

NANOSTRUCTURED COPPER OXIDE THIN FILMS VIA RAPID HYDROTHERMAL ROUTE FOR ELECTROCHEMICAL ENERGY STORAGE

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Abstract

This study examines the rapid hydrothermal production of nanostructured copper oxide (CuO) thin films as efficient electrode materials for supercapacitors. Supercapacitors are esteemed for their fast charging and discharging capabilities and elevated power density, making CuO a desirable material owing to its substantial theoretical capacitance, adequate conductivity, and eco-friendliness. Nanostructuring CuO increases surface area and reduces ion diffusion distances, improving electrochemical performance. The synthesis process utilizes a hydrothermal approach that is energy-efficient, cost-effective, and sustainable, using deionized water as a solvent. Critical factors like temperature, pH, and reaction duration are adjusted to produce CuO with nanostructures that enhance electrochemical properties. The synthesized CuO is applied to nickel foam or stainless-steel substrates by dip-coating or electrochemical deposition. Characterization methods include X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM), offering insights into structural and morphological attributes. XRD verifies phase purity, SEM analyzes surface appearance, and TEM elucidates nanostructure dimensions and crystallinity. The electrochemical performance is evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). CV investigation reveals pseudo-capacitive behavior, with specific capacitance reaching 60 Fg^{-1} . GCD testing demonstrates efficient charging-discharging characteristics, whilst EIS indicates little internal resistance and advantageous charge transfer. The research finds that hydrothermally produced CuO thin films are advantageous for supercapacitor applications. They offer a sustainable method to create high-capacity, stable, and economical materials for improved energy storage systems.

Keywords: Supercapacitors, cyclic voltammetry-ray diffraction, copper oxide, thin films

Introduction

Supercapacitors are receiving considerable interest as energy storage devices owing to their capacity for quick charging and discharging, extended cycle life, and elevated power densities. [1-2] With the increasing need for efficient and sustainable energy storage, there is an urgent requirement for cost-effective, high-performance electrode materials. Transition metal oxides,

especially copper oxide (CuO), are advantageous options owing to their elevated theoretical capacitance, mild conductivity, and environmentally benign characteristics. [3] Copper oxide (CuO), a naturally prevalent and economical substance, has remarkable redox activity that improves charge storage capacity, particularly when fabricated as nanostructures. Nanostructuring CuO enhances its surface area and reduces ion diffusion distances, both essential for augmenting electrochemical performance in supercapacitors. [4]

Nevertheless, conventional synthesis techniques for nanostructured CuO are often laborious and costly. The fast hydrothermal synthesis method offers a scalable, eco-friendly, and effective solution for the production of CuO thin films with precisely controlled nanostructures. This work seeks to examine the quick hydrothermal production of nanostructured CuO thin films and assess their electrochemical characteristics as supercapacitor electrodes. This optimised synthesis process advances the development of sustainable, high-performance materials for next-generation energy storage devices. [5]

Nanoscale structuring of copper oxide (CuO) into thin films improves its electrochemical performance, making it suitable for supercapacitors. This enhancement results from three primary factors: augmented surface area, facilitating more active sites and more charge storage; reduced ion-diffusion pathways, permitting expedited charging and discharging; and enhanced active surface sites, fostering efficient redox reactions. These structural advantages provide nanostructured CuO thin films as very efficient electrode materials for rapid, high-capacity energy storage.

Hydrothermal synthesis is optimal for generating nanostructured CuO thin films owing to its meticulous control of particle size, shape, and crystallinity, hence improving electrochemical performance. It is scalable for extensive manufacturing and ecologically sustainable, often using water as a solvent without necessitating high-energy inputs or hazardous chemicals. These benefits provide it a flexible and sustainable approach for producing high-performance materials for energy storage applications. [5]

The aim of this research provides a quick hydrothermal synthesis technique for the fabrication of nanostructured copper oxide (CuO) thin films, specially tailored for electrochemical energy storage applications, particularly in supercapacitors. This work seeks to illustrate that optimizing the hydrothermal process may provide economical, high-performance CuO electrodes with improved capacitance, stability, and charge/discharge efficiency. The importance is in the development of sustainable and efficient materials for next-generation supercapacitor technology, addressing the increasing need for rapid and dependable energy storage. [6]

