UNIVERSITI TEKNIKAL MALAYSIA MELAKA

EFFECT OF SPINNING RATE AND SINTERING TEMPERATURE OF TiO_2 SOL-GEL VIA SPIN COATING

This report is submitted in accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor of Manufacturing Engineering Technology (Process and Technology) with Honours.

By

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APPROVAL

This report is submitted to the Faculty of Engineering Technology of UTeM as a partial fulfilment of the requirement for the degree of Bachelor of Manufacturing Engineering Technology (Process and Technology) with Honours. The member of the supervisory is as follow:

Signature : ______________________________

Supervisor's Name : Associate Professor Ts. Dr. Zulkifli Bin Mohd Rosli

Date : 30th November 2018

DEDICATION

To my beloved father, Tan Hun Teng, and mother, Chiew Yoke Har.

ABSTRACT

In these few decades, Titanium Dioxide (TiO_2) exist as an important topic that being studied. This is due to its benefits that brought to the society. Furthermore, there are several functions which is beneficial to the current science and technology industry. For instance, the self-cleaning function of TiO_2 when coated in a substrate. TiO_2 can be classified into three different crystalline phase which are rutile, anatase and brooktie. In this study, researcher will focus on the study of TiO_2 in brookite phase. The uniqueness of TiO_2 in brookite phase is about the photocatalysis ability after being coated in the surface of the substrate. Brookite TiO_2 is able to carry out photocatalytic activities under visible light while anatase TiO_2 perform a better photocatalytic activity under UV light. The technique used to coat the substrate is using sol-gel via spin coating. Spin coating is a suitable method to coat TiO_2 onto a substrate because it can produce flat and thin layer of coating. Characterization method used to analyse the effect of specimen are using Scanning Electron Microscope (SEM) to analyse the morphology while using X-Ray Diffraction (XRD) to analyse the crystalline phase. Researcher found that the higher the spinning rate during spin coating process will produce a thinner cross section thickness of TiO_2 sol-gel thin film. Beside this, the sintering temperature used for this experiment is not sufficient to change the crystalline phase of the TiO_2. The surface morphology of the TiO_2 thin film is uniform and denser due to the catalyst used in this experiment when synthesizing TiO_2 sol-gel. Researcher suggest that to set a higher temperature to observe the effect of sintering temperature on coating surface quality in the future research.

Key words: sol-gel, Titanium Dioxide, crystalline phase, morphology, spin coating

ABSTRAK

Titanium Dioksida (TiO_2) merupakan topik yang dikajikan dalam masa beberapa dekad yang lalu. Hal ini disebabkan bahawa bahan ini memberi banyak manfaat kepada manusia. Di samping itu, bahan ini menpunyai kegunaan yang penting kepada bidang sains dan teknologi. Sebagai contohnya, TiO_2 menpunyai fungsi pembersihan sendiri apabila disalut pada substrat. TiO_2 boleh diklasifikasikan kepada beberapa fasa kristal seperti rutile, anatase dan brookite. Dalam projek ini, fasa kristal yang dititikberatkan adalah TiO_2 dalam fasa brookite kerana brookite mempunyai kelebihan yang unik untuk dikajikan. Keunikan brookite adalah kuasa fotokatalisisnya berbanding dengan anatase dan rutile. TiO_2 dalam fasa kristal dapat mengjalankan aktiviti fotokatalisis dalam kewujudan cahaya yang boleh dilihat oleh mata kasar manakala fasa anatasa hanya boleh menjalankan aktivit fotokatalisis dalam melalui cahaya UV. Teknik salutan yang digunakan dalam projek ini adalah menggunakan sol-gel melalui teknik salutan putaran (spin coating). Teknik ini dapat menyalut TiO_2 pada permukaan substrat secara rata dan nipis. Teknik pencirian yang dipilih untuk menganalisis spesimen yang telah disalut adalah melalui mesin Scanning Electron Microscope (SEM) untuk mengkaji tentang permukaan morfologi manankala mesin X-Ray Diffraction (XRD) digunakan untuk mengkaji fasa kristal spesimen. Pengkaji mendapati bahawa kadar pemutaran yang tinggi menghasilkan salutan yang nipis. Di samping itu, suhu yang digunakan tidak dapat membawa sebarang perubahan dan perbezaan yang jelas. Permukaan morfologi yang dihasilkan secara uniform dan padat kerana pemangkin yang digunkan dalam kajian ini. Pengkaji mencadang bahawa memilih suhu yang lebih tinggi untuk rawatan haba bagi spesimen supaya dapat melihat perbezaan dan perubahan yang jelas dalam kajian masa depan.

