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Preparation and Electrochemical Performance of N,S,F Co-Doped Porous Carbon Derived from FCC Slurry via Synergistic Doping and Pore Regulation for High-Performance Supercapacitors

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Abstract: Utilizing fluid catalytic cracking (FCC) slurry as a carbon precursor represents a promising approach for the high-value conversion of industrial by-products, yet its application is restricted by inorganic impurities, limited pore accessibility, and insufficient active sites. In this work, a synergistic strategy combining ammonium sulfate-assisted in-situ N,S co-doping, KOH activation, and lithium fluoride–hydrochloric acid etching is developed to fabricate high-performance porous carbon. The incorporation of $(\text{NH}_4)_2\text{SO}_4$ enables simultaneous pore formation and heteroatom doping, while KOH activation constructs a hierarchical porous structure with enhanced surface area and ion transport pathways. Meanwhile, LiF–HCl etching effectively removes residual inorganic species and introduces fluorine functionalities, thereby modulating surface chemistry and pore architecture. Comprehensive structural analysis confirms the formation of a defect-rich carbon framework with uniformly distributed N, S, and F heteroatoms. The optimized sample (CNK-2) exhibits a high specific surface area of $2847 \text{ m}^2 \text{ g}^{-1}$ and a well-developed pore structure. Electrochemical measurements reveal a high specific capacitance of 401 F g^{-1} at 1 A g^{-1} with excellent rate capability and 87% capacitance retention after 10,000 cycles. These results highlight the synergistic effects of hierarchical porosity and multi-heteroatom doping, demonstrating significant potential for advanced supercapacitor applications.

Key words: FCC slurry; Hierarchical porous carbon; Multi-heteroatom doping; Pore structure regulation; Supercapacitors

1 Introduction

The large-scale deployment of renewable energy is essential for achieving global sustainability goals^[1]; however, its inherent intermittency and fluctuation pose significant challenges to the stability of modern power systems^[2]. Advanced energy storage technologies are therefore required to balance energy supply and demand, playing a key role in building modern power systems and supporting carbon neutrality and peak carbon emission goals^[3,4]. Among various candidates, supercapacitors have attracted considerable attention due to their high power density, rapid charge–discharge capability, and excellent cycling stability^[5,6]. Nevertheless, their relatively low energy density compared to batteries remains a major limitation for practical applications^[7]. Therefore, enhancing the energy density of supercapacitors while maintaining high power density and rapid charge–discharge performance remains a critical research challenge^[8].

Supercapacitors typically consist of electrodes, electrolytes, current collectors, separators, and other auxiliary components^[9]. The electrochemical performance of supercapacitors is predominantly determined by electrode materials^[10]. Carbon-based materials are widely considered as promising electrodes owing to their high surface area, tunable pore structure, and outstanding chemical stability^[11]. However, conventional carbon precursors such as metal–organic frameworks (MOFs) and covalent organic frameworks (COFs) often involve complex synthesis procedures, high cost, and environmental concerns^[12]. Therefore, developing low-cost, sustainable carbon materials with high electrochemical performance is of great importance^[11,12].

Fluid catalytic cracking (FCC) slurry, an abundant industrial by-product, represents a promising carbon precursor due to its high aromatic content and inherent heteroatoms^[13,14]. Its utilization not only reduces environmental burden but also provides a cost-effective route for carbon material production^[15,16]. However, direct pyrolysis of FCC slurry typically results in

porous carbon with limited performance due to several intrinsic drawbacks. Residual inorganic impurities (e.g., SiO_2 and Al_2O_3) can block pore channels and deteriorate structural stability, while the resulting carbon framework often exhibits low specific surface area, poor pore connectivity, and insufficient active sites^[14,17]. These factors collectively restrict ion transport and charge storage, leading to unsatisfactory electrochemical performance^[18].

To address these challenges, significant efforts have been devoted to pore structure engineering and heteroatom doping^[19,20]. Template-assisted methods and chemical activation strategies have been widely employed to construct hierarchical porous structures^[21,22]. For example, Liu et al. prepared hierarchical porous carbon from coal tar pitch by combining a molten salt ($\text{NaCl}/\text{ZnCl}_2$) template with KOH chemical activation. The salt served as a water-removable sacrificial template to generate mesopores, while KOH activation further introduced micropores, yielding a specific surface area of up to $2984 \text{ m}^2 \text{ g}^{-1}$. This work clearly demonstrates the effectiveness of coupling template-assisted and chemical activation strategies for constructing hierarchical porous structures^[23]. While heteroatom doping (e.g., N, S et al.) can effectively modulate the electronic structure and introduce additional active sites^[24,25]. For instance, Zhao et al. prepared N,S co-doped porous carbon from FCC slurry via acid leaching, urea-assisted doping, and KOH activation, achieving a high specific surface area of up to $2587 \text{ m}^2/\text{g}$ along with excellent electrochemical performance^[14]. Despite these advances, current approaches often suffer from high cost, complex synthesis procedures. In particular, the synergistic effects between hierarchical porosity and multi-heteroatom doping, as well as their roles in governing electrochemical behavior, remain insufficiently understood^[26].

Herein, we propose an integrated strategy for the preparation of high-performance porous carbon from FCC slurry by coupling pore structure regulation with multi-heteroatom doping. This strategy enables simultaneous impurity removal, pore architecture optimization, and surface chemical modulation. Specifically, in situ decomposition of ammonium sulfate introduces initial porosity and N,S co-doping, followed by KOH activation to construct a hierarchical porous framework, and LiF-HCl etching to remove inorganic impurities and further tailor the pore structure while introducing fluorine species. Through this synergistic design, the interplay between pore structure and multi-heteroatom doping is systematically regulated. This work not only enhances the electrochemical performance of FCC-derived carbon materials but also provides new insights into the structure–property relationship, offering an effective pathway for the high-value utilization of FCC slurry-derived in advanced supercapacitor applications.

