

# Synthesis and Characterization of Nanocube Cu<sub>2</sub>O Thin Film at Room Temperature for Methylene Blue Photodegradation Application

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## Abstract

Methylene Blue is a synthetic dye with a complex structure thus making it hard to decompose naturally. Among the decomposition methods of synthetic dyes is photodegradation using a semiconductor material. In this study, Cu<sub>2</sub>O semiconductor nanoparticle has been synthesized on the surface of conductive substrate indium tin oxide using the electrodeposition method at room temperature. The X-ray diffractometer analysis provides information on the presence of Cu<sub>2</sub>O in the sample and the shape of the Cu<sub>2</sub>O crystal system which is a nanocube. Scanning electron microscopy with energy-dispersive X-ray spectroscopy provides distribution mapping information based on the morphology and atomic composition of the sample. Impedance measured a maximum resistance to charge transfer value of 2500 Ω. Photodegradation test towards methylene blue achieved a percent of degradation was 62.00% for 120 minutes under visible light irradiation with initial and final absorbance values of 1.56351 abs and 0.896875 abs respectively.

**Keywords:** Cu<sub>2</sub>O, photodegradation, methylene blue, thin film.

## 1. Introduction

Most synthetic dyes are complex organic molecules with high stability [1]. Methylene blue (MB) is one of the dyes that are commonly found in industrial applications. Waste disposal of MB could affect the environment because MB is toxic, carcinogenic, and mutagenic to organisms [2]. These are the reasons why MB needs to be treated before being disposed of in the environment. One method to decompose synthetic dyes is the photodegradation method. The photodegradation method uses a semiconductor material to decompose organic substances structures. The semiconductor can absorb light at a certain wavelength which causes a redox reaction in water on the surface of the material that produces radical. These radicals can oxidize organic compounds including MB resulting in decomposing of the structure [3]. Photodegradation methods have superiority such as low cost, ease of process, and environmental friendliness [4].

A previous study by Abdulla *et al.* successfully synthesized BiVO<sub>4</sub>-CuO using the precipitation method [5]. BiVO<sub>4</sub>-CuO in this study has a degradation efficiency at MB and natural pH in the range of 40-90% based on CuO-doped variants and another study by Budi *et al.*, synthesized a CoNi-decorated Zn-doped Cu<sub>2</sub>O via electrodeposition technique on an indium tin oxide-coated polyethylene terephthalate substrate exhibited 42.19% photocatalytic degradation of MB [6].

Both Cu<sub>2</sub>O and CuO have potential ability for photodegradation. However, Cu<sub>2</sub>O is better in terms of carrier concentration because Cu<sub>2</sub>O has a larger bandgap with a value of 2.0-2.2 eV [7]. Apart from that, Cu<sub>2</sub>O has superiorities such as being easy to process, low production cost, non-toxic, and having a high optic absorption at visible light wavelength regions [8].

Many methods could be used to synthesize Cu<sub>2</sub>O such as sol-gel, sonochemical, sputtering, hydrothermal, and electrodeposition [9-14]. Among these methods, electrodeposition has high potential because of its

superiority in morphology control such as deposition time, temperature, frequency, applied potential, and pH, thus enabling to control of the final product specifically [13]. Furthermore, electrodeposition is a method with low cost and is environmentally friendly [14].

To explore the potential of pure  $\text{Cu}_2\text{O}$  as photocatalyst material,  $\text{Cu}_2\text{O}$  thin films were synthesized using the electrodeposition method at room temperature for MB photodegradation. Methylene blue is chosen as the synthetic dyes because MB has high stability which makes it hard to decompose naturally. This compound could be used as a reference when photodegrading other synthetic dyes [15].

## 2. Materials and Method

The materials used in this study were copper II sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), potassium chloride (KCl), lactic acid ( $\text{C}_3\text{H}_5\text{O}_3$ ), sodium hydroxide (NaOH), and indium tin oxide (ITO) substrates were used for the  $\text{Cu}_2\text{O}$  electrodeposition.

