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
°C	Degree celcius
°C/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