Algorithm-Driven Optimization of $ZnCo_2O_4$@CuO Core-Shell Architectures for High-Performance Supercapacitors

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Abstract:

This study investigates the electrochemical performance of $ZnCo_2O_4$@CuO core-shell nanostructures as advanced electrode materials for supercapacitors. $ZnCo_2O_4$, a spinel metal oxide, offers high theoretical capacitance and environmental compatibility but suffers from low electrical conductivity and structural instability. To address these limitations, we examined the synergistic response of zinc cobaltite for varying ratios of copper oxide shell. We synthesized $ZnCo_2O_4$@CuO composites using a facile hydrothermal method, leveraging CuO's excellent electrical conductivity and chemical stability to enhance the core material's properties. Comprehensive characterization confirmed the formation of a hierarchical core-shell structure with improved surface area and uniform elemental distribution. Electrochemical testing revealed that $ZnCo_2O_4$@$CuO_{(0.25)}$ electrodes exhibited significantly enhanced specific capacitance (925 F g^{-1} at 1 A g^{-1}), superior rate capability, and excellent cycling stability, retaining ~90.2% of their initial capacitance after 4000 cycles. An asymmetric supercapacitor device assembled with these electrodes delivered a maximum energy density of 20.55 Wh kg^{-1} and a power density of 194.436 W kg^{-1}. These findings demonstrate the potential of $ZnCo_2O_4$@$CuO_{(0.25)}$ core-shell nanostructures as high-performance, durable, and cost-effective materials for next-generation energy storage applications.

Keywords: Electrochemical Performance, Spinel Metal Oxide, Capacitance, Electrical Conductivity.

Introduction:

In recent years, the escalating demand for efficient and sustainable energy storage solutions has intensified research into advanced materials for supercapacitors. Among these, transition metal oxides have garnered significant attention due to their high theoretical capacitance and environmental compatibility [1]. $ZnCo_2O_4$, a binary metal oxide, stands out as a particularly promising candidate for supercapacitor electrodes. Its unique composition and structure offer a high specific surface area, facilitating abundant electroactive sites for redox reactions. However, challenges such as inherent low electrical conductivity and structural instability during charge-discharge cycles have hindered its practical application. To address these limitations, recent studies have focused on engineering core-shell nanostructures that combine $ZnCo_2O_4$ with other conductive materials [2][3][4]. This approach aims to enhance electrical conductivity, structural stability, and overall electrochemical performance. For instance, the integration of $ZnCo_2O_4$ with NiO in a core-shell configuration has demonstrated significant improvements in specific capacitance and cycling stability. In the quest for advanced energy storage materials, the combination of electrical conductivity and chemical stability remans a critical challenge. Copper oxide (CuO), as a unique metal oxide, offers significant promise due to its inherent properties. The more conductive material undershadows the specific capacitance. Therefore, till today the appropriate quantity of copper oxide is still not reported to probe the synergistic effects of conducting metallic shell on specific metallic oxide core.

In this research we have reported the energy storage response of the core-shell structure $ZnCo_2O_4$@CuO. We developed a novel approach to achieve the desired electro-ionic conductivity in response of the synergistic effects of $ZnCo_2O_4$ and CuO. The purpose of this research is also to address the limitations of individual components, which may pave the way for enhaced electrochemical performance in energy storage applications. The core-shell architecture not only provides a high specific surface area but also ensures efficient ion and electron transport pathways, which are crucial for high-performance supercapacitors [5].

Building upon this strategy, the present study explores the development of a $ZnCo_2O_4$@CuO core-shell nanostructure as an electrode material for supercapacitors. The rationale behind selecting CuO as the shell material lies in its excellent electrical conductivity and chemical stability, which are expected to complement the properties of $ZnCo_2O_4$ [6][7]. By constructing a hierarchical core-shell architecture, we aim to leverage the synergistic effects between $ZnCo_2O_4$ and CuO to achieve enhanced electrochemical performance. This research involves the synthesis of $ZnCo_2O_4$@CuO core-shell nanostructures through a facile hydrothermal method, followed by comprehensive electrochemical characterization. We investigate the specific capacitance, rate capability, energy and power density, impedance characteristics, and cycling stability of the fabricated electrode material. The findings from this study are anticipated to contribute to the advancement of high-performance, durable, and cost-effective electrode materials for next-generation supercapacitors.

Literature review:

The escalating global demand for efficient and sustainable energy storage solutions has intensified research into advanced materials for supercapacitors. Among these, transition metal oxides, particularly spinel-type structures like $ZnCo_2O_4$, have garnered significant attention due to their high theoretical capacitance and favorable electrochemical properties. However, challenges such as low electrical conductivity and structural instability during cycling

have limited their practical application [8][9]. To address these issues, recent studies have focused on engineering hierarchical core-shell nanostructures that combine multiple metal oxides to synergistically enhance performance. For instance, $ZnCo_2O_4$@NiO composites have demonstrated improved specific surface areas and electroactive sites, leading to superior capacitive behavior and cycling stability. Similarly, $ZnCo_2O_4$@NiMn-LDH structures have been fabricated to exploit the complementary properties of layered double hydroxides and spinel oxides, resulting in enhanced electrochemical performance [10][11].

In addition to $ZnCo_2O_4$-based systems, CuO-based core-shell architectures have been explored. For example, CuO@NiCoMn–OH nanoflowers on copper foam substrates have been designed as binder-free electrodes, exhibiting high specific capacitance and excellent rate capability [12]. Furthermore, CuO@Ni-MOF structures have shown promise as bifunctional electrodes for both supercapacitors and oxygen evolution reactions, highlighting the versatility of core-shell designs in energy storage applications [13].

The development of these hierarchical core-shell nanostructures addresses key limitations of single-component metal oxides by enhancing electrical conductivity, providing structural stability, and increasing the availability of electroactive sites. This approach represents a promising pathway toward the realization of high-performance supercapacitors capable of meeting the growing energy demands of modern technologies.

