ISSN: 1410-8917
Jurnal Kimia Sains & Aplikasi
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 25 (12) (2022): 442–449

Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry

Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

Effect of Ascorbic Acid Concentration on Cu_2O Production for Photoelectrochemical Water Splitting on Photocathode Thin Films

Kharisma Luthfiaratri Rahayu [a], Abdul Haris [a], Gunawan [a,*]

[a] Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Tembalang, Semarang, Indonesia

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

https://doi.org/10.14710/jksa.25.12.442-449

Article Info

Article history:

Received: 29th August 2022
Revised: 18th November 2022
Accepted: 21st December 2022
Online: 31st December 2022

Keywords:
Cu_2O; ascorbic acid; photocathode; water splitting

Abstract

Hydrogen energy has great potential as a renewable energy source. Electrochemical water-splitting can be employed to obtain hydrogen by converting solar energy into hydrogen. In this study, Cu_2O thin film electrodes have been successfully synthesized using ascorbic acid using the spin coating method. This study aimed to determine the effect of ascorbic acid in manufacturing Cu_2O semiconductors as photocathodes and their activity for electrochemical water-splitting. The results indicated that ascorbate affected the photon current and onset potential of the Cu_2O semiconductor. The synthesis results found that Cu_2O at C1 (lower concentration than Cu^{2+}) yielded 95.69%, and the yield for Cu_2O at C2 (concentration equal to Cu^{2+}) was 96.2%. The yield for Cu_2O at C3 (concentration greater than Cu^{2+}) was 99.82%. The photon currents generated by adding 3%, 6%, and 9% ascorbate solution were 1.18, 1.69, and 1.78 mA/cm^2, respectively, at 0.3 V vs. RHE (Reversible Hydrogen Electrode). X-ray diffraction analysis revealed that the sample consisted of Cu_2O C3 with an average grain size of 17.55 nm. Meanwhile, Cu_2O C1 and Cu_2O C2 had average grain sizes of 38.99 nm and 36.42 nm, respectively. SEM analysis showed the presence of Cu_2O with a cuboid and flower-like morphology. EDX analysis showed that the samples contained elements of Cu: O, 73.97%: 26.03%; 79.89%: 20.11% and 98.43%: 1.57% respectively.

1. Introduction

Fossil energy sources that can meet human needs on a large scale for the next few years are increasingly scarce, causing humans to still depend on fossil energy sources. Humans are trying to find alternative energy that is environmentally friendly due to the depletion of fossil energy reserves. Hydrogen energy has great potential as a renewable energy source [1]. Electrochemical water splitting can be employed to obtain hydrogen by converting solar energy into hydrogen. Photoelectrochemical water-splitting is a method for converting solar energy into hydrogen. In this approach, sunlight is absorbed by the semiconductor in electrolysis, thereby providing energy to drive the water-splitting reaction [2]. In the photoelectrochemical water-splitting process, the semiconductor electrode must have a minimum bandgap of 1.5-2.5 eV [3].

A semiconductor is a material with electrons in at least two energy bands separated by a band without electrons [4]. Copper(I) oxide, one of the copper-based metal oxide semiconductors, has advantages such as being utilized as a semiconductor material, non-toxic, easy to synthesize, low manufacturing costs, and having a band gap of around 2, 2.1, 2.2, 2.35 and 2.45 eV [5]. Copper(I) oxide semiconductor is a p-type semiconductor that has applications in solar cells [6] and photoelectrochemical water-splitting [7]. Copper(I) oxide semiconductors can be obtained using several methods, including ultrasonic spray, hydrothermal, sol-gel, precipitation, and electrodeposition [8].

Cu_2O is produced by reducing Cu^{2+} to Cu^{+} ions with the help of reducing agents such as hydrazine hydrate [9], glucose [10], sodium boride [11], a plant containing an aldehyde group such as *Tridax procumbens* [12] and ascorbic acid [13]. In previous studies, Cu_2O was

synthesized using glucose as a reducing sugar [10]. However, this study used ascorbate as a substitute for reducing sugar using the Fehling method because it has good properties, especially in alkaline conditions. This reducing agent can be used for carbohydrate identification and quantitative analysis. This property is seen in the redox reactions of metal ions such as Cu^{2+}, which are present in synthesizing specific reactions [14]. Thus, this research is expected to give better results than previous studies using glucose as a reducing agent.

Ascorbic acid (vitamin C) is a lactone (ester-in hydroxycarboxylic acid) that is characterized by the presence of an enediol group as a strong reducing agent, where this group can reduce Cu^{2+} to Cu^{+} or Cu [15].

In this study, Cu_2O prepared using ascorbic acid as a reducing agent was used to produce Cu_2O thin films through a spin-coating approach. This method has advantages such as a simple production process, producing materials with good morphology, not requiring high temperatures, and being environmentally friendly. The thin layer produced by this method has a high degree of homogeneity. The desired coating thickness can be controlled based on the time and rotation speed of the spin coater [16].

