

Short Communication

Electrosynthesis and Characterization of $\text{Cu}(\text{OH})_2$ Nanoparticle using Cu and Cu-PVC Electrodes in Alkaline Solution

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$\text{Cu}(\text{OH})_2$ have been synthesized by electrochemistry technique using Cu and Cu-PVC electrodes in alkaline solution. The electrolysis process was carried out in 0.1 M KOH supporting electrode at room temperature. Experiments were performed in a three electrodes system using Cu and Cu-PVC as a working electrode, SCE as reference electrode and platinum wire as the counter electrode. The electrolysis of was performed using potential constant (1050 mV) in 50 mL capacity glass electrochemical cell. Universal Pulsa Dynamic EIS, Cyclic Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for electrochemical behavior measurements. XRD and XPS have been used to characterize the morphology, structure, and composition of the compounds at electrode surface. The results of this experiment shown the $\text{Cu}(\text{OH})_2$ is main product and higher purity. The advantages of our method for the $\text{Cu}(\text{OH})_2$ synthesis are low temperature, simple, inexpensive, non-toxic raw materials and environmentally friendly

Keywords: Electrosynthesis, $\text{Cu}(\text{OH})_2$, nanoparticle, Cu and Cu-PVC, alkaline solution

1. INTRODUCTION

Nano scale copper compounds are of research interest for the many applications. Synthesis of copper compounds nano scale has been actively researched for many decades because copper compounds is an important industrial material due to its novel physical and chemical properties. Among all metals used in modern electronic circuits, Cu is the most common one because of its excellent electrical conductivity and low cost. Copper compounds are one of the most normal

conductors in modern technologies and could be used widely in nano device. Therefore the development of copper compounds uniform nano particles has been intensively pursued [1].

$\text{Cu}(\text{OH})_2$ nano particle is a copper compounds are many applications. One of the main uses for copper hydroxide is a fungicide and nematocide. Copper hydroxide is the most toxic compound against *E. vermiculata* [2]. People also use it for insecticides for walnuts, wine grapes, and peaches among many other types of fruits and nuts commonly grown for agricultural purposes throughout the world. Copper hydroxide is used as fungicide on fruits, vegetables, ornamentals, the manufacture of rayon, as a source for copper salts, as a mordant, kill mold in paints. It can be used to color ceramics, as a catalyst, as an alternative to the bordeaux mixture, nematocide. Copper hydroxide is also occasionally used as ceramic colorant, combined with latex paint, making a product designed to control root growth in potted plants [1,3].

Synthesis of copper hydroxide ($\text{Cu}(\text{OH})_2$) nanoparticles attracted increased attention due to reliable low cost, specific size, well-defined morphologies and wide range of potential applications. Various methods for synthesis of copper hydroxide nanoparticles have been development with various methods, including biosynthesis [3], chemical co-precipitation method [4,5], a two-step template approach [6], wet chemical route [7,8], anion exchange method [9], and an electrochemical method [10,11].

This electrochemical method has an advantage over other methods in that the shape and atomic compositions of final copper compound films can be controlled by means of modulating the potential, reaction time, and the integrated charge passed through the cell [10]. Copper (II) hydroxide nano particles were synthesized via chemical co precipitation method from Copper Sulphate and Sodium Hydroxide [4]. Copper hydroxide nanowires were synthesized from copper chloride dihydrate and sodium hydroxide in the presence of Pistachio leaf extract at room temperature [3].

Composite based on conductive phase dispersed in polymeric matrices are recommended in order to obtain reproducible electroanalytical result, enhance electroactivity or selectivity [12]. These methods of pretreatment frequently cause changes to the surface composition, the surface roughness, the production of surface bound functional groups or the intercalation compounds owing to the insertion of ion, atoms and molecules into its interplanar space. These pretreated or modified electrodes are commonly used in electroanalysis, biosensors, electrochromism and electrocatalysis. This preparation method in comparison with the compression techniques is easier, economical and produces larger surface over apparent electrode area ratio. The use of metallic copper as an electrode for the electrochemical oxidation has been studied by several authors [13]. Although considerable currents were observed for some metals, the oxidation over potential for copper electrodes was much higher than those obtained when platinum or gold electrodes were used. The activity of the copper bound to nafion was related to the presence of Cu (II) and Cu (III) surface oxides.

