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ANODIC TITANIUM DIOXIDE LAYERS: 
SYNTHESIS, PROPERTIES AND APPLICATIONS

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Anodic Titanium Dioxide Layers: Synthesis, Properties and Applications

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A thesis submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy

Mar 2010
DECLARATION

I hereby declare that this thesis entitled “Anodic Titanium Dioxide Layers: Synthesis, Properties and Applications” has not been, either in whole or in part, previously submitted to any other institution for a degree or other qualification, and contains no material previously published or written by another person, except where due references is made in the text.

(Signed)

HUANG Chuanjun (Name of student)
ABSTRACT

Highly-ordered, self-organized TiO$_2$ nanotube arrays obtained through electrochemical anodization in F$^-$ ions containing electrolytes have received considerable attention in the past decade due to their easy fabrication and anticipated high potential for technological application. Although extensive research has been conducted, there is still much to be learned about the fabrications, characterizations and applications of the anodic TiO$_2$ layer. Research interest is aroused by tailoring of the morphology of the anodic TiO$_2$ nanotube arrays through precisely controlled anodization parameters and carefully prepared electrolytes. TiO$_2$ layers obtained through anodizing titanium in F$^-$ ions containing electrolyte, which have the advantage of attaching onto the metallic substrate, significantly extend the advanced applications of nanocrystalline TiO$_2$. These applications are strongly related to the semiconductor nature, chemical stability, high surface-to-volume ratio and tunable geometries of these layers. The development of anodic TiO$_2$ layers with tunable geometry through anodization of titanium and titanium alloys, and the investigation of their properties and applications, have both scientific and practical significance.

In this thesis, investigations of the TiO$_2$ layer formed through anodizing titanium and NiTi alloy in different electrolytes were conducted. In F$^-$ ions containing aqueous solution, research emphasis was placed on the effects of duration of anodization, addition of phosphoric acid, and applied potential on the morphology of the TiO$_2$ layer. Highly-ordered TiO$_2$ nanotube arrays and hybrid material consisting of TiO$_2$ nanotube arrays and bamboo-shoot-like structures were developed and examined by field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Using selected-area electron diffraction (SAED) and Raman spectroscopy, the as-prepared bamboo-shoot-like structure was determined to be anatase, and through X-ray diffraction (XRD) the as-prepared TiO$_2$ nanotube array was found to be amorphous. The formation of the bamboo-shoot-like structures was ascribed to ageing induced dielectric breakdown
under potentiostatic anodization at special applied potentials in HF solution containing H₃PO₄. For F⁻ ions containing hybrid electrolyte, the influence of applied potentials on the surface morphology of the TiO₂ layer was demonstrated and the critical role of the electrical field was studied. TiO₂ layers including micro-, meso- and macro-porous structures, corresponding to the applied potential, were obtained. The formation of a nanoporous TiO₂ layer under various applied voltages in F⁻ ions containing hybrid solution was attributed to the non-uniform electrical field on the metal surface. For a non-aqueous solution containing NH₄HF₂ and ethylene glycol, the effects of applied potential on the surface morphology and growth rate of the TiO₂ layer were investigated. Highly-ordered TiO₂ nanotube arrays, which were covered with nanowires, were observed by FESEM. Growth rate related to applied potential was calculated according to tube length and anodization time. It was found that a high applied voltage leads to a high growth rate but loose nanotube array. An optimal applied voltage in view of order of the TiO₂ nanotube arrays and the growth rate is suggested. These anodic TiO₂ layers with their various geometries provided sufficient scope for studying the influence of geometry on their properties, for investigating the associated effect as a support for other functional materials, and for examining the influence of architecture on the cell performance of dye-sensitized solar cells. Anodization of NiTi alloy in diluted HF solution was carried out. A surface oxide layer with enhanced surface roughness was observed through FESEM and scanning probe microscopy (SPM). The composition of the oxide layer was characterized using X-ray photoelectron spectroscopy (XPS). By investigation through electrochemical potentiodynamic in Hanks’ based salt solution, it was found that the surface oxide layer exhibited improved corrosion resistance.

The semiconductor property and the geometry of TiO₂ layers attached to a titanium substrate make them a favorable heterogeneous photocatalyst. The photocatalytic properties of the bamboo-shoot-like structure/TiO₂ nanotube arrays hybrid material and the nanoporous TiO₂ layers were examined through decomposition of a kind of non-biodegradable dye-AO7 under weak UV irradiation. The data from photocatalytic measurement were plotted as logarithms of the time-dependent normalized dye concentration and it was found that the photocatalytic
activity followed pseudo-first-order kinetics. When investigating the influence of morphology on photocatalytic efficiency, it was found that the hybrid material exhibited higher photocatalytic efficiency than the TiO$_2$ nanotube arrays. Moreover, the influence of post-annealing treatment on the photocatalytic activity was studied and it was demonstrated that samples annealed at 550 °C resulted in maximum photocatalytic efficiency, which was attributed to the formation of the anatase/rutile junction. The enhanced photocatalytic activity of TiO$_2$ layers annealed at 550 °C was attributed to the increase in charge-separation. Among various structures including micro-, meso- and macro-porous TiO$_2$ layers, ordered TiO$_2$ nanotube arrays exhibit the highest photocatalytic activity in decomposition of dye AO7 under UV illumination. A fixed-bed flow-through photoreactor, which scaled up the decomposition of waste solution, was designed and examined. It was found that the anodic TiO$_2$ nanotube arrays/Ti is a good alternative to the commonly used TiO$_2$ nanoparticle photocatalyst.

Due to their highly accessible surface, electrochemical behavior and chemical stability, anodic TiO$_2$ nanotube arrays have attracted considerable interest for energy-storage applications. The electrochemical double layer capacitance (EDLC) of the TiO$_2$ nanotube arrays obtained from aqueous solution was studied in alkaline and acidic solutions through cyclic voltammetry (CV) and galvanostatic charge-discharge techniques. It was found that the EDLC of the anodic TiO$_2$ nanotube array was very low and it depended on the ions (OH$^-$ or H$^+$) in the electrolyte employed. Decorating the anodic TiO$_2$ nanotube arrays with electroactive materials including NiO-Ni(OH)$_2$ and RuO$_2$ was carried out through an electrochemical deposition method for redox supercapacitor application. The redox supercapacitance of the NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti and RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites was examined. In both cases, it was found that the crystalline structure of the anodic TiO$_2$ nanotube arrays influenced the charge-discharge behavior. Moreover, extension of the potential of the operational windows of the redox supercapacitor was obtained compared with that obtained through the deposition of electroactive materials on metallic titanium substrate. These findings indicate that the anodic TiO$_2$ nanotube arrays/Ti is a good alternative support
material for supercapacitor applications.

The semiconductor nature and the geometry of anodic TiO$_2$ nanotube arrays make them suitable for use as electrode material in photon-to-electric conversion devices, especially dye-sensitized solar cells (DSSCs). Liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays obtained through anodization in non-aqueous solutions as photoanode were assembled and examined. First, anodic TiO$_2$ nanotube arrays were fabricated through potentiostatic anodization in ethylene glycol solution with NH$_4$HF$_2$, and liquid-junction DSSCs based on the annealed structures were assembled and characterized. The assembling and sealing process was investigated and it was found that the commonly used sealing material, Surlyn film, was not suitable for the liquid-junction DSSCs. Epoxy adhesive slowed down evaporation of the solvents but leakage of the electrolyte was unavoidable. Treatment of the anodic TiO$_2$ nanotube arrays with TiCl$_4$ solution was performed and the results demonstrated that the treatment increased photocurrent and consequently enhanced the performance of the cell. Anodic TiO$_2$ nanotube arrays with special surface nanostructures were fabricated through two-step anodization in non-aqueous electrolyte containing NH$_4$F and ethylene glycol. It was found that the special surface nanostructure resulted in improvement of cell performance. The electron transport properties of the liquid-junction DSSCs, especially the electron lifetime, were investigated through electrochemical impedance spectroscopy and open-circuit voltage decay approaches. The influence of the addition of a kind of ionic liquid into redox electrolyte was investigated and it was found that it led to an increase in the electron lifetime and enhancement of the cell performance.
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LIST OF ABBREVIATIONS AND NOTATION

AES: Auger electron spectroscopy
ALD: atomic layer deposition
AM: air mass
APCE: absorbed photon-to-current efficiency
ATO: anodic titanium oxide
CB: conduction band
CV: cyclic voltammetry
DSSCs: dye-sensitized solar cells
DOS: density of states
EDLC: electrochemical double layer capacitor
EG: ethylene glycol
EIS: electrochemical impedance spectra
ESR: equivalent series resistance
FESEM: field-emission scanning electron microscopy
FTO: Fluorine doped tin oxide glass
HOMO: highest occupied molecular orbital
HRTEM: high-resolution transmission electron microscopy
IPCE: incident photon-to-current conversion efficiency
IMPS: intensity modulated photovoltage spectroscopy
LbL: layer-by-layer
LHE: light harvesting efficiency
LUMO: lowest unoccupied molecular orbital
OCP: open-circuit potential
SAED: selected-area electron diffraction
SCE: saturated calomel electrode
SHE: standard hydrogen electrode
SPM: scanning probe microscopy
SRC: standard reporting conditions
STM: scanning tunneling microscopy
VB: valance band
XPS: X-ray photoelectron spectroscopy
XRD: X-ray diffraction
TBP: 4-tert-butylpyridine
TCO: transparent conducting oxide
TEM: transmission electron microscopy
$E_g$: band gap energy
$L_{ni}$: electron diffusion length
$\tau_n$: electron lifetime
$D_n$: diffusion coefficient
$E_{BD}(V)$: Breakdown potential
$\lambda$(nm): Wavelength
$I_{corr}$: corrosion current density
$V_{oc}$: open-circuit voltage
$J_{sc}$: short-circuit current
$ff$: fill factor
Chapter 1 Introduction

The formation of highly-ordered, self-organized TiO$_2$ nanotube arrays through electrochemical anodization approaches can be traced back to 1999. In that year, Zwilling and his co-workers grew the first tubular TiO$_2$ nanostructures by anodizing titanium and titanium alloy in F$^-$ ions containing electrolytes [1, 2]. Since then there has been considerable interest in the formation of anodic TiO$_2$ nanotube arrays, due to their high surface-to-volume ratio, tunable nanostructure, size-dependent properties, and semiconductor nature. A variety of reports in the literature have testified to the unique properties of this special nanotubular architecture, making it of considerable scientific interest as well as potential practical importance.

In the early years of development of anodic TiO$_2$ nanotube arrays, researchers focused mainly on extending the geometry, including the pore size, wall thickness, and thickness of the nanotube arrays. Generally speaking, anodic TiO$_2$ nanotube arrays have gone through three generations according to the aspect ratio of the nanotube, which has more recently been as high as 10,000:1. TiO$_2$ layers with advanced geometries such as nanolace, bamboo-type nanotubes, and multilayered nanotubes have been fabricated through precise adjustment of electrochemical parameters including the nature of the electrolytes, the applied potential, and even the steps of anodization. Although it is well known that the properties of electrolytes and applied potentials play a critical role in the final morphology of the TiO$_2$ oxide layer, the current literature lacks comprehensiveness. Furthermore, a few reports have revealed conflicting views about the effects of the applied voltage.

Despite the limited thickness of the TiO$_2$ layer, anodization of titanium in F$^-$ ions containing aqueous solutions has been extensively investigated due to the easy preparation and low cost of the electrolyte. It is commonly postulated that the limitation of thickness results from the equilibrium of chemical etching and growth of the nanotube, which implies that the length of the nanotube arrays is independent of anodization time. No research has been conducted on the duration of anodization
in aqueous solution with H$_3$PO$_4$ as an additive. Moreover, mixed or hybrid electrolytes, which allow for continuous adjustment of the electrolyte properties, have received little attention in investigating the formation of anodic TiO$_2$ structures. During the past few years, anodic TiO$_2$ nanotube arrays with high aspect ratios have been widely investigated through electrochemical anodization in non-aqueous solutions. However, little attention has been devoted to investigating the influence of the applied potential on the morphology and growth rate of the nanotube arrays.

Alongside the fabrication of anodic TiO$_2$ nanotube arrays with tunable dimensions, various applications have been investigated on the basis of their unique architecture and semiconductor nature. Among these advanced applications, photocatalytic decomposition of organic waste and photocatalytic water splitting, using as photoanode for dye-sensitized solar cells (to be abbreviated DSSCs hereafter), have received considerable recent attention. These applications depend strongly on the geometry and properties of the anodic TiO$_2$ nanotube arrays. Little research has been carried out to investigate the effects of morphology on these applications. Due to their high aspect surface area and semiconductor properties, the anodic TiO$_2$ nanotube arrays can be coated with various functional materials for advanced applications. Little attention has been directed to coating anodic TiO$_2$ nanotube arrays with electroactive materials as redox supercapacitor. On the other hand, these advanced applications stimulate research activities of the anodic TiO$_2$ layer with tunable architecture and new structures. Then it is necessary to systematically investigate the influence of anodization parameters in various solutions, such as duration of anodization and applied potential, on morphology of the anodic TiO$_2$ layer. Moreover, investigation of properties and applications of the anodic TiO$_2$ layer exhibits practical and scientific significance.

In view of the above, this study sets out to fabricate TiO$_2$ layers via anodization of titanium in F$^-$ ions containing aqueous, mixed, and non-aqueous solutions. The influence of applied potentials on surface morphology was investigated. Then anodic TiO$_2$ layers with different geometries were investigated as photocatalyst. To scale up the photocatalytic decomposition of organic waste, a photoreactor using anodic TiO$_2$
nanotube arrays as photocatalyst was designed and manufactured, followed by examination of photocatalytic efficiency. A further application of anodic TiO₂ nanotube arrays focused on support material in a supercapacitor with nickel oxide and ruthenium oxide as electroactive materials. Finally, anodic TiO₂ nanotube arrays obtained through anodization of titanium in organic solutions were investigated for photoanode of liquid-junction DSSCs.

1.1 Aim and Objectives

The aim and objectives of the thesis are listed as follows:

1. To fabricate TiO₂ layers through electrochemical anodization method: one of the objectives is to fabricate various TiO₂ layers with tunable surface morphologies. The relationships between anodic parameters such as composition of the electrolyte, applied potential, anodic current density and geometry of the oxide layer are investigated and analyzed.

2. To understand the formation mechanism of TiO₂ layers obtained under various anodic parameters and in various electrolytes: The influences of the anodic parameters and the nature of the electrolyte on the morphology of the TiO₂ layer are investigated.

3. To understand the photoresponse properties of TiO₂ layers with various geometries and post-treatment processes: The photocatalytic decomposition of organic waste in solution is studied. A fixed-bed flow-through photoreactor employing anodic TiO₂ layer as photocatalyst is designed and examined.

4. To coat anodic TiO₂ nanotube arrays with electroactive materials: NiO-Ni(OH)₂/anodic TiO₂ nanotube arrays/Ti and RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites are synthesized through electrochemical deposition and these arrays are investigated for electrochemical supercapacitor application.
To fabricate liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays as photoanode: Liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays obtained from non-aqueous solutions with post-treatment as photoanode are assembled and the effects of surface morphology on cell performance are investigated.

1.2 Outline of Thesis

*Literature review*

Literature detailing recent research into the background of anodizing titanium and the development of anodic TiO$_2$ nanotube arrays through anodization in F$^-$ ions containing electrolytes is addressed in Chapter 2. Limitations and gaps in current understanding are presented, which stimulate present research. Various applications of the anodic TiO$_2$ nanotube arrays are reviewed, with the main focus on photocatalysis, redox supercapacitor and photoanode in liquid-junction DSSCs, which are closely related to the present project.

*Anodizing titanium and NiTi alloy in various solutions*

Anodization of titanium in aqueous, mixed and non-aqueous solutions containing F$^-$ ions and anodization of NiTi alloy in diluted HF aqueous solution are carried out in Chapter 3. For anodization of titanium in an aqueous solution, the influences of an additive-H$_3$PO$_4$, anodization duration, and applied potential on the morphology of the TiO$_2$ layer are investigated. For anodization in the mixed solution, the influence of applied potentials on the morphology of the TiO$_2$ layer is investigated. For anodization in the non-aqueous solution, the effect of applied potentials on the morphology and growth rate of the TiO$_2$ layer is investigated. Finally, anodization of the NiTi alloy in diluted HF aqueous solution is investigated.

*Photocatalytic decomposition of organic dye in solution using anodic TiO$_2$ layers*

The photocatalytic properties of an anodic TiO$_2$ layer obtained through
anodization in aqueous and mixed solutions are investigated in Chapter 4. The influences of the morphology and crystalline structure of anodic TiO₂ layers on photocatalytic activity are studied. Finally, a fixed-bed flow-through photoreactor using anodic TiO₂ nanotube arrays as photocatalyst is demonstrated.

*Anodic TiO₂ nanotube arrays as support material for redox supercapacitor*

The electrochemical double-layer capacitance of anodic TiO₂ nanotube arrays and the redox capacitance of NiO-Ni(OH)₂/anodic TiO₂ nanotube arrays/Ti, RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites are presented in Chapter 5. NiO-Ni(OH)₂/anodic TiO₂ nanotube arrays/Ti and RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites are fabricated through an electrochemical deposition method and are investigated for electrochemical supercapacitor application.

*Liquid-junction DSSCs using anodic TiO₂ nanotube arrays as photoanode*

Liquid-junction DSSCs using anodic TiO₂ nanotube arrays obtained through anodization in non-aqueous solutions are fabricated and characterized in Chapter 6. DSSCs based on anodic TiO₂ nanotube arrays with surface treatment are assembled and investigated. DSSCs using anodic TiO₂ nanotube arrays with special surface nanostructures obtained through two-step anodization method in non-aqueous solution are fabricated and characterized.

*Concluding remarks and suggestions for future research*

The conclusions of the thesis are presented in the last chapter. A preview of proposed future work is also presented.
Chapter 2 Literature Review

2.1 Introduction

Titanium is the ninth most abundant element and the second most abundant transition metal in the Earth’s crust. The most common compound of titanium is titanium dioxide (TiO₂), which is often used for many applications ranging from anticorrosion, self-cleaning coating, photocatalyst and paint to DSSCs. In general, titanium spontaneously forms a stable, protective, and strongly adherent oxide layer when it is exposed to air or other oxygen containing environments. This is because titanium exhibits strong affinity towards oxygen in any environments where a trace of moisture or oxygen is present. Moreover, titanium is capable of healing ruptures in the oxide layer instantly in oxygen containing environments. Including titanium, the so-called valve metals, such as aluminum (Al) tantalum (Ta), niobium (Nb), vanadium (V), hafnium (Hf) and wolfram (W) show the similar properties whose surfaces are immediately covered with a native oxide layer of a few nanometers, when these metals are exposed to oxygen containing surroundings [3]. Typically, the native oxide passive layer is about 1.5 to 10 nm in thickness in air at room temperature [4]. The native oxide layer consists mainly of morphologically homogeneous TiO₂ with amorphous crystalline structure. Besides amorphous, in nature, TiO₂ is known to exist mainly in crystal structures of anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic).

Many applications result from the excellent properties of TiO₂. For instance, TiO₂ is the most widely used white pigment because of its brightness and very high refractive index (n = 2.4). The application for sunscreen depends on the nature of its ultraviolet (UV) adsorption capability. A well known application of TiO₂ is to use it as a photocatalyst for the environmental remediation. Other important applications are used for sensors, paints to DSSCs, and biomedical engineering material. All these applications strongly relate to the microstructures and crystallization of TiO₂.

The TiO₂ layer formed in air is thin and un-tunable so that its applications are
limited. To modify the morphology of the TiO$_2$ layer on titanium, many attempts have been examined, for example, thermal oxidization in oxygen at high temperature. Electrochemical oxidation (also named anodization or anodic oxidation) is a well-established surface modification technique for titanium and it has been used in aerospace and other industries [5].

In this chapter, an overview of electrochemical oxidation of titanium in various solutions is provided, especially formation of highly-ordered, self-organized TiO$_2$ nanotube arrays in F$^-$ ions containing electrolytes. Other approaches for synthesis of TiO$_2$ nanotubes are briefly summarized. Then applications of the TiO$_2$ are briefly reviewed with emphases focused on photocatalyst, support for supercapacitors and photoanode for DSSCs.

2.2 Anodization of titanium or titanium alloys in electrolytes without F$^-$ ions

2.2.1 Formation of titanium oxide layer

When a potential or current is applied between the anode and cathode, electrode reactions (oxidation and reduction) in combination with field-driven ion diffusion, as shown in Figure 2-1, lead to the formation of titanium oxide layer on the surface of the anode. The titanium oxide layer results from the competition between field-enhanced oxidation, and dissolution including field-enhanced dissolution and chemical dissolution. The chemical reactions driven by electric field specifically for anodization of titanium are described as [6]:

At Ti/Ti oxide interface:

$$\text{Ti} \leftrightarrow \text{Ti}^{2+} + 2e^-$$  \hspace{1cm} (2-1)

At Ti oxide/electrolyte interface:

$$2\text{H}_2\text{O} \leftrightarrow 2\text{O}^{2-} + 4\text{H}^+ + 4e^-$$  \hspace{1cm} (2-2)

(Oxygen ions react with Ti to form oxide)

$$2\text{H}_2\text{O} \leftrightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$$  \hspace{1cm} (2-3)

(O$_2$ gas evolves or sticks at electrode surface)
At both interfaces:

\[ \text{Ti}^{2+} + 2\text{O}^{2-} \leftrightarrow \text{TiO}_2 + 2\text{e}^- \]  \hspace{1cm} (2-4)

![Diagram](image)

Figure 2-1 Schematic diagram of ions diffusion under an electric field [5, 6].

Sometimes, the TiO\(_2\) layer on titanium can heal itself. In other words, the as-formed TiO\(_2\) layer can be protective and prohibit further oxidation. This is because the as-formed TiO\(_2\) layer is passive due to inhibition of active dissolution by the more or less spontaneous formation of a dense passive layer of limited ionic conductivity. The stability of the TiO\(_2\) layer is found to be dependent on the surrounding environments. The TiO\(_2\) layer formed in acidic environments shows high corrosion resistance, which is attacked only by hot concentrated HCl or H\(_2\)SO\(_4\), and HF. The famous Pourbaix diagram or the potential-pH diagram provides the graphical representation of the reversible potential as a function of the pH. The stability domains of dissolved cations (anodic dissolution) and of solid species supposed to be adherent and protective (passivity) can be inferred in the Pourbaix diagram [7]. However, it is difficult to draw a conclusion about whether corrosion or protection states actually settle and occur at which rate. Usually, the Pourbaix diagram cannot be used to interpret kinetic phenomena such as the formation of duplex layers with different oxidation state, and the stability of passive metals in acid solution.
2.2.2 Morphology, composition and properties of titanium oxide layer

Anodization of titanium in alkaline or acid electrolytes without F\(^-\) ions results in an improved thickness but few changes of morphology of the TiO\(_2\) layer. In contrast to the 1.5-10 nm native scale formed in air, the thickness of the TiO\(_2\) layer obtained by anodization in alkaline or acid electrolytes is much greater. TiO\(_2\) layer of 1000 nm thickness was obtained through anodization in CH\(_3\)COOH electrolyte [4]. Numerous studies indicate that the thickness of TiO\(_2\) layer is almost linear dependent on the applied potential:

\[
d \approx aU
\]  

(2-5)

where \(d\) is the thickness of the TiO\(_2\) layer, \(a\), a constant within the range of 1.5-3 nm V\(^{-1}\), and \(U\) is the applied potential [5, 6, 8]. It was revealed that the so-called growth constant (\(a\)) depends on the nature of electrolyte. In an aqueous solution, the applied voltage drops mainly over the TiO\(_2\) layer rather than the electrolyte and the metallic contact. Many passive layers are found to be of the barrier type, i.e. they show low ionic and electronic conductivity at low and medium field strength (\(E_s \ll 1 \text{ MV} \cdot \text{cm}^{-1}\)) [3]. As long as the electric field is strong enough to drive ion conduction through the oxide layer, it keeps growing, which qualitatively gives the almost linear relationship between the thickness of oxide layer and the applied potential.

The formation of the TiO\(_2\) layer is often limited by breakdown potential. If the applied potential exceeds the dielectric breakdown limit of the TiO\(_2\) layer, vigorous oxygen evolution and sparking occur [6]. The breakdown potential (\(E_{BD}\)) of the TiO\(_2\) layer depends heavily on the nature of electrolyte. Different electrochemical behaviors such as slow down of voltage increase, attainment of maximum voltage, appearance of visible sparking, occurrence of audible cracking and rapid voltage fluctuation were employed by researchers to identify the dielectric breakdown [9]. It was reported that the passivity breakdown stemmed from dielectric breakdown due to high field strength, corrosion, aggressive ions penetrating into the TiO\(_2\) layer and hydrogen incorporating into the TiO\(_2\) layer at low potentials [3]. The dielectric
breakdown indicated by irregular current peaks, visible sparks, potential fluctuations or audible cracking, means a spontaneous local increase of conductivity. Ikonopisov and co-workers proposed a theoretical model of dielectric breakdown caused by an avalanche of electron injections at the electrolyte/oxide interface [10, 11]. In this model, an electronic current, called primary electronic current, is injected from the electrolyte into the oxide conduction band. High field strength accelerates these injected electrons to an energy which is sufficient to free other (secondary) electrons by impact ionization, so that an avalanche occurs when a certain critical current is reached, leading to dielectric breakdown [9]. The dielectric breakdown is found to depend on the oxide band gap, composition and concentration of the electrolyte, but it is almost independent of current density, temperature, surface roughness, hydrodynamics, movements of the electrolytes and history of the oxide layer [11].

The breakdown of tantalum oxide layer was interpreted by the local formation of electron avalanches due to high field strength, initiating at inhomogeneities in the interface oxide/electrolyte [12]. The inhomogeneities was associated with flaws in the substrate, which were an effect of impurities [13].

The influences of the electrolyte concentration on the anodization behavior were intensively studied. In general, the anodic forming voltage decreases apparently with increase of the electrolyte concentration, which is interpreted on the basis of the “electrical double layer” model [8]. As shown in Figure 2-2, the electrical double layer consists of an excess or deficit of electrons on the metal side and of an excess or deficit of ions on the electrolyte side, resulting in a certain gradient of concentration distribution of the electrolyte. If an increase of the electrolyte concentration is sufficient to heighten the lowered concentration of the inner layer, the electrochemical reaction at the interface accelerates and then the electrical resistance will be reduced. Eventually, the anodic forming voltage decreases with increase of the electrolyte concentration.

The structure, composition and crystallization of the anodic TiO$_2$ layer were extensively investigated. It was reported that rapidly grown oxide layers indicated the presence of higher defect density and revealed a higher dissolution rate [8, 14].
The compact anodic TiO$_2$ layer contained defects, whose concentration was determined by the growth constant, while the high defect densities were reduced by additional heat treatment [15]. In view of the composition or stoichiometry, oxygen overstoichiometry in upper-most layer and an intermediate suboxide TiO$_{2-x}$ between the deep TiO layer of the titanium substrate and the more superficial TiO$_2$ layer of the TiO$_2$ were revealed by Rutherford backscatter method [14, 16, 17]. The oxygen overstoichiometry in the outer parts of the oxide layer was attributed to the formation of hydration, which was confirmed by elastic recoil detection analysis (ERA) [16]. A few authors claimed that the anodic TiO$_2$ layer was hydrated [16, 18]. In view of the crystalline structure of the TiO$_2$ layer, previous findings were controversial. Most of researchers considered that the crystallization of the anodic TiO$_2$ layer was mainly determined by the applied potential. However, quantitative description of the applied voltages and the crystalline structures including amorphous, anatase or rutile was difficult. The crystallinity of TiO$_2$ obtained under various applied potentials was investigated by series methods such as XRD, TEM and Raman spectra. Recently, local crystallinity of the anodic TiO$_2$ layer was revealed by STM, which occurred at very low applied potential as -50 mV in 0.1 M H$_2$SO$_4$ solution [19]. A few authors believed that the composition of the anodic TiO$_2$ layer depended on the whole history, indicating that it may change during the anodization process, even if the conditions were kept identical [16].

Ageing of the anodic TiO$_2$ layer has received much attention during the past decades. Various transformations such as stoichiometric changes, swelling or dehydration, corrosion, further growth, recrystallination, or depletion of defects were found when duration of anodization was conducted. Property varieties of the TiO$_2$ layer including ionic and electronic conductivities, potential distribution were reported under duration of anodization [3].
Figure 2-2 Schematic structure of electrical double layer at the titanium oxide/electrolyte interface, A: metal/oxide interface, B-C: defect layer of electrons, C: oxide/electrolyte interface, D: gradient line of the concentration distribution, D-E: excess layer of anions [8].

2.3 Formation of highly-ordered, self-organized TiO$_2$ nanotube arrays by anodization of titanium or titanium alloys in electrolytes with F$^-$ ions

Date back to 1999, Zwilling and his coworkers grew the first self-organized, highly-ordered tubular TiO$_2$ nanostructures by anodization of titanium and titanium alloys in F$^-$ ions containing electrolytes [1, 2]. However, there is a debate about the pioneered work on the formation of the TiO$_2$ nanotube arrays obtained through anodization. Grimes’ group in America claimed that they were the first one to fabricate the anodic TiO$_2$ nanotube arrays in 2001 [20], while Schmuki’s group in Germany generally referred to Zwilling’s work as the first contribution. More and more work followed soon thereafter and the geometries of the anodic TiO$_2$ nanotube arrays, especially the length, were optimized through controlling electrochemical processes.

2.3.1 Approaches to synthesizing TiO$_2$ nanotubes

To date, three approaches are developed to synthesize TiO$_2$ nanotubes, namely, template method, electrochemical anodization method and alkaline hydrothermal method. A timeline describing the development of TiO$_2$-related nanotubular
structures is shown in Figure 2-3.

![Figure 2-3 Simplified timeline describing development of TiO\textsubscript{2} nanotubes.](image)

Figure 2-3: Simplified timeline describing development of TiO\textsubscript{2} nanotubes.

Figure 2-4 (a): schematic representation of template method, and (b): SEM image of the TiO\textsubscript{2} nanotube array [21] (Figure reprinted with permission from Hoper Copyright (1996) American Chemical Society).

Template method utilizes the morphological properties of known and characterized materials (so-called template) to construct materials with a similar morphology through reactive deposition and dissolution processes [21]. TiO\textsubscript{2}
nanotube array was first synthesized through the template method in 1996, as shown in Figure 2-4 [22]. The typical deposition approaches include electrodeposition, atomic layer deposition (ALD) and layer-by-layer (LbL) self-assembly technique. In this way, regular TiO$_2$ nanotube array is obtained. However, the template is sacrificial in most cases, and is required to be removed after synthesis, leading to an increase in cost.

Hydrothermal method starts with amorphous or crystalline TiO$_2$ powders, followed by treatment in a concentrated sodium hydroxide (NaOH) solution at an elevated temperature. In this way, TiO$_2$ nanotubes with conversion efficiency of almost 100% are performed. TiO$_2$ nanotubes were first fabricated through the hydrothermal method in 1998, as shown in Figure 2-5[23].

![Figure 2-5 (a): The start material, and (b): TiO$_2$ nanotubes obtained through a hydrothermal method][23] (Figure reprinted with permission from Kasuga et al. Copyright (1998) American Chemical Society).

In contrast to the template and the hydrothermal method, electrochemical anodization method attracts wide interest due to its facile, low cost and straight-forward properties [24]. Growth of highly-ordered oxides with pore
structures through anodization method is demonstrated for almost all valve metals. Among these metals, aluminum is extensively studied and it has been known for a few decades that porous alumina layer can be obtained by anodization in an acidic electrolyte [25]. In 1995, Masuda and Fukuda demonstrated that porous alumina with very high degree of order was achieved by adjustment the anodization conditions [26]. Metallic alloys of valve metals such as TiNb, TiZr, TiAl or even more complex Ti6Al7Nb and Ti6Al4V, Ti29Nb13Ta4.6Zr or Ti25Nb3Mo3Zr2.2Sn were demonstrated to successfully form self-organized pore structures.

2.3.2 Formation of anodic TiO₂ nanotube arrays

The electrode reaction (oxidation) and field-driven ion diffusion occur simultaneously during the anodization process. Similar to that occurring in electrolytes without F⁻ ions, anode reaction under sufficiently high applied voltage, as shown in Figure 2-1, is described as [27]:

i) Ti⁰ is oxidized to Ti⁴⁺ or Ti²⁺ at the metal-oxide interface and the cations migrate outwards (under the applied electric field); and

ii) O²⁻ ions are incorporated in the layer and migrate towards the metal-oxide interface.

These reactions result in the formation of a compact titanium oxide layer. Depending on the transfer properties in the oxide lattice for the anions in comparison with the cations, the TiO₂ layer may grow at the outer or inner of the oxide interface. When the electrolyte contains F⁻ ions, dissolution of titanium and titanium oxide occurs simultaneously due to a chemical etching process, which is described as [28]:

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

(2-6)

In other words, the formation of the highly-ordered TiO₂ nanotube arrays results from these following three simultaneously occurring processes [29]:

i) Field-assisted oxidation of Ti metal to form titanium oxide;
ii) Field-assisted dissolution of Ti metal ions in the electrolyte; and

iii) Chemical dissolution of Ti and TiO$_2$ due to the chemical etching by F$^-$ ions.

The final chemical dissolution of TiO$_2$ in the F$^-$ ions containing electrolyte plays a crucial role in the formation of the highly-ordered TiO$_2$ nanotube arrays rather than the compact oxide layer.

The initial stages of the anodization process in the F$^-$ ions containing electrolyte were extensively investigated. It was reported that the field-assisted dissolution dominates chemical dissolution due to the relatively large electric field across the titanium oxide layer [30]. Then small pits form due to the localized dissolution of the titanium oxide, as described by Equation (2-6), acting as starting pore centers. Subsequently, these pits are converted into bigger pores and the pore density increases, followed by pores covering uniformly over the surface. The understanding of the formation of the anodic TiO$_2$ nanotube arrays stemmed from that of the prototype anodization system, aluminum. Parkhutik and Shershulskii developed a model describing the procedures of the formation of alumina pores [31], as shown in Figure 2-6. At beginning of the anodization process, a compact, uniform titanium oxide layer formed on the surface, as shown in Figure 2-6a. The distribution of electric field in the oxide layer was strongly related to surface morphological fluctuations, playing critical role in the formation of the pore structures, as shown in Figure 2-6b [27]. Then the pores started to form, which resulted from the localized field-enhanced dissolution in the compact oxide layer, as illustrated in Figure 2-6c. Eventually, the pores grew steadily and uniformly distributed pores were obtained, as shown in Figure 2-6d. The current density-time relationship is shown in Figure 2-6e, revealing details about the timescales of different stages of the growth process and about the corresponding morphologies under constant-voltage or alternating-voltage conditions [32]. The influence of volume expansion and local acidity on the pore growth is shown in Figures 2-6f and 2-6g, respectively.

To date, the most popular prototype for the self-assemble process of the anodic alumina is a mechanical model developed by Gosele’s group [33, 34], in which the formation of the hexagonally-ordered pore arrays resulted from repulsive force
between neighboring pores caused by expansion of aluminum during the oxide formation. The volume expansion coefficient, which stems from participation of O atoms, is calculated according to the following formula [35]:

\[
\xi = \frac{Md}{nAD}
\]  

(2-7)

where \(M\), \(A\), \(d\), \(D\) and \(n\) is molecular weight of titania (or alumina), atomic weight of titanium (or aluminum), density of titanium (or aluminum), density of titania (or alumina) and the number of titanium (or aluminum) atoms in titania (or alumina), respectively. For titanium, the volume expansion coefficient is about 2.11 if the density of titanium and titania are 4.5 and 4 g.cm\(^{-3}\), respectively [35]. The mechanical model considered the following factors [36]:

i) The oxidation occurs at the entire metal/oxide interface mainly by the migration of oxygen containing ions (\(O^{2-}\) or \(OH^-\)) from the electrolyte;

ii) The dissolution and thinning of the oxide layer results mainly from hydration reaction of the as-formed oxide layer;

iii) In the case of barrier-type oxide growth without pore formation, all Al\(^{3+}\) ions reaching the electrolyte/oxide interface contribute to oxide formation. On the other hand, porous alumina is formed when Al\(^{3+}\) ions drift through the oxide layer. Some of them are ejected into the electrolyte without contributing to the oxide formation;

iv) Pores grow perpendicular to the surface when the field-enhanced dissolution at the electrolyte/oxide interface is equilibrated with oxide growth at the oxide/metal interface;

v) The as-formed alumina is assumed to be Al\(_2\)O\(_3\). Therefore, the atomic density of aluminum in alumina is by a factor of 2 lower than in metallic aluminum. This means that the volume of the anodized alumina expands to about twice the original volume; and

vi) The volume expansion leads to compressive stress during the formation of the oxide in the oxide/metal interface. The expansion in the vertical direction pushes the pore walls upwards.
More recently, it was reported that a critical field strength was responsible for the self-ordering of the pore structures [37]. In this model, the crucial ordering factor was ascribed to the electric field in the oxide layer (that has to be maximum) to obtain a maximum but not supercritical ionic current density [27].

Although it often draws analogy with aluminum, there are several differences between titanium and aluminum. It was demonstrated that for aluminum a pre-requisite for pore formation is sufficiently acidic electrolyte or an electrolyte containing Al$^{3+}$- complexing ions to solvate a certain amount of cations [27, 38]. In view of titanium, however, compact oxide layer can be obtained under almost all anodization conditions. A low pH is found to be not sufficient to create porous oxide
layer. This is because a low pH is sufficient to solvate cations (Ti^{4+}). When the electrolyte contains fluoride ions, the formation of water-soluble TiF$_6^{2-}$ complexes aids the prevention of Ti-oxide layer formation at the tube bottom and leads to mild but permanent chemical dissolution of the formed TiO$_2$ [27]. Moreover, F$^-$ ions enter the growing TiO$_2$ lattice due to the small ionic radius and are transported by the electric field through the oxide to the metal-oxide interfaces [39].

Among various factors being considered to form the rounded shapes tube/pore bottoms, mainly three factors are considered to be crucial [27]:

i) Volume expansion (the volume of the formed oxide is greater than the space available due to metal loss-this generates stress at the interface);

ii) Field distribution (there is field line concentration at the inner tube bottom);
and,

iii) Local acidity (typically anodization processes generate cations that when hydrolyzed create local acidity-this pH gradient at the pore tip may enhance chemical dissolution of oxides [24, 40].

The composition of the highly-ordered TiO$_2$ nanotube arrays has been investigated recently [39]. Investigation through high-resolution TEM (HRTEM) indicates that there is a double-wall structure of the as-prepared nanotube synthesized in F$^-$ ions containing electrolyte. The inner part of the as-prepared nanotube is found to be largely incorporated with electrolyte species, revealed by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) analysis, as shown in Figure 2-7b. A fluoride rich layer is detected at the bottom of the tubes (accumulated due to the higher migration velocity of fluorides compared with O$_2^-$). Moreover, the tube wall is also predicted to be in the presence of fluoride rich layer, leading to the tube separation. This is because the boundaries between oxide cells are prone to be attacked (dissolution). Similar results were reported for the anodic alumina nanotubes, indicating that the compositions of the inner part and the out part of an individual pore are significantly different [30], as shown in Figure 2-7a. The inner part is rich with electrolyte species, while the outer part consists essentially of pure alumina [41]. More recently, it was suggested that the outer part
is titanium dioxide hydroxide (TiO$_2$·xH$_2$O) and the separation of nanotubes results from dehydration of the layer [42].