### 2.1 Fabrication of $\text{Cu}_2\text{O}$ thin film

The electrodeposition method was conducted using a 3-electrode system with Pt as a counter electrode, Ag/AgCl as the reference electrode, and ITO as the working electrode. The  $\text{Cu}_2\text{O}$  preparation was carried out for 1 h with a constant current at -0,3 V using an electrolyte solution containing  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  0.049875 M and lactic acid as the solvent.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution was added with  $\text{Na}_2\text{SO}_4$  0.202591 M with aquadest as a solvent until the volume was 25 mL, then the pH of the solution was controlled at 10 by the addition of solid NaOH.

### 2.2 Characterization

Identification of  $\text{Cu}_2\text{O}$  Crystal structure and the size of the crystallite was accomplished using an X-ray diffractometer (XRD) (PANalytical Aeris with PIXcel1D-Medipix3 detector, and  $\text{CuK}\alpha$  radiation source). Then for analysis morphological and compositional  $\text{Cu}_2\text{O}$  crystal used scanning electron microscope - energy dispersive X-ray (SEM-EDX, FEI brand type: Inspect-S50). SEM-EDX results are used to observe the morphology that is formed at the thin film and find out the elements that are contained in the substrate layer.

### 2.3 Electrochemical impedance spectroscopy test

In this process, the electrolyte used is KCl 0.5 M in 25 mL aquadest. These solutions are used in the 3-electrode system with the thin film  $\text{Cu}_2\text{O}$  sample as the working electrode, Ag/AgCl (KCl 3 M) as the reference electrode,

and Pt as the counter electrode. The test was carried out with a frequency rate of 1 Hz to 100.000 kHz under irradiation.

### 2.4 Photoelectrochemical test

Photoelectrochemical cell tests are conducted in bright and dark conditions. The electrolyte used is 50 mL  $\text{Na}_2\text{SO}_4$  0.5 M. Each test is conducted in the voltage range of -0.5 to 1.5 V at room temperature using 3-electrode system with  $\text{Cu}_2\text{O}$  thin film sample as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode.

### 2.5 Photodegradation Test

The photocatalytic activity was measured using photodegradation of 5 ppm of MB solution under visible light irradiation. The measurement of MB concentrations is conducted for 120 minutes with the data taken every 5 minutes using spectrophotometry UV-Vis (GB Cintra 2020) to observe the concentration changes in the interval times.

## 3. Results and Discussion

The XRD patterns of the  $\text{Cu}_2\text{O}$  sample are shown in Fig. 1 the crystallinity of  $\text{Cu}_2\text{O}$  was confirmed according to the COD reference data No. #900-57-69. The peak  $\text{Cu}_2\text{O}$  crystallinity was observed at  $2\theta = 36.430^\circ$ ;  $42.371^\circ$ ; and  $63.538^\circ$  corresponding with miller indices (111), (200), (220) representing crystal planes of cubic  $\text{Cu}_2\text{O}$  [16].

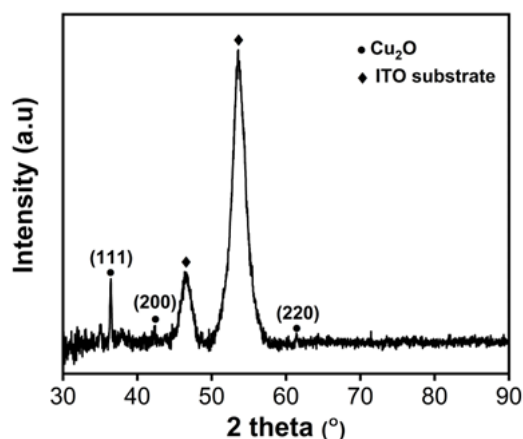


Figure 1. XRD diffractogram of  $\text{Cu}_2\text{O}$  thin film.

SEM micrographs are shown in Fig. 2 which show the morphology of  $\text{Cu}_2\text{O}$  synthesized using the electrodeposition method. From SEM analysis size-distribution and shapes of  $\text{Cu}_2\text{O}$  crystal are shown. Based on the analysis, the shape of  $\text{Cu}_2\text{O}$  crystals formed has a cubic shape on the surface of the ITO substrate [17]. In Addition, the particle size was also examined by SEM which

showed that  $\text{Cu}_2\text{O}$  consisted of a relatively uniform size with the crystal having an average diameter of 0.416  $\mu\text{m}$ . Moreover, Fig. 3 shows the EDX result confirming the presence of Cu and O elements on the thin film.

