UNIVERSITI TEKNIKAL MALAYSIA MELAKA

FORMATION OF SELF-ORGANIZED ZrO_2 NANOTUBES BY ELECTROCHEMICAL PROCESS

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

by

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ABSTRAK

Pembentukan sendiri tiub nano ZrO_2 yang dihasilkan oleh proses elektrokimia. Kajian tiub nano ZrO_2 dipilih kerana pelbagai aplikasi tiub nano ZrO_2 yang meluas dikaji oleh ramai penyelidik di seluruh dunia. Perkembangan bahan nano adalah selari dengan permintaan kehendak dalam teknologi dan proses. Dalam tesis ini, terdapat tiga objektif kajian iaitu untuk mensintesis tiub nano ZrO_2 oleh proses elektrokimia dalam elektrolit berkarbonat, menyiasat kesan parameter anodik pada pembentukan ZrO_2 dan mendapatkan keadaan optimum dan juga untuk mengkaji sifat fotopemangkinan dalam tiub nano ZrO_2 yang telah dihasilkan. Peringkat-peringkat utama metodologi dalam kerja-kerja ini adalah penganodan, pencirian dan juga ujian pemfotorosotaan. Secara umumnya, penganodan melibatkan proses elektrokimia untuk membuat lapisan oksida filem nipis di bawah keadaan penganodan. Kaedah pencirian yang digunakan untuk mengkaji morfologi dan struktur tiub nano yang telah dibentuk adalah dengan menggunakan Mikroskop Imbasan Elektron (SEM), sinar-X pembelauan dan Tenaga serakan X-ray spektrometer. Akhir sekali, ujian cahaya degradasi dilakukan dengan menguji degradasi Methyl Orange. Ia dilakukan adalah untuk menilai fotopemangkinan daripada tiub nanoZrO_2. Struktur yang terhasil adalah struktur liang nano. Kandungan optimum untuk pembentukan liang nano dalam akueus dan organic elektrolit adalah masing-masing 0.3 dan 0.5 g of Na_2CO_3.

ABSTRACT

This project studies is the formation of self-organized ZrO_2 nanotubes by electrochemical process. The title of this research has stated clearly, the main purpose of this work. The study of ZrO_2 nanotubes is chosen due to their various promising application of ZrO_2 nanotubes that have widely investigated by many researchers in over the world. The study of nanomaterials is recommended as their development is parallel to the requirement demand in technology and processes. In this thesis, there are three stated research objectives; to synthesize ZrO_2 nanotubes by electrochemical process, to investigate the effects of anodic parameters on ZrO_2 nanotubes hence to obtain an optimum anodization condition and last but not least to study the photocatalytic properties in ZrO_2 nanotubes produced. Generally, anodization involve of electrochemical process to make an oxide layer of thin film under anodization condition. The characterization methods used to investigate the morphology and structure of the formed nanotubes are by using Scanning Electron Microscope (SEM), X-ray diffraction and Energy Dispersive X-ray spectrometer. Then, the photodegradation test by degradation of Methyl Orange is done to evaluate the photocatalytic properties of the ZrO_2 nanotubes. The results of the structures are in formed of spongy-like nanoporous structure. The optimum carbonate content in aqueous and organic electrolyte is 0.3 and 0.5 g of Na_2CO_3 respectively. After annealed, the crystallization increased for both samples. Last but not least, the highest degradation rate of methyl orange is showed when used annealed sample of 0.3 g of Na_2CO_3 formed in aqueous electrolyte.

DEDICATION

To my beloved family

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim,

I would like to convey my gratitude to Allah S.W.T for giving me strength and willingness to be able to complete this final year project. And also, I would like to thank the Faculty of Manufacturing Engineering (FKP) of Universiti Teknikal Malaysia Melaka (UTeM) for providing the opportunity through my final year of bachelor degree program. This final year project allows me to experience the effective approach in handling an engineering project as well as write appropriate project report writing. My thanks and appreciation is given to Dr. Syahriza Ismail for the guidance throughout my final year project as my supervisor. Her effective advice during discussion time on my final year project is a great help for my advance in this project. Without these opportunity and advices, the completion of the first part of my final year project would be impossible. And not to be forgotten, I also would like to thank, Mr Bahatiar, Mr Hairulhisyam and all the technicians and friends that involved directly and indirectly upon completing this project.

