



## Optimization of Cu<sub>2</sub>O Thickness to Enhance Photocatalytic Properties of Electrodeposited Cu<sub>2</sub>O/FTO Photoanode

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### Abstract

Currently, n-type cuprous oxide (Cu<sub>2</sub>O) is a promising material as photocatalyst because of its energy gap of 2 eV that absorbs visible light up to a wavelength of 600 nm. As a photoelectrode, the thickness of Cu<sub>2</sub>O is crucial, where the improper thickness may worsen the photocatalytic properties. This work aimed to enhance the photocatalytic properties of Cu<sub>2</sub>O electrodeposited on fluorine-doped tin oxide (FTO), called Cu<sub>2</sub>O/FTO, by optimizing the Cu<sub>2</sub>O thickness. The thickness of Cu<sub>2</sub>O was controlled by adjusting the deposition time in the electrochemical deposition of Cu<sub>2</sub>O/FTO. By changing the deposition time from 5 to 45 min, the morphology of Cu<sub>2</sub>O changed from a leaf-like shape to an irregular facet shape with highly dense coverage, and the average thickness increased from 370 to 1100 nm. The increasing Cu<sub>2</sub>O thickness resulted in the increasing light absorption. The Cu<sub>2</sub>O/FTO demonstrated anodic photocurrent, which increased with the Cu<sub>2</sub>O thickness up to a threshold value of 1000 nm (35 min deposition time). At a thickness of 1000 nm, Cu<sub>2</sub>O/FTO achieved the highest photocurrent (150 and 58 μA under irradiation of 365 and 470 nm, respectively) due to the highly dense morphology and high absorption. In addition, with a thickness of 1000 nm, the charge diffusion was still good. Further, the increase of Cu<sub>2</sub>O film thickness higher than 1000 nm caused low photocatalytic properties even though the morphology was highly dense, and the absorption was the highest. This condition could be due to the relatively too-high resistance of Cu<sub>2</sub>O that caused poor charge diffusion.

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**Keywords:** Cu<sub>2</sub>O; thickness; photocatalytic properties; electrochemical deposition; deposition time

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### 1. Introduction

Photocatalysis is a field of research that is much in demand because of its application utilizing sunlight energy to produce hydrogen gas (H<sub>2</sub>) through photocatalytic water splitting [1] and to overcome water pollution through photocatalytic degradation of pollutants [2]. Cuprous oxide (Cu<sub>2</sub>O) is a promising material for photocatalysis that works under visible light irradiation because it has a narrow energy gap (2.0 – 2.6 eV) [3,4]. The valence band (VB) and

conduction band (CB) edge positions of Cu<sub>2</sub>O coincide with the redox potentials of water. At pH 7, the VB of Cu<sub>2</sub>O (0.65 vs. Ag/AgCl) is at a more positive potential than the oxidation potential of H<sub>2</sub>O to O<sub>2</sub> (0.62 vs. Ag/AgCl), and the CB of Cu<sub>2</sub>O (-1.35 V vs. Ag/AgCl) is at a more negative potential than the reduction potential of H<sup>+</sup> to H<sub>2</sub> (-0.62 vs. Ag/AgCl) [5]. Furthermore, Cu<sub>2</sub>O photocatalysis is extremely widespread because it is non-toxic, abundant in nature, and inexpensive [6]. Typically, Cu<sub>2</sub>O is a p-type semiconductor because of copper vacancies in the crystal lattice [7,8]. The p-type Cu<sub>2</sub>O acts as a photocathode used for photocatalytic reduction reactions [8,9]. Currently, many researchers prepared Cu<sub>2</sub>O as an

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n-type semiconductor, which is formed due to oxygen vacancies [10–12]. The n-type  $\text{Cu}_2\text{O}$  acts as photoanode and is applied for photocatalytic oxidation reactions [11,12]. The n-type  $\text{Cu}_2\text{O}$  is interesting to study widely because of its application for photocatalytic degradation of dyes that pollute the environment.

$\text{Cu}_2\text{O}$  can be fabricated using various methods, such as sputtering [13], thermal oxidation [14], chemical immersion [15], electrochemical deposition [16], and others. Among various thin film deposition methods, the electrochemical deposition method is the most popular method for fabricating  $\text{Cu}_2\text{O}$  because it is cheap, highly scalable, and easy to operate. This method can control conductivity type, morphology, facets, and thickness by adjusting electrochemical deposition parameters, such as voltage, time, and solution pH [7]. For example, the fabrication of  $\text{Cu}_2\text{O}$  photoelectrode prepared at pH 6.2 exhibited n-type conductivity, while those obtained at pH 11 showed p-type conductivity [17]. Furthermore, the variation of deposition time can change the morphology and thickness of n-type  $\text{Cu}_2\text{O}$  [18]. Several works have attempted to enhance the photocatalytic performance of n-type  $\text{Cu}_2\text{O}$  by changing the deposition parameters in the electrochemical deposition method [10–12,19]. As a photoelectrode, thickness of  $\text{Cu}_2\text{O}$  film can affect the photon absorption and charge diffusion, where the increase of film thickness can increase the light absorption, but reduce the charge diffusion [20]. Hence, the optimization of the  $\text{Cu}_2\text{O}$  film thickness is crucial to achieve the highest photocatalytic activity of n-type  $\text{Cu}_2\text{O}$ . However, the optimized film thickness of n-type  $\text{Cu}_2\text{O}$  for enhancing its photocatalytic properties has not been studied.

