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Photoelectrochemical characterisation of direct and pulse electrodeposited copper on fluorine-doped tin oxide glass

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ABSTRACT

Electrodeposition (ED) is applied in several applications since it is one of the most user-friendly and cost-effective techniques. The increasing popularity of this technique is due to its capacity to control the morphology and chemical composition of the target materials. Copper (Cu) is one of the metals that can be discovered in the greatest abundance on earth. It has been used as an alternative to noble metals to improve the photo electrochemical (PEC) activity for hydrogen generation. This research involved the electrochemical deposition of Cu metal onto fluorine-doped tin oxide (FTO) glass using direct and pulse ED. The objective of this study is to investigate the PEC performance of Cu metal electrodeposited on FTO glass by evaluating its efficiency under light illumination. The deposition of the Cu films was successful, resulting in a thin layer of Cu films onto the FTO. The PEC response of metallic Cu was analysed by doing an LSV study on the thin films, in relation to the ED technique, applied voltage, ED time, and pulse cycle. The results show that the FTO/Cu −0.8 V samples produced via pulse ED have the highest PEC activity. The deposition of strongly adhering and improved morphology of Cu thin film is important especially for interconnect in semiconductor applications.

1. INTRODUCTION

Hydrogen technology has emerged as a highly promising alternative for achieving a pure and sustainable energy future in light of recent advancements. Carbon dioxide (CO_2) and other greenhouse gases (GHGs) cannot be produced when hydrogen is used as a storage medium for energy. This exceptional property has

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garnered considerable attention and inspired optimism regarding hydrogen's potential role in influencing the future energy landscape (Ahmad et al., 2020; Karim, 2021; Kovač et al., 2021). Solar-powered water splitting may effectively produce hydrogen from renewable sources (Li et al., 2021b; Mohd Shah et al., 2021; Rosman et al., 2018). Solar hydrogen production by water splitting is acknowledged as one of the most promising alternatives to the use of fossil fuels due to its negligible influence on the surrounding ecology and the abundance of water supplies (Yao et al., 2018).

Copper (Cu), which can be found in large quantities on earth and is famous for the high conductivity it possesses, is a material that has been extensively utilised as an input for a wide range of applications (Rajput et al., 2021; Schnebele et al., 2019). Due to its ability to facilitate the transfer of electrons, Cu possesses the potential to function as an electrocatalyst in photo-electrochemistry. Because of this, Cu is used in a vast number of industries, including those that produce solar cells, capacitors, and many others (Chakraborty et al., 2020; Kannimuthu et al., 2021; Rajput et al., 2021). Cu is one of the low-cost options that can substitute noble metals to boost photocatalytic hydrogen production and has garnered a lot of interest as of the current day (Rocha et al., 2014; Xiao et al., 2015).

In photo-electrochemistry, increasing the light-trapping efficiency of a photoelectrode can be accomplished in several methods, including doping with elements, creating nanostructures, and modifying the surface with plasmonic metallic nanoparticles. Plasmonic metal nanoparticles have been included to improve efficiency, with the ability of these nanoparticles to capture light. Cu nanoparticles may display localized surface plasmon resonance, often known as LSPR, in the visible region of the electromagnetic spectrum. Consequently, it plays a crucial role in the increased absorption of the visible light region of the Cu photoelectrode, which is anticipated to boost the PEC activity caused by the irradiation of visible light (He et al., 2018). Hence, it also plays a significant role in the improved photocatalytic activity of Cu photoelectrodes.

Electrodeposition (ED) is among the most economical and user-friendly techniques. As a result, it has found its way into various applications, including photoelectrode manufacturing (Satar et al., 2018). This form of material manufacture has gained fraction in recent years and is currently the preferred option for a low-cost technique. This is because, it allows for more control over the morphology and chemical content of the materials being deposited (Kale et al., 2021; Taherinia et al., 2022; Xiao et al., 2008; Zhang et al., 2022). Cu ED has been utilised in various fields for over a century as it can be performed in vast quantities (Ma et al., 2019). One reason for this is that it can provide extremely high yields. Simple and direct ED, which can deposit thin films on flat conductive surfaces, has resulted in a non-uniform coating. This causes the deposition of aggregated particles on the top and an uncoated surface on the bottom (Kang et al., 2015; Tang et al., 2015a; Tang et al., 2015b). Meanwhile, pulse electrodeposition, on the other hand, can potentially enhance the homogeneity of thin films produced on conductive substrates (Wu et al., 2018).

