INFLUENCE OF ADDITIVES ON SOL-GEL NANOPOROUS TiO_2 THIN FILM

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

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DECLARATION

I hereby, declared this report entitled "Influence of Additives on Sol-Gel Nanoporous TiO_2 Thin Film" is the results of my own study except as cited in references.

Signature : ………………………………

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment to the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

……………………………………..

(Prof Madya Dr. Zulkifli Bin Mohd Rosli)

ABSTRAK

Cecair Titanium Dioksida (TiO_2) telah disediakan melalui process percampuran Titanium Tetraisopropoxide (TTiP) ke dalam Hidroklorik asid (HCl), etanol (C_2H_6O) dan air suling pada suhu dan tekanan bilik. Prestasi fotopemangkin dapat dipertingkatkan dengan mencampur pemangkin ke cecair TiO_2 kerana pemangkin membantu penukaran microstruktur dalam filem nipis TiO_2. Polietilena glikol (PEG) dan serbuk Degussa P25 telah digunakan sebagai pemangkin dalam kajian ini. PEG menggalakkan pembentukan filem nipis TiO_2 yang bebas daripada retak dan berliang dalam nano saiz. Selain itu, serbuk Degussa P25 digunakan untuk meningkatkan kristal anatase dalam fasa penkristalan kerana ia terdiri daripada gabungan fasa anatase dan rutil fasa dengan nisbah 70:30. Filem nipis TiO_2 dibentuk dengan pencelupan substrat ke dalam cecair TiO_2 melalui proses celupan yang terkawal. Sebanyak 5 celupan telah dilakukan berturut-turut untuk menghasilkan ketabalan saput nipis yang optima pada permukaan substrat. Pemanasan dan pengkalsinan terhadap substrat yang telup dicelup denggan TiO_2 telah dijalankan pasa suhu yang agak tinggi iaitu 500 ˚C untuk memastikan pengkristalan berlaku. Filem nipis TiO_2 didapati dalam keadaan baik iaitu ia melekat dengan sempurna terhadap permukaan substrat. Penggunaan pancaran kemikroskopan electron imbasan (SEM) telah menunjukkan substrat bersalut dengan TiO_2 dan TiO_2/PEG mempunyai morfologi permukaan yang sama; kedua-dua substrat tersebut membetuk permukaan yang retak dan medakan putih. Substrat dicelup dengan TiO_2/PEG menunjukkan retakan yang lebih rendah kerana PEG menghalang pembentukan retak. Substrat dicelup dengan TiO_2/Degussa P25 menghasilkan struktur salutan yang padat densiti, bebas daripada retakan dan aglomerasi P25 nano partikel berlaku atas salutan. Ia juga mempunyai liang kecil yang bersaiz 2 μm. Ciri-ciri tersebut diperlukan untuk mendapatkan keadaan fotopemangkin yang terbaik.

ABSTRACT

Titanium Dioxide (TiO_2) sol was prepared at room temperature, approximately 27 ˚C and ambient pressure by hydrolysis of Titanium Tetraisopropoxide (TTiP) in acidic aqueous solution (Hydrochloric acid, HCl), ethanol (C_2H_6O) and distilled water. Additives were added into TiO_2 sol as it can enhanced in the photocatalytic performance by changing the microstructure of the TiO_2 thin film formed. Polyethylene glycol (PEG) and Degussa P25 were the additives used in this study. PEG can promote the formation of crack free and nanoporous TiO_2 thin film. Besides, Degussa P25 powder was used to increase the anatase phase presence in the crystalline phase as it consists of a combination phases of anatase and rutile phases with the ratio of 70:30. The TiO_2 thin films are deposited on microscope glass slides from the as-prepared TiO_2 sol by a dip coating process at room temperature and ambient pressure. TiO_2 layers on the substrate were thickened by 5 consecutive coatings. Heat treatment was applied at a higher temperature at 500 ˚C to improve crystallization. Eventually, TiO_2 thin film was found to be in well adhesion through the substrates. Scanning electron microscope (SEM) investigations revealed that substrates coated with TiO_2 and TiO_2/PEG exhibited same surface morphology; both formed coating with severe cracks and some white precipitates. However, amount of cracks were observed to be reduced in TiO_2/PEG coating compared to TiO_2 coating because PEG tend to inhibit the growth of cracks. TiO_2/Degussa P25 formed a denser structure coating which was free of crack and P25 nanoparticles tend to agglomerates on the final coating. Fine pores with estimated size of 2 μm were formed also. These are the characteristics that are proned to achieve high photocatalytic performance.

