TITANIUM DIOXIDE FORMATION VIA ANODIZATION AND THERMAL OXIDATION FOR PHOTOREDUCTION OF CHROMIUM (VI)

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by

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LIST OF SYMBOLS

g/cm^3	Gram per centimeter cube
%	Percentage
<	Less than
>	More than
°	Degree
℃	Degree celcius
℃/min	Degree celcius per minute
θ	Bragg angle
λ	Wavelength
$\bullet O_2^-$	Superoxide radical
•OOH	Hydroperoxyl radical
•OH	Hydroxyls radical
A	Ampere
Å	Angstrom (10^{-10} m)
cm	Centimeter
E_g	Band gap
cm^3	Centimeter cube
E_{CB}	Conduction band edge potential
I	Current
i	Critical current density
D	Diameter
e^-	Electron
eV	electronvolt

g	Gram
h	hour
L	Length
mg	Milligram
μm	Micrometer
mm	millimeter
mL	Milliliter
M	Molarity
min	Minute
nm	Nanometer
d	Oxide thickness
hν	Photon energy
%	Percentage
s	Second
T	Temperature
E_{VB}	Valence band edge potential
V	Volt
wt.%	Weight percentage
2θ	Diffraction angle

LIST OF ABBREVIATIONS

1D	One-dimensional
a.u.	Arbitrary unit
CB	Conduction band
Cr(III)	Trivalent chromium
Cr(VI)	Hexavalent chromium
DI	Deionized
DOE	Department of Environment
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy dispersive X-ray
EG	Ethylene glycol
EPA	Environmental Protection Agency
FESEM	Field Emission Scanning Electron Microscope
FRL	Fluoride-rich layer
FTIR	Fourier-transform Infrared
FWHM	Full width height maximum
IARC	International Agency for Research on Cancer
IR	Infrared
ISO	International Organization for Standardization
J-t	Current density-time
NHE	Normal hydrogen electrode
NPs	Nanoparticles
NTs	Nanotubes
NWs	Nanowires

PDF	Powder diffraction file
pH	Hydrogen potential
SC	Semiconductor
TEM	Transmission Electron Microscope
TNTs	Titanium dioxide nanotubes
US-EPA	US Environmental Protection Agency
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
VB	Valence band
vs	Versus
WHO	World Health Organization
XRD	X-ray Diffraction

PENGHASILAN TITANIUM DIOKSIDA MELALUI PENGANODAN DAN PENGOKSIDAAN TERMAL UNTUK FOTOMANGKIN KROMIUM (VI)

ABSTRAK

Kajian ini menyiasat kebolehan fotomangkin untuk menurunkan Cr(VI) kepada Cr(III) di dalam larutan akueus TiO_2 berstrukturnano (tiubnano (TNTs) dan dawainano (NWs)) melalui pengoksidaan anodik dan termal, masing-masing. TNTs dihasilkan dalam elektrolit yang mengandungi fluorida sementara NWs TiO_2 di hasilkan dalam persekitaran oksida yang mengandungi potassium. Semasa proses penghasilannya, di jumpai TiO_2 mengandungi ion-ion yang kewujudannya diperlukan bagi menghasilkan struktur nano. Bahan cemar utama yang menduduki dalam oksida NTs dan NWs ialah ion fluorida dan potassium, masing-masing. EDX dan SEM telah digunakan untuk mengkaji kuantiti bahan cemar di dalam oksida tersebut. TNTs mengandungi 1.89 wt% fluorin. NWs mengandungi 7.54% potassium. Oleh hal yang demikian, bagi membandingkan sama ada bahan cemar tersebut memberi kesan terhadap proses penurunan Cr(VI), filem TiO_2 telah di hasilkan secara pengoksidaan anodik dan termal tanpa kehadiran ion fluorida dan potasium, masing-masing. Hasilnya ialah filem berstruktur padat tanpa sebarang kehadiran struktur nano. Mengikut EDX, filem-filem itu bebas daripada bahan cemar. Fasa penghabluran bagi oksida TiO_2 anodik dan termal ini juga di kaji. TNTs mengandungi anatase seperti mana di dapati daripada XRD dan spektroskopi Raman sementara anodik TiO_2 padat mengandungi amorfus dan rutile. Kedua-dua oksida termal TiO_2 mengandungi rutile. Filem NTs, NWs dan padat TiO_2 telah di uji di dalam eksperimen fotokatalisis bagi menurunkan Cr(VI) kepada Cr(III). Anodik TiO_2 padat berjaya menurunkan sebanyak 48.36% Cr(VI) selepas 20 minit. Manakala, TNTs yang telah di sepuh lindap dapat menurunkan 5.86% Cr(VI) selepas 20 minit. Ini menunjukkan TNT mempunyai kurang keupayaan menurunkan Cr(VI) berbanding filem padat anodik. Dalam masa yang sama,

TiO_2 padat yang telah di oksida secara termal menurunkan 28.04% Cr(VI) berbanding 14.48% oleh NWs selepas 20 minit. Walaubagaimanapun, selepas 50 minit, kesemua empat struktur TiO_2 telah menghampiri 100% tahap penurunan.

TITANIUM DIOXIDE FORMATION VIA ANODIZATION AND THERMAL OXIDATION FOR PHOTOREDUCTION OF CHROMIUM (VI)

