Nanostructured CuO thin film deposited on stainless steel using spray pyrolysis as supercapacitor electrode

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Abstract
We investigated the effects of different annealing temperatures on cupric oxide (CuO) films as supercapacitor electrode. CuO films were grown on stainless steel substrates via spray pyrolysis and annealed for two hours at different temperatures of 160 °C, 250 °C, and 400 °C. X-ray diffractometry (XRD) and micro-Raman spectroscopy (MRS) confirmed the monoclinic phase of CuO films. At higher annealing temperatures, narrower XRD peaks were observed due to reduced defects and increased grain size. The supercapacitive properties of the CuO electrode were evaluated using three-electrode cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in 1.0 M aqueous sodium sulfate (Na2SO4) electrolyte. At a scan rate of 10 mV s⁻¹, the highest specific capacitance of 87.06 F g⁻¹ was achieved from the CuO electrode annealed at 400 °C. Furthermore, repeated CV scans up to the 1000th cycle revealed that the CV plots have retained its shape and capacitance up to 84.68% of the original value. The obtained results revealed that the CuO nanostructures grown by spray pyrolysis can be used as an electrode for supercapacitors.

1. Introduction
The increase in demand for electrical energy storage due to the fast-growing market for portable electronic devices, stand-by power, and hybrid electric vehicles has motivated intensive research and development of new materials to improve the performance of current energy storage devices [1–6]. Supercapacitor also known as electrochemical capacitors (ECs) are energy storage devices which utilize high-surface area, porous material electrode materials, and thin separator to achieve capacitances several orders of magnitude larger than conventional capacitors [1, 3, 6, 7]. In a supercapacitor, energy is stored on the surface of the active material. Hence, its charging-discharging occurs at faster rates which results to high-power densities, high efficiency, high-cycling stability, and excellent lifespan [5, 7–9]. These features positioned supercapacitors as one of the most promising energy storage systems in addition to batteries.

Supercapacitors can be classified as either an electric double layer capacitor (EDLC) or pseudocapacitor depending on whether the charge transfer is non-faradic or faradic respectively. EDLC stores charge in an electric double layer that is formed at the electrode/electrolyte interface and therefore this charge storage is faradic [5, 8, 10]. Carbon based materials are used in EDLC because of its large surface area, good electronic conductivity, low cost, and long cycling stability [11–13]. For example, Xue et al fabricated N/O self-doped hollow carbon nanorods (HCNs) based on deep eutectic solvents as all-in-one talent acting as C/N/O precursor, self-template, and self-doping reagent. The HCN exhibit a high capacitance of 382 F g⁻¹ at 1.0 A g⁻¹ which ascribed to its high surface area that provides abundant active sites for ions, enhanced accessibility for ion storage and its hollow structure that enhances the electron transport along the walls and allow electrolyte ion permeation inside the internal channels, which expose more active sites [14]. On the other hand, pseudocapacitor stores the charge utilizing faradic redox reactions as well as non-faradic electric double layer formation which allows higher energy storage than that of EDLC [5–9]. Transition metal oxide (TMO) is
considered as the best candidate for pseudocapacitors. Among the TMOs, ruthenium oxide (Ru2O3) is the most promising due to its high theoretical specific capacitance, high cycling stability, and large potential window. However, its high cost and toxicity of Ru prohibits its large scale application. Therefore, research interests have been focused on other TMOs [9, 15].

