Efficient light harvesting with double-sided anodic titania nanotube arrays in dye-sensitized solar cells

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**EFFICIENT LIGHT HARVESTING WITH DOUBLE-SIDED
ANODIC TITANIA NANOTUBE ARRAYS IN DYE-
SENSITIZED SOLAR CELLS**

**SUN LIDONG
SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING
2011**

EFFICIENT LIGHT HARVESTING WITH DOUBLE-SIDED ANODIC TITANIA NANOTUBE ARRAYS IN DYE- SENSITIZED SOLAR CELLS

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Abstract

In the past decade, anodic titania nanotube arrays have been vigorously investigated in dye-sensitized solar cells so as to reduce electron scattering and energy loss that present in conventional titania nanoparticle photoanodes. However, the photovoltaic efficiency of the cells based on the nanotubes is not as efficient as that on the nanoparticles. This is due to the low photocurrent induced by the low dye loading amount of the nanotube photoanodes. As such, in this project a novel parallel configuration of dye-sensitized solar cells is proposed on the basis of double-sided nanotubes.

To achieve the parallel structure, anodic nanotube growth is studied first with reference to electric field which is believed to be an essential factor influencing the tube geometry, although the geometry has been reported to be affected by a number of factors (e.g., applied potential, working distance, water content, temperature, and so forth). Electric field originating from the potential drop over the oxide layer results in linear increase in pore diameter while exponential increment in growth rate. Electric field emanating from the potential drop in the organic electrolyte also contributes to the growth rate by promoting the ionic flux in the electrolyte. The effect of the field can be explained by an ion flux model.

More detailed investigation on the role of electric field in the electrolyte is carried out by double-sided nanotube growth. Nanotube arrays are grown simultaneously on both sides of a titanium foil using a typical two-electrode method. Tube length at the frontside is longer than that at the backside, as a consequence of higher ionic flux induced by the electric field at the frontside. The tube length is thus tailored to be comparable at both sides through adjusting the field.

Transition from nanotubes to nanowires is investigated subsequently in order to obtain clear tube surface suitable for application in dye-sensitized solar cells. The results demonstrate that the transition requires a large number of H^+ ions to reduce the passivated area of tube walls, therefore can be observed only under an intermediate chemical dissolution environment. Ultrasonic cleaning is found effective in clearing away the nanowires on top of the nanotubes due to formation of quasi-nanosprings.

The parallel configuration of dye-sensitized solar cells is achieved using the double-sided nanotubes as the photoanodes. The photovoltaic performance of the cells exhibits an average 70% increment in photocurrent and 30% enhancement in conversion efficiency, as a consequence of highly increased surface area and considerably reduced series resistance. A theoretical calculation and relevant fitting results indicate that a tube length of $\sim 30\text{ }\mu\text{m}$ is optimal for the nanotubes used in the current work. This parallel structure is effective in promoting the light harvesting of dye-sensitized solar cells based on anodic nanotube arrays.

List of Publications

Journal Papers:

1. L. Sun, S. Zhang, X. Wang, X. W. Sun, D. Y. Ong, X. Wang, D. Zhao, Transition from anodic titania nanotubes to nanowires: arising from nanotube growth to application in dye-sensitized solar cells, *ChemPhysChem* **2011**, DOI: 10.1002/cphc.201100450 (in press).
2. L. Sun, S. Zhang, X. Wang, X. W. Sun, D. Y. Ong, A. K. K. Kyaw, A novel parallel configuration of dye-sensitized solar cells with double-sided anodic nanotube arrays, *Energy Environ. Sci.* **2011**, *4*, 2240-2248.
 - Highlighted in *COSMOS (Proceedings of the Singapore National Academy of Science)* **2011**, *7*, 8-9.
3. L. Sun, S. Zhang, X. W. Sun, X. Wang, Y. Cai, Double-sided anodic titania nanotube arrays: a lopsided growth process, *Langmuir* **2010**, *26*, 18424-18429.
4. L. Sun, S. Zhang, X. Sun, X. He, Effect of the geometry of the anodized titania nanotube array on the performance of dye-sensitized solar cells, *J. Nanosci. Nanotechnol.* **2010**, *10*, 4551-4561.
5. L. Sun, S. Zhang, X. W. Sun, X. He, Effect of electric field strength on the length of anodized nanotube arrays, *J. Electroanal. Chem.* **2009**, *637*, 6-12.
6. X. Wang, S. Zhang, L. Sun, A two-step anodization to grow high-aspect-ratio TiO₂ nanotubes, *Thin Solid Films* **2011**, *519*, 4694-4698.

Book Chapter:

L. Sun, S. Zhang, X. W. Sun, X. He, Anodized titania nanotube array and its application in dye-sensitized solar cells. In *Handbook of Nanostructured Thin Films and Coatings*, Vol. 3 (Ed: S. Zhang), Taylor & Francis, New York **2010**, Ch. 2, 57-108.

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List of Symbols and Abbreviations

a	Lattice Constant
$a(\lambda)$	Energy Absorption at Wavelength λ
c	Concentration
d	Thickness
$f_{\min}$	Peak Frequency
h	Height of a Column
i	Current Density
i_0	Reverse Saturation Current
k_{inj}	Fraction of Injected Electrons
k_{deact}	Fraction of Deactivated Electrons
l	Electrode Distance
m	Layers of Dye Molecules beyond Critical Tube Length
n	Total Layers of Dye Molecules
p	Porosity of Nanotube Surface Layer
q	Electron Elementary Charge
r	Radius of a Nanoparticle
$r(\lambda)$	Energy Loss of Incident Light at Wavelength λ
u	Ionic Mobility
u_i	Mobility of Species i
w	Width of Space Charge Layer
x	Number of Nanoparticles
y	Number of Nanotubes

A	Surface Area, Active Area
A_d	Active Area at the Side via Direct Illumination
A_r	Active Area at the Side via Mirror Reflection
A_{tot}	Total Active Area
D	Pore Diameter of Nanotubes, Diffusion Coefficient
$\mathbf{D}_i$	Diffusion Coefficient of Species i
D_n	Electron Diffusion Coefficient
E	Electric Field Strength
E_{abs}	Total Energy Absorption
E_d	Incident Irradiance by Direct Illumination
E_F	Fermi Energy Level
E_{loss}	Total Energy Loss
E_r	Incident Irradiance by Mirror Reflection
E_{tot}	Total Incident Irradiance
F	Faraday Constant
FF	Fill Factor
$F(\lambda)$	Incident Photon Flux Density at Wavelength λ
I	Current Flow
I_p	Photocurrent of a Parallel Cell
I_s	Photocurrent of a Single Cell
I_{sc}	Short-Circuit Photocurrent
$IPCE(\lambda)$	Incident Photon to Current Efficiency at Wavelength λ
J_b	Ionic Flux at Frontside

J_f	Ionic Flux at Backside
$\mathbf{J}_i$	Ionic Flux of Species i
J_{mpp}	Photocurrent Density at Maximum Power Point
J_{sc}	Short-Circuit Photocurrent Density
$J_{\text{sc-d}}$	Photocurrent Density from a Cell under Direct Illumination
$J_{\text{sc-r}}$	Photocurrent Density from a Cell under Mirror Reflection
L	Nanotube Length
L_n	Electron Diffusion Length
L_{NP}	Optimal Film Thickness of Nanoparticles
L_{NT}	Optimal Length of Nanotubes
L_0	Critical Tube Length
$LHE(\lambda)$	Light-Harvesting Efficiency at Wavelength λ
N	Charge Carrier Concentration
P_{in}	Incident Photon Flux Density, Power Input
P_{max}	Maximum Power Output
P_{out}	Power Output
R	Gas Constant, Radius of a Nanotube, Resistance
R_h	Internal Ohmic Resistance
R_p	Charge Transfer Impedance
R_{Parallel}	Impedance of a Parallel Cell
R_r	Recombination Impedance
R_s	Series Resistance
$R_{\text{Single-B}}$	Impedance of a Single-B Cell

$R_{\text{Single-F}}$	Impedance of a Single-F Cell
T	Kelvin Temperature, Tube Wall Thickness
U	Electrode Potential, Potential Drop
U_{fb}	Flat-Band Potential
V	Volume
V_{B}	Amount of Band Bending
V_{mpp}	Photovoltage at Maximum Power Point
V_{oc}	Open-Circuit Photovoltage
Z_{w1}	Diffusion Impedance
Z_{w2}	Warburg Impedance
α	Degradation Factor, Portion of Energy Absorption
ε	Dielectric Constant
ε_0	Permittivity of Free Space
η	Overall Conversion Efficiency
η_{cc}	Charge Collecting Efficiency
η_{NP}	Packing Factor of Nanoparticles
η_{NT}	Packing Factor of Nanotubes
η_{p}	Efficiency of a Parallel Cell
η_{s}	Efficiency of a Single Cell
κ	Conductivity
λ	Wavelength
σ	Optical Absorption Cross Section

τ_c	Electron Transport Time
τ_n	Electron Lifetime
ϕ_{inj}	Quantum Yield of Charge Injection
ω_{min}	Peak Frequency
Γ	Dye Loading Amount per Projected Surface Area
ΔI	Difference in Photocurrent
ΔJ	Difference in Ionic Flux
ΔL	Difference in Tube Length
$\Delta \eta$	Difference in Efficiency
A	Anatase
AAO	Anodic Aluminum Oxide
ALD	Atomic Layer Deposition
AM	Air Mass
AOI	Angle of Incidence
AZO	Aluminum-Doped Zinc Oxide
B	Backside
BET	Brunauer-Emmett-Teller
CE	Counter Electrode
CPE1	Double Layer Capacitance
CPE2	Constant Phase Element
CIGS	Copper Indium Gallium Diselenide

DB	Double-Sided Anodization
DI	Deionized
DSSC	Dye-Sensitized Solar Cell
EIS	Electrochemical Impedance Spectroscopy
F	Frontside
FCC	Face-Centered Cubic
FESEM	Field Emission Scanning Electron Microscope
FTO	Fluorine-Doped Tin Oxide
IMPS	Intensity-Modulated Photocurrent Spectroscopy
IMVS	Intensity-Modulated Photovoltage Spectroscopy
IPCE	Incident Photon to Current Efficiency
ITO	Indium-Tin Oxide
LHE	Light Harvesting Efficiency
M	Mirror
NHE	Normal Hydrogen Electrode
NT	Nanotubes
NTA	Nanotube Array
NW	Nanowires
SEM	Scanning Electron Microscope
SGprot	Single-Sided Anodization with Protection
SGunprot	Single-Sided Anodization without Protection
T	Titanium
TCO	Transparent Conducting Oxide

TEM	Transmission Electron Microscope
TW	Terawatts
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Chapter 1 Introduction

1.1 Prelude

To date, the world's total energy consumption is about 4.1×10^{20} joules per year, equivalent to a continuous power consumption of 13×10^{12} Watts, or 13 terawatts (TW).^[1] World demand for energy is estimated to be more than double by 2050 and more than triple by the end of this century. Improvements in existing energy networks are obviously inadequate in meeting this demand. Therefore, looking for sufficient supplies of clean energy for the future becomes one of the most challenging endeavors of the present mankind.

Fortunately, the sun supplies 120,000 TW of radiation on the surface of the earth, far exceeding human needs even in the most aggressive energy demand scenarios.^[1] In other words, 20 TW of power is obtainable provided that 0.16% of the land on the earth is covered with 10% efficient solar conversion systems, which is nearly twice the world's consumption of fossil energy or equivalent to 20,000 nuclear fission plants of 1 gigawatt. It is evident that the solar energy can be exploited on the needed scale to meet global energy needs without significantly influencing the solar resource.

Conventional photovoltaic devices are based on the concept of charge separation at an interface of two materials with different conduction mechanism, which are capable of converting solar energy directly into electricity. Currently, the photovoltaic market is dominated by solid-state *p-n* junction based devices, and profits from the experience and material availability from semiconductor industry. For the sake of reducing production cost, thin film technologies are attractive and effective. To date, there are a variety of thin film

solar cells, such as copper indium gallium diselenide (CIGS, maximum cell efficiency of $19.4 \pm 0.6\%$), cadmium telluride (CdTe, maximum cell efficiency of $16.7 \pm 0.5\%$), gallium arsenide (GaAs, maximum cell efficiency of $26.1 \pm 0.8\%$), amorphous (maximum cell efficiency of $10.1 \pm 0.3\%$) and nanocrystalline (maximum cell efficiency of $10.1 \pm 0.2\%$) silicon thin film solar cells.^[2] Yet all of them have their own deficiencies. The use of indium and gallium in CIGS increases the manufacturing cost due to limited supply. The cadmium in CdTe solar cells is toxic and environment unfriendly. Although GaAs achieves the highest cell efficiency, it is the most expensive one.^[3] Low stability and questionable durability are the main limiting factors of amorphous silicon thin film solar cells.^[4] As for micro/nanocrystalline silicon thin film solar cells, the low growth rate with high hydrogen dilution may be problematic in manufacturing.^[3]

Alternatively, dye-sensitized solar cell (DSSC) is one of the most promising thin film photovoltaic devices for cost reduction, due to a number of merits compared to inorganic *p-n* junction solar cells. These advantages include ease of fabrication, low cost of scale-up (without high-vacuum, high-temperature, and ultra-clean environment), compatibility with flexible substrates, insensitive to light intensity (or incident angle), and so forth.^[5]

The current version of dye sensitized solar cells was first reported in 1991 by O'Regan and Grätzel with an overall conversion efficiency of 7.1~7.9%.^[6] Thereafter, this photovoltaic conversion system has been widely investigated and significantly improved. The cell efficiency reached 10% in 1993,^[7] 10.4% in 2001,^[8] and 11.18% in 2005^[9] with different sensitizers by Grätzel's group. An efficiency of 10.2% was also achieved by another group in 2005 through optimized design of each cell components.^[10] Certified efficiencies exceeding

11% were reported for laboratory cells (Sharp) and 6%~7% of efficiency for modules.^[11-14] Tandem versions of the cell reached 15% conversion efficiencies.^[15] However, an assessment from U.S. Department of Energy concluded that a photovoltaic efficiency of 20% was obtainable by developing the scientific underpinning to exploit the unique properties of the sensitized systems, and such studies may further lay the scientific foundation for developing nanostructural systems with efficiencies beyond the Shockley-Queisser limit of 32%.^[1] Apparently the current version is far below the limiting ceiling, and there is still a large room for improvement. Although the challenge of realizing this vision is considerable and requires substantial advances in understanding each component as well as physical process affecting the performance and stability of the devices, it is yet the most intriguing and promising way to offer cheap, renewable, and clean energy for mankind on the earth.

1.2 Overview

In conventional titania nanoparticle based dye-sensitized solar cells,^[6] the overall conversion efficiency is hindered by electron scattering (e.g., at nanoparticle connections, defects, impurities, etc.) and energy loss (i.e., in the red and near-infrared region). To solve these problems, diverse one-dimensional nanostructures have been studied, such as nanowires^[16] and nanotubes,^[17] which are found to accelerate electron transport and increase light scattering. In particular, highly oriented titania nanotube arrays prepared by electrochemical anodization have been vigorously investigated, for controllable geometry (e.g., tube length,^[18-22] pore diameter,^[23-25] wall thickness,^[26] intertube spacing,^[27] wall roughness,^[28] etc.) in comparison to template-assisted method.^[29]

To date, dye-sensitized solar cells based on anodic nanotubes have two major configurations:^[30] frontside and backside illumination. In frontside illumination, nanotubes are produced from a titanium thin film sputtered on a transparent conducting oxide, thereafter assembled into DSSCs.^[31] The most efficient cell of this type achieved a conversion efficiency of 6.86% with tube length of $\sim 17.6\ \mu\text{m}$.^[32] In backside illumination, nanotubes are directly grown on titanium foil, and assembled into DSSCs.^[33] A conversion efficiency of 6.89% was achieved with approximately 20- μm -long nanotubes also by Grimes' group.^[19]

Apparently the use of anodic titania nanotube arrays is not as efficient as that of titania nanoparticles (i.e., 7% vs. 11%).^[9, 11] One of the most important factors is the striking difference in effective surface areas which directly result in different dye loadings and hence the light harvesting efficiency and eventually the conversion efficiency. It is estimated that,^[34] to produce a comparable surface area under the same photoanode volume, the radius ratio of a single nanotube (assuming regular cylindrical tube) with respect to a single nanoparticle (assuming regular sphere) has to be 5:3. This requires the tube pore diameter to be at most 30 nm to generate a comparable surface area with that of nanoparticles of 18 nm in diameter (normally in the range of 15~20 nm).^[35] By means of electrochemical anodization, practically, it is difficult to achieve this kind of nanotube array with enough length believed to be tens of micrometers^[36, 37] for DSSC application. This is because the tube pore diameter proportionally decreases with the potential drop over the oxide layer, while the growth rate exponentially decreases.^[38]

In view of these, to increase light harvesting and thus achieve high photovoltaic efficiency, it is essential to promote the dye loading ability of the nanotubes by increasing the effective surface area available for dye adsorption.

1.3 Objectives

This project aims at increasing the light harvesting of dye-sensitized solar cells based on anodic nanotube arrays by promoting the dye loading amount of the photoanodes. To achieve this, a novel parallel configuration of dye-sensitized solar cells is proposed with double-sided nanotube arrays. Accordingly, double-sided nanotube growth is investigated first on the basis of single-sided nanotube fabrication.

1.4 Scope

This project consists of two major parts, that is, investigation of nanotube growth for better geometry control and study of dye-sensitized solar cells with a novel parallel configuration. In growth of the nanotubes, tube geometry is tailored by varying the electric field which plays an essential role in the growing process. In application of the nanotubes, dye-sensitized solar cells are assembled with different parameters, for example, dye category, TiCl_4 treatment duration, UV-ozone treatment, substrate thickness, tube length, and so on. Optimal assembling conditions are presented and discussed based on experimental results and theoretical calculation.

1.5 Organization

This thesis is divided into six parts. Chapter 1 introduces research background of the project. Chapter 2 reviews current status of nanotube fabrication and application of the nanotubes in dye-sensitized solar cells. Chapter 3 summarizes challenges in DSSCs with anodic nanotubes, presents proposed solution in this project, and describes the experimental details. Chapter 4 discusses the essential role of electric field in anodic nanotube growth and

exhibits the methods to tailor the tube geometry and morphology. Chapter 5 focuses on application of the nanotubes in dye-sensitized solar cells. Finally, conclusions and future work are given in Chapter 6.

Chapter 2 Anodic Titania Nanotube Array and Its Application in Dye-Sensitized Solar Cells

2.1 Anodic Titania Nanotube Array

The emergence of anodic aluminum oxide has triggered development of a spectrum of nanostructured materials with highly ordered porous structure as template. CdS nanowire arrays,^[39] carbon nanotubes,^[40] titanium dioxide (titania) nanotube arrays,^[41] are a few examples. In the past decade, various metal oxide nanoporous or nanotube structures were directly produced using the same electrochemical anodizing method, in the absence of the templates. Examples include titanium,^[42] zirconium,^[43] hafnium,^[44] niobium,^[45] tantalum,^[46] tungsten,^[47] to name but a few. In particular, the anodic titania nanotube arrays with highly oriented alignment have generated worldwide interest, owing to its intriguing performance when applied in dye-sensitized solar cells,^[17, 32] gas sensors,^[48, 49] water splitting,^[26, 50] and so forth.

In 1999, anodic columnar porous film was formed on titanium in fluorinated electrolyte by Zwilling and co-workers.^[51] Two years later, anodic titania nanotube array was first reported by Grimes and co-workers.^[42] Thereafter it has been vigorously investigated, profiting from its high surface area and highly oriented alignment, and extensively explored in versatile applications. In dye-sensitized solar cells, the high surface area enables large dye loading while the highly ordered configuration facilitates electron transport,^[36] thus rendering great potential for further efficiency enhancement. However, these unique properties can only be capitalized when the nanotube growth process is well studied for better geometry control.

In this section, mechanism of nanotube growth by electrochemical anodization is presented first. Thereafter, various factors influencing the geometry of the nanotubes are reviewed and discussed. These are the basis for further application of the nanotubes in dye-sensitized solar cells.

2.1.1 Nanotube Growth by Electrochemical Anodization

Electrochemical anodization is an electrochemical process to form passivated oxide layer on metal surface originally used for protection of metal components against corrosion, especially for aluminum and aluminum alloys. In the case of pure aluminum, a native dense amorphous aluminum oxide with a thickness of 2 to 3 nm^[52] is formed on the surface at room temperature once it is exposed to the air, or any environment containing oxygen. This layer prevents aluminum from further oxidation or corrosion. But for aluminum alloy, the corrosion resistance is greatly decreased because of the alloying elements or impurities, such as copper, iron, and silicon.^[52] Therefore, electrochemical anodization is employed to increase the thickness of passivated oxide layer for better protection.

In Figure 2.1, a typical experimental setup of the electrochemical anodization with a simple two-electrode configuration is illustrated, where a titanium foil is employed as the working electrode (or anodic electrode) and a platinum foil (or sheet, gauze, mesh, etc.) is adopted as the counter electrode (or cathodic electrode). The anodization process can be carried out by galvanostatic method (control the current passing the working electrode while measure the potential applied to it) or potentiostatic method (control the potential applied to the working electrode while measure the current passed). In both cases, anions in the electrolyte migrate toward the working electrode and cations toward the counter electrode under electric field.

The electrolyte solutions used are relatively extensive from aqueous solution to organic solution. However, it is recognized that fluorine ions are essential in formation of nanotube structures instead of compact films,^[53] though the titania nanotube arrays can also be obtained in fluoride-free electrolytes.^[54-56] During electrochemical anodization, magnetic stirring is frequently employed to reduce the thickness of double layer at metal-electrolyte interface,^[57] ensure uniform local current density as well as temperature over the surface,^[58] and facilitate ion diffusion in the electrolyte.^[59]

Figure 2.1 Schematic diagram of an electrochemical anodization with a simple two-electrode configuration.

In the process of anodizing titanium in fluoride-free electrolyte, generally barrier-type anodic films form through the following reaction^[24, 60]

After formation of the initial oxide on the titanium surface, further film growth takes place at metal-oxide and oxide-electrolyte interfaces by Ti^{4+} egress and O^{2-} ingress under the electric field,^[53, 61] as illustrated in Figure 2.2 (a). The outwardly mobile Ti^{4+} ions can also form hydroxide on the film surface, which is revealed by X-ray photoelectron spectroscopy (XPS) measurement.^[62] The anodic current density decreases with prolonged duration, as a result of progressively increased film thickness. The film growth terminates eventually by dielectric breakdown.

Figure 2.2 Schematic presentation of anodizing titanium in (a) absence of fluorides (results in barrier-type film), and (b) presence of fluorides (results in tube growth).^[53]

The anodic film growth process in fluoride-containing electrolyte is totally different, which gives rise to formation of nanotube structure rather than the barrier-type film, as shown in Figure 2.2 (b). In this scenario, the fashioned anodic films at oxide-electrolyte interface experience chemical dissolution as follows^[24, 60, 63]

In addition, direct ejection (or direct complexiation) of the outwardly mobile Ti^{4+} ions into the electrolyte also occurs under the electric field, which can be presented as ^[53, 63]

To date, the mechanism of anodic nanotube growth is not well established as that of the porous anodic alumina films.^[57, 59, 60, 62, 64, 65] Most growth mechanisms are elucidated based on the anodic alumina films. Mor and co-workers studied the surface morphology of the nanotubes prepared at 20 V for different anodizing durations and revealed the evolution of the nanotubes.^[57] Accordingly, a possible mechanism is proposed as follows.

Figure 2.3 is a typical current transient during nanotube growth under potentiostatic anodization. It shows that, upon commencement of the anodization, the current density decreases drastically, corresponding to the formation of the initial oxide layer on metal surface (see Figure 2.4 (a)). In the presence of fluorine ions, chemical dissolution of the oxide layer takes place in regions especially under the electric field which, in turn, polarizes and weakens the Ti–O bonds.^[57] In this case, small pits are formed on the oxide surface (see Figure 2.4 (b)), which act as the embryo pores for subsequent nanotube growth. This results in mildly decreased slope of the curve, as displayed in Figure 2.3 (the region between 15 seconds and P1). In this scenario, field strength beneath the embryo pores is relatively larger than that between the pores,^[66] hence giving rise to rapid ion transport at the pore base. This effectively accelerates the development of the embryo pores both in vertical and lateral directions, as illustrated in Figure 2.4 (c). As the pores develop progressively, the anodic current density increases accordingly (the region between P1 and P2 in Figure 2.3) due to reduced thickness of the oxide layer.

