Experimental study of $CuBi_2O_4$ photocathode synthesized by spray pyrolysis and electrochemical deposition methods for visible light harvesting in photoelectrochemical cells

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This research examined methods that are suitable, easy to fabricate, and low-cost for producing $CuBi_2O_4$ photocathodes for application in photoelectrochemical cells. Both spray pyrolysis and electrochemical deposition techniques were used to produce thin films for various types of semiconductor electrodes. The $CuBi_2O_4$ thin film was coated on fluorine-doped tin oxide (FTO) using spray pyrolysis and electrochemical deposition, followed by annealing in an oxygen atmosphere. X-ray diffraction (XRD) characterized the crystal structures, confirming them as Kusachiite. Scanning electron microscopy (SEM) analysis revealed that $CuBi_2O_4$ fabricated by electrochemical deposition exhibited smaller particles, while the spray pyrolysis method produced a plate-like structure. The optical properties were investigated using UV-visible reflection, and the energy bandgaps of the products were estimated using Tauc plots, showing slight differences. Chopped light voltammetry (CLV) was used to evaluate the photon conversion efficiency of the synthesized photocathodes. Results indicated that the photocathode made by electrochemical deposition responded better to light compared to the one made by spray pyrolysis. With 0.5 M Na_2SO_3 as a sacrificial agent, the highest photocurrent density obtained was 0.2 mA/cm², while with 0.5 M $NaHCO_3$, the highest photocurrent was 0.5 μA/cm², indicating poorer performance.

(Received November 19, 2024; Accepted January 24, 2025)

Keywords: Kusachiite, Photoelectrochemical cells, Photocathode, Electrochemical deposition, Spray pyrolysis

1. Introduction

Research on photocatalyst materials for water splitting reactions has focused on developing materials suitable for converting light into chemical energy. This conversion is achieved using a device called a photoelectrochemical cell (PEC) [1], which consists of two electrodes based on the semiconductor materials used. When using a p-type semiconductor, two electrodes are required: one is the photocathode, and the other is the platinum (Pt) counter electrode. Upon light irradiation, the photocathode generates hydrogen (H_2) gas, while the Pt electrode generates oxygen (O_2) gas. In the case of an n-type semiconductor, the roles are reversed. Both p-type and n-type configurations require an external power supply to drive the electrons needed to generate O_2 or H_2. The final type of PEC is the tandem cell [2-3], which comprises a photocathode (p-type) and a photoanode (n-type) semiconductor without the need for an external power supply.

For p-type semiconductors, a key advantage is their low energy bandgap compared to n-type semiconductors.[4] Due to this advantage, many materials [5], such as CuO [6-9], Cu_2O [10-15], and $CuBi_2O_4$ [16-19], have been studied for PEC applications. Our research focuses on CuBi2O4, which has shown great potential for converting photons into chemical energy. The energy bandgap of $CuBi_2O_4$ is 1.8 eV [20], making it highly suitable for harvesting solar energy. $CuBi_2O_4$ can be synthesized as nanoparticles and deposited on conductive transparent oxide (CTO) glass. One advantage of depositing the material on CTO glass is its strong adhesion. To use nanoparticles for coating on CTO, an additional binder is required, which can be annealed until only the semiconductor material remains on the CTO substrate. However, this process can lead to instability

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https://doi.org/10.15251/DJNB.2025.201.113

of the material on the CTO substrate, making it susceptible to degradation during the water splitting reaction.

The electrochemical deposition and the spray pyrolysis are both employed to fabricate the semiconductor thin film on the CTO substrate. For example, Y. Nakabayashi et al. [20]., fabricated the photocathode by an electrodeposition method. His work was started from depositing Bi_2O_3 and CuO, and heat treatment to obtain the $CuBi_2O_4$. The energy band gap of $CuBi_2O_4$ was 1.8 eV. Moreover, the method of $CuBi_2O_4$ fabrication and comparison was done by B. Meena et al. [16] There were three main methods compared, namely, drop-casting, hydrothermal, and electrodeposition methods and then was further studied as a tandem PEC. In the case of the spray pyrolysis, F. Wang et al. [21] was studied the solution for highly homogeneous $CuBi_2O_4$ thin film. There were many solvents were studied, e.g. triethyl orthoformate, and polyethylene glycol. Furthermore, Y. Wang et al. [22] was also investigated the fast evaporated solvent to from $CuBi_2O_4$ photocathode for water splitting. The result was the highest photocurrent density of 0.3 mA/cm^2. In our respect, the spray pyrolysis and electrochemical deposition are generally methods to fabricate the thin film for PEC. However, which method is the best practical and more reliable to use is not be a research topic.

