Synthesis of Cu2 O from modified Fehling reaction for the preparation of Cu2 O thin film photocathode by using the spin coating method, characterization, and its photoelectrochemical properties

by Gunawan Gunawan

16
Journal of Physics: Conference Series

PAPER · OPEN ACCESS

Synthesis of Cu_2O from modified Fehling reaction for the preparation of Cu_2O thin film photocathode by using the spin coating method, characterization, and its photoelectrochemical properties

4
To cite this article: Sulat *et al* 2021 *J. Phys.: Conf. Ser.* **1943** 012179

Synthesis of Cu_2O from modified Fehling reaction for the preparation of Cu_2O thin film photocathode by using the spin coating method, characterization, and its photoelectrochemical properties

Sulat, Gunawan, R A Lusiana, A Haris, D S Widodo

Chemistry Department, Diponegoro University, Semarang, Indonesia

Corresponding author: gunawan@live.undip.ac.id

Abstract. Hydrogen energy has the potency as a renewable energy source to replace the fossil energy. It can be obtained through the process of photoelectrochemical (PEC) water splitting with the help of a semiconductor as a photocathode to capture photon energy. One of the copper-based metal oxide semiconductors that can be used in the water splitting process is copper(I) oxide (Cu_2O), because it has non-toxic advantage, requires an easy synthesis process, low production cost, and has a low band gap (2-2.45 *e*V). This study aims to determine the effect of Fehling's modification using citrate in Cu_2O synthesis as material to prepare Cu_2O thin film photocathode using spin-coating method. The prepared photocathode consists of three stages, namely variations of Cu_2O synthesis with mole ratios of copper:citrate of 1:1; 1:2; 1:4, thin film preparation and heating. Then the obtained thin film was characterized using SEM, EDX and XRD. *J-V* curves of the photocathodes gave current densities, onset potential and applied bias to photon efficiency (ABPE) for Cu_2O thin film photocathode prepared by copper:citrate mole ratios of 1:1; 1:2; 1:4 namely 0.09; 0.18; 0.12 mA/cm^2 at potential of 0.2 V (*vs*. RHE), 0.04; 0.08; 0.02 V (*vs*. RHE), and 0.062, 0.057, 0.058 %, respectively. SEM analysis result showed a spherical morphology of Cu_2O. EDX analysis showed that the sample contained copper and oxygen with 78% Cu and 22% O. XRD analysis results showed the presence of Cu_2O with an average crystal grain size of 38.08 nm.

1. Introduction

Nowadays, the world community relies on fossil energy as the main energy source. However, the availability of fossil energy is very limited, so renewable energy is needed that can replace the fossil energy. Hydrogen energy has great potential to become one of the renewable energy sources. Hydrogen can be obtained through the process of photoelectrochemical water splitting by using solar energy. The process occurs in which sunlight is absorbed by semiconductor materials in an electrolyte solution, resulting in photovoltage which is used to generate water splitting reactions [1]. Semiconductors that can be used in the photoelectrochemical process of water splitting are semiconductors that have a band gap of 1.5-2.5 eV [2]. The position of the valence band and conduction band of a semiconductor material that can be used for photocathode and photoanode in photoelectrochemical water spitting coincide with the redox potential of H_2O [3].

Recently it is of great concern in semiconductor applications as photocathodes, namely metal oxides. This is because metal oxide semiconductors have a band gap of 1.5–3.2 eV [4], making it possible to absorb most of the solar spectrum. One of the copper-based metal oxide semiconductors is

copper(I) oxide (Cu_2O) because it has the advantage that it can be used as a semiconductor, non-toxic, easy synthesis process, low production costs with a band gap value of around 2-2.45 eV [5]. Cu_2O semiconductor is *p*-type semiconductor that can be used in photoelectrochemical (PEC) water splitting because they have a band gap range that allows them to absorb most of the sun's spectrum [6]. Cu_2O film shows good activity against the hydrogen formation reaction so it has the potential to be used as a photocathode [5].

