Proceeding The 1st IBSC: Towards The Extended Use Of Basic Science For Enhancing Health, Environment, Energy And Biotechnology
ISBN: 978-602-60569-5-5

Synthesis of Zinc Oxide (ZnO) Nanoparticle By Mechano-Chemical Method

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Abstract— Zinc Oxide nanoparticle have been synthesized by mechano-chemical method. The method is reacting zinc chloride (ZnCl2), Natrium Carbonate (Na2CO3), Sodium Chloride (NaCl) into Zinc Carbonate (ZnCO3) and Sodium Chloride (NaCl). This research focuses on the effect of variations in the length of time milling to the size of particles formed. Milling time used in this research are 0 hours, 15 minutes, 1 hour, 3 hours, 5 hours, 7 hours, 8 hours respectively. Calcination to remove CO2 carried out at a temperature of 4500C for 2 hours. This process may lead to aggregation of the particles so that the particles will swell due to the merger between the particles. Sodium Chloride (NaCl) removed by dissolving in aquadestilata with sonicator for 30 minutes a speed of 60 Hz. Characterization of the size of the particles formed is done using the Particle Size Analyzer. The measurement results show that the particles formed yet reached below 100 nm. 3 hours long milling time provides the best particle size is 135.6 nm. The particle size obtained when milling 1 and 7 hours respectively were 183.8 nm, 877.7 nm. ZnO compounds are formed for a variation of milling time 0 hours, 1 hour and 8 hours respectively was 12.55%, 13.31%, 14.8%.

Keywords: Mechano-Chemical, Nanoparticle

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.

One of material that is often studied to the nanoscale material is Zinc Oxide (ZnO). In Indonesia this material available in large quantities [1]. 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.

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. 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. 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. 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. Therefore, level controlled process parameters indispensable in mechano-chemical method. 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.

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.

RESULTS AND DISCUSSION

Milling process is determined by the length of time milling parameters. Variations milling time is used to determine the length of milling time best 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 4500 C for 2 hours is used to remove CO2 from ZnCO3 and NaCl. After calcination, the powder obtained ZnO and

NaCl and CO2 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.

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. 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. Data obtained from the deposition time of the observations that have been made for each variation of milling time stated in Table 1. Table 1 shows that the deposition time is directly proportional to the time of milling. This phenomenon occurs until a certain time. After that, the precipitation decreases.

Table 1. The relationship between milling and deposition

Milling time (minute)	Deposition time (minute)
0	126
15	203
60	335
180	480
300	328
420	279
480	143

The result of particle size using the Particle Size Analyzer obtained varied sizes, as stated in Table 2. The particle size for the milling time 1 hour, 3 hours and 7 hours respectively is 183.8 nm, 135.6 nm and 877, 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.

Table 2. The Size particle produce

Milling time (minute)	Particle size (nm)
60	183.8
180	135.6
420	877.7

The results of XRD spectra in analysis using Xpowder program with the database used is ICDD Pcpdfwin 1998. Results XRD spectra for 1 hour prior to analysis can be seen in Figure 1.. XRD observations made when the sample has not dissolved into aqua bidestilata and samples still contained a dominant element sodium chloride.

XRD observation results for the milling time of 0 hours 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. The XRD results for the three samples could be seen figure 2

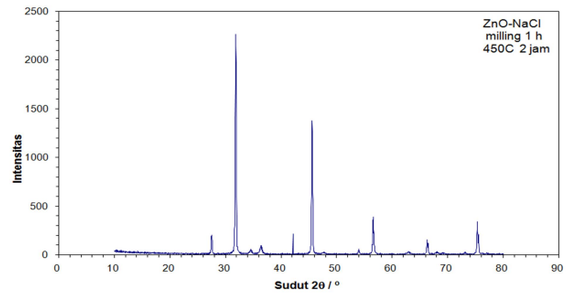

Figure 1. The XRD results for samples calcined one hour

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% ZnCO3. The process of formation of ZnO compound has not been perfect for 1 hour milling time due to zinc carbonate. For milling time of 8 hours, the percentage of ZnO, NaCl, and ZnCO3 respectively by 14, 8%, 84% and 1.20%. Results ZnO for 8 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 ZnCO3. Percentage of compounds ZnCl2, Na2CO3, NaCl, ZnO and ZnCO3 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.

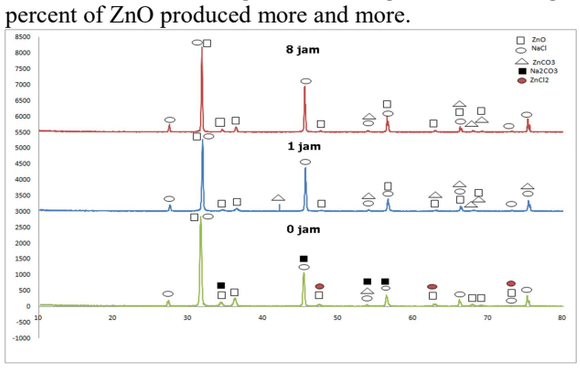

Figure 2. The XRD spectra for three samples i.e . 0 hour, 1 hour , and 8 hours.

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

Compound	Milling 0 hour	Milling 1 hour	Milling 8 hours
Zinc Chloride (ZnCl2)	0,9%	-	-
Sodium Carbonate (Na_2CO_3)	32,9%	-	-
Sodium Chloride (NaCl)	52,4%	85,6%	84,0%
Zinc Oxide (ZnO)	12,5%	13,3%	14,8%
Zinc Carbonate (Zn CO_3)	1,40%	1,1%	1,20%

The size of the crystal to milling for 1 hour obtained 35.50 ± 7.32 nm and for milling 8 hours obtained the crystal size is 50.65 ± 9.25 nm as well as the size of the crystals obtained without milling was 64.49 ± 22.49 nm (see table 4). The size of the crystals can grow large because of the influence of calcination and milling processes which cause agglomeration.

Table 3. Crystal size of the sample

Milling time	Size of crystal
1 jam	35,50±7,32nm
8 jam	50,65 ±9,25
0 jam	64,49±22,49

CONCLUSION

The synthesis of ZnO nanoparticles obtained from the reaction of ZnCl2 and Na2CO3 in a solvent NaCl will form ZnCO3 then calcination to form ZnO with the

ISBN: 978-602-60569-5-5

smallest particle size is 136.5 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.

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