DEDICATION

I would like to dedicate this work to my beloved parents, lecturers and friends whose have guided and inspired me through this education journey. Also thanks to their support, belief and motivation.

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LIST OF ABBREVIATIONS

TiO_2	-	Titanium Dioxide
CVD	-	Chemical Vapor Deposition
PVD	-	Physical Vapor Deposition
PEG	-	Polyethylene Glycol
ZnO	-	Zinc Oxide
SiO_2	-	Silicon Dioxide
DSSCs	-	Dye-sensitized Solar Cells
TCO	-	Transparent Conductive Oxide
HCl	-	Hydrochloric Acid
CMC	-	Carboxy Methyl Cellulose
PVP	-	Polyvinyl Pyrrolidon
HCC	-	Hydroxylpropy Cellulose
PTA	-	Peroxotitanic Acide
IUPAC	-	International Union of Pure and Applied Chemistry
TTiP	-	Titanium Tetraisopropoxide
SEM	-	Scanning Electron Microscope
XRD	-	X-ray Diffraction
PMMA	-	Polymethylmethacrylate
CMM	-	Coordinate Measuring Machine
EDX	-	Energy Dispersive X-ray

CHAPTER 1

INTRODUCTION

This chapter gives an overview about this project. Problem statement, objectives and scopes are also discussed in the following section.

1.1 Background Study

In recent decades, Titanium Dioxide (TiO_2) becomes one of the world‟s most popular photocatalytic materials. In 1972, Fujishima and Honda have discovered the important role of TiO_2 in photocatalytic activities. The main reasons behind the use of TiO_2 over other materials are related to its high chemical stability, low cost, absolutely non-toxic and highly photoactive that this type of material presents. There are several existing crystalline phases of TiO_2 in nature which are anatase, brookite and rutile. Among these, anatase is widely used in most researches because it has a high photocatalytic activity. The resulting coatings have great potentials in a vast range of applications including antimicrobial coating, photocatalytic system, anti-fogging and self-cleaning technology as well as humidity sensor (Guo *et al*., 2004).

Oshani *et al.* (2014) stated that there are numerous of techniques such as chemical vapor deposition (CVD), spray pyrolysis, sputtering and sol-gel have been employed to prepare TiO_2 thin films. Each of these techniques has its own superiorities and weaknesses. The relatively simple sol-gel method is a well-known and suitable method for the preparation of porous TiO_2 thin films (Tristantini *et al*., 2011). The sol-gel method of preparing thin films offers greater advantages over other techniques: low temperature processing, easy coating of large surface, low cost equipment and good optical properties (Attia *et al*., 2012). It is significantly easy to operate and therefore, it can be used to deposit TiO_2 films on almost all substrates.

Some critical factors such as crystal phases and porosity contributed to the photocatalytic performance of TiO_2 thin films significantly (Guo *et al*., 2004). By incorporating additives into the TiO_2 thin film can change the microstructure of the thin film coating. For instance, the use of Polyethylene glycol (PEG) additives in modifying TiO_2 thin films had been done by other researches (Tristantini *et al*.,2011). According to previous researches Guo *et al.* (2004), PEG acts as a structure-directing agent and it is responsible for the generation of porous structure in the films. In other words, PEG content strongly influenced the formation of nanoporous and crack-free TiO_2 with adjustable sizes.

In the present research, constant amount of PEG and Degussa P25 will be added and systematically studied to make a nanoporous TiO_2 thin film prepared by sol-gel method. For better understanding on the impact of additive on TiO_2 thin film properties, analysis on its morphological will be performed.

1.2 Problem Statement

TiO_2 thin films coating have attracted wide spread attraction due to their employment in many applications and its outstanding ability to be deposited well on a variety of substrates.

It is well known that the photocatalytic activities of TiO_2 films are strongly depend on crystal phase structure and porosity of the films. In terms of crystal phase structure, TiO_2 existed in several phases such as brookite, rutile and anatase. Among these phases, anatase phase has been widely used because it has a high photocatalytic activity; whereas for the porosity factor in producing the films, a higher porous surface structure is desirable because it offers a much greater number of catalytic sites compared to a dense film.

Additive can plays a critical role in determining the features of the film produced. Previous studies have manipulated the utilizing of additives in synthesizing the TiO_2 films in order to increase the photocatalytic sites. For instance, Degussa P25 and Polyethylene glycol (PEG) are additives that make a huge influence on the formation of crack free films with greater amount of nanoporous surface structure.

In other words, additive plays a vital role in determining the TiO_2 film"s microstructure. Thus, a study is carried out systematically to evaluate the effect of additives, e.g. Degussa P25 and Polyethylene glycol (PEG), on the properties of the thin TiO_2 thin films produced by sol-gel dip coating method.

