UNIVERSITI TEKNIKAL MALAYSIA MELAKA

PSM TITLE: FORMATION OF COBALT-DOPED ZINC OXIDE PHOTOCATALYST FOR SYNTHETIC METHYL ORANGE DEGRADATION

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

(Engineering Materials) (Hons.)

by

KATERINA ANAK BIRANG

B051310018

920415136244

FACULTY OF MANUFACTURING ENGINEERING

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Materials) (Hons.). The member of the supervisory is as follow:

…….

(Project Supervisor)

ABSTRAK

Proses doping merupakan satu cara untuk meningkatkan reaksi fotokatalis iaitu bahan oksida di dalam pewarna oren. Laporan ini merangkumi proses penyediaan kobalt (II) asetat tetrahidrat yang diserap ke dalam oksida zink (dalam bentuk serbuk) menggunakan kaedah sol-gel. Proses pencirian bahan dilakukan dengan menggunakan FESEM, XRD, FTIR dan RAMAN untuk mengenalpasti morfologi dan struktur oksida zink tulen dan oksida zink terdop kobalt. Kehadiran struktur heksagon wurtzite dan struktur zincite dikenalpasti melalui analisis XRD manakala oksida zink dalam bentuk nanorod dan nanodisk wujud di dalam fotokatalis dikenalpasti melalui analysis FESEM. Morfologi dan struktur oksida zink ini akan memberi impak kepada prestasi degradasi pewarna oren. Doping akan menyebabkan ion daripada kobalt menggantikan ion zink di dalam kekisi kristal zink oksida. Aktiviti fotokatalis telah dianalisis dengan mendedahkan pewarna oren yang mengandungi photokatalis kepada sinaran UV. Semakin lama pewarna oren didedahkan kepada sinaran UV, semakin berkurang kepekatan pewarna oren. Hasil yang mengejutkan ditemui apabila zink oksida tulen menunjukkan prestasi aktiviti fotokatalis paling tinggi berbanding sampel fotokatalis yang mengandungi kobalt. Fenomena ini berkait rapat dengan jumlah tahap bahan doping yang digunakan dan juga kekosongan oksigen di dalam fotokatalis. Selepas pendedahan sinaran UV selama 6 jam, zink oksida tulen menunjukkan 100 % degradasi ke atas pewarna oren, 1 peratus berat Co (47 %), 3 peratus berat Co (39 %), 6 peratus berat Co (23 %), 9 peratus berat Co (27 %) dan 12 peratus berat Co (22 %).

ABSTRACT

Doping process is one of the method to enhance the photocatalytic activity of metal oxide in methyl orange (MO) dye solution. This report covers on doping of Cobalt (II) acetate tetrahydrate into zinc oxide (powder form) by using sol gel method. Material characterization done using FESEM, XRD, FTIR and RAMAN to identify the morphology and structure of pure ZnO and Co-doped ZnO. The presence of hexagonal wurtzite structure and zincite structure is confirmed using XRD analysis whereas ZnO nanorod and nanodisk morphology presence in photocatalysts analysed using FESEM image. Morphology and structure of ZnO give effect on degradation performance of methyl orange. Doping process makes Co ions substituted ZnO ions in ZnO crystal lattice. Photocatalytic activity analysed by exposed MO dye solution contain photocatalyst to UV light irradiation. As the exposure time increase, the concentration of dye solution decrease. Surprisingly, pure ZnO shows high photocatalytic activity than Co-doped ZnO. This phenomena correlates to amount of dopant level and also oxygen vacancy of photocatalyst. After 6 hours of UV light irradiation, pure ZnO shows 100 % degradation of MO dye, 1wt % Co (47 %), 3wt % Co (39 %), 6wt % Co (23 %), 9wt % Co (27 %) and 12wt % Co (22 %).

DEDICATION

I would like to dedicate this project to my beloved parents, Birang anak Nyelang and Ampa anak Kubu who haven given me external and unconditional support such as patience, love, financial and courage in order for me to complete my final year project. Also to my siblings especially my first brother, Vincent Meringgai that always support, give opinion and knowledge in order to complete and produce a good report. This project is also dedicated to everyone that have intention to continue this research as their references and make some improvements on reducing organic pollutant.

