EFFECT OF DEGUSSA ADDITION AND Ag CONTENTS ON THE CHARACTERISTIC AND PHOTOCATALYTIC PERFORMANCE OF Ag-TiO_2 COATING DEPOSITED ON CERAMIC TILES

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in fulfillment of the requirements for the degree of
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DEDICATION

To my family member especially my beloved parents,

To the people who have supported me throughout the journey,

And future endeavours.

This humble work is dedicated to all of you.

ABSTRACT

TiO_2 coating has drawn great attention in various field of application including the ceramic industry. The limitation of TiO_2 photocatalytic activity that only reacts on short-wavelength ultraviolet irradiation has brought an effort to extend its potential to visible range by reducing the fast rate of electron-hole pair recombination. Hence, doping with semiconductor such as silver (Ag) incorporated TiO_2 is proposed. However, Ag incorporated TiO_2 had some issues where the use of Ag with high concentration decreases the surface charge that can cause an agglomeration of Ag species and reduction to Ag^o particles on TiO_2 surface. Lowering the amount of Ag concentration thereafter contributed to the formation of AgO, Ag_2O and Ag^o. The amount of Ag that can control the particles size, surface area, thermal stability and band gap that contributes towards good photocatalytic performance is still vague and continuously studied. Yet, the works of Ag-TiO_2 coating reported mostly on the surface of glass, metal and fabric instead of ceramic surfaces. Therefore, in this study, the deposition of Ag-TiO_2 coating was carried out on unglazed and glazed ceramic tiles. Firstly, the effect of Degussa P25 on the Ag-TiO_2 coating was studied to decide the needs of Degussa P25 in synthesizing Ag-TiO_2 sol formulation. Later, the effect of Ag content (2.5, 5.0 and 7.5 mol %) on the microstructure (crystalline phase, crystal size, elemental distribution, morphology and cross section surface) of the Ag-TiO_2 coated ceramic tiles (unglazed and glazed) were examined and its photocatalytic performance were tested. This yield to the self-cleaning properties of the intended antibacterial ceramic tiles application. The coatings were heat treated at 500 ºC and characterized by Glancing angle X-ray diffraction (GAXRD) and Scanning electron microscopy (SEM), Field electron scanning microscopy (FESEM) coupled Energy-Dispersive X-ray Spectrometer (EDX) and further tested for environmental application using methylene blue degradation (MB) under ultraviolet (UV) and visible light irradiation. The results of the present study suggest that Ag-TiO_2 sol can be synthesized without the aid of Degussa P25 where Degussa P25 possibly hinders the formation of Ag metallic. Ag-TiO_2 coating deposited on the unglazed tile was observed sip into the pores of ceramic surfaces. The finding highlights that Ag-TiO_2 coating deposited on unglazed and glazed improved photocatalytic performances at 5.0 mol % Ag content under visible light irradiation. This is because 5.0 mol % Ag content presented uneven small density of cracks over the surface with more Ag demonstrated by surface morphology and elemental mapping. Also, it can be related to their active crystallites that react well upon visible irradiation. Hence it can be deduced that the amount of Ag needed for good photocatalytic performance needs to take into account the substrate and surrounding condition.

KESAN PENAMBAHAN DEGUSSA DAN KANDUNGAN Ag KE ATAS CIRI DAN PRESTASI PEMANGKIN-FOTO SALUTAN Ag-TiO_2 DIENDAPKAN PADA JUBIN SERAMIK

