SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
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FORMATION OF TITANIA NANOTUBES AND ITS APPLICATION IN REDUCING Cr(VI)

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DECLARATION

I hereby declare that I have conducted, completed the research work, and written the dissertation entitled **"Formation of Titania Nanotubes and Its Application in Reducing Cr(VI)"**. I also declared that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any examining body or University.

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PEMBENTUKAN NANOTIUB TITANIA DAN APLIKASI BAGI MENURUNKAN Cr(VI)

ABSTRAK

Cr(VI) adalah logam berat toksik yang telah diklasifikasikan sebagai karsinogen kepada manusia. Sumber-sumber industri Cr(VI) termasuk aloi dan pembuatan keluli, kemasan logam, dan penyamakan kulit. Kajian ini mengkaji keupayaan TiO_2 nanotiub (TNTs) untuk penyingkiran Cr(VI) daripada larutan akueus. TNTs telah disintesis oleh teknik penganodan dalam tiga elektrolit yang berbeza iaitu, Etilina Glikol/NH_4F, Gliserol/NH_4F, dan Na_2SO_4/NH_4F pada waktu dan voltan yang dioptimumkan. Pembentukan TNTs kemudiannya dicirikan oleh FESEM, XRD, TEM, dan FTIR. Dua parameter utama telah dikaji yang merupakan kesan masa penganodan dan kesan voltan penganodan kepada pembentukan TNTs yang mempunyai panjang yang sama tetapi dengan diameter yang berbeza dalam elektrolit yang berbeza. Sampel optimum ditakrifkan oleh, TNTs dengan panjang $\sim 2 \pm 0.5\ \mu m$ telah dibentuk oleh penganodan dalam Etilina Glikol/NH_4F pada 60V dalam masa 30 minit, Gliserol/NH_4F pada 40V dalam masa 12 jam, dan Na_2SO_4/NH_4F pada 20V dalam masa 90 minit. Sampel kemudian dianil pada 400^oC selama tiga jam di udara untuk membentuk struktur kristal daripada TNTs dan di dalam gas N_2 untuk mendapatkan TNTs didopkan nitrogen. Sampel anil menjalani pencirian XRD dan FTIR untuk mengesahkan penghabluran TNTs yang terbentuk. Kemudian, sampel optimum yang dianil di udara dan gas N_2 bersama-sama dengan sampel dianodkan telah diuji untuk keupayaan photocatalytic mereka di bawah cahaya matahari dan cahaya UV selama dua jam. Keputusan photocatalytic diperolehi oleh spektroskopi UV-Vis dan data C_t/C_o melawan masa telah diplot.

FORMATION OF TITANIA NANOTUBES AND ITS APPLICATION IN REDUCING CR(VI)

ABSTRACT

Cr(VI) is a toxic heavy metal which has been classified as carcinogenic to humans. The industrial sources of Cr(VI) include alloy and steel manufacturing, metal finishing, and leather tanning. This study investigated the applicability of TiO_2 nanotubes (TNTs) for the removal of Cr(VI) from aqueous solution. The TNTs were synthesized by anodization technique in three different electrolytes which are Ethylene Glycol/NH_4F, Glycerol/NH_4F, and Na_2SO_4/NH_4F at optimized times and voltages. The TNTs formation were then characterized by Field Emission Scanning Electron Microscope (FESEM), X-Ray Diffraction (XRD), Transmission Electron Microscope (TEM), and Fourier Transform Infrared (FTIR). Two main parameters were investigated which were the effects of anodization time and the effect of anodization voltage to the formation of TNTs with similar length but with different diameter in different electrolytes. The optimum sample defined by TNTs with length ~ 2 ± 0.5 μm were formed by anodization in Ethylene Glycol/NH_4F for 60V in 30 minutes, Glycerol/NH_4F for 40V in 12 hours, and Na_2SO_4/NH_4F for 20V in 90 minutes. The samples were then being annealed at 400^{o}C for three hours in air to form crystalline structure of the TNTs and in N_2 gas to get the N-doped TNTs. The annealed samples undergo XRD and FTIR characterization to confirm the crystallinity of TNTs formed. Then, the optimized samples that were annealed in air and N_2 gas along with as anodized samples were tested for their photocatalytic ability under sunlight and UV light for two hours. The photocatalytic results were obtained by UV-VIS spectroscopy and the data of C_t/C_o versus time were plotted.

CHAPTER 1

INTRODUCTION

1.1 Nanotechnology

Science and engineering that is involved in the design, synthesis, characterization, and application of materials which is at least one dimensional and on the nanometer scale are defined as nanotechnology (Silva et al., 2004). Nanotechnology encompasses the synthesis routes and applications of materials, structures, systems and devices that have unique and novel properties due to their size. Other than that, nanotechnology also includes technologies that allow nanoscale materials to be viewed. For example, Field Emission Scanning Electron Microscopes and Transmission Electron Microscopes allowed the surface topography, morphology, and composition of nanoscale's solid materials to be viewed and discovered. The equipment produces clearer and less electrostatically distorted images with spatial resolution down to $1^{1/2}$ nm that allows the nanoscales to be seen clearly.

The origin of the term 'nanotechnology' can be traced back to a speech given by Richard Feynman at California Institute of Technology in December 1959 called "There's Plenty of Room at the Bottom" (Allhoff et al., 2009). He talked about the principles of miniaturization and atomic-level precision and how the concepts do not violate the law of physics. The word "nanotechnology" was introduced by N. Taniguchi in 1974 at the international conference on industrial production in Tokyo. He used the word to describe the superthin processing of materials with nanometer accuracy and creation of nano-sized mechanisms. In the late 1980s to early 1990s more research on nanotechnology was done and the revolution in nanotechnology begins with the discovery of one-dimensional (1D) nanostructure in the form of carbon nanotubes by Iijima. The unique properties offered by materials in nanoscale together with many possible applications have encouraged more research and development in the field of nanotechnology. The formation of oxide materials with 1-D nanotubular shape started off in early 1990s but started to become more prominent when anodisation process was reported to enable the formation of TiO_2 nanotubes. Early works, Hoye, the first person who used an electrochemical deposition method into an ordered alumina template to produce titania nanotubes. Followed by sol–gel techniques, and hydro/solvothermal methods with or without templates and atomic layer deposition (ALD) into the template (Macak, 2007).

