



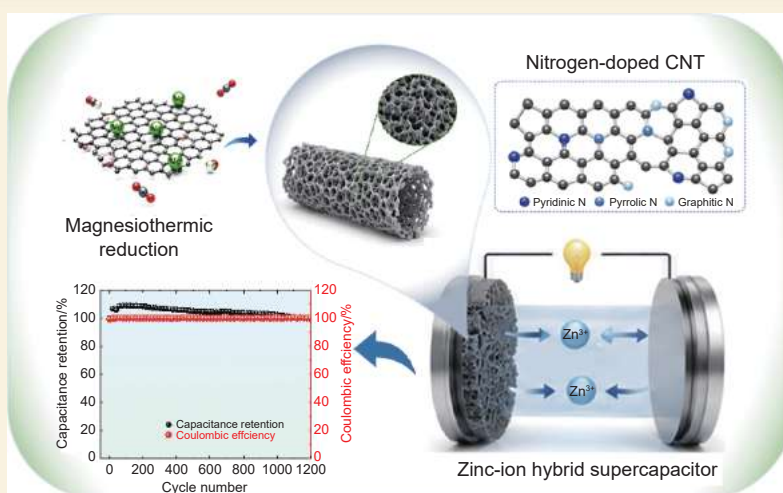
Nitrogen-doped carbon nanotube foams prepared by a modified magnesiothermic reduction reaction for zinc-ion hybrid supercapacitors

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Abstract: Carbon-based materials are promising candidates for the cathode of zinc-ion hybrid supercapacitors (ZHSCs) because of their excellent electronic conductivity, outstanding chemical stability, low toxicity, and environmental sustainability. However, the limited capacitance of conventional porous carbon cathodes and the mismatch in the charge-storage capacity between carbon cathodes and Zn metal anodes remain major challenges for their practical development. We report a green and scalable one-step modified magnesiothermic reduction strategy for the direct synthesis of nitrogen-doped carbon nanotube foam (N-CNTF) using CO₂ and urea as the carbon and nitrogen sources, respectively. During the reaction, the thermal decomposition of urea releases NH₃, which induces the selective etching of carbon nanotube walls to form pores while enabling nitrogen doping of the carbon framework. ZHSCs assembled with a N-CNTF cathode have an ultrahigh areal capacitance of 2501.51 mF cm⁻² at a current density of 1 mA cm⁻², along with an excellent cycling stability, retaining 79.9% of its initial capacity after 10 000 cycles at 20 mA cm⁻². This work provides a sustainable and efficient route for converting CO₂ into high-value nitrogen-doped porous carbon electrodes and offers a promising strategy for the scalable development of next-generation aqueous energy-storage systems.

Key words: CNT; Porous carbon materials; Magnesiothermic reduction; Nitrogen-doped; Zinc-ion hybrid supercapacitors



1 Introduction

Aqueous zinc-ion hybrid supercapacitors (ZHSCs) have garnered widespread attention due to their advantages of metallic zinc anodes, including high theoretical capacity, low redox potential, low cost, and environmental friendliness. They may be the most promising energy storage device alternatives for portable and large-scale electronic devices in the future^[1–2]. However, the cathode capacity of aqueous ZHSCs, originating from particularly carbon-based materials (porous carbon, graphene), fails to match the high theoretical capacity of the zinc anode, which re-

stricts the development and practical applications of aqueous ZHSCs^[3–6]. Even though carbon-based materials possess a large specific surface area and porous structure, the electrical double-layer capacitance (EDLC) capacity based on a reversible physical adsorption/desorption mechanism has a certain upper limit. Consequently, the design and creation of suit-

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able porous carbon-based cathode materials with rational pore architectures, abundant active sites, and superior conductivity continue to be the most difficult obstacles to enhance the energy storage performance of ZHSCs^[7–10]. Current methods for preparing porous carbon-based materials are often hindered by complex procedures, long processing times, and harsh reaction conditions (e.g., strong acid/base treatments, temperatures exceeding 1000 °C), making it difficult to achieve a balance between environmental friendliness and electrochemical performance^[11].

As a classical chemical reduction method, the magnesiothermic reduction reaction offers distinct advantages in the synthesis of functional carbon materials^[12]. By leveraging the strong reducing capability of magnesium, this reaction enables the direct conversion of carbon-containing gases such as CO₂ into solid carbon under relatively mild conditions, facilitating not only the valorization of greenhouse gases but also aligning with the strategic goals of carbon peak and carbon neutrality. Ma et al. have demonstrated that by controlling the reaction temperature, carbon materials with diverse morphologies, such as graphene, carbon nanotubes, and hollow carbon nanoboxes, can be synthesized from CO₂. They further elucidated the critical role of interfacial reaction in governing the nucleation and growth of these carbon materials. The resulting graphene achieved an energy density of up to 80 Wh/kg in supercapacitors, significantly outperforming conventional activated carbon^[13]. Wang et al. introduced a modified magnesiothermic reduction approach using nickel foam as a template to directly construct three-dimensional (3D) interconnected carbon nanotube foams from CO₂^[14–16]. These foams exhibit both excellent conductivity and light-weight characteristics. When composited with Ni(OH)₂, the hybrid electrode delivered a high specific capacitance of 259 F/g in 6 mol/L KOH electrolyte, along with favorable rate capability and cycling stability^[17]. Ji et al. refined the substrate design through the in-situ growth of flexible three-dimensional carbon nanotube foams on carbon cloth, enabling active material coatings with mass loadings of more than 10 mg/cm²^[18]. Such

high mass loadings are particularly important for practical ZHSCs^[19]. Furthermore, through the precise tuning of surface oxygen functional groups via a mild air activation strategy, the optimized material exhibited remarkable improvements in specific surface area, porosity and electrolyte wettability. The assembled flexible quasi-solid-state zinc-ion hybrid capacitor achieved a high areal capacitance of 1635.7 mF/cm² at a current density of 1 mA/cm² and maintained excellent electrochemical stability even under bending conditions^[20].

Despite the outstanding performance of carbon materials prepared via these methods, studies on achieving heteroatom doping in a single-step magnesiothermic reduction process remain less-reported, even though this represents a crucial pathway for enhancing the capacitance of carbon-based materials^[21–23]. The incorporation of heteroatoms such as nitrogen, phosphorus, and sulfur could modulate the electronic structure of the carbon framework, introduce additional defect sites, improve surface wettability, and contribute extra pseudocapacitance through Faradaic redox reactions^[24–25]. For instance, Liu et al. prepared nitrogen/phosphorus/oxygen co-doped hierarchical porous carbon via a molecular engineering strategy, achieving a high specific capacity of 139.2 mAh/g in Zn²⁺ hybrid capacitors^[26]. Jin et al. synthesized boron/nitrogen co-doped carbon nanosheet superstructures using a template-directed approach, and the assembled zinc-ion hybrid capacitors exhibited outstanding rate capability (84.5 mAh/g retained at 30 A/g) and exceptional cycling stability (98.7% capacity retention after 30 000 cycles), attributed to the synergistic effect of boron and nitrogen co-doping^[27]. However, these methods often involve complex multi-step synthesis and post-treatment processes, and the resulting products are typically in powder form, requiring the addition of binders and conductive agents before coating the porous carbons onto current collectors. This not only introduces dead mass into the electrode but also adds additional interfacial resistance. Therefore, the development of a green, facile preparation method that enables one-step

in situ heteroatom doping and the formation of 3D self-supporting carbon materials is of great significance for advancing high-performance energy storage devices.

