UNIVERSITI PUTRA MALAYSIA

ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF TITANIA NANOTUBE THIN FILM

LIM YING CHIN

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By

LIM YING CHIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the degree of Doctor of Philosophy

June 2013

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DEDICATION

Dedicated to my beloved parents and Huey Woon for their love, support, understanding and encouragement.....

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Doctor of Philosophy

ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF TITANIA NANOTUBE THIN FILM

By

LIM YING CHIN

June 2013

Chairman: Professor Zulkarnain Zainal, PhD

Faculty: Science

Titania nanotubes (TNT) have gained increasing interest due to their high surface area, fewer interfacial grain boundaries and excellent charge transfer between interfaces; all are critical properties in photoelectrochemical and photocatalysis application. In this study, TNT thin film electrodes were synthesized by electrochemical anodisation of pure Ti in a standard two-electrode cell containing NH_4F solution. Parameters affecting the morphological, structural and geometry of TNT were investigated in three different electrolytic medium namely the acidic aqueous solution (NH_4F/H_2O), mixture of aqueous-organic solution (NH_4F/H_2O/EG) and an organic neutral solution (NH_4F/EG).

The characteristic of TNT were analyzed using Field Emission Scanning Electron Microscopy (FESEM), X-ray Diffractometry (XRD), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Analysis (EDX) and UV Visible Diffuse Reflectance Spectroscopy (UV-DRS). Meanwhile, the photoelectrochemical responses of TNT were investigated using Liner Sweep Photovoltammetry (LSPV) and their photoefficiency was evaluated in 0.1 M KOH under UV illumination. The

thermal stability of short TNT (400 nm in length) and its morphological, structural, optical and photoelectrochemical changes as a result of heat treatment at 200-800 ^{o}C were also studied.

In NH_4F/H_2O electrolyte, sample morphology was affected by electrolyte pH and fluoride concentration whereby nanotubes dimensions and their growth rate can be manipulated via anodisation voltage, bath temperature, anodisation duration and the addition of EDTA. Voltage range and NH_4F concentration used for TNT formation varied depending on the electrolytic medium used during anodisation. Higher voltage range could be used in NH_4F/EG to obtain larger diameter and longer length tube. An optimum fluoride concentration is required to achieve well-defined and long tube as higher amount of F^- leads to faster chemical dissolution.

Choice of electrolytic medium also has an influence on the crystalline structure, regularity, morphology, elemental composition and band gap of TNT. XRD results showed that pure anatase phase was obtained in $NH_4F/EG/H_2O$ and NH_4F/EG solution while mixture of anatase and rutile co-existed for TNT prepared in NH_4F/H_2O solution. As opposed to irregular nanotubes with ripples formed in NH_4F/H_2O, regular and smooth TNT with variation in length were obtained in NH_4F/EG.

The as-anodised TNT is amorphous and transformed to anatase phase at 300 ^{o}C. Crystallization of anatase phase increases on elevating calcination temperature and rutile phase co-existed at 500 ^{o}C. TNT is thermally stable up to temperature < 600 ^{o}C, above which changes in morphology and dimensions of TNT occurred. Calcination of

TNT at 500 ^{o}C appeared to be the most favorable condition to retain the nanotubular structure with desired crystal phase and photoelectrochemical properties.

The morphology and geometry of the TNT are important factors influencing the photoelectrochemical response, with higher photocurrent response are generally associated with thicker layer of TNT. Photoefficiency for TNT synthesized in different electrolytes medium was tested under halogen and UV light illumination. Highest photoefficiency was obtained for TNT prepared in NH_4/EG compared to those prepared in other electrolytes due to formation of longer length tube.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS ELEKTROKIMIA DAN PENCIRIAN LAPISAN FILEM NIPIS TITANIA NANOTIUB

Oleh

LIM YING CHIN

Jun 2013

Pengerusi: **Profesor Zulkarnain bin Zainal, PhD**

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Nanotiub titanium dioksida (TNT) telah menarik perhatian disebabkan luas permukaan yang tinggi, sempadan butiran antara muka yang rendah dan pemindahan cas yang cemerlang di antara muka, yang mana semua ini merupakan ciri-ciri kritikal dalam aplikasi fotoelektrokimia and fotopemangkinan. Dalam kajian ini, TNT telah disediakan melalui penganodan plat titanium tulen dalam sel piawai 2-elektrod mengandungi larutan NH_4F. Parameter yang mempengaruhi morfologi, struktur dan geometri TNT telah dikaji dalam tiga media elektrolisis yang berbeza iaitu larutan akua berasid (NH_4F/H_2O), campuran larutan akua-organik ($NH_4F/EG/H_2O$) dan larutan organik neutral (NH_4F/EG).