Figure 2.3 A typical current transient for anodization of a titanium thin film prepared by magnetron sputtering. Inset is a corresponding current transient for anodization of a titanium foil, with vertical axis being the current density and horizontal axis being the anodization time. The kinetics of nanotube growth is the same for either thin films or foils.^[30]

All the above processes are similar to the formation of porous anodic alumina films. Although there are a number of common features in anodizing titanium and aluminum,^[65] the difference in key features is obvious: anodization of titanium gives rise to individual nanotubes while anodization of aluminum results in integrated nanoporous structure. Mor and co-workers^[57] assumed that only pores with thin walls could form, owing to relatively low ion mobility and high chemical solubility of the oxides. Consequently, unanodized metallic portions can initially present between the pores. With pores deepened, the electric field in these metallic regions is enhanced, thus resulting in the formation of intertube spacing, as exhibited in Figure 2.4 (d). Thereafter, the pores and voids (or intertube spacing) develop equally and yield exclusive nanotube structure (see Figure 2.4 (e)). At the same time, the current gradually decreases with the prolonged anodizing duration (see Figure 2.3 in the range of P2~P4), as a consequence of steadily increased nanotube length.

Figure 2.4 Schematic diagram of the evolution of straight nanotubes at a constant anodizing voltage, as follows: (a) oxide layer formation; (b) pit formation on the oxide layer; (c) growth of the pit into scallop-shape pores; (d) the metallic part between the pores undergoes oxidation and field-assisted dissolution; and (e) fully developed nanotubes with a corresponding top views.^[57]

Chemical dissolution plays an important role in nanotube growth, since the fashioned nanotubes can be dissolved by fluoride-containing electrolyte especially for aqueous electrolyte. In general, there are three essential processes during nanotube growth, i.e. field-assisted oxidation at metal-oxide interface, field-assisted dissolution at oxide-electrolyte interface, and chemical dissolution at tube mouth-electrolyte interface. These three processes contribute to two important rates. One is electrochemical etching rate at tube base,

determined by field-assisted oxidation and dissolution. At steady anodizing state, this rate is constant since the field-assisted oxidation and dissolution are equal to each other. The other rate is the chemical dissolution rate at tube mouth, which progressively consumes the formed nanotubes. If these two rates are comparable during anodizing of titanium, the nanotube length will keep constant in the subsequent anodizing process, as illustrated in Figure 2.3 from P4 to P5. The effect of these three processes and two rates will be discussed in detail in Section 4.1.

2.1.2 Geometry Control of Anodic Nanotubes

For application of anodic nanotubes in dye-sensitized solar cells, the cell performance is seriously affected by the tube geometry, for example, tube length, pore diameter, wall thickness, intertube spacing, wall roughness, and so on. These geometrical characteristics are, in turn, influenced by a number of factors, such as applied potential, electrolyte composition, pH value, magnetic stirring, temperature, and anodizing duration. To better control the nanotube geometry, effect of these anodizing parameters on the tube features (especially for tube length and pore diameter) is reviewed in the following subsections.

2.1.2.1 Effect of Applied Potential

In growth of anodic nanotubes, the driving force for ion transport in the oxide layer is the electric field which originates from the potential drop over the oxide layer. The lateral component of the field contributes to evolution of pore diameter of the tubes. As such, the applied potential is one of the most important factors influencing the tube length and pore diameter. Bauer *et al.* ^[23] tailored the geometry of the anodic nanotubes in $\text{H}_3\text{PO}_4/\text{HF}$ electrolytes by changing applied potentials, as illustrated in Figure 2.5. In Figure 2.6, it

clearly shows both pore diameter and length (or layer thickness) of these nanotubes increase linearly with applied potential. Similar results were also reported by other researchers in various electrolytes.^[24, 42, 53, 59, 67, 68]

2.1.2.2 Effect of Electrolyte Composition

Macak *et al.*^[59] investigated the influence of fluoride concentration on tube configuration. The results reveal that only compact oxide layer is formed in fluoride-free electrolyte, as shown Figure 2.7, similar to the discussion in Section 2.1.1. In all other cases, nanotube structures are produced in the presence of fluoride in the electrolyte. It also indicates the length of the nanotubes increases with the fluoride concentration, as illustrated in the insets of Figure 2.7, suggesting promoted growth rate at increased concentration. However, formation of the nanotubes is not homogeneous over the entire Ti surface at very high F⁻ concentration (e.g. 0.54 M), in agreement with that reported by Bauer and co-workers.^[23] As shown in Figure 2.8, the anodization with concentrations of fluoride ions < 0.1 wt% results in compact oxide layer (see Figure 2.8 (a)), while with a concentration of 0.5 wt% HF or more etching of the surface is observed (see Figure 2.8 (c)). In view of these, it seems that there exists an optimal concentration of fluorine ions for a given electrolyte to generate nanotube structure with a desired growth rate. Below a lower critical concentration, no nanotubes can be obtained, whereas etching of nanotubes takes place above certain fluoride concentration.

Figure 2.5 SEM images of TiO₂ nanotubes formed in 1 M H₃PO₄ + 0.3 wt% HF at: 1 V (a), 2.5 V (b), 5 V (c), 10 V (d), 15 V (e), 20 V (f) and 25 V (g) for 1 h.^[23]

Figure 2.6 Diameters and thickness of nanotube layers formed in 1 M H_3PO_4 + 0.3 wt% HF at different potentials (values extracted from Figure 2.5).^[23]

Figure 2.7 SEM images of samples anodized in water/glycerol electrolyte (50:50 vol%) at 20 V during 3 h with different NH_4F concentrations.^[59]

Figure 2.8 SEM images of TiO₂ layers formed at 10 V for 2 h in 1 M H₃PO₄ with different additions of HF: (a) 0.025 wt%, (b) 0.3 wt% and, (c) 0.5 wt%.^[23]

Figure 2.7 suggests that pore diameter of the nanotubes is not strongly influenced by concentration of the fluorine ions (0.135; 0.27; 0.54 M NH₄F), echoing the results from

Macak and co-workers^[69] in which anodic titania nanotubes were grown in Na₂SO₄ (1 M) electrolyte with different NaF concentration (0.5; 0.7; 1 wt% NaF). The pore diameter is not significantly depending on the NaF concentration. However, these results are obtained within one individual electrolyte regime, i.e. in a particular solution whilst varying the fluoride concentration. Nevertheless, pore diameters of the nanotubes differ in different electrolytes. For example, pore diameters of ~20 nm are obtained at 10 V in acetic acid electrolyte containing 0.5 wt% NH₄F,^[70] whereas ~50 nm at 10 V and 100 nm at 20 V in 1 M phosphoric acid electrolyte containing 0.3 wt% HF,^[23] ~140 nm at 20 V in 1 M sulphuric acid electrolyte containing 0.15 wt% HF.^[71] These examples indicate that the pH value of the electrolyte plays an important role in determination of pore diameter, which will be discussed in the following section.

In addition, it was reported that the nanotube wall thickness decreases with increasing NH₄F concentration during anodization of Ti-Zr alloy at 20 V in 1 M (NH₄)₂SO₄ solution.^[64]

2.1.2.3 Effect of pH Value

Ghicov *et al.*^[72] studied titania nanotubes prepared in phosphate electrolytes. The results show that nanotube pore diameter increases with HF concentration from 30 nm in 0.3 wt% HF, to 50 nm in 0.5 wt% HF, and to 70 nm in 0.7 wt% HF. Feng and co-workers^[73] prepared titania nanotubes over a wide pH range. Their results indicate that the nanotube length increases significantly with the electrolyte pH value, and the corresponding growth rate is larger in basic conditions than in acidic conditions. The authors attributed it to the different chemical dissolution rates at pore mouth under different pH values, considering the three processes during tube growth that mentioned in Section 2.1.1.

Since electrochemical formation of titania nanotubes was first reported in 2001,^[42] many researchers have devoted themselves to promoting the nanotube length. It was revealed that the tube length of only hundreds of nanometers (so-called First Generation) could be obtained in aqueous or acidic HF solutions,^[23, 42, 57, 70, 71] as a result of high chemical dissolution rate of the fashioned nanotubes. To solve this problem, researchers proposed to use pH buffer species and adopt relatively mild solutions in preparation of anodic nanotubes.^[62, 69, 72, 74] In this case, nanotubes of a few micrometers (so-called Second Generation) were achieved. However, this length was still far from the ideal values for the sake of applications. To further suppress the chemical dissolution process, organic electrolyte was employed,^[18-22] which boomed the tube length to hundreds of micrometers and even millimeters (so-called Third Generation).

In anodic growth of nanotubes in organic electrolyte, water content becomes a crucial factor in producing and tailoring the tube structure, since the chemical dissolution rate increases with the water content. Raja *et al.*^[75] investigated the effect of water content on formation of the nanotubes. Their results demonstrate that a minimum of about 0.18 wt% water is required to produce a well ordered nanotubes in the ethylene glycol + 0.2 wt% NH₄F solution. With water content more than 0.18 wt%, no significant change in morphology of the nanotubes is observed. However, with very high water content (> 0.5 wt%) ripples are present on the nanotube walls and the number of the ripples increases with water content. In general, the ripples are commonly observed in the nanotubes prepared in aqueous solutions, owing to the current oscillation induced by pH burst during nanotube growth,^[76] whereas smooth wall is normally obtained in organic electrolyte. The same results were also reported by Macak and co-workers,^[59] as shown in Figure 2.9 where ripples on the nanotube walls

become more obvious as water content increases. Additionally these authors claim that the pore diameter of the nanotubes increases with water content, i.e. 45 ± 6 nm for 0 vol% H_2O , 60 ± 7 nm for 0.67 vol% H_2O , 75 ± 8 nm for 6.7 vol% H_2O , and 105 ± 10 nm for 16.7 vol% H_2O . This may be attributed to the decreasing IR drop with increased water content, thus producing higher effective potential on the working electrode (Ti foil) with higher water addition.

Figure 2.9 SEM high-magnification images of the tube walls showing different features depending on the water content.^[59]

2.1.2.4 Effect of Temperature and Stirring

Yasuda and Schmuki^[64] demonstrated that the length limiting factor of the nanotube growth is controlled by diffusion of ionic species in the electrolyte. The ion diffusion process,

in turn, is affected by anodizing temperature and magnetic stirring; therefore these two factors are introduced together in this section.

Macak and Schmuki ^[25] investigated the influence of electrolyte viscosity and temperature on morphology of anodic titania nanotubes. Clearly their results reveal that both tube length and pore diameter increase with elevated temperature, as illustrated in Figure 2.10. In the case of anodization at a temperature higher than 40 °C, only unstable bundles of the tubes are formed, whereas no regular and mechanically stable nanotube architectures are obtained. The strong temperature dependence of the nanotube geometry reflects the important role of ion diffusion in the growth of anodic nanotubes.

Figure 2.10 Titania nanotubes prepared in glycerol + 0.5 wt% NH_4F electrolytes at 20 V during 6 h at different temperatures.^[25]

To further clarify the effect of diffusion process, magnetic stirring is employed during nanotube growth and studied in comparison to that without stirring.^[25, 59, 77] The results

indicate that the current density is higher in stirred electrolyte than that in static. Moreover, the length of the nanotubes produced in the stirred electrolyte is much longer. For example,^[64] the nanotubes anodized at 20 V in 1 M $(\text{NH}_4)_2\text{SO}_4$ + 0.5 wt% NH_4F electrolyte has a length of 16.9 μm with magnetic stirring. In contrast, only 10.7 μm is obtained in static electrolyte. This again suggests ion diffusion controls the nanotube growth process.

2.2 Application of Anodic Titania Nanotube Arrays in Dye-Sensitized Solar Cells

In this section, the typical structure and working principle of a dye-sensitized solar cell are introduced first. The factors influencing the cell performance are presented. The reasons to choose anodic nanotube arrays as the photoanodes are elucidated in detail. Thereafter, effect of tube geometry on photovoltaic performance of the DSSCs is reviewed and discussed.

2.2.1 Typical Structure and Working Principle

A typical nanocrystalline based dye-sensitized solar cell consists of transparent conducting oxide (TCO), dye molecules anchored to the surface of TiO_2 nanoparticle network employed as the photoanode, redox electrolyte penetrating through the photoanode, and platinized counter electrode, as depicted in Figure 2.11.

For the materials of the TCO, indium-tin oxide (ITO), fluorine-doped tin oxide (FTO), and recently developed aluminum-doped zinc oxide (AZO) are commonly used as the front contacts of DSSCs for light trapping and electron collection.

Figure 2.11 Schematic diagram of a typical architecture of a dye-sensitized solar cell with TiO₂ nanocrystalline photoanode. Inset is local magnification as well as corresponding energy level of the sensitized system.^[5]

The core component of a DSSC system is the mesoporous semiconductor photoanode, which is generally placed in contact with a redox electrolyte or an organic hole conductor. The material used widely has been anatase TiO₂, though alternative ZnO,^[78, 79, 80] SnO₂,^[81, 82] and Nb₂O₅^[83] have also been investigated. The mesoporous TiO₂ photoanode is sintered at 450 °C for a short time (e.g., 30 min) after prepared on the TCO substrate to ensure that the particles are electronically interconnected. The TiO₂ particle size is typically 15–30 nm, and real surface area of the film with a thickness of 10 μm is 1000 times larger than that of the projected area.^[84] The much higher surface area renders larger dye loading ability for sufficient absorption of the incident photon energy.

Attached to the surface of the mesoporous TiO_2 film is a monolayer of sensitizers or dye molecules. The sensitizer is usually ruthenium compounds which are known for their outstanding stability. *cis*-Di(thiocyanato)bis(2,2'-bipyridyl)-4,4'-dicarboxylate ruthenium(II), coded as N3 or N-719 dye depending on whether it contains four or two protons, is found to be an excellent solar light absorber and charge-transfer sensitizer.^[5] Figure 2.12 shows the structures of three different ruthenium sensitizers and their corresponding appearances loaded by mesoporous TiO_2 film. The center one is the so-called N3 sensitizer (also shown in inset of Figure 2.11). The sensitizers are adsorbed onto the mesoporous film surface by dip coating in the dye solutions for certain time (e.g., 48 h).

Figure 2.12 Structures of three different ruthenium sensitizers RuL_3 (yellow), *cis*- $\text{RuL}_2(\text{NCS})_2$ (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 nanocrystalline TiO_2 films loaded with a monolayer of the respective sensitizers.^[5]

The redox electrolyte usually containing I^-/I_3^- ions is filled in the pores of the mesoporous film after sensitized by dye molecules. The oxidized dye molecules are regenerated by

electron donation from the redox couple ($3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^-$). On the other hand, regeneration of the redox couple occurs via collecting electrons from the counter electrode ($\text{I}_3^- + 2\text{e}^- \rightarrow 3\text{I}^-$).

The platinized TCO is widely employed as the standard counter electrode to reduce the redox couple or collect the holes from hole conducting materials in solid-state DSSCs, where the platinum acts as catalyst.^[85] In addition, other kinds of counter electrode are also studied, such as single wall carbon nanotube on glass,^[86] carbon black on FTO,^[87] and carbon black on stainless steel.^[88]

Once a dye-sensitized solar cell is soaked under the sun, photons are absorbed by dye molecules (or sensitizers), thus resulting in electron excitation from ground states to excited states of the dye molecules, as illustrated in the inset of Figure 2.11. Electron injection takes place subsequently from dye molecules into the conduction band of the photoanode, due to its relatively lower energy level. The injected electrons percolate through the nanoparticle network to the collecting electrode via trapping/de-trapping mechanism.^[89-91] In the mean time, the original state of the dye molecules is restored by electron donation from the I^-/I_3^- redox couple in the electrolyte, while the iodide is regenerated in turn by the reduction of triiodide at the platinized counter electrode. The circuit is eventually completed via electron migration through the external load. The theoretical maximum open-circuit photovoltage produced under illumination corresponds to the difference between the quasi-Fermi level of the photoanode and the chemical potential of the electrolyte. The conduction band level of the TiO_2 photoanode and the redox potential of I^-/I_3^- are estimated to be -0.5 V versus normal hydrogen electrode (NHE) and 0.4 V versus NHE, respectively.^[92] Therefore, in the case of a DSSC using TiO_2 photoanode and I^-/I_3^- redox mediator, the maximum

photovoltage is expected to be approximately 0.9 V, depending on the electrolyte components because the Fermi level of the TiO_2 electrode depends on the electrolyte components and their concentrations.^[93]

2.2.2 Efficiency Limiting Factors

The overall conversion efficiency (η) of a (dye-sensitized) solar cell can be calculated as

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (2.4)$$

where J_{sc} is the short-circuit photocurrent density, V_{oc} is the open-circuit photovoltage, FF is the fill factor, and P_{in} is the incident photon flux density. The equation indicates that, under certain incident photon energy, it is necessary to maximize the three parameters in the numerators so as to promote the global efficiency. Figure 2.13 is a typical I - V curve for a solar cell, from which the J_{sc} and V_{oc} can be directly obtained as illustrated in the figure. The dotted line represents dark current.

The fill factor is mainly related to the shunt and series resistance of a dye-sensitized solar cell, which is determined by

$$FF = \frac{J_{mpp} \cdot V_{mpp}}{J_{sc} \cdot V_{oc}} \quad (2.5)$$

Here the J_{mpp} and V_{mpp} are photocurrent density and photovoltage at maximum power point, respectively. Both can be obtained from the I - V curve as in Figure 2.13. Han *et al.*^[94] proposed an equivalent circuit for modelling DSSCs based on electrochemical impedance spectroscopy measurement. Their further study shows that the series resistance of a DSSC

consists of three resistance elements, namely, the sheet resistance of TCO, the resistance of ionic diffusion in electrolyte, and the resistance at the interface of counter electrode and electrolyte.^[10] The FF increases with decrease in the internal resistance elements, and a conversion efficiency of 10.2% was obtained by optimization design of each DSSC component. Accordingly, a large FF can be achieved by reducing the series resistance.

Figure 2.13 A typical I-V curve for efficiency calculation of a (dye-sensitized) solar cell.

The J_{sc} can be computed by integrating the incident photon flux density $F(\lambda)$ and the incident photon to current efficiency $IPCE(\lambda)$ ^[11]

$$J_{sc} = \int qF(\lambda)(1-r(\lambda))IPCE(\lambda)d\lambda \quad (2.6)$$

where q is the electron elementary charge, $r(\lambda)$ is the energy loss via absorption and reflection at the transparent conducting oxide. The $IPCE(\lambda)$ is a product of the light

harvesting efficiency $LHE(\lambda)$, the quantum yield of charge injection ϕ_{inj} , and the charge collecting efficiency η_{cc} , as follows ^[7]

$$IPCE(\lambda) = LHE(\lambda)\phi_{inj}\eta_{cc} \quad (2.7)$$

The $LHE(\lambda)$ is used to measure the absorption of incident photon energy by available dye molecules and given by ^[7]

$$LHE(\lambda) = 1 - 10^{-\Gamma\sigma(\lambda)} \quad (2.8)$$

Here Γ is the dye loading amount per square centimeter of projected surface area of the photoanode and σ is the absorption cross section of the dye molecules at the wavelength λ .

The quantum yield of charge injection ϕ_{inj} can be expressed as ^[5]

$$\phi_{inj} = \frac{k_{inj}}{k_{deact} + k_{inj}} \quad (2.9)$$

where k_{inj} is the fraction of excited electrons injected into the conduction band of the photoanode, while k_{deact} is the fraction of the deactivated electrons. To achieve a good quantum yield ϕ_{inj} , the rate constant for charge injection should be at least 100 times higher than k_{deact} .^[5] This is achievable by employing the sensitizers with special functional group, for instance, carboxylate, hydroxamate, or phosphonate moieties that anchor the sensitizer to the oxide surface.^[95] In general, photons absorbed by dye molecules are converted to conduction band electrons efficiently. An estimation reveals the value of $\phi_{inj} > 99.9\%$ under certain conditions.^[7]

Equations 2.6~2.9 show that, under constant incident photon flux density, the photocurrent of a dye-sensitized solar cell is determined by the following parameters: $r(\lambda)$, Γ , σ , ϕ_{inj} , and η_{cc} . The $r(\lambda)$ is a property of the transparent conducting oxide, which can be reduced by optimizing the doping concentration and increasing light-trapping via surface texturing.^[96] The σ and ϕ_{inj} are closely related to the property of the sensitizer, with ϕ_{inj} normally being very efficient as presented above. The Γ is the dye loading amount per projected surface area of the photoanode. The charge collection efficiency η_{cc} is mainly determined by the competition between charge transport and recombination in the photoanode.^[17] So as to increase η_{cc} , charge transport should be enhanced, while charge recombination should be suppressed. In view of these, the most important factor influencing the photocurrent is the property of the photoanode (i.e., Γ and η_{cc}). As such, to achieve high photocurrent, it is essential to produce photoanode with high surface area, efficient electron transport, and effectively suppressed recombination. This is the motivation of the current project, which will be discussed in detail in Section 2.2.3.

Equation 2.8 demonstrates that increment in dye loading amount is crucial to achieve light harvesting. The dye loading amount is, in turn, dependent on surface area of the photoanode. Accordingly, it is effective to increase the thickness of nanoparticle film (or photoanode) for higher dye loading amount. However, quantitative collection of charge carriers can be achieved only when the electron diffusion length (L_n) is greater than the film thickness (d)

$$L_n > d \quad (2.10)$$

The electron diffusion length can be calculated using Einstein's relationship

$$L_n = \sqrt{D_n \tau_n} \quad (2.11)$$

where D_n and τ_n are the electron diffusion coefficient and lifetime in the photoanode, respectively. This has restricted the thickness of the conventional nanocrystalline DSSCs to an order of a few microns, which depends on the optical cross section of the sensitizer or quantum dot and their concentration in the film. Ito *et al.* ^[97] reported the procedures to fabricate standard DSSCs and presented the optimum film thickness to produce highly efficient DSSCs being 12~14 μm . In addition, the $LHE(\lambda)$ can be further promoted by mixing larger anatase particles to enhance light scattering in the mesoporous film, and thus give rise to higher photocurrent. Han *et al.* ^[11] reported an overall conversion efficiency of 11.1% and J_{sc} of 21 mA/cm^2 by using TiO_2 electrodes with high haze controlled via addition of submicron particles (400 nm diameter). Chou *et al.* ^[98] published the same effect of light scattering on efficiency enhancement of DSSCs.

The open-circuit photovoltage can be computed from the diode equation ^[84]

$$V_{oc} = \left(\frac{nRT}{F} \right) \ln \left[\frac{i_{sc}}{i_o} - 1 \right] \quad (2.12)$$

where n is the ideality factor between 1 and 2 for the DSSCs, i_o is the reverse saturation current induced by recombination, R is the gas constant, T is the Kelvin temperature, F is the Faraday constant. Accordingly, a 59 mV gain in V_{oc} is achievable at room temperature for each order of magnitude decrease in the dark current.^[99] This dark current (dashed line in Figure 2.13) reflects the recombination taking place in the DSSC system. In general, two major recombination processes affect the V_{oc} significantly: the injected electron (e_{cb}^-)

recaptured by the oxidized dye molecule (S^+) or recombined with the triiodide (I_3^-) in the electrolyte. The reactions are as follows ^[100]

In these two processes, the recombination between injected electrons and the triiodide (Reaction 2.14) is dominant, because regeneration of dye molecules by the iodide in the electrolyte normally takes place at an order of nanosecond, which is fast enough to compete with the recombination process (Reaction 2.13). Consequently, a blocking layer is used to hinder the electron back reaction with the electrolyte.^[101, 102] Another effective method to suppress the recombination is incorporation of one dimensional nanostructures (e.g., nanowire, nanotube, nanorod, etc.), which will be discussed in the following section.

