Novel Nanostructured Titania and Titania Nanocomposites for Photovoltaics and Photocatalysis

Xinning Luan
Louisiana State University and Agricultural and Mechanical College

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NOVEL NANOSTRUCTURED TITANIA AND TITANIA NANOCOMPOSITES FOR PHOTOVOLTAICS AND PHOTOCATALYSIS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Mechanical and Industrial Engineering

by

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August 2014
To my late grandparents,
Peihan Feng
and
Jie Cao
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TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................... iii

LIST OF TABLES .................................................................................................................. vi

LIST OF FIGURES ................................................................................................................ vii

LIST OF ABBREVIATIONS ................................................................................................... xii

ABSTRACT ............................................................................................................................... xiv

CHAPTER 1 OVERVIEW ......................................................................................................... 1
  1.1 Energy Crisis and Renewable Sources ............................................................................. 1
  1.2 Dye-Sensitized Solar Cells ............................................................................................. 2
    1.2.1 Three Generations of Photovoltaics ........................................................................ 2
    1.2.2 Principle of Dye-Sensitized Solar Cells .................................................................. 4
    1.2.3 Evaluation of Dye-Sensitized Solar Cells ............................................................... 7
  1.3 Semiconductor Photocatalysis ....................................................................................... 9
    1.3.1 Principle of Semiconductor Photocatalysis ............................................................ 9
    1.3.2 Modifications of TiO₂ for Enhanced Photocatalytic Activity ................................. 11
  1.4 Objectives of the Present Work ..................................................................................... 13
  1.5 References ..................................................................................................................... 14

CHAPTER 2 FACILE SYNTHESIS AND MORPHOLOGY CONTROL
OF BAMBOO-TYPE TiO₂ NANOTUBE ARRAYS FOR
HIGH-EFFICIENCY DYE-SENSITIZED SOLAR CELLS ...................................................... 19
  2.1 Introduction ................................................................................................................. 19
  2.2 Experimental .............................................................................................................. 21
  2.3 Results and Discussion ............................................................................................... 22
  2.4 Conclusion ............................................................................................................... 31
  2.5 References ................................................................................................................. 31

CHAPTER 3 PLASMON-ENHANCED PERFORMANCE OF
DYE-SENSITIZED SOLAR CELLS BASED ON
ELECTRODEPOSITED Ag NANOPARTICLES ...................................................................... 36
  3.1 Introduction ................................................................................................................. 36
  3.2 Experimental .............................................................................................................. 38
  3.3 Results and Discussion ............................................................................................... 39
  3.4 Conclusion ............................................................................................................... 47
  3.5 References ................................................................................................................. 48
LIST OF TABLES

Table 2.1 Photovoltaic characteristics of dye-sensitized solar cells shown in Figure 2.7 .................................................................................................................................................. 30

Table 3.1 Photovoltaic characteristics of dye-sensitized solar cells shown in Figure 3.6 .................................................................................................................................................. 43

Table 3.2 Photovoltaic characteristics of dye-sensitized solar cells shown in Figure 3.8 .................................................................................................................................................. 46

Table 4.1 Photovoltaic characteristics of DSSCs based on unmodified and RGO-modified TiO$_2$ nanotube arrays via EPD time of 15 s, 30 s, 1 min, and 5 min shown in Figure 4.5 .................................................................................................................................................. 58

Table 4.2 Photovoltaic characteristics of DSSCs based on unmodified and RGO-modified bamboo-type TiO$_2$ nanotube arrays via EPD time of 30 s as shown in Figure 4.9 .................................................................................................................................................. 62

Table 5.1 Photovoltaic characteristics of DSSCs based on TiO$_2$ nanosheet films with different thicknesses as shown in Figure 5.4 .................................................................................................................................................. 72

Table 5.2 Photovoltaic characteristics of DSSCs based on 8.8 μm-thick TiO$_2$ nanosheet films with and without TiCl$_4$ treatment as shown in Figure 5.5 .................................................................................................................................................. 74

Table 6.1 Kinetic characteristics of photocatalytic degradation of MB on crystalline TiO$_2$ nanotubes shown in Figure 6.5 .................................................................................................................................................. 86

Table 6.2 Kinetic characteristics of photocatalytic degradation of MB on crystalline TiO$_2$ nanotubes shown in Figure 6.7 .................................................................................................................................................. 90
LIST OF FIGURES

Figure 1.1 Worldwide energy consumption within 250 years ................................................. 1

Figure 1.2 Growth of wind power and photovoltaics ................................................................. 2

Figure 1.3 Efficiency and cost projections for first (I), second (II), and third generation (III) PV technologies ................................................................. 3

Figure 1.4 Typical structure of DSSC ...................................................................................... 5

Figure 1.5 Schematic showing working mechanism of DSSCs .................................................... 6

Figure 1.6 Schematic showing the primary (green) and recombination (red) electron transfer processes and timescale of DSSCs ......................................................... 6

Figure 1.7 AM1.5 global standard solar spectrum ......................................................................... 7

Figure 1.8 Current–voltage (J–V) curve of solar cell ................................................................... 8

Figure 1.9 Simplified scheme of semiconductor activation ......................................................... 10

Figure 1.10 Relationship between the band structures of some selected metal oxides and non-oxide semiconductors and the redox potentials of water splitting ................................................................. 10

Figure 1.11 Bulk crystal structures of rutile and anatase ............................................................ 12

Figure 2.1 Anodization sequence for the formation of bamboo-type TiO₂ nanotube arrays .......................................................................................................................... 21

Figure 2.2 SEM images of bamboo-type and smooth-walled TiO₂ nanotube arrays of 8.0-μm thickness. The tubes were synthesized in EG electrolytes containing 0.3 wt% NH₄F and 5 vol% H₂O under different anodization sequence of (a, b) Smooth-walled: 60 V for 60 min; (c, d) Bamboo-type-4: 60 V for 4 min, 10 V for 4 min, and 20 cycles; (e, f) Bamboo-type-2: 60 V for 2 min, 10 V for 2 min and, 40 cycles; (g, h) Bamboo-type-1: 60 V for 1 min, 10 V for 1 min, and 80 cycles ................................................................. 23

Figure 2.3 Overview of bamboo-type and smooth-walled TiO₂ nanotube arrays of 8.0-μm thickness. The tubes were synthesized in EG electrolytes containing 0.3 wt% NH₄F and 5 vol% H₂O under different anodization sequence of (a) Smooth-walled: 60 V for 60 min; (b) Bamboo-type-4: 60 V for 4 min, 10 V for 4 min, and 20 cycles; (c) Bamboo-type-2: 60 V for 2 min,
10 V for 2 min and, 40 cycles; (d) Bamboo-type-1: 60 V for 1 min, 10 V for 1 min, and 80 cycles

Figure 2.4 Schematic showing growth of bamboo-type TiO₂ nanotubes via anodic oxidation: (a) pH gradient profile in nanotubes during their steady growth at 1ˢᵗ high voltage step, (b) less steep pH gradient and pore formation at the 1ˢᵗ low voltage step, (c) formation of a ridge between the 1ˢᵗ section and 2ⁿᵈ section of nanotubes at the 2ⁿᵈ high voltage step, (d) pore formation at the 2ⁿᵈ low voltage step, (e) ridge formation between the 2ⁿᵈ section and 3ʳᵈ section of nanotubes at the 3ʳᵈ high voltage step.

Figure 2.5 SEM images of bamboo-type nanotube arrays synthesized (a, b) in EG electrolytes containing 0.3 wt% NH₄F and 5 vol% H₂O under the anodization sequence of 60 V for 1 min, 10 V for 1 min, and 160 cycles; (c, d) in EG electrolytes containing 0.3 wt% NH₄F and 2 vol% H₂O under the anodize sequence of 60 V for 1 min, 10 V for 1 min, and 80 cycles.

Figure 2.6 XRD diffraction patterns of bamboo-type TiO₂ nanotubes produced by anodization sequence of 60 V for 1 min, 10 V for 1 min, and 80 cycles in EG electrolyte containing 0.3 wt% NH₄F and 5 vol% H₂O (a) As-prepared TiO₂ nanotube; (b) Anatase TiO₂ nanotube formed after annealing at 450 °C.

Figure 2.7 J–V characteristics of DSSCs using different TiO₂ nanotube arrays. (SW: smooth-walled nanotube synthesized at 60 V for 60min; BT-4: bamboo-type nanotube synthesized at 60 V for 4 min, 10 V for 4 min, and 20 cycles; BT-2: bamboo-type nanotube synthesized at 60 V for 2 min, 10 V for 2 min and, 40 cycles; BT-1: bamboo-type nanotube synthesized at 60 V for 1 min, 10 V for 1 min and, 80 cycles; BT*: bamboo-type nanotube synthesized in the electrolyte containing 2 vol% H₂O at 60 V for 1 min, 10 V for 1 min, and 80 cycles.

Figure 3.1 Schematic showing the pulse current process for electrochemical deposition of Ag with a rectangular pulse shape composed of alternating on-times and off-times for 100 deposition cycles.

Figure 3.2 X-ray diffraction pattern of bare TiO₂ nanotube array annealed at 450 °C in air for 2 h.

Figure 3.3, a, b) Cross-sectional, c) top-view SEM images, and d) EDX spectrum of TiO₂ nanotube arrays modified with Ag nanoparticles via pulse deposition time of 1 s/3 s.
Figure 3.4 TEM image of a TiO$_2$ nanotube modified with Ag nanoparticles via pulse deposition time of 1 s/3 s. ................................................................. 41

Figure 3.5, a) XPS spectra and b) Ag3d XPS peak of TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 1 s/3 s. ......................... 42

Figure 3.6 $J−V$ characteristics of DSSCs based on different TiO$_2$ nanotube arrays. (Ag@TiO$_2$ 0.5 s/1.5 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 0.5 s/1.5 s; Ag@TiO$_2$ 1 s/3 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 1 s/3 s; Ag@TiO$_2$ 2 s/6 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 2 s/6 s; Bare TiO$_2$: unmodified TiO$_2$ nanotubes.) .................................................................................. 44

Figure 3.7 TEM image of a TiO$_2$ nanotube modified with Ag nanoparticles via pulse deposition time of 2 s/6 s. .................................................................................. 44

Figure 3.8 $J−V$ characteristics of DSSCs based on different TiCl$_4$-treated TiO$_2$ nanotube arrays. (Ag@TiO$_2$-TiCl$_4$ 0.5 s/1.5 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 0.5 s/1.5 s; Ag@TiO$_2$-TiCl$_4$ 1 s/3 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 1 s/3 s; Ag@TiO$_2$-TiCl$_4$ 2 s/6 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 2 s/6 s; Bare TiO$_2$-TiCl$_4$: unmodified TiO$_2$ nanotubes.) .............................................................................. 45

Figure 3.9, a, b, c) Cross-sectional and top-view SEM images of TiCl$_4$ treated bare TiO$_2$ nanotube arrays; d, e, f) Cross-sectional and top-view of SEM images of TiCl$_4$-treated TiO$_2$ nanotube arrays modified with Ag nanoparticles via pulse deposition time of 2 s/6 s. .............................................................................. 47

Figure 4.1 Schematic showing the anodization sequence for the formation of bamboo-type TiO$_2$ nanotube arrays. .............................................................................. 52

Figure 4.2 X-ray diffraction pattern of smooth-walled TiO$_2$ nanotube array annealed at 450 °C in air for 3 h, which indicate that as-prepared sample is indexed as anatase. .............................................................................. 54

Figure 4.3, a) Cross-sectional and b) top-view SEM images of smooth-walled TiO$_2$ nanotube arrays; Top-view SEM images of smooth-walled TiO$_2$ nanotube arrays modified with RGO via EDP time of c) 1 min and d) 5 min. .............................................................................. 55

Figure 4.4, a) C 1s and b) Ti 2p XPS spectra of smooth-walled TiO$_2$ nanotubes unmodified and modified with RGO s via EPD for 1h. ................................. 56
Figure 4.5 $J-V$ characteristics of DSSCs based on unmodified and RGO-modified TiO$_2$ nanotube arrays via EPD time of 15 s, 30 s, 1 min, and 5 min. .......................................................... 58

Figure 4.6 Electrochemical impedance spectra of DSSCs consisting of unmodified smooth-walled TiO$_2$ nanotubes and smooth-walled TiO$_2$ nanotubes modified with RGO s via EPD for 30 sec. .......................................................... 59

Figure 4.7 Cross-sectional SEM images of bamboo-type TiO$_2$ nanotube arrays a, b) before and c, d) after TiCl$_4$ treatment. .......................................................... 60

Figure 4.8 Top-view SEM images of a) bamboo-type TiO$_2$ nanotube arrays and b) TiCl$_4$-treated bamboo-type TiO$_2$ nanotubes modified with RGO via EDP time of 30 s. .......................................................... 60

Figure 4.9 $J-V$ characteristics of DSSCs based on unmodified and RGO-modified bamboo-type TiO$_2$ nanotube arrays via EPD time of 30 s. .......................................................... 61

Figure 5.1 X-ray diffraction patterns of samples before and after exfoliation: (a) calcinated cesium titanate (b) TBA$^+$-intercalated Ti$_{0.91}$O$_2$ nanosheets (dried sample), and (c) TiO$_2$ nanosheets obtained via thermal annealing of reassembled Ti$_{0.91}$O$_2$ nanosheets at 450 °C for 3 h. .......................................................... 69

Figure 5.2 SEM images of (a) calcinated cesium titanate, (b) reassembled Ti$_{0.91}$O$_2$ nanosheets in a gelation form using HCl solution, and (c) TiO$_2$ nanosheets obtained via thermal annealing of Ti$_{0.91}$O$_2$ nanosheets at 450 °C for 3 h. .......................................................... 70

Figure 5.3 TEM images of (a) Ti$_{0.91}$O$_2$ nanosheets, (b) TiO$_2$ nanosheets, (c) photograph, and (d) polarized microscopic image of TBA$^+$-intercalated Ti$_{0.91}$O$_2$ NS colloidal dispersion. .......................................................... 71

Figure 5.4 $J-V$ characteristics of DSSCs based on TiO$_2$ nanosheet films with different thickness (3.5, 5.8, 8.8 and 17.2 µm). .......................................................... 72

Figure 5.5, a) $J-V$ characteristics of DSSCs based on 8.8 µm-thick TiO$_2$ nanosheet film with and without TiCl$_4$ treatment, b) SEM image of TiO$_2$ NSs after TiCl$_4$ treatment. .......................................................... 73

Figure 6.1 Schematic showing a) an anodization sequence for the formation of bamboo-type TiO$_2$ nanotube arrays, b) pulse current process for electrochemical deposition of Ag with a rectangular pulse shape composed of alternating on-times and off-times for 100 deposition cycles. ................................. 80
Figure 6.2 X-ray diffraction pattern of bamboo-type TiO$_2$ nanotube array annealed at 450 °C in air for 3 h. ................................................................. 82

Figure 6. 3 Cross-sectional view SEM images of a, b) smooth-walled TiO$_2$ nanotube arrays, c, d) Ag-modified smooth-walled TiO$_2$ nanotube arrays, and e, f) bamboo-type TiO$_2$ nanotube arrays. ............................................................................ 83

Figure 6.4 EDX spectrum of Ag-modified smooth-walled TiO$_2$ nanotubes arrays...................................................................................................................... 84

Figure 6.5, a) Photocatalytic degradation ratios of MB on the anodic smooth-walled (SW-TiO$_2$), Ag-modified smooth-walled (SW-TiO$_2$@Ag), and bamboo-type TiO$_2$ nanotubes arrays (BT-TiO$_2$), and b) corresponding photodegradation kinetic curves of MB photodegradation, where $C_0$ and $C$ are the initial and reaction concentration of MB aqueous solution, respectively. ................................................................................... 85

Figure 6.6 Cross-sectional and top-view SEM images of bamboo-type TiO$_2$ nanotube arrays modified with Ag nanoparticles via different pulse deposition time of a, b) 0.5 s/1.5 s, c, d) 1 s/3 s, and e, f) 2 s/6 s. ................................................. 87

Figure 6.7, a) Photocatalytic degradation ratios of MB on the anodic bamboo-type TiO$_2$ nanotubes arrays modified with Ag nanoparticles via pulse deposition time of 0.1 s/0.3 s (BT-TiO$_2$@Ag-0.1/0.3), 0.5 s/1.5 s (BT-TiO$_2$@Ag-0.5/1.5), 1 s/3 s (BT-TiO$_2$@Ag-1/3), and 2 s/6 s (BT-TiO$_2$@Ag-2/6), and b) corresponding photodegradation kinetic curves of MB photodegradation, where $C_0$ and $C$ are the initial and reaction concentration of MB aqueous solution, respectively. ......................................................... 89

Figure 6.8 Schematic diagram showing interfacial charge-transfer processes for Ag/bamboo-type TiO$_2$ composite under UV light irradiation. ....................... 91
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM 1.5 G</td>
<td>incident air mass 1.5 global spectrum</td>
</tr>
<tr>
<td>AV</td>
<td>alternating voltage</td>
</tr>
<tr>
<td>Ag</td>
<td>silver</td>
</tr>
<tr>
<td>BT</td>
<td>bamboo-type</td>
</tr>
<tr>
<td>CE</td>
<td>counter electrode</td>
</tr>
<tr>
<td>CV</td>
<td>constant voltage</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye sensitized solar cell</td>
</tr>
<tr>
<td>$e_{CB}$</td>
<td>conduction band potential</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EF</td>
<td>quasi-Fermi energy level</td>
</tr>
<tr>
<td>$E_g$</td>
<td>band gap</td>
</tr>
<tr>
<td>e-h</td>
<td>electron-hole</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>$e_{VB}$</td>
<td>valance band potential</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FTO</td>
<td>fluorine doped tin oxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>J</td>
<td>current density</td>
</tr>
<tr>
<td>$J_{max}$</td>
<td>current density of $P_{max}$</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>short-circuit current density</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>N719</td>
<td>cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)- ruthenium(II) bis-tetrabutylammonium</td>
</tr>
<tr>
<td>$P_{in}$</td>
<td>power of incident light</td>
</tr>
<tr>
<td>$P_{max}$</td>
<td>maximum power output</td>
</tr>
<tr>
<td>Pt</td>
<td>platinum</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
</tbody>
</table>
RGO  reduced graphene oxide
S    sensitizer
SEM  scanning electron microscopy
TEM  transmission electron microscopy
TiO$_2$ titania
UV-Vis ultraviolet-visible
V    voltage
$V_{\text{max}}$ voltage of $P_{\text{max}}$
$V_{\text{oc}}$ open circuit voltage
XPS X-ray photoelectron spectroscopy
XRD X-ray Diffraction
Z    impedance
$Z'$ real impedance
$Z''$ imaginary impedance
$\lambda$ wavelength
$\eta$ power conversion efficiency
$\sigma$ standard deviation of power conversion efficiency
ABSTRACT

With the consumption of energy continually increasing around the world and the main source of this energy, fossil fuels, slowly being depleted, the need for alternate sources of energy is becoming more and more pertinent. Demand for solar energy has experienced exponential increase over the last decade. Nanostructured TiO$_2$ has attracted significant attention due to its nontoxicity, low cost and wide applications in photovoltaics and photocatalysis. This research is focused on novel synthesis and surface modification of TiO$_2$ nanotube arrays for applications in advanced dye-sensitized solar cells (DSSCs) and efficient photocatalysis. The first part of this work entails fast synthesis of bamboo-type TiO$_2$ nanotube arrays with large surface area via anodization of Ti substrates for applications as photo-anodes in high-efficiency DSSCs. In addition, titania nanotubes are modified with other nanomaterials for further increased efficiency of DSSCs. For example, uniformly-sized Ag nanoparticles are deposited onto TiO$_2$ nanotube array via pulse electrodeposition for plasmon effect, leading to enhanced light absorption in DSSCs. Also, reduced graphene oxide nanosheets are deposited onto a TiO$_2$ nanotube array using electrophoretic deposition, for increased electronic conductivity and improved electron transport in DSSCs. Additionally, ultra-thin two dimensional TiO$_2$ nanosheets are synthesized via exfoliation of layered protonated titanate into separate layers using bulky organic ions, for application as photo-anodes with enhanced light scattering and dye loading in high-efficiency DSSCs. The second part of the work concentrates on synthesis of Ag-modified bamboo-type TiO$_2$ nanotube arrays for efficient photocatalysis. Such novel titania-based nanocomposite structure provides large surface area for organic pollutant absorption and subsequent degradation; the ordered structure of nanotube array also offers direct pathway for fast electron transport. Moreover, Ag nanoparticles deposited onto TiO$_2$ nanotubes function as reservoirs for photogenerated electrons to improve charge separation and facilitate catalytic reactions.
CHAPTER 1 OVERVIEW

1.1 Energy Crisis and Renewable Sources

Energy crisis in current century poses challenges and requires immediate attention. In the past decades, fossil fuels, including coal, petroleum and nature gas, have been the main source to satisfy the world’s energy consumption. Consequently, the severe negative side effects of combusting fossil fuels have become evident. On one hand, by-products of fossil fuel synthesis and combustion generate a massive amount of carbon oxides (e.g. CO₂, CO), sulfides and waste water, which can have detrimental effects on the atmospheric conditions of the earth. The excess generation of by-products could have profound effects on the surface climate of the earth including global warming and severe weather pattern shifts. On the other hand, the remaining short supply of the non-renewable fuels has appeared as a big issue. This problem becomes more aggravating because of the exponentially increased demand for energy, especially for fossil fuel supplies. Since the amount of fossil fuels left for garnering is dwindling, alternate energy sources need to be found as quickly as possible to avoid more severe atmospheric effects and/or depletion of current primary energy source.

As can be seen from Figure 1.1, fossil fuels are by far the most important contributors to the world’s current energy consumption. Renewables and nuclear power are making increasing contributions since the related technologies boomed in 1990 [1]. During the past decade, with the economic crises and rise of oil prices, the dire need for an alternate energy source has become more and more urgent. This necessity has initiated floods of research towards developing a source worthy enough to replace fossil fuels – the current dominant energy source.

![Graph showing energy consumption over time.](image)

Figure 1.1 Worldwide energy consumption within 250 years [2].
Renewable energy includes such sources as wind, photovoltaic, thermal solar, tidal and wave power. While its global contribution is still minor, it shows enormous promise on energy supply. At present, renewable technologies supply less than 1% of the world's total energy needs, but its growth rate is exceptional. Since the end of 2004, worldwide renewable energy capacity has grown at a rate of 10–60% annually [3]. Solar energy, for example, has experienced an annual growth rate of 33% over the last decade [4-6]. Even though wind is regarded as the fastest growing energy source, energy supply via photovoltaics has been increasing at twice the rate of wind since 2007— an average of 63.6%/year, due to the reduction in cost. By 2014 the installed capacity of photovoltaics will likely exceed that of wind, and becomes the most commendable and promising source for fossil fuel replacement (Figure 1.2).

Figure 1.2 Growth of wind power and photovoltaics [3].

The profound future prospects of photovoltaics are due to its direct utilization of solar radiation to produce electricity, providing an ideal way to utilize the nature's renewable energy flow. With photovoltaic cells, power can be produced near the end users of electricity, thus avoid transmission losses and costs. Moreover, solar panels operate without noise, toxic and greenhouse gas emissions, and require very little maintenance. Therefore, these advantages of solar electricity make it attractive for large-scale utilization.

1.2 Dye-Sensitized Solar Cells

1.2.1 Three Generations of Photovoltaics

With the emerging photovoltaic technologies, solar cells are classified into three generations: First generation solar cells consisting of silicon-based family of solar cells (monocrystalline/polycrystalline) are currently the most efficient solar cells available for
residential use and constitute most of the photovoltaic market. These solar cells are manufactured by using a single junction for extracting energy from photons and deliver very high efficiencies, approaching their theoretical maximum efficiency of 33%. The manufacturing involves extremely pure silicon, thus the major downfall to the first generation solar cells is the high cost greater than $1/watt for the production of extremely pure silicon (Figure 1.3) [7]. About 5% increase in efficiency (~10% to ~15%), the cost/m² would double ($200/m² to $400/m²). Therefore, high cost is associated with the production of high-efficiency solar cell devices.