Kata kunci: sol-gel, Titanium Dioksida, Fasa Kristal, Morfologi, salutan putaran

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

DI	- Deionized Water
HCL	- Hydrochloric Acid
pH value	- Power of hydrogen value
SEM	- Scanning Electron Microscope
TiO_2	- Titanium Dioxide
TTIP	- Titanium Isopropoxide
XRD	- X-Ray Diffraction
β	- Line broadening at half the maximum intensity
θ	- Bragg angle
λ	- Wavelength of X-Rays
ω	- Spinning speed during spin coating process

CHAPTER 1

INTRODUCTION

1.0 Introduction

This chapter describe the background of the research, the problem statements and objectives needed to be achieved in this research. Moreover, scope covered is being stated in this chapter.

1.1 Background of Study

Titanium dioxide, TiO_2 thin film is a popular topic in recent decades and it is being intensively studied by researchers due to its potential applications such as optoelectronic applications, electric appliances like refrigerators, water purifications such as removal of hazardous substances and disinfection, and photocatalytic activities (for examples, self-cleaning glass). TiO_2 normally existed in several form which are anatase, rutile and brookite.

By comparing the three form (anatase, rutile and brookite), brookite is the rarest form. Brookite is a structure formed by octahedral with titanium oxygen ion at every vertices while anatase and rutile with the structure of tetragonal. Brookite with largest cell volume and least dense compare to the other two forms. It is rare to use for experimental investigation. Hence, this study will focus on investigating the coating properties of brookite form TiO_2 thin films. Further discussion on brookite form TiO_2 is being discussed in the literature review chapter.

TiO_2 thin films can be prepared by various technique. For examples, chemical vapour deposition, hydrolysis deposition, electrodeposition, chemical spray pyrolysis and sol-gel method. In comparison, sol-gel is more often and more preferable used because of its good homogeneity, advantages on controlling the parameters of characterizations such as particle size, morphology and film thickness. Furthermore, sol-gel technique has the advantage of purity and it is more economic. Sol-gel technique permits the production of thin films with better adhesion properties which is applicable to complex geometries and not only constraint to metallic substrate because of its low sintering temperatures, (Juhasz et al., 2011).

Performance of TiO_2 thin film will be influenced by the synthesis parameters and the coating conditions. In this study, researcher are going to study and analyse the effect of different coating condition on the characteristics of the coated thin film. The parameters set as manipulation variables in this study is the spinning rate and the sintering temperature. Three different spinning rate and three vary sintering temperature had been fixed for this study. After the coating process, specimens are being analyse by scientific method like by using Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD) to analyse the morphology, grain size and crystalline phase of the specimens. Different coating parameters results to different properties of the substrates.

The spinning rate of spin-coating as it plays an important role in the post coating effect. According to Bhargava et al. (2018), in centrifugal spinning, there is a competition between surface tension of the sol and centrifugal forces. When the centrifugal forces is high enough to against the surface tension, the sol is able pulled to form fibres. In other word, the higher the spinning rate will reduce the thickness of the coating on the substrate because of the inversely proportional relationship between the spinning rate and the thickness of the film.

At the same time, the sintering temperature is also an important coating parameters that effect the characterization properties of the spin coating process. Sintering temperature will affect the densification and grain growth of the material. When sintering temperature raise during sintering process will increase the ionic mobility which enable the densification and grain growth much easier to be observed, (Costa et al., 2003).

From the various coating parameters done in this research, there is a different of effect of TiO_2 coating. In this study, the morphology and crystalline phase of the specimens are being analyse. Scanning Electron Microscope (SEM) is being used to observe the morphology of the coating while the crystalline phase is being investigated by using X-ray Diffraction (XRD).

In a nutshell, it is important to study the effect of spinning rate and sintering temperature of TiO_2 sol-gel via spin coating because these are interrelated and play crucial role in determine the crystal growth of the TiO_2 thin film.

