Harmonized edge/graphitic-nitrogen doped carbon nanopolyhedron@nanosheet composite via salt-confined strategy for advanced K-ion hybrid capacitors

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Abstract
Nitrogen doping has readily emerged as an efficient solution to boost potassium-ion storage of carbonaceous materials. Nevertheless, the capacity and lifespan enhancement of derived electrodes is still plagued by the incompetent in coordinating the dopant configurations. In the realm of emerging potassium-ion hybrid capacitor (PIHC) device, dictating nitrogen doping to enhance pseudocapacitive behavior and improve K⁺ diffusion kinetics of carbonaceous anodes is scarcely demonstrated. Herein, we report the design of hierarchical N-doped carbon nanopolyhedron@nanosheet composite via a salt-confined synthetic strategy with tunable doping configurations toward advanced PIHC anode. A harmonized edge- to graphitic-nitrogen ratio in such dual-carbon materials enables outstanding rate capability (130 mAh g⁻¹ at 10.0 A g⁻¹) and cyclic performance (with a capacity retention of 80% after 2000 cycles at 5.0 A g⁻¹) in half-cell tests. As expected, the thus-assembled PIHC full device with a working voltage of 4.2 V presents a high energy/power density (146 Wh kg⁻¹/8000 W kg⁻¹) and favorable cyclicability. This work is anticipated to offer an innovative insight into the coordination of nitrogen doping configurations in heteroatom-doped carbon anode targeting high-performance PIHC applications.

KEYWORDS
carbon nanopolyhedron@nanosheet composite, edge-nitrogen, graphitic-nitrogen, potassium-ion hybrid capacitor, salt-confined synthesis
1 | INTRODUCTION

The wide implementation of electric vehicles and electronic gadgets have stimulated massive exploration of emerging energy storage systems especially potassium-ion hybrid capacitors (PIHCs).\textsuperscript{1-9} Indeed, K-based energy storage devices have readily demonstrated great potentials to replace Li-based counterparts because of their collective merits, which include (i) the wide availability of K resources due to abundant earth’s crust (K ~ 2.09 wt% vs. Li ~ 0.0017 wt%); (ii) the low-cost aspect of carbonate-based electrolytes; and (iii) the cost-effectiveness of current collectors, where Al foil could replace Cu foil at the anode side. Basically, PIHCs synergize the merits of a high-energy battery-type anode and a high-power capacitor-type cathode. Nevertheless, their development remains at a nascent stage: the challenge mainly lies in the kinetic imbalance between the two electrodes and the large amount of K\(^+\) consumption in the electrolyte of the first charge/discharge cycle. On the latter concern, the preincorporated K\(^+\) can reduce the potential of the anode as well as provide additional K-ion sources to compensate the initial irreversible potassium loss due to the formation of a solid electrolyte interface (SEI) layer on the anode surface, thereby improving the energy density of the entire device. As a result, the primary bottleneck is to deal with the optimization in the rate capability of the anode and improvement of the specific capacity of the cathode to boost the final energy density and power density.\textsuperscript{10,11} KOH-pretreated commercial activated carbon (AC) has normally been employed as the cathode candidate, readily demonstrating favorable performance. In this regard, it is urgent to explore the matching anode materials.

To date, a variety of anode materials encompassing metals (Sn, Bi),\textsuperscript{12-16} transition metal compounds and MXene-based composites have been extensively studied,\textsuperscript{17-25} manifesting outstanding reversible capacity for K-ion storage. However, their cyclic stability and lifespan still cannot satisfy the practical needs. Carbon-based materials harnessing low cost, production scalability and superb conductivity have been considered as appealing candidates to render high-performance PIHC anodes. Typical graphite anodes based on K-ion intercalation/extraction otherwise suffer from low specific capacity and poor rate performance, mainly stemming from huge volume variation and limited ion diffusivity upon discharge/charge.\textsuperscript{26,27} Accordingly, unremitting efforts have been devoted to exploring amorphous carbons (e.g., soft carbon, hard carbon) with heteroatom dopants and porous architectures, aiming to realize better accommodation of K\(^+\) throughout supplementary adsorption pathway.\textsuperscript{28-33} In this respect, nitrogen doping in hierarchical carbon skeletons has been experimentally and theoretically recognized as an effective solution to substantially boost K-ion storage with facile electrokinetics. For instance, Qiu et al. managed to prepare N-doped carbons with a high doping level (15.5 at\%) as PIHC anode materials. Thus-derived device in turn showed outstanding cyclability (81.5% capacity retention for 5000 cycles at 5 A g\(^{-1}\)).\textsuperscript{34} Despite fruitful progress achieved in designing N-doped carbon nanostructures, it is still questionable (i) whether elevating the total content of nitrogen dopants would be ultimately beneficial to improving the anode performance and (ii) whether designing enriched edge-nitrogen doping would lead to better K-ion storage. Note that most existing studies highlighted the significance of high nitrogen contents and dominant edge-nitrogen species yet failed to pinpoint the contribution from graphitic-nitrogen dopant.\textsuperscript{35-38} In other words, there has been no systematic study whatsoever on the harmonization of edge- and graphitic-nitrogen in regulating the potassium storage properties. Especially in the realm of PIHC anodes, adjusting nitrogen doping configurations in carbonaceous materials to realize better pseudocapacitive activity and improve K\(^+\) diffusion kinetics is scarcely demonstrated.

