DEVELOPMENT OF ZIRCONIA NANOTUBES AND IRON OXIDE NANOPORES BY ANODIZATION METHOD FOR PHOTOACTIVE MATERIAL

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UNIVERSITI SAINS MALAYSIA

2018

DEVELOPMENT OF ZIRCONIA NANOTUBES AND IRON OXIDE NANOPORES BY ANODIZATION METHOD FOR PHOTOACTIVE MATERIAL

by

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Thesis submitted in fulfillment of the

requirements for the degree of

Doctor of Philosophy

May 2018

DECLARATION

I hereby declare that I have conducted, completed the research work and written the thesis entitles "Development of Zirconia Nanotubes and Iron Oxide Nanopores by Anodization Method for Photoactive Material". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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Date: 4 May 2018

Witness by

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Date: 4 May 2018

ACKNOWLEDGEMENT

In the name of ALLAH, the Most Gracious and the Most Merciful.

Alhamdulillaah, all praises to ALLAH for the strengths and His blessing in completing this study. Nothing happens except in accordance with ALLAH's will.

First of all, I would like to express my most sincere gratitude to my supervisor, Assoc. Prof. Dr. Zainovia Lockman for her patience, guidance and perpetual encouragement throughout my doctoral study. It would not have been possible for me to complete this thesis without her help and constant support. I am indebted to her for introducing me to materials science and giving me an opportunity to work on nanomaterials. I really admire her in so many ways.

I also would like to thank Prof. Atsunori Matsuda from Toyohashi University of Technology (TUT) for his guidance, Dr. Go Kawamura and Dr. Tan Wai Kian for their help during my attachment at TUT, Dr. Teruhisa Okuno, Dr. Nguyen Huu Huy Phuc and Adrian Ashari for their kindly help to guide me on operating various material characterization machines.

I am deeply thankful to School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (USM) for offering an opportunity to pursue doctoral degree with great supports from academic, technical, and administrative staffs. I am grateful to ASEAN University Network/Southeast Asia Engineering Education Development Network (AUN/SEED-Net) and Japan International Cooperation Agency (JICA) for financial support and great opportunity for collaborative research with TUT. My sincere gratitude goes to Long Term Research Grant Scheme (LRGS) under OneBAJA project from Ministry of Higher Education Malaysia for partially support laboratory expenses for this research work.

Many people have highlighted my life experience in USM and deserve mentioning. I benefited greatly from the intellectual interaction with Assoc. Prof. Dr. Syafrudin Masri and his wife, Dr. Adhi Kusumastuti and her husband, Madam Fong, Encik Mohd Azzam Rejab, Puan Haslina Zulkifli, Encik Kemuridan Md. Desa and Encik Mohammad Azrul Zainol Abidin. I thank Encik Abdul Rashid Selamat and Encik Muhammad Khairi Khalid for their kindly help to train me on operating Scanning Electron Microscope. I also thank for social interactions to my colleagues at Electronics Lab and GEMS group, particularly to Mustaffa Ali Azhar Taib, Nurhaswani Alias, Nurul Izza Soaid and Nurul Nadia Mohd Zorkipli. Not forget to Dr. Muhammad Syukron, Dr. Khairul Arifah Saharudin, Ervina Junaidi, Nor Azlina Ahmad and Chow Yuh Nien. Their friendship is a blessing.

Finally, I would like to express special gratitude to my beloved parents; Erniwati, S.H and Iroza for their pray and unconditional love. It is impossible for me to finish this doctoral study without their support financially and morally. I also thank my sister; Chichi Rosalinda, S.E., M.M. and her kids for their love. Last but not least, to everybody who painted the story in accomplishment of this study successfully, thank you.

Monna Rozana

4 May 2018

TABLE OF CONTENTS

CHAPTER THREE : METHODOLOGY

CHAPTER FOUR : RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

1-D	1 dimensional
AAO	Anodic aluminium oxide
Al	Aluminum
AM 1.5	Air Mass Solar Spectrum (100 mW cm^{-2})
BE	Binding energy
BET	Brunauere Emmette Teller
CB	Conduction band
D	Crystallite size
EG	Ethylene glycol
EHPs	Electron-hole pairs
EFTEM	Energy Filtered Transmission Electron Microscopy
ESI	Electron Spectroscopic Imaging
FESEM	Field Emission Scanning Electron Microscopy
FRL	Flouride-rich layer
FTIR	Fourier Transform Infrared
FNPs	α–Fe_2O_3 nanopores
FNTs	α–Fe_2O_3 nanotubes
FS-ZNTs	Freestanding ZrO_2 nanotubes
HRTEM	High-Resolution Transmission Electron Microscopy
M	Metal
MO	Methyl orange
NIR	Near infrared
PDF	Powder Diffraction File
PEC	Photoelectrochemical
PL	Photoluminescence
SAED	Selected Area Electron Diffraction
SHE	Standard hydrogen electrode
TEM	Transmission Electron Microscopy
TNTs	TiO_2 nanotubes
UV	Ultraviolet
UV-Vis	Ultraviolet-visible

VB	Valence band
XRD	X-ray Diffraction
XPS	X-ray photoelectron spectroscopy
YSZ	Yttria-stabilized zirconia
ZNTs	ZrO_2 nanotubes

LIST OF SYMBOLS

%	Percentage
<	Less than
>	Greater than
°	Degree
wt.%	Weight percentage
M	Molarity
ppm	Parts per million
eV	Electron volt
λ	Wavelength
$h\nu$	Photon energy
α	Absorption coefficient
2θ	Diffraction angle
X	Electronegativity
E^e	Energy of free electrons on the hydrogen scale
E_g	Bandgap energy
E_{VB}	Valence band edge potential
E_{CB}	Conduction band edge potential

PENGEMBANGAN TIUB NANO ZIRKONIA DAN LIANG NANO FERUM OKSIDA MELALUI KAEDAH PENGANODAN UNTUK BAHAN TERAKTIF FOTO

ABSTRAK

Tenaga solar boleh digunakan untuk penjanaan elektrik dan pembersihan air. Untuk menangkap foton solar, bahan teraktif foto diperlukan. Walau bagaimanapun, beberapa masalah telah dikenalpasti pada penggunaan oksida sebagai bahan teraktif foto: (1) penggabungan semula pasangan fotojana elektron-lohong, (2) penggunaan sinaran boleh nampak dan (3) oksida amorf membatasi penggunaan. Dalam tesis ini, tiub nano ZrO_2 (ZNTs), liang nano α–Fe_2O_3 (FNPs) dan tiub nano α–Fe_2O_3 (FNTs) telah berjaya difabrikasikan dalam elektrolit ammonium fluorit (NH_4F)/glikol etilena (EG) yang mengandungi pelbagai penyedia O^{2-} dan/atau OH^- (H_2O, KOH, LiOH or H_2O_2) melalui kaedah penganodan. ZNTs, FNPs dan FNTs digunakan sebagai fotoanod dalam sel fotoelektrokimia (PEC) untuk menghasilkan arusfoto dan sebagai fotopemangkin untuk degradasi metil oren. ZNTs berlapis ganda dimana tiub diameter 45 nm di lapisan atas dan tiub yang lebih besar (140 nm) di lapisan bawah dihasilkan dalam KOH/NH_4F/EG. ZNTs dengan panjang 7.4 μm dihasilkan dalam LiOH/NH_4F/EG, namun mempunyai permukaan ZNTs ditutupi oleh pencemaran anion/kation (OH^-, F^-, CO_3^{2-}, NH_4^+, and Li^+). Sementara itu, ZNTs yang berdiri bebas (FS-ZNTs) difabrikasikan dalam H_2O_2/NH_4F/EG disebabkan oleh kekosongan oksigen yang membantu melemahkan kelekatan ZNTs pada Zr. ZNTs yang dihasilkan dalam LiOH/NH_4F/EG mempunyai sebahagian besar kristalit tetragonal ZrO_2 disebabkan oleh kewujudan kekosongan oksigen, OH^- dan bendasing. Setelah penyepuhlindapan, ZNTs mempunyai sebahagian besar monoklinik ZrO_2 sementara