![Efficiency and cost projections for first (I), second (II), and third generation (III) PV technologies](image_url)

Second-generation solar cells are usually called thin-film solar cells based on III-V or II-VI group compounds, such as GaAs, GaN, CdTe, GaInP and copper indium gallium selenide. Compared to crystalline silicon based cells, they are made from binary and multi-junction semiconductor materials only a few micrometers thick. The combination of using less material and less expensive manufacturing processes allow the production cost as low as $0.50/watt [7]. However, the biggest problem for the 2nd generation solar cells is also due to the reduced materials amount and thus thinner cells, there is less light-absorbing material to generate photocurrent leading to lower efficiencies of 10-15%.

Third-generation solar cell is a promising device, aiming to achieve high-efficiency cells with low cost in comparison with expensive first-generation solar cells and low-efficiency second-generation solar cells. In particular, a third-generation device known as dye-sensitized solar cell (DSSC) is a promising alternative to silicon and multijunction solar cells. By utilizing nanomaterials to broaden the potential for optimized energy conversion efficiency, DSSCs have the potential to be as efficient as silicon solar cells with a fraction of the cost of silicon and multijunction solar cells.
Since the electrical power generated from a solar cell is the product of the current and voltage, a compromise is made and in an idealized solar cell, the maximum theoretically efficiency in a single junction device is just over 30%, achievable by harvesting UV to near IR photons up to 1.1 eV [8]. For the single junction solar cell, 100% of the solar light is harvested up to the optical bandgap of the absorber, and all the charge is collected with unity efficiency up to an open-circuit voltage equivalent to the optical bandgap. Henry Snaith pointed out the origin of photovoltaic loss in DSSCs, in sequential order from light absorption to current collection: i) The first loss can arise from incomplete light harvesting, or light harvesting in a non-optimal wavelength range. ii) A second loss can arise from inefficient photoinduced electron transfer, where there can be a direct loss of absorbed photon to non-injecting channels. iii) Accompanying this, it must be energetically favorable for the photoexcited dye to transfer an electron to the metal oxide. iv) Further to this, if the photoexcited dye relaxes prior to electron transfer, to possibly form a relaxed exciton, then this will result in a conformational change to the dye, which will cost energy, with the electron being transferred into the oxide at a lower energy. v) Once the electron has been transferred into the oxide, the hole residing on the dye is regenerated by the electrolyte. The dye regeneration is most probably the largest single source for loss-in-potential in the device. vi) Further losses include resistive losses for charge transport through the solar cell; if these are high then a significant IR drop will occur manifesting itself as a drop in potential. vii) Finally, if there are any resistive losses or potential barriers at the electrodes, then once again this will reduce the attainable open-circuit voltage and fill factor of the device [9].

1.2.2 Principle of Dye-Sensitized Solar Cells

Dye-sensitized solar cells were invented by Michael Grätzel in the 1990s. Currently, the highest efficiency from DSSCs using ruthenium complexes is 11.1% with a theoretical efficiency of 31% [8,10,11]. DSSCs use a layer of dye-sensitized nanocrystalline semiconductor oxide particles which are far cheaper than crystalline silicon and multijunction solar cells, primarily due to the abundant use of inexpensive materials and utilization of high surface area from nanomaterials.

DSSCs are typically constructed with five components: conductive anode support, wide-band-gap semiconductor oxide film, sensitizer (dye), redox electrolyte, and platinized conductive counter electrode. Figure 1.4 shows a typical structure of DSSC with mesoporous TiO$_2$ film as photoanode and front side illumination. The anode and cathode supports are generally transparent conductive oxide (TCO), such as fluorine-doped SnO$_2$ (FTO) on glass. TiO$_2$ cannot efficiently absorb the solar spectrum due to its wide band gap as large as 3.2 eV [12,13]. Dyes adsorbed on the surface of TiO$_2$ can serve as the light absorbers. Ruthenium Dyes are the most common dyes that are chemically adsorbed on TiO$_2$ through carboxylic, sulfonic, and phosphonic acid groups [14,15]. The TiO$_2$ semiconductor film is typically a 10-µm thick mesoporous network composed of 10-20 nm anatase particles, which has sufficient surface area to allow a monolayer of dye molecules to absorb nearly all incident photons with energies above the maximum dye absorbance. By using nanocrystalline TiO$_2$ as working electrode, an approximate 1000
fold increase in surface area is achieved compared to a planar single crystal. Such remarkably enhanced surface area allows a considerable amount of dye to be loaded onto a cell, which in turn makes it a thin and efficient solar cell.

Figure 1.4 Typical structure of DSSC [16].

Basic principle of DSSCs is illustrated in Figure 1.5. In DSSCs, electrons of dye are excited to a higher energy state by solar energy absorption and the electrons from photo-excited dye are transferred from the excited energy level of dye to the conduction band of photo-anode TiO$_2$. The electrons then diffuse through TiO$_2$ nanocrystalline network to the electrode, and subsequently reach the counter electrode through an external circuit. The dye molecules regain electrons from a redox couple iodide/triiodide (I$^-$/I$_3^-$) in the electrolyte. The iodide is regenerated in turn by the reduction of triiodide at the counter electrode, and this process requires a catalytic functionality of Pt on the cathode surface. This photo-conversion process is regenerative. The operating cycle can be summarized in the following chemical reactions:

Anode: \[ S + \text{hv} \rightarrow S^* \] Absorption (1)

\[ S^* \rightarrow S^+ + e^- (\text{TiO}_2) \] Electron injection (2)

\[ 2S^+ + 3I^- \rightarrow 2S + I_3^- \] Regeneration (3)

Cathode: \[ I_3^- + 2e^- (\text{Pt}) \rightarrow 3I^- \] (4)

Unfortunately, competitive transitions also take place, which reduces energy conversion efficiency. Upon excitation, a process known as recombination occurs in which dye molecules decay from the excited state to the ground state in nanoseconds. The electron recombination can also transfer electrons in milliseconds from the conduction band of TiO$_2$ to the ground state of a dye or to the electrolyte mediator (Figure 1.6). Many research efforts have been performed to overcome recombination processes and increase conversion efficiency.
Figure 1.5 Schematic showing working mechanism of DSSCs [17].

Figure 1.6 Schematic showing the primary (green) and recombination (red) electron transfer processes and timescale of DSSCs.
1.2.3 Evaluation of Dye-Sensitized Solar Cells

A solar cell is a device that converts incident light to electrical energy. Evaluation of DSSC performance involves measurement of current as a function of voltage under illumination to determine energy conversion efficiency. Generally, a solar simulator containing a xenon arc lamp is used as a light source which is calibrated by using an air mass filter (AM 1.5 G) to generate a spectrum comparable to solar irradiance spectrum (Figure 1.7). Under illumination, a difference in the potential between the working and counter electrodes of a solar cell causes electrons to migrate through the cell and generate current.

![Figure 1.7 AM1.5 global standard solar spectrum [18].](image)

The current-voltage ($J$–$V$) curve of a cell under certain illumination is displayed in Figure 1.8. The critical parameters that can be extracted from the $J$–$V$ curve are short circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor ($FF$), and efficiency ($\eta$). When the cell is short circuited under illumination, the maximum current, $J_{sc}$ is generated, while under open circuit conditions no current can flow and the voltage is at its maximum, which is $V_{oc}$. The point in the $J$–$V$ curve yielding maximum product of current and voltage, $P_{max}$, is called the maximum power point. The corresponding current and voltage are called $J_{max}$ and $V_{max}$, respectively. The theoretical power ($P_{theo}$) of the device is calculated by multiplying the short circuit current density by the open voltage. Another important characteristics of solar cell performance is the fill factor ($FF$), defined as the maximum power produced by the cell ($P_{max}$) divided by the theoretical power ($P_{theo}$).

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} = \frac{P_{max}}{P_{theo}}$$
The last parameter and probably the most critical device characteristic is energy conversion efficiency, defined as the ratio of $P_{\text{max}}$ to the power input ($P_{\text{in}}$) on the representative area.

$$\eta = \frac{I_{\text{sc}} \times V_{\text{oc}} \times FF}{P_{\text{in}}} \times 100\%$$

A standard measurement condition has been developed to facilitate comparable testing of solar cells in different laboratories. Under the standard condition, the power input is generally maintained at 100 mW cm$^{-2}$ by the solar simulator and the spectral distribution of the light source is AM 1.5 global standard solar spectrum.

![Figure 1.8 Current–voltage (J–V) curve of solar cell.](image)

Photovoltaic performance depends on several factors, such as light harvesting, charge separation and charge collection. It is maximized by materials selection and cell design. In a DSSC, the dye-adsorbed TiO$_2$ film plays an important role because it serves as a pathway for photo-injected electrons. It is no doubt that nanocrystalline TiO$_2$ film with higher surface area is able to utilize more photons due to a large amount of adsorbed dye. Increasing the TiO$_2$ film thickness would be one day to enlarge the total surface area. However, this method is restricted because the increased surface area can also act as recombination centers [19,20]. In addition, the use of only nanocrystalline TiO$_2$ particles with about 20 nm in diameter allows light to pass through the film, which deteriorates light harvesting efficiency. To address this problem, one dimensional (1D) TiO$_2$ nanotube array is selected as an alternate photoanode for DSSC due to the following reasons [21-27]. First, 1D nanotubes have less grain boundaries that electrons have to pass; thus electron mobility is increased, leading to fast transport of excited electrons. Second, ordered TiO$_2$ nanotubes provide a vertical pathway for electron transport along the tube, and thus minimize electron loss during diffusion process.

There are other approaches that have been applied to improve electron transport in DSSCs, such as surface modification with noble metal [28-30], using quantum dots [31], developing new sensitizers [32-34], and designing new morphology of photoanodes.
The purposes of these methods are either to enhance light harvesting ability or to suppress recombination of photogenerated electron-hole (e-h) pairs.

1.3 Semiconductor Photocatalysis

Environmental pollution, such as contaminated water or polluted air, has become a global issue threatening the health of human kind. Typical pollution sources are toxic organic molecules or exhausted gas compounds which are released from household waste and local industries. Many research efforts have been focused on searching new alternatives and ecologically sustainable methods for cleaning up environmental contamination. Photocatalysis is an effective solution that has attracted tremendous research interests since the early 1970s, when Fujishima and Honda discovered the photocatalytic splitting of water on TiO$_2$ electrodes [37]. Considering that we get “free” light from the sun, the idea of using solar light energy as a source to clean up the environment is an ideal and extremely promising approach.

1.3.1 Principle of Semiconductor Photocatalysis

Photocatalysis is generally defined as the initiation of a chemical reaction or changing its rate when exposed to ultraviolet, visible or infrared radiation in the presence of a substance – the photocatalyst – that absorbs light and is involved in chemical degradation of organic pollutants. Figure 1.9 shows a simple scheme of semiconductor activation. When a catalyst is exposed to UV radiation and the energy of incident photons matches or exceeds the band gap of the semiconductor catalyst, electrons are promoted from the valence band (VB) to the conduction band (CB) of the catalyst leaving an equal number of holes. As a result, an electron–hole (e-h) pair is produced, where $e_{cb}^-$ and $h_{vb}^+$ are the electron in the conduction band and the electron vacancy in the valence band, respectively. Both excited electrons and holes migrate to the surface of photocatalyst, where they react with absorbed electron donors and electron acceptors, respectively, by a redox reaction. In the photoreduction reaction, the photo-generated electrons can be transferred to surface-adsorbed O$_2$ rapidly to produce activated •O$_2^-$ (superoxide radical anion of oxygen). The activated •O$_2^-$ further produces •OH (active hydroxyl radicals) via a series of reaction with H$^+$. In the photo-oxidation reaction, the photogenerated holes can also react with surface bound H$_2$O to give rise to •OH radicals. The photo-reduction and photo-oxidation steps both generate •OH which is a strong oxidizing agent for oxidative degradation and ultimate mineralization of organic pollutants, and thus the adsorbed organic pollutants are continuously decomposed to CO$_2$ and H$_2$O on the catalyst surface. More organic pollutants transfer from the bulk solution to the surface for consumption, and thereby the concentration of organic pollutant drops as UV illumination continues.
The probability and the rate of such charge transfer processes depend on the positions of the conduction and valence band edges and on the redox potentials of the adsorbed species. For example, when a semiconductor is used as a photocatalyst in the environmental remediation involving photodecomposition of organic pollutants, it should be capable of generating a hole in the valence band with a redox potential that is positive enough to oxidize the organic pollutant. At the same time the photo-generated electron in the conduction band should have a potential negative enough to reduce adsorbed $O_2$ to superoxide radical anion [38]. Figure 1.10 shows the values of band gaps of different semiconductors and their ranking on the electrochemical scale. A substrate can only successfully interact with some semiconductors: it is necessary that the electrochemical potential of the electron acceptor is more positive than the potential of the semiconductor conduction band and that the potential of the electron donor is more negative (up in the graph) than that of the semiconductor valence band. A photocatalytic reaction can take place only under such conditions.

![Figure 1.9 Simplified scheme of semiconductor activation.](image)

![Figure 1.10 Relationship between the band structures of some selected metal oxides and non-oxide semiconductors and the redox potentials of water splitting [39].](image)
Recombination of electron-hole pairs can occur, in competition with charge transfer to adsorbed species. This phenomenon represents the major deactivation path which could significantly decrease the overall photocatalytic efficiency. Thus, taking TiO₂ as an example of semiconductor photocatalyst, the main reaction scheme of a photocatalytic process can be summarized in the following equations and depicted in Figure 1.9.

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow e^-_{cb} + h^+_{vb} \quad \text{Charge separation (1)} \\
e^-_{cb} + \text{O}_2 & \rightarrow \cdot\text{O}_2^- \quad \text{Surface trapping (2)} \\
\cdot\text{O}_2^- + \text{H}^+ & \rightarrow \cdot\text{OOH} \rightarrow \cdot\text{OH} \quad (3) \\
h^+_{vb} + \text{H}_2\text{O} & \rightarrow \cdot\text{OH} + \text{H}^+ \quad (4)
\end{align*}
\]

A photocatalyst must be stable and not prone to decompose due to long exposure to light. Among different semiconductor photocatalysts, TiO₂ appears as the most active and most suitable one for a wide variety of energy and environmental applications. In fact, TiO₂ has a high oxidation ability, its photogenerated holes being at \(E_0 = 2.9\) V vs. NHE at pH 0. Moreover, it is biologically and chemically inert, photo-stable and cost effective. Finally the location of the bottom of conduction band (Figure 1.10) makes it suitable for photocatalytic production of hydrogen from water; thus titania has received extensive attention in the last decade owing to its potential applications in the field of solar energy harvesting, conversion and storage [39-40].

The crystalline form of TiO₂ is also very important. The crystalline forms of TiO₂ are anatase, rutile, and brookite. Rutile and anatase phases are most commonly used in photocatalytic studies (Figure 1.11). Differences in lattice structures of these two phases result in different mass densities and electronic band structures for anatase and rutile TiO₂. In particular, titanium dioxide is characterized by an indirect band gap, which is equal to 3.2 and 3.0 eV, respectively, for anatase and rutile phase.

1.3.2 Modifications of TiO₂ for Enhanced Photocatalytic Activity

Though TiO₂ remains as the most active and suitable semiconductor photocatalyst for a wide variety of energy and environmental applications, the following factors limit its photocatalytic efficiency and activity: (i) Relatively large band gap which determines the energy necessary to create e-h pairs in the semiconductor to innervate photocatalytic processes. For example, the band gap of TiO₂ (anatase phase) is 3.2 eV. It absorbs light in the UV region, so that only a small portion of sunlight can be used for photocatalytic processes. (ii) Low mobility of charge carriers in the migrating process results in fast recombination of most photo-generated e-h pairs in competition with charge transfer to adsorbed species on the surface.

In order to extend the spectral width and increase efficiency of TiO₂ photo-response, many approaches have been applied to improve the photocatalytic properties of TiO₂ by shifting the band gap towards lower energy and improving the charge separation efficiency. Particularly, deposition of noble metals on its surface to change the band gap is found to be
an effective approach [41-43]. Tunc et al. reported a reduced band gap of Ag-TiO$_2$ composites (2.75 eV) compared to that of pure TiO$_2$ nanoparticles (3.7 eV) and an electron charge transfer to Ag occurring upon UV irradiation [44]. Since there is a difference in Fermi levels of TiO$_2$ and Ag, Ag can act as a reservoir for photo-generated electrons, improving charge separation as well as promoting the interfacial charge-transfer kinetics at the Ag/TiO$_2$ interface and facilitating catalytic reactions in which electrons are involved. Also, surface plasmon induced by Ag nanoparticles (NPs) has been reported to significantly increase photon absorption efficiency of visible light [45]. However, under the strong absorption of UV-light, the small change in plasmon absorption is too weak to be probed [28]. Several methods have been reported to deposit Ag NPs onto TiO$_2$ such as magnetron sputtering [46], photo reduction deposition [47], and electrochemical deposition [48]. However, none is able to prevent the aggregation of Ag particles and to keep structure uniform during the Ag deposition process. Chou et al. synthesized Ag/TiO$_2$ composites via dry coating process showing agglomeration of Ag NPs with a wide particle size distribution of 20-100 nm [49]. Agarwala et al. also deposited Ag NPs onto TiO$_2$ nanotubes by using a photo reduction method; the resulted particle size is larger than 70 nm and the nanoparticles are mixed with some rod-like structures [50]. On the other hand, Lai et al. developed a simple method using pulse current deposition to deposit uniformly distributed spherical Ag NPs (2-10 nm) on the surface of TiO$_2$ nanotube arrays [51]. This process is easy to implement and can effectively suppress the agglomeration of Ag particles by taking advantage of high nucleation rate of Ag under the pulse current condition.

Figure 1.11 Bulk crystal structures of rutile and anatase [52].
1.4 Objectives of the Present Work

The aim of this work is to synthesize and modify novel TiO$_2$ nanostructures and nanocomposites for their enhanced performances in photovoltaics and photocatalysis. In chapter 2, fast synthesis of bamboo-type TiO$_2$ nanotube arrays via anodization of Ti under alternating voltage condition is introduced, for applications as photo-anodes in high-efficiency dye-sensitized solar cells. Compared with DSSCs based on smooth-walled nanotubes synthesized under constant voltage condition, DSSCs based on bamboo-type TiO$_2$ nanotube arrays with the same tube length show higher efficiencies, due to enhanced surface area of bamboo-type structure for more dye loading. Moreover, longer bamboo-type TiO$_2$ nanotubes can be synthesized via decreasing water content in electrolyte for further increased DSSC efficiency.

Chapter 3 and 4 focus on modifications of TiO$_2$ nanotube arrays with Ag and reduced graphene oxide, respectively, for applications in DSSCs. In Chapter 3, Pulse current deposition is used to deposit uniformly-sized Ag nanoparticles onto a TiO$_2$ nanotube array for application as photoelectrode in dye-sensitized solar cells, and the size and amount of loaded Ag nanoparticles can be controlled by the pulse deposition time. Due to the enhanced light absorption and electron-hole separation caused by plasmon effect, DSSCs based on Ag-modified TiO$_2$ nanotube arrays show higher energy conversion efficiencies than those based on bare nanotubes with the same tube length. Particularly, high-concentration TiCl$_4$ treatment on TiO$_2$ nanotube arrays can further increase the DSSC efficiencies. In Chapter 4, electrophoretic deposition is used to deposit reduced graphene oxide (RGO) nanosheets onto a TiO$_2$ nanotube array for application as photoelectrode in dye-sensitized solar cells. The as-deposited RGO nanosheets are very uniform and can be obtained with controllable thickness. Due to the enhanced electronic conductivity caused by RGO, the short-circuit current of DSSCs based on RGO-modified TiO$_2$ nanotube arrays is much higher than that of DSSCs based on unmodified TiO$_2$ nanotube arrays.

Chapter 5 concentrates on synthesis of TiO$_2$ nanosheets (NSs) via a soft-chemical exfoliation method. Colloidal Ti$_{0.91}$O$_2$ NSs are first prepared via chemical exfoliation of a layered precursor (H$_x$Ti$_{2-x/4}$[x/4]O$_4$ • H$_2$O) through ion exchange with bulky tetrabutylammonium ions. Subsequent acid treatment induces colloidal Ti$_{0.91}$O$_2$ NSs to reassemble and precipitate into a gelation form, followed by thermal annealing to convert to anatase TiO$_2$ for applications as photoanode materials in DSSCs. DSSC based on TiO$_2$ nanosheet film with optimized thickness delivers the highest energy conversion efficiency and higher efficiency than DSSCs consisting of TiO$_2$ NSs synthesized via other methods reported in literature. Additionally, TiCl$_4$ treatment of TiO$_2$ nanosheets can further enhance efficiency of DSSC by increasing surface area of TiO$_2$ nanosheets for more dye loading.

Photocatalytic property of TiO$_2$ is investigated for application in degradation of methylene blue dye in Chapter 6. Enhanced methylene blue degradation efficiency is achieved by depositing Ag nanoparticles onto bamboo-type TiO$_2$ nanotube array. Ag nanoparticles act as reservoirs for photo-generated electrons, improving charge separation and facilitating catalytic reactions in which electrons are involved. The photocatalytic
activity and kinetic behavior of Ag-modified bamboo-type TiO₂ nanotube arrays are also optimized by tuning pulse deposition time of Ag nanoparticles.

1.5 References


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CHAPTER 2 FACILE SYNTHESIS AND MORPHOLOGY CONTROL OF BAMBOO-TYPE TiO$_2$ NANOTUBE ARRAYS FOR HIGH-EFFICIENCY DYE-SENSITIZED SOLAR CELLS

2.1 Introduction

As fossil fuel reserves become depleted, the long-lasting and source-free solar energy is becoming an economically viable source of energy to offer a clean solution to the current energy crisis [1,2]. However, conventional silicon solar cells are still expensive due to high production costs. Since dye-sensitized solar cell (DSSC) was first invented in 1991, it has attracted intensive attention for their low cost and easy fabrication [3-8]. Hence, DSSC is regarded as one of the promising alternatives to traditional silicon solar cells. In DSSCs, electrons of dye are excited by solar energy adsorption and the electrons from photo-excited dye inject into conduction band of photo-anode titanium dioxide (TiO$_2$). The electrons then diffuse through TiO$_2$ layer to the electrode, and subsequently reach the counter electrode through an external circuit. The dye molecules regain electrons from a redox couple iodide/triiodide (I$^-$/I$_3^-$) in an electrolyte. The iodide is regenerated in turn by the reduction of triiodide at the counter electrode, and this process requires a catalytic functionality of Pt on the cathode surface. This photo-conversion process is regenerative.

Up to now, energy conversion efficiencies of DSSCs reported in literature are still lower than those of traditional silicon solar cells [9]. One of the most efficient approaches to enhance DSSC efficiency is to reduce the recombination losses in the random network of TiO$_2$ nanocrystalline [10-12]. To reduce electron recombination with excited dye and I$_3^-$ in electrolyte, one-dimensional (1D) nanotubes have been investigated to enhance the electron transport owing to several advantages as follows [13-19]. First, 1D nanotubes have less grain boundaries that electrons have to pass; thus electron mobility is increased, leading to fast transport of excited electrons. Second, ordered TiO$_2$ nanotubes provide a vertical pathway for electron transport along the tube, and thus minimize electron loss during diffusion process. Third, the vertically-ordered tubular structure will facilitate the filling of new sensitizer or solid-state electrolyte for further increase of efficiency and improvement of stability, while the disordered mesoporous structure of conventional TiO$_2$ nanocrystalline film makes infiltration of solid or viscous electrolyte difficult and ineffective [20,21].

As such, self-aligned TiO$_2$ nanotube arrays have been widely studied for applications as photo-anodes in DSSCs and anodic oxidation of Ti has been the most common method for synthesis of these nanotube arrays [17,22-28]. However, the 1D nanotube structure typically has a low surface area compared to mesoporous films, resulting in insufficient dye loading and low light-harvesting efficiency. In general, DSSCs based on TiO$_2$ nanotube arrays with a length of 10-30 μm only showed energy conversion efficiencies within the range of 1-3%. For example, Li et al fabricated TiO$_2$ nanotube arrays of various lengths (10, 17, and 22 μm-long) by anodic oxidation, and DSSCs based on these nanotube arrays exhibited efficiencies of 1.08%, 1.25%, and 1.39%, respectively [29]. Kim et al also reported synthesis of TiO$_2$ nanotube arrays up to 10, 20 and 30 μm in length, with
corresponding DSSC efficiencies of 2.33%, 2.88%, and 2.87% [30]. To increase the DSSC efficiency, nanotubes with length up to 100 μm have been produced to increase the surface area for dye loading [31,32]. Shankar et al even obtained ultra-long TiO$_2$ nanotubes with length over 200 μm which delivered significantly improved DSSC efficiency of 6.89% [32]. However, synthesis of these ultra-long nanotubes costs much time (more than 10 hours) and electricity for anodization process, and the reported efficiencies of TiO$_2$-nanotube-array-based DSSCs are still lower than DSSCs based on mesoporous TiO$_2$ films, due to the relative low internal surface area for dye loading of nanotube arrays [33-35].