ABSTRACT

This study investigated on the photocatalytic performance to reduce Cr(VI) to Cr(III) in aqueous solution of TiO_2 nanotubes (NTs) and nanowires (NWs) synthesised by oxidation of titanium, anodically and thermally, respectively. TiO_2 NTs were produced in fluoride containing electrolyte whereas TiO_2 NWs were produced in potassium containing oxidation environment. During these fabrication processes, TiO_2 was found to contain ions which were required for the growth of the nanostructures. In NWs, potassium ions were found to be the main impurity whereas in NTs, fluoride ions were detected to be incorporated within the oxide. EDX in SEM was used to study the amount of impurities in the oxide. It was found that anodic TNTs were consisted of 1.89 wt % of fluorine. Thermally oxidised NWs contained 7.54 wt% of potassium contamination. Therefore, as to compare if the impurities affect the Cr(VI) reduction process, TiO_2 films were also created either by anodic or thermal oxidation in the absence of fluoride ions and potassium ions, respectively. The resulting films were compact without any noticeable nanostructures and from EDX the films were free from contamination. The crystal phases of the anodic or thermal oxidised TiO_2 were also studied. It was found that anodic NTs were comprised of anatase as shown from XRD and Raman spectroscopy whereas compact TiO_2 was consisted of a mixture of amorphous and rutile. Thermally oxidised TiO_2 compact and NWs on the other hand were consisted of both rutile oxide. NTs, NWs and compact TiO_2 were tested in a photocatalysis experiment to reduce Cr(VI) to Cr(III). It was found that compact anodised TiO_2 can reduce down to 48.36% after 20 minutes. Whereas annealed NTs

can reduce 5.86% after 20 min. This indicated that the NTs have less ability to reduce Cr(VI) compared to compact anodic film. Similarly, thermally oxidised titanium with compact structure can reduce 28.04% compared to 14.48% NWs after 20 min. However, it was found that after 50 min , all four samples has reach almost 100% of reduction.

CHAPTER 1

INTRODUCTION

1.1 Background

Industrial growth has many advantages. However, the flow of the unregulated industrial waste especially wastewater into the waterways has resulted in pollution-related diseases to animals, plants and humans. According to Schneider (2014), in the recent two decades, the pollutants, coming from a variety of industrial activities, are contaminating surface and ground water to an unacceptable level all over the world. The discharged water if not properly treated is contaminated with toxic organic and inorganic compounds (Chen et al., 2000) which are harmful to the environment.

Examples of inorganic compounds are heavy metal ions. Heavy metals are elements with an atomic density greater than 6 g/cm^3. They are one of the most persistent pollutants in wastewater. Among the various manufacturing sectors that contribute to the high concentrations of heavy metal ions in their wastewater are metal finishing processes including steel polishing, chrome plating and etching. Textile industries also contribute to heavy metal such as cadmium (Cd), lead (Pb), chromium (Cr) and copper (Cu) pollutions as many dyes and pigments washed away in the waste water containing heavy metal ions (Pang and Abdullah, 2013). Indeed, there have been many studies evaluating the distribution of heavy metals such as zinc (Zn) (Mokhtar et al., 2015), nickel (Ni) (Sakai et al., 2017), iron (Fe) (Khodami et al., 2017), arsenic (As) (Looi et al., 2013), mercury (Hg) (Looi et al., 2015), cadmium (Cd) (Khodami et al., 2017) and chromium (Cr) (Praveena and Lin, 2015) in the water near to industrial areas. All of these works reach a consensus that the problem of heavy metal pollution,

despite can be controlled, must be acknowledged as to reduce the amount of such pollutants in the water.

In Malaysia, 51 rivers (11%) are reported to be polluted based on the Department of Environment Malaysia (DOE), Malaysia report in 2017. Among the pollutants reported are As, Fe, Manganese (Mn) and Ni (Affandi and Ishak, 2018). The presence of these metals or metalloids in water can induce perturbation of ecological and geological equilibrium because they have generally infinite lifetimes (Litter, 2015). There is therefore an urgent need to ensure manufacturers and waste generating industries are compliant with the environmental acts as to ensure zero contamination and there should also be better control of pollution from wastewater in the country.

Hexavalent Cr or Cr(VI) is a heavily toxic, mutagenic and carcinogenic metal to most of the living organisms (Suksabye et al., 2009) when its concentration level is higher than 0.05 ppm. Cr(VI) is also corrosive and extremely mobile than Cr(III) (Ku and Jung, 2001). However, Cr(VI) compounds have been widely utilized in various industrial processes especially steel and plating industries for centuries. Cr(VI) has also been used as pigments, dyes (Halimoon and Yin, 2010), chemical manufacture, leather tannery (Chen et al., 2012), metal plating (Cavaco et al., 2007), and fertilizer manufacturer (Bankole et al., 2014). These manufacturers can also be responsible in high level of Cr(VI) pollution in river water. Unless properly treated, Cr(VI) can be easily discharged to the environment.

There have been reports recently on the amount of Cr in Malaysia. For example, Praveena and Lin (2015) reported that the levels of Cr in some of the fish in Port Dickson such as Selaroides spp (2.34 mg/kg) and Sardinella spp (1.42 mg/kg) had exceeded the limit (1 mg/kg) enforced by the Malaysian Food Regulations (1985). Another researcher also found high concentration of Cr (4.205 mg/kg) in red snapper

fish in Pulau Ketam near Port Klang, Selangor. Apart from red snapper, Cr has also been detected in many other types of fish (Widad and Abdullah, 2013, Poon et al., 2016). Existence of Cr in seafood must be taken as serious issue due to the danger of accumulation in the food chain. Upon consumption, Cr(VI) can retain in human body, in which it accumulates throughout life. Excessive exposure of Cr(VI) can result in acute irritant to human leading to allergen. Not only that, when Cr(VI) is digested for instance by consuming water or seafood contaminated by Cr(VI), it can cause diarrhoea, internal haemorrhage or kidney damage. Hence, assessment on the amount of Cr(VI) released from the industrial establishment as well as method of removal of Cr(VI) from wastewater is very much needed. In this work, a process to remove Cr(VI) from stimulated wastewater is proposed via photocatalytic reduction.

1.1.1 Chromium

Chromium has five oxidation states. Oxidation state of +3 is considered essential for good health in moderate intake, however, chromium in oxidation state of +6 (Cr(VI)) is considered harmful even in small intake quantity (Guertin et al., 2016). Cr(VI) is the second most stable oxidation state of chromium and has been categorised as Group 1 materials which is human carcinogen by International Agency for Research on Cancer (IARC), France by inhalation. On the other hand, consuming excessive amount of Cr(VI) can cause severe health problems such as damage of liver and kidney as well as the central nerve system (Sharma, 2014).