FS-ZNTs mempunyai sebahagian besar tetragonal ZrO_2 dengan jurang tenaga ~5 eV. FS-ZNTs menunjukkan 34% degradasi MO setelah 2 jam terdedah di bawah cahaya UV, sementara 9.5% degradasi MO diperhatikan setelah 2 jam terdedah cahaya tampak. Ini menunjukkan ZNTs dapat diaktifkan di bawah cahaya tampak untuk degradasi MO. ZNTs yang terbuat dalam LiOH menghasilkan arusfoto 2.18 mA cm^{-2} pada 1 $V_{Ag/AgCl}$ dibawah UV, tetapi di bawah cahaya tampak arusfoto terhasil sangat rendah 1.69 x 10^{-4} mA cm^{-2} pada 1 $V_{Ag/AgCl}$. ZNTs mungkin tidak sesuai digunakan sebagai fotoanod dalam sel PEC dibawah cahaya tampak, walaupun jurang tenaga telah disempitkan disebabkan kecacatan dalam jurang tenaga. Bahan dengan jurang tenaga yang lebih kecil α–Fe_2O_3 difabrikasi melalui penganodan besi (Fe) dalam usaha menghasilkan bahan teraktif cahaya tampak. Penganodan Fe dalam H_2O, KOH atau LiOH/NH_4F/EG menghasilkan FNPs. FNPs setelah dianod dalam KOH atau LiOH elektrolit mempunyai FeOOH kristal kerana kandungan OH^- yang tinggi. FNTs dengan permukaan berumput terhasil dalam H_2O_2/NH_4F/EG. Selepas penyepuhlindapan, FNPs/FNTs mempunyai sebahagian besar fasa α–Fe_2O_3. FNPs yang terbentuk dalam H_2O/NH_4F/EG menghasilkan arusfoto tertinggi iaitu 25.6 mA cm^{-2} pada 1 $V_{Ag/AgCl}$ kerana kehadiran α–Fe_2O_3 dan lapisan antara muka yang nipis. Arusfoto terendah 2.8 mA cm^{-2} pada 1 $V_{Ag/AgCl}$ dihasilkan daripada FNTs. Arusfoto berkurangan disebabkan oleh morfologi dan kewujudan Fe_3O_4. Penyepuhlindapan mesti dilakukan dalam nitrogen untuk mengurangkan pertumbuhan Fe_3O_4. FNPs yang terbentuk dalam LiOH menunjukkan 34% degradasi MO selepas 2 jam pendedahan cahaya tampak. Sampel ini mempunyai jurang tenaga 2.2 eV dan kecacatan pada 1.9 eV disebabkan oleh kekosongan oksigen mengakibatkan peningkatan kepadatan lohong bebas, lalu meninggikan degradasi MO.

DEVELOPMENT OF ZIRCONIA NANOTUBES AND IRON OXIDE NANOPORES BY ANODIZATION METHOD FOR PHOTOACTIVE MATERIAL

ABSTRACT

Solar energy can be utilized for electricity generation and water purification. To capture solar photons, photoactive materials are required. However, several problems were identified on the use of oxide as photoactive material: (1) recombination of photogenerated electron-hole pairs, (2) visible light utilization and (3) amorphous oxide limits the application. In this thesis, ZrO_2 nanotubes (ZNTs), α–Fe_2O_3 nanopores (FNPs) and α–Fe_2O_3 nanotubes (FNTs) were successfully fabricated by anodization in ammonium flouride (NH_4F)/ethylene glycol (EG) electrolyte containing various O^{2-} and/or OH^- providers (H_2O, KOH, LiOH or H_2O_2) to overcome the mentioned problems. The ZNTs, FNPs and FNTs were used as photoanode in a photoelectrochemical cell to generate photocurrent and as photocatalyst to degrade methyl orange (MO). Double layered ZNTs with top layer tube diameter of 45 nm and larger nanotubes (140 nm) at bottom layer were obtained in KOH/NH_4F/EG. 7.4 μm length ZNTs was formed in LiOH/NH_4F/EG, however the surface was covered by anion/cation contamination (OH^-, F^-, CO_3^{2-}, NH_4^+, and Li^+). Meanwhile freestanding ZNTs (FS-ZNTs) were fabricated in H_2O_2/NH_4F/EG due to oxygen evolution which aids in weakening the adherence of the ZNTs from Zr. As-anodized ZNTs formed in LiOH/NH_4F/EG have tetragonal ZrO_2 crystallite due to the existence of oxygen vacancies, OH^- and impurities. After annealing, ZNTs have majority monoclinic ZrO_2 whereas FS-ZNTs have majority tetragonal ZrO_2 with bandgap of ~5 eV. FS-ZNTs exhibited 34% MO degradation after 2 h of UV light whereas 9.5% MO degradation was observed after 2 h of visible light exposure.

These indicate ZNTs can be activated under visible light to degrade MO. LiOH derived ZNTs with good adherence with Zr generated high photocurrent of 2.18 mA cm^{-2} at 1 $V_{Ag/AgCl}$ under UV, but under visible light very small current of 1.69 x 10^{-4} mA cm^{-2} at 1 $V_{Ag/AgCl}$ were generated. ZNTs may not suitable to be used as photoanode in a PEC cell under visible light despite the band narrowing due to defects within their energy gap. A smaller bandgap material α–Fe_2O_3 was fabricated by anodization of iron (Fe) in an attempt to produce visible light activated material. Anodization of Fe in H_2O, KOH, or LiOH/NH_4F/EG produced FNPs. The as-anodized FNPs formed in KOH or LiOH electrolyte have crystalline FeOOH due to the high content of OH^-. FNTs with grassy surface were formed in H_2O_2/NH_4F/EG. After annealing, FNPs/FNTs have majority α–Fe_2O_3 phase. FNPs formed in H_2O/NH_4F/EG generated highest photocurrent of 25.6 mA cm^{-2} at 1 $V_{Ag/AgCl}$ due to the presence of α–Fe_2O_3 and thin interfacial layer. The lowest photocurrent of 2.8 mA cm^{-2} at 1 $V_{Ag/AgCl}$ was produced from FNTs. The reduced photocurrent may be due the morphologies and the existence of Fe_3O_4. Annealing must be done in nitrogen to reduce the growth of Fe_3O_4. As for the MO degradation, LiOH derived FNPs exhibited 34% degradation after 2 h of visible light exposure. The sample has bandgap energy of 2.2 eV and defect state at 1.9 eV due to oxygen vacancies resulted in increasing free holes density, hence enhanced MO degradation.