Generally, Cu_2O synthesis is carried out by oxidizing pure copper or obtained by reducing Cu^{2+}. The most common method is by reducing Cu^{2+} to Cu^{+} using Fehling's solution and glucose. Fehling's solution contains tartrate ions in addition as a complex for Cu^{2+} and sodium hydroxide. The tartrate ion acts as a complexing agent to keep the copper ions in the solution. Without the tartrate ion, the copper hydroxide, $Cu(OH)_2$, will precipitate directly from the basic Cu^{2+} solution. Heating Fehling's solution with a reducing agent such as glucose, causes the reduction of Cu^{2+} to Cu^{+}. Tartrate ion cannot form complex copper Cu^{+} ions, so the reduction of Cu^{2+} to Cu^{+} with the help of glucose can form an orange solution into brick-red Cu_2O deposits and carboxylic acid filtrate resulting from the oxidation of aldehyde groups in glucose [7]. On the other hand, citrate ion has similar properties as tartate, where citrate is softer and more stable in keeping copper ions in solution. Based on research conducted by [8] using disodium citrate dihydrate as a substitute for tartrate in the synthesis of Cu_2O from Cu-acetate base solution, Cu_2O monodisperse crystal solid ball with a diameter of 168 to 265 nm was obtained. When viewed from the structure, the citrate ion has a more complex structure, so that the citrate ion can be used as a capping ligand which is more stable to react with Cu^{2+}. In addition, the presence of citrate ions can prevent $Cu(OH)_2$ precipitation, slow down nucleation, and to stabilize Cu^{2+} precursors in solution and is used to increase product size so that the resulting Cu_2O is smaller [8]. It is hoped that the replacement of tartrate ion to citrate will result in a more stable Cu_2O crystal with a smaller size so that it will be more evenly applied to the film. This study aims to determine the effect of Fehling's modification using citrate in Cu_2O synthesis as a material for the preparation of Cu_2O photocathode using spin-coating method and used in the photoelectrochemical water splitting process. Furthermore, characterization was carried out using X-Ray diffraction to determine the crystallinity of Cu_2O, SEM-EDX to determine the surface morphology of Cu_2O and its composition, and UV-Vis Spectrophotometry to determine the effect of citrate in Fehling's reagent modification.

2. Experimental methods

2.1. Materials

Materials used include: FTO (Fluorine-doped tin oxide) glass (sigma aldrich), copper(II) sulfate pentahydrate (Merck), sodium citrate dihydrate (Merck), NaOH (Merck), Glucose (Merck), Na_2SO_4 (Merck), Ethanol, tea tree essential oil.

2.2. Equipments

Glasswares (Pyrex), analytical balance (Ohaus), Hot plate and magnetic stirrer (Thermo Scientific), multimeter (Krisbow), Furnace (homemade), Sonication (Best CJ-008), Oven (Kirin KBO-90M), Spin-coating (homemade), Potentiostat (Corr Test CS-150), UV-Vis Spectrophotometer (PG Instruments T60 Spectrophotometer), X-ray Diffraction (PANalytical X Pert3 Powder), SEM-EDX (Phenom Pro-X desktop SEM with EDX).

2.3. Research procedures

The research began with the synthesis of Cu_2O using the citrate modified Fehling method as a complexing agent with Cu:citrate mole ratios of 1:1; 1:2; 1:4. Then, the obtained Cu_2O was used for preparing a Cu_2O thin film on FTO using the spin coating method and followed by annealing. The powder sample was analyzed using SEM-EDX to determine its morphology and composition and XRD analysis to determine its crystallinity. In addition, the initial reagents of cupper, citrate, and tartrate ions were investigated by a UV-Vis spectrophotometer to see their spectrum profiles.

Meanwhile, the current density and onset potential of Cu_2O thin film were measured to determine its photoelectrochemical properties.

2.3.1. Synthesis of Cu_2O. Synthesis of Cu_2O was initiated by making modified Fehling A and B solutions. Fehling A's solution was prepared by dissolving copper(II) sulfate pentahydrate (0.02 mol) in distilled water (100 mL). Then proceed to vary the citrate-modified Fehling B solution by dissolving trisodium citrate dihydrate by varying the mole of the Cu:sodium citrate ratios of 1:1; 1:2; 1:4 (0.0275 mol, 0.055 mol, and 0.11 mol) and sodium hydroxide (0.0552 mol) in distilled water (100 mL). After the Fehling A and B solutions were prepared, then mixed each solution and stirred for 15 min. After that, 100 mL glucose 10 g was added to the mixture as a reducing agent. Then the final mixture was heated at 60 °C and stirred. After obtaining Cu_2O brick red color solid then washed with distilled water (3 times) and ethanol (2 times) and dried in an oven at 80 °C for 2 h.

2.3.2. Preparation of FTO glass. The preparation was conducted by cleaning 1cm x 2 cm FTO glass with 10 mL of 0.1 M nitric acid, acetone, ethanol, and distilled water successively to remove impurities.

2.3.3. Characterization of Cu_2O. After obtaining Cu_2O, then it was characterized using X-Ray Diffraction to determine the crystallinity of Cu_2O, SEM-EDX to determine the surface morphology of Cu_2O and its composition, scanning wavelength UV-Vis spectrophotometry was used to prove that the Cu-citrate complex was formed and compared with Cu-tartrate.

