HYDROTHERMAL PROCESS ROUTE IN THE SYNTHESIS OF ZINC OXIDE POWDER

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HYDROTHERMAL PROCESS ROUTE IN THE SYNTHESIS OF ZINC OXIDE POWDER

by

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requirement for the degree of
Master of Science
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DECLARATION

I declare that the content which is presented in the dissertation is my own work which was done at Universiti Sains Malaysia unless informed otherwise. The dissertation has not been previously submitted for any other degree.

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TABLE OF CONTENTS

		Page
ACKNOWLEDGEMENTS		ii
TABLE OF CONTENTS		iii
LIST OF TABLES		vi
LIST OF FIGURES		vii
LIST OF SYMBOLS		xi
LIST OF ABBREVIATIONS		xi
LIST OF CHEMICAL FORMULAS		xii
LIST OF APPENDICES		xii
ABSTRAK		xiii
ABSTRACT		xiv
CHAPTER ONE : INTRODUCTION		
1.1	Research Background	1
1.2	Objectives of Research	3
1.3	Significant of Project	4
1.4	Scope of Project	5
CHAPTER 2 : LITERATURE REVIEW		
2.1	Zinc Oxide and Applications	6
2.2	Overview on Nanotechnology	7
2.3	Nanostructured Zinc Oxide, Properties and Applications	9
2.4	Wet-Chemical Techniques	10
	2.4.1 Sol-gel	11
	2.4.2 Chemical Vapour Deposition	12
	2.4.3 Sonochemical	14
	2.4.4 Aqueous solution route	15
	2.4.5 Hydrothermal	17
2.5	Filtration	21
2.6	Washing The Precipitates	24

2.7 Drying of Samples 25
2.8 Material Characterization Techniques
2.8.1 X-Ray Diffraction Analysis 28
2.8.2 Scanning Electron Microscope and Energy Dispersive X-ray Spectrometer 33
2.8.3 X-Ray Fluorescence Analysis 37
2.8.4 Thermal Analysis 39

CHAPTER 3 : METHODOLOGY

3.1 Experimental 46
3.2 Reagent and Chemicals 49
3.3 Apparatus 50
3.4 Solution Preparation
3.4.1 Zinc nitrate hexahydrate and urea solutions 50
3.4.2 Buffer solution 51
3.4.3 Sodium Hydroxide Solution for pH Adjustment 51
3.5 Hydrothermal Process Route 52
3.6 Filtration after the hydrothermal method 52
3.7 Washing the precipitates 53
3.8 Drying and Calcination 53
3.9 Characterization Techniques of Sample
3.9.1 Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometry 54
3.9.2 X-Ray Diffraction Analysis 54
3.9.3 Spectral Mapping 54
3.9.4 X-Ray Fluorescence 55
3.9.5 Thermal Analysis 55

CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Process Chemistry 56
4.2 Low Concentration Synthesis 57

4.2.1 Product Morphology and Elemental Analysis 58
4.2.2 Phase Identification 66
4.3 High Concentration Synthesis 70
4.3.1 Product Morphology and Elemental Analysis 70
4.3.2 Phase Identification 79
4.4 Spatial Distribution Determination 82
4.5 Chemical Composition Determination 84
4.6 Thermal Analysis 84
4.7 Physical Appearance and Colour of the Product 86

CHAPTER 5 : CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions 88
5.2 Recommendations for Future Work 90

REFERENCES 92

APPENDICES

Appendix A- Calculation on Solutions Preparation 98

LIST OF TABLES

		Page
2.1	Methods of synthesis and investigation of nanomaterials	8
3.1	Summary of the parameter studied at varying concentration, time and temperature with respective to the coding of the product	49
3.2	List of chemicals	49
3.3	List of apparatus	50
3.4	pH of acetic acid-sodium acetate buffer mixtures	51
4.1	Summary of morphology observed in the nano zinc oxide sample synthesized with the low concentration chemical precursors	66
4.2	Summary of crystallite size of nano zinc oxide synthesized at low concentration of chemical precursors	70
4.3	Summary of morphology observed in the nano zinc oxide sample synthesized with the low concentration chemical precursors	78
4.4	Summary of crystallite size of nano zinc oxide synthesized at high concentration of chemical precursors	82
4.5	XRF results of calcined zinc oxide product (NZO3) synthesized at high concentration synthesis under the temperature of 150°C with the reaction time of 3 hours	84
5.1	Summary of crystallite size and morphologies of nano zinc oxide	90

LIST OF FIGURES

		Page
1.1	Commercial zinc oxide powder with particle size below 5μm (AR grade)	3
2.1	Mechanisms of filtration	23
2.2	Phase diagram of water	26
2.3	Specific volume of water vapour as a function of the water vapour pressure. The temperature of the vapour in this diagram is that of ice	26
2.4	Freeze-drying system	27
2.5	X-ray diffraction	29
2.6	XRD patterns for nano-sized ZnO powders	32
2.7	XRD pattern of ZnO nanocrystal	32
2.8	Low and high resolution FESEM photomicrograph of triangular shaped, plate like agglomerated nanoparticles	35
2.9	FESEM photomicrograph of a) lamellar b) flake-like c) flake-like and hexagonal and d) hexagonal structure of zinc oxide	35
2.10	a) SEM photomicrograph b) EDX spectrum of ZnO nanocrystal	36
2.11	a) SEM photomicrograph b) EDX spectrum of nanosized ZnO powder	37
2.12	Evaluation of a typical curve with single-step loss of mass	41
2.13	Evaluation of a typical curve for two step loss of mass	42
2.14	Evaluation of a multistep loss of mass where the mass does not remain constant between the various steps	43
2.15	TGA–DTA curves of the precursors of ZnO	45
2.16	TGA curves of a) as-precipitated powders and b) as-milled powders	45
3.1	Research methodology adopted in the synthesis of ZnO powder via hydrothermal process route	48
3.2	Pressure reactor	52

