DEVELOPMENT OF WO_3-TiO_2 NANOTUBE ARRAYS FOR WATER ELECTROLYSIS

by

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LIST OF ABBREVIATIONS

AR	Aspect ratio
APT	Ammonium paratungstate
C_B	Conduction band
CBD	Chemical bath deposition
DFT	Density functional theory
DI	Deionized water
EDX	Energy dispersive X-ray spectroscopy
E_B	Band-gap energy
E_F	Fermi level
EG	Ethylene glycol
EISA	Evaporation-induced self-assembly
FESEM	Field emission scanning electron microscopy
G	Geometric surface area factor
GLAD	Glancing angle deposition
LSP	Linear sweep potential
MB	Methyl blue
MO	Methyl orange
NHE	Normal hydrogen electrode
PEC	Photoelectrochemical
PL	Photoluminescence
RF	Radio Frequency
RT	Room temperature
SCE	Saturated calomel electrode
SEM	Scanning electron microscope
TEM	Transmission electron microscopy
UV	Ultraviolet
V_B	Valence band
V_{fb}	Flat band potential
V_{oc}	Open-circuit potential
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

$h\nu$	Photon energy
Å	Angstrom
atm	Standard atmosphere
at%	Atomic percentage
cm	Centimeter
e^-	Electron
h	Hour
h^+	Hole
eV	Electronvolt
ΔG°	Gibbs free energy
I_o	Power density of the incident light
j_p	Photocurrent density
kHz	Kilohertz
M	Molar
mA	Milliampere
mL	Milliliter
mm	Millimeter
mM	Millimolar
min	Minute
nm	Nanometer
s	Second
µm	Micrometer
V	Voltage
Voc	Open-circuit voltage
W	Watt
wt%	Weight percentage
λ	Radiation wavelength
η	Photoconversion efficiency
θ	Diffraction angle
°C	Degree Celsius
φ	Work function

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PEMBANGUNAN SUSUNAN TIUBNANO WO_3-TiO_2 DALAM ELEKTROLISIS AIR

ABSTRAK

Penjanaan hidrogen solar melalui elektrolisis air adalah sasaran utama untuk pembangunan ekonomi hidrogen secara lestari bagi sistem tenaga masa depan. Pembentukan TiO_2 tiubnano yang bebas daripada kelompok adalah penting dalam aplikasi elektrolisis air supaya mencapai kecekapan yang tinggi. Kajian terperinci terhadap kesan komposisi elektrolit, masa penganodan, keupayaan elektrik, suhu penganodan dan suhu penyepuhlindapan telah dilaksanakan bagi mengawal susunan dan geometri tiubnano. Susunan tiubnano TiO_2 yang mempunyai permukaan dinding licin dan nisbah aspek yang tinggi telah berjaya disintesis dalam glikol etilena yang mengandungi 5 wt% NH_4F dan 5 wt% H_2O_2 melalui kaedah penganodan pada 60 V selama 1 jam. H_2O_2 digunakan sebagai pembekal oksigen untuk meningkatkan kadar pengoksidaan dan seterusnya meningkatkan kadar pembentukan tiubnano dalam kajian ini. Sehubungan dengan itu, didapati bahawa penambahan hidrogen peroksida ke dalam elektrolit dalam selang masa 10 min menghasilkan tiubnano yang lebih panjang (~ 13 µm) dengan diameter ~ 140 nm. Usaha berterusan telah dilaksanakan bagi meningkatkan lagi prestasi elektrolisis air dengan mendeposisi WO_3 pada TiO_2 tiubnano melalui teknik pemercikan RF dan pengisitepuan basah. WO_3-TiO_2 tiubnano yang dipercik dengan daya pemercikan 50 W selama 0.5 min serta disepuhlindap pada 400 °C telah menunjukkan foto-arus sebanyak 2.4 mA/cm^2 yang tinggi dengan kecekapan penukaran foto sebanyak 6.2 %. Peningkatan prestasi sebanyak dua kali ganda telah dicatatkan berbanding dengan TiO_2 tiubnano yang asal. Sebaliknya, TiO_2 tiubnano yang dicelupkan dalam 0.3 mM larutan APT selama 1

jam menunjukkan foto-arus sebanyak 2.1 mA/cm^2 dengan kecekapan penukaran foto sebanyak 5.1 %. WO_3-TiO_2 tiubnano yang dihasilkan melalui teknik pemercikan RF mencatatkan prestasi elektrolisis air yang lebih tinggi berbanding dengan teknik pengisitepuan basah. Penemuan ini menunjukkan bahawa pengenapan W^{6+} spesies dalam kekisi TiO_2 dengan tenaga kinetik yang tinggi (pemercikan RF) mencapai prestasi elektrolisis air yang lebih baik berbanding dengan proses resapan daripada W^{6+} spesies ke dalam kekisi TiO_2 (pengisitepuan basah). Kehadiran unsur W di bawah 1 at% dalam TiO_2 menunjukkan peningkatan foto-arus dan kecekapan penukaran foto kerana ia akan bertindak sebagai pengantara yang berkesan untuk memerangkap elektron dan mengurangkan rekombinasi elektron-lohong. Sebaliknya, kandungan WO_3 yang berlebihan akan membentuk akumulasi pada permukaan tiubnano dan mengakibatkan prestasi elektrolisis air menjadi rendah kerana lapisan asing ini akan bertindak sebagai pusat rekombinasi elektron-lohong.

DEVELOPMENT OF WO_3-TiO_2 NANOTUBE ARRAYS FOR WATER ELECTROLYSIS

ABSTRACT

Solar hydrogen generation from water electrolysis is a key target for the development of sustainable hydrogen economy for future energy system. The formation of self-organized TiO_2 nanotubes without bundling is essential for high efficiency in photoelectrochemical (PEC) water electrolysis application. Comprehensive investigations on different parameters, such as composition of electrolyte, anodization time, anodization voltage, anodization temperature and heat treatment temperature were conducted in order to control the specific architecture of nanotubes. Highly ordered and smooth TiO_2 nanotubes were successfully synthesized through anodization of Ti foil in ethylene glycol containing 5 wt% of NH_4F and 5 wt% of H_2O_2 at 60 V for 1 h. In this study, H_2O_2 was used as oxygen provider to increase the oxidation rate for synthesizing nanotubes at a rapid rate. It was found that addition of H_2O_2 at 10 min intervals formed longer nanotubes (~ 13 μm) with larger pore diameter (~ 140 nm). Continuous efforts have been exerted to further improve the PEC water splitting performance by incorporating an optimum content of WO_3 into TiO_2 nanotubes using RF sputtering and wet impregnation techniques. It was found that TiO_2 nanotubes sputtered at 50 W for 0.5 min and subsequently heat treated at 400 °C demonstrated a maximum photocurrent density of ~ 2.4 mA/cm^2 with photoconversion efficiency ~ 6.2 %. This performance was approximately two times higher than the pure TiO_2 nanotubes. On the other hand, TiO_2 nanotubes that dipped into the 0.3 mM ammonium paratungstate (APT) solution for 1 h showed photocurrent density of ~ 2.1 mA/cm^2 with photoconversion