CHAPTER ONE

INTRODUCTION

1.1. Background

This thesis is on the synthesis, characterization and utilization of photoactive semiconductor oxides for energy and environmental protection purposes. Two main materials synthesized in nanoscale were studied: ZrO_2 and α–Fe_2O_3. This chapter introduces the background that leads to the use of these photoactive semiconductor oxides as light-to-electric current (photocurrent) converter, and as photocatalyst for water purification from dyes contamination. Problem statements and gap of knowledge on nanostructured ZrO_2 and α–Fe_2O_3 formation process, and their photoactivity properties are introduced along with the main aim and specific objectives of the thesis.

1.1.1. Electricity generation

One of the driving forces in achieving economic development is energy. Fulfilling energy demand from large number of population is a great challenge especially for developing countries, like Malaysia. As the third largest energy consumer in Southeast Asian countries after Indonesia and Thailand (IEA, 2015), Malaysia's energy demand of 2013 population of nearly 30 million people was 89 million tonnes of oil equivalent. Population and energy demand are predicted to increase to 40 million and 160 million tonnes of oil equivalent respectively in 2040 (Table 1.1), hence the country needs more energy in the future.

Table 1.1: Key indicators for Malaysia (IEA, 2015)

Indicator	Unit	Year		
		2000	**2013**	**2040**
Population	million	23	30	40
Energy demand	million tonnes of oil equivalent	50	89	160
Electricity demand	TWh	61	124	400
CO_2 emission	million tonnes	118	211	430

According to Malaysia Energy Statistics Handbook 2015 (Tenaga, 2015) natural gas and coal provided about 88% of electricity generation in 2013. Based on IEA forecasting, the country's electricity generation will reach 400 TWh in 2040 with natural gas and coal as the largest sources for electricity generation. Given the continuing dominance of fossil fuels in the country's energy mix, the CO_2 emission will be increased from 211 million tonnes in 2013 to almost 430 milllion tonnes by 2040 as shown in Table 1.1. The impact on environment caused by CO_2 emission is a serious concern. Therefore, to reduce the dependence on fossil fuels and to limit CO_2 emission, the use of renewable energy source need to be considered.

Among various renewable energies, solar energy is seen as the only source of renewable energy that has high potential to meet energy demands (Lewis and Crabtree, 2005; Lewis and Nocera, 2006), especially in Malaysia. More importantly solar energy does not contribute to CO_2 emission (Solangi *et al.*, 2011). As Malaysia lies entirely in the equatorial region and has abundant solar radiation, the utilization of solar energy is extremely logical for electricity generation. A summary of yearly average solar radiation in various towns in the country is shown in Table 1.2. The Northern region (Mekhilef *et al.*, 2012) has the highest potential hence every effort in converting solar energy for electricity generation is important.

Table 1.2: Solar intensity in Malaysia (Mekhilef *et al.*, 2012)

Location	Yearly intensity average ($kWh\ m^{-2}$)
Kuching	1470
Kuala Lumpur	1571
Johor Bahru	1625
Ipoh	1739
George Town	1785
Bayan Lepas	1809
Kota Kinabalu	1900

Various technologies can be utilized to capture solar energy and turn it into electricity. One way is to capture solar photons by a photoelectrochemical (PEC) cell utilizing aqueous electrolyte and converting them to photocurrent which at the same time can lead to hydrogen generation. PEC-type cells can also have various different functions (Gratzel, 2001), but in this work, focus was given to convert solar to photocurrent. Based on International Union of Pure and Applied Chemistry (IUPAC) Recommendations 2011, definition of photocurrent is photogeneration and movement of charge between two electrodes in a photovoltaic cell or a PEC cell as a result of photoprocesses induced by light absorption (Braslavsky *et al.*, 2011). A PEC cell requires a photoactive material; a material that can be activated under light irradiation, to generate the photocurrent. A photoanode in a PEC cell is consisted of photoactive oxide semiconductor as shown in Figure 1.1. In this thesis, two oxides; ZrO_2 and α–Fe_2O_3 made in nanoscale and their ability to generate photocurrent were studied. As shall be explained later, the selected oxide materials also have the properties to split water and through the process of water splitting, hydrogen gas is produced.

One of the advantages of a PEC cell is that hydrogen and oxygen gases are produced at separate electrode. The photogenerated electrons reduce water to form

hydrogen at platinum counter electrode, while holes oxidize water to form oxygen on photoanode. This allows easy separation of these gases without considering post separation. Another advantage of PEC cell is that it can be conducted at room temperature. Hydrogen gas can be converted into electricity and used as chemical fuels to power vehicles.

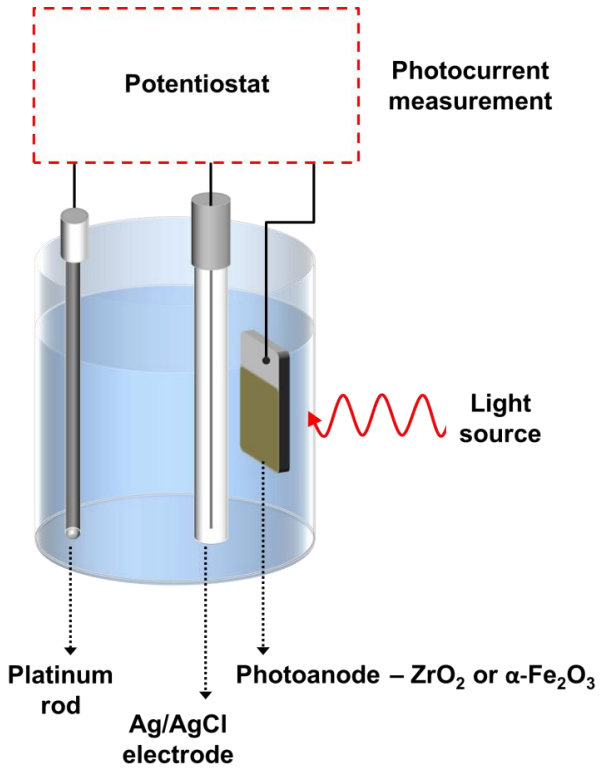

Figure 1.1: The position of photoanode in a PEC cell.

1.1.2. Dye pollution in water

On a different note, Malaysia is known as a net exporter of textiles and apparel. In 2014 the textiles industry contributed 1.6% share of the country's export of manufactured goods (MIDA, 2015). Investment in the Malaysian textile and clothing industry is expected to increase more than US$ 3 billion in 2020. Textile industry is also expected to continue fulfilling an important role in the country's economic development. Unfortunately textile industry utilizes huge amount of water

and produces high quantity of waste water. A major source of water pollution from textile industry is the release of dyes into environment during textile fiber dying (Pang and Abdullah, 2013). A wide variety of health problems can be caused by dyes contamination, like skin rashes, headaches, diarrhea, muscle and joint pain, dizziness, difficulty in breathing, and irregular heartbeat (Chavan, 2011).

Since the presence of dyes in waste water is unwanted, there are several treatment methods to treat waste water from textile industry before it can be safely release to the environment like adsorption, ion exchange, membrane filtration, biological method (aerobic and anaerobic process), chemical coagulation, and photocatalysis (Pang and Abdullah, 2013). Energy consumption, efficiency, cost and easy operation need to be considered to select the best method. Among various methods mentioned, photocatalysis is believed to be an efficient, relatively easy and a cost effective method to remove dyes in water, thus is seen as a promising technique for water purification (Ajmal *et al.*, 2014; Khataee and Kasiri, 2010).

