Synthesis and Characterization of Cu/ZnO Electrocatalyst Nanoparticle via Solvothermal Method

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Abstract. The global warming is triggered by an increase in greenhouse gases that mostly contain CO_2. It is a great concern to the whole world to reduce CO_2 levels in the atmosphere. To reduce CO2 at low over potential and high kinetics, here we synthesize the bimetallic of Cu and Zn. The synthesis method is carried out by solvothermal method with variations in temperature and concentration of precursors. The synthesis results are then characterized using SEM, XRD, and XRF. The relationship between solvothermal temperature and ZnO particle size is directly proportional. In addition, the greater the concentration of cu precursors used, the easier cu particles are formed. At a solvothermal temperature of 150°C, there is only one sample of Cu3Zn1 (75% Cu precursor and 25% Zn precursor) that can produce Cu particles.

Keywords: CO_2, Catalyst, Synthesis, Precursor, Solvothermal**.**

1 Introduction

The increasing industry and motor vehicles have been proven to cause global warming [1]. Global warming is a major problem that is being faced by all countries in the world. Global warming is defined as an increase in the earth's surface temperature that impacts climate conditions in all parts of the earth and has the potential to cause disasters in various countries. The main contributing factor to global warming is the increase in greenhouse gases. CO_2 is the largest constituent component of greenhouse gases (about 72%), followed by CH_4 by 18%, and NOx by 9% [2]. Reducing greenhouse gasses is important to avoid the effects of climate change.

Carbon Capture Storage (CCS) is the most widely used method to reduce CO_2 gas emissions in the atmosphere. However, the CCS method requires large operating and energy costs [3]. As research progresses, a method is found to reduce CO_2 emissions more effectively, namely CO_2 reduction. Electrochemical CO_2 reduction reaction (CO_2RR) method is widely used because it is closest to commercialization application, relatively cheap, and more flexible [4]. However, compare to other electrochemical reduction reactions such as Hydrogen evolution reaction (HER) and Oxygen reduction reaction (ORR), CO_2RR confronts much more complications. Some of the challenges in CO_2RR is the products selectivity and high overpotential. In addition, the CO_2RR require multiple protons-coupled multiple-electron

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processes which is a huge challenge kinetically. Besides, the CO_2RR is often conducted in aqueous environment which will further lower the reaction kinetic due to competition with HER. Hence, catalyst design which will able lower the over potential, increase the reaction kinetics, and suppress the HER is essential.

Cu and Cu based catalysts are the most widely used and widely studied material in CO_2RR. Cu is known to be very active to reduce CO2, however, the product selectivity of using this catalyst is very low. Combining Cu with other metal such as Sn with different Cu/Sn ratio have shown can improve their selectivity.

Recently, Cu-Zn bimetallic or Cu and Zn based composite have gained an increase attention since both Cu and Zn are cheap and abundant. Addition of Zn to Cu is expected to inhibit HER, since Zn is not selective for HER. The good conductivity of Cu can reduce the resistance and thus improve the mass transport and overall kinetic of the reaction.

Here we present a simple route to synthesize the bimetallic of Cu and ZnO using solvothermal method. Solvothermal method are widely used method in producing chemical compound. The reaction takes place in a solvent at a temperature higher than its boiling point in a sealed vessel. This method of synthesis can produce nanomaterials and bimetallic in large quantity, making the up-scaling process feasible. In addition, this process only generates small amount of waste.

In electrocatalysis reaction, smaller size of the catalysts can prove large active surface area for the reaction. Thus, nanosized of electrocatalysts are usually preferred since it can provide large surface area for the CO_2RR and as a result improve overall kinetic of the reaction. In this present research, the temperature of the solvothermal reaction is optimized to give Zn with a small and uniform particle size. Thereafter that optimum condition is used to synthesize bimetallic of CuZnO.