efficiency of ~ 5.1 %. The WO_3-TiO_2 nanotubes prepared by RF sputtering exhibited higher PEC water splitting performance than that of wet impregnation. These findings deduced that W^{6+} species incorporated within TiO_2 lattice by high kinetic energy process (RF sputtering) exhibited better PEC performance than the diffusion of W^{6+} species into TiO_2 lattice (wet impregnation). The presence of W element below 1 at% in TiO_2 showed an improvement of photocurrent density and photoconversion efficiency because it acted as an effective mediator to trap the photo-induced electrons and minimize the recombination of charge carriers. By contrast, excessive content of WO_3 loading on the wall surface of TiO_2 nanotubes resulted in poor PEC water splitting performance because it formed independent layers that acted as recombination centers for the charge carriers.

CHAPTER 1

INTRODUCTION

1.1 Introduction

At present, modern society is habituated to a high degree of mobility, fast communication and daily comfort, all of which require considerable energy input (Grimes *et al*., 2008). These energy inputs largely consist of fossil fuel, which in turn, after combustion, contributes to the greenhouse gases and increases the carbon footprint in the earth's atmosphere. The addition of greenhouse gases are said to be largely responsible for increasing extreme climate conditions, which have wrought havoc on many nations across the world in the past several years (Ohi, 2005; Yu and Chen, 2009). Many scientists aware that the extraction and combustion of fossil fuels will release significant amount of greenhouse gases to the atmosphere and this is a major threat to the environment because it causes land damage, smog, acid rain and atmospheric changes (Bockris, 2002; Ghicov and Schmuki, 2009). Environmental damage and atmospheric changes may soon alter the weather and climate patterns of the earth, resulting in grave problems of all its inhabitants.

One of the steps taken by many countries to aid the earth and minimizing environmental problems is applying sustainable development. It seems that sustainable development is a strategic goal of modern society reflecting contemporary demand for economic, social, political and environmental development (Turner, 1999; Aroutiounian *et al*., 2005; Jefferson, 2006). Therefore, executing research for generating green and renewable energy resource has been the passion for scientists, which can provide us energy in sustainable manner. The finding of alternative clean energy source is crucial in leading a high quality of life, which is in harmony with nature (Kreuter and Hofmann, 1998; Marsen *et al*., 2007).

To date, hydrogen (H_2) has been established as a potential future energy carrier and possibly the best substitute for fossil fuel to secure the future supply of a clean and sustainable energy (Funk, 2001; Tromp *et al.*, 2003; Ewan and Allen, 2005). The novel feature of H_2 is that it can be produced from water using solar energy, which are readily available and renewable resources without carbon emission (Tryk *et al.* 2000; Bak *et al*. 2002; Grätzel, 2003; Mahajan *et al.*, 2008; Maeda *et al.*, 2010). However, the future will certainly not be based on a simple replacement of fossil fuels by H_2 fuel as a commercial source of energy. H_2 must be produced and made available at cheaper cost for everyone to utilize it without creating any misbalance in global ecology. Among viable renewable H_2 production approaches, the use of photoelectrochemical (PEC) water splitting system has become one of the most promising methods and has high potential in the H_2 economy to secure the future supply of clean and recyclable H_2 energy (Grätzel, 2003; Paulose *et al.*, 2006; Liu *et al.*, 2011).

In order to bring H_2 to the point of commercial readiness and establish H_2 economy, substantial research on the development of semiconductor for water splitting process using solar energy has been developed lately (Leung *et al.*, 2010; Kubacka *et al.*, 2012). Although a number of semiconductor have been reported to be active photocatalysts for the overall water splitting reaction, most of them only function under ultraviolet (UV) light ($\lambda < 400$ nm) owing to the wide band gap energy. Since nearly half of the solar energy incident on the earth's surface falls in the visible region ($400 < \lambda < 800$ nm), the efficient use of visible light is essential for generating H_2 gas through water splitting process (Ni *et al.*, 2007; Ahn *et al.*, 2007; Shon *et al.*, 2008; Fujishima *et al.*, 2008). Unfortunately, overall PEC water splitting using visible light is difficult to achieve due to the band level of the semiconductor is rather difficult to be tuned to visible region (Kitano *et al*., 2007; Abe *et al*., 2011; Tong *et al*., 2012). To date, no known semiconductor has been discovered that simultaneously meets all the criteria required for economical H_2 production (Grimes *et al*., 2008; Kubacka *et al*., 2012).

In fact, a suitable candidate as a photoelectrode for H_2 production must have three basic criteria as shown below (Grimes and Mor, 2009):

i. Stability:

   The semiconductor must be photochemically stable in aqueous solution, in which it will not be photocorroded during the photoelectrolysis process.

ii. Band gap:

   The semiconductor must have a band gap about 1.7-2.0 eV as considering the overpontential losses and energy required for water splitting process.

iii. Energy Level:

   For spontaneous water splitting process, the oxidation and reduction potential must lie between the valence and conduction band edges of the semiconductor.

In the field of photocatalysis today, titanium dioxide (TiO_2) has emerged as the leading candidate as an efficient photoelectrode in PEC water splitting system because of its unique characteristics, such as high stability against corrosion, non-toxicity, strong oxidation ability, good photocatalytic property, self-cleaning property, and ready availability (Ho *et al*., 2006; Grimes, 2007; Roy *et al*., 2011). However, an obvious hindrance to the widespread use of TiO_2 as a photoelectrode is its poor visible light response resulting from its large band gap (3.2 eV on the anatase polymorph) and the rapid recombination of photo-induced electron/hole pairs (Ahn *et al*., 2007; Hathway *et al*., 2009; Leung *et al*., 2010). Several researchers have argued that the visible light absorption of TiO_2 can be improved in the past few years. This can be done by coupling TiO_2 with another semiconductor, which will lead to additional electronic state in the band-gap, which in turn affect a change in the optical, electronic and functionality of TiO_2. (Mohapatra *et al*., 2008; Shen *et al*., 2008; Zhang *et al*., 2010; Nah *et al*., 2010; Bang and Kamat, 2010; Costi *et al*., 2010; Das *et al*., 2011). Other than poor response of TiO_2 to visible light, the multi-component semiconductors are complex materials. Making intuitive guesses on their properties are more or less impossible, and a focused research on the area is a very challenging task.

