POST ANNEALING TREATMENT OF TiO_2 NANOTUBES FOR DEFECTIVE BLACK OXIDE FORMATION AND APPLICATION IN HEAVY METAL REMOVAL

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POST ANNEALING TREATMENT OF TiO_2 NANOTUBES FOR DEFECTIVE BLACK OXIDE FORMATION AND APPLICATION IN HEAVY METAL REMOVAL

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DECLARATION

I hereby declared that I have conducted, completed the research work and written the dissertation entitled: “**Post Annealing Treatment of TiO_2 Nanotubes for Defective Black Oxide Formation and Application in Heavy Metal Removal**”. I also declared that it has not been previously submitted for the award for any degree and diploma or other similar title of this for any other examining body or University.

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LIST OF ABBREVIATIONS

1D	One-dimensional
a.u.	Arbitrary unit
Cr(III)	Trivalent chromium
Cr(VI)	Hexavalent chromium
EDTA	Ethylenediamine tetraacetic acid
EDX	Energy Dispersive X-ray
EG	Ethylene glycol
EPR	Electron Paramagnetic Resonance
ESR	Electron Spin Resonance
FESEM	Field Emission Scanning Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
ICDD	International Centre for Diffraction Data
ISO	International Organization for Standardization
NH_4F	Ammonium fluoride
NHE	Normal Hydrogen Electrode
NTs	Nanotubes
PL	Photoluminescence
UV-Vis	Ultraviolet-visible Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

LIST OF SYMBOLS

°	Degree
°C	Degree Celsius
$\bullet HO_2$	Superoxide acid
$\bullet O_2^-$	Superoxide anion radicals
$\bullet OH$	Hydroxyl radicals
2θ	Diffraction angle
Å	Angstrom (10^{-10} m)
e^-	Electrons
eV	Electronvolt
h^+	Holes
H_2/Ar	Mixed gas of 10% hydrogen gas and 90% argon gas
hv	Photon energy
nm	Nanometer
ppm	Part per million
$TiO_{(2-x)}$	Black / oxygen-vacancy rich titanium dioxide
TiO_2	Titanium dioxide
V^{2-}	Oxygen vacancy
wt%	Weight percent

RAWATAN SELEPAS PENYEPUHLINDAPAN TIUB NANO TIO_2 UNTUK PEMBENTUKAN OKSIDA HITAM DAN APLIKASI DALAM PEMBUANGAN LOGAM BERAT

ABSTRAK

Pencemaran alam sekitar oleh air sisa akibat kewujudan ion kromium adalah salah satu isu serius di seluruh dunia kerana ketoksikan dan tidak terbiodegradasinya. Rawatan air sisa boleh dijalankan dengan proses fotomangkin dengan kehadiran TiO_2 sebagai fotomangkin. Namun, TiO_2 hanya boleh diaktifkan di bawah sinaran ultraungu kerana jurang jalurnya yang luas. Penghasilan oksida dengan kecacatan melalui penghidrogenan akan mewujudkan jurang pertengahan yang mengecilkan jurang jalur dan membolehkan penjanaan pembawa caj oleh cahaya matahari. Oleh itu, objektif projek ini adalah untuk menilai keberkesanan TiO_2 nanotiub yang tulen dan hitam untuk penyingkiran ion Cr(VI). Sintesis TiO_2 nanotiub dilakukan melalui anodisasi dengan voltan yang berbeza, diikuti dengan pengyepuhlindapan dalam udara. Dua set TiO_2 nanotiub hitam disediakan: (i) penghidrogenan selepas penyepuhlindapan dalam udara dan (ii) penghidrogenan selepas anodisasi tanpa penyepuhlindapan dalam udara. Penambahan diameter tiub nano diperolehi apabila voltan anodisasi meningkat. Kehadiran fasa anatase disahkan dalam TiO_2 NTs selepas penyepuhlindapan. TiO_2 nanotiub dengan penghidrogenan selepas penyepuhlindapan dalam udara mempunyai penggabungan semula pembawa caj yang terendah kerana adanya kekosongan oksigen dan ion Ti^{3+}. Kecekapan penyingkiran Cr(VI) tertinggi dicapai oleh TiO_2 NTs beranil udara dan dihidrogenasi yang disintesis pada 60 V dengan 43.43% di bawah cahaya matahari. Uuntuk keadaan penyepuhlindapan yang berbeza, TiO_2 nanotiub dengan penghidrogenan selepas penyepuhlindapan dalam udara mencapai kecekapan penyingkiran Cr(VI) tertinggi dengan 42.23% .

POST ANNEALING TREATMENT OF TiO_2 NANOTUBES FOR DEFECTIVE BLACK OXIDE FORMATION AND APPLICATION IN HEAVY METAL REMOVAL

ABSTRACT

Environmental pollution by wastewater due to presence of chromium ions is one of the serious issues around the world owing to its toxicity and non-biodegradability. Wastewater treatment can be done by photocatalytic process in the presence of TiO_2 as photocatalyst. However, TiO_2 can only be activated under ultraviolet radiation owing to its wide band gap. Producing defective oxide via hydrogenation will create mid-gap states to narrow the band gap and allow generation of charge carriers by sunlight. Thus, the objective of this project is to assess the effectiveness of pristine and defective black TiO_2 nanotubes for removal of Cr(VI) ions. The synthesis of TiO_2 nanotubes is performed via anodization with different anodization voltage, followed by annealing in air. Two sets of defective black TiO_2 nanotubes are prepared: (i) hydrogenation after annealing in air and (ii) hydrogenation after anodization without annealing in air. Increment in diameter of nanotubes is observed when anodization voltage increased. The presence of anatase phase is confirmed in nanotubes after annealing. TiO_2 nanotubes subjected to annealing in air and hydrogenation show the lowest recombination of charge carriers due to presence of oxygen vacancies and Ti^{3+} ions. For different anodization voltage, the highest Cr(VI) removal efficiency is achieved by air-annealed + hydrogenated TiO_2 nanotubes synthesized at 60 V with 43.43% under sunlight irradiation. For different annealing conditions, TiO_2 nanotubes subjected to both annealing in air and hydrogenation show highest removal efficiency of 42.23%.