2 Method

The ingredients used in this study were cooper acetate monohydrate ($Cu(CH_3COO)_2.H_2O$, 99.9%) and zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$, 99.9%), purchased from Sigma-Aldrich, sodium hydroxide (NaOH, 98%) ethylene glycol 99.8%, analytical ethanol 98% purchased from Merck, and aquades. The methodology on this research is divided into 3 main parts, they are (1) Optimization of ZnO nanoparticle synthesis by solvothermal method (2) Synthesis of Cu/ZnO nanoparticles (3) Drying process. ZnO nanoparticle synthesis by dissolved Zn precursor in 35 mL of ethylene glycol (EG) and 5 mL of H_2O to form solution 1, and 914 mg of NaOH dissolved in 17 mL EG and 3 mL of H_2O to form solution 2. Then, solution 2 is added to the solution 1 drop by drop. After 10 minutes, a vigorous stirring is carried out. The mixture of the two solutions is then transferred into the autoclave and put in the oven for 12 hours with a temperature variation of 120℃, 150℃, 180℃, 200℃, and 240℃ to analyze the particle size of ZnO. ZnO with the smallest particle size will be used as a synthesis temperature.

In synthesis Cu/ZnO composite is performed in the same way as the process of synthesis of ZnO nanoparticles. However, at this synthesis is used optimum temperature in the previous ZnO synthesis process (120℃ and 150℃) and variation concentration of precursors as Table 1.

Table 1. Sample With Variation Concerntration of Precursors

Sample	Solution 1	
	$Cu(CH_3COO)_2.H_2O$	$Zn(CH_3COO)_2.2H_2O$
	(mg)	(mg)
Cu	1,085	0
Cu3Zn1	1,085	419
Cu1Zn1	1,085	1,228
Cu1Zn3	1,085	3,731
ZnO	0	1,100

The mixture that has been put in the oven, then removed and cooled at room temperature. The precipitate are separated by centrifuge at 7000 rpm for 10 minutes and then washed twice with H_2O and ethanol. Next, the sample is put in a vacuum oven at 60 °C for one night until the sample is obtained in powder form.

3 Result and discussion

A. Synthesis of ZnO Nanoparticle

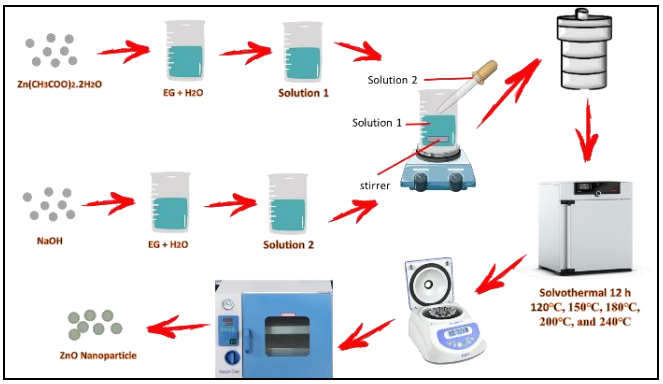


Fig. 1. ZnO Nanoparticle Synthesis Scheme with Solvothermal Method. Example of an unacceptable low-resolution image

In ZnO nanoparticle synthesis, the reaction was performed in an alkaline solution by adding NaOH solution as a source of –OH. With the addition of NaOH solution can trigger the formation of metal hydroxide precipitate. The addition of ethylene glycol to this process aims to prevent agglomeration. The reaction of zinc acetate dihydrate with ethylene glycol involves only water exchange of hydration with ethylene molecules without disrupting zinc-acetate bonding with the following reaction [12]

$$Zn(CH_3COO)_2.2H_2O + 2R\text{-}OH \longrightarrow Zn(CH_3COO)_2.2R\text{-}OH + 2H_2O$$

In **Figure 2** the ZnO solution is colorless which indicates that all Zn salts dissolve in a mixture of water and ethylene glycol. After the addition of NaOH, ZnO solution turns cloudy. This indicates that there is a precipitate occurring.

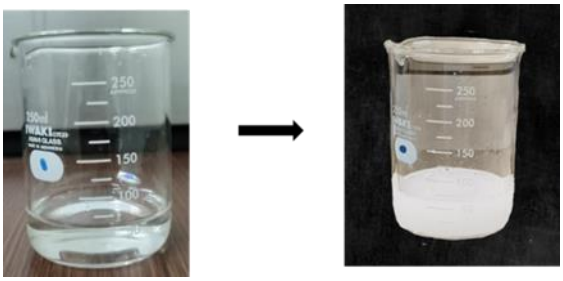


Fig. 2. Zinc Acetate Solution Before and After NaOH Is Added.

