

RESEARCH ARTICLE



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* **Corresponding author.**

Tel: +91-9440281769
drdevaprasadraju@gmail.com

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Surfactant assisted morphological transformation of rod-like ZnCo_2O_4 into hexagonal-like structures for high-performance supercapacitors

Kumcham Prasad¹, Gutturu Rajasekhara Reddy¹, Borelli Deva Prasad Raju^{2*}

¹ Department of Instrumentation, Sri Venkateswara University, Tirupati, 517502, India

² Department of Physics, Sri Venkateswara University, Tirupati, 517502, India. Tel.: +91-9440281769

Abstract

Objectives: To develop the microstructures of rod-shaped ZnCo_2O_4 (ZCO-Urea) and hexagonal-shaped ZnCo_2O_4 (ZCO- NH_4F) through the change of surfactants such as urea and NH_4F in the reaction and to investigate the physicochemical and electrochemical properties for high-performance supercapacitors. **Methods:** The structural and morphological characteristics of two prepared samples were analyzed through X-ray diffraction analysis (XRD), Scanning electron microscope (SEM) analysis, and Transmission electron microscope (TEM) analysis, respectively. The electrochemical performance was evaluated using Cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), and Electrochemical impedance spectroscopy (EIS) analysis. **Findings:** The crystalline nature and phase purity of the as prepared samples were confirmed from XRD, and the structural parameters such as lattice parameter (a), microstrain (ϵ), dislocation density (δ), cell volume (v), and average crystalline size (D) for both the samples were determined. The SEM and TEM analysis revealed morphological characteristics of the samples. The electrochemical analysis of ZCO-Urea and ZCO- NH_4F electrodes were tested for supercapacitor application in 1M of aqueous KOH electrolyte and exhibit an areal capacitance of 31 mF cm^{-2} , and 41.43 mF cm^{-2} , respectively, obtained at a current density of $10 \mu\text{A cm}^{-2}$. And also showed outstanding cyclic stability over 1000 charge-discharge cycles. **Applications:** The simple and inexpensive method of synthesized surfactant-assisted morphological transformation of ZCO microstructures will introduce new directions in this emerging energy field.

Keywords: ZnCo_2O_4 ; Urea; NH_4F ; areal capacitance; supercapacitors

1 Introduction

As the non-renewable energy resources such as fossil fuels become rarer and the increasing demand for energy to meet current energy requirements leads to an intense search for alternative energy sources and the use of energy devices. This is further

stressed by the rapid increment in possession of consumer electronic goods and portable devices^(1–4). In this scenario, supercapacitors (SCs) are studied as one of the best-suited technologies for energy storage devices due to their longer cycle life, higher power density, faster charging-discharging ability, smaller size, and safe operation, and eco-friendly characteristics than many other energy storage devices. Apart from the advantages of SCs, the successful exploitation of renewable energy resources still requires more efficient, low-cost, reliable, and eco-friendly characteristics^(5,6).

SCs can be generally sorted in terms of their charge storage mechanism into two classes as electric double-layer capacitors (EDLCs) in which the charge is stored due to non-faradaic reversible ion adsorption at the electrode/electrolyte's interface. Still, it is achieved for pseudocapacitors (PCs) due to the reversible faradaic redox reactions of the active electrode material⁽⁷⁾. Since the electrode material is one of the significant components in enhancing the energy storage device's electrochemical performance, novel materials and materials with varying morphological characteristics have been investigated. Carbonaceous materials, conducting polymers, and transition metal oxides (TMOs) are the various types of most commonly used electrode materials. The latter was widely explored for PCs due to their high theoretical capacitance and abundant oxidation states. The PCs exhibit higher charge storage ability than EDLCs, but their usage is still rendered by their high cost and poor cycling stability. The electrochemical performance of PCs mainly depending on the size, morphology, architecture of the electroactive material and can be enhanced by using nanostructured materials⁽⁸⁾.

In this view, most of the current research work has been focussed on the rational design of porous structures, novel heterostructures, and hierarchical architectures of the electrode materials using various strategies like introducing structure-directing agents, ligands to synthesize more effective electroactive materials with special structures^(9,10). Among the TMOs, the AB₂O₄ type binary transition metal oxides (BTMOs) like NiCo₂O₄⁽¹¹⁾, MnCo₂O₄⁽¹²⁾, ZnCo₂O₄⁽¹³⁾, CuCo₂O₄⁽¹⁴⁾, and ZnFe₂O₄⁽¹⁵⁾ are the most explored electrode materials for supercapacitors than their corresponding single-component metal oxides due to the advantages like rich redox chemistry, combined contributions of both the metal ions, etc. ZnCo₂O₄, as one of the most promising BTMOs, has been widely explored as active electrode material for energy storage applications like supercapacitors. This is due to its advantages like high theoretical specific capacitance, variable oxidation states, low-cost, environmental-friendly characteristics, and easy availability. Further, both zinc and cobalt cations' contributions offer a synergetic effect on the redox chemistry of ZnCo₂O₄ electrode material. This is due to the Co ions' high capacitance and the greater number of electron transportation channels provided by the Zn ions^(16,17). A wide range of micro/nanostructures of ZnCo₂O₄ were synthesized through different methods to date^(18–20).

The morphology of the ZnCo₂O₄ depends on mainly the reaction or experiment parameters such as reaction time and temperature, solvent and surfactant type, and precursors concentration. In our previous reported papers, different types of morphologies were synthesized by adjusting the synthesis parameters and investigated the physicochemical, textural and electrochemical properties for supercapacitors in terms of specific capacitance (F/g). The novelty of the present work involves, to prepare two different morphologies by varying the surfactant in the hydrothermal reaction and other synthesis conditions are the same. Hexagonal and rod-like morphologies were obtained and exhibits different electrochemical performance for supercapacitors in terms of areal capacitance. Furthermore, the prepared two electrodes exhibit outstanding cyclic performance over 1000 cycles^(21–23).