To split water under visible light, the incorporation of WO_3 into TiO_2 photocatalyst has received much more attention in the literatures recently due to the interesting and unique features of the resultant binary oxide system (Fernandez-Garcia *et al*., 2005; Higashimoto *et al*., 2008; Sajjad *et al*., 2010; Wang *et al*., 2011). In this manner, coupling TiO_2 with small band-gap of WO_3 that possess different redox energy level for their valence band and conduction band, which provides another attractive approach to achieve more efficient charge separation under visible light (Barreca *et al*., 2011). A hybrid of WO_3-TiO_2 nanotubes, acting as a photoelectrode in PEC water splitting system has been developed in our study recently. Results suggest that the hybrid WO_3-TiO_2 nanotubes demonstrate significant advantages of promoting the separation of electron/hole pairs and responsive to the visible light in PEC water splitting system.

1.2 Problem statement

The exceptional chemical and physical properties of TiO_2 have been long recognized since the discovery of water photoelectrolysis on TiO_2 by Fujishima and

Honda in 1972. To date, one-dimensional (1D) structure of well-aligned TiO_2 nanotubes by a simple electrochemical oxidation reaction of a Ti substrate under a specific set of environment conditions have been widely reported (Mishra *et al.*, 2003; Raja *et al.*, 2005; Mor *et al.*, 2006; Paulose *et al*. 2006). However, TiO_2 nanotubes are still far from becoming a potential candidate for PEC water splitting system. Bundling problem (disorder arrangement of nanotube arrays) and weak adherence of the nanotube arrays on Ti substrate remains as a great challenge. In addition, poor visible light absorption and rapid recombination of charge carriers limit the widespread use of TiO_2 nanotubes (Ahn *et al.*, 2007; Zhang *et al.*, 2010; Márquez *et al.*, 2011; Kubacka *et al.*, 2012). Thus, in order to produce high efficient PEC water splitting system using TiO_2 nanotubes as a photoelectrode is challenging unless several issues have pointed out are addressed.

One of the ways to improve the PEC water splitting performance of TiO_2 is creating 1D nanotubular structures with desired length, pore diameter and wall thickness through anodization method. Anodization is the most feasible method due to its ability to create self-organized anodic oxides in the form of nanotubular structures with almost perfect vertical alignment. Moreover, anodization is relatively simple; it can be adopted for large-scale industrial production (Todorova *et al.*, 2008; Yasuda *et al.*, 2007; Roy *et al.*, 2011). However, in getting the right dimensions and morphologies, a controlled synthesis procedure for the production of well-aligned 1D TiO_2 nanotubes must be investigated and optimized. Generally, highly ordered TiO_2 nanotubes result in undesirable bundling problems, which significantly decrease the photoconversion efficiencies in the PEC water splitting system (Zhu *et al.*, 2007; Kim *et al.*, 2008; Baker and Kamat, 2009). Therefore, in the present study, considerable efforts have been devoted to the synthesis of stable (good photoresponse and high chemical stability), clean (bundle-free), and highly ordered TiO_2 nanotubes that could increase the PEC water splitting performance.

To resolve the above listed problems of the TiO_2, continuous efforts have been conducted by coupling a narrow band-gap semiconductor with TiO_2 in order to enhance the charge separation efficiency (Mohapatra *et al*., 2008; Shen *et al*., 2008; Costi *et al*., 2010; Das *et al*., 2011). In this case, the narrow band-gap semiconductor must fulfill several basic requirements for better charge separation efficiency, such as the conduction band of narrow band-gap semiconductor should be more positive than that of the TiO_2, responsive to visible light and photo-corrosion free condition (Navarro Yerga *et al*., 2009).

In the present study, WO_3 was selected as a suitable semiconductor to be coupled with TiO_2 nanotubes due to suitable band edge position relative to TiO_2, strong reversible field-aided ion intercalation, and exhibit higher surface acidity to absorb more ionic species on the surface of TiO_2. In this manner, conduction band electrons from TiO_2 can be injected to the WO_3 due to the internal electrostatic field from the interpretation of inter-band state (Nah *et al*., 2008; Benoit *et al*., 2009; Gong *et al*., 2011). Besides, WO_3 offers relatively small band gap energy (2.5 eV to 2.8 eV) and exhibit strong absorption within solar spectrum (Abe *et al*., 2011; Song *et al*., 2011). Another important reason for using hybrid WO_3-TiO_2 as photoelectrode in PEC water splitting system is because of long term inertness to chemical environment and resilience to photocorrosion over a wide pH range in aqueous solution under evolving oxygen conditions (Fernandez-Garcia *et al*., 2005; Kim *et al*., 2009; Márquez *et al*., 2011).

1.3 Research objectives

The objectives of this study are listed as follow:-

i. To study the effect of electrochemical parameters on the formation of TiO_2 nanotubes (e.g., composition of electrolyte, time, temperature, cleaning methods, heat treatment temperature) by anodization method.

ii. To study the effect of geometry (e.g., aspect ratio, surface morphology, crystal structure) of the anodized TiO_2 nanotubes on the PEC characteristic studies.

iii. To study the formation of WO_3-TiO_2 nanotubes via RF sputtering technique (e.g., sputtering time, sputtering power) and wet impregnation technique (e.g., molarity of precursor, soaking time).

iv. To study the PEC characteristic studies (e.g., photocurrent density, photoresponse, photoconversion efficiency and amount of H_2 generation) of WO_3-TiO_2 nanotubes as compared to the pure TiO_2 nanotubes.

1.4 Scope of research

Anodization is the most feasible method for synthesis of TiO_2 nanostructures because it yields anodic oxides with nanotubular structures in a well-aligned manner. Thus, TiO_2 nanotubes with controlled dimensional features and free from bundling or clustering are essential prior to WO_3 incorporation. Therefore, in the present study, the formation of TiO_2 nanotubes in organic electrolyte (ethylene glycol) was investigated. Then, the possibility of forming TiO_2 nanotubes at faster rate in the presence of hydrogen peroxide (H_2O_2) in ethylene glycol electrolyte was investigated in detail. In addition, the effect of the composition of electrolyte, anodization time, applied voltage, anodization temperature and heat treatment temperature on the nanotube geometry (e.g., length, pore diameter and wall thickness) were studied in order to understand the optimum architecture of nanotube arrays for high efficient PEC water splitting performance. Unlike other works, H_2O_2 is used in here instead of water as oxygen provider to accelerate the field assisted oxidation and thus high aspect ratio nanotubes could be achieved. Furthermore, the use of H_2O_2 in ethylene glycol electrolyte was found to be beneficial in addressing bundling and adherence problems of nanotube arrays. The growth mechanism of TiO_2 nanotubes in such electrolyte was investigated too.