According to World Health Organization (WHO) International Standards for Drinking water, the maximum allowable concentration of Cr(VI) is 0.05 mg/L (Organization, 2011). In the United States, the Environmental Protection Agency

(EPA) under the authority of the Safe Drinking Water Act (SDWA) has set the maximum contaminant level of Cr(VI) at 0.10 mg/L while in Malaysia, parameter limits of effluent of Cr(VI) is 0.005 mg/L based on Environmental Quality Act, 1974 and the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, 1999, 2000. Chromium (III) is an essential element in humans, with a daily intake of 50 to 200 μg/d recommended for adults. Ensuring water free from Cr(VI) contamination is crucial.

There are many methods that can be used to remove Cr(VI) from wastewater such as biological method, ion exchange (Rengaraj et al., 2003), bioremediation , membrane separation (Modrzejewska and Kaminski, 1999), adsorption (Rao et al., 2002), biosorption (Ziagova et al., 2007), chemical precipitation (Chen et al., 2007), ozonation chemical reduction and photocatalytic reduction (Athanasekou et al., 2017, Chen et al., 2017, Cheng et al., 2015, Li et al., 2017). However, apart from photocatalytic reduction, many of them suffer from limitations such as generating sludge, not fully precipitating, high operational cost and zero removal is almost impossible (Güell et al., 2008, Litter, 2015). Photocatalysts reduction can be adopted for Cr(VI) removal whereby Cr(VI) is reduced to Cr(III) in the presence of photocatalysts under light illumination. Photocatalysis is a one-step removal process, therefore it also has the advantage to be more practical and cleaner than chemical reduction, hence, it is a preferred method to transform Cr(VI) to Cr(III).

1.1.2 Reduction of Cr(VI) to Cr(III) by photocatalysis process

Photocatalysis is a process that uses photons from the UV-near visible region (Barakat, 2011) to illuminate a solid catalyst as to generate free electrons within the material (Kisch and Hennig, 1983, Serpone and Pelizzetti, 1989). A photocatalyst is

often oxide semiconductor. When the semiconductor (SC) is irradiated by photon with energy higher than its band gap energy which is illustrated in Figure 1.1, the electron-hole pairs are formed on the surface of the SC. The excitation process occurs when electrons in the valence band of the SC absorbed the photon energy and make a transition to the conduction band leaving behind holes. Photogenerated electrons can be used for reduction processes whereas photogenerated holes can be used for oxidation to happen. As for Cr(VI) reduction, holes can lead to the transformation of H_2O to oxygen and Cr(VI) to Cr(III) reduction can be done by the electrons (Litter, 2015).

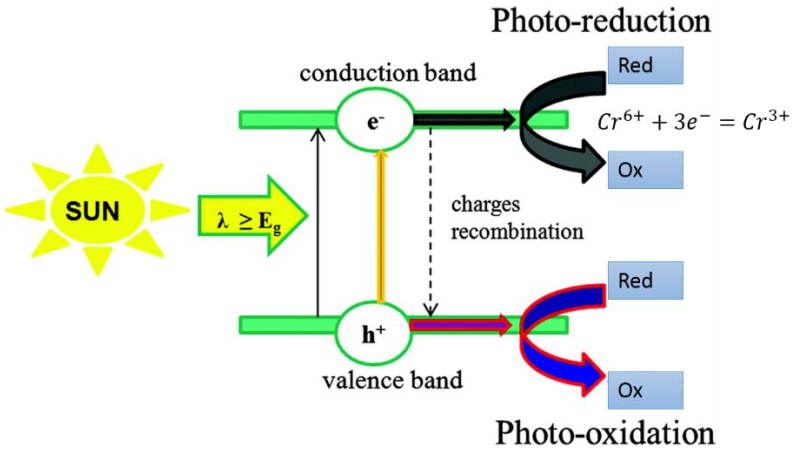

Figure 1.1 Photo-activation of a semiconductor and primary reactions occurring on its surface (Colmenares and Luque, 2014).

1.1.3 Photocatalyst materials for reduction of Cr(VI)

A desired photocatalyst must possess high photocatalytic efficiency, high activity, ability to utilize visible and/or near UV light, photostable (durable), reusable, insoluble under most condition, non-toxic, chemically and biologically inert, low density, good biocompatibility and cheap. There are many SC photocatalyst such as NiO (Hashemzadeh et al., 2015), Cu_2O (Qin et al., 2015), ZnO (Cheng et al., 2015) , ZrO_2

(Rozana et al., 2017) , Fe_2O_3 (Xu et al., 2012), WO_3 (Ou et al., 2013) and TiO_2 (Trejo-Valdez et al., 2019, Rahmat et al., 2018) that can be used for Cr(VI) reduction. Of all different SC photocatalysts reported in literature, TiO_2 appears to be the most extensively used for photocatalysis processes (Barbeni et al., 1985, Chen and Ray, 1998, Herrmann et al., 1983, Chen and Ray, 2001).

To achieve the photoreduction of Cr(VI), the photogenerated electrons at the CB of the TiO_2 SC must be more be more negative than the reduction potential of Cr(VI) (~0.36 eV at pH 7). Since the electrons energy in the conduction band of the SC is ~ -0.42 eV hence the oxide is therefore possible to reduce Cr(VI) to Cr(III). Moreover, the position of CB and VB is influenced by the pH. Higher pH of electrolyte solution will shift the VB and CB towards more cathodic potentials by 59 mV/pH. The reduction potential of Cr(VI) becomes more negative at higher pH than the photogenerated electrons. This leads to the photocatalytic reduction of the Cr(VI) is favoured at a lower pH. Although the driving force of the Cr(VI) reduction decreases with increasing their concentration, it can be reduced photocatalytically to down to 10^{-12} M. According to Chen et al. (2001), since the potential of Cr(III) is more negative than that Cr(VI), it cannot be reduced photocatalytically to lower Cr of lower oxidation states and hence the reduction of Cr(VI) to Cr(III) stops after the Cr(IV) ions have all been transformed to Cr(III). Cr(III) can be precipitated out from the solution by hydroxide treatment.

