UNIVERSITI TEKNIKAL MALAYSIA MELAKA

PSM TITLE (Synthesis of TiO_2 Nanotubes via Anodic Oxidation in Carbonated Bath)

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

STUDENT NAME (Nur Nadia Binti Muhamad Arshad)
MATRIX NUMBER (B051110100)
IC NUMBER (920109-01-5268)

FACULTY OF MANUFACTURING ENGINEERING
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(DR. SYAHRIZA BINTI ISMAIL)

DECLARATION

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

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ABSTRAK

Nanotube TiO_2 telah disintesis pada kepingan Ti foil tulen dengan kaedah proses pengoksidaan anodik. Beberapa parameter telah disiasat seperti kesan daripada jumlah Na2CO3 dan kesan penyepuhlindapan dalam keadaan cecair dan organik larutan elektrolit. Morfologi dan fasa TiO_2 nanotube dibentuk dicirikan. Kesan penyepuhlindapan dibentuk nanotube TiO2 struktur kristal dan beberapa fasa dapat diperhatikan seperti anatase dan rutil. Sampel optimum adalah dalam larutan elektrolit akueus yang mengandungi 95 ml 1M daripada Na_2SO_4 ditambah kepadanya, 5 ml H_2SO_4, 0.3 g ammonium florida (NH_4F) dengan jumlah 0.3 g Na_2CO_3 C adalah tertakluk pada ujian fotopemangkinan. Bidang Pelepasan Mikroskop Imbasan Elektron (FESEM) untuk pengimejan pembesaran Ultra-tinggi dalam pemerhatian. EDX menunjukkan unsur-unsur yang terkandung di dalam TiO_2 nanotube sementara sifat-sifat yang mempengaruhi fotopemangkinan juga ditemui dengan menggunakan degradasi metil oren. Pembelauan sinar-X (XRD) dijalankan kuantiti fasa yang menggunakan keamatan nisbah rutil dan anatase. Selain daripada itu, Raman microspektroskop juga adalah cara berkesan untuk membezakan anatase dan rutil. Ujian fotopemangkinan adalah murah, sangat stabil secara kimia dan sangat pengoksidaan manakala pengoksidaan anodik juga kos rendah, proses yang mudah, proses yang efektif dan cepat serta pemboleh-ubah parameter yang boleh disesuaikan untuk keadaan yang optimum. Kesimpulannya, TiO_2 nanotube yang dihasilkan oleh penganodan foil Ti dijalankan di fluorin berkarbonat dan metil oren diuji untuk proses pemfotorosotaan.

ABSTRACT

TiO_2 nanotubes is synthesized on pure Ti foil by an anodic oxidation process approach. Several parameters were investigated such as the effect of the amount Na_2CO_3 and effect of annealing in aqueous and organic electrolyte solutions. The morphologies and phases of TiO_2 nanotubes formed were characterized using Field Emission Scanning Electron Microscope (FESEM) for Ultra-high magnification imaging. The effect of annealing formed the crystalline TiO_2 nanotubes of crystal structure and several phases were observed such as anatase and rutile. The optimum sample was in aqueous electrolyte solution containing 95 ml 1M of Na_2SO_4 added to it, 5 ml of H_2SO_4, 0.3 g of ammonium floride (NH_4F) with the amount 0.3 g of Na_2CO_3 C. Energy Dispersive X-Ray (EDX) showed the elements inside of TiO_2 nanotubes while the properties that influence the photocatalytic were also discovered by using degradation of methyl orange. X-ray diffraction (XRD) measurement is carried out for the quantification of phase which utilises the intensity ratios of the rutile and anatase. Raman microspectroscopy was employed effectively to differentiate the anatase and rutile. Photocatalytic testing are inexpensive, highly chemically stable and highly oxidizing whereas anodic oxidation are low cost, simple process, in vary rapid process and the parameter can be adjusted for optimum conditions. As a conclusion, TiO2 nanotubes produced by anodization of Ti foil conducted in fluorine carbonated bath and methyl orange is tested for photodegradation.

