FORMATION OF ZIRCONIA SHEETS WITH NANOTUBULAR STRUCTURE PREPARED BY ANODIZATION OF ZIRCONIUM

by

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DECLARATION

I declare that this thesis is the result of my own research, does not incorporate without acknowledgement any material submitted for the degree or diploma in any university and does not contain any materials previously published, written or produced by another person except where due references are made in the text.

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LIST OF ABBREVIATIONS

ZNT'S	Zirconium oxide nanotubes
ZrO_2	Zirconium Oxide
C	Cubic
T	Tetragonal
M	Monoclinic
MO	Methyl Orange
PC	Photocatalyst
FESEM	Field Emission Scanning Electron Microscopy
XRD	X-ray Diffraction
TEM	Transmission Electron Microscope

LIST OF SYMBOLS

%	Percentage
<	Less than
>	More than
^{o}C	Degree Celsius
cm	Centimetre
h	Hour
L	Liter
m	Metre
min	Minute
ml	Millilitre
mm	Millimetre
wt%	Weight percent
V	Voltage
nm	Nanometre
g	Gram
s	Second
eV	Electron volt
λ	Wave length
T	Temperatur

ABSTRAK

Dalam karya ini, proses anodik dilakukan untuk menghasilkan lapisan anodik yang terdiri daripada tiub nano ZrO_2. Lapisan anodik kemudian dikeluarkan dari kepingan Zr untuk menghasilkan berdiri bebas lembaran ZrO_2 tiub nano. Jenis-jenis karbonat, berbeza kepekatan karbonat, voltan penganodan dan juga masa penganodan telah dieksperimen bertujuan untuk membentuk lembaran ZNTs. Kehadiran karbonat, Na_2CO_3 dan K_2CO_3 sebagai penambah memainkan peranan yang penting dalam pembentukan kepingan tiub nano. Untuk membandingkan, dalam EG ditambah dengan 3 ml 1 M K_2CO_3 menunjukkan lebih pembentukan kepingan tiub nano berbanding EG dengan Na_2CO_3. Dalam pembentukan ZNTs, H^+ dilepaskan dalam tiub nano dan apabila H^+ bertindak balas dengan CO_3^{2-}, gas CO_2 dilepaskan. Pembentukan gas CO_2 memberi kesan kepada lekatan filem ZrO_2 dari foil. Kesan kepekatan K_2CO_3 yang berbeza menambah, jumlah kepingan tiub nano yang terbentuk. Bagi kesan voltan penganodan dan masa, didapati bahawa pada 40 V dan 60 V, jumlah ZNTs dibentuk dan pada 60 V, filem itu adalah lebih mudah untuk dikeluarkan daripada foil Zr. Bagi kesan masa penganodan, ia seolah-olah bahawa pada masa yang lebih lama, tindak balas lebih bagi CO_3^{2-} dan H^+ berlaku membentuk lebih CO_2. Gas CO_2 yang dihasilkan daripada tindak balas CO_3^{2-} dan H^+ terkumpul pada antara muka logam dan oksida dan membuat filem oksida anodik untuk menanggalkan dengan mudah dari Zr substrat tanpa memerlukan prarawatan. Lembaran tiub nano ZrO_2 didapati amorfus, oleh itu ia telah disepuh lindap pada tiga suhu yang berbeza 200 ^{0}C, 400 ^{0}C dan 600 ^{0}C. Pembentukan fasa dan perubahan pada setiap suhu diperhatikan dengan semua tetragon (T), padu (C), dan wujud bersama-monoklinik (M) fasa selepas penyepuhlindapan pada 400 ^{0}C dan 600 ^{0}C

Aktiviti lembaran tiub nano ZrO_2 anil adalah kajian oleh degradasi MO. Selepas 300 minit, kira-kira 37% daripada MO telah di hina oleh sampel disepuh lindap pada 600 ^oC, 35% daripada MO dihina oleh sampel anil pada 400 ^oC dan 22% daripada MO dihina oleh sampel disepuh lindap pada 200 ^oC. Ini menunjukkan bahawa penghabluran adalah penting dalam fotopemangkinan.

