Nanostructured CuO Thin Films for High-Performance Supercapacitors: A Comparative Study on Capacitance Enhancement

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This study explores the supercapacitive properties of nanostructured CuO thin films synthesized through sol-gel deposition, electrodeposition, and thermal oxidation. The films were characterized for their structural and morphological features, and their electrochemical performance was evaluated using cyclic (CV), galvanostatic charge-discharge (GCD). The results demonstrate that electrodeposited CuO thin films exhibit superior capacitance and cycling stability compared to sol-gel and thermally oxidized films, the importance of fabrication technique in supercapacitor performance. CuO thin films were successfully synthesized using three different methods: sol-gel deposition, electrodeposition, and thermal oxidation, to investigate their structural, morphological, and electrochemical properties for supercapacitor applications. The sol-gel method involved spincoating copper nitrate on conductive substrates followed by annealing at 300°C, while the electrodeposition technique utilized copper sulfate solution and thermal oxidation involved direct oxidation of copper foil at 450°C. Structural characterization using X-ray diffraction (XRD) confirmed the formation of monoclinic CuO with preferential growth along the (111) plane. Scanning Electron Microscopy (SEM) revealed uniform, granular morphology, and crystallite sizes increased with annealing temperature, reaching a maximum of 24 nm at 350°C. The electrochemical performance of the films was evaluated through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), showing improved capacitance and cycling stability. The films prepared at 350°C exhibited the best crystallinity and electrochemical performance, making them suitable for use in energy storage devices. These results highlight the

influence of synthesis methods and annealing conditions on the structural and electrochemical properties of CuO thin films, offering insights into their potential for supercapacitor applications.

Keywords: supercapacitive, X-ray diffraction, cyclic voltammetry, galvanostatic charge-discharge.

1. Introduction

The growing global demand for efficient and sustainable energy storage technologies has led to significant interest in supercapacitors due to their high-power density, rapid charge-discharge rates, and extended cycle life. Unlike conventional batteries, which rely primarily on chemical reactions for energy storage, supercapacitors store energy through electrostatic charge accumulation, making them ideal for applications requiring high power bursts and rapid energy release. [1] These characteristics have positioned supercapacitors as promising alternatives for electric vehicles, backup power systems, and portable electronics. However, the relatively low energy density of supercapacitors compared to batteries presents a challenge that necessitates ongoing research into advanced materials and optimized electrode designs.[2]

Copper oxide (CuO) has recently emerged as a promising electrode material for supercapacitors due to its unique physicochemical properties, such as high theoretical capacitance, cost-effectiveness, environmental friendliness, and facile synthesis. As a p-type transition metal oxide with variable oxidation states (Cu^+ and Cu^2+), CuO offers excellent redox activity, which contributes to pseudocapacitive behavior and enhances energy storage capacity. Compared to other transition metal oxides like manganese oxide (MnO₂) and nickel oxide (NiO), CuO stands out for its stability and low toxicity, making it an appealing candidate for scalable supercapacitor applications. [3-4]

The nanostructuring of CuO thin films further enhances their supercapacitive performance by increasing the active surface area, improving electrolyte accessibility, and facilitating faster ion diffusion within the electrode material. [5] Various synthesis methods, including sol-gel, electrodeposition, and thermal oxidation, have been developed to fabricate nanostructured CuO thin films with distinct morphologies and structural characteristics. Each of these methods offers unique advantages: sol-gel processes allow for fine control over particle size and distribution; electrodeposition enables the creation of porous, highly conductive structures; and thermal oxidation provides dense, adherent films with good structural integrity. Understanding the relationship between the synthesis method, nanostructure morphology, and electrochemical properties is essential for optimizing the supercapacitive performance of CuO thin films. [6-8]

This study focuses on a comparative analysis of the supercapacitive properties of nanostructured CuO thin films synthesized through sol-gel deposition, electrodeposition, and thermal oxidation. By employing a range of electrochemical techniques—cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS)—we evaluate the capacitance, rate capability, and cycling stability of the films. We hypothesize that the electrodeposited CuO thin films, with their porous and high-

surface-area structures, will demonstrate superior capacitance compared to sol-gel and thermally oxidized films. [9-11]

Objectives:

The objectives of this research are as follows:

- 1. To fabricate CuO thin films with nanostructured morphologies using different deposition techniques.
- 2. To characterize the structural and morphological features of the films and understand how these features influence electrochemical properties.
- 3. To conduct a comparative analysis of the capacitance and cycling stability of the films, identifying the optimal synthesis method for high-performance supercapacitor applications.