2.2.3 Photoanodes from Nanoparticle Network to Nanotube Array

It is widely recognized that two major factors have limited the conversion efficiency of conventional nanoparticle based dye-sensitized solar cells. One is the slow percolation of electrons through the random nanocrystalline network. The injected electrons repeatedly interact with a distribution of traps as they undertake a random walk through the mesoporous film.^[16] The structural disorder at the contact between two crystalline nanoparticles leads to aggravated scattering of free electrons,^[103] thus reducing electron mobility. The electron diffusion coefficient, $D_n \leq 10^{-4} \text{ cm}^2\text{s}^{-1}$, is several orders of magnitude smaller than that in TiO_2 or ZnO single crystal.^[104, 105] The other factor is the poor absorption of low-energy photons by available dye molecules especially in red and near-IR region. The incident photon

to current efficiency as a function of wavelength for commonly used sensitizers, i.e., N3 (red line) and black dye (black line), is shown in Figure 2.14 (a). The absorption spectra of the sensitizers cover a large region, even extending to 800nm for N3 and 900 nm for black dye. For comparison, the IPCE spectra of DSSCs with commonly nanocrystalline TiO_2 photoanode employing black dye as the sensitizer is displayed in Figure 2.14 (b). The solid line marked with Haze 3% presents the performance of the traditional nanocrystalline DSSCs. Haze, defined as the ratio of diffuse transmittance to total transmittance, are controlled by addition of submicron particles (400 nm diameter) to the TiO_2 photoanodes.^[11] Although the IPCE of black dye can reach 80% in the visible light region, the normal nanocrystalline DSSCs only have a value of 60%. Especially for the wavelength in the region of 800 to 900 nm, the IPCE of conventional nanocrystalline DSSCs is relatively lower than that achieved by the black dye, as illustrated in Figure 2.14.

Figure 2.14 (a) Photocurrent action spectra obtained with the N3 (ligand L) and the black dye (ligand L') as sensitizer.^[99] The photocurrent response of a bare TiO_2 films is also shown for comparison; (b) Dependence of IPCE spectra on haze of TiO_2 electrodes.^[11] Black dye is employed as the sensitizer. The vertical dashed lines are added for clarity. L = 4,4'-COOH-2,2'-bipyridine, L' = 4,4',4''-COOH'-2,2':6',2''-terpyridine.

In view of these, various one dimensional nanostructures (e.g., nanotube, nanowire, nanorod, etc.) have generated worldwide interest, owing to the intriguing properties when

applied in dye-sensitized solar cells. Law *et al.* ^[16] reported a new DSSC architecture employing ZnO nanowire array as the photoanode, as shown in Figure 2.15. In this array, the nanowire length and diameter vary from 16 to 17 μm and 130 to 200 nm, respectively. The authors estimate an electron diffusion coefficient of $D_n=0.05\sim0.5\text{ cm}^2\text{s}^{-1}$ for single dry nanowire, which is several hundred times larger than that for the operating cells (i.e., $D_n\leq 10^{-4}\text{ cm}^2\text{s}^{-1}$, as mentioned above), suggesting fast electron transport in the nanowire structure. Moreover, the conductivity of the nanowire arrays is increased by 5~20% when bathed in the standard DSSC electrolyte. Besides, the electron injection in nanowire ($\sim 5\text{ ps}$) is much faster than that in nanoparticle ($\sim 100\text{ ps}$). All these characteristics enable a high incident photon to current efficiency.

Figure 2.15 The nanowire dye-sensitized cell, based on a ZnO wire array. (a) Schematic diagram of the cell. Light is incident through the bottom electrode. (b) Typical scanning electron microscopy cross-section of a cleaved nanowire array on FTO. The wires are in direct contact with the substrate, with no intervening particle layer. Scale bar, 5 μm .^[16]

However, the ZnO nanowire DSSCs exhibit a performance of $J_{\text{sc}} = 5.3\sim 5.85\text{ mA/cm}^2$, $V_{\text{oc}} = 0.61\sim 0.71\text{ V}$, $FF = 0.36\sim 0.38$, and overall conversion efficiency $\eta = 1.2\sim 1.5\%$ under AM 1.5 illumination. The relatively small J_{sc} is resulted from low dye loading amount of the nanowire film, as shown in Figure 2.16. It demonstrates that, for the same J_{sc} of 6 mA/cm^2 ,

the dye loading amount of ZnO nanowire film with a thickness of 18~24 μm is comparable with that of conventional TiO_2 nanoparticle film with a thickness of only 2.2 μm . This can be attributed to the large diameter of ZnO nanowire (i.e., 130~200 nm) in comparison to the conventional TiO_2 nanoparticle size of 15~20 nm, leading to much lower surface area for dye adsorption. On the other hand, the comparable J_{sc} also implies the desirable electron transport property in nanowire structure. The poor FF exhibits great potential for further improvement of this DSSC architecture, and it is robust with respect to alteration of the nanowire electrical properties and electrolyte concentration.

Considering the superior electron injection and transport properties but relatively low dye loading ability of the nanowire structure that discussed above, the nanotube architecture is proposed as a result of similar configuration while with much higher surface area induced by additional interior tube surface. Conventional methods for TiO_2 nanotube preparation include hydrothermal, sol-gel, template synthesis, and so forth. However, the nanotubes fabricated by these methods are unsuitable for application in DSSCs. Titania nanotubes prepared by hydrothermal and sol-gel methods are generally randomly packed with limited length. And the fabrication process needs to be prosecuted in rigorous conditions and is time consuming. The template-assisted method requires porous alumina or polymer as the template; moreover, the dimension of the tubes is restricted and determined by the original template features, thus resulting in limited output and bad patterns.

Figure 2.16 Comparative performance of nanowire and nanoparticle cells.^[16]

Figure 2.17 is the transmission electron microscopy (TEM) images of TiO_2 nanotubes prepared by sol-gel method.^[106] The disordered nanotubes with closed (see Figure 2.17 (b)) or open (see Figure 2.17 (c)) tips are visible. Employing these tubes as photoanode, Flores and co-workers demonstrated an efficiency of $\eta = 5.64\%$ (under light intensity 100 mW/cm^2) with $J_{\text{sc}} = 12.47 \text{ mA/cm}^2$, $V_{\text{oc}} = 0.829 \text{ V}$, and $FF = 0.55$. Although the morphology of the nanotubes is disordered, the J_{sc} and V_{oc} are still highly promoted compared to nanoparticle based DSSCs. The superior performance is attributed to the high surface area of the photoanode that allowing more ruthenium dyes to be anchored to the oxide surface and creating ample ion path for fast ionic motion from the bulk to the inner parts of the film. The outstanding property of electron transport of TiO_2 nanotube photoanode also renders an intriguing alternative for more efficient solid-state DSSCs. However, the randomly packed structure is undesirable in view of electron scattering at the connections between tubes. Nevertheless, the uncontrollable tip features are not preferred either.

Figure 2.17 TEM images of the TiO_2 nanotubes prepared by sol-gel method at different magnifications.^[106]

Figure 2.18 is the scanning electron microscopy image of ZnO nanotubes fabricated by template-assisted synthesis, based on commercially available 60- μm -thick anodic aluminum oxide (AAO) membrane as the template.^[107] The nominally 60 μm thick membrane with 200 nm pores was coated with ZnO by atomic layer deposition (ALD) and then 1 μm thick electrode composed of transparent conducting aluminum-doped zinc oxide was deposited on one side of the membrane by ALD. The membrane was subsequently applied to assemble DSSCs as the photoanode. The most efficient cell with 7 nm thick ZnO nanotubes, deposited on the pore wall, exhibited a performance of $J_{\text{sc}} = 3.3 \text{ mA/cm}^2$, $V_{\text{oc}} = 0.739 \text{ V}$, $FF = 0.64$, and $\eta = 1.6\%$ under light intensity 100 mW/cm^2 . Obviously the lower J_{sc} has limited the cell performance, which originates from the low dye loading ability due to large pore diameter and the low charge collection efficiency owing to the large thickness of the photoanode. It is evident that the two limiting factors seriously depend on the initial template properties.

Figure 2.18 SEM images of ZnO nanotube photoanode prepared by template synthesis. (a) Cross-sectional SEM image of commercial anodic aluminum oxide membrane face coated with transparent conductive oxide AZO. (b) Cross-sectional SEM image of commercial AAO membrane pores coated with 20 nm of ZnO by atomic layer deposition.^[107]

In contrast, titania nanotube arrays prepared by electrochemical anodization exhibit highly ordered alignment that perpendicular to the substrate and controllable tube geometry (see Section 2.1.2 for more details). All these are desirable virtues for application in dye-sensitized solar cells, making it of considerable scientific interest as well as practical importance. To date, dye-sensitized solar cells based on anodic nanotubes have two major configurations:^[30] frontside and backside illumination. In frontside illumination, nanotubes are produced on a transparent conducting oxide, thereafter assembled into DSSCs, as illustrated in Figure 2.19 (a).^[31] This normally requires a number of complicated steps before the nanotubes can be used in DSSCs, for example, sputtering a titanium thin film onto the TCO glass and then growing the nanotubes,^[32] or growing the nanotubes first on a titanium foil, peeling off these nanotubes, and transferring onto the TCO glass.^[108, 109] Since light can enter directly from the TCO substrate, this kind of DSSC is termed as the front-side illuminated DSSC. In backside illumination, nanotubes are directly grown on commercial titanium foils and assembled into DSSCs, as shown in Figure 2.19 (b).^[33] As the opaque

nature of the substrate (usually with a thickness of 100 or 250 μm), illumination needs to perform from the platinized counter electrode, on top of the nanotube array. This type of DSSC is termed as back-side illuminated DSSC.

Mor and co-workers ^[31] prepared highly ordered TiO_2 nanotube arrays (46 nm in pore diameter, 17 nm in wall thickness, 360 nm in length) by means of anodic oxidation of titanium thin film sputtered on the FTO. Thereafter, front-side illuminated DSSCs were obtained using these nanotube arrays as the photoanodes. The front-side illuminated DSSCs presented J_{sc} of 7.87 mA/cm^2 , V_{oc} of 0.75 V and FF of 0.49, with an overall conversion efficiency of $\eta = 2.9\%$ under light intensity 100 mW/cm^2 . It is necessary to highlight that the length of the nanotubes is only 0.36 μm , whereas the performance of photovoltaic device is superior to that of the 60- μm -thick ZnO nanotube DSSCs prepared by template synthesis that presented above. The low J_{sc} is attributed to the short tube length with less dye loadings, while the low FF is due to the inevitable barrier layer and poor contact between barrier layer and FTO substrate. In comparison to conventional TiO_2 nanoparticle based DSSCs, the nanotube photoanodes effectively suppress the recombination, thus giving rise to higher V_{oc} . The longer lifetimes also indicate fewer recombination centers in the nanotubular films. Therefore, the highly oriented architecture allows for improved charge separation and transport properties as compared to conventional nanoparticle DSSCs, while comparable dye loadings are achievable if the tubes are long enough.

Figure 2.19 Schematic diagram of anodic TiO_2 nanotube-based DSSCs: (a) Front-side illuminated type, cell components from top to bottom in the sequence of the arrows: Counter Electrode: FTO sputtered with 25 nm platinum, I^-/I_3^- electrolyte, N-719 sensitized TiO_2 nanotubes, TiO_2 barrier layer, FTO glass substrate; (b) back-side illuminated type, cell components from top to bottom in the sequence of the arrows: Conducting glass sputtered with 0.8 nm platinum, I^-/I_3^- electrolyte, N-719 sensitized TiO_2 nanotubes, TiO_2 barrier layer, Ti metal substrate.^[30]

Zhu and co-workers^[17] investigated the back-side illuminated DSSCs. The obtained nanotube arrays have the following features: several micrometers in length, 8~10 nm in wall thicknesses and intertube spaces, 30 nm in pore diameter. Dye molecules are found to cover both the interior and exterior walls of the nanotubes. Besides improved electron transport and suppressed recombination, the authors demonstrate that strong internal light-scattering effect is discovered in nanotube based DSSCs, which improves the light-harvesting efficiency.

These two examples reveal that tube geometry affects the photovoltaic characteristics significantly. Therefore, to achieve light harvesting as well as high conversion efficiency, the effect of tube geometry on performance of dye-sensitized solar cells is subsequently discussed in Section 2.2.4.

2.2.4 Effect of Nanotube Geometry on Performance of Dye-Sensitized Solar Cells

The nanotube arrays as the photoanodes eliminate the particle-to-particle contacts necessary in the randomly packed configuration for electron transport. This largely reduces electron scattering at the joining points.^[106, 110] In nanotubes, usually the grains are stretched in the tube growth direction. This further decreases possible electron losses at grain boundaries.^[111-114] Other obvious benefit in nanotube photoanode includes vectorial transport of electrons to minimize trapping/detrapping events before collection.^[111, 112, 115] In the case of anodic nanotube array, a barrier layer exists between the photoanode and the collecting electrode. Electrons collected are thus separated from the redox couple (e.g., I^-/I_3^- couple) in the electrolyte,^[33, 110] making it impossible for further recombination. However, performance of the nanotube array based DSSCs is greatly affected by the tube geometry. This section dissects this geometry to look into the details of the influence of wall thickness, tube length, pore diameter, and intertube spacing to cast light into better design for high efficiency.

2.2.4.1 Wall Thickness

The initial chemical potential of electrons in a semiconductor and an electrolyte is determined by Fermi level of the semiconductor and redox potential of the redox couples in the electrolyte, respectively. When the semiconductor is submerged in the electrolyte and the initial chemical potential of the electrons is different for the two phases, a space charge layer (also called a depletion layer) develops in the semiconductor adjacent to the electrolyte, and a Helmholtz layer^[116, 117] forms in the electrolyte in contact with the semiconductor. As illustrated below, in the case of TiO_2 nanoparticles, the size (usually in the range of 15~20 nm) of the particle is too small to support the space charge layer.^[16, 99, 118, 119]

The width of the space charge layer in the semiconductor can be determined by ^[116]

$$w = \sqrt{\frac{2\epsilon\epsilon_0 V_B}{qN}} \quad (2.15)$$

where ϵ is the dielectric constant of the semiconductor, ϵ_0 is the permittivity of free space, q is the electronic charge, N is the charge carrier concentration in the semiconductor, and V_B is the amount of band bending in the depletion layer. The value of V_B is given by ^[116]

$$V_B = U - U_{fb} \quad (2.16)$$

Here U is the electrode potential (Fermi level) of the semiconductor, and U_{fb} is the flat-band potential of the semiconductor. For titanium dioxide with anatase structure which is widely employed in the conventional DSSCs, the width of space charge layer is about 15~20 nm, using $\epsilon = 31$, ^[120, 121] $N = 10^{18} \sim 10^{19} \text{ cm}^{-3}$, ^[120-122] $U = -4.2 \text{ eV}$ (quasi-Fermi level of anatase TiO_2 under illumination), ^[123, 124] and U_{fb} (usually depends on pH value of the electrolyte). ^[122, 125-128] Consequently, the size of a TiO_2 particle must be at least 30~40 nm to support space charge layer in the particle.

Now consider the photoanode of highly oriented TiO_2 nanotube array. If the wall thickness of the nanotube exceeds the critical value estimated above, the space charge layer forms. As a result, the conduction and valence band edges are upwardly bent ^[119] so that potential barriers are created near both inner and outer surfaces of the tubes against further electron transfer into the redox couples in the electrolyte, ^[116, 117] as shown in Figure 2.20 (a). Once the electrons are injected into this “high speed lane” by dye molecules, they are confined in because of the potential barrier and move away from the source of the electron generation to form the drift current. This results in high J_{sc} and V_{oc} . Figure 2.20 (c) depicts the illumination

process at a DSSC with a photoanode of nanotube array, where the light illuminates through a TCO layer to be absorbed in the nanotube array.

In the event that the nanotube wall becomes too thin to support the space charge layer, negligibly small or even no band bending occurs,^[119] the “high speed lane” will not form. In this case, cations in the electrolyte are adsorbed on the surfaces of the nanotubes ^[5, 129, 130] (i.e., Helmholtz layer) leading to increased recombination between the electrons in the channel and the triiodide in the electrolyte, as illustrated Figure 2.20 (b). Consequently, the electron transport degrades to that in the photoanode based on nanoparticles. The electron transport is thus a diffusion process (as in contrast to the drift process in the case of existence of space charge layer), which can be explained by random walk model.^[89, 115, 131]

Figure 2.20 Schematic diagram of electron percolation in a thick-walled (a) and thin-walled (b) nanotube, and its corresponding band structure as well as line of electric force in the cell. (c) Instruction of the symbols and presentation of the 3D structure of the cell as well as the circuit under illumination.

Zhu and co-workers^[17] were surprised that the electron transport in the photoanode of highly oriented anodic TiO₂ nanotube array was comparable with that in the randomly packed TiO₂ nanoparticles, as shown in Figure 2.21 (a). In fact, the wall thickness of their tubes is about 8 nm and the size of the particles is around 24 nm. As discussed afore, the existence of the space charge layer needs a particle or wall thickness of at least 30 to 40 nm. Obviously, the tube wall thickness and particle size are both below this critical size. As such, no “high speed lane” forms, electron transport in both cases is dominated by the same diffusion process, resulting in comparable electron transport. Similar phenomena were reported in TiO₂ nanotubes prepared by sol-gel (10 nm in diameter),^[112] randomly oriented nanowire (diameter of about 20 nm),^[132] and nanoparticle-fused nanorod (effective diameter less than 5 nm)^[111] structures. All these cells did not show advantage of electron transport over nanoparticles, most likely because of nonexistence of the space charge layer due to small size.

Figure 2.21 (a) Comparison of transport time constants for nanotube and nanoparticle based DSSCs as a function of the incident photon flux. (b) Transport (IMPS, solid symbols) and recombination (IMVS, open symbols) time constants for dye-sensitized nanotube films of various thicknesses as a function of the incident photon flux. The film thicknesses are (a) 1.9 μm ($\bullet$, $\circ$), (b) 3.2 μm ($\blacksquare$, $\square$), (c) 4.3 μm ($\blacktriangle$, $\triangle$), (d) 5.7 μm ($\blacktriangledown$, $\triangledown$).^[17]

Even without the “high speed lane”, thicker nanotube walls give rise to higher open-circuit voltage, as revealed in Table 2.1. It puts together the geometries of various TiO₂ nanotube array based DSSCs and their performances. The following observations are highlighted:

1. There seems no direct relationship between the open circuit voltage and the length of the tubes (V_{oc} vs L).
2. The pore diameters varied from about 30 to 130 nm while the open circuit voltage only varied from 0.6 to 0.8 V. Thus the pore diameter does not affect V_{oc} noticeably.
3. The influence of the wall thickness can be extracted from separating the cells into two groups: group I with the same wall thickness of 8 nm (cell # 2, 3, 4 and 5), and Group II with thickness more than its double, i.e., 17 to 24 nm (cell # 1, 6, 7 and 8). Although the wall thickness of both groups is below the critical thickness (30 nm) for “high speed lane” formation, thicker walled nanotubes still result in higher open-circuit voltage (0.8 V vs 0.6 V), as a result of lower chances of electrons interfacing with redox electrolyte thus lower chances of recombination.
4. Cell # 11 achieved very high current density (16 mA/cm²). However, it only achieved a conversion efficiency of 4.8%, likely due to its thin wall thickness (20 nm) which restricted the open-circuit voltage (only 0.43 V).

To allow fast and uninterrupted transportation of electrons through the nanotube, it is crucial that the tube wall is thick enough for the space charge layer to form.

Table 2.1 Performance of DSSCs with TiO₂ Nanotube Array Photoanodes ^a

Cell No.	<i>L</i> (μm)	<i>T</i> (nm)	<i>D</i> (nm)	<i>J</i> _{sc} (mA/cm ²)	<i>V</i> _{oc} (V)	<i>FF</i>	<i>η</i> (%)	Ref.
Back-Side Illumination								
1	0.36	17±2	46±8	2.40	0.786	0.69	1.3	¹¹⁰
2	1.9	8±1	30±4	4.4	0.64	0.60	1.7	¹⁷
3	3.2	8±1	30±4	6.6	0.63	0.58	2.4	¹⁷
4	4.3	8±1	30±4	7.8	0.61	0.57	2.7	¹⁷
5	5.7	8±1	30±4	9.0	0.61	0.55	3.0	¹⁷
6	6±0.3	20	110	8.79	0.84	0.57	4.24	³³
7	6.2±0.3	20±2	110±10	10.6	0.82	0.51	4.4	¹¹⁰
8	20	24	132	12.72	0.817	0.663	6.89	¹⁹
Front-Side Illumination								
9	0.36	17±2	46±8	7.87	0.75	0.49	2.9	³¹
10	3.6	17	46	10.3	0.84	0.54	4.7	¹¹⁰
11	5	20	100	16	0.43	0.70	4.8	¹³³

^a(Cell # 1~10 by electrochemical anodization, Cell # 11 by template-assisted method)

L: tube length; *T*: wall thickness; *D*: pore diameter;

*J*_{sc}: short-circuit current density; *V*_{oc}: open-circuit voltage; *FF*: fill factor;

η: overall conversion efficiency

2.2.4.2 Tube Length

Table 2.1 shows that the short-circuit current density (from 2.4 to about 13 mA/cm²) and the overall conversion efficiency increase (from 1.3% to about 7%) with the tube length (from about 0.4 to 20 μm). This is resulted from the increment in dye loading amount.

To obtain high conversion efficiency, the electrons injected into the conduction band of the TiO₂ photoanode should be collected as many as possible. A key parameter determining this process is the electron diffusion length (see Equation 2.11). Effective collection of electrons can be realized only when the electron diffusion length is larger than the film thickness (or tube length), as given by Equation 2.10. In a typical TiO₂ nanoparticle photoanode, the optimal film thickness is about 10 μm,^[90] that is

$$L_{NP} = 10\mu\text{m} \quad (2.17)$$

Figure 2.21 (b) displays virtually no change in electron transport time as the tube length changes from 1.9 to 5.7 μm. As discussed in Section 2.2.4.1, under thin-walled condition, the electron transport time (τ_c) is about the same in nanoparticle-based DSSCs (cf., Figure 2.21 (a)), which can be expressed as^[115]

$$\tau_c \approx L^2 / 2.35D_n \quad (2.18)$$

Therefore, the electron diffusion coefficient in nanotubes is to some extent similar to that in nanoparticles. Based on the results of Zhu and co-workers,^[17] the recombination time in nanotubes is an order of magnitude (10 times) greater than that in nanoparticles (similar result was also obtained in nanorod structure^[111]). If so, Equation 2.11 thus gives rise to the electron diffusion length in nanotubes being $\sqrt{10}$ times that in a typical nanoparticle

photoanode. As such, using Equations 2.11 and 2.17, the optimal length of TiO_2 nanotubes (L_{NT}) should be around

$$L_{\text{NT}} = \sqrt{10}L_{\text{NP}} = \sqrt{10} \times 10 \mu\text{m} \approx 30 \mu\text{m} \quad (2.19)$$

Shankar and co-workers^[19] suggested the optimal nanotube length is nominally 20 μm (cell # 8 in Table 2.1). Kim and co-workers^[134] assembled nanotube array based DSSCs with different lengths, as shown in Table 2.2. Maximum conversion efficiency seems to be with nanotube length of close to 30 μm . An evaluation of the photocurrent for dye-sensitized TiO_2 nanotube arrays,^[53] as displayed in Figure 2.22, also indicates that the maximum photocurrent occurs at close to tube length of $\sim 30 \mu\text{m}$.

Table 2.2 Performance of DSSCs with Different Nanotube Lengths^[134]

	L (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
NT	10	7.77	0.65	0.458	2.33
NT	20	9.62	0.66	0.450	2.88
NT	30	10.40	0.64	0.430	2.87
NGF-NT	10	7.52	0.71	0.539	2.87
NGF-NT	20	8.56	0.69	0.516	3.05
NGF-NT	30	9.39	0.67	0.468	2.94

It is noteworthy that the optimal nanotube length of about 30 μm discussed afore is based on back-side illuminated DSSCs. Usually back-side illuminated DSSCs have much lower

efficiency than the front-side illuminated counterpart. For example, cells # 1 and 9 in Table 2.1 have the same geometry, but # 1 is back-side illuminated and # 9 is front-side illuminated. Cell # 9 has much higher short-circuit current density (7.87 mA/cm^2 vs. 2.4 mA/cm^2) and much higher conversion efficiency (2.9% vs. 1.3%), which is more than 2-fold increase in efficiency.