Despite these developments, there is still room for improving the morphological structures, which have a significant character in enhancing a device's energy storage ability, using low-cost materials and more straightforward synthesis methods. In this regard, researchers have focused on varying the material's morphological properties and controlling the size by using materials as surfactants and precipitants^(24–28). Herein we proposed a work focussed on tuning the morphology of ZnCo₂O₄ (ZCO) material by varying surfactants like Urea and Ammonium fluoride using the hydrothermal method and represented as ZCO-Urea and ZCO-NH₄F, respectively, throughout the study. The as-prepared materials are systematically studied using various physicochemical and electrochemical techniques. These results ensure that as-prepared materials are potential candidates for supercapacitors applications.

2 Materials and Methods

2.1 Materials

Zinc nitrate hexa-hydrate [Zn(NO₃)₂·6H₂O], cobalt nitrate hexa-hydrate [Co(NO₃)₂·6H₂O], urea [Co(NH₂)₂], ammonium fluoride (NH₄F), ethanol (C₂H₅OH) and potassium hydroxide (KOH) were purchased from Sigma-Aldrich (India). All the chemicals above mentioned were AR grade and directly used after purchase. The solvent used is DI water with a resistivity of 18.2 MΩ cm for all the experiments.

2.2 Synthesis of rod/hexagonal-like ZnCo_2O_4

In a typical synthesis procedure, for rod-like ZnCo_2O_4 (ZCO-Urea) 10 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 20 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 1 g of $[\text{CO}(\text{NH}_2)_2]$ was dissolved in 35 ml of DI water and thoroughly stirred for 10 minutes. The obtained homogeneous clear solution was then transferred into a Teflon-lined stainless-steel autoclave of 50 mL volume and heated up to 180°C at a ramping rate of $2^\circ\text{C}/\text{min}$ and maintained at that temperature for 12 hours and allowed to cool down naturally to room temperature. After the reaction was over, the precipitate is collected and subjected to washing with DI water followed by absolute ethanol several times to remove the residual nanoparticle debris and allowed to dry at 80°C for 12 hours. Finally, the powder samples obtained are annealed at 400°C for 3 hours at a ramping rate of $2^\circ\text{C}/\text{min}$ resulting in the formation of rod-like ZnCo_2O_4 nanostructures. The synthesis procedure for hexagonal-like ZnCo_2O_4 (ZCO- NH_4F) was similar to rod-like ZnCo_2O_4 (ZCO-Urea), except $\text{CO}(\text{NH}_2)_2$ is replaced by NH_4F .

2.3 Materials characterization

The crystalline nature and phase purity of the as prepared ZCO samples was determined using X-ray diffraction (XRD) analysis with a diffractometer (PANalytical X'Pert PRO, Malvern, UK) facilitated with $\text{Cu K}\alpha$ ($\lambda = 1.5405980 \text{ \AA}$) as the radiation source, functioning voltage of 40 kV and a current of 30 mA within a 2θ range of $10\text{--}80^\circ$ with a step size of 0.02° . The morphological characteristics were analyzed with a scanning electron microscope (SEM) (Model number FE-SEM, S-4800, Hitachi, Japan). During SEM measurements, an ultra-thin layer of Pt was sputter-coated (E-1030 Ion Sputter, Hitachi, Japan) onto the samples to increase the conductivity. The microstructures were examined using a transmission electron microscope (TEM) (HRTEM, Tecnai G2 F20 S-Twin, Hillsboro, USA). The electrochemical measurements of the samples were carried out on an electrochemical workstation (CHI 760E, CH instruments, USA) using a three-electrode system with 1 M KOH aqueous solution as the electrolyte at room temperature. A platinum wire was used as the counter electrode, Ag/AgCl acted as the reference electrode, and the as-prepared ZnCo_2O_4 was used as the working electrode for all the measurements. The cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were carried out to evaluate the electrochemical performance of the ZCO samples.

2.4 GCE preparation

For conducting the electrochemical measurements, a homogeneous suspension of 4 mg of active material in 2 mL of ethanol was prepared and $10 \mu\text{L}$ of the resulting suspension was uniformly deposited on the glassy carbon electrode over an area of 0.06 cm^2 . The electrode had been dried under an infrared lamp and then washed thoroughly with de-ionized water before conducting the electrochemical measurements.

3 Results and discussion

3.1 X-ray diffraction analysis

The crystallinity of the as-prepared ZnCo_2O_4 microstructures was studied by XRD analysis. The characteristic peaks centered at the 2θ values of 18.89, 31.35, 36.76, 38.49, 44.67, 59.28, and 65.23° were well indexed to the planes of (111), (220), (311), (222), (400), (511), and (440) respectively as shown in Figure 1, confirms the cubic and spinel phase of the prepared ZnCo_2O_4 microstructures belongs to the space group of $\text{Fd}3\text{m}$ (JCPDS No: 23-1390)⁽²⁹⁾. Furthermore, some weak diffraction peaks centered at 2θ values of 31.94, 34.48, 47.66, 62.49, and 66.67° were observed, denoting a significantly less fraction of ZnO in the as-prepared samples formed during the synthesis⁽³⁰⁾.