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LIST ABBREVIATIONS, SYMBOLS AND NOMENCLATURES

~	approximately
°C	Degree Celsius
Å	Angstrom
C	Carbon
EG	Ethylene glycol
h	Hour
H_2O	Water
H_2O_2	Hydrogen Peroxide
HF	Hydrofluoric Acid
NH_4F	Ammonium Floride
Na_2CO_3	Sodium Carbonate
Na_2SO_4	Sodium Sulphate
g	Gram
H^+	Hydrogen Ion
M	Molarity
ml	milliliter
nm	nanometer
O_2	Oxygen
OH^-	Hydroxide Ion
V	Volt
Zr	Zirconium
ZrO_2	Zirconia

CHAPTER 1

INTRODUCTION

1.1 Background

As a fundamental for a healthy life, one of the most important aspects is an adequate supply of safe drinking water however the infection like waterbone disease is still a main reason of death in many parts of the world. Drinking water generally come from two essential sources, which are groundwater and also surface waters, such as rivers (Fawell & Nieuwenhuijsen, 2003). The pollution of this water can be very harmful to human being as water is a basic need for human to stay alive in this world. Other than that, it also will give bad effects to ecological environment. There are many factors that will contribute for contamination to happen; one of them is when there is a possibility of spills of chemicals from industry, agriculture and also slurries from intensive farm units that can contain pathogens. Generally, in consumer's premises, contamination also can take place either from the back-flow of liquids into the distribution system due to of improper connections or from materials used in plumbing, such as lead or copper.

There are several different technologies and processes are currently used including membrane filtration, adsorption on new adsorbents, photocatalysis and electrodialysis (Kurniawan, Chan, Lo, & Babel, 2006). Evidently, from survey, the most frequently studied and widely applied for the treatment of metal-contaminated wastewater are adsorbents and membrane filtration. However, recently it was reported, the photocatalysis is the most promising methods to treat such complex systems in which it consume cheap photons from the UV-near visible region (Barakat, 2011). Table 1.1 shows the comparison between different processes in wastewater treatment. The advantages and disadvantages of chemical precipitation, adsorption with new adsorbents, membrane filtration, electrodialysis and photocatalysis are stated as shown in Table 1.1.

Table 1.1: Advantages and disadvantages of various processes of water treatment in waste water. *(Adapted from New trends in removing heavy metals from industrial wastewater by Barakat, 2011*)

No.	Treatment technique	Advantages	Disadvantages
1	Chemical precipitation	The capital cost is low and the operation is simple.	Sludge generation, extra operational cost for sludge disposal.
2	Adsorption with new adsorbents	Cost is low, operating conditions is easy, having wide pH range, high metal binding capacities.	Low selectivity, production of waste product.
No.	Treatment technique	Advantages	Disadvantages
3	Membrane	Space requirement is small,	High operational cost due to

	filtration	low pressure, high separation selectivity.	membrane fouling.
4	Electrodialysis	High separation selectivity	High operational cost due to membrane fouling and energy consumption.
5	Photocatalysis	Removal of metal and organic pollutant simultaneously, less harmful by-products.	Long duration time, limited application.

Recently, to suggest the material to treat wastewater, materials categorized under nanoparticle have been proposed. This is because of their plasmon resonance in the nanoparticles (NPs) of noble metals that can strongly absorb visible light, which is deeply affected by their morphology and size. To important applications such as colorimetric sensors, photovoltaic devices, photochromic devices, and photocatalysts, it is gives rise by the phenomenon of plasmon resonance (P. Wang et al., 2008). A nanostructured material is defined as a solid material formed by units (or building blocks) that have dimensions at the nanometer scale. NPs constitute the basic building blocks for nanotechnology. Since nanosized oxides have various nanostructure morphologies, it has been seen as a potential material architecture to be used as adsorption materials to treat wastewater from industrial areas. For most practical applications, the NPs have to be organized into a specific structure (in one, two or three dimensions), similar to how atoms and molecules are assembled into matter (Izquierdo & en Química, 2012).