Precipitate formed at room temperature in this process are $Zn(OH)_2$ precipitate as in the following reactions [13] :

$$Zn(CH_3COO)_2.2H_2O + 2\ NaOH \longrightarrow Zn(OH)_2 + 2CH_3COONa$$

In general, all $Zn(OH)_2$ polymorphs are more soluble and less stable compared to ZnO so $Zn(OH)_2$ can be converted quickly into ZnO in the presence of heat [13]. The reactions that occur in this process are:

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

B. Analysis of Composition and Average Crystal Size of ZnO

In **Figure 3** it can be seen that ZnO synthesis without the use of solvothermal method or known as precipitation method, ZnO nanoparticles can also be produced. This can occur due to the heat received by the sample during the drying process in the vacuum oven at a temperature of 60 °C and a time of 28 hours so that the precipitate of Zn(OH)2 can be converted into ZnO nanoparticles [14].

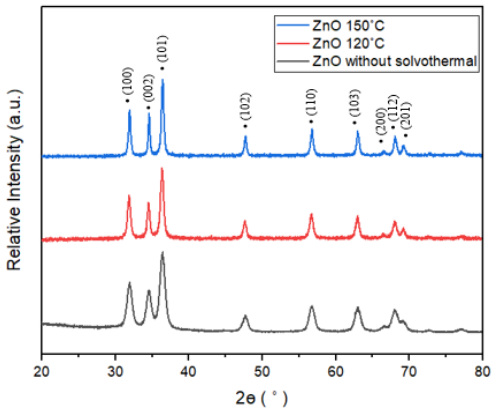


Fig. 3. XRD Graph of ZnO Synthesis Results at Solvothermal Temperatures of 120°C and 150°C, and Without Solvothermal Method.

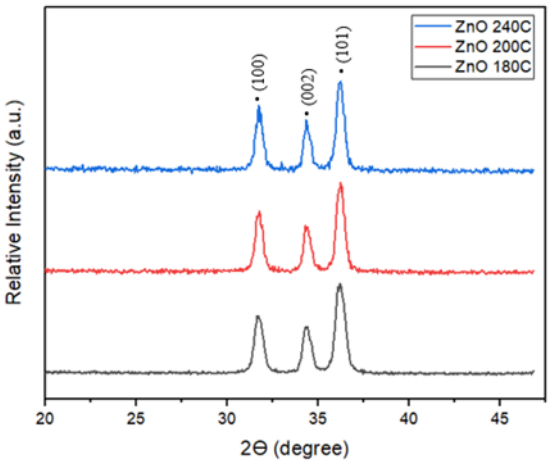


Fig. 4. XRD Graph of ZnO Synthesis Results at Solvothermal Temperatures of 180°C, 200°C, and 240°C.

From the resulting ZnO diffraction graph, miller index at 150°C depicts the field of wurtzite hexagonal crystals and corresponds to JCPDS 36-1451 data as in Table 2.

Table 2. Reference Data for Zin Oxide Hexagonal Wurtzite

2Θ (°)	Peak Number	h	k	l
31.7694	1	1	0	0
34.4211	2	0	0	2
36.2521	3	1	0	1
47.5376	4	1	0	2
56.6015	5	1	1	0
62.8626	6	1	0	3
66.3783	7	2	0	0
67.9608	8	1	1	2
69.0981	9	2	0	1

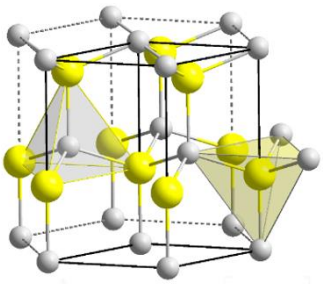


Fig. 5. Unit Cell Wurtzite

In addition, from the diffraction graphs in **Figure 3** and **Figure 4** can be calculated crystal size of ZnO synthesis at various temperature using the scherrer equation as follows:
Where k is a scherrer constant that depends on the crystalline shape and can be considered as

$$D = \frac{k\lambda}{B \cos\theta} \quad (1) \qquad (1)$$

0.89. λ indicates the x-ray wavelength of Cu radiation of 0.154 nm. B is the FWHM value of the width of the diffraction peak at half the maximum intensity, and Θ is the peak diffraction angle in radians. ZnO crystal size in Table 3 is calculated based on FWHM at peak (101).