Recent years have witnessed a growing attention in utilizing metal–organic framework (MOF)-derived carbons in energy storage and catalysis owing to their tailored architecture, considerable surface area and ample heteroatom doping.\textsuperscript{39-42} In the realm of anode design for K-ion storage, a representative work by Yu and colleagues reported the preparation of macroporous ZIF-8 carbonized three-dimensional (3D) N-doped hierarchical porous carbon, which harvested favorable electrochemical performance (94 mAh g\(^{-1}\) at 10.0 A g\(^{-1}\)).\textsuperscript{40} However, direct pyrolysis of MOFs usually results in uncontrollable manipulation of nitrogen species. Robust approaches to dictate the type/concentration of nitrogen doping in MOF-derived carbons still remain elusive.

Herein, we exploit a salt-confined strategy to produce hierarchical N-doped carbon nanopolyhedron@nanosheet composite with tunable doping configurations for the first time targeting high-performance PIHC anode. Throughout sealing ZIF-8 within the NaCl crystals upon pyrolysis, 3D architecture can be obtained by simultaneously forming carbon nanopolyhedrons from ZIF-8 and carbon nanosheets from salt compartments. By varying the pyrolysis temperature at 700°C, 800°C and 900°C, N-doped dual-carbon composites (NC-700, NC-800 and NC-900) bearing different content ratios of edge- to graphitic-nitrogen can be constructed. Electrochemical evaluation indicates that NC-800 exhibits the best rate capability (130 mAh g\(^{-1}\) at 10.0 A g\(^{-1}\)) and cyclic performance (with a capacity retention of 80% after 2000 cycles at 5.0 A g\(^{-1}\)) for potassium storage. Note that NC-800 affords a total nitrogen content of 14.7 at
% with an edge-to-graphitic-nitrogen ratio of 2, lower than that of NC-700 (a total content of 20.1 at% with a ratio of 6), implying the significance of harmonizing nitrogen species. This is systematically verified by in situ/ex situ analytical characterizations combined with density functional theory (DFT) simulations. Impressively, the advance of NC-800 further results in improved anode performances to enable PIHC full-cell implementation. When coupled with AC cathode, thus-assembled PIHC deliver high energy and power density (146 Wh kg$^{-1}$/8000 W kg$^{-1}$).

2 | RESULTS AND DISCUSSION

The preparation procedure of N-doped carbon nanopolyhedron@nanosheet composite is schematically illustrated in Figure 1(A). First, ZIF-8 powder was obtained by using the precursors of Zn(NO$_3$)$_2$·6H$_2$O and 2-methylimidazole. Thus-produced ZIF-8 crystals were evenly distributed in a saturated NaCl salt solution by ultrasonic treatment under stirring. Upon continuously adding ethanol, a NaCl recrystallization process occurred.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (A) Schematic illustration of the salt-confined synthetic procedure of N-doped dual-carbons. (B) Real photograph showing the original salt, ZIF-8@NaCl and NC production. (C) Low-magnification transmission electron microscopy (TEM) image of NC-800. (D) Scanning transmission electron microscopy (STEM) image and corresponding energy-dispersive spectrometry (EDS) mapping of NC-800. High-resolution TEM (HRTEM) images of (E) NC-700, (F) NC-800 and (G) NC-900.
in such mixed solution. Subsequently, N-doped carbon hybrid/NaCl can be fabricated throughout a one-step pyrolysis at an elevated temperature (e.g., 700°C, 800°C and 900°C) in an Ar atmosphere. In this respect, a decomposition process occurs in the salt-sealed MOFs. The decomposed intermediate species were trapped within the NaCl salt reactor to initiate an in situ self-assembly process. Further carbonization results in the formation of graphitic-like carbon nanosheets. The dual-carbon architecture was finally synthesized after the facile removal of the salt seal. In this regard, NC-700, NC-800 and NC-900 products were accordingly obtained. Such a salt-confined synthetic route obviously possesses collective advantages, including large scalability, cost-effectiveness and ease-of-preparation (Figure 1B).

