TiO$_2$ nanotubes and WO$_3$ nanostructures for dye-sensitized solar cells

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

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Author’s Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

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Haidong Zheng

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Haidong (Rick) Zheng (age 27)
Abstract

The study of dye-sensitized solar cells (DSCs) photoanodes have been so far mainly focused on TiO$_2$ nanoparticles, however, other TiO$_2$ morphologies or metal oxides can also be used as viable photoanode layers. In this PhD thesis, the author pursued the research on novel DSC photoanodes based on anodic titania nanotubes (ATN) and WO$_3$ nanostructures. To the best of the author’s knowledge, this thesis is the first detailed investigation on high-voltage efficient growth of ATN on fluorine-dope tin oxide (FTO) and WO$_3$-based DSCs.

In recent years, TiO$_2$ nanotubes have gained enormous attention for their incorporation in DSCs. It has been reported that the electron diffusion length in the ATN-DSCs can be up to 100 µm, which is almost 4 times longer than that of the current commercial TiO$_2$ nanoparticle DSCs. This unique charge transport property of ATN has led to the explosion of research activities on ATN for DSCs, however, the author recognizes that there are still important areas of ATN-DSCs to be explored. A survey of literature in this thesis reveals some of the fundamental properties of TiO$_2$, as well as the techniques for anodizing Ti for obtaining the self-organized and vertically-oriented nanotubular structures. However, most of the ATN structures reported today are synthesized on Ti metal foils that back-side illumination has to be employed. As much as 20% of light is lost using this configuration. In order to tackle this problem, the author focused on obtaining ATN films on FTO glass substrates. In this work, Ti films were sputtered on the transparent FTO glass substrates and anodized in the fluoride-containing organic electrolyte in the presence of H$_2$O. ATN films as thick as 9.2±0.3 µm were obtained with extraordinarily high growth rate of 0.6±0.3 µm min$^{-1}$, which had been rarely reported before. The ATN films exhibited excellent uniformity and adhesion to the substrates. This study demonstrated that the optimum anodization conditions for ATN growth on foreign substrates were within the range of 0.3 to
0.5% (wt) NH\textsubscript{4}F, with 3 to 5% (vol) H\textsubscript{2}O at 60 V. The actual volume estimation, X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectrometry (ICP-MS) were utilized to elucidate the reason for the unexpectedly large increase of film thickness from the sputtered Ti film to their ATN forms. From these measurements, it was found that this large increase of film thickness was caused by the incorporation of the polarized TiF\textsubscript{4} into the already-formed oxide structure, hence, the author proposed a new mechanism to describe the ATN growth under high voltage and optimum anodization conditions. The DSCs fabricated using high quality ATN films on FTO glass achieved up to 3.11% efficiency, compared to the 2.59% obtained for the foil-based ATN-DSC. This performance enhancement is clearly enabled by the fact that front-side illumination is viable by the ATN on FTO glass and the degree of improvement matches with the light loss due to the back-side illumination.

After a comprehensive literature review, the candidate of this PhD study realized that the fundamental properties of WO\textsubscript{3} is similar to TiO\textsubscript{2} and there is a wide range of techniques for synthesizing various WO\textsubscript{3} nanostructures. However, in the research on the alternative photoanode materials for DSCs, there has been rarely any report on WO\textsubscript{3}, probably due to its acidic surface and more positive (vs NHE) conduction band edge position compared to TiO\textsubscript{2} or ZnO. Crystalline WO\textsubscript{3} is an extremely chemical-stable metal oxide and its application in DSCs has the potential to address the stability issue of photoanode material. Therefore, the author devoted the rest of this thesis to the investigation of WO\textsubscript{3}-DSCs. This work reports the first electrochemical anodization of sputtered W thin films on FTO glass. A novel high pressure sputtering method was utilized to produce W films of low intrinsic stress with a high degree of adhesion to the transparent substrates. Structurally and uniformly porous WO\textsubscript{3} films were obtained under optimized anodization conditions in fluorine-containing
electrolyte. In addition, WO$_3$ nanoparticles films of different thicknesses were prepared as another nanostructure for the application in DSCs. 24 hrs ball milling of the WO$_3$ nanoparticle paste was found to be very effective for forming smooth photoanode layers. Crystalline WO$_3$ was obtained after annealing the films at 480 ºC. Scanning electron microscopy (SEM), Raman and X-ray diffraction (XRD) characterization techniques were used to determine the surface morphology and crystal structure of the WO$_3$ films. For the first time, DSCs based on WO$_3$ films were successfully fabricated by the author. However, the anodic nanoporous WO$_3$ films were found to be unsuitable as the photoanode layer due to their small thicknesses. In contrast, WO$_3$ nanoparticle DSCs with efficiency of up to 0.75% were obtained. It was found that significant performance enhancement could be obtained from treating the WO$_3$ nanoparticle film with TiCl$_4$ and the TiCl$_4$ treated WO$_3$ DSCs was recorded with efficiency reaching 1.46%.

In summary, the author believes that this PhD thesis provides readers with in-depth investigation of FTO-ATN-DSCs and WO$_3$-DSCs from the points of material reviews, syntheses, characterizations as well as device fabrications and testing. The author also believes that this study has contributed significantly to the research of alternative photoanodes for DSCs.
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Chapter 1 – Introduction

1.1 Introduction

As the development of world economy continues to advance, the need of energy is ever increasing. Currently the primary energy consumption in the world is close to 500 exajoules per annum and it is estimated to jump to 760 exajoules by 2030.[1] Almost 90% of the world energy is sourced from fossil fuels which mainly fall into oil, natural gas and coal, however these natural resources will be depleted in this century given today’s rate of energy need.[2] Besides the demand of energy, the problems of pollution and climate change associated with the burning of fossil fuels are clearly witnessed today. Therefore energy issue is and will remain on the centre stage of discussion in the human history.

Development of renewable and clean energies sourced from solar, wind, geothermal, nuclear and tide should be of strategic importance. Among these renewable energy sources, photovoltaics has been used commercially for more than half a century and it is still one of the hottest topics in today’s research and development. Photovoltaic devices convert solar irradiation directly to electricity with zero emission and it has the potential to supply the whole world’s energy demand. The reason is that the earth receives approximately 3 yottajoules per year from the sun, thus the present demand of the world’s energy can be met by simply covering only 0.13% of the earth surface with 10% efficient solar cells.[3] In this chapter, short history of photovoltaics and the introduction of dye-sensitized solar cells (DSCs) are presented. Then the areas of research within the topic of DSCs are discussed and it is followed by the objective of this work and the content structure of this thesis.
1.2 Photovoltaics – a brief history

The history of human being harvesting power from the sun can be dated back nearly 2500 years ago, however, photovoltaic effect was first discovered in mid-19th century by French physicist Edmund Bacquerel.[4] In 1876, William Grylls Adams and his student, Richard Evans Day, made the first solar cell by contacting a sample of selenium with two heated platinum contacts and produced a stable photon-electricity conversion.[5] Seven years later, an American inventor, Charles Fritts, detailed the first large area solar cells from selenium wafers.[5] However, these solar cells had conversion efficiency far less than 1% and deteriorated very rapidly when exposed to strong sunlight.

In 1901, Max Planck introduced the spectral distribution of solar spectrum by his famous Planck's law,[6] while Albert Einstein published his famous description of photoelectric effect four years later.[7] This is the theoretical basis for all semiconductor-based photovoltaic devices, where electrons are excited by incident photons and jump out of the valence band and into the conduction band and then they are collected and transported to the external circuit.

Around the same period of time, Wilhelm Hallwachs, Walter Schottky, Neville Mott and others contributed tremendously in understanding the semiconductor-junction (Schottky barrier) devices,[5] the theories and the prototype devices they pioneered were fundamental to the development to efficient photovoltaic devices. In 1932, Audubert and Stora discovered the photovoltaic effect in cadmium sulfide (CdS), which leads to the exploration of solar cells based on II-VI materials.[5] The breakthrough in photovoltaic devices came in the 1950s with the development of silicon electronics. Fuller, a Bell chemist, intuitively made near-surface p-n junctions by a boron trichloride treatment of n type silicon wafers,[5] which greatly enhanced the charge separation. Using these substrates, Chapin obtained near 6% conversion
efficiency - 50 times higher than any other previous solar cells.[5] Inspired by this achievement, p-n junctions with CdS, GaAs, InP and CdTe were studied to obtain higher efficiency. However, the cost of these solar devices was so high (several hundred dollars per Watt) that they remained experimental projects in laboratories and only NASA could afford to use this technology for space applications. Crystallisation of materials accounts for over 40% of the overall cost in solar cell manufacturing. Therefore more research effort has switched to material crystallisation techniques. After taking several technical measures, a team led by Berman at Solar Power Corporation cut the cost of single crystal module down to US$10 - 20 per Watt in the early 1970s.[8]

During the 70s, the second generation (gen-2) of solar cells were developed with the goal to achieve higher conversion efficiency but turned out to be advantageous in production cost compared to the single crystal solar cells. The materials in the gen-2 solar cells include polycrystalline and amorphous thin-film silicon, CdTe, CuInSe₂, (CIS) and Cu(In,Ga)Se₂ (CIGS). The multi-junction solar cell technology was also developed during this period of time. In the 90s, new concepts for photovoltaics emerged. These technologies mainly include dye-sensitized solar cells, polymer solar cells and nanocrystalline solar cells, all of which are now known as the third generation (gen-3) photovoltaics because they are very different from the previous semiconductor devices. The gen-3 solar cells do not rely on a traditional p-n heterojunction to separate photogenerated charge carriers. Instead, they tend to form a ‘bulky’ junction, where charge separation takes place. These solar cells mainly require low-cost materials and facile fabrication processes, thus they are expected to take a significant stake in the fast growing photovoltaic market.
1.3 The emergence of dye-sensitized solar cells

Dye-sensitized solar cells (DSCs) are considered to be one of the most promising photovoltaic technologies and it is currently under intense fundamental research and commercial development. The early work on semiconductor sensitisation was reported in photography by Vogel in 1873.[9] He investigated the sensitisation of silver halide emulsions with dyes, finding the photoresponse significantly extended into the red and even infrared. Photoelectric effect was found 15 years later by using the dye on silver halide electrodes.[5] Continuous research activities were seen on this field, however, the charge generation and transfer process were still little known. In the 1960s, a number of scientists found that the electron injection process best described the operating mechanism of these cells.[5] In brief, the light excitation of molecular dyes creates free electrons which are injected to the conduction band of the semiconductor where the dye is anchored to; the oxidised dye molecules have to be reduced for the ongoing light excitation and liquid electrolyte containing redox species is usually used to remediate the system. The early DSCs were mainly based on planar surface of ZnO, these devices experienced very weak light absorption and produced only 1-2% efficiency.[10]

The very first efficient DSC was presented by Brian O’Regan and Michael Gratzel in 1991 achieving conversion efficiencies of 7.1-7.9% under solar illumination and 12% under diffused daylight.[11] The genius of the Gratzel cells lie into the sensitization of TiO$_2$ nanoparticle thin films. These photoelectrodes with greatly enhanced surface-to-volume ratio enable the capture of most incident light by a monolayer of dye molecules with a high molar extinction coefficient. With the discovery of a new generation of dye sensitizers such as N3 and “black dye”, light harvesting is further stretched towards the longer wavelength of the visible spectrum and efficiencies were recorded to be approaching 12% under
illumination.[12] In a typical DSC device, a sandwich structure is adopted. This structure is composed of a transparent conductive oxide (TCO) electrode, a layer of mesoporous photoanode material, a monolayer of dye molecules which are chemisorbed onto the photoanode surface, a layer of electrolyte, which contains redox species such as $\Gamma/\Gamma_3^-$ and finally a counter electrode which is a TCO layer coated with a metal such as Pt.

### 1.4 Areas of exploration in DSC research

Today, there are thousands of publications on the research of DSCs and a number of companies such as Dyesol Pty Ltd and SONY Corporation on the verge of releasing fully commercialised DSCs, however this technology is still surrounded by many unknowns. The research and development of DSCs can be categorised by components as follow:

#### 1.4.1 TCO electrodes

Traditionally the contact TCO is fluorine-doped tin oxide (FTO), because FTO has good transparency over the visible range and its conductivity remains relatively unchanged when heated up to 550°C as the crystallisation of TiO$_2$ requires at least 450°C. However, FTO is expensive due to its relatively low production volume in industry. The relatively cheaper, yet more conductive indium tin oxide (ITO) is also being experimented with in DSCs. Unfortunately, processes which involve with ITO have to be kept below 250 °C due to its low thermal tolerance. Thus, replacing FTO with contact material that is less expensive, visibly transparent and heat resistant can be very advantageous for advancing DSCs to commercialisation. One possible candidate is graphene. Recent work conducted by Wang et al.[13] showed that these graphene films fabricated from exfoliation exhibit a high conductivity of 550 S/cm and a transparency of more than 70% over 1000-3000 nm. They also show high chemical and thermal stabilities. However, the efficiencies of the graphene-based DSCs are still in the order of 50% less than the standard ones.[13]
1.4.2 Semiconductors (photoanode)

The photoanode layer is one of the most important components in DSCs. This photoanode material has to satisfy a number of requirements: suitable band structure; wide bandgap, corrosion resistance and ease of structural manipulation. The reasons why TiO$_2$ was chosen at the first place were less documented, however, as research on DSCs advanced, people started to realise that TiO$_2$ somehow meets all the requirements above. TiO$_2$ is a wide bandgap semiconductor which means that it is visibly transparent and does not interfere with the light-absorption by dye molecules; its conduction band (CB) position is negative (vs NHE) enough for a good open-circuit voltage while positive enough for electron injection from the excited dyes; TiO$_2$ remains quite stable under the exposure to a certain range of acids; and most importantly, TiO$_2$ in nanoparticles form can be obtained easily in large quantity as the enhanced surface-to-volume ratio of the photoanode is crucial for maximum light absorption.

Research on the photoanode material has been highly focused on TiO$_2$. Crystal phase of TiO$_2$ is a major area of exploration, as anatase TiO$_2$ is known to be the best for DSCs, not the more symmetrical rutile phase. However, the reason is still very much in debate. On the synthesis of TiO$_2$, researchers also explore ways to induce anatase phase at low temperature. Surface morphology of TiO$_2$ is another important area and TiO$_2$ in nanowire and nanotube forms are used for DSCs as these organised and vertical structures are thought to be more efficient for electron transfer. On the other hand, different semiconductor materials have also been studied for DSCs. Most notably, ZnO-based DSCs achieved comparable conversion efficiency to the TiO$_2$-based devices. ZnO is a wide-bandgap material with a similar band structure to TiO$_2$ and comparable electron injection dynamics. In nanoparticles form, ZnO possesses higher electronic conductivity than TiO$_2$. The high isoelectric point (ISP) on ZnO surface (approximately pH =9) is desirable...
for maximum dye loading [21] and most advantageously nanostructured ZnO is highly amenable in a range of fabrication processes.[20] Another metal oxide that has the potential to make efficient DSCs is SnO$_2$. The SnO$_2$ carrier mobility, in nanoparticles form, is as high as 240 cm$^2$/(V s), which is reported to be 100 times more than that of TiO$_2$.[22] The wider bandgap of SnO$_2$ means less direct response to sunlight, which is believed to reduce the chance of direct oxidation of the electrolyte, thus improving the long-term stability of the device.[21] However, when used alone, SnO$_2$-based DSCs have a low $V_{oc}$ due to a more positive (vs NHE) CB position. Also, the low ISP of SnO$_2$ hinders the dye adsorption on the oxide surface.[21] To overcome these problems, SnO$_2$ is normally coated with a thin layer of TiO$_2$ or ZnO before it is immersed into the dye solution.[21] Such DSCs claim to have obtained efficiency of up to 8%.[23] There are also reports on DSCs using other metal oxides such as Nb$_2$O$_5$,[24] In$_2$O$_3$,[24] and SrTiO$_3$[25] as the alternative photoanodes. Although they all show inferior performance in comparison to the TiO$_2$-based DSCs, such materials have provided important and fundamental understanding of the electronic mechanism within the DSC systems.

1.4.3 Sensitizers

Dye is the heart of DSCs. In traditional DSSC, the standard dye is a ruthenium-based organic complex which has a chemical formula of tris(2,2’-bipyridyl-4,4’- carboxylate) Ru (II) (N3 dye).[26] The dye must carry functional groups such as carboxylate or phosphonate to firmly attach itself to the photoanode surface by chemisorptions. These groups ensure that the dye spontaneously assembles as a molecular layer upon exposing the oxide films to it. The N3 dye is the most efficient sensitizer so far since its first synthesis in the late 90s. Molecular engineering on dyes focuses on molecular extinction coefficient and extending light absorption in the red region and a credible challenger to the N3 dye is recently
developed as the “black dye”. The “black dye” has a chemical formula of tri(cyanato-2,2',2''-terpyridyl 4,4',4''-tricarboxylate)Ru(II) with response extends 100 nm further into the IR than the N3 dye. Ruthenium is an expensive and rare transition metal and for years people have been trying to replace it with other more available elements such as copper. However ruthenium based dyes remain the most efficient sensitizers so far. Instead of organic dyes, innovative concept of using inorganic sensitizers such as narrow bandgap semiconductor CdS nanocrystals was also proposed. Compared to organic dyes, inorganic sensitizers are more stable and have higher temperature tolerance; however the disadvantages of inorganic sensitizers are their narrow spectrum of light absorption and poor attachment to the oxide surface. Finally, dye adsorption onto photoanode surface is a slow process, as the full dye coverage usually takes 24hrs. Engineering on the chemisorption component of the dye molecule for more efficient attachment is beneficial to shorten the devices fabrication time.