Herein, a modified magnesiothermic reduction strategy is developed to realize nitrogen doping of carbon nanotube foams (N-CNTF). In contrast to previously reported CNT foams and N-doped carbon cathodes, this method is green, facile, and one-step, using urea and CO_2 (a greenhouse gas) as the N and C sources, respectively. The resulting N-CNTF maintains a robust 3D interconnected conductive network and a self-supporting structure, unlike the powder form commonly obtained for N-doped porous carbon cathodes in previous studies. Meanwhile, nitrogen incorporation enriches the electrochemically active sites and introduces significant pseudocapacitive contributions. The impact of nitrogen doping level, tuned via the urea dosage, on the morphological evolution, structural integrity, hydrophilicity, and electrochemical properties of the carbon nanotube foams is systematically examined. A zinc-ion hybrid supercapacitor based on this architecture delivers an exceptional areal capacitance of 2501.51 mF/cm^2 at 1 mA/cm^2 and retains 79.9% of its initial capacity after 10 000 cycles, highlighting a promising pathway toward high-performance energy storage.

2 Experiment

2.1 Substrate activation and catalyst immersion

Initially, carbon cloth (CC) was ultrasonically cleaned sequentially in acetone, ethanol, and deionized water for 30 min each solvent, followed by repeated rinsing with deionized water and drying in a vacuum oven at 60°C for 24 h. Subsequently, the CC was subjected to air activation in a muffle furnace, where it was heated to 450°C at a heat ramp rate of 2°C min^{-1} , held at that temperature for 6 h, and then naturally cooled to room temperature. The activated CC (ACC) was then immersed in the catalyst solution for 20 min. The catalyst solution was prepared according to our previously reported method^[18]. After immersion, the ACC was removed from the solution and

dried in an oven at 60°C for 30 min.

2.2 One-step fabrication of nitrogen-doped carbon nanotubes

First, 1.5 g of magnesium powder was uniformly spread in an alumina boat ($20 \text{ cm} \times 60 \text{ cm} \times 90 \text{ mm}$). A piece of ACC ($3 \text{ cm} \times 3 \text{ cm}$) pre-coated with catalyst precursors was placed flat on top of the magnesium powder. This boat was then positioned at the center of the high-temperature zone on the outlet side of a two-zone tube furnace (OTF-1200X, Hefei Kejing Materials Technology Co., Ltd.). Separately, a specific amount of urea was evenly distributed in another alumina boat and placed in the low-temperature zone on the inlet side of the furnace. The furnace was heated to 800°C at a ramp rate of 2°C/min under an Ar/H_2 atmosphere with a flow rate of 50 mL/min and held at this temperature for 1 h. Subsequently, CO_2 gas was introduced with a flow rate of 50 mL/min for 0.5 h to initiate the growth of carbon nanotubes. After the reaction, the CO_2 flow was stopped, and the furnace was cooled to room temperature under an Ar/H_2 atmosphere. The resulting 3D N-doped carbon nanotubes were obtained by etching away NiO, MgO and Al_2O_3 in a 3 mol/L HCl aqueous solution for 24 h. The product was then gently rinsed several times with deionized water until the pH of the rinse solution became neutral, and finally dried thoroughly in a vacuum oven at 60°C for 24 h. Depending on the amount of urea used, the resulting N-doped CNT foams were designated as N-CNTF-1, N-CNTF-2 and N-CNTF-3, corresponding to urea additions of 2, 4 and 6 g, respectively.

3 Results and discussion

Nitrogen-doped carbon nanotube foams (N-CNTF) were fabricated via a one-step magnesiothermic reduction method (Fig. 1). Before synthesis, the CC was subjected to activation treatment and catalyst immersion. The activation process significantly improved the surface pore structure and hydrophilicity of the CC (Fig. S1). The activated carbon cloth loaded with magnesium catalyst precursors served as the supporting substrate for the growth of three-dimension-

ally interconnected carbon nanotubes. During heating, the catalyst precursors were converted into catalytically active nanoparticles. When the temperature reached 800 °C, the magnesium powder began to melt, while the urea introduced at the inlet underwent thermal decomposition. In the reaction, CO₂ was reduced by magnesium, leading to the direct synthesis of carbon nanotubes within the interstices of the ACC. Concurrently, the decomposition of urea generated ammonia, which etched the carbon under high-temperature conditions, enabling in-situ nitrogen doping and the formation of additional micro- and mesopores. After removal of the byproducts (NiO, MgO and Al₂O₃), hierarchically structured N-CNTF was obtained.

The amount of urea added significantly influences the morphology, pore structure, hydrophilicity and electrochemical performance of the N-CNTF. The microstructure of the samples was characterized by scanning electron microscopy (SEM) (Fig. 2a-c). The macroscopic morphologies of the N-CNTF obtained with different amounts of urea generally show the same morphology, all exhibiting a 3D interconnected hierarchical structure composed of ultralong carbon nanotubes. Such a structure maintains good self-supporting capability and provides interconnected chan-

nels for rapid ion transfer during the charging and discharging process^[19]. At higher magnification, distinct changes in the surface morphology of the carbon nanotubes are observed with increasing urea content. For N-CNTF-1 (Fig. 2a), the nanotube surfaces show slight roughening, with localized fine nanoscale protrusions or shallow pits, indicating mild etching by urea decomposition products (NH₃). When the urea content increases to 4 g (N-CNTF-2), the surfaces become considerably rougher, with a high density of nanoscale pores, forming a well-developed hierarchical porous structure (Fig. 2b). This is primarily attributed to the selective etching of carbon by NH₃ at elevated temperatures, where NH₃ preferentially reacts with structural defects and the regions of low crystallinity^[28-29]. When the urea content is further increased to 6 g (N-CNTF-3, Fig. 2c), the surface morphology evolves into a distinct scaly structure, containing numerous macropores.

To further investigate the microstructural evolution induced by activation, additional TEM and HRTEM analyses were performed on both N-CNTF-1 and N-CNTF-2 samples (Fig. S2). The TEM images reveal that both materials maintain a tubular carbon nanotube morphology, while N-CNTF-2 exhibits a significantly roughened outer surface compared with