Many studies highlighted the coupling mechanism between WO_3 and TiO_2 to facilitate better charge carrier separation and visible light response (Higashimoto *et al.*, 2008; Das *et al.*, 2011; Gong *et al.*, 2011). However, most of these studies involved WO_3-TiO_2 photocatalysts in the form of particles/spheres or thin films, which do not possess high enough surface area for photon absorption (Yan and Zhou, 2011; Kubacka *et al.*, 2012). Moreover, most scholars mainly focused on the photodegradation of organic pollutants rather than the PEC water splitting application. Therefore, detail studies regarding the relationship of the WO_3 content incorporated into TiO_2 nanotubes for PEC water splitting performance has been established in this work. To the best of our knowledge, incorporation of WO_3 into 1D TiO_2 nanotubes using radio frequency (RF) sputtering technique to improve PEC water splitting performance is not available. Meanwhile, little information is known regarding the formation of WO_3-TiO_2 nanotubes photoelectrode through wet impregnation technique, especially in PEC water splitting application. Thus, a comprehensive study was conducted to optimize RF sputtering parameters (e.g., sputtering time and sputtering power) and wet impregnation parameters (e.g., molarity of precursor and soaking time) to obtain the desired WO_3-TiO_2 nanotubes, resulting in best PEC water splitting performance.

The surface and cross-sectional morphologies of the anodized Ti foils was viewed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The elemental analysis was determined with energy dispersion X-ray (EDX). Besides, X-ray diffraction (XRD) was used to investigate the crystallinity and phase transition of the sample. In addition, Raman analysis was used to obtain the vibrational information specific to the chemical bonds and symmetrical of molecules in the sample. Meanwhile, high sensitive surface analysis of X-ray photoelectron spectroscopy (XPS) was selected to identify and quantify the elemental composition and oxidation state from the sample surface. Then, the fundamental information on the properties of the energy levels lying within the band gap as well as the efficiency of charge carrier trapping, immigration and transfer was investigating using photoluminescence (PL) measurement.

The PEC water splitting performance of the samples were characterized using a three-electrodes PEC cell with TiO_2 nanotubes as the working photoelectrode, a platinum rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte used in the PEC cell consisted of 1 M potassium hydroxide (KOH) aqueous solution. All of the three electrodes were connected to a potentiostat (µAutolab III), and the current and voltage were measured. A 150 W Xenon arc lamp solar simulator (Zolix LSP-X150) with an intensity of 800 W/m^2 was used to produce a largely continuous and uniform spectrum. The photocurrent densities of the samples were measured. Next, the responsiveness of the samples to the interrupted illumination and the H_2 evolution measurements were studied. The evolved H_2 gas was collected using a reverted burette.

1.5 Outline of dissertation

This dissertation is organized in five chapters consecutively. In chapter 1, the introduction of this research work, research objectives, problem statement, the scope of research as well as dissertation overview are presented. Chapter 2 provides an overview of the principles, and the research progress of solar H_2 generation production via the water splitting reaction using TiO_2 nanotubes. In addition, chapter 2 comprises literature review on the WO_3 incorporated TiO_2 photocatalyst using different approaches. The specifications of the raw materials, research methodology, and the characterizations employed in this research work are described in chapter 3. The results of characterizations and the discussions are presented in chapter 4. Chapter 5 summarizes the conclusion of the study as well as several suggestions and recommendations for the future work. Such finding will aid in building the fundamentals of TiO_2 nanotubes modification with WO_3 in the development of H_2 fuel cell for sustainable energy system.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Nowadays, public concern about the environment, climate change and limited fossil fuel resources have given rise to the urgent need of fostering development in the area of renewable energies, which are inexhaustible and non-polluting (Turner, 1999; Ohi, 2005; Jefferson, 2006). The production of H_2 gas is one of the most promising prospects for efficient renewable resources (Funk, 2001; Bockris, 2002; Tromp *et al*., 2003; Ewan and Allen, 2005). To bring H_2 to the point of commercial readiness and viability in terms of performance and cost, substantial research on the development of n-type semiconductor for PEC water splitting process using solar energy is necessary (Tryk *et al*. 2000; Bak *et al*. 2002).

Recent studies have indicated that TiO_2 has emerged as the leading candidate for PEC water splitting cell because of its low cost, non-toxicity, self-cleaning property, ready availability and strong photocatalytic activity and stability against photocorrosion (Raja *et al.*, 2005; Ho *et al*., 2006; Grimes, 2007; Paulose *et al*., 2007). The high efficiency of TiO_2 as a photoelectrode in a PEC water splitting cell requires a suitable architecture that minimizes electron loss at nanostructure connections and maximizes photon absorption (Mahajan *et al*., 2008; Dholam *et al*., 2009; Sun *et al*., 2010). In order to further improve the immigration of photo-induced charge carriers, considerable effort has to be exerted to further improve the water splitting performance under visible light illumination (Knorr *et al*., 2008; Li *et al*., 2010). Lately, interesting and unique features of WO_3-TiO_2 binary oxide photocatalyst system have gained much attention and became favourite research matter among various groups of scientists. The relationship between the WO_3 on

TiO_2 photocatalyst as well as their PEC water splitting performance was still a matter of debate and remains unclear. It was noted that the properties of this binary oxide primarily depend on the nature of the preparation method and the role of optimum WO_3 content incorporated into the TiO_2. Therefore the development of efficient visible light responsive photocatalyst remains to be determined. In the subsequent section, the historical overview, basic principal, material selection and work done by various researchers with regards to the TiO_2 nanotubes as well as WO_3-TiO_2 nanotubes applied in PEC water splitting application will be reviewed in detail.

2.2 Historical overview of PEC water splitting

As the drive to seek alternative energy sources significantly increases across the world, there is a growing interest in low-cost, easily manufactured, and high efficiency energy sources (Kreuter and Hofmann, 1998). One of those sources is the harnessing of the sun light energy through the excitation of semiconductor materials, later coined as semiconductor photocatalyst (Aroutiounian *et al*., 2005; Barreca *et al*., 2011; Tong *et al*., 2012). The early work on semiconductor photocatalysis was reported by Becquerel (1839). He reported that a silver chloride electrode connected to a counter electrode and immersed in an electrolyte solution, generates a voltage and an electric current during illumination of sunlight. The discovery that the energy of sunlight can be captured and converting into electric power had brought out lots of great ideas for scientists and researchers, whom seek alternative energy sources. Later, the photoelectric effect was first applied to a device by Charles Fritts (1883) with the development of a selenium and gold *pn* junction device with approximately 1% efficiency. However, the literature regarding to the photocatalyst was limited at the early part of the last century.

In 1954, the first *pn* junction solar cell design was published and reported by Bell Laboratories with an efficiency of 6% (Chapin *et al.*, 1954). The innovation by Bell Laboratories produced the first viable commercial solar cell, which has been revolutionized the photovoltaic industry. Since then, the improvements have been made to give photovoltaic more accessibility in the global energy market. The conversion of sunlight to electrical power has been dominated by solid-state junction devices, often made of silicon (Solanki, 2009; Okamoto *et al.*, 2011). However, this dominance is now being challenged by the emergence of the new generation of PEC water splitting cell (integration of photovoltaic system with an electrolyzer to generate clean and portable H_2 energy carrier). The main disadvantage of the photovoltaic is that it does not operate well at night or during the period of bad weather. Thus, storage of energy as chemical fuel in the H_2 form is essential (Grätzel, 2001; Currao, 2007; Barreca *et al.*, 2011).