This work aimed to study the threshold thickness of n-type  $\text{Cu}_2\text{O}$  in enhancing the photocatalytic properties of n-type  $\text{Cu}_2\text{O}$  deposited on fluorine-doped tin oxide (FTO) by the electrochemical deposition method. The thickness of  $\text{Cu}_2\text{O}$  was adjusted by controlling the deposition time. The variation of deposition times from 5 to 45 min resulted in the transformation of  $\text{Cu}_2\text{O}$  morphology from a leaf-like shape (thickness of 370 nm) to an irregular faceted shape (thickness of 1100 nm) with a highly dense coverage. The increase of  $\text{Cu}_2\text{O}$  thickness resulted in the increase of light absorption. The  $\text{Cu}_2\text{O}$  with a deposition time of 35 min (thickness of 1000 nm) showed the highest anodic photocurrent response (150 and 58  $\mu\text{A}$  under irradiation with wavelengths of 365 and 470 nm, respectively) among all the investigated  $\text{Cu}_2\text{O}$ , indicating that the threshold film thickness was 1000 nm. In this condition, the  $\text{Cu}_2\text{O}$ , with a thickness of 1000 nm, exhibited a highly dense morphology and high absorption. Additionally, the charge diffusion was

still good. The  $\text{Cu}_2\text{O}$  film with a thickness higher than 1000 nm resulted in poor photocatalytic properties even though the morphology was highly dense, and the absorption was the highest. The relatively too-high resistance of  $\text{Cu}_2\text{O}$  with a thickness higher than 1000 nm might cause poor charge diffusion, leading to the poor photocatalytic properties.

## 2. Materials and Methods

### 2.1 Preparation of $\text{Cu}_2\text{O}/\text{FTO}$

$\text{Cu}_2\text{O}$  film was fabricated using the electrochemical deposition method in a three-electrode cell using an electrochemical workstation (Zahner Zennium, Germany) [12]. The working electrode was FTO, the reference electrode was Ag/AgCl, and the counter electrode was a Pt plate. The electrolyte for the electrodeposition of  $\text{Cu}_2\text{O}/\text{FTO}$  was a mixed solution of 0.02 M  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (Powder, 99.9%, Sigma-Aldrich) and 0.1 M  $\text{NaCH}_3\text{COO}$  (Powder, 99%, Sigma-Aldrich) in 40 mL of deionized (DI) water. The pH of the electrolyte was adjusted to 6.5 via 0.5 M  $\text{CH}_3\text{COOH}$  (Powder, 99.8%, Sigma-Aldrich). Repurification was not required because all chemicals were in good purity. Before deposition began, the FTO was washed using a solution of acetone, ethanol, and DI water in an ultrasonic cleaner sequentially for 10 min each. Next, the electrochemical deposition was carried out at a voltage of  $-0.2$  V vs. Ag/AgCl under different deposition times (5, 15, 25, 35, and 45 min). During the deposition process, the electrolyte temperature was kept constant at 60 °C. After that, the as-prepared sample, called  $\text{Cu}_2\text{O}/\text{FTO}$ , was washed using DI water and then dried using nitrogen gas for approximately 5 min.

$\text{Cu}_2\text{O}/\text{FTO}$  was also prepared with a “step height” on its surface for thickness measurement. The sample preparation process followed the same procedure as original  $\text{Cu}_2\text{O}/\text{FTO}$ . However, the FTO was modified before the electrodeposition process. A tape (0.5 cm  $\times$  1 cm) was attached to the middle of the FTO surface. Next, the electrochemical deposition was carried out at a voltage of  $-0.2$  V vs. Ag/AgCl and electrolyte temperature of 60 °C under different deposition times (5, 15, 25, 35, and 45 min). Once finished, the tape on the FTO surface was peeled off. After that, the as-prepared  $\text{Cu}_2\text{O}/\text{FTO}$  having a “step height” was washed using DI water and then dried using nitrogen gas for approximately 5 min.

### 2.2 Characterization of $\text{Cu}_2\text{O}/\text{FTO}$

$\text{Cu}_2\text{O}/\text{FTO}$  was characterized using several techniques. Before the characterization, the  $\text{Cu}_2\text{O}/\text{FTO}$  was purged with nitrogen gas for approximately 5 min to remove the dust from the

surface. The topography of  $\text{Cu}_2\text{O}$  was observed using Atomic Force Microscopy (AFM) (PicoScan-AFM, Molecular Imaging Inc; now known as Agilent Technologies, USA). The thickness of  $\text{Cu}_2\text{O}$  was measured by AFM. For this measurement, the  $\text{Cu}_2\text{O}/\text{FTO}$  was prepared in as a step height sample. The crystal structure was recorded using X-ray diffractometry (XRD) (PANalytical X'Pert PRO, Netherlands) at an incidence wavelength of 1.5401 Å (Cu- $K\alpha$  radiation). The vibration modes were measured using Raman spectroscopy (NTEGRA Spectra, NT-MDT, Netherlands) under excitation of 532 nm-wavelength ( $2.1 \text{ mW}\cdot\mu\text{m}^{-2}$ ). The light absorption spectra were measured using ultraviolet–visible (UV–vis) spectroscopy equipped with an integration sphere and a Xe lamp.

### 2.3 Measurement of Photocatalytic Properties of $\text{Cu}_2\text{O}/\text{FTO}$

The photocatalytic properties of  $\text{Cu}_2\text{O}/\text{FTO}$  were investigated by measuring the photocurrent under light irradiation with wavelengths of 365 and 470 nm at a light intensity of  $5 \text{ mW}\cdot\text{cm}^{-2}$ . The photocurrent measurement was performed using a source meter (Keithley 2400) under a two-electrode cell configuration without a bias. The  $\text{Cu}_2\text{O}/\text{FTO}$  acted as the working electrode and a Pt plate acted as the counter electrode. The electrolyte solution was 0.05 M  $\text{Na}_2\text{SO}_4$ . Furthermore, the photocatalytic activity of the  $\text{Cu}_2\text{O}/\text{FTO}$  was examined by measuring the degradation of methylene blue (MB) under dark and light irradiation of 365 nm ( $38 \text{ mW}\cdot\text{cm}^{-2}$ ) through monitoring the decrease in absorbance peak of MB solution at a wavelength of 664 nm [21]. The photocatalytic degradation of MB was measured without bias, with an initial MB concentration of 5  $\mu\text{M}$  in the electrolyte of 0.05 M  $\text{Na}_2\text{SO}_4$ .