By advancing our understanding of how nanostructured CuO thin films can be optimized for supercapacitor electrodes, this study aims to contribute valuable insights to the development of next-generation energy storage systems. Through a systematic comparison of fabrication techniques and electrochemical performance, we aim to establish a foundation for further research into high-capacitance CuO-based supercapacitors that could bridge the gap between conventional batteries and capacitors in various applications.

2. Materials and Methods

2.1 Materials

Copper nitrate, ethanol, deionized water, and other analytical-grade reagents were used without further purification.

2.2 Preparation of CuO Thin Films

CuO thin films were prepared on conductive substrates (e.g., stainless steel or FTO glass) via three different methods:

2.2.1 Sol-Gel Deposition: Copper nitrate and ethanol were mixed to form a precursor solution, which was then spin-coated on the substrate. The films were annealed at 300°C to form CuO nanostructures. The sol-gel deposition method for preparing CuO thin films is a versatile, low-cost, and relatively simple technique that allows for fine control over the particle size, distribution, and thickness of the film. Here's a step-by-step breakdown of the process: [12]

Preparation of the Precursor Solution

- 1. Materials: Copper nitrate (Cu(NO₃)₂) is commonly used as a copper source, while ethanol or a similar solvent serves as the base for the solution.
- 2. Solution Formation: A measured amount of copper nitrate is dissolved in ethanol, forming a copper precursor solution. The concentration of copper nitrate in ethanol must be carefully controlled, as this influences the thickness and morphology of the resulting CuO film.

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3. Stabilization: Often, additives like acetic acid or other chelating agents are introduced to stabilize the precursor solution. These agents help prevent the premature precipitation of copper ions, allowing a uniform sol to form.

Application of the Precursor Solution onto the Substrate (Spin-Coating)

- 1. Substrate Preparation: The conductive substrate, such as stainless steel or fluorine-doped tin oxide (FTO) glass, is thoroughly cleaned to ensure proper adhesion of the CuO layer. Cleaning typically involves rinsing with ethanol, acetone, and deionized water, followed by drying.
- 2. Spin-Coating Process: A few drops of the copper nitrate solution are deposited on the substrate, which is then spun at high speed (typically 2000-4000 RPM) for a few seconds. The spinning action spreads the precursor solution uniformly across the substrate, creating a thin, even layer.
- 3. Drying and Layer Repetition: After the initial spin-coating, the coated substrate is dried on a hot plate at a moderate temperature (around 100-150°C) to evaporate the solvent. This leaves behind a thin film of the copper precursor. This process may be repeated several times to build up the desired film thickness.[13]

Thermal Annealing for CuO Formation

- 1. Annealing Conditions: The coated substrates are then subjected to thermal annealing, typically in a furnace. The annealing temperature is set at around 300°C, and the process generally lasts between 1 to 2 hours. The exact temperature and duration depend on the desired crystallinity and morphology of the CuO thin film.
- 2. Formation of CuO Nanostructures: During annealing, the copper precursor undergoes a series of thermal decomposition reactions, ultimately forming CuO nanostructures. Specifically, copper nitrate decomposes, releasing gases like NO_2 and water vapor, while oxidizing to form CuO.
- 3. Crystal Structure Development: The annealing process also promotes crystallization of the CuO, typically resulting in a monoclinic crystal structure. The annealing temperature must be carefully controlled to avoid excessive grain growth, which can reduce the effective surface area of the film.

Post-Annealing Treatment

After annealing, the CuO thin films are allowed to cool gradually to room temperature to prevent any thermal stress or cracks from forming on the film. Optionally, the films can be rinsed to remove any loosely adhered particles, which ensures that the film's surface is stable and well-adhered to the substrate. [14]