1.3 Objectives

The objectives of this research are:

(a) To deposit a nanoporous TiO_2 thin films via sol-gel method.
(b) To analyse the effect of varying additives in producing a nanoporous TiO_2 thin film coating via sol-gel method.

1.4 Scope

The scope of this research is focused on the coating microstructure analysis that determined by the additives used. TiO_2 thin film is coated onto the substrate surface and the substrate is microscope glass slides. Sol-gel dip coating is used to manufacture TiO_2 thin film in this study due to its economical cost and low processing temperature. The characteristics study is to analyse the surface morphology such as porosity of the crystallization structure of the coating. The significance of this study is to enhance the performance of photocatalytic by using the TiO_2 formulation with a method of sol-gel dip coating deposition. Thus, improved photocatalytic efficiency TiO_2 thin film coating will be applied to all related photocatalytic applications.

CHAPTER 2

LITERATURE REVIEW

The present chapter discusses the brief theory of thin film technology and highlights the fundamentals of TiO_2. Apart from this, sol-gel derived coating - dip coating method is used to synthesize TiO_2 while highlighting the different additives incorporated in this technique.

2.1 Thin Film Technology

Technologies for synthesizing thin films and nanostructured coatings have been under steady development at least since 1950s. Thin film technologies have been a source of intense interest in a variety of industrial applications still today. Basically, a thin film is a layer of material deposited on a substrate in which the thickness typically ranging from nanometer to several micrometers (Granqvist, 2012). Accordingly, thin film features mostly come from its thickness deposited on the substrate. These thin films used to manipulate and improve the physical properties of various substrates by employing the properties of the selective coating materials on the substrate surface. Hence, unique functional surfaces can be fabricated on the specific substrates.

2.1.1 Titanium dioxide (TiO_2) thin film

TiO_2 is white and opaque naturally occurring oxide of titanium. TiO_2 catalyst generally comes in powder form and additional treatment is required before it coated on substrate"s surfaces (Tristantini *et al.*, 2011). Another drawback of TiO_2 is that,

TiO_2 is very difficult to be separated from suspension after its fabrication. Therefore, great attention has been given to developing TiO_2 powder catalyst to TiO_2 thin film catalyst and it is the innovative solution to the problems. Up to now, many researches had been done to enhance photocatalytic activity in TiO_2 thin film form (Eufinger *et al.*, 2008).

2.1.2 Advantages and disadvantages of TiO_2

In 1821, Titanium dioxide (TiO_2) was discovered. However, it could only be massively produced until 1916 by that modern technology had progressed at that time (Shon *et al.*, 2008). In recent years, TiO_2 is extensively used as thin film on many substrates such as soda lime glass, quartz glass, Silicon wafer and stainless steel in kinds of applications with regard to its remarkable chemical and physical properties.

Among the materials available such as Zinc oxide (ZnO) and Silicon dioxide (SiO_2), TiO_2 is the most promising material used as a photocatalyst with respect to its much more advantages. Despite its promising properties, unfortunately, there are some major apparent disadvantages in TiO_2. The superiorities and weaknesses of TiO_2 are clearly summarized in the provided Table 2.1.

Table 2.1: Superiorities and Weakness of Titanium Dioxide (TiO_2).

Superiorities	Weakness
• High chemical Stability • Highly Photoactive • Excellent durability • Non-toxicity • Low cost	• Relatively large band gap (Eg = 3.2 eV for anatase phase)

2.1.3 Applications of TiO_2 thin film

A numerous of the sol-gel derived films have been manufactured for different applications. TiO_2 thin film have been extensive applied in vary industrial applications lately due to its remarkable properties. Accordingly, the scientific community has started to explore the great potential applications of TiO_2 thin film.

According to Lam *et al.* (2008) and Tristantini *et al.* (2011), anti-fogging and self-cleaning application is one of the possible applications. Outdoor materials such as window, side mirror of car and windshield have been exposed to dust in air, rain and environment pollution can become dirty easier as compared to indoor materials. Consequently, a frequent cleaning is required to maintain clear transparency and visualization of the materials. However, preparation of cleaning chemicals, equipment and also manpower for traditional cleaning method could be complex and costly. In order to improve the current situation, TiO_2 thin film with strong oxidation power and excellent hydrophilic wetting properties is broadly used. Hydrophilic wetting properties of TiO_2 degrade the pollutants on TiO_2 coated surfaces and make it easy to be eliminated (Tristantini *et al.,* 2011).