![Diagram of anodic Al$_2$O$_3$ pores and nanotubes](image)

Figure 2-7 (a): The inner part of anodic Al$_2$O$_3$ pores consisting of an anion rich layer, and (b): schematic representation of inner and outer parts of anodic TiO$_2$ nanotubes (IST: inner shell tube; OST: outer shell tube; FRL: fluoride-rich layer) [27].

F$^-$ ions play a critical role in the formation of the anodic TiO$_2$ nanotube arrays. However, it was reported that the anodic TiO$_2$ nanotube arrays are successfully fabricated in Cl$^-$ or Br$^-$ ions containing electrolytes. This is because similar reaction occurs and forms water-soluble complexes. However, there are differences of anodization between in Cl$^-$ or Br$^-$ ions containing and in F$^-$ ions containing electrolytes. For example, growth rate in Cl$^-$ and/or Br$^-$ ions containing electrolytes is found to be much greater than that in F$^-$ ions containing electrolytes [43]. Moreover, growth behavior in aqueous and viscous electrolytes seems to be the opposite of that in F$^-$ ions containing electrolytes [44].
2.3.3 Three generations of anodic TiO$_2$ nanotube arrays

In early stages of the anodic TiO$_2$ nanotube arrays, three generations were classified according to the aspect ratio [45]. The so-called first generation of TiO$_2$ nanotube arrays, which had a limited length around 500 nm, was obtained in hydrofluoric acid based electrolytes [20, 46]. The limitation of the aspect ratio is ascribed to a high rate of the chemical dissolution of the formed TiO$_2$. This is because the thickness of the TiO$_2$ layer is essentially the result of an equilibrium between the electrochemical formation of TiO$_2$ at the bottom and the chemical dissolution of TiO$_2$ in the F$^-$ ions containing solution [40]. Anodic TiO$_2$ nanotube arrays with length up to several micrometers, which were called the second generation of nanotube, were produced through controlling the self-induced acidification at the pore bottom, as shown in Figure 2-8 [28, 40, 47]. Using a buffered neutral solution as the electrolyte and adjusting the anodic current flow, acidic condition was created at the pore bottom while higher pH values were established at the pore mouth as a resulting of migration and diffusion effects of the pH buffer species (for example NH$_4$F, (NH$_4$)$_2$SO$_4$) [40]. The steady-state current and the desired pH profile were achieved through a voltage-sweep technique. Anodic TiO$_2$ nanotube arrays with aspect ratio up to more than one hundred, the so-called third generation of nanotubes, were obtained through controlling the local concentration fluctuations and pH burst in viscous electrolytes [45, 48]. In view of the anodic current transients, it was found that regular current oscillations occurred during anodization of Ti in an aqueous solution. This phenomenon is attributed to the ridges on the nanotube walls and the variations in the wall thickness, which is interpreted by the fact that every current transient was accompanied by a pH burst at the pore tip. To balance local acidification, control of diffusion is a good choice and suppressing pH bursts to damp the fluctuations was employed through decreasing the diffusion constant of ions. Considering the Stokes-Einstein relation:

$$D = \frac{k_BT}{6\pi\eta a}$$

(2-8)
where $k_B$ is Boltzmann’s constant, $T$, the absolute temperature, $\eta$, the dynamic viscosity and $\alpha$ is the radius of a spherical body, increase of viscosity results in low diffusion constant. So the electrolytes with high viscosity electrolyte such as glycerol, ethylene glycol (EG) were used [45]. Using electrolytes with high viscosity, anodic TiO$_2$ nanotube arrays with very smooth wall and high aspect ratio were fabricated. As a result of change in the diffusion behavior and the improved confinement of the acidic area at the pore tip, anodic TiO$_2$ nanotube arrays with thickness up to 7 $\mu$m were achieved [45]. Soon thereafter, anodic TiO$_2$ nanotube arrays with thickness over 100 $\mu$m were fabricated in electrolytes with water content less than 5 wt % or non-aqueous solutions [29, 49]. Recently, TiO$_2$ nanotube arrays with thickness up to 1000 $\mu$m, which aspect ratio reaches about 10000:1, was synthesized in NH$_4$F + EG electrolyte with a small amount of water [50].

![Figure 2-8](image)

Figure 2-8 Schematic diagram of tuning the electrochemical conditions to achieve high-aspect-ratio structures. (a): schematic representation of dissolution reactions and mechanism, (b): pH profile within a pore, (c): dissolution-rate profile within a pore wall, and (d): experimental determination of the dissolution rate, $R_{\text{diss}}$, of anodic TiO$_2$ depending on the pH value [40].

2.3.4 Pore size and wall thickness controlling

The geometries of the anodic TiO$_2$ nanotube arrays including pore size and wall thickness can be tailored in a wide range [51]. It was demonstrated that the pore size could be varied from 12 nm [52] to 242 nm [49] and the outer diameters could be tuned from 48 nm [53] to 256 nm [29]. The wall thickness could also be varied from 5 nm [52] to 34 nm [54] while the tube-to-tube spacing could be tuned from several tens of nanometers to effectively nothing.
The pore size or tube diameter is found to be dependent almost linearly on the applied potential [55]. TiO$_2$ nanotube arrays with pore size from 10 to 250 nm were achieved at the anodization potentials range of 1-45 V in an HF/H$_3$PO$_4$ aqueous solution [55, 56]. However, it is interesting that the anodic TiO$_2$ nanotube arrays were obtained even at applied potentials as low as 1 V, although the surface morphology showed a web like structure rather than a clear tubular morphology [24]. The tunable behavior of diameter makes the anodic TiO$_2$ nanotube arrays suitable for applications where the tube diameter is required to be tailored for specific use.

The wall thickness of the anodic TiO$_2$ nanotubes was tailored through controlling electrolyte temperature. It was demonstrated that the wall thickness could be tailored in the range of 9 to 34 nm when electrolyte temperature was changed from 50 °C to 5 °C, as illustrated in Figure 2-9 [54]. This is ascribed to the chemical etching process being functions of the electrolyte temperature.

![Figure 2-9 Diagram representation of relationship between wall thickness and electrolyte temperature.](image)

2.3.5 Influences of anodization time on morphology of anodic TiO$_2$ nanotube arrays

The effect of ageing or duration of anodization on the morphology of the anodic TiO$_2$ layer is limited. Generally, duration of anodization determines thickness of the anodic TiO$_2$ nanotube arrays if other electrochemical parameters are kept constant. However, it was found that there is a maximum thickness of TiO$_2$ nanotube arrays...
obtained by anodization in an aqueous solution, which is attributable to an equilibrium between the tube growth at bottom and the chemical/electrochemical dissolution at top when a steady-state condition reaches [57]. To obtain a long nanotube, low dissolution is necessary thus typically low electrolyte acidity and low Fions concentration are desired. In acidic electrolyte, typical only a few percent of current efficiency for tube growth was reported [58]. In neutral [59] or alkaline [60] electrolytes considerable longer nanotube was obtained. Different behavior was observed for anodization in a non-aqueous electrolyte or an organic solution with a small amount of water, indicating that the length of the TiO2 nanotube arrays keeps increasing when the anodization lasts. For example, nanotube with length up to 1000 μm was fabricated through anodization in an organic solution with small amount of water for 216 h [50].

Other phenomena such as thinning of nanotube walls, “grassy” remnants on the top of nanotube arrays were observed when duration of anodization process lasted for a long time. However, the influence of duration of the anodization process on the morphology of the TiO2 layer is still limited. It is significant to investigate the effects of duration of the anodization process on morphology and properties of the TiO2 layer.

2.3.6 Advanced geometries of anodic TiO2 nanotube

Apart from TiO2 nanotube arrays, advanced geometries including nanobamboo, nanolace, branched tube, double walled nanotubes and ordered porous TiO2 were fabricated through precisely controlling electrochemical parameters as well as electrochemical process. Bamboo-type nanotubes [32], nanolace [32], branched nanotubes, inter-tubes and multilayer nanotubes [61] were obtained through altering the applied voltage. Bamboo-tubes were observed when the applied voltage was pulsed put between two level, as shown in Figure 2-10a. The nanolace structure was obtained through extended etching of the bamboo, as shown in Figure 2-10b. Double walled TiO2 nanotubes, as shown in Figure 2-10c, was obtained by a suitable annealing treatment [39]. The anodic TiO2 nanotube arrays with improved degree of
order were obtained through employing of titanium with high purity or repeating anodization of titanium [62, 63]. Fascinating surface morphology of anodic nanotube arrays with high degree of order, as shown in Figures 2-10d and 2-10e, was fabricated through so-called self-templating method, in which anodization started from the metallic titanium substrate after removal pre-anodized TiO$_2$ nanotube arrays [63].

![Figure 2-10 Advanced geometries of TiO$_2$ nanotubes, (a): bamboo type nanotubes [32] (Figure reprinted with permission from Sergiu et al. Copyright (2008) Wiley-VCH), (b): nanolace [32] (Figure reprinted with permission from Sergiu et al. Copyright (2008) Wiley-VCH), (c): double walled nanotubes [39] (Figure reprinted with permission from Albu et al. Copyright (2008) Wiley-VCH), (d): nanotube](image)
2.3.7 Properties of anodic TiO$_2$ nanotube arrays

*Crystallization of the as-prepared anodic TiO$_2$ nanotube arrays*

Now it was found that the as-prepared anodic TiO$_2$ nanotube arrays typically are amorphous. Thermal treatments above 300 °C converts the amorphous material to anatase, or a mixture of anatase and rutile [39, 64, 65]. However, a complete conversion to pure rutile has not been achieved up to now. This is because conversion to rutile requires heat treatment at an elevated temperature, while annealing at around 700 °C results in significant morphologies deterioration. When annealed in an oxygen ambient, the nanotube walls were found to be transformed to anatase phase, while the barrier layer were converted to rutile [65, 66]. Investigation by XRD and HRTEM revealed that the nanotube was polycrystalline whereas entire truly single crystalline nanotubes have never been found.

In contrast to anatase, rutile has a minimum free energy so it is more thermodynamically stable. To convert anatase to rutile, annealing at high temperature is necessary. However, the temperature at which such conversion happened to rutile depended on serverl factors such as the presence of impurities, feature size, texture, sand strain. Morphologies deterioration was usually observed after sintering process due to nucleation-growth type of phase transformations if the annealed temperature was too high [67].

The properties of the anodic TiO$_2$ nanotube arrays depend heavily on their crystallization, and hence the applications vary for TiO$_2$ with different phases. In general, anatase is preferred in charge-separating devices such as DSSCs and photocatalysis whereas the rutile TiO$_2$ is usually used for gas sensors. This is because the anatase exhibits a significantly greater carrier mobility than rutile [68], which makes it suitable for photoelectrochemical appllications. The requirement of annealing to induce crystallization transition limits utilization them as
temperature-sensitive materials and other applications, hence direct formation of crystallized anodic TiO$_2$ nanotube arrays without post-annealing treatment is desired. Recently, approach for anodic formation of crystalline (anatase) TiO$_2$ nanotube arrays without post-annealing treatment is developed through anodization of a pre-treated crystalline TiO$_2$ layer [69]. However, the limitation of this method is that it is hard to obtain long crystalline TiO$_2$ nanotube. More recently, it was reported that polyol electrolytes (such as diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol) as well as the applied potential were employed to induce sort of crystallization the anodic TiO$_2$ nanotube arrays [70, 71].

**Chemistry and doping**

The chemical composition of the as-prepared anodic TiO$_2$ nanotube arrays was investigated and it was found that a considerably high amount (5 at %) of F$^-$ ions was detected. This “doping” results from incorporation of anions from the electrolyte during anodization process [72]. The bulk properties of the as-formed layer such as mobility of ions, conductivity, dielectric properties, growth rate, corrosion process and optical properties, were found to be influenced by the “doing” effect [73]. The fluoride content was found to be significantly reduced through watering the nanotubes for sufficient time or through thermal annealing [59]. Annealing treatemnt at around 300 °C led to almost complete loss of the fluorides [74].

Deliberate doping of the anodic TiO$_2$ nanotube arrays was extensively investigated to modify the electronic properties so that photoelectrochemical applications can be extended to visible light. Doping of the anodic TiO$_2$ nanotube arrays by transition metals and non-metal elements was investigated through various methods. Carbon-doped anodic TiO$_2$ nanotube arrays was synthesized through reduction of carbon monoxide [75], acetylene reduction [76], treatment at 500 °C under a mixed flux of nitrogen and acetylene, or flame annealing process [77]. Sonoelectrochemical anodization method using an ethylene glycol-ammonium fluoride solution and annealing the as-prepared sample under reducing atmosphere
(H₂), led to conversion the amorphous nanotubes to anatase phase and doping with the carbon simultaneously [78]. Nitrogen-doping was also investigated to narrow the band gap. The approaches to doping TiO₂ with nitrogen included nitrogen/hydrogen gas plasma treatment, annealing in ammonia gas [79], N-ion bombardment [80], or in situ anodization doping process [81].

**Photoelectrochemical properties of the anodic TiO₂ nanotube arrays**

The photoresponse property of the anodic TiO₂ nanotube arrays results from their semiconductor nature. Typical photocurrent characteristics for the as-prepared and the annealed anodic TiO₂ nanotube arrays are shown in Figure 2-11 as IPCE (incident photon-to-current conversion efficiency: IPCE)-plots [64]. The indirect band gap of the material is determined from the \( \text{IPCE} \ hν^{1/2} \) vs. \( hν \) plots, as shown in inset of Figure 2-11. The strong enhancement of IPCE of the annealed anodic TiO₂ nanotube arrays compared to that of the as-prepared samples was ascribed to nanotube walls conversion from amorphous to anatase. In view of the as-prepared sample, it was found that most of the photocurrent was generated at the bottom of the TiO₂ nanotubes and contributions of the nanotube walls were negligible because amorphous structures contain a high number of defects that led to a high carrier recombination rate [64].

![Figure 2-11 Photocurrent spectra recorded for the as-prepared and the annealed (450]
anodic TiO$_2$ nanotube arrays, an example of the band gap energy ($E_g$) evaluation is given as an inset [24]. (Figure reprinted with permission from Macak et al. Copyright (2007) Elsevier).

Compared to nanoparticulate based TiO$_2$ layer, the anodic TiO$_2$ nanotube arrays are expected to exhibit different photoelectrochemical properties, which can be described as following [27]:

i) a much lower degree of distorted crystal structures at grain boundaries that enhance electron scattering (reducing the electron mobility);

ii) smooth tube walls that may provide a lower surface state density—thus reducing surface state recombination effects; and

iii) suppression of an extensive random walk path through a porous network due to the 1D nature of the tube.

However, the photoresponse of the anodic TiO$_2$ nanotube arrays is found to depend strongly on the following two competing factors [24]:

i) the longer the nanotubes, the higher the total light absorption; and

ii) the longer the tubes, the higher the recombination loss.

Although the influence of nanotube structures on the photoelectrochemical properties was extensively investigated, the optimized geometry (length, diameter, wall thickness) of the anodic TiO$_2$ nanotube arrays for photoresponse is still limited. Moreover, the photoelectrochemical properties of anodic TiO$_2$ layers with advanced geometries are also limited.

2.4 Applications of anodic TiO$_2$ nanotube arrays

The unique physicochemical properties of the anodic TiO$_2$ nanotube arrays as well as their special morphologies, render these materials very promising for many applications. A summary of various applications of nanostructured titanates and TiO$_2$ was provided in reference [21].

In principle, any applications where TiO$_2$ in solid/compact or powder form is currently used as listed in Table 2-1, may be a potential application for the anodic TiO$_2$ nanotube arrays. In many of these applications the defined architecture of the
nanotube arrays brings specific advantages. Here lists some applications of the anodic TiO$_2$ nanotube arrays including electrochromic effect, biomedical applications, sensor, photocatalysis, support for supercapacitor, and photoanode of dye-sensitized solar cells.

Table 2-1 Potential applications of titanate and TiO$_2$ nanotubes [21]

<table>
<thead>
<tr>
<th>Application</th>
<th>Example</th>
<th>Utilized properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst support</td>
<td>Au/TiO$_2$, CO oxidation, Ru(III)/TiO$_2$</td>
<td>Ion-exchange capacity, mesoporous, strong metal-support interaction,</td>
</tr>
<tr>
<td>Photocatalysis</td>
<td>CdS/TiO$_2$, Zn$^{2+}$/TiO$_2$, oxidation reaction</td>
<td>Photocatalytic activity, interfacial charge transfer</td>
</tr>
<tr>
<td>Electrocatalysis</td>
<td>Pd/TiO$_2$, oxidation methanol, RuO$_2$/TiO$_2$, reduction CO$_2$</td>
<td>Mesoporous morphology, Electrical conductivity</td>
</tr>
<tr>
<td>H$_2$ storage and separation</td>
<td>Sorption of hydrogen in pore of TiO$_2$ nanotubes</td>
<td>Slit pores, OH groups</td>
</tr>
<tr>
<td>H$_2$ sensing</td>
<td>Anodic TiO$_2$ nanotube arrays</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>Lithium batteries</td>
<td>Negative electrode for rechargeable Li cells</td>
<td>Effective transport of Li, Electrical conductivity</td>
</tr>
<tr>
<td>Photovoltaic cells</td>
<td>Dye-sensitized solar cells</td>
<td>Semiconductor, Electrical conductivity</td>
</tr>
</tbody>
</table>

Anodic TiO$_2$ nanotube arrays were employed as electrochromic material due to their semiconductor nature with a lattice structure that allows easy proton or Li$^+$ ion intercalation. The insertion procession of TiO$_2$ is accompanied by a reduction process, which is described as:

$$\text{TiO}_2 + M^+ + xe^- \leftrightarrow MTiO_2$$

(2-9)
where \( M \) can be H or Li. The formation of Ti\(^{3+}\) species results in a color change. The anodic TiO\(_2\) nanotube arrays were found to exhibit a very high electrochromic effect as well as high switching speed and to be more stable against cycling deterioration than layers made of nanoparticles [82].

Titanium and its alloys were used for biomaterial for a long time due to their good mechanical properties and biocompatibility [5]. Recently, the anodic TiO\(_2\) nanotube arrays are extensively investigated for biomedical applications, which mainly stems from their unique architecture and excellent biocompatibility. Anodic TiO\(_2\) nanotube arrays were found to successfully enhance interaction between implant and tissue. Recent work indicated that growth behavior of hydroxyapatite was significantly enhanced on anodic nanotubular surfaces [83] or implant alloys such as Ti6Al4V or Ti6Al7Nb. Interaction of living cells with anodic TiO\(_2\) nanotube arrays attracted much interest in the past few years. Adhesion, spreading and growth of stem cells were found to depend dramatically on the pore size of the TiO\(_2\) nanotube arrays [84]. Recently, anodic TiO\(_2\) nanotube arrays were found an application for drug delivery and controlled release due to their tubular structure [85].

The anodic TiO\(_2\) nanotube arrays were used as an electrode for photocatalytic water splitting. The production of hydrogen (H\(_2\)) and oxygen (O\(_2\)) through the photocatalytic decomposition of water under solar light illumination receives a great deal of attention due to increasing energy demand and decreasing traditional energy resources. Although there are many methods to generate hydrogen, photoelectrolysis is often considered as a promising approach which may put the hydrogen in the hydrogen economy. Pioneering work of photocatalysis on TiO\(_2\) material was initiated by Fujishima and Honda in 1972, reporting the first photo-assisted production of H\(_2\) and O\(_2\) from water utilizing a photoelectrochemical cell [86]. The special geometry of the anodic TiO\(_2\) nanotube arrays provided large effective surface area in close proximity with the electrolyte, reducing the recombination of photogenerated holes with electrons, thus significantly enhancing the quantum yield efficiency. Hydrogen generation rate of 7.6 mL.h\(^{-1}\), equivalent to 80 mL.W\(^{-1}\).h\(^{-1}\) (for
1 cm² electrode area under 98 mW.cm⁻² illumination with wavelength 320~400 nm) with a photoconversion efficiency of 12.25 % was obtained using the anodic TiO₂ nanotube arrays [87]. The conversion efficiency for water-splitting application was found to be controlled mainly by the wall thickness of the TiO₂ nanotube arrays [54]. An enhanced photoconversion efficiency of 16.25 % was achieved using anodic TiO₂ nanotube arrays of 45 μm in length under UV illumination [29]. Visible light induced water-photoelectrolysis using the anodic TiO₂ nanotube arrays was also studied and hydrogen generation rate of 175 μL.h⁻¹ with a conversion efficiency of 0.6 % was obtained [88].

2.4.1 TiO₂ used as photocatalyst

Human are faced with a tremendous set of environmental problems related to the remediation of hazardous wastes, contaminated groundwaters, and the control of toxic air contaminants. Heterogeneous photocatalyst has received great attention as an alternative method for air and water purification due to its strong oxidizing power under UV illumination since 1972 [86]. When the heterogeneous photocatalyst is irradiated by UV light, the absorbed organic compounds and micro-organisms in air and wastewaters such as herbicides, pesticides, aliphatics, aromatics, polymers and dyes, can be either totally or partially decomposed and mineralized to carbon dioxide, water and mineral acids via direct oxidation or via photo-generated holes or OH radicals [89]. In comparison to traditional oxidation approaches, heterogeneous photocatalysis takes advantages of the following characterizations: completely decomposition of waste into carbon dioxide and water and mineral acids; taking place at ambient temperature and pressure; without special oxygen necessary; low cost, easily available and repeatable of photocatalytic materials; without waste disposal problem [90]. Including TiO₂, a large range of semiconductors are investigated for heterogeneous photocatalysis, such as ZnO,WO₃, Fe₂O₃, CdS, SrTiO₃. In general, the ideal photocatalyst must have the following properties: high photoactivity, biological and chemical inertness, stability toward photocorrosion, suitability towards visible or near UV light, low cost, and lack of toxicity [91].
Among these photocatalytic materials, TiO$_2$ is regarded as the most efficient and environmentally benign photocatalyst. Moreover, TiO$_2$ is also a promising material for antibacterial application, even killing tumor cells. In the past three decades, studies including interpretations of fundamental mechanism, enhancements of photocatalytic efficiency and applications of TiO$_2$ in environmental remediation have been extensively conducted.

Photocatalytic processes include following four behaviors: generation of electron-hole ($e_{cb}^- - h_{vb}^+$) pairs, recombination of electron-hole pairs, charge-carrier trapping and photocatalytic degradation. When photons with energy higher or equal to the band gap energy of TiO$_2$ ($E_g = 3.2$ eV for anatase [68, 92], $3.0$ eV for rutile [93], and $3.2$-$3.5$ eV for amorphous [94]) are absorbed by the photocatalyst, electrons are promoted from the valance band (VB) to the conduction band (CB) with simultaneous generation of a hole ($h^+$) in the VB. Some of the $e_{cb}^- - h_{vb}^+$ pairs recombines on the surface or in the bulk of the TiO$_2$ in a few nanoseconds and heat energy is dissipated. Moreover, some of electrons and holes are trapped at surface or bulk of the TiO$_2$. The trapped holes are detected as O$^-$ species, generated from lattice O$_2^-$ in the VB, while the electrons are witnessed either as Ti$^{3+}$ species or as electrons captured in the CB [95]. It was demonstrated that the lifetime of the trapped charge carrier depends on the ambient temperature [95]. Some of the charge carriers migrates to surface and reacts with donor (D) or acceptor (A) species absorbed or close to the surface of TiO$_2$. Subsequently, anodic and cathodic redox reactions occur, as shown in Figure 2-12. The characteristic times of these dynamic processes, including generation of electron-hole pair, charge-carrier trapping, charge-carrier recombination and interfacial charge transfer are given in Table 2-2 [90].

The photodegradation process usually involves one or more radicals or intermediate species such as $\cdot$OH, O$_2^-$, H$_2$O$_2$, or O$_2$, playing an important role in the photocatalytic reaction. It was demonstrated that the photocatalytic activity of a semiconductor is largely controlled by the following properties: the light absorption properties, reduction and oxidation rates on the surface by the electron and hole, and the electron-hole recombination rate.
The ability of TiO₂ to undergo photoinduced electron transfer to absorbed species on its surface is governed by the band energy positions of the semiconductor and the redox potentials of the adsorbate. The relevant potential level of the acceptor species is thermodynamically required to be below (more positive than) the CB potential of the semiconductor. The potential level of the donor is required to be above (more negative than) the VB position of the semiconductor in order to donate

**Table 2-2 Dynamic processes and characteristic times of photocatalysis** [90]

<table>
<thead>
<tr>
<th>Dynamic process</th>
<th>Characteristic times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation of electron-hole pair</td>
<td>fs</td>
</tr>
<tr>
<td>Charge-carrier trapping</td>
<td></td>
</tr>
<tr>
<td>$h^*_b + \rightarrow Ti^{IV}OH \rightarrow { &gt; Ti^{IV}OH }^+$</td>
<td>fast (10 ns)</td>
</tr>
<tr>
<td>$e^*_{cb} + \rightarrow Ti^{IV}OH \leftrightarrow { &gt; Ti^{III}OH }$</td>
<td>shallow trap (100 ps)</td>
</tr>
<tr>
<td>$e^*_{cb} + \rightarrow Ti^{IV} \rightarrow Ti^{III}$</td>
<td>deep trap (10 ns)</td>
</tr>
<tr>
<td></td>
<td>(dynamic equilibrium)</td>
</tr>
<tr>
<td></td>
<td>(irreversible)</td>
</tr>
<tr>
<td>Charge carrier recombination</td>
<td></td>
</tr>
<tr>
<td>$e^*_{cb} + { &gt; Ti^{IV}OH }^+ \rightarrow Ti^{IV}OH$</td>
<td>slow (100 ns)</td>
</tr>
<tr>
<td>$h^*_b + { &gt; Ti^{III}OH } \rightarrow Ti^{IV}OH$</td>
<td>fast (10 ns)</td>
</tr>
<tr>
<td>Interfacial charge transfer</td>
<td></td>
</tr>
<tr>
<td>${ &gt; Ti^{IV}OH }^+ + Red \rightarrow Ti^{IV}OH + Red^+$</td>
<td>slow (100 ns)</td>
</tr>
<tr>
<td>$e^-_{\text{red}} + O_X \rightarrow Ti^{IV}OH + O_X^+$</td>
<td>very slow (ms)</td>
</tr>
</tbody>
</table>
an electron to the vacant hole [96]. The band-edge positions of several semiconductors including TiO₂ are presented in Figure 2-13. The positions were derived from the flat band potentials in a contact solution of aqueous electrolyte at pH = 1. Generally, the pH of the electrolyte solution influences the band edge positions of these various semiconductors compared with redox potentials for the adsorbate.

To date, three generations of TiO₂ based photocatalyst are developed, i.e., pure TiO₂ nanomaterials, metal-doped TiO₂ nanomaterials and nonmetal-doped TiO₂ nanomaterials [97]. The first generation utilizes the high surface-to-volume ratio and high surface reaction activity of nanocrystalline TiO₂ to enhance the catalytic activity. Furthermore, the increase in the band gap energy with decreasing nanoparticle size potentially enhances the redox potential of the VB holes and the CB electrons, allowing for photoredox reactions [97]. Generally, it is believed that the nanostructured TiO₂ results in improvement of photocatalytic efficiency [98]. However, there is conflicting result indicating that the nanostructured TiO₂ is less photoactive than their bulk-phase counterparts due to surface defect density [99]. One obvious disadvantage of pure TiO₂ nanomaterials is limited light absorption, which is a small percentage of sunlight (~ 3 %). To utilize the visible light of the solar spectrum, doping with metal ions such as Fe³⁺, Mo⁵⁺, Ru³⁺, Os³⁺, Re⁵⁺, V⁴⁺, Rh³⁺, Co³⁺ and Al³⁺, has been extensively investigated over the past decades. However, doping with cations was found to exhibit both positive and negative effects on the photocatalytic activity [100]. A number of authors claimed that metal ions decreased the photothreshold energy of TiO₂ but served as a recombination center for electrons and holes [101]. Nonmetal-doped TiO₂ nanomaterials, which are regarded as the third generation photocatalyst, are demonstrated to be the most promising visible light photocatalyst [97]. Various nonmetal elements including nitrogen, carbon, sulfur, phosphorus and fluorine are investigated for visible light photocatalytic application. The idea of doping TiO₂ materials with nitrogen and other nonmetal species was first presented in 2001 [102], in which theoretical results from the substitution of N, C, or S for oxygen atoms in the TiO₂ lattice were
reported. Among these nonmetal elements-doped TiO\textsubscript{2}, N-modified TiO\textsubscript{2} in particular receives considerable attention. Nowadays, three methods are developed to synthesize N-doped TiO\textsubscript{2}, namely, sputtering and implantation technique, high-temperature sintering of TiO\textsubscript{2} under nitrogen-containing atmospheres generated by nitrogen compounds including ammonia and urea, and sol-gel method. However, it is still controversial about the mechanism governing the increase of photocatalytic efficiency under visible light illumination. Density of states (DOS) calculations for anatase TiO\textsubscript{2} suggested that substitutional-type doping (interstitial type doping and a mixture of both substitutional and interstitial type were both found to be ineffective) using nitrogen was effective due to the mixing of N\textsubscript{2p} states with O\textsubscript{2p} states, thus led to a significant decrease in the width of the overall band gap [100]. Results obtained by \textit{ab initio} band calculations indicated that band gap narrowing due to the S doping originated from mixing the S\textsubscript{3p} states with valence band led to an increase in the VB width [103]. It was found that both band gap narrowing and the overlap between the O\textsubscript{2p} state and dopant-introduced states were responsible for the enhanced photoactivities of the anion-doped TiO\textsubscript{2} materials using similar \textit{ab initio} electronic-structure method [104].

![Figure 2-13 Relative dispositions of various semiconductor band edge positions shown both on vacuum scale and with respect to the standard hydrogen electrode](image-url)
The photocatalytic efficiency of TiO$_2$ depends heavily on its morphologies and phase compositions. This is because TiO$_2$ with high aspect surface area provides lots of reaction sites at solid/liquid interface as well as light absorption. Furthermore, optimal architecture of TiO$_2$ reduces the photo-generated carrier recombination. The anodic TiO$_2$ nanotube arrays are excepted to be a promising photocatalyst due to their special geometries. It was demonstrated that the anodic TiO$_2$ arrays exhibited greater photocatalytic efficiency than commercially available Degussa P25 film. Provided the photocatalysis process was activation- or diffusion-controlled [106] as well as depending on the location of the reactive site within the nanotube structure, it was ascribed to these following factors [107]:

i) The TiO$_2$ nanotube provides an optimized geometry with significantly shorter carrier-diffusion paths in the tube walls (10-15 nm [64]), including lower trapping and recombination kinetics of photo-generated e$_{cb}^-$ - h$_{ob}^+$ pairs comparing to Degussa P25 layer; and

ii) The tubular geometry provides a short (straight) diffusion path for dye molecules from the solution to the active surface area, whereas the convoluted porous structure in the Degussa P25 layer contains a broad spectrum of diffusion paths (including very long diffusion lengths).

However, these descriptions were doubted due to lack of experimental evidence [108]. Although no direct support was found, it was demonstrated that the half life of the photogenerated hole of the TiO$_2$ nanotubes was significantly longer as compared to that of TiO$_2$ nanoparticles [109]. Investigation by time-resolved diffuse reflectance spectroscopy demonstrated that remarkably long-lived radical cations of the substrate and trapped electron of TiO$_2$ nanotubes were observed compared with those of TiO$_2$ nanoparticles [110]. Furthermore, a higher diffusion length of charge carriers was claimed to result in the higher efficiency of electron transport in TiO$_2$-nanotube electrodes compared with analogous electrodes of TiO$_2$ nanoparticles, as shown in Figure 2-14 [111]. Moreover, it was reported that the TiO$_2$ nanotube
arrays geometry offered the ability to influence the absorption and propagation of light through the architecture by precisely designing and controlling the architectural parameters including diameter, wall thickness, and length [29, 112].

It was demonstrated that the photocatalytic activity of the anodic TiO$_2$ nanotube arrays was enhanced by noble metal deposition onto the layers [113] or by applying an external bias [114]. More recently, advanced applications including cancer killing [115], photoinduced release of active proteins [116], were investigated.

![Figure 2-14 Schematic representation of the advantages derived from the use of TiO$_2$ nanotube, the aspect ratio favors the photocatalytic activity [108].](image)

Although there are a number of examples indicating the outstanding photocatalytic activity of the anodic TiO$_2$ nanotube arrays, the specific features of photocatalytic are still limited and more examples are desired. The influence of geometries and compositions on the photocatalytic efficiency is still unclear and there is plenty of room using the anodic TiO$_2$ nanotube arrays for photocatalytic applications. Futhermore, the photocatalytic activity of the anodic TiO$_2$ layers with advanced geometries is also exxcepted to be interpreted.

2.4.2 TiO$_2$ used as a support in supercapacitor

Electrochemical capacitors, also known as supercapacitors or ultracapacitors, are devices having higher specific energy densities than conventional dielectric capacitors and that possessing higher specific powers than most batteries. The
supercapacitor first appeared on the market in 1978, providing computer memory backup power [117]. Due to urgent need of sources providing power densities over 1 kW.kg⁻¹, energy densities over 5 Wh.kg⁻¹ (18 J.g⁻¹) or 11 Wh.L⁻¹ (39.6 J.cm⁻³) for a number of technologically important systems, supercapacitors have been extensively investigated and developed [118]. These systems include acceleration power for electric vehicles, electrical regenerative braking storage for electric drive systems, power assist to hybrid vehicles, starting power for fuel cells, plus power for mobile telecommunications and other electronic devices that require high power to operate.

Traditional dielectric capacitors (including electrolytic capacitors or metalized layer capacitors) provide power densities many times over 1 kW.kg⁻¹ and exhibit very long cycle life (> 10⁶), but they show low energy densities. The rechargeable batteries provide high energy density but low power densities and short cycle life (< 10⁴). The supercapacitors provide the best opportunity to meet both the power and the energy requirements. The reason why electrochemical capacitors receive considerable attentions are visualized in Figure 2-15, in which typical energy storage and conversion devices are presented in the so called “Ragone plot (that is, the plot of volumetric against gravimetric energy density [119])” in terms of their specific energy and specific power. In addition, when supercapacitors are coupled with batteries, they can reduce the peak power requirement, prolong the life times and reduce the energy requirement (or the size) of the battery. Although today’s lithium-ion batteries are improved greatly, they still require 3~5 min for charging, versus ~1 s for a supercapacitor. Another advantage of supercapacitor is their safety comparing with lithium-ion batteries during high rate charge and discharge processes [117]. The comparison of batteries, capacitors and supercapacitors is given in Table 2-3.

In view of supercapacitors, two kinds of energy-storage mechanisms are used: the electrochemical double layer capacitors (EDLCs), where the charge storage is electrostatic in nature, and the redox-capacitors, where the charge implies a Faradic process, or a partial Faradic transfer, such as electrosorption or a redox process involving the electroactive materials [120]. For the former, energy storage is
electrostatic and the electrodes are high surface area porous materials, in which the capacitance arises from charge separation at the interface between the solid electrode surface and the liquid electrolyte. For the latter, fast Faradaic charge transfers occurs at the electrode materials, as in a battery, and gives rise to what is called pseudo-capacitance. The pseudo-electrochemical capacitance involves voltage-dependent Faradaic reactions between the electrode and the electrolyte, either in the form of surface adsorption/desorption of ions, redox reactions with the electrolyte, or doping/undoping of the electrode materials. Due to the charge-discharge mechanism involving all the active mass and not only the surface, the obvious advantage of the redox supercapacitor is that its specific capacitance is much greater than that of EDLCs [121].

![Figure 2-15 Simplified Ragone plot of the energy storage domains for the various electrochemical energy conversion systems compared to an internal combustion engine and turbines and conventional capacitors [122]. (Figure reprinted with permission from Kotz and Carlen. Copyright (2000) Elsevier).](image)

Commonly EDLCs store the electric energy in an electrochemical double layer (Helmholtz Layer) formed at a solid/electrolyte interface. Positive and negative ionic charges within the electrolyte accumulate at the surface of the solid electrode and compensate for the electronic charge at the electrode surface. The thickness of the double layer is found to depend strongly on the concentration of the employed
electrolyte and on the size of the ions and it is in the order of 5-10 Å for a concentrated electrolyte. The EDLC is about 10-20 μF.cm⁻² for a smooth electrode in concentrated electrolyte and can be estimated according to:

\[ C = \frac{A\varepsilon}{d} \]  

(2-10)

where \( C \) is capacitance, \( A \), the surface-area, \( \varepsilon \), the dielectric constant of the electrical double-layer region, and \( d \) is the thickness of the electrical double layer.

Table 2-3 Energy storage component property comparisons [123].

<table>
<thead>
<tr>
<th></th>
<th>Capacitors</th>
<th>EDLCs</th>
<th>Batteries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density (Wh.kg⁻¹)</td>
<td>0.1</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>Power density (W.kg⁻¹)</td>
<td>( 10^7 )</td>
<td>3000</td>
<td>100</td>
</tr>
<tr>
<td>Time of charge (s)</td>
<td>( 10^{-3} \sim 10^{-6} )</td>
<td>0.3–30</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Time of discharge (s)</td>
<td>( 10^{-3} \sim 10^{-6} )</td>
<td>0.3–30</td>
<td>1000–10000</td>
</tr>
<tr>
<td>Cyclability</td>
<td>( 10^{10} )</td>
<td>( 10^6 )</td>
<td>1000</td>
</tr>
<tr>
<td>Typical lifetime (years)</td>
<td>30</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>&gt;95</td>
<td>85–98</td>
<td>70–85</td>
</tr>
</tbody>
</table>

In contrast to conventional capacitors which exhibit total capacitance in range of pF or μF, the capacitance of the EDLCs is rather high [122]. A simple schematic representation of carbon electrode and the electrolytic solution is shown in Figure 2-16. Each electrode is treated as a single capacitor of capacitance \( (C_1) \) or \( (C_2) \) and the total capacitance is described as:

\[ \frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \]  

(2-11)

The interpretation of EDLCs goes mainly through three stages [124]. The first model was developed by von Helmholtz in the 19th century, as shown in Figure 2-17a, stating that two layers of opposite charge form at the electrode/electrolyte interface and distribute in atomic distance. This simple model was further developed
by Gouy and Chapman based on consideration of a continuous distribution of electrolyte ions (both cations and anions) in the electrolyte, driven by thermal motion, which was referred to as the diffuse layer, as shown in Figure 2-17b. However, the Gouy-Chapman model results in an overestimation of the electronic double layer capacitance. This is because the capacitance of two separated arrays of charges increases inversely with their separation distance, causing a very large capacitance value in the case of point charge ions close to the electrode surface. On the basis of the Helmholtz model and Gouy-Chapman model, Stern recognized two regions of ion distribution—the inner region (which is named as the compact layer or Stern layer) and the diffuse layer, as shown in Figure 2-17c. In the inner layer, ions (very often hydrated) are strongly adsorbed by the electrode. Furthermore, the inner layer consists of specifically adsorbed ions (in most cases they are anions irrespective of the charge nature of the electrode) and non-specifically adsorbed counter-ions. The inner Helmholtz plane and outer Helmholtz plane are used to distinguish the two types of adsorbed ions.
Figure 2-17 Models of the electrical double layer at a positively charged surface, (a): the Helmholtz model, (b): the Gouy–Chapman model, and (c): the Stern model, showing the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). The IHP refers to the distance of closest approach of specifically adsorbed ions (generally anions) and OHP refers to that of the non-specifically adsorbed ions. The OHP is also the plane where the diffuse layer begins. $d$ is the double layer distance described by the Helmholtz model. $\varphi_a$ and $\varphi$ are the potentials at the electrode surface and the electrode/electrolyte interface, respectively [124].

