UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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EFFECT OF HCl CONCENTRATION, ANODIZATION VOLTAGE AND TIME ON MICROSTRUCTURE, PHASE AND PHOTOCATALYSIS ACTIVITY OF TITANIUM DIOXIDE FILM

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

by

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DECLARATION

I hereby, declared this report entitled "Effect of HCl Concentration, Anodization Voltage and Time on Microstructure, Phase and Photocatalysis Activity of Titanium Dioxide Film" is the results of my own research except as cited in the references.

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Date	: 02 Jun 2015

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Material) (Hons.). The members of the supervisory committee are as follow:

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(Dr. Shahriza binti Ismail)

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(Dr. Lau Kok Tee)

ABSTRAK

Titanium dioksida (TiO_2) telah digunakan secara meluas untuk aplikasi fotopemangkinan. Secara konvensional, TiO_2 dihasilkan oleh teknik seperti proses sol-gel dan kimia wap pemendapan. Walau bagaimanapun, teknik ini sama ada mahal, rumit, atau menghasilkan filem TiO_2 dengan sifat-sifat mekanikal yang lemah. Oleh itu, projek ini adalah bertujuan untuk membuat filem TiO_2 dengan penganodan daripada foil Ti. Parameter penganodan seperti voltan, masa dan kepekatan HCl adalah penting untuk menghasilkan filem TiO_2 yang sesuai untuk aplikasi tertentu. . Objektif projek ini adalah, mensintesis filem TiO_2 oleh penganodan foil titanium, mencirikan filem morfologi TiO_2 mikrostruktur dan permukaan mencirikan sifat-sifat fotopemangkinan filem TiO_2. Raman Spectra menunjukkan anatase dan rutil lebih sukar untuk membentuk dalam HCl elektrolit pada voltan yang lebih tinggi dan masa penganodan yang lebih lama. Bidang Pelepasan Mengimbas mikroskopi elektron Keputusan menunjukkan tiada nanopore diperhatikan dalam mikrostruktur permukaan tidak seragam sampel. Filem TiO_2 dikesan foil Ti dan telah disahkan oleh tenaga spektroskopi serakan. Mikroskop imbasan elektron menunjukkan peningkatan voltan dan penganodan gunaan masa, menyumbang kepada kekasaran permukaan yang lebih tinggi pada sampel penganodan. Sampel menunjukkan peningkatan dalam kekasaran permukaan. Didapati sampel penganodan di 10 min dan 5 V menunjukkan prestasi fotopemangkinan lebih rendah berbanding sampel anodized pada masa yang lebih lama (iaitu 20 min). Parameter terbaik untuk filem TiO_2 disintesis oleh penganodan foil Ti adalah lebih rendah voltan 5 V dan lebih pendek tempoh masa 10 min.

ABSTRACT

Titanium dioxide (TiO_2) is used for wide photocatalysis applications. Conventionally, TiO_2 was produced by techniques such as sol-gel process and chemical vapor deposition. However, these techniques are either costly, complicated, or produces TiO_2 film with poor mechanical properties. Hence, this project was serves to fabricate the TiO_2 film by anodization of titanium foil. Anodization parameters such as voltage, time and HCl concentration were important to produce TiO_2 film that suits to particular applications. The objectives of this project is, to synthesize TiO_2 film by anodization of titanium foil, characterize the microstructure, phase composition and photocatalysis properties of the photocatalysis TiO_2 film. Raman Spectra show anatase and rutile are more difficult to form in HCl electrolyte at higher voltage and longer anodization time. Field Emission Scanning electron microscopy (FESEM) results showed no nanopore observed in the non-uniform surface microstructure of the sample. Nanothickness TiO_2 film was detected Ti foil and was verified by energy dispersive spectroscopy (EDS). Scanning electron microscopy (SEM) result showed an increase of applied voltage and anodization time, contributed to higher surface roughness on the anodized samples. Samples exhibited an increase in surface roughness. It was found the sample anodized at 10 min and 5 V exhibited lower photocatalytic performance as compared to samples anodized at longer time (i.e. 20 min). Hence, the best parameter for TiO_2 film synthesized by anodization of Ti foil was in lower voltage 5 V and shorter time duration 10 min.