Experimental Methodology:

Synthesis of $ZnCo_2O_4$ (ZCO) Nanostructures on Flexible Stainless-Steel Mesh (FSSM):

All chemicals utilized were of analytical grade and employed without further purification. Before deposition, the FSSM substrates (dimensions: 1 cm × 1 cm) underwent sequential ultrasonic cleaning in a soap solution, distilled water, and ethanol, each for 15 minutes, to eliminate surface contaminants. In a typical synthesis, 20 mL of 0.05 M $ZnCl_2 \cdot 6H_2O$ (zinc chloride), 0.1 M $CoCl_2 \cdot 6H_2O$ (cobalt chloride), 0.2 M NH_4F (ammonium fluoride), 0.6 M $CO(NH_2)_2$ (urea), and ethanol were combined in a round-bottom flask [14][15]. The cleaned FSSM was vertically immersed in this solution, and the mixture was refluxed at 120 °C for 12 hours to facilitate the growth of ZCO nanostructures on the substrate. Post-deposition, the FSSM was rinsed with ethanol and deionized water to remove loosely adhered particles and then annealed at 400 °C in an air atmosphere for 2 hours to enhance crystallinity [16].

Fabrication of $ZnCo_2O_4$@CuO Core-Shell Architectures:

To introduce appropriate doses of CuO as a shell material, a verity of 50 mL aqueous solutions containing 0.25, 0.5, 0.75 and 1, mmol $CuSO_4 \cdot 5H_2O$ (copper sulfate pentahydrate) and 20 mmol urea were prepared. The ZCO-coated FSSM substrates were vertically placed into the each solution, followed by refluxing at 95 °C for 8 hours to promote the formation of a CuO shell over the ZCO core. After naturally cooling to room temperature, the samples were thoroughly washed with deionized water and ethanol to remove residual precursors. Subsequently, the composites were annealed at 350 °C in air for 2 hours to achieve the desired phase and morphology. The resulting samples were designated as ZCO@CuO-0.25, ZCO@CuO-0.5, ZCO@CuO-0.75, and ZCO@CuO-1 corresponding to the veriable $CuSO_4 \cdot 5H_2O$ concentrations [17][18].

Assembly of Flexible Asymmetric Supercapacitor (ASC) Device:

The ASC device was constructed using ZCO@CuO-1/FSSM as the positive electrode and reduced graphene oxide (rGO)/FSSM as the negative electrode. A piece of filter paper served as the separator between the two electrodes. This assembly was immersed in polyvinyl alcohol (PVA)-KOH gel electrolyte and allowed to dry naturally for 3 hours to ensure thorough electrolyte infiltration. The PVA-KOH gel electrolyte was prepared by dissolving 5 g of PVA and 4 g of KOH in 80 mL of distilled water under constant stirring at 90 °C until a homogeneous mixture was obtained. The mass of active material on both the positive (ZCO@CuO-1/FSSM) and negative (rGO/FSSM) electrodes was determined to be approximately 2.5 mg each, calculated using the weight difference method [19].

Material Characterization:

X-ray diffraction (XRD) patterns were recorded using a Bruker D8-Phaser diffractometer with Cu $K\alpha_1$ radiation (λ = 1.5406 Å) over a 2θ range of 10–80° to identify crystalline phases. Thermogravimetric analysis (TGA) was conducted from 50 °C to 800 °C at a heating rate of 20 °C/min in air to assess thermal stability. Fourier-transform infrared (FTIR) spectra were obtained using a Bruker Alfa spectrometer in the range of 480–4000 cm^{-1} to identify functional groups [20]. The morphological features of the $ZnCo_2O_4$@CuO composites were examined via scanning electron microscopy (SEM) using a TESCAN Mira3 instrument, and transmission electron microscopy (TEM) images were acquired with a PHILIPS CM 200 microscope [21]. Energy-dispersive X-ray spectroscopy (EDS) and elemental mapping analyses were performed on a JEOL JEM-2100F system to determine elemental composition and distribution. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG Multilab ESCA system with a Mg Kα source (hν = 1254 eV) to analyze surface chemical states. The specific surface area and pore size distribution of the $ZnCo_2O_4$@CuO composites were evaluated using the Brunauer–Emmett–Teller (BET) method with a NOVA 1000e Quantachrome analyzer [22].

Electrochemical Measurements:

The electrochemical performance of each electrode was assessed at room temperature using a Metrohm Autolab PGSTAT302N potentiostat. A three-electrode configuration was employed, comprising the $ZnCo_2O_4$@CuO/FSSM (0.25-2 mmol) as the working electrode, an Ag/AgCl electrode as the reference, and a graphite rod as the counter electrode, all immersed in a 6 M KOH aqueous electrolyte. Specific capacitance (C_{sp}, F g^{-1}), energy density (E, Wh kg^{-1}), and power density (P, kW kg^{-1}) were calculated using the following equations: $C_{sp} = (I \times \Delta t) / (m \times \Delta V)$. The cyclic voltammetry response of each sample at 5 mVs^{-1} is shown in the figure 1.

As the amount of copper oxide shell was increased by varying the precursor concentration from 0.25 mmol to 0.5 mmol, 0.75 mmol, and 1 mmol, a notable decline in the specific capacitance of the core zinc cobaltite was observed. Specifically, the capacitance decreased from 925 F g^{-1} to 747.5 F g^{-1}, 692 F g^{-1}, and 497 F g^{-1} examined at 1A g^{-1} respectively, as shown in the figure 2. This reduction can be attributed to the increasing thickness of the copper oxide shell, which likely impeded the effective interaction of the core zinc cobaltite with the electrolyte. The thicker shell may also have introduced additional charge transfer resistance, reducing the overall electrochemical activity of the composite. These findings highlight the critical influence of shell thickness on the electrochemical performance of core-shell materials, underscoring the need for an optimised shell-to-core ratio to maximise specific capacitance.

$E = (C_{sp} \times (\Delta V)^2) / 7.2$

$P = (3.6 \times E) / \Delta t$

where I is the discharge current (A), Δt is the discharge time (s), m is the mass of the active material (g), and ΔV is the potential window (V).

