Anodic TiO₂ nanotube arrays with high surface area for dye-sensitized solar cells

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2013

Wang, X. (2013). Anodic TiO₂ nanotube arrays with high surface area for dye-sensitized solar cells. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/55152>

<https://doi.org/10.32657/10356/55152>

NANYANG
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**Anodic TiO₂ Nanotube Arrays with High Surface Area
for Dye-Sensitized Solar Cells**

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2013

Acknowledgement

I would like to express my sincere and deepest gratitude to my supervisor Prof. Sam Zhang Shanyong of School of Mechanical and Aerospace Engineering, Nanyang Technological University, for his valuable academic guidance and endless patience. Without his continuous encouragement and support, I can't complete this work.

I wish to express my sincere thanks to my senior Dr. Sun Lidong for his considerable help, invaluable instruction and discussion. I also want to thank all the members in our group, Dr. Zhang Wali, Dr. Wang Huili, Dr. Shang Lei, Dr. Cai Yanli, Dr. Li Fengji, Ms. Zhang Zhe, Dr. Wang Yuxi for their help and care.

I'm grateful to my collaborators Ms. Wang Xiu and Ms. Ong Duenyang from School of Material Science and Engineering for their assistance and help in solar cell testing. I would like to extend my thanks to the technicians in Materials Lab 1 for their helpful support in my experimental sections, especially Mr. Chang Set Chiang, Ms. Yong Mei Yoke, Ms. Chow Shiau Kee, Mr. Leong Kwok Phui and Ms. Sandy Seah.

I sincerely thank all my friends for their help and caring in the past years.

I deeply thank my parents and little brother for their constant caring, love, understanding and support.

Finally, I shall thank Nanyang Technological University for providing research scholarship and various equipments for the conduct of my project.

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Abstract

Dye-sensitized solar cells (DSSCs) have received worldwide research interest as a promising and competitive candidate for low-cost photovoltaics. Highly-ordered TiO₂ nanotube arrays prepared by electrochemical anodization have been developed as an intriguing photoanode owing to vertical tube alignment for one-dimensional electron transport and available inner and outer tube surface for dye attachment. For nanotubes based DSSCs, one main efficiency limitation factor is the relatively low tube surface area due to accessible large diameter (usually ~ 100 nm).

This project aims to enlarge tube surface area for high dye loading amount and in turn enhance conversion efficiency of DSSC devices. Two approaches are adopted to increase the surface area of nanotubes. One method is synthesis of nanotube/nanoparticle composite by a facile hydrothermal treatment. The other one is fabrication of long nanotubes of small diameter by an optimized two-step anodization.

The results show that hydrothermal treatment of anodic nanotubes is facile and effective to create TiO₂ nanoparticles on tube walls. With optimized treatment duration for a particular tube length, an optimal nanotube/nanoparticle composite structure is obtained. The composite electrode greatly improves the conversion efficiency of DSSCs, due to the combined advantages of high surface area from nanoparticles and vertical electron transport from nanotubes.

Two-step anodization by adjusting voltage from high to low produces double-layered nanotubes. In the double-layered structure, the top layer sacrifices itself to protect the bottom layer from significant chemical dissolution during growth of the bottom nanotubes, resulting in longer tubes. Furthermore, the second layer nanotubes are tailored to seed from upper tube bottoms by interim treatment to facilitate ion diffusion. Subsequently, the two-step anodization is optimized and long enough nanotubes of small diameter are achieved, that is, with tube length of 31 μm and diameter of ~ 35 nm. This overcomes tube length limitation challenge of small diameter tubes in conventional one-step anodization. Small diameter tubes greatly enlarge the dye loading amount and thus increase solar cell efficiency, in contrast to large diameter tubes. The small diameter tubes with a length of 23 μm yield a high conversion efficiency of 5.02% in dye-sensitized solar cells.

List of Publications

1. **Xiaoyan Wang**, Lidong Sun, Sam Zhang, Xiu Wang, Kaifu Huo, Jijiang Fu, Hairong Wang, Dongliang Zhao, A composite electrode of TiO₂ nanotubes and nanoparticles by hydrothermal treatment for dye-sensitized solar cells, RSC Advances, 2013, 3 (27), 11001 – 11006 (Impact Factor: 2.562).
2. **Xiaoyan Wang**, Lidong Sun, Sam Zhang, Dongliang Zhao, On seeding of the second layer in growth of double-layered TiO₂ nanotube arrays, Electrochimica Acta, 2013, 107, 200-208 (Impact Factor: 3.777).
3. **Xiaoyan Wang**, Sam Zhang and Lidong Sun, A two-step anodization to grow high-aspect-ratio TiO₂ nanotubes, Thin Solid Films, 2011, 519 (15), 4694-4698 (Impact Factor: 1.604).
4. **Xiaoyan Wang**, Sam Zhang, Lidong Sun, Xiu Wang, Dongliang Zhao, Ultra-long, small diameter TiO₂ nanotubes achieved by an optimized two-step anodization for highly efficient dye-sensitized solar cells, ACS Applied Materials & Interfaces, under review (Impact Factor: 5.008).
5. Shaojun Yuan, Gordon Xiong, **Xiaoyan Wang**, Sam Zhang and Cleo Choong, Surface modification of polycaprolactone substrates using collagen-conjugated poly(methacrylic acid) brushes for the regulation of cell proliferation and endothelialisation, Journal of Materials Chemistry, 2012, 22, 13039–13049 (Impact Factor: 5.968).
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the role of anions in hydrotalcite for quasi-solid state dye-sensitized solar cells application, Journal of Materials Chemistry A, 2013, 1, 4345-4351(Impact Factor: NA).

7. Lidong Sun, Sam Zhang, Xiao Wei Sun, **Xiaoyan Wang**, and Yanli Cai, Double-sided anodic titania nanotube arrays: a lopsided growth process, Langmuir, 2010, 26 (23), 18424–18429 (Impact Factor: 4.187).

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List of Symbols and Abbreviations

a	Radius of a Spherical Body
c	Concentration
d	Thickness
n	Ideality Factor
p	Porosity
q	Electron Charge
r	Incident Light Loss
D	Diffusion Coefficient
F	Faraday Constant
J	Ions Flux
L	Nanotube Length
R	Gas Constant
T	Kelvin Temperature
$F(\lambda)$	Incident Photon Flux Density
D_e	Electron Diffusion Coefficient
L_n	Electron Diffusion Length
J_{max}	Current at Maximum Power Output
J_{sc}	Short-Circuit Photocurrent Density
P_{in}	Input Power Density
V_{max}	Voltage at Maximum Power Output
V_{oc}	Open-Circuit Photovoltage

α	Light Absorption
σ	Optical Absorption Cross Section
λ	Wavelength
η	Dynamic Viscosity
τ_r	Electron Life
x_0	Thicknesses of Diffusion Layer
f_{growth}	Growth Factor
k_B	Boltzmann's Constant
k_{inj}	Rate Constant of Electron Injection
k_{deact}	Rate Constant of Electron Deactivation
ϕ_{inj}	Quantum Yield for Electron Injection
η_{coll}	Electron Collection Efficiency
η_{global}	Overall Conversion Efficiency
BET	Brunauer-Emmett-Teller
CIGS	Copper Indium Gallium Selenide
DI	Deionized
DSSC	Dye-Sensitized Solar Cell
FESEM	Field Emission Scanning Electron Microscopy
FF	Fill Factor
FTO	Fluorine-doped Tin Oxide
GRXRD	Glancing Angle X-Ray Diffraction

IMPV	Intensity-Modulated Photocurrent Spectroscopy
IMVS	Intensity-Modulated Photovoltage Spectroscopy
IPCE	Incident Photon to Current Efficiency
ITO	Indium-Tin Oxide
LHE	Light-Harvest Efficiency
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TCO	Transparent Conducting Oxide
TEM	Transmission Electron Microscope
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Chapter 1 Introduction

In this chapter, the research background of this project regarding TiO₂ nanotube arrays for application in dye-sensitized solar cells (DSSC) is introduced. And the current problem in this area is stated. The corresponding solutions are proposed and the project objective is described. The project scope and thesis organization are given finally.

1.1 Background

Energy plays a crucial role in our economy growth and daily life. Demand for energy will double by 2050 and triple by the end of the 21th century [1]. The energy source from fossil fuels, including oil, coal and nature gas, are exhausting at an alarming rate and will not be able to sustain the exponentially increasing energy needs [2]. Additionally, air pollution and global warming from fossil fuel bring threats to the environment of the earth. Seeking clean and renewable energy is the most important scientific and technical challenge in 21th century to solve energy shortage problem and environmental issues.

Solar energy is the ideal source of renewable energy due to its environmental friendliness and gigantic supply, i.e., 3×10^{24} J year⁻¹ or 10,000 times the average global consumption. That is to say, covering 0.1% of the earth's surface with solar cells with an efficiency of 10% would satisfy the present needs [3].

Solar energy can be converted into electricity by conventional photovoltaic devices, which are based on the concept of charge separation at an interface of two materials with different conduction mechanism, that is, *p-n* junction photovoltaics. To date, the

photovoltaics market is mainly dominated by crystalline silicon solar cells, including multicrystalline and monocrystalline silicon solar cells with an efficiency of 12%-16% in commercial modules and 24.4% in laboratory cell [4]. However, the silicon photovoltaics suffer high expensive production cost. To undercut the cost, thin film solar cells are developed based on thin film crystalline silicon, amorphous silicon, cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) [4, 5]. Low stability of amorphous silicon, the inherent toxicity of CdTe and the expensive CIGS limit their mass production [6]. Hence, extensive researches are carried out to reduce the fabrication cost and increase the conversion efficiency.

One breakthrough is the invention of dye-sensitized solar cell by O'Regan and Grätzel in 1991 [7]. In DSSC, light is absorbed by dye molecules, which are anchored to the surface of a wide band semiconductor, such as TiO_2 , ZnO and Nb_2O_5 . Photo excitation of the dye sensitizer results in electron injection from the dye into the conduction band of the semiconductor. Then electrons transport through the semiconductor to the collecting electrode for electricity generation via external circuit. DSSCs have received worldwide research interest as a promising and competitive candidate for low-cost photovoltaics due to the low production cost, compatibility with flexible substrate, insensitivity to defects, stable performance, environmental-friendly raw material, etc. [6, 8]. Despite its light-to-electricity conversion efficiency being lower than that of solid-state p - n junction photovoltaics, its price-to-performance ratio is high enough to allow it to be the most promising candidate for photovoltaic devices.

1.2 Problem statement

In DSSCs, the typical photoanode is a thin film (10~15 μm) of TiO_2 nanoparticles with a size of ~20 nm, which provide high surface area for dye adsorption and hence lead to high photocurrent and conversion efficiency [9-11]. The nanoparticles based DSSCs yielded a high efficiency of 7.12% in 1991 [7], and 11.1% in 2005 [12] and up to 12.3% in 2011 [13]. The further efficiency improvement is greatly hindered by much electron loss from electron scattering and trapping at nanoparticle boundaries during electron transport [11].

As such, one-dimensional nanostructures (e.g., nanowires [14, 15], nanotubes [16, 17] and nanorods [18]) are adopted as alternative photoanodes for efficient electron transport. The one of particular interest is TiO_2 nanotube arrays fabricated by electrochemical anodization, which renders an oriented alignment for vectorial electron transport and provides available inner and outer surface for dye attachment. However, nanotubes based DSSCs exhibit lower conversion efficiency than that based on nanoparticles. The most efficient device based on nanotubes yields an efficiency of ~8% in comparison to ~12% for nanoparticles, as detailed in one recent review paper [19]. One main limiting factor is the relatively low tube surface area due to accessible large tube diameter (usually ~ 100 nm).

Small diameter nanotubes are desired for highly efficient DSSCs [20-22]. It is calculated that when tube diameter is decreased to be ~ 30 nm, nanotubes can provide as high surface area as conventional nanoparticles of ~ 18 nm for the same film thickness [23]. Since tube diameter mainly depends on applied voltage [24-26], small diameter tubes are achieved at low voltage (< 30 V). However, at low voltage, the

relatively high chemical dissolution rate at tube tops and slow tube growth rate at tube bottoms limits the tube length to only several micrometers [21, 26, 27], far from the optimal value of 20~30 μm in DSSCs [22]. For instance, Zhu *et al.* prepared nanotubes with pore diameter of ~ 30 nm at 20 V in glycerol electrolyte but tube length was only ~ 5.7 μm after 70 h [17]; Grimes' group obtained nanotubes with inner diameter of ~ 45 nm at 20 V in ethylene glycol with 0.3 wt % NH_4F and tube length was only 5 μm after 17 h [27]; Schmuki's group produced much smaller diameter nanotubes of ~ 15 nm at 10 V in ethylene glycol solution, and their tube length was barely ~ 1 μm after 24 h [21]. To date, it remains a huge challenge to grow small diameter nanotubes to high length.

Consequently, high voltage (> 30 V) is generally adopted to produce long nanotubes in a short time but at the expense of large tube diameters (usually ~ 100 nm when voltage is higher than 50 V). For example, Grimes *et al.* found that nanotubes grown at 50 V reached up to ~ 45 μm after 17-anodization while pore diameter is 90 nm; and at 60 V, the tube length can even grew to ~ 165 μm after 17 h with a pore diameter of 105 nm [27].

In view of these, small tube diameter and high tube length are a dilemma regarding conventional anodic growth of TiO_2 nanotubes, which limits the tube surface area for dye attachment in application of DSSCs. Essentially, enlarging tube surface area for high dye loading amount will enhance light harvesting and solar cell efficiency.

1.3 Proposals

Based on the problem statement, two approaches are proposed to increase surface area of TiO_2 nanotube arrays. For large diameter nanotubes, hydrothermal treatment is

performed to generate TiO_2 nanoparticles on tube walls. The nanotube/nanoparticle composite is expected to provide larger surface area than the pristine tubes. For small diameter tubes, two-step anodization is adopted to increase tube length to optimal value. The resultant long nanotubes of small diameter will render high surface area for dye attachment.

1.3.1 Hydrothermal treatment to produce nanotube/nanoparticle composite

TiO_2 nanotubes are fabricated by electrochemical anodization at high voltage (i.e., 50 V) in short time (several hours). Subsequently, the as-anodized nanotubes are subjected to hydrothermal treatment in water at 90 °C for short periods, as illustrated in Figure 1.1. With hydrothermal treatment, nanoparticles are generated on the nanotube walls. With optimized treatment duration for a particular tube length, an optimal nanotubes/nanoparticles composite structure can be attained to combine the merits of high surface area from nanoparticles and vectorial electron transport from the still preserved nanotubes. Hence, the nanoparticles/nanotubes composite will greatly enhance the efficiency of DSSCs, in contrast to the pristine, smooth nanotubes.

Figure 1.1 Schematic illustration of hydrothermal treatment of anodic TiO_2 nanotubes to form TiO_2 nanotube/nanoparticle composite.

1.3.2 Two-step anodization to grow long nanotubes of small diameter

In two-step anodization, a top layer is created to protect the desired bottom nanotubes from substantial chemical dissolution, enabling achievement of longer tubes, as illustrated in Figure 1.2. In the first anodization, a protective top layer is formed at high voltage, as presented in Figure 1.2(a). In the second anodization at low voltage, the bottom tubes of small diameter grow underneath to form double-layered structure (see Figure 1.2(b)). During growth of the bottom tubes, the top layer gradually dissolves to protect the bottom layer from chemical dissolution, as depicted in Figure 1.2(c). Eventually, the top layer is totally dissolved and the desired bottom tubes grow to high length, as displayed in Figure 1.2(d). The resultant long nanotubes of small diameter are favored for efficient DSSC devices.

Figure 1.2 Schematic illustration of two-step anodization to grow long TiO_2 nanotubes of small diameter: (a) top layer is created in the first anodization; (b) bottom layer is grown under the top layer to form double-layered structure; (c) top layer is partially dissolved during growth of the bottom layer; (d) top layer is completely dissolved and bottom layer nanotubes grow to high length.

1.4 Objectives

This project aims to enlarge surface area of anodic TiO₂ nanotube arrays for high dye loading amount, and thus promote efficient light harvest and enhance conversion efficiency of dye-sensitized solar cells. To achieve this goal, nanotube/nanoparticle composites are obtained by hydrothermal treatment, and long nanotubes of small diameter are achieved by optimized two-step anodization. Their corresponding dye loading amounts and solar cell performances are investigated accordingly.

1.5 Scope

The whole project mainly consists of two parts. One part is synthesis of nanotube/nanoparticle composite by hydrothermal treatment for application in DSSCs. The tube morphology and phase evolution with treatment duration is systematically studied. Accordingly, the composite electrodes are used in DSSCs. The corresponding dye loading amount and solar cell performance are studied. The other part is fabrication of long TiO₂ nanotube of small diameter in two-step anodization for efficient DSSCs. In this part, protective effect of the top layer in double-layered structure is investigated and subsequently seeding sites of the second layer nanotubes are tailored. Based on these knowledge, two-step anodization is optimized and ultra-long, small diameter tubes are finally achieved. The improvement of dye loading amount and solar cell efficiency based on the small diameter nanotubes is measured.

1.6 Organization

The thesis includes six chapters. Chapter 1 introduces the research background, and states the current problem concerning TiO₂ nanotubes based DSSCs and then provides

the solutions. In chapter 2 presents literature reviews on dye-sensitized solar cells and anodic TiO₂ nanotube arrays. Chapter 3 gives the project overview and describes the experimental methodology. Chapter 4 shows the results regarding synthesis of nanotube/nanoparticle composite and their application in DSSCs. Chapter 5 deals with fabrication of long nanotubes of small diameter in two-step anodization for efficient DSSCs. The corresponding conclusions and recommendations are presented in chapter 6.

Chapter 2 Literature Review

In this chapter, the fundamental knowledge of TiO_2 nanoparticles based dye-sensitized solar cells are reviewed firstly, including their typical structure, working principle and conversion efficiency. Subsequently, the application of highly-ordered TiO_2 nanotube arrays in DSSCs is introduced and the effects of tube geometries and crystalline structure on solar cell efficiency are presented. To tailor the tube geometries for efficient DSSCs, the growth process of TiO_2 nanotubes by electrochemical anodization and the effect of anodization parameters on tube geometries are discussed accordingly. Some novel nanotube-based hierarchical nanostructures are also briefly introduced herein.

2.1 Conventional TiO_2 nanoparticles based dye-sensitized solar cells

Since first reported by O'Regan and Grätzel in 1991[7], dye-sensitized solar cells have received worldwide research interest as a promising, low-cost photovoltaics. DSSC typically comprises a thin layer of mesoporous TiO_2 nanoparticles covered by a monolayer of dye molecules on a transparent conducting oxide (TCO), a platinized counter electrode and an electrolyte containing iodide ion/triiodide ion redox couple between the two electrodes [9-11]. The working principle and conversion efficiency of DSSCs are introduced as following.