The basic operation of a single-cell supercapacitor consisting of two electrodes is illustrated in Figure 2-18. $C_a$ and $C_c$ are the capacitance of the anode and cathode respectively (the specific capacitance of a single electrode reported in the literature is based on a three-electrode cell configuration). $R_s$ is the equivalent series resistance (ESR) of the cell. $R_F$ is the resistance responsible for the self-discharge of a single electrode and the notation for anode and cathode are $R_{Fa}$ and $R_{Fc}$, respectively.

Figure 2-18 A RC equivalent circuit representation illustrates the basic operation of a single-cell supercapacitor [124].

The energy stored in a capacitor is given by:
where \( C \) is the capacitance and \( U \) is the cell voltage. To improve the energy stored, the cell voltage should be enhanced for a capacitor. The maximum voltage of a supercapacitor depends strongly on the employed electrolyte. For aqueous medium, it is suggested the maximum operating voltage of a supercapacitor does not exceed 0.8 V (even if the thermodynamic stability window of water is 1.23 V) [125]. An organic medium based on a salt, e.g. TEABF4 (tetraethyl ammonium tetrafluoroborate) dissolved in an acetonitrile permits supercapacitor to be charged up to 2.0 V or 2.3 V. To increase working voltage range of supercapacitor, ionic liquids are employed, which are characterized by thermally stable salts synthesized by combining a bulky organic cations with different anions and characterized as high thermal stability and negligible vapor pressure [126]. However, ionic liquids often show high viscosity which complicates a good wetting behavior of mesoporous electrode. The high viscosity and low conductivity usually leads to slightly reduced performance of supercapacitor [125]. Moreover, the energy stored in supercapacitors depends on the double layer capacitance, the specific surface area of the respective electrode material, and the wetting behavior of the pores [122].

The power of a supercapacitor is given by [125]:

\[
P = \frac{U^2}{4R_c}
\]

(2-13)

where \( R_c \) stands for the ESR, which stems from various types of resistance such as the intrinsic electronic properties of the electrode matrix and the electrolyte, mass transfer resistance of the ions in the electrode material, and contact resistance between the current collector and the electrode material [124]. Clearly, simultaneous increase of capacitance as well as operating voltage and decrease of ESR are desired for a supercapacitor with high performance.

Experimentally, the specific capacitance can be investigated by charge-discharge characterization and it is calculated by the following equation:
\[ C_s = \frac{C}{S} = \frac{i \cdot t}{\Delta V \cdot S} \quad (2-14) \]

where \( I \) is charge-discharge current density, \( t \), discharge time, \( \Delta V \), corresponding potential window, and \( S \) is apparent surface area. Alternatively, the capacitance can be investigated by cyclic voltammetry at different scan rates and the specific capacitance \( C \) in F.g\(^{-1}\) is calculated as [127]:

\[ C = \frac{1}{mv(E_b-E_a)} \int_{E_a}^{E_b} I(E) dE \quad (2-15) \]

where \( m \) is the mass of the active material in the electrode, \( v \), the scan rate, \( E_a \) and \( E_b \), the integration limits of the voltammetric curve, and \( I(E) \) is the voltammetric charging current.

**Redox supercapacitors**

In contrast to EDLC which results from pure electrostatic charge accumulation at the electrode/electrolyte interface, pseudo-capacitance arises from thermodynamic reasons. This is because fast and reversible redox reactions between the electrolyte and electro-active species result in charge acceptance (\( \Delta q \)) and a change in potential (\( \Delta V \)). The derivative \( C = \frac{d(\Delta q)}{d(\Delta V)} \) corresponds to a capacitance. In view of an ideal EDLC, the capacitance \( (dq/dV) \) is constant and is independent of operating potential. In view of a redox supercapacitor, however, the charge transferred in the fast Faradic reactions is voltage dependent, leading to the pseudo-capacitance \( (C = \frac{d(\Delta q)}{d(\Delta V)}) \) also being voltage dependent [128]. To date, two classes of pseudo-capacitive materials are investigated and developed: the transition metal oxides and the conjugated conducting polymers.

Three types of electrochemical processes are utilized in the development of redox-supercapacitors, i.e., surface adsorption of ions from the electrolyte, redox reactions involving ions from the electrolyte, and the doping/undoping processes for conducting polymer materials [128]. The first two processes were primarily surface mechanism, indicating that the capacitance depends strongly on the surface area of
the electrode materials. Metal oxides such as NiO, IrO₂, MnO₂, V₂O₅, MoO₃, Co₃O₄, and RuO₂ show ideal pseudo-capacitance properties in aqueous or organic solutions. However, pseudo-capacitance and EDLC are hardly separated in most cases. It is now known that carbon-based EDLCs exhibit perhaps 1-5 % their capacitance as pseudo-capacitance due to Faradic reactivity of surface (edge) oxygen-functions. On the other hand, redox supercapacitors always exhibit some EDLC component to their electrochemically accessible interfacial areas-probably about 5-10 % [129].

*Nickel oxide and nickel hydroxide as supercapacitor electrode materials*

Nickel oxide (NiO) as well as nickel hydroxide (Ni(OH)₂) are extensively investigated for rechargeable batteries and supercapacitors, owing to their low cost, easy availability and comparable electrochemical behavior. NiO is a p-type semiconductor and has an indirect band gap of 3.55 eV. The capacitance of NiO stems from reversible electrochemical oxidation of the Ni atoms locating at the NiO/electrolyte interface in both aqueous and non-aqueous electrolytes [130]. It was shown that the redox potential for the electrochemical oxidation of NiO was pH-dependent in an aqueous electrolyte and depended on the type of cation in aprotic electrolytes, suggesting that the oxidation was coupled with desorption of protons or cations adsorbing at the surface oxygen atoms [130]. In a non-aqueous electrolyte, the type of cation was found to determine the shape and position of the cyclic voltammogram properties. Nowadays, it is commonly accepted that the reaction of Ni²⁺ to Ni³⁺ occurs at the surface of NiO according to [131]:

\[
\text{NiO} + \text{OH}^- \rightleftharpoons \text{NiOOH} + e^- \quad (2-16)
\]

Ni(OH)₂ is also a p-type semiconductor [132], with applications for electrode materials in alkaline rechargeable battery [133] and energy storage coupled with TiO₂ in photocatalysis [134]. The capacitance of the Ni(OH)₂ stems from reversible electrochemical oxidation which is described as [131]:

\[
\text{Ni(OH)₂} + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (2-17)
\]
However, the clear limitation of low capacitance made the NiO and Ni(OH)$_2$ very
difficult to substitute RuO$_2$ and IrO$_2$ for supercapacitors. Thus efforts have been
devoted to enhancing their reactivity, surface area and utilization efficiency. Several
methods such as chemical precipitation, electrodeposition and sol-gel techniques are
adopted to prepare NiO or Ni(OH)$_2$. The capacitances of the NiO prepared via
different methods are different due to its morphology.

Mesoporous NiO was prepared by a template method and a maximum
capacitance of 124 F.g$^{-1}$ was obtained, demonstrating that the modification of
morphology and microstructure of the active material could be a very feasible
approach for capacitance promotion [131]. Loading of NiO on TiO$_2$ nanotubes
prepared by a hydrothermal method was investigated and enhancement of
capacitance of NiO was obtained, which was attributable to strongly improve the
utilization of the electroactive material by the TiO$_2$ nanotubes [135]. This is because
the three dimensional TiO$_2$ nanotube network offers a solid support structure for the
NiO, allowing the electroactive material to be readily accessible for redox reactions,
and then increasing the efficiency of the active materials [135]. Polyhedron NiO
particle with high surface areas (179 m$^2$.g$^{-1}$) and narrow pore distributions was
synthesized by controlled thermal decomposition of the oxalate precursor and best
specific capacitance of 165 F.g$^{-1}$ was obtained [136].

*Ruthenium oxide as supercapacitor electrode materials*

RuO$_2$ exhibits a continuous redox activity over a wide voltage range and very
high, surface-area-independent capacitance, high conductivity, good electrochemical
reversibility, high power and energy density and long cyclic life [137]. The concept
and utilization of RuO$_2$ as a new interesting electrode material dated back to 1971
[138]. However, the high cost of ruthenium metal limited it except for military
application [139]. Then renewed interest in RuO$_2$ as a supercapacitor material
moved to improvement in synthesis methods and development of composites aiming
to increase the utilization of ruthenium oxide. However, to date, the specific
capacitances of RuO$_2$ based supercapacitors are far away from its theoretical value
of 2000 F.g⁻¹ [140]. The pseudo-capacitance of the ruthenium oxides (RuO₂ and RuO₂ₓH₂O) arises from very fast and reversible Faradaic protonation processes on the surface and/or in the bulk. The electrochemical reactions for RuO₂-based positive and negative electrodes are described as [141]:

\[
\text{(discharge)} \quad \text{HRuO}_2 \rightleftharpoons H_{1-\delta}\text{RuO}_2 + \delta H^+ + \delta e^- \quad \text{(charge)} \tag{2-18}
\]

\[
\text{(discharge)} \quad \text{HRuO}_2 + \delta H^+ + \delta e^- \rightleftharpoons H_{1-\delta}\text{RuO}_2 \quad \text{(charge)} \tag{2-19}
\]

The overall reaction is:

\[
\text{(discharge)} \quad \text{HRuO}_2 + \text{HRuO}_2 \rightleftharpoons H_{1-\delta}\text{RuO}_2 + H_{1+\delta}\text{RuO}_2 \quad \text{(charge)} \tag{2-20}
\]

where \(0 < \delta < 1\) (similar reactions take place in RuO₂ₓH₂O).

The transport of proton from one electrode to the counter electrode via the electrolyte solution, and RuO₂ and H₂RuO₂, respectively, represents the positive and the negative electrodes at the fully charged state of the cell. This kind of supercapacitors keep the salt concentration of the employed electrolyte constant during the charge and discharge processes, differenting from the carbon-based EDLC and the n/p-type polymer supercapacitors. The high specific capacitance of RuO₂ results from the fact that the Faradaic reaction occurs not only at the surface of the electrode material but also in the bulk, as the proton can easily enter the bulk of the amorphous RuO₂ₓH₂O. Thus amorphous hydrous RuO₂ₓH₂O was an especially promising material due to its high capacitance, good conductivity and electrochemical reversibility [142]. It was found that the best specific capacitance value for crystalline RuO₂ was 380 F.g⁻¹ for a surface area of 130 m².g⁻¹, whereas a specific capacitance of 768 F.g⁻¹ was reported for an amorphous hydrous RuO₂ of a surface area of 68.6 m².g⁻¹ [143].

The high specific capacitance of RuO₂ and RuO₂ₓH₂O makes themselves favorable electrode materials in electrochemical capacitors for space or military applications. However, the high cost and limited supply of ruthenium metal are a
major disadvantage for use in large-scale application as supercapacitors. In the past few decades, extensive efforts have been done to improve the electrochemical utilization of the electroactive ruthenium oxides. Nowadays, there are two ways to enhance utilization of the expensive ruthenium oxide, enhancement the capacitance of RuO₂ itself and development RuO₂ based composite electrode to low RuO₂ content.

It was reported that the key factors determining the performance of the RuO₂-based supercapacitors include [144]:

1) Electrochemical reversibility of the electroactive materials;
2) Electronic resistance between and within the electroactive materials;
3) Contact resistance at the interface between current collector and electroactive materials;
4) Proton conductivity and diffusivity between and within the electroactive materials; and
5) Pore structure and surface area.

Based on these rules/directions, various RuO₂ and RuO₂-based composite electrodes were investigated by controlling hydration, crystallinity, texture, and surface area of RuO₂.

The electrical and electrochemical properties of RuO₂ are related closely to the amount of water within its structure and the degree of structural order. Hydrous ruthenium oxide, RuO₂ₓH₂O (x=0.2~2), exhibits mixed electronic/prontonic conductivities combined with high capacitance. The hydrous regions, mostly near the surface, allow for facile proton permeation through the material, which make them efficient for charge storage. The capacitance is attributed to the redox transitions of superficial RuO₂ involving the double injection/expel of protons and electrons, according to [145]:

$$\text{Ru}^{(IV)}O_{a}(OH)_{b} + \delta H^{+} + \delta e^{-} = \text{Ru}^{(III)}O_{a-\delta}(OH_{b+\delta})$$  \hspace{1cm} (2-21)

The capacitance of hydrous or anhydrous RuO₂ was optimized when the electronic
and protonic transports were balanced according to the mechanism of double injection/expel of protons and electrons [146]. Anhydrous RuO₂ obtained by heat treatment in air, whose lost water is irreversible in the structure, was found to lead to a decrease in the volume of protonic transport paths but an increase in the metallic conduction paths [146]. In addition, heat treatment in air was found to result in destroy of fine-tuned nanostructure and reduction of in specific surface area of the hydrous RuO₂, except for increase in proton diffusion barrier [147]. Moreover, the high specific capacitance of hydrous RuO₂ₓH₂O was found to stem from the diffusion and intercalation of protons into the bulk of the material, while the proton reactions were found to be limited to the surface of the anhydrous RuO₂ material [137]. These results indicate that RuO₂ₓH₂O annealed at temperatures lower than 100 °C and higher than 200 °C showed relatively restrained proton dynamics/diffusive motion. In contrast, samples annealed at temperatures between 100 and 200 °C was found to exhibit relatively low activation energies, implying that the protons could easily diffuse into the bulk of the material. It is believed that these phenomena were related to changes of local structure of hydrous RuO₂ₓH₂O due to varying annealing temperatures [148]. The interaction between the structural water and the local structure of hydrous RuO₂ₓH₂O was found to play an extremely crucial role in hydrogen transfer in the bulk material [149]. These findings indicate that the synthesis approaches and post-annealing processes play a critical role in hydration of ruthenium oxide.

Various approaches to synthesis of anhydrous and hydrous ruthenium oxides with different specific capacitance are developed. Anodization of ruthenium metal to obtain RuO₂ was conducted by multi-cyclic voltammetry in H₂SO₄ electrolyte [150, 151]. Chemical oxidation of RuCl₃ or (NH₄)₃RuCl₆ to produce RuO₂ powder, followed by coating them on metallic substrate for current collector with a suitable binder such as PVdF (polyvinylidenfluoride) and NMP (N-methyl-2-pyrrolidone), was investigated for supercapacitor application [143, 152, 153]. Cathodic galvanostatic deposition of RuO₂ on metallic current collector such as nickel, titanium was accomplished via hydrolysis of RuCl₃ by electrochemically generated
It was found that condensation of hydroxyl groups accompanied with particle coalescence and crystal growth of amorphous RuO$_2$-xH$_2$O particulates resulted from heat treatment at temperatures above 150 °C in air, destroying the original nanostructure, reducing the water content and increasing the proton diffusion barrier, and made a great loss in active sites and specific capacitance. Hydrothermal method was also used and was found to restrict crystallization of RuO$_2$ within the primary RuO$_2$-xH$_2$O nanoparticles without significant condensation of superficial hydroxyl groups between particles, due to water molecules in the hydrothermal bath serving as a barrier for particulate aggregation [155]. The best reported capacitance of a hydrous RuO$_2$ synthesized from an aqueous solution of RuCl$_3$.xH$_2$O was between 600 and 900 F.g$^{-1}$, which were obtained for RuO$_2$.0.5H$_2$O [145, 153, 156, 157].

It was reported that the amorphous RuO$_2$ had a much higher capacitance than the crystalline RuO$_2$ in a bulk-type supercapacitor [143, 158]. The specific capacitance of the amorphous RuO$_2$.0.5H$_2$O was found to be more than 1000 times greater than that of the highly crystalline, anhydrous RuO$_2$ (0.75 F.g$^{-1}$), although only a 2-fold difference in their specific surface area was detected [143, 156]. Crystalline anhydrous RuO$_2$ was determined to be d-band metallic conductor with a single-crystal conductivity of 10$^4$ S.cm$^{-1}$, which is much larger than that of hydrous RuO$_2$ (which can be designed as RuO$_x$H$_y$ or RuO$_2$.xH$_2$O) in the order of 1 S cm$^{-1}$ [156, 159].

Since the simultaneous maintenance of a 3D porous architecture for facile electrolyte penetration, of high water content for proton exchange, and of the crystalline structure for metallic conductivity for hydrous RuO$_2$ was challenge [147, 159]. Coalescence of RuO$_2$ particulates prepared by sol-gel process and hydrothermal process was investigated [159]. These findings indicate that crystal growth of hydrous RuO$_2$ prepared by sol-gel process upon annealing at/above 200 °C was effectively inhibited by the formation of RuO$_2$.nH$_2$O nanocrystalline in a hydrothermal process, maintaining high water content, nanocrystalline structure, and porous nature of RuO$_2$.nH$_2$O [159]. Because the morphology and composition of
the RuO$_2$ electrode depend strongly on the synthesis method, suitable approach is required to prepare anhydrous and hydrous RuO$_2$. In addition, reduction of ruthenium content is pursued in different ways. One way is development of Ru-based binary oxide electrode such as RuO$_2$-VO$_x$/Ti, RuO$_2$-MoO$_x$/Ti, RuO$_2$-tungsten oxide, doping RuO$_2$ with Cr, strontium ruthenate perovskite and Pb/Ru pyrochlore (Pb$_2$Ru$_2$O$_{6.5}$). Other approach to minimize Ru content is through combining large surface area materials with RuO$_2$.

Considering the benefits of anodic TiO$_2$ nanotube arrays/Ti such as three-dimensional, mesoporous, ordered/aperiodic architectures, it should be a promising support material for electroactive materials such as NiO and RuO$_2$. Decoration of anodic TiO$_2$ arrays with metal oxides exhibits practical and scientific significance. However, there is no related study till now.

2.4.3 TiO$_2$ used as photoanode material of dye-sensitized solar cells

Photovoltaic devices are based on charge separation at an interface of two materials of different conduction mechanism under light illumination. To date, this field is dominated by solid-state junction devices, usually silicon, and profiting from the experience and material availability resulting from the semiconductor industry. However, it requires expensive and energy intensive high temperature, and high vacuum processes. So-called excitonic solar cells [160], including organic, hybrid organic-inorganic and DSSCs are promising photovoltaic devices for inexpensive, large-scale solar energy conversion. Among these photovoltaic devices, DSSCs offer the prospect of very low-cost fabrication and present a range of attractive features that will facilitate market entry.

In 1991, O’Regan and Gratzel first demonstrated DSSCs with high power conversion efficiency up to 7 % could be fabricated using a mesoporous layer of TiO$_2$ sensitized by a ruthenium based dye [161]. Since then, DSSCs have received considerable attention as they offer the possibility of extremely inexpensive and efficient solar energy conversion. Important results of DSSCs under standard reporting conditions (SRC) of 1000 W.m$^{-2}$, 25 °C and air mass 1.5 (AM1.5) are list
in Table 2-4.

Table 2-4 Some top efficiency results of DSSCs.

<table>
<thead>
<tr>
<th>Year</th>
<th>Efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991</td>
<td>7.1-7.9</td>
<td>[161]</td>
</tr>
<tr>
<td>1993</td>
<td>10.0</td>
<td>[162]</td>
</tr>
<tr>
<td>2005</td>
<td>11.18</td>
<td>[163]</td>
</tr>
</tbody>
</table>

To characterize solar cells and prevent the researcher from adjusting the reporting conditions to maximize the power conversion efficiency, the standard reporting conditions were established, consisting of temperature, spectral irradiance and total irradiance [164]. The air mass is a measure of how absorption in the atmosphere affects the spectral content and intensity of the solar radiation reaching the Earth’s surface, which can be described to [164]:

Air Mass = \( \frac{1}{\cos \theta} \)  

(2-22)

where \( \theta \) is the angle of incidence (\( \theta = 0 \) when the sun is directly overhead). The schematic diagram of AM1.5, AM1.0 and AM2.0 is illustrated in Figure 2-19. The AM1.5 spectrum, which is normalized to a total power density of 1 kW.m\(^{-2}\), is the preferred standard spectrum for solar cell efficiency measurements in literature. The spectral content of sunlight at the Earth’s surface has a diffuse (indirect) component owing to scattering and reflection in the atmosphere and surrounding landscape and accounts for up to 20% of the light incident on a solar. The AM number is therefore further defined by whether or not the measured spectrum includes the diffuse component. An AM1.5G (global) spectrum includes the diffuse component, while an AM1.5D (direct) does not. Virtually all of the solar irradiation reaching the earth’s surface falls between wavelengths of 300 and 2500 nm, with roughly half of the available power (and roughly a third of the available photons) in the range of 400 to
750 nm [165]. In fact, neither the direct reference spectrum (AM1.5D) nor the global reference spectrum (AM1.5G) actually integrates to exactly 1000 W.m$^{-2}$. The global reference spectrum integrates to approximately 963 W.m$^{-2}$ and the direct reference spectrum integrates to approximately 768 W.m$^{-2}$ [164]. The PV community has arbitrarily taken the term “one sun” to mean a total irradiance of 1000 W.m$^{-2}$ [166].

![Figure 2-19 Schematic diagram of AM1.0, AM1.5 and AM2.0: the path length of the solar radiation through the Earth’s atmosphere in units of Air Mass increases with the angle from the zenith. It increases from unity for 0° (zenith) to 1.5 for 48° and 2.0 for 60°.]

The power conversion efficiency ($\eta$) is calculated from the measured maximum or peak PV power ($P_{\text{max}}$), device area ($A$), and total incident irradiance ($E_{\text{tot}}$):

$$\eta = \frac{P_{\text{max}}}{E_{\text{tot}} A} \times 100$$

(2-23)

Usually, as shown in Figure 2-20, the overall solar conversion, $\eta$, is also given by a product of the short-circuit current density, $J_{sc}$, the open-circuit photovoltage, $V_{oc}$, and the fill factor, $FF(or \, ff)$, according to:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

(2-24)

where $P_{in}$ is the total solar power incident on the cell.
Figure 2-20 Typical I-V curve of PV solar cells, the overall efficiency ($\eta$) of a PV cell is the product of integral photocurrent density ($I_{sc}$: current obtained at short-circuit conditions, divided by the cell area), the open-circuit voltage ($V_{oc}$) and the fill factor ($FF$: defined as $V_{MP}/V_{oc}I_{sc}$).

Figure 2-21 Schematic diagram of a liquid-junction DSSC.

The structure of a typical liquid-junction DSSC is shown in Figure 2-21, which consists mainly of the following parts: transparent conducting oxide (TCO)-coated...
glass, photoanode, dye molecule, redox electrolyte, platinized TCO-coated glass and sealing material. Due to leakage of the redox electrolyte of the liquid-junction DSSC, quasi-solid-state and solid-state DSSCs are developed.

The operational principle of the liquid-junction DSSC is illustrated in Figure 2-22. The primary steps of converting photons to current can be described as:

i. Ru complex photo-sensitizers (dye molecule) anchored on the semiconductor surface absorb incident photon flux;

ii. The dye molecule is excited from the ground state ($S$) to the excited state ($S^*$) owing to the metal-to-ligand charge-transfer transition. The excited electrons are injected into the CB of the semiconductor electrode, resulting in the oxidation of the dye molecule:

\[
S + h\nu \rightarrow S^* \tag{2-25}
\]

\[
S^* \rightarrow S^+ + e^- \tag{2-26}
\]

iii. Injected electrons in the CB of semiconductor diffuse towards the back contact (TCO-coated glass) and consequently reach the counter electrode through the external load and wiring;

iv. The oxidized dye molecule ($S^+$) accepts electrons from the $\Gamma$ ion redox mediator, regenerating the ground state ($S$), and $\Gamma$ is oxidized to the oxidized state, $I_3^-$,

\[
S^+ + e^- \rightarrow S \tag{2-27}
\]; and

v. The oxidized redox mediator, $I_3^-$, diffuses towards the counter electrode and is reduced to $\Gamma$ ions,

\[
I_3^- + 2e^- \rightarrow 3\Gamma^- \tag{2-28}
\]

The voltage generated under solar illumination relates to the gap between the Fermi level of the electron in the semiconductor and the redox potential of the
electrolyte, as shown in Figure 2-22. Overall, the device generates electric power from light without suffering any permanent chemical transformation [164, 167]. Clearly, the charge separation process for DSSCs is different from that of p-n junction solar cells, whose photo-generated charges are separated by the electric field in the space charge layer. The differences between p-n junction solar cells and DSSCs are listed in Table 2-5 [168].

The kinetics and dynamics of charge transport are studied by many researchers through experimental and computational methods. As illustrated in Figure 2-23, the different time scales of relevant processes are depicted [169]. For each time constant, the value given in Figure 2-23 is the most current literature datum measured on a standard cell under operating conditions, preferably at the maximum power point (about 700 mV). The details of these time constants are listed in Table 2-6.

To relate these processes to PV performance, the charge dynamics are viewed on a modified energy level diagram, as indicated in Figure 2-24, with potentials taken from literature reports, as listed in Table 2-7.
Table 2-5 Comparison between p-n junction solar cell and DSSC [168].

<table>
<thead>
<tr>
<th>p-n junction solar cell</th>
<th>DSSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge separation in space charge field</td>
<td>No significant space charge region</td>
</tr>
<tr>
<td>Grain boundaries, high recombination probability at junction should be avoided or minimized</td>
<td>Grain surface maximization necessary up to $10^3$ times increased contact area</td>
</tr>
<tr>
<td>Photovoltage from neutralization of internal built-in field</td>
<td>Existence (and importance) of an electric field not established</td>
</tr>
<tr>
<td>Both minority and majority carriers are present in the semiconductor</td>
<td>Carriers of only one type are present in the semiconductor</td>
</tr>
</tbody>
</table>

![Figure 2-23 Kinetic processes in a liquid-junction DSSC [169].](image)

The mechanism of electron transport in the semiconductor photoanode and the kinetics of electron transfer at semiconductor/electrolyte interface are still controversial.

Table 2-6 Time constants of various kinetic processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Half-life</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron injection</td>
<td>150 ps</td>
<td>[170]</td>
</tr>
<tr>
<td>Relaxation</td>
<td>12 ns</td>
<td>[171]</td>
</tr>
</tbody>
</table>
Recharge regeneration 1 µs [172]
Recombination 3 µs [173]
Charge transport 100 µs [174]
Charge interception 1 ms [174]

Figure 2-24 Kinetic processes in DSSCs on a modified energy level [169].

Table 2-7 Potentials relevant to DSSC operation [169].

<table>
<thead>
<tr>
<th>Potential vs. SCE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2 Ecb/q</td>
<td>-0.9 V</td>
</tr>
<tr>
<td>TiO2 Evb/q</td>
<td>2.2 V</td>
</tr>
<tr>
<td>N719*+/+</td>
<td>-1.04 V</td>
</tr>
<tr>
<td>N719^o+/+</td>
<td>0.71 V (N3^o+/ = 0.87 V)</td>
</tr>
<tr>
<td>I^+/I^-</td>
<td>0.23 V</td>
</tr>
</tbody>
</table>
The details of the components of a typical liquid-junction DSSC are described as follows:

**TCO-coated glass:** TCO-coated glass is used as a support for the semiconductor material. For DSSCs with high performance, the TCO-coated glass is required to have low sheet resistance (electrical conductivity: an order of magnitude of $10^4$ S.cm$^{-1}$) and high transparency (better than 80 % visible wavelengths). Sometimes, sheet resistance is required to be nearly independent of the temperature up to 500 °C due to calcinations process of TiO$_2$. Currently, tin doped indium oxide (In$_2$O$_3$:Sn or ITO) and fluorine doped tin oxide (SnO$_2$:F or FTO) are commonly used. The most widely used is FTO, due to its thermal steadiness and low cost. ITO is also used in DSSCs due to its higher specific conductivity. However, ITO does not remain stable at high temperatures and thence it is specifically used in flexible cell technologies in which heat treatment temperatures are usually lower (typically 200 °C or less) [178].

**Dye molecule:** In DSSCs, the dye molecules anchored to the semiconductor surface act as light-harvesting intermediates, absorbing visible and near-infrared solar irradiation and efficiently injecting the resultant excited-state electrons into the CB of the semiconductor photoanode. As shown in Figure 2-22, the energy of the dye excited-state necessarily must be higher than the CB edge to generate a photocurrent. High quantum efficiency for electron injection is achieved when the dye lowest unoccupied molecular orbital (LUMO) is both energetically matched and reasonably strongly coupled to the underlying semiconductor. The dye molecule is excepted to absorb strongly from the blue end of the visible spectrum to the near infrared. The anticipated short-circuit current ($J_{sc}$) for a given dye and cell design can be determined by integrating the IPCE, with the AM1.5 terrestrial solar spectrum. The IPCE can be given by:

\[
IPCE(\lambda) = LHE(\lambda) \times \Phi_{inj} \times \eta_c = LHE(\lambda) \times APCE
\]  

(2-29)

where LHE is the light harvesting efficiency at a given wavelength, $\Phi_{inj}$, the electron injection efficiency, $\eta_c$, the charge collection efficiency, and the product of
\( \Phi_{\text{inj}} \) and \( \eta_c \) is the absorbed photon-to-current efficiency (APCE). IPCE is also given by:

\[
\text{IPCE} (\%) = \frac{1240 [eV \times nm] \times J_{\text{SC}} [\mu A \text{ cm}^{-2}]}{\lambda [\text{nm}] \times \Phi [\mu W \text{ cm}^{-2}]} \times 100
\]

(2-30)

where \( J_{\text{SC}} \) is the short-circuit photocurrent density for monochromatic irradiation, \( \lambda \), the wavelength, and \( \Phi \) is the monochromatic light intensity. LHE is the fraction of photons absorbed at that wavelength, which can be described using Beer’s law [165]:

\[
\text{LHE} = 1 - T = 1 - 10^{-\varepsilon(\lambda) L_n C}
\]

(2-31)

where \( \varepsilon(\lambda) \) is the extinction coefficient, \( C \), concentration (which is determined by the effective photoanode roughness), and \( L_n \) is the shorter of the diffusion length or electrode thickness.

In the most highly optimized DSSCs, both \( \Phi_{\text{inj}} \) and \( \eta_c \) are approximately unity (APCE~1). In these cells, the combination of dye extinction and electrode roughness is sufficient that the LHE is close to unity for a large portion of the visible spectrum, then tailoring off close to the dye’s optical gap. The measured maximum IPCE, however, is generally limited to 80 % due to light reflection losses and absorption by FTO.

To date, the most efficient (> 10 %) DSSCs incorporate the ruthenium polypyridyl complex N3, the closely related tetrabutylylammonium salt (N719), or the black dye. These dyes show strong coupling to the underlying semiconductor and minimal recombination as evidence by nearly quantitative APCE. For dye N719, the IPCE reached 80 % for wavelength below 650 nm and then tailed off at longer wavelength (750 nm) due to minimal LHE (~10 %). A lot of photons in the 750-900 nm region of the solar spectrum can be absorbed by dye N3 and the black dye extend the range of sunlight that can be absorbed. A fundamental limitation of ruthenium polypyridyl dyes is their low molar absorptivity (\( \varepsilon_{\text{max}} \sim 1.4 \times 10^4 \)
Hundreds of adsorbed dye monolayers were required to collect at least 90% of the light at the most strongly absorbing wavelength. That was why nanocrystalline semiconductor, which effective surface area was roughly 1200 times the geometric area and a capping light scattering layer was needed sometimes, was used as photoanode.

**Electrolyte:** Currently, there are three types of electrolyte used in DSSCs: liquid electrolyte, quasi-solid state electrolyte and solid state electrolyte. According to solvent employed, liquid electrolyte is into organic solvent electrolyte and ionic liquid electrolyte. Organic solvent electrolytes are widely used and extensively investigated due to their low viscosity, fast ion diffusion, high efficiency, easy to be designed and high pervasion into nanocrystalline film electrode. Usually, the electrolyte consists of solvent(s), redox couple and additives. Organic solvents used in organic liquid electrolyte include nitrile such as acetonitrile, valeronitrile, 3-methoxypropionitrile, and esters such as ethylene carbonate (EC), propylene carbonate (PC), γ-butyrolactone.

Typical redox couple used in liquid-junction DSSCs contains I-/I$_3^-$ redox ions, mediating electrons transfer between the dye molecular and the counter electrode and completing the electrochemical circuit. Mixtures of iodides such as LiI, NaI, KI, tetraalkylammonium iodide (R$_4$NI), and imidazolium-derivative iodides with concentrations of 0.1 to 0.5 M and 0.05 to 0.1 M I$_2$ dissolved in nonprotonic solvents, were commonly employed. There are two kinetics constants for a successful redox shuttle: it must reduce the dye cation before the dye cation recombines with an electron in the photoanode, but not allow the oxidized form of the shuttle to intercept an electron from the photoanode [165]. The dual criteria of fast dye regeneration and slow interception play a very challenging constraint in identifying effective redox shuttles. The uniquely good performance of I$_3^-/I^-$ was attributed to efficient dye regeneration combined with exceedingly slow electron transfer from TiO$_2$ to I$_3^-$. DSSCs with highly-polarizable organic dyes were found to exhibit much higher dark current densities than those sensitized with conventional ruthenium polypyridyl complexes when I$_3^-/I^-$ was used as redox shuttle [180].
undesirable consequence of high dark current density was low open-circuit voltage [165].

To suppress the dark current and improve the photoelectric conversion efficiency, additives including 4-tert-butylpyridine (TBP) and N-methylbenzimidazole were commonly introduced into the redox shuttle of liquid-junction DSSCs. It was demonstrated that the addition of TBP could reduce the recombination of electrons in the CB of semiconductor and the electron acceptor in the redox electrolyte [181, 182]. TBP in the electrolyte was believed to play an important role in increasing of both \( V_{oc} \) and \( ff \) through remedying the dye-uncovered surface of the semiconductor electrode [162]. Furthermore, it was demonstrated that the addition of TBP containing Li\(^+\) ions in the electrolyte increased the \( V_{oc} \) through reducing the surface positive charge, which shifted the CB potential of TiO\(_2\) toward negative by reducing the amount of adsorbed Li cations [181, 183].

**Counter electrode**: The counter electrode converts the tri-iodide ions (I\(_3^-\)) to I\(^-\) ions. To reduce the tri-iodide ions, the counter electrode is required to have high electrolytic activity. Platinized (5-10 \( \mu \)g.cm\(^{-2}\) or approximately 200-nm thickness) TCO-coated or carbon were usually used the counter electrode [164].

**Sealing materials**: Sealing materials are required to prevent the leakage of liquid electrolyte and the evaporation of solvent. Chemical and photochemical stability of the sealing materials against the electrolyte component, iodine, and the solvent are required. Surlyn (Du Pont), a copolymer of ethylene and acrylic acid, met these requirements [164].

**Photoanode**: The purpose of the photoanode is to facilitate light harvesting, electron injection, electron collection and transport to TCO-coated glass. To maximize light harvesting, the photoanode is required to be transparency or semi-transparency for the unsensitized semiconductor framework and sufficiently high internal area to enable absorptivities for surface-anchored dye molecules to exceed 1 over the spectral region of interest. \( \eta_{inj} \) is maximized by having a large density of unpopulated states in the photoanode at potentials positive of the dye\(^{+/-}\) potential (i.e. lower in energy than the thermalized dye excited-state on an absolute
energy level). The ideal photoanode is required to exhibit fast electron transport as well as high transparency, high and tunable surface area and high porosity.

The electron collection depends on the effective rate of electron diffusion (the rate at which electrons are collected), electron lifetime (governed by rates of interception and recombination) and the electron recombination. When recombination is neglected, the electron collection efficiency is determined by the kinetic competition between the electron diffusion and electron lifetime. The diffusion rate is dependent on both the apparent diffusion coefficient, $D_n$, and the diffusion length, $L_n$ (diffusion rate $\propto D_n L_n^2$), which is described as [167]:

$$L_n = \sqrt{D_n \tau_n}$$  \hspace{1cm} (2-32)

where $\tau_n$ is the electron lifetime, which relates to the quasi-Fermi level of electrons in the photoanode, and shows trap density dependence. Quantitative collection of electrons is achieved only if the electron diffusion length is greater than the photoanode thickness ($d$):

$$L_n > d$$  \hspace{1cm} (2-33)

However, the photoanode, in turn, is required to be significantly thicker than the light absorption length ($1/\alpha$) to ascertain nearly quantitative light harvesting in the spectral absorption range of the dye molecule:

$$d > 1/\alpha$$  \hspace{1cm} (2-34)

TiO$_2$ nanoparticles-based photoanode was largely responsible for the first large successes with DSSCs and remained to be a key component of the most efficient DSSCs, due to its optical transparency and large internal surface area for dye loading. Photoanode based on TiO$_2$ nanoparticles offers low material cost, ready scalability and tremendous chemical stability. Optimized photoanode consisted of 10-20 nm spherical particles with 12 µm-thick transparent structure. The surface
area enhancement is described by the roughness factor, which is defined as ratio of actual surface area to the projected surface area. Roughness factors in excess of 1000 were achieved for TiO$_2$ nanoparticles-based photoanode. To enhance the absorption of red and near-IR light in the solar spectrum, a ~ 4 µm thick film of much larger (~ 400 nm) TiO$_2$ particles was subsequently deposited on the photoanode [184]. However, it was believed that the introduction of larger particles into nanocrystalline films unavoidably reduced the internal surface area of the photoanode film [184]. The TiO$_2$ nanoparticles-based photoanode was usually prepared by the doctor blade technique or screen printing method.

To date, photoelectrode of DSSCs predominantly employs nanocrystalline TiO$_2$ nanoparticle network film. In view of crystalline form of TiO$_2$, anatase is widely used because it exhibits a high band gap energy (3.2 eV, and absorbs only irradiation below 388 nm), making it invisible to most of the solar spectrum, reducing the recombination rate of photoinjected electrons [178]. Rutile TiO$_2$ was also employed as photoanode of DSSCs. However, a higher dark current due to low band gap (3.0 eV) was found and it showed less effective and less chemically stable because of photoexcitation within the band gap generating holes acting as oxidants [178, 185]. The photovoltages of DSSCs using rutile or anatase nanoparticles as photoanode with the same thickness were found to be essentially the same, whereas the $J_{sc}$ of the rutile-based cell was about 30 % lower than that of the anatase-based cell [185].

Other metal oxides such as ZnO, SnO$_2$, Nb$_2$O$_5$, In$_2$O$_3$, NiO, SiTiO$_3$ are investigated for DSSCs. Among these alternative materials, ZnO receives much attention. This is because the ZnO exhibits similar band gap and energy position to that of TiO$_2$, as shown in Figure 2-13. The electron transport times and light intensity dependence of ZnO was found to be similar to those of TiO$_2$ [186]. Furthermore, ZnO shows higher electron mobility ~115-155 cm$^2$.V$^{-1}$.s$^{-2}$ than that of anatase TiO$_2$, which was determined to be ~10$^{-5}$ cm$^2$.V$^{-1}$.s$^{-2}$ [187]. Investigation through intensity modulated photovoltage spectroscopy (IMPS) under open-circuit conditions indicated that the electron lifetime of DSSCs using ZnO as photoanode was significantly higher than those using TiO$_2$ [186]. The electron recombination
rate of DSSCs using ZnO as photoanode with triiodide in the electrolyte was found to be lower than those using TiO$_2$ [186]. Moreover, ZnO shows more flexibility in synthesis and morphology than TiO$_2$. Various morphologies of ZnO including nanoparticles, nanowires and nanotubes have been synthesized with relative ease. However, the best device performance of DSSCs using ZnO as photoanode so far was much lower than those using TiO$_2$ as photoanode. One possible reason for the low device performance is its interior stability than that of TiO$_2$, which was demonstrated to be compromised in solvent-rich or acidic environments. Dye adsorption behavior of ZnO was found to be worse than that of TiO$_2$ due to low chemical stability [188]. In addition, dissolution of ZnO and formation of complexes precipitation consisting of the dye and Zn$^{2+}$ ions occurred due to high acidity of the dye molecule, stemming from the presence of carboxylic acid binding groups [186]. Thus dye concentration and immersion time were required to be optimized for DSSCs using ZnO as photoanode [187]. Furthermore, a low electron injection efficiency from excited dye molecules into the CB of ZnO and/or a low dye regeneration efficiency of DSSCs were suggested to cause the relatively low performance compared to those using TiO$_2$ as photoanode [186].