Referring to IUPAC Recommendations 2011, the definition of photocatalysis is the change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance – the photocatalyst – that absorbs light and is involved in chemical transformation of the reaction partners (Braslavsky *et al.*, 2011). It is clearly stated that ultraviolet, visible, or infrared radiation are needed on photocatalysis and all these radiations are included in the solar spectrum. As mentioned, Malaysia has abundant solar radiation, hence the utilization of solar energy for water purification from dye contaminant for instance by photocatalysis will be a potential solution for treating waste water from textile industry in Malaysia. Similar to the materials used to generate useful photocurrent, photoactive oxide semiconductors can be utilized as

photocatalysts (Figure 1.2). Similarly, ZrO_2 and α–Fe_2O_3 were selected to be investigated as photocatalysts in this thesis.

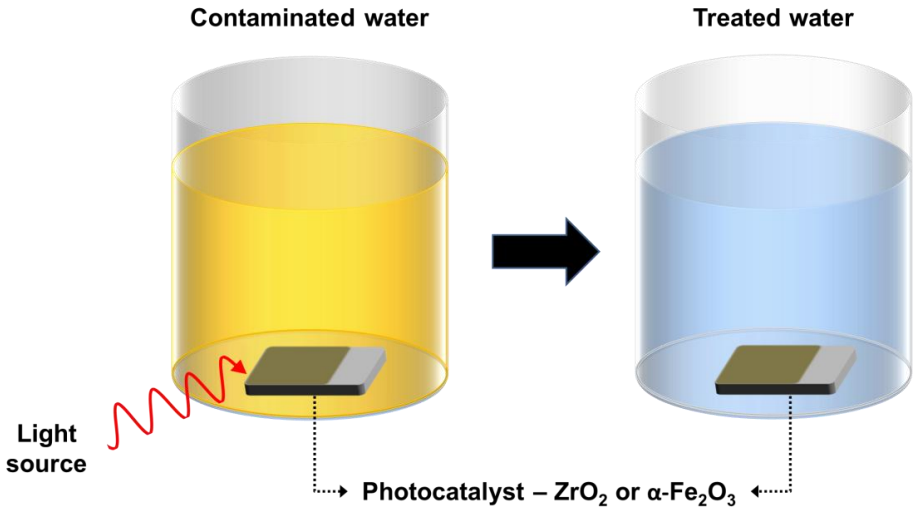

Figure 1.2: ZrO_2 or α–Fe_2O_3 as photocatalyst to treat water from dyes contamination.

1.2. Photoactive material

Practical uses of solar energy on electricity generation and water purification are summarized in Figure 1.3. To generate photocurrent in a PEC cell and for photocatalysis applications, a material that can be activated under light irradiation is needed (or called photoactive). A semiconductor is a material that can generate electron-hole pairs (EHPs) through optical excitation. The valence band is the highest energy band filled with electrons while conduction band is the lowest unoccupied band. The absorption of photons with larger energy than the band gap of a semiconductor will produce EHPs which are useful carriers to either provide sufficient electric current (photocurrent) or to perform oxidation or reduction process via electron or hole transfers (photocatalyst). To ensure EHPs play the role in driving the photoactivity process, they must not be allowed to recombine and ought to be separated as fast as possible. They must have a long life time until they can

travel to the surface of the semiconductor to be transferred to either adsorbed species or to the electrolyte. Therefore, to able the use of photoactive oxides as photoanode or photocatalyst, the following properties are required:

- high light absorption coefficient (in order 10^3 cm^{-1})
- suitable bandgap energy to produce EHPs
- position of conduction and valence band straddles the redox potential of water
- efficient EHPs separation
- able to transport carrier to semiconductor interface as quick as possible

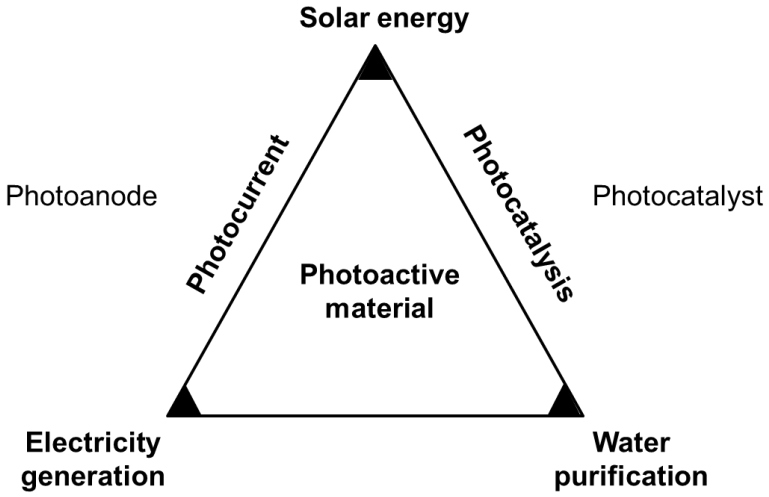

Figure 1.3: Practical uses of solar energy for electricity generation and water purification.

As mentioned, there were two semiconductor oxide materials studied here: ZrO_2 and α–Fe_2O_3. ZrO_2 is also a wide band gap semiconductor but the high conduction band position is enough to initiate photocatalytic processes in aqueous solution (Asmatulu *et al.*, 2015; Gerischer, 1981). ZrO_2 exists as monoclinic, tetragonal, and cubic phases (Keramidas and White, 1974). The three phases of ZrO_2

(monoclinic, tetragonal, and cubic) have bandgap energies of 5.1 eV, 5.2 eV, and 5.2 eV respectively from theoretical data (French *et al.*, 1994) and 3 – 6 eV from experimental data (Anandan *et al.*, 2017; Goharshadi and Hadadian, 2012; McComb, 1996; Nicoloso *et al.*, 1992; Sathyaseelan *et al.*, 2017; Xu *et al.*, 2016). While the monoclinic phase is stable at room temperature, tetragonal or cubic are high temperature phases. Therefore, they must be stabilized at room temperature or else the tetragonal or cubic phase will revert to monoclinic when cooled to room temperature. To stabilize tetragonal and cubic phase at room temperature, ZrO_2 has to be made oxygen deficient (Fabris *et al.*, 2002; Liu *et al.*, 2014). Often this is achieved by Y^{3+} or Ce^{3+} doping and significant defects are introduced in the oxide. The main defect is oxygen vacancy.

Since ZrO_2 has a rather wide energy gap, it can only be activated under UV irradiation, similar to TiO_2. Despite its wide bandgap, ZrO_2 has shown significant photoactivity (Emeline *et al.*, 2005). Among various reasons to account for this is the existence of defects which successfully modify the electronic properties of the oxide. In this thesis, ZrO_2 was synthesized as thin film with nanotubular structure by anodization process. The reason of nanostructuring will be explained later but suffice to say is to increase the surface area of the oxide. Anodization process requires oxygen ions migration across oxide film for film growth. The migration is electric field dependent. Because of this, the formed anodic ZrO_2 is often very defective and is consisted of oxygen vacancies (Bashirom *et al.*, 2017; Fang *et al.*, 2013). Two effects are seen from the existence of oxygen defects:

(i) Stabilization of tetragonal or cubic ZrO_2 at room temperature

(ii) Modification of electronic band structure of ZrO_2

while the former is interesting as no dopants are needed for anodic ZrO_2 to be in tetragonal phase, the latter is useful since the presence of defects levels within the wide bandgap of ZrO_2 can aid in visible light activation of the oxide. From photoluminescence spectra of tetragonal phase, it was reported that oxygen vacancy narrows the gap to 2.04 eV (Liang *et al.*, 2002). This can be translated to 608 nm wavelength of light (i.e. within visible light region). Oxygen vacancies introduce a level near valence band of ZrO_2 (Kumar and Ojha, 2015), narrowing the energy gap of the oxide.

