PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF SILVER DOPED ZINC OXIDE PHOTOCATALYSTS

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By

ELISA RASOULI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

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DEDICATIONS

This thesis is lovingly dedicated to my beloved parents, brother and sisters whose endless care supported me all through the way

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PREPARATION, CHARACTERIZATION AND PHOTOCATALYTIC ACTIVITY OF SILVER DOPED ZINC OXIDE PHOTOCATALYSTS

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Chairman: Associate Professor Abdul Halim bin Abdullah, PhD

Faculty: Science

In this study, silver doped zinc oxide and undoped zinc oxide photocatalysts were synthesized through precipitation-irradiation method. In order to evaluate the effect of irradiation time during synthesis, the photocatalysts were prepared at different irradiation duration of 12, 24 and 48 hours. The effect of Ag on the properties and photocatalytic performance of ZnO was also evaluated by preparing Ag-doped ZnO catalyst with different silver loading from 1 to 3 wt%. The resulting catalysts were characterized by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Total surface Area Measurement (BET Method) and Band Gap Measurement. XRD patterns showed hexagonal structure of zinc oxide. FESEM results confirmed hexagonal structure of zinc oxide and also showed flake morphology with increasing irradiation time. However, both FESEM and TEM images showed high agglomerated particles but it should be noticed that agglomeration decreased with increasing irradiation time. In addition, increasing silver percentage doped on zinc oxide decreased the flake morphology and led to more agglomerated particles. The surface area of ZnO decreases with increasing irradiation time and with addition of Ag. The band gap energy of the ZnO remained constant with increasing radiation time but increased with the addition of 2 wt. % Ag. Due to high agglomeration, measurement of photocatalysts particle size was not conducted.

The efficiency of produced ZnO and Ag doped ZnO was examined for degradation of Methyl orange as a model of pollutant under UV-irradiation. Influence of different parameters on degradation performance of Methyl orange such as mass of catalyst, initial concentration of dye, and initial pH were tested. The results showed that the efficiency of catalyst decreased with increasing irradiation time. It was observed that the removal percentage of dye increased with increasing silver loading on zinc oxide and the mass of catalysts up to an optimum amount. Furthermore, the maximum removal percentage was achieved at pH 5. In conclusion, the highest photodegradation activity of 81% of 10 ppm MO was achieved using 0.8 g of 2% Ag/ZnO catalyst at pH 5.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN, PENCIRIAN DAN AKTIVITI FOTO PEMANGKINAN OLEH ARGENTUM/ZINK OKSIDA

Oleh

ELISA RASOULI

November 2014

Pengerusi: Professor Madya Abdul Halim bin Abdullah, PhD

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Dalam kajian ini, fotomangkin zink oksida dan argentum/ zink oksida telah disintesis melalui kaedah pemendakan-penyinaran. Untuk menilai kesan masa penyinaran, pemangkin disediakan pada masa penyinaran yang berbeza iaitu 12, 24 dan 48 jam. Kesan Ag terhadap sifat dan prestasi fotopemangkinan ZnO juga dinilai dengan menyediakan mangkin Ag-didopkan ZnO dengan muatan argentum yang berbeza antara 1 hingga 3% berat. Mangkin yang terhasil telah dicirikan menggunakan Pembelauan sinaran-X (XRD) , Mikroskopi Medan Pancaran Imbasan Elektron (FESEM), Mikroskopi Transmisi Elektron (TEM) , luas permukaan (Kaedah BET) dan luang tenaga. Analysis XRD dan FESEM menunjukkan struktur heksagon zink oksida berbentuk kepingan telah diperolehi dengan peningkatan masa penyinaran. Kedua-dua imej FESEM dan TEM menunjukkan penggumpalan zarah yang tinggi tetapi tahap penggumpalan berkurangan dengan peningkatan masa penyinaran. Penambahan argentum pada zink oksida mengurangkan zarah yang bermorfologi kepingan tetapi menjadikan zarah lebih menggumpal. Luas permukaan ZnO berkurangan dengan peningkatan masa sinaran dan dengan penambahan Ag. Nilai luang tenaga daripada ZnO tidak berubah dengan peningkatan masa radiasi tetapi meningkat dengan tambahan 2 wt. % Ag.

