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Boosting charge storage in $ZnFe_2O_4$ nanostructures through morphological tuning using Fluoride-Ion Mediation ☆

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ABSTRACT

$ZnFe_2O_4$ (ZFO) nanostructures were synthesized via a hydrothermal method using NH_4F as a morphology-directing agent, enabling controlled evolution from spherical nanoparticles to uniform nanorods (50–100 nm length, 10–20 nm diameter). XRD confirmed the pure cubic spinel phase, while TEM/EDS verified the polycrystalline nature and stoichiometric Zn:Fe:O $\approx$ 1:2:4 composition. Electrochemical studies revealed that ZFO-0.12M-AF nanorods exhibited superior performance due to their anisotropic architecture, which promoted ion diffusion and enhanced redox activity. The nanorods delivered a high specific capacitance of 189 F/g at 11 A/g, with a 93 % diffusion-controlled contribution, improved diffusion coefficient, and reduced series resistance (1.7 Ω vs. 2.0 Ω at 0.03 M). They also achieved notable areal (3.16 F/cm^2) and volumetric (19.77 F/cm^3) capacitances. In an asymmetric device (ZFO-0.12M-AF//AC), the electrode delivered 8.23 Wh/kg at 539.32 W/kg with 89 % capacitance retention after 10,000 cycles. This study highlights NH_4F's dual role in morphology control and performance enhancement.

1. Introduction

Energy is a fundamental driver of modern development, yet the overreliance on finite fossil fuels has raised serious concerns regarding sustainability, energy security, and environmental impact. With global primary energy consumption reaching 157,064 TWh in 2019, the rising demand, particularly in developing nations, underscores the urgent need for efficient and sustainable energy storage systems. Renewable energy sources such as solar, wind, and hydroelectric power offer promising alternatives, but their intermittent nature necessitates the integration of advanced storage technologies [1–4]. Among these, supercapacitors (SCs) stand out for their high power density, rapid charge–discharge characteristics, and long cycling life, bridging the gap between conventional capacitors and batteries. Based on charge storage mechanisms, SCs are categorized into Electric Double-Layer Capacitors (EDLCs), relying on electrostatic adsorption at the electrode–electrolyte interface, and pseudocapacitors, which utilize fast, reversible redox reactions. While transition metal oxides like RuO_2, MnO_2, and NiO have demonstrated excellent pseudocapacitive performance [5–11], their cost and toxicity drive the exploration of cost-effective, eco-friendly alternatives [12–14].

In this context, zinc ferrite ($ZnFe_2O_4$) has emerged as a highly promising pseudocapacitive electrode material due to its natural abundance, non-toxicity, high theoretical capacitance, and excellent electrical conductivity. Its nanoscale morphology further enhances ion transport and redox activity, making it attractive for next-generation energy storage compared to other ternary transition metal oxides (TTMOs) such as $NiCo_2O_4$ [15], $Co_3V_2O_8$ [16], $Ni_3V_2O_8$ [17], $CuCo_2O_4$ [18], and $ZnCo_2O_4$ [19]. These metal oxides have been synthesized by various chemical and physical approaches, including the solvothermal method [20], sol–gel, co-precipitation [21], and hydrothermal synthesis [22]. Among these, hydrothermal synthesis is particularly effective for

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tailoring $ZnFe_2O_4$ nanostructures by precisely controlling particle size, crystallinity, and morphology. Beyond transition metal oxides, natural materials are also gaining increasing importance in energy storage research. Biopolymers such as cellulose, chitosan, and lignin have been investigated as green binders and electrolytes, while bio-derived nanofillers, including carbon nanostructures and clay-based materials, have been utilized to enhance the electrochemical stability and conductivity of electrodes in EDLCs and batteries. The incorporation of such sustainable and renewable materials not only reduces reliance on costly or toxic precursors but also aligns with the broader goal of environmentally responsible energy storage solutions [23–25].

This study focuses on the hydrothermal synthesis of $ZnFe_2O_4$ nanorods using ammonium fluoride (NH_4F) as a morphology-directing agent, a novel approach to fine-tuning surface properties and redox accessibility. We systematically investigate the interplay between NH_4F concentration, nanorod aspect ratio, and electrochemical performance, employing cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) to quantify pseudocapacitive contributions, diffusion coefficients, and charge transfer kinetics. Furthermore, we evaluate the practical viability of the optimized $ZnFe_2O_4$ electrode in an asymmetric supercapacitor (ASC) configuration paired with activated carbon (AC), assessing metrics such as energy density, power density, and long-term cycling stability.

2. Experimental

2.1. Materials

Zinc nitrate ($Zn(NO_3)_2$ (98 %), ferric nitrate ($Fe(NO_3)_3$ (98 %), ammonium fluoride (NH_4F) (98 %), urea ($CO(NH_2)_2$) (99 %), ethanol (C_2H_5OH) (95 %), and acetone (CH_3COCH_3) (98 %) were purchased from Loba Chemie Pvt. Ltd., Mumbai, India. Nickel foam was purchased from MTI, South Korea. Polyvinylidene fluoride (PVDF), N-methyl-2-pyrrolidone (NMP) (99 %), activated carbon, carbon black (CB), and potassium hydroxide (KOH) (99.95 %) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl) (30 %) was purchased from Daejung Chemicals, South Korea. All chemicals were used directly without further purification for the typical synthesis of ZFO nanostructures via a cost-effective and low-temperature hydrothermal method.

