Article

Synthesis of ZnO/CuO Composite by The Electrochemical Method in The Acetat Acid Solution

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Abstract. The metal oxide composite is used to the microelectronic circuit, piezoelectric, fuel cell, sensor, catalyst, coating for preventing corrosion, and solar cell. The ZnO/CuO is one of the metal oxide composites. The combination of ZnO and CuO is the potential composite used to the catalyst and the anti-bacterial agent. The method used in this research was the electrochemical method in the acetate acid solution. The acetate acid solution used in this research is cheaper than the succinite acid used in the previous research. The electrochemical method has advantages due the easy to control and cheap. The composite resulted was analyzed by the XRD and the FTIR. The aims of this analysis are to know the crystallite phase, structure, and the functional groups of the particle resulted. The analysis showed that the ZnO-CuO composite can be resulted by the electrochemical method.

Keywords: ZnO/CuO, electrochemical, synthesis, composite, acetate acid

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1. Introduction

The semiconductor of the metals oxide was used as the microelectronic circuit[1], piezoelectric[2], fuel cell[3], sensor[4], catalyst[5], coating for preventing corrosion[6], and the solar cell[7]. These cause the research on the metals oxide to be interesting for researchers. The ZnO is the good antibacterial agent due to the photocatalytic properties but has a large band gap of 3.2 – 3.5 eV. This high band gap can reduce the photocatalytic properties of ZnO. For that, it requires a mixture of materials which can reduce the band gap value. Addition of CuO to ZnO can reduce the band gap value([8]. The combination of these two metals oxide can produce composites that can be used for catalysts[9], [10], degradation chemical[11], photodetector[12], photochemical cell[13] and antibacterial substances[14]. The ZnO/CuO is a type of metal oxide semiconductor composite.

There are several methods of synthesizing ZnO/CuO composites, including sonochemistry[15], sol-gel method[16], ultrasound assisted co-precipitation method[17], hydrothermal synthesis method[18], and electrochemistry[19]. The advantages of the electrochemical method compared to the other methods are simpler, cheaper, and easy to control.

Electrosynthesis of CuO/ZnO has been successfully carried out in the succinic acid (Das and Srivastava, 2017). However, the succinic acid raw material used is difficult to obtain and the price is relatively expensive. For this reason, the cheaper and easier solution to obtain replacement is needed. One alternative that can be used is the acetic acid solution. Acetic acid is an organic and weak acid group like succinic acid but has a cheaper and easier to obtain than succinic acid. Acetic acid has a better level of solubility in water than succinic acid. The purpose of this research is to synthesize the ZnO/CuO composite by the electrochemical method in the acetic acid electrolyte solution

2. Experimental

The reagents used to the synthesis of ZnO/CuO composite by the electrochemical method are acetic acid, NaOH, and succinic acid. The reagents were purchased from Merck and used without further purification. The 2.5 x 5 cm Zn and Cu plates were used as the source of ZnO/CuO composite. The 0.15 M 200 mL acetate acid solution was used as the electrolyte solution. The 1 M NaOH was added to the electrolyte solution until the pH is 7. The electrolysis was done in a 400 mL beaker glass as a cell. The cell had three electrodes. The Zn plate is used as the cathode and the Zn and Cu plates are used as the anode. the distance between the plates is 2 cm. The dimensions of electrodes were 5 × 2.5 cm. The electrodes were immersed in the electrolyte solution at a depth of 2 cm and connected to DC power supply (Zhaoxin PS-3005D). The synthesis of ZnO/CuO composite was done at constant voltage 17 V for 2 and 3 hours under 300 rpm constant stirring and room temperature. Fig 1 shows the schematic diagram of the experimental setup. The particles were filtrated by filter paper and washed by aquadest. The particles were dried at 80°C for the overnight. The particles were calcinated at 500 ^{o}C for 5 hours. The 0.15M succinic acid solution is also used as an electrolyte solution for comparison. The particles were analyzed by XRD, FTIR, and SEM.

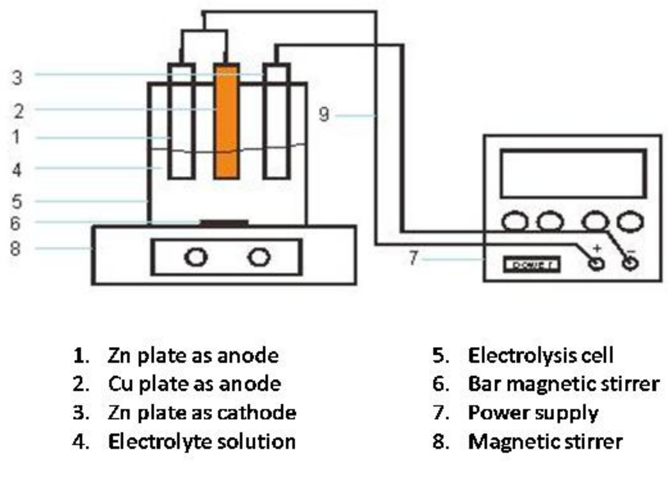

Fig. 1. The schematic diagram of the experimental setup.

3. Result and Discussion

The ZnO/CuO composite synthesized by the electrochemical method follow the reactions:

- Anode

$$Zn \rightarrow Zn^{+2} + 2e^- \quad (1)$$

$$Cu \rightarrow Cu^{+2} + 2e^- \quad (2)$$

- Cathode

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

At the pH of the solution 7, the Zn^{+2} ions react with OH^- ions to form $Zn(OH)^+$ ions while the Cu^{+2} ions react with OH^- ions to form $Cu(OH)^+$ ions.

$$Zn^{+2} + OH^- \rightarrow Zn(OH)^+ \quad (4)$$

$$Cu^{+2} + OH- \rightarrow Cu(OH)^+ \quad (5)$$

The further oxidation produces particles :

$$Zn(OH)^+ \rightarrow ZnO\downarrow + H^+ + e^- \quad (6)$$

$$Cu(OH)^+ \rightarrow CuO\downarrow + H^+ + e^- \quad (7)$$

The black particles was resulted. The SEM images of the particles is shown in Fig. 2.

