

Effect of Deposition Time on the Photoelectrochemical Properties of Cupric Oxide Thin Films Synthesized via Electrodeposition Method

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Abstract. The main aim of this study was to investigate the effect of deposition time on the physicochemical and photoelectrochemical properties of cupric oxide (CuO) thin films synthesized via electrodeposition method. Firstly, the electrodeposition of amorphous CuO films on fluorine-doped tin oxide (FTO) working electrodes with varying deposition time between 5 and 30 min was carried out, followed by annealing treatment at 500 °C. Resultant nanocrystalline CuO thin films were characterised using field emission-scanning electron microscopy (FE-SEM), photocurrent density, and photoluminescence measurements. Through FE-SEM analysis, it was observed that the surface of thin films was composed of irregular-sized CuO nanocrystals. A smaller CuO nanocrystals size will lead to a higher photoactivity due to the increase in overall catalytic surface area. In addition, the smaller CuO nanocrystals size will prolongs the electron-hole recombination rate due to the increase in copious amount of surface defects. From this study, it was revealed that the relationship between deposition time and CuO film thickness was non-linear. This could be due to the detachment of CuO thin films from the FTO surface at an increasing amount of CuO mass being deposited. It was observed that the amount of light absorbed by CuO thin films increased with film thickness until a certain extent whereby, any further increase in the film thickness will result in a reduction of light photon penetration. Therefore, the CuO nanocrystals size and film thickness have to be compromised in order to yield a higher catalytic surface area and a lower rate of surface charge recombination. Finally, it was found that the deposition time of 15 min resulted in an average CuO nanocrystals size of 73.7 nm, optimum film thickness of 0.73 μm , and corresponding photocurrent density of 0.23 mA/cm^2 at the potential bias of - 0.3 V (versus Ag/AgCl). The PL spectra for the deposition time of 15 min has the lowest rate of recombination of photogenerated electron-hole pairs by referring to its lowest PL intensity.

1 Introduction

Photoelectrochemical (PEC) water splitting is a photo-driven conversion process of water molecules into hydrogen and oxygen molecules through the use of semiconductor metal oxides photocatalysts [1]. In a PEC cell, minority charge carriers will be generated when the amount of light photons being absorbed by the semiconductor photocatalyst used is greater than its corresponding bandgap energy level [2]. Therefore, the type of semiconductor photocatalysts used in the PEC water splitting process will affect the efficiency of water-to-hydrogen conversion process due to their inherent bandgap characteristics.

To date, the synthesis of nanostructured semiconductor metal oxides photocatalysts have attracted much attention due to their promising properties in different fields of application ranging from sensors, optoelectronics, and electronics to catalysis. Binary copper semiconductors have attracted much research interests owing to their high photoactivity, inexpensive and that copper is a relatively abundant element [2]. Cupric oxide (CuO) is one of the *p*-type binary copper semiconductors with a narrow bandgap of 1.3 to 1.9 eV, and a corresponding theoretical photocurrent density of 35 mA/cm^2 [3, 4].

The physical and chemical properties of CuO thin films are strongly dependent on the method of preparation. There are various synthesis methods used to

synthesize CuO thin films, such as pulsed laser deposition [5], electrodeposition [6], chemical vapor deposition [7], and sol-gel method [8]. Among all, electrodeposition is a simple and straightforward method that can be operated at ambient operating pressure and temperature, as well as being an inexpensive method. The electrodeposition method is also enabling the direct control of film thickness by systematically manipulating the synthesis parameters [9]. It was reported that controlling the CuO film thickness could have a profound effect on the photocurrent density, and subsequently leading to a higher efficiency in the water-to-hydrogen conversion process [10].

Previously, Patake et al. [11] have prepared porous and amorphous CuO thin films via cathodic electrodeposition method, and subsequently studied for their potential application as supercapacitor and their characteristics. Lim et al. [4] studied the deposition of Cu₂O and CuO thin films by a sol-gel spin-coating process, and enhanced the PEC performance by depositing a thin layer of NiO_x co-catalyst. Wang et al. [6] investigated the effect of deposition voltage on the morphology of CuO thin films. Although these previous studies have discussed on the growth, characterisation and application of CuO thin films, there is less information available that detailed on the relationship between deposition time, nanocrystals size, film thickness, and photocurrent density.