The morphologies of NC-700, NC-800 and NC-900 were inspected by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The pure NaCl crystal, ZIF-8 nanopolyhedron and salt-sealed NC upon pyrolysis were probed, as shown in Figures S1 and S2, Supporting Information. After the removal of salt by washing in water, 3D carbon nanopolyhedron@nanosheet architecture can be witnessed by SEM (Figure S3, Supporting Information). Figure 1C displays a typical low-magnification TEM image of the NC-800, manifesting the existence of a dual-carbon configuration. Corresponding scanning transmission electron microscopy (STEM) image

![Figure 2](image-url)

**Figure 2** (A) X-ray diffraction (XRD) patterns and (B) Raman spectra of NC-700, NC-800 and NC-900. (C) X-ray photoelectron spectroscopy (XPS) Na 1s spectrum of NC-800 upon fabrication. XPS N 1s spectra of (D) NC-700, (E) NC-800 and (F) NC-900. (G) N$_2$ adsorption/desorption isotherms of NC-700, NC-800 and NC-900. (H) The corresponding pore size distribution of NC-800. (I) Schematic illustration of as-obtained N-doped dual-carbon architecture.
and energy-dispersive spectrometry mappings show homogeneous distribution of C, N and O elements (Figure 1D). High-resolution TEM observations indicate that the pyrolysis temperature exerts a profound impact on the degrees of structural order (Figure 1E–G). By elevating the carbonization temperature, the detailed structure varies from amorphous (NC-700) through short-range ordered (NC-800) to nanocrystalline (NC-900). The interplanar spacings of NC-800 (0.391 nm) and NC-900 (0.38 nm) become progressively clear (Figure S4, Supporting Information).

As-designed N-doped dual-carbons were further examined by a suite of characterization tools including X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and N₂ adsorption/desorption analyzer. Figure 2(A) presents XRD patterns of obtained samples, all of which display a broad peak centered at ~25°, corresponding to the (002) plane of graphite. It is evident that the positions of these peaks shift to smaller angles as compared with that of natural graphite, suggestive of increased interlayer distance. As such, the peak at 22° of NC-800 can be ascribed to the interlayer spacing of 0.39 nm according to Bragg equation. The extended distance is mainly due to heteroatom doping,32,43,44 in favor of augmenting the active sites and accelerating the diffusion of alkali metal ions. As depicted in Figure 2(B), Raman spectra of NC-700, NC-800 and NC-900 show two characteristic signals at 1340 and 1591 cm⁻¹, corresponding to the D-band and G-band peak, respectively. It is noted that the I_D/I_G value becomes smaller when escalating the pyrolysis temperature (Table S1, Supporting Information), indicative of higher graphitization with declined defect density. Sheet resistance (Rₛ) distribution maps of NC-700, NC-800 and NC-900 were further collected. It can be observed that the NC-900 film manifests an average Rₛ value of 327 Ω sq⁻¹, suggesting a superior electrical conductivity (Figure S5, Supporting Information). XPS measurements were performed to probe the elemental constitutions and nitrogen doping levels of NC-700, NC-800 and NC-900. The full spectrum of NC-800 contains C, N and O elements, accounting for 82.6 at%, 14.7 at% and 2.7 at%, respectively (Figure S6, Supporting Information). The detection of tiny oxygen content might be related to the surface-bound oxygen when handling the products in air. High-resolution Na 1s spectrum shows the absence of sodium signals, indicating the thorough removal of salt seal (Figure 2C). With the increase of pyrolysis temperature, the sp² carbon proportion becomes higher in the C 1s spectrum, corroborating enhanced carbonization degree (Figure S7, Supporting Information). Figure 2(D–F) displays the high-resolution N 1s spectra, which could well fit into three components corresponding to pyridinic N (N-6, 398.4 eV), pyrrolic N (N-5, 400.2 eV) and graphitic N (N-Q, 401.1 eV) contribution. Graphitic N represents that a nitrogen atom replaces a carbon atom in the hexagonal ring; whereas pyridinic N and pyrrolic N are classified as edge-nitrogen dopants. Interestingly, the contents of edge- and graphitic-nitrogen dopants, along with the total nitrogen concentrations, can be tuned by varying the pyrolysis temperature (Table S1, Supporting Information). Meanwhile, under the identical processing temperature, the nitrogen content of the NC-800 is higher than that of the pure NC-800 prepared without salt confinement, suggesting the protective growth effect of salt (Figure S8 and Table S2, Supporting Information). Figure 2(G) manifests N₂ adsorption/desorption isotherms of NC-700, NC-800 and NC-900, with the calculated surface area values marked. As shown in Figure 2(H), NC-800 obviously displays a suitable value (1174 m² g⁻¹) in comparison with its counterparts and affords the presence of micropores (1.78 nm). In contrast, NC-900 possessing a considerable surface area value might result in excessive consumption of electrolyte. The surface area value of NC-700 is otherwise too small to have sufficient ion/electron transport channels. Collectively, the N-doped carbon nanopolyhedron@nanosheet composite manufactured via our salt-confined strategy possesses special advantages such as 3D porous framework, dual-carbon architecture and harmonized nitrogen content, which is ultimately conducive to the K-ion diffusion, electron transport and volume change buffer (Figure 2I).