CHAPTER 1

INTRODUCTION

1.1 Research Background

In the modern age, environmental pollution issue is getting more serious. The well-known contaminants that lead to environmental pollution is heavy metals. Water pollution is one of the serious environmental pollutions caused by presence of heavy metals. However, water is the basic need for human, animals and aquatic life. Thus, heavy metal pollution in water source may cause serious threats to both marine life and wild populations, as well as severe diseases in human body such as cancer, birth defects, kidney dysfunction, immune system dysfunction and etc. (Balali-Mood *et al*., 2021). This is because heavy metals have different toxicity, non-degradable and tend to accumulate in human and animal life. Thus, this work is on synthesis of black titanium dioxide nanotubes for heavy metal removal in water.

1.2 Heavy Metal Pollution

Heavy metals are described as natural occurring elements which have atomic number greater than 20 and relatively high density. As the name suggests, heavy metals are categorized under metals and metalloids. Heavy metals are usually non-biodegradable and toxic even at ppb levels. Examples of heavy metals are copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), nickel (Ni), cobalt (Co), cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As) and chromium (Cr) (Y. Liu *et al*., 2017).

Heavy metals are commonly released into environment through anthropogenic activities, such as release of industrial wastewater and automobile exhaust, electroplating, mining, incineration of fossil fuels and smelting (Sharma *et al*., 2020). As heavy metals are classified as inorganic pollutants, the existence of heavy metals in the ecological environment may pose harms to human health and ecosystem. Thus, heavy metal pollution is one of the serious issues which will affect human, ecosystem and environment and this issue is gaining more attention nowadays.

1.3 Chromium Pollution

Chromium is a metallic element with steel grey appearance, high melting point (1907°C) and density of 7.19 gcm^{-3}, thus it is classified as heavy metal (Lunk, 2015). Chromium rarely exists as pure state (Cr (0)) in nature and it is usually obtained from chromite ores ($FeCr_2O_4$). It will transform into green chromic oxide (Cr_2O_3) due to heating (Shanker, 2019). It is categorized as highly toxic metal and release of chromium to the environment may cause adverse impact to human health and ecosystems with long term exposure. In this world, the production of chromium is approximate 10^7 metric tons per year, where 60 to 70% of the production is used in metal alloy and stainless-steel production, while another 15% is used in chemical and industrial processes (N. Sharma *et al.*, 2020).

In Malaysia, the source of water used for consumption and agricultural are mainly come from the rivers. Thus, the quality and cleanliness of river water need to be controlled properly as water is essential for human survival and ecological sustainability. According to World Health Organization (2010), the concentration of Cr(VI) ions in drinking water should not exceed 0.05mg/L. However, there is report on the chromium pollution in the sediments of Sungai Kelantan with the range of 16 – 172 µg/g due to sand mining, logging, land reclamation activities, as well as rainfall events which leads to terrestrial runoff (Rahim *et al.*, 2019). Another research by Ahmed *et al.* (2020) on the concentration of chromium in Langat River shows that chromium was detected in the river but still within the permissible limit. The increasing of chromium concentration in Langat River is said to be due to the weathering of serpentinite rock-derived oxisols and metal finishing activities from the industries near to the river.

Chromium pollution not only happens in Malaysia, but also in other countries. In India, Karunanidhi *et al.* (2021) reported that the mean concentration of chromium in the groundwater reached 0.09 mg/L, which has exceeded the permissible limit of chromium stated by World Health Organization. The source of chromium pollution is reported to be the existence of leather tanning industries in massive scale. Mani Tripathi and Chaurasia (2020) also reported that the concentration of chromium detected in the water collected from Dharamkata, India was 2070 µg/L, exceeding the permissible limit. The rise in chromium concentration is due to discharge of untreated tannery effluents. Ahmad *et al.* (2021) has conducted a study on the chromium concentration in water due to emission from automobile in Pakistan. The range of chromium concentration in water is from 0.50 to 1.14 mg/kg, indicating environmental pollution due to release of chromium by emission of smokes from automobiles. According to He and Li (2020), surface water of Luo River in China has high concentration of chromium which cause water pollution and environmental issue. The chromium pollutant is coming from the groundwater which has high chromium concentration. Different samples from rivers which are connected with Luo River shown chromium concentration detection within the range of 0.005 to 0.251 mg/L. Meanwhile, in North Carolina, the chromium concentration from 0.012 to 22.9 µg/L was detected in the Piedmont groundwater. However, the source of the chromium was not stated clearly (Vengosh *et al.*, 2016).

The major anthropogenic source of chromium release to environment is from industrial activities, such as metal processing, welding, production of ferrochrome and chrome pigment, tannery facilities and chromate production. High concentration of chromium in environment is commonly related to the release of wastewater and air containing chromium from the industries (Tchounwou *et al*., 2012).

Chromium consists of many oxidation states, ranging from -2 to +6. However, the existence of chromium in nature usually is in the states of trivalent chromium and hexavalent chromium. Trivalent chromium is the most stable state, followed by hexavalent chromium (Tumolo *et al*., 2020). At low pH, Cr(III) and Cr(VI) will exist as $[Cr(OH_2)_6]^{3+}$ and $Cr_2O_7^{2-}$, respectively. Meanwhile at high pH, Cr(III) exists as $[Cr(OH)_4]^-$ and Cr(VI) exists as CrO_4^{2-} (Lunk, 2015).

1.4 Nanomaterials

According to ISO/TS 80004-1:2010, nanomaterials are defined as material built with any external dimensions, internal structure or surface structure in nanoscale range, which is within the range of 1 to 100nm. Thus, nanomaterials can be classified into four categories as shown in Figure 1.1, which includes zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D), depending on the number of dimensions fall within nanoscale range. 0-D nanomaterials refer to the material with all dimensions (x-, y- and z-axis) in nanoscale range, for instance nanoparticles. 1-D nanomaterial is the material with two dimensions (x- and y-axis) in nanoscale range, such as nanotubes, nanorods, nanowires and nanofibers. Meanwhile, 2-D nanomaterial is the material with one dimension, usually thickness, in nanoscale range. Examples of two-dimensional nanomaterial are nanosheets, nanofilms, nanolayers and graphene. The nanomaterial with all three dimensions falls outside nanoscale range is known as 3-D nanomaterial. The three-dimensional material is usually made up of multiple arrangement of nanosized materials such as nanoparticles, nanotubes, nanorods or nanolayers in different orientation, forming dimensions greater than 100 nm.