α–Fe_2O_3 on the other hand is already a narrow gap semiconductor with bandgap energy of ~2.2 eV, hence light absorption from green-yellow colour in visible region until UV region for EHPs formation is possible. The oxide therefore can be activated readily under solar spectrum. α–Fe_2O_3 is abundant and relatively inert in most electrolyte over a wide range of pH (Forster *et al.*, 2015). Iron oxide mostly exists in the form of magnetite (Fe_3O_4), maghemite (γ–Fe_2O_3) and hematite (α–Fe_2O_3) (Cornell and Schwertmann, 2003). But among all these phases, α–Fe_2O_3 has been used as a photoanode in PEC cells (Bassi *et al.*, 2014; Sivula *et al.*, 2011) to give photocurrent.

Here ZrO_2 and α–Fe_2O_3 films were produced on Zr and Fe foils respectively, with the film consisted of nanotubes or nanopores structure. The International Organization for Standardization (ISO) defines nanomaterial as a material with any external dimensions in the nanoscale or having internal structure or surface structure in the nanoscale (ISO, 2010; Boverhof *et al.*, 2015). The ISO definition of nanoscale is in the range of 1 – 100 nm. The use of photoactive materials in nanoscale has been suggested due to high surface area hence larger area for light absorption is expected (Satsangi *et al.*, 2010). In addition, the use of semiconductor in nanoscale is also to

minimize the distance for photogenerated carriers to reach semiconductor|electrolyte interface, thus reducing the probability of recombination (Walter *et al.*, 2010).

1.3. Synthesis method of nanostructured ZrO_2 and α–Fe_2O_3

There are various different ways to form metal oxide with nanotubular and nanoporous structure such as template based method (Bao *et al.*, 2002; Cochran *et al.*, 2007; Ogihara *et al.*, 2006; Rao *et al.*, 1997), sol-gel (Gundiah *et al.*, 2003; Huo *et al.*, 2014), atomic layer deposition (Bachmann *et al.*, 2007; Shin *et al.*, 2004), and anodization (Ismail *et al.*, 2011a; Ismail *et al.*, 2011b; Mushove *et al.*, 2015; Tsuchiya *et al.*, 2005; Wang *et al.*, 2015). Here, the structures were grown from metal foil by anodization as illustrated in Figure 1.4.

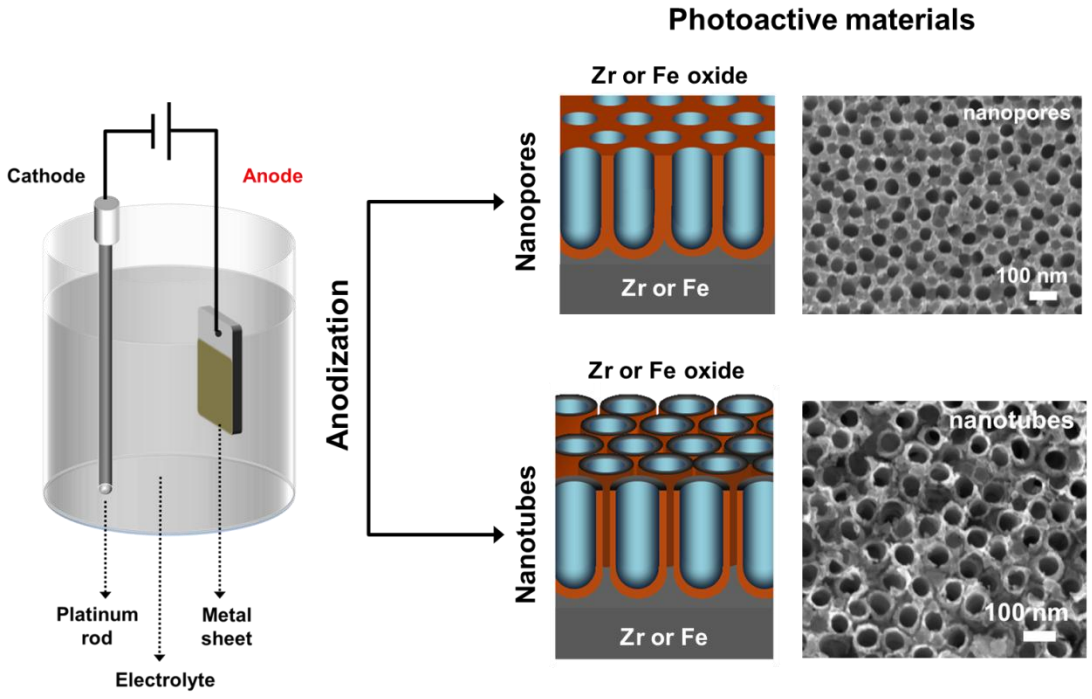

Figure 1.4: Schematic illustration for nanopores and nanotubes metal oxides formation by anodization as photoactive materials.

Anodization offers a simple, quick, and cost effective process of fabrication of elongated nanoporous and nanotubular metal oxides. As seen from Figure 1.4, it is

carried out typically in a cell containing suitable electrolyte, with metal foil of interest as anode and an inert platinum rod as cathode. Moreover as mentioned, the use of anodization process is unique since it can form a high temperature stable cubic or tetragonal ZrO_2 phase (Habazaki *et al.*, 2000) without the need of intentional doping process. As will be discussed later, in this work anodization of Zr resulted in ZrO_2 nanotubes (ZNTs) and on iron foil either α–Fe_2O_3 nanopores (FNPs) or α–Fe_2O_3 nanotubes (FNTs) can be produced (Figure 1.4).

As stated earlier, ZrO_2 has a wide bandgap 3 – 6 eV which means that EHPs generation only can happen under UV light irradiation. For the case of TiO_2, metal dopants have been used to produce energy levels or states above the valence band and oxygen vacancies near the conduction band (Nakamura *et al.*, 2000). These new energy levels narrows the bandgap. For example electron can be excited to the oxygen vacancy states under visible light (Kim *et al.*, 2016) as shown in Figure 1.5. Adopting this idea, defective ZNTs were produced hence it can be visible light active. Formation of oxygen vacancies was introduced by anodization process and the presence of K^+, Li^+ or F^- in the electrolyte may induce unintentionally doping during nanotubes synthesis process.

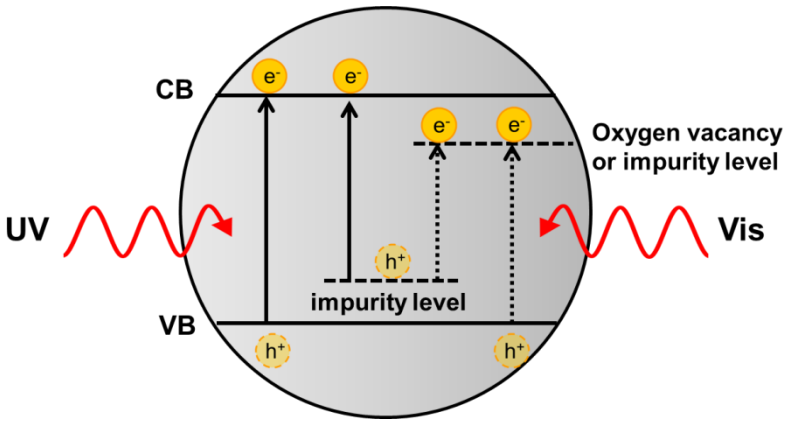

Figure 1.5: Band gap modification of photoactive oxide semiconductors by oxygen vacancies or impurities (where VB and CB is valence band and conduction band respectively).