In this work, the $CuBi_2O_4$ was employed the electrochemical deposition and the spray pyrolysis to fabricate. The main aim of this study is to compare the method which one is the best suitable for $CuBi_2O_4$ fabrication with the greatest photocurrent density. Hence, the effect of solvent was our limit parameter where only the deionized water was solely used as a solvent only. The thin film coated on the FTO substrate was investigated by XRD, SEM and UV-Visible spectroscopy. The performance of specimens was tested by CLV method which is the photo-conversion efficiency upon a light irradiation only.

2. Material and methods

For the materials, the Bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) and Copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) were purchased from Merck and applied without purified. For the substrate, the FTO substrate (Merck, 7Ω/sq) was cut into 2 cm × 2 cm and then cleaned by acetone, ethanal and DI water ultrasonically for 10 min each.

The Bi and Cu precursors were mixed at the Bi:Cu ratio of 2:1 in order to from $CuBi_2O_4$ materials on FTO substrate. To simplify, the 10 mmol of $Bi(NO_3)_3 \cdot 5H_2O$ and 5 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in the DI water. It is to note that the $Bi(NO_3)_3 \cdot 5H_2O$ was difficult to dissolve in water, thus the 3 mL of HCl (37%, Merck) was dropwise to help the $Bi(NO_3)_3 \cdot 5H_2O$ to dissolve. There is no further additive was added. Then, the Bi and Cu precursor was applied to fabricate on the FTO substrate. In the case of spray pyrolysis, the substrate was heat up to 500 °C for 30 min then the mixed of Cu and Bi solvent was spray to the substrate for 1 min where the black brown thin film was noticeable observed. In the case of electrochemical deposition, the FTO and the Pt were submerged into the Bi and Cu mixed solution where the FTO electrode was set at a negative pole and the Pt wire was set at a positive pole of precision power supply. The voltage was fixed at 2 V while the current was limited at 10 mA. The deposited time was set to 10 min where the Bi and Cu ions was homogeneous well from on the FTO substrate. Then, the as-prepared $CuBi_2O_4$ thin film was further annealed at 500 °C in O_2 atmosphere.

The crystal structure formed on the FTO substrate was characterized by XRD (Bruker D8, eco). The surface morphology of this film was investigated by SEM (JEOL JEM-IT800). The optical property was studied by the UV-Visible absorption spectroscopy (Shimazu UV 2600). The CLV and electrochemical imprudence spectroscopy (EIS) was studied by potentiostate (Zennium pro, Zahner electrik). All light illumination was employed the white LED solar simulator from Zahner electrik.

3. Results and discussions

Fig. 1 shows the crystal structure of $CuBi_2O_4$ was analyzed by XRD technique. When compared to the PDF#01-071-1774 database [23], both spectra are match well to this phase. Thus, it is confirmed that the electrochemical deposition [24] and spray pyrolysis method [22,25] can be successfully synthesis. In both cases, it was found another CuO phases was mixed the main $CuBi_2O_4$. The small diffraction peak located at 32.5°, 36.7°, and 38.9° were assigned as the CuO phase.

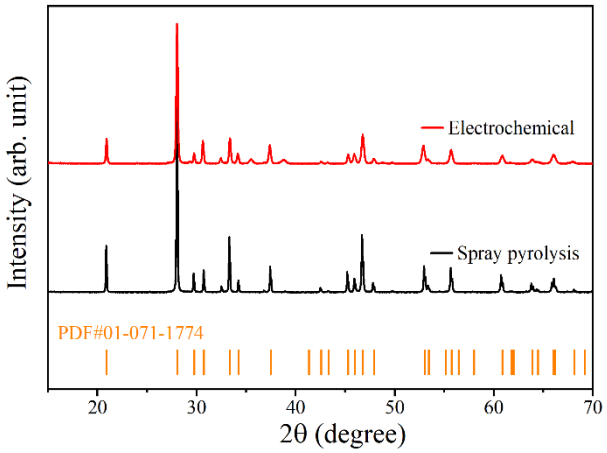

Fig. 1. XRD patterns of $CuBi_2O_4$ fabricated by the electrochemical deposition and spray pyrolysis methods.