The potassium storage properties of the obtained N-doped dual-carbon materials were investigated in K-ion half-cell using potassium metal as the counter electrode and KPF₆ as the electrolyte. As shown in Figure S9, Supporting Information, the first three cycled cyclic voltammetry (CV) profiles of NC-700, NC-800 and NC-900 in the voltage range of 0.01–3.0 V (vs. K/K⁺) at a scan rate of 0.1 mV s⁻¹ were collected. During the first discharge cycle, a broad peak appears at 0.6 V and disappears in the subsequent cycles, which can be ascribed to the formation of SEI. The sharp intensification of current response at low voltage indicates the insertion reaction of K⁺. Meanwhile, the CV shapes of following two cycles present no significant change, revealing excellent reaction stability of NCs. The obvious capacity loss at the first cycle is mainly concerned with the formation of SEI and the irreversible reaction on the electrode surface, resulting in the limited initial Coulombic efficiency (ICE) (Figure S10, Supporting Information).45,46 The low ICE might also originate from the large surface area and ample defects of the dual-carbon composite. In the realm of PIHC device, note that the low ICE could be compensated by a prevailing prepotassiation strategy. Figure 3(A) displays the rate performances of NC-700, NC-800 and
NC-900 electrodes at various current densities. As such, NC-800 shows reversible capacities of 366, 299, 247, 209, 181 and 147 mAh g\(^{-1}\) at the current densities of 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 A g\(^{-1}\), respectively. Even at a high current density of 10.0 A g\(^{-1}\), it enables a compelling capacity of 130 mAh g\(^{-1}\), indicative of favorable rate capability. In contrast, the NC-700 has a high initial capacity yet accompanied by rapid decays, while NC-900 has good stability but delivers low specific capacity. To prevent the data randomness, multipoint statistics was adopted by plotting the interval graph of first-cycle charging capacity values (Figure S11, Supporting Information), again showing the superiority of NC-800. Compared to the recently published studies based on nitrogen-doped carbon anodes, our NC-800 harvests an advanced rate performance especially at high current densities (Figure 3B).\(^{24,33,36,40,47-51}\)

The cycling performances of these N-doped dual-carbon electrodes were consequently evaluated under different current densities. As shown in Figure 3(C), NC-800 presents a high cyclic stability to retain a reversible capacity of 240 mAh g\(^{-1}\) after 300 cycles at 0.2 A g\(^{-1}\). In contrast, NC-700 harnessing both higher nitrogen total content and larger edge-nitrogen proportion shows a conspicuous capacity fading under the same current density. At a current density of 1.0 A g\(^{-1}\), NC-800 could realize an initial capacity of 207 mAh g\(^{-1}\) and maintain 150.1 mAh g\(^{-1}\) upon 1900 cycles, corresponding to a capacity retention of 73% (Figure 3D). The related activation for the first 10 cycles of NC-800 is displayed in Figure S12, Supporting Information. This performance is clearly superior to those of its counterparts (NC-700 and NC-900). Encouragingly, when the current density is escalated to 5.0 A g\(^{-1}\), NC-800 can still retain ~80% of the

