UNIVERSITI TEKNIKAL MALAYSIA MELAKA

(Synthesis of TiO_2 Nanostructure by Anodic Oxidation)

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

by

(Nurul Asyikin Binti Ahmad Nor Hisham)

(B051310006)

(920213-08-6170)

FACULTY OF MANUFACTURING ENGINEERING

2016

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

TAJUK: Synthesis of TiO_2 Nanostructure by Anodic Oxidation

SESI PENGAJIAN: 2013/14 Semester 2

Saya **NURUL ASYIKIN BINTI AHMAD NOR HISHAM**

mengakumembenarkanLaporan PSM inidisimpan di Perpustakaan Universiti Teknikal Malaysia Melaka (UTeM) dengansyarat-syaratkegunaansepertiberikut:

1. Laporan PSM adalah hak milik Universiti Teknikal Malaysia Melaka dan penulis.
2. Perpustakaan Universiti Teknikal Malaysia Melaka dibenarkan membuat salinan untuk tujuan pengajian sahaja dengan izin penulis.
3. Perpustakaan dibenarkan membuat salinan laporan PSM ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. **Silatandakan (✓)

☐ SULIT (Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia sebagaimana yang termaktub dalam AKTA RAHSIA RASMI 1972)

☐ TERHAD (Mengndungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)

☐ TIDAK TERHAD

Disahkanoleh:

_________________________ _________________________

AlamatTetap:
NO 33, Lorong 27,
Taman Desa Jana 3,
34600 Kamunting,Perak

Cop Rasmi:

Tarikh: _________________________

Tarikh: _________________________

** Jika Laporan PSM ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa / organisasi berkenaan dengan menyatakan sekali sebab dan tempoh laporan PSM ini perlu dikelaskan sebagai SULIT atau TERHAD.

DECLARATION

I hereby, declared this report entitled "Synthesis of TiO_2 Nanotubes by Anodic Oxidation" is the results of my own research except as cited in references.

Signature : ……………………………………………………….

Author's Name : NURUL ASYIKIN BINTI AHMAD NOR HISHAM

Date : ……………………………………………………...

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfilment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

…………………………………………………………………………..

(DR.SYAHRIZA BINTI ISMAIL)

ABSTRAK

TiO_2 nanotiub telah disintesis pada kepingan Ti tulen dengan kaedah pengoksidaan anodic. Beberapa parameter telah disiasat seperti kesan voltan dan masa. Morfologi dan fasa TiO_2 nanotiub yang dibentuk telah dicirikan. Kesan penyepuhlindapan dibentuk nanotube TiO_2 struktur kristal dan beberapa fasa dapat diperhatikan seperti anatase dan rutile. Sample optimum adalah dalam larutan elektrolit organik yang mengandungi 95 ml 1M daripada EG ditambah kepadanya, 5 ml H_2O_2 dan 0.3 g ammonium florida (NH_4F) mengikuti disepuh lindap pada 450^oC adalah tertakluk pada ujian fotopemangkinan. Bidang Pelepasan Mikroskop Imbasan Elektron (FESEM) untuk pengimejan pembesaran Ultra-tinggi dalam permerhatian. XRD dan spectroskopi Raman mengesahkan fasa-fasa seperti anatase dan rutile yang terbentuk selepas proses penyepuhlindapan. Raman spektroskopi telah digunakan untuk menyokong morfologi dan fasa yang diperolehi darI analisis FESEM dan XRD. Sebagai kesimpulan, struktur TiO_2 nanotiub dibentuk pada kepingan Ti tulen ada 30 minit, 60 V dalam elektrolit semasa pengoksidaan anodi, diikuti dengan penyepuhlindapan pada 450^oC menghasilkan morfologi dan fasa yang terbaik. Sample yang mempunyai optimum parameter diuji dengan metil oren untuk proses pemfotorosotan.

