DEVELOPMENT OF CARBON AND POTASSIUM-INCORPORATED TITANIUM DIOXIDE NANOTUBE ARRAYS FOR SOLAR ENERGY HARVESTING APPLICATIONS

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DEVELOPMENT OF CARBON AND POTASSIUM-INCORPORATED TITANIUM DIOXIDE NANOTUBE ARRAYS FOR SOLAR ENERGY HARVESTING APPLICATIONS

by

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Thesis submitted in fulfillment of the requirements
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DECLARATION

I hereby declare that I have conducted, completed the research work and written the thesis entitle; *DEVELOPMENT OF CARBON AND POTASSIUM-INCORPORATED TITANIUM DIOXIDE NANOTUBE ARRAYS FOR SOLAR ENERGY HARVESTING APPLICATIONS.* This thesis has not been previously submitted for the degree or diploma in any university, it and does not contain any materials previously published, written or produced by another person.

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Thank you.

Warapong Krengvirat

May 2013

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AC	Alternating Current
AR	Aspect ratio
BET	Brunauer, Emmet, and Teller theory
C_B	Conduction band
D	Pore size
DC	Direct Current
DEG	Diethylene glycol
DI	Deionized water
DLOS	Deep-level spectroscopy
DMSO	Dimethyl sulfoxide
DSSC	Dye-sensitized solar cell
E_F	Fermi level
EG	Ethylene glycol
EIS	Electrochemical impedance spectroscopy
E_{redox}	Reduction/oxidation potential
$E_{counter}$	Electrical potential of the working electrode at open circuit conditions
E_{meas}	Electrical potential of the working electrode under illumination
FA	Formamide
FF	Fill Factors
FESEM	Field-emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
FTO	Fluorine-doped tin oxide

G	Geometric surface area factor
GOF	Goodness of fit
HRTEM	High-resolution transmission electron microscopy
ICSD	Inorganic crystal structure database standard
IPCE	Photon to current conversion efficiency
ITO	Tin oxide glass
J	Current density
J_{mp}	Current at maximum power
j_p	Photocurrent density
J-t	Current density-time transient
J-V	Current density - Voltage
LDA	Local-density approximation
MB	Methylene blue
MEK	Methylethylketone
MO	Methyl orange
MS	Mott-Schottky measurement
N_d	Charge carrier density
NHE	Normal Hydrogen Electrode
NMF	*N*-methylformamide
P_D	Residual concentration of MB after photodegradation
P_{max}	Maximum power
P-V	Power density - Voltage
PEC	Photoelectrochemical water splitting
PEG	polyethylene glycol
PEMFC	Proton exchange membrane fuel cells

PL	Photoluminescence spectroscopy
PTFE	Teflon
R	Resistance
RCA	Radio Corporation of America cleaning method
R_{exp}	Minimum reachable value of R_{wp}
R_{p}	Diameter of semi-circle of impedance spectrum
R_{s}	High frequency intersection of impedance spectrum
R_{wp}	Weight residual error
SAED	Selected area electron diffraction
TEG	Triethylene glycol
TEM	Transmission electron microscopy
UV-Vis	UV-Visible spectroscopy
V_{B}	valence band
VBM	Maximum valence-band
V_{fb}	Flat band potential
V_{mp}	Voltage at maximum power
V_{oc}	Open-circuit voltage
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Z	Impedance
Z'	Real impedance
$V_O^{\bullet\bullet}$	Oxygen vacancies

LIST OF SYMBOLS

hv	Photon energy
$\in$	Dielectric constant of anatase TiO$_2$ (48 F m^{-1})
$\in_0$	Permittivity of the free space charge ($8.86 \times 10\text{-}12$ F m^{-1})
E_{rev}^0	Reversible potential for water splitting
2θ	Diffraction angle
a	Interpore distance
Å	Angstrom
β	Full-Width at Half-Maximum (radius)
C	Capacitance
C'	Estimated capacitance
e	Electronic charge unit (1.6×10^{19} C)
e^-	Electrons
f	Applied frequency
η	Photoconversion efficiency
h^+	Holes
λ	Wavelength
μ	Growth rate
μ_v	Viscosity
θ	Bragg angle
σ	Ionic conductivity
τ	Crystallite size
τ_{rxn}	Time constant of electrochemical reaction

v	Interpore voids distance
w	Wall thickness
ω_{max}	Frequency at a maximum imaginary impedance

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LIST OF PUBLICATIONS

International journals

1   **Krengvirat W.**, Sreekantan S., Noor A.-F.M., Negishi N., Oh S.Y., Kawamura G., Muto H., Matsuda A. (2012) Carbon-incorporated TiO_2 photoelectrodes prepared via rapid-anodic oxidation for efficient visible-light hydrogen generation, *International Journal of Hydrogen Energy* 37 p.10046−10056.

2   **Krengvirat W.**, Sreekantan S., Noor A.-F.M., Negishi N., Kawamura G., Muto H., Matsuda A. (2013) Low-temperature crystallization of TiO_2 nanotube arrays via hot water treatment and their photocatalytic properties under visible-light irradiation, *Materials Chemistry and Physics* 137 p.991−998.

3   **Krengvirat W.**, Sreekantan S., Noor A.-F.M., Kawamura G., Muto H., Matsuda A. (2013) Single-step growth of carbon and potassium-embedded TiO_2 nanotube arrays for efficient photoelectrochemical hydrogen generation, *Electrochimica Acta* 89 p.585−593.

4   Wei L.C., Sreekantan S., San E.P., **Krengvirat W.** (2012) Photoelectrochemical characterization of WO_3-loaded TiO_2 nanotube arrays via radio frequency sputtering, *Electrochimica Acta* 77 p.128−136.

5   Sreekantan S., E P.S., Wei L.C., **Krengvirat W.** (2011) Nanotubular transition metal oxide for hydrogen production, *Advanced Materials Research: Nanomaterials* 364 p.494−499.

Proceedings

1   **Krengvirat W.**, Sreekantan S., Noor A.-F.M., Kawamura G., Muto H., Matsuda A. (2012) Low temperature formation of anatase nanocrystals in anodized titania nanotube arrays with hot water treatment, *The 53th Symposium on Glass and Photonics Materials* p.8−9, Japan.

2   **Krengvirat W.**, Sreekantan S., Noor A.-F.M., Kawamura G., Muto H., Matsuda A. (2012) Bimetallic transition oxide nanotubes photoelectrode for the production of hydrogen from water, *The 4th International Conference on Applied Energy* p.3221−3226, China.

3   **Krengvirat W.**, Sreekantan S., Noor A.-F.M., Kawamura G., Muto H., Matsuda A. (2012) Enhance photoresponse property of titania nanotube arrays by hot-water treatment technique, *The 50th Anniversary Symposium on Basic Science of Ceramics* p.197, Japan.

4   **Krengvirat W.**, Sreekantan S., Noor A.-F.M., Matsuda A., Chinwanitcharoen C. (2011) Water content: an essential factor for the preparation of well-aligned TiO$_2$ nanotubes via anodic oxidation in ethylene glycol electrolyte, *Science and Technology Community Development 2011 & International Symposium on Material Science Engineering and Energy Technology* p.110−119, Thailand.

5   **Krengvirat W.**, Sreekantan S., Noor A.-F.M., Matsuda A., Chinwanitcharoen C. (2011) Formation of Self-organized Titanium Oxide by Anodic Oxidation at Different Electrical Potentials and its Photocatalytic Property, *International Conference on Materials Processing Technology 2011* p.27−31, Thailand.

6.   Sreekantan S., Lai C.W., E P.S., **Krengvirat W.** (2011) Nanotubular transition metal oxide for hydrogen production, *International Conference of Nanomaterials Synthesis and Characterization* 2011, Malaysia.

Award

1   Sreekantan S., Arifin Z.A., Lai C.W., Saharudin K.A. and **Krengvirat W.** (2011) Korea International Women's Invention Exposition 2011, Seoul, Korea, hosted by the Korean Intellectual Property Office (KIPO) and organized by the Korea Women Inventors Association (KWIA) on 4 – 7th May 2011, for project entitle: Nanopurifier- A sustainable way of destroying contaminants in air and water.