The manufacture of thin films as solar cells from bulk synthesis with an anti-solvent protocol has become the most effective method to achieve a photon-to-current conversion efficiency (PCE) of more than 20% [17]. Thus, the novelty of this research is the formation of a thin layer semiconductor from Cu_2O powder on Fluorine Tin Oxide (FTO) glass obtained by the Fehling method by reducing ascorbate using the spin coating method and essential oil as a precursor solution.

The morphology of Cu_2O crystal films was measured using scanning electron microscopy (SEM). The crystal structure of Cu_2O was observed using an X-ray diffractometer (XRD).

2. Methods

2.1. Materials and Instruments

Copper(II) sulfate ($CuSO_4$) (Merck), HCl 37% (Merck), ascorbate (Merck), sodium sulfate (Na_2SO_4) (Merck), sodium hydroxide (NaOH) (Merck), potassium sodium tartrate (K-Na tartrate) (Merck) were pro-analysis grade. Acetone and ethanol were technical grade, FTO glass (Sigma Aldrich), distilled water (UNDIP Integrated Laboratory), and essential oil. UV-Vis Spectrophotometer, SEM EDX (Phenom Pro X desktop SEM with EDX), X-Ray Diffraction (PANalytical X Pert Powder).

2.2. Synthesis of Cu_2O

The preparation of Cu_2O was conducted in several stages. The first stage was the preparation of Cu_2O powder by reacting 50 mL of 1 M $CuSO_4$ with 50 mL of Fehling B consisting of K-Na tartrate and NaOH with stirring for 15 minutes. Then, 50 mL of ascorbate was added with stirring for 60 minutes at 600°C at different concentrations: C1 (concentration less than Cu^{2+} or ascorbate concentration of 3%), C2 (concentration equal to Cu^{2+} of 6%) and C3 (concentration greater of Cu^{2+}, or an ascorbate concentration of 9%). The varied concentration aimed to determine the effect of reducing sugar concentrations on the quality of Cu_2O semiconductors. The mixture was washed with distilled water and ethanol to remove impurities and dried at 800°C for 3 hours.

2.3. Production of Cu_2O Thin Films on FTO

The spin-coating process was initiated by dissolving Cu_2O powder in essential oil. FTO glass was cut into 1 x 2 cm and cleaned with 10 mL nitric acid, acetone, ethanol, and distilled water to remove impurities. Cu_2O in essential oil solution was dripped onto the surface of the FTO glass using the spin-coating method at 500 rpm. The glass was evaporated by heating on a hotplate for 5 minutes at 1000°C so that Cu_2O adhered. The subsequent drip was repeated up to 50 times. The process was continued by annealing the Cu_2O solution for 60 minutes at 4000°C to evaporate the impurities. The next step was photoelectrochemical measurements in a 0.1 M sodium sulfate solution pH 9.0 using a simulated light of 1.5 AM (100 Mw/cm^2).

2.4. Photoelectrochemical Measurement

In this study, photoelectrochemical measurements used a potentiostat with three electrodes. Cu_2O as the working electrode, platinum as the cathode, and Ag/AgCl as the reference electrode in an electrolyte solution of 0.1 M sodium sulfate pH 9.0. were done at an initial potential of 0.5 V to a final potential of 1.0 V vs. Ag/AgCl at a scan rate of 10 mV/s under and without irradiation using a simulated light of 1.5 AM (100 mW/cm^2) every 5 seconds. Photoelectrochemical measurements consist of current density, onset potential, and ABPE.

2.5. Characterization of Cu_2O Semiconductors

The synthesized Cu_2O was then characterized using XRD, SEM–EDX, and UV-Vis spectrophotometers. The crystal structure and grain size of the films were analyzed by X-ray diffraction (XRD). When an X-ray beam hits a crystalline solid, the crystal field will refract X-rays with a wavelength equal to the distance between the layers in the crystal. The refracted light will be interpreted as a diffraction peak. After the diffraction peaks are identified, the results of these compounds can be compared using JCPDS and RRUFF data.

The surface morphology of the films was evaluated using Scanning Electron Microscopy (SEM). Electrons can be diffracted by a charged sample, thus forming a pattern that describes the structure of the sample. The current from the light absorbed by the specimen can be detected and used to create an image of the spread of the specimen current. Electronic amplifiers amplify the signal, displayed as brightness on the cathode tube. Analysis images can be taken from high-resolution cathode ray tube photography and saved to a computer hard disk.

The atomic composition was analyzed by Energy Dispersive X-ray Spectroscopy (EDX). A sample to be analyzed using EDX will be subjected to high-energy

electrons on the sample's surface so that the electrons in the inner shell of the sample atom will be excited. This results in a vacancy of electrons in the shell, allowing the composition of a compound to be determined from the transfer of electrons.

3. Results and Discussion

3.1. Fabrication of Cu_2O Semiconductor Thin Films

Thin films of Cu_2O semiconductors have been successfully synthesized using the spin coating method, whose physical appearance can be seen in Figure 1. Semiconductor Cu_2O with a concentration of C2 shows a brighter brick-red color than C1 and C3. The red color indicates that copper is completely reduced to form Cu_2O when the concentration reaches equilibrium. The color of the sample at C1 tends to be brownish, revealing that the formation of Cu_2O is not optimal due to the lack of reducing sugars. Meanwhile, the reduced sugar content in samples with C3 concentration causes the color of the synthesized product to be yellowish orange. Sample C1 yielded 95.69% Cu_2O, while C2 and C3 yielded 96.2% and 99.82%, respectively.