ABSTRACT

TiO_2 nanotubes have been synthesized in pure Ti sheet by anodic oxidation method. Various parameters were investigated such as the effect of voltages and time. TiO_2 nanotube morphology and phase formed were characterized. Annealing effect of TiO_2 nanotubes formed crystal structures and phases can be observed as anatase and rutile. The optimum sample is in the organic electrolyte solution containing 95 ml of the EG added to 1M, 5 ml H_2O_2 and 0.3 g of ammonium fluoride (NH_4F) followed annealed at 450^oC is subject to photocatalytic tests. The Field Emission Scanning Electron Microscope (FESEM) used for Ultra-high magnification imaging observation. XRD and Raman Spectroscopies confirm phases such as anatase and rutile formed after the annealing process. Raman spectroscopy used to support the morphology and phase obtained from FESEM and XRD analysis. In conclusion, the structure of TiO_2 nanotubes formed on sheets of pure Ti is 30 minutes, 60 V in the electrolyte during oxidation anode, followed by annealing at 450^oC to produce the best morphology and phase. The sample has tested the optimal parameters for process degredation of methyl orange.

DEDICATION

To my beloved parent and husband.

ACKNOWLEDGEMENT

It takes tons of hard work to complete this thesis, with the help from many kind and supportive persons. I would like to take this opportunity to express my gratefulness and gratitude to those who have rendered their valuable advice, support and guidance to me during the long journey of completing this thesis. First and foremost, I would like to thank my supervisor Dr.Syahriza Binti Ismail for her relentless support, advices and guidance throughout the entire project. Not to forget the research team: Katerina Anak Birang dan Noor Farah Iddayu Binti Abu Bakar for all assistance and guidance provided all this while. I am greatly touched by the commitments and dedications they shown. Without the support and guidance, I would not be able to completed this study. Besides, I would like to thank Universiti Teknikal Malaysia Melaka (UTeM) for the willingness to give me an opportunity to gain knowledge, widen my experience, explore my talent and prepared my future for the past four years. I really appreciate helps provided by Faculty Manufacturing Engineering in term of the facilities, equipment and advices for me to complete my challenging final year project. Without the moral support and understanding from my family, it would be impossible for me to complete this thesis. I wish to express my biggest gratefulness and love to my family members.

TABLE OF CONTENT

CHAPTER 4: RESULT & DISCUSSION

LIST OF TABLES

LIST OF FIGURE

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

0D	-	Zero Dimensional.
1D	-	One Dimensional.
2D	-	Two Dimensional.
Et al	-	etalii
FESEM	-	Field Emission Scanning Electron Microscope
SEM	-	Scanning Electron Microscope
XRD	-	X-Ray Diffraction
EG	-	Ethylene Glycol
NH_4F	-	Ammonium Fluoride
NaOH	-	Sodium Hydroxide
H_2O_2	-	Hydrogen Peroxide
H_2O	-	Hydrogen Oxide
H^+	-	Hydrogen Ion
OH^-	-	Hydroxide Ion
TiO_2	-	Titanium Dioxide
UV	-	Ultra Violet
Nm	-	Nanometer

CHAPTER 1

1.1 INTRODUCTION

This chapter will introduce the background of the study as well as problem statement, objectives and scopes. The substance of this chapter explains more or less why this research was carried out.

1.2 Background of Study

Nanostructures can be defined as any structure with one or more dimensions measuring in the nanometer (10−9m) range (Abbas et al, 2014). Previously, many definitions discussing about this, their expressing that a nanostructure should have a characteristic dimension that is between 1nm and 100 nm, putting nanostructures as intermediate in size between a particle and a bacterium (Clive et al., 2009). Hoffmann et al. (1995) reported that nanostructured TiO_2 material shows high bio-compatibility, low toxicity and good retention of biological activity of protein binding (Hoffmann et al., 1995). TiO_2 has also shown to deliver low monetary value of titanium oxide, which is a desirable characteristic for economic viability compared to other methods and materials (Hoffmann et al., 1995). Based on Yuan and members on 2004, titanium oxide (TiO_2) is an n-type semiconductor and a typical photocatalyst, attracting much attention from both fundamental and practical viewpoint. It has been used in many industrial areas including environment purification, solar cell, gas sensor, pigments and cosmetics. Based on the exploration approaches for the nanostructured titania of various natures with the ascendancy of the particle size in nanometer-scale and the sound structure become quite interesting. Addition to it, since the carrying into action of titanium in its various applications tie up with on its crystalline phase state, dimensions and morphology (Liu et al., 2004). Therefore, several specific features relevant to TiO_2 nanostructures will make these materials outstanding (Patrik et al., 2011) (Figure 1.1).

