

DECLARATION

I hereby declare that I have conducted, completed the research work and written thesis entitled: “THE EFFECT OF Cu BASED TiO₂ NANOTUBES ARRAY FOR HEAVY METAL REMOVAL”. I also declare that it has not been previously submitted for the award for any degree or other similar title of this for any other examining body or university

Signature :

Candidate's name : SYAZWANI BT MOHD ZAKI

Date : 15 JANUARY 2014

Signature :

Supervisor's name : ASSOC. PROF. DR. SRIMALA SREEKANTAN

Date : 15 JANUARY 2014

**THE EFFECT OF Cu BASED TiO₂ NANOTUBES ARRAY FOR
HEAVY METAL REMOVAL**

by

SYAZWANI BT MOHD ZAKI

**Thesis submitted in fulfillment of the
requirement for the degree of
Master of Science**

JANUARY 2014

ACKNOWLEDGEMENT

Firstly, I would like to express my gratitude to Universiti Sains Malaysia (USM) especially School of Materials and Mineral Resources Engineering (SMMRE) for offering an opportunity and providing a comprehensive and conducive research environment with sufficient facilities to complete my research project. I would like to acknowledge the University Islam Antarabangsa Malaysia (UIA) and Kementerian Pengajian Tinggi (KPT) for providing the financial support.

I would like to take this opportunity to thank my heartfelt gratitude to my supervisor, Assoc. Prof. Dr. Srimala Sreekantan for her invaluable guidance and patience throughout the project. Her continuous support and guidance have led this research to an accomplishment. This thesis would have not completed without her constant guidance.

On top of that, special thank goes to all academic and technical staffs of SMMRE for their advices and assistance in handling laboratory equipment and analyzing the samples. My special thanks are especially dedicated to my family for the moral encouragement and mental support. Their encouragement and comforting efforts will always be remembered throughout my life. I am also indebted to my friends for their support throughout the years. Last but not least, I would like to extend my gratitude to everyone whom may have contributed in one way or another to make this thesis a reality. Thank you very much.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	i
TABLE OF CONTENTS	ii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF ABBREVIATIONS	x
LIST OF SYMBOLS	xii
LIST OF PUBLICATIONS	xiii
ABSTRAK	xiv
ABSTRACT	xvi
CHAPTER 1	
1.1 Introduction	1
1.2 Problem Statement	3
1.3 Research Objectives	5
1.4 Scope of research	5
1.5 Project Outline	7
CHAPTER 2	
2.1 Introduction	8
2.2 Electronic waste (e-waste)	9
2.3 Heavy metal	11
2.3.1 Lead	12
2.3.2 Removal of heavy metal	14
2.3.2.1 Adsorption	14
2.3.2.2 Membrane separation	15
2.3.2.3 Chemical precipitation	15
2.3.2.4 Ion exchanger	16
2.3.2.5 Ultrafiltration	16

2.3.2.6	Electrolytic recovery	17
2.3.2.7	Photocatalysis	17
2.4	TiO ₂ nanotubes	20
2.4.1	Properties of TiO ₂	21
2.5	Formation TiO ₂ nanotubes	24
2.5.1	Sol-gel technique.	24
2.5.2	Hydrothermal technique	25
2.5.3	Anodization	26
2.5.3.1	Mechanistic model of TiO ₂ nanotubes	28
2.5.3.2	Generation of TiO ₂	31
2.6	Modification of TiO ₂	34
2.6.1	Metal ion doping	35
2.6.2	Copper incorporated TiO ₂ photocatalyst	40
CHAPTER 3		
3.1	Introduction	46
3.2	Raw materials and apparatus	47
3.2.1	Titanium preparation	47
3.2.2	Ammonium fluoride	47
3.2.3	Ethylene Glycol (EG)	48
3.2.4	Copper nitrate	48
3.2.5	Acetone	48
3.2.6	Lead (II) stock solution	48
3.3	Procedure of anodization experiment	49
3.3.1	Foil preparation	49
3.3.2	Electrolytes preparation	49
3.3.3	Anodization procedure	50
3.3.4	Cleaning TiO ₂ nanotubes	51
3.5	Annealing process	51
3.6	Experimental design	52
3.6.1	Anodization at optimized condition	52

3.6.2. Wet Impregnation	53
3.6.2.1 The effect of substrate (as-anodized vs. as-annealed)	53
3.6.2.2 The effect of initial concentration	54
3.6.2.3 The effect of temperature of wet impregnation	55
3.7 Heavy metal removal	56
3.7.1 The effect of pH on Pb(II) solution	56
3.7.2 The effect of concentration of Pb(II) solution	56
3.8 Characterization techniques	57
3.8.1 Field emission scanning electron microscopy (FESEM)	57
3.8.2 Transmission electron microscopy (TEM)	59
3.8.3 X-Ray diffraction (XRD)	60
3.8.4 X-ray photoelectron spectroscopy (XPS)	61
3.8.5 Atomic absorption spectrometer (AAS)	62
3.8.6 UV-Vis spectroscopy (Uv-Vis)	63
3.8.7 Photoluminescence (PL) spectroscopy	64

CHAPTER 4

4.1 Introduction	65
4.2 Anodization of TiO ₂ nanotubes in optimized condition	65
4.2 Wet impregnation	69
4.2.1 Wet impregnation on as anodized vs. annealed TiO ₂	69
4.2.2 Effect of Post annealing treatment after impregnation	72
4.3 The effect of temperature	76
4.3.1 Structural characteristics of the nanotube arrays	76
4.3.2 Phase formation	80
4.4 The effect of Cu concentration	82
4.4.1 Structural characteristics of the nanotube arrays	82
4.4.2 Phase formation	85
4.4.3 Light absorption characteristics	86
4.4.4 X-Ray photoelectron spectroscopy (ARXPS) depth profiling	89
4.4.5 Chemical state and electronic state by XPS Analysis	91
4.5 Heavy metal removal	96

4.5.1	Dark adsorption of Pb on TiO ₂ nanotubes	96
4.5.3	The effect of pH on photocatalytic oxidation of Pb(II)	102
4.5.4	The effect of Pb concentration on photocatalytic oxidation of Pb	105

CHAPTER 5

5.1	Conclusions	109
5.2	Suggestions	110

REFERENCES		111
-------------------	--	-----

LIST OF TABLES

Table 2.1	: The Maximum Contaminant Level (MCL) standard for the most hazardous heavy metal (Babel and Kurniawan, 2003).	11
Table 2.2	: Various methods of lead (II) removal at different initial concentration	20
Table 2.3:	: Summary of fourth synthesis generation of TiO ₂ nanotubes.	33
Table 2.4	: Summary of the works reported on the different metal ions incorporated TiO ₂ photocatalysts.	38
Table 2.5	: Cu doped TiO ₂ photocatalyst at various concentrations and methods.	45
Table 3.1	: Parameters at optimized condition for anodization process.	52
Table 3.2	: Constant parameter of wet impregnation technique.	55
Table 3.3	: Constant parameter for the effect of temperature	55
Table 4.1	: Pb accumulated on Cu-TiO ₂ surface under UV illumination	105

