OPTICAL AND STRUCTURAL PROPERTIES OF ZINC OXIDE NANOPARTICLES SYNTHESIZED BY DIFFERENT SOL-GEL ROUTES

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To my beloved mother and father
To my dear wife and son Osamah

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ABSTRACT

Transformation into nanoscale from bulk structures involves an outstanding modification in the properties of materials. It gives an opportunity to get a novel behaviour such as size dependent in structural and optical properties. Zinc oxide nanoparticle is a promising material for many applications especially optical devices. There are many methods to synthesis these nanoparticles. In this work ZnO nanoparticles are synthesized by sol-gel method using different routes with different stirring temperatures. The structural, morphological and optical properties of ZnO nanoparticles are studied. The result of the XRD shows that the average particle size of ZnO particles decreases with increasing stirring temperature. By using Williamson-Hall formula to calculate the average size of ZnO nanoparticles it reveals that the Zinc Acetate precursor gives smaller nanoparticles than Zinc Nitrate (at 70 ^{o} C ~22 and ~50 nm respectively). FESEM images display the semi-spherical shaped of the synthesized nanoparticles and emphasise that the nanoparticles synthesized by Zinc Acetate are finer and more homogenous than those synthesized with Zinc Nitrate. Furthermore, the photoluminescence result shows that the band energy of the zinc oxide nanoparticles synthesized by Zinc Nitrate is 3.02 eV while for those synthesized with Zinc Acetate is 3.10 eV. The excellent features of the result suggest that this work may constitute a basis for the tuneable synthesis of ZnO nanoparticles suitable for optoelectronics devices.

ABSTRAK

Transformasi kepada skala nano dari struktur berskala besar melibatkan pengubahsuaian luar biasa (ketara) di dalam sifat-sifat suatu bahan. Ia memberi peluang untuk memperolehi kelakuan novel seperti kebergantungan saiz di dalam sifat struktur dan optik. Nanopartikel zink oksida merupakan bahan yang baik untuk pelbagai aplikasi terutama peranti optik. Terdapat pelbagai kaedah boleh digunakan dalam proses sintesis nanopartikel. Di dalam kajian ini, nanopartikel zink oksida telah disintesis melalui kaedah sol-gel dengan menggunakan bahan kimia) berbeza dengan suhu kacau yang berbeza. Sifat struktur, morfologi dan optik terhadap nanopartikel zink oksida dikaji. Hasil pencirian XRD menunjukkan bahawa saiz purata partikel ZnO berkurangan apabila suhu kacau ditambah. Dengan menggunakan formula Williamson-Hall bagi kiraan saiz purata nanopartikel ZnO, hasil menunjukkan bahawa pelopor zink acetat memberikan saiz nanopartikel lebih kecil berbanding pelopor zink nitrat (pada suhu 70º iaitu 22 dan 50 nm). Imej FESEM menunjukkan bahawa nanopartikel ZnO yang terbentuk adalah semi-sfera serta menunjukkan permukaan nanopartikel yang disintesis menerusi zink acetat lebih halus dan sekata berbanding zink nitrat. Tambahan lagi, hasil pencirian kefotopendarcahayaan (fotoluminasi) menunjukkan bahawa jurang jalur tenaga bagi sampel nanopartikel ZnO bagi zink nitrat adalah 3.02 eV manakala bagi zink acetat adalah 3.10 eV. Hasil terbaik pencirian yang diperolehi dicadangkan bahawa kajian ini mampu memberikan asas kepada sintesis nanopartikel ZnO sesuai bagi aplikasi peranti optoelektronik.

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LIST OF ABBREVIATION

1D	-	One Dimensional
2D	-	Two Dimensional
3D	-	Three Dimensional
Å	-	Angstrom (=10^{-10} m)
arb. u.	-	Arbitrary Unit
C.B	-	Conduction Band
DC	-	Direct Current
DOS	-	Density of State
EHR	-	Electron-Hole Recombination
eV	-	Electron Volt
FESEM	-	Field Emission Scanning Electron Microscopy
FWHM	-	Full Width Half Maximum
GaAs	-	Gallium Arsenide
Ge	-	Germanium
IR	-	Infra Red
JCPDS	-	Joint Committee on Powder Diffraction Standard
nm	-	Nanometer
NPs	-	Nanoparticles
LED	-	Light Emitting Diodes
O_i	-	Oxygen Interstitial
PL	-	Photoluminescence
QD	-	Quantum Dot
Rad.	-	Radian
Si	-	Silicon
S_o	-	Singlet State
T	-	Temperature

