Development of ZnO/SiO<sub>2</sub> Nanocomposites Using Sol Gel Method

by

Asnadila binti Amris

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

### CERTIFICATION OF APPROVAL

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Asnadila binti Amris

A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

(Assoc. Prof. Dr. Anita binti Ramli)

DR ANITA RAMLI Associate Professor Fundamental & Applied Sciences Department Universiti Teknologi PETRONAS, PERAK

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2009

### **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ASNADÍLA BINTI AMRIS

### ABSTRACT

In this study, nanocomposite of ZnO-SiO<sub>2</sub> was prepared by through in situ sol gel method in which ZnO nanoparticles were dispersed in the silica glassy matrix. Zinc Nitrate was added to Tetraethoxysilane at ratio molarity of Zinc Nitrate:Tetraethoxysilane at 0.3:0.3 and 0.1:0.5. To promote the reaction, the Nitric Acid and base, Sodium Hydroxide was added for the dried get formation purpose. The prepared dried gel of ZnO-SiO<sub>2</sub> at 120°C was heated to different calcination temperatures which are at 400°C, 500°C, 600°C and 700°C. The structure and thermal behavior of nanocomposite was identified through X-Ray Diffraction (XRD), Fourier Transform Infrared Spectrometry (FTIR), Scanning Electron Microscope (SEM) and Thermo Gravimetric Analysis (TGA). Throughout this report will be discussed more on the structure and characteristic the synthesis nanoparticles for its physical and chemical properties.

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## CHAPTER 1 INTRODUCTION

### 1.1 BACKGROUND OF STUDY

ZnO-SiO<sub>2</sub> nanocomposite thin films have attracted much attention for a wide range of device applications based on their specific optical and electrical properties [1]. ZnO-based nanocomposites are of considerable interest in ceramics technology for applications as varistors, sensor elements and photoluminescent materials [2]. In particular, varistors used in high voltage applications require a small grain size in order to keep the varistor volume low, while the overall properties of varistors are greatly improved by the reduction of the zinc oxide particles to nanometer range. A potential application in the optoelectronic industry stems from the size-dependent optical properties, associated with the quantum size effect and with the existence of a high percentage of atoms at the nanoparticle surface. Several preparation methods, like sol gel, impregnation and molecular capping, have been proposed for the dispersion of ZnO nanoparticles in silica or polymeric matrices in order to avoid the tendency of nanoparticles to aggregate [2]. Among these methods, the sol-gel preparation is more preferable due to its numerous advantages which were easy control of chemical components, and fabrication of thin film at low cost to investigate structure and optical properties of ZnO thin film [3]. This research is focused on nanoparticles materials. synthesize ZnO-SiO<sub>2</sub> using sol gel method and check the characteristic of the synthesis nanoparticles for its physical chemical properties. The effect of the solvent, composition and temperature is investigated. Structural evolution of the samples towards thermal treatments and chemical modifications of the precursor deposited onto silica are studied by XRD, SEM, TGA and FTIR.

### **1.2 PROBLEM STATEMENT**

Zinc oxide nanoparticles have been investigated in recent years, owing to their applications in catalytic, luminescent, and electronic devices, pigments and components for pharmaceutical and cosmetic industries [4]. The reasons makes ZnO is ready for commercialization is that it is not an exotic nanomaterial, but rather a material that is inexpensive, plentiful and well understood. ZnO is also chemically stable, easy to prepare and non-toxic. Another area where ZnO seems to have a unique opportunity is an area that has already been mentioned: transparent electronics. In this area, transparent ZnO TFTs would be used to create entirely transparent displays by all accounts a useful feature for certain military, medical, automotive and industrial market [5].

However, not all commercially interesting applications for ZnO provide a large niche that is uniquely suited to ZnO. In many of these areas, ZnO have low metal surface area and have to compete with other materials and in some cases, ZnO's competitive advantages may not be so clear. This is true even for older applications for ZnO such as conductive coatings; there are dozens of materials that are more widely used in this application. In particular, ZnO has sometimes been proposed as an effective substitute for ITO under certain circumstances, because ZnO coatings can serve as a transparent conductive coating. However, ZnO in its usual form has much lower conductivity than ITO, and while other alternatives to ITO have the same problem, some of them (nanomaterials in particular) seem well positioned for improvement on ITO at some time in the future. In addition, some ITO alternatives-especially organic materials and (again) nanomaterials-promise greater suitability for deposition on the flexible substrates of the future [5].

However, none of this should be taken as an assertion that ZnO is in some way always second best. There are important areas where ZnO has established itself as the dominant material in a certain market segment, even though there are other possible alternatives.

### 1.3 OBJECTIVES AND SCOPE OF STUDY

There are few main objectives of this project which are:

- 1) To synthesize ZnO SiO<sub>2</sub> using Sol Gel Methods.
- 2) To characterize the synthesis nanoparticles for its physical and chemical properties.

In order to fulfill the need of the objectives, Sodium Hydroxide (NaOH) and Nitric Acid (HNO<sub>3</sub>) will be use to promote the reaction using this Sol Gel methods. , the sample will be characterized using several types of equipment for instance, X-Ray Diffraction Analysis (XRD), Scanning Electron Microscope (SEM), Thermal Gravimetric Analysis (TGA) and Infrared-Spectroscopy (FT-IR).

### CHAPTER 2 LITERATURE REVIEW

### 2.1 NANOCOMPOSITE

Nanocomposite Science and Technology Book, define nanocomposite as multiphase solid materials where one of the phases has a dimension of less than 100 nanometers (nm) [15]. It can be considered solid structures having nanometer scale dimensional repeat distances between the different phases that make up the material. In *Concise encyclopedia of composites materials*, the size limits for these effects have been proposed by Kamigaito which are; <5nm for catalytic activity, <20nm for making a hard magnetic material soft, <50nm for refractive index changes, and <100nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement.