1.4.4 Electrolytes

The redox species are the core elements in DSCs electrolytes. Currently the most popular choice of redox species is iodine/triiodine complex. However, this redox species are corrosive, thus it may be a problem for the sealant and the photoanode material. Also iodine is light yellow, therefore it induces unwanted light absorption when light has to go through the electrolyte first. Thus exploring on redox species which are neutral and transparent can benefit device long-term stability and allow illumination from the back. Recently disulfide/thiolate redox couple that has negligible absorption in the visible spectral range has been reported. Making electrolyte into solid state is another important area of research for DSCs, since the solvent of the liquid electrolyte is mainly evaporative; leakage of electrolyte is the upmost long-term stability issue for DSCs. However, solid state electrolyte introduces
less than ideal contact to the dye molecules. Also charge carrier movements in the solid state electrolyte are less efficient than that in the liquid electrolyte. Currently, the solid state electrolytes can be derived into: p-type semiconductors (organic or inorganic); ionic conductors; and conductive polymers.[32] The most efficient solid state DSCs reported are around 8.1%, which are based on ion conducting polymer of poly(ethylene oxide-co-propylene oxide) trimethacrylate oligomers.[32]

1.4.5 Substrates

Normally the substrates that the TCO is deposited on are glass slides. These DSCs are rigid and have limitations in applications such as solar cells for curved surface, solar cells integration on clothing and tents. The deposition of TCO on flexible substrates such as plastic and metal sheets can open up more markets for DSCs. The integration of plastic or metal sheets as substrates can also adapt to some standard industrial manufacturing process such as roll-to-roll process, thus reducing the total cost for DSCs. However, due to the low temperature tolerance of plastic sheets, novel fabrication techniques need to be developed so that high-temperature annealing can be avoided. As for the metal sheets, high corrosion-resistance should be the key selection criteria because the iodine in the electrolyte is corrosive. Recently, 7.2% efficient flexible DSCs were demonstrated using Ti metal sheets.[33]

1.5 Objectives

Compared to the research on dyes and electrolytes, study on the photoanode material has been relatively less attended. This PhD study investigated the TiO₂ nanotubes obtained using electrochemical anodization as the photoanode for DSCs and presented the first detailed study of WO₃ being used as alternative photoanode.
TiO$_2$ in nanotubular form was initially presented about 10 years ago[17] and the majority are obtained using hydrothermal[34] and electrochemical anodization methods.[17] However, electrochemical anodization synthesis is considered to be the most popular choice, as the process is relatively simple with a great degree of controllability on structural properties.[17] TiO$_2$ nanotubes produced by anodization are well-ordered, self-organised and vertically aligned to the substrate, the typical scanning electron microscopy (SEM) image of such structure is shown in Figure 1.1. Electron transfer within this structure is thought to be straight forward without intervention, whereas electrons have to hop from one particle to another in the nanoparticle system.[35] Most of the TiO$_2$ nanotubular films are anodized from Ti metal sheets, as a result when it is used in DSCs, devices have to be illuminated from the counter electrode that a portion of light is absorbed by the electrolyte. Thus growing transparent anodic TiO$_2$ nanotubes (ATNs) directly on FTO glass is highly desirable for DSC application. Therefore, the first objective of this work is devoted to the efficient synthesis of thick and transparent ATN films on FTO glasses and the evaluation of DSCs performance with the incorporation of these films.

![Figure 1.1](image)

**Figure 1.1** Typical scanning electron microscopy (SEM) images of anodic titania nanotubes (a) top view, (b) cross-sectional view.
As mentioned earlier, the reasons why TiO$_2$ was chosen initially were not clearly defined and it is still the subject of discussion. Although the most efficient DSCs now are all based on TiO$_2$, search for alternative photoanode materials should not be discouraged as more suitable semiconductors may emerge or in certain circumstances TiO$_2$ simply cannot be used. To the best of the author’s knowledge, there is no detailed report found for WO$_3$ being used as the photoanode for DSC applications. WO$_3$ is a transition metal oxide with a bandgap that is commonly observed in a range from 2.6 to 3.25 eV for most of its crystal phases,[36] which responds to the blue-UV region of the light spectrum. This bandgap energy is in the same order of that of anatase TiO$_2$ and Figure 1.2 shows the energy band diagram of WO$_3$ in comparison to TiO$_2$ as well as a number of other semiconductors. WO$_3$ itself is an extremely stable material that can survive most harsh environments such as exposure to strong acids, thus this has the potential to enable the usage of more efficient electrolyte with greater acidity. The carrier mobility in WO$_3$ is also reported to be within the range of TiO$_2$.[37] Furthermore, WO$_3$ can be obtained in a number of nanostructured forms such as nanoporous,[38] nanoplatelets,[39] nanoparticles,[40] and nanowires [41] to increase the surface-to-volume ratio for maximum dye loading. Taking all these into considerations, the author believes that WO$_3$ has the potential to be used as the photoanode material in DSC with acceptable efficiency. Thus the other objective of this work is to obtain and investigate suitable WO$_3$ nanostructures from anodization as well as from commercially available sources for DSCs.
Figure 1.2 CB and valence band (VB) energy levels of WO$_3$ in comparison with a number of semiconductors. Reproduce with the permission from [3]. Copyright 2001 Nature.

1.6 Thesis organisation

This thesis aims to provide readers with an appreciation for the study of alternative photoanode morphology and materials for DSCs. This thesis is divided to 6 Chapters with Chapter 1 provides introductive information on photovoltaics and DSCs as well as the objectives of this work; Chapter 2 presents the detailed literature reviews on DSCs, material properties of TiO$_2$ and WO$_3$ and the nanostructuring processes these two materials; Chapter 3 and 4 encompass the synthesis and characterization of ATNs and WO$_3$ nanostructures on FTO glass substrates, respectively; Chapter 5 investigates the performances of DSCs which are fabricated using ATN films and WO$_3$ nanostructures; finally Chapter 6 provides the concluding remarks and outlooks of this PhD thesis.

1.7 References

Chapter 1 – Introduction


Chapter 2 – Literature review

2.1 Introduction

This chapter presents all the relevant concepts in dye sensitized solar cells (DSCs), as well as the review on TiO$_2$ and WO$_3$ as the DSC photoanode material. The operating principles, device structure and materials as well as the charge dynamics are three most basic, yet extremely important items for understanding DSCs. Following the discussion on DSCs, fundamental properties of TiO$_2$, including crystal phases, surface defects, non-stoichiometry, band structure, optical and electrical characteristics will be introduced. One of the prime focuses of this thesis is on the anodic titania nanotubes (ATNs) and a comparison of charge transport between the ATN and the TiO$_2$ in nanoparticle form will be studied. Furthermore the anodization of Ti and the formation mechanism of ATNs will also be reviewed. At the same time, tungsten trioxide (WO$_3$) and its non-stoichiometric form WO$_{x}$, are unique materials that have been rigorously studied for their chromism, photocatalysis and sensing capabilities. However, this material has received relatively less attention in the use of DSCs. This chapter also presents a general review of nanostructured WO$_3$ – some of their fundamental properties and methods of nanostructuring synthesis.

2.2 Operating principle of DSCs

Today, the operating principle of DSCs is still subject to further exploration. The most widely accepted mechanism is considered to be different from the conventional p-n heterojunction solar cells.[1] Conventional solar cells convert light into electricity by exploiting the photovoltaic effect that exists at the semiconductor junctions. In the case of illumination, photons with energy higher than the energy band gap ($E_g$) of the semiconductor generate excitons whose interactions are determined by columbic forces. These excitons
recombine after a certain time with emission of photons or heat and only those created in or close to the space charge layer can be separated by the built-in electric field and contribute to the photocurrent as seen in Figure 2.1. Conventional p-n junction solar cells are also called the minority carrier devices, since only the photo-generated electrons in the p-type material are collected to the outer circuit, thus their efficiencies are highly dependent on the crystallinity of the semiconductor material.[2]

![Energy band diagram of a conventional p-n junction solar cell under illumination.](image)

**Figure 2.1** Energy band diagram of a conventional p-n junction solar cell under illumination.

On the contrary, the generation and separation of charge carriers in DSCs are performed by different materials which are illustrated in Figure 2.2. The generation of charge carriers is realized by light absorption of the dye (S) monolayer which is attached onto the photoanode semiconductor surface. After being irradiated by light, the dye molecules are on excited states (S*) and free electrons are generated from these excited dyes. At the same time, charge separation takes place via the photoanode as well as the electrolyte (or hole conductor). [3] The generated electrons are transferred to the conduction band (CB) of the photoanode
semiconductor from the excited dyes via a process called “injection”.[3] The electron transport in the photoanode is mainly diffusion,[4] and electrons are eventually collected to the electrode. When the excited dye molecules inject electrons to the photoanode, they become oxidized with positive charges (S\(^+\) or holes). The original state of the dye (S\(^o\)) is subsequently remediated by electron donation from the electrolyte, usually an organic solvent containing redox species, such as the iodide/triiodide couple, in a process called “regeneration”.[3] The iodide is regenerated in turn by the reduction of triiodide at the counter electrode. In this process, oxidised dye molecules can be viewed as positive charges which are separated through the electrolyte. The theoretical maximum open circuit voltage (V\(_{oc}\)) that a DSC could deliver is determined by the difference between the redox potential of the redox species and the quasi-Fermi level of the electrons in the semiconductor.[4]

Figure 2.2 Energy band diagram of a typical DSC with I/I\(_3^-\) in the electrolyte under illumination.
2.2.1 Structure and materials of DSCs

DSCs typically take on a sandwich structure, that the materials are fitted between two electrodes. Figure 2.3 depicts the standard structure of DSCs.

![Diagram of DSC structure](image)

**Figure 2.3** A typical device architecture of DSCs.

The DCS components, shown in Figure 2.3, are as follows (from left to right):

1. **Working electrode** – this electrode is usually made from transparent conductive oxide (TCO), such as fluorine doped tin oxide (FTO) on glass substrate. The reason why FTO is the most popular choice of TCO is that it is highly resistant to acidic environment and can tolerate high processing temperatures of up to 550 °C. The working electrode can also be other conductors such as metal sheets, however, the cells have to be illuminated from the back side if non-transparent working electrode is used.[5]
2. Photoanode – the photoanode layer is made of semiconductors and usually deposited on top of the working electrode. The most common semiconductor photoanode layer is made of TiO$_2$ nanoparticles of the optimum radius of approximately 15 nm and thickness in the range of 12-15 $\mu$m.[3]

3. Sensitizer – the sensitizer is typically a monolayer of dye molecules anchored on the photoanode surface via carboxylate groups.

4. Electrolyte – This layer is liquid phase, which infiltrates the mesoporous photoanode network. Acetonitrile is normally used as the solvent of the electrolyte and redox species such as iodide/triiodide are added to it.[3] Solid phase electrolyte can also be implemented.

5. Counter electrode – FTO glass is also used for this layer of DSCs, however, for achieving high efficiency, the counter electrode is usually coated with a few nm of Pt as the catalyst to the electrolyte.[4]

2.2.2 Charge dynamics in DSCs

DSCs are photoelectrochemical devices where a number of parallel electron transfer processes compete with each other. Upon illumination, the sensitizer is excited in a few femtoseconds[6] and the electron injection from S$^*$ to the photoanode (TiO$_2$) is in the subpicosecond scale.[6] The injected electrons are then rapidly (less than 10 fs) thermalized by lattice collisions and phonon emissions.[7] The nanosecond-ranged relaxation of S$^*$ is rather slow compared to that of injection, ensuring sufficient time for the electron injection to take place.[8] The ground state of the sensitizer is then replenished by I$^-$ in the microsecond domain (dye regeneration).[8] This time scale effectively lowers the chance of S$^+$ recombining with the injected electron in photoanode, which usually takes millisecond.[8] This is followed by the two other important processes: electron percolation across the
photoanode structure and the capture of electrons by the oxidized I (which forms I$_3^-$) within milliseconds or even seconds.[9] The perfect matching of time constants of these processes is the key for achieving high conversion efficiencies in DSCs.[8]

2.3 TiO$_2$ for DSCs

TiO$_2$ or titania, has long been the focus of photoanode material investigations in DSCs, since the most efficient DSCs incorporate TiO$_2$ and most theoretical models of DSCs are also based on TiO$_2$. In the following sections, a number of typical characteristics of TiO$_2$ are reviewed together with the electrochemical anodization for synthesizing TiO$_2$ nanotubular structure, which is the emphasis of this PhD thesis.

2.3.1 Fundamental properties of TiO$_2$

This section reviews some of the fundamental properties of TiO$_2$. It begins with the discussion of the typical crystal phases exist in TiO$_2$. The structural defects and the non-stoichiometry of TiO$_2$ are also detailed as they may be present when the material is used in DSCs. This is followed by the description of other fundamental properties including electronic band structure, optical and electrical characteristics.

2.3.1.1 Crystal phases and transition

Three major crystal phases exist for TiO$_2$, they are: rutile (tetragonal), anatase (tetragonal) and brookite (rhombohedral).[10] Other crystal structures are also present, for example, cotunnite TiO$_2$ has been reported to be obtained in high-pressure synthesis and is believed to be one of the hardest polycrystalline materials known.[10] However, only anatase and rutile TiO$_2$ have been intensively studied for their properties and applications. The unit cells of rutile and anatase TiO$_2$ are shown in Figure 2.4, where the basic building block is composed of a titanium atom surrounded by six oxygen atoms in octahedral configuration.[11] In each structure, the bond between the titanium and the oxygen atoms at the top of the
octahedron is slightly longer. The neighbouring octahedra shares one corner along the (110) direction in the rutile structure. While in anatase, the corner-sharing octahedra forms (001) planes, which are connected with the edges of the octahedra below.[11] A sizable variation from the 90° bond angle is also evident in anatase. The phase transition from anatase to rutile can be achieved by annealing and it is generally reported to take place at 700-900 °C.[10]

Figure 2.4 Crystal structures of rutile and anatase TiO$_2$ showing their basic building blocks. Reproduce with the permission from [10]. Copyright 2002 Elsevier.

For DSC applications, anatase TiO$_2$ is mostly used. Rutile TiO$_2$ receives relatively less attention, since rutile TiO$_2$-DSCs are generally 20-30% less efficient than the anatase ones.[12] Although TiO$_2$ in the rutile phase can scatter more white light and is more chemically stable compared to anatase phase, the reason why anatase TiO$_2$-DSCs perform better is still a heated debate.[13] Generally it is believed that the electron transport is slower in the rutile TiO$_2$ nanoparticle layer than in the anatase layer. This may be due to the
differences in the extent of inter-particle connectivity, as the much higher temperature required to induce the rutile phase, which tends to reduce the particle packing density.[12]

2.3.1.2 Defects and non-stoichiometry

It has been reported that many stable phases with a variety of crystal structures exist within the whole titanium-oxygen phase.[10, 14, 15] In the region of $\text{Ti}_2\text{O}_3 - \text{TiO}_2$, the presences of $\text{Ti}_3\text{O}_5$ and seven discrete phases of the homologous $\text{Ti}_n\text{O}_{2n-1}$ (magneli phases) are commonly observed.[10] $\text{TiO}_2$ can be easily reduced, resulting in a color change from transparent to light and eventually dark blue. This intrinsic defect effectively induces n-type doping and higher conductivity for the material.[14] The bulk structure of non-stoichiometric $\text{TiO}_2$ crystals is rather complex with a wide range of defects such as doubly charged oxygen vacancies, $\text{Ti}^{3+}$ and $\text{Ti}^{4+}$ interstitials and planar defects.[10] These defect structures vary with oxygen deficiencies which are highly dependent on temperature, gas pressure and impurities in the synthesis process.

2.3.1.3 Electronic band structure

$\text{TiO}_2$ is one of the most important wide bandgap ($E_g$) transition metal oxides. The reported experimental $E_g$ of anatase $\text{TiO}_2$ is $\sim 3.2$ eV, which is approximately 0.2 eV larger than that of rutile $\text{TiO}_2$.[14] Theoretical calculations show that the upper valence band (VB) which is composed of $\text{O}_{2p}$ has a width of 5.17 eV for anatase $\text{TiO}_2$ and the lower $\text{O}_{2s}$ band is 1.76 eV wide and lies 17.88 eV below the CB minimum, which is filled with $\text{Ti}_{3d}$.[14] The general features of electronic band structure of rutile $\text{TiO}_2$ is quite similar to anatase. It was found that the upper VB width of rutile $\text{TiO}_2$ is 1 eV wider than that of anatase and the lower $\text{O}_{2s}$ band is 1.94 eV for rutile.[14] Electronic band structure of brookite $\text{TiO}_2$ has also been reported to be similar to anatase $\text{TiO}_2$ with only minor difference in the local crystal environment.[10]
2.3.1.4 Optical properties

Since the energy bandgap for both anatase and rutile TiO$_2$ is over 3 eV, they are essentially transparent to visible light. Figure 2.5 presents the optical transmittance spectra for TiO$_2$ thin films with different phase compositions.[16] It is seen that the transparency of the films exhibits a sharp decrease in the UV region. This decrease is caused by the fundamental absorption of light. It can also be seen that the absorption edge of the transmittance is slightly shifted to the red for the films with more rutile phase, as rutile TiO$_2$ has a slightly smaller $E_g$ compared to that of anatase.[16] In the visible region, the absorption coefficient $\alpha$, is influenced by the scattering of light on the surface roughness.[17] However, at shorter wavelengths close to the optical band gap, the scattering losses are dominated by the fundamental absorption. Above the threshold of fundamental absorption, the dependence of $\alpha$ on incident light energy is given by:[17]

$$\varepsilon\alpha \propto (\varepsilon - E_g)^\eta$$  \hspace{1cm} (2.1)

where $\varepsilon$ is the photon energy and $\eta = 2$ is used since TiO$_2$ has indirect transitions.
Figure 2.5 Transmittance spectra of TiO$_2$ thin films sputtered onto glass substrates, A$_{gl}$: 60% anatase, 40% rutile, B$_{gl}$ and C$_{gl}$: 99.9% anatase, D$_{gl}$: 90% anatase, 10% rutile. Reproduce with the permission from [16]. Copyright 1999 Elsevier.