Our study aims to contribute novel insights into the PEC performance of Cu by examining the impact of different ED techniques-specifically direct and pulse electrodeposition-on FTO glass. While previous studies have focused primarily on the morphology and elemental composition of the electrodeposited Cu (Adris et al., 2023), limited research has explored the direct comparison of these deposition techniques and their influence on PEC activity. By systematically varying ED parameters such as applied voltage, deposition time, and cycles, this study investigates the optimal conditions for enhancing the PEC performance of the Cu thin films. In this work, we explore the effects of direct and pulse ED of Cu towards its PEC behaviour. This finding is expected to provide valuable insights into improving Cu-based photocathodes for water splitting applications in the field of sustainable hydrogen production.

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2. METHODOLOGY

2.1 Materials

Analytical-grade copper sulphate pentahydrate (R&M Chemicals), sodium sulphate (Sigma-Aldrich), ethanol (QReC), and acetone (QReC) were used as received. The FTO glass substrate was ultrasonically cleaned for five minutes in acetone, ethanol, and deionized water, respectively. Cu was deposited using an Ametek Versastat 4 equipped with a three-electrode setup for the process of electrodeposition.

2.2 Fabrication of FTO/Cu via direct electrodeposition

The Cu thin film was fabricated via direct electrodeposition (DD) in an electrolyte solution of 0.01 M Cu_2SO_4•$5H_2O$ and 0.2 M Na_2SO_4 in deionised water. Electrodeposition was performed using a chronoamperometric function at room temperature. FTO glass substrate, Pt mesh, and Ag/AgCl saturated in 3 M KCl served as working, counter, and reference electrodes, respectively (Fig. 1). Electrodeposition of Cu was carried out at a constant voltage ranging from −0.2 V to −0.8 V versus silver-silver chloride (Ag/AgCl), and the electrodeposition period ranged from 300 to 1200 seconds. The magnetic stirring was done at 150 revolutions per minute to maintain a constant electrolyte content. The fabricated FTO/Cu sample was thoroughly rinsed with deionised water before drying.

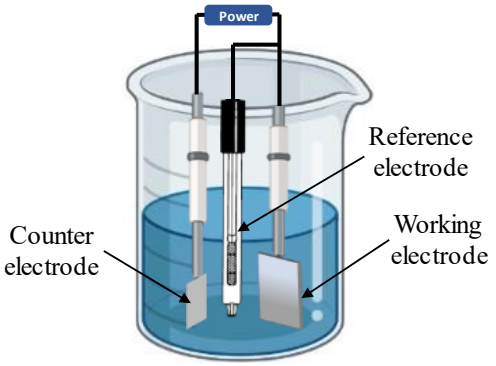

Fig. 1. Schematic diagram of ED method with three-electrode setup

Source: Authors' own illustration

2.3 Fabrication of FTO/Cu via pulse electrodeposition

The applied voltage was repeatedly turned on and off for pulse electrodeposition (PD) of Cu onto FTO glass. The experimental setup is similar to DD (Fig. 1). The deposition process was carried out in recurrent voltage pulses mode with pulse cycles ranging from 100 cycles to 400 cycles. When the power was on, the voltage values were in the cathodic range (−0.6 V), but when it was off, the voltage was 0 V, as shown in Fig. 2. The Ton (−0.6 V) is a period where the current is applied to allow copper ions to be reduced and deposited on the FTO substrate. Meanwhile, Toff (0 V) is a period where there is no current applied to allow for the replenishment of ions near the electrode surface and promotes uniform deposition. After completed the electrodeposition process, the fabricated FTO/Cu samples were thoroughly rinsed with deionised water and dried.

