Faculty of Manufacturing Engineering

SYNTHESIS OF TITANIUM DIOXIDE THIN FILM FOR PHOTOCATALYTIC ACTIVITY VIA GREEN SOL-GEL ROUTE

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Master of Science in Manufacturing Engineering

2020

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A thesis submitted
in fulfillment of the requirements for the degree of Master of Science in Manufacturing Engineering

Faculty of Manufacturing Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2020

DECLARATION

I declare that this thesis entitled "Synthesis of Titanium Dioxide Thin Film for Photocatalytic Activity via Green Sol-Gel Route" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :..

Name : NURUL SHUHADAH BINTI ABD YAZID

Date :..

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.

Signature :...

Supervisor Name :...

Date :...

ABSTRACT

TiO_2 thin film coating has been a scope of interest for the purpose of photocatalytic application due to its superior photocatalyst properties. Nowadays, complex formulation or various techniques are deployed due to the drawbacks of TiO_2 itself which has large band gap and low efficiency towards visible region. Thus, in this research, the main objective is to produce TiO_2 thin film photocatalyst coating via sol-gel dip coating method using green sol-gel formulation (without solvent). First objective is to investigate the influences of solvent with ethanol (E_{16} and E_8) and without ethanol (E_0) at five and ten dipping numbers and heat treatment (500°C and 600°C) on the characteristic of the deposited TiO_2 thin film. The main characteristics such as crystalline phases, crystallites size, phase composition, and surface morphology of the deposited thin films are reported. Second objective is to synthesis the hydrolysis ratio, ***r*** (16, 10, 8, and 5) between deionized water and TTiP precursor on the deposited TiO_2 thin film especially its photocatalytic characteristics particularly focusing on the green sol-gel route. Third objective is to evaluate the photocatalytic performance of the deposited TiO_2 thin film via green sol-gel route under UV-light and visible light using photo degradation method of methylene blue. TiO_2 thin film characteristic such as its crystalline phases were analysed using XRD and RAMAN, while the crystallites size and phases composition were calculated using Scherrer's equation and Spurr's equation respectively. The surface morphologies and films thicknesses were analysed using SEM. The band gap value was obtained from UV-vis spectrum and Tauc plot equation. The photocatalytic test was conducted using color degradation method of methylene blue exposed under irradiation of UV-light and visible light for five hours. It is found that TiO_2 thin film fabricated via novel green sol gel route with the hydrolysis ratio, ***r***=5 ($R_{32:6}$) showed the best photocatalytic characteristic and performance which possess an important characteristic of without ethanol (E_0), mixed crystalline phases of anatase and rutile and consume low heat treatment temperature of 500°C. The crystallites size produced were large and in the range of photocatalytic crystallites size with an average of 17.2 nm to 28.9 nm. It phases composition also showed the best applicable composition with a mixture of 70% anatase and 30% rutile in addition with small thickness of 2.9μm as well as with small band gap of 2.85 eV which are good in enhancing photocatalytic activity. Further analysis with color degradation method confirmed that the fabricated TiO_2 thin film of green sol gel with ***r*** = 5 showed the highest photodegraded of methylene blue of 97%± 0.5 under UV-light region and 86%± 1.8 under visible light region for five hours' duration. As a conclusion, TiO_2 thin film of novel green sol gel route is successfully fabricated for better photocatalytic performance under both UV-light region and visible light region.