1.2 Problem Statement

The microstructure and characterization of TiO_2 thin film depends on various factors. For instance, the sol-gel synthesis parameters like pH value, heat treatment temperature, and additive selected for the process. Beside the synthesis parameters, the coating parameters and condition is important as well. In this study, researcher will study about what is the difference on crystalline phase, grain size, and film thickness of the thin film TiO_2 spin coated under different spinning rate and sintering temperature.

As discussed earlier, the spinning rate is inversely proportional to the thickness of the thin film formed which means that the higher the spinning rate will result to a thinner thin film deposited on substrate via spin-coating. According to Balzarotti, Cristiani and Francis (2017), the coating thickness reduce with an increment of spinning rate. On flat substrate, the coating thickness is determined by the centrifugal force driving the solution off the substrate. Beside this, researcher found that the spinning time is a key that will affect the coating thickness. Hence, in this study, spinning time is set a fix variable.

Furthermore, researcher will choose three various sintering temperature to carry out this study. From the different sintering temperature, the phases and morphology of thin film is being observed technically with SEM and XRD. At last, comparison between different sintering temperature and spinning rate on the effect of morphology and phases will be analyse and recorded.

1.3 Objectives

The objectives of this study are:-

1. To investigate the effect of spinning rate on coating quality.

2. To investigate the effect of sintering temperature on coating quality.

1.4 Scope

The scope of this research will be focused on the spinning rate and sintering temperature on the coating quality of TiO_2 sol-gel via spin coating process. Analysis of coating properties of thin film which coated with nine combinations of different spinning rates and sintering temperature will be carried mainly on the morphological and crystalline phases of TiO_2 thin film.

In addition, this research will only discuss on the sol-gel method used to synthesis TiO_2 thin film. The film is bring coated via spin coating technique. The sintering time is fix at 1hr and the volume of coating solvent is fixed at 360µm as these effect on morphology and crystalline phases are not the main concerns in this research.

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

The purpose of this chapter is to refer all the researches and information obtained from the previous study from journals, articles, books, websites etc. The project title will segment into tiny sections for further discussion and elaborations. From this chapter, readers are able to extend the idea of this project title through the summary of each section.

2.1 Brookite

Brookite is one of the orthorhombic species of TiO_2. According to Paola et al. (2007), brookite is the rarest among other species which able to carry out photocatalytic activity such as anatase and rutile. The brookite structure is formed by octahedral with titanium oxygen ion at every vertices. Octahedron shares three edges with septal octahedral, built an orthorhombic structure (Pauling, 1928).

Crystals of brookite usually tabular, stretch and striated parallel to length. It can also be pyramidal, pseudo-hexagonal or epitaxial relationship (mindat.org, 2011). Brookite is usually in brown colour or sometime in yellowish and reddish brown or black (Handbook of Mineralogy, 2005).

Figure 2.1: Figure of Crystal Brookite (Handbook of Mineralogy, 2005).

According to Handbook of Mineralogy (2005), brookite is a brittle substance with non-uniform fracture and low cleavage in single direction parallel to the c crystal axis and traced of cleavage in a direction perpendicular to both a and b crystal axes.

2.2 Titanium Dioxide

Titanium dioxide (TiO_2) also known as titanium (IV) oxide or titania. There is more than 1000 of articles related to TiO_2 were published from year 2015 to 2018. This showed the significant value of study of TiO_2 is improving and being focused by researchers. According to Juengsuwattananon et al. (2008), TiO_2 is admitted as one of the most useful materials. It is used in environmental protection procedures.

Generally, TiO_2 exist in three (3) crystalline forms: anatase, rutile, and brookite. According to Johari et al. (2017), TiO_2 in brookite form is the rarest crystallographic phases but with extremely high photocatalytic activities compare to anatase and rutile. There are several methods to prepare TiO_2 such as sol-gel, hydrothermal, pyrolysis and chemical precipitation. Among all these methods, sol-gel is the most efficient method use to prepare noncrystalline TiO_2 with high purity and possess low crystallite size (Juengsuwattananon et al., 2008).