LIST OF FIGURES

Figure 2.1	: Waste generation rates in the Southeast Asian Nations (Nguyen et al., 2003).	10
Figure 2.2	: The top ten industrial sources contributing to disease. Lead-acid battery recycling is the largest contributor to the burden of disease when measured in disability-adjusted life years (the years lost to ill-health, disability or early death). Photograph: Green Cross Switzerland.	13
Figure 2.3	: The conceptual reaction path of photocatalysis over TiO_2 (Barakat, 2011b)	19
Figure 2.4	: Illustrative top and cross sectional FESEM images of titania nanotubes arrays synthesis by anodization of Ti films in an ethylene glycol electrolyte (Grimes and Mor, 2009)	21
Figure 2.5	: Structure of Anatase and Rutile (Linsebigler et al. 1999)	23
Figure 2.7	: Formation of TiO_2 Nanotubes Array by anodization (Grimes and Mor, 2009)	29
Figure 3.1	: Flow chart of overall process in this research study	47
Figure 3.2	: Anodization method	50
Figure 3.3	: The profile for annealing process	51
Figure 3.4	: Wet impregnation method (As annealed)	54
Figure 4.1	: The I-t curve of titanium anodized in electrolyte for 60 min. Inset show the pits formation on the oxide layer at A2 (after 5 minutes of anodization)	66
Figure 4.2	: TiO_2 nanotubes formed after 60 minutes of anodization(a) top view (b) side view	67
Figure 4.3	: XRD patterns of TiO_2 nanotube arrays (a) as anodized and (b) annealed 400°C	68
Figure 4.4	: EDX elemental composition for (a) as-anodized TiO_2 nanotubes and (b) as annealed TiO_2 nanotubes	69

Figure 4.5	: The top view FESEM images of the Cu-TiO ₂ on (a) as-anodized TiO ₂ (b) annealed TiO ₂	71
Figure 4.6	: Overall image of the wet impregnated foils; (a) as-anodized (a) as-annealed	72
Figure 4.7	: FESEM image shows the presence of well aligned TiO ₂ nanotubes without any peeling of problem	73
Figure 4.8	: EDX elemental composition for Cu-TiO ₂ nanotubes	74
Figure 4.9	: XRD pattern of TiO ₂ nanotube (a) without post annealing and (b) with post annealing treatment after impregnation	75
Figure 4.10	: Photocatalytic activity of methyl orange degradation for post annealed and without post-annealed sample	76
Figure 4.11	: FESEM morphology of Cu-TiO ₂ nanotubes prepared at (a) 60°C and (b) 80°C	77
Figure 4.12	: TEM image of (a) TiO ₂ -nanotubes (b) 60°C Cu-TiO ₂	79
Figure 4.13	: Formation of TiO ₂ nanotubes array by anodization method (Grimes and Mor, 2009)	80
Figure 4.14	: The dehydration consequently occurs and the structure of two octahedral sharing one edge is formed to form anatase phase.	81
Figure 4.15	: FESEM image of TiO ₂ nanotubes dipped in different concentration of Cu(NO ₃) ₂ solutions (a) 0.01 M (b) 0.06 M (c) 0.1 M (d) 2 M	84
Figure 4.16	: XRD patterns of (a) pure TiO ₂ and Cu-TiO ₂ prepared in (b) 0.01 M, (c) 0.06 M, (d) 0.1 M, (e) 0.6 M Cu(NO ₃) ₂ solutions followed by annealing at 400°C.	85
Figure 4.17	: PL spectra of TiO ₂ and Cu-TiO ₂ prepared in (a) 0.01 M, (b) 0.06 M, (c) 0.1 M, (d) 0.6 M Cu(NO ₃) ₂ solutions, (e) Pure-TiO ₂ nanotubes	87
Figure 4.18	: Depth profiling by XPS for confirmation Cu (0.01 M) incorporated TiO ₂ at 0.01 M (a) 0° (b) 15° (c) 30° (d) 45° (e) 50°	90
Figure 4.19	: XPS spectrum of (a) TiO ₂ and (b) Cu-TiO ₂ nanotubes	91

Figure 4.20	: XPS spectrum for Ti 2p for (a) TiO ₂ nanotubes and (b) 0.01 M	92
Figure 4.21	: XPS spectrum of Cu 2p for (a) pure TiO ₂ and (b) 0.01 M Cu-TiO ₂	94
Figure 4.22	: C 1s spectra for (a) TiO ₂ nanotubes and (b) 0.01 M Cu-TiO ₂	95
Figure 4.23	: O1s spectrum of (a) TiO ₂ nanotubes and (b) 0.01 M Cu-TiO ₂	96
Figure 4.24	: Percentage (%) of Pb(II) removal conducted in dark region at (a) pH 5 (b) pH 11	97
Figure 4.25	: FESEM images and EDX analysis of pure TiO ₂ nanotubes at (a) pH 5 (b) pH 11	98
Figure 4.26	: Percentage (%) of Pb(II) removal conducted in UV and dark region at different pH with initial concentration of 100 ppm	99
Figure 4.27	: EDX analysis of Cu-TiO ₂ at (a) pH5 (b) pH 11	101
Figure 4.28	: Photocatalysis oxidation of Pb(II) as a function pH in dark environment and under illumination	103
Figure 4.29	: Percentage (%) of Pb(II) removal by Cu-TiO ₂ nanotubes at pH 5 with different concentration of Pb(II)	106
Figure 4.30	: Percentage (%) of Pb(II) removal by Cu-TiO ₂ nanotubes at pH 11 with different concentration of Pb(II)	106
Figure 4.31	: Schematic diagram illustrating the formation of PbO/PbOH layer on TiO ₂ retard the photocatalytic reaction for more Pb(II) removal	108
Figure 4.32	: Atomic percentage (At%) of Pb on TiO ₂ nanotubes at different concentration of Pb(II)	108

LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometer
ARXPS	Angle resolves X-Ray photoelectron spectroscopy
At%	Atomic percentage
CB	Conduction band
DI	Deionized
E-waste	Electronic waste
EEE	Electrical and electronic equipments
EPA	Environmental protection agency
USEPA	U.S. environmental protection agency
E&E	Electrical & electronics
EELS	Electron energy loss spectroscopy
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
HRTEM	High resolution transmission electron spectroscopy
ICDD	International centre of diffraction data
MCL	Maximum level contaminants
NIR	Near infrared
PL	Photoluminescence
PCs	Personal computers
PBT	Persistent, bio-accumulatives and Toxic
RT	Room temperature