4.1	SEM photomicrograph of calcined nano zinc oxide produced from low concentration synthesis at temperature of 130°C, 3 hours reaction time (NZO1) with magnification of a) 500x and b) 53.77kx	60
4.2	EDX spectrum of calcined nano zinc oxide produced from low concentration synthesis at temperature of 130°C, 3 hours reaction time (NZO1)	61
4.3	SEM photomicrograph of calcined nano zinc oxide produced from low concentration synthesis at temperature of 130°C, 5 hours reaction time (NZO2) with magnification of a) 500x b) 3kx and c) 11.17kx	61
4.4	EDX spectrum of calcined nano zinc oxide produced from low concentration synthesis at temperature of 130°C, 5 hours reaction time (NZO2)	63
4.5	SEM photomicrograph of calcined nano zinc oxide produced from low concentration synthesis at temperature of 150°C, 3 hours reaction time (NZO5) with the magnification of a) 500x and b) 100.00kx	63
4.6	EDX spectrum of calcined nano zinc oxide produced from low concentration synthesis at temperature of 150°C, 3 hours reaction time (NZO5)	64
4.7	SEM photomicrograph of calcined nano zinc oxide produced from low concentration synthesis at temperature of 150°C, 5 hours reaction time (NZO8) with magnification of a) 500x and b) 50.00kx	65
4.8	EDX spectrum of calcined nano zinc oxide produced from low concentration synthesis at temperature of 150°C, 5 hours reaction time (NZO8)	66
4.9	XRD diffractogram of calcined nano zinc oxide produced from low concentration synthesis at the temperature of 130°C a) NZO1 (reaction time-3 hours) and b) NZO2 (reaction time-5 hours)	68
4.10	XRD diffractogram of calcined nano zinc oxide produced from low concentration synthesis at the temperature of 150°C a) NZO5 (reaction time-3 hours) and b) NZO8 (reaction time-5 hours)	69
4.11	SEM photomicrograph of calcined nano zinc oxide produced from high concentration synthesis at temperature of 130°C, 3 hours reaction time (NZO4) with the magnification of a) 500x and b) 97.94kx	72

4.12	EDX spectrum of calcined nano zinc oxide produced from high concentration synthesis at temperature of 130°C, 3 hours reaction time (NZO4)	73
4.13	SEM photomicrograph of calcined nano zinc oxide produced from high concentration synthesis at temperature of 130°C, 5 hours reaction time (NZO6) with the magnification of a) 500x b) 10.00kx and c) 50.00kx	73
4.14	EDX spectrum of calcined nano zinc oxide produced from high concentration synthesis at temperature of 130°C, 5 hours reaction time (NZO6)	75
4.15	SEM photomicrograph of nano zinc oxide produced from high concentration synthesis at temperature of 150°C, 3 hours reaction time (NZO3) with the magnification of a) 500x and b) 5.00kx	75
4.16	EDX spectrum of calcined nano zinc oxide produced from high concentration synthesis at temperature of 150°C, 3 hours reaction time (NZO3)	76
4.17	SEM photomicrograph of calcined nano size zinc oxide produced from high concentration synthesis at temperature of 150°C, 5 hours reaction time (NZO7) with magnification of a) 500x and b) 20.00kx	77
4.18	EDX spectrum of calcined nano zinc oxide produced from high concentration synthesis at temperature of 150°C, 5 hours reaction time (NZO7)	78
4.19	XRD diffractogram of calcined nano zinc oxide produced from high concentration synthesis at the temperature of 130°C a) NZO4 (reaction time-3 hours) and b) NZO6 (reaction time-5 hours)	81
4.20	XRD diffractogram of calcined nano zinc oxide produced from high concentration synthesis at the temperature of 150°C a) NZO3 (reaction time-3 hours) and b) NZO7 (reaction time-5 hours)	81
4.21	Spectral mapping for nano zinc oxide powder produced from high concentration synthesis at temperature of 130°C with 3 hours reaction time (NZO4)	83
4.22	TGA/DTA curves of calcined nano zinc oxide powder (NZO1) produced from low concentration synthesis at temperature of 130°C with the reaction time of 3 hours	85

4.23	TGA/DTA curves of calcined nano zinc oxide powder (NZO4) produced from high concentration synthesis at temperature of 130°C with the reaction time of 3 hours	86
4.28	Nano zinc oxide powder	87

LIST OF SYMBOLS

°C	Celcius
Å	Angstron, 10^{-10}
nm	10^{-9}
µm	10^{-6}
ml	Mililiter
g	Gram
M	Molar

LIST OF ABBREVIATIONS

XRD	X-ray diffraction
XRF	X-ray fluorescence
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray Spectrometer
TGA	Thermogravimetric Analysis
DTA	Differential Thermal Analysis
TEM	Transmission Electron Microscope
CVD	Chemical vapour Deposition

LIST OF CHEMICAL FORMULAS

$Zn(NO_3)_2.6H_2O$	Zinc nitrate hexahydrate
$CO(NH_2)_2$	Urea
CH_3COONa	Sodium acetate
CH_3COOH	Acetic acid
NaOH	Sodium hydroxide
CH_3OH	Methanol
H_2O	Water
CO_2	Carbon dioxide
ZnO	Zinc oxide

LIST OF APPENDICES

Appendix A	Calculation on Solutions Preparation

PROSES HIDROTERMAL DALAM SINTESIS KIMIA SERBUK ZINK OKSIDA

ABSTRAK

Dalam projek penyelidikan ini, serbuk zink oksida disintesis dengan menggunakan kaedah hidroterma. Dalam prosedur penghasilan nano zink oksida, larutan penimbal asetat, larutan natrium hidroksida, larutan zink nitrat heksahidrat (0.1 M and 1.0 M) dan larutan urea (0.2 M and 2.0 M) dicampurkan dalam keadaan pengadukkan ke dalam reaktor tekanan. Nisbah kepekatan molar zink nitrat heksahidrat kepada urea ialah 1:2. Tempoh masa tindakbalas yang dikaji ialah 3 jam dan 5 jam pada suhu 130°C dan 150°C. Mendakan yang dibiarkan kering selepas turasan dan kemudian pengkalsinan dijalankan pada 400°C. Analisis SEM menunjukkan berlainan jenis morfologi serbuk yang dihasilkan pada tempoh dan suhu tindakbalas yang berlainan iaitu bentuk nano kepingan, rod dan rod heksagonal. Purata ketebalan struktur nano kepingan yang diperoleh berada dalam lingkungan 7.49nm hingga 63.21nm. Bagi partikel berbentuk rod, lebar dan panjang rod adalah 1.724μm dan 10.63μm. Keseluruhan keputusan EDX, tidak menunjukkan kehadiran puncak-puncak elemen yang lain. Daripada keputusan analisis XRD, saiz kristalit sampel-sampel yang diperoleh berada dalam lingkungan 197.4Å hingga 662.9Å. Peratusan zink oksida dalam sampel daripada analisis XRF adalah lebih kurang 98.8%. Keputusan analisis terma (TGA/DTA) menunjukkan kesemua sampel zink oksida adalah stabil kerana tiada perubahan jisim yang ketara. Serbuk zink oksida dengan taburan homogenus struktur nano kepingan boleh disintesiskan melalui proses hidroterma di bawah kepekatan rendah prapenanda kimia, suhu tindakbalas yang rendah dan masa tindakbalas yang lebih singkat dipilih.