Zwilling and co-workers in 1999 claimed to be the first person produced self-organized anodic oxides on titanium by anodization in chromic acid electrolytes containing hydrofluoric acid. This work showed that organized nanotube layers of up to about 500 nm in thickness. The tube structure was not highly organized and the tubes showed considerable sidewall inhomogeneity. In 1979, (Kelly et al.) explored the influence of fluorides on the passivity of titanium and concluded that porous oxide layers formed for low fluoride concentrations, but they did not perform electron microscopy at a sufficiently high resolution to resolve the presence of self-organized TiO_2 nanotube layers. After 1999, several approaches that used acidic fluoride-containing electrolytes essentially confirmed Zwillings findings. This early work established that the as-formed material is amorphous but may contain some crystallites. Most crucial improvements to the geometry of the tubes were established (Macak et al.). Furthermore, an optimized two-step anodization treatment similar to the one reported for porous anodic alumina can lead to virtually perfect hexagonally ordered arrays of TiO_2 nanotubes.

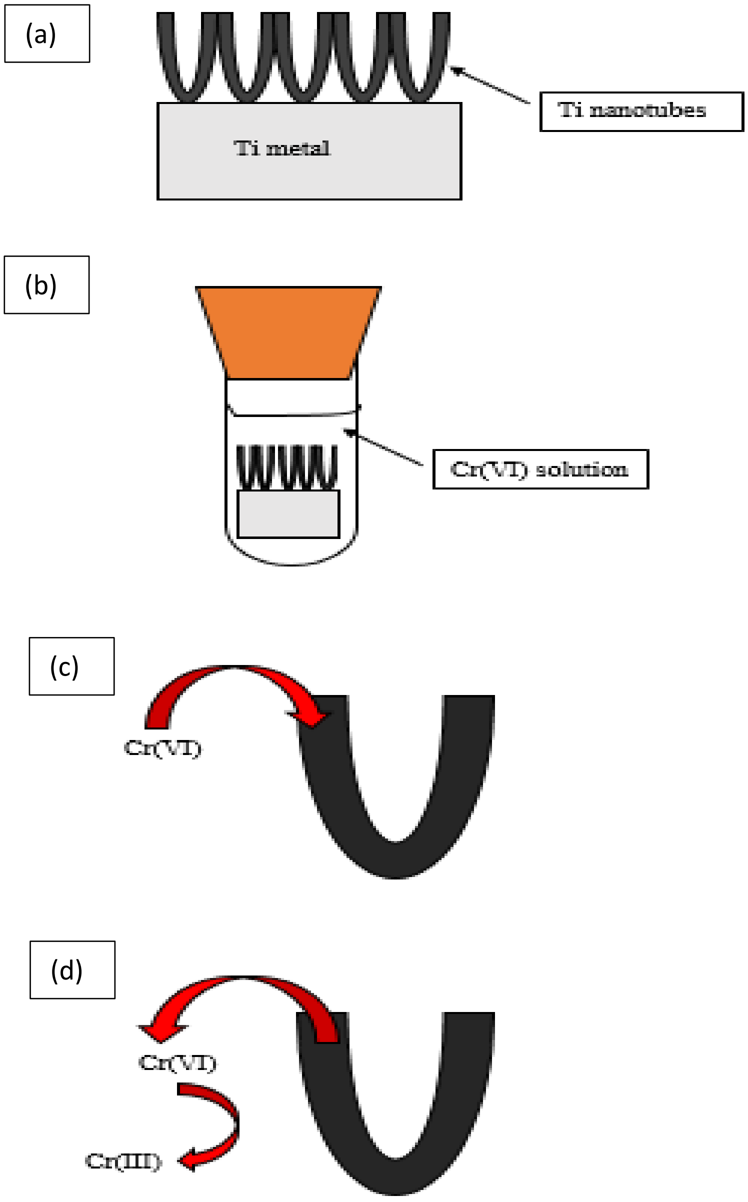
1.2 Nanomaterials

A material where some relevant dimension which is controllable is in the scale of 100nm or less is called as nanomaterials (Ramesh, 2009). Nanomaterials are newly developed materials whereby the controlled structure has a dominant effect on the desired behaviour of the material or device. Nanomaterials can be divided classified into: (i) discrete nanomaterials, (ii) nanoscale device materials, and (iii) bulk nanomaterials.

Discrete nanomaterials are materials that are self-supporting with the scale in the range of 1–10 nm and in at least one dimension. Discrete nanomaterials can be further classified into:

(i) Zero-dimensional (0-D) nanostructures) for example Fullerenes,
(ii) One-dimensional (1-D) nanostructures for example Carbon Nanotubes,
(iii) Two-dimensions (2-D) for example Graphene, and
(iv) Three-dimensions (3-D) for example Graphite

Nanoscale device materials are nanoscale material elements that are contained within devices. Usually nanoscale device materials are in the form of 2-D thin film. Bulk nanomaterials on the other hand are materials that are available in bulk quantities but yet the structure is controlled at nanoscale. Bulk nanomaterials may be built up of discrete nanomaterials or nanoscale device materials which when grouped together will form three-dimensional (3D) nanostructures. In this project, anodisation was done to produce discrete nanotubes of TiO_2 but the nanotubes are supported on a Ti foil. This makes a 3-D nanostructure assembly with the arrays of nanotubes on 1 cm x 1 cm Ti foil. Sketch in Figure 1.1 shows the flow process of anodization and utilization as Cr(VI) adsorbent and photocatalytic to reduce to Cr(III). This project was on the formation of the TiO_2 nanotubes (TNTs) bby anodisation process. Anodization process was conducted in various electrolytes.