2.3.1.5 Electrical conductivity

For n-type semiconductor such as TiO$_2$, donor-type defects, including oxygen vacancies and titanium interstitials, are mainly responsible for the n-type conductivity and the nonstoichiometry.[18] The electrical conductivity of n-type semiconductor is the product of both electron concentration and mobility terms, which is expressed by the following formula:[19]

$$\sigma = en\mu_n$$  \hspace{1cm} (2.2)

where $e$ is the elementary charge, $n$ is the concentration of electrons and $\mu_n$ is their mobility. However, recent studies have shown that oxidized TiO$_2$ may also exhibit p-type semiconducting properties owing to the concurrent presence of acceptor-type defects in the form of titanium vacancies.[19]
2.3.2 TiO$_2$ nanotubes

TiO$_2$ is one of the most important metal oxides in nanotechnology research, therefore, there is a large number of synthesis techniques reported for obtaining a wide range of TiO$_2$ nanostructures. However, titania nanotubular structure in particular receives the greatest attention. This is probably due to this elongated one-dimensional nanostructure which is believed to be highly efficient for charge transport.[20] Also the double-sided-wall nature of this tubular structure can significantly enhance the surface-to-volume ratio of the material.[21] In addition, this interesting shape has led to some new research which extends the functionality of titania. For example, the titania nanotubular membrane was reported to be used as a UV-induced microfluidic valve.[22] Titania nanotubular structure is commonly obtained using templating sol-gel technique,[23] hydrothermal methods[24] and electrochemical anodization of Ti.[21] However, the titania nanotubes obtained using hydrothermal method are randomly distributed and non-directional. The ones produced from templating sol-gel process tend to have problems on uniformity and stability of the structure. Only titania nanotubes obtained using anodization of Ti are rigid, uniform and vertically attached to the substrate. Therefore, most of fundamental research on titania nanotubes is based on electrochemical anodization synthesis and this technique is investigated for DSCs in this work.

2.3.2.1 Anodic TiO$_2$ nanotubes vs TiO$_2$ nanoparticles

Since the TiO$_2$ nanotube structure obtained using anodization was first reported,[25] a large number of literature has focused on the electronic transfer properties of this vertical nanostructure. When electron injection takes place in the TiO$_2$ nanoparticle film, the charges move toward the contact either by hopping between sites or by a random walk process as illustrated in Figure 2.6a. During this transfer process, the electrons may be immobilized in trap sites.[20] Also the electrons may be localized near the surface, they may be captured by
the redox species. Whereas for the case of anodic titania nanotube (ATN), the vertical structure provides the injected electrons with a direct transfer pathway (Figure 2.6b).[20] The collection efficiency of the injected electrons is determined by the competition between electron transport to the anode and electron transfer to \( \text{I}_3^- \) ions in the electrolyte. A key parameter in this efficiency is the electron diffusion length:[20]

\[
L_n = (D_0 \tau_0)^{1/2}
\]  

(2.3)

where \( D_0 \) is the free electron diffusion coefficient and \( \tau_0 \) is the free electron lifetime. One of the important characteristics of highly efficient DSCs is that the \( L_n \) values are considerably larger than the \( \text{TiO}_2 \) film thickness.[26] It is experimentally found that the \( L_n \) of ATN can be as high as 100 µm, which is significantly longer than the 24 µm measured with the \( \text{TiO}_2 \) nanoparticles.[20]

Figure 2.6 (a) SEM image of a typical \( \text{TiO}_2 \) nanoparticle film, where injected electrons hop from one site to another in random fashion, (b) injected electrons transfer directly from the top to the contact in the anodic \( \text{TiO}_2 \) nanotube film.
Therefore, the use of TiO$_2$ nanotube structure in DSC is of great interest. The reports on such DSCs recorded overall conversion efficiency of up to 6% with 30 µm thick ATN films on Ti substrate.[26, 27] These ATN films are generally treated with TiCl$_4$ solution to increase the surface roughness on the tube.[27] It was found that the short-circuit current, hence the efficiency of ATN-DSCs, decreases if the film thickness was over 30 µm, indicating that the film thickness is approaching the electron diffusion length in ATN.[27] This usable film thickness is till significantly larger in comparison to the standard DSCs, where the maximum thickness of the TiO$_2$ nanoparticle film is approximately 14 µm. The tube diameter is also an important parameter affecting the performance of ATN-DSCs, as the diameter determines the aspect ratio of the ATN film. It has been reported that ATN with 100-120 nm tube diameter is more suitable for DSC applications.[27]

2.3.2.2 Electrochemical anodization of Ti

Electrochemical anodization, or simply anodization, is a well established electrolytic passivation process to increase the thickness of the natural oxide layer on the surface of metal. Anodization changes the microscopic texture of the surface and alters the crystal structure of the metal near the surface. It is conventionally used to increase the corrosion resistance and wear resistance of metals and provide better adhesion for paint primers and glues.[28]

In a typical anodization process, the sample is connected to the positive electrode (anode) and a conductor is connected to the negative electrode (cathode) serving as the counter electrode as shown in Figure 2.7. A direct current is passed through the two electrodes in an electrolytic solution and the current releases hydrogen at the counter electrode and oxygen at the surface of the sample, building up a layer of oxide. For having a precise control over the anodization process, a reference electrode and a pH meter can also be implemented.
Most electrolytic solutions contain acids or other corrosive species as a balance force to make pores on the oxide layer. The formation of pores allows the electrolyte and the current to reach inside the oxide layer enabling further oxidation of the sample material, thus a thicker oxide layer can be produced. The anodization voltage is another important control for the process and it is applied in a range from 1 to 300 V, although most fall within 10-20 V.\textsuperscript{[28]} The pore size and oxide layer thickness have a great dependency on anodization voltage. Other conditions such as electrolyte acidity and temperature can also be tuned to optimise the formation of a consistent oxide layer. Since the discovery of self-organised nanoporous structure of alumina by anodizing aluminium,\textsuperscript{[29]} anodization has been explored to achieve similar nanostructures for many other metal oxides. Ti metal was one of the early anodization targets and the electrolyte used usually contains fluorine species as the corrosive. Self-organised nanotubular titania that was vertically aligned to the substrate was first reported in 2001 by Gong and co-workers using an aqueous HF electrolytic solution.\textsuperscript{[25]}
2.3.2.3 Formation mechanism of anodic titania nanotubes

The titanium samples were anodized, resulting in uniform nanotube arrays grown on top of the supporting titanium metal foils, with an electrically insulating barrier layer separating the nanotubes from the conducting titanium foil. The formation mechanism of ATNs can be directly interpreted using the anodic current transient recorded during the process. The typical anodic current transient curve is shown in Figure 2.8a, while Figure 2.8b illustrates the different stages during the ATN formation. At the initial stage, the anodic current drops sharply indicating the formation of the compact oxide layer when the Ti metal interacts with the $\text{O}^{2-}$ or $\text{OH}^-$ ions. As the oxide layer grows thicker, the current reaches a minimum as it is more difficult for the electrons to move through a thick insulating oxide layer. Then small pores start to be developed by chemical dissolution, enabling bigger current flow. Under the electric field, electrochemical etching dominates over chemical dissolution. The Ti ions from the metal as well as from the oxide (Ti-O bond is weakened by the electric filed) are field-drifted towards the interface of oxide and electrolyte and complex with $\text{F}^-$ to form $\text{TiF}_4$ which is then dissolved in water. At the same time, oxide formation is also in action, as the out-bound Ti ions can be oxygenated. Since the bottom of the pore is closer to the anode, the electric field is stronger, that more fluorine ions and oxygen ions are present around this location. Therefore, both electrochemical etching and oxidation are concentrated at the bottom of the pore, thus making the pore deeper. When the anodic current reaches an equilibrium stage, the forces of electrochemical etching and oxidation balance out each other, however the pores are getting deeper, eventually forming tubes.
Figure 2.8 (a) A typical anodic current transient for Ti anodization, (b) A general illustration of the formation mechanism of ATNs.

2.4 WO$_3$ for DSCs

Although WO$_3$ is a wide-bandgap transition metal oxide which has similar properties to TiO$_2$, there is rarely a detailed report on its use for DSCs. As mentioned in Chapter 1, WO$_3$ possesses suitable charge dynamics and electronic band structures for its implementation in
DSCs. Further to this, the biggest advantage of WO$_3$ is its inertness in most acidic environments. This property of WO$_3$ may provide possible solution to address the long-term stability issue of DSCs and extend the use of electrolyte to the ones with more acidity. In the following sections, some of the fundamental properties of WO$_3$ and synthesis techniques for obtaining nanostructured WO$_3$ are reviewed.

2.4.1 Fundamental properties of WO$_3$

This section focuses on the fundamental properties of nanostructured WO$_3$ which start with its various crystal structures and the conditions for phase transitions between these structures. The structure of non-stoichiometric WO$_x$ and WO$_3$ hydrates are also discussed. The other fundamental properties including electronic band structure, optical and electrical characteristics are presented next.

2.4.1.1 Crystal structures and phase transition

WO$_3$ crystals are generally formed by corner and edge sharing of WO$_6$ octahedra. The following phases are obtained by corner sharing: monoclinic II (ε-WO$_3$), triclinic (δ-WO$_3$), monoclinic I (γ-WO$_3$), orthorhombic (β-WO$_3$), tetragonal (α-WO$_3$) and cubic WO$_3$. However, cubic WO$_3$ is not commonly observed experimentally. The detail of the polyhedral representations of these six structures is shown in Figure 2.9.[30] The phase classification is based on the tilting angles and rotation direction of WO$_6$ octahedra with reference to the “ideal” cubic structure (ReO$_3$ type).
Like other metal oxides, WO$_3$ crystal phase transitions can take place during annealing and cooling. It has been widely reported that for WO$_3$, in bulk form, phase transformation occurs in the following sequence:[31, 32]

monoclinic II (ε-WO$_3$, $<-43^\circ$C) $\rightarrow$ triclinic (δ-WO$_3$, $-43^\circ$C to 17°C) $\rightarrow$ monoclinic I (γ-WO$_3$, 17°C to 330°C) $\rightarrow$ orthorhombic (β-WO$_3$, 330°C to 740°C) $\rightarrow$ tetragonal (α-WO$_3$, $>740^\circ$C)

The above phase transitions of WO$_3$ has been reported to be partially reversible. At room temperature, monoclinic I (γ-WO$_3$) has been reported as the most stable phase, with triclinic (δ-WO$_3$) also being observed.[31] In addition to the aforementioned crystal phases, another possible stable phase for WO$_3$ is hexagonal (h-WO$_3$). The phase transition behavior in nanostructured WO$_x$ can be quite complex, as it mainly depends on the material’s
morphology, which is greatly affected by the nanostructure synthesis process and the initial precursors used. Proposed by the Gibbs-Thomson expression,[33] the reduction of size of WO$_x$ crystallites enhances the surface energy of the system and this enhanced surface energy decreases melting and sublimation temperatures. Therefore, generally lower annealing temperatures, compared to the ones mentioned for the bulk WO$_x$, are needed to induce the crystal phase transitions in the nanostructured form.[34]

2.4.1.2 Non-stoichiometric tungsten oxide (WO$_x$) and WO$_3$ hydrates

WO$_3$ is a transition metal oxide made up of perovskite units, which is well-known for its non-stoichiometric properties, as the lattice can withstand a considerable amount of oxygen deficiency.[35] Only a partial loss of the WO$_3$ oxygen content is needed to affect its electronic band structure and increase its conductivity by a large amount.[36] However, the reduction of WO$_3$ is usually accompanied by structural changes.[35] Some of the better known non-stoichiometric WO$_x$ compositions are W$_{20}$O$_{58}$, W$_{18}$O$_{49}$ and W$_{24}$O$_{68}$. Such oxides are formed by corner-sharing WO$_6$, which alternate with octahedra that are partially established by edge-sharing.[35]

Investigations of WO$_3$ hydrates (WO$_3$·nH$_2$O) or “tungstic acids” are important as they are closely related to WO$_x$. The reports on these hydrates can be traced back to almost a century ago,[37, 38] with the four most studied classes presented as WO$_3$·2H$_2$O (dihydrate); WO$_3$·H$_2$O (monohydrate); WO$_3$·0.5H$_2$O (hemihydrate); and WO$_3$·0.33H$_2$O. The crystal structures of WO$_3$ hydrates are highly dependent on their water content.[38]

2.4.1.3 Electronic band structure

WO$_3$ is a wide bandgap n-type semiconductor, with an $E_g$, corresponding to the difference between the energy levels of the valence band, formed by filled O2p orbitals and the conduction band formed by empty W5d orbitals.[39] As mentioned earlier, the crystal
phase of WO$_3$ transits in a sequence that is determined by the degree of distortion from the ideal cubic phase and in principle, this transition is also accompanied by a change in $E_g$, as the occupied levels of the W5d states change. Amorphous WO$_3$, with the most distorted structure, normally possesses a relatively large $E_g$ on the order of $\sim 3.25$ eV, whereas monoclinic WO$_3$ in bulk form, has been reported to show a typical $E_g$ of $\sim 2.62$ eV at room temperature. In nanostructured WO$_3$, the bandgap generally increases with reducing grain size. Experimentally, this is often observed as a blue shift of the optical absorption band-edge as the nanostructure dimensions are reduced. It is widely accepted that this observed blue shift can be attributed to the quantum confinement (QC) effect.

2.4.1.4 Optical properties

The optical properties of WO$_3$ in the visible region are dominated by the absorption threshold, which is defined by the bandgap energy of the material. The bandgap of nanostructured WO$_3$ is blue shifted compared to the bulk form, with reported values ranging widely from $E_g = 2.60$ to $3.25$ eV. Therefore, WO$_3$ (stoichiometric) is essentially transparent to most visible wavelengths with a slightly yellow tint for smaller bandgap samples, which absorb part of the blue spectrum. This indicates that the absorption of WO$_3$ film do not interfere with the light absorption by the dye if WO$_3$ was used in DSCs. For photon energies greater than the bandgap energy, the light absorption $\alpha$ can be approximated by the equation 2.1, where $\varepsilon$ is the photon energy and $\eta = 2$ indicating that for WO$_3$ indirect transitions are allowed. Typical optical transmission spectra for nanostructured WO$_3$ can be seen in Figure 2.10 with a clear absorption edge evident at ultraviolet (UV) to blue wavelengths. The oxygen-deficient WO$_x$ (non-stoichiometric) are mostly found to be light green, which is caused by an additional broad absorption peak in the red to infrared with a transmission window remaining in the blue-green range. This additional absorption peak is due to the electron transfer from W$^{6+}$ to W$^{5+}$. It is also noteworthy to mention that the
refractive index of WO₃ is large, in the range of 2-2.5 and hence, it is important to consider this parameter in the design of WO₃ based optical devices. [45]

![Transmittance spectra of the RF sputtered WO₃ thin films at different substrate temperatures. Reproduce with permission from [39]. Copyright 2010 American Institute of Physics.](image)

**Figure 2.10** Transmittance spectra of the RF sputtered WO₃ thin films at different substrate temperatures. Reproduce with permission from [39]. Copyright 2010 American Institute of Physics.

### 2.4.1.5 Electrical conductivity

The electrical conductivity of single crystal WO₃ ranges from 10 to 10⁻⁴ S cm⁻¹ depending on the stoichiometry.[36] In addition structural factors such as grain size, grain boundary, film thickness, specific phase and dopants (if any) also have a great influence on the material’s conductivity.[46] Therefore, the electrical properties of WO₃ are strongly dependent on the synthesis techniques and the growth conditions. For example, it has been reported that a relatively high carrier concentration (5×10¹⁹ cm⁻³) and electron mobility (6.5 cm² V⁻¹ s⁻¹) have been observed for WO₃ films synthesized using an elevated substrate temperature during sputtering and thermal evaporation depositions.[47] High substrate temperature tends to detach oxygen ions under vacuum conditions, allowing more free electrons for conduction. It has been suggested that by confining the free carriers’ movement to within well oriented one or two dimensional crystal structures, with smooth boundaries,
the carrier mobility increases as the scattering effects are reduced. This increase in mobility has been successfully shown in other metal oxides such as ZnO nanorods.[48] For WO$_3$ such reports are rare. However recently, the carrier mobility of a single W$_{18}$O$_{49}$ nanowire was measured by Rui et al.[49] to be as high as 40 cm$^2$ V$^{-1}$ s$^{-1}$.

2.4.2 WO$_3$ nanostructure syntheses

Many different approaches for the syntheses of nanostructured WO$_3$ have been implemented using both vapor and liquid phase based methods. As there is no report on WO$_3$ being used in DSCs, the choice of WO$_3$ nanostructure is open and it depends on the synthesis conditions and availability of equipments in this work. In this section, the most common synthetic methods for obtaining nanostructured WO$_3$ are presented.

2.4.2.1 Vapor-phase synthesis

The category of vapor-phase deposition includes a wide range of material synthesis techniques. In general, it involves the condensation of vaporized source material onto the targeted substrates.[50] To obtain nanostructured WO$_x$, physical vapor deposition (PVD) is more commonly used. The PVD process can be purely physical, starting with the WO$_x$ material source in the form of a solid target or powder, which is energetically evaporated (sublimed) by many possible techniques. Ion bombardment[51, 52, 53, 54], heat,[55] electron beam,[56] and laser irradiation[57] are among the most commonly reported energetic sources. With careful control on the process parameters, the evaporated species can condense into a nanostructured form with desired dimensions, crystallinity and nanoscale morphology. The starter material source is not necessarily WO$_x$, it can also be W metal in the form of powder or filament.[58] In this case, oxygen gas or oxidants must be added to the vapor to form WO$_x$. In many cases, the as-synthesized material resulting from PVD is WO$_x$ rather than WO$_3$. The color of the deposited material is a good indicator of the species stoichiometry.[58, 59]
Usually black films are obtained because of severe lack of oxygen content within the material; translucent dark blue films are observed for WO$_x$ with $x = 2.7 \pm 0.2;[58]$ and a light green-yellow color is observed for WO$_3.[59]$ Generally post annealing can be utilized to obtain the desired oxygen content as well as crystal phase and stoichiometry. In the following text, a number of popular vapor-phase syntheses for obtaining nanostructured WO$_x$ are described.