2. Materials and Methods

2.1 Materials

The following materials were used in the production of CuO thin films by the hydrothermal method:

Copper precursor: Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$)

Solvent: Deionised water (H_2O)

Reducing agent: Sodium hydroxide (NaOH)

Substrates: Nickel foam (Ni foam) or stainless steel (SS) films for deposition

Surfactant (optional): Polyvinyl alcohol (PVA) or stabilizing agents

2.2 Synthesis of Nanostructured Copper Oxide Thin Films

2.2.1 Parameters for Hydrothermal Synthesis

The hydrothermal approach for synthesizing nanostructured CuO thin films adheres to a systematic protocol that enables meticulous regulation of the films' shape, crystallinity, and electrochemical characteristics. The parameters of the hydrothermal synthesis process are as follows: A copper precursor solution is produced by dissolving 0.1 M copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) in deionised water. Sodium hydroxide (NaOH) is incrementally added to the copper precursor solution to modify the pH and start the precipitation process. A final NaOH concentration of roughly 0.2 M is often used to facilitate the synthesis of CuO under hydrothermal conditions. The reaction occurs at a temperature of 180°C , sustained for a period of 1 to 2 hours. This temperature is sufficient to initiate the hydrothermal process, promoting the production of CuO and enabling nanostructuring. Reaction time: An expedited synthesis method is used, decreasing the reaction duration to around 1-2 hours. Minimised reaction durations are optimised to reduce energy consumption and enhance material efficiency while guaranteeing the correct phase and nanostructure development. The precursor solution is introduced into a sealed autoclave, where the reaction occurs under high pressure to facilitate crystal growth and the development of well-defined CuO nanostructures. This expedited hydrothermal method aims to facilitate rapid nucleation and development of CuO nanostructures, enhancing the material's electrochemical efficacy for supercapacitor applications. [7]

2.2.2 Deposition onto Substrates

Following the synthesis of CuO in the hydrothermal reactor, the subsequent step involves the deposition of the nanostructured CuO onto a conductive substrate. The procedure for preparation and deposition is as follows:

Substrate preparation: Conductive substrates, like nickel foam (Ni foam) and stainless steel (SS) sheets, are used for their superior electrical conductivity and mechanical durability. The substrates undergo comprehensive cleaning by ultrasonic treatment in acetone, ethanol, and deionised water to eliminate organic impurities, thereafter dried in an oven at 60°C .

Film deposition: Following washing, the substrates are submerged in the synthesised CuO solution. Deposition is often accomplished by two methods:

Dip-coating: The purified conductive substrates are submerged in the CuO precursor solution and then extracted at a regulated velocity to create a thin, uniform layer of CuO. The substrate is then dried at 60°C to eliminate surplus solvent.

Electrochemical deposition (when used with hydrothermal synthesis): A continuous voltage is provided between the substrate (working electrode) and a counter electrode inside the CuO

solution. This technique may further improve the adherence and homogeneity of the CuO coating on the substrate. [8]

2.3 Characterization Techniques

2.3.1 Structural and Morphological Examination: X-ray diffraction (XRD) is used to ascertain the phase purity, crystallinity, and structural characteristics of the synthesised CuO thin films. The XRD examination verifies the production of CuO and elucidates the crystalline structure of the material. Films are generally analysed using a Bragg-Brentano geometry utilising Cu K α radiation (wavelength = 1.5406 Å). The distinctive diffraction peaks associated with CuO are noted at 2θ values around 35.5°, 38.7°, 48.8°, 58.5°, and 68.1°, aligning with the typical CuO diffraction pattern (JCPDS No. 48-1548). The XRD patterns may elucidate the crystallinity of the films by analysing the full-width at half maximum (FWHM) of the peaks, which is associated with the size of the crystallites. [9]