Figure 2.22 Photocurrent evaluation of the dye-sensitized nanotube layers grown to different tube length based on the photocurrent transients at 650 nm.^[53]

The lower efficiency of the backside illumination type originates from the following drawbacks: (1) energy loss due to reflection and absorption by the platinized counter electrode; (2) absorption of the photon energy by the iodine in the electrolyte^[33, 110] before reaching the nanotube array; (3) after the electrons are generated, they have to travel all the way through the photoanode to reach the collecting electrode. The increased distance of travel drastically increased the chances of recombination. In contrast, front-side illumination has the advantage of not having the above problems. In addition, since there is no such loss

of photon energy, the electron density in the front-side illuminated photoanode is much higher under light soaking. As such, some of the electrons fall into the trapping states in the bandgap of the oxide, paving way for other electrons to move more freely. Since the traps that participate in the electron motion affect the value of the diffusion coefficient,^[5] the reduction of quantity of traps results in increase in the electron diffusion coefficient D_n . As illustrated in Equation 2.11, the electron diffusion length L_n is also related to electron lifetime τ_n . According to Paulose and co-workers,^[110] the electron lifetime for both illumination types is comparable. Consequently, the electron diffusion length in front-side illuminated photoanode should be larger than that in back-side illuminated architecture, which in turn, gives rise to longer optimal tube length. One recent estimation of the electron diffusion length suggests that the optimal tube length is in the order of 100 μm in TiO_2 nanotube array based DSSCs,^[37] using a method taking into account the fact that the occupancies of electron traps are substantially different under open-circuit and short-circuit conditions.

2.2.4.3 Pore Diameter and Intertube Spacing

The pore diameter and intertube spacing have significant influence on surface roughness factor and porosity of nanotube arrays,^[17, 19] thus affecting the performance of dye-sensitized solar cells. The anodic nanotubes have a unique close-end structure in which air may be trapped in during dye loading and electrolyte injection. This is more serious in the case of nanotubes with small pore diameters. Conventional nanoparticles used in DSSCs are of 15~20 nm in diameter, which gives rise to very large surface area for possible generation of electrons. In nanotube arrays, however, the surface area is drastically reduced due to the tube structure and it becomes worse when large pore diameter tubes are used.

Compared to other one-dimensional nanostructures, nanotubes have inner tube surface available for dye loading thus capable of producing more electrons to inject into the photoanode. The outer surface, however, may not be completely available for dye loading. This happens when the tubes are touching one another to form a strand or bundle of tubes.^[27] In this case, the dye molecules and redox electrolyte will not be able to wet each of the nanotube, thus drastically reduce the effective dye loading area. This, in turn, reduces the overall conversion efficiency, as illustrated in Table 2.3. Ideally, the each individual tube should stand alone leaving enough space to facilitate infiltration of dye molecules and electrolyte as well as faster electron transportation.

Table 2.3 Performance of DSSCs with Bundle and Bundle-Free Nanotube Structure^[27]

	L (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
bundle structure	6.1	4.9	0.60	0.53	1.6
bundle-free structure	6.1	5.7	0.58	0.56	1.9

Roughness of the outer surface of the nanotubes also affects the efficiency in DSSCs. The bamboo-type nanotubes prepared by modulating electrochemical anodization process,^[28] as displayed in Figure 2.23, results in increased short-circuit current density ($8.76 \text{ mA}/\text{cm}^2$ vs. $5.93 \text{ mA}/\text{cm}^2$) and overall conversion efficiency (2.96% vs. 1.90%) as compared to smooth nanotube outer surface. This is because of the increased dye loading amount per unit volume of the photoanode. The additional area provided by the bamboo rings may allow both inner and outer surfaces to be covered by dye molecules as well.^[28]

Figure 2.23 SEM images of anodized TiO₂ nanotube array with smooth wall (a), and bamboo-type wall (b) and (c).^[28]

2.2.4.4 Summary

This section reviews the effect of anodic nanotube geometry on the performance of dye-sensitized solar cells. The following points are worth highlighting:

1. There seems to exist a critical wall thickness for fast electron transportation. The critical thickness comes from the formation of the space charge layer. If the wall is too thin to support this layer, the electron transport will be degraded to that of the nanoparticle case. The estimated critical wall thickness is about 30 to 40 nm.
2. There also exists an optimal nanotube length for optimal electron collection in consideration of dye loading capacity and electron diffusion length. In back-side illuminated dye-sensitized solar cells, the optimal length is close to 30 μm . Under front-side illumination, the value could even be a lot greater.
3. The pore diameter should be as small as possible to increase surface area and the nanotubes should ideally be free of bundling to facilitate dye and electrolyte infiltration.

2.2.5 Crystallization of Nanotubes for Dye-Sensitized Solar Cells

Titania minerals have three crystallographic structures: anatase, rutile, and brookite. It is widely recognized that the anatase structure is preferred for application in dye-sensitized solar cells, especially for the one with exposed facets having (101) orientation.^[5] Because the anatase structure exhibits superior photocatalytic properties while the lowest energy surface of (101) orientation is desirable for dye adsorption. In the case of anodic nanotubes, generally the as-grown tubes are amorphous, though anatase tubes are obtainable directly in a strong oxidizing electrolyte with certain surface treatment prior to anodization.^[135, 136] Therefore, thermal annealing is required to crystallize the nanotubes into anatase phase for DSSC application. The crystallinity closely related to the annealing conditions influence the cell performance through the following aspects: preferential exposed facets, surface defects, bulk defects. The exposed facets determine the dye loading amount and hence the photocurrent. The surface defects affect electron transfer and recombination by incorporating electron trapping sites in the band gap of anatase TiO_2 , and also the dye adsorption. The bulk defects influence electron transport in the photoanode. In view of these, the crystallization of anodic nanotubes is reviewed in this section for application in dye-sensitized solar cells.

In 2003, Varghese and co-workers reported the crystallization and structural stability of TiO_2 nanotube arrays with a length of approximately 400 nm.^[137] The results show that the amorphous tubes start to crystallize into anatase at $\sim 280^\circ\text{C}$ and transform from anatase to rutile at $\sim 480^\circ\text{C}$ in a dry oxygen environment. The transformation completes at $\sim 620^\circ\text{C}$ in dry oxygen and $\sim 570^\circ\text{C}$ in humid argon. A model is proposed to interpret the transformation process. The rutile crystals nucleate at around 430°C at the TiO_2/Ti interface, and grow at

higher temperature especially for the anatase crystals in the tube walls contacting with the rutile crystals at the interface region. This model was confirmed further by Yang *et al.* who studied the crystallization of the nanotube arrays with a length of $\sim 4\ \mu\text{m}$.^[138] They found that the tube length decreases with elevated temperature and in the meanwhile a relatively compact layer thickens gradually between Ti substrate and the tubes. This is attributed to the transformation from anatase to rutile structure for the anatase crystals in contact with the rutile crystals at the interface region. The above results indicate that the titanium metal substrate plays an important part in the transformation process. Accordingly, more stable anatase tubes are attainable in the absence of the substrate. This was consolidated when annealing the nanotube membranes (i.e., without titanium substrate) which retained an anatase structure up to $800\ ^\circ\text{C}$.^[139] All of the above results reveal that a pure anatase phase forms between $280\ ^\circ\text{C}$ and $480\ ^\circ\text{C}$ while a rutile phase starts to nucleate at a temperature above $480\ ^\circ\text{C}$. As a consequence, the annealing temperature between $280\ ^\circ\text{C}$ and $480\ ^\circ\text{C}$ can be used for DSSC application in view of the preference of anatase phase. However, more factors affecting the cell performance should be considered when determining an exact temperature to be adopted, as will be discussed below.

Zhu *et al.* investigated the effect of annealing temperature on the charge collection and light harvesting properties of nanotube photoanodes in dye-sensitized solar cells.^[140] The $2\text{-}\mu\text{m}$ -thick tubes present amorphous features at $200\ ^\circ\text{C}$, only anatase phases at $300\ ^\circ\text{C}$ and $400\ ^\circ\text{C}$, and a mixed structure of anatase and rutile at $500\ ^\circ\text{C}$ and $600\ ^\circ\text{C}$. These phenomena are consistent with the previous reports and significantly affect the dye loading amount of the nanotubes. Figure 2.24 shows that the dye loading amount increases with the annealing temperature from $200\ ^\circ\text{C}$ to $300\ ^\circ\text{C}$ due to enhanced crystallinity of anatase phase, keeps

nearly constant from 300 °C to 400 °C, while drops above 400 °C due to the emergence of rutile phase. This indicates that anatase structure with high crystallinity is favored for dye adsorption, thus explaining the dependence of annealing sequence on dye loading.^[141] Figure 2.24 also reveals that the short-circuit current density of the tubes annealed at 400 °C is higher than that at 300 °C even though both tubes have similar dye loading amount. This is partially attributed to the higher crystallinity which, in turn, results in fewer defects (both surface and bulk defects) in the tubes and thus leads to superior electron transport and slower recombination. The electron diffusion coefficient and recombination current density are subsequently analyzed with reference to the annealing temperature, which exhibits the best performance for the tubes annealed at 400 °C. One recent report shows that higher crystallinity can be obtained with an ethanol vapor treatment and increases the photoelectrochemical performance as well.^[142]

Figure 2.24 Dependence of the short-circuit photocurrent density and dye loading on annealing temperatures of nanotube films used in DSSCs illuminated with 680 nm laser light.^[140]

The crystallites in the tube walls are usually oriented along the length rather than across the thickness.^[137] This on the other hand gives rise to a vectorial electron transport in the tubes, and reduces electron trapping and detrapping events before being collected. In addition, the crystallite size in the tube walls is reported to be at least 50 nm in length with (101) facets,^[17, 137, 140] which is about twice the crystallite size of commonly used P25 nanoparticles. As a result, the grain boundaries in the tubes are significantly reduced, thereby facilitating electron transport.

On the basis of the above discussion, an annealing temperature of 450 °C is used in this work considering both the tube length and cell performance.

Chapter 3 Methodology

3.1 Challenges and Proposal

To date, the highest efficiencies achieved by dye-sensitized solar cells based on titania nanoparticles are ~11%.^[8-11, 143] Whereas the most efficient DSSCs based on anodic titania nanotube arrays are ~7%.^[19, 32, 144] It is expected that performance of the latter should be better as a result of superior electron transport and suppressed recombination behaviors. However, the use of the nanotubes is not as efficient as that of the nanoparticles. Table 2.1 reveals that the cell performance is greatly restricted by the low photocurrent (i.e., ~13 mA/cm² vs. >20 mA/cm² for nanotubes with respect to nanoparticle). In Section 2.2.2, the factors influencing the photocurrent are dissected. It shows that, under constant incident photon flux density, the photocurrent of a dye-sensitized solar cell is determined by the following parameters: $r(\lambda)$, Γ , σ , ϕ_{nj} , and η_{cc} . Two of these parameters are related to the photoanode, that is, the dye loading amount per projected surface area of the photoanode (Γ) and the charge collecting efficiency (η_{cc}). Zhu and co-workers^[17] reported that the η_{cc} in the nanotubes is improved by 25% as compared to the nanoparticles. As such, it is the Γ that limits the photocurrent in the DSSCs based on the nanotubes, which in turn is directly related to the surface area of the photoanode.

To illustrate this point, surface areas of nanoparticle and nanotube photoanodes are calculated based on the following assumptions: (1) the nanoparticles are sphere and the nanotubes are regular cylindrical tube; (2) the wall thickness and bottom area of the nanotubes are negligible; (3) the contact areas between nanoparticles or nanotubes are ignored.

The face-centered cubic (FCC) structure is the most closely packed form of spheres in the space with $ABCABC\dots$ sequence, as illustrated in Figure 3.1 (a). In this architecture, the packing factor of nanoparticles (η_{NP}) can be calculated as

$$n = \frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4 \quad (3.1)$$

$$4r = \sqrt{2}a \quad (3.2)$$

$$\eta_{NP} = \frac{V_{NP}}{V} = \frac{\frac{4}{3}\pi r^3 \cdot n}{a^3} = 74.05\% \quad (3.3)$$

Here n is the number of nanoparticles in a unit cell, r is the radius of a nanoparticle, a is the lattice constant of the unit cell. As for nanotubes, the space arrangement can only be $ABABAB\dots$ sequence, as shown in Figure 3.1 (b). To facilitate further calculation, the packing factor of nanotubes (η_{NT}) is calculated assuming that the inner tube is solid instead of hollow (i.e., nanorod structure),

$$n = 1 + \frac{1}{3} \times 6 = 3 \quad (3.4)$$

$$2R = a \quad (3.5)$$

$$\eta_{NT} = \frac{V_{NT}}{V} = \frac{\pi R^2 h \cdot n}{\frac{\sqrt{3}}{4} a^2 \cdot 6 \cdot h} = 90.69\% \quad (3.6)$$

where n is the number of solid nanotubes (i.e., nanorods) in a hexagonal column (see dashed line in Figure 3.1 (b)), R is the radius of a nanotube, a is the lattice constant of the hexagonal unit cell, h is the height of the column.

Figure 3.1 (a) Face-centered cubic structure of close packed nanoparticles; (b) hexagonal close packed structure of ideal nanotube arrays.

The key point concerned herein is how to obtain comparable surface areas of nanoparticle and nanotube photoanodes under the same volume. Assuming there are x nanoparticles and y nanotubes in the respective photoanode under the same volume V , therefore

$$\frac{4}{3}\pi r^3 \cdot x = \eta_{\text{NP}} V = 74.05\% V \quad (\text{for nanoparticles}) \quad (3.7)$$

$$\pi R^2 h \cdot y = \eta_{\text{NT}} V = 90.69\% V \quad (\text{for nanotubes}) \quad (3.8)$$

$$4\pi r^2 \cdot x = 2\pi R \cdot h \cdot 2 \cdot y \quad (\text{for the same surface area}) \quad (3.9)$$

Equation 3.9 denotes that x nanoparticles and y nanotubes have the same surface area. Note that the second number 2 on the right of the equation originates from the two surfaces (both inner and outer surfaces) of each nanotube. On the basis of Equations 3.7–3.9, the following relation can be attained

$$\frac{r}{R} \approx \frac{3}{5} \quad (3.10)$$

Equation 3.10 indicates that, to obtain comparable surface areas between nanoparticle and nanotube photoanodes under the same photoanode volume, the radius ratio has to be 3:5 for a single particle with respect to a single tube. In conventional titania nanoparticle based dye-sensitized solar cells, the particle size is normally in the range of 15~20 nm. Taking the particle size of 18 nm for example, it requires the tube diameter to go down to 30 nm to generate comparable surface area. As discussed in Section 2.1.2.1, both inner and outer diameters of the anodic nanotubes decrease with applied potential. The small diameter (e.g., 30 nm) can only be achieved under a low potential (e.g., < 20 V). On the other hand, the growth rate decreases drastically at such a low potential. In other words, it is difficult to produce anodic nanotubes of 30 nm in diameter with enough length (e.g., 30 μm as discussed in Section 2.2.4.2). This is reflected in Table 2.1 where most nanotubes used in DSSCs are larger than 30 nm in diameter. Even though the required 30 nm is achieved, the utilization of both inner and outer nanotube surfaces remains another challenging issue, as shown in Section 2.2.4.3. In view of these factors, in general, the effective surface area per unit volume of photoanode is relatively small for nanotubes as compared to the nanoparticles, thus resulting in less dye loading amount which, in turn, gives rise to low photocurrent and low conversion efficiency.

The above discussion is based on the calculation without taking into account the nanotube wall thickness and bottom area (i.e., assumption # 2). If these factors are considered, in the case of funnel shaped tube inner walls,^[20, 64, 145, 146] Equation 3.10 becomes

$$\frac{r}{R} > \frac{3}{5} \quad (3.11)$$

This is because the second number 2 on the right of the Equation 3.9 should be substituted with a relatively smaller number due to reduced inner tube surface area. In this scenario, it requires even smaller tube diameter to generate comparable surface area with reference to the conventional nanoparticle photoanode, which is even more difficult to achieve.

As such, the key challenge in dye-sensitized solar cells based on anodic nanotubes is to promote the dye loading amount of the photoanode and hence increase the photocurrent and eventually the conversion efficiency. This can be achieved by enlarging the surface area available for dye adsorption in the photoanode. In view of this, the following architecture of a dye-sensitized solar cell is proposed in this project, as illustrated in Figure 3.2. The double-sided nanotubes separated by a layer of titanium metal are sandwiched between two platinized counter electrodes, thus rendering a natural parallel cell structure after electrolyte injection. This configuration makes full use of both surfaces of a photoanode, therefore significantly increases the dye loading amount of the photoanode, which is the determining figure of merit for the photocurrent. In application, the light source directly illuminates one side of the cell while a dielectric mirror is adopted to reflect the light onto the other side. In practice, this can be easily done (Mirrors and even lenses are already used in concentrator solar cells to concentrate sunlight onto the photovoltaic cells.^[147, 148]).

In this proposal, titania nanotube arrays are produced on both sides of a titanium foil and then assembled into dye-sensitized solar cells. In principle, the dye loading amount of the photoanode is two times larger than that of the normal single-sided nanotubes, provided that the tube length at both sides is comparable, hence will give rise to at least 100% increase in photocurrent. At the same time, the superior electron transport and suppressed recombination

properties are maintained in the nanotubes. As a consequence, the cell performance will be highly promoted.

Figure 3.2 Schematic diagram of a parallel configuration dye-sensitized solar cell with double-sided nanotube arrays. Cell components (from left to right): FTO-Pt/electrolyte/dye-nanotubes/Ti/nanotubes-dye/electrolyte/Pt-FTO. A dielectric mirror (M, $\Phi 2''$, which is much larger than the active area of the solar cells) is used for light reflection.

3.2 Project Overview

To achieve the cell structure that proposed in Figure 3.2, the initial requirement is to prepare the double-sided nanotube arrays which are adopted as the photoanodes of the solar cells. Therefore, the current project consists of two major parts: investigation of anodic nanotube growth and application of the nanotubes in dye-sensitized solar cells. In growth of the nanotubes, the tube geometry is first tailored by changing the electric field which is an essential factor affecting tube growth. Transition from anodic nanotubes to nanowires is studied for better tube morphology used in DSSCs. With these two fundamental work, the double-sided nanotube growth is investigated subsequently. Dye-sensitized solar cells are

assembled with both single and parallel configurations. The photovoltaic characteristics of the cells are explored. An overview of the project is given in Figure 3.3.

Figure 3.3 Overview of the current project

3.3 Experimental

In this section, detailed methods to grow and characterize the nanotubes, assemble and test the solar cells, calculate and determine the surface porosity are discussed in respective subsections.

3.3.1 Growth of Anodic Titania Nanotube Arrays

Electrochemical anodization was carried out using a typical two-electrode configuration, as illustrated in Figure 2.1, with a titanium foil as the working electrode and platinum gauze (100 mesh, 99.9% trace metals basis, Sigma-Aldrich) as the counter electrode. Prior to anodization, titanium foils (0.25 mm or 0.127 mm, 99.7% purity, Sigma-Aldrich) were cleaned ultrasonically in acetone, ethanol, and deionized (DI) water for 10 min each. The foils were then dried with air stream. The thickness used was dependent on the purpose, for example, the 0.25-mm foils were usually adopted to study the nanotube growth while the 0.127-mm foils were normally applied in assembling solar cells (the reasons will be discussed in Section 5.3). The anodizing electrolyte solution used was ethylene glycol (anhydrous, 99.8%, Sigma-Aldrich) with 0.3 wt.% ammonium fluoride (NH_4F , 98 + %, ACS reagent, Sigma-Aldrich) and 2 vol.% deionized water, unless otherwise indicated. After each run, fresh electrolyte was prepared and used for the next. A Keithley 2400 SourceMeter was employed as power supply for the anodization and to record current transients during the process. Target potentials were directly applied onto the electrodes without ramping. The distance between electrodes was controlled by a specially designed electrolytic cell (PMMA, 60 mm $\times$ 50 mm $\times$ 50 mm). Most experiments were performed at room temperature ($\sim 20^\circ\text{C}$) and some were at a designated temperature controlled by water bath ($\pm 0.25^\circ\text{C}$, PolyScience). All the experiments were carried out without stirring, unless otherwise highlighted. After each anodization, the sample was rinsed with DI water and dried in air. For use in dye-sensitized solar cells, the as-grown nanotubes were cleaned in deionized water ultrasonically for 20 min after anodization and dried in air (the reasons will be discussed in Section 4.3).

3.3.2 Assembly of Dye-Sensitized Solar Cells

For use in dye-sensitized solar cells, the as-grown nanotubes were annealed in air at 450° C for 3 h with heating and cooling rate of 5 °C min⁻¹. The TiCl₄ treatment was carried out in 40 mM aqueous solutions of titanium tetrachloride (TiCl₄, ~0.1 M in 20% HCl, Sigma-Aldrich) at 70 °C for different durations. The TiCl₄ solution prepared under ice-cooled condition was loaded into a closed vessel with one sample in partial vacuum each time. The resultant samples were annealed at 450 ° C for 30 min with heating and cooling rate of 5 °C min⁻¹. The UV-ozone treatment was conducted using a UV surface decontamination system (PSD-UV, Novascan) for 20 min.

The obtained nanotubes were sensitized with 0.3 mM N719 dye (*cis*-diisothiocyanato-bis(2, 2'-bipyridyl-4, 4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium), Solaronix) in acetonitrile/*tert*-butanol (1:1, v/v) solvent for 24 h at room temperature. The dye loading process was performed in partial vacuum. Transparent platinized counter electrodes were prepared by drop spreading a 0.6 M H₂PtCl₆/isopropanol solution on fluorine-doped tin oxide (15 Ω/sq) glass substrate, and followed by thermal decomposition at 400 °C for 15 min. For cell assembly, two counter electrodes were placed at each side of a sample. A hot-molten spacer (SX1170, Solaronix, 60 μm) was sandwiched between the sample and the counter electrode. Electrolyte solution (EL HPE, Dyesol) containing iodide/tri-iodide redox couple was introduced into the cells from one hole at the frontside (under partial vacuum) while two holes at the backside (under air pressure).

3.3.3 Characterization of Nanotubes and Testing of Solar Cells

The morphology of the nanotubes was characterized by field emission scanning electron microscope (FESEM, JEOL, JSM-6340F) at an acceleration voltage of 5.0 kV and working

distance of 8~10 mm. Some cross-sectional views with low magnification were obtained by scanning electron microscope (SEM, JEOL, JSM-5910LV) at an acceleration voltage of 15.0 kV and working distance of 16 mm. To examine the cross section by optical microscope, the nanotubes were first mounted in epoxy resin and ground with silicon carbide abrasive paper, and then polished with alumina suspension (BUEHLER, 0.05 μm) for a scratch free mirror surface.

The X-ray photoelectron spectroscopy (XPS, KRATOS, AXIS ULTRA) measurements were carried out by using a monochromated Al K α (1486.7 eV) X-ray source at power of 150 W (15 kV $\times$ 10 mA). The XPS analysis was performed at room temperature under a typical pressure in the range of $4.0 \times 10^{-7} \sim 8.0 \times 10^{-7}$ Pa, at take-off angle relative to the surface holder of 90°. A charge neutralizer was employed to neutralize charge accumulation during the analysis. All the spectra were referenced to the binding energy of C 1s peak (285.0 eV) arising from adventitious carbon. Prior to peak deconvolution, the inelastic background (Shirley-type) was subtracted. To obtain the concentrations at the tube surface and bottom (Section 4.1), each sample was measured before and after argon ion etching at 4.0 kV and 15 mA for 5 min to remove possible surface contaminants. Bottom concentration of the nanotubes was obtained by measuring the bottom sides of lift-off pieces. To make a comparison between nanowire and nanotube structures (Section 4.3), the XPS measurements were applied onto the surface of bulk nanowires and the cross section of the same lift-off nanotube membrane. Phase composition of the nanotubes was obtained by X-ray diffraction (XRD, Philips, PW1830).

The photocurrent-voltage characteristics were measured using an AM 1.5 solar simulator (Oriel, 300 W Xenon lamp) with an active area of 0.26 cm^2 . Dye desorption measurements were carried out by immersing the dye-sensitized samples in 3 ml of 0.1 mol L^{-1} NaOH solution in a mixed solvent (water/ethanol = 1:1, v/v) for 1 h, thereafter the UV-vis absorption spectrum of the resultant solution was measured to estimate the dye loading amount. Electrochemical impedance spectroscopy (EIS) measurements were conducted using an electrochemical workstation (Autolab, PGSTAT302N) under a forward bias (-0.75 V) in the dark. The testing frequency varied from 10^{-2} Hz to 10^5 Hz with AC amplitude of 10 mA .