Kecekapan mangkin ZnO dan Ag didopkan ZnO yang dihasilkan telah diuji untuk degradasi pewarna Metil Jingga (MO) sebagai model bahan pencemar di bawah sinaran UV. Pengaruh parameter yang berbeza terhadap prestasi degradasi MO seperti jisim mangkin, kepekatan awal pewarna, dan pH awal telah diuji. Hasil kajian menunjukkan bahawa kecekapan pemangkin menurun dengan peningkatan masa penyinaran. Ia diperhatikan bahawa peratusan penyingkiran pewarna meningkat dengan peningkatan muatan argentum dalam zink oksida dan jisim pemangkin sehingga satu jumlah yang optimum. Tambahan pula, peratusan penyingkiran maksimum dicapai pada pH 5. Kesimpulannya, aktiviti fotodegradasi tertinggi sebanyak 81% daripada 10 ppm MO telah dicapai dengan menggunakan 0.8g mangkin 2% Ag/ZnO pada pH 5.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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LIST OF ABBREVIATIONS

ZnO	-	Zinc Oxide
AgZnO	-	Silver-doped Zinc Oxide
MO	-	Methyl Orange
FSP	-	Flame Spray Pyrolysis
nm	-	Nanometer
XRD	-	X-ray Diffractometry
FESEM	-	Field Emission Scanning Electron Microscopy
TEM	-	Transmission Electron Microscopy
BET	-	Brunauer, Emmett and Teller Theory
EDA	-	ethylendiamine
CTAB	-	Cetyltrimethyl ammonium bromide
ZEH	-	Zinc 2-ethylhexanoate
TMAH	-	Tetramethylammonium hydroxide
CB	-	Conduction Band
VB	-	Valance Band
UV	-	Ultraviolet
OA	-	O_2 Absorbed
[M[n	-	Nobel Metal
λ	-	Wavelength
eV	-	Electron Volt
*C*0	-	initial concentration of *Methyl orange*,
*C*t	-	concentration of *Methyl orange*
HCl	-	Hydrochloric acid
NaOH	-	Sodium hydroxide
$AgNO_3$	-	Silver nitrate
$Zn(NO_3)_2.6H_2O$	-	Zinc nitrate hex-hydrate
θ	-	fraction of surface covered by the substrate
K	-	L-H constant of adsorption equilibrium
C	-	concentration of the organic substrate
t	-	irradiation time

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Environmental issues become one of the important concerns to governments and societies in recent years. Waste water has significantly contaminate the environment and affect public health because of the increase in toxicity level and high effect of colour on environment directly.

Water pollution is a serious global problem. Industries, specially tanneries and dyeing industries have heavily polluted the water, and researchers from both academic and industrial sectors has to identify methods to remove toxic compounds form the water bodies, and consequently guarantee the health succours of water creatures and humans lives. As these pollutants might cause heavy ecological imbalance, it is essential to find means to protect the ecological systems.

Generally, dyes are pollutant that can be easily seen in waste water, as they are extremely visible, even in very low quantities (<1ppm for some dyes) (Abdessalem et al., 2010; Monteagudo et al., 2010). Dyes are commonly used in many current technological fields (Modirshahla et al., 2007) . There are more than 100,000 commercially available dyes, and more than 735 tonnes of dyes produced every year (Tehrani-Bagha et al., 2010). Textile industry is one of the major consumers of dyes; generally textile industries use synthetic dyes.

It has been approximated that about 15% of the total world production of dyes is lost during the dyeing process and then released to the environment through textile effluents (Bouasla et al., 2010). In addition to the textile industries, leather tanning industries (Habibi andTalebian, 2007; W. Zhang et al., 2009), paper industry (Ayed et al., 2010), food technology (Zhao et al., 2006), hair colorings (Chen et al., 2008; Vahdat et al., 2010), photo electrochemical cells (Andronic et al., 2009; Dajka et al., 2003) , and light-harvesting arrays (El-Bahy et al., 2009; Mohamed andAl-Esaimi, 2006) also discharge dyes through sewage. These are serious issues that, majority of the dyes used in industries are toxic and carcinogenic, which eventually creates a severe danger to marine organisms. Therefore, a number of studies have been conducted to address this serious issue (Diebold, 2003; Xie andLi, 2006).

As there is significant demanding limitations on the organic composition of industrial effluents, it is crucial to remove dyes from waste water, prior to discharging them into the environment. Nevertheless, a lot of dyes are difficult to decolorize, due to their synthetic nature and complicated structure.

During the last decades advanced oxidation processes (AOPs) have been applied for the removal of organic pollutants using combination of oxidants, ultraviolet (UV) light or UV with photocatalyst to convert the pollutants into CO_2, H_2O and harmless chemicals. Among all variety of AOPs heterogeneous photocatalysis as an emerging destructive technology attained effective colorization of most organic pollutants (Karkmaz et al. 2004; Mozia et al. 2005).