2.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is used to examine the surface appearance and structure of CuO thin films. SEM pictures provide high-resolution depictions of the nanostructure, facilitating the examination of the homogeneity, thickness, and morphology of the CuO nanostructures. The surface roughness, porosity, and dispersion of CuO nanoparticles may also be evaluated. Scanning Electron Microscopy (SEM) may be conducted at many magnifications to examine various facets of the film's morphology, including nanosheet and nanowire formations, which are critical determinants of the electrochemical performance of supercapacitors. [10]

2.3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) provides an enhanced understanding of the intricate morphology, crystalline structure, and size distribution of individual CuO nanoparticles or nanostructures inside the thin film. Transmission electron microscopy (TEM) is very effective for examining the lattice structure and verifying the crystalline characteristics of CuO at the atomic scale. High-resolution TEM pictures may elucidate interplanar spacing and facilitate the estimation of crystallite size, which is beneficial for linking structural characteristics with electrochemical performance. [11-12]

2.3.4 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is used to examine the electrochemical properties of CuO thin films by assessing the current response relative to the applied voltage. CV curves offer critical insights into the redox behaviour, capacitive performance, and stability of the material. The morphology and region under the CV curve signify the specific capacitance and the reversibility of electrochemical processes. A standard CV curve for CuO in a supercapacitor configuration will exhibit distinct peaks indicative of the oxidation and reduction processes of CuO, offering insights into its efficacy for charge storage. [13]

2.3.5 Galvanostatic Charge-Discharge (GCD) Assessments

Galvanostatic charge-discharge (GCD) experiments are performed to assess the specific capacitance and cycle stability of the CuO thin films. In these tests, the material undergoes

charging and discharging at a constant current, and the resultant voltage-time curve is examined. The specific capacitance (C) is determined using the formula:

$$C = \frac{I \cdot \Delta t}{m \cdot \Delta V}$$

where I represent the current, Δt denotes the discharge duration, m signifies the mass of the CuO film, and ΔV indicates the voltage range. GCD testing offers insights into the efficiency, rate capability, and overall performance of CuO thin films under actual working settings.[14]

2.3.6 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is used to assess the internal resistance and charge transfer kinetics of CuO thin films. The method employs an alternating current voltage signal across several frequencies and assesses the impedance response. The resultant Nyquist plot (impedance against frequency) elucidates the charge transfer resistance (R_{ct}), the electrolyte resistance (R_s), and the comprehensive electrochemical performance of the supercapacitor. Low R_{ct} values signify effective charge transfer, but a nearly vertical line at higher frequencies indicates favourable capacitive characteristics. EIS is important in evaluating the stability and conductivity of CuO films throughout several charge/discharge cycles. [15]

3. Results and Discussion

3.1 XRD Analysis:

XRD Analysis: The structural characteristics of the CuO thin films were assessed using XRD analysis. The diffraction angles and relative intensities of lines from the produced thin films were compared to the JCPDS standard for phase analysis. Figure 1 displays the XRD patterns of CuO thin films, including the reference spectrum for the pure CuO monoclinic phase (JCPDS card No. 00-048-1548) and the Cu₂O cubic phase (JCPDS No. 01-078-2076).

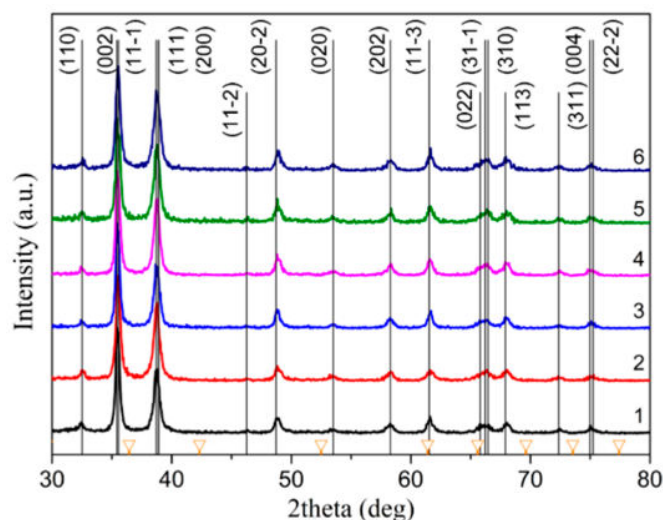


Figure 1. XRD patterns from synthesized CuO films at different substrate temperatures T_s , K: (1) 600, (2) 625, (3) 650, (4) 675, (5) 700, and (6) 725. (Black vertical lines correspond to CuO;

orange lines with the triangles show the location of the cubic Cu_2O peaks (JCPDS No. 01-078-2076)).