3.3.4 Determination of Surface Porosity Based on Electron Microscopy Image

Although there are several methods to measure the porosity of bulk materials, e.g., direct measurement (weighting mass to determine the theoretical volume and measuring the dimension to obtain the real volume), Brunauer-Emmett-Teller (BET) method, mercury intrusion porosimetry, gas expansion method, it is difficult to solely determine the surface porosity of the nanotubes that presented in Figure 3.4 (a), especially to separate the single-sided surface porosity from the double-sided nanotubes on the same substrate. Direct calculation based on the FESEM images is also complicated, as a result of the irregular pore shape and the random pore distribution. An alternative approach to determine the surface porosity is explored in this work and presented as follows.

A typical surface morphology of the as-grown nanotubes is given in Figure 3.4 (a). Obviously the pore size and distribution are nonuniform. Two major pore types are present in the image: penetrating and semi-penetrating pores, as shown in Figure 3.4 (b). It is believed that both types contribute to the ionic flux during nanotube growth, as a result, both are

considered in the subsequent porosity calculation. Using the regions (two circles and one semicircle) highlighted in Figure 3.4 (c), porosity of Figure 3.4 (b) is easily determined to be 27.73%. However, this calculation is only limited to the regular pore shapes while impossible to be applied to Figure 3.4 (a).

Figure 3.4 Surface morphology of nanotubes at the backside formed at 60 V for 30 min (a) FESEM original image; (b) magnified rectangular region in (a); (c) highlighted pore regions used for porosity calculation; (d) distribution of grayscale intensity of (b) used for porosity calculation.

Considering the bitmap format of electron microscopy image, Figure 3.4 (b) can be converted into values of grayscale intensity using OriginPro 8 software, varying from black

(or a value of 0) at the weakest intensity to white (or a value of 65535) at the strongest. Accordingly, grayscale intensity distribution of Figure 3.4 (b) is plotted in Figure 3.4 (d). Herein average surface height of the porous layer is defined to be the mean value of the normal distribution curve as marked in Figure 3.4 (d). A 50% drop of the grayscale intensity, from the mean value (e.g., 24000 in Figure 3.4 (d)) to the minimum value (e.g., 0 in Figure 3.4 (d)), is identified to be the critical value (e.g., 12000 in Figure 3.4 (d)) of effective pores including both penetrating and semi-penetrating types. As such, the porosity of Figure 3.4 (b) is determined to be 27.71%, in line with the value calculated above. Apparently this method shows no dependence on pore shape and distribution, therefore can be used to calculate surface porosity of the nanotubes displayed in Figure 3.4 (a). This method is thus adopted to calculate the surface porosity of the nanotubes that discussed in Section 4.2.

Chapter 4 Essential Role of Electric Field in Nanotube Growth

4.1 Tailoring Nanotube Geometry via Changing Electric Field

Section 2.1.2.3 reviews that, in the last decade, length of anodic titania nanotubes increased from initial hundreds of nanometers to a few micrometers,^[24, 42, 71, 74] and to hundreds of micrometers,^[18-21] even millimeters.^[22] This huge progress was achieved by adopting different anodizing electrolyte to reduce chemical dissolution of the fashioned nanotubes, i.e., from the initial acidic electrolyte to mild aqueous electrolyte, and to organic electrolyte. In the case of organic electrolyte, electric field originating from potential drop in the electrolyte played an important part in the nanotube growth (as will be revealed in this section). On the other hand, pore diameter of the nanotubes was reported to be influenced by a number of factors in organic electrolyte, e.g., applied potential,^[67] water content,^[59] and temperature,^[25] which was more than two times smaller than that in aqueous electrolyte.^[76] All these results can be ascribed to the variation of effective field strength at the working electrode (i.e., titanium foil), since initiation and evolution of the pores are intensively related to the lateral components of the field strength.^[66, 149] As such, it is meaningful to clarify the role of electric field in nanotube growth for better geometry control.

In view of these, considering the significant IR drop in organic electrolyte^[53, 59, 70] which directly reduces the effective field strength at the working electrode, an electrolyte of ethylene glycol and a specially designed electrolytic cell are adopted in this section. The field strength is adjusted by changing the applied potential and the working distance between the electrodes. These two factors are straightforward in tailoring the field strength and thus employed to study the essential role of the electric field.

4.1.1 Determination of Field Strength from Current Density

Figure 4.1 (a) is the time dependence of current density during growth of TiO₂ nanotube arrays under different applied potentials. It shows that the current density at steady-stage anodization increases with the augment of applied potential, owing to the larger driving force of ion transport induced by higher potential. In addition, the initial current density at high voltage is also larger than that at low voltage, as displayed in the inset of Figure 4.1 (a). The relation between anodic current density (i) and field strength (E) can be presented as ^[21, 66, 150, 151]

$$i = A \exp(BE) \quad (4.1)$$

where A and B are constants related to temperature, and the field strength E is the ratio of the potential drop across the oxide layer to barrier layer thickness. Accordingly, the field strength can be reflected from the current density level for a given temperature. Therefore, from Figure 4.1 (a), it is obvious that the relevant field strength increases with applied potential. For the same electrochemical anodizing system, the applicability of Equation 4.1 (or in terms of the High Field Mode ^[150, 151]) has been validated using Macdonald and co-workers' diagnostic criteria ^[152] by Prakasam *et al.* ^[21]

The current transients for different working distances are shown in Figure 4.1 (b). Clearly the current density at steady stage decreases gradually as the distance increases, so does the electric field strength because of the IR drop in the electrolyte. The IR drop in the present organic solution is substantial and considerable, as a result of relatively low conductivity which is about 460 $\mu\text{S cm}^{-1}$. ^[21]

Figure 4.1 Plot of current density vs. time during growth of TiO₂ nanotube arrays for (a) varying applied potential at fixed working distance, and (b) varying working distance at fixed applied potential. Insets are current transients in the first 100 seconds.

Rewriting Equation 4.1 as

$$\ln i = \ln A + BE \quad (4.2)$$

Therefore, field strength is proportional to $\ln i$ for a given temperature. In Figure 4.2, plot of $\ln i$ vs. time for different applied potentials and working distances is illustrated. Evidently the field strength increases with applied potential whereas decreases with increased working distance. Moreover, the variation of field strength when changing working distance in the range of 13~40 mm at 60 V corresponds to that when changing applied potential in the range of 60~50 V (keeping distance constant at about 13 mm). To present the field strength effect in a more direct way later, parameters of potential and distance are assigned with E_n ($n = 0\sim6$) to denote their corresponding field strength with reference to the sequence illustrated in Figure 4.2.

Figure 4.2 Re-plotting of data from Figure 4.1 in terms of $\ln i$ vs. time: the influence of the potential and distance on the logarithm of current density (or electric field strength).

Figure 4.3 shows the surface morphology of the nanotubes prepared at different potentials and distances, suggesting strong dependence of tube diameter on the relevant anodizing parameters. There is a thin layer of titanium oxides on each surface to be discussed later. The corresponding tube inner (or pore) diameters are summarized in Figure 4.4 (a). It is apparent that pore diameter of the nanotubes increases with applied potential, in agreement with the reported results.^[23, 24, 42, 53, 67, 68] The pore diameter slightly decreases with increased working distance, which can be attributed to the significant IR drop in organic electrolyte^[53, 59, 70] thus reducing effective field strength at the working electrode. Similar trends are also reflected in the nanotube length changes, as illustrated in Figure 4.4 (b). It indicates growth rate of the nanotubes increases with applied potential whereas decrease with increase of working distance.

Figure 4.3 FESEM images of TiO_2 nanotube arrays prepared at (a) 25 V, (b) 40 V, (c) 50 V, (d) 60 V with working distances of 13 mm; and at 60 V for different distances between working electrode and counter electrode: (e) 40 mm, (f) 30 mm, (g) 20 mm, (h) 13 mm. The anodization durations for all these experiments are two hours. Cracking regions were specially selected to observe the tube diameters due to the coverage by the initial porous oxide layer.

Figure 4.4 Tube diameter (a) and length (b) of TiO_2 nanotube arrays as a function of applied potential (bottom axis) and working distance (top axis). The anodization durations for all these experiments are two hours.

To uncover the effect of electric field strength, Equation 4.2 is formulated in the following forms

$$\Delta \ln i = B \Delta E \quad (4.3)$$

$$\ln i_n - \ln i_0 = B (E_n - E_0) \quad (4.4)$$

where E_n ($n = 0 \sim 6$) is the pertinent field strength at different applied potentials or working distances as in Figure 4.2, and $\ln i_n$ is the corresponding ordinate (in Figure 4.2) at steady-state anodization. In Equation 4.4, the field strength at 25 V (i.e., E_0) is designated as the ground field strength, while the others are presented with relative values with reference to E_0 . In this case, variations of nanotube length and pore diameter are plotted against this relative field strength, as shown in Figure 4.5. Obviously pore diameter presents a linear increase with relative field strength, as a result of proportionally enhanced lateral components of the field. In contrast, the tube length (also growth rate in the first two hours) displays an exponential relationship with the relative field strength. Taking into account the exponential relation (Equation 4.1), it suggests that growth rate of the nanotubes is proportional to the anodic current density, i.e., the higher the current density the higher the growth rate. On the other hand, the current density is a reflection of the ion transport in the anodic barrier layer (or ion migration in the electrolyte) which is strongly associated with the field strength in this layer (or field strength in the electrolyte). In other words, it is the field strength that essentially affects the nanotube growth rate as well as the length.

Figure 4.5 Effect of the relative field strength $E_n - E_0$ ($n = 0 \sim 6$) on nanotube length and pore diameter (raw data from Figure 4.2 and Figure 4.4).

4.1.2 Nanotube Growth at Steady State (An Ion Flux Model)

Figure 4.2 reveals the maximum and minimum field strength is produced at 60 V and 25 V, respectively. In view of this, to further figure out the effect of field strength, titania nanotubes were produced and studied at 60 V and 25 V (with respective working distance of 13 mm) at prolonged anodization durations.

It is widely recognized that there are three key processes during the growth of nanotube arrays, that is, field-assisted oxidation at metal/oxide interface, field-assisted dissolution at oxide/electrolyte interface at tube bottom, and chemical dissolution of produced nanotubes at tube mouth.^[18, 19, 42, 57] And these processes are responsible for two crucial rates which in turn determine the final length of nanotube arrays. One is the electrochemical etching rate, determined by field-assisted oxidation and dissolution, being constant when these two processes reach equilibrium. The relevant chemical reactions are given in Reactions 2.1 and 2.2. The other is the chemical dissolution rate, the speed under which the fashioned TiO_2

nanotube array is dissolved through the same Reaction 2.2. As a consequence, longer nanotubes are attainable for a given duration if the electrochemical etching rate at tube bottom is faster than the chemical dissolution rate at tube mouth, otherwise shorter or even no nanotubes are obtained.^[42]

Figure 4.6 illustrates tube length as a function of anodizing duration at selected potentials which produces desired maximum and minimum field strengths. Growth rate of nanotubes can be attained from the slope, which is the combined result of electrochemical etching rate and chemical dissolution rate. The slope is positive if the former is faster than the latter, and it is negative if the former is slower than the latter and equals to zero if these two rates are comparable. Moreover, the larger is the slope, the more apparent is the discrepancy between these two rates. The figure reveals that the growth rate at 60 V in the initial two hours is $\sim 7.81 \mu\text{m/h}$, more than nine times higher than that at 25 V (which is only $\sim 0.80 \mu\text{m/h}$), and it increases slightly as duration extends and decreases finally for long anodization periods. The growth rate at 25 V shows the same trend in the primary duration, whereas becomes negative for long anodization periods. The results suggest electrochemical etching at high field strength is prominent, while chemical dissolution at low field strength dominates the growing process.

The prevailing process of electrochemical etching at high field strength can be seen from the steep slope at 60 V in contrast to that at 25 V (see Figure 4.6). The dominant process of chemical dissolution at low field strength can be deduced from the changes in surface morphology with prolonged duration. In Figure 4.3, the pore diameters of TiO_2 nanotube arrays anodized for two hours cannot be seen clearly and the wall thicknesses cannot even be distinguished, except for some special regions such as within the cracks. Because there is a

thin layer of TiO_2 oxides on top of the nanotube arrays formed in the first few tens of seconds (see the drastic drop of current density in the insets of Figure 4.1) after commencement of anodization. Although the pores are partially shaded, nanotube arrays grow beneath the initial oxides, and the pore entrances (the initial oxides) are not affected by field-assisted dissolution and hence remain relatively narrow.^[57, 59, 134] Therefore, the initial oxides on the surfaces can only be eliminated by chemical dissolution that mentioned above.^[60] Figure 4.7 is top and lateral view of TiO_2 nanotube arrays prepared at 25 V for different durations. It reveals that the surface becomes much planar as time increasing, and the pores gradually become clear, as visible from the insets. In particular, the remnant initial oxides present on the surface of 2 h anodization (see Figure 4.7 (a)) are dissolved after long anodizing periods (e.g., 14 h in Figure 4.7 (b)). Moreover, nonuniform and relatively thick-wall nanotubes are observed after anodization for 24 h, which can be attributed to the permanent chemical dissolution of the nanotubes in consideration of the characteristic V-shape profile in wall thickness.^[20, 64, 145, 146] In addition, progressively decreased tube length is exhibited in Figure 4.7 (d)~(f), which is adopted in the plot of Figure 4.6. All these results demonstrate that chemical dissolution is substantial at low field strength.

To elucidate the influence of electric field on the growth rate of the nanotubes, it helps to look into the details of ion migration under electric field in the electrolyte. (This electric field originates from IR drop in the organic electrolyte, which is the driving force of ion migration. Although it is different from the electric field in the oxide layer discussed afore, the relationship of field strength between different parameters is consistent with that illustrated in Figure 4.2.) Reported results^[53, 59, 64] indicate, in aqueous electrolyte, steady-state growth of anodic nanotubes is controlled by ion diffusion. However, in organic electrolyte, the effect of

electric field should be considered. This is exactly the case of the present work. In principle, the flux of ions in the presence of electric field can be expressed as

$$\mathbf{J}_i = -\mathbf{D}_i \frac{\partial c_i}{\partial x} - u_i c_i \mathbf{E} \quad (4.5)$$

Where, $\mathbf{J}_i$ is the flux of species i of concentration c_i in direction x , $\partial c/\partial x$ is the concentration gradient, $\mathbf{D}_i$ is the diffusion coefficient, u_i is the mobility of species i , and $\mathbf{E}$ is the electric field strength.

Figure 4.6 Time dependence of length of TiO_2 nanotube arrays prepared at 60 V and 25 V. Inset is a local magnified region.

Evidently ion transport in electrolyte is significantly affected by field strength, since ion migration under electric field is considerable in comparison to the process of ion diffusion under concentration gradient. In addition, Reactions 2.1 and 2.2 suggest H^+ and F^- ions play an important part in growth of the nanotubes. As the reaction products, $[\text{TiF}_6]^{2-}$ ions also influence the growth process, which will be discussed later. Let the vertical axis be the length

of the tube, and the horizontal axis the concentration of ions, as illustrated in Figure 4.8. Let us consider H^+ and F^- ion concentration profile within a single nanotube: H^+ ions are produced during anodization only at tube bottom,^[74] and the concentration is constant at steady-state anodization. Under electric field, H^+ ions migrate in the electrolyte toward negative electrodes (the estuary direction). Therefore, H^+ concentration decreases from the tube bottom to the mouth. F^- ion concentration, on the other hand, is the maximum at the estuary, i.e., comparable with that in the bulk electrolyte thus remains constant. Under electric field, F^- ions migrate in the electrolyte toward the positive electrode (the bottom direction). As such, the concentration of F^- ions decreases from the tube mouth to the bottom, as shown in Figure 4.8.

In Figure 4.8 (a), as tube length increases (from solid line to dot line, then to dash line and to dash-dot line), the F^- concentration at the bottom decreases gradually because of the increase in ionic migration pathway (increase of tube length). The variation of H^+ profile strongly depends on the F^- concentration at the bottom. From Reactions 2.1 and 2.2, it can be seen that most H^+ ions produced through Reaction 2.1 immediately participate in Reaction 2.2 as long as there is enough F^- ions (e.g., at the intersection of solid line in Figure 4.8 (a)). As such, there is not much accumulation of H^+ ions, i.e., H^+ concentration profile is small and is in the vicinity of the tube bottom (solid line in H^+ profiles). At this stage, electrochemical etching is dominant as there is almost no H^+ ion at tube mouth. In this scenario, the tube grows at nearly constant rate (cf., Figure 4.6).

Figure 4.7 Illustrative FESEM top images of TiO₂ nanotube arrays prepared by electrochemical anodization at 25 V for (a) 2 h, (b) 14 h, (c) 24 h, and their corresponding SEM cross-sectional view (d), (e) and (f). Insets are local magnified images.

Figure 4.8 Schematic diagram of H^+ and F^- concentration profiles within a single nanotube during electrochemical anodization: (a) for different tube lengths (the arrow denotes length increase direction, and the cross on the axis represents the critical concentration point), (b) at different field strengths for the same tube length.

As tube length increases, the F^- concentration at the bottom decreases while the H^+ concentration keeps constant at the steady state. Therefore, there exists a critical concentration of F^- ions, which is approximately $[H^+]/[F^-]=2:3$ according to Reaction 2.2. At this point (marked with a cross in Figure 4.8 (a)), the F^- concentration is just enough to meet the needs of Reaction 2.2 (in addition to possible direct reaction through Reaction 2.3 or migration into the oxides under the electric field). At this point, the concentration gradient of H^+ ions is still small and confined at the bottom area, as shown with the dot line of the H^+ profiles in Figure 4.8 (a). The electrochemical etching is still prevailing at this stage.

Further increase in the tube length results in F^- concentration falling below the critical point at the bottom. When this happens, the F^- ions at tube bottom can no longer meet the needs of Reaction 2.2. Consequently, extra H^+ ions at the bottom will migrate toward the estuary under the electric field, giving rise to significant change in H^+ concentration profile to the dash line in Figure 4.8 (a). At this stage, though electrochemical etching is still dominant, the nanotube growth rate is decreased (due to slowdown of Reaction 2.2). This can be confirmed from the turning point in Figure 4.6 (at 60 V after 8 hours the slope of curve is dipped).

As the process continues and the H^+ ion accumulates at the estuary (dash-dot profile of H^+), chemical dissolution of the fashioned nanotubes takes place, again through Reaction 2.2, but this time the tube at the mouth (TiO_2) is consumed, resulting in decreased growth rate. At the steady state, where the rate of Reaction 2.2 at the tube mouth (dissolution) increases to that at the tube bottom (tube growth), the net growth of the tube stops. This has been widely observed in the growth of anodic nanotubes.^[42, 59, 68, 69, 71] At the bottom of the tube, the reaction product $[TiF_6]^{2-}$ accumulates gradually, which reduces the chemical reaction rate. At certain extent, the dissolution at the top becomes faster than the growth at the bottom, a negative net growth occurs, i.e., reduction of the total tube length (as happened at 25 V during long time anodization in Figure 4.6).

The role of the electric field strength can be clearly seen in Figure 4.8 (b). According to Equation 4.5, higher field strength results in higher ion flux in the electrolyte. At the same tube length, under high field strength, F^- concentration at tube bottom will be higher than that under low field strength. Therefore, it requires longer time for bottom F^- concentration to

drop to the critical value. In this process, the H^+ ions are mainly confined in the vicinity of tube bottom. As a result, electrochemical etching (or tube growth) process maintains for a longer time. As is shown in Figure 4.6, at 60 V, the tube still grows after 10 hours but at 25 V the tube growth stops at around 5 hours (and further increase in time only results in shortening of the tube). Therefore, at low field strength, the chemical dissolution kicks in much faster than at high field strength. Since the chemical dissolution takes place at the tube estuary and depends on the accumulation of the H^+ ions, reduction in the H^+ concentration at the mouth should effectively prolong the growth. As such, an anodization run at 25 V was continuously stirred for 24 h. Without stirring, the final tube length is only $\sim 2.5 \mu\text{m}$, whereas with stirring, the final tube length becomes $8.4\sim 12.7 \mu\text{m}$, or an increase by a factor of three to five. Of course, this increase in length did not come from the reduction in chemical dissolution alone: the other reason is the increase in flux as a result of forced convection and enhanced ion diffusion (first term in Equation 4.5)^[53, 59, 64, 77] due to stirring.

As an evidence of the fluorine ion concentration gradient in the electrolyte during the anodization process, the fluorine gradient in the as-grown tubes is observed via X-ray photoelectron spectroscopy. In the nanotube array prepared at 60 V for 8 h (length of $\sim 120 \mu\text{m}$), the XPS composition analysis reveals 13.52 at% F at the mouth and 8.38 at% at the bottom (or, 28.68 at% Ti, 57.80 at% O and 13.52 at% F at tube mouth; 30.76 at% Ti, 60.86 at% O and 8.38 at% at tube bottom).

4.2 Double-Sided Anodic Titania Nanotube Arrays: A Lopsided Growth Process

In Section 4.1, two electric fields are concerned: the field originating from the potential drop over the oxide layer and that in the electrolyte. The former is essential in determining pore diameter and growth rate while the latter also plays an important part in affecting the growth rate. However, the latter is only discussed qualitatively in terms of an Ion Flux Model. In this section, the role of electric field in the electrolyte is revealed directly through a double-sided nanotube growth. Anodic titania nanotube arrays are grown simultaneously at both sides of a titanium foil. The tube length as well as the surface porosity increases with applied potential at each side, while longer nanotubes are obtained at the frontside in comparison to the backside. This lopsided growth is attributed to the higher ionic flux induced by electric field at the frontside. Accordingly, the double-sided nanotubes are tailored to be comparable by adjusting the electric field in the electrolyte. The tube growth rate under different anodizing configurations is also compared. It shows that the fastest growth is obtained with this simple two-electrode method. In addition, fabrication of the double-sided nanotubes is also a basic requirement for further application in dye-sensitized solar cells of parallel configuration as proposed in Section 3.1 (see Figure 3.2).

4.2.1 Single-Sided Anodization for Double-Sided Nanotube Growth

In growth of double-sided nanotube arrays, the same two-electrode configuration was employed, where a titanium foil was used as working electrode and a piece of platinum gauze as counter electrode. The backside of the titanium foil was directly exposed to the electrolyte without any protection, as shown in Figure 4.9 (a). In the same electrochemical system, the nanotube arrays grown at the frontside (i.e., the side facing the counter electrode) have been investigated extensively (e.g., in Section 4.1), but the backside seems always ignored. Figure 4.9 (b) is a cross-sectional view of the titanium foil anodized at 60 V for 30 min. Titanium

oxide layers exist at both sides of the foil, and the layer at the frontside is thicker than that at the backside. FESEM characterization reveals that both the layers are highly ordered nanotubes, as shown in Figure 4.9 (c) and (d), with the tube length at the frontside being longer than that at the backside.

Figure 4.9 (a) Schematic diagram of a two-electrode electrochemical anodization; (b) optical microscope image of the titanium foil in (a) anodized at 60 V for 30 min; and FESEM cross-sectional images of the nanotube arrays prepared in (a) at 25 V for 30 min: (c) frontside and (d) backside.

Surface morphology of the nanotubes grown at different applied potentials is shown in Figure 4.10. Obviously all the nanotubes are covered by a thin layer of porous oxides that formed at the very beginning of anodization, because no significant chemical dissolution takes place during such a short duration (i.e., 30 min). Even so, the pore size as well as the tube length at both sides increases with applied potential. With prolonged anodizing duration

(see Figure 4.7) or elevated temperature (see Figure 4.11), the tubes become clearer as a result of enhanced dissolution at the top surface. This will affect the final length of the nanotubes and thus the net growth rate. As such, a series of experiments was carried out at room temperature for 30 min only to study the lopsided growth process.

Figure 4.10 FESEM top-view images of the nanotubes grown at 25 V (a, b), 40 V (c, d), 50 V (e, f), and 60 V (g, h) for 30 min. The left and right columns are nanotubes at the frontside and backside, respectively. Insets are local magnifications or corresponding SEM cross-sectional views.

The length of nanotubes prepared at different applied potentials is summarized in Figure 4.12 (a). The tube length increases with the applied potential at each side, with the frontside

being longer than the backside at all the applied potentials studied. This difference in tube length is attributed to different ionic fluxes in the electrolyte between the frontside and backside, which will be discussed in detail in the following sections.