Table 3. Zinc Oxide Crystal Size with Temperature Variation

Method	Solvothermal Temperature (℃)	Crystal Size (Å)	Crystal Size (nm)
Precipitation	-	116.341	11.634
Solvothermal	120	144.317	14.432
	150	150.831	15.083
	180	166.904	16.690
	200	196.993	19.699
	240	219.781	21.978

From the results in Table 3 shows that the higher the solvothermal temperature used, the larger the crystal size of ZnO will also be. This happens because with high system temperatures, the solubility of metal oxides decreases drastically which causes system supersaturation. Rapid supersaturation of the system can trigger a rapid nucleation process that forms the nuclei of particles and continues to grow [15]. Moreover, using the precipitation method produces a smaller ZnO crystal size compared to using the solvothermal method.

C. Size Analysis of ZnO Particle Diameter

Analyze ZnO particle size from synthesis using Scanning Electron Microscopy (SEM). All ZnO sample has a rounded shape (sphere). From the SEM results, ZnO samples will be more agglomerated with increasing solvothermal temperature.

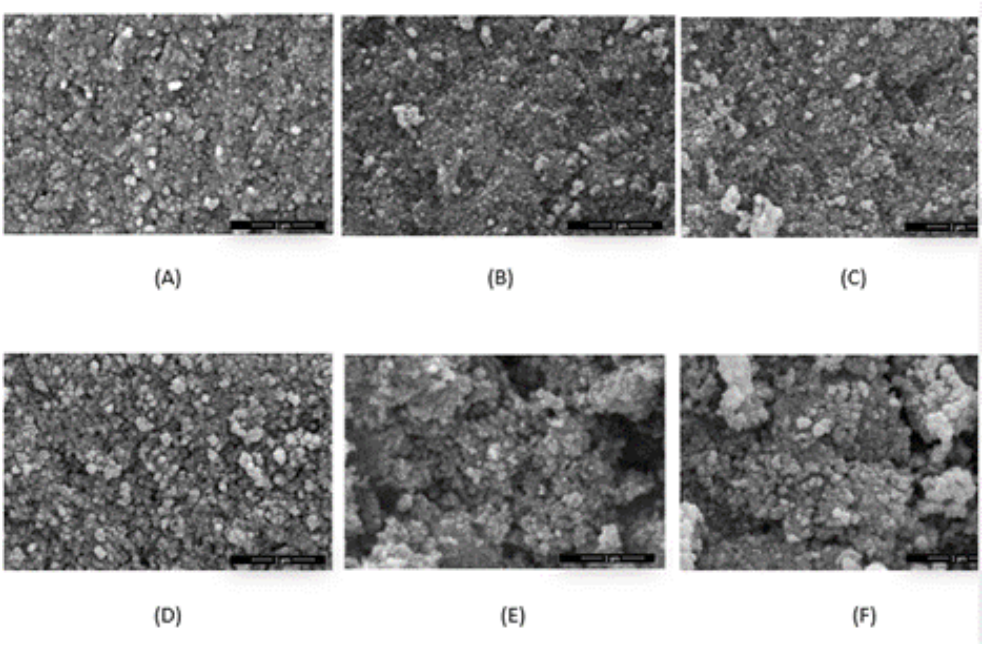


Fig. 6. SEM Result of ZnO (A) No Solvothermal (B) Temperature 120 °C (C) Temperature 150 °C (D) Temperature 180 °C, (E) Temperature 200 °C, and (F) Temperature 240 °C.

From the SEM results, the average diameter of particles and the distribution of ZnO particle diameters resulting from synthesis with temperature variations using ImageJ and origin software.