SEM	Scanning electron microscopy
SE	Secondary electron
SiLi	Silicon lithium
TTIP	Titanium tetraisopropoxide
TMP	Tran-membrane pressure
TEM	Transmission electron microscopy
UF	Ultrafiltration
UV	Ultraviolet
UHV	Ultra-high-vacuum
UV-Vis	Ultraviolet visible spectroscopy
Vol%	Volume percent
VB	Valence band
Wt %	Weight percent
WEP	World environmental protection
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

Å	Armstrong
°C	Celsius
cm	Centimeter
d	Crystal lattice
eV	Electron volt
e^-	Electron
g	Gram
h^+	Hole
kV	Kilo volt
L	Litre
M	Molar
mV	Millivolt
mm	Millimeter
μm	Micrometer
ml	Milliliter
nm	Nanometer
ppm	Part per million
V	Voltage
W	Watt
λ	Radiation wavelength
θ	Diffraction angle

LIST OF PUBLICATIONS

1. Srimala Sreekantan, Lai Chin Wei, **Syazwani Mohd Zaki** (2014) “The Influence of Lead Concentration on Photocatalytic Reduction of Pb(II) Ions Assisted by Cu-TiO₂Nanotubes, *International Journal of Photoenergy*, Volume 2014 (2014), Article ID 839106, 7 pages.
2. Sreekantan, S. & **Zaki, S.M.** (2011). Preparation and characterization of Cu loaded TiO₂ nanotube arrays and their photocatalytic Activity, *The International Conference for Nanomaterials Synthesis and Characterization 2011, 4th-5th July 2011*, Mines Wellness Hotel, Seri Kembangan, Selangor, Malaysia
3. Sreekantan, S. & **Zaki, S.M.** (2013). The Effect of Cu Concentration on TiO₂ nanotubes for low Concentration of Pb (II) removal, *The 3rd ISESCO Internal Conference On Nanotechnology 2012 (IWCN2012)*, 5th-7th Dec 2012, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia

KESAN KUPRUM BERASASKAN TATASUSUNAN TIUB NANO TiO₂ TERHADAP PENYINGKIRAN LOGAM BERAT

ABSTRAK

Pencemaran logam berat terutamanya plumbum (Pb) dalam air sisa telah menjadi satu ancaman utama kepada kesihatan manusia dan alam sekitar. Teknik-teknik konvensional yang telah digunakan tidak mampu memenuhi keperluan Agensi Perlindungan Alam Sekitar (EPA) (<0.005 mg/L) yang merupakan tahap maksimum pencemaran yang dibenarkan. Oleh itu, teknik foto pemangkinan telah diterokai untuk menyingkirkan Pb(II) dalam penyelidikan. Untuk meningkatkan kecekapan penyingkiran Pb(II), tiub nano TiO₂ telah dihasilkan menggunakan proses penganodan. Kepingan Titanium (Ti) ditenggelamkan dalam etilena glikol yang mengandungi 0.3 g NH₄F dan 1 ml daripada H₂O pada 60 V selama 1 jam. Tiub nano TiO₂ dengan diameter 95 nm dan panjang 13 μm telah diperolehi melalui penganodan. Usaha telah diteruskan untuk meningkatkan lagi aktiviti foto pemangkin dengan menggabungkan Cu pada TiO₂ tiub nano dengan menggunakan teknik pengisitepuan basah. Kesan ke atas substrat yang telah melalui proses penganodan dengan substrat yang telah melalui rawatan haba, kepekatan larutan Cu(NO₃)₂ dan kesan ke atas suhu ketika proses pengisitepuan basah telah disiasat untuk memperoleh jumlah optimum penganapan Cu spesis dalam TiO₂ tiub nano. Ia telah mendapati bahawa 0.8 at% Cu yang diperolehi menggunakan 0.01M Cu(NO₃)₂ menunjukkan prestasi yang terbaik dalam aktiviti foto pemangkin iaitu 40% lebih baik daripada yang TiO₂ tiub nano asli. Seterusnya kajian telah dijalankan untuk mengkaji kesan pH dan penyerapan kepekatan awal Pb(II) oleh 0.01 M Cu-TiO₂ tiub

nano dalam Ultraviolet (UV) dan di dalam persekitaran gelap. Ia telah mendapati bahawa penyingkiran Pb(II) adalah tinggi (~ 99.7%) apabila pH larutan adalah 11 dan kepekatan Pb(II) kurang daripada 60 ppm.

THE EFFECT OF Cu BASED TiO₂ NANOTUBES ARRAY FOR HEAVY METAL REMOVAL

ABSTRACT

Heavy metals contamination especially lead (Pb) in wastewater has become a major threat to the health of mankind and environment. The conventional techniques that have been used are not capable of fulfill the requirement of Environmental Protection Agency (EPA) on maximum heavy metal concentration in stream. The maximum contaminant level of Pb(II) is 0.005 mg/L. Therefore, photocatalysis technique was explored to remove Pb(II) in this work. To increase the efficiency of Pb(II) removal, highly order TiO₂ nanotubes array was synthesized using anodization method. The Ti foil was anodized in ethylene glycol containing 0.3 g NH₄F and 1 ml of H₂O at 60 V for 1 hour. TiO₂ nanotubes with diameter of 90 nm and length of 13 μm were obtained upon anodization. Continuous efforts have been exerted to further improve the photocatalytic activity by incorporating Cu in TiO₂ nanotubes by using wet impregnation technique. The effect of as-anodized vs. as-annealed substrate, Cu(NO₃)₂ concentration and temperature were investigated in order to incorporate optimum amount of Cu in TiO₂ nanotubes. It was found that 0.8 wt% of Cu that was incorporated using 0.01M Cu(NO₃)₂ demonstrated the best performance in photocatalytic activity which is 40% better than pristine TiO₂ nanotubes. Further studies were carried out to investigate the effect of pH and initial concentration of Pb(II) absorption by 0.01 M Cu-TiO₂ nanotubes in Ultraviolet (UV) and dark environment. It was found that the removal of Pb(II) was

high (~99.7%) when the pH of the solution is 11 and the concentration of Pb(II) is below 60 ppm.

CHAPTER 1

1.1 Introduction

The rapid growth of volumes of electronic waste (e-waste) in the ASEAN region has increasingly drawn international attention. Economies face huge demands for electrical and electronic products, while governments are confronted with difficulties dealing with increasing volumes of e-waste. Due to economic growth and increased living standards, demand for electrical and electronic equipment (EEE) is growing. So are the streams of waste from these same devices. Volumes of e-waste are growing three times faster than volumes of average solid waste (Goosey, 2004). It was estimated that 50 million tons of e-waste are produced each year (Sthiannopkao and Wong, 2012). USA discards 30 million computers each year and 100 million phones are disposed of in Europe each year. The Environmental Protection Agency (EPA) estimates that only 15-20% of e-waste is recycled, the rest of these electronics go directly into landfills and incinerators (ICF, 2011). To tackle this serious heavy metal problem, strategic efforts need to be undertaken.