PEMBENTUKAN TITANIUM DIOKSIDA TIUBNANO DIGABUNG KARBON DAN KALIUM UNTUK APLIKASI PENGUJAAN SOLAR

ABSTRAK

Tiubnano TiO_2 telah menarik perhatian ramai sebagai bahan yang paling sesuai untuk aplikasi menggunakan tenaga solar. Walaubagaimanapun penyerapan cahaya nampak yang rendah dan rekombinasi cas pembawa yang tinggi masih kekal sebagai isu yang mencabar untuk aplikasi praktikal. Oleh itu , objektif penyelidikan ini adalah untuk membentuk tiubnano TiO_2 untuk aplikasi menggunakan tenaga solar, seperti fotopemerosotan, sel fotoelektrokimia (PEC) dan pewarna-tersensitis sel solar (DSSC). Hasil penyelidikan ini menunjukkan tiubnano TiO_2 yang responsif kepada cahaya nampak telah dibentuk dengan kadar yang pantas ~289 nm min^{-1} melalui pengoksidaan anodik dalam etilena glikol (EG) yang mengandungi 0.5 wt% ammonium fluorida (NH_4F) dan 1 wt% H_2O. Kehadiran spesis karbonat-terjerap dan karbon pada celahan dalam tiubnano TiO_2 yang berasal daripada pirogenasi EG telah didapati telah didapati menghasilkan jalur setempat di dalam jurang tenaga, lalu mempertingkatkan kebolehan penyerapan cahaya nampak. Tiubnano TiO_2 anatas dengan luas permukaan tinggi (~110.9 m^2 g^{-1}) telah diperolehi setelah merendam tiubnano yang dianodik di dalam air panas pada ~90°C. Tiubnano yang dirawat dengan air panas mempamerkan fotopemerosotaan metilena biru yang cekap di bawah cahaya nampak dengan kadar penguraian sebanyak ~11% h^{-1}; nilai ini lebih tinggi daripada tiubnano yang telah di rawatan haba (~9 % h^{-1}) dan serbuk P25 (~2 % h^{-1}). Walau bagaimanapun, rawatan haba pada 400 °C selama 4 jam merupakan satu pendekatan penting untuk mendapatkan tahap kehabluran yang baik untuk

mempertingkatkan sifat PEC dan DSSC. Tiubnano TiO_2 yang diberi rawatan haba yang mempunyai panjang purata sebanyak ~18 µm, ketebalan dinding (~13 nm) dan saiz liang yang besar (~115 nm) dengan nisbah aspek yang tinggi (~142.5) mempamerkan keupayaan luar biasa untuk menjana H_2 pada kadar ~508.3 µL min^{-1} cm^{-2} dan kecekapan fotoubahan (η) daripada ~2.3 %. Pertumbuhan tiubnano TiO_2 dan sifat elektrokimianya telah diperbaiki lagi dengan penambahan kalium hidroksida (KOH) ke dalam florin-EG. Gabungan 1 wt% 1.0 M KOH menyebabkan pertumbuhan seimbang tiubnano dengan kadar ~353 nm min^{-1}. Spesis kalium-terjerap meningkatkan lagi penyerapan cahaya nampak kepada ~780 nm. Selain itu, sifat e^- daripada kalium-terjerap menggalakkan penambahan pembawa cas (9.7 × 10^{21} cm^{-3}). Tiubnano TiO_2 yang mengandungi karbon dan kalium dengan nisbah aspek ~140.5 menunjukkan sifat fotoelektrokimia yang unggul dan mempunyai kebolehan untuk menjana H_2 dengan kadar evolusi ~658.3 µL min^{-1} cm^{-2} dan η daripada ~2.5 %; iaitu ~30 % lebih tinggi daripada TiO_2 tanpa kalium. Tiubnano TiO_2 yang mempunyai karbon dan kalium digunakan untuk penghasilan DSSCs pencahayaan belakang dengan menggunakan pewarna N719 dan elektrolit iodida/triodideredox. Tiubnano yang tersusun baik dengan panjang purata sebanyak 18 µm, tebal dinding (~13 nm), dan saiz liang~130 nm didapati membenarkan penembusan $h\nu$ teruja yang lebih banyak dan memudahkan resapan pembawa cas. Tambahan pula, luas permukaan geometri yang tinggi sebanyak ~755 dapat menguja penjerapan pewarna yang tinggi. η maksimum sebanyak 2.78 % telah dicapai daripada tiubnano TiO_2 yang mempuyai panjang sebanyak 17.8 µm dengan potensi litar terbuka sebanyak 0.67 V, ketumpatan arus 8.95 mA cm^{-2}, dan faktor terisi 46.39 %.

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ABSTRACT

TiO_2 nanotube arrays have attracted great interest as the most promising candidate for solar energy harvesting applications. However, poor visible-light absorption and high recombination of charge carriers still remain as challenging issues for their practical applications. Hence, the objective of this work was to develop carbon and potassium-incorporated TiO_2 nanotube arrays for solar energy harvesting applications, including photodecolorization, photoelectrochemical cell (PEC) and dye-sensitized solar cells (DSSC). Visible-light responsive TiO_2 nanotube arrays were rapidly grown with a rate of ~289 nm min^{-1} by anodic oxidation in ethylene glycol (EG) containing 0.5 wt% ammonium fluoride (NH_4F) and 1 wt% H_2O. The presence of adsorbed-carbonate species and interstitial carbon in TiO_2 nanotubes originated from the pyrogenation of EG resulted in the generation of localized state, and thus enabled the visible-light absorption. Anatase TiO_2 nanotube arrays with high surface area (~110.9 m^2 g^{-1}) were obtained by facile immersion of as-anodized nanotube arrays in hot water at ~90°C. Such hot water-treated nanotube arrays exhibited efficient visible-light photodegradation of methylene blue with the decomposition rate of ~11 % h^{-1}. This value is relatively higher than heat-treated arrays (~9 % h^{-1}) and P25 powder (~2 % h^{-1}). However, heat treatment at 400°C for 4 h was found as essential approach to obtain better crystallinity for high PEC and DSSC properties. Heat-treated TiO_2 nanotube arrays with average nanotube lengths