4.2.2 Nanotube Growth from Initiation to Steady State

Yasuda and Schmuki ^[64] demonstrated ionic diffusion in the electrolyte was the rate-determining step of zirconium titanate nanotube growth in aqueous electrolyte. In the case of titania nanotubes grown in organic electrolyte, the influence of electric field should also be taken into account, as presented in Section 4.1. To interpret the lopsided growth and reveal the role of electric field, two major diffusion processes are considered, i.e., H^+ ion diffusion toward the counter electrode and F^- ion diffusion toward the working electrode, as illustrated in Figure 4.8.

As discussed in Section 4.1, Reactions 2.1 and 2.2 take place at the working electrode in anodic growth of titania nanotube arrays. Reaction 2.1 is responsible for field-assisted oxidation, while Reaction 2.2 contributes to field-assisted dissolution. Nanotube growth is an adjustment between these two processes. Essentially fluorine ion is a crucial factor in formation of nanotubes, in absence of which only compact titanium oxide layer is formed through Reaction 2.1.^[23, 59] In the presence of fluorine ions, field-assisted dissolution takes place provided that enough H^+ and F^- ions are present at the oxide surface simultaneously. Otherwise, the growth process is controlled either by field-assisted oxidation or field-assisted dissolution, depending on whether F^- or H^+ ions are abundant at the oxide surface.

Figure 4.11 Surface morphology of nanotubes formed at 25 V and 40 °C for 30 min: (a) frontside and (b) backside. The temperature is controlled by water bath.

Figure 4.12 (a) Titania nanotube length as a function of applied potential for both frontside and backside (data are from Figure 4.9 and Figure 4.10). (b) Current transients during nanotube growth at different applied potentials. Inset is a local region.

For nanotube growth in the present organic electrolyte, the required H^+ ions originate mainly from field-assisted oxidation through Reaction 2.1.^[74] Gas emission is observed from both titanium and platinum surfaces in the first tens of seconds after commencement of the electrochemical process. This suggests the existence of the following reactions under DC condition:

Figure 4.12 (b) is the current transients during nanotube growth at different applied potentials. It shows the current density drastically decreases in the initial tens of seconds, along with the observation, indicating that field-assisted oxidation is dominant at this stage. This results in a high H^+ concentration at the oxide surface through Reactions 2.1 and 4.6. On the other hand, the required F^- ions for tube growth are from the bulk electrolyte by diffusion process. In view of these, the initial stage of nanotube growth is controlled by F^- flux toward working electrode (i.e., the field-assisted dissolution process or Reaction 2.2), as a result of abundant H^+ ions at the oxide surface, as illustrated in Figure 4.13 (a) (see Stage I).

As the process progresses, the F^- ions are continuously transported toward the oxide surface. As such, the H^+ ions are gradually consumed through Reaction 2.2 until its concentration drops to a steady value, thus resulting in progressively increased tube length (Stage II in Figure 4.13 (a)). This steady value is the H^+ concentration produced only through Reaction 2.1. After reaching the steady H^+ concentration, F^- concentration increases with anodizing duration because of enhanced surface porosity. At a particular moment (Stage III in Figure 4.13 (a)), a critical ratio between H^+ and F^- concentration achieves, i.e., 2:3 according to Reaction 2.2. Thereafter, the nanotube growth will be controlled by H^+ generation (i.e., the field-assisted oxidation process or Reaction 2.1), owing to the abundance of F^- ions at the oxide surface (Stage IV in Figure 4.13 (a)).

Figure 4.13 (a) Schematic diagram of evolution of H^+ (green dots) and F^- (red dots) ions during nanotube growth. FA-Dis and FA-Ox denote field-assisted dissolution and field-assisted oxidation, respectively. (b) (Bottom) nanotube length as a function of anodizing duration at 60 V for both the frontside and backside. (Top) corresponding length difference between frontside and backside.

Existence of this transition process, that is, from field-assisted dissolution control to field-assisted oxidation control, is reflected in Figure 4.13 (b). It reveals that nanotube length at both sides increases with anodizing duration. Importantly there is an abrupt increase in the growth rate at about 2 h. This indicates nanotube growth process is controlled by field-assisted dissolution before 2 h and by field-assisted oxidation after 2 h, as marked in Figure 4.13 (b). However, the growth rate will eventually decrease again for long anodizing durations, which will be discussed later.

4.2.3 Influence of Electric Field

Now let us return to Figure 4.12 (a). The tube length at the frontside is longer than that at the backside at all applied potentials. Since the anodizing duration is 30 min for all these experiments, the tube growth process is controlled by field-assisted dissolution or exactly the F^- flux toward working electrode. Therefore, the higher the F^- flux, the longer the tubes. As

such, the longer tubes at the frontside originate from the larger F^- flux. Considering potential drop in the organic electrolyte, ionic flux at the frontside should consist of two parts: ion diffusion under concentration gradient and ion migration under electric field. In contrast, only ion diffusion exists at the backside, as follows:

$$J_f = -pD \frac{\partial c}{\partial x} + ucE \quad (4.8)$$

$$J_b = -pD \frac{\partial c}{\partial x} \quad (4.9)$$

where, J_f and J_b are ionic fluxes at the frontside and backside, respectively, p is the porosity of the nanotube surface layer, D is the diffusion coefficient, c is the concentration, $\partial c/\partial x$ is the concentration gradient, u is the ion mobility, and E is the electric field strength in the electrolyte. In theory, mass transport in solution occurs by diffusion, migration, or convection. In this study, all the experiments were carried out under near constant ambient temperature ($\sim 20^\circ\text{C}$) for 30 min only (in this case, possible natural convection due to thermal gradients was negligible) without stirring (i.e., no forced convection), therefore effect of convection can be neglected. Normally the following conditions are chosen to minimize the migration effect in an electrochemical cell:^[153] using a large quantity ($> 0.1\text{ M}$) of inert electrolyte (or supporting electrolyte), reducing electroactive species to a concentration of 5 mM or less, minimizing the distance between working electrode and counter electrode, employing electrodes of small sizes (e.g., microelectrodes), and so forth. Accordingly, the migration effect must be considered in the present study, in view of the conditions used: in the absence of inert electrolyte (i.e., ethylene glycol + 0.3 wt% NH_4F + 2 vol% deionized water, a solution volume of 77 ml in a rectangular vessel of 60 mm $\times$ 50 mm $\times$ 50 mm), large

concentration of electroactive species (i.e., 0.3 wt%, or 0.09 M for NH_4F), considerable distance between the electrodes (i.e., 13 mm), large sizes of the planar electrodes (i.e., $\sim 11 \text{ mm} \times 20 \text{ mm}$ on average for titanium foils and $15 \text{ mm} \times 25 \text{ mm}$ for the platinum mesh).

For the terms of ion diffusion in Equations 4.8 and 4.9, a factor of surface porosity p is involved to illustrate its impact on the flux. The surface porosity of the nanotubes (as displayed in Figure 4.10) is evaluated using a method that presented in Section 3.6. Figure 4.14 (a) reveals that the porosity linearly increases with the applied potential at each side and is comparable under the same condition for both sides. Under pure diffusion control at the backside, plot of tube length against porosity exhibits a proportional relationship, as shown in Figure 4.14 (b). In consideration of Equation 4.9, this gives rise to

$$L \propto J \tag{4.10}$$

Herein, L is the nanotube length. Consequently, it is the applied potential that affects the surface porosity and thus the ionic flux and eventually the tube growth rate. The potential dependence of ionic flux is also reflected in the inset of Figure 4.12 (b). In the first tens of seconds, the current density decreases drastically. At a particular moment, a turning point appears, indicating occurrence of obvious dissolution (i.e., formation of pore embryos). This turning point (marked with arrows in Figure 4.12 (b)) presents earlier at relatively higher applied potential, as a consequence of higher ionic flux.

Figure 4.14 (a) Potential dependence of surface porosity at frontside and backside. Data are from Figure 4.10. (b) Plot of nanotube length vs. surface porosity at the backside. Data are from Figure 4.12 (a) and Figure 4.14 (a).

In Equation 4.8, an additional term of ion migration is produced owing to the potential drop in organic electrolyte at the frontside. This potential drop (U) can be estimated using Ohm's Law

$$U = IR = I \frac{1}{\kappa} \frac{l}{A} = i \frac{l}{\kappa} \quad (4.11)$$

where I is the current flow, R is the electrolyte resistance between the working and counter electrode, κ is the ion conductivity in the electrolyte, l is the distance between the two electrodes, A is the effective surface area of the working electrode, i is the relevant current density. Note that herein the current density is computed using the one-side surface area only (i.e., A instead of $2A$). Accordingly, the pertinent electric field strength in the electrolyte can be written as

$$E = \frac{U}{l} = \frac{i}{\kappa} \quad (4.12)$$

Based on Equations 4.8~4.12 and the comparable surface porosity at the frontside and backside (cf. Figure 4.14 (a)), the following relationship stands

$$\Delta L \propto \Delta J \propto E \quad (4.13)$$

Here ΔL and ΔJ are the difference in length and F^- flux between frontside and backside, respectively. As such, ΔL is directly proportional to the electric field strength E . In Figure 4.15, plot of ΔL vs. E is presented. It is evident that the nanotube length difference increases linearly with the electric field strength, in line with the above discussion. More important, this straight line passes through the origin. This predicts that the length difference will eventually disappear as E approaches zero. Equation 4.12 shows the value of E is proportional to current density i and inversely proportional to conductivity κ . The conductivity of the organic solution used is about $460 \mu\text{S cm}^{-1}$,^[21] which is small enough to magnify the electric field strength thus giving rise to distinctly different tube lengths at the frontside and backside. To demonstrate the effect of the electric field, anodization was carried out in another electrolyte of much higher conductivity (i.e., 1 M $(\text{NH}_4)_2\text{SO}_4$ + 0.5 wt.% NH_4F , $\kappa \approx 4.45 \times 10^4 \mu\text{S cm}^{-1}$, about 100 times larger than the normal electrolyte) also at 25 V for 30 min. The obtained nanotube arrays are shown in Figure 4.16, which are not as regular as that in the organic electrolyte (cf. Figure 4.9 (c) and (d)) due to significant chemical dissolution. However, the bottoms of the nanotubes can be clearly discerned and remnant oxides at the surface can be observed as well. This morphology is in agreement with that reported by Taveira and co-workers.^[62] It is apparent that the length of the nanotubes is comparable at the frontside and backside, identical with the above prediction and discussion. The results demonstrate additional electric field at the frontside contributes to ion migration

in the electrolyte and gives rise to higher ionic flux, therefore resulting in longer nanotubes than the backside.

Figure 4.15 Plot of difference in nanotube length between frontside and backside vs. electric field strength in the electrolyte. Data are from Figure 4.12. The value of conductivity (κ) used is $460 \mu\text{S cm}^{-1}$.

Figure 4.16 FESEM cross-sectional images of as-grown titania nanotube arrays prepared at 25 V for 30 min in 1 M $(\text{NH}_4)_2\text{SO}_4$ with 0.5 wt.% NH_4F : (a) frontside and (b) backside. The arrows indicate the thickness of the nanotube layer.

In Section 4.1.2, anodic nanotube growth at steady state (i.e., the growth process controlled by field-assisted oxidation) is discussed in detail using an Ion Flux Model. This model illustrates significant chemical dissolution of fashioned nanotubes kicks off much faster under low electric field, because of relatively smaller ionic flux in the electrolyte. Accordingly, in the current work, dissolution of the nanotubes at the backside should be triggered much earlier than that at the frontside. This is confirmed in Figure 4.13 (b). It shows the tube growth rate at the backside declines after approximately 4 h, and the corresponding length difference (top curve) keeps increasing thereafter, as a consequence of substantial chemical dissolution. Figure 4.17 is the pertinent surface morphology of the nanotubes (or nanowires^[154-158] on top of the nanotubes, which will be discussed in Section 4.3) at the frontside and backside for 8-hour anodization. It is evident that remnant original oxide layer (porous surface) can still be observed at the frontside, whereas this layer has totally disappeared at the backside. This directly reveals chemical dissolution initiates much faster at the backside. On the other hand, it further proves ionic flux at the backside is smaller than that at the frontside, echoing the above discussion.

Figure 4.17 FESEM top-view images of as-grown titania nanotube arrays prepared at 60 V for 8 h: (a) frontside and (b) backside.

4.2.4 Comparison between Single- and Double-Sided Anodization

In the normal anodizing process, as illustrated in Figure 4.9 (a) (hereafter referred to as “SGunprot” for “single-sided anodization with titanium backside unprotected”), titania nanotubes develop simultaneously at both sides of a titanium substrate. A general question is what will happen to the frontside if the backside growth is hindered or accelerated. As such, two more experiments were set up. In one case, the backside of the titanium foil was protected by epoxy resin (hereafter referred to as “SGprot” for “single-sided anodization with titanium backside protected”). In yet another setup, two platinum counter electrodes were placed at each side of the titanium foil to establish a double-sided anodization (hereafter referred to as “DB” for “double-sided anodization”).

Potential dependence of the tube length at the frontside is given in Figure 4.18. It reveals that the tube length increases with applied potential regardless of conditions, due to relatively higher F^- flux produced at higher potential. The pertinent growth rate presents the largest for SGunprot and the smallest for SGprot, with DB in between at nearly each applied potential.

In the case of single-sided anodization including SGunprot and SGprot, there are one electronic pathway and one ionic pathway in the electrochemical system. During nanotube growth, electrons are generated at the working electrode through Reaction 2.1 as well as Reaction 4.6, and consumed at the counter electrode through Reaction 4.7. In the SGunprot system, extra nanotube growth at the backside will produce more electrons in comparison to the SGprot system, resulting in relatively higher current flow. Since there is only one ionic pathway, the relevant current density at the frontside will be increased accordingly. On the basis of Equation 4.12, this increased current density will, in turn, promote the electric field

in the electrolyte, thereby giving rise to higher ionic flux (cf. Equation 4.8) and hence the growth rate. With respect to double-sided anodization, there are two electronic pathways and two ionic pathways. In this system, nanotubes grown at the backside will no longer contribute to current density of the frontside. This is the reason why growth rate at the frontside, for DB system, is smaller than that for SGunprot system. As a consequence, SGunprot system gives rise to the largest growth rate among all the conditions. In addition, it is believed that the relatively higher nanotube growth rate for DB system originates from the higher ionic flux (or higher current density), due to relatively lower resistance in the parallel circuit in contrast to the SGprot system.

Figure 4.18 Potential dependence of nanotube length at the frontside under different backside environments. Data are from Figure 4.9, Figure 4.10, and Figure 4.19. SGprot, SGunprot, and DB denote single-sided anodization with titanium backside protected, single-sided anodization with titanium backside unprotected, and double-sided anodization, respectively. The anodizing duration is 30 min for all the experiments.

Figure 4.19 Cross-sectional views of the nanotubes obtained at 25 V (a, e), 40 V (b, f), 50 V (c, g), and 60 V (d, h). The upper and bottom rows are grown under SGprot and DB, respectively.

4.3 Transition from Anodic Nanotubes to Nanowires

In Sections 4.1 and 4.2, nanotubes grown under different conditions are investigated and discussed with reference to the essential role of electric field. However, to achieve the structure that proposed in Section 3.1, another important work has to be carried out, that is, to obtain regular tube surface. This normally arises when organic electrolyte is adopted to produce the nanotubes, as shown in Figures 4.3, 4.10 and 4.17 where the tubes are covered by a layer of porous oxide or nanowires.

Recently a few researchers reported formation of titania nanowires on top of the nanotubes in organic electrolyte.^[154-158] This structure is undesirable in most applications where the open tube tops are required, for example, to facilitate dye loading and electrolyte infiltration in dye-sensitized solar cells. To date, two major methods have been exploited to obtain ordered tube surface: pre-treatment of the titanium foils or post-treatment of the titania

nanotubes. The pre-treatment method is used to suppress formation of the nanowires, such as growing a compact rutile layer,^[156] producing a photoresist coating,^[159] or polishing titanium foils prior to anodization.^[134] These techniques cannot really solve the problem, since the nanowire formation is an intrinsic stage during nanotube growth in organic electrolyte (to be demonstrated in this section). In other words, the nanowires will appear eventually after etching away the pre-formed layers. The post-treatment method, on the other hand, is employed to eliminate the fashioned nanowires after anodization, for example, by ultrasonication.^[160] This process is effective in clearing away the nanowires. However, it is only limited to certain conditions, as will be revealed in this section, and the cleaning mechanism has not been reported.

The formation of the nanowires has been interpreted using a bamboo-splitting model^[154] based on alumina nanowires and nanotubes produced by etching alumina templates.^[161] Although there are a number of common features in anodizing titanium and aluminum,^[65] the difference in key features is obvious: anodization of titanium gives rise to individual nanotubes while anodization of aluminum results in integrated nanoporous structure. Thus, the formation mechanism may not be totally the same.

In this section, transition from titania nanotubes to nanowires is investigated by varying anodizing conditions. The x-ray photoelectron spectroscopy measurements indicate that the transition requires a large number of H^+ ions to reduce the passivated area of tube walls, therefore can be observed only under an intermediate chemical dissolution environment. Ultrasonic cleaning proves an effective way in ridding off the surface nanowires to reveal the nanotubes, due to formation of the quasi-nanosprings. A possible model is proposed to interpret the transition process.

4.3.1 Formation and Elimination of Nanowires

Figure 4.20 (a) shows the nanowires produced by electrochemical anodization, beneath which the nanotubes can be clearly visible. Similar structures were previously reported elsewhere^[154, 155, 157] and explained using a bamboo-splitting model.^[154] However, a number of phenomena are difficult to explain with this model. In Figure 4.20 (b), each single tube presents a spring-like structure, bends and elongates. Generally only one single nanowire initiates from each nanotube, as revealed in Figure 4.20 (c). The tubes are already transformed into quasi-nanosprings before formation of the nanowires, as shown in Figure 4.20 (d).

Figure 4.20 Top-view FESEM images of as-grown anodic titania nanotubes prepared at 25 V and 40 °C for 2 h: (a) nanowires on top of nanotubes; (b) and (c) are local magnifications in (a); (d) nanotubes below the nanowires.

The transition from nanotubes to nanowires can be observed only under an intermediate chemical dissolution environment. At high chemical dissolution rate, for example, in aqueous^[62, 69] or acidic electrolyte,^[23, 71] no nanowire forms due to fast dissolution. Under this condition, the spring-like structure can still be observed near the tube mouth (see Figure 2.5). At low chemical dissolution rate, for instance, in organic electrolyte at room temperature for short anodizing durations, the tube arrays are covered by a thin layer of porous oxide, as

shown in Figure 4.21 (a), thereby no nanowire forms either. Figure 4.21 (b) shows that the pore size of the oxide layer is larger at 40 °C than that at room temperature (cf. Figure 4.21 (a)) owing to the increased dissolution, and the nanotubes beneath the oxide layer are exposed in regions. The spring-like structure also appears at the tube mouth, as illustrated in the inset. Prolonged anodization at 40 °C results in the formation of the wires as displayed in Figure 4.20. In contrast, no wire is fashioned at room temperature under the same duration (see Figures 4.3 (a) and 4.7 (a)). This indicates chemical dissolution plays an essential role in the transition process from tubes to wires, thus interpreting the effect of water content^[154, 155, 158] on formation of the nanowires. As the water content increases, chemical dissolution rate increases and hence facilitates development of the nanowires. Therefore, under the same condition but with relatively higher water content, nanowires can initiate at lower potential,^[154] in shorter time,^[155] or with lower threshold content when HF instead of water is used.^[158]

Figure 4.21 Top-view FESEM images of as-grown anodic titania nanotubes prepared at 25 V for 30 min: (a) at room temperature (~20 °C) and (b) at 40 °C. Inset is a local region.

In growth of anodic titania nanotubes, the chemical dissolution rate increases with anodizing duration (cf. Figure 4.21 (a) and Figure 4.3 (a)) due to localized acidification,^[74] therefore it is believed that the nanotubes will eventually evolve into nanowires for long durations in organic electrolyte at room temperature. This has been revealed in Figure 4.22 (a) where the nanowires grown at 25 V and room temperature for 14 h are displayed. Similar transition can also be obtained at higher potential for relatively shorter durations (e.g., at 60 V and room temperature for 8 h, as shown in Figure 4.17). Consequently, the pre-treatment method is unable to prevent formation of the nanowires. As the pre-treated layers are etched away by chemical dissolution, the wires will eventually initiate and grow.

Figure 4.22 Surface morphology of as-grown anodic titania nanotubes prepared at 25 V and room temperature ($\sim 20^\circ\text{C}$) for 14 h: (a) without ultrasonic cleaning; (b) with ultrasonic cleaning for 10 min after anodization. Inset is a local magnification showing the quasi-nanosprings at the tube mouth.

Existence of a layer of nanowires on top of nanotube array blocks the way the nanotubes are meant to function, for example, in dye-sensitized solar cells to facilitate dye loading and electrolyte infiltration, thus this layer of wires is undesirable and should be removed. However, once formed, the nanowires cannot completely self-dissolve during anodization.

Ultrasonic cleaning is effective in clearing away the wires, as shown in Figure 4.22 (b). It is noteworthy that the nanowires grown for “short” durations (e.g., at 25 V and 40 °C for 2 h, 4 h, and 6 h) are unable to be eliminated even under ultrasonic cleaning, as presented in Figure 4.23 (a). In the first 6 hours, the length of nanotubes together with nanowires increases linearly. The corresponding growth rate is $\sim 1.39 \mu\text{m/h}$, which drops after 6 h since the lengthened nanowires keep curving and collapse on the tube surface as displayed in Figure 4.23 (b) and Figure 4.24. Two values of tube length are given at 8 h in Figure 4.23 (a), with the top one for nanotubes and nanowires together (i.e., before the nanowires are cleared away, see Figure 4.23 (b)) while the bottom one for nanotubes only (i.e., after the nanowires are cleared away, see Figure 4.23(c)). Thereafter, clear nanotubes are obtainable via ultrasonic cleaning. The resultant net tube growth rate is $\sim 0.37 \mu\text{m/h}$. The reason why clear tube surface (i.e., free of wires) can be obtained by ultrasonication only after long anodizing duration will be discussed in Section 4.3.2.

Figure 4.23 (a) Length of nanotubes formed at 25 V and 40 °C for different anodizing durations; FESEM cross-sectional images at 8 h: (b) without ultrasonic cleaning, (c) with ultrasonic cleaning for 10 min after anodization. NT and NW denote nanotubes and nanowires, respectively.

Figure 4.24 Top-view FESEM image of as-grown anodic titania nanotubes prepared at 25 V and 40 °C for 8 h. Inset is a local magnification with a scale bar of 100 nm.

4.3.2 Mechanism of Nanowire Formation

Based on the above results in Section 4.3.1, a possible model to illustrate the transition process is proposed in Figure 4.25. Initially the nanotubes grow steadily underneath a compact oxide layer that formed at the very beginning of anodization, as illustrated in Figure 4.25 (a). In the meanwhile, periodical rings form on the tube walls (as shown Figure 4.26), which play an important part in the subsequent transition process. As the anodization prolongs, thinning of the tube walls takes place especially near the tube mouth. This thinning process is unsymmetrical over the tube walls due to the uneven thickness, and proceeds slowly at relatively thicker parts (e.g., at the rings), as depicted in Figure 4.25 (b). At the tube mouth, spring-like structure (see the inset of Figure 4.21 (b)) arises under significant etching after the initial oxide layer is etched away (or detached from the nanotubes). The above course is widely recognized as a pure chemical dissolution process at the tube mouths.

However, it cannot be achieved without the assistant of an electric field, as the Ti–O bonds are polarized and weakened along the tube axial direction under the field.^[57] This in turn makes the bonds broken easily in the presence of H^+ and F^- ions.

Figure 4.25 Schematic diagram of the transition from nanotubes to nanowires: (a) steady growth of a nanotube underneath an initial oxide layer; (b) thinning of the tube mouth and formation of the quasi-nanosprings under an intermediate chemical dissolution environment; *Stretching Mode*: (c) propagation of a crack along the quasi-nanosprings under an electric field; (d) stretching of a nanowire under the field; *Splitting Mode*: (e) bending of the quasi-nanosprings, the sketch on the right-hand side is a corresponding side view of the rectangular region; (f) initiation of a single nanowire due to splitting. The red and blue arrows denote tensile and compressive stresses, respectively.

Continuous dissolution results in progressive thinning of the tube walls and eventually the formation of quasi-nanosprings for long durations, as shown in Figure 4.20 (d) and the inset of Figure 4.22 (b). This could be the reason why nanowires grown for long durations can be cleared away by an ultrasonic cleaning, since the cracks on the quasi-nanosprings propagate easily along the rings under the ultrasonication.

