The Effect of Furnace Temperature and Precursor Concentration Ratio to The Characteristics of Nanocomposite ZnO-Silica

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Abstract— ***Zinc Oxide is a semiconductor with relatively non-toxic, cheap and abundant properties which can be applied to LEDs. ZnO colloids are unstable due to further chemical reactions and coagulation so the addition of silica is needed to inhibit the growth of ZnO. ZnO was synthesized using sol-gel method by hydrolyze zinc acetate dihydrate in ethanol solution. Silica colloids was prepared by dissolving waterglass in distilled water at a temperature of 60 °C then passed into cation resin that has been activated using 2N HCl for ion exchange with Na+ to H+. In this study, the spray drying method was used to produce ZnO-silica nanocomposite. Morphological characterization of particles formed was analyzed using Scanning Electrostatic Microscope (SEM) (Zeiss Evo MA LS, Cambridge, England). X-Ray Diffraction (XRD) (Cu-Kα 1.54 A0, 40 kV, 30 mA, X'pert Pro, PAN alytical, Netherlands) and Fourier Transform Infrared (FTIR) (Therniscientific Nicolet iS10, US) were used to analyze the crystallinity and group functionalization, respectively. The results show that more particles are formed on 10% concentration volume of ZnO colloids rather than 5%.***

Keywords—Spray Drying, Sol-Gel Method.

I. Introduction

Increasing energy demands cause the availability of fossil fuels decrease so that it needs to develop a new renewable energy sources as alternative energy. This alternative energy source is expected to have a high level of efficiency and environmentally friendly. Making of energy saving lamps such as LEDs (Light Emitting Diodes) are one of the alternative energy sources in the field of lighting. LEDs have been often used for lighting source because of the small energy consumption. LEDs are electronic components from semiconductor materials. The resulting color depends on the semiconducting material used. Zinc oxide (ZnO) is a semiconductor material that is equivalent to Gallium Nitrite (GaN) LEDs for application [1].

Spanhel and Anderson successfully synthesized ZnO particles with a diameter below 10 nm by hydrolyze zinc acetate dihydrate in ethanol solution [2]. ZnO colloid is unstable due to the agglomeration of particles of ZnO. To produce ZnO particles with a homogeneous size and stable for long periods without any agglomeration is by dispersing the silica colloids into ZnO colloids. The time and the process of dispersing needed to be considered at the time of silica colloids dispersion into ZnO colloids. Silica selected as composite materials because these materials are transparent in the visible light region so not disturb the ZnO luminescence. Silica colloids was successfully synthesized using waterglass [3]. However, silica colloids was gelled when the silica concentration larger than 50 mole % mixture [4].

In the application of ZnO which used as energy-efficient lighting we used particles with size below 1μm so the formation of gel should be avoided. Spray drying method is able to produce particles in the range of 100 nanometers to a few micrometers in large numbers, with uniform morphology, spherical shaped, low operating cost and simple equipment [5]. Colloids suspension temperature that are used has to be more than 450 oC because below 450 oC the Si-O-Si bond becomes unstable [6]. This study is expected to determine the effect of furnace temperature and the ratio of precursor concentration on the characteristics of ZnO-silica nanocomposite.

II. Method

The ethanolic ZnO were pepared by dissolving 0.1 M zinc acetate dehydrate in 200 mL absolute ethanol under stirring at 78oC in a flask equipped with a condenser for 180 min until 80 ml solution remaining in the flask. Next, a solution of 0.14 M LiOH in 120 mL absolute ethanol was then added to the ethanolic solution. This process performed at 0 oC for 10 min into an ultrasonic bath. Schematic apparatus is shown in Figure 1.

In the second step, the silica colloids were prepared by dissolving 0.1 M waterglass in 200 ml distilled water at 60 °C. After that, the solution was passed to the cation exchange resin column to replace Na+ ions from the solution with H+ ions. The cation exchange resin column was activated by treatment with 2 N HCl. The pH value of the colloids was adjusted to the desired value using kalium hydroxide (0.1 M KOH).The pH of the colloids was ~7. Schematic apparatus is shown in Figure 2.