HYDROTHERMAL PROCESS ROUTE IN THE SYNTHESIS OF ZINC OXIDE POWDER

ABSTRACT

In this work, zinc oxide powder is synthesized via the hydrothermal method. In the experimental procedure producing the ZnO powder, acetate buffer solution, sodium hydroxide, zinc nitrate hexahydrate solution (0.1 M and 1.0 M) and urea solution (0.2 M and 2.0M) are mixed under stirred condition in a pressure reactor. The molar concentration ratio of zinc nitrate hexahydrate to urea is 1:2. The reaction time studied was at 3 hours and 5 hours at temperatures of 130°C and 150°C. The precipitates were dried after filtration and then calcination at 400°C. SEM analysis showed different types of morphology observed in the powders produced at varying reaction time and temperature. They were nano flakes-like shape, rod shape and hexagonal rod shape. The average thickness of the nano flakes structure obtained range from 7.49nm to 63.21nm. As for the rod shape particles, the width and length of the rod is 1.724μm and 10.63μm respectively. Overall EDX results, did not show the presence of other elemental peaks. From XRD analysis, the crystallite size of the samples produced range from 197.4Å to 662.9Å. The percentage of zinc oxide present in the sample from the XRF analysis is around 98.8 %. Results from thermal analysis (TGA/DTA) showed that the zinc oxide powder produced are stable with no significant change in mass. Zinc oxide powder with homogeneous distribution of nano flakes-like structure can be synthesized via hydrothermal process under low concentration of chemical precursors and at low reaction temperature and shorter reaction time.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Zinc oxide with the chemical formula of ZnO which is shown in Figure 1.1 is a white to grey to yellowish powder with no odor but bitter taste (Schlager, et al., 2006). Other names of zinc oxide are chinese white, philosopher's wool, zinc white, flowers of zinc and etc. It occurs in nature as the mineral zincite. It is almost insoluble in water but soluble in dilute acids and bases. It has a melting point of around 1975°C with the specific gravity of ~5.6.

According Schlager, et al. (2006), zinc oxide can be produced by heating of either zinc metal or an ore containing zinc to obtain zinc vapour. This vapour is then reacted with oxygen to obtain zinc oxide. The chemical reaction formula is shown in equation 1.1. The other method takes place in an aqueous solution. In this process, zinc are leached out of ores and converted to zinc carbonate ($ZnCO_3 . 2Zn(OH)_2$). The zinc carbonate is decomposed by heating to produce pure zinc oxide shown in equation 1.2

$$2Zn + O_2 \longrightarrow 2\ ZnO \qquad (1.1)$$

$$ZnCO_3 . 2Zn(OH)_2 \longrightarrow 3ZnO + CO_2 + 2H_2O \qquad (1.2)$$

As for the nano zinc oxide, the particle size range is from 1-100 nm in at least one dimension. It can be obtained through synthesizing using either physical or

chemical method. According to most of the researchers, variety of morphological type of nano zinc oxide has been produced using different method namely the physical (Cao, 2004) and chemical methods (Schwarz, et al., 2004). Physical methods are like thermal oxidation (Yu and Pan, 2009), vapor phase transport and condensation deposition process (Wen, et al., 2003) and others. Chemical methods involved sol-gel method (Wahab, et al., 2007), aqueous precipitation (Xie, et al., 2008), hydrothermal route (Ismail et al., 2005) and many more. The microstructure produced are like nanosheets (Xiao, et al., 2007), hexagonal prismatic rod (Lu, et al., 2008), rosette-like nanostructures (Wahab, et al., 2009) and others.

In this research, zinc oxide is produced using wet chemical synthesis method that is via the hydrothermal route. The experiments can be conducted in high temperature and pressure in a sealed vessel preventing the solution to leak out that cause waste and this method is able to synthesis the powder with well-controlled chemical compositions, narrow size distribution, uniform particle morphology and the process can be conducted without any sophisticated instrumental setup (Lu, et al., 2008).

Based on the of Chen, et al, (2008) and Wu, et al., (2006) research work, the hydrothermal process is conducted under 160°C for 5 and 20 hours and 100°C for 6 hours respectively. The high reaction temperature and long hours of reaction time are conducted at their work. Therefore, in this research, the finding of mild condition of hydrothermal process is of concerned. The adding point of this research compared to others is that the buffer solution is added in to stabilize the acidic system because pH value can change the quantity of zinc oxide nuclei and of growth unit based on Rani

et al. (2008) research. Besides, the characteristics of zinc oxide powder depend on the pH of the starting solutions.

Figure 1.1 Commercial zinc oxide powder with particle size below 5μm (AR grade)

1.2 Objectives of Research

The aim of this research work is to carry out a study with the following objectives:

i. To adopt hydrothermal method in the chemical synthesis of zinc oxide powder at low and high concentration of zinc nitrate hexahydrate and urea with respect to reaction temperature and time to understand the chemical processes involved.

ii. To study how different reaction condition has an effect on the structural morphology of the zinc oxide powder produced.

iii. To select a suitable and economical method in the chemical synthesis of zinc oxide powder via hydrothermal process route to produce a powder with homogeneous particle or aggregates for a particular application.

1.3 Significant of Project

This research was conducted due to the increasing demand of nano zinc oxide. Zinc oxide powders are used in numerous fields of applications. Zinc oxide is used in many products like cosmetics, rubber, plastics, ceramic, automobile parts, electronic components and many more. This shows that nano zinc oxide possesses a broad spectrum of applications. From the project, various factors that govern the wet-chemical reaction can be studied in depth. Various parameters involved are concentration, temperature, and time of process. Moreover, the process chemistry can be comprehended.