Thus, the main aim of this study was to systematically investigate the effect of deposition time on the physicochemical and PEC properties of CuO thin films synthesized via electrodeposition method. Initially, the *p*-type CuO thin films of different film thicknesses were synthesized on fluorine-doped tin oxide (FTO) working electrodes by varying the deposition time between 5 and 30 min, followed by annealing treatment at 500 °C. The resultant *p*-type CuO thin films were further characterised using field emission-scanning electron microscopy (FE-SEM), photocurrent density, and photoluminescence (PL) measurements.

2 Materials and methods

Materials. Copper (II) sulphate (CuSO₄), di-potassium hydrogen phosphate (K₂HPO₄), potassium hydroxide (KOH), lactic acid (C₃H₆O₃), and sodium sulfate (Na₂SO₄) were purchased from Merck Malaysia. All the reagents are of analytical grade and used without further purification.

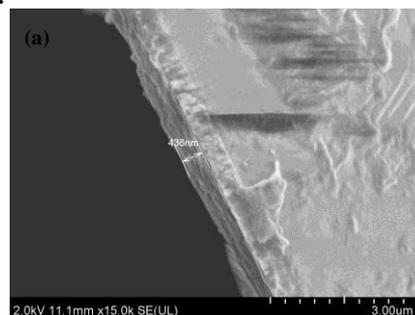
Preparation of CuO thin films. Electrodeposition of CuO thin films was carried out in a three-electrode PEC cell that comprised of FTO, a platinum (Pt) rod, and a saturated silver/silver chloride (Ag/AgCl) electrode used as the working, counter, and reference electrodes, respectively. Before the electrodeposition synthesis process, FTO glass slides (ChemSoln, USA; resistivity of

14 Ω/sq) were cleaned ultrasonically using acetone, ethanol, and deionised water for 20 min, before being dried in the oven. The electrolyte used for the electrodeposition synthesis process was made up of 0.2M CuSO₄ and 3 M lactic acid solution in deionised water with 0.5M K₂HPO₄ buffer. Following this, the electrodeposition process was carried out at pH 9 by adjusting the pH of the solution using 2M KOH. The electrodeposition synthesis process was conducted potentiostatically with an applied potential of -0.4 V versus Ag/AgCl. The deposition time was varied between 5 and 30 min. After the electrodeposition process, the FTO glass slides were washed with deionised water to remove the presence of any ion followed by annealing treatment at 500 °C for 30 min.

Characterisation of CuO thin films. Different thicknesses of CuO thin films were examined using FE-SEM (FEI Nova NanoSEM; accelerating voltage 1kV). Photocurrent density measurements were carried out in a standard three-electrode assembly using an applied potentiostat/galvanostat (Metrohm PGSTAT 204 model, Netherlands). Similarly, the saturated Ag/AgCl electrode and Pt rod were used as the reference and counter electrodes, respectively. The photocurrent density measurements were conducted inside a dark box at room temperature. A 100 W halogen lamp restricted at a frequency of 0.05 Hz was used as the light source during the photocurrent density measurements. The intensity of incident light flux was measured using a digital light meter to be 8700 mW/m² at a light source-to-sample distance of 10 cm. The FTO working electrode was estimated to be approximately 1.32 cm². All the photocurrent experiments were conducted in a 0.5M aqueous Na₂SO₄ solution. PL measurements were carried out using a fluorescence spectrophotometer (LS 55, Perkin Elmer) at room temperature. The excitation wavelength was 325 nm with a scanning speed of 500 nm/min, while the emission spectra were scanned from 600 to 700 nm.

3 Results and Discussion

FE-SEM.



