Faculty of Manufacturing Engineering

INFLUENCE OF SOL AND DEPOSITION METHOD IN DEVELOPING TiO_2 BROOKITE COATINGS

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DECLARATION

I declare that this thesis entitled “Influence of Sol and Deposition Method in Developing Sol-Gel in TiO_2 Brookite Coatings” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Manufacturing Engineering.

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DEDICATION

To my beloved family

ABSTRACT

Brookite is highly promising photocatalyst due to its high photoactivity performance and significant hydrophilic ability. However, the development and application of pure sol-gel brookite coating is less reported. Therefore, the main objective of this research is to deposit brookite TiO_2 sol-gel coatings derived from 'green formulated sol' for self-cleaning application. The TiO_2 coatings were fabricated from various hydrolysis ratio, temperatures and deposition method. The hydrolysis ratio of water to titanium (IV) isopropoxide (TTiP) used are 32:4 (W_{32}), 48:4 (W_{48}) and 64:4 (W_{64}). In this work, two deposition methods which are dip and spin coating are used to compare the influence of deposition methods on TiO_2 coating phase formation, particularly on identifying the brookite presence. The deposited TiO_2 coatings were then heated at various temperatures such as 200 °C, 300 °C, 400 °C and 500 °C and soaked for 3 hours. For phase analysis, X-ray diffraction (XRD) and Raman spectroscopy are used to examine the influence of sol and deposition method towards phase formation. The surface and cross sectional morphological of TiO_2 coating were analyzed by scanning electron microscope (SEM) observation. The crystallite size was calculated using Scherrer's equation. The optical and hydrophilic properties were conducted to examine the TiO_2 coating characteristic. Results show that the different sol formulations and deposition methods have an influence in brookite TiO_2 coating's development. XRD result indicate that a single peak emerged at 31.9° from spin method was referred to the (111) plane of brookite crystal. For the spin coating, Raman spectroscopy also indicate a dominant brookite characteristic (band at 322 cm^{-1} and 363 cm^{-1}). SEM analysis revealed that the spin coating produced a uniform coating compared to the dip coating. Besides, the surface coating of the deposited TiO_2 coating via dip coating showed cracks regardless of temperature used. The thickness of the TiO_2 coating via spin coating is thinner (447 nm) compared to the dip coating (887 nm). The crystallite size of the TiO_2 spin coating was larger (63.2 nm) compared to the crystallite size of the spin coated (18.7 nm). The band gap value of the TiO_2 spin coating was in the range of 3.32 eV - 3.46 eV (brookite characteristic) whereas for the TiO_2 dip coating, their band gap value was in the range of 3.05 eV - 3.18 eV (anatase characteristic). Furthermore, the TiO_2 spin coating exhibited more hydrophilic characteristic compared to the TiO_2 dip coating**.** For photoactivity performances, the brookite TiO_2 coating was found to be more effective in the degradation of methylene blue (90.65%) and photo-induced hydrophilicity (15.21°). As a conclusion, it is found that spin coating deposition with W_{64} sol formulation is preferable for brookite formation whereas dip coating is more suitable for anatase and rutile.