_Sputtering_ – Conventionally, quality anhydrous WO$_x$ ($x = 3 \pm 0.1$) thin films can be obtained using DC or RF sputtering techniques with metallic W or WO$_x$ targets in an oxygen-rich environment. The as-synthesized materials usually exhibit a columnar structure that consists of micro- or nano-sized grains that are tightly packed forming.[51, 52, 53, 54] However, this compact structure is not going to be suitable for the photoanode of DSCs, as large surface-to-volume ratio is required.

_Thermal evaporation_ – For the deposition, the source material can be either W metal or WO$_3$, which is either in powder or condensed form. Due to the low pressure environment, vaporization of the source material can usually be conducted at a temperature that is lower than the melting point of WO$_3$ (~ 1470 °C).[55] In general, WO$_x$ nanowires can be obtained under optimum thermal evaporation conditions and the physical mechanism for the nanostructure condensation has been described using the vapor-solid growth mechanism. Thangala _et al._[55] describes the vapor-solid process as follows. Firstly, the supersaturated WO$_x$ vapor condenses to form solid WO$_x$ clusters in a nucleation step. Then, the WO$_x$ clusters are further oxidized to form a nanocrystalline ‘tip’ on the substrate. Finally this crystalline tip acts as a seed for further crystal growth and exhibits enhanced adsorption of the WO$_2$/WO$_3$ species. Depending on the crystallinity of this seed, the nucleation point will either grow preferentially in the vertical dimension, forming a one-dimensional (1D) nanowire structure, or can grow in both lateral and vertical dimensions forming small aggregated nanoparticles through the use of higher substrate temperature.[55] Since high
substrate temperature is generally required in this synthesis, it is not viable for the WO$_3$-DSCs due to the use FTO glass substrate.

*Spray pyrolysis* – A typical spray pyrolysis process can be conducted either in vacuum or under atmospheric pressure. During the deposition, the precursor solution is pumped to an atomizer and then sprayed through the carrier gas as a fine mist of very small droplets onto heated substrates. Subsequently the droplets undergo evaporation, solute condensation and thermal decomposition, which then result in film formation.\[60\] WO$_x$ films prepared by this method are generally produced from tungsten chloride or ammonium tungstate solutions and oxygen or air is used as the carrier gas.\[61, 62, 63, 64, 65\] Such films are typically of compact structure, consisting of 100-200 nm grains. More recently, Bathe *et al.*\[66\] obtained WO$_3$ films of interconnected nanofibres using pulsed spray pyrolysis to avoid the unwanted substrate cooling caused by continuous spraying of mist. The relatively large particle size may be problematic in terms of photoanode surface area and the equipments described in the literature are generally not available for this work.

2.4.2.2 *Liquid-phase synthesis*

Liquid-phase synthesis (LPS) methods are generally chosen when the high capital cost of vapor phase deposition equipment cannot be justified. LPS offers better control of the material morphology when compared to the vapor-phase methods. LPS can also be implemented at relatively low temperatures, hence not deteriorating the quality of low heat tolerance substrates during the deposition process. Over the years, a vast number of liquid-phase synthesis routes have been developed for synthesizing WO$_3$ in various nanostructured forms. Hydrolysis, condensation, etching and oxidation are the four most important chemical processes in LPS.
**Sol-gel** – Film deposition is generally conducted during the gelation process, where the “sol-gel” is dip-coated, spun or drop-cast onto the substrates. In most WO₅₃ sol-gel syntheses, hydrated WO₃ is produced even after calcination at 300 °C. The author’s group recently reported[67] a new technique for preparing a tungstic acid solution in which the mixing of Na₂WO₄ solution and HNO₃ was conducted using a microfluidic “Y” connector with a controlled flow rate rather than mixing the two solutions at once. Micro- and nano-textured tungsten oxide in a randomly aligned flake-like structure (thickness: 10-30 nm) was obtained using a slow flow rate. The humidity of the aging process was also found to affect the material’s morphology as enhanced film porosity was obtained in a more humid environment. Peroxotungstic acid solutions are probably the most widely used precursors in WO₃ sol-gel syntheses due to their excellent stability in an ambient environment.[68] A typical surface morphology of the WO₃ films obtained using peroxotungstic acid is a highly mesoporous network of interconnected particles (diameter: 100-200 nm).

**Templating** – this synthesis is a modification of the sol-gel synthesis technique and can be very effective for the preparation of meso- or nano-structured WO₅. The produced morphology of WO₅ using this method is highly dependent on the templates used, which can be a wide range of materials. Some of the more popular templates are alumina membrane (AAM) with self-organized nanopores,[69, 70] meso- or nano-porous silica substrate,[71] carbon based structures (e.g. carbon microspheres[72]) and organic compounds such as polyethylene glycol (PEG),[73, 74] polymethyl methacrylate (PMMA)[75] and other block copolymers.[76, 77, 78, 79, 80]

**Hydrothermal** – Hydrothermal treatment is a facile, cost-effective and well-studied liquid-phase technique, which has the capability of producing WO₅ of different nano-morphologies. In most cases, the hydrothermal synthesis of nanostructured WO₅ starts with the preparation of a tungstic acid solution (H₂WO₄) as the precursor. This solution is then
kept at an elevated temperature (120-300 °C) for a certain period of time,[81] allowing the nucleation and growth of crystallites. Such synthetic processes generally produce layered WO$_3$·nH$_2$O flakes of lateral dimensions in the range of several tens of nanometers to several micrometers and thicknesses in the nanometre range. Recent reports have shown that, high aspect ratio 1D WO$_x$ nanostructures such as nanowire, nanorod and other interesting configurations can be synthesized using the hydrothermal technique by adding sulfates and certain types of organic acids to the tungsten acid precursor solution as structure-directing and dispersing agents. The type of nanostructure and crystallinity can be controlled through the use of different kinds of sulfates and organic acids.[81]

**Electrochemical anodization** – This is the WO$_3$ nanostructure synthesis technique that this thesis features and the typical experimental setup and mechanism are detailed in Ti anodization in Chapter 4. Grimes *et al.*[82] reported the first use of anodization to produce WO$_3$ nanostructures. This demonstration used a W foil in an oxalic acid electrolyte resulting in the production of a thin nanoporous WO$_3$ layer on the W foil surface. This experiment was followed by the demonstration of more uniform and thicker films (with thickness up to 500 nm) by anodizing W foils in fluorine-containing electrolyte, where the fluorine species were found to greatly enhance the electrochemical etching and chemical corrosion processes.[83, 84, 85]

**Electrodeposition** – this process can be considered the reverse of electrochemical anodization. For the electrodeposition of WO$_x$, the most popular choice of electrolyte is the peroxotungstic acid solution.[86] Alcohol (isopropanol or ethanol) can be added to the solution to increase the stability.[86] Typically the process requires only a small applied voltage (e.g. −0.5 V vs Ag/AgCl) and the deposition duration is in the range of 1-30 mins. Excessive applied voltages and prolonged processing time can result in creating compact
films with low porosity.[87, 88] Under optimal conditions, electrodeposition can produce porous WO$_3$ films with grains of 20-100 nm in diameters.

2.4.3 Why nanostructured WO$_3$ photoanode?

As mentioned earlier in the Introduction section, there is not yet a detailed report found for WO$_3$-DSCs. ZnO and SnO$_2$ are two most studied alternative photoanode materials, even though the efficiencies of the DSCs made using these two materials, respectively, are still far behind the TiO$_2$ DSCs. The research on alternative photoanode materials provide more fundamental understanding to the charge transfer dynamics in DSCs, also these research activities are justified by the material’s own merit, extremely high electron mobility in SnO$_2$ and ease of nanostructuring for ZnO. As shown previously, crystalline WO$_3$ has similar properties to TiO$_2$. Crystalline WO$_3$ itself is very inert metal oxide, it was found that crystalline WO$_3$ films, under strong acidic environment (glycerin-H$_2$SO$_4$ 10:1), have a very slow dissolution rate of 18 Å per day in room temperature.[89] Figure 2.11 depicts a typical energy state diagram for DSC where WO$_3$ is the photoanode and TiO$_2$ is shown as dashed lines as a reference. As can be seen, the CB edge position of WO$_3$ is generally more positive than TiO$_2$ and it was reported to be in the region of 0V relative to NHE.[1] This position is below the excited state of dye and above the redox potential of electrolyte, thus capable of producing useful open-circuit voltages ($V_{oc}$). Since it is widely accepted that the $V_{oc}$ is regulated by the difference of the metal oxide Fermi level and the redox potential of the electrolyte ($\sim$-0.4V vs NHE for I/I$_3$), thus the $V_{oc}$ of the WO$_3$-DSC could be on the order of 400 mV. Assuming $J_{sc} = 10$ mA cm$^{-2}$ and a fill factor of 0.7, the estimated efficiency for WO$_3$-DSC is approximately 2.8%. Nanostructure is also a very important aspect for photoanode material, as it is essential for maximum dye loading. It has been reviewed that WO$_3$ nanostructures and their syntheses have a large variety. For the scope of this thesis, anodic WO$_3$ nanostructure and WO$_3$ nanoparticles are investigated for DSCs.
Figure 2.11 Energy states diagram for aWO$_3$-based DSC featuring the operation principle.

The dashed line shows the electron transfer route for the TiO$_2$-coated WO$_3$-based DSC.

2.5 Chapter Summary

In this chapter, a literature review of the general concepts relevant to DSCs was firstly presented. The operating principles, structure and materials as well as the charge dynamics within the operation were described, respectively. These theoretical concepts are very important in understanding of device fabrication and evaluation, which will be discussed in following Chapters. The review on general DSCs was followed by the study of the most popular DSC photoanode material, TiO$_2$. Typical fundamental properties of TiO$_2$ were discussed. Anodic titania nanotube was reported to be more favourable for electron transport in compassion to its nanoparticle form and the synthesis technique of anodization for
obtaining TiO$_2$ nanotubes was also explained. Finally, fundamental properties of WO$_3$ as a DSC photoanode material and its various synthesis techniques for producing nanostructured WO$_3$ were reviewed.

2.6 References


Chapter 2 – Literature review


33. P. J. Desre, \textit{A thermodynamic model for the nanocrystal to glass transition of intermetallic compounds subjected to high deformation by mechanical attrition-application to \textit{Ll}(2) phases}, Nanostruct. Mater. 8 (1997), no. 6, 687-701.


Chapter 3 – Synthesis of titania nanotubes on TCO glasses

3.1 Introduction

The experimental details of anodic titania nanotubes (ATNs) synthesized on transparent conductive oxide (TCO) glass substrates, conducted by the author of this thesis, are presented in this Chapter. Up until now, most of the Ti anodization reports focus on metal foil substrates, however, this native metal substrate limits the applications of ATNs, especially for optical devices. Formation of the ATN films on transparent substrates, such as glass, quartz and TCO glass, is very important for expanding the use of this self-organized vertical nanostructure. However, the synthesis of ATN films on foreign substrates is technically more difficult than that on the native Ti foil due to the exfoliation force that is exerted on the deposited Ti films caused by the anodization.

As a strategy for obtaining high quality ATN films on TCO glasses, the author implemented an efficient ATN growth technique that is developed for growing long ATN (>100 µm) on the Ti foil. The key justification for using this strategy is to minimize the anodization duration to reduce the effect of chemical dissolution and film exfoliation caused by the high voltage. The surface morphology, crystal phase and structural composition are characterized. Also the details of structural changes influenced by the anodization conditions are provided.

3.2 Evolution of anodic titania nanotubes – towards efficient growth of structure

The first generation ATNs are generally considered to be the ones that are formed in aqueous electrolyte with HF. These anodizations are conducted on Ti foils at 3 – 20 V in 0.5% wt HF aqueous solution. At low voltages (<10 V), the morphology of the produced films is similar to sponge-like porous structure with typical pore size of 15 – 30 nm. When
voltage increases to 10 V, tubular features start to appear. The inner diameter and the length of the tube are dependent on the voltage. With a 20 V anodization for 45 mins, tubes have an average inner diameter of ~80 nm and maximum length of ~500 nm. However, the nanotubular morphology seems to be broken up at higher anodization voltages.

Due to the high etching rate of the oxide by the HF solution, the first generation ATNs suffers problems of insufficient length and irregular morphology. These problems are improved by replacing HF with KF or NaF and increasing the pH of the aqueous solution with NaOH. Using NaF solution with pH set at 4.5, titania nanotubes of a few microns are obtained at 25 V and this type of ATNs is regarded as the second generation. It is interesting to note that the electrolyte pH affects both the electrochemical etching and chemical dissolution during the process. With increasing pH, the hydrolysis of titanium ions on the oxide surface increases, therefore slows the rates of electrochemical etching and chemical dissolution, allowing longer tubes to be formed.

Although relatively longer ATNs can be produced, the formation rate is still too low, as more than 90 hrs is required to obtain ATNs of just approximately 4 µm. The third generation is aiming at achieving much longer ATNs. It is found that the key is to use organic electrolyte and to decrease the water content in the electrolyte to less than 5%. In this electrolyte composition, the generation of the oxide layer is more difficult in comparison to the aqueous solution. At the same time, the low water content reduces the chemical dissolution of the oxide in the fluorine containing electrolyte thus producing longer nanotubes. The typical organic electrolytes used are formamide, N-methylformamide and ethylene glycol (EG). For the third generation ATNs, up to 1 mm length is obtained and much higher anodization voltages can be implemented to speed up the ATNs formation process.
3.3 ATNs on TCO glass

Most ATN structures obtained today are based on Ti metal foils. Anodization on Ti foils provides ease of fabrication for ATNs, however, the metal substrates come with a number of disadvantages, such as non-transparency; low tolerance for mechanical vibration and low heat-resistance. For the application of dye sensitized solar cells (DSCs), having a non-transparent working electrode for the photoanode means only back-side illumination is viable. When light has to travel through the Pt coating and the I\textsubscript{3}/I\textsubscript{3}electrolyte, as much as 25% of the input power is lost.\cite{4} Therefore, it is highly desirable to obtain ATN structures on TCO glass substrates. Although successful transfer of ATN layers via a lift-off process onto foreign substrates has been reported,\cite{5} such a method requires delicate handling of the ATN films and suffers from poor adhesion between the films and the substrates. Grimes and co-workers pioneered the direct fabrication of the ATN films on TCO glasses with controllable thickness.\cite{6} Later, these films were implemented in DSCs and achieved up to 6.9% efficiency by front-side illumination.\cite{7} However in their reports, the fabrication of ATNs involves a series of prolonged sputtering processes to obtain Ti metal films of tens of micron thick. During the deposition of such thick films, it is not uncommon to observe cracks and peeling-off due to the enormous amount of film stress. Also the anodization of such thick sputtered Ti films can take up to many hours and the produced ATN films can detach from the TCO substrate easily since chemical dissolution becomes dominant in the later stage of the prolonged anodization process.

Therefore, to produce quality ATN films on TCO glass substrates more efficiently is essential from the commercialization point of view. A high anodization voltage (40 – 120 V) combining with EG is known to produce uniform ATN films very efficiently on Ti foil.\cite{1} Anodization voltage is the main control for the reaction rate and a higher voltage can induce a
faster ion movement thus increasing the ATN growth rate. However, this increased growth rate always comes with irregular structure, thus the use of high voltage has to be balanced with viscous electrolyte such as EG to regulate the ion movement. The author of this thesis investigated such problems and found the optimum anodization parameters, which are presented in the following sections.

3.3.1 Anodization of Ti sputtered on ITO glass

The first attempt to obtain ATN films on transparent TCO glass is conducted by anodizing Ti metal films sputtered on indium tin oxide (ITO) glass substrates.[8] For this experiment, titanium films of 1.2 µm thickness were first deposited onto ITO glass substrates using radio frequency (RF) sputtering technique from a 99.99% pure Ti target. A RF power of 140 W was applied during the deposition process. The sputtering chamber was pumped down to the background pressure of 10⁻⁵ Torr before introducing the sputtering gas of 100% Ar with a pressure of 2 × 10⁻² Torr. The substrate temperatures were kept at room temperature and 300 °C and the deposition time was 60 min. Anodization was performed in a neutral electrolyte medium of 0.5% (wt) NH₄F/ethylene glycol solution using a platinum foil cathode at room temperature. Scanning electron microscopy (SEM) and x-ray diffraction (XRD) were used to characterize the sputtered Ti films as well as the produced ATN films.

Only sputtered Ti films with a substrate temperature at 300 °C were able to be converted to ATN films after the anodization. It can be seen (Figure 3.1) that at the start of the anodization process perpendicular holes were formed into these hexagonal surfaces of Ti crystallites in high temperature deposited films. These holes were homogeneously distributed, which eventually initiate the well-ordered nanotubes. After the anodization process, anatase TiO₂ was confirmed by the XRD which is shown in Figure 3.2. In contrast, similar patterns were not observed for the room temperature deposited films. For such films, etching starts in
the grain boundaries and gradually expanded toward different directions. However, some randomly oriented nanopores and short tubes were obtained within grain boundaries. The XRD of these as-anodized films still shows predominant Ti metal peak, which is an indication of less than ideal oxide formation.

Figure 3.1 SEM images of 300 °C RF sputtered films at 20 V anodization, showing a sequence of steps: (a) after 5 min, (b) after 10 min, (c) after 45 min and (d) after 80 min.

ITO glass is famous for its high transparency in the visible spectrum and excellent conductivity. However, it is also known for its instability in high temperature and acidic environments. It is found that the sheet resistance of the ITO glass increases dramatically after the 300 °C RF sputtering process, which is also confirmed by XRD (Figure 3.2) that the
oxygen ions from the ITO tend to complex with the bombarded Ti ions.[8] In addition, the ITO layer is seen to be easily etched away during the course of the anodization. Taking these observations, it is concluded that, as a working electrode, ITO glass substrate is not suitable for obtaining ATN films which are used in DSCs. Therefore, the author did not pursue these ATN films on ITO glass for further characterization and application in this thesis and the investigation of fluorine-doped tin oxide (FTO) glass was experimented with due to its superior thermal stability and chemical inertness.