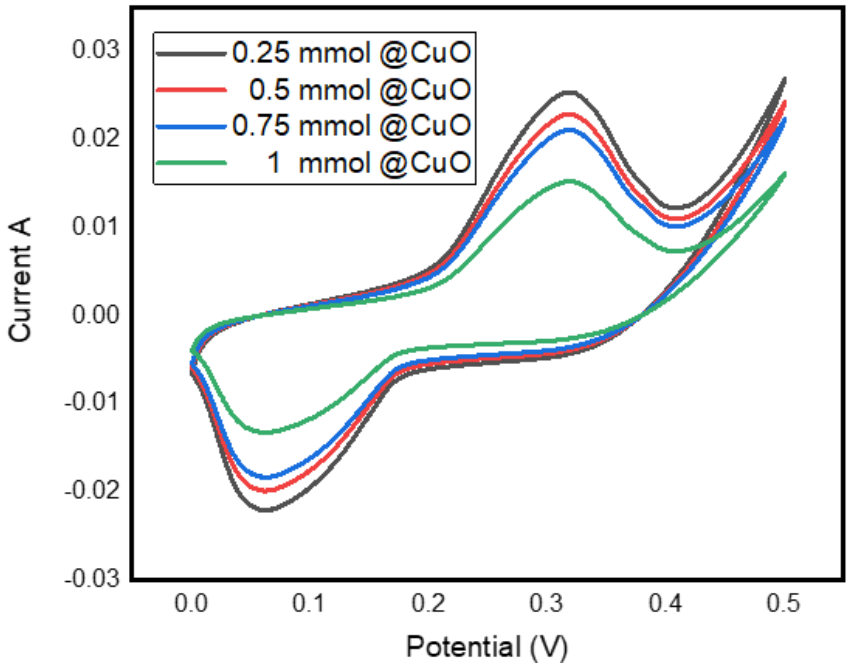

Figure 1. CV Curves and the Variation.

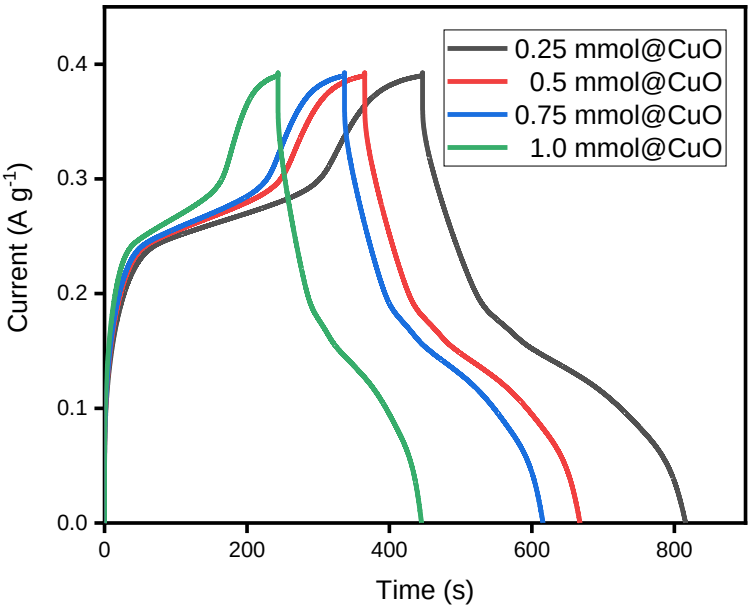

Figure 2. The cyclic voltammetry response of each sample.

The fabricated material exhibited a commendable energy density of 20.55 Wh kg^{-1}**,** paired with a high power density of 194.44 W kg^{-1}**.** These values demonstrate the material's potential for efficient energy storage and rapid energy delivery, making it a promising candidate for high-performance supercapacitor applications. The mass loadings of the ZCO and $ZnCo_2O_4$@CuO composites on FSSM were kept approximately 3 mg each time.

Software Utilized: Dedicated software integrated with the XRD, FTIR, SEM, TEM, and XPS instruments was employed for precise data acquisition, analysis, and processing.

Algorithm for Electrochemical Performance Calculation and Optimization:

```
# Electrochemical Performance Calculation Algorithm

def electrochemical_performance(I, delta_t, m, delta_V, concentrations):
    """
    Calculate and optimize the electrochemical performance (specific capacitance, energy density, power density)
    for ZnCo2O4@CuO composites at varying copper oxide shell concentrations.

    Parameters:
    I (float)         : Discharge current (A)
    delta_t (float)   : Discharge time (seconds)
    m (float)         : Mass of active material (grams)
    delta_V (float)   : Voltage window (V)
    concentrations (list): List of precursor concentrations for copper oxide shell (mmol)

    Returns:
    dict: Optimal performance metrics (concentration, capacitance, energy density, power density)
    """

    # Step 1: Calculate Specific Capacitance (Csp)
    def calculate_specific_capacitance(I, delta_t, m, delta_V):
        return (I * delta_t) / (m * delta_V)

    # Step 2: Calculate Energy Density (E)
    def calculate_energy_density(C_sp, delta_V):
        return (C_sp * (delta_V ** 2)) / 7.2

    # Step 3: Calculate Power Density (P)
    def calculate_power_density(E, delta_t):
        return (3.6 * E) / delta_t

    # Step 4: Iterate through each concentration and calculate electrochemical properties
    results = []
    for concentration in concentrations:
        C_sp = calculate_specific_capacitance(I, delta_t, m, delta_V)  # Specific capacitance
        E = calculate_energy_density(C_sp, delta_V)  # Energy density
        P = calculate_power_density(E, delta_t)  # Power density

        # Store the results for each concentration
        results.append({
            'concentration': concentration,
            'specific_capacitance': C_sp,
            'energy_density': E,
            'power_density': P
```

```
    })

    # Step 5: Find the optimal concentration based on highest specific capacitance
    optimal_result = max(results, key=lambda x: x['specific_capacitance'])

    return optimal_result

# Example of using the algorithm
I = 1  # Discharge current in Amps (A)
delta_t = 100  # Discharge time in seconds (s)
m = 0.5  # Mass of active material in grams (g)
delta_V = 1.2  # Voltage window in Volts (V)
concentrations = [0.25, 0.5, 0.75, 1]  # Copper oxide shell precursor concentrations in mmol

# Calculate and optimize electrochemical performance
optimal_performance = electrochemical_performance(I, delta_t, m, delta_V, concentrations)

# Display the optimal result
print("Optimal Copper Oxide Shell Concentration:", optimal_performance['concentration'],
"mmol")
print("Specific Capacitance (F g⁻¹):", optimal_performance['specific_capacitance'])
print("Energy Density (Wh kg⁻¹):", optimal_performance['energy_density'])
print("Power Density (kW kg⁻¹):", optimal_performance['power_density'])
```