Some recent efforts have been made to further increase surface area of TiO$_2$ nanotube arrays for enhanced efficiencies of DSSCs, such as fabricating bamboo-type TiO$_2$ nanotube arrays with ridges on tube sidewalls. Schmuki’s group reported an effective strategy to synthesize bamboo-type TiO$_2$ nanotube arrays via anodization under an alternating voltage (AV) condition [36,37]. Such bamboo structure gained enhanced surface area owing to the ridges and yielded a photo conversion efficiency which was 55% higher than that of smooth-walled nanotubes with identical film thickness of 8.0 μm when used in DSSCs. However, these bamboo-type TiO$_2$ nanotube arrays were grown by using an electrolyte containing environmentally hazardous HF and a rather high voltage (120 V) for more than 10 hours, and efficiency of DSSCs based on the bamboo-type TiO$_2$ nanotube arrays was still relatively low (2.96%). Zhang et al. synthesized bamboo-type TiO$_2$ nanotube arrays using an alternating current condition by using relatively high voltages (85 V and 55 V), and reported a slightly improved DSSC efficiency of 3.47% [38]. It is noted that synthesis of these bamboo-type TiO$_2$ nanotube arrays is not very efficient as it takes long time and high voltages. Though formation process of bamboo-type TiO$_2$ nanotubes is outlined, there is no report about fundamental explorations about growth mechanism and no clear understanding of factors that control morphological features such as ridge spacing. More importantly, the efficiencies of DSSCs based on these bamboo-type nanotubes have not shown appreciable improvement compared to DSSCs based on smooth-walled TiO$_2$ nanotube arrays [37-39].

In this report, we employ a facile anodic oxidation method to fabricate bamboo-type TiO$_2$ nanotube arrays for enhanced efficiencies of DSSCs. In comparison with former syntheses reported in literature [36-38], we use ethylene glycol-based electrolyte that contains NH$_4$F and H$_2$O but not the hazardous HF. In addition, the synthesis consumes much less energy and takes shorter time, since our bamboo-type nanotubes with comparable lengths can be achieved by anodizing Ti at lower voltage (60 V) for less than 3 hours. The formation mechanism of bamboo-typed TiO$_2$ nanotubes synthesized via alternating high and low-voltage anodization steps is explored as well. As the AV pulse duration is directly correlated to the tube/ridge growth, the morphological features of nanotubes such as ridge spacing can be precisely manipulated. The nanotube length can also be tuned by changing water content in electrolyte. Such fast synthesis and facile morphology control of bamboo-type TiO$_2$ nanotube arrays allows for optimization of nanotubes to achieve high-efficiency DSSCs.
2.2 Experimental

Ti foils (0.25 mm thickness, 99.5 wt% purity, Alfa Aesar) were degreased by sonicating in acetone, deionized (DI) water, and ethanol for 15 min, respectively, then rinsed with ethanol and dried in a nitrogen stream. Electrochemical anodization of the Ti foils was carried out in a two-electrode cell, with a platinum mesh as the counter electrode at room temperature. The electrolyte for anodization was prepared with anhydrous ethylene glycol (EG) with NH₄F (0.3 wt%) and H₂O (5 vol% for shorter TiO₂ nanotube arrays; 2 vol% for longer TiO₂ nanotube arrays). The voltage was supplied by a DC power supply with digital display (Model 1623A, PK Precision). To prepare bamboo-type TiO₂ nanotube arrays, the anodization process consists of multiple cycles of alternating high and low-voltage steps, as shown in Figure 2.1. The voltage is first increased from zero to \( V_{\text{high}} \) (60 V) and being kept at \( V_{\text{high}} \) for a time \( t \), then drops to \( V_{\text{low}} \) (10 V) and is also held at \( V_{\text{low}} \) for a time \( t \), followed by increasing to \( V_{\text{high}} \) (60 V) again and being kept at for a time \( t \). Each voltage alternate from 60 V to 10 V is regarded as one cycle. High voltage of 60 V in the first cycle is reached via a voltage ramp of 1 V/s, while other voltage steps are switched without ramp. The AV pulse duration, \( t \), is kept the same for \( V_{\text{high}} \) and \( V_{\text{low}} \) during the anodization process. To produce bamboo-type TiO₂ nanotube arrays with different ridge spacing, \( t \) is varied (1 min, 2 min, and 4 min). For comparison purposes, smooth-walled TiO₂ nanotube array was prepared by anodization of Ti under constant-voltage condition (CV) at 60 V for 1 h. After anodization, the samples were rinsed in deionized water and dried in air, followed by heat treatment at 450 °C in air for 3 h to produce anatase phase. The annealed TiO₂ nanotube arrays were soaked in 100 mL of 0.2 M TiCl₄ aqueous solution at 70 °C for 30 min and then annealed in at 450 °C in air for 30 min.

![Figure 2.1 Anodization sequence for the formation of bamboo-type TiO₂ nanotube arrays.](image)

To fabricate DSSCs, the as-prepared TiO₂ nanotube arrays were soaked in anhydrous ethanol containing 0.2 mM N719 dye (Ru[LL’-(NCS)]₂, L=2,2’-bipyridyl-4,4’-dicarboxylic acid, L’=2,2’-bipyridyl-4,4’- ditetraethylammonium carboxylate, Solaronix Co.) and sensitized for 24 h at room temperature. Afterwards, these
films were rinsed with acetonitrile in order to remove physisorbed N719 dye molecules. Platinized counter electrode was fabricated by drop casting 0.5 mM H$_2$PtCl$_6$/isopropanol solution on FTO glass substrate that has a hole for electrolyte injection later on, followed by heating at 400 °C in air for 20 min. The dye-sensitized TiO$_2$ nanotube arrays were sandwiched together with Pt-coated FTO glass by applying a 100 μm thick hot-melt sealing film as the spacer (Meltonix 1170-100, Solaronix Co.). DSSCs were sealed by applying heat and pressure with a hot press at 110 °C. A $\Gamma$/I$_3^-$ based electrolyte, which contained 0.10 M GTC in a mixture of acetonitrile and valeronitrile (85:15 v/v) (No. ES-0004, IoLiTec Inc., Germany) was injected through the hole on the Pt-coated FTO into DSSC.

A FEI Quanta 3D FEG scanning electron microscope (SEM) was used to characterize morphology of TiO$_2$ nanotube arrays. Crystal structure of TiO$_2$ nanotube arrays was determined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu Kα radiation operated at 30 kV and 15 mA with a scan rate of 2°/min. The current–voltage (J–V) characteristics of DSSCs were recorded using a Keithley 2400 source meter. A solar light simulator (Model: 67005, Oriel) was used to simulate sunlight under one sun AM 1.5 G (100 mW/cm$^2$) illumination provided by a 150 W Xenon arc lamp (Model: 6256, Oriel) and calibrated using a Si solar reference cell (Model: 91150V, Oriel). Backside illumination mode was used, since the photo-anode consists of TiO$_2$ nanotube array on Ti substrate which is not transparent to light.

2.3 Results and Discussion

Morphology of anodic TiO$_2$ nanotube arrays can be adjusted by tuning synthesis conditions such as voltages, electrolyte composition and anodization time. Figure 2.2 displays smooth-walled nanotubes and bamboo-type nanotubes synthesized by anodizing Ti in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O under CV and AV conditions, respectively. CV anodization at 60 V for 1 h leads to formation of ordered TiO$_2$ nanotubes with smooth walls, as shown in Figure 2.2, a and b. They are hollow inside with an open entrance on the top, showing an average pore diameter ~150 nm (Figure 2.3, a). As can be seen from Figure 2.2, a, the whole nanotube array is perpendicular to the Ti substrate, with a thickness of ~8.0 μm. In contrast to CV conditions, AV anodization processes produce bamboo-type TiO$_2$ nanotubes with rough walls, as shown in Figure 2.2, c and d (BT-4), e and f (BT-2), and g and h (BT-1) with AV pulse duration time of 4 min, 2 min and 1 min, respectively. BT-4 is formed under an AV condition with a sequence of 4 min at 60 V and 4 min at 10 V for 20 cycles as shown in Figure 2.2, c and d. Total time of this anodization sequence is 160 min; the resultant bamboo-type nanotube array (BT-4) has a thickness of 8 μm and the spacing between neighboring bamboo ridges is 400 nm. These bamboo-type TiO$_2$ nanotubes have clear top surfaces and open entrances, easy for infiltration of dye and redox electrolytes (Figure 2.3, b, c, and d).
Figure 2.2 SEM images of bamboo-type and smooth-walled TiO$_2$ nanotube arrays of 8.0-μm thickness. The tubes were synthesized in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O under different anodization sequence of (a, b) Smooth-walled: 60 V for 60 min; (c, d) Bamboo-type-4: 60 V for 4 min, 10 V for 4 min, and 20 cycles; (e, f) Bamboo-type-2: 60 V for 2 min, 10 V for 2 min and, 40 cycles; (g, h) Bamboo-type-1: 60 V for 1 min, 10 V for 1 min, and 80 cycles.
Figure 2.3 Overview of bamboo-type and smooth-walled TiO$_2$ nanotube arrays of 8.0-µm thickness. The tubes were synthesized in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O under different anodization sequence of (a) Smooth-walled: 60 V for 60 min; (b) Bamboo-type-4: 60 V for 4 min, 10 V for 4 min, and 20 cycles; (c) Bamboo-type-2: 60 V for 2 min, 10 V for 2 min and, 40 cycles; (d) Bamboo-type-1: 60 V for 1 min, 10 V for 1 min, and 80 cycles.

Figure 2.2, e and f present SEM images of BT-2 sample using AV condition with a sequence of 2 min at 60 V and 2 min at 10 V for 40 cycles. In comparison with BT-4 in Figure 2.2, c and d, the length of BT-2 nanotubes remains 8 µm as shown in Figure 2.2, e, but the spacing between two neighboring bamboo ridges is decreased to 200 nm as can be seen from Figure 2.2, f. In other words, ridge density is doubled in BT-2 compared to BT-4. To further increase surface area of bamboo-type nanotube arrays by increasing ridge density, AV pulse duration time is further reduced to 1 min and number of AV cycles is increased to 80, yielding BT-1 sample as shown in Figure 2.2, g and h. The nanotube length stays at 8 µm (Figure 2.2, g), but the spacing between neighboring bamboo ridges is further reduced to 100 nm (Figure 2.2, h). Comparing the cross-section SEM images of BT-4, BT-2, and BT-1 in Figure 2.2, d, f, and h, ridge spacing of bamboo-type nanotubes decreases linearly with AV pulse duration time, while the nanotube length is the same as the total high-voltage anodization time is the same. Our other work shows that a proper low-voltage duration time is required for ridge formation while ridge spacing is dependent
on the time of high-voltage step. Since the ridge spacing relies on the high-voltage period, it can be seen the total length of bamboo-type nanotubes is decided by the whole time of high-voltage steps. Therefore, morphology control of bamboo-type TiO$_2$ nanotube arrays can be achieved by simply adjusting AV pulse duration time and cycle numbers. Nanotube arrays with larger surface area can be obtained by using shorter pulse duration for denser ridges and more cycle numbers for longer tubes, for maximizing energy conversion efficiency of DSSCs.

The controllable formation of bamboo ridges via AV oxidation is related to the growth behaviors of anodic TiO$_2$ nanotube arrays under CV conditions. Once a constant voltage is applied, three fundamentally different morphologies of an oxide film emerge successively on Ti substrate. At the beginning, a compact oxide layer is formed; later, pits and pores originate in the compact layer and turn it into a porous structure; finally, these pores are separated by inter-pore cavities, eventually yielding an ordered tubular layer. Three chemical reactions occur simultaneously to complete such morphological evolution: (1) Field-assisted oxidation of titanium: water decomposes near the metal and produce O$^{2-}$ and H$^+$ ions; the O$^{2-}$ ions then migrate across an electrolyte-oxide interface to oxidize Ti. The reactions are described as:

\[
H_2O \rightarrow 2H^+ + O^{2-} \quad \text{(water decomposition)} \quad (1)
\]

\[
Ti + 2O^{2-} \rightarrow TiO_2 + 4e \quad \text{(metal oxidation)} \quad (2)
\]

(2) Field-assisted dissolution of titanium oxides: due to the electric field, Ti–O bond undergoes polarization and is weakened, promoting dissolution of the oxides. (3) Chemical dissolution of titanium oxides: therefore, Ti$^{4+}$ cations become soluble hexafluorotitanium complexes [TiF$_6$]$^{2-}$ that enter the electrolyte, while the free O$^{2-}$ anions travel to the oxide–metal interface and react with metal. The reaction is described as:

\[
TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \quad \text{(oxide dissolution)} \quad (3)
\]

After the anodization starts, pH and ion diffusion gradients are quickly established inside the tubular layer, which finally allows stable growth of TiO$_2$ nanotubes under a high voltage (Figure 2.4, a). In this situation, water decomposes at the bottom of tubes and cavities (eqn(1)), and produces H$^+$ ions there. Some H$^+$ ions diffuse outward to cause a stable pH gradient, while others participate in the dissolution of surrounding oxides, together with F$^-$ ions from outside [25]. The substrate is continuously oxidized (eqn(2)) and the barrier layer at the bottom keeps moving towards the substrate, resulting in steady growth of single-layer TiO$_2$ nanotubes.

Once this system is altered quickly to a lower voltage, fewer H$^+$ ions are yielded and fewer F$^-$ ions diffuse to reach the tube bottom. Hence, pH gradient or ion concentration profiles are gradually adjusted to less steep gradients until compatible with the low-voltage condition (Figure 2.4, b). Fewer H$^+$ ions make dissolution of oxides slower, yielding a thicker barrier layer at the tube bottom or cavity bottom. After a short time, tiny pores originate in the barrier layer which can be considered as the first stage of tube formation as introduced above. At this moment, a fast step back to the high voltage (60 V) will restart the growth of tubes and cavities towards the metal, and pores formed at low voltage are
eaten by the re-grown large tubes. The thick barrier layer under the tubes and cavities continued to be dissolved and pushed toward the substrate, but the part between two neighboring tubes survives and remains on the tube walls to form ridges, yielding bamboo-type nanotubes with two sections in vertical direction (Figure 2.4, c). Likewise, when this system is switched to the low voltage again, the pH gradient profile inside bamboo-type tubes tends to be less steep, and a second pore formation occurs at the base of these tubes, followed by origination of a second ridge between the 2nd and 3rd tube sections (Figure 2.4, d and e). In an anodization process consisting of multiple alternating high-voltage and low-voltage steps, such ridge formation event is repeated and the length of TiO$_2$ nanotubes with multiple sections is increased accordingly.

![Diagram showing growth of bamboo-type TiO$_2$ nanotubes via anodic oxidation](image)

Figure 2.4 Schematic showing growth of bamboo-type TiO$_2$ nanotubes via anodic oxidation: (a) pH gradient profile in nanotubes during their steady growth at 1st high voltage step, (b) less steep pH gradient and pore formation at the 1st low voltage step, (c) formation of a ridge between the 1st section and 2nd section of nanotubes at the 2nd high voltage step, (d) pore formation at the 2nd low voltage step, (e) ridge formation between the 2nd section and 3rd section of nanotubes at the 3rd high voltage step.
In addition to modifying the sidewall morphology, length of bamboo-type TiO₂ nanotubes can also be tuned to grow ultra-long nanotubes to further enhance surface area. Simply increasing the number of anodization cycles or time of anodization sequence does not necessarily lead to longer nanotubes due to dissolution of oxides in electrolyte. For example, an anodization sequence with 1 min at 60 V and 1 min at 10 V for 160 cycles (total time = 320 min, doubled time compared to anodization in Figure 2.2, g) yields bamboo-type TiO₂ nanotube arrays with a thickness of 7 μm (Figure 2.5, a) which is even shorter than 8-μm-long BT-1 nanotubes in Figure 2.2, g. During the anodization oxidation process, the nanotube length typically increases with anodization duration time at the beginning of anodization. However, after the nanotube length reaches to a critical value, the longer nanotube limits the diffusion of ionic species to the metal/oxide interface, and chemical dissolution begins to dominate the anodization kinetics, resulting in decrease of nanotube length. Moreover, water content in electrolyte has significant effect on the tube length as well as the ridge spacing in bamboo-type nanotubes. So far we use EG electrolytes containing 0.3 wt% NH₄F and 5 vol% water. Reducing water content to 2 vol% and using the same anodization sequence for growing BT-1 earlier in Figure 2.2, g yield bamboo-type TiO₂ nanotube arrays (BT-L) as long as 16.5 μm (Figure 2.5, c), which is significantly longer than BT-1 (8 μm). However, ridge spacing is increased to 230 nm, larger than 100 nm for BT-1 in Figure 2.2, h. Less water in electrolyte allows formation of thinner barrier layers at the substrate because the donation of oxygen becomes difficult (eqn (1) and (2)) and results in a reduced tendency to form oxide [40,41]. Ionic transport across the barrier layer is enhanced, and thus the motion of this layer toward substrate is accelerated, yielding faster growth of nanotubes. Meanwhile, as water content decreases, few H⁺ ions are produced and diffusion of electrolyte species is slowed down, which makes difficult for origination of bamboo ridges, as evidenced by weakened and less clear ridges shown in the SEM image of Figure 2.5, d.

The as-prepared anodic TiO₂ nanotubes are amorphous and they are heated at high temperature to convert to anatase phase for applications in DSSCs. Figure 2.6 shows XRD patterns of bamboo-type TiO₂ nanotubes (BT-1) produced by an anodization sequence of 60 V for 1 min, 10 V for 1 min, and 80 cycles in EG electrolyte containing 0.3 wt% NH₄F and 5 vol% H₂O. The XRD pattern of as-prepared bamboo-type nanotubes only has diffraction peaks of Ti, indicating that the as-prepared bamboo-type nanotubes are amorphous. After heat treatment in air at 450 °C for 2 h, the TiO₂ nanotubes are converted into crystalline forms. The emergence of (101) and (200) peaks of metastable anatase suggested the transformation of amorphous TiO₂ to anatase TiO₂.

High concentration TiCl₄ treatment is carried in this work in order to improve short circuit current for DSSC applications. It has been reported in literature that TiCl₄ treatment can enhance dye absorption on the surface, improve the electron transport properties in nanocrystalline TiO₂ films, and increase the charge separation efficiency [42-44]. After being treated in TiCl₄ aqueous solution, TiO₂ nanotube arrays are sensitized by N719 dye, and are integrated into DSSCs. Figure 2.7 presents J–V curves of DSSCs based on 8-μm-long smooth-walled TiO₂ nanotubes (SW), 8-μm-long bamboo-type nanotube arrays with different ridge spacing (100 nm, 200 nm, 400 nm) (BT-1, BT-2, BT-4), and 16.5-μm-long bamboo-type nanotubes with a ridge spacing of 230 nm (BT-L).
Photovoltaic characteristics of these DSSCs such as short-circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor ($FF$), and efficiency ($\eta$) are summarized in Table 2.1. It is evident that all the bamboo-type nanotube arrays (BT-4, BT-2, and BT-1) show higher short circuit currents than smooth-walled nanotube array (SW) of the same length, since the bamboo ridges on sidewalls enhance the surface area of nanotube arrays for dye chemisorption. Among the three bamboo-type nanotube arrays with the same length of 8 µm, BT-1 with highest ridge density delivers the highest energy conversion efficiency (5.64%) compared to BT-2 and BT-4, exhibiting $V_{oc}$ of 0.81 V, $J_{sc}$ of 11.60 mA/cm$^2$, $FF$ of 0.60 (Table 2.1), which represents a 44.6% increase in cell efficiency compared to SW. Similarly, DSSC based on BT-2 with higher ridge density shows better performance than DSSC based on BT-4. These results indicate that bamboo-type TiO$_2$ nanotube arrays (same length) with higher ridge density enhance DSSC performance more due to larger surface area for dye loading and the regular bamboo-ridges for enhanced electron transport.

Figure 2.5 SEM images of bamboo-type nanotube arrays synthesized (a, b) in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O under the anodization sequence of 60 V for 1 min, 10 V for 1 min, and 160 cycles; (c, d) in EG electrolytes containing 0.3 wt% NH$_4$F and 2 vol% H$_2$O under the anodize sequence of 60 V for 1 min, 10 V for 1 min, and 80 cycles.
Figure 2.6 XRD diffraction patterns of bamboo-type TiO$_2$ nanotubes produced by anodization sequence of 60 V for 1 min, 10 V for 1 min, and 80 cycles in EG electrolyte containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O (a) As-prepared TiO$_2$ nanotube; (b) Anatase TiO$_2$ nanotube formed after annealing at 450 °C.

Figure 2.7 $J$–$V$ characteristics of DSSCs using different TiO$_2$ nanotube arrays. (SW: smooth-walled nanotube synthesized at 60 V for 60min; BT-4: bamboo-type nanotube synthesized at 60 V for 4 min, 10 V for 4 min, and 20 cycles; BT-2: bamboo-type nanotube synthesized at 60 V for 2 min, 10 V for 2 min and, 40 cycles; BT-1: bamboo-type nanotube synthesized at 60 V for 1 min, 10 V for 1 min and, 80 cycles; BT*: bamboo-type nanotube synthesized in the electrolyte containing 2 vol% H$_2$O at 60 V for 1 min, 10 V for 1 min, and 80 cycles.
Table 2.1 Photovoltaic characteristics of dye-sensitized solar cells shown in Figure 2.7

<table>
<thead>
<tr>
<th>Tube length (µm)</th>
<th>(J_{sc}) (mA/cm²)</th>
<th>(V_{oc}) (V)</th>
<th>FF(^a)</th>
<th>(\eta)(^b) (%)</th>
<th>(\sigma)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW</td>
<td>6.96</td>
<td>0.85</td>
<td>0.66</td>
<td>3.90</td>
<td>0.16%</td>
</tr>
<tr>
<td>BT-4</td>
<td>7.91</td>
<td>0.83</td>
<td>0.60</td>
<td>3.94</td>
<td>0.29%</td>
</tr>
<tr>
<td>BT-2</td>
<td>9.44</td>
<td>0.78</td>
<td>0.60</td>
<td>4.42</td>
<td>0.06%</td>
</tr>
<tr>
<td>BT-1</td>
<td>11.60</td>
<td>0.81</td>
<td>0.60</td>
<td>5.64</td>
<td>0.31%</td>
</tr>
<tr>
<td>BT-L</td>
<td>13.95</td>
<td>0.87</td>
<td>0.56</td>
<td>6.80</td>
<td>0.26%</td>
</tr>
</tbody>
</table>

\(a\) Fill-factor (FF) = \(P_{max}/(J_{sc}\times V_{oc})\);  
\(b\) Power conversion efficiency (\(\eta\)) = \(J_{sc}(\text{mA/cm}^2)\times V_{oc}(\text{V})\times FF/[100(\text{mW/cm}^2)]\times 100\%\);  
\(c\) Standard deviation of power conversion efficiency.