2.1.1 Working principle and typical components

The working principle of a typical DSSC is schematically depicted in Figure 2.1. Sunlight passes through TCO and then is absorbed by the dye sensitizers which are

anchored to the surface of TiO_2 nanoparticles. Sensitizer is thus raised from its ground state to electronically excited state ($S^0 + h\nu \rightarrow S^*$). Photo-induced electrons from sensitizers inject to conduction band (CB) of TiO_2 ($S^* \rightarrow S^+ + e^-$) and percolate through mesoporous network to the collecting electrode. The oxidized sensitizers (S^+) subsequently restores to its original state (S^0) by electron donation from the redox electrolyte, which is usually an organic solvent containing redox system, such as the iodide/triiodide couple (I^-/I_3^-) containing electrolyte. The redox electrolyte itself is regenerated in turn at counter electrode by electrons passed through the load. Finally the circuit is completed by electron migration through external load. The open circuit voltage of DSSC corresponds to the difference between the Fermi level of the TiO_2 film indicated with a dashed line in Figure 2.1 and the redox potential of electrolyte [10].

Figure 2.1 Working principle of TiO_2 nanoparticles based dye-sensitized solar cell. S^0 : ground state of sensitizer, S^+ : oxidized sensitizer, S^0/S^+ : the ground/oxidized state of sensitizer, S^* : electronically excited sensitizer, CB: conduction band of TiO_2 , $h\nu$: light energy [10].

The embodiment of TiO_2 nanoparticles based DSSC is shown in Figure 2.2. The materials of TCO mainly include fluorine-doped tin oxide (FTO) or indium-tin oxide (ITO). A typical TiO_2 nanoparticles film is deposited by doctor blade or screen printing on a TCO covered glass substrate. Then a short sintering process is performed to ensure that the nanoparticles are electronically interconnected for electron transport. TiO_2 has three crystal structures: brookite, anatase and rutile. The DSSCs mainly use anatase titania which has the best photoelectric property with a band gap of ~ 3.2 eV. Apart from TiO_2 , alternative wide-gap-oxides ZnO [28], Nb_2O_5 [29], SnO_2 [30] have also been studied for use in DSSCs. Up to now, TiO_2 is still regarded as the best choice. The TiO_2 film thickness is usually $10\sim 15\ \mu\text{m}$ with an average particle size of ~ 20 nm. For a $10\text{-}\mu\text{m}$ thick film, the surface area is enlarged 1000 times than the flat surface for highly efficient light harvesting by the absorbed sensitizer [10].

Figure 2.2 Schematic diagram of typical architecture of TiO_2 nanoparticles based DSSC. Inset is local magnification of a TiO_2 nanoparticle attached by a dye molecule [10].

The sensitizer anchored to mesoporous TiO_2 nanoparticle film is usually polypyridyl complexes of ruthenium and osmium, which has attachment group such as carboxylate or phosphonate to firmly graft it to the surface of TiO_2 particles, as shown in the inset of Figure 2.2. The chemical structures of dyes and corresponding colors after loading of three different ruthenium sensitizers in nanoparticle films are shown in Figure 2.3. The most widely used dye sensitizer for the DSSC has been the N3 (or N719), i.e., cis- $\text{Ru}(\text{SCN})_2\text{L}_2$ ($\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylate), as displayed in Figure 2.3(center). “Black dye”, tri(cyanato)-2,2'2"-terpyridyl-4,4'4"-tricarboxylate) $\text{Ru}(\text{II})$ is another comparable sensitizer with N3, as depicted in Figure 2.3(right) [10]. In order to obtain a broad optical absorption extending throughout the visible and infrared region, a combination of two dyes has been used to mesoporous TiO_2 films, resulting in additive optical effects. Semiconductor quantum dots such as CdSe , CdS , PbS , which absorb light in visible region, are also attractive candidates for sensitizers of solar cell [31, 32].

Figure 2.3 Chemical structure of the ruthenium sensitizers RuL_3 (yellow) $\text{cis-RuL}_2(\text{NCS})_2$ (red) and $\text{RuL}'(\text{NCS})_3$ (green) where $\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid and $\text{L}' = 2,2',2''$ -terpyridyl-4,4',4''-tricarboxylic acid. The lower part of the picture shows TiO_2 nanoparticles films loaded with a monolayer of the respective sensitizer [11].

The redox electrolyte between the photoanode and counter electrode is liquid organic solvent containing I^-/I_3^- couple. This kind of redox electrolyte is volatile and unstable under long-term illumination [10]. Recently, non-volatile electrolytes, e.g., ionic liquid [33, 34], quasi-solid-state polymer gel electrolyte [35, 36], solid-state hole conductor [37, 38] have been employed in DSSCs for better stability and durability.

The counter electrode widely adopts platinum coated TCO glass, which serves to transfer electrons from external circuit to iodine and triiodide in the electrolyte. However, the platinized TCO is relatively expensive. Alternatively, cheap carbon materials have been investigated to be counter electrode [39, 40].

2.1.2 Conversion efficiency

In the following part, the conversion efficiency of dye-sensitized solar cells will be introduced, including the incident photon to current efficiency (IPCE) and the overall conversion efficiency.

(1) Incident photon to current efficiencies

The incident photon to current conversion efficiency (IPCE, also known as external quantum efficiency) is the ratio of the number of electrons measured as photocurrent in the external circuit to the monochromatic photon flux that strikes the cell. IPCE relates

to the response of a solar cell to the various wavelengths in the spectrum of light shining on the cell. IPCE can be expressed as [11]

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda) \phi_{\text{inj}} \eta_{\text{coll}} \quad (2.1)$$

Where $\text{LHE}(\lambda)$ is the light-harvest efficiency for photons of wavelength λ , ϕ_{inj} is the quantum yield for electron injection from excited sensitizer into the conduction band of the semiconductor oxide, and η_{coll} is the electron collection efficiency. All the efforts to increase $\text{LHE}(\lambda)$, ϕ_{inj} , η_{coll} will enhance IPCE of DSSCs.

(a) Light-harvest efficiency $\text{LHE}(\lambda)$

Light is efficiently harvested by a monolayer of dyes which are anchored to the surface of mesoporous TiO_2 nanoparticle films. The light absorption α is described by Beer-Lambert's law in terms of reciprocal absorption length [11]

$$\alpha = \sigma c \quad (2.2)$$

Where σ and c are the optical absorption cross section of the sensitizer and its concentration. The absorption cross section is determined by the kind of dye. Increasing the concentration of sensitizer can enhance light absorption.

The light-harvest efficiency is derived from the reciprocal absorption length via [11]

$$\text{LHE}(\lambda) = 1 - 10^{-\alpha d} \quad (2.3)$$

where d is the thickness of the nanoparticle film. So increasing the film thickness is a good method to improve LHE, although the maximum thickness is restricted by electron diffusion length L_n . Beside, LHE can be further enhanced by incorporating

large anatase particles of 100~400 nm which significantly increase the absorption of red and near-infrared photons [11].

(b) Heterogeneous electron injection ϕ_{inj}

As illustrated in Figure 2.4, electron injection from excited sensitizer into the conduction band of the semiconductor (Process 3) competes with other radiative or radiationless deactivation channels (Process 2). The quantum yield of electron injection indicates the fraction of electrons captured by dye sensitizer that are converted into conduction band electrons. It can be expressed as [11]

$$\phi_{inj} = k_{inj}/(k_{deact} + k_{inj}) \quad (2.4)$$

where k_{inj} is the rate constant of electron injection, and k_{deact} is sum of the rate constant of radiative or radiationless electron deactivation.

Figure 2.4 Photoinduced processes occurring during photovoltaic energy conversion at the surface of the titania nanoparticle films: (1) sensitizer (S) excitation by light; (2) radiative and nonradiative deactivation of the sensitizer; (3) electron injection in the conduction band, followed by electron trapping and diffusion to the particle surface; (4) recapture of the conduction band electron by the oxidized sensitizer (S^+); (5) recapture of the conduction band electrons by the oxidized form of the redox couple regenerating the sensitizer and transporting the positive charge to the counter electrode. Gray spheres: titania nanoparticles. Red dots: sensitizer. Green and blue dots: oxidized and reduced forms of the redox couple [11].

Typical k_{deact} values lie in the range from 10^3 to 10^{10} s^{-1} . The present sensitizers, such as N3 and N719, can firmly anchor to the surface of TiO_2 particles and thus the injection times are usually in the pico- or femtosecond range. This can satisfy the rate constant for electron injection k_{inj} at least 100 times higher than k_{deact} , which result in the quantum yield of charge injection generally exceeding 90%.

(c) Electron collection efficiency η_{coll}

During the electrons percolation over the mesoscopic particle network, there are two main electron losses to affect collection efficiency: electron recapture by the oxidized dyes (Process 4 in Figure 2.4) and electron recapture by the oxidized form of the redox couple in the electrolyte (Process 5 in Figure 2.4).

Figure 2.5 illustrates the dynamic competition of the different processes during the conversion of light to electric power. Electron injection into the TiO_2 conduction band is extremely rapid, much faster than its back reaction with the oxidized dye, leading to a complete charge separation. Dye regeneration through electron donation from the redox couple is also very quick, in nanosecond time scale, so very few electrons are captured by oxidized dye. Nevertheless, recapture of the electrons by the oxidized redox couple in the electrolyte and electron transport in the nanocrystalline film take place within millisecond or even second, which are crucial to electron collection. The production of electron diffusion coefficient D_e and electron life τ_r determines electron diffusion length L_n via [11]

$$L_n = \sqrt{D_e \tau_r} \quad (2.5)$$

Figure 2.5 Dynamics of redox processes during conversion of light to electric power in DSSCs [11].

Electron is efficiently collected only if the electron diffusion length is greater than the film thickness (d) [11]:

$$L_n > d \quad (2.6)$$

In nanoporous nanoparticle films, the calculated electron transport length lies in the range of 10~20 μm , in line with experimental results. Electron transport length can be increased by adopting one-dimensional nanostructure, such as nanorod [18, 41], nanowire [14, 42], nanotube [17, 43], by increasing electron diffusion coefficient and decreasing interfacial recombination.

Furthermore, the thickness of the nanoparticle film should be larger than light absorption length ($1/\alpha$) for the sufficient light harvesting in the spectral absorption region of the sensitizer [11]:

$$d > 1/\alpha \quad (2.7)$$

Typically, to satisfy this equation, the film is a few microns thick, depending on the optical cross section of the sensitizer and their concentration in the film.

(2) Overall conversion efficiency

The overall conversion efficiency of DSSC (η_{global}) is calculated from the short-circuit photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and input power density (P_{in}) [44]

$$\eta_{global} = \frac{J_{sc}V_{oc}FF}{P_{in}} \quad (2.8)$$

And the fill factor FF is defined as [28]

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}} \quad (2.9)$$

Where V_{max} and I_{max} are the voltage and current at maximum power output, respectively. P_{in} is 1000 W/m^2 under sunlight AM 1.5. Equation (2.8) indicates that the overall efficiency of DSSC can be improved through increasing the three parameters J_{sc} , V_{oc} and FF .

J_{sc} can be described by integrating the product of the incident photon flux density $F(\lambda)$ and $IPCE(\lambda)$ of the cell over the wavelength (λ) of the incident light, expressed as

$$J_{sc} = \int qF(\lambda)(1 - r(\lambda))IPCE(\lambda)d\lambda \quad (2.10)$$

Where q is the electron charge and $r(\lambda)$ is the incident light loss in light absorption and reflection by the conducting glass. All the approaches to reduce incident light loss $r(\lambda)$ and increase $IPCE(\lambda)$ will improve J_{sc} . Recently much research effort to increase J_{sc} focuses on two ways. One aspect is improving light harvest by developing new panchromatic dyes [45] which can absorb incident light of longer length or by adding submicron particles in nanocrystalline film to enhance light scattering [11]. The other is improving electron collection by adopting one-dimensional nanostructures.

The open-circuit voltage V_{oc} can be calculated from the diode equation [9]:

$$V_{oc} = \left(\frac{nRT}{F}\right) \ln\left[\frac{J_{sc}}{i_o} - 1\right] \quad (2.11)$$

where n is the ideality factor whose value is between 1 and 2 for DSSC, R is the gas constant, T is the Kelvin temperature, F is the Faraday constant and i_o is the reverse saturation current. In DSSC, the reverse charge flow (i.e. dark current) is from recapture of the electron by the electrolyte. It can be suppressed by a tightly packed insulating monolayer at the surface of the oxide particles. At room temperature, each order of magnitude decrease in reverse current will lead to the gain of 59 mV in V_{oc} [9]. So effort in this direction is indispensable to enhance the efficiency of the DSSC over the limit of 15%.

Fill factor FF is mainly related to the series internal resistance of DSSC, which will increase with reduction of the internal resistance. The series resistance of DSSC comprises the sheet resistance of TCO, the resistance of ionic diffusion in the

electrolyte, and the resistance at the interface between the counter electrode and the electrolyte [44]. The series internal resistance can be measured with electrochemical impedance spectroscopy based on an equivalent circuit. It has been found that efficiency of DSSC can be raised by reduction of series internal resistance [46].

2.2 Anodic TiO₂ nanotube arrays based dye-sensitized solar cells

In DSSC, the nanostructures of TiO₂ electrode are essentially important because it has two crucial functions. One role is providing high surface area for dye attachment to enable efficient sunlight harvest. And the other is accepting electron injection and serving as electron transport medium to the collecting TCO substrate. In conventional TiO₂ nanoparticles based DSSCs, the main efficiency limiting factors are the electron loss via much interfacial recombination at the nanoparticle boundaries and poor absorption of low-energy photons by available dyes [47]. The electron transport is comparably slow in the disordered nanoparticle networks due to electron trapping/detrapping in three-dimensional random pathways, as depicted in the left image of Figure 2.6. Electron trapping sites, such as defects, surface state, nanoparticle grain boundaries etc., slow down electron diffusion and give rise to electron recombination, thereby decreasing electron collection efficiency [15, 22, 48].

Figure 2.6 Comparison of the electron pathways through a nanoparticulate TiO_2 film and a nanotubular TiO_2 film [22].

To enhance the electron collection efficiency, one promising approach is using one-dimensional, high-ordered nanostructures, such as nanorod [18, 41], nanowire [14, 15], nanotube [16, 17, 48, 49] and so on. The one-dimensional nanostructures aligned perpendicular to TCO substrate significantly improve the electron transport due to unidirectional electron mobility and reduce interfacial recombination, as depicted in the right image of Figure 2.6.

The electron diffusion length in TiO_2 nanotubes based DSSC is estimated to be of the order of 100 μm , which is in line with experiment observation that the electron collection efficiency is close to 100% for 20 μm -thick nanotube films [43]. In ZnO nanotube arrays based DSSC, electrons are efficiently collected over the entire 64 μm -thick photoanode arrays and the effective electron diffusion coefficient is measured to be 3 order of magnitude greater than in any DSSC photoanode to date [50]. The enhanced electron diffusion length also allows for using much thick films, which enable higher light harvest via increasing dye loading and improving the absorption of low energy photos in the red and infrared regions [14, 47].

Among the various one-dimensional nanostructures, TiO_2 nanotube arrays are receiving considerable attention which provide both inner and outer surface area for dye loading. Many techniques have been used to fabricate nanotube arrays, such as hydrothermal approach [51, 52], template-assisted synthesis [53, 54], electrochemical anodization [55-59], and so on. In particular, highly ordered, self-organized TiO_2 nanotubes by electrochemical anodization of titanium substrate attract significant research interest, owing to relatively simple synthesis and well-controlled tube geometry for use in DSSCs.

2.2.1 Two types of illumination configuration

There are two types of illumination in nanotube array based DSSCs, that is, front-side and back-side illumination, which are determined by light transmission of the substrate for nanotube growth. TiO_2 nanotubes fabricated by anodization of a titanium film on transparent glass can be assembled in front-side illuminated DSSCs. Nanotubes directly grown on opaque titanium foil require back-side illumination.

(1) Front-side illuminated dye sensitized solar cell

The configuration of transparent TiO_2 nanotube films based front-illuminated DSSC is illustrated in Figure 2.7. The nanotube arrays are directly grown on transparent FTO glass. The transparent nanotube/FTO electrode allows sunlight passing through the photoanode and being harvested by nanotubes, that is, front-side illumination.

Figure 2.7 Schematic diagram of front-side illuminated dye-sensitized solar cell architecture based on transparent nanotube arrays on FTO glass [60].

The transparent nanotube arrays are synthesized by anodization of a titanium film sputtered on the TCO substrate. The as-anodized nanotubes become optical transparent after subsequent annealing at 450 °C for 3 h to form crystalline structure. The key stages in synthesis of transparent nanotubes film are shown in Figure 2.8. The high ordered nanotube arrays renders vectorial electron transfer to TCO substrate resulting in superior electron lifetime and fast electron transport, in contrast to nanoparticulate system. DSSC based on a 360-nm-thick nanotube film could obtain a photocurrent efficiency of 2.9%, suggesting transparent nanotubes to be a very promising electrode material [16]. The further improvement of efficiency is using much longer nanotube arrays, which is limited by the technological challenge to sputter enough thick Ti film (tens of micrometers) with high quality on TCO substrate [60]. In 2009, the fabrication

difficulty is overcome by Grimes' group and TiO_2 nanotube arrays up to 33 μm were achieved. These long vertical nanotubes were assembled in DSSCs and a maximum power conversion efficiency of 6.9% was attained based on 17- μm -thick nanotube arrays [61].

Figure 2.8 The key stages in fabrication of a transparent TiO_2 nanotubes film: (a) sputter deposition of a high quality Ti thin film; (b) anodization of resulting film and (c) heat treatment to oxidize remaining metallic islands [60].

Apart from direct oxidation of Ti film sputtered on TCO substrate, TiO_2 nanotubes can be separated from Ti foil substrate and transferred to TCO for front-side illuminated dye sensitized solar cells [62-65]. Figure 2.9 shows the process of transferring nanotube arrays on FTO [62]. The key step is detachment of nanotubes from Ti substrate by selectively dissolution in particular solution containing such as HCl [62], $\text{CH}_3\text{OH}/\text{Br}_2$ [66], or H_2O_2 [64, 65]. This method is relatively simple and cost-efficient to assemble front-illuminated DSSC with high conversion efficiency. In 2010, it was reported that

the bottom end of the transferred nanotubes can be opened by chemical etching. This end-opened TiO_2 nanotube arrays were used in front-side illuminated DSSC, in which a high efficiency of 9.1% is obtained [65].

Figure 2.9 Scheme of transferring TiO_2 nanotube arrays from Ti substrate to FTO glass [62].

(2) Back-side illuminated dye sensitized solar cell

Nanotubes based back-illuminated DSSC is presented in Figure 2.10. TiO_2 nanotube arrays are grown on Ti foil substrate. Then the nanotube/Ti substrate is directly assembled in DSSC devices. Since the underlying Ti substrate is opaque, light must pass through platinum coated TCO counter electrode, in which platinum film is thin enough (~ 1.6 nm) for light transmission. This is so-called back-illuminated dye sensitized solar cell. Backside illumination is not optimal for achieving highly efficient

DSSC, since ~25% incident light energy loss from light reflection by counter electrode and light absorption by electrolyte [47, 61]. There is about 4% efficiency decrease for back-side illumination compared to front-side illumination at same film thickness [67].

Figure 2.10 Schematic diagram of back-side illuminated dye-sensitized solar cell architecture based on nanotube arrays on opaque titanium substrate [60].