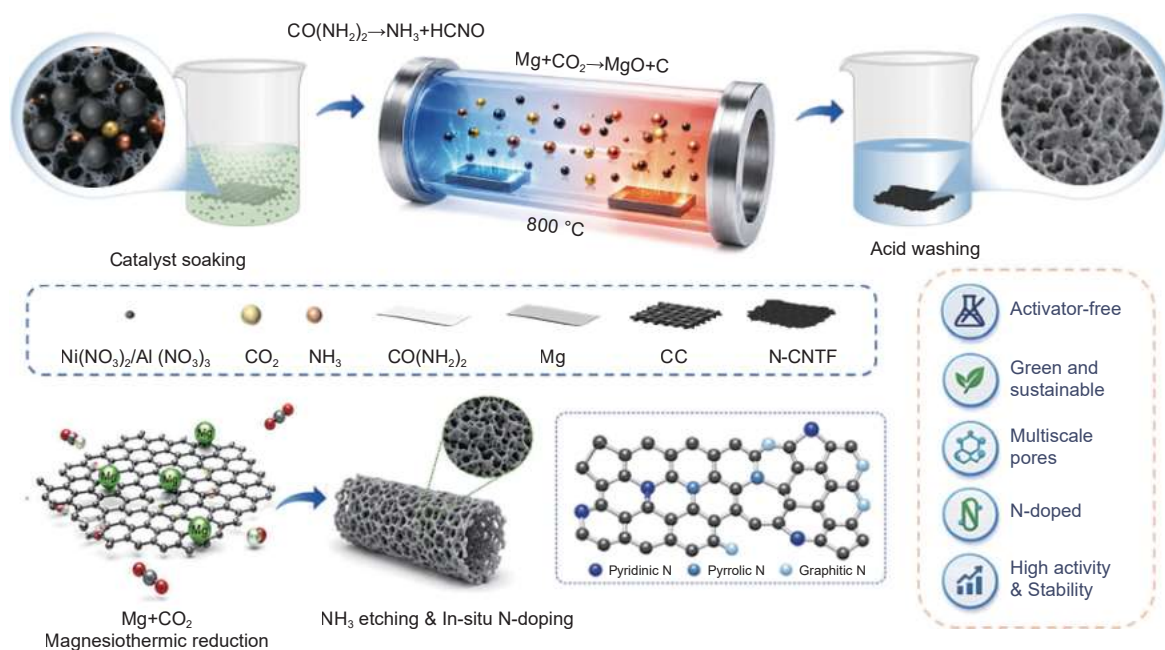


Fig. 1 Schematic illustration of the magnesiothermic reduction process for the synthesis of N-CNTF by an in-situ nitrogen doping strategy

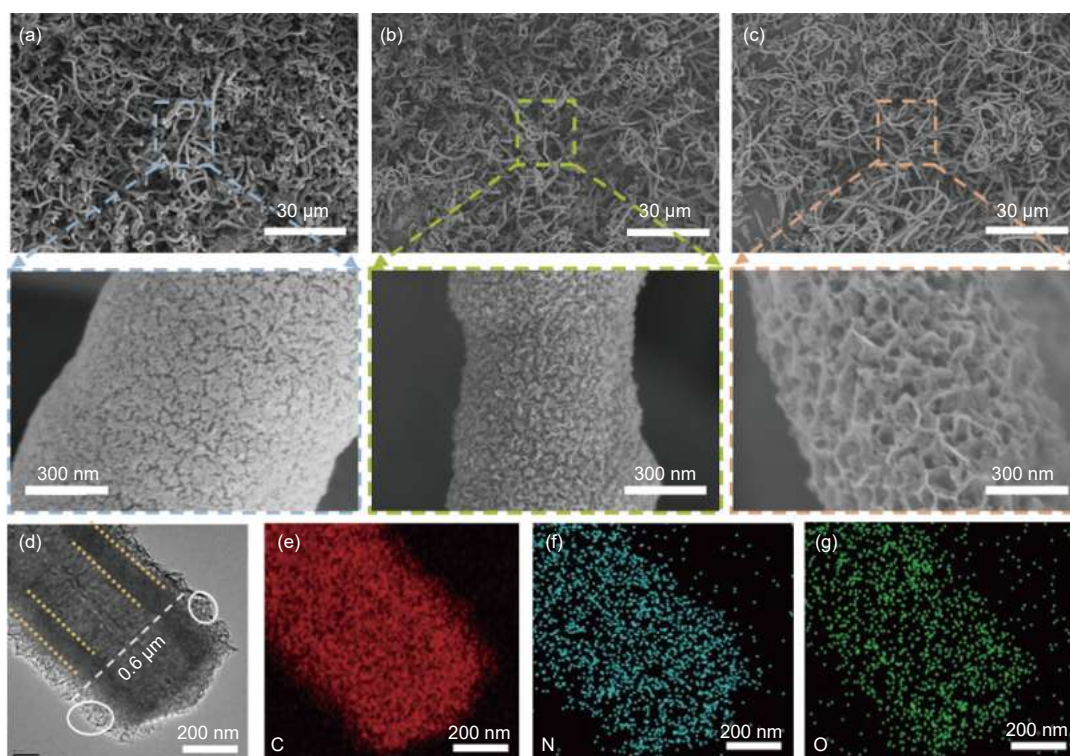


Fig. 2 SEM images of (a) N-CNTF-1, (b) N-CNTF-2 and (c) N-CNTF-3. (d) TEM image of N-CNTF-2. Elemental mapping images of (e) C, (f) N and (g) O

N-CNTF-1, indicating the occurrence of activation-induced surface reconstruction. High-magnification TEM images further show that the activation process generates a porous and defect-rich outer region surrounding the nanotube framework. HRTEM images provide further insight into the structural changes after activation. The pristine N-CNTF-1 displays relatively continuous and well-aligned graphitic lattice fringes, suggesting a higher degree of graphitic ordering. In contrast, N-CNTF-2 exhibits shorter, curved, and partially discontinuous graphitic fringes, indicating the introduction of structural defects and local disorder during activation. Nevertheless, graphitic domains remain observable, confirming that the activation process increases defect density while preserving the conductive graphitic framework. Such a defect-rich structure is beneficial for increasing accessible active sites, improving electrolyte penetration, and enhancing electrochemical charge storage performance. Furthermore, TEM-EDS elemental mapping confirms the homogeneous distribution of C, N and O elements throughout the N-CNTF-2 and N-CNTF-1 framework (Fig. 2d-g and S2e). The uniform nitrogen incorporation indicates successful nitrogen doping, while the O-containing

species are mainly associated with defect sites generated during activation. The synergistic combination of interconnected nanotube networks, defect-rich graphitic domains, and uniformly distributed heteroatoms is expected to promote electrolyte accessibility, accelerate charge-transfer kinetics, and enhance overall electrochemical performance. Contact angle measurements (Fig. S3) show that the contact angle increases with urea dosage, reaching 61° at 6 g, which hinders electrolyte permeation. This indicates that excessive urea leads to over-etching. Although over-etching may introduce more N-containing functional groups, the oxygen content decreases (Table S1) and the intrinsic structure of the carbon nanotubes is compromised, thereby reducing hydrophilicity, structural stability and electrochemical performance.

The crystalline structure and graphitization degree of the N-CNTF-X samples were characterized using X-ray diffraction (XRD) and Raman spectroscopy. As shown in the XRD patterns (Fig. 3a), all samples exhibit 2 distinct diffraction peaks located at approximately 26.1° and 43.1° , corresponding to the (002) and (100) planes of graphitic carbon, respectively. Notably, the intensity and sharpness of the