1.4. Problem statements

This study was aimed at the formation of ZNTs and FNPs/FNTs by anodization to be used as photoactive materials: photoanode for photocurrent generation and photocatalyst for water purification from dye contamination. Limited studies exist for both on the formation of ZNTs and FNPs/FNTs by anodization and their applications as photoactive materials as most published works are on the well-known material: TiO_2 (Grimes and Mor, 2009; Lee *et al.*, 2014b; Ochiai and Fujishima, 2012; Paramasivam *et al.*, 2012; Roy *et al.*, 2011). The rationale of using both ZrO_2 and α–Fe_2O_3 is that their band gap energies are sufficient for promoting a wide range of chemical reactions of environmental interest. However there are several material related challenges needed to be overcome: (1) minimizing recombination, (2) utilization of solar spectrum for catalyst activation, and (3) formation of crystalline oxide as the as-made oxides are amorphous which limits their applications.

In a thin compact film, the direction of light absorption is the same across the film with photogenerated carriers transfer from the surface and the bulk of the film to the back contact (Walter *et al.*, 2010) to give photocurrent (Figure 1.6(a)). The distance of holes can diffuse before recombination (or holes diffusion length) must be larger than $1/\alpha$ (where α is absorption coefficient of semiconductor near bandgap) in order to reduce recombination. Nevertheless, oxide semiconductor have small hole diffusion coefficient making them easily recombine with electrons. In order to overcome the holes diffusion problem, the semiconductor needs to be as thin as possible. But in a compact film, the film must be thick enough to absorb significant light that can be converted into useful EHPs. Instead of compact film, nanostructuring of the oxide film is believed to enable the creation of thicker oxide film but with much reduce recombination problem. Nanostructuring can be done by

creating thin film comprising of perfect arrays of nanotubes or nanopores. As seen in Figure 1.6(c), nanotubes have thin walls hence once created; the holes must only travel at a shorter distance to reach the surface. If the walls can be made much smaller than the mean free path and the diffusion coefficient of the holes, the carriers are thought to be able to move with minimum resistance and recombination.

It is well known that film with nanostructures have higher surface area than compact film. This will allows larger area for absorption of light. Nanopores also have thin walls, but their walls are not separated (Figure 1.6(b)) whereas nanotubes have well separated pore cells (discrete), and hence light absorption and EHPs formation are thought to be more efficient (Figure 1.6(c)). Moreover, the as mentioned, distance travelled of carriers from the pore walls to the side for transfer process will be much reduced as well. By utilizing nanostructured film, harvesting light from the source is thought to be much improved translating to higher density of electrons and holes in the surface of the catalysts. Therefore, in this thesis anodic method to produce oxide films comprising of either nanotubes or nanopores structure were explored in great depth.

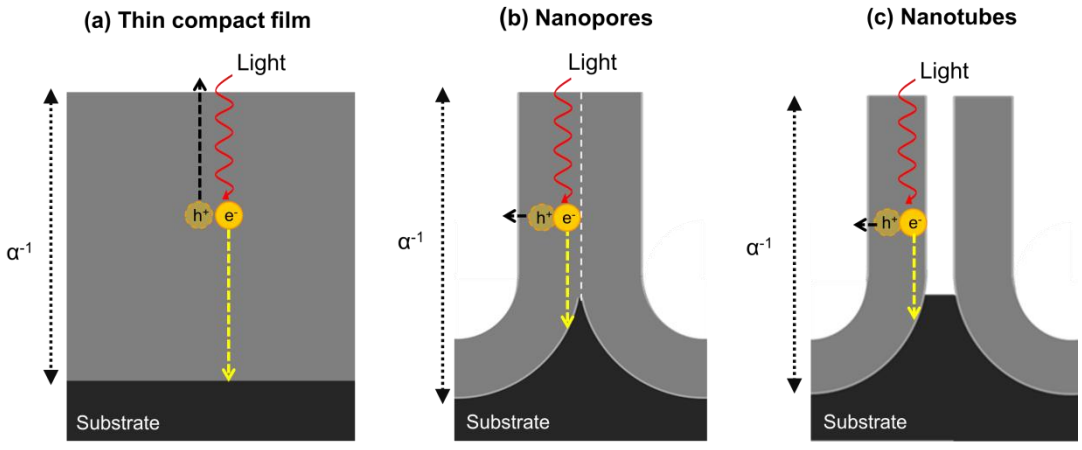

Figure 1.6: In a thin compact film (a), photogenerated carriers must traverse the entire thickness of the film, α^{-1} (where α is the absorption coefficient), before collection. In a nanopores film (b) and nanotube-array film (c), carriers must only reach the nanotube surface before recombination.

The peak of solar spectrum (AM 1.5) is at a greenish wavelength of 502 nm within the visible region (Bak *et al.*, 2002; Tsui and Zangari, 2014). On the shorter wavelength side, the spectrum extends to the visible purple range and falls sharply within the ultraviolet (UV) region. On the longer wavelength side, the spectrum extends much more into the infrared region (Zhu and Yu, 2016). A solar spectrum is therefore consisted of UV light (< 400 nm), visible light (400 – 700 nm), and infrared regions (> 700 nm). In order to harvest the visible part of the spectrum, photoactive materials used must have energy gap within the energy of visible light photons. Second generation photoactive materials can be classified as semiconductors that have greater absorption of light in visible region (Emeline *et al.*, 2012). Wide band gap semiconductor like ZrO_2 is not suitable to be used under visible light. However in this thesis ZNTs were made rather defective, hence it can be activated under visible part of the solar spectrum. To achieve defective ZNTs, various metal ions impurities like F^-, K^+, and Li^+ and oxygen vacancies were introduced. O^{2-} and hydroxyl ion (OH^-) are needed for oxide formation, but with the field effect ionic migration process occurring during anodic process, the anodic ZNTs tend to have defects especially oxygen vacancies. The existence of such defect can narrow down the energy gap of the oxide. On the other hand, α–Fe_2O_3 is an intrinsically narrow gap semiconductor whereby the oxide can be activated readily under visible part of the solar spectrum. The oxide has however problem related to short hole diffusion length.