Despite of this limitation, backside illumination is still very important and useful type in application of DSSC due to many other advantages. Firstly, the desired tube geometries (i.e., length, diameter, wall thickness, etc.) of nanotube arrays grown on Ti foil are easily controllable and obtainable in appropriate anodization condition. Secondly, the open circuit voltage (V_{oc}) is typically larger than 770 mV with values as high as 860 mV being observed. It is higher than that in conventional front-side illuminated nanocrystalline solar cells (V_{oc} is typically 700~750 mV) [47]. Thirdly, TiO₂ nanotubes grown on Ti foil substrate are promising photoanode materials for flexible dye sensitized solar cells. It is currently a research interest due to their potential for large area fabrication and the low production cost [68-70].

2.2.2 Critical factors for the conversion efficiency

The geometrical and structural features of TiO_2 nanotubes arrays (e.g. tube length, diameter, top morphology, crystalline structure, etc.) play great roles on the conversion efficiency of dye sensitized solar cells. The geometries should be tailored to yield a high surface area for dye loading, which is an important key factor determining the efficiency. Dye loading not only depends on the tube geometry, but also depends on tube crystalline structure and the dye sensitization conditions. Apart from dye loading, the electron collection efficiency along the tube walls is another factor to affect solar cell efficiency. The factors are discussed in details below.

(1) Tube length

Figure 2.11 (A) shows the IPCE curves of DSSCs with different tube lengths. When tube length increases from 1 μm to 20 μm , IPCE steadily increases from approx. 5% to more than 80%. It is apparent that increasing the tube length will lead to an increase of dye loading, which is attributed to enlarge available surface area. In Figure 2.11(B), it can be seen that the short circuit current J_{sc} increases with tube length from 1 μm to 24 μm , in line with the results of IPCE. Both the J_{sc} and IPCE shows light harvest is enhanced by higher dye loading with longer nanotubes. However, the open circuit voltage V_{oc} is slightly decreased with an increase of tube length from 8 μm to 32 μm . The decrease of V_{oc} is ascribed to higher number of recombination centers along longer tubes and higher series resistance. So the overall conversion efficiency of solar cells is almost similar for tubes with length of 16~24 μm . When tube length is longer than 10 μm , further increasing tube length has small improvement of conversion efficiency. Many experiment results show the optimum tube length for high efficient DSSC is in

the range of 16~24 μm [22, 61, 70], which is consistent with the calculated tube length of 30 μm [17, 71].

Figure 2.11 (A) Comparison of measured (solid line) and calculated (dotted line) IPCE values for different thicknesses of TiO₂ nanotube layers. (B) Photocurrent-Voltage characteristics of solar cells based on TiO₂ nanotube layers with different lengths [22].

(2) Tube diameter

Beside tube length, tube diameter is another key parameter to influence the available surface area for dye loading. In nanotubes based DSSCs, for the same tube length, small diameter tubes provide larger surface area for dye attachment, resulting in higher conversion efficiency, as shown in Figure 2.12(A). Figure 2.12(B) displays more results obtained from different tube geometries by different researchers. It shows a clear trend that smaller diameter tubes (for comparable tube length) increase the solar cell efficiency, as illustrated in the inset in Figure 2.12(B). This is ascribed to larger surface area for dye loading. So decreasing tube diameter is a much promising approach to enhance the efficiency of DSSCs [20].

Figure 2.12 (A) Photocurrent-voltage characteristics of DSSCs based on TiO₂ nanotubes with different diameters (empty symbols correspond to 8 μ m and filled symbols correspond to 16 μ m layer thickness) [20]; (B) Influence of tube geometry: illustrating the effect of tube length and diameter. Inset is schematic trend of solar cell performances based on large and small diameter nanotubes [22].

At present, the conversion efficiency of DSSCs based on the nanotubes is still much lower than that based on nanocrystallines (the highest efficiency $\sim 8\%$ vs. $\sim 12\%$ [19]). The main limiting factor is that TiO₂ nanotubes provide a relatively lower specific surface area due to accessible large tube diameter (usually around 100 nm). Surface area can be measured by BET (Brunauer-Emmett-Teller) method, e.g., $BET_{tubes} \approx 30 \text{ m}^2 \text{ g}^{-1}$; $BET_{nanoparticles} \approx 80 \text{ m}^2 \text{ g}^{-1}$ [22]. This in turn results in lower dye loading and photocurrent compared to ~ 20 nm sized nanoparticles. It is estimated that the specific surface areas of nanotube and nanoparticle photoanodes are comparable provided that the radius ratio of a single nanotube to nanoparticle is 5:3 [23]. Taking a particle size of 18 nm for example, it requires the nanotube diameter to be ~ 30 nm. Frank and co-workers [17] reported that nanotubes with an average inner diameter of 30 ± 4 have

comparable surface area and dye loading amount with 24-nm-sized nanoparticles for a given film thickness. The corresponding photocurrent-voltage property of this kind of nanotube and nanoparticle based DSSCs is displayed in Table 2.1. For the same film thickness, DSSCs based on nanotubes can produce a higher photocurrent than those based on nanoparticles, owing to enhanced electron collection efficiencies and light scattering.

Table 2.1 Photovoltaic performance parameters of DSSCs based on nanotubes and nanoparticles [17]

film type	L (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
NT	1.9	4.4	0.64	0.60	1.7
	3.2	6.6	0.63	0.58	2.4
	4.3	7.8	0.61	0.57	2.7
	5.7	9.0	0.61	0.55	3.0
NP	2.5	4.6	0.65	0.69	2.1
	4.2	6.5	0.63	0.63	2.6
	7.3	7.9	0.61	0.66	3.2

(3) Top morphology

The top morphology of nanotube arrays will also affect dye loading and electron transport, and consequently influence the conversion efficiency of DSSC. During growth of long tubes (more than 10 μm), the top parts of tubes may bundle together, or forms nanowires or nanograss. It is because of chemical etching, which thins the tube walls during the extended exposure in fluoride containing electrolyte [72, 73].

The influence of tube top morphology is shown in Figure 2.13. The disordered bundling nanotubes slow electron transport (a combination of one and three dimensional electron transport), increase surface recombination centers and decrease dye loading, leading to a decrease of cell efficiency [73]. Several methods have been

proposed to remove or eliminate the disordered structures, e.g., drying as-anodized tubes in super-critical CO₂ to obtain bundling-free nanotube arrays [73], creating preformed rutile oxide layer to eliminate the formation of nanograss [72], and using photoresist layer to get well-defined and open tube tops [74]. All these efforts on growth of nanograss-free nanotubes improve the conversion efficiency of solar cells. Furthermore, additional measures to increase specific surface area are taken, such as TiCl₄ treatment [75].

Figure 2.13 Influence of tube top morphology on the conversion efficiency of DSSCs: ‘nanograss-free’ and ‘grassy’ TiO₂ tube tops [22].

(4) Crystalline structure

Other than geometrical features, the crystalline structure also has significant effect on electron transport, dye loading and the electron collection efficiency [22]. From X-ray diffraction (XRD) technique, it is found that the as-anodized nanotubes are amorphous and converted into anatase or rutile upon thermal annealing at temperature higher than 250 °C, as shown in Figure 2.14(a). Under annealing treatment in the range of 300

$^{\circ}\text{C}$ ~500 $^{\circ}\text{C}$, anatase phase is obtained and rutile titania forms at a higher temperature of 550 $^{\circ}\text{C}$.

The corresponding photovoltaic performances of DSSCs are presented in Figure 2.14(b). Amorphous tubes yield very low almost negligible conversion efficiency due to a large number of recombination defect sites. Tubes upon annealing at 450 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$ exhibit the best conversion efficiency. The annealed nanotubes at 350 $^{\circ}\text{C}$ has faster electron transport but much lower dye loading, leading to lower efficiency, in comparison to tubes annealed at 450 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$. When tubes annealed at 550 $^{\circ}\text{C}$, the comparably lower efficiency can be ascribed to the formation of a detrimental rutile layer beneath the nanotube arrays at high temperate [20].

Figure 2.14 (a) XRD patterns of as-prepared and annealed TiO_2 nanotube arrays at different temperatures for 1 h in air. A, R, and T denotes anatase, rutile, and Ti substrate, respectively. (b) Photocurrent-voltage characteristics of DSSCs based on as-prepared and annealed tubes in the range 250 $^{\circ}\text{C}$ ~ 550 $^{\circ}\text{C}$ [20].

(5) Dye sensitization conditions

Besides tube geometries and crystalline structure, dye loading amount is also greatly affected by dye sensitization conditions, e.g., dye loading time, dye solution concentration, solution viscosity, pH value, loading temperature, and so on. When the tube samples are immersed in dye solution, the dye molecules gradually attach on the tube surface. After a certain time, a monolayer of dyes covers the surface area completely and the dye adsorption reaches saturation.

The dye loading amount of TiO₂ nanotubes increase with loading time. After the saturation of dye loading, the dye amount keeps almost unchanged. For the popular N719 dye solution, P. Roy et al. revealed that the dye adsorption amount greatly increased with sensitization time within 1 day [22], and then dye loading amount didn't increase with prolonged duration of 3 days, as illustrated by the red line in Figure 2.15. It indicates that dye adsorption has reached saturation by 1-day immersion in dye solution. A monolayer of dye molecules has been covered on TiO₂ surface completely. Further prolonged sensitization time can't promote the dye adsorption, as depicted by the black line in Figure 2.15. The dye amount decreased slightly with a longer duration of 7 days due to the dye aggregation [20]. Therefore, dye sensitization in N719 solution is generally carried out for 1 or 2 days in most reported work. For the other kinds of dye solution, there also exists an optimal dye sensitization time.

Figure 2.15 Influence of dye sensitization durations: an overview graph for non-TiCl₄-treated as well as TiCl₄-treated tubes for different dye sensitization durations [22].

Dye concentration also affects the dye loading amount. Higher dye concentration will accelerate the dye adsorption. It is found that a higher and lower dye concentration requires a shorter and longer loading time [76]. In addition, dye solution viscosity affects the dyes diffusion the nanotube films. A lower solution viscosity facilitates the dye loading process and shortens the loading time. A higher solution viscosity affects the dye solution infiltration in nanotubes and thus hinders the dye loading process.

Since the dye molecules usually contain several carboxylic acid binding group for dye attachment on TiO₂ surface, dye solution is high acid. If the dye solution contains higher concentration of carboxylic groups, the dye solution has a lower pH value. In this case, it needs shorter time for the dye sensitization process. However, the lower pH value don't damage can lead to the dissolution of ZnO electrode [77]. The TiO₂ nanostructures are not affected by the pH value.

Sensitization temperature also plays an important role in dye sensitization. High dye sensitization temperature, such as 40 °C, leads to a fast dye adsorption. It can be ascribed to a possible fast dehydration reaction when the carboxylic acid group anchors on the TiO₂ surface [22].

2.3 Fabrication of TiO₂ nanotube arrays by anodization

In 1999, Zwilling and co-workers reported that porous titania film with a regular columnar structure formed in the fluorine species containing electrolyte by anodization of titanium [78]. In 2001, Gong and co-workers reported the formation of uniform, high-ordered TiO₂ nanotube arrays in a HF electrolyte [55]. Since then, self-organized, vertically-oriented titania nanotube arrays fabricated by anodization of titanium have been extensively and vigorously investigated, due to their relatively simple synthesis and well-controlled geometry for various application in photocatalysis [79], photocleavage of water [80], and dye sensitized solar cells [22], and so on.

Anodization of titanium foils is conducted using two-electrode or three-electrode system. In two-electrode system, the set-up for anodization is shown in Figure 2.16. Titanium foil is performed as the working electrode and platinum mesh is used as the counter electrode. In most electrolytes, only compact TiO₂ is formed. While in the fluoride-containing electrolyte, self-organized TiO₂ nanotubes can be produced under applied voltage.

Figure 2.16 Schematic diagram of electrochemical anodization set-up and anodic growth of TiO_2 nanotubes on a Ti-metal sheet [22].

Formation of TiO_2 nanotubes are governed by three simultaneously occurring processes and the corresponding chemical reactions are shown as below.

The three key processes are: field assisted oxidation of Ti to form titanium oxide at metal/oxide interface according to Reaction 2.12; field assisted dissolution of TiO_2 and Ti^{4+} at metal/electrolyte interface at tube bottom through Reactions 2.13 and 2.14, and chemical dissolution of the formed TiO_2 by fluoride ion in the electrolyte based on Reaction 2.13, which is much fast in acid solution [26, 56, 58].

Figure 2.17(A) illustrates the field-assisted oxidation and dissolution. Under the draw force of applied electric field, anions such as O^{2-} and F^- migrate through the oxide layer to the metal/oxide interface. O^{2-} reacts with Ti metal, resulting in the oxide growth. At

the same time, metal ion Ti^{4+} moves from the metal substrate through oxide layer to the oxide/electrolyte interface by aid of electric field. Ti^{4+} is directly reacted with F^- to form soluble TiF_6^{2-} complexes according to reaction (14) and then ejected into the electrolyte. At the tube bottom, the formed oxides are gradually dissolved by etching of F^- ion. The applied electric field promotes the dissolution of oxides through polarizing and weakening the Ti-O bond. The field-assisted oxidation moves the metal/oxide interface forwards into the metal substrate and thickens the oxide layer. The field-assisted dissolution moves the oxide/electrolyte interface into the formed oxide layer and thins the oxide layer. After a certain time, the field-assisted oxide growth rate and dissolution rate becomes equal. The steady state is established and the thickness of the oxide layer remains unchanged although it moves further into the metal making the tubes longer [58].

Figure 2.17 (A) Schematic representation of the Ti anodization in presence of fluorides (results in the tube growth); (B) steady state growth situation characterized by equal rates of TiO_2 dissolution (v_1) and formation (v_2) [58].

The length of nanotubes will be determined by the pore growth rate (electrochemical etching rate) at tube bottom and the chemical dissolution rate of fashioned oxides at tube mouth, as illustrated in Figure 2.17(B). When these two rates become equal, the nanotubes reach the maximum length. Before this point, the tube length will increase with anodization time. After the time of reaching maximum length, chemical dissolution is faster than pore growth, and thus the tube length will decrease with prolonged duration. In fact, chemical dissolution occurs over the entire tube length, while much faster at tube mouth than at tube bottom. Hence the tube possesses V-shape morphology after extended anodization duration.

The initiation and growth of nanotube is schematically shown in Figure 2.18 and the corresponding current density transition with anodization time is depicted in Figure 2.19. At the very beginning of anodization, a compact titanium oxide barrier layer forms (Figure 2.18(a)). Hence, the current density abruptly decreases with barrier thickening until to a minimal value (point P1 in Figure 2.19). Due to the presence of fluoride ion in the electrolyte, dissolution and breakdown of the barrier layer occur randomly on the surface (Figure 2.18(b)) and the current begins increasing (from P1 to P2 in Figure 2.19). When the breakdown pits reach saturation, the maximal current is obtained (P2 in Figure 2.19). These breakdown sites act as pore nucleation seeds and a disordered wormlike porous structure grows towards into the metal substrate (see Figure 2.18(c)). The anodization current then gradually drops with an increase of pore depth (point P3~P4 in Figure 2.19). A pH gradient is established between the pore top and bottom. The electrochemical etching rate of the oxide is accelerated at the pore bottom due to the local acidification. After the competition and natural selection between the initial pores, ordered nanotubes are formed (see Figure 2.18 (d)) and the

current becomes steady (see point P4 in Figure 2.19). The time to generate nanotubes is very short, usually several minutes. During subsequent anodization, the nanotubes become longer and the current gradually decreases. The initial barrier layer at the surface is gradually dissolved and finally removed by chemical dissolution, leaving the high-ordered nanotube pores, as shown in Figure 2.18(e).

Figure 2.18 Schematic representation of the TiO₂ nanotube arrays formation: (a) compact layer growth to the maximum thickness, (b) breakdown of the barrier film, (c) growth of the pores resulting in a worm-like structure, (d) more ordered structure, and (e) regular self-organized porous TiO₂ structure [81].

Figure 2.19 Anodization behaviour of a 400 nm Ti thin film anodized at 10 V in HF-based electrolyte at room temperature. Inset shows a typical current density transition observed for a titanium foil (one face protected with polymer coating) anodized at the same potential and electrolyte [56].

The growth of nanotubes is diffusion controlled process after the nanotubular structure forms (generally several minutes). The diffusion model is schematically given in Figure 2.20. The F^- ions diffuse from the bulk electrolyte to the tube bottom and are consumed through reaction with TiO_2 or Ti^{4+} . It is presumed that the concentrations of F^- in the bulk electrolyte and tube bottom are c_0 and 0, respectively. The reacted TiF_6^{2-} ions are produced at the tube bottom and diffuse to the electrolyte. Its concentrations are supposed to decrease from c_0 to 0 between tube bottom and the electrolyte. So the flux of ions (J) in the diffusion layer and nanotube layer are expressed as [25],

$$J = -D \frac{\partial c}{\partial x} \quad (-x_0 \leq x \leq 0) \quad (2.15)$$

$$J = -pD \frac{\partial c}{\partial x} \quad (0 \leq x \leq L) \quad (2.16)$$

where D , p , c , x_0 , and L are the diffusion coefficient, porosity of the nanotube layer, concentration of the ionic species, thicknesses of the diffusion layer and nanotube length, respectively.

Figure 2.20 Schematic drawing of the diffusion model for ionic species during the anodization [25].

From Equation 2.15 and 2.16, it can be seen that improving diffusion coefficient can increase the flux of ions, leading to accelerated growth rate of nanotubes. That is the reason that higher temperature during anodization can increase the tube length [82]. Stirring can reduce the thickness of the diffusion layer and therefore increase diffusion rate, resulting in longer tube length [25].

2.4 Effect of anodization parameters on tube geometries

The geometries of TiO_2 nanotube arrays can be affected by many anodization parameters, including electrolyte composition, applied voltage, anodization duration,

temperature, stirring, and so on. The effects of these anodization factors on the tube geometries are introduced in the following.

2.4.1 Effect of electrolyte composition

The electrolyte compositions, such as pH, concentration of fluoride ion, water content, and so on, play a great role on the geometries of nanotubes, especially on the tube length. In aqueous electrolyte, pH affects both the electrochemical etching at tube bottom and chemical dissolution along tube walls. In strong acidic electrolyte ($\text{pH} < 1$), chemical dissolution is rapid and thus prolonging anodization duration doesn't increase tube length. That is the reason that maximum tube length is only ~ 500 nm in HF electrolyte. When increasing pH, the rate of chemical dissolution is reduced. Therefore, in weaker acid electrolyte, longer nanotubes will be obtained after enough long time. However, the tube diameter doesn't depend on pH at a particular voltage [56, 83].

Besides pH value, the chemical dissolution of oxide is also determined by the fluoride concentration. No nanotubes are formed when the chemical dissolution is too low or too fast. So only in a certain range of F^- concentration, nanotubes can be produced. And the anodization voltage to fabricate nanotubes is related with fluoride concentration. Large voltage requires high fluoride concentration in the electrolyte [83]. The concentration of fluoride species is also a mainly important factor to affect the wall thickness. It has been found at same condition, nanotube wall thickness decreases with fluoride concentration, due to the enhanced chemical dissolution [25, 84]. Under the same anodization voltage, when increasing the F^- concentration, the growth rate of the nanotubes will be increased, in turn resulting into longer tubes in a short time [27, 84, 85].

