EFFECTS OF CARBON CONTENT ON THE PHOTOCATALYTIC ACTIVITY OF ZINC OXIDE UNDER VISIBLE LIGHT IRRADIATION

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DEDICATION

This thesis is dedicated to my beloved mother, Salmah binti Mohd Sapiee, who always shows and taught me that everything can be accomplish with patience and effort.

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ABSTRACT

The research described in this thesis is an attempt to correlate structural and physicochemical properties of ZnO photocatalysts with their photocatalytic properties. ZnO photocatalysts were synthesized by sol-gel method from zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) in methanolic medium, either with or without the addition of cetyl-trimethyl ammonium bromide (CTAB) and sodium hydroxide. The ZnO powders synthesized with the addition of CTAB were calcined at 300, 400, 500, 600 and 700°C to produce ZnO that contained carbon. ZnO was also synthesized by a similar method without CTAB addition and calcined at 500°C. The structural and electronic properties of ZnO synthesized with the addition of CTAB (C-ZnO) and ZnO synthesized without the addition of CTAB (ZnO-500) were analysed. X-Ray diffraction pattern proved that the ZnO samples were crystalline hexagonal ZnO wurtzite with crystallite size range of 23-34 nm. Field emission scanning electron microscopic morphology of ZnO samples showed irregular-shape particles in the prepared C-ZnO and ZnO samples. Particle size of ZnO increased as the calcination temperature of ZnO was increased. The particle sizes of ZnO samples were distributed from 40 to 300 nm. The presence of carbon in ZnO samples after calcination was confirmed by Fourier transform infrared spectroscopy, thermogravimetric analysis and X-ray photoelectron spectroscopy. The photocatalytic oxidation of styrene in H_2O_2 catalyzed by ZnO photocatalysts was selective towards the production of styrene oxide. Among ZnO samples, ZnO-500 showed the highest selectivity towards styrene oxide which is 96.8%. This was explained by the presence of amorphous carbon in ZnO-500 indicated by the weight loss in thermogravimetric analysis which is due to the oxidation of amorphous carbon. The amorphous carbon caused the grey colour in ZnO-500, C-ZnO-300 and C-ZnO-400 due to aggregation of acetate during ZnO synthesis, and this was supported by C=C aromatic absorption peaks observed by Fourier transform infrared spectroscopy. White colour of C-ZnO-500, C-ZnO-600 and C-ZnO-700 was due to high content of organized carbon formed from the trapped acetate in CTAB during ZnO synthesis. Density functional theory (DFT) calculations were carried out to study the effects of carbon on the electronic properties of C-ZnO. The results showed lowest band gap energy caused by carbon substituted with oxygen.