Recently, researchers became interested on CuO as an electrode for supercapacitor application due to its electrochemical properties, low cost, chemically stability, easy preparation, abundant resources, and desirable optical and electrical properties [16–22]. Numerous methods have been developed to synthesize various CuO nanostructures with diverse morphologies, sizes, and dimensions using various chemical and physical strategies for supercapacitor application [22]. Pawar et al fabricated Cu2O and CuO nanorods on stainless steel substrates by using reactive radio frequency (RF) magnetron sputtering. The nanorods exhibited maximum capacitance of 272 F g\(^{-1}\) at 10 mV s\(^{-1}\) in 6 M KOH electrolyte [4]. Reddy et al also grew their copper oxide nanorods on stainless steel substrate using the same method [23]. Vidhyadharan et al prepared copper oxide nanowires via electrospinning method which exhibited a capacitance of 710 F g\(^{-1}\) at 2 mV s\(^{-1}\) in 6 M KOH electrolyte [10]. Arrays of CuO nanowires and nanosheets on copper foam prepared by Li et al via anodization of copper foam followed by thermal treatments reported a maximum specific capacitance of 133 F g\(^{-1}\) in 0.2 M ionic liquid [21]. These methods proved effective in obtaining copper oxide nanostructures with high specific capacitances, however they have prohibitive costs and complicated fabrication processes.

In this paper, we present a simple, cost-effective, straightforward, and scalable process for obtaining CuO film electrode on stainless steel for supercapacitor applications. CuO film electrodes were fabricated on stainless steel substrates using spray pyrolysis method to obtain nanostructure with improved electrochemical performance. This method has several advantages, like fast and easy diffusion of electrolyte ions, good contact with current collector, and better cycling stability [19]. As post-deposition treatments might be useful to control and improve the morphology, structural and electrochemical characteristics of the films. As-deposited films were annealed for two hours in air at 160 °C, 250 °C and 400 °C. These methods proved effective in obtaining copper oxide nanostructures with high specific capacitances, however they have prohibitive costs and complicated fabrication processes.

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2. Experimental

2.1. Preparation of electrodes

Cu\(_2\)O nanostructures were synthesized via spray pyrolysis on clean 1.5 cm × 5 cm stainless steel substrates. The substrates were cleaned via standard degreasing procedures. A 50 mM precursor solution of copper acetate monohydrate [Cu(CH\(_3\)COO)\(_2\)-H\(_2\)O, CuAc] was dissolved in a 3:1 deionized water to ethanol solvent ratio, with a total volume of 100 ml [24, 25]. The precursor solution was transferred in an atomizer and sprayed onto the surface of pre-heated substrates until the solution has emptied. The substrate temperature was kept at 100 °C during the deposition. A 10-second interval between the sprays was maintained to ensure that chemicals other than the desired products will evaporate. The as-deposited Cu\(_2\)O films had undergone a post-heat treatment for two hours with different annealing temperatures of 160 °C, 250 °C, and 400 °C and were designated as A160, A250, and A400, respectively. As-deposited sample was also included in the sample set.

2.2. Characterization of electrodes

The surface morphology of Cu\(_2\)O nanostructures were analyzed using a field emission scanning electron microscope (FEI XL30 Sirion) with an accelerating voltage of 10 V. The crystallographic study was employed using XRD (Bruker D8 Discover) with a CuK\(_\alpha\) radiation measured at 40 kV and 40 mA. Full-angle scans between 20 °C to 80 °C were taken with a scanning speed of 0.01 min\(^{-1}\). The average crystallite size was calculated using the Scherrer equation given in equation (1) [26–28],

\[
D = \frac{k\lambda}{\beta \cos \theta}
\]

where, \(k\) is the shape factor, \(\lambda = 1.5406 \text{ Å}\) is the x-ray wavelength, \(\beta\) is the full width at half maximum (FWHM) and \(\theta\) is the angle of the diffraction peak. Complementary to XRD, Raman spectroscopy was employed using a Ventus diode-pumped solid-state (DPSS) laser with ∼532 nm wavelength for photoexcitation in the wavenumber region 100–1000 cm\(^{-1}\). The Raman signal was recorded using an iHR500 spectrophotometer equipped with charge-coupled device detector. All measurements were carried out at room temperature.

