UNIVERSITI PUTRA MALAYSIA

PREPARATION AND PHYSICOCHEMICAL PROPERTIES OF ZINC OXIDE NANOPARTICLES

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ITMA 2011 20

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By

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

April 2011

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

PREPARATION AND PHYSICOCHEMICAL PROPERTIES OF ZINC OXIDE NANOPARTICLES.

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April 2011

Chairperson : Professor Mohd Zobir bin Hussein, PhD

Institute : Institute of Advanced Technology

Zinc oxide nanoparticles are important inorganic particles which receive great interest over the past few years because of the wide nanotechnology application in various fields of material physics and chemistry. The physicochemical properties of resulting ZnO nanoparticles can be controlled by the synthesis route, method of preparation and parameters related to condition processing. In this study, ZnO nanoparticles were successfully synthesized by three different methods namely polyol method, solvothermal method and co-precipitation method. X-ray diffraction (XRD) patterns show that the all resulting ZnO nanoparticles materials which were synthesized by all the three different methods are pure phase with good crystalinity and completely matched the hexagonal-wurzite structure. The presence of a broad and sharp absorption band at around 440 cm^{-1} in the FTIR spectrum further confirmed the existence of ZnO phase.

In polyol method, ZnO nanoparticles were successfully synthesized under hydrothermal condition. Zinc acetate (ZnAc) was dissolved and heated in three different glycol solutions, namely ethylene glycol (EG), diethylene glycol (DEG) and trietyleneglycol (TEG). The effect of different glycol solutions and calcination on the formation of ZnO nanoparticles was investigated. Single-modal narrow particle size distribution of ZnO nanoparticles with average particles size of 2 ± 1 nm, 12 ± 1nm and 13 ± 1 nm were obtained when EG, DEG and TEG were used in the synthesis, respectively. The broadness of the size distribution of the ZnO nanoparticles can be given as EG > DEG >TEG. The specific surface areas of all the resulting materials however show very similar values ranging from 12.2 to 13.5 m^2g^{-1}.

The low-temperature solvothermal process was employed as the second method to synthesize ZnO nanoparticles. The initial concentration of zinc acetate was controlled and this process is based on the decomposition of zinc acetate and sodium hydroxide (NaOH) in a mixture solution of ethanol and EG. The effect of different zinc acetate concentration and the effect of organic solvent mixtures solution between ethanol and EG can be shown by a single modal narrow particle size distribution with the average size below 25 ± 1 nm. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) analysis revealed that less macroscopic agglomeration of ZnO nanoparticles, indicating that the effect of low temperature process in the mixtures solution also contributed to the higher specific surface area of about 40 m^2g^{-1}. Further effect of high calcinations temperature on the physicochemical properties of the resulting ZnO nanoparticles shows more crystalline and pure phase.

However, the increasing particles size resulted in the decreasing of specific surface area due to the compact agglomeration of ZnO particles.

Lastly, an intermediate zinc oxalate phase was synthesized by oxalate coprecipitation from nearly saturated solution of zinc acetate and 2-propanol of oxalic acid solution. Highly crystallized and pure phase ZnO nanoparticles were successfully synthesized by thermal treatment at 400 to 600 ^{o}C for 4 hours. Single-modal narrow particle size distribution of ZnO nanoparticles with the average particles size of 3± 1 nm , 28 ± 1 nm and 25 ± 1 nm are obtained at 400, 500 and 600 ^{o}C, respectively. FESEM and TEM also revealed the different surface structure and morphology of ZnO nanoparticles obtained at calcination temperatures. A huge reduction of specific surface area of ZnO nanoparticles from 22.9 m^2g^{-1} to 2.6 m^2g^{-1} was observed when the calcination temperature is increased from 400 to 600 ^{o}C.

This study verified, a good crystallinity, high purity, small particle size and large specific surface area of ZnO nanoparticles can be obtained using all the methods. The effect of preparation parameters in each method gives the most influence to physichochemical properties of the resulting material.

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

PENYEDIAN DAN SIFAT KIMIA-FIZIKAL PARTIKEL NANO ZINK OKSIDA

Oleh

KHAIRUL BASYAR BIN BAHARUDIN

April 2011

Pengerusi : Profesor Mohd Zobir Bin Hussein, PhD

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Partikel nano Zink oksida adalah partikel tak organik penting yang menerima perhatian tinggi dalam tahun kebelakangan ini kerana mempunyai aplikasi nanoteknologi yang meluas dalam pelbagai bidang fizik bahan dan kimia. Sifat kimia-fizikal partikel nano ZnO yang dihasilkan dapat dikawal melalui laluan sintesis, kaedah persiapan dan parameter yang sesuai dengan keadaan proses. Dalam kajian ini, partikel nano ZnO telah berjaya disintesis dengan tiga kaedah yang berbeza iaitu kaedah poliol, kaedah solvoterma dan kaedah ko-pemendapan. Corak pembelauan sinar-X menunjukkan bahawa semua bahan partikel nano ZnO yang disintesis melalui ketiga-tiga kaedah yang berbeza menghasilkan hablur yang baik dengan fasa tulen yang bersesuaian dengan struktur heksagon-wurzite. Kehadiran satu jalur penyerapan yang luas dan tajam sekitar 440 cm^{-1} pada spectrum FTIR membuktikan lebih lanjut kewujudan fasa ZnO.