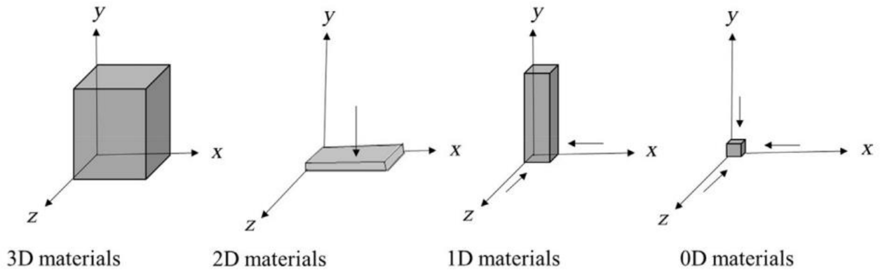

Figure 1.1: Dimensions of materials with nano-scale size (Kebede and Imae, 2019)

1.5 Photocatalytic Process on TiO_2 and Black TiO_2

Photocatalytic process is an advanced process which uses photocatalysts and light, such as ultraviolet or visible light, as source of energy to trigger oxidation and reduction process for removal of heavy metals from industrial wastewater. The photocatalysts required for this process are commonly semiconductor, for instance titanium dioxide (TiO_2), zinc oxide (ZnO) and etc, which consists of filled valence band and empty conduction band for excitation of electrons and generation of holes with the presence of photon energy which are greater than the band gap energy (X. Gao and Meng, 2021). In short, photocatalytic process includes transformation of ionic species into solid metal and deposition of solid metal on the surface of catalysts (Litter, 2015). Photocatalytic process also involves separation of photogenerated holes and electrons and recombination of charge carriers which will reduce the number of excited charge carriers. Thus, photocatalysts with narrower band gap are preferred for photocatalytic process in removing heavy metals by capturing more visible light (Ren *et al.*, 2021).

Titanium dioxide (TiO_2) is a semiconductor and common photocatalyst used for photocatalytic reaction as it possess high chemical stability and photostability, good commercial availability, low toxicity, cost effective, good thermal stability and excellent resistance to light-induced corrosion (Z. Li *et al.*, 2022). The photocatalytic reaction is strongly depends on the ability of photocatalysts to generate charge carriers which leads to formation of electrons that responsible for heavy metal removal or degradation (Sreekantan *et al.*, 2014). The conduction band of TiO_2 has a reduction potential of -0.3 V vs. NHE, while the potential for valence band is 2.9 V vs. NHE (Humayun *et al.*, 2018). Meanwhile, the reduction potential of $Cr_2O_7^{2-}/Cr^{3+}$ is +1.33 V vs. NHE, which is more positive than the conduction band, thus photocatalytic reduction of Cr(VI) as shown in Figure 1.2 is possible.

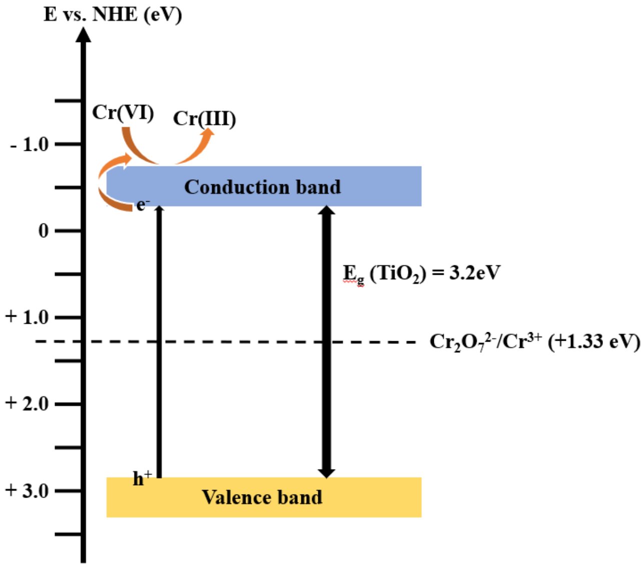

Figure 1.2: Photocatalytic reduction of Cr(VI) with TiO_2

Meanwhile, defective black TiO_2 is the titanium dioxide with band gap modification which formed with surface disorders and existence of oxygen vacancies and Ti^{3+} defects (Y. Zhang *et al.*, 2022). This is because TiO_2 nanotubes usually exhibit large band gap and rapid recombination of charge carriers, which will then lead to reduction in the performance of TiO_2 in photocatalytic reactions. Defective black TiO_2 is synthesised by introducing defects, such as surface disorders and oxygen vacancies into the TiO_2. Through introduction of defects, the photocatalytic performance can be improved as the band gap of TiO_2 will be reduced for visible light absorption and the recombination rate of charge carriers will also be lowered for effective separation of photogenerated charge carriers (Y. Zhang *et al.*, 2022).

In this work, the TiO_2 nanotubes synthesised by anodization will be annealed in reducing atmosphere, which is 10% H_2 / 90% Ar gas, for hydrogenation process to produce black TiO_2 nanotubes. The hydrogenation time for this proposed work is shorter than other studies that will be discussed later in Section 2.8.1. For anodized TiO_2 nanotubes, annealing in air usually will be done to improve the crystallinity of nanotubes before hydrogenation. As hydrogenation process requires temperature similar to annealing in air, the hydrogenation process without annealing in air after anodization is proposed in this work. Next, the hydrogenated TiO_2 nanotubes without annealing in air will be used for chromium(VI) reduction which is not done before.