2.2. Synthesis of $ZnFe_2O_4$ nanostructures

The synthesis of zinc ferrite ($ZnFe_2O_4$) nanostructures was conducted via a hydrothermal method to investigate the influence of ammonium fluoride (NH_4F) as a morphology-directing agent. The synthesis of $ZnFe_2O_4$ nanoparticles via hydrothermal method were shown in scheme 1. Four distinct samples were prepared by systematically varying NH_4F concentrations (0.03 M, 0.06 M, 0.09 M, and 0.12 M) while maintaining fixed molar ratios of other precursors: 25 mM zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), 50 mM ferric nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), and 15 mM urea ($CO(NH_2)_2$), all dissolved in 80 mL deionized water. Urea acted as a precipitating agent, facilitating the formation of metal hydroxides, while NH_4F modulated crystal growth and nanostructure morphology. Each solution was magnetically stirred until homogenized, ensuring uniform precursor distribution. For hydrothermal synthesis, the mixtures were transferred into 100 mL Teflon-lined stainless-steel autoclaves, sealed, and heated at 140 °C for 10 h. After finishing reaction and natural cooling, the precipitates were washed repeatedly with deionized water and ethanol to remove unreacted ions and organic residues, ensuring purity. The washed products were dried at 80 °C for 12 h, and labelled ZFO-0.03 M−AF (30 mM NH_4F), ZFO-0.06 M−AF (60 mM NH_4F), ZFO-0.09 M−AF (90 mM NH_4F), and ZFO-0.12 M−AF (120 mM NH_4F). The dried powders were annealed in a muffle furnace at 400 °C for 3 h to enhance crystallinity and stabilize the spinel structure of $ZnFe_2O_4$, which is critical for electrochemical performance. Annealing eliminates residual organics, reduces lattice defects, and improves electrical conductivity and the final prepare nanoparticle were used for further study.

2.3. Material characterizations

The synthesized ZFO powder was systematically characterized using various analytical techniques. Crystalline structure was analyzed by X-ray diffraction (XRD) on a Rigaku Miniflex-600 diffractometer with Cu K_α radiation ($\lambda = 0.15425$ nm), scanned over the 2θ range of $10°$-$80°$. The morphology and elemental distribution were studied using field emission scanning electron microscopy (FE-SEM, Hitachi S4800) equipped with energy-dispersive spectroscopy (EDS). High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL

Scheme 1. Schematic representation of the hydrothermal synthesis of $ZnFe_2O_4$ nanoparticles at different concentrations of ammonium fluoride.

JEM-ARM200F NEOARM operating at 200 keV to further probe the nanostructure. Surface chemical states were examined by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific ESCALAB 250 system with Al K_α radiation. Electrochemical performance of the ZFO-AF electrodes was evaluated on a Wonatech ZIVE SP5 electrochemical workstation.

2.4. Electrode preparation and electrochemical study

The synthesized $ZnFe_2O_4$ (ZFO) nanoparticles were utilized to fabricate working electrodes for electrochemical analysis. For the positive electrode, ZFO nanoparticles were employed, while activated carbon (AC) served as the negative electrode. Both electrodes were prepared by mixing the active material (ZFO or AC), polyvinylidene fluoride (PVDF) binder, and carbon black (CB) in a mass ratio of 80:10:10 with N-methyl-2-pyrrolidone (NMP) as the solvent. The mixture was homogenized into a slurry via ultrasonication. Prior to electrode fabrication, nickel (Ni) foam substrates were cleaned with 2 M HCl to remove surface oxides, rinsed thoroughly with deionized water, and dried overnight at 60 °C. The slurry for both electrodes was drop-casted onto the pre-treated Ni foam substrates and dried in an oven at 60 °C for 12 h. Electrochemical characterization of the ZFO electrode was performed using a three-electrode system in 2 M KOH electrolyte, where a platinum (Pt) wire acted as the counter electrode, the ZFO-coated Ni foam as the working electrode, and an Ag/AgCl electrode as the reference. For the asymmetric supercapacitor (ASC), the optimized ZFO-0.12 M−AF electrode (positive) and AC electrode (negative) were immersed in 2 M KOH electrolyte. The two electrodes were separated by a Whatman filter paper soaked in the same electrolyte, and the assembly was encapsulated using parafilm. The electrochemical performance of the ASC, including cyclic stability and capacitance, was evaluated under controlled conditions.

3. Results and discussion

3.1. X-ray diffraction analysis

XRD analysis was performed to investigate the crystallinity and phase purity of the synthesized $ZnFe_2O_4$ (ZFO) nanostructures. Fig. 1 shows the XRD pattern of ZFO nanostructures synthesized via a one-step hydrothermal method. The presence of multiple peaks indicates the polycrystalline nature of the material. Major diffraction peaks were observed at 2θ values of 18.19°, 29.92°, 35.26°, 53.11°, 56.63°, and 62.21°, corresponding to the (111), (220), (311), (422), (511), and (440) crystallographic planes, respectively.

These peaks align well with the standard cubic ZFO structure (JCPDS card #22–1012, space group: Fd3m, space group number: 227), with lattice parameters calculated as a = b = c = 8.4 Å [26,27]. The peaks were observed at 24.16°, 33.18°, 35.65°, 49.48°, 54.09°, and 63.92°, corresponding to the (1 1 0), (121), (−1 1 0), (220), (231) and (−211) planes of Fe_2O_3 (JCPDS card #01–073-2234) and its intensity were decrease with increase molar concentration of the ammonium fluoride as reported in prior studies [28]. Additional peaks at 31.92° and 36.26° were attributed to ammonium hydrogen fluoride (NH_4HF_2). Notably, the intensity of these NH_4HF_2-related peaks increased with higher ammonium fluoride (NH_4F) molarity during synthesis. A slight peak shift at 36.26° was also observed, which correlated with improved electrochemical performance of the electrode.

Fig. 1. XRD pattern of the $ZnFe_2O_4$ nanoparticles at 0.03 M, 0.06 M, 0.09 M and 0.12 M concentration of the ammonium fluoride.