Figure 4.26 Cross-sectional FESEM image of as-grown anodic titania nanotubes prepared at 25 V and 40 °C. Ripples on the tube walls are clearly visible.

After formation of the quasi-nanosprings in Figure 4.25 (b), nanowires start to fashion in two manners: stretching and splitting. In the stretching mode, cracks at the tube mouths (see the inset of Figure 4.21 (b)) propagate in a direction perpendicular to the electric field or with an angle, because of the polarized and weakened Ti–O bonds along the field, as illustrated in Figure 4.25 (c). In the meanwhile, the broken tubes will stretch out with the motion of ionic species in the electrolyte, thereby forming the primal nanowires, as shown in Figure 4.25 (d). To prove this mode, a series of experiments were designed purposely. First of all, the

essential role of electric field is studied with reference to nanowire evolution. After formation of the quasi-nanosprings and initiation of the cracks at tube mouths (see Figure 4.21 (b)), the nanotubes were etched under the same conditions in the absence of the field (i.e., leaving the samples in the electrolyte after switching off the power supplier) for 1.5 h. The results reveal that no nanowires are formed without the assistant of the field, as shown in Figure 4.27 (a), in contrast to that under the field (cf. Figure 4.20). The same results are obtained when etching the tubes for even 7.5 h (cf. Figure 4.24 and Figure 4.27 (b)). These demonstrate that an electric field is required to trigger the transition from the tubes to wires. Secondly, after formation of the structure in Figure 4.21 (b), the anodization was continued to carry out in ethylene glycol with 2 vol% H₂O only (i.e., removing the ionic species of NH₄F) at 25 V and 40 °C for 1.5 h or 7.5 h. It shows that no nanowires are fashioned in the absence of NH₄F either, as displayed in Figure 4.28. The above experiments disclose two requisites for the transition: an electric field to polarize the Ti–O bonds and an ionic species to attack the weakened bonds. Accordingly, the nanowires stretching out of the tube surface can be observed if adopting a relatively weaker electrolyte. As such, after formation of the initial structure in Figure 4.21 (b), the anodization was continued further in an electrolyte of ethylene glycol containing 0.09 M NaCl and 2 vol% H₂O for 1.5 h, considering the possibility to grow nanotubes using a chlorine-based solution.^[55] Figure 4.29 (a) exhibits that a number of short nanowires appear on the tube surface after the anodization. Under the current anodizing conditions, no substance can be deposited on the surface. Therefore, these wires originate from the tubes underneath the porous oxide layer, as can be confirmed from one end of each wire anchoring to the surface, as shown in Figure 4.29 (b)~(d). Obviously, the wires protruding the surface can only be achieved via an approach that proposed in

Figure 4.25 (c) and (d). The stretching mode can be further consolidated with the zigzag edges of the wires, emanating from the crack propagation across the rings. And also the wires keep curving when long enough (see Figure 4.24).

Figure 4.27 Surface morphology of the nanotubes anodized at 25 V and 40 °C in ethylene glycol with 0.3 wt% NH_4F and 2 vol% H_2O for 30 min first, and then etched (i.e., switch off the power supplier) in the same electrolyte solution for (a) 1.5 h and (b) 7.5 h.

Figure 4.28 Surface morphology of the nanotubes anodized at 25 V and 40 °C in ethylene glycol with 0.3 wt% NH_4F and 2 vol% H_2O for 30 min first, and then in ethylene glycol with 2 vol% H_2O only for (a) 1.5 h and (b) 7.5 h.

Figure 4.29 Surface morphology of the nanotubes anodized at 25 V and 40 °C in ethylene glycol with 0.3 wt% NH_4F (or 0.09 M) and 2 vol% H_2O for 30 min first, and then in ethylene glycol with 0.09 M NaCl and 2 vol% H_2O for 1.5 h. The four images are at different locations and with different magnifications.

In the other manner of spitting, the resultant quasi-nanosprings (as in Figure 4.25 (b)) can bend, elongate, and swing in the electrolyte, especially for the ones with enough room. When two neighbored nanotubes bend toward opposite directions, cracks initiate, coalesce, and propagate, as shown in Figure 4.20 (b). In principle, the bending gives rise to tensile stress for one side of a quasi-nanospring while compressive stress for the other side, as illustrated in Figure 4.25 (e). This will accelerate the chemical dissolution of the regions under tensile

stress, especially with the assistant of an electric field. As a consequence, the regions finally break up and thus forming the primal nanowire structure, as illustrated in Figure 4.25 (f) and revealed in Figure 4.20 (c). The splitting mode requires a certain room for bending and hence takes place at the cracking regions only.

In Figure 4.30, the XPS spectra of as-grown nanowires and nanotubes are compared. The oxidation state of Ti element (Ti 2p_{3/2}, binding energy 458.9 eV; Ti 2p_{1/2}, binding energy 464.7 eV) in both nanostructures is identical to Ti⁴⁺,^[162, 163] together with the major peak of O 1s (binding energy 530.3 eV), indicating the pertinent bonding structure is TiO₂. The binding energy of F 1s is 684.6 eV, in line with the F⁻ ions that physically adsorbed on the TiO₂ surface.^[164] Obviously, both the O 1s peaks are asymmetric and can be deconvolved into two peaks, as shown in Figure 4.30 (d) and (e). The smaller peaks at the shoulders (binding energy 532.0 eV) are assigned to surface species (i.e., Ti–OH and Ti–O–O–) as reported elsewhere.^[162, 165, 166] Corresponding content of these species in the O 1s peak is ~20% and ~45% for nanowires and nanotubes, respectively. The atomic ratio of Ti:O:F is about 1:2.25:0.27 in nanowires and 1:2.89:0.37 in nanotubes based on the relevant peak areas displayed in Figure 4.30 (a)~(c). Accordingly, the number of F⁻ ions per surface Ti is 2.7:1.8 (i.e., $0.27/[1-2.25\times(1-20\%)\times(1/2)]=2.7$ for nanowires and $0.37/[1-2.89\times(1-45\%)\times(1/2)]=1.8$ for nanotubes, herein the terms in square brackets are the percentage of Ti elements bonding with surface species only) for nanowires with respect to nanotubes.

Figure 4.30 Comparison of XPS spectra between as-grown nanowires and nanotubes prepared at 60 V for 8 h: (a) Ti 2p core level, (b) O 1s core level, (c) F 1s core level; (d) and (e) are respective curve fitting results of the O 1s peaks. The relevant photoelectrons are from bulk nanowires (see Figure 4.17 (b)) and nanotube sidewalls (see Figure 4.26).

As such, the following scenario is figured out. Initially a large number of anions (mainly F^- and OH^- ions) are adsorbed on the nanotube surface. Considering the chemical dissolution process, that is, $TiO_2 + 4H^+ + 6F^- \rightarrow [TiF_6]^{2-} + 2H_2O$, only the regions with F^- ions are activated and able to be etched, while the regions with OH^- ions are passivated. According to the calculation above, the activated region is only 45% ($1.8/4 = 45\%$) for the nanotubes whereas $\sim 68\%$ ($2.7/4 \approx 68\%$) for the nanowires. To trigger the transition, more H^+ ions are required to react with OH^- ions and pave the way for F^- adsorption. This is the reason why nanotube-nanowire transition takes place only under an intermediate chemical dissolution environment (e.g., at elevated temperature or prolonged duration in organic electrolyte) that presented afore. On the other hand, this result also elucidates high-aspect-ratio nanotubes are obtainable in organic electrolyte because of the passivated tube walls.

4.4 Summary

In this chapter, the role of electric field is studied in growth of titania nanotubes through electrochemical anodization. Two electric fields are concerned: the field originating from the potential drop over the oxide layer and that in the electrolyte. Pore diameter increases linearly while tube length (or growth rate) increases exponentially with the former. The latter also affects the growth rate via increasing ionic flux in the electrolyte. At higher field strength, growth of the tube maintains longer time as a result of higher ion concentration at tube bottom. The growth of the tubes and the influence of the field are elucidated by an Ion Flux Model where H^+ and F^- ion concentration profiles are considered in a single tube.

To further study the effect of the latter (i.e., electric field in the electrolyte), double-sided nanotubes are grown simultaneously at both sides of a titanium foil using a two-electrode

anodizing method. The tube length and surface porosity at both sides increase with applied potential. Under normal conditions, longer nanotubes are obtained at the frontside comparing to the backside. This lopsided growth process is attributed to the higher ionic flux induced by electric field at the frontside. The double-sided nanotubes are tailored to be comparable by adjusting the electric field in the electrolyte. Comparative study reveals that this simple two-electrode anodizing configuration gives rise to the largest tube growth rate.

For application in dye-sensitized solar cells, clear tube surface is required to facilitate dye loading and electrolyte injection, therefore formation and elimination of nanowires on top of the nanotubes are investigated. The results indicate that transition from anodic nanotubes to nanowires is an intrinsic stage during tube growth in organic electrolyte, thus cannot be eliminated by pre-treatment methods. The transition requires a large number of H^+ ions to reduce the passivated area of tube walls, therefore can be observed only under an intermediate chemical dissolution environment, such as at elevated temperature or prolonged duration in organic electrolyte. The nanowires grown for long duration (e.g., ≥ 8 h at 25 V and 40 °C) can be cleared away with ultrasonic cleaning (a post-treatment method) due to formation of the quasi-nanosprings.

Chapter 5 Novel Approach for Light Harvesting in Dye-Sensitized Solar Cells

Chapter 2 reviews that, up till now, dye-sensitized solar cells based on anodic nanotubes have two major configurations.^[30] frontside and backside illumination. In frontside illumination (see Figure 2.19 (a)), nanotubes are produced on a transparent conducting oxide, thereafter assembled into DSSCs.^[31] This normally requires a number of complicated steps before the nanotubes can be used in DSSCs, for example, sputtering a titanium thin film onto the TCO glass and then growing the nanotubes,^[32] or growing the nanotubes first on a titanium foil, peeling off these nanotubes, and transferring onto the TCO glass.^[108, 109] All these procedures will substantially increase the costs of production, therefore should be minimized. In backside illumination (see Figure 2.19 (b)), nanotubes are directly grown on commercial titanium foils and assembled into DSSCs.^[33] Although this structure suffers energy loss via light reflection and electrolyte absorption, a comparable conversion efficiency was achieved with pristine nanotubes (no additional processing except for the necessary TiCl_4 treatment) by Grimes' group, that is, 6.89%^[19] as compared to 6.86%^[32] in the frontside illumination. Very recently, an efficiency of 7.6% was reported by Li and co-workers also adopting the same configuration.^[144] This renders a great potential to produce efficient while low cost DSSCs based on the backside illumination. However, the reduced photocurrent via energy loss has hindered its development.

Accordingly, two methods are proposed to promote the photocurrent in backside-illuminated configuration: reducing energy loss or increasing energy absorption. The former can be realized by using counter electrodes of high transmittance or cell spacers of small

thickness.^[144] The latter can be achieved by increasing the surface area of the photoanode that available for dye adsorption, as discussed and proposed in Section 3.1.

In this chapter, the parallel configuration of dye-sensitized solar cells is investigated based on double-sided nanotube arrays which drastically increase the energy absorption of the photoanodes, and as a result, the conversion rate. Electrochemical impedance spectroscopy measurements confirm the parallel connection of the double-sided solar cells. Photovoltaic performance of the parallel cells exhibits an average 70% photocurrent increment and 30% efficiency enhancement as compared to that of the single cells, due to significantly increased surface area and highly reduced series resistance. The formation of nanowires that discussed in Section 4.3 also arises when the tubes are directly used in dye-sensitized solar cells. A TiCl_4 treatment for ~10 h is found effective in suppressing the formation of nanowires and thus improve the photovoltaic properties of the solar cells. An optimal tube length for backside illumination is determined to be ~30 μm on the basis of theoretical calculation and experimental fitting results.

5.1 Parallel Configuration and Efficiency Calculation

In Section 4.2, double-sided nanotubes are grown simultaneously on both sides of a titanium foil using a two-electrode configuration, with the tubes at the frontside being longer than that at the backside (in general, nanotubes grown at the side facing to the counter electrode is referred to as the “frontside” while that at the other side is referred to as the “backside”). To obtain clear tube surface for dye loading and electrolyte infiltration, ultrasonic cleaning is proposed to rid off the nanowires on top of the nanotubes in Section 4.3. As such, the tube lengths at both sides are tailored to be comparable after anodization at 25 V

and 40 °C for 14 h with ultrasonication for 20 min, i.e., $11.1 \pm 1.4 \mu\text{m}$ for the frontside and $11.2 \pm 1.3 \mu\text{m}$ for the backside (based on 5 samples), as shown in Figure 5.1. This tube length is employed in most experiments below, unless otherwise indicated. The resultant double-sided nanotubes are displayed in Figure 5.2. It reveals that no obvious difference is present between the nanotubes at the frontside and backside.

Figure 5.1 SEM cross-sectional views of the nanotubes grown at 25 V and 40 °C for 14 h after ultrasonic cleaning for 20 min: (a) frontside, (b) backside.

Figure 5.2 (a) Optical microscope image showing double-sided nanotube arrays (TiO_2 , blue color) on a titanium substrate (Ti, white color). (b, c) Top and (d, e) cross-sectional FESEM images of the nanotubes used in this work: (b, d) frontside, (c, e) backside.

The as-grown amorphous nanotubes crystallized into almost 100% anatase structure when annealed in air at 450 °C for 3 h, as displayed in Figure 5.3. The crystallite size is estimated

to be ~53 nm using Scherrer equation, in line with the values reported elsewhere.^[17, 137, 140] This crystal size can facilitate electron transport and the preferential facet of (101) orientation is also favored for dye adsorption, as discussed in Section 2.2.5. Titanium peaks from the underlayer of metal substrate are also detected. It is evident that the crystallographic structures are nearly the same for the tubes on both sides. The above results indicate highly oriented nanotubes at both sides exhibit no distinct difference before assembled into dye-sensitized solar cells.

Figure 5.3 XRD patterns of the as-grown and annealed nanotubes at the frontside (F) and backside (B). A and T represent anatase and titanium phase, respectively.

In Figure 3.2, a dye-sensitized solar cell of parallel configuration proposed in this project is illustrated. The cell structure is described again as follows. The double-sided nanotubes separated by a layer of titanium metal are sandwiched between two platinized counter electrodes, thus rendering a natural parallel cell structure after electrolyte injection. This configuration makes full use of both surfaces of a photoanode, therefore significantly

increases the dye loading amount of the photoanode, which is the determining figure of merit for the photocurrent. In application, the light source directly illuminates one side of the cell while a dielectric mirror is adopted to reflect the light onto the other side. In practice, this can be easily done (Mirrors and even lenses are already used in concentrator solar cells to concentrate sunlight onto the photovoltaic cells.^[147, 148]). Although a reflection rate over 99% can be achieved in the range of 400~850 nm (see Figure 5.4), the reflected light intensity is only $35 \pm 5 \text{ mW/cm}^2$ (measured by an Ophir Optronics power-meter Nova reader) in contrast to the 100 mW/cm^2 obtained from direct illumination, because of increased light pathway and tilted incident angle.

Figure 5.4 Transmittance spectra of the dielectric mirror used for light reflection in the current project. AOI denotes angle of incidence. Data are provided by PHOTONIK (SINGAPORE) PTE LTD.

To determine the reflected light intensity exactly at the cell surface, photovoltaic responses of the cells were tested under different light intensities, as shown in Figure 5.5. In general, the short-circuit current density increases linearly with light intensity in a typical dye-sensitized solar cell where transport kinetics of redox couples in the electrolyte are fast enough to regenerate the dye molecules.^[7, 167] This linearity is present in Figure 5.5 especially at low intensity, which deviates when longer nanotubes are used and/or at higher intensity. After fitting the J_{sc} obtained by mirror reflection (empty symbols in Figure 5.5) into the dashed lines, the reflected light intensity at cell surface is determined to be 38 mW/cm^2 . This value is within the scope measured by the Nova reader and therefore adopted in the subsequent efficiency calculation.

Figure 5.5 Influence of light intensity on short-circuit current density of the cells with nanotubes of different lengths. Solid symbols are obtained by direct illumination while the empty symbols are attained by mirror reflection.

Photovoltaic conversion efficiency of a parallel cell is calculated using the following equation

$$\eta(\%) = \frac{P_{\text{out}}}{P_{\text{in}}} \times 100 = \frac{P_{\text{max}}}{E_{\text{tot}} A_{\text{tot}}} \times 100 = \frac{I_{\text{sc}} V_{\text{oc}} FF}{E_{\text{d}} A_{\text{d}} + E_{\text{r}} A_{\text{r}}} \times 100 \quad (5.1)$$

where P_{out} is the power output, P_{in} is the power input, P_{max} is the maximum or peak power output, E_{tot} is the total incident irradiance, E_{d} is the incident irradiance by direct illumination (i.e., 100 mW/cm²), E_{r} is the incident irradiance by mirror reflection (i.e., 38 mW/cm²), I_{sc} is the short-circuit photocurrent, V_{oc} is the open-circuit photovoltage, FF is the fill factor, A_{tot} is the total active area, A_{d} and A_{r} are the active area at the side via direct illumination and mirror reflection, respectively.

In particular, the following relations stand in the current study

$$A_{\text{r}} = A_{\text{d}} = A \quad (5.2)$$

$$E_{\text{r}} = \alpha E_{\text{d}} \quad (5.3)$$

where α is a degradation factor of the incident irradiance via mirror reflection. Consequently, Equation 5.1 can be rewritten as

$$\eta(\%) = \frac{I_{\text{sc}} V_{\text{oc}} FF}{(1 + \alpha) E_{\text{d}} A} \times 100 = \frac{J_{\text{sc}} V_{\text{oc}} FF}{(1 + \alpha) E_{\text{d}}} \times 100 \quad (5.4)$$

It reveals that Equation 5.4 can be used to calculate the conversion efficiency of a single cell when $\alpha = 0$ and that of a parallel cell when $\alpha = 0.38$ in this study. Note that herein the method to determine the J_{sc} of a photovoltaic cell remains the same for both single and parallel structures, that is, dividing the I_{sc} with A on the basis of Equation 5.4.

5.2 Verification of Parallel Connection

Typical performance of one parallel solar cell under different illumination modes is compared in Figure 5.6 (a). In one case, photovoltaic behavior of a single cell (i.e., the cell at each side) was tested separately: “Single-F” and “Single-B” represent the solar cell assembled with the nanotubes at the frontside and backside, respectively. In the other case, performance of a parallel cell (i.e., the cells at both sides) was tested: “Parallel-FB” means direct illuminating the F while reflecting on the B, and “Parallel-BF” denotes direct illuminating the B while reflecting on the F. The cell performance of Single-B is superior to that of the Single-F. The relatively higher J_{sc} may originate from the longer nanotubes on B considering the standard deviation of the tube length (see Section 5.1). The larger V_{oc} is ascribed to the longer electron lifetime in the nanotubes at the backside. The respective electron lifetime is determined to be 43 ms, 31 ms, 31 ms for Single-B, Single-F, and Parallel cells in the dark, based on the peak frequency in Figure 5.6 (b) by $\tau_n = 1/\omega_{min} = 1/2\pi f_{min}$.^[168, 169] The photovoltaic behaviors of Parallel-BF and Parallel-FB are nearly the same except for a little higher J_{sc} of the Parallel-BF. This is understandable in light of possible longer nanotubes at the backside. Interestingly, the V_{oc} of both parallel cases is comparable with that of the Single-F. Taking into account the similar electron lifetimes in the Parallel and Single-F cells, it suggests that lifetime in the parallel structure is limited by that of the shorter one in the individual single cells.

In Figure 5.6 (c), Nyquist plots of the pertinent cells are presented. In general, three semicircles appear in a typical Nyquist diagram of DSSCs, which are associated with (in the order of decreasing frequency) charge transfer at the counter electrode, electron transport in the photoanode and charge transfer at the photoanode/electrolyte interface, and Nernst

diffusion within the electrolyte.^[169, 170] Accordingly, the following parameters are obtained by fitting the equivalent circuit illustrated in Figure 5.7: internal ohmic resistance (R_h), charge transfer impedance at the electrolyte/Pt-FTO interface (R_p), and recombination (or dark reaction) impedance (R_r) at the nanotubes/electrolyte interface, as listed in Table 5.1. The R_h , mainly related to the sheet resistance of FTO and titanium foil, is determined by the first intercept of the semicircles (frequency $> 10^5$ Hz).^[94, 171] The R_p and R_r are attained from the diameters of the small and large semicircles, respectively.^[170, 172] All the measured values of the three parameters satisfy the following relationship

$$\frac{1}{R_{\text{Parallel}}} = \frac{1}{R_{\text{Single-F}}} + \frac{1}{R_{\text{Single-B}}} \quad (5.5)$$

Here $R_{\text{Single-F}}$, $R_{\text{Single-B}}$, and R_{Parallel} are impedance of the Single-F, Single-B, and Parallel cells, respectively. The calculated values of R_{Parallel} using Equation 5.5 are also given in Table 5.1, which are in good agreement with the measurements. This directly discloses the parallel connection of the double-sided solar cells.

Figure 5.6 (a) Photocurrent-voltage characteristics of a parallel configuration dye-sensitized solar cell under different illumination modes. Electrochemical impedance spectra of the cell in (a) measured under -0.75 V applied bias in the dark: (b) Bode phase plots, (c) Nyquist plots. Inset is a local magnification. The lines in (b) and (c) show the fitted results ($\chi^2 < 0.01$).

Figure 5.7 Equivalent circuit of DSSCs. (A) internal ohmic resistance (R_h); (B) charge transfer at the electrolyte/Pt-FTO interface (R_p , charge transfer impedance; $CPE1$, double layer capacitance); (C) electron transport in the nanotubes and charge transfer at nanotubes/electrolyte interface (Z_{w1} , diffusion impedance; R_r , recombination impedance; $CPE2$, constant phase element); (D) Nernst diffusion in the electrolyte (Z_{w2} , Warburg impedance).

Table 5.1 Values of Impedance Determined by EIS Measurements

	R_h (Ω)	R_p (Ω)	R_r (Ω)
$R_{\text{Single-F}}$	17.15	2.89	44.50
$R_{\text{Single-B}}$	15.35	3.04	62.50
R_{Parallel}	8.60	1.26	24.29
R_{Parallel} (calculated)	8.10	1.48	25.99

5.3 Photovoltaic Characteristics of Parallel Dye-Sensitized Solar Cells

Table 5.1 indicates that the parallel structure merits the photovoltaic performance by substantially reducing the series resistance (R_s) of the solar cells, as the R_h and R_p are assigned to be the components of R_s .^[171] In view of this, to reduce the R_h and therefore the R_s , the same double-sided nanotubes were grown on titanium foils of 0.127 mm instead of the normal 0.250 mm. Moreover, UV-ozone treatment was applied onto the nanotubes before dye loading, which is believed to benefit the cells by reducing surface states in the nanotubes according to the results of Zhang and co-workers.^[172] Photovoltaic behaviors of the cells on

0.127-mm foils surpass that on 0.250-mm foils, as shown in Figure 5.8. Remarkably the following relation is obtained as expected

$$R_{s, 0.250\text{-mm Single}} > R_{s, 0.127\text{-mm Single}} > R_{s, 0.250\text{-mm Parallel}} > R_{s, 0.127\text{-mm Parallel}} \quad (5.6)$$

where the subscripts correspond to the labels in Figure 5.8. It further demonstrates that the parallel configuration contributes to cell performance by decreasing the series resistance. This, in turn, increases the photocurrent in a parallel system, as revealed in Figure 5.9. By simply adding the photocurrent at the frontside under 1 sun illumination (i.e., Curve III) and that at the backside under mirror reflection (i.e., Curve I), photocurrent of a parallel cell is calculated to be as Curve (I + III), which is smaller than the measured value (i.e., Curve IV) over the whole testing range. This deviation in photocurrent is resulted from the reduced series resistance in the parallel configuration. In addition, the cell exhibits serious nonlinearity (i.e., efficiency: 3.37% under 0.38 sun vs. 1.72% under 1 sun for Curve I vs. Curve II) due to increased tube length, in line with the measurements in Figure 5.5.

Figure 5.8 Photovoltaic performance of dye-sensitized solar cells with nanotubes grown on different thicknesses of titanium foils. All the nanotubes are under UV-ozone treatment for 20 min before dye loading.

