STRUCTURAL AND OPTICAL PROPERTIES OF ZINC OXIDE NANOPARTICLES SYNTHESIZE VIA SOL GEL AUTO COMBUSTION METHOD

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Material) (Hons.)

by

LEE SEIH CHUNG

B051310063

930112-14-5097

FACULTY OF MANUFACTURING ENGINEERING

DEDICATION

Only

my beloved father, Lee Kam Choon

my appreciated mother, Poy Lai Ling

my adored brothers, Seih Punt and Seih Hein

for giving me moral support, money, cooperation, encouragement and also understandings

Thank You So Much & Love You All Forever

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TABLE CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ag	-	Silver
c/n	-	Citrate to Nitrate Ratio
CB	-	Conduction Band
$C_2H_5NO_2$	-	Glycine
$C_6H_8O_7$	-	Citric Acid
$C_6H_6O_6$	-	Aconitic Acid
$C_5H_6O_4$	-	Itaconic Acid
$C_5H_4O_3$	-	Itaconic Anhydride
$CO(NH_2)_2$	-	Urea
CO_2	-	Carbon Dioxide
CO_3	-	Carbonate Group
CuO	-	Copper Oxide
DOS	-	Density of Sate
DTA	-	Differential Thermal Analysis
F	-	Flourine
F/O	-	Fuel to Oxidizer Ratio
FE	-	Free Exciton
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared Spectrometer
GOD	-	Glucose Oxidase
H_2O	-	Water
IR	-	Infrared
JCPDS	-	Joint Committee on Powder Diffraction Satndards
LEED	-	Low Energy Electron Diffraction
N_2	-	Nitrogen Gas
$NaNO_3$	-	Sodium Nitrate
NaOH	-	Sodium Hydroxide

NH_4OH	-	Ammonia Solution
NH_4NO_3	-	Ammonia Nitrate
O	-	Oxygen
OH	-	Hydroxyl Group
O_2	-	Oxygen Gas
SEM	-	Scanning Electron Microscope
SHS	-	Self-propagating High Temperature Synthesis
$SiCl_4$	-	Silicon tetrachloride
TEM	-	Transmission Electron Microscope
TGA	-	Thermogravimetric Analysis
UV	-	Ultra-violet
UV-Vis	-	Ultraviolet-visible Spectroscope
VB	-	Valence Band
VCS	-	Volume Combustion Synthesis
XRD	-	X-ray Diffraction
Zn	-	Zinc
$Zn(NO_3)_2$	-	Zinc Nitrate
$Zn(OH)_2$	-	Zinc Hydroxide
Zn_2SnO_4	-	Zinc Stannate
$Zn_5(CO_3)_2(OH)_6$	-	Hydrozincite
$ZnCrO_4$	-	Zinc Chromate
ZnO	-	Zinc Oxide

LIST OF SYMBOLS

%	-	Percentage
m_h^*	-	Effective Mass of Hole
m_e^*	-	Effective Mass of Electron
μ	-	The Reduced Effective Mass of the Electron-hole Pair of
∞	-	Infinity
Å	-	Angstrom
a	-	Lattice Constant
c	-	Lattice Constant
cm^{-1}	-	Wavenumber
D_p	-	Crystalline Size
E	-	Energy Level
		Effective Mass of the Exciton
E_g	-	Activation Energy
$Eg(\infty)$	-	Bulk Band Gap
eV	-	Electron Volt
Eε	-	Bulk Optical Dielectric Constant
g	-	Gram
h	-	Planck's Constant
K	-	Constant
kV	-	Kilo Volt
m^{-1}	-	Per meter
M	-	Mole
m_e	-	Free Electron Mass
meV	-	Milli Electron Volt
min^{-1}	-	Per Minute
ml	-	Milli Litre
mm	-	Millimetre

mol	-	Molarity
MPa	-	Mega Pascal
n	-	Quantum Number
nm	-	Nanometer
^{o}	-	Degree of Angle
^{o}C	-	Degree Celsius
pH	-	The Measure of Acidity
t	-	Thickness of Sample
T	-	Transmittance
u	-	Bond Length
v	-	Velocity
x	-	Magnification
α	-	Absorption Coefficient
β	-	Broadening at Diffracion Line
$\varepsilon / \varepsilon_0$	-	Relative Dielectric Constant
θ	-	Delta
λ	-	Wavelength
π	-	Pi
σ	-	Sigma