ABSTRACT

In this work, anodic process was done to produce anodic layer of comprising of ZrO_2 nanotubes. The anodic layer was then removed from the Zr foil to produce free standing ZrO_2 nanotube sheets. Types of carbonates, different concentration of carbonates, anodization voltage and also anodization time were experimented aiming at forming ZNTs sheets. The presence of carbonates, K_2CO_3 and Na_2CO_3 as an additive plays an important role during the formation of the nanotube sheets. To compare, in EG added with 3 ml 1 M K_2CO_3 shows more nanotube sheets formation compared to EG with Na_2CO_3. In ZNTs formation, H^+ is released in the nanotubes and when H^+ reacts with CO_3^{2-}, CO_2 gas is released. The formation of CO_2 gas effect the adhesion of ZrO_2 film from the foil. Effect of different concentrations of K_2CO_3 added, the amount of nanotube sheets that formed was also increased. As for the effect of anodization voltage and time, it appears that at 40 V and 60 V, the amount of ZNTs were formed and at 60 V, the film was easier to be removed from Zr foil. As for the effect of anodization time, it seems that at longer time, more reaction between the CO_3^{2-} and H^+ occurs forming more CO_2. The CO_2 gas produced from the reaction of CO_3^{2-} and H^+ accumulated at the metal and oxide interface and makes the anodic oxide film to detach easily from Zr substrate without the need of pretreatment. The ZrO2 nanotube sheets were found to be amorphous, thus it were annealed at three different temperatures of 200 ^{0}C, 400 ^{0}C and 600 ^{0}C. The phase formation and transformation at each temperature was observed with all tetragonal (T), cubic (C), and monoclinic (M) phase co-exist after annealing at 400 ^{0}C and 600 ^{0}C. The activity of the annealed ZrO_2 nanotube sheets was study by degradation of MO. After 300 min, about 37 % of the MO was degraded by the annealed

sample at 600 ^{0}C, 35 % of MO degraded by sample annealed at 400 ^{0}C and 22 % of MO degraded by sample annealed at 200 ^{0}C. This indicates that crystallinity is important in photocatalysis

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CHAPTER 1

INTRODUCTION

1.1 Nanomaterials

In order to achieve a modern science and technology development, nanotechnology had been recognized to have a big potential in bringing benefits to many areas of research. This technology had been attracting rapid increasing investment from government and from industry in many parts of the world. According to Halimaton et. al., (2007), nanotechnology can be defined as the science of materials and systems with structures and components which display improved novel physical, chemical and biological properties. This phenomenon exists in the nano size scale (1-100 nm) where a nanometer (nm) is one billionth of a meter (Halimaton et *al*., 2007).

The term nanotechnology was first used by Norio Taniguchi to refer to the precise and accurate tolerances required for machining and finishing materials. The term nano derives from the Greek word for dwarf. It is used as a prefix for any unit such as a second or a meter, and it means a billionth of that unit. People are interested at the nanoscale because at this scale that the properties of materials can be very different from those at a larger scale. Nanomaterial has a relatively larger surface area when compared to same mass of materials produced in a larger form. This can make materials more chemically active and affect their strength or electrical properties.

To properly understand and appreciate the diversity of nanomaterial, some form of categorization is required. Currently, the most typical way of classifying nanomaterial is to identify them according to their dimensions. Nanomaterials can be classified as zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D). This classification is based on the number of dimensions, which are not confined to the nanoscale range (<100nm). Zero-dimensional nanomaterials are materials where in all the dimensions are measured within the nanoscale (larger than 100nm). These nanomaterials can be amorphous or crystalline, be single crystalline or polycrystalline, be composed of single or multichemical elements and exhibit various shapes or form. On the other hand, 1-D nanomaterials differ from 0-D nanomaterials in that the former have one dimension that is outside the nanoscale. One-dimensional nanomaterials include nanotubes, nanorods, and nanowires. These 1-D nanomaterials can be amorphous or crystalline, can be single crystalline or polycrystalline, can be chemically pure or impure and it also can be standalone materials or embedded in within another medium.