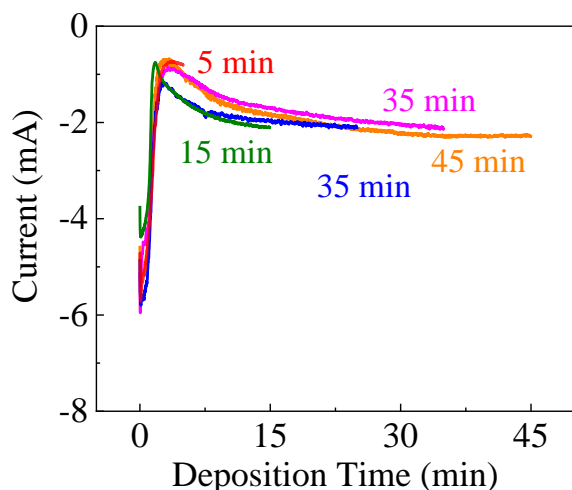


Figure 1. Current of  $\text{Cu}_2\text{O}/\text{FTO}$  recorded during electrochemical deposition process under different deposition times.

## 3. Results and Discussion

### 3.1 Effect of Deposition Time on Morphology, Thickness, and Properties of $\text{Cu}_2\text{O}/\text{FTO}$

$\text{Cu}_2\text{O}/\text{FTO}$  was fabricated using an electrochemical deposition method by applying a constant voltage ( $-0.2 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$ ) with varying deposition times from 5 to 45 min. The formation of  $\text{Cu}_2\text{O}$  on the FTO substrate in the solution containing  $\text{Cu}(\text{CH}_3\text{COO})_2$  occurred following the reaction of  $2\text{Cu}^{2+} + 2\text{OH}^- + 2e^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$  [22]. During the deposition process, the current resulting from the deposition process was recorded against the deposition time, as seen in Figure 1. The deposition current clearly showed the  $\text{Cu}_2\text{O}$  nucleation-growth step, where there are three regions [23,24]. Initially, the first current region showed that the  $\text{Cu}_2\text{O}$  growth process began with the nucleation of  $\text{Cu}_2\text{O}$  grains on the FTO surface, characterized by a high cathodic current quickly around 30 s because of the conductive FTO with a sheet resistance of  $22 \Omega/\text{sq}$  [12]. The cathodic current increased rapidly, indicating that the deposition rate of  $\text{Cu}_2\text{O}$  was controlled by surface diffusion of  $\text{Cu}^{2+}$  with uniform incoming flux [25,26]. After that, as time increased (the second current region), the number of  $\text{Cu}_2\text{O}$  grains increased and covered the FTO surface, causing the higher resistance on the FTO surface, indicated by the decrease of the cathodic current until reaching its maximum before decaying. In this condition, each  $\text{Cu}_2\text{O}$  grains developed in the diffusion zone. In the third current region (more than 5 min), the cathodic current decayed to equilibrium, and the development of  $\text{Cu}_2\text{O}$  material on the FTO surface was more abundant. Finally,  $\text{Cu}_2\text{O}$  material covered the whole surface of FTO. The surface diffusion could control the morphology and roughness of  $\text{Cu}_2\text{O}$  on the FTO surface [26]. The number of  $\text{Cu}_2\text{O}$  material on the FTO surface depended on the deposition times, where the total charge (electric current times deposition time) during the electrochemical deposition process determined the grain number. Hence, the number of  $\text{Cu}_2\text{O}$  grains increased as the deposition time increased, leading to the increase of the  $\text{Cu}_2\text{O}$  film thickness [18].

The topography of  $\text{Cu}_2\text{O}/\text{FTO}$  was observed with AFM, presented in Figure 2. The morphology of  $\text{Cu}_2\text{O}$  on the FTO substrate depended on the deposition time. The change in the morphology of  $\text{Cu}_2\text{O}$  corresponded to the form of the deposition current (Figure 1). As shown in Figure 2(a),  $\text{Cu}_2\text{O}$  deposited for 5 min demonstrated three leaf-like grains with dendritic branches of 500 – 800 nm length. The  $\text{Cu}_2\text{O}$  grains deposited on the FTO surface showed branching dendritic development because the surface diffusion of  $\text{Cu}^{2+}$  in the plating solution could not refill the deposition [24]. This

leaf-like shape of  $\text{Cu}_2\text{O}$  grains was also observed by other studies [24,27].  $\text{Cu}_2\text{O}$  branches grew vertically, resulting in a thicker  $\text{Cu}_2\text{O}$  film, thus covering the leaf-like shape of  $\text{Cu}_2\text{O}$  grains, as seen in  $\text{Cu}_2\text{O}$  deposited for 15 min (Figure 2(b)) and 25 min (Figure 2(c)). In this condition, the  $\text{Cu}_2\text{O}$  surface showed a porous structure. The leaf-like morphology of  $\text{Cu}_2\text{O}$  was no longer visible in the deposition time of 35 min (Figure 2(d)) and 45 min

(Figure 2(e)). In this situation, the  $\text{Cu}_2\text{O}$  surface exhibited an irregular faceted shape with a highly dense coverage, which could be caused by the nonuniform distribution of  $\text{Cu}^{2+}$  during the electrodeposition.