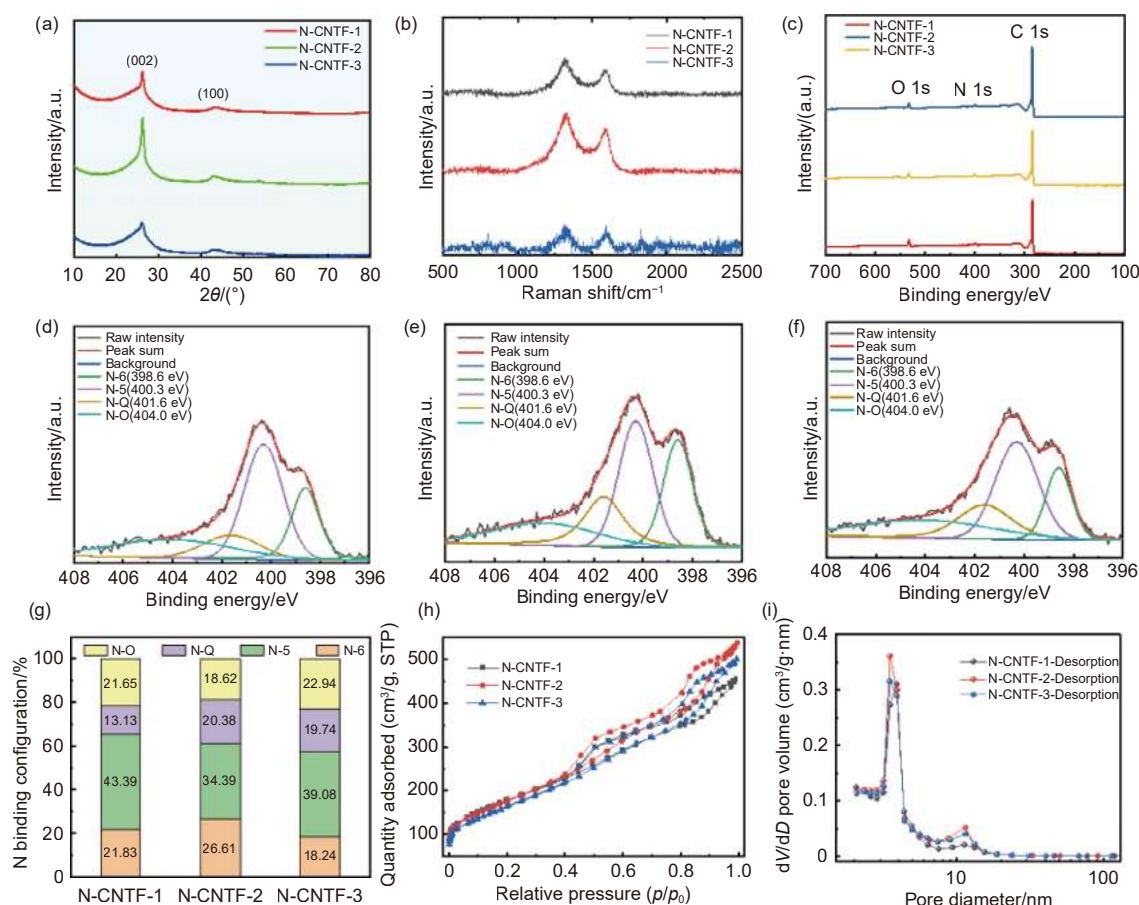


Fig. 3 Structural and compositional characterizations of N-CNTF-X samples. (a) XRD patterns. (b) Raman spectra. (c) XPS survey spectra. High-resolution N 1s XPS spectra of (d) N-CNTF-1, (e) N-CNTF-2 and (f) N-CNTF-3, with peak deconvolution. (g) Relative percentages of different nitrogen species derived from XPS analysis. (h) Nitrogen adsorption-desorption isotherms. (i) Corresponding pore size distribution curves

(002) peak vary with the degree of N doping. Specifically, N-CNTF-2 displays the most intense and sharpest (002) diffraction peak among the series. The observed changes in the (002) peak are primarily attributed to the combined effects of NH_3 etching on the C nanotube framework and in-situ N incorporation. During the synthesis, NH_3 preferentially removes amorphous carbon and disordered regions, thereby enhancing the overall structural ordering of the graphitic lattice^[26, 30]. These structural variations are further corroborated by Raman spectroscopy (Fig. 3b). All samples show two prominent bands: the D-band at 1330 cm^{-1} and the G-band at 1581 cm^{-1} . The intensity ratio between these bands (I_D/I_G) serves as a critical indicator of defect density and graphitic ordering. The calculated I_D/I_G values for N-CNTF-1, N-CNTF-2 and N-CNTF-3 are 2.1769, 2.3961 and 1.5693, respectively. These values indicate the generation of a more disordered porous architecture, which is in excellent

agreement with the TEM observations. The markedly increased I_D/I_G value of N-CNTF-2 suggests an optimal balance between the preservation of graphitic ordering and the introduction of nitrogen-induced defects. This synergistic effect confers N-CNTF-2 with both high electrical conductivities, derived from the well-ordered graphitic structure and abundant electrochemically active sites, imparted by the nitrogen heteroatoms.

X-ray photoelectron spectroscopy (XPS) was employed to characterize the elemental composition and surface chemical states of the as-prepared samples. All binding energies were calibrated with reference to the adventitious C 1s peak at 284.8 eV to eliminate the effect of surface charging. As shown in Fig. 3c, all survey spectra exhibit 3 distinct characteristic peaks centered at 284.8 , 399.8 and 531.8 eV , which are assigned to C 1s, N 1s and O 1s, respectively, confirming the coexistence of C, N, and O ele-

ments on the material surface. The dominant C 1s signal indicates that the samples are mainly composed of carbon-based structures, consistent with the intrinsic carbon nanotube framework of the materials (Fig. S4). The well-resolved N 1s XPS peak confirms the successful doping of nitrogen heteroatoms into the carbon lattice^[31]. Meanwhile, the O 1s signal demonstrates the presence of oxygen-containing functional groups on the sample surface (Fig. S5). As summarized in Table S1, with the increase of urea dosage, the O content of the samples shows a slight decrease from 5.47% to 3.55% (atom fraction), which is mainly attributed to the partial decomposition and removal of unstable O-containing functional groups during the high-temperature urea activation process^[32]. Meanwhile, the total nitrogen content increases moderately from 2.78% to 3.00% (atom fraction). This trend arises from the thermal decomposition of urea at high temperature releasing NH₃. The etching effect of NH₃ creates abundant defective sites on the carbon nanotube framework, which provide effective anchoring sites for nitrogen doping, thus elevating the nitrogen content of N-CNTF^[33].

The high-resolution N 1s XPS spectra of the N-CNTF samples (Fig. 3d-f) were deconvoluted into 4 characteristic components, corresponding to pyridinic N (N-6, 398.6 eV), pyrrolic N (N-5, 400.3 eV), graphitic N (N-Q, 401.6 eV), and oxidized N (N-O, 404.0 eV)^[34]. Among these species, pyridinic N, pyrrolic N, and graphitic N are characteristic of N atoms substitutionally doped into the carbon lattice. Pyridinic N and pyrrolic N, which are mainly located at the edge or defect sites of the carbon framework, could provide abundant electrochemically active sites and contribute additional pseudocapacitance via reversible Faradaic reactions^[35]. In addition, elemental mapping (EDS) confirms that nitrogen is uniformly distributed throughout the carbon nanotube walls rather than being enriched only on the surface (Fig. 2f and Fig. S2e). These findings collectively confirm that N atoms are incorporated into the carbon framework via lattice doping, rather than being merely surface-functionalized. Graphitic N doped in the basal plane

of the carbon framework can effectively improve the intrinsic electronic conductivity of the material and accelerate electron transfer, thus boosting the electrochemical reaction kinetics. Quantitative analysis of the relative content of each nitrogen species (Fig. 3g) reveals that the proportion of different nitrogen configurations varies significantly among the samples with increasing urea dosage. Specifically, the total relative content of pyridinic N and pyrrolic N in N-CNTF-2 reaches 61%, among which the relative content of pyridinic N is 26.61%, significantly higher than that of the other control samples. The synergistic effect of the above nitrogen configurations is expected to simultaneously provide abundant active sites and excellent electronic conductivity for N-CNTF electrodes, thus effectively improving their electrochemical performances. Furthermore, by comparing the total nitrogen doping content of the 3 samples (Table S1), it could be found that increasing the urea dosage has a limited effect on the total nitrogen content of the samples, but can effectively regulate the relative proportion of different nitrogen-containing functional groups on the carbon nanotube surface.

