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ZINC OXIDE AND COPPER OXIDE SYNTHESIZED BY THERMAL TREATMENT METHOD

LEE PHIN JIT

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By

LEE PHIN JIT

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

ZINC OXIDE AND COPPER OXIDE SYNTHESIZED BY THERMAL TREATMENT METHOD

By

LEE PHIN JIT

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Chair : Professor Elias Saion, PhD
Faculty : Science

In this work, zinc oxide and copper oxide nanoparticles have been synthesized via thermal treatment method. In a typical work, salt nitrate as precursor and polyvinyl pyrrolidone as capping agent were dissolved and stirred in deionized water (as solvent) using magnetic stirrer accompanied with heating. Then, the hot mixture dried in oven for 24 hr was ground with mortar for at least 20 min to form fine powder. Lastly, the fine powder was underwent heat treatment at temperature ranged from 400 to 900 ^{o}C. The oxides nanoparticles formed were characterized using thermogravimetric analysis (TGA), X-ray diffraction (XRD), Fourrier Transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), and ultraviolet-visible (UV-Vis) spectroscopy. From TGA, it was found that the capping agent, polyvinyl pyrrolidone can be removed by calcination at temperature 450 and 500 ^{o}C to form pure copper oxide and zinc oxide respectively. This result was testified by FT-IR such that no characteristic absorption bands of polyvinyl pyrrolidone was detected in copper oxide and zinc oxide calcined at temperature 450 and 500 ^{o}C respectively, except corresponded oxide bands. In XRD analysis, broad diffraction peaks of zinc oxide and copper oxide nanoparticles were observed at temperature of 400 ^{o}C, showed that hexagonal wurzite structure and monoclinic structure crystals corresponded to zinc oxide and copper oxide have formed at this temperature. By increasing the heating temperature from 400 to 900 ^{o}C, the crystallites size of zinc oxide and copper oxide nanoparticles increased from ~18.9 to 96.4 nm and from ~19.5 to 36.2 nm, respectively. Meanwhile, TEM also showed that particle size of zinc oxide and copper oxide increased with increasing heating temperature. It was found that zinc oxide nanoparticles demonstrated spherical shape while copper oxide showed rod shape at temperature below 700 ^{o}C and then spherical shape as heating temperature increased. From UV-Vis measurement, estimated direct energy band gap of zinc oxide and copper oxide decreased with increased heating temperature while indirect energy band gap of copper oxide showed increasing trend.