Nanocomposites are important class of materials because many of their physical and chemical properties show particle size dependence. Nano structured metal (Zn, Mg, Ca) aluminate, with spinel structure, dispersed in SiO<sub>2</sub> glassy matrix materials are found to exhibit improved properties such as great thermal stability, hardness, etc. and thus, gained interesting importance in the technological applications like optical, refectories and high alumina cement oxidation catalysts [6]. Nanocomposite materials can be obtained by controlling both the size and polydispersity of the particles in the host matrix through various synthesis methods, under specific conditions, like sol-gel, solid state reaction, etc. Wide varieties of glass, glass-ceramic monoliths and nano structured powders are synthesized through sol-gel technique, since it has many advantages over other methods like low temperature processing, high chemical homogeneity and purity. Hence, the above mentioned advantages focused our attention to synthesize nanocrystals of spinel structured ZnO dispersed in SiO<sub>2</sub> glassy matrix through insitu sol-gel reaction and characterize by XRD, TGA, SEM and FTIR.

### 2.2 MAGNETIC NANOPARTICLES

Magnetic nanoparticles are a class of nanoparticle which can be manipulated using magnetic field. These particles have been the focus of much research recently because they possess attractive properties which could see potential use in catalysis, biomedicine, magnetic resonance imaging, data storage and environmental remediation. The established methods of magnetic nanoparticle synthesis include: Co-precipitation, Thermal decomposition and Microemulsion.

- i. Co-precipitation is a facile and convenient way to synthesize iron oxides (either  $Fe_3O_4$  or  $\gamma$ - $Fe_2O_3$ ) from aqueous  $Fe^{2+}/Fe^{3+}$  salt solutions by the addition of a base under inert atmosphere at room temperature or at elevated temperature. The size, shape, and composition of the magnetic nanoparticles very much depends on the type of salts used (e.g. chlorides, sulfates, nitrates), the  $Fe^{2+}/Fe^{3+}$  ratio, the reaction temperature, the pH value and ionic strength of the media.
- ii. Monodisperse magnetic nanocrystals with smaller size can essentially be synthesized through the thermal decomposition of organometallic compounds in high-boiling organic solvents containing stabilizing surfactants
- iii. Using the microemulsion technique, metallic cobalt, cobalt/platinum alloys, and gold-coated cobalt/platinum nanoparticles have been synthesized in reverse micelles of cetyltrimethlyammonium bromide, using 1-butanol as the cosurfactant and octane as the oil phase.

These particles have been the focus of much research recently because they possess attractive properties which could see potential use in catalysis, biomedicine, magnetic resonance imaging, data storage and environmental remediation.

### 2.3 SOL GEL METHOD

Sol is refer to a stable suspension of colloidal solid particles or polymers in a liquid while gel is refer to porous, three-dimensional, continuous solid network surrounding acontinuous liquid phase. Sol-gel process involved, hydrolysis,

5

condensation, gelation, ageing, drying and densification. Sol-gel method of synthesizing nanomaterial is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

Step 1: Formation of different stable solutions of the alkoxide or solvated metal precursor (the sol).

**Step 2:** Gelation resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation or polyesterification reaction that results in a dramatic increase in the viscosity of the solution.

**Step 3:** Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

**Step 4:** Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv)the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.

Step 5: Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to  $800^{0}$ C.

**Step 6:** Densification and decomposition of the gels at high temperatures (T>800<sup>o</sup>C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.



Figure 1: Sol-gel Process.

Above figure shows the process of sol gel methods. It involved the steps mentioned in the previous paragraph.[18]

### 2.4 ANALYSIS

### X-Ray Diffraction Analysis (XRD)

A research was done by Yoritsugu Shino and Hirotoshi Nakabayashi (2004), shown from the Figure 2 below, the X-Ray diffraction patterns of the ZnO-SiO<sub>2</sub> binary oxides prepared by the calcinations at various temperatures, with the specific surface areas measured by BET method. The diffraction patterns assignable to ZnO phase were only observed at the temperatures lower than 1073K, indicating that the binary oxides were composed of ZnO crystalline phase and nanocrystalline SiO<sub>2</sub> phase [10]. In general, the phase diagram depicts that the Zn<sub>2</sub> SiO<sub>4</sub> phase is formed by the solid-phase reaction, which is caused at very high temperatures around 1573 K. However, the solgel derived Zn<sub>2</sub>SiO<sub>4</sub> is elaborated by the calcination at the lower temperatures. Because the sol-gel technique readily offers the finely divided particles as well as the homogeneously dispersed particles, the Zn<sub>2</sub>SiO<sub>4</sub> phase must be formed at the temperature lower than 1573 K. [10]



Figure 2: X-Ray diffraction patterns and surface area of ZnO-SiO<sub>2</sub>

While in the other researcher stated that, the crystallization of ZnO thin film occurs in the heat treatment at over  $400^{\circ}$ C [3]. In Figure 3, ZnO thin film appears to have a polycrystalline structure, because of a crystal plane of (002) and (101). The (002) plane peak rises larger with the increase in annealing temperature between 400 °C and 600 °C, however, the peak decreases instead at 700 °C. It appears that the crystallinity of ZnO thin film in high annealing temperature is a result of the volatilization of Zn particles. (Byeong Kyun Choi and Dong Hoon Chang, 2006). [3]



Figure 3: XRD patterns of ZnO thin film with various annealing temperatures

From this XRD analysis, the grain size increases from 21.817 to 21.997 nm with the increase of annealing temperature from 400 to 600  $^{\circ}$ C, after then the grain is decrease to 21.834 nm at 700  $^{\circ}$ C. These grain sizes are obtained using the Scherrer's equation as follows.

$$d = \frac{K\lambda}{\beta\cos\theta}$$

Where;

d = crystallite size;

K = 0.9;

 $\lambda = 1.5406$ ; the wavelength of the diffraction peaks;

 $\theta$  = the Bragg's angle at maximum peak;

A research was done by V.Musat and E. Fortunato (2008), shows the XRD patterns of the thin films deposed using the sol II at 20 cm/min and 30 cm/min (samples S3 and S4) are presented in Figure 4 and show wurtzite tipe ZnO nanocrystalline phase with preferential (100) crystalline orientation, embedded in an amorphous silica matrix. [1] The thin films deposed at lower withdrawal speed or using the sols I and III didn't show well defined peaks of ZnO phase. [1]



Figure 4: XRD patterns of the samples S3 and S4.