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ZnO	-	Zinc Oxide
Co	-	Cobalt
MO	-	Methyl Orange
HCl	-	Hydrochloric acid
UV	-	Ultra-violet
pH	-	Potential of hydrogen
wt%	-	weight percent
FESEM	-	Field Emission Scanning Electron Microscope
XRD	-	X-Ray Diffraction
µm	-	micrometer
EHP	-	electron-hole pair
e−	-	electron
•OH	-	hydroxyl free radical
O^{2-}	-	oxide ion
CO_2	-	Carbon dioxide
H_2O	-	Water
nm	-	nanometer
Å	-	Angstrom
AR	-	Alizarin red
pzc	-	point zero charge
FTIR	-	Fourier Transform Infrared Spectroscopy
eV	-	Electronvolt

CHAPTER 1

INTRODUCTION

1.1 Research Background

The issue of environmental pollution is absolutely unavoidable for centuries. Over the years, many researches have been conducted to solve this problem because the health of the human and aquatic life are at risk. One of the causes of pollution in wastewater is due to the traces of organic dyes that are present in textiles, paper goods and cosmetic. The organic dyes must be eliminated from wastewater as it contains chemicals that are toxic, carcinogenic (benzidine, naphthalene) or mutagenic in nature, that contribute to organic pollutant (Suteu et.al 2009). If these dyes are not removed, they will remain in the environment for a long duration. There are several technique suitable to remove the colour from the textiles effluents such as adsorption, precipitation, air stripping, flocculation, reverse osmosis and ultra-filtration (Carmen et.al 2012).

Semiconductor photocatalyst such as titanium oxide (TiO_2) and zinc oxide (ZnO) have been introduced by many researchers for wastewater treatment due to its simplicity and enhanced photodegradation efficiency (Mondal et al 2014). As Mondal(2014) cited in his studies, TiO_2 and ZnO have the ability to obtain full mineralization of organic contaminants under ambient pressure and temperature. Zinc oxide shows a potential solution for environmental remediation among all the semiconductor photocatalyst. Therefore, it is most widely used for the degradation of toxic organic pollutants. Doping ZnO nanostructures with transition metals such as manganese

(Mn), iron (Fe), nickel (Ni), copper (Cu), and cobalt (Co) have been proven to be able to increase the photocatalytic activities. 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 et.al 2012). Contrastive type of dopant will give a unique impact on crystal lattice of the metal oxide (ZnO). In a previous research, a cobalt ion was doped into the zinc oxide nanocrystals. The outcome from the reaction shows a significant shift in the band gap energy which supports in transferring of electron at the surface or interface and adjust the Fermi-level of ZnO (Yongchun et.al 2011).

For the dye solution, the most preferable is methyl orange (MO) as it has excellent solubility in water. It also gives a pleasant and noticeable colour change. Furthermore, MO gives a sharper end point but does not obtain a full spectrum colour change. When the dye solution MO is exposed to UV light irradiation, it will switch the dye solution into non-toxic and simple compounds such as water, carbon dioxide and hydrochloric acid (HCL). However, there are some researchers that use 4-nitrophenol or other dye solution tested for photodegradation. Rajamanickam et. al (2012) emphasized in his research that 4-nitrophenol (organic pollutant) used as a dye solution successfully degraded by ZnO under solar light irradiation. The results from his studies shows the pH value of adsorption reach maximum pH 5. Adsorption technique might be a favourable process for removal of 4-nitrophenol but it has a major disadvantage where it needs extra treatment since it does not serve a real degradation of compounds. Moreover, it only shifts them from diluted to concentrated steams.

1.2 Problem Statement

A previous research by He at.al (2012) stated the root cause of the low photocatalytic activity of the Co doped ZnO than the pure ZnO where under UV light exposure, the generation of the mid-gap energy levels related to the recombination centers regardless of the type of nanostructure and the synthesis process. Low photocatalytic activity is an unacceptable result for photodegradation. The surface area, surface defects, band gap and the oxygen vacancies of the photocatalyst plays important role to execute a good photodegradation (Sunandan et.al 2012). Smaller size ZnO which is in nanosize (range from 1nm-100nm) has high surface to volume ratio. ZnO nanorod is an excellent nanostructure since it is surface independent and can evolve on any type of membranes through proper surface treatment (Sunandan et al 2012). Furthermore, the high surface defect and large oxygen vacancies of photocatalyst mandatory to help the efficient migration of the charge at the ZnO surface. If there is a reduction in the oxygen vacancy, the performance of photocatalytic activities will decrease. Therefore, the smaller size of ZnO with a convenient preparation technique such as sol-gel, hydrothermal reaction, or co-precipitation method is essential to get the desirable condition (surface defect, oxygen vacancy, band gap) that will lead to the high photodegradation.