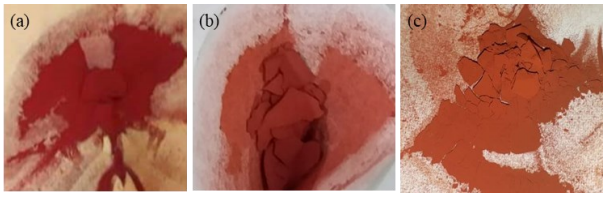

Figure 1. Cu_2O synthesized in (a) C1, (b) C2, and (c) C3

The production of thin films of Cu_2O semiconductors was carried out using the homemade spin coating method at a speed of 500 rpm by dissolving 100 mg of synthesized Cu_2O in 2.5 mL of essential oil. The addition of essential oil functions as a solvent so that it can attach Cu_2O powder to an FTO glass previously washed with 10 mL of nitric acid, acetone, ethanol, and distilled water to remove impurities. Then, the spin coating process was performed by dripping one drop of Cu_2O solution on the FTO glass at 500 rpm for 15 seconds. Then the glass was heated on a hot plate at 100°C for 5 minutes to attach Cu_2O to the glass. Dropping was repeated up to 50 times with the same process.

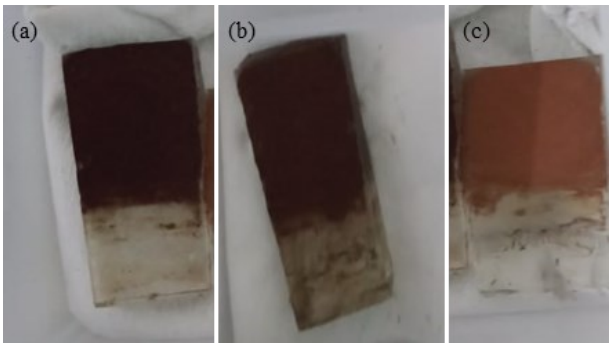

Figure 2. Semiconductor coating results on FTO after annealing on Cu_2O (a) C1, (b) C2, and (c) C3

The next step was the annealing process on the FTO coated with Cu_2O. Annealing is the process of heating a material at a specific temperature and time and then cooling it slowly to reach the desired temperature. This process aims to form CuO oxide and decompose organic compounds as the temperature increases. According to research by Chauhan *et al.* [18], the annealing process is optimal for synthesizing CuO in annealing at a temperature of 400-650°C.

3.2. UV-Vis Spectra of Formation of Cu_2O

UV-Vis spectrophotometry analysis aims to determine the shift in wavelength between reactants and the interactions between one reactant and another so that redox reactions can form Cu_2O precipitates. The results of UV-Vis characterization can be seen in Figure 3.

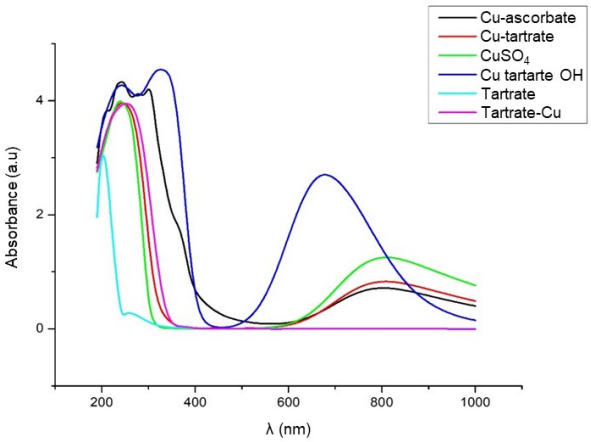

Figure 3. UV-Vis analysis results

Based on the results of UV-Vis characterization, the reagent that plays a role in Cu precipitation is NaOH. Before the presence of NaOH, the absorbance peaks of $CuSO_4$ and $CuSO_4$ tartrate did not experience a shift, only the absorbance intensity increased at 811 nm. After adding NaOH, the absorbance peak shifted to the left at 625 nm. Meanwhile, ascorbate is also proven to increase the resulting precipitate. This is because the peak shifts towards UV, which causes the precipitate to increase [19].

As a result of the peak shift, it causes a complex formation reaction. Hydroxide ions displace hydrogen ions from the air ligands and then attach to the copper ions. This can be seen in the following reaction equation:

$$[Cu\ (H_2O)_6{}^{2+}] + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2]_{(s)} + 2H_2O \quad (1)$$

3.3. XRD Characterization

Figure 4 shows the XRD patterns of the newly produced Cu_2O. The XRD patterns of Cu_2O at varied ascorbic acid concentrations are shown in Figure 4. Figure 4 demonstrates that the Cu_2O C3 XRD peak is not clearly visible and that impurity phases like CuO and Cu_2O may instead be seen. The sharp and strong peaks reveal that the Cu nanocrystalline is highly oriented. At the same time, no characteristic peaks of oxide impurities can be detected. This indicates that only pure Cu and CuO nanoparticles were obtained under synthetic conditions, whereas copper oxide was not formed. Meanwhile, in the sample Cu2O C1 (less than equilibrium) and C2 (at equilibrium) showed peaks of Cu_2O.