The energy can be stored in H_2 fuel within a fuel cell can then be efficiently converted into electrical energy and to be available at all times. This cell normally is based on nanocrystalline materials, which offers the prospect of cheap fabrication together with other attractive feature such as high chemical stability and flexibility in aqueous solution under evolving O_2. Those materials also have reasonably high incident light to current generation when operated in a PEC water splitting cell (Grätzel, 2001; Grimes *et al.*, 2007; Allam *et al.*, 2008; Centi and Perathoner, 2009). In 1972, Fujishima and Honda discovered the PEC water splitting process for H_2 generation using TiO_2 electrodes. This breakthrough has triggered the subsequent interests in photocatalysis research by scientists and researchers from all over the world on TiO_2 and made TiO_2 as an important component in many practical applications.

2.3 Basic principle of PEC water splitting

PEC water splitting process is the general term for a chemical reaction in which water is separated into O_2 and H_2 using photocatalyst that catalyze the water splitting reaction. A basic schematic diagram of such overall water splitting reaction using a semiconductor photocatalyst is presented in Figure 2.1.

$$2H_2O\ (l) \rightarrow O_2\ (g) + 2H_2\ (g) \qquad \text{(equation 2.1)}$$

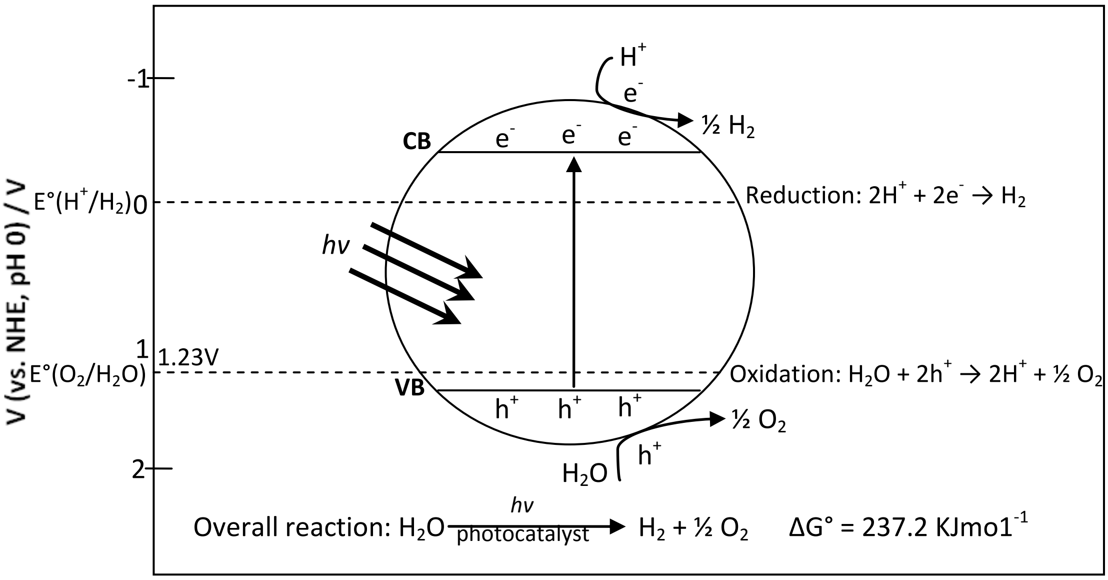

Figure 2.1: Basic principle of the overall water splitting reaction on a semiconductor photocatalyst (Leung *et al.*, 2010).

The overall water splitting reaction is considered as a thermodynamically uphill reaction with a large a Gibbs free energy of $\Delta G^0 = + 237.2$ KJ mol^{-1} (equation 2.1). This indicates that photon energy is required to overcome the large positive change in Gibbs free energy through PEC water splitting (Leung *et al.*, 2010). The light-driven water splitting process is triggered when n-type TiO_2 photocatalyst absorbs photons (*hv*) with energies greater than its band gap energy. This light absorption generates electrons in the conduction band and holes in the valence band (equation 2.2). The holes perform work at the TiO_2 electrolyte interface oxidizing water molecules to create O_2 and H^+ ions (equation 2.3). The electrons will move through the external circuit to the platinum electrode where they reduce H^+ ions creating H_2 molecules due to the electric field or under external bias (equation 2.4).

$$TiO_2 + 2\,h\nu \rightarrow TiO_2 + 2e^- + 2h^+ \qquad \text{(equation 2.2)}$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \qquad \text{(equation 2.3)}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{(equation 2.4)}$$

If these reactions are to proceed with success, the band gap of the semiconductor photocatalyst must satisfy certain requirements. It is necessary that the photon delivering energy to the reaction has enough energy to perform both the oxidation and reduction reactions of water on its surface. In the case of PEC water splitting, this means that the incoming energy must be at least equilibrium with cell potential for water electrolysis, which is 1.23 eV at 25 °C and 1 atm.

A Schottky contact is formed between metal (Ti foil) and semiconductor (TiO_2 nanotubes) as presented in Figure 2.2. In this manner, Fermi level must be constant throughout the sample; otherwise no electric current will flow. A potential gradient along the interface is formed and then will lead to the band bending. Thus, photo-induced electrons will force to transfer from semiconductor to the metal. Then, these photo-induced electrons will drift to the counter electrode and reduce the H^+ ions into H_2 gases under external bias.

However, there is unavoidable energy losses associated with any solar energy conversion process involving semiconductor photocatalyst. When solar illumination strikes the photocatalyst, any photons absorption with the energy higher than band gap of the photocatalyst will excite the electrons from the valence band into conduction band. In this case, recombination of electron/hole pairs can be acted very rapid and release energy in the form of unproductive heat or photons (Grimes *et al.*, 2007). Other possible reasons for the energy losses includes electrons transport within the sample during charge carriers separation, transport of electrons from photoanode to counter electrode, and Joule heating due to the electrons flow through the external circuit (Leung *et al*., 2010). In a practical PEC water splitting system, energy losses can be greater than 0.8 eV (Ni *et al*., 2007; Navarro Yerga *et al*., 2009). Thus, the optimum band gap of semiconductor photocatalyst applied to PEC water splitting cell must be approximately 2.0 eV (Grimes *et al*., 2007).