 $<sup>\</sup>beta$  = the full width of the XRD peak at half maximum intensity of the peak (FWHM).

### FourierTransform Infrared-Spectroscopy (FT-IR)

The formation in the matrix of the heteropolynuclear complex combination, its thermal decomposition and the behavior during the thermal treatment of the silica matrix system, have been studied by IR spectrometry. The FT-IR spectra are shown in Figure 5 below. The frequencies of the IR main absorption bands corresponding to the studied samples and the assignment of these bands are shown in Table 1. This analysis is to indentify the various functional group that are not fully decomposed in the sample. [13]



Figure 5: FT-IR Spectra.

Table	1:1	К	frequencies	of	mai	n a	bsorption	i banc	ls	of	the	studied	sam	ples
-------	-----	---	-------------	----	-----	-----	-----------	--------	----	----	-----	---------	-----	------

	•	<u>IR fi</u>	equencies	[cm ']			Assignment
Ţ	2	3	4	5	6	7	······································
3360	3426	3426	3438	3368	3427	3400	3440 cm <sup>-1</sup> ; v(H <sub>2</sub> O)
2959	2947	2936	-	-	2940	2947	$2950 \text{ cm}^{-1} \text{ v}_{s}$ (CH <sub>3</sub> )
2880	2880	-	-	-	-	2860	2880 cm <sup>-1</sup> : v(CH)
1623	1610	1615	1627	1638	1620		1640 cm <sup>-1</sup> : 5(H,O)
-	-	-	•	-	-	1615	1620 cm <sup>-1</sup> : V <sub>ab</sub> (COO)
-	-	1393	-	-	-	1386	1390 cm <sup>-1</sup> ; v.(COO)
13\$0	1380	-	-	1380	-	-	1380 cm <sup>-1</sup> : (NO.)
-	-	1364	1358	•	-	1358	1360 cm <sup>-1</sup> ; &(OH)
-	-	1312	1312	-	-	1312	1320 cm <sup>-1</sup> : v.(CO)
•	-	-	-	-	-	1218	1220cm1 v(OE)+8(OE
1180	11\$\$	1183	1200	1194	1194	-	1200 cm <sup>-1</sup> : v <sub>a</sub> (Si-O-5
-	-	-	-	-	-	1073	1080 cm <sup>-1</sup> : v(COH)
1072	1062	1065	1065	1065	1065	-	1075 cm <sup>-1</sup> ; v_(Si-O-5
960	960	•	÷	948	950	•	960 cm <sup>-1</sup> ; v(Si-OH)
792	794	\$00	800	796	790	•	\$00 cm 1: v.(Si-O-Si)
-		-	-	+	-	\$00	780cm : 5(0C0)-v(M0
-	+	•	-	-	-	715	715 cm <sup>2</sup> : 0(H,O)
452	445	446	450	446	434	490	480

### Scanning Electron Microscope (SEM)

The microstructure of the samples sintered at 700°C is shown in Figure 6. One can observe that the grain boundaries are not well-defined for all the samples but the aggregated crystallites can be seen for samples  $Ni_{0.7}Zn_{0.3}Fe_2O_4$  and  $Ni_{0.6}Zn_{0.4}Fe_2O_4$ . This is due to the sintering temperature not high enough for the complete formation of the microstructure [11].



Figure 6: The morphology of nickel-zinc-ferrite after sintering at 700°C

(a)  $Ni_{0.8}Zn_{0.2}Fe_2O_4$ , (b)  $Ni_{0.7}Zn_{0.3}Fe_2O_4$ (c)  $Ni_{0.6}Zn_{0.4}Fe_2O_4$  (d)  $Ni_{0.5}Zn_{0.5}Fe_2O_4$ 

### **CHAPTER 3**

### **METHODOLOGY**

### **3.1 PROJECT PROCESS FLOW**

No	Detail/ Week	1	2	3	4	5	6	7	8	9	19. J.	10	11	12	13	14	15	16
1	Project Work Continue					-					 			<u> </u>				
2	Progress Report 1																 	
3	Project Work Continue	 											<u></u>					
4	Progress Report 2	 																
5	Seminar																	
6	Project Work Continue																	
7	Poster Exhibition																	
8	Dissertation(softbound)														^ <i></i>			
8	Oral Presentation																	
9	Dissertation(hardbound)				- - -													

Figure 7: Gantt Chart

### 3.2 MATERIALS AND APPARATUS

### 3.2.1 Apparatus

- Hot plate
- Magnetic Stirrer
- Beaker
- pH Meter
- Furnace

### 3.2.2 Chemicals

- Zinc Nitrate, Zn(NO<sub>3</sub>)<sub>2</sub>6H<sub>2</sub>O
- Tetraethoxysilane, TEOS
- Ethanol, EtOH
- Sodium Hydroxide, NaOH
- Acid Nitric, HNO<sub>3</sub>

### 3.2.3 Equipment

- X-Ray Diffraction Analysis (XRD)
- Fourier Transform Infrared-Spectroscopy (FT-IR)
- Scanning Electron Microscope (SEM)
- Thermal Gravimetric Analysis (TGA)
- CHNS Analyzer

### 3.3 MIXTURE COMPOSITION

In this study, Zinc Nitrate with water was added to Tetraethoxysilane with ethanol at ratio molarity of Zinc Nitrate:Tetraethoxysilane at 0.3:0.3 and 0.1:0.5. To promote the reaction, the Nitric Acid was added until the solution pH reach 2 and addition of base, Sodium Hydroxide until the pH reach 4.