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**FIGURE 3**  (A) Rate performances of NC-700, NC-800 and NC-900. (B) Comparison of the rate performances between NC-800 in this work and other reported carbonaceous anodes. Cyclic performances of different NC electrodes at (C) 0.2 A g\(^{-1}\), (D) 1.0 A g\(^{-1}\) and (E) 5.0 A g\(^{-1}\).
initial capacity value after 2000 cycles. Nevertheless, NC-700 gradually malfunctions to cycle under such a high current density, as shown in Figure 3(E) and Figure S13, Supporting Information. In addition, the electrochemical performance of pure NC-800 without salt confinement was also evaluated, displaying inferior rate capability and cycling stability as compared to those of NC-800 (Figures S14 and S15, Supporting Information). This further confirms the advancement of dual-carbon architecture with harmonized nitrogen doping configurations.

To gain a better understanding of the favorable K-ion storage performance of NC-800, the N-doping environments and electrochemical kinetics were analyzed. Figure 4(A) plots the fundamental differences in the proportions of N-doping among the three examined electrodes. Obviously, the optimal performance has been achieved when the ratio of edge-nitrogen to graphitic nitrogen reaches ~2. In this respect, edge-nitrogen is beneficial to adsorbing K ions for inducing surface-driven pseudocapacitive behavior, while graphitic-nitrogen possesses high stability and high electrical conductivity: the coordination between these two would ultimately maximize the advantages of NC-800. On such basis, Figure 4(B) draws the comparison of the galvanostatic charge/discharge (GCD) curves (the 2nd cycle) collected at 0.05 A g\(^{-1}\) between NC-700, NC-800 and NC-900 electrodes. It is evident to observe that NC-800 offers the highest capacity value, implying that NC-800 is more
suitable as a battery-anode for high-energy PIHCs. To specify the reaction kinetics, electrochemical impedance spectroscopy (EIS) tests during the first cycle among three electrodes were carried out. As presented in the Nyquist plots in Figure 4(C), the sloping lines at the low-frequency regime reflect K-ion diffusion. NC-800 discloses more facile diffusion as compared to the other counterparts. To further quantify the ion diffusion process, galvanostatic intermittent titration technique (GITT) was utilized to ascertain the K-ion diffusion coefficient ($D_{K^+}$) in NC-700, NC-800 and NC-900 electrodes. This was carried out by using a series of pulse current at 80 mA g$^{-1}$ for 20 min between rest intervals for 60 min during the first cycle. Based on the GITT profiles shown in Figure 4(D), Figure 4(E) discloses the calculated $D_{K^+}$ values of the three electrodes during 2nd-cycle potassiation/depotassiation stage. The diffusion coefficient of NC-800 at the open-circuit voltage point is the largest, which is in good agreement with the EIS results. It is also found that all $D_{K^+}$ values decline with the reduction of the voltage during potassiation process, indicating that the diffusion-limited intercalation kinetics mainly occurs at the low potential. Meanwhile, to explore the stability of K-ion diffusion, GITT profiles were in addition recorded after 200 cycles (Figure 4(F)). In this regard, NC-800 possesses the highest ion diffusion stability (Figure 4(G)), echoing well with the foregoing rate and cyclic performances.

To fully clarify the electrochemical kinetics of edge- and graphitic-nitrogen synergies for K-ion storage, the pseudocapacitive contribution was probed. CV profiles of NC-700, NC-800 and NC-900 electrodes at different scan rates from 0.1 to 2.0 mV s$^{-1}$ were firstly collected (Figure S16, Supporting Information). In the CV curves, the peak current ($i$) and scan rate ($\nu$) obey a power law: $i = a\nu^b$, where the $b$ value can be derived by the slope of $\log(i)$ versus $\log(\nu)$ plot. A $b$ value of 0.5 represents a diffusion-controlled process, while the $b$ value of 1 suggests a capacitive-dominant process. As revealed in Figure 4(H), NC-800 harvests a $b$ value of 0.88, indicative of a combined diffusion-controlled and pseudocapacitive mechanism. In this regard, the pseudocapacitive contribution to the total capacity can be distinguished by using the equation: $i = k_1\nu^{1/2} + k_2\nu$, where $k_1\nu^{1/2}$ and $k_2\nu$ represent the diffusion-controlled and capacitive-controlled contribution, respectively. As for the NC-800 electrode, the capacitive contribution rises with the increase of the scan rates, reaching 83% at a scan rate of 2 mV s$^{-1}$ (Figure S17, Supporting Information).

