Journal of Physics: Conference Series **1445** (2020) 012014 doi:10.1088/1742-6596/1445/1/012014

Synthesis of ZnO Nanoparticles Using Mechano-Chemical Method By Utilizing 3D HEM (High Energy Milling)

Siswanto[1*] and Mayasari Hariyanto[1]
[1]Physics Departmen, Faculty of Science and Technology, Universitas Airlangga, Indonesia.

[*]Corresponding email address : siswanto_fst@yahoo.co.id

Abstract. The synthesis of ZnO nanoparticle by mechano-chemical method using 3D HEM already has been done. The chemical reaction process is done by 3D HEM with 1500 rpm. The concern of this research is milling time there are 0 minute, 15 minutes, 60 minutes, 180 minutes, 300 minutes, 420 minutes and 480 minutes. Through this method is done a chemical reaction of materials, Zinc Chloride ($ZnCl_2$), Natrium Carbonate (Na_2CO_3), Sodium Chloride (NaCl) become Zinc Carbonate ($ZnCO_3$) and Sodium Chloride (NaCl). The calcination is done at a temperature 450 ^oC for 2 hours. That calcination process is also causing aggregation which makes the particle size increase. The sodium chloride is removed by dissolving in aqua bidestilata and using sonicator for 30 minutes with its velocity 60Hz. For minimalize of Sodium Chloride (NaCl) is dissolving the sample in aquades and then deposited. The duration of precipitation shows the particle size of ZnO that formed. Precipitation is caused by gravitation force and the particle size that didn't affect by the force is under 50 nm. Therefore, the observation of particle size only did on the sample that has long time of precipitation and short time of precipitation as comparator. The result of PSA observation shows the smallest particle size that formed is (135.6 ± 35,8) nm, with the milling time for 180 minutes. Meanwhile, the particle size is obtained at 1 hour and 7 hours milling time are (183.8 ± 46,6) nm and (877.7 ± 228,7) nm. Besides that, all the crystal size that formed is nanometer. In addition, the result of XRD shows the volume fraction of ZnO for 0 minute, 60 minutes and 180 minutes milling time are still small relatively, there are 12.55%, 13.31 % and 14.8 %.

1. Introduction

Currently nanotechnology is research studies are of interest to the global community. This phenomenon is associated with the application which can cover almost all areas of life. In addition, nanotechnology is able to bring us anything new, including computers are getting smaller and faster, anti-stain clothes, molecular sensors, and even cancer therapies centered [1].

One of material that is often studied to the nanoscale material is Zinc Oxide (ZnO). In Indonesia this material available in large quantities [2]. These materials in everyday life used to mix food ingredients due to its anti-bacterial and non-toxic. In the human body, ZnO will be zinc ions. These zinc ions is needed to cure the disease Zinc defiency Syndrome. ZnO material relating to anti bacteria can be used as a mixture of deodorant and sunscreen (sunscreen). In addition, this material is also used for dental cement material as an anti-bacterial [3].

In its application, bulk ZnO material has weaknesses. As food, anti-bacterial properties of ZnO material is not functioning optimally. This is due to breakdown of the ions into the ion Zn takes a long time. Moreover, it also caused problems of uneven distribution. For applications such materials as deodorant and sunscreen in general will leave white scars on the skin. As a material for the manufacture of dental cement, anti-bacterial effect of ZnO in bulk size is not the maximum[4].. This is caused by uneven distribution and can not seep into the pores of the dental cement. Therefore, changes in the size of the ZnO into nano-sized particles are expected to improve the material weakness.

There are two methods that have been used to synthesize ZnO nano namely mechanical alloying and plasma. Mechanical alloying method using the process and mechanical equipment in the

manufacture of nanoparticles. Temperature is a parameter that must be considered [5]. In addition, the chemical reaction process is not carried out during milling so that no phase change. While plasma methods require high temperatures for the formation of nanoscale materials. In addition, the plasma process is not easy to do because of the high risk at the time of oxidation or burning.

Mechanical-chemical method of nanoparticle formation is the process of using a ball mill type of High Energy Milling. The parameters that influence the formation of ZnO nanoparticles milling process are: speed, time, mass ratio of the mass of the ball and the material will be milling[6].. Additionally, the diameter of the balls used also affects the particle size to be produced. Changes of parameters used will affect the energy generated during the collision process[7].. Therefore, level controlled process parameters indispensable in mechano-chemical method[8].. In this paper, show the influence of parameter changes long milling time on the formation of ZnO nanoparticles. For the parameters of speed, mass ratio of ball milling and material, as well as the diameter of the sphere is made constant.