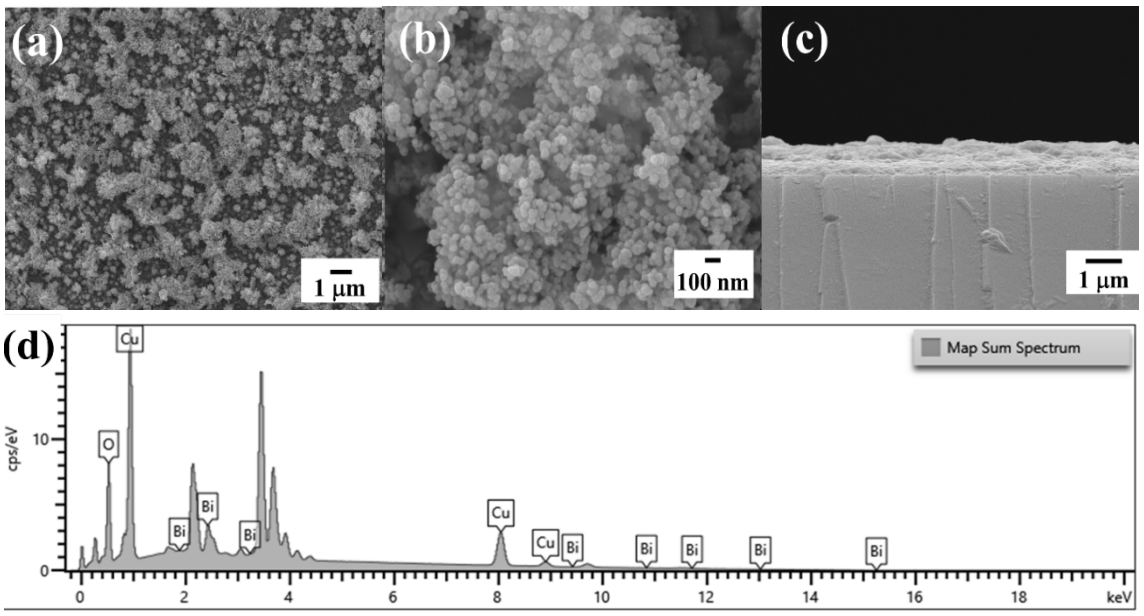

Fig. 2. SEM image of $CuBi_2O_4$ synthesized by the electrochemical deposition.

The surface morphology of sample was studied by SEM. In Fig. 2a showed the overall surface morphology of $CuBi_2O_4$ synthesized by the electrochemical deposition. From the result, the $CuBi_2O_4$ nanoparticles were most coated on the FTO substrate. Fig. 2b showed the magnification of Fig. 2a which one can estimate the size of $CuBi_2O_4$. From the scale bar, the estimated diameter of $CuBi_2O_4$ nanoparticle is around 50 – 100 nm. The shape of the particle is look like the nanosphere. Fig. 2c revealed the thickness of $CuBi_2O_4$ coated on the FTO substrate, which is around 1 μm height.

Fig. 2d shows the energy dispersive X-ray spectroscopy analysis (EDX) of the film, that reveal the majority composition of Cu, Bi, and O atoms on the FTO film.