TiO_2 nanotubes formation on Ti metal

Experimental putting TNTs inside Cr(VI) solutions for photocatalytic process

Absorption of Cr(VI) into TNTs

Photoreduction of Cr(VI).

The reduction of Cr(VI) to Cr(III)

Figure 1.1: The flow process of anodization and utilization as Cr(VI) adsorbent and photocatalytic to reduce to Cr(III)

1.3 Heavy metal pollution

The term “heavy metals” refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration (Lenntech, 2004). “Heavy metals” is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water (Duruibe et al. 2007). Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed.

Information on the levels of heavy metals in the Malaysian aquatic environment is scarce and limited to a few studies. Most of the coastal resources, agriculture and economic activities and human population, are concentrated on the west coast of Peninsular Malaysia, and as such most of the studies on heavy metals have been focused in this area (Abdullah et al., 1999). The Straits of Malacca on the west coast is a major international shipping lane and the related maritime activities may also contribute to the pollution of the marine environment of Malaysia. Oil and gas-related industries are developing rapidly along the east coast of Malaysia with most of the development located in the states of Pahang and Terengganu.

1.4 Removal of heavy metal pollution via nanotechnology

Recently, nanomaterials have been suggested to be used as heavy metal treatment due to its cost-effective, environmental friendly, and efficiency (Xu, *et al*). Nanomaterials can be used as an efficient water-purification catalysts due their large surface areas and their size and shape-dependent electronic and catalytic properties (Savage & Diallo, 2005).

The size and shape of nanomaterials were both important factors to affect the adsorption performances. The nanostructure comprising of highly ordered nanotubes on a substrate has been seen as a potential architecture to be used as adsorption medium to treat heavy metal's water pollution.

Nowadays, the new technique has been developed for the removal of dissolved metal ions in wastewater that is the reduction by semiconductor photocatalysis technology. One of the most promising examples of photocatalysts is titanium dioxide, TiO_2. The strong interest in TiO_2 lies in the fact that it is non-toxic, inexpensive, highly photoactive, and easily synthesized and handled (Rengaraj et al., 2007). Photocatalyst is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. Figure 1.2 shows the mechanisms of photocatalysis.

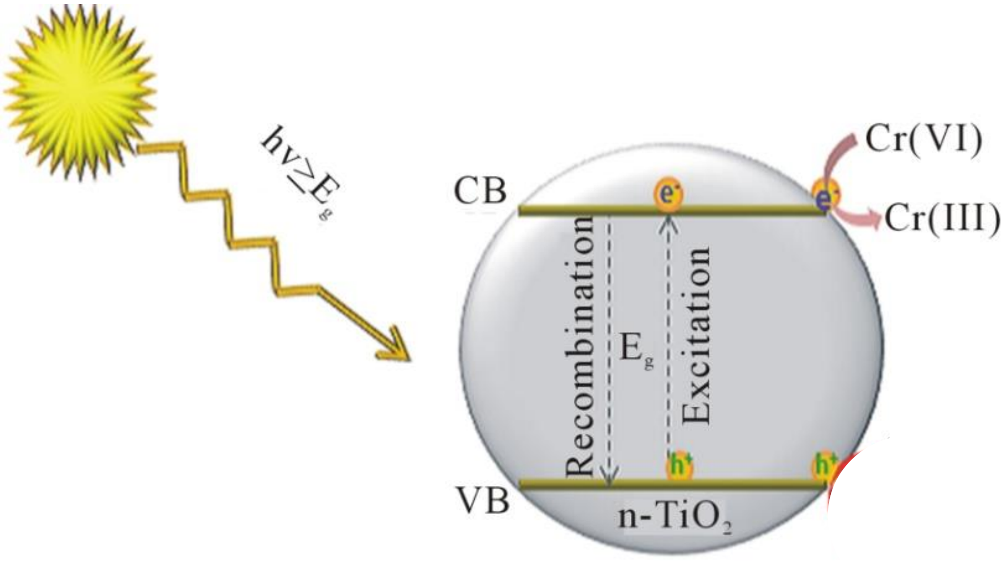


Figure 1.2: Mechanisms of Photocatalysis

Cr(VI) usually exists in wastewater as chromate $(CrO_4)^{2-}$ and dichromate $(Cr_2O_7)^{2-}$ anions and does not precipitate easily using conventional methods. However, they can be removed by absorbtion and reduction by TNTs. The photo-reduction of Cr(VI) to Cr(III) can be achieved via a photocatalytic process with a mechanism as follows:

$$TiO_2 + hv \rightarrow h^+ + e^- \qquad \text{(Eq. 1.1)}$$

$$Cr_2O_7^{2-} + 14\,H + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad \text{(Eq. 1.2)}$$

Where,

h^+ = holes, and

e^- = electrons

1.5 Problem Statement

Chromium is widely distributed in the earth’s crust. It can exist in oxidation states of +2 to +6. Soils and rocks may contain small amounts of chromium, and mostly the trivalent state. Hence, chromium has been transported to the water through the disposal from industrial and lead to dangerous diseases to human body. To control the chromium waste, reduction of Cr(VI) to Cr(III) has been done by several methods such as nanomaterials application method, and the photocatalytic method. This process can effectively clean the environment by reducing Cr(VI) to Cr(III). TiO_2 nanotubes are being used for photoreduction process of Cr(VI). However, TiO_2 has large band gap that allows the material to absorb light only in the UV range, which means that only about 7% of the solar spectrum can be absorbed. Different dimensions of nanotubes give different effects to the photocatalytic for reduction of Cr(VI).