Among all the TiO\(_2\) nanotube arrays, BT-L (16.5 µm long, ridge spacing of 230 nm) shows the highest DSSC efficiency of 6.80%, owning to its doubled length. Obviously, the significantly increased nanotube length leads to the enhanced short circuit current (13.95 mA/cm²) which contributes to the high DSSC efficiency. Efficiency of DSSC based on BT-L is almost twice the highest cell efficiency (3.43%) from DSSCs based on bamboo-type TiO\(_2\) nanotubes reported in literature to date [38]. However, it is noted that \(J_{sc}\) does not increase linearly with the length of nanotubes. This phenomenon is consistent with others’ work on anodic TiO\(_2\) nanotube arrays. For example, Li et al fabricated various smooth-walled TiO\(_2\) nanotube arrays with the increasing thickness of 10, 17, and 22 µm which exhibited the increasing but non-linear \(J_{sc}\) of 3.16, 3.85, and 4.29 mA/cm² and efficiencies of 1.08%, 1.25%, and 1.39%, respectively [29]. Likewise, Kim et al reported synthesis of TiO\(_2\) nanotube arrays with 10, 20 and 30 µm in length and corresponding non-linearly increasing \(J_{sc}\) of 7.77, 9.62, and 10.40 mA/cm² and efficiency of 2.33%, 2.88%, and 2.87% [30]. It has been discovered that the inner diameter of nanotubes is decreasing from the tube entrance to tube bottom, due to continuous dissolution of formed tube walls, yielding a V-like hollow structure [45]. Accordingly, the inter-tube cavities tend to be narrower at the bottom where the roots of nanotubes are closely contacted. The narrowing gaps make it difficult to achieve full filling of dye solution or redox electrolytes, resulting in an undesired loss of outer surface area especially in long TiO\(_2\) nanotube arrays. This limitation is probably responsible for a fact that DSSCs based on ultra-long TiO\(_2\) nanotubes with a length of several hundreds of micrometers do not show much improved \(J_{sc}\) [32]. On the other hand, if surface area of long nanotubes is fully utilized by dye loading and electrolyte infiltration, a linear increase in \(J_{sc}\) with the tube length could be observed. For example, Gao et al. synthesized vertically aligned TiO\(_2\) nanotubes with identical diameters but with lengths varying from 10 to 20 µm, by using long ZnO nanowires as templates [46]. Gaps between these long nanotubes are wide enough for complete dye
absorption and electrolyte infiltration, and thus the related $J_{sc}$ increases linearly from 6.5 to 12.2 mA/cm$^2$ when the nanotube length is doubled.

2.4 Conclusion

We employ a facile anodic oxidation method to synthesize bamboo-type TiO$_2$ nanotube arrays with controllable ridge density and tube length by applying alternating voltage sequence, for enhanced efficiencies of dye-sensitized solar cells (DSSCs). Synthesis in this work involves non-hazardous electrolyte and is much more efficient than those reported in literature. Using less than one third of the anodization time and half of the voltage that were reported in literature yields bamboo-type TiO$_2$ nanotubes with comparable tube length and ridge density. Formation mechanism for these bamboo-type TiO$_2$ nanotube arrays is also discussed. Wall morphology and length of these nanotubes can be manipulated by tuning high-voltage anodization time and electrolyte composition, which can be used to improve and maximize efficiency of DSSCs. For instance, DSSC based on 8-μm-long bamboo-type TiO$_2$ nanotubes with ridge spacing of 100 nm exhibits a significantly improved efficiency of 5.64% due to the enhanced surface area and light scattering provided by the bamboo ridges, while DSSC based on smooth-walled nanotubes of the same length shows an efficiency of 3.90%. In addition, ultra-long (16.5 μm) bamboo-type TiO$_2$ nanotube array can be fabricated by decreasing water content in electrolyte, to further increase surface area and improve DSSC efficiency to 6.80%. Such facile synthesis and morphology control of bamboo-type TiO$_2$ nanotube arrays allow for optimizations of nanotubes for maximized efficiency of DSSCs and will advance the DSSC technology.

2.5 References


CHAPTER 3 PLASMON-ENHANCED PERFORMANCE OF DYE-SENSITIZED SOLAR CELLS BASED ON ELECTRODEPOSITED AG NANOPARTICLES

3.1 Introduction

Numerous approaches and strategies have been investigated so as to enhance photoelectric conversion efficiency of DSSC by surface modification with noble metal [1-3], using semiconductor quantum dots [4,5], developing new dyes [6-8], and designing new morphology [9-11]. The purposes of these methods are to either increase the surface area for dye loading or increase the light harvesting ability and/or suppress the recombination of photogenerated electron-hole pairs.

Among these approaches, surface modification by noble metal has been considered a very effective approach to enhance energy conversion efficiency of DSSC by improving its light harvesting. Surface plasmon induced by noble metals has the potential for enhancing the optical absorption. The surface plasmon effect is caused by light-driven collective oscillations of conduction electrons in metallic nanoparticles. The nanoparticles must be smaller than the wavelength of exciting light for electrons to oscillate with the electric field of light. When these conditions are met, an enhanced electromagnetic field is found nearby the surface of nanoparticle. The enhanced electromagnetic field is highly dependent upon the wavelength of incident light, as well as the shape, size and aggregation state of the nanoparticle. Atwater et al. have recently outlined three types of plasmonic light-trapping geometries for incorporating metal nanoparticles [12]: i) Far-field scattering. When light is scattered from noble metal nanoparticles in DSSC, light is preferentially scattered and trapped into the semiconductor by multiple and high-angle scattering, causing an increase in the effective optical path length in the cell. ii) Near-field scattering. When the wavelength of the irradiation sources are correlated with the optical absorption of the surface plasmon resonance, an increase in local electromagnetic field is found nearby metal surface. The photo-excited particles’ near-field causes the creation of electron-hole (h-e) pairs in semiconductor and suppresses the recombination of electrons in dye and/or electrolyte. iii) Surface plasmon polaritons at the metal/semiconductor interface. A corrugated metallic film on the back of semiconductor can couple sunlight into surface plasmon polaritons at metal/semiconductor interface. Therefore, utilization of plasmon effect for enhancement of light is a promising procedure for improving the efficiency of DSSC.

Till now, surface plasmon arising from metal nanoparticles has mostly been applied to increase optical absorption and/or photo current in the field of silicon solar cells [13-16] and organic solar cells [17,18]. Not many examples of this concept have been introduced and demonstrated in DSSCs. Considering plasmon effect of various noble metals, Ag is one of the most suitable candidates for practical applications due to its easy preparation and lower cost than others. Several methods have been reported to deposit Ag nanoparticles onto TiO$_2$ such as photo-induced deposition, calcination reduction, and electrochemical deposition. However, none is able to prevent the aggregation of Ag particles and keep...
structures uniform during the deposition process. Chou et al. synthesized TiO$_2$/Ag composites via dry coating process and investigated their applications in DSSCs [19]. Such a nano-metal modified DSSC yielded a photo conversion efficiency of 0.93%, which was higher than DSSC based on unmodified nanotubes (0.71%) with identical film thickness of 8.0 μm. However, this efficiency of 0.93% was still low, which was ascribed to agglomeration of Ag nanoparticles and a wide particle size distribution of 20-100 nm. Agarwala et al. also prepared Ag nanoparticles onto TiO$_2$ nanotubes by using a photo reduction method, to scatter light and generate surface plasmon effect [20]. The DSSC efficiency was enhanced by 22% after being modified with Ag nanoparticles. However, the particle size was larger than 70 nm and the nanoparticles were mixed with some rod like structures, resulting in lower dye absorption and less scattering effect. On the other hand, Lai et al. developed a simple method using pulse current (PC) deposition to deposit uniformly distributed spherical Ag nanoparticles (2-10 nm) on the surface of prepared TiO$_2$ nanotube arrays. The generated photocurrent was found to be 36% higher than that of randomly distributed Ag particles prepared by photocatalytic reduction [21]. PC electrodeposition is considered as a facile method for controlling the electrocrystallization process and hence depositing materials with unique structures and properties. By tuning current-on time ($t_{on}$) and current-off time ($t_{off}$), instantaneous current density applied by pulse control can lead to ultrafine-grained structures and homogenous surface appearance of the deposit. Therefore, PC electrodeposition can form evenly distributed and uniformly nano-sized Ag. On the other hand, direct current (DC) electrodeposition results in inhomogeneous Ag with rough surface; hence, it is not a suitable method for producing Ag nanoparticles [22].

As summarized above, size of Ag nanoparticles synthesized via photo reduction deposition method is too large and uncontrollable; as a result, these commonly-used methods are not suitable choices for enhancing plasmon effect in DSSCs. However, the enhancement of plasmon effect can be easily achieved by using pulse current deposition method, which can produce evenly distributed nanoparticles with controllable size distribution by tuning pulse current. However, this method has never been used for depositing metallic particles for plasmon effect in DSSCs. The present work is the first effort to employ pulse current deposition method for enhancing plasmon effect in DSSCs. TiO$_2$ nanotube arrays are prepared via anodization and followed by deposition of uniformly distributed spherical Ag nanoparticles via pulse current deposition. This process is easy to implement and can effectively suppress the agglomeration of Ag particles by taking advantage of high nucleation rate of Ag under the PC condition. DSSCs based on Ag-modified TiO$_2$ nanotube arrays show significantly enhanced performance than DSSCs consisting of bare TiO$_2$ nanotube arrays. Efficiency of such DSSCs can also be maximized by tuning pulse deposition time of Ag nanoparticles. Moreover, efficiency of DSSCs can be further improved by treating TiO$_2$ nanotubes with high concentration TiCl$_4$ prior to Ag deposition.
3.2 Experimental

Ti foils (0.25 mm thickness, 99.5 wt% purity, Alfa Aesar) were degreased by sonicating in acetone, deionized (DI) water, and ethanol for 15 min, respectively, then rinsed with ethanol and dried in a nitrogen stream. Electrochemical anodization of the Ti foils was carried out in a two-electrode cell, with a platinum mesh as the counter electrode at room temperature. The electrolyte for anodization was prepared with anhydrous ethylene glycol (EG) with NH₄F (0.3 wt%) and H₂O (5 vol%). The voltage was supplied by a DC power supply with digital display (Model 1623A, PK Precision). After anodization, the samples were rinsed in deionized water (DI water) and dried in air, followed by heat treatment at 450 °C in air for 3 h to produce anatase phase. Optional TiCl₄ treatment was performed on TiO₂ nanotube arrays by soaking annealed nanotube in 100 mL of 0.2 M TiCl₄ aqueous solution at 70 °C for 30 min and then annealing at 450 °C in air for 30 min.

Pulse-current electrodeposition of Ag nanoparticles was carried out by immersing the as-prepared TiO₂ nanotube in an aqueous electrolyte composed of 10 mM AgNO₃ and 100 mM NaNO₃ at room temperature. The TiO₂ nanotube array and a platinum mesh were used as the working and counter electrodes, respectively. A pulse-current of 10 mA cm⁻² with different alternating on-times and off-times (0.5 s/1.5 s, 1 s/3 s, 2 s/6 s) for 100 cycles were applied. Figure 3.1 shows a scheme showing the pulse current process for electrochemical deposition of Ag nanoparticles with a rectangular pulse shape composed of an alternating on-time and off-time for 100 deposition cycles. The Ag-deposited samples were then rinsed with DI water and dried in vacuum at 50 °C overnight.

Figure 3.1 Schematic showing the pulse current process for electrochemical deposition of Ag with a rectangular pulse shape composed of alternating on-times and off-times for 100 deposition cycles.
To fabricate DSSCs, TiO$_2$ nanotube arrays with or without Ag modifications were soaked in anhydrous ethanol containing 0.2 mM N719 dye (Ru[LL’-(NCS)$_2$], L=2,2’-bipyridyl-4,4’-dicarboxylic acid, L’=2,2’-bipyridyl-4,4’-ditetra-butyl-ammonium carboxylate, Solaronix Co.) and sensitized for 24 h at room temperature. Afterwards, these dye-sensitized TiO$_2$ nanotube arrays with an active area of approximately 0.25 cm$^2$ were rinsed with acetonitrile in order to remove physisorbed N719 dye molecules. Platinized counter electrode was fabricated by drop casting 0.5 mM H$_2$PtCl$_6$/isopropanol solution on FTO glass substrate that had a hole for electrolyte injection later on, followed by heating at 400 °C in air for 20 min. The dye-sensitized TiO$_2$ nanotube arrays with or without Ag modifications were sandwiched together with Pt-coated FTO glass by using a 100 μm thick hot-melt sealing film as the spacer (Meltonix 1170-100, Solaronix Co.). DSSCs were sealed by applying heat and pressure with a hot press at 110 °C. A I$^*/$I$^3^-$ based electrolyte, which contained 0.10 M GTC in a mixture of acetonitrile and valeronitrile (85:15 v/v) (No. ES-0004, IoLiTec Inc., Germany) was injected through the hole on the Pt-coated FTO into DSSC.

Crystal structure of TiO$_2$ nanotube arrays was determined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu Kα radiation operated at 30 kV and 15 mA with a scan rate of 2°/min. A FEI Quanta 3D FEG scanning electron microscope (SEM) at an accelerating voltage of 5-20 kV was used to characterize morphology of TiO$_2$ nanotube arrays. Chemical composition of these nanotubes was studied by energy dispersive X-ray spectroscopy (EDX) on a Hitachi S-3600N SEM. Surface composition of TiO$_2$ nanotube arrays were analyzed via an X-ray photoelectron spectroscopy (XPS) on the AXIS-165 XPS (Kratos Analytical Ltd.) with an AXIS 165 spectrometer from Kratos Analytical LTD by using a twin-anode Al Kα (1486.6 eV) X-ray source. Transmission electron microscopy (TEM, JEM-1011, JEOL LTD.) with an accelerating voltage of 80 kV was used to characterize the morphology of Ag-modified TiO$_2$ nanotubes. The current–voltage (J–V) characteristics of DSSCs were recorded using a Keithley 2400 source meter. A solar light simulator (Model: 67005, Oriel) was used to simulate sunlight under one sun AM 1.5 G (100 mW/cm$^2$) illumination provided by a 150 W Xenon arc lamp (Model: 6256, Oriel) and calibrated using a Si solar reference cell (Model: 91150V, Oriel). Backside illumination mode was used, since the photo-anode consists of TiO$_2$ nanotube array on Ti substrate which was not transparent to light.

### 3.3 Results and Discussion

XRD analysis is utilized to examine the crystallinity of TiO$_2$ nanotubes. Figure 3.2 shows XRD patterns of bare TiO$_2$ nanotube arrays annealed at 450 °C in air for 2 h. The peaks at 20 = 25.4° and 20 = 48.0° correspond to (101) and (200) in TiO$_2$ anatase phase, and all of the other dominant peaks correspond to the reflection of Ti foil substrate. This result suggests that the as-prepared anodic TiO$_2$ nanotubes convert to anatase phase after heated at high temperature, which can be used as photo-anodes in DSSCs.
Figure 3.2 X-ray diffraction pattern of bare TiO$_2$ nanotube array annealed at 450 °C in air for 2 h.

Figure 3.3 shows SEM images and EDX spectrum of TiO$_2$ nanotube arrays modified with Ag nanoparticles (NPs) via pulse deposition time of 1 s/3 s. The cross-section SEM image in Figure 3.3, a shows that the structure of TiO$_2$ nanotube arrays preserves well after the PC deposition. Thickness of the TiO$_2$ nanotube arrays is estimated to be ~6.1 μm, and the average diameter of these nanotubes is ~120 nm. It is important to note that Ag NPs are uniformly distributed and anchored along the surface of the tube structure. It is observed from Figure 3.3, b that most of Ag nanoparticles have a size in range of 10-40 nm. The top-view SEM image in Figure 3.3, c shows Ag NPs deposited on the open entrances of TiO$_2$ nanotube arrays. It can be seen Ag NPs deposited on the top open entrances of TiO$_2$ nanotubes (showing a particle size up to 60 nm) are larger than Ag NPs on the tube walls. Meanwhile, Ag NPs deposited on the top open entrances of TiO$_2$ nanotubes are denser (without any obvious agglomeration) than Ag NPs on the tube walls. Such a larger particle size and denser distribution of Ag NPs on the top of TiO$_2$ nanotubes are possibly due to the top open entrances of TiO$_2$ nanotubes being more exposed to electrochemical deposition. Figure 3.3, d displays the EDX spectrum of these TiO$_2$ nanotubes arrays modified with Ag NPs. A small amount of Ag element is detected, as evidenced by its weak but discernible peaks in the EDX spectrum.

To further study details about Ag NPs deposited on TiO$_2$ nanotube arrays via pulse deposition time of 1 s/3 s, its TEM image is obtained as shown in Figure 3.4. The average diameter of Ag NPs shown in the TEM image is approximately 20 nm, which is consistent with the particle size shown in the SEM images earlier. This homogeneous dispersion of Ag NPs on TiO$_2$ nanotube arrays is desirable for efficient light harvesting, yielding high plasmon-induced activity for electron transportation.
Figure 3.3, a, b) Cross-sectional, c) top-view SEM images, and d) EDX spectrum of TiO$_2$ nanotube arrays modified with Ag nanoparticles via pulse deposition time of 1 s/3 s.

Figure 3.4 TEM image of a TiO$_2$ nanotube modified with Ag nanoparticles via pulse deposition time of 1 s/3 s.
To further confirm the formation of Ag NPs from the pulse deposition, XPS is also employed to study surface composition of Ag modified TiO$_2$ nanotubes arrays. The XPS spectrum taken from TiO$_2$ nanotubes arrays modified with Ag NPs via pulse deposition time of 1 s/3 s exhibits the Ag3d peak in Figure 3.5, a. In Figure 3.5, b, the peaks observed at 368.1 eV and 374.2 eV are ascribed to metallic Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ respectively, confirming metallic Ag existent on the surface of TiO$_2$ nanotube arrays. These findings reveal that Ag-modified TiO$_2$ nanotube arrays are successfully achieved by electrochemical deposition of Ag in AgNO$_3$-containing solution.

Figure 3.5, a) XPS spectra and b) Ag3d XPS peak of TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 1 s/3 s.
Performances of DSSCs based on bare and Ag-modified TiO\textsubscript{2} nanotubes electrodes are examined under 1 sun AM 1.5 simulated sunlight. Figure 3.6 presents $J$-$V$ curves of DSSCs based on 6.1-\textmu m-long TiO\textsubscript{2} nanotubes arrays modified with Ag NPs using different pulse deposition times (0.5 s/1.5 s, 1 s/3 s, and 2 s/6 s). Photovoltaic characteristics of these DSSCs, such as short-circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and efficiency ($\eta$) are summarized in Table 3.1. It is evident that the short circuit currents of all Ag-modified TiO\textsubscript{2} nanotubes based DSSCs (0.5 s/1.5 s, 1 s/3 s, and 2 s/6 s) are larger than that of bare TiO\textsubscript{2} nanotubes based DSSCs, since the Ag NPs on sidewalls enhance absorption and charge separation, while there are no substantial differences in the photovoltages. DSSC based on Ag@TiO\textsubscript{2} (Ag-modified TiO\textsubscript{2} nanotubes) synthesized via the shorter pulse deposition time of 0.5 s/1.5 s, delivers an energy conversion efficiency of 1.28%, which is just slightly higher than the efficiency (1.20%) of DSSC based on bare nanotube, possibly because the amount of Ag NPs loading is too low to show any plasmon effect. The DSSC based on Ag@TiO\textsubscript{2} 1 s/3 s (Ag-modified TiO\textsubscript{2} via pulse deposition time of 1 s/3 s) delivers the highest energy conversion efficiency (1.68%) exhibiting $V_{oc}$ of 0.79 V, $J_{sc}$ of 4.37 mA/cm\textsuperscript{2}, and FF of 0.49, which represents a 40.0% increase in cell efficiency compared to DSSC consisting of bare TiO\textsubscript{2} nanotube array (1.20%). In theory, the maximum voltage ($V_{\text{max}}$) generated by DSSC is the difference between the (quasi-) Fermi level of the TiO\textsubscript{2} and the redox potential of the electrolyte, about 0.7 V under solar illumination conditions. Since the loaded Ag nanoparticles do not affect the Fermi level of TiO\textsubscript{2} and redox potential of electrolyte much, Ag deposition on TiO\textsubscript{2} would not improve $V_{oc}$. The improved $J_{sc}$ is resulted from higher plasmon resonance effect caused by coverage of Ag NPs on the TiO\textsubscript{2} nanotube surface, which increases the number of photoelectrons generated and improves the effective separation of electron-hole pairs. Therefore, the loaded Ag nanoparticles can improve short-circuit current rather than the open-circuit voltage in these DSSCs. Interestingly, the efficiency of DSSC based on Ag-modified TiO\textsubscript{2} nanotube array decreases again, as the pulse deposition time used for depositing Ag nanoparticles is increased to 2 s/6 s, due to agglomeration of Ag NPs and formation of some particles with larger size resulted from longer pulse deposition time as shown in Figure 3.7. Such agglomeration of Ag NPs on TiO\textsubscript{2} nanotubes result in less surface area for dye loading as well as ineffective light absorption and charge separation.

Table 3.1 Photovoltaic characteristics of dye-sensitized solar cells shown in Figure 3.6

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm\textsuperscript{2})</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag@TiO\textsubscript{2} 0.5 s/1.5 s</td>
<td>2.56</td>
<td>0.77</td>
<td>0.65</td>
<td>1.28</td>
<td>0.07%</td>
</tr>
<tr>
<td>Ag@TiO\textsubscript{2} 1 s/3 s</td>
<td>4.37</td>
<td>0.79</td>
<td>0.49</td>
<td>1.68</td>
<td>0.09%</td>
</tr>
<tr>
<td>Ag@TiO\textsubscript{2} 2 s/6 s</td>
<td>3.71</td>
<td>0.82</td>
<td>0.47</td>
<td>1.42</td>
<td>0.02%</td>
</tr>
<tr>
<td>Bare-TiO\textsubscript{2}</td>
<td>2.27</td>
<td>0.78</td>
<td>0.68</td>
<td>1.20</td>
<td>0.05%</td>
</tr>
</tbody>
</table>
Figure 3.6 $J-V$ characteristics of DSSCs based on different TiO$_2$ nanotube arrays. (Ag@TiO$_2$ 0.5 s/1.5 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 0.5 s/1.5 s; Ag@TiO$_2$ 1 s/3 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 1 s/3 s; Ag@TiO$_2$ 2 s/6 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 2 s/6 s; Bare TiO$_2$: unmodified TiO$_2$ nanotubes.)

Figure 3.7 TEM image of a TiO$_2$ nanotube modified with Ag nanoparticles via pulse deposition time of 2 s/6 s.

To further improve energy conversion efficiency of DSSC based on TiO$_2$ nanotubes, treatment of TiO$_2$ nanotubes with high concentration TiCl$_4$ is carried out in this work. It has been reported that TiCl$_4$ treatment can enhance dye absorption on the surface, improve the electron transport properties in nanocrystalline TiO$_2$ films, and increase the charge
After being treated in TiCl$_4$ aqueous solution, TiO$_2$ nanotube arrays are sensitized with N719 dye and then integrated into DSSCs. Figure 3.8 compares the $J$–$V$ characteristics of DSSCs based on TiCl$_4$ treated bare and Ag-modified TiO$_2$ nanotubes as a function of different pulse deposition times (0.5 s/1.5 s, 1 s/3 s, and 2 s/6 s). Detailed photovoltaic performance parameters are presented in Table 3.2. Compared to untreated bare TiO$_2$ nanotubes, the energy conversion efficiency of DSSC based on TiCl$_4$ treated bare TiO$_2$ nanotubes is increased to 2.61%, and such enhancement is mainly originated from the increased short-circuit current density. Likewise, the efficiency of DSSC based on Ag@TiO$_2$-TiCl$_4$ 0.5 s/1.5 s (TiCl$_4$-treated TiO$_2$ nanotubes modified with Ag NPs via pulse deposition time of 0.5 s/1.5 s) increase to 2.56% presenting a 100% enhancement of efficiency compared to DSSC based on Ag@TiO$_2$ 0.5 s/1.5 s (1.28%). The short-circuit current density of DSSC based on Ag@TiO$_2$-TiCl$_4$ 0.5 s/1.5 s shows slight enhancement than that of DSSC based on bare TiO$_2$-TiCl$_4$ and the enhancement is not significant due to small amount of Ag loading resulted from short pulse deposition time of Ag. In particular, the effect of Ag modification to enhance energy conversion efficiency is more significant for DSSC based on Ag@TiO$_2$-TiCl$_4$ 1 s/3 s (TiCl$_4$ treated TiO$_2$ modified with Ag NPs via pulse deposition time of 1 s/3 s), which delivers the highest energy conversion efficiency (3.82%) with $V_{oc}$ of 0.75 V, $J_{sc}$ of 9.27 mA/cm$^2$ and FF of 0.55 (Table 3.2), which represents a 46.4% increase in cell efficiency compared to that of DSSC based on bare TiO$_2$-TiCl$_4$ (TiCl$_4$-treated TiO$_2$ nanotubes) nanotube array (2.61%). These results confirm that Ag NPs loaded on TiO$_2$ nanotube surface significantly increase the performance of DSSCs.