ABSTRAK

Penyelidikan yang diterangkan dalam tesis ini adalah satu percubaan untuk mengaitkan sifat-sifat fisikokimia fotomangkin ZnO dengan sifat fotopemangkinannya. Mangkin ZnO telah disediakan daripada zink asetat dihidrat ($Zn(CH_3COO)_2.2H_2O$) dengan kaedah sol-gel di dalam medium metanol sama ada dengan atau tanpa penambahan setil-trimetil ammonium bromida (CTAB) dan dengan kehadiran natrium hidroksida. Serbuk ZnO yang disediakan dengan penambahan CTAB telah dikalsin pada 300, 400, 500, 600 dan 700°C untuk menghasilkan ZnO yang mengandungi karbon. ZnO juga disediakan dengan kaedah yang serupa tanpa penambahan CTAB dan dikalsin pada 500°C. Sifat struktur dan elektronik ZnO yang disediakan dengan penambahan CTAB (C-ZnO) dan ZnO yang disediakan tanpa penambahan CTAB (ZnO-500) telah dianalisis. Corak pembelauan sinar-X membuktikan bahawa sampel ZnO adalah kristal ZnO wurtzite heksagon dengan julat saiz kristal 23-34 nm. Morfologi mikroskopi elektron pengimbas menunjukkan bahawa sampel C-ZnO dan ZnO yang disediakan menunjukkan zarah yang tidak teratur di dalam sampel C-ZnO dan ZnO. Saiz zarah ZnO meningkat apabila suhu pengkalsinan ZnO ditingkatkan. Taburan saiz partikel sampel ZnO adalah dari 40 hingga 300 nm. Kehadiran karbon di dalam sampel ZnO selepas pengkalsinan telah dibuktikan dengan spektroskopi inframerah transformasi Fourier, analisis termogravimetri dan spektroskopi fotoelektron sinar-X. Pengoksidaan fotopemangkinan stirena di dalam H_2O_2 dimangkinkan fotomangkin ZnO mempunyai kepilihan terhadap penghasilan stirena oksida. Di antara sampel ZnO, ZnO-500 menunjukkan kepilihan tertinggi terhadap stirena oksida iaitu 96.8%. Ini dijelaskan dengan kehadiran karbon amorfus di dalam ZnO-500 yang dibuktikan dengan penurunan berat dalam analisis termogravimetri disebabkan oleh pengoksidaan karbon amorfus. Karbon amorfus menyebabkan ZnO-500, C-ZnO-300 dan C-ZnO-400 berwarna kelabu disebabkan oleh pengumpalan asetat semasa penyediaan ZnO, dan ini disokong oleh puncak penyerapan aromatik C=C yang dapat diperhatikan dengan spektroskopi inframerah transformasi Fourier. Warna putih C-ZnO-500, C-ZnO-600 dan C-ZnO-700 adalah disebabkan oleh kandungan karbon tersusun yang tinggi yang terbentuk daripada asetat yang terperangkap di dalam CTAB semasa penyediaan ZnO. Pengiraan teori fungsi ketumpatan (DFT) telah dijalankan untuk mengkaji kesan karbon terhadap sifat elektronik C-ZnO. Hasilnya menunjukkan tenaga luang jalur terendah disebabkan oleh karbon yang digantikan dengan oksigen.

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LIST OF ABBREVIATIONS

UV-Vis	-	Ultraviolet-Visible
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier transform infrared
ZnO	-	Zinc oxide
DFT	-	Density functional theory
XPS	-	X-Ray Photoelectron Spectroscopy
H_2O_2	-	Hydrogen peroxide
PL	-	Photoluminescence
CB	-	Conduction band
VB	-	Valence band
CTAB	-	Cetyltrimethyl ammonium bromide
TGA	-	Thermalgravimetric Analysis
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

•OH	-	Hydroxyl radical
h^+	-	Positive hole
e^-	-	Electron
ZnO	-	Zinc oxide
H_2O_2	-	Hydrogen peroxide

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

In the recent years, the scientific research has spent many efforts in new development in field of photocatalysis, especially because the importance of both technological and economical photocatalysis has increased over the past decades. A range of photocatalysis applications have been developed including anti-fogging, anti-microbial, self-cleaning surfaces, water and air purification, and solar induced hydrogen production (Pawar and Lee, 2015). Among these applications, many of them have been successfully commercialized. However, continuous research is done to further optimize photocatalysis technology and to broaden the scale of potential applications.

Semiconductors are widely used as photocatalysts because of a favorable combination of electronic structure, light absorption properties, charge transport characteristics and excited-state lifetimes (Khan and Adil, 2015). Among the oxide semiconductors, TiO_2 has broad application especially in photocatalysis. Besides TiO_2, ZnO is also recognized as one of the excellent materials for the photocatalytic activity since it has almost similar band gap energy as TiO_2, which is nontoxic in nature and provide low cost (Haibo *et al.*, 2013). Therefore, recent studies are more focus on optimization of ZnO photocatalyst to widen its application in photocatalyst. ZnO has direct and wide band gap energy near the UV spectral region, about 3.37 eV at room temperature (Janotti & Walle, 2009). This wide band gap of ZnO photocalyst is useful to decrease the time for the recombination of electron-hole pair in photocatalytic activity. However, the application of ZnO photocatalyst is limited to the UV light photocatalyst only, because the energy emitted from UV light is high enough to promote electron from valence band to conduction band. The main problem in the photocatalysis is to develop an economical photocatalyst, which one

of the solutions is by using solar energy, but photocatalyst only active under UV light irradiation.