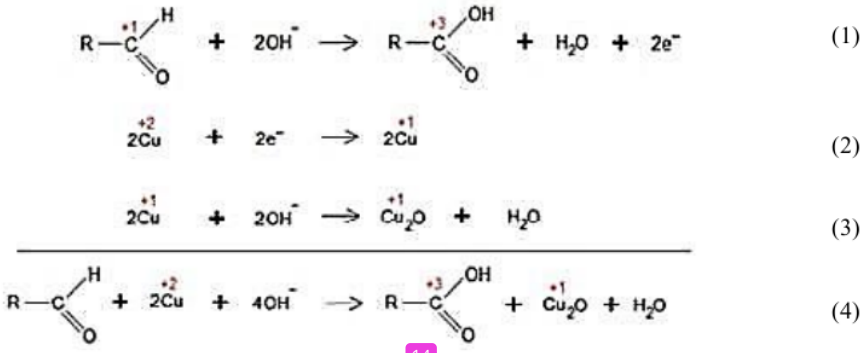
2.3.4. Preparation of Cu_2O thin film Semiconductors. Preparation of Cu_2O thin film semiconductor was done by dissolving 0.1 g of Cu_2O into 5 mL of tea tree essential oil. The solution was stirred using a magnetic stirrer for 1 h then sonicated at room temperature for 10 min to make a homogeneous solution of Cu_2O in the solution. Then, 1 drop of the solution was put on FTO glass and the FTO was spinned using spin-coater at 500 rpm for 15 s. Further, after spin coating process the FTO was heated at 110 °C for 5 min. This step was repeated up to 15 drops. After that, the thin layer was annealed at 400 °C for 30 min.

2.3.5. Photoelectrochemical Measurements. Photoelectrochemical measurements used potentiostat (CorrTest CS-150) in a chamber containing three electrodes of Cu_2O thin layer on FTO as a working electrode, platinum as anode, and Ag/AgCl as a reference, and electrolyte solution of 0.1 M Na_2SO_4 at pH 9.0. The measurements was carried out at an initial potential of 0.1 V to the final potential of -1.0 V *vs* Ag/AgCl with a scan rate of 10 mV/s in the conditions with and without irradiation using 1.5 AM simulated light.

3. Results and discussion

3.1. Synthesis of Cu_2O by Modified Fehling Reagent

Synthesis of Cu_2O was carried out using the modified Fehling method by replacing potassium sodium tartrate with sodium citrate in Fehling B's solution. Based on the research conducted by Kooti & Matouri [7] Cu_2O was successfully prepared by using Fehling's reagent, through this method, Fehling's modification was carried out with sodium citrate solution. In this study, the variation of Cu_2O synthesis was carried out with the variation of sodium citrate used, namely three variations of the synthesis with the addition of less, balance, and excess citrates. The use of citrate is adjusted to the stoichiometric reaction from Kooti & Matouri [7] recipe to calculate the moles used. Based on stoichiometric calculations, the mole ratio of Cu:sodium citrate is obtained with a variation of 1:1; 1:2; 1:4. The mechanism of Cu_2O formation is through a redox reaction with Fehling's reagent according to the following reaction [9].



(1)

(2)

(3)

(4)

Figure 1. Reaction mechanism for the formation of Cu_2O.

The reaction mechanism for the formation of Cu_2O using citrate complexes is as follows:

$$CuSO_4\ (aq) + 2NaOH\ (aq) + 2Na_3C_6H_5O_7\ (aq) \rightarrow [Cu(C_6H_7O_7)_2]\ (aq) + 4Na_2SO_4\ (aq) \quad (5)$$

$$[Cu(C_6H_7O_7)_2]\ (aq) + C_6H_{12}O_6\ (aq)\ (reductor) \rightarrow Cu_2O\ (s) + carbocyclic\ acid\ (aq) \quad (6)$$

The total reaction is as follows:

$$CuSO_4\ (aq) + 2NaOH\ (aq) + 2Na_3C_6H_5O_7\ (aq) + C_6H_{12}O_6\ (aq)\ (reductor) \rightarrow$$
$$Cu_2O\ (s) + 4Na_2SO_4\ (aq) + carbocyclic\ acid\ (aq) \quad (7)$$

Powders of Cu_2O were obtained for Cu:citrate mole ratios of 1:1, 1:2, 1:4 with a yield of 89.3; 98.7 and 96.4%, respectively.

3.2. Characterization of Copper Complex Formation by UV-Vis Spectrophotometer

Characterization of complex formation with UV-Vis spectrophotometer aims to determine the effect of citrate addition as a complexing agent in the synthesis of Cu_2O with Fehling's reagent modification. The results of this characterization can distinguish between the complexing agent in Fehling's reagent using tartrate and citrate ions based on the shift in wavelengths formed.

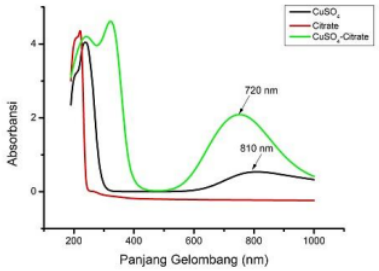


Figure 2. UV-Vis Scanning Graph of $CuSO_4$, sodium citrate and Cu-citrate mixtures.