The present study was technique with rapid, clean, non-toxic, and environmentally friendly for the synthesis of copper hydroxide nano particle by electrosynthesis method using Cu and Cu-PVC composite electrode at room temperature.

2. EXPERIMENT

2.1. Preparation copper electrode

Cu metal sheet (99.98% purity, 0.5 mm thick, Aldrich Chemical Company) was used to prepare Cu electrode. The metal sheet electrodes were prepared in square cut of 1 cm by length and wide respectively. The metal sheet electrodes were connected to silver wire with silver conducting paint prior covered with epoxy gum.

2.2. Preparation of a copper powder electrode (Cu-PVC)

Cu powder (< 2 micron in size and 99.9% purity, Aldrich Chemical Company) and PVC in 4 ml tetrahydrofuran (THF) solvent and swirled flatly to homogeneous followed by drying in an oven at 100°C for 3 hours. The mixture was placed in 1 cm diameter stainless steel mould and pressed at 10 ton/cm². A typical pellet contained approximately amount of Cu (95%) powder, and approximately 5% of PVC polymer. The total weighed of pellet obtained is approximately 1.5 g.

2.3. Characterization using XPS and XRD

The XPS was obtained from a Kratos Analytical, Digital 500, Ion pump system controller, Glassman High Voltage Inc. Minibeam Gun Control and Mg K α (1253.6 eV) X-ray. While a diffraction pattern was obtained using a X-ray diffraction (XRD) from a Phillips X-ray Diffractometer employing Ni filtered CuK α radiation (40 kV) at scan rate of 1/2° min⁻¹.

2.4. Electrochemical behavior of the electrodes

Universal Pula Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for electrochemical behavior measurements; data acquisition was accomplished using the voltmaster 4 software. Cyclic voltammetry experiments were performed in a three electrodes system using Cu metal sheet and Cu-PVC as a working electrode, an Ag/AgCl (saturated KCl) or SCE as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the SCE reference electrode.

2.5. Experimental procedure

The electrolysis process was carried out in 0.1 M KOH at room temperature. Experiments were performed in a three electrodes system using Cu and Cu-PVC as a working electrode, SCE as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the SCE. The electrolysis of Cu and Cu-PVC electrodes in 0.1 M KOH was performed using potential constant (1050 mV) in 50 mL capacity glass electrochemical cell.

3. RESULT AND DISCUSSION

3.1. Cyclic voltammetry of response using Cu and Cu-PVC electrodes

Figure 1A and 1B shows the cyclic voltammogram of Cu and Cu-PVC electrodes with anodic sweep from -700 to 700 mV in of 0.1 M KOH. Peaks A1, A2, A3 and A4 were due to the oxidation of Cu which is easily oxidized to form oxide compound. The alkaline medium would force the forming of coating of Cu₂O, CuO, and Cu(OH)₂ on the electrode surface. Beside that other species, might be deposited on the electrode surface depending on the potential, pH of the solution, the mass-transport conditions and ageing and surface restructuring processes [14].

