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.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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).

REFFERENCES

Absalan, E. (2010). Comparative study of ZnO thin films prepared by different sol-gel route. *ACTA Physica Polonica A, 118*.

AlSalhi, S., Atif, M., Ansari, A., Khun, K., Ibupoto, H., and Willander, M. (2013). Growth and characterization of ZnO nanowires for optical applications. *Laser Physics, 23*(6).

Aneesh, P., Vanaja, K., and Jayaraj, M. (2007). Synthesis of ZnO nanoparticles by hydrothermal method. Paper presented at the NanoScience+ Engineering.

Capper, P., Kasap, S., Willoughby, A., Litton, W., Collins, C., and Reynolds, C. (2011). *Zinc oxide materials for electronic and optoelectronic device applications*: John Wiley & Sons.

Cole, D. (1951). On a quasi-linear parabolic equation occurring in aerodynamics. *Quarterly of applied mathematics, 9*(3), 225-236.

Das, P. (2010). Mesoscopic systems in the quantum realm: fundamental science and applications. *Advances in Natural Sciences: Nanoscience and Nanotechnology, 1*(4), 043001.

De Angelis, F., and Armelao, L. (2011). Optical properties of ZnO nanostructures: a hybrid DFT/TDDFT investigation. *Physical Chemistry Chemical Physics, 13*(2), 467-475.

Dhanaraj, G., Byrappa, K., Prasad, V., and Dudley, M. (2010). *Springer handbook of crystal growth*: Springer.

Duo-Fa, W., Lei, L., Jin-Chai, L., Qiang, F., Ming-Zeng, P., and Jun-Ming, Z. (2005). Synthesis and optical properties of ZnO nanostructures. *Chinese Physics Letters, 22*(8), 2084.

Efros, L., and Rosen, M. (1998). Quantum size level structure of narrow-gap semiconductor nanocrystals: Effect of band coupling. *Physical Review B, 58*(11), 7120.

Ehrenreich, H., and Spaepen, F. (2001). *Solid state physics*: Academic Press.

Fan, Z., and Lu, G. (2005). Zinc oxide nanostructures: synthesis and properties. *Journal of nanoscience and nanotechnology, 5*(10), 1561-1573.

Gaponenko, V. (1998). *Optical properties of semiconductor nanocrystals*. (Vol. 23): Cambridge university press.

Geetha, D., and Thilagavathi, T. (2010). Hydrothermal synthesis of nano ZnO structures from CTAB. *Digest Journal of Nanomaterials & Biostructures, 5*(2).

Gfroerer, H. (2000). Photoluminescence in analysis of surfaces and interfaces. *Encyclopedia of Analytical Chemistry*.

Ghosh, P. (2012). *Synthesis and characterization of zinc oxide nanoparticles by sol-gel process.*

Gupta, M. C., and Ballato, J. (2012). *The handbook of photonics*: CRC press.

Heisenberg, W. (1927). Über den anschaulichen Inhalt der quantentheoretischen Kinematik und Mechanik. *Zeitschrift für Physik, 43*(3-4), 172-198.

Hoshino, Y. (2002). *Synthesis and Optical Property of PbS quantum dot materials by the sol-gel method*: University of California, Los Angeles.

Jagadish, C., and Pearton, J. (2011). *Zinc oxide bulk, thin films and nanostructures: processing, properties, and applications*: Elsevier.

Janotti, A., and Van de Walle, G. (2009). Fundamentals of zinc oxide as a semiconductor. *Reports on Progress in Physics, 72*(12), 126501.

Kamat, V., Dimitrijevic, M., and Nozik, A. (1989). Dynamic Burstein-Moss shift in semiconductor colloids. *The Journal of Physical Chemistry, 93*(8), 2873-2875.

Kim, S., Tai, P., and Shu, J. (2005). Effect of preheating temperature on structural and optical properties of ZnO thin films by sol–gel process. *Thin Solid Films, 491*(1), 153-160.

Klingshirn, F., Klingshirn, C., and Klingshirn, C. (2007). *Semiconductor optics* (Vol. 3): Springer.

Kubo, R. (1962). Electronic properties of metallic fine particles. *Journal of the Physical Society of Japan, 17*(6), 975-986.

Li, G., Sundararajan, A., Mouti, A., Chang, J., Lupini, R., Pennycook, J., and Guiton, S. (2013). Synthesis and characterization of p-n homojunction-containing zinc oxide nanowires. *Nanoscale, 5*(6), 2259-2263.

Lim, H., Kang, K., Kim, K., Park, K., Hwang, K., and Park, J. (2006). UV electroluminescence emission from ZnO light-emitting diodes grown by high-temperature radiofrequency sputtering. *Advanced Materials, 18*(20), 2720-2724.

Lin, B., Fu, Z., Jia, Y., and Liao, G. (2001). Defect photoluminescence of undoping ZnO films and its dependence on annealing conditions. *Journal of the Electrochemical Society, 148*(3), G110-G113.

Look, C., and Claflin, B. (2004). P-type doping and devices based on ZnO. *physica status solidi (b), 241*(3), 624-630.