As such, the photocurrent of a parallel solar cell benefits from three contributions: the cell at the frontside, the cell at the backside, and the interaction between the two individual cells which reduces the series resistance through the parallel connection as in Figure 5.9. In contrast, the photocurrent of a single cell depends on one cell only. Consequently, the parallel configuration substantially promotes the photocurrent in a unit solar cell through two ways: additionally utilizing the back surface and considerably reducing the series resistance.

Figure 5.9 Photovoltaic performance (solid lines) of a parallel dye-sensitized solar cell under mirror reflection (or 0.38 sun) at the backside only (I), 1 sun illumination at the backside only (II), 1 sun illumination at the frontside only (III), 1 sun illumination at the frontside and mirror reflection (or 0.38 sun) at the backside (IV). The (I + III) is a calculation (dash line) by adding the photocurrent of I and III together. The lengths of the nanotubes used are 39.1 μm at the frontside (F) and 27.5 μm at the backside (B), respectively.

Photovoltaic characteristics of DSSCs with nanotubes under TiCl_4 treatment for different durations are summarized in Table 5.2. The reasons to vary the TiCl_4 treatment duration will be discussed in Section 5.4. In all cases, the parallel cells exhibit superior performance over

the single cells. Considerable improvements in photocurrent and series resistance are obtained, consistent with the above discussion. In principle, the dye loading amount of the photoanode in a parallel cell is two times larger than that in a single cell, provided that the tube length at both sides is comparable, hence will give rise to at least 100% increase in photocurrent. However, on average only a 70% increment is achieved (based on more than 30 cells). This is attributed to the lower incident intensity at the backside via light reflection (i.e., 38 mW/cm^2), which produces less electrons as compared to direct illumination (i.e., 100 mW/cm^2). Fill factor of the cells increases slightly, due to highly reduced R_s in the parallel configuration, as shown in Table 5.2: more than halved as compared to that in the single cells. A comparable V_{oc} is obtained in both structures, as electron lifetime in the parallel system is limited by that of the shorter one in the individual single cells. At the given conditions, an average efficiency enhancement of 30% (based on more than 30 cells) is achieved in the parallel cells. In addition, the cell performance increases with the duration of TiCl_4 treatment, which may originate from the increased surface area as more tiny nanoparticles form on tube surface, as will be discussed in Section 5.4.

In Section 5.1, the method to calculate the conversion efficiency of a photovoltaic cell is presented on the basis of solar cell fundamentals. Accordingly, an average 30% increment in conversion efficiency is determined for parallel configuration. In general, a solar cell is regarded as a current source; therefore the photocurrent produced in a unit solar cell is essential in view of real application. In this project, an average 70% increase in photocurrent is achieved with the parallel configuration. To further highlight the virtues of the parallel configuration, a scenario in real application is considered as follows.

Table 5.2 Comparison of Photovoltaic Characteristics between
Single and Parallel Structures ^a

Solar Cells		I_{sc} (mA)	ΔI^b	V_{oc} (V)	FF	R_s $\Omega \text{ cm}^2$	η^c (%)	$\Delta \eta^d$
15 h	Single	0.653	57%	0.698	0.606	62.26	1.06	23%
	Parallel	1.024		0.692	0.656	26.49	1.30	
20 h	Single	0.728	67%	0.688	0.580	59.44	1.12	46%
	Parallel	1.217		0.694	0.695	25.10	1.64	
25 h	Single	0.832	70%	0.697	0.544	58.50	1.21	44%
	Parallel	1.412		0.699	0.634	25.14	1.74	

^a Data are obtained from the average of two cells; ^b $\Delta I = (I_p - I_s)/I_s$; ^c Calculated using Equation 5.4; ^d $\Delta \eta = (\eta_p - \eta_s)/\eta_s$

Consider a tall building with a limited roof area to supply the electrical power with solar panels. Using the single cell configuration, it is assumed that 100 pieces of panels are required to power the building, that is, $P=100P_{\text{single}}=100 \times (I_{sc} V_{oc} FF)$. In contrast, only 59 pieces of panels are required when adopting the parallel cell configuration, since 1.7 times photocurrents can be produced in a unit panel provided that similar mirrors are used (i.e., $P'=59P_{\text{parallel}}=59 \times (1.7I_{sc} V_{oc} FF)=100P_{\text{single}}$). As such, less solar panel is needed for the same requirement of electrical power, or more electrical power is generated with the same quantity of panels using the parallel configuration. Therefore, the promoted power output in a unit solar cell is another intriguing characteristic of the parallel cell structure, since power input is less considered in real application as the sun continuously supplies sufficient energy to the earth.

5.4 Optimal Duration for TiCl_4 Treatment

Section 4.3 shows that transition from nanotubes to nanowires takes place during nanotube growth under an intermediate chemical dissolution environment. Interestingly the formation of nanowires also arises during application of nanotubes in dye-sensitized solar cells. In Figure 5.10 (a), the original nanotubes (i.e., without TiCl_4 treatment or at 0 h) exhibit regular tube surface with some cracks resulted from the formation of initial nanowires (see Figures 4.20 and 4.22). After assembled into DSSCs, the nanotubes bundle together, especially along the cracks as shown in Figure 5.10 (b) at 0 h. Detailed observation reveals that nanowires appear once again at the bundling regions, as displayed in Figure 5.10 (c) where the quasi-nanosprings can also be seen. Obviously this transition process is detrimental in view of the long term stability of the solar cells.

Considering the similar transition process that occurs during nanotube growth, thinning of tube walls is a crucial factor in forming the nanowires. Accordingly, a counter strategy to thicken the tube walls is proposed to suppress the formation of nanowires. One effective method is the TiCl_4 treatment which is frequently used to promote the photovoltaic performance of DSSCs by forming an additional highly pure TiO_2 layer on the original nanoparticles,^[7] improving electron percolation,^[167] and increasing the surface area.^[173] A TiO_2 layer of 1 nm on the surface of nanoparticles was obtained by Grätzel's group using 40 mM aqueous TiCl_4 solution at 70 °C for 30 min.^[97] Under the same condition but adopting 0.2 M solution, TiO_2 layers of ~13 nm were formed on both the inner and outer walls of the anodic nanotubes by Schmuki's group.^[141, 174] As such, the concentration of 40 mM was selected in light of the closely packed configuration of the nanotubes used in this study,

otherwise higher concentration may result in clogging of the intertube spacing and even the tube tops as in ref. [141].

Figure 5.10 Surface morphology of the nanotubes used in dye-sensitized solar cells: (a) before and (b) after assembled into devices; (c) typical nanowire and quasi-nanospring structures present in (b) at 0 h. The times on the images indicate the durations of TiCl_4 treatment on the relevant nanotubes.

Figure 5.10 (a) shows that the surface morphology of the nanotubes changes little with the duration of the TiCl_4 treatment, whereas the pertinent tube stability has been improved significantly as displayed in Figure 5.10 (b). In comparison to the pristine (i.e., Figure 5.10 (b))

at 0 h) as well as the original (i.e., Figure 5.10 (a)) nanotubes, a treatment duration of 10 h and above gives rise to relatively more stable tube structure.

Photovoltaic performance of the relevant solar cells is shown in Figure 5.11 and summarized in Figure 5.12 (a). The open-circuit voltage of cells with nanotubes under TiCl_4 treatment is higher than that without the treatment. This is attributed to the improved electron percolation in the nanotubes, especially in the quasi-nanosprings where the connections between rings may act as the electron trapping sites. No obvious changes in V_{oc} can be observed as the duration prolongs.

Figure 5.11 Photocurrent-voltage characteristics of dye-sensitized solar cells with the nanotubes under TiCl_4 treatments for different durations.

Figure 5.12 (a) Photovoltaic characteristics of dye-sensitized solar cells as a function of TiCl₄ treatment duration; (b) series resistances and dye loadings of the relevant solar cells; surface morphology of the nanotubes under TiCl₄ treatment for (c) 5 h, (d) 10 h, (e) 15 h, and (f) 20 h. Data are obtained from the average of two cells.

The short-circuit current density drastically enhances upon treatment (cf. 0 h and 0.5 h) and gradually increases thereafter (i.e., from 0.5 h to 10 h), whereas drops dramatically between 10 h and 15 h while increases steadily after 15 h. This trend is in good agreement with the dye desorption measurement presented in Figure 5.12 (b). Clearly there is also an abrupt decrease in dye loading amount that adsorbed on the nanotubes in the range of 10 h ~ 15 h. In general, the dye loading amount is closely related to the surface area of the photoanode. Accordingly, the surface area of the nanotubes increases with the treatment duration, as more tiny particles form on both the inner and outer tube walls.^[173, 141] However, the surface area will diminish considerably when intertube spacing (or at least that near the tube tops, considering the diffusion process in the solution for the hydrolysis) is fully filled by the

nanoparticles, since the outer surface of the nanotubes is hardly to be used any more. This is corroborated by the morphology changes shown in Figure 5.12 (c)~(f). After 10 h, the intertube spacing is too small for the dye molecules to access the outer tube walls, particularly when taking into account the dye loading process which normally occurs by diffusion process from tube tops to the bottoms. It is believed that the progressive increment in J_{sc} after 15 h originates from the increased inner tube surface.

Figure 5.12 (a) also reveals that the fill factor of the solar cells is improved by the $TiCl_4$ treatment while degrades gradually after 10 h. This is in line with the variation in series resistance (cf. Figure 5.12 (b)). Eventually the most efficient cell is obtained with the nanotubes under $TiCl_4$ treatment for 10 h. The above results demonstrate that $TiCl_4$ treatment duration over 5 h is necessary and effective in suppressing the formation of nanowires thus increasing the stability of the nanotubes. On the other hand, longer treatment duration (over 10 h) will result in degradation of photovoltaic performance, due to failure in using the outer tube surface. Therefore, the treatment duration of ~10 h is optimal for the current study. It also suggests that an optimal treatment condition should exist for all the anodic nanotubes, which varies with the concentration of the solution, treating temperature, and also the nanotubes used.

5.5 Optimal Tube Length for Parallel Dye-Sensitized Solar Cells

The photocurrent of a dye-sensitized solar cell is closely related to dye loading amount of the photoanode which, in turn, is significantly affected by length of the nanotubes. Figure 5.13 (a) shows that photovoltaic properties of the single cells increase with length of the nanotubes up to 25.5 μm and decline when longer tubes are used. Similar trend is also

present in parallel cells, as shown in Figure 5.13 (b). An efficient cell exhibits a conversion efficiency of 2.57% for single structure and 3.38% for parallel configuration, an efficiency enhancement over 30%. Obviously the cell performance strongly depends on the photocurrent.

Figure 5.13 Effect of nanotube length on photovoltaic properties of single cells (a) and parallel cells (b). The parallel cells are tested with nanotubes at the frontside (F) under 1 sun illumination and that at the backside (B) under mirror reflection (or 0.38 sun).

In general, the longer the tubes, the more the dye loading amount and thus the photocurrent. However, electron diffusion length in the tubes, on the other hand, limits the length to an optimal value. This optimal length is particularly significant for dye-sensitized solar cells with backside-illuminated configuration. In this structure, photon energy is first absorbed at the tube tops where electron injection takes place predominantly. Thereafter, the injected electrons have to percolate all the way through the tubes to the collecting electrode. In this scenario, charge collecting efficiency of the cell decreases seriously when the tube length exceeds the electron diffusion length, since a majority of electrons generated at the tube tops

can no longer be collected. As such, it is important to determine the optimal tube length in backside-illuminated solar cells for higher photocurrent.

Let us consider solar cells with single structure first. In principle, the short-circuit photocurrent density of a dye-sensitized solar cell under backside illumination can be expressed as (similar to Equation 2.6)

$$J_{sc} = \int qF(\lambda)[1 - r(\lambda) - a(\lambda)]IPCE(\lambda)d\lambda \quad (5.7)$$

where q is the electron elementary charge, $F(\lambda)$ is the incident photon flux density, $r(\lambda)$ is the energy loss due to reflection by the counter electrode, $a(\lambda)$ is the energy loss owing to absorption by the counter electrode and electrolyte, $IPCE(\lambda)$ is the incident photon to current efficiency. Accordingly, the photon flux density incident on the nanotubes is as follows

$$f(\lambda) = F(\lambda)[1 - r(\lambda) - a(\lambda)] \quad (5.8)$$

The $IPCE(\lambda)$ is a product of the light harvesting efficiency $LHE(\lambda)$, the quantum yield of charge injection ϕ_{inj} , and the charge collecting efficiency η_{cc} , which is given in Equation 2.7. The $LHE(\lambda)$ is used to measure the absorption of incident photon energy by available dye molecules and given by Equation 2.8.

To obtain a relation between the J_{sc} and nanotube length L and hence determine the optimal tube length, the following assumptions are used to derive the light harvesting efficiency in terms of L instead of λ : (1) dye molecules are adsorbed uniformly on both inner and outer surfaces of the tubes, as illustrated in Figure 5.14 (a); (2) global dye loading amount is the sum of n layers of dye molecules along the tubes, with the thickness of each layer being the

dimension (l) of a dye molecule, i.e., $L = nl$; (3) each layer absorbs the same portion (α) of the incident photon energy.

Figure 5.14 Models used to calculate light harvesting efficiency of the solar cells under backside illumination with nanotube length (a) $L \leq L_0$, and (b) $L > L_0$. Inset illustrates the magnification of a tube attached with dye molecules (red dots) on both inner and outer surfaces.

As such, the light harvesting efficiency can be calculated as

$$LHE(n) = \frac{\alpha f(\lambda) + \alpha(1-\alpha)f(\lambda) + \alpha(1-\alpha)^2 f(\lambda) + \cdots + \alpha(1-\alpha)^{n-1} f(\lambda)}{f(\lambda)} \quad (5.9)$$

Here the numerator is the total absorption of the incident photon energy by n layers of dye molecules while the denominator is the incident photon flux density as in Equation 5.8. As a consequence,

$$LHE(n) = 1 - (1 - \alpha)^n \quad (5.10)$$

Apparently the light harvesting efficiency will be close to unity when there are infinite layers of dye molecules. With the above equations, Equation 5.7 can be written as

$$J_{sc} = \int qf(\lambda) LHE(n) \phi_{inj} \eta_{cc} d\lambda = LHE(n) \phi_{inj} \eta_{cc} \int qf(\lambda) d\lambda = [1 - (1 - \alpha)^n] \eta_{cc} C \quad (5.11)$$

where

$$C = \phi_{inj} \int qf(\lambda) d\lambda \quad (5.12)$$

As photons absorbed by dye molecules are converted to conduction band electrons efficiently, e.g., $\phi_{inj} > 99.9\%$ under certain conditions,^[7] the value of C is approximately constant for single or parallel configuration in this study, which depends on electrolyte category, spacer thickness, counter electrode, and incident photon flux density.

In the case of nanotube length being shorter than electron diffusion length (L_0) within the tubes, as shown in Figure 5.14 (a),

$$\eta_{cc} = 1 \quad (L \leq L_0) \quad (5.13)$$

Therefore,

$$J_{sc} = C[1 - (1 - \alpha)^{L/l}] \quad (L \leq L_0) \quad (5.14)$$

With the tube length being longer than L_0 , as illustrated in Figure 5.14 (b), electrons injected at the part beyond L_0 cannot be collected any more. Assuming this part contains m layers ($L - L_0 = ml$) of dye molecules, the total energy loss (E_{loss}) is presented as

$$E_{\text{loss}} = \alpha f(\lambda) + \alpha(1-\alpha)f(\lambda) + \alpha(1-\alpha)^2 f(\lambda) + \cdots + \alpha(1-\alpha)^{m-1} f(\lambda) \quad (5.15)$$

The total energy absorption (E_{abs}) is

$$E_{\text{abs}} = \alpha f(\lambda) + \alpha(1-\alpha)f(\lambda) + \alpha(1-\alpha)^2 f(\lambda) + \cdots + \alpha(1-\alpha)^{n-1} f(\lambda) \quad (5.16)$$

Accordingly, the charge collecting efficiency is determined to be

$$\eta_{\text{cc}} = \frac{E_{\text{abs}} - E_{\text{loss}}}{E_{\text{abs}}} = \frac{(1-\alpha)^m - (1-\alpha)^n}{1 - (1-\alpha)^n} \quad (L > L_0) \quad (5.17)$$

Thus,

$$J_{\text{sc}} = C(1-\alpha)^{L/l} [(1-\alpha)^{-L_0/l} - 1] \quad (L > L_0) \quad (5.18)$$

Using $l = 0.0015 \mu\text{m}$ (1.5 nm)^[167] and fitting Equations 5.14 and 5.18 with the data given in Figure 5.13 (a), the short-circuit photocurrent density for a single cell is presented as

$$J_{\text{sc}} = \begin{cases} 11.5 \times (1 - 0.97^L) & (L \leq L_0) \\ 17.3 \times 0.97^L & (L > L_0) \end{cases} \quad (5.19)$$

with $\alpha = 4.36 \times 10^{-5}$ and $L_0 = 30.03 \mu\text{m}$, as displayed in Figure 5.15. It indicates that, under backside illumination, the optimal tube length is around 30 μm for the nanotubes used in the

current study, in line with our previous estimation in Section 2.2.4.2. Obviously the photocurrent decreases drastically once tube length exceeds the electron diffusion length.

Figure 5.15 Plot of short-circuit current density vs. nanotube length. Data (□ single cells, Δ parallel cells) are from Figure 5.13. The curves are fitted based on the calculation in the text with solid lines for single structure and dashed lines for parallel configuration.

Now let us consider parallel configuration. In the parallel configuration, the photocurrent from the cell under direct illumination (J_{sc-d}) follows Equation 5.19 while that from the cell under mirror reflection (J_{sc-r}) differs as a result of relatively smaller incident photon flux density. This gives rise to a smaller value (referred to as C') of Equation 5.12 via mirror reflection. As the electron diffusion length is expected to be independent of light intensity,^[90] it is assumed that electron diffusion length under mirror reflection is the same as that under direct illumination, that is, $L_0 = 30.03 \mu\text{m}$. Therefore, the short-circuit current density of a parallel cell is computed as

$$J_{sc} = J_{sc-d} + J_{sc-r} = 11.5 \times (1 - 0.97^L) + C' \eta_{cc} [1 - (1 - \alpha)^{L/l}] \quad (L \leq L_0)$$

$$(5.20)$$

$$J_{sc} = J_{sc-d} + J_{sc-r} = 17.3 \times 0.97^L + C' \eta_{cc} [1 - (1 - \alpha)^{L/l}] \quad (L > L_0) \quad (5.21)$$

By fitting Equations 5.20 and 5.21 with the data given in Figure 5.13 (b), the J_{sc} for a parallel cell is determined to be

$$J_{sc} = \begin{cases} 20.8 \times (1 - 0.97^L) & (L \leq L_0) \\ 31.3 \times 0.97^L & (L > L_0) \end{cases} \quad (5.22)$$

The relevant fitting curves are shown in Figure 5.15.

The above results demonstrate that photocurrent of a dye-sensitized solar cell under backside illumination is affected by tube length significantly, with an optimal length being $\sim 30 \mu\text{m}$ in this study. Within this length, the photocurrent is promoted with the parallel configuration as in Figure 5.15, due to additional utilization of back surface or increment in energy absorption (light harvesting). Equations 5.19 and 5.22 reveal that the constant C also plays an important part in promoting the photocurrent, which is closely related to the photon energy incident on the nanotubes. To enlarge C and hence increase the photocurrent, it is effective to decrease the energy loss at the counter electrode and that in the electrolyte.

5.6 Summary

A novel parallel configuration of dye-sensitized solar cells is achieved in this study based on double-sided anodic titania nanotube arrays. The parallel connection is verified by electrochemical impedance spectroscopy measurement. Photovoltaic performance of the

parallel cells exhibits an average 70% increment in photocurrent and 30% enhancement in conversion efficiency, benefiting from additional utilization of the back surface and considerable reduction of the series resistance. A theoretical calculation and relevant fitting results indicate that a tube length of $\sim 30\text{ }\mu\text{m}$ is optimal for the nanotubes used in the current work. In addition, transition from nanotubes to nanowires also arises during application of the nanotubes in dye-sensitized solar cells. To suppress formation of the nanowires thus improve the photovoltaic performance, a 10 h treatment with 40 mM TiCl_4 solution at $70\text{ }^\circ\text{C}$ is effective for the nanotubes used in this study.

Chapter 6 Conclusions and Future Work

6.1 Conclusions

In this project, growth of anodic titania nanotube arrays is investigated with reference to the essential role of electric field. Two fields are concerned herein: electric field originating from potential drop over the oxide layer and that in the organic electrolyte. The results reveal that pore diameter of the tubes increases linearly with the former, since evolution of tube pores is closely related to the lateral components of the electric field. Tube growth rate shows an exponential increase with the former as a result of enhanced ionic transport through the oxide layer. The tube growth rate is also promoted by the latter which contributes to ionic flux in the electrolyte. This can be explained using an ion flux model where H^+ and F^- ion concentration profiles are considered in a single tube.

To further demonstrate the role of electric field in the organic electrolyte (i.e., the latter), double-sided nanotube growth is studied by a simple two-electrode configuration. Anodic nanotubes are grown simultaneously at both sides of a titanium foil, with tube length being longer at the frontside than that at the backside. This lopsided tube growth is attributed to higher ionic flux induced by the electric field at the frontside. Accordingly, the tube length is tailored to be comparable at both sides by adjusting the field. In addition, comparative study reveals that this simple two-electrode anodizing configuration gives rise to the largest tube growth rate.

For application of the nanotubes in dye-sensitized solar cells, open tube tops are required to facilitate dye loading and electrolyte infiltration. As such, transition from nanotubes to

nanowires is investigated to obtain clear tube surface. It shows that the transition is an intrinsic stage during nanotube growth in organic electrolyte, thus cannot be eliminated by pre-treatment methods. The transition requires a large number of H^+ ions to reduce the passivated area of tube walls, therefore takes place only under an intermediate chemical dissolution environment, such as at elevated temperature or prolonged duration in organic electrolyte. The nanowires grown for long duration (e.g., ≥ 8 h at 25 V and 40 °C) can be cleared away with ultrasonic cleaning (a post-treatment method) due to formation of the quasi-nanosprings.

In dye-sensitized solar cells based on anodic titania nanotubes, the low photocurrent has hindered their development, which is intimately associated with the dye loading amount of the photoanode. In view of this, a novel parallel configuration of dye-sensitized solar cell is achieved on the basis of the double-sided nanotubes. The parallel connection is verified by electrochemical impedance spectroscopy measurement. Photovoltaic performance of the parallel cells exhibits an average 70% increment in photocurrent and 30% enhancement in conversion efficiency, as a consequence of highly increased surface area and considerably reduced series resistance. A theoretical calculation and relevant fitting results indicate that a tube length of ~ 30 μm is optimal for the nanotubes used in the current work. In addition, transition from nanotubes to nanowires also arises during application of the nanotubes in dye-sensitized solar cells. To suppress formation of the nanowires thus improve the photovoltaic performance, a 10 h treatment with 40 mM $TiCl_4$ solution at 70 °C is effective for the nanotubes used in this study.

6.2 Future Work

In Chapter 2, dye-sensitized solar cells based on conventional titania nanoparticles are reviewed. The following two major points have hampered their further development: electron scattering at numerous nanoparticle connections and energy loss in long wavelength. However, the large dye loading ability is desirable in view of light harvesting. In contrast, the dye loading ability of anodic nanotube based DSSCs has restricted the efficiency, whereas the superior electron transport and suppressed electron recombination properties are favourable. In view of these, a composite electrode consisting of nanoparticles and nanotubes is promising to promote the cell efficiency further, which aims at combining the merits of the above two systems while overcoming the demerits. The composite electrode can be achieved via electrodeposition, in which the pores of the nanotubes are filled with the nanoparticles, as illustrated in Figure 6.1.

Figure 6.1 Schematic diagram of nanoparticle-nanotube composite electrode.

In Section 2.2.5, the effect of crystallization on cell performance is discussed. It reveals that the crystallinity as well as the crystallite size influences the electron transport and recombination in the nanotube photoanodes. In view of this, it is meaningful to investigate

the pertinent photovoltaic characteristics through changing the crystallinity and crystallite size systemically in the future.

In addition, as one of the examiners of this thesis pointed out, the power conversion efficiency of DSSCs varies widely from lab to lab depending on the experiences and skills in assembly of dye-sensitized solar cells. It will be useful to assemble DSSCs using commercially available titania nanoparticles, in order to compare with the nanotube-based dye-sensitized solar cells.

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