



UNIVERSITI PUTRA MALAYSIA

***DEVELOPMENT OF COBALT-DOPED ZINC OXIDE PHOTOCATALYST
NANOPARTICLES FOR REMOVAL OF NITROBENZENE***

LIMAN MUHAMMAD GIDADO

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By

LIMAN MUHAMMAD GIDADO

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

December 2015



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DEDICATION

This thesis is dedicated to my late father (Liman Muhammad Bello) and the entire Muslim Ummah.



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Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Doctor of Philosophy

DEVELOPMENT OF COBALT-DOPED ZINC OXIDE PHOTOCATALYST NANOPARTICLES FOR REMOVAL OF NITROBENZENE

By

LIMAN MUHAMMAD GIDADO

December 2015

Chairman : Associate Professor Abdul Halim Abdullah, PhD
Faculty : Science

The increasing rise of world population and rapid industrial development across the globe is not without problem, especially in terms of availability of potable drinking water. The photocatalytic oxidation of zinc oxide, ZnO, under UV irradiation on organic pollutants in water is well established and nitrobenzene, NB, has been classified under persistent organic pollutants and reported as being carcinogenic. In this study, ZnO catalyst was synthesized via sol-gel and, for the first time, via combination of sol-gel and hydrothermal method, in the presence of ethylene and polyethylene glycol surfactants. The resulting powder was calcined at different temperatures (400, 500, 600°C) and for a different calcination periods (2, 4, 6 hours). The prepared samples were characterized using X-ray Diffraction (XRD, Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), Surface Area Measurement (BET method), Diffuse Reflectance Spectroscopy (DRS), X-ray Fluorescence (XRF) and Electron Diffraction Spectroscopy (EDS). All ZnO samples were spherical with hexagonal structure and particle size ranges from 16 to 96 nm. The variation in surfactants, calcination temperature and calcination time have no significant effect on the properties of ZnO. The photocatalytic activity of the prepared ZnO was evaluated by degradation of NB, under 2h of UV light irradiation. ZnO prepared by a combined sol-gel and hydrothermal method, exhibits the highest photocatalytic activity (75% of NB removal). This is attributed to high surface area and small particle size. In order to enhance its photoactivity, the ZnO catalyst was doped with various percentage of cobalt, Co. The addition of Co onto ZnO did not change the morphology of the catalyst. There was no remarkable change in the band gap (3.20 eV for the 0.5% Co-doped ZnO and 3.22 eV for the undoped ZnO) but an increase in the surface area (12.6 m²/g for undoped ZnO to 17.6 m²/g for the 0.5% Co-doped ZnO) was observed. The photocatalytic activity of Co-doped ZnO catalysts in degradation of NB under UV light irradiation is 86% which is higher than that of ZnO (SGHP).

The effects of catalyst mass, NB concentration as well as the solution pH were examined using the Co-doped ZnO catalyst, SP2. The best conditions for degrading NB were 0.75 g catalyst loading, 20 ppm NB and at a solution pH of 7. Under these conditions and for a 2 hours irradiation time, SP2 removed 86% and 83% of NB under UV light and visible light irradiation, respectively. The ability of the SP2 catalyst to

effect 83% NB removal under visible light irradiation is a landmark achievement because greater part of solar radiation consists of visible light. The degradation of NB follows first-order reaction with a rate constant k_1 equals to $2.16 \times 10^{-2} \text{ mgL}^{-1} \text{ min}^{-1}$ and a half-life period of 32 min. Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) analyses, after a 2 hour photodegradation period, showed a 79% and 66% removal of NB, respectively, indicating a substantial degradation of the pollutant. The SP2 catalyst showed no significant loss in photoactivity after 5 cycles of photodegradation reaction suggesting that many more cycles are possible before reaching 50% drop in the photoactivity; a pointer to its reusability.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