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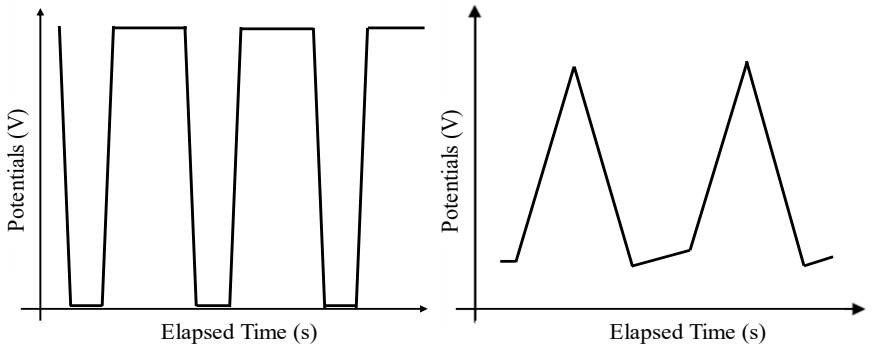

Fig. 2. Schematic representation of pulse electrodeposition (PD)

Source: Authors' own data

2.4 Photoelectrochemical Analysis

Using a three-electrode configuration system, photoelectrochemical (PEC) analysis was performed. The electrodes were submerged in a 0.5 M Na_2SO_4 electrolyte solution (pH 7), and a 30-minute purging step with N_2 gas was undertaken prior to their use to remove any dissolved oxygen. The PEC study utilised a linear scan voltammetry function with a scan rate of 1 mV/s under chopped light illumination (100 mW/cm^2 of Xenon lamp with AM1.5 filter). The impedance measurements were conducted using the same instrument to estimate the photoelectrode's resistance at 10 mV amplitude with a frequency range of 0.01 to 1 kHz.

3. RESULTS AND DISCUSSION

3.1 Effect of electrodeposition (ED) potential

The metallic brown Cu thin films were successfully deposited on the FTO glass substrate using direct and pulse ED methods. Cu is one of the low-cost and effective materials used to replace noble metals as the photocatalyst, as it can increase the conductivity and charge separation of the electrode. Plasmonic metallic nanoparticles deposited on the surface of a semiconductor are also an effective surface modification for enhancing light harvesting (Cao et al., 2020; Chen et al., 2018; Li et al., 2021a; Xin et al., 2021). To determine the photoactivity of the deposited Cu, PEC experiments were done under chopped light illumination to test the PEC performance of the metallic Cu. Fig. 3 shows the J−V responses of the FTO/Cu in 0.5 M Na_2SO_4 solution at pH 7. The positive and negative transient spikes observed in the chopped LSV are important indicators of the photoelectrode's behaviour. The positive photocurrent spikes represent hole accumulation under illumination, while the negative transients after switching off the light are due to the recombination of bulk electrons with the holes in the space charge layer. These transients offer valuable insights into the photoelectrode's dynamics, which would be lost in a continuous light or dark measurement.

As shown in Fig. 3 (a), FTO/Cu −0.8 V has the highest current density at 0 V_{RHE} compared to the others. It also clearly shows that the photoactivity of FTO/Cu degraded at 0.3 V_{RHE} and was left with only an increasing dark current. The photoactivity of Cu may degrade due to the dissolution of Cu and the loss of its structural and electrical properties when Cu performs a chemical interaction with the electrolyte in the presence of light (Weng et al., 2019). However, Cu metal has unconditional conductive properties; thus, it can be used in semiconductor technology as an interconnector between elements. Fig. 3 (b) shows that