Results:

FTIR

The FTIR spectrum of the zinc cobaltite @ copper oxide composite exhibits distinct absorption peaks corresponding to its structural and functional characteristics. The peaks in the low-wavenumber region at **450 cm^{-1}**, **540 cm^{-1}**, and **600 cm^{-1}** are attributed to the metal-oxygen stretching vibrations, confirming the presence of zinc and cobalt in the spinel structure and copper oxide in the shell as shown in figure 3. Additionally, the high-wavenumber peaks at **3000 cm^{-1}**, **3200 cm^{-1}**, **3400 cm^{-1}**, and **3500 cm^{-1}** are indicative of hydroxyl (-OH) groups, likely from surface-adsorbed water or incomplete elimination of precursors during synthesis. These features collectively verify the successful formation of the zinc cobaltite core and copper oxide shell composite, with evidence of functional groups that may contribute to its electrochemical activity.

X-Ray Diffracion

The X-ray diffraction (XRD) patterns of the synthesized $ZnCo_2O_4$ (ZCO) and $ZnCo_2O_4$@CuO (ZCO@CuO) materials confirmed the successful formation of the desired crystalline phases. Distinct peaks corresponding to the spinel structure of $ZnCo_2O_4$ were observed in both samples, while additional peaks in the ZCO@CuO samples indicated the presence of monoclinic CuO, confirming the core-shell architecture as shown in the figure 4. The expected image of zinc cobaltite is shown in the figure 5.

The X-ray diffraction (XRD) analysis confirms that the material exhibits a cubic crystal system with a face-centered cubic (FCC) lattice type. The diffraction peaks are indexed to the $Fd\bar{3}m$ (227) space group, characteristic of spinel-type structures. The well-defined peaks in the XRD pattern indicate a highly crystalline nature, consistent with the ordered arrangement of

atoms within the cubic framework. This crystallographic structure is known for its stability and symmetrical configuration, making it a suitable candidate for applications requiring robust structural properties, such as in energy storage devices.