DEDICATION

To my beloved parents

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, advice and guidance throughout the entire project. Not to forget the research team: Nurazreen Binti A B N Sy B S ' o c c ov this while. I am greatly touched by the commitments and dedications they have shown. Without the support and guidance, I would not be able to complete 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 prepare 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. Finally, I wish to say that I treasure very much the friendship of my friends who have been very supportive in providing all necessary help and advice during the long journey of completing this study.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

0D	-	Zero Dimensional
1D	-	One Dimensional
2D	-	Two Dimensional
Et al	-	et alii
FESEM	-	Field Emission Scanning Electron Microscope
SEM	-	Scanning Electron Microscope
XRD	-	X-Ray Diffraction
EG	-	Ethylene Glycol
NH_4F	-	Ammonium Floride
NaOH	-	Sodium Hydroxide
H_2O_2	-	Hydrogen Peroxide
H^+	-	Hydrogen Ion
OH^-	-	Hydroxide Ion
TiO_2	-	Titanium Dioxide
MITC	-	Melaka International Trade Centre
UV	-	Ultra VIolet
>	-	More than
Nm	-	Nanometer

CHAPTER 1
INTRODUCTION

This chapter will introduce the background of the study as well as problem statement, objectives and scopes. The content of this chapter explained about why this research was carried out.

1.1 Background of Study

Nanostructured TiO_2 materials focus on protein binding show high biocompatibility, low toxicity and good retention of biological activity. The effects and large specific areas for these properties of TiO_2 nanostructure materials were mainly ascribed to their quantum-confinement (Wan et al., 2009). Based on Macak and Schmuki (2006), there are several properties of TiO_2 nanotubes have already been explored for instance, the nanotubes show a high photoresponse, when annealed they show extremely high sensitivity to hydrogen when used as gas-sensor, they can extremely change their surface wettability, they show significant light conversion efficiencies when dye-sensitized they can act as a catalyst in order to make a photocatalyst active in the visible light. Moreover, TiO_2 is a very useful non-toxic, environmentally friendly, corrosion-resistant material due to the frequently used in paint, white pigments and sun blockers (Schmuki et al., 2011). The intrinsic properties of TiO_2 which provide the basics for many outstanding functional features however, is the main reason why TiO_2 nanotubes are currently attracting such a vary high interest. Thus, there are several specific features relevant to TiO_2 nanotubes that make this materials outstanding (Figure 1.1). The schematic image of nanotubes is shown in Figure 1.2 where hollow tubes are aligned and organized.

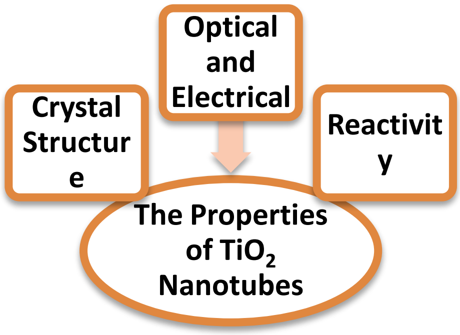

Figure 1.1 : The properties of TiO_2 nanotubes

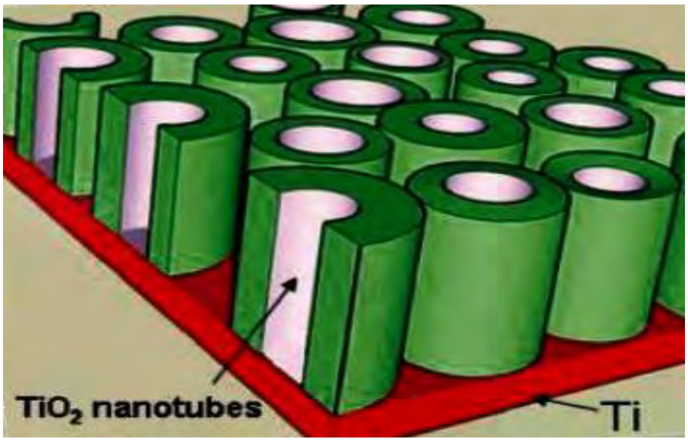

Figure 1.2 : The schematic nanotubes structure of TiO_2

Basically, nanosized oxides can be classified into three categories, zero-dimensional (0D), one-dimensional (1D) and two-dimensional (2D) (Ashby et al., 2009). Figure 1.3 shows the samples of different shape nanosized oxides can have under category of nanomaterials which are 0D, 1D and 2D whereas Figure 1.4 shows more details classification of nanomaterials. A high electron mobility or quantum confinement effects, a very high specific surface area, and even show a very high mechanical strength are some of the unique electronic properties of one-dimensional (1D) nanostructure (Schmuki et al., 2011).