### 3.4 EXPERIMENTAL

In this project, 0.1 mol Zinc Nitrate is mixed up with 0.5 mol Tetraethoxysilane with addition of Nitric Acid until the pH = 2. After two hours heating and stirring, base which is Sodium Hydroxide is added to make the pH = 4. Wait until the solution form gel and overheated at 110°C overnight in the oven before calcinations at high temperature and check the characteristic using the respective equipment. The procedure is presented in the below Figure 8:



Figure 8: Methodology of preparing ZnO/SiO<sub>2</sub> nanocomposites.

Below shown the apparatus setup of the experiment involved several equipment that have been used.



Figure 9: Apparatus Setup (Sol gel methods)

### 3.5 SAMPLE TESTING

For catalyst characterization, there will be several methods being used which are as per details below:

### 3.5.1 X-Ray Diffraction (XRD)

In XRD, diffraction occurs when a sample is irradiated with electromagnetic radiation, in this case X-rays, and there is interaction with a structure where the repeat distance is on the same order as the wavelength of the electromagnetic radiation. The wavelengths of X-rays are angstroms in magnitude, which is in the range of the repeat distance in most crystalline solid materials. Diffraction occurs based on Bragg's law,

which is shown in Equation below, where n is an integer,  $\lambda$  is the wavelength, d is the repeat distance, and  $\theta$  is the angle of diffraction.

### $n\lambda = d\sin\theta$

The output from XRD analysis yields a plot, which shows intensity versus diffraction angle, as shown in Figure 3. From this one can determine the crystallographic planes that are being diffracted and since the wavelength and diffraction angle is known, using Bragg's law the repeat distance, d, can be calculated, which can be utilized to create a map of the crystal structure. Alternatively, a collection of standards can be utilized to compare the peaks in the diffractogram with literature values, allowing one to identify crystal planes. Furthermore, the equipment can be configured to have a detector to measure X-ray absorption. This detector has been utilized in the work of Hormes et al. Each element has a unique absorption spectrum so utilizing X-ray diffraction and absorption elemental identification is obtained as well as the repeat distance. Schevchenko et al, utilized XRD in order to evaluate peak broadening with size decrease and their results are shown in Figure 10.



Figure 10: Size-dependent XRD Pattern of CoPt<sub>3</sub> Nano-crystals

### 3.5.2 Fourier Transform Infrared Spectrometry (FT-IR)



Figure 11: Infrared-Spectroscopy (FT-IR)

Infrared spectroscopy is a technique used to identify various functional groups in unknown substances through the identification of different covalent bonds that are present in the compound. By identifying the different covalent bonds that are present in a compound, the types of functional groups present can be established. By comparing the absorptions seen in an experimental spectrum to the literature absorptions of various functional groups, therefore the list of possible identities for the bonds present can be determined.

### 3.5.3 Scanning Electron Microscopy (SEM)

It is possible to utilize an XRD equipped with X-ray absorption detector to extract particle size and shape data, however, a scanning electron microscope is a better tool for extraction of size and shape data because it yields real images from which measurements can be made.

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.



Figure 12: SEM Image of Nano-particles.

### 3.5.4 Thermogravimetric Analysis (TGA)

TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. Again, interpretation is limited without further modifications and disconsolation of the overlapping peaks may be required.

Analysis is carried out by raising the temperature gradually and plotting weight against temperature. The temperature in many testing methods routinely reaches 1000°C or greater, but the oven is so greatly insulated that an operator would not be aware of any change in temperature even if standing directly in front of the device. After the data is obtained, curve smoothing and other operations may be done such as to find the exact points of inflection (John Lynch, 2003).

TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

### **CHAPTER 4**

### **RESULT & DISCUSSION**

### 4.1 DATA GATHERING & ANALYSIS

Two solutions have been prepared, they were:

- 1. Solution of *Zinc Nitrate* with water was added into *Tetraethoxysilane* with ethanol at molarity, *0.1:0.5*, Zinc Nitrate:Tetraethoxysilane respectively with the present of Nitric Acid to promote the reaction.
- 2. Solution of *Zinc Nitrate* with water was added into *Tetraethoxysilane* with ethanol at molarity, *0.3:0.3*, Zinc Nitrate: Tetraethoxysilane respectively with the present of Nitric Acid to promote the reaction.

The mixture was stirred at a room temperature with rapid mixing rate. At the beginning, the pH of the mixture is 1.5 after the addition of the Nitric Acid.

About 2 hours starting at pH = 1.5, base solution of Sodium Hydroxide, NaOH concentrated was added until pH of the mixture reached 4. Within 30 minits, wet gel was formed. (refer Figure 13).

After forming the wet gel, then it have been heated overnight at temperature 120°C in the oven. Continue with calcinations in the furnace for 3 hours at 400 °C, 500 °C, 600 °C and 700 °C. Dry sample was produced. (refer Figure 14).



Figure 13: Sample Zinc Nitrate and Tetraethoxysilane after forming wet gel.



Figure 14: Sample of Zinc Nitrate and Tetraethoxysilane after calcinations process.

From the figure 13 above, the wet gel was formed and figure 14, was final condition of the mixture after calcinations at high temperature.