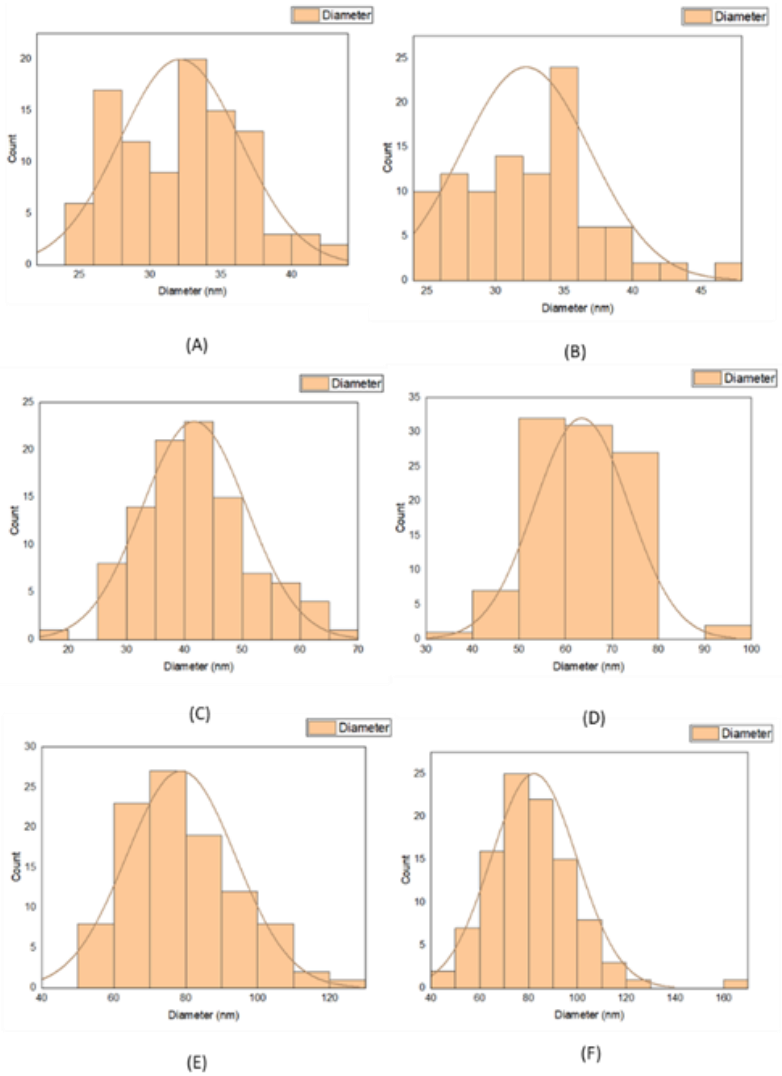


Fig. 7. Diameter distribution of ZnO (A) Without Solvothermal (B) Temperature 120 °C (C) Temperature 150 °C (D) Temperature 180 °C, (E) Temperature 200 °C, and (F) Temperature 240 °C.

From the diameter distribution diagram obtained the average diameter of ZnO particles at various temperatures as follows:

Table 4. Average Particle Diameter of Zinc Oxide with Solvothermal Temperature Variation

Method	Solvothermal Temperature (°C)	Particle Diameter (nm)
Precipitation	-	32.111
Solvothermal	120	32.224

	150	41.726
	180	63.482
	200	78.664
	240	82.289

Thus, it can be describe by the graphs of the relationship between the average particle diameter and the solvothermal temperature used in the synthesis of ZnO nanoparticles as follows:

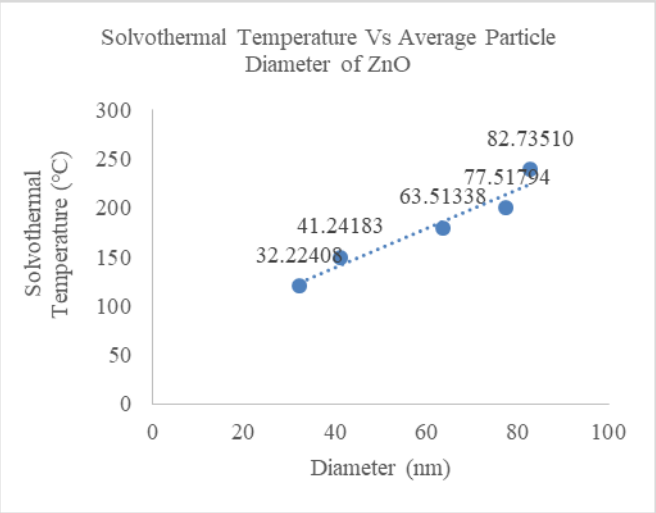


Fig. 8. Graph of Solvothermal Temperature Vs Average Diameter of ZnO Particles

The higher the solvothermal temperature used in the ZnO synthesis process, the greater the average diameter of the particle. Because at high temperatures particles begin to agglomerated caused by Ostwald Ripening. Where higher temperatures are used, small solid grains will have higher solubility and a large steam pressure than large solid grains, consequently thermodynamically unstable. To achieve equilibrium conditions, small solid grain molecules diffuse from one solid grain to another resulting in large solid grains growing [16]. Thus, in this study, optimum temperature was used for the synthesis of Cu/ZnO nanoparticles are 120°C and 150°C.