3.2. FE-SEM analysis

The surface characteristics and elemental composition of zinc ferrite ($ZnFe_2O_4$, ZFO) nanostructures synthesized via hydrothermal routes were systematically investigated using field electron scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDAX). These analytical techniques provided critical insights into the morphological evolution and chemical purity of the nanostructures as a function of ammonium fluoride (AF) molar concentration. Fig. 2**(a-d)** presents SEM micrographs of hydrothermally synthesized ZFO nanostructures at four distinct AF molar concentrations: 0.03 M (ZFO-0.03M−AF), 0.06M (ZFO-0.06M−AF), 0.09M (ZFO-0.09M−AF), and 0.12M (ZFO-0.12M−AF). Each sample was imaged at incremental magnifications of 10k, 40k, 60k, and 80k to resolve fine structural details. The SEM micrographs in Figs. 2(a) and 2(b) reveal that ZFO-0.03M−AF and ZFO-0.06M−AF nanoparticles exhibit predominantly spherical morphologies with an average particle size of ∼ 100 nm. These particles display moderate agglomeration, a common phenomenon in nanoparticle synthesis due to high surface energy and van der Waals interactions. However, the size distribution remains relatively homogeneous, suggesting that the hydrothermal reaction conditions-temperature (140°C), time and (10h), promote uniform nucleation and growth kinetics at lower AF concentrations. The spherical shape is consistent with the isotropic growth behavior of cubic spinel $ZnFe_2O_4$ under thermodynamic control, where minimization of surface energy favors symmetrical geometries. In contrast, Fig. 2(c) (ZFO-0.09M−AF) demonstrates a morphological transition from spherical to mixed spherical-rod structures. This evolution highlights the role of AF concentration in modulating crystal growth pathways. Ammonium fluoride acts as both a mineralizer and a structure-directing agent in hydrothermal synthesis. At higher concentrations (0.09M), the increased F^- ion availability alters the supersaturation ratio, promoting anisotropic growth. The rod-like structures likely arise from selective adsorption of F^- ions on specific crystallographic planes, which suppresses growth along certain axes while favoring elongation along others. This phenomenon aligns with the oriented attachment mechanism, where primary nanoparticles align and fuse along preferential crystallographic directions to form one-dimensional nanostructures. Fig. 2(d) (ZFO-0.12M−AF) further corroborates this trend, showing uniformly distributed nanorods with dimensions of 50–100 nm in length and 10–20 nm in diameter. The absence of spherical particles at this concentration underscores the dominance of kinetic control over thermodynamic equilibrium at elevated AF levels. The narrow size distribution of the nanorods suggests that the reaction system achieves a steady-state growth regime, where the rate of precursor depletion balances the growth rate. Such morphological precision is critical for applications requiring high surface-to-volume ratios, in energy storage.

The EDAX analysis Fig. 3**a-d** was performed to verify the elemental composition and stoichiometric integrity of the ZFO nanostructures. The spectra for all samples confirm the presence of zinc (Zn), iron (Fe), and oxygen (O) as the primary constituents, with no detectable impurities. Quantitative EDAX data reveal atomic ratios close to the theoretical stoichiometry of $ZnFe_2O_4$ (Zn:Fe:O ≈ 1:2:4). For instance, ZFO-

Fig. 2. FESEM micrograph at different magnifications of the (a1-a4) ZFO-0.03M−AF, (b1-b4) ZFO-0.06M−AF, (c1-c4) ZFO-0.09M−AF, (d1-d4) ZFO-0.12M−AF nanorods.

0.12M−AF exhibits atomic percentages of 14.2 % Zn, 28.5 % Fe, and 57.3 % O, deviating by less than 2 % from ideal values. This consistency validates the phase purity of the synthesized material and the efficacy of the hydrothermal method in preserving stoichiometric ratios. The transition from spherical nanoparticles to nanorods with increasing AF concentration can be rationalized through classical nucleation theory and growth kinetics. At lower AF concentrations (0.03–0.06M), the reaction medium has a lower ionic strength, leading to rapid nucleation and the formation of numerous small nuclei. These nuclei grow isotropically due to uniform diffusion of ions to all crystal facets, resulting in spherical particles. However, as AF concentration increases (0.09–0.12M), the elevated F^- ion concentration alters the interfacial energy of specific crystal planes. F^- ions adsorb preferentially on high-energy facets, effectively passivating them and forcing growth to occur along the crystal directions. This anisotropic growth is further amplified by the chelating action of NH_4^+ ions, which stabilize intermediate complexes and modulate the release of Zn^{2+} and Fe^{3+} ions into the solution.

3.3. TEM analysis

Transmission electron microscopy (TEM) was employed to further validate the morphological and structural characteristics of hydrothermally synthesized zinc ferrite ($ZnFe_2O_4$, ZFO) nanostructures. This technique provided nanoscale resolution to corroborate the findings from field electron scanning electron microscopy (FESEM), while also offering insights into crystallinity, elemental distribution, and phase purity. Fig. 4 presents a comprehensive TEM analysis of the ZFO-0.12M−AF nanostructures. Fig. 4**(a)–(c)** display bright-field TEM micrographs captured at progressively higher magnifications. The low-magnification image (Fig. 4a) reveals the overall morphology of the nanostructures, showing aggregated particles with irregular shapes. At intermediate magnification (Fig. 4b), the granular texture and porous architecture of the ZFO become apparent, consistent with the FESEM-derived morphological data. The high-resolution TEM (HRTEM) image in Fig. 4(c) resolves lattice fringes within individual crystallites. The presence of lattice fringes with varying orientations across adjacent crystallites confirms the polycrystalline nature of the synthesized ZFO nanoparticles, a characteristic attributed to the nucleation-dominated growth mechanism typical of hydrothermal synthesis. The selected-area electron diffraction (SAED) pattern (Fig. 4e) further substantiates the polycrystallinity of the material. The diffuse intensity distribution within the rings, rather than discrete spots, reflects crystallites nature of the ZFO, a feature common in nanoscale polycrystalline systems.