DEDICATION

Dedicated to my beloved family members especially my parents, lecturers, and also to all my friends.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

CO	-	Carbon Monoxide
Cr	-	Chromium
EDS	-	Energy Dispersive Spectroscopy
Fe	-	Iron
FESEM	-	Field-emission scanning electron microscopy
HCl	-	Hydrocloric Acid
Hg	-	Mercury
H_2	-	Hydrogen Gas
H_2O	-	Water
H_2S	-	hydrogen Sulfide
Ti	-	Titanium
TiO_2	-	Titanium Dioxide
TiO_6	-	Titanium octahedron
UV	-	Ultraviolet
M	-	Molarity
MB	-	Methylene blue
Ni	-	Nickel
N_2	-	Nitrogen

NO_2	-	Nitrogen Dioxide
NO	-	nitric Oxide
PVD	-	Physical Vapor Deposition
S	-	Sulfur
SEM	-	Scanning Electron Microscopy
SO_2	-	Sulphur dioxide
Ti	-	Titanium
Å	-	Angstrom
λ	-	Wavelength
ε	-	Strain
ω	-	Omega
α	-	Alpha
β	-	Beta
γ	-	Lambda
e^-	-	Negative electron
h^+	-	Positive hole

CHAPTER 1

INTRODUCTION

1.1 Background History and Application

Photocatalyst can be in form such powders and coating. In 1938 there are a report on photobleaching of dyes where it was happen when the UV absorption produces an active oxygen species on the TiO_2 surface (Hashimoto et al; 2005).

In 1970's, TiO_2 was used to produce hydrogen gas (H_2) using photocatalytics. TiO_2 was used in form of electrode where it was contributed to the production sites of the H_2 and O_2 gases, and then recombine back into water (Hashimoto et al; 2005). By the mid 1980"s, H_2 production by TiO_2 photocatalyst became unattractive as other semiconductors were better suited for future research and development (Hashimoto et al; 2005).

In early 1990s, TiO_2 film photocatalysis have been investigated under weak UV light for photocatalytic cleaning, antibacterial, and hydrophilic characterization. Photocatalytic antibacterial effect decomposition reaction of photocatalytic can be applicable to microorganisms. In fact, Escherichia coli (E. coli) cells can completely eliminated by photocatalysis of TiO_2 after about one week under a UV irradiation of 1 mW/cm^2 (Hashimoto et al; 2005).

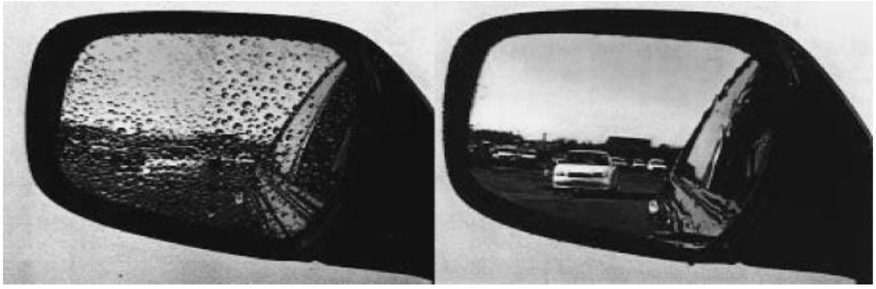

Figure 1.1: Anti-fogging effect of automobile side-view mirror: conventional mirror (left) and TiO_2-coated mirror (right) (Hashimoto et al; 2005).

The design of nanostructure of TiO_2 was introduced in 21st century (Hashimoto et al.; 2005). Sensitivity of TiO_2 was extended to visible light range by substituting. Cr, Fe or Ni for Ti site, but the method was not accepted wider due to the lack of reproducibility and chemical stability (Hashimoto et al; 2005). Commercial cements containing TiO_2 that was introduces to reduce surface pollution. The notable Italcementi‟s projects is the Jubilee church in Rome, shown in Figure 1.2 and constructed using white cement containing TiO_2 (Hashimoto et al; 2005).