To further investigate the effect of urea addition on the surface pore structure of carbon nanotubes, nitrogen adsorption-desorption measurements were performed to investigate the porous structure characteristics of the as-fabricated N-CNTF-1, N-CNTF-2 and N-CNTF-3 samples, with the corresponding isotherms, pore size distribution (PSD) curves, and detailed pore structure parameters presented in Fig. 3h-3i and Table S2, respectively. All three samples display typical type IV isotherms with distinct H3-type hysteresis loops in the relative pressure (p/p_0) range of 0.4–1.0, revealing the dominant mesoporous feature with slit-like pore channels derived from the interconnected and stacked carbon nanotube networks, which is further confirmed by the PSD curves calculated via the Barrett-Joyner-Halenda (BJH) method from the desorption branch, showing a concentrated pore size distribution mainly in the range of 2–10 nm along with a small fraction of macropores above 10 nm for all samples. The BET surface areas of N-CNTF-1, N-

CNTF-2 and N-CNTF-3 are 629.43, 636.96 and 593.25 $\text{m}^2 \text{g}^{-1}$, respectively. Meanwhile, N-CNTF-2 and N-CNTF-3 display comparable average pore sizes of 4.87 and 4.89 nm, respectively, both slightly larger than that of N-CNTF-1 (4.15 nm).

To systematically evaluate the effect of nitrogen doping on the electrochemical performance of the cathode, and to screen out the optimal nitrogen doping condition, cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) tests were performed on the as-prepared N-CNTF- X ($X = 1, 2, 3$) electrodes in a two-electrode configuration. Fig. S6 shows the CV curves of the electrodes at scan rates ranging from 5 to 50 mV s^{-1} . All CV curves exhibit approximately rectangular profiles with a pair of weak and broad redox humps, indicating dominant electric double-layer capacitance (EDLC) behavior accompanied by a pseudocapacitive contribution, as well as excellent

electrochemical reversibility. The CV curves of the 3 N-CNTF- X electrodes were compared at a low scan rate of 5 mV s^{-1} and a low current density of 1 mA cm^{-2} , respectively. As shown in Fig. 4a, all devices exhibit well-resolved broad redox peaks in the voltage ranges of 0.4–0.8 V and 1.0–1.4 V, further confirming the additional pseudocapacitance contribution derived from nitrogen doping-induced active sites. Among the three samples, the N-CNTF-2 electrode presents the largest integrated CV area under identical test conditions, verifying its highest charge storage capacity and the most efficient utilization of electrochemically active sites at low scan rate/current density, which is in good agreement with the previous performance test results. To further reveal the intrinsic origin of the excellent electrochemical performance of the N-CNTF-2 electrode, in-depth electrochemical kinetic analysis was carried out based on CV

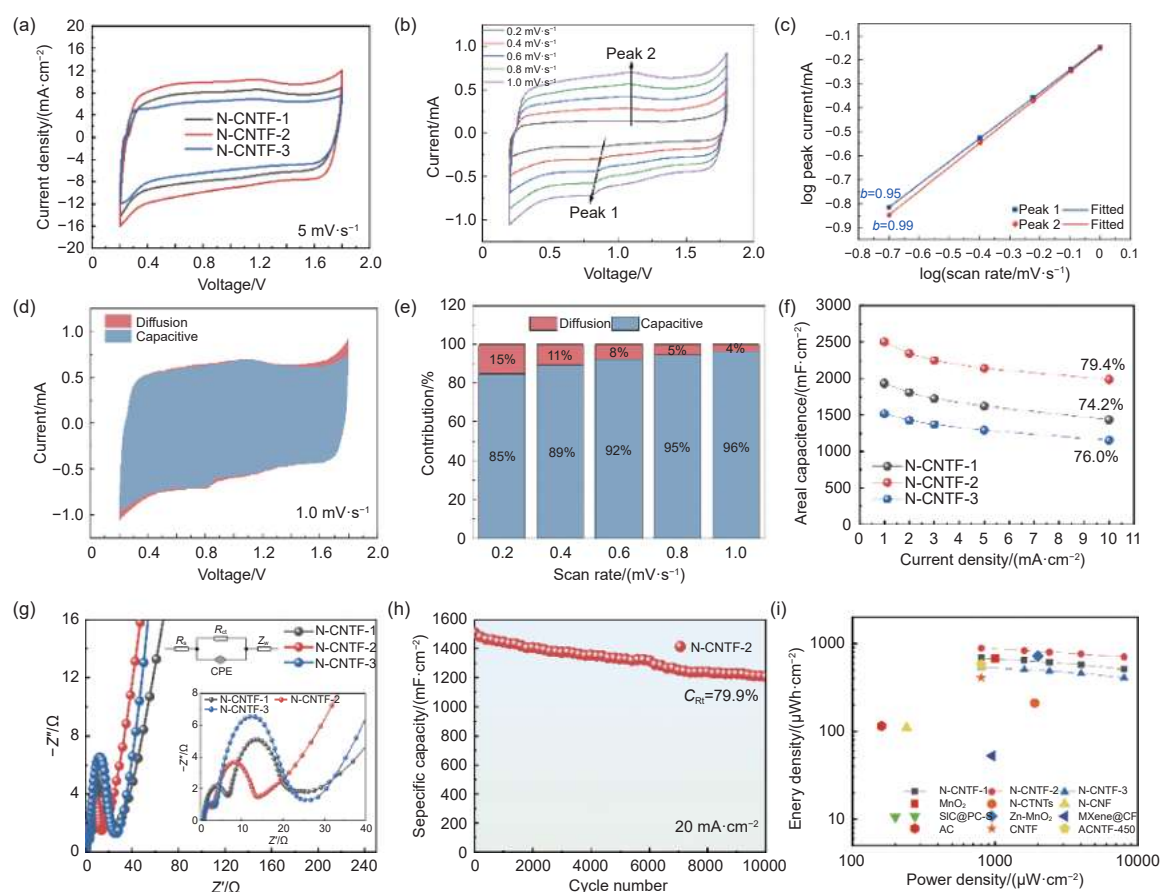


Fig. 4 Electrochemical performances of the assembled ZHSCs. (a) CV curves of N-CNTF- X at a scan rate of 5 mV s^{-1} . (b) CV curves at scan rates of 0.2–1.0 mV s^{-1} . (c) $\log(i)$ vs. $\log(v)$ fitting plots for b -value calculation. (d) Capacitive contribution (red shaded area) at 1.0 mV s^{-1} . (e) Contribution ratios of capacitive and diffusion-controlled processes at varied scan rates. (f) Areal capacitance of different electrodes. (g) EIS curves of the N-CNTF- X electrodes. (h) Long-term cycling stability of the optimized N-CNTF-2 electrode at a current density of 20 mA cm^{-2} . (i) Ragone plot of the devices