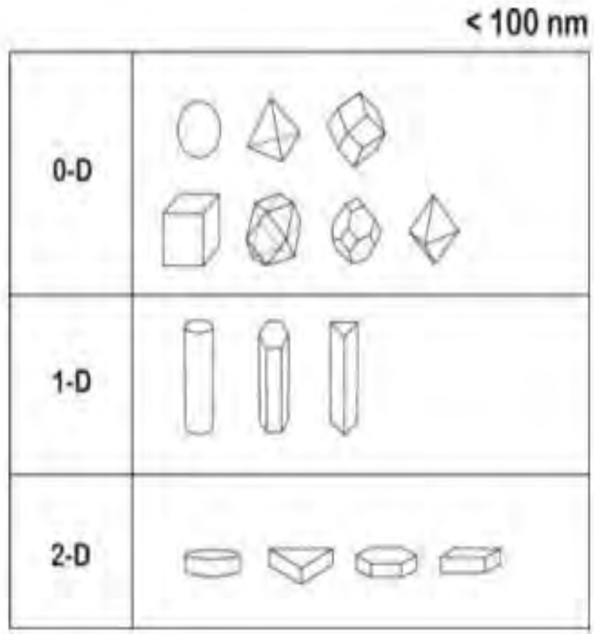

Figure 1.1: Geometrical shapes of basic NP building blocks at the nanometer scale. (*Retrieved from Synthesis of Nanoparticles and Nanostructured Materials by Self-Assembly by Izquierdo & en Quimica, 2012*)

One easy way to decide the dimension is to think how many sides of the structure are bigger than the others. The dimension of nanomaterials can be summarizes as:

- 0D = espherical nanoparticles (all dimensions are the same and in the in the nanometric behavior)
- 1D = nanorods, etc (1 dimension bigger than the other 2)
- 2D = nanosheets, etc (2 dimensions bigger than the other 1)
- 3D = other nanomaterials.

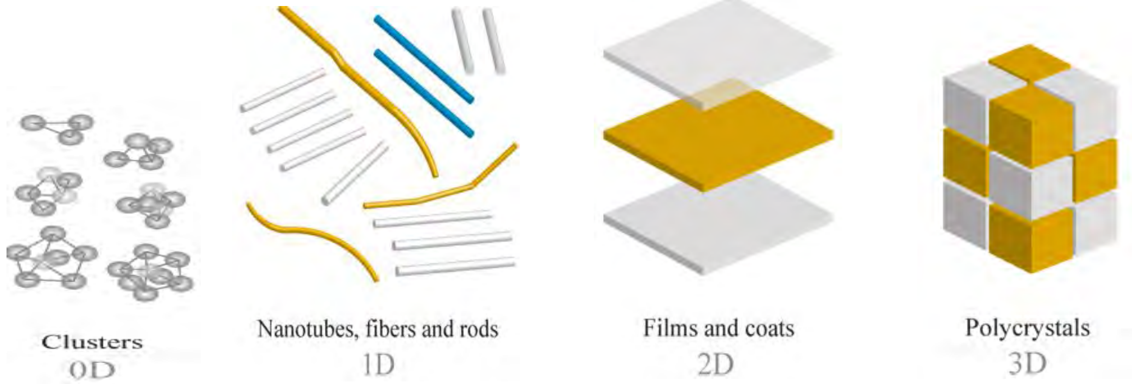

Figure 1.2: Types of nanocrystalline materials by size of their structural elements (0D, 1D, 2D, 3D)