of ~18 μm, thick walls (~13 nm) and large pore sizes (~115 nm), with high aspect ratio (~123.6) exhibited remarkable ability to generate H_2 at a rate of ~508.3 μL min^{-1} cm^{-2} and photoconversion efficiency (η) of ~2.3%. The growth of TiO_2 nanotube arrays and their electrochemical properties were further improved by simple addition of potassium hydroxide (KOH) into fluorinated-EG. The incorporation of 1 wt% of 1.0 M KOH facilitated an equilibrium growth of nanotube arrays with a rate of ~353 nm min^{-1}. The adsorbed-potassium species further extended the light visible-light absorption to ~780 nm. Furthermore, the electron donation nature of adsorbed-potassium promoted larger number of charge carriers (9.7×10^{21} cm^{-3}). Carbon and potassium-incorporated TiO_2 nanotube arrays with aspect ratio of ~140.5 exhibited superior photoelectrochemical H_2 generation with an evolution rate of ~658.3 μL min^{-1} cm^{-2} and η of ~2.5%, which is ~30 % higher than that of without potassium. Carbon and potassium-incorporated TiO_2 nanotube arrays were assembled to back-side illumination DSSCs using N719 dye and iodide/triodide redox electrolyte. Well-aligned nanotubes with average nanotube lengths of 18 μm, thick walls (~13 nm), and large pore sizes (~130 nm) allowed a greater penetration of excited $h\nu$ and ease charge carrier diffusion. Furthermore, high geometric surface area up to ~755 could harvest higher dye adsorption. A maximum η of 2.78% was achieved from a 17.8 μm length TiO_2 nanotube arrays, with open circuit potential of 0.67V, current density of 8.95 mA cm^{-2}, and filled factor of 46.39%.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Global warming is an important issue faced by humankind, which causes an unprecedented onslaught of deadly and costly weather disasters, such as severe storms, droughts, heat waves, rising seas and floods throughout the world. The combustion of fossil fuel from human activities, such as transportation and industry massively increase the energy consumption thus contributes to global warming by releasing billion tons of greenhouse gases, such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and fluorinated gases into atmosphere. Figure 1.1 shows statistic data of fossil fuel consumption and CO_2 emission reported by British Petroleum public limited company; BP (British Petroleum, 2012). The fossil fuel consumption increases continuously year by year and the overall consumptions are estimated approximately eight times higher than alternative sources, for example nuclear- and hydro-energy.
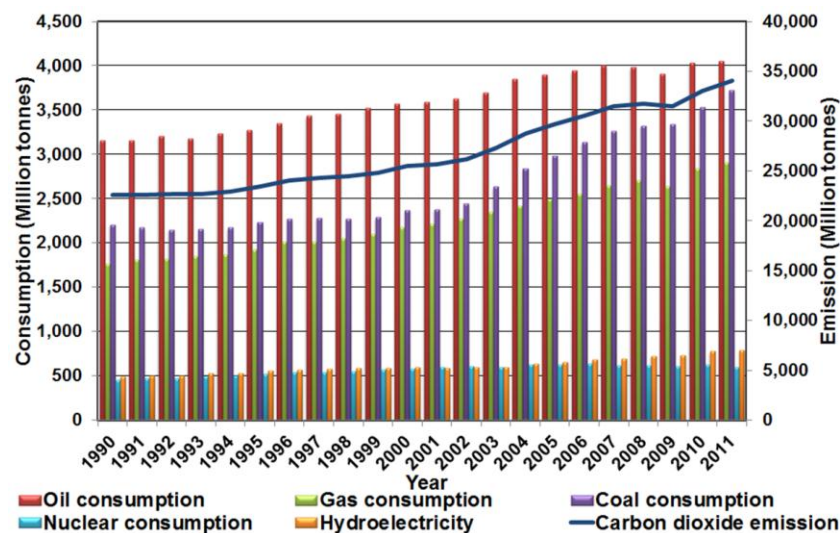
Figure 1.1 Statistic data of global energy consumption and CO_2 emission during 1990-2011 – plotted from statistic data from British Petroleum, (2012).

High consumption of fossil fuel also leads to energy crisis which strongly impacts the economic globalization by arising the energy price. Besides, the emissions of effluents gaseous or wasted water from human activities contribute to the deleterious effects on an environment and the earth ecosystems (Akpan *et al.*, 2009). Pursuant to aforementioned issues, it is indispensable to explore sustainable solutions to safe the earth and mankind. Over the last decades, abundant resources, including geothermal, solar and wind have drawn considerable attention as alternative resources for inexhaustible and non-polluting "GREEN" energy. However, they can subsidies approximately 15% of overall electricity generation (Figure 1.2).
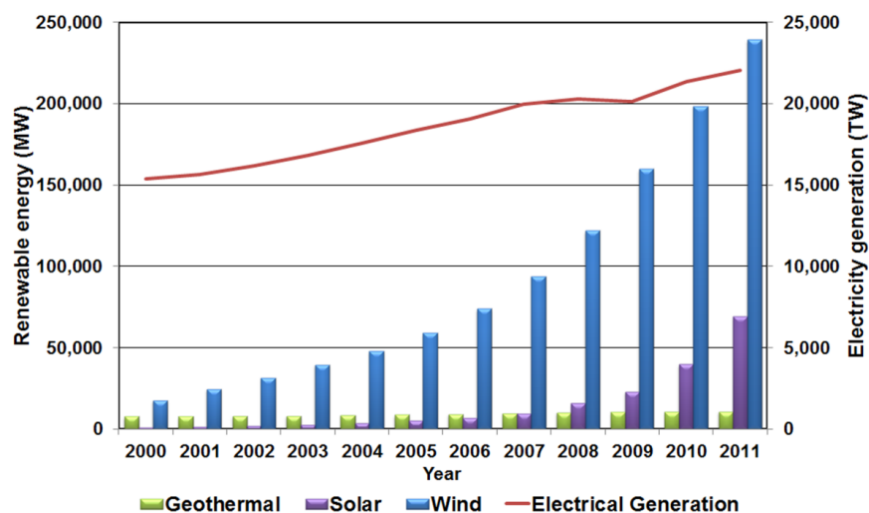
Figure 1.2 Statistic data of global electricity generation and renewable energy during 1990-2011 – plotted from statistic data from British Petroleum, (2012).

Solar energy; radiant light and heat from the sun, is the most abundant clean energy source available. Despite the fact that solar energy strikes the earth in an hour is relatively higher than energy consumed by humans for an entire year (Lewis, 2007). Hence, extensive research and development of materials that can efficiently harvest solar irradiation and convert it to clean and renewable energy are essential. Photocatalysis which utilizes solar energy to activate the chemical reactions via

oxidation and reduction is a sustainable technology to provide solution for energy crisis and environmental issues (Kudo and Miseki, 2008; Vinu and Madras, 2010). Photoelectrochemical water splitting; PEC (Fujishima and Honda, 1972) and dye-sensitized solar cell; DSSC (O'regan and Gratzel, 1991) appear as potential means to convert solar energy to hydrogen (H_2) fuel and electricity, respectively. Several types of photocatalyst, such as TiO_2, ZnO, Fe_2O_3, ZrO_2, V_2O_5, Nb_2O_5 and WO_3 have been used in PECs and DSSCs. Among them, TiO_2 is one of the most promising candidates because of its superior properties, *e.g.*, light absorption capabilities, chemical inertness and stability (Ni *et al*., 2007; Chen *et al*., 2007; Varghese *et al*., 2009). It possesses suitable band-edge positions that enable its use in PECs and DSSCs. Furthermore, its strong oxidation nature offers a great ability in detoxifying hazardous waste and air contaminant (Fujishima and Honda, 1972).

One-dimension (1D) nanostructured material has been discovered (Iljima, 1991), and it has been trigged enormous effort in physics, chemistry, and materials science. TiO_2 with well-aligned nanotubular structure provides unique electronic properties, such as high e^- mobility, low quantum confinement effects, high specific surface area, excellent ability to harvest photon energy (*hv*), and high mechanical strength (Mohapatra *et al.*, 2007; Baker and Kamat, 2009; Roy *et al.*, 2011). Furthermore, vectorial charge transport facilitates the photoelectrochemical properties and photocatalytic efficiency (Baker and Kamat, 2009; Mohamed and Rohani, 2011). These advantages render TiO_2 nanotube arrays as a promising candidate for various applications, such as for pollutant detoxification (Chen *et al.*, 2009; Sreekantan *et al.*, 2010; Sangpour *et al.*, 2010), PECs (Park *et al.*, 2006; Mohapatra *et al.*, 2007; Palmas *et al.*, 2010) and DSSCs (Jennings *et al.*, 2008; Lei *et*

al., 2010; Premalal *et al.*, 2012; Chang *et al.*, 2012). Although a promising structure of TiO_2 has been established, poor visible-light absorption of wide bandgap semiconductor (*c.a.* 3.2 eV) and high recombination of charge carriers restrict its use under solar irradiation. Therefore, this research established an efficient approach to form carbon-incorporated TiO_2 nanotube arrays via anodic oxidation in ethylene glycol (EG) containing excessive fluoride ions (F^-) for solar harvesting applications.

The growth of TiO_2 nanotube arrays was further improved by incorporation of alkali-species through the addition of potassium hydroxide (KOH) into EG. This approach allowed the simultaneous control of electrochemical oxidation and chemical dissolution, thereby enhancing the growth rate and structural morphologies of nanotube arrays. Adsorbed-potassium species on TiO_2 nanotubes contributed to their visible-light absorption and photoelectrochemical properties. This research also demonstrated an alternative method to crystallize TiO_2 nanotube arrays at low-temperature via water treatment. In addition, the crystallization behavior and structural stability of nanotube arrays was also determined by thermal annealing at high temperature. The photoelectrochemical water splitting and photodegradation under solar irradiation were carried out in custom made reactors. Furthermore, back-side illumination DSSCs were fabricated in order to further determine the performance of nanotube arrays to harvest the solar energy.