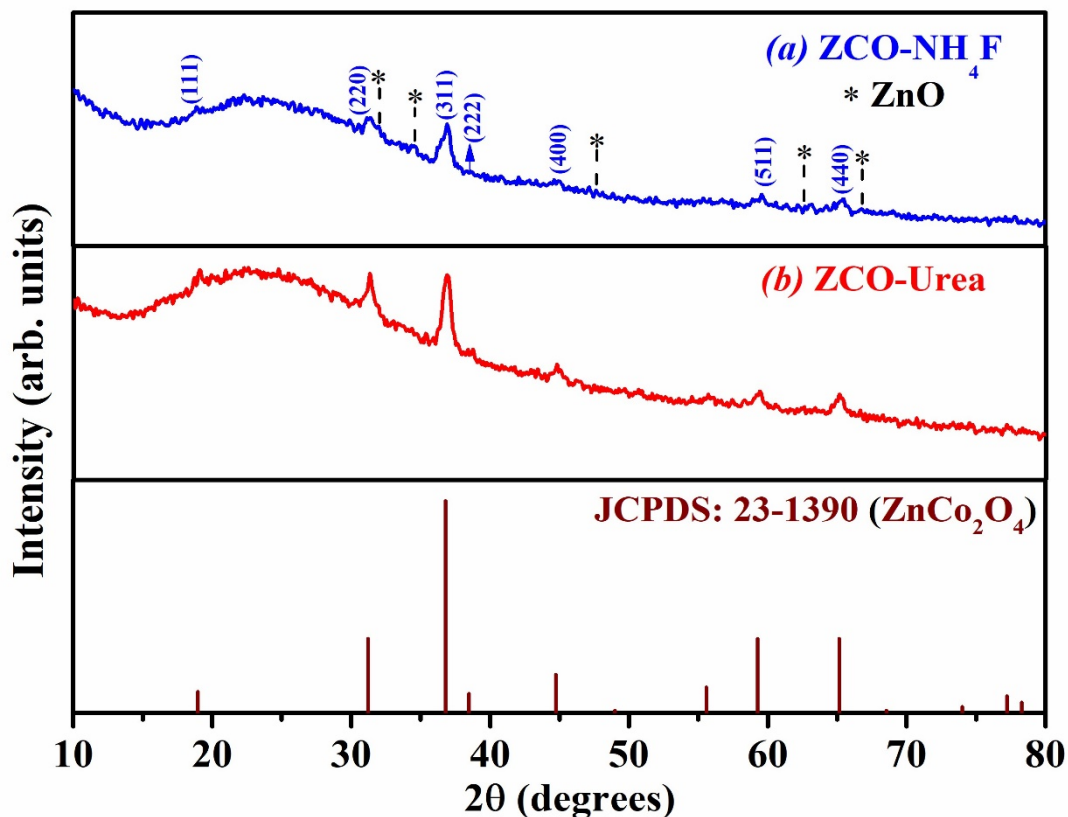


Fig 1. X-ray diffraction (XRD) pattern of ZCO-NH₄F (a) and ZCO-Urea (b)

The XRD details of the as-prepared materials were analyzed, compared with the standard data, and shown in Table 1.

Table 1. Obtained XRD data for ZCO-Urea and ZCO-NH₄F

h k l	2θ (°)			d-spacing (Å)		JCPDS No.	Composition	
	Standard value	Observed value		Standard value	Observed value			
		ZCO-Urea	ZCO- NH ₄ F		ZCO-Urea			ZCO- NH ₄ F
111	18.96	19.12	18.89	4.68	4.53	4.81	23-1390 ZnCo ₂ O ₄	
220	31.21	31.30	31.30	2.86	2.85	2.85		
311	36.80	36.93	36.83	2.44	2.41	2.41		
222	38.48	38.84	38.51	2.34	2.33	2.33		
400	44.74	44.81	44.61	2.02	2.03	2.03		
511	59.28	59.47	59.47	1.55	1.54	1.54		
440	65.14	65.23	65.35	1.43	1.43	1.43		

The lattice parameter (a), microstrain (ε), dislocation density (δ), cell volume (v), and average crystalline size (D) for both ZCO-Urea and ZCO-NH₄F microstructures were determined using the following formulae for the dominant peak (311) from the XRD data and represented in Table 2^(31,32).

$$2d_{hkl} \sin \theta_{hkl} = \lambda \quad (1)$$

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (2)$$

$$\text{microstrain}(\varepsilon) = \frac{H \cos \theta}{4} \quad (3)$$

$$\text{dislocation density } (\delta) = \frac{1}{D^2} \quad (4)$$

$$\text{cell volume } (v) = abc \sin \beta \quad (5)$$

$$\text{crystalline size } (D) = \frac{K\lambda}{H \cos \theta} \quad (6)$$

Where K is the shape factor, D is the crystallite size in nm, θ is the peak position in $^\circ$, H is full width at half maximum in radians, and d is the interplanar distance in \AA and h, k, l are the Miller indices and a, b, c, β are the lattice parameters.

Table 2. Structural parameters of ZCO-Urea and ZCO-NH₄F

Physical quantity (symbol) (units)	ZCO-Urea	ZCO- NH ₄ F
Lattice parameter (a) (\AA)	8.35	9.46
Micro strain (ε) $\times 10^{-3}$	1.56	1.67
Dislocation density (δ) $\times 10^{-15}$	2.11	2.38
Cell volume (v) ($\approx \text{nm}^3$)	0.52	0.84
Crystalline size (D) (nm)	21.79	20.49

The sharp and broadened diffraction peaks reveal the poor crystallinity and small crystallite size of the ZCO-NH₄F that play a vital role in enhancing the electrode material's electrochemical behavior than ZCO-Urea. This enhancement was achieved due to the availability of more transportation channels in a low crystalline material compared to a highly crystalline one^(33,34).