Based on the analysis on the topography images, the roughness and surface area also varied with the deposition time. Under the deposition times of 5, 15, 25, 35, and 45 min, the

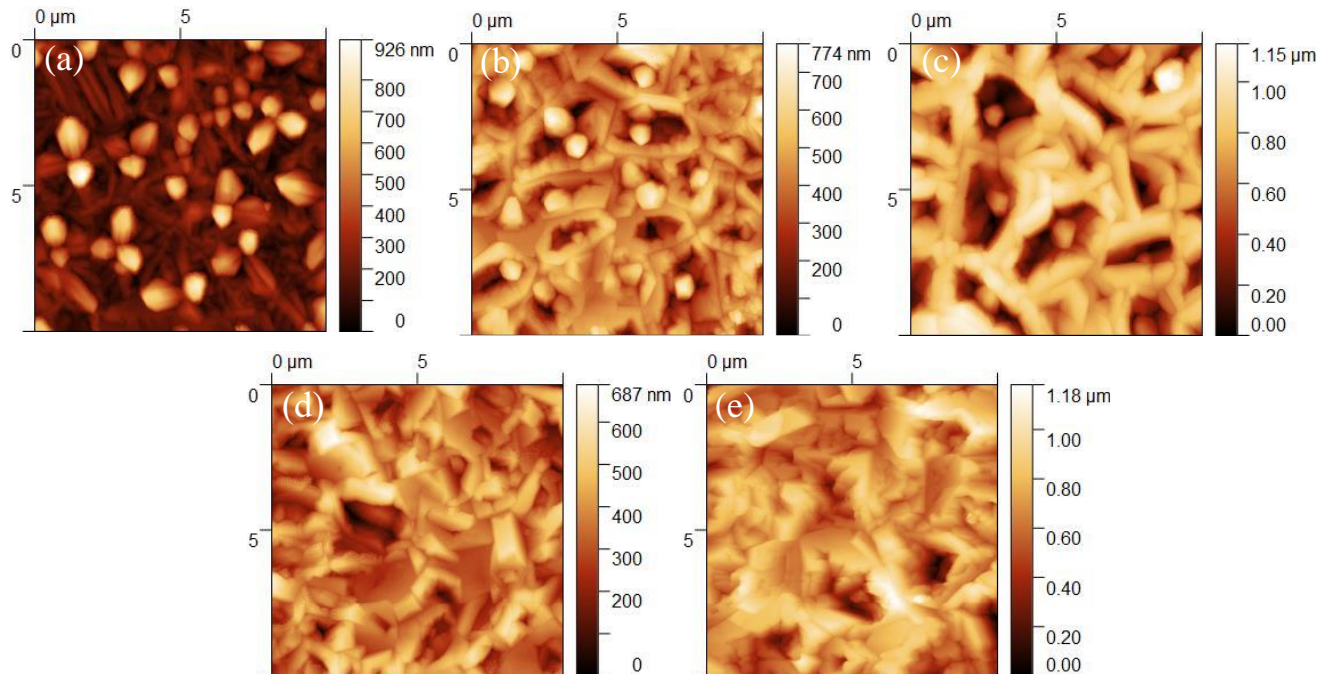


Figure 2. 2D AFM images showing topography of  $\text{Cu}_2\text{O}/\text{FTO}$  deposited under deposition times of (a) 5 min, (b) 15 min, (c) 25 min, (d) 35 min, and (e) 45 min.

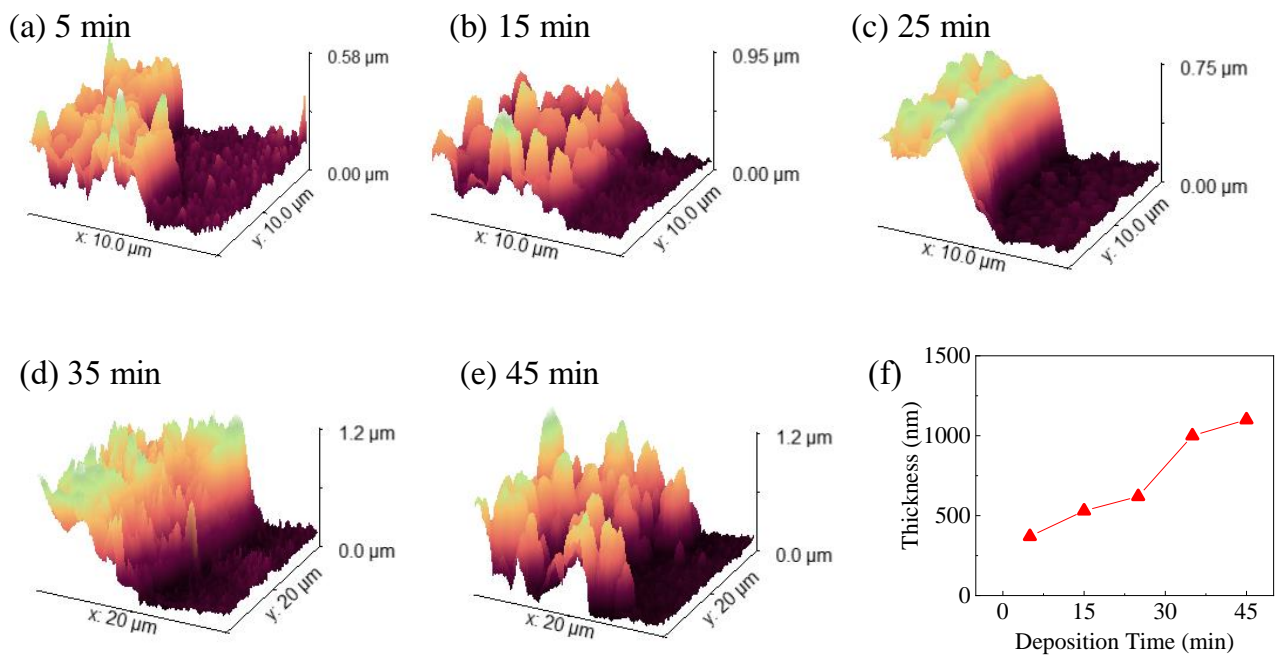


Figure 3. 3D AFM images showing thicknesses of  $\text{Cu}_2\text{O}$  on FTO substrate deposited under different deposition times.



roughnesses of Cu<sub>2</sub>O were 151.5, 133.5, 220.7, 122.8, and 159.2 nm, respectively. Meanwhile, the surface areas were 130.3, 123.9, 133.5, 115.7, and 123.7 μm<sup>2</sup>. In addition to the substrate conductivity, the variations of morphology, roughness, and surface area with the deposition time were caused by the surface diffusion of Cu<sup>2+</sup> in the electrodeposition [26].