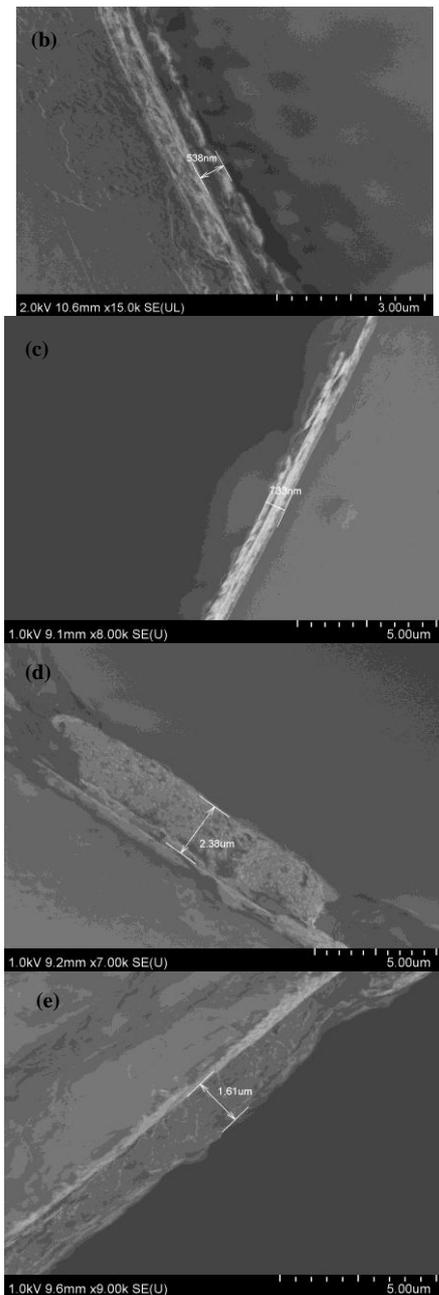


Figure 1. Cross-sectional FE-SEM images of CuO thin films at different deposition time of: (a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min and ; (e) 30 min.

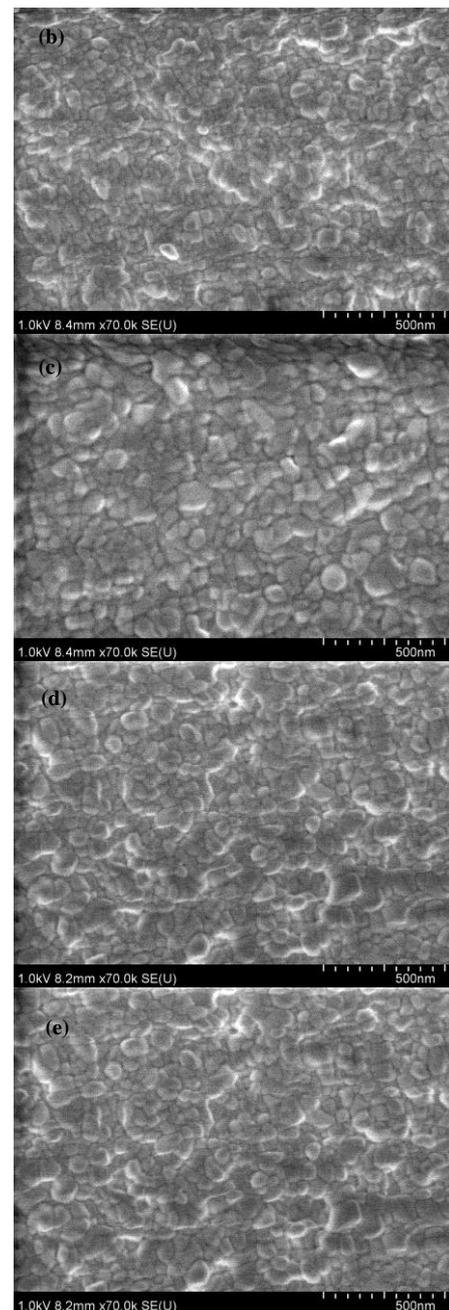
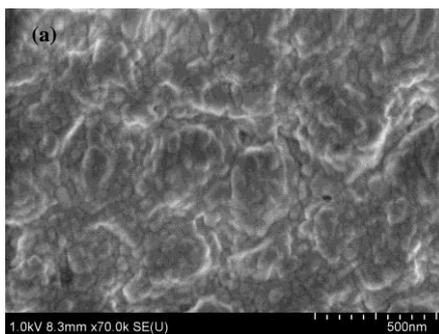


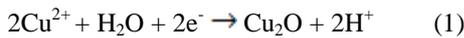
Figure 2. Top view FE-SEM images of CuO thin films at different deposition time of: (a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min and; (e) 30 min.

Table 1. Relationship between deposition time, CuO film thickness and nanocrystals size.