Although these metal oxides have been extensively investigated, DSSCs using nanocrystalline TiO$_2$ as photoanode show the best performance. However, the TiO$_2$ nanoparticles are not suitable for the next generation DSSC due to obvious disadvantages such as relatively low porosity [189], limited materials generality and tedious particle synthesis [165]. The primary weakness of the TiO$_2$ nanoparticle based photoanode is the extraordinarily small apparent diffusion coefficient ($D_n$). Slow electron transport in photoanode strongly limits the choice of dye regenerator (redox shuttle), which, in turn, limits photovoltage and constrains the choice of light absorber.

To date, it is commonly accepted that the electron transport in the nanoparticle network film is controlled by diffusion. The slow electron transport governed by diffusion mechanism ultimately restricts the diversity of feasible redox mediators. Otherwise, the small collection of suitable mediators was found to limit both
understanding of an intriguing heterogeneous system and the performance of these devices [169]. In 2001, Gratzel first predicted that the DSSCs using aligned structures as photoanode could increase the energy conversion efficiency compared with those using fractal nanoparticle network film as photoanode [190]. In 2005, DSSCs using an array of aligned nanowires of ZnO as photoanode was first demonstrated by generation of a layer of ZnO nanowires on a TCO glass [191]. The schematic representation of a DSSC using ZnO nanowires as photoanode is given in Figure 2-25. However, the roughness factor of the ZnO nanowires based photoanode was determined to be around 125, which was significantly lower than that of nanoparticle based photoanode (roughness factor >1000). Lacking in roughness factor resulted in reduction of $J_{sc}$ and therefore limited energy conversion efficiency to 1.5 % [191]. In marked contrast to the limited roughness factor of nanowires array, a second route to low dimensionality photoanodes of DSSCs is established in the form of nanotube arrays, which enhances the roughness factor through the internal area. More recently, electron diffusion coefficient of polycrystalline ZnO nanotubes of a thickness of 64 $\mu$m is determined to be up to 0.4 cm$^2$.s$^{-1}$, which is about 3 orders of magnitude greater than those of any photoanode previously reported [192].

TiO$_2$ nanotubes synthesized by various methods are extensively investigated as photoanode of DSSCs. In 2002, TiO$_2$ nanotubes obtained by a hydrothermal method was first employed as photoanode of liquid-junction DSSCs [193]. In 2005, anodic TiO$_2$ nanotube arrays was pioneered used as photoanode of liquid-junction DSSCs and a power conversion efficiency of 3.3 % was reported [194]. Since then, anodic TiO$_2$ nanotube arrays have attracted much interest of application for DSSCs due to their easy synthesis and special architecture. Moreover, the pronounced charge transport along the length of the TiO$_2$ nanotube is possible to differentiate dramatically from random charge hopping across and trapping at nanoparticles’ grain boundaries. However, this requires the assumption that the charge transport in mesoporous TiO$_2$ is dominated by inter-particle traps and that the crystal size in the nanotube was greater than that of the nanoparticles [195]. If the surface trapping [196] rather than the interparticle trapping dominates the charge transport process,
the advantage of nanotube arrays will not be directly apparent [195].

![Schematic diagram of a highly-ordered nanowires based DSSC](image)

Figure 2-25 Schematic diagram of a highly-ordered nanowires based DSSC [191]. (Figure reprinted with permission from Law et al. Copyright (2005) Nature Publishing Group).

There were many evidences revealed that the advantages of TiO$_2$ nanotube used as photoanode of DSSCs. For example, TiO$_2$ nanotubes, synthesized by a hydrothermal method, were revealed to have a longer electron lifetime and larger diffusion length than the photoanode made of P25 nanoparticles [111]. Anodic TiO$_2$ nanotube arrays were found to exhibit inhibited recombination behaviors with longer electron lifetimes, indicating fewer recombination centers in the nanotubular photoanode compared with that of nanoparticles [197]. This is attributed to less surface defects for the anodic TiO$_2$ nanotubes. However, investigation by IMPS indicated that the transport times of nanotube and nanoparticle for DSSCs were similar [197]. This is ascribed to the crystal size (30 nm) in the TiO$_2$ nanotubes being comparable with the standard particle size (20 nm), with transport limited by inter-grain electron transfer [195]. More recently, it was directly revealed through a range of complementary experimental techniques and the electron diffusion length of anodic TiO$_2$ nanotube arrays was determined to be up to the order of 100 μm, which is remarkably greater than that of typical DSSCs using TiO$_2$ nanoparticle network film as photoanode [198]. These results revealed that the collection
efficiency for electrons was close to 100% for these anodic TiO$_2$ nanotube arrays based devices [198].

One obvious limitation of DSSCs using anodic TiO$_2$ nanotube arrays on titanium foil as photoanode is that the device requires illumination from the back-side (through the platinized TCO glass). The schematic diagrams of front-side illumination and back-side illumination are shown in Figure 2-26 [199]. The back-side illumination is not an optimal configuration for liquid-junction DSSCs due to reflection of solar light by platinum on FTO and adsorption of photons at lower wavelength by iodine in the redox electrolyte [195]. Grimes and co-workers compared the efficiency of the front-side illuminated and the back-side illuminated TiO$_2$ nanotube arrays-based DSSCs sensitized by dye N719, indicating that the front-side illuminated DSSCs showed a power conversion efficiency of 4.7% compared with 4.4% for a back-side illuminated DSSC [199]. Although the front-side illumination can be realized through sputtering titanium onto a FTO and subsequent anodization, there are several challenges including limitation of film thickness and uniformity of the TiO$_2$ nanotubes.

It was demonstrated that the top morphology of anodic TiO$_2$ nanotube arrays played an important role in the photovoltaic performance of DSSCs. An increase in power conversion efficiency from 1.6% to 1.9% was demonstrated through removing the surface layer covering on the TiO$_2$ nanotube arrays [200]. Similar enhancement of power conversion efficiency was demonstrated through removing the bundled “nanograss” at the top of the TiO$_2$ nanotube arrays [201]. Dye-loading property was also found to be a critical parameter to influence the cell performance. The limitation of commonly employed dye-loading process may result in low level of dye adsorption, especially the inner surface of the TiO$_2$ nanotube, and dye aggregation at mouth of the TiO$_2$ nanotube. This may be attributed to the relatively small tube diameter and the closed tube bottom (the deeper TiO$_2$ nanotubes were more difficult to be sensitized due to the capillary effect).
Figure 2-26 Schematic representation of (a): front-side illumination, and (b): back-side illumination of DSSCs using anodic TiO$_2$ nanotube arrays as photoanode [199]. (Figure reprinted with permission from Paulose et al. Copyright (2006) IOP Publishing Limited).

Although the special architecture provided vectorial electron transfer pathway and reduction of electron recombination, the best power conversion efficiency achieved so far for liquid-junction DSSCs based on anodic TiO$_2$ nanotube arrays is much lower than that using TiO$_2$ nanoparticle network film photoanode [202]. Moreover, previous results were conflicting with parameters influencing the power conversion efficiency of DSSCs using anodic TiO$_2$ nanotube arrays as photoanode. For example, Grime and co-workers reported that DSSCs employing long TiO$_2$
nanotube arrays of 220 µm in length showed a best power conversion efficiency [49], while others demonstrated that TiO$_2$ nanotube arrays of 20 µm in length were optimized for DSSCs [202]. Considering the geometries of the anodic TiO$_2$ nanotube arrays can be tailored over a wide range [51], the nanostructures as well as other parameters including dye-loading process are far from being optimized for liquid-junction DSSCs. On the other hand, the assembling and sealing processes of liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays as photoanode are different from those typical liquid-junction DSSCs using nanoparticle network film as photoanode and they are rarely investigated, or investigated but rarely reported. Hence, investigation of assembling, sealing processes and of influence of surface morphology on photovoltaic performance of DSSCs, has both practical and scientific significance.
3.1 Introduction

To date, it is generally recognized that nanoscale control of TiO$_2$ architectures permits significant enhancement in corresponding applications, including photocatalysis, photoanodes for DSSCs, and support for redox supercapacitors. Although numerous studies of anodization of titanium and other valve metals have been published over the past decade, understanding is still limited. This chapter is into four parts: anodization of titanium in an aqueous solution consisting of HF and H$_3$PO$_4$, anodization of titanium in F$^-$ ions containing a hybrid solution, anodization of titanium in a non-aqueous solution consisting of NH$_4$HF$_2$ and ethylene glycol, and anodization of NiTi alloy in a diluted HF solution.

3.2 Anodization of titanium in an aqueous solution and formation of TiO$_2$ nanotube arrays and bamboo-shoot-like structures/TiO$_2$ nanotube arrays hybrid material

Although TiO$_2$ nanotube arrays obtained through anodization in aqueous electrolytes exhibit limited thickness, they are still very attractive due to their easy preparation and the low cost of the electrolytes. Moreover, there is limited knowledge of the anodization of titanium in aqueous solution and the influence of various additives; for example, the influence of ageing of anodization on the morphology and properties of the TiO$_2$ layer. In the present work, the effects of anodization duration and applied potential in an aqueous electrolyte consisting of HF and H$_3$PO$_4$ on the morphology of the TiO$_2$ layer were investigated.

Anodization of titanium in aqueous solution containing HF and H$_3$PO$_4$

Titanium foils of 0.20 mm thickness and 99.6 % purity, supplied by Strem Chemical in the USA (hereafter all related studies employ this kind of titanium
except where specially noted) were used. Prior to anodization, samples (cut into pieces of 2*5 cm) were degreased by sonicating in acetone, isopropanol and methanol, followed by rinsing with deionized water (DW) and drying in air. The anodization was performed in a two-electrode configuration with a Ti foil as the working electrode and a platinum foil of the same shape as counter electrode. The two electrodes were parallel clamped to two copper clips with a fixed distance of 20 mm and immersed directly in a mixture of 0.125 M HF and 0.5 M H₃PO₄. All electrolytes were prepared from reagent grade chemicals. The anode-to-cathode potential was supplied by a program-controlled Agilent DC resource (Model N5751A) and the current was recorded. A schematic diagram of the anodization apparatus is shown in Figure 3-1. The anodic treatment consisted of a potential ramp at a sweep rate of 0.1 V.s⁻¹ from 0 V to designated voltages, followed by maintaining the applied potentials for different durations. After anodization, the as-prepared samples were rinsed in DW and dried in air at room temperature.

Figure 3-1 Schematic diagram of an apparatus used for anodization, A: anode (titanium), B: cathode (Platinum), C: electrolyte, D: Aglient DC resource, E: computer, F: magnetic stirrer, G: magnetic stirrer plate, H: clamp, and I: USB cable.

The morphology of the as-formed TiO₂ layer was investigated using FESEM (JEOL JSM-6335F). Cross-sectional and inferior-view images of the TiO₂ layer were obtained from mechanically bent samples. Surface morphology was examined by scanning probe microscopy (SPM) (NanoScope IV, digital instrument) working at
tapping mode. A bamboo-shoot-like structure was obtained by sonicating the as-prepared sample in ethanol for 1 h and was then characterized by TEM (JEOL JEM-2010) with selected-area electron diffraction (SAED) and electron dispersive spectroscopy (EDS). Micro-Raman spectra were recorded at room temperature with a Jobin-Yvon HR800 Raman Spectrometer working at 488 nm.

Formation of highly-ordered TiO$_2$ nanotube arrays

Surface morphologies of Ti foils anodized in HF/H$_3$PO$_4$ electrolyte at various applied potentials are shown in Figure 3-2 (a-c). These results indicate that regular TiO$_2$ nanotube arrays with diameters of 35 nm, 78 nm and 136 nm were formed at 10 V, 20V and 30 V respectively. The thickness of the TiO$_2$ nanotube arrays formed by anodization at 30 V for 4 h was about 600 nm (as indicated in Figure 3-2d) and the maximum length was found to be independent of anodization time, which is consistent with the findings in reference [55]. This is because the thickness of the TiO$_2$ layer is essentially the result of an equilibrium between the electrochemical formation of the TiO$_2$ and the chemical dissolution of the TiO$_2$ in an F$^-$ ion containing solution [40]. The TiO$_2$ nanotubes formed at 10 V were connected to each other, unlike the isolated nanotubes formed at higher voltages. The controlling parameters for the formation of connected and isolated TiO$_2$ nanotubes included the applied potential and properties of the electrolytes. It is reasonable to assume that isolated TiO$_2$ nanotube arrays could be obtained even at low applied potential when an increased concentration of HF and H$_3$PO$_4$ is applied.

As shown in Figure 3-3, the diameter of the TiO$_2$ nanotube was found to depend linearly on the applied potential, which is in line with the finding reported in reference [55]. These results provide a method for preparation of highly-ordered TiO$_2$ nanotube arrays with geometries that are easily tunable by adjustment of the applied potential and electrolyte. The surface roughness of the highly-ordered TiO$_2$ nanotube arrays was investigated through SPM. As shown in Figures 3-4a and 3-4b, the surface of the anodic highly-ordered TiO$_2$ nanotube arrays was found to be very smooth.
Figure 3-2 FESEM images of TiO$_2$ nanotube arrays formed by anodic oxidation in 0.125 M HF + 0.5 M H$_3$PO$_4$ for 4 h at different potentials, (a): 10 V, (b): 20 V, (c): 30 V, and (d): cross-section view of the TiO$_2$ nanotube array by anodic oxidation at 30 V for 4 h.

Figure 3-3 Diameters of TiO$_2$ nanotube formed in 0.125 M HF + 0.5 M H$_3$PO$_4$ at 10 V, 20 V and 30 V (values extracted from Figure 3-2(a-c)).
Figure 3-4 SPM images of anodic TiO$_2$ nanotube arrays obtained in 0.125 M HF + 0.5 M H$_3$PO$_4$ at 30 V for 2 hr, (a): 2-D, and (b): 3-D images.
Figure 3-5 Bamboo-shoot-like structures formed by anodization at 30 V for 4 h, (a): top view of the bamboo-shoot-like structures/TiO$_2$ nanotube array, (b): large view of a bamboo-shoot-like structure grown out of nanotube arrays, (c): a bamboo-shoot-like structure with conical bottom, and (d): large pit in the titanium substrate by removal a bamboo-shoot-like structure using ultrasonication, the surrounded small conical surface resulting from TiO$_2$ nanotubes.

**Formation of TiO$_2$ nanotube arrays containing bamboo-shoot-like structures**

Many bamboo-shoot-like structures were obtained within TiO$_2$ nanotube arrays when the duration of the anodization was 4 h at 30 V. These special structures, which are much larger than the nanotube, were randomly located on the TiO$_2$ nanotube array, as shown in Figure 3-5a. It is evident that these special structures grow out of the TiO$_2$ nanotube array and have laminar structure, as shown in Figure 3-5b. Through bending the sample, a bamboo-shoot-like structure was obtained, as shown in Figure 3-5c, which had a reciprocal conical-shape bottom. The bamboo-shoot-like structure was determined to be around 7.5 $\mu$m in length and 2.8 $\mu$m in diameter. A large pit was found after removing the bamboo-shoot-like structure through ultrasonication, as shown in Figure 3-5d, indicating that the bamboo-shoot-like structure was deeply inserted into the titanium substrate.

This special architecture had an empty core, which could be observed in a cracked bamboo-shoot-like structure, as indicated in Figure 3-6a. Through ultrasonication a cracked sample was obtained, shown in Figure 3-6b, which clearly reveals a cavity inside the bamboo-shoot-like structure. It is reasonable to believe that every bamboo-shoot-like structure has an internal cavity; more examples are shown in Figure 3-6c.
Figure 3-6 (a): a cracked bamboo-shoot-like structure with cavity inside, (b): a cracked bamboo-shoot-like structure through ultrasonication, an empty core is observed, and (c): more cracked bamboo-shoot-like structures with empty cores inside.

Figure 3-7 Optical image of the bamboo-shoot-like structures/TiO$_2$ nanotube arrays hybrid material, the red arrow demonstrates the rich distribution of bamboo-shoot-like structures.

As shown in Figure 3-5a, the distribution of the bamboo-shoot like structures was disordered. However, in macro-morphology, it was observed that the distribution of these special structures aligned along a particular direction, as shown in Figure 3-7. A similar result has been observed for titanium by Goodfellow. The
titanium was made by a roll-to-roll process and it was found that these bamboo-shoot-like structures aligned the direction of the roll-to-roll processing.

Figure 3-8 (a): TEM image of a cracked bamboo-shoot-like structure, (b): laminar structure of a cracked bamboo-shoot-structure, and (c): SADE of a cracked bamboo-shoot-like structure.

Figure 3-9 EDS of an as-prepared bamboo-shoot-like structure.
The TEM images confirmed again that the special structure has a conical shape, as shown in Figure 3-8a. It was also found that the cracked bamboo-shoot-like structure contains laminar structures, as shown in Figure 3-8b.

**Composition of the as-formed bamboo-shoot like structure**

SADE of the cracked bamboo-shoot like structure is shown in Figure 3-8c. Clearly (101), (004), (200), (105), (204), and (220) diffraction patterns, which were determined to be anatase phase of TiO₂ [197, 203], are observed. These polycrystalline SAED patterns indicate that the as-prepared bamboo-shoot-like structure consisted of polycrystalline anatase TiO₂.

Phosphorus was detected through EDS in the as-prepared bamboo-shoot-like structure, as shown in Figure 3-9. This was due to the incorporation of anions (PO₄³⁻) in the electrolyte during anodization. It has been reported that presence of 4 % P was detected through XPS on the surface of anodic TiO₂ nanotubes formed in electrolyte containing HF/H₃PO₄ [55]. However, those indicated that the element P was present only in the region close to the surface; P was barely detected when the sputter depth was greater than 40 nm. It has been demonstrated that few anions including SO₄²⁻ were incorporated and only trace amounts (≪ 1 %) could be found [55].

XRD is sensitive to the long-range order of materials, thus providing average structural information across several unit cells. In contrast, Raman scattering is a local probe and very sensitive to the local properties of materials [204]. Thus, micro-Raman spectrum was adopted in this study to investigate the properties of the localized bamboo-shoot-like structures. The Raman spectra of an as-prepared bamboo-shoot-like structure and an optical image of the hybrid material are shown in Figures 3-10a and 3-10b, respectively. As shown in Figure 3-10a, sharp peaks at 144, 399, 513 and 639 cm⁻¹ were recorded for the as-grown bamboo-shoot-like structure. A weak peak at 197 cm⁻¹ was also detected for the as-prepared bamboo-shoot-like structure. It has been reported that anatase TiO₂ has six Raman-active fundamentals in the vibrational spectrum: three E₉ modes centered around 144, 197 and 639 cm⁻¹ (usually designated E₉(1), E₉(2) and E₉(3) respectively),
two $B_{1g}$ modes at 399 and 519 cm$^{-1}$ (designated $B_{1g(1)}$ and $B_{1g(2d)}$), and an $A_{1g}$ mode at 513 cm$^{-1}$ [97, 205]. For the as-prepared bamboo-shoot like structure, the most intense modes were $E_{g(1)}$ and $E_{g(3)}$ whereas the intensity of the $E_{g(2)}$ mode was very weak, as shown in Figure 3-10a. The shifts of 399 and 515 cm$^{-1}$ have been determined to be from $B_{1g}$ mode [205, 206]. These modes were clearly identified in the micro-Raman spectra of the as-prepared bamboo-shoot-like structures, verifying the formation of well-crystallized anatase TiO$_2$, in line with the SAED results. For the as-prepared TiO$_2$ nanotube arrays formed at 30 V for 4h, as shown in Figure 3-10a, only broadening peaks of micro-Raman spectra were recorded and these were determined to be amorphous TiO$_2$, which is consistent with that reported in reference [65].
Anodic current density and effects of $H_3PO_4$ addition

The anodic current density behavior under potentiostatic anodization was recorded and shown in Figure 3-11. It has been suggested that the behavior of anodic current density reveals growth stages of the TiO$_2$ layer, and typically three stages can be identified: an exponential drop due to the formation of a compact oxide layer; a rapid increase due to the migration of fluoride ions and oxide dissolution; and a slow decrease due to the stable, regular growth of TiO$_2$ nanotubes [32]. As shown in the inset of Figure 3-11, a sharp drop in anodic current density was observed after the applied potentials reached the target values. A low anodic current density was obtained for high applied potential, indicating that a compact oxide layer of high thickness was formed at high applied potential. Then the anodic current densities increased slowly due to the formation of nanotubes, reached extremum, and then followed the third stage in experiments at 10 and 20 V. However, different behavior was observed in the anodic current density at the third stage for anodization at 30 V, in that the anodic current density kept increasing rather than slowly decreasing. The increase of anodic current density recorded at 30 V fell into two stages: a slow increase and an exponential increase after 2 h. It was determined that the bamboo-shoot-like structure was formed at the later stage during an exponential increase in current density.

The open-circuit potential (OCP, also referred to as the equilibrium potential or the corrosion potential) is the potential at which there is no current. The OCP of titanium in HF/$H_3PO_4$ aqueous solution is shown in Figure 3-12. It was found that the OCP increased when electrolyte with a high concentration of $H_3PO_4$ was employed. The potentiodynamic polarization behavior of titanium in an aqueous solution containing HF/$H_3PO_4$ was investigated and is shown in Figure 3-13. Comparing Figure 3-13a with Figure 3-13b, it is evident that the corrosion current density ($I_{\text{corr}}$) decreased with increased concentration of $H_3PO_4$. In this study it was revealed that addition of $H_3PO_4$ into electrolyte containing HF causes the corrosion
potential to be more positive and decreases the passive current density. This is consistent with results reported in reference [207].

Figure 3-11 Anodic current density-anodization time curves at different applied potentials in 0.125 M HF + 0.5 M H₃PO₄ aqueous solution.

Figure 3-12 Open-circuit potential of titanium in HF/H₃PO₄ aqueous solutions.

It was found that the concentration of phosphoric acid plays a critical role in the formation of the bamboo-shoot-like structures. These special structures were never found in 0.125 M HF solution without H₃PO₄ under various anodization conditions. Nor could the special structure be obtained when the concentration of H₃PO₄ was
below 0.25 M for potentiostatic anodization at 30 V. The anodic current densities under potentiostatic anodization in electrolytes containing various concentrations of H₃PO₄ were recorded and are shown in Figure 3-14. A dramatic increase in the anodic current density was observed when the concentration of H₃PO₄ was equal or greater than 0.5 M, and the bamboo-shoot-like structures were detected on samples anodized in these electrolytes.

Figure 3-13 Anodic potentiodynamic polarization curves of titanium in (a): 0.125 M HF + 0.5 M H₃PO₄, and (b): 0.125 M HF + 1 M H₃PO₄.
Figure 3-14 Anodic current density-anodization time behaviors of potentiostatic anodization at 30 V in electrolytes containing various concentration of H$_3$PO$_4$.

It has been reported that the addition of H$_3$PO$_4$, which usually acts as a buffering medium, extends the anodization voltage windows for forming TiO$_2$ nanotube arrays [208]. This may result from adjustment of local acidification during pore growth [40, 55]. In the present work, a similar result was demonstrated. It was found that highly-ordered TiO$_2$ nanotube arrays could not be obtained in electrolyte containing 0.125 M HF when the applied potential was greater than 25 V. However, TiO$_2$ nanotube arrays were obtained even at 30 V when 0.5 M H$_3$PO$_4$ was introduced into the electrolyte. Furthermore, the increase in the anodic current density was also observed in 3 M HCl + 0.07 M H$_3$PO$_4$ aqueous solution at 15 V [208]. A similar result was demonstrated by Raja and co-workers [207], who reported that a longer duration of anodization resulted in perturbation of the steady-state of the anodic current density, and the current began to increase in HF/H$_3$PO$_4$ aqueous solution, which was attributed to localized breakdown of the barrier layer and possibly nucleation of the secondary oxide particles [207]. These authors related the instability of the barrier layer to two competing forces, namely surface energy (a stabilizing force) and an increase in strain energy due to electrostriction, electrostatic, and re-crystallization stresses (a destabilizing force) [207].
Figure 3-15 Duration of anodization for 4 h and then (a): secondly anodization in a new electrolyte, and (b): secondly anodization in the used electrolyte.

It was found that the increase of anodic current density was independent of the electrolyte. Firstly, samples were treated under potentiostatic anodization in 0.125 M HF + 0.5 M H$_3$PO$_4$ for 4 h and then taken out of the electrolyte and thoroughly rinsed with DI water. They were then immersed into old and fresh electrolytes respectively, followed by potentiostatic anodization at the same applied potential. The recorded anodic current densities, as shown in Figures 3-15a and 3-15b, exhibited identical behavior. The rapid increase of anodic current density during the
second-step anodization indicated that it resulted from the nature of the anodic TiO$_2$ layer rather than the influence of the electrolyte employed.

*Growth process of the bamboo-shoot like structure/TiO$_2$ nanotube arrays hybrid material*

Vigorous oxygen evolution at the anode was found to be associated with the significant increase of the anodic current density. It has been reported that oxygen evolution on an anode resulted from an increase of electronic conductivity on crystalline regions [209]. The as-prepared bamboo-shoot like structures were determined to be anatase, which exhibited higher electronic conductivity than that of the amorphous TiO$_2$ nanotube arrays, so that vigorous oxygen evolution was observed.

In contrast to formation of the amorphous anodic TiO$_2$ nanotube arrays, the formation of the crystalline bamboo-shoot like structures was of interest. The crystalline TiO$_2$ has been attributed to several factors such as impurity elements in the substrate, growth stresses, electrostriction, and ionic transport under high electric field [210]. Considering that these special structures aligned along the direction of roll-to-roll processing, it is reasonable to believe that the nucleation began at sites with residual stresses in the titanium substrate. Based on these findings, the following growth process of the bamboo-shoot-like structure is proposed. At the first stage, self-organized TiO$_2$ nanotube arrays form on the surface of the titanium, as shown in Figure 3-16a. After a period of anodization and the passage of a certain amount of charges, the oxygen species that have migrated inward aggregate at these sites and form oxygen voids, as shown in Figure 3-16b. The crystallization of TiO$_2$ has previously been ascribed to the inward migration of oxygen species during anodization [210]. Apart from the diffusion of ions as shown in Figure 2-1, oxygen species can migrate into the oxide layer and titanium substrate during the period of anodization. These voids grow rapidly due to the aggregation of more oxygen species, and crystallization starts around these voids, as shown in Figure 3-16c. The crystallization of TiO$_2$ may result from the high pressure of oxygen in the voids.
Finally, the voids and surrounding crystalline TiO$_2$ grow out of the anodic TiO$_2$ nanotube arrays and form the bamboo-shoot-like structures, as illustrated in Figure 3-16d. The formation of the bamboo-shoot-like structures may result directly from the extension of voids and crystalline TiO$_2$, as suggested by the evidence of a cavity inside of the bamboo-shoot-like structure as investigated through FESEM.

Figure 3-16 Schematic representation of formation of bamboo-shoot like structure, (a): formation of anodic TiO$_2$ nanotube arrays, (b): inward migration and aggregation of oxygen species, (c): rapid growth and crystalline of TiO$_2$, and (d): TiO$_2$ growth out of anodic TiO$_2$ nanotube arrays and formation of the bamboo-shoot-like structure.

Spontaneous occurrence of oxygen evolution and crystallization has been defined as the main characteristics of the breakdown of anodic TiO$_2$ [209]. In this study, the breakdown is attributed to ageing of the anodic TiO$_2$ oxide layer under potentiostatic anodization. Ageing induced breakdown of anodic TiO$_2$ and formation of bamboo-shoot-like structures were controlled by the applied voltage, concentration and composition of the electrolyte and anodization time. Dielectric breakdown also
occurred under galvanostatic anodization, which is characterized by a significant
decrease in voltage gradient, gas evolution, sparking, crystallization, or a
combination of these factors [3, 209].

Figure 3-17 Two steps anodization of titanium in HF/H₃PO₄ electrolyte, firstly
anodization under potentiostatic and then under galvanostatic at (a): 1 mA.cm⁻², and
(b): 2 mA.cm⁻².

To investigate the influence of galvanostatic anodization on morphology of
anodic TiO₂ layer, samples were pre-treated under a potentiostatic anodization in
electrolyte containing HF/H₃PO₄ for 2 or 3 h to form TiO₂ nanotube arrays. Then they were treated under galvanostatic condition. The anodization under constant current densities for 1 mA.cm⁻² and 2 mA.cm⁻² is shown in Figures 3-17a and 3-17b, respectively. Perturbations of the applied voltage are clearly observed and dielectric breakdown took place under the constant current anodization condition. However, only anodic TiO₂ nanotube arrays rather than bamboo-shoot-like structures were obtained when the galvanostatic anodization was controlled under 1 mA.cm⁻². When the galvanostatic anodization was conducted under 2 mA.cm⁻², the anodic TiO₂ nanotube arrays which formed during the potentiostatic anodization disappeared.

3.3 Anodization of titanium in a hybrid solution and formation of nanoporous TiO₂ layer

To investigate the influence of applied potential on localized chemical etching processes and the surface morphologies of the TiO₂ layer, a mixed solution containing water, fluoric acid, phosphoric acid, and ethylene glycol (EG) was used as electrolyte, since the properties of the mixed solvent could be continuously tuned by varying the mixing ratio of the components [211]. The morphologies of the TiO₂ layers formed at different applied potentials were examined and described.

Anodization of titanium in hybrid solution

Ti foils of 0.25 mm thickness (99.6 % purity, Goodfellow, England), were degreased according to procedures described in Section 3.2, and then chemically polished in strong acidic solution of HF (3.5 M) and HNO₃ (5.6 M) for 10 s to remove the natural titanium oxide layer, followed by rinsing with deionized (DI) water and drying in a nitrogen stream. The anodization was performed using the same equipment and identical procedures to those described in Section 3.2. The electrolyte consisted of 0.125 M HF, 0.5 M H₃PO₄, and 50 vol % ethylene glycol (EG). The post-treatment procedures and characterization of the morphology of the samples were identical to those described in Section 3.2.
**Formation of nanoporous TiO$_2$ layer**

As shown in Figure 3-18, uniform pores with diameter about a few nanometers are formed on the surface of titanium foil by anodization at 5 V for 2h in the mixed solvent. The result indicates that microporous or mesoporous TiO$_2$ layer can be obtained even at low anodization potential in F$^-$ ions containing electrolyte. However, these TiO$_2$ nanotubes are connected, which is different from those isolated nanotubes.

Figure 3-18 FESEM image of the TiO$_2$ layer prepared by anodization at 5 V for 2 h.
Figure 3-19 FESEM images of the TiO$_2$ layer prepared by anodization for 2 h at (a): 10 V, (b): 20 V, (c): 30 V, (d): cross section view of (c), (e): bottom view of (c), and (f): relationship between diameters of nanotube and anodization potentials.

As shown in Figure 3-19a, a relatively regular nanotube array, with diameter and wall thickness about 30 nm and 15 nm respectively, was observed on the surface of titanium foil after anodization at 10 V for 2 h. When the applied potential was increased to 20 V and 30 V, nanotube arrays with diameter about 60 nm (Figure 3-19b) and 100 nm (Figure 3-19c) respectively were obtained. These findings imply that the diameter of TiO$_2$ nanotube increased linearly with the anodization potential (as illustrated in Figure 3-19f). When these findings are compared with those obtained through anodization in aqueous electrolyte containing HF/H$_3$PO$_4$ (as discussed in Section 3.3), it is notable that a small pore size of TiO$_2$ nanotube could be obtained in the hybrid solution. This may result from the high permittivity of the hybrid electrolyte. As shown in Figure 3-19d, a self-aligned TiO$_2$ nanotube array with a thickness about 800 nm was formed after anodization for 2 h at 30 V. The bottom of the TiO$_2$ nanotube array had a paraboloid shape, and a corresponding parabolic surface remained on the titanium (as shown in Figure 3-19e). Comparing the top view with the bottom view, it was found that the nanotube array was not compact at the mouth, due to chemical dissolution of the TiO$_2$.

Different surface structures were formed when the anodization potential was increased. A mixed of nanotube and porous structure, as shown in Figure 3-20a, was obtained upon anodization at 40 V for 2 h. When the anodization potential was increased to 70 V, macroporous TiO$_2$ with pore size about 200 nm, as shown in
Figure 3-20b, was obtained. When the applied potential was raised to 150 V, macroporous TiO$_2$ with pore size about 500 nm, as shown in Figure 3-20c, was obtained.

![Figure 3-20 FESEM images of the TiO$_2$ layer prepared by anodization for 2 h at (a): 40 V, (b): 70 V, and (c): 150V.](image)

The surface morphologies of TiO$_2$ layers synthesized by anodization at different potentials are summarized in Figure 3-21. When the anodization potential was low but above the OCP, microporous and mesoporous structures were formed. The pore size of nanoporous TiO$_2$ could be increased by improving the applied potential. Regular mesoporous and macroporous structures, i.e., self-aligned TiO$_2$ nanotube arrays, could be formed in a special potential range determined by the properties of the electrolyte employed. Irregular macroporous structures were formed by anodization at high applied potentials. The surface morphology of the TiO$_2$ layer depended not only on the applied potential but also on the properties of the electrolyte including concentration of F$^-$ ions, temperature, conductivity, and
permittivity. These findings will contribute to the synthesis of nanoporous TiO$_2$
layers on titanium substrate, with surface morphology tunable by easy and feasible
adjustment of anodization potential.

Based on the obtained findings, which indicate that surface morphology depends
on the applied potentials, the formation process of nanoporous TiO$_2$ by anodization
in F$^-$ ions containing a mixed solution is proposed here. The nanopores originate
from random breakdown of the barrier TiO$_2$ layer formed on the surface of titanium
foils [47], which takes place when the potential is above the OCP. The breakdown
occurs due to chemical dissolution of the TiO$_2$, and the formed sites act as seeds for
the final pores. The formed sites make the metal surface rough, and then
non-uniform electric fields generate near that surface. Provided that the charge
transport at the interface of metal/oxide is omitted, the metal substrate can be dealt
with as an isopotential body. Considering that the relationship between an electric
field and potential can be described as: $\vec{E} = -\nabla \phi$, where $\vec{E}$ represents the electric
field and $\phi$ is the potential, the electric field is vertical to the surface of the
equipotential body. Then a non-uniform electric field forms near the pore, as shown
in Figure 3-22a. The non-uniform electric field confines F$^-$ ions and other anions at
locations where the electric field intensity is high, which causes the formation of a
concentration gradient of F$^-$ ions (as shown in Figure 3-22b). The anisotropy of the
chemical dissolution which forms the nanoporous TiO$_2$ layer on the titanium stems
from the concentration gradient of the F$^-$ ions. At low applied potential, the
confinement of F$^-$ ions by the non-uniform electric field is weak. At that stage the
chemical etching is almost isotropic, so that the nanotubes are connected and the
depth of the pores formed at low applied potential does not change greatly even after
a long anodization period. When the applied potential is increased, the non-uniform
electric field can strongly modify the distribution of F$^-$ ions so that a higher
concentration of F$^-$ ions is obtained at bottom of the pores and a low concentration at
the top. The concentration gradient of F$^-$ ions causes different etching rates in
different locations, and finally nanotubes are formed at the bottom along the
direction of the electric field. When a higher potential is applied, more F⁻ ions are confined at the bottom of the pore and the size of zone with a high concentration of F⁻ ions is so large that nanotubes with greater diameter are formed. It should be mentioned that the potential range for formation of regular nanotubes depends on factors related to the electrolyte employed such as the concentration of F⁻, the conductivity, and the temperature. When the applied potential is above 40 V, more F⁻ ions are confined at the bottom of the pores and the violent reaction between the F⁻ ions and the TiO₂ layer results in the formation of an irregular macroporous structure.

Figure 3-21 Surface morphologies of the TiO₂ layer prepared by anodization at different applied potential.

The confinement of OH⁻ by the non-uniform electric field, which increased the pH value, also occurred at the bottom of the pores. However, water electrolysis reactions occurred at the bottom of the pores due to a high electric potential, so that rich H⁺ ions generate at the bottom. This is because the reactions $2\text{H}_2\text{O} \rightarrow 2\text{O}^{2-} + 4\text{H}^+$ and $2\text{H}_2\text{O} \rightarrow \text{O}^{2-} + 4\text{H}^+ + 4\text{e}^-$ occur at the Ti oxide/electrolyte interface, oxygen ions reacting with Ti to form oxide, oxygen gas evolving or sticking to the electrode surface. An abundance of H⁺ ions results in a relatively low pH value at the bottom
which aids the chemical etching reaction together with the confinement of F- ions by the electric field. The increased viscosity of the mixed solvent due to ethylene glycol also contributes to the gradient of pH at the bottom and top of the pore because of the process of ions diffusion in the Stoke-Einstein manner, according to Equation (2-8) [48].

![Figure 3-22 Schematic diagrams of formation of (a): non-uniform electric field, and (b): confinement of F- ions by the electric field. The grey area and arrows show the TiO2 layers and directions of electric field, respectively.]

3.4 Anodization of titanium in a non-aqueous solution and formation of TiO2 nanotube arrays

Anodization of titanium in a non-aqueous polar electrolyte containing F- ions results in highly-ordered TiO2 nanotube arrays with very high aspect ratios. For example, TiO2 nanotube arrays greater than 1000 μm in thickness have recently been fabricated in organic solution [50]. This has been attributed to an accelerated rate of nanotube growth rate in the non-aqueous solution containing F- ions, which results from the high dielectric constants and polarity. High electrolyte capacitance induces the formation of more charges on the oxide layer and subsequently improves extraction of the Ti4+ ions [29]. High electrolyte polarity allows HF or NH4F to be easy dissolved, thus increasing their availability at the TiO2/electrolyte interface [29]. Another key point is that the formation of long TiO2 nanotube arrays results from
minimizing water content in the electrolyte [212]. Currently, most studies have employed electrolytes containing HF or \( \text{NH}_4\text{F} \) in organic solvent with a small amount of water. In the present study, non-aqueous electrolytes containing \( \text{NH}_4\text{HF}_2/\text{EG} \) were employed for anodization of the titanium. The surface morphology and growth behavior of the TiO\(_2\) layer were investigated.

**Anodization of titanium in non-aqueous solution consisting of \( \text{NH}_4\text{HF}_2 \) and EG**

Ti samples were degreased according to the procedures described in Section 3.2. The anodization was performed using the same equipment and procedures as described in that section. The electrolyte consisted of ethylene glycol (EG) and 0.25 wt % ammonium hydrogenfluoride (\( \text{NH}_4\text{HF}_2 \), 95 % purity, Sigma-Aldrich). The post-treatment procedures and morphology characterization of the samples were identical to those described in Section 3.2.