In addition, the various types of zinc oxide particles morphologies can be adopted in different application. Therefore, the powder produced from the research with specific morphology can be used in particular application. As for examples, the synthesis of various shapes of ZnO, such as wires, flower-like structures and others are expected to have more potential applications in building functional electronic devices with special architectures and distinctive optoelectronic properties (Xie, et al., 2008). Rod like structures are suitable for application in solar cell, gas sensors, short wavelength light emitting and field effect devices (Dedova et al.). As for ribbon like structure it is used in sensor (Wang, 2004). Therefore, the hope to obtain the various morphologies of nano zinc oxide is of concerned.

Vast research work has been carried out in the synthesis of especially nano zinc oxide powder. The problem lies in controlling the shape and size of the powder according to a particular application. Therefore, in this research we are trying to produce zinc oxide powder in nanoscale using the hydrothermal approach that has a homogeneous distribution of particles shape and size as well as high purity.

1.4 Scope of Project

In this research, zinc oxide powder is produced using the hydrothermal approach where the reaction of the substances occurred under certain temperature and pressure using the pressure reactor. Acetate buffer solution (pH 3.48) is added in moderate rate into the zinc nitrate hexahydrate solution under stirred condition. Then, sodium hydroxide (2.0M) solution is added drop wise to adjust the pH of the mixture to pH5. After that, urea solution is poured into the beaker containing the mixtures. The mixed substances are later transferred into the pressure reactor. The temperatures are set at 130°C and 150°C for 3 hours and 5 hours. At the end of the reaction time, the mixtures are left to cool before filtration process. The next step of the experiment is washing. In this step, waterfree methanol is used to wash the precipitate to remove the impurities that present. The precipitated are left to dry in the oven at 105°C before sending for calcinations using the furnace at temperature of 400°C for 2 hours. The powders produced are sent for characterization using SEM, EDX, XRD, XRF, spectral mapping, and TGA/DTA.

CHAPTER 2

LITERATURE REVIEW

2.1 Zinc Oxide and Applications

Zinc oxide plays an important role in a wide range of applications in various fields. Zinc oxide is usually added in sunblock to protect a person from sunburn as it has the ability to absorb ultraviolet light in sunlight (Schlager, et al., 2006). The same property applies for other essential applications for zinc oxide, such as their use in rubber and plastic products. Possessing the ability to absorb ultraviolet light, zinc oxide protects the rubber or plastic from decomposing (Schlager, et al., 2006). The compound also has other uses in the rubber and plastic industries. Zinc oxide is added as fungicidal additive to rubber and plastic in preventing fungi from attacking (Schlager, et al., 2006) and destroying products made from those materials and also as accelerator activator and excellence anti-aging in rubber. Zinc oxide also has the ability to impart heat resistance properties in plastics.

Besides its major applications in the rubber and plastic industries, zinc oxide has a number of utilities in other field such as in coating in automotive components (Platts, 1990), cosmetic, paints and coatings, glass and ceramic materials (Schlager, et al., 2006), in the manufacture of specialized types of sealants and adhesives (Schlager, et al., 2006) and many more. In cosmetic products, zinc oxide is used in the production of lotions, sunscreens, diaper rash prevention creams and as UV absorber in cosmetic products

(www.ghchemicals.com/zinc_oxide_applications.htm). Besides, zinc oxide also act as a pigment and brightener, an additive which absorbs UV rays to extend colour retention and a good inhibitor of fungi in paints and coatings (www.ghchemicals.com/zinc_oxide_applications.htm). As in the glass and ceramic materials, zinc oxide play its role as an additive to provide greater heat resistance, resistance to breakage by shock (Schlager, et al., 2006) due to the low coefficient of thermal expansion, high luster and as an opacifier or whitener. Due to the wide band gap of 3.37eV and 60meV of binding energy (Lu, et al., 2008), zinc oxide is employed in optoelectronic devices, solar cells, piezoelectric sensors, varistor (Zhang, et al, 2002).

The different between zinc oxide and nano zinc oxide is in terms of particle size. Zinc oxide is considered nano size when the particle size falls between the range of 1-100nm in at least one dimension. Nanomaterials exhibit surface effect, small size effect, macroscopic quantum tunnel effect and etc. For an example, both zinc oxide and nano zinc oxide can be used in rubber product but using the nano zinc oxide could reduce the dosage required. In addition, by using nano zinc oxide the surface interaction between the rubber and nano zinc oxide will be improved due to the large surface area.

2.2 Overview on Nanotechnology

Nanotechnology is known as an innovative manufacturing technology of the twenty first century involving multidisciplinary research issues that rely on the

understanding and control of substances at the nanoscale length of around 1-100nm. Similarly, nanoparticles refer to ultrafine particles whose sizes are less than 100nm.

Nanotechnology has been recognized as an area which brings about new advancement in materials, devices and processes (Matsunaga and Okamura, 2002). The growth of nanoscience and technology is due to the availability of new approaches for the synthesis of nanomaterials and new tools of characterization and manipulation. Table 2.1 illustrates the methods of synthesis and investigation of nanomaterials.

Table 2.1 Methods of synthesis and investigation of nanomaterials (Roa, et al., 2004).

Scale (approx.)	Synthesis Method	Structural Tool	Theory and simulation
0.1 to ~ 10nm	Covalent synthesis	Vibrational spectroscopy NMR Diffraction methods	Electronic structure
<1 to 100nm	Techniques of self-assembly	Scanning probe microscopies	Molecular dynamics and mechanics
100nm to ~1μm	Processing modifications	SEM, TEM	Coarse-grained model and etc.

The popularity of nanomaterials have grown in the industries due to the high-priced that commercial companies have to pay for introducing new materials into the market. Nanotechnology enables these industries to obtain new properties using old and recognized materials by just reducing their particle size (Gedanken, 2004).

The knowledge of the existing technologies is the stepping stone towards the development of the nanoscience technology. The further research from the

foundation is the key in developing various methods in synthesizing nanomaterials. The objectives of the science and technology of nanomaterials are to fully master the synthesis of isolated nanostructures (building blocks) and their assemblies with the desired properties, to explore and establish nanodevice concepts and systems architectures, to generate new classes of high performance materials, to connect nanoscience to molecular electronics and biology and last but not least to improve known tools while discovering better tools of investigation of nanostructures (Roa, et al., 2004).