According to Liang *et al.* (2010), TiO_2 film is of great and increasing importance for dye-sensitized solar cells (DSSCs). In recent years, relatively low cost manufacturing DSSCs with high photo-to-electric efficiency properties have become the favorite research titles of many researchers due to the increasingly concern of public to the environment. Large surface area of TiO_2 films has conducted a good connection between the TiO_2/TiO_2 gains and TiO_2/transparent conductive oxide (TCO) glass interface are important to the performance of DSSCs (Liang *et al.,* 2010). TiO_2 film that incorporated with increasing of molecular weight of polyethylene glycol (PEG) increases the number of porosity of the films. As a result, a higher surface area of TiO_2 film was created in which leads to the increased dye loading as well as performance of DSSCs.

According to Biju and Jain (2007), TiO_2 thin films have attracted numerous applications including humidity sensors. The measurement and control of humidity air is a critical issue in many areas such as meteorology, industrial and agricultural fields and food production line. Nanocrystalline TiO_2 thin film is a potential candidate for humidity sensing and it has been frequently reported for the application of humidity sensors. The special feature of TiO_2 thin film provides a large surface area that enhances the adsorption process of water and hence, it leads to high humidity sensitivity (Biju and Jain, 2007).

2.2 Thin Film Deposition Methods: Sol-gel Technique

According to Sakka (2003), sol-gel technology plays a vital role in the development of modern nanotechnology as almost all gel products involved nanoparticles. Sol-gel technique has been developed and employed to prepare various materials because it has main advantage of easy control of chemical composition and low temperature synthesis that are very important for thin film formation.

The sol-gel process is known also soft chemistry („chimie douce‟). It is a wet-chemical technique to form colloidal solution or known as sol for thin film deposition used. A sol is a colloidal suspension of solid particles in a liquid with small dispersed phase (1-1000nm). In brief, sol-gel method describes a formation of solid material from a solution by using sol or gel as an intermediate step. In 1845, M. Ebelmen was discovered the earliest sol-gel derived material in France (Attia *et al.*, 2002). The specific uses of sol-gel processed thin film coatings are derived from various materials and forms in different structure.

The primary chemical system of sol-gel process consists of four main constituents, namely precursor, solvent, catalyst and additive. Catalyst is the substance that speeds up a chemical reaction without changing itself. Acid and base are the two types of catalysts and each reaction of the catalyst will be different. Unique combinations of molar ratio of these four chemicals are used to form a thin film coating. HCl is used in the present work because it plays an important role in the synthesis of the anatase phase of TiO_2 (Funda *et al.*, 2005).

2.2.1 Process Routes

The sol-gel process can be done by a series of distinct steps that involving chemical and physical processes associated with hydrolysis, polymerization, gelation, condensation, drying and densification. Figure 2.1 shown the general steps in the sol-gel process. Attia *et al.* (2002) stated that sol-gel process involved the steps as below:

(a) Preparing a stable homogenous solution of precursor in organic solvent miscible with distilled water
(b) Formation of sol from the solution by hydrolysis
(c) Conversion of the sol to a gel by polycondensation
(d) Shaping the gel to finally desired forms such as thin film in this study
(e) Sintering and densification process at temperature (~500˚C)