Figure 1 illustrates that all XRD patterns exhibit diffraction peaks at angles of 32.5° (110), 35.5° (11-1), 38.7° (111), 48.7° (20-2), 53.4° (020), 58.2° (202), 61.5° (11-3), 66.2° (31-1), 68.0° (113), 72.2° (311), and 75.0° (004), which correspond to the designated reflections from the crystallographic planes [33]. The findings align completely with the usual JCPDS card data and validate the monoclinic structure of the produced CuO thin film (space group C2/c). No supplementary peaks of secondary phases or uncontrolled contaminants were seen in the XRD patterns. This signifies a rather high purity of the produced thin films, which are single-phase and only include the CuO phase. [16]

3.2 Scanning Electron Microscopy (SEM)

Figure 2 shows SEM pictures of the surface of the synthesised CuO thin films. The nanostructured thin CuO films exhibit considerable homogeneity, a distinct polycrystalline structure, significant surface roughness, and the presence of tiny holes. No macroscopic flaws, including exfoliation, voids, or perforations, were observed. Figure 3 illustrates that the grains of the produced thin films exhibit heterogeneity in both size and form. They get spherical, cubic, lamellar, and several other forms. Simultaneously, the samples produced at elevated substrate temperatures exhibited primarily cubic-like crystallites. Elevating the substrate temperature results in an augmentation of the crystallite size in the thin films, with an average grain diameter of around 90 nm. [17-18]

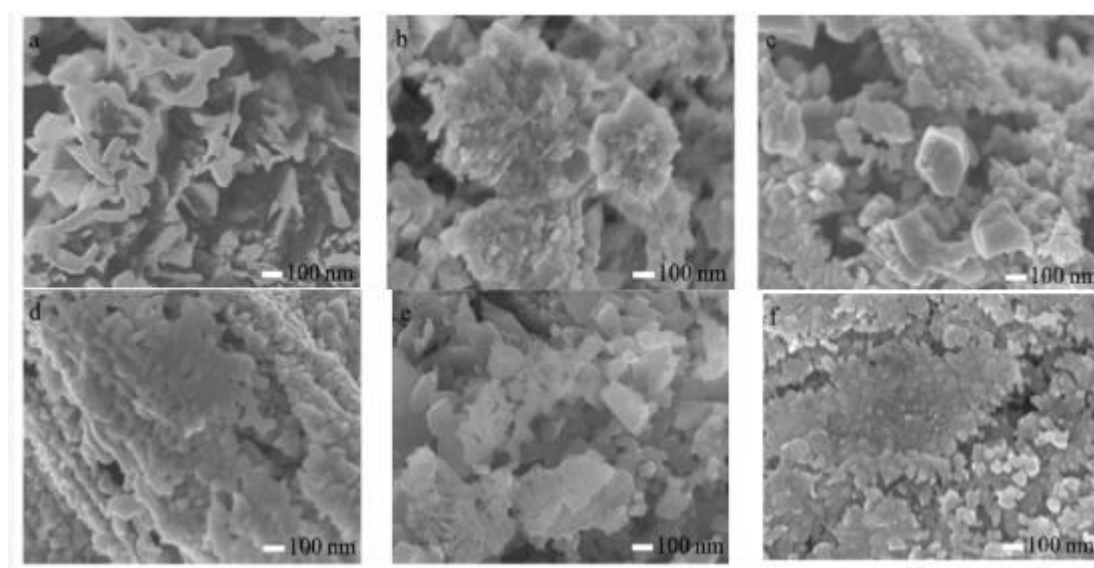


Figure 2. SEM images of the surface of the CuO thin films deposited at different substrate temperatures (50 k magnification), T_s , K: (a) 600, (b) 625, (c) 650, (d) 675, (e) 700, (f) 725.