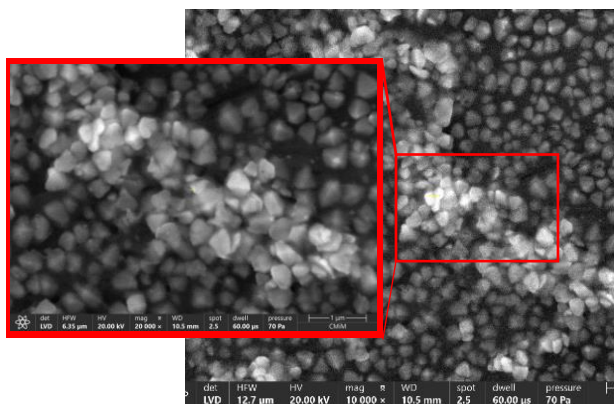


Figure 2. SEM micrograph of the  $\text{Cu}_2\text{O}$  thin film.

Photoelectrochemical (PEC) test is used to analyze the photoelectrochemistry response of  $\text{Cu}_2\text{O}$ . In the PEC,  $\text{Cu}_2\text{O}$  was irradiated with visible light to trigger a photochemistry reaction on the surface. Figure 4 shows the relation of the potential electrode with the current density. Based on the analysis of  $\text{Cu}_2\text{O}$  film from Fig. 4  $\text{Cu}_2\text{O}$  has a current density maximum of 0.1434  $\text{mA}/\text{cm}^2$  at 0.55 V vs. Ag/AgCl (KCl 3 M) under visible light irradiation.

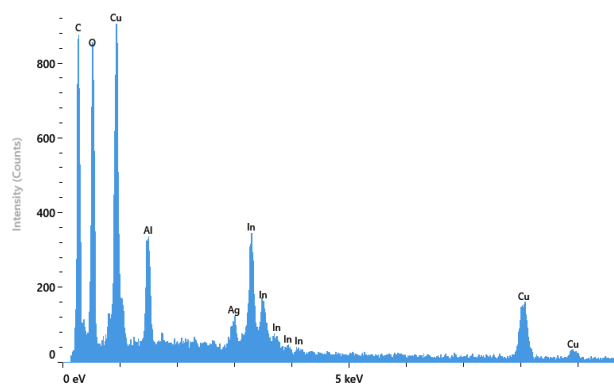


Figure 3. EDX spectrum of  $\text{Cu}_2\text{O}$  thin film.

The electrochemical impedance spectroscopy (EIS) measurement was performed to evaluate the current transfer resistance ( $R_{ct}$ ) of the  $\text{Cu}_2\text{O}$  thin film surface in its use as a photocatalyst. EIS generates a Nyquist plot which can be used to analyze the impedance of  $\text{Cu}_2\text{O}$  [18]. Figure 5 shows a Nyquist plot between a real impedance ( $Z'$ ) and an imaginary impedance ( $Z''$ ) for  $\text{Cu}_2\text{O}$  thin film. The resistance of  $\text{Cu}_2\text{O}$  is reflected by the half-circle of the Nyquist plot. A smaller arc radius of a plot indicates the higher efficiency of charge transfer and the value of  $R_{ct}$  will be lower [19]. In this study,  $\text{Cu}_2\text{O}$  thin film has an  $R_{ct}$

maximum of  $\sim 2500 \Omega$ .  $R_{ct}$  is associated with electron transfer reactions such as hole-electron recombination with  $\text{Cu}_2\text{O}$ . Thus, the lower  $R_{ct}$  is more desirable for the application of photodegradation [20].