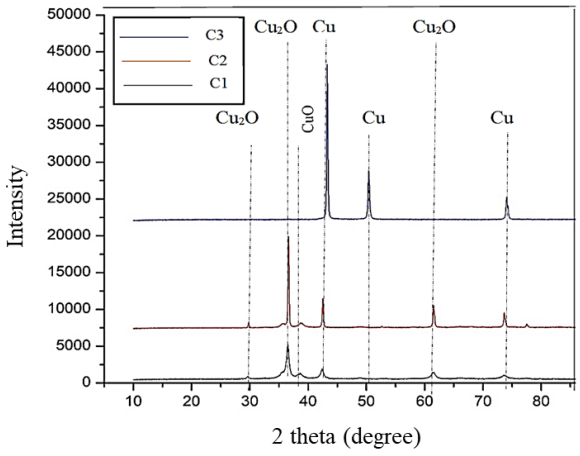

Figure 4. XRD analysis of Cu_2O with different ascorbate concentrations

XRD analysis can also calculate the average grain size of the crystals formed. The calculation of the average grain size is obtained from the FWHM (Full Width Half Maximum) value using the Debye Scherrer equation. The average grain size of Cu crystals can be seen in Table 1.

Table 1. 2θ value, FWHM, and size of Cu crystals

Semiconductor	2θ (°)	θ	FWHM	D (nm)	Average (nm)
Cu_2O (C1)	43.2917	21.6458	0.226	38.24	38.9925
	50.4115	25.2057	0.2472	35.92	
	74.0671	37.0335	0.2387	42.448	
	89.8547	44.9273	0.2882	39.362	
Cu_2O (C2)	29.793	14.8965	0.187	44.45	36.4216
	35.833	17.9165	0.196	43.07	
	36.638	18.319	0.807	10.485	
	38.807	19.4035	0.204	41.749	
	42.515	21.2575	0.211	40.851	
	61.554	30.777	0.218	43.268	
	73.671	36.8355	0.48	46.04	
	77.525	38.7625	0.211	21.46	
Cu_2O (C3)	29.646	14.823	0.48	17.89	17.5575
	35.114	17.557	0.5375	18.27	
	38.529	19.2645	1.008	8.442	
	42.388	21.194	0.5602	15.38	
	61.466	30.733	0.7886	17.103	
	73.638	36.819	1.009	28.26	

The synthesis results show that Cu_2O C1 has the largest average grain size of 38.9925 nm. Meanwhile, the smallest average grain size of 17.5575 nm was achieved by Cu_2O C3, followed by Cu_2O C2, with a size of 36.4216 nm. It can be concluded that additional ascorbic acid as a reducing sugar resulted in a smaller Cu_2O crystal size. Increasing the ascorbate concentration allows nucleation growth to decrease and causes a decrease in particle size [19]. The FWHM value is related to the crystallinity of a material. If the resulting FWHM value is small, the material's crystallinity will be greater. Crystallinity affects charge separation and charge transfer. The more crystalline a substance is, the easier it is to transport a charge due to its decreased resistance, resulting in a greater current density [20].

3.4. Scanning Electron Microscopy (SEM) Analysis

SEM-based characterization and analysis aim to determine the surface morphology of semiconductors. The SEM analysis of the Cu_2O semiconductor is presented in Figure 4, showing that the Cu_2O C1 surface has a cubic shape with long sides. Meanwhile, Cu_2O C3 revealed a more homogeneous flower-like surface morphology. Surface morphology plays a role in the interaction of light with the surface in the electron and hole formation mechanism. A more even and homogeneous surface will increase the light absorption process. The greater absorption of light by a semiconductor generates more electrons and holes, hence increasing the efficiency of the water-splitting process.

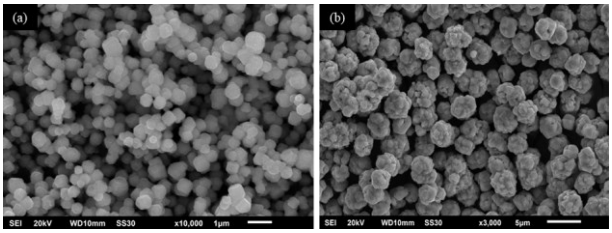

Figure 5. (a) Cu_2O C1 and (b) Cu_2O C3 with 5000 times magnification

3.5. Characterization with Energy Dispersive X-ray Spectroscopy (EDX)

The characterization using EDX aims to quantitatively determine the synthesized Cu2O semiconductor's elemental composition. The results of the EDX analysis can be seen in Table 2.