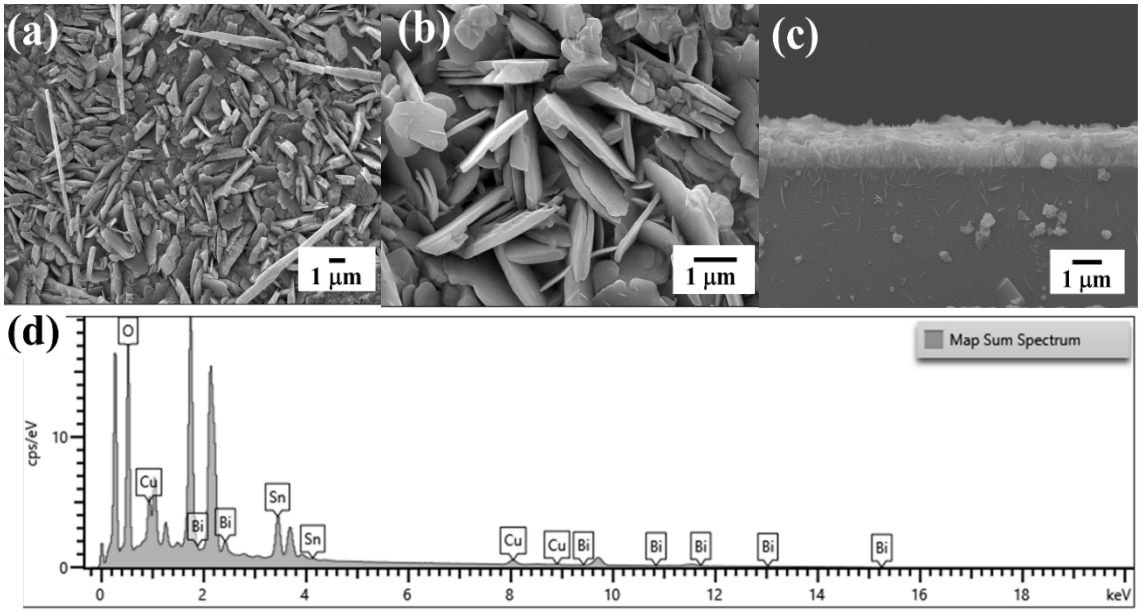

Fig. 3. SEM image of $CuBi_2O_4$ synthesized by the spray pyrolysis deposition.

In contract to the $CuBi_2O_4$ fabricated by spray pyrolysis method, the overall surface morphology of the film as shown in Fig. 3a and its magnified shown in Fig. 3b are different. The plate-like $CuBi_2O_4$ was coated on the FTO substate where the film thickness about 1.2 µm long. When compared to the electrochemical deposition, the film was denser and thicker. Fig. 3d shows EDX of the film, that reveal the majority composition of Cu, Bi, and O atoms on the FTO film.

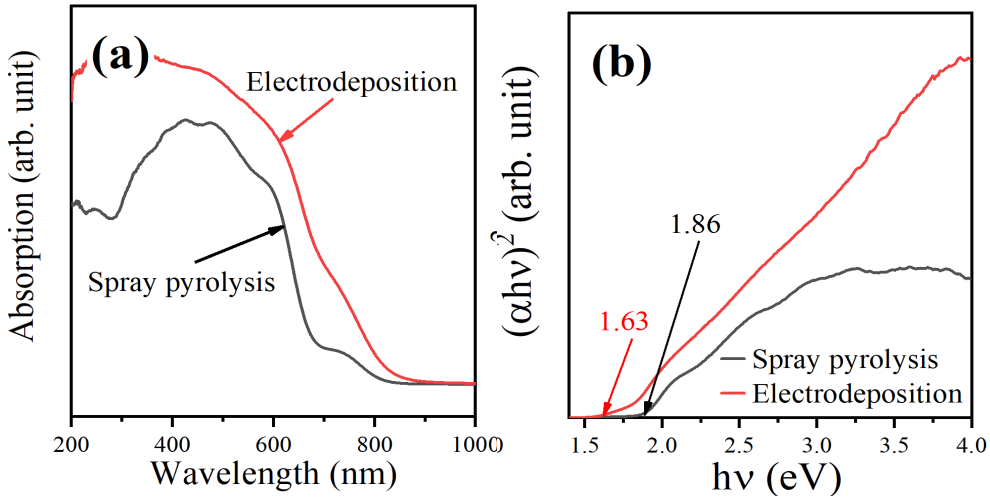

Fig. 4. (a) UV visible absorption spectra and (b) Tauc plot of $CuBi_2O_4$ fabricated by different methods.

Fig. 4 showed the optical property and the estimated energy bandgap of $CuBi_2O_4$ materials at different synthesis methods. In Fig. 4a, the absorption spectra of materials were obtained by the

Kubelka transformation from the UV-visible reflection spectra of each $CuBi_2O_4$. As a result, the over energy spectra of both exhibited visible light absorption. The energy band edge of $CuBi_2O_4$ synthesized by electrochemical deposition methods was a bit extend than the $CuBi_2O_4$ synthesized by spray pyrolysis method. By plotting the relation between the photon energy and $(\alpha h\nu)^2$, the extrapolated on x-axis is showed the energy gap of the materials. The case of $CuBi_2O_4$ fabricated by spray pyrolysis obtained 1.86 eV while another fabrication was obtained 1.63 eV.