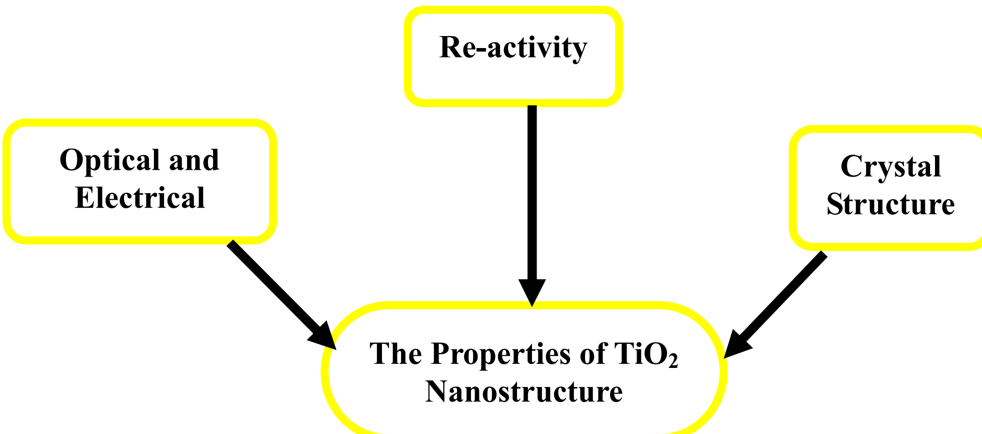

Figure 1.1: The properties of TiO_2 Nanostructure (Patrik et al., 2011)

Furthermore, these properties of TiO_2 nanostructure materials were primarily attributed to their quantum-confinement effects and large specific areas. One type of them was one-dimention (1D) structured materials such as nanorods, nanowires, and nanotubes (Younan et al., 2003).Basically, nanosized oxides can be separated into three categories, zero-dimention (0D), one-dimensional (1D) and two-dimensional (2D) (Ashby et al., 2009). In this work, 1D TiO_2 nanostructure will be investigated (Yuan et al., 2004) (Figure 1.2).

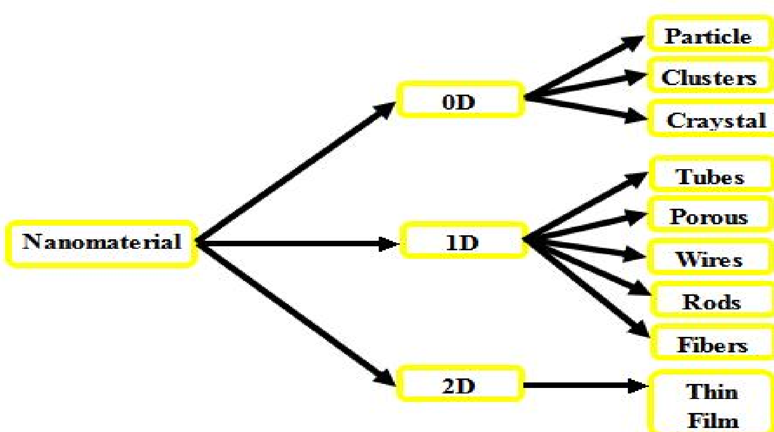

Figure 1.2: The classification of nanomaterials (Yuan etal., 2004)