1.6 Problem Statement

The presence of heavy metals in the environment and long exposure to the heavy metals may cause harmful effect to human health due to their high toxicity. One of the methods to remove heavy metal ions in wastewater is through photocatalytic reduction. Titanium dioxide (TiO_2) is a semiconductor which commonly used as photocatalyst. However, TiO_2 in nanoparticular forms tend to agglomerate after solution treatment, leading to difficulty in separation from the tested solution. Thus, in this project, TiO_2 photocatalyst will be synthesised in the form of nanotubes via anodization using titanium foils. Nanotubes with different dimensions due to application of different anodization voltage will give different effects in photocatalytic reduction of Cr(VI).

Besides that, amorphous TiO_2 shows low photocatalytic activity due to presence of large amounts of imperfections which will act as recombination centres for electron and hole pairs. Although anatase TiO_2 is commonly used as photocatalysts, TiO_2 has several limitations such as wide band gap and rapid recombination of electron and hole pairs. Thus, TiO_2 can only absorb light in ultraviolet range, which is only about 7% of the solar spectrum. The photocatalytic activity of TiO_2 nanotubes under sunlight is limited. Anodized nanotubes subjected to different annealing conditions may give different crystallinity and defects to the nanotube structures. Thus, the annealing conditions need to be studied to overcome the wide band gap and rapid recombination of electron and hole pairs in TiO_2 nanotubes. Besides that, the application of TiO_2 nanotubes subjected to different annealing conditions in photocatalytic reduction of chromium(VI) has not been extensively studied.

1.7 Objectives

1. To investigate the effect of anodization voltage on the morphology of TiO_2 nanotubes.
2. To compare the effect of annealing condition on the morphology, structure, crystallinity and electron-hole recombination of TiO_2 nanotubes and black TiO_2 nanotubes.
3. To compare the Cr(VI) removal efficiency of TiO_2 nanotubes and black TiO_2 nanotubes synthesized by different anodization voltages and different annealing conditions.

1.8 Scopes of Work

This project included the investigation on the formation of black TiO_2 nanotubes via anodization and annealing, followed by hydrogenation. To synthesis TiO_2 nanotubes, titanium foil was used as substrate for growth of nanotubes by immersing in EG electrolyte with alteration of anodization voltage. After anodization, one set of the TiO_2 nanotubes was annealed in air to transform the amorphous phase to anatase phase.

Meanwhile, another set of TiO_2 nanotubes was annealed in reducing atmosphere without annealing in air. Black TiO_2 nanotubes were then synthesized via annealing in reducing atmosphere with flowing of 10% H_2 / 90% Ar gas in tube furnace. The crystalline phase, structure and morphology of white and black TiO_2 nanotubes were determined using XRD, Raman Spectroscopy, FESEM and HRTEM. The chemical state and electron-hole recombination behavior of TiO_2 nanotubes were determined using XPS and PL Spectroscopy. The removal efficiency of white and black TiO_2 nanotubes was determined using Cr(VI) aqueous solution. The concentration of chromium ions remained in the solution after exposure to sunlight together with TiO_2 nanotubes for a period of time was measured using UV-Vis spectroscopy. The overview flowchart for this work is shown in Figure 1.3.

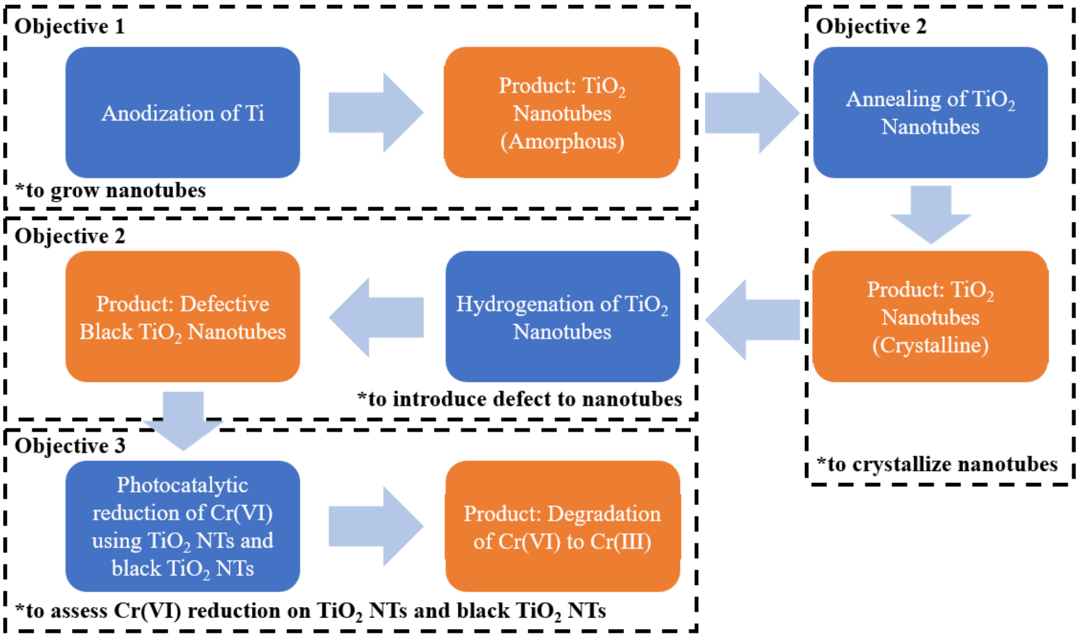

Figure 1.3: Overview flowchart for this work

1.9 Outline of Chapters

This project consists of five main chapters. The chapter one discusses on the introduction, problem statement, objectives and scope of this project. In second chapter, the literature review, basic concept and theory related to nanomaterials, chromium and its removal techniques, white and black TiO_2 nanomaterials and their synthesis methods, and photocatalysis will be discussed. The materials, experimental procedures and characterization techniques will be discussed in chapter three. Meanwhile, chapter four consists of results and discussions regarding this work. Lastly, chapter five includes the conclusion of this project and suggestion of recommendation for future works.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This project is focused on the formation of TiO_2 nanotubes (NTs) on titanium foil by anodization and black TiO_2 nanotubes (NTs) via hydrogenation. The application of TiO_2 NTs and black TiO_2 NTs as photocatalyst for removal of hexavalent chromium (Cr(VI)) is also one of the focuses for this project. In this chapter, the toxicity and pollution of hexavalent chromium in wastewater will be discussed. This chapter also discusses on the techniques that can be used for removal of hexavalent chromium from wastewater and synthesis methods for TiO_2 NTs and black TiO_2 NTs.

