UNIVERSITI TEKNIKAL MALAYSIA MELAKA

POROUS PHOTOCATALYTIC NANOTITANIA (TiO_2) THIN FILMS FOR ENVIRONMENTAL SELF-CLEANING APPLICATIONS

Thesis submitted in accordance with requirements of the Technical University of Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) with Honours.

by

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This PSM submitted to the senate of UTeM and has been as partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials). The member of the supervisory committee is as follow:

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Mr. Jeefferie Bin Abd Razak

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DECLARATION

I hereby, declared this report entitled "Porous Photocatalytic Nanotitania (TiO_2) Thin Films for Environmental Self-Cleaning Applications" is the results of my own research except as cited in references.

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ABSTRACT

Titanium dioxide photocatalysis is one of the most promising mechanisms for absolute mineralization of organic pollutants. This research, deals with the modification of the sol gel process for the synthesis of the porous TiO_2-PEG thin films with good structural integrity for water treatment. Relatively by adding the PEG, it can influence the formation of TiO_2 films structure and adhesion. Then, high porosity induced by the combination effect of the template such as the PEG with titania sol can be beneficial to the maximum exposure of the nanocrystallites. Moreover, the formation of TiO_2 associated with larger pores will accelerate the mass transfer of the treated contaminants in the larger pore channels. For the mesoporous TiO_2 thin films prepared by a PEG 300, PEG 400 and PEG 600 through the sol gel method, porous structure and larger film thickness will be obtained. The advantages of the unique structures of the as-prepared TiO_2 films in the application of environmental self-cleaning systems are extensively studied. In this research, details information on the preparation method, synthesis route and its mechanism, crystallographic and structural properties, and photocatalytic activity of the nanocrystalline TiO_2 particles with thermal stability will be investigated. Due to this research, five characteristic techniques applied for the characteristic the photocatalytic coating of TiO_2 thin films such as X-ray Diffraction (XRD), Atomic Force Microscoe (AFM), Transmission Electron Microscopy (TEM) and Brunner-Emmet-Teller (BET) surface area. Adhesion of TiO_2 thin films become smooth and better surface while increasing the coating layers. Besides that, the films structure of TiO_2 thin films produced high anatase peak while increase the coating layer over the five layers coating and the increasing the PEG molecular weight. From the other view, this research will provide the investigation of new nanotechnology product development of high efficient photocatalytic TiO_2 particles films that will be used in the self cleaning and disinfection application.

ABSTRAK

Titanium dioksida photocatalysis adalah salah satu mekanisme yang paling baik untuk menjernihkan pencemaran organic. Kajian ini, berkaitan dengan pengubahsuaian proses sol gel untuk sintesis dari TiO_2-PEG porous filem tipis dengan integriti struktur yang baik untuk pemprosesan air. Relatif dengan menambah PEG, boleh mempengaruhi pembentukan struktur filem TiO_2 dan adhesif. Kemudian, kualiti porositi disebabkan oleh kesan gabungan dari template seperti polietilen glikol (PEG) dengan sol Titania dapat bermanfaat untuk pendedahan maksimum nanokristalografi di lapisan dalam ke antara muka padat-cair. Selain itu, pembentukan TiO_2 berkaitan dengan pori-pori yang lebih besar akan mempercepatkan pemindahan massa dari kontaminan dirawat di saluran pori yang lebih besar. Untuk TiO_2 filem tipis poros disiapkan oleh struktur melalui kaedah sol gel PEG 300, PEG Peg 400 dan 600, mesoporos bimodal dan ketebalan filem yang lebih besar akan diperolehi. Keuntungan dari struktur unik dari TiO_2 filem dalam aplikasi sistem pembersihan sendiri dipelajari. Kerana kajian ini, lima teknik karakteristik tersirat untuk pelapisan fotokatalitik karakteristik filem tipis TiO2 seperti Koheren sinar-X (XRD), Atomic Force Microscoe (AFM), Mikroskop Elektron Transmisi (TEM) dan Brunner-Emmet-Teller (BET) luas permukaan. Adhesi filem tipis TiO2 menjadi halus dan permukaan yang lebih baik sekaligus meningkatkan lapisan coating. Selain itu, struktur film film tipis TiO2 yang dihasilkan puncak anatase quality sementara meningkatkan lapisan lapisan atas lima lapisan coating dan berat molekul PEG peningkatan.Dalam kajian ini, butiran maklumat mengenai kaedah persiapan dan mekanisme sintesis, sifat kristalografi dan struktur, dan aktiviti fotokatalitik dari TiO_2 Nanostrukutral zarah dengan kestabilan terma akan diselidiki. Dari aspek lain, kajian ini akan menyediakan produk pembangunan penyelidikan nanoteknologi baru yang akan digunakan dalam aplikasi system pembersihan persekitaran sendiri dan desinfeksi.

