FORMATION OF COBALT DOPED ZINC OXIDE PHOTOCATALYST

This report is submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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I hereby, declared this report entitled "Formation of Cobalt Doped Zinc Oxide Photocatalyst" is the result of my own research except as cited in references.

Signature : ....

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons). The member of the supervisory committee is as follow:

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ABSTRAK

Matlamat dalam penyelidikan ini adalah untuk mangkaji aktiviti fotokatalis zink oksida yang didopkan dengan kobalt. Proses doping adalah salah satu cara untuk meningkatkan aktiviti fotokatalis osida logam di dalam pewarna oren. Dalam kajian ini, kaedah sol-gel digunakan untuk dope kobalt (II) asetat tetrahidrat ke dalam serbuk zink oxide. Selain itu, XRD, FESEM, RAMAN dan FTIR merupakan cara pencirian bahan untuk mengenalpasti struktur dan morfologi zink oksida tulen dan kobalt doped zink oksida. XRD digunakan untuk mengenalpasti kewujudan struktur heksagon wurtzite manakala keguanan FESEM adalah untuk meganalisis bentuk nanorod dan nanodisk dalam fotokatalis. Prestasi degradasi pewarna oren akan dipengaruhi oleh morfologi dan struktur zink oxoda. Pewarna oren yang mempunyai fotokatalis akan terdedah kepada sinaran UV kemudian menganalsi aktiviti fotokatlis sampel tersebut. Kepekatan pewarna oren akan semakin kurang apabila masa pendedahan kepada sinaran UV semakin lama. Hasil yang mengejutkan ditemui apabila kobalt dop zink oxida menunjukkan prestasi yang tidak memuaskan berbanding dengan zink oxida tulen. Fenomena ini mungkin disebabkan jumlah bahan doping yang digunakan dan juga kekosongan oksigen dalam fotokatalis. Dalam penyelidikan ini, peratus degradasi pewarna oren untuk fotokatalis zink oksida tulen (C0), 0.25 peratus berat Co (C1), 0.5 peratus berat Co (C2), 1.0 peratus berat Co (C3), 1.25 peratus berat Co (C4) dan 1.5 peratus berat Co (C5) adalah 93%, 77%, 74%, 57%, 39% dan 37% masing-masing selepas 6 jam pendedahan kepada sinaran UV.

ABSTRACT

The aim of this research is to study the photocatalytic activity of zinc oxide that doped with cobalt. Doping process is one of the method to improve the photocatalytic activity of metal oxide in methyl orange (MO) dye solution. In this research, sol gel method is used to dope the Cobalt (II) acetate tetrahydrate into zinc oxide powder. Besides that, material characterization was done using XRD, FESEM, RAMAN and FTIR in order to identify the structure and morphology of pure ZnO and Co-doped ZnO. XRD was used to confirm the presence of hexagonal wurtzite structure whereas FESEM showed the nanorod and nanodisk morphology of ZnO that presence in the photocatalysts. The degradation performance of methyl orange is affected by the morphology and structure of ZnO. MO dye solution that contain photocatalyst was exposed to UV light irradiation and then analysed the photocatalytic activity of the samples. The concentration of the MO dye solution decreases as exposure time to UV light increases. Surprisingly, the Co doped ZnO photocatalyst shows poorer performance of photocatalytic activity as compared to pure ZnO photocatalyst. This may due to the amount of dopant applied and the oxygen vacancies in the photocatalyst. In this research, after 6 hours irradiation of UV light, the percentage degradation of MO dye solution for pure ZnO (C0), 0.25 wt% Co (C1), 0.5 wt% Co (C2), 1.0 wt% Co (C3), 1.25 wt% Co (C4) and 1.5 wt% Co (C5) are 93%, 77%, 74%, 57%, 39% and 37% respectively.

DEDICATION

I would like to dedicate this project to my beloved father, Mr. Chin and my dearest mother, Mrs. Sam who have given me external and unconditional support such as love, patience, financial, encouragement and understanding for me to complete my final year project successfully. Furthermore, also to my siblings Pui Yee and Kean that always motivate, mentally support, opinion and knowledge to me in order to produce a good and quality report. Thank you so much and my love to you all can never be quantified.