Figure 1.2: Jubilee Church of Rome, Exterior made from Italcementi Concrete Containing TiO_2 (Hashimoto et al; 2005)

1.2 Applications

Table 1.1: Applications of TiO_2 (Abdullah & Sorrell; 2010)

Application	**Explanation / Applications**
White pigments	Used in paint, plastic, inks, paper, leather, textiles and cosmetic products
Metal oxide semiconductor field effect transistor (MOSFET)	High dielectric constants ($\varepsilon = 100$)
Varistors	Used in ceramic and electric devices
Gas sensors	As humidity control To control the air/fuel mixture in car engines Utilized in determination of oxygen and CO at high temperatures (>600˚C)
Biomaterials	Bone implant coatings As bone substituent As reinforcing mechanical support
Photo-assisted degradation of organic molecules	Purification of waste water Used in operating rooms in hospital Self-cleaning coating on car windshields
Anti cancer treatment	Photochemical treatment
As thin film optical interference coating	Antireflective coating Dielectric mirrors for lasers Metal mirrors with enhanced reflection Filters
As a protective coating	Corrosion resistant barriers
Photocatalysts (solar cells)	Used in the production of hydrogen and electric energy As anti-reflection coatings
Sunscreen	As UV absorber in sunscreen cream with high sun protection factors

Food	Foodstuff, food colouring (E-171)
Pharmaceuticals	As tablet coating, toothpaste
As catalysts	Selective reduction of NOx to N_2, Hydrogen production by gas shift production, CO oxidation by O_2, H_2S oxidation to S, Reduction of SO_2 to S by CO, NO_2 storage
Used in fluxes and ceramics	Raw materials
Li-based batteries	Anatase form is used as anode material
Electrochromic devices	Thin film coating

1.3 Problem Statement

Photocatalytic degradation is an effective way of transforming organic pollutants into harmless end products at ambient conditions using light and photocatalyst. TiO_2 shows different characteristics and properties in different phases. Anatase, brookite, and rutile are three different phases (crystalline forms) of TiO_2. There have different thermal stability, crystal size, and reactive surface area. Surface area and microstructure of TiO_2 easily affect its photocatalysis properties (Hanaor & Sorrell; 2010). An increases of total surface area increases the pollution reduction potential of TiO_2 as it increases the surface area for reaction with pollutants (Hanaor & Sorrell; 2010).

Suitable processing method and parameters are important to produce TiO_2 film that suits to particular applications. Nevertheless, the choice of synthesis method is determined by cost control, quality of product, safety issues, etc. Current available production synthesis such as physical vapour deposition method is costly or involving complicated process (Erol et al; 2014). Anodization is a less expensive electrochemical method to produce TiO_2 film. TiO_2 film synthesized by this technique has anti-galling and wear resistant properties. The film is continuous and does not flake off in highly stressed areas and has increase in fatigue strength increase of 15-20% due to its homogeneous surface treatment.

1.4 Objective

The purpose of this research is to synthesize TiO_2 thin film on titanium substrates using anodization method. Below are the specific objectives for this research;

a) To synthesize TiO_2 film by anodization of titanium foil.
b) To characterize microstructure and phase composition of the TiO_2 film.
c) To characterize photocatalysis property of the TiO_2 film.

1.5 Scope

Investigation of the relationship between anodization parameters, phase composition and microstructure of TiO_2 film were conducted. Effect of three anodization parameters: voltage, anodizing duration and HCl acid concentration were studied. Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FESEM) are used to characterize the microstructure of TiO_2 film. Raman spectroscopy is used to characterize phase composition of the TiO_2 film. The decomposition rate of methylene blue is used to asses the photocatalytic activity of the TiO_2 film.