Meyer, B., Alves, H., Hofmann, D., Kriegseis, W., Forster, D., Bertram, F., and Dworzak, M. (2004). Bound exciton and donor–acceptor pair recombinations in ZnO. *physica status solidi (b), 241*(2), 231-260.

Micheroni, C. (2013). *Fabrication and characterization of defect-free UV-emitting ZnO nanoparticles.* Villavova University.

Morkoç, H., and Özgür, Ü. (2008). *Zinc oxide: fundamentals, materials and device technology*: John Wiley & Sons.

Mote, V., Purushotham, Y., and Dole, B. (2012). Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles. *Journal of Theoretical and Applied Physics, 6*(1), 1-8.

Nair, V., Ramaniah, M., and Rustagi, C. (1992). Electron states in a quantum dot in an effective-bond-orbital model. *Physical Review B, 45*(11), 5969.

Pecharsky, V., and Zavalij, P. (2008). *Fundamentals of powder diffraction and structural characterization of materials*: Springer.

Ramaniah, L. M., and Nair, S. V. (1993). Optical absorption in semiconductor quantum dots: A tight-binding approach. *Physical Review B, 47*(12), 7132.

Ren, T., Baker, H. R., and Poduska, K. M. (2007). Optical absorption edge shifts in electrodeposited ZnO thin films. *Thin Solid Films, 515*(20), 7976-7983.

Sattler, K. D. (2010). *Handbook of nanophysics: clusters and fullerenes*: CRC press.

Schmidt-Mende, L., and MacManus-Driscoll, J. L. (2007). ZnO – nanostructures, defects, and devices. *Materials today, 10*(5), 40-48.

Schmidt Mende, L., and L, M. D. a. J. (2007). ZnO–nanostructures, defects and devices. *Materials today, 10*(5), 40-48.

Schwenzer, B., Gomm, R., and Morse, E. (2006). Substrate-induced growth of nanostructured zinc oxide films at room temperature using concepts of biomimetic catalysis. *Langmuir, 22*(24), 9829-9831.

Shaoqiang, C., Jian, Z., Xiao, F., Xiaohua, W., Yanling, S., Qingsong, X., and Ziqiang, Z. (2005). Nanocrystalline ZnO thin films on porous silicon/silicon substrates obtained by sol–gel technique. *Applied Surface Science, 241*(3), 384-391.

Sharma, R., Bisen, D., Shukla, U., and Sharma, B. (2012). X-ray diffraction: a powerful method of characterizing nanomaterials. *Recent Research in Science & Technology, 4*(8).

Sivakumar, S. (2006). *Lanthanide-doped nanoparticles in sol-gel matrices: improved optical properties and new opportunities.*

Sokol, A., French, A., Bromley, T., Catlow, A., van Dam, J., and Sherwood, P. (2007). Point defects in ZnO. *Faraday discussions, 134*, 267-282.

Stampfl, C., Van de Walle, C. G., Vogel, D., Krüger, P., and Pollmann, J. (2000). Native defects and impurities in InN: First-principles studies using the local-density approximation and self-interaction and relaxation-corrected pseudopotentials. *Physical Review B, 61*(12), R7846-R7849.

Takahashi, K., Yoshikawa, A., and Sandhu, A. (2007). *Wide bandgap semiconductors: fundamental properties and modern photonic and electronic devices*: Springer.

Terasako, T., Yagi, M., Ishizaki, M., Senda, Y., Matsuura, H., and Shirakata, S. (2007). Growth of zinc oxide films and nanowires by atmospheric-pressure chemical vapor deposition using zinc powder and water as source materials. *Surface and Coatings Technology, 201*(22), 8924-8930.

Uche, V. (2013). Sol-gel technique: A veritable tool for crystal growth. *Advances in applied Sci Res, 4*(1), 506-510.

Umar, A., Hajry, A., Al-Heniti, S., and Hahn, Y.B. (2008). Hierarchical ZnO nanostructures: growth and optical properties. *Journal of nanoscience and nanotechnology, 8*(12), 6355-6360.

Wang, D. (2010). *Preparation and characterisation of transparent conducting oxides and thin films.* Dongxin Wang.

Wang, Q., Zhang, D. h., Xue, Z. y., CHEN, S. h., and MA, H. l. (2003). Luminescence properties of ZnO films prepared by RF magnetron sputtering. *Chinese Journal of Luminescence, 24*, 69-72.

Wooten, F. (1972). *Optical properties of solids* (Vol. 111): Academic press New York.

Yamamoto, T., and Katayama-Yoshida, H. (2001). Physics and control of valence states in ZnO by codoping method. *Physica B: Condensed Matter, 302*, 155-162.

Yao, B., Chan, Y., and Wang, N. (2002). Formation of ZnO nanostructures by a simple way of thermal evaporation. *Applied Physics Letters, 81*(4), 757-759.

Zhang, C., Xiaoyuan Zhou, and Guozhong Cao. (2009). ZnO nanostructures for dye-sensitized solar cells. *21*, 22.

Zhang, J., Gao, D., Yang, G., Zhu, Z., Zhang, J., and Shi, Z. (2012). Study on synthesis and optical properties of ZnO hierarchical nanostructures by hydrothermal method. *International Journal of Material and Mechanical Engineering*, *1*(2).