Table 2. EDX analysis results of Cu_2O Semiconductor

Element	Cu_2O semiconductor		
	C1 (%)	C2 (%)	C3 (%)
Cu	73.97	79.89	98.43
O	26.03	20.11	1.57

The results of the EDX analysis in Table 2 show that pure Cu and O elements have been formed. The semiconductors Cu_2O C1, C2, and C3 revealed the same percentage of elemental composition. There are more Cu elements than O elements. The difference in mass of these elements is due to the formation of Cu_2O oxide while adding an ascorbate solution. Thus, this indicates that Cu_2O has been formed by reacting Fehling A and Fehling B and ascorbic acid solution as reducing sugar. This is also reinforced by the X-ray diffraction analysis, which proves that Cu_2O peaks have formed in the semiconductor sample on the diffractogram.

3.6. Photoelectrochemical Measurement under Simulated Light

Photoelectrochemical measurements under the simulated light aim to determine the ability of synthesized semiconductors to function as photocathodes in the photoelectrochemical water-splitting process. This measurement used the CorrTest 150 tool and the CS Studio 5 application using three electrodes with platinum metal as the anode, Ag/AgCl as the reference electrode, and FTO glass as the cathode. Sodium sulfate solution (0.1 M, pH 9.0) as an electrolyte solution by irradiating with a simulated light of 1.5 AM (100 mW/cm^2) for 5 seconds with a scan rate of 10 mW/scan at a current of 0.5 mV to -1 mV.

3.7. Measurement of Current Density and Onset Potential on Cu_2O Semiconductors

The current density and onset potential were measured with and without irradiation every 5 seconds in Na_2SO_4 solution to determine the actual current density in photoelectrochemical water-splitting applications. The results of measuring the current density in the Na_2SO_4 solution are presented in the JV curve in Figure 6.

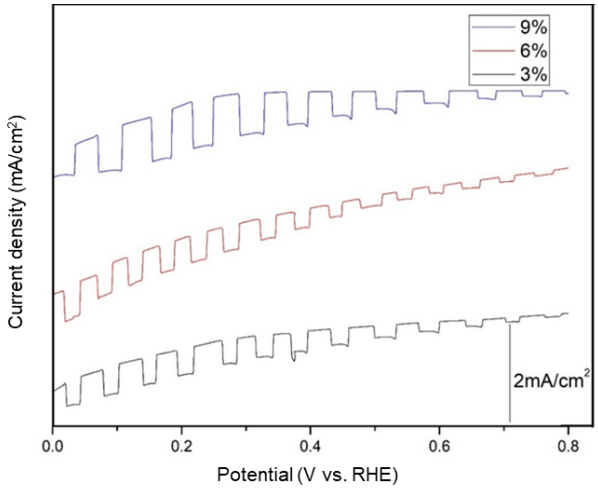

Figure 6. The results of Cu_2O current measurements in various reducing sugars C1(3%), C2 (6%), and C3 (9%) with and without the 1.5 AM simulated sunlight using Na_2SO_4 solution (pH 9)

Figure 6 depicts the current density that arises under irradiation (light on) and returns to zero without irradiation (light off). This shows that the presence of light affects the performance of semiconductors. This light functions in the excitation of electrons and valence band towards the conduction band and produces pairs of electron holes (e^-/h^+) which play a role in oxidation-reduction reactions. The electrons will then be excited from the valence band to the conduction band, decreasing H_2O to H_2 gas, as evidenced by the existence of bubbles on the cathode surface (platinum). In contrast, the holes will oxidize H_2O to oxygen [21].

The concentration of an ascorbic acid solution affects the resulting current density in the Cu_2O semiconductor. The resulting current density value at a potential of 0.3 V vs. RHE (Reversible Hydrogen Electrode) in Na_2SO_4 solution is presented in Table 3.

Table 3. Current density of Cu2O semiconductor at various ascorbate concentrations at a voltage of 0.3 V

Cu_2O samples	Current Density (mA /cm^2)
C1	1.186
C2	1.693
C3	1.787

The resulting current density in the Cu_2O semiconductor with variations in the addition of ascorbic acid C1, C2, and C3 was respectively 1.186, 1.693, and 1.787 mA/cm^2 at 0.3 RHE. The highest photon current was produced when the concentration of 9% ascorbate solution was added (C3). Thus, it can be concluded that the more the addition of ascorbic acid solution, the higher the photon current generated on the Cu_2O semiconductor thin layer. This is because the formation of Cu_2O has become more evenly distributed, resulting in a greater photon current.

The current density generated by the doctor blade method is the semiconductor layer deposition by flattening the paste on the glass substrate using a stirrer, followed by drying and centrifugation at a certain temperature and time [16]. In the doctor blade method, DMSO was used as a solvent and stirrer for the doctor blade coating process. After levelling with a stirrer, the FTO glass was heated on a hot plate at 90°C. The results of measuring the current density in the Na_2SO_4 solution are presented in the JV curve in Figure 7.