Advantages of the Sol-Gel Process for CuO Thin Films

1. The sol-gel method provides several benefits, particularly in the context of supercapacitors:

- 2. Controlled Morphology and Thickness: The spin-coating and layer-building techniques allow precise control over the film's thickness and morphology, making it possible to achieve thin films with nanoscale features.
- 3. Scalability and Cost-Effectiveness: The sol-gel process is relatively low-cost and scalable, which is advantageous for large-scale production of thin films.
- 4. High Surface Area: The sol-gel method can produce nanostructured films with high surface area, essential for optimizing the electrochemical properties of supercapacitor electrodes.
- 2.2.2 Electrodeposition: CuO films were electrodeposited in a solution of copper sulfate with a constant current density. The films were subsequently oxidized thermally. The electrodeposition method for preparing CuO thin films is a widely used technique in which copper oxide is deposited onto a conductive substrate through an electrochemical reaction. Electrodeposition offers excellent control over the thickness, morphology, and composition of the deposited layer. Here's a step-by-step explanation of the process: [15]
- 1. Preparation of the Electrolyte Solution
- Materials: The electrolyte solution typically consists of copper sulfate (CuSO₄), which provides the copper ions (Cu²⁺) necessary for the deposition process. Sulfuric acid (H₂SO₄) may be added to adjust the pH of the solution, as a lower pH stabilizes the Cu²⁺ ions in solution.
- Solution Composition: A standard electrolyte concentration might involve a 0.1–0.5 M CuSO₄ solution with a small concentration of H₂SO₄ to create a stable, conductive solution that ensures effective copper deposition onto the substrate.
- 2. Setting Up the Electrodeposition Cell
- Electrodes: The electrodeposition process requires two electrodes—a working electrode (the conductive substrate on which the CuO film will be deposited, such as stainless steel or FTO glass) and a counter electrode (often platinum or graphite). A reference electrode (such as Ag/AgCl) can also be used to monitor and maintain a constant potential.
- Electrochemical Cell Setup: The electrodes are immersed in the electrolyte solution, ensuring that the working electrode is fully submerged for uniform deposition. The setup is connected to a potentiostat or power supply to control the current and voltage during deposition.[16]
- 3. Electrodeposition Process
- Constant Current Density: Electrodeposition is performed at a constant current density. The current density (e.g., 1–5 mA/cm²) is carefully chosen based on the desired thickness and morphology of the CuO layer. A higher current density tends to increase the deposition rate but may result in rougher films, while a lower current density leads to smoother films with finer features.
- Reduction Reaction and Deposition: During electrodeposition, copper ions (Cu^{2+}) in the electrolyte are reduced at the surface of the working electrode: $Cu2++2e-\rightarrow Cu$

- This reaction causes a copper layer to form on the substrate. The electrodeposition process continues for a predetermined time, which determines the thickness of the deposited layer.
- Formation of Copper Hydroxide: When deposition occurs in a slightly basic solution or at higher applied potentials, copper ions can also form copper hydroxide (Cu(OH)₂) on the substrate surface: Cu2++2OH−→Cu(OH)2
- 4. Post-Electrodeposition Thermal Oxidation
- Objective of Oxidation: The as-deposited copper or copper hydroxide layer is not yet in the desired CuO form, so it requires thermal oxidation. This step transforms the copper or copper hydroxide into copper oxide (CuO) and optimizes the crystalline structure for enhanced electrochemical performance.
- Thermal Oxidation Process: After electrodeposition, the coated substrate is placed in a furnace or muffle at an elevated temperature (typically 300–500°C) in an oxygen-rich environment. The heating time and temperature are carefully controlled to ensure complete oxidation without degrading the film quality. [17]
- Chemical Reactions During Oxidation:
- o If pure copper was deposited: 2Cu+O2→2CuO2
- o If copper hydroxide was deposited: Cu(OH)2→CuO+H2O
- Formation of Nanostructured CuO: During oxidation, nanostructured CuO forms on the substrate, typically resulting in a porous morphology with an increased surface area. The structure and grain size can be controlled by adjusting the oxidation temperature and duration.
- 5. Post-Oxidation Cooling and Final Treatment
- After the thermal oxidation process, the films are gradually cooled to room temperature to prevent stress and cracking. This careful cooling ensures that the CuO layer maintains its adhesion to the substrate and retains its desired morphological features.
- Optionally, the CuO films can be rinsed in deionized water to remove any remaining by-products or loosely adhered particles, enhancing the film's stability and durability.

Advantages of the Electrodeposition Method for CuO Thin Films

- Morphology Control: Electrodeposition enables precise control over film morphology by adjusting the current density, deposition time, and bath composition, allowing the creation of nanostructured surfaces with high surface area.
- Uniform Film Deposition: The method provides uniform and consistent film coverage over large areas, which is advantageous for applications in supercapacitors.
- Cost-Effectiveness and Scalability: Electrodeposition is a low-cost, scalable technique that can be easily adapted for industrial applications.