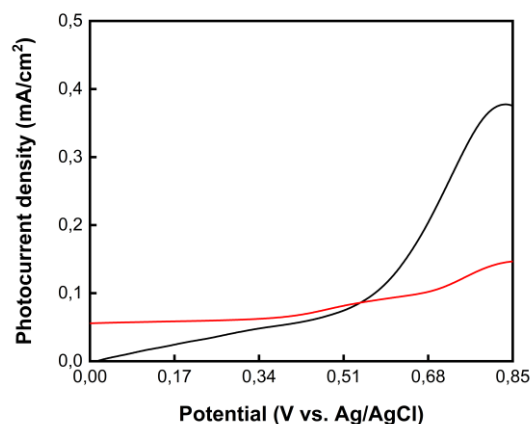


Figure 4. Photoelectrochemical graphic of thin film  $\text{Cu}_2\text{O}$ .

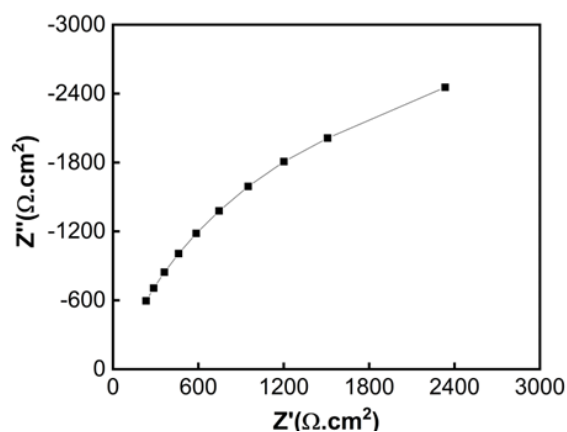
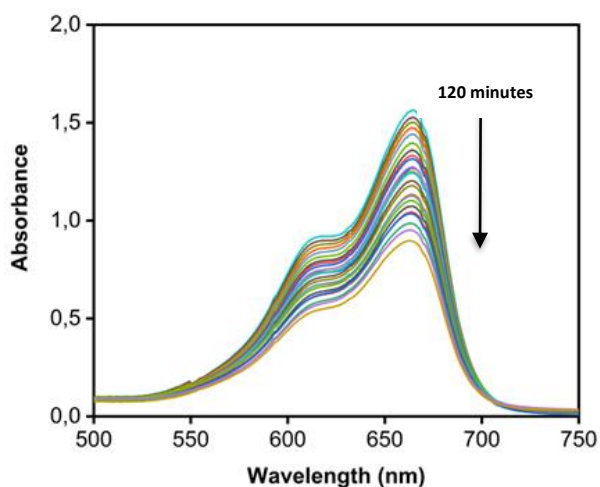


Figure 5. Nyquist plot of thin film  $\text{Cu}_2\text{O}$  under visible light irradiation.

The photodegradation analysis toward MB under visible light irradiation is shown in Fig. 6. Figure 6 shows the absorption spectra of the MB for 120 minutes. It is observed that the maximum absorbance of MB was recorded at a wavelength of 664 nm. The degradation of MB can be analyzed from the decrease in absorbance rate over time [21]. The result is consistent with the theory that shows the longer the irradiation time, the higher the photodegradation results [22]. The degradation of MB is based on energy absorbed by the semiconductor material that is used in separating current electrons ( $e^-$ ) and holes ( $h^+$ ) to form radicals that decompose organic molecule structures [23]. In this study, MB percentage decreased over time with a recorded degradation of 62.00% at 120

minutes with initial and final absorbance values of 1.56351 abs and 0.896875 abs respectively.



**Figure 6.** Photodegradation graphic of methylene blue under Visible Light Irradiation.

#### 4. Conclusion

Copper (I) oxide thin films were successfully synthesized on indium tin oxide as substrates by electrodeposition method at room temperature to exhibit a potential  $\text{Cu}_2\text{O}$  for photodegradation methylene blue application. The result shown in this study is that  $\text{Cu}_2\text{O}$  has a cubic structure. Moreover, the  $R_{ct}$  value is obtained which shows the charge transfer photocatalyst that occurs on the photocatalyst on the  $\text{Cu}_2\text{O}$  surface with a maximum value at  $\sim 2500 \Omega$ . The photocatalytic performance of  $\text{Cu}_2\text{O}$  was evaluated by the MB solution degradation at an absorption wavelength of 664 nm under visible light irradiation for 120 minutes. The result shows that the  $\text{Cu}_2\text{O}$  film has a percent degradation of 62.00%.

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