Water content is another important factor during tube growth. In aqueous electrolyte, longer nanotubes are difficult to be obtained, due to high rate of chemical dissolution. In organic electrolyte, increasing water content from <1 vol.% to 50 vol.%, tube length is greatly decreased, because of faster chemical dissolution. Meanwhile, the tube diameter is increased, which is ascribed to larger effective electric field across the oxide film due to decreasing IR drop in the electrolyte [86, 87]. It is also observed that there are many ripples on the tube walls when water content exceed 5 vol.%, resembling with nanotubes grown in aqueous electrolyte. In order to obtain smooth and long nanotubes, the water content is lower than 5 vol.% in organic solution [86].

The development of anodic nanotubes can be classified into four generations based on modification of electrolyte composition [59]. The tube length has a significant increase from 500 nm [55] to approx. 1000 μm [88]. The first generation of TiO_2 nanotubes was formed on Ti foil in HF aqueous electrolyte at 10 V~23 V. The maximum tube length is up to 500 nm, due to rapid chemical dissolution by the acid. In order to reduce the chemical dissolution of as-fashioned nanotubes, an aqueous buffered electrolyte containing KF or NaF to tailor PH in weaker acid was proposed by Cai and co-workers [83]. It opened up the second generation synthesis technique. The tube length was increased to approximately 7 μm , an order of magnitude longer than the first generation tubes [89]. Growth of much longer nanotubes is limited by high water content in aqueous electrolyte, which is responsible for the rapid chemical dissolution of as-formed nanotubes. And the tube walls of first and second generation are rough with considerable thickness variations (ripples) caused by current oscillation in aqueous electrolyte [90]. The third generation nanotubes were fabricated in polar organic electrolyte with much low water content. As a result, tubes of several hundred

micrometers [85, 91, 92] even one millimeter [88] were achieved. And the tube walls are much smooth due to suppressing current fluctuation in viscous organic electrolyte [90]. Other than in fluoride containing electrolyte, nanotube arrays also can be fabricated in non-fluoride based electrolyte consisting of HCl or H₂O₂ or their mixtures with NH₄Cl [93]. This is regarded as the fourth generation synthesis techniques. The typical tube features of these four generation synthesis are shown in Figure 2.21.

Figure 2.21 Cross-sectional SEM images of (A) a 500 nm long first generation nanotube arrays prepared by HF based electrolyte at 20 V [59]; (B) a 1.5 μm long second generation nanotube arrays prepared by KF based electrolyte at 25 V [83]; (C) 165 μm long third generation nanotube arrays prepared by ethylene glycol based electrolyte at 60 V [59]; (D) 300 nm long fourth generation nanotube arrays prepared at 13 V in 3 M HCl for 10 min [93]. Insets are corresponding top-view images.

2.4.2 Effect of voltage

Voltage is an important factor to determine the tube length and diameter during the growth of nanotube arrays. It has been found that the tube length and diameter both increase with applied voltage [24, 26], as shown in Figure 2.22. The tube length increase with anodization voltage is attributed to the enhanced electric driving force for ion transport through the barrier layer at the tube bottom. This results in faster movement of Ti/TiO₂ interface into the Ti metal. At high voltage, the electrochemical etching rate at tube bottom is much faster than the chemical dissolution at tube top, and nanotubes can grow very long after enough anodization time. Hence using high voltage is the most effective approach to obtain ultra-long nanotubes in organic electrolyte. At low voltage, the growth rate of nanotubes is slow. And the tube length is short after long anodization duration.

Figure 2.22 Diameters and thicknesses of TiO₂ nanotube layers formed in 1 M H₃PO₄ + 0.3 wt% HF at different potentials [24].

Anodization voltage is the key factor to control the tube diameter. The linear potential-dependency of nanotube diameter is explained by the model in Figure 2.23. The model assumes that the oxide growth starts from the tip of the tube bottom and grows immediately in all directions leading to a hemispherical oxide structure. The maximum oxide thickness (i.e., tube radius) is equal to the compact oxide layer thickness, which determined by [94, 95]

$$R = f_{\text{growth}} U \quad (2.17)$$

where f_{growth} is the growth factor. For the case of Ti/TiO₂, the growth factor $f_{\text{growth}} = 2.5 \text{ nm V}^{-1}$. So the diameter of TiO₂ nanotubes can be expressed as $D = 2f_{\text{growth}} U = 5.0 \text{ nm V}^{-1} U$.

Figure 2.23 Proposed mechanism explaining the potential-dependency of the nanotube diameter [95].

2.4.3 Effect of anodization time

Anodization time is an important factor to affect tube length. Tube length will increase with anodization time until it reaches the maximum length. After that, tube length will

shorten with prolonged duration. The maximum length is determined by electrochemical etching rate at tube bottom and chemical dissolution rate at tube mouth. Tubes reach to maximum length when these two rates are comparable [26]. In aqueous electrolyte, since the chemical dissolution is fast, prolonging anodization time can't obtain enough long tubes. In organic electrolyte, the time to maximum length is mainly depends on the anodization voltage. The lower the voltage is, the sooner the maximum is reached, as displayed in Figure 2.24. At high voltage, e.g., 60 V, high electric field strength enables fast electrochemical etching rate, resulting in fast tube growth and much long time for maximum length. In optimized organic electrolyte, TiO₂ nanotubes can grow up to several hundred [27, 85, 91] even to one millimeter [88] after extended anodization duration (17 h~216 h) at a high voltage of 60 V. At low voltage, e.g., 25 V, the tube length reaches to maximum of several micrometers after short time. It is because that the chemical dissolution rate at tube tops becomes comparable with the tube growth rate at tube bottom. Therefore, the tubes grown at low voltage are usually short even after long anodization time.

Figure 2.24 Time dependence of length of TiO₂ nanotube arrays prepared at 60 V and 25 V. Inset is a local magnified region [26].

2.4.4 Effect of temperature

The influence of temperature on the growth of nanotube arrays has been widely investigated. At higher temperature, ion diffusion in electrolyte become quicker, in turn the current density during tube growth is increased, resulting in longer nanotubes. And tube diameter also increases linearly with temperature [82], as shown in Figure 2.25. Based on the diffusion controlled process of nanotube growth, the diffusion constant D is determined by [82]

$$D = \frac{k_B T}{6\pi\eta a} \quad (2.18)$$

where k_B is Boltzmann's constant, T is the absolute temperature, η is the dynamic viscosity and a is radius of a spherical body. The dynamic viscosity decreases with

temperature (mainly for organic electrolyte), and therefore the ion diffusion increases temperature, resulting in longer nanotubes.

Figure 2.25 Temperature dependence of diameter and length of TiO_2 nanotubes in glycerol electrolytes [82].

Regarding the temperature-dependence of tube diameter, it can be explained from the increased effective electric field. At higher temperature, the ionic diffusion is enhanced and the ionic conductivity of the electrolyte is increased. The IR drop in the electrolyte is decreased and thus in turn the potential across the nanotube layer is increased. Hence the diameter of the nanotubes is increased with temperature. The relationship is just suitable to the organic electrolyte, because the IR drop is greatly affected by temperature in viscous electrolyte. In aqueous electrolyte, the tube diameters are almost the same in different temperatures [56]. It is because the IR drop across the aqueous electrolyte is hardly affected by temperature. However, in aqueous electrolyte, the wall thickness is greatly decreased with anodization temperature [56].

2.4.5 Effect of stirring

As discussed above, growth of TiO_2 nanotubes is a diffusion control process in the steady state. Stirring in the electrolyte will affect the diffusion rate. It has been found that stirring can significantly increase current density. Hence the tube growth rate is enhanced, leading to an increased tube length [25, 26, 87, 96]. This can be ascribed to increased diffusion rate by reducing the thickness of the diffusion layer during the stirring process, as schematically depicted in Figure 2.26.

Figure 2.26 Concentration profiles of the species in the outer and inner diffusion area of the tubes with and without stirring [87].

The ion diffusion actually occurs in the diffusion layer and the nanotube layer. Stirring mainly affects the diffusion layer in the electrolyte and reduces its thickness. The concentration gradient becomes much larger than in static electrolyte, and in turn the diffusion rate is increased. That is the reason that the current density and tube length is

increased. Therefore, longer nanotubes can be obtained in stirring condition. The effect of stirring on the current density further confirms the diffusion controlled process.

Tube surface morphology is also affected by stirring. In the static electrolyte, the tube top is homogenous due to the steady ionic diffusion process. While stirring produces much rough tube surface. In order to fabricate uniform nanotube arrays, static electrolyte is preferred [25, 87].

2.5 TiO₂ nanotube-based hierarchical architectures

Based on the extensive studies on growth of TiO₂ nanotube arrays, more complicated nanostructures have been produced by modified anodization. Double or multi-layered nanotubes have been fabricated by two or multi-step anodization. Bamboo-typed nanotubes can be prepared by using alternative voltage. Furthermore, hybrid nanostructures have also been obtained by hydrothermal treatment or water soaking of the as-anodized nanotubes. These nanostructures are introduced below in detail.

2.5.1 Double-layered nanotubes

Since the anodization parameters (i.e., electrolyte, voltage, temperature, et. al.) affect the tube geometry, double-layered TiO₂ nanotubes can be fabricated with a two-step anodization by changing electrolyte [97-99], adjusting applied voltage [99-104], or varying bath temperature [105]. The double-layered nanotubes open up new possibilities to vertically tailor the properties for new applications.

2.5.1.1 Double-layered TiO₂ nanotube formed in different electrolytes

Double-layered nanotubes can form with a two-step anodization in two different electrolytes at the same voltage, e.g., in aqueous and organic electrolyte, respectively [97, 98]. When the first anodization is performed in an aqueous electrolyte, followed by the second anodization in an organic electrolyte, the as-formed double-layered structure is presented in Figure 2.27. The top layer grown in the aqueous electrolyte has a large tube diameter and the bottom tubes have relatively smaller diameters. From the interface morphology in Figure 2.27(B), it is obvious that the small tubes penetrate through the tube bottoms of the first layer. In comparison to the aqueous electrolyte, there is a large IR drop in the organic electrolyte and hence the effective electric potential across the oxide layer is reduced, leading to the small diameter tubes in the organic electrolyte.

Figure 2.27 SEM images of the interface of the double-layered TiO_2 nanotubes: (A) in the top view and (B) in the cross-sectional view showing channels at the bottoms of the first layer [97].

However, it is reported that the double-layered structure can't be observed when the anodization sequence is reversed, i.e., first anodization is carried out in organic electrolyte for 6 h and subsequently the second anodization is performed in aqueous HF containing electrolyte for 2 h [98]. It can be explained from the fast chemical dissolution in the HF containing aqueous electrolyte. The as-formed top tubes are totally dissolved after 2 h in the second anodization. Therefore, the anodization sequence and corresponding duration are important for the resultant double-layered nanostructure in different electrolytes.

2.5.1.2 Double-layered TiO₂ nanotube formed by adjusting voltage

Voltage is an important anodization parameter during growth of TiO₂ nanotubes. Adjusting voltage is much simple and straightforward approach to produce double-layered nanotubes, in contrast to changing electrolytes. Multi-layered anodic porous alumina nanostructures with branched channels by reducing voltage or increasing voltage has been widely investigated [106, 107]. Branched double-layered TiO₂ nanotubes are achieved by decreasing voltage by a factor of $\frac{1}{\sqrt{n}}$ in the high voltage range of 85 V to 28 V [102], as shown in Figure 2.28. With decreasing voltage, a large tube is branched into several small tubes.

Figure 2.28 Branched TiO₂ nanotubes by reducing voltage from 85 V to 60 V [102].

In some cases of low voltage schemes, adjusting voltage leads to the stacked double-layered structure, as shown in Figure 2.29. When decreasing voltage from 20 V to 10 V, small diameter tubes form beneath the upper large tubes and seed from in the intertube gaps of the top layer, as depicted in Figure 2.29(a). It is different from the case in Figure 2.28. This indicates that the oxide thickness at intertube gaps is thinner than that at the bottom and thus the sites between the gaps are more chemically active, leading to formation of new tubes in the gaps of the existing tubes [94]. When increasing voltage from 20 V to 40 V, large tubes grow beneath the upper small tubes, as presented in Figure 2.29(b). It can be seen the tube bottom of the first layer is still closed and the second layer grows beneath them, exhibiting a stacked structure.

Figure 2.29 Cross-sectional SEM images of the TiO_2 nanotubes prepared in a two-step anodization for Ti-Zr alloy. The first anodization was conducted at 20 V for 15 min. The second anodization was conducted at (a) 10 V and (b) 40 V for 15 min after opening the circuit for 1 min and then sweeping the voltage from 20 V to the end value at a rate of 0.1 Vs^{-1} [100] .

2.5.2 Bamboo-type nanotubes

Alternating voltage with cyclic high-low voltage sequence can produce novel bamboo-typed nanotubes [103, 108, 109], as presented in Figure 2.30. The tubes are grown at the high voltage (i.e., 120 V) for 1~5min. Then the voltage is switched to a low voltage (i.e., 40 V) for 5 min. During the low voltage period, the tube growth is terminated while the pH and ion-diffusion gradients inside tubes are reduced. A subsequent anodization at the high voltage will produce an initial compact oxide again, leading to the formation of bamboo-rings along tubes. Essentially, using appropriate alternating voltage cycling allows a switch between conditions that enable tube growth and conditions enable compact layer generation for determinant formation of a bamboo-type structure. The distance of bamboo rings are determined by the tube length grown at high voltage, in turn facilely tailored by the anodization time of the high-voltage

step [103, 108, 109]. In Figure 2.29(b, c), the bamboo ring distance is reduced by shortening the anodization time from 5 min to 1 min at 120 V.

Figure 2.30 SEM images of 8 μm thick TiO_2 layers: (a) smooth walled nanotube layers, grown under constant-voltage conditions at 120 V for 2 h; (b) bamboo-type tubes (B-NT1), grown under alternating voltage conditions, with a sequence of 5 min at 120 V and 5 min at 40 V for 4 h; (c) bamboo-type tubes (B-NT2), grown under alternating voltage conditions, with a sequence of 1 min at 120 V and 5 min at 40 V for 12 h. For panels a-c, images on the right show cross-sectional views for each sample [108].

In comparison with the conventional smooth nanotubes, the bamboo-type nanotubes can substantially increase tube surface area and the efficiency of dye-sensitized solar cell [108, 109], as shown in Figure 2.31. The higher photocurrent can be attributed to the higher surface area arising from the bamboo-rings for higher dye loading amount. Furthermore, higher density of the bamboo-rings, that is, smaller ring spacing, leads to higher solar cell efficiency [108, 109].

Figure 2.31 (a) IPCE values and (b) I-V characteristics of DSSCs based on smooth and bamboo-typed TiO₂ nanotube layers shown in Figure 2.29: smooth (NT) and bamboo type (B-NT1 and B-NT2). The inset in panel a shows a photocurrent transient acquired at 520 nm wavelength [108].

2.5.3 Hybrid nanostructures

After post-treatment of the as-formed TiO₂ nanotubes, hybrid nanostructures consisting of nanotubes and nanoparticles or nanowires have been fabricated. TiCl₄ treatment has been widely employed to decorate nanoparticles on the tube walls before assembling nanotubes in the DSSC devices [75, 110, 111]. TiO₂ Nanoparticles with a size of ~3nm are precipitated on the surface of tubes after TiCl₄ treatment, as shown in Figure 2.32. The conversion efficiency of DSSCs based on TiCl₄ treated nanotubes are

enhanced due to the enlarged surface area by the coated nanoparticles for dye loading amount [75, 110, 111].

Figure 2.32 SEM images of TiO_2 nanotubes before (a) and after TiCl_4 treatment (b) [75].

Hydrothermal treatment was another approach to generate nanoparticles on tube wall in $(\text{NH}_4)_2\text{TiF}_6$ [112] or P25-nanoparticles-containing aqueous solution [113]. After hydrothermal treatment, smooth nanotubes are converted into nanoscopic tubes composed of a large number of nanoparticles, as presented in Figure 2.33.

Figure 2.33 SEM images of hierarchically structured TiO_2 nanotube arrays composed of nanoparticles by a facile combination of two-step electrochemical anodization with a hydrothermal process: (a) top view; (b) cross-sectional view [112].

Water soaking of as-anodized nanotubes is also a facile method to convert nanotubes partially or entirely into nanowires or nanoparticles [114, 115]. The amount of nanowires or nanoparticles increases with water soaking time, as displayed in Figure 2.34. It usually takes 1~3 days for the formation of nanowires. In contrast to as-anodized nanotubes, these novel hybrid nanostructures have a remarkably enlarged surface area for dye loading, resulting into enhanced efficiency [115].

Figure 2.34 SEM characterization of the morphological evolution as a function of water-soaking time: (a, b) as-anodized TiO_2 nanotube arrays; (c, d) intermediate double-walled nanotube arrays obtained by water soaking for 15-25 h; (e, f) intermediate wire-in-tube nanoarchitectures formed by water soaking for 25-72 h; (g, h) mesoporous nanowire arrays obtained by a long-term water soaking (>72 h). Scale bars: 500 nm. The insets of panels a, c, e, and g denote the morphologies of the nanostructure arrays after scratching the top porous layer off. Scale bars: 200 nm [114].

Chapter 3 Project Overview and Methodology

As stated in Chapter 1 and reviewed in Chapter 2, one of the main efficiency limitation factors in TiO_2 nanotube arrays based DSSCs is low tube surface area for dye attachment, resulting in insufficient light harvest. For large diameter tubes, the tube length is long enough while the large tube diameter limits available surface area. For favored small diameter tubes, the tube length is short, due to high chemical dissolution rate at low voltage. Consequently, this project proposed two solutions to enlarge tube surface area for efficient DSSCs, as illustrated in Figure 1.1 and 1.2 in Chapter 1. In this chapter, the project overview is presented and the experimental methodology is given.

3.1 Project overview

The project includes two parts, as illustrated in the project overview in Figure 3.1. In the first part, nanotube/nanoparticle composite is produced by hydrothermal treatment. Tube morphology and phase evolution with hydrothermal duration are systematically investigated. The performances of DSSCs based on the composites are studied by varying the composite morphology and tube length. In the second part, long nanotubes of small diameter tubes are achieved by two-step anodization. Protective effect of the top layer in double-layered structure is revealed. The seeding of the second layer is investigated and the resultant branched structure is obtained by tailoring the voltage decrease rate. Based on the fundamental knowledge, long enough nanotubes of small diameter are attained by an optimized two-step anodization and the corresponding DSSC performances are measured.

Figure 3.1 Overview of the project

3.2 Experimental

This section presents detailed experimental procedures to fabricate TiO₂ nanotubes and TiO₂ nanotube/nanoparticle composite and assembly process of DSSC devices. Accordingly, nanotube characterization and solar cell testing are introduced.

3.2.1 Synthesis of TiO₂ nanotube arrays and nanotube/nanoparticle composite

Highly ordered TiO₂ nanotube arrays were fabricated by electrochemical anodization with titanium foil (0.25 mm, 99.5% purity, Alfa Aesar) as the working electrode and platinum gauze as the counter electrode, as shown in Figure 3.2(a). Prior to the anodization, the foils were degreased in acetone, ethanol and deionized (DI) water for 20 min each and dried by air stream. The distance between electrodes was set at 22 mm. The electrolyte solution was ethylene glycol (extra pure, Merck) containing 0.3 wt. % ammonium fluoride (98+%, Reagent, Sigma-Aldrich) and 2 vol. % DI water. All

the anodizations were conducted at room temperature ($\sim 20^\circ\text{C}$). During anodization, a digital multimeter (Agilent, 34401A, $6\frac{1}{2}$ Digit) was used to record the current transitions, as displayed in Figure 3.2(b).