2 Experimental

2.1 Materials

The chemical substances employed in the experiment, such as HCl, KOH, absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$), and all analytical-grade reagents, were procured from Sinopharm Chemical Reagent Co., Ltd. $(\text{NH}_4)_2\text{SO}_4$ was obtained from Shanghai Maclin Biochemical Technology Co., Ltd., and LiF was purchased from Shandong Keyuan Biochemical Co., Ltd. High-purity nitrogen (Ar, 99.999%) was supplied by Jinan Deyang Special Gas Co., Ltd. Ultrapure water utilized throughout the experimental procedure was prepared using a Swiss Milli-Q ultrapure water system. The catalytic cracking slurry was provided by Shandong Chambroad Petrochemicals Co., Ltd. The elemental analysis of the FCC slurry is presented in Table 1, and its fundamental properties are shown in Table 2.

Table 1 Elemental analysis of FCC slurry (ultimate analysis)

C	H	O*	N	S
89.56%	7.30%	1.16%	0.69%	1.29%

*Oxygen was determined by the difference method.

Table 2 Basic properties of FCC slurry

Property	Data
Density, g/cm ³	1.012
Metal content, µg/g	
Ni	36
Al	575
V	16
Ethnic composition, %	
Saturates	8.7
Aromatics	51.5
Resins	31.3
Asphaltenes	8.5

2.2 Preparation of porous carbons

Figure 1 depicts a comprehensive flow chart that outlines this multi - stage synthesis approach, which includes precursor modification, staged pyrolysis, alkaline activation, and post - treatment procedures.

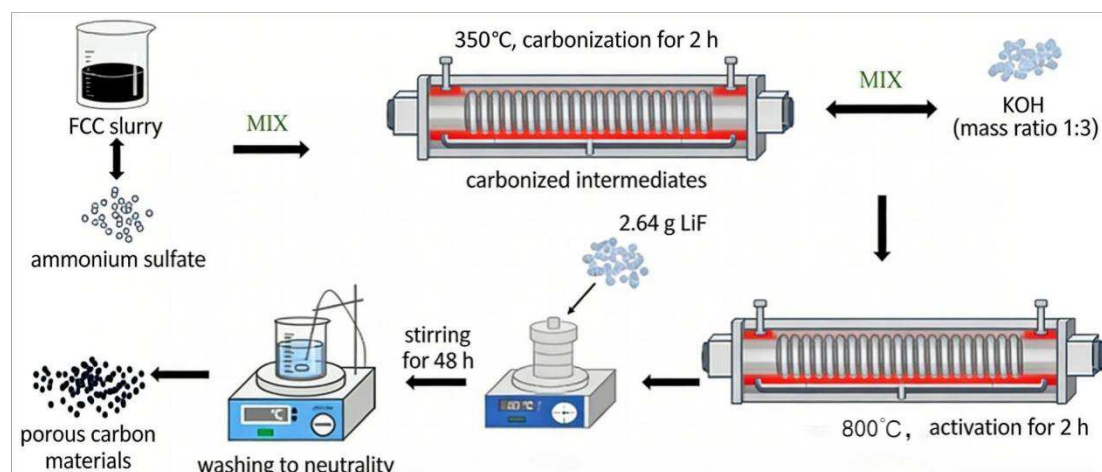


Figure 1 Synthesis of FCC Slurry-Based Porous Carbon

The synthesis procedure commenced with the preparation of precursor mixtures utilizing FCC slurry and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). Precursor batches, each with a mass of 10 grams, were homogenized at mass ratios of 4:0, 4:1, 4:2, 4:3, and 4:4 (FCC slurry: $(\text{NH}_4)_2\text{SO}_4$), leading to the generation of samples labeled as CNK-X, where X (0-4) denotes the percentage of ammonium sulfate doping relative to the FCC matrix.

Primary pyrolysis was carried out in a horizontal tube furnace under a nitrogen flow rate of 1 L/min. Samples CK (control) and CNK1-4 were subjected to a precisely controlled thermal program: heating at a rate of 1°C/min to 350°C with a 2-hour isothermal holding period, followed by natural cooling. This process yielded preliminary carbonized intermediates.

For chemical activation, the pyrolyzed products were mixed with KOH at a mass ratio of 1:3 (carbon:KOH). The mixtures underwent secondary pyrolysis under the same nitrogen flow conditions, being heated at a rate of 5°C/min to target temperatures of 800°C, with a 2-hour dwell at the peak temperature, ultimately resulting in the production of activated carbon materials.

A specialized etching solution was prepared by dissolving 2.64 g of LiF in 40 mL of 6 M HCl under continuous magnetic stirring at a speed of 400 rpm for 10 minutes. After activation, the samples were subjected to dual washing protocols: treatment with the etching solution or washing with concentrated HCl, each accompanied by 3 hours of agitation. Subsequent purification involved

repeated rinsing with ultrapure water until the pH reached neutrality, followed by vacuum drying at 80°C.

2.3 Characterization

To comprehensively explore the chemical and physical properties of the materials, a series of characterization experiments were carried out. The elemental composition of the catalytic cracking oil slurry was analyzed by means of an organic element analyzer (EA, Elimonta UNCUBE). The surface topographies of the samples were inspected using scanning electron microscopy (SEM, (SLGMA HD series, Germany). Powder X-ray diffraction (XRD) was employed to identify the phase structure on a Rigaku SmartLab instrument with Cu-K β (40 kV/30 mA) radiation and a step size of 0.01° in the wide-angle range of 5–90°. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific K α instrument from Thermo Fisher Scientific, USA, utilizing a monochromatized Al K α radiation source with an energy step size of 1 eV. The graphitization degree of the samples was analyzed using a Raman spectrometer (HORIBA Scientific LabRAM HR Evolution, Japan). N₂ adsorption–desorption analysis was performed on a JW-BK100 surface area and porosity analyzer from JWGB Sci. & Tech., China. The specific surface area and pore geometries of the activated carbon were determined respectively using the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda models.