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LIST OF ABBREVIATIONS

Al	-	Aluminium
C	-	Carbon
Co	-	Cobalt
CO_2	-	Carbon Dioxide
Cr	-	Chromium
Cu	-	Copper
C_2H_6O	-	Ethanol
EHP	-	Electron Hole Pair
Fe	-	Iron
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared Spectroscopy
Ge	-	Germanium
HCL	-	Hydrochloric acid
H_2 O	-	Water
KOH	-	Potassium Hydroxide
LiOH	-	Lithium Hydroxide
Mn	-	Manganese
MO	-	Methyl Orange
N	-	Nitrogen
NaOH	-	Sodium Hydroxide
NH_4OH	-	Ammonium Hydroxide
Ni	-	Nickel
PbS	-	Lead (II) Sulphide
pH	-	Potential Hydrogen
S	-	Sulphur
Si	-	Silicon
TMAH	-	Tetramethylammonium Hydroxide

TiO_2	-	Titanium Dioxide
UV	-	Ultra-violet
XRD	-	X-ray Diffraction
ZEH	-	2-ethylexanoate
ZnO	-	Zinc Oxide
ZnS	-	Zinc Sulphide

LIST OF SYMBOLS

eV	-	Electronvolt
K	-	Kelvin
RT	-	Room Temperature
wt%	-	Weight Percentage
•OH	-	Hydroxyl radicals
e^-	-	Electron
h^+	-	Holes
O_2^-	-	Oxide ion
µm	-	Micrometer
°C	-	Degree Celsius
mol%	-	Mol percentage
Co^{2+}	-	Cobalt ion
Zn^{2+}	-	Zinc ion
g	-	Gram
rpm	-	Revolution per Minute
°F	-	Degree Fahrenheit
cm^{-1}	-	Wavenumber
Å	-	Angstrom

CHAPTER 1

INTRODUCTION

1.1 Research Background

This research is induced by a common problem which is undeniably a problem faced by every country in the world, environmental pollution in particularly, water pollution. Among all the causes of water pollution, the traces of organic dyes that can be found in cosmetic, paper goods and textiles is the main factor as a result of the development of industry and economy. These toxic organic dyes are better to be eliminated through chemical process as their self-decomposition reaction is too long.

Over the years, there are several techniques used to remove organic dyes from the textiles effluents such as adsorption, precipitation, air stripping, flocculation, reverse osmosis and ultra-filtration (Carmen & Daniela, 2010). However, since Fujishima & Honda (1972) introduced the evolution of oxygen and hydrogen from titanium oxide electrode in the electrolyte cell under irradiation of light, photocatalysis has been regarded as one of the most effective ways in removing organic dyes. Various photocatalysts, especially metal oxide photocatalysts such as titanium oxide, tin oxide, and zinc oxide (ZnO) are promising materials for degradation of organic pollutants by utilizing UV or solar light.

Among the various semiconductor photocatalysts, ZnO shows potential solution for degradation of organic pollutants. The potential use of ZnO nanostructures with various morphologies such as nanoparticles, nanorods, nanoballs, nanoflowers for photocatalytic degradation of organic dyes has attracted increased attention in recent years (Kuriakose *et al.*, 2015). Besides, ZnO has outstanding properties such as low cost, non-toxic nature and ability utilize abundantly available sunlight. However, ZnO nanostructures suffer from the drawback such as too rapid of recombination of photoexcited electrons and holes (Xu *et al.*, 2014). Indirectly, this will cause ZnO to have low photocatalytic efficiency. Doping of ZnO nanostructures with transition metals will enhance their photocatalysts. There are various types of transition metals such as manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), and cobalt (Co). There are two types of doping: anionic and cationic doping. The example of cation doping to the metal oxide are aluminium (Al), chromium (Cr), manganese (Mn), iron (Fe), whereas for anion doping are nitrogen (N), carbon (C) and sulphur (S) (Ali & Muhammad, 2012). As Ali & Muhammad (2012) cited in their studies, cobalt doping to ZnO will give significant shift of the energy band gap which support in transferring of electrons at the surface or interface.

Methyl orange (MO) has been chosen as the dye solution because it has excellent solubility in water and also gives a pleasant and significant colour change. Moreover, MO gives a shaper end point but does not obtain a full spectrum colour change. Furthermore, the MO dye solution will change into non-toxic, simple compounds such as water, carbon dioxide (CO_2) and hydrochloric acid (HCL) when it exposed to UV light irradiation.

