Faculty of Manufacturing Engineering

CHARACTERIZATION OF BROOKITE THIN FILM DEPOSITED BY SPIN COATING METHOD WITH GREEN SOL-GEL ROUTE

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DECLARATION

I declare that this thesis entitled “Characterization of Brookite Thin Film Deposited by Spin Coating Method with Green Sol-Gel Route” 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.

Signature : ....

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Date : 26/07/2022

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 Doctor of Philosophy.

Signature : ………………………………………………..

Supervisor Name : Profesor Madya Ts. Dr. Zulkifli Mohd Rosli

Date : 26/07/2022

DEDICATION

To my beloved father and mother,

my husband and daughters,

my family and family in law,

my supervisor and my supportive friends that accompanying me along the difficult pathway in my university life.

ABSTRACT

Brookite thin film is one of the great interests as a photocatalyst for water treatment in photocatalytic applications. Brookite has several advantages, but its applicability has been mainly limited because of the inability to synthesize brookite in pure phase due to its high purity and large surface area. One way to overcome such limitation is to establish the brookite phase by optimizing the synthesizing technique and sol-gel formulation. The current study was focused on the comparative deposition methods between dip and spin coating in order to evaluate the brookite phase. The green sol used was made free from solvent as an attempt for a green sol–gel route. The heat treatment temperature is varied and fixed at 200°C, 300°C, 400°C and 500°C for 3 h. The produced thin films were characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier-transform infrared spectroscopy (FTIR). Results showed that deposition methods influence the type of phase formation and crystallinity. TiO_2 thin films via dip coating composed of anatase (101) at $2\theta = 25°$ and rutile (110) at $2\theta = 27°$ while spin coating produce single brookite (111) at $2\theta = 31°$. The crystallite size of brookite thin film was larger (47.9 nm and 58.4 nm) compared to dip coating (5.0 nm to 28.8 nm). Raman shows that the TiO_2 thin film via dip and spin coating has a mixture of anatase, rutile and brookite. SEM analysis shows that the brookite thin film deposited via spin coating produced uniform and crack free coating at 200°C and 300°C. Brookite thin film had a crack coating with a width of 3.1 μm at 400°C and 1.5 μm at 500°C. In comparison to the TiO_2 thin film deposited via dip coating, which had a dense coating and cracks ranging in width from 0.4 μm to 4.3 μm. The coating thickness of brookite thin films via spin coating was in the range of 350.6 nm to 618.7 nm and TiO_2 thin films via dip coating was in the range of 320.5 nm to 1005.9 nm. TEM analysis on the films deposited via spin coating confirmed the presence of only brookite crystallites with lattice fringes of 0.28 nm compared to films via dip coating, which show anatase with lattice fringes of 0.35 nm and rutile with lattice fringes of 0.33 nm. FTIR results shows the TiO_2 thin film obtained via dip and spin coating contained the hydroxyl group on the surface of thin film. Next, the properties of brookite thin films via spin coating, which is band gap energy were in the range of 3.37 eV to 3.90 eV at 200°C to 500°C. The water contact angle of brookite thin films via spin coating was between 11.79° to 19.64° at 200°C to 500°C. The degradation of methylene blue shows the brookite thin film at 300°C and 200°C exhibit the highest degradation of methylene blue under UV light (67.7% and 63.0% after 4 h) and visible light (97.8% and 95.4% after 4 h) irradiation, respectively. The larger crystallite size (47.9 nm and 58.4 nm) and lower band gap energy value (3.37 eV) influenced the degradation of methylene blue. Thus, from the results, the brookite thin film coating was shown to be more effective in the degradation of methylene blue under visible light irradiation compared to under UV light irradiation in decomposing water contaminants by transforming them into benign substances.

