PREPARATION OF COBALT DECORATED TITANIUM DIOXIDE NANOTUBES BY ELECTRODEPOSITION

This report is submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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I hereby, declared this report entitled "Preparation of Cobalt Decorated Titanium Dioxide Nanotubes by Electrodeposition" is the result of my own research except as cited in references.

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Date : 31 May 2017

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons). The member of the supervisory committee are as follow:

………………………................................

(Dr. Syahriza Binti Ismail)

ABSTRAK

Kobalt titanium dioksida nanotube telah disintesis melalui kaedah pengenapan. Keputusan XRD menunjukkan Co-TiO_2 nanotube sahaja terdiri daripada fasa anatase. Struktur dan morfologi kobalt dalam TiO_2 nanotube dianalisa oleh FESEM, Raman Spektroskopi, X-ray Diffraction (XRD) dan sifat-sifat fotokatalitik diuji dengan lampu UV. Peningkatan kepekatan kobalt mempertingkatkan degradasi metil oren (MO) di penyerapan spectrum UV-vis. Kobalt menghalang pertumbuhan bijirin TiO_2, aglomerasi dan beralih penyerapan band TiO_2 dari ultraviolet (UV) ke rantau kelihatan. Aktiviti fotokatalitik sampel dianalisa untuk menguji kemerosotan degradasi metil oren (MO). Kehadiran 0.05mM kepekatan kobalt klorida dalam TiO_2 menyebabkan pemangkin dengan aktiviti tertinggi di rantau kelihatan.

ABSTRACT

Cobalt decorated titanium dioxide nanotubes were synthesized by electrodeposition method. X-Ray diffraction (XRD) results showed that Co-TiO_2 nanotubes only include anatase phase. The framework substitution of Co in TiO_2 nanotubes were established by Field Emission Scanning Electron Microscope (FESEM), Raman Spectroscopy, X-ray Diffraction (XRD) and the photocatalytic properties is tested by UV lamp chamber. The increase of cobalt concentration enhanced degradation of methyl orange (MO) in the UV-Vis absorption spectra. The Co suppressed the growth of TiO_2 grains, agglomerates them and shifts the band absorption of TiO_2 from ultraviolet (UV) to visible region. The photocatalytic activity of samples were tested for degradation of methyl orange (MO) solutions. The presence of 0.05 mM of cobalt chloride concentration in TiO_2 resulted in a catalyst with the highest activity under visible irradiation.

DEDICATION

Only

my beloved father, Wee Poh Hock

my appreciated mother, Marilyn Lenih Lihan

my adored brother and sisters,

Hillary Wee Ching Kun

Christy Wee Fui Yen

Eileen Wee Hui Yien

Kathy Wee Mi Lang

my friend, Chai Chang Wei

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LIST OF ABBREVIATIONS

1D	-	One-Dimensional
2D	-	Two-Dimensional
3D	-	Three-Dimensional
$C_2H_6O_2$	-	Ethylene Glycol
$C_3H_8O_3$	-	Glycerol
CBD	-	Chemical Bath Deposition
Co	-	Cobalt
$CO\ (CH_3)_2$	-	Acetone
FESEM	-	Field Emission Scanning Electron Microscope
H_2O_2	-	Hydrogen Peroxide
H_3BO_3	-	Boric Acid
HER	-	Hydrogen Evolution Reaction
MO	-	Methyl Orange
NH_4F	-	Ammonium Fluoride
NHE	-	Normal Hydrogen Electrode
PEC	-	Photoelectrochemical
SnO_2	-	Tin Dioxide
TiO_2	-	Titanium Dioxide
UV	-	Ultraviolet
VB	-	Valence Band
WBGS	-	Wide Band Gap Semiconductor
XRD	-	X-ray Diffraction
ZnO	-	Zinc Oxide