PENGARUH KAEDAH PEMENDAPAN DAN SOL DALAM PEMBENTUKAN SALUTAN TiO_2 BROOKITE

ABSTRAK

Brookite adalah fotokatalis yang sangat menarik kerana fotoaktiviti yang tinggi dan keupayaan hidrofilik yang ketara. Walau bagaimanapun, kemajuan dan aplikasi kepada brookite tulen salutan adalah kurang dilaporkan. Oleh itu, tujuan utama objektif kajian ini adalah untuk menghasilkan salutan brookite TiO_2 yang berasal dari 'sol larutan hijau' untuk aplikasi pembersihan diri. Salutan TiO_2 tersebut diperbuat daripada pelbagai nisbah hidrolisis, suhu dan kaedah pemendapan. Nisbah hidrolisis air ke TTiP yang digunakan adalah 32:4(W_{32}), 48:4(W_{48}) dan 64:4(W_{64}). Dalam penyelidikan ini, dua kaedah pemendapan iaitu salutan celup dan putaran telah digunakan untuk membandingkan pengaruh kaedah pemendapan pada pembentukan fasa salutan TiO_2, terutamanya dalam mengenal pasti kehadiran brookite. Salutan TiO_2 dipanaskan pada pelbagai suhu seperti 200^0C, 300^0C, 400^0C dan 500^0C dan direhatkan selama 3 jam. Untuk analisis fasa, XRD dan spektroskopi Raman digunakan untuk mengkaji pengaruh sol dan proses pemendapan dalam pembentukan fasa. Salutan dan morfologi keratan rentas salutan TiO_2 dianalisis oleh pemerhatian SEM. Saiz kristal dihitung menggunakan persamaan Scherrer. Sifat optik dan hidrofilik dijalankan untuk mengkaji ciri-ciri salutan TiO_2. Keputusan menunjukkan bahawa formulasi sol dan kaedah pemendapan yang berbeza mempengaruhi dalam pembentukan salutan brookite TiO_2. Keputusan XRD dikaitkan dengan puncak tunggal pada 31.9° yang dirujuk kepada satah kristal brookite (111). Spektroskopi Raman juga menunjukkan ciri-ciri brookite (band pada 322 cm^{-1} dan 363 cm^{-1}). Imej SEM dengan lebih lanjut mendedahkan bahawa TiO_2 yang disalut secara putaran menghasilkan salutan seragam berbanding TiO_2 yang disalut secara celupan. Sementara itu, imej SEM permukaan salutan TiO_2 melalui salutan celupan menunjukkan salutan retak tanpa mengira sebarang suhu. Selain itu, ketebalan salutan TiO_2 salutan melalui salutan putaran adalah lebih nipis berbanding ketebalan salutan celup TiO_2 dengan 447 nm dan 887 nm. Saiz kristal TiO_2 yang disalut secara putaran adalah lebih besar (63.2 nm) berbanding saiz kristal TiO_2 yang disalut secara celupan (18.7 nm). Nilai jurang band TiO_2 disalut secara putaran didapati dalam lingkungan 3.32 eV - 3.46 eV (ciri-ciri brookite) manakala bagi TiO_2 disalut secara celupan, nilai jurang band didapati dalam lingkungan 3.05 eV – 3.18 eV (ciri-ciri anatase).Tambahan lagi, TiO_2 yang disalut secara proses putaran menunjukkan sifat hidrofilik yang lebih tinggi berbanding TiO_2 yang disalut secara celupan. Untuk keupayaan fotoaktiviti, salutan brookite TiO_2 didapati lebih berkesan dalam penurunan kadar metil biru (90.65%) dan fotoinduksi hidrofilik (15.21^0). Sebagai kesimpulan, didapati proses pemendapan salutan putaran dengan formulasi sol W_{64} adalah lebih baik untuk pembentukan brookite manakala salutan celupan lebih sesuai untuk anatase dan rutile.

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LIST OF ABBREVIATIONS

AOPs	-	Advanced Oxidation Processes
CA	-	Contact angle
CeO_2	-	Cerium Oxide
CVD	-	Chemical Vapor Deposition
EDX	-	Energy Dispersive X-Ray
H_2O	-	Water
HCl	-	Hydrochloric Acid
MB	-	Methylene Blue
OH	-	Hydroxyl
SnO_2	-	Tin Oxide
PVD	-	Physical Vapor Depsoition
SEM	-	Scanning Electron Microscopy
TiO_2	-	Titanium Dioxide
TTiP	-	Titanium (IV) Isopropoxide
UV Vis	-	Ultraviolet Visible
WO_3	-	Tungsten Trioxide
XRD	-	X-Ray Powder Diffraction
ZnO	-	Zinc Oxide
ZnS	-	Zinc Sulfide

LIST OF SYMBOLS

e	-	Electron
λ	-	Wavelength
eV	-	Energy Gap
cm	-	Centimeter
nm	-	Nanometer
h	-	Hour
°C	-	Degree celcius
%	-	Percentage
g/cm^3	-	Gram per cubic centrimetre

LIST OF PUBLICATIONS

Suzaim, F. H., Rosli, Z. M., and Juoi, J. M., T. Moriga, 2019. Effect of heating temperature on brookite TiO_2 sol-gel coating for photo-induced hydrophilicity. Accepted for publication in *Journal of Advanced Manufacturing Technology*.

Suzaim, F. H., Rosli, Z. M., and Juoi, J. M., 2018. Influence of water volume and heating temperatures on type of phases and crystallite size of sol-gel thin films deposited without solvent. *International Journal of Engineering & Technology*, 7(4), pp. 5067–5071.

CHAPTER 1

INTRODUCTION

1.1 Background of study

Since the encounter of the prevalent waste water treatment, compelling methods to degrade organic pollutants and microorganisms has been widely explored to provide fresh and clean water. Advanced Oxidation Processes (AOPs) methods agree upon a better environmental technological approach to produce the potential for excellent removal of organic pollutant and microorganisms in order to deal with increasing wastewater problem and develop cost-effective to societies (Bhattacharya et al., 2013). Furthermore, the present of recent advanced technology in modern economy and society requires good technical efficiency, low cost and various nanostructure for removal treatment process (Savage et al., 2005; Samantha et al., 2016).