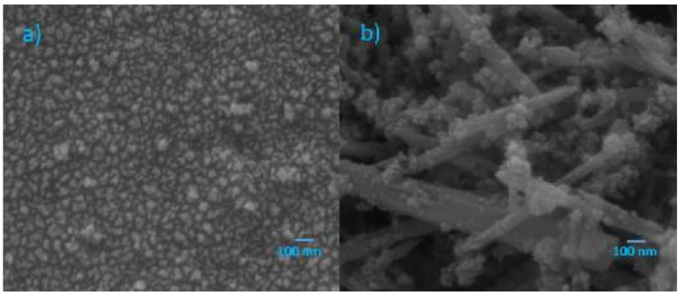

Fig. 2. SEM Image of the particles resulted (a) 2 hrs and (b) 3 hrs

The particles have the uniform sphere-shaped 30 to 80 nm at the 2 hrs electrolysis time. The rod and sphere-shaped particles were formed at the 3 hrs electrolysis time.

Fig. 3 shows the results of FTIR analysis. The Cu-O bonds are located in the wave number 700-400 cm^{-1}. There is the peak at the wave number around 560 cm^{-1} which indicates the formation of Cu-O bonds in the sample. The Zn-O functional group is characterized by the formation of the peak at 400 cm^{-1} to 480 cm^{-1}. The O-H functional group is formed in the range of wave numbers about 3400 cm^{-1}. The presence of O-H groups comes from CH_3COOH and NaOH. The presence of the peak at wave numbers 2850 to 2950 cm^{-1} indicates the presence of the C-H bonds which comes from CH_3COOH. The CO_2 group appears at wave number 2300 cm^{-1}. This CO_2 group is from the air.

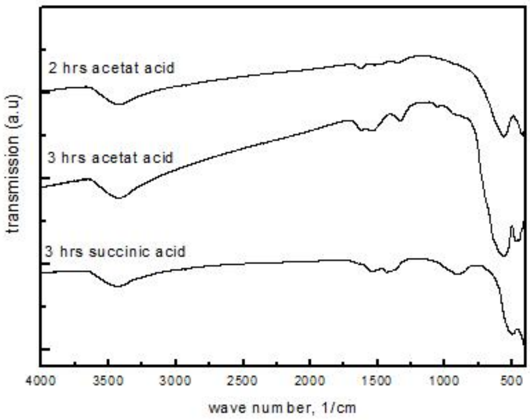

Fig. 3. The FT-IR spectrum of the particles resulted

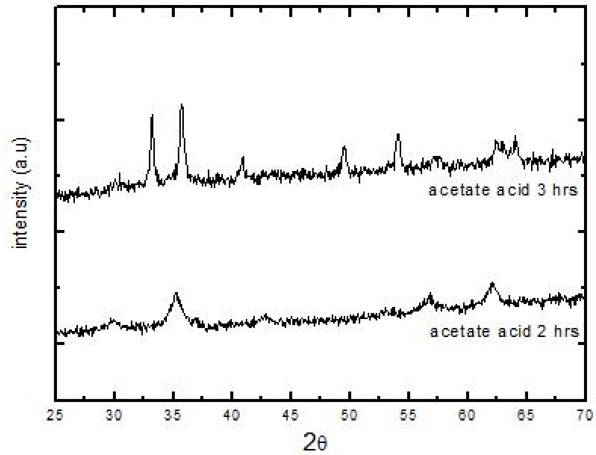

Fig. 4. The XRD patterns of the particles resulted

Fig. 4. was shown the XRD patterns of the particles resulted for 2 and 3 hrs the electrolysis time. The ZnO particles have three characteristic peaks about 31°, 34 °, and 36 ° and the CuO has one characteristic peak about 35 °. The composition and highest peak are determined by Match! 3 software. The result shows that the particles synthesized for 2 hrs the electrolysis time consist of the 61.2% ZnO and 38.8% CuO. The particles synthesized for 3 hrs the electrolysis time consist of the 8.4% ZnO and 91.6% CuO. The highest peak data was used to determine the size of the nanocrystal composite by the Scherrer equation. The results of calculating the size of the nanocrystal composite are shown in Table 1. Based on XRD analysis, the ZnO particles have a hexagonal structure that matches the COD (Crystallography Open Database) no. 96-101-1260. The CuO particles have a monoclinic structure that matches the COD database no. 96-101-1149.

Table 1. The highest peak and the crystallite size of the particles resulted

The electrolysis time	The highest peak (°2θ)	The crystallite size (nm)
2 hrs	35.22	24.39
3 hrs	35.46	47.08

4. Conclusion

The acetic acid solution can be used as the electrolyte solution in the synthesis of ZnO/CuO composite by the electrochemical method. The Zn plate is used as the cathode and the Zn and Cu plates are used as the anode. The synthesis of ZnO/CuO composite was done at constant voltage 17 V for 2 and 3 hours under 300 rpm constant stirring and room temperature. The result shows that the particles synthesized for 2 hrs the electrolysis time consist of the 61.2% ZnO and 38.8% CuO. The particles synthesized for 3 hrs the electrolysis time consist of the 8.4% ZnO and 91.6% CuO.

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