UNIVERSITI PUTRA MALAYSIA

SYNTHESIS, CHARACTERIZATION, AND ANTIBACTERIAL ACTIVITY OF COPPER OXIDE NANOSHEETS

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FS 2013 65

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By

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

July 2013

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

SYNTHESIS, CHARACTERIZATION, AND ANTIBACTERIAL ACTIVITY OF COPPER OXIDE NANOSHEETS

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July 2013

Chairman: Nor Azowa Ibrahim, PhD
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The investigation on nanoparticles, which includes fabrication and characterization of the structural, physical, and chemical properties and their functions in various field of technology, is a fundamental cornerstone of nanotechnology and nanoscience. The applications of nanoparticles are known in many fields, such as catalysis, coating, semiconductors, and electronics. Among all practical matters that are produced at the nanometer scale, metal oxides are mainly attractive candidates from a technological and scientific point of view. Amongst all metal oxide nanoparticles, copper oxide (CuO) has gained the most interest because of its wide applications. During the past decades different methods have been proposed to synthesis CuO nanoparticles. Some of these methods have limitations due to requirements for high temperature, expensive instruments and special catalysis. In this study fabrication of CuO nanosheets in polyvinylpyrrolidone (PVP) by the quick precipitation method was investigated. The main advantages of this method compared to other methods are environmentally

friendly, cost-effectiveness, producing pure materials and simplicity of operation. Synthesis parameters include pH, concentration of stabilizer, and molar ratio of Cu^{2+} and OH^- were varied and their influences on the properties of CuO were investigated. Copper nitrate trihydrate $Cu(NO_3)_2.3H_2O$, polyvinylpyrrolidone (PVP) and sodium hydroxide (NaOH) were utilized as copper precursor, stabilizer and reducing agent, respectively. As evidenced by XRD analysis, all the products synthesized at pH 10 and 12 were CuO with monoclinic structure and all the products obtained under acidic pH were copper hydroxyl nitrate ($Cu_2(OH)_3NO_3$). Electron microscopy analysis illustrated that nanocrystals have a sheet-like geometry. By careful observation of electron microscopy revealed that oriented attachment mechanism was responsible for formation nanosheets from nanosized subunits. EDAX clearly confirmed the existence of Cu and O with an atomic ratio of 1:1 in all samples synthesized at pH 10 and 12. Diffuse reflectance spectroscopy studies revealed that the band gap of CuO nanosheets was found to be size-dependant. FT-IR spectroscopy was applied in this work to study the bonding at the surface of the synthesized CuO nanosheets. The result of FT-IR indicated that C=O in PVP Coordinated with CuO nanosheets and formed a protection layer. Investigation of effect of molar ratios of Cu^{2+} and OH^- on CuO indicated that when the molar ratio of Cu^{2+} and OH^- is 1:1, the final product is not pure. The pure monoclinic CuO were formed at the molar ratio of 1:3 and 1:4. From electron microscopy studies, sheet-like CuO at the molar ratio of 1:3 and 1:4 and ellipsoid-shape at a molar ratio of 1:1 were formed. The as synthesized CuO nanosheets were examined for antibacterial activity against four human pathogens, including two Gram-positive (*Staphylococcus. areas* and *Bacillus. subtilis*) and two Gram-negative (*Salmonella* and *Klebsiella pneumonia*). The antibacterial activity of CuO nanosheets was found to be size-dependent. The zone of inhibition increased as particle size decreased. The main observation was that CuO nanosheets indicated greater antimicrobial activity against Gram-positive bacteria. The inhibition zone for all microorganisms reached the maximum using CuO nanosheets fabricated in PVP 5% wt at pH 10.

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

SINTESIS, PENCIRIAN DAN AKTIVITI ANTIBAKTERIA DARI OKSIDA KUPRUM HELAIAN NANO

Oleh

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Siasatan pada nanopartikel, yang termasuk fabrikasi dan pencirian struktur, fizikal dan sifat-sifat kimia dan fungsi mereka dalam pelbagai bidang teknologi, adalah asas asas nanoteknologi dan nanosains. Aplikasi nanopartikel dikenali dalam banyak bidang, seperti pemangkinan, salutan, semikonduktor, dan elektronik. Antara semua perkara-perkara yang praktikal yang dihasilkan pada skala nanometer, oksida logam adalah calon-calon yang menarik terutamanya dari segi teknologi dan saintifik pandangan. Antara semua nanozarah logam oksida, kuprum oksida (CuO) telah mendapat faedah yang paling kerana aplikasi luas. Dalam dekad yang lalu kaedah yang berbeza telah dicadangkan untuk sintesis CuO. Beberapa kaedah mempunyai had kerana keperluan untuk suhu yang tinggi, alat mahal dan pemangkinan khas. Dalam kajian ini fabrikasi CuO helaian nano di polivinilpirrolidon (PVP) melalui kaedah pemendakan cepat telah disiasat. Kelebihan utama kaedah ini ialah berbanding dengan kaedah lain ianya mesra alam, keberkesanan kos, menghasilkan bahan-bahan tulen dan operasi yang ringkas.

