



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS AND CHARACTERISATION OF COPPER OXIDE DOPED
ZINC OXIDE NANOPHOTOCATALYST AND ITS PHOTOCATALYTIC
ABILITY IN METHYL ORANGE DYE DEGRADATION**

NORZAFIRAH BINTI RAZALI

FS 2011 70

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UNIVERSITI PUTRA MALAYSIA**

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NORZAFIRAH BINTI RAZALI

**Thesis Submitted to the School of Graduate Studies, University Putra Malaysia,
in Fulfillment of the Requirements for the degree of Master of Science**

August 2011

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

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OXIDE NANOPHOTOCATALYST AND ITS PHOTOCATALYTIC
ABILITY IN METHYL ORANGE DYE DEGRADATION**

By

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August 2011

Chairman : Associate Prof. Abdul Halim Bin Abdullah, PhD

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CuO-doped ZnO (CuO-ZnO) nanophotocatalyst was synthesized by stirring CuO and ZnO in absolute methanol solution overnight, at ambient pressure and temperature. CuO was initially produced from four different precursors namely copper acetate, copper sulphate, copper chloride, and copper nitrate while the precursor of ZnO was produced from zinc acetate. Effects of different precursors to the properties of CuO (CA, CS, CCl, CN) were investigated. Next, the produced CuOs were doped onto ZnO (CZA, CZS, CZCl, CZN) and the properties were studied. Thermogravimetry analysis (TGA), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-Ray Fluorescence (XRF), Atomic Absorption Spectroscopy (AAS), surface area and pore distribution

(BET and BJH), and Zeta potential were used to characterize the synthesized ZnO, CuO and CuO-ZnO nanophotocatalysts. In photocatalysis, the ability of ZnO, CuO and CuO-ZnO nanophotocatalysts in decolorizing methyl orange (MO) dye were evaluated using UV-Vis spectroscopy while the degradation process was determined through Total Organic Carbon (TOC) analysis.

Interaction between intermediates and by-products during the synthesis process of CuO affected the crystallinity, morphology and particle size of synthesized CuOs. Although no significant changes in most of the physical properties of ZnO was observed, the introduction of CuO had improved the photoactivity of ZnO. This attributed to the enhancement in surface area of the CuO-ZnO photocatalyst and the ability of CuO to act as electron acceptor that prolongs charge separation which resulted in a better photodegradation process. Among the prepared CuO-ZnO nanophotocatalysts, CZN (CuO produced from copper nitrate) exhibited the highest rate of methyl orange photodegradation.

In order to determine the optimum % of CuO to be doped on ZnO, 0.5 – 2.0 % CuO-ZnO photocatalyst were synthesized using CZN. No significant changes in the properties of ZnO as the % of CuO doped were varied. In photodegrading MO, 1.0% of CuO-ZnO nanophotocatalyst showed the highest degradation rate. The optimum condition in degradation of MO was obtained at dye concentration of 30 ppm and pH of 7 by using 1.5g of 1.0% of CuO-ZnO photocatalyst. The photoactivity of CuO-ZnO was maintained until fifth cycle in the study of reusability. 1.0% of CuO had significantly improved the photoactivity of bare ZnO under visible-light irradiation. The potential of 1.0% CuO-ZnO nanophotocatalyst in degrading real dye-containing industrial

wastewater from one of textile factories at Melaka was evaluated. From the TOC analysis, 22% of total organic carbon in the real wastewater was degraded within 60 min.



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

**SINTESIS DAN PENCIRIAN NANO-FOTOMANGKIN ZINK OKSIDA DIDOP
DENGAN KUPRUM OKSIDA DAN KEMAMPUAN
FOTOPEMANGKINANNYA DALAM MENDEGRADASI PEWARNA METIL
OREN**

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Nanofotomangkin ZnO yang didop dengan CuO doped ZnO (CuO-ZnO) disintesis dengan mengacau serbuk CuO dan ZnO di dalam larutan metanol mutlak semalaman pada suhu dan tekanan bilik. CuO yang digunakan disintesis daripada prekursor berbeza iaitu kuprum sulfat, kuprum nitrat, kuprum klorida dan kuprum asetat manakala ZnO dihasilkan daripada zink asetat. Pengaruh pelbagai prekursor terhadap sifat CuO telah dikaji. Selanjutnya, CuO yang dihasilkan didopkan pada ZnO dan sifatnya diselidiki. ZnO, CuO dan CuO-ZnO nano-fotomangkin yang terhasil dikaji dengan menggunakan analisis termogravimetri (TGA), pembelauan sinar X (XRD), mikroskop pengimbas electron (SEM), mikroskop pembiasan elektron (TEM), sinar-X

berpendarfluor (XRF), analisa luas permukaan dan taburan liang pori, jerapan Atom Spektrofotometer (AAS), pengubah inframerah fourier (FTIR) dan analisa potensi zeta. Dalam kajian fotopemangkinan, kemampuan ZnO, CuO dan CuO-ZnO dalam menyahwarna pewarna metal jingga dimulai dengan menggunakan UV-vis spektroskopi dan proses degradasi ditentukan melalui analisa jumlah karbon organik (TOC).

Interaksi antara bahan pengantara dengan hasil sampingan telah mempengaruhi kehabluran, morfologi dan saiz partikel CuO yang disintesis. Walaupun tiada perubahan yang ketara pada hampir kesemua sifat fizikal ZnO, kehadiran CuO telah meningkatkan fotoaktiviti ZnO. Ini adalah disebabkan oleh penambahan luas permukaan dan kemampuan fotomangkin CuO-ZnO. CuO berperanan sebagai penerima elektron yang memanjangkan masa pemisahan cas yang menghasilkan fotodegradasi yang lebih baik. Antara CuO-ZnO fotomangkin yang disediakan, CZN (CuO yang terhasil daripada kuprum nitrat) menunjukkan fotodegradasi metal jingga yang paling tinggi.