LIST OF SYMBOLS

°C	-	Degree Celsius
Eg	-	Energy Gap
eV	-	Electron Volt
g	-	Gram
kV	-	Kilo Volt
ml	-	Milliliter
mM	-	Milli Molar
nm	-	Nanometer
ppm	-	Parts Per Million
rpm	-	Revolutions Per Minute
V	-	Volt

CHAPTER 1

INTRODUCTION

1.1 Background Study

The first report in 1999 described how easy and how difficult it was through comprehensible yet perfect electrochemical anodization of a titanium foil to develop ordered channel arrays of Titanium Dioxide (TiO_2) nanotubes. This recommendation has encouraged passionate fieldwork activities that emphasis the adjustment, development, properties together with the application. As a matter of fact, including all of the transition-metal oxides, the most substantially research material is TiO_2 (over 40 000 publications within 10 years), that compose TiO_2 to become among the most studied compounds in science material (Roy et al., 2011).

TiO_2 is n-type and wide band gap semiconductor (WBGS) which allows them to function at higher voltage, temperatures and frequencies compared to ordinary semiconductor. We also know that TiO_2 has outstanding stability, effective photoactivity, non-toxic and low cost. Whereas in nanotubes category, TiO_2 shows high aspect ratio and surface area in semiconductor nature. Not to mention, there are two types of photochemical reaction which are photo-induce hydrophilic conversion of TiO_2 and photo-induce redox reaction of adsorbed substance on TiO_2 surface area when radiated with UV light. To upgrade the optical and electronics properties of TiO_2, this metal oxide is usually being doped or hybrid with other metal or element. This is to improve the ability of the performance for certain application such as photocurrent and photocatalytic (Roy et al., 2011).

There are few techniques that can used to produce nanotube oxide such as sol-gel technique, hydrothermal synthesis, co-precipitation and thermal decomposition. This process would produce nanotube structure. Alternatively, electrodeposition method can be used to deposit the cobalt layer on the TiO_2. This method uses electric current to allow the ions transfer and in the end it will form metal coating on the electrode. The reason for this process being used is because electrodeposition is a low cost and able to improve the mechanical characteristics of metals (Pelaez et al., 2012).

This research aimed to prepare cobalt decorated TiO_2 nanotubes by electrodeposition. The photocatalytic properties of the formed structures will be used for the photocatalysis applications. At the moment, there are not so many research regarding TiO_2 cobalt decorated.

1.2 Problem Statement

There are two types of photochemical reaction which are photo-induce hydrophilic conversion of TiO_2 and photo-induce redox reaction of adsorbed substance. These two purposes have made TiO_2 as an alternative choice as photocatalyst. Even so, TiO_2 can only be actuate by UV light from solar or manufactured radiation sources, and has high rates of recombination of electron-hole pairs that will restrict the photocatalysis effectiveness. To point out, there are two major problems for TiO_2 semiconductor; grow their parameter of activation into visible parameter and lessen the photogenerated electron-hole pair recombination.

For this reason, it is suggested that the concept of cobalt decorated TiO_2 that will have dissimilar conduction band level to form bi-component semiconductor. Cobalt is a p-type semiconductor material with narrow band gap that can be activated by visible light. Nonetheless, it has poor stability. Therefore, by incorporate these materials, n-p type's semiconductor can be created. This contemporary n-p type semiconductor can be actuate by visible light. The configuration of new bi-component semiconductor can lead to the electron hole recombination rate reduction. Consequently, it can be applied using radiation of visible light. This pair can boost the efficiency and semiconductor properties as photocatalyst.

Firstly, anodization method will be used to form TiO_2 nanotubes then the cobalt will be deposit via electrodeposition method. Also, the synthesis bi-component TiO_2-cobalt nanotubes semiconductor by electrodeposition process is scrutinized as well as the morphology and structural of the structures. The evaluation of photoelectrochemical properties such as photocurrent density, photoresponse and photoconversion efficiency of the semiconductor will be done by radiating the oxide using visible light.