The results of UV-Vis analysis on $CuSO_4.5H_2O$ in distilled water appeared an absorption peak at a wavelength of 810 nm, while in the complex compound [Cu(II)-$(C_6H_6O_7)_2$] the absorption peak appeared at a wavelength of 710 nm, whereas in a solution of trisodium citrate dihydrate in distilled water there is no peak absorption because the solution is colorless (Figure 2). In the figure, it can be seen that there is a shift in the maximum peak towards a smaller wavelength. Research conducted by [10] was able to produce complex [Cu(II)-$(C_6H_6O_7)_2$] with the addition of citric acid to $CuSO_4$ solution. Based on this result indicates the formation of a complex compound [Cu(II)-$(C_6H_6O_7)_2$] has

occurred. When compared with the complex formation in Fehling's reagent using tartrate ions, the results obtained show different peaks with the addition of citrate ions, as shown in figure 3.

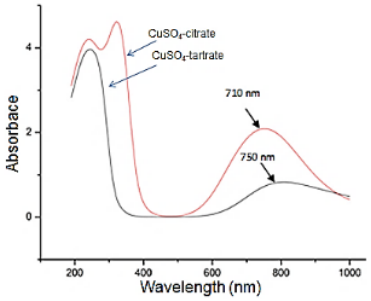


Figure 3. UV-Vis spectra of Cu-citrate and Cu-tartrate.

These results indicate that the Cu-tartrate complex appears at a wavelength of 750 nm, while in the Cu-citrate complex an absorption peak appears at a wavelength of 710 nm. The figure shows a shift in wavelength towards short wavelengths from the Cu-tartrate complex to Cu-citrate which is commonly called the blue shift. The blue shift will increase the energy value of the crystal field splitting of the complex compounds that will be formed, so that it will increase the energy of crystal field stabilization which will affect the crystals to be formed. $Na_3Cit•2H_2O$ was used as a capping ligand to react with Cu^{2+} to stabilize the Cu^{2+} precursor and slow down the nucleation.

The diameter of the as prepared single-crystal solid Cu_2O spheres have been successfully synthesized to reach sizes 168 nm to 265 nm by varying the amount of sodium citrate [8]. Meanwhile, the reduction of Fehling's solution (alkaline solution of copper sulfate and tartaric ions) by glucose only yielded Cu_2O nanoparticles with a diameter of about 30 nm [7]. From these results, it can be concluded that the use of citrate as a complexing agent is better than tartrate, because the complex formed will be more stable.

3.3. Characterization of Cu_2O powder by SEM-EDX

Figure 4 shows SEM analysis of Cu_2O powder. The presence of Cu_2O is indicated by spherical morphology [11] in accordance with the SEM results, where at mole ratio of 1:1 Cu:citrate of Cu_2O morphology is spherical with small clustered sizes. The ratio of 1:2 has the morphological form of clustered polyhedron balls with a size greater than the addition of less and excess citrate. Whereas the 1: 4 variation shows the spherical morphological shape and some irregular cubic shapes.

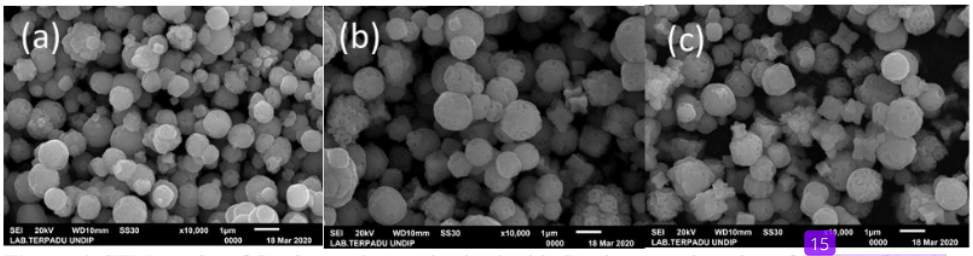


Figure 4. SEM results of Cu_2O powder synthesized with Cu:citrate mole ratios of (a) 1:1; (b) 1:2; (c) 1:4.

Table 1. EDX analysis results for Cu_2O powder.

Ratio of Cu:citrate	Percentage (%)	
	Cu	O
1:1	78.84	21.16
1:2	77.62	22.38
1:4	76.14	23.86

EDX analysis results for Cu_2O powder with Cu:citrate of 1:1; 1:2; 1:4 ratios have different values of Cu and O elements for each variation, as shown in table 1. From this table, it can be seen that the more citrate used, the lower the Cu percentage and the higher the O percentage. This difference shows that the addition of citrate affects the Cu_2O results obtained. Probably it was influenced by the complex compounds formed with the Cu as a central atom that makes it more stable with the increasing amount of citrate added. However, the percentage of Cu is greater than that of O. It is probably due to the incomplete reduction of Cu^{2+}.