2.3 Nanostructured Zinc Oxide, Properties and Applications

Nano zinc oxide has drawn researchers' attention due to their notable performance in electronics, optics and photonics. Owing to their utilities as sensors, transducers and catalysts, the synthesis of zinc oxide films has started since the 1960's. A few decades back, ever since the nanotechnology idea led by the United State, study of one dimensional (1D) materials has become an important discovery in nanoscience and nanotechnology. The novel electrical, mechanical, chemical and optical properties are introduced with the reduction in size, which are largely believed to be the result of surface and quantum confinement effects. Nanowire-like structures are the promising system for studying the transport process in 1D confined objects, which are of advantage not only for understanding the fundamental phenomena in low dimensional systems, but also for developing new generation nanodevices with high performance (Wang, 2004). The lack of a centre of symmetry in wurtzite structure of zinc oxide, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties which make zinc oxide a

suitable material used in mechanical actuators and piezoelectric sensors (Wang, 2004).

Additionally, zinc oxide possesses a wide band-gap of 3.37eV compound semiconductors that make it suitable for short wavelength optoelectronic applications. The large exciton binding energy of 60meV in zinc oxide crystal enable efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence has been described in disordered nanoparticles and thin films (Wang, 2004). Zinc oxide has a various group of growth morphologies, such as nanocombs, nanorings, nanohelixes/nanosprings, nanobelts, nanowires, and nanocages. The nanostructures could have novel applications in optoelectronics, sensors, transducers and biomedical sciences (Wang, 2004). The application of ZnO nanobelts as nanosensors, nanocantilevers, field effect transistors and nanoresonators is explained by Wang (2004).

2.4 Wet-Chemical Techniques

There are various wet-chemical methods in synthesizing zinc oxide nanoparticles such as by sol-gel (Rani et al., 2008; Wahab, et al., 2007), ultra mist-chemical vapour deposition method (Singh, et al., 2008), aqueous solution route (Xie, et al., 2008; Chen, et al., 2008; Liu, et al., 2007), hydrothermal (Lu, et al., 2008; Wu, et al., 2006; Baruwati, et al., 2006; Dem'yanets, et al., 2006) approaches and others. All these approaches produce various types of morphologies and particle size of zinc oxide.

As for examples, a hexagonal shape of zinc oxide nanoparticles with the particle size of 14-16nm were obtained by Rani et al. (2008) using the sol-gel route. Besides, Chen et al., (2008) managed to produce zinc oxide nanorods using the hydrothermal synthesis and as for Wahab, et al. (2009) research work, they were able to synthesize zinc oxide in the form of rosette-like nanostructure. This shows that wet chemical analysis possesses the capability to produced nanoparticles and not just only the physical methods did. Chemical methods have the benefits over physical methods in several aspects like low cost, higher productivity level and ease of maintenance (Luan et al., 1998).

2.4.1 Sol-gel

The sol-gel process is a wet-chemical technique or also known as chemical solution deposition for the synthesis of colloidal dispersions of inorganic organic-inorganic hybrid materials, especially oxides and oxide-based hybrid in various forms of powders, fibers, thin films and monoliths (Charinpanitkul, et al., 2008). The precipitated powder obtained is amorphous in nature, therefore, further heat treatment is usually required for crystallization (Charinpanitkul, et al., 2008). This process is typically for the fabrication of metal oxides starting from a chemical solution that reacts to produce nanosized colloidal particles (sol). Typical precursors (gel) are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a broad range of solid-liquid (and/or liquid-liquid) mixtures, all of which contain distinct solid (and/or liquid) particles which are dispersed to various degrees in a liquid medium. The result is a system composed of solid particles dispersed in a solvent. Formation of a metal oxide involves connecting

the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.

Wahab and co-workers (Wahab, et al., 2007) have conducted a research on synthesis and characterization of hydrozincite and its conversion into zinc oxide nanoparticles. The zinc oxide nanoparticles are obtained through thermal annealing of hydrozincite powder at various temperatures in air for 2 hours using sol-gel method by refluxing for 6 hours at 70°C. The chemical used in this method are zinc acetate dehydrate ($Zn(CH_3COOH)_2.2H_2O$) and urea (NH_2CONH_2). By using the FESEM, the microstructure of the hydrozincite powder where plate like structure. This structure will then converted into zinc oxide powder when annealed at 300°C, 500°C, 700°C, 900°C. A circular and elongated microstructure of the nanoparticles can be clearly observed at annealing temperature of 300°C with particle sizes of approximately 20–30 nm. Annealing at 500°C showed agglomeration as aggregated particles with particle size of around 50–60 nm. An increase is particle size from 50 to 100 nm is observed with increased annealing temperature at 700°C, with grains changing from circular to faceted particles. Hydrozincite powder which annealed at 900°C shows the increased in particles size to about 250 nm. The nanoparticles tend to agglomerate with each other and there are neck formations between the particles. This phenomenon may lead to the densification of the particles.

2.4.2 Chemical Vapour Deposition

Chemical vapor deposition (CVD) is a chemical process used to deposit films by reacting chemical vapour to produce a film on the substrate. It is also used to

produce high-purity, high-performance solid materials. The reactions using this method may be activated by heat (CVD), RF-energy (plasma enhanced-PECVD) or by light (photon induced-PHCVD). The process is often used in the semiconductor industry to produce thin films.

Rose-like zinc oxide nanoflowers were successfully synthesized on SiC substrate via a simple chemical vapor deposition method by a group of researchers (Zhang, et al., 2008). These rose-like zinc oxide nanoflowers are composed of nanosheets layer by layer. Furthermore, some other shapes of zinc oxide microstructures such as microplates, micro-palmerworms, and self-assembled nanosheets were also synthesized. It can be seen that all crystals have flower-like multilayered structure with size about 1–2 μm and resemble beautiful roses in nature. The top of a nanoflower, which exhibits clearly that thickness and width of the nanosheets are about 50–80 nm and 500–600 nm, respectively. These researchers believed that these rose-like ZnO nanoflowers maybe have a good prospect in scientific and industrial applications.