Pb(O), Pb(II) and Pb(IV) is a toxic metal ion frequently found in electronic waste (e-waste). Elevated levels of Pb in drinking water can result in delayed physical and mental development, attention deficits, kidney disorders and high blood pressure. In addition, studies have shown that young children, infants and pregnant women are particularly susceptible to the unsafe of Pb level. The maximum contaminant level (MCL) of Pb that has

been established by U.S. Environmental Protection Agency (USEPA) is 0.15 mg/L if the water is coming from a community water distribution system and a level of 0.005 mg/L if the water is coming directly from the source into the home.

Various conventional methods such as precipitation-filtration, ion-exchange, reverse osmosis, oxidation reduction, electrochemical recovery and membrane separation are commonly used to treat heavy metals. All these methods have their own advantages and disadvantages. However, those methods were not able to achieve the requirement of USEPA. Lately, photocatalyst is seen as an emerging technique to overcome the aforementioned problem. The major advantages of this technology are as follows:

- (i) Photocatalysis offers a good substitute for the energy-intensive conventional treatment methods with the capacity for using renewable and pollution-free solar energy.
- (ii) Unlike conventional treatment measures which transfer pollutants from one medium to another, photocatalysis leads to the formation of innocuous products.
- (iii) This process can be used to destroy a variety of hazardous compounds in different wastewater streams.
- (iv) It can be applied to aqueous and gaseous-phase treatments, as well as solid-soil phase treatments to some extent.
- (v) No further treatment for secondary disposable methods.

Among various photocatalyst material, TiO_2 have captivated much attention because of their, favorable surface chemistry and good biocompatibility (Xiao et al., 2008). However, it has its own limitation such as fast charge carrier recombination and low interfacial charge transfer rates of photo generated carrier. In order to overcome these difficulties, TiO_2 nanotubes was produced by anodization method and subsequently wet impregnate in $\text{Cu}(\text{NO}_3)_2$. It is believed that by incorporating optimum amount of Cu into TiO_2 lattice, the recombination losses of charge carrier can be reduced.

1.2 Problem Statement

Various methods such as conventional physical-chemical treatment methods which include precipitation-filtration, ion-exchange, reverse osmosis, oxidation reduction, electrochemical recovery, membrane separation and other techniques, are commonly used to treat heavy metals. However, among all the available methods, photocatalytic emerged as a promising one because it is able to destroy and transform variety of pollutants by oxidative or reductive mechanism and can remove metal and organic pollutants simultaneously. In addition, this process also assists removal of toxic organics and microbiological pollution. Unlike other method, photocatalytic is believed capable of removing heavy metal contaminants to low concentration (less than 20 ppm). However, to date, there is limited study regarding heavy metal removal at low concentration by

photocatalytic activity of TiO₂ nanotubes. Therefore, comprehensive work on heavy metal removal by TiO₂ nanotubes photocatalyst is essential to be explored.

Though TiO₂ is regarded as one of the most efficient and environmentally benign photocatalyst for photo-degradation of various pollutants, TiO₂ exhibits intrinsic drawbacks which limit its widespread technological applications. The use of the pristine TiO₂ phases presents some drawbacks such as (i) high recombination rate for the photo produced electron-hole pairs (ii) difficulty to significantly improve the performances by incorporating or doping with foreign species that often work as recombination centers, (iii) difficulty to support powdered TiO₂ on the substrate. Many studies highlighted the coupling mechanism between Cu and TiO₂ to facilitate a better charge carrier separation and visible light response (Zhang *et al.*, 2004, Xin *et al.*, 2008, Xu *et al.*, 2011). However, most of these studies involved Cu-TiO₂ photocatalysts in the form of particles/spheres or thin films, which do not possess high enough surface area for photon absorption (Yan and Zhou, 2011, Kubacka *et al.*, 2012). Moreover, most scholars mainly focused on the photo degradation of organic pollutants rather than the inorganic pollutants. Therefore, in the present study, TiO₂ in nanotubular structure was developed by anodization process and subsequently incorporated with Cu by wet impregnation method to study the feasibility of those nanotubes in removing Pb. A detail studies regarding the synergistic relationship of Cu incorporated TiO₂ nanotubes on Pb removal has been established in this work. Thus, a comprehensive study was conducted

to optimize wet impregnation parameters (e.g., substrate effect, concentration of precursor and temperature) to obtain the preferred Cu-TiO₂ nanotubes, resulting in the best performance of Pb(II) removal.

1.3 Research Objectives

Following are the objectives of the research conducted:

- i) To grow TiO₂ nanotubes by anodization using optimized condition
- ii) To study the formation of Cu-TiO₂ nanotubes in terms of substrate, concentration of Cu(NO₃)₂, temperature and time by wet impregnation method.
- iii) To study the Pb removal by TiO₂ /Cu-TiO₂ nanotubes and postulates the mechanism of Pb removal.

1.4 Scope of research

In order to achieve high efficiency of heavy metal removal, it is essential to have TiO₂ nanotubes with control dimensional structure and free from bundling problem (disorder arrangement of nanotube array) because the removal process occurs at the surface and through narrow channel of nanotubes. Therefore, anodization was conducted in optimized condition based on our preliminary work (Sreekantan *et al.*, 2010). The obtained TiO₂ nanotubes were then annealed at 400°C and wet impregnated in Cu(NO₃)₂. Effect of substrate, concentration of Cu(NO₃)₂, time and temperature was investigated. The best sample was then selected to study the heavy metal removal.

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

Heavy metal removal by Cu-TiO₂ nanotubes was evaluated by Atomic Absorption Spectrometer (AAS). The stock solution was prepared by diluting 1000 ppm of selected heavy metal solution to the required concentration. The area of foil that was soaked in the stock solution is 1cm x 4cm. The photocatalytic reaction for heavy metal removal was performed in a quartz tube (200 ml) equipped in 120 W germicidal light (UV-C) as the light source. The photocatalytic activity was carried out at room temperature (RT), 25°C for 5 hours. Lead was diluted in 100 ml of ultra-pure deionized (DI) water to obtain different concentration. The performance of Cu-TiO₂ nanotubes was compared with the pristine TiO₂ nanotubes. The remnant concentration of Pb(II) after photocatalytic reaction was quantified by AAS.