3.4. Characterization of Cu_2O powder by XRD

XRD characterization was carried out only for synthesized Cu_2O powder with Cu:citrate mole ratio of 1:2, because based on the SEM-EDX characterization shows almost the same results between the Cu_2O synthesized results from Cu:citrate ratios of 1:1; 1:2; 1:4. The XRD analysis is presented in Figure 5.

Figure 5 shows there are three strong peaks, namely peaks located in the 2nd, 4th and 5th peak sequence with a value of 2θ of 36.54; 42.43; and 61.47° as the peaks of Cu_2O. Whereas at 2θ of 36.99° is the Cu peak, where Cu^{2+} is completely reduced to form Cu. The Cu_2O polycrystalline average size is calculated from the value of Full Width High Maximum (FWHM) based on the diffractogram peaks using the Debye-Schererr equation.

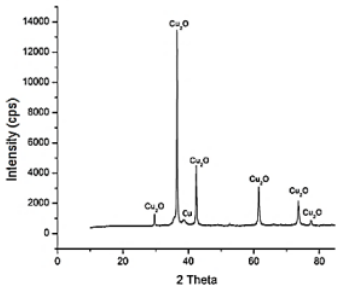


Figure 5. XRD results of Cu_2O powder from synthesis with a Cu:citrate mole ratio of 1: 2.

Table 2 presents the polycrystalline size data and the FWHM values from the results of X-ray diffraction analysis of Cu_2O powder samples. This is consistent with the Debye-Schererr equation that the grain size is inversely proportional to the FWHM value, where the greater the FWHM value, the smaller the grain size and the greater the diffraction pattern so that the crystallinity decreases. Vice versa, if the smaller the FWHM value, the crystal size will be bigger, and the solid will be more crystalline. From the calculation results in table 2 can be confirmed that the synthesized Cu_2O is crystals. The average grain size of Cu_2O is 38.08 nm. Crystallinity affects charge separation and charge transfer [12]. Crystalline solids have a regular arrangement; the more crystalline a solid is, the easier the charge separation and charge transfer will be because there are only a few obstacles, so the resulting current density will also be greater [13].

Table 2. Polycrystalline Cu_2O sizes and FWHM values.

2θ (°)	θ (°)	FWHM	D (nm)
29.6899	14.8449	0.2213	38.7913
36.5435	18.2717	0.2118	41.2586
42.4736	21.2368	0.2218	40.1377
61.4736	30.7368	0.2664	36.2393
73.2986	36.6493	0.2872	36.0372
73.5999	36.7999	0.2878	36.0076

3.5. Photoelectrochemical Measurement with Simulated Light

Photoelectrochemical measurement aims to determine the potential first time the current appears at the time of light exposure (onset potential) and the maximum current density produced by the photocathode when irradiating the Cu_2O semiconductor from the modified Fehling reaction. CorrTest CS-150 with CS Studio 5 application was used to measure the onset potential and maximum current density at the photocathode. The series of measurements are the photocathode as the working electrode, platinum as the anode, while Ag/AgCl as the reference electrode in the sodium sulfate electrolyte solution. The electrolyte solution serves to increase the conductivity of the solution because it contains ions that can conduct electricity. If the photoelectrochemical measurement uses only water, the redox reaction will take place slowly. Measurements were made with an initial potential of 0.1 V to a final potential of -1.0 V vs Ag/AgCl with a scanning rate of 10 mV/s under and without irradiation (chopped) using a simulated light of 1.5 AM (100 mW/cm^2) every 5 seconds. This irradiation aims to determine the effect of artificial sunlight on the current density produced by the photocathode.

3.5.1. Measurement of Current Density and Potential Onset. Measurement of current density and onset potential was carried out with and without irradiation every 5 seconds in Na_2SO_4 solution (pH 9) to determine the actual current density in water solution applications. The result of the current density measurement is presented in Figure 6.

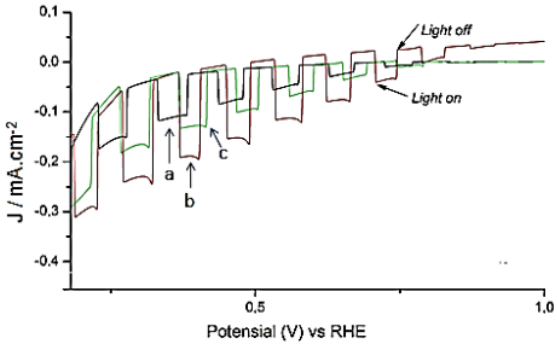


Figure 6. J-V curves of Cu_2O prepared by Cu:citrate mole ratios of (a) 1:1, (b)1:2, and (c) 1:4 measured in 0.1 M Na_2SO_4 under chopped 1.5 AM irradiation.

Figure 6 shows the current density appears when there is irradiation (light on) and returns to zero when there is no illumination (light off). This shows that the presence of light affects the performance of the photocathode. Light functions in the process of exciting electrons from the valence band to the conduction band, and produces electron-hole pairs (e^-/h^+), which play a role in redox reactions. Electrons reduce H_2O and form hydrogen gas, while the holes will oxidize water to form oxygen gas [6]. In the absence of light the usual electrochemical process has not been achieved so that on the curve, no current is generated.