DEDICATION

Emak & All My Family Members, My supervisor Mr. Jeefferie Bin Abd Razak, Head of Department Nanomaterials AMREC Dr. Abd Kadir Bin Masrom & AMREC Staff, FKP Staffs, Classmates & UTeM 2007-2010.

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscope
BET	-	Brunner-Emmet-Teller
CB	-	Conduction Band
CSG	-	Composite-Sol-Gel
CVD	-	Chemical Vapor Deposition
D.I water	-	Distilled water
HCL	-	Acid Hydrochloride
MB	-	Methylene Blue
NIR	-	Near Infrared
PCA	-	Photocatalytic Activity
PEG	-	Polyethylene Glycol
SEM	-	Scanning Electron Microscope
SiO_2	-	Silica Oxide
SnO_2	-	Stanium Oxide
TEM	-	Transmission Electron Microscopy
TiO_2	-	Titanium Dioxide
UV	-	Ultraviolet
VB	-	Valence Band
XRD	-	X-Ray Diffraction
ZnO	-	Zinc Oxide
α-F_e2O_3	-	α Ferrite Oxide

CHAPTER 1

INTRODUCTION

1.1 Research Title

Porous photocatalytic Nanotitania (TiO_2) thin films for environmental self-cleaning applications.

1.2 Introduction

This research is to provide solution of more than 99% clean up of organic and biological contaminants that impact the health and safety of the inhabitant through the utilization of the novel photocatalytic system. Basically, the susceptibility of nanotitanium dioxide (TiO_2) photocatalytic system to absorb the photon energy from the ultraviolet (UV) of the solar spectrum and its reaction with water molecules to produce radicals that could be used to create self-cleaning surfaces are tested. Photocatalyst can break down almost any organic compound and a number of extensively research efforts have been done to take advantage of this reactivity by developing a wide range of environmentally useful products. Not only organic contaminants can be destroyed by TiO_2 particles, but also microorganisms can be deactivated. Overall process are including transfer of the reactants in the fluid phase to the surface, adsorption of at least one of the reactants, reaction in the adsorbed phase, desorption of the products and removal of the products from the interface region (Herrmann, 1999).

The photocatalytic reaction occurs in the adsorbed phase. The only difference with conventional catalysis is the type of activation of the catalyst in which the thermal activation is replaced by a photonic activation. Hydroxyl radicals are formed and will break down the cell. The outer membrane allowing cell contents to pour out and TiO_2 particles to enter. Thus, causing the cell damage and loss in the presences of water (Lee, 2004). This only can be happened when a microorganism is in contact with the TiO_2 surface that exposed to the UV light of the wavelength below 385 nm. Development of high efficient TiO_2 photocatalytic particulate and continuous fibrous systems were done by modifying the TiO_2 electronic structure with additive and increasing the reactive surface area of the catalysts. Photocatalyst design, synthesis and its characterization with the environmental engineering sciences (microbial evaluation) applied the contemporary knowledge of nanotechnology.This combination is to improve the conventional water and air purification quality systems.

The innovation of this research lies in the combination effects introduced by the most reactive photocatalyst TiO_2. Up until now, TiO_2 photocatalysis has been proven to be the most effective for the degradation of several toxic organic contaminants in water and air environment. In the applications deal with the water purification, reactors utilizing the TiO_2 catalyst as immobilized films on the suitable support have a unique advantage over reactors utilizing suspended TiO_2 particles. The sol–gel method is considered as an effective way for the preparation of immobilized TiO_2 films on the variety of substrates surfaces. In this method, heat treatment at higher firing temperature is usually required to obtain the desired crystal phase and good adherence to the surface of the support material such as glass and stainless steel. However, at higher than optimum firing temperature, it will frequently lead to a significant reduction in the photocatalytic activity of TiO_2 films. This is mainly due to the reduction in surface area caused by crystal sintering and collapsing of pore as well as due to the crystal phase transformation from anatase to rutile phase.

TiO_2 modified-sol-gel method can yield relatively thick TiO_2 films with the enhanced of the photocatalytic activity, excellent adherence to the support and much densification compared to those obtained by using the unmodified sol–gel procedure.

This research is actually to evaluate the photocatalytic activity of these immobilized TiO_2 films. Therefore, by incorporating additive into a precursor titania sol, it is expected to show good strategy for developing high performance immobilized TiO_2 films with excellent mechanical stability.