2.3. Electrochemical measurement

The electrochemical properties of the Cu\(_2\)O electrodes were evaluated via cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Both setups utilized a three-electrode electrochemical cell which
was connected to a potentiostat (eDAQ EA163). The Cu_{x}O films served as the working electrode, platinum (Pt) disk as the counter electrode and silver/silver chloride (Ag/AgCl, filled with 3 M KCl with a potential of 0.2 V versus hydrogen). The electrodes were tested in 1.0 M Na_{2}SO_{4} electrolyte. CV measurements were done using an ED410 data recorder connected to the potentiostat. In the E-Chem software, the voltage window was set from 0 to −700 mV while the scan rates were varied from 10 mV s^{-1} to 100 mV s^{-1}. The specific capacitance, C_s (F g^{-1}) can be determined by CV curves by using equation (2) [10, 20]:

\[ C_s = \frac{1}{2mnv(E_2 - E_1)} \int_{E_1}^{E_2} I(E) dE \]  

where \( m \) is the mass of active material (g), \( v \) is the scan rate (mV s^{-1}), and \( I \) is the response current from the applied potentials from initial \( (E_1) \) and final \( (E_2) \) voltages. The weight of the active is equivalent to 1 mg. EIS measurements were carried out using an ERZ100 impedance analyzer in the frequency range of 1 mHz to 10 kHz with an applied alternating current potential of 100 mV. EIS data was typically expressed as Nyquist plot, -Z’ versus Z’, where -Z’ and Z’ is the imaginary impedance and real part of the complex impedance, respectively. The impedance data were modelled using ZMAN to provide the equivalent circuit to determine whether the resistances came from the electrolyte, double layer capacitance, charge transfer, and/or diffusion.

3. Results and discussion

3.1. Structure and morphology

SEM images of the as-deposited and post-annealed Cu_{x}O films at different temperatures are shown in figure 1. All micrographs show a successful growth of highly uniform and homogeneous nanostructures of Cu_{x}O. Figure 1(a) displays the as-deposited film wherein the spray pyrolysis deposition method resulted to even and smooth surface. When post-heat treatment was introduced at 160 °C, A160 has a slight increase in grain size but with no distinct boundaries as shown in figure 1(b). When the annealing temperature was raised to 250 °C, visible crevices between each grain were revealed from the A250 film in figure 1(c). At 400 °C, larger grains formed and the presence of crevices were more distinguished in A400 (figure 1(d)). SEM results show that raising the annealing temperature leads to larger grain boundaries and particle size possibly due to reduced overall surface energy [29]. It is evident that the surface morphology and its sizes can be controlled by varying the annealing temperature.

XRD was performed on the as-deposited and annealed films are illustrated in figure 2. Diffraction peaks occurred at angles of 32.7°, 35.8° and 38.8° which correspond to the (110), (−111), and (111) peaks of CuO with monoclinic phase. No formation of Cu_{2}O phase or any impurities was detected with an increase in the annealing temperature. The peak intensities increase with the annealing temperature which suggests improved crystallinity.
of the copper oxide films [27, 29–31]. In addition, the FWHM of the XRD peaks decreases with increasing annealing temperature. Crystallite size can be determined from equation (1) given the diffraction angle and FWHM extracted from the diffraction profile. The FWHM and crystallite size as a function of the annealing temperature is shown in figure 3. The calculated crystallite sizes increased from 6.9 nm to 17.1 nm and 6.67 nm to 17.73 nm for the \((111)\) and \((111)\) planes, respectively, as annealing temperature increased from 100 °C to 400 °C. The largest crystallite size was observed at an annealing temperature of 400 °C. This can be attributed to the sufficient thermal energy produced which enable small crystallites to coalesce with each other resulting in bigger crystallites. The broadening of the diffraction peak (larger FWHM) observed at the as-deposited and A160 films is caused by poor crystallinity due to lattice imperfections such as defects and grain boundaries. Annealing at higher temperature caused the film to undergo a recrystallization process which decreased the defects in the crystalline structure resulting in narrower diffraction peaks [29, 31, 32]. Therefore, XRD analysis shows the formation of high quality CuO films at higher annealing temperature.