Figure 3.8 $J$–$V$ characteristics of DSSCs based on different TiCl$_4$-treated TiO$_2$ nanotube arrays. (Ag@TiO$_2$-TiCl$_4$ 0.5 s/1.5 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 0.5 s/1.5 s; Ag@TiO$_2$-TiCl$_4$ 1 s/3 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 1 s/3 s; Ag@TiO$_2$-TiCl$_4$ 2 s/6 s: TiO$_2$ nanotubes modified with Ag nanoparticles via pulse deposition time of 2 s/6 s; Bare TiO$_2$-TiCl$_4$: unmodified TiO$_2$ nanotubes.)
Table 3.2 Photovoltaic characteristics of dye-sensitized solar cells shown in Figure 3.8

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag@TiO$_2$-TiCl$_4$ 0.5 s/1.5 s</td>
<td>5.41</td>
<td>0.78</td>
<td>0.61</td>
<td>2.56</td>
<td>0.08%</td>
</tr>
<tr>
<td>Ag@TiO$_2$-TiCl$_4$ 1 s/3 s</td>
<td>9.27</td>
<td>0.75</td>
<td>0.55</td>
<td>3.82</td>
<td>0.09%</td>
</tr>
<tr>
<td>Ag@TiO$_2$-TiCl$_4$ 2 s/6 s</td>
<td>3.66</td>
<td>0.63</td>
<td>0.67</td>
<td>1.55</td>
<td>0.05%</td>
</tr>
<tr>
<td>Bare TiO$_2$-TiCl$_4$</td>
<td>5.39</td>
<td>0.75</td>
<td>0.64</td>
<td>2.61</td>
<td>0.10%</td>
</tr>
</tbody>
</table>

It is, however, noteworthy that DSSC based on Ag@TiO$_2$-TiCl$_4$ 2 s/6 s shows a large decrease in efficiency compared to DSSC based on TiCl$_4$ treated bare TiO$_2$ nanotubes. DSSC based on Ag@TiO$_2$-TiCl$_4$ 2 s/6 s (TiCl$_4$ treated TiO$_2$ nanotubes modified with Ag NPs via pulse deposition time of 2 s/6 s) delivers a low energy conversion efficiency of 1.55% with $V_{oc}$ of 0.63 V, $J_{sc}$ of 3.66 mA/cm$^2$, FF of 0.67, as summarized in Table 3.2. It can be observed that the drastic efficiency drop of DSSCs based on Ag@TiO$_2$-TiCl$_4$ 2 s/6 is mainly originated from the decreased short-circuit current. The decrease of short-circuit current may be attributed to the following reasons. Long pulse deposition time (2 s/6 s) may cause agglomeration of Ag NPs on the TiO$_2$ nanotubes surface and this effect is more distinct for TiO$_2$ nanotubes treated with TiCl$_4$. TiCl$_4$ treatment yields very tiny TiO$_2$ nanoparticles on the surface of TiO$_2$ nanotubes (Figure 3.9, a-b), some of which may partially plug the top entrances of TiO$_2$ nanotubes (Figure 3.9, c), resulting in more sites for Ag deposition. When the deposition time is very long and since the tops of TiO$_2$ nanotubes are partially plugged and are much more exposed to electrochemical deposition than tube walls, large agglomerates of Ag NPs would form on the top of TiO$_2$ nanotubes without much deposition of Ag NPs along tube walls (Figure 3.9, d-f), leading to reduced plasmon effect and decreased surface area for dye loading. In the case of surface plasmon, metallic nanoparticles must be smaller than the wavelength of the exciting light in order for electrons to oscillate together in response to the electric field of the excitation light. Agglomerates of Ag NPs as well as those with larger particle size (more than 200nm) are much more difficult to be excited by radical light. Another issue is that Ag agglomerates or larger Ag particles have more severe plasmon decay. The intensity of electrons transferred to TiO$_2$ depends on the distance that plasmon travel from radical light impact position to TiO$_2$. Vesseur [26] has pointed out that plasmon excited by radical light, which are emitted radially from the impact position, are lost through absorption unless they are converted to a target. Therefore, plasmon excited on the surface of TiO$_2$ decays when transferred to the bottom of nanotube. Hence, plasmon decay is more severe in the case of Ag@TiO$_2$-TiCl$_4$ 2 s/6, which has large Ag agglomerates or particles on the tops of TiO$_2$ nanotubes and few Ag nanoparticles along the walls.
Figure 3.9, a, b, c) Cross-sectional and top-view SEM images of TiCl$_4$ treated bare TiO$_2$ nanotube arrays; d, e, f) Cross-sectional and top-view of SEM images of TiCl$_4$-treated TiO$_2$ nanotube arrays modified with Ag nanoparticles via pulse deposition time of 2 s/6 s.

If we compare Figure 3.6 and 3.8, DSSCs based on TiCl$_4$ treated TiO$_2$ nanotubes show higher energy conversion efficiency than DSSCs based on untreated TiO$_2$ nanotube, due to larger surface area of TiO$_2$ nanotube resulted from TiCl$_4$ treatment. It can also be observed that the effect of Ag NPs to improve energy conversion efficiency and short-circuit current is more distinct for DSSCs based on Ag@TiO$_2$-TiCl$_4$ 1 s/3 s than DSSCs consisting of TiO$_2$ nanotubes modified with Ag via other shorter or longer pulse deposition time, because this pulse deposition time (1 s/3 s) yields evenly-distributed and uniformly-sized Ag nanoparticles, leading to enhanced surface plasmon resonance and subsequent improved optical absorption. The particle size of Ag NPs synthesized via commonly-used methods such as photo reduction deposition methods is too large and uncontrollable, while pulse current deposition can provide uniformly distributed nanoparticles which are necessary for plasmon effect in DSSC.

3.4 Conclusion

In summary, TiO$_2$ nanotube arrays are synthesized by anodizing Ti foils in EG electrolytes with a small amount of NH$_4$F and H$_2$O under alternating-voltage conditions, and subsequent heat treatment transforms them to anatase phase for modification with Ag nanoparticles via electrochemical deposition, for enhanced efficiencies of DSSCs. Ag nanoparticles with a size distribution up to 10-40 nm are formed on the side walls of TiO$_2$ nanotubes. Metallic Ag formation is confirmed by EDX and XPS analyses. In addition,
the loading amount of Ag nanoparticle can be easily optimized by adjusting pulse deposition time. Most of DSSCs based on Ag-modified TiO$_2$ nanotube arrays show significantly higher energy conversion efficiencies than DSSC consisting of bare nanotube array of same length. Such enhancement is ascribed to the surface plasmon resonance induced by uniformly deposited Ag NPs. Increasing the Ag deposition content is able to further improve the plasmon effect, but superfluous Ag content yields not as good as or worse photovoltaic performance, and DSSC based on TiO$_2$ nanotubes modified with Ag via pulse deposition time of 1 s/3 s display the highest energy conversion efficiency. TiCl$_4$ treatment for TiO$_2$ nanotubes can further enhance energy conversion efficiency of DSSCs by increasing surface area of TiO$_2$ nanotubes for more dye loading. Our results confirm that modifying anodic TiO$_2$ nanotube arrays with noble metal nanoparticles is an effective approach for maximizing efficiency of DSSCs and will advance the DSSC technology.

3.5 References


CHAPTER 4 ELECTROPHORETIC DEPOSITION OF REDUCED GRAPHENE OXIDE NANOSHEETS ON TiO$_2$ NANOTUBE ARRAYS FOR DYE-SENSITIZED SOLAR CELLS

4.1 Introduction

TiO$_2$ nanotubes can be commonly synthesized using anodization and morphology of these TiO$_2$ nanotubes can be easily tailored by varying anodization parameters such as voltage, time, and electrolyte composition. However, DSSC based on TiO$_2$ nanotube array exhibits limited energy conversion efficiency owning to the recombination of photogenerated electron-hole (e-h) pairs between TiO$_2$ and dye molecular/electrolyte and its low surface area for dye loading [1-4]. Therefore, many research efforts have been focused on the following two aspects: increasing the surface area of TiO$_2$ nanotube electrodes and suppressing the recombination of e-h pairs. Our group has recently fabricated bamboo-type TiO$_2$ (BT-TiO$_2$) nanotubes arrays under alternating-voltage (AV) condition and evaluated the effect of bamboo ridges on efficiency of DSSCs [5]. It is found that bamboo ridges provide extra surface area and greatly facilitate dye absorption on their surface, which makes BT-TiO$_2$ nanotube array a better photo-anode than smooth-walled nanotube array in DSSC.

There are other approaches that have been applied to improve efficient electron transport to counter electrode in DSSCs, such as surface modification with noble metal [6-8], using quantum dots [9,10], developing new sensitizers [11-13], and designing new morphology of photo-anodes [5,14,15]. The purposes of these methods are either to increase the surface area for dye loading or to enhance light harvesting ability and/or suppress recombination of photogenerated e-h pairs. Graphene has recently drawn considerable interest for applications in photovoltaic devices owning to its very light weight, large surface area, and extremely high electron mobility (\(~15 \text{,000 cm}^2 \text{ V}^{-1} \text{ s}^{-1}\)) at room temperature [16-18]. It has been demonstrated that the incorporation of graphene into TiO$_2$ nanoparticle film greatly facilitates electron transport. However, there are few reports about graphene/TiO$_2$ composites, due to the challenge of combining two-dimensional (2D) graphene with one-dimensional (1D) TiO$_2$ nanotubes. Song et al. developed a simple dip-and-dry method to deposit graphene oxide on the surface of TiO$_2$ nanotube arrays in order to improve the photoelectrochemical response of TiO$_2$ nanotube arrays in the visible light region [19]. Liu et al. deposited reduced graphene oxide (RGO) on the surface of TiO$_2$ nanotube arrays by using a cyclic voltammetric method [20]; the incorporation of RGO onto TiO$_2$ improved the light absorption and facilitated separation of e-h on TiO$_2$ nanotubes. Yun et al. presented a method involving combined electrophoretic deposition and anodization to produce RGO-nanotube film, which allowed simultaneous anodic growth of TiO$_2$ nanotubes and electrophoretic deposition of RGO, to improve the photocurrent and photoelectrochemical properties of TiO$_2$ [21]. However, to the best of our knowledge, there are no reports on the incorporation of graphene onto TiO$_2$ nanotube arrays for application in DSSCs.
In this paper, smooth-walled and bamboo-type TiO$_2$ nanotubes arrays are first synthesized via anodization and then modified with RGO via electrophoretic deposition (EPD). In the process of EPD, negatively charged RGO sheets are well dispersed in distilled water and migrate toward the positively charged TiO$_2$ nanotube arrays under an applied electric field. The as-prepared RGO on TiO$_2$ nanotube arrays is very uniform and can be obtained with controllable thickness. This work is the first effort to employ EPD method to incorporate RGO onto TiO$_2$ nanotube arrays for the enhanced energy conversion efficiency of DSSCs. The enhancement of DSSC efficiency can be optimized by controlling amount of RGO loading via changing EPD time. Moreover, BT-TiO$_2$ nanotube arrays with higher surface area synthesized under AV condition is a favorable candidate for RGO deposition. DSSC consisting of RGO modified BT-TiO$_2$ nanotube array show further increased energy conversion efficiencies due to higher surface area from BT-TiO$_2$ nanotubes and improved charge transfer from RGO.

4.2 Experimental

Ti foils (0.25 mm thick, 99.5 wt% purity, Alfa Aesar) were degreased by sonicating in acetone, deionized (DI) water, and ethanol for 15 min, respectively, then rinsed with ethanol and dried in a nitrogen stream. Electrochemical anodization of the Ti foils was carried out in a two-electrode cell, with a platinum foil as the counter electrode at room temperature. The electrolyte for anodization was prepared by mixing anhydrous ethylene glycol (EG) with NH$_4$F (0.3 wt%) and H$_2$O (5 vol% for smooth-walled TiO$_2$ nanotube arrays; 2 vol% for bamboo-type TiO$_2$ nanotube arrays). Electric field was applied by using a DC power supply with digital display (Model 1623A, PK Precision). Smooth-walled TiO$_2$ nanotube array was synthesized via anodization of Ti under constant-voltage condition (CV) at 60 V for 1 h. To prepare bamboo-type TiO$_2$ nanotube arrays, the anodization process consists of 80 cycles of alternating high and low-voltage steps, as shown in Figure 4.1 [5].

![Figure 4.1 Schematic showing the anodization sequence for the formation of bamboo-type TiO$_2$ nanotube arrays.](image)

The voltage is first increased from zero to 60 V and being kept at 60 V for 1 min, then drops to 10 V and is also held at 10 V for 1 min. Each voltage alternating from 60 V to 10 V
is regarded as one cycle. After anodization, the samples were rinsed in DI water and dried in air, followed by heat treatment at 450 °C in air for 3 h to produce anatase phase. TiCl₄ treatment was performed on TiO₂ nanotube arrays by soaking annealed nanotubes in 100 mL of 40 mM TiCl₄ aqueous solution at 70 °C for 30 min and then annealed again at 450 °C in air for 30 min.

Single layer graphene oxide (GO) (ACS Material, LLC) was milled into fine powder before being subject to chemical reduction. In the chemical reduction process to reduce GO to RGO, 100 mg of GO powder was dispersed in 200 ml of DI water under the ultrasonic treatment for 15 min. A concentration of 0.5 mg ml⁻¹ was selected. 1 ml hydrazine hydrate solution (Aldrich, 80%) was added to the GO solution and the suspension was heated to 85 °C for 6 h under vigorous stirring [21]. Subsequently, the resultant RGO was retrieved from the suspension by a centrifuge (4000 rpm, 3 times) and washed thoroughly with DI water.

Purified RGO was dispersed in DI water, and then sonicated for 1 hr to produce a uniform suspension. The as-prepared TiO₂ nanotube array was used as the substrate. A platinum foil used as the counter electrode was kept parallel to TiO₂ electrode at 1 cm in the RGO suspension. The electrophoretic deposition was carried out by applying a constant DC voltage of 60 V for 15 s, 30 s, 1 min, and 5 min with the as-deposited RGO-TiO₂ nanotube arrays named as RGO-TiO₂ 15 s, RGO-TiO₂ 30 s, RGO-TiO₂ 1 min, and RGO-TiO₂ 5 min. The RGO-deposited samples were then rinsed with DI water and dried at 50 °C overnight.

To fabricate DSSCs, TiO₂ nanotube arrays with or without RGO modifications were soaked in anhydrous ethanol containing 0.2 mM N719 dye (Ru[LL’-(NCS)₂], L=2,2’-bipyridyl-4,4’-dicarboxylic acid, L’=2,2’-bipyridyl-4,4’-ditetramethyl-ammonium carboxylate, Solaronix Co.) and sensitized for 24 h at room temperature. Afterwards, these dye-sensitized TiO₂ nanotube arrays with an active area of approximately 0.25 cm² were rinsed with acetonitrile in order to remove physisorbed N719 dye molecules. Platinized counter electrode was fabricated by drop casting 0.5 mM H₂PtCl₆/isopropanol solution on FTO glass substrate that had a hole for electrolyte injection later on, followed by heating at 400 °C in air for 20 min. The dye-sensitized TiO₂ nanotube arrays with or without RGO modifications were sandwiched together with Pt-coated FTO glass by using a 100 μm thick hot-melt sealing film as the spacer (Meltonix 1170-100, Solaronix Co.). DSSCs were sealed by applying heat and pressure with a hot press at 110 °C. A I/I₃⁻ based electrolyte, which contained 0.10 M GTC in a mixture of acetonitrile and valeronitrile (85:15 v/v) (No. ES-0004, IoLiTec Inc., Germany) was injected through the hole on the Pt-coated FTO into DSSC.

Crystal structure of TiO₂ nanotube arrays was determined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu Kα radiation operated at 30 kV and 15 mA with a scan rate of 2° min⁻¹. A FEI Quanta 3D FEG scanning electron microscope (SEM) at an accelerating voltage of 5 kV was used to characterize morphology of TiO₂ nanotube arrays with or without RGO modification. Surface composition of TiO₂ nanotube arrays with or without RGO modification was analyzed via an X-ray photoelectron spectroscopy (XPS) on Hemispherical Energy Analyzer (PHOIBOS 150) and FOCUS 500 X-Ray Monochromator with Al Kα X-ray source. The current–voltage (J–V) characteristics of
DSSCs were recorded using a Keithley 2400 source meter. A solar light simulator (Model: 67005, Oriel) was used to simulate sunlight under one sun AM 1.5 G (100 mW cm\(^{-2}\)) illumination provided by a 150 W Xenon arc lamp (Model: 6256, Oriel) and calibrated using a Si solar reference cell (Model: 91150V, Oriel). Backside illumination mode was used, since the photo-anode (TiO\(_2\) nanotube array on Ti substrate) was not transparent to solar light. The electrochemical impedance spectroscopy (EIS) measurements were performed using a VersaSTAT MC electrochemical analyzer (Princeton Applied Research) with the frequency range from 10 mHz to 100 kHz by applying an AC amplitude of 10 mV. The impedance measurements were carried out under forward bias of -0.70 V in the dark.

### 4.3 Results and Discussion

The as-prepared anodic TiO\(_2\) nanotubes are heated at high temperature to convert to anatase phase. Figure 4.2 shows XRD pattern of bare TiO\(_2\) nanotube arrays annealed at 450 °C in air for 3 h. Typical diffraction peaks at \(2\theta = 25.4^\circ\) and \(2\theta = 48.0^\circ\) correspond to (101) and (200) in TiO\(_2\) anatase phase (PDF #21-1272, JCPDS). Diffraction peaks of Ti substrate are also found in this XRD pattern, with (002) peak at \(2\theta = 38.4^\circ\) and (101) peak at \(2\theta = 40.1^\circ\). These results indicate that heat treatment converts amorphous as-prepared TiO\(_2\) nanotubes to a crystalline phase (anatase) that are subsequently used for RGO modification and as photo-anodes in DSSCs. The XRD pattern of RGO-modified TiO\(_2\) nanotube arrays is identical with that of bare TiO\(_2\) nanotube arrays shown in Figure 4.2, indicating that RGO modification would not affect crystalline phase of TiO\(_2\).

![X-ray diffraction pattern](image)

Figure 4.2 X-ray diffraction pattern of smooth-walled TiO\(_2\) nanotube array annealed at 450 °C in air for 3 h, which indicate that as-prepared sample is indexed as anatase.

Morphologies of unmodified and RGO-modified TiO\(_2\) nanotube arrays are investigated via SEM. CV anodization leads to formation of ordered TiO\(_2\) nanotubes with smooth walls, as shown in Figure 4.3, a and b. As can be seen from Figure 4.3, a, the highly
ordered nanotube array is perpendicular to the Ti substrate, with a thickness of ~6.8 μm. The tubes are hollow inside with an open entrance on the top, showing an average pore diameter ~150 nm. After EPD is performed in well dispersed RGO suspension, RGO nanosheets are uniformly deposited on the top of TiO₂ nanotube arrays. Figure 4.3, c and d present top-view SEM images of TiO₂ nanotube arrays modified with RGO via EPD time of 1 min and 5 min, respectively. It should be noted that the thickness of RGO coverage is dependent on EPD time. When 1 min is used for EPD of RGO sheets, an ultra-thin and translucent layer of RGO nanosheet covers the top of TiO₂ nanotubes uniformly at large scale (Figure 4.3, c). While for EPD time of 5 min, the as-deposited RGO sheets are thicker and top entrances of TiO₂ nanotubes are less discernible as they are covered by thicker RGO sheets (Figure 4.3, d). These results suggest that thickness of RGO nanosheets on TiO₂ nanotubes can be manipulated by optimizing EPD time. It is also important to note that deposited RGO nanosheets are uniformly covered and highly-ordered stacked on top of TiO₂ nanotubes which makes it an ideal candidate for photovoltaic application.

Figure 4.3, a) Cross-sectional and b) top-view SEM images of smooth-walled TiO₂ nanotube arrays; Top-view SEM images of smooth-walled TiO₂ nanotube arrays modified with RGO via EDP time of c) 1 min and d) 5 min.
XPS was employed to study the chemical states of the as-prepared samples. The obtained data were all calibrated by using contaminant carbon at binding energy of 284.6 eV [22-23]. Figure 4.4, a and b show the C 1s and Ti 2p XPS spectra of the as-prepared TiO$_2$ nanotube arrays, respectively. In Figure 4.4, a, the C 1s XPS spectra of unmodified and RGO-modified TiO$_2$ nanotubes clearly shows the presence of C-C group (284.6 eV), C-O-R group (285.5 eV), and O=C-OH group (288.8 eV) [24]. The C-C group at 284.6 eV can be assigned either to carbon contamination adsorbed from the ambient atmosphere or to the C-C bond (sp$^2$) of graphene [23]. After EPD of RGO, the peak area of C-C group in RGO-modified TiO$_2$ nanotube array shows a drastic increase, indicating the effective deposition of RGO nanosheets. In addition, it can be seen the peak intensity of oxygen-containing groups C-O-R, and O=C-OH increase considerably after EPD. These results indicate that the residue of epoxide and hydroxyl function groups originate from GO surface which are not completely reduced by hydrazine hydrate solution, and thus provide strong evidence for deposition of RGO on TiO$_2$ nanotubes. To further confirm the deposition of RGO nanosheets onto TiO$_2$ nanotubes, the change in peak intensity and binding energy of Ti 2p XPS peaks after RGO-modification is evaluated as displayed in Figure 4.4, b. The two peaks located at binding energies of 458.5 and 464.2 eV are assigned to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$, respectively, with a 5.7 eV peak-to-peak separation [24,25]. Compared to unmodified TiO$_2$ nanotubes, the slight decrease of Ti 2p peak intensity indicates that the surface of TiO$_2$ nanotubes is covered by ultra-thin layers of RGO nanosheets. Furthermore, after deposition of RGO, Ti 2p peaks from the RGO-modified TiO$_2$ nanotubes show a shift to the lower binding energy, suggesting the formation of chemical bonds between RGO and TiO$_2$ nanotubes during EPD. These results reveal that RGO-modified TiO$_2$ nanotube arrays are successfully achieved via EPD in RGO suspensions.