Elemental composition and spatial distribution were probed using TEM-coupled energy-dispersive X-ray spectroscopy (TEM-EDS). The EDS spectrum (Fig. 4d) exhibits distinct peaks for zinc (Zn), iron (Fe), and oxygen (O), with no extraneous peaks, confirming the absence of impurities. Quantitative analysis of the peak intensities yields an atomic ratio of Zn:Fe:O $\approx$ 1:2:4, consistent with the stoichiometry of $ZnFe_2O_4$. Fig. 4**(f)–(h)** show the elemental mapping profiles for Zn (red), Fe (green), and O (blue), respectively. The homogeneous spatial distribution of all three elements across the mapped region demonstrates the uniformity of the ZFO nanostructures. The color density gradients correlate with local elemental concentrations, revealing no phase segregation or elemental clustering, which further validates the phase

Fig. 3. EDS spectra of the (a) ZFO-0.03M−AF, (b) ZFO-0.06M−AF, (c) ZFO-0.09M−AF, (d) ZFO-0.12M−AF nanoparticles.

purity inferred from XRD and XPS. The polycrystalline nature of ZFO, evidenced by the lattice fringe orientations and SAED pattern, arises from the kinetic control inherent to hydrothermal synthesis. Under moderate temperatures and prolonged reaction times, nucleation occurs at multiple sites, leading to the formation of small crystallites that aggregate into larger particles. This growth mechanism minimizes interfacial energy but preserves the spinel framework, as reflected in the coherent lattice fringes and diffraction patterns. The absence of secondary phases in EDS mapping and the stoichiometric Zn:Fe:O ratio confirm that the hydrothermal conditions (precursor concentration, and temperature) were optimized to prevent the formation of competing phases such as ZnO or Fe_3O_4. The combined TEM-EDS results not only reinforce the XRD and XPS conclusions but also provide critical nanoscale evidence of the material's structural integrity. The consistency across multiple characterization techniques- FESEM (morphology), XRD (crystallographic phase), XPS (surface chemistry and oxidation states), and TEM (nanoscale structure and elemental distribution)-establishes a robust framework for confirming the successful synthesis of phase-pure, polycrystalline ZFO nanoparticles. These structural attributes are particularly advantageous for applications such as energy storage, homogeneous elemental distribution are critical. TEM analysis serves as a cornerstone for validating the structural and compositional properties of ZFO nanostructures. The HRTEM lattice imaging, SAED pattern, and EDS mapping collectively confirm the polycrystalline spinel phase, stoichiometric homogeneity, and absence of impurities, thereby underscoring the efficacy of the hydrothermal method in producing high-quality $ZnFe_2O_4$ for advanced functional applications.

3.4. *XPS analysis*

X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical composition and surface state of zinc ferrite ($ZnFe_2O_4$, abbreviated as ZFO) nanostructures synthesized via a simple hydrothermal method. The XPS analysis provided critical insights into the elemental composition, oxidation states, and bonding environment of the constituent elements, thereby corroborating the successful formation of phase-pure ZFO. Fig. 5(a) presents the XPS survey spectrum, which confirms the presence of iron (Fe), zinc (Zn), and oxygen (O) as the primary elements in the nanostructure. No extraneous peaks corresponding to impurities or contaminants were detected, indicating the high purity of the synthesized material. The characteristic peaks observed at binding energies of 529.5 eV, 710.4 eV, and 1021.3 eV are attributed to the O 1s, Fe 2p, and Zn 2p orbitals, respectively, aligning with the expected electronic transitions in a spinel-structured $ZnFe_2O_4$ lattice. A detailed examination of the Zn 2p core-level spectrum (Fig. 5b) reveals two distinct peaks centered at binding energies of 1021.3 eV and 1044.5 eV, corresponding to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ spin–orbit doublets [29–31]. The energy separation between these peaks is approximately 23 eV, a value consistent with the Zn^{2+} oxidation state in a spinel oxide framework. This observation strongly supports the incorporation of Zn^{2+} ions into the tetrahedral sites of the $ZnFe_2O_4$ structure, as predicted by its spinel configuration. Furthermore, the absence of satellite peaks or shifts in the Zn 2p spectrum suggests minimal surface defects or secondary phases, reinforcing the phase purity of the synthesized material. The Fe 2p core-level spectrum (Fig. 5c) exhibits two prominent peaks at 710.37 eV and 723.5 eV, assigned to the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ transitions, respectively [32]. The Fe $2p_{3/2}$ peak position at 710.37 eV, coupled with the absence of lower binding energy contributions, confirms the dominance of the Fe^{3+} oxidation state in the ZFO nanostructure. This is a hallmark of Fe^{3+} ions occupying octahedral coordination sites within the spinel lattice, as required by the stoichiometry of $ZnFe_2O_4$. The energy difference of $\sim$ 13.1 eV between the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks further validates the trivalent state of iron, which is characteristic of well-crystallized spinel ferrites. Additionally, the slight asymmetry in the Fe 2p peaks may arise from ligand-field effects or minor surface hydroxylation, though these do not detract from the overall conclusion that Fe exists predominantly in the $+3$ oxidation state. The O 1s spectrum (Fig. 5d) displays a strong,

Fig. 4. TEM image at different magnification (a-c), EDS spectra (d), SAED pattern (e), elemental mapping Zn (f), Fe (g) and O (h) of ZFO-0.12M−AF nanoparticles.