3.3 Transmission Electron Microscopy (TEM)

Figure 3 shows the transmission electron micrograph of the most sensitive nanostructured CuO thin films acquired by the scratching of the thin film. The powder was dissolved with ethanol. A copper grid was used to contain the powder. The TEM picture clearly indicates that the grains are nanostructured and almost spherical, with sizes less than 9 nm. [19]

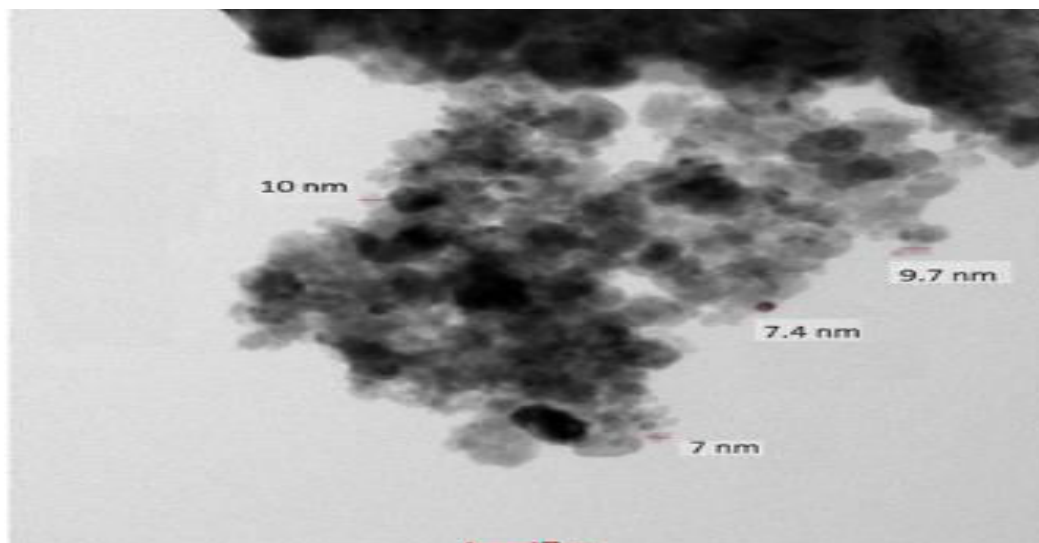
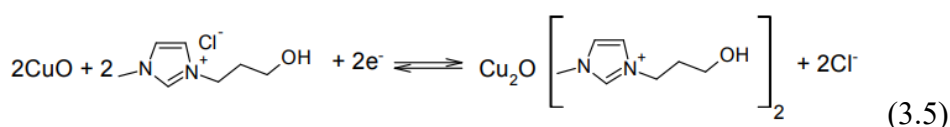


Figure 3: TEM images of the most sensitive nanostructured CuO thin film

3.4 Cyclic Voltammetry (CV): The voltage ranges from -0.3 to 0.2 V relative to SCE was covered by recording cycle voltammograms (CV) in 0.1 M [HPMIM][Cl] ionic liquid at a scan rate of 10 mV/s for each sample. So, we found the oxidation and reduction potentials of CuO and how the electrochemical performance changed as a function of CuSO₄ concentration. An approach to lowering Cu²⁺ to Cu¹⁺ is linked to the flow of cathodic current, which occurs to a potential of -0.3 V relative to SCE when the CuO sample is shifted. A similar vein applies to the anodic current flows connected to the Cu¹⁺ ↔ Cu²⁺ oxidation behave in a positive potential state. This is an example of pseudo capacitance behavior, and the subsequent reaction is a picture of the cell's redox process:



An electrolyte containing [HPMIM][Cl] IL using a 0.1 M concentration in water has been suggested for use as a CuO electrode for charge storage:



Shaikh et al. demonstrated comparable reactions using a Ru-doped CuO electrode in an electrolyte containing 3-carboxymethyl-1-methylimidazolium bisulfate [CMIM] [HSO₄]. The redox process that causes the pseudo capacitive behavior is found to occur at the point where the electrolyte meets the electrodes.