2.4 Electrochemical Measurement

The electrochemical tests were conducted using a CHI 760e electrochemical workstation (Chenhua, Shanghai). A three-electrode system was adopted to perform galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) tests. Porous carbon, conductive carbon black, and polytetrafluoroethylene were uniformly blended at a mass ratio of 8:1:1, coated, and pressed on 1×1 cm² nickel foam to fabricate a working electrode. In the three-electrode test, the prepared electrodes, Ag/AgCl, and platinum foil were respectively used as the working, reference, and counter electrodes to assess the electrochemical performance of the synthesized porous carbon. GCD measurements were carried out at current densities ranging from 0.5 to 20 A • g⁻¹, while CV measurements were obtained at sweep rates of 10, 20, 50, and 100 mV/s within a voltage window range from -1 to 0 V in a 6 mol/L KOH electrolyte. EIS measurements were performed at frequencies from 10⁻² to 10⁵ Hz under open-circuit voltage, with an amplitude of 0.005V.

In the three-electrode system, the gravimetric specific capacitances CS (unit: F • g⁻¹) of the CKX were calculated using Equation (1):

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (1)$$

where I denotes the discharge current, A, Δt is the discharge time, s, m is the mass of the active material in the working electrode, g, and ΔV is the voltage change after the ohmic drop during the discharge process, V.

3 Results and discussion

3.1 Morphological and structural characterization

To elucidate the effect of (NH₄)₂SO₄ doping on pore structure evolution, N₂ adsorption–desorption measurements were conducted for all samples, and the corresponding isotherms and pore size distributions are presented in Figure 2, with detailed parameters summarized in Table 3. SEM and TEM images (Figure 3) further provide structural evidence at the micro- and nanoscale.

As shown in Fig. 2(a), all samples exhibit a sharp increase in N₂ adsorption at low relative pressures ($P/P_0 < 0.1$), indicating the presence of abundant microporous structures. The undoped CK sample displays a typical Type I isotherm, characteristic of predominantly microporous

materials with limited meso-/macropore contribution. In contrast, all $(\text{NH}_4)_2\text{SO}_4$ -treated samples present Type IV isotherms with pronounced hysteresis loops in the high relative pressure region ($P/P_0 > 0.5$), which can be attributed to capillary condensation within mesopores. This feature confirms the formation of a hierarchical pore structure with the coexistence of micropores and mesopores. The transition from Type I to Type IV isotherms demonstrates that $(\text{NH}_4)_2\text{SO}_4$ treatment plays a crucial role in tailoring the pore architecture, facilitating mesopore development while preserving abundant micropores. The pore size distribution curves (Fig. 2(b)) further reveal that micropores (0.1–0.9 nm) dominate across all samples, whereas the secondary distribution in the range of 2–5 nm corresponds to mesopores. Notably, the CK sample is enriched with ultramicropores (<0.5 nm), while CNK-2 exhibits a broadened micropore distribution centered at ~ 0.7 nm, indicating an enlarged effective pore size and improved pore accessibility. Such structural evolution suggests that appropriate $(\text{NH}_4)_2\text{SO}_4$ incorporation promotes pore widening and enhances pore connectivity, which is beneficial for ion transport and diffusion.

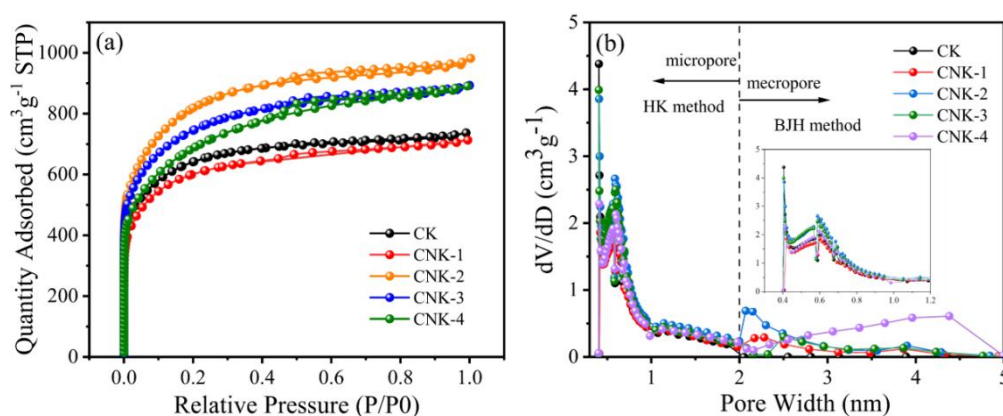


Figure 2 N_2 adsorption–desorption isotherms and pore size distributions of CK, CNK-1, CNK-2, CNK-3 and CNK-4. (a) N_2 adsorption–desorption isotherms and (b) Pore size distributions.

As summarized in Table 3, the specific surface area follows the order: $\text{CNK-2} > \text{CNK-3} > \text{CNK-4} > \text{CNK-1} > \text{CK}$, with CNK-2 reaching a maximum value of $2847 \text{ m}^2 \text{ g}^{-1}$, which is approximately 31% higher than that of CK. This result indicates that an appropriate $(\text{NH}_4)_2\text{SO}_4$ dosage effectively promotes pore generation, whereas insufficient doping (CNK-1) leads to incomplete pore development, and excessive doping (CNK-4) results in structural over-etching. Further analysis of the pore composition reveals that CNK-2 achieves the most optimized micropore–mesopore balance, featuring a high micropore surface area ($2179 \text{ m}^2 \text{ g}^{-1}$) and micropore volume ($0.99 \text{ cm}^3 \text{ g}^{-1}$), along with an average pore size of 2.11 nm. In contrast, excessive doping significantly reduces the micropore contribution (down to 59.6% for CNK-4) while increasing the meso-/macropore volume, indicating the collapse and merging of micropores. This phenomenon can be attributed to an over-activation effect, where excessive gas evolution and etching processes lead to the thinning and eventual destruction of pore walls, thereby deteriorating the microporous framework. As a result, the pore structure evolution follows a typical “generation–optimization–collapse” trend with increasing $(\text{NH}_4)_2\text{SO}_4$ dosage. Notably, moderate doping (CNK-2) enables the construction of a hierarchical porous structure with a well-balanced micro/mesopore distribution and a high specific surface area. Such structural characteristics are conducive to enhanced ion transport and efficient charge storage, which ultimately contribute to

the improved electrochemical performance.