Basic building blocks can be classified by crystal symmetry and dimensionality (Figure 1.1). The zero-dimensional (0-D) building blocks such a small (dot) spheres, icosahedrons, and cubes are the most familiar shapes at the nanoscales. Rods, cylinders and wires are examples of one-dimensional (1-D) building blocks, whereas disks, plates, and polygon shape structures belong to two-dimensional (2-D) building blocks group (Izquierdo & en Química, 2012). Figure 1.3 shows the classification of nanomaterials, which are under 0D there are particles, clusters, and crystalline while under 1D there are tubes, porous, wires, rods and fibres, last but not least under 2D there is only thin film

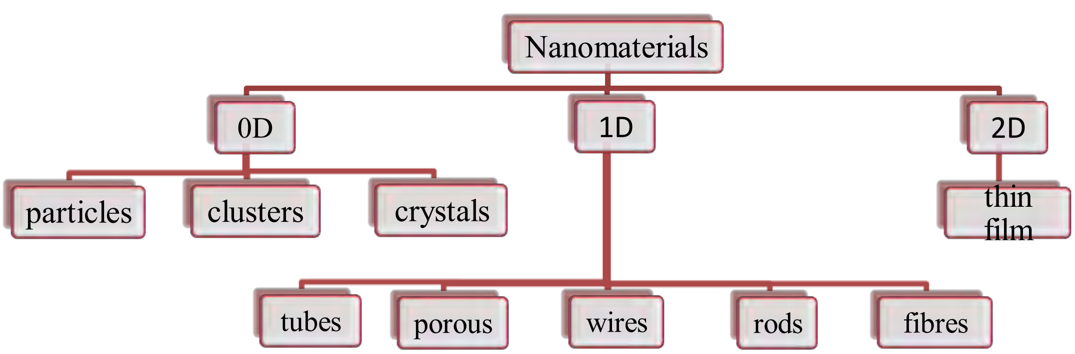

Figure 1.3: Classification of nanomaterials.

Among the available nanosized oxides, zirconium oxides nanotubes are chosen to be the material studied in this work. This material is categorized under 1D nanomaterials. The diameter is in nanoscale while the length could be in nano. ZrO_2 has attractive technological properties, including high thermal and chemical stability, good mechanical strength and wear resistance, excellent diaelectric properties (as oxides of a "valve metal") and good ion-exchange properties (Muratore et al., 2011). In particular, due to their unique physical and chemical properties, ZrO_2 nanotubes have generated a lot of interest in nanotechnology world. They are significantly different from their microcrystalline counterparts due to their enhanced surface area to volume ratio, quantum confinement, and changes in lattice parameters (Guo, Zhao, Wang, Xu, & Li, 2009). Furthermore, ZrO_2 is widely investigated because of its broad application. ZrO_2 nanotubes have wide potential applications in the field of electronic, magnetic, optical and heterogenous catalysis, etc (Zhao et al., 2008). It is a promising material for catalyst or catalyst support, sensor, solid electrolyte etc (Guo et al., 2009). In this study, the photocatalyst properties of ZrO_2 in nanotubes structure will be investigated and explored. Due to the attractive properties of zirconia, various applications can be applied to ZrO_2 nanotubes. The potential application of ZrO_2 nanotubes can be summarized as in Figure1.4.