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

ZINK OKSIDA DAN KUPRUM OKSIDA DISINTESIS MENGGUNAKAN KAEDAH RAWATAN TERMA

Oleh

LEE PHIN JIT

Mei 2014

Pengerusi : Profesor Elias Saion, PhD
Fakulti : Sains

Dalam kajian ini, zink oksida dan kuprum oksida nanopartikel telah disintesis dengan menggunakan kaedah rawatan terma. Dalam suatu kajian lazim, garam nitrat sebagai pelopor dan polivinil pyrrolidon sebagai ejen pelitupan telah dilarut dan dikacau dalam air ternyahion (sebagai pelarut) dengan menggunakan pengacau magnet disertai dengan pemanasan. Kemudian, campuran dikeringkan di dalam ketuhar selama 24 jam dan kemudiannya dikisar dengan mortar untuk sekurang-kurangnya 20 minit untuk membentuk serbuk halus. Akhir sekali, serbuk halus menjalani rawatan terma pada suhu antara 400 hingga 900 ^oC. Nanopartikel oksida terbentuk telah dicirikan dengan menggunakan analisis thermogravimetric (TGA), sinar-X (XRD), spektroscopi Fourrier Transform inframerah (FT-IR), mikroscop transmisi elektron (TEM), dan spektroskopi ultraungu-tampak (UV-Vis). Dari TGA, didapati bahawa ejen peliputan, polivinil pyrrolidon disingkirkan dengan pengkalsinan pada suhu 450 dan 500 ^oC untuk masing-masing membentuk kuprum oksida dan zink oksida tulen. Keputusan ini disokong oleh FT-IR bahawa tiada ciri-ciri jalur penyerapan polivinil pyrrolidon dikesan di dalam kuprum oksida dan zink oksida dikalsin pada suhu 450 dan 500 ^oC masing-masing, kecuali jalur oksida berkenaan. Dalam analisis XRD, puncak pembelauan zink oksida dan kuprum oksida nanopartikel yang lebar dapat diperhatikan pada suhu 400 ^oC, menunjukkan bahawa hablur berstruktur wurzite heksagon dan monoklinik mewakili zink oksida dan kuprum oksida terbentuk pada suhu ini. Dengan meningkatkan suhu pemanasan daripada 400 kepada 900 ^oC, saiz hablur zink oksida dan kuprum oksida nanopartikel meningkat daripada ~18.9 kepada 96.4 nm dan daripada ~19.5 ke 36.2 nm, masing-masing. Sementara itu, TEM juga menunjukkan bahawa saiz partikel zink oksida dan kuprum oksida meningkat dengan peningkatan suhu pemanasan. Didapati bahawa nanopartikel zink oksida menunjukkan bentuk sfera manakala kuprum oksida menunjukkan bentuk rod pada suhu di bawah 700 ^oC dan kemudian bentuk bulat dengan meningkatkan suhu pemanasan. Daripada penilaian UV-Vis, anggaran jurang jalur tenaga terus zink oksida dan kuprum oksida menurun dengan peningkatan suhu pemanasan manakala jurang tenaga tidak terus kuprum oksida menunjukkan peningkatan.

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I certify that a Thesis Examination Committee has met on 19 May 2014 to conduct the final examination of Lee Phin Jit on her thesis entitled "On Zinc Oxide and Copper Oxide Synthesized by Thermal Treatment Method" 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.

Members of the Thesis Examination Committee were as follows:

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Faculty of Science
Universiti Putra Malaysia
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Associate Professor
Faculty of Science
Universiti Putra Malaysia
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Khamirul Amin B Matori, PhD
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Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Yussof Wahab, PhD
Professor
Universiti Teknologi Malaysia
Malaysia
(External Examiner)

NORITAH OMAR, PhD
Associate Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 21 July 2014

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

Elias B. Saion, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mazliana Bt. Kamarudin, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

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LIST OF ABBREVIATIONS

c/a	Ratio of lattice parameter c to a
Cu	Copper
$Cu(NO_3)_2·3H_2O$	Copper nitrate trihydrate
Cu_2O	Copper (I) oxide
Cu_4O_3	Paramelaconite (copper oxide)
CuO	Copper (II) oxide
FeO	Ferrite
FT-IR	Fourrier transform infrared spectroscopy
FWHM	Full width at half maximum
HCP	Hexagonal closed pack
ICDD	International Centre for Diffraction Data
LED	Light emitting diode
Mid-IR	Middle infrared
MnO	Manganese oxide
Nd:YAG	Neodymium-doped yttrium aluminium garnet
NIR	Near infrared
O_i	Interstitial oxygen
O_{Zn}	Substitution of oxygen on zinc site
PVP	Polyvinyl pyrrolidone
S/V	Surface-to-volume ratio
SPR	Surface Plasmon resonance
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
UV	Ultraviolet
UV/Vis/NIR	Ultraviolet-visible light-near infrared
UV-Vis	Ultraviolet-visible light
V_o	Oxygen vacancy
V_{Zn}	Zinc vacancy
wt%	Weight percentage
XRD	X-ray diffraction
Zn	Zinc
$Zn(NO_3)_2·6H_2O$	Zinc nitrate hexahydrate
Zn_i	Interstitial zinc
ZnO	Zinc oxide