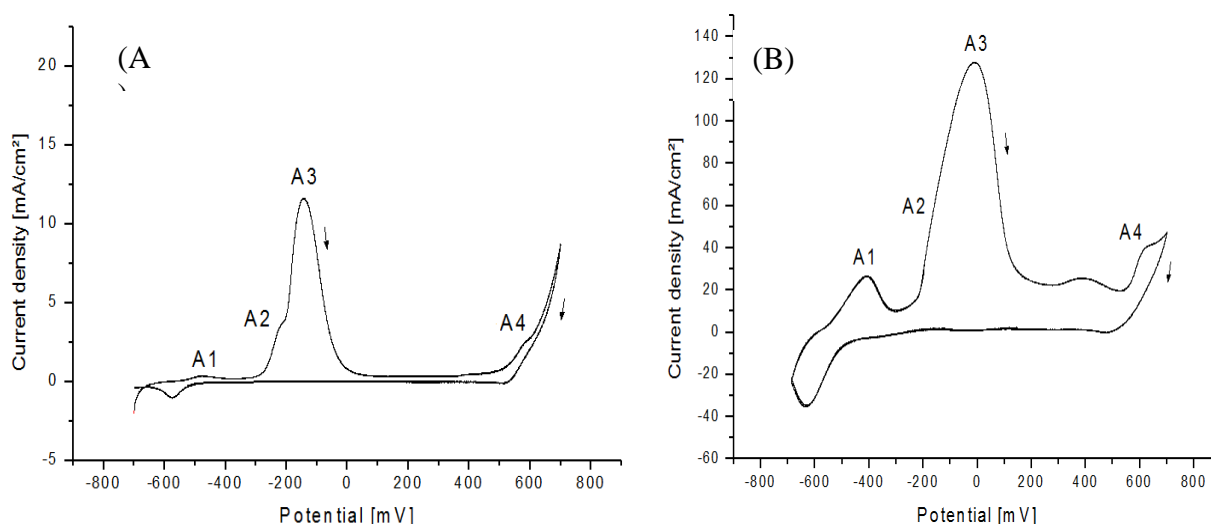
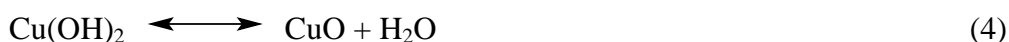
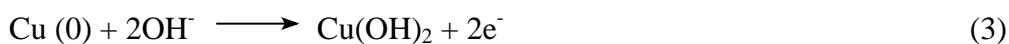


Figure 1. Cyclic voltammogram of (A) Cu metal and (B) Cu-PVC electrodes in 0.1 M KOH. Scan rate 10 mV/Sec.

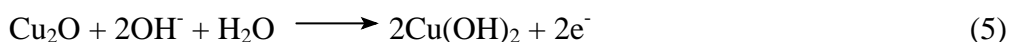
A1 peak which occurred -500 mV represent the oxidation of Cu (0) or Cu metal to Cu (I) which were in the form of CuOH and/or Cu₂O. Cu₂O represent intermediate of layer according to the following mechanism [15, 16]:



A2 peak which is the biggest and highest peak represent the oxidation of Cu (0) to Cu (II) and Cu (I) to Cu (II), with the following reaction:

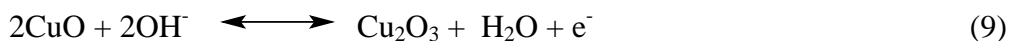
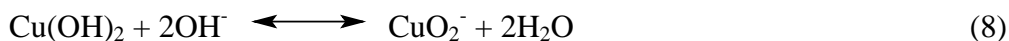
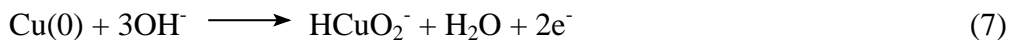


Oxidation reaction also come from Cu₂O which represent the layer on the surface of electrode.





While A3 peak of represent further oxidation of Cu (II) to Cu (III). Cu (III) species are more easily formed, and indeed detected at high hydroxide concentration, which reaction is [15]:

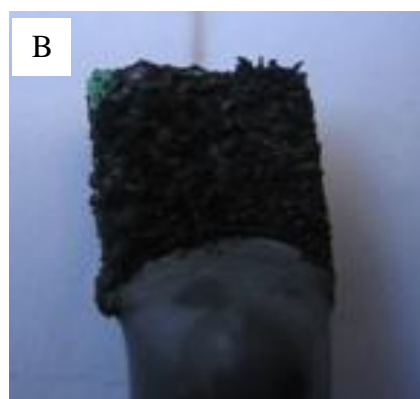
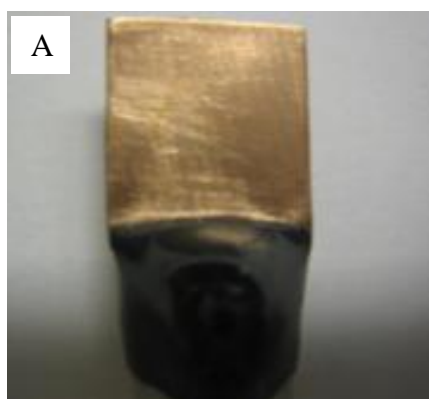


Cu (III) was detected at a potential of 0.6 V during the positive scan. The formation of Cu (III) species at $E > 0.6$ V may have a similar role in the electro catalytic process. Figure 1B shows the peak at 600 mV which represents the oxidation peak of Cu (II) to Cu (III). The differences between CV voltammogram between Cu and Cu-PVC electrodes is current density. Very much higher current density was produced when Cu-PVC electrode was used compared Cu electrode. The Cu-PVC electrode, prepared in pellets, showed good mechanical strength with electrical resistivity lower than 1 Ωcm , which is similar to that of composites as reported earlier [16]. The Cu-PVC composites are a hydrophobic electrode material. At about 0.6 V the formation of a soluble Cu (III) species takes place.