2. MATERIALS AND PREPARATION

The materials used in this study is $ZnCl_2$, Na_2CO_3 and NaCl solvent. All materials used Merck, where Zinc Chloride has a purity of 99.99%, Sodium Carbonate have a purity of 99.99% and the solvent has a purity of 99.99%. The tools used are divided into two, namely mechanical and synthesis tools. Synthesis tools used are: paper scales, spatula, tongs, cursible, sample bottles, glass beaker, measuring cup, mortar, pipette and furnace. Mechanical device used is a digital balance, Sonicator (Sonics Vibra Cell) and ball mill type of High Energy Milling E-3D. The tools used for the characterization is Particle Size Analyzer (PSA), to determine the particle size; X-Ray Diffraction (XRD) to determine the compound and structure of the atom contained in these materials.

The molar ratio between $SnCl_2$ and NaCl is 1: 8, so that the composition of the materials needed for $ZnCl_2$, Na_2CO_3 and NaCl respectively was 1.365 grams; 1.06 grams and 3.51 grams. Prior to synthesis, washing vials and ball milling to avoid contamination of other compounds that the attachment using ethanol and silica. Also did coating to the vial using NaCl to minimize the occurrence of corrosion and samples obtained are not attached to the vial. Then, the material zinc chloride, sodium chloride and sodium carbonate milling processed using the High Energy Milling. The time variation used is 0 hours, 15 minutes, 1 hour, 3 hours, 5 hours, 7 hours and 8 hours. Comparison between ball milling and materials used 15: 1. Furthermore, calcinate powder of CaCO3 and NaCl at a temperature of 450^0C for 2 hours. To eliminate the NaCl from the calcination of ZnO and NaCl by dissolving 2 grams of sample into the aqua bidestilata and then at Sonic Vibra Cell sonicator for 30 minutes. Then do the observation time of deposition of the solution.

3. RESULTS AND DISCUSSION

Milling process is determined by time parameter. The time milling parameter is used to determine the best time for produce ZnO nanoparticles. Variation of time spent not continuously due to see the difference of the diameter of the particles produced.

The milling results in a state of powder that is ZnCO3 and NaCl are already sized nanoparticles. The milling process function reacting material to form a compound ZnCO3 and NaCl. Milling at the same time also serves to destroy particles formed so that the nano-sized particles. Variations time 0 hours milling is done by grinding the material using a mortar to react the material.

Calcination is carried out at a temperature of 450^0 C for 2 hours is used to remove CO_2 from $ZnCO_3$ and NaCl. After calcination, the powder obtained ZnO and NaCl and CO_2 element would evaporate during calcination. The calcination process can cause agglomeration or clumping nanoparticles. This phenomenon can occur because when calcining compounds organic compounds are released that will cause the volume to shrink. Volume shrinkage will cause the particles to join or

collide with other particles so that it becomes one of large particles. This calcination process causes the resulting nanoparticle size enlarges. Figure 1 is an example of a calcined product with a 3-hour milling time.

Sonic is done to eliminate the NaCl contained in ZnO. Dissolution using aqua bidestilata sterile, because NaCl is soluble in water. ZnO compounds are not soluble and does not react with water. Solvents stable for ZnO is Isopropanol, not water. And NaCl is insoluble in isopropanol. Sonic is done with a speed of 60 Hz, serve to break back in the cracks due to the agglomeration of particles when calcination.

Subsequently, the sample is dissolved back into distilled water to reduce the high concentration of NaCl. High concentration of NaCl which can affect the long deposition and will result in the particles tend to recombine. Examples of diluted solution samples with 3-hour milling time can be seen in Figure 2. Merging the particles can occur because there is no emulsifier which protects the particles, so the dilution with the addition of distilled water into the sample.

The resulting ZnO concentration is very small. This is due to the resulting ZnO ratio and the NaCl solvent being 1: 8 so that only few particles are produced. Observation of the sample after diluted the data obtained by the time of precipitation. The precipitation time is related to the diameter of the resulting particles. The smaller the particle diameter increasingly unaffected by the force of gravity. The particle size not affected by the gravitational force is below 50 nm. Precipitation time can represent the size of the particle obtained. Data obtained from the precipitation time of the observations that have been made for each variation of milling time showed in Table 1. From this table shows that the precipitation time is directly proportional to the time of milling. This phenomenon occurs until a certain time. After that, the precipitation decreases.

