FORMATION OF COBALT COATED TiO_2 NANOTUBES BY WET IMPREGNATION

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UNIVERSITI TEKNIKAL MALAYSIA MELAKA
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FORMATION OF COBALT COATED TiO_2 NANOTUBES BY WET IMPREGNATION

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

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons). The member of the supervisory committee are as follow:

……………………...............................

(Dr. Syahriza binti Ismail)

ABSTRAK

Titanium dioksida (TiO_2), juga dikenali sebagai titania adalah bahan semikonduktor terkenal di mana digunakan secara meluas dalam pelbagai aplikasi seperti fotopemangkinan, sel solar, sensing gas, bioperubatan dan lain-lain. 1D tatasusunan tiubnano telah menarik perhatian yang lebih kerana sifat cemerlang mereka oleh nisbah aspek yang tinggi. Berbanding dengan bahan-bahan pukal, tiubnano struktur pula mempunyai banyak ciri-ciri yang baik di mana sangat relevan untuk prestasi yang lebih baik dalam pelbagai aplikasi. Dalam kajian ini, susunan tiubnano TiO_2 yang mempunyai nisbah aspek yang tinggi dan selaras telah berjaya disintesis dalam glikol etilena yang mengandungi NH_4F dan H_2O_2 melalui kaedah penganodan pada 60 V selama 30 minit. Salutan kobalt telah digunakan untuk menyelesaikan kelemahan TiO_2. Jurang band TiO_2 yang luas dan kadar penggabungan semula yang tinggi telah mengehadkan penggunaan TiO_2 fotokatalis dalam spektrum solar. Kobalt bersalut TiO_2 tiubnano telah dibentuk oleh teknik pengisitepuan basah. TiO_2 tiubnano telah direndam di dalam $CoCl_2$ prekursor dalam tempoh rendaman tertentu. Proses pengisitepuan basah ini adalah masa bergantung, akan mengubah jumlah kobalt yang dimuatkan dalam nanotube permukaan. Dengan kehadiran kobalt, ia didapati bahawa aktiviti pemfotorosotaan dalam cahaya penyinaran UV telah banyak dipertingkatkan berbanding dengan semata-mata TiO_2 tiubnano. Kobalt yang telah dimuatkan boleh bertindak sebagai perangkap yang boleh membantu untuk mengasingkan elektron-lohong. Sebaliknya, kandungan kobalt yang berlebihan pada permukaan dinding TiO_2 tiubnano akan merendahkan prestasi photocatalytic kerana lapisan asing yang dibentuk ini akan bertindak sebagai pusat rekombinasi elektron-lohong.

ABSTRACT

Titanium dioxide (TiO_2), also known as titania is a well known semiconducting material where widely used in many applications such as photocatalysis, solar cell, gas sensing, biomedical and many more. 1D nanotube arrays have attracted more attention due to their outstanding properties by its relatively high aspect ratio. Compared to bulk materials, nanotubes structure posses many favourable characteristics that highly relevant for the improved performance in numerous applications. In this study, highly ordered and well aligned TiO_2 nanotubes were successfully synthesized through anodization of Ti foil in ethylene glycol ($C_2H_6O_2$) containing ammonium fluoride (NH_4F) and hydrogen peroxide (H_2O_2) at 60 V for 30 minutes. Cobalt coating was applied to solve the TiO_2 drawbacks. The wide band gap and high recombination rate restricted the utilization of TiO_2 photocatalyst in solar spectrum. Cobalt coated TiO_2 nanotubes were formed by wet impregnation technique. TiO_2 nanotubes were dipped into $CoCl_2$ precursor for certain soaking period. This diffusion interstitial process via wet impregnation was time dependent, which altered the amount of cobalt loaded in the nanotubes surface. With the presence of cobalt, it was found that the photodegradation activity under UV light irradiation was greatly enhanced as compared to bare TiO_2 nanotubes. The cobalt loaded may act as the shallow traps that can help to separate photo-induced charge carriers effectively. By contrast, excessive content of cobalt existing on the wall surface of TiO_2 nanotubes resulted in poorer photocatalytic performance because it formed independent layers that acted as recombination centers for the charge carriers.