3.2. Sponge at Electrodes Surface Cu and Cu-PVC

Figure 2 (A) shows the Cu solid electrode that is ready to use, yellowish and not oxidized. Cu solid electrode is very essay to oxidation in the air will be form Cu oxide compounds at electrode surface. Cu solid electrode must be cleaned using sand paper and washed with deionized distilled water. Figure 2 (B) and (C) shows the sponge formed on the Cu solid electrode after electrolysis 0.1 M KOH, electrolysis time of 6 hours at a potential of 1050 mV. Figure 2 (D) shows the sponge formed on the Cu-PVC composite electrode after electrolysis 0.1 M KOH, electrolysis time of 6 hours at a potential of 1050 mV.

Figure 2 shows the Cu solid electrode have a good reactivity in KOH solution. Electrolysis 0.1 M KOH using Cu solid electrode will be form a black, green and light blue sponge.



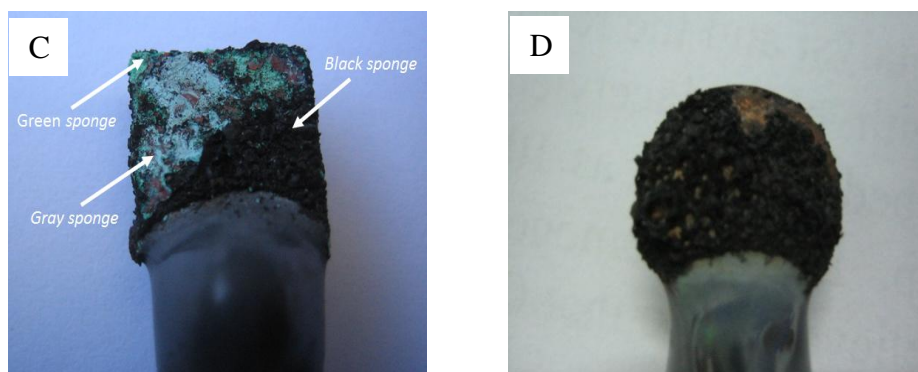
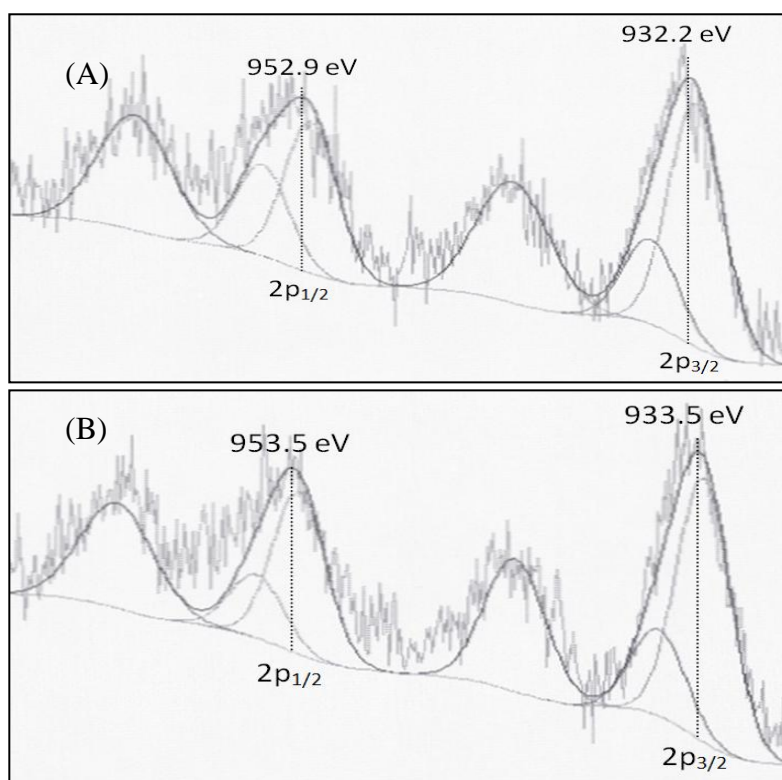