The concentration of citrate added in the Cu_2O formation reaction affects the current density produced by the photocathode. The value of the current density produced by the Cu_2O photocathode in Na_2SO_4 solution is presented in Table 3.

Tabel 3. Current density of Cu_2O prepared by varied Cu:citrate mole ratio at 0.2 V *vs* RHE

Cu_2O prepared by Cu:citrate mole ratio	Current density (mA/cm^2)
1:1	0.09
1:2	0.18
1:4	0.12

The current density produced by Cu_2O in the synthesis results with a Cu:citrate ratio of 1:1 has a very small current density value of 0.09 mA/cm^2, while the Cu:citrate ratio 1:2 has the largest current density value, namely 0.18 mA/cm^2, and for the Cu: citrate ratio of 1:4, the current density value was lower than that of the Cu:citrate 1:2 ratio, which was 0.12 mA/cm^2 at 0.2 V *vs* RHE. From these results indicate that in equilibrium or with a Cu:citrate ratio of 1:2 in the citrate modified Fehling reaction, the Cu_2O photocatode has the highest current. This is possible because at equilibrium, the modified Fehling reagent has completely reacted to produce Cu_2O precipitates, so that there is no impurity in Cu_2O powder which has been made for Cu_2O thin layer photocathode. Meanwhile, the Cu:citrate ratio of 1:1 and 1:4 produces Cu_2O which still has a lot of impurities so that it affects the process of measuring the current.

The concentration variation of citrate addition in Cu_2O synthesis also shows a shift in the onset potential. The onset potential is the initial potential that the current appears when the photocathode is irradiated. Determination of the onset potential is done by plotting J^2 vs potential for each photocathode. The intersection of the dotted line and the straight line on the curve indicates the photocathode onset potential [12]. The onset potential at various concentrations of citrate addition to the synthesis of Cu_2O used as a photocathode is shown in Figure 7.

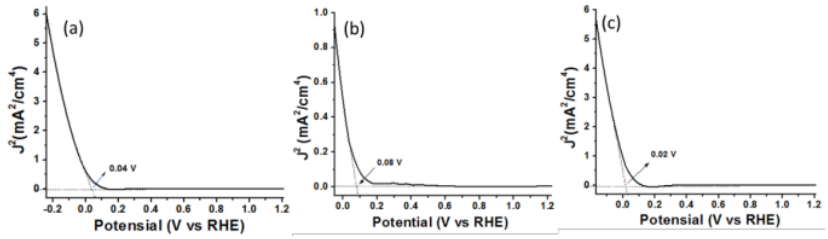


Figure 7. Onset potentials of Cu_2O semiconductors prepared by the mole ratio of Cu:sodium citrate (a) 1:1; (b) 1:2; (c) 1:4.

From these results, it can be seen that the onset potential of Cu_2O semiconductors with variations in the concentration addition is shown in Table 4.

Table 4. Measurement results for onset potential.

Cu_2O prepared by Cu:citrate ratio	**Onset potential (V *vs* RHE)**
1:1	0.04
1:2	0.08
1:4	0.02

A semiconductor with a Cu:citrate ratio of 1:2 have the highest onset potential value. So it can be concluded that in equilibrium it produces pure Cu_2O with a high value of photon currents and a high onset potential. While under and over citrate conditions obtain lower onset potential and current density. It is possible that the resulting Cu_2O is impure or impurities are still present.

3.5.2. Applied Bias Photon-to-Current Efficiency (ABPE) Measurement. ABPE measurement aims to determine the efficiency of the photocathode in responding to photons/light energy into an electric current under a given voltage. In determining the ABPE value on the photocathode previously, the photocurrent (current density) was measured using 3 electrodes, namely Cu_2O as the working electrode, platinum as the anode, and the Ag/AgCl electrode as the reference electrode, which was inserted into the Na_2SO_4 electrolyte solution (pH 9) which is ideally used in the process of measuring the efficiency of water splitting by photoelectrochemistry. The curve of the ABPE (%) value in Na_2SO_4 solution is presented in Figure 8. The figure shows the effect of variations in the addition of citrate on the ABPE, and the maximum values are summarized in Table 5.

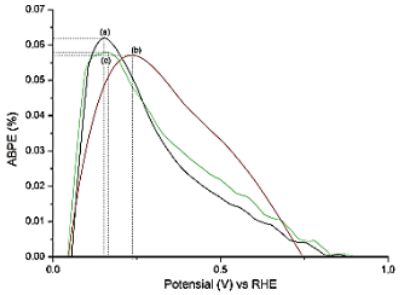


Figure 8. ABPE curves for Cu_2O semiconductors prepared by Cu:citrate ratio of (a) 1:1, (b) 1:2, (c) 1:4.