Deposition time (min)	Film thickness (μm)	Nanocrystals size (nm)
5	0.43	53.8
10	0.56	74.6
15	0.73	73.7
20	2.57	74.0
30	1.61	83.6

Figure 1 and 2 show the FE-SEM images used to determining the CuO film thickness and nanocrystals size at varying deposition time. From the FE-SEM images, it

was observed that the surface of thin films is composed of irregular-sized CuO nanocrystals. Moreover, it was observed that the longer the deposition time, the rougher the CuO film surface. This is expected because the larger the CuO grains size will results in a rougher surface. Table 1 shows how the variation in deposition time affects the CuO film thickness and nanocrystals size. From Table 1, it was observed that CuO films with different thicknesses were synthesized by effectively manipulating the deposition time. Generally, the CuO film thickness was found to increase with increasing deposition time due to that more Cu²⁺ ions being diffused to the FTO surface, underwent reduction reaction, and subsequently deposited on it as shown in Eq. (1).



However, the relationship between deposition time and CuO film thickness was non-linear. It was observed that the CuO film thickness decreased when the deposition time was increased to more than 20 min. This could be due to the porous structure formation of CuO films, and caused the falling-off of porous deposits [1]. On the other hand, the CuO nanocrystals size was found to increase with increasing deposition time. This trend is expected due to the coalescence of growing CuO grains after they have attained a given size.

Photocurrent Density Measurements.

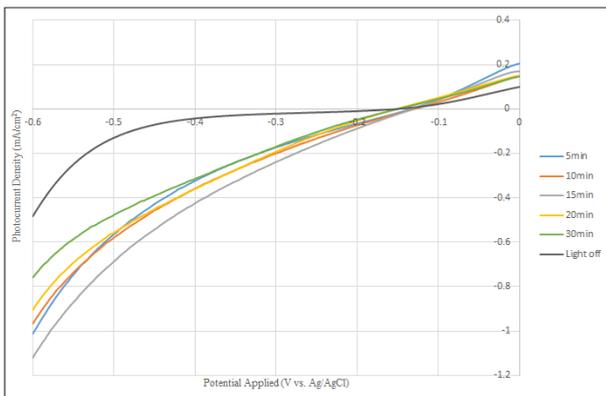


Figure 3. Photocurrent density profiles for CuO thin films under dark and irradiated conditions.

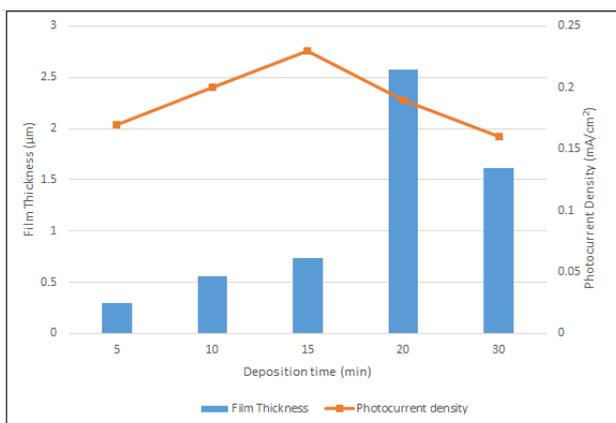


Figure 4. Effect of deposition time on CuO film thickness and photocurrent density.

Figure 3 shows the photocurrent density profiles for CuO thin films under dark and irradiated conditions. As the potential swept towards the negative direction from 0 V to -0.6 V (vs. Ag/AgCl), cathodic photocurrents were observed. Generally, the photocurrent density of CuO thin films is increasing with the increase in applied potential. This is due to the higher band-bending at the working electrode/electrolyte interface, which leads to a higher mobility of the photogenerated excitons and expansion of the depletion width with increasing applied potential [2]. In this study, the potential bias of -0.3 V (vs. Ag/AgCl) on the CuO thin films was used for the comparison of photocurrent density for different CuO thin films formed under varying deposition time. From Figure 4, it can be seen that the photocurrent density of CuO thin films increased with increasing film thickness. This could be due to the formation of steep band bending that enhances the charge separation of electrode and reduced carrier recombination in the bulk [3]. However, the photocurrent density started to decrease when the deposition time used was more than 15 min. As the CuO film thickness increases, more light can be absorbed until a certain thickness, whereby the CuO films will reduce the light photon penetration. This will increase the electron-hole pair recombination rate and results in a lower water-to-hydrogen conversion efficiency [4].