3.2 FT-IR analysis

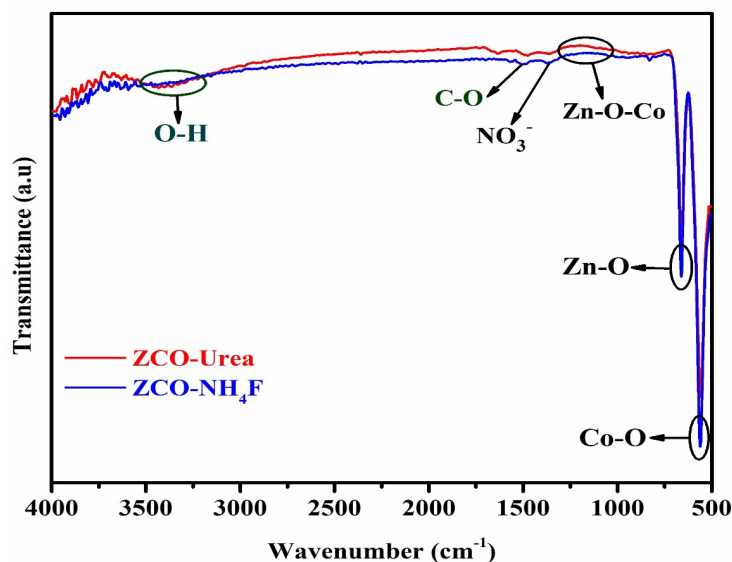


Fig 2. FT-IR spectrum of ZCO-Urea and ZCO-NH₄F

FT-IR spectroscopy is used to identify the major functional groups and chemical species present in the as-prepared ZCO microstructures and presented in Figure 2. The broadband at around $3360\text{--}3460\text{ cm}^{-1}$ can be attributed to the OH- group's stretching vibrations. The low-intensity band at about 1477 cm^{-1} can be attributed to the C-O stretching vibration. The peak observed at around 1385 cm^{-1} represents the presence of NO_3^- ions, originated from the precursor medium. The band observed at about 1105 cm^{-1} confirms the formation of the Zn-O-Co bond. The sharp peaks observed at 665 and 564 cm^{-1} represent the presence of Zn-O and Co-O stretching vibrations, respectively, for both the samples^(35–37).

3.3 Morphological analysis

The surface morphology and structural features of the ZCO samples were analyzed through FE-SEM analysis. The ZCO-Urea sample exhibits rod-like microstructures (Figure 3 (a)) with in homogeneous aspect ratios having an average length of several micrometres whose surface comprises several agglomerated nanoparticles. Further, when the urea is replaced by ammonium fluoride (NH_4F), the ZCO sample exhibit hexagonal-shaped microstructures. These microstructures are uniform-sized and consist of numerous irregular micropores formed during the sample's annealing treatment. The high aspect ratio and surface to volume ratios, and high porosity of uniformly distributed hexagonal microstructures provide more surface area to access the electrolyte, increasing the number of electroactive sites resulting in better charge transfer kinetics that leads to the improved electrochemical performance⁽³⁸⁾.

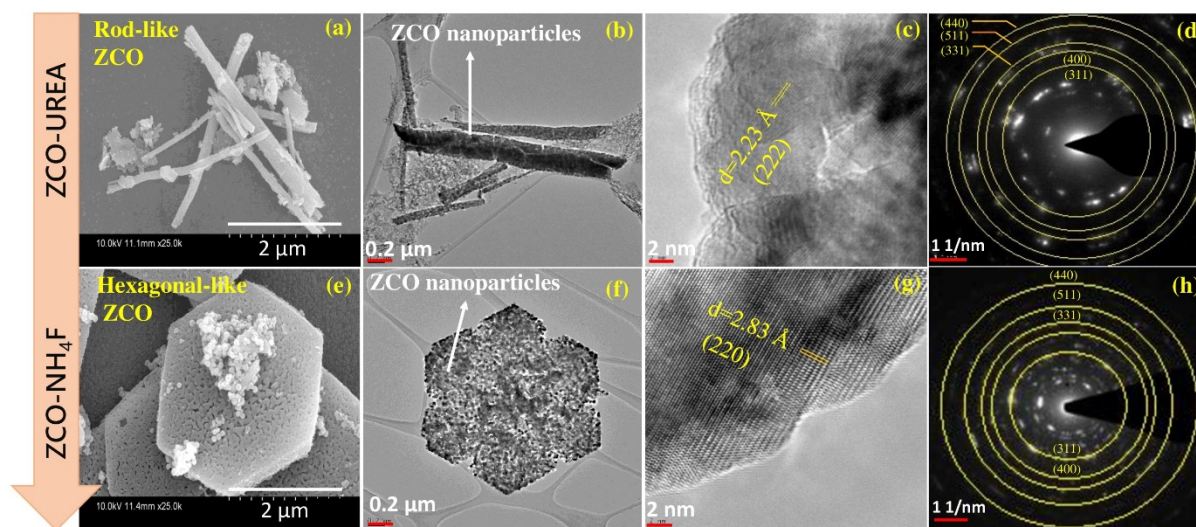


Fig 3. SEM (a, e), TEM (b, c, f, g) images and SAED pattern (d, h) of ZCO-Urea and ZCO- NH_4F , respectively

TEM and High-Resolution TEM analyses were carried out for the detailed evaluation of morphology for both rod-like and hexagonal-like structures of the as-prepared ZCO samples. From the TEM images (Figure 3(b, f)), it can be observed that a lot of ZCO nanoparticles aggregated to form rod-like microstructures, whereas most of the pure ZCO nanoparticles piled up to form hexagonal-like microstructures. The interplanar distance (d-spacing) and its corresponding lattice planes of both ZCO-Urea and ZCO- NH_4F were determined to be 2.23 \AA , 2.83 \AA , respectively, from the HR-TEM image. The porous nature of the hexagonal microstructures can be observed from the TEM analysis, inconsistent with the SEM analysis. The microstructures' porosity provides a more specific surface area and shortens the ion diffusion paths between the electrolyte and active material of the electrode. This improves the number of redox electroactive sites and their utilization ability, which leads to the enhanced electrochemical performance of the hexagonal-like microstructures of the ZCO sample. The selected area electron diffraction (SAED) pattern of both ZCO-Urea and ZCO- NH_4F samples exhibit regular diffraction fringes as shown in Figure 3(d) and (h) represent the polycrystalline nature of the as-prepared samples which is consistency with the XRD analysis^(39,40).

3.4 Mechanism

Surfactants play a crucial role in obtaining various microstructures. Growth process of nanomaterials occur in three main stages: nucleation, coalescence, and island formation. During hydrothermal treatment, the process of nucleation begins. After that, in the coalescence stage, small particles start to coagulate, which leads to the aggregation of particles. At this stage, surfactants

are used to control the aggregation rate and initiate morphological changes on the material's surface. During the process of nanoparticle synthesis, surfactants can be assembled into various forms such as monolayer micelles, spherical micelles, rod-like micelles, reverse micelles, and vesicle formation with single/multi-component⁽⁴¹⁾. A layer of H₂O surrounds the inorganic material of the precursor, and both particles and water droplets are attached with a single/multilayer surfactant. This leads to the formation of different morphological microstructures⁽⁴²⁾.