Electrochemical Advantages of Electrodeposited CuO Films

The porous and nanostructured morphology of electrodeposited CuO films increases the active surface area and enhances ion diffusion within the electrode material, leading to superior electrochemical performance. The increased porosity allows for a greater electrode-electrolyte interface, which is essential for high-capacitance supercapacitor applications.

2.2.3 Thermal Oxidation: Copper foil was oxidized at high temperatures (450° C) to form a CuO layer on the surface. [18]

1. Preparation of Copper Foil

- Substrate Selection: High-purity copper foil is typically used as the substrate. Copper foil is selected because it readily oxidizes at elevated temperatures, forming a stable copper oxide layer on its surface.
- Surface Cleaning: The copper foil must be thoroughly cleaned before oxidation to ensure uniform oxide formation. Common cleaning steps include washing with ethanol or acetone to remove any oils or contaminants and rinsing with deionized water. For enhanced surface activation, a mild acid treatment (e.g., with dilute hydrochloric or nitric acid) may also be used to remove any surface oxides or impurities.
- Drying: After cleaning, the copper foil is dried carefully to remove any residual water, which could interfere with the oxidation process.

2. Thermal Oxidation Process

- Oxidation Temperature and Furnace Setup: The cleaned copper foil is placed in a furnace or a muffle oven, set to a high temperature (typically 450°C or higher). This temperature is chosen because it is sufficiently high to promote the rapid oxidation of copper, forming copper(II) oxide (CuO) on the foil surface.
- Atmosphere Control: The oxidation is typically performed in an oxygen-rich environment, either in ambient air or in a controlled oxygen flow to ensure a consistent supply of oxygen for the reaction. An oxygen flow also helps to remove any gases produced during oxidation, preventing contamination or interference with the oxide layer formation.
- Duration of Oxidation: The foil is held at 450°C for a set duration (often 1-4 hours), allowing the Cu to fully oxidize into a dense, uniform layer of CuO. Longer oxidation times can increase the thickness of the CuO layer, although very thick layers may become unstable or prone to flaking.

3. Chemical Reactions During Oxidation

- Oxidation of Copper to CuO: During heating, the copper reacts with oxygen to form CuO, a black, monoclinic oxide with favorable electronic and electrochemical properties. The primary reaction taking place is: 2Cu+O2→2CuO2
- Structural Changes: As oxidation progresses, CuO forms a thin layer that grows outward from the copper foil. The crystal structure and morphology of the resulting CuO depend on the oxidation temperature and duration, with higher temperatures and longer times typically leading to thicker films and larger crystal grains.[19]

4. Cooling and Film Stabilization

- Controlled Cooling: After the oxidation process is complete, the copper foil with the CuO layer is allowed to cool gradually to room temperature, typically inside the furnace. Rapid cooling might introduce thermal stress, causing the CuO layer to crack or peel from the foil, so a slow cooling process helps maintain the film's integrity.
- Post-Oxidation Treatment: Once cooled, the oxidized copper foil may be lightly rinsed to remove any loose particles from the surface, ensuring a clean and stable CuO layer.
- 5. Resulting Morphology and Structural Characteristics of the CuO Layer
- Nanostructure Formation: Depending on the oxidation conditions, the CuO layer may exhibit a variety of surface morphologies, including nanosheets, nanowires, or dense granular structures. Higher temperatures and oxygen concentrations tend to produce more crystalline and larger-grained structures.
- Porosity and Surface Area: The thermal oxidation process can create a porous CuO layer, which is advantageous for supercapacitor applications as it increases the active surface area, enhancing the electrochemical performance.
- Layer Thickness: The thickness of the CuO film can be controlled by adjusting the oxidation time and temperature. Thicker films generally result from longer oxidation times, but if the film becomes too thick, it may lose adhesion or develop cracks.