To the best of our knowledge, there seems to be a consensus reached in recent studies that a high total nitrogen content in N-doped carbons typically leads to good electrochemical performance (as compared to counterparts with relatively low total contents) and that a predominant edge-nitrogen doping (N-5 and N-6) is beneficial to extraordinary cyclability. The results shown in our work somewhat deviate from those achieved therein: NC-700 possessing a high total doping concentration (20.1 at%) and an edge-enriched configuration (85.7%) otherwise exhibits relatively poor rate and cyclic performance. This might suggest that excessive doping especially by dominating edge-nitrogen contribution could escalate the degree of the electrode instability. In contrast, NC-800 affording declined total nitrogen content (14.7 at%) and harmonized edge- to graphitic-nitrogen ratio demonstrates unprecedented potassium storage stability. In fact, the balance/contribution from graphitic-nitrogen (N-Q) species has been normally overlooked in the realm of potassium storage. Since nitrogen is more electronegative than carbon, the incorporation of N-Q not only sustains the electrical conductivity of the material but also improves the system stability toward potassium storage. More significantly, the higher charging capacity delivered by NC-800 in the low voltage range as compared to NC-700 and NC-900 renders it even more suitable for practical anodes in full-cell applications. As shown in Table S3, Supporting Information, NC-800 with balanced N-doping configuration delivers favorable electrochemical performance to rival the state-of-the-art carbonaceous anodes with pure N-doping.

To systematically investigate the K-ion storage mechanism of NC-800, *operando* EIS and ex situ XPS/TEM characterizations were carried out during the process of potassiation/depotassiation. Figure 5(A) displays *operando* EIS analysis at different states, with the corresponding first-cycle GCD profiles acquired at 0.2 A g$^{-1}$. During the discharge process, a significant increase followed by a decrease in the semicircles at high/medium-frequency regions could be observed. The increase might be related to the formation of SEI films and some irreversible side reactions. The subsequent decline is mainly due to the intercalation of K$^+$, which is conducive to the ionic conductivity of NC-800 and hence, influence the resistance of SEI. In the subsequent charging process, the impedance spectra basically recover to the initial state. This serves as a solid proof for the good reversibility of the NC-800. XPS K 2p and C 1s spectra at different voltage states during the first cycle were recorded (Figure S18, Supporting Information). As for the initial state, the carbon signal is quite strong with no K signal detected. Along with the discharge process, the C 1s peak decreases its intensity, while the K 2p peak reaches the highest intensity at the end of discharge (0.01 V). This phenomenon reflects the uptake of potassium ions. During the charging stage, with the release of K$^+$, the intensity of K 2p peak decreases obviously, indicative of good reversibility. In further contexts, ex situ
TEM examination reveals that no significantly morphological change of NC-800 can be found after 200 cycles, again confirming good electrode stability (Figure S19, Supporting Information).

To unravel the synergistic effect of edge- and graphitic-nitrogen doping, theoretical simulations based on DFT calculations were carried out. Thermodynamic stability and electronic structures are evaluated based on graphitic-nitrogen (N-Q) and two typical edge-nitrogen structures, N-5 and N-6. As shown in Figure 5(B), the formation energy \( E_f \) of the N-Q is around 20 times lower than that of edge nitrogen, N-5 and N-6. It can be ascribed to the energetic preference for N-Q in a perfect pristine graphene sheet. Assuming a Boltzmann distribution that the average equilibrium concentration of a certain type of noninteracting defects is proportional to \( \exp(-E_f/k_B T) \), at an experimental temperature \( \sim 800^\circ \text{C} \), N-5 and N-6 are much difficult to be directly formed as compared to N-Q in pristine graphene. The formation of N-5 or N-6 is accompanied by the generation of carbon vacancies (or holes). This is the reason that they are usually found in the edges or existing defects. The above formation energy was calculated at a relatively N-deficient environment, which accords well with the operating conditions of our experiment. The formation energy of N-doped carbon structures on different chemical conditions \( (\mu_N) \) is further shown (Figure S20A, Supporting Information), where N-6 could be dominant under N-rich conditions, in good agreement with the other results.\(^{57,58}\) N-doped structures are found to be stabilized further with an N-Q to substitute N-5 (Figure S20B, Supporting Information). Therefore, the presence of N-Q in the bulk helps to stabilize the system under a given nitrogen doping degree. Figure 5(C) shows the binding energy \( E_b \) of a K atom on different N-doping structures. Although pure N-Q defects show poor binding strength with K atoms, edge-nitrogen doped carbon structures with one more N-Q are more preferable for K adsorption to those without the presence of N-Q. For instance, the N-5_N-Q architecture shows a lower \( E_b \) \((-3.42 \text{ eV})\) than that of 1N-5 \((-2.86 \text{ eV})\) or the counterpart with the same number of nitrogen atoms 2N-5 \((-3.31 \text{ eV})\). Among them,
2N-5_N-Q (edge-N: graphitic-N = 2:1) has the lowest $E_b$, indicating advanced K adsorption ability. Figure 5(D) depicts the density of states of the N-doped carbon structures with the harmonization of N-Q. In comparison with the architectures with N-5_N-Q and N-6_N-Q defects, the 2N-5_N-Q is metallic and has more states near Fermi level, implying better electrical conductivity.