As mentioned above, TiO_2 is the most preferred photocatalyst for Cr(VI) removal in environment. Nanostructured TiO_2 especially in a form of 1-dimensional nanotubes (NTs) and nanowires (NWs) can be fabricated as an effective photocatalyst to reduce Cr(VI) to Cr(III). NTs and NWs have unique and improved properties compared to bulk TiO_2 due to their high surface area which render them to have higher

surface energy. NTs or NWs with high aspect ratio can facilitate rapid diffusion of free electron to the surface of the photocatalyst for efficient electron transfer process. There are many methods that can be used to produce TiO_2 nanotubes (TNTs) and NWs. In this work, oxidation processes; thermal and anodic were chosen as the methods to produce NWs and NTs respectively.

1.1.4 Anodic and thermal oxidation for TiO_2 Nanotubes and Nanowires Formation

Many approaches have been employed for the synthesis of TiO_2 with nanotubular structures such as anodic oxidation (Nyein et al., 2016), templating (Kang et al., 2009), sol-gel (Lee et al., 2010), hydrothermal (Suzuki and Yoshikawa, 2004) and photo-electrochemical etching (Macak et al., 2007, Kang et al., 2008). Of these, anodic oxidation is a widely used technique to fabricate TNTs with excellent ordering on a surface of titanium foil (Ghicov and Schmuki, 2009, Macak et al., 2007). Anodization is also preferred because it is a relatively simple (Minagar et al., 2012) and efficient process to fabricate well-aligned TNTs (Gong et al., 2001). Anodization can be conducted in an electrochemical bath with anode (titanium) and cathode (platinum) immersed in fluoride electrolyte. The existence of fluoride ions induces the formation of nanotubes.

On the other hand TiO_2 NW can be synthesized by subjecting titanium foil to high temperature in the presence of oxidising environment with suitable catalyst. The process is a simple, inexpensive and highly scalable process (Arafat et al., 2016).

However, these two methods may induce contamination from the processing route itself. Anodic oxidation for example requires fluoride ions and hence the insertion of the fluoride ions induce the formation of fluoride rich TiO_2 layer which is

not semiconducting. Thermal oxidation as mentioned requires the existence of catalyst like potassium compound, therefore the nanowires formed are often said to comprise of a thin layer of potassium-rich TiO_2 which can also influence the photocatalytic properties of the oxide. Therefore, despite the success in the formation of the desired nanostructures, the existence of the contamination may influence the properties of the oxide. Hence, in this work, fabrication of compact layer of TiO_2 using the same anodic and thermal oxidation were done as to compare oxide properties with the nanostructures produced from the process.

1.2 Problem Statement

There are many studies done evaluating the distribution of heavy metal in the coastal and river water in Malaysia. This includes areas in Port Dickson (Praveena and Lin, 2015), Ketam Island in Selangor (Sobihah et al., 2018), Simpang Empat River in Pulau Pinang (Widad and Abdullah, 2013) and Langat River estuary in Selangor (Mokhtar et al., 2015). As mentioned, the toxic Cr(VI) can enter water bodies by unregulated wastewater from electroplating, textile, leather tannering and fertilizer industry. Removal of Cr(VI) can be done by using TiO_2 as photocatalyst in the photocatalysis process.

However, there are very limited amount of work reported on the use of TiO_2 for Cr(VI) reduction. Majority of reported works are on the use of TiO_2 in Advanced Oxidation Process (AOP). AOP is a promising treatment that utilizes highly reactive hydroxyl radicals generated from photogenerated holes for achieving complete mineralization of the organic pollutants such as methylene orange (Taib et al., 2017) into carbon dioxide and water (Krishnan et al., 2017). Reduction on the other hand uses photogenerated electrons in the conduction band of the semiconductor. To date,

there are not many literatures on the use of photoelectrons in TiO_2 to perform reduction of pollutants.

Therefore, in this work, TiO_2 was selected as a photocatalyst semiconductor to reduce Cr(VI), however, to avoid from oxidation of Cr(III) back to Cr(VI), the Cr(VI) solution treated was added with EDTA as scavenger. The EDTA was used to scavenge oxygen (Liu et al., 2017, Tran et al., 2017) and hence oxidation process on TiO_2 will be much reduced. As mentioned, nanostructured TiO_2 such as NWs or NTs is hypothesised to have much better catalytic properties due to the high surface area and high volume ratio is has. There are many reports on the formation of TiO_2 NWs and NTs supported on titanium (Ti) substrate. For the NTs formation, anodic oxidation has been routinely done in fluoride containing electrolyte (Zwilling et al., 1999, Gong et al., 2001, Beranek et al., 2003). The role of the fluoride ions is obvious for the NTs formation. Nevertheless, the NTs contain fluoride contamination in its structure. According to Albu et al. (2008), EDX analysis revealed the presence of fluoride species all over the nanotubular layer which are along the nanotube and at the oxide|metal interface (Habazaki et al., 2007). The TNTs containing fluoride rich layer at the oxide|metal interface can be ascribed to the twice as fast migration rate of the fluoride ions in the high-field barrier oxide (tube bottom). The fluoride has been proved by XPS sputter profiles from the tube bottom sides (Albu et al., 2008). Water soluble $(TiF_6)^{2-}$ (Macak et al., 2008) and TiF_4 complexes are both stable compound that can be found on the walls of the nanotubes. The fluorine incorporation in the nanotubes is not in the TiO_2 lattice but forming compound with titanium. This contamination could affect the semiconducting properties of TiO_2.

On the other hand, one dimensional nanowires fabricated from thermal oxidation of titanium is often done in potassium containing environment. The role of

the potassium ions are obvious for the NWs formation. However, the NWs will have contamination of potassium compound (Lee, 2014). This can be explained by 5-8 % of potassium found in EDX analysis (Cheung et al., 2007). It is assumed that the significant contamination of these elements is due to the process formation itself. Therefore, the performance of those nanostructured TiO_2 as a photocatalyst during the photoreduction of Cr(VI) to Cr(III) may get affected. Nevertheless, there is no work devotes to study on the effect of the contamination from the fabrication process to the properties of the TiO_2.

Therefore, in this work, thin and compact layer of titanium dioxide was formed by using the same methods to produce the nanotubes and nanowires; anodic and thermal oxidation respectively. The synthesized compact TiO_2 films were expected to be free from any significant contamination as no NH_4F or KOH was involved in the fabrication process. To the best of knowledge, there is limited amount of publications regarding comparison of photoreduction performance (Cr(VI) to Cr(III)) between TiO_2 nanostructures (NTs and NWs) with compact oxide of TiO_2, fabricated both by anodic and thermal oxidation.