CHAPTER 2

LITERATURE REVIEW

The literature review of the titanium dioxide (TiO_2) was discussed in this chapter. The TiO_2 material and its general physical properties and crystallography is discussed in the first section. Next, the photocatalyst properties are reviewed in relationship to TiO_2 is being used as the thin film coating on titanium. Anodization is discussed and compared with other fabrication techniques.

2.1 General Materials Properties

TiO_2 exists in three different polymorphous structures: Anatese, rutile, and brookite. Anatase and brookite appear as metastable phases compared to more stable rutile phase (Hanaor & Sorrell; 2010).

Rutile has a tetragonal cystalline stucture (refer Figure 2.1(a)), anatase has a tetragonal cystalline stucture (refer Figure 2.1(b)), and brookite has an orthorhombic cystalline stucture (refer Figure 2.1(c)) (Pavemaintenance, 2014). Details of crystallographic and physical properties of the rutile, anatase and brookite are summarized in Table 2.1.

(a) (b) (c)

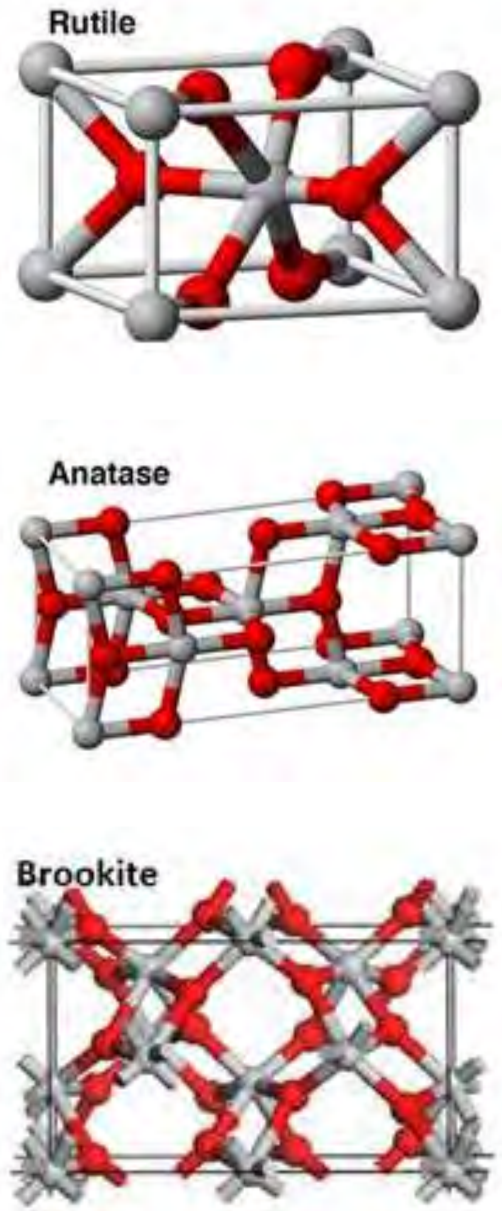

Figure 2.1: Crystal structure of: (a) Rutile, (b) Anatase, and (c) Brookite (Grey coloured atoms – Titanium, Red coloured atoms – Oxygen) (Pavemaintenance; 2014)

Table 2.1: Crystallographic and Physical Properties of Rutile, Anatase & Brookite. (Nakaruk; 2010)

Polymorphs Structure		**Rutile**	**Anatase**	**Brookite**
Chemical Formula		TiO_2	TiO_2	TiO_2
Crystal System		Tetragonal	Tetragonal	Orthorhombic
Point group according to Schonflies		D_{2h}	D_{2d}	C1
Unit cell parameter (nm)	a	0.459	0.536	0.915
	b	0.459	0.536	0.544
	c	0.296	0.953	0.514
Moh"s Hardness		7.00-7.25	5.5-6.0	5.5-6.0
Density (g/cm^3)		4.13	3.79	3.99
Refractive Index (25˚C) (λ = 5893 Å)		2.61	2.56	2.58