To prepare a precursor solution for the spray drying process, the silica colloids mixed with the as-prepared solution of 0.1 M ZnO colloids. Schematic apparatus is shown in Figure 3. Next, a precursor solution was put in Ultrasonic nebulizer (OMRON Ultrasonic Nebulisers, Model NE-U17) to produce the droplets of precursor

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solution then it was sprayed into the heating zone with frequency 1.7 MHz. Air from the compressor (8L Krisbow 1HP compressor direct driven) flows through steel pipes which contains silica gel to get dried air and then passed flowmeter (KUFLOCRK 1200, Japan) as a measure of the carrier gas flow rate. Air flow is set at 1.5 liters / min (T = 20oC, P = 101.325 kPa). Air flow into the Ultrasonic nebulizer (OMRON Ultrasonic Nebulisers, Model NE-U17) and brought the droplet to the tubular electrical furnace reactor (ASH, Japan) which was equipped with a temperature controller. In addition there is also a precursor flow into the ultrasonic nebulizer which were made continuously using a peristaltic pump. It was intended that the obtained particles can have a uniform size. Particles which were formed in the reactor were collected in the electrostatic precipitator. Schematic apparatus is shown in Figure 4. Then, its morphological characterization was analyzed using scanning electrostatic microscope (SEM) (Zeiss Evo MA LS, Cambridge, England). Particles size distribution used two dimensional measurements from SEM picture. X-Ray Diffraction (XRD) (Cu-Kα 1,54 A0, 40 kV, 30 mA, X'pert Pro, PANalytical, Netherlands) and Fourier Transform Infrared (FTIR) (Therniscientific Nicolet iS10, US) are used to analyze crystallinity and group characterization, respectively.

III. Result and Discussion

Making variations of percent volume of the silica colloids dispersed into ZnO colloids and furnaces temperature to optimize the synthesis of ZnO-silica nanocomposite particles are shown in table 1.

In this study were also made pure silica particles and pure ZnO particles. Silica particles could be formed at 400 °C and 600 °C. Meanwhile, ZnO particles were only formed at 400 °C because there was fire that appeared from furnace to ultrasonic nebulizer at 600 oC. This could be occurred because the solvent is flammable. The concentration of ethanol in pure ZnO colloids was higher than at ZnO-silica colloid mixture. The addition of ZnO cause concentration changes silica colloids. The time of evaporation ZnO colloids faster than ZnO-silica colloids.

Furthermore, to determine the effect of furnace temperature on the characteristics of ZnO-silica nanocomposite particles by calculating the average particle diameter (Dp) of 200 particles sample from SEM images. The average particles diameter of silica is 676.78 nm and 639.78 nm, respectively at 400 oC and 600 oC. The average diameter particles ZnO colloids at 400 oC is 482.73 nm. The particle size of ZnO is smaller than silica particles.pressure (point E or A). And the cycle repeats itself.

The SEM image shows that more spherical particles were obtained on 10%concentration volume ZnO colloids than at 5%. However, at 15% to 20% concentration ZnO colloid particles were not formed. This is because higher concentration ZnO colloids makes it difficult to be atomized. When compared in morphologic forms ZnO-silica nanocomposite particles which were formed at 600 °C is better than at 400 °C. Particles can be formed in each of the various volumes silica colloids that dispersed into ZnO colloids at 600 °C.

The XRD analysis result for ZnO-silica nanocomposite particles is shown in Figure 7 and 8. The analysis results are then compared with the JCPDS (Joint Committee on Powder Diffraction Standards) 01.071.3830 to know the profile of the crystal structure and nanocomposite particles degrees which were formed. According JCPDS 01.071.3830 the structure of ZnO is hexagonal. The higher concentration of silica colloids in precursor caused peak height reduced because the growth size of ZnO particles was inhibited by addition silica colloids. Paticles size diameter at 80% concentration silica colloids is 98.653 nm and 123,33 nm, respectively at 400 °C and 600 °C.

The FTIR analysis shows that the absorbance band of Si-O-Zn at 1277.59 cm^{-1}. The absorbance band of Si-O-Zn group was also smaller at 600 °C than 400 °C. This was caused by at high temperature the Si-O-Zn structure will be lost. The increasing amount of ZnO caused the increasing absorbance band of the Si-O-Zn group. The increasing amount of ZnO caused the higher of –OH absorbance band. The –OH absorbance band indicated the existing of silanol group of silica.