Figure 4.4. a) C 1s and b) Ti 2p XPS spectra of smooth-walled TiO$_2$ nanotubes unmodified and modified with RGO s via EPD for 1h.
The TiCl₄ treatment is carried out in this work in order to enhance the surface area of TiO₂ nanotubes and subsequently increase the short circuit current for DSSC applications [26-28]. After being treated in TiCl₄ aqueous solution, TiO₂ nanotube arrays are sensitized by N719 dye, and are integrated into DSSCs. Figure 4.5 presents J–V curves of DSSCs based on unmodified and RGO-modified TiO₂ nanotube arrays via EPD time of 15 s, 30 s, 1 min, and 5 min; these RGO-modified TiO₂ nanotube arrays are named as RGO-TiO₂ 15 s, RGO-TiO₂ 30 s, RGO-TiO₂ 1 min, and RGO-TiO₂ 5 min. Photovoltaic characteristics of these DSSCs, such as short-circuit current (Jₛ𝑐), open circuit voltage (𝑉ₒ𝑐), fill factor (FF), and efficiency (η) are summarized in Table 4.1. It can be seen that the performances of DSSCs based on RGO-modified TiO₂ nanotube arrays are dependent on the RGO loading amount. Jₛ𝑐 of DSSCs consisting of RGO-modified TiO₂ nanotube arrays increase higher than that of DSSCs based on unmodified TiO₂ nanotube arrays and Jₛ𝑐 increases gradually with the increasing EPD time and reaches a peak value of 8.87 mA cm⁻² at an EPD time of 30 s, followed by Jₛ𝑐 decreasing sharply with a further increase of EPD time later. Among the RGO-modified TiO₂ nanotube arrays with the same length of 6.8 µm, DSSC consisting of TiO₂-RGO 30 s delivers the highest energy conversion efficiency of 4.10%, exhibiting 𝑉ₒ𝑐 of 0.77 V, Jₛ𝑐 of 8.87 mA cm⁻², FF of 0.60 (Table 4.1), which represents a 38.0% increase in cell efficiency compared to that of DSSC based on unmodified TiO₂ nanotube arrays (2.97%). Likewise, the efficiency of DSSC based on TiO₂-RGO 15 s is 3.44%, presenting a 15.8% enhancement of efficiency compared to DSSC based on unmodified TiO₂ nanotube arrays (2.97%). The energy conversion efficiency of DSSC based on TiO₂-RGO 15 s is not as high as the efficiency of DSSC based on TiO₂-RGO 30 s, possibly because RGO nanosheet is too thin or does not fully cover on TiO₂ nanotubes in TiO₂-RGO 15 s. Interestingly, as the EPD time increases to 1 min, the efficiency of DSSC based on TiO₂-RGO 1min (3.32%) is still higher than that of DSSC based on unmodified TiO₂ nanotube arrays (2.97%), but lower than that of DSSC based on TiO₂-RGO 30 s (4.10%). The initial increase of efficiency is attributed to the enhanced electronic conductivity from the increased RGO loading amount [29-31]. After EPD for 30 s, the RGO nanosheets become thicker and result in some ineffective light absorption and charge separation, resulting in a decrease in DSSC efficiency. When the EPD time is increased to 5 min, DSSC consisting of TiO₂-RGO 5 min delivers a low energy conversion efficiency of 2.50% with 𝑉ₒ𝑐 of 0.60 V, Jₛ𝑐 of 5.68 mA cm⁻², FF of 0.73, as summarized in Table 4.1. This efficiency is even slightly lower than that of DSSC based on unmodified TiO₂ nanotubes, possibly due to the overly thick RGO nanosheets deposited on TiO₂ nanotube array. The restacking of thick RGO nanosheets on TiO₂ nanotube array may lead to graphite-like structure through strong π-π stacking interactions, and thus result in slower electron transfer and lower efficiency of DSSC [32]. In addition, the thicker layer of RGO nanosheets on the top entrances of TiO₂ nanotubes may hinder dye-absorption and electrolyte infiltration.
Figure 4.5 $J-V$ characteristics of DSSCs based on unmodified and RGO-modified TiO$_2$ nanotube arrays via EPD time of 15 s, 30 s, 1 min, and 5 min.

Table 4.1 Photovoltaic characteristics of DSSCs based on unmodified and RGO-modified TiO$_2$ nanotube arrays via EPD time of 15 s, 30 s, 1 min, and 5 min shown in Figure 4.5

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>6.24</td>
<td>0.73</td>
<td>0.652</td>
<td>2.97</td>
<td>0.34%</td>
</tr>
<tr>
<td>TiO$_2$-RGO 15 s</td>
<td>7.62</td>
<td>0.67</td>
<td>0.674</td>
<td>3.44</td>
<td>0.11%</td>
</tr>
<tr>
<td>TiO$_2$-RGO 30 s</td>
<td>8.87</td>
<td>0.77</td>
<td>0.600</td>
<td>4.10</td>
<td>0.08%</td>
</tr>
<tr>
<td>TiO$_2$-RGO 1 min</td>
<td>7.49</td>
<td>0.69</td>
<td>0.642</td>
<td>3.32</td>
<td>0.02%</td>
</tr>
<tr>
<td>TiO$_2$-RGO 5 min</td>
<td>5.68</td>
<td>0.60</td>
<td>0.734</td>
<td>2.50</td>
<td>0.11%</td>
</tr>
</tbody>
</table>

Electrochemical impedance spectroscopy (EIS) is performed to investigate the dynamics of interfacial charge transfer process in DSSCs. Figure 4.6 shows the Nyquist plots of DSSCs based on unmodified and RGO-modified TiO$_2$ nanotubes at -0.7 V bias in the dark. In general, the first semicircle at the high frequency regime in the impedance spectrum of a DSSC is attributed to the charge transfer at counter electrode, while the second semicircle corresponds to the electron recombination at the TiO$_2$/dye/electrolyte
interface. It can be seen from Figure 4.6 that charge transfer at the counter electrode in the DSSC based on unmodified TiO₂ nanotubes is similar to that in the DSSC based on RGO-modified TiO₂ nanotubes. It is also observed that EIS of the DSSC based on RGO-modified TiO₂ nanotubes exhibits a larger radius of the second semicircle, indicating that electron recombination resistance between TiO₂ and electrolyte is increased by introducing RGO. Therefore, the interfacial electron recombination during the electron transfer from conduction band of TiO₂ to I₃⁻ in electrolyte in the DSSC would be retarded by RGO modification, which leads to the increased Vₗ and Jₘ in Figure 4.5 and the significantly enhanced over all power conversion efficiency.

![Electrochemical impedance spectra of DSSCs](image)

Figure 4.6 Electrochemical impedance spectra of DSSCs consisting of unmodified smooth-walled TiO₂ nanotubes and smooth-walled TiO₂ nanotubes modified with RGO s via EPD for 30 sec.

To further improve energy conversion efficiency of DSSCs based on TiO₂ nanotubes, bamboo-type TiO₂ nanotubes with higher surface area are synthesized under alternative-voltage condition. AV anodization yields bamboo-type TiO₂ nanotubes with rough walls and longer nanotubes are obtained by reducing water content in electrolyte to 2 vol%. Figure 4.7 displays bamboo-type nanotubes synthesized by anodizing Ti in EG electrolytes containing 0.3 wt% NH₄F and 2 vol% H₂O under AV condition. BT-TiO₂ nanotube array is formed under an AV condition with a sequence of 1 min at 60 V and 1 min at 10 V for 80 cycles. As shown in Figure 4.7, a and b, the resultant bamboo-type nanotube array has a thickness of 16.8 μm, and the spacing between two neighboring bamboo ridges is about 230 nm. The bamboo-type TiO₂ nanotubes are hollow inside with an open entrance on the top, showing an average pore diameter ~150 nm (Figure 4.8). The cross-sectional SEM images of TiCl₄ treated BT-TiO₂ nanotube arrays are shown in Figure 4.7, c and d. It is observed that after being treated in TiCl₄ aqueous solution, BT-TiO₂ nanotube array shows a rough surface and preserves the same tube thickness of 16.8 μm.
Figure 4.7 Cross-sectional SEM images of bamboo-type TiO$_2$ nanotube arrays a, b) before and c, d) after TiCl$_4$ treatment.

Figure 4.8 Top-view SEM images of a) bamboo-type TiO$_2$ nanotube arrays and b) TiCl$_4$-treated bamboo-type TiO$_2$ nanotubes modified with RGO via EDP time of 30 s.
It has been reported by our group earlier that bamboo ridges provide extra surface area to TiO$_2$ nanotubes and thus can increase the energy conversion efficiency of TiO$_2$-nanotube-based DSSC. Figure 4.9 compares the $J-V$ characteristics of DSSCs based on RGO-modified and unmodified BT-TiO$_2$ nanotube arrays via EPD time of 30 s, with corresponding photovoltaic parameters summarized in Table 4.2. DSSC based on BT-TiO$_2$-RGO 30 s (bamboo-type TiO$_2$ nanotubes modified with RGO via EPD time of 30 s) delivers the highest energy conversion efficiency (6.01%) with $V_{oc}$ of 0.77 V, $J_{sc}$ of 12.51 mA cm$^{-2}$ and $FF$ of 0.62 (Table 4.2), which represents a 13.8% increase in cell efficiency compared to that of DSSC based on unmodified BT-TiO$_2$ nanotube array (5.28%). These results confirm that RGO deposited on BT-TiO$_2$ nanotube surface significantly increase the performance of DSSCs. It is also noted that the efficiency enhancement from RGO on BT-TiO$_2$ nanotubes is not as high as that from RGO on smooth walled TiO$_2$ nanotubes by comparing the DSSC parameters in Tables 4.1 and 4.2, possibly due to the following reasons. The much longer BT-TiO$_2$ nanotubes are synthesized using longer anodization time, which causes partial dissolution of the tops of BT nanotubes, resulting in disordered TiO$_2$ nanograss on the top of BT nanotubes (Figure 4.8, a). The less enhancement in DSSC efficiency from RGO-modified BT-TiO$_2$ nanotubes is probably owing to randomly distributed RGO nanosheets deposited on the disordered TiO$_2$ nanoglass on the top of BT nanotubes (Figure 4.8, b). Since longer anodization time is used for growth of TiO$_2$ BT nanotubes than smooth-walled nanotubes, chemical etching of the tube tops is more severe for BT nanotubes, leading to thinning and disintegration of some tube walls and formation of grass-like structure on the tube tops. Such disordered TiO$_2$ nanoglass structure would cause an increased recombination rate and affect light permeation and thus result in less improved electron transfer [33].

![Figure 4.9 $J-V$ characteristics of DSSCs based on unmodified and RGO-modified bamboo-type TiO$_2$ nanotube arrays via EPD time of 30 s.](image-url)
Table 4.2: Photovoltaic characteristics of DSSCs based on unmodified and RGO-modified bamboo-type TiO$_2$ nanotube arrays via EPD time of 30 s as shown in Figure 4.9

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$\sigma$%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT-TiO$_2$</td>
<td>11.37</td>
<td>0.72</td>
<td>0.645</td>
<td>5.28</td>
<td>0.08%</td>
</tr>
<tr>
<td>BT-TiO$_2$-RGO 30 s</td>
<td>12.51</td>
<td>0.77</td>
<td>0.624</td>
<td>6.01</td>
<td>0.20%</td>
</tr>
</tbody>
</table>

4.4 Conclusions

In summary, TiO$_2$ nanotube arrays are synthesized by anodizing Ti foils in EG electrolytes with a small amount of NH$_4$F and H$_2$O under constant-voltage conditions, and subsequent heat treatment transforms them to anatase phase for modification with RGO nanosheets via electrophoretic deposition, for enhanced energy conversion efficiency of DSSCs. Deposition of RGO on TiO$_2$ nanotube arrays is confirmed by SEM and XPS analyses. In addition, thickness or amount of RGO nanosheets deposited on TiO$_2$ nanotube arrays can be easily optimized by adjusting EPD time, for maximized efficiency of DSSCs. When EPD time for RGO deposition is not too long, DSSCs based on RGO-modified TiO$_2$ nanotube arrays show significantly higher energy conversion efficiencies than DSSC consisting of bare TiO$_2$ nanotube array of the same length. Such enhancement is ascribed to the significantly improved electronic conductivity of photo-anodes induced by RGO. Increasing the EPD time is able to further improve the electron transport, but superfluous RGO deposition yields less good or worse photovoltaic performance, and DSSC based on RGO-modified TiO$_2$ nanotube arrays displays the highest energy conversion efficiency of 6.01%. Such significant enhancement in DSSC efficiency is attributed to higher surface area from bamboo-type TiO$_2$ nanotubes for dye loading and the improved charge transfer and retarded charge recombination from RGO-modified photo-anodes. Our results confirm that RGO nanosheets can be facilely deposited onto bamboo-type or smooth-walled TiO$_2$ nanotube arrays by EPD with controllable thickness for applications as photo-anodes in high-efficiency DSSCs.

4.5 References


CHAPTER 5 DYE-SENSITIZED SOLAR CELLS BASED ON UNIFORM ULTRATHIN TiO\textsubscript{2} NANOSHEETS SYNTHESIZED VIA EXFOLIATION AND ANNEALING

5.1 Introduction

Dye-sensitized solar cell (DSSC) is a promising photovoltaic device for converting sunlight into electrical energy, which has attracted significant attention due to its easy processing and low cost production. Since nanoscaled TiO\textsubscript{2} with high surface area was used as photoanode for the first time as reported by Grätzel et al. in 1991, the energy conversion efficiency of DSSC has reached a value as high as 12.3\% [1-7]. Recently, various attempts have been made to improve the efficiency of DSSCs by designing photoanodes with different structures. TiO\textsubscript{2} is the most common photoanode material used in current DSSCs and is typically in the form of nanoparticle film which provides a large surface area for dye loading. However, electron transport in TiO\textsubscript{2} nanoparticle film is random and needs to pass many grain boundaries before reaching electrode and may easily recombine with the oxidizing species, which limits DSSC efficiency. Also, it is important to incorporate large submicron structures (100 to 400 nm) as light-scattering centers to enhance light-harvesting [8-12]. One-dimensional (1D) TiO\textsubscript{2} nanostructures and two-dimensional (2D) nanosheets (NSs) have attracted much attention as the photoanode materials in DSSCs because their ordered structures can facilitate electron transport and their larger dimensions can scatter incident light and enhance light-harvesting efficiency [13-16].

In particular, 2D TiO\textsubscript{2} NSs have been investigated as a promising photoanode material in DSSCs owing to several advantages described as follows. First, TiO\textsubscript{2} NSs can serve as hosting materials to load guest functional nanomaterials and the resulted nanocomposite structure has advantages of both components in addition to other unique new properties. Second, 2D TiO\textsubscript{2} NSs and its derived nanocomposite materials can transform from 2D to 1D structure by scrolling into nanorolls or nanotubes [17]. Third, TiO\textsubscript{2} NS provides large interaction area between TiO\textsubscript{2} photoanode and FTO conducting glass; thus it would block the direct contact between electrolytes and FTO glass. Therefore, TiO\textsubscript{2} NSs demonstrate as a very promising photoanode material for application in DSSCs.

TiO\textsubscript{2} NSs can be commonly synthesized via hydrothermal method using titanium salts as the precursor and hydrofluoric acid as the solvent. Yu and co-workers reported synthesis of anatase TiO\textsubscript{2} NSs with exposed \{001\} facets, using a simple one-pot hydrothermal route with HF as a morphology controlling agent and Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4} as precursor [18]. Such TiO\textsubscript{2} NSs based solar cells exhibited higher photoelectric conversion efficiency (4.56\%) than those of DSSCs based on TiO\textsubscript{2} nanoparticles (NPs) (3.64\%) and commercial P25 particles (4.24\%) with the same titania film thickness of 10 \(\mu\)m, due to good crystallinity, high pore volume, large lateral size, and enhanced light scattering of TiO\textsubscript{2} NSs. Zhao et al. developed a novel TiO\textsubscript{2} double light-scattering layer (TiO\textsubscript{2}-DLL) film consisting of TiO\textsubscript{2} hollow spheres (TiO\textsubscript{2}-HS) as the top layer and TiO\textsubscript{2} NSs as the...
lower layer for application as photoanode in DSSCs [19]. It was found that such TiO$_2$-DLL film based cell achieved the highest conversion efficiency of 5.08%, which was 23.3% higher than that of TiO$_2$-HS film based cell (3.62%) and 8.3% higher than that of TiO$_2$ NS film based cell (4.31%) with identical film thickness of 25 μm under a constant irradiation of 100 mW cm$^{-2}$. The presence of TiO$_2$ NS in the lower layer provided larger contact area between TiO$_2$ photoanode and FTO glass and blocked contact between electrolyte and FTO glass. However, the solvent hydrofluoric acid used in this hydrothermal method was corrosive and needed to be handled with extreme care. Another disadvantage is that hydrothermal method relying on sealed autoclaves limits large scale production of TiO$_2$ NSs [20].

It is critical to develop an effective and environmental friendly method to prepare TiO$_2$ NSs with high crystallinity and controllable dimensions. Sasaki T et al. synthesized 2D colloidal titanium oxide nanosheets, with well-defined chemical composition of Ti$_{0.91}$O$_2$, by completely delaminating a lepidocrocite-type layered protonic titanate H$_x$Ti$_{2-x/4}$O$_4$ • H$_2$O (x = 0.7, □: vacancy) into its single layers with tetrabutylammonium (TBA$^+$) ions using a soft-chemical exfoliation method [21,22]. The exfoliated Ti$_{0.91}$O$_2$ NS has a unique structure with an extremely small thickness of 1 nm and a lateral size of micrometers. With such extremely high 2D anisotropy, the as-prepared Ti$_{0.91}$O$_2$ NS exhibits distinctive physical and chemical properties such as a larger band gap energy than anatase TiO$_2$ due to quantum size effects [23,24]. In addition, the exfoliated Ti$_{0.91}$O$_2$ NSs, which behave as an anionic inorganic polyelectrolyte, can be self-assembled into multilayer thin films by using alternating layer by layer (LBL) method [25,26]. As Ti$_{0.91}$O$_2$ NS is inherently negatively charged due to vacancies at Ti positions, it is possible to assemble unilamellar Ti$_{0.91}$O$_2$ NSs with positively charged guest sheets into multilayer films via LBL [23,24]. With these advantages, Ti$_{0.91}$O$_2$ NSs are expected to be a promising candidate for synthesizing TiO$_2$ NSs as photonanode material used in high efficiency DSSCs.

To the best of our knowledge, anatase TiO$_2$ NSs fabricated via a soft-chemical exfoliation method have never been used as photoanode materials in DSSCs. Herein, we fabricate colloidal Ti$_{0.91}$O$_2$ NSs via chemical exfoliation of a layered precursor (H$_x$Ti$_{2-x/4}$O$_4$ • H$_2$O) through ion exchange with bulky organic ions (TBA$^+$). Subsequent acid treatment induces colloidal Ti$_{0.91}$O$_2$ to reassemble and precipitate into a gelation form. Then, thermal annealing is carried out to convert Ti$_{0.91}$O$_2$ gelation into anatase TiO$_2$ for applications as photoanode materials in DSSCs.

5.2 Experimental

Lamellar solids of lepidocrocite-type cesium titanate Cs$_x$Ti$_{2-x/4}$O$_4$ (□: vacancy, x~0.7) was synthesized via a conventional solid-state calcination method [27,28]. A stoichiometric mixture of Cs$_2$CO$_3$ (Alfa Aser, 99.99%) and TiO$_2$ (anatase, 99%, Sigma Aldrich) was calcinated with a molar ratio of 1:5.3 at 1073 K for 20 hours. After cooling, the products were ground and calcinated repeatedly. Subsequent acid leaching converted them into a protonated form of H$_x$Ti$_{2-x/4}$O$_4$ • H$_2$O [21,22]. The protonated titanate was derived through repeated ion exchange of Cs with proton. The resulted powder (~2 g)
was stirred in 200 ml hydrochloric acid solution with a concentration of 1 mol l$^{-1}$ for 24 hours. After Cs extraction was completed via four cycles of ion exchange, the acid-treated product was thoroughly washed with water to remove acid residue and dried under ambient condition.

The as-prepared \( H_xTi_{2-x/4}O_{4} \cdot H_2O \) was treated with tetrabutylammonium hydroxide (TBAOH, (C$_4$H$_9$)$_4$NOH, ~40% solution, Fluka) to delaminate into \( Ti_{0.91}O_2 \) NSs. A weighed amount (2 g) of \( H_xTi_{2-x/4}O_{4} \cdot H_2O \) was shaken vigorously in an aqueous solution (500 ml) of TBA hydroxide, ((C$_4$H$_9$)$_4$NOH, ~40% solution, Fluka) for two weeks at room temperature. The amount of TBA hydroxide was 5-fold excess to the exchangeable capacity of \( H_xTi_{2-x/4}O_{4} \cdot H_2O \) (4.12 meq g$^{-1}$). Typically, 100 ml colloidal suspension of \( Ti_{0.91}O_2 \) NSs was poured into 100 ml of HCl solution (1 mol l$^{-1}$). Wool-like precipitates were yielded and the mixture was stirred overnight. After filtration and washing with distilled water, a post-calcination process is necessary for removing organic residues and forming a high-crystalline phase. The obtained solids were then heated at 450 °C in air for 3 h to produce anatase TiO$_2$ NSs. The TiO$_2$ NS electrodes were fabricated by a doctor blade method. TiCl$_4$ treatment was performed on TiO$_2$ NS electrodes by soaking annealed solids in 100 mL of 40 mM TiCl$_4$ aqueous solution at 70 °C. Platinized counter electrode was fabricated by drop casting 0.5 mM H$_2$PtCl$_6$/isopropanol solution on FTO glass substrate that had a hole for electrolyte injection later on, followed by heating at 400 °C in air for 20 min. The dye-sensitized TiO$_2$ NS photoanode was sandwiched together with Pt-coated FTO glass by using a 60 μm thick hot-melt sealing film as the spacer (Meltonix 1170-100, Solaronix Co.). DSSCs were sealed by applying heat and pressure with a hot press at 110 °C. An I$_3^-$ based electrolyte, which contained 0.10 M GTC (guanidine thiocyanate) in a mixture of acetonitrile and valeronitrile (85:15 vol/vol) (No. ES-0004, IoLiTec Inc., Germany) was injected through the hole on the Pt-coated FTO into DSSC.

Crystal structure of TiO$_2$ NSs was determined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu Kα radiation operated at 30 kV and 15 mA with a scan rate of 2°/min. Morphology of naosheets was characterized by FEI Quanta 3D FEG scanning electron microscope (SEM) at an accelerating voltage of 10 kV. High-resolution transmission electron microscopic (HRTEM) images of the as-prepared naosheets were taken using JEOL HRTEM (JEM-1400 electron microscope) with an acceleration voltage of 120 kV. The samples were also observed under a polarized optical microscope using an Olympus BX-51 microscope. The current–voltage (J–V) characteristics of DSSCs were recorded using a Keithley 2400 source meter. A solar light simulator (Model: 67005, Oriel) was used to simulate sunlight under one sun AM 1.5 G (100 mW cm$^{-2}$) illumination provided by a 150 W Xenon arc lamp (Model: 6256, Oriel) and calibrated using a Si solar reference cell (Model: 91150V, Oriel).
5.3 Results and Discussion

Figure 5.1 shows XRD patterns of calcinated cesium titanate, TBA\(^+\)-intercalated Ti\(_{0.91}\)O\(_2\) NS (dried sample), and exfoliated TiO\(_2\) nanosheets. XRD pattern in Figure 5.1, a shows that the calcinated product is identified as a homogeneous single phase of lepidocrocite-type cesium titanate Cs\(_{0.7}\)Ti\(_{1.825}\)O\(_4\)\(_{0.175}\) (JCPDS #40-0827) which is synthesized using TiO\(_2\) and Cs\(_2\)CO\(_3\) with a molar ratio of 5.3:1 followed by heat treatment at 800 °C for 20 h. As reported by Sasaki et al. [28,29], the protonated titanate H\(_x\)Ti\(_{2-x/4}\)O\(_4\)\(_{x/4}\)\(\cdot\)H\(_2\)O is then produced through repeated ion exchange of Cs ions with protons. Afterwards, H\(_x\)Ti\(_{2-x/4}\)O\(_4\)\(_{x/4}\)\(\cdot\)H\(_2\)O reacts with TBAOH, intercalating TBA\(^+\) ions into the interlayer space of H\(_x\)Ti\(_{2-x/4}\)O\(_4\)\(_{x/4}\)\(\cdot\)H\(_2\)O through ion exchange of TBA with protons. The obtained stable colloidal suspensions consist of well-dispersed exfoliated nanosheets of hydrated Ti\(_{0.91}\)O\(_2\), with a thickness of approximately 1 nm [29]. The TBA\(^+\)-intercalated Ti\(_{0.91}\)O\(_2\) NS is dried at room temperature and shows relatively small XRD diffraction peaks as shown in Figure 5.1, b; this crystalline phase is probably an intermediate phase before forming final product. Subsequent acid treatment performed on stable colloidal Ti\(_{0.91}\)O\(_2\) NSs induces reassembly and aggregation of NSs and converts Ti\(_{0.91}\)O\(_2\) NSs into a gelation form. Thermal annealing is carried out to convert the reassembled gelation to anatase phase. Figure 5.1, c displays XRD pattern of exfoliated TiO\(_2\) NSs after annealing Ti\(_{0.91}\)O\(_2\) NSs gelation at 450 °C for 3 h. Typical diffraction peaks at 20 = 25.4° and 20 = 48.0° correspond to (101) and (200) in TiO\(_2\) anatase phase (PDF #21-1272, JCPDS). These results indicate that heat treatment converts Ti\(_{0.91}\)O\(_2\) NSs to crystalline phase (anatase) that is subsequently used as photo-anodes in DSSCs.