Parameter sintesis termasuk pH, kepekatan penstabil, dan nisbah molar Cu^{2+} dan OH^- telah diubah dan pengaruh mereka pada sifat CuO telah disiasat. Kuprum trihidrat nitrat ($Cu(NO_3)_2.3H_2O$), polivinilpirrolidon (PVP) dan natrium hidroksida (NaOH) telah digunakan sebagai pelopor, penstabil dan agen penurunan untuk kuprum, masing-masing. Seperti yang dibuktikan oleh analisis XRD, semua produk yang disintesis pada pH 10 dan 12 adalah CuO dengan struktur monoklinik dan semua produk yang diperolehi dalam keadaan pH berasid adalah kuprum hidroksil nitrat ($Cu_2(OH)_3NO_3$). Analisis mikroskopi elektron menunjukan bahawa nanokristal tersebut mempunyai geometri seperti helaian. Daripada pemerhatian yang teliti mikroskop elektron mendedahkan bahawa mekanisma lampiran berorientasikan memberikan pembentukan helaian nano daripada subunit bersaiz nano. EDAX jelas mengesahkan kewujudan Cu dan O dengan nisbah atom 1:1 dalam semua sampel yang disintesis pada pH 10 dan 12. Kajian spektroskopi pantulan meresap mendedahkan bahawa jurang jalur helaian nano CuO didapati bergantung kepada saiz. FT-IR telah digunakan dalam kerja-kerja ini untuk mengkaji ikatan pada permukaan CuO helaian nano disintesis. Hasil daripada FT-IR menunjukkan bahawa C=O di PVP terselaras dengan helaian nano CuO dan membentuk satu lapisan perlindungan. Penyiasatan kesan nisbah molar Cu^{2+} dan OH^- kepada CuO menunjukkan bahawa apabila nisbah molar Cu^{2+} dan OH^- 1:01, produk akhir adalah tidak tulen. Monoklinik tulen CuO telah dibentuk pada nisbah molar 1:3 dan 1:4. Dari kajian mikroskopi elektron, seperti lembaran-CuO pada nisbah molar 1:3 dan 1:4 dan ellipsoid-bentuk pada nisbah molar 1:1 telah dibentuk. CuO yang telah disintesis telah diperiksa untuk aktiviti antibakteria terhadap empat patogen manusia, termasuk dua (*Staphylococcus. aureus dan Bacillus subtilis*) Gram-positif dan dua Gram-negatif (*Salmonella dan Klebsiella pneumonia*). Aktiviti antibakteria helaian nano

CuO didapati bergantung kepada saiz. Zon perencatan meningkat apabila saiz zarah menurun. Pemerhatian utama menunjukkan bahawa helaian nano CuO memberikan aktiviti antimikrob yg lebih tinggi terhadap bakteria Gram-positif. Zon perencatan untuk semua mikroorganisma mencapai maksimum menggunakan helaian nano CuO yang difabrikkan dalam 5% PVP pada pH 10.

ACKNOWLEDGEMENTS

First of all, praise is to “Allah “the cherisher, and the sustainers of the world for giving me strengths, health and determination to complete this thesis. I wish to express my deep and sincere appreciation to the chairperson of my supervisory committee Dr.Nor Azowa Ibrahim for her valuable ideas and support during the course of my thesis and for the direction and guidance provided during the entire period of my study. I appreciate her patience and sincere approach to motivate, help, advice and guide me to finish my study. My deepest appreciation goes to Professor Dr. Wan Md. Zin Wan Yunus and Dr. Norhazlin Zainuddin, for their guidance and advice for me to complete this project.

I wish to acknowledge my best friend, Dr. Nabi Motallebi who supported me along these years with his kindness and generosity.

I am deeply indebted to my parents for all their love, support and their patience during these years. I warmly thank my parents for always offering a helping hand when needed.

Most importantly, I would like to thank my wife. She fulfils my life with unconditional love, constant patience, and great deal of understanding. I am extremely grateful for her devotion to our life so that I could successfully finish my graduate studies. To my wife, I dedicated this thesis to thank her for everything that she did for me during these years.

I certify that a Thesis Examination Committee has met on 18 July 2013 to conduct the final examination of Mahdi Shahmiri on his thesis entitled "Synthesis, Characterization, and Antibacterial Activity of Copper Oxide Nanosheets" 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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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment for the degree of Master of Science. The members of Supervisory committee are as follows:

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DECLARATION

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

MAHDI SHAHMIRI

Date: 18 July 2013

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CHAPTER ONE

INTRODUCTION

1.1 Background of Research

There are two types of copper oxide, copper (I) oxide (Cu_2O) and copper (II) oxide (CuO), which Cu_2O is known as cuprous oxide and CuO is referred as cupric oxide (Jusang *et al.*, 2010). Even though they have the same components, they each have somewhat different characteristics. In mineralogy, CuO is known as tenorite. Its molecular weight is 79.54 g mol^{-1} and melts at 1603 K. CuO is a transition metal oxide, p-type semiconducting matter with a monoclinic crystal structure (Jun *et al.*, 2009). The lattice parameters for CuO are a = 4.68 Å, b = 3.42 Å, c = 5.13 Å, $\alpha = 90°$, $\beta = 99.54°$ and $\gamma = 90°$ (Ching *et al.*, 1989). CuO is stable to air and moisture at room temperature. It is virtually insoluble in water or alcohols. The oxide dissolves slowly in ammonia solution but quickly in an ammonium carbonate solution; it is dissolved by alkali metal cyanides and by strong acid solutions. Hot formic acid and boiling acetic acid solutions readily dissolve the oxide (Hong *et al.*, 2002). CuO decomposes to Cu_2O at 1303 K and at atmospheric pressure. The reduction can proceed at lower temperature in a vacuum. Carbon monoxide and hydrogen reduce CuO to the copper metal at 523 K and to Cu_2O at about 423 K. Ammonia gas reduces CuO to copper metal and Cu_2O at 698-973 K (DeSisto *et al.*, 1989). Metal oxide nanoparticles are the main attractive candidates among all functional materials to be synthesized at the nanometer scale. The distinctive characteristics of metal oxides make them the most varied classes of materials, with properties covering almost all aspects of solid-state physics and materials science

(Niederberger, 2009). Among all metal oxides nanoparticles, CuO has gained the best interest because of their possible wide applications. Many different physical and chemical routes have been suggested to fabricate CuO nanoparticles, such as thermal decomposition (Kim *et al.*, 2006), Sonochemical method (Kumar *et al.*, 2000), microwave irradiation (Zhu *et al.*, 2007) and quick precipitation method (Zhu *et al.*, 2004). Some of these methods have limitations due to requirements for high temperature, expensive instruments and special catalyst. For cost-effectiveness and simplicity of operation, quick-precipitation is preferred. (Wu *et al.*, 2010)

1.2 Structure of Copper Oxide

The structure of CuO (Figure1.1) is unique, Copper ions (light brown) are coordinated by four oxygen ions (dark red) in an approximately square planar configuration and a tetrahedral arrangement of 4 Cu atoms around each oxygen atom (Figure1.1). The Cu-O distance is 1.95 Å (Forsyth *et al.*, 1991).

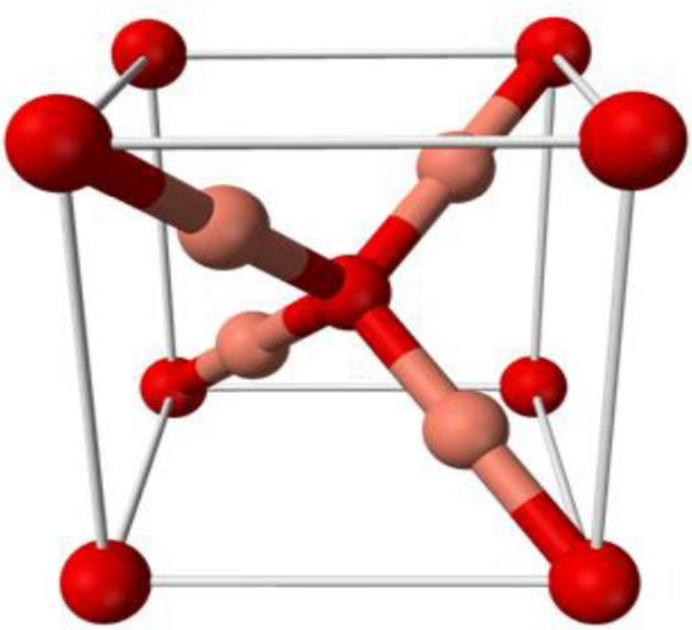

Figure1.1. Copper ions (light brown) are coordinated by four oxygen ions (dark red)

1.3 Problem Statement

General background for nanoparticles, their applications, different approaches to synthesize them, their advantages and disadvantages of approaches are given in chapter two. It will be explained that some of those methods, reported in the literature have limitations due to requirements for high temperature (hydrothermal), expensive instruments (sonochemical), formation of large particles (thermal decomposition), and need to organic solvent and oil (reverse Micellar). The significance of the current study is possibility of production capped copper oxide nanostructures by varying precipitation parameters without using high temperature, costly instruments, and organic solvents. The reaction temperature was set at 60°C.

1.4 Scope of Study

This investigation was conducted to synthesis copper oxide (CuO) nanostructures at low reaction temperature using quick precipitation method. The project will be focused on the study of synthesis parameters include pH, concentration of stabilizer, and different molar ratios of Cu^{2+} and OH^- and their influences on the antibacterial activity of final products.

1.5 Objectives of Research

1. To synthesis copper oxide nanostructures in PVP by the quick precipitation method.
2. To characterize copper oxide (CuO) nanostructures.
3. To study the effect of precipitation parameters, including the effect of pH, effect of concentration of stabilizer (PVP) and effect of molar ratios of Cu^{2+} / OH^-on the size and shape of final products.
4. To investigate the antibacterial activity of copper oxide nanostructures.

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