2.2 Nanomaterials for Photocatalytic Reaction

Nanomaterials are widely studied nowadays as they may possess remarkable size-dependent properties which are not exist in their larger forms due to its high surface-to-volume ratio. Thus, nanomaterials may have different physical, chemical, electrical and optical properties as compared to the larger forms of same materials due to the differences in size and surface area for reaction to occur. The ability to fine-tune the properties of nanomaterials also contribute to the wide application of nanomaterials in photocatalytic reaction. For photocatalytic reaction, nanomaterials with higher surface area and more active sites for reaction to occur will be required to improve the reaction rate for better photocatalytic performance. Besides that, nanomaterials are very small in size where they are generally within nanoscale range, thus reducing the distance for photogenerated electrons and holes to reach the surface faster for photocatalytic reaction, leading to lower recombination rate of electron and hole pairs (Tahir *et al.*, 2020). The comparison of size between nanomaterials and bulk materials was shown in Figure 2.1. Some examples of nanomaterials for photocatalytic reaction are shown in Table 2.1..

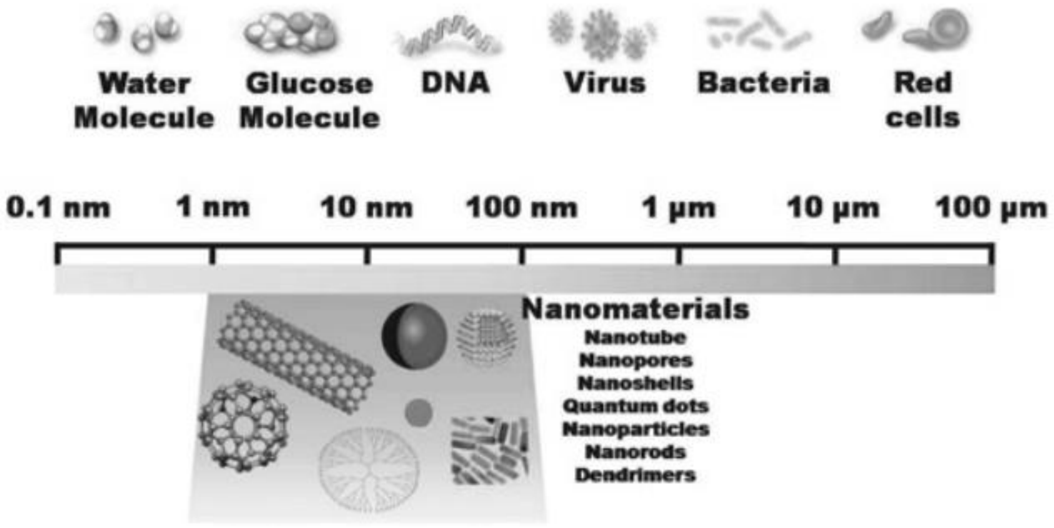

Figure 2.1: Comparison of size between nanomaterials and bulk materials (A. Roy, 2014)

Table 2.1: Examples of nanomaterials for photocatalytic reaction

Nanomaterials	**Photocatalytic application**	**Reference**
TiO_2 nanotubes	Degradation of methylene blue (MB) and paracetamol	(Farrugia *et al.*, 2021)
Fe_2O_2 nanoparticles	Degradation of Rhodamine B (RhB)	(Kusior *et al.*, 2019)
Bi-doped carbon quantum dots / CdS	Photocatalytic hydrogen evolution	(Y. Wang *et al.*, 2018)
Cu-doped TiO_2 nanoparticles	Degradation of MB	(Mingmongkol *et al.*, 2022)
TiO_2 nanoparticles	Removal of cadmium (II) and lead (II)	(Fatehizadeh *et al.*, 2014)
r-GO/Ag nanocomposite	Degradation of MB and RhB	*(Pratheesya et al.*, 2019)
Cobalt oxide-loaded TiO_2/reduced graphene oxide nanocomposite	Degradation of 2-chlorophenol	(A. Sharma and Lee, 2016)

Nanomaterials can be classified into four categories, which are zero-dimensional, one-dimensional, two-dimensional and three-dimensional. Among the four categories of nanomaterials, one dimensional nanomaterial such as nanotube is more preferable to use as photocatalyst in contrast to nanoparticles as nanoparticles have higher tendency to form agglomeration when in contact with liquid, thus reduce the photocatalytic performance. Nanotubes also allow better carrier transport as compared to nanoparticles. The highly ordered and self-organized tubular structure of nanotubes also provide effective site for adherence and reaction (Indira *et al*., 2015).

2.3 Fundamental and Toxicity of Chromium

Chromium is one of the metallic elements with steel grey appearance and high melting point (1907°C). It has body-centered cubic (BCC) crystal structure and the density of 7.19 gcm^{-3} (Lunk, 2015). Chromium is usually obtained from chromite ores ($FeCr_2O_4$). It will transform into green chromic oxide (Cr_2O_3) due to heating. With presence of oxygen, chromium will produce thin oxide layer on surface which is impermeable to oxygen and thus provide protection for metal from corrosion (Shanker, 2019).

The common exposure route for chromium is through ingestion, inhalation and dermal exposures, eventually deposits in body organs, such as heart, lungs, kidney and liver. Excessive amount of chromium accumulated in organs will possess health risk or potential threats to human health as chromium is carcinogenic to humans. Consumption of high concentration of chromium may lead to respiratory, cardiovascular, gastrointestinal, skin ulcerations, nausea, hepatic and renal systems and hematological issue (Karunanidhi *et al.*, 2021). According to Occupational Safety and Health Administration of United States Department of Labor, the exposure limit of chromium should not exceed an airborne concentration of 5μg/m^3. United States Environmental Protection Agency also reported that the acceptable concentration of chromium in drinking water is within 0.1ppm. Meanwhile, the recommended concentration of chromium discharged in water is within the range of 0.05 to 2ppm (Tumolo *et al*., 2020).