1.3 Objectives

i. To synthesis cobalt decorated TiO_2 nanotubes by electrodeposition.
ii. To characterize the structural and morphology properties of cobalt decorated TiO_2 nanotubes by electrodeposition.
iii. To study the photocatalytic properties in TiO_2 based materials for the photocatalysis applications.

1.4 Scope

This research covered the literature study on TiO_2 nanotubes, the preparation of cobalt decorated TiO_2 nanotubes and also the photocatalytic properties of TiO_2. The synthesis of TiO_2 nanotubes is by electrodeposition process or known as electroplating process. The parameters such as molarity and time are studied. The phase, microstructure and morphology characterization on TiO_2 nanotubes was determined by using Field Emission Scanning Electron Microscope (FESEM), Raman Spectroscopy, X-ray Diffraction (XRD) and the photocatalytic properties is tested by UV lamp chamber.

1.5 Limitation of Study

The limitations of this study are:

i. The weak bonding between cobalt and TiO_2 nanotubes prevent the effective electron transfer.
ii. In situ preparation of cobalt decorated TiO_2 on nanotubes to promote electron transfer efficiency is still demanding and difficult.

CHAPTER 2

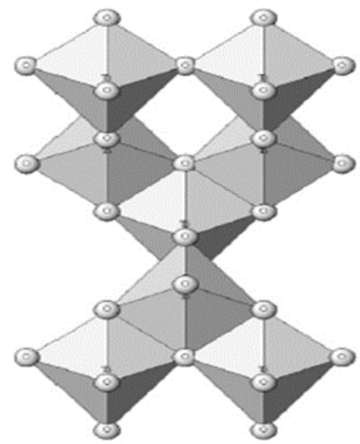
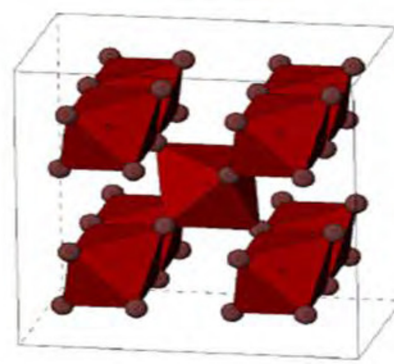
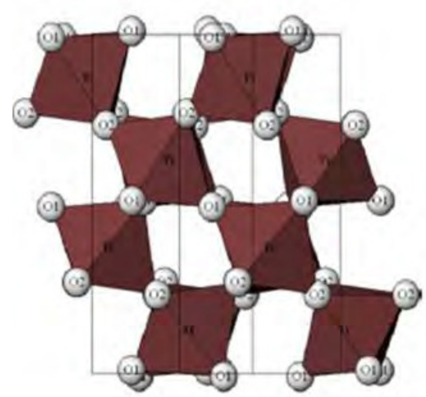
LITERATURE REVIEW

This chapter will discuss more on the literature review that associated to the general information of Titanium Dioxide (TiO_2), its advantages and properties. The later section will concentrate on the Cobalt. Next is the TiO_2 nanotubes, its general properties and formation. The fabrication is concerned mostly on the growth of TiO_2 nanotubes by anodization. The use of TiO_2 as photocatalyst and the electrodeposition for cobalt decorated on TiO_2 will be addressed. Lastly, the photocatalytic ability for the photocatalytic degradation of TiO_2 nanotubes in particular will be reviewed as well.

2.1 Titanium Dioxide (TiO_2)

TiO_2 can be found in three phases (rutile, anatase and brookite) and it has different crystal structure and also physical properties. In photocatalytic, the most energetic crystal phases are anatase and rutile while brookite is seldom being used. The order of this alteration is due to the atom of titanium encircled octahedral by the atom of oxygen. Anatase has a cubic close oxygen atom packing with half of the tetrahedral space loaded with titanium and it has the lowest density and refractive index. But there is not much difference between the phases of TiO_2. While rutile, it has the hexagonal close oxygen atoms packing with half of the octahedral space loaded with titanium and it has the highest density and refractive index among all the TiO_2 phases. Finally, brookite has the orthorhombic crystal structure and six oxygen atoms encircle the titanium atom which located at the centre. More than 973K temperature where it is stable in thermodynamic, both anatase and brookite will become rutile (Nguyen et al., 2016).