1.5 Project Outline

This dissertation is organized in five chapters consecutively. In chapter 1, the introduction of this research work, research objectives, problem statement, the scope of research as well as dissertation overview are presented. Chapter 2 provides an overview of TiO₂ principles and the research progress of heavy metal removal using of TiO₂ by photocatalytic activity. In addition, chapter 2 comprises literature review on Cu incorporated TiO₂ nanotubes and its application in environmental remediation. The specifications of the raw materials, research methodology and the characterizations employed in this research work are described in chapter 3. The results of characterizations and the discussions are presented in chapter 4. Chapter 5 summarizes the conclusion of the study as well as several suggestions and recommendations for the future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Due to rapid development and industrialization all over the world, the levels of industrial pollution have been steadily rising. The pollution problem of industrial wastewater became more and more serious in the entire world. Consequently, the treatment of polluted industrial wastewater remains a topic of global concern. Wastewater containing heavy metals are considered to be hazardous to both human life and the environment due to their acute toxicity and non-biodegradability, even when heavy metals are present in trace concentration. Lead (Pb) is one of the most toxic heavy metal, also being mutagenic to aquatic organisms and humans. Therefore the discharge limit permitted by Environmental Protection Agency (EPA) is 0.005 mg/L from both natural and anthropogenic resources which is harmful to human and living things. Long-term drinking water containing high level of lead will cause serious health problems such as nerve disorder, anemia, kidney diseases and mental retardation (Xu *et al.*, 2008).

Photocatalysis is considered to be a 'green' method for water decontamination, as it can lead to fast and complete decomposition of contaminants without leaving harmful intermediates (Zhang, 2010). Therefore, development of photocatalyst for heavy metal contaminants is the aim of this work. In the following section, the details of electronic waste (e-waste), heavy metal, photocatalytic activity, TiO₂ nanotubes

formation and Cu incorporated TiO₂ nanotubes are reviewed in details. As this dissertation is concerned mainly on the effect of Cu incorporation TiO₂ nanotubes, this subject matter is addressed in the literature too. The final part appraised the application of TiO₂ nanotubes in heavy metal removal.

2.2 Electronic waste (e-waste)

Volumes of e-waste are growing three times faster than volumes of average solid waste (Goosey, 2004). It is estimated that 50 million tons of e-waste are produced each year (Sthiannopkao and Wong, 2012). The USA discards 30 million computers each year and 100 million phones are disposed of in Europe each year. The volume of obsolete PCs in developing countries is estimated to surpass those of the developed countries by 2016 to 2018. By 2030, some 400 to 700 million personal computers will become obsolete in the developing countries (Yu *et al.*, 2010). Many Asian countries will be experiencing a rapid rise in the volume of e-waste. Figure 2.1 shows waste generation in the Southeast Asian nations. Malaysia generated an estimated 5475,000 tons of solid waste in 2001, which is about 0.81 kg/cap/day (Hassan *et al.*, 2001). However, the Environmental Protection Agency (EPA) estimates that only 15-20% of e-waste is recycled, the rest of these electronics go directly into landfills and incinerators (ICF, 2011)

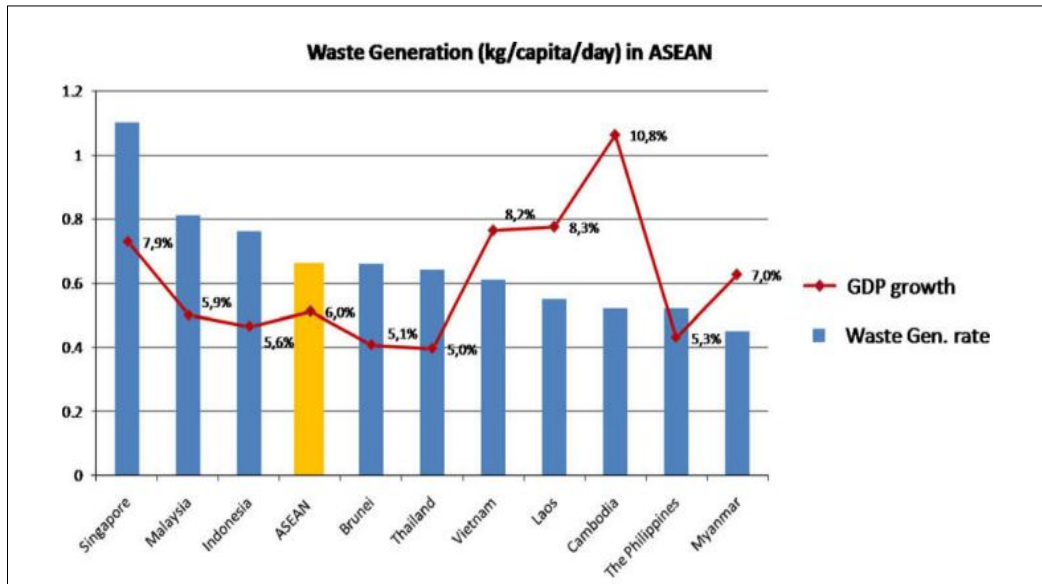


Figure 2.1: Waste generation rates in the Southeast Asian Nations (Nguyen *et al.*, 2003).

The electrical & electronics (E&E) industry is the leading sector in Malaysia's manufacturing sector, contributing significantly to the country's manufacturing output (26.94 per cent), exports (48.7 per cent) and employment (32.5 per cent) (Malaysian Investment Development Authority, 2013). However, Malaysia lacks a domestic recycling scheme that can handle the mounting streams of e-waste. The amount of e-waste being discarded is estimated to equal 1.165 billion units (or over 21,000 million tonnes) by 2020 (Basel Convention, 2009). The country suffers from heavy metal produced from e-waste. In 2008, the whole country only had 107 licensed contractors for collecting and processing such e-waste (Pariatamby and Victor, 2011). As a result, only a small fraction of the e-waste is treated properly. The government of Malaysia is currently working on a draft for regulating the control and management of e-waste and it needs an urgent attention to save the environment and improve the health of mankind.

2.3 Heavy metal

Heavy metals are the major contaminants of e-waste. Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava and Majumder, 2008). Heavy metal contamination in the aquatic environment including arsenic (As), cadmium (Cd), lead (Pb), chromium (Cr) and mercury (Hg) poses an eco-toxicological hazard to living organisms. Some of these metal pollutants come from fertilizer and sewage but the biggest source is definitely the effluent industrial discharged from various industries such as electronic industry, mining, electroplating and battery manufacturing. Since heavy metals cause serious health effect, wastewater regulations are established to minimize human and environmental exposure to hazardous chemical. The summary of various heavy metals and their permitted concentration is shown in the Table 2.1:

Table 2.1: The Maximum Contaminant Level (MCL) standard for the most hazardous heavy metal (Babel and Kurniawan, 2003).