tests at low scan rates. As shown in Fig. 4b, the CV curves of the N-CNTF-2 electrode at scan rates ranging from 0.2 to 1.0 mV s⁻¹ maintain well-preserved shapes with negligible peak position shift and shape distortion as the scan rate increases, indicating outstanding electrochemical reversibility and rapid kinetic response of the electrode. The charge storage mechanism of the electrode was quantitatively clarified via the classic power-law relationship between peak current (i) and scan rate (v), which can be described as $i = av^b$, where a and b are adjustable parameters^[36]. The b -value is a core indicator to distinguish the charge storage mode: a b -value close to 0.5 indicates a diffusion-controlled battery-type process, while a b -value approaching 1.0 corresponds to a surface-dominated capacitive-controlled process (including electric double-layer capacitance and pseudocapacitance). As shown in Fig. 4c, the linear fitting of $\log(i)$ versus $\log(v)$ delivers b -values of 0.99 for the cathodic peak (peak 1) and 0.95 for the anodic peak (peak 2), both of which are extremely close to 1.0. This result unambiguously demonstrates that the charge storage process of the N-CNTF-2 electrode is dominated by the capacitive-controlled behavior, which is well consistent with the nearly rectangular CV profiles. To further quantify the specific contribution ratio of the 2 charge storage mechanism, the current response at a fixed potential was divided into 2 parts: the capacitive-controlled contribution (k_1v) and the diffusion-controlled contribution ($k_2v^{1/2}$), following the formula $i(V) = k_1v + k_2v^{1/2}$. Fig. 4d visually presents the capacitive-controlled current contribution (red shaded area) at a scan rate of 1.0 mV s⁻¹, which occupies the clear majority of the total current, further verifying the dominant capacitive charge storage feature. The normalized contribution ratios at different scan rates are summarized in Fig. 4e. The capacitive contribution ratio increases continuously from 85% to 96% as the scan rate rises from 0.2 to 1.0 mV s⁻¹, and it still maintains an absolute dominant position even at the lowest scan rate. Fig. S7 presents the GCD curves of the N-CNTF-X electrodes at various current densities from 1 to 10 mA cm⁻². All curves display nearly sym-

metric triangular shapes without distinct voltage plateaus, which is well consistent with the CV test results, verifying that the energy storage mechanism is dominated by EDLC with a minor pseudocapacitive contribution. At the current density of 1 mA cm⁻², the N-CNTF-2 electrode delivers the longest charge-discharge time, in good agreement with the CV analysis results. The areal capacitances calculated from the discharge curves are summarized in Fig. 4f: at 1 mA cm⁻², N-CNTF-1, N-CNTF-2 and N-CNTF-3 achieve areal capacitances of 1933.29, 2501.51 and 1516.41 mF cm⁻², respectively. To further evaluate the contribution of the nitrogen-doped carbon nanotube framework, activated carbon cloth (ACC) was employed as a control electrode under identical testing conditions. As shown in Fig. S8, the ACC electrode delivers an areal capacitance of 1266.55 mF cm⁻² at a current density of 1 mA cm⁻², which is significantly lower than that of N-CNTF-2 (2501.51 mF cm⁻²). Furthermore, with a high current density of 10 mA cm⁻², the N-CNTF-2 electrode maintains an areal capacitance of 1985.67 mF cm⁻², corresponding to a capacitance retention of 79.4% relative to the initial capacitance at 1 mA cm⁻². This value is significantly higher than those of N-CNTF-1 (74.2%) and N-CNTF-3 (76.0%), demonstrating the outstanding rate capability of the N-CNTF-2 electrode.

To further investigate the charge-transfer and ion-transport behavior of the electrodes, electrochemical impedance spectroscopy (EIS) measurements were performed and fitted using the equivalent circuit model $R_s - (R_{ct} \parallel CPE) - Z_w$ (Fig. 4g). The fitted parameters are summarized in Table S3. R_s represents the equivalent series resistance, including the electrolyte resistance, intrinsic electrode resistance, and contact resistance, whereas R_{ct} corresponds to the charge-transfer resistance at the electrode/electrolyte interface. The constant phase element (CPE) accounts for the non-ideal capacitive behavior arising from surface heterogeneity and porous structures, while Z_w reflects the ion diffusion process within the porous electrode framework. Among the three samples, N-CNTF-2 ex-

hibits the lowest R_s value (3.81 Ω), which is significantly lower than those of N-CNTF-1 (5.12 Ω) and N-CNTF-3 (6.89 Ω), indicating improved electronic conductivity and reduced internal resistance. More importantly, N-CNTF-2 shows the smallest charge-transfer resistance (16.37 Ω), compared with 24.65 Ω for N-CNTF-1 and 26.94 Ω for N-CNTF-3, demonstrating faster electron-transfer kinetics at the electrode/electrolyte interface. The lower impedance of N-CNTF-2 can be attributed to its optimized hierarchical porous structure and uniform nitrogen incorporation, which provide efficient ion-transport pathways while maintaining continuous conductive networks. Furthermore, the steeper low-frequency region of the Nyquist plot suggests enhanced ion diffusion behavior, which is beneficial for rapid charge storage and discharge processes. These results confirm that N-CNTF-2 possesses the most favorable charge-transfer and ion-transport characteristics, consistent with its superior electrochemical performance.

Based on the above analysis, the N-CNTF-2 electrode was identified as the optimal cathode candidate for ZIHSCs, and its long-term cycling stability was further evaluated (Fig. 4h). After 10 000 consecutive charge-discharge cycles at a high current density of 20 mA cm⁻², the N-CNTF-2 electrode achieves a capacitance retention of 79.9% relative to its initial capacitance, with the coulombic efficiency maintained at nearly 100% throughout the whole cycling process. Moreover, the GCD curves of the electrode before and after cycling show negligible shape distortion, demonstrating the excellent structural stability of the carbon framework and the highly reversible electrochemical reactions during long-term repeated charge and discharge. As presented in Table S4, the areal capacitance, rate capability, and cycling stability of our N-CNTF cathode significantly surpass those of previously reported ZIHSC cathodes. Benefiting from nitrogen doping and abundant pore structure, N-CNTF-2 can reach an impressive energy density of 886.3 $\mu\text{Wh cm}^{-2}$ (797.1 $\mu\text{W cm}^{-2}$), surpassing previously documented ZHSC values (such as MnO₂^[37], N-CTNTs^[38], N-CNF^[39], SiC@PC-S^[40], Zn-MnO₂^[41],

MXene@CF^[42], AC^[43], CNTF^[20] and ACNTF-450^[20]) (Fig. 4i).

To verify the practical application potential of the as-prepared electrode, a quasi-solid-state zinc-ion hybrid supercapacitor (ZHSC) was assembled with the optimized N-CNTF-2 as the cathode, zinc foil as the anode, and a polyacrylamide (PAM) hydrogel soaked in 2 mol/L ZnSO₄ electrolyte for 24 h as the gel electrolyte (which also serves as the separator), as illustrated in Fig. 5a. The electrochemical performance of the as-assembled quasi-solid-state device was systematically investigated. Fig. 5b and 5c show the CV curves at various scan rates and GCD curves at different current densities of the quasi-solid-state ZHSCs, respectively. The CV curves at low scan rates exhibit a quasi-rectangular profile coupled with a pair of distinct broad redox peaks, indicating a synergistic charge storage mechanism dominated by EDLC, accompanied by a pseudocapacitive contribution, which is well consistent with the electrochemical behavior of the liquid system mentioned above. Calculated from the GCD curves, the quasi-solid-state device delivers a high areal capacitance of 2248 mF cm⁻² at a current density of 1 mA cm⁻². The N-CNTF-2 electrode was identified as the optimal cathode candidate for ZHSCs, and its long-term cycling stability was further evaluated (Fig. 5d). After 1200 consecutive charge-discharge cycles at a high current density of 20 mA cm⁻², the N-CNTF-2 electrode achieved a capacitance retention of 98% relative to its initial capacitance, with the coulombic efficiency maintained at nearly 100% throughout the whole cycling process. Notably, the long-term cycling test normalized capacitance retention to the stability test's first cycle. Slight increases above 100% occur during some early cycles due to an electrochemical activation process. In early cycles, the electrolyte begins to penetrate the electrode's hierarchical porous structure, enabling sites that were previously inaccessible to electrochemical reactions. The first cycle of the stability test does not fully capture this process, which is why capacitance in subsequent cycles is higher. Once the process is completed, capacitance stabilizes and exhibits ex-