ABSTRAK

Salutan TiO_2 telah menarik perhatian pelbagai bidang aplikasi termasuk industri seramik. Had aktiviti fotobermangkin TiO_2 yang hanya bertindak balas pada penyinaran gelombang pendek ultraungu telah mencetuskan usaha untuk meluaskan potensinya pada gelombang julat boleh dilihat dengan cara mengurangkan kadar pantas penggabungan semula pasangan elektron-lubang. Oleh itu pengedopan dengan bahan separuh pengalir seperti perak (Ag) telah dicadangkan ke dalam TiO_2. Walau bagaimanapun, Ag yang dimasukkan ke dalam TiO_2 dengan kepekatan tinggi boleh mengurangkan cas permukaan yang akan menyebabkan penggumpalan spesies Ag dan penurunan kepada zarah Ag^{o} pada permukaan TiO_2. Sebaliknya, pengurangan jumlah kepekatan Ag menyumbang kepada pembentukan AgO, Ag_2O dan Ag^{o}. Jumlah Ag yang boleh mengawal saiz zarah, luas permukaan, kestabilan terma dan jurang jalur kearah prestasi fotobermangkin yang bagus masih kabur dan terus dikaji. Namun, kerja-kerja salutan Ag-TiO_2 yang dilaporkan kebanyakannya adalah pada permukaan kaca, logam dan fabrik dan bukannya permukaan seramik. Dalam kajian ini, pengendapan salutan Ag-TiO_2 telah dijalankan pada jubin seramik tidak berlicau dan licau. Pertama, kesan Degussa P25 pada salutan Ag-TiO_2 telah dikaji untuk menentukan keperluan Degussa P25 dalam mensintesis formulasi sol Ag-TiO_2. Kemudian, kesan kandungan Ag (2.5, 5.0 dan 7.5 mol %) ke atas mikrostruktur (fasa hablur, saiz kristal, taburan unsur, morfologi dan permukaan keratan rentas) jubin seramik tidak berlicau dan licau bersalut Ag-TiO_2 telah diperiksa dan prestasi fotobermangkinnya telah diuji. Ini menghasilkan sifat pembersihan kendiri bagi jubin seramik antibakteria. Salutan telah dirawat haba pada 500 ^{o}C dan dicirikan melalui sudut kerling pembelauan sinar-X (GAXRD) dan Mikroskop pengimbasan elektron (SEM), Mikroskop pancaran medan pengimbasan electron (FESEM) ditambah Spektrometer Serakan Tenaga Sinar-X (EDX) dan diuji untuk aplikasi alam sekitar menggunakan degradasi metilena biru (MB) di bawah sinaran ultraungu (UV) dan cahaya nampak. Keputusan kajian ini mencadangkan bahawa sol Ag-TiO_2 boleh disintesis tanpa bantuan Degussa P25 di mana Degussa P25 mungkin menghalang pembentukan logam Ag. Salutan Ag-TiO_2 yang dimendapkan pada jubin tidak berlicau meresap ke dalam liang permukaan seramik. Penemuan ini menyerlahkan bahawa salutan Ag-TiO_2 yang diendapkan pada jubin seramik tidak berlicau dan berlicau meningkatkan prestasi fotobermangkin pada 5.0 mol % Ag di bawah penyinaran cahaya boleh nampak. Ini kerana 5.0 mol % Ag menunjukkan kehadiran rekahan yang tidak sekata dengan ketumpatan kecil di atas permukaan dan lebih banyak Ag hadir pada morfologi permukaan. Ia juga dikaitkan dengan kumin hablur aktif yang bertindak balas dengan baik terhadap sinaran boleh nampak. Oleh itu, dapat disimpulkan bahawa jumlah Ag yang diperlukan untuk prestasi fotobermangkin yang baik perlu mengambil kira substrat dan keadaan sekeliling.

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LIST OF ABBREVIATIONS

A	-	Ampere
Ag	-	Silver
Au	-	Gold
Al	-	Aluminium
$AgNO_3$	-	Silver nitrate
Ag/TiO_2	-	Silver doped TiO_2
Ba	-	Barium
Ca	-	Calcium
Cl	-	Chlorine
CuO	-	Copper oxide
DI	-	Dionised
DSCCs	-	Dye Sensitized Solar Cells
EDX	-	Energy dispersive X-ray spectroscopy
EtOH	-	Ethanol
Fe	-	Ferum
FWHM	-	Full width half maximum
GAXRD	-	Glancing Angle X-ray diffraction
HCl	-	Hydrochloric acid
H_2O	-	Water
ITO	-	Indium tin oxide
ISO	-	International Organization for Standard
JCPDS	-	Joint committee on powder diffraction standards
K	-	Potassium
MB	-	Methylene Blue
Mg	-	Magnesium
MWCNT	-	Multi-Walled Carbon Nanotubes
N	-	Nitrogen
O	-	Oxygen
PAD	-	Photo-Assisted Deposition

Pt	-	Platinum
pH	-	Potential Hydrogen
ppm	-	Part per million
P25	-	Degussa 25
rpm	-	Revolution per minute
ROS	-	Reactive Oxygen Species
SEM	-	Scanning Electron Microscope
SPR	-	Surface resonance
Sn	-	Tin
Si	-	Silicon
Ti	-	Titanium
TiO_2	-	Titanium dioxide
TTiP	-	Titanium tetraisopropoxide
TBOT	-	Tetrabutyl orthotitanate
UV	-	Ultra-violet
UV-Vis	-	Ultra-violet visible
VOC	-	Volatile organic compound
Wt		weight
XRD	-	X-ray Diffraction
Zn	-	Zinc