The Raman spectra of all CuO films at room temperature are shown in figure 4. Theoretically, CuO has 12 phonon branches as expressed in equation (3). These branches are divided into: (i) \([A_u + 2B_g]\) symmetry, which corresponds to 3 the acoustic phonon modes; (ii) \([3A_u + 3B_u]\) symmetry which has 6 infrared-active modes, and; (iii) \([A_g + 2B_d]\) symmetry which are 3 Raman-active modes [23, 31, 33].

\[
\Gamma_{\text{vibr}} = 4A_u + 5B_u + A_g + 2B_d
\]  

(3)

In the measured Raman spectra from the films, three peaks (297 cm\(^{-1}\), 347 cm\(^{-1}\) and 605 cm\(^{-1}\)) were observed which were identified as the first order phonon scattering and assigned to \(A_g\) and \(2B_d\) CuO phonon modes [23, 31, 33]. These peaks intensify along with annealing temperature indicating crystallization in the CuO film at high temperature anneals in accordance with the XRD results. Raman and XRD analysis confirm that only the CuO phase exist in the prepared thin films and that annealing enhanced the crystallinity of the film.

3.2. Electrochemical properties

Cyclic voltammetry was used to evaluate the supercapacitive performance of CuO films annealed at different temperatures. Figure 5 displays the cyclic voltammograms (CVs) of each electrode in 1.0 M Na\(_2\)SO\(_4\) aqueous electrolyte in the voltage window 0 to 0.7 V at different scan rates from 10 to 100 mV s\(^{-1}\). In the charging state, CuO (and/or Cu(OH)\(_2\)) gains electrons and is converted to Cu\(_2O\) (and/or CuOH) during the reduction process which resulted in cathodic peaks. Meanwhile, during electrochemical discharge, anodic peaks were present which can be attributed to the oxidation of Cu\(_2O\) (and/or CuOH) to CuO (and/or Cu(OH)\(_2\)). Based on previous reports and these observations, the charging and discharging processes for CuO electrodes, respectively, are summarized in equations (4) and (5) [4, 10, 20, 21, 34]:

\[
2\text{CuO} + \text{H}_2\text{O} + 2e^- \leftrightarrow \text{Cu}_2\text{O} + 2\text{OH}^-
\]  

(4)

\[
\text{Cu(OH)_2} + e^- \leftrightarrow \text{CuOH} + \text{OH}^-
\]  

(5)

Both anodic and cathodic peaks, which correspond to the reduction and oxidation reactions during electrochemical process respectively, were present in the CV profiles of all CuO electrodes investigated. This result confirmed the pseudocapacitive nature of the CuO electrodes. The shifting of the anodic peak towards the
positive potential and the cathodic peak towards the negative potential with an increase in the scan rate demonstrates the quasi-reversible nature of the redox reaction [35]. This behavior has been conventionally observed [10, 23, 34, 36]. The shape of the CV curves remains nearly the same for all scan rates which indicates excellent capacitive behavior.

Figure 3. Calculated FWHM and grain size as a function of annealing temperature (a) (−111) plane, (b) (111) plane.

Figure 4. Raman spectra of copper oxide thin films annealed at different temperatures.
The specific capacitance, \( C_s \), of the electrodes at different scan rate were estimated using equation (2) and shown in figure 6. A decrease in \( C_s \) at higher scan rate was observed for all samples which suggest material utilization. The redox reaction responsible for the pseudocapacitive behavior of CuO electrodes depends on the diffusion of ions from the electrolyte into available active sites of the electrode. A lower scan rate allows longer duration for the electrolyte ions to penetrate the bulk of the electrode thus utilizing most of the active site in the material leading to high \( C_s \). Meanwhile, high scan rates restrict the interaction between ions and electrode at the outer surface of the electrode leading to smaller \( C_s \). The maximum \( C_s \) of 87.06 F g\(^{-1}\) was recorded for electrode

![Cyclic voltammogram of copper oxide electrodes at different scan rate.](image1)