Heavy Metal	Toxicities	MCL (ppm)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis nausea, chronic asthma, coughing , human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of kidney, circulatory system, and nervous system	0.005
Mercury	Rheumatoid arthritis and diseases of kidneys, circulatory and nervous system.	0.00003

Among various heavy metals shown in the Table 2.1, Pb is our special concern due to persistency and recalcitrant of Pb in the environment. According to World Environmental Protection (WEP), Pb accounts for 98% of the total disposal or other releases of persistent, bio-accumulatives and toxic (PBT) chemicals. In addition, EPA has reported that the disposal or other releases of PBT chemicals increased by 50%, mainly due to increases in Pb and Pb compounds. Total disposal or other releases of lead and lead compounds increased 51% in 2010. Thus, Pb contaminants need urgent attention in order to save the environment and to overcome the adverse health risk of mankind.

2.3.1 Lead

Lead is a toxic metal ion frequently found in wastewater coming from industrial effluents. Lead exists in three oxidation states; Pb(O), Pb(II) and Pb(VI). Metallic lead, Pb (O) exists in nature but its occurrence is rare. In the environment, Pb is commonly found combined with two or more other elements to form lead compounds and it usually exists as Pb(II). Pb(II) is a toxic metal ion frequently found in wastewater coming from industrial effluents. As for Pb(VI), it is only formed under extremely oxidizing condition.

The major industrial sources for lead pollution originate from industrial waste/municipal sewages, mining, chemical manufacture and other sources. In addition, this element can be found as a component of insecticides batteries and water pipes. Pb also is widely used in car batteries, electronic items and ammunitions. The improper disposal from these industries contributes to the rise level of Pb in the aquatic

environment. Moreover, Pb also can enter into drinking water through corrosion of leaded pipelines in water transporting system and more to happen when the water is slightly acidic (Al-Rasheed, 2005).

Figure 2.2 depicts the top ten industrial sources contributing to disease and lead-acid battery recycling is the largest contributor to the problem of disease which causes the disability or early death. Lead smelting is in the second rank for industrial pollutant source. We can conclude that lead is the major problem released by various industrials.



Figure 2.2: The top ten industrial sources contributing to disease. Lead-acid battery recycling is the largest contributor to the burden of disease when measured in disability-adjusted life years (the years lost to ill-health, disability or early death). Photograph: Green Cross Switzerland.

2.3.2 Removal of heavy metal

Recently, numerous approaches have been studied for the development of cheaper and more effective technologies to reduce the amount of wastewater and to improve the quality of treated effluent. The conventional process for removing heavy metals from wastewater includes chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition. In addition, neutralization, electrolysis, chemical oxidation-reduction, extraction, adsorption, precipitation, ion exchange, membrane separation and electrodialysis were often used for wastewater containing heavy metal ions (Zhang *et al.*, 2012b, Kabra *et al.*, 2004, Rao *et al.*, 2007). These techniques can play a role more or less. However, the effectiveness for wastewater containing low concentration heavy metal is still questionable. Moreover, most of these technologies are simple physical separation process, and pollutants did not really change into harmless substance. So it is easy to cause secondary pollution (Fu and Wang, 2011). Therefore, search for adsorbents with high adsorption capacities that could remove the Pb up to 0.05 mg/L is still in great need.

2.3.2.1 Adsorption

In recent years, adsorption has become one of the alternative treatments because the search for low cost adsorbents that have metal binding capacities has intensified (Leung *et.al* 2000). The adsorbent maybe of mineral, organic or biological origin, zeolites, industrial by products, agriculture wastes, biomass and polymeric materials (Kurniawan *et.all* 2005). Adsorption is a process that occurs when gas or liquid solute (adsorbate) accumulates on the surface of a solid or more rarely, in a liquid (absorbent)

to form a molecular or atomic film. The exact nature of bonding depends on the adsorbate and adsorbent species involved in the reaction but the adsorption process is generally classified as chemisorption (involving weak van der Waals force) and physisorption (involving strong covalent bond). The major shortcomings of adsorption process are high operating cost, inability to regenerate, low adsorption capacities and large sludge disposal (Srivastava, 2013, Vigneswaran *et al.*, 2004)

2.3.2.2 Membrane separation

Membrane separation has been increasingly used recently for the treatment of inorganic effluent due to its convenient operation. Membrane filtration is capable in removing not only suspended solid and organic compounds but also inorganic contaminants such as heavy metals (Barakat, 2011a). It separates heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size and molecular weight of the separating compounds (Vigneswaran *et al.*, 2004). However, the decrease in the performance due to membrane fouling has hindered it from wider application in wastewater treatment. Fouling has adverse effects on the membrane system such as flux decline, high pressure which resulted in high operational cost for membrane system (Kurniawan *et al.*, 2006).

2.3.2.3 Chemical precipitation

Chemical precipitation is widely used in heavy metal removal from inorganic effluent. The theoretical mechanism of heavy metal removal by chemical precipitation is presented in the equation 2.7.1. (Wang *et al.* 2004):



where M^{2+} represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide. However chemical precipitation requires a large amount of chemical to reduce metal to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long term environmental impacts of sludge disposal (Aziz et.al 2008).

2.3.2.4 Ion exchanger

Ion exchanger is another method has been used successfully in the industry for the removal of heavy metals from effluent. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover, ion exchange is nonselective and is highly sensitive to the pH of the solution (Barakat, 2011a) .

2.3.2.5 Ultrafiltration

Ultrafiltration (UF) membrane is useful in removing macromolecules, colloids and suspended solids. This technique allows the channel of water and low-molecular weight solutes but maintains macromolecules whose size is larger than the pore size of the membrane (Vigneswaran *et al.*, 2004). Moreover, it possesses some advantages such as lower driving force and a smaller space requirement due to its high packing density. It also enables concentration, purification, and fractionation of macromolecules in solution

at ambient temperature and without phase change or addition of solvents. However, the decrease in UF performance due to membrane fouling has hindered it from a wider application in wastewater treatment. Fouling has many adverse effects on the membrane system such as flux decline, an increase in trans-membrane pressure (TMP) and the biodegradation of the membrane materials (Kurniawan et.al 2006). These effects result in high operational costs for the membrane system. In view of these, the search and development of a more outstanding and cost-effective adsorbing materials have been intensified recently.