In this study, urea is used as a forced hydrolysis agent because of its water solubility at 80 to 100 °C, then gradually decomposes into NH₃ and CO₂⁽⁴³⁾. Also, NH₃ reacts with water to give NH_4^+ and OH^- . In the process of oxide crystal growth, fine crystal nuclei are formed. The nanoparticles of this oxide are precipitated due to the increase in pH by NH_4^+ ions generated from NH₃ from the decomposition of urea with increasing temperature. Hydrolysis of urea raises the pH due to the increased release of NH_4^+ from the solution. Under milder conditions and lower urea content, urea hydrolysis proceeds slowly, and primary solutions undergo supersaturation of metal hydroxide species. Thus, the formation of metal-hydroxide crystals occurs by the nucleation process in the crystal's desired growth direction. In addition, increasing the hydrothermal system's pressure and the formation of gas molecules disrupted the growth of crystals, leading to the formation of rod-like morphology^(44,45).

Since NH₄F is an acidic mineralizing agent, it has been used so far to increase the crystallinity and crystal size of various materials grown in the solution method^(46,47). In this study, the highly ordered hexagonal-like ZCO microstructure was obtained with the addition of NH₄F as shown in Figure 3(e, f). NH₄F can dissociate into NH_4^+ and F^- ions in precursor solutions and further increase the precursor's solubility and the chemical potential of the solution through F^- , which is more favorable for microstructure growth. Strong coordination of F^- ions with metal cations (Zn²⁺ and Co²⁺) reduce the rate of release of metal ions and further slows the nucleation rate of ZnCo₂O₄ precursors resulting in the aggregation of particles to the hexagonal-like morphology. F^- ion can improve ions' mobility by reducing the solution's viscosity^(48–50).

3.5 Electrochemical analysis

The electrochemical performance of as-prepared electrodes was evaluated to explore the advantages of the morphologies for the application of supercapacitors. The cyclic voltammetry (CV), chronopotentiometry (GCD), and electrochemical impedance spectroscopy (EIS) measurements were conducted using a three-electrode system with 1 M KOH as electrolyte solution at room temperature. Figure 4 (a), (b) shows the obtained CV curves of ZCO-Urea and ZCO-NH₄F samples, respectively, within the potential window of 0–0.6 V at different scan rates from 5 to 100 mV s^{−1}. A pair of reduction and oxidation peaks are observed for all the CV curves representing the materials' pseudocapacitive nature. For this, a couple of reduction and oxidation peaks are identified at 0.45 V and 0.49 V for ZCO-Urea microstructures and 0.39 V and 0.48 V for ZCO-NH₄F microstructures respectively for the scan rate of 5 mV s^{−1}. The ZCO-NH₄F electrode possesses a larger integral part surrounded by the CV curve and higher redox current density than that of the ZCO-Urea electrode. It represents the superior super capacitive performance of the ZCO-NH₄F electrode (Figure 4(c)).

Moreover, the oxidation and reduction peaks shift towards higher and lower potentials as the scan rate increases from 5 to 100 mV s^{−1}, indicating the reaction kinetics are reversible during the redox process due to the internal resistance polarization effect of the electrodes. The electrochemical reaction mechanism can be explained with the diffusion of OH^- ions into the electrode in 1M KOH electrolyte. The corresponding chemical equations associated with the faradaic redox reactions are represented as follows^(51,52).



Furthermore, to explain the process associated with the electrodes' electrochemical reactions, the relationship between the peak current and its corresponding square root of the scan rates is studied using the power law⁽²²⁾.

$$i = av^b \quad (9)$$

Where *i*, *v* are peak current and scan rates, respectively. The *a*, *b* are the appropriate constants. The value of the constants can determine the charge storage mechanism present in the reaction. If *b* = 0.5, represents the diffusion-controlled nature of the electrochemical process and if *b* = 1, represents the non-diffusion-controlled surface redox process⁽²²⁾.