SINTESIS FILEM NIPIS TITANIUM DIOKSIDA UNTUK AKTIVITI FOTOBERMANGKIN MELALUI LALUAN SOL-GEL HIJAU

ABSTRAK

*Lapisan filem nipis titanium dioksida (TiO_2) telah menjadi tarikan utama dalam bidang fotopemangkinan kerana sifat-sifat fotopemangkinannya yang unggul. Pada masa kini, pelbagai formulasi yang rumit atau teknik telah dicuba bagi mengatasi kelemahan TiO_2 iaitu mempunyai jurang jalur tenaga yang tinggi serta tindakbalas yang rendah terhadap cahaya nampak. Oleh itu, objektif utama dalam kajian ini ialah menghasilkan lapisan filem nipis fotopemangkinan TiO_2 melalui kaedah celupan sol-gel dengan menggunakan formulasi sol-gel hijau (tanpa pelarut). Objektif pertama adalah untuk membandingkan pengaruh etanol (E_{16} dan E_8) dan tanpa etanol (E_0) di dalam pensintesisan sol pada ciri filem nipis TiO_2 yang dimendakkan pada setiap lima dan sepuluh celupan serta mengkaji pengaruh rawatan haba (500°C dan 600°C) terhadap filem nipis TiO_2 yang terhasil. Ciri-ciri utama pada filem yang terbentuk seperti fasa hablur, saiz hablur, komposisi fasa, morfologi permukaan dan ketebalan filem dilaporkan terutamanya kepada filem nipis TiO_2 yang didepositkan tanpa etanol (E_0) sebagai formulasi sol gel hijau. Objektif kedua adalah mengubah suai formulasi sol-gel hijau dengan mengubah nisbah hidrolisis, **r** [16 ($R_{64:\ 4}$), 10 ($R_{64:\ 6}$), 8 ($R_{32:\ 4}$), 5 ($R_{32:\ 6}$)] iaitu air dengan TTiP. Ciri filem nipis TiO_2 seperti fasa hablur dianalisis dengan menggunakan XRD dan RAMAN, manakala saiz hablur dan komposisi fasa dihitung menggunakan persamaan Scherrer dan persamaan Spurr. Morfologi permukaan dan ketebalan filem pula dianalisis dengan menggunakan SEM. Nilai jurang jalur tenaga diperolehi daripada spektrum UV-Vis dan persamaan Tauc-Plot. Ujian photocatalytic pula dijalankan dengan menggunakan kaedah degradasi warna biru metilena yang didedahkan di bawah sinaran UV-cahaya dan cahaya nampak selama lima jam. Keputusan menunjukkan filem nipis TiO_2 sol gel hijau (E_0)pada nisbah hidrolisis, **r** = 5 ($R_{32:\ 6}$) adalah terunggul serta menunjukkan ciri fotopemangkinan yang terbaik iaitu menghasilkan campuran fasa anatase dan rutil pada suhu rawatan haba yang rendah iaitu 500 °C. Saiz hablur yang dihasilkan juga adalah dalam lingkungan saiz hablur yang diperlukan bagi aktiviti fotopemangkinan dengan purata 17.2 nm kepada 28.9 nm. Komposisi fasanya juga menunjukkan campuran 70% anatase dan 30% rutile selain ketebalan yang nipis iaitu 2.9µm dan juga jurang jalur tenaga yang kecil iaitu 2.85 eV. Selain itu, analisis kaedah degradasi warna juga menunjukkan fabrikasi filem nipis TiO_2 sol gel hijau dengan r = 5 memberi bacaan fotodegrasi metilena biru tertinggi iaitu 97% ± 0.5 di bawah cahaya UV serta 86% ± 1.8 di bawah cahaya nampak dalam tempoh lima jam. Kesimpulannya, filem nipis TiO_2 sol gel hijau telah berjaya dihasilkan untuk fotopemangkinan yang lebih baik di bawah sinaran UV dan cahaya tanpa pengaruh etanol atau bahan pelarut.*

ACKNOWLEDGEMENTS

Thanks to Allah SWT for giving this opportunity to make my dream success in completing the study in master. First of all, I would like to give my respect to my supervisor, Associate Professor Ts. Dr. Zulkifli Bin Mohd Rosli who always give me full of motivation, support, knowledge, inspiration, and kindness during this study. Also, I would like to thank to my parents, husband, siblings and my teammate at UTeM.

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LIST OF ABBREVIATIONS

Ag	-	Argentum
ALD	-	Atomic layer deposition
Au	-	Aurum
C	-	Carbon
Cu	-	Copper
CVD	-	Chemical vapor deposition
DI	-	Deionized water
EtOH	-	Ethanol
Fe	-	Ferum
HCl	-	Hydrochloric acid
H_2O_2	-	Hydrogen peroxide
MB	-	Methylene blue
Mn	-	Manganese
SEM	-	Scanning electron microscopic
TiO_2	-	Titanium dioxide
TTiP	-	Titanium (IV) isopropoxide
TNTs	-	Titanium dioxide nonotubes
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet spectroscopy
XRD	-	X-ray diffracti

LIST OF SYMBOLS

°C	-	Degree celsius
eV	-	Electron volt
nm	-	Nanometres
mm	-	Millimetres
µm	-	Micrometres
λ	-	Wavelength
θ	-	Bragg angle
kV	-	Kilo volt
mA	-	Milliampere
ppm	-	Parts per million
s	-	Seconds
W	-	Watt

LIST OF PUBLICATIONS

Yazid, S.A., Rosli, Z.M., and Juoi, J.M., 2019. Effect of Titanium (IV) Isopropoxide Molarity on the Crystallinity and Photocatalytic Activity of Titanium Dioxide Thin Film Deposited via Green Sol-Gel Route. *Journal of Materials Research and Technology*, 8(1), pp. 1434–1439.