For this project, the fundamental reactions that take place during sol-gel process are showed below:



The hydrolysis reaction, through addition of water, replaces alkoxide groups (OR) with hydroxyl groups (OH). In normal conditions, the hydrolysis reaction is very slow. It is most rapid and complete when catalyst (acid and base) are employed. Normally, base-catalyzed hydrolysis proceeds much more slowly than acid-catalyzed hydrolysis at an equivalent catalyst concentration. Base on this experiment, they might be some others factors that can influence the gelation process and formation of the final product. They are, the pH used for the mixture, composition of starting solution, method of mixing the reagents, gelation temperature, gel aging, heat treatment methods, rate of solvent elimination and maximum temperature of heat treatment (Piccaluga et al, 2000).

### 4.2 RESULTS & ANALYSIS

### X-Ray Diffraction



Figure 15: Ratio 0.3:0.3, ZnO:SiO<sub>2</sub>

Based on the Figure 15 above, the sharp peaks have confirmed the dispersion of crystalline ZnO in the  $SiO_2$  glassy matrix. The roughness shows in the diffractogram represent the amorphous which is the silica it self.



Figure 16: Ratio 0.1:0.5 ZnO:SiO<sub>2</sub>

While, for Figure 16 above, only reflection appear. The diffractogram did not give clear peak since the main compound in the sample is silica. From this, one can observe that the composition of chemical been used effected the result. Since the ratio of the composition is widely different which is 0.1:0.5 ZnO:SiO<sub>2</sub> therefore it give more Silica in the sample compared to the balance composition of ratio 0.3:0.3 ZnO:SiO<sub>2</sub>, the crystalline phase of ZnO appear as observe in the diffractogram.

Besides that, XRD result reveals the crystal system of the compound at the highest intensity. All Zinc Oxide compound is hexagonal system where  $\alpha = \beta \neq \gamma$  and for Zinc Silicate is tetragonal/orthorhom system where  $\alpha = \beta = \gamma = 90$ . Analysis shows that, as increase the temperature Zinc Oxide crystal system is maintain the same while Zinc Silicate crystal system change from tetragonal system to orthorhom system. The table below shows the details of XRD analysis.

	Compound			Alpha,	Beta,	Gamma,
Sample Name	Name	Formula	System	a	β	Ŷ
0.3:0.3	Zinc Oxide	ZnO	Hexagonal	90	90	120
ZnO:SiO2			·····	_		
(400°C)	Zinc Silicate	ZnOSiO4	Tetragonal	90	90	90
0.3:0.3	Zinc Oxide	ZnO	Hexagonal	.90	90	120
ZnO:SiO2						
(500°C)	Zinc Silicate	ZnOSiO4	Tetragonal	90	90	90
0.3:0.3	Zinc Oxide	ZnO	Hexagonal	90	90	120
ZnO:SiO2						
(600°C)	Zinc Silicate	ZnOSiO4	Orthorhom	90	90	90
0.3:0.3	Zinc Oxide	ZnO	Hexagonal	90	90	120
2n0:Si02 (700°C)	Zinc Silicate	ZnOSiO4	Orthorhom	90	90	90

Table 2: Crystal System of the Compound for 0.3:0.3 ZnO:SiO<sub>2</sub>

Sample	Compound		, 4,, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1	Alpha,	Beta,	Gamma,
Name	Name	Formula	System	α	β	γ
0.1:0.5 ZnO:SiO2	Zinc Oxide	ZnO	Hexagonal	90	90	120
(400°C)	Zinc Silicate	ZnOSiO4	Tetragonal	90	90	90
0.1:0.5 ZnO:SiO:	Zinc Oxide	ZnO	Hexagonal	90	90	120
(500°C)	Zinc Silicate	ZnOSiO4	Tetragonal	90	90	90
0.1:0.5 ZnQ:SiQ2	Zinc Oxide	ZnO	Hexagonal	90	90	120
(600°C)	Zinc Silicate	ZnOSiO4	Orthorhom	90	90	90
0.1:0.5 ZnO:SiO2	Zinc Oxide	ZnO	Hexagonal	90	90	120
(700°C)	Zinc Silicate	ZnOSiO4	Orthorhom	90	90	90

Table 3: Crystal System of the Compound for 0.1:0.5 ZnO:SiO<sub>2</sub>

From XRD analysis, crystallite size can be calculated using Scherer formula:

$$d = \frac{K\lambda}{\beta \cos\theta}$$

Where;

d = crystallite size;

K = 0.9;

 $\lambda$  = the wavelength of the diffraction peaks;

 $\theta$  = the Bragg's angle at maximum peak;

 $\beta$  = the full width of the XRD peak at half maximum intensity of the peak (FWHM).

The Scherrer equation predicts crystallite thickness if crystals are smaller than 1000Å. Broadening of a diffraction peak is expected to reflect some large scale feature in the crystal.

Calcination Temp(°C)	к	Wavelength(Å)	Obs. Max 20°	FWHM (20°)	Crystal size(nm)
400	0.9	1.5406	36.253	0.321	0.930
500	0.9	1.5406	36.305	0.323	0.924
600	0.9	1.5406	36.26	0.341	0.875
700	0.9	1.5406	31.705	0.251	1.190

Table 4: Crystal Size for Sample 0.3:0.3 ZnO:SiO<sub>2</sub>

Table 5: Crystal Size for 0.1:0.3 ZnO:SiO<sub>2</sub>

Calcination Temp(°C)	K	Wavelength(Å)	Obs. Max 20°	FWHM (20°)	Crystal size(nm)
400	0.9	1.5406	31.883	0.76	0.393
500	0.9	1.5406	34.577	1.759	0.170
600	0.9	1.5406	22.707	0.412	0.724
700	0.9	1.5406	22.043	1.248	0.239



Figure 17: Graph of Crystal Size Respect to Calcinations Temperature

From the figure 17 above, sample 0.3:0.3 ZnO:SiO<sub>2</sub>, shows the crystal size increase as the temperature increase. The increasing trend of the crystallite size with increasing sintering temperature may due to rapid crystal growth at the beginning of sintering process that cause voids and the particles to grow together to form crystallite grains. While for sample 0.1:0.5 ZnO:SiO<sub>2</sub>, the crystal size is not constant (decreasing and increasing) when the temperature increase. Since the preparation condition of this particular sample was inconsistent with others, the results become entirely different.