Table 3 Porosity characteristics of CK、CNK-1、CNK-2、CNK-3 and CNK-4

Sample	S_{BET} (m^2/g)	S_{mic} (m^2/g)	V_{Total} (cm^3/g)	V_{mic} (cm^3/g)	$V_{\text{mec}+\text{mac}}$ (cm^3/g)	D_{a} (nm)	$S_{\text{mic}}/S_{\text{BET}}$ (%)
CK	2175	1746	1.10	0.75	0.35	2.02	81.3
CNK-1	2300	1874	1.13	0.96	0.17	1.98	81.4
CNK-2	2847	2179	1.50	0.99	0.51	2.11	80.3
CNK-3	2635	1952	1.37	0.86	0.51	2.08	74.1
CNK-4	2366	1409	1.37	0.65	0.72	2.32	59.6

The morphology and microstructure evolution of the samples with varying $(\text{NH}_4)_2\text{SO}_4$ doping ratios were investigated by SEM and TEM (Figure 3). The undoped CK sample exhibits a loose bulk structure with irregular surface features and limited pore development, indicating an underdeveloped porous framework. With the introduction of $(\text{NH}_4)_2\text{SO}_4$ (CNK-1), the surface becomes more uniform and porous, suggesting that initial doping promotes pore formation and improves structural homogeneity. With further increase in doping level, CNK-2 displays a well-defined three-dimensional porous architecture composed of interconnected channels linking the surface and interior. This highly open and continuous network significantly enhances pore accessibility and mass transport pathways. TEM analysis further reveals a layered structure with abundant pores and no discernible lattice fringes, confirming the amorphous nature of the carbon framework. The combination of layered morphology and interconnected porosity provides abundant active sites and efficient ion transport channels, which are essential for enhanced electrochemical performance. However, excessive $(\text{NH}_4)_2\text{SO}_4$ doping leads to structural deterioration. In CNK-3 and CNK-4, granular aggregates are observed on the surface, accompanied by partial pore blockage and reduced structural uniformity. The pore network becomes increasingly disrupted, with decreased connectivity and collapsed local structures. This phenomenon can be attributed to over-activation and excessive gas evolution during pyrolysis, which induces pore wall thinning and structural instability. Overall, the microstructure evolution follows a clear “formation–optimization–degradation” trend with increasing $(\text{NH}_4)_2\text{SO}_4$ dosage. Moderate doping (CNK-2) enables the construction of a hierarchical porous network with well-balanced pore distribution and high structural integrity, whereas insufficient or excessive doping results in incomplete pore development or structural collapse. This optimized architecture, featuring interconnected channels and abundant active sites, is highly favorable for ion transport and charge storage, thereby accounting for the superior electrochemical performance observed for CNK-2.

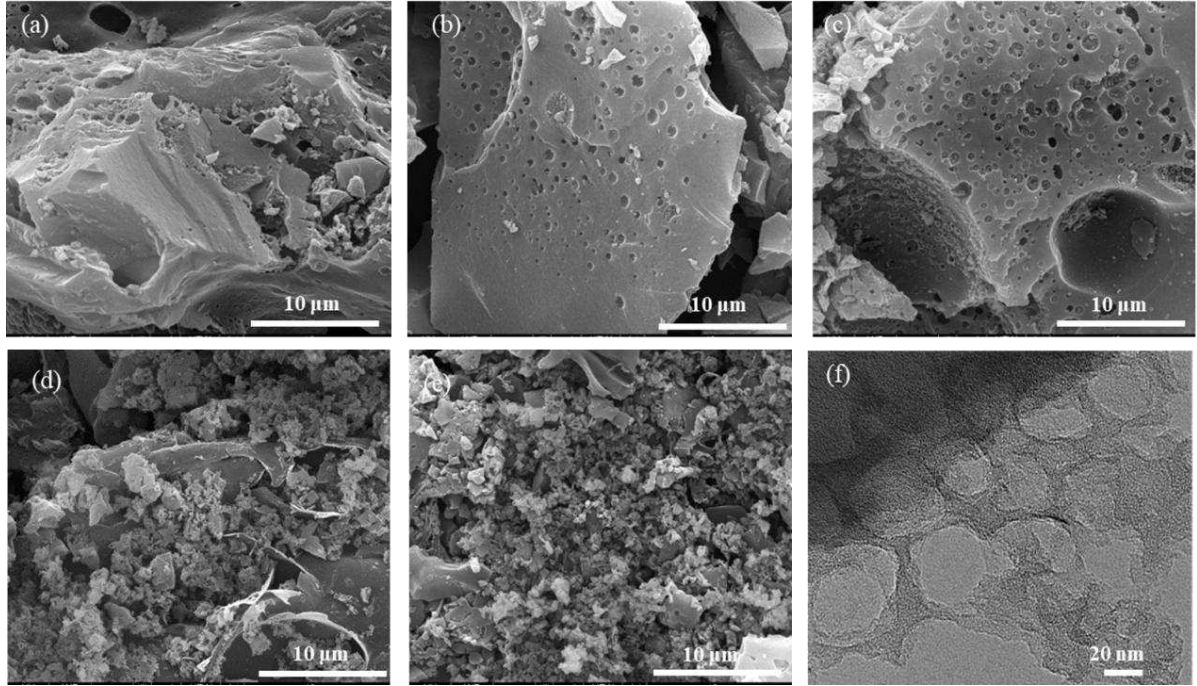


Figure 3 Electron micrographs of porous carbons CK, CNK-1, CNK-2, CNK-3 and CNK-4. (a) SEM image of CK, (b) SEM image of CNK-1, (c) SEM image of CNK-2, (d) SEM image of CNK-3, (e) SEM image of CNK-4 and (f) TEM image of CNK-2.