The thickness of Cu<sub>2</sub>O on the FTO substrate was measured by AFM. However, because Cu<sub>2</sub>O was not reflective enough, it was difficult to see the “step height” via camera (CCD) in AFM system. Hence, the Cu<sub>2</sub>O/FTO having a “step height” was placed on top of the Au/glass so that the boundaries between FTO and Cu<sub>2</sub>O were clearly seen because of the reflective Au/glass. Next, the position of AFM cantilever was adjusted so that it was exactly positioned on the boundary between Cu<sub>2</sub>O and FTO. Next, AFM scanning was performed horizontally, and a “step height” profile was obtained, shown in Figure 3. In addition to

better density and coverage of Cu<sub>2</sub>O grains on the FTO surface, the thickness of the Cu<sub>2</sub>O film increased from 370 to 1100 nm with the increasing deposition time [18,28]. This result was consistent with the increase in total charge during electrochemical deposition.

The XRD and Raman scattering were measured to identify the presence of Cu<sub>2</sub>O on the FTO surface. Figure 4(a) shows the XRD patterns of Cu<sub>2</sub>O/FTO deposited under different deposition times from 5 to 45 min. The XRD patterns exhibited several peaks with 2θ values of 36.58, 42.29, and 61.30°, corresponding to the (111), (200), and (220) crystal planes of pure Cu<sub>2</sub>O (ICSD No. 98-006-0719), respectively [3,7]. The intensity of the (111) peak was higher than those of peaks indexed to (200) and (220), indicating the preferential growth of Cu<sub>2</sub>O along the (111) direction. The intensity of (111) and (200) peaks changed with deposition time, where increasing the deposition time increased the crystallinity in

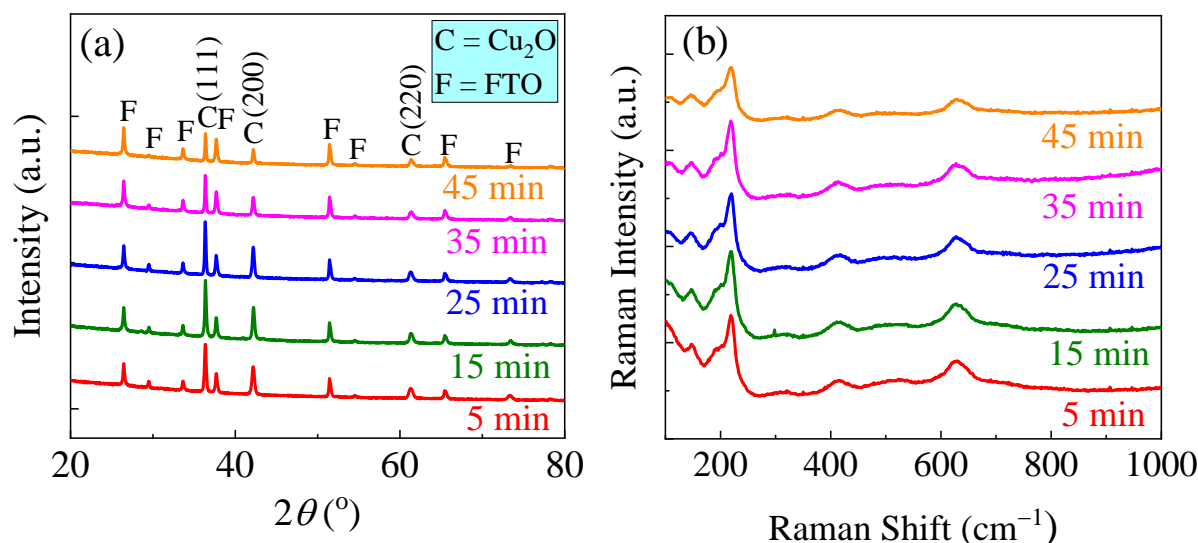


Figure 4. (a) XRD patterns and (b) Raman spectra of Cu<sub>2</sub>O/FTO deposited under different deposition times.

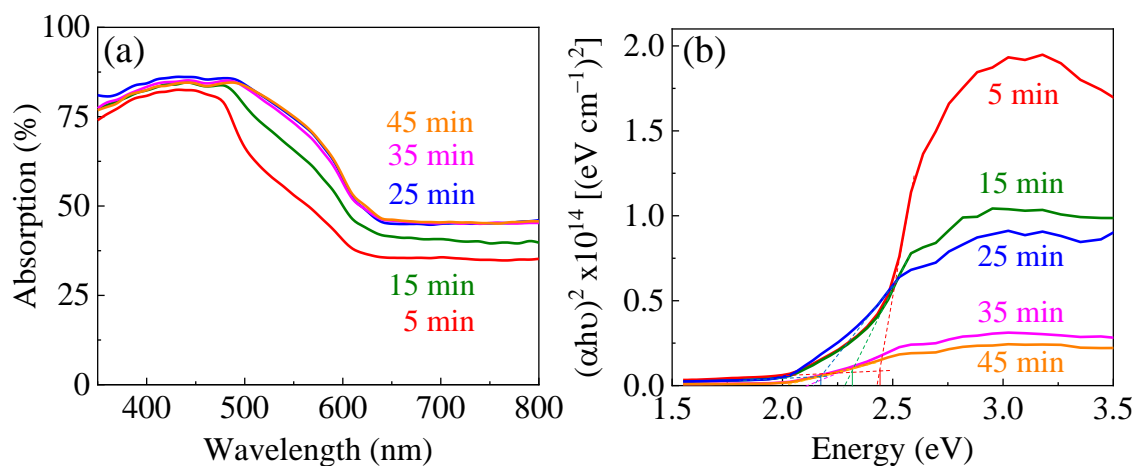


Figure 5. (a) Absorption spectra and (b) Tauc-plots of Cu<sub>2</sub>O/FTO deposited under different deposition times.