IV. Conclusion

Based on the result and discussion, it can be concluded as follows:

1. ZnO-silica nanocomposite particles has been produced by a combination of sol-gel and spray drying which was carried out continuously.
2. Effect of the ZnO-silica concentration ratio is optimum in 10% ZnO volume.
3. Effect of temperature furnace with optimum results at 600 ° C, with a more uniform size.

Acknowledgement

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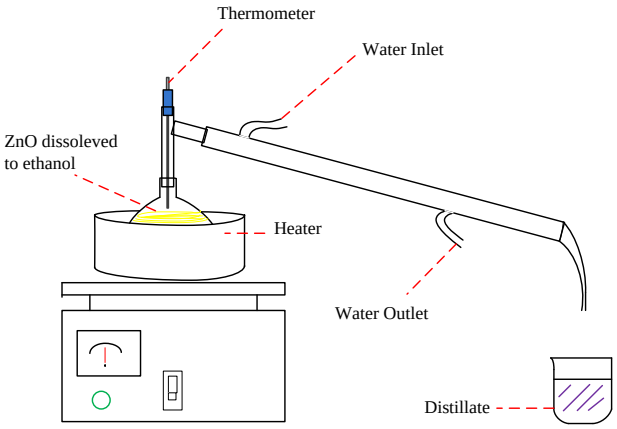