Surface chemical properties

To elucidate the effect of $(\text{NH}_4)_2\text{SO}_4$ doping on the electronic structure and surface chemistry of the porous carbon, XRD, Raman spectroscopy, and XPS analyses were systematically conducted (Figures 4 and 5). These complementary techniques provide insights into the structural ordering, defect evolution, and heteroatom incorporation of the carbon framework. As shown in Figure 4(a), all samples exhibit two broad diffraction peaks corresponding to the (002) and (100) planes, indicating a predominantly amorphous carbon structure. Upon $(\text{NH}_4)_2\text{SO}_4$ doping, the (002) peak intensity decreases, suggesting reduced graphitic stacking and increased structural disorder. This trend is further supported by Raman analysis (Figure 4(b)), where the D band ($\sim 1360\text{ cm}^{-1}$) and G band ($\sim 1560\text{ cm}^{-1}$) represent disordered carbon and graphitic domains, respectively. The $I_{\text{D}}/I_{\text{G}}$ ratio initially decreases from 0.96 (CK) to 0.89 (CNK-2), indicating improved structural ordering at moderate doping levels, and then increases for CNK-3 and CNK-4, reflecting the introduction of excessive defects under high doping conditions. This evolution reveals that $(\text{NH}_4)_2\text{SO}_4$ doping regulates the balance between graphitization and defect generation. The surface chemical composition and bonding states were further analyzed by XPS (Figure 4(c)). The survey spectra show dominant peaks of C 1s, O 1s, and F 1s for all samples, while additional N 1s and S 2p signals are observed in the CNK series, confirming successful heteroatom incorporation. Quantitative analysis (Table 4) indicates that the N and S contents increase with doping amount, reaching maximum values of 1.37% and 1.57%, respectively. Notably, LiF-HCl treatment effectively removes inorganic impurities (e.g., SiO_2 and Al_2O_3), while introducing fluorine species into the carbon framework. The formation of semi-ionic C-F bonds is expected to modulate the surface electronic structure and enhance charge transport. Overall, the combined XRD, Raman, and XPS results demonstrate that moderate $(\text{NH}_4)_2\text{SO}_4$ doping (CNK-2) achieves an optimal balance between structural ordering and defect density, while enabling effective multi-heteroatom

incorporation. This synergistic regulation of electronic structure and surface chemistry is critical for improving charge storage behavior and electrochemical performance.

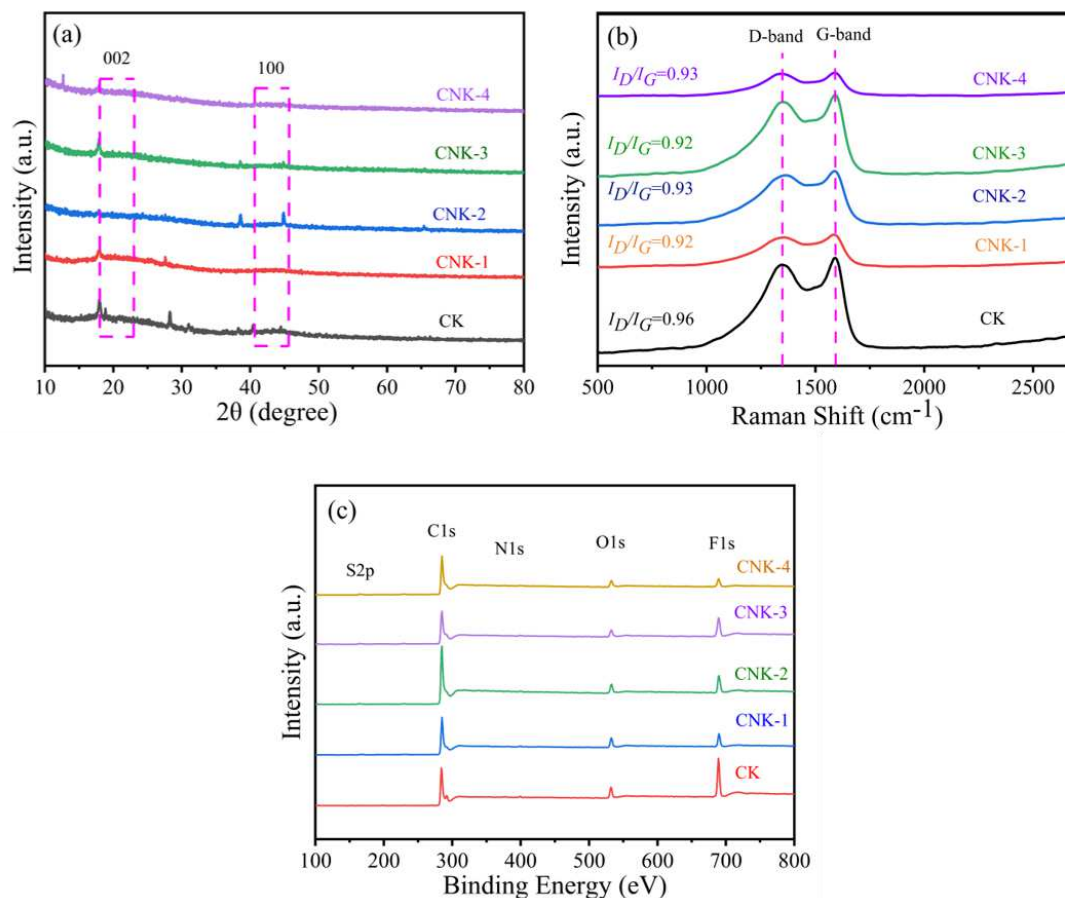


Figure 4 (a) The X-ray diffraction (XRD) patterns of CK, CNK-1, CNK-2, CNK-3, and CNK-4, (b) Raman spectra of CK, CNK-1, CNK-2, CNK-3, and CNK-4, and (c) XPS full spectrum of CK, CNK-1, CNK-2, CNK-3 and CNK-4.