the (111) and (200) orientations, as shown in the deposition time of Cu<sub>2</sub>O/FTO for 5 to 25 min. However, Cu<sub>2</sub>O/FTO deposited for 35 and 45 min showed a decrease in (111) and (200) orientations, which could be attributed to the absence of leaf-like morphology in Cu<sub>2</sub>O/FTO (see AFM images). Another peak in the XRD pattern originates from the FTO substrate. The Raman spectra of the Cu<sub>2</sub>O/FTO are shown in Figure 4(b). Several peaks at Raman shifts of 146, 218.5, 413.7, 503.1, and 628.8 cm<sup>-1</sup> were observed, corresponding to the Raman spectrum of Cu<sub>2</sub>O [29]. The Raman peaks did not change much with the deposition times. The XRD patterns and Raman scattering spectrum confirmed that the electrodeposition of Cu<sub>2</sub>O was successful. Only Cu<sub>2</sub>O was grown on the FTO surface, and no other phases of copper oxide were found.

The light absorption spectra of Cu<sub>2</sub>O/FTO were recorded using UV-vis spectroscopy. Cu<sub>2</sub>O/FTO exhibited high light absorption in the spectral region of 350–600 nm, as shown in Figure 5(a), in agreement with other studies [4,24,30]. The light absorption increased as the deposition time increased. It indicated that the higher Cu<sub>2</sub>O thickness yielded the higher light absorption, which was proportional to the amount of Cu<sub>2</sub>O materials on the FTO substrate caused by the

longer deposition time. With a higher thickness, the distribution of the intensity of the radiant energy inside the Cu<sub>2</sub>O was also higher [20]. A red shift at the absorption edge was observed with the increasing deposition times, consistent with the Cu<sub>2</sub>O color changing from yellow to reddish. The apparent absorption observed at wavelengths greater than 600 nm originated from light scattering losses during the measurement. Tauc-plots of Cu<sub>2</sub>O/FTO, calculated from the absorption coefficient assuming a direct band gap,  $(ah\nu)^2$  [31], showed that the Cu<sub>2</sub>O/FTO had a bandgap energy of 2.4, 2.3, 2.2, 2.1, and 2.0 eV, for deposition time of 5, 15, 25, 35, and 45 min, respectively (Figure 5(b)). With a band gap energy of around 2 eV, Cu<sub>2</sub>O could absorb visible light from the sun [4,8]. The higher the deposition time, the longer the wavelength of light that can be absorbed.

### 3.2 Effect of Cu<sub>2</sub>O Thickness on Photocatalytic Properties of Cu<sub>2</sub>O/FTO

The current intensity of Cu<sub>2</sub>O/FTO was measured in the electrolyte of 0.05 M Na<sub>2</sub>SO<sub>4</sub> without additional bias under chopped monochromatic light irradiation of 366 and 470 nm (5 mW.cm<sup>-2</sup>), shown in Figures 6(a) and 6(b). Under dark conditions, the current intensity of the

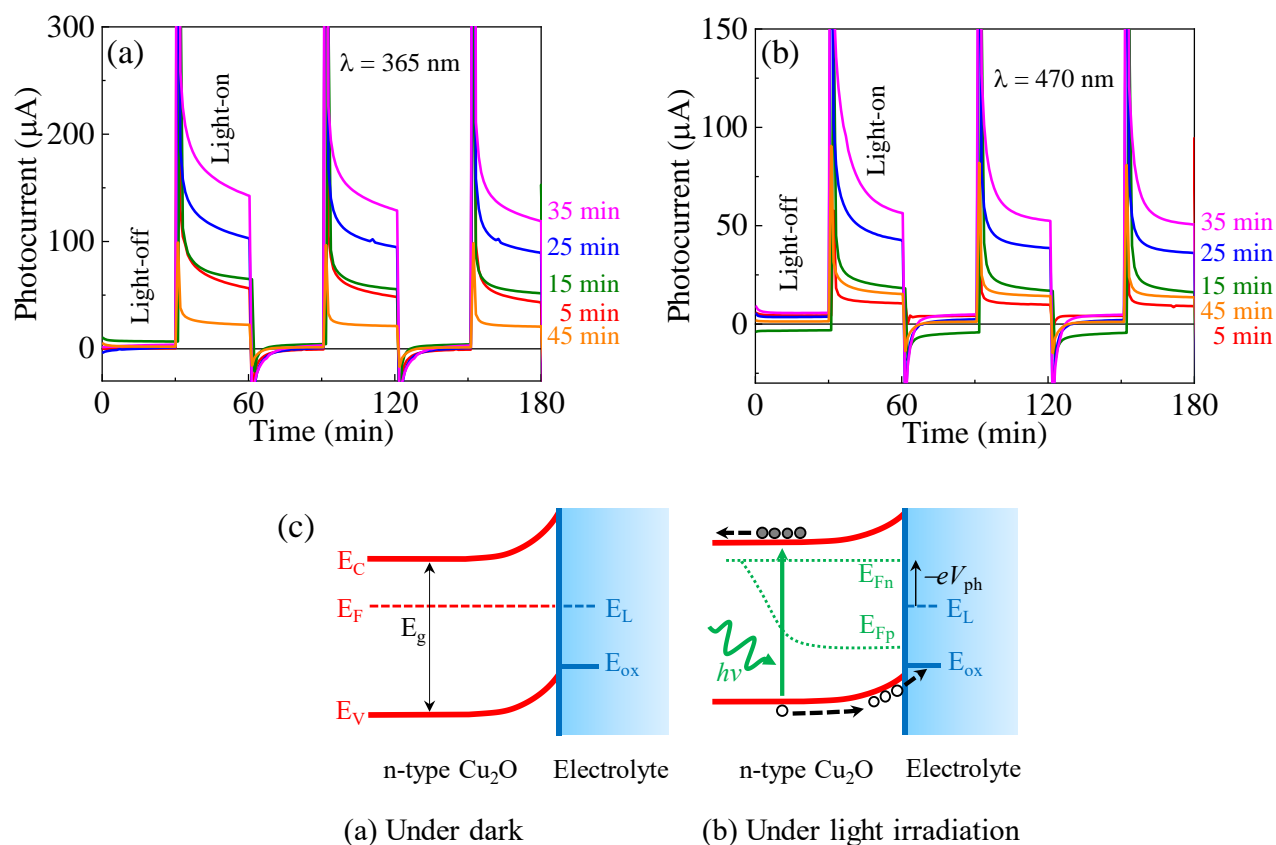


Figure 6. Photocurrent of Cu<sub>2</sub>O/FTO deposited under different deposition times, irradiated with wavelengths: (a) 365 nm and (b) 470 nm. (c) Schematic energy band diagram of n-type Cu<sub>2</sub>O/electrolyte under dark and light irradiation conditions [12].