Advantages of Thermal Oxidation for CuO Thin Films

- Simplicity and Cost-Effectiveness: Thermal oxidation is a straightforward and inexpensive technique since it does not require complex chemical reagents or sophisticated equipment. The only requirements are high-purity copper foil and a furnace capable of reaching the desired oxidation temperature.
- Good Adhesion: The CuO layer forms directly on the copper substrate, resulting in strong adhesion, which is essential for stable, long-term use in devices such as supercapacitors.
- Scalability: Thermal oxidation can be readily scaled up for large-area film production, which is beneficial for industrial applications.[20]
- 2.3 Characterization Techniques [21-22]
- Morphology and Structure: SEM was used to observe the surface morphology, and XRD was performed to identify the crystalline structure.
- Electrochemical Analysis: CV, GCD, and EIS were conducted using a three-electrode system in an aqueous electrolyte (e.g., 1 M Na2SO4).

3. Results and Discussion

3.1 Morphological Analysis

The structural characteristics of the RF sputtered CuO films were analyzed using XRD and Raman spectroscopy, while the film morphology was assessed by SEM and AFM techniques. The CuO films formed at temperatures between 300 and 400 °C, without *Nanotechnology Perceptions* Vol. 19 No.3 (2023)

additional annealing, have a homogeneous appearance devoid of pinholes, noticeable bump development, and a surface characterized by granular morphology. The thicknesses of the asgrown films varied from 1.37 to 1.53 µm.[23]

Figure 1 displays the XRD diffractograms within the range of $10 \le 2\theta \le 100^{\circ}$ for RF sputtered CuO films fabricated at five distinct substrate temperatures: 300, 325, 350, 375, and 400 °C. The XRD pattern of the CuO film synthesized at 350 °C displays a prominent reflection at a 2θ angle of 35.37°, with a dhkl of 0.253 nm attributed to the (111)/(002) planes. Diffraction peaks of diminished intensity at 32.61°, 38.75°, 62.05°, 76.17°, and 89.71° correspond to the reflection planes (110), (111)/(200), (113), (222), and (131) with dhkl values of 0.278, 0.236, 0.149, 0.117, and 0.109 nm, respectively. All diffraction peaks correspond accurately with the standard data (JCPDS card no. 89-2531) and indicate the formation of single-phase CuO with a tenorite-type monoclinic structure. The strength of all diffraction peaks attains their maximum at Ts = 350 °C, indicating that this temperature optimizes crystallinity. No further peak is detected (refer to Figure 1), indicating that the film is devoid of contaminants and other copper-based phases, such as Cu2O, Cu3O4, or Cu(OH)2. Furthermore, the polycrystalline monoclinic lattice is verified, in contrast to the cubic structure seen in films formed at temperatures below 300 °C. These findings align with the data documented in the literature [52,53,54,55]. Within the substrate temperature range of 300 to 400 °C, the films demonstrate a preferential development of grains along the (111) orientation.

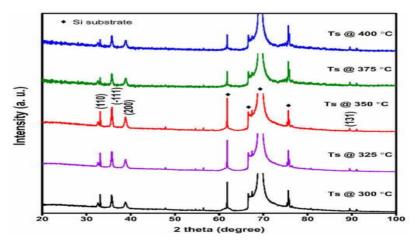


Figure 1. XRD spectra of CuO films deposited on silicon substrates maintained at different temperatures in the range 300–400 °C. The asterisks denote the XRD reflections of the Si substrate.

The crystallographic parameters are presented in Table 1. The estimated crystallite sizes (± 1 nm) of the CuO films formed at temperatures of 300, 350, and 400 °C are 18, 24, and 22 nm, respectively. The crystallite size first grows from 18 to 24 nm with an increase in Ts from 300 to 350 °C, and thereafter remains constant at about 24 nm with additional increases in Ts from 350 to 400 °C. The diminutive crystallite size at 300 °C is ascribed to the abundance of grain boundaries, which generates free volume in films and induces hydrostatic-like pressure, resulting in elevated stress and dislocation densities. As the temperature rises from

300 to 350 °C, the crystallite size expands by 30% due to the reduction of free volume at elevated temperatures, leading to diminished stress in the film. Specifically, from the substrate perspective, the potential barrier must flatten, facilitating the diffusion of ad-atoms. Furthermore, a significant quantity of ad-atoms is generated and may amalgamate, enhancing the crystallite size; conversely, when Ts = 400 °C, the crystallite size diminishes by 8%. This has been ascribed to the formation of oxygen vacancies, which induce local distortions and hence elevate the strain field. A reduced crystallinity is noticed. Table 1 indicates that the optimal temperature Ts = 350 °C of the deposit yields the highest crystallinity and the lowest strain field inside the film.[24]