Photocatalysis is the field of study on the photocatalyst and its photocatalytic process. Photocatalytic process begins when photons of energy higher or equal to the band gap energy are absorbed by a semiconductor particle resulting the transferred electron (e^-) from the valence band (VB) to the conduction band (CB) and generating a hole (h^+) in the VB (Hernández-Ramírez and Medina-Ramírez, 2015). Figure 1.1 shows the general mechanism of photocatalysis. The electron of the valence band becomes excited when irradiated by light. The absorption of the photons creates a bulk of electron–hole pairs, where free photo-electrons (e^-) are located in the conduction band and photo-holes (h^+) are located in the valence band. The recombination of e^- and h^+ take places either on the surface or in the bulk of the particle releasing the energy in the form of heat. The e^- and h^+ can migrate to the surface of the particle, where they can react with adsorbed molecules if the recombination process is suppressed (Hernández-Ramírez and Medina-Ramírez, 2015). The adsorbed species could be either reduced by CB electrons or oxidized by positive holes in VB. If the adsorbed species is water, electrons from water molecule will transfer to the positive holes to produce •OH radicals which are powerful oxidants and react with organic and toxic compounds. •OH radicals is responsible to initiate the oxidation reactions, especially for substances that adsorb weakly on the photocatalyst surface. This oxidation pathway is known as indirect oxidation to differentiate it from the direct oxidation by holes (Hernández-Ramírez and Medina-Ramírez, 2015).

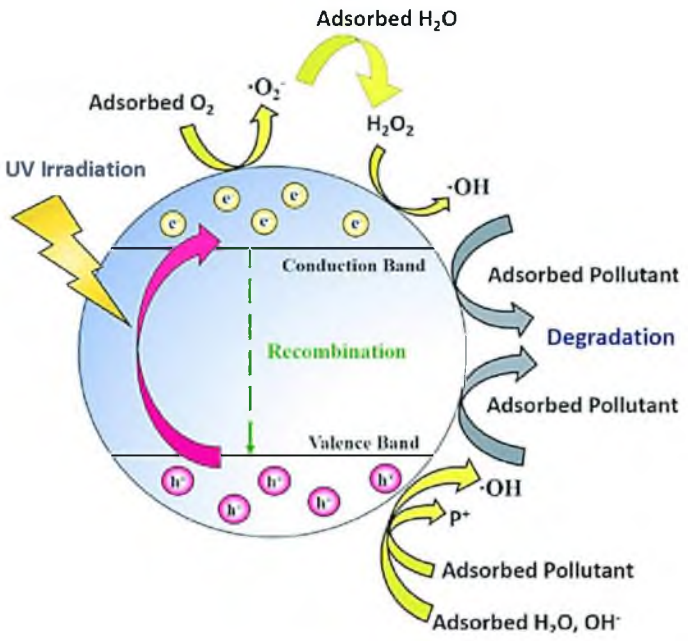

Figure 1.1 Photocatalysis mechanism of metal oxide for pollutant degradation (Leong *et al*. 2016)

Sunlight or known as solar energy is a free and most abundance energy source in the world. In order to maximal utilization of free solar energy, research study is focusing on the visible-light driven photocatalyst since visible light covers 39% of sunlight (Joesten, *et al.*, 2006). The problem is ZnO has wide band gap energy which limits the absorption of visible light, this is because the energy emitted from visible light is not strong enough to excite electron from valence band to conduction band. Therefore, it is very crucial to lower the band gap of ZnO to allow the absorption of visible light region, and also promote maximum utilization of solar energy. Many studies have reported the proper methods in the development of visible-light driven photocatalyst, which are ion doped semiconductor, semiconductor coupling (Hernandez-Ramirez & Medina-Ramirez 2015), surface organic coating, surface hybridization with carbon and doping method either with metal (Benhebal *et al*. 2014) such as copper (Ahmad *et al*. 2013) or non-metal elements such as carbon (C), nitrogen (N) and sulphur (S) (Tan *et al*. 2007).