1.3 Research Objectives

1. To synthesize compact and NTs and NWs of TiO_2 by using anodic and thermal oxidation methods, respectively.
2. To evaluate the Cr(VI) reduction on TiO_2 NTs and NWs by comparing with compact films fabricated by the similar processes.

1.4 Research Scope

This thesis describes the research study on the formation of bulk and nanostructures (NTs and NWs) of TiO_2 by using anodic and thermal oxidation. The

oxidation parameters include presence of NH_4F as etchant, oxidation voltage, presence of KOH catalyst and oxidation temperature. The samples were characterized by Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction Spectroscopy (XRD), Raman Spectroscopy, Fourier Transform Infrared (FTIR) spectrometer and Transmission Electron Microscopy (TEM). The samples also were used as photocatalyst for Cr(VI) removal in simulated Cr(VI) solution. The photoactive materials performance were studied via Ultraviolet-Visible (UV-Vis) spectrophotometer.

1.5 Thesis Outline

This thesis consists of five chapters. Chapter 1 explains the background of this research study, problem statements, objectives, research scope and thesis outline. Chapter 2 provides the fundamental knowledge of Ti as a metal, TiO_2 as a semiconductor material, its properties, crystal structures and importance in applications. The literature review continues with the mechanism of bulk and nanostructures (NTs and NWs) of TiO_2 formation. In chapter 3, all the materials, chemicals, experimental work procedures and characterization techniques are explained in detail. Chapter 4 contains results and data of the project. The results are analyzed and discussed further. Different microstructures of the compact oxide layer, NTs and NWs of TiO_2, phases formation, crystallinity and transformation as well as its photocatalytic performance were presented. Lastly, chapter 5 concludes this research study and give suggestions and recommendation for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter consists of theories and previous research findings that can be divided into four main parts. Firstly, it is about the main material involved in this project which is TiO_2. Its originality, properties, phases and crystal structures are described in details. Secondly, fundamental of nanomaterials, TiO_2 nanostructures as well as the properties and application are reviewed. The third part reveals two types of synthesis methods which are anodic and thermal oxidation that were used to fabricate the TiO_2. Two parameters from each method are elaborated further with the mechanism of each of the material formation. The final part reviews on materials used to reduce Cr(VI) to Cr(III) as well as on the summary of proposed for Cr(VI) reduction by photocatalysts.

2.2 Titanium

Titanium (Ti) is a very popular metal in metallurgy world which it is known to have an outstanding properties such as high specific strength and excellent corrosion resistant. It was first found by a chemist named William Gregor in 1791. He found it in the form of black sand or also known as ilmenite in Menaccan Valley, Cornwall, England. It is actually titanium iron oxide, $FeTiO_3$. He examined the sand and later named it as manaccanite in regard of the place name. Following that, in Germany, a chemist, Martin Heinrich Klaproth also found a compound containing Ti which is ore rutile, TiO_2. Rutile is a common phase of Ti found on the earth. Among all the top titanium producing countries for instance Canada, Norway, China, Japan and United

States of America, Malaysia is also considered as one of the Ti metal producer in the world (Clark et al., 2018, Leyens and Peters, 2003).

There are many ways to classify an element from periodic table. Ti can be categorized as a metallic, non-ferrous transitional, valve and light metal. The separation between light and heavy metal is 5 g cm^{-3}. Ti has density of 4.51 g cm^{-3}. There are two main crystal structures available for Ti which are hexagonal close-packed (HCP) and body face centered (BCC). Ti has these two crystal structures based on what temperature it experiences. At low temperature, Ti has hexagonal closed packed (HCP) crystal structure or commonly known as α. Meanwhile, at temperature higher than 882℃, Ti has body centered cubic (BCC) structure or known as β. The phase transformation from α to β crystal structure is called as an allotropic transformation. The illustrations of both crystal structures can be seen in Figure 2.1. Table 2.1 depicts comparison between Ti and other metals in terms of their characteristics and properties.

Table 2.1 Characteristics of Ti when compared to other metals (Lütjering and Williams, 2007)

	Ti	**Fe**	**Ni**	**Al**
Melting Temperature (℃)	1670	1538	1455	660
Allotropic Transformation (℃)	882 (β to α)	912 (γ to α)	-	-
Crystal Structure	BCC to HCP	FCC to BCC	FCC	FCC
Room Temperature E (GPa)	115	215	200	72
Yield Stress Level (MPa)	1000	1000	1000	500
Density (g/cm^3)	4.5	7.9	8.9	2.7

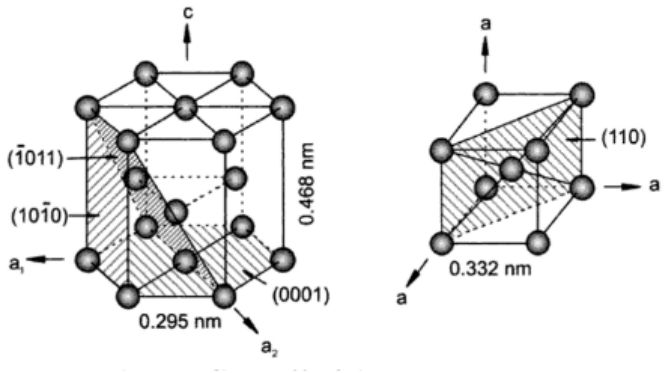

Figure 2.1 Crystal structure of HCP and BCC phase (Layens and Peters, 2003).

In the metallic group, Ti is the fourth most abundant metal found on the earth after aluminium (Al), iron (Fe) and silicon (Si). Meanwhile, Ti is the ninth most abundant element in the earth's crust. Despite the huge amount of the metal, Ti is sold at a very high price. It is heavily used in many fields such as aerospace and biomedical applications.