Figure 3.2 Photos of electrochemical anodization set-up: (a) anodization cell; (a) equipment connections.

After anodization, all samples were rinsed with DI water and dried in air. For application in dye-sensitized solar cells, the as-formed nanotubes were cleaned ultrasonically in DI water for 20 min to remove nanograss on tube tops and subsequently dried in air.

(1) Hydrothermal treatment to produce nanotube/nanoparticle composite

TiO₂ nanotube arrays were prepared by electrochemical anodization at 50 V for different time at room temperature ($\sim 20^\circ\text{C}$). The resultant nanotubes were ultrasonically cleaned in ethanol/DI water (1:1, v/v) for 30 min to remove the nanowires accumulated on tube tops. Prior to ultrasonication, the as-anodized

nanotubes were annealed at 200 °C for 2 h to increase the adhesion strength between the tubes and titanium substrate.

Subsequently the cleaned and top-opened nanotubes were immersed into 20 mL DI water in a Teflon-lined stainless steel autoclave for hydrothermal treatment. The autoclave was kept in oven at 90 °C for different durations (< 5 h). After cooling down to room temperature in oven, the samples were rinsed with DI water and dried in air.

(2) Two-step anodization to grow ultra-long, small diameter tubes

Double-layered TiO₂ nanotubes were prepared with a two-step anodization by adjusting applied voltage in the same electrolyte. Two voltage sequences were used: from high voltage to low and from low voltage to high. Applied voltage and anodization duration were chosen on purpose for systemic investigation. To promote the tube growth, magnetic stirring was applied at a speed rate of 250 rpm.

In search for the rules that govern the choice of the “seeding sites” of the second layer, interim treatment conditions were changed under the same voltage sequence, i.e., at 30 V in the first step and subsequently at 15 V in the second step. Before the second anodization, five different interim treatments were applied separately: annealing the first layer nanotubes at 450 °C for 3 h; drying the first layer nanotubes in air for 24 h; interrupting power supply for 5 min; decreasing voltage abruptly from 30 V to 15 V; reducing voltage gradually from 30 V to 15 V at a rate of 1.5 V/min.

3.2.2 Assembly of DSSC devices

For use in DSSC devices, the as-grown and hydrothermal-treated nanotubes were subjected to thermally annealing at 450 °C for 3 h in air to convert amorphous titanium oxide into anatase. To enhance the solar cell efficiency, pristine nanotubes arrays were selectively subjected to TiCl_4 treatment in 40 mM aqueous solutions of titanium tetrachloride (99.9%, Reagent, Sigma-Aldrich) at 70 °C for 10 h. The TiCl_4 solution prepared under ice-cooled condition was loaded into a closed vessel with one sample in partial vacuum each time. The resultant samples were rinsed with ethanol to remove excess TiCl_4 and then annealed at 450 °C for 30 min to crystallize the decorated nanoparticles.

The crystallized nanotubes were sensitized by soaking in 0.3 mM N719 dye (*cis*-diisothiocyanato-bis(2,20-bipyridyl-4,40-dicarboxylato)ruthenium(II)bis(tetrabutylammonium), Solaronix) in acetonitrile/*tert*-butanol (1:1, v/v) solvent for 48 h. To facilitate dye penetration into nanotubes, each sample was sealed in closed-vessel each time and the dye loading process was performed in partial vacuum. The sensitized nanotube arrays were assembled into DSSCs with platinized FTO glasses as the counter electrode, which were prepared by thermal decomposition of H_2PtCl_6 solution (0.6 mM) at 400 °C for 15 min. The two electrodes were spaced by hot-melt films (SX1170, Solaronix, Switzerland) with a thickness of 25 μm or 60 μm . The electrolyte (EL HPE, Dyesol) containing iodide/tri-iodide redox couple was introduced from one hole on the counter electrode under partial vacuum. The active area of the cells was 0.26 cm^2 . A schematic of DSSC device is shown in Figure 3.3.

Figure 3.3 Schematic representation of Ti/Nanotubes based dye-sensitized solar cell

3.2.3 Tube characterizations

Top and cross-sectional views of TiO_2 nanotube arrays were characterized by field emission scanning electron microscope (FESEM, JEOL, JSM-7600F). Some cross-sectional views with long nanotubes were observed by scanning electron microscope (SEM, JEOL, 5600LV). Morphology and structure of nanotubes were also obtained by transmission electron microscope (TEM, JEOL, JEM-2010, 200 kV). The phase compositions were examined by glancing angle X-ray diffraction (GAXRD, PANalytical Empyrean, $\text{Cu K}\alpha$ radiation). Chemical composition of the titanium oxide was detected by X-ray photoelectron spectroscopy (XPS, KRATOS, AXIS ULTRA) by using a monochromated $\text{Al K}\alpha$ (1486.7 eV) X-ray source at a power of 150 W (15 kV $\times$ 10 mA). The binding energy of C 1s peak at 285.0 eV was used as the reference for all the spectra.

3.2.4 Solar cell testing

The photocurrent-voltage characteristics of DSSCs were measured with a digital source meter (Keithley 2400) under simulated AM 1.5 illumination (100 mW cm^{-2}) from a solar simulator (1 kW xenon with AM 1.5 filter, Müller). Dye loading amount of the nanotube films was determined by measuring the UV-vis absorption spectra of the desorbed dye solutions. The dye molecules were desorbed by immersing the sensitized samples in 0.1 M NaOH solution in a mixed solvent (water/ethanol = 1:1, v/v).

Chapter 4 TiO₂ Nanotube/Nanoparticle Composite for Dye-Sensitized Solar Cells

As reviewed in Chapter 2, high tube length and small tube diameter are favored for highly efficient dye-sensitized solar cells. Long TiO₂ nanotubes are easily achieved at high voltage, while the corresponding tube diameters are large. Their relatively low surface areas limit dye loading amount and thus the conversion efficiency of DSSCs.

Several methods have been exploited to decorate nanoparticles on nanotube walls to enlarge the available surface area. TiCl₄ treatment has been widely employed to precipitate very small nanoparticles (~3 nm) on tube walls before assembling solar cells [75, 110]. Recently, hydrothermal treatment has been reported to form the nanoparticles piled nanotubes electrode in (NH₄)₂TiF₆ [112] or P25-nanoparticles-containing aqueous solution [113]. Water soaking is another facile method to convert nanotubes partially or entirely into nanoparticles or nanowires [114, 115]. This process is performed without any additional chemicals at room temperature, but it takes a very long period of time (2~3 days) to form the composite architecture. In all these cases, the obtained structures render high surface area for dye loading and hence give rise to appreciable efficiency enhancement when applying in DSSCs. Nevertheless, the outer tube walls are unlikely to be used any more, as intertube spacings are filled or blocked by the newly formed nanoparticles (see Figures 2.32~2.34 in Chapter 2). Additionally, electron transport in these electrodes is deteriorated, as the integrity of the tubes has already been destroyed.

In this study, nanotubes/nanoparticles composite electrodes are prepared by a facile hydrothermal treatment of nanotubes in DI water at 90 °C for short periods (< 5 h), as illustrated in Figure 1.1 of Chapter 1. The work aims to figure out the formation process of the composites and produce an optimal nanotube/nanoparticle composite structure to utilize both the inner and outer tube walls while maintaining the tube features, thus increasing the power conversion efficiency. Synthesis of the composite electrode is investigated systematically and the corresponding performances of dye-sensitized solar cells are measured.

4.1 Synthesis of the composite electrodes by hydrothermal treatment

TiO₂ nanotubes were prepared by electrochemical anodization in ethylene glycol containing 0.3 wt. % ammonium fluoride and 5 vol. % DI water at 50 V for 2 h. Then the as-anodized nanotubes were hydrothermally treated in water at 90 °C for different durations. The tube morphology and phase evolution with hydrothermal treatment duration are discussed below.

4.1.1 Tube morphology evolution with hydrothermal treatment duration

Figure 4.1 shows the pristine smooth TiO₂ nanotubes. The nanotubes exhibit a uniform, highly ordered morphology with pores diameter of 92 ± 5 nm and tube length of ~ 6.5 μm . The top-opened tubes are obtained after clearing away the undesired nanowires on tube tops [111]. Compared with conventional nanoparticles in DSSCs, the large diameter tubes provide much lower surface area for dye adsorption. In order to increase the surface area, the nanotubes were therefore subjected to hydrothermal treatment in water at 90 °C.

Figure 4.1 FESEM top (a, b) and cross-sectional (c, d) images of pristine TiO₂ nanotube arrays of 6.5 μm after ultrasonic cleaning.

After 30 min treatment, only a few small particles of several nanometers form on both inner and outer tube walls, as presented in Figure 4.2(a, b). As the duration prolongs to 45 min, more particles of larger size (ca. 20~40 nm) are obtained, as shown in Figure 4.2(c, d). The newly formed particles on the tubes will enlarge the available surface area for dye adsorption. Meanwhile, the preserved tubular structure can provide vectorial pathway for electron transport. Hence, the composite electrode will combine the merits of nanoparticles and nanotubes, which is desirable for efficient DSSCs. This is the most intriguing feature in contrast to the other reported composite structures [112, 114] where the integrity of the tubes is destroyed.

Figure 4.2 FESEM top (a, c) and cross-sectional (b, d) images of TiO₂ nanotube arrays of 6.5 μm under hydrothermal treatment for 30 min (a, b) and 45 min (c, d).

As the hydrothermal duration increases to 1 h, the tubes almost convert into nanoparticles completely so that the top surface nearly loses tube features, as presented in Figure 4.3(a). Although the vertical alignment is still discernible in Figure 4.3(b), the relevant magnifications reveal that the integrity of tube walls is nearly destroyed and each tube is composed of numerous nanoparticle segments, as detailed in the insets of Figure 4.3(b). Figure 4.3(c)~(e) shows that the upper part of the tubes is still hollow while the middle part is partially blocked and the lower part is completely filled with nanoparticles. This is ascribed to abundant TiO₂ source near tube bottoms for nanoparticle formation, in view of the V-shaped tube inner pores. When further increasing the duration (e.g., 3 or 5 h), the nanotube arrays exhibit similar morphology.

Figure 4.3 FESEM images of TiO₂ nanotubes of 6.5 μm under hydrothermal treatment for 1 h: (a) top morphology; (b) cross-sectional morphology; (c) hollow tubes at the upper part; (d) partially blocked tubes at the middle part; (e) solid tubes at the lower part. The insets in (b) are the corresponding magnified upper, middle and lower tubes.

4.1.2. Tube phase evolution with hydrothermal treatment duration

Accompanying the morphology evolution, structure of TiO₂ nanotubes also changes with hydrothermal duration, as shown in Figure 4.4(a). For pristine nanotubes, only titanium peaks from the substrate are detected. Therefore, the original TiO₂ nanotubes are still amorphous after annealing at 200 °C for 2 h to increase the adhesion between the nanotubes and titanium substrate. Upon hydrothermal treatment, anatase phase emerges and the peak intensity increases with treatment duration. It can be concluded that hydrothermal process in water induces the phase transformation from amorphous

to anatase, in line with the results reported elsewhere [114, 116]. To apply in DSSCs, all these nanotubes were annealed at 450 °C for 3 h. Figure 4.4(b) reveals that all the nanotubes entirely convert into anatase structure upon annealing.

Figure 4.4 XRD patterns of the pristine and hydrothermally modified TiO₂ nanotube arrays for different durations before (a) and after (b) annealing at 450 °C for 3 h.

To gain further insight into the tube evolution upon hydrothermal treatment, the relevant nanotubes were characterized by transmission electron microscopy (TEM). Figure 4.5(a) displays representative morphology of one pristine nanotube which exhibits smooth hollow tubular structure with thick walls. The corresponding selected area electron diffraction (SAED) pattern indicates that the pristine tubes are amorphous. After hydrothermal treatment for 30 min, tube walls partially convert into nanoparticles while keeping the hollow tube structure, as illustrated in Figure 4.5(b). The corresponding SAED pattern shows weak diffractions, confirming the presence of crystallites. This is in consistence with the pertinent XRD patterns in Figure 4.4(a). When further prolonging the treatment to 45 min, the original tubular structure is still discernible with the tube being filled with big particles, as shown in Figure 4.5(c), and more crystallites are thus formed (see the relevant inset). After 1 h, the tubes are transformed into nanoparticles completely, losing the tubular structure, as depicted in Figure 4.5(d). The corresponding SAED pattern shows a typical feature of nanocrystals. The TEM results are in fairly good agreement with the morphology and phase evolutions presented in Figures 4.1~4.4.

Figure 4.5 TEM images of one pristine TiO₂ nanotube (a), and nanotubes after hydrothermal treatment for 30 min (b), 45 min (c), and 1 h (d). The insets are corresponding selected area electron diffraction patterns.

Hydrothermal generation of TiO₂ nanoparticles is based on a dissolution-precipitation process where water molecule plays an essential role [114, 116, 117]. The as-anodized TiO₂ nanotubes are amorphous and thermodynamically unstable in water. Water molecules adsorb on the surface of the amorphous titania to combine with the basic titania unit of TiO₆²⁻ octahedra. Subsequently the dehydration of water leads to regular arrangement of octahedral and crystallization. Noticeably, stably crystallized tubes can hardly induce the dissolution-precipitation process, resulting in limited changes in tube

morphology and structure [118]. In this process, the ambient temperature and pressure affect the nucleation and growth of the crystallites, influencing the final electrode configuration. Under the current experimental conditions, i.e., hydrothermal treatment at 90 °C, the size and amount of the nanoparticles increase with treatment duration. For short durations (below 1 h), amorphous tube walls partially dissolve and precipitate to form crystalline nanoparticles on the tubes. For long durations (above 1 h), the whole tubes convert into columnar structure consisting of nanoparticles and no discernible morphology change is observed for further prolonged duration. Meanwhile, the relevant crystallinity enhances with the treatment duration, as can be seen from the increased intensity of the XRD (Figure 4.4 (a)) and SAED patterns (Figure 4.5). It demonstrates that the morphology evolution and phase transformation simultaneously occur in the dissolution and precipitation process. As compared to previous reports [114, 115], the hydrothermal treatment at elevated temperature (i.e., 90 °C) in this study drastically shortens the transformation time (i.e., ~1 h vs. 2~3 days). Furthermore, the nanoparticle size is much larger than that formed at the room temperature (i.e., 20~40 nm vs. 3~10 nm [114]) because the higher temperature and pressure facilitate the particle growth.

4.2 Application of the composite electrodes in DSSCs

As discussed above, tube morphology evolves with hydrothermal treatment to form nanotube/nanoparticle composite. Subsequently, the pristine and hydrothermally treated TiO₂ nanotubes will be assembled in DSSCs and the corresponding solar cell performances will be characterized in the following. Accordingly, the advantages of

the composite electrodes will be evaluated and the optimal composite structure will be figured out for further cell efficiency enhancement.

4.2.1 DSSC performances depending on tube morphology

To use in DSSCs, the pristine and hydrothermally treated TiO₂ nanotubes were subjected to thermal annealing at 450 °C for 3 h in air. The annealing treatment converted all these tubes into anatase completely, as revealed from the XRD patterns in Figure 4.4(b). The tube morphologies after annealing are displayed in Figure 4.6. Upon annealing treatment, the pristine tubes are still smooth (Figure 4.6(a)), which is as same as the ones before annealing (Figure 4.1(b)). For hydrothermally treated tubes (Figure 4.6(b~f)), tube morphologies also keep unchanged after annealing treatment in comparison to the corresponding tubes before annealing (Figure 4.2 and 4.3).

Figure 4.6 FESEM top views of pristine and hydrothermally treated TiO₂ nanotubes with a length of 6.5 μm after annealing treatment at 450 °C for 3 h in air: (a) pristine tubes; (b) 30-min-treated tubes; (c) 45-min-treated tubes; (d) 1-h-treated tubes; (e) 3-h-treated tubes and (f) 5-h-treated tubes.

Thereafter, these annealed nanotubes are exploited as photoanodes in DSSCs. The photocurrent-voltage characteristics are shown in Figure 4.7(a). Compared to solar cells based on pristine nanotubes, those based on the treated nanotubes exhibit higher power conversion efficiencies. The efficiency as a function of hydrothermal duration is summarized in the inset of Figure 4.7(a). It shows that the efficiency dramatically increases from 1.04% to 2.04% and then slightly drops to 1.63% as the duration increases. The enhancement in efficiency can be ascribed to the nanoparticle formation under hydrothermal treatment which enlarges dye adsorption ability.

Figure 4.7 Photocurrent-voltage characteristics of DSSCs based on pristine and hydrothermally treated TiO₂ nanotube arrays of 6.5 μm (a) and corresponding dye loading amount (b). The inset is the efficiency as a function of hydrothermal duration.

Figure 4.7(b) shows the relevant dye loading amount. From 30 min to 45 min, the remarkable increment in dye loading amount contributes to the abrupt efficiency enhancement, which in turn originates from the enlarged surface area by forming big nanoparticles (see Figures 4.2 and 4.5). Further increased duration has little influence on the dye amount, as the tubes convert into nanoparticles completely around 1 h (see Figures 4.3 and 4.5). In addition, the filled tube bottoms and intertube spacings after long durations (see Figure 4.3) on the other hand reduce the surface area for dye adsorption, thus lowering the photocurrent and power conversion efficiency. Moreover, the destroyed integrity of the nanotubes may deteriorate the charge collection process and therefore affect the cell performance, as evidenced from the decreased photocurrent with increased treatment duration (from 45 min to 5 h in Figure 4.7(a)) under similar dye loading amount (see Figure 4.7(b)). Eventually, the nanotubes under hydrothermal treatment of 45 min exhibit the highest efficiency in the present study, since it combines the advantages of nanoparticles and nanotubes.

4.2.2 DSSC performances depending on tube length

Based on the discussion above, 6.5- μm tubes under 45-min hydrothermal treatment exhibits the optimal nanotube/nanoparticle structure for best conversion efficiency. To further enhance DSSC efficiency, much longer tubes are desired. Hence the as-anodized TiO₂ nanotubes with different tube lengths (3.5~20.5 μm) were subjected to hydrothermal treatment for 45 min to study the length effect.

The corresponding photocurrent-voltage characteristics are given in Figure 4.8(a). It shows that the cell photocurrent increases with tube length from 1.90 mA/cm² at 3.5 μm to 5.26 mA/cm² abruptly at 6.5 μm and then to 6.04 mA/cm² at 16.5 μm and final

up to 6.77 mA/cm² at 20.5 μ m. This trend is in good agreement with the measurement of dye loading amount, as exhibited in Figure 4.8(b). The cell photocurrent enhancement is ascribed to the corresponding dye loading increase for efficient light absorption.

Figure 4.8 Photocurrent-voltage characteristics of DSSCs based on TiO₂ nanotubes of different lengths (a) and corresponding dye loading amount (b) under hydrothermal treatment of 45 min.