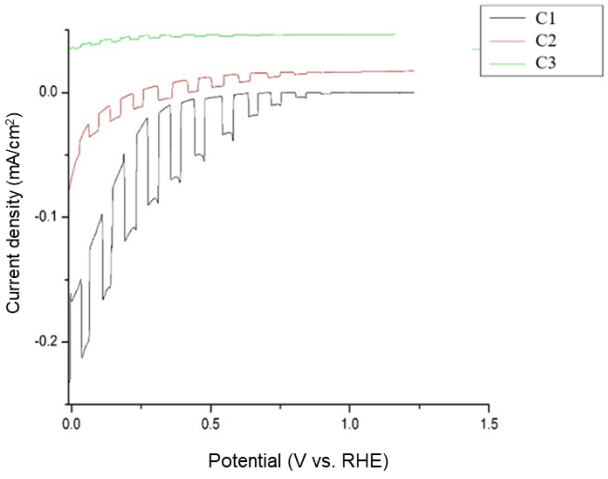

Figure 7. The results of measuring the current density of Cu_2O with various reducing sugars of C1(3%), C2(6%) and C3 (9%) using the doctor blade method

The resulting current density in the Cu_2O semiconductor using the doctor blade method with variations in the addition of ascorbic acid C1, C2, and C3 were respectively 0.006, 0.048, and 0.147 mA/cm^2 at 0.26 V vs. RHE. The highest photon current was produced when the concentration of 9% ascorbate solution (C3) was added.

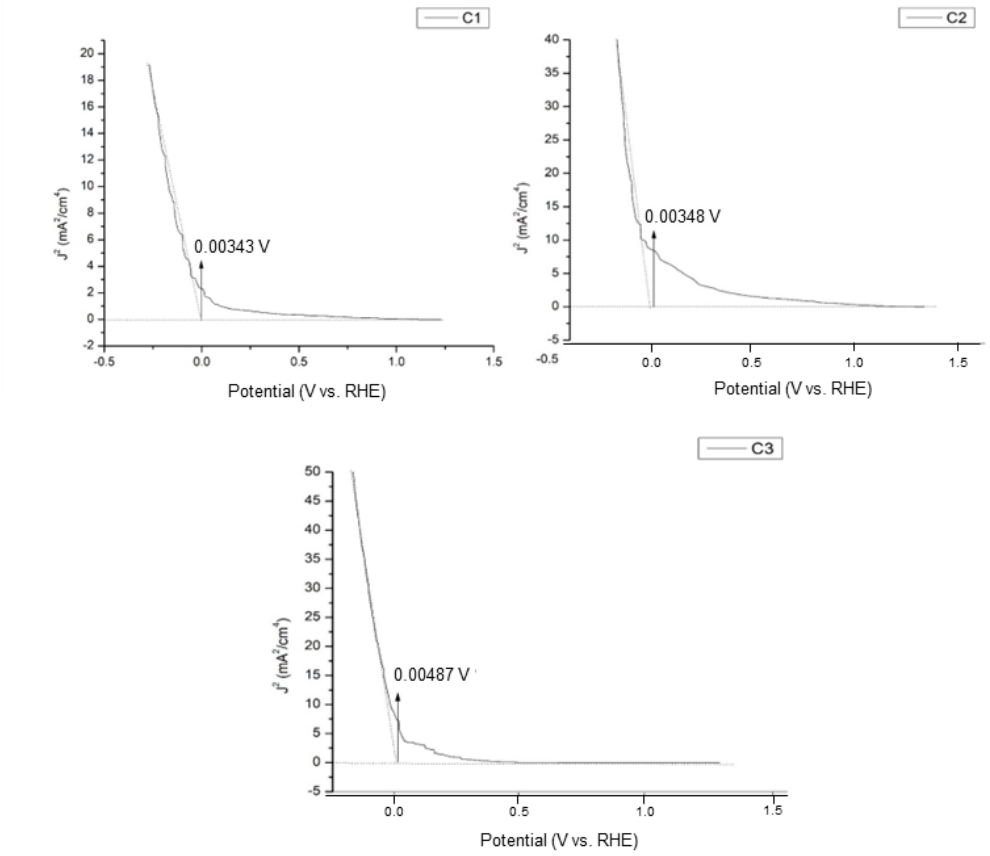

Figure 8. Cu_2O semiconductor onset potential curve with variations in the addition of C1, C2, and C3 ascorbate concentration

Thus, the spin coating method produced a higher current than the doctor blade method. The spin coating method has better results than the doctor blade method because the homogeneity of the solution is well calcined on the substrate so that it can be deposited on the FTO glass with the maximum [22].

Next, the potential onset measurement was performed on the Cu_2O semiconductor. The onset potential is the initial potential for a current to appear in a semiconductor when it is illuminated by light. The determination of the onset potential is shown in the plot of the current density squared (J2) to the potential (V). The Cu_2O semiconductor onset potential curve can be seen in Figure 8.

Figure 8 shows the current density squared (J2) plot to the potential (V). The onset potential is determined from the intersection of the linear lines on the curve [20]. Semiconductor Cu_2O with varying concentrations of glucose solutions C1, C2, and C3 produced potentials of 0.00343 V, 0.00348 V, and 0.00487 V, respectively. The onset potential affects the performance of the semiconductor. To be able to work as a photocathode, it must have an onset potential of more than zero so that there is an intersection between the onset potential and the photocathode (maximum operating current density). The water-splitting does not require an external bias when the intersection occurs. Thus, the reaction can take place spontaneously without any additional stress. Therefore, the more positive the onset potential, the higher the performance of the photocathode. Semiconductor Cu_2O, with the addition of C3 solution concentration, has the highest onset potential. Thus, it can be concluded that the additional ascorbate affects the photon current and onset potential produced by the Cu_2O semiconductor. The greater the concentration of an ascorbic acid solution, the higher the photon current and onset potential generated by the Cu_2O semiconductor.