According to Linsebigler et al. (Linsebigler et al., 1995) heterogeneous photocatalysis is classified into catalysed and sensitized photoreactions. Basically, the photocatalytic effect begins as soon as the photo-generated electron and energy are transferred to (ground state) molecules adsorbed onto its surface, by the excited semiconductor. In sensitized photoreactions, the preliminary optical excitation happens in the molecules, which are adsorbed onto the catalyst surface; and this is followed by a molecular reaction, with the catalyst at its ground state.

Nowadays, semiconductor photo-catalysis attracts increased attention since it has a great potential to contribute to such environmental problems. The usage of ZnO and TiO_2 as semiconductor photocatalyst has been widely applied in the removal of organic contaminants (Sakthivel et al., 2003, Akyol et al., 2004 and Irmak et al., 2004).

Semiconductor materials comprise valence bands, which are filled up with low-energy electrons, and empty higher-energy conduction bands. A band gap exists between valence and conduction bands. The band-gap structure of semiconductors lacks constant regions, as opposed to metals. In photocatalysis, the light irradiate the solution and semiconductor absorb the irradiated light, the electrons from the valence band migrated to the conduction band. As a result the electron-hole pairs generated and will be active only to pico-seconds; nevertheless, it is adequate for the photo-generated electrons and holes to be transported to the adsorbed species on the semiconductor surface.

Heterogeneous photo-catalysis is the process that the stability of the semiconductor is maintained and the exchange of charges to the adsorbed species stays lasting and exothermic. The heterogeneous photo-catalysis is subdivided into gas–solid and liquid–solid photo-catalysis (Linsebigler et al., 1995), and both vary in their reaction mechanisms. When heterogeneous photo-catalysis is applied to the oxidation of pollutants both O_2 and H_2O are necessary. However, O_2 plays a predominant role in gas–solid photo-catalytic processes (the actual oxidant is $\cdot O_2$, O^-), as does H_2O in liquid–solid photo-catalytic processes (the oxidant is $\cdot OH$, $\cdot O_2H$).

Photocatalysis process will start as soon as the semiconductor photo-catalyst absorbs the radiation with energy, which is corresponding or higher than that of the band gap, the electrons are promoted from the valence band to the conduction band (Figure 1, path1) and generating electron-hole pair. Although the electron-hole pairs are active only to pico-seconds, the following three additional pathways can be taken by the excited electrons and holes: photo-generated electron–hole pairs recombine (Figure 1, path 2) or after attaining the surface, the photo-generated electrons react with electron acceptors

(Figure 1, path 3) while the photo-generated holes react with electron donors absorbed on the semiconductor surface (Figure 1, path 4).

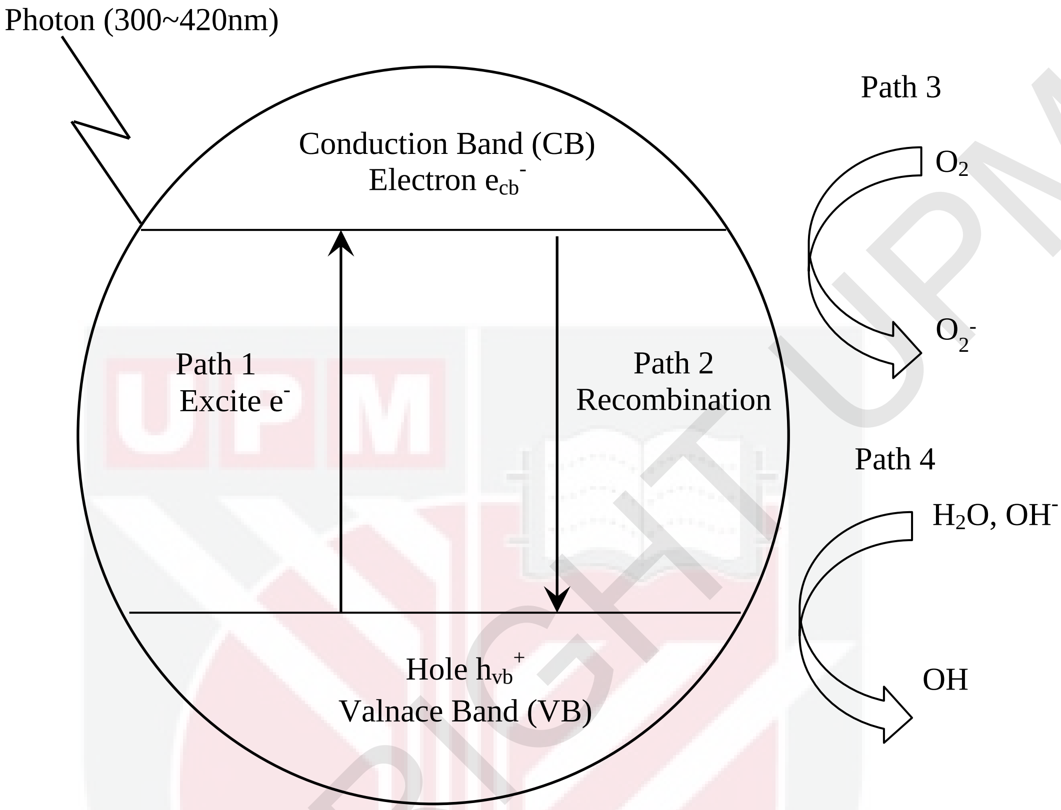

Figure 1: Schematic Diagram of Mechanism of Semiconductor Photo-catalysis (Kwon et al., 2008).