Table 4 XPS analysis of CK, CNK-1, CNK-2, CNK-3, CNK-4 and CNK-2-H

Samples	C 1s (%)	N 1s (%)	S 2p (%)	O 1s (%)	F (%)
CK	69.60	1.17	-	7.01	22.22
CNK-1	84.01	0.97	0.85	5.63	8.53
CNK-2	77.06	1.13	1.09	6.08	14.65
CNK-3	84.92	1.18	1.37	6.24	6.31
CNK-4	76.19	1.57	1.30	10.19	10.76

Focusing on the optimized CNK-2 sample, high-resolution XPS analysis (Figure 5) was performed to elucidate the surface chemical states and their roles in electrochemical performance. The C 1s spectra (Figure 5(a)) and O 1s spectra (Figure 5(b)) reveal the coexistence of graphitic carbon and oxygen-containing functional groups (e.g., C–O and C=O), indicating a partially

graphitized carbon framework with abundant surface functionalities, which can enhance wettability and facilitate electrolyte access. The S 2p spectrum (Figure 5(c)) confirms the presence of both thiophene-like sulfur (C–S–C) and oxidized sulfur species, suggesting that sulfur is successfully incorporated into the carbon lattice and contributes to electronic structure modulation. Meanwhile, the N 1s spectrum (Figure 5(d)) is dominated by pyridinic and pyrrolic nitrogen species, which are widely recognized as electrochemically active sites that can provide additional pseudocapacitance and improve charge storage capability. In addition, the introduction of fluorine species (Figure 4(c)) leads to the formation of semi-ionic C–F bonds, which can induce strong electron-withdrawing effects and promote charge redistribution within the carbon framework, thereby enhancing electrical conductivity and interfacial charge transfer. TEM imaging and elemental mapping further confirm the porous structure and the uniform distribution of heteroatoms, ensuring the effective utilization of active sites. Overall, the results demonstrate that moderate $(\text{NH}_4)_2\text{SO}_4$ doping enables a synergistic regulation of surface chemistry and electronic structure, characterized by the coexistence of conductive carbon domains and abundant heteroatom-induced active sites. This optimized configuration facilitates both electric double-layer capacitance and pseudocapacitive contributions, thereby leading to enhanced electrochemical performance. In contrast, excessive doping introduces excessive defects and disrupts structural integrity, resulting in deteriorated surface properties and performance decline.

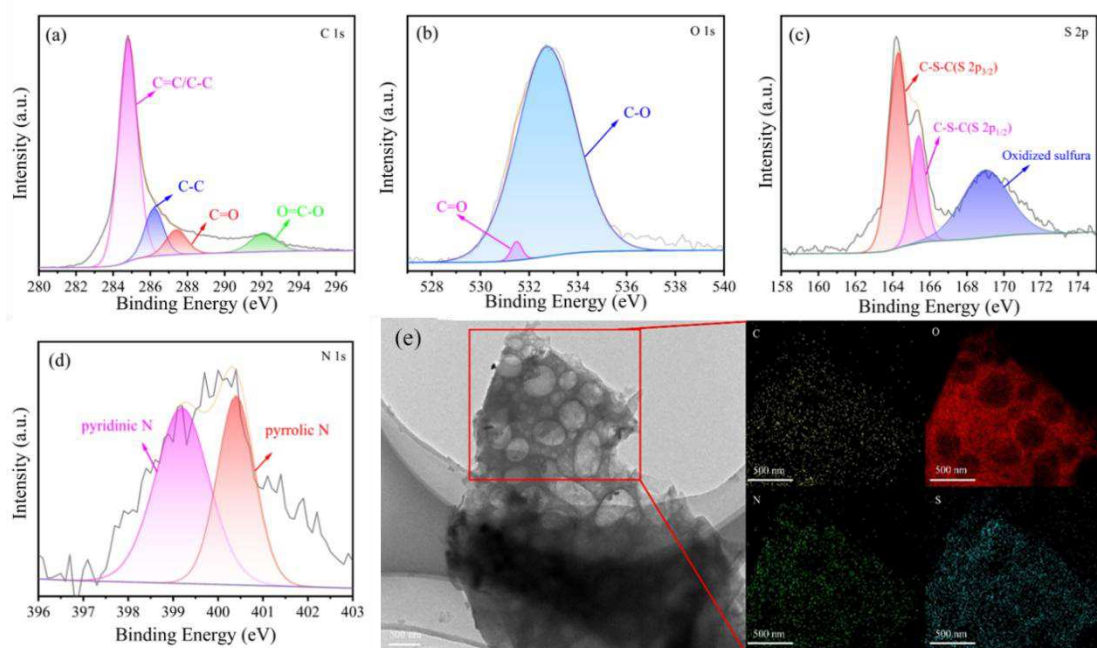


Figure 5 XPS map and TEM element image of CNK-2. (a) X-ray photoelectron spectra of C 1s region, (b) X-ray photoelectron spectra of O 1s region, (c) X-ray photoelectron spectra of S 1s region, (d) X-ray photoelectron spectra of N 1s region, (e) TEM diagram and element map of C, O, N, and S.

3.3 Electrochemical performance

To evaluate the electrochemical energy storage behavior of the as-prepared carbon materials, cyclic voltammetry (CV) measurements were conducted for all samples (CK, CNK-1, CNK-2, CNK-3, and CNK-4) at scan rates ranging from 10 to 200 mV s^{-1} (Figure 6). As shown in Figures

6(a) - 6(e), all samples exhibit quasi-rectangular CV curves, indicating typical electric double-layer capacitance (EDLC) behavior dominated by reversible ion adsorption/desorption at the electrode–electrolyte interface. Notably, the CV profiles remain well preserved even at a high scan rate of 200 mV s^{-1} , suggesting rapid charge propagation and low internal resistance, which can be attributed to the well-developed porous structure and good electrical conductivity. Among all samples, CNK-2 displays the most ideal rectangular shape with excellent symmetry, particularly at high scan rates, indicating superior rate capability and electrochemical reversibility. As shown in Figure 6(f), CNK-2 also exhibits the largest enclosed CV area at 10 mV s^{-1} , followed by CNK-3, implying a higher charge storage capacity. This trend is consistent with the pore structure analysis, where CNK-2 possesses an optimized hierarchical porosity and high specific surface area, enabling efficient ion transport and enhanced electrolyte accessibility. Furthermore, the improved capacitive behavior can be attributed to the synergistic effect of pore structure and heteroatom doping. The hierarchical porous network facilitates ion diffusion, while the introduction of N, S, and F heteroatoms modulates the surface electronic structure and provides additional active sites, thereby contributing to both EDLC and pseudocapacitive processes. These combined effects account for the superior electrochemical performance observed for CNK-2.