**Surface morphology and growth rate of TiO\(_2\) layer**

Figure 3-23 shows the surface morphology, cross-section and bottom view of anodic TiO\(_2\) nanotube arrays obtained at different applied potentials. A bundle layer, consisting of nanowires, was obtained at all applied potentials. The formation of nanowire in a non-aqueous solution consisting of \( \text{NH}_4\text{F} \) and EG was interpreted using the so-called bamboo-splitting model [213]. This model demonstrated that the nanowires on the surface resulted from vertical splitting of the anodic TiO\(_2\) nanotube arrays, which was attributed to electric-field-directed chemical etching. During the anodization process, a small amount of water provided by atmospheric moisture adsorption or by water addition is essential for the formation of the nanowires on top of the anodic TiO\(_2\) nanotube arrays, and the amount of water required for the generation of nanowires significantly relates to the applied potentials. As shown in Figure 3-23, the amount of nanowires was dependent on the applied potential. At low applied potentials, including 20, 30, and 40 V, few nanowires were obtained, as shown in Figure 3-23(a-d). Large amounts of the nanowires were observed for TiO\(_2\) nanotube arrays obtained through anodization at moderate applied potentials.
including 50, 60 and 70 V, as shown in Figure 3-23(e-f). In the sample obtained through anodization at 70 V, the anodic TiO₂ nanotube array was fully covered by a bundle layer of nanowires, as shown in Figure 3-23f. At high applied potentials including 80 and 90 V, very thin nanowire layers were obtained, as shown in Figures 3-23g and 3-23h.

It was found that the regularity of the anodic TiO₂ nanotube arrays depended on the applied potential. At a low applied potential such as 20 V, there was only fair regularity, as shown in Figure 3-23a. However, improved regularity was found in arrays obtained through anodization at applied potentials from 30 to 70 V. At high applied potentials including 80 and 90 V the regularity deteriorated, as shown in Figures 3-23g and 3-23h. Comparing Figure 3-23c with 3-23h, it is evident that the regularity of the bottom obtained at 40 V was much better than that obtained at 90 V. As shown in Figure 3-23h, the bottom of the anodic TiO₂ nanotube arrays was not as compact as that obtained at moderate applied potentials such as 40 V and 60 V.
Figure 3-23 FESEM images of the anodic TiO$_2$ nanotube by anodization in 0.25 wt % NH$_4$HF$_2$+ EG at various potentials for 2 h at (a): 20, (b): 30, (c): 40, (d): 50, (e): 60, (f): 70, (g): 80 V, and (h): 90 V, all the samples were obtained from the backside of the titanium.

Different morphology was observed for the anodic TiO$_2$ nanotube arrays obtained at 90 V. Firstly, the macro-morphologies of the counter-side and back-side of the titanium differed. The back-side was compact whereas the counter-side was porous, as shown in Figures 3-24a and 3-24b respectively. FESEM investigation demonstrated that the protrusions in the counter-side of the titanium consisted of anodic TiO$_2$ arrays as shown in Figure 3-25a. Unlike those obtained at low and moderate applied potentials, the nanotube arrays were less compact and less regular. Under the protruded layer there was an anodic TiO$_2$ array with has large wall thickness and small pore size, as illustrated in Figure 3-25b. When potentiostatic anodization was conducted at 100 V, as shown in Figure 3-26a, a porous structure rather than nanotube arrays were obtained on the surface. However, the bottoms of the TiO$_2$ nanotubes featured loose and irregular structures, as shown in Figure 3-26b.
These porous structures resulted from the high electric field at the surface of the titanium foil.

Figure 3-24 Optical images of the anodic TiO$_2$ nanotube/Ti obtained at 90 V in 0.25 wt % NH$_4$HF$_2$ + EG, (a): backside, and (b): counter-side.

Figure 3-25 FESEM images of anodic TiO$_2$ nanotube obtained by anodization in 0.25 wt % + EG at 90 V, (a): magnified view of counter-side, and (b): counter-side.

Figure 3-26 FESEM images of the anodic TiO$_2$ layer by anodization in 0.25 wt % NH$_4$HF$_2$+EG at 100 V for 2 h, (a): top-view, and (b): bottom-view.
Figure 3-27 Thickness of the anodic TiO$_2$ nanotube arrays obtained in 0.25 wt % NH$_4$HF$_2$ + EG for 2 h at various applied potential.

The thickness of the anodic TiO$_2$ arrays was dependent on the applied potentials, as shown in Figure 3-27. The growth rate could be calculated and it was found to be about 10 $\mu m \cdot h^{-1}$ for anodization at 80 V whereas it was only about 3 $\mu m \cdot h^{-1}$ for anodization at 60 V. The growth rate for anodization in solution consisting of NH$_4$HF$_2$ and EG was lower than that obtained for anodization in electrolyte consisting of NH$_4$F and EG, where the growth rate of the latter has been determined to be around 15 $\mu m \cdot h^{-1}$ [51, 214]. This may be the result of increased concentration of F$^-$ and H$^+$ in solution containing NH$_4$HF$_2$, which enhanced the chemical etching rate of the as-formed anodic TiO$_2$ nanotube arrays and resulted in nanowires on the surface.
Figure 3-28 FESEM images of anodic TiO$_2$ nanotube by anodization at 60 V, (a): top-view, (b): bottom-view, (c): cross-sectional view of TiO$_2$ nanotube, and (d): cross-sectional view of TiO$_2$ nanotube arrays obtained for 12 h.

Although the potentiostatic anodization at 80 V exhibited a high growth rate, it led to low irregularity of the anodic TiO$_2$ nanotube arrays, as shown in Figure 3-23g. Potentiostatic anodization at 60 V seems to be good choice in view of the growth rate and the nanotube array structure. As seen in Figure 3-28(a-c), the TiO$_2$ nanotube arrays obtained through anodization at 60 V showed good regularity and compact structures. Figure 3-28d shows the cross-section of anodic TiO$_2$ nanotube arrays obtained through anodization for 12 h. The thickness was found to be 36.8 $\mu$m, confirming that the growth rate was about $3 \mu m.h^{-1}$ when potentiostatic anodization was conducted at 60 V.

The surface profiles of the anodic TiO$_2$ nanotube arrays obtained through anodization at 60 V were investigated by SPM. Figure 3-29a shows the 2D and 3D surface images of the anodic TiO$_2$ nanotube arrays, again demonstrating the formation of nanowires on the surface. SPM images of the bottom of anodic TiO$_2$ nanotube arrays are given in Figure 3-29b, indicating slight fluctuation in the range of 100 nm. Figure 3-29c exhibits the SPM images of the titanium substrate after removing the as-prepared anodic TiO$_2$ nanotube arrays.
3.5 Anodization of NiTi alloy in an aqueous solution containing F⁻ ions

Surface roughness of the NiTi alloy plays an important role in cell proliferation. It has been demonstrated that cell proliferation could be improved by enhancing surface roughness but it became difficult when the surface roughness was in a micrometer scale [215]. Improved surface roughness and irregularity contributed to biomechanical interlocking which was responsible for reinforce of osseointegration between implant and bone [6]. Cell-implant interactions have been controlled by

Figure 3-29 SPM images of the anodic TiO₂ nanotube obtained in 0.25 wt % NH₄HF₂ + EG at 60 V for 4 h, (a): surface images, (b): bottom images, and (c): metallic substrate after removal TiO₂ nanotubes.
surface roughness [216]. Exploration of approaches to surface modification is worthwhile to increase corrosion resistance and surface roughness.

In the present study, commercially available NiTi alloys were electrochemically anodized in diluted HF electrolyte. The surface morphologies and compositions of the anodized layer were characterized by FESEM equipped with EDS, SPM and XPS. The corrosion resistance of treated NiTi alloy was conducted by cyclic polarization testing in Hanks’ based salt solution at 37 °C and pH 7.4.

Anodization of NiTi alloy and characterization of oxide layer

Commercial NiTi alloy (Memry, USA, 56.0 wt % Ni) was used. Before anodization, the NiTi specimen was cleaned in a mixture of concentrated HF and HNO₃ for 20 s and was then rinsed with deionized (DI) water. The anodization was performed using the same equipment and procedures as described in Section 3.2 in a diluted HF aqueous solution. The post-treatment procedures and characterization of the morphology of the samples were identical to those described in Section 3.2. Reference samples were obtained from anodization in H₃PO₄ electrolyte.

The as-prepared specimens were investigated using FESEM equipped with an EDS device. The surface morphology was examined by SPM working in tapping mode. The composition of the surface layer was investigated by XPS with a Shengyang SKL-12 electron spectrometer equipped with a VG CLAM 4 MCD electron energy analyzer. Non-monochromatic Mg Kα at a current of 15 mA was used during the experiments. The surface hardness of the untreated and the modified NiTi alloy was tested on a Hysitron triboindenter. Three repeated measurements were conducted for each depth and the average hardness values were reported.

The potentiodynamic polarization experiments were performed in Hanks’ based salt solution at 37 °C and pH 7.4. The solution was a physiological salt buffer and its composition is listed in Table 3-1 [217]. Before testing, the solution was purged with nitrogen gas for 30 min. A GAMRY system (model CMS100) was used to record anodic polarization curves with a scanning rate of 0.5 mV s⁻¹. The treated and untreated NiTi alloys served as working electrode, a Pt sheet as counter electrode,
and the all potentials were expressed with reference to a SCE. The polarization scan was conducted from -600 mV to +1600 mV.

Surface properties of anodized NiTi alloy

Figure 3-30 shows the surface morphology and EDS result of NiTi alloy anodized in 0.075 M HF solution at 20V for 1 h. The surface color of the as-prepared NiTi alloy was light yellow, similar to the color of that anodized in H₃PO₄ electrolyte, due to the formation of TiO₂. Similar color changes occurred for titanium anodized in acid and alkaline electrolytes and has been found that the surface color depended on anodization parameters such as anodization potential, composition of electrolyte, and anodization time [218]. It was found that more nanoscale cavities were formed on the surface layer (as shown in Figure 3-30a). This finding indicates that the surface was rougher than that anodized in H₃PO₄ electrolyte (as shown in Figure 3-31a). It is known that surface roughness in all three scales, macro-, micro-, and nano-scale is desirable for implant applications, and micro-roughness of implants is easily obtained by polishing and mechanical grinding. In this study, enhanced nano-roughness was obtained by anodizing in diluted HF electrolyte. The EDS results for surface layers anodized in diluted HF solution and in H₃PO₄ indicated that the atom number of the nickel decreased (as shown in Figures 3-30b and 3-31b, respectively) compared with the untreated NiTi alloy. Reduction of the nickel element in the surface layer anodized in HF electrolytes resulted from preferential dissolution of the nickel element. After anodization in HF solution for a long period the diameter of the NiTi reduced markedly (as shown in Figure 3-32). This implies that both nickel and titanium elements were consumed during the anodization process. When anodized in HF electrolyte, both nickel and titanium in the NiTi alloy lost electrons and formed oxides due to field-assisted oxidation. Then the formed TiO₂ dissolved due to chemical dissolution as follows [28]:

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow (\text{TiF}_6)^{2-} + 2\text{H}_2\text{O}
\]  (3-1)
Others believe that the dissolution of TiO$_2$ is attributed to formation of titanium fluoride or titanium oxide fluoride [219]:

$$\text{TiO}_2 + 4\text{H}^+ + 4\text{F}^- \rightarrow \text{TiF}_4 + 2\text{H}_2\text{O}$$  \hspace{1cm} (3-2)

$$\text{TiO}_2 + 2\text{H}^+ + 2\text{F}^- \rightarrow \text{TiOF}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (3-3)

Because of the chemical dissolution of TiO$_2$, only a very thin oxide layer remained on the surface of the NiTi alloy, which was confirmed by the light yellow color and paucity of oxygen element found by EDS. This was also confirmed by the phenomena of the surface morphologies which depended on the composition of the electrolyte and applied potential but was independent of the anodization time after a critical value. When anodized in fluoric ions containing aqueous solution, a limited TiO$_2$ layer and consumption of the matrix were also observed for titanium and other titanium alloys. It is known that self-aligned, highly-ordered TiO$_2$ nanotube arrays can be generated on the surface of titanium and titanium alloys such as Ti6Al4V,

![Figure 3-30](image)

Figure 3-30 (a): FESEM image of NiTi anodized in 0.075 M HF at 20 V, the inset shows zoom in view of NiTi wire after anodization for 4 h, and (b): EDS result [220].

Ti6Al7Nb, Ti29Nb13Ta4.6Zr, and Ti45Nb due to the simultaneous occurrence of field-assisted oxidation, field-assisted dissolution, and localized chemical
dissolution. Here the irregular surface layer rather than nanotube arrays which formed on the surface of the NiTi alloy in HF might result from the high chemical dissolution rate of Ni which disturbs the localized chemical dissolution.

Figure 3-31 (a): FESEM image of NiTi alloy anodized in 0.5 M H$_3$PO$_4$ at 20 V for 1 h, the inset shows zoom in view of NiTi wire, and (b): EDS result [220].

Figure 3-32 Change in diameter of NiTi wire during anodization in a diluted HF solution [220].

Enhanced surface roughness of the NiTi alloy after anodization in diluted HF was also revealed by SPM. As shown in Figure 3-33a, the oxide layer grown on the NiTi alloy treated in HF was significantly rougher than that treated in H$_3$PO$_4$ (as shown in Figure 3-33b). For samples treated in HF, the mean roughness $R_a$ was
about 53 nm, which is greater than the 11 nm obtained from samples anodized in H$_3$PO$_4$.

Figure 3-33 SPM images of NiTi alloy treated in (a): HF, and (b): H$_3$PO$_4$ [220].
Figure 3-34a shows the XPS surface survey results of NiTi alloys after anodic oxidation in diluted HF solution. The atomic ratio of Ni/Ti in the treated NiTi alloy surface was considerably reduced (with a Ni/Ti element ratio of 0.15). The reduction of the Ni/Ti element ratio at the surface was ascribed to preferential dissolution of nickel. This finding indicates that NiTi alloy anodized in HF will enhance biocompatibility through the formation of TiO$_2$ and the reduction of nickel ions [221]. For titanium, two peaks were detected at 459 and 465 eV corresponding to Ti 2P$_{3/2}$ and Ti 2P$_{1/2}$ spectral lines (data not shown), respectively. Only one O 1s was observed at 530 eV, as shown in Figure 3-34b, which was determined to correspond very well with titanium oxide [222]. This result indicates that the oxide layer consisted of titanium oxide. The Ni/Ti element ratio revealed by XPS was much lower than that revealed by EDS. This is because that XPS explores only a few nm from the top of the surface.

Surface hardness as a function of indentation depth for the untreated NiTi alloy and the NiTi alloy anodized in HF electrolyte is shown in Figure 3-35. With a range of 300–500 nm, the hardness of the NiTi alloy anodized in HF electrolyte showed lower values than the untreated NiTi alloy due to formation of nano-roughness on
the surface. When the indent depth was greater than a certain number of micrometers (about 3000 nm), the hardness in both cases tended to a constant value which depended on the hardness of the NiTi alloy matrix. It has been reported that the formation of a surface oxide layer dramatically improves the surface hardness of NiTi alloy [223]. However, our finding revealed that anodization in HF decreased the surface hardness of the NiTi alloy. This is because the formation of the nanoporous structures on the NiTi alloy surface reduced the surface hardness.

The polarization curves for treated and untreated NiTi alloys in Hanks’ based salt solution at pH = 7.4 and 37 °C are given in Figure 3-36. For the NiTi alloy anodized in HF solution, the corrosion current density ($I_{corr}$), which can be obtained from Tafel extrapolation and the Stern-Geary equation, is significantly higher than that of the untreated sample. For the breakdown potential ($E_{bd}$), which is defined as the least noble potential where pitting or crevice corrosion, or both initiate and propagate, the value for the treated NiTi alloy (about 1000 mV) is larger than that of the untreated NiTi alloy (about 200 mV).

Table 3-1 Composition of Hanks’ based salt solution used for potentiodynamic polarization testing [220].

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g.L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>8.0</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.14</td>
</tr>
<tr>
<td>KCl</td>
<td>0.4</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.35</td>
</tr>
<tr>
<td>MgCl₂.6H₂O</td>
<td>0.1</td>
</tr>
<tr>
<td>Na₂HPO₄.2H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.06</td>
</tr>
<tr>
<td>MgSO₄.7H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>Glucose</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 3-35 Nanohardness of NiTi alloy anodized in HF and untreated NiTi alloy [220].

Figure 3-36 Anodic potentiodynamic polarization curves of treated and untreated NiTi alloys in Hanks’ based salt solution: $I_{\text{corr}}$, corrosion current, $E_{\text{bd}}$, breakdown potential [220].

3.6 Conclusions

In this chapter, anodization of titanium and NiTi alloy in various electrolytes was investigated. The conclusions are listed as follows:
1. The potentiostatic anodization of titanium in aqueous electrolyte containing HF and H₃PO₄ under different applied potentials and anodization times was studied. Highly-ordered TiO₂ nanotube arrays were obtained through anodization at 10, 20 and 30 V and the diameter of the TiO₂ nanotubes was found to depend linearly on the applied potential. Bamboo-shoot-like structure/TiO₂ nanotube arrays hybrid material was obtained through anodization under potentiostatic anodization at 30 V by ageing the anodization process. Through SAED and Raman microscopy the as-prepared bamboo-shoot-like structures were determined to be anatase and the as-prepared TiO₂ nanotube arrays were amorphous. A strong increase in the anodic current density and vigorous oxygen evolution were observed when the bamboo-shoot-like structures were formed. It was revealed that the formation of the bamboo-shoot-like structures stemmed from ageing-induced breakdown of anodic TiO₂.

2. A nanoporous TiO₂ layer including microporous, mesoporous, and macroporous structures was obtained through anodization of titanium foils at different applied potentials in mixed solvents containing F⁻ ions. It was found that regular self-aligned TiO₂ nanotube arrays formed at specific applied potentials only. The chemical dissolution of TiO₂ by localized confinement of F⁻ ions was responsible for the nanoporous structure obtained. The concentration gradient of F⁻ ions stemmed from the non-uniform electric field near the metal surface, whose intensity could be adjusted by changing the applied potential.

3. The surface morphology of the TiO₂ layer obtained through anodization in a non-aqueous electrolyte consisting of NH₄HF₂ and EG, and the influence of applied potential were investigated. It was found that highly-ordered TiO₂ nanotube arrays could be obtained within a wide range of the applied potentials. It was demonstrated that TiO₂ nanotube arrays with compact and highly regular structure could be fabricated at moderate applied potentials, although anodization at high applied potentials increased the growth rate. The optimal applied potential in a non-aqueous
electrolyte consisting of 0.25 wt % NH₄HF₂ and EG was 60 V.

4. Surface modification of the NiTi alloy through anodic oxidization in diluted hydrogen fluoride was investigated. It was found that a light yellow surface oxide layer was formed by potentiostatic anodization in diluted hydrogen fluoride solution. As determined by XPS, the oxide layer consisted of titanium dioxide. The surface oxide layer formed by anodization in HF was considerably rougher than that formed in the phosphoric acid electrolyte. Nanoindentation results revealed that the surface hardness of the NiTi alloy anodized in HF was lower than that of the untreated alloy, which contributed to the formation of the nanoporous surface. Corrosion behavior in Hanks’ based salt solution was investigated and the enhanced corrosion resistance obtained was found to be due to the formation of an oxide layer. These findings indicate that surface modification of the NiTi alloy using anodization in diluted HF solution was effective in enhancing surface roughness and corrosion resistance.
Chapter 4 Photocatalytic Decomposition of Organic Waste in Solution Using Anodic TiO$_2$ Layers

4.1 Introduction

The photocatalytic activity of TiO$_2$ material results from its semiconductor nature and band-edge positions suitable to allow the formation of highly oxidative species from aqueous environments [224]. To obtain high-efficiency photocatalysis, TiO$_2$ with high specific surface area is typically favored. It has been reported that anodic TiO$_2$ nanotube arrays could be a promising photocatalyst. However, there are still unclear aspects in the photocatalytic activity of such arrays. It is commonly accepted nowadays that the morphology of the TiO$_2$ plays an important role in the photocatalytic activity. The influence of the morphology of an anodic TiO$_2$ layer on photocatalytic is limited and need to be interpreted. Furthermore, the photocatalytic efficiency of the TiO$_2$ depends strongly on the compositions its phase, which can be influenced by the post-annealing process. On the other hand, annealing treatment may distort the morphology of the TiO$_2$, again influencing the photocatalytic activity. So interest is stimulated to investigate the effects of morphology and post-annealing processes on the photocatalytic activity of TiO$_2$ layers obtained through anodization. This chapter is into two parts, firstly photocatalytic activity of the anodic TiO$_2$ layer, and secondly design of a fixed-bed flow-through photoreactor. The former includes photocatalytic activity of the bamboo-shoot-like structure/TiO$_2$ nanotube arrays hybrid materials and photocatalytic activity of anodic TiO$_2$ oxide layers with different morphologies including micro-, meso- and macro-porous structures.

4.2 Photocatalytic activity of anodic TiO$_2$ layers

The structures as well as the crystallization of TiO$_2$ play a critical role in the photoresponse properties. A few examples have indicated that anodic TiO$_2$ nanotube arrays exhibit enhanced photocatalytic activity due to enhanced light adsorption and reduced carrier recombination compared with nanoparticulate TiO$_2$ [107]. For
example, the photocatalytic activity of anodic TiO\textsubscript{2} nanotube arrays synthesized in an electrolyte with 0.5 wt \% HF at 10 V, 15 V, and 20 V, following annealing in air at various temperatures, has been examined and the results indicated that the samples anodized at 20 V and annealed at 450 °C exhibited the highest photocatalytic efficiency [225]. However, that study reported decreased photocatalytic activity for samples annealed at temperatures above 450 °C, and this was ascribed to the formation of excessive rutile phase and a decrease in surface area [225]. Others have demonstrated that optimal photocatalytic activity was obtained for anodic TiO\textsubscript{2} nanotube arrays with a thickness of 2.5 \(\mu\)m and the it was only slightly influenced by pore size [226]. For anodic TiO\textsubscript{2} layers obtained from organic electrolyte, it has been reported that the crystal structure as well as the width of the space charge layer of the nanotube arrays were critical factors for photocatalytic decomposition of methylene blue [227]. Others have demonstrated that short nanotube arrays exhibit better photoelectrocatalytic activity than long ones, which was attributed to reduced recombination effects [63]. In brief, the influence of geometry as well as crystalline structure on the photocatalytic efficiency seems to be controversial. In this study, the effects of morphology and the composition of the anodic TiO\textsubscript{2} layers were investigated.

### 4.2.1 Photocatalytic activity of bamboo-shoot-like structures/TiO\textsubscript{2} nanotube arrays hybrid material

*Formation, annealing and characterizations of anodic TiO\textsubscript{2} layer*

The anodization of titanium in aqueous solution containing HF and H\textsubscript{3}PO\textsubscript{4} was described in Section 3.2. The surface morphology was investigated and discussed in Section 3.2. Next, as-prepared hybrid structures and TiO\textsubscript{2} nanotube arrays were annealed in air at various temperatures for different times with a heating rate of 5 °C.min\textsuperscript{-1}. To confirm the compositions of the as-prepared structure, XPS with a Shengyang SKL-12 electron spectrometer equipped with a VG CLAM 4 MCD electron energy analyzer was used. Non-monochromatic Mg Kα at a current of 15 mA was used during the experiments. The as-prepared and annealed hybrid
structures were examined with a Philips diffractometer (Philips PW3020). Raman spectra were recorded at room temperature with a Jobin-Yvon HR800 Raman Spectrometer working at 488 nm.

**Measurement of photoresponse and photocatalytic activity**

The photoelectrochemical properties were investigated using a three-electrode configuration with the TiO₂ layer/Ti as a photoanode, a saturated calomel electrode (SCE) as reference electrode, and platinum foil as a counter electrode. A 1.0 M KOH aqueous solution was used as the electrolyte. An electrochemical workstation (CH Instruments, model CHI 660C) was used to measure dark and illuminated currents at a scan rate of 10 mV.s⁻¹. For illuminated current characterization, the samples were irradiated by General Electric F20T12/BLB 20 W fluorescent lamp which emitted at wavelength 310 - 410 nm with a peak maximum at 365 nm. The UV irradiance was determined to be 0.6 mW.cm⁻².

Photocatalytic activity of the TiO₂ layers was evaluated by degrading of a model organic pollutant-Acid Orange 7 (AO7, C₁₆H₁₁N₂O₄SNa, a textile dye), which is a non-biodegradable dye used in the textile industry and often considered a standard dye for examining photocatalytic activity [107]. The dye AO7 takes advantage of its minimum adsorption at around the irradiation wavelength of UV illumination so that the majority of the incident light is absorbed by the TiO₂. The dye and its reaction products have strong adsorption in the visible spectra, which can be detected by UV/Vis spectrophotometer. Samples (size: 3 x 3 cm) were immersed in 6 mL of AO7 solution (C_{initial} = 2.5 x 10⁻⁵ mol.L⁻¹, PH = 5.3) for 20 min to establish dye adsorption/desorption equilibrium. Then the samples were irradiated by the same lamp as described in characterization of photoresponse activity. For comparison, P25/Ti samples were prepared through a spin-coating method, followed by annealing at 350 °C for 1 h in air. The thickness of the P25 film was determined to be around 400 nm by FESEM. The absorbance of the testing solutions irradiated for 1 h, 2 h, 3 h, and 4 h, was examined using a UV/Vis spectrophotometer (Shimadzu UV-2550).
Composition and crystalline structure of TiO$_2$ layers

The composition of the as-prepared hybrid material was investigated through XPS. A peak at 530 eV related to O 1s was detected, which corresponded well to the oxygen peak in TiO$_2$. For titanium, two peaks at 459 eV and 465 eV, corresponding to Ti 2P$_{3/2}$ and Ti 2P$_{1/2}$, were detected. Trace of F was also observed at 685 eV, which comes from the HF in the electrolyte. As indicated in Figure 4-1, a peak at 133 eV related to P$_{2p}$ was detected on the surface of the hybrid material. It has been reported that the PO$_4^{3-}$ ions can be absorbed more strongly on the TiO$_2$ surface than other ions such as SO$_4^{2-}$ [55].

Figure 4-1 XPS P$_{2p}$ peak of the hybrid material obtained by anodization in H$_3$PO$_4$/HF electrolyte.

Figure 4-2 Distortion of the TiO$_2$ nanotube arrays after annealing at 650 °C for 8 h.
Figure 4-3 XRD patterns of TiO$_2$ structure/Ti annealed at (a): 450 °C for 3 h, (b): 550 °C for 3 h, (c): 650 °C for 8 h, and of (d): P25/Ti.

To induce phase transition, the hybrid materials were annealed at 450 °C/3 h, 550 °C/3 h, and 650 °C/8 h, respectively. No discernible sign of bamboo-shoot-like structures disintegration was observed after the samples were annealed at these temperatures. In the nanotube arrays, slight distortion was detected for samples annealed at 650 °C for 8 h, as shown in Figure 4-2, but no discernible disintegration was observed for samples annealed at 450 °C and 550 °C. The crystallization of the as-prepared and annealed hybrid materials was investigated by XRD. The as-prepared TiO$_2$ nanotube arrays were confirmed by XRD results to be amorphous (result not shown here). Figure 4-3 shows XRD patterns of bamboo-shoot-like structure/TiO$_2$ nanotube array/Ti materials calcined at various temperatures. With annealing at 450 °C for 3 h, peaks at 2θ = 25.3° and 48.1° corresponding to the (101) and (200) planes diffraction of anatase TiO$_2$ respectively were observed, as shown in Figure 4-3a. The broadening of the diffraction peak resulted from the small crystalline size and weak crystallization [228]. As shown in Figure 4-3b, the peak intensities of the anatase increased due to enhancement of crystallization when calcinated at 550 °C for 3 h. Weak diffractions from the rutile phase are observed in Figure 4-3b. These indicate that the enhanced crystallization of anatase and a small amount of rutile TiO$_2$ could be obtained by annealing at 550 °C for 3 h. The phase-transformation temperature of anatase to rutile is around 500 °C. Upon an
increase in the calcination temperature to 650 °C for 8 h, as indicated in Figure 4-3c, the rutile phase became the major phase of the material as evident from the higher ratio of rutile 110 peak to anatase 101 peak. Crystal size can be determined by Scherrer’s equation:

\[ D = \frac{0.89\lambda}{\beta \cos \theta} \]  

(4-1)

where \( D \) is the crystal size, \( \lambda \) is the wavelength of the X-ray radiation (0.154 nm for Cu K\textsubscript{α}l), \( \beta \) is the full width at half-maximum, and \( \theta \) is the diffraction angle.

The crystal sizes of hybrid materials annealed at various temperatures are listed in Table 4-1. The XRD pattern of P25/Ti, which can be indexed into anatase and rutile, is shown in Figure 4-3d. For composite materials consisting of anatase and rutile, the rutile content can be calculated based on the intensities of the peaks for anatase and rutile as follows [229]:

\[ \chi_R = (1 + 0.8 \frac{I_A}{I_R})^{-1} \]  

(4-2)

and the content of anatase can be obtained by \( \chi_A = 1 - \chi_R \), where \( \chi_R \) is the weight fraction of the rutile phase in the composite, and \( I_A \) and \( I_R \) are the integrated x-ray intensities of the (101) reflection of anatase at \( 2\theta = 25.4^\circ \) and the (110) reflection of rutile at \( 2\theta = 27.5^\circ \) respectively. In this study, X’Pert high score software was employed to calculate the intensities of anatase (101) and rutile (110) patterns, and the mass fractions of anatase and rutile of the hybrid materials annealed at different temperatures are shown in Table 4-2.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Crystal size of anatase</th>
<th>Crystal size of rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 °C</td>
<td>22.3</td>
<td>--</td>
</tr>
<tr>
<td>550 °C</td>
<td>18.1</td>
<td>12.6</td>
</tr>
<tr>
<td>650 °C</td>
<td>15.5</td>
<td>30.4</td>
</tr>
</tbody>
</table>
Table 4-2 Mass fraction of anatase and rutile of the hybrid material annealed at various temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>weight fraction of Anatase</th>
<th>weight fraction of Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 °C</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>550 °C</td>
<td>0.89</td>
<td>0.11</td>
</tr>
<tr>
<td>650 °C</td>
<td>0.39</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Figure 4-4 Photocurrent densities of the hybrid material annealed at various temperatures.

Figure 4-4 shows the photocurrent density of the hybrid materials annealed at various temperatures under UV irradiation. As shown in Figure 4-4, the photocurrent density of the hybrid material annealed at 550 °C for 3 h under 0.6 mW.cm\(^{-2}\) illumination was significantly greater than that of the hybrid material annealed at 450 °C for 3 h or at 650 °C for 8 h. Comparing the photocurrent densities of the samples annealed at 450 °C and at 650 °C, it was observed that the photocurrent density of the former was slightly lower than that of the latter. Considering the fact that the hybrid materials were synthesized through an identical process except for the post-calcination process, it is reasonable to assume that the difference resulted from the composition of the hybrid materials. This result indicates that hybrid material containing anatase/rutile in a mass ratio of 0.89:0.11, exhibits a significantly higher photocurrent density than those containing only anatase.
However, the photocurrent density decreased when the hybrid materials contained 61 wt % rutile and 39 wt % anatase. This may stem from disintegration of the nanotube arrays annealed at 650 °C and the low charge carrier mobility of rutile compared with anatase [68].

![Absorption Spectrum](image)

Figure 4-5 UV/Vis adsorption spectra of an AO7 solution.

![Rate Constants](image)

Figure 4-6 Apparent rate constants of P25 and anodic TiO₂ layers with different morphologies and various post-annealing temperature (data extracted from Table 4-1).
Photodecomposition properties of TiO$_2$ layer and analysis of the data

Figure 4-5 shows the UV/Vis adsorption of AO7 solution. It was found that the wavelength of maximum adsorption was 485 nm, which could therefore be used to determine the concentration of AO7 at that wavelength. As shown in Figure 4-5, the minimum adsorption of AO7 solution was at around 350 nm, which resulted in weak adsorption of UV irradiation by the solution, so that the majority of the incident light was absorbed by the TiO$_2$ nanotube arrays. The data from photocatalytic measurement were plotted as logarithms of the time-dependent normalized dye concentration, which was the ratio between the initial concentration C$_0$ and the real-time actual dye concentration C. The degradation curves were almost linear,
indicating that the decomposition kinetics essentially followed a pseudo-first-order kinetics:

\[ \ln(C/C_0) = \kappa \tau \]  

(4-3)

where \( \kappa \) is the apparent rate constant and \( \tau \) is time [106]. The apparent rate constants of various samples are listed in Table 4-3 and schematically represented in Figure 4-6. Blank (control) experiment revealed that the decomposition of AO7 by UV irradiation with wavelength around 360 nm was negligible. In the as-prepared TiO\(_2\) nanotube arrays obtained through anodization for 2 h, it was found that the photocatalytic activity was very weak. This was because the amorphous TiO\(_2\) was not photoactive [230]. The photocatalytic activity of the TiO\(_2\) nanotube arrays obtained through anodization for 2 h is higher than that obtained through anodization for 1 h, indicating that the photocatalytic activity of the TiO\(_2\) nanotube arrays depended on their thickness. As shown in Figure 4-7, Degussa P25, which has a high specific surface area, ca. 50 m\(^2\)g\(^{-1}\), has often been used as a benchmark for photocatalysis. The TiO\(_2\) nanotube arrays showed higher photocatalytic activity than P25 film of similar thickness, which is in line with findings reported by Schmuki’s group [107]. The enhanced photocatalytic activity of the regular TiO\(_2\) nanotube arrays resulted from low trap and recombination of electron-hole pairs and easy diffusion from solution to the active surface area [107].

### Table 4-3 Photocatalytic activities for AO7 oxidation.

<table>
<thead>
<tr>
<th>Photocatalyst Annealed Temperature</th>
<th>Morphologies</th>
<th>Crystalline*</th>
<th>-κ (h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td></td>
<td>0.006</td>
</tr>
<tr>
<td>30V/1h</td>
<td>450 °C/3 h</td>
<td>NT</td>
<td>A</td>
</tr>
<tr>
<td>30V/2h</td>
<td>as-prepared</td>
<td>NT</td>
<td>α</td>
</tr>
<tr>
<td>30V/2h</td>
<td>450 °C/3 h</td>
<td>NT</td>
<td>A</td>
</tr>
<tr>
<td>30V/3h</td>
<td>450 °C/3 h</td>
<td>hybrid</td>
<td>A</td>
</tr>
</tbody>
</table>

123
The as-prepared hybrid materials showed low photocatalytic activity due to the bamboo-shoot-like structures, which were directly crystallized during anodization. Samples obtained through anodization for 3 h after annealing at 450 °C showed higher photocatalytic activity than those obtained through anodization for 2 h after calcination at 450 °C, due to the formation of the bamboo-shoot-like structures which had higher photocatalytic activity than the nanotube arrays. Improved photocatalytic activity was obtained when more bamboo-shoot-like structures were formed. The high photocatalytic efficiency of the bamboo-shoot-like structures may be ascribed to the layered geometry, which could improve the efficiency of adsorption light and the diffusion rates of reactants. Although the dimensions of the bamboo-shoot-like structures were in micrometer scale, they consisted of many layered structures which were found to be nanocrystalline anatase TiO$_2$, as determined by XRD and HRTEM as shown in Figure 4-8, which shows a crystal size of about 25 nm and a clear lattice of anatase. The nanocrystalline anatase TiO$_2$ with high specific surface area provided a high population of coordinately unsaturated titanium sites and oxygen vacancies existing at crystallite corners and edge locations, which enhanced the photocatalytic performance [231].

The highest photocatalytic efficiency was obtained for sample annealed at 550 °C, which consisted of a mixture of anatase and rutile phases revealed by XRD. The crystalline structure of TiO$_2$ plays a key role in photocatalysis, except for the specific surface area, reactants diffusion rate. It is generally recognized that the anatase phase of TiO$_2$ shows higher photocatalytic efficiency than the rutile phase. This has been ascribed to several factors, including a higher amplitude of

<table>
<thead>
<tr>
<th>Condition</th>
<th>Treatment</th>
<th>Type</th>
<th>Material</th>
<th>α/A</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>30V/4h</td>
<td>as-prepared</td>
<td>hybrid</td>
<td>α/A</td>
<td>0.129</td>
<td></td>
</tr>
<tr>
<td>30V/4h</td>
<td>450 °C/3 h</td>
<td>hybrid</td>
<td>A</td>
<td>0.339</td>
<td></td>
</tr>
<tr>
<td>30V/4h</td>
<td>550 °C/3 h</td>
<td>hybrid</td>
<td>A/R</td>
<td>0.567</td>
<td></td>
</tr>
<tr>
<td>30V/4h</td>
<td>650 °C/8 h</td>
<td>hybrid</td>
<td>A/R</td>
<td>0.239</td>
<td></td>
</tr>
<tr>
<td>P25/Ti</td>
<td>NP</td>
<td>A/R</td>
<td>0.224</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*α: amorphous; A: Anatase; R: Rutile
photoadsorption of oxygen and a lower relative electron-hole recombination rate of anatase compared with rutile [232]. On the other hand, reduction of the recombination of photogenerated electron-hole pairs and enhancement of photocatalytic activity can be achieved by compositing two phases of the same semiconductor [228]. The high photocatalytic activity of commercially available P25, which contains anatase (78 % in mass fraction) and rutile (22 % in mass fraction) phases, has been attributed to the increase in charge-separation efficiency resulting from interfacial electron transfer from the anatase conduction band to the rutile conduction band, which exhibits much higher photocatalytic efficiency of CH₃CHO than either pure anatase or rutile [233]. It has been demonstrated that the enhanced charge separation, which is responsible for the improved photocatalytic property of P25, results from the rapid electron transfer from the rutile conduction band to lower energy anatase lattice trapping sites [234]. The electron-transfer process, which is critically dependent on the small particle size of the rutile phase and intimate contact between the two phases, results in the existence of catalytic hot-spots at the anatase/rutile interface [234]. Recently, it has been found that the photocatalytic activity of TiO₂ depends directly on the surface phase and it can be greatly enhanced by the formation of intimate anatase-rutile phase junctions so that carrier transfer between the two phases occurs smoothly [235]. More recently, rutile-anatase core-shell structured nanocrystalline TiO₂ has been developed and investigated for photocatalytic application [236]. In our study, photocatalytic efficiency decreases severely due to disintegration of the nanotube arrays and formation of considerable rutile phase when the samples were annealed at 650 °C for 8 h. This result is well in line with photocurrent results of hybrid materials annealed at various temperatures.

When the photocatalytic activity of the hybrid materials was compared with that of the nanotube arrays, as shown in Table 4-3 and Figure 4-6, it was found that the photocatalytic efficiency of the former was significantly higher. This may have resulted mainly from the hybrid structure of the bamboo-shoot-like structures, whose hierarchically macro/meso-structure favored photocatalytic activity due to the
minimization or intra-diffusion resistance and enhancement of photoadsorption efficiency [237]. Moreover, the high hydrophilicity of the hybrid material compared to the regular nanotube arrays enhanced the reactions at the interface of solid/electrolyte and thus enhanced the photocatalytic activity. It was found that the photocatalytic efficiency of the TiO$_2$ nanotube arrays depended on the anodization time for the same annealing process, as shown in Figure 4-6 and Table 4-3. This was because the photoresponse was mainly dominated by two controversial factors, namely light adsorption and recombination of photogenerated electron-hole pairs, which both depend on the length of the nanotube. It has been demonstrated that nanotube arrays with thickness of 1 µm are the optimal structure for UV conversion [24]. In our study, as the thickness of both kinds of nanotube arrays was less than 1µm, the longer nanotube arrays exhibited relatively high photocatalytic efficiency due to their enhanced light adsorption.