symmetrical peak at 529.55 eV, attributed to lattice oxygen (O_I) in the Zn-O-Fe framework. This binding energy is typical of metal–oxygen bonds in transition metal oxides and aligns with the oxygen environment in spinel-structured $ZnFe_2O_4$. A peak centered at 530.75 eV, attributed to surface oxygen (O_{II}), and a higher binding energy peak at 532.14 eV, ascribed to chemisorbed oxygen species (O_{III})[33,34]. The XPS findings are in excellent agreement with the X-ray diffraction (XRD) results, which previously confirmed the cubic spinel phase of $ZnFe_2O_4$. Specifically, the binding energies and spin–orbit splitting's observed in the Zn 2p, Fe 2p, and O 1s spectra match the electronic structure expected for $ZnFe_2O_4$, as reported in prior studies of spinel ferrites. The combined data conclusively demonstrate that the hydrothermal synthesis route yields phase-pure ZFO nanostructures without requiring post-treatment steps such as calcination. This underscores the efficacy of the hydrothermal method in producing well-defined spinel oxides with controlled stoichiometry and minimal defects. The XPS analysis not only validates the presence of Zn^{2+}, Fe^{3+}, and O^{2-} in the synthesized material but also provides atomic-level evidence of their bonding environment, oxidation states, and coordination geometry. These results, when integrated with XRD data, confirm the successful synthesis of high-purity $ZnFe_2O_4$ nanostructures via a facile hydrothermal approach, highlighting the method's potential for scalable production of spinel ferrites for applications in energy storage.

3.5. Electrochemical study

The electrochemical performance of zinc ferrite ($ZnFe_2O_4$, ZFO) nanostructures, synthesized via a hydrothermal route with varying

Fig. 5. XPS spectra Survey scan (a), Zn 2p (b), Fe 2p (c), and O1s (d) of the ZFO-0.12 M−AF nanoparticles.

molar concentrations of ammonium fluoride (NH_4F: 0.03 M, 0.06 M, 0.09 M, 0.12 M), was systematically investigated using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS).

Electrodes were prepared by depositing ZFO nanoparticles onto nickel foam substrates using a polyvinylidene fluoride (PVDF) binder (10 wt%), as detailed in the Materials section. Comparative analyses of these electrodes revealed significant correlations between NH_4F concentration, surface morphology, and energy storage performance. Fig. 6a displays CV profiles for all electrodes at a scan rate of 15 mV/s within a potential window of 0–0.6 V (vs. Ag/AgCl). The ZFO-0.12M−AF electrode exhibits the largest enclosed CV area, indicating superior charge storage capacity compared to ZFO-0.03M−AF, ZFO-0.06M−AF, and ZFO-0.09M−AF. This enhancement is attributed to its nanorod-dominated microstructure (50–100 nm length, 10–20 nm diameter), as confirmed by FESEM. The nanorods provide a high surface-to-volume ratio, which facilitate rapid electrolyte ion (OH^-) diffusion and expose abundant redox-active sites. The CV profile of the all electrode at different scan rated were shown in Fig. 7**(a-d)**. In contrast, electrodes synthesized with lower NH_4F concentrations (0.03–0.09 M) feature spherical nanoparticles (FESEM data in Fig. 2**a-c**) with agglomeration due to insufficient passivation of high-energy crystal facets. These agglomerates restrict electrolyte access and reduce effective surface area, resulting in smaller CV areas. The CV curves also reveal redox peaks at ~ 0.1 V and ~ 0.45 V (vs. Ag/AgCl), corresponding to reversible Faradaic reactions involving Zn^{2+}/Fe^{3+} redox couples:

$$ZnFe_2O_4 + OH^- + H_2O \leftrightarrow ZnO + 2FeOOH + e^- \tag{1}$$

The quasi-rectangular shape of the CV profiles confirms a hybrid charge storage mechanism combining electric double-layer capacitance (EDLC) and pseudocapacitance. Fig. 6b compares GCD curves for all electrodes at a current density of 11 mA/cm^2. The ZFO-0.12M−AF electrode demonstrates the longest charge–discharge duration, while ZFO-0.03M−AF shows the shortest. The GCD profile of the all electrode at different current density were shown in Fig. 8**(a-d)**. The extended duration for high-NH_4F electrodes correlates with their nanorod morphology, which enhances ion diffusion kinetics and reduces charge-transfer resistance. Specific capacitance (C_s), areal capacitance (C_a), and volumetric capacitance (C_v) were calculated using equation 2,3,4[19]:

$$C_s = \frac{I \times T_d}{m \times \Delta V} \tag{2}$$

$$C_a = \frac{I \times T_d}{A \times \Delta V} \tag{3}$$

$$C_v = \frac{I \times T_d}{V \times \Delta V} \tag{4}$$

Energy density ($ED_{s,a,v}$)= $\frac{\Delta V^2 \times C_{s,a,v}}{7.2}$ (5).

Power density ($PD_{s,a,v}$)= $\frac{3600 \times EDs,a,v}{T_d}$ (6).