1.6 Research objectives

This project focused on the fabrication of titanium nanotubes by anodization method which is controlled by a few parameters such as anodization time, and anodization voltage. Therefore, the objectives of this study are:

i) To find the most optimum condition for producing TNTs with similar length of 2 μm in Ethylene Glycol/NH_4F, Glycerol/NH_4F, and Na_2SO_4/NH_4F electrolytes

ii) To investigate the influence of electrolytes on the properties of TNTs formed morphologies, phases and structural

iii) To investigate the effect of annealing atmosphere on the properties of TNTs as photocatalysts for Cr(VI) photoreduction process

1.7 Scope of project

The scope of this study is to synthesis TiO_2 nanotubes by anodization method. The temperature of the anodization was fixed at room temperature. The anodization was carried out in three different electrolytes with specific voltage and time. The temperature during annealing process was fixed at $400^{o}C$ but the atmosphere were different that was in N_2 and in air. The nanotubes formed were characterized by Field Emission Scanning Electron Microscope, X-Ray Diffraction, Energy Disperse X-ray, and Fourier Transform Infrared. Finally, TiO_2 nanotubes undergo photoreduction under sunlight and UV light for certain period of time for Cr(VI) reduction purposes before the characteristic of photocatalyst for TiO_2 nanotubes being studied using UV-Vis spectroscopy.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter is on the review of relevant literatures on: (1) general properties of chromium, (2) Chromium VI (Cr(VI)) treatment technologies to remove Cr(VI), and (3) Formation of TiO_2 nanotubes via anodization methods.

2.2 Properties of Chromium

Chromium is one of the minerals that is widely distributed in the earth's crust. According to the World Health Organization, 1988, Chromium occurs most frequently as Cr(VI) or Cr(III) in aqueous solutions (Dakiky et al. 2002). The World Health Organization (WHO) declared that the parameter limit of Cr(VI) effluent in water is 0.05 mg/L3, hence discharge of Cr(VI) to the aquatic environment must be avoided or the Cr(VI) need to be treated with proper treatment first before being discharged to the environment (Budiman et al. 2016). The two oxidation states that are +3 and +6 have different chemical, biological and environmental properties. Table 2.1 shows the physiochemical properties of Chromium and the compounds containing Cr(III) and Cr(VI) (Fawell et. al, 2003). Cr (VI) exists mostly as CrO_4^{2+} of $HCrO_4^-$ and Cr (III) as $CrOH^{2+}$ and $Cr(OH)_3$ in the environment.

Table 2.1: Physiochemical properties of Chromium and the Chromium compound (Fawell et. al, 2003).

Property	**Cr**	**$CrCl_3$**	**K_2CrO_4**	**Cr_2O_3**	**CrO_3**
Melting point (ºC)	1857	1152	968.3	2266	196
Boiling point (ºC)	2672	-	-	4000	-
Solubility (g/L)	Insoluble	Slightly soluble	790	Insoluble	624
Density (g/cm^3)	7.14	2.76	2.73	5.21	2.70

There are some chemical characteristics of chromium that are fundamental to its use in many commercial applications as well as to the environment and human health as summarized in the following statements.

1. The dominant naturally occurring form of chromium is the trivalent oxide.
2. Other forms will tend to be converted to the trivalent oxide when in contact with the natural environment.
3. Even when put in environments where it is not thermodynamically stable, trivalent chromium oxide is slow to react (Barnhart 1997).

2.2.1 Disadvantages of Chromium (VI) to Environment and Human Body

Cr(VI) is toxic (Schrank, José, & Moreira, 2002). Cr(VI) can act as carcinogens, mutagens, and teratogens in biological systems.

The estimated chromium intake for human body is only 0.5-2 micrograms of absorbable chromium (III) from water, food, and air (Zhang and Li, 1987). Because of the high solubility of chromium in the aquatic environments, living organisms are able to absorb the chromium. Then, once the living organisms enter the food chain, large concentrations of chromium may accumulate in the human body and can cause serious health disorder due to the ingestion of the human body systems.

Ten years have elapsed since the International Agency for Research on Cancer (IARC) evaluated the carcinogenicity of chromium and chromium compounds (Flora 2000). A huge literature have been covered the activity of chromium compounds on genetic related effects in *in vitro* test systems. De Flora *et. al* reviewed more than 700 sets of data obtained by testing 32 chromium compounds in as many as 132 experimental systems having cellular targets. Chromium levels in blood and urine reflects the amount of chromium which has been taken by human body.

A number of occupational activities involve the production of chromium (Flora 2000).

2.3 Cr (VI) Treatment Technologies

The conventional processes for removing heavy metals from wastewater include many processes (Barakat 2011). Various methods have been employed to remove Cr(VI) from wastewater like membrane filtration, electrochemical treatment, chemical precipitation, ion exchange and adsorption (Budiman et al. 2016). In this section, the Cr(VI) treatment technologies will be explained briefly including the summarization of advantages and disadvantages of these technologies. The summarization were shown in Table 2.3.

2.3.1 Membrane Filtration

Application of membrane technology to wastewater treatment has expanded over the last decades. In particular, the absolute retention of all microorganisms by membrane makes it possible to treat wastewater effectively (Chang & Kim 2005). In addition, membrane technology has been used for a tertiary waste- water treatment process. After secondary biological waste- water treatment, a membrane filtration of secondary effluents has been applied for an advanced wastewater treatment regime. Membrane filtration systems are categorized by pore size, which is from larger to smaller pore size including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (Guertin et. al, 2004)

2.3.2 Electrochemical Treatment

Recently, electrochemical techniques have been proposed for the wastewater treatment that contains organic pollutants which considered as toxic. In this process, electroconversion and electrocombustion reactions transform the non-biodegradable organic species which are dissolved in aqueous solutions to biodegradable organic compounds or final inorganic ones, like CO_2 and H_2O (Panizza 2001).