The toxicity of chromium is affected by its oxidation state. Hexavalent chromium is highly toxic pollutant as several researches proved that chromium(VI) is more toxic than chromium(III) and study of chromium(VI) even at part per billion also shows toxicity (Pradhan *et al.,* 2017). Besides that, as chromium(VI) is strong oxidizing agent with the ability to accelerate generation of reactive oxygen species, it will have higher toxicity than chromium(III) (Shanker, 2019). However, chromium released into environment due to anthropogenic activity are usually in the form of chromium(VI) (Tchounwou *et al*., 2012).

2.4 Environmental Pollution by Wastewater Containing Hexavalent Chromium

Although around 70% of earth is composed of water, however only 3% of them is fresh water and 0.06% can be used without any contaminants or problems (Ahuja, 2021). Production of wastewater from industry is one of the major sources of water and environmental pollution, especially wastewater that containing heavy metal ions such as chromium, cadmium, lead, arsenic and etc. The presence of heavy metal ions is not desirable in water sources especially drinking water as the heavy metal ions in high concentration may be carcinogenic and causes serious threats to human health and ecological systems. As chromium(VI) is highly soluble in water, it may form $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ (Hudaya *et al*., 2013). Long and continuous exposure to chromium even at very low concentration also may cause adverse effect to organs and immune system. Chromium(VI) can be easily reduced to chromium(III) which is less toxic with the aid of reducing agent.

Chromium(VI) in wastewater usually comes from industrial or anthropogenic activities, such as mining, metal and alloys production and finishing, paint manufacturing, wood processing, electroplating or coating, paper processing, and etc. For instance, chromium(VI) salts can be used for wood preservation, while chromium carbide can be used as additive for production of hard metals and preparation of coating materials. Chromic acids will also be used for electroplating or chromizing which will produce chromium layer on the metal surface for specific purposes, such as improve wear and corrosion resistance. Chromium is also commonly used to produce stainless steel owing to the ability to resist corrosion by forming hard, self-healing oxide layer on the metal surface which can prevent the oxygen from penetrating and reacting with the iron underneath. Besides that, the generation of energy and second-generation fertilizers from incineration of municipal waste may release ashes which will increase the chromium(VI) content in water and soil, is also an important concern that need to be aware *(Tumolo et al.*, 2020). Chromium is also used as chromium based catalysts for various chemical processes, such as oxidative dehydrogenation of light alkanes, ethylene oligomerization and etc. (Malinowski *et al.*, 2020; P. Liu *et al.*, 2021). With the rapid growth and development of industrialization, the release of wastewater that containing heavy metals ions became a huge issue which receiving increased attention.

2.5 Wastewater Treatments for Chromium Removal

Wastewater are usually discharged from domestic activities and industrial processes on daily basis which containing various organic and inorganic chemical compounds. This may pose serious threats to humans and ecosystem as the wastewater may contain pollutants or toxic materials owing to the absence of proper treatment before release into environment. Presence of heavy metal in wastewater also may leads to water crisis due to the toxicity and non-biodegradable nature of heavy metal ions (Ahuja, 2021). Thus, wastewater treatment can be said as the plausible solution to the problems and challenges related to wastewater in order to transform toxic pollutants into less or non-toxic materials.

Conventional wastewater treatments used to remove chromium include chemical precipitation, electrochemical technology, ion exchange, membrane filtration, coagulation and adsorption. All these techniques have their own advantages and drawbacks. For instance, the wastewater treatments are not able to remove heavy metal ions completely and they tend to generate secondary waste products which require additional process for disposal. Some of the wastewater treatments also may requires expensive materials and equipment. Thus, research and development of the wastewater treatment method with maximum effectiveness and efficiency to remove heavy metal ions still under progress. Advanced technologies such as photocatalysis was developed for wastewater treatment with some improvement such as higher removal efficiency and lower sludge or waste generation.

2.5.1 Adsorption

Adsorption is one of the most popular methods for wastewater treatment as it can utilizes both natural and synthetic materials as adsorbents. It is done where the molecules to be removed are concentrated and adhered on the surface of adsorbent by being adsorbed in the pores of adsorbent. However, the high production and regeneration cost of activated carbon has limited the usage of activated carbon for wastewater treatment. A cheaper and more sustainable technology for adsorption technique has been developed where the agricultural by-products and industrial wastes are used as bio-sorbent for removal and recovery of chromium ions from wastewater (Owlad *et al*., 2009).

2.5.2 Chemical Precipitation

The working principle of chemical precipitation in wastewater treatment is conversion of heavy metal ions into insoluble solid as shown in Figure 2.2 under basic conditions which will be adjusted using alkali. According to Pourbaix Diagram, precipitate of chromium (III) hydroxide ($Cr(OH)_3$) will be formed at pH range from 8 to 11 (Mella *et al*., 2015). Precipitation reagent will also be added to aid the formation of insoluble solids in the solutions. To remove the precipitates or insoluble solids, chemical coagulation can be done to convert the precipitates into clump and remove by filtration or sedimentation.

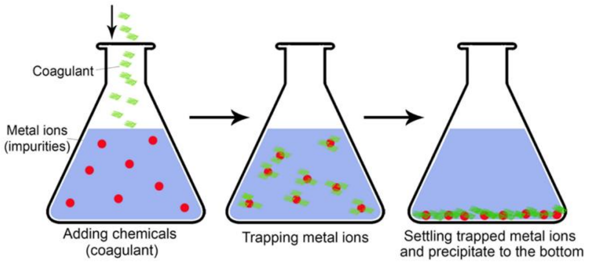

Figure 2.2: Schematic diagram of chemical precipitation for heavy metal removal (Qasem *et al*., 2021).