D. Synthesis of Cu/ZnO Nanoparticle

Fig. 9. Cu/ZnO Nanoparticle Synthesis Scheme with Solvothermal Method

At the time of the addition of NaOH to the Cu and Zn solution, the originally transparent blue solution became murky blue as shown in fig.10. This occurs due to the presence of $Zn(OH)_2$ precipitate formed. In the Process of Cu/ZnO synthesis using solvothermal method, Zn precursors are not reduced and only Cu is reduced, this is because Cu (Eo = 0.153 V) has a greater standard reduction potential compared to Zn (Eo = -0.7618 V) [17].

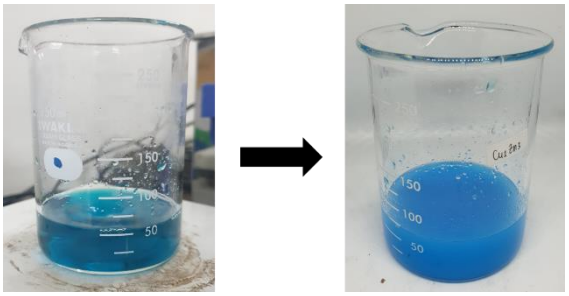
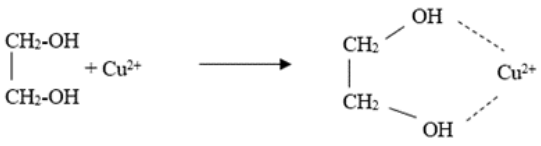


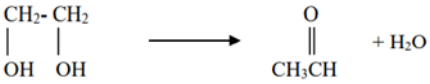
Fig. 10. Cu-Zn Solution Before and After NaOH Is Added.

After the addition of cu precursors in ethylene glycol solution, Cu^{2+} ions interact with ethylene glycol molecules and form a complex $[Cu(II)EG^{2+}]$ according to the following equation [18]:

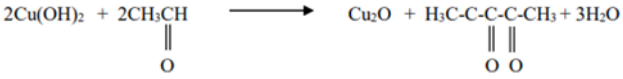


Furthermore, in the presence of water, the complex is converted into a Precipitate $Cu(OH)_2$ because the constant stability of the complex is smaller than $Cu(OH)_2$ [18].

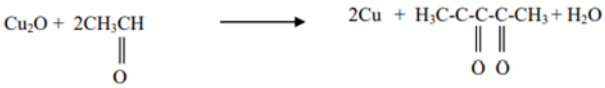
During the reaction, the acetaldehyde molecule is formed by dehydration of ethylene glycol [18].



Then, the precipitate of $Cu(OH)_2$ is reduced to Cu_2O at high temperatures [18].



Due to instability, the subsequent formation is reduced by acetaldehyde to form Cu particle [18].



The synthesis of Cu/ZnO powder can be seen in **Figure 11**.

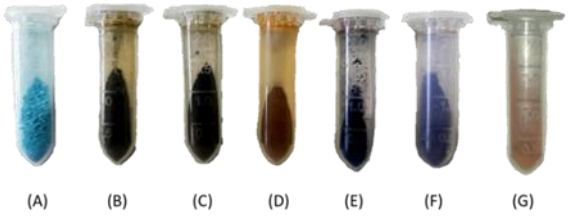


Fig. 11. Synthesis Result (A) Cu3Zn1 No Solvothermal (B) Cu3Zn1 120°C (C) Cu1Zn1 120°C (D) Cu1Zn1 150°C (E) Cu3Zn1 150°C (F) Cu1Zn3 150°C (G) Cu pure 150°C.

The color in the Cu3Zn1 sample without solvothermal is still the same as the color of the Cu and Zn precursor mixture solution after NaOH is added. For samples synthesized via solvothermal method has different colors when performed variations in temperature and concentration.