ABSTRAK

Tujuan kajian ini adalah untuk menilai sifat-sifat struktur dan optik nanopartikel ZnO disintesis melalui gel sol kaedah pembakaran auto. Pertama, nitrat zink dan asid sitrik akan dicampurkan bersama-sama dan dipanaskan pada 250 ^{o}C. penyelesaian ammonia kemudian ditambah kepada penyelesaian untuk meneutralkan kepada pH 7. Produk abu yang dihasilkan dalam warna hitam meneruskan proses pengkalsinan untuk mengeluarkan kekotoran dalam abu. Kaedah ini digunakan kurang tenaga berbanding dengan kaedah lain untuk mensintesis nanopartikel ZnO. Sitrat berbeza kepada nisbah nitrat dirumuskan dalam kajian ini untuk mencapai auto tindak balas pembakaran. Ia menghasilkan ketulenan tinggi nanopartikels ZnO selepas proses pengkalsinan. Reaksi semasa proses sintesis disiasat melalui penilaian haba. Sifat-sifat struktur nanopartikel ZnO dicirikan oleh pembelauan sinar-X (XRD) untuk mengkaji penghabluran, kekisi yang berterusan, dan saiz kristal. Kehadiran nanopartikel ZnO telah disahkan oleh Fourier Transform Infrared (FTIR) dan X-ray pembelauan (XRD). Ultra-violet Spektroskopi yang boleh dilihat adalah satu kaedah yang berguna untuk menyiasat sifat-sifat optik hartanah ZnO nanopaticles.Optical nanopartikel ZnO dipengaruhi oleh zarah-zarah nano. Ia boleh diperhatikan bahawa partikels yang lebih besar saiz zarah, lebih baik ciri-ciri optik. Kerja ini menunjukkan bahawa gel sol tindak balas pembakaran auto adalah satu kaedah yang berkesan untuk mensintesis nanopartikel ZnO.

ABSTRACT

The aim of this study is to evaluate the structural and optical properties of ZnO nanoparticles synthesized via sol gel auto combustion method. Firstly, zinc nitrate and citric acid mixed together and heated at 250 ^{o}C. Ammonia solution was then added to the solution to neutralize it to the pH 7. Products ashes were produced in black color are proceed to the calcinations process to remove the impurities in the ashes. This method consumed less energy compared to other method to synthesize ZnO nanoparticles. Different citrate to nitrate ratio is formulated in this study to achieve auto combustion reaction. It yielded high purity of ZnO nanoparticles after the calcinations process. The reaction during the synthesis processes were investigated via the thermal evaluations. The structural properties of ZnO nanoparticles was characterized by X-ray diffraction (XRD) to study the crystallinity, lattice constant, and crystallite size. The presence of ZnO nanoparticles was confirmed by Fourier Transform Infrared (FTIR) and X-ray diffraction (XRD). Ultra-violet Visible Spectroscopy is a useful method to investigate the optical properties of ZnO nanopaticles.Optical properties of ZnO nanoparticles were influenced by the nanoscale particles. It was observed that the larger the particle size, the better the optical properties. This work shows that the sol gel auto combustion reaction is an effective method to synthesize ZnO nanoparticles.

CHAPTER 1
INTRODUCTION

1.1 Background Study

Zinc oxide (ZnO) invite potential attention because their fascinating properties on electrical and optical. ZnO is a II-IV semiconductor that exhibit a direct band gap of 3.37eV at ambient condition, high optical gain, high electrical conductivity, high optical transmittance in visible region, and large binding energy (Rusu *et al.*, 2011). Physical properties such as electronic band structure, cleavage, and optical transparency are highly depend on the lattice symmetry and the crystal structure of ZnO (Elfadill *et al.*, 2015). ZnO usually form in zinc blende crystal structure and hexagonal wurtzite crystal structure.

Various form of ZnO materials such as thin films, nanoparticles, and powder have been reported and synthesized earlier (Shankar *et al.*, 2015). Thin films of ZnO is used on graphene for thin film transistor due to its high electronic transportation and optical properties (Lim *et al.*, 2008). Doping action of fluorine improves the feature of antibacterial of ZnO nanopowders (Ravichandran *et al.*, 2014). Currently organic dyes are widely used in textile, rubber, paper, and plastics industries. Due to the toxicity of dyes, environmental problems are getting serious. An advanced adsorption materials, ZnO nanoparticles, are used as a dye adsorbents for dye removal (Zhang *et al.*, 2016).