PEMBANGUNAN FOTOMANGKIN KOBALT-DIDOPKAN ZINK OKSIDA NANOPARTIKEL BAGI PENYINGKIRAN NITROBENZENA

Oleh

MUHAMMAD GIDADO LIMAN

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Peningkatan kepadatan penduduk dunia dan pembangunan industri yang pesat di seluruh dunia bukan tanpa masalah, terutamanya dari segi ketersediaan air minuman yang boleh diminum. Proses pengoksidaan pencemar organik dalam air berfotopemangkinan zink oksida, ZnO, di bawah sinaran UV telah pun mantap dan nitrobenzena, NB, telah diklasifikasikan di bawah pencemar organik kekal dan dilaporkan sebagai karsinogenik. Dalam kajian ini, mangkin ZnO telah disintesis melalui kaedah sol gel dan untuk pertama kalinya melalui gabungan kaedah sol gel dan hidroterma dengan kehadiran surfaktan etilena dan polietilena glikol. Serbuk yang terhasil dikalsin pada suhu yang berbeza (400, 500, 600°C) dan bagi tempoh pengkalsinan yang berbeza (2, 4, 6 jam). Sampel yang tersedia dicirikan menggunakan Pembelauan sinar-X (XRD), Mikroskopi Transmisi Elektron (TEM), Mikroskopi Medan Pancaran Pengimbas Elektron (FESEM), pengukuran luas permukaan (kaedah BET), Spektroskopi Pantulan Resap (DRS), Pendaflor sinar-X (XRF) dan Spektroskopi Pembelauan Elektron (EDS). Semua sampel ZnO berbentuk sfera dengan struktur heksagon dan dengan saiz zarah antara 16-96 nm. Perubahan jenis surfaktan, suhu pengkalsinan dan masa pengkalsinan tidak memberi kesan yang besar ke atas sifat ZnO. Aktiviti fotopemangkinan ZnO yang disediakan telah dinilai dengan mendegradasi NB di bawah sinaran cahaya UV selama 2 jam. ZnO yang disediakan dengan kaedah gabungan sol-gel dan hidroterma mempamerkan aktiviti fotopemangkinan tertinggi (75% penyingkiran NB). Ini adalah disebabkan oleh luas permukaan yang tinggi dan saiz zarah yang kecil. Dalam usaha untuk meningkatkan fotoaktivitinya, pemangkin ZnO telah didop dengan pelbagai peratusan kobalt (Co). Penambahan Co ke ZnO tidak mengubah morfologi pemangkin. Tiada perubahan yang ketara dalam jurang jalur tenaga (3.20 eV bagi 0.5% Co didop ke ZnO dan 3.22 eV bagi ZnO) tetapi peningkatan luas permukaan (12.6 m²/g bagi ZnO ke 17.6 m²/g bagi 0.5% Co didop ke ZnO) telah diperhatikan. Aktiviti fotopemangkinan Co didop ke ZnO dalam mendegradasikan NB di bawah sinaran cahaya UV adalah 86% iaitu lebih tinggi dengan yang dicatatkan oleh ZnO (SGHP).

Kesan jisim mangkin, kepekatan NB serta pH larutan telah dikaji menggunakan mangkin Co didop ke ZnO, SP2. Keadaan yang terbaik untuk mendegradasikan NB adalah 0.75 g mangkin, 20 ppm NB dan pada pH larutan 7. Di bawah keadaan ini, dan

untuk 2 jam masa penyinaran, SP2 menyingkirkan 86% dan 82% NB, masing-masing, di bawah sinaran cahaya UV dan cahaya nampak. Keupayaan pemangkin SP2 dalam penyingkiran 83% NB di bawah sinaran cahaya nampak adalah satu pencapaian mercu tanda kerana sebahagian besar sinaran suria terdiri daripada cahaya nampak. Degradasi NB mengikut tertib pertama tindak balas dengan pemalar kadar, k_1 , bersamaan dengan $2.16 \times 10^{-2} \text{ mgL}^{-1} \text{ min}^{-1}$ dan dengan tempoh separuh hayat selama 32 min. Analisa keperluan oksigen kimia (COD) dan jumlah karbon organik (TOC), selepas 2 jam fotodegradasi, menunjukkan penyingkiran NB, masing-masing 79% dan 66%, menunjukkan degradasi bahan pencemar yang besar. Pemangkin SP2 tidak menunjukkan sebarang kehilangan fotoaktiviti yang ketara selepas 5 kitaran tindak balas fotodegradasi menunjukkan kemungkinan lebih banyak kitaran sebelum penurunan fotoaktiviti mencapai 50%; petunjuk bagi kebolegunaan pemangkin tersebut.