Ciri TNT telah dianalisis menggunakan mikroskopi pengimbasan elektron pancaran medan (FESEM), pembelauan sinar-X (XRD), mikroskopi pancaran elektron (TEM), analisis penyerakan tanaga sinar-X (EDX) dan spektroskopi ultra lembayung nampak-pantulan resapan (UV-DRS). Sementara itu, gerak balas fotoelektrokimia TNT dianalisis menggunakan ujian fotovoltammetri pengimbasan linear dan kecekapan foto TNT dinilai dalam larutan 0.1 M KOH di bawah sinaran cahaya UV. Kestabilan haba

bagi TNT pendek (400 nm panjang) dan perubahan morfologi, struktur, optik dan fotoelektrokimia TNT hasil daripada pemanasan pada suhu 200-800 ^{o}C turut dikaji.

Dalam elektrolit NH_4F/H_2O, morfologi sampel dipengaruhi oleh pH elektrolit dan kepekatan fluorida manakala dimensi nanotiub dan kadar pembesarannya boleh dimanipulasi melalui voltan penganodan, suhu rendaman, tempoh penganodan dan penambahan EDTA. Julat voltan dan kepekatan fluorida yang diguna untuk pembentukan TNT berbeza bergantung kepada media elektrolisis yang digunakan semasa penganodan. Voltan yang lebih tinggi boleh diguna dalam NH_4F/EG untuk mendapatakan diameter tiub yang lebih besar dan tiub yang lebih panjang. Suatu kepekatan fluorida yang optimum diperlukan untuk mencapai tiub yang tertakrif rapi dan panjang memandangkan jumlah F^- yang tinggi menyebabkan pelartuan kimia yang lebih cepat.

Pilihan media elektrolisis juga memberi kesan ke atas struktur hablur, keteraturan, morfologi, komposisi unsur dan julang jalur TNT. Keputusan XRD menunjukkan fasa anatas dapat diperolehi dalam larutan $NH_4F/EG/H_2O$ dan NH_4F/EG manakala campuran anatas dan rutil wujud bersama untuk TNT yang disediakan dalam larutan NH_4F/H_2O. Berlawanan kepada pembentukan tiub yang tidak sekata dengan riak dalam NH_4F/H_2O, TNT yang sekata dan licin dengan ubahan panjang boleh diperolehi dalam NH_4F/EG.

TNT hasil daripada penganodan bersifat amorfus dan ditransfomasi ke fasa anatas pada 300 ^{o}C. Penghabluran fasa anatas meningkat dengan peningkatan suhu pemanasan dan fasa rutil wujud bersama pada 500 ^{o}C. TNT stabil secara terma

sehingga suhu < 600 ^{o}C yang mana suhu yang lebih tinggi menyebabkan berlakunya perubahan dalam morfologi dan dimensi TNT. Pemanasan TNT pada 500 ^{o}C merupakan keadaan yang sesuai untuk mengekalkan struktur nanotiub dalam fasa hablur dan ciri fotoelektokimia yang dijangka.

Morfologi dan geometri TNT merupakan faktor yang penting mempengaruhi gerak balas fotoelektrokimia. Gerak balas fotoarus yang tinggi secara umumnya boleh dikaitkan dengan lapisan TNT yang lebih tebal. Kecekapan foto TNT yang disintesis dalam media elekrolisis yang berlainan diuji di bawah sinaran cahaya lampu halogen dan UV. Kecekapan foto yang paling baik dicapai menggunakan TNT yang disediakan dalam NH_4F/EG berbanding dengan elektrolit lain disebabkan pembentukan tiub yang lebih panjang.

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I certify that a Thesis Examination Committee has met on 24 June 2013 to conduct the final examination of Lim Ying Chin on her thesis entitled "Electrochemical Synthesis and Characterization of Titania Nanotube Thin Film" in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

_____

LIM YING CHIN

Date: 24 June 2013

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LIST OF ABBREVIATIONS AND SYMBOLS

AOTNT/EG	As-anodised titania nanotubes synthesized in ethylene glycol
AOTNT/EGH_2O	As-anodised titania nanotubes synthesized in ethylene glycol and water mixtures
AOTNT/H_2O	As-anodised titania nanotubes synthesized in aqueous solution
C2TNT	Titania nanotubes calcined at 200 ^oC
C3TNT	Titania nanotubes calcined at 300 ^oC
C4TNT	Titania nanotubes calcined at 400 ^oC
C5TNT	Titania nanotubes calcined at 500 ^oC
C6TNT	Titania nanotubes calcined at 600 ^oC
C7TNT	Titania nanotubes calcined at 700 ^oC
C8TNT	Titania nanotubes calcined at 800 ^oC
C5TNT/EG	Calcined titania nanotubes at 500 ^oC synthesized in ethylene glycol
C5TNT/EGH_2O	Calcined titania nanotubes at 500 ^oC synthesized in mixture of ethylene glycol and water
C5TNT/H_2O	Calcined titania nanotubes at 500 ^oC synthesized in aqueous solution
DC	Direct current
E_C	Conduction band
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersion X-ray
E_F	Fermi energy level
E_g	Band gap energy
E_V	Valence band
eV	Electron volt
FESEM	Field Emission Scanning Electron Microscopy