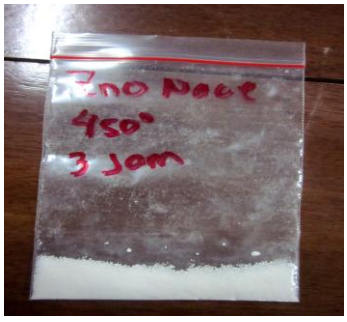


Figure1. Sample with 3 - hours calcination

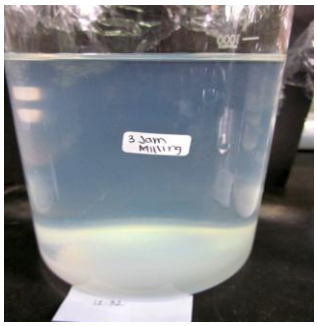
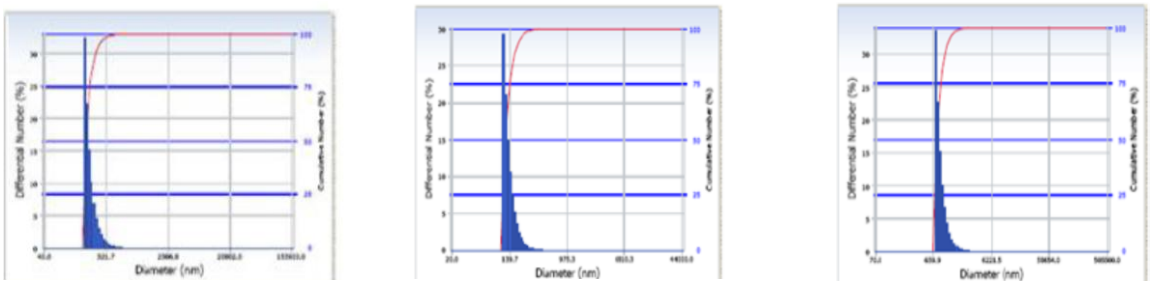


Figure 2. Dilution sample with 180 minutes milling

Table 1. The relationship between milling time and precipitation

Milling time (minutes)	Deposition time (minute)
0	126
15	203
60	335
180	480
300	328
420	279

Based on table 1, only three samples were tested by Particle Size Analyzer that is sample with precipitation duration 60 , 180 and 420 minutes. The reason is that the PSA can only measure a maximum of 1000 nm and the duration of precipitation shows the size of the particle. The result of particle size using the Particle Size Analyzer obtained varied sizes, as showed in figure 3 and Table 2. The particle size for the precipitation duration 60 ,180 and 420 minutes respectively is (183.8 ± 46,6) nm, (135.6 ± 35,8) and (877.7 ± 228,7) nm. The particle size corresponds to the length of time the deposition solution so that the size of the particles to milling time 0 hours, 15 minutes, 1 hour and 8 hours greater than 877.7 nm. The longer the milling time, the smaller the particle size. Then, starting point milling time 3 hours, the particle size enlarged with increasing length of time milling. This phenomenon occurs because due to collisions between the nano particles when milling.



(a) (b) (c)

Figure 3. PSA of samples with milling time (a) 60 minutes ,(b) 180 minutes, (c) 420

Table 2. The Size particle

Milling time (minutes)	Particle size (nm)
60	(183.8 ± 46,6)
180	(135.6 ± 35,8)
420	(877.7 ± 228,7)

XRD observation results for the milling time of 0 hour is still a pure compound constituent is NaCl, Na_2CO_3, and $ZnCl_2$. This shows that without milling the compound does not react. ZnCO3 compound is not formed because the constituent compounds do not react, but to form ZnO with small amounts. ZnO compounds formed from compounds $ZnCl_2$ due calcination temperature above its boiling point is 565 K so $ZnCl_2$ react to form ZnO[9].. The XRD results for the three samples could be seen Figure 4

The results of XRD observations can also be used to determine the percentage of ZnO is formed. For milling time 1 hour obtained 13.31% of ZnO, NaCl amounted to 85.6% and 1.1% $ZnCO_3$. The process of formation of ZnO compound has not been perfect for 1 hour milling time due to zinc carbonate. For milling time of 3 hours, the percentage of ZnO, NaCl, and $ZnCO_3$ respectively by 14, 8%, 84% and 1.20%. Results ZnO for 3 hours milling time increased but the resulting formation of ZnO is not perfect because of the persistence of the zinc carbonate remaining unreacted due to the calcination process entirely. Results obtained samples without milling is still the dominant constituent elements and not formed $ZnCO_3$. Percentage of compounds $ZnCl_2$, Na_2CO_3, NaCl, ZnO and $ZnCO_3$ respectively was 0.9%; 32.9%; 52.4%; 12.5% and 1.40%. The percentage value of 1.40% Zinc Carbonate there is only one peak so can not be said to have formed Zinc Carbonate (see table 3). It can be concluded that the longer the milling time, the weight percent of ZnO produced more and more.