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I certify that a Thesis Examination Committee has met on 18 December 2015 to conduct the final examination of Liman Muhammad Gidado on his thesis entitled "Development of Cobalt-Doped Zinc Oxide Photocatalyst Nanoparticles for Removal of Nitrobenzene" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBRAVIATIONS

BET	Brunauer – Emmet – Teller
BJH	Barret – Joyner – Haalenda
COD	Chemical Oxygen Demand
DRS	Diffuse Reflectance Spectroscopy
EDS	Electron Diffraction Spectroscopy/Energy Dispersive (X-ray) Spectroscopy
EG	Ethylene glycol
FESEM	Field Emission Scanning Electron Microscopy/Microscope
FWHM	Full Width at Half Maximum
HPLC	High Performance Liquid Chromatography
IC	Inorganic Carbon
JCPDS	Joint Committee of Powder Diffraction Standards
NB	Nitrobenzene
PEG	Polyethelene glycol
S400	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 400 °C for 2 hours.
S500	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 500 °C for 2 hours.
S600	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 600 °C for 2 hours.
SGE1	Zinc oxide synthesized using ethylene glycol surfactant via sol-gel method and calcined at 500 °C for 2 hours.
SGE2	Zinc oxide synthesized using ethylene glycol surfactant via sol-gel method and calcined at 500 °C for 4 hours.
SGE3	Zinc oxide synthesized using ethylene glycol surfactant via sol-gel method and calcined at 500 °C for 6 hours.
SGP1	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 500 °C for 2 hours.
SGP2	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 500 °C for 4 hours.
SGP3	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel method and calcined at 500 °C for 6 hours.
SGHP	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel-hydrothermal method and calcined at 500 °C for 2 hours.

SP1	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel-hydrothermal method modified with 0.25% Co and calcined at 500 °C for 2 hours.
SP2	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel-hydrothermal method modified with 0.50% Co and calcined at 500 °C for 2 hours.
SP3	Zinc oxide synthesized using polyethelene glycol surfactant via sol-gel-hydrothermal method modified with 1.0% Co and calcined at 500 °C for 2 hours.
TEM	Transmission Electron Microscopy/Microscope
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
UHPLC	Ultra High Performance Liquid Chromatography
UV	Ultraviolet
Vis	Visible
XRD	X-ray Diffraction
XRF	X-ray Fluorescence
ZC	Commercial zinc oxide (Sigma-Aldrich)

CHAPTER 1

INTRODUCTION

1.1 Background

There is no disputing the fact that, rapid globalization and industrialization brought about by advancement in science and technology has been a source of blessing to this world. However, the development has not been without many challenges. The major of these challenges is inadequacy of clean and sanitized drinking water. It was estimated that around 4 billion people worldwide are suffering from clean and sanitized water supply and millions people died due to severe water borne diseases annually (Malato et al., 2009). Richardson (2008) and Wintgens et al., (2008) reported that, the discharge of wastewater and chemical spillage from industries into water channels has exacerbated the water quality crisis. For instance, Yang and Cheng (2007) and Lu et al., (2009) have reported that, by-products of disinfection process generated from chlorination are carcinogenic to human health, thus leading the world researches to develop more efficient water treatment technologies to remove the persistent organic contaminants from wastewater. Many efforts have been devoted to develop technologies that are capable to eradicate the hazardous materials from wastewater (Orloff, 2003 and Pera-Titus et al., 2004). Among many options, the development of processes to transform the toxic and hazardous pollutants into harmless compounds is one of the most effective solutions. However, initially, traditional methods were employed in the purification of water which later turns out to be nondestructive (Abramovic et al., 2004), because of their inability to degrade the organic pollutants. Allegre et al., (2004), Padmanabhan et al., (2006), and Gaya and Abdullah (2008) indicated that further treatment is required to destroy the pollutants into final harmless products such as CO_2 and H_2O , which indirectly increases operational cost (Gaya & Abdullah, 2008). Other researchers who worked on Advanced Oxidation Processes includes, Kaniou et al., (2005), Erquez and Pichat (2006), Parida et al., (2006), Uddin et al., (2007), Kaneco et al., (2009) and (Rao et al., (2009). The advanced - oxidation processes -are designed based on the generation of highly reactive species such as H_2O_2 , $\cdot\text{OH}$, $\cdot\text{O}_2^-$ and O_3 for the complete destruction of refractory organic compounds (Konstantinou and Albanis, 2004 and Pera-Titus et al., 2004). The commonly used semiconductors employed in the photocatalytic processes includes, TiO_2 , ZnO , CuO , Nb_2O_5 and ZnS . The photocatalytic process is normally undertaken under ambient condition and atmospheric oxygen (Chatterjee and Dasgupta, 2005). Fujishima, Rao, & Tryk, (2000), Carp et al., (2004), Grasian (2005) and Zainal et al., (2005) have identified TiO_2 as the main semiconductor used owing to its inertness (chemically and biologically), efficiency, cost effectiveness and being readily available. However, Daneshvar, Salari, & Khataee, (2004) and Akyol et al., (2004) both viewed ZnO as a suitable alternative to TiO_2 because of the former's having nearly the same band gap as the latter, follows the same mechanism of photodegradation and sometimes rated high in photocatalytic performance. Gaya and Abdullah (2008) have extensively reviewed the papers related to the use of TiO_2 in heterogeneous photocatalytic degradation of organic contaminants. In their review,

