Binding Se into nitrogen-doped porous carbon nanosheets for high-performance potassium storage

Huijuan Huang1 | Xiao Luo1 | Yu Yao1 | Xuefeng Zhou1 | Yu Jiang1 | Chunli Guo2 | Jiaqin Liu3 | Xiaojun Wu1 | Yan Yu1,4

1Hefei National Laboratory for Physical Sciences at the Microscale, Department of Materials Science and Engineering, CAS Key Laboratory of Materials for Energy Conversion, University of Science and Technology of China, Hefei, China
2College of Environmental Science and Engineering, Taiyuan University of Technology, Taiyuan, China
3Institute of Industry & Equipment Technology, Key Laboratory of Advanced Functional Materials & Devices of Anhui Province, Hefei University of Technology, Hefei, China
4Dalian National Laboratory for Clean Energy (DNL), Chinese Academy of Sciences (CAS), Dalian, China

Correspondence
Yan Yu, Hefei National Laboratory for Physical Sciences at the Microscale, Department of Materials Science and Engineering, CAS Key Laboratory of Materials for Energy Conversion, University of Science and Technology of China, Hefei, Anhui 230026, China. Email: yanyumse@ustc.edu.cn

Abstract
Selenium cathode has been demonstrated as a promising candidate of cathode material for low-cost and high-energy density potassium ion batteries (PIBs). Nevertheless, their applications are prevented by poor electrochemical performance due to the shuttle effect of high-order polyselenides, the sluggish diffusion of bigger K+, and the huge volumetric expansion during cycling. In this work, we design a multifunctional Se host (N-HCNS) by grafting ZIF-8-derived microporous carbon onto the surface of N-doped porous carbon nanosheets. The obtained N-HCNS carbon matrix integrates conductivity, captivity, and immobility abilities, which inhibits the polyselenides shuttle, improves the Se utilization, and buffers the volume change during cycling. The 3D hollow carbon skeleton enhances the infiltration of electrolytes. As an cathode for PIBs, the Se@N-HCNS electrode delivers an unprecedented life-span (260 mAh g⁻¹ at 1.0 A g⁻¹ after 2000 cycles) and exhibits a remarkable rate capacity (339 mAh g⁻¹ at 5.0 A g⁻¹). Density functional theory (DFT) calculation reveals the effective adsorption of K₂Se with pyridine and pyrrole nitrogen doping in carbon matrix. The unique synergetic design of electrode not only gives insight into the reaction mechanism but also highly emphasizes the potential capabilities of N-doped carbon in K-Se batteries.

KEYWORDS
nitrogen-doped carbon, potassium-selenium batteries (K-Se batteries), selenium cathodes
1 | INTRODUCTION

Lithium-ion batteries (LIBs) are the most popular electrochemical energy storage technology. Nonetheless, the low abundance and geographic scarcity of lithium limit the application of LIBs in the large-scale stationary. The exploration of alternative alkali metal-ion batteries using more abundant elements (such as sodium and potassium) has attracted more and more attention, especially for large-scale energy storage. Compared to sodium ion batteries (SIBs), potassium ion batteries (PIBs) show more advantages: (a) Potassium has a lower redox voltage than Na, which implies a relatively high voltage for a full battery; (b) Potassium possesses a smaller Stokes’ radius in carbonate solvents because it has a weaker Lewis acidity than Na; (c) Potassium ions show the highest ion conductivity and ion mobility than both Li ions and Na ions in carbonate electrolyte. Therefore, the PIB has advantages: (a) Potassium has a lower redox voltage than Na; (b) Potassium possesses a smaller Stokes’ radius in carbonate solvents because it has a weaker Lewis acidity than Na; (c) Potassium ions show the highest ion conductivity and ion mobility than both Li ions and Na ions in carbonate electrolyte. Therefore, the PIB has been regarded as a most promising candidate for next-generation low-cost energy storage system. The real challenge of PIBs is to develop high performance anode and cathode materials. Recently, many efforts have been devoted to searching anode materials (i.e. carbon-based and conversion reaction materials) with long cycle life and high capacity. Among these cathode materials, selenium has attracted considerable attention because it possesses better electrical conductivity (5 x 10^{-2} S m^{-1}) than S (1 x 10^{-3} S m^{-1}), and similar volumetric capacity (3250 mAh cm^{-3}) with sulfur (3470 mAh cm^{-3}). Moreover, the high electronic conductivity of Se leads to a highutilization rate of the active materials in batteries. All these merits make it an attractive energy storage system with both high power and high volumetric energy densities. However, the application of K-Se battery are prevented by the poor cycle life that results from the following issues: (1) Larger radius of K^+ leads to sluggish diffusion; (2) Shuttle effect of high-order polyselenides during redox reaction causes low Coulombic efficiency and short cycling lifespan; (3) Dramatic volume expansion during cycling results from a solid-phase reaction of alkali metal and selenium phase, leading to pulverization of the active materials. Many approaches have been reported to address the abovementioned issues. One of the most effective ways is to encapsulate the high-order polyselenides inside porous carbon host materials that can also enhance the conductivity of Se cathodes. Another approach is to design chemical bonds between the Se and the carbon matrix, which anchors polyselenide and suppresses the shuttle effect the polyselenides. Obviously, it is highly desirable to design a carbon host that can not only physical entrap Se and polyselenides but also form strong chemical binding to Se-contained species, simultaneously.