Light intensity plays an important role on the percentage of dye degradation. There will be a huge difference in outcome between the high intensity of light irradiation and poor intensity of light irradiation. The minor percentage of degradation might be found on the poor intensity of light irradiation due to the reduction in the formation of the free radicals (Mondal et.al 2014) which leads to the segregation of the electron-hole pair competes with recombination. Close supervision on light irradiation will affect the result of photodegradation.

There are several conditions that must be emphasized to study the degradation of Methyl Orange, (MO) so that the results from the study will be presented in clear and achievable objectives. One of the parameters that should be considered is the pH value for the reason that it affects the performance of the photocatalytic degradation by the adsorptions of pollutants at the surface of the photocatalyst. The adjustment of the pH value must be performed correctly, recorded before irradiation process and cannot be

controlled during the course of reaction (Rajamanickam et.al 2012). Sharma (2014) declared that pH values that are sufficient are in the range of 3 (acidic) to 13 (alkaline).

1.3 Objectives

1. To synthesize different concentration of cobalt-doped zinc oxide for photocatalytic studies.
2. To characterize the morphology and structure of Co doped ZnO.
3. To analyse the degradation rate of methyl orange (MO) using Co doped ZnO.

1.4 Scopes

This research will aim to investigate only on the objectives stated as follows:

a. To achieve the first objective, it will cover on:
    i. The synthesis of the photocatalyst with different concentration of Co (3wt %, 6wt %, 9wt % and 12wt %) by sol-gel method.
b. For the second objectives, the scope will cover on:
    i. Co effect on the ZnO nanostructure that will indicate the morphology (surface nanostructure) and structure (crystal lattice) using FESEM, X-ray diffraction, FTIR, and RAMAN.
    ii. The effect of the doping level of Co on the photocatalytic activity.

c. The last objective will cover on:
    i. Analyse the percentage of MO degradation at specified time under UV light.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Pure zinc oxide (ZnO) and Cobalt (Co) used widely to study photocatalytic activities of methyl orange. In this work, ZnO is doped using Co from transition metal group to enhance and improve the characteristics and properties of ZnO. The properties of ZnO and Co is studied. The doping process with Co is done by a process called cationic doping. The role of photocatalyst is discussed and factor affect the photocatalytic activities is viewed in detail. A suitable technique for synthesized samples is chosen based on the advantage and disadvantages.

2.2 Zinc oxide (ZnO)

An excellent photocatalyst should be able to absorb light efficiently in the visible light and UV light. ZnO is widely used as the perfect photocatalyst and has been rigorously studied. It is also abundant in nature, non-toxic nature and environmental friendly (Mondal et.al, 2014). Compared to TiO_2, ZnO might not promise a stable and high sensitivity towards photo corrosion. However, ZnO assures a better stability in nanometric dimension as it offers a better crystallinity and smaller defects (Radzimska et.al 2014). Photocatalytic activity of the ZnO can be improved by adding some other components into it. This can be done by doping process where the range of visible

spectrum will be extended. Furthermore, Zinc oxide exhibits properties that are required for photodegradation of dye solution (Radzimska et.al 2014). The properties are as follows:

a. High chemical stability
b. Low electrical constant
c. High electrochemical coupling index
d. Wide range of radiation or UV absorption
e. High photo stability
f. Biocompatibility and biodegradability

Zinc oxide is a material that can activate itself by taking the energy from photons for photocatalytic activities. Besides, photocatalyst adsorb enough amount of oxygen and organic pollutant molecules will contribute to the formation of the adsorption site. The high specific surface area and open porous structure of material are preferable. The reactions must occur at ambient temperature (Mondal et.al 2014).

Table 2.1: The band gap energies of common semiconductor materials at 0K. (Sharma et.al 2014)

Semiconductor materials	**Band gap energy (eV)**
Titanium oxide, TiO_2	3.03
Zinc oxide, ZnO	3.36
Zinc Sulphide, ZnS	3.60
Tin Dioxide, SnO_2	3.54

From Table 2.1, ZnO shows favourable band gap energy with 3.36 eV at wavelength 388 mm. It has been proved that the large excitation binding energy of 60 meV is desirable to act as a photocatalyst. The photocatalytic activities can only be conducted with the presence of UV light (Poongodi et.al 2015). Since it has wide band gap, it can only utilize solar energy at percentage range of 3% to 5%.