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the photocurrent density of the Cu thin films deposited at lower cathodic potential is not high, with a ca. −1.2 μA/cm^2 at 0.4 V_{RHE}. However, when deposited at a higher cathodic potential (−0.6 V), the FTO/Cu exhibits enhanced photoactivity compared to the Cu at a lower cathodic potential. The photocurrent density of FTO/Cu −0.6 V is ca. −12.95 μA/cm^2, which is 10 times higher than the FTO blank (without Cu deposited). It has been discovered that when the reduction potential of copper is smaller, the deposition of copper can be slowed down or prevented entirely. If the reduction potential is lower, the deposition of copper on the surface may be delayed as a result (Bhardwaj et al., 2019). Because of this, the reduction potential of copper plays a role in the process of copper's deposition on a surface. However, higher deposition potentials have been found to lead to better photoactivity (Doong & Liao, 2017). Deposition at a higher potential can resulted in smaller nuclei and more adherent and compact Cu layer on the substrate, potentially leading to improved morphology (Grujicic & Pesic, 2002), and thus improved photoelectrochemical performance.

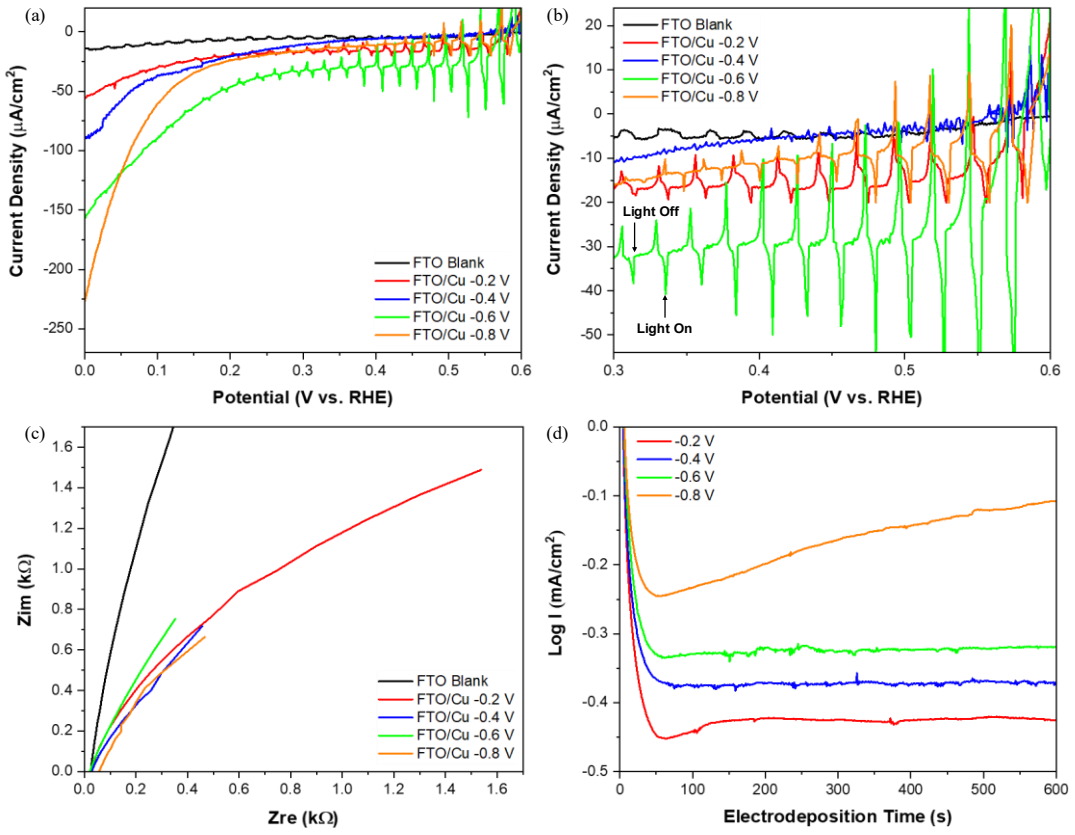

Fig. 3. (a-b) J−V curve of FTO/Cu with voltage range from −0.2 V to −0.8 V and its enlarged curve; (c) EIS plot, and (d) Log I vs. Cu ED time