![X-ray diffraction patterns](image)

Figure 5.1 X-ray diffraction patterns of samples before and after exfoliation: (a) calcinated cesium titanate (b) TBA\(^+\)-intercalated Ti\(_{0.91}\)O\(_2\) nanosheets (dried sample), and (c) TiO\(_2\) nanosheets obtained via thermal annealing of reassembled Ti\(_{0.91}\)O\(_2\) nanosheets at 450 °C for 3 h.
Morphologies of cesium titanate, $\text{CsTi}_0.91\text{O}_2$ NS, and $\text{TiO}_2$ NSs are investigated via SEM shown in Figure 5.2. As can be seen from Figure 5.2, a, cesium titanate consists of plate-like particles with widths at sub-micron scale and lengths up to one micron. It has been reported that protonated titanate can be stabilized in a suspension containing TBA$^+\text{OH}^-$; in this system, $\text{H}^+$ ions in the interlayer structure of titanate are replaced by much larger TBA$^+$ ions, increasing the interlayer space of titanate [21,22]. During vigorous stirring, the interlayer spacing might also be expanded due to intercalation of water and the increased water content in the interlayer space, which significantly reduces the electrostatic interaction between neighboring sheets [17]. During the flocculation using HCl solution, TBA$^+$-intercalated colloidal $\text{Ti}_{0.91}\text{O}_2$ NS suspension becomes unstable and the nanosheets become stacked and reassembled due to the intercalated TBAOH reacting with HCl solution. As shown in Figure 5.2, b, $\text{Ti}_{0.91}\text{O}_2$ NS sheets are well dispersed by delaminating layered precursor of protonated titanate. Most of the dispersed nanosheets exhibit lateral curling indicating successful delamination of layered precursor. Figure 5.2, c shows the morphology of $\text{TiO}_2$ NSs through annealing $\text{Ti}_{0.91}\text{O}_2$ NSs gelation at 450 °C for 3 h. At 450 °C, the $\text{Ti}_{0.91}\text{O}_2$ NSs in the gelation form are restacked together and convert to anatase $\text{TiO}_2$ NSs.

Figure 5.2 SEM images of (a) calcinated cesium titanate, (b) reassembled $\text{Ti}_{0.91}\text{O}_2$ nanosheets in a gelation form using HCl solution, and (c) $\text{TiO}_2$ nanosheets obtained via thermal annealing of $\text{Ti}_{0.91}\text{O}_2$ nanosheets at 450 °C for 3 h.

TEM images in Figure 5.3, a and b further reveal dimensions and structural details of $\text{Ti}_{0.91}\text{O}_2$ NSs in gelation form and $\text{TiO}_2$ NSs. Figure 5.3, a shows TEM image of $\text{Ti}_{0.91}\text{O}_2$ NSs with a lateral size up to micron scale, which is consistent with the size of the starting material (cesium titanate) that is used to synthesize $\text{Ti}_{0.91}\text{O}_2$ NSs. Curling and folding of $\text{Ti}_{0.91}\text{O}_2$ NS into itself indicates its ultra-thin thickness. After heat treatment, a large amount of $\text{TiO}_2$ NSs with a lateral size of 20 - 100 nm can be clearly observed in Figure 5.3, b. These $\text{TiO}_2$ NSs are crystalline as lattice fringes are also observed in Figure 5.3, b. It can also been seen in Figure 5.3, a and b that both $\text{Ti}_{0.91}\text{O}_2$ NSs and $\text{TiO}_2$ NSs are almost transparent or translucent, indicating their ultra-thin thickness. Moreover, crystallinity of TBA$^+$-intercalated $\text{Ti}_{0.91}\text{O}_2$ NSs suspension is detected by naked eyes and polarized microscopy due to birefringence of colloids. Figure 5.3, c shows a photo of the colloidal suspension containing TBA$^+$-intercalated $\text{Ti}_{0.91}\text{O}_2$ NSs, which appears
translucent and homogeneous. This colloidal dispersion is stable for several weeks, indicating Ti$_{0.91}$O$_2$ NSs with ultra-thin thickness are uniformly dispersed and stable in the solvent. Figure 5.3, d shows a polarized microscopy image of TBA$^+$-intercalated Ti$_{0.91}$O$_2$ NS colloidal dispersion, in which crystallinity of TBA$^+$-intercalated Ti$_{0.91}$O$_2$ NS suspension is confirmed by birefringence of colloids. However, crystallinity observed by polarized microscopy is not uniform, indicating the TBA$^+$-intercalated Ti$_{0.91}$O$_2$ NSs may not be completely crystallized. Therefore, a post-calcination process is needed to form a well-crystalline phase.

Figure 5.3 TEM images of (a) Ti$_{0.91}$O$_2$ nanosheets, (b) TiO$_2$ nanosheets, (c) photograph, and (d) polarized microscopic image of TBA$^+$-intercalated Ti$_{0.91}$O$_2$ NS colloidal dispersion.

Performances of DSSCs based on TiO$_2$ NS electrodes are examined under 1 sun AM 1.5 simulated sunlight. Figure 5.4 presents $J$–$V$ curves of DSSCs based on TiO$_2$ NSs with different film thickness (3.5, 5.8, 8.8 and 17.2 µm). Photovoltaic characteristics of these DSSCs, such as short-circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor ($FF$), and efficiency ($\eta$) are summarized in Table 5.1. As the thickness of TiO$_2$ NS film increases from 3.5 µm to 8.8 µm, $V_{oc}$ remains almost the same, while $J_{sc}$ ascends from 6.30 mA cm$^{-2}$ to 9.30 mA cm$^{-2}$, with fill factor ($FF$) staying around 0.66, and efficiency of DSSCs increases from 3.14% to 4.76%. It is evident that the short circuit current increases with
film thickness due to the enhanced surface area of TiO₂ NSs for dye chemisorption, resulting in the enhanced efficiency of DSSC. The highest efficiency is achieved from DSSC consisting of 8.8-µm-thick TiO₂ NS film with three main factors contributing to this high efficiency: i) high light harvesting efficiency due to TiO₂ NSs; ii) ultra-thin layers of TiO₂ NSs provide enhanced surface area of TiO₂ for dye loading; and iii) well-distributed TiO₂ NSs with submicron lateral sizes embedded on FTO glass providing good contact between TiO₂ NSs and FTO glass and blocking the direct contact between electrolyte and FTO glass. However, as thickness of TiO₂ NS film increases to 17.2 µm, $V_{oc}$, $J_{sc}$ and efficiency of DSSC all decrease to 0.72 V, 8.25 mA cm$^{-2}$ and 4.08% respectively. Such overly thick TiO₂ NS film will not further increase DSSC efficiency because a too thick film results in longer pathway for electron transport and more electron-hole recombination.

![Graph showing J-V characteristics of DSSCs](image)

Figure 5.4 $J-V$ characteristics of DSSCs based on TiO₂ nanosheet films with different thickness (3.5, 5.8, 8.8 and 17.2 µm).

Table 5.1 Photovoltaic characteristics of DSSCs based on TiO₂ nanosheet films with different thicknesses as shown in Figure 5.4

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$\sigma$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>6.30</td>
<td>0.75</td>
<td>0.66</td>
<td>3.14</td>
<td>0.09%</td>
</tr>
<tr>
<td>5.8</td>
<td>8.12</td>
<td>0.77</td>
<td>0.66</td>
<td>4.14</td>
<td>0.27%</td>
</tr>
<tr>
<td>8.8</td>
<td>9.30</td>
<td>0.76</td>
<td>0.67</td>
<td>4.76</td>
<td>0.39%</td>
</tr>
<tr>
<td>17.2</td>
<td>8.25</td>
<td>0.72</td>
<td>0.69</td>
<td>4.08</td>
<td>0.20%</td>
</tr>
</tbody>
</table>
To further improve energy conversion efficiency of DSSC based on TiO$_2$ NSs, TiCl$_4$ treatment is carried out to further enhance surface area of TiO$_2$ NSs and subsequently increase the short circuit current of DSSC [30-32]. After being treated in TiCl$_4$ aqueous solution, TiO$_2$ NS film is sensitized by N719 dye and integrated into DSSC. Figure 5.5, a compares $J$–$V$ characteristics of DSSCs based on TiCl$_4$ treated and untreated TiO$_2$ NS film with the same thickness of 8.8 µm. Representative photovoltaic performance parameters are presented in Table 5.2. Compared to untreated TiO$_2$ NSs, DSSC consisting of TiCl$_4$ treated TiO$_2$ NS film delivers the highest energy conversion efficiency (6.44%) with $J_{sc}$ of 12.81 mA/cm$^2$, $V_{oc}$ of 0.76 V and FF of 0.66, which represents a 35.3% increase in cell efficiency compared to that of DSSC based on untreated TiO$_2$ NS film (4.76%). Figure 5.5, b presents SEM image of TiO$_2$ NSs after TiCl$_4$ treatment, showing very tiny TiO$_2$ nanoparticles on the surface of TiO$_2$ nanosheets resulted from TiCl$_4$ treatment contributing to rougher surface with higher surface area. Therefore, TiCl$_4$ treatment of TiO$_2$ NSs increases the energy conversion efficiencies by significantly enhancing surface area for dye loading. Compared to the commonly used hydrothermal method which involves corrosive hydrofluoric acid, chemical exfoliation provides a safe, environmental friendly, and effective approach. Moreover, DSSCs based on the as-prepared 8.8-µm-thick TiO$_2$ NS films with and without TiCl$_4$ treatment both exhibit higher efficiency (6.44% and 4.76%) than DSSC consisting of 10-µm-thick TiO$_2$ NSs synthesized via hydrothermal method (4.56%) that has been reported by other research group [18]. Also, efficiency of our DSSC based on 8.8-µm-thick TiCl$_4$-treated TiO$_2$ NS film (6.44%) is higher than that of DSSC based on 25-µm-thick TiO$_2$ double light-scattering layer (TiO$_2$-DLL) film consisting of TiO$_2$ hollow spheres as the top layer and TiO$_2$ NSs as the lower layer (5.08%) reported by Zhao et al. [19]. Therefore, TiO$_2$ nanosheets synthesized via chemical exfoliation and heat treatment can serve as very promising photo-anode materials for future high-efficiency DSSCs, due to their unique extremely high 2D anisotropy structure, large surface area resulted from their ultrathin thickness, and enhanced light scattering owing to their submicron lateral size.

![Figure 5.5](image-url)  
Figure 5.5, a) $J$–$V$ characteristics of DSSCs based on 8.8 µm-thick TiO$_2$ nanosheet film with and without TiCl$_4$ treatment, b) SEM image of TiO$_2$ NSs after TiCl$_4$ treatment.
Table 5.2 Potovoltaic characteristics of DSSCs based on 8.8 μm-thick TiO₂ nanosheet films with and without TiCl₄ treatment as shown in Figure 5.5

<table>
<thead>
<tr>
<th></th>
<th>J_sc (mA/cm²)</th>
<th>V_oc (V)</th>
<th>FF</th>
<th>η (%)</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ nanosheets</td>
<td>9.30</td>
<td>0.76</td>
<td>0.67</td>
<td>4.76</td>
<td>0.39%</td>
</tr>
<tr>
<td>TiCl₄-TiO₂ nanosheets</td>
<td>12.81</td>
<td>0.76</td>
<td>0.66</td>
<td>6.44</td>
<td>0.49%</td>
</tr>
</tbody>
</table>

5.4 Conclusions

In summary, ultra-thin 2D anatase TiO₂ nanosheets are synthesized by ion exchange between hydrochloric acid with cesium titanate followed by chemical exfoliation via intercalation of TBA⁺ ions, HCl treatment, and subsequent heat treatment for applications as photoanode materials in dye-sensitized solar cells. In this process, the intermediate Ti₀.₉¹O₂ NSs resulted from chemical exfoliation of layered pronated titanate are well-dispersed exhibiting ultra-thin thickness with a lateral size up to a few micrometers. Subsequent acid treatment induces colloidal Ti₀.₉¹O₂ to reassemble and precipitate into a gelation form. Thermal annealing is carried out to convert the Ti₀.₉¹O₂ in gel form to antase phase TiO₂ for application as photoanode material in DSSCs. DSSC based on 8.8 μm-thick TiO₂ nanosheet film delivers a high energy conversion efficiency of 4.76%. TiCl₄ treatment of TiO₂ nanosheets can further enhance energy conversion efficiency of DSSC to 6.44% by increasing surface area of TiO₂ nanosheets for more dye loading. Such results are attributed to the large surface area of TiO₂ NSs, good contact with FTO provided by the ultrathin two-dimensional sheet structure, and enhanced light scattering owing to the submicron lateral size of nanosheets. Our results confirm that TiO₂ nanosheets synthesized via exfoliation method and post heat treatment are promising photo-anode materials for maximizing efficiency of DSSCs and will advance the DSSC technology.

5.5 References


CHAPTER 6 PREPARATION AND PHOTOCATALYTIC ACTIVITY OF AG/BAMBOO-TYPE TiO_2 NANOTUBE COMPOSITE ELECTRODES FOR METHYLENE BLUE DEGRADATION

6.1 Introduction

Environmental pollution and energy shortage have become urgent worldwide issues due to the booming development of science and technology in the past two decades. Semiconductor photocatalysis has emerged with an increasing demand of environmental remediation and alternative clean energy supplies, because it can easily utilize the clean and abundant solar energy. Semiconductive titania has been attracting considerable attention in the fields of renewable energy and environmental protection such as photocatalysis [1-5], dye-sensitized solar cells (DSSCs) [6-10], gas sensing [11-13], water splitting [14-16], biomedical materials [17-20], and lithium-ion batteries [21] due to its good chemical stability, non-toxicity, and readily available raw materials. Since the photocatalytic properties of TiO_2 were published by Akira Fujishima in 1972, great progress has been achieved to improve the activity of TiO_2-based photocatalysts and to understanding the detailed mechanisms behind the photo-degradation of various organic compounds in eliminating pollutants [22]. However, despite intensive efforts have been dedicated to improve the photocatalytic activity of TiO_2, the energy transformation efficiency is still too low for practical utilization of TiO_2-based photoanodes for degradation of pollutants [23-27]. Two main problems of TiO_2-application in photocatalysis are (i) relatively large band gap which determines the energy necessary to create e-h pairs in the semiconductor to innervate photocatalytic processes, and (ii) low mobility of charge carriers in the process of migrating to the catalyst surface resulting in recombination of most of photogenerated e-h pairs.

Many approaches have been applied to improve the photocatalytic properties of TiO_2 by shifting the band gap towards lower energies and improving the charge separation efficiency. Particularly, deposition of noble metals on its surface to change the band gap is found to be an effective approach [28-30]. Tunc et al. reported a reduced band gap of Ag-TiO_2 composites (2.75 eV) compared to that of pure TiO_2 nanoparticles (3.7 eV) and an electron charge transfer to Ag occurring upon UV irradiation [31]. Since there is a difference in Fermi levels of TiO_2 and Ag, the presence of Ag may act as a reservoir for photogenerated electrons, improving charge separation as well as promoting the interfacial charge-transfer kinetics on Ag/TiO_2 interface and facilitating catalytic reactions in which electrons are involved. Also, surface plasmon induced by Ag nanoparticles (NPs) has been reported to have the potential for leading a significant increase of photon absorption efficiency of visible light [31,33]. However, under the strong absorption of UV-light, the small change in plasmon absorption is too weak to be probed [34]. Several methods have been reported to deposit Ag NPs onto TiO_2 such as magnetron sputtering [34], photo reduction deposition [35,36], and electrochemical deposition [37]. However, none is able to prevent the aggregation of Ag particles and to keep structure uniform during the deposition process. Chou et al. synthesized Ag/TiO_2 composites via dry coating process
showing agglomeration of Ag NPs with a wide particle size distribution of 20-100 nm [38]. Agarwala et al. also deposited Ag NPs onto TiO$_2$ nanotubes by using a photo reduction method; the resulted particle size is larger than 70 nm and the nanoparticles are mixed with some rod-like structures [39]. On the other hand, Lai et al. developed a simple method using pulse current deposition to deposit uniformly distributed spherical Ag NPs (2-10 nm) on the surface of TiO$_2$ nanotube arrays [40]. This process is easy to implement and can effectively suppress the agglomeration of Ag particles by taking advantage of high nucleation rate of Ag under the pulse current condition.

Morphology also strongly affects photocatalytic activity of TiO$_2$ due to its influence on the charge separation efficiency. Anodic TiO$_2$ nanotubes have been investigated to enhance the electron transport owning to its promising morphology and tailored features for photochemical applications. The ordered TiO$_2$ nanotubes provide a vertical pathway for electron transport along the tube and thus minimize the electron loss during the diffusion process. Also, one-dimensional nanotubes have less grain boundaries that electrons have to pass; thus electron mobility is increased, leading to faster transport of excited electrons. In this regard, remarkable progress has been made in the ordered alignment of one-dimensional nanostructures for the construction of functional photocatalytic devices. In recent years, bamboo-type TiO$_2$ nanotube arrays formed by anodic oxidation under alternating-voltage (AV) conditions have attracted extensive interest for applications in DSSCs [41-43]. Our group recently explored the formation mechanism of bamboo-type TiO$_2$ nanotubes arrays and discovered the significant influence of bamboo ridges on photocatalysis [41]. The results suggest that bamboo ridges provide extra surface area to TiO$_2$ nanotubes and greatly facilitate chemical reactions on their surface, which enables bamboo-type TiO$_2$ nanotubes to be a better candidate than smooth-walled nanotubes in photocatalytic applications as well. These results motivate us to study photocatalytic activity of bamboo-type TiO$_2$ nanotubes further modified with Ag NPs. To the best of our knowledge, there are no reports on the photocatalytic activity of Ag-modified TiO$_2$ nanotubes with bamboo-structure.

In the present work, we first investigate photocatalytic property of Ag-modified TiO$_2$ bamboo-type nanotubes by degradation of methylene blue (C$_{16}$H$_{18}$N$_3$-SCl, MB) dye under UV light irradiation. Ag-modified bamboo-type nanotubes, Ag-modified smooth-walled nanotubes, and smooth-walled nanotubes of the same length are compared in photocatalytic degradation of MB dye. Metallic Ag NPs are uniformly loaded on TiO$_2$ nanotube arrays via the pulse current deposition method. Morphology-controllable bamboo-type TiO$_2$ nanotube arrays are prepared via an AV anodization process as described in our previous work [41]. Either Ag modification or morphology manipulation of TiO$_2$ nanotubes plays an important role in the degradation of MB and leads to enhanced photocatalytic activities than bare smooth-walled TiO$_2$ nanotubes of the same length. In this work, we combine Ag surface modification for enhanced charge separation efficiency and morphology manipulation for larger surface area, by synthesizing Ag-modified bamboo-type nanotubes that demonstrate further improved photocatalytic effect. The photocatalytic activity of Ag-modified bamboo-type nanotubes can be further maximized by tuning pulse deposition time of Ag NPs.
6.2 Experimental

Ti foils (20 x 20 x 0.25 mm$^3$, 99.5 wt% purity, Alfa Aesar) were degreased by sonicating in acetone, deionized (DI) water, and ethanol for 15 min, respectively, then rinsed with ethanol and dried in a nitrogen stream prior to any electrochemical treatment. Electrochemical anodization of the Ti foils was carried out in a two-electrode cell, with a platinum mesh as the counter electrode at room temperature. The electrolyte for anodization was prepared with anhydrous ethylene glycol (EG) with $\text{NH}_4\text{F}$ (0.3 wt%) and $\text{H}_2\text{O}$ (5 vol%). The voltage was supplied by a DC power supply with digital display (Model 1623A, PK Precision). Smooth-walled TiO$_2$ nanotube array was prepared by anodization of Ti under constant-voltage condition (CV) at 60 V for 1 h. To prepare bamboo-type TiO$_2$ nanotube arrays, the anodization process consists of multiple cycles of alternating high and low-voltage steps, as shown in Figure 6.1, a. The voltage is first increased from 0 V to $V_{\text{high}}$ (60 V) and being kept at $V_{\text{high}}$ for a time $t$, then drops to $V_{\text{low}}$ (10 V) and is also held at $V_{\text{low}}$ for a time $t$, followed by increasing to $V_{\text{high}}$ (60 V) again and being kept at for a time $t$. High voltage of 60 V in the first cycle is reached via a voltage ramp of 1 V/s, while other voltage steps are switched without ramp. Each voltage alternate from 60 V to 10 V is regarded as one cycle. The AV pulse duration, $t$, is kept as 1 min for $V_{\text{high}}$ and $V_{\text{low}}$ during the anodization process. After anodization, the samples were rinsed in deionized water and dried in air, followed by heat treatment at 450 °C in air for 3 h to produce anatase phase.

![Figure 6.1](image)

Figure 6.1 Schematic showing a) an anodization sequence for the formation of bamboo-type TiO$_2$ nanotube arrays, b) pulse current process for electrochemical deposition of Ag with a rectangular pulse shape composed of alternating on-times and off-times for 100 deposition cycles.

Pulse-current electrodeposition of Ag NPs was carried out by immersing the as-prepared TiO$_2$ nanotubes (smooth-walled or bamboo-type) in an aqueous electrolyte composed of 10 mM AgNO$_3$ and 100 mM NaNO$_3$ at room temperature. The TiO$_2$ nanotube array and a platinum mesh were used as the working and counter electrodes, respectively. A pulse-current of 10 mA cm$^{-2}$ with different alternating on-times, $t_{\text{on}}$, and off-times, $t_{\text{off}}$, (0.1 s/0.3 s, 0.5 s/1.5 s, 1 s/3 s, and 2 s/6 s) for 100 cycles were applied. Figure 6.1, b shows the
schematic pulse current process for electrochemical deposition of Ag NPs with a rectangular pulse shape composed of an alternating on-time and off-time for 100 deposition cycles. The Ag-deposited samples were then rinsed with DI water and dried in vacuum at 50 °C overnight.

Crystal structure of bamboo-type TiO$_2$ nanotube arrays was determined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu Kα radiation operated at 30 kV and 15 mA with a scan rate of 2°/min. A FEI Quanta 3D FEG scanning electron microscope (SEM) was used to characterize morphology of TiO$_2$ nanotube arrays. Chemical composition of these nanotubes was studied by energy dispersive X-ray spectroscopy (EDX) on a Hitachi S-3600N SEM. Surface composition of TiO$_2$ nanotube arrays were analyzed via an X-ray photoelectron spectroscopy (XPS) on the AXIS-165 XPS (Kratos Analytical Ltd.) with an AXIS 165 spectrometer from Kratos Analytical LTD by using a twin-anode Al Kα (1486.6 eV) X-ray source. The photocatalytic activities of TiO$_2$ nanotube arrays were evaluated by degradation of MB dye in aqueous solution. A SpectrolineSB-100P UV Lamp (Spectronics Co., USA) emitting a light intensity of 4800 μW cm$^{-2}$ at a wavelength of 365 nm was used to vertically irradiate 50 ml of MB aqueous solutions in beakers with an initial concentration of 12 mg L$^{-1}$. The distance between the lamp head and liquid surface was ~4 cm. The anodized foils were first immersed into MB solutions in darkness and the solution was vigorously stirred with a magnetic stirrer for 1 h to establish an adsorption/desorption equilibrium. Subsequently, the solution was irradiated with the UV light. Changes in the MB concentration were monitored every 30 min by the variations in absorption intensity at 664 nm by using an UV-vis spectrophotometer (Evolution 600, Thermo Scientific), because a linear relation between UV absorbance (A) and MB concentration (C) was found at this wavelength and described as A = 0.206 C + 0.00942.