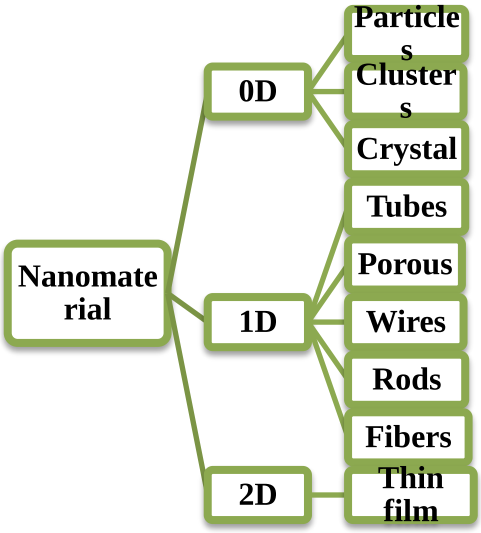

Figure 1.3 : The classification of nanomaterials

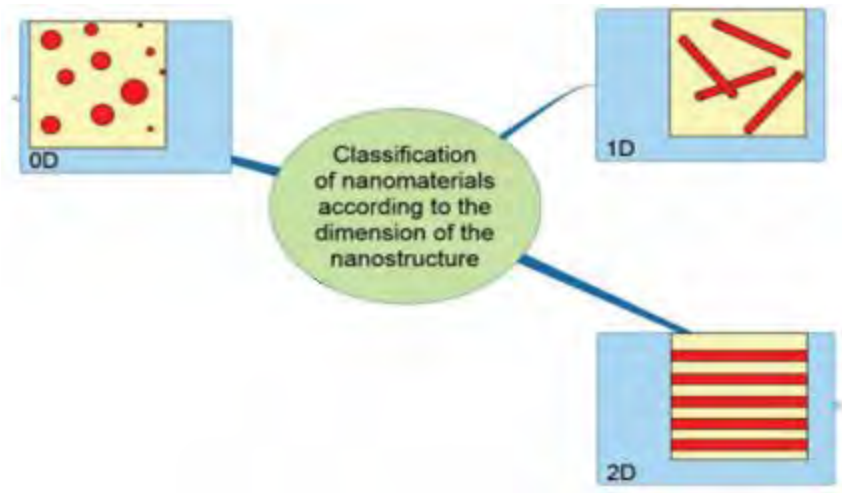

Figure 1.4 : The classification of nanomaterial according 0D, 1D, 2D and 3D

To summarize, 0D nanomaterials contain spheres or clusters which are considered as point-like particles. While 1D nanomaterials contain nanofibres, wires, tubes and others. For 2D structures, films, plates, multilayers or networks is identifies and 3D structures are nanophase material consisting of aquiaxed nanometer-sized grains. In this work, 1D TiO_2 nanotubes will be investigate since this structure have enhanced properties compared to any other form of metal oxide for applications. The example of TiO_2 nanotubes are shown in Figure 1.5.

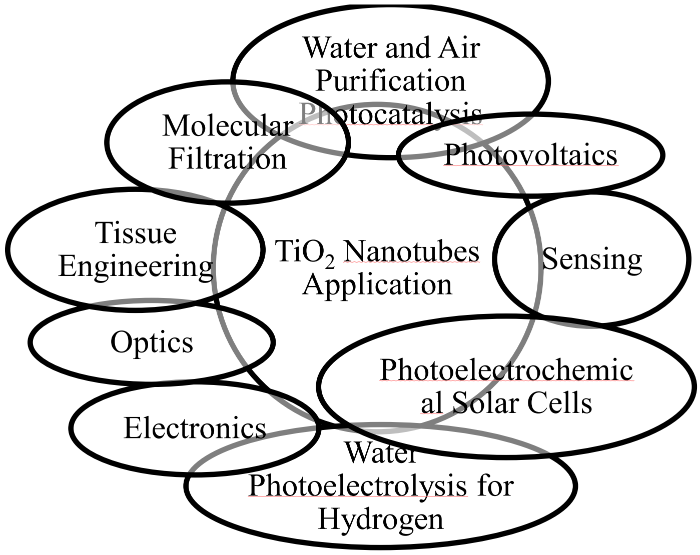

Figure 1.5 : The example of TiO_2 nanotubes application

Wastewater are harmful to human beings and ecological environment, it is a must to control the harmful effects improve the human living environment (Xu et al., 2012). In this work, the application of photocatalysis is focused by using TiO_2 nanotubes as the photocatalyst. The pollution degradation, water splitting and organic synthesis are the main classic of photocatalytic area. Research on photocatalytic pollutant degradation is increasing day by day because its practical use has drawn great attention in industry (Schmuki et al., 2011). Similarly, TiO_2 nanotube layers were used as irritants for the destruction of gaseous pollutants (Paramasivam et al., 2012). Besides, TiO_2 nanotubes is widely perceived as the best and often the most suitable photocatalyst for environmental applications particularly due to stability, inexpensive, highly stable chemically and the holes are highly oxidizing. A good photocatalyst must have a small size and large surface area to allow more absorption and oxidation of pollutants.