Source: Authors' own data

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Fig. 3 (b) demonstrates that at an applied potential of −0.4 V_{RHE}, the photocurrent density initially increases as the deposition potential rises, subsequently followed by a decline (FTO/Cu −0.8 V). However, it is noteworthy that the overall current density of FTO/Cu −0.8 V remains the highest. This finding suggests that the FTO/Cu −0.8 V exhibits superior performance in terms of dark electrolysis for the hydrogen evolution reaction (HER). The Nyquist plot shown in Fig. 3 (c), which is obtained from the analysis of electrochemical impedance spectra (EIS) measured under illumination at 0 V_{RHE}, provides insights into the interfacial charge transfer processes between FTO/Cu and the electrolyte. Apart from the FTO blank, the highest charge transfer resistance of 3.52 kΩ belongs to the FTO/Cu −0.2 V, which also has the lowest current density performance, followed by the FTO/Cu −0.4V (3.05 kΩ) and FTO/Cu −0.6V (2.71 kΩ). Meanwhile, the smallest charge transfer resistance (1.56 kΩ) calculated for FTO/Cu −0.8 V indicates that the resistance across the electrode/electrolyte interface is the lowest among other samples. This correlates with the highest current density performance illustrated in Fig. 3 (a). Furthermore, this result substantiates a significant improvement in the interface charge carrier transfer, thereby leading to a higher overall current density (Yu et al., 2021).

In this study, it was observed that the overall current density of the Cu thin film exhibits a significant enhancement as the electrodeposition potential became more cathodic. The current density generated increased from −73 μA/cm^2 to −232 μA/cm^2 at higher cathodic potentials. However, even though Cu deposited at −0.8 V exhibits the highest current density, its lower photocurrent activity suggests that the increased current may primarily be due to dark electrolysis or non-photoactive processes, likely related to the formation of dendritic structures or surface roughness that enhance charge transfer but not necessarily photoactivity. Previous studies have demonstrated that the electrodeposition voltage has a substantial influence on the structure of the electrodeposited Cu thin films (Nishikawa et al., 2013; Xu et al., 2019). Therefore, to further investigate this, the current log density–time plot was examined to explore the possibility of dendritic formation, as shown in Fig. 3 (d). At potentials ranging from −0.2 V to −0.6 V, the slope of the current density remained constant, indicating the absence of dendritic growth. However, at a potential −0.8 V, the slope of the current density started to increase around 160 seconds, signifying a change in the growth mechanism of the deposited Cu. This phenomenon corresponds to the induction period, where dendrite precursors form prior to the onset of dendritic growth. These findings suggest that at higher cathodic potential (−0.8 V vs. Ag/AgCl), there is a notable evolution of dendrite formation (Popov & Nikolić, 2012). Consequently, the electrodeposition time/cycle was further investigated while maintaining a fixed electrodeposition potential of −0.8 V.

The formation of dendritic structures at −0.8 V has a considerable impact on the morphology of the electrodeposited Cu thin films (Adris et al., 2023). Dendrites, with their branched and porous morphology, offer a high surface area, enhancing electron transfer and increasing active sites for the hydrogen evolution reaction (HER) during PEC analysis (Li et al., 2019; Sui et al., 2021). This larger surface area improves the overall PEC performance of the Cu thin films by facilitating better interaction between the electrode and electrolyte. However, dendritic structures may also introduce mechanical instability and surface roughness, potentially leading to issues such as film detachment and irregular electron flow over time (Li et al., 2022). Therefore, optimising electrodeposition conditions is crucial to balance the benefits of increased PEC activity with the potential drawbacks of dendritic growth.