It was reported that doping with non-metal elements like carbon (C), nitrogen (N) and sulphur (S) had the ability to decrease the band gap of ZnO and served as p type semiconductor photocatalyst (Tan *et al*. 2007). Furthermore, C, N and S doped

ZnO were proven to give higher photocatalytic activity compared to pure ZnO (Yu *et al.* 2016). However, among the non-metal dopants, C has been reported to be very efficient for visible light driven photocatalysis (Liu *et al.* 2011; Haibo *et al.* 2013). ZnO is an n-type semiconductor and change into p-type semiconductor by doping of carbon which promotes the changes in its electrical and optical properties, and creates unique properties (Haibo *et al.* 2013). Thus, for the last 10 years, carbon-doped ZnO photocatalyst has gained significant attention as one of the promising technique in the degradation of various organic pollutants such as organic dyes and phenolic compounds.

The ZnO doped with carbon has been successfully prepared by calcination of zinc compound with various organic agents, such as gluconic acid, ethylene glycol, vitamin C (Cho *et al.* 2010), and polystyrene opal (Lin *et al.* 2012). Urea which is synthesized from inorganic compound has been successfully used as carbon source in synthesis of ZnO doped with carbon (Zhang *et al.* 2015). Other precursors, zinc gluconate (Haibo *et al.* 2013), zinc acetate dihydrate (Bechambi *et al.* 2015), zinc carbonate hexahydrate (Liu *et al.* 2011) and zinc nitrate dihydrate (Lavand & Malghe 2015) are also being used in the synthesis of ZnO doped with carbon. ZnO doped with carbon synthesized from urea with band gap energy ~2.37 eV has excellent photocatalytic activity for methylene blue photodegradation under visible light irradiation after 2 hours irradiation with 90.2% efficiency (Zhang *et al.* 2015). Therefore, to ensure that the ZnO doped with carbon is absorbing visible-light, the value of band gap energy should be around ~2.37 eV as reported by Zhang *et al* (2015). Hydrothermal reaction, thermal plasma inflight technique, pulse-laser deposition and pyrolysis are the common method used in preparation of ZnO doped with carbon. However, sol-gel method is a common method done in the preparing of ZnO due to its advantages. Sol gel method is known as one of the convenient method to synthesize nanoparticles from various precursors. It is flexible, economical and less complex as compared to other conventional methods for nanoparticles synthesis and it also uses relatively low temperatures (Kumar *et al.* 2015).

From the recent study, ZnO doped with carbon has been successfully used as visible driven photocatalysts in the photodegradation of organic pollutant and dyes. In dyes degradation, ZnO doped with carbon is active for the photodegradation of

malachite green (Lavand & Malghe 2015) , orange II (Cho *et al.* 2010), rhodamine B (Haibo *et al.* 2013) and methylene blue (Zhang *et al.* 2015). ZnO doped with carbon is also successfully used for solar water splitting, with polystyrene opal as the carbon precursor (Lin *et al.* 2012). In this study, the effect of carbon doped on the ZnO and its photocatalytic activity in styrene oxidation was evaluated by several spectroscopic analysis and DFT simulation.