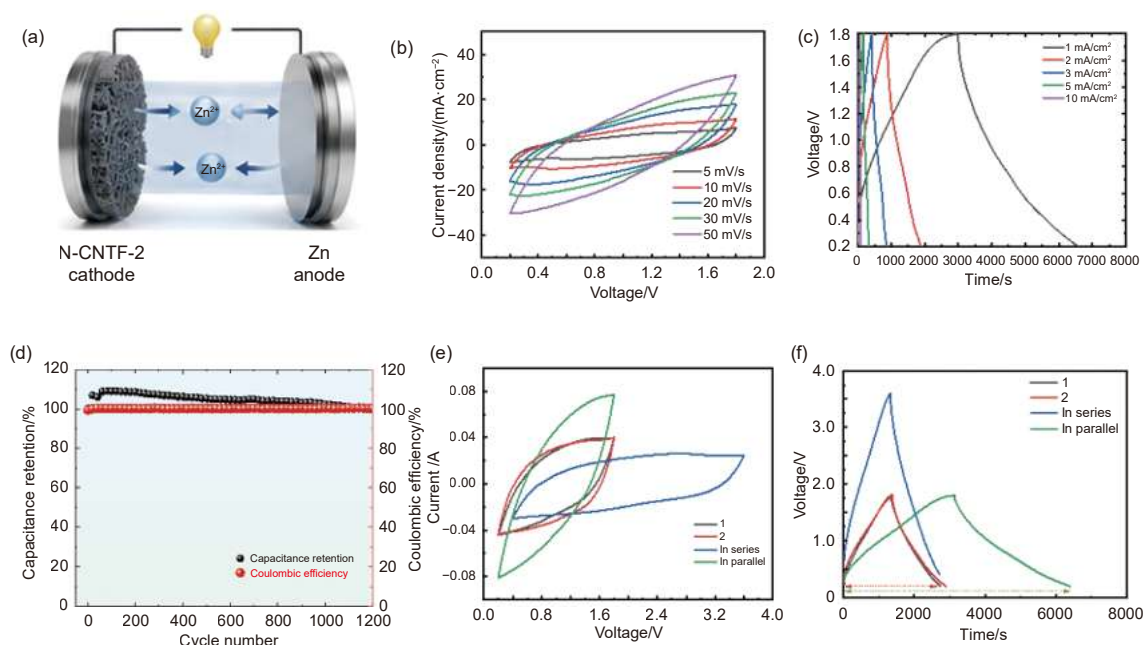


Fig. 5 (a) Electrode assembly of ZHSCs quasi-solid electrode. (b–c) Device CV and GCD measurement. (d) The long cycling performance. (e) CV and (f) GCD measurement of a single device and two devices connected in parallel/in series

cellent and stable retention during the long-term cycling test, confirming the N-CNTF-2 electrode's excellent structural stability. To further demonstrate the scalable output voltage and capacitance for practical applications, two identical quasi-solid-state ZHSCs were assembled in series and in parallel, respectively. As shown in Fig. 5e (CV curves at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$) and Fig. 5f (GCD curves at a current density of $2 \text{ mA} \cdot \text{cm}^{-2}$), the two devices connected in series can double the output voltage window, while the parallel configuration can double the areal capacitance, exhibiting outstanding scalability and bright practical application prospects.

4 Conclusions

In this work, N-CNTF was successfully fabricated via a facile one-step magnesiothermic reduction strategy. The NH_3 released from the thermal decomposition of low-cost urea plays a dual synergistic role, and simultaneously enables efficient in-situ nitrogen doping into the carbon lattice with tunable nitrogen configurations. By tuning the urea dosage, the optimized N-CNTF-2 cathode for ZHSCs delivers an ultrahigh areal capacitance of $2501.51 \text{ mF cm}^{-2}$ at a current density of 1 mA cm^{-2} , excellent rate capability

with 79.4% capacitance retention at 10 mA cm^{-2} , and robust long-term cycling stability with 79.9% capacitance retention after 10 000 consecutive cycles at 20 mA cm^{-2} . Furthermore, the series/parallel assembled quasi-solid-state flexible ZHSCs realize linear and controllable expansion of output voltage and capacitance, demonstrating great application potential in flexible and wearable electronics. This work provides a facile, low-cost and scalable synthetic strategy for the rational design of high-performance carbon-based ZHSC cathodes, and offers valuable experimental guidance for the development of advanced carbon-based energy storage devices.