A nanoparticles is a form of structures with sizes in the nm range. In principle any particles which bonded together or individual with size less than 100nm can be considered as nanoparticles. In the past few decades, nanoparticles have attracted scientists due to the unique properties. Differences between nanoparticles and bulk material are nanoparticles possess novel electrical and optical properties due to quantum confinement effect leading to wide applications (Anugop *et al.*, 2016). The bridge between bulk materials and atomic or molecular structures are effectively defined by nanoparticles.

Despite the nanoparticles are widely applied in this modern era but it has a long history. In the century of Mesopotamia, nanoparticles were used by artisans to produce glittering effect on the pot surface. Gold nanoparticles was developed by Turkevich and then improved by Frens with electrochemistry techniques (Zhong 2009). In early 1900s, polycrystalline ZnO was used for medical and pharmaceutical industries and medical technology (Litton *et al.*, 2011). In 1930s, the photoluminescence and electroluminescence properties were being included in some of the research activities and this early work was documented and reviewed, which were cited by Klingshirn (Feng, 2013). In 1960s, a novel piezoelectric properties of ZnO has been discovered which the first electronic application applied as a thin layer for surface acoustic wave devices (Ellmer *et al.*, 2008). In recent year, from 2005 until now, the amount of publication of ZnO related to nano-structure and application is increasing.

Properties such as electrical, optical and magnetic have been significantly defined by nanoparticles due to the nano scale. The high surface area to weight ratio of nanoparticles leads to an excellent chemical interactions at the interface (Ghafari *et al.*, 2016). Optical properties of metal oxide nanostructures strongly depend on their shape, it is often highly desired to control shape to achieve different optical properties for both fundamental studies and applications (Zhong 2009).

According to Duo *et al.* (2016), in order to exploit a new function of ZnO nanoparticles, the development of synthetic strategies for well-defined three-three dimensional interconnection or self-assembly of micro-and nano-structured building blocks into desired hierarchical structures is one of the key issue and significant challenges. Javed *et al.* (2016) stated that ZnO nanoparticles are stable and their synthesis is low cost but instability happened when agglomeration of chemically synthesized nanoparticles due to high surface energy results in size increase.

In order to obtain the nanoparticles, the synthesis method is critical. The parameters involved in the synthesis of nanoparticles are greatly influenced the sizes, shapes, structures, and properties of the nanoparticles. There are several methods which are commonly used for synthesis of nanoparticles such as solid state reaction (Sun *et al.*, 2006), sol gel method (Addonizio *et al.*, 2014), precipitation method (Sharma & Ghose 2014), hydrothermal method (Yuan *et al.*, 2009), and auto-combustion reaction (Wang *et al.*, 2015).

1.2 Problem Statement

In the previous studied, particle size is the key parameter to the structural and optical properties of zinc oxide (Ungula & Dejene 2016). Optical properties such as scattering, transmittance, refractive index, reflectivity and etcetera mainly depend on how the structure formed. Nanoscale materials have been extensively studied due to their potential in the field of optical. The properties of the nanostructures are strongly dependent on their structures and morphologies. Thus, it is important to synthesize the nanostructures with different morphologies such as rod-like, spindle-like, and sheet-like to explore their possible unique properties in optical. Potential sources such as interface effect, localized/internal strain and surface defects are greatly influence the optical properties of the nanomaterial of zinc oxide. Therefore in this project, the improvement in scaling of zinc oxide synthesized by sol-gel auto combustion method by mixing the zinc nitrate ($Zn(NO_3)_2$) and citric acid ($C_6H_8O_7$) then followed by ammonia solution (NH_4OH). The nitrate to citrate ratio was optimized in order to achieve the homogenous dispersion of zinc oxide nanoparticles.

1.3 Objectives

The objectives of this project are summarized below:

- To synthesis ZnO nanoparticles using sol-gel auto combustion method
- To characterize structural and optical properties of synthesized ZnO nanoparticles
- To investigate the relationship between the optical properties and the nanostructure of zinc oxide

1.4 Research Scope

This research work scopes are synthesizing and characterizing ZnO nanoparticles via sol-gel auto combustion method with specified amounts of citrate-nitrate ratio which are 0.3, 0.4, 0.5, 0.6, and 0.7. Citrate-nitrate ratio is the key parameter to control the degree of homogeneity of the particles distribution in the ZnO nanoparticles. The raw materials are zinc nitrate powder, citric acid powder, and ammonia solution. Processes involved during synthesis of ZnO nanoparticles are solution mixing, auto combustion and calcination. The combustion profile and the thermal stability of as-prepared gel were determined by using thermal analyzer at increasing temperature. Structural properties such as lattice constant, crystallite size, microstructure, and morphology of ZnO nanoparticles were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) to investigate the outcomes of each parameter. A scanning electron microscope (SEM) was employed to characterize the morphology of the ZnO nanoparticles to obtain the high resolution image with magnification of 10,000x. The optical absorption and specifications for characterization were set within the range of value of 400 to 4000 cm^{-1} for spectral and 0.3 cm^{-1} for resolution for fourier transform infrared spectroscope.