Dalam menentukan % CuO yang optimum untuk didop ke atas ZnO, 0.5 – 2.0 % CuO-ZnO fotomangkin telah disintesis menggunakan CZN. Tiada perubahan yang ketara dikesan melalui analisa pada sifat-sifat asal ZnO setelah didop CuO pada peratusan berbeza. Dalam fotodegradasi MO, 1.0% CuO-ZnO fotomangkin menunjukkan tahap degradasi tertinggi. Keadaan optimum dalam degradasi MO diperolehi pada 30 ppm kepekatan pewarna dan pH 7 dengan menggunakan 1.5g 1.0% CuO-ZnO fotomangkin.

Dalam kajian penggunaan semula mangkin, fotoaktiviti CuO-ZnO adalah kekal sehingga kitaran ke-5. 1.0% CuO-ZnO juga mempamerkan peningkatan yang mendadak dalam peratusan degradasi dibawah sinaran cahaya nampak berbanding dengan ZnO. Potensi 1.0% CuO-ZnO fotokatalis dalam mendegradasi air buangan kilang dari salah sebuah

kilang di Melaka telah dinilai. Daripada analisa TOC, 22% dari jumlah karbon organik dalam air buangan tersebut telah didegradasikan dalam tempoh 60 minit.



ACKNOWLEDGEMENT

Allamdulillah and thank you to ALLAH S.W.T for the strength, health and knowledge that HE give to me. With HIS blessing and mercy, I am proud to finally finish my research and wrote this thesis. THANK YOU ALLAH.

I would like to thank those who continuously support and encourage me during my research and always be my side in my ups and downs. The top person in my list is my mother, Pn. Asiah binti Palidin who always believe at me and pray for my successful. To my siblings, there are no words can describe my appreciation to you of being my supporters whenever I felt sad and down. You guys are the best thing that happens in my life!

He smiles, he laughs and he always shared his knowledges and ideas to his students and never let his student lost in their research and study. He is Prof. Madya. Dr. Abdul Halim Bin Abdullah. Here, I would like to thank him for his guidance and patient to me during my course of study. Thank you Dr. Halim!

Millions of thank to all staff in Department of Chemistry, Institute of Advanced Technology (ITMA), and Institute of Bioscience, UPM for their kindness and services especially to En Ismayadi Ismail (FESEM), Pn. Nor Azlina Shari (TGA), Pn. Rusnani Amirudin (FTIR), Pn. Kamsiah Alias (XRD), Kak Aminah (SEM and TEM), En. Mohd. Shah Ibrahim (XRF) and Zainal Zahari Zakaria (AAS). Finally, I wish to thank to all students of Lab BASL 103 and AMNL for their guidance, ideas, and help during my study. Thank you guys.

I certify that a Thesis Examination Committee has met on 18th August 2011 to conduct the final examination of **Norzafirah binti Razali** on her **Master of Science** thesis entitled “**Synthesis and characterisation of Copper oxide doped Zinc oxide nanophotocatalyst and its photocatalytic ability in methyl orange dye degradation**” 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 Master of Science.

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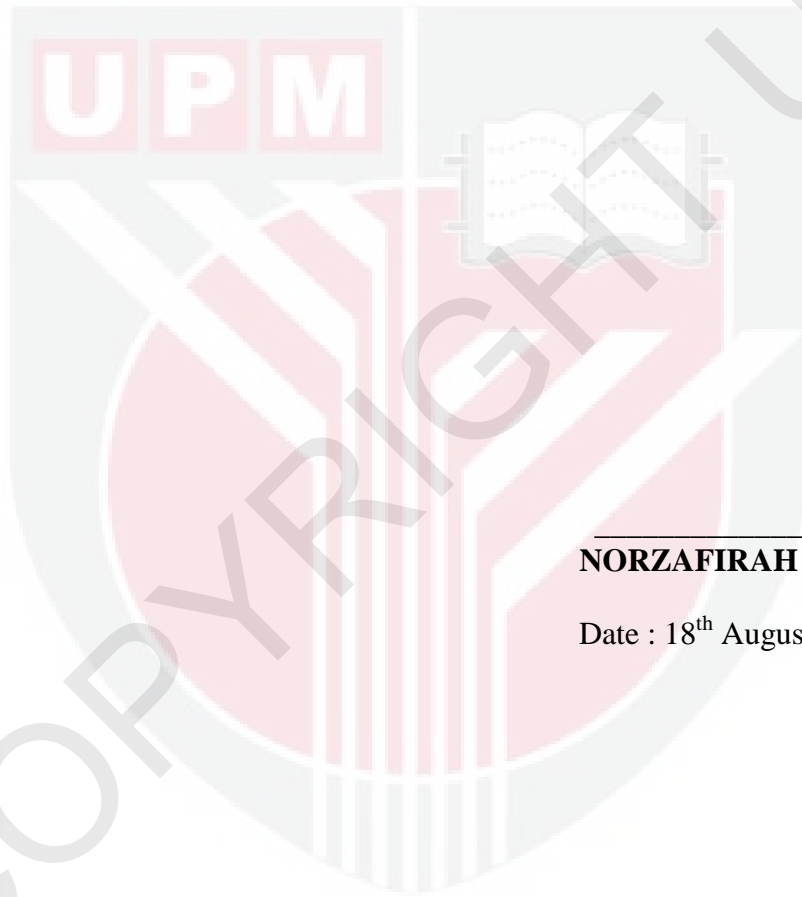
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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



NORZAFIRAH BINTI RAZALI

Date : 18th August 2011

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