Herein, we develop nitrogen-doped porous carbon nanosheets with multiple adsorptive/catalytic sites that can simultaneously physically entrap and chemical anchor Se and polyselenides. This special two-dimensional (2D) hierarchical micro-mesoporous carbon nanosheets (denoted as N-HCNS) is fabricated by delicately integrating ZIF-8 and N-doped porous carbon nanosheets. The porous carbon matrix has the following merits: (1) 2D ultra-thin nanostructure with high porosity facilitates the liquid electrolyte to soak in and alleviates the volumetric change during potassiation/depotassiation; (2) Synergistic effect of chemical binding and physical trapping usually enhances stability and utilization of Se cathode after long cycling; (3) 3D flower-like carbon-based framework provides more active sites, and increase both ion mobility and electronic conductivity; (4) The N-doping in carbon skeleton introduces abundant defect in the carbon matrix that enhances chemical adsorption to polyselenides intermediates. After infiltration Se into the N-HCNS, the obtained Se@N-HCNS electrode exhibits unprecedented electrochemical performance in terms of high reversible capacity (542 mAh g^{-1} at 0.1 A g^{-1}), excellent rate capacity (339 mAh g^{-1} at 5.0 A g^{-1}) and ultralong life span (260 mAh g^{-1} after 2000 cycles at 1.0 A g^{-1}). The results of the Galvanostatic Intermittent Titration Technique (GITT) demonstrate enhanced carrier diffusivity of the Se@N-HCNS. The DFT calculation further verifies the N-5/N-6 doping structures are favorable for adsorption of K2Se, leading to improved electrochemical performance.

2 | RESULTS

Figure 1 shows the synthesis procedure of the Se@N-HCNS. Firstly, small-sized ZIF-8 with diameter ~ 30 nm was loaded on the MgO template through a one-step synthesis process (Figure S1A,B). The growth of the ZIF-8 on the MgO nanosheets was verified by the X-ray diffraction (XRD) patterns of the ZIF-8 and MgO@ZIF-8 (Figure S2A,B). The peaks at 43° and 62° of MgO@ZIF-8 correspond to the (200) and (220) planes of the MgO nanosheet, respectively. The MgO@ZIF-8 template was coated by carbon layer that derived from evaporation of the phenyl carbon (PC) in vacuumed. After removing the MgO template and following activation with KOH to create micro pores, nitrogen-doped 3D hierarchical carbon nanosheets (N-HCNS) were obtained. Finally, Se was infiltrated into the pores of the N-HCNS to prepare the Se@N-HCNS. For comparison, the N-doped mesoporous carbon nanosheets (N-MCNS) was prepared by a similar
process except ZIF-8 free. Moreover, the nitrogen doped microporous carbon (N-MC) was obtained by calcination of ZIF-8 directly. The Se@N-MCNS and the Se@N-MC were fabricated using the same infiltration process.

The morphologies of the MgO, the MgO@ZIF-8, the N-HCNS, and the Se@N-HCNS were investigated by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In Figure 2A,B, the ZIF-8 particles were homogenously loaded on the 2D MgO nanosheets (thickness: ~100 nm). The N-HCNS replicates the morphology of 2D MgO@ZIF-8 template after the self-assembly mesoporous carbon covering uniformly (Figure 2C). Figure 2D confirms that the ZIF-8 derived N-MC is encapsulated in the carbon nanosheets. After removing the MgO template by HCl, the N-HCNS nanosheets display a hollow structure consisting of the uniform carbon nanocapsules with an average size of 50 nm. Figure S3 shows the morphology and structure of the N-MCNS and the N-MC. The N-MCNS shows the 2D porous carbon nanosheets which are also composed of hollow capsules with a diameter of about 50 nm. The N-MC inherits the structure of zif-8. Figure 2E reveals the morphology of the Se@N-HCNS. No obvious Se particles are observed on the surface of the N-HCNS, revealing Se uniformly infiltrates into the pores of the carbon host through the melt diffusion process. The high-resolution transmission electron microscopy (HRTEM) of the Se@N-HCNS (Figure 2F) displays no obvious fringes or any other lattice structure and labels the amorphous Se species from the contrast of carbon, indicating the homogeneous encapsulation of Se. The images of scanning transmission electron microscopy (STEM) and corresponding element mapping are shown in Figure 2G–I, revealing a uniform dispersion of C, N, and Se species.