References

- [1] Chen X D, Zhang H, Gao Y, et al. Zinc-ion hybrid supercapacitors: design strategies, challenges, and perspectives[J]. *Carbon Neutralization*, 2022, 1(2): 159-188.
- [2] Tang H, Yao J J, Zhu Y R. Recent developments and future prospects for zinc-ion hybrid capacitors: a review[J]. *Advanced Energy Materials*, 2021, 11(14): 2003994.
- [3] Liu S, Tian Z, Wang Y, et al. The doping of coal-based activated carbon with both B and N for use as the cathode of high performance aqueous zinc-ion hybrid capacitors[J]. *New Carbon Materials*, 2026, 41(2): 379-392.
- [4] Liu Y, Song L H, Li C Z, et al. Recent advances in high-performance carbon-based electrodes for zinc-ion hybrid capacitors[J]. *Batteries*, 2024, 10(11): 396.
- [5] Zhang Y F, Liang H Y, Zhu C L, et al. Unlocking the potential of multifunctional carbon nanomaterials for zinc-ion hybrid capacitors: Mechanisms, applications, and challenges[J]. *Coordination Chemistry Reviews*, 2026, 549: 217338.
- [6] Lu Y P, Wang H X, Liu L T, et al. Boron and nitrogen co-doped sodium alginate-based porous carbons for durable and fast Zn-ion hybrid capacitors[J]. *New Carbon Materials*, 2024, 39(3): 506-514.
- [7] Liu Y, Wu L J. Recent advances of cathode materials for zinc-ion hybrid capacitors[J]. *Nano Energy*, 2023, 109: 108290.
- [8] Javed M S, Najam T, Hussain I, et al. Fundamentals and scientific challenges in structural design of cathode materials for zinc-ion hybrid supercapacitors[J]. *Advanced Energy Materials*, 2023, 13(3): 2202303.
- [9] Li J X, Ge K K, Grammenos A O, et al. Understanding multi-stage charge storage on nanoporous carbons in zn-ion hybrid capacitors[J]. *Advanced Materials*, 2025, 37(24): 2502422.
- [10] Li Y R, Jin X H, Yang Y, et al. Temperature-driven boosting of zinc-ion hybrid capacitor cathode performance via one-step construction of hierarchical porous carbon[J]. *Journal of Energy Storage*, 2026, 146: 120047.
- [11] Yu C C, Chen X X, Gao W Y, et al. Advance in design techniques and synthesis strategies of porous carbon positive electrodes for aqueous zinc-ion hybrid capacitors[J]. *Chemical Engineering Journal*, 2025, 514: 162914.
- [12] Zhang J M, He H N, Tang Y G, et al. Advanced materials prepared via metallic reduction reactions for electrochemical energy storage[J]. *Small Methods*, 2020, 4(10): 2000613.
- [13] Zhang H T, Zhang X, Sun X Z, et al. Shape-controlled synthesis of nanocarbons through direct conversion of carbon dioxide[J]. *Scientific Reports*, 2013, 3(1): 3534.
- [14] Wang C L, Han Q Q, Xie R H, et al. Fabrication of petal-like Ni₃S₂ nanosheets on 3D carbon nanotube foams as high-performance anode materials for Li-ion batteries[J]. *Electrochimica Acta*, 2020, 331: 135383.
- [15] Wang C L, Qu H L, Peng T, et al. Large scale α -Co(OH)₂ needle arrays grown on carbon nanotube foams as free-standing electrodes for supercapacitors[J]. *Electrochimica Acta*, 2016, 191: 133-141.
- [16] Wang C L, Feng Y J, Sun X C, et al. Fabrication and activation of carbon nanotube foam and its application in energy storage[J]. *Electrochimica Acta*, 2017, 236: 343-350.
- [17] Wang C L, Li F T, Qu H, et al. Fabrication of three dimensional carbon nanotube foam by direct conversion carbon dioxide and its application in supercapacitor[J]. *Electrochimica Acta*, 2015, 158: 35-41.
- [18] Ji Z C, Liu C C, Xie W H, et al. Interfacial engineered PANI/carbon nanotube electrode for 1.8 V ultrahigh voltage aqueous supercapacitors[J]. *Nanotechnology*, 2023, 34(16): 165401.
- [19] Wan C, Huang J, Chen K, et al. Hierarchical porous N-doped carbon fibers enable ultrafast electron and ion transport for Zn-ion storage at high mass loadings[J]. *Energy Storage Materials*, 2024, 69: 103384.
- [20] Ji Z C, Jin H X, Wang Z Y, et al. Controllable oxygen group modification on CNT foam for high-performance flexible zinc-ion hybrid supercapacitors[J]. *Chemical Engineering Journal*, 2025, 523: 168381.
- [21] Wei F, Zeng Y S, Guo Y C, et al. Recent progress on the heteroatom-doped carbon cathode for zinc ion hybrid capacitors[J]. *Chemical Engineering Journal*, 2023, 468: 143576.
- [22] Wang S C, Wei F, Geng W Y, et al. Multi-heteroatoms doped hierarchical porous carbons from rice husk for zinc ion hybrid capacitors[J]. *Chemical Engineering Journal*, 2025, 515: 163462.
- [23] Gao S T, Wei F, Zhu X Y, et al. Electronically modified hierarchical porous carbon by N, P heteroatoms for zinc ion hybrid capacitor[J]. *Applied Surface Science*, 2024, 644: 158758.
- [24] Ni J, Chen W J, Zhang X Y, et al. Nitrogen doped hierarchical porous carbon for supercapacitors and zinc ion hybrid capacitors[J]. *Industrial Chemistry & Materials*, 2025, 3(4): 475-484.
- [25] Pang C R, Wang T W, Song C C, et al. A dual-surfactant template system for fabricating N-doped porous carbon nanorods for use as supercapacitor electrodes[J]. *New Carbon Materials*, 2025, 5: 1123-1134.
- [26] Liu M Q, Wu F, Feng X, et al. Molecular engineering toward sustainable development of multiple-doped hierarchical porous carbons for superior zinc ion storage[J]. *Science China Materials*, 2023, 66(2): 541-555.
- [27] Jin C J, Guo F J, Mi H Y, et al. Template-oriented synthesis of boron/nitrogen-rich carbon nanoflake superstructure for high-performance Zn-ion hybrid capacitors[J]. *Carbon Energy*, 2025, 7(3): e673.
- [28] Dong Y, Zhang Q J, Tian Z Q, et al. Ammonia thermal treatment toward topological defects in porous carbon for enhanced carbon dioxide electroreduction[J]. *Advanced Materials*, 2020, 32(28): 2001300.
- [29] Li X F, Lian K Y, Liu L, et al. Unraveling the formation mechanism of graphitic nitrogen-doping in thermally treated graphene with ammonia[J]. *Scientific Reports*, 2016, 6(1): 23495.
- [30] Yu K H, Wang X R, Yang H Y, et al. Insight to defects regulation on sugarcane waste-derived hard carbon anode for sodium-ion batteries[J]. *Journal of Energy Chemistry*, 2021, 55: 499-508.
- [31] Lin T Q, Chen I W, Liu F X, et al. Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage[J]. *Science*, 2015, 350(6267): 1508-1513.
- [32] Dai C C, Wan J F, Yang J, et al. H₃PO₄ solution hydrothermal carbonization combined with KOH activation to prepare argy wormwood-based porous carbon for high-performance supercapacitors[J]. *Applied Surface Science*, 2018, 444: 105-117.

- [33] Huang C B, Yu Y X, Xu H P, et al. Urea-assisted dual-shell hollow Zn-MOF microsphere-derived carbon for a Zinc ion capacitor[J]. *ACS Applied Energy Materials*, 2026, 9(5): 2871-2883.
- [34] Zhu X Q, Guo F J, Yang Q, et al. Boosting zinc-ion storage capability by engineering hierarchically porous nitrogen-doped carbon nanocage framework[J]. *Journal of Power Sources*, 2021, 506: 230224.
- [35] Wei F, Wei Y C, Wang J F, et al. N, P dual doped foamy-like carbons with abundant defect sites for zinc ion hybrid capacitors[J]. *Chemical Engineering Journal*, 2022, 450: 137919.
- [36] Lu Y Y, Li Z W, Bai Z Y, et al. High energy-power Zn-ion hybrid supercapacitors enabled by layered B/N co-doped carbon cathode[J]. *Nano Energy*, 2019, 66: 104132.
- [37] Zhang Z W, Liu Y D, Wang L Y, et al. High load, long cycle and flexible zinc-ion hybrid supercapacitors[J]. *Journal of Energy Storage*, 2024, 79: 110241.
- [38] Gong Y, Fu D X, Fan M M, et al. Multilayer core-sheath wires with radially aligned N-doped carbon nanohole arrays for boosting energy storage in zinc-ion hybrid supercapacitors[J]. *ACS Applied Materials & Interfaces*, 2024, 16(4): 4793-4802.
- [39] Amiri A, Naraghi M, Polycarpou A A. Zinc-ion hybrid supercapacitors with ultrahigh areal and gravimetric energy densities and long cycling life[J]. *Journal of Energy Chemistry*, 2022, 70: 480-491.
- [40] Yang Y, Wang R Y, Chen S L, et al. High-performance Zn-ion hybrid supercapacitors enabled by rationally designed hierarchical SiC@C quasi-aligned nanoarrays[J]. *Journal of Energy Storage*, 2023, 67: 107526.
- [41] Li K D, Cai B, Wang L Y, et al. A flexible axial Zn ion hybrid supercapacitor with high surface capacitance and long cycle life[J]. *Journal of Alloys and Compounds*, 2023, 953: 169995.
- [42] Shi B, Chen L, Jen T C, et al. Vertical arrangement of Ti_2CT_x MXene nanosheets on carbon fibers for high-performance and flexible Zn-ion supercapacitors[J]. *ACS Applied Nano Materials*, 2022, 6(1): 315-322.
- [43] Zhang P P, Li Y, Wang G, et al. Zn-ion hybrid micro-supercapacitors with ultrahigh areal energy density and long-term durability[J]. *Advanced Materials*, 2019, 31(3): 1806005.