2.3.3 Chemical Precipitation

For inorganic effluent, chemical precipitation method is the most widely being used for heavy metal removal. Eq 1 shows the conceptual mechanisms of heavy metal removal by precipitation (Wang *et al*., 2005)

$$M^{2+} + 2(OH)^{-} = M\ (OH)^{-} \qquad (2.1)$$

Lime, caustic, and sodium carbonates are the commonly used chemicals for precipitation of metals. Common precipitants include hydroxide $(OH)^{-}$, sulphide $(S)^{2-}$, cyanide, and carbonate. Precipitation of salts is a fairly rapid process, where it was performed by adjusting concentrations and other conditions so that ionic constituents to be removed change from dissolved ionic phase to solid salt (Wang *et al.*, 2005). There are two steps processes for removal of Cr(VI) by using chemical reduction process that are; (1) reduction of Cr(VI) under acidic conditions (pH 2 to 3) and (2) the precipitation of Cr(III) as hydroxyl species (Madhavi *et al.,* 2013).

2.3.4 Ion Exchange

Ion exchange is the process which the ions on the surface of the solid has been exchanged for ions of the similar in the solution with which the solid is in contact. The dissolved Cr(VI) will binded to the resin and displace the previously bound ions (Cl^- or OH^-) when water flows through it (Guertin *et al.,* 2004).

2.3.5 Adsorption

Adsorption is commonly employed as a polishing step to remove organic and inorganic contaminants in water and wastewater treatment. Efficiency of conventional adsorbents is usually limited by the surface area or active sites, the lack of selectivity, and the adsorption kinetics. Nano-adsorbents offer significant improvement with their extremely high specific surface area and associated sorption sites, short intraparticle diffusion distance, and tuneable pore size and surface chemistry(Qu et al. 2013).

Adsorption is now recognized as a promising method for heavy metal wastewater treatment due to its effectiveness and economic. The adsorption process offers flexibility in design and operation and in many cases will produce high quality treated effluent. Moreover, some adsorbents can be regenerated by suitable desorption method. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid. There are two possible types of bond between the adsorbent and adsorbate molecules (Raj, 1978).

i. Mutual interactions such as those between molecules in the solid surface, the Van der Waals forces, prevail between the adsorbent and adsorbate molecules. This phenomenon is referred to as physical adsorption or physisorption.

ii. A very strong, almost chemical bond exists between the adsorbent and adsorbate atoms. This phenomenon is referred to as chemisorption.

Table 2.2 shows the summarization of differences between physiosorption and chemisorption.

Table 2.2: Summarizes differences between physiosorption and chemisorption (Raj, 1978)

	Physiosorption	**Chemisorption**
Electronic force	Van der Waals bond	Chemical bond
Interaction	Weak	Strong
Type of reaction	Reversible	Irreversible
Site reaction	A function of coverage of surface (no specific location)	At fixed site of the surface (specific location)
Electron sharing	Do not sharing electrons	Have electron sharing
Saturation uptake	Multilayer	Monolayer
Adsorption enthalpy	Low (40 kJ/mol)	High (40-400 kJ/mol)
Adsorbate	Not very specific	Often very specific

Kinetics of adsorption	Fast- Instantaneous process	Rapid or slow- Often activated process

2.3.6 Photocatalytic

The process of photocatalytic is known to be a rapid and efficient method for the removal of environmental various pollutants including for the reduction of Cr(VI) to less harmful Cr(III) (Bashirom et al. 2017).

Nowadays, photocatalytic process in aqueous suspension of semiconductor has gain bright attention in view of solar energy conversion. This photocatalytic process was achieved for rapid and efficient destruction of environmental pollutants (Barakat 2011). Photocatalytic reduction of Cr(VI) over TiO2 catalysts was investigated in both the absence and presence of organic compounds (Papadama et al., 2007; Wang et al., 2008).

Figure 2.1 shows the conceptual reaction path of photocatalysis over titanium dioxide particle. The mechanism of photocatalysis over titanium dioxide particle was reported (Zhang and Itoh, 2006). To avoid recombination, the generated electron hole pairs must be trapped. Then, hydroxyl ions (OH^-) are the likely traps for holes make hydroxyl radicals as strong oxidant agents, while the traps for electrons are adsorbed oxygen species, leading to the formation of superoxide species($O2^-$) which are unstable, reactive and may evolve in several ways (Barakat 2011).

For photocatalytic activity, one of the most used nanomaterials was TiO_2 nanomaterials because it can be done in UV and possibly visible light range, low human toxicity, high stability, low cost (Qu et al. 2013).

Figure 2.2 shows the principle of the photocatalytic decomposition on a semiconductor electrode. Photons from a light source that have sufficient energy, that is, higher than the bandgap energy, Eg, of the semiconductor, excite electrons from the valence band to the conduction band of the semiconductor and charge-carrier pairs (consisting of a hole h+ and electron e^-) are formed which either recombine inside the particle, or migrate to its surface, where they can react with adsorbed molecules. In aqueous solutions positively charged valence-band holes typically form hydroxyl radicals, HOC, while electrons in the conduction band mainly reduce dissolved molecular oxygen to superoxide $CO2^-$ radical anion (Macak et al. 2007)