1.2   Problem statements

Since scientific studies of TiO_2 has been established in the early of 20th century (Keidel, 1929), TiO_2 has become one of the most widely used materials due to its unique physio-chemical properties (Hashimoto *et al.*, 2005). However, their

poor visible-light absorption and high recombination of charge carriers restrict their use under solar irradiation (Sennik *et al*., 2010; Sreekantan *et al.*, 2010). The recombination of photogenerated charge carrier due the diffusion length of ~10 – 30 nm (Lei *et al.*, 2010) can be overcame by the use of nanotubular structure. Recently, synthesis of TiO_2 nanotube arrays by anodic oxidation has been attracting considerable interest to aforementioned purposes. Effects of various synthesis parameters, *e.g.*, electrical potential (Gong *et al.*, 2001; Paulose *et al.*, 2007), anodization time (Wan *et al.*, 2009; Palmas *et al.*, 2010), electrolyte type and chemical composition (Shankar *et al.*, 2007; Hu *et al.*, 2008) have been extensively investigated.

The anodic oxidation in EG has been suggested as an efficient method to form well-aligned TiO_2 nanotube arrays with ultra-high aspect ratios (Paulose *et al.*, 2006; Shankar *et al.*, 2007). Furthermore, it is the only process that allows the incorporation of carbon species into nanotubes without any additional processing (Hu *et al.*, 2007; Park *et al.*, 2006; Raja et al., 2007). The adsorbed-carbon species from EG induce the generation of a localized C$2p$ state above O$2p$ states, thereby enabling the visible-light absorption (Mohapatra *et al.*, 2007; Liu *et al.*, 2009). Numerous researchers have achieved the formation of ultra-long TiO_2 nanotube arrays up to 1000 μm (Paulose *et al.*, 2007; Shankar *et al.*, 2007; Prakasam *et al*., 2007). In these reported works, the formation of long nanotube arrays however requires long production time of ~17 – 216 h. Such conditions suppress the utilization of anodic oxidation to be applied in the industrial scales and thus hinder the usage of TiO_2 nanotube arrays. From these aspects, the development of an

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anodization process for the rapid formation of TiO$_2$ nanotube arrays turns into an attractive subject of this study.

The anodic-growth of TiO$_2$ nanotube arrays is well-known as the equilibrium reaction between electrochemical oxidation and chemical dissolution (Sreekantan *et al.*, 2010; Sennik *et al.*, 2010). The growth of long nanotubes is significantly hindered by high chemical dissolution at the top of nanotubes (Macak et al., 2006; Shankar et al., 2007). Wang *et al.* (2011) have recently proposed the solution to control the chemical dissolution in EG containing ammonium fluoride (NH$_4$F) electrolyte by addition of sodium carbonate (NaCO$_3$) which allowed the formation of nanotube arrays with fast growth rate. This implies the potential of alkali additives to improve the balance between electrochemical oxidation and chemical dissolution. Besides, the incorporation of alkali species into TiO$_2$ nanotube arrays contributed to better photoelectrochemical properties as demonstrated by the anodic growth of TiO$_2$ nanotube arrays in hydrofluoric acid electrolyte containing potassium salt (Richter *et al.*, 2009). Although high growth rate has been achieved, the photoelectrochemical properties of nanotube arrays obtained from EG containing alkali species remains to be determined. Hence, this research devotes to develop carbon and potassium-incorporated TiO$_2$ nanotube arrays with enhanced electrochemical properties by rapid-anodic oxidation in fluorinated-EG containing alkali species.

Besides, heat treatment process has also drawn an essential role in determining the crystal structure of TiO$_2$ nanotube arrays. High annealing temperature to form high crystallinity anatase phase (*c.a.* $280 - 600°C$) induces the formation of thick barrier layer and thus lowers the photocatalytic efficiency of TiO$_2$

nanotube arrays by the recombination of charge carriers. Therefore, the investigation of crystallization behavior and structural stability of TiO_2 nanotube arrays at different heat treatment temperature are crucial to define their morphology and crystallinity, as well as the integration of this nanostructure into the devices. The development of low temperature crystallization of TiO_2 nanotube arrays is essential to the integration of TiO_2 nanotube arrays with polymeric substrates or temperature-sensitive devices. Alternatively, Matsuda *et al.* (2000) have suggested a facile approach to crystallize titanate-based thin films by immersion of the oxide into hot water. The products showed superior characteristics, *e.g.*, wettability, optical properties, photocatalytic efficiency and photovoltaic performance. Therefore, the mechanistic study for the crystallization of carbon-incorporated TiO_2 nanotube arrays by hot water treatment is essential to be explored as an alternative to thermal annealing.

TiO_2 nanotube arrays have widely been used in photoelectrochemical and photocatalytic applications. However, the understanding in the influence of structural characteristics of nanotube arrays on their efficiency remains unclear. For example, Park *et al.* (2006) suggested that the photoelectrochemical efficiency of nanotube arrays is proportional to the nanotube length. Liu *et al.* (2009) later demonstrated that the pore diameter has a greater effect rather than the nanotube length. It is of interest to study the influence of structural characteristics of TiO_2 nanotube arrays for solar energy harvesting applications. The role of carbon and potassium species in nanotubes on the visible-light response and their properties is also essential to address. Hence, comprehensive studies need to be conducted to obtain mechanistic model on how the carbon and potassium species improve the visible-light absorption, as well as photocatalytic and photoelectrochemical efficiency. Therefore, it is of

interest to gain fundamental knowledge on the fabrication of PEC and DSSC devices using carbon and potassium-incorporated TiO_2 nanotube arrays as photoelectrodes.

1.3   Objectives

The objectives of this research work are described as follows;

1. To study rapid formation of carbon incorporated TiO_2 nanotube arrays by anodization method in EG.

2. To improve the growth and properties of carbon incorporated TiO_2 nanotube arrays with KOH addition in EG.

3. To study the crystallization of TiO_2 nanotube arrays via hot water treatment and thermal treatment.

4. To investigate the photocatalytic and photoelectrochemical properties of visible-light responsive TiO_2 nanotube arrays.

1.4   Expected outcome

The ultimate outcomes of this research work are detailed as follows;

- Fundamental knowledge on the formation visible-light responsive TiO_2 nanotube arrays for solar energy harvesting applications is the main outcomes of this research work.

- With the fundamental knowledge of the formation gathered from this research work, a mechanistic model on the growth of TiO_2 nanotube arrays is proposed which is essential for the control of structural morphologies of TiO_2 nanotube arrays by controlling the anodic oxidation parameters.

- Data on the electrochemical, chemical, structural, electronic, morphological and optical properties, as well as photocatalytic and photoelectrochemical properties

would contribute towards the knowledge of microstructure-properties relation of photocatalysts in nanoscale.

- Eventually, by acquiring this important fundamental knowledge on the formation of visible-light responsive TiO_2 nanotube arrays and their usage in PECs and DSSCs, the project is believed to benefit the Universities as well as the countries in the development of high efficiency PECs and DSSCs.

1.5   Thesis overview

This thesis is organized in five chapters consequently. Chapter 1 describes a brief introduction, problem statements, objectives and outcomes of the research. In chapter 2, a comprehensive review on the formation of TiO_2 nanotube arrays and fundamental concepts of photocatalysis and functional applications of TiO_2 nanotube arrays, including photoelectrochemical water splitting and dye-sensitized solar cells are elaborated. This includes a comprehensive review on the enhancement of photocalytic efficiency by the incorporation of noble loading, metal ion and anion doping, composite semiconductors and sensitization. Chapter 3 details the experiment procedures that were used in this study. This included the experimental design and the preparation of TiO_2 nanotube arrays with the incorporation of carbon and potassium species. The characterization techniques are described in detail. This covers a brief explanation on the characterization equipment, their operation principles and sample preparation.