6.3 Results and Discussion

The as-prepared anodic TiO$_2$ nanotubes are heated at high temperature to convert to anatase phase. Crystallinity of bamboo-type TiO$_2$ nanotubes is examined by XRD analysis after the nanotube arrays are annealed at 450 °C in air for 3 h, as shown in Figure 6.2. Typical diffraction peaks located at 2θ = 25.4° and 2θ = 48.0° correspond to (101) and (200) of TiO$_2$ anatase phase (PDF #21-1272, JSPDS). Diffraction peaks of Ti substrate are also found in the XRD pattern of Figure 6.2, with (002) peak at 2θ = 38.4° and (101) peak at 2θ = 40.1°. These results indicate that heat treatment converts amorphous as-prepared TiO$_2$ nanotubes to a crystalline phase (anatase) that are subsequently used for Ag electrodeposition.
Morphology of anodic TiO$_2$ nanotube arrays can be adjusted by tuning synthesis conditions such as voltages and anodization time. Figure 6.3 displays the cross-sectional view SEM images of smooth-walled TiO$_2$ nanotube array (a, b), Ag-modified smooth-walled TiO$_2$ nanotube array (c, d), and bamboo-type TiO$_2$ nanotube array (e, f). CV anodization at 60 V for 1 h leads to formation of ordered TiO$_2$ nanotubes with smooth walls, as shown in Figure 6.3, a and b. The self-organized nanotube array is perpendicular to the Ti substrate with highly ordered structure. Thickness of the as-prepared TiO$_2$ nanotube array is estimated to be ~6.1 μm, and the diameter of these nanotubes is in a range of 120-150 nm. Metallic Ag NPs are uniformly deposited on TiO$_2$ nanotube arrays via pulse current deposition method. Figure 6.3, c and d show SEM images of Ag-modified smooth-walled TiO$_2$ nanotube arrays via pulse deposition time of 1 s/3 s. It is observed that the structure of smooth-walled TiO$_2$ nanotube arrays preserves well after the pulse current deposition. Ag NPs are uniformly distributed and anchored on the surface of the tube structure. It is observed from Figure 6.3, d that most Ag NPs have a size in the range of 10-40 nm. To confirm the formation of Ag NPs from pulse deposition, EDX is then employed to study surface composition of Ag-modified TiO$_2$ nanotubes arrays. Figure 6.4 shows EDX spectrum of Ag-modified smooth-walled TiO$_2$ nanotubes arrays. A small amount of Ag element is detected, as evidenced by its weak but discernible peak in the EDX spectrum. These findings reveal that Ag-modified TiO$_2$ nanotube arrays are successfully achieved by electrochemical deposition of Ag in AgNO$_3$-containing solution. In addition to the expected peaks of Ag 3d, XPS peaks of C 1s, Ti 2p, and O 1s are also detected from Ag-modified TiO$_2$ nanotube arrays. In contrast to CV conditions, AV anodization processes produce bamboo-type TiO$_2$ nanotubes with rough walls, as shown in Figure 6.3, e and f.
Figure 6.3 Cross-sectional view SEM images of a, b) smooth-walled TiO$_2$ nanotube arrays, c, d) Ag-modified smooth-walled TiO$_2$ nanotube arrays, and e, f) bamboo-type TiO$_2$ nanotube arrays.
Figure 6.4 EDX spectrum of Ag-modified smooth-walled TiO$_2$ nanotubes arrays.

In comparison with smooth-walled TiO$_2$ nanotubes in Figure 6.3, a and b, the length of bamboo-type nanotubes remains the same length (~6.1 μm), but a bamboo-type sidewall morphology is observed. As shown in Figure 6.3, f, the spacing between two neighboring bamboo ridges is ~100 nm. It can be seen that the bamboo structure gains more surface area owing to the bamboo ridges. The ridge density can be maximized by simply adjusting AV pulse duration time and number of cycle.

The photocatalytic activities of Ag-modified TiO$_2$ smooth-walled nanotube (SW-TiO$_2$@Ag) and bamboo-type nanotube arrays (BT-TiO$_2$) are evaluated by degradation of MB and are compared with that of smooth-walled TiO$_2$ nanotube arrays (SW-TiO$_2$). Figure 6.5, a presents the photocatalytic degradation ratios of MB based on these crystalline TiO$_2$ nanotubes. It is found that SW-TiO$_2$@Ag has a higher MB degradation efficiency than that of SW-TiO$_2$. MB concentration is reduced by 44.4% in 3 h on SW-TiO$_2$. With Ag NPs deposited on smooth-walled nanotubes, the removal amount of MB on SW-TiO$_2$@Ag increases to 52.6%, almost 18.5% faster than MB disposal on smooth-walled TiO$_2$ nanotubes. The presence of Ag is believed to retard recombination of e-h pairs by serving as an electron sink and to facilitate the interfacial electron transfer to surface-absorbed O$_2$ to produce activated $\bullet$O$_2^-$. It is also noted that MB decomposes faster on the bamboo-type nanotubes than on the smooth tubes of the same length. Using BT-TiO$_2$ as electrodes, the removal amount of MB in 3 h is significantly increased to 64.4%, almost 45.0% faster than MB disposal on SW-TiO$_2$. This result indicates that photocatalytic reaction is greatly facilitated by the extra surface area of bamboo ridges. Furthermore, bamboo-type TiO$_2$ nanotubes provide larger surface area not only to allow more electrons and holes generated from photoexcitation process to reach their interface, but to absorb more MB dye molecules for degradation.
Figure 6.5, a) Photocatalytic degradation ratios of MB on the anodic smooth-walled (SW-TiO$_2$), Ag-modified smooth-walled (SW-TiO$_2$@Ag), and bamboo-type TiO$_2$ nanotubes arrays (BT-TiO$_2$), and b) corresponding photodegradation kinetic curves of MB photodegradation, where C$_0$ and C are the initial and reaction concentration of MB aqueous solution, respectively.

The photocatalytic degradation rate of organic compounds is commonly described by the following Langmuir–Hinshelwood mechanism [44]:

\[
\ln\left(\frac{C_0}{C}\right) = kt
\]  

(1)

where k is the apparent rate constant of pseudo-first-order, t is the irradiation time, and C$_0$ and C are the initial and residual concentration of MB solution, respectively. Figure 6.5, b compares the kinetic behavior of MB photodegradation on SW-TiO$_2$, SW-TiO$_2$@Ag, and BT-TiO$_2$. The corresponding kinetic constants of MB degradation are given in Table 6.1.
The enhanced k value of Ag-modified nanotubes (0.0042 min\(^{-1}\)) indicates chemical reaction of MB degradation becomes faster with Ag loaded on the tube structure. The resulted k values show that bamboo-type nanotubes yield the highest apparent rate constant (0.0057 min\(^{-1}\)), 72.7% higher than that of smooth-walled nanotubes. This is ascribed to the larger surface area of bamboo-type TiO\(_2\) nanotube arrays with respect to smooth TiO\(_2\) nanotube arrays.

Table 6.1 Kinetic characteristics of photocatalytic degradation of MB on crystalline TiO\(_2\) nanotubes shown in Figure 6.5

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<th>((C_0-C)/C_0), %</th>
<th>k (^b)</th>
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<td>SW-TiO(_2)</td>
<td>44.4</td>
<td>0.0033</td>
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<tr>
<td>SW-TiO(_2)@Ag</td>
<td>52.6</td>
<td>0.0042</td>
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<tr>
<td>BT-TiO(_2)</td>
<td>64.4</td>
<td>0.0057</td>
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\(^a\)\((C_0-C)/C_0\), photocatalytic degradation ratio of MB on TiO\(_2\) nanotube arrays; 
\(^b\) k, apparent rate constant of photocatalytic degradation of MB on TiO\(_2\) nanotube arrays.

To further increase the photocatalytic activities of TiO\(_2\) nanotube arrays, bamboo-type nanotube arrays with larger surface area are deposited with Ag NPs. The amount of Ag deposited on nanotube arrays can be optimized easily by varying on-times and off-times of pulse deposition. Figure 6.6 shows the cross-sectional and top-view SEM images of 6.1-\(\mu\)m-long bamboo-type TiO\(_2\) nanotubes arrays modified with Ag NPs deposited via different pulse deposition times (0.5 s/1.5 s, 1 s/3 s, and 2 s/6 s). When the pulse deposition time is 0.5 s/1.5 s, Ag NPs are evenly distributed and anchored on the sidewall of bamboo-type nanotubes with a very uniform size of \(\sim\)20 nm, as shown in Figure 6.6, a. The top-view SEM image in Figure 6.6, b shows Ag NPs deposited on the open entrances of TiO\(_2\) nanotube arrays (showing a size in the range of 20-40 nm) are larger than Ag NPs on the tube walls. Meanwhile, Ag NPs deposited on the top open entrances of TiO\(_2\) nanotubes are denser (without any obvious agglomeration) than Ag NPs on the tube walls. The larger particle size and denser distribution of Ag NPs on the top of TiO\(_2\) nanotubes are possibly due to the top open entrances of TiO\(_2\) nanotubes being more exposed to electrochemical deposition than tube walls. When the pulse deposition time is increased to 1 s/3 s, the size and the amount of Ag NPs on TiO\(_2\) nanotubes increase as well. It can be seen from Figure 6.6, c and d that some extremely large Ag particles (\(\sim\)100 nm) and agglomerates of Ag NPs are observed on the surface of the tube structure as well as the top open entrances. While the pulse deposition time is further increased to 2 s/6 s, large agglomerates and large Ag particles (\(\sim\)150 nm) would form both on the top of TiO\(_2\) nanotubes and along tube walls, as shown in Figure 6.6, e and f. It can also be seen that the top entrances of TiO\(_2\) nanotubes are clogged by larger and denser Ag NPs.
Figure 6.6 Cross-sectional and top-view SEM images of bamboo-type TiO$_2$ nanotube arrays modified with Ag nanoparticles via different pulse deposition time of a, b) 0.5 s/1.5 s, c, d) 1 s/3 s, and e, f) 2 s/6 s.
The photocatalytic processes are then performed on these different Ag-modified bamboo-type nanotube arrays as above. Figure 6.7, a compares the photocatalytic degradation ratios of MB on these nanotubes as a function of different pulse deposition times (0.1 s/0.3 s, 0.5 s/1.5 s, 1 s/3 s, and 2 s/6 s), respectively, which are designated as BT-TiO\textsubscript{2}@Ag-0.1/0.3, BT-TiO\textsubscript{2}@Ag-0.5/1.5, BT-TiO\textsubscript{2}@Ag-1/3, and BT-TiO\textsubscript{2}@Ag-2/6. BT-TiO\textsubscript{2}@Ag-0.1/0.3 shows slight enhancement of degradation ratio (68.8%) than that of bare bamboo-type nanotubes (64.4%) and the enhancement is not significant due to the small amount of Ag loading resulted from short pulse deposition time of Ag. In particular, the effect of Ag modification to MB degradation efficiency is more significant for BT-TiO\textsubscript{2}@Ag-0.5/1.5, which delivers the highest photocatalytic degradation ratios (78.5%) representing 21.9% and 76.8% increase in degradation efficiency compared to those of bare bamboo-type (BT-TiO\textsubscript{2}) and bare smooth-walled nanotubes (SW-TiO\textsubscript{2}). These results confirm that Ag NPs loaded on TiO\textsubscript{2} nanotubes significantly increase the efficiency of photocatalytic degradation of MB under UV light. Likewise, BT-TiO\textsubscript{2}@Ag-1/3 shows a higher degradation efficiency of 75.5% than that of bare bamboo-type nanotubes, but slightly low than that of BT-TiO\textsubscript{2}@Ag-0.5/1.5. The slightly low degradation efficiency of BT-TiO\textsubscript{2}@Ag-1/3 compared to BT-TiO\textsubscript{2}@Ag-0.5/1.5 may be attributed to larger Ag particles along the tube structure and agglomerates of Ag NPs on the top open entrances of TiO\textsubscript{2} nanotubes of BT-TiO\textsubscript{2}@Ag-1/3, as shown in Figure 6.6, c and d. This conclusion can be further confirmed by decomposing of MB on BT-TiO\textsubscript{2}@Ag-2/6. It is noted that the MB degradation efficiency by BT-TiO\textsubscript{2}@Ag-2/6 (62.9%) is much lower than that on BT-TiO\textsubscript{2}. Similarly, the low efficiency is due to large Ag NPs and agglomerates on the top entrances of TiO\textsubscript{2} nanotubes resulted from long pulse deposition time of Ag. It is noted that large Ag particles anchored on the TiO\textsubscript{2} nanotubes and agglomerates plugged the top open entrances of nanotubes result in an undesirable loss of outer surface area and less efficient MB degradation.

Figure 6.7, b summarizes the kinetic behavior of MB photodegradation by various Ag-modified bamboo-type nanotube arrays as a function of different pulse deposition times (0.1 s/0.3 s, 0.5 s/1.5 s, 1 s/3 s, and 2 s/6 s). Corresponding kinetic constants of MB degradation on these nanotubes are presented in Table 6.2. The k value of BT-TiO\textsubscript{2}@Ag-0.5/1.5 (0.0079 min\textsuperscript{-1}) shows a maximum enhancement of 38.6% than that of BT-TiO\textsubscript{2} (0.0057 min\textsuperscript{-1}), indicating that a proper amount of Ag loading can maximize the photocatalytic efficiency. It can be seen that decomposition of MB becomes significantly faster with the increase of the pulse deposition times from 0.1 s/0.3 s to 1 s/3 s, reaching a maximum at 0.5 s/1.5 s, and then becomes slower with the further increase of the pulse deposition time at 2 s/6 s. It is concluded that photocatalytic behavior of Ag on TiO\textsubscript{2} degradation of MB under UV light has a bi-functional effect. With an appropriate amount of Ag NPs deposited on TiO\textsubscript{2} nanotubes, efficient charge separation of the photogenerated e-h pairs can be achieved. Chang and co-workers reported the photocatalytic performance of the as-fabricated TiO\textsubscript{2}-nanotube arrays by evaluating the photo-degradation of methyl blue (5 mg L\textsuperscript{-1}). The TiO\textsubscript{2}-nanotube arrays exhibited a photocatalytic degradation efficiency of 48.7% after 120 min of UV-vis light irradiation [45]. He and co-workers reported synthesis of 8 μm long Ag/TiO\textsubscript{2}-nanotube composite
with Ag particle size of 10 nm [46]. The pseudo first-rate kinetic constant \( k \) of MB (30 mg L\(^{-1}\)) over the Ag/TiO\(_2\)-nanotube composite arrays is about 0.0022 min\(^{-1}\), which is much smaller than the k value (0.0084 min\(^{-1}\)) of BT-TiO\(_2\)@Ag-1/3 reported in our result.

Figure 6.7, a) Photocatalytic degradation ratios of MB on the anodic bamboo-type TiO\(_2\) nanotubes arrays modified with Ag nanoparticles via pulse deposition time of 0.1 s/0.3 s (BT-TiO\(_2\)@Ag-0.1/0.3), 0.5 s/1.5 s (BT-TiO\(_2\)@Ag-0.5/1.5), 1 s/3 s (BT-TiO\(_2\)@Ag-1/3), and 2 s/6 s (BT-TiO\(_2\)@Ag-2/6), and b) corresponding photodegradation kinetic curves of MB photodegradation, where \( C_0 \) and \( C \) are the initial and reaction concentration of MB aqueous solution, respectively.
Table 6.2 Kinetic characteristics of photocatalytic degradation of MB on crystalline TiO$_2$ nanotubes shown in Figure 6.7

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<td>0.0084</td>
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<td>BT-TiO$_2$@Ag-1/3</td>
<td>75.5</td>
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<tr>
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<td>62.9</td>
<td>0.0053</td>
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Figure 6.8 illustrates the main interfacial charge-transfer processes for Ag/bamboo-type TiO$_2$ composite under UV light irradiation. Bamboo ridges provide extra surface area to TiO$_2$ nanotubes and greatly facilitate chemical reactions on their surface by absorbing more organic pollutant and Ag NPs. The photocatalytic reactions involved with Ag NPs are summarized below:

\[ e_{cb}^- + \text{Ag} \rightarrow \text{Ag}(e_{cb}^-) \] (2)

\[ \text{Ag}(e_{cb}^-) + \text{O}_2 \rightarrow \cdot \text{O}_2^- \] (3)

The electrons are excited to the conduction band and the holes are left in the valence band. Since the Fermi energy of Ag is lower than that of TiO$_2$, the Schottky barriers are formed between Ag NPs and TiO$_2$ nanotubes after Ag NPs are loaded on the TiO$_2$ surface [28, 47-49]. The Schottky barriers facilitate the separation of e-h pairs by trapping more photogenerated electrons from the conduction band of TiO$_2$ to Ag. During this process, e-h recombination is largely suppressed, leading to high photocatalytic activity. On the other hand, large silver particles and agglomerations formed through overly long pulse time would retard photocatalytic reaction. Large silver particles anchored on tube walls and agglomerations clogged the top of TiO$_2$ nanotubes as shown in Figure 6.6, e and f, would provide more sites for e-h recombination in Ag. Therefore, photocatalytic efficiency would decrease due to the enhanced e-h recombination in Ag agglomeration. It is also speculated that large Ag agglomerates covered on TiO$_2$ surface would result in an undesirable loss of surface area of TiO$_2$ nanotubes for absorbing UV light and contact between TiO$_2$ and MB dye, which reduces the efficiency of photocatalytic reaction.
6.4 Conclusions

In summary, we use pulse deposition method to synthesize Ag-modified bamboo-type TiO$_2$ nanotubes, which show more efficient MB degradation than Ag-modified or bare smooth-walled nanotubes of the same length. The enhanced degradation efficiency is ascribed to extra surface area provided by bamboo ridges on the tube side walls and enhanced electron-hole separation assisted by Ag NPs. In addition, the loading content of Ag nanoparticle can be easily optimized by adjusting pulse deposition time, to maximize the MB degradation efficiency by Ag-modified bamboo-type TiO$_2$ nanotube arrays. Increasing the Ag content is able to improve the MB degradation efficiency, but superfluous Ag content results in less good or worse photocatalytic performance. Bamboo-type TiO$_2$ nanotubes modified with Ag NPs via pulse deposition time of 0.5 s/1.5 s demonstrate the highest MB degradation efficiency. These results confirm that bamboo-type TiO$_2$ nanotube array modified with noble metal nanoparticles shows potential as an excellent photocatalyst which can be used for efficient decomposition of organic pollutant disposal and can find wide applications in other devices such as gas sensors and dye-sensitized solar cells.

6.5 References


31. Tunc, I.; Bruns, M.; Gliemann, H.; Grunze, M.; Koelsch, P., Bandgap determination and charge separation in Ag@TiO$_2$ core shell nanoparticle films. Surface and Interface Analysis 2010, 42 (6-7), 835-841.


CHAPTER 7 CONCLUSIONS

This research is focused on synthesis and surface modification of novel titania-based nanostructures and nanocomposites for applications in advanced dye-sensitized solar cells (DSSCs) and efficient photocatalysis. The work is divided into two major categories. The first part of the work entails facile synthesis of bamboo-type TiO$_2$ nanotube arrays with controllable ridge density and tube length by using alternating voltage anodization, for increased efficiencies of DSSCs. Formation mechanism of bamboo-type TiO$_2$ nanotube arrays is also discussed. The low-voltage step reduces pH and ion-diffusion gradient inside TiO$_2$ nanotubes and induces formation of bamboo ridges on outer tube walls during the following high-voltage step. Ridge spacing and length of bamboo-type nanotubes can be facilely tuned by adjusting duration time of high-voltage step and electrolyte composition. Wall morphology and length of these nanotubes can be manipulated by tuning high-voltage anodization time and electrolyte composition, which can be used to improve and maximize efficiency of DSSCs to a value as high as 6.80% by using 16.5 μm-long TiO$_2$ bamboo-type nanotubes.

In addition, titania nanotubes are modified with other nanomaterials for further increased efficiency of DSSCs. Uniformly-sized Ag nanoparticles are deposited onto TiO$_2$ nanotube array via pulse electrodeposition for plasmon effect, leading to enhanced light absorption in DSSCs. Due to the enhanced light absorption and electron-hole seperation caused by plasmon effect, DSSCs based on Ag-modified TiO$_2$ nanotube arrays show significantly higher energy conversion efficiencies than DSSC consisting of bare nanotube array of the same length. High-concentration TiCl$_4$ treatment on TiO$_2$ nanotube arrays can further increase the energy conversion efficiencies by significantly creating more surface area for dye loading.

Moreover, reduced graphene oxide nanosheets are deposited onto a TiO$_2$ nanotube array using electrophoretic deposition, for increased electronic conductivity and improved electron transport in TiO$_2$-based DSSCs. The as-deposited RGO nanosheets are very uniform and can be obtained with controllable thickness. Long bamboo-type TiO$_2$ nanotubes with rough walls are synthesized under alternative-voltage condition for modification with RGO nanosheets and subsequent integration into DSSCs. The as-fabricated DSSCs deliver a further increased efficiency of 6.01%. Such significant enhancement in DSSC efficiency is attributed to higher surface area from bamboo-type TiO$_2$ nanotubes for dye loading and the improved charge transfer and retarded charge recombination from RGO-modified photo-anodes.

In addition one-dimensional TiO$_2$ nanotubes, ultra-thin two dimensional TiO$_2$ nanosheets are synthesized via soft-chemical exfoliation of layered protonated titanate into separate layers with bulky organic ions, for application as photo-anodes in high-efficiency DSSCs. In this process, the intermediate Ti$_{0.91}$O$_2$ NSs resulted from chemical exfoliation of layered pronated titanate are well-dispersed exhibiting ultra-thin thickness with a lateral size up to several micrometers. Subsequent acid treatment induces colloidal Ti$_{0.91}$O$_2$ to reassemble into a gelation form which is then converted to antase phase TiO$_2$ via heat treatment. DSSC based on TiO$_2$ nanosheet film with an optimized thickness of 8.8 μm delivers the highest energy conversion efficiency of 4.76%. The efficiency of DSSCs based
on exfoliated TiO₂ nanosheets after TiCl₄ treatment can reach as high as 6.44%, due to enhancing light scattering and dye loading of ultra-thin TiO₂ nanosheets structure. Both efficiencies are higher than those of DSSCs consisting of TiO₂ nanosheets synthesized via other methods reported in literature.

The second part of the work concentrates on synthesis of Ag-modified bamboo-type TiO₂ nanotube arrays for efficient photocatalysis. The improved photocatalytic degradation of methylene blue dye in aqueous solution is achieved by using bamboo-type TiO₂ nanotubes deposited with Ag nanoparticles via electrochemical deposition. Both Ag-modified bamboo-type and smooth-walled nanotube arrays show improved photocatalytic degradation efficiencies compared to bare smooth-walled TiO₂ nanotubes of the same length, due to the enhanced electron-hole separation and more surface area provided by bamboo ridges. Bamboo-type nanotubes deposited with Ag nanoparticles via pulse deposition shows the highest methylene blue degradation efficiency of 78.5%, which represents 21.9% and 76.8% enhancement of efficiency compared to those of bare bamboo-type and smooth-walled nanotubes, respectively, indicating that a proper amount of Ag nanoparticles on TiO₂ can maximize the photocatalytic processes. Such novel titania-based nanocomposite structure provides large surface area for organic pollutant absorption and subsequent degradation; the ordered structure of nanotube array also offers direct pathway for fast electron transport. Moreover, Ag nanoparticles deposited onto TiO₂ nanotube arrays act as reservoirs for photo-generated electrons, improving charge separation and facilitating catalytic reactions in which electrons are involved. Therefore, the bamboo-type TiO₂ nanotube array modified with noble metal nanoparticles shows potential as an excellent photocatalyst which can be used for efficient decomposition of organic pollutant disposal and can find wide applications in other devices such as gas sensors and dye-sensitized solar cells.
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Xinning Luan was born and grew up in Shenyang, Liaoning, China. In the year of 2002, Xinning graduated with a B.E. degree in Metallurgical Engineering from Central South University in China. During her undergraduate study, she participated in summer internships at Shaoguan Smelter in 2004 and Chinese Aluminum Co., Ltd. in 2005. Knowing that she did not wish to stop her education, she turned to graduate school and joined the lab of Dr. Guorong Hu at Central South University. Her research was focusing on cathode material of Lithium ion batteries with high energy. Xinning graduated with a M.S. degree in Metallurgical Engineering from Central South University in 2006. Xinning also received her M.S. degree in Material Science and Engineering at the South Dakota School Mines and Technology in 2011. She joined Dr. Ying Wang’s group in the Department of Mechanical and Industrial Engineering at Louisiana State University (LSU) in 2011, to pursue her Ph.D. study. Xinning has received several honors during her Ph.D. study at LSU including Enrichment Award, Materials Initiative Assistantship, and Economic Development Assistantships. During her Ph.D. career at LSU, Xinning has gained research expertise in the areas of nanomaterials synthesis, photovoltaics, and photocatalysis. She also published 7 professional publications and attended 4 conference presentations during her Ph.D. study at LSU. Xinning expects to graduate with the degree of Ph.D. in Mechanical Engineering from LSU in August 2014.