In addition, TiO_2 is a very valuable non-toxic, environmentally friendly, corrosion-resistant material due to the commonly used in pigment, white pigments and sun blockers (Patrik et al., 2011). TiO_2 can be produced by using anodic oxidation processes. The anodic oxidation of the substrates was carried away at room temperature passing an electric D.C current between the substrate (as an anode) and a platinum wire (as a cathode), both separated by a length of 5 cm and submerged in a beaker containing a 1M solution H_2O_4 (as electrolyte). In each instance, a constant voltage was kept up for 1 min. The voltage applied ranged from 10 to 60 V (Maria et al., 2013). TiO_2 was produced by anodization at 60 V in a bath with electrolytes composed of ethylene glycol (EG), ammonium fluoride (NH_4F) and hydrogen peroxide (H_2O_2). The H_2O_2 was used to take place the H_2O as an oxygen supplier to increase the oxidation rate for synthesizing highly ordered and smooth TiO_2 at a speedy pace. As anodization time was increased, the rate was reduced slightly (Sreekantan el al., 2011).

They're having several influence factors in anodic oxidation such as anodizing potential, potential ricing rates, the oxidation time, pH and concentrations of F^- and lastly solution (Qiang et al., 2014). TiO_2 can be formed at the right potential range, which is generally called potential window (Cai et al., 2005). When the oxidation potential is lower than the potential window, the only nonporous film is formed on the Ti film; however, when the potential is too high, a sponge oxide layer (Lockman et al.,2010) is formed. The potential window generally ranges from 10 V to 40 V. The upper bound of the potential window can reach 220 V in some special solution system. Potential rising rate (PRR) means the rising rate for the applied potential to the predetermined one of the open circuit potential in anodic oxidation processes. The PRR affects the morphologies of oxide layer greatly; if it is too large, the disorder porous TiO_2 layers are formed. The PRRs are different in different solutions, and it is generally larger in the organic solutions than that in aqueous solutions. The oxidation time (OT) is some other significant element in the anodic oxidation process. If the OT is too short, the electrochemical reaction has not yet reached a final equilibrium state, then the resulting product is a disordered porous oxide layer, and no ordered TiO_2 nanostructures can be formed. When the OT is too long, the tubes' top and bed will crack due to excessive corrosion, and the wires (Xu et al., 2011) or porous walls (Fang et al., 2011) will be formed, then an appropriate OT is important for the tube shaping. The last factor that will affect the anodic oxidation process is aqueous solution and the organic solution that is used in the fabrication of TiO_2 by anodic oxidation method. Broadly speaking, the TiO_2 architectures dissolve faster in aqueous solutions than that in organic solution. Compared with an aqueous solution, TiO_2 prepared in organic solution has uniform shape and are very regular, and the extra-long tubes with smooth surface can be obtained.

1.3 Problem Statement

Subject field of nanomaterials metal oxide includes titania, tungsten, zirconia and alumina had started since early year 2000 and research interests on it were progressively increasing in 2005 (Jianling, 2005). The multifunction and properties of TiO_2 had been discovered and had attracted interest. For this study, have two main problem that have been focusing. First is about the weakness of fluorine (F^-) in aqueous solution . The second problem statement is about the pollution in the environment.

Metal oxide nanotubes have become a widely investigated material, more specifically, self-organized titania nanotube arrays synthesized by electrochemical anodization. Dawei et al., proposed the titanium oxide nanotubes were fabricated by anodic oxidation of a pure titanium sheet in an aqueous solution containing 0.5 to 3.5 wt% hydrofluoric acid. The formation of longer nanotubes with high aspect ratio in aqueous electrolyte is difficult to achieve since after reaching certain critical length, the nanotubes collapse (Michal et al., 2014). Beside, the contained of fluoride in aqueous solution is difficult to control chemical dissolution.

Next, on that point are critical issue worldwide due to population increase and speedy evolution of industrialization and give effect to human beings in the long-term many of years. Then it will harmful the living things and environment. Based on the previous studies, only a little report on the photo-catalytic application of TiO_2 nanostructure used in water treatment. Thus, the properties that influence the photo-catalytic will be