LIST OF SYMBOLS

A	Absorbance
C	Contant
c	Speed of light
$Cu\ K_{\alpha}$	Wavelength of copper anode
D	Average crystallite size
d_{hkl}	*d*-spacing of plane
E	Activation energy
E_g	Energy band gap
$F(R)$	Kubelka-Munk function
h	Planck's constant
$h\nu$	Photon energy
I_R	Intensity of reference
I_S	Intensity of sample
m	Direct or indirect transition
R	Gas constant
R	Absolute reflectance
R_{sample}	Reflectance of sample
$R_{standard}$	Reflectance of baseline
T	Absolute temperature
α	Absorption coefficient
β	Full-width at half maximum
θ	Incident ray angle
λ	X-ray wavelength
λ_c	Cut off wavelength

CHAPTER 1

INTRODUCTION

1.1. Introduction

The innovation of nanoscale materials has been investigated over last two decades since for the past centuries the development of micron materials or bulky materials dominated our technology. Nanoscale materials are defined as the materials that have at least one of their dimensions the size of less than 100 nm, including larger materials (like colloids or thin films) that can exhibit amazing size-dependent properties which are different from their bulk form. Nanoscale materials can presence in different dimensions, for example nanoparticles, nanowire, nanorod, nanobelt, and nanoflower, depending on the synthesis routes that applied. These to allow their increase surface area usage to fulfil the demand of diverse technologies such that different types and sizes of dimension show unlikely properties.

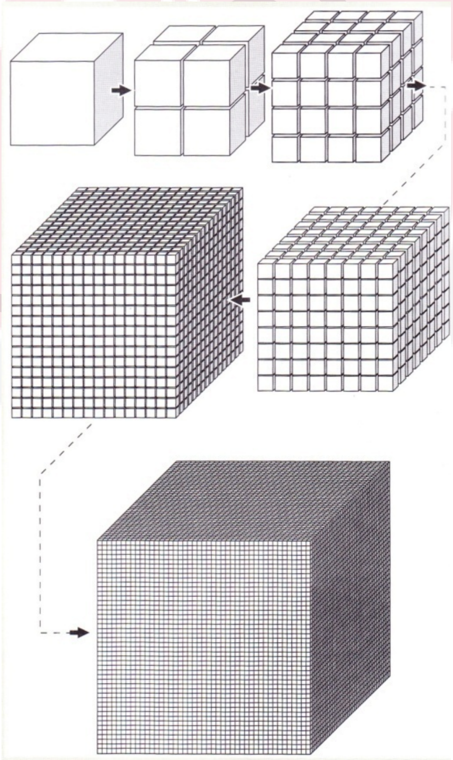

Figure 1.1: The division of a cube into smaller cubes of same volume result larger ratio of surface-to-volume. (Source: Hornyak *et al.*, 2008)

The properties of nanomaterials are very dependent on the effect of surface area which related to the size and shape of the particles. Hornyak *et al.* (2008) state that, "collective surface area and the surface-to-volume ratio are inversely proportional to the size of the particle", which the collective surface area is the total surface areas of an individual material (bulk or subdivided into nanomaterial) while surface-to-volume ratio (S/V) is the ratio of collective surface area to the volume of the same material. This can be more understandable with the illustration show in Figure 1.1. The collective surface area increases drastically when the dimension of a material is divided into smaller size with same volume. For an example, when a cube of micron size has a volume of $1x10^{-18}$ m^3 and collective surface area of $6x10^{-12}$ m^2 is break up into nanosize ($1x10^9$ nanocubes), the collective surface area turns out to be $6x10^{-9}$ m^2, which means the S/V ratio of nanomaterials is 1000 times more than micron material (or bulk material). In addition to that, particle shape also influences the surface area of nanomaterials such that a cube appears to have larger surface area compared to a sphere with same volume.

Nanoscale materials are given significantly attentions due to the remarkable properties these materials have showed such as magnetic, electrical, catalytic, photoelectric, and optical, not only limited to the general features such as mechanical hardness, thermal or chemical stability (Jolivet, 1994). Among the various nanoscale materials, metal oxides have shown promises criteria that most of metal oxides exist with more than one novel property than its bulky phase and have assorted applications.