![Specific capacitance of copper oxide electrode annealed at different temperature at varying scan rate from 10 mV s\(^{-1}\) to 100 mV.](image2)
A400 at scan rate of 10 mV s\(^{-1}\). A250, A160 and as-deposited electrodes follow with 54.52 F g\(^{-1}\), 33.67 F g\(^{-1}\) and 18.28 F g\(^{-1}\), respectively. The increase in specific capacitance of A400, relative to other electrodes can be attributed to the improved conductivity and increase in surface area as a result of annealing. This improvement resulted in reduced area of grain boundary and interfaces and consequently to reduced resistance of the material and improved carrier mobility. In addition, the crevices in A400 became an open structure in the electrode’s surface which increased the diffusion of ions into the material. The recorded specific capacitance is comparable to recently reported solution-based method in fabricating copper oxide film as an electrode for supercapacitor application \([16, 17, 34]\). As mentioned above, such enhancement in capacitance is attributed to the improvement of the electrical conductivity with annealing. This improved conductivity is further confirmed by EIS. Figure 7 shows the Nyquist plot of the electrodes annealed at different temperatures. At very high frequency, the y-intercept of the Nyquist plot is the equivalent series resistance (Rs). The Rs arises due to electrolyte resistance, internal resistance of the electro active material, and the contact resistance between the active material and current collector \([10, 37, 38]\). The Rs are 24.65 \(\Omega\), 24.89 \(\Omega\), 24.72 \(\Omega\), and 23.72 \(\Omega\) for as-deposited, A160, A250 and A400 respectively. A semicircle arc displays at the high frequency region represents the redox reaction between CuO and Cu\(_2\)O (as indicated in equations (4) and (5)) at electrolyte/electrode interface. The diameter of the semicircle is the kinetic resistance due to the charge transfer process, known as charge transfer resistance (Rct). Thus, smaller semicircle reflects lower Rct. Among the four electrodes, A400 has the lowest Rs and much smaller semicircle suggesting the electrode’s high conductivity due to increased carrier mobility.

According to the result, we identified the A400, among the four samples as the optimum electrode as it provides superior crystallinity, large grain size, high conductivity and the highest specific capacitance. Apart from these properties, the cycling stability is also one key factor in finding supercapacitor electrodes for many practical applications. Repeated CVs up to 1000 cycles at a scan rate of 100 mV s\(^{-1}\) were performed on A400. Its capacity retention with respect to cycle number is shown in figure 8. Inset of figure 8 is the CV curves of the 1st, 500th and 1000th cycles. The capacitance is maintained for the first 130 cycle but decreased by approximately 9.8% from its original capacitance as it reached the 200th cycle. The specific capacitance decreased continuously after 200th cycles, however, it was able to maintain 15.32% of its original capacitance after 1000th cycle. This decrease of C\(_s\) with the number of cycles is presumably related to the delamination of active electrode material.
during cycling probably due to stresses induced during measurements at such fast scan rate and poor adherence of the active material onto the substrate [2, 18, 20].

4. Conclusion

CuO films were successfully deposited on stainless steel substrate by a simple, cost-effective, straight forward and scalable spray pyrolysis techniques for supercapacitor application. The effect of post annealing temperature on the morphology, structure and performance of supercapacitor behavior was studied. SEM showed significant grain growth for A400. XRD and Raman confirm the monoclinic CuO structure of the films. It was found that specific capacitance values are better for electrodes annealed at higher temperature in 1.0 M Na₂SO₄ electrolyte. A maximum capacitance of 80.86 F g⁻¹ was recorded on A400 at a scan rate of 10 mV s⁻¹. The increase in capacitance of the electrode is attributed to the improved conductivity and increase in surface area as a result of annealing. EIS show that the equivalent series resistance and internal resistance of A400 is low owing to the decrease in grain boundary that enhanced the carrier mobility. Repeated cyclic voltammetry up to 1000 cycles reveal loss of capacitance which is attributed to the delamination of active electrode material during cycling. Our results demonstrate that the present CuO films from spray pyrolysis are viable supercapacitor electrodes.

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