3.8. Applied Bias Photon to Current Efficiency (ABPE) Measurement

The ABPE measurement aims to determine the efficiency of the photocathode in responding to photon/light energy into an electric current under the applied voltage. To determine the ABPE value at the photocathode, previously carried out measurements of photocurrent (current density) on the photocathode using three electrodes, $CuSO_4$ as the working electrode, platinum as the cathode, and Ag/AgCl as the reference electrode, which is inserted into the Na_2SO_4 electrolyte solution to determine the theoretical ABPE value ideally used for the process of measuring the efficiency of photoelectrochemical water splitting. The curve of ABPE value (%) in the Na_2SO_4 solution is presented in Figure 9.

ABPE is determined by converting the current density value (J) to potential (V). Figure 9 shows a change in the % ABPE Cu_2O value. The Cu_2O C3, C2, and C1 produced photocathode efficiencies of 1.3012%, 1.252%, and 1.281%, respectively. Thus, the higher the ascorbate concentration, the greater the efficiency in photoelectrochemical water splitting.

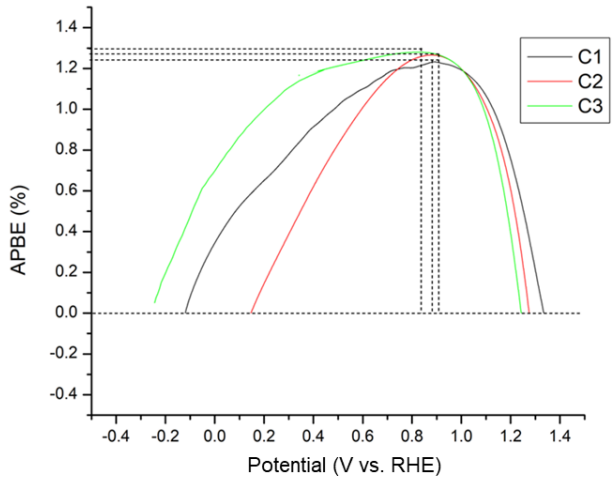

Figure 9. ABPE curves of Cu_2O semiconductors C1, C2 and C3

4. Conclusion

Semiconductor Cu_2O was successfully synthesized via spin-coating with additional ascorbic acid at various concentrations. The Cu_2O C3 semiconductor (9% ascorbic acid concentration) showed the highest %ABPE due to its high crystallinity, which made the charge transfer process unchallenging. This is supported by the resulting high density and onset potential of 0.147 mA/cm² at 0.26 V vs. RHE and 0.00487 V, respectively. Current density measurement using the spin-coating method gives maximum results compared to the doctor blade method because of the homogeneity of the solution adequately calcined on the substrate so that it can be deposited on the FTO glass with the maximum. SEM analysis showed that the surface morphology of Cu_2O C3 was more homogeneous in flower-like shape. The higher concentration of ascorbic acid causes the Cu_2O semiconductor to have the potential as an efficient material for photoelectrochemical water-splitting.

References

[1] David Sebastián, Isabel Suelves, Rafael Moliner, María Jesús Lázaro, Alessandro Stassi, Vincenzo Baglio, Antonino Salvatore Aricò, Optimizing the synthesis of carbon nanofiber based electrocatalysts for fuel cells, *Applied Catalysis B: Environmental*, 132-133, (2013), 22-27 https://doi.org/10.1016/j.apcatb.2012.11.023

[2] Wilman Septina, Rajiv Ramanujam Prabhakar, Rene Wick, Thomas Moehl, S. David Tilley, Stabilized solar hydrogen production with CuO/CdS heterojunction thin film photocathodes, *Chemistry of Materials*, 29, 4, (2017), 1735-1743 https://doi.org/10.1021/acs.chemmater.6b05248

[3] Dong Joo Choi, Jeong-Ki Kim, Haseob Seong, Min-Seok Jang, Young-Ho Kim, The formation of Cu_2O nanoparticles in polyimide using Cu electrodes via chemical curing, and their application in flexible polymer memory devices, *Organic Electronics*, 27, (2015), 65-71 https://doi.org/10.1016/j.orgel.2015.09.007

[4] D. P. Halliday, M. D. G. Potter, J. T. Mullins, A. W. Brinkman, Photoluminescence study of a bulk vapour grown CdTe crystal, *Journal of Crystal Growth*, 220, 1-2, (2000), 30-38 https://doi.org/10.1016/S0022-0248(00)00755-7

[5] Necmi Serin, Tülay Serin, Şeyda Horzum, Yasemin Celik, Annealing effects on the properties of copper oxide thin films prepared by chemical deposition, *Semiconductor Science and Technology*, 20, 5, (2005), 398 https://doi.org/10.1088/0268-1242/20/5/012