Through chemical precipitation, the heavy metal usually precipitates in the form of oxides, hydroxides, sulphide or carbonate for removal from wastewater. According to Peng and Guo (2020), direct precipitation of Cr(VI) without the need of reduction to Cr(III) can be done using lead sulphate as precipitating agent and the chromium removed as $PbCrO_4$. However, lead sulfate is one of the second pollutants which will cause harms to the environment, making it not an effective solution for wastewater treatment.

2.5.3 Electrochemical Technology

Electrochemical reduction is a process where the chromium removal is done by reducing chromium(VI) under an acidic condition using acidic medium such as sulphuric acid (H_2SO_4). This is because the reduction of chromium(VI) is acid-dependent and the reduction efficiency of chromium(VI) can be improved by increasing the acid concentration. As the name mentioned, this method is related to electricity, thus electrode will be needed for this process. With the application of DC power supply, free electrons will be supplied as reducing agent into the process for reduction of chromium Peng and Guo (2020). To remove the chromium(III) in the form of precipitates, reagent need to be added into the highly acidic solution after electrochemical reduction in order to allow precipitation of chromium(III) to proceed in an alkaline medium (Shrestha *et al*., 2021).

2.5.4 Ion Exchange

Ion exchange is a reversible stoichiometric chemical process where the heavy metal is removed from wastewater using solid which has the capability for exchange of cations or anions. In other words, the ions from the solution or electrolyte can be exchanged with a similarly charged ions that attached to an insoluble solid to maintain the overall electroneutrality between the solid and electrolyte. For chromium removal, insoluble resin is commonly used by releasing ions of similar charge for exchange without causing structural change in the resin. Resin is the most popular selection for ion exchange process (Peng and Guo, 2020). The efficiency of heavy metal removal by ion exchange method is also depending on the ionic strength and pH where high ionic strength and presence of free acids will reduce the heavy metal removal efficiency (Shrestha *et al*., 2021). The schematic diagram of ion exchange process is shown in Figure 2.3.

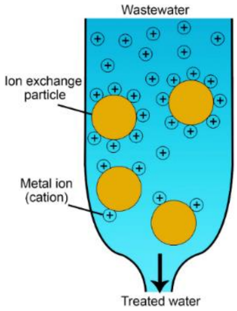

Figure 2.3: Schematic diagram of ion exchange process (Qasem *et al*., 2021)

2.5.5 Membrane Filtration

Membrane filtration is a method where the heavy metals are separated from the wastewater by forcing the wastewater through a semi-permeable membrane via diffusion. The diffusion rate of feed water through the membrane for different type of membrane filtration for heavy metal separation is depending on the concentration of ions present in the water, pressure and temperature applied (Shrestha *et al*., 2021). The schematic diagram of membrane filtration process for heavy metal removal is shown in Figure 2.4.

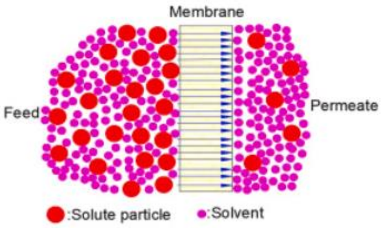

Figure 2.4: Schematic diagram of membrane filtration process for removal of heavy metal (Shrestha *et al*., 2021)

2.5.6 Photocatalytic Reaction

Photocatalytic reaction is a green technique which can be activated by sunlight or ultraviolet light and works by either oxidizing or reducing the heavy metals in the wastewater to be treated. It is gaining more attention as compared to conventional techniques as it is cleaner, cheaper, more practical and it is a promising solution to achieve environmental sustainability. During photocatalytic reaction, the photocatalysts will generate highly reducing photogenerated electrons which will transfer to the conduction band (CB) and strongly oxidizing photogenerated holes in valence band (VB) with irradiation of light which have higher photon energy than the band gap of photocatalysts (X. Gao and Meng, 2021).

Photocatalytic process includes transformation of ionic species into solid metal and deposition of solid metal on the surface of catalysts (Litter, 2015). Photocatalytic process also involves separation of photogenerated holes and electrons, as well as recombination of charge carriers which will reduce the number of excited charge carriers. During the photocatalytic reaction to remove chromium from wastewater, chromium(VI) will be reduced by the photogenerated electron, while the photogenerated holes in valence band will leads to oxidation of water to generate hydroxyl radicals and hydrogen gas. The hydroxyl radical produced during the photocatalytic reaction has strong oxidation power with high oxidation potential (2.80 eV). The hydroxyl radical can be used to decompose organic compounds in water into less harmful compounds in order to treat and clean the industrial wastewater (Lee and Park, 2013). The mechanism of photoreduction of chromium by photocatalyst is shown below (Malakootian and Mansuri, 2015):

$$\text{Photocatalyst} + \text{photon (hv)} \rightarrow h_{VB}^{+} + e_{CB}^{-} \qquad \text{Equation 2.1}$$

$$h_{VB}^{+} + H_2O \rightarrow \bullet OH \text{ (hydroxyl radical)} + H^{+} \qquad \text{Equation 2.2}$$

$$Cr_2O_7^{2-} + 14H^{+} + 6e_{CB}^{-} \rightarrow 2Cr^{3+} + 7H_2O \qquad \text{Equation 2.3}$$

Photocatalytic reduction is also greatly influenced by the pH value. According to Pourbaix diagram, chromium(VI) exists as H_2CrO_4 which is neutral molecule when pH value is below 2.0. Meanwhile, when pH value is greater than 2.0, the predominant chromium species are $HCrO_4^{-}$, CrO_4^{2-} and $Cr_2O_7^{2-}$ which are negatively charged. The surface charge of photocatalysts which serves for heavy metal adsorption purpose will be affected by the pH of solution. At the same time, different photocatalysts have different point of zero ionic charge. When the pH of solution is below the point of zero charge, the surface charge of photocatalysts will be positively charged, leads to stronger adsorption of oppositely charged heavy metal species on the surface of photocatalyst and thus better photocatalytic performance. Thus, the negatively charged chromium(VI) species will be strongly adsorbed to the surface of photocatalysts with positive charge at pH value greater than 2.0 due to the electrostatic interaction between opposite charges (Hudaya *et al.*, 2013). However, the surface charge of photocatalysts will also decrease at pH value above 4.0. The optimum pH value for photocatalytic reduction is in the range of 2.0 to 4.0, where the concentration of anions, such as CrO_4^{2-} and $HCrO_4^-$, is higher, thus enhancing the adsorption of chromium(VI) (Zhao *et al.*, 2019).