Chapter 4 presents the experimental results and comprehensive discussion on the formation of TiO_2 nanotube arrays via rapid-anodic oxidation and their applications under solar light irradiation. The content consists of main three parts,

including 1) the detail investigation on the growth behavior of visible-light responsive TiO_2 nanotube arrays by varying anodic oxidation parameters (*e.g.*, electrolyte composition, applied potential and anodization time) and effect of structural characteristics on their photoelectrochemical properties, 2) the crystallization of nanotube arrays via hot water treatment at different temperatures and exposure times, and the thermal stability of nanotube arrays at different temperatures, and 3) the formation of carbon and potassium-incorporated TiO_2 nanotube arrays by incorporation of KOH solution into fluorinated-EG electrolyte. The potential for newly-developed TiO_2 nanotube arrays for solar energy harvesting applications, such as photoelectrochemical water splitting and photodegradation under solar irradiation, as well as dye-sensitized solar cell are discussed in detail. Finally, chapter 5 is devoted to the conclusions of this research work and suggestions for future work.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

TiO$_2$ nanotube arrays have attracted scientific interest due to the combination of functional material properties with controllable nanostructure. Superior properties of TiO$_2$ nanotube arrays, including vectorial pathway of e^- transport, minimized e^- recombination, and high specific surface area render them as the most promising candidate for solar energy harvesting applications. Photoelectrochemical cells (PECs) and dye-sensitized solar cells (DSSCs) assembled with TiO$_2$ nanotube arrays have attracted great interest due to their outstanding potential to convert solar energy to hydrogen (H$_2$) fuel and electricity, respectively. However, the performance of PECs and DSSCs are greatly determined by structural morphologies of nanotube arrays. Hence, related literatures on the development of TiO$_2$ nanotube arrays for solar harvesting applications are elaborated in this chapter.

This chapter provides comprehensive review on the following topics: 1) basic principle of photocatalyst, PECs and DSSCs, 2) formation mechanism of oxide via anodization, and effects of anodization parameters to the formation of TiO$_2$ nanotube arrays, 3) electronic structure modification strategies, *e.g.*, noble metal loading, metal doping, nonmetal doping, semiconductor composite and sensitization for efficient solar harvesting applications, 4) the crystallization of TiO$_2$ nanotube arrays, and 5) the significance of structural morphologies of nanotube arrays on the performance of PECs and DSSCs.

2.2 Solar energy harvesting technologies

Innovations in materials science related to photoelectrochemical technology play a key role in the paradigm shift from fossil fuel to clean and renewable sources (Varghese *et al.*, 2009). PECs (Fujishima and Honda, 1972) and DSSCs (O'regan and Gratzel, 1991) have been recognized as potential technologies to aforementioned transition by generating clean and renewable energy from solar energy. Photoelectrochemical solar energy conversion devices involve photosensitizers that absorb light and engage in electron-transfer reaction (Kalyanasundaram and Gratzel, 1998). Figure 2.1 illustrates the main steps involved in photocatalytic water splitting process under illumination.
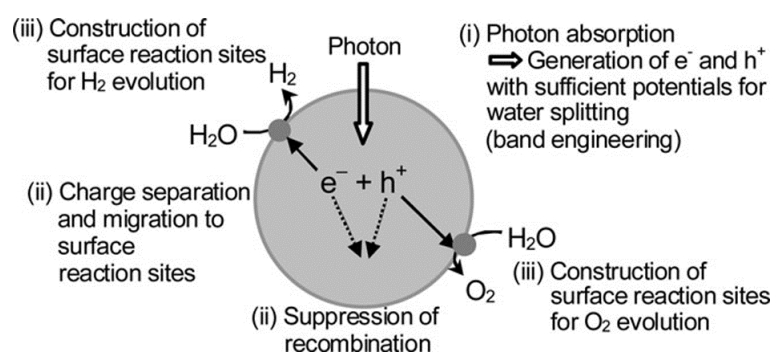
Figure 2.1 Main processes in photocatalytic water splitting (Kudo and Miseki, 2008).

Numerous n-type semiconductors, such as TiO_2, ZnO, Fe_2O_3, ZrO_2, V_2O_5, Nb_2O_5 and WO_3 have been integrated for PECs and DSSCs as photoanodes (Kalyanasundaram and Gratzel, 1998; Chicov and Schmuki, 2009). However, relative positions of band edges play a key role in determining their chemical applications. For PEC, the bottom level of conduction band (C_B) edge needs to be more negative than the redox potential of H^+/H_2 (0 V *vs.* normal hydrogen electrode: NHE), while the top level of the valence band (V_B) be more positive than the redox potential of H_2O/O_2 (*c.a.*, 1.23

eV) –refer to Figure 2.2. Therefore, the theoretical minimum band gap energy for water splitting is 1.23 eV that corresponds to the wavelength (λ) of light at approximately 1,100 nm (Kudo and Miseki, 2008; Ghicov and Schmuki, 2009).
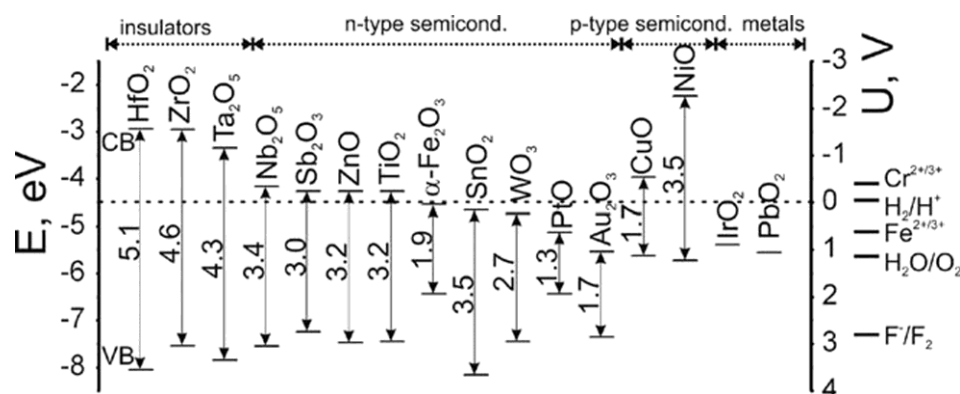
Figure 2.2 Electronic structures of different metal oxides and relative position of their band edges *vs.* some important redox potential (Ghicov and Schmuki, 2009).

Among qualified candidates, TiO_2 is the most promising candidate to be used as photoelectrode because of its superior properties, for example strong oxidation, high stability and against photocorrosion (Chen *et al*., 2007; Varghese *et al*., 2009; Lei *et al*., 2010). TiO_2 exists in three different structures (anatase, rutile and brookite), the anatase and rutile phases have been widely used for solar energy harvesting applications (Mohapatra *et al.*, 2007; Kang *et al.*, 2009; Premalal *et al.*, 2012). The band gap energies of anatase and rutile are 3.2 and 3.0 eV, corresponding to absorption thresholds at 390 and 415 nm, respectively (Rao *et al*., 1980). This infers that rutile phase can absorb a more extensive range of light. The V_B positions of these two phases is almost the same (*c.a.* 3.0 V), but the C_B positions are slightly different (Figure 2.3). The C_B potential of rutile is slightly different from the NHE potential, whereas anatase is shifted cathodically by 0.2 V. This indicates relatively high

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driving force of anatase phase for the reduction of water as compared to rutile phase (Lueng *et al.*, 2010).
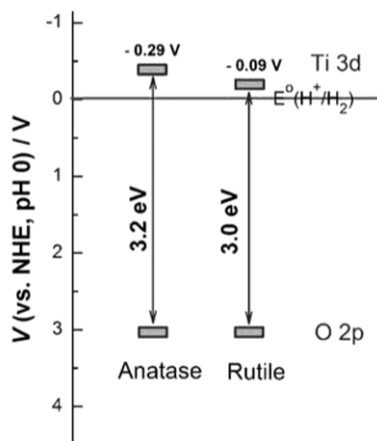
Figure 2.3 Band structures of anatase and rutile TiO_2 (Leung *et al*., 2010).