Figure 2. Sponge at Cu surface electrodes (A) fresh Cu solid electrode (B) black sponge (C) black, green and gray sponge (D) black sponge at Cu-PVC surface electrode

Sponge with different colors indicates different species of compounds. Cu (0) will be oxidation to Cu (I), Cu (I) to Cu (II) and Cu (II) to Cu (III). Green sponge is CuO or Cu(OH)₂, a light blue sponge is CuOH or Cu₂O and black sponge is Cu₂O₃.

3.3. Analysis of Sponge at Electrodes Surface using XPS

Figure 3A shows the spectrum of the Cu 2p from green sponge with binding energy 2p_{3/2} dan 2p_{1/2} is 932.2 and 952.9 eV, respectively. Table 1 shows the binding energy 2p_{3/2} dan 2p_{1/2} from the reference and this work.



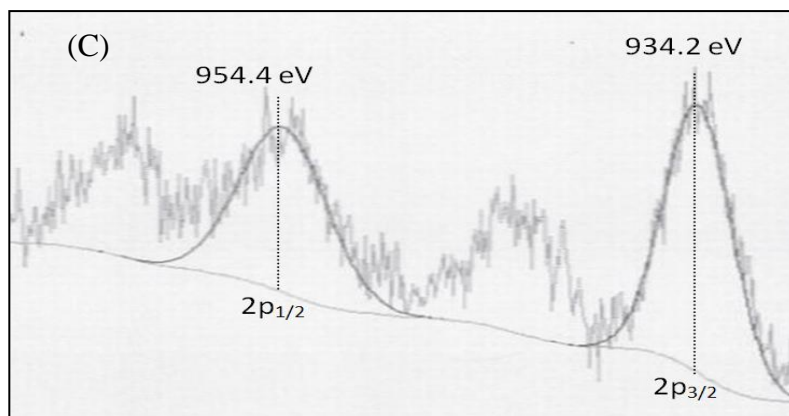
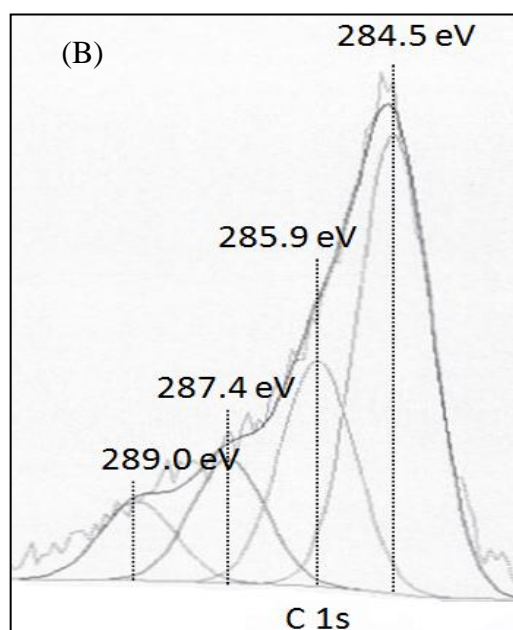
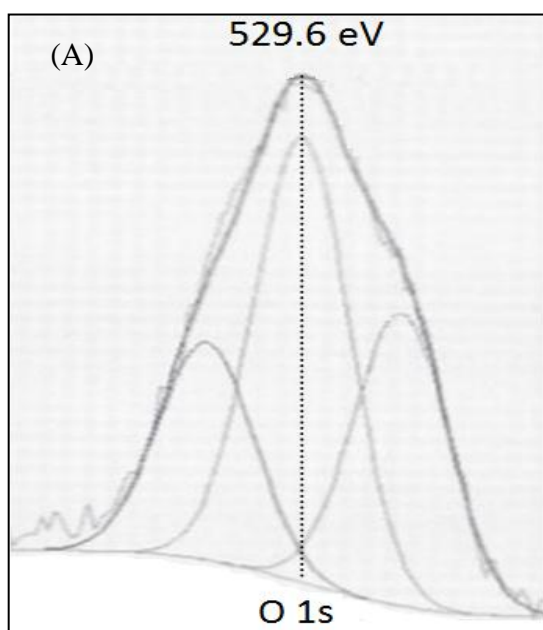