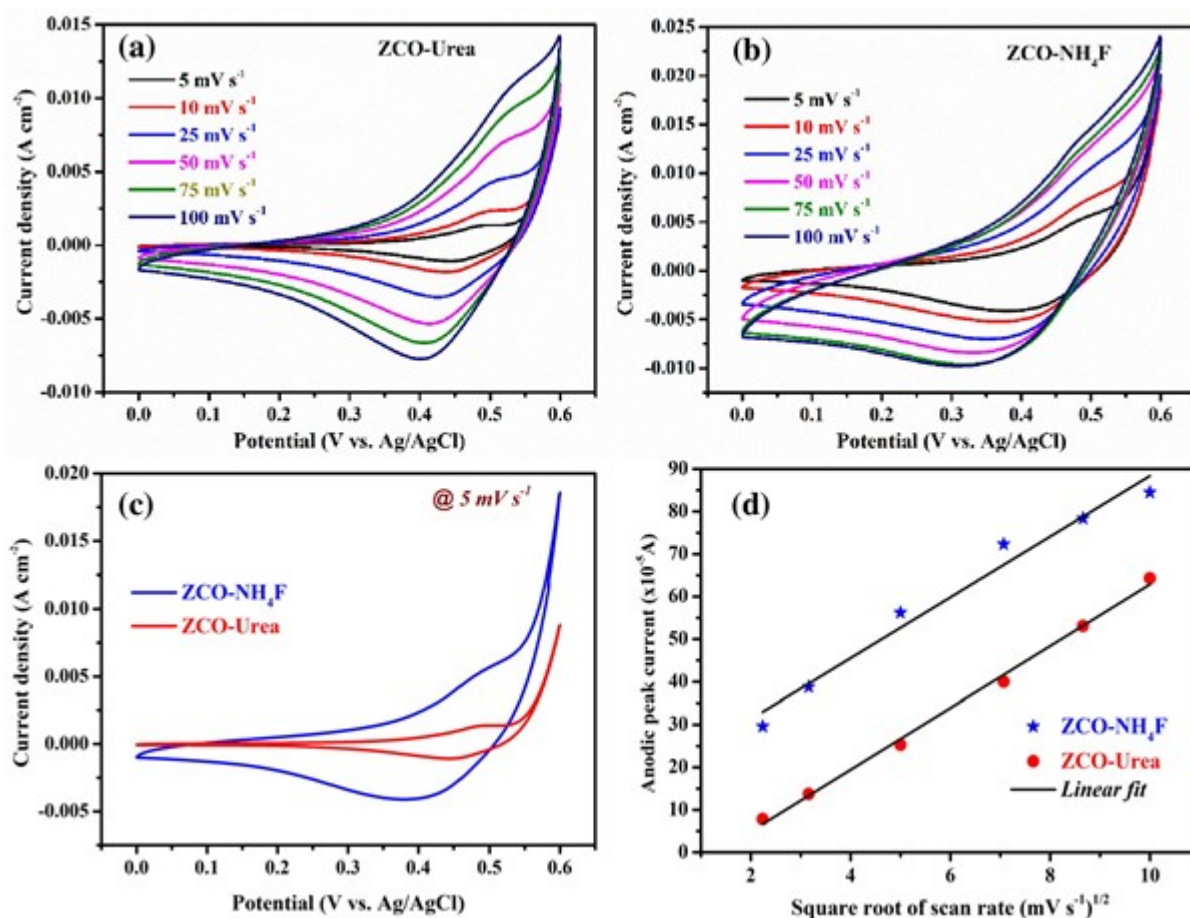


Fig 4. Cyclic voltammetry (CV) curves of ZCO-Urea (a) and ZCO-NH₄F (b) Comparison of CV curves obtained at the scan rate of 5 mV s⁻¹ (c), Anodic peak current vs. square root of corresponding scan rate plots of both ZCO-Urea and ZCO-NH₄F microstructures (d)

The anodic peaks of ZCO-Urea and ZCO-NH₄F electrodes in Figure 4 (d) have *b* values of 0.54, 0.58 respectively. Since these values are very close to 0.5, it confirms the diffusion-controlled electrochemical process of both electrodes. It is further evidenced by the linearity between the anodic peak current and the square root of their corresponding scan rates and the increase in the integral area surrounded by the cv curves with increasing scan rates⁽⁵³⁾. Further, the higher current responses of the ZCO-NH₄F electrode can be observed from the diffusion-controlled process plot compared to the ZCO-Urea electrode, which represents that the ZCO-NH₄F electrode possesses an excellent electrochemical performance⁽⁵⁴⁾. The GCD measurements were carried out to further evaluate the electrodes' electrochemical characteristics in the potential range of 0-0.4 V at various current densities of 10 to 1,000 $\mu\text{A cm}^{-2}$.

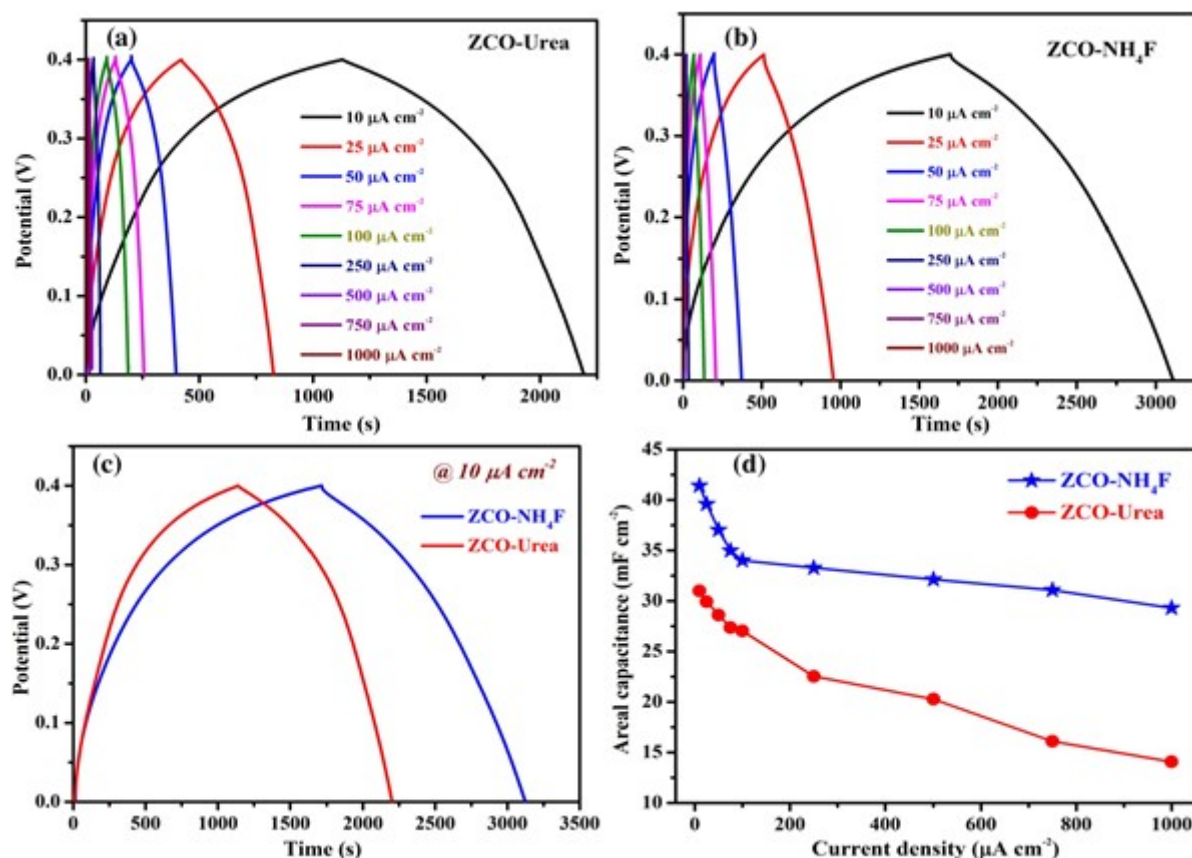


Fig 5. Galvanostatic charge-discharge (GCD) curves of ZCO-Urea (a) and ZCO-NH₄F (b). Comparison of GCD curves obtained at the current density of 10 $\mu\text{A cm}^{-2}$ (c) and variation of calculated areal capacitance values of both ZCO-Urea and ZCO-NH₄F as a function of various current densities (d)