Table 2.1: Crystalline structures of Titanium Dioxide, TiO_2 (Pelaez et al., 2012).

Phases	Structure	Diagram
Anatase	Tetragonal	
Rutile	Tetragonal	
Brookite	Orthorhombic	

2.1.1 Advantages of TiO_2

The benefits of titanium dioxide (TiO_2) are due to the low price, non-toxic and stable in chemical of the compound itself. Not to mention, TiO_2 had acquire attention in degradation of photocatalytic for the organic pollutant. Among distinct configuration of TiO_2, anatase is chosen for photocatalytic constituent because of its outstanding transfer or charge properties (Nguyen et al., 2016).

Anatase and rutile are acknowledged to be materials which are potentially active for numerous applications. It consist of three phases (anatase, rutile and brookite), of which TiO_2 can be found. However, the major disadvantages from all these applications is their UV region absorption, which matches to only not more than 5 % of solar radiation. Uniquely, to give it a better choice for photocatalysis applications, incorporating of a little impurity ions concentration alters its absorption to the visible region (Choudhury et al., 2012).

Provided that their capability in photocatalytic activity for degradation of hazardous contaminant, semiconductors that are suitable for photocatalytic such as ZnO, SnO_2 and TiO_2, are being recognized by more researchers. Owing to its environmental safety and good stability, TiO_2 is believed to be among one of the most favorable materials (Jiang et al., 2015).

2.1.2 Properties of TiO_2

2.1.2.1 Photocatalytic properties

In spite of sustaining the outstanding photocatalytic properties of TiO_2 and to enhance its light-absorption properties, altering TiO_2 with noble metals (gold, silver or platinum), lower band-gap semiconductors and ternary semiconductors are being done (Nguyen et al., 2016). TiO_2 doped with noble metal is proven to be one of the perfect techniques to produce hydrogen. This is because of its potential to boost electron-holes pair dissociation and the methods of photoinduced reduction. TiO_2 conduction band has higher energy compared to Fermi level of the noble metal. The photo promoted electrons can drift to the metal, ditching TiO_2 valence band with the holes (Sadanandam et al., 2013).

Moreover, when low band-gap semiconductors incorporate with TiO_2, they will produce outstanding photoelectrochemical properties because the incorporate band-edge levels, under visible light irradiation are able to drive the water redox process (Nguyen et al., 2016).

However, the ultraviolet part of solar spectrum absorption is limited due to the TiO_2 intrinsic band gap. Additionally, TiO_2 electron transfer rate is low because of its poor conductivity, triggering the electron-hole pair's recombination, and restrict their broad applications (Wang et al., 2016).

2.1.2.2 Optical properties

In the meantime, they are various ventures and trials in the process of altering the physical, chemical and TiO_2 optical properties through transition metal oxides doping. Through doping with metals, its photoelectrochemical activities and its photocatalytic activities of TiO_2 thin films is boosted up. Doping with the impurity and annealing intensify the properties of the structural and the optical. Although few other dopants have been considered, yet Co doped with TiO_2 thin films is leading due to the ferromagnetism properties at the state of room temperature that makes them meet the requirements of spintronic applications not forgetting the photocatalytic properties in the visible parameter region (Subramanian et al., 2008).

Subramanian et al. (2008) also stated that the crystallinity and the films optical properties were determined from sol–gel process and the organic materials from which it is formed. When undergo heat treatment at elevated temperature, the films get compact and the crystallinity are increasing, because of its organic materials evaporate, and upgrading the films refractive index. The index is increasing with the increase of concentration of cobalt dopant and this is probably because of the density in film increases.