where I = current density, T_d = discharge time, m = active mass (g), A = electrode area (cm^2), V = electrode volume (cm^3), and ΔV = potential window. ZFO-0.12M−AF achieves C_s =189 F/g, C_a = 3.16 F/cm^2,and C_v=19.77 F/cm^3,outperforming ZFO-0.03M AF(C_s=85 F/g, C_a=1.42 F/cm^2, C_v= 8.87 F/cm^3). The comparative specific capacitance, areal capacitance and volumetric capacitance of all electrode were shown in Fig. 6**d-f** with different current density. EIS Nyquist plots (Fig. 6c) reveal the impedance characteristics of all electrodes. The series resistance (R_s), derived from the x-intercept of the high-frequency semicircle, decreases progressively with increasing NH_4F concentration: R_s=2.0Ω (ZFO-0.03M−F), 1.77Ω (ZFO-0.06M−AF), 1.74Ω (ZFO-0.09M−AF), and 1.7Ω (ZFO-0.12M−AF). The reduced R_s for ZFO-0.12M−AF reflects enhanced electrode–electrolyte interaction due to its nanorod morphology, which minimizes interfacial resistance and improves charge transfer. Fig. 6**g-i** present Ragone plots comparing energy density (Wh/kg or mWh/cm^2) and power density (W/kg or mW/cm^2). ZFO-0.12M−AF achieves 7.96 Wh/kg at 181W/kg, significantly higher than ZFO-0.03M−AF (2.1Wh/kg at 85W/kg). This performance is attributed to the nanorods' ability to balance high surface area with efficient charge transport, enabling sustained redox reactions even at elevated power demands. FESEM images (Fig. 2) illustrate the structural

Fig. 6. Comparative CV profile (a), GCD profile (b), EIS spectra (c), specific capacitance (d), Areal capacitance (e), volumetric capacitance (f), Ragone plot corresponding to specific capacitance (g), corresponding to Areal capacitance (h), corresponding to volumetric capacitance (i) of $ZnFe_2O_4$ electrode at different molar concentration of the ammonium fluoride.

transition from agglomerated spherical nanoparticles (ZFO-0.03M−AF, ZFO-0.06M−AF) to uniform nanorods (ZFO-0.09M−AF, ZFO-0.12M−AF).

At low NH_4F concentrations (0.03–0.06M), limited F^- ions fail to passivate crystal facets, promoting isotropic growth and particle agglomeration. Higher NH_4F concentrations (0.09–0.12M) induce anisotropic growth by selective adsorption of F^- ions onto facets, resulting in elongated nanorods. The nanorods' dimensions (50–100 nm length, 10–20 nm diameter) provide optimal surface accessibility and shortened ion diffusion paths (<20 nm), which directly enhance capacitance and energy density.

Ammonium fluoride acts as both a mineralizer and structure-directing agent during hydrothermal synthesis. At high concentrations, F^- ions form stable complexes with Zn^{2+} and Fe^{3+} (e.g., $[ZnF_4]^{2-}$, $[FeF_6]^{3-}$), slowing nucleation rates and promoting oriented attachment into nanorods. Concurrently, NH_4^+ ions buffer the solution, stabilizing the spinel $ZnFe_2O_4$ phase against competing oxides like ZnO or Fe_2O_3. The electrochemical kinetics and charge storage mechanisms of $ZnFe_2O_4$ (ZFO)-based electrodes were systematically investigated using cyclic voltammetry (CV) to elucidate the interplay between diffusion-controlled and capacitive processes. Key parameters, including the b-value, diffusion coefficient (D), charge transfer rate constant (k^0), and transfer coefficient (α), were derived from CV profiles to quantify the redox behavior and ion transport dynamics. These analyses provided critical insights into the structural advantages of ZFO electrodes, particularly the nanorod morphology of the optimized ZFO-0.12M−AF electrode, which exhibited superior electrochemical performance. The charge storage mechanism was first evaluated using the power-law relationship (Equation7) [35,36]:

$i = a\cdot \nu^b$ (7).

where i is the peak current, ν is the scan rate, a is a proportionality constant, and b is an exponent determined from the slope of log(i) vs log (ν). The b-value distinguishes between diffusion-controlled (b=0.5) and capacitive (b=1.0) processes. For the ZFO-0.12M−AF electrode, a b-value of 0.37 (Figs. 9a,b) confirmed diffusion-dominated charge storage, attributed to its unique nanorod morphology. This structure facilitates rapid ion charging and discharging by providing short diffusion pathways. b-values (Table 1), reflecting greater capacitive contributions due to limited ion accessibility. To further resolve the contributions of capacitive and diffusion-controlled processes, the current deconvolution method (Equation8) was applied [37,38]:

$i(V) = k_1\cdot \nu + k_2\cdot \nu^{0.5}$ (8).

Here, k_1 represents the capacitive current (surface-controlled), while k_2 corresponds to the diffusion-limited current (bulk redox reactions). At 5 mV/s, the ZFO-0.12M−AF electrode demonstrated 93 % diffusion-controlled contribution (Fig. 9c), consistent with its low b-value. This dominance persisted across scan rates (Fig. 9d), though capacitive contributions increased marginally at higher scan rate as surface

Fig. 7. CV profile at different scan rate of the (a) ZFO-0.03M−AF, (b) ZFO-0.06M−AF, (c) ZFO-0.09M−AF, (d) ZFO-0.12M−AF electrode.

Fig. 8. CV profile at different current density of the (a) ZFO-0.03M−AF, (b) ZFO-0.06M−AF, (c) ZFO-0.09M−AF, (d) ZFO-0.12M−AF electrode.

adsorption became kinetically favorable. The diffusion coefficient (D) was calculated using the Randles-Sevcik equation (Equation (9) [39,40]:

$$i_p = 2.69 \times 10^5 \times \sqrt{n} \times A \times \sqrt{D} \times C\sqrt{\nu} \tag{8}$$

where i_p is the peak current, n is the number of electrons transferred, A is the electrode area, and C is the ion concentration. The ZFO-0.12M−AF electrode exhibited the highest D value among all tested electrodes (Table 1), attributed to its hierarchical nanorod architecture. This morphology enhances electrolyte penetration and reduces tortuosity, enabling faster ion diffusion. Comparatively, electrodes with irregular or dense structures showed lower D values due to hindered ion mobility. The reversibility of redox reactions was assessed using Laviron's theory, which relates the peak potential separation (ΔE_p) to k^0 and α (Equation (9) [40,41]:

p

Fig. 9. plot for b value (a,b) of $ZnFe_2O_4$ electrode, capacitive and diffusive current contribution at 5 mV/s scan rate (c), capacitive and diffusive current contribution at different scan rate (d) of ZFO-0.12M−AF electrode, plot for diffusion coefficient (e-f), plot for k^0 and α (g-h) of $ZnFe_2O_4$ electrode.

$$i_p = 0.227nFACk^0exp\left[-\left(\frac{\propto nF}{RT}\right)\left(E_p - E^0\right)\right] \tag{9}$$

For quasi-reversible systems, k^0 lies between 10^{-5} and 10^{-1} cm/s, and $0<\alpha<1$. The ZFO-0.12M−AF electrode exhibited k^0=0.00037492 cm/s and α=0.16 (Figs. 9g, h), confirming quasi-reversible redox behavior.