Cu<sub>2</sub>O/FTO was minuscule (<1 μA), indicating that the adsorption and catalysis were very weak and negligible without any specific analytes. Cu<sub>2</sub>O/FTO exhibited an anodic photocurrent that increased with the increase of the deposition time but decreased after 35 min deposition time, indicating that the threshold thickness of Cu<sub>2</sub>O was approximately 1000 nm. The anodic photocurrent is established as the behaviour of n-type semiconductors in contact with an electrolyte [11,12].

The schematic diagram of n-type Cu<sub>2</sub>O/electrolyte under dark and irradiation conditions is illustrated in Figure 6(c) [12]. In equilibrium under dark conditions, the Fermi energy of Cu<sub>2</sub>O ( $E_F$ ) and Fermi energy of liquid water ( $E_L$ ) aligned, forming a Schottky junction. Under light irradiation, the Cu<sub>2</sub>O absorbed light with an energy higher than its band gap energy, yielding photogenerated electron-hole pairs in the Cu<sub>2</sub>O. The photogenerated electrons were excited into the CB of Cu<sub>2</sub>O, while the photogenerated holes remain in the VB of Cu<sub>2</sub>O. In this situation, the  $E_F$  of Cu<sub>2</sub>O splitted into quasi-Fermi level of electron ( $E_{Fn}$ ) and quasi-Fermi level of the hole ( $E_{Fp}$ ). In the photoelectrochemical cell, the photogenerated electrons in the CB moved to FTO and then transferred to the Pt plate via an external circuit. The remaining photogenerated holes in the VB were transferred to the electrolyte for the oxygen evolution reaction. Thus, an anodic photocurrent was generated [12]. The photocurrent was much higher than the dark current, indicating that the oxidation reaction in the Cu<sub>2</sub>O/electrolyte was dominated by photocatalysis.

Determination of the correct deposition time during the Cu<sub>2</sub>O deposition process was very important. Under irradiation of 365 nm, the

photocurrent increased from 60 to 150 μA when the deposition time increased from 5 to 35 min and decreased drastically to 24 μA when the deposition time was adjusted to 45 min. The same behavior was also observed under irradiation of 470 nm. The Cu<sub>2</sub>O/FTO deposited at 35 min exhibited the highest photocurrent (58 μA) among all the investigated Cu<sub>2</sub>O/FTO. This means that 35 min was the suitable deposition time to prepare Cu<sub>2</sub>O/FTO to produce the highest photocurrent. It also indicated that the suitable thickness to achieve the highest photocurrent was approximately 1000 nm. With a thickness of 1000 nm, Cu<sub>2</sub>O had a highly dense coverage and high light absorption. The higher light absorption resulted in the higher photogenerated electron and hole, which led to the higher photocurrent. In addition, the charge diffusions, which were the transfers of electrons from Cu<sub>2</sub>O to FTO and holes from Cu<sub>2</sub>O to electrolyte, still proceed quite well [20]. The charge transfer could be characterized by electrochemical impedance spectroscopy [32]. On the other hand, the Cu<sub>2</sub>O/FTO deposited for 45 min, having a thickness higher than 1000 nm, showed the lowest photocurrent even though the morphology of Cu<sub>2</sub>O exhibited a highly dense coverage and the light absorption was high. It means that there was another reason causing the low photocurrent of Cu<sub>2</sub>O/FTO deposited at 45 min. It indicated that if Cu<sub>2</sub>O was too thick, photogenerated electrons and holes could not diffuse and transfer optimally, which mean the resistance of Cu<sub>2</sub>O was too large. Therefore, Cu<sub>2</sub>O/FTO with a sufficient Cu<sub>2</sub>O thickness could produce the optimal light absorption and a good charge transfer process, resulting in highest photocurrent.

The photocatalytic activity of Cu<sub>2</sub>O/FTO electrodeposited at 35 min was examined by