The dye amount is in turn influenced by available surface area of the nanotubes. For the shortest tubes of 3.5 μm , it shows only a few small nanoparticles on the tube surface while the tube walls are still smooth, as shown in Figure 4.9(a, b). When the tube length increases to 6.5 μm , many big nanoparticles of 20~40 nm decorate on the tube walls after the same treatment duration (Figure 4.2(c, d)). In this case, the surface area is greatly enlarged. This explains why the dye loading and efficiency are nearly tripled when tube length increases from 3.5 μm to 6.5 μm . For longer tubes of 16.5 μm , the whole tubes are converted into nanoparticles (see Figure 4.9(c, d)) which lead to further increase in surface area for higher dye amount. However, at the part near tube bottoms, it is evident that the original tubes have been filled with nanoparticles completely and become solid nanocolumns, as depicted in the inset of Figure 4.9(d). As the length increases to 20.5 μm , the treated nanotube tops are almost covered with nanoparticles completely, as compared to that of the 16.5- μm -long tubes, as illustrated in Figure 4.9(e, f). The solid structures at lower parts of tubes are difficult for dye attachment. This is why the dye loading amount does not increase greatly with longer nanotubes. Additionally, with longer tubes (>16.5 μm), the photovoltage is reduced due to increased electron recombination in longer tubes. The reduction of voltage offsets the increase of photocurrent and eventually results in similar conversion efficiency for solar cells with tube length being over 16.5 μm (~2.2%). Therefore, nanoparticle formation under hydrothermal treatment is accelerated in longer tubes, due to abundant titania source for dissolution-precipitation process to occur.

Figure 4.9 FESEM images of top (a, c, e) and cross-sectional (b, d, f) morphologies for 45-min-treated TiO₂ nanotube arrays with lengths of 3.5 μm (a, b), 16.5 μm (c, d), and 20.5 μm (e, f). The inset in (d) is the corresponding tubes near the bottom part.

4.2.3 DSSC performances based on long tubes with optimized hydrothermal treatment duration

As discussed in Section 4.2.2, longer TiO₂ nanotubes ($> 6.5 \mu\text{m}$) has been converted into nanoparticles completely after 45-min treatment due to the accelerated dissolution-precipitation process. Therefore, for longer tubes ($> 6.5 \mu\text{m}$), the

hydrothermal duration should be adjusted accordingly to obtain preferred composite electrode of nanotubes and nanoparticles.

Taking an example of 16.5- μm nanotubes, the hydrothermal treatment is shortened to be 30 min, 15 min and 10 min. The DSSC devices exhibit the best performance when the duration is reduced to around 15 min, as presented in Figure 4.10. All the photovoltaic characteristics are improved as compared to the devices with 45-min-treated tubes (photocurrent: 8.82 vs. 6.04 mA/cm^2 , photovoltage: 0.70 vs. 0.67 V, and fill factor: 0.57 vs. 0.55). Eventually a power conversion efficiency of 3.54% is achieved. Therefore, optimal treatment duration exists for a particular tube length. For long tubes, the hydrothermal duration should be shortened for formation of an optimized nanotube/nanoparticle composite structure, which makes full use of both outer and inner tube walls while reserving the tube features.

Figure 4.10 Photocurrent-voltage characteristics of DSSCs based on pristine and hydrothermally treated TiO₂ nanotube arrays of 16.5 μm for different durations.

4.3 Summary

In this chapter, a facile and effective hydrothermal treatment of anodic TiO₂ nanotubes in water was adopted to create nanoparticles on the tube walls. The tube morphology and structure evolution with hydrothermal duration were systematically studied. The size and amount of nanoparticles increased with treatment time. For the tubes of 6.5 μm in length, within 1 hour titania nanoparticles formed on both inner and outer tube walls while keeping the integrity of the tubes. At prolonged time of exceeding 1 hour, the nanotubes were entirely converted into nanoparticles. Along with the morphology evolution, the amorphous tubes were gradually converted into anatase nanoparticles.

The performance of DSSCs based on the hydrothermally treated nanotubes was investigated. With the same length (i.e., 6.5 μm) but different durations, the nanotubes by hydrothermally treated for 45 min yielded the best photovoltaic performance, due to the combined merits of high surface area from the nanoparticles and vectorial electron transport from the nanotubes. Under the same duration (i.e., 45 min) but with different lengths, the formation of nanoparticles was accelerated in longer tubes. The parts near the tube bottoms were constantly filled with the nanoparticles, limiting the cell efficiency to about 2.23% with the length being over 16.5 μm . Accordingly, further efficiency enhancement up to 3.54% was achieved with the tubes of 16.5 μm in length by shortening the duration of hydrothermal treatment to 15 min only.

Chapter 5 Long TiO₂ Nanotubes of Small Diameter for Dye-Sensitized Solar Cells

As stated in Chapter 1, small diameter TiO₂ nanotubes are favored for highly efficient DSSCs. However, it is still a huge challenge to grow very long nanotubes of small diameter. Therefore, much effort has been focused on decorating nanoparticles on large tubes to increase surface area for dye attachment (Chapter 4). This project also aims to overcome the length limitation of small diameter nanotubes for application in DSSCs. Thus a two-step anodization is proposed for realizing this target, as illustrated in Figure 1.2 of Chapter 1.

In this chapter, the formation of double-layered nanotubes by a two-step anodization is presented and the protective effect of the top layer is revealed. Subsequently, the seeding sites of the second layer nanotubes are tailored by interim treatment and the seeding mechanism is interpreted. The resultant branched double-layered structure is favored for growth of longer nanotubes in the second layer. Finally, the two-step anodization is optimized and very long nanotubes of small diameter are eventually achieved and used in DSSC devices.

5.1 Protective effect of the top layer in double-layered structure

In growth of anodic TiO₂ nanotubes, chemical dissolution plays an important role in determining the final tube length. To obtain very long nanotubes, organic electrolyte was used to suppress the chemical dissolution [119, 120]. As a result, nanotubes with length of hundreds of micrometers [85, 92] and even a few millimeters [88] were

achieved. Nevertheless, these nanotubes are generally grown at high applied voltage (60 V or above). Meanwhile, the tube diameters are large, usually larger than 100 nm.

Small diameter nanotubes are achieved at low voltage. The top morphology of TiO₂ nanotubes grown at 15 V is shown in Figure 5.1. The tubes are uniform with an average inner diameter of 35 ± 3 nm and outer diameter of 45 ± 4 nm. The value is close to the estimated ideal tube diameter of 30 nm, which could provide comparable specific surface area with conventional nanoparticles [23]. Frank and co-workers [17] also reported that nanotubes with an average inner diameter of 30 ± 4 nm have comparable surface area and dye loading with nanoparticle films with a particle size of ~ 24 nm for a given film thickness. Consequently, the diameter of TiO₂ nanotubes produced at 15 V satisfies the requirement of highly efficient DSSCs. In this project, 15 V is adopted as the low voltage to grow desired small diameter nanotubes.

Figure 5.1 FESEM top views of TiO₂ nanotubes grown at 15 V for 4 h. The inset is a local magnification.

However, under low voltage, the unavoidable chemical dissolution at tube tops become comparable with tube growth rate at the bottom, leading to the difficulty of growing long tubes of small diameter by conventional one-step anodization.

In this section, two kinds of double-layered TiO₂ nanotube arrays were prepared by changing voltage from high to low (i.e., from 30 V to 15 V) or from low to high (i.e., from 15 V to 30 V) in a two-step anodization. It is found the top layer can serve as a sacrificial layer to protect the continuous growth of the bottom layer from chemical dissolution. Accordingly, the two-step anodization from high voltage to low voltage is adopted to produce longer TiO₂ nanotubes of small diameter in view of the protective effect of the top layer. The results and discussion are introduced in the following.

5.1.1 Formation of double-layered nanotubes by adjusting voltage from high to low

To date, double-layered TiO₂ nanotubes can be fabricated with a two-step anodization by changing electrolyte [97-99], adjusting applied voltage [99-104] or varying bath temperature [105]. In particular, adjusting voltage is relatively easy and straightforward.

In this work, two-step anodization by adjusting applied voltage is used to produce double-layered TiO₂ nanotubes. In the first step, the anodization was performed at 30 V (or 15 V) for different durations (1 h, 2 h, or 3 h) to grow the top layer (the sacrificial layer). The second step began 5 min later after completion of the first anodization and was carried out at 15 V (or 30 V) for different durations (3 h, 2 h or 1 h) to grow the bottom layer (the desired layer). The total anodizing duration was 4 h (i.e., 1 h + 3 h or 2 h + 2 h, etc.). For longer bottom tubes, the second anodization duration was prolonged. As reference, single-layered nanotubes at 30 V and 15 V were also grown.

The corresponding tube lengths under different anodization conditions are systematically studied and summarized in Table 5.1. For the same anodization duration of 4 h (Exps. 1~6), double-layered structure are obtained in Exps. 1, 2, and 6, whereas only one layer is observed in Exps. 3~5.

Table 5.1 Lengths of nanotubes grown under different anodizing conditions (Unit: μm)

Exp.	anodizing conditions	total length	top layer	bottom layer
1	30 V 1 h-stop 5 min-15 V 3 h	2.81 ± 0.17	1.55 ± 0.14	1.21 ± 0.05
2	30 V 2 h-stop 5 min-15 V 2 h	4.34 ± 0.13	3.79 ± 0.10	0.47 ± 0.03
3	30 V 3 h-stop 5 min-15 V 1 h	5.08 ± 0.26	5.08 ± 0.26	0
4	15 V 1 h-stop 5 min-30 V 3 h	5.97 ± 0.15	0	5.97 ± 0.15
5	15 V 2 h-stop 5 min-30 V 2 h	4.54 ± 0.25	0	4.54 ± 0.25
6	15 V 3 h-stop 5 min-30 V 1 h	2.85 ± 0.15	0.16 ± 0.05	2.69 ± 0.03
7	30 V 1 h	3.03 ± 0.21	—	—
8	15 V 3 h (in used electrolyte of 7)	1.03 ± 0.05	—	—
9	30 V 1 h-stop 5 min-15 V 6 h	2.17 ± 0.06	0	2.17 ± 0.06
10	15 V 6 h (in used electrolyte of 7)	1.07 ± 0.06	—	—
11	30 V 3 h-stop 5 min-15 V 3 h	4.79 ± 0.30	4.33 ± 0.28	0.56 ± 0.12
12	15 V 3 h-stop 5 min-30 V 10 min	1.30 ± 0.15	0.86 ± 0.07	0.53 ± 0.02

Exps. 1~3 were performed by decreasing voltage from 30 V to 15 V with 5-min interrupting in between two anodizations. Double-layered nanotubes are achieved in Exps. 1 and 2 with large diameter tubes on the top and small diameter tubes at the bottom, as displayed in Figure 5.2(a). In Exp. 3, only one layer is observed. The

interface region between two layers is shown in the inset of Figure 5.2(a). It reveals that the tubes of second layer are grown from the intertube gaps of the first layer, in line with the previous report [100]. During the second anodization, small pores nucleate from intertube gaps of upper tubes for growth of new tubes.

Figure 5.2 Cross-sectional FESEM images of (a) double-layered TiO₂ nanotubes grown at 30 V 1 h- stop 5 min-15 V 3 h; (b) a single layer grown at 30 V for 1 h; (c) a single layer grown at 15 V for 3 h in the electrolyte used once in (b); (d) nanotubes grown at 30 V 1 h- stop 5 min-15 V 6 h; (e) a single layer grown at 15 V for 6 h in the electrolyte used once in (b). Insets are local magnification (a) and corresponding top views (b, c).

To investigate the effect of top layer on the growth of bottom layer, one-step anodizations were carried out individually at 30 V and 15 V. In particular, to compare with double-layered TiO₂ nanotubes grown at 30 V for 1 h and subsequently at 15 V for

3 h (Exp. 1), the 15 V anodizations were performed for 3 h (Exp. 8) in the electrolytes used once at 30 V for 1 h (Exp. 7). The relevant surface and cross-sectional morphologies are shown in Figure 5.2(a~c). The nanotubes grown at 30 V for 1 h by one-step anodization (Exp. 7) are longer than that of the top layer obtained by two-step anodization (Exp. 1). This is because the top layer is gradually dissolved in the subsequent 3 h anodization for bottom nanotube growth, as shown in Figure 5.2(a) where the top nanotubes are bundling together as a consequence of chemical etching. Comparatively only regular porous layer can be observed for the one-step anodization (cf. Figure 5.2(b)). Under the same condition, the tube length by the one-step anodization at 15 V for 3 h (Exp. 8) is shorter (see Figure 5.2(c)) than that of the bottom layer by the two-step anodization (Exp. 1). This can also be attributed to the chemical dissolution during anodization, as displayed in the inset of Figure 5.2(c), in line with the above discussion. In contrast, the bottom layer by two-step anodization is protected by the top layer, hence resulting in longer nanotubes.

In Figure 5.2(d), the nanotubes grown at 30 V for 1 h and then at 15 V for 6 h (Exp.9) are presented. It indicates the tube length of the bottom layer increases with anodizing duration in the presence of the top layer, i.e., ~2.17 μm in Exp. 9 compared with ~1.21 μm in Exp. 1. During growth of the bottom layer, the top layer is progressively dissolved leaving only a few remnant nanotubes, and almost disappeared (see Figure 5.2(d)) after 6 h. This indicates that the top layer facilitates nanotube growth of the bottom layer by sacrificing itself gradually. Comparatively, the unprotected single layer grown at 15 V for 6 h in the electrolyte used once at 30 V for 1 h (cf. Exp. 10) just reaches ~1.07 μm , as shown in Figure 5.2(e). Therefore, the existence of top layer protects the bottom layer from chemical dissolution. Accordingly, thicker top layer

enables longer nanotube growth at the bottom. As the steady-state growth of anodic TiO₂ nanotubes is controlled by diffusion [25, 121], the thicker top layer, on the other hand, will decrease the bottom nanotube growth rate through increasing ionic diffusion length. The bottom layer grown at 15 V for 3 h under a thicker top layer (Exp.11) is much shorter than that also grown at 15 V for 3 h under a relatively thinner top layer (Exp. 1) (i.e. ~0.56 μm vs. ~1.21 μm). This further confirms that longer tube length of top layer slows down the growth rate of bottom layer. Therefore, only one layer is observed in the two-step anodization of Exp. 3. As such, there exists an optimal thickness of the top layer to produce enough long nanotubes at the bottom for application in dye-sensitized solar cells.

5.1.2. Formation of double-layered nanotubes by adjusting voltage from low to high

Exps. 4~6 were carried out by increasing voltage from 15 V to 30 V with the first anodizing duration of 1 h, 2 h, 3 h and the second duration of 3 h, 2 h, 1 h, respectively (see Table 5.1). In Exps. 4 and 5, only the bottom layer grown at 30 V can be observed. A thin top layer (~160 nm) is observed from Exp. 6. So the top layer grown at low voltage (i.e., 15 V) is easily dissolved during the subsequent anodization. Double-layered nanotube arrays grown at 15 V for 3 h (as the first step) and then at 30 V for 10 min (as the second step) (Exp. 12) are shown in Figure 5.3(a), and the top layer with small tube diameter is clearly observed. Significant chemical dissolution takes place at the top layer, giving rise to disordered surface morphology, as illustrated in Figure 5.3(b). It is noteworthy that the bottom layer grew at 30 V for only 10 min. With prolonged duration (1 h) of the bottom layer (Exp. 6), the top layer is very thin, as

shown in Figure 5.3(c). This demonstrates the chemical dissolution of the top layer grown at low voltage is substantial during the growth of bottom layer at high voltage. As such, it is difficult to produce double-layered nanotubes from low voltage to high provided that long anodization duration is adopted at high voltage (see Exps. 4~6 and Figure 5.3(d)). This may be the reason for few reports on double-layered nanotubes obtained from low voltage to high. On the other hand, it also indicates that the top layer grown at low voltage is impossible to be employed as the protector for the nanotubes growth at the bottom.

Figure 5.3 FESEM images of double-layered TiO₂ nanotubes grown at 15 V 3 h-stop 5 min-30 V 10 min: (a) cross-sectional view and (b) top view; Cross-sectional FESEM images of TiO₂ nanotubes prepared by two-step anodization at (c) 15 V 3 h-stop 5 min-30 V 1 h, (d) 15 V 2 h-stop 5 min-30 V 2 h.

5.1.3 Growth of the bottom nanotubes under the protective top layer

Based on the above discussion, a method to grow long nanotubes at low voltage is proposed in Figure 5.4, which employs the top layer grown at high voltage as a protective layer to facilitate bottom tube growth. The anodization sequence is proposed only from high voltage to low voltage, since the top layer grown at low voltage will be dissolved easily in the subsequent anodization. After formation of the top layer (Figure 5.4(a)), small diameter nanotubes will grow beneath by reducing the applied voltage from high to low, as illustrated in Figure 5.4(b). As the second anodization prolongs, the tube length at the bottom progressively increases while the top layer is gradually dissolved (see Figure 5.4(c)). The single-layered nanotubes with high length will be achieved when the top layer is totally dissolved eventually, as shown in Figure 5.4(d).

Figure 5.4 Schematic illustration of two-step anodization to grow long TiO₂ nanotubes of small diameter: (a) top layer is created in the first anodization; (b) bottom layer is grown under the top layer to form double-layered structure; (c) top layer is partially dissolved during growth of the bottom layer; (d) top layer is completely dissolved and bottom layer grows to high length (same as Figure 1.2).

Among the above results (Exps. 1~12 in Table 5.1), the longest tube length achieved at 15 V is only $\sim 2.17 \mu\text{m}$ under the protection of a top layer grown at 30 V for 1 h (Exp. 9). To grow longer nanotubes, thicker top layer and longer anodization duration should be employed. Accordingly, the lengths of nanotubes grown at 15 V under protection of a top layer for different time are plotted in Figure 5.5. The up-triangle and down-triangle symbols indicate the tube lengths obtained under the protective layer grown at 30 V for 1 h and 2 h, respectively. For comparison, the tubes prepared at 15 V in conventional one-step anodization are also plotted by cycle symbols. It shows that nanotubes can grow longer under the protection of a top layer. Thicker top layer can protect the desired bottom layer for longer time, enabling the achievement of longer tubes. Under the protection of thicker layer grown at 30 V for 2 h, the nanotubes reach up to $11.0 \pm 0.5 \mu\text{m}$ after 46-h anodization at 15 V.

Figure 5.5 Lengths of TiO₂ nanotubes prepared at 15 V for different time: without protection (circle symbols) or under protection of top layer grown at 30 V for 1 h (up triangle symbols) and for 2 h (down triangle symbols).

FESEM images of the nanotube arrays grown at 15 V provide more clear information, as displayed in Figure 5.6. The images in the left column present the tubes prepared by one-step anodization and the ones in right column show tubes fabricated under protection of a top layer. Obviously, longer nanotubes are achieved under the protection layer. A thin top layer grown at 30 V for 1 h is completely dissolved after 10 h (Figure 5.6(d)). Thicker top layer grown at 30 V for 2 h can protect within 20 h (Figure 5.6(g)). After 20 h, the bottom tubes achieve a length of $\sim 4.89\ \mu\text{m}$, which is much longer than that grown by one-step anodization ($\sim 2.84\ \mu\text{m}$, in Figure 5.6(f)). Afterwards, the bottom tube growth is equal to the unprotected one-step anodization. When prolonging the anodization to be 46 h, the tube lengths reach up to $\sim 7.6\ \mu\text{m}$ and $\sim 10.9\ \mu\text{m}$ without and with protection, respectively, as shown in Figure 5.6(h, j). While there are some cavities appearing at the top portion of as-fashioned tubes which is attributed to serious chemical etching after long anodization duration.