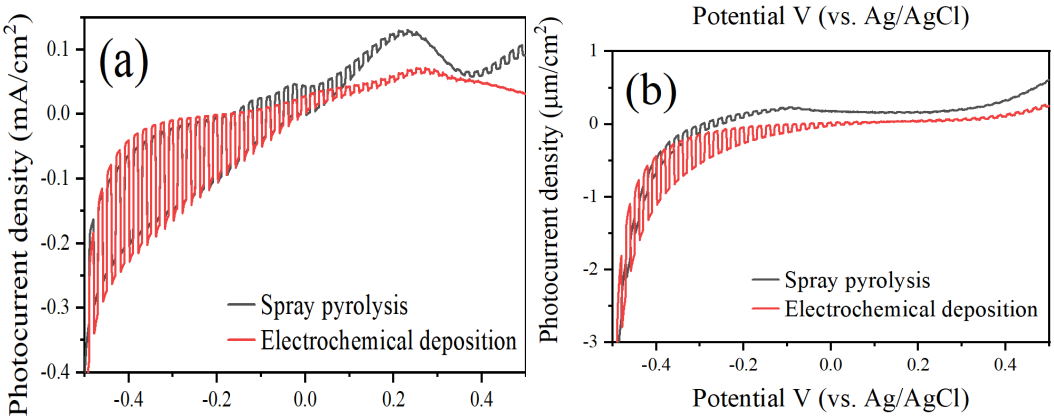

Fig. 5. CLV of $CuBi_2O_4$ fabricated by electrochemical deposition method and spray pyrolysis method were tested in (a) 0.5 M Na_2SO_3 and (b) 0.5 M $NaHCO_3$ electrolytes.

The performance of photocathode was examined by the CLV method. In the CLV test, the light was turned on and off in a period of time. The amount of photocurrent density obtained from the light irradiation is concerned to the electron promotion and separation in the photocathode. The transferred electrons across the electrode is due to the applied the external bias voltage. Hence, the most responded and efficiency photocathode should have at most photocurrent density. Fig 5a showed the CLV of photocathode using 0.5 M Na_2SO_3 as an electrolyte. Considered at the applied -0.4 bias voltage vs. Ag/AgCl, the photocurrent density of $CuBi_2O_4$ photocathode made by the electrochemical deposition exhibited the greater respond to the light than the $CuBi_2O_4$ photocathode made by the spray pyrolysis method.

In addition, Fig. 5b showed the efficiency of photocathode with different electrolyte. In this study, the $NaHCO_3$ is the source of CO_2. From the result, the $CuBi_2O_4$ made from the electrochemical deposition still showed the better performance to reduce the CO_2 to from another chemical spices. However, the magnitude of photocurrent density is less than by using Na_2SO_3 by about 1,000 times. In order to apply this electrode, it is required to improve the photocatalytic activity of the $CuBi_2O_4$ surface as shown in the literatures.

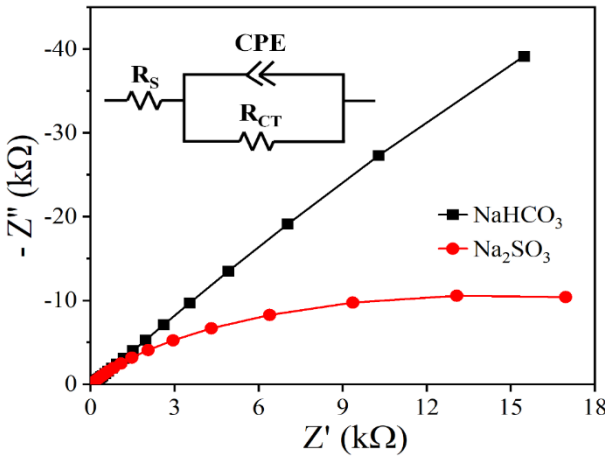

Fig. 6. Nyquist plot of $CuBi_2O_4$ photocathode tested at applied -0.3 V (vs. Ag/AgCl) under visible light illumination.

The EIS study of $CuBi_2O_4$ photocathode made by electrochemical deposition method was showed in Fig. 6. The EIS technique can be allowed us to estimate the internal resistance of the PEC when its operates. Therefore, the test should be performed at the selected condition that PEC can be operated ready. In Fig. 6, the compare internal resistance occurred when the PEC operated with different electrolytes, which are in Na_2SO_3 and $NaHCO_3$. According to the fitting model, the arc radius is referred to the internal resistance (R_{CT}). The Na_2SO_3 is the best electrolyte for the $CuBi_2O_4$ photocathode as its lowest internal resistance causing the greater photocurrent density supporting to the result in Fig. 5.

4. Conclusions

This work was compared the suitable method, which are the electrochemical deposition method and the spray pyrolysis method, to fabricate the $CuBi_2O_4$ thin film coated directed on the FTO substrate. The products were characterized by XRD, SEM and UV-visible absorption spectroscopy. The XRD confirmed the $CuBi_2O_4$ was obtained by both synthesis method. It was found that the surface morphology obtained from both synthesis technique was different and effected to the photocathode performance. The value obtained in this studied may be improved in the next further research.

Acknowledgements

This study was funded by King Mongkut's University of Technology North Bangkok (contract no. KMUTNB-66-KNOW-06).

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