LIST OF SYMBOLS

A	-	Absorbance
cm	-	Centimeter
ca.	-	Circa/approximately
D, d	-	Diameter
e.g	-	Exempli gratia
E_P		Radiation intensity
eV	-	Electron volt
g	-	Gram
k	-	Scherrer coefficient
M	-	Molarity
m	-	Meter
ml	-	Milliliter
mm	-	Millimeter
n	-	Nano
nm	-	Nanometer
P_{MB}	-	Specific photocatalytic activity
ppm	-	Parts per million
R	-	Specific degradation rate
R_a	-	Surface roughness
s	-	Second
t_{ave}	-	Average thickness
V	-	Volume
W	-	Watt
ζ_{MB}	-	Photonic efficiency
µ	-	Micro
λ	-	Wavelength
^{o}	-	Degree
^oC	-	Degree celcius
%	-	Percentage

θ	-	Bragg angle
$\geq$	-	More than or equal to
$\leq$	-	Less than or equal to
$\pm$	-	Plus minus
ΔA_{λ}		Absorption difference

LIST OF APPENDICES

LIST OF PUBLICATIONS

Journals

1. **Hafizah, N. Z.,** Juoi, J. M., Zulkifli, M. R., and Musa, M.A, 2020. Effect of Silver Content on the Crystalline Phase and Microstructure of TiO_2 Coating Deposited on Unglazed Ceramics Tile. *International Journal of Automotive and Mechanical Engineering (IJAME)*, 17(3), pp. 8179 – 8185.

2. **Hafizah**, **N. Z.,** Juoi, J. M., Zulkifli, M. R., and Johari, N. D., 2023. Effect of Silver Doping on the Microstructure and Photocatalytic Performance of Ag-TiO_2 Coatings on Unglazed Ceramic. *Journal of Advanced Research in Micro and Nano Engineering*, 15(3) - accepted and submitted to publication 2024.

Conferences and Proceedings

1. **Hafizah, N. Z.,** Juoi, J.M., Zulkifli, M. R., Musa, M.A., 2019. Investigation on the Method of Ag Addition into TiO_2 Coating Deposited on Unglazed Ceramic Tile. *Proceedings of Innovative Research and Industrial Dialogue 2018* (IRID'18), pp. 142 – 143.

2. Paper presentation: Effect of Silver Content on the Crystalline Phase and Microstructure of TiO_2 Coating Deposited on Unglazed Ceramics Tiles. **In** *11th Malaysian Technical Universities Conference on Engineering & Technology "Communitising Technology in the Context of Industrial Revolution 4.0*"(MUCET 2019). 19 – 22 November 2019. Bukit Gambang Resort City, Kuantan.

Exhibitions

1. Poster presentation: Addition of Ag into TiO_2 Coating via Dipping and Precursor Method. **In** *Research Showcase of Innovative Research and Industrial Dialogue 2018* (IRID'18). 18 July 2018. Block B, FKP and PPS Auditorium

CHAPTER 1

INTRODUCTION

1.1 Background

Ceramic materials are one of the widely use material in various different field. It includes such as automotive, military, refractory, biotechnology, electrical, electronic and magnetic fields. The applications select its own appropriate property from ceramic materials and that's why ceramic are used in almost every field. In military, ceramic was used for making weapons, missile guidance and defence system because of the hardness and nonreactive properties. A certain use of refractories involved high technology ceramic and for biotechnology to strengthen tissues organ (Dash et al., 2023). The application of ceramic has been well developed and proposed frequently. The product of ceramic tile meanwhile is gaining popularity in both residential and commercial use because of its limitless potential. Tile is the most favourite use design materials for both in dry and wet area. Often can be seen in kitchen and bathroom renovation. The requirement of clean surfaces in every edge of our everyday live is a priority need because it involves our healthy lifestyle. Therefore, the simple easy cleaning or self-cleaning surfaces has been under the focus of nanotechnology.

Surfaces of different structure and nanocoating had become an interest among the researcher. Coating is priority in the furnishing process of a product. It was done on most of the surfaces such as ceramics, metals, polymers and wooden surfaces. There are two types of surface coating that are liquid base coating and powder coating. Both of them have different purposes and benefits. Liquid base surface coating mainly focus on corrosion