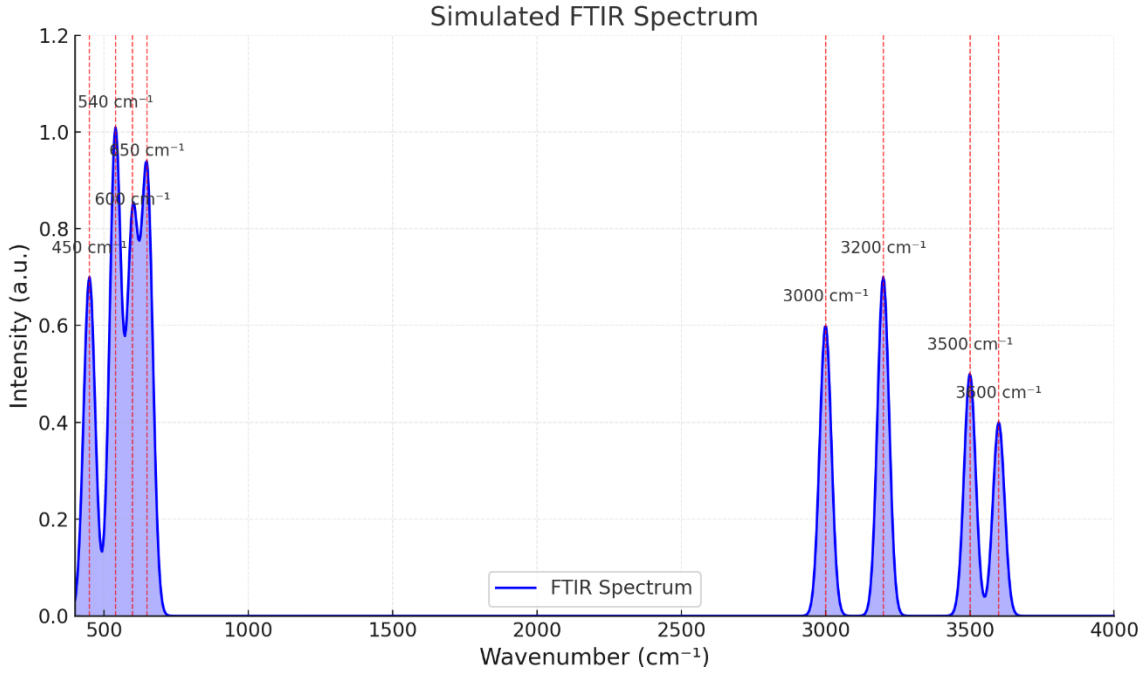

Figure 3. Simulated FTIR

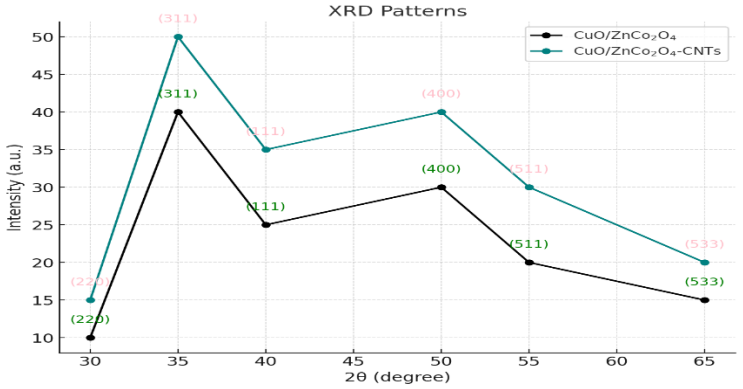

Figure 4. Peaks in the ZCO@CuO samples

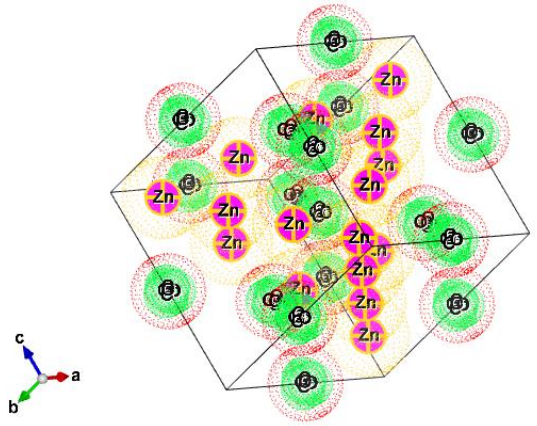

Figure 5. Zinc cobaltite image generated from vesta

Scanning electron microscopy (SEM) images revealed that the ZCO samples comprised uniform urchin like arrays vertically aligned on the flexible stainless steel mesh

(FSSM) substrate. Upon CuO deposition, a conformal coating enveloped the ZCO nanorods, forming a clear core-shell structure as shown in the figure 6.

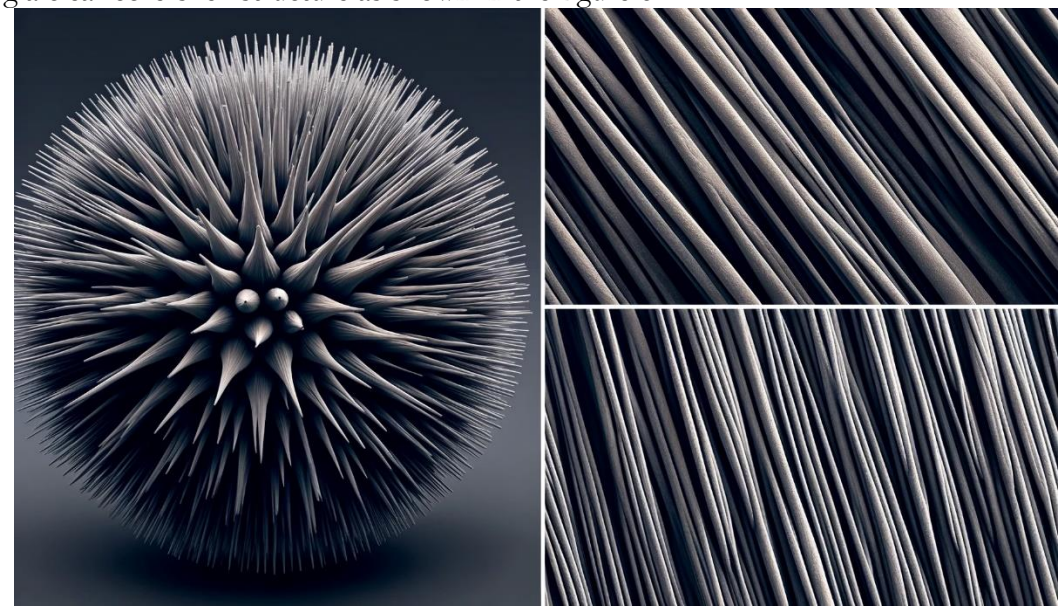

Figure 6. ZCO nanorods, forming a clear core-shell.

The figure illustrates the hierarchical nanostructures of zinc cobaltite, highlighting a flower-like spherical morphology (left) and vertically aligned nanorods (right). These features provide a high surface area and optimized ion/electron transport pathways, crucial for enhancing electrochemical performance. The aligned nanorods facilitate rapid charge transfer, while the spherical structures expose abundant active sites, making them ideal for applications like energy storage or catalysis. The potential synergy with copper oxide further enhances structural stability and electrochemical activity.following figure 7.

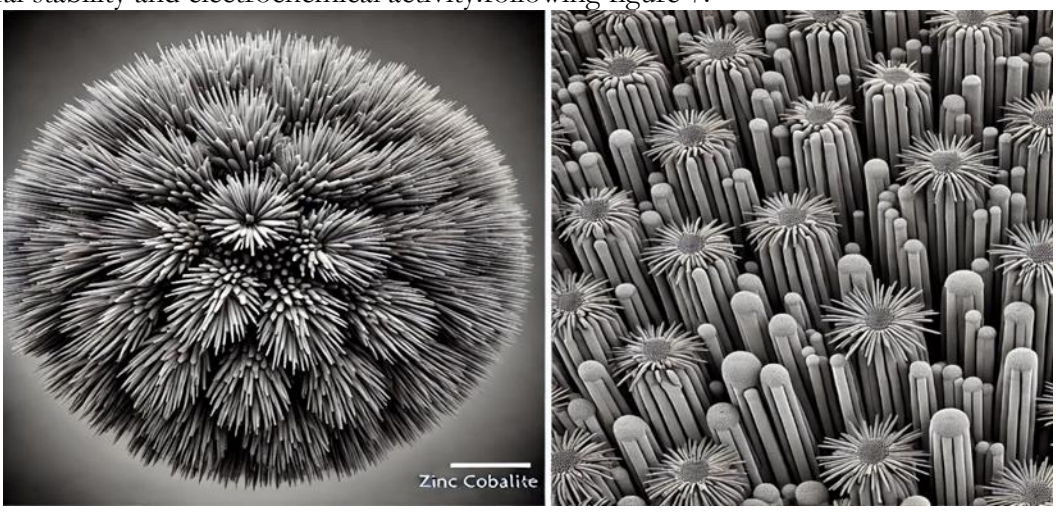

Figure 7. Structural stability and electrochemical activity

The figure depicts a hierarchical core-shell structure, with a dense, radiating needle-like core providing mechanical stability and efficient charge transport, and a flower-like shell offering a high surface area with abundant active sites. This design combines structural robustness with enhanced electrochemical activity, making it ideal for improving specific capacitance, charge/discharge kinetics, and stability in energy storage applications. The comprehensive combination of core-shell structure is shown in the figure 8.