4.2.2 Photocatalytic activity of nanoporous TiO$_2$ layers

*Formation, annealing and characterizations of nanoporous TiO$_2$ layer*

The anodization of titanium and characterization of the nanoporous TiO$_2$ layer were described in Section 3.2. To crystallize TiO$_2$, the as-prepared samples were annealed at different temperatures in air, with a heating rate of 5 °C.min$^{-1}$. Then the crystallization was characterized by X-ray diffractometer. The photocatalytic activity was examined according to the description in the previous section. The surface morphologies of the nanoporous anodic oxide layer through anodization at various applied potentials were described in Section 3.2.

The crystalline nature of the as-prepared nanoporous TiO$_2$ was revealed to be amorphous (data not shown). Figure 4-9 shows XRD patterns of TiO$_2$ anodic titanium oxide (ATO)/Ti materials annealed at various temperatures. With annealing at 450 °C for 3 h, peaks at 20 = 25.3° and 48.1° corresponding to the (101) and (200) planes diffraction of anatase respectively were observed (shown in Figure 4-9a). As shown in Figure 4-9b, the peak intensity of the anatase increased due to enhancement of crystallization when annealed at 550 °C for 3 h. Weak diffractions
from the rutile phase can be seen in Figure 4-3b. These results indicate that enhanced crystallization of anatase and a small amount of rutile TiO₂ could be obtained by annealing at 550 °C for 3 h. When the calcination temperature was increased to 650 °C for 3 h, as indicated in Figure 4-9c, rutile became the major phase of the materials, as evident from the higher ratio of the rutile 110 peak to the anatase 101 peak.

Figure 4-9 XRD patterns of anodic TiO₂/Ti annealed at (a): 450 °C, (b): 550 °C, and (c): 650 °C for 3 h.

Photocatalytic activity of nanoporous TiO₂ layer

The data from photocatalytic measurement were plotted as logarithms of the time-dependent normalized dye concentration according to the approach detailed in the previous section. It was found that the degradation curves were almost linear, indicating that the decomposition kinetics followed essentially pseudo-first-order kinetics as described by Equation (4-3). The photocatalytic efficiency of the nanoporous TiO₂ layer obtained through anodization at different applied voltages and then annealed at 450 °C for 3 h is shown in Figure 4-10a. It was found that the regular TiO₂ nanotube arrays formed at 30V exhibited the highest photocatalytic efficiency. The influence of thickness of the anodic TiO₂ nanotube arrays on the photocatalytic performance was investigated. As shown in Figure 4-10b, the photocatalytic efficiency of the regular TiO₂ nanotube arrays depended linearly on
the anodization time, indicating that the photocatalytic activity of the anodic TiO₂ nanotube arrays depended on their thickness. The effects of the annealed temperature on photocatalytic activity were examined. It was found that the photocatalytic activity was controlled by the annealed temperature, as indicated in Figure 4-10c. The photocatalytic efficiency of the annealed TiO₂ nanotube arrays annealed at 550 °C was higher than that of the arrays treated at 450°C and those treated at 650 °C. It has been reported that the photocatalytic activity of anatase is higher than that of rutile. The decrease of the photocatalytic efficiency of the anodic TiO₂ nanotube arrays annealed at 650 °C resulted from the increase of rutile TiO₂ (as shown in Figure 4-10c). However, the photocatalytic activity would be improved if appropriate rutile TiO₂ was formed. This is because photocatalytic activity could be enhanced by the anatase-rutile phase junction, as discussed in Section 4.2. Moreover, annealing at 650 °C caused distortion of the TiO₂ nanotube arrays, which reduced photocatalytic efficiency. The apparent rate constants of the nanoporous TiO₂ layers annealed at different temperatures are shown in Table 4-4 and Figure 4-11.
Figure 4-10 Photocatalytic activity of nanoporous TiO$_2$ layers formed at (a): various voltages and treated at 450 °C/3 h, (b): 30V for different anodization times and treated at 450 °C/3 h, and (c): 30 V/2 h annealed at different temperatures.

Table 4-4 Photocatalytic activities of anodic oxide layer for AO7 oxidation.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Annealed temp</th>
<th>Morphologies</th>
<th>Crystalline $^*$</th>
<th>$\kappa$</th>
<th>R-square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td></td>
<td>NT</td>
<td>A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATO/10V/2h</td>
<td>450 °C/3 h</td>
<td>NT</td>
<td>A</td>
<td>0.142</td>
<td>0.99</td>
</tr>
<tr>
<td>ATO/20V/2h</td>
<td>450 °C/3 h</td>
<td>NT</td>
<td>A</td>
<td>0.294</td>
<td>0.98</td>
</tr>
<tr>
<td>Sample</td>
<td>Temperature</td>
<td>Porosity</td>
<td>Phase</td>
<td>k_{app} (A)</td>
<td>η (%)</td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>----------</td>
<td>--------</td>
<td>-------------</td>
<td>-------</td>
</tr>
<tr>
<td>ATO/70V/2h</td>
<td>450 °C/3 h</td>
<td>porous</td>
<td>A</td>
<td>0.247</td>
<td>0.98</td>
</tr>
<tr>
<td>ATO/30V/0.5h</td>
<td>450 °C/3 h</td>
<td>NT</td>
<td>A</td>
<td>0.141</td>
<td>0.98</td>
</tr>
<tr>
<td>ATO/30V/1.0h</td>
<td>450 °C/3 h</td>
<td>NT</td>
<td>A</td>
<td>0.300</td>
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<tr>
<td>ATO/30V/1.5h</td>
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<td>A</td>
<td>0.461</td>
<td>0.99</td>
</tr>
<tr>
<td>ATO/30V/2h</td>
<td>450 °C/3 h</td>
<td>NT</td>
<td>A</td>
<td>0.509</td>
<td>0.98</td>
</tr>
<tr>
<td>ATO/30V/2h</td>
<td>550 °C/3 h</td>
<td>NT</td>
<td>A/R</td>
<td>0.546</td>
<td>0.99</td>
</tr>
<tr>
<td>ATO/30V/2h</td>
<td>650 °C/3 h</td>
<td>NT</td>
<td>A/R</td>
<td>0.320</td>
<td>0.98</td>
</tr>
</tbody>
</table>

* A: anatase, R: rutile

Figure 4-11 Apparent rate constants of nanoporous TiO_2 layers with different morphologies and various post-annealing temperatures (data extracted from Table 4-4).

4.3 Design of a fixed-bed flow-through reactor using anodic TiO_2 nanotube arrays for photocatalytic decomposition of organic waste in solution

To utilize photocatalysis to decompose organic waste or bacteria in air or solution, the design of a reactor with increased efficiency is necessary [238, 239]. To design a continuous photocatalytic reactor of industrial scale, the most important parameters to consider include the catalyst configuration, the specific illuminated surface area, the mass transfer rate, the light efficiency, the UV source, the scaling-up possibilities, and the intrinsic reaction kinetics [240]. Regarding the
photocatalyst configuration, current reactors fall into two types: those with the photocatalyst suspended (photoreactors that use a photocatalyst as the suspension form are called suspended photoreactors, sometimes also called slurry photoreactors) and those with the photocatalyst immobilized on a carrier material or substrate (reactors that use an immobilized photocatalyst are called immobilized photoreactors) [241]. Suspended systems are often more efficient than immobilized ones due to the absence of limitation of mass transfer and the large specific surface area of the nanometer-scale particles. However, suspended systems are limited by a separation step required to retrieve the photocatalyst after the purification process and by limited penetration depth into the slurry of light. These disadvantages can be avoided by using an immobilized system, which usually consists of TiO₂ thin film prepared by deposition, sol-gel or anodization methods. Limitations of this system include inefficient mass transfer and limited specific area for the reactants.

Nowadays, photocatalytic reactors, both suspended and immobilized, usually use TiO₂ nanoparticles as the photocatalyst. Little is known about anodic TiO₂ nanotube arrays, although it has been demonstrated that they have higher photocatalytic efficiency than the commercially available Degussa P25 nanoparticles [107]. Furthermore, many laboratory reactors used for photocatalytic studies have a small capacity of 100 to 500 ml [242]. Here we designed a fixed-bed flow-through immobilized photoreactor with a capacity of 3000 ml, using highly-ordered anodic TiO₂ nanotube arrays as the photocatalyst.

**Photoreactor configuration**

A schematic diagram of the fixed-bed flow-through photoreactor is shown in Figure 4-12. It consisted of three main parts: a treatment box with anodic TiO₂ nanotubes arrays/Ti foils attached, a UV illumination system and a cyclic water supply system. The treatment box, made from Polymethyl Methacrylate (PMMA) sheets with a thickness of 5 mm, was divided into three small units with size of 60*70*220 mm so that water could flow through them one by one, as shown in Figure 4-13. The TiO₂ nanotube arrays/Ti foils were attached on copper foils, as
shown in Figure 4-14, and then the copper foils were attached on the inner surfaces of the small units beside the bottom. Three quartz shells $\phi 50 \text{mm}\times 210 \text{mm}$ in size were put into the treatment box to separate the water with UV lamps, as shown in Figure 4-15(a-d). The UV lamps were from Osram with a power of 18 W each, which emitted irradiation with a peak maximum at 365 nm. The cyclic water supply system was composed of an electrical pump with a power of 9 W, a water tank 120*70*230 mm in size and contact pipes. A diagram of the photoreactor in operation is shown in Figure 4-16.

![Figure 4-12 Schematic representation of the fixed-bed, flow-through photoreactor.](image1)

![Figure 4-13 Schematic representation of flow through in treatment box.](image2)
Figure 4-14 TiO$_2$ nanotube arrays/Ti foils attached on copper foils.

Figure 4-15 Diagrams of (a): treatment box, (b): UV lamps, (c): quartz shells, and (d): assemble of them.

Figure 4-16 Diagram of fixed-bed flow-through photoreactor.
Formation and annealing of anodic TiO$_2$ nanotube arrays

Anodization was performed as described in Section 3.2 at 20 V for 2 h. Then the as-prepared samples were rinsed in DI water and dried in air, followed by post-annealing at 450 °C for 3 h. The morphology and composition of the TiO$_2$ layers were investigated by FESEM and XRD respectively and the results were provided in Section 3.2.

An optical image of the titanium foil after anodization in aqueous solution containing HF and H$_3$PO$_4$ is shown in Figure 4-17. The yellow part consists of TiO$_2$ nanotube arrays, which had been investigated through FESEM and the relevant results shown Section 3.2. The diameter and length of the TiO$_2$ nanotube arrays were 130 nm and 600 nm respectively. After annealing at 450 °C for 3 h in air, the as-prepared anodic TiO$_2$ nanotube arrays were transferred to anatase.

![Figure 4-17 Optical image of Titanium foil after anodization in HF/H$_3$PO$_4$ aqueous solution (the uniform yellow part consisting of anodic oxide layer, the silver-grey part is pure titanium for clamping).](image)

Decomposition of dye AO7 using the photoreactor

Photocatalytic activity was tested by decomposing AO7 solution, as described in the previous section. Before the experiments, the TiO$_2$ nanotube arrays/Ti/copper foils were immersed in dye solution for 20 min to establish equilibrium of dye adsorption/desorption. Then the three UV lamps and the pump were opened. For comparison, P25/Cu foils of the same size were prepared through the dip-coating
method, followed by annealing at 350 °C for 1 h in air, and the thickness of the P25 film was determined to be around 500 nm. The absorbance of the testing solutions irradiated for 1 h, 2 h, …, and 8 h, was examined using a UV/Vis spectrophotometer (Spectronic Genesys 2) at wavelength $\lambda = 484.5$ nm.

**Analysis of photocatalytic decomposition properties of the photoreactor**

The data from photocatalytic measurement were plotted as logarithms of the time-dependent normalized dye concentration, which was described in Section 4.1. As shown in Figure 4-18, the decomposition of the AO7 dye by UV irradiation without the photocatalyst was negligible. The degradations curves of the annealed anodic TiO$_2$ nanotube arrays/Ti foils and P25/Cu sheets were almost linear, as shown in Figure 4-18, indicating that the decomposition kinetics essentially followed a pseudo-first-order kinetics described by Equation (4-3). The apparent constants were extracted from Figure 4-18 and are listed in Table 4-5. The absolute apparent rate constant of the photoreactor using the anodic TiO$_2$ was about $0.127 \text{ h}^{-1}$, which was about twice of that using P25/Cu sheets. This finding indicates that the anodic TiO$_2$ nanotube arrays/Ti is a promising photocatalyst for photoreactors. The color change of the AO7 solution through the photoreactor using anodic TiO$_2$ nanotube arrays as photocatalyst is shown in Figure 4-19.

In comparisons of the absolute apparent rate constant of the anodic TiO$_2$ nanotube arrays in the photoreactor with that found in Section 4.2.1 and Section 4.2.2, it was found that the former is much lower than either of the latter. This may stem from several factors. Firstly, according to Beer’s law, UV irradiation attenuates rapidly. In our system, the minimum displacement between the quartz shell and the TiO$_2$ nanotube arrays/Ti foils was greater than 10 mm. In fact, the demand for catalyst illumination adds engineering complexity in photoreactor design, in addition to complications of scale-up in conventional reactors such as mixing and mass transfer, reactant-catalyst contact, flow patterns, reaction kinetics, catalyst installation, temperature control, etc. [242]. On the other hand, the dye solution flowed through the treatment box at a relatively high flow velocity of 11.7 mL.s$^{-1}$. 

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This caused the dye solution to flow rapidly through the surface of the anodic TiO$_2$ nanotube arrays, decreasing the efficiency of photocatalytic decomposition. Furthermore, the amount of active photocatalyst in the photoreactor was limited and even though individual degradation processes might be relatively efficient, the photocatalytic efficiency of the photoreactor was still low. The parameters including the inner surface and volume of the treatment box of the photoreactor are listed in Table 4-6.

![Photocatalytic activity of fixed-bed flow-through photoreactor using anodic TiO$_2$ nanotube arrays/Ti, P25/Cu and only UV illumination.]

Table 4-5 Apparent rate constants of (data extracted from Figure 4-22)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition*</th>
<th>$-\kappa$/h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UVA</td>
<td></td>
<td>0.019</td>
</tr>
<tr>
<td>P25/copper</td>
<td>A/R</td>
<td>0.064</td>
</tr>
<tr>
<td>TiO$_2$ NT arrays/Ti</td>
<td>A</td>
<td>0.127</td>
</tr>
</tbody>
</table>

A: anatase, R: rutile

Table 4-6 Parameters of fixed-bed, flow-through photoreactor

<p>| Volume of reactor (cm$^3$) | 1814 |</p>
<table>
<thead>
<tr>
<th>Volume of water tank (cm$^3$)</th>
<th>1276</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocatalyst surface area (cm$^2$)</td>
<td>600</td>
</tr>
<tr>
<td>Volumetric flow rate (cm$^3$.s$^{-1}$)</td>
<td>11.7</td>
</tr>
<tr>
<td>Electrical energy input (W)</td>
<td>62</td>
</tr>
</tbody>
</table>

Figure 4-19 Color change of AO7 solution during UV illumination in photoreactor using the anodic TiO$_2$ nanotube arrays as photocatalyst.

4.4 Conclusions

In this chapter, the photocatalytic activity of the TiO$_2$ layers obtained through anodization in aqueous and hybrid solutions was investigated through photodecomposition of a non-biodegradable dye, AO7. To scale up the photocatalytic decomposition, a fixed-bed flow-through photoreactor was designed and examined. The conclusions are listed as follows:

1. The photocatalytic properties of the TiO$_2$ layer obtained by anodization in an aqueous solution containing HF and H$_3$PO$_4$, following treatment through annealing in air at different temperatures for phase transformation, were investigated through degradation of dye AO7 under UV illumination. It was found that the bamboo-shoot-like structures/TiO$_2$ nanotube arrays hybrid material exhibited higher photocatalytic efficiency than the anodic TiO$_2$ nanotube arrays and P25 film. The
influence of the composition of the TiO$_2$ layer on the photocatalytic performance was investigated and it was found that sample annealed at 550 °C showed the highest photocatalytic efficiency. XRD investigation revealed that the sample annealed at 550 °C consisted of anatase and rutile. The enhancement of photocatalytic activity was attributed to the formation of anatase/rutile junctions.

2. The photocatalytic performance of nanoporous TiO$_2$ layers obtained through anodization in a hybrid solution containing F$^-$ ions was investigated. It was found that the regular TiO$_2$ nanotube arrays obtained through anodization at 30 V exhibited higher photocatalytic efficiency than other nanoporous TiO$_2$ layers. The photocatalytic activity of the anodic TiO$_2$ nanotube arrays depended on the nanotube length, and it was found that anodic TiO$_2$ nanotube arrays with increased thickness showed enhanced photocatalytic efficiency.

3. A fixed-bed flow-through photocatalytic reactor was designed and fabricated. The photocatalytic reactor consisted mainly of a treatment box divided into three units, a UV illumination system containing three UV lamps, and a cyclic water system supplied by a pump. It was found that the photocatalytic decomposition efficiency of dye AO7 solution using the anodic TiO$_2$ nanotube arrays as photocatalyst was significantly higher than that using P25 film. However, the photocatalytic efficiency of the photoreactor was lower than that of the anodic TiO$_2$ nanotube arrays in static experiment. This finding was ascribed to several factors including weak UV irradiation and limited photocatalyst in relation to the capacity of the photocatalytic reactor.
5.1 Introduction

Nanocrystalline TiO$_2$ has been used as a model material to investigate systems that combine both pseudo-capacitance and lithium intercalation. As well designed 1D-nanostructured architecture, anodic TiO$_2$ nanotube arrays have recently attracted considerable interest for energy-storage applications due to their highly accessible surface, electrochemical behavior and chemical stability [243, 244]. Through integrating some noble or transition metal oxides, TiO$_2$ nanotube based nanocomposites have been successfully fabricated for supercapacitor applications [135]. Due to their unique architecture, these anodic TiO$_2$ nanotube arrays can act as the electrode substrate of a supercapacitor. Furthermore, the well-aligned nanotubular structure also provides more available spaces for electrochemical reactions. Therefore, fabrication of electroactive materials/anodic TiO$_2$ nanotube arrays/current collector composites has become an effective way of promoting the full utilization and also lessening the fading effect of electroactive materials during continuous charge-discharge processes. In contrast to a typical redox supercapacitor, in which the electroactive material was attached on a metallic current collector obtained through deposition or sol-gel methods, the composites developed here have a sandwich structure of electroactive materials/anodic TiO$_2$ nanotube arrays/Ti. The composites are excepted to exhibit different behaviors since charges must penetrate the semiconducting anodic TiO$_2$ nanotube arrays during operation of the redox supercapacitor whereas charges directly transferred to metallic current collector for a traditional redox supercapacitor.

In this chapter, the electrochemical double layer capacitance (EDLC) of anodic TiO$_2$ nanotube arrays is first investigated. Then, NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti and RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites obtained through electrochemical deposition are investigated for redox supercapacitor application.
5.2 EDLC of anodic TiO$_2$ nanotube arrays

The charge storage of EDLC results from the adsorption of ions on the surface of the electrode materials, which depends directly on the accessible surface area. Therefore, nanostructured materials should be promising as electrodes for EDLC due to their provision of relatively short electronic and ion transport [245]. The unique architecture of anodic TiO$_2$ nanotube arrays favors the adsorption of ions as well as facilitating charge transport with very low resistance. In the present work, the EDLC of as-prepared and annealed anodic TiO$_2$ nanotube arrays was investigated.

Measurement of EDLC of anodic TiO$_2$ nanotube

For comparison, anodic TiO$_2$ nanotube arrays were synthesized through anodization in two different electrolytes, HF solution and HF/H$_3$PO$_4$ solution. The selection of materials and the anodization process used were exactly identical to those described in Chapter 3. Anodization in pure HF (0.125 M) solution was conducted at 20 V for 0.5 h, and anodization in 0.125 M HF + 0.5 M H$_3$PO$_4$ was conducted at 25 V for 1.5 h. To crystallize the anodic TiO$_2$ nanotube arrays, they were annealed in air at 450 °C for 2 h. The as-prepared and annealed samples obtained through anodization in HF solution were denoted ANTF20-asp and ANTF20-450 respectively. Similarly, the as-prepared and annealed samples obtained through anodization in HF/H$_3$PO$_4$ at 25 V were denoted ANTFP25-asp and ANTFP25-450 respectively. To enhance the surface area, the annealed samples were immersed in 40 mM TiCl$_4$ aqueous solution at 70 °C for 0.5 h, following calcination at 350 °C for 0.5 h, and these samples were denoted ANTF20-450-P. The morphology and composition of the as-prepared and annealed anodic TiO$_2$ nanotube arrays were examined and the findings were provided Chapters 3 and 4. The length of the anodic TiO$_2$ nanotube arrays obtained from the HF electrolyte was about 300 nm, which was shorter than that obtained from the electrolyte containing HF and H$_3$PO$_4$, i.e., 700 nm. Both these anodic TiO$_2$ nanotube arrays have similar pore size and wall thickness, 100 nm and 15 nm respectively. For the annealed samples, no
discernible disintegration of nanotube arrays was detected through FESEM. The composition of the annealed sample investigated by XRD was shown in Chapter 4 and it was determined to be anatase.

The EDLC of the anodic TiO$_2$ nanotube arrays was investigated through cyclic voltammetry and galvanostatic charge-discharge techniques using an electrochemical workstation VersaSTAT 3 (Princeton, USA). The anodic TiO$_2$ nanotube arrays/Ti material was used as a working electrode, platinum foil as a counter electrode, and a SCE as a reference electrode. Electrochemical impedance spectroscopy (EIS) was carried out in a frequency range from 0.1 Hz to 100 kHz under a constant potential of 0 V and ac-voltage amplitude of 10 mV. Two kind of aqueous solutions (1 M H$_2$SO$_4$ and 1 M KOH) were employed for the cyclic voltammetry and galvanostatic charge-discharge characterizations.

**Analysis of EDLC of anodic TiO$_2$ nanotube arrays**

The cyclic voltammetry (CV) behavior of the ANTFP25-asp in 1 M H$_2$SO$_4$ solution is shown in Figure 5-1a. It was found that the CV curves are close to an ideal rectangle, indicating an EDLC-type energy-storage mechanism. As shown in the insert in Figure 5-1a, the current densities increased almost linearly as a function of the scan rate, and it was found that the shapes were maintained at a high scan rate, indicating good power properties [246, 247]. The CV behavior of the ANTFP25-asp in 1 M KOH solution is given in Figure 5-1b. Comparing Figure 5-1b with 5-1a, it is evident that the current density obtained in the alkaline solution was significantly smaller than that obtained in the acidic solution, indicating the EDLC of the ANTFP25-asp in KOH was lower than that in H$_2$SO$_4$ solution. This was attributed to a physical adsorption of the OH$^-$ ions from the basic electrolyte which participate in the hole-trapping process [248]. The physisorbed OH$^-$ ions on the TiO$_2$ nanotube arrays would interfere with the formation of the electric double layer, resulting in a lower specific capacitance [246].
The kinetic characterization of the adsorption/desorption of ions and electron transport can be investigated through EIS. The impedance spectra of the ANTFP25-asp and the ANTFP25-450 are given in Figure 5-2. Comparison of the impedance response of the ANTFP25-asp with that of the ANTFP25-450 showed that the resistance of the annealed anodic TiO$_2$ nanotube arrays was much lower than that of the as-prepared anodic TiO$_2$ nanotube arrays. Generally, the impedance spectrum consisted of three distinct parts, depending on the frequency range [246]. The high frequency region related to the electrolyte properties whereas the behavior
in the mid-frequency region corresponded to the electrode/electrolyte interface process [249]. The almost vertical dependence of the imaginary part for the as-prepared anodic TiO$_2$ nanotube arrays demonstrated good capacitive behavior without any diffusion limitations [250]. However, different behavior was detected for the annealed anodic TiO$_2$ nanotube arrays, as shown in Figure 5-2.

![Figure 5-2 EIS of the as-prepared and the annealed anodic TiO$_2$ nanotube arrays.](image)

The typical galvanostatic charge-discharge curve of the anodic TiO$_2$ nanotube arrays in 1 M H$_2$SO$_4$ solution is shown in Figure 5-3. For the charge and discharge process, nearly linear behavior of the electrode potential was obtained, as shown in Figure 5-3, which was a very similar response to that of the AC-based EDLC [246]. The long-term stability of the EDLC is demonstrated in Figure 5-4, which indicates that the EDLC could be maintained at nearly 100 % after 500 cycles.

The specific capacitance of the anodic TiO$_2$ nanotube arrays in 1 M H$_2$SO$_4$ aqueous solution is given in Table 5-1a. As shown in Table 5-1a, the specific capacitance of the ANTF20-asp was about 130 $\mu$F cm$^{-2}$. It should be noted that the surface area employed here was the apparent area. However, this value was much lower than that reported in reference [246]. For the ANTFP25-asp, the specific capacitance was about 212 $\mu$F cm$^{-2}$, which was much greater than that of the
ANTF20-asp. This is because the thickness of the ANTFP25-asp was greater than that of the ANTF20-asp, resulting in an enhanced surface area. Although the surface area of the ANTFP25-asp was twice that of the ANTF20-asp, the specific capacitance of the former was not twice that of the latter, which indicated that not all the inner surface area was accessible by the ions in the electrolyte. This is similar to carbon material capacitors, which have some inaccessible surface for ions in electrolyte [251].

For the ANTF20-450-P, which had been obtained through treatment with TiCl4 solution, the specific capacitance was significantly greater than that of the untreated ANTF20-450. This is because the treatment with TiCl4 solution produced many TiO2 nanoparticles on the surface of the nanotube arrays, significantly enhancing the accessible surface area. The specific capacitance of the anodic TiO2 nanotube arrays in 1 M KOH aqueous solution is given in Table 5-1b. Compared with the specific capacitance obtained in 1 M H2SO4 solution, the value obtained in 1 M KOH was much lower, which is in line with the results obtained through CV measurement.

When the as-prepared anodic TiO2 nanotube arrays were compared with the annealed ones, it was found that the former exhibited higher specific capacitance. This result is similar to reference [246]. In that study, the authors observed that the specific capacitance of the anodic TiO2 nanotube arrays annealed above 400 °C decreased significantly, which they attributed to the disruption of the nanotubes as well as the breakdown of the inlet of the nanotubes, disturbing the movements of the electrons. However, others have demonstrated that no discernible morphology change was found for anodic TiO2 nanotube arrays with annealing treatment at 450 °C for 1 h in air [252]. In our work described in Chapter 4, no discernible disintegration was been found for the anodic TiO2 nanotube arrays even annealed at 550 °C.
Figure 5-3 Galvanostatic charge-discharge curve at a current density of 0.01 mA.cm\(^{-2}\) of ANTFP25-asp in 1 M H\(_2\)SO\(_4\) solution.

Figure 5-4 Galvanostatic charge-discharge curve at a current density of 0.05 mA.cm\(^{-2}\) of the ANTFP25-asp in 1 M H\(_2\)SO\(_4\) solution.

Table 5-1a Specific capacitance of anodic TiO\(_2\) nanotube arrays in 1 M H\(_2\)SO\(_4\) solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Charge-discharge current density/time mA.cm(^{-2})/s</th>
<th>Voltage V</th>
<th>specific capacitance (\mu F.cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANTF20- asp</td>
<td>0.001/20</td>
<td>0.35-0.51</td>
<td>135.1±1.1</td>
</tr>
<tr>
<td>Sample</td>
<td>Charge-discharge current density/time</td>
<td>Voltage</td>
<td>Specific capacitance</td>
</tr>
<tr>
<td>-----------------</td>
<td>--------------------------------------</td>
<td>---------</td>
<td>----------------------</td>
</tr>
<tr>
<td>ANT20-asp</td>
<td>0.001/10</td>
<td>-0.09/-0.40</td>
<td>22.3±0.2</td>
</tr>
<tr>
<td>ANT20-450</td>
<td>0.001/5</td>
<td>-0.08/-0.40</td>
<td>10.7±0.1</td>
</tr>
<tr>
<td>ANTFP25-asp</td>
<td>0.001/20</td>
<td>-0.20/-0.30</td>
<td>44.3±0.3</td>
</tr>
<tr>
<td>ANTFP25-450</td>
<td>0.001/10</td>
<td>-0.20/-0.60</td>
<td>12.2±0.3</td>
</tr>
</tbody>
</table>

5.3 Redox supercapacitance of NiO-Ni(OH)₂/anodic TiO₂ nanotube arrays/Ti nanocomposites

Nickel oxide and nickel hydroxide have received considerable attention for application in rechargeable batteries and redox supercapacitors due to their low cost, easy availability and comparable electrochemical behavior [253]. However, due to low specific capacitance of the bulk material, considerable effort should be devoted to improving the reactivity, surface area and effective utilization of the electroactive material. For example, it has been found that modification of morphology and
microstructure of the NiO was a very feasible approach for capacitance enhancement [131]. In general, micro- and meso-porous structures with large surface areas can significantly improve interfacial ion and charge transfer compared with compact electrode materials. Recently, nanostructured TiO$_2$ has been shown to be a promising electrode material for energy-storage applications due to its high accessible surface, electrochemical behavior and chemical stability [254]. Especially, powdery TiO$_2$ nanotubes decorated with noble or transition metal oxides, have been used to fabricate composite electrodes for supercapacitor applications [135]. However, these powdery TiO$_2$ nanotubes, synthesized by a hydrothermal method, usually have a random distribution and a small tube size (below 10 nm), making the inner surface inaccessible due to high interfacial intension energy. Anodic TiO$_2$ nanotube arrays have a regular architecture and could function well as an electrode substrate of electroactive materials for energy-storage devices, due to their tubular channels offering a solid support structure that permits a feasible loading of various designated electroactive materials and easy access by electrolyte ions. The decorated configuration provides more readily available spaces for electrochemical reactions, eventually promoting full utilization of these electroactive materials. In the present work, the anodic TiO$_2$ nanotube arrays were decorated by electroactive Ni(OH)$_2$ and NiO and the redox capacitance of the nanocomposites was investigated.

*Fabrication and characterization of NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites*

TiO$_2$ nanotube arrays/Ti material was prepared by a potentiostatic anodization of Ti foils, as described in Chapter 3, at 25 V for 1.5 h in 0.125 M HF + 0.5 M H$_3$PO$_4$. These samples were denoted ANTFP25-asp. Post-annealing at 450 °C for 2 h in air was conducted for a phase transformation and those samples were denoted ANTFP25-450. Either electrochemical deposition or hydrothermal synthesis was adopted for the preparation of NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti composites. To lower the surface intension energy and improve interfacial ion adsorption, ultrasonic pre-treatment of the TiO$_2$ nanotube arrays/Ti was conducted
for 2 h in a saturated nickel acetate (Ni(Ac)_2) 30 % (v/v) ethanol hybrid solution or a 0.5 M Ni(NO_3)_2 aqueous solution with 0.1 M sodium dodecyl benzene sulfonate (SDBS). Hydrothermal synthesis was conducted at 180 °C for 18 h in 0.1 M Ni(NO_3)_2 aqueous solution with the pre-adjusted pH value of 7.3 through KOH. Initial cyclic voltammetry (CV) experiments were carried out to determine the optimized conditions for controlled deposition. Electrochemical deposition was conducted by potentiostatic electrodeposition at -1.0 V in 0.02 M Ni(Ac)_2 aqueous solution (pH = 6.2 at 18.6 °C) for 30 min or in 0.1 M Ni(NO_3)_2 aqueous solution (pH = 1.4 at 16.4 °C, with 0.2 M NaNO_3 to keep the concentration of NO_3^- around 0.4 M [255]) for 10 min. The electrode was then transferred into a 1.0 M KOH solution and the working potential was cycled 10 times from 0 V to 1 V versus SCE to ensure complete formation of the nickel hydroxide instead of metallic nickel [255]. Finally, heating treatment at 300 °C for 2 h at a ramp rate of 5 °C.min^{-1} was carried out to convert the nickel hydroxide to nickel oxide.

The surface morphology and microstructure of the TiO_2 nanotube arrays and the NiO-Ni(OH)_2/anodic TiO_2 nanotube arrays/Ti nanocomposite were investigated by FESEM. To determine the crystal phase behavior, XRD measurements were conducted using a Bruker D8 discover operation on 40 kV with a current 20 mA.

A conventional cell with a three-electrode configuration was used for electrochemical characterization. A NiO-Ni(OH)_2/anodic TiO_2 nanotube arrays/Ti nanocomposite was employed as the working electrode, a platinum sheet as counter electrode and a SCE as reference electrode. Electrochemical measurements were performed in 1.0 M KOH aqueous solution using an electrochemical workstation.

In general, the cathodic electrochemical deposition process caused formation of metallic nickel on the surface of the TiO_2 nanotube arrays through the reduction reaction of nickel ions. The subsequent positive cyclic scan in an alkaline solution led to the in situ synthesis of nickel hydroxide through the electro-oxidation reaction of the metal nickel. The temporal current density curves during the electrochemical deposition processes are given in Figure 5-5.
Figure 5-5 Potentiostatic electrodeposition curves on various substrates in (a): 0.02 M Ni(Ac)$_2$, and (b): 0.1 M Ni(NO$_3$)$_2$ solutions.

The cathodic electrochemical deposition of nickel oxide and nickel hydroxide on the anodic TiO$_2$ nanotube arrays/Ti electrodes was conducted through a potentiostatic process (-1.0 V vs. SCE) in 20 mM nickel acetate for 30 min or 0.1 M nickel nitrate aqueous solution for 10 min. As shown in Figures 5-5a and 5-5b, it was found that the current densities in the electrochemical deposition reaction were highly consistent in the potentiostatic deposition process. Considering the standard redox potential of -0.257 V versus NHE for Ni$^{2+} + 2e^- \rightarrow$ Ni and 0 V for 2H$^+ + 2e^- \rightarrow$ H$_2$, metallic nickel could be well formed on the surface of the TiO$_2$ nanotube
arrays along with the electrochemical generation of hydrogen under the above experimental conditions. In view of the high oxidative potential of $\text{Ni}^{2+} + \text{OH}^- - xe^- \leftrightarrow \text{Ni(OH)}_2$ at + 0.72 V versus NHE, a cyclic scan process was carried out 10 times with the potential range from 0 to 1 V to ensure complete formation of the Ni(OH)$_2$. Typical cyclic voltammograms of the electrodeposited Ni-TiO$_2$ nanotube arrays/Ti or Ni/Ti electrodes are given in Figure 5-6 (a-f). Comparing Figure 5-6a with 5-6c or 5-6b with 5-6d, it can be seen that the current densities of the samples deposited on titanium substrate were much greater than the current densities of those deposited on the anodic TiO$_2$ nanotube arrays/Ti substrate. This is because the anodic TiO$_2$ nanotube arrays exhibited a significantly higher resistance than the pure titanium. As shown in Figure 5-6(a-g), the positions of the oxidative peaks and the reductive peaks depended on the substrates and the electrolytes. The oxidation peaks have been ascribed to both the electrodeposited nickel to Ni(OH)$_2$ and the newly formed Ni(OH)$_2$ to NiO$_x$(OH)$_{2-x}$ [256]. Upon reversal of the scan, the reductive peaks are observed and have been ascribed to the reduction of the NiO$_x$(OH)$_{2-x}$ back to Ni(OH)$_2$ [256]. This reversible redox reaction could be described schematically as \[ \text{Ni(OH)}_2 + x\text{OH}^- - xe^- \leftrightarrow \text{NiO}_x(\text{OH})_{2-x} + x\text{H}_2\text{O} \] [257]. After several continuous cycles, both oxidative and reductive waves approached a current plateau and a stable voltammetric response was obtained. These voltammetric findings were in agreement with those reported in reference [258]. Alternatively, for comparison, Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposite was prepared by a hydrothermal method, in which Ni(OH)$_2$ nanocrystallites were expected to grow and deposit on the surface of the TiO$_2$ nanotube arrays through dissolution and re-crystallization processes in a strong alkali solution under high-temperature and high-pressure conditions [259]. The cyclic voltammogram of the hydrothermal sample is shown in Figure 5-6g, revealing that the capacitance was very low.
Figure 5-6 Cyclic voltammetries in 1 M KOH aqueous solution of samples obtained by deposition from (a): Ni(Ac)$_2$ on Ti, (b): Ni(Ac)$_2$ on ANTFP25-asp/Ti, (c): Ni(NO$_3$)$_2$ on ANTFP25-asp/Ti, (d): Ni(NO$_3$)$_2$ on ANTFP25-450/Ti, (e): Ni(AC)$_2$ on
ANTFP25-450/Ti, (f): Ni(NO₂)₂ on ANTFP25-450/Ti, and by (g): a hydrothermal method.

The surface morphology and cross-sectional views of the anodic TiO₂ nanotube arrays were shown in Chapter 3. Figure 5-7a shows the surface morphology of the Ni(OH)₂/anodic TiO₂ nanotube arrays/Ti nanocomposites obtained through the hydrothermal method, and it was found the nanoparticles of nickel hydroxide formed on the surface. A compact layer of Ni(OH)₂ on the surface of the anodic TiO₂ nanotube arrays was obtained through electrochemical deposition in Ni(NO₃)₂ solution, as shown in Figure 5-7b. However, cracks and detachment of nickel hydroxide were found. The surface morphology of the NiO-Ni(OH)₂/Ti nanocomposites obtained through deposition in Ni(Ac)₂ solution on titanium substrate is shown in Figure 5-7c, where a crack in the NiO-Ni(OH)₂ layer is found. An example of the surface morphology of the NiO-Ni(OH)₂/ANTFP25-asp/Ti nanocomposites is shown in Figure 5-7d, in which flower-like structures are observed on the surface. Significantly, this binary metal oxide composite could form a cross-linked multi-porous structure with open channels and a narrow pore size. Such an open porous structure could benefit the charge and mass transfer through ion diffusion at the electrode/electrolyte interface, which is crucial for the promotion of the capacitance performance [131]. Such architecture would lead to a higher reaction surface area and also to a better cycling stability.
Figure 5-7 FESEM images of (a): hydrothermal sample, (b): Ni(OH)$_2$/ANTFP25-asp/Ti deposition from Ni(NO$_3$)$_2$, (c): NiO-Ni(OH)$_2$/Ti deposition from Ni(Ac)$_2$, and (d): NiO-Ni(OH)$_2$/ANTFP25-asp/Ti deposition from Ni(Ac)$_2$.

Figure 5-8 XRD patterns of samples obtained by (a): hydrothermal sample, deposition from (b): Ni(Ac)$_2$ on ANTFP25-asp, (c): Ni(Ac)$_2$ on ANTFP25-asp, followed by annealing at 300 °C for 2 h, and (d): Ni(NO$_3$)$_2$ on ANTFP25-asp.

XRD patterns of the nanocomposites are shown in Figure 5-8. Having the same electrode substrate material, all samples exhibit similar characteristic diffraction peaks, which were ascribed to diffractions of titanium metal (JCPDS file No. 89-5009). For the sample obtained through the hydrothermal method, only a weak diffraction peak at $2\theta = 19.3^\circ$ was found, which has been indexed to diffraction of $hkl$ (001) for Ni(OH)$_2$ (JCPDS file No. 14-0117). For the sample obtained through deposition in 0.02 Ni(Ac)$_2$ solution, as shown in Figure 5-8b, a strong diffraction peak at $2\theta = 43.5^\circ$ was found, which was ascribed to diffraction of $hkl$ (200) for crystal NiO with cubic syngony (JCPDS file No. 89-5881), and a weak diffraction
peak at $2\theta = 19.3^\circ$ was also found. These findings indicate that the depositions on the surface of the anodic TiO$_2$ nanotube arrays consisted of nickel oxide and nickel hydroxide. Through post-annealing treatment at 300 °C for 2 h, it was found that the nickel hydroxide had been completely transferred to nickel oxide, as shown in Figure 5-8c. For the sample obtained through deposition in Ni(NO$_3$)$_2$ solution, as shown in Figure 5-8d, only weak diffraction of the nickel hydroxide was detected. This finding indicates that only nickel hydroxide was formed through electrochemical deposition in nickel nitrate solution.