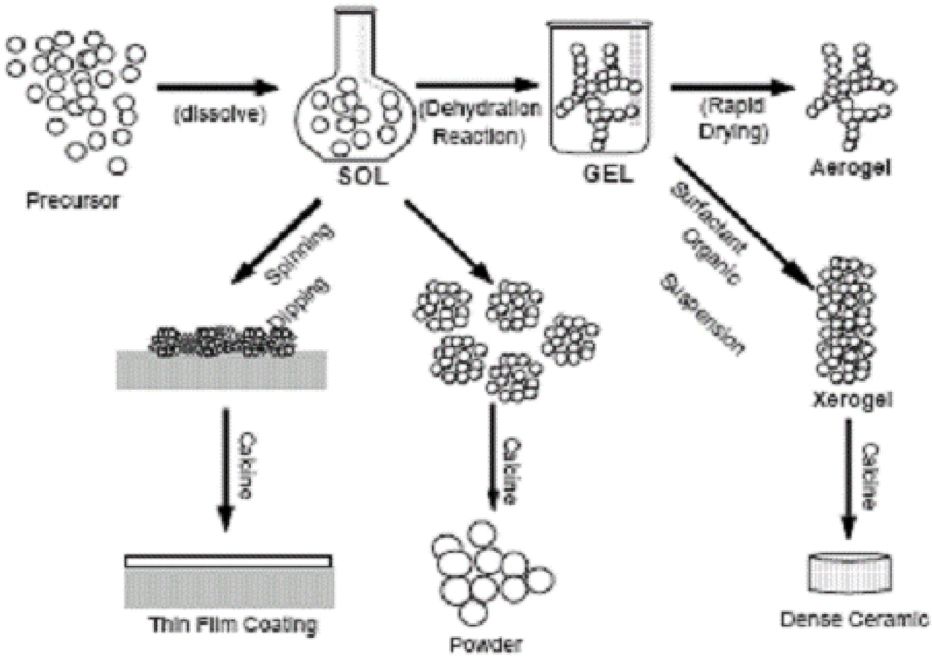

Figure 2.1: Schematic representation of sol-gel process.
(Source: http://www.gitam.edu/eresource/nano/nanotechnology/bottamup%20app.htm)

This study is concern of preparing of thin film coating by dip coating the substrate in sol via sol-gel method. It is not up to stage of dehydration to a gel and dry networks.

2.2.2 Comparison of thin film deposition methods

Thin film and coating technologies are of intense interest today. There are two primary deposition methods used today in terms of chemical and physical principles of operations: chemical vapor deposition (CVD) and physical vapor deposition (PVD). In fact, CVD of films involve the chemical reactions of gaseous reactants occur on substrate surface and leading to the deposition of a solid film (Choy, 2003). In contrast, there is no chemical reaction involved of vapors in PVD. Each method has some advantages and disadvantages that are summarized in Table 2.2.

Table 2.2: Comparison of thin film deposition methods (Brinker *et al.*, 1991; Mattox *et al.*, 1998; Park and Sudarshan, 2001; Brundle and Evan, 2001).

Methods		Advantages	Disadvantages
Physcial Vapor Deposition (PVD)	Sputtering	• Any material can be sputtered including element, alloy or compound • Uniform thickness over large substrate	• Often Expensive • Low deposition rate • Substrate damage due to ion bombardment
	Electron Beam Evaporation	• Thickness of films can be controlled easily • Deposit on a wide range of materials • Can form multiple layers of films	• High capital equipment coast • Line-of-sight process
	Pulsed Laser Deposition (PLD)	• Versatile method • Simple • Cost-effective	• Splashing of particulates • Non-conformal coverage
Chemical gas phase methods	Spray Pyrolysis	• Low cost • High Purity Product • Uniform deposition scaled for large area	• Poor control of product morphology : porous and hollow particles are often formed
	Chemical Vapor Deposition (CVD)	• Conformal films formed • High deposition rate	• High process temperature • Hazardous, toxic and corrosive process
	Sol-Gel Method	• Low temperature processing • Relatively small thickness of films produced. • Easy coating on large surface • Simple	• Often a large volume shrinkage and cracking during drying • Relatively expensive of raw materials

In this study, sol-gel method has been chosen for TiO_2 thin film deposition along with its noticeable advantages and disadvantages presented. The value of sol-gel method makes it attractive and competitive to other thin film deposition methods.

2.2.3 Sol-gel derived coating: dip coating

A variety of sol-gel derived coating techniques are available in fabricating TiO_2 thin film such as dip coating, spin coating, spray coating, flow coating, capillary coating and roll coating. However, in many cases, most of the coating techniques have not been effective. Based on the previous researches, many works have been done by using dip coating techniques (Anastasescu *et al*., 2004; Oshani *et al*., 2014; Lam, 2008; Andronic *et al*., 2013). It is a popular way of making thin film coated materials.

Dip coating techniques is a process where the substrate to be coated is immersed in a fluid sol and then withdrawn with a suitable withdrawal speed under controlled conditions. Sol-gel dip coating results in the deposition of a solid film on the substrates (Brinker *et al*., 1991). Dip coating can be divided into five stages: immersion, start up, deposition, evaporation and finally drainage as summarized in Figure 2.2. Attia *et al*. (2002) reported that gelation process begins when the surrounding environment condition controls the solvents from evaporates in dip coating process. This results in the formation of a transparent film on the substrate.

There are several crucial factors should be taken into consideration as they may influence the deposited film thickness. One of the significant factors is substrate speed. In particular, a thinner film can be produced with a slower substrate withdrawal speed (Klein, 1994). In contrast, the faster the substrate speed, the thicker the film deposited. Nevertheless, viscosity of the liquid governs the film thickness. The coating can be differing from 20 nm up to 50 nm as well as maintaining excellent optical properties by selecting the appropriate viscosity (Attia *et al*., 2002). It is possible to customize the pore size and surface area as well as pore volume with a good control of these factors.