they have identified important achievements and problems recorded in recent work done until 2007 (Gaya & Abdullah, 2008).

Nitroaromatic compounds such as nitrobenzene and nitrophenols are largely synthesized and particularly often occur in water bodies as toxic pollutants. The degradation of these compounds in the environment via direct photolysis and by biological treatment is difficult and usually slow. Experimental results suggested the UV:H₂O₂ process as an effective and efficient technology for complete mineralization of nitrobenzene and nitrophenols. Comprehensive reaction mechanism for nitrobenzene photolysis was proposed with detailed discussions (Bing et al., 2006). The degradation mechanism of p-nitrophenol (p-NP) exposed to 254 nm UV light was studied in the presence and absence of oxygen respectively via both steady-state photolysis and time-resolved laser flash photolysis (LFP) experiments (S. Zhao et al., 2010).

1.2 Research problem and Objectives

1.2.1 Research problem

Although, substantial research reports are available on the semiconductor photocatalytic activity in the removal of many organic pollutants very little has been reported on nitrobenzene removal. There are reports on the removal of chlorinated phenolic compounds using TiO₂. (Sehili et al., (1989, 1991) reported the use of ZnO on the removal of 4-chloro phenol and 2,4-dichloro phenol in the presence of UV light. Also, there are many reports on the removal of chlorophenoxy herbicides by titania (Tanaka and Reddy 2002; Kamble et al., 2006; Bahnemann et al., 2007; Giri et al., 2007; and (Singh et al., 2007; Singh et al., 2007) with few reports on the same herbicides utilizing ZnO (Djebbar and Sehili, 1998). Nitrobenzene is a nitro aromatic hydrocarbon used to produce aniline and it was nominated by the National Institute of Environmental Health Sciences for listing in the Report on carcinogens based on the conclusions of an International Agency for Research on Cancer (IARC) working group that there is sufficient evidence of its carcinogenicity in experimental animals and that it is possibly carcinogenic to humans (Technology Planning and Management Corporation, 2002). Minero et al., (1994) reported that degradation of nitrophenols is slightly faster than that of nitrobenzene. They also reported that TiO₂ showed better efficiency on the degradation of nitrobenzene than ZnO. Nitrobenzene is considered to be highly toxic aromatic compound which is widely used in explosives, pesticides, prepharmo, and dye production (Li et al., 2006) yet very little work was conducted on its removal. Li et al., (2006) reported the use of excimer UV lamp ($\lambda = 172$ nm) in degrading nitrobenzene and confirmed that, the degradation is more efficient with UV/H₂O₂ combination than using UV alone. Many synthesis methods were reported for the preparation of semiconductor photocatalysts including using mixed oxides/couple semiconductor, combined methods, doping etc. But no report has been seen where ZnO was synthesized via the combination of sol-gel and hydrothermal method, especially the one utilizing polyethelene glycol or ethylene glycol surfactants. Hence, the reason why this research focuses its attention on the removal of this persistent organic pollutant using ZnO, particularly ZnO prepared via a combined method of sol-gel and hydrothermal methods.

The use of ZnO synthesized via different methods and the comparison with commercial ZnO in terms of photoactivity in degrading organic pollutants vis-a-vis its characteristic properties are well documented by various researchers. The literatures provide the strength and weakness of most methods and suggest ways of improving them. In another part, some literatures studied and compared the role of ZnO in degrading organic pollutants in comparison with some other semiconductor photocatalysts, more especially, TiO₂. In many instances, it was reported that doping semiconductor with metals/metal oxides is capable of enhancing its photoactivity and ZnO was not an exception. Method of synthesis has also been linked up with the photoactivity of synthesized photocatalysts because of its capability to affect its characteristics by transforming its physical and chemical properties. To objectively contribute to the world of photocatalysis especially in organic pollutants degradation, one needs to critically, select the right semiconductor to use; select the synthesis method that is perceived to be economical, friendly and capable of producing a high catalytic product; assess the need or otherwise for modification and also optimize the operational conditions for the photocatalytic reactions. The ZnO nanoparticle has been not to perform very well in degrading many organic pollutant within the UV region but act poorly when exposed to visible light radiation. The fast depleting non renewable energy sources has tilted the attention of many researchers towards harnessing energy from the renewable source towards meeting the world's high energy demand. One of the readily available and affordable source is the solar radiation (46% of which is in the visible region). Therefore, getting a semiconductor that can perform very well in the visible region will a remarkable achievement.