![Complex impedance plots of samples obtained by deposition from Ni(Ac)$_2$ on (a): Ti, (b): as-prepared nanotube arrays, and (c): annealed TiO$_2$ nanotube arrays. The EIS was measured at 0 V vs. SCE in a frequency range of 0.1–100,000 Hz.](image)

EIS was carried out over a frequency range from 0.01 Hz to 100 kHz under a constant potential of 0 V and ac-voltage amplitude of 10 mV in 1 M KOH solution. Typical Nyquist plots of the nanocomposites are shown in Figure 5-9. Generally, the complex impedance consisted of a charge-transfer resistance in series with a mass transfer impedance containing linear and nonlinear diffusion terms, whose value mostly depended upon the electrical resistance and capacitance of electrode materials, charge and mass transfer resistance, and constant phase element [260].
The depressed semicircles within the entire frequency range in the Nyquist plots indicate that these nanocomposite electrodes predominantly conducted a kinetics-controlled electrochemical process, and the complex impedance was determined mainly by the charge-transfer resistance at the interface of electrolyte/electroactive material/substrate. Our research demonstrated that the bare TiO_2 nanotube arrays/Ti electrodes exhibited a negligible Warburg region with a 45° slope at low frequencies which resulted from the semi-infinite ion diffusion into the TiO_2 nanotubes [256]. Of special relevance to the two designated NiO/anodic TiO_2 nanotube arrays/Ti electrodes, the difference of impedance curves at high frequencies has been mainly ascribed to the degree of limitation of the interfacial charge transfer between the nanocomposite and the electrolyte [256]. Corresponding electrical resistance could be qualitatively estimated by comparing the diameter of the semicircle-like arc at high frequencies in the Nyquist plots [256]. Impedance results, as shown in Figure 5-9, indicated that deposition on the anodic TiO_2 nanotube arrays resulted in increased resistance between the electroactive material and substrate than that of deposition on metallic titanium, which could make the electrode exhibit poorer performance. When the sample obtained through deposition on the as-prepared anodic TiO_2 nanotube arrays/Ti was compared with that obtained through deposition on the annealed anodic TiO_2 nanotube arrays, it was found that the former exhibited higher resistance than the latter, as shown in Figure 5-9.

**Analysis of redox supercapacitance of the nanocomposites**

To investigate the redox supercapacitance of the nanocomposites, cyclic voltammetry was conducted in 1 M KOH solution between −0.6 -- 1.0 V, as shown in Figure 5-10(a-c). As shown in Section 5.1, the anodic TiO_2 nanotube arrays/Ti electrode alone had a negligible integral area on the basis of the current–potential curve, suggesting that the nanotube array itself had a very small specific capacitance (which was determined to be in the order of hundreds of μF). It has been reported that non-faradic adsorption of OH^− and a possible double-layer charging process occurred during the initial stage from 0 V to 0.33 V during the anodic scan process.
Then, owing to the appearance of the redox peak pair, faradic reaction must have occurred to bring about a good performance of faradic capacitance. This capacitance characteristic of NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti was different from that of the EDLC, which usually produced a CV curve close to an ideal rectangular shape with a potential-independent current response. Herein, the measured capacitance was based mainly on the reversible redox reaction mechanism due to the quasi-reversible electron transfer process. The characteristic redox peaks appearing on the CV curves corresponded to the formation of nickel oxy-hydroxide and its back conversion to a nickel oxide product, whose corresponding electrode reaction is shown as:

$$\text{NiO} + z\text{OH}^- - ze^- \leftrightarrow \text{NiO(OH)} + (1 - z)\text{NiO} \quad (5-1)$$

The CV curves of the NiO-Ni(OH)$_2$/Ti, NiO-Ni(OH)$_2$/ANTFP25-asp, and NiO-Ni(OH)$_2$/ANTFP25-450 in 1 M KOH are shown in Figures 5-10a, 5-10b and 5-10c, respectively. Due to the surrounded area of the CV curve corresponding to the capacitance according to Equation (2-15), it was found that the capacitance of the NiO-Ni(OH)$_2$/Ti nanocomposites obtained through deposition on metallic titanium substrate was much greater than that obtained through deposition on the anodic TiO$_2$ nanotube arrays/Ti. For the NiO-Ni(OH)$_2$/Ti nanocomposite, a couple of redox peaks were found within the potential range 0.3 to 0.8 V, where the anodic peak resulted from the oxidation of NiO to NiOOH and the cathodic peak resulted from the reverse reaction. However, small potential windows were obtained for the NiO-Ni(OH)$_2$/Ti nanocomposites, significantly smaller than those for the NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites, as shown in Figure 5-10. Comparison of Figures 5-10b and 5-10c shows that there was a reaction peak at around - 0.3 V versus SCE for NiO-Ni(OH)$_2$/ANTFP25-450. For all nanocomposites, the shape of the CV curves depended on the scan rates, which was consistent with results reported in reference [262]. When the scan rate is increased, the anodic peak potential and cathodic peak potential shifted more in the anodic and
cathodic directions, respectively. Moreover, the capacitance decreased when the scan rate was increased, which was similar to CV characterization of RuO$_2$ [263].

The galvanostatic charge-discharge technique was employed to investigate the redox capacitance of the nanocomposites. Figure 5-11(a-c) shows the galvanostatic discharge curves of the nanocomposites in 1 M KOH solution. During the galvanostatic charge process, the oxidation reaction of NiO and formation of NiOOH occurred, which associated with increase of potential, which was in agreement with the behavior during CV characterization. The discharge process started with a sharp drop in voltage due to the internal resistance [264]. Then a slow drop of potential followed due to the reaction of the electroactive material. Comparison of Figure 5-11a with 5-11b or 5-11c shows that the redox capacitance of the electroactive materials deposited on the anodic TiO$_2$ nanotube arrays was significantly lower than that deposited on the titanium substrate. However, extension of operational-potential windows was achieved for the nanocomposites obtained through deposition on the anodic TiO$_2$ nanotube arrays. It was found that the redox capacitance depended on the discharge current density. When the discharge current density was increased, a large potential drop was produced and the redox capacitance decreased. This was ascribed to limited OH$^-$ ion diffusion processes during charge/discharge of electroactive materials [265]. At a high scan rate or discharge current density, significant OH$^-$ ions are required to intercalate swiftly at the interface of electroactive material/electrolyte interface. However, if the relatively low concentration of OH$^-$ ions cannot meet that requirement then the processes would be determined by ion diffusion [262, 265].

Usually in the galvanostatic charge–discharge process, bare TiO$_2$ would contribute a non-faradic capacitance with a very low value. So the capacitance resulting from EDLC type energy-storage mechanism of the anodic TiO$_2$ nanotube arrays could be completely negligible for the redox capacitive evaluation of the nanocomposites. The redox capacitances was determined to be 57 mF.cm$^{-2}$ for NiO-Ni(OH)$_2$/ANTFP25-450 at a discharge current density of 0.5 mA.cm$^{-2}$. Presumably, such a redox capacitance could be further improved by increasing the
NiO loading inside the TiO$_2$ nanotubes, since a larger surface area of the electroactive NiO would benefit redox reaction in the process of charge storage. Furthermore, the charge–discharge curves exhibited a reversible characteristic without apparent deviation in each cycle. This observation means that the NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites had good electrochemical stability to resist the corrosion loss of electroactive NiO from the TiO$_2$ nanotube arrays during a continuous charge-discharge operation.

Figure 5-10 CV curves of (a): NiO-Ni(OH)$_2$/Ti, (b): NiO-Ni(OH)$_2$/ANTFP25-asp/Ti, and (c): NiO-Ni(OH)$_2$/ANTFP25-450 in 1 M KOH at various scan rates.
Figure 5-11 Galvanostatic discharge curves of (a): NiO-Ni(OH)$_2$/Ti, (b): NiO-Ni(OH)$_2$/ANTFP25-asp, and (c): NiO-Ni(OH)$_2$/ANTFP25-450 in 1 M KOH at various current densities.

5.4 Redox capacitance of RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites

RuO$_2$ has been regarded as the best example of a redox supercapacitor material, as it shows continuous redox activity over a wide potential range and very high, surface-area-independent capacitance, high conductivity, good electrochemical reversibility, high power and energy density, and a long cyclic life [137]. The charge-discharge mechanism of RuO$_2$ is attributed to the reversible redox reaction between Ru$^{4+}$ and Ru$^{3+}$ through a simultaneous electron and proton insertion, which can be described as [145, 155]:

$$\text{Ru}^{(IV)}\text{O}_a\text{(OH)}_b + \delta\text{H}^+ + \delta\text{e}^- = \text{Ru}^{(III)}\text{O}_{a-\delta}\text{(OH)}_{b+\delta}$$  \hspace{1cm} (5-2)

Although RuO$_2$ exhibits a great number of advantages, its use is still limited except for military applications due to the obvious high cost. However, the considerable interest in RuO$_2$ as a supercapacitor material has led to improvement of synthesis methods and development of composites aimed at increasing its utilization. Anodic TiO$_2$ nanotube arrays/Ti material contributes a very high specific surface area and vertically aligned structure, which functions well as support for electroactive materials. In the present study, an electrodereduction-oxidation process was employed to decorate the anodic TiO$_2$ nanotube arrays/Ti with electroactive RuO$_2$ for redox
supercapacitor application.

**Formation of RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites**

Anodic TiO$_2$ nanotube arrays/Ti was prepared by a potentiostatic anodization of Ti foils, as described in Chapter 3, at 25 V for 1.5 h in 0.125 M HF + 0.5 M H$_3$PO$_4$. These samples were denoted ANTFP25-asp. Post-treatment through annealing at 450 °C for 2 h in air was conducted for phase transformation and those samples were denoted ANTFP25-450. Either electrochemical deposition or hydrothermal synthesis was adopted for preparation of RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites. Hydrothermal synthesis was conducted at 180 °C for 18 h in 0.02 M RuCl$_3$.xH$_2$O solution (pH = 1.30). An electrochemical deposition method was employed and initial cyclic voltammetry experiments were performed to determine the optimal conditions for controlled deposition. The electrochemical deposition was conducted by potentiostatic deposition at -1.0 V in 0.02 M RuCl$_3$.xH$_2$O + 0.01 M NaAc solution (pH = 1.53) for 30 min. The specific mass of the electroactive material was determined according to the weight difference before and after RuO$_2$ deposition (both were dried at 150 °C for 2 h in air) using an electronic balance with 0.01 mg sensitivity (FACT mettler AT201). To investigate the influence of crystallization on the capacitance, annealing treatment at 200 °C, 300 °C and 400 °C for 2 h at a ramp rate of 5 °C.min$^{-1}$ was conducted and the annealed nanocomposites were denoted RuO$_2$/ANTFP**/200, RuO$_2$/ANTFP**/300, and RuO$_2$/ANTFP**/400, respectively.

The surface morphology and microstructure of the RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites were investigated by FESEM. To determine the crystal phase behavior, XRD measurements were conducted using a Bruker D8 discover operation on 40 kV with a current 20 mA.

A conventional cell with a three-electrode configuration was used for electrochemical characterization. RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti electrode was employed as the working electrode, a platinum sheet as the counter electrode and a SCE as the reference electrode. Electrochemical measurements were
performed in 1.0 M H₂SO₄ aqueous solution using an electrochemical workstation.

Initial cyclic voltammetry of the ANTFP25-asp and the ANTFP25-450 was conducted to find the optimized conditions for controlled deposition. As shown in Figure 5-12, the reduction of Ru(III) ions occurred at 0 to -0.2 V versus SCE whereas hydrogen evolution took place at potential negative to -0.2 V versus SCE. To achieve optimal deposition efficiency, which could be described as weight of deposits per Coulomb charge passed \( \frac{M_{\text{dep}}}{Q_p} \), cathodic potential at -0.9 V versus SCE in 0.01 M RuCl₃ + 0.1 M KCl aqueous solution with pH = 2 was demonstrated for deposition on titanium substrate [266]. Generally, cathodic deposition results in composites of metallic ruthenium and ruthenium oxides [266]. Moreover, cathodic depositions have commonly been conducted in acidic electrolytes due to the formation of Ru(OH)₃ precipitation when the pH of the solution is above 4.0 [267].

In the present work, cathodic deposition was conducted at -1.0 V versus SCE in 0.02 M RuCl₃ + 0.01 M NaAc aqueous solution with pH = 1.53. The current density-time behaviors of the ANTFP25-450 and the ANTFP25-asp are shown in Figure 5-13. The current density for the as-prepared ANTFP25-asp is found to be slightly greater than that for the annealed ANTFP25-450.

The surface morphology of samples obtained through the hydrothermal method and electrodeposition is shown in Figure 5-14(a-c). As with the samples obtained through the hydrothermal method in Ni(NO₃)₂ solution, no discernible TiO₂ nanotube arrays could be obtained due to the high pressure and high temperature, as shown in Figure 5-14a. Figure 5-14b shows the RuO₂ layer on the surface of the anodic TiO₂ nanotube arrays. A cross-sectional view of the RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites is shown in Figure 5-14c, revealing a very thin layer of RuO₂ compared with the thick nanotube arrays. The specific mass of the RuO₂ on the surface of the anodic TiO₂ nanotube arrays/Ti substrate was determined to be 0.10 mg.cm⁻² obtained through the electronic balance.
Figure 5-12 CV curves of ANTFP25-asp and ANTFP25-450 in 20 mM RuCl$_3$ + 10 mM NaAc solution.

Figure 5-13 Potentiostatic electrodeposition curves of ANTFP25-asp and ANTFP25-450 at -1 V vs. SCE in 0.02 M RuCl$_3$ + 0.01 M NaAc solution.
Figure 5-14 FESEM images of (a): sample obtained through hydrothermal method, (b): RuO₂/ANTFP25-asp nanocomposite obtained by deposition on ANTFP25-asp, and (c): cross-sectional view of RuO₂/ANTFP25-asp.

Analysis of redox supercapacitance of the RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites

Cyclic voltammograms of the RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites were investigated in 1 M H₂SO₄ solution at various scan rates, as shown in Figure 5-15(a-h). The CV curves were found to be close to an ideal rectangular shape, indicating a good capacitance behavior in the examined potential range, which is different from the potentials related to hydrogen or oxygen evolution through electrolyzing water reaction (below - 0.2 V or above 1.2 V vs. SCE). The redox capacitances of the RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites could be determined through cyclic voltammetry at various scan rates according to Equation (2-15).

The hydrothermal sample exhibited very low capacitance, as shown in Figure 5-15h. Comparison Figure 5-15a with 5-15c or 5-15e shows that the annealing treatment of the nanocomposites obtained through deposition on the as-prepared anodic TiO₂ nanotube arrays, resulted in a reduction of redox supercapacitance. A similar result was found for the nanocomposites obtained through deposition on the annealed anodic TiO₂ nanotube arrays, as shown in Figures 5-15b, 5-15d, and 5-15f.
Figure 5-15 CV behaviors in 1 M H₂SO₄ solution at various scan rates of (a): RuO₂/ANTFP25-asp/200, (b): RuO₂/ANTFP25-450/200, (c): RuO₂/ANTFP25-asp/300, (d): RuO₂/ANTFP25-450/300, (e): RuO₂/ANTFp25-asp/400, (f): RuO₂
The influences of the substrate on the capacitance of RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites were found to be complex. The redox supercapacitance of the nanocomposites depended slightly on whether annealing treatment was used. A very small redox supercapacitance was obtained for the RuO$_2$/ANTFP25-450/400, as shown in Figure 5-15f. Calculation of capacitance according to Equation (2-15) showed that the redox capacitance of the nanocomposite obtained at high scan rates was lower than that obtained at low scan rates. This has been ascribed to the rate of electrochemical protonation depending on the diffusion of the proton-donating species in the RuO$_2$ electrode [156, 268]. The $e^{-}/H^{+}$ charge storage occurs at a hydrous RuO$_2$ surface layer and the voltammetric charge ($q_{cv}$) depends on the potential scan rate ($v$). RuO$_x$H$_y$ located in areas such as micropores and cracks precludes facile access by protons as the scan rate is increased thereby progressively excluding more RuO$_x$H$_y$ sites. The rate of electrochemical protonation, and thus the voltammetric charge, is then limited by the diffusion of the proton-donating species to those sites. It has been reported that the voltammetric charge responds linearly with $v^{-1/2}$ given a semi-infinite diffusion process [156].

Figure 5-16(a-e) shows the galvanostatic discharge diagrams of the RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites in 1 M H$_2$SO$_4$ electrolyte at different current densities. Like that of the NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites, the discharge behavior started with a sharp drop of potential due to internal resistance, as shown in Figure 5-16(a-e). Then followed a slow drop in potential, which resulted from the reaction of the electroactive material according to Equation (5-2). The slow drop in potential was found below 0.1 V. This was in line with the result obtained through the CV characterization, in which there was a rapid increase of current density, as shown in Figure 5-15. The specific capacitance of the RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites was calculated according to:

$$C_m = \frac{c}{m} = \frac{I*t}{\Delta V*m} \quad (5-3)$$
where $I$ is charge-discharge current, $t$, discharge time, $\Delta V$, the corresponding potential window, and $m$ is the mass of electroactive material. Table 5-2 shows the specific capacitances of the RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites.

![Figure 5-16 Galvanosatic discharge curves of (a): RuO$_2$/ANTFP25-asp/200, (b): RuO$_2$/ANTFP25-450/200, (c): RuO$_2$/ANTFP25-asp/300, (d): RuO$_2$/ANTFP25-450/300, (e): RuO$_2$/ANTFP25-asp/400, and (f): RuO$_2$/ANTFP25-asp/400.](image)

It was found that the specific capacitance decreased significantly when high galvanostatic discharge current density was employed. This has been attributed to
the significant barrier for the penetration and diffusion of H⁺ ions in electrolyte into a relatively thick film and/or the relatively poor electronic conductivity of electroactive material [269].

Figure 5-17 XRD patterns of RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites annealed at 200 °C, 300 °C, and 400 °C for 2 h.

In investigation of the influence of the annealing treatment on specific capacitance, it was found that annealing treatment of the nanocomposites at temperatures above 200 °C resulted in a significant decrease of the specific capacitance. Very small specific capacitances were observed for samples annealed at 400 °C for 2 h. A maximum specific capacitance of 487.5 F g⁻¹ was obtained for the RuO₂/ANTFP25-asp/200 nanocomposite. The reduction of the specific capacitance for the annealed samples at the elevated temperatures was ascribed to the formation of crystal RuO₂ and loss of water, resulting in low capacitance. The XRD patterns of the RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites annealed at various temperatures are shown in Figure 5-17. For samples annealed at 200 °C for 2 h, no pattern of crystal RuO₂ was detected. When annealing temperatures reached 300 °C and 400 °C, clear diffraction peaks at 2θ = 28.0 ° and 35.0 ° were obtained, which were been indexed to diffraction of hkl (110) and hkl (101) for RuO₂ (JCPDS file No. 00-040-1290). In all samples, metallic ruthenium was found, which showed a diffraction peak at 2θ = 44.0 ° (JCPDS file No. 00-006-0663).

The EIS of the RuO₂/anodic TiO₂ nanotube arrays/Ti nanocomposites was
investigated over a frequency range from 100 kHz to 0.1 Hz and with an amplitude of 10 mV in 1 M H$_2$SO$_4$ solution. As shown in the inset in Figure 5-18a, effective series resistance (ESR), which corresponded to the high frequency range [270], was about 1.0 $\Omega$ for samples obtained through deposition on the as-prepared anodic TiO$_2$ nanotube arrays. However, the ERS increased dramatically to 80.0 $\Omega$ in the case of deposition on the annealed anodic TiO$_2$ nanotube arrays, as shown in inset in Figure 5-18b. The ESR included contact resistance between current collector and external wires, titanium plate resistance, the electronic resistance of the RuO$_2$ and contact resistance between RuO$_2$ and the anodic TiO$_2$ nanotube arrays. Generally, crystallization of the anodic TiO$_2$ nanotube arrays upon annealing treatment resulted in a significant reduction of electronic resistance. It is reasonable to believe that the increase in resistance stemmed mainly from contact resistance between the RuO$_2$ and the anodic TiO$_2$ nanotube arrays. When the nanocomposites were annealed at 300 $^\circ$C for 2 h, as shown in Figures 5-18c and 5-18d, both exhibited relatively low resistance. For the nanocomposites annealed at 400 $^\circ$C for 2 h, as shown in Figure 5-18e, very high resistance was found for the nanocomposite obtained through deposition on the as-prepared anodic TiO$_2$ nanotube arrays. However, the resistance was relatively low for the nanocomposite obtained through deposition on the annealed nanotube arrays, as shown in Figure 5-18f. These findings indicated that obtaining the nanocomposites through electrodeposition on the as-prepared nanotube arrays with post-annealing at 400 $^\circ$C resulted in high contact resistance, whereas using electrodeposition on the annealed nanotube arrays resulted in relatively low contact resistance.

Table 5-2 Specific capacitance of the RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites obtained through galvanostatic discharge.

<table>
<thead>
<tr>
<th>Sample</th>
<th>discharge current density mA.cm$^{-2}$</th>
<th>specific capacitance* F.g$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>RuO$_2$/ANTFP25-asp/200</td>
<td>2.0</td>
<td>300.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>388.5</td>
</tr>
<tr>
<td>Material</td>
<td>Capacity</td>
<td>Energy</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>RuO₂/ANTFP25-450/200</td>
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<td>487.5</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>250.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>300.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>356.0</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
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<td>125.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>175.0</td>
</tr>
<tr>
<td>RuO₂/ANTFP25-450/300</td>
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<td>225.0</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>237.5</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>237.5</td>
</tr>
<tr>
<td>RuO₂/ANTFP25-asp/400</td>
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<td>50.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>56.0</td>
</tr>
<tr>
<td>RuO₂/ANTFP25-400/400</td>
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<td>56.0</td>
</tr>
<tr>
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<td>62.5</td>
</tr>
</tbody>
</table>

![Graphs](image-url)

5.5 Conclusions

In this chapter, the EDLC of the anodic TiO$_2$ nanotube arrays was first investigated. Then NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti and RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites were fabricated through electrochemical deposition and were examined for redox supercapacitor application. The conclusions are listed as follows:

1. The EDLC of the anodic TiO$_2$ nanotube arrays was investigated through cyclic voltammetry and galvanostatic charge-discharge in basic and acidic electrolytes. The anodic TiO$_2$ nanotube arrays were found to exhibit EDLC in the order of hundreds $\mu F.cm^{-2}$. The EDLC could be enhanced through extending the length of the TiO$_2$ nanotubes arrays. The EDLC of the anodic TiO$_2$ nanotube arrays depended on the electrolyte, and it was found that the specific capacitance in acidic solution was higher than that in basic electrolyte.

2. Ni(OH)$_2$-NiO/anodic TiO$_2$ nanotube arrays/Ti nanocomposites were fabricated through cathodic electrodeposition in Ni(NO$_3$)$_2$ or Ni(Ac)$_2$ solutions. A mixture of NiO and Ni(OH)$_2$ was formed obtained through deposition in Ni(Ac)$_2$ solution whereas Ni(OH)$_2$ was obtained through deposition in Ni(NO$_3$)$_2$ solution. The
specific capacitances of the nanocomposites were investigated through cyclic voltammetry and galvanostatic charge-discharge in KOH solution. Redox supercapacitance of the nanocomposites obtained through deposition in Ni(Ac)$_2$ solution was higher than that obtained through deposition in Ni(NO$_3$)$_2$ solution. A maximum redox supercapacitance of 57 mF.cm$^{-2}$ was obtained.

3. RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites were synthesized through cathodic electrodeposition from RuCl$_3$ solution. The specific capacitances of the nanocomposites were investigated through cyclic voltammetry and galvanostatic charge-discharge in H$_2$SO$_4$ solution. The influence of annealing treatment of the nanocomposites at 200 °C, 300 °C and 400 °C on the redox supercapacitance was investigated. A maximum specific capacitance of 487.5 F.g$^{-1}$ was obtained for the sample annealed at 200 °C. A significantly decrease in specific capacitance was observed for the nanocomposites annealed at temperatures above 200 °C. Investigation by XRD revealed that annealing at temperatures over 300 °C led to crystal RuO$_2$, which has low capacitance.
Chapter 6 Liquid-junction Dye-Sensitized Solar Cells Using Anodic TiO$_2$
Nanotube Arrays as Photoanode

6.1 Introduction

Dye-sensitized solar cells (DSSCs) represent one of the most promising of several alternative, cost-effective concepts for photon-to-electric conversion, and over the past decades have presented considerable challenge to conventional silicon solar cells. The configuration of a liquid-junction DSSC consists of a wide band gap semiconductor photoanode, dye sensitizer, redox electrolyte, and platinized-FTO counter electrode. Among various wide band gap semiconductors such as ZnO, SnO$_2$, Nb$_2$O$_5$ and TiO$_2$, TiO$_2$ is still regarded as by far the best choice. Commonly, TiO$_2$ nanoparticle network film prepared by doctor blade technique or screen printing methods is used as the photoanode material. However, lattice mismatches at the grain boundaries in the nanoparticle network film influence charge transport due to scattering and act as traps. It has been reported that approximately $10^6$ grain boundaries exist for a TiO$_2$ nanoparticle network film with a thickness of 10 $\mu m$ [271]. Charge transport is retarded thereby, resulting in charge accumulation in the nanoparticles which can recombine with either the redox electrolyte or the reduced dye. In contrast to TiO$_2$ nanoparticle network film, 1D TiO$_2$ nanostructures such as nanowires, nanorods, or nanotubes can effectively improve charge transport properties due to the absence of an extended random walk network and grain boundary effects. Among various 1D TiO$_2$ nanostructures, anodic TiO$_2$ nanotube arrays, which can be easily prepared by the electrochemical anodization approach, are suggested to be superior in photoelectrochemical performance due to their 1D architecture which provides vectorial electron transfer pathway and reduced recombination [29, 197, 200]. The outstanding charge transport properties of 1D TiO$_2$ nanotube arrays result from smooth directional electron mobility (limiting random walk in the wide nanocrystalline network) as well as decreased inter-crystalline contact, which accelerates charge transport and reduces charge recombination.
recombination. Moreover, 1D TiO$_2$ nanostructures are excepted to absorb more dye sensitizer than nanoparticle network film of the same thickness. For example, it has been demonstrated that the TiO$_2$ nanowires allowed for greater adsorption of dye than P25 nanoparticle network film of identical thickness [272]. Furthermore, anodic TiO$_2$ nanotube arrays facilitate greater light-harvesting efficiency, especially at the long-wavelength end of the visible and in the near red-infrared region than that of conventional TiO$_2$ nanoparticle network film of the same thickness [197]. Although extensive investigation of anodic TiO$_2$ nanotube arrays/Ti for the photoanode material of the liquid-junction or solid-state DSSCs has been conducted [194, 201, 273, 274], there is limited knowledge of the effects of the architecture of the anodic TiO$_2$ nanotube arrays on cell performance, and the geometry of the anodic TiO$_2$ nanotube arrays currently used is far from optimized.

In this chapter, liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays obtained through anodization in non-aqueous solution consisting of NH$_4$HF$_2$ and EG as photoanode were investigated. The assembling and sealing processes of the liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays, which were different from those of the conventional liquid-junction DSSCs using two FTO based electrodes, were studied. Then, liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays with special surface nanostructure as photoanode, which were obtained through two-step anodization in non-aqueous solution consisting of NH$_4$F and EG, were fabricated and characterized.

6.2 Liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays as photoanode

Anodic TiO$_2$ nanotube arrays consist of well-aligned, parallel 1D nanostructures, vertically aligned on the metallic titanium substrate. It is believed that the charge transport along each nanotube is enhanced due to the reduced scattering at grain boundaries and reduced structural disorder compared to the nanoparticle network film photoanode. Recently, it has been reported that the electron diffusion length in the anodic TiO$_2$ nanotube arrays based photoanode is much greater than that in the nanoparticle network film photoanode [198]. The enhancement of electron transport
also allows for improvement in light-harvesting efficiency, as thicker anodic TiO₂ nanotube arrays can be used to increase optical density, thus improving the adsorption of low-energy photons in the red and infrared spectra. It is therefore expected that such ordered and strongly interconnected photoanodes will help improve electron transport, leading to higher overall power conversion efficiency of liquid-junction DSSCs. However, many unclear aspects, even technical issues, need to be clarified. In the present work, liquid-junction DSSCs using anodic TiO₂ nanotube arrays of different thicknesses as photoanode were assembled and characterized.

**Fabrication of anodic TiO₂ nanotube arrays of various thicknesses**

Anodic TiO₂ nanotube arrays/Ti material was prepared by a potentiostatic anodization of Ti foils at 60 V in a non-aqueous solution consisting of 0.25 wt % or 0.5 wt % of NH₄HF₂ and EG. The anodization process was detailed in Chapter 3. The titanium sheets were cut into pieces of 1.0 x 2.0 cm², in each of which a hole of Φ 0.7 mm was drilled. To avoid detachment of the as-prepared anodic TiO₂ nanotube arrays from the metallic substrate, the as-prepared samples were immersed overnight in ethanol or methanol. Then, the samples were cleaned through ultrasonication for 30 s in DI water with 4 wt % alumina particles (average diameter: 0.3 μm). Post-calcination treatment was conducted in air with a ramp rate of 1 °C.min⁻¹ at various temperatures for phase transformation. The surface morphology of the anodic TiO₂ nanotube arrays was investigated by FESEM and the main findings were presented in Chapter 3. It was found that anodization at 60 V resulted in nanotube arrays with an optimal structure and a growth rate of 3 μm.h⁻¹. To investigate the influence of the mass fraction of NH₄HF₂ on the thickness of the nanotube arrays, anodization was conducted at 60 V in EG solutions containing 0.25 wt % or 0.5 wt % NH₄HF₂ for various anodization times. As shown in Figure 6-1, it was found that the thickness of the anodic TiO₂ arrays increased slightly with mass fraction of NH₄HF₂ and the thickness was almost linearly dependent on the anodization time. In general, the as-prepared anodic TiO₂ nanotube arrays suffered
from capillary stress created during the evaporation of solvents from the mesopores of dense arrays, which resulted in bundling of the nanotubes and formation of microcracks, as shown in Figure 6-2. The capillary stress led to severe peeling of the as-prepared anodic TiO$_2$ nanotube arrays from the metallic titanium substrate at room temperature. Moreover, the large stress/strain between the anodic TiO$_2$ nanotube arrays, and between the arrays and the metallic substrate, especially in very long TiO$_2$ nanotube arrays, resulted in peeling of the anodic TiO$_2$ nanotube arrays at room temperature. On the other hand, peeling off and curling of the TiO$_2$ nanotube arrays were also found after the annealing process, as shown in Figure 6-3, which may be attributable to thermal stress between the TiO$_2$ nanotube arrays and the metallic substrate. It has been demonstrated that the supercritical carbon dioxide drying technique could be employed to produce bundle-free and crack-free anodic TiO$_2$ nanotube arrays [200]. In the present study, the as-prepared anodic TiO$_2$ nanotube arrays were immersed in methanol or ethanol overnight, which exhibited low surface tension than the EG, following evaporation of these solvents. It was found that this treatment retarded detachment of the anodic TiO$_2$ nanotube arrays from the titanium substrate during the subsequent ultrasonication and annealing processes.

Figure 6-1 Relationship between thickness of nanotube arrays and anodization time.
Figure 6-2 (a): Bundling of TiO$_2$ nanotube arrays, and (b): microcrack of TiO$_2$ nanotube arrays.

As shown in Chapter 3, the as-prepared anodic TiO$_2$ nanotube arrays were covered with many nanowires and other debris. Since the dye-loading and the light-harvesting properties may be adversely affected by these structures, they were removed through ultrasonication in Al$_2$O$_3$ suspension. Figure 6-4 shows that these undesired structures were successfully removed. Moreover, it was demonstrated that the thickness of the anodic TiO$_2$ nanotube arrays was slightly reduced by the ultrasonication treatment. To increase the surface area of the nanotube arrays, they were immersed in a 40 mM TiCl$_4$ aqueous solution at 70°C for 0.5 h, followed by annealing at 350 °C in air for 0.5 h. FESEM images of the anodic TiO$_2$ nanotube arrays with the ultrasonication treatment and then with TiCl$_4$ treatment are shown in Figures 6-5a and 6-5b, respectively. It was found that the treatment with TiCl$_4$ increased the surface area of the TiO$_2$ nanotube arrays.
In general, DSSCs favor anatase TiO$_2$, which may result from its higher conduction-band edge energy. To completely crystallize the as-prepared TiO$_2$ nanotube arrays, the samples were annealed at 450 °C, 550 °C, and 600 °C for 4 h in air. Investigation through FESEM revealed no discernible morphology change in the TiO$_2$ nanotubes for samples annealed at 450 °C. Only anatase was detected through XRD for the samples annealed at 450 °C. However, the annealing treatment at 450 °C for 4 h resulted in serious cracking of the anodic TiO$_2$ arrays, as shown in Figure 6-6. For samples annealed at 550 °C for 4 h, a mixture of anatase and rutile was obtained. Marked distortion of the TiO$_2$ nanotube arrays was found with a temperature of 600 °C, as shown in Figure 6-7. In the present study, optimal annealing treatment was performed at 450 °C for 4 h in air with a ramp rate of 1 °C.min$^{-1}$.

![Figure 6-4](image1.png)

Figure 6-4 Top-view of TiO$_2$ nanotube arrays after removal surface debris and nanowires through ultrasonication in Al$_2$O$_3$ suspension.

![Figure 6-5](image2.png)

Figure 6-5 Top-view of the TiO$_2$ nanotube arrays, (a): treatment with ultrasonication,
and (b): treatments with ultrasonication and then TiCl₄.

Figure 6-6 Cracks of the nanotube arrays induced by annealing treatment.

Figure 6-7 Top-view of the TiO₂ nanotube arrays after removing surface debris and then annealing at 600 °C for 2 h.

Assembling of liquid-junction DSSCs using anodic TiO₂ nanotube arrays as photoanode

The annealed TiO₂ nanotube arrays/Ti, which was used as a working electrode (photoanode), was immersed in 0.5 mM N719 [(Bu₄N)₂[Ru(dc bpyH)₂(NCS)₂] (dc bpy)=4,4’-dicarboxy-2,2’-bipyridyl, Dyesol) acetonitrile solution at 70 °C for 8 h to absorb sufficient sensitizer for light harvesting. To evaluate the amount of dye sensitizer on the photoanode, a dye desorption experiment was conducted by immersing the dye-loaded sample in 10 ml of 10 mM KOH solution for 1 h, followed by UV/Vis spectra characteristics for concentration measurements [275]. A fluorine-doped tin oxide glass (typical size of 1.0 x 2.5 cm²) with Pt nanoparticles
was used as a counter electrode (cathode). The FTO glass was platinized through thermal decomposition of 5 mM H₂PtCl₆ in isopropanol at 375 °C for 10 min [276] and the amount of Pt was about 5 μg.cm⁻². Surlyn film with thickness of 25 μm with a hole of Φ 5.5 mm was used as a spacer and as sealing material. The redox electrolyte consisted of lithium iodide (LiI, 0.1 M), diiodine (I₂, 0.01 M), 4-tert-butylpyridine (TBP, 0.5 M), and Guanidinium thiocyanate (GuNCS, 0.1 M) in acetonitrile.

To assemble a liquid-junction DSSC, the photoanode with dye loading, Surlyn spacer and Pt-FTO were first assembled in a sandwich structure, as shown in Figure 6-8. Then the sandwich structure was heated at 80 °C for a few minutes on a hotplate. Generally, Surlyn film has been used as a sealing material to adhere working and counter electrodes which were both made of FTO. Surlyn film has been proved to be chemically and photochemically stable against liquid electrolyte components. However, it has seemed less effective in liquid-junction DSSCs using anodic TiO₂ nanotube arrays as photoanode. This was ascribed to the Surlyn film exhibiting low affinity with the TiO₂ nanotube arrays so that leakage of the redox electrolyte and evaporation of the solvents were unavoidable. In our study, sealing of the photoanode, spacer layer and Pt-FTO was achieved through an epoxy adhesive (Araldite). The sealed liquid-junction DSSCs are shown in Figure 6-9. Then the redox electrolyte was introduced into the space in the DSSC through the hole in the photoanode using a device shown in Figure 6-10. To introduce the liquid electrolyte, the valve 2 was first closed and the samples were degassed by a mechanical pump. Then valve 1 was closed and the redox electrolyte was introduced through valve 2. In this way, the redox electrolyte was introduced into the space in the sandwich structure through the small hole in the photoanode and no discernible bubbles were observed. Finally, the small hole was sealed using the epoxy adhesive. However, leakage of the electrolyte was found to be unavoidable for the liquid-junction DSSCs using epoxy adhesive as the sealing material and no liquid electrolyte could be found a few days later.
Figure 6-8 Schematic diagrams of assembling a liquid-junction DSSC, (a): dye-loaded photoanode, (b): Surlyn spacer layer, (c): platinized-FTO, and (d): assemble of (a), (b) and (c).

Figure 6-9 Optical image of the liquid-junction DSSCs using the TiO₂ nanotube arrays as photoanode.

Figure 6-10 Device for introducing liquid redox electrolyte into liquid-junction DSSCs.
Photovoltaic performance of the liquid-junction DSSCs using anodic TiO₂ nanotube arrays as photoanode

In this study dye N719 was employed, which exhibits strong adsorption in visible light and tails off at a longer wavelength (750 nm), as shown in Figure 6-11. The amount of dye sensitizer on the TiO₂ nanotube arrays obtained through anodization for 4 h has been determined to be around 289 nmol.cm⁻², which is slightly higher than that of TiO₂ nanoparticle network film photoanode [162].

The I-V characterization of the liquid-junction DSSCs was performed by applying an external potential bias to the solar cell and measuring the photocurrent using a digital source meter (Keithley 2400, GPIB interface with PC). The solar cell was subjected to one-solar AM 1.5 Global irradiation from a solar simulator (Scienctech, SS500, Ca.,) calibrated with a Si-based reference cell (RC2-B-RTD).