Two-dimensional nanomaterials are somewhat more difficult to classify. However, 2-D nanomaterials are materials in which two of the dimensions are not confined in the nanoscale. As a result, 2-D nanomaterials exhibit platelike shapes. Two-dimensional nanomaterials include nanofilm, nanolayers and nanocoatings. This nanomaterial can exhibit properties of amorphous or crystalline, made up of various chemical compositions, used as a single layer or multilayer structures, deposited on substrates and integrated in surrounding matrix materials. Three-dimensional of nanomaterials, also known as bulk nanomaterials are relatively difficult to classify also. However, it is true to say bulk nanomaterials are materials that are not confined in nanoscale in any dimension. Three-dimensional nanomaterials can have the properties of amorphous or crystalline, chemically pure or impure, composite materials and composed of multi nano layers.

In this work, thin film comprising of ZrO_2 nanotube arrays were formed then the film was separated to form freestanding ZrO_2 nanotube sheets. The nanotube arrays that been produced consist of 1-D structure because it is in the form of nanotubular structure and the sheets are not in nanoscale, the end product in this experiment has 2-D nanostructure. However, if the thickness of the ZrO_2 sheets exceeds 10µm, thus this nanotube sheets also will experience three-dimensional structure. As a result, the ZrO_2 nanotube sheets compiled of all these three dimensions in it structure.

$ZrO_{2,}$ zirconium dioxide has been investigated extensively due to its many interesting properties. The typical properties exhibited by ZrO_2 that are commonly utilized include high strength, excellent wear resistance, high toughness and ionic conductivity. ZrO_2 has three polymorphs that are monoclinic (M), tetragonal (T) and cubic (C). T and C of ZrO_2 are stable at high temperatures. Monoclinic is the most stable phase at room temperature. However, most engineering applications make use of the T and C phases.

1.2 ZrO_2 Nanotube Photocatalyst

The oxidation of most hydrocarbons proceeds rather slowly in absence of a catalytic active substance. A photocatalyst decrease the activation energy and photoinduced processes occur. A photocatalytic system consists of semiconductor particles which are in close contact with a liquid or gaseous reaction medium. Exposing the catalyst to ultraviolet light processes like redox reactions and melocular transformations take place (Wiemhofer et. al., 1992). This property is important because the photocatalytic reaction can stabilizied the harmful organic compounds into degradable substances.

Advanced Oxidation process (AOP) is a well-known method for wastewater treatment due to its ability to degrade and mineralize organic pollutants. One of the ways to initiate the AOPs is by using semiconductor heterogeneous photocatalyst. Heterogeneous photocatalysis can be described as the acceleration of photoreaction in the presence of photocatalyst. In heterogeneous photocatalyst, two or more phases are used in the photocatalytic reaction. A light source is used to initiate the photoreaction. Thus, the semiconductor material will promote electrons from the valance bond to the excited states in the conduction band if the material is illuminated by photons having energy greater than or equal to its band gap. The generation of electron and hole pair leading to the formation of hydroxyl radical and superoxide radical. These radicals are the primary oxidizing species in the photocatalytic oxidation process (AOP).

ZrO_2 is an important material widely used in heterogeneous catalysis (Corma et. al., 1995). It has been considered recently as a photocatalyst in photochemical heterogenous reaction due to its nature as n-type semiconductor. The reported value of the energy of the bandgap (Eg) of ZrO_2 is in the range between 3.25 and 5.1 eV, depending on the preparation technique of the sample. The most frequent and accepted value of ZrO_2 is 5.0 eV, with a conduction band potential of -1.0V vs. NHE at pH 0. Accordingly, the corresponding value of the valence band potential is +4.0 V vs. NHE. The relatively wide E_g value and the high negative value of the conduction band potential allowed its use as a photocatalyst in the production of hydrogen through water decomposition. Although ZrO_2 presents an absorption maximum around 250 nm, some samples show a non-negligible absorption in the near UV range (290-390 nm). Moreover, some photocatalytic reactions can be performed under irradiation in this range without the participant of light of higher energy (Botta et. al., 1999).

In a photocatalytic reaction, the oxide material is the one which is responsible in the adsorption and degradation of organic compounds and the presence of the Zr foil does not gives any direct influence to the reaction. As the foil is seen as redundant for the photocatalytic process, in this project, the anodic film comprising of the nanotubes was removed from the Zr foil and the nanotube sheets alone were weighed and added to the solution to be degraded. It is also thought that when the anodic film is removed from the foil, the area for reaction can also be increased as both sides of the foil can now be used.