Table 5 shows the efficiency of photocathodes in responding to light. The ABPE value in Cu_2O from the Cu:citrate ratio 1:1 has the highest efficiency, which is 0.062%. Meanwhile, Cu_2O from an equilibrium state (1:2) has the lowest efficiency value of 0.057%. Although the efficiency of the photocathode on Cu_2O from equilibrium has a low ABPE value, when it is used as a photocathode in water splitting it has a higher current than Cu_2O from the addition of less citrate.

Table 5. ABPE values (%) for each photocatode

Cu_2O prepared by Cu:citrate mole ratio	**Potential (V) *vs* RHE**	**ABPE (%)**
1:1	0.154	0.062
1:2	0.239	0.057
1:3	0.165	0.058

4. Conclusion

Modification of Fehling's reagent using sodium citrate has effects on the measurement of current and onset potential of Cu_2O semiconductor under equilibrium conditions. The Cu_2O thin film semiconductor has been successfully prepared using the spin coating method. SEM analysis results showed Cu_2O with spherical morphology. The EDX analysis results confirmed that the sample contained 78 and 22% of Cu and O elements, respectively. The XRD analysis results revealed the presence of Cu_2O with an average grain size of 38.08 nm. Meanwhile, based on UV-Vis spectrophotometry, measurement showed that Cu-citrate was complexed better than Cu-tartrate. The results of current and onset potential measurements for Cu_2O photocathode from the Cu:citrate mole ratio of 1:2 gave the highest values, namely 0.18 mA/cm^2 and 0.09V, respectively. However, the highest efficiency (ABPE) was found for photocathode of Cu_2O prepared by Cu:citrate of 1:1.

Acknowledgment
The authors are thankful to the Faculty of Science and Mathematics at Diponegoro University for supporting this work (Non-APBN FSM UNDIP 2020).

References

[1] Septina W, Prabhakar R R, Wick R, Moehl T and Tilley S D 2017 *Chem. Mater.* **29** 4 1735–1743
[2] Chen Z, Dinh H N and Miller E 2013 *Photoelectrochemical Water Splitting SpringerBriefs in Energy* (London: Springer)
[3] Zhang Z, Zhang S, Liu S, Wang M, Fu G, He L, Yang Y and Fang S 2015 *Sens. Actuators B. Chem.* **220** 184–191
[4] Tamirat A G, Rick J, Dubale A A, Su, W-N and Hwang B-J 2016 *Nanoscale Horiz.* **1** 4 243–267
[5] Serin N, Serin T, Horzum Ş and Çelik Y 2005 *Semicon. Sci. Technol.* **20** 5 398–401
[6] Ma Q-B, Hofmann J P, Litke A and Hensen E J M 2015 *Sol. Energy Mater. Sol. Cells* **141** 178–186
[7] [illegible]oti M and Matour L 2010 *IEE Trans. Nanotechnol.* **17** 1
[8] Bi J, Wu S, Xia H, Li L and Zhang S 2019 *J. Mater. Chem. C* **7** 15 4551–4558
[9] Asthana S, Samanta C, Voolapalli R K and Saha B 2017 *J. Mater. Chem. A* **5** 6 2649–2663
[10] Barry R W and DuBois F W 1952 *J. Am. Soc.* **74** 15 3749–3753
[11] Feng L, Zhang C, Gao G and Cui D 2012 *Nanoscale Res. Lett.* **7** 1 276.
[12] Chen Z, Jaramillo T F, Deutsch T G, Kleiman shwarsctein, A, Forman A J, Gaillard N, Garland R, Takanabe K, Heske C, Sunkara M, Mcfarlan E W, Domen K, Miller E L, Turner J A and Dinh H N 2010 *J. Mater. Res.* **25** 1 3–16
[13] Nurosyid F, Purnama B and Ayuni L A 2008 *Jurnal Ilmu Dasar* **9** 9–14

Synthesis of Cu2 O from modified Fehling reaction for the preparation of Cu2 O thin film photocathode by using the spin coating method, characterization, and its photoelectrochemical properties

ORIGINALITY REPORT

9%	6%	7%	3%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	Submitted to University of Greenwich Student Paper	1%
2	Jiajie Bi, Suli Wu, Hongbo Xia, Lu Li, Shufen Zhang. " Synthesis of monodisperse single-crystal Cu O spheres and their application in generating structural colors ", Journal of Materials Chemistry C, 2019 Publication	1%
3	F. Janene, H. Dhaouadi, N. Etteyeb, F. Touati. "Flower-like cuprous oxide: hydrothermal synthesis, optical, and electrochemical properties", Ionics, 2014 Publication	1%
4	doc-pak.undip.ac.id Internet Source	1%
5	www.mdpi.com Internet Source	1%