The last two reactions (Figure 1, paths 3 and 4) are essential for photo-catalysis; while, the first path (Figure 1, path 2) is detrimental, and must be restricted. In a suitable reaction with trapping the photo-generated electron, the preferred redox-reaction occurs at the surface of the catalyst, and the recombination of electron and hole is averted.

The following reaction equation show the photoreactions of each path in more detail:

Path 1: $ZnO + hv \rightarrow ZnO\ (e^-_{CB} + h^+_{VB})$

Path 2: $e^-_{CB} + h^+_{VB} \rightarrow heat$

Path 3: $O_2 + e^- \rightarrow \cdot O_2^-$

$H_2O + O_2^- \rightarrow \cdot OOH + OH^-$

$2\ \cdot OOH \rightarrow O_2 + H_2O_2$

$\cdot OOH + H_2O + e^- \rightarrow H_2O_2 + OH^-$

$H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + O_2 + OH^-$

Path 4: $H_2O + h^+ \rightarrow OH + H^+$

$OH^- + h^+ \rightarrow OH$

$h^+_{VB} + dye \rightarrow dye^{\cdot +} \rightarrow$ oxidation of the dye

The oxidizing potential of the electron hole is directly or indirectly exploited by majority of the photo-catalytic oxidation reactions. Apart from, the hydroxyl radical ·OH, the ·OOH radical, and the super-oxide ion radical $\cdot O_2^-$, which takes part in the reduction reaction.

1.2 Problem Statement

Recently, ZnO and TiO_2 are the most widely used photo-catalysts, because of their physical and chemical stability, high oxidative capacity, low cost and ease of availability (Periyat et al., 2008). Among the semiconducting materials, ZnO offers significant prospect in providing electronic, photonic, and spin-based functionality (spintronics) because of its direct wide band gap (3.37 ev).

The main advantage of ZnO over TiO_2 is that, it absorbs over a larger fraction of UV range (Deng et al., 2010). The high chemical stability and low toxicity also make ZnO a suitable choice in the area of photo-catalyst.

Theoretically, modification of semiconductors with the noble metals increase photo-catalytic activity and also acting as a sink of photo-induced charge carriers and promoting interfacial charge-transfer processes. Modification of semiconductors with nobel metals appears to be an essential factor for maximizing the efficiency of photocatalytic water splitting reactions and the processes of the photo induced degradation of toxic organics.

Silver can trap the photo-generated electrons from the semiconductor and allow the holes to form hydroxyl radicals which results in the degradation reaction of organic species present. Moreover, silver can enhance the photo-catalytic activity by creating a local electric field and the optical vibration of surface Plasmon in silver can make a reasonable enhancement in this electric field (Stathatos et al., 2001).

So far, many methods have been used to synthesize Ag/ZnO heterostructures such as hydrothermal or solvothermal method (Lu et al., 2008 and Zheng et al., 2007), electro spinning method (Lin et al., 2009), sol-gel (Jang et al. 2010), Flame Spray Pyrolysis (FSP) (Height et al., 2006), RF magnetron sputtering (Tan et al., 2008), and so on. However, most of these methods are either inefficient, or need expensive instruments.

In this study, we synthesized ZnO and Ag/ZnO photocatalysts with different Ag content using precipitation-irradiation technique under different irradiation time to improve and evaluate the photo catalytic activity of synthesized photocatalysts in degrading Methyl orange dye as organic pollutant.

1.3 Research Objectives

According to existing problem in the literature for removing organic pollutant from wastewaters, it is necessary to find a simple synthesis procedure to produce photo-catalysts with high performance and at low cost. Thus in this study we are going to:

1. Synthesize ZnO and Ag/ZnO photo-catalysts with different Ag content using precipitation-irradiation technique under different irradiation time

2. Characterize the resulting ZnO and Ag/ZnO photo-catalysts using X-ray Diffraction (XRD, Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Total Surface Area Measurement (BET Method), Band Gap Measurement.

3. Evaluate the photo-catalytic performance of the catalyst in degrading methyl orange dye under different reaction conditions.

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