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Effect of Glucose Concentration on Preparation of Cu_2O Semiconductors as a Photocathode in Photoelectro-Chemical Water Splitting

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Abstract: Synthesis of Cu_2O semiconductor thin layer as a photocathode in photoelectrochemical water splitting had been done. Before the Synthesis of Cu_2O photocathode, on FTO was covered with copper thin film by applying electrodeposition method using a potentiostat. Then the Cu-FTO was covered Cu_2O by then reacting with Fehling B solution with varied glucose concentrations (2, 4, and 6 %) . Characterization with XRD, SEM-EDX and UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) was chosen for Cu_2O that gave the highest current density and the most positive onset potential. The results showed photoelectrochemical property revealed the greater concentration of glucose solution, the greater the current density, Cu_2O with a concentration of 6% produced the highest current density, namely 0.413 mA/cm^2 and onset potential of 0.23 V. The results of X-ray diffraction showed that the sample contained Cu_2O crystals with grain size averaged 87.82 nm. The results of SEM characterization of spherical crystalline morphology Cu_2O, and EDX results showed the presence of Cu and O elements.The results of UV-Vis DRS showed that the energy band gap of Cu_2O was 2.13 eV.

Keywords: water splitting, photocatode, Cu_2O, electrodeposition, glucose.

I. INTRODUCTION

Activities of human life increasingly depend on the availability of energy. Hydrogen energy has a great potential for renewable energy sources[1], One way to obtain hydrogen is through the photoelectrochemical water splitting process. Photoelectrochemical water splitting is a method to convert solar energy into hydrogen. In this approach, sunlight is absorbed by the semiconductor material located in the electrolyte solution, resulting photovoltage used to push the water splitting reaction, In the photoelectrochemical water splitting process, the electrode of semiconductor band gap must have a minimum (1.5–2.5 eV)[2].

Copper (I) oxide has several advantages, including use as a semiconductor material, non-toxic, the synthesis process is relatively easy, since it has the band gap value of 2, 2.1; 2.2; 2.35 and 2.45 eV[3], Cu_2O semiconductor is *p*-type semiconductor that has applications in solar cells[4], a glucose sensor[5], photocatalyst[6], hybriddiode[7], biosensors[6], photoelectrochemicalwater splitting (PEC)[8], gassensor[9], chemiluminescence[10], polymer memory devices[11], transistor [12] and lithium ion batteries[13].One of Cu synthesis is carried out by electrodeposition, because it is simple, able to be deposited in large scale, the morphology can be controlled, and it does not require high temperatures and environmentally friendly[14]. The formation of Cu_2O through the process of reaction with Fehling's solution B and glucose. Glucose is as a reducing agent of Cu^{2+} to Cu^{+}. Fehling's solution B serves as a complexing agent to keep the copper ions in solution. The Cu_2O preparation was grown over a copper covered FTO subtrate.

This research was aimed to prepare a thin layer of Cu_2Oon Cu-FTO with varied concentration of glucose solutions(2, 4, and 6%) to form Cu_2O as photocathode in photoelectrochemical water splitting.

II. METHODS

1.Materials and Tools

a. Material used are $CuSO_4.5H_2O$ pa (Merck), $C_6H_8O_7$ pa (Merck), $Na_3C_6H_5O_7$ pa (Merck), H_2SO_4 pa (Merck), Na_2SO_4 pa (Merck), NaOH pa (Merck), HNO_3 pa (Merck), HNO_3 pa (Merck), technical Acetone, Ethanol technical, technical Fehling's solution B, Glucose (Merck), Pt Electrodes, Electrodes Ag / AgCl, Glass FTO (Sigma-Aldrich, surface resistivity ~ 7Ω / sa).

b. The tools used in this research are glassware laboratory standards, a pH meter (Trans Instruments), analytical balance (Ohaus), potentiostat (CorrTest CS 150), Multimeter (Krisbow), hotplate (IKA C-MAG HS 7), X-raysdiffraction Instrument (PANalytical), Instruments SEM-EDX (X pro Phenom desktop SEM with EDX), UV-Vis instruments Diffuse Reflectance Spectroscopy (UV-Vis DRS) (Agilent Carry-100).

2. Preparation of electrolytesolution and electrodes

Preparation of the solution for the deposition of Cuused 0.623 g $CuSO_4.5H_2O$; 2.5426 g and 2.2057 g $Na_3C_6H_5O_7$ $C_6H_8O_7$, then dissolved in distilled water until 50 mL. Then the pH was set 2.5 by addition with 1 M H_2SO_4.The electrode used for Cu deposition was FTO (2 cm x1 cm) with the deposition area 1 cm^2. Then the FTO was washed with nitric acid, acetone, ethanol and distilled water successively for every 15 mins to remove impurities.