6	exp-nanoandes2012.blogspot.com Internet Source	1 %
7	pubs.rsc.org Internet Source	<1 %
8	Yingpan Song, Chuanpan Guo, Hongfei Ji, Shuai Zhang, Minghua Wang, Linghao He, Donglai Peng, Zhihong Zhang. "CuxO@DNA sphere-based electrochemical bioassay for sensitive detection of Pb2+", Microchimica Acta, 2018 Publication	<1 %
9	Submitted to The International School Bangalore Student Paper	<1 %
10	d-nb.info Internet Source	<1 %
11	Guvenc Akgul, Funda Aksoy Akgul, Emre Mulazimoglu, Husnu Emrah Unalan, Rasit Turan. "Fabrication and characterization of copper oxide-silicon nanowire heterojunction photodiodes", Journal of Physics D: Applied Physics, 2014 Publication	<1 %
12	Submitted to King Saud University Student Paper	<1 %
13	link.springer.com Internet Source	

		<1%
14	F. A. Harraz. "Pore filling of macropores prepared in p-type silicon by copper deposition", physica status solidi (a), 06/2005 Publication	<1%
15	assets.researchsquare.com Internet Source	<1%
16	repository.lppm.unila.ac.id Internet Source	<1%
17	wiredspace.wits.ac.za Internet Source	<1%
18	G. Wisz, P. Sawicka-Chudy, P. Potera, M. Sibiński, R. Yavorskyi, Ł. Głowa, B. Cieniek, M. Cholewa. " Morphology, composition, structure and optical properties of thermally annealed Cu O thin films prepared by reactive DC sputtering method ", Molecular Crystals and Liquid Crystals, 2019 Publication	<1%
19	Palaska, P.. "Sensitive detection of cyclophosphamide using DNA-modified carbon paste, pencil graphite and hanging mercury drop electrodes", Talanta, 20070515 Publication	<1%

20	Xiaojiao Yu, Jie Zhang, Xiyan Tang, Yuchen Wei, Song Kou, Jinfen Niu, Binghua Yao. "Preparation and performance of non-enzymatic glucose sensor electrode based on nanometer cuprous oxide", Nanomaterials and Nanotechnology, 2018 Publication	<1 %
21	apr.psk.or.kr Internet Source	<1 %
22	doku.pub Internet Source	<1 %
23	escholarship.org Internet Source	<1 %
24	Iqbal Singh, R. K. Bedi. "Influence of pH on the synthesis and characterization of CuO powder for thick film room-temperature NH3 gas sensor", Journal of Materials Science, 2011 Publication	<1 %
25	Kunjal Patel, G. K. Solanki, K. D. Patel, Pratik Pataniya, V. M. Pathak, Mohit Tannarana, Payal Chauhan, Megha Patel. "Flat band potential determination of NbSe2 photoelectrode using Mott-Schottky plot", AIP Publishing, 2019 Publication	<1 %
26	Sharma, P.. "Synthesis of fluorescent hollow and porous Cu"2O nanopolyhedras in the	<1 %

presence of poly(vinyl pyrrolidone)", Materials Chemistry and Physics, 20090415
Publication

---

27 Yu, Xiaojiao, Yuchen Wei, Linzhu Huang, Jinfen Niu, Jian Zhang, Xinming Li, and Binghua Yao. "Fabrication, morphology formation mechanism and properties of nanometer Cu2O thin film with KCl-doping", Materials Chemistry and Physics, 2014.
Publication

<1 %

---

28 Zeinab Rahmati, Mahmoud Roushani, Hadi Hosseini, Hamzeh Choobin. "Electrochemical immunosensor with Cu2O nanocube coating for detection of SARS-CoV-2 spike protein", Microchimica Acta, 2021
Publication

<1 %

---

29 John P. Hart, Adrian Crew, Eric Crouch, Kevin C. Honeychurch, Roy M. Pemberton. "Some Recent Designs and Developments of Screen‐Printed Carbon Electrochemical Sensors/Biosensors for Biomedical, Environmental, and Industrial Analyses", Analytical Letters, 2007
Publication

<1 %

---

30 Yi-Hsuan Chiu, Sarah A. Lindley, Chun-Wen Tsao, Ming-Yu Kuo, Jason K. Cooper, Yung-Jung Hsu, Jin Z. Zhang. " Hollow Au Nanosphere-Cu O Core–Shell Nanostructures

<1 %

with Controllable Core Surface Morphology ",
The Journal of Physical Chemistry C, 2020
Publication

Exclude quotes	Off	Exclude matches	Off
Exclude bibliography	Off		

Synthesis of Cu2 O from modified Fehling reaction for the preparation of Cu2 O thin film photocathode by using the spin coating method, characterization, and its photoelectrochemical properties

GRADEMARK REPORT

FINAL GRADE

/0

GENERAL COMMENTS

Instructor

PAGE 1

PAGE 2

PAGE 3

PAGE 4

PAGE 5

PAGE 6

PAGE 7

PAGE 8

PAGE 9

PAGE 10

PAGE 11