The liquid-junction DSSC was examined under standard reporting conditions (20 °C, AM1.5 Global, 100 mW.cm⁻²). Figures 6-12a and 6-12b exhibit the J-V characteristics of the liquid-junction DSSCs using the anodic TiO₂ nanotube arrays through anodization for various times without and with TiCl₄ treatments, respectively. As shown in Figure 6-12a, different J-V behaviors were found for these liquid-junction DSSCs. Considering all treatment procedures were identical except for the anodization time, it is reasonable to believe that the different photovoltaic properties of these liquid-junction DSSCs resulted from the various thicknesses of the anodic TiO₂ nanotube arrays. The short-circuit current (Jsc) density of the liquid-junction DSSC using the anodic TiO₂ nanotube arrays obtained through anodization for 6 h was significantly higher than that using the anodic TiO₂ arrays obtained through anodization for 2 h and 4 h. This was ascribed to the thick nanotube arrays offering a larger surface area for dye adsorption and thereby enhancing the light harvesting, leading to improved cell performance. However, the photovoltaic performance of the liquid-junction DSSCs using the TiO₂ nanotube arrays obtained through anodization for 8 h was inferior to worse than that using the TiO₂ nanotube arrays obtained through anodization for 6 h. As shown in Figure 6-1,
the thickness of the anodic TiO$_2$ nanotube arrays obtained through anodization for 6 h has been determined to be about 20 $\mu$m. In the present work, the optimal thickness of the TiO$_2$ nanotube arrays for liquid-junction DSSCs with backside-illumination configuration was about 20 $\mu$m. The liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays with thickness greater than 20 $\mu$m exhibited inferior performance, which may be attributed to considerable electron recombination for the long nanotubes [202]. As listed in Table 6-1, the most effective liquid-junction DSSCs showed a $V_{oc}$, $J_{sc}$, fill factor ($ff$), and power conversion efficiency of 0.69 V, 8.23 mA.cm$^{-2}$, 0.40 and 2.27 $\%$, respectively.

Figure 6-11 UV/Vis spectra of a N719 solution.

Figure 6-12 $J$-$V$ curves of liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays as photoanode, (a): photoanode without TiCl$_4$ treatment, and (b): photoanode with TiCl$_4$ treatment.
The $J$-$V$ characteristics of the liquid-junction DSSCs using the TiO$_2$ nanotube arrays with TiCl$_4$ treatment were shown in Figure 6-12b. In contrast to those using the TiO$_2$ nanotube arrays without TiCl$_4$ treatment, enhanced photocurrent was obtained. This is because the treatment of anodic TiO$_2$ nanotube arrays with TiCl$_4$ resulted in significant enhancement of the surface area, as shown in Figure 6-5, and consequently resulted in improvement of dye adsorption [277]. The enhancement of the specific surface area and improvement of dye adsorption improved light harvesting and then increased photoelectron generation. Moreover, it was demonstrated that treatment with TiCl$_4$ led to a downward shift in the conduction band of the TiO$_2$ and a reduction in the electron recombination with electrolyte, increasing the quantum efficiency of charge separation at the interface and then improve the photocurrent [278]. As listed in Table 6-1, the most effective liquid-junction DSSCs using the anodic TiO$_2$ nanotube arrays with TiCl$_4$ treatment exhibited a $V_{oc}$, $J_{sc}$, fill factor ($ff$), and power conversion efficiency of 0.72 V, 9.80 mA.cm$^{-2}$, 0.45 and 3.18 %, respectively.

Table 6-1 Characterizations of liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays with different thicknesses, without and with TiCl$_4$ treatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ /mA.cm$^{-2}$</th>
<th>$V_{oc}$ /V</th>
<th>$ff$</th>
<th>efficiency /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANT/2h</td>
<td>4.83</td>
<td>0.72</td>
<td>0.34</td>
<td>1.18</td>
</tr>
<tr>
<td>ANT/2h-TiCl$_4$</td>
<td>7.86</td>
<td>0.75</td>
<td>0.40</td>
<td>2.35</td>
</tr>
<tr>
<td>ANT/4h</td>
<td>6.29</td>
<td>0.68</td>
<td>0.32</td>
<td>1.36</td>
</tr>
<tr>
<td>ANT/4h-TiCl$_4$</td>
<td>8.81</td>
<td>0.69</td>
<td>0.42</td>
<td>2.55</td>
</tr>
<tr>
<td>ANT/6h</td>
<td>8.23</td>
<td>0.69</td>
<td>0.40</td>
<td>2.27</td>
</tr>
<tr>
<td>ANT/6h-TiCl$_4$</td>
<td>9.80</td>
<td>0.72</td>
<td>0.38</td>
<td>2.68</td>
</tr>
<tr>
<td>ANT/8h</td>
<td>6.52</td>
<td>0.71</td>
<td>0.40</td>
<td>1.86</td>
</tr>
<tr>
<td>ANT/8h-TiCl$_4$</td>
<td>9.80</td>
<td>0.72</td>
<td>0.45</td>
<td>3.18</td>
</tr>
</tbody>
</table>

In general, the photocurrent of liquid-junction DSSCs results from several
factors including the geometry of the photoanode, the dye-loading property, and the redox shuttles. Anodic TiO₂ nanotube arrays are believed to be a promising material for the photoanode of the liquid-junction DSSCs. Several studies have indicated that DSSCs using 1D TiO₂ nanostructures as photoanode exhibited superior performance to those using nanoparticle network film as photoanode, which stemmed from reduction in grain boundaries, enhancement of specific surface area and then dye loading, and lower recombination rates [200]. As shown in Figures 6-12a and 6-12b, it was found that these liquid-junction DSSCs exhibited relatively high dark current density. The dark current of the liquid-junction DSSCs is basically indicative of the back-reaction rate, in this case indicating that the recombination rate of electrons in TiO₂ with I⁻ in the electrolyte was high. This was ascribed to the formation of dye - I⁻ complexes and the resulting large local concentration of I⁻ at the semiconductor/dye interface [165]. Moreover, as shown in Figure 6-12 and Table 6-1, all these liquid-junction DSSCs suffered from a very low fill factor, which severely limited the power conversion efficiency. The fill factor of the liquid-junction DSSCs corresponds to several factors, such as the architecture of photoanode, the components of the redox electrolyte and even the sealing technology. In the present study, the low fill factor of the liquid-junction DSSCs may have stemmed mainly from the geometry of the photoanode and the redox electrolyte. Although they were treated through ultrasonication in Al₂O₃ suspension, debris and nanowires remained on the surface, which decreased dye adsorption and light harvesting. It is desired that the redox electrolyte be optimized to reduce the recombination of electrons in TiO₂ with I⁻ in the electrolyte.

6.3 Liquid-junction DSSCs using anodic TiO₂ nanotube arrays with special surface nanostructure as photoanode

As shown in Chapter 3, the as-prepared TiO₂ nanotube arrays obtained from non-aqueous solution consisting of NH₄HF₂ and EG were covered by debris and nanowires, which reduce dye adsorption and light harvesting [201]. Although post-treatment by ultrasonication in Al₂O₃ suspension can effectively remove the
debris and nanowires, as shown in the previous section, the liquid-junction DSSCs showed a low fill factor which was ascribed to the limited surface area of the TiO$_2$ nanotube arrays. In the present work, anodic TiO$_2$ nanotube arrays with special surface architecture were fabricated through two-step anodization in an organic solution consisting of NH$_4$F and EG. Liquid-junction DSSCs using the anodic TiO$_2$ nanotube arrays with the special surface nanostructure were fabricated and characterized.

*Fabrication and characterization of TiO$_2$ nanotube arrays with special surface morphology*

TiO$_2$ nanotube arrays with special surface morphology were fabricated using two-step anodization in a non-aqueous solution. First, TiO$_2$ nanotube arrays were prepared by potentiostatic anodization of Ti foils at 60 V in a non-aqueous solution consisting of 0.25 wt % NH$_4$F and EG. The anodization process was identical to that in organic solution consisting of NH$_4$HF$_2$ and EG, which was described in Chapter 3. Then the as-prepared anodic TiO$_2$ nanotube arrays were removed through ultrasonication in DI water. As shown in Figure 6-13, after removal of the TiO$_2$ nanotube arrays the metallic titanium had many concavities on its surface, which resulted from the bottom of the TiO$_2$ nanotube arrays. Investigated through SPM, the surface fluctuation was less than 200 nm, as shown in Figure 3-29c. The second-step anodization was carried out by potentiostatic anodization at 60 V in the same electrolyte. Unlike the first-step anodization, the second-step anodization consisted of a rapid potential ramp, i.e., at a sweep rate of 5 V.s$^{-1}$ [63]. The geometry of the titanium sheets and the post-treatment of the anodic TiO$_2$ nanotube arrays were identical to those described in the last section.

The surface morphology of the anodic TiO$_2$ nanotube arrays obtained through two-step anodization is shown in Figure 6-14. The particular structure was attributed to the combination of the remaining concave surface of the titanium after removal of the TiO$_2$ nanotube arrays obtained from the first-step anodization and the rapid potential ramp in the second-step anodization, which has been called the
self-templating method [63]. If a low potential ramp below 1 V.s\(^{-1}\) was employed during the second-step anodization, the special surface morphology was never observed. Another key point in the formation the TiO\(_2\) nanotube arrays with the special surface nanostructure is that the second-step anodization must be conducted in the used (old) electrolyte; it was never found when the second-step anodization both was conducted in new electrolyte. This was because the relatively strong chemical etching in new electrolyte removed the surface of the TiO\(_2\) nanotube arrays.

Figure 6-13 Surface morphology of Ti substrate after removing the anodic TiO\(_2\) nanotube arrays.

Figure 6-14 (a): top-view, and (b): large view images of anodic TiO\(_2\) nanotube arrays after the second-step anodization in the used electrolyte for 2 h.

The special surface nanostructure became very thin when the second-step
anodization lasted for 4 h, as shown in Figures 6-15a and 6-15b. Sometimes, cracking and disappearance of the special structure, as shown in Figure 6-15a, was observed through FESEM. The thickness of the TiO$_2$ nanotube arrays after second-step anodization for 4 h was determined to be around 12 \( \mu \text{m} \), as shown in Figure 6-16. This indicates that the growth rate of the second-step anodization in the used electrolyte was significantly lower than that of the first-step anodization in new electrolyte, which was determined to be about 15 \( \mu \text{m.h}^{-1} \) [51, 214].

It was very difficult to obtain very long TiO$_2$ nanotubes with the special surface nanostructure, although it was possible by second-step anodization in used electrolyte, in which case the thickness of the anodic TiO$_2$ nanotube arrays could be over ten micrometers. However, the duration of the second-step anodization in used electrolyte resulted in thinning or disappearance of the special surface nanostructure. Partial disappearance of the anodic TiO$_2$ nanotube arrays was found for the second-step anodization in the used electrolyte, as shown in Figure 6-17. In contrast to the highly-ordered TiO$_2$ nanotube arrays under the special surface nanostructure, the thickness of the latter was very small, as shown in Figure 6-16. It is expected that the special surface nanostructure could enhance light-harvesting efficiency and then improve the power conversion efficiency of the liquid-junction DSSCs when employed as photoanode.

Figure 6-15 (a): top-view, and (b): large view of the anodic TiO$_2$ nanotube arrays after the second-step anodization in the used electrolyte for 4 h.
Figure 6-16 Cross-section view of the anodic TiO$_2$ nanotube arrays after the second-step anodization in the used electrolyte for 4 h.

Figure 6-17 Partial disappearance of as-prepared anodic TiO$_2$ nanotube arrays during the second-step anodization in the used electrolyte.

Photovoltaic performance of liquid-junction DSSCs with anodic TiO$_2$ nanotube arrays with special surface nanostructure as photoanode

The annealed anodic TiO$_2$ nanotube arrays/Ti, which was used as working electrode (anode), was immersed in dye N719 solutions using acetonitrile or ethanol as solvent at 70 °C for 8 h to absorb sufficient dye molecules for light harvesting. A fluorine-doped tin oxide glass with Pt nanoparticles was used as a counter electrode (cathode). The redox electrolyte consisted of lithium iodide (LiI), diiodine (I$_2$), 4-tert-butylpyridine (TBP), guanidinium thiocyanate (GuCNS) and 1-propyl-3-methyl-imidazolium iodide (PMII) in a mixture of acetonitrile and valeronitrile (v/v = 15/1). Assembly of the liquid-junction DSSCs using the anodic TiO$_2$ nanotube arrays as photoanode was identical to that described in the previous section. The characterization of the liquid-junction DSSCs was also the same as that
described in the previous section.

The $J-V$ characteristics of the liquid-junction DSSCs using the anodic TiO$_2$ nanotube arrays obtained through the two-step anodization approach with and without TiCl$_4$ treatment are shown in Figure 6-18. It was found that treatment with TiCl$_4$ significantly enhances the photocurrent density of the liquid-junction DSSCs, which was ascribed to improvement of the specific surface area for dye adsorption and light-harvesting efficiency. Moreover, treatment with TiCl$_4$ resulted in improvement of the electron transport properties, such as the electron lifetime, which is associated with the charge recombination process between the semiconductor and the redox electrolyte at the TiO$_2$/electrolyte interface. Investigated through EIS, the electron lifetime can be determined according to [279]:

$$\tau_n = 1/(2\pi f_{\text{min}}) \quad (6-1)$$

where $f_{\text{min}}$ is the middle frequency. EIS measurement was conducted over a frequency range of 0.1 Hz to 100 000 Hz at an open-circuit potential and ac-voltage amplitude of 5 mV. As shown in Figure 6-19, treatment with TiCl$_4$ shifted the peak of the middle frequency in the negative direction, indicating that it increased the electron lifetime and then reduced the recombination rate [280]. Reduction of the recombination rate effectively improves the performance of liquid-junction DSSCs. As listed in Table 6-2, the most effective liquid-junction DSSC using the anodic TiO$_2$ arrays with the special surface nanostructure with TiCl$_4$ treatment exhibited a $V_{oc}$, $J_{sc}$, fill factor ($ff$), and power conversion efficiency of 0.67 V, 7.05 mA.cm$^{-2}$, 0.72 and 3.40 %, respectively, when the redox electrolyte consisted of 0.1 M LiI, 0.01 M I$_2$, 0.5 M TBP, 0.1 M GuCNS and 0.6 M PMII in a mixture of acetonitrile and valeronitrile ($v/v = 15/1$).
Figure 6-18 J-V curves of liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays obtained by two-step anodization in the used electrolyte, with and without TiCl$_4$ treatment as photoanode.

Figure 6-19 Imaginary part of EIS as a function of frequency of liquid-junction DSSCs using the anodic TiO$_2$ nanotube arrays with special surface nanostructure obtained through two-step anodization in the used electrolyte with and without TiCl$_4$ treatment as photoanode.
Table 6-2 Characterization of liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays, obtained by two-step anodization in the used electrolyte, without and with TiCl$_4$ treatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$/mA.cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>$ff$</th>
<th>efficiency/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANT/2h</td>
<td>2.91</td>
<td>0.78</td>
<td>0.60</td>
<td>1.37</td>
</tr>
<tr>
<td>ANT/2h/TiCl$_4$</td>
<td>3.94</td>
<td>0.78</td>
<td>0.62</td>
<td>1.90</td>
</tr>
<tr>
<td>ANT/4h</td>
<td>4.98</td>
<td>0.76</td>
<td>0.56</td>
<td>2.12</td>
</tr>
<tr>
<td>ANT/4h/TiCl$_4$</td>
<td>5.63</td>
<td>0.71</td>
<td>0.59</td>
<td>2.35</td>
</tr>
<tr>
<td>ANT/6h</td>
<td>5.98</td>
<td>0.67</td>
<td>0.71</td>
<td>2.80</td>
</tr>
<tr>
<td>ANT/6h/TiCl$_4$</td>
<td>7.05</td>
<td>0.67</td>
<td>0.72</td>
<td>3.40</td>
</tr>
</tbody>
</table>

Effects of redox electrolyte on performance of liquid-junction DSSCs

In general, redox electrolyte mediates electron transfer between the dye molecular and the counter electrode, and completes the electrochemical circuit. On the other hand, it provides a location for electron recombination in the conduction band of the TiO$_2$ with I$_3^-$ ions in the electrolyte, increasing the dark current and consequently decreasing the cell performance. It has been demonstrated that adjustment of the components of the redox electrolyte can effectively reduce the recombination rate [281]. In the present study, three types of redox electrolyte were investigated, whose components are listed in Table 6-3. Comparing electrolyte 1 (E1) with electrolyte 2 (E2), the former contains a kind of ionic liquid-PMII. In contrast to E1 and E2, electrolyte 3 (E3) consists of high concentration of LiI and I$_2$, but without GuCNS and PMII.

The performance of the liquid-junction DSSCs employing different redox electrolytes is shown in Figure 6-20. As other processes such as the anodization of the titanium, the annealing process and the dye-loading procedure remained identical, it is reasonable to believe that the differences in the cell performance resulted from the redox electrolyte. As shown in Figure 6-20, the liquid-junction DSSCs employing electrolyte E3 exhibited a higher short-circuit current density ($J_{sc}$) than those using E1 and E2. However, they showed a significantly low open-circuit
voltage ($V_{oc}$, 0.62 V) and a low fill factor ($ff$, 0.48), which were significantly lower than those of liquid-junction DSSCs using E1 and E2. Generally, a high concentration of I/I$_3^-$ ions in the redox electrolyte could rapidly reduce excited dye molecular and then improve the photocurrent. On the other hand, high concentration of I/I$_3^-$ ions simultaneously increased the recombination of electrons in the conduction band of the TiO$_2$ with I$_3^-$ ions in the redox electrolyte. Moreover, it strongly increased light adsorption by the redox electrolyte in the liquid-junction DSSCs with backside-illumination configuration due to the high concentration of iodine. It has been reported that about 25% of the incident light will be attenuated by the Pt-FTO counter electrode and the redox electrolyte in liquid-junction DSSCs with backside-illumination configuration [282]. Comparison of electrolyte E1 with E2 showed that liquid-junction DSSCs employing electrolyte E1 exhibited higher short-circuit current density and fill factor, as shown in Figure 6-20 and Table 6-3.

Electron recombination in the conduction band of the TiO$_2$ with I$_3^-$ in the redox electrolyte can be characterized by means of the electron lifetime. It can be determined through the open-circuit voltage decay method, which is based on the reciprocal time derivative of the open-circuit voltage decay, normalized to the thermal voltage [283]:

$$\tau_n = -\frac{k_BT}{q} \left(\frac{dV_{oc}}{dt}\right)^{-1}$$  \hspace{1cm} (6-1)

where $K_B$ is Boltzmann’s constant, $T$, the absolute temperature, and $q$ is the elementary charge. The solar cell was illuminated with one-sun light for a few minutes and the irradiation was stopped through a shuttle on the solar simulator. The open-circuit potential of the solar cell was recorded using an electrochemical workstation (VersaSTAT 3). As shown in Figure 6-21, the electron lifetimes of the liquid-junction DSSCs employing electrolyte E1 and E2 were higher than those using electrolyte E3. Comparison of the electron lifetime of the cell employing electrolyte E1 and that employing electrolyte E2 showed that the former was much longer than the latter. This difference can be attributed to the influence of the
addition of the ionic liquid-PMII. It has been reported that PMII can effectively slow the $I_3^-$ ion transport in the redox electrolyte and thus dramatically reduce the recombination rate of liquid-junction DSSCs [284].

Alternatively, the electron lifetime can be investigated through EIS according to Equation (6-1). As shown in Figure 6-22, the peak shift of the middle frequency in the low frequency region in the negative direction indicates an increase of the electron lifetime, which is in line with the results obtained from the open-circuit voltage decay method. Comparison of the electron lifetime obtained from open-circuit voltage decay technique with that obtained from EIS demonstrated that the latter was significantly longer than the former. This has been rationalized in terms of different local $I_3^-$ concentrations present in the pores of the nanocrystalline TiO$_2$ network [284]. In the present work, it can be ascribed to the relatively higher $I_3^-$ concentration caused by full sunlight illumination in the EIS measurement. EIS is a steady-state method measuring the current response to the application of an ac voltage as a function of the frequency, which takes advantage of using tiny ac voltage amplitudes exerting a very small perturbation on the system [285].

Typical EIS of the liquid-junction DSSCs at full sunlight intensity and open-circuit potential is shown in Figure 6-23. In general, three typical semicircles in the Nyquist plots or three typical characterization frequency peaks in the Bode phase plots were observed in EIS of the liquid-junction DSSCs, which corresponded to the $I_3^-$ transport in the electrolyte, electron recombination at the TiO$_2$/electrolyte interface together with electron transport in the TiO$_2$ network, and charge transfer at the counter electrode in order of increasing frequency [284-286]. In the present study, the EIS was investigated over frequencies from 0.1 Hz to 100 kHz so that only two semicircles or two typical characterization frequency peaks were observed for the Nyquist plots or Bode phase plots respectively, as shown in Figure 6-23. It has been demonstrated that the resistance $R_h$ relates to the sheet resistance of TCO in DSSC [287]. As shown in Figure 6-22, $R_h$ was determined to be over ten ohms, which corresponded to resistance between the titanium substrate and the TiO$_2$ nanotube arrays. It has been reported that the barrier layer between metallic substrate and
nanotube arrays acts as a carrier trap and hinders electron transfer to the metal [288]. To improve the photovoltaic performance of liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays as photoanode, the resistance between the metallic substrate and the nanotube arrays should be reduced. The first semicircle corresponds to the charge transfer at the counter electrode, and the corresponding resistance $R_1$ has been determined to be reciprocally proportional to the roughness factor of the Pt-FTO counter electrode [287]. The second semicircle observed at low frequencies relates to the charge transfer resistance ($R_2$) of the recombination process and the chemical capacitance of the TiO$_2$ network [286]. A reduction of the resistance $R_h$ and an increase in the resistance $R_2$ are favored to optimize the performance of liquid-junction DSSCs.

![Figure 6-20](image)

Figure 6-20 $J$-$V$ curves of liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays obtained by two-step anodization in the used electrolyte for 2 h employing various redox electrolytes.
Table 6-3 Compositions of the redox electrolytes (unit: M).

<table>
<thead>
<tr>
<th>Sample</th>
<th>LiI</th>
<th>I$_2$</th>
<th>TBP</th>
<th>GuNCS</th>
<th>PMII</th>
<th>solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>0.1</td>
<td>0.01</td>
<td>0.5</td>
<td>0.1</td>
<td>0.6</td>
<td>acetonitrile/valeronitrile (v/v = 15/1)</td>
</tr>
<tr>
<td>E2</td>
<td>0.1</td>
<td>0.01</td>
<td>0.5</td>
<td>0.1</td>
<td>---</td>
<td>acetonitrile/valeronitrile (v/v = 15/1)</td>
</tr>
<tr>
<td>E3</td>
<td>0.5</td>
<td>0.05</td>
<td>0.5</td>
<td>---</td>
<td>---</td>
<td>acetonitrile</td>
</tr>
</tbody>
</table>

Table 6-4 Characterization of the liquid-junction DSSCs employing different redox electrolytes

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ /mA.cm$^{-2}$</th>
<th>$V_{oc}$ /V</th>
<th>$ff$</th>
<th>efficiency /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>4.62</td>
<td>0.69</td>
<td>0.63</td>
<td>2.00</td>
</tr>
<tr>
<td>E2</td>
<td>3.41</td>
<td>0.70</td>
<td>0.48</td>
<td>1.14</td>
</tr>
<tr>
<td>E3</td>
<td>4.93</td>
<td>0.62</td>
<td>0.41</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Figure 6-21 Electron lifetime of the liquid-junction DSSCs employing different redox electrolytes obtained through open-circuit voltage decay method.
The addition of the PMII increased the electron lifetime and then reduced the charge recombination. However, introduction of the ionic liquid-PMII would increase the viscosity of the liquid electrolyte, which lead to a mass-transfer limitation on the photocurrent in full sunlight. Figure 6-24 shows the short-circuit densities of the solar cell employing electrolyte E1 under various illumination intensities. The almost linear relationship between the $J_{sc}$ and light intensities.
indicates no mass-transport limitation for liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays with special surface nanostructure as photoanode employing redox electrolyte containing ionic liquid [289].

Figure 6-24 Short-circuit current density ($J_{sc}$) of liquid-junction DSSCs employing redox electrolyte E1 under different illumination intensities.

Effect of dye concentration and solvent on cell performance

The effects of dye concentration and solvent on the performance of the liquid-junction DSSCs using the anodic TiO$_2$ nanotube arrays with special surface nanostructure as photoanode were investigated through measurement of the $I-V$ characteristics. The dye-loading process for the anodic TiO$_2$ nanotube arrays obtained through two-step anodization for 3 h was carried out through immersion in various dye solutions at 70 °C for 8 h. As shown in Figure 6-25, it was found that dye-loading in different solvents led to different short-circuit current densities for the liquid-junction DSSCs employing redox electrolyte E1. Moreover, all cells exhibited similar open-circuit voltage ($V_{oc}$). As listed in Table 6-5, liquid-junction DSSCs using the dye-loading process through immersion in 0.6 mM N719 in ethanol solvent exhibited the best performance, which was significantly superior to that of liquid-junction DSSCs using dye-loading processes through immersion in 0.3 mM or 0.9 mM N719 in ethanol solvent. Investigation of the influence of solvent on the cell performance showed that the liquid-junction DSSCs using anodic TiO$_2$
nanotube arrays photoanode through immersion in ethanol solvent showed higher power conversion efficiency than those obtained through immersion in acetonitrile solvent. This may have been due to lower solubility of dye N719 in acetonitrile than in ethanol.

Figure 6-25 $J-V$ curves of liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays obtained by two-step anodization for 3 h, using different dye-loading processes.

Table 6-5 Characterization of DSSCs using the anodic TiO$_2$ nanotube arrays obtained through two-step anodization for 3 h using different dye-loading processes.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>$J_{sc}$ /mA.cm$^{-2}$</th>
<th>$V_{oc}$ /V</th>
<th>$ff$</th>
<th>efficiency /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>3.70</td>
<td>0.69</td>
<td>0.62</td>
<td>1.58</td>
</tr>
<tr>
<td>D2</td>
<td>4.58</td>
<td>0.69</td>
<td>0.57</td>
<td>1.80</td>
</tr>
<tr>
<td>D3</td>
<td>5.47</td>
<td>0.69</td>
<td>0.61</td>
<td>2.32</td>
</tr>
<tr>
<td>D4</td>
<td>3.99</td>
<td>0.70</td>
<td>0.63</td>
<td>1.75</td>
</tr>
<tr>
<td>D5</td>
<td>4.24</td>
<td>0.71</td>
<td>0.61</td>
<td>1.83</td>
</tr>
</tbody>
</table>

*: D1: 0.3 mM N719 in ethanol, D2: 0.3 mM N719 in acetonitrile, D3: 0.6 mM N719 in ethanol, D4: 0.6 mM N719 in acetonitrile, and D5 0.9 mM N719 in ethanol.
6.4 Conclusions

In this chapter, liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays obtained through anodization in non-aqueous solutions and anodic TiO$_2$ nanotube arrays with special surface nanostructure obtained through two-step anodization as photoanode were fabricated and characterized. The conclusions are listed as follows:

1. Liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays as photoanode were fabricated and characterized. The TiO$_2$ nanotube arrays were synthesized through potentiostatic anodization in a non-aqueous solution consisting of NH$_4$HF$_2$ and EG. To remove debris and nanowires, the as-formed anodic TiO$_2$ nanotube arrays were treated through ultrasonication in alumina suspension. The liquid-junction DSSCs consisted of a sandwich structure of anodic TiO$_2$ nanotube arrays with dye sensitizer, Surlyn film as spacer and platinized–FTO, which was then sealed using a kind of epoxy adhesive. The redox electrolyte was introduced through a hole in the photoanode which was then sealed using epoxy resin. It was found that the epoxy adhesive slowed evaporation of the solvents but leakage of the electrolyte was unavoidable. It was found that the power conversion efficiency of the liquid-junction DSSCs depended on the thickness of the TiO$_2$ nanotube arrays. Treatment of anodic TiO$_2$ nanotube arrays with TiCl$_4$ solution resulted in improvement of the photocurrent of the cell. Maximum power conversion efficiency of 3.2 % was obtained under one sun illumination with an AM 1.5 Global filter.

2. Liquid-junction DSSCs using anodic TiO$_2$ nanotube arrays with special surface morphology as photoanode were fabricated and characterized. Anodic TiO$_2$ nanotube arrays with special surface nanostructure were fabricated through a two-step anodization method in a non-aqueous solution consisting of NH$_4$F and EG. The second-step anodization started with the metallic surface after removing the anodic TiO$_2$ nanotube arrays and it was conducted in old electrolyte. The liquid-junction DSSCs using the anodic TiO$_2$ nanotube arrays with special surface nanostructure exhibited enhanced fill factor and maximum power conversion
efficiency of 3.2 % was obtained. The influence of the redox electrolyte on electron transport of the liquid-junction DSSCs was investigated. It was found that high concentrations of LiI and I₂ in the redox electrolyte resulted in a high short-circuit current density and a low fill factor. The addition of ionic liquid-PMII into the redox electrode was found to significantly increase the electron lifetime and subsequently reduced the recombination rate.
Chapter 7 Concluding Remarks and Suggestions for Future Research

7.1 Concluding Remarks

Anodization of titanium and NiTi alloy was conducted in various solutions. The morphology, properties, and advanced applications of the anodic TiO\textsubscript{2} layer attached on the metallic titanium substrate for photocatalyst, support for the supercapacitor, and the photoanode of liquid-junction DSSCs were investigated. The conclusions are given as follows:

Potentiostatic anodization of titanium in an aqueous electrolyte containing H\textsubscript{3}PO\textsubscript{4} and HF at different applied potentials was studied. Ordered anodic TiO\textsubscript{2} nanotube arrays were obtained at 10, 20 and 30 V and it was found that the diameter of the TiO\textsubscript{2} nanotube depends linearly on the applied potential. Novel TiO\textsubscript{2} nanotube arrays containing bamboo-shoot-like structures were obtained under potentiostatic anodization at 30 V by ageing the anodization process. The as-prepared bamboo-shoot-like structures were investigated through SAED and Raman spectroscopy and were determined to be anatase, while the as-formed TiO\textsubscript{2} nanotube array investigated through XRD was amorphous. A strong increase of anodic current density and vigorous oxygen evolution were observed when the bamboo-shoot-like structures were formed, indicating that the formation of the special structures stemmed from ageing-induced dielectric breakdown.

A nanoporous TiO\textsubscript{2} layer including micro-, meso-, and macro-porous structures was obtained by anodization of titanium foils at different applied potentials in a hybrid solution containing F\textsuperscript{-} ions. It was found that regular, self-aligned TiO\textsubscript{2} nanotube arrays could be formed only at special applied potentials. The formation of the nanoporous TiO\textsubscript{2} layer was ascribed to chemical dissolution of the TiO\textsubscript{2} by localized confinement of F\textsuperscript{-} ions, whereas the concentration gradient of the F\textsuperscript{-} ions stemmed from the non-uniform electric field near the metal surface. The strength of the non-uniform electric field depended on the applied potential, so that TiO\textsubscript{2} layers with various surface structures could be obtained.
Potentiostatic anodization of titanium in a non-aqueous solution containing 0.25 wt % NH₄HF₂ and ethylene glycol was conducted and the influences of applied voltage on the morphology and growth behavior of the TiO₂ layer were investigated. It was found that highly-ordered TiO₂ nanotube arrays, which were covered by nanowires, could be obtained in a wide range of applied potentials from 20 to 90 V. It was found that the growth rate of the TiO₂ nanotube arrays depended on the applied potential. TiO₂ nanotube arrays with compact and highly regular structures were fabricated at moderate applied potentials, and anodization at high applied potentials resulted in an increased growth rate. The optimal applied potential was suggested to be 60 V in non-aqueous electrolyte containing 0.25 wt % NH₄HF₂ and EG.

Anodization of NiTi alloy in diluted HF aqueous solution was investigated. A light yellow oxide layer was formed on the surface, which was found by XPS to consist of TiO₂. In contrast to the smooth surface obtained through anodization in H₃PO₄ solution, the oxide layer obtained by anodization in diluted HF exhibited considerable roughness. The corrosion behavior of the oxide layer in Hanks’ based salt solution was investigated and enhanced corrosion resistance was obtained due to the formation of TiO₂. These findings indicated that surface modification of NiTi alloy by potentiostatic anodization in diluted HF solution was effective in enhancing surface roughness and corrosion resistance.

The photocatalytic activity of the TiO₂ layer obtained through anodization in an aqueous solution consisting of HF and H₃PO₄ was studied by decomposition of a dye AO7 solution under UV illumination. Investigated through FESEM, no discernible disintegration of the TiO₂ nanotube arrays was found for samples annealed at temperatures below 600 °C in air. Distortion of the TiO₂ nanotube arrays was observed, however, for samples annealed at 650 °C. The bamboo-shoot-like structures/TiO₂ nanotube arrays hybrid material with post-annealing at 550 °C exhibited the best photocatalytic activity. The maximum absolute apparent rate constant for decomposition of the dye AO7 solution was determined to be 0.567 h⁻¹. As determined by XRD, the TiO₂ layer annealed at 550 °C consisted of anatase.
and rutile. The high photocatalytic activity of these samples was ascribed to the formation of anatase/rutile junction, which led to an increase in charge-separation efficiency resulting from interfacial electron transfer from the conduction band of the anatase to the conduction band of the rutile. Nanoporous TiO$_2$ layers obtained through anodization of titanium at various applied potentials in hybrid solvents were investigated for photocatalytic application. The influence of morphology of the TiO$_2$ layers on the photocatalytic efficiency was examined through decomposition of AO7 under UV illumination. It was found that the ordered TiO$_2$ nanotube arrays obtained through anodization at 30 V showed higher photocatalytic efficiency than other nanoporous TiO$_2$ oxide layers. The photocatalytic efficiency of the anodic TiO$_2$ nanotube arrays depended on the thickness of the nanotube arrays and it was found that thick nanotube arrays exhibited better photocatalytic activity than thin nanotube arrays.

The EDLC of TiO$_2$ nanotube arrays and the redox capacitance of electroactive materials/anodic TiO$_2$ nanotube arrays/Ti nanocomposites were investigated through CV and galvanostatic charge-discharge techniques. It was found that the EDLC of the anodic TiO$_2$ nanotube arrays obtained through anodization in aqueous solution was in the order of a few hundreds of $\mu F.cm^{-2}$. Moreover, the EDLC depended on the ions (OH$^-$ or H$^+$) in the electrolyte, and the capacitance in acidic solution was higher than that in alkaline solution. It was found that not all of the inner surfaces of the nanotube could be accessed by the ions in the electrolyte. NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposite was fabricated through electrochemical deposition in Ni(Ac)$_2$ or Ni(NO$_3$)$_2$ aqueous solutions. It was found that the anodic TiO$_2$ nanotube arrays exhibited distinct advantages such as suppressing structural distortion, improving reversibility and cycling stability, and providing more active sites for redox reaction and ion delivery. Regarding the charge storage properties of the novel redox supercapacitor, a superior capacitance performance was achieved for the well-tailored NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti electrode. The redox capacitance of 57 $mF.cm^{-2}$ was obtained for the NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposite. Comparing with the NiO-Ni(OH)$_2$/Ti
nanocomposite, extension of the operational window of supercapacitor potential was found for the NiO-Ni(OH)$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposite. RuO$_2$/anodic TiO$_2$ nanotube arrays/Ti nanocomposites were prepared through electrochemical deposition in RuCl$_3$ solution. It was found that the anodic TiO$_2$ nanotube array was fully decorated by electroactive RuO$_2$ with particular aggregates and the specific mass of electroactive material was about 0.10 mg.cm$^{-2}$. The maximum redox specific capacitance of 487.5 F.g$^{-1}$ was obtained for RuO$_2$ deposited on the as-prepared anodic TiO$_2$ nanotube arrays with post-annealing treatment at 200 °C for 2 h. A significant decrease in specific capacitance was found when the nanocomposites were annealed at temperature above 200 °C.

Liquid-junction dye-sensitized solar cells based on anodic TiO$_2$ nanotube arrays obtained from non-aqueous solutions were assembled and characterized. For the assembling process, it was found that the commonly used Surlyn film exhibited low affinity with the anodic TiO$_2$ nanotube arrays and a kind of epoxy adhesive slowed down the evaporation of the solvents and leakage of the electrolyte. A maximum power conversion efficiency of 3.2 % was obtained for the liquid-junction DSSC based on the anodic TiO$_2$ nanotube arrays obtained through anodization in 0.25 wt % (NH$_4$)HF$_2$ in EG for 8 h with ultrasonication and TiCl$_4$ treatments. Anodic TiO$_2$ nanotube arrays with special surface morphology were prepared through two-step anodization in organic solution containing 0.25 wt % NH$_4$F and EG. Liquid-junction DSSCs based on these anodic TiO$_2$ nanotube arrays were fabricated and investigated. Devices with improved performance, especially in the fill factor, were demonstrated, and a maximum power conversion efficiency of 3.4 % was obtained. The electron lifetime of the liquid-junction DSSCs was investigated through electrochemical impedance spectroscopy and open-circuit voltage decay methods. It was found that the addition of ionic liquid in the redox electrolyte increased electron lifetime, and then reduced electron recombination and increased cell performance.

As a conclusion, TiO$_2$ layers with tunable morphology and properties could be achieved through the anodization approach in various solutions. The TiO$_2$ layer obtained through the anodization method is valuable material for use as a
photocatalyst, support for a redox supercapacitor, and use as a photoanode for liquid-junction DSSCs.

7.2 Suggestions for Future Research

The limitations of the current work and suggestions for future research are presented as follows:

Quantitative characterization of the relationship between various surface morphologies of the TiO$_2$ layer and the applied potentials is limited. It is found that the morphology of the TiO$_2$ layer depends on both the applied potentials and the electrolyte. Investigation is suggested of the relationship between the morphology of the TiO$_2$ layer and the applied potential, using a simulation approach. To achieve exact characterization, the distribution of the electric field, properties of the oxide, properties of the electrolyte, and even the charge transport at the interfaces should be considered. Such quantitative characterization will help to extend the geometries of the TiO$_2$ layer and consequently to develop advanced applications. Moreover, it might pave the way for fabrication of TiO$_2$ layers with advanced architectures through the anodization approach.

The fixed-bed flow-through photoreactor using anodic TiO$_2$ nanotube arrays as photocatalyst exhibited low photocatalytic efficiency, although the treatment contents were scaled up. Optimization of the photoreactor should be carried out to increase the photocatalytic activity. Full utilization of UV irradiation, modification of the rate of flow, and installation of anodic TiO$_2$ nanotube arrays should be carefully considered in new photoreactor design.

For electroactive material/anodic TiO$_2$ nanotube arrays/Ti nanocomposites, a coaxial structure of electroactive materials and TiO$_2$ nanotube may be a prerequisite for a redox supercapacitor in terms of charge transport. It is difficult to obtain coaxial structure by the electrochemical deposition method. A new approach is desired to prepare the coaxial structure. Furthermore, it was observed that the operational-potential windows of the electroactive material/anodic TiO$_2$ nanotube arrays/Ti nanocomposite were extended compared with that obtained through
deposition on the metallic substrate. This may be ascribed to the associated effect between the semiconductor anodic TiO₂ nanotube arrays and the electroactive material. Interpretation of the mechanism is an issue for future investigation.

It is commonly believed nowadays that liquid-junction DSSCs using anodic TiO₂ nanotube arrays as photoanode exhibit enhanced cell performance, and the presented liquid-junction DSSCs show fair power conversion efficiency. There are many scientific and even technical problems for liquid-junction DSSCs using anodic TiO₂ nanotube arrays as photoanode, for example, effective dye-loading into the inner nanotube. The influence of the barrier layer on the charge transport of the liquid-junction DSSCs should be interpreted and subsequently enhancement of power conversion efficiency may be achieved.
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1 Chuanjun Huang, Limin Zhou, Haitao Huang, Formation of Bamboo-shoot-like structures in H$_3$PO$_4$/HF Electrolyte, Presented at EMRS, Jun 8-12, 2009, Strasbourg, France.

3 Chuanjun Huang, Yibing Xie, Limin Zhou and Haitao Huang, Nanoporous TiO₂ Film Prepared by Anodization in F⁻ Ions Containing Mixed Solvent and its photocatalytic activity, presented at the 6th International Forum on Advanced Material Science and Technology, Hong Kong, 12-14 June, 2008.