To envisage the practical applications of our designed N-doped dual-carbons, PIHC full-cells were further assembled (Figure 6A) by employing NC-800 as the anode and activated AC (AAC) as the cathode (denoted as NC-800//AAC). As for the cathode fabrication, commercial AC was further treated with KOH to obtain AAC with a specific surface area of 2101 m$^2$ g$^{-1}$ (Figures S21 and S22, Supporting Information). The electrochemical performance of the AAC in half-cell is systematically shown (Figures S23–S25, Supporting Information).

According to the charge balance theory of anode and cathode ($m_{\text{anode}}C_{\text{anode}} = m_{\text{cathode}}C_{\text{cathode}}$), the performance of our PIHC full-cell has been optimized when the mass ratio of cathode and anode reaches 2. In turn, the voltage window of PIHC is adjusted to be 0.01–4.2 V, as disclosed in Figure 6(B). The GCD profiles of thus-constructed PIHC display typical hybrid capacitor behavior (Figure 6C). Figure 6(D) manifests the specific capacity at different current densities. Even at 5.0 A g$^{-1}$, the specific capacity can still maintain 31 mAh g$^{-1}$. The excellent rate performance indicates the perfect match between NC-800 and AAC electrodes as well as the facile kinetics. Encouragingly, our PIHC harvests a maximum energy density of 146 Wh kg$^{-1}$. Even at a power density of 8000 W kg$^{-1}$, it enables an energy density of

![Figure 6](image_url)
56 Wh kg⁻¹ (at 10.0 A g⁻¹). Such a high-energy/high-power feature compares favorably with the state-of-the-art PIHCs reported recently, including Ca₀.₅Ti₂(PO₄)₃//AC,⁵⁹ soft carbon//AC,⁹ K₂TP//AC,⁶₀ KTO//NGC,⁶¹ S-NPCNs//AC⁶² and NHCS//ANHCS (Figure 6E).⁶³ In addition, the PIHC demonstrates remarkable cycling stability by exhibiting a long lifespan with a capacity retention of 78% over 8000 cycles at 0.5 A g⁻¹, corresponding to only 0.0027% decay rate per cycle (Figure 6f).

3 | CONCLUSION

In summary, hierarchical N-doped carbon nanopolyhedron@nanosheet composite has been fabricated via a salt-confined strategy and introduced for the first time to investigate the tailorable N-doping effect on PIHCs. Thus-derived 3D dual-carbon architecture not only optimizes the electron/K-ion diffusion pathway but also cushions the structural change during potassiation/depotassiation, thereby anticipating excellent rate and cyclic performance. Harmonized edge-to-graphitic-nitrogen dopant configurations are realized to benefit high-rate capability of 130 mA h g⁻¹ at 10.0 A g⁻¹. The pseudocapacitive potassium storage mechanism of our N-doped dual-carbon material is systematically verified by in situ/ex situ analytical characterizations and corroborated by theoretical simulations. Impressively, assembled PIHC full-cells on a basis of NC-800 anode and activated AC cathode manage to deliver high energy/power density (186 Wh kg⁻¹ /8000 W kg⁻¹), offering new insights into practical energy storage applications.

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CONFLICT OF INTEREST

The authors declared no potential conflicts of interest.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of this article.

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