Effect of Reaction Time on the Morphology of CuO Nanostructured Electrode for Pseudocapacitor Application

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Abstract. CuO nanostructured electrodes were successfully synthesized via a chemical bath deposition at room temperature for pseudocapacitor application. Changing the reaction time leads to the formation of different morphological nanostructures such as uniformed nanoneedles, nanotubes, nanosheets, and microflowers during oxidation. The electrodes were electrochemically characterized via cyclic voltammetry and galvanostatic charge-discharge using 6 M KOH electrolyte at different scan rates of 2-50 mV/s and current densities of 2-5 mA/cm², respectively. The electrodes exhibited good electrochemical performance with specific capacitance ranging from 88-231 mF/cm² at 2 mV/s.

1. Introduction
With the rapid development of the global economy and the exponential growth of the population, the large increase in energy demand has been one of the world’s biggest and most urgent problems. Currently, about 80% of the world’s energy mix is generated from the burning of oil, coal, and natural gas. Despite being the primary source of energy, fossil fuels are expected to be unsustainable in the coming years due to their depleting reserves, as well as the long-term devastating impact on the environment [1-2]. Thus, the development of clean, sustainable, efficient, and low-cost energy, such as renewables, must be urgently addressed.

Renewable energy is generated from natural resources such as sunlight, wind, tides, and geothermal, which are vast and naturally replenished. However, renewable energy is highly dependent on natural conditions making it vulnerable to climate change. Further, due to its intermittency, the incorporation of energy storage devices, such as batteries, has been used to efficiently capture and store energy [3-5]. However, batteries have their drawbacks, particularly their limited life span due to deterioration over cycles of charge-discharge process [6-7]. Therefore, it is crucial to develop additional efficient energy storage devices that will further support the transition to a clean and sustainable energy source.

Among other energy storage and conversion technologies, electrochemical supercapacitor (ES) has been the subject of extensive research due to its high-power density, reversibility, operating safety, environment benignity, fast charging/discharging rate, and long-term cycle stability. A supercapacitor is classified into two types based on charge storage mechanism: electric double-layer capacitors (EDLC) and pseudocapacitors [8-10]. EDLC stores energy in a non-Faradaic manner. Charge storage happens during ion adsorption/desorption at the interface between the electrode and electrolyte. Carbon-based materials are usually used for EDLCs. However, EDLC has limited specific capacitance compared to pseudocapacitors due to its double-layer charge storage mechanism [10-11].

On the other hand, pseudocapacitors store energy by Faradaic battery-type oxidation-reduction reaction, leading to pseudocapacitive behavior where electron transfers between the electrode and
electrolyte. Transition metal oxides and conducting polymers are typically used as active materials in pseudocapacitor electrodes [10,12]. Ruthenium oxide (RuO$_2$) has been the most widely employed transition metal oxide for pseudocapacitors due to its high specific capacitance of about 1400-2000 F/g. However, due to its toxicity and high cost, alternative transition metal oxides are currently being explored [13].

Among other transition metal oxides, copper oxide (CuO) has been considered due to its elemental abundance, low cost, environmentally benignity, and relatively high specific capacitance but has low conductivity and poor cyclic stability. Thus, most studies on CuO nanostructures have been focused on tuning the morphology to increase the number of pathways for electrolyte penetration using various synthesis techniques, such as hydrothermal process [14], electrodeposition [15], thermal reduction [16], microwave-assisted synthesis [17], etc. However, among those methods, chemical bath deposition (CBD) offers several advantages, such as low cost, and simplicity, and ease of fabrication [18-19].

In this work, various CuO nanostructures were synthesized via a facile chemical bath deposition method at room temperature for applications in binderless pseudocapacitor electrodes. The effects of CBD reaction time on the morphology, phase composition, and crystal structure of the CuO nanostructures on the surface of both Cu foil were investigated. The electrochemical performance of the binderless CuO nanostructured electrode was characterized using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD).

2. Experimental

2.1. Chemical bath deposition of CuO nanostructured electrode

All chemicals were analytical grade and used without further purification. In a typical experiment, 1.0 x 1.0 cm pieces of copper (Cu) foils were ultrasonically cleaned in acetone (Technical grade), ethanol (AR grade, RCI Labscan), and deionized water consecutively for 10 min. The substrates were immersed in 1.0 M hydrochloric acid (HCl, Macron Fine Chemicals) solution to remove surface oxides and impurities. The pre-cleaned Cu foils were dried in air. Nail enamel was used to cover one side of the substrate. The substrates were then immersed in a solution containing 12.0 mL 10.0 M sodium hydroxide (NaOH, Macron Fine Chemicals), 6.0 mL 1.0 M ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$, Himedia), and 27.0 mL deionized water for 30-120 min. The substrates were rinsed with ethanol and deionized water, followed by air drying.