Remarkable advantages of anatase TiO_2 render them as efficient photoanode in DSSCs (O'regan and Gratzel, 1991; Jenning *et al*., 2008; Lei *et al*., 2010; Wang *et al*., 2010). However, the photoconversion efficiency of DSSCs is strongly dependent on the dye semiconductor and a redox mediator (Kalyanasundaram and Gratzel, 1998; Adachi *et al*., 2007). Therefore, it is dispensable to understand the operation principle of PEC and DSSC in order to utilize TiO_2 nanotube arrays as efficient photoanode for solar energy harvesting applications.

2.2.1   Principle of photoelectrochemical water splitting

Hydrogen is an ideal, renewable and clean energy carrier and one of the most promising alternates for the fossil fuel in the future. The utilization photocatalyst for solar energy harvesting using PEC is essential for sustainable H_2 production (Zhang *et al*., 2010; Gong *et al*., 2010). The PEC system consists of a semiconductor working electrode (*i.e.* nanocrystalline TiO_2 film) and platinum (Pt) counter

electrode, both immersed in an aqueous electrolyte (Fujishima and Honda, 1972) as illustrated in Figure 2.4.
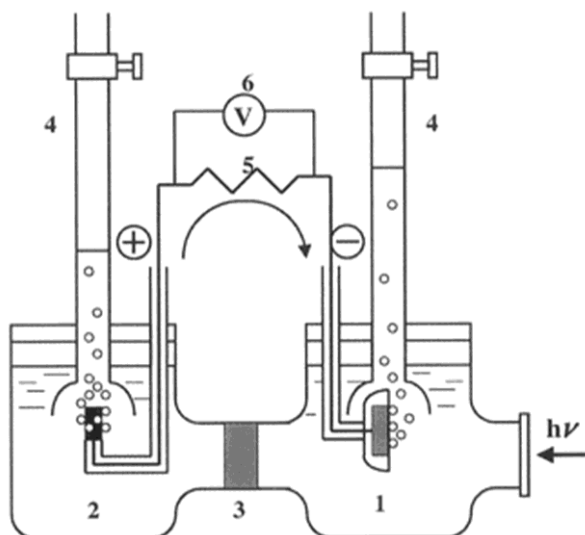
Figure 2.4 Schematic diagram of electrochemical cell. (1) n-type TiO_2 electrode; (2) Pt counter electrode; (3) ionically conducting separator; (4) gas burette; (5) load resistance; and (6) voltmeter (Hashimoto *et al*., 2005).

Upon illumination with sufficient light energy (hv), electrons (e^-) in the V_B are excited into the C_B, creating an electron-hole pairs in the semiconductor. The e^- are transported from the C_B via an external wire to the Pt cathode where the H_2 evolution reaction occurs through the reduction of water (H_2O). On the other hand, the holes (h^+) are transported to the photoanode surface where they oxidize H_2O to produce oxygen gas (O_2). By this means, H_2 and O_2 are produced at different electrodes, and can be collected in separate storage volumes. The electrochemical reactions at the cathode and photoanode are:

$$TiO_2 + hv \rightarrow e^- + h^+ \qquad \text{(Reaction 2.1)}$$

Anode: $\qquad 2H_2O + 4h^+ \rightarrow O_2 + 4H^+$ $\qquad$ (Reaction 2.2)

Cathode: $2H^+ + 2\,e^- \rightarrow H_2$ (Reaction 2.3)

Overall: $2H_2O + 4h\nu \rightarrow 2H_2 + O_2$ (Reaction 2.4)
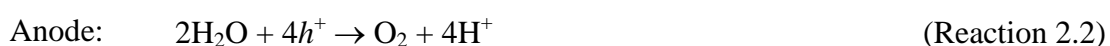
In addition, the flat band potential (V_{fb}) at the photoanode/electrolyte interface is also essential to determine the efficiency of PEC. The band bending at the photoanode/electrolyte interface is a result of solid-electrolyte interface phenomena (Figure 2.5). The Fermi level (E_F) in a semiconductor and electrochemical reactions in the electrolyte (E_{redox}) are equal at the equilibrium state. The space charge region is formed at the interface. This space charge region provides a strong electric field that is indispensable for an effective separation of photoexcited e^- from h^+. On the other hand, if light is absorbed in the bulk of the photoanode, the photoexcited e^- and h^+ are created, but there is a high possibility for recombination to occur during water photolysis (Redeka *et al.*, 2008).
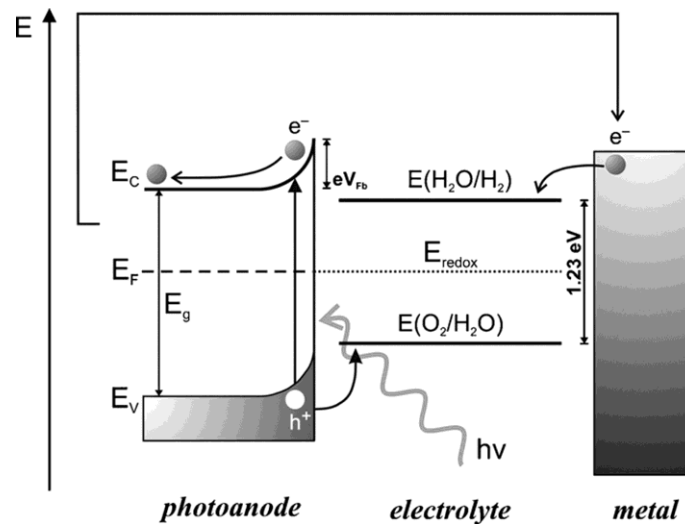
Figure 2.5 Energy diagram of the semiconducting photoanode/liquid electrolyte/metallic cathode system for water photolysis (Radecka *et al.*, 2008).

2.2.2 Principle of dye-sensitized solar cell

Dye-sensitized solar cell has been recognized as a viable competitor to the well-developed silicon solar cell which is relatively expensive (Varghese *et al.*, 2009; Lei *et al.*, 2010). A typical DSSC is assembled with a nanocrystalline TiO_2 film on fluorine-doped tin oxide (FTO) glass which is covered with a monolayer of dye molecules, redox mediator, and Pt-coated FTO glass (O'regan and Gratzel, 1991; Wang and Lin, 2010). Several types of ruthenium bipyridyl dyes (*i.e.*, black dye, N3 and N719) are often used as the dye, while iodide/tri-iodide (I^-/I_3^-) redox electrolyte is used as the redox mediator (Adachi *et al.*, 2007; Lei *et al.*, 2010; Zhang *et al.*, 2011). Considerable efforts have been devoted to develop TiO_2 nanotube arrays on FTO glass and use as photoanode (TiO_2/FTO) for front-side illumination –refer to Figure 2.6a (Varghese *et al.*, 2009; Lei *et al.*, 2010). However, the fabrication of TiO_2/FTO involves the sputtering of Ti-films on FTO glass, thus leading to high fabrication cost (Lei *et al.*, 2010).
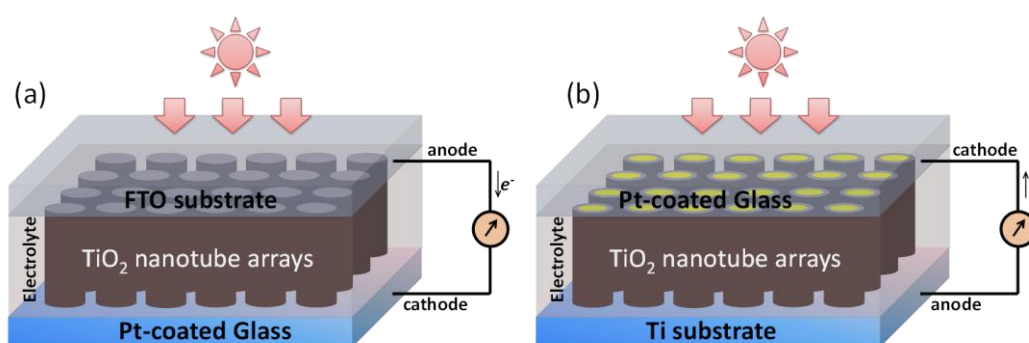
Figure 2.6 Schematic diagrams of (a) front-side and (b) back-side illumination modes DSSCs using TiO_2 nanotube arrays.