Table 6: Maximum Inte	ensity respect to (	Calcination Temperature	e of 0.3:0.3 ZnO:SiO2
-----------------------	---------------------	-------------------------	-----------------------

Calcination Temp(°C)	Max Int. (Cps)
400	105
500	107
600	97.2
700	116

Calcination Temp(°C)	Max Int. (Cps)
400	24.2
500	24.2
600	28
700	24.7



Figure 18: Graph of Maximum Intensity Respect to Calcinations Temperature

From the figure 18 above, sample 0.3:0.3 ZnO:SiO<sub>2</sub>, shows the intensity increase as the temperature increase. While for sample 0.1:0.5 ZnO:SiO<sub>2</sub>, the intensity is quite constant with the changes of temperature. Interrelated with the previous graph, the optimum calcinations temperature for good crystallization behaviour of ZnO/SiO<sub>2</sub> is at 700°C since it shows balance result which has highest intensity and highest crystallite size compare to the other temperature.

Intensity of each peak can be obtained in the XRD analysis. In the literature (Basic in XRD@2001, Buker AXS) stated that, intensity of each peak is caused by the crystallographic structure, the position of the atoms within the elementary cell and their thermal vibration. The line width and shape of the peaks may be derived from conditions of measuring and properties like particle size of the sample material. After determined the crystallographic structure above, the below table shows data of maximum intensity with respect to the calcination temperature.

### FTIR Analysis

The formations of ZnO, its thermal decomposition and the behaviour during the thermal treatment of the silica matrix system, have been studied by IR spectrorometry. The FT-IR spectra are shown in Figure 19 and Figure 20.



Figure 19: FT-IR Spectra: (a) gel from synthesis 1 *(Zinc Nitrate:Tetraethoxysilane, 0.3:0.3)*, calcined at 400°C, (b) gel from synthesis 1, calcined at 500°C, (c) gel from synthesis 1, calcined at 600°C, (d) gel from synthesis 1, calcined at 700°C.



Figure 20: FT-IR Spectra: (a) gel from synthesis 1 (Zinc Nitrate: Tetraethoxysilane, 0.1:0.5), calcined at 400°C, (b) gel from synthesis 1, calcined at 500°C, (c) gel from synthesis 1, calcined at 600°C, (d) gel from synthesis 1, calcined at 700°C.

The frequencies of the IR main absorption bands, functional group and assginment corresponding to the studied samples are shown in Table 7.

		IR fr	equenci	es (cm-1	]			Functional Group	Assignment
1	2	3	4	5	6	7	8		
3552	3523	ŀ	3552	3569	3533	-	-	Alcohol	3500 cm-1: O-H
-	-	3411	3465	3469	-	3415	3411	Water	3440 cm-1: n(H2O)
2426	2426	2426	2426	-	-	-	-	Alkanes	2880 cm-1: n(CH)
1637	1637	1639	1633	1627	1625	1627	1627	Water	1640 cm-1: d(H2O)
1560	1560	1562	-		-	-	_	Amides	Amide II unassoc.
1384	1380	1384	1384	1384	5		-	Carboxylic acids	1390 cm-1: ns(COO)
-	1222	-	1174	-	1228	1220	-	Carboxylic acids	1220cm-1:n(OH)+d(OH)
-	-	-	-	1066	1074	1066	-	Silicon	1075 cm-1: nas(Si-O-Si)
-	-	906	-	-	-	-	-	Silicon	960 cm-1: n(Si-OH)
829	-	-	848	-	-		-	Silicon	800 cm-1: ns(Si-O-Si)
	784	786	767	798	798	796	798	Silicon	780cm-1: d(OCO)+n(MO)
667	665	667	-	-	-	-	-	Amides	Amide V (α & β)
549	-	580	530	-	518	-	-	Amides	Amide VI amorph
435	439	420	482	472	499	447	489	Alkyl halides	480 cm-1: n(MO)

Table 8: IR frequencies of main absorption bands of the studied samples.

### TGA Analysis

This analysis determined changes in weight in relation to change in temperature. TGA normally is performed on dried samples to study and determine at what temperature the decomposition will occur. Figure 21 and Figure 22 below show the analysis on calcine samples.



Figure 21: TGA Analysis of 0.3:0.3, ZnO:SiO2



Figure 22: TGA Analysis of 0.1:0.5, ZnO:SiO2

Figure 21 above shows the weight for sample 400°C and 500 °C decrease from the beginning starting at 50°C. While the weight for sample 600 °C and 700 °C decreases starting at 770 °C. Figure 22 above shows the weight for all sample gradually decrease from the beginning starting at 50°C. Since the weight loss are still occurs and not yet constant thus, it shows the organic groups such as hydroxyl group, carboxyl group and others are not fully decompose after 3 hours calcination. For a better samples, the calcination hour need to be increased for few more hours.

### **SEM** Analysis



The microstructure of the samples shown in Figure 23 and Figure 24 below.

Figure 23: (a) 0.1:0.5, ZnO:SiO<sub>2</sub> at 400°C (b) 0.1:0.5, ZnO:SiO<sub>2</sub>, at 500°C, (c) 0.1:0.5, ZnO:SiO<sub>2</sub>, at 600°C, (d) 0.1:0.5, ZnO:SiO<sub>2</sub>, at 700°C.