2.3 **Titanium dioxide**

Titanium dioxide has many importance in many technical field such as in civil as nano-paint (self-cleaning), antibacterial agents, catalysis and photocatalysis. With that, it can be seen that the number of publications on TiO_2 has been increasing gradually from 1975 and reach a steep gradient at early 2000 (Diebold, 2003). The innovation on TiO_2 research has been revolutionizing year by year. From bulk structure, to miniaturization and now surface manipulation of the TiO_2. This is because of its excellent properties such as low density, excellent biocompatibility and chemical stability. There are quite a number of its application in many technical field for instance (Diebold, 2003),

- As a photocatalyst in heterogeneous catalysis
- To produce hydrogen and electric energy in solar cells

- As a gas sensor to control air/fuel mixture in car engines
- As white pigment in paints and cosmetic products as it has high refractive index
- As a protective coating against environmental damage
- As a self-cleaning coating on car windshields
- As an optical coating in ceramics and in electric devices
- In the biocompatibility of bone implants
- In Li-based batteries and electrochromic devices in nanostructured form

TiO_2 has many different phases. It can be seen in Table 2.2.

Table 2.2 Different phases of TiO_2 (Hanaor and Sorrell, 2011).

Phases of TiO_2
Rutile
Anatase
Brookite
TiO_2 II or srilankite, an orthorhombic polymorphs of the lead oxide structure
Cubic fluorite-type polymorph
Pyrite-type polymorph
Monoclinic baddeleyite-type polymorph

Rutile, anatase and brookite are the only naturally occurring oxide of titanium at atmospheric pressure. Rutile is a stable phase while the other two are metastable. Rutile phase have been investigated extensively. Meanwhile, surface science research on the technologically quite important anatase phase is just starting (Diebold, 2003). And last one is brookite. The last five phases are of high-pressure phases of TiO_2. They have minor significance for research and development application due to their phase stability issue (Hanaor and Sorrell, 2011). Figure 2.2 shows the crystal structures of anatase, rutile and brookite.

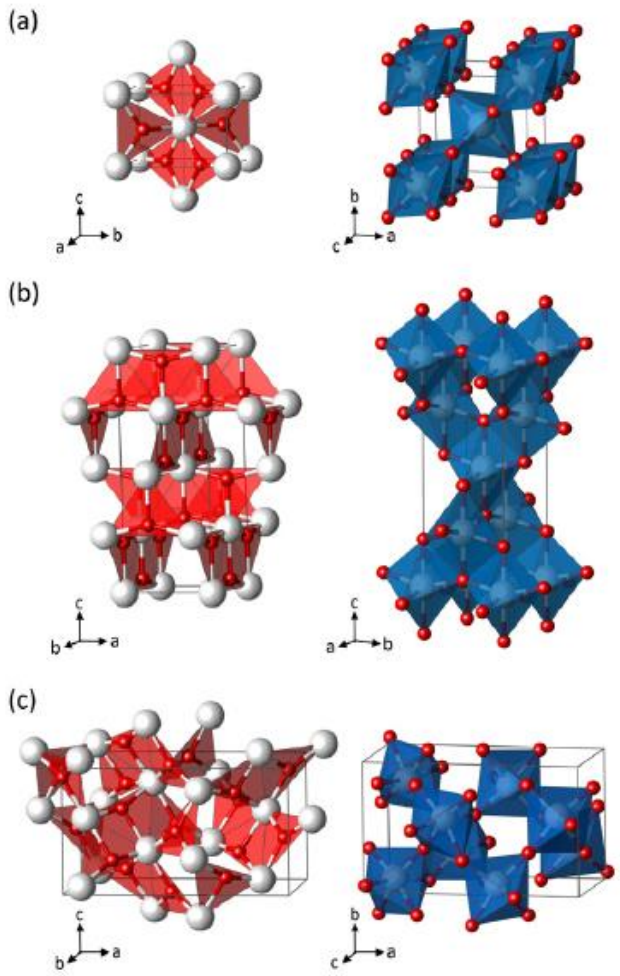

Figure 2.2 Planar Ti_3O building-block representation (left) and Ti_6O polyhedral (right) for the TiO_2 phases rutile (a), anatase (b) and brookite (c) (Ti (white); O (red)) (Landmann et al., 2012).

Table 2.3 Bulk properties of titanium dioxide with its crystal structures (Diebold, 2003).

Properties		**Crystal structure**			**Reference**
		Anatase	**Rutile**	**Brookite**	
Atomic radius (nm)					
O	0.066 (covalent)				
Ti	0.146 (metallic)				
Ionic radius (nm)					
O (-2)	0.14				
Ti (+4)	0.064				
System		Tetragonal	Tetragonal	Rhombohedral	(Diebold, 2003)
	a	0.3733	0.4584	0.5436	(Diebold, 2003)
	b	-	-	0.9166	

Lattice constants (nm)	c	0.937	0.2953	0.5135	
	c/a	2.51	0.644	0.944	
Atom per unit cell (Z)		4	2		(Paufler, 1988, Burdett et al., 1987)
Unit cell volume (nm^3)		0.1363	0.0624		
Density (kg/m^3)		3830	4240	4170	(Diebold, 2003)
Electrical resistance (Ω m)	773 K	-	3×10^5	-	(Diebold, 2003)
	1073 K	-	1.2×10^2	-	
	1473 K	-	8.5×10^2	-	
Electron mobility (µm)		~ 10	~ 1	-	(Diebold, 2003)
Calculated indirect bandgap					(Beltrán et al., 2006, Madhusudan Reddy et al., 2003, Serpone, 2006)
(eV)		3.23-3.59	3.02-3.24		
(nm)		345.4-383.9	382.7-410.1		
Experimental bandgap					(Beltrán et al., 2006, Mardare et al., 2000)
(eV)		~ 3.2	~ 3.0		
(nm)		~ 387	~ 413		
Refractive index	n_g	2.488	2.908	2.7004	(Diebold, 2003)
	n_m	-	-	2.5843	
	n_p	2.561	2.621	2.5831	
Solubility in water		Insoluble	Insoluble		(Fisher and Egerton, 2001)

2.3.1 Rutile

According to many thermodynamics studies, rutile is considered to be more stable than anatase at all temperatures and pressures. In order for anatase to be more stable, negative pressures are needed.