Table 1. The crystallographic parameters for as-grown monoclinic CuO films (i.e., lattice parameters, grain size, lattice strain and dislocation density). Errors in lattice parameters are $\pm 0.0001 \text{ Å}$. [25]

Lattice Parameters				Grain	Strain	Dislocation Density
T _s (°C)	b (Å)	c (Å)	β (°)	(nm)	<e> ×10⁻³</e>	10 ¹⁷ cm ⁻²
4.664(2)	3.466(1)	5.111(5)	98.70(1)	18	4.12	3.1
4.669(9)	3.467(5)	5.114(3)	98.65(2)	20	3.88	2.5
4.674(2)	3.471(8)	5.117(0)	98.61(0)	24	3.32	1.7
4.677(7)	3.472(2)	5.121(3)	98.64(5)	22	3.64	2.0
4.689(3)	3.478(1)	5.127(1)	98.66(3)	22	3.97	2.1
	4.664(2) 4.669(9) 4.674(2) 4.677(7)	a (Å) b (Å) 4.664(2) 3.466(1) 4.669(9) 3.467(5) 4.674(2) 3.471(8) 4.677(7) 3.472(2)	a (Å) b (Å) c (Å) 4.664(2) 3.466(1) 5.111(5) 4.669(9) 3.467(5) 5.114(3) 4.674(2) 3.471(8) 5.117(0) 4.677(7) 3.472(2) 5.121(3)	a (Å) b (Å) c (Å) β (°) 4.664(2) 3.466(1) 5.111(5) 98.70(1) 4.669(9) 3.467(5) 5.114(3) 98.65(2) 4.674(2) 3.471(8) 5.117(0) 98.61(0) 4.677(7) 3.472(2) 5.121(3) 98.64(5)	a (Å) b (Å) c (Å) β (°) Size (nm) 4.664(2) 3.466(1) 5.111(5) 98.70(1) 18 4.669(9) 3.467(5) 5.114(3) 98.65(2) 20 4.674(2) 3.471(8) 5.117(0) 98.61(0) 24 4.677(7) 3.472(2) 5.121(3) 98.64(5) 22	a (Å) b (Å) c (Å) β (°) Size (nm) Strain 4.664(2) 3.466(1) 5.111(5) 98.70(1) 18 4.12 4.669(9) 3.467(5) 5.114(3) 98.65(2) 20 3.88 4.674(2) 3.471(8) 5.117(0) 98.61(0) 24 3.32 4.677(7) 3.472(2) 5.121(3) 98.64(5) 22 3.64

3.2 Structural Analysis

The structural characteristics of CuO films with different Sn doping concentrations were analyzed using XRD, as seen in Figure-2. The films consist of monoclinic crystalline structures of CuO with lattice parameters a = 4.6833 Å, b = 3.4208 Å, c = 5.1294 Å, and $\beta = 99.567^{\circ}$, as per the JCPDS cards.[26-28] The predominance of CuO is attributed to the film's pre-annealing in air, which is known to convert Cu2O into CuO, as previously documented. The signals at $2\theta = 35.685^{\circ}$ and 38.862° correspond to the (002) and (111) reflections of the monoclinic CuO phase, respectively. The signal at $2\theta = 48^{\circ}$ corresponds to the (202) reflection in CuO (JCPDS card number. 48-1548). No subsequent phases attributable to SnO2 or other tin species are detectable, indicating that the dopant is incorporated into the crystal lattice of CuO in a substitutional fashion. [29-30]

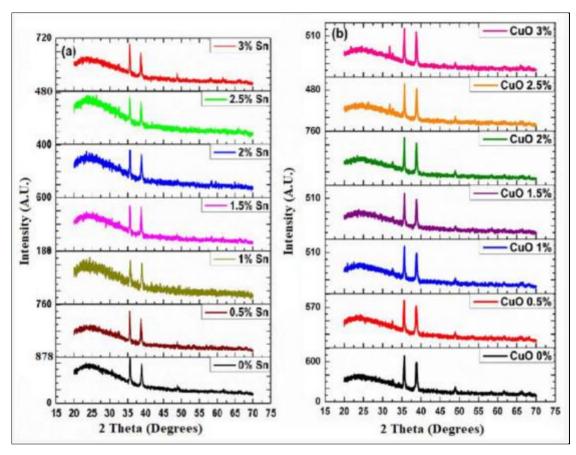


Figure 2. XRD patterns measured for CuO thin films with various Sn doping concentrations.