Figure 1.The experimental apparatus to form ethanolic solution

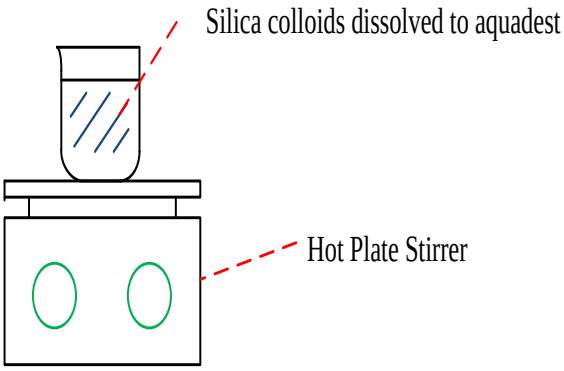

Figure 2.The experimental apparatus to form silica colloids

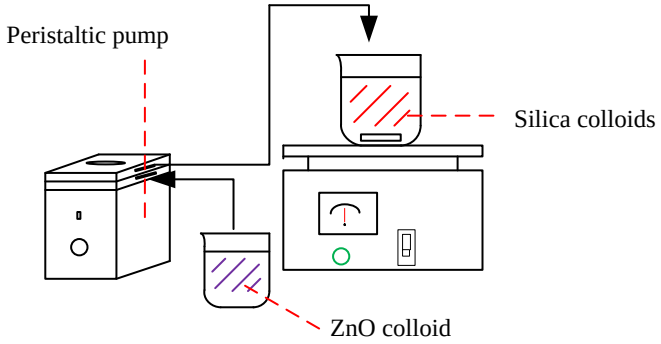

Figure 3.The experimental apparatus to form precursor

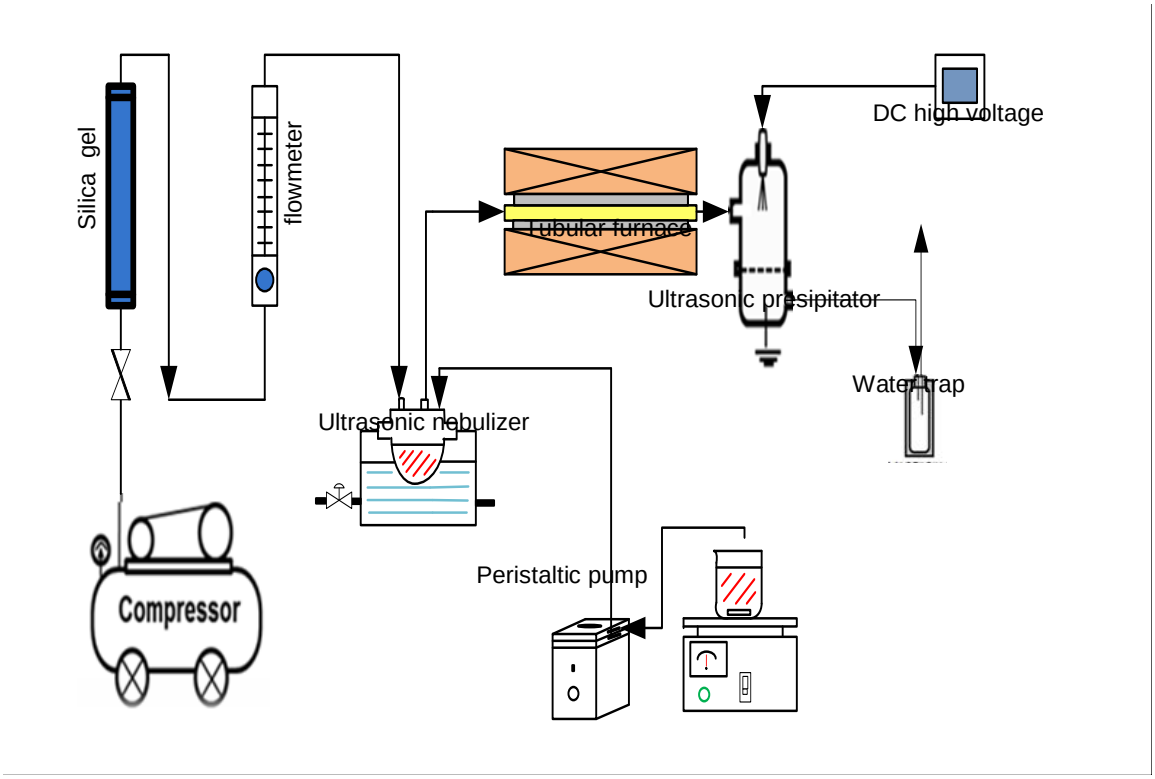

Figure 4.Experimental set up of spray drying using an ultrasonic nebulizer as the atomizer