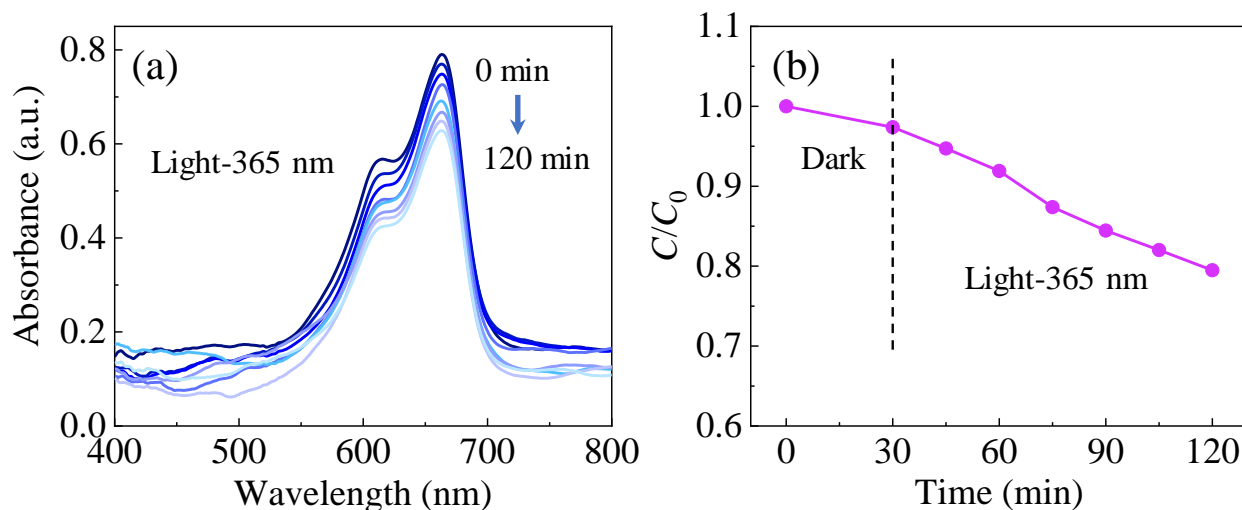


Figure 7. (a) Decrease in the MB absorbance peak by the photocatalyst of Cu<sub>2</sub>O/FTO electrodeposited at 35 min under dark from 0 to 30 min and under light irradiation of 365 nm wavelength from 30 to 120 min. (b) Photocatalytic degradation of MB ( $C/C_0$ ) by Cu<sub>2</sub>O electrodeposited at 35 min.

measuring the degradation of MB in the electrolyte of 0.05 M Na<sub>2</sub>SO<sub>4</sub> without a bias. The MB was mixed with Na<sub>2</sub>SO<sub>4</sub> electrolyte to increase the conductivity of the wastewater solution containing MB. The solution conductivity could affect the current efficiency and consumption of electrical energy in the photocatalytic degradation [33]. The degradation of MB was measured by monitoring the decrease in absorbance peak of MB solution at a wavelength of 664 nm under dark for the first 30 min and light irradiation of 365 nm (38 mW cm<sup>-2</sup>) for 90 min afterward (Figure 7(a)). Figure 7(b) shows the photocatalytic degradation in the MB concentration ( $C/C_0$ ) by the Cu<sub>2</sub>O/FTO. Under dark conditions, the Cu<sub>2</sub>O/FTO could degrade the MB by approximately 2.6% in 30 min. The MB was degraded through the adsorption and catalysis processes in the dark [21]. Under light irradiation of 365 nm, the degradation percentage increased to 22.9 % for a total time of 120 min. In addition to the adsorption and catalysis processes, the MB degradation was due to the photocatalysis through photooxidation process [21,34]. Hence, the Cu<sub>2</sub>O/FTO was a good photocatalyst for MB degradation due to the synergetic effect among the adsorption, catalysis, and photocatalysis.

The investigation on n-type Cu<sub>2</sub>O under different deposition times provided an optimal thickness for Cu<sub>2</sub>O photocatalyst. However, the produced photocurrent density (30 μA.cm<sup>-2</sup> under irradiation of 365 nm and 11.6 μA.cm<sup>-2</sup> under irradiation of 470 nm) is still low compared with the theoretical photocurrent. Theoretically, Cu<sub>2</sub>O exhibits a solar-to-hydrogen (STH) efficiency of 18%, corresponding to the photocurrent density of 14 mA.cm<sup>-2</sup> [35]. The high recombination of photogenerated charges may cause the low photocurrent of the as-prepared Cu<sub>2</sub>O [36]. In future research, n-type Cu<sub>2</sub>O can be combined with p-type Cu<sub>2</sub>O to reduce the charge recombination. In addition, the photocurrent exhibited a decay with time under light irradiation (Figures 6(a) and 6(b)), indicating the poor photostability in aqueous solution [37,38]. Poor photostability is possible because Cu<sub>2</sub>O undergoes photo-corrosion, where reduction and oxidation potentials of Cu<sub>2</sub>O lie between the bandgap of Cu<sub>2</sub>O [36]. Hence, annealing and protection with a capacitive coating layer can be good ways to improve the photostability of Cu<sub>2</sub>O in future research.

#### 4. Conclusions

The photocatalytic properties of n-type Cu<sub>2</sub>O under different Cu<sub>2</sub>O thicknesses were investigated. The Cu<sub>2</sub>O was deposited on an FTO substrate using an electrochemical deposition method. The Cu<sub>2</sub>O film thickness was controlled by

adjusting the deposition time from 5 to 45 min. The quality of the Cu<sub>2</sub>O/FTO was characterized using several techniques, consisting of AFM, XRD, Raman spectroscopy, and UV-vis spectroscopy. The Cu<sub>2</sub>O exhibited a morphological form that depended on the deposition time, where the Cu<sub>2</sub>O coverage become denser with the increase of deposition time. The Cu<sub>2</sub>O thickness increased as the deposition time increased. The Cu<sub>2</sub>O/FTO could absorb light up to a wavelength of 600 nm (band gap energy 2.0 eV). The absorption of the Cu<sub>2</sub>O/FTO increased as the deposition time increased because of the increase in film thickness. The photocatalytic properties of the Cu<sub>2</sub>O/FTO were investigated by measuring the photocurrent under UV and visible light irradiation. The Cu<sub>2</sub>O/FTO demonstrated an anodic photocurrent behaviour and tended to increase with the increasing deposition time but decreased after a deposition time of 35 min, showing a threshold thickness of approximately 1000 nm. With the thickness of 1000 nm, the Cu<sub>2</sub>O/FTO exhibited the highest anodic photocurrent, which was attributed by the optimal thickness for light absorption, highly dense of Cu<sub>2</sub>O coverage, and quite well charge diffusion. Further increasing Cu<sub>2</sub>O thickness, no photocurrent enhancement was obtained. The photocatalytic properties of the Cu<sub>2</sub>O/FTO deposited at 45 min was the lowest even though the morphology showed a highly dense coverage, and the absorption was high, attributed to the relatively too-high resistance of Cu<sub>2</sub>O that caused poor charge diffusion.

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#### CRedit Author Statement

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