[6] Junie Jhon Magdadaro Vequizo, C. Zhang, Masaya Ichimura, Fabrication of Cu_2O/Fe–O heterojunction solar cells by electrodeposition, *Thin Solid Films*, 597, (2015), 83-87 https://doi.org/10.1016/j.tsf.2015.11.034

[7] Kulandaivelu Kaviyarasan, Sambandam Anandan, Ramalinga Viswanathan Mangalaraja, Thirugnanasambandam Sivasankar, Muthupandian Ashokkumar, Sonochemical synthesis of Cu_2O nanocubes for enhanced chemiluminescence applications, *Ultrasonics Sonochemistry*, 29, (2016), 388-393 https://doi.org/10.1016/j.ultsonch.2015.10.018

[8] Javeed Mahmood, Feng Li, Sun-Min Jung, Mahmut Sait Okyay, Ishfaq Ahmad, Seok-Jin Kim, Noejung Park, Hu Young Jeong, Jong-Beom Baek, An efficient and pH-universal ruthenium-based catalyst for the hydrogen evolution reaction, *Nature Nanotechnology*, 12, (2017), 441-446 https://doi.org/10.1038/nnano.2016.304

[9] G. Jimenez-Cadena, E. Comini, M. Ferroni, G. Sberveglieri, Synthesis of Cu_2O bi-pyramids by reduction of $Cu(OH)_2$ in solution, *Materials Letters*, 64, 3, (2010), 469-471 https://doi.org/10.1016/j.matlet.2009.11.051

[10] M. Kooti, L. Matouri, Fabrication of nanosized cuprous oxide using fehling's solution, *Scientia Iranica*, 17, 1, (2010), 73-78

[11] Mehmet Zahmakiran, Saim Ozkar, Zeolite-confined ruthenium(0) nanoclusters catalyst: record catalytic activity, reusability, and lifetime in hydrogen generation from the hydrolysis of sodium borohydride, *Langmuir*, 25, 5, (2009), 2667-2678 https://doi.org/10.1021/la803391c

[12] K. Gopalakrishnan, C. Ramesh, V. Ragunathan, M. Thamilselvan, Antibacterial activity of Cu_2O nanoparticles on *E. coli* synthesized from *Tridax procumbens* leaf extract and surface coating with polyaniline, *Digest Journal of Nanomaterials and Biostructures*, 7, 2, (2012), 833-839

[13] H. Sekhar, D. Narayana Rao, Preparation, characterization and nonlinear absorption studies of cuprous oxide nanoclusters, micro-cubes and micro-particles, *Journal of Nanoparticle Research*, 14, 976, (2012), 1-11 https://doi.org/10.1007/s11051-012-0976-4

[14] Hui-Bog Noh, Kyung-Sun Lee, Pranjal Chandra, Mi-Sook Won, Yoon-Bo Shim, Application of a Cu–Co alloy dendrite on glucose and hydrogen peroxide sensors, *Electrochimica Acta*, 61, (2012), 36-43 https://doi.org/10.1016/j.electacta.2011.11.066

[15] Fadime Eryılmaz Pehlivan, Vitamin C: An antioxidant agent, in: A.H. Hamza (Ed.) *Vitamin C*, IntechOpen, 2017, https://doi.org/10.5772/intechopen.69660

[16] Gregory A. Luurtsema, Spin coating for rectangular substrates, Department of Electrical Engineering

and Computer Sciences, University of California, Berkeley, 1997

[17] Praduman Arora, Aadesh P. Singh, Bodh R. Mehta, Suddhasatwa Basu, Metal doped tubular carbon nitride (tC_3N_4) based hematite photoanode for enhanced photoelectrochemical performance, *Vacuum*, 146, (2017), 570-577 https://doi.org/10.1016/j.vacuum.2017.07.010

[18] Diwakar Chauhan, V. R. Satsangi, Sahab Dass, Rohit Shrivastav, Preparation and characterization of nanostructured CuO thin films for photoelectrochemical splitting of water, *Bulletin of Materials Science*, 29, 7, (2006)

[19] Shahrzad Arshadi-Rastabi, Javad Moghaddam, Mohammad Reza Eskandarian, Synthesis, characterization and stability of Cu_2O nanoparticles produced via supersaturation method considering operational parameters effect, *Journal of Industrial and Engineering Chemistry*, 22, (2015), 34-40 https://doi.org/10.1016/j.jiec.2014.06.022

[20] Zhebo Chen, Huyen N. Dinh, Eric Miller, *Photoelectrochemical water splitting*, 1 ed., Springer, New York, 2013, https://doi.org/10.1007/978-1-4614-8298-7

[21] Josny Joy, Jinu Mathew, Soney C. George, Nanomaterials for photoelectrochemical water splitting–review, *International Journal of Hydrogen Energy*, 43, 10, (2018), 4804-4817 https://doi.org/10.1016/j.ijhydene.2018.01.099

[22] Vitriany Ekasari, Gatut Yudoyono, Fabrikasi DSSC dengan dye ekstrak jahe merah (*Zingiber officinale* linn var. rubrum) variasi larutan TiO_2 nanopartikel berfase anatase dengan teknik pelapisan spin coating, *Jurnal Sains dan Seni ITS*, 2, 1, (2013), B15-B20