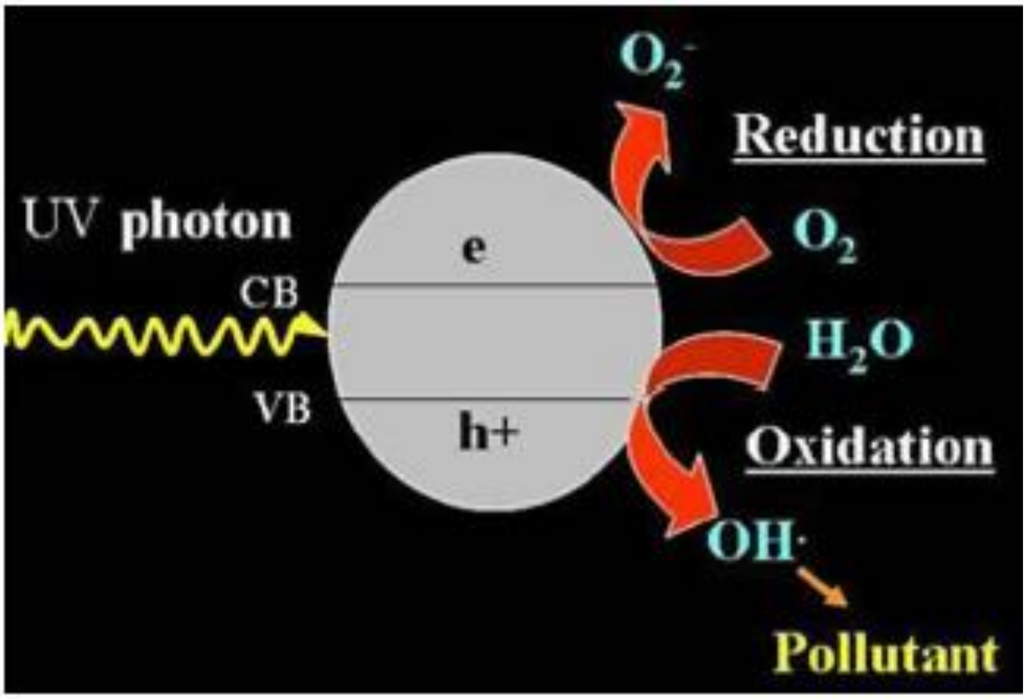


Figure 2.1: The conceptual reaction path of photocatalysis over TiO_2 (Herrmann, 1999)

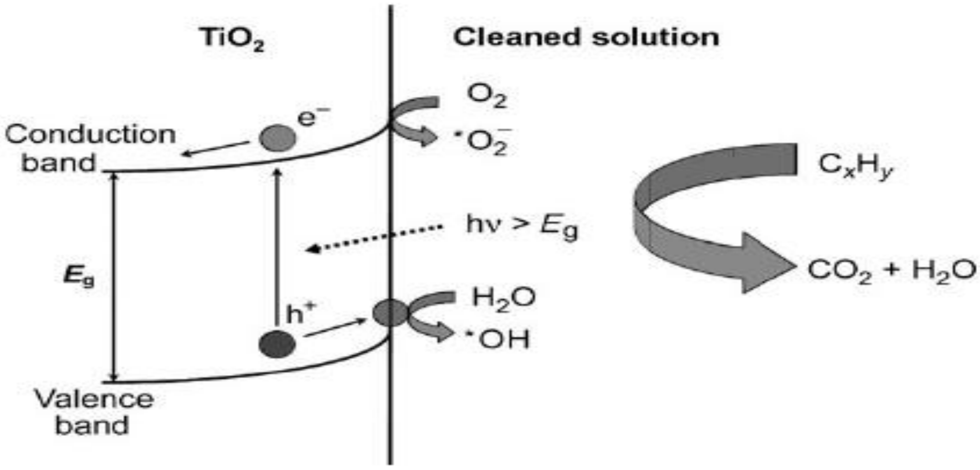


Figure 2.2: Principles of photocatalytic decomposition on semiconductor TiO2 surfaces (Macak et al. 2007).

2.3.7 Comparison of Cr(VI) Removal Techniques

The process of photocatalytic has become one of the preferred methods for the removal of toxic contaminants from wastewater. The summary along with the advantages and disadvantages of the methods used for removal Cr(VI) were shown in Table 2.3.

Table 2.3: Advantages and disadvantages of various Cr(VI) treatment techniques

Technologies	Advantages	Disadvantages
Membrane filtration (Fu *et al.*,2011)(Barakat,2010)	○ High efficiency, easy operation ○ Space saving ○ Low pressure ○ High separation selectivity	○ High cost, process complexity ○ Membrane fouling, low permeate flux
Electrochemical (Fu *et al.*,2011)	○ Fast treatment process ○ Require fewer chemicals ○ Provide good reduction yields	○ Relatively large capital investment

	○ Produce less sludge	○ Expensive electricity supply
Chemical precipitation (Fu *et al.,* 2011)(Barakat,2010)	○ Simple operation ○ Low capital cost	○ Ineffective to treat water with low metal ion concentration ○ Mot economical ○ Produced large amount of sludge resulting long-term environment impact ○ Slow metal precipitation, poor settling
Ion exchange (Fu *et al.*,2011)(Barakat,2010)	○ High treatment capacity ○ High removal efficiency ○ Fast kinetics	○ Ion exchange resins must be regenerated ○ Regeneration caused secondary pollution ○ Expensive (when large amount water with low metal ion concentration) ○ Not suitable for large scale
Adsorption (Fu *et al.*,2011)	○ Effective and economic ○ Adsorbents can be regenerated ○ No secondary pollutant produce ○ Can use for the low concentration of heavy metals in wastewater ○ Easy operating conditions	○ Absorption efficiency and capacity depends on type of adsorbents
Photocatalytic (Qu et al. 2013)(Barakat, 2011)	○ Removal of metals and organic pollutant simultaneously ○ less harmful by-products	○ Long duration time, ○ limited applications

2.4 Formation of TiO_2 Nanotubes (TNTs)

Zwilling et al. have been reported on the electrochemical formation of self-assembled TiO_2 nanotubes (p-TiO_2) by the anodization of Ti in 1999 (Tio 2005).