1.3 Problem Statements

Quality of life is becoming a major issue in modern urban living. Comfortness, mobility, energy resources and the environmental awareness are of the key points of interest in future smart materials developments. Environmental problems linked with the treatment of pollutants in air and water environment is a major important focused for the society. Over the last decade, environmental pollution remediation has arisen as a high national and global priority (Hoffmann *et al.,* 1995). However, the issues of environmental remediation are poorly addressed by conventional technologies. Recently, there are so many efforts to overcome this seriously endangered situation. One of the strategies used to treat the pollution is by utilizing the photocatalyst technique.

There are several oxides that have a promising potential in the photocatalyst activity such as TiO_2, ZnO, SnO_2 and α-Fe_2O_3. Among these oxide, anatase- TiO_2 that has been popular for its superior photocatalytic ability and is most widely used for water and air purification, odour control, and sterilization (Fujishima *et al.,* 2000). In fact, anatase TiO_2 is currently the most commonly applied efficient photocatalyst (Anpo, 2000, Liu *et al.,* 2000). Specifically, TiO_2 is an ideal to be used as photocatalyst because of the chemical stability and corrosion resistance behaviors. TiO_2 is used because it may absorb photon energy from the UV end of the solar spectrum and then react with water molecules to produce radicals that could be used to create self-cleaning surfaces. Although, TiO_2 films prepared is fired at high firing temperature often leads to robust crystal structure and good adhesion, however the as-prepared TiO_2 films often suffered from low catalyst activity due to low Brunner-Emmet-Teller (BET) surface area, smaller than optimum pore size, and low porosity. As a result, their UV light reactivity efficiency is not optimum and consequently their photocatalytic activity is less than optimum.

In addition, an increase in the number of coating layers can lead to an increase in photocatalytic activity of porous TiO_2 films. However, this is accompanied with longer and more costly synthesis process. Moreover, thick films may suffer from several problems including mass transfer limitation between the treated contaminants and active sites in the inner layers due to non-optimized pore structure, crack formation, and formation of undesirable crystalline phases due to multiple heat treatment cycles. Therefore, it is crucial to carry out systematic research for in depth understanding on the interrelated aspects of the process and to overcome the earliest mentioned problems and challenges. Development of meaningful strategies for the synthesis of highly active and mechanical stable are compulsory films in order to achieve the stated objectives. Thus, this research was designed innovatively to incorporate polyethylene glycol (PEG) into the precursor sol during the synthesis of thick photocatalytic films on the glass surfaces, since, there is lack of information on the effect of some important preparation conditions, such as the TiO_2 sol and the firing temperature to the effect of the photocatalytic activity. Finally, the characterization of TiO_2 thin films will be extensively studied.

1.4 Objectives of Research

The main aim of this research was to study the photocatalytic activity TiO_2 by preparing the composite sol-gel TiO_2. The specific objectives are as follows:

i. To develop photocatalytic coating for the self-cleaning application.
ii. To obtain a fundamental understanding on the effect of important titania sol on the film structure, adhesion and photocatalytic activity.
iii. To produce TiO_2 sol for enhance photocatalytic activity by adding the formulation of TiO_2 sol using polyethylene glycol (PEG) additive.

1.5 Scope of Research

The research project will focus primarily on the development of photocatalytic composite sol-gel (CSG) for the deposition into thick porous films. In addition, it also to design the photocatalytic nanocomposite systems which have higher photocatalytic efficiency for both surface properties and quantum yield. Development of CSG titania is done by binding the pre-calcined TiO_2 sol which have a relatively high surface area and good resistance against the mechanical stress and abrasion. Besides that, the formation of TiO_2 associated with larger pores induced by decomposition of PEG additive is considered as an important reason for dramatic enhancement in photocatalytic activity of TiO_2 composite films.

1.6 Hypothesis

These photocatalytic TiO_2 thin films and membranes have great potential in developing high efficient self-cleaning systems because of their multiple and simultaneous functions such as decomposition of organic pollutants. It is projected; increasing the loading the PEG additive into TiO_2 sol will enhance the photocatalytic activity of TiO_2 thin films. It is also expected that the repetition of the coating procedure made it possible to control the physical properties of the TiO_2 layer such as the coating thickness, catalyst amount, photocatalytic activity and water permeability. Consequently, it will improve the final photocatalytic activities of the fabricated TiO_2 thin films.

1.7 Importance of the Research

It is hope that this research will contribute to the development of new or novel photocatalytic system for self-cleaning application. Besides that, it is also expected to contribute to the future development of smart materials which facilitate the water treatment application by reacting with water molecules to produce radicals that assist self-cleaning surfaces activity.