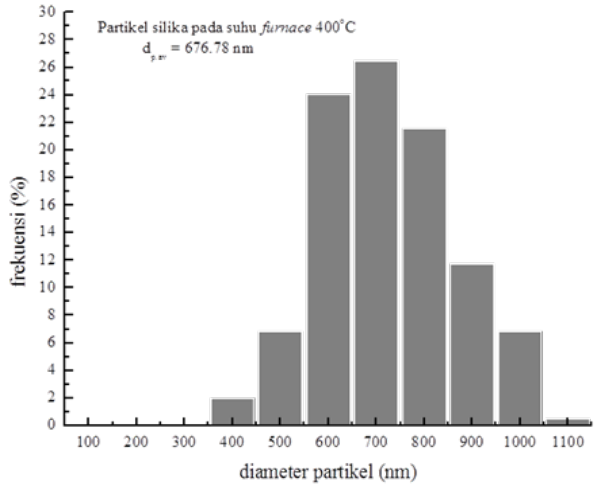

Figure 5.Particle size distribution of silica at temperatures 400 °C

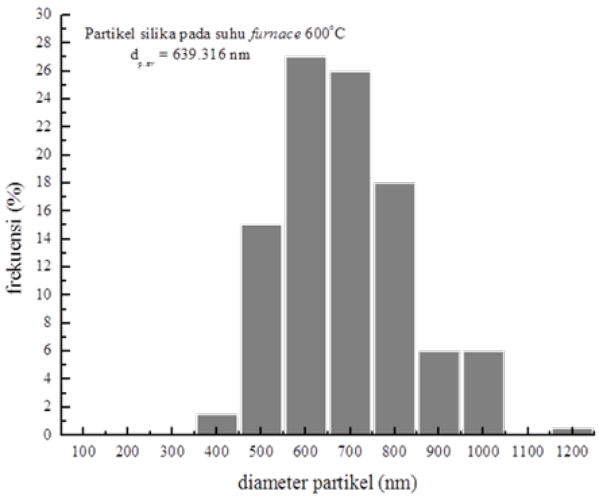

Figure 6.Particle size distribution of silica at temperatures 600 °C

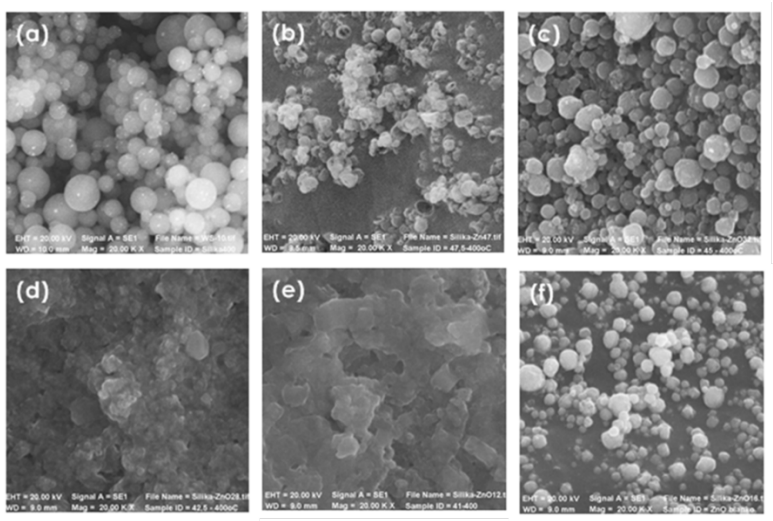

Figure 7. SEM image of nanocrystalline ZnO powders modified using various concentration silica colloids were dispersed into ZnO colloids at 400 ºC (a) 100% silica colloids (b) 95% volume silica colloids, (c) 90% volume silica colloids (d) 85% volume silica colloids (e) 80% volume silica colloids (f) 0% silica colloids

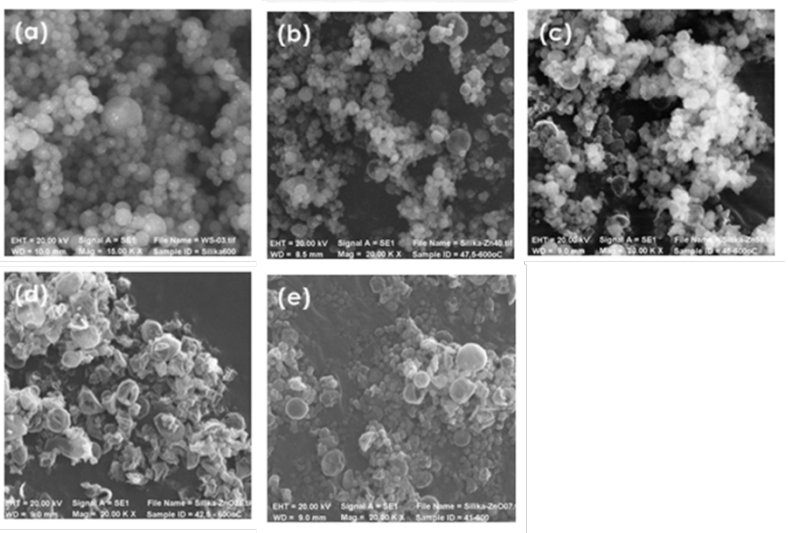

Figure 8. SEM image of nanocrystalline ZnO powders modified using various concentration silica colloids were dispersed into ZnO colloids at 600 ºC (a) 0% silica colloids (b) 95% volume silica colloids, (c) 90% volume silica colloids (d) 85% volume silica colloids (e) 80% volume silica colloids

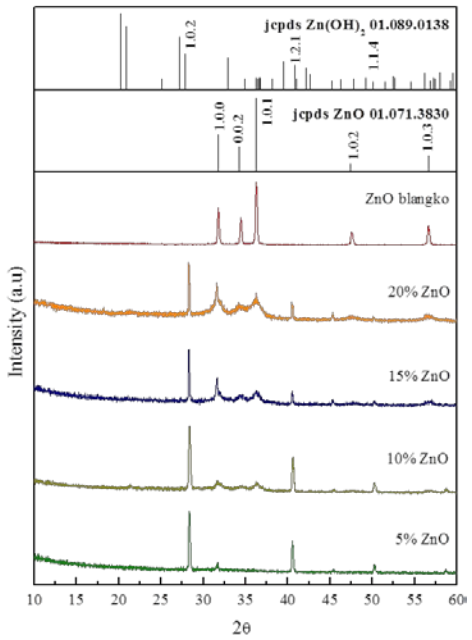

Figure 9. XRD patterns of nanocrystalline ZnO powders modified with variety of volume ZnO colloids at a temperature 400 º C