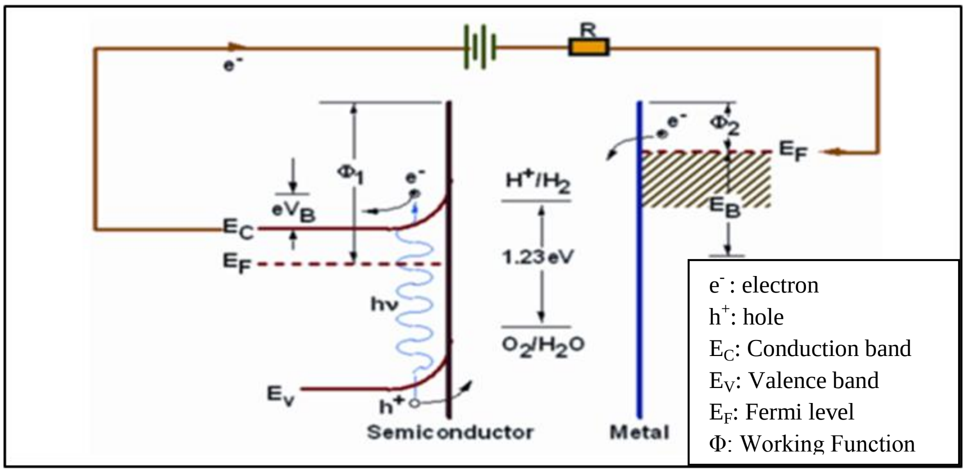

Figure 2.2: Energy diagram for an n-type semiconductor-metal in photoelectrolysis cell (Neelkanth *et al*., 2009).

However, there is unavoidable energy losses associated with any solar energy conversion process involving semiconductor photocatalyst. When solar illumination strikes the photocatalyst, any photons absorption with the energy higher than band gap of the photocatalyst is lost as heat. There is only a partial fraction of the excited state energy can be used to separate electrons from their atomic bonds to produce electron/hole pairs (Grimes *et al*., 2007). Other possible reasons for the energy losses includes electrons transport within the photoanode during charge carriers separation, transport of electrons from photoanode to platinum electrode, and Joule heating due to the electrons flow through the external circuit (Leung *et al*., 2010). In a practical PEC water splitting system, energy losses can be greater than 0.8 eV (Ni *et al*., 2007; Navarro Yerga *et al*., 2009). Thus, the optimum band gap of semiconductor photocatalyst applied to PEC water splitting cell is approximately 2.0 eV (Grimes *et al*., 2007).

2.4 Material selection for PEC water splitting

Taking into account of the processes involved in the dissociation of water on particulate photocatalysts under visible light irradiation, the materials used as photocatalysts must satisfy several functional requirements with respect to band gap energy and electrochemical properties as shown below:

i. Band edge position: The conduction band level should be more negative than H_2 production level ($E_{H2/H2O}$) while valence band level should be more positive than water oxidation level ($E_{O2/H2O}$) for efficient H_2 generation (Ni *et al*., 2007).
ii. Band-gap: The electronic band gap should be low for most of the solar light spectrum so that can be used for photoexcitation (Misra *et al*., 2009).
iii. Transportation of charge carriers: Charge carriers should be transported with minimal losses from the bulk oxide material to the counter electrode for high efficient H_2 generation. (Grimes *et al*., 2007).
iv. Stability: The photocatalyst must be stable against photocorrosion in electrolyte (Misra *et al*., 2009).

Besides, light-harvesting ability of a photocatalyst is an important criterion to produce maximum photo-induced charge carriers. The basic parameter that governs the light-harvesting ability of the photocatalyst is its electronic structure, which determines its band gap energy. Various wide band-gap metal oxide semiconductor (TiO_2, WO_3, ZnO, Fe_2O_3, SnO_2, SiC) and non-oxide semiconductors (CdS, CdSe, GaAs, GaP) have been identified as attractive materials for stable and highly efficient renewable energy devices (Ahn *et al.*, 2007; Marsen *et al.*, 2007). Figure 2.3 illustrates the positions of band edges of various semiconductors regarding to the normal hydrogen electrode (NHE) as standard for zero potential for water-oxidation/ reduction processes. As viewed from the band positions, CdSe, CdS, ZnO, TiO_2 and SiC fulfill the thermodynamic requirements for overall water splitting.

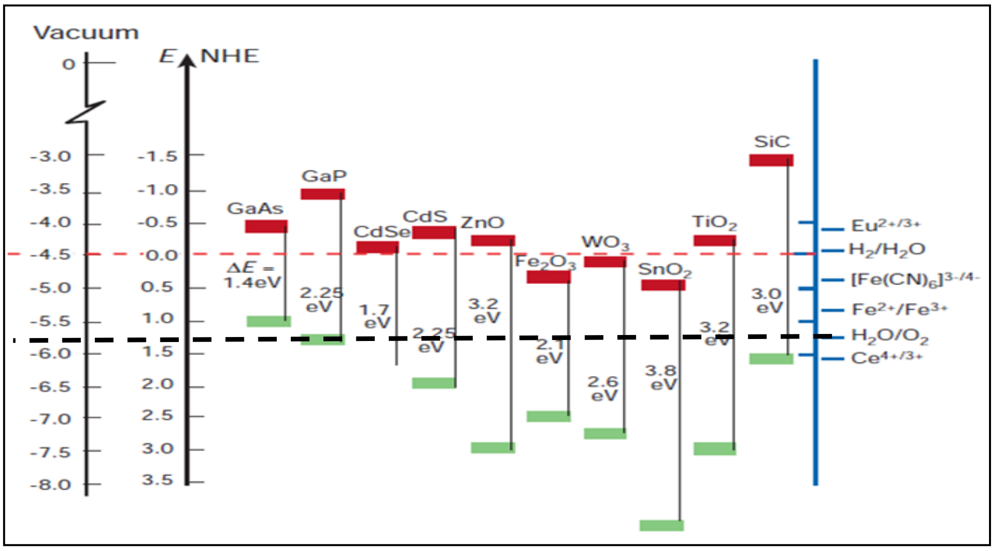

Figure 2.3: Electronic structure of different semiconductors and the relative position of their band edge vs. some key redox potentials (Grätzel, 2001).

Among these semiconductors, CdS and CdSe showed lower band gap and suitable band edge position. However, CdS, and CdSe are unstable in the water oxidation reaction because anions of these materials are more susceptible to oxidation than water, causing both (i.e., CdS and CdSe) to degrade by oxidation (Neelkanth *et al.*, 2009, Ni *et al*. 2007). ZnO fulfills the thermodynamic requirements for PEC water splitting reactions. However, ZnO is more likely to form nanowires and nanorods with random distribution arrangement as well as difficult to grow into self-organized and highly order nanotubes architecture. In this manner, ZnO nano-architecture will result in inadequate light absorption, higher surface recombination and limit its practical application in PEC water splitting. Among all of the available semiconductor photocatalysts, TiO_2 offers great promise for PEC water splitting applications and it is perfectly suitable as a photoelectrode in PEC water splitting system, which has a positive impact on the PEC utility of the material (Misra *et al*., 2009; Leung *et al*., 2010; Nah *et al*., 2010).