![Figure 3.2 XRD patterns of room temperature and 300 °C RF sputtered Ti films: before and after anodization.](image)

**Figure 3.2** XRD patterns of room temperature and 300 °C RF sputtered Ti films: before and after anodization.

### 3.3.2 Rapid formation of ATN films on FTO glass

The Ti films of various thicknesses were deposited using a RF sputtering system fitted with a Ti target of 99.995% purity.[9] Ti was sputtered on the commercial FTO glass (13 Ω square$^{-1}$). The base pressure in the system was 10 μTorr. Sputtering was conducted in argon at
Chapter 3 – Synthesis of titania nanotubes on TCO glasses

20 mTorr with 1.78 W cm\(^{-2}\) applied RF power density and substrate temperature of 300 °C. Anodization of the sputtered Ti films was carried out at room temperature by a conventional anode (target sample) – cathode (platinum plate) system specified in Chapter 2. The electrolyte was composed of 0.1 to 1.5% (wt) NH\(_4\)F in EG, with the addition of 0 – 10% (vol) of deionised H\(_2\)O. Anodization voltages in the range of 20V to 80V were studied in the process. Upon the completion of the anodization process, samples were washed using acetone and isopropanol and dried in N\(_2\). Anatase TiO\(_2\) was obtained by annealing the anodized samples in a standard laboratory furnace at 480 °C for 120 mins, in ambient air, with a ramp up and ramp down rate of 2 °C min\(^{-1}\).

The ATN films were characterized by SEM, XRD and X-ray photoelectron spectroscopy (XPS). Inductively coupled plasma mass spectrometry (ICP-MS) was also conducted on the electrolytic solutions before and after anodization. Optical transmission measurements were obtained using a broadband DH-2000-BAL UV-NIR deuterium tungsten halogen source fitted with a spectrum analyzer.

Figure 3.3 shows the SEM of the sputtered Ti surface on FTO glass substrate. As can be seen, the surface of sputtered Ti is relatively flat and exceptionally compact and it is comprised of Ti platelets. The cross-sectional view shows that the compactness is throughout the whole film.
Figure 3.3 Surface morphology of the Ti metal film on FTO glass obtained using RF sputtering at 1.78 W cm$^{-2}$ and 300 °C for 180 mins. Insert: cross-sectional view of the film.

3.3.2.1 Effect of voltage, NH$_4$F concentration and H$_2$O content

The anodization voltage has the dominant effect on the structural properties and the growth rate of nanotubes. In this work, the average inner diameter of the nanotubes was found to be highly dependent on the applied voltages. The top views of the nanotubes obtained using different voltages with the same anodization duration are shown in Figure 3.4. As can be seen, only 30 – 40 nm holes are developed with 20 V; while tubular structure with 60 – 70 nm inner diameter was obtained at 60 V and nanotubes with 80 – 90 nm openings were evident for 80 V. Also the wall thickness of the tube decreased with increasing the anodization voltage.
Figure 3.4 SEM images of ATNs obtained at 0.5%(wt) NH$_4$F 3%(vol) H$_2$O for 16 mins, (a) 20V, (b) 60 V, (c) 80 V.

The author also found that the growth of ATN films produced from prolonged anodization due to low growth rates (20 – 30 V or less than 0.3% (wt) of NH$_4$F) was not uniform. Some areas of such ATN films were etched away, while some areas were still metallic. In contrast, extremely high growth rates in the range of 1 - 1.76 µm min$^{-1}$ were associated with either very high applied voltages (70 - 80 V), or high NH$_4$F concentrations (1 - 1.5% wt), however this high growth rate always induced irregular structures which seemed to cause partial film delamination from the substrates. Figure 3.5a depicts the physical photo of such ATN film where the etched-away portions are clearly visible and the SEM image on the etched-away spot is shown in Figure 3.5b where the ATNs are aggregated in bundles. It is believed that the extremely strong electrochemical etching in very high voltage or NH$_4$F concentration conditions is responsible for this low quality ATN films.[10]
Figure 3.5 (a) Physical photo of a ATN film on FTO obtained at 60V, 1.5 % (wt) NH$_4$F 3% (vol) H$_2$O, (b) SEM image of the over-etched spot of such ATN films.

It is known from experiments that minimizing H$_2$O content is the key for achieving efficient ATN growth.\[11\] The anodic current transients recorded during anodization with different water contents are displayed in Figure 3.6. With aqueous electrolyte or high water content (10% vol), a large amount of hydroxyl ions are injected to the oxide surface suppressing the ion transport on this interface, hence depressing the ATN growth.\[12\] The steady-state anodic current increases with the decrease of water content in the electrolyte composition. Also it is suggested that the chemical dissolution of oxide is weaker with less water content, hence promoting the growth of longer nanotubes.\[12\] In organic electrolytes such as EG with 0% (vol) H$_2$O, the oxygen evolution on the anode is more difficult comparing to aqueous electrolyte thus reducing the formation of oxide and making the whole system very conductive for ions transport.\[1\] Additionally, the nanotubular structure obtained using this composition is very disordered due to the enhanced electrochemical etching associated with high anodic current.
Figure 3.6 Anodic current transients recorded during 60 V anodization, 0.5 % (wt) NH$_4$F with 0 – 10 % (vol) H$_2$O added.

As a result, it is very important to control the anodization parameters so that uniform and efficient transformation of transparent ATN films from the sputtered Ti films can be achieved. After a series of experiments, the author found that such high quality ATN films were produced with steady-state anodic currents ranging from 10 – 20 mA cm$^{-2}$. In this current range, the anodization voltage was kept at 60 V and electrolyte solutions contained 0.3 to 0.5% (wt) NH$_4$F with 2 to 3% (vol) H$_2$O. The resultant films had excellent adhesion to the substrates, as after the post-anodization cleaning and over 20 mins of sonication, no delamination of the ATN films from the substrate or structural changes, were observed.[9] Therefore, only sputtered Ti films anodized using 0.5% (wt) NH$_4$F with 3% (vol) H$_2$O at 60 V was investigated for the remaining of the thesis.
3.3.2.2 SEM analysis

For 0.5% (wt) NH$_4$F with 3% (vol) H$_2$O at 60 V, 3 sputtered Ti films on FTO with different film thicknesses were anodized and the details are summarized in Table 3.1.

**Table 3.1** Characteristics of the sputtered Ti anodizations at 0.5% (wt) NH$_4$F, 3% (vol) H$_2$O and 60 V

<table>
<thead>
<tr>
<th>Ti film thickness (µm)</th>
<th>Anodization duration (min)</th>
<th>ATN film thickness (µm)</th>
<th>Ratio of thickness increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>3.5</td>
<td>2.2</td>
<td>2.44</td>
</tr>
<tr>
<td>1.8</td>
<td>8</td>
<td>4.8</td>
<td>2.67</td>
</tr>
<tr>
<td>3.2</td>
<td>16</td>
<td>9.5</td>
<td>2.97</td>
</tr>
</tbody>
</table>

It is clear that the formation of the ATN films on FTO substrates is very efficient. An up to 9.5 µm thick ATN film was obtained after only 16 mins of anodization. The ATN growth rate at these anodization parameters is ~0.6 µm min$^{-1}$. Figure 3.7 shows the SEM images of the produced ATN films. The surface of the sputtered Ti became nanoporous as seen in Figure 3.7a, nanotubes are actually formed beneath this upper nanoporous layer (Figure 3.7b) and that these pores lead to the openings of the tubes (Figure 3.7b insert). Conventionally, this upper porous layer would be etched away by chemical dissolution, in the later stage of the anodization of Ti foil over several hours. However, this fast anodization process has minimized chemical dissolution and preserved the upper porous layer, while generating uniform transformation from the sputtered Ti film to ATNs, with no or maybe a few nanometres of remaining sputtered Ti left except for the areas near the interface between the sputtered Ti and the ATN film (Figure 3.7c-e). The increase of the ATN film thickness from the original sputtered Ti film is directly depicted in Figure 3.7e. At the interface between the
sputtered Ti and the ATNs, there is a thin layer of remaining Ti close to the interface and the ATNs are also shorter than the ones at the centre of the film.

**Figure 3.7** SEM images of sputtered Ti films anodized in 0.5% (wt) NH₄F - 3% (vol) H₂O at 60V. (c, d) 45° tilted view of the samples, the ATNs are on top of the FTO with no or very little amount of remaining Ti, (e) 45° tilted view of the interface between the ATN film and sputtered Ti film featuring the increase of film thickness.
3.3.2.3 ATN film transmittance and XRD patterns

The digital photos of the three ATN films specified in Table 3.1 as well as one of the annealed samples are shown in Figure 3.8a. The transmission spectra of the samples and the FTO glass as a reference are displayed in Figure 3.8b. As can be seen, the 2.2 µm ATN film has the greatest absolute transmission of average 85% in the visible spectrum if the FTO glass spectrum was subtracted. The spectrum is similar to the ones reviewed in Chapter 2. It is also observed that the transmission of ATN films is inversely proportional to its thickness, as more light is scattered by the longer structure. Annealed ATN films generally experience 15 – 20 % reduction of transmission when compared with non-annealed ATN films, however, the cause of this requires further investigation. The XRD patterns (Figure 3.8c) confirm that the anodized titania films were mainly amorphous, which are undesirable for electron transport. TiO$_2$ of anatase phase was obtained by annealing the anodized samples, which was identified by the strong anatase signature peak at 2θ = 25.15°.
Chapter 3 – Synthesis of titania nanotubes on TCO glasses

3.3.3 Analysis of film thickness variation before and after anodization

After metal transforms to metal oxide, it is not uncommon to observe that the thickness of the formed oxide is larger than the original thickness of metal. This phenomenon is caused by volume expansion and the Pilling-Bedworth ratio is used for describing the difference of the volume of a metal oxide to the volume of the corresponding metal which forms that oxide.[13] The Pilling-Bedworth ratio for Ti is ~1.9,[13] as a result, the expected

Figure 3.8 (a) The photos of ATN films obtained at 0.5% (wt) NH$_4$F - 3% (vol) H$_2$O at 60V, (b) transmission spectra of FTO glass substrate, ATN films on FTO glass before annealing and after annealing, (c) the XRD patterns of the FTO glass substrate, sputtered Ti films on FTO, ATN films before and after annealing.
film thickness after anodization for the three Ti films in Table 3.1 should be equal to 1.71, 3.42 and 6.08 µm, respectively. Apparently the expected ATN film thicknesses are largely different from the characterized values. Relying on the conventional ATN formation mechanism described in Chapter 2, oxide formation and corrosion happen simultaneously and the Ti ions are drifted out to complex with F\(^-\) to form TiF\(_4\). However, the TiF\(_4\) is dissolved in the electrolyte during corrosion that it is highly unlikely for such a large increase of thickness due to the loss of Ti ions.

3.3.3.1 Actual volume evaluation for the ATN films

In order to find out the exact mechanism behind the unexpectedly large increase of film thickness, before and after anodization, the author evaluated the geometric models of single nanotube for the three samples specified in Table 3.1 with dimensions based on the average values obtained from SEM characterizations. The average dimension data are displayed in Figure 3.9a. Taken these data, the evaluated volumes are summarized in Table 3.2 and the calculation was conducted using the following equations:

\[
V_{\text{tube}} = \pi \times h \times \left[ \left( \frac{d_o}{2} \right)^2 - \frac{1}{2} \times \left( \frac{d_i}{2} \right)^2 + \left( \frac{d_{ib}}{2} \right)^2 \right]
\]

\hspace{1cm} (3.1)

where \(V_{\text{tube}}\) : volume of a single nanotube; \(h\) : average height of nanotube; \(d_o\) : average tube outer diameter; \(d_i\) : average tube inner diameter; and \(d_{ib}\) : average tube inner diameter at the bottom.

\[
V = \frac{S}{a} \times V_{\text{tube}} \times 18
\]

\hspace{1cm} (3.2)
where $V$ : volume of the ATN film; $S$ : area of the ATN film; $a$ : a defined area of 0.25 µm$^2$; for average 130 nm tube outer diameters; maximum 18 tubes present in 0.25 µm$^2$ area.

**Table 3.2 Volume evaluation data for three different ATN films.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Estimated V (cm$^3$)</th>
<th>Volume of consumed Ti film (cm$^3$)</th>
<th>Volume expansion ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2 µm</td>
<td>0.000255</td>
<td>0.000140</td>
<td>1.82</td>
</tr>
<tr>
<td>4.8 µm</td>
<td>0.000270</td>
<td>0.000145</td>
<td>1.85</td>
</tr>
<tr>
<td>9.5 µm</td>
<td>0.000828</td>
<td>0.000461</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The expansion ratios derived from the evaluated titania volumes and the consumed Ti volumes for all three cases are within the range of the Pilling-Bedworth ratio for compact TiO$_2$ oxide which is approximately 1.9. This indicates that the oxide growth of the three ATN films was indeed very close to 100% efficiency. This highly efficient growth is further confirmed by Figure 3.9b, where the evaluated volumes of the three ATN films and their respective total charge recorded during anodization are plotted against the volumes of compact titania predicted by Faraday’s Law. The relationship between the formed titania volume and the used charge under Faraday’s Law can be expressed as:

$$V_{TiO_2} = \frac{Q \times M_{TiO_2} \times \eta}{z \times F \times \rho_{TiO_2}}$$

(3.3)

where, $V_{TiO_2}$ : volume of formed oxide; $Q$ : total charge used, $M_{TiO_2}$ : molar weight of TiO$_2$ = 79.88 g mol$^{-1}$, $\eta$ : oxidation efficiency = 1, assuming 100% efficient; $z$ : = 4, assuming a four-electron reaction; $F$ : Faraday’s constant = 96500 C mol$^{-1}$; $\rho_{TiO_2}$ : density of TiO$_2$ = 3.89 g cm$^{-3}$. As can be seen, the cases of 2.2 and 4.8 µm ATN films have a very good match with the prediction from the Faraday’s law, while for the case of 9.5 µm ATN film, the
recorded charge of 21.91 C produced a smaller oxide volume than the prediction. It is believed the extra charge was taken for more gas evolution at the electrode surface during its relatively longer anodization.

Figure 3.9 (a) geometric models of a single nanotube for all three samples to evaluate the volume of the ATN films, (b) relationship between formed oxide volume and total charge predicted by Faraday’s Law; the estimated volumes of ATN films of all three samples are plotted against the total charge recorded during their respective anodization.

3.3.3.2 XPS and ICP-MS measurements

Figure 3.10a presents the XPS patterns which were obtained by the author to study the composition of the ATN films. It depicts that the Ti2p binding energy peaks at 458.6 eV, which is the value for a standard TiO₂ bond. Fluorine is found to be the only impurity in the ATN film; this anion intake is common in electrochemical formation of oxide and the large increase of film thickness is unlikely to be caused by such small element. After annealing, the
presence of fluorine species was negligible. The author also used ICP-MS to determine the composition of the post-anodization electrolytes of the three cases and a fresh electrolyte and one that has been used for over 3 hours was also analyzed. Figure 3.10b shows that the concentrations of Ti ions in the first three electrolytes are all less than 50 ppm. This would suggest that, most of the Ti ions from the sputtered films are used to form the tubular oxide structure and remain in the oxide after brief periods of anodization.

**Figure 3.10** (a) The XPS spectra of the ATN film before and after annealing, (b) Ti ion concentration in 50 mL electrolyte after anodization normalized to fresh electrolyte, column 1, 2, 3 and 4 corresponds to electrolyte used to anodize 0.9 µm, 1.8 µm, 3.2 µm Ti films and Ti film for >3 hours.

### 3.3.4 Mechanism for the rapid formation of ATN

Considering all the analyses above, it is evident that this rapid formation of ATN films on FTO glass is somehow contradictory to the conventional model, that no Ti ions are lost during the process. Therefore, the author proposes a modified ATN formation mechanism, as illustrated in Figure 3.11. Under particular anodization conditions, e.g. 10 – 20 mA cm$^{-2}$ steady-state anodic current density and relatively short anodization time, the
TiF$_6^{2-}$ ions produced from the complexation of Ti$^{4+}$ and F$^-$ ions are driven back towards the anode by the electric field. The TiF$_6^{2-}$ ions are polarized again near the already-formed titania structure and contribute Ti$^{4+}$ ions to the formation of new oxide. This new oxide formation may have played an important role to the large thickness increase from the sputtered Ti films to ATN films. Understanding the mechanism of this rapid formation of ATN films on FTO glass is very important for producing high quality film on a consistent basis, which is a crucial factor for the successful implementation of this material to DSCs application.

Figure 3.11 Illustration of the modified ATN formation mechanism for the rapid growth of ATN films on FTO under optimum anodization conditions.

3.4 Chapter summary

It was shown that ATNs come through different stages of development and the most efficient growth of ATN films is achieved by the combination of organic electrolyte, low water content and high anodization voltage. However, most Ti anodizations are carried out using Ti foils, thus the DSCs made using foil-based ATN films have a major disadvantage as
the amount of receivable light energy is reduced, when it is illuminated from the back-side. In a quest to fabricate transparent ATN films on TCO glass substrates, the efficient ATN film growth strategy is required to be implemented. However, the author found that ITO glass was degraded by the substrate heating during the sputtering process. For the FTO case, only certain settings of the anodization parameters are capable of producing high quality ATN on the FTO glass. During the course of anodizing sputtered Ti films, much greater than expected increase of film thickness was observed when comparing the films before and after anodization. This film thickness variation was explained using a number of analytical tools and all the analyses lead to the development of the novel mechanism for the rapid formation of ATN film which is different from the conventional model.

3.5 References


nanotube arrays sensitized with a donor-antenna dye, Nano Lett. 8 (2008), no. 6, 1654-1659.