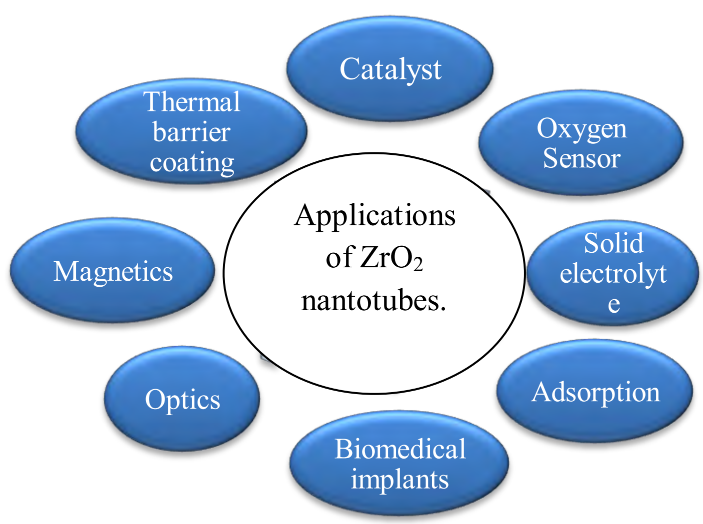

Figure 1.4: Various promising applications of ZrO_2 nanotubes.

There are several techniques that can be used in the formation of nanotubes oxide such as sol-gel technique, hydrothermal synthesis, co-precipitation and thermal decomposition. Alternatively, oxidation method can be used in the formation of ZrO_2 nanotubes layer onto a metal substrates. Generally, oxidation processes is divided into two types which are thermal and anodic oxidations. However, in this work, anodic oxidation process will be used for the formation of self-organized ZrO_2 nanotubes. The meaning of anodic oxidation is the making of thin oxide film on a metallic substrate by electrochemical process. The reason of this process was used because anodic oxidation process is a low cost process yet it is very effective in synthesizing large area materials.

This research was aimed for the formation of self-organized ZrO_2 nanotubes by anodization process in fluoride and carbonated bath electrolyte. The photocatalytic properties of the ZrO_2 nanotubes are then will be studied. The morphology & structured of ZrO_2 nanotubes will be studied as the main objective is to form the self-organized ZrO_2 nanotubes on Zr foil. Despite, many works have been reported on formation of ZrO_2 nanotubes but only a little works was reported on formation of ZrO_2 nanotubes in fluoride carbonate electrolyte.

1.2 Problem Statement

Study of formation of ZrO_2 nanotubes by electrochemical process has recently attracts many researchers to work on it. The formation of electrochemical growth self ordered ZrO_2 nanotubes are produced with various types of electrolyte such as H_2SO_4 + NH_4F (Tsuchiya, Macak, Sieber, & Schmuki, 2006), Na_2SO_4 + HF (Stępień, Handzlik, & Fitzner, 2014), FA+ GE + HCl (Guo et al., 2009) and etc.

It is found that HF used as electrolyte is highly influence the formation of the ZrO_2 nanotubes. However the used of HF has brought many problems. Since the chemical is hazardous to human as the fluoride ion readily causing destruction of deep tissue layers, penetrates the skin, and even bone (Anderson & Anderson, 1988). Hydrofluoric acid produces dehydration and corrosions of tissues due to free hydrogen ions. However, unlike others acids, the dissociated fluoride ion, F^-, produce critical toxicity (Bertolini, 1992). Besides, the material handling of HF is not practical. Because of it is known that HF is highly toxic, extremely corrosive, and hazardous, so it always needs fume hood and special tools to handle it. Then, the used of HF as an electrolyte is not recommended. In this project, a suggestion will be given to encounter this problem.

Recently, many of works on the formation of ZrO_2 nanotubes are done in acidic & aqueous electrolyte H_2SO_4, $(NH_4)_2SO_4$ and etc. However, only a little works on the formation of self-organized ZrO_2 nanotubes in fluoride carbonate electrolyte. So, in this work, we are planning to produce and study the formation of self-organized ZrO_2 nanotubes by electrochemical process in fluoride carbonate electrolyte. Also, the effects of anodic parameter on anodic ZrO_2 nanotubes is be investigate hence an optimum condition to produce it is suggested. The anodic parameters that will be study is the various concentrations and applied voltage for ZrO_2 nanotubes formed. In this present work, the morphology, microstructure and photocatalytic property of ZrO_2 nanotubes produced in carbonated bath is study. Thus, scanning electron microscope (SEM), x-ray diffraction (XRD) and UV lamb chamber are used. Last but not least, the photocatalytic properties of ZrO_2 nanotubes is study.