1.2. Problem Statement

Zinc oxide (ZnO) and copper oxide (CuO) are two of the very common materials being used in fabrication of semiconductor devices since past centuries as zinc (Zn) and copper (Cu) raw materials are abundant and easy to obtain from earth crust as well as their trusted physical and mechanical properties in bulk structure. On the other hand, these oxides fabricated in nanosize have shown magnificent properties besides properties of bulk structure, for examples: electrical, magnetic, catalytic, optical, and etc, as reported by many researches in the past decades. Due to their amazing properties shown in nanoscale, promising nanosize metal oxides can be synthesized through miscellaneous of methods such as electrochemical deposition and wet chemical reduction synthesis, solid state thermal and hydrothermal method, as well as biological green synthesis. However, most of these methods involve expensive equipments, complexity of operation procedure and preparation, handling of highly dangerous toxic chemicals, and presence of unwanted by-products as well that restrict their potential of large scale production. Thus, seeking for method that enable to overcome these problems is very vital for future nanotechnology development.

In this study, a thermal treatment method originated from our research group (Naseri *et al.*, 2011) was adopted to overcome some of the undesired problems. By implementing this method in fabrication of ZnO and CuO nanoparticles, complication of fabrication method of ZnO and CuO nanoparticles can be simplified by using non-toxic chemicals, low cost instruments, and easily perform typical preparation procedures at the mean time enhance or at least maintaining their astonishing properties by producing metal oxides that are free from impurities and the size remains in nanoscale.

1.3. Significance of Study

Thermal treatment method is a technique that taking capping agent or stabilizer at front step to suppress the growth of particles followed by calcination process to remove undesirable organic compounds and simultaneously controls the particles' growth rate. The advantages of thermal treatment method are:

- Simple to carry out without complex procedures
- Low cost due to low temperature and lack of expensive equipment usage
- No chemical or organic reducing agent
- Usage of non-toxic chemicals which is safe to handle
- Environmentally friendly such that no production of toxic by-products.

1.4. Research Objectives

In this study, zinc oxide (ZnO) and copper (II) oxide (CuO) nanoparticles were prepared by using thermal treatment method with metal nitrates as metal precursors, polyvinyl pyrrolidone (PVP) as capping agent and deionized water as solvent in nanoparticles sample preparation.

Due to the rapid and extensive development of nanotechnology, feasible materials shall have features such that it has large availability, an abundant element on Earth, and non-toxic to environments. For that reason, zinc and copper are suitable materials in nanomaterials fabrication. Moreover, to the best of my knowledge, synthesis of ZnO and CuO nanoparticles with aid of PVP using thermal treatment method have not yet been reported.

Hence, the objectives of this research are:

1) to show that ZnO and CuO nanoparticles can be prepared via thermal treatment method.
2) to study the effects of calcination temperature on structural properties of synthesized ZnO and CuO nanoparticles.
3) to obtain the optical band gap value of synthesized ZnO and CuO nanoparticles.

1.5. Scope of Study

The scope of the study is to show that ZnO and CuO nanoparticles can be prepared via thermal treatment method with the aid of PVP. By considering the effects of calcination temperature on synthesized ZnO and CuO nanoparticles, the structural properties of nanoparticles calcined at temperature range from 400 to 900 ^{o}C was studied. Beside of that, the quantitative and qualitative aspects of optical properties of ZnO and CuO nanoparticles prepared were determined in terms of optical band gap.

1.6. Outline of the Thesis

This thesis explores the possibility of fabrication of ZnO and CuO nanoparticles through thermal treatment method by investigating the effects of calcination temperature on the structural properties and optical properties. Typically, this thesis consists of five chapters starting from Chapter 1 about introduction to this work and Chapter 2 for reviews from other researches related to this work. Next, is Chapter 3 which included all the materials used in nanoparticles fabrication and research methodology as well as instruments and equipments utilized in investigation of structural and optical properties. Every result obtained and discussions including tables, figures, and graphs regarding the effects of calcination temperature on properties of ZnO and CuO nanoparticles are all comprised in Chapter 4. The conclusions and future works of research are laid in Chapter 5.

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APPENDICES

X-ray diffraction analysis