Fig. 4 shows that the current density rises from 0.1 to 0.2 M CuSO₄ concentration, but then decreases with subsequent concentration increases. This might be because the samples have

superior conductivity. Based on We derived an equation using the CV curves to get the samples' specific capacitance:

$$C_s = \frac{\int idV}{2m \times \Delta V \times S} \quad (3.6)$$

in such case C_s is the capacitance, $\int idV$ The Integral area of the cyclic voltammetry (CV) curve, where S denotes the scan rate, m represents the mass of the active material, and ΔV indicates the potential range. The inset displays a graph illustrating the fluctuation in specific capacitance in relation to CuSO_4 concentration. Table 1 presents the energy densities, specific capacitances, deposited masses, and sample codes.[20]

Table No. 1: Specific capacitance value for different concentrations

Sample code	Deposited mass (mg)	Specific capacitance (Fg^{-1})	Energy Density (Wh kg^{-1})
CuO0.1M	0.08	57	0.79
CuO0.2M	0.09	60	1.18
CuO0.3M	0.10	55	0.51
CuO0.4M	0.13	43	0.46
CuO0.5M	0.09	31	50.3

Based on current estimates, the maximum specific capacitance should be 60 Fg^{-1} or $\text{CuO}_{0.2\text{M}}$ at 10 mVs^{-1} . Because nano petals on microgranular shape increase electrical conductivity, sample $\text{CuO}_{0.2\text{M}}$ has a high specific capacitance. The absence of electrochemical stability is caused by microcracks that appear in CuO samples made with a greater concentration of CuSO_4 , which cause the mass deposited to peel off during measurements.

Inset of Figure 5 displays the $\text{CuO}_{0.2\text{M}}$ sample's CV curves, obtained at different potential scan speeds. Additionally, the precise capacitance readings are shown. Cathodic shifts in reduction peaks and anodic shifts in oxidation peaks both become more pronounced as scan rates rise. more apparent, accompanied by an augmentation in the region under the curvature. Scan rates are inversely proportional to specific capacitance. Pseudo capacitance is explained by elerostatic surface buildup and ion intercalation from the electrolyte to the CuO locations. Given that the electrolyte concentration remains constant, the concentration gradient is presumably uniform across all samples; thus, the specific capacitance is primarily determined

by the number of ions incorporated within the bulk and accumulated on the surface, which relies on the concentration gradient and the duration required for the intercalation process. At reduced scan speeds, the specific capacitance is elevated due to the sufficient time allowed for the intercalating ions to complete the operation; at lower scan rates, the specific capacitance is low because fewer ions are intercalated because the intercalating ions are subjected to shorter time intervals to complete the process.

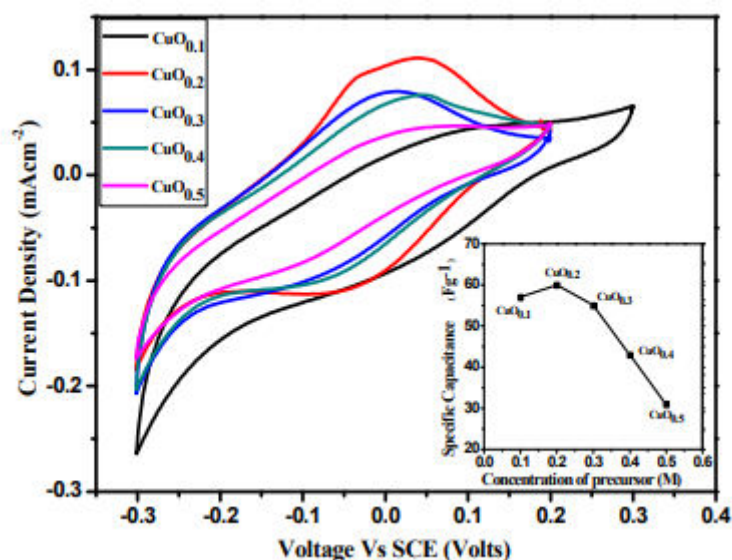


Figure 4: Statistical analysis of the samples' cyclic voltammograms from -0.3V to 0.2V