2.2. Characterization of CuO nanostructured electrode

A scanning electron microscope (SEM, JEOL Ltd., JSM-5310) was used to investigate the morphology of the Cu products at different reaction times. The phase composition and crystal structure were examined by X-ray diffraction (Shimadzu MaXima XRD-700, Cu K radiation, $\lambda=0.1542$ nm, 30 mA).

2.3. Electrochemical characterization of CuO nanostructured electrode

Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were carried out using a potentiostat/galvanostat (SP-150, Biologic) to determine the specific capacitance of the electrode. A three-electrode set-up was used with Ag/AgCl (KCl electrolyte: 3 mol/L, Metrohm), platinum wire (8 cm wide), and the CuO/Cu sheet electrode (1.0 cm x 1.0 cm) as the reference, counter, and working electrodes, respectively. Measurement was performed in a 6.0 M potassium hydroxide (KOH, A.R., HiMedia) aqueous solution at different scan rates of 2 to 50 mV/s. The CV was measured between -0.3 to 0.6 V vs Ag/AgCl. The GCD was carried out under different current densities from 2 to 5 mA/cm$^2$ at a potential window of 0 to 0.4 V vs Ag/AgCl.

3. Results and discussion

3.1. Effect of Reaction Time on Chemical Bath Deposition

Fig. 1 shows the SEM images of Cu nanostructures on Cu foil after chemical bath deposition at different reaction times at room temperature. At 30 min, a uniformed needle-like structure was formed.
with an average length of 5 µm and a width of 289 nm as shown in Fig. 1a. These nanostructures correspond to the formation of blue to greenish film on the surface of the Cu foil. After 60 min, micro-flowers and nanotubes were observed as in Fig. 1b. The micro-flower consists of connecting nanosheets forming into petals with triangular tips. The micro-flowers have an average width of 4 µm while the nanotubes have an average diameter of 222 nm. Prolonging the reaction time to 100-120 min in Fig. 1c-d resulted in the formation of nanosheets covering the whole area of the Cu substrates. The Cu surface also changed to black. Further, spherical flower-like structures with an average diameter of 2.9 and 3.4 µm were also observed together with the nanosheets after 100 and 120 min, respectively.

![Image](image-url)

**Figure 1.** SEM images of Cu foil after immersion in NaOH/(NH₄)₂S₂O₈ aqueous solution at different reaction times of (a) 30, (b) 60, (c) 100, and (d) 120 min

Fig. 2 shows the XRD pattern of Cu nanostructures on Cu foil at different CBD reaction times. Cu peaks at 2θ = 43.7° and 50.7° correspond to planes (111) and (200) were present for all electrodes at different reaction times. At 30 min reaction time, diffraction peaks at 2θ = 24.28°, 34.36°, 35.82°, 38.74°, 40.1° were attributed to (021), (002), (111), (022), (130), (132) planes of the orthorhombic Cu(OH)₂. This indicates that the needle-like structures in Fig. 1a are Cu(OH)₂. On the other hand, only weak peaks of (111) and (022) Cu(OH)₂ were observed after 60 min reaction time. The absence of other Cu(OH)₂ peaks could be attributed to the change in the morphology of the product to nanotubes and micro-flowers. Increasing the immersion time up to 100 min resulted in the appearance of CuO and Cu₂O peaks. The (200) Cu₂O peak coincided with the (111) Cu peaks, which explains the increase in the intensity of this peak. CuO planes (110), (002) (111), (-112), (-202), (020), (202), (-113), (-311) and (220) at 2θ = 32.6°, 35.87°, 39.1°, 46.5°, 49.2°, 53.7°, 58.47°, 61.92°, 66.7°, and 68.3° were observed. This indicates the transformation of the product from Cu(OH)₂ to Cu oxides, which coincides with the change in color of the film to black [18-19]. This also signifies that the nanosheets in Fig. 1b-c are Cu oxides. Similarly, Cu oxides were identified from the XRD pattern in Fig. 2d. However, the strongest peaks were due to CuO, suggesting it is the dominant Cu oxide phase. The (200) Cu peak decreased in intensity after 100-120 min, indicating thicker Cu oxide film. The color
change on the surface of the Cu foil from rose gold, blue, and then black demonstrates the oxidation on the surface of the substrate from Cu, Cu(OH)$_2$, Cu$_2$O to CuO during 30-120 min chemical bath deposition. The reactions can be expressed by the equations below:

\[
\begin{align*}
\text{Cu} + 4 \text{NaOH} + (\text{NH}_4)_2\text{S}_2\text{O}_8 \xrightarrow{30\text{ min}} & \text{Cu(OH)}_2 + 2\text{Na}_2\text{SO}_4 + 4\text{NH}_3 \uparrow + 2\text{H}_2\text{O} \\
2\text{Cu} + 8 \text{NaOH} + 2(\text{NH}_4)_2\text{S}_2\text{O}_8 \xrightarrow{60\text{ min}} & \text{CuO} + \text{Cu(OH)}_2 + 4\text{Na}_2\text{SO}_4 + 4\text{NH}_3 \uparrow + 5\text{H}_2\text{O} \\
\text{Cu} + 4 \text{NaOH} + (\text{NH}_4)_2\text{S}_2\text{O}_8 \xrightarrow{100/120\text{ min}} & \text{CuO} + 2\text{Na}_2\text{SO}_4 + 2\text{NH}_3 \uparrow + 3\text{H}_2\text{O}
\end{align*}
\]

**Figure 2.** XRD of Cu foil after immersion in NaOH/(NH$_4$)$_2$S$_2$O$_8$ aqueous solution at different reaction times of (a) 30, (b) 60, (c) 100, and (d) 120 min

### 3.2. Electrochemical Analysis

Cyclic voltammetry (CV) of the CuO electrodes was performed in a three-electrode system in 6 M KOH aqueous electrolyte at the potential window of -0.3 to 0.6 V vs Ag/AgCl. Fig. 3a shows the CV curves of the Cu(OH)$_2$ electrode prepared after 30 min CBD at different scan rates of 2-50 mV/s. The CV curves display anodic and cathodic peaks attributed to the redox reactions of Cu(OH)$_2$, Cu$_2$O, and CuO, which indicates the pseudocapacitance behavior of the fabricated electrodes. The quasi-reversible redox reaction between Cu(I) and Cu(II) species are expressed below [20]:

\[
\begin{align*}
2\text{Cu(OH)}_2 + 2e^- & \leftrightarrow \text{Cu}_2\text{O} + 2\text{OH}^- + \text{H}_2\text{O} \\
\text{Cu}_2\text{O} - 2e^- + 2\text{OH}^- & \leftrightarrow 2\text{CuO} + \text{H}_2\text{O}
\end{align*}
\]

The 30 min electrode has an increasing specific capacitance from 50 to 88 mF/cm$^2$ at decreasing scan rates. This indicates that a lower scan rate allows the ions from the electrolyte to access the bulk active material of the electrode for a longer time [20-21].

Fig. 3b shows the CV curves of the electrodes prepared after 30-120 min at 2 mV/s scan rate. For the electrodes prepared after 100 and 120 min, the anodic peaks on the CV curves were in the range of -0.4 to -0.2, and -0.1 to 0 vs. Ag/AgCl, which correspond to the oxidation of Cu/Cu$_2$O and Cu$_2$O/CuO, respectively. The reverse reactions are indicated by the cathodic peaks in the range of -0.1 to 0, and 0.2 to 0.3 V vs. Ag/AgCl at 100-120 min electrodes. The specific capacitance of the 30, 60, 100, and 120 min electrodes were 88, 167, 113, and 231 mF/cm$^2$ at 2 mV/s, respectively. The 120 min electrode displays the highest specific capacitance, which is attributed to its morphology. The
combination of nanosheets and micro-flowers may offer more active sites for interaction with the electrolyte, which leads to a more efficient redox reaction compared to the other three electrodes [20-22].

Figure 3c displays the galvanostatic charge-discharge of the 30 min electrode at different current densities of 2-5 mA/cm². It can be observed that charge-discharge curves have a non-linear shape indicating pseudocapacitance from the redox reactions of the electrodes [20,22]. The electrode showed a maximum potential of 0.4 V. Decreasing the current density from 5 to 2 mA/cm² resulted in an increase in the specific capacitance from 71.3 to 130 mF/cm².

**Figure 3.** Cyclic voltammetry curve of (a) the 30 min electrode at scan rates of 2-50 mV/s and (b) the 30-120 min electrodes at 2 mV/s scan rate (c) Galvanostatic charge-discharge of the 30 min electrode at current densities of 2-5 mA/cm²

### 4. Conclusion

CuO nanostructured electrodes were synthesized in a chemical bath deposition at different reaction times. Different morphological structures were formed after increasing reaction time of 30-120 min, including uniformed needle-like structure with an average length of 5 µm and width of 289 nm, nanotubes with an average diameter of 222 nm, and microflowers with diameters in the range of 2.9-3.4 µm. The specific capacitance at 2 mV/s of the 30, 60, 100, and 120 min electrodes were 88, 167, 113, 231 mF/cm², respectively. The 120 min electrode displays the highest specific capacitance of 231 mF/cm² at 2 mV/s which is attributed to its morphology that offers more active sites for redox reactions.

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