2.3.2.6 Electrolytic recovery

Electrolytic recovery is also one of the many technologies used to remove metals from process water streams. This process uses electricity to pass current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantages was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Kurniawan et al., 2006)

2.3.2.7 Photocatalysis

Photocatalysis is an innovative and the most promising and emerging technique for efficient destruction and transform a variety of pollutants by oxidative or reductive mechanisms (Murrini *et al.*, 2007). In this way, organic and inorganic compounds and even microorganisms are degraded and transformed into less harmful substances. Upon

an illumination of semiconductor electrolyte interface with light energy greater than the semiconductor band gap, electron-hole pairs (e^-/h^+) are formed in the conduction band and the valence band of semiconductor, respectively (Hermann,1999). Industrial bearing heavy metals that could be removed by photocatalysis are Cd, Cr, Ni, Pb and Zn, which are the most hazardous among the chemicals industries. Various semiconductors have been used in photocatalysis study such as TiO_2 , ZnO, CeO_2 , CdS and ZnS. As generally observed, the best photocatalytic performance with maximum quantum yields (number of times a specific event occurs per photon absorbed by the system) are always obtained with TiO_2 .

Figure 2.3 depicts the conceptual reaction path of photocatalysis over TiO_2 . Generally, photocatalyst creates strong oxidation agent and electronic holes to breakdown the organic matter to carbon dioxide and water in the presence of photocatalyst, light and water. Mechanism involved when photocatalyst TiO_2 absorbs Ultraviolet (UV) irradiation from sunlight or illuminated light source, it will produce pairs of electrons and holes. The electron of the valence band TiO_2 becomes excited when illuminated by light. The excess energy electron promoted the electron to the conduction band of TiO_2 therefore creating the negative-electron (e^-) and positive-hole (h^+) pair. This stage is referred as semiconductor photo excitation state.

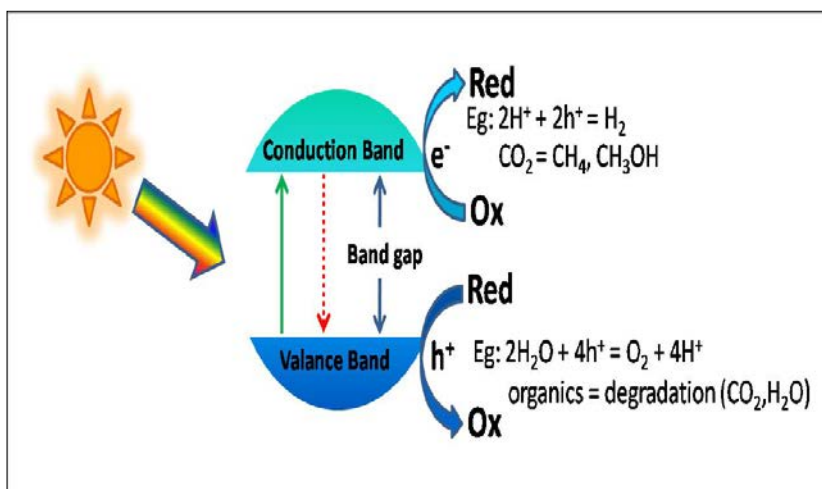


Figure 2.3 : The conceptual reaction path of photocatalysis over TiO₂ (Barakat, 2011b).

Photocatalysis is mainly applicable to the oxidation of organic compounds and reduction of inorganic species. The oxidation-reduction behavior of species in contact with TiO₂ determines whether the material will be photooxidized or photoreduced. Mollers et.al (1974) suggested that oxidation is the initial step that determines reduction. The redox reactions of this process have versatile applications especially for transformation of metal ions. Table 2.2 shows work done by various researchers on lead removal using photocatalyst and adsorption method. As seen, photocatalysis can be envisaged as convenient method for eliminating Pb(II) from aqueous solution. However, efficiency of heavy metal removal is relatively low because most of the study involved nanoparticles/nanopowders. Therefore, photocatalytic reaction for heavy metal removal using nanotubes is worth exploring. Furthermore, the mechanisms involved for heavy metal removal by photocatalytic process are not still completely understood, thus efforts for their elucidation seem valuable. A major advantage of photocatalysis is that the process can be used to destroy a variety of hazardous of compounds in different

wastewater streams. The reactions of photocatalysis are mild, reaction time is modest and lesser chemical input is required. Option for recovery can also be explored for metals which are converted to their less toxic or non-toxic metallic.

Table 2.2: Various methods of Pb(II) removal at different initial concentration.

Method	Initial Concentration (ppm)	Efficiency (%)	Time (h)	Structure	Reference
Photocatalysis	198	27.2	1	Nanopowder	(Chen and K Ray, 2001)
Photocatalysis	100	93	5	Nanoparticle	(Murruni <i>et al.</i> , 2007)
Photocatalysis	10	95.8	3	Nanoparticle	(Samarghandi <i>et al.</i> , 2007)
Photocatalysis	198	98.8	3	Nanoparticle	(Joshi and Shrivastava, 2010)
Photocatalysis	165	57	4	Nanopowder	(Murruni <i>et al.</i> , 2008)
Photocatalysis	100	7	1	Nanoparticle	(Mishra <i>et al.</i> , 2007)

2.4 TiO₂ nanotubes

Titania Nanotubes (TiO₂) have captivated much attention because of their large specific surface area, favorable surface chemistry and good biocompatibility (Xiao *et al.*, 2008). It is a highly functional material that has been used in several applications such as hydrogen generation, solar cell and photo oxidation of organic compounds (Okour *et al.*, 2010). Besides, TiO₂ nanotubes arrays were found to possess outstanding charge

transport and carrier lifetime properties enabling a variety of advanced applications. TiO₂ nanotubes have a tube-like structure with a circular nanotubular opening with the range of diameter within 20 nm-200 nm. The typical wall thickness can be produced ranges from 10 nm to 20 nm. By optimizing the local electrochemical condition within these tube layers, these ordered nanotubes with length as long as 100 μm can be produced. SEM images of the top of anodized foil gave an appearance in the Figure 2.4.

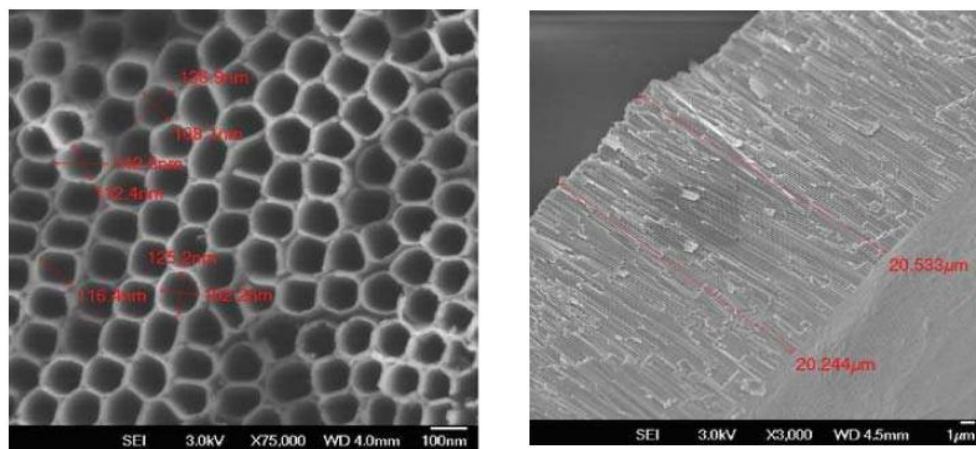


Figure 2.4: Illustrative top and cross sectional FESEM images of titania nanotubes arrays synthesized by anodization of Ti films in an ethylene glycol electrolyte (Grimes and Mor, 2009) .