$h\nu$	Photon energy
JCPDS	Joint Committee of Powder Diffraction Standard
kV	Kilo volt
LSPV	Linear Sweep Photovoltammetry
MO	Methyl orange
NH_4F/H_2O	Aqueous NH_4F solution adjusted to pH 4
$NH_4F/EG/H_2O$	Mixture NH_4F, ethylene glycol and 50 vol.% H_2O solution
NH_4F/EG	Ethylene glycol containing NH_4F
nm	nanometer
ppm	Parts per million
TEM	Transmission Electron Microscopy
TNT	Titania nanotubes
TNT4.5	Titania nanotubes prepared at pH 4.5 in NH_4F/H_2O
TNT4.5/EDTA	Titania nanotubes prepared at pH 4.5 in NH_4F/H_2O and EDTA
UV-DRS	Ultraviolet visible Diffuse Reflectance Spectroscopy
μm	Micrometer
μA	Microampere
V	Voltage
vol.%	Volume percent
W	Watt
wt.%	Weight percent
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Over the past few decades, the world's energy demands have increased tremendously and therefore accelerate the research on renewable energy. Sunlight or solar energy derived from the sun's electromagnetic radiation is the widely available energy source. Thus, harvesting solar energy and convert it into electrical power through the photovoltaic process with suitable materials appeared to be one of the promising energy conversion processes. Although p-n junction semiconductors have demonstrated high efficiency in solar energy harvesting, expensive materials such as silicon is often required in such photovoltaic cell. Titanium dioxide (TiO_2) has extensively been investigated for its unique and remarkable properties including chemically stable, high corrosion stability and comparable low cost of preparation. In addition, TiO_2 exhibits high photocatalytic efficiency and its photogenerated holes are highly oxidizing. Thus, it has found enormous applications in photocatalysis, photoelectrochemical water splitting and self-cleaning application. In addition, high level biocompatibility nature of titania facilitates its application in biomedical field where TiO_2 layers on Ti or Ti alloys are in direct contact with biological tissue in dental implants and orthopedic applications (Kar *et al*., 2006; Popat *et al*., 2007c).

However, bulk TiO_2 materials have low surface area and therefore exhibit low adsorption property. Moreover, fast recombination rate of the photogenerated charge carriers deteriorate the performance of such materials especially in photoelectrochemical applications. In order to overcome such problems, synthesis of nanocrystalline TiO_2 materials which exhibit unique properties, such as quantum size

effect and high surface area is of great interest among researchers in recent years. As such, TiO_2 nanoparticles are frequently used in replacement to their bulk counterparts in such applications.

However, the suspended nanoparticles encountered two technical problems which set the limitation of this system towards industrial application. Firstly, the need for separation of the suspended TiO_2 nanoparticles such as in catalysis application can be very costly and difficult. Secondly, agglomeration of nanoparticles occurs especially at high concentrations which reduce the active sites of photoactive TiO_2. Nanostructured thin films are often more desirable for applications involving catalysis and filtration compared to the powdery forms. Thus, development of various methods to immobilize TiO_2 thin films on the solid substrates has been carried out including sol-gel, sputtering, chemical vapor deposition, and liquid-phase deposition. However, overall active surface area has been greatly reduced in the immobilized system compared to the corresponding slurries leading to the lower efficiency of such system in photoelectrochemical application.

Apart from high surface area which is beneficial for photoelectrochemical application, material with a faster electron transport and low recombination rate of photogenerated charge carrier is a key issue in achieving high efficiency in a photoelectrochemical cell. Much effort has been focused on fabrication of highly efficient materials with suitable architecture to minimize the recombination of electron-hole pairs. In this context, formation of highly ordered and oriented nanotubular or porous geometry is advantageous due to high surface-to-volume ratio and short diffusion path within enclosed nanoscale compartment (Masuda and

Fukuda, 1995). Self-organized growth of nanotubular TiO_2 thin films is of great interest in this research due to its unique physical properties including larger surface area in a small geometrical area, fewer interfacial grain boundaries and superior charge transport, of which all are important properties governing its performance as photoanode in a photoelectrochemical cell.