There is some of the renewable energy technologies are applied to treat wastewater in the long term period such as bio-fuel, solar energy, biomass and wind power. In particular, AOPs is being used as water purification due to its ability in absorbing energy, high efficiency and becoming more critcal to eliminate pollutants in wastewater. It is imperative that the increase of energy during AOPs reaction is sought after as the effectiveness of performance is measured by these conditions (Martin et al., 2011; Taknabe et al., 2017).

Among the available AOPs, the development of heterogenous photocatalysis has performed as the most favourable for the approaching wastewater experiment. In the recent decade, heterogenous photocatalysis has been widely studied which used solid catalyst under light irradiation (UV and visible light) to totally degrade organic pollutant and microorganisms present in water. Moreover, some potentially semiconductor metal oxide

materials with enough sufficient band gap energy like titanium dioxide (TiO_2), cerium oxide (CeO_2), zinc oxide (ZnO) as well as tin oxide (SnO_2) are mainly acting as heterogenous photocatalysts and being used in photocatalytic application (Ibhadon and Fitzpatrick 2013; Byrne et al., 2015; Hodges et al., 2018). The present of available semiconductor catalyst such as low wavelength absorption, instability for catalysis, toxicity and low recombination rate have constrained the performance of the photocatalytic reaction. With these limitations, there is a need to circumvent the issue in order to improve high performance of photocatalytic reaction with greater rate of light absorption and longer lifecycle of catalyst (Rochkind et al., 2015).

To date, TiO_2 is is the most suitable being used as semicoductor photocatalyst due to the excitation of the semiconductor catalyst under UV light irradiation (Lu et al., 2011; Leong et al., 2014; Tsang et al., 2019). The efficiency of the TiO_2 photocatalytic properties is depended on the particle size, crystallinity, surface area, crystallite phase and composition, porosity, band gap, surface defects and the density of surface hydroxyl (Yasmina et al., 2014; Pawar et al., 2018). Another property that can be measured by exposing TiO_2 surface under UV light is its hydrophilicity which is known as photoinduced hydrophilicity (Zhang et al., 2012). Photo-induced hydrophilicity phenomenon is a mechanism when the formation of the hydroxyl group with TiO_2 surface interacts with the presence of UV light (Machida et al., 2018). Theoretically, photoinduced hydrophilicity efficiency increases as the hydroxyl group (OH-) increases (Jun et al., 2015a). The more interface of the hydroxyl group along the TiO_2 surface, the more the water droplet will spread out onto the surface. Thus, the mutual action between the hydrophilicity and the photocatalytic activities will reinforce each other and can be used as a self-cleaning application (Guan et al., 2005).

In comparion with TiO_2 powder, the TiO_2 coating does not form conglomeration and provide high surface activity, allowing the material use in wide industrial applications including self-cleaning and anti-bacterial (Chen et al., 2009). TiO_2 coating can be prepared through numerous procedures such as sol-gel method, hydrolysis deposition, chemical vapor deposition, electrodeposition and chemical spray pyrolysis. Among the many techniques, sol gel method is considered the most suitable to be used due to its ability to provide excellent homogenity and easy on controlling the particle size and morphology (Alzamani et al., 2013; Danks et al., 2016; Liang et al., 2018). Thus, in order to deposit TiO_2 coating on glass substrate, a dip and spin-coating technique are going to be used in this study. Dip and spin coating method is commonly adopted for depositing TiO_2 on glass substrate because it easy to conduct and has advantage to control the thickness of TiO_2 coating.

Thus, the application of TiO_2 is attractive for many reason. TiO_2 has been intensively used in photocatalytic activities, hotoinduced hydrophillicity (for example self cleaning glass), solar cells, optoelectronic applications and gas sensors. In recent decade, TiO_2 photocatalysis become more attractive and considered as the most promising semiconductor for purification of water and air (Liu et al., 2006; Nakamura et al., 2010). Morevover, the TiO_2 photocatalyst and hydrophillic properties can react concurrently on the same surface even if the reaction is entirely different (Banerjee et al., 2015). The formation of water droplet on the TiO_2 coating surface and the photocatalytic degradation of organic poluttans resulted in self-cleaning effect. Recently, the researchers began to pay attention to the development of self-cleaning material due to its wide applications in view of environment, indoor application, solar panel and building material. Figure 1.1 displays the main area of TiO_2 depending on its photocatalysis activity.