Figure 5.6 Cross-sectional FESEM images of TiO₂ nanotube arrays grown at 15 V for 6 h (a, b), 10 h (c, d, e), 20 h (f, g), 46 h (h, i) by one-step anodization (a, c, f, h) and two-step anodization under a thinner top layer grown at 30 V for 1 h (b, d) or a thicker top layer created at 30 V for 2 h (e, g, i). The insets are local magnifications or corresponding top morphology.

5.2 Seeding of the second layer nanotubes in double-layered structure

In Section 5.1, two-step anodization was proposed to grow longer nanotubes of small diameter (~ 35 nm) in an attempt to increase the dye loading ability. The longest tubes obtained was only ~ 11 μm after 46-h anodization, which is far from the optimal tube length of 20~30 μm in DSSCs. Hence, the double-layered structure should be optimized for achievement of longer tubes. The presence of an interface between the two adjacent layers (see Figure 5.2(a)) hinders growth of the bottom tubes by slowing down mass transport. It is expected that much longer tubes can be obtained without interfacial blocking, where the lower tubes penetrate through the bottoms of the upper tube arrays. This will provide a direct ion supply for the lower tube growth. Therefore, tailoring the interfacial structure of the double-layered nanotubes is essential in growing long tubes of small diameter.

Two major double-layered structures have been reported so far: branched and stacked structures. In branched nanotubes, one single large tube diverges into several small tubes, as obtained by stepping down voltage, e.g., from 120 V to 40 V [103], from one particular voltage to another one locating at a special region [101] or by a factor of $\frac{1}{\sqrt{n}}$ in the range of 85 V to 28 V [102]. In stacked structure, new tubes grow from the intertube gaps to form a second layer underneath, as attained by decreasing voltage from 20 V to 10 V at a rate of 0.1 V/s or repeated anodization at 20 V after interrupting the power supply for 1 min [100]. Obviously, the newly formed nanotubes can seed either from the tube bottoms of the first layer (branched structure) or from the intertube gaps (stacked structure) under similar conditions, i.e., stepping down voltage from high

to low in the same electrolyte. It also seems that branched structures can be formed easily under high voltage (e.g., above 20 V) [101-103] while stacked structures are usually under low voltage (e.g., below 20 V) [100, 104]. On the other hand, small diameter nanotubes can only be achieved under low voltage, e.g., 15 V in this work. This has raised another challenging issue: how to produce branched structure under low voltage?

In this section, we change the interim treatment conditions under a low voltage scheme (i.e., from 30 V to 15 V) to induce seeding of the second layer nanotubes at intertube gaps, tube bottoms, or random positions in search for the rules that govern the choice of the “seeding sites”. Seeding of new tubes under the existing layer is investigated and interpreted. This work provides a useful insight into tailoring the double-layered configuration for growing long nanotubes of small diameter.

5.2.1 Seeding sites of the second layer nanotubes

Double-layered TiO₂ nanotubes were prepared with a two-step anodization under the same voltage sequence, i.e., at 30 V in the first step and subsequently at 15 V in the second step. Before the second anodization, five different interim treatments were applied separately: Scenario 1, annealing the first layer nanotubes at 450 °C for 3 h; Scenario 2, drying the first layer nanotubes in air for 24 h; Scenario 3, interrupting power supply for 5 min; Scenario 4, decreasing voltage abruptly from 30 V to 15 V; Scenario 5, reducing voltage gradually from 30 V to 15 V at a rate of 1.5 V/min.

Different interim treatments result in different seeding sites of the second layer nanotubes, as detailed below from Scenario 1 to 5.

In Scenario 1, nanotubes of the first layer were annealed at 450 °C for 3 h prior to the second anodization. The as-grown double-layered structure is presented in Figure 5.7(a). The larger tubes on the top belong to the first layer while the smaller tubes at the down-left and top-right corners are from the second layer. In between, a compact interlayer is present, originating from the thermal annealing. This interlayer is around 25 nm, as shown in Figure 5.7(b). Figure 5.7(c) displays the tube bottoms of the first layer and also the compact interlayer. Obviously, the tube bottoms are closed. Some remnant tube tops from the second layer are discernible from the interlayer surface. These demonstrate that small tubes of the second layer initiate randomly beneath the compact interlayer without any preferential seeding sites.

Figure 5.7 FESEM images of double-layered TiO₂ nanotubes grown under Scenario 1 (anodized at 30 V for 1 h, annealed at 450 °C for 3 h, and then anodized at 15 V for 1 h): (a) top view; (b) interfacial region; (c) bottom view of the first layer and the compact interlayer. Inset is local magnification. (d) XRD patterns of the relevant nanotubes. A: anatase; T: titanium.

Figure 5.7(d) shows the relevant XRD patterns of the nanotubes at different stages. Annealing the first layer at 450 °C for 3 h transforms the nanotubes from amorphous into anatase. The phase components keep unchanged after growing the double-layered structure. To examine the phase of the interlayer, the nanotubes of the first layer were removed intentionally (see Figure 5.8). Figure 5.7(d) reveals that the interlayer is of anatase structure, considering the amorphous nature of the as-grown tubes. The anatase interlayer originates from thermal oxidation of the titanium substrate beneath the upper nanotubes upon annealing [122]. Therefore, no preferential seeding sites exist in the presence of thermal annealing, due to formation of a thick anatase interlayer underneath the upper tubes.

Figure 5.8 FESEM top view of the second layer nanotubes covered by the compact interlayer after removing the first layer nanotubes.

In Scenario 2, prior to the second anodization, nanotubes of the first layer were dried in air. The double-layered structure is shown in Figure 5.9(a), with larger tubes stacking on top of the smaller ones. There exists a thin interlayer (~10 nm) consisting of annular

cells, as displayed in Figure 5.9(b). Small tubes grow beneath the interlayer. Figure 5.9(c) reveals that tube bottoms of the first layer are closed. The interlayer is thus developed from the pits left by the closed bottoms, as illustrated in Figure 5.9(d). Each annular cell in the interlayer corresponds to one tube bottom of the first layer. Small holes form randomly on the interlayer which features a lotus-root-shaped structure. The small holes penetrate the interlayer and subsequently deepen into the substrate to form lower tubes, leaving a porous appearance of the interlayer. This discloses that the second layer tubes also seed randomly on a thin interlayer.

Figure 5.9 FESEM images of double-layered TiO₂ nanotubes grown under Scenario 2 (anodized at 30 V for 1 h, followed by drying in air, and then anodized at 15 V for 6 h): (a) cross-sectional view; (b) interfacial region; (c) bottom view of the first layer with the second layer attachment; (d) top view of the second layer with the first layer attachment.

In Scenario 3, power supply was interrupted for 5 min between two anodizations. The stacked double-layered nanotubes are shown in Figure 5.10(a). Similarly, small tubes grow underneath the larger ones. At the interface, small channels are formed on the upper tube walls, which are the remnant of lower tube tops, as revealed in the inset in Figure 5.10(a). Figure 5.10(b) displays the tube bottoms of the first layer, where the tube tops of the second layer initiate from intertube gaps and organize surrounding each tube bottom, as illustrated by dashed circles. This indicates that new tubes of the second layer seed from the intertube gaps of the first layer, in line with the previous report [100]. Additionally, a very thin interlayer exists beneath the tube bottoms of the first layer, as highlighted by the arrow in Figure 5.10(c). Since the lower tubes of small diameter at intertube gaps can hardly occupy the total area of the titanium substrate, new tubes subsequently form to fill up the vacancy under each tube bottom, as depicted by the circles in Figure 5.10(d). These circled regions match well with those shown in Figure 5.10(b). Hence, nanotubes of the second layer seed preferentially at the intertube gaps in the presence of a very thin interlayer.

Figure 5.10 FESEM images of double-layered TiO₂ nanotubes grown under Scenario 3 (anodized at 30 V for 1 h, followed by interrupting power supply for 5 min, and then anodized at 15 V for 3 h): (a) cross-sectional view; (b, c) bottom views of the first layer at different locations; (d) top view of the second layer. The insets are corresponding local magnifications. The dashed circles illustrate the arrangement of new tubes. The arrow in (c) highlights the very thin interlayer beneath tube bottoms of the first layer.

In Scenario 4, applied potential was reduced abruptly from 30 V to 15 V. The seeding sites are also from the intertube gaps, as shown in Figure 5.11(a). The structure is similar to that in Scenario 3, while no obvious interlayer is observed under the current condition, as displayed in Figure 5.11(b). The absence of the interlayer may explain why the two layers tend to separate under the same mechanical force when preparing SEM samples, in contrast to Scenario 3. Besides, the seeding is not as uniform as that in Scenario 3, since some of the intertube gaps are untouched and the new tubes are not

well-organized surrounding the tube bottoms. This suggests that subsequent tube formation is possible to fill up the vacancies under the untouched regions after seeding. Thus, the seeding sites also locate preferentially at the intertube gaps in the absence of a clear interlayer.

Figure 5.11 FESEM images of double-layered TiO₂ nanotubes grown under Scenario 4 (anodized at 30 V for 1 h and then at 15 V for another 1 h with an abrupt voltage reduction): (a) bottom view of the first layer; (b) cross-sectional view. The inset is corresponding local magnification.

In Scenario 5, applied potential was gradually reduced from 30 V to 15 V at a rate of 1.5 V/min. The branched double-layered TiO₂ nanotubes are achieved, as presented in Figure 5.12(a). New tubes of the second layer penetrate through tube bottoms of the first layer. Figure 5.12(b) shows one trunk tube diverging into two or three smaller tubes. This is distinct from the above Scenario 1~4 where tube bottoms of the upper layer are closed. It is noteworthy that new tubes can also form at the intertube gaps while cease eventually due to spacing limitation by neighboring branched tubes, as indicated by arrows in Figure 5.12(a). Consequently, seeding of the second layer takes

place by penetrating through the upper tube bottoms when decreasing the voltage gradually.

Figure 5.12 FESEM images of double-layered TiO₂ nanotubes grown under Scenario 5 (anodized at 30 V for 1 h and then at 15 V for another 1 h with a voltage reduction rate of 1.5 V/min): (a) cross-sectional view; (b) top view of the first layer (large tubes) and second layer (small tubes). The arrows in (a) indicate the seeding of new tubes at intertube gaps.

The above results reveal that the interfacial region between two adjacent nanotube layers is affected by interim treatments significantly. The interlayer in turn plays an essential role in seeding of the second nanotube layer. As the interlayer attenuates and disappears eventually, seeding evolves from random sites to intertube gaps, and finally to upper tube bottoms. The branched structure is thus realized under low voltage (i.e., 15 V) in Scenario 5, which is preferred to grow long nanotubes of small diameter, owing to a direct ion pathway for lower tube growth.

5.2.2 Seeding mechanism of the second layer nanotubes

To look into the seeding mechanism of the second layer, the growth process of titania nanotubes with conventional one-step anodization is briefed below. Growth of anodic

nanotubes is mainly governed by the following two processes [26, 56, 58]: field-assisted oxidation of titanium metal at TiO₂/Ti interface and field-assisted dissolution of titanium oxide at TiO₂/electrolyte interface, as illustrated in Figure 5.13. The relevant chemical reactions during the processes are as follow [56, 83, 121]:

Figure 5.13 Illustration of two active locations, where field-assisted dissolution takes place for seeding under existing TiO₂ nanotubes. A: tube bottoms; B: intertube gaps. The thin oxide layer between the tubes and substrate is fluoride-rich layer. The ripples on tube walls are visible from Figure 5.12 (a) and also other cross-sectional FESEM images.

Formation of TiO₂ nanotubes mainly goes through three stages, as shown in the inset of Figure 5.14(a). In the initial stage (Stage I), a compact titanium oxide layer is formed by field-assisted oxidation via Reaction 5.1, resulting in an abrupt decrease of current. Subsequently (Stage II), the compact oxide is etched by dominant field-

assisted chemical dissolution through Reaction 5.2 to form dissoluble TiF_6^{2-} complex, in turn leading to occurrence of small pores. At the pore bottoms, electric field is concentrated due to smaller thickness. The field-assisted oxidation and dissolution accelerate each other at the bottoms [94], and thus the current density is increased to a local maximum where the pore density reaches saturation. After the competitive selection process of the initial pores, steady growth of nanotubes is established (Stage III). Afterwards, the current density gradually drops with pore depth increase. In steady state, the oxidation and dissolution processes reach equilibrium and thereby the barrier layer thickness (see Figure 5.13) at tube bottoms keeps unchanged. The barrier layer thickness is closely related to the applied potential. In general, the larger the potential is, the thicker the barrier layer will be [94, 95]. Accordingly, in this study the barrier layer grown at 30 V is much thicker than that at 15 V, yielding a larger critical thickness to maintain steady-state tube growth at 30 V.

Figure 5.14 Current transients during growth of double-layered TiO₂ nanotubes in a two-step anodization with different interim treatments: (a) first anodization at 30 V for 1 h and (b) second anodization at 15 V for 1 h in which direct growth of single layered nanotubes is added for comparison. The inset is current transition in the first 600 s at 30 V, which has been divided into three stages.

The as-formed oxide is titanium oxide containing fluoride, as seen from XPS data in Figure 5.15. The content of incorporated fluorine in nanotubes is ~5 wt.% and can be removed by thermal annealing [95, 123]. Since the movement speed of F⁻ ions in the growing oxide is twice the migration of O²⁻ ions under the electric field, fluoride is accumulated in the TiO₂/Ti interface to form a thin fluoride-rich TiO₂ layer [95, 124], as indicated in Figure 5.13. The intertube gap formation is proposed to originate from chemical dissolution of the thin fluoride-rich layer between tubes [86, 124] or mechanical force from the volume expansion from metal to oxide [94]. The oxide at intertube gap (Location B in Figure 5.13) has a smaller thickness, higher fluoride content, in comparison to that at tube bottom (Location A in Figure 5.13) [124, 125].

Figure 5.15 XPS spectra of titanium oxide layer after initial anodization at 30 V for 1 min: wide scan (a) and narrow scans of Ti 2p (b); O 1s(c); F 1s(d).

When decreasing voltage from 30 V to 15 V suddenly (Scenarios 1~4), the electric field is nearly halved as it is determined by potential drop across the barrier layer [26, 27]. As a result, the field-assisted oxidation is slowed down or may be even terminated, since the electric field (at 15 V) is too weak to drive the ions passing through the thick barrier layer (formed at 30 V). In this case, nanotubes cannot grow further until the barrier layer thickness is reduced to a critical value by field-assisted dissolution process to enable ion transport at 15 V.

Therefore, seeding of new tubes occurs at the sites where the oxide layer is dissolved faster to the critical thickness maintaining steady-state tube growth at 15 V. There are

two different active locations suffering the dissolution: tube bottoms (Location A) and intertube gaps (Location B), as illustrated in Figure 5.13. These two locations compete with each other and new pores form preferentially at the one where the oxide layer is etched faster to the critical thickness.

The current transitions provide more insight into tube seeding in the second anodization, as presented Figure 5.14(b). In comparison to conventional one-step anodization at 15 V, the current density is much smaller since ions have to diffuse in the upper tubes and transport through the barrier layer. The tube seeding process (Stage II) requires much longer time in view of the upper layer. During this period, chemical dissolution at the electrochemical active locations competes with each other for preferential pore nucleation. It will be discussed in detailed below.

For clarification, five interim treatments, i.e., annealing or drying the nanotubes, interrupting the power supply, reducing the voltage abruptly or gradually, are denoted as T_A , T_D , T_I , T_{AR} , and T_{GR} below, respectively.

T_A converts the nanotubes from amorphous to anatase (see Figure 5.7(d)) and meanwhile produces a crystallized compact oxide layer underneath (see Figure 5.7(b)). The crystallized titanium oxide has a good conductivity and small resistance in comparison to amorphous oxide [126]. Hence, the electric field is large enough to drive ions through the thick interlayer either from upper tube bottoms or intertube gaps, resulting in a relatively high current density, in contrast to the other interim treatments in Figure 5.14(b). The crystallized compact interlayer is difficult to be dissolved. Hence, the chemical etching rates at tube bottoms (Location A) and intertube gaps (Location B) are both extremely slow. In this case, no preferential seeding sites are

present. As a result, new tubes seed under the thick crystalline interlayer randomly, equivalent to a regrowth process, as illustrated in Schematic 1 of Table 5.2.

T_D affects the surface state of as-grown amorphous titanium oxide. The oxide is enriched in Ti cations and deficient in oxygen anions, forming TiO_{2-x} oxide which has many oxygen vacancies [125, 127]. When drying the first layer in air for 24 h, oxygen molecules are adsorbed on the surface of TiO_{2-x} oxides and fill the oxygen vacancies [127-129]. The adsorbed oxygen promotes the initial oxidation of titanium by providing direct oxygen source rather than decomposition of H₂O in the electrolyte, as evident from the highest current density at the very moment of the second anodization in Figure 5.14(b). As the original oxide layer at intertube gaps is much thinner than that at tube bottoms (see Figure 5.13), a relatively thicker oxide is produced underneath the Location B upon the second anodization, as displayed in Figure 5.9 (b, d). In this case, a thin interlayer with a lotus-root-shaped structure is developed under tube bottoms (see Figure 5.9(b, d)). Consequently, new tubes seed randomly underneath the thin interlayer, which is still a regrowth process, as presented in Schematic 2 of Table 5.2. This is in consistence with the previous report regarding two-step anodization with peeling off the first layer in air [130].

Table 5.2 Interfacial structures and seeding sites of the second layer nanotubes under different interim treatments

Treatments	Schematics	Interfacial structures	Seeding sites
Scenario 1: Annealing the first layer		Thick interlayer	Random
Scenario 2: Drying the first layer		Thin interlayer	Random
Scenario 3: Interrupting power supply		Very thin interlayer	Intertube gaps
Scenario 4: Reducing voltage abruptly		No interlayer but interface	Intertube gaps
Scenario 5: Reducing voltage gradually		Branched structure	Upper tube bottoms

T_f gradually attenuates the ion concentration gradient that established at 30 V. During the period (i.e., 5 min) without electric field, the first layer nanotubes suffer from

chemical attacking by F⁻ and H⁺ ions produced at 30 V, leading to thinning of the oxide [131]. Hence, in the very moment when 15 V is applied, current density is high and then abruptly decreases to a local-minimal value, as displayed in blue line in Figure 5.14(b). This produces a very thin interlayer as revealed in Figure 5.10(c). Together with this thin interlayer, the oxide layer is still much thinner at Location B, as illustrated in Figure 5.13. As a result, seeding of the new pores occurs preferentially at intertube gaps (see Figure 5.10), in line with the previous report in which multi-layered zirconium titanate nanotubes were prepared by repeated anodization with 1 min interrupting intervals in between [94, 100]. The double-layered structure is presented in Schematic 3 of Table 5.2.

T_{AR} makes the ion concentration gradient less steep in a very short time when abruptly reducing the voltage from 30 V to 15 V [103]. In the initial stage, the oxidation is almost ceased under the low electric field, and hence no obvious interlayer is formed. The seeding of tubes in the second anodization is similar to that under TI, as illustrated in Schematic 4 of Table 5.2. New tubes preferentially seed at intertube gaps and subsequently beneath the tube bottom. The barrier layer at tube bottom (Location A) is too thick to be etched to critical thickness during the pore nucleation, leading to the closed-end.