Nanomaterials are a class of novel materials with at least one of its dimensions in the nanoscale range (< 100 nm). Nanomaterials can be classified according to the number of dimensions not confined to the nanoscale range as zero-dimensional (0-D), one dimensional (1-D), two dimensional (2-D) and three dimensional (3-D). Nanomaterials can exist in aggregated or agglomerated forms with different shape such as spherical, tubular, rod, ribbon or irregular shape. 0-D TiO_2 materials such as sphere have very high specific area. For 1-D TiO_2 materials such as nanotubes or nanowires, apart from having high surface area, they exhibit added advantages with regard to less recombination due to short diffusion path for charge carrier and light scattering properties. Hence, synthesis of titania nanotubes (TNT) is more favorable over nanowires in this study due to its additional surface area resulted from the hollow structure.

There are two approaches namely the top-down and bottom up approach in the synthesis of nanomaterials. The top down approach refers to slicing or successive cutting of bulk material into nanosized particles such as photolithography and electron beam machining. Generally, it is an expensive and complex approach in actual implementation. Whereas, bottom up approach refers to the building of nanostructures up from the bottom either atom-by-atom or molecular-by-molecular

such as in sol-gel deposition and chemical bath deposition or self-assembly droplets. This type of fabrication is much less expensive compared to the top-down approach. Apart from this, bottom up approach is also more promising in obtaining nanostructures with less defects, more homogenous chemical composition and better ordering. Therefore, the bottom up approach such as electrochemical anodisation of Ti was chosen in synthesizing titania nanotubes with desired dimension and uniform size distribution. Moreover, high temperature and pressure are often not required in electrochemical synthesis of titania nanotubes, making it a simple and cost effective process.

Producing TNT with desired dimensions, crystallinity and microstructure in a controlled and reproducible way is of great challenge. Besides, a full knowledge of the effect of electrochemical condition on the physicochemical properties is important to develop a greater fundamental science for this material. Even though potentiostatic anodisation of Ti has been used to fabricate TNT, most of the studies employed corrosive and toxic hydrofluoric acid as electrolyte in the synthesizing process. In view of this, development of environmental benign or green electrolyte is crucial for industrial scale application. Hence, the main objective of the present work was to synthesize TNT in a relatively mild aqueous NH_4F (with small amount of H_2SO_4 only to adjust the pH) and in non-aqueous ethylene glycol solution followed by investigation of the effect of electrochemical conditions on the formation, structural and photoelectrochemical properties of TNT.

In addition, the effect of complexing agent on the dimensional changes of TNT formed in organic electrolyte has been reported in literature. However, no published

study has been reported on the growth of TNT in aqueous solution. In this study, the effect of EDTA on the formation and nanotubes' growth of TNT in mild aqueous NH_4F solution has been investigated and reported. The TNT thin films were also subjected to heat treatment in open air to study the annealing effect on the thermal stability, structural, morphological, optical and photoelectrochemical properties of this material.

1.2 Objectives of the Study

The objectives of the present work are summarized as follow:

1. to synthesize titania nanotubes thin films via electrochemical anodisation of Ti in aqueous NH_4F solution, in mixture of aqueous NH_4F and ethylene glycol and in viscous ethylene glycol solution.
2. to investigate the effect of electrochemical parameters on the morphology and dimensions of titania nanotubes thin films.
3. to determine the crystal structure, surface morphology and elemental composition of the titania nanotubes thin films.
4. to evaluate the photoelectrochemical and optical properties of the titania nanotubes thin films.
5. to study the annealing effect on the morphology, crystal structure, optical and photoelectrochemical properties of 400 nm long titania nanotubes.

1.3 Structure of the Thesis

The thesis is organized into 5 chapters. After an introduction that describes the background of the study in Chapter 1, the outline structure of the remaining part of the thesis is as follow.

Chapter 2 gives the literature review on previous work relates to titania nanotubes. Intensive background information covering the preparation method and factors governing the formation and dimensions of nanotubes is given. The properties of titania nanotubes and possible mechanism for nanotubes formation is also presented and discussed.

The experimental details on the electrochemical anodisation of Ti in three different electrolytic medium are given in Chapter 3. Experimental set up and characterization techniques used such as XRD, FESEM, TEM, EDX and UV-DRS are briefly mentioned.

The experimental results for synthesis of titania nanotubes in three different electrolytes medium namely in aqueous NH_4F solution, in mixture of aqueous NH_4F-non aqueous ethylene glycol solution and in viscous ethylene glycol solution are presented one by one in Chapter 4. Electrochemical parameters affecting the morphology and dimensions of titania nanotubes are discussed comprehensively. Elemental composition, optical properties and photoefficiency of different nanotubes are also compared. Study of annealing effect on the morphology, crystal structure, optical and photoelectrochemical properties of short nanotubes are also elaborated in detail.

Finally, Chapter 5 summarizes all the present analysis work and provides conclusions on observation obtained beyond previously published work. Recommendations are also given for future research directions.

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