In EG electrolyte, H_2O has been vastly used as an O^{2-} and/or OH^- provider (Lee *et al.*, 2014a; Schrebler *et al.*, 2014; Wang *et al.*, 2015). But instead of H_2O, the addition of KOH into EG electrolyte has been proposed as oxygen provider (oxidant) to produce TiO_2 nanotubes (TNTs) (Krengvirat *et al.*, 2013; Nyein *et al.*, 2017; Taib

et al., 2017). K^+ was also shown to be inserted into TNTs and resulting high photoactivity (Krengvirat *et al.*, 2013). K^+ added TNTs required applied bias lower than that pure TNTs for photocurrent generation (Richter *et al.*, 2009; Richter and Menon, 2010). In addition, hydroxyl group (OH^-) was found on the surface of TNTs produced in KOH/NH_4F/EG electrolyte and surface OH^- affects the photoactivity performance whereby they can trap holes at the lattice oxygen atoms to form OH radicals ($OH^\bullet$) (Taib *et al.*, 2017). Similarly, Li^+ insertion to TNTs was reported to enhance photocurrent and PEC efficiency (Kang and Park, 2013; Meekins and Kamat, 2009). In addition, LiOH and H_2O_2 can be used as an O^{2-} and/or OH^- provider in EG electrolyte to induce faster growth rate and aspect ratio TNTs (Joseph and Sagayaraj, 2015; Lin *et al.*, 2008; Raj and Prasanth, 2015; Raj *et al.*, 2015; Sreekantan *et al.*, 2011; Wang *et al.*, 2011). As to date, despite various works reported on TNTs, there is no report on the effect of the addition of these different O^{2-} and/or OH^- providers into EG electrolyte on morphology, crystallinity, optical property and photoactivity performance of both ZNTs and FNPs/FNTs. This thesis reports on the characteristics of ZNTs and FNPs/FNTs formed by anodization process in KOH, LiOH or H_2O_2 added NH_4F/EG electrolyte. Experiments were done to build further understanding on how the ZNTs produced in various O^{2-} and/or OH^- providers behave as photocatalyst or as photoanode in PEC cell under UV and visible light irradiation. The photoactive properties of FNPs/FNTs produced in EG added with various O^{2-} and/or OH^- providers were also studied by measuring photocurrent or dye degradation (photocatalytic experiments) under visible light irradiation.

Another challenge associated with anodic ZNTs and FNPs/FNTs are that they are amorphous (Ismail *et al.*, 2011a; Stępień *et al.*, 2014; Zhao *et al.*, 2008). The amorphous structure limits their application as photoactive materials as amorphosity

reduce chances for EHPs formation and promotes recombination. Amorphous structure also demonstrates the lack of stability in a solution of low pH level (Stępień *et al.*, 2014) and hence when used in liquid (as in when immersed in solution for photocatalytic process), the oxide tends to be dissolving or absorbing significant amount of water. In order to convert the amorphous into crystalline structure, annealing is required. Nevertheless, annealing may also induce grain growth and sintering, thus destroying the nanotubular or nanoporous structure. As the optical and electronic properties of annealed ZNTs have not been thoroughly explored, it is the intention here to report on detailed analysis on what happened when these oxides were annealed. Morphologies of the oxides were viewed as a function of annealing temperatures. The photoactivities of the annealed oxides were then studied. It was later observed that the substrate material also oxidized during the course of annealing

It was realized that Zr foil is rather expensive and hence recycling of the substrate material is preferred. In one part of this thesis, a study on the formation of freestanding ZNTs (FS-ZNTs) – the film detached from the foil is reported. There are more advantages of the use of FS-ZNTs, for instance by utilizing FS-ZNTs, the influence of the substrate can be eliminated during annealing. It is also of interest to have liquid penetrating inside the interior of the nanotubes for more oxide-liquid interaction, therefore by using FS-ZNTs, both sides of the film can be used as oppose to when it is fixed on the Zr. In this thesis, ZNTs were formed in H_2O_2/NH_4F/EG electrolyte as to weaken the adherence of the oxide film to the Zr hence FS-ZNTs were produced. To the best of knowledge, the use of this method has not been reported in current literature and thus there were various parameters studied and reported in this thesis. Similar to the other samples, photocatalytic properties of FS-ZNTs were also assessed.

1.5. Research objectives

The main objectives of this thesis are:

1. To study the formation of ZNTs on the Zr and FNPs/FNTs on Fe by anodization in NH_4F/EG electrolyte added with varying O^{2-} and/or OH^- provider
2. To investigate the influence of annealing on ZNTs and FNPs/FNTs to their morphology, crystallinity, and property
3. To elucidate FS-ZNTs formation by anodic process
4. To assess the photoactivity performance (as photocatalyts for dye degradation or as photoanode for photocurrent generation in a PEC cell) of ZNTs/FS-ZNTs and FNPs/FNTs under visible light irradiation.

1.6. Research scope

In this research work, three main aspects to discuss are the formation of ZNTs and FNPs in various O^{2-} and/or OH^- providers, characterization, and performance evaluation as photoactive materials. The scope of this research covered:

1. Anodization process was done only with EG as the bulk electrolyte added to it NH_4F and different O^{2-} and/or OH^- providers added (H_2O, KOH, LiOH, and H_2O_2). Aqueous electrolyte and other organic electrolyte were not studied.
2. ZNTs and FNPs/FNTs formed by anodization were characterized by Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Energy Filtered Transmission Electron Microscopy (EFTEM), Electron Spectroscopic Imaging (ESI), X-ray Diffraction (XRD), Raman spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Fourier Transform

Infrared (FTIR) spectrometer, Ultraviolet-visible spectrophotometry (UV-Vis), and Photoluminescence (PL) spectral measurements only.

3. Photoactive material performance was studied by measuring photocurrent in a simple PEC cell utilizing NaOH as electrolyte. No other electrolyte or another more complex system was studied. Photocatalytic process was done by measuring the reduction of concentration in organic dye under light illumination. No other experiments were done.

1.7. Thesis outline

The thesis is consisted of five chapters. Chapter 1 is the overall introduction for the whole thesis. Chapter 2 presents the literature review of the anodization process in NH_4F/EG electrolyte and mechanism of nanopores and nanotube formation. The literature review of application of ZNTs and FNPs/FNTs as photoactive materials is presented in that chapter as well. Chapter 3 deals with the material, chemicals used, and experimental procedure of this study. Chapter 4 focuses on presenting the overall results and discussion on formation of ZNTs and FNPs/FNTs, their properties and photoactivity performance. Chapter 5 is on the conclusion and suggestions for further studies on this work.

CHAPTER TWO

LITERATURE REVIEW

2.1. Introduction

This chapter emphasizes on three main parts. First part reviews the anodization process for nanostructuring. The second part reviews the anodization of Zr metal for ZrO_2 nanotubes (ZNTs) formation which includes: (1) progress in Zr metal anodization in various types of electrolyte until the discovery of ZNTs, (2) growth mechanism model and factors affecting the growth of ZNTs, (3) methods to form freestanding ZNTs, (4) crystallinity and phase stabilization, and (5) properties and photoactivity of ZNTs. The last part reviews the anodization of Fe metal for α–Fe_2O_3 nanopores/nanotubes (FNPs/FNTs) formation and their photocurrent generation.

2.2. Anodization process for nanostructuring

Anodic oxidation or anodization of metals has been used to protect metal components from corrosion and for decorative purposes for more than 10 decades (Aladjem, 1973). However, anodization has become a technique not only for protection or to increase the aesthetic appearance of the metal components but explicitly done to produce a thin oxide film. Anodic thin oxide film on a metal has many unique properties leading to various interesting applications. For instance anodizing aluminum (Al) resulted in Al_2O_3 film which has raised substantial scientific and technological interest in recent years due to the dielectric property of the oxide which can be used in electrolytic capacitors (Ban *et al.,* 2014). Anodized titanium (Ti) on the other hand has been widely investigated as the TiO_2 film

produced, being a photoactive semiconductor has many applications especially in the field of solar energy utilization (Grimes and Mor, 2009; Kowalski *et al.*, 2013; Sauvage *et al.*, 2010). TiO_2 is also a well-known photocatalysts hence anodizing Ti can be used to produce TiO_2 photocatalyst that can degrade organic pollutants in contaminated air and water (Ao and Lee, 2005; Lee and Park, 2013; Sreekantan *et al.*, 2009).