3.2 Effect of electrodeposition time/cycle

The properties and performance of an electrode are greatly influenced by the thickness of the metal coating. The thickness of a metal coating can impact its ability to absorb light. Thus, in this study, the impact of different electrodeposition times and cycles on the PEC performance of electrodeposited Cu was thoroughly investigated and is shown in Fig. 4. It was observed that as the electrodeposition time increased, the generated overall current density produced also increased, while the electrical resistivity decreased. However, a significant decrease in the overall current density generation was observed at the electrodeposition times of 900 s to 1200 s and 400 cycles. Thicker Cu thin film may absorb more light,

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resulting in an increase in optical absorption and possibly an increase in photoconversion efficiency (Giurlani et al., 2020). However, there may be an optimal thickness beyond which surplus thickness may result in light trapping and diminished performance due to reabsorption or reflection. Excessive thickness of Cu coating may lead to light shielding effects and a reduction in the efficiency of the photocatalyst (He et al., 2018; Shen et al., 2021), consequently impacting the overall current density generation. Hence, the best PEC performance was achieved with the FTO/Cu electrodeposited for 600 s (DD) and 300 cycles (PD).

The photocurrent density values obtained for the FTO/Cu films synthesised in this study were compared with those reported in the literature. He et al. (2018) reported a photocurrent density of 0.05 mA/cm² for FTO/Cu thin films deposited using the electrodeposition method, while Liu et al. (2017) achieved a photocurrent density of 4.7 μA/cm² for FTO/Cu synthesised using the hydrothermal method. In our study, the FTO/Cu films deposited via DD and PD methods exhibited photocurrent densities of 9.9 μA/cm² and 11.81 μA/cm², respectively. These values indicate a significant improvement in the photocurrent density compared to Liu et al. (2017) and are comparable with He et al. (2017), although slightly lower in magnitude. This finding is consistent with the analysis of charge transfer resistance for FTO/Cu, as shown in Fig. 4 (b) and Fig. 4 (d), where the electrodeposition times (600 s) and cycles (300 cycles) exhibited the smallest charge transfer resistance of 0.47 kΩ and 0.27 kΩ , respectively, compared to the other electrodeposition conditions.