CHAPTER 2
LITERATURE REVIEW

2.1 Zinc Oxide

Zinc oxide is an inorganic compound with the chemical formula of ZnO. Zinc oxide possesses special properties such as high chemical stability, high electrochemical coupling coefficient, good radiation absorption, and better photostability (Segets *et al.*, 2009). It is also useful in ceramic industry due to its hardness, rigidity, and piezoelectric constant in nature (Özgür *et al.*, 2005). Zinc oxide is one of the semiconductor having wide band gap of 3.37eV at room temperature, high optical transmittance, and high optical gain of 300 cm^{-1} (Purohit *et al.*, 2015). ZnO is a semiconductor with direct band gap and high excitation binding energy, due to this properties its shows a great promise for application of high efficiency and short wavelength light-emitting devices which means it allows efficient excitonic emissions at high temperature (Bagnall *et al.*, 1998). ZnO as a semiconducting material and has been extensively study in the early 1950s and 1970s (Ellmer *et al.*, 2008).

In the early century, zinc oxide used in various field of applications such as rubber industry, ceramic industry, animal feed, catalyst, and paint industry. Due to the development of rubber industry, the demand of zinc oxide is high. Zinc oxide is one of the agents to activate the sulfur cross-linking of rubber and it provides pigmentary behavior that able to improve the capability to absorb heat from frictional force. Zinc oxide is essential to reduce the melting temperature of the glaze which is greatly reduces the energy required for the machine. It also provides the zinc source for the animal to maintain their body's metabolism.

2.1.1 Structural Properties of Zinc Oxide

Zinc oxide possesses three type of form of crystal structure which are hexagonal wurtzite, rocksalt, and cubic zincblende. Among the crystal structures, wurtzite crystal structure is the most stable form in the ambient condition with the binding energy of 60 meV. ZnO usually form a wurtzite crystal structure with lattice constant of *a* = 3.250 Å and *c* = 5.207 Å. Cubic zincblende can be stabilized by growing on the substrates. ZnO have been extensively investigated and interpreted in term of the band theory of semiconductors as distinct from the tight binding or Heitler-London model (Thomas 1959). The electronic configuration of Zn is $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^2$ $(3p)^6$ $(3d)^{10}$ $(4d)^2$ and O is $(1s)^2$ $(2s)^2$ $(2p)^4$ (Klingshirn *et al.*, 2010). The Zn atom is tetrahedrally bonded with four O atoms, the electrons from *d* orbital of Zn atom hybridized with the electros from *p* orbital of O atom, as shown in Figure 2.1. Undoped ZnO is normally attributed to interstitials of Zn, vacancies of hydrogen or oxygen for electron doping action (Wang *et al.*, 2007).

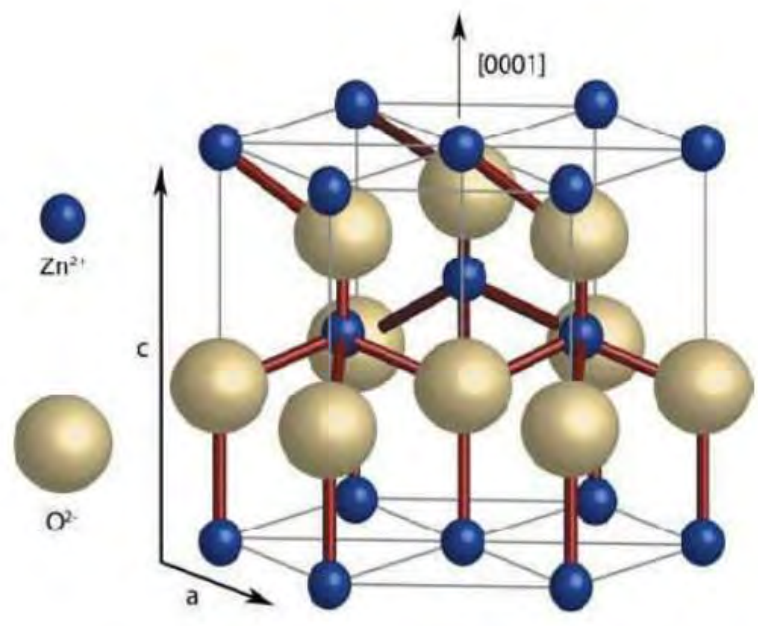

Figure 2.1:Hexagonal wurtzite structure of ZnO (Umar *et al*. 2009).