TiO_2 nanotube arrays on Ti substrate (TiO_2/Ti) have later been developed to overcome aforementioned problem (Kuang *et al.*, 2008). TiO_2/Ti-based DSSCs require back-side illumination (Figure 2.6b), which limits the enhancement of

photoelectrochemical performance because the platinized-counter electrode partially reflects light, and also induce high resistance at the metal/oxide interface (Varghese *et al.*, 2009; Wang and Lin, 2010). Figure 2.7 illustrates the reaction in DSSC under illumination. Optical excitation of the dye with $h\nu$ leads to the transition of e^- in the dye from equilibrium state to an excited state (Reaction 2.5). Photoexcited e^- rapidly moves from dye into the C_B of TiO_2, thereby remaining a positively charged state (Reaction 2.6). The dye accepts e^-, then regenerate I_3^- from $3I^-$ in the electrolyte (Reaction 2.7). The I_3^- formed in the dye regeneration process diffuse through the liquid phase to the cathode, where they are reduced back to $3I^-$ to complete the cycle by receiving an e^- from redox mediator –refer to Reaction 2.8 (Kalyanasundaram and Gratzel, 1998; Adachi *et al.*, 2007; Jennings *et al.*, 2008).

$$Dye + h\nu \rightarrow Dye* \qquad \text{(Reaction 2.5)}$$

$$Dye* + TiO_2 \rightarrow TiO_2^{\bullet} + Dye^+ \qquad \text{(Reaction 2.6)}$$

$$Dye^+ + 3I^- \rightarrow Dye + I_3^- \qquad \text{(Reaction 2.7)}$$

$$I_3^- + CE\text{-}^{\bullet} \rightarrow 3I^- + CE \qquad \text{(Reaction 2.8)}$$
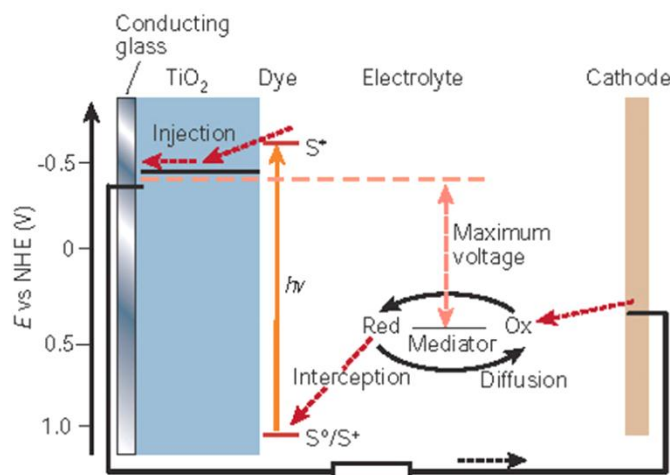
Figure 2.7 Schematic of operation of the DSSC (Gratzel, 2001).

In either model, the e^- may be localized near the surface or in the bulk, and during their transit the e^- may partially loss by transfer across the solid/liquid interface to I_3^-. The efficiency of collecting the photoexcited e^-, which is determined by competition between electron transport to the anode and electron transfer to I_3^- in the electrolyte, is critical to enhance the device performance (Jennings *et al.*, 2008).

2.3   TiO$_2$ nanotube arrays

Particulate TiO$_2$ film has been used since the discovery of PEC (Fujishima and Honda, 1972) and DSSC (O'regan and Gratzel, 1991). However, random pathway of e^- transport in particulate TiO$_2$ film leads to the recombination through trapping/detrapping of photogenerated e^-/h^+ (Kudo amd Miseki, 2008; Lei *et al.*, 2010; Mohamed and Rohani, 2011). 1D nanostructures have trigged enormous effort in physics, chemistry, and materials science of nanomaterials. TiO$_2$ with well-aligned nanotubular structure provides unique electronic properties, such as high e^- mobility, low quantum confinement effects, high specific surface area, excellent ability to absorb *hv*, and high mechanical strength (Mohapatra *et al.*, 2007; Baker and Kamat, 2009; Roy *et al.*, 2011). Furthermore, vectorial charge transport in well-aligned tubular structure greatly contributes to better photoelectrochemical properties and photocatalytic efficiency as compared to randomly-oriented nanoparticles (Baker and Kamat, 2009; Mohamed and Rohani, 2011). These advantages render TiO$_2$ nanotube arrays as promising candidate for various applications; pollutant decomposition (Chen *et al.*, 2009; Sangpour *et al.*, 2010), PEC (Park *et al.*, 2006; Mohapatra *et al.*, 2007; Palmas *et al.*, 2010) and DSSC (Jennings *et al.*, 2008; Lei *et al.*, 2010; Premalal *et al.*, 2012; Chang *et al.*, 2012). Hence, the correlation of structural

morphologies and performance of TiO$_2$ nanotube arrays is elaborated in subsequent section.

2.3.1   Anodic growth of self-organized TiO$_2$ nanotube arrays

TiO$_2$ nanotubes have been fabricated through various methods, such as sol-gel (Maiyalagan *et al*., 2006; Kang *et al*., 2009), hydrothermal (Yu *et al*., 2008; Sreekantan and Lai, 2010), chemical vapor deposition (Hsieh *et al*., 2010) and electrochemical anodization (Gong *et al.*, 2001; Macak and Schmuki, 2006; Sohrab and Ahmed, 2009). However, electrochemical anodization has been recognized as an efficient and facile approach to produce integrative, vertically-oriented highly-ordered nanotube arrays with controllable structural morphologies without any additional process (Roy *et al*., 2011; Mohamed and Rohani, 2011).

Electrochemical anodization can be defined as well-desired electrochemical growth of an oxide film on a metal substrate by polarizing the metal anodically in an electrochemical cell. Anodization can be conducted by *i*) applying a constant potential difference between anode and cathode; potentiostatic mode, *ii*) by imposing constant current; galvanostatic mode, or *iii*) by sweeping the anode potential at given rate; potentiodynamic mode (Pasquale *et al*., 2006; Kaneco *et al*., 2007; Miraghaei *et al*., 2011; Vanhumbeeck and Proost, 2011). Potentiostatic anodization has widely been used to grow oxide films due to its extreme simplicity (Mohapatra *et al.*, 2007; Baker and Kamat, 2009; Roy *et al.*, 2011). Zwilling *et al.* (1999) first demonstrated the formation of self-organized porous TiO$_2$ via potentiostatic anodization of Ti in chromic acid (H$_2$CrO$_4$) containing hydrofluoric acid (HF). The obtained tube-like structure was not highly organized, and it showed considerable sidewall

inhomogeneity. From this origin, the presence of fluoride ions (F⁻) in electrolyte has been recognized as an essential in anodic growth self-organized oxide structures. The anodic growth of self-organized structure mainly involves with electrochemical oxidation and chemical dissolution. A compact oxide layer initially forms on the metal surface; M involving metal ion formation; M^{z+} (Reaction 2.9), and consequently reacted with oxide ion (O^{2-}) and/or hydroxyl ions (OH⁻) via field-assisted oxidation –refer to Reaction 2.10 – 2.11 (Shankar *et al*., 2007; Roy *et al.*, 2011). The oxide formation mechanism on a metal is illustrated in Figure 2.8a.