Chapter 4 – Preparations of nanostructured WO₃ on FTO glasses

4.1 Introduction

As reviewed in Chapter 2, there is a large variety of synthesis techniques for obtaining nanostructured WO₃, however, this PhD study focus only on nanostructuring WO₃ through anodization and the preparation of WO₃ nanoparticle films. Similar to the synthesis of anodic titania tube (ATN) films on fluorine-doped tin oxide (FTO) glass, anodization of W is also conducted on sputtered W metal films on FTO glass to achieve a transparent and nanostructured photoelectrode.

TiO₂ nanoparticles are normally used for dye-sensitized solar cells (DSCs), therefore, it is directly comparable to also experiment WO₃ nanoparticles in DSC applications. Since WO₃ nanoparticles are widely available as a commercial product, the synthesis of WO₃ of this nanostructure form is not the subject of this work. Instead, the techniques of the preparation of WO₃ nanoparticle films and their characterizations are described in the second half of this Chapter.

4.2 Tungsten anodization

The galvanostatic anodization of W foil in oxalic acid electrolyte, producing nanoporous WO₃, was first reported in 2003 by Grimes et al.[1] This was followed by the demonstration of the self-organized nanoporous WO₃ anodized using NaF electrolyte.[2] During the anodization of W, it was shown that the porosity of WO₃ can be controlled by varying either the fluoride concentration or the applied voltage, or both at the same time. With high surface to volume ratio and enhanced electro-optical properties, the anodized surfaces have a great potential for the fabrication of optical and electronic devices. Schmuki et al.[3] obtained a large photocurrent response of 170 mA cm⁻² (with 0.75 V applied potential and
photocurrent normalized to 1 W lamp output) and 33 % incident photon-to-current conversion efficiency (IPCE) in the UV region with the annealed porous WO$_3$ layer obtained from a W foil. It is believed that the openness of the structure created much more electrolyte – WO$_3$ interfaces and resulted in such excellent photo-response. Unlike the attention received on the Ti anodization, there are only a handful of reports [4, 5, 6, 7, 8, 9] on W anodization and almost all the results obtained are based on anodizing the W metal foil, which is again a limiting factor to fully utilize the nanoporous WO$_3$. Similar to the Ti anodization discussion in the previous chapter, it is quite necessary to synthesize the nanoporous WO$_3$ structure directly on the FTO glass substrates for the DSC application.

4.2.1 Tungsten sputtering on FTO glass and the anodization conditions

The tungsten films used in this work were prepared by the same RF sputtering system, which was used for the Ti sputtering. A cathode W target of 99.95% purity was placed at 70 mm over the stage. The sheet resistance of the FTO glass substrates, which tungsten was sputtered on were 35 Ω square$^{-1}$. The base pressure of the sputtering chamber was 10 µTorr. Pure argon was introduced into the chamber, prior to sputtering, as the process gas and the process pressure was controlled at 20 mTorr; 35 mTorr; and 50 mTorr for different depositions. A constant 100 W RF power was used in the process, whereas the substrate temperature was chosen to be either room temperature or 300 ºC. The film thickness for each deposition was examined by scanning electron microscopy (SEM).

The anodization of the sputtered W films was carried out by the setup, which was described in Chapter 2. The chemical medium used in the system was an organic electrolyte, ethylene glycol (EG) with 0.5% (wt) NH$_4$F. Upon the completion of anodization, samples were washed using acetone and isopropanol and allowed to dry naturally. Crystalline WO$_3$
was obtained from the anodized samples through annealing by a standard laboratory furnace at 480 °C for 2 hours in 90% O₂ with a temperature ramping rate of 2 °C min⁻¹.

Photocurrent measurements were conducted using a broadband DH-2000-BAL UV-NIR deuterium tungsten halogen source (Ocean Optics) with 0.1 M of Na₂SO₄ electrolyte against a platinum electrode.

4.2.2 Characteristics of the sputtered tungsten films

During the process of sputtering of W onto FTO glasses, shattered films, due to interfacial stress, were always obtained using the process parameters similar to the Ti film sputtering. Literature suggests that the stress presents in a sputtered W film is caused partially by substrate expansion via heating and is due primarily to the increase of the film thickness,[10] and highly stressed films delaminate from the substrate in most cases. To tackle this problem, the author used high process gas pressure and high quality W films of 750 nm, 2.1 µm and 3.85 µm were produced at 50 mTorr in this work. However, cracking and delamination of films occurred at lower process pressures. The relationship between the stress of the sputtered W films and the process gas pressure was studied by Shen et al.[11] and they showed that the intrinsic stress of the RF sputtered W films gradually moves to zero pressure point, when the process gas pressure exceeds 60 mTorr. It is suggested that this could be due to the increase in the number of argon particles present in the chamber which provides a softer landing for the bombarded W particles. [11] The SEM images of the optically reflective and smooth W films are shown in Figure 4.1. For all 750 nm, 2.1 µm and 3.85 µm cases, the tungsten films show strong degree of adhesion to the FTO glass. It was observed that the sputtered W films consisted of extremely compact nanorods perpendicular to the substrate. Such nanorods have widths ranging from 10 to 100 nm and are made of arrow-head shaped W platelets (5 to 100 nm – at a 45° angle to the surface) stacked on top of each other.
Chapter 4 – Preparations of nanostructured WO$_3$ on FTO glasses

Figure 4.1 SEM images of the RF sputtered 3.85 µm W film on FTO glass, (a) top view, (b) cross sectional view.

4.2.3 Formation mechanism and SEM characterization of the anodic WO$_3$ films

The as-sputtered W films were anodized at three different voltages (20 V, 40 V and 60 V) in 0.5% (wt) NH$_4$F / ethylene glycol electrolyte for one hour. Unlike for the Ti anodization, the electrolyte used in the W anodization process is anhydrous, since the author found that the addition of water induced pinholes on the anodic films. The recorded anodization current transients are shown in Figure 4.2a; the initial anodization current density strongly depends on the anodization voltages, which were 25 mA cm$^{-2}$, 50 mA cm$^{-2}$ and 83 mA cm$^{-2}$ respectively for the 20 V, 40 V and 60 V cases. All three cases of anodization show similar trends in their current transients. These current transient curves are analogous to the ones from Ti anodization, which indicates that the formation mechanism of anodic nanoporous WO$_3$ and ATNs are similar. As can be seen, anodization currents drop sharply from their respective initial values down to 0.2 mA cm$^{-2}$ in less than 250 seconds, due to the rapid formation of oxide layers assisted by the applied electric field. Then the electric field-drifted fluoride ions arrive at the interface of the film and electrolyte, where they interact with
the newly-formed oxide layer and W ions, developing pores on the oxide layer. The electric field is strengthened locally by the porosified oxide layer, during which the current slightly increases from its initial local minimum. Eventually all anodization currents reach a similar steady state; which implies that the rate of dissolution of the oxide layer balances with the formation of the oxide layer.

SEM studies were carried out on the as-anodized 750 nm, 2.1 µm and 3.85 µm tungsten films and it was observed that different anodization voltages produced similar surface morphologies independent of the film thickness. In Figure 4.2b – d, the 20 V anodized W film shows no porous structure and the general morphology of the sputtered film is still apparent with etched-like jagged nanostructures being produced. Pores started to appear along the grain boundaries when 40 V was applied; but it is clear that the 60 V-anodization produces a more uniformly-distributed porous structure (pore sizes of 60 – 100 nm). A larger current transient during the initial and the steady-state stages may have contributed to more severe and homogenous etching of the surface in the 60 V anodization of W thin film. The cross-sectional view of the nanoporous WO$_3$ film is shown in Figure 4.2d insert. It is clear that the nanoporous structure is present throughout the film and the pores are interconnected. However, the thickness of the nanoporous film is only ~400 nm and it is independent of the anodization duration, voltage and electrolyte composition. This relatively small thickness of anodic nanoporous WO$_3$ may be problematic for dye sensitization, reducing the generation of photocurrent. Nonetheless, to the best of the author’s knowledge, this is the first ever reported anodization of sputtered W films on FTO glass.[12]
Figure 4.2 (a) Current transient curves recorded during the anodization at different voltages with 0.5% (wt) NH₄F / ethylene glycol electrolyte and the resulting surface morphologies of anodized W films at (b) 20V, (c) 40V, (d) 60V (insert: cross sectional SEM image).

4.2.4 XRD patterns and physical images of the anodic WO₃ films

In Figure 4.3a, the author presents the XRD patterns obtained for the pure FTO substrate, sputtered W film (750 nm) and anodized tungsten films (750 nm) before and after annealing. Three well-defined peaks indicative of the presence of β-tungsten (ICDD no. [47-1319]) are clearly seen in the sputtered film. The XRD data of the anodized sample revealed that the tungsten metal film had changed to a poorly-oxidized form of tungsten (W₃O) (ICDD
no. [41-1230]) and not into the fully oxidized WO$_3$. It is also likely that a small amount of tungsten metal remains underneath the porous layer, as evident by the broad and unsymmetrical peaks at 35.3, 39.8 and 43.8° 2θ. After annealing, the nanoporous films clearly displayed the crystal structure of orthorhombic WO$_3$ (ICDD no. [20-1324]). It is interesting to note that the WO$_3$ has a much more intense peak in the (001) plane at 2θ = 23.25°. The XRD data of the pure FTO substrate is shown as a reference and tin oxide (SnO$_2$) peaks from the FTO substrate are clearly visible in the XRD data of the other samples due to the small thickness of W and WO$_3$.

A comparison of physical images of the samples is shown in Figure 4.3b, where photos of sputtered W films (750 nm) before and after anodization; and the anodized film after annealing were presented. Clearly, anodization has changed the metallic finish of the sputtered W film. The anodized W film before annealing has quite a dark color, since W film was only slightly oxidized after the anodization process. However, a great degree of transparency was obtained for the anodized sample after annealing, indicating the tungsten film is fully oxidized. This is in agreement with the XRD pattern of the annealed-anodized sample.
Figure 4.3 (a) XRD patterns of the FTO substrate, the plain sputtered 750 nm W film as well as the 60V-anodized 750 nm W films before and after annealing, (b) digital photos of 750 nm (left) sputtered W film; (middle) after 60V anodization; (right) as-anodized film after annealing, (c) photocurrent responses of nanoporous WO\textsubscript{3} and sputtered WO\textsubscript{3} in broad UV-vis illumination with no biased voltage. The switch-on / -off periods are both 10 seconds; electrolyte is 0.1 M Na\textsubscript{2}SO\textsubscript{4} aqueous solution.
4.2.5 Enhanced photocurrent produced by anodic \( \text{WO}_3 \) films

Photocurrent measurements were performed by the author on the 60 V-anodized annealed nanoporous \( \text{WO}_3 \) film vs compact \( \text{WO}_3 \) (deposited using reactive RF sputtering with 90% \( \text{O}_2 \) and 10% \( \text{Ar} \)) of the same thickness to validate the enhanced performance of nanoporous structure and the results are displayed in Figure 4.3c. Under a broad UV-vis source and no external voltage applied, a photocurrent density of 27 \( \mu \text{A cm}^{-2} \) was generated by the annealed nanoporous \( \text{WO}_3 \), whereas only 4.8 \( \mu \text{A cm}^{-2} \) was produced by the compact \( \text{WO}_3 \) under the same conditions. Furthermore, the annealed nanoporous \( \text{WO}_3 \) has quicker responses to both light-on and light-off instants. These results indicate that the inter-network of pores allows the electrolyte to diffuse more easily and nanoporous structure provides a much larger surface exposed to the electrolyte, hence producing a larger photocurrent.

4.3 Fabrication of \( \text{WO}_3 \) nanoparticle films

In order to obtain thick nanostructured \( \text{WO}_3 \) films in the order of tens of microns for the implementation in DSCs, \( \text{WO}_3 \) nanoparticles were prepared in ways analogous to the typical \( \text{TiO}_2 \) nanoparticle films used for standard DSCs.[13] These \( \text{WO}_3 \) nanoparticles were purchased from Nabond Technologies Co. Ltd, with the particle size specified in the range of 20 to 200 nm. Prior to the use, the \( \text{WO}_3 \) nanoparticles were refined firstly by precipitation and then by centrifugation to remove the larger particles. The size of the particles used in the experiments was determined to be mainly around 40 nm using SEM.

The \( \text{WO}_3 \) paste used in this study adapted from the recipe of \( \text{TiO}_2 \) paste for screen-printing.[13] The refined \( \text{WO}_3 \) nanoparticles were firstly mixed with ethyl cellulose and terpineol in the ratio of 18:9:73, then absolute ethanol was added to the mixture to help dissolve the cellulose. In order to obtain a homogenous \( \text{WO}_3 \) paste free of aggregates and clumps, the final mixture was stirred overnight and then ball milled for 24 hours.
Subsequently, it was placed into a rotary evaporator to remove all the ethanol content. These processes resulted in a metal oxide paste with 18% (wt) WO$_3$ of light green color. Recipes for doctor-blade and spin coating techniques were also tried on preparing the WO$_3$ paste, however cracks were found on the films made using these methods.

To deposit the WO$_3$ nanoparticle film, a scotch tape with a cut-out area in the middle was firstly placed onto the FTO glass substrate (30 $\Omega$ square$^{-1}$), then the WO$_3$ paste was dropped in the cut-out area and formed into films by running a Razor blade on the scotch tape. The thickness of the film could be conveniently increased by repeating this deposition process on top of the already-annealed film. The author found that a small amount of ethanol added to the paste would facilitate the process, which resulted in more uniform films. The as-prepared samples were annealed at 490 °C for 2 hrs to burn out the cellulose and terpineol; the annealing process also helped the WO$_3$ nanoparticles join together and induced strong adhesion between the WO$_3$ films and the FTO glass substrates.

SEM was employed to characterize the particle size and surface morphology of the WO$_3$ film. Raman measurements were conducted using a 514 nm laser source and an Ocean Optics QE65000 spectrometer with the spectra resolution of 6 wavenumbers. The XRD analysis was utilised to depict the crystal structure of the WO$_3$ nanoparticles.

4.3.1 SEM characterization of the WO$_3$ nanoparticle films

For efficient DSCs, the implementation of uniformly porous metal oxide nanoparticle films as the photoanode layer is essential, as it truly allows photocurrent enhancements due to the large surface to volume ratio. In the preparation of these WO$_3$ nanoparticle films, the author found that the key in obtaining uniform WO$_3$ nanoparticle films is to ball mill the WO$_3$ nanoparticle paste before it is applied onto the FTO glasses. The effect of ball milling is
clearly displayed in Figure 4.4a and b, where large clumps of \( \text{WO}_3 \) nanoparticles were observed for films without ball milling (Figure 4.4a). These large clumps severely degrade the quality of the film and promote cracks on the film during the annealing process. On the contrast, high quality \( \text{WO}_3 \) nanoparticle films are obtained from the paste that has been ball milled for 24 hrs (Figure 4.4b). Figure 4.4c depicts the top view of high quality \( \text{WO}_3 \) film, which possesses a high degree of porosity. The magnified view of the film can be seen in the insert of Figure 4.4c, where the size of the nanoparticles ranges from 10 to 100 nm, however, the majorities are around 40 nm. The cross-sectional view in Figure 4.4d shows the porosity and the particle size is uniform across the whole film.

**Figure 4.4** SEM images showing the surface of the \( \text{WO}_3 \) nanoparticle film deposited on FTO glass. (a) The \( \text{WO}_3 \) nanoparticle paste was applied directly without ball milling, (b) with 24 hr ball milling before use, (c) the close-up view of the \( \text{WO}_3 \) film, insert: magnified view featuring the particle size of \( \text{WO}_3 \) and (d) the cross-sectional view of the \( \text{WO}_3 \) nanoparticle film.
4.3.2 Crystal phases of the annealed-WO$_3$ nanoparticle films

In the literature review of this thesis, the author has revealed that, for TiO$_2$ based DSCs, anatase is the most superior material compared with rutile as well as the amorphous TiO$_2$,[14] although the reasons for choosing anatase TiO$_2$ are not agreed upon entirely. Therefore, it is highly desirable to compare the DSC performances based on WO$_3$ with different crystalline structures, despite the fact that the crystal structure of WO$_3$ is much more complex than TiO$_2$ which was stated in Chapter 2. Since removing the cellulose content in the WO$_3$ paste requires at least 420 °C, only the crystal structure of the films annealed above this temperature were examined. The Raman spectra in Figure 4.5a shows that the as-purchased WO$_3$ powder has broad and stretched peaks which are the indication of poor crystallinity and presence of hydrated WO$_3$.[15] For the WO$_3$ films annealed at 490 and 630 °C, the Raman spectra peaks are in similar locations and both show highly crystalline structures. As reported in one of the author’s publications[16], the Raman peaks at 278, 333, 718 and 815 cm$^{-1}$ attribute mainly to the monoclinic phase, however Raman peaks for the orthorhombic phase are also adjacent to the wavenumbers mentioned above, as a result the authors believe that both phases are likely to co-exist in the material. This multi-crystalline property of the WO$_3$ nanoparticle is further confirmed by the XRD analysis presented in Figure 4.5b, where very similar XRD patterns of the two WO$_3$ films show both monoclinic and orthorhombic peaks, with peaks that tend to overlap with each other. Although generally reported [17] that liquid phase synthesized WO$_3$ turns into orthorhombic and monoclinic at 320 °C and 150 °C annealing temperatures, respectively; the as-purchased WO$_3$ was gas phase synthesized, which was already partly crystalline with prominently monoclinic phase. It is suggested that annealing temperatures up to 750 °C [18] are used for obtaining tetragonal WO$_3$, unfortunately, this crystal phase has to be ruled out in this research as such high temperatures
are not practical for the FTO glass substrates. As a result, strictly mono-crystalline WO$_3$ could not be investigated and only multi-crystalline WO$_3$ was studied. Therefore, only the 490 °C-annealed WO$_3$ were implemented in DSC characterization.