T_1 - Triplet State

UV - Ultra-Violet

V.B - Valence Band

V_o - Oxygen Vacancy

XRD - X-Ray Diffraction

W-H - Williamson-Hall

Zn_i - Zinc Interstitial

ZnO - Zinc Oxide

LIST OF SYMBOLS

A/V - Surface to Volume Ratio

d - Size of Particles

E - Energy

E_g - Band Gap Energy

ξ - Electric Field

k - Shape Factor

β - Full Width Half Maximum

λ - Wavelength

θ - Angle of Diffraction

ε - Strain of Particles

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Recently design, characterization, production, and application of materials, which involves the manipulation of matter at the smallest scale (from 1 to 100 nm), have been widely used as current meaning of nanotechnology rather than just materials. Three distinct aspects can be considered for evolution of nanotechnology: indirect, direct, and conceptual. The advanced miniaturization of obtainable technologies, which open new areas of application for those technologies, can be explained by indirect aspect. Direct refers to the application of novel nanoscale artifacts to improve the performance of presented process and materials or for completely novel purposes. Finally, there is a conceptual aspect of nanotechnology, in which all materials and process considered from molecular or even atomic viewpoint especially in living system and biology. Now a few areas of technology are exempt from the advantages of nanotechnology. The information and communication systems such as novel semiconductor and optoelectronic device, environment (filtration), energy (reduction of energy, consumption increasing, the efficiency of energy production nuclear accident cleanup and waste storage), heavy industry (aerospace and catalysis), and consumer goods are some applications of nanotechnology (Capper *et al.*, 2011; Jagadish *et al.*, 2011).

Zinc oxide (ZnO) is a chemical compound which commonly grows in a white powder form that is insoluble in water. This powder is mostly used as an additive into numerous materials and products such as ceramics, plastics, glass etc. Although ZnO exists as a mineral zincite in the Earth crust, most of the commercially usage is produced synthetically. Zinc and oxygen belong to the second and sixth groups in the periodic table respectively (Morkoç *et al.*, 2008).

ZnO nanoparticles have been used extensively as the preferable semiconductor because of their potential applications, as piezoelectric transducers, optical waveguides, acousto-optic media, surface acoustic wave devices, conductive gas sensors, transparent conductive electrodes, solar cell windows, and varistors for about two decade (Kim *et al.*, 2005; Look *et al.*, 2004; Schwenzer *et al.*, 2006; Shaoqiang *et al.*, 2005). ZnO is a II–VI semiconductor which has wide-band gap of ~3.37 eV and large exciton binding energy of 60meV (Yamamoto *et al.*, 2001) therefore, it is now known as a promising candidate for blue and ultraviolet light-emitting diodes (Goyal and Kachhwaha, 2012), laser diodes, and LEDs for general illuminations such as traffic signals, backlight for liquid-crystal display (LCD), mobile phone, and automotive lighting. The large exciton binding energy allows excitonic absorption and recombination even at room temperature, which makes this material interesting for optoelectronic devices (Schwenzer *et al.*, 2006; Yamamoto *et al.*, 2001).

1.2 Problem Statement

Controlled synthesis and fabrication of semiconductor nanostructure by simplicities and cost effectiveness method is challenging for electronic, optoelectronic and sensor application. Research shows that, through metal oxide semiconductor nanoparticles, the ZnO semiconductor is a preferred engineering material for its advantages including its wide bandgap (3.37 eV). ZnO presents itself as one of the potential and important material for the fabrication of light emitting diodes, laser diodes, optical switches and so on (Jagadish *et al.*, 2011; Takahashi *et* *al.*, 2007; Zhang *et al.*, 2012). Moreover, the high exciton binding energy (60 meV) makes it as an appropriate choice for the room temperature ultraviolet laser diodes (Lim *et al.*, 2006).

Remarkably, a variety of techniques has been used to control the size of ZnO particles in the nanometer range. Experimental observation requires further verification and surface modification require further studies. The results generated from sol-gel method need to be compared with other techniques. However it can be observed from the previous studies that to attain ZnO nanostructure usually catalyst or additives with a high temperature and/or low pressure is required (Umar *et al.*, 2008).

Consequently, there is a need to improve an effective and simple method to synthesis these types of nanoparticles in a large quantity with a high quality at low-temperature without using catalyst or additives. The easy and economic nature of our method is suitable for the fabrication of varieties of other nanostructures to understand the fundamental physics of nanoscale structure under different synthesis condition is also important.

1.3 Research Objectives

The aims of this research will focus on the following points:

- To determine the structural properties of ZnO nanoparticles synthesized by two different sol-gel routes with different stirring temperatures using X-Ray diffraction (XRD).

- To investigate the surface morphology of the nanoparticles by Field Emission Scanning Electron Microscopy (FESEM).

- To characterize the optical behaviour using photoluminescence spectroscopy.

1.4 Scope and Significance of Study

Sol-gel method with two different routes is employed to synthesis ZnO nanoparticles. X-ray diffraction and Field emission scanning electron microscopy (FESEM) are used to characterize the structural properties and surface morphology of the samples. The effect of synthesis parameters on optical behaviour are studied by photoluminescence (PL) spectroscopy.

Nanostructuring of semiconductors is a novel means of developing new electronic and optoelectronic devices. In particular, the discovery of room-temperature visible photoluminescence (PL) from ZnO nanostructures has stimulated much interest in these particular kinds of nanostructures and in small semiconductor particles. Easy and economic fabrication technique would be developed. The instrumentation for large-scale fabrication has social economic impact. The fundamental physics behind the synthesis would be understood.

ZnO nanoparticles can be exploited extensively for the use in optoelectronic devices such as high bright full color light emitting diodes (LED), high quality flat panel displays, high efficiency blue laser and low threshold optical pumped laser applications at room temperature (Wang *et al.*, 2003).

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