In line with the above criteria and in cognizance with available information in the literature, this research will focus its synthesis on using a combined sol-gel and hydrothermal methods and the modification of the samples using cobalt nitrate. Each of this two methods has merits and demerits in terms of producing a desired product, however, the combination of the two methods is believed to be promising in producing a product with better activity than a product produced via either of the two methods. A combination of the two methods is capable of producing product with high purity, reduced particle size, high crystallinity, nanoscale product, high light harvesting character and which is ecofriendly (Vijayan et. al., 2006). The aim of modification of a semiconductor by doping is to improve the photocatalytic activity of the semiconductor and most probably avoid surface recombination. However, different metal/metal oxide has varied contribution they make towards improving photoactivity of a semiconductor, it is therefore pertinent to note the right metal/metal oxide to select in effecting doping. Cobalt is one of the many transition metals used in doping semiconductor and it has been reported in some literature (Barakat et al., 2005; Walsh et al., 2008); Rasouli et al., 2011; Udayakumar et al., 2012; Zhao et al., 2012; (Caglar, 2013); (Fu et al., 2013); (Rajbongshi & Samdarshi, 2014) that, it is capable of reducing the particle size of the semiconductor, capable of producing extra absorption peak, capable of producing semiconductor that favors red shift, capable of reducing the band gap energy of the semiconductor. These qualities of cobalt and the fact that its ionic size is almost the same with that of zinc ion informed our choice of cobalt for the modification process. Based on broad literature review, we did not see any work where synthesis of ZnO nanoparticle via a combination of sol-gel and hydrothermal using PEG2000 surfactant and modified using cobalt, was reported. And very few research work on the removal of nitrobenzene by semiconductor photocatalysts were reported, in particular no report has been made on the removal of nitrobenzene using ZnO synthesized via this method. Therefore, this research study with potentials of producing ZnO nanoparticle via

combined sol-gel and hydrothermal and modified with cobalt; capable of degrading nitrobenzene utilizing both UV and visible light sources will be an immense contribution, especially considering the fact that most of the photocatalytic activities of ZnO utilizes UV light.

1.2.2 Project objectives

The main aim of this study is to synthesize cobalt doped ZnO via a combination of sol-gel and hydrothermal methods for the removal of nitrobenzene. The scope of my research includes and limited to synthesizing ZnO nanoparticles via Solgel and combination of Solgel and Hydrothermal methods utilizing ethylene glycol and polyethelene glycol surfactants as well as the modification of some selected samples with cobalt. The Solgel synthesized samples using both surfactants would be subjected to different time of calcinations (2, 4 and 6 hours) while the samples from the best surfactant would further be subjected to different calcination temperature (400, 500 and 600 °C). Various samples synthesized would be characterize using different techniques to ascertain its properties. The samples characterized would be applied in the removal of nitrobenzene using known concentration, as well as relating the characteristic properties of the samples with their photoactivity against nitrobenzene.

The specific research objectives include:

1. To synthesize ZnO nanoparticles via sol-gel and Solgel-hydrothermal methods using ethylene glycol and polyethelene glycol surfactants under different synthesis conditions and subsequent modification (via doping) of the sample with cobalt.
2. To characterize the different synthesized samples in terms of its phase, crystallinity, surface area, morphology, and band gap using XRD, TEM, FESEM, DRS, BET, EDX and XRF
3. To study the removal of nitrobenzene using the various samples under different operating conditions and ascertain the extent of mineralization of the nitrobenzene.

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LIST OF PUBLICATIONS

- M. G. Liman, A. H. Abdullah, M. Z. Hussein and Z. Zainal, Photodegradation of Nitrobenzene Using Cobalt Modified Zinc Oxide Particles, *Asian Journal of Chemistry*, 2014. **26**: S287 – S290. **Impact 2013 0.335**
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