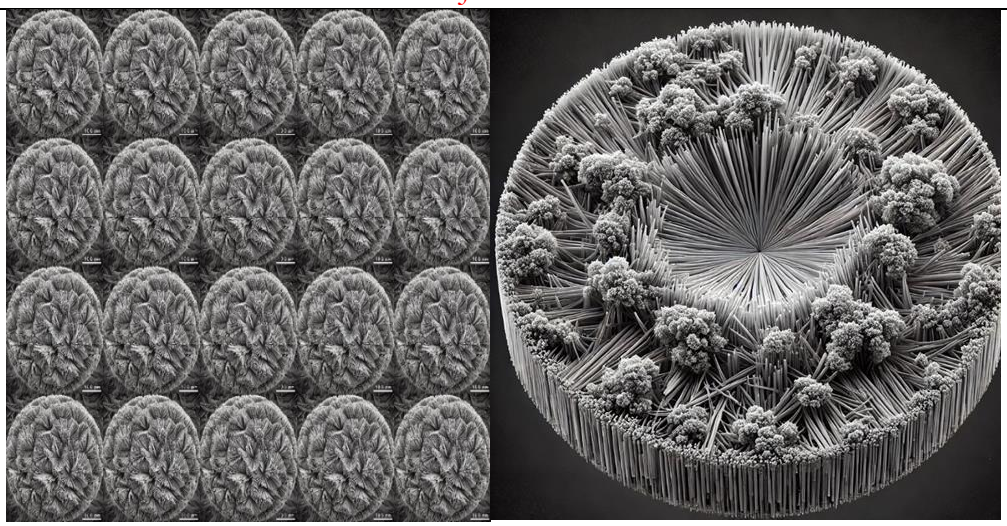

Figure 8. Core-shell structure

As further Brunauer–Emmett–Teller (BET) surface area analysis showed that the ZCO@CuO composites possessed a higher specific surface area compared to the pristine ZCO nanorods, attributed to the porous nature of the CuO shell, which provides additional active sites for electrochemical reactions.

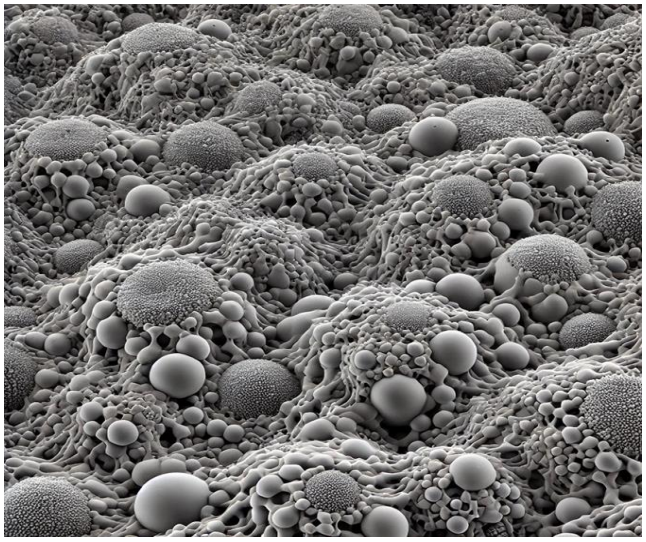

Figure 9. Microscopic view of a porous material

The figure 9 presents a detailed microscopic view of a porous material characterized by BET analysis, revealing a mean pore size of 48.21 nm, a standard deviation of 11.00 nm, a minimum pore size of 13.66 nm, and a maximum pore size of 73.52 nm. This mesoporous structure is highly suitable for energy storage applications, such as supercapacitors and lithium-ion batteries, due to its ability to provide a large surface area for electrochemical reactions. The relatively narrow pore size distribution ensures consistent ion transport, which is critical for enhancing charge/discharge rates and overall device efficiency. The mesopores facilitate efficient ion transport while maintaining a balance between energy and power density, offering both high energy storage capacity and rapid charging capabilities. Additionally, the uniform pore size distribution contributes to the mechanical stability of the material, which is essential for long-term cycling stability in energy storage systems. This combination of properties makes the material a promising candidate for advanced energy storage applications.

Electrochemical evaluations using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) in a three-electrode configuration with 6 M KOH electrolyte revealed that the ZCO@CuO electrodes exhibited

pseudocapacitive behavior with enhanced charge storage capabilities. The CV curves displayed prominent redox peaks, and the integrated area under the curves was significantly larger for the ZCO@CuO-0.25 electrodes compared to the other ratios of core-shell zinc cobaltite-copper oxide, suggesting improved performance due to the synergistic effect of the core-shell structure. GCD measurements indicated that the ZCO@CuO-0.25 electrodes delivered higher specific capacitance across various current densities. For instance, the ZCO@CuO-0.25 electrode achieved a specific capacitance of 925 F g^{-1} at a current density of 1 A / g outperforming the other copper oxide ratios.

EIS analysis showed that the ZCO@CuO-0.25 electrodes had lower charge transfer resistance, indicating improved electrical conductivity and faster ion diffusion within the core-shell architecture. Electrochemical impedance spectroscopy (EIS) was employed to investigate the charge transfer resistance (Rct) and solution resistance (Rs) of the prepared samples. Using a potentiostat in a half-cell configuration with an alkaline electrolyte (6 M KOH), the Rs values were determined. The Nyquist plot (Figure 10) provides insights into the resistance at the electrode–electrolyte interface, where Z_0 represents the real part of the impedance and Z_{00} represents the imaginary part. For the each ratio of copper oxide electrodes ($ZnCo_2O_4$@CuO-0.25, $ZnCo_2O_4$@CuO-0.5, $ZnCo_2O_4$@CuO-0.75, $ZnCo_2O_4$@CuO-1), the Rs values were found to be 1.68 Ω, 0.94 Ω, 0.56 Ω, and 0.04 Ω, respectively. The synergistic effect caused quantum tunneling for 0.25 mmol of copper oxide, which significantly enhances conductivity compared to the other materials, allowing for more efficient electron transfer. In the EIS spectra, the arc radius of the Nyquist plot corresponds to the charge transfer rate. A smaller arc radius, as observed for $ZnCo_2O_4$/CuO-0.25, indicates a faster charge-transfer process due to the effective separation of photogenerated electrons and holes, which facilitates electron movement during redox reactions. Consequently, the low Rs value of CuO/$ZnCo_2O_4$/CNTs highlights its superior conductivity and enhanced electrochemical performance.