DEDICATION

Only

my beloved father, Kok Sin Kew

my appreciated mother, Chong Yew Thai

my adored brother and sisters, Wei Khong, Fie Ping, Fie Ni and Fie May

for giving me moral support, money, cooperation, encouragement and also understandings

Thank You So Much & Love You All Forever

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LIST OF ABBREVIATIONS

ALD	-	Atomic layer deposition
C_B	-	Conduction band
$C_2H_6O_2$	-	Ethylene glycol
Co	-	Cobalt
$CoCl_2$	-	Cobalt chloride
CO_2	-	Carbon dioxide
DI	-	Deionized water
DC	-	Direct current
E_g	-	Band gap energy
EG	-	Ethylene glycol
FESEM	-	Field emission scanning electron microscopy
H_2O	-	Water
H_2O_2	-	Hydrogen peroxide
MB	-	Methylene blue
MO	-	Methyl orange
NH_4F	-	Ammonium fluoride
RT	-	Room temperature
Ti	-	Titanium
TiO_2	-	Titanium dioxide
UV	-	Ultravoilet
V_B	-	Valance band
WO_3	-	Tungsten trioxide
XRD	-	X-ray diffraction

LIST OF SYMBOLS

$h\nu$	-	Photon energy
e^-	-	Electron
h	-	Hour
h^+	-	Hole
λ	-	Radiation wavelength
eV	-	Electronvolt
°C	-	Degree Celsius
rpm	-	Revolution per minute
ns	-	Nanosecond
nm	-	Nanometer
mm	-	Millimeter
mL	-	Milliliter
µm	-	Micrometer
W	-	Watt
ppm	-	Parts per million
g	-	Gram
min	-	Minute
V	-	Voltage
kV	-	kiloVolt
s	-	Second
M	-	Molar
%	-	Percent
wt%	-	Weight percentage
at%	-	Atomic weight percentage
Θ	-	Diffraction angle

CHAPTER 1

INTRODUCTION

1.1 Research background

In 1972, photocatalytic water splitting of TiO_2 electrodes was first discovered by Fujishima and Honda , which also known as Honda-Fujishima effect, the TiO_2 has become one of the most studied compounds in the following years. This material has attracted a lot of interest in semiconductor photocatalyst application due to its outstanding properties, such as excellent chemically stability, non-toxic and high catalytic activity (Li *et al*., 2016). Recently, the study on the titanium nanostructured morphology is more imperative, which it mostly relies to their properties (Arruda *et al*., 2015). TiO_2 nanostructures are widely used in various functional applications such as photocatalysis, dye sensitized solar cells, gas sensors, hydrogen storage and biomedical materials (Riboni *et al*., 2016).

Among the several nanostructures such as nanoparticles, nanotubes, nanowires, nanorods and nanofilms, the hollow structures of tubular materials leads to a high surface-to-volume ratio (Meng *et al*., 2013). These characteristics are significantly contributed to an enhancement of reaction rate and preferred dimensionality to the system (Roy *et al*., 2011). Since carbon nanotubes has been identified by Iijima in 1991, the chemical synthesis of 1D nanoscale structures for transition metal oxide has been greatly reported. First report by Zwilling *et al*. in 1999 showed the growth of highly ordered TiO_2 nanotubes arrays by electrochemical anodization by using titanium metal sheet. This successful finding is then led to a dramatic increase in the following research activities from the aspects of the growth, mechanisms, properties, and applications of the one-dimensional nanostructures (Regonini *et al*., 2013).

For the photocatalysis application, a photocatalyst is generally used in degradation systems (Blaskov *et al*., 2012). The nano-structured TiO_2 is a well-known photocatalyst among the metal oxides for its high efficiency and non-corrosive property (Tan *et al*., 2011). It has shown an excellent photocatalytic performance due to its stability and high oxidizing power that essential for degrading organic pollutants (Macak *et al*., 2007). Compared with traditional advanced oxidation processes, the technology of photocatalysis is preferred due to their advantages, such as ease of setup and operation at ambient temperatures, no need for postprocesses, low energy consumption and relatively low cost.

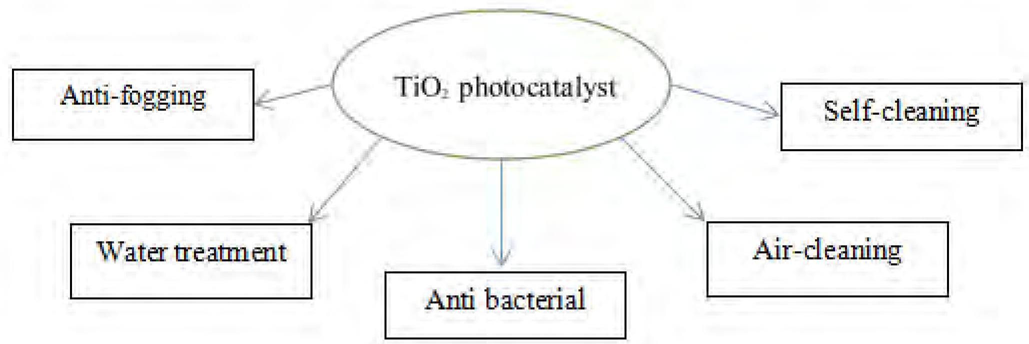


Figure 1.1: Applications of TiO_2 photocatalyst.