$$M \rightarrow M^{z+} + ze^- \qquad \text{(Reaction 2.9)}$$

$$M + \frac{z}{2}H_2O \rightarrow MO_{z/2} + zH^+ + ze^- \qquad \text{(Reaction 2.10a)}$$

$$M^{z+} + zH_2O \rightarrow M(OH)_z + zH^+ \qquad \text{(Reaction 2.10b)}$$

$$M(OH)_z \rightarrow MO_{z/2} + \frac{z}{2}H_2O \qquad \text{(Reaction 2.11)}$$

In principle, four different morphologies, including compact structure, random porous structure, oriented porous structure and oriented tubular structure can be obtained by anodization (Figure 2.8b). Chemical dissolution plays an important role to determine the structural morphologies of anodic oxide. After the formation of an initial oxide layer, the O^{2-} and/or OH⁻ ions migrate through the oxide layer reaching the metal/oxide interface and then react with the metal. High electric field at initial oxide layer dominates the polarization of the $M^{z+}-$O bond (Mor et al., 2006; Zhang *et al*., 2010). The M^{z+} consequently migrates from the metal at the metal/oxide interface and moves outwards the oxide/electrolyte interface.
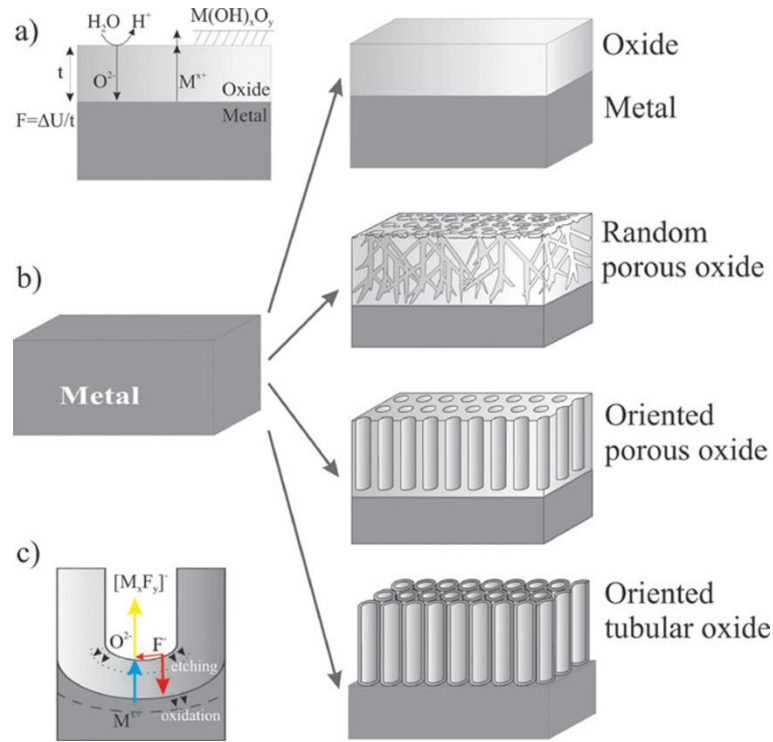
Figure 2.8 (a) Oxide formation mechanism on a metal. (b) Morphologies which can be obtained by anodization of Ti metal −a compact oxide film, a disordered nanoporous layer, a self-ordered nanoporous or a self-ordered nanotube layer. (c) Nanotube formation mechanism (Ghicov and Schumuki, 2009).

Besides, the presence of F^- in electrolyte strongly affects the anodization process, as F^- subsequently forms soluble complex $[MF_z]^{2-}$ species (Figure 2.8c). On the other hand, complexation occurs with M^{z+} ion migrated from the oxide/electrolyte interface (Reaction 2.12), and consequently attaches to the formed oxide −refer to Reaction 2.13 (Ghicov and Schumuki, 2009; Roy *et al.*, 2011).

$$M^{z+} + zF^- \rightarrow [MF_z]^{2-} \qquad \text{(Reaction 2.12)}$$

$$MO_z + zF^- + zH^+ \rightarrow [MF_z]^{2-} + H_2O \qquad \text{(Reaction 2.13)}$$
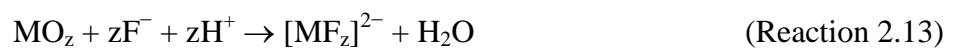
Gong *et al*. (2001) investigated the significance of electrochemical dissolution and chemical dissolution in aqueous electrolyte on the anodic growth of TiO_2 oxide by

varying applied potential over the range of 5 – 20 V, and HF concentration of 0.5 – 3.5 wt%. Porous and particulate structure was formed in aqueous electrolyte containing 0.5 wt% HF under applied potential lower than 10 V. Self-organized tubular structure was successfully formed at 10 – 20 V. It was noticeable that an appropriate applied potential for the formation of TiO_2 nanotube arrays is disproportional to the HF concentration. These reveal the essential of anodization parameters on the formation and structural morphologies of TiO_2 nanotube arrays.

2.3.2 Factors affecting geometry and composition

The anodic growth of self-organized tubular structure is well known as the equilibrium reaction between electrochemical oxidation at the metal/electrolyte interface and chemical dissolution at the oxide/electrolyte interface (Macak *et al.*, 2005; Shankar *et al.*, 2007). The structural characteristics of the nanotube arrays can be controlled through various synthesis parameters, including applied potential (Cai *et al.*, 2005; Paulose *et al.*, 2007; Lockman *et al.*, 2010), anodization time (Cai *et al.*, 2005; Wan *et al.*, 2009; Antony *et al.*, 2012), electrolyte type and chemical composition (Macak *et al.*, 2005; Ruan *et al.*, 2005; Shankar *et al.*, 2007). Therefore, this section provides a comprehensive review on the influence of aforementioned parameters on the formation of TiO_2 nanotube arrays.

2.3.2.1 Nanotube arrays synthesis using aqueous electrolytes

Gong and co-workers (2001) first obtained self-organized, highly-uniform TiO_2 nanotube arrays by anodizing Ti in aqueous electrolyte containing 0.5 wt% HF under applied potential of 10 – 20 V. The pore size increased with increasing applied potential while the nanotube length was dependent on the anodization time.

However, the length of nanotubes was limited to a maximum of ~500 nm, due to the restriction imposed by high chemical dissolution of formed oxide by strong acidity of HF aqueous electrolyte, *c.a.*, pH < 2 (Cai *et al.*, 2005; Mohamed and Rohani, 2011). The chemical dissolution of the formed oxide is determined by the F^- concentration and the pH value of the solution –refer to Reaction 2.13 (Cai *et al.*, 2005). Large number of F^- and H^+ ions in HF aqueous electrolyte dominates high chemical dissolution and thus hinders the equilibrium growth of the nanotube arrays (Macak *et al.*, 2005). Beranek *et al.* (2003) found that the incorporation of low concentration of HF aqueous electrolyte with acetic acid (H_2SO_4) addition could reduce the chemical dissolution, and thus allows the formation of porous TiO_2 with improved structural morphologies. This basis was later used to obtain TiO_2 nanotube arrays with well-defined tubular structure over applied potential range of 10 V to 25 V (Cai *et al.*, 2005). The nanotube length and pore diameter increased linearly with increasing applied potential. In summary, the structural morphologies of anodic growth oxides can be controlled by the acidity of electrolyte (Sreekantan *et al.*, 2009).

Macak *et al.* (2005) investigated the influence of the electrolyte acidity on the growth of nanotube arrays using HF, potassium fluoride (KF) and sodium fluoride (NaF) as F^- sources. TiO_2 nanotube arrays with ~280 nm long and ~40 nm pore diameter were formed in strong acidity (pH < 1) HF aqueous electrolyte after 2 h of anodization at 10 V. The increase in the pH value of electrolyte to 1.3 and 2.8 by using KF and NaF instead of HF resulted in the formation of TiO_2 nanotube arrays with the nanotube length of ~320 nm and 590 nm, respectively. TiO_2 nanotube arrays with a maximum length of 1.5 μm were achieved at 25 V (Figure 2.9a – c). Moreover, the nanotube length is proportional to the anodization time, and thus