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Yazid, S.A., Rosli, Z.M., Juoi, J.M. and Johari, N.D., 2018. Raman Spectroscopy and XRD investigation on TiO_2 sol-gel dip coating thin films synthesizes with and without solvents. In *MATEC Web of Conferences* (Vol. 150, p. 04007). EDP Sciences.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter lays out a brief explanation on introduction which comprises a short background, problem statement, research objectives, research hypothesis, scope of works and organization of the thesis. Titanium dioxide has been a subject of study to seek an optimum quality of green TiO_2 thin film coating for photocatalytic performance in ultra-violet (UV) and visible region via green sol-gel route. The overall chronology and the aim of the research study will be discussed in detail in this chapter.

1.2 Background

Water crisis or water pollution imposes deadly risk to health and environment. Nowadays, increased in water contaminants and colouring in residual waters from industries have been reported (Fagnern et al. 2012; Castro-beltrán et al. 2018; Fu et al. 2018). Many measures have been taken to eliminate the colorants in water like adsorption, flocculation, ozonation and photocatalysis (Khoshnavazi et al. 2016). Photocatalysis is a promising, efficient and economic method to decompose water contaminant by transform them to benign substances (Khoshnavazi et al. 2016).

Therefore, introducing titanium dioxide (TiO_2) as a photocatalyst, has drawn attention due to non-toxicity, low cost, simple synthesis, high catalytic activity and high photo-thermal stability (Sayilkan et al. 2005; Fagnern et al. 2012; Alzamani et al. 2016; Komaraiah et al. 2016). TiO_2 exist with three different polymorphs: anatase, rutile and brookite. All these different polymorphs have their own functioning towards photocatalytic but mixed TiO_2 polymorphs are reported can give a good sign in photodegradation of methylene blue compared to single polymorphs. Similar finding is affirmed by Fischer et al. 2017, which were mixed polymorphs of anatase and rutile will reduced the photo-generated towards the electrons holes thus increased the light absorption activity. Moreover, mixture polymorphs of rutile and brookite as well as anatase and brookite also reportedly will generated fast degradation rate in organic molecules (Hanaor et al. 2012; Fischer et al. 2017; Monai et al. 2017). About 70:30 phase composition ratio of anatase to rutile, 91:9 phase composition ratio of anatase to brookite and 61:27:12 phase composition ratio of anatase to rutile to brookite had generated high photocatalytic performance with more than 39% degradation of methylene blue solution in one (1) hour irradiation imposed by UV light reactor (Fischer et al. 2017). Furthermore, few researchers had also reported that mixed polymorphs of anatase and rutile with phase composition ratio of 70:30 were exhibits more than or equal to 65% of methylene blue solution photodegradation at above one hour irradiation imposed by UV light reactor (Eshaghi et al. 2011; Šegota et al. 2011). Meanwhile, pure brookite with 100% composition was reported to exhibit good degradation of methylene blue solution with 92% of photodegradation with four (4) hours irradiation under visible light reactor compared to mixed phases of TiO_2 deposited (Komaraiah et al. 2016). Thus, all three polymorphs were believed can do act as a catalyst or reaction agent in photodegradation activity.

Furthermore, crystalline phases, mixed phases, phase compositions, degree of crystallinity, morphology structure, thickness of the film, crystallites size, band gap value and surface area of TiO_2 thin film have a substantial influence in determining the photocatalytic performance (Eshaghi et al. 2011; Šegota et al. 2011). For example, high degree of crystallinity of TiO_2 polymorphs and low crystallites size with the large surface area were persistently good in photocatalytic performance (Hafizah et al. 2012). Meanwhile, Lopez claimed that, rapid degradation of methyl orange with the fastest degradation rate was obtained with the morphologies structure (Lopez et al. 2013). Uniform coating surface of TiO_2 thin film with some cracking or patches surface with few pores structure deposited on the glass substrate also influenced the excitation of the photo recombination of TiO_2 thin film coating in the light absorption efficiency. Then, the cracking or patches surface structured are expected to reduce the surface area of the deposited TiO_2 thin film coating and hence increased the photocatalytic performance when the TiO_2 thin film coating have been exposed to UV-light and visible light reactor. Moreover, it is also reported that smaller crystallites size of TiO_2 thin film coating also can enhance the photocatalytic activity performance. Anatase phase with crystallites size of ~19 nm which was present in the deposited TiO_2 thin film exhibited good photo degradation reported by Lopez et al. 2013. According to (Zhang and Banfield, 2000), different polymorphs of anatase, rutile and brookite can achieved thermodynamically and hence enhanced the photocatalytic activity performance if small crystallites size below 40 nm were formed. Anatase is the highly thermodynamically stable if the crystallite size produced is less than 11 nm while brookite is highly stable if the crystallite size produced is between 11 nm and 35 nm and above 35 nm, rutile is extremely stable. Hence, crystallites size below 40 nm is believed can enhance the photo degradation reaction due to small surface area exposed in the TiO_2 thin film. Energy band value or band gap value between electron valence and conduction band of TiO_2 thin film coating deposited also plays an important role in the light reactor penetration. Low energy band or band gap value resulted in good photocatalytic performance in the UV-light and visible light region (Yazid et al. 2019). The mixtures of anatase and rutile has been reported to hinder the rate of recombination. The reduction of anatase phase from its pure phases by 40 % leads to the reduction of the band gap value of 2.82 eV (Castrejón et al. 2014).