Jung et al. (2008) commented that TiO_2 is a new technology which can degrade several type of organic contaminants in effect. According to Salame et al. (2017), TiO_2 Nanoparticles can avoid microbial proliferation or effectively decrease the number of microorganisms that stay or increase on the external layer of building materials. Nanoparticles in TiO_2 is often used to mix with the commercial paints as a brightener and use as the powder for the bright white lines on tennis courts, according to Les, 2008. TiO_2 is an opacifier which act as a pigment to whiten products (Koleske, 1995). Hence, TiO_2 is a useful material that can be used in various field of industries.

2.3 Spin Coating

Spin coating being admitted that is the most direct and easy technique to fabricated thin film or layer of solvent onto a substrate. This technique had been used for several decade in the application of coating technology. It is a way to apply liquid-based coatings onto a rotating substrate. In spin coating process, a drop of sol is deposited on the surface of the substrate. Spin coating continuously removes solvent and transform to thin film under a centrifugal force. Under the centrifugal draining, the centrifugal force drives the flow radially outward while viscous force (friction) acts radially inward. Consequently, the deposited film become thin and tends to be uniformly flat due to the equilibrium force between the centrifugal force and friction. According to Sahu et al. (2009), there are 4 key stages to carry out spin coating process. The steps are deposition, spin-up, stable fluid outflow and evaporation.

Generally speaking, thickness of a spin coated film is inversely proportional to the squared root of spinning speed (ossila.com). Equation are shown as below:

$$\boldsymbol{t} \propto \frac{\mathbf{1}}{\sqrt{\boldsymbol{\omega}}}$$

Keys:

t = Film thickness

ω = Spinning speed of spinner

Sahu et al. (2009) commented that one of the advantage of spin coating is that the thickness is easier to control by manipulating the spinning speed of the spinner. Beside this, spin coating able to form more uniform and flat on the surface and it is a more economic coating processes. In another hand, the disadvantages of spin coating is large substrates cannot be spun at a sufficiently high rate in order to permit the film to become thinner. Furthermore, lack of material efficiency is another disadvantages for spin coating.

In spin coating, the material that are going to coat must be dissolved or dispersed into a solvent. Spin coating is widely used in many industries. For example, photoresist for defining patterns in microcircuit fabrication, magnetic disk coating and flat screen display coating (Birnie et al., 2005).

2.4 Sol-gel Synthesis Parameters

2.4.1 Effects that influence coating performance

In general, there are various factors affect the performance of TiO_2 coating. This is due to the sensitivity and precision of the material used to produce TiO_2 especially for sol-gel technique. Optimal synthesis parameters for the preparation of TiO_2 nano-sized particles is essential to determine the effectiveness of sol-gel deposition. One of the method to obtain high purity TiO_2 is by using sol-gel. According to Montoya et al. (1992), beside the process of hydrolysis of an alkoxide to form a sol, gelling, ageing, drying and thermal stabilization is essential steps to be taken. Every process must look into details and controlled to get a specific material, large surface areas, narrow pore size and narrow particles size distribution.

Combination of the synthesized material is one of the essential factor that affect the coating performance. Ratio of combination or ingredients to synthesize the material are the examples for this. According to an experiment done by Costa et al. (2003), there are several factors been investigated on the effect of microstructure of Barium Bismuth Titanate (BBT) thin film. BBT thin film with different viscosity will lead to a different microstructure although other factors like heating condition, thickness and spinning rate. The study showed that lower viscosity is easier to prepare the BBT films with the outcome of better morphologic characterises and surface quality.

Liquid film thickness is depending on the properties of the coating solution, viscosity is one of the property that needed to be studied and controlled (Chisneros-Zecallos et al., 2006).

According to the 2nd edition Compendium of Chemical Terminology by MaNaught et al. (1997), concentration in chemistry defined as the sufficiency of a constituent divided by the total volume of mixture. Thus, there is a difference between concentration and viscosity which defined as a measure of a resistance of liquid to gradual deformation by shear stress or tensile stress (Merriam-Webster Dictionary, 2018). According to Zhang et al. (2015), the vapour cell used as a coating agent had a different result between "Air Exposure" and "Wet Solution method preparation. That of using "Wet Solution" preparation method with high water concentration yielded on average the longest relation times and indicated the best reproducibility. According to He et al. (2014), nanocomposite prepared with 2.3wt. % and 3.5wt. % coating solution concentration treatment have the best shear properties. This include the shear strength, elongation at break and fracture work.