2.3.2 Anatase

As mentioned, TiO_2 can be fabricated by many methods and usually it will first crystallize in anatase form (Okada et al., 2001, Shin et al., 2005). This could be of two reasons. First, structurally, anatase has less-constrained molecular construction compared to rutile. Therefore, it is easier for the short-range ordered TiO_6 octahedra to arrange themselves into a long-range ordered of anatase structure (Matthews, 1976). Secondly, in a thermodynamic angle, it is known that anatase has lower surface free energy compared to rutile. Hence, it can be said that the more rapid recrystallization of anatase is due to that factor although it has higher Gibbs free energy compared to rutile.

2.3.3 Semiconductor materials

Titanium dioxide (TiO_2) is a semiconductor material that has been studied extensively in the last few decades due to its chemical stability, nontoxicity and high photocatalytic activity (Mahajan et al., 2008). Depending on the crystal phases, TiO_2 has energy band gap ranging from 3.02 eV to 3.59 eV.

2.4 Nanostructure of TiO_2

2.4.1 Nanomaterials

According to International Organization for Standardization (2015), any material with any external dimension, internal structure or surface structure in the nanoscale is considered as nanomaterial. Following that, nanoscale can be defined as

length range approximately from 1 nm to 100 nm. Nanomaterials can be classified into four main classes: zero, one, two and three dimensional nanomaterials. In this work, one dimensional (1D) of TiO_2 was fabricated and investigated. Examples of 1D nanomaterials are nanowires, nanorods and nanotubes. These materials have at least one dimension in nanoscale. A bulk material is significantly different than a material in nanoscale (nanomaterial) even thought has the same chemical composition. This is mainly due to the dimensional confinement which lead to having high surface area to volume ratio. For example bulk Pt is an inert material. It remains unaffected with any single mineral acid. However, in nanoscale, Pt is very reactive that it can act as a catalyst in a catalytic activity (Bai et al., 2016). The higher surface area to volume ratio of a material, the higher reactive it gets towards its environment. Similarly, TiO_2 in nanoscale can have properties which are markedly different than bulk material.

Nanomaterial fabrication can be divided into two categories which are bottom up and top down approach. Bottom up approach can be defined as building up of any dimensional category of nanomaterial from the bottom. It can be atom by atom, molecule by molecule or cluster by cluster. For example, sol-gel, templated, and salt reduction. Meanwhile, top down approach can be defined by slicing or successive cutting of a bulk material to get nano-sized particle. For instance, milling, etching and lithography methods. As mentioned, anodic and thermal oxidation method were used in this work.

2.4.2 Nanostructure of TiO_2

A good photocatalyst must have a high surface area for more catalytic sites. Nanoparticles are zero dimensional nanomaterials which have higher surface area compared to NTs and NWs which is 1D nanomaterials. However, many literatures

stated that 1D TiO_2 has better photocatalytic reaction compared to nanoparticles. Figure 2.3 shows comparison of electron pathways through nanoparticles NTs and NWs. Although TiO_2 NPs have higher surface area compared to NTs and NWs, they have shorter diffusion length of the electron, hence increasing recombination of the electrons (Javed et al., 2014). Moreover, 1D geometrical structure of TNTs facilitates rapid diffusion-free electron transport along the longest direction and reduce interface charge recombination greatly. Nevertheless, the characteristic of a material is always associated with the fabrication processes. The challenge remains which is to investigate the exact properties of the 1D TiO_2 derived by processes which allows for perfect its formation and to compare with bulk material.

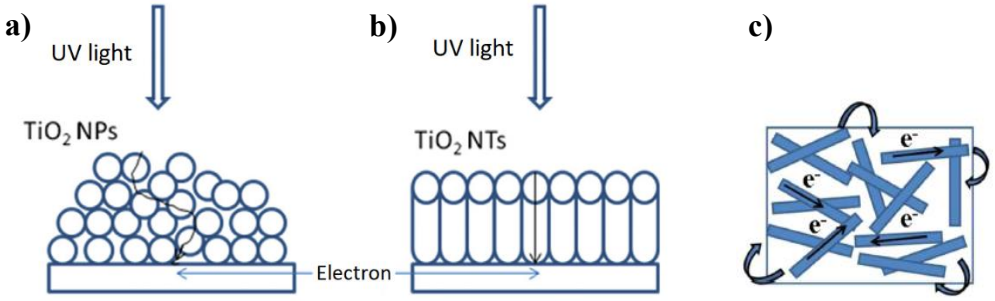

Figure 2.3 Comparison of electron pathways through TiO_2 nanoparticles (NPs), nanotubes (NTs) and nanorods (NRs). (a-b) (Javed et al., 2014) (c) (Sengupta et al., 2016)

2.5 Synthesis of titanium dioxide

There are many fabrication techniques that can be used to produce TiO_2 in the form of 1D nanotubes or nanowires depending on what is desired for the end application. As for photocatalyst, supported oxide NTs on a metal substrate is preferred as it will be easier to remove the catalyst after use. Several methods have been identified to grow oxide on metal substrate. One relatively straight forward process is by oxidizing the metal substrate either by polarizing it in an electrochemical bath or by heating it up at

high temperature in an oxidizing environment. Both processes will result in the formation of thin oxide film of the parent metal. Oxidising titanium results in the formation of TiO_2 film.

2.5.1 Electrochemical anodic oxidation method

Anodization is an electrochemical process conducted on a metal to produce a layer of metal oxide on the metals surface. The anodization process is performed in an electrochemical cell consisting of two electrodes, the working electrode or the anode and the counter electrode or the cathode. The metal is employed as an anode and oxidation process starts on the anode when external voltage is applied between anode and cathode electrodes in an electrolyte (Abedinisohi, 2013). Electrochemical anodic oxidation or so called anodization is a well-established method to produce metal oxide (Sibert, 1963). This method has been used to grow a thick and uniform oxide layer on metals for a decade or so (Minagar et al., 2012). Anodic oxidation is a widely used technique to fabricate TiO_2 film comprising of self-ordered nanotubular structure, because it is a relatively simple and efficient process to fabricate well-aligned and highly ordered NTs. Figure 2.4 is a schematic drawing of an electrochemical anodization cell. Often, Pt is used as the cathode while Ti is used as the anode Moreover, anodization can produce TiO_2 nanotube layer which grows normal to the surface with regular diameter, in contrast with other techniques such as solvothermal and hydrothermal methods, in which nanotubes are obtained in a free form but have a lower degree of organization (Dumitriu et al., 2015, Ng et al., 2010).