1.2 Problem Statement

A poor photocatalytic activity is faced by ZnO nanostructures due to the high electron hole recombination rate and the inefficient utilization of sun light (Xu *et al.*, 2014). Overall, low photocatalytic activity is not adequate to give satisfaction result for photodegradation. Baruah *et al.* (2012) showed in an empirical study that the nanosize (range 1mm-100mm) of ZnO has high surface to volume ratio. As Baruah *et al.* (2012) cited in his studies, ZnO nanorod is a very good nanostructure since it can evolve different type of membranes through proper surface treatment and it is surface independent. Moreover, the high surface defect and large oxygen vacancies of photocatalyst play an important role to help the efficient migration of the charge at the ZnO surface. Therefore, in order to get the desirable condition (surface defect, oxygen vacancy, band gap) that will lead to the high photodegradation, the smaller size of ZnO must go through some convenient techniques such as sol-gel, hydrothermal reaction or co-precipitation method. Besides, by controlling the structure of ZnO itself, the efficiency of ZnO can also be obtained by incorporation of other metal such as by dopant or hybridization.

Doping with transition metal cations to ZnO could change the coordination environment of Zn in the lattice and modify the electronic energy band structure of ZnO. Among the transition metals, cobalt is the most preferable metal to dope with ZnO. This is because cobalt can tune both electronic and optical properties due to its abundant electronic states as well as its minor influence on the ZnO lattice structure. Furthermore, doping of Co ions in ZnO nanostructure will give a significant change in band gap energy favouring the electron transfer and tuning of the Fermi level of ZnO. Moreover, the number of oxygen vacancies in ZnO nanostructure increases due to the incorporation of transition metal ions and the oxygen vacancies in ZnO nanostructure which usually promote efficient separation of phootogenerated charge carriers.

On the other hand, environmental pollution also is one of the concern in this research. The pollution like contamination in air, water and soil is the current world problems. As we know, water is a fundamental requirement in our daily life. This water pollution is highly due to toxic chemical as well as biological contamination. Application of nanotechnology using engineered catalysts exploiting unique properties of nanomaterials is capable making an impact to control the environmental pollution. In order to purify or eliminate the toxic pollutant in waste water, photocatalysis using visible light has been reported through doping of semiconductors with transition metals (Baruah *et al.*, 2012). The used of doped semiconductor materials have demonstrate a better photocatalytic process. The photocatalysis is considered as one of the successful techniques that offer highly reactive oxidant named hydroxyl radicals (OH^-). This oxidant is capable of destroying wide range of organic pollutant in water and wastewater. The process can completely degrade the organic pollutant into harmless substance such as H_2O and CO_2.

1.3 Objectives

i. To synthesize different concentration of cobalt-doped zinc oxide for photocatalytic studies.

ii. To characterize the morphology and structural of Co doped ZnO.

iii. To analyze the degradation rate of methyl orange (MO) using Co doped ZnO.

1.4 Scopes

This research aims to investigate the synthesis of the photocatalyst with different concentrations of Co (0.25 wt%, 0.5 wt%, 1 wt% and 1.2 5wt %, 1.5 wt %) by sol-gel method. Furthermore, this research also covers on the Co effect on the ZnO nanostructure in order to study the morphology (surface nanostructure) and structure (crystal lattice) using FESEM, X-ray diffraction, FTIR, and RAMAN. Moreover, the effect of the doping level of Co on the photocatalytic activity also will be investigated. Lastly, this research covers on the analysis of the percentage of MO degradation at specified time under UV light.

1.5 Outline of Project

This report divides into five chapters which include introduction, literature review, methodology, results and discussion, and conclusion and recommendation. In PSM 1, there are three chapters contributed. Chapter one is the introductory chapter about the project which consists of the research background, problem statement, objectives, and scope of project, as well as the outline of the project.

Literature review is focusing on the discussion of the published information that related to the title of this research and will be done in chapter 2. This step is important in guiding the entire research and it gives an overview on the relevant title. It also provides a solid background for the research investigation to understand the previous work that have done. Hence, improvement and new development can be made toward the limitations and drawbacks of the conducted research.

Chapter three discusses the methodology of the research. This chapter includes the methods to carry out the project and the theoretical analysis of the body of the methods by using material characterization methods.