Karkare, 2014, had found that the TiO_2 nanoparticles prepared via sol–gel route is highly crystalline, heterogeneous, produces uniform coating and smaller crystallite size as compared to the one prepared by hydrothermal method. Therefore, TiO_2 thin film by sol-gel dip method is the most convenient method to produce TiO_2 thin film because it offers low temperature processing, provides high surface homogeneity, easy coating in large surface area and low cost (Fagnern et al. 2012).

In sol gel, precursor, solvent, water and catalyst are the known basic parameters which can control the TiO_2 properties for photocatalytic activity such as phase content, phase transfer kinetics, crystallite size distribution, surface area, morphology structure, and degree of crystallinity of the TiO_2 thin film. Precursor is used to derive the TiO_2 polymorphs and its degree of crystallinity was reported by Hafizah et al. 2012. There are many types of precursor that have been used such as titanium (IV) isopropoxide (TTiP), titanium tetrachloride, and titanium tetrabutoxide and titanium alkoxides. Besides, TTiP is relatively a good precursor in producing stable solution at low hydrolysis ratio (Simonsen and Søgaard, 2010). Moreover, solvent (Alzamani et al. 2013), catalyst (Sayilkan et al. 2005) and water (Hanaor et al. 2012) also play a role in hydrolysis and condensation rate to form a stable TiO_2 solution.

The nature of solvent was reported to affect the rate of hydrolysis and condensation. Higher reaction rates of hydrolysis and condensation will lead to the formation of larger particles with rough surface films whereas lower reaction rate tend to form columnar particles with a smooth surface (Hu et al. 1992). In the work of (Edusi et al. 2012), they used aerosol-assisted CVD technique to deposit TiO_2 phases and found that solvents like ethanol or propanol will lead to anatase phases while rutile phase produced when methanol was used. They concluded that, the use of different solvents can have a direct effect in controlling the TiO_2 phases when deposited as a film. However, Hanaor et al. 2012 reported that excessive water led to formation rutile from the deposited of mixed anatase-brookite if the composition ratio between water and TTiP close to hydrolysis ratio, $\boldsymbol{r}$ =100. The rutile phase also can be established even when the heating temperature used is below 500°C. At $\boldsymbol{r}$ =6, amorphous type structure occurred and crystallinity of anatase can only be produced for temperature above 300°C and the transformation of rutile can only be produced for temperature above 500°C . Thus, it can be concluded that, high content of water ratio ($\boldsymbol{r}$=100) can be form mixed phases of anatase-brookite-rutile compared to low water ratio ($\boldsymbol{r}$=6). Next, concentration of precursors also plays a pivotal role in TiO_2 properties. Concentration of precursor helps in determining TiO_2 structure, crystallite size, mixed phases and degree of crystallinity that can enhance photocatalytic performance.

However, simple formulation like basic sol parameters such as precursors, catalyst and water has been ignored in order to go with the less chemical consumption move by the 5th principles of green chemistry (waste prevention, design of safer, non-persistent, biodegradable chemicals and inherently safer chemistry for accident prevention). Therefore, it is important to synthesize the TiO_2 with three main element (precursors, catalyst and water) to produce green TiO_2 thin film by green sol-gel route without ethanol as a solvent. First, studying the role of ethanol as a solvent in terms of dipping number and heat treatment on the deposited TiO_2 thin film. Then synthesize the hydrolysis ratio,$\boldsymbol{r}$ between water and precursor in producing green TiO_2 sol-gel composition and ideal TiO_2 thin film coating properties for photocatalytic activity. Next, the characteristics of thin film such as crystalline phases, crystallite size, phase composition, morphology structure, degree of crystallinity and band gap also need to be characterize due to enhance the photocatalytic behaviour. Lastly, the TiO_2 thin film with green sol-gel will undergo photocatalytic activity via UV-light and visible light irradiation by methylene blue (MB) degradation.