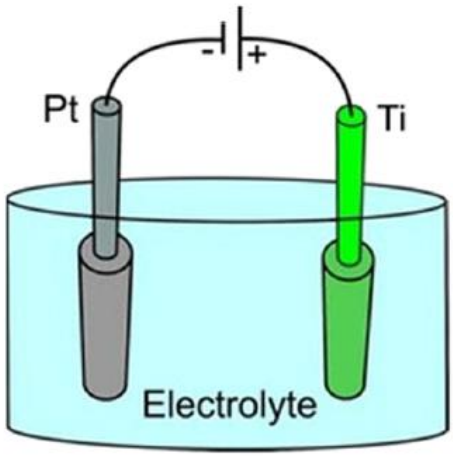

Figure 2.4 Schematic drawing for Titanium anodization cell (Galstyan et al., 2013).

2.5.1(a) Mechanism of compact and dense TiO_2 formation

The formation of oxide by electrochemical process is a well-documented topic. At the beginning of the anodization where the voltage is applied, polarization happen at the Ti metal foil surface (Equation 2.1). Then in the presence of oxidants, oxide will form (Equation 2.2 – 2.3). Anodic oxidation can be represented by Equation 2.4 (Brunette et al., 2012).

$$Ti \Leftrightarrow Ti^{4+} + 4e^{-} \qquad \text{Equation 2.1}$$

$$2H_2O \Leftrightarrow 2O^{2-} + 4H^{+} \qquad \text{Equation 2.2}$$

$$Ti^{2+} + 2O^{2-} \Leftrightarrow TiO_2 \qquad \text{Equation 2.3}$$

$$Ti + 2H_2O \Leftrightarrow TiO_2 + 4H^{+} + 4e \qquad \text{Equation 2.4}$$

When the anodic electrolyte is comprised of only oxidant, the resulting film is often compact. TiO_2 has low conductivity compared with the electrolyte and the metal substrate, therefore the ions and charge transfer from the electrolyte to the metal surface, and vice versa, are controlled by the applied voltage.

With the absence of fluoride ions in the electrolyte, a layer of metal oxide will be formed according to the Equation 2.3 and 2.4, where the oxygen ions required for the oxidation process are supplied by water molecules within the electrolyte. As the oxide layer has a low conductivity, it works as an insulator, which hinders the transport of oxygen and titanium ions, the continued growth of the oxide layer has controlled by field aid. As there is no fluoride source in the electrolyte, no chemical dissolution occur for further pore growth. Figure 2.5 is a schematic drawing for the anodization of titanium in an electrolyte free from fluoride (Taveira et al., 2005).

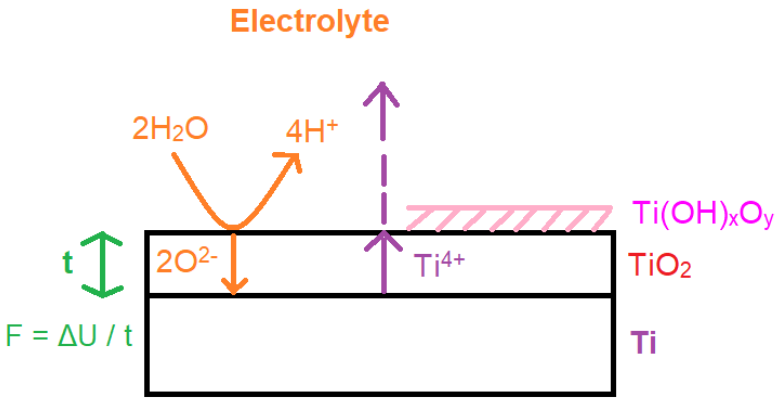

Figure 2.5 Schematic drawing for anodization of titanium in an electrolyte free from fluoride ions (Macak et al., 2007)

2.5.1(b) Mechanism of nanotubes TiO_2 formation

Nevertheless, when fluoride ions are added in the electrolyte, the oxide formation is accompanied by chemical dissolution processes. In fluoride electrolyte, three consecutive steps for nanotubes formation are (Awad et al., 2017, Keller et al., 1953, Khudhair et al., 2016):

- Initial stage: polarisation of Ti, where dissolution of Ti and the formation of the Ti ions that dissolve in the solution can happen
- Intermediate stage: the interaction of Ti^{4+} with oxygen ions supplied by the water molecules in the electrolyte to form TiO_2 on titanium surface

- Steady state: chemical dissolution of the oxide forming porous TiO_2 which then followed by steady state competition between oxide formation and oxide dissolution reactions for nanotubes formation

The oxide grows as a result of the movement of ions under the action of an applied electric field. As the oxide film grows thicker and its overall electrical resistance increases, it acts as a barrier to the flow of ions and electrons. The oxide that is formed is generally a barrier type film. The anodizing ratio, defined as the maximum oxide thickness obtainable per unit volt, is in the range 1–3 nm/V. The presence of a pore free barrier layer limits the final thickness of the oxide to within a few hundred nanometers.

TNTs can be formed by using certain kinds of electrolytes. Self-organized TiO_2 layers can be formed using fluoride containing electrolyte. Meanwhile, bundles of TNTs (i.e. not self-organized) can be formed by using perchlorate, chloride, bromide or sulphuric acid containing electrolytes.

This typical current density (mA/cm^2) against time (s) graph as in Figure 2.6 can be obtained during anodization process. It can be seen that there are three significant stages in the process. The first stage, from a – b, polarization occur due to coulombic attraction between positive charge and negative charge. The positive charge comes from the metal which is Ti^{4+}. Meanwhile, negative charge comes from the electrolyte which are O^{2-} and OH^-. In addition, F^- also involve for fluoride-containing electrolyte. After that, an oxide barrier layer of TiO_2 starts to form. Therefore, it can be seen in the first stage, current decreases. Oxidation process continue to occur forming a very high resistance oxide barrier layer (Regonini et al., 2013).