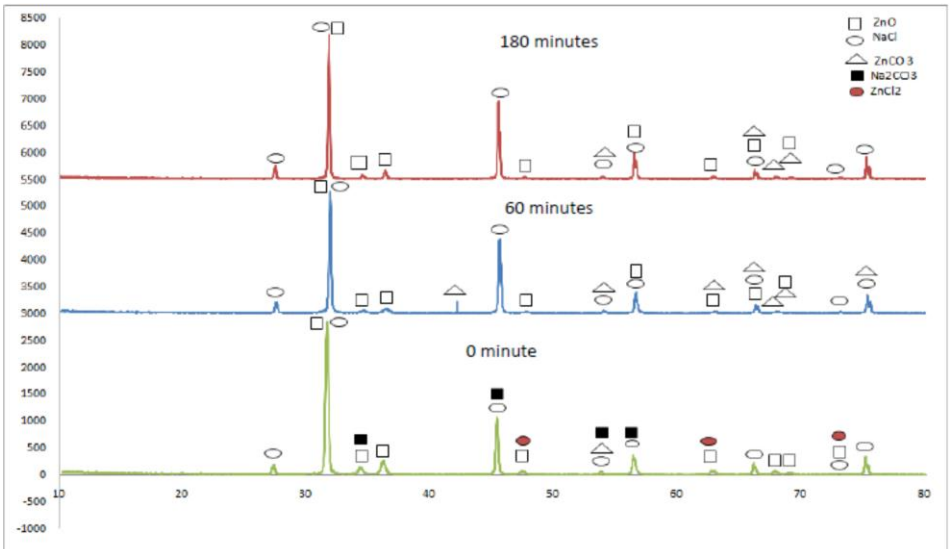


Figure 4. The XRD spectra for three samples i.e . 0 minute, 60 minutes , and 180 minutes.

Table 3. The percentage of compound formed a function of milling time

Compound	Milling time (minutes)		
	0	60	180
Zinc Chloride ($ZnCl_2$)	0,90 %	-	-
Sodium Carbonate (Na_2CO_3)	32,90 %	-	-
Sodium Chloride (NaCl)	52,40 %	85,60 %	84,00 %
Zinc Oxide (ZnO)	12,50 %	13,30 %	14,80 %
Zinc Carbonate (Zn CO_3)	1,40 %	1,10 %	1,20 %

4. Conclusion

The synthesis of ZnO nanoparticles obtained from the reaction of ZnCl2 and Na_2CO_3 in a solvent NaCl will form $ZnCO_3$ then calcination to form ZnO with the smallest particle size is (135.6 ± 35,8) nm. One of the factors that heavily influence the mechano-Chemical processes are milling time. From the time variation of milling indicate that the optimum point occurs at the time of 3 hours. The optimum point produces the best nanoparticle size. The resulting nanoparticles are still exceeding the size of the nano which is sized between 0.1 to 100 nm. This is due to the calcination process is very influential on the merger or an agglomeration of particles which could cause enlarged particle size. In the mechanochemical method ZnO is formed in a matrix of NaCl so that should be a separation between ZnO and NaCl are formed by means of dissolution.

5. References

[1] Guo, Xiuying., Dong Xiang, Guanghong Duan, Peng Moua, 2010, Tsinghua University, China, Journal Waste Management 30 (2010) 4–10

[2] Sinaga, P., 2009, Effect of Annealing temperature on microstructure, electrical properties and optical properties of conductive oxide thin films transparent ZnO: Al made by screen printing techniques, Final Project of Department of Physics Education, FPMIPA, Universitas pendidikan indonesia, Jakarta

[3] Weiqin., Junqin Li, Huaming Yang, Xierong Zeng, Xiaocui Ma, 2006, Powder Technology, Volume 168, Issue 3 p. 148-151

[4] Balaz, P., Alacova, A., Achimovicova, M., Ficeriova, J., Godocizkov, E., 2005, Journal Hydrometallurgy 77, p. 9–17.

[5] Aghababazadeh, R., B Mazinani, A Mirhabibi, And M Tamizifar, 2006, Metallurgy and Materials Department, Iran university of Science and Technology, Tehran, Iran, Journal of Physics: Conference Series 26, p. 312–314

[6] Kusumawati, Wheni., 2009, The effect of increasing hydroxyapatite concentration on the characteristics of Co-Cr composites as bone implant material, Final Project of Physics Program Sudy, University of Airlangga , Surabaya .

[7] Lin, I.J., 1998, , Journal of Thermal Analysis and Calorimetry 52(2), p. 453–461

[8] Heintz, A.S., Fink, M.J., Mitchell, B.S., 2007,, Journal Advanced Materials19 (22), p. 3894–3900.

[9] Ding, J., W.F. Miao, P.G. McCormick, R. Street, 1995, , Journal Appl. Phys., Lett. 67 , p. 3804