Dalam kaedah poliol, partikel nano ZnO telah berjaya disintesis dalam keadaan hidroterma. Zink asetat (ZnAc) dilarutkan dan dipanaskan dalam tiga larutan glikol yang berbeza, iaitu etilina glikol (EG), dietilina glikol (DEG) dan trietilina glikol (TEG). Kesan terhadap larutan glikol berbeza dan pemanasan pada pembentukan partikel nano ZnO telah dikaji. Taburan sempit modal tunggal partikel nano ZnO dengan saiz purata partikel adalah 2, 12 dan 13 nm masing-masing diperolehi semasa EG, DEG dan TEG digunakan semasa sintesis. Keluasan saiz taburan partikel nano ZnO boleh ditunjukan dengan urutan EG> DEG> TEG. Luas permukaan khusus semua bahan yang dihasilkan walaubagaimanapun menunjukkan nilai yang hampir iaitu disekitar 12.2 sehingga 13.5 m^2g^{-1}.

Proses solvoterma suhu rendah digunakan sebagai kaedah kedua untuk sintesis partikel nano ZnO. Kepekatan awal ZnAc dikawal dan proses ini berdasarkan pada penguraian ZnAc dan natrium hidroksida (NaOH) di dalam campuran larutan etanol dan EG. Kesan kepekatan ZnAc yang berbeza dan kesan larutan campuran pelarut organik diantara etanol dan EG boleh ditunjukkan oleh taburan sempit modal tunggal saiz partikel dengan ukuran purata di bawah 25 nm. Mikroskopi pengimbasan elektron pancaran medan (FESEM) dan Mikroskop penghantaran elektron (TEM) analisa mendedahkan bahawa agelomerasi makroskopik partikel nano ZnO yang kurang, menandakan bahawa kesan suhu yang rendah dalam campuran larutan juga menyumbangkan terhadap luas permukaan khusus lebih tinggi iaitu sekitar 40 m^2g^{-1}. Kesan lanjutan terhadap suhu kalsinasi tinggi pada sifat kimia-fizikal partikel nano ZnO yang dihasilkan menunjukkan penghasilan fasa hablur dan ketulenan bahan akhir yang lebih tinggi. Namun demikian,

peningkatan saiz partikel mengakibatkan penurunan luas permukaan khusus kerana kepadatan agelomerasi partikel ZnO.

Kaedah terakhir, fasa pertengahan zinc oksalat disintesis melalui kopemendapan oksalat dari larutan hampir tepu ZnAc dengan larutan asid oksalat yang disediakan daripada pelarut 2-propanol. Penghabluran yang tinggi dan fasa ZnO yang tulen telah berjaya disintesis dengan pemanasan selama 4 jam pada suhu 400 sehingga 600 ^{o}C.Taburan saiz modal tunggal sempit partikel nano ZnO dengan saiz purata partikel adalah 3, 28 dan 25 nm diperolehi masing-masing pada 400, 500 dan 600 ^{o}C. FESEM dan TEM juga mendedahkan struktur permukaan dan morfologi partikel nano ZnO yang berbeza diperolehi dalam suhu kalsinasi yang lebih tinggi. Penurunan besar luas permukaan khusus partikel nano ZnO dari 22.9 m^2g^{-1} kepada 2.6 m^2g^{-1} diperhatikan ketika suhu kalsinasi meningkat dari 400 kepada 600 ^{o}C.

Kajian mengesahkan semua kaedah penyediaan menghasilkan partikel nano ZnO yang baik penghabluran, tinggi ketulenan , saiz partikel kecil dan luas permukaan khusus yang besar. Kesan parameter penyediaan melalui kaedah masing-masing memberikan pengaruh besar terhadap sifat akhir kimia-fizikal bahan yang dihasilkan

ACKNOWLEDGEMENT

Alhamdulillah, praise to ALLAH the Almighty for blessing the completion of this study and to all individuals who contribute to this project.

First of all, I would like to express my sincere gratitude to my project supervisor, Professor Dr. Mohd Zobir bin Hussein for his valuable advice, excellent guidance, ideas, kindness and great encouragement throughout this project.

My special appreciation and thanks to the staff of Chemistry Department, Faculty of Science, UPM, Institute of Advanced Technology UPM, Institute of Bioscience UPM and lastly Universiti Islam Antrabangsa Malaysia. My appreciation and thanks also goes to all post graduate students at ITMA and not forgotten the postgraduate students in Old Chemistry Laboratory 2 for the support and helpful in finishing my project.

To my beloved parents and family, thank you very much for giving me the encouragement and moral support throughout my study in UPM.

To all my friends and the rest whom have helped to complete my study, 'THANK YOU'

I certify that an Examination Committee has met on 19 April 2011 to conduct the final examination of Khairul Basyar Bin Baharudin on his Master of Science thesis entitled "**Preparation and Physicochemical Properties of Zinc Oxide Nanoparticle**" in accordance with University Pertanian Malaysia (Higher Degree) Act 1980 and University Pertanian Malaysia (Higher Degree) regulation 1981. The Committee recommends that the student be awarded the relevant degree.

Members of the examination Committee were as follows:

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DECLRATION

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

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KHAIRUL BASYAR BAHARUDIN

DATE: 19 April 2011

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