3. Electrodeposition

Electrodeposition process was carried out to cover FTO with Cu thin film. Electrodeposition process was run by three electrode system (FTO, Ag/AgCl and Pt as on Pt working, reference, and counter electrodes, respectively). Linear Sweep Voltametry (LSV) with the potentials from 0 to -1.5 V was applied by using potentiostat. Cu was deposited at the potential that gave the highest current for 1800 s. The Cu covered FTO glass was washed with distilled water and dried with N_2 gas.

4. Characterization of Cu_2O thin film

Characterization of Cu_2O thin film was done using XRD, SEM-EDX, SEM and UV-Vis DRS.

5. Photoelectrochemical (PEC) measurement

After synthesis of Cu_2Oon Cu-FTO semiconductor layer, a PEC measurement was performed in 1M Na_2SO_4 solutionat pH 9 using a potentiostat instrument in which the semiconductor layer on the FTO glass as the working electrode, Pt as the counter electrode and Ag/AgCl as the reference electrode was then immersed into the sodium sulfate solution. In this measurement the chopped irradiation (on-off) treatment was performed for 10 s with irradiation using 100 mWatt/cm^2 power light. A potentiostat instrument masured the current by using a linear sweep voltametry program with initial and final potentials of 0.1 and -1.4 V, respectively.

III. RESULTS AND DISCUSSION

1.Determination of CurrentApplication

Copper electrodeposition using a solution of copper sulfate, citric acid and sodium citrate (pH 2.5). Before electrodeposition it was done by the determination of application flows using Linear Sweep Voltametry (LSV). It was obtained copper deposition at the highest current at 3 mA. Then the copper electrodeposition was done at a steady current for 30 min. The thin film precipitate formed was reacted with Fehling's Bsolution and glucose solutions at varied concentrations of of 2, 4, and 6% to form Cu_2O. Cu_2O formation reaction can be seen in Figure 1.

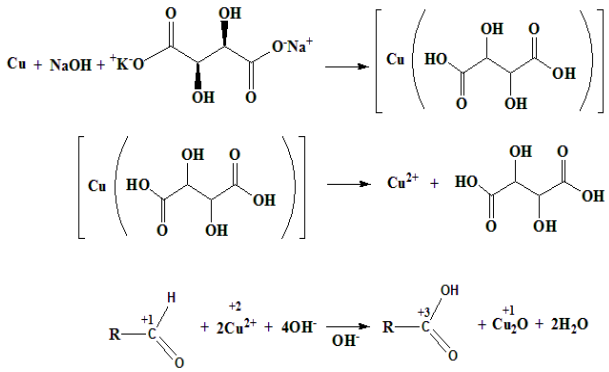

Figure 1.The reaction of Fehling's Bsolution with glucose

In the reactionprocess with Fehling's Bsolution occurred glucose reduction reaction of copper (II) to copper (I). Qualitatively, the concentration of 2, 4, and 6% gave the color of red brick, slightly dark red brick, and dark red brick precipitates, respectively.

2.Photoelectrochemical measurements of Cu_2O thin film photocathode

The next stage was photoelectrochemical measurements to determine the first current appear at the time given beam (onset potential) and the maximum current generated by the photocathode of Cu_2O with varying glucose concentrations. Photoelectrochemical measurements was performed with and without radiation every 10 seconds. Irradiation aims to determine the effect of artificial sunlight to the current produced by the photocathode, irradiation role in photocatalytic activity associated with the formation of the electron and hole and confirms the semiconducting property.Figure 2 shows J-V curves of Cu_2O photocathode resulted from varied glucose concentration.

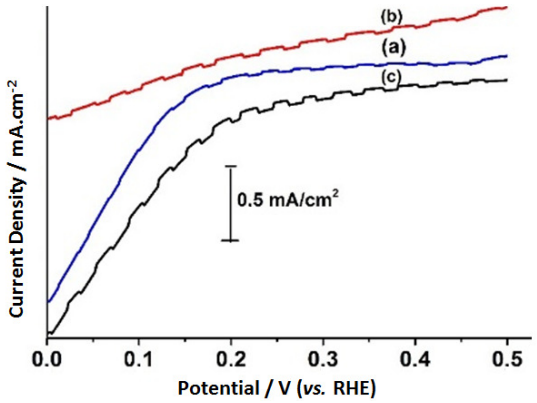

Figure 2.J-V Curves of Cu_2Ophotocathodes resulted from varied glucose concentrations (a) 2, (b) 4, (c) 6%.

Table 1. Current density and onset potensial semiconductor Cu_2O with variations addition of glucose concentration (a) 2% (b) 4% (c) 6%.

Cu_2O prepared with glucose	Current Density (mA/cm^2)	OnsetPotential (V)
2%	0.264	0.17
4%	0.329	0.18
6%	0.413	0.23

Based on table 1it can be

concluded that the higher concentration of glucose solution, the greater current density and onsetpotential. The high current density alsodemonstrated the high light absorbed by semicoductor, so the more electron-hole that plays a role in the reduction and oxidation reactions.