The arrangement of ions and atoms of a material is known as crystal structure. The lattice structure in a solid is defines as the arrangement of the atoms or ions in a specified manner. Zhong (2009), stated that, for the same materials, reducing the size to nanoscale could change their crystal structure but in practice most materials retain their crystal structures as that of bulk, down to a few nanometers. Because of the large surface-to-volume ratio, the surface area of the material plays an important role to explore unique properties. Wurtzite crystal structure is the mainly form of structure of ZnO. The lattice constants of ZnO for the wurtzite structure are *a* and *c* and under the class of dihexagonal-pyramidal crystal where the ratio for $c/a = \frac{\sqrt{8}}{3}$ and this ratio indicates the ideal wurtizite structure. This class of crystal is belongs to hexagonal crystal system. ZnO has a space group of C_{6v}^{4}-$P6_{3}mc$. Every single atom is fourfold coordinated, which means there are four atoms were surrounded. The bond length of these atoms is defined as:

$$u = \frac{1}{3}\frac{a^2}{c^2} + \frac{1}{4} \tag{2.1}$$

where *u* is bond length, *a* and *c* are lattice constant. From the Equation (2.1), there is a strong relationship between *c/a* ratio and *u* parameter, that is, when the *c/a* ratio is increases, the *u* parameter is decreases.

2.1.2 Optical Properties of Zinc Oxide

Intrinsic and extrinsic effect is the main sources of the optical properties of a material. Optical properties which affected by intrinsic effect occur between the electron in the conduction band and holes in the valence band. Exciton can be categories into two, bound and free exciton. The optical absorption and reflectance are affects by the dopants/impurities that can produce electronic states between the band gaps. There are several optical properties such as optical transmission, absorption, reflection, and etcetera.

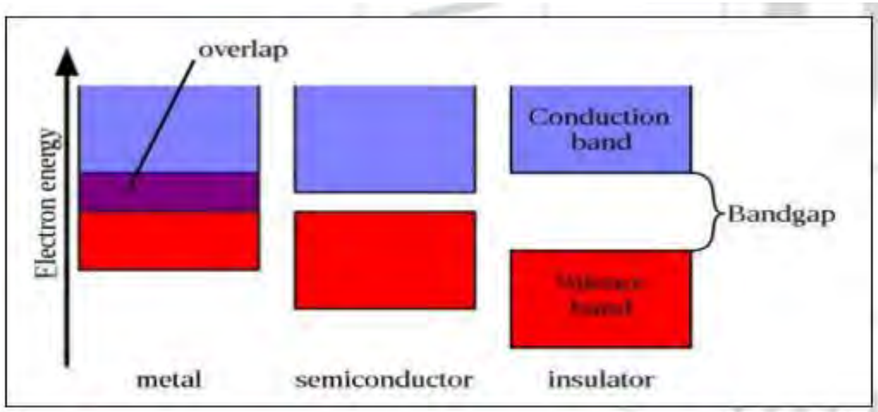

Figure 2.2: Energy band gap of insulator, semiconductor, and overlap in metal (Bilya & Sani 2016) .

Figure 2.2 shows the energy band gap among metal, semiconductor, and insulator. Conduction band and valence band in metal, semiconductor, and insulator are overlap, separate in small band gap, and separate in big band gap respectively. Zinc oxide exhibits both UV emission band and broad emission band at room temperature. The free exciton (FE) emission determined the UV emission. The broad emission band referred to the 420 and 700nm range of wavelength. Figure 2.3 shows the optical transmittance of zinc oxide between range of 300 to 1100 nm. Zinc oxide is highly transmitted to visible light with an average of transmittance of 95 %. The absorption coefficient is calculated from the transmittance with the Equation (2.2).

$$\alpha = -\frac{1}{t}\ln(T) \tag{2.2}$$

where T is the transmittance and *t* is the thickness of sample. The absorbance coefficient is used to determine the band energy of zinc oxide. Thus, the band energy (E_g) is calculated by Equation (2.3) for the direct transition of valence band and conduction band, where K is a constant.

$$\alpha\, hv = K(hv - E_g)^{1/2} \tag{2.3}$$