2.5 TiO_2 photocatalyst for PEC water splitting

In 1972, PEC water splitting using TiO_2 as photoelectrode was successfully reported by Fujishima and Honda. Since then, TiO_2 has been extensively used as an efficient photoelectrode in PEC water splitting system for H_2 generation because of its unique characteristics (Kitano *et al*., 2007; Shankar *et al*., 2008; Dholam *et al*., 2008; Yan and Zhou, 2011). Particles/spheres of TiO_2 as photoelectrode in PEC water splitting system has been reported in earlier studies, either freely suspended in solution or compacted to a robust photoelectrode. However, the drawbacks of such photoelectrode include the presence of defects or trapping sites, more grain boundaries, and disordered contact areas between two particles/spheres (Sun *et al*., 2010; Roy *et al*., 2011). Hence, the electron transporting time in the bulk phase of TiO_2 particles/spheres is rather long, which leads to more recombination losses and scattering problems of photo-induced electrons. Furthermore, the use of TiO_2 particle/sphere photoelectrode requires appropriate substrates as support for the catalysts in PEC system to ease the filtration procedure after photoreaction (Yang *et al*., 2010). Recently, two-dimensional TiO_2 thin film photoelectrode has been used in PEC water splitting system because of their capability to eliminate the above listed problems and still be reusable (Ghicov and Schmuki, 2009; Liu *et al*., 2011; Sun *et al*., 2011). However, two-dimensional TiO_2 thin film photoelectrode generally does not possess large active surface area for PEC reactions (Yang *et al*., 2010). Therefore, maximizing the specific surface area of TiO_2 thin film is crucial. 1D TiO_2 nanotube arrays are considered an ideal photoelectrode because of their inner and outer wall surface area of nanotube that greatly increases the density of the active sites available for photon absorption (Nah *et al.*, 2010; Zhang *et al.*, 2010; Krengvirat *et al.*, 2012; So *et al.*, 2012). Therefore, the use of 1D TiO_2 nanotubes is much better and effective way to improve the PEC water splitting performance.

Synthesis of 1D TiO_2 nanostructures can be achieved by various approaches such as sol-gel synthesis (Hoyer *et al.*, 1996; Liu *et al.*, 2000; Yuan and Su, 2004), hydrothermal synthesis (Kasuga *et al.*, 1999; Zhang *et al.*, 2004; Kasuga, 2005), and anodization technique (Mor *et al.*, 2003; Mishra *et al.*, 2003; Mor *et al.*, 2006; Paulose *et al.* 2006). Among all of these methods, anodization technique is the most feasible due to its ability to create self-organized anodic oxides in the form of nanotubular structures with almost perfect vertical alignment. Moreover, anodization is relatively simple and can be adopted for large-scale industrial production (Macak *et al.*, 2006; Ghicov and Schmuki, 2009). Most importantly, 1D TiO_2 nanotube arrays provides a unidirectional electrical channel for photo-induced charge carrier transfer, at where TiO_2 grains are stretched in the tube growth direction. Thus, vertical transportation of charge carriers could be enhanced and improved the PEC water splitting performance due to low recombination losses at grain boundaries (Roy *et al.*, 2011). In order to get the right dimensions and morphologies, a controlled synthesis procedure for the production of nanotube arrays must be investigated and optimized by tuning the length, wall thickness, pore diameter, and intertube spacing through the synthesizing process. However, massive organic waste will be produced after the anodization process, thus, proper organic waste management and disposal is required. In the following section, TiO_2 nanotube arrays and the formation by various authors will be reviewed.

2.6 TiO_2 nanotube arrays

Highly ordered and self-aligned 1D TiO_2 nanotube arrays is commonly produced by anodization method (Paulose *et al.*, 2007; Macak *et al.*, 2008). Vertically oriented nanotube arrays offer large specific surface area, which have tube-like structures with circular nanotubular opening serve as a scaffold to anchor light-harvesting assemblies (Grimes, 2007; Sun *et al.*, 2010). The diameter of the opening ranges from 20 nm to 350 nm and the length of the tube can vary from 0.2 μm to 1000 μm depending on the processing parameter. The bottom part of the nanotubes which are in the form of domes is called barrier layer with typical shape of hexagonal or pentagonal (Mohapatra *et al*, 2007). Figure 2.4 shows FESEM images of the cross section, top viewed and bottom part of typical self organized TiO_2 nanotube arrays, respectively. The formation of nanotubes by anodization technique will be reviewed in the preceding section.

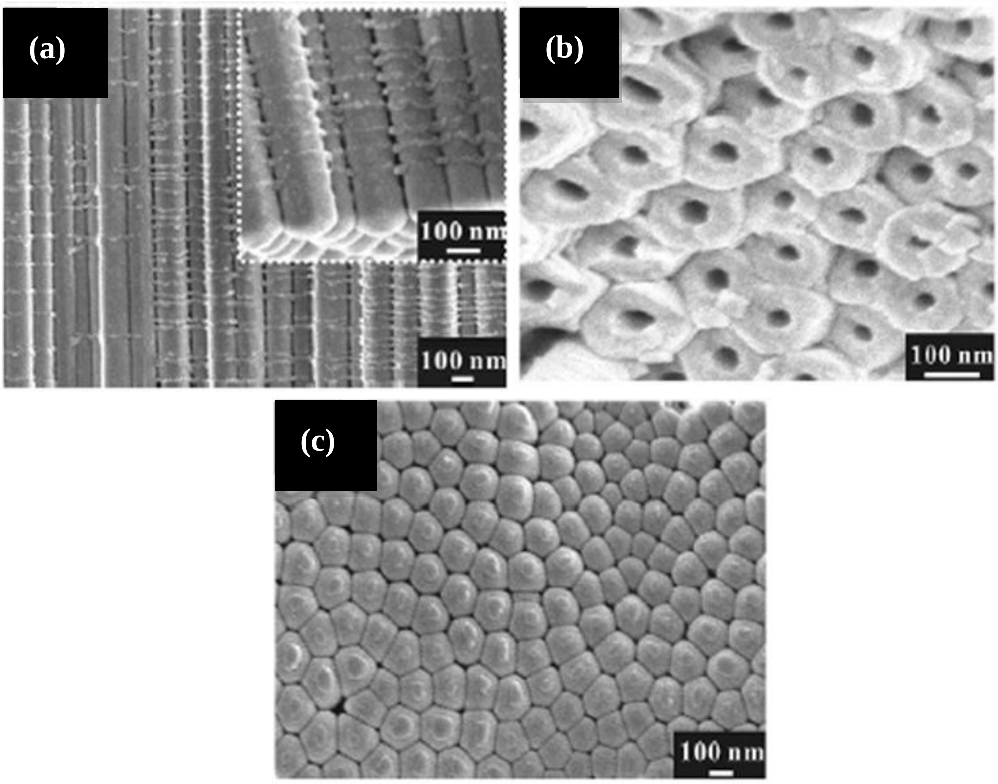

Figure 2.4: SEM images of (a) cross sectional image of TiO_2 nanotubes, inset is the image with higher magnification, (b) top view of TiO_2 nanotubes, and (c) bottom of TiO_2 nanotubes (Zhang *et al.*, 2010).