Singh and a group of researchers (Singh, et al., 2008) have reported zinc oxide nanocrystalline powder can be synthesis by ultrasonic mist-chemical vapour deposition route where this type of production is a combination of more than one technique. This method according to the researchers is suitable for large-area deposition at low temperatures and taking into consideration on its simplicity, inexpensiveness and safety. The experimental set up consisted of 3 zones, namely the ultrasonic spray zone, evaporation zone and deposition zone. The FESEM and TEM results revealed that the powder containing mixture of nanoparticles with

different size in the range of 50 to 100 nm. The XRD results indicated that the zinc oxide nanocrystalline had the pure wurtzite structure.

2.4.3 Sonochemical

Sonochemistry is one of the earliest techniques used to prepare nanosized compounds (Gedanken, 2004). Sonochemistry is the research area in which molecules undergo a chemical reaction due to the presence of powerful ultrasound radiation or ultrasound range from 20 kHz–10 MHz. The physical phenomenon responsible for the sonochemical process is acoustic cavitation (Gedanken, 2004). Sonochemical synthesis, which has become a common method for preparing a wide variety of nanostructured materials, is based on acoustic cavitation resulting from the continuous formation, growth and implosive collapse of bubbles in a liquid (Xiao, et al., 2008). Sonochemistry can be used as a synthetic tool for the creation of inorganic materials. Ultrasound has proved extremely useful in the synthesis of a broad spectrum of nanostructured materials, including high-surface-area transition metals, alloys, carbides, oxides, and colloids.

ZnO nanosheets have been successfully synthesized by Xiao, et al. (2008) using sonochemical method under ambient air in alkali aqueous solution without any template. It is discovered that the microstructure of as-prepared ZnO powders noticeably depends on the pH of starting solutions, and the microstructure of ZnO powders prepared at pH 12.5 is rod-like and sheet-like shapes. ZnO powder exhibited sheet-like shapes using $ZnCl_2$ and $ZnSO_4$ as zinc resources.

A group of researchers (Zhang, et al., 2005) synthesized ZnO nanorods and trigonal-shaped ZnO ultrafine particles by sonochemical method through the decomposition of zinc acetate dihydrate in paraffin oil. The time-framed synthesis of ZnO with trigonal-shaped structure with the width of 300nm and length of 500nm and nanorod-like structure with the width of about 40–80nm and length of 150–300nm. In a simple single step sonochemical method synthesis is economically viable. Fluorescence spectrum shows that ZnO ultrafine particles have a perfect crystal form. They concluded that these single-crystalline ZnO ultrafine particles might be useful in future application such as optoelectronic devices, miniature gas sensor and other devices.

2.4.4 Aqueous solution route

Precipitation is a popular and a widely used industrial process in production of crystalline powders (Mullin, 1972). Chemical precipitation means formation of a solid substance where soluble metal ions are transformed into an insoluble form by altering the composition of the aqueous solution in order to reduce the solubility of the metal ions.

There are two concepts behind the precipitation theory. Supersaturation is considered a driving force for precipitation and spontaneous formation of a stable state solid from solution must accompanied by a decrease in free energy (Demopoulos, 2008). These concepts are linked to the phenomena of nucleation and crystal growth.

There are various types of nucleation mechanism. The most important mechanisms are the homogeneous, heterogeneous and surface nucleation. Homogeneous nucleation is a primary production of nuclei in the absence of the surface (Demopoulos, 2008). As for the heterogeneous nucleation, the primary nuclei produced on a foreign surface (Demopoulos, 2008). Lastly, surface nucleation is the secondary production of nuclei on the surface of a solid of the same kind with the one which precipitates (Demopoulos, 2008). After nucleation has taken place, small nuclei may reduce their free energy further by growing to larger sizes. This phenomenon is known as crystal growth.

By using the simple aqueous route, monodispersed needle-like ZnO whiskers and flower-like ZnO microstructures composed of different building blocks were successfully prepared at low temperature. The solution basicity, Zn^{2+}:OH^-, determines not only the composition of the precursor but also the morphology of the final product. During the pre-stirring step, the reaction solutions are clear all along when Zn^{2+}:OH^- = 1:8 and1:9, while some white solids appear in the range of Zn^{2+}:OH^- =1:4–1:7. The solids at Zn^{2+}:OH^- = 1:4 and 1:5 are amorphous, while perfectly regular crystals are achieved at Zn^{2+}:OH^- = 1:6 and1:7 (Xie, et al., 2008). From this research, the results show that the solution basicity plays an important role in the composition of the precursor, which has determinative effects on the morphology of the obtained ZnO microparticles by interfering the nucleation and crystal growth rate.

The synthesis of nano-sized zinc oxide using the direct precipitation method was performed by Chen and co-workers in year 2008. The precursor precipitates of

zinc oxide were obtained from the reaction between zinc nitrate and ammonium carbonate in aqueous solutions with suitable concentration. The synthesized ZnO powders had a pure wurtzite structure and the average nano-particle sizes were about 35.2 nm. However, the inconsistency of ZnO particle sizes derived from the BET methods and the XRD analysis indicated that a fraction of nanosized ZnO powders were in the form of aggregates.

Nano-zinc oxide crystals, produced by adapting homogeneous precipitation method using urea and zinc nitrate as raw materials with 0.1M Zn^{2+} (0.2M urea) concentration, show structures with orientation adhesion according to Liu et al. (2007). Orientation adhesion is the connection between the positive and negative polar faces in the direction of pole axis to form crystal. However, Liu et al. (2007) agreed that nano-zinc oxide crystals prepared by hydrothermal method should show good dispersion properties and less orientation adhesion. This is because crystal grain grows freely under hydrothermal condition. When prepared by homogeneous precipitation method, zinc oxide nanocrystals are formed from intermediate precipitate product zinc carbonate hydroxide hydrate and thus zinc oxide nanocrystals would crystallize under forced state in this case (Liu et al, 2007).