Figure S4 shows the XRD spectra of pure Se, the N-HCNS, and the Se@N-HCNS. The sharp characteristic peaks of pure Se feature a crystallized trigonal structure. No peaks of Se of the Se@N-HCNS appear, showing that Se is encapsulated into the pores of N-HCNS. Two broad peaks at ~24° and 43° were observed both in the XRD patterns of the N-HCNS and the Se@N-HCNS, corresponding to the amorphous carbon and short-range order carbon domains, respectively. The N-MCNS and the N-MC display the similar amorphous structures (Figure S4B,C). Raman spectra patterns of pure Se powder and the Se@N-HCNS are showed in Figure S5. Compared to pure Se, the peak of Se in the Se@N-HCNS shifts from 237 cm\(^{-1}\) to 254 cm\(^{-1}\), indicating that the trigonal Se transforms to short Se\(_n\) chains during the melt infusion process.\(^{27}\) As shown in Figure S6, the peaks centered at 1347 cm\(^{-1}\) and 1587 cm\(^{-1}\) in three samples feature the D-band of disordered sp\(^3\) carbon and vibrational G-band, respectively. The D/G intensity ratio (I\(_D\)/I\(_G\)) of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC are 0.94, 0.97, and 0.89, respectively, indicating the amorphous state of the carbon matrices.

Figure S7A–C compare the adsorption–desorption isotherms of the N-HCNS, the N-MCNS and the N-MC before and after infiltration Se. The Brunauer–Emmett–Teller
(BET) specific surface area is 1236 m² g⁻¹ for the N-HCNS and substantially decreases to 220 m² g⁻¹ for the Se@N-HCNS (Figure S7A), confirming that the Se is successfully embedded in the N-HCNS matrix. Abundantly available interspace in the N-HCNS can not only infiltrate more chain-like selenium phase but also release the volume expansion during cycling. The BET specific surface area for the N-MCNS and the N-MC are 622 and 2365 m² g⁻¹, respectively (Figure S7B,C). After infiltration of Se, the BET surface areas of the Se@N-MCNS and the Se@N-MC significantly decrease to 210 and 43 m² g⁻¹, respectively. It indicates that the Se particles encapsulated in the porous carbon matrix. After loading Se, the pore volume of the N-HCNS (0.83 cm³ g⁻¹) sharply reduces to 0.334 cm³ g⁻¹ for the Se@N-HCNS (Figure S7D), implying the efficient infiltration of Se into pores. The pore-size distributions of the N-HCNS are 0.55, 1.41, and 2.77 nm, which decreased sharply after the infiltration of Se. The hierarchical pore structure of the N-HCNS is inherited from the mesopores N-MCNS (Figure S7E) and the micropores N-MC (Figure S7F), which not only ensures an efficient confinement of Se but also buffers the volume change during cycling. Thermo Gravimetric Analysis (TGA) results (Figure S8A–C) indicate the Se contents of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC are 45.6, 45.1, and 44.4 wt.%, respectively. X-ray photoelectron spectroscopy (XPS) (Figure S9) reveals the chemical bonding configuration of Se in the Se@N-HCNS, the Se@N-MCNS and the N-MC. The peaks at 56.4 and 55.6 eV correspond to the Se 3d⁵/₂ and 3d³/₂ peaks, respectively. The peak located at 59.5 eV could be attributed to the Se-O and Se-N bonds, indicating the strong incorporation of the Se species with the N-doped 3D carbon framework. The nitrogen doping contents of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC are 1.09, 4.42, and 6.5 at.% (Table S1), respectively. The high-resolution N1s spectrum analysis of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC (Figure S10A–C) visualize four species of nitrogen, pyridinic N (398.4 eV), pyrrolic N (400.0 eV), quaternary N (401.1 eV), and N-O bonds (402.3 eV), respectively. The total content of pyridinic N (N-6) and pyrrolic N (N-5) in the Se@N-HCNS is 79.2 wt.%, higher than those of the other two samples (Table S2). It has been demonstrated that N-6 and N-5 have an electron negative inductive effect, leading to more exposed chemical reactive sites than electron-donating quaternary N (N-Q), which
optimizes the intrinsic reaction kinetics and facilitates the
electron conduction. Figure S11 shows Fourier-
transform infrared (FT-IR) spectra of the N-HCNS and the
Se@N-HCNS. They share the common peaks at 3450,
1642, 1611, and 834 cm\(^{-1}\), corresponding to the characteristic peak of hydrogen bond, C=O bond, C≡N bond, and C≡N bond, respectively. The peak of the Se@N-HCNS at 438 cm\(^{-1}\) attributable to the C-Se bond, which verifies the stabilize bond cooperation between the selenium phase and the carbon skeleton at the atomic scale.

The Se@N-HCNS electrode is expected to provide enhanced electrochemical