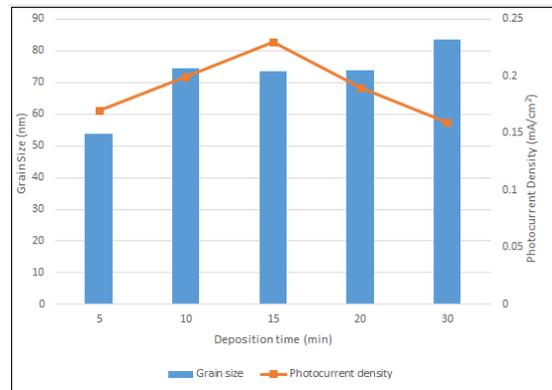


Figure 5. Effect of deposition time on CuO nanocrystals size and photocurrent density.

From Figure 5, it was found that the photocurrent density increased with increasing CuO nanocrystals size. It was observed that the CuO nanocrystals size remained almost constant for the deposition time of 10 - 20 min, while the corresponding photocurrent densities varied. Therefore, it can be concluded that the change in the photocurrent densities was not solely due to the change in CuO nanocrystals size. The photocurrent density started to decrease when the CuO nanocrystals size was larger than 73.7 nm. This observation could be explained by the larger CuO nanocrystals size and correspondingly lower catalytic surface area. This will result in a longer average minority carrier transport distance to the electrolyte interface and therefore, lower the collection efficiency.

Photoluminescence Measurements.

PL quenching effect is an efficient method to understand the emission mechanism and the charge transfer of the

material. The PL intensity is representing the rate of recombination of photogenerated electron-hole pairs. Therefore, a lower PL intensity indicates that more photoinduced electrons are trapped and stably transferred through the interface. Otherwise, the more intense PL spectrum dictates the fast recombination rate of electron-hole pairs. Figure 6 shows the PL spectra of CuO thin films synthesized at varying deposition time of 5 - 30 min. It was found that the PL spectra are composed of a sharp emission peak in the red region (662 nm). The emission peak at 662 nm arises due to the band-to-band transition of CuO and other defects arising in the nanostructured mixture. The PL spectra for the deposition time of 15 min has the lowest rate of recombination of photogenerated electron-hole pairs by referring to its lowest intensity shown in Figure 6. A further comparison study of PL data and the photocurrent density measurements showed that the obtained results are consistent with each other.

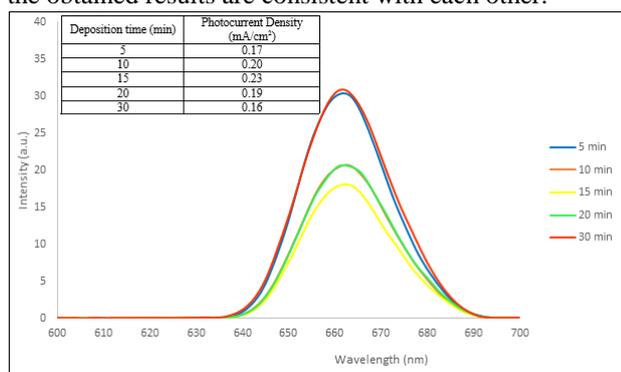


Figure 6. PL measurements of CuO thin films at different deposition time.

4 Conclusion

In conclusion, the effect of deposition time on the physicochemical and PEC properties of CuO thin films synthesized via electrodeposition method was systematically investigated. A smaller CuO nanocrystals size will lead to a higher photoactivity due to the increase in overall catalytic surface area. In addition, the smaller CuO nanocrystals size will prolongs the electron-hole recombination rate due to the increase in copious amount of surface defects. From this study, it was revealed that the relationship between deposition time and CuO film thickness was non-linear. This could be due to the detachment of CuO thin films from the FTO surface at an increasing amount of CuO mass being deposited. It was observed that the amount of light absorbed by CuO thin films increased with film thickness until a certain extent whereby, any further increase in the film thickness will result in a reduction of light photon penetration. Therefore, the CuO nanocrystals size and film thickness have to be compromised in order to yield a higher catalytic surface area and a lower rate of surface charge recombination. Finally, it was found that the deposition time of 15 min resulted in an average CuO nanocrystals size of 73.7 nm, optimum film thickness of 0.73 μm , and corresponding photocurrent density of 0.23 mA/cm² at the potential bias of - 0.3 V (versus Ag/AgCl). The PL spectra for the deposition time of 15 min has the lowest rate of recombination of photogenerated electron-hole pairs by referring to its lowest PL intensity.

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