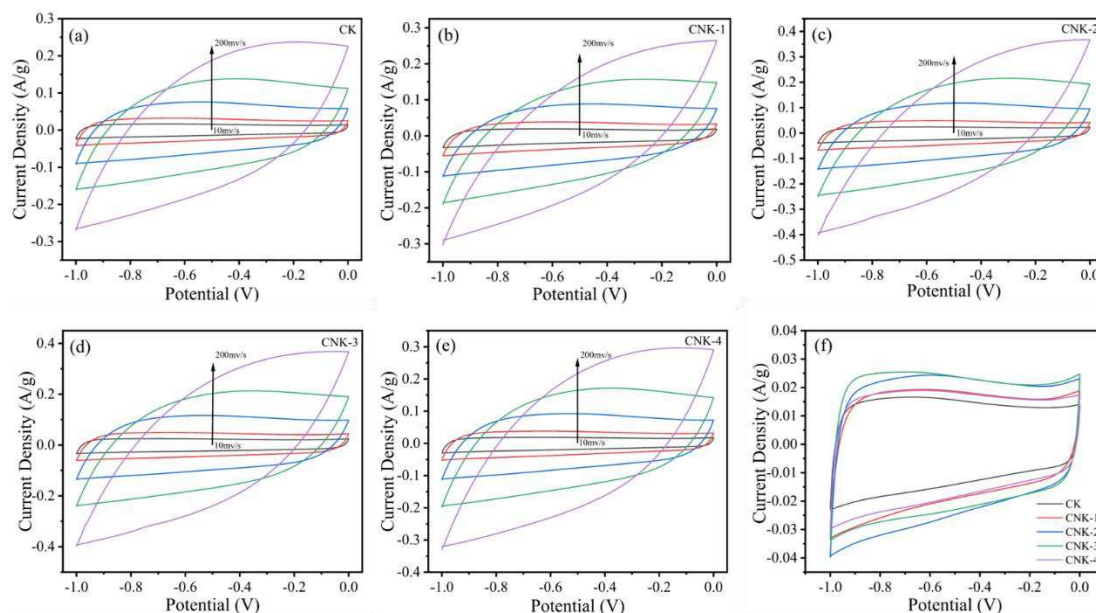


Figure 6 (a) CV curve of CK with a scan rate of 10–200 mV/s , (b) CV curve of CNK-1 with a scan rate of 10–200 mV/s , (c) CV curve of CNK-2 with a scan rate of 10–200 mV/s , (d) CV curve of CNK-3 with a scan rate of 10–200 mV/s , (e) CV curve of CNK-4 with a scan rate of 10–200 mV/s and (f) CV curves of CK, CNK-1, CNK-2, CNK-3 and CNK-4 with a scan rate of 10 mV/s .

Galvanostatic charge–discharge (GCD) measurements were conducted to further evaluate the charge storage behavior of the as-prepared electrodes (Figure 7). As shown in Figure 7a, all samples exhibit nearly symmetric triangular GCD curves at 1 A g^{-1} with negligible IR drop, indicating typical electric double-layer capacitive behavior with high reversibility and low internal resistance. Among them, CNK-2 displays the longest discharge time, corresponding to the highest specific capacitance. The capacitance values follow the order: CNK-2 (401 F g^{-1}) > CNK-3 (329 F g^{-1}) > CNK-4 (285 F g^{-1}) > CNK-1 (275 F g^{-1}) > CK (226 F g^{-1}), which is consistent with the

evolution of pore structure and surface area. The rate capability of CNK-2 was further examined at current densities ranging from 0.5 to 10 A g⁻¹ (Figure 7(b)). With increasing current density, the discharge time decreases, while the GCD curves retain good symmetry, indicating fast charge propagation and excellent electrochemical reversibility. As shown in Figure 7c, although the specific capacitance of all samples decreases at higher current densities due to limited ion diffusion, CNK-2 maintains the highest capacitance across the entire range, demonstrating superior rate performance. This behavior can be attributed to its optimized hierarchical pore structure, which ensures efficient ion transport pathways, as well as the presence of heteroatom-induced active sites that contribute to additional charge storage. Electrochemical impedance spectroscopy (EIS) was employed to investigate the charge transfer and ion diffusion kinetics (Figure 7(d)). All samples exhibit similar solution resistance (R_s), indicating comparable intrinsic conductivity and electrolyte accessibility. Notably, CNK-2 shows the smallest semicircle in the high-to-medium frequency region, corresponding to the lowest charge transfer resistance (R_{ct}), which suggests more efficient interfacial electron transport. In the low-frequency region, CNK-2 presents a nearly vertical line with the highest slope, indicative of ideal capacitive behavior and rapid ion diffusion. These results confirm that CNK-2 possesses optimized charge transport kinetics, benefiting from the synergistic effects of hierarchical porosity and multi-heteroatom doping. Overall, the superior electrochemical performance of CNK-2 originates from the combined advantages of well-developed pore architecture and regulated surface chemistry, which together facilitate efficient ion diffusion, rapid charge transfer, and enhanced charge storage capability.

Figure 7(e) shows the cycling stability of the optimized CNK-2 electrode was evaluated over 10,000 charge–discharge cycles at a current density of 1 A g⁻¹. The capacitance retention remains as high as 87%, decreasing only from 401 to 349 F g⁻¹, indicating excellent long-term electrochemical stability. Notably, the capacitance evolution shows a stable and nearly linear profile without significant fluctuation or abrupt decay, suggesting high reversibility during repeated charge–discharge processes. This outstanding stability can be attributed to the robust structural integrity of the hierarchical porous framework, which effectively mitigates pore collapse and maintains continuous ion transport pathways. In addition, the stable performance implies that the surface functional groups and heteroatom configurations remain electrochemically stable during prolonged cycling. The synergistic effect of well-developed pore architecture and multi-heteroatom doping not only enhances charge storage capability but also suppresses irreversible side reactions, thereby ensuring sustained electrochemical performance. Overall, the excellent cycling durability of CNK-2 demonstrates that the optimized structure–chemistry coupling is highly effective in maintaining both structural and electrochemical stability, highlighting its strong potential for practical supercapacitor applications.