E. Composition Analysis and Metal Content of Cu/ZnO Composite

At a solvothermal temperature of 150°C for Cu3Zn1 there is a peak Cu formed. This can happen because with the higher solvothermal temperature, the precipitate of $Cu(OH)_2$ can be reduced to Cu_2O. The **Figure 13** shows that without the solvothermal method, there is no Cu_2O and Cu are formed in the Cu3Zn1 sample. Thus, it can be concluded that in the absence

of heat from the solvothermal reaction, $Cu(OH)_2$ cannot be reduced to Cu_2O and Cu. Thus, in the synthesis of Cu/ZnO is then used temperature 150 °C and obtained XRD graph for all catalyst samples as shown in **Figure 14**. In the sample Cu1zn1 and Cu1Zn3 there is no formation of Cu but Cu_2O because the number of precursors Zn is too much as can be seen in Table 1. So that ethylene glycol will be more widely used as a capping agent for ZnO synthesis reactions that cause the least ethylene glycol left to reduce precursors Cu.

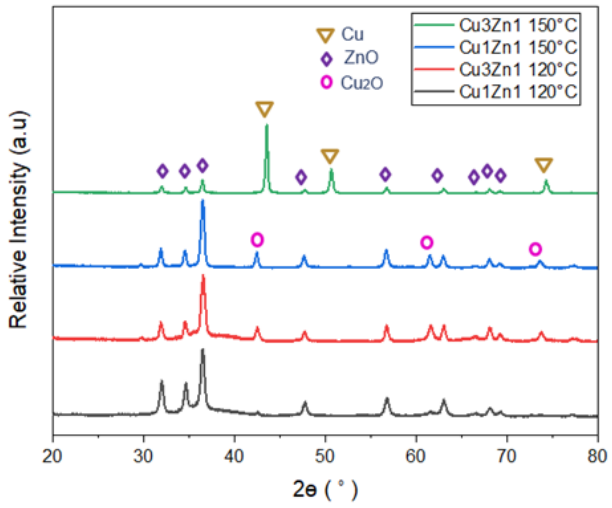


Fig. 12. XRD Graph Of Synthesis Results Cu3Zn1 and Cu1Zn1 with Solvothermal Temperature 120°C Vs 150°C

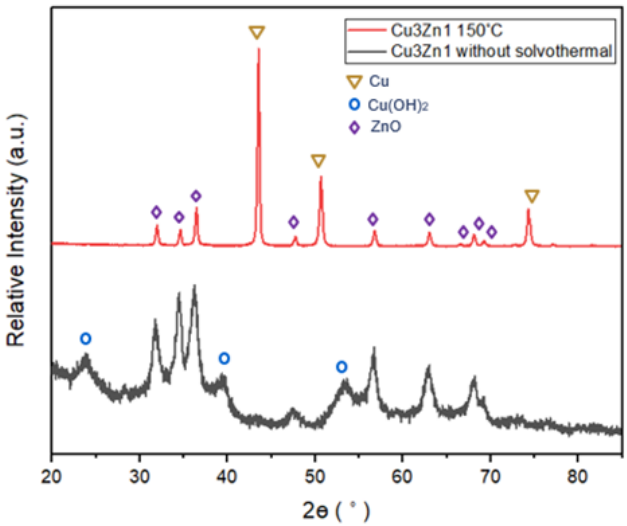


Fig. 13. XRD Graph Cu3Zn1 without Solvothermal Vs Cu3Zn1 150°C.

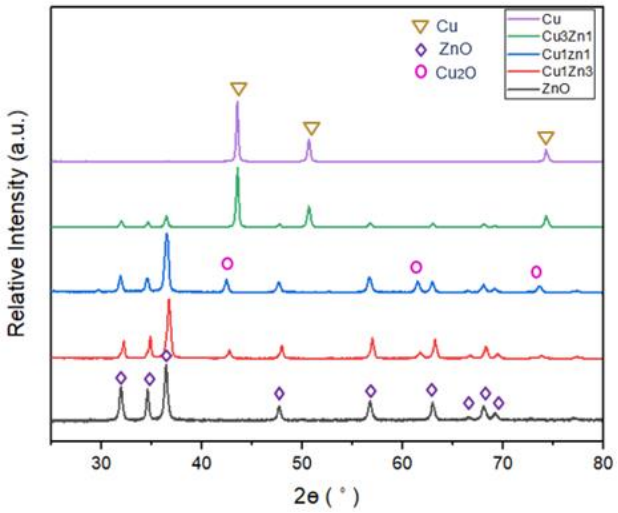


Fig. 14. XRD Graph of Cu/ZnO with Solvothermal Temperature of 150°C.