1.8 Organization

Chapter One gives about an introduction to the projects which include objectives, scope of works, and background of the study. In this chapter, it describes the background of photocatalyst activity and its major application. Next, Chapter Two presents the literature review on titanium dioxide (TiO_2) photocatalysis and its application to the environmental cleaning related to previous research finding, photocatalytic disinfection of biological contaminants, design and synthesis of highly enhanced photocatalyst system binded with pre-calcined of TiO_2 and TiO_2 nanocoating. Then, Chapter Three focused about description on the methodology and parameter used in this research for overall study. All the research flow, raw materials, procedure of the research and the characterization analysis involved during this research, were described details for this chapter. Next, Chapter Four involved the results and discussions which are included all the characterization analysis of various properties and microstructure, area explained in details. Besides that, this chapter also included the comparison of previous research finding with this research. Chapter Five is a summary of the research which is concludes the whole finding of the research. In the same time, Chapter Five also provides the recommendations for future implementation or improvement for research effectiveness.

CHAPTER 2

LITERATURE REVIEW

2.0 Photocatalyst

Photocatalyst can be defined as the acceleration of a photoreaction in the presence of a catalyst. In catalyzed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis the photocatalytic activity (PCA) is depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (hydroxyl radical of-OH) that able to undergo the secondary reactions. Generally, the defining factor is the production and the use of the hydroxyl radical. There are several materials considered as photocatalyst such as titanium oxide (TiO_2), zinc sulfide (ZnS), stanium oxide (SnO_2), strontium titanate (SrTiO3) and zinc oxide (ZnO). Titanium oxide (TiO_2) is used as photocalyst material for further research. Considering its excellent characteristic for this application. TiO_2 also is very stable without chemically dissolving in acid and alkali. Furthermore, TiO_2 is oxidative in nature and with the 3.2eV of energy band, it is very suitable to be used for the photocatalytic application. In addition, TiO_2 also are Inexpensive when produced on a large scale as white pigment.

2.1 Photocatalyst TiO_2

Akira Fujishima (1967) discovered the photocatalytic water decomposition activity on TiO_2 surface that is called Honda-Fujishima effect. Thus great discovery of self-cleaning activities of TiO_2 brought major revolution in development of ceramic and glass with antimicrobial application. It is found that the water decomposition reaction by TiO_2 electrodes can be done without electricity. In general, photocatalyst can break down almost any organic compound and a number of research groups have been work out to take advantage of this unique reactivity by developing a wide range of environmentally innovative products. Not only organic contaminants can be destroyed by TiO_2 particles but microorganism's activity also can be deactivated. When the microorganism is in contact with the TiO_2 surface that exposed to the UV light at the wavelength of below 385 nm, the hydroxyl radicals will form and break down the cell wall and outer membrane which later the allowing cell contents to leak out and the TiO_2 particles to enter. Thereby causing cell damage and death in the presence of water (Lee,S.W., 2004). Photocatalysis can be carried out in various media such as gas phase, pure organic liquid phases, and at the aqueous solutions. As for standard heterogeneous catalysis, the overall process can be divided into five independent steps. First steps will be the transfer of the reactants in the fluid phase to the surface. Next, will be the adsorption of at least one of the reactants. The reaction will be occurred in the absorbed phase. Later, the desorption of the products will be occurred. Finally, the removal of the product was happen at the interface region (Chang, 2008).

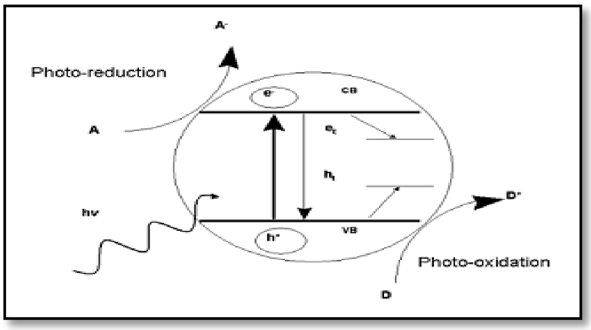

Figure 2.1: Basic principle of photocatalyst (http://www.civil.northwestern.edu/EHE/HTML_KAG/Kimweb/Photocatalysis.html online on 5 October 2009).

The only difference with the conventional catalysis is the type of activation system which the thermal activation is replaced by a photonic activation. Photocatalysis over a semiconductor such as TiO_2 is initiated by the absorption of a photon with energy equal to or greater than the band gap of the semiconductor (3.2 eV for TiO_2), producing electron-hole (e-/h+) pairs, that dissociate into free photoelectrons in the conduction band and photoholes in the valence band (Lee,S.W., 2004). At the same