1.2 Problem Statement

ZnO with doped carbon photocatalysts have gained significant attention as one of the promising technique in the photodegradation and photocatalytic oxidation of organic molecules. Recently, ZnO with doped carbon is widely studied as driven visible light photocotalyst since it is proved that carbon is able to lower the band gap energy of ZnO and allows the absorption of visible light. However, less study successfully describe the effect of carbon in the ZnO to the photocatalytic performance of ZnO under visible light. The ZnO contained carbon was prepared from zinc acetate dihydrate via sol-gel method with the addition of CTAB or without it, and further calcined at different temperatures. Zinc acetate dihydrate acts as both precursors of Zn and carbon in the ZnO synthesis Therefore, this method will be the most convenient method to synthesis ZnO with carbon content without any external sources of carbon. The addition of CTAB and various calcination temperature in the ZnO synthesis was believed to affect the carbon formed, and deliberately affect the structure and properties of ZnO. Therefore, this study was conducted to determine the effect of carbon in ZnO, CTAB addition and calcination temperature based on the structure and properties. The relationship between structure-properties of ZnO towards the photocatalytic performance under visible light irradiation for photocatalytic oxidation of styrene was described in this study.

1.3 Research Objectives

The objectives of this study were:

- To synthesize ZnO from zinc acetate dihydrate with and without CTAB by sol-gel method.
- To characterize the physical chemical properties of the prepared ZnO photocatalysts.
- To study the relationship of structure-properties of ZnO with the photocatalytic performance under visible light irradiation for photocatalytic oxidation of styrene, and to study effect of carbon to the electronic properties of carbon-ZnO by DFT calculation.

1.4 Scopes of the Study

The study was focused on the effect of carbon in ZnO, addition of CTAB and calcination temperatures in ZnO synthesis towards the visible light photocatalytic activity for styrene oxidation. The carbon-ZnO were synthesis from zinc acetate dihydrate via sol-gel method with and without CTAB addition. Zinc acetate dihydrate was used as the precursors of Zn and carbon. Carbon sourced from acetate after calcination would likely formed in different form such amorphous and organized carbon, which also being affected by the addition of CTAB. The dried ZnO samples were calcined at different temperatures from 300 to 700 ^{o}C to study the effect of temperature to the carbon content in ZnO, and the structures-properties of ZnO.

Several spectroscopic analysis such as Fourier Transform Infrared Spectrometer (FTIR), DR UV VIS Spectrophotometer (DR UV-vis), Photoluminescence Spectrometer (PL) and X-Ray Photoelectron Spectrometer (XPS) were used to study the electronic properties and other properties of ZnO photocatalysts. Other analysis such as Field emission scanning electron microscope (FESEM), X-Ray Diffractometer (XRD) and Thermogravimetric analyzer (TGA)

instrumentations were also utilized to study the morphology, crystallinity and weight loss percentage of ZnO photocatalysts.

In general, density functional theory (DFT) calculation is one of the quantum theories based on Schrödinger equation. The DFT was first introduced and explained by Thomas-Fermi model in 1920s and later being completed by Kohn, Hohenberg and Sham by introducing the calculation using electron density. The electron density determines the number of electron, ground state wave function and all other electronic properties of the system. This DFT calculation is advantages for bigger structures where the bigger structures give more reliable result since they are more stable. Previous study on DFT calculation has widely studied on ZnO wurtzite, however, there are less DFT study focusing on effect of carbon in ZnO. Therefore, in this study DFT calculation was used to determine the electronic properties of carbon-ZnO. Gaussian 09 package was used, and a supercell model for ZnO consist of 24 Zn atom and 24 O atom were proposed and evaluated in the DFT simulation using B2PLYP/6-311G(D) method.

1.5 Significance of the Study

The study is important for the photocatalysis, especially in describing the effect of carbon in the metal oxide or semiconductors likes ZnO. Different forms of carbon like amorphous carbon will have different effect towards the structures, properties and photocatalytic performance of the ZnO photocatalyst. The study provides significant information on the relation between the structural and physical properties of ZnO with its photocatalytic activity. Therefore, the effect of carbon in ZnO structures and properties were evaluated using several instrumentation techniques and the effect of carbon in the photocatalytic performance of ZnO were described.

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