The highly symmetric and non-linear GCD curves as shown in Figure 5 (a), (b) represent the fast-faradaic redox reactions that occurred at the interface of the electrode/electrolyte and ideal pseudocapacitive behavior, which is inconsistent with the CV analysis⁽⁵⁵⁾. The ZCO-Urea and ZCO-NH₄F samples' areal capacitance is calculated using the following formula⁽⁵⁶⁾.

$$C_s = \frac{I \times \Delta t}{S \times \Delta V}$$

Where I is the discharging current in Amperes, Δt is the discharging time in seconds, S is the area of the glassy carbon electrode in cm^2 , and ΔV is the potential drop during discharge in volts. An areal capacitance of 31.00, 29.94, 28.62, 27.37, 27.04, 22.54, 20.28, 16.11 and 14.08 mF cm^{-2} for ZCO-Urea and 41.43, 39.61, 37.04, 34.99, 34.02, 33.29, 32.14, 31.08 and 29.31 mF cm^{-2} for ZCO-NH₄F samples was obtained at the current densities of 10, 25, 50, 75, 100, 250, 500, 750 and 1000 $\mu\text{A cm}^{-2}$ respectively. The variation in the electrodes' areal capacitance with respect to the current density was represented in Figure 5(d). The decrease in the areal capacitance with an increase in the current densities is observed and can be attributed to the internal resistance, polarization of the electrodes, and the mechanical stress produced due to the insertion and removal of the electrolyte ions^(29,57). Further, a rate capability of 45.4% and 70.7% of initial capacitance was retained even when the current density increased from 10 to 1000 $\mu\text{A cm}^{-2}$ for ZCO-Urea and ZCO-NH₄F samples respectively. The areal capacitance of the two electrodes of the present work is compared with different transition metal oxides and their combinations and represented in Table 3. From the comparison, one can suggest them for the application of electrode material for supercapacitors.

The cyclic stability test was further used to investigate the supercapacitor performance of the electrodes. Figure 5(a) and (b) represents the cyclic stability of ZCO-Urea and ZCO-NH₄F samples for 1,000 continuous charge-discharge cycles at a constant current density of 500 $\mu\text{A cm}^{-2}$ in the potential range of 0–0.4 V. Impressively, 156.1% and 150.7% of initial areal capacitance were

Table 3. The areal capacitance of different metal oxides in comparison with present work

Different metal oxides and combinations	Synthesis method	Areal capacitance	Ref.
2D-LiCoO ₂	Electrochemical deposition	310 mF cm ⁻² @ 5 mV s ⁻¹	(58)
Hexagonal-like ZnCo ₂ O ₄	Hydrothermal	41.43 mF cm ⁻² @ 10 μ A cm ⁻²	Present
NiCo ₂ O ₄	Sol-gel method	40.6 mF cm ⁻² @ 0.133 mA cm ⁻²	(59)
Rod-like ZnCo ₂ O ₄	Hydrothermal	31.00 mF cm ⁻² @ 10 μ A cm ⁻²	Present
TiO ₂	Electrochemical anodization	23.24 mF cm ⁻² @ 2 mV s ⁻¹	(60)
Co(OH) ₂ /Ni	Electrochemical deposition	22.9 mF cm ⁻² @ 5 mV s ⁻¹	(61)
MnO ₂ /MoS ₂	Magnetron sputtering	22.4 mF cm ⁻² @ 0.1 mA cm ⁻²	(62)
sheet-like ZnCo ₂ O ₄	Hydrothermal	16.13 mF cm ⁻² @ 10 μ A cm ⁻²	(56)

retained for ZCO-Urea and ZCO-NH₄F samples respectively, after cycling for 1,000 cycles indicates the outstanding cycling stability of the as-prepared electrodes.

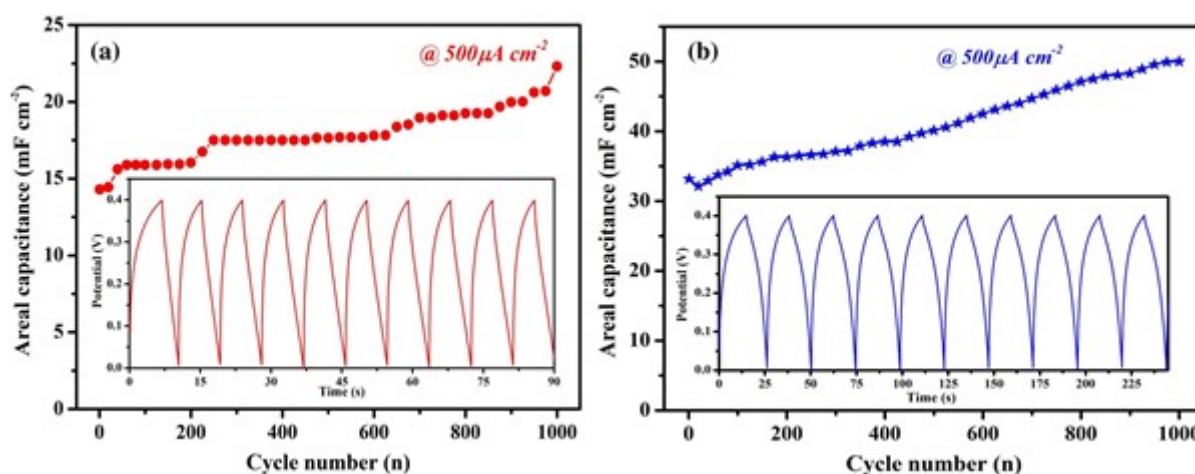


Fig 6. Cycling performance of ZCO-Urea (a) and ZCO-NH₄F (b) for 1,000 continuous charge-discharge cycles. (Insets of (a) and (b) represents GCD curves of the first ten cycles of ZCO-Urea and ZCO-NH₄F, respectively).