ABPE measurement serves to determine the efficiency of a photocathode in response to photon/light to electric current under an applied voltage. ABPE measurement results are in figure 3.

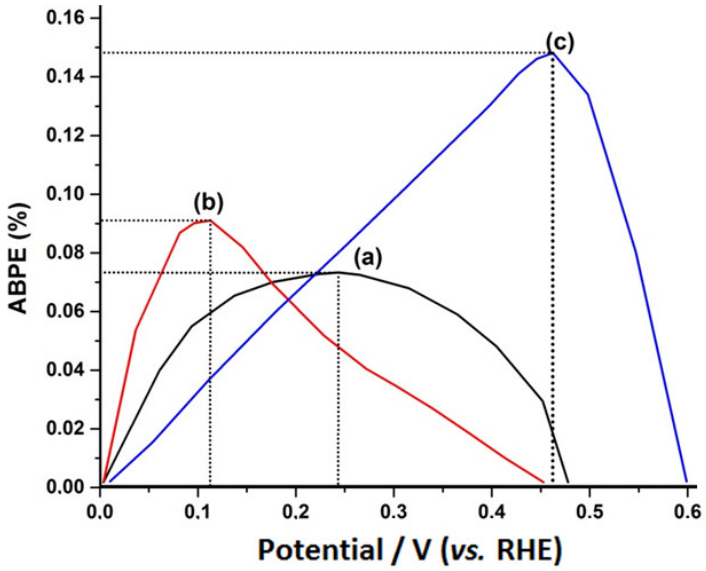

Figure 3. ABPE curves of the semiconductor Cu_2O with a variation of the addition of glucose concentration (a) 2, (b) 4, and (c) 6%.

Table 2.ABPE value (%) in each photocathode

Cu_2O	APBE (%)
2%	0.07
4%	0.11
6%	0.14

Based onfigure 2,Cu_2O with a concentration of 6% has the highest photocathode efficiency; it indicates that the semiconductor Cu_2O made of Cu with Fehling's solution B and the addition of glucose concentration 6% increase efficiency photocathode in response to light.

3.Characterization with XRD

Characterization by X-ray diffraction was performed to identify synthesized Cu_2O on FTO glass. X-ray diffraction analysis of the sample in the range of diffraction angle (2θ) of 20-80^o with $K_{\alpha 1}$ Cu radiation (λ = 1.541874 Å). The result of XRD analysis is shown in figure 4.

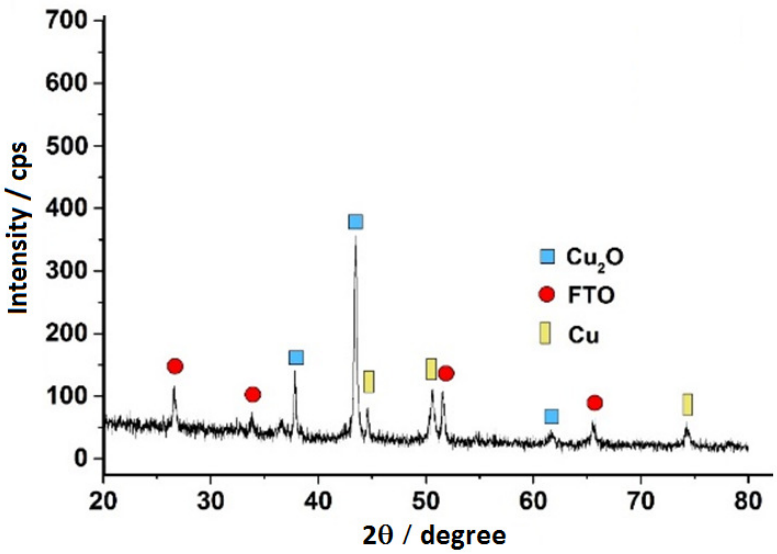

Figure 4. X-ray diffractogram of Cu_2Osemiconductor prepared by addition of 6% glucose solution.

Cu_2O standard diffraction patterns are indicated by peaks at 2θ values of 36.43; 42.38; and 61,65°. These peaks coincide with the peak of synthesized Cu_2O diffractogram intensity prepared by the addition of glucose6%. Therefore, the sample of synthesizedCu_2Ohad been formed on FTO glass. Then to calculate the average size of a Cu_2O crystal uses Debye-Schererr equation and the result as shown in table 3.