The nanorod structure likely enhances electron transfer kinetics by providing conductive pathways and active sites for redox reactions. In contrast, electrodes with poor crystallinity or defective surfaces showed lower k^0, indicating sluggish kinetics. The performance of ZFO-0.12M−AF stems from its nanorod network, which offers three key advantages nanorods, facilitates electrolyte interaction and accommodates volume changes during cycling. Nanorods shorten the path for ion transport, enhancing D. Interconnected rods promote electron transfer, improving k^0. Electrodes with spherical or aggregated particles lacked these features, leading to lower D and higher capacitive contributions. The dominance of diffusion-controlled processes in ZFO-0.12M−AF makes it ideal for battery-type electrodes, where bulk redox reactions are critical. However, the coexistence of capacitive contributions at high v suggests versatility in hybrid supercapacitor applications. The quasi-reversible kinetics further indicate stable cycling performance, as moderate k^0 values balance reaction rates with structural integrity. Through systematic CV analysis, the ZFO-0.12M−AF electrode demonstrated superior diffusion coefficients (D), quasi-reversible kinetics (k^0), and a predominantly diffusion-controlled charge storage mechanism. These properties are directly linked to its nanorod morphology, which optimizes ion/electron transport and redox activity. Impact of the ammonium fluoride underscores the importance of morphological engineering in tailoring electrochemical performance, providing.

To assess the practical viability of the ZFO-0.12M−AF electrode, an asymmetric supercapacitor.

3.6. Asymmetric supercapacitor (ASC)

ASC was assembled using ZFO-0.12M−AF as the battery-type positive electrode and activated carbon (AC) as the capacitive negative electrode. This configuration leverages the complementary charge storage mechanisms of the two materials: the ZFO electrode enables Faradaic redox reactions, while the AC electrode contributes electric double-layer capacitance (EDLC), thereby extending the operational voltage window and enhancing energy density. The ASC was fabricated between the two electrodes, as detailed in the experimental section. The operational voltage window of the ASC was determined by analyzing the individual stable potential ranges of the ZFO-0.12M−AF and AC electrodes via cyclic voltammetry (CV) (Fig. 10a).

Table 1

Comparative capacitance, energy density, b value, diffusion coefficient, Standard rate constant, Transfer coefficient of ZFO electrode.

Parameter	ZFO-0.03M−AF	ZFO-0.06M-AF	ZFO-0.09M−AF	ZFO-0.12M−AF
Specific capacitance (F/g)	97	149	168	189
Sepcific energy density(Wh/kg)	4.10	6.28	7.07	7.96
Areal Capacitance (F/cm^2)	1.6	2.5	2.8	3.1
Areal energy density (mWh/cm^2)	0.068	0.105	0.118	0.132
Volumetric capacitance (F/cm^3)	10.1	15.6	17.5	19.7
Volumetric energy density (mWh/cm^3)	0.428	0.656	0.738	0.830
b value	0.46	0.35	0.4	0.38
Diffusion coefficient (D) × 10^{-7}(cm^2/s)	0.96	5.30	5.31	6.14
Standard rate constant k0 × 10^{-4} (cm/s)	2.69	2.97	1.99	3.74
Transfer coefficient (α)	0.15	0.16	0.18	0.16

The ZFO electrode exhibited a redox-active window of 0–0.6 V (vs. Ag/AgCl), while the AC electrode showed capacitive behavior up to −1.0 V. The combined stable window of the ASC was thus set to 1.8 V (0–1.8 V), avoiding electrolyte decomposition. CV profiles of the ASC at scan rates from 10-90 mV/s (Fig. 10b) revealed quasi-rectangular shapes with redox humps, confirming hybrid charge storage (EDLC + pseudocapacitance). The retention of shape at higher scan rates indicated fast ion kinetics, attributed to the nanorod morphology of ZFO-0.12M−AF, which facilitates rapid charge transfer.

Galvanostatic charge–discharge (GCD) curves (Fig. 10c) at current densities of 16–24 mA/cm^2 displayed symmetric triangular profiles with minimal voltage drop (IR drop = 0.12 V at 10 A/g), underscoring low internal resistance and efficient charge storage. CV, GCD and EIS spectra of the AC were shown in Fig. 11**(a-c)**. The specific capacitance (C_s) of the ASC was calculated using equation (2),3,4). The ASC delivered a C_s of 18.31F/g at 16mA/cm^2, with areal and volumetric capacitances of 1.42F/cm^2 and 24.6F/cm^3, respectively (Figs. 10d,f) and volumetric capacitance were shown in Fig. 11d. A comparative analysis of the electrochemical properties of the ASC with previously reported devices is presented in Table 2.The energy density (ED) and power density (PD) were derived using equation 6,7. At 16 mA/cm^2, the ASC achieved an energy density of 8.23 Wh/kg at a power density of 539.32 W/kg (Figs. 10e,g). The Ragone plot of ASC corresponding to specific capacitance and areal capacitance were shown in Figs. 10e,g and corresponding to volumetric capacitance shown in Fig. 11e. Cyclic stability, a critical metric for real-world deployment, was evaluated over 10 k GCD

Fig. 10. CV profile of AC and ZFE-0.12M−AF (a), CV profile at different scan rate (b), GCD profile at different current density (c), specific capacitance (C_s) at different current density (d), Ragone plot corresponding to C_s (e), Aral capacitance (C_a) at different current density (f), Ragone plot corresponding to C_a (g), Cyclic stability over 10 k GCD cycles (h), EIS spectra before and after cyclic stability (i) of ASC.