As mentioned, anodization is a process that resulted in the formation of thin oxide film on a metal substrate. When a metal (M) is exposed to a sufficiently high anodic applied voltage in an oxidizing electrolyte, an oxidation reaction will take place. Generally the reaction can be written as Equation 2.1:

$$M \rightarrow M^{n+} + ne \qquad \text{Equation 2.1}$$

If the metal ions, M^{n+} are solvatized in the electrolyte, no anodic film will form and the metal will continuously dissolve. Depending on the rate of dissolution, the metal components can be completely corroded or only a thin layer will be removed as a typical process in electropolishing of metal. If the electrolyte is comprised of oxidant species that can react with the solvated ions, then a metal oxide (MO) can be formed (Equation 2.2).

$$M^{n+} + O^{2-} \rightarrow MO \qquad \text{Equation 2.2}$$

Now the properties of MO will determine the fate of the underlying metal. If the MO is easily dissolved then the metal will not be protected. If the MO is not dissolving, a barrier layer is formed and such a compact film may protect the underlying metal from further corrosion. Normally this can be achieved at relatively low anodizing voltage and by an appropriate choice of electrolyte. A competition between solvatization and oxide formation can also be observed whereby the anodic

film will dissolve but at the same time oxidized to form MO. Therefore, depending on the electrolyte used, the surface oxide formed on anodized metal can either be compact or porous. Porous film can be further classified as a film consisted of random pores, ordered pores or pores formed by loosely bounded small particulates on the metal surface forming a three dimensional network of interconnected particles.

Ordered pores can be in a form of discreet pores, characterized by elongated holes forming perpendicular to the underlying metal substrate. The pores can be of micron of depth but the diameter is normally less than 100 nm hence they are termed nanopores. An anodic oxide film with such morphology is called nanoporous oxide. Anodizing Al in acidic electrolyte is a well-known example whereby the resulting anodic Al_2O_3 is consisted of such nanopores (Sulka, 2008). Moreover, not only the nanopores formed are elongated, forming channels of equal diameter and length, the channels are actually highly densely packed in hexagonal arrangements. The first work reported on this observation is by Masuda and Fukuda whereby they mentioned that under specific experimental conditions pores growth is highly organized (Masuda and Fukuda, 1995). Applications of such structure are endless and one of it is as a template to produce nanowires or nanotubes. The use of nanoporous Al_2O_3 or termed anodic aluminium oxide (AAO) as a template for synthesis of 1-D nanomaterials is reported by Uosaki et al. (Uosaki *et al.*, 1990). Following this pioneering work, many reports have appeared on the use of AAO as 1-D nanostructures template material. The AAO pores are filled with the desired material; metal, polymer or semiconductors, then the AAO template will be etched away to yield nanorods or nanotubes.

Anodic process to yield self-organized pores on other metals such as W (Ismail *et al.*, 2016; Ng *et al.*, 2015), Nb (Kim *et al.*, 2016; Stojadinović *et al.*, 2015), Ti (Dikici *et al.*, 2017; Lee, 2017; Toshiaki *et al.*, 2016), Zr (Amer *et al.*, 2014; Berger *et al.*, 2008b; Wierzbicka *et al.*, 2016), and Fe (Cheng *et al.*, 2012b; Konno *et al.*, 2012; Wang *et al.*, 2015) and semiconductors like Si (Kim *et al.*, 2004) and InP (Li *et al.*, 2016; Sato *et al.*, 2006) have then received more attention. In the early works, focus was given on the formation of anodic oxide with similar morphology: close-packed cells in a hexagonal arrangement with nanopores at their centers. Optimization of the process to have control over pore diameter and length has been done. Anodization voltage has a strong influence the diameter and length of the nanopores formed. When the morphology of the AAO is inspected further, the pore cell is found to consist of scalloped shaped bottom. This is readily observed especially when the oxide layer is removed from the metallic substrate; exploring this allows for the proposal of several mechanistic models that describe the occurrence of the self-organized AAO.

The mechanisms of formation have then been adopted to explain the development of similar structure on other metals examples as mentioned earlier. Among the metals (and semiconductors) stated, Ti has been the most studied considering the anodic layer (i.e. TiO_2) possesses many excellent properties for applications in environment remedy and energy production as stated before (Chen and Mao, 2007; Mor *et al.*, 2006). Work published by Zwilling et al can be regarded as the first report on the formation of self-organized TiO_2 nanostructure by anodic process (Zwilling *et al.*, 1999). In the said work chromic acid electrolyte containing hydrofluoric acid was used to form what appears to be nanotubular structure. Despite the poor wall appearance, this work presents the most significant findings

such that fluoride ions are needed in the electrolyte to allow the transformation of nanopores to nanotubes. Following this, more reports have emerged on the formation of oxide nanotubes especially TiO_2 with fluoride ions as the main ingredient in the electrolyte that allows for pores to tubes transformation (Wang *et al.*, 2009; Wang and Lin, 2009).

There are four main components in the process of anodization: metal foil, platinum, power supply and electrolyte. The electrolyte can be consisted of fluoride ions (F^-), oxygen ions (O^{2-}) and hydroxide ions (OH^-) in viscous electrolyte. The positively charged electrode is the anode where the oxidation reaction occurs and the negatively charged electrode is the cathode where reduction reaction is dominating. When the anode is metal (and platinum as cathode), the applied voltage generates an electric field across the metal and causes the anodic film in form of barrier oxide layer to grow as O^{2-} ions migrate inward under the influence of the electric field and the metal ions eject out from the metal. Anodic film has different volume than the parent metal, thus it is expected to be under compressive stress. Following the flow concept for the growth of porous anodic Al_2O_3 (Houser and Hebert, 2009), oxide flow is assumed to originate from the plasticity of the barrier oxide layer generated by compressive stresses. To minimize stress the oxide behaves viscoplastically and it is continually being pushed upwards from the metal|oxide interface forming scalloped structure which will then develop into pores. The transition from pores to tubes structures can occur by dissolving interpores boundaries which is consisted of flouride-rich layer. This layer is soluble in water, hence sufficient amount of water is needed to dissolve it and then tube can be produced.

2.3. Anodization of Zr metal for ZNTs formation

This section reviews the history of Zr anodization in various electrolytes to form ZrO_2 compact oxide layer, nanopores, or nanotubes. There has been a significant progress made regarding the synthesis of ZNTs which has led to: first generation ZNTs prepared in aqueous electrolyte containing NaF or NH_4F, second generation ZNTs grown in hydrofluoric acid (HF), third generation smooth ZNTs in organic electrolyte and finally fourth generation ZNTs in fluoride free electrolyte. This thesis focuses on ZNTs formed in organic electrolyte, specifically in ethylene glycol containing NH_4F and various types of oxidant. Growth mechanism model and factor affecting the growth of ZNTs in organic electrolyte, the phases of ZrO_2 and stabilization of certain phases, properties and photoactivity of ZNTs are reviewed here.

2.3.1. Progress in Zr metal anodization in various types of electrolyte

Cox in 1970 anodized Zr to form a compact oxide layer of up to several hundred nanometers thickness. The Zr metal was first etched in mixed nitric/hydrofluoric acid then anodized in aqueous electrolyte (Cox, 1970). F^- ions in ammonium borate electrolyte was used to anodize Zr as reported by Archibald and Leach (Archibald and Leach, 1977a; Archibald and Leach, 1977b) to produce compact ZrO_2 as well. In 1988, Khalil et al. reported on the anodization of Zr in various aqueous electrolytes and showed the formation of hydrated layer on the oxide surface (Khalil *et al.*, 1988).