1.2 Problem Statement

TiO_2 possesses a very suitable band-edge position that results in a high photocatalytic performance (Roy *et al*., 2011). The main advantages of the TiO_2 nanotubes are highly ordered nanostructure, large surface area and efficient unidirectional charge transport routes. However, there are two main drawbacks existed in TiO_2 photocatalyst which severely hinder its applicability. First of all, the fast recombination of photogenerated charge carriers (electron-hole pairs) brings a decreased quantum yield and poor photocatalytic activity. Then, the relatively wide band gap of TiO_2 leads to its absorption restricted in UV region (Lozzi *et al*., 2016). The photocatalyst application has been limited in the ultilization of visible light of the solar spectrum (Momeni & Ghayeb, 2015).

Serpone et al. (1995) found that about more than 90% of the photoinduced electrons recombine within 10 ns. This relatively high recombination rate greatly decreases the overall quantum efficiency in semiconductor photocatalysis. According to Pelaez *et al*. (2012), when recombination of the photogenerated electron hole pairs occurs, those excited electron will return back to valance band without any reactions with the adsorbed species for degradation. Energy will then dissipated in the form of light or heat. The absence of hydroxyl radicals and superoxide anions brings an ineffective photocatalysis application. Thus, organic pollutants cannot degrade into carbon dioxide and water.

For electron-holes pairs to be generated, TiO_2 photocatalysts need to absorb enough amount of photon energy. Once the adequate input of radiation equal to or higher than the band gap energy, the photocatalytic reaction can be initiated (Li *et al*., 2016). In fact, TiO_2 semiconductor has a wide band gap, where the energy band gaps (E_g) for anatase is 3.2 eV while rutile is 3.0eV accordingly. Its photocatalytic reaction only can be activated under ultraviolet (UV) irradiation, which means that it only corresponds to a relatively small fraction (~5%) of total solar spectrum. (Tobaldi *et al*., 2013)

To resolve these problems, photocatalytic activity of TiO_2 need to be enhanced and the absorption in visible light region need to be improved. So, numerous methods such as doping with transition metals, non-metals and rare earth elements were introduced for the modification of TiO_2 nanotubes (Nischk *et al*., 2016). Doping of cobalt has been proved to minimize the TiO_2 band gap that effectively enhance the photocatalysis in the visible range (Hsieh *et al*., 2009). However, the coating of the nanotubes by transition metals such as Cobalt was not illustrated and implied in detail. Meanwhile, till now, there are few studies has been done that prepare cobalt coated TiO_2 nanotubes formation by the wet impregnation technique.

There are some reasons for choosing cobalt to be coated the TiO_2 nanotubes. According to Amadelli *et al*. (2008), cobalt is present as the divalent form which is cobalt (II) and cobalt (III) ions and Co(II) states are located within the band gap of TiO_2. Cobalt ions loaded on the nanotubes can act as shallow traps to separate the photo-induced carriers. It was responsible to extend the spectrum response visible range and thus increase the photocatalytic capability of TiO_2.

1.3 Objectives

The objectives are as follows:

(a) To synthesis cobalt coated TiO_2 nanotubes by wet impregnation.

(b) To characterize the structural and morphology properties of cobalt coated TiO_2 nanotubes produced by wet impregnation.

(c) To study the photocatalytic properties of the cobalt coated TiO_2 nanotubes.

1.4 Scopes of the Research

This research will covered the study on the formation of cobalt coated TiO_2 nanotubes by wet impregnation and its photocatalytic properties. The parameters for the synthesis such as molarity of precursor and soaking time of $CoCl_2$ solution will be investigated in this study to obtain the optimized cobalt coated TiO_2 nanotubes. The phase formation, structural morphology and characterization on the coated TiO_2 nanotubes will be determined by field emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD) and also Raman spectroscopy. Photodegradation test by methyl orange (MO) aqueous solution will be used to evaluate the photocatalytic activities of the nanotubes. This study aims to modify the band gap energy of cobalt coated TiO_2 nanotubes towards the visible spectral region for an improved photocatalyst.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 mainly describes the theory and research that have been defined and done by various researcher years ago. Related information of previous studies are extracted as references and discussion based on their research about TiO_2, synthesis method, mechanism of TiO_2 nanotubes formation and photocatalyst.