Fig. 11. GCD profile (a), CV profile (b), EIS spectra (c) of AC, volumetric capacitance (C_v) (d), Ragone plot corresponding to C_v (e) of ASC.

Table 2

Comparative analysis of the electrochemical properties of symmetric supercapacitor devices.

Compound	Electrolyte	Potential range (V)	Energy density (Wh/kg)	Power density (W/ kg)	Reference
ZFO-1.2 M−AF//AC	2 M KOH	0 to1.8 V	8.23	539.32	Present work
ZFO-ACF	2 M KOH	0 to 1.1 V	7.6	523.6	[42]
Carbon	L-KOH	0 to 1 V	7.4	200	[43]
ZFO/rGO	2 M KOH	0 to 1.2 V	6.7	300	[13]
$ZnFe_2O_4$/NRG	1 M KOH	0 to 1.2 V	6.7	3000	[44]
AC//AC	BMIMCl:EC:PC:$TEABF_4$	0 to 1 V	5.6	1660	[45]
ZFO/FLGR carbon	3 M KOH	0 to 0.5 V	5.42	5.00	[46]
ZFO	PVA-$LiClO_4$	0 to 1	4.5	277	[47]
$Co(OH)_2$	L-1 M KOH	0 to 1.2 V	3.96	42(kW/kg1	[48]
AC//AC	MC-NH_4NO_3-PEG	0 to 0.85 V	3.9	140	[49]
MnO_2	L-$LiPF_6$	0 to 1 V	3.4	370	[50]
AC//AC	PS-MC-NH_4NO_3-GL	0 to 1 V	2.2	385	[51]
AC//AC	CS-MC-NH_4I-GL	0 to 0.9 V	1.1	578	[52]
AC//AC	C:St:$LiClO_4$:SiO_2	0 to 1 V	0.9	135	[53]
AC//AC	PVA:$LiClO_4$:TiO_2	0 to 1 V	0.36	1.56	[54]

cycles at 30 mA/cm^2 (Fig. 10h). The ASC retained 87 % of its initial capacitance with a near-ideal Columbic efficiency of 99 %, indicating minimal parasitic reactions. The gradual capacitance fade (13 % over 10k cycles) aligns with typical pseudo capacitive materials and is attributed to partial dissolution of active material or subtle structural rearrangements in the ZFO nanorods. Post-cycling electrochemical impedance spectroscopy (EIS) (Fig. 10i) revealed an increase in series resistance (R_s) from 0.73Ω to 1.05Ω and charge transfer resistance (R_{ct}) from 0.26Ω to 1.73Ω, likely due to electrode surface passivation or electrolyte dry-out. However, the low absolute R_s values confirm sustained ionic conductivity, validating the electrode's mechanical and electrochemical resilience. The superior performance of ZFO-0.12M−AF stems from its nanorod morphology, synthesized via a hydrothermal route with 0.12M ammonium fluoride (NH_4F) as a structure-directing agent. NH_4F promotes anisotropic growth by selectively etching certain crystal planes, yielding high-aspect-ratio nanorods (Fig. 2d). This morphology provides: Short Ion Diffusion Paths: Reduced diffusion length enhances D (Table 1). Nanorods Facilitates electrolyte access and redox site utilization. Mechanical Robustness: Interconnected rods mitigate pulverization during cycling. The ZFO-0.12M−AF//AC ASC demonstrates excellent energy storage capabilities. Its high energy density (8.23 Wh/kg), cyclability (87% retention), and rapid charge–discharge kinetics position it as a promising candidate for grid storage, EVs, and portable electronics. This study underscores the pivotal role of morphological engineering in advancing hybrid energy storage systems.

4. Conclusion

This study demonstrates that controlled hydrothermal synthesis using NH_4F as a morphology-directing agent enables precise tuning of $ZnFe_2O_4$ nanostructures from spherical nanoparticles to uniform nanorods, with the optimized ZFO-0.12M−AF sample exhibiting superior electrochemical performance. The nanorod architecture enhanced ion diffusion, lowered series resistance, and delivered a high specific capacitance of 189F/g, alongside excellent areal and volumetric capacitances. When integrated into an asymmetric supercapacitor with activated carbon, the electrode achieved an energy density of 8.23 Wh/kg with 89 % retention after 10,000 cycles, underscoring both high performance and durability. Despite these promising results, limitations remain. The specific capacitance, while improved, is still lower than theoretical values, suggesting incomplete utilization of active sites. In addition, the hydrothermal synthesis requires precise control of NH_4F concentration and reaction parameters, which may pose challenges for large-scale production. Future work should focus on hybridizing $ZnFe_2O_4$ nanorods with conductive carbons or biopolymer-based binders to further enhance charge transport and mechanical stability. Expanding this strategy to other transition metal oxides and exploring scalable, green synthesis approaches will be crucial for translating these findings into practical next-generation energy storage systems.

CRediT authorship contribution statement

A.B. Bhorde: Data curation. **M.A. Yewale:** Conceptualization. **S.B. Madake:** Data curation. **A.A Jadhawar:** Formal analysis. **A.A. Al-Kahtani:** Data curation. **DK. Shin:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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