Figure 3. XPS Spectrum of Cu 2p from *sponge* at Cu solid electrode surface result of the electrolysis 0.1 M KOH, electrolysis time 6 hours and potential at 1050 mV with (A) green (B) light blue and (C) black color

Table 1. Binding Energy (eV) XPS Cu 2p_{3/2} green, light-blue and black sponge from references and this work

Compounds	Cassela & Gatta (2000) [17]	He et al. (2006) [18]	Moulder et al. (1992) [19]	This Work		
				Green Sponge	Light-blue Sponge	Black Sponge
Cu metal	-	-	932.7	-	-	-
Cu ₂ O	932.3 ± 0.3	932.4	932.5	932.2	-	-
CuO	933.4 ± 0.3	933.4-933.5	933.7	-	933.5	-
Cu(OH) ₂	934.5 ± 0.3	934.5-934.9	935.1	-	-	934.2



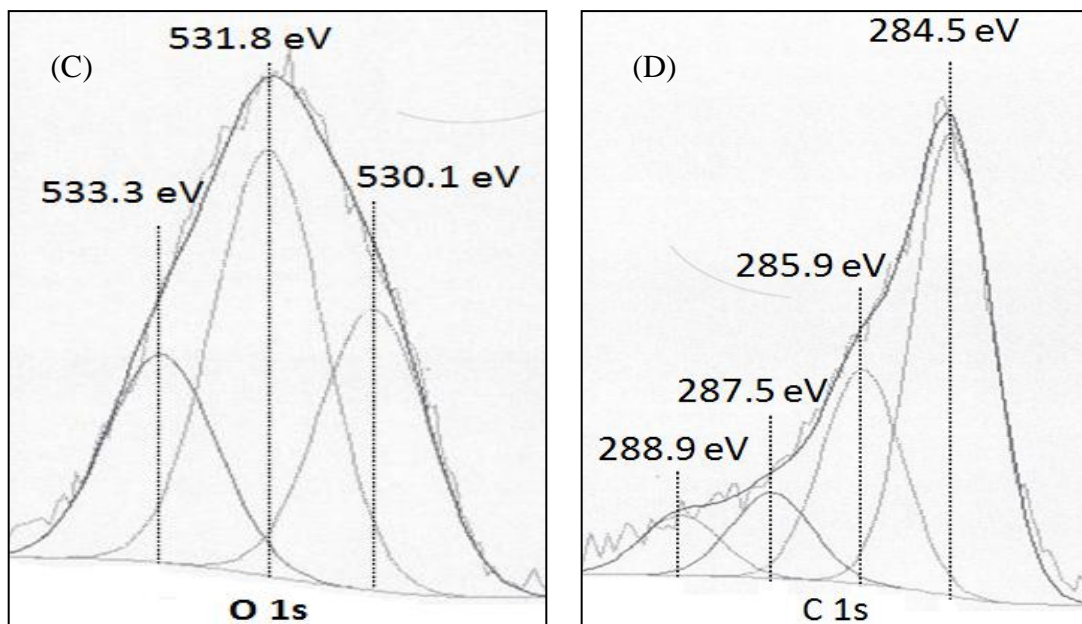


Figure 4. XPS Spectrum *sponge* at Cu solid electrode surface result of the electrolysis 0.1 M KOH, electrolysis time 6 hours and potential at 1050 mV, with are (A) O 1s green sponge (B) C 1s green sponge (C) O 1s light-blue sponge and (D) C 1s light-blue sponge

Based on the binding energy at Table 1, green sponge have the same binding energy between the sample and the reference that is, Cu_2O . It is a compound than the Cu (I) is formed before the compound Cu (II) and Cu (III). The results of this study supported by the spectrum XPS at O 1s and C 1s (Figure 4A and 4B). Figure 4A shown indicates that the compound Cu_2O has O 1s binding energy is 529.6 eV. According to Casella and Gatta [17] and Stefanov et al. [20] O 1s have binding energy of 530 ± 0.3 eV. This compound is Cu_2O . Thus, it was concluded that the first compound (green color) is formed of the Cu solid electrode surface is Cu_2O .