**Figure 4.5** (a) Raman spectra of the as-purchased WO$_3$ powder, 490 and 630 °C annealed WO$_3$ films, (b) XRD patterns of the 490 and 630 °C annealed WO$_3$ films. The labelled peaks correspond to monoclinic WO$_3$ (Δ, ICDD no. 00-043-1035 C), orthorhombic WO$_3$ (●, ICDD no. 00-020-1324 I) and FTO substrate (◊).
4.3 Chapter summary

The synthesis details of anodic nanoporous WO$_3$ and the preparation of WO$_3$ nanoparticle films were outlined in this Chapter. The author showed that the quality of the sputtered W films on FTO glass is found to be heavily dependent on the processing gas pressure. The anodization of sputtered W films was able to produce a uniform and nanoporous structure, where the surface morphology was mainly controlled by the applied voltage. Using the anodic current transient analysis, the author believes that the formation of anodic nanoporous WO$_3$ has a similar mechanism as to Ti anodization. The obtained WO$_3$ nanoporous film was visibly transparent and had significantly higher photocurrent generation when it is compared with a similar compact WO$_3$ film.

Also in this Chapter, the preparation of the WO$_3$ nanoparticle films adapted the technique, which is used in standard TiO$_2$-DSC fabrication, was performed by the author. Ball milling treatment to the WO$_3$ nanoparticle paste is crucial for forming high quality films, as it can efficiently break up particle clusters that are developed during the paste formation. However, dual crystal phases were found in these WO$_3$ nanoparticle films after high temperature annealing, although mono crystal phase may be more preferable for the analysis of WO$_3$ used as a photoanode material for DSCs. Nonetheless, the film thickness of WO$_3$ nanoparticles was highly controllable.

4.5 References

Chapter 4 – Preparations of nanostructured $\text{WO}_3$ on FTO glasses


Chapter 5 – DSCs preparations and testing results

5.1 Introduction

In this chapter, the experimental methodology and solar cell performances based on the nanomaterials described in Chapter 3 and 4 will be presented. The fabrication of these devices follows the standard process reported in literature. The custom designed solar cell testing station was used for characterizing the $J-V$ curves of each individual device. These cell performances are also plotted against the controlled devices.

5.2 Device fabrication process

One of the main advantages of the dye-sensitized solar cells (DSCs) is their ease of fabrication and Figure 5.1 illustrates the process for the DSCs fabrication in this work. The DSCs are based on both anodic titania nanotubes (ATNs) glass and WO$_3$ nanostructures on fluorine-doped tin oxide (FTO) which were described in the previous chapters.

![DSCs fabrication process](image)

Figure 5.1 DSCs fabrication process.
Photoelectrode sensitization – after obtaining a transparent ATN film or WO$_3$ nanostructure film on the FTO glass substrate, the photoanode layer together with the working electrode (which can be termed as “photoelectrode”) is annealed at 480 ºC for 2 hrs to induce the crystallinity. As the annealed photoelectrode cools down to approximately 80 ºC, it is then immediately immersed into a 20 mM N3 dye (tris(2,2’-bipyridyl-4,4’-carboxylate) Ru (II), DYESOL Ltd) solution to minimize the absorption of air moisture on the photoelectrode. The duration for the sensitization is generally 24 hrs and ethanol is used as the solvent for the dye.

Packaging – The counter electrode, which a 10 nm layer of Pt is sputtered onto the FTO, is drilled with a 0.5 mm hole. Packaging of the cell is done by placing a heat-cure gasket (~25 µm thickness, ionomer Surlyn 1702, Dupont) with a cut-out area slightly bigger than the photoanode layer onto the working electrode and then the counter electrode is pressed firmly against the working electrode. To cure the gasket, the cell is heat treated at ~125 ºC for no more than 30 s. During the heat curing, adequate pressure needs to be applied on the counter electrode to squeeze out the air, which is trapped between the gasket edges and the glass substrate.

Electrolyte filling – Finally a drop of electrolyte (DYESOL high performance electrolyte (EL-HPE) with I$_3^-$/I$_2$ as the redox species, inorganic iodide salt, organic iodide salt and pyridine derivative as the additives dissolved in acetonitrile and valeronitrile) is placed onto the hole at the counter electrode and the cell is filled with electrolyte via vacuum back filling technique. The hole on the counter electrode is then sealed to prevent electrolyte evaporation. To make electrical contacts, normal electrical wires are bonded to the two electrodes using silver paste.
The physical images of such DSCs are shown in Figure 5.2, from left to right, ATN obtained on Ti foil, ATN obtained on FTO glass and WO$_3$ nanoparticle film based device.

**Figure 5.2** Photos of DSCs that are made from ATN on Ti foil (left), on FTO glass substrate (middle) and one that is based on WO$_3$ nanoparticle film (right).

### 5.3 Solar cells testing apparatus and calculations of performance characteristics

The performances of the fabricated DSCs were characterized by the author using a custom-made solar cell testing station. It consists of a ABET Technologies LS-150 solar light source fitted with an AM 1.5 filter which produces a spectrum as shown in Figure 5.3. The illumination power density on the surface of the cells is consistently kept at 90 mW cm$^{-2}$. For each $J$-$V$ measurement, the power is calibrated using a Thorlab PM100 Light power consol fitted with a S120C light sensor (400-1000 nm). The Keithly 2602 source meter is utilized to output the voltage which is against the one produced by the cell at a sweeping rate of 0.01 V s$^{-1}$. At the same time, this source meter records the current generated by the cell in negative polarity. These $I$-$V$ characteristics are then fed to a Labview program which produced the $J$-$V$ data based in the active area of the cell. The incident-photon-to-electron conversion efficiency (IPCE) measurements were conducted using a 1000 W Xe lamp and a
monochromator. The monochromator is controlled by a computer, which sets the wavelength scan rate and range. The range used in this work is from 400 to 800 nm.

Figure 5.3 The solar spectrum produced by the LS-120 solar simulator fitted with an AM 1.5 filter.

For the measurements of DSC performance parameters, the short-circuit current density \( J_{sc} \) and the open-circuit voltage \( V_{oc} \) are observed as depicted in Figure 5.4. This Figure also shows the indications of the maximum current density \( J_m \) and the maximum voltage \( V_m \). The other parameters are calculated as follows:\[1\]

**Maximum power density:**

\[
P_m = |J_m| \times V_m \tag{5.1}
\]

**Fill factor:**

\[
F.F. = \frac{P_m}{|J_{sc}| \times V_{sc}} \tag{5.2}
\]

**Efficiency:**

\[
\eta = \frac{P_m}{90 \ (mW \cdot cm^2)} \times 100\% \tag{5.3}
\]
5.4 Testing results for ATN-DSCs with front side illumination

The DSC performances of ATN on FTO, with the comparison to the ones on Ti foil as well as TiO$_2$ nanoparticles DSC are represented by the respective $J$-$V$ characteristics curves in Figure 5.5a. In addition, Figure 5.5b shows the $J$-$V$ characteristics of the front-side illuminated ATN DSCs with 5.5 µm and 9.5 µm thick ATN films, respectively. The $J_{sc}$ becomes positive when the applied voltage exceeds the $V_{oc}$ generated by the cell. The performance data of these cells are summarized in Table 5.1.

**Table 5.1** Performances of TiO$_2$-DSCs made with a variety of parameters.

<table>
<thead>
<tr>
<th>Cell type</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>Fill Factor (F.F.)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5µm TiO$_2$ nanotube on FTO</td>
<td>650</td>
<td>-8.44</td>
<td>0.51</td>
<td>3.11</td>
</tr>
<tr>
<td>5.5µm TiO$_2$ nanotube on FTO</td>
<td>650</td>
<td>-6.66</td>
<td>0.51</td>
<td>2.44</td>
</tr>
<tr>
<td>11µm TiO$_2$ nanotube on Ti foil</td>
<td>670</td>
<td>-7.02</td>
<td>0.5</td>
<td>2.59</td>
</tr>
<tr>
<td>12µm TiO$_2$ nanoparticle on FTO</td>
<td>770</td>
<td>-8.81</td>
<td>0.63</td>
<td>4.78</td>
</tr>
</tbody>
</table>
Despite the fact that the reported electron diffusion length and electron life time are both much greater for ATN than for TiO_2 nanoparticle network, the efficiency of ATN-DSCs is still lower in comparison to that of TiO_2 nanoparticle DSCs. In particular, both the open-circuit voltage and the fill factor need to be improved. A recent publication experimentally showed that the electron mobility in ATNs is high, however, the injected electrons can be immobilized in the trap sites which are created by the nitrogen and fluorine impurities in the structure.[2] For comparable thickness of ATN photoanode layer, it is clearly seen that the short-circuit current density of FTO-based ATN-DSC is significantly higher than that of Ti foil-based ATN-DSC, hence the efficiency is improved by 20% (from 2.59 to 3.11%). The author believes that this significant enhancement can be directly ascribed to the benefit from front-side illumination and the degree of improvement corresponds to the percentage of loss of light when illuminating from the back-side. Furthermore, FTO-based ATN-DSCs with different photoanode layer thickness were investigated. With an increase of ATN film thickness from 5.5 to 9.5 µm, \( J_{sc} \) increases from -6.66 mA cm\(^{-2}\) to -8.44 mA cm\(^{-2}\). However, thicker ATN films could not be studied for DSCs in this work due to degradation of film quality, when FTO-based ATN film thickness increases beyond 10 µm.
Figure 5.5 $J-V$ characteristics for (a) front-side illuminated ATN-DSC, back-side illuminated ATN-DSC and the DSC bases on TiO$_2$ nanoparticle, (b) front-side illuminated ATN-DSCs, the thickness of the ATN is 5.5 and 9.5 µm, respectively.

5.5 WO$_3$ nanostructures for DSCs

The performances of WO$_3$-DSCs were evaluated by the author using two types of nanostructures: anodic nanoporous WO$_3$ and WO$_3$ nanoparticles. The following analysis provides the first experimental detail on DSCs that are based on a new photoanode material, WO$_3$. These results are fundamental in the research of DSCs and the investigation of WO$_3$ nanoparticle-DSCs was published in Langmuir by the author.[3]

5.5.1 DSCs based on anodic nanoporous WO$_3$

After dye sensitization, there was no visible color change observed on the anodic nanoporous WO$_3$ films. This is probably due to the relatively small thickness of the film. Also the isoelectric point (ISP) of WO$_3$ is commonly measured to be in a range from pH 0.2
to 0.5,[4] which suggests that negative charges are present on the surface of the WO$_3$ when it is immersed in the dye solution. Unfortunately, since the anchoring ligand of the N3 dye is the carboxylic group that is also negatively charged, dye adsorption on WO$_3$ films is slow and the dye may not be able to cover the entire WO$_3$ surface.[5] The $J$-$V$ characteristic of such DSC is shown in Figure 5.6. Since there is little dye attached onto the WO$_3$ surface, both $V_{oc}$ and $J_{sc}$ are very small, 0.13 V and -0.37 mA cm$^{-2}$, respectively. Also the unsettled dark current curve indicates the fill factor is poor which is highly likely caused by severe charge recombination.

![J-V characteristics of DSC based on anodic nanoporous WO$_3$ as the photoanode layer.](image)

**Figure 5.6** $J$-$V$ characteristics of DSC based on anodic nanoporous WO$_3$ as the photoanode layer.

5.5.2 Nanoparticle WO$_3$ for DSCs

Taking into consideration the low ISP of WO$_3$, the author carried out all the dye soaking processes for the nanoparticle WO$_3$-DSCs for at least 48 hours in order to achieve
better dye adsorption. Table 5.2 and Figure 5.7, respectively, present the cell performances and $J$-$V$ characteristics of the DSC based on WO$_3$ nanoparticle films of different thicknesses.

**Table 5.2** Performances of nanoparticle WO$_3$-DSCs made with a variety of parameters.

<table>
<thead>
<tr>
<th>Cell type</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>Fill Factor (F.F.)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5 µm WO$_3$ DSC</td>
<td>380</td>
<td>-3.29</td>
<td>0.4127</td>
<td>0.5733</td>
</tr>
<tr>
<td>6.5 µm WO$_3$ DSC</td>
<td>370</td>
<td>-3.84</td>
<td>0.4223</td>
<td>0.6667</td>
</tr>
<tr>
<td>12 µm WO$_3$ DSC</td>
<td>390</td>
<td>-4.61</td>
<td>0.3752</td>
<td>0.7495</td>
</tr>
<tr>
<td>15 µm WO$_3$ DSC</td>
<td>380</td>
<td>-4.67</td>
<td>0.3733</td>
<td>0.7361</td>
</tr>
<tr>
<td>630 ºC 4.5 µm WO$_3$ DSC</td>
<td>370</td>
<td>-3.35</td>
<td>0.4095</td>
<td>0.5640</td>
</tr>
</tbody>
</table>

**Figure 5.7** (a) $J$-$V$ characteristics and dark currents for the N3 dye sensitized solar cells based on nanoparticle WO$_3$ in film thicknesses of 4.5, 6.5 and 15 µm and (b) IPCE for all the cells described in (a).

It was found that the efficiency of the best nanoparticle WO$_3$ DSC reached 0.75%. The $V_{oc}$ of cells were recorded to be approximately 390 mV, which was very close to the initial prediction in Chapter 2. The DSCs obtained using 630 ºC-annealed WO$_3$ nanoparticle
films have similar performance as to the ones with 490 °C–annealed films. As expected, the increase of film thickness enhances the photocurrent. A maximum ~ -4.60 to -4.70 mA cm$^{-2}$ ($J_{sc}$) was obtained for such DSCs with the layer thickness of 12 µm or more. The current started to be saturated for devices obtained using samples with WO$_3$ nanoparticle film thickness of over 12 µm, as there was not much difference in the measured $J_{sc}$ between 12 µm (-4.61 mA/cm$^2$) and the 15 µm (-4.67 mA/cm$^2$) cells. This is likely due to the fact that the film thickness started to exceed the electron diffusion length.[6] In Figure 5.7a, it is clear that the $J$-$V$ characteristics of WO$_3$ based DSCs cannot match with the qualities of TiO$_2$ based DCSs. The relatively larger dark current and poorer F.F. may be caused by the fact that severe charge recombination is present within all the WO$_3$ based DSCs. As mentioned earlier, the dye coverage on the WO$_3$ film was less than ideal, resulting in direct contact between the electrolyte and WO$_3$ surface to some extent, as illustrated in Figure 5.8. As electrons are injected to the CB of WO$_3$ and transferred within the structure, some of them are likely to have interaction with the redox species on the WO$_3$ – electrolyte interface. Since I$_3^-$ is an active oxidant which can easily combine with electrons on the WO$_3$ surface and be reduced back to I$^-$.\[7\] Thus, via this route, some of the injected electrons are transferred to the counter electrode. This flow of electrons is opposite to the direction of photocurrent and directly contributes to increase the level of the dark current. It is also noticed that WO$_3$ DSC made from thicker nanoparticle film is seen to produce slightly lower F.F., which can be explained by the trend of the dark current density curves. Dark current increases with the film thickness, indicating that more charge recombination takes place in the WO$_3$-DSC with a larger film thickness. Considering the IPCE (Figure 5.7b), the 15 µm WO$_3$ DCS has the best IPCE as more light is absorbed by thicker films and a peak quantum efficiency of 45% in the 500 - 530 nm region was obtained. In comparison to the TiO$_2$-DSCs, WO$_3$ based DSCs efficiency is still much less. As discussed above, the amount of dye molecules adsorbed on
the WO₃ surface is believed to be the major problem, which leads to small photocurrents and the unfavorable charge recombination.

![Illustration of possible mechanism for the charge recombination in nanoparticle WO₃-DSCs.](image)

**Figure 5.8** Illustration of possible mechanism for the charge recombination in nanoparticle WO₃-DSCs.

### 5.5.3 TiCl₄-treated nanoparticle WO₃ for DSCs

As mentioned in the Introduction chapter, coating the SnO₂ with TiO₂ or ZnO for DSC can greatly minimize the problems of insufficient dye attachment and low $V_{oc}$.[8] Similar to this approach, the author improves the performances of WO₃-DSCs via coating the WO₃ with TiO₂. This coating provides a more basic oxide surface, which favors the dye adsorption. Furthermore, $V_{oc}$ should be larger because the excited electrons can now be injected to the more negative CB of TiO₂ then step down to the CB of WO₃, which was depicted in Figure 2.11.

Coating the WO₃ nanoparticle surface with TiO₂ was experimented by treating the sample using aqueous TiCl₄ solution at the elevated temperature of 70°C, in which the thermal hydrolysis of TiCl₄ takes place. Prior to making the TiCl₄ solution, both the TiCl₄
stock and de-ionized water were kept at 4 °C as TiCl$_4$ can be easily hydrolyzed to Ti(OH)$_4$ and HCl at room temperature. The annealed WO$_3$ electrodes were then immersed in 40 mM aqueous TiCl$_4$ solution at 70 °C environment for 1 hr. After the process, the WO$_3$ electrodes were washed thoroughly by ethanol and re-annealed at 480 °C for 30 mins to induce anatase TiO$_2$ coating. The surface morphology of the modified samples is examined by SEM and the Ti element is confirmed by energy-dispersive X-ray spectroscopy (EDX).

As shown in Figure 5.9a, the TiCl$_4$ treated WO$_3$ surface morphology is dramatically different from the plain nanoparticle WO$_3$. It is evident that small flakes and dots are now developed around the WO$_3$ nanoparticles. It was seen that the modifications occurred in the whole bulk of the thin film and the strong presence of Ti element was detected by EDX analysis (Figure 5.9b and insert). After immersing in the dye solution, the physical photos in Figure 5c shows that the treated WO$_3$ film looked remarkably deeper in color compared with the sensitization of untreated WO$_3$. The performance of a 12 µm treated WO$_3$-DSC is shown in Figure 5.9c, exceptional improvements are found in every aspect with a $V_{oc}$ of 490 mV, $J_{sc}$ of -6.67 mA cm$^{-2}$ and a nearly doubled overall efficiency reaching 1.46%. While Figure 5.9c depicts the improvement on $J$-$V$ characteristics made by the TiCl$_4$ treatment, Figure 5.9d presents that the quantum efficiency of nanoparticle WO$_3$-DSC is also enhanced by the treatment, as the peak efficiency approached 55% and a broader peak range of 460 to 570 nm was observed. However, the TiCl$_4$ treated WO$_3$ DSC still performed in the lower end compared with the standard TiO$_2$-DSCs, because the TiO$_2$ coating did not form a complete shell structure to fully insulate the WO$_3$ surface. Therefore, the charge recombination level within the cell could still be very high.
Figure 5.9 (a) top view of the TiCl$_4$ treated WO$_3$ nanoparticle film and the magnified view as insert, (b) cross-sectional view of the film, insert: EDX showing the presence of Ti element, (c) J-V characteristics of the TiCl$_4$ treated 12 µmWO$_3$-DSC in comparison with the untreated one and their corresponding physical photos and (d) the IPCE for the TiCl$_4$ treated 12 µmWO$_3$-DSC.