T_{GR} gradually reduces the potential at a very low rate (i.e., 1.5 V/min in Scenario 5) so that ion concentration keeps almost unchanged during the early stage. Therefore, the chemical dissolution rate at tube bottoms (Location A) is approximately as high as that in the first anodization. The barrier layer at tube bottoms is thus thinned faster to a critical thickness, in view of the larger ionic flux as compared to the intertube gaps

(Location B). New tubes grow steadily at tube bottoms to form branched structure, as shown in Schematic 5 of Table 5.2.

Therefore, seeding of new tubes originates from the sites where oxide layer is dissolved faster to a critical thickness. This depends on dissolution ability of the existing oxide layer, electric field, ion concentration profile, etc. In a two-step anodization by stepping down voltage, the intrinsic factor affecting the structure of double-layered nanotubes is the chemical dissolution rate at respective electrochemical active locations.

5.2.3 Growth of the second layer nanotubes based on branched structure

As discussed above, stacked and branched double-layered nanotubes can be obtained by interim treatment. The protective effect of the top layer in Section 5.1 is investigated based on the stacked structure, where the second layer nanotubes seed from intertube gaps of the upper layer (see Figure 5.2). Branched structure, where the lower tubes penetrate through tube bottoms of the upper layer, is expected to facilitate ion diffusion for bottom tube growth. Hence, growth of the second layer nanotubes based on the branched structure is studied herein.

Under a top layer grown at 30 V for 1 h, the bottom tubes grow to be ~2.1 μm at 15 V after 6 h based on the stacked structure, as shown in Figure 5.16(a). In contrast, in branched double-layered structure, length of the bottom nanotubes is a little longer, i.e., ~2.4 μm , as displayed in Figure 5.16(b). However, the top layer has been dissolved mostly after 6 h. To achieve longer bottom tubes, the anodization duration should be prolonged and thus a thicker top layer is required for longer protective time.

Figure 5.16 FESEM cross-sectional views of TiO₂ nanotubes grown in a two-step anodization at 30 V for 1 h and then 15 V for 6 h based on different double-layered structures: (a) stacked structure; (b) branched structure. Insets are the corresponding schematics of double-layered structures.

Under a thicker top layer grown at 30 V for 2 h, stacked double-layered structure is achieved by interrupting power supply or reducing voltage abruptly, as displayed in Figure 5.17(a, b). Branched structure is formed by gradual voltage reduction. A reduction rate of 1.5 V/min from 30 V to 15 V leads to new tubes seeding at both intertube gaps and upper tube bottoms, as shown in Figure 5.17(c, d). Therefore, with thicker first layer, a much smaller decrease rate is required to keep relatively higher chemical dissolution at tube bottom rather than intertube gaps. Finally, a stepwise reduction rate of 1.5 V/min from 30 V to 22.5 V and then 0.5 V/min from 22.5 V to 15 V, results in the preferential seeding at tube bottom to form branching structure, as presented in Figure 5.17(e, f).

Figure 5.17 FESEM images of double-layered TiO₂ nanotubes grown at 30 V for 2 h and then at 15 V for 2h with different interim treatments: (a) interrupting power supply for 5 min between two anodizations; (b) reducing voltage abruptly or (c, d) at 1.5 V/min and (e, f) 1.5 V/min from 30 V to 22.5 V and then 0.5 V/min from 22.5 V to 15 V. (a, b, d) is bottom view of the first layer; (c, e) are cross-section views; (f) is top view of the second layer. The insets are corresponding local magnifications.

With a thicker top layer created at 30 V for 2 h, the bottom nanotubes grown at 15 V for 20 h are presented in Figure 5.18. In the stacked structure, the second layer tubes reach to $\sim 4.0 \mu\text{m}$ meanwhile the top layer is dissolved completely, as displayed in

Figure 5.18(a). In contrast, based on the branched structure, the nanotubes of the second layer obtain a higher length of $\sim 6.1\ \mu\text{m}$, as shown in Figure 5.18(b). The longer tubes in branched structure are ascribed to the direct ion diffusion paths for bottom tube growth. This confirms that branched double-layered structure is favored to grow long nanotubes of small diameters.

Figure 5.18 FESEM cross-sectional views of TiO₂ nanotubes grown in a two-step anodization at 30 V for 2 h and then 15 V for 20 h based on different double-layered structures: (a) stacked structure; (b) branched structure. Insets are the corresponding schematics of double-layered structures.

5.3 Long nanotubes of small diameter achieved by an optimized two-step anodization for application in DSSCs

In Section 5.1, it is revealed that two-step anodization is capable of growing longer TiO₂ nanotubes of small diameter in view of the protective effect of the top layer. In Section 5.2, branched double-layered structure is achieved by tailoring interim treatment for providing direct ion diffusion paths, enabling faster tube growth at the bottom. However, the lengths of small diameter tubes are still far from the optimal

value (i.e., 20~30 μm) in DSSCs. Therefore, two-step anodization is optimized to grow enough long nanotubes of small diameter for efficient dye-sensitized solar cells.

5.3.1 Long nanotubes of small diameter achieved by an optimized two-step anodization

The scheme of an optimized two-step anodization is illustrated in Figure 5.19. A much high voltage is used to create a protective top layer with thick tube walls for high chemical resistance and large tube diameters for ion diffusion. Subsequently the voltage is reduced from high to low at an appropriate rate to form branched structure. Thereafter, magnetic stirring is applied to further promote tube growth at low voltage. After enough long time, the protective top layer is dissolved completely and the small tubes are expected to grow to very high length.

Figure 5.19 Fabrication of long TiO₂ nanotubes of small diameter by an optimized two-step anodization.

In the previous results, 30 V is employed to grow the protective layer. However, the top layer grown at 30 V for 2 h ($\sim 4\ \mu\text{m}$) dissolved completely within 20 h (see Figure 5.18). The chemical resistance of nanotubes is closely related with tube wall thickness, which is in turn affected by applied voltage. A higher voltage can produce nanotubes with thicker walls and larger diameters, which are favored for the protective layer. Therefore, in an optimized two-step anodization, a high voltage of 50 V is adopted to grow the top layer and 15 V is still used to grow desired small diameter tubes at the bottom.

To achieve branched double-layered structure, voltage reduction rate is essential, as discussed in Section 5.2. When reducing voltage from 30 V to 15 V, branched structure is obtained by a small voltage reduction rate of 1.5 V/min. It is reported that it takes shorter time to reduce the barrier layer to critical thickness at higher voltage scheme and vice versa [102]. Therefore, the two-step anodization from 50 V to 25 V at different decreasing rates is investigated firstly.

When decreasing voltage from 50 V to 25 V at a small rate of 1 V/min, branching occurs at different levels on the tubes, as displayed in Figure 5.20(a). A large tube diverges into two smaller ones (see Figure 5.20(b)). In particular, the branching tubes exhibit an oval shape, as highlighted by dashed lines in Figure 5.20(b). Furthermore, a faster voltage reduction rate of 5 V/min result in branching at the same level, as shown in Figure 5.20(c). Figure 5.20(d) shows that two or three smaller tubes penetrate through the larger tube bottoms. When abruptly reducing voltage from 50 V to 25 V, branched double-layered structure is still obtained, as shown in Figure 5.20(e, f), while the tube walls are much thin at the interface of the adjacent two layers.

Figure 5.20 FESEM images of branched TiO₂ nanotubes grown at 50 V for 15 min and then at 25 V for 1 h with different voltage reduction rates: (a, b) 1 V/min, (c, d) 5 V/min and (e, f) abrupt decrease. (a, c, e) are cross-sectional views and (b, d, f) are top views of the branching interfaces. Insets are corresponding local magnifications.

The above results reveal that at high voltage scheme (i.e., from 50 V to 25 V), a much fast voltage decrease rate can leads to the formation of branched structure. It can be

attributed to the high electric field which keeps the relative higher chemical dissolution rate at tube bottoms than intertube gaps.

Consequently, in the two-step anodization from 50 V to 15 V, the voltage reduction rate is stepwise controlled, by using a faster reduction rate from 50 V to 25 V and a smaller rate from 25 V to 15 V. From 50 V to 25 V, the voltage reduction rate is set as 5 V/min, since it leads to branching at same level and produce thick tube walls at interface of the two layers.

In the two-step anodizations by decreasing voltage from 50 V to 25 V at 5 V/min and then from 25 V to 15 V at 2 V/min, 1 V/min and 0.5 V/min, respectively, the as-formed double-layered structures are presented in Figure 5.21. In the case of 2 V/min, seeding of the second layer nanotubes at both upper tube bottom and intertube gaps, as shown in Figure 5.21(a, b). A smaller reduction rate of 1 V/min gives rise to tube branching while a few new tubes can still grow from intertube gaps, leading to the irregular nanotube alignment, as displayed in Figure 5.21(c, d). Eventually, a much slow rate of 0.5 V/min result in the formation of branched nanotubes, in which large tubes diverge into several small tubes at the same level, as shown in Figure 5.21 (e, f).

Figure 5.21 FESEM images of double-layered TiO₂ nanotube arrays grown at 50 V for 15 min and then at 15 V for 1 h with voltage reduction rate of 5 V/min from 50 V to 25 V and then at (a, b) 2 V/min, (c, d) 1 V/min and (e, f) 0.5 V/min from 25 V to 15 V. (a, c~f) are cross-sectional views and (b) is corresponding bottom views.

Subsequently, the branched double-layered structure formed by decreasing voltage from 50 V to 15 V is used to grow nanotubes of small diameter, as presented in Figure 5.22 (a). The top tubes grown at 50 V for 15 min have a length of $\sim 2.5 \mu\text{m}$. The tubes wall thickness is $\sim 27 \text{ nm}$ and the outer diameter is $\sim 125 \text{ nm}$ (see Figure 5.22(b)). At the interface, large upper tubes branch into several small tubes, as displayed in Figure

5.22(c). The small tubes at the bottom will grow longer with prolonged anodization time. To further increase tube growth at 15 V, magnetic stirring with a speed of 250 rpm is applied. After 45-h anodization, the top layer is completely dissolved and the bottom tubes reach up to $\sim 31\ \mu\text{m}$, as shown in Figure 5.22(d). To our best knowledge, this is the longest nanotubes achieved at 15 V at room temperature. Therefore, the optimized two-step anodization is effective to grow small diameter nanotubes to enough length. Through tailoring the thickness of the protective layer and the duration of the second anodization, length of small diameter tubes can be controlled.

Figure 5.22 Cross-sectional FESEM images of double-layered TiO₂ nanotubes grown at 50 V for 15 min and then at 15 V for 1 h with voltage reduction rate of 5 V/min from 50 V to 25 V and then 0.5 V/min from 25 V to 15 V (a), the magnified images of the top nanotubes (b) and interface structure (c). (d) is long nanotubes achieved by 45-h anodization with stirring under the top layer in (a).

5.3.2 Solar cell performances based on long nanotubes of small diameter

Since long TiO₂ nanotubes of small diameter have been achieved by the optimized two-step anodization, their performances in DSSC devices are studied in this section. As reported by extensive literatures, solar cell efficiency increases with tube length and it is found that the optimal tube length is $\sim 25\ \mu\text{m}$ for achieving highest solar cell efficiency [22, 61]. Therefore, in this study, 23- μm nanotubes of small diameter are prepared for highly efficient DSSCs. And the small pore diameter is $\sim 35\ \text{nm}$, as presented in Figure 5.23(a). They were prepared by the two-step anodization at 50 V for 10 min and then at 15 V for 30 h under stirring. For comparison purpose, 23- μm , large tubes with a pore diameter of $\sim 95\ \text{nm}$ was also grown by anodization at 50 V for 4 h, as shown in Figure 5.23(b).

Figure 5.23 Cross-sectional views of small diameter nanotubes (a) and large diameter nanotubes (b) with the identical length of $\sim 23\ \mu\text{m}$. Small tubes is grown in a two-step anodization at 50 V 10 min-15 V 30 h with stirring and large tubes were grown at 50 V for 4 h. Insets are corresponding magnified top morphologies.

The as-anodized small and large tubes are amorphous, as revealed from the XRD patterns in Figure 5.24. For use in DSSC devices, they were subjected to thermal

annealing at 450 °C for 3 h. All the amorphous nanotubes are converted into anatase upon annealing treatment, as evident in Figure 5.24.

Figure 5.24 XRD patterns of as-anodized and annealed TiO₂ nanotubes of small and large diameter. A and T represent anatase and titanium peaks, respectively.

The two kinds of TiO₂ nanotubes are assembled in DSSCs and the photocurrent-voltage characteristics are presented in Figure 5.25. Obviously, with the same tube length of 23 μm , small diameter nanotubes yield much higher photocurrents than the large tubes, i.e., 9.04 vs. 5.96 mA/cm² for pristine tubes and 12.16 vs. 9.13 mA/cm² for TiCl₄ treated tubes. The corresponding photovoltaic parameters are summarized in Table 5.3. From the small tubes, the higher photocurrents are attributed to larger surface area for dye attachment, as displayed in Table 5.3. This leads to efficient light harvesting and thus higher conversion efficiency. After TiCl₄ treatment, a much high efficiency of 5.02% is attained for 35-nm tubes. Hence, long nanotubes of small diameter are effective to produce highly efficient DSSCs.

Figure 5.25 Photocurrent-voltage characteristics of DSSCs based on pristine and TiCl₄ treated TiO₂ nanotubes with different tube diameters and the same tube length (~23 μm).

Table 5.3 Photovoltaic performance parameters of DSSC devices and dye loading amount

Samples	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	Dye loading
					(10 ⁻⁹ mol/cm ²)
Pristine large tubes	5.96	0.70	0.62	2.59	67.3
Pristine small tubes	9.04	0.70	0.55	3.48	99.9
TiCl ₄ treated large tubes	9.13	0.75	0.54	3.70	105.6
TiCl ₄ treated small tubes	12.16	0.75	0.55	5.02	169.2

5.4 Summary

In this chapter, double-layered TiO₂ nanotubes were fabricated with two-step anodization by adjusting voltage. Subsequently, two-step anodization by decreasing voltage from high to low was adopted to grow long nanotubes of small diameter. The

top layer could protect the desired bottom tubes of small diameter from chemical dissolution, enabling longer tubes.

In the double-layered nanotubes, seeding sites of the bottom nanotubes were tailored to be at upper tube bottoms, intertube gaps or random position on an interlayer by varying interim treatments. The results revealed that new tubes formed preferentially at the location where the oxide layer was etched faster to critical thickness for pore nucleation. Branched configuration was the preferred double-layered structure capable of producing long TiO₂ nanotubes of small diameter, due to the direct ion diffusion path.

Finally, the two-step anodization was optimized, i.e., creating a more protective layer by adopting a much higher voltage, tailoring the branching interface by controlling voltage reduction rate and increasing bottom tube growth by applying magnetic stirring. Ultra-long, small diameter TiO₂ nanotubes were thus achieved, that is, with tube length of 31 μm and pore diameter of ~ 35 nm. This overcame tube length limitation challenge for small diameter tubes in conventional one-step anodization. The small diameter tubes with tube length of 23 μm yielded a high conversion efficiency of 5.02% in dye-sensitized solar cells.

Chapter 6 Conclusions and Recommendations

In this project, the surface area of TiO_2 nanotubes has been enlarged for efficient dye-sensitized solar cells, including synthesis of nanotube/nanoparticle composite by hydrothermal treatment for application in DSSCs (Chapter 4) and growth of long nanotubes of small diameter by two-step anodization for application in DSSCs (Chapter 5). In this chapter, the conclusions based on these results are presented and some interesting work is recommended for further investigation.

6.1 Conclusions

Based on the results in Chapter 4 and Chapter 5, the corresponding conclusions were drawn as below.

(1) Hydrothermal treatment of as-anodized TiO_2 nanotubes in water was facile and effective to create nanoparticles on tube walls. The tube morphology and structure evolved with hydrothermal duration. For tubes of $6.5\ \mu\text{m}$, within 1 hour titania nanoparticles formed on both inner and outer tube walls while keeping the integrity of the tubes. At prolonged time of exceeding 1 hour, the nanotubes were entirely converted into nanoparticles. Meanwhile, the tubes were gradually converted from amorphous into anatase with hydrothermal treatment.

(2) With the same tube length (i.e., $6.5\ \mu\text{m}$) but different durations, nanotubes under hydrothermal treatment for 45 min yielded the best photovoltaic performance, due to combined advantages of high surface area from nanoparticles and vectorial electron transport from nanotubes.

(3) For tubes of different lengths under the same treatment duration (i.e., 45 min), the efficiency of solar cells increased with tube length while kept nearly constant over 16.5 μm . This was owing to the accelerated particle formation in longer tubes, which filled the lower parts of the tubes and hence reduced the available surface area for dye attachment. Accordingly, further efficiency enhancement of 3.54% was achieved with nanotubes of 16.5 μm by shortening the treatment duration.

(4) A two-step anodization by adjusting voltage from high to low was utilized to grow long TiO_2 nanotubes of small diameter. In the double-layered structure, the top layer served as a sacrificial layer to protect the desired bottom tubes from chemical dissolution.

(5) In double-layered TiO_2 nanotube arrays, seeding sites of the second layer nanotubes were tailored to initiate from intertube gaps, tube bottoms, and random positions of the upper tubes by controlling interim treatments. The branched feature was the preferred double-layered structure capable of producing high-aspect-ratio TiO_2 nanotubes of small diameters.

(6) An optimized two-step anodization was thus developed to achieve ultra-long, small diameter TiO_2 nanotubes, that is, with tube length of 31 μm and pore diameter of ~ 35 nm. This overcame tube length limitation for small diameter tubes by one-step anodization. Compared to large diameter tubes, the small diameter tubes exhibited a remarkably higher efficiency of 5.02% for tube length of 23 μm after TiCl_4 treatment.

6.2 Recommendations

In this project, much effort has been made to develop two approaches to enlarge tube surface area for higher dye loading amount and thus enhance conversion efficiency of DSSCs. Based on the current results, there are some interesting work worthy to be further studied, as detailed below.

(1) Electron transport and recombination in the nanotube/nanoparticle composite electrode and long nanotubes of small diameter

Electron transport and recombination are also important issues to understand the DSSC system and their photovoltaic performances. Electron transport properties can be measured by IMPV (intensity-modulated photocurrent spectroscopy). And electron recombination can be examined by IMVS (intensity-modulated photovoltage spectroscopy).

(2) Front-side illuminated DSSCs based on the nanotube/nanoparticle composite electrode and long nanotubes of small diameter

As reviewed in Chapter 2, there are two types of configurations for nanotubes based DSSC devices: front-side and back-side illumination. Our current projects employed the back-side illuminated DSSC architecture. The nanotubes on opaque titanium substrate are assembled directly in DSSC devices, which require light passing through the counter electrode. Backside illumination has more light energy loss due to light reflection by counter electrode and light absorption by electrolyte.

To further increase the solar cell efficiency, the nanotube/nanoparticle composite and the long nanotubes of small diameter should be separated from the opaque titanium

substrate by appropriate methods. Then the free-standing membranes should be carefully transferred to transparent FTO glass and adhered to FTO by a thin film of nanoparticles paste for front-side illuminated DSSC assembly. Based on the front-side illumination, the conversion efficiency of DSSCs will be further improved.

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