Table 1 shown the light-blue sponge have binding energy spectrum Cu $2p_{3/2}$ is 933.5 eV. Base on the binding energy from various references (Table 1) show CuO compounds. Thus, light blue colored compound formed on the surface of the Cu electrode is CuO. It is formed from the result of oxidation of Cu (I) to Cu (II). The results of this study supported by the spectrum of O 1s and C 1s shows the formation of bonds between carbon atoms with atomic O and H (Figure 4C and 4D). According to Casella and Gatta the spectrum of the C 1s have binding energy is 284.5 eV, the formation of CH bonds, when the C 1s have binding energy are 285.9, 287.5 and 288.9 eV, indicate the formation of a bond the C-OH, C = O, and COOH [17].

Figure 2B, 2C and 2D shown black sponge at the Cu electrode surface are dominant. Sponges with black colors are very stable and not change color at long time electrolysis. The longer electrolysis black sponge run more and more formed. Base on binding energy of Cu $2p$ spectra are the black sponge is, 934.2 eV, corresponding compound is $\text{Cu}(\text{OH})_2$ (Table 1). Table 1 shown binding energy of Cu $2p$ spectra not match with $\text{Cu}(\text{OH})_2$, because black sponge is a mixture of $\text{Cu}(\text{OH})_2$ and CuOOH . Base on Figure 5 and values for the binding energy this compound is CuOOH . This species is very stable, it does not change color during electrolysis.

3.4. Analysis of Sponge at Electrodes Surface using XRD

Figure 5 shown the XRD pattern of the copper hydroxide nanoparticles (black sponge). XRD studies indicate that copper hydroxide particles are nanoparticles and crystalline. Based on 2θ angle black color can be determined [18, 21]. The peak of Cu indicated by the angle 2θ at 43.3° and 50.5° . Peaks with 2θ angle at 32.5° , 38.7° , 53.2° and 57.9° are specific peaks for compound $\text{Cu}(\text{OH})_2$. Peaks with 2θ angle at 28.9° , 35.6° and 61.5° represent Cu_2O . Based on the XRD analysis showed the black sponge is a mixture of $\text{Cu}(\text{OH})_2$ and Cu_2O . Concentrations of $\text{Cu}(\text{OH})_2$ is larger compared to Cu_2O , it is shown the highest peaks at the 2θ angle is 38.7° . Particle size was calculated using Debye-Scherrer equation [3, 11, 24-25]:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where, D is the particle size of copper hydroxide, K is the Scherrer constant with value from 0.9 to 1, λ represents wavelength of x-ray source used in XRD (Radiation/wavelength Cu K-alpha is 0.15418 nm), θ is the Bragg angle is $2\theta = 38.699^\circ$; $\theta = 19.3495^\circ$ (Figure 5). β is the full width at half maximum of the diffraction peak. β is the difference in angles at half max.

$$\beta = (2\theta \text{ High}) - (2\theta \text{ Low}) * \pi / 180$$

$$\beta = (39.0 - 38.2) * 3.14 / 180$$

$$\beta = (39.0 - 38.2) * 3.14 / 180$$

$$\beta = 0.01396$$

$$D = \frac{0.9 \times 0.15418}{0.01396 \times \cos 19.3495} = 10.5352 \text{ nm}$$

The particle size of the copper hydroxide was found to be 10.5352 nm. Copper hydroxide of the compounds formed in the Cu electrode surface are nanoparticles, because have particle size between 1-100 nm.

Figure 6 shown cross section of the compounds formed in the Cu electrode surface. Figure 6 shown the Cu electrode surface form three layer after used for electrolysis in 0.1 M KOH solution. The first layer (green color) on the Cu electrode surface is Cu_2O compound. The second layer (light-blue) is CuO and the third layer (black color) is $\text{Cu}(\text{OH})_2$ and CuOOH . The dominant species at the Cu electrode surface after used for electrolysis in 0.1 M KOH is $\text{Cu}(\text{OH})_2$. Cu metal is easily oxidized to form oxide compounds in the alkaline medium, which would formed oxide coating on the surface of the electrode, Cu_2O , CuO, and $\text{Cu}(\text{OH})_2$, besides the other species depending on the potential, pH of the solution, the mass-transport conditions, ageing and surface restructuring processes [22, 23].