Synthesis of 1D TiO_2 nanostructures may be achieved by various route including sol-gel methods, template assisted method, hydrothermal approach, electrochemical means and by others. However, the focus on self-organised TiO_2 nanotubes layer. These layers can be formed using a simple electrochemical oxidation reaction of a Ti foil under a specific set to achieve the optimum conditions. The synthesis is carried out by a low-cost parallel process which conventional electrochemical anodization. In addition, the self-ordering anodization approach is not limited to form highly aligned oxide nanotube of titanium but can be applied to a large range of other transition metals or alloys (Schmuki et al., 2011).

This project was aimed at the formation of TiO_2 nanotubes to be used as photocatalyst to remove pollution degradation from industrial waste water. Despite there are works on the formation of the anodic oxide of TiO_2, not much has been explored on the formation of nanotubes in carbonated bath. In here, anodic oxidation technique is used because of it is a simple process, low cost and applicable for fabrication of large area of metal substrate.

1.2 Problem Statement

Study 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 (Longtu Li, 2005). The multi functions and properties of TiO_2 nanotubes had been discovered and had attracted interests. The increasing interest can be easily seen from publication which based on research paper and journal published at ScienceDirect, Springer, IOP, ScientificNet, RSC, and others.

There are three generations of fluorine-containing electrolytes have been reported by Yin et al., (2009) for anodization of Ti foil to produce TiO_2 nanotubes. The first generation electrolyte is based on dilute hydrofluoride (HF) acid aqueous solution in which the maximum thickness of TiO_2 nanotubes arrays to just several hundred nanometers due to high rate of chemical dissolution of TiO_2. By using HF, it give effect to the environment and the material handling of HF is not practical. The second generation electrolyte, a fluorine-containing buffer solution by controlling the pH gradient within the growing nanotubes arrays of TiO_2 nanotubes several micrometers in length can be achieved. The third generation electrolyte can produce TiO_2 nanotubes arrays with an ultrahigh aspect ratio which consists of fluoride and a viscous organic electrolyte such as ethylene glycol (EG) or glycerol. Hence, using NH_4F as a resolution agent. However, the effect of fluoride ions was not illustrated in detail (Liang et al., 2011). Furthermore, the effect of NH_4F carbonated bath on the dimension nanotubes will be discussed.

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To date, there are crtical issue worldwide due to population growth and rapid development of industrialization and give effect to human being in long-term many of years.thus it will hamful the living things and environment. According to the previous works, only a little report on the photocatalytic application of TiO_2 nanotubes for water treatment, therefore the properties that influence the photocatalytic will be investigate. By forming nanotubes structures, there would presence the exciton-like trap states which is superior for electron transport properties that are needed for high photocatalytic efficiency. As an alternative, a simple model for water treatment is designed, built, and tested using TiO_2 nanotubes formed. Wastewater are harmful to human beings and ecological environment, it is a must to control the harmful effects improve the human living environment (Xu et al., 2012).

1.3 Objectives

There are two main objectives in this research are:

i. To produce the TiO_2 nanotubes by anodic oxidation in fluorine carbonated bath.
ii. To study the photocatalytic properties in TiO_2 nanotubes produced by anodization.

1.4 Scope of Work

This research covered the study on the formation of self-organised TiO_2 nanotubes and the properties of photocatalytic produced of TiO_2 produced. The synthesis of TiO_2 nanotubes is by electrochemical process and also known as anodic oxidation. The effects of anodic parameters such as applied voltage, concentration and pH are studied. The phase formation, morphology, structural and characterization on TiO_2 nanotubes was determined by scanning electron microscope (SEM), x-ray diffraction (XRD), energy dispersive x-ray (EDX) and UV lamp chamber.

1.5 Outline of Chapters

This thesis consists of five chapters. Chapter one discusses on the introduction, background of thesis, objectives, and scopes of work regarding the project. Meanwhile, concept and literature review related to formation of TiO_2 nanotubes by using anodic oxidation method are explained in Chapter two. In Chapter three, the methodology or experimental details are explained. Then, Chapter four focuses on the results and discussion in vary details about this research. Finally, conclusion and recommendations of future work are explained in Chapter five.