2.1 Titanium dioxide, TiO_2

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurred oxide form of titanium. According to Macak *et al*. (2007), TiO_2 is a material that has been used in many functional applications due to their numbers of unique properties. It becomes one of the preferrable materials for semiconductor oxide photocatalyst based on its interesting properties, for example photostability, oxidation ability (Murakami *et al*., 2008) and low toxicity (Pelaez *et al*., 2012).

2.1.1 Crystal structure

TiO_2 exists in three distinct crystalline phases; which are anatase, rutile and brookite (Pelaez *et al*., 2012). The anatase and rutile structures were first described by Vegard (1916), while brookite structure was identified by Pauling and Strurdivant. Brookite is extremely more difficult to synthesize compared with the other two phases. Rutile is generally considered to be the most stable phase compared to other two phases. The metastable anatase and brookite will transform to the thermodynamically stable rutile upon heating (Hu *et al*., 2003).

For their structure, Titanium (Ti^{4+}) atoms are coordinated to six oxygen (O^{2-}) atoms to form TiO_6 octahedra (Tobaldi *et al*., 2013). The way of the TiO_6 octahedra linked are different in these three polymorphs. The anatase is made of distorted TiO_6 octahedral sites sharing four corners in a tetragonal structure. The orthorhombic structure of brookite is formed where each octahedron shares three edges with adjacent octahedra. The rutile consists of the chains of TiO_6 octahedra that share vertex along c-axis to give a tetragonal structure.

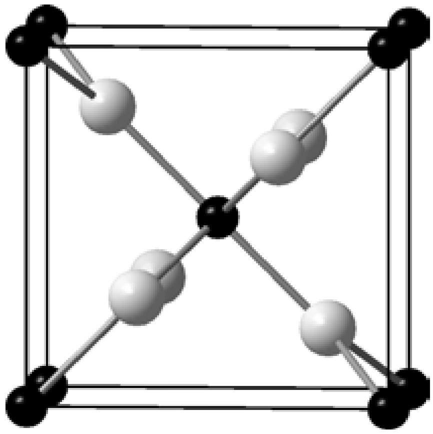
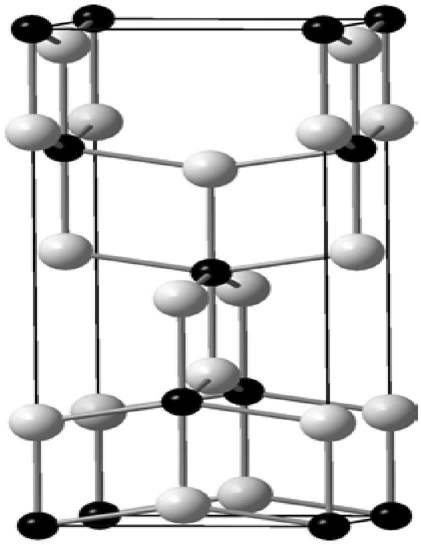
All of the polymorphs exist as wide band gap semiconductors, transparent in the visible region, and with a high refractive index. The two forms, rutile and anatase, absorb at different sections of the spectrum. Rutile is able to absorb violet light with a wavelength of 415 nm which is just within the visible region. For anatase, it only absorbs at the edge of visible light and near-UV light, at 385 nm. So, the present of the rutile is used to move the photocatalytic activity of the titanium dioxide into the visible region wherease anatase phase is preferred because its promising efficiency for photocatlysis usage (Janisch *et al*., 2005).

According to Li *et al*. (2015), the phase transformation of the TiO_2 nanotube film occurred when increase the annealing temperature. TiO_2 phases become the most critical parameter in determining the material properties such as photocatalytic properties.

Table 2.1: TiO_2 phases exists by different annealing temperature (Li *et al*., 2015).

Annealing temperature (^oC)	TiO_2 phases
Without annealing	Amorphous
200	Amorphous
300-500	Anatase
600	Rutile
600-700	Rutile + Anatase
800	Rutile

Table 2.2: Crystalline structures of titanium dioxide, TiO_2 (Janisch *et al*., 2005).

Polymorph	Structure	Figure
Anatase	Tetragonal	
Rutile	Tetragonal	
Brookite	Orthorhombic