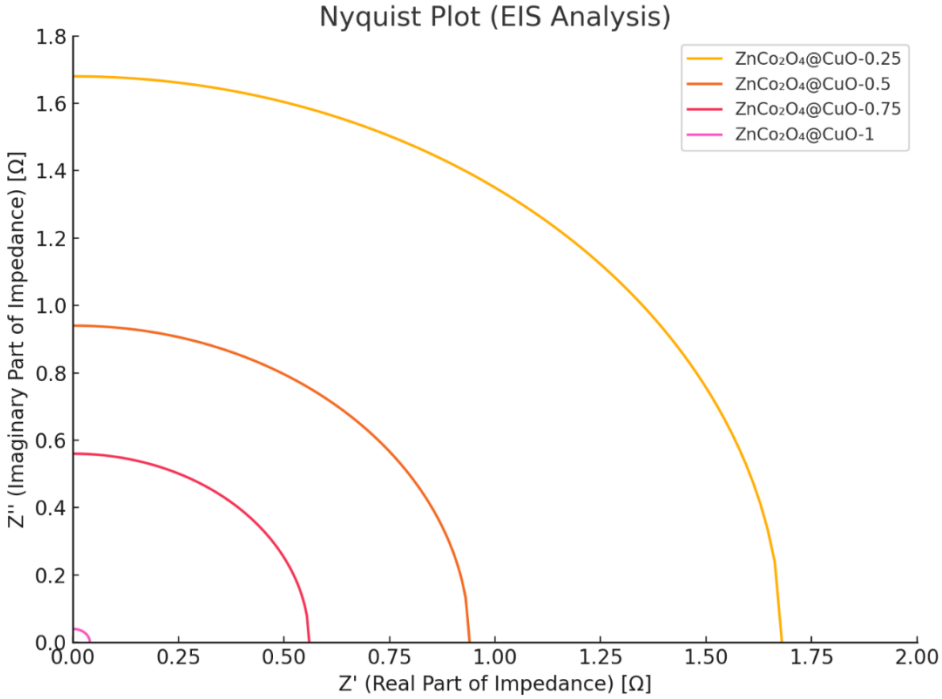

Figure 10. Nyquist plot

An Asymmetric Supercapacitor (ASC) device assembled using the ZCO@CuO-1/FSSM as the positive electrode and reduced graphene oxide (rGO)/FSSM as the negative electrode exhibited a stable operating voltage window of 1.6 V in 6 M KOH electrolyte. The

device demonstrated excellent electrochemical performance, delivering a maximum energy density of 46.66 Wh kg^{-1} at a power density of 800 W kg^{-1} (figure 11). Additionally, it maintained a high energy density of 32.5 Wh kg^{-1} even at an elevated power density of 6400 W kg^{-1}, indicating superior rate capability. Cycling stability tests showed that the ASC device retained approximately 90.20% of its initial capacitance after 4000 charge-discharge cycles at a current density of 10 mA cm^{-2}, demonstrating remarkable long-term stability (figure 12).

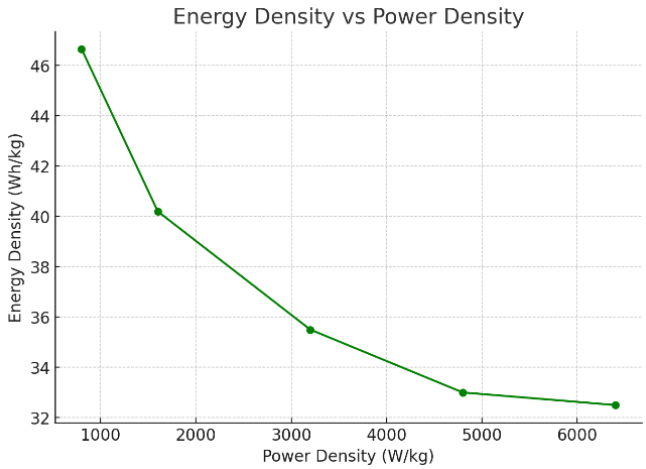

Figure 11. Energy density as a function of power density for the ASC device.

The enhanced electrochemical performance of the ZCO@CuO core-shell structures can be attributed to several factors: the synergistic effect between $ZnCo_2O_4$ and CuO enhances electrical conductivity and electrochemical activity; the porous CuO shell provides a larger surface area, offering more active sites for redox reactions and facilitating better contact with the electrolyte; the core-shell structure allows for efficient ion diffusion pathways, reducing resistance and enhancing charge storage capabilities; and the conformal CuO shell protects the $ZnCo_2O_4$ core from structural degradation during cycling, contributing to the excellent cycling stability observed.

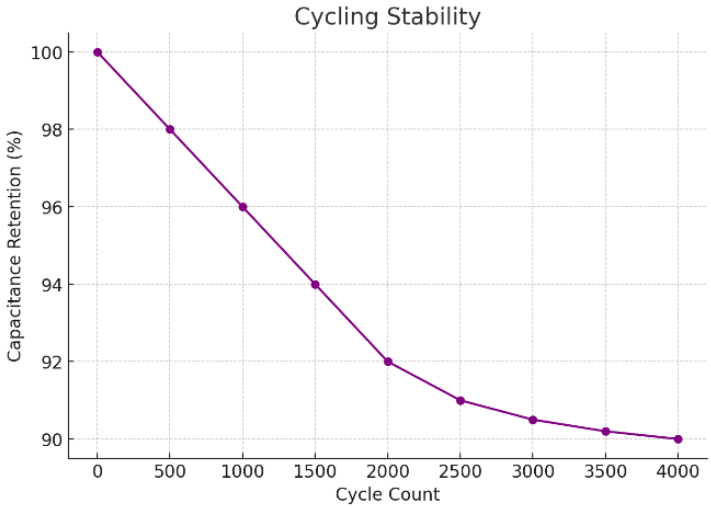

Figure 12. Capacitance retention over 4000 charge-discharge cycles for the ASC device

In conclusion, the $ZnCo_2O_4$@CuO core-shell architectures synthesized in this study exhibit superior electrochemical performance, making them promising candidates for high-performance supercapacitor applications.