PENCIRIAN FILEM NIPIS BROKIT DIENDAP OLEH KAEDAH PENYALUTAN BERPUTAR DENGAN LALUAN SOL-GEL HIJAU

ABSTRAK

Penyalutan filem nipis brokit sangat menarik sebagai permangkin untuk rawatan air dalam aplikasi fotopemangkinan. Terdapat pelbagai kelebihan Brokit, tetapi ianya terhad kerana ketidakmampuannya disintesis atas faktor ketulenan yang tinggi dan luas permukaan yang besar. Salah satu cara untuk mengatasi perkara tersebut adalah dengan mewujudkan fasa brokit melalui pengoptimuman teknik sintesis dan formulasi sol-gel. Kajian semasa adalah memfokuskan kepada perbandingan kaedah endapan antara penyalutan celup dan penyalutan berputar bagi menilai fasa brokit. Sol hijau yang dihasilkan bebas daripada pelarut sebagai percubaan menghasilkan sol-gel hijau. Suhu rawatan haba dibezakan pada 200°C, 300°C, 400°C dan 500°C selama 3 jam. Pencirian filem nipis menggunakan pembelauan sinar-X (XRD), spektroskopi raman, mikroskop elektron imbasan (SEM), elektron penghantaran mikroskopik (TEM) dan spektroskopi Fourier-jelmaan inframerah (FTIR). Keputusan menunjukkan kaedah pengendapan mempengaruhi jenis pembentukan fasa dan penghabluran. Filem nipis TiO_2 dihasilkan melalui penyalutan celup yang terurai daripada anatas (101) di $2\theta = 25°$ dan rutil (110) di $2\theta = 27°$ manakala penyalutan berputar menghasilkan hanya brokit (111) di di $2\theta = 31°$. Saiz kristal filem nipis brookit adalah besar (47.9 nm dan 58.4 nm) berbanding penyalutan celup (5.0 nm hingga 28.8 nm). Raman menunjukkan filem nipis TiO_2 daripada penyalutan celup dan berputar mempunyai campuran anatas, rutil dan brokit. Analisis SEM pada filem nipis brokit melalui penyalutan berputar pada suhu 200°C dan 300°C, menunjukkan salutannya seragam dan tiada retakan. Pada suhu 400°C dan 500°C, terdapat retakan dengan lebar 3.1 µm dan 1.5 µm. Berbanding filem nipis TiO_2 melalui penyalutan celup, salutannya padat dan retakannya antara 0.4 µm hingga 4.3 µm. Ketebalan filem melalui penyalutan mejam adalah di antara 350.6 nm hingga 618.7 nm dan penyalutan celup adalah di antara 320.5 nm hingga 1005.9 nm. Analisis TEM untuk filem dimendapkan melalui penyalutan berputar mengesahkan kehadiran hanya kristal brokit dengan pinggir kekisi 0.28 nm berbanding filem melalui penyalutan celup yang pinggir kekisi anatas 0.35 nm dan pinggir kekisi rutil 0.33 nm. Keputusan FTIR menunjukkan filem nipis TiO_2 dihasilkan dari penyalutan celup dan berputar mengandungi kumpulan hidroksi pada permukaan filem. Seterusnya, sifat filem nipis brokit melalui penyalutan berputar mempunyai jurang tenaga di antara 3.37 eV hingga 3.90 eV. Sudut sentuh air filem nipis brokit melalui penyalutan berputar adalah di antara 11.79° hingga 19.64°. Degradasi metilena biru menunjukkan filem nipis brokit pada 300°C dan 200°C mempunyai degradasi metilena biru paling tinggi di bawah penyinaran cahaya UV (67.7% dan 63.0% selepas 4 jam) dan penyinaran cahaya nampak (97.8% dan 95.4% selepas 4 jam). Saiz kristal yang besar (47.9 nm dan 58.4 nm) dan jurang tenaga yang rendah (3.37 eV) mempengaruhi degradasi metilena biru. Oleh itu, salutan filem nipis brokit lebih berkesan pada degradasi metilena biru di bawah penyinaran cahaya nampak berbanding penyinaran cahaya UV dalam mengurai bahan cemar air.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	-	American Society for Testing and Materials
BSE	-	Back-scattered electrons
CB	-	Conduction band
P25	-	Degussa
DEA	-	Diethanolamine
EDX	-	Energy Dispersive X-ray
FFT	-	Fast Fourier transform
FTIR	-	Fourier-transform infrared spectroscopy
IR	-	Infrared
ICDD	-	International Centre for Diffraction Data
JCPDS	-	Joint Committee on Powder Diffraction Standards
MB	-	Methylene blue
M	-	Molarity
PEG	-	Polyethylene glycol
RS	-	Raman spectroscopy
SEM	-	Scanning electron microscopy
SE	-	Secondary electrons
SAED	-	Selected area (electron) diffraction
SAXS	-	Small-Angle X-Ray Scattering
TDMAT	-	Tetrakis dimethylamino titanium
TTIP	-	Titanium (IV) tetraisopropoxide

TTB	-	Titanium tetrabutoxide
TEM	-	Transmission electron microscopy
UV	-	Ultra-violet
UV-Vis	-	Ultraviolet-Visible Spectrometer
VB	-	Valence band
WAXS	-	Wide-Angle X-Ray Scattering
XRD	-	X-ray diffraction
YSZ	-	Yttria-stabilized zirconia

LIST OF SYMBOLS

Å	-	Angstrom
θ	-	Contact angle
D	-	Crystallite size
°	-	Degree
°C	-	Degree celsius
eV	-	Electronvolt
h	-	Hour
µl	-	Microliter
µm	-	Micrometer
mg	-	Milligram
ml	-	Milliliter
mm/s	-	Millimeters per second
mTorr	-	Millitorr
M	-	Molarity
nm	-	Nanometer
ppm	-	Parts per million

cm^{-1}	-	Per centimeter
min^{-1}	-	Per minute
%	-	Percentage
rpm	-	Rotation per minute
s	-	Second
W	-	Watt

LIST OF APPENDICES

LIST OF PUBLICATIONS

Journal

1. Johari, N.D., Rosli, Z.M. and Juoi, J.M., 2022. Effect of Heat Treatment Temperature on the Structural, Morphological, Optical and Water Contact Angle Properties of Brookite TiO_2 Thin Film Deposited Via Green Sol–Gel Route for Photocatalytic Activity. *Journal of Materials Science: Materials in Electronics*, 33, pp. 15143-15155.
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CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter provides a quick overview of the introduction, which includes the background of study, problem statement, research objectives, scope of research, and thesis outline. The brookite TiO_2 has been the subject of study to seek an optimum quality brookite thin film coating for the photocatalytic activity under ultra-violet (UV) and visible light irradiation via green sol-gel route.

1.2 Background of Study

Today's fast global population growth and extensive industrialisation are mostly to blame for massive environmental degradation produced by a variety of hazardous waste and organic pollutants. Water pollution results from the continual release of organic pollutants such as dyes into water resources, which affects not only human health but also aquatic life in water bodies (Pedanekar et al., 2020). Also, increased colouring in residual waterways from sectors such as textiles, pharmaceuticals, plastics, and cosmetics has recently become a major health and environmental concern (Srinivasan and Viraraghavan, 2010). Based on the current Lancet Commission on Pollution and Health, water-borne illnesses cause about 1.8 million deaths globally. The colouring structure consists of aromatic rings, metallic and halide ions which has high toxicity and low biodegradability that is known as an organic compound (Chen et al., 2014; Sadeghzadeh-Attar, 2018). There are many techniques available to eliminate the organic compound such as biodegradation,