2.4.5 Hydrothermal

Hydrothermal processing is a non-conventional method to obtain nanocrystalline inorganic material. In this method water plays an important role in the precursor material transformation at elevated temperatures. Based on phase diagram of water, below 100°C the equilibrium vapour pressure of liquid water is

below 1 bar and above the boiling point of water, the hydrothermal pressure range is available (Schäf, et al., 2002). In hydrothermal, temperature plays an important role in kinetics of product formation and thermodynamic stability of the product phase. The solubility of the product formation is depended on the pressure. The supersaturation range directing the crystallization process and the thermodynamic stability of the product phase. Too high the synthesis pressure will lead to the crystallization of the denser phases (Schäf, et al., 2002). The other vital parameter in this mode of synthesis is time. The reason is the synthesis of kinetically stable phases is favoured in short term processes while the thermodynamically stable phases are usually formed in long term experiments. This is caused by resolution and recrystallization of the already formed phases (Schäf, et al., 2002).

Hydrothermal processing also can be labeled as any heterogeneous reaction in the presence of aqueous solvents under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Byrappa and Adschiri (2007) define hydrothermal as any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above the room temperature and at pressure greater than 1 atm in a closed system. Today, hydrothermal technology will not be just limited to the crystal growth, or leaching of metals, but it is going to take a very broad shape covering several interdisciplinary branches of science. The instrumentation needed in material processing using hydrothermal method is a pressure vessel or autoclave which capable of containing a highly corrosive solvent at high temperature and pressure.

Hydrothermal technique is used by Ismail and co-workers (2005) in producing zinc oxide nanoparticles. In their research, they used zinc acetate and sodium hydroxide in the presence of hexamethylenetetramine (HMTA) which acts as surfactant. A Teflon-lined autoclave was used for the experiment. They managed to obtain zinc oxide nanoparticles with the particle size of 55-110nm.

Shang and co-workers (2007) reported on the formation of nanoplates, flower-like nanostructure composed of nanorods of ZnO were successfully synthesized by employing zinc sulphate heptahydrate and sodium hydroxide as the starting materials at 120°C under hydrothermal condition. Keeping the same parameters, ZnO urchin shape was obtained by addition of vitamin C as a directing agent at 190°C. The directing agent is to direct the morphology and structure of chemical compounds produced (McGarvey and Owen, 1995). In this research, the hydrothermal technique is used to produce the nano zinc oxide powder.

Based on Chen et al. (2008) research work by adopting the hydrothermal method, they managed to obtain zinc oxide nanorods with the length of 9-10μm and diameter of 0.5μm. Zinc nitrate hexahydrate, sodium hydroxide, hexamethylenetetramine and ethanol are the reactants used. The synthesis was done at 160°C for 5 hours and 20 hours respectively. The growth of zinc oxide nanorods can be summarized in three steps. There are nucleation and growth of nanoparticles having equal diameter and length (Chen et al., 2008), growth of nanorods mainly in length direction (Chen et al., 2008) and formation of 3D network due to entanglement of the nanorods (Chen et al., 2008).

Baruah and Dutta (2009), have conducted a study on the effect of pH variation on the dimension and morphology of ZnO nanorods. ZnO nanorods with diameters varying between 220 nm and 1.8 mm and lengths between 1 and 5.6 mm were synthesized by adopting the simple hydrothermal method, using the same concentration and the same growth duration, merely by controlling the pH of the reaction bath during the growth process. Factors that affect the growth of the ZnO nanorods are concentration of the chemical bath, temperature, duration of growth, pH, etc., which directly affect the final morphology of the rods grown. In basic condition, the growth rate for both lateral and longitudinal direction is higher compared to growth rate in acidic conditions because ZnO nanorods are believed to get eroded in acidic conditions. Hydrothermal crystallization of ZnO carried out at various basic pH values in Baruah and Dutta work showed the transition of morphology from rod like to flower like with a shift towards more basic pH. Even the types of alkaline sources influence the structural and morphological of the ZnO powder produced. According to Lu and co-workers, the morphology of the powders synthesized using NH_4OH showed well hexagonal prismatic rods with a diameter of 0.3–0.4μm and length of 4–6μm.When MEA was used the rod-shaped microstructure was transformed into a flower-like morphology consisting of many petals. When DEA and TEA was employed, the powders consisted of aggregated spherical petals a large number of uniformly distributed spheres were obtained respectively (Lu, et al., 2008). The alkaline sources also affect the crystal orientation, particle size and crystallinity of the formed ZnO particles.

2.5 Filtration

Filtration or solid/liquid separation involves the separation of 2 phases from a suspension by passing the solution through a porous medium or membrane (Wakeman and Tarleton, 2005; Cheremisinoff, 1998). As the solution or suspension is forced through the porous medium, the solid particles are retained on the medium's surface or on the walls of the pores. The fluid that passed through is referred to as filtrate. Filtration is used in many processes with the purposes of recovering the valuable solid components where the liquid being discarded, recovering of liquid and the solids being discarded, recovering of both solids and liquid phases or recovering neither phases (when a liquid is being cleaned prior to discharge as the prevention of water pollution) (Wakeman and Tarleton, 2005).

The filter media plays an important role in ensuring a clear separation of particulates from the solution with the minimum consumption of energy (Wakeman and Tarleton, 2005). According to Cheremisinoff (1998), a filter media is inhomogeneous with non-uniform pores size, uneven in geometry and not uniformly distributed over the media surface by nature. Besides, the flow through the medium happens through the pores only, the micro-rate of liquid flow may cause large differences over the filter surface and this shows that the initial layers of the produced filter cake are heterogeneous. The phenomena are established based on the structure and properties of the filter medium. The precipitates primary structure depends on the initial layers because the number of pore passages in the precipitates is big compared to the number in the filter medium. This brings to the conclusion that the precipitates and filter medium influence each other (Cheremisinoff, 1998).

The examples of filter media are woven fabrics, non-woven media, fibrous materials, polymeric and ceramic sheets, sintered metals and perforated sheets (Wakeman and Tarleton, 2005). Other common types of filter media are sand, diatomite, coal, porous plates of quartz, chamotte and many more (Cheremisinoff, 1998).