In summary, the images (a) shows, least pores at lower temperature compared to image (d) shows, many pores at high temperature.



Figure 24: (a) 0.3:0.3, ZnO:SiO<sub>2</sub> at 400°C (b) 0.3:0.3, ZnO:SiO<sub>2</sub>, at 500°C, (c) 0.3:0.3, ZnO:SiO<sub>2</sub>, at 600°C, (d) 0.3:0.3, ZnO:SiO<sub>2</sub>, at 700°C.

The overall images shows, many pores with bigger support size compared to the sample ratio of 0.1:0.5, ZnO:SiO<sub>2</sub>.

One can observe that the grain boundaries are not well-defined. This is because the main surface of the sample is silica in stead of the metal which is ZnO itself. From the images, Silica is the support size of the sample while ZnO is embedded to the silica for a small amount only. For clearer picture, the below Figure 25 summarize the statement earlier. Image a, shows many pores and bigger support size in the sample, thus it will give higher surface area while image b, shows the least pores and small support size in the sample thus, it will give small surface area.



Figure 25: Picture of the support size and the metal.

For same ratio composition of the sample, can been seen from figure 18, much evolution had occurred in the samples. In the other side, from figure 17 for different ratio composition of sample, the appearance of nanoparticles also not constant for each sample since most of the figure shows plane surface (silica as support size). This is due to the sintering temperature not high enough for the complete formation of the microstructure.

### CHAPTER 5

### **CONCLUSION & RECOMMENDATION**

### 5.1 CONCLUSON

 $ZnO-SiO_2$  nanocomposites were prepared by sol-gel method. It provides suitable route for the nanoparticles preparation since the method easy control of chemical components and low cost to investigate the structure. The characteristics of the nanoparticles are analyzed by XRD, FTIR, SEM and TGA. Many parameters and operational condition have been determined and tested in order to check the porous structure of silica and to obtain satisfactory results of nanocomposite.

From the relation of XRD and SEM analysis, it can be conclude that, the ZnO crystalline phase give hexagonal system. Where as increasing the calcinations temperature it will increase the crystal size, intensity and surface area. While from the relation of FT-IR and TGA analysis, shows that the organic groups are not fully decomposed. Further the calcinations process are required in order to have fully decomposed sample.

The experimental observation of XRD, SEM, TGA and FT-IR analysis prove that porous structure of the silica matrix; number, shape and volume of the pores will depends on amount of precursor salt. In addition of that, it proves that the variety of parameters and operational condition can influenced the porous structure of silica in order to obtain good result of the satisfactory nanoparticles.

### 5.2 **RECOMMENDATION**

- 1. Using correct composition of chemical used; Zinc Nitrate solution/Tetraethoxysilane/nitric acid/Sodium Hydroxide. It must be studied and tested to get good results of nanocomposite.
- 2. Alert with gelation time and parameters that affect gelation time (such as pH, chemical ratio) of the mixture to avoid over stirred.
- Determined suitable time for calcinations hour to make sure all others organic group are fully decomposed.
- 4. Use organic additives for example citric acid to increase the formation of mesopores and increase in ZnO dispersion.
- Analyze the sample using FT-IR before and after calcinations process thus, can compare the result and clearly detect the functional group that have been fully decomposed.
- 6. Run the experiment for many set of ratio thus, can compare the result and clearly get the best composition of chemical in order to obtain satisfactory nanoparticles.
- 7. Further study will be conducted to utilize it for electrical device application.

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### **APPENDICES**

# Infrared Spectroscopy

# **IR Absorptions for Representative Functional Groups**

	anna an an anna anna anna anna anna an	
nctional Group	Molecular Motion	Wavenumber (cm <sup>-1</sup> )
	C-H stretch	2950-2800
	CH <sub>2</sub> bend	~1465
anes	$CH_3$ bend	~1375
	CH <sub>2</sub> bend (4 or more)	~720
<u>na se anna a spine ann an ann an an ann an ann an ann an</u>	=CH stretch	3100-3010
	C=C stretch (isolated)	1690-1630
	C=C stretch (conjugated)	1640-1610
	C-H in-plane bend	1430-1290
enes	C-H bend (monosubstituted)	~990 & ~910
	C-H bend (disubstituted - E)	~970
	C-H bend (disubstituted - 1,1)	~890
	C-H bend (disubstituted - Z)	~700
	C-H bend (trisubstituted)	~815
	acetylenic C-H stretch	~3300
ynes	C,C triple bond stretch	~2150
	acetylenic C-H bend	650-600
	C-H stretch	3020-3000
	C=C stretch	~1600 & ~1475
matics	C-H bend (mono)	770-730 & 715-685
inauco	C-H bend (ortho)	770-735
	C-H bend (meta)	~880 & ~780 & ~690
	C-H bend (para)	850-800
ahala	O-H stretch	~3650 or 3400-3300
UNUS	C-O stretch	1260-1000

hemistry.ccsu.edu/.../table.html

2009	Table of IR Absorptions Page	
iers	C-O-C stretch (dialkyl)	1300-1000
	C-O-C stretch (diaryl)	~1250 & ~1120
lehvdes	C-H aldehyde stretch	~2850 & ~2750
	C=O stretch	~1725
tones	C=O stretch	~1715
	C-C stretch	1300-1100
	O-H stretch	3400-2400
rhowlic acids	C=O stretch	1730-1700
	C-O stretch	1320-1210
	O-H bend	1440-1400
	C=O stretch	1750-1735
iers	C-C(O)-C stretch (acetates)	1260-1230
	C-C(O)-C stretch (all others)	1210-1160
d chlorides	C=O stretch	1810-1775
	C-CI stretch	730-550
vdrides	C=O stretch	1830-1800&1775-1740
iyunaco	C-O stretch	1300-900
	N-H stretch (1 per N-H bond)	3500-3300
	N-H bend	1640-1500
ines	C-N Stretch (alkyl)	1200-1025
	C-N Stretch (aryl)	1360-1250
	N-H bend (oop)	~800
	N-H stretch	3500-3180
ides	C=O stretch	1680-1630
1405	N-H bend	1640-1550
	N-H bend (1 <sup>o</sup> )	1570-1515
	C-F stretch	1400-1000
<i>l</i> balides	C-CI stretch	785-540
yi naliues	C-Br stretch	650-510