A second generation of nanotubes have been studied with lengths up to several micrometers and aspect ratios up to 50 can be formed by adjusting the pH gradient within the growing nanotube. The results of these studies, the side walls of the tubes show strong irregularities which the side-wall profiles show considerable thickness variations (ripples) as shown in Figure 2.2. In previous work it has been established that the length of the nanotubes is essentially the result of a steady-state situation between electrochemical formation of TiO_2 at the pore tip and the chemical dissolution of formed TiO_2 by fluorides from the electrolyte (Tio 2005).

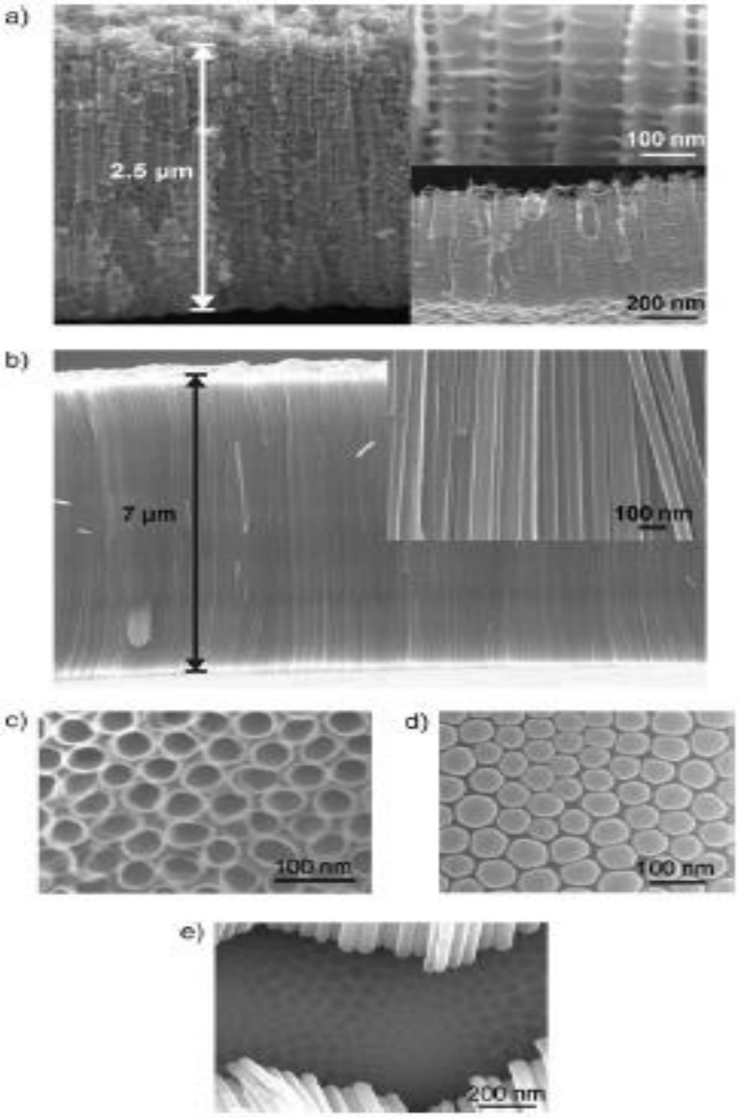


Figure 2.3: a) SEM images of conventional anodic TiO_2 nanotubes with a magnification of the structure (top) and an example of ripples on short tubes formed in 1m H_2SO_4 with 0.15 wt% HF (bottom). b) Smooth TiO_2 nanotubes 7-mm long produced in glycerol electrolyte with 0.5 wt% NH_4F. The inset shows the walls of the nanotubes in more detail. c)– e) SEM images of smooth TiO_2 nanotubes 7-mm long produced in glycerol electrolyte: c) top view; d) bottom view. The average nanotube diameter is approximately 40 nm and the average pore spacing is approximately 60 nm. e) Top view of an anodized sample after removal of some arrays of nanotubes. The lower part of the tubes and part of the Ti substrate surface are visible. Clearly the convex shape of the nanotube bottoms is reflected in the surface of the Ti substrate (Tio 2005).

There are various techniques on synthesizing TiO_2 nanostructures including sol–gel methods, template-assisted methods, hydro/solvothermal approaches, and by electrochemical means (Roy et al. 2011). TiO_2 offers unique properties and a high functionality for various applications such as photocatalysis, self-cleaning surfaces, solar energy conversion, catalysis, biomedicine, sensors, and optical coatings (Berger et al. 2010).

Self-organized TiO_2 nanotube layers can be formed by a simple substrate under a specific set of environmental conditions as shown in Figure 2.3 (a). These TiO_2 nanotube structures represent a unique combination of the highly functional features of TiO_2 with a regular and controllable nanoscale geometry (length, tube diameter, and self-ordering can be adjusted over large length scales). The synthesis is carried out by a low-cost parallel process which is the conventional electrochemical anodization. It is furthermore remarkable that the self-ordering anodization approach is not limited to titanium but can be applied to a large range of other transition metals or alloys to form highly aligned oxide nanotube or pore structures (Roy et al. 2011).