There are 2 ways in retaining the particles on filter media. There are the cake and depth filtration. Cake filtration means when particles are larger than the sizes of pores in the filter medium, they form a layer of sediment on the surface of the medium and known as filter cake. Depth filtration process is due to the mechanical or surface chemical effect. In this process, when the particles are smaller than the pores size of the filter medium, deposition occurs within the internal structure of the medium. Some very small particles have the possibility to pass through the medium and be collected in liquid form known as filtrate. The mechanism of filtration or so-called laws of filtration can be seen at Figure 2.1. Depth filtration occurs by the standard blocking law that describes gradual accumulation of particles in the medium, and most cake filtrations occur by a combination of blocking and bridging (Wakeman and Tarleton, 2005). An Intermediate blocking mechanism allows for the particles to cause both pore blocking and cake formation (Wakeman and Tarleton, 2005). Figure 2.1a illustrated the principle of depth filtration. The complete blocking which happens at the microscopic scale cake filtration and achieved by a combination of 2 primary mechanisms can be seen in Figure 2.1b. Bridging (Figure 2.1c) occurs when particles size are smaller than the pore size of the filter medium form a cake. Bridging happens when the particles are at a higher concentration in feed. Some of the particles fail to pass through at the surface of the filter medium

and this leads to the forming of bridge over the pore entrance (Wakeman and Tarleton, 2005).

There is variety types of filtration equipment used in the industries. The selection of this equipment is based on the slurry to be handled, precipitates properties, anticipated capacities and process operating conditions (Cheremisinoff, 1998). Examples of filters are rotary drum filters, drum vacuum filters with external filtering surfaces, internal rotary-drum filters, Nutsch filters, horizontal rotary filters, belt filters, cross mode filters, filter press, leaf filters, disk filters, cartridge filters, diaphragm filters, high pressure, thin cake filters and others (Cheremisinoff, 1998).

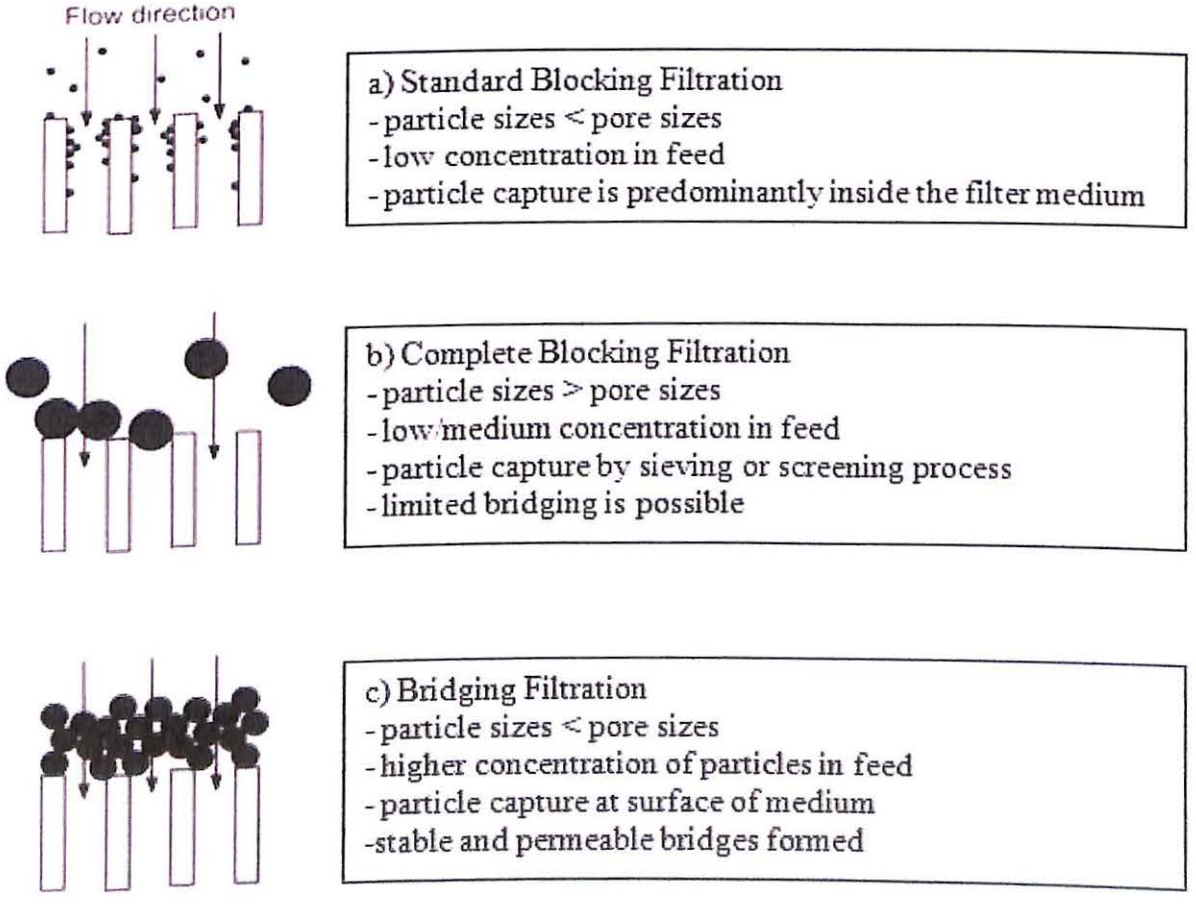

Figure 2.1 Mechanisms of filtration (Wakeman and Tarleton, 2005).

2.6 Washing The Precipitates

Washing are conducted either to remove liquid impurities from a valuable solid product or to increase the recovery of a liquid product from the precipitates (cake). Generally, this process would be continued until the concentration of solute in the precipitates has reached to some acceptable level or until the maximum allowable degree of dilution of the collected filtrate has been achieved.

Residual liquor is normally removed by either one of the three available methods. The first method is displacement washing where wash liquor is passed through the cake once (Wakeman and Tarleton, 2005). The second type is countercurrent washing where all or some portion of the wash liquor (sometimes mixed with filtrate) emanating from a downstream section of the cake is passed through a section of the cake farther upstream (Wakeman and Tarleton, 2005). The last method is reslurried washing where the cake is discharged from the filter and then mixed with wash liquid in a separate vessel before being filtered again (Wakeman and Tarleton, 2005). The operation of this method is sometimes done on the filter.

The rate of permeation of the wash liquid into the pores of the filter cake as well as mass transfer processes depend on the efficiency of washing. The pore structure of the voids, of which the pore size distribution is most essential, in the filter cake affects the wash liquid flow hence also the effectiveness of washing (Wakeman and Tarleton, 2005).