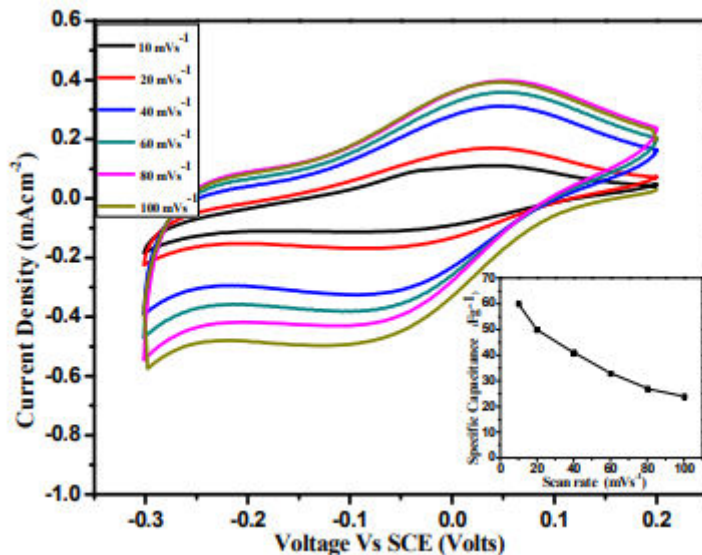


Figure 5: Sample CuO_{0.2} cyclic voltammograms ranging from -0.3 V to 0.2 V vs SCE at different scan speeds in a 0.1 M [HPMIM][Cl] electrolyte liv.

3.5 Galvanostatic Charging-Discharging (GCD)/Chronopotentiometry (CP) Along with CV, GCD data is also used to evaluate specific capacitance CCD, energy and power densities. These measurements carried out at different charge densities, for example, 1Ag⁻ 1, 2 Ag⁻ 1 and so on that record potential variation with time. Cyclic stability is determined by GCD curve by

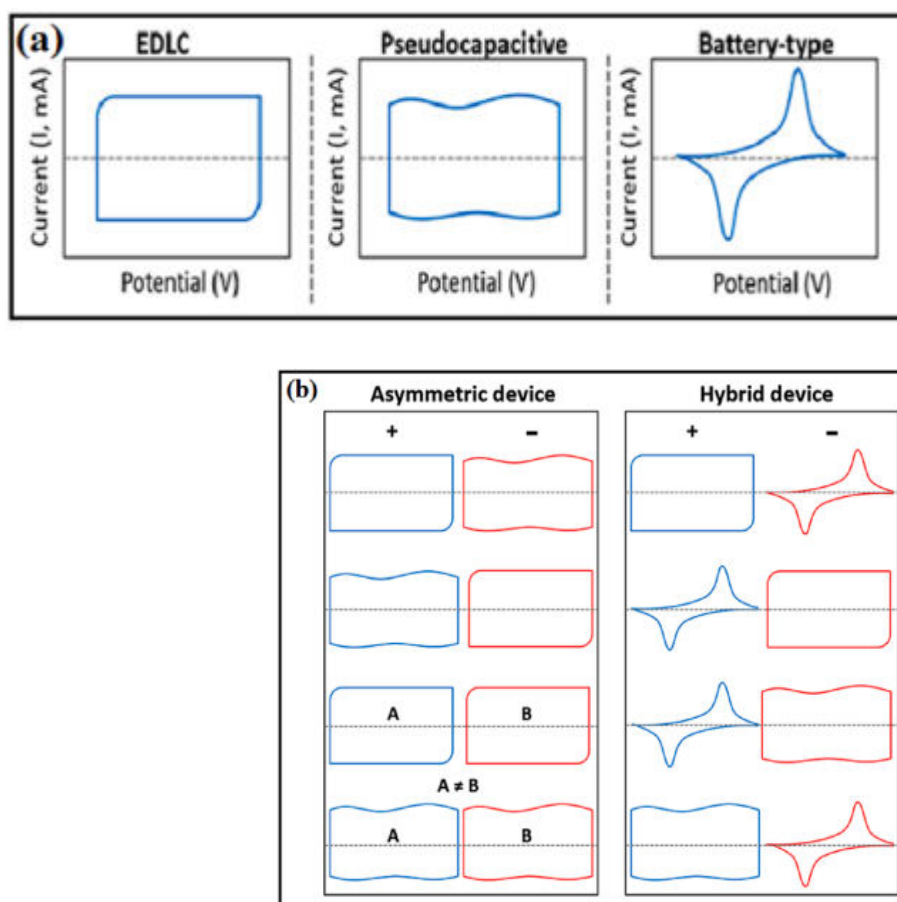
measuring its charging-discharging time. Current density and specific capacitance have inversely proportional relationship. For EDLC materials, GCD curve is linear and value of b is always equal to 1, indicating good electrochemical capacitive nature. For pseudocapacitive materials, charging-discharging profiles have non-linear variation due to quasi reversible faradic reactions as shown in Table 2. Charge/voltage ratio of these faradic reactions no longer remains constant and varies with time, give non-symmetric curve. For battery type materials, GCD curve has plateaus as shown in Fig. 5(a-d). Specific capacitance of fabricated electrode from GCD data is calculated using equation.