009	Table of IR Absorptions Page	
	C-I stretch	600-485
iles	C,N triple bond stretch	~2250
cyanates	-N=C=O stretch	~2270
thiocyanates	-N=C=S stretch	~2125
nes	R <sub>2</sub> C=N-R stretch	1690-1640
	-NO <sub>2</sub> (aliphatic)	1600-1530&1390-1300
U groups	-NO <sub>2</sub> (aromatic)	1550-1490&1355-1315
rcaptans	S-H stretch	~2550
foxides	S=O stretch	~1050
fones	S=O stretch	~1300 & ~1150
fonates	S=O stretch	~1350 & ~11750
IUnales	S-O stretch	1000-750
senhinee	P-H stretch	2320-2270
JSPINICS	PH bend	1090-810
osphine oxides	P=O	1210-1140

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# MID RANGE IR ASSIGNMENTS FOR POLYAMIDE TYPES STUDIED IN THE THESIS

here. Results from the literature in differing crystallographic environments are provided along with the measured values Appendix C gives a table of FTIR spectroscopy peak frequencies in the mid infrared region for the four polyamides studied from photoacoustic experiments on the polyamides with their morphology from formation in ampoules.

# C.1 Mid range IR and hydrogen bond interactions

The table presented below is a compilation of assignments from various literature sources along with measured values of peak wavelengths found from ampoule samples of the polyamides and from some quenched samples also measured.

FTIR Assignment	PA46	PA46	PA46	PA6	PA6 a or	PA6 Y	PA6	PA69	PA69	PA612	PA612
		Gaymans	Meas.	Amorph.	£		Meas.		Meas		Meas.
Hydrogen bonded N-H	3305	3300	3304		3290	3290	3302	3302	3302		3300
stretch											
N-H band	3066	3070	3067		3070	3090	3069	3090	3090		3063
CH <sub>2</sub> asym stretch	2944	2945	2944		2930	2930	2935	2930	2930		2921
CH <sub>2</sub> sym stretch	2872	2870	2872		2865	2860	2868	2854	2854		2853
Amide I unassoc					1667	1650	1652		1652		1652
Amide I ordered					1647	1643	1647		1645		1645
Amide I	1652	1638	1652		1642	1642	1636	1636	1636		1634

Table C-1 Assignments for polyamide bands **Bold**=[99, pp.85-88], *Italic* [48, p. 504]. Normal from ampoule samples and PA46 Gaymans are solution cast FTIR peaks from [122] in cm<sup>-1</sup>

FTIR Assignment	PA46	PA46	PA46	PA6	PA6 a or	PA6 Y	PA6	PA69	PA69	PA612	PA612
		Gaymans	Meas.	Amorph.	ß		Meas.		Meas		Meas.
C=O stretch											
Atnide II	1540	1540			1545	1562	1559	1558	1558		
CN stretch + C(O)-N-H											
bend											
Amide II unassoc.				1560	1540	1560	1541				
									1541		1540
N vic, CH <sub>2</sub> bend ( $\alpha$ )	1476				1476		1476	1471	1471	1474	1474
CH <sub>2</sub> bend	1464		1459		1464	1463	1463	1466	1466	1467	
CH <sub>2</sub> bend	1438			1440	1436	1442	1437	1436	1436	1436	1438
CO vic, CH2 bend (a)	1418		1419		1417		1418	1420	1419	1419	1419
	1363		1363		1374	1369	1373	1371	1368	1369	1370
Amide III ( <sub>7</sub> )	1279	1280	1281	1281	1265	1269	1266		1277	1276	1277
								1249	1250	1237	1237
						1236	1242			1218	1217
(α)	1201		1200		1199		1201	1194	1196	1188	1188
(y),amorph				1170	1170	1170	1170	1180	1189	1180	1188
Amorph	1140		1142	1124				1131	1126	1116	1116
						1121	1123	1111	1112		
					1060	1079	1071	1072	1072	1064	1064
			1027		1029	1048	1029	1026	1017	1036	1026
	984		686			1002		. 886	988	886	987
C-CO stretch $\alpha$ or $\gamma$					959	977	968				
C-CO stretch $\alpha$ or $\gamma$	944	940	943		930	922	929	940	942	937	938
	906		906					006	899	897	899

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FTIR Assignment	PA46	PA46	PA46	PA6	PA6 a or	<b>ΡΑ6</b> γ	PA6	<b>PA69</b>	PA69	PA612	PA612
		Gaymans	Meas.	Amorph.	ą		Meas.		Meas		Meas.
					834		833	853	842		853
						777		797	799	162	792
ĊH₂ wag	733	730	731		731	730	730	727	728	731	730
										720	721
Amide V (y)						712					
N-H out of plane				,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,							
Arnide V (α & β)	693	690	692		691		691	689	695	069	692
Amide VI (y)						623			627		612
C=O out of plane											-
Amide VI (α)	581	575	581		579		579	588	574	582	582
Amide VI amorph				578					574		
	524	520	525		522	521	522	532	535	539	539