1.3 Research Objectives

The purpose of this research is to produce self-organized ZrO_2 by using electrochemical process. Below are the specific objectives for this research:

i. To synthesize ZrO_2 nanotubes by electrochemical process (anodization) in aqueous and organic carbonated electrolyte.
ii. To investigate the effects of amount of Na_2CO_3 on ZrO_2 nanotubes hence to obtained an optimum anodization condition.
iii. To study the photocatalytic properties in ZrO_2 nanotubes produced by electrochemical process (anodization) in carbonated electrolyte.

1.4 Research Scope

This research covered the study on the formation of self-organized ZrO_2 nanotubes and the photocatalytic properties of ZrO_2. The synthesis of ZrO_2 nanotubes is by electrochemical process or known as anodic oxidation process. The anodic parameter such as effect of various concentration and effect of applied voltage studied. The phase, microstructure and morphology characterization on ZrO_2 nanotubes was determined by using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Raman Spectroscopy, Energy Dispersy X-ray Spectrometer (EDX) and the photocatalytic properties is tested by UV lamb chamber.

1.5 Outline of Chapters

In overall, this thesis consists of five chapters. Chapter one is a chapter that discuss on the introduction, background of thesis, thesis objectives and scopes of work regarding the project. Meanwhile, the concept and literature review relate to formation of ZrO_2 nanotubes by using electrochemical process are explained in Chapter two. Then, in

Chapter three, the methodology or experimental details are explained. In Chapter four, it is focused on the result and discussion of this research. Last but not least, the conclusion of this research and also recommendations of future work are declared in Chapter five

CHAPTER 2

LITERATURE REVIEW

This chapter discusses the literature review on specific topics related to formation of ZrO_2 nanotubes. As the Zr foil (valve metal) were anodized for formation of self-organized ZrO_2 nanotubes, the topic of anodization process and nanotubes formation are reviewed in here. Literature survey on ZrO_2 nanotubes, properties as well as the applications of ZrO_2 nanotubes are presented here.

2.1 Introduction to Nanomaterials

Nanostructured material and device have attracted a great deal of technological and scientific attention in over the world. The word "Nano" means dwarf in Greek and it is exemplified as length of hydrogen atom line up in a row. A nanometer is define as one billionth of meter (10^{-9} or 10^{-7} cm), about a thousand times smaller than a red blood cell, about half the size of the diameter of DNA or one hundred thousand times smaller than the diameter of a human hair (Scott & Chen, 2013). From the point of view of discovering new physical phenomena as well as their exploitation possibilities in novel devices, it is found that nanostructured materials are of enormous interest. They have generated a lot of great expectations not only in the academic community but also among investors, the government, and industry, seeing many interesting properties can be harvested from them (Serrano, Rus, & Garcia-Martinez, 2009).

Generally, quantum effects and surface energy are strongly affecting the properties of nanomaterials. If compared to the same materials in bulk scale, nanomaterials posses a different in optical, magnetic and electronic properties. Those differences are due to the electronic structure and surface area to volume ratio changes as the size of the materials is reduced to nanosize (El-Sayed, 2001). Instead of the size control, wires or flakes in the nanoscale region possess novel properties. The fact it is, the exclusive properties of these different types of intentionally produced nanomaterials give them novel catalytic, electrical, mechanical, magnetic, thermal or imaging features that are highly desirable for applications in commercial, agricultural, military, medical and environmental sectors (Boisselier & Astruc, 2009).

Several kinds of nanomaterials such as TiO_2 nanomaterials as well as ZrO_2 nanomaterials have been widely studied by many researchers all around the world including Schmuki's group, Zhao's group, Skeldon's group and many others research groups. All the works done by them on formation of ZrO_2 nanotubes is reviewed in other sub-section.

2.2 Valve metal oxide

Recently, numerous valve metals such as Hf, Ta, Nb, Ti, W and Zr have been used to grown self-organized arrays of metal oxide nanotubes under appropriate anodizing