1.3 Problem statement

Typically TiO_2 thin film coating is good for photocatalytic activity that can treat water pollution which is seriously imposes to health and environment. Therefore, TiO_2 thin film coating must produce some characteristic that can improve photocatalytic activity such as mixed anatase-rutile phases, small crystallites size (10 nm- 40 nm), optimal composition of anatase-rutile (70% : 30%), optimal thickness as well as small bandgap (2.8 eV to 3.1eV). Also fine cracking surface is needed to produce active site surface of deposited TiO_2 thin film coating. Besides, sol-gel dip method is used to produce the deposited TiO_2 thin film coating due to easy to coat homogenous coating and low cost as well as only basic sols parameters are used such as water, precursor, solvent and catalyst. But nowadays, most of researcher are focusing on complex sols formulation such as doping element was added to produce above characteristic to achieve high photocatalytic activity, thus ignoring simple formulation.

Introducing ethanol as a solvent into basic sol parameters has been reported to slow down the rate of hydrolysis and condensation and thus producing specific surface area and surface state of TiO_2 which is good for photocatalytic activity. Ethanol also can produced anatase crystalline at low temperature (~ 350 °C and 400 °C) but can't produce mixture of anatase-rutile. However, it is also reported that the use of ethanol can reduce the anatase formation and form amorphous structure thus produce large crystallites size. Nevertheless, ethanol is volatile organic compounds (VOCs) that can harm the environment and human health (Johari et al. 2019). It were also reported by (Uzma et al. 2008; koteswararao et al. 2014) long terms of organic solvents exposure to the air environment can lead to the highly risk air pollution thus deleterious effects on thyroid, haematological and respiratory functioning.

Therefore, 5^{th} principle of green chemistry (waste prevention, design of safer, non-persistent, biodegradable chemicals and inherently safer chemistry for accident prevention) are introduce in this research to minimize the solvent applications during the preparation of TiO_2 sols. Basic sol parameters such as precursors, catalyst and water are the three main element need to maintain in producing green sol-gel route of TiO_2 sols which is less chemical consumption and save cost. Therefore, synthesis of hyrolysis ratio, ***r*** between TTiP and DI water are believes plays an important role in producing deposited TiO_2 thin film coating with mixed anatase-rutile, small crystallites size, fine cracking surface as well as small band gap due to steric hindrance produced.

1.4 Objectives

The main objective of this study is to investigate the coating properties of the deposited TiO_2 thin film via sol-gel dip coating method without ethanol as a green route approach in fabricating photocatalytic coating. Thus, three specific objectives have been set to fulfil this aim which are:

1. To investigate the influences of solvent with ethanol (E_{16} and E_8) and without ethanol (E_0) at five and ten dipping numbers and heat treatment (500°C and 600°C) on the characteristic of the deposited TiO_2 thin film.
2. To synthesis the hydrolysis ratio, ***r*** (16, 10, 8, and 5) between deionized water and TTiP precursor on the deposited TiO_2 thin film especially its photocatalytic characteristics particularly focusing on the green sol-gel route.

3. To evaluate the photocatalytic performance of the deposited TiO_2 thin film via green sol-gel route under UV-light and visible light using photo degradation method of methylene blue.

1.5 Research questions

Understanding the relationship between coating quality and its synthesizing parameter:

1. What is the role of ethanol, dipping numbers and heat treatment in producing deposited TiO_2 thin film?
2. How the hydrolysis ratio, ***r*** (16, 10, 8, and 5) between deionized water and TTiP precursor affect the deposited TiO_2 thin film especially its photocatalytic characteristics particularly focusing on the green sol-gel route?
3. How the deposited TiO_2 thin film via green sol-gel route will promotes photocatalytic performance under UV-light and visible light using photo degradation method of methylene blue?

1.6 Scope of work

This research aims to investigate the implication of ethanol as a solvent on the deposited TiO_2 thin film crystalline phases and crystallite size by varying the dipping numbers of five (5) and ten (10) with different heat treatment of 500°C and 600°C. Next, the relationship between water and TTiP ratio will be studied to seek the optimum quality of crystalline phases, phase composition, crystallite size, morphology structure, thin film thickness and band gap value of TiO_2 thin film coating for green coating. Therefore, X-ray diffraction (XRD) analysis is used to analyse the crystalline phases, degree of crystallinity, phase compositions and crystallite size while RAMAN spectroscopy is used for the