5.6 Chapter summary

From the testing results obtained for ATN, it is clear that the DSC made using the ATN on FTO outperforms the one produced using ATN on Ti foil. The efficiency of the FTO-based ATN-DSC fabricated in this work achieved 3.11%, compared to the 2.59%
obtained for the foil-based ATN-DSC. This performance enhancement is mainly contributed by the fact that front-side illumination is enabled by the ATN on FTO configuration and the degree of improvement matches with the light loss due to the back-side illumination. The devices based on ATN on FTO glass are still considerably less efficient than DSCs made using TiO$_2$ nanoparticles film. Despite some reports have indicated the electron diffusion length and life time are superior in ATN than in the TiO$_2$ nanoparticle structure, there is not yet a report on ATN-DSC which has a greater efficiency than that of the standard TiO$_2$ nanoparticle devices. The reason for this discrepancy is still an unknown, however, the recent report in Nature Nanotechnology found that the impurities in the ATN structure may be responsible for the lower efficiency, experienced by the ATN-DSCs.[2]

For WO$_3$-DSCs, the author has found that the anodic nanoporous WO$_3$ film was unsuitable to be used as a photoanode layer, as this nanostructured layer was rather thin. Thus, extremely small amount of dye molecules were able to anchor onto the oxide surface. DSCs made using thicker WO$_3$ nanoparticle films produced more readable results. However, the performances were less than ideal, as all the efficiencies recorded were less than 1%. The author attributes the subdued performance of WO$_3$-DSCs to the sever charge recombination within the device. The very low ISP of the WO$_3$ surface was not favorable for dye attachment and this poor dye coverage was believed to create a large amount of electrolyte-WO$_3$ interfaces, where the charge recombination most likely takes place. Coating the WO$_3$ with TiO$_2$ was taken as the mitigation strategy. The TiO$_2$-coated WO$_3$ DSC was up to 1.5% efficient.
Chapter 5 – DSCs preparations and testing results

5.7 References


Chapter 6 – Conclusions and future work

8.1 Conclusions

During his PhD candidature, the author focused on a holistic, yet comprehensive approach for the development of alternative photoanode nano-morphology and material for the use in dye sensitized solar cells (DSCs). Chapter 1 of this thesis introduces the background information on today’s energy issues, photovoltaics and DSCs and also briefly explains the motivations for studying anodic titania nanotubes (ATNs) and WO₃ for developing DSCs. Chapter 2 provides the readers with a general review on the basic principles of DSCs, the fundamental properties of TiO₂ and WO₃ and the synthesis methods for obtaining ATNs as well as various WO₃ nanostructures. The experimental details of obtaining ATN on transparent conductive oxide (TCO) glasses as well as the characterizations of the films are presented in Chapter 3. In Chapter 4, the synthesis of anodic nanoporous WO₃ and the preparation of WO₃ nanoparticle films are described. The author presents the performance data of the DSCs fabricated using ATN and nanostructured WO₃ on fluorine-doped tin oxide (FTO) glass, respectively in Chapter 5. Finally, the last Chapter gives conclusive comments from the works that have been presented and indentifies areas for future investigations.

In summary, the novel outcomes, which have been presented by the author of this thesis, can be divided to three major areas:

1. Synthesis of ATN films on TCO glasses

Due to the disadvantages of the ATN films produced from Ti anodization on Ti foil substrates, this PhD study investigated the possibility of efficiently growing ATN films directly on TCO glasses. The author and his colleague demonstrated that nanotubular structures can be obtained by anodizing Ti metal films RF sputtered on indium tin oxide...
(ITO) glasses. However, only Ti films which were sputtered with 300 °C substrate temperature can sustain the anodization process and were able to be transformed to ATN films. Unfortunately this high substrate temperature significantly reduces the conductivity of the ITO surface, thus leading to lower efficiency when it is used as the working electrode in DSCs.

The other TCO glass is FTO glass, which has better thermal and chemical stability than ITO glass. Ti metal films are also RF sputtered on the FTO glass substrates at 300 °C by the author. It was found that efficient anodization (high voltage, organic electrolyte and low water content) of the Ti films could produce high quality ATN films in relatively short durations. These ATN films formed only within the steady-state anodic currents range of 10 – 20 mA cm\(^{-2}\). This anodic current range corresponds to anodization parameters of 60 V and electrolyte solutions containing 0.3 to 0.5% (wt) NH\(_4\)F with 2 to 3% (vol) H\(_2\)O. The effect of typical anodization conditions on the as-synthesized ATN films are summarized as follows:

- **Voltage** – tube diameter increases from 40 nm to 90 nm when voltage is raised from 20 V to 80V. In contrast, the thickness of tube wall is inversely proportional to the voltage. The author believes that the voltage is the main control over the ATN morphology. Voltage was also found to affect the growth rate of ATNs, as the movement of ions is faster when larger drifting force is present due to higher applied voltage.

- **NH\(_4\)F concentration** – high fluorine content (>1% wt) always induces high growth rate, which irregular structures tend to be produced causing film delamination. However, if the concentration was too low (<0.3% wt), the duration of anodization prolonged and this can also damage the films due to chemical dissolution which becomes increasingly dominant at the equilibrium stage of the anodization process.
• **Water content** – the effect of water content in the electrolyte can be directly seen from the anodic current transients. It is shown that anhydrous electrolytes induced the largest steady-state current in comparison to the electrolytes with 2 – 10% (vol) H₂O. The author believes that the generation of oxygen ions is more difficult with insufficient water in the electrolyte; hence the system is less resistive due to less oxide formation. On the other hand, excessive water content suppresses ionic conduction on the oxide-electrolyte interface.

With optimum anodization conditions, the growth of ATN films is rapid with average rate of 0.6 µm min⁻¹. The resultant ATN films had excellent adhesion to the substrates with high transparency in the visible spectrum and anatase phase can be easily induced by annealing the films at 480 °C for 2 hrs. The high efficiency and facile synthesis process are very important in the commercialization of these ATN films.

The author’s investigation on the as-prepared ATN films also revealed that the increase of film thickness greatly exceeds what would have normally been obtained in the case of Ti metal converting to compact TiO₂. After using a number of analytical tools, including actual volume estimation, Faraday’s law, x-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectroscopy (ICP-MS), it was found that there is little loss of Ti ions to the electrolyte during this rapid formation of ATN films. All the initially-etched Ti ions are most likely repolarized under the strong electric field and reused in the formation of the structure. The author believes this finding is fundamentally important to the research of formation mechanism of ATNs. Also, understanding physics behind this thickness variation is crucial for producing high-quality ATN films on FTO glass on a consistent basis.
2. Preparations of WO₃ nanostructures

Diversity of photoanode materials is key to the expansion of DSC applications and finding systems with high efficiency. To the knowledge of the author, WO₃ has never been investigated for DSCs, despite its similar properties as to TiO₂ and it is one of the most acid-stable metal oxides known today. As one of the objectives set out for this PhD study, WO₃ was investigated for the use as an alternative photoanode material in DSCs. Since nanostructuring of the photoanode layer is one of the most critical elements of DSCs, different synthesis methods obtaining various nanostructured WO₃ were reviewed by the author. Due to the scope of this thesis and the time constrains of the PhD candidature, only electrochemical anodization as well as commercially available nanoparticles were considered for constructing the nanostructured WO₃ photoanode layer.

Similar to the description of Ti anodization, the W anodization was also carried out on the RF sputtered W metal films on FTO glass using the standard experimental setup. The author found that the sputtering of W required higher-than-usual process gas pressure (50 mTorr) to produce high quality films. Uniformly nanoporous structures were obtained after the as-sputtered W films were anodized at 60 V in 0.5% (wt) NH₄F / ethylene glycol electrolyte for one hour. The pores size from 60 to 100 nm and they are interconnected throughout the whole thickness of the film. This as-prepared anodic nanoporous WO₃ film is visibly transparent and orthorhombic phase could be obtained after 480ºC-annealing processes. In the author’s opinions, this nanoporous structure is highly favorable for applications, where gas or liquid electrolyte requires to efficiently infiltrate the structure, creating more reaction interfaces. This was confirmed by photocurrent measurements where the nanoporous film produced more than 5 times larger response than that of the compact film. However, the maximum thickness of the anodic nanoporous WO₃ film that can be
achieved so far is only approximately 400 nm and this relatively small thickness limits the use of this nanoporous structures as the photoanode layer in DSCs.

As to the WO$_3$ nanoparticle films, the preparation technique and the material characterizations were presented in this thesis. In order to make a direct comparison to the standard DSCs, the author adapted a process similar to the one used in TiO$_2$ nanoparticle film preparation to fabricate the WO$_3$ nanoparticle films. The WO$_3$ nanoparticles were firstly refined, then prepared in paste form and finally deposited on the FTO glass using the “Doctor blading” technique. Before the film deposition, overnight ball milling of the WO$_3$ nanoparticle paste was found to be essential for breaking up the particle clusters, ensuring the uniform distribution of the nanoparticles. The thickness of these nanoparticle films was highly controllable and could be increased by just repeating the deposition after drying the previous layer. The nominal size of the WO$_3$ nanoparticles was measured to be approximately 40 nm using scanning electron microscopy (SEM), while the crystal phases exist in the 490 ºC annealed films were characterized to be monoclinic as well as orthorhombic by x-ray diffraction (XRD) and Raman spectrometry. Although monocrystallinity is preferred for the analysis WO$_3$-DSCs, it could not be achieved in this work, as the annealed-WO$_3$ nanoparticle films tend to retain the orthorhombic phase to a certain extent after cooling down and these orthorhombic phase partially reversed back to monoclinic at room temperature. Tetragonal WO$_3$ was also not viable for device fabrication in this study, as the high temperature required to induce tetragonal phase exceeds the thermal tolerance of FTO glass.

3. DSCs results

The final subject in this PhD study was to evaluate the performances of DSCs made using ATN on FTO and WO$_3$ nanostructures, respectively. The author demonstrated that high quality ATN films are able to be obtained efficiently and directly on FTO glass. DSCs based on 9.5 µm ATN films on FTO glass have an efficiency of up to 3.11%. These devices clearly
outperformed the ones based on the ATN films on foils, with 20% improvement in the short-circuit current. Base on these results, the author believes that, for DSC applications, back-side illumination should be avoided when possible, as the generation of photocurrent is significantly reduced due to the loss of incident light energy. However, the efficiencies of all the ATN-DSCs fabricated in this work were lower in comparison with the standard TiO$_2$ nanoparticle DSCs, despite all the reported advantages associated with ATNs. In the author’s opinions, the impurities within the ATN structures may be the cause of this issue.

Using the anodic nanoporous WO$_3$ films, DSCs were also fabricated. However, due to the relatively small thickness of the photoanode layer and the very low isoelectric point (ISP) of the WO$_3$ surface, there was no significant visual change in color after the dye sensitization process. The photovoltaic this performance for this device is rather poor, with very small $V_{oc}$ and $J_{sc}$, of 0.13 V and -0.37 mA cm$^{-2}$, respectively.

DSCs fabricated using WO$_3$ nanoparticle films have much better results than that of the anodic nanoporous WO$_3$ films. The highest efficiency recorded was approximately 0.75% and ~ -4.60 mA cm$^{-2}$ of $J_{sc}$ and 390 mV of $V_{oc}$ were obtained with photoanode layer thickness of 12 µm. The fill factor of the devices was relatively low, at ~0.37. The author believed that this is most likely caused by severe charge recombination within these WO$_3$-DSCs. Since the dye coverage on the WO$_3$ surface was insufficient, it created many oxide-electrolyte interfaces, where injected electrons could recombine with the oxidation specie in the electrolyte. The author solved this problem to some extent by coating the WO$_3$ surface with a layer of TiO$_2$, which has higher ISP and more negative conduction band (CB) edges. With this surface modification, more dye molecules were attached to the oxide surface, furthermore, the photo-excited electrons could be injected to the CB of TiO$_2$ then step down to the CB of WO$_3$, producing higher $V_{oc}$. The performance of a 12 µm TiO$_2$ treated WO$_3$-
DSC has a $V_{oc}$ of 490 mV, $J_{sc}$ of -6.67 mA cm$^{-2}$ and a nearly doubled overall efficiency reaching 1.46%.

In conclusion to this thesis, the research results presented correspond to the objectives set out at the beginning. The author has reported the efficient synthesis of high quality ATN films for the first time and this finding contributes new and fundamental knowledge to the area of Ti anodization. Such FTO-ATN films enabled the front-side illumination and such devices demonstrated to be more efficient than in back-side illumination. To the best of the author’s knowledge, this thesis is the first detailed investigation of DSCs based on multi-crystalline WO$_3$ nanostructure films, which presents itself as an alternative photoanode for DSCs. Despite the lack of previous reports in this area, WO$_3$ DSCs were successfully fabricated, generating acceptable efficiencies.

8.2 Publications and other achievements

Within his PhD candidature, the author has published in a wide range of refereed, high impact factor scientific journals, covering many areas including: material synthesis, surface science, DSCs fabrication and characterization and general review of materials. The summary of publications is shown in Table 8.1 and full detail of them can be found in the Appendix.
Table 8.1 Publication summary

<table>
<thead>
<tr>
<th>Journal name</th>
<th>Research area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir (3 papers)</td>
<td>material synthesis / DSC fabrication and characterization</td>
</tr>
<tr>
<td>Electrochemistry Communications (2 papers)</td>
<td>material synthesis</td>
</tr>
<tr>
<td>Applied Surface Science (1 Paper)</td>
<td>surface science</td>
</tr>
<tr>
<td>Sensors and Actuators B – Chemical (1 paper)</td>
<td>material synthesis / sensors</td>
</tr>
<tr>
<td>Chemistry of Materials (1 paper)</td>
<td>material synthesis</td>
</tr>
<tr>
<td>Advanced Functional Materials (1 paper)</td>
<td>general review of materials</td>
</tr>
<tr>
<td>Physical Chemistry Chemical Physics (1 paper)</td>
<td>material synthesis / sensors</td>
</tr>
</tbody>
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Many of the contents of this thesis are based on peer-reviewed journal papers published by the author. These contents are as follow:

- Synthesis of ATNs on ITO glass: *Anodization of Ti Thin Film Deposited on ITO* in Langmuir.
- Synthesis of ATNs on FTO glass: *Fast formation of thick and transparent titania nanotubular films from sputtered Ti* in Electrochemistry Communications.
• WO$_3$-DSCs characterizations: Dye-Sensitized Solar Cells Based on WO$_3$ in Langmuir.

Further to the research activity, the author attended a number of scientific conferences, including International Conference on Nanoscience and Nanotechnology (ICONN) 2008, Melbourne, Australia; Nano Today 2009, Singapore and Materials Research Society (MRS) fall meeting 2009, Boston, USA. The author was also the recipient of “2009 Excellent Self-funded Overseas Chinese Postgraduate Award”, which was presented by the Chinese government. In addition, during the period of July – November 2009, the author completed a postgraduate certificate on research commercialization, which was provided by the Australian Technology Network.

8.3 Future work

This thesis has presented a number of advances in both theoretical and applied sciences, with the outcomes published in several high impact factor journals. Throughout the author’s PhD candidature, several future directions that are related to this work were identified, which are listed as follows:

• The efficiency of any ATN-DSCs has never been able to reach the level that standard TiO$_2$ nanoparticle DSCs have set, even though a fair amount of reports state that the electron diffusion length in ATN-DSCs is much greater than that of TiO$_2$ nanoparticle DSCs. In contrast, there is also a report stated that the electron mobility in ATNs is high, however, there are nitrogen and fluorine impurities in the structure, creating trap sites which immobilize the injected electrons. These impurities was found to be incorporated from the electrolyte during the synthesis process, therefore, obtaining ATN using non-fluorine as well as non-nitrogen electrolytes should be noteworthy for further development and analysis.
• The synthesis of anodic nanoporous WO$_3$ films has encountered the problem of relatively small film thickness. It is likely that an oxide barrier layer is developed and overwhelms the etching and dissolution reactions. Since WO$_3$ can be dissolved in basic solution such as NaOH, it is worth trying to increase the pH value of the electrolyte solution when anodizing W.

• The low ISP of WO$_3$ surface is identified to be the major hurdle for it to be used in highly efficient DSCs, due to the poor dye adsorption. The author suggests that the anchoring ligand, carboxylic acid, can be neutralized by adding HCl into the dye solution. In this way, carboxylic acid is protonated by the H$^+$, thus losing the negative charges and making better attachment to the WO$_3$ surface.

• It is important to investigate the effect of smaller dimensional particles for WO$_3$ based DSCs. The optimum TiO$_2$ nanoparticle dimensions used for DSCs is generally in the order of 15-20 nm, while the WO$_3$ nanoparticle dimensions in this work were in the order of 40 nm. It is expected that by reducing these sizes the efficiency of WO$_3$ based DSCs can be enhanced further due to greater surface to volume ratio. In addition, smaller nanoparticle sizes may allow WO$_3$ to retain the whole orthorhombic phase after annealing and transform to tetragonal with much lower annealing temperature.

• For the measurement of WO$_3$-DSCs, it is highly desirable to conduct impedance spectroscopy to determine the charge dynamics within these devices and compare them to the TiO$_2$-DSCs.
Appendix – List of publications