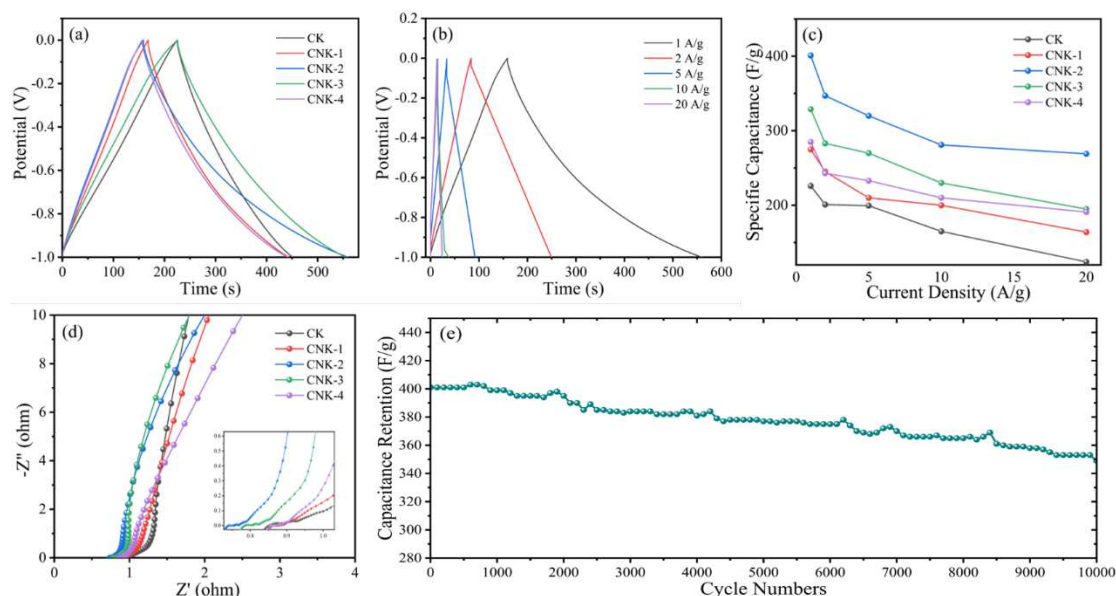


Figure 7 Constant current charge and discharge curve, impedance spectrum of CK、CNK-1、CNK-2、CNK-3 and CNK-4. (a) GCD curves for a current density of $1 \text{ A} \cdot \text{g}^{-1}$, (b) GCD curves of CNK-2 for a current density of $0.5\text{--}10 \text{ A} \cdot \text{g}^{-1}$, (c) Capacitances versus current densities, (d) Nyquist plots in the $10^{-2}\text{--}10^5$ frequency range and (e) Cycling stability of CNK-2 at $1 \text{ A} \cdot \text{g}^{-1}$

Overall, the CNK-2 sample, obtained with an optimal $(\text{NH}_4)_2\text{SO}_4$ doping level, exhibits the best electrochemical performance among all samples. It delivers a high specific capacitance of 401 F g^{-1} at 1 A g^{-1} , together with excellent rate capability and rapid charge–discharge kinetics, as well as outstanding cycling stability with 87% capacitance retention after 10,000 cycles. The superior performance of CNK-2 can be attributed to the synergistic coupling between its hierarchical porous architecture and multi-heteroatom-regulated surface chemistry. The well-developed pore structure ensures efficient ion transport and electrolyte accessibility, while N, S, and F doping modulates the electronic structure and introduces additional active sites, thereby enhancing both electric double-layer capacitance and pseudocapacitive contributions. These combined advantages endow CNK-2 with enhanced charge storage capability and structural stability, highlighting its strong potential as a high-performance electrode material for advanced supercapacitor applications.

4 Results and Discussion

Sulfur–nitrogen co-doped porous carbon with enhanced electrochemical performance was successfully prepared from fluid catalytic cracking (FCC) slurry via a synergistic strategy integrating in situ heteroatom doping, chemical activation, and post-etching purification. This integrated approach enables the simultaneous regulation of pore structure and surface chemistry, which is essential for overcoming the intrinsic limitations of FCC-derived carbon materials.

During the synthesis process, ammonium sulfate induces initial pore formation while enabling uniform N,S co-doping, thereby introducing abundant active sites and modulating the electronic structure. Subsequent KOH activation promotes the development of a hierarchical porous framework with improved connectivity through catalytic gasification. Meanwhile, LiF–HCl etching effectively removes inert inorganic impurities (e.g., SiO_2 and Al_2O_3) and introduces fluorine species, forming

semi-ionic C–F bonds that further optimize the pore structure and facilitate electron transport. The synergistic coupling of pore architecture and multi-heteroatom doping establishes a well-balanced structure–property relationship.

As a result, the optimized CNK-2 sample exhibits a high specific surface area of $2847\text{ m}^2\text{ g}^{-1}$, a total pore volume of $1.50\text{ cm}^3\text{ g}^{-1}$, and an average pore size of 2.11 nm , along with uniformly distributed heteroatoms. Benefiting from these structural advantages, the CNK-2 electrode delivers a high specific capacitance of 401 F g^{-1} at 1 A g^{-1} in 6 M KOH , while retaining 269 F g^{-1} at 20 A g^{-1} , indicating excellent rate capability. In addition, 87% capacitance retention is maintained after 10,000 cycles, demonstrating outstanding cycling stability.

Overall, this work provides an effective and scalable strategy for integrating impurity removal, pore structure engineering, and multi-heteroatom regulation in FCC-derived carbon materials. It not only enhances electrochemical performance but also offers a sustainable pathway for the high-value utilization of industrial waste, providing important insights for the rational design of advanced carbon electrodes in supercapacitor applications.

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