UNIVERSITI TEKNOLOGI MARA

SYNTHESIS, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF PRISTINE AND DOPED ZnO (Mn, Fe, Ag and Ni) NANOMATERIAL

AHMAD KHAIRUL AZFAR BIN DARMAN

MSc

October 2021

AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

Name of Student	:	Ahmad Khairul Azfar Bin Darman
Student I.D. No.	:	2017867404
Programme	:	Master of Science (Applied Chemistry) – AS757
Faculty	:	Applied Sciences
Thesis Title	:	Synthesis, Characterization and Photocatalytic Activity of Pristine and Doped ZnO (Mn, Fe, Ag, Ni) Nanomaterial
Signature of Student	:	………………………………………………..
Date	:	October 2021

ABSTRACT

Pristine and doped ZnO (Mn-, Fe-, Ag- and Ni) nanomaterial were successfully synthesized by a simplified sol-gel method at different stoichiometry, which are $Zn_{(x)}Mn_{(x-1)}O$, $Zn_{(x)}Fe_{(x-1)}O$, $Zn_{(x)}Ag_{(x-1)}O$ and $Zn_{(x)}Ni_{(x-1)}O$ (x = 1 %, 3 %, 5 %, 7 % and 10 %) respectively. In this work, all the nanomaterials were systematically studied based on several factors affecting their performances, which are phase study, morphological study, band gap study, textural properties, and the number of active sites presence on the surface of the nanomaterial using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), UV-Vis Spectrophotometer, Brunauer-Emmett-Teller (BET) analysis and Temperature Programmed Desorption (TPD – CO_2) respectively. This synthesis method of sol-gel was modified by omitting the use of chelating agent to reduce the preparation time obtaining precursor. X-ray Diffraction (XRD) confirmed that the existence of substitutional/pure doping for Mn/ZnO and Fe/ZnO because it depicts the same pattern as pristine ZnO nanomaterial, allowing the dopants ions to substitute in the host's lattice. Interstitial/impure doping for Ag/ZnO, Ni/ZnO was noted due to the presence of other known crystalline phase known as impurities in which the dopants ions are not slotted into the lattice. Morphological study from (FESEM) showed two significant shapes possessed, which are nanorods and spherical with a variation in diameter and lengthwise. Nanorods which has a smaller diameter compared to spherical will give larger surface area on the surface of nanomaterial. Therefore, condition of synthesis has been accomplished about the nanoscale obtained. Band gap study expressed that all stoichiometry for doped ZnO managed to lower down the wide energy gap value of 3.34 eV pristine ZnO and has a potential for visible light responsive photocatalysis, as well as better photocatalyic activity under UV light irradiation, except 1% Mn/ZnO and 10 % Ni/ZnO because of higher energy gap value at 3.37 eV and 3.35 eV respectively which is mainly due to smaller crystallite size giving rise to apparent separation of energy levels. In terms of the (BET) analysis, the effect of 1 % dopant of Mn/ZnO, Fe/ZnO and Ni/ZnO contributed to a larger surface area with 16.371 m^2g^{-1}, 17.457 m^2g^{-1} and 11.970 m^2g^{-1} than that of pristine ZnO (11.671 m^2g^{-1}), which supposedly favour photocatalytic activity. Interestingly, amongst all dopants, 5 % Ag/ZnO showed highest photocatalytic activity at 99.93 %, producing at least 14^{th} cycles of nanomaterial reusability on degradation of methyl orange under UV irradiation. This substantial result on nanomaterial reusability has successfully overcomed the problem arose from the synthesis part. The condition of photocatalysis set up was constructed uniformly for all nanomaterials. Larger surface area of 1 % Mn/ZnO, Fe/ZnO and Ni/ZnO nanomaterial showed poor photocatalytic performance at 28.43 %, 73.24 % and 35.68 %. Active sites of nanomaterial is proposed to be an additional factor contributing towards photocatalysis in this work besides band gap, size, morphology and surface area. TPD – CO_2 showed that the incorporation of Ag into ZnO lattice has enhanced the number of active sites on the surface of the nanomaterial (166.53 μmol/g) whereas incorporation of Mn/ZnO, Fe/ZnO and Ni/ZnO lowered the number of active sites with respect to pristine ZnO. Active sites measurement is effective and significant, providing opportunities in developing an intensive study as an additional factor. This research work aims to propose and find the key player in photocatalytic performance in which the study is focusing more on the number of active sites present on the surface of nanomaterials. This is because the presence of a larger number of active sites will promote the formation of active radicals.

ACKNOWLEDGEMENT

All praises and thanks to Allah, The Almighty, The Most Beneficient and The Most Merciful who has bestowed me good health and ability to strive until chequered flag.

I wish to thank myself for putting every hard work, patience and time management throughout completing this project. These three elements motivated and helped me a lot as I successfully managed to grab my target on this project.

Special thanks to my supervisor, Dr Muhd Firdaus Bin Kasim for his time, thorough guidance on the project and motivation on work-life balance.

I would love to express my gratitude to perfectly comprehensive lab officer, Mr Mohamad Fikrey Bin Ramli, Madam Hasdiyana Binti Hashim, Madam Norashikin Binti Kamarudin and Mr Zaidi Bin Marlan for their relentless efforts, always deliver their best enhancing my skills in laboratory and taught me brand new knowledge to gain worth experiences.

Inevitable thanks to my beloved parents for their countless advice every single time. It is hard when both of you not around, but I know you're somewhere out there smiling down. Memories give me the strength that I need to proceed and believe. Because in my heart, where I always keep you.

Thanks to all my friends and to those who had helped me in giving suggestions day in day out.

TABLE OF CONTENTS