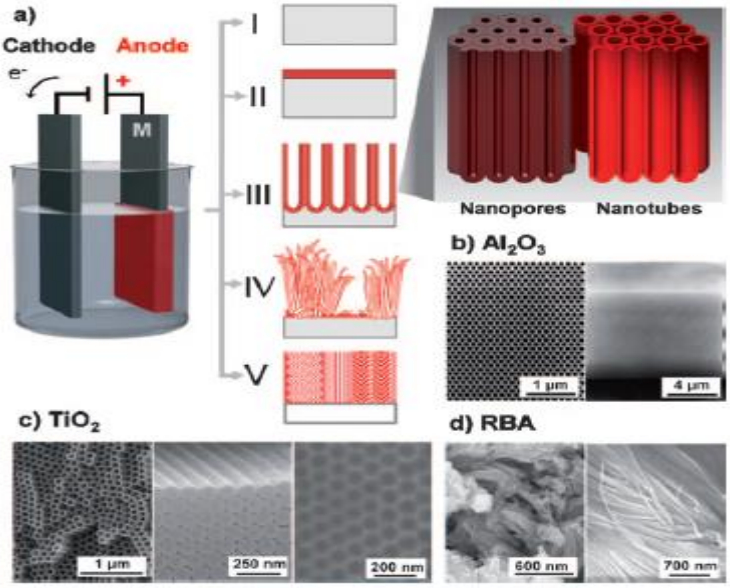


Figure 2.4: The electrochemical anodization process and possible anodic morphologies: a) I) metal electropolishing, II) formation of compact anodic oxides, III) self-ordered oxides (nanotubes or nanopores), IV) rapid (disorganized) oxide nanotube formation, V) ordered nanoporous layers. Examples of morphologies of obtained structures: b) Classical highly organized nanoporous, c) highly ordered TiO2 nanotubes (in top and side view) with dimpled structure (right) on metal surface when tubes are removed, d) disordered TiO2 nanotubes growing in bundles. [RBA=rapid-breakdown anodization.] (Roy et al. 2011)

2.5 Mechanisms of Nanotubes Formation

Since the discovery of carbon nanotubes, much attention has been given to the study of nanotube structures and their formation mechanisms. The sound understanding of carbon nanotube formation mechanisms related to their structure characteristics has stimulated intensive research on the synthesis and characterization of other nanotube structures from compound layered materials (Nath, *et.al*, 2001).

For the formation of TiO_2 nanotubes, initially, titanium reacts with electrolyte to form a TiO_2 layer on the surface. The TiO_2 layer reacts with NH_4F when F^- is the dominant ion in the system. In this case, the compact oxide begins to be dissolved in some areas that is also known as etching. The etching rate varies at different areas of the oxide layer due to the differences in the magnitude of stress on the surface of oxide film. This selective etching produces porous structures on the surface. The nanotubular structures are formed through two processes: oxidation of titanium and oxide dissolution, which can be summarized as two reactions as shown in Eq. 2.1 (Shokuhfar, *et.al*).

$$\text{Oxidation: } Ti + 4H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$$

$$\text{Dissolution: } TiO_2 + 6F_2 + 4H^+ \text{ A } [TiF_6]^{22} + 2H_2O \qquad \text{(Eq. 2.1)}$$

Figure 2.5 shows the Schematic diagram of TiO2 nanotube formation. Panel (a) shows the oxide layer formation, (b) pore growth due to dissolution reaction, (c) nanotube formation layer by layer, and (d) an SEM image of the layered structure in nanotubes.

The electrical field can enhance the migration of metal ions, a process called field-enhanced dissolution. With increasing the pore size, the electrolyte has a chance to penetrate into the interface of the oxide layer and metal and the second oxide layer will form and then be etched again due to the effect of the electrical field.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

Generally, this research work was divided into three stages including anodization, annealing, and photoreduction process as shown in flow chart in Figure 3.1. In anodization process, a set of experiment was conducted as summarized in Figure 3.2. The samples that have been prepared through this process were characterized by Field Emission Microscope (FESEM) and X-Ray Diffraction (XRD). Next, in annealing process, the samples were annealed in two different atmosphere, that is in Nitrogen (N_2) atmosphere and in air atmosphere at fixed temperature 400˚C for 3 hours soaking time. The annealing profile was shown in Figure 3.3(a) and the annealing process flow chart was shown in Figure 3.3(b). While in photoreduction process, several experiments were conducted as summarized in Figure 3.4(a) and parameters applied in Figure 3.4(b).

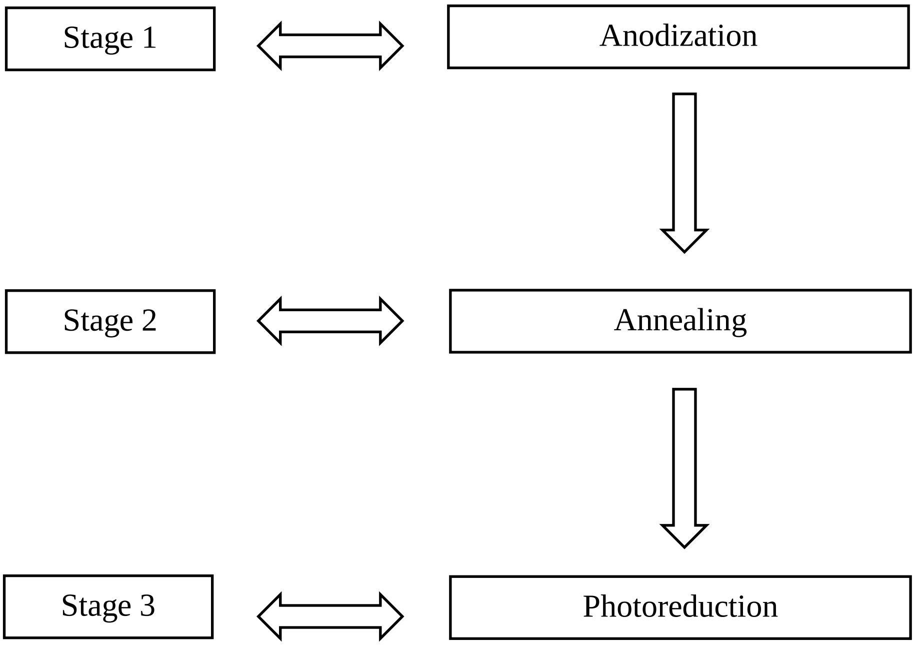


Figure 3.1: Flowchart of of overall experiment