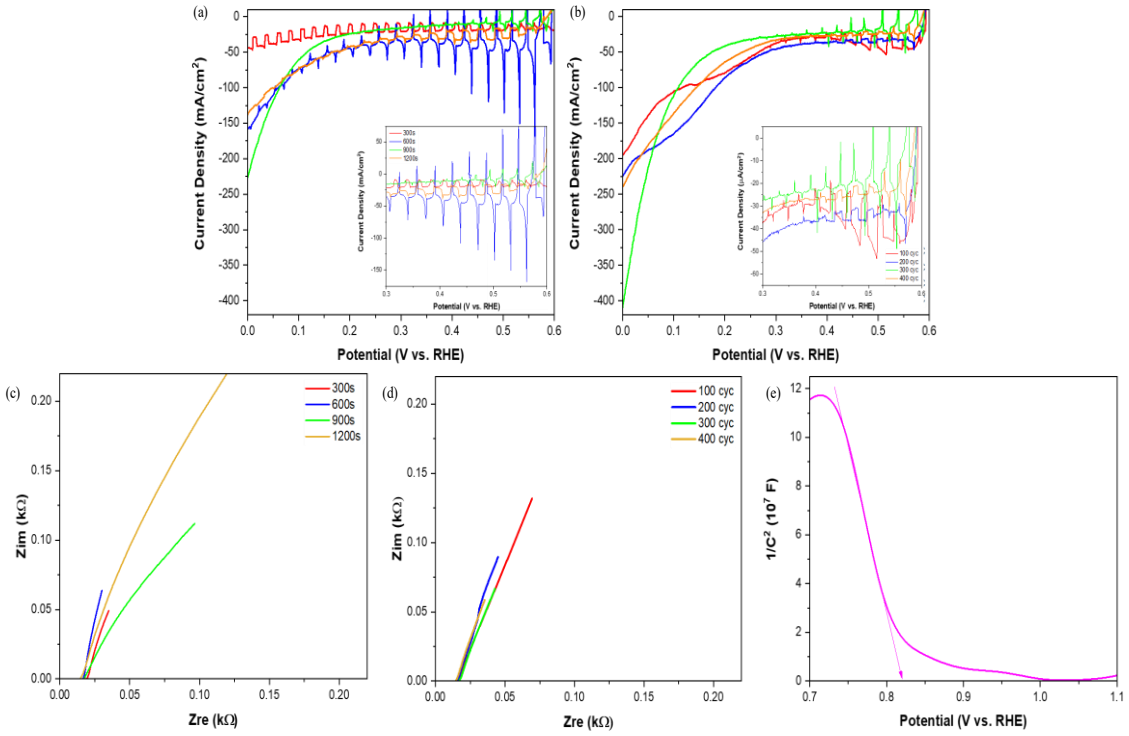

Fig. 4. J–V and EIS plot of FTO/Cu deposited via (a,c) DD, (b,d) PD, and (e) Mott-Schottky plot of the FTO/Cu

Source: Authors' own data

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The enhanced performance observed in this study can be attributed to the optimisation of the electrodeposition parameters, particularly the use of pulse electrodeposition, which has been demonstrated to yield a more homogeneous, denser nanostructured Cu layer. Furthermore, the negative slope observed in the Mott-Schottky plot (Fig. 5 (e)) confirms that the FTO/Cu fabricated in this study functions as a p-type photoelectrode. In the parameters tested such as electrodeposition potential, time, or cycle, the pulse electrodeposited FTO/Cu has the best performance compared to the direct electrodeposition method in this study. This superior performance can be attributed to several factors associated with pulse electrodeposition. Firstly, pulse electrodeposition facilitates the attainment of improved homogeneity, reduced porosity, and a denser nanostructured Cu coating (Ma et al., 2011). The altered transport mechanisms induced by pulse electrodeposition can influence the nucleation rate and growth mechanisms of the deposited Cu (Seyedraoufi & Mirdamadi, 2014). Furthermore, when the current is intermittently interrupted during pulse electrodeposition, the ions supplied by the intermittent power source attain an equilibrium concentration (Lin et al., 2018). Previous studies have also highlighted that materials deposited via pulse electrodeposition tend to exhibit denser packing and more uniform coverage (Hayakawa et al., 2008; Simpson et al., 2019; Wasekar et al., 2018; Zhang et al., 2021). However, it introduces complexity and potential trade-offs such as longer deposition times and the risk of dendritic growth (Sierra-Herrera et al., 2017; Yang et al., 2014). Proper optimisation of pulse parameters can mitigate some of these limitations, but it remains a more technically demanding approach than continuous deposition methods.

4. CONCLUSIONS

This study successfully employed direct and pulse electrodeposition methods to fabricate metallic brown Cu thin films on FTO glass substrates. The Cu deposited at−0.6 V shows the best PEC performance while minimising unwanted dark processes. Besides, the presence of nanostructured Cu in the FTO/Cu films played a critical role in enhancing visible light absorption, thereby improving the visible-light-driven photocatalytic activity of the material. The EIS Nyquist plot further confirmed that the FTO/Cu electrodeposited at −0.6 V demonstrated superior performance compared to those deposited at lower or higher cathodic potential. When comparing two methods, PD produced more efficient thin films than DD, as PD allowed for better control over film structure and uniformity. Therefore, while high cathodic voltage enhances PEC performance in both methods, the PD method yields the highest overall performance. Consequently, this investigation underscores the significance of the deposition potential as a crucial factor influencing the performance of Cu nanoparticles. The insights gained from this study hold potential for the development of highly efficient photocatalytic materials.

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CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare the absence of conflicting interests with the funders.

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AUTHORS CONTRIBUTIONS

Nur Azlina Adris: Conceptualisation, methodology, formal analysis, investigation, and writing-original draft; **Lorna Jeffery Minggu**: Project administration, conceptualisation, data analysis, supervision, and writing- review and editing; **Rozan Mohamad Yunus**: Data analysis and validation, supervision, writing-review and editing; **Khuzaimah Arifin**: Data analysis and validation, supervision, and writing- review and editing; **Mohamad Azuwa Mohamed**: Data analysis and validation, supervision, and writing- review and editing; **Mohammad B. Kassim**: Data analysis and validation, and supervision.

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