$$CCD = 2I_m V / \int V^+ V^- V dt$$

Where, CCD = charging-discharging capacitance, V = operational voltage window, I_m is current density in $A g^{-1}$, $\int V^+ V^- V dt$ is current integral area. Or simply, it can also be written as, $C_s = I \times \Delta t / \Delta V \times m$ Where I , Δt , ΔV , m corresponds to discharge current (A), discharge time (s), potential window (V) and the mass of active materials (g), respectively. For better electrochemical performance of supercapacitor rapid charge-discharge and negligible voltage drop (low internal resistance) is required. With increase in current density, power density decreases and energy density, on contrary increases. The specific energy density E in unit of watt-hours per kilogram is shown in equation.

$$E = \frac{1}{2} C_s (\Delta V)^2$$

Where, ΔV is operational voltage window, C_s = Specific capacitance of fabricated electrode. The specific power density P in unit of watt per kilogram is described in equation.



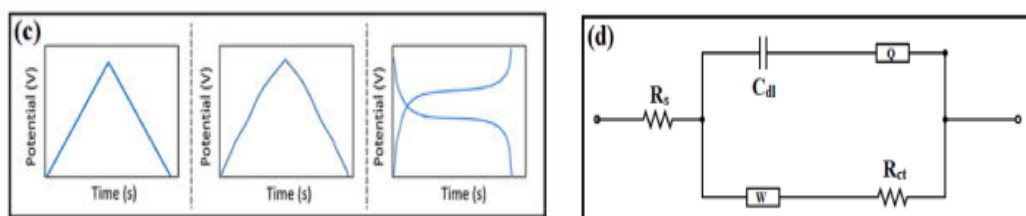


Fig. 5. (a) Distinct shape of CV for EDLC, pseudo capacitive and battery type material. (b) Asymmetric and hybrid different configurations of distinct CV by combining materials A and B. (c) GCD profile to distinguish EDLC, pseudo capacitive and battery type material [(d) General circuit diagram for electrochemical impedance spectroscopy (EIS).

4. Conclusion

This study shows that nanostructured CuO thin films, produced by an improved hydrothermal method, have favorable electrochemical characteristics for supercapacitor applications. The structural benefits provided by nanostructuring, such as increased surface area, decreased ion transport paths, and improved active sites, substantially boost the material's charge storage capacity. The quick synthesis and regulated deposition techniques enhance the scalability and sustainability of this process. The CuO thin films demonstrate elevated specific capacitance, energy density, and consistent charge-discharge behavior, establishing them as promising candidates for high-performance energy storage devices. The results highlight the promise of CuO nanostructures in meeting the increasing need for efficient and environmentally sustainable supercapacitor technology.

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