2.4.1 Properties of TiO₂

In photocatalysis system, TiO₂ exists in nature in three main polymorphs: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). However, the two main crystallographic forms are anatase and rutile. The band gap energy of anatase is 3.23 eV, 3.02 eV for rutile and 3.13 eV for brookite. It is found that the transformation sequence and thermodynamic phase stability of various TiO₂ phases are depended on the particles size. At particles size below 11 nm, anatase was thermodynamically stable whereas

rutile was stable for sizes more than 35 nm. On the other hand, brookite phase achieves its stability when particles size lies between 11 and 35 nm (Zhang and Banfield, 2000) . The anatase polymorph is prevalently used as photocatalyst, rutile in optical devices whilst the physico-chemical properties of brookite are not much known because pure brookite without rutile or anatase is rather difficult to be prepared (Lazzeri *et al.*, 2001). As a result, most of the studies have been carried with either anatase or rutile due to their simple preparation method and high photocatalytic activity.

The structure of rutile and anatase can be described in terms of chains of TiO_6 octahedral. The two crystal structures differ by the distortion of each octahedron and by the assembly pattern of the octahedral chains. Figure 2.5 shows the unit cell structures of the rutile and anatase crystal. Each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions. The octahedron in rutile is not regular, showing a slight orthorhombic distortion. The octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are greater (3.79 and 3.04 Å vs 3.57 and 2.96 Å in rutile) whereas the Ti-O distances are shorter than in rutile (1.934 and 1.980 Å in anatase vs 1.949 and 1.980 Å in rutile). In the rutile structure each octahedron is in contact with 10 neighbor octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms) while in the anatase structure each octahedron is in contact with eight neighbors (four sharing an edge and four sharing a corner). These differences in lattice structures cause different mass densities and electronic band structures between the two forms of TiO_2 , as indicated in Figure 2.5 (Linsebigler *et al.*, 1995)

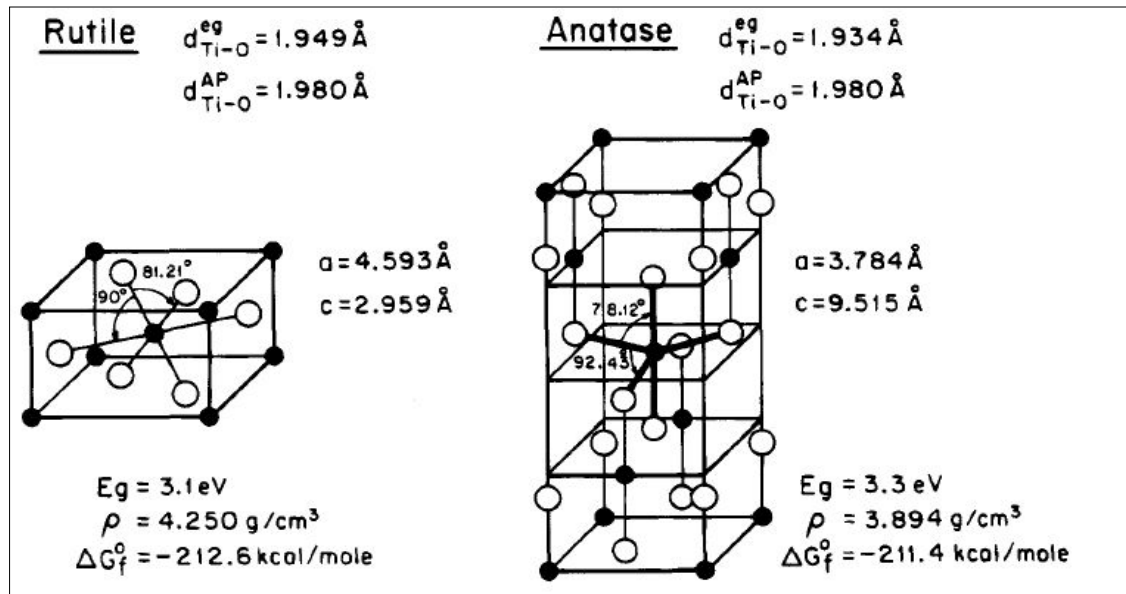


Figure 2.5: Structure of anatase and rutile (Linsebigler *et al.*, 1995)

In the past few years, high surface area and nanoporous TiO₂ nanotubes have attracted much attention for their potential use in several practical applications requiring an interconnected and large internal surface area. More recently, titania nanotubes with different sizes and various geometrical shapes were prepared using various physical and chemical synthesis routes such as sol-gel (Jung *et al.*, 2002), hydrothermal process (Bavykin *et al.*, 2004, Khan *et al.*, 2006), and anodization (Grimes and Mor, 2009). As an effective fabrication technology, the electrochemical anodization process is useful because of its low cost, large area fabrication, good mechanical adhesion, and electrical conductivity due to the nanotubes being directly connected to the substrate, while the limited thickness of these anodic TiO₂ nanotubes must be adjusted by controlling the anodic conditions, such as the applied voltage, electrolyte composition,

the pH of the electrolyte, duration, and magnetic agitation. The different techniques for TiO₂ formation were reviewed briefly in the next section.

2.5 Formation TiO₂ nanotubes

There are few common approaches for synthesizing TiO₂ in nanotubular structure namely sol-gel, hydrothermal, template assisted fabrication and anodization of titanium (Xiao *et al.*, 2008). The details are reviewed in the following section.

2.5.1 Sol-gel technique

Sol-gel hydrolysis is widely employed due to its capability in controlling the textural and surface properties of the resulting oxides. This method used primarily for the fabrication of mix-metal oxides, starting from a colloidal solution (sol). In 1998, Tomoko and co-workers demonstrated a detailed study to obtain very fine TiO₂ powder using by sol gel method using a metal alkoxide. These fabrication methods yield TiO₂ particles smaller than several hundreds of nanometers in size. It has been reported that TiO₂-based powders doped with a small amount of SiO₂ prepared by the sol- gel method with subsequent heat treatment have large specific surface areas. However, the sol gel technique suffers some drawback such as the raw materials that currently used are expensive, time consuming and existence of large number of pores in the gel during drying process.

Previously, the nanostructured titania used in photochemical were obtained by casting a colloidal sol, with the resulting film consisting of a three-dimensional network of interconnected nanometer-sized particles. The small size of the crystalline particles