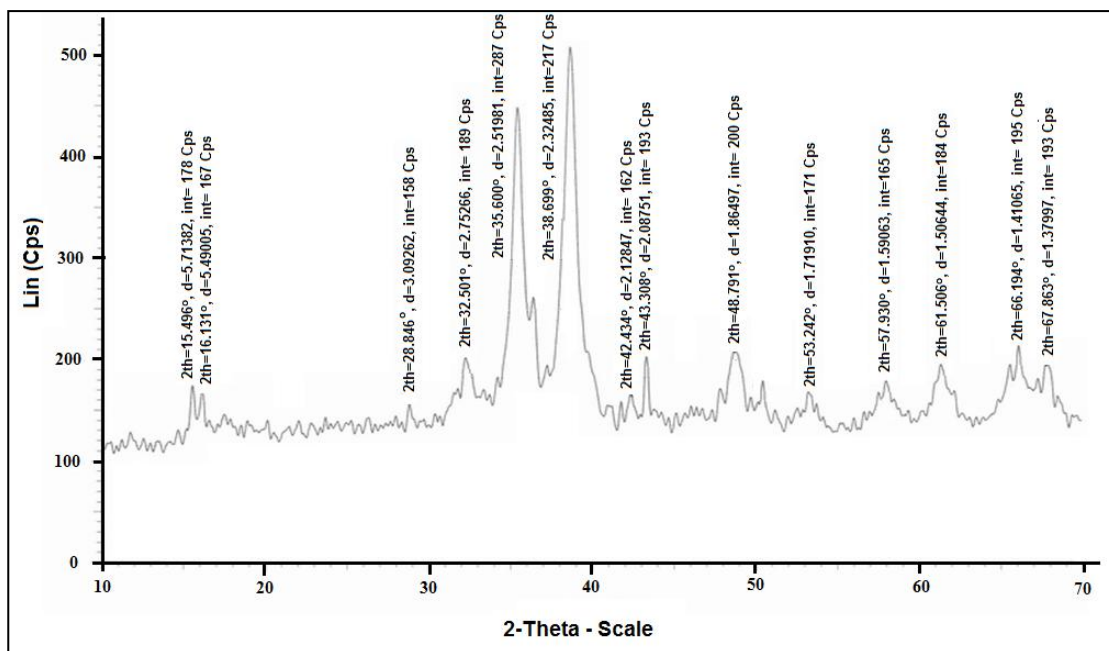


Figure 5. XRD pattern of the copper hydroxides from sponge with black colour

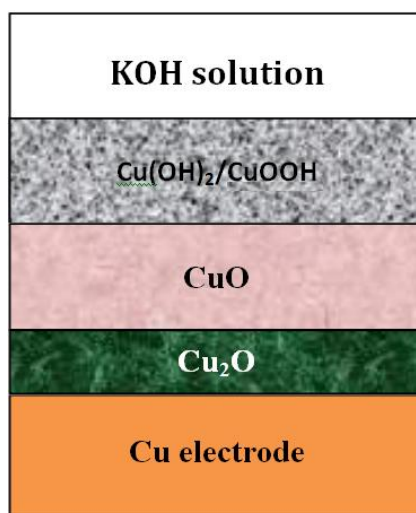


Figure 6. Cross section of the compounds formed at the Cu electrode surface after used for electrolysis in 0.1 M KOH

4. CONCLUSIONS

A new and simple synthesis approach has been successfully developed to synthesize copper hydroxide $\text{Cu}(\text{OH})_2$ nanoparticle using electrosynthesis methods. XPS and XRD analysis shown copper hydroxide $\text{Cu}(\text{OH})_2$ have high purity, nanoparticle and dominant species. Base on the XRD analysis shown copper hydroxide $\text{Cu}(\text{OH})_2$ suggests that the particle size is in the nanoparticle range

(10.5352 nm). The electrosynthesis methods are environmentally friendly, simple, very low cost, inexpensive and non-toxic materials and several important advantageous features.

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