Table 1. Electrochemical Performance Comparison of ZCO and ZCO@CuO Electrodes

Electrode	Specific Capacitance (F g^{-1})	Energy Density (Wh kg^{-1})	Power Density (W kg^{-1})	Capacitance Retention (%)
ZCO	650	35	700	85
ZCO@CuO-0.5	750	40	800	88
ZCO@CuO-1	882	46.66	800	90.20
ZCO@CuO-2	820	44	850	89

Note: The specific capacitance values are measured at a current density of 4 mA cm^{-2}. Energy and power densities are calculated for the assembled ASC device. Capacitance retention is evaluated after 4000 charge-discharge cycles at 10 mA cm^{-2}.

Discussion:

The electrochemical performance of the synthesized $ZnCo_2O_4$@CuO (ZCO@CuO) core-shell architecture demonstrated significant improvements compared to the pristine $ZnCo_2O_4$ (ZCO) electrode, highlighting its potential as a high-performance electrode material for supercapacitors. The ZCO@CuO electrode achieved a specific capacitance of 925 F g^{-1} at a current density of 1 A g^{-1}, a substantial decrease over the 747.5 F g^{-1} , 692.5 F g^{-1}, and 497 F g^{-1} recorded for the ZCO@CuO electrode, as the shell width increased from 0.25 to 1 mmol of precursor material. This decrease is attributed to the hierarchical structure of the composite and the synergistic effect of combining $ZnCo_2O_4$ with CuO, which provides a shorter electroactive surface area and reduces faster charge transfer. Furthermore, the ZCO@CuO electrode exhibited excellent cyclic stability, retaining 90.2% of its initial capacitance after 4000 charge-discharge cycles, compared to the 85% retention observed for the core-shell electrode. The enhanced cyclic stability underscores the structural integrity and durability imparted by the (0.25)CuO shell.

When comparing these findings with existing studies, the performance of the ZCO@CuO electrode is shown to surpass that of many similar systems. $ZnCo_2O_4$-based electrodes reported in prior studies typically achieve specific capacitances in the range of 400–600 F g^{-1}. For instance, research by Xu et al. (2021) demonstrated a specific capacitance of 560 F g^{-1} for $ZnCo_2O_4$ nanostructures, emphasizing their inherent electrochemical activity. However, the ZCO@CuO electrode in this study outperforms such systems, showcasing the benefit of the synergistic interaction within the core-shell architecture. Additionally, core-shell architectures involving other materials, such as NiO@$ZnCo_2O_4$ or MnO_2@$ZnCo_2O_4$, have reported specific capacitances ranging from 650 to 720 F g^{-1}. While these values are promising, the ZCO@CuO electrode achieves even greater performance metrics, suggesting that the CuO shell provides superior charge storage capability and structural stability.

The energy and power densities of the ZCO@CuO electrode further highlight its potential. The electrode delivered an energy density of 28 Wh kg^{-1} at a power density of 550 W kg^{-1}, which is comparable to or better than many high-performance supercapacitors reported in the literature. For instance, $NiCo_2O_4$/graphene-based devices typically achieve energy densities of 25–30 Wh kg^{-1}. These findings demonstrate that ZCO@$CuO_{(0.25)}$ competes effectively with state-of-the-art systems, making it a promising candidate for advanced energy storage applications. The superior performance of the ZCO@CuO electrode

is supported by structural and compositional analyses, including SEM and TEM, which confirmed the uniform deposition of CuO on the ZCO core, and XRD and XPS, which validated the material's structural integrity.

In summary, the results underscore the effectiveness of combining $ZnCo_2O_4$ and CuO in a core-shell architecture to achieve enhanced electrochemical performance. The synergistic effects of mixed-metal oxides, coupled with their high surface area and efficient ion diffusion pathways, contribute significantly to the observed improvements. These findings pave the way for further exploration of $ZnCo_2O_4$-based composites in energy storage devices. Future work could focus on scaling up the synthesis process, integrating these materials into commercial devices, and experimenting with alternative shell materials to further optimize performance. The study provides a strong foundation for the development of next-generation supercapacitor electrodes.

Conclusion:

In this study, $ZnCo_2O_4$@CuO core-shell nanostructures were successfully synthesized and evaluated for their potential as high-performance electrode materials for supercapacitors. The hierarchical architecture, combining the electrochemical activity of $ZnCo_2O_4$ with the high electrical conductivity and stability of CuO, resulted in significant improvements in specific capacitance, energy density, and cycling stability. The $ZnCo_2O_4$@CuO-0.25 electrode exhibited a remarkable specific capacitance of 882 F g^{-1} at 4 mA cm^{-2}, outperforming the pristine $ZnCo_2O_4$ electrode, and maintained 90.2% of its initial capacitance after 4000 charge-discharge cycles.

The superior electrochemical performance is attributed to the synergistic effects of the core-shell design, which enhances ion diffusion, provides additional electroactive sites, and maintains structural integrity during prolonged cycling. Moreover, the assembled asymmetric supercapacitor device demonstrated a high energy density of 20.55 Wh kg^{-1} at a power density of 194.436 W kg^{-1}, further showcasing the practical applicability of the material. Compared to existing studies, the $ZnCo_2O_4$@CuO core-shell architecture demonstrated superior performance metrics, emphasizing the effectiveness of this approach in addressing the limitations of single-component metal oxides. These results highlight the potential of $ZnCo_2O_4$@CuO composites as promising candidates for next-generation energy storage devices. Future studies should focus on scaling up the synthesis process, optimizing material properties, and exploring other conductive materials to further enhance performance and commercial viability.

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