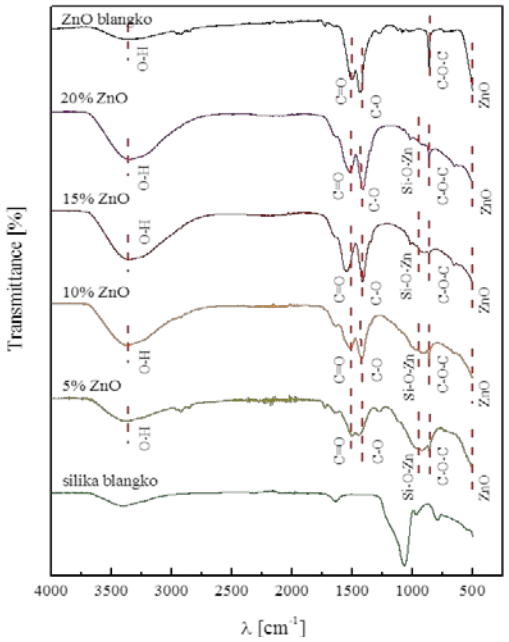

Figure 11. FTIR spectrum for various %volume ZnO colloids at 400 º C

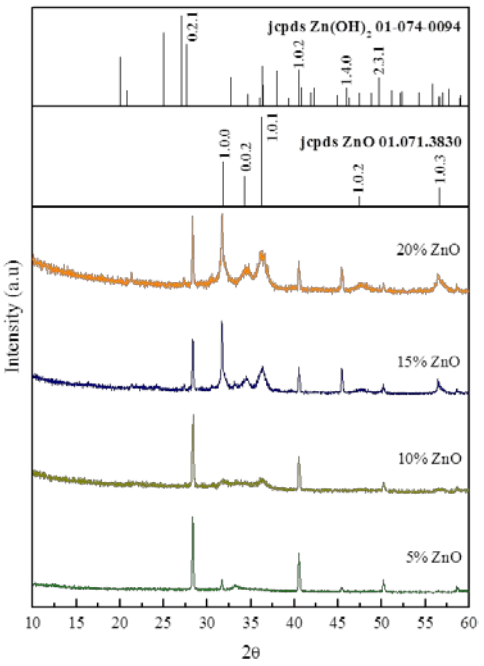

Figure 10. XRD patterns of nanocrystalline ZnO powders modified with variety of volume ZnO colloids at a temperature 600 º C

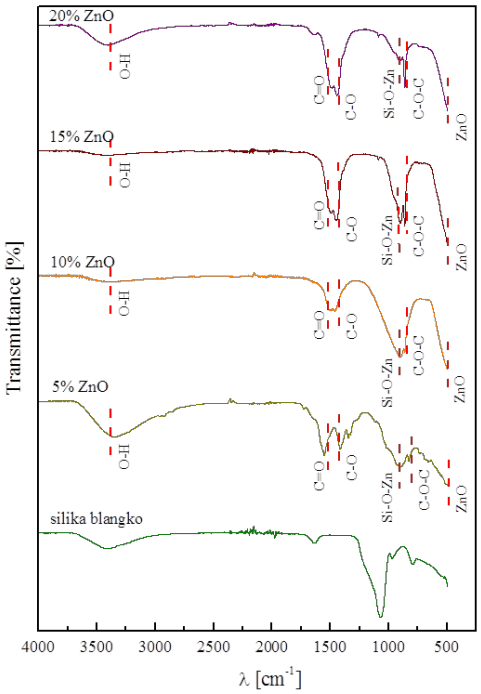

Figure 12. FTIR spectrum for various %volume ZnO colloids at a temperature 600 º C

TABLE 1.
VARIATIONS THE VOLUME OF SILICA COLLOIDS

Variable (%volume)	Volume (mL)		Temperature (ºC)	Furnace
	Silica	ZnO	400	600
80	40	10	✓	✓
85	42.5	7.5	✓	✓
90	45	5	✓	✓
95	47.5	2.5	✓	✓