Table 3.Cu_2O crystal size and FWHMvalue

2θ	θ	FWHM	*d* (nm)
36.43	18.215	0.1003	84.31
42.38	21,190	0.1003	85.89
61.65	30.825	.1003	93.26

Debye-Schererr equation, the value of FWHM is inversely proportional to the size of the crystals. The results shows that the synthesis of Cu_2O smaller FWHM values that have increasingly large crystal size, the size of a large crystal having high crystallinity. So it can be concluded that Cu_2Osynthesis productis a crystalline. The average Cu_2O grainsize is 87.82 nm. Crystallinity affects the charge separation and charge transfer [2]. Crystalline solid has a regular arrangement. Therefore, in crystalline solid charge separation and charge transfer will be easier because it has a little resistance so that the resulting current density will also increase.

4.Characterization using SEM-EDX

Characterization by SEM was conducted to determine the surface morphology of Cu_2O, while EDX performed to determine the percent Cu_2O composition that has formed on the FTO glass quantitatively. The results of SEM-EDX analysis of semiconductors Cu_2O concentration of glucose solution with the addition of 6% in figure 5.

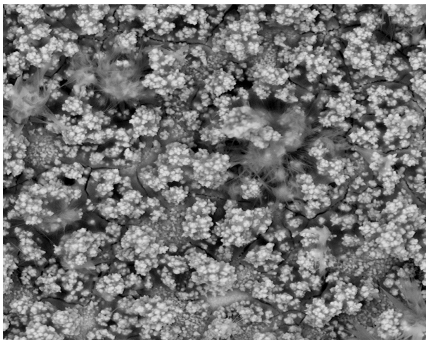

Figure 5. SEM analysis of semiconductors Cu_2Oprepared by addition of glucose concentration 6%.

SEM analysis shows that the surface morphology of Cu_2O with the addition of 6% glucose solution is spherical. The surface morphology will play a role in the interaction of light with the surface of the formation mechanism of electrons. Uniform and homogeneous surface will increase light absorption. Good light absorption will increase the more the electrons and holes are formed.

Elemental compositions of Cu_2O semiconductor are known through EDX analysis. Table 4 shows the EDXresult of Cu_2Osemiconductor.

Table 4. The results of EDX analysis of Cu_2Osemiconductor prepared by glucose concentration of 6%.

Element	Relative mass (%)
O	22
Cu	78
Total	100

The results of EDX analysis on Cu_2Osemiconductor shows that the most dominant elements are copper and oxygen, namely 78, and 22 %, respectively. Cu element has more percentage than that of O. The elemental mass difference is possible during the process of adding a glucose solution, Cu_2O formation has not been evenly distributed, so there are still many elements of Cu. Not only that, the results of the synthesis of semiconductor thin layers is possible on certain surfaces there are elements of O is less than the Cu element. This indicates that it has formed a semiconductor Cu_2O above FTO glass on the addition of glucose solution concentration of 6%. It is also strengthened by the presence of X-ray diffraction analysis proved that the semiconductor sample has formed as the peaks of Cu_2O.

5.Characterization by UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS)

The band gap value of copper (I) oxide (Cu_2O) can be determined by using a spectrophotometer UV-Vis DRS. UV-Vis DRS is based on measuring the intensity of UV-Vis light that are reflected or scattered by the sample. Measurements were made at a wavelength of 200-800 nm. Figure 6 shows the relationship between Eg with $[F(R) hv]^{1/2}$ is used to determine the value of the band gap compound of copper (I) oxide synthesis result prepared by addition of glucose 6%.

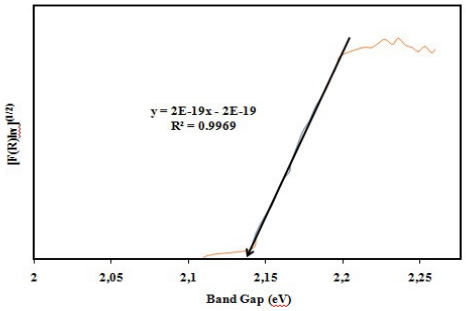

Figure 6.Curve for obtaining of Cu_2Osemiconductor band gap.

Band gap valuefor copper (I) oxide compoundobtained from the calculation of Kubelka - Munk by making a graph of hν as the x-axis with $[F(R)\ h\nu]^{1/2}$ as the y-axis and by extrapolating using straight line in the spectrum ofhv vs. $[F(R)\ h\nu]^{1/2}$ to cut energy axis (x-axis). Values of Cu_2Osemiconductor band gap is 2.13 eV for Cu2O prepared by addition of 6% glucose solution. The band gap value is in the ranges of previous work for Cu_2Othat is from 2,0 until 2.45 eV[3].

IV. CONCLUSION

The variation of glucose concentration in the preparation of semiconductor Cu_2O effects on the higher current density generated by the semiconductor. Semiconductor Cu_2O with a concentration of 6% produce the highest current 0.413 mA/cm^2 and the onset potential of 0.23 V (vs RHE). The band gap of the Cu_2O is 2.13 eV.

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