There are various techniques that can be used for chromium removal from wastewater and they will be selected based on the criteria that are required based on different situation and condition. The advantages and disadvantages of the wastewater treatment techniques are being discussed in Table 2.2. In this project, the technique selected for chromium removal is photocatalytic reaction.

Table 2.2: Comparison of advantages and disadvantages of various wastewater treatment method (Peng and Guo, 2020) (Crini and Lichtfouse, 2018) (Shrestha *et al.*, 2021)

Wastewater treatment method	**Advantages**	**Disadvantages**
Adsorption	☑ Simple equipment ☑ High effectiveness with fast kinetics for adsorption ☑ Possible use of biosorbent for sustainability	☒ Non-selective of materials for adsorption ☒ High regeneration cost for adsorbent

Chemical precipitation	☑ Simple tools and equipment ☑ Suitable for wastewater with high loads of pollutant ☑ Cost effective and efficient	☒ Production of large amount of sludge / secondary pollution ☒ Less effective for wastewater with high acid content and low heavy metal ions concentration
Electrochemical technology	☑ Rapid and well-controlled operation for separation of pollutants ☑ Less sludge generation ☑ Biodegradable and environmental friendly	☒ High equipment and maintenance cost, and power consumption ☒ pH sensitive process ☒ Requires addition of chemicals
Ion exchange	☑ Rapid and efficient treatment ☑ Capability for selective metal removal and recovery ☑ Lower sludge production	☒ High initial cost due to utilization of resin and high maintenance cost ☒ Tendency to contaminate or foul ion exchange media
Membrane filtration	☑ Little or no generation of additional pollutants ☑ No addition of chemicals required ☑ No phase change	☒ Fouling or clogging of membrane ☒ High operation and maintenance cost
Photocatalytic reaction	☑ Low secondary pollution or sludge generation ☑ Low cost, high stability ☑ Rapid removal or degradation of pollutants	☒ Must be activated by light energy ☒ Light absorption range depends on the width of band gap of photocatalysts

2.6 Titanium and Titanium Dioxide (TiO_2)

Titanium (Ti) is a metallic element located in the Group 4 of periodic table with silvery or greyish appearance. It is the fourth most abundant metallic element distributed in the Earth's crust. However, it is rarely appearing as pure state in nature. Titanium usually can be found in mineral salts, such as ilmenite ($FeTiO_3$). Titanium has low density, which is only 4.51 gcm^{-3}. Titanium will crystallize in hexagonal close packed (hcp) structure, which also known as α-titanium at low temperature, but exhibit body-centered cubic (bcc) structure at high temperature, which also called β-titanium, as shown in Figure 2.5 (Leyens *et al.*, 2003).

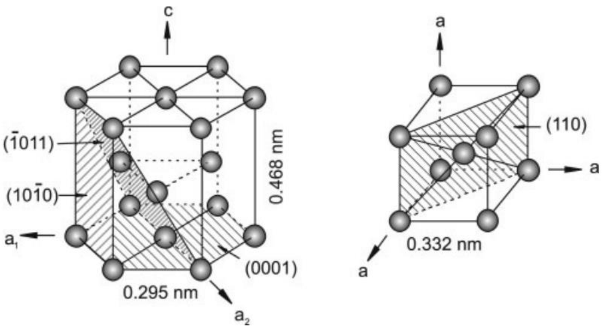

Figure 2.5: Crystal structure of hcp α and bcc β titanium phase (Leyens *et al.*, 2003)

Titanium dioxide (TiO_2), which also known as titania, is made up of titanium and oxygen with covalent bonds and partial ionic character (Sousa and Illas, 1994). It is generally white in colours. TiO_2 is gaining lots of interest from researchers due to its contribution to many applications and fields, for instance photocatalytic reduction of heavy metals and pollutants, pigment, food technology, cosmetics, electronic and electrical devices, building materials, drug delivery system, biomedical materials, antibacterial agents and etc. (Haider *et al.*, 2019). TiO_2 is a semiconductor with wide band gap of 3.0 – 3.2eV which limits its light absorption to ultraviolet light range. In other words, the photon energy needs to have energies higher than the band gap energy of TiO_2

in order for electron transport between valence band and conduction band and creation of holes in valence band.

2.7 TiO_2 Nanomaterials as Photocatalysts

Photocatalyst is a material which play an important role in photocatalysis to speed up the reaction for heavy metal removal with photon. As a semiconductor photocatalyst, TiO_2 need to fulfil several conditions, where it should not possess any form and properties changes during the photocatalytic reaction and it is required to provide different mechanism routes to achieve acceleration in the rate of photocatalytic reaction (Lee and Park, 2013). TiO_2 is a common photocatalyst used for photocatalytic reaction as it possesses high chemical stability and photostability, good commercial availability, low toxicity, cost effective, good thermal stability and excellent resistance to light-induced corrosion (Z. Li *et al*., 2022).

For photocatalytic reaction, the photogenerated electrons need to be reduced to form superoxide acid ($\bullet HO_2$) and superoxide anion radicals ($\bullet O_2^-$) as shown in Equation 2.4 and 2.5 respectively. Meanwhile, photogenerated holes are required for oxidation of OH^- to form hydroxyl radicals ($\bullet OH$) as demonstrated in Equation 2.6. The superoxide anion radicals and hydroxyl radicals are strong oxidizing agents which will oxidize numerous organic and inorganic compounds and pollutants (Yan *et al*., 2013).

$$O_2 + H^+ + e^- \rightarrow \bullet HO_2 \qquad \text{Equation 2.4}$$

$$O_2 + e^- \rightarrow \bullet O_2^- \qquad \text{Equation 2.5}$$

$$OH^- + h^+ \rightarrow \bullet OH \qquad \text{Equation 2.6}$$