For pure zinc oxide, the energy gained from the visible light is inadequate to initiate the photocatalytic activities. However, the reaction will become impressive if the sample is capable to absorb both ultra-violet radiation and visible light. In addition, the photocatalytic properties of ZnO are based on the surface morphology size, crystal

structure, aspect ratio, density of the crystal and crystallographic orientation (Mondal et.al 2014).

2.2.1 Photocatalytic mechanism for ZnO photocatalyst

The concept of the photocatalytic reaction that related to the generation of electron-hole pair (EHP) into semiconductor material and the movement of electron need to be understood. The outcome from the interaction of photocatalyst and organic solvent such as methyl orange and methyl blue are influenced by (Mondal et.al 2014):

a. Band gap energy
b. Electronic configurations
c. Ability to absorb light
d. Time consuming for excitation

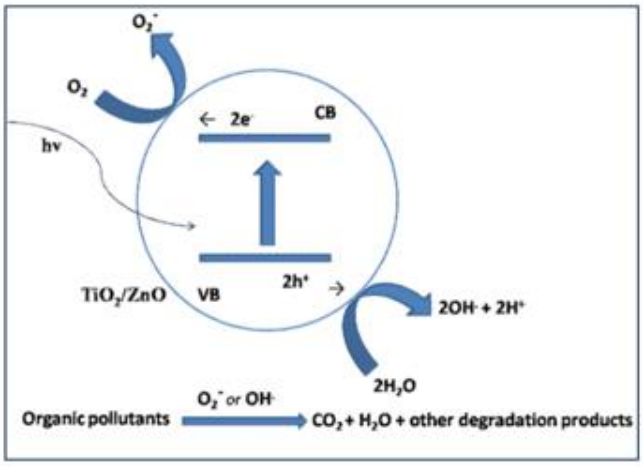

Figure 2.1: The schematic of the photocatalytic mechanism for ZnO photocatalyst (Mondal et.al 2014)

The figure above shows the principal of reaction mechanism of ZnO. The reaction are as follows:

a. The radiation energy is applied to the ZnO where the amount of radiation required must be equal or greater than band gap energy.
b. The positive charges are produced in the valence band whereas negative charge in conduction band.

c. When there is enough energy for excitation process, electron from valence band will excite to conduction band. An electron-hole pair will be produced.
d. Electron from conduction band will release oxygen which then absorbed by ZnO to become superoxide ion (O^{2-}).
e. The holes that carry positive charge will oxidize directly to organic pollutants (disintegrate harmful and toxic dyes) or indirectly by water (to produce hydroxyl free radical •OH).
f. The •OH and O^{2-} will act as a powerful oxidizer in the degradation of dyes and convert them to CO_2 and H_2O.

2.3 Cobalt (Co)

Cobalt is a metal with shiny blue silver appearance which contain three tiny particles which are proton (positively charge), neutron (no charge) and electron (negatively charge). Susan (2007) in her book states that cobalt have a potential to act as a magnet (ferromagnetism) where it can stay magnetic at maximum temperature of 1100°C. The oxidation number of Co is based on the amount of charge (gain or loss) to form a compound. Cobalt have variation of oxidation state that describe the joining of element to form compound as shown in Figure 2.2. The variation is due to unfilled inner electron shell of Cobalt.

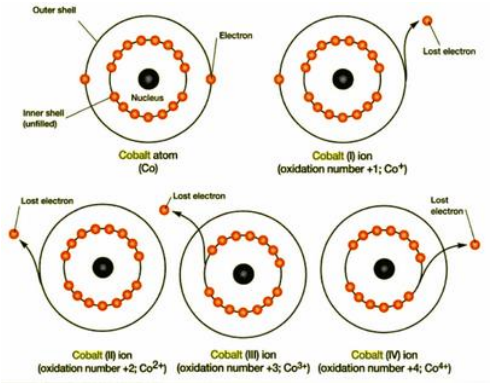

Figure 2.2: Oxidation state of Cobalt (Susan, 2007)