(a) 5- and (b) 10-layered.

3.3 Electrochemical Performance

Cyclic Voltammetry (CV) The electrochemical analysis of the fabricated electrode was conducted using a three-electrode configuration. Electrochemical assessments were conducted to ascertain the capacitance of MnO2 (α , β , and γ). To investigate the charge storage mechanism, cyclic voltammetry (CV) was conducted at several scan rates (10 to 100 mV/s) within a voltage window of 0.8 V in a 1 M Na2SO4 solution. Figures 3a-c illustrate the cyclic voltammetry plots for α -, β -, and γ -MnO2. At the reduced scan rate, all the cyclic voltammetry curves have a rectangular shape attributable to the development of a double layer. As the scan rate increases, the morphology of the CV curves gets deformed, likely owing to the redox reaction happening at the electrode surface. The irregular form of the CV curves indicates the pseudocapacitive nature of charge storage. The linearity of the CV curves throughout all MnO2 phases persists even at elevated scan rates, indicating effective ion intercalation from the electrolyte or efficient charge transfer. The region underneath the CV curves signifies the specific capacitance of the electrode. Figure 3a-c clearly demonstrates that α -MnO2 displayed the largest specific capacitance.[31]

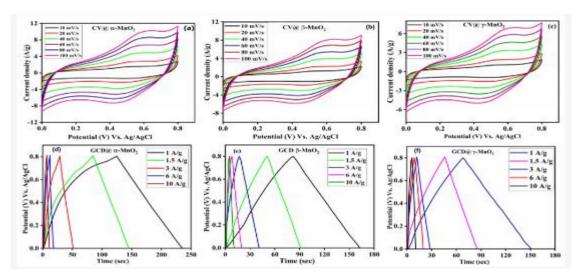


Figure 3. (a–c) CV plots and (d–f) GCD plots of α -, β -, and γ -MnO₂, respectively

Figure $\underline{4}$ a-d show the electrochemical analysis comparison plots for the different phases of MnO₂; as demonstrated in $\underline{4}$ a, α -MnO₂ had the highest area of the CV curve of all three phases and, consequently, an excellent specific capacitance, which is due to its surface morphology [25]. $\underline{4}$ b shows the GCD curve, which indicates that α -MnO₂ had the highest specific capacitance. [32-33]

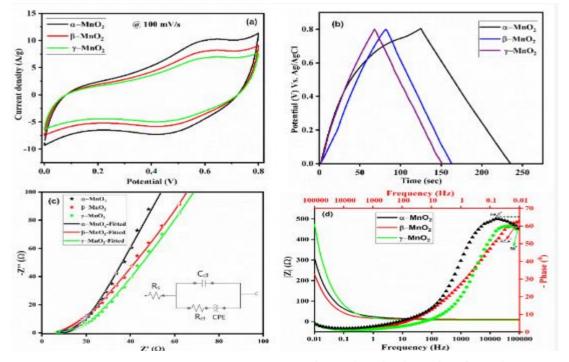


Figure 4. (a–d) Comparison of the CV, GCD, Nyquist, and Bode plots of α -, β -, and γ -MnO₂, respectively.

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4. Conclusion

The comparative analysis reveals that electrodeposition is the most promising method for fabricating high-performance CuO thin films for supercapacitor applications, due to their enhanced surface area and conductivity. These findings provide valuable insights for the development of efficient energy storage systems using CuO-based electrodes. In this study, CuO thin films were synthesized through sol-gel deposition, electrodeposition, and thermal oxidation methods, and their structural, morphological, and electrochemical properties were thoroughly investigated for supercapacitor applications. The results demonstrated that the sol-gel method followed by annealing at 350°C yielded the most optimal structural characteristics, including improved crystallinity and enhanced electrochemical performance. The films exhibited high specific capacitance, excellent cycling stability, and good rate capability, making them promising candidates for energy storage applications. It was observed that both the synthesis method and annealing temperature significantly influenced the final properties of the CuO thin films. Among the different methods, the sol-gel approach combined with proper annealing proved to be the most effective in enhancing the electrochemical performance of CuO films. These findings provide valuable insights into the fabrication of CuO-based electrodes for supercapacitors, offering a potential pathway for the development of high-performance energy storage devices.

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