The increase in the electrodes' areal capacitance after cycling is due to the full activation of the electrode material. This activation occurs due to the slow insertion of the electrolyte solution into the bulk structure of the active material and the diffusion of more ions that create a more significant number of electroactive sites within the electrode material⁽⁶³⁾. A high symmetric nature in the shape of the GCD curves for the first ten charge-discharge cycles was observed for both ZCO-Urea and ZCO-NH₄F, as shown in the insets of Figure 6 (a) and (b), represents the superior reversible redox behavior of the electrodes⁽²⁹⁾.

To further study the two electrodes' electrochemical behavior, EIS was performed before and after conducting the cycling stability test within the frequency range of 0.001 Hz to 100 kHz at an open circuit potential with an AC perturbation of 5 mV amplitude. All the Nyquist plots exhibit a straight line in the low-frequency section and a semi-circle in the high-frequency area represented in Figure 7 (a) and (b).

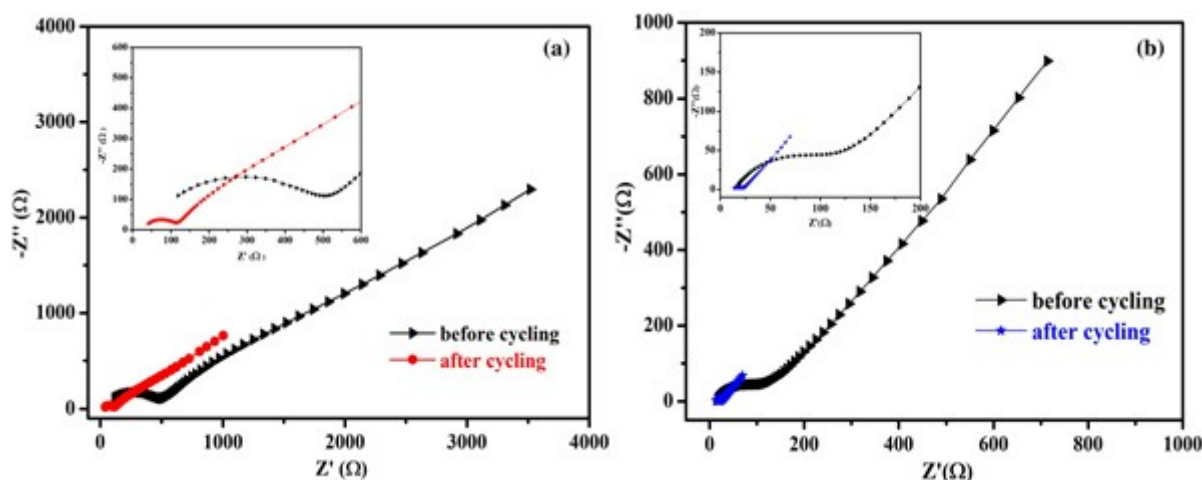


Fig 7. Nyquist plots of ZCO-Urea (a) and ZCO-NH₄F (b) before and after cycling for 1000 cycles. (Inset shows the magnified images of Nyquist plots of ZCO-Urea and ZCO-NH₄F, respectively).

Firstly, the internal resistance (R_s), which includes the electrolyte resistance, electrode resistance, and contact resistance at the electrode/electrolyte interface of the electrochemical system, was estimated at the intercept of the high-frequency region with the real axis. The R_s values are measured for both ZCO-Urea and ZCO-NH₄F samples are shown in Table 4. The ZCO-NH₄F electrode's R_s is lower than the ZCO-Urea electrode, indicating its good rate capability^(64,65). Secondly, the slope of the linear part of the Nyquist diagrams at the low-frequency region represents the Warburg impedance (W), associated with the ion's diffusion of electrolyte into the electrode surface. The lower slope of the straight line for both ZCO-Urea and ZCO-NH₄F samples after cycling indicates a gradual decrement in ion transfer rates between electrode and electrolyte that helps in utilizing more active material. However, the ZCO-NH₄F electrode shown less Warburg impedance represents its greater ions diffusion of electrolyte with the electrode surface than the ZCO-Urea electrode. Thirdly, the diameter semi-circle in the high-frequency section represents interfacial charge transfer resistance (R_{ct}) associated with the faradaic reactions. The decrease in the semi-circle diameter is observed after cycling in both the electrodes indicating their improved electronic conductivity (Table 4).

Table 4. Series resistance (R_s) and charge transfer resistance (R_{ct}) of ZCO-Urea and ZCO-NH₄F before and after cycling.

Resistance	ZCO-Urea		ZCO-NH ₄ F	
	Before cycling	After cycling	Before cycling	After cycling
R_s (Ω)	473	39.8	16.9	13.7
R_{ct} (Ω)	134.5	82.9	128.6	82.4

However, the lowest R_{ct} of the ZCO-NH₄F electrode shows its improved electronic conductivity than the ZCO-Urea electrode. The decrease in R_{ct} after cycling can be attributed to sufficient electrolyte penetration and wetting within the electrode's interior that helps for the rapid transportation of electrons, thus enhancing the electronic conductivity. These results conclude that the ZCO-NH₄F electrode, after cycling with desirable properties like fast ion transport rates and charge transfer kinetics shows excellent electrochemical properties^(36,66,67).

4 Conclusions

The hexagonal/rod-shaped ZCO microstructures were synthesized by replacing the surfactant in the reaction by a simple hydrothermal method followed by further annealing. The structural characteristics and morphology were assessed by XRD, FE-SEM, HR-TEM, and SAED analyses. ZCO's two different microstructures were evaluated as electrode materials for supercapacitors through electrochemical studies such as CV, GCD, and EIS. A high areal capacitance (41.43 mF cm⁻² for ZCO-NH₄F and 31.00 mF cm⁻² for ZCO-Urea at 10 μA cm⁻²) and superior cycling stability (150.7% for ZCO-NH₄F, 156.1% for ZCO-Urea of initial capacitance retained after 1,000 cycles) and good rate capability (70.7% for ZCO-NH₄F, 45.4% for ZCO-Urea when the current density was increased from 10 μA cm⁻² to 1,000 μA cm⁻²) were obtained for both the electrodes. The unique hierarchical architectures with porous material nature helped in obtaining the results mentioned above.

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