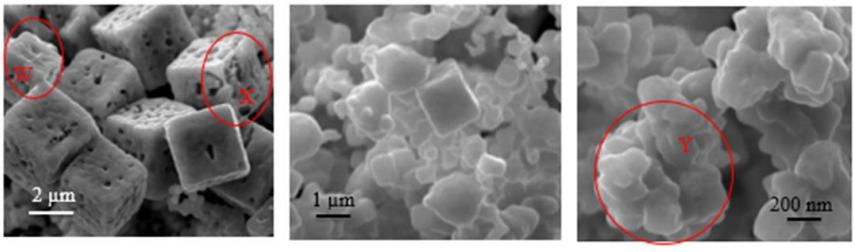
Using X-Ray Fluoresence (XRF) analysis, percent weight of Cu and Zn metal were obtained for each sample of Cu/ZnO nanoparticles as follows:

Table 5. Cu and Zn Metal Content in Cu/ZnO Samples

Sample	Wt %	
	Cu	Zn
Cu1Zn1	49.4765	50.5218
Cu3Zn1	61.8317	38.1656
Cu1Zn3	32.0929	67.8762

In each sample Cu / ZnO synthesis results have wt% that is not as it should be, this can be caused by a less long stirring time so that the precipitate of metal hydroxide that occurs less homogeneous which causes a less perfect precipitation process [19].

F. SEM Analysis for Cu/ZnO Sample



(A) (B) (C)

Fig. 15. SEM of Cu Pure with Solvothermal Temperature 150°C At Magnification (A) 20000 (B) 25000 (C) 50000 times.

Morphology of Cu pure samples displayed at low and high magnification. In the sample, Cu pure has a cubic form and a wide size distribution that is nano-sized to submicronous. Micro-sized particles are dominant and have rough surfaces as shown in W and X particles. Some of these cubic Cu are an array of nano-sized particles, as evidenced by the Y particle at a higher magnification. In the process of synthesis, ethylene glycol used not only serves as a solvent, it also has a role as a surfactant favoring the oriented packing of small Cu particles [11]. Agglomeration in small particles, especially nano-structures, can be driven by a reduction in surface energy and the agglomeration can occur due to the presence of ethylene glycol surfactants. So that the arrangement can be reflected as a submicron-sized Cu particle as in the W and X particles.

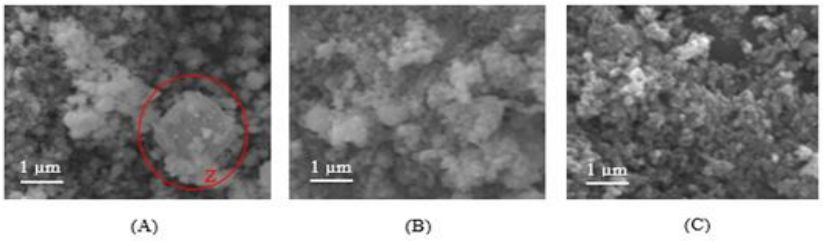


Fig. 15. SEM of Cu Pure with Solvothermal Temperature 150°C At Magnification (A) 20000 (B) 25000 (C) 50000 times.

For Cu3Zn1 sample it can be clearly observed that there are two particle forms that are round (sphere) that indicate the formation of ZnO and cubic as in the Z particle that indicates the formation of Cu in the sample. When compared to the other two samples, Cu1Zn1 and Cu1Zn3 cannot be clearly observed the presence of cubic-shaped particles.

4 Conclusion

ZnO and Cu/ZnO Composite nanoparticles can be synthesized using solvothermal methods with precursors cooper acetate monohydrate ($Cu(CH_3COO)_2.H_2O$) and zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) because, in the presence of heat it can convert metal hydroxide into ZnO and Cu particles. The higher the solvothermal temperature used in the ZnO synthesis process, the greater the average diameter and crystal size of the particle. Cu-Zn ratio can be easily controlled by variating of precursors concentration. It is also indicates that we can also produce tunable H_2/CO ratio. The Cu/ZnO electrocatalyst from this study is potentially used in CO_2 reduction reactions to syngas because ZnO particles have a diameter of about 20-60 nm. So, it has a larger surface area so that many sites are active for CO_2 reduction reactions according to experiments conducted before [11].

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