2.6.1 Formation of TiO_2 nanotube arrays

Ti foil can be used to grow an oxide film via electrochemical process. In anodizing cell, Ti is used as an anode and it is connected to positive terminal of power source, whereas platinum is used as cathode and being connected to negative terminal of power source. There are few other candidates for cathode, which consist of carbon, lead, nickel or stainless steel. The cathode has to be an inert electrode and non-reactive in the electrolyte bath (Mor *et al*., 2006; Allam and Grimes, 2008). Figure 2.5 shows a typical experimental setup of anodization and typical structure of TiO_2 nanotubes after anodization process. When the circuit is connected, electrons will flow from the anode, allowing the ions on the metal surface to react with electrolyte to produce oxide layer on the metal. During anodization process, magnetic stirring is commonly used to reduce the thickness of the double layer at the Ti foil/electrolyte interface, and ensure the uniform local current density as well as temperature over the Ti electrode (Macak *et al*., 2006, Paulose *et al*., 2006). The electrochemical condition such as voltage, time, concentration of electrolyte, temperature, and pH of electrolyte will determine the morphological and structural of TiO_2 nanotubes (Muti *et al*, 2008). In the next section, synthesis generations of TiO_2 nanotubes formation are discussed and several mechanism models are presented.

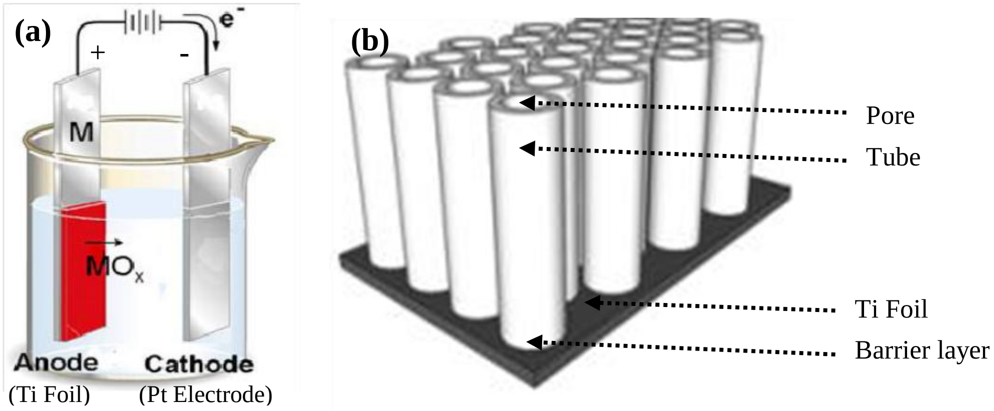

Figure 2.5: (a) Typical experimental setup of anodization system and (b) schematic diagram of the typical structure of TiO_2 nanotubes after anodization process (Macak *et al*., 2007).

2.6.2 The four synthesis generation of TiO_2 nanotubes

The first generation of the TiO_2 nanotube arrays synthesis was achieved by aqueous electrolytes (HF-based electrolyte), such as HNO_3/HF, H_2SO_4/HF, H_2CrO_7/HF, H_2SO_4/NH_4F and CH_3COOH/NH_4F electrolyte. A report in 1999 by Zwilling and co-workers suggested that self-organized porous TiO_2 can be obtained by anodizing a Ti-based alloy in an acidic, fluoride-based electrolyte. In 2001, Gong and co-workers fabricated a form of self-organized, highly uniform TiO_2 nanotubes by anodizing Ti in an aqueous electrolyte that contains dilute HF. Maximum nanotube lengths in this first synthesis generation were approximately 500 nm. It was found that the short nanotubes mainly attributed to the higher surface etching rate at the tip of nanotubes due to the excessive H^+ ions in the electrolyte.

In the second generation, the length of TiO_2 nanotubes was increased to approximately 7 µm by controlling the pH of the electrolyte. Cai and co-workers (2005) were first to fabricate TiO_2 nanotubes of several µm in length using KF and NaF electrolytes by varying electrolyte pH. They found that the difference in electrolyte pH, in turn controlled the surface etching rate at the tip of the nanotubes and chemical dissolution rate at the barrier layer of nanotubes. This condition leads to significant variation in tube length and pore diameter.

In the third-generation, TiO_2 nanotubes with lengths of up to approximately 1000 µm were achieved using non-aqueous and polar organic electrolytes such as formamide, dimethylsulfoxide, ethylene glycol or diethylene glycol (Ruan *et al.*, 2006). The key for successfully growing long nanotube arrays was to keep the water content below 5 wt% in the anodization bath. A few studies discovered that the addition of optimum amount of water results in high growth rate (i.e., over 10 nm/min) of organic electrolyte (Poulose *et al.*, 2006; Prakasam *et al.*, 2007; Raja *et* *al*., 2007; Sohn *et al*., 2008; Chang *et al*., 2009; Wan *et al*., 2009). In those studies, water was observed to act as an oxygen provider, which supplied sufficient amount of O^{2-} ions needed for oxidation. Besides, the use of high fluoride content in an organic electrolyte containing optimum amount of water was noticed to accelerate the chemical dissolution at the bottom of the nanotubes, resulting in longer nanotube arrays (Paulose *et al.,* 2006; Shankar *et al.,* 2007; Sreekantan *et al*., 2010).

The fourth synthesis generation was non-fluoride-based anodization chemistries. In 2006, Nakayama *et al.* reported the formation of TiO_2 nanotubes by anodization in a perchloric acid solution. Richter *et al.* (2007) grew similar nanotubes in oxalic acid, formic acid, and sulfuric acid solutions containing 0.3–0.6 M NH_4Cl. However, the nanotubes were in bundles form rather than arrays. The length of nanotubes was approximately 60 µm. There was no obvious dependence of nanotube diameter upon voltage; all tubes diameters were between 15 and 35 nm with wall thickness of about 5 nm (Hahn *et al.*, 2007). The finding indirectly showed the importance role of the fluoride ions in the formation of well-aligned and highly ordered nanotube arrays. Therefore, in the present work, organic electrolyte containing fluoride ions was used for producing TiO_2 nanotube arrays.

2.6.3 Mechanism of formation of TiO_2 nanotubes

In this section, the formation mechanisms of TiO_2 nanotubes proposed by various authors are reviewed. There are mainly three mechanistic models of TiO_2 nanotubes formation via anodization technique. In early 2004, Choi *et al.* developed a mechanistic model of TiO_2 nanotube formation by describing the formation of porous TiO_2 due to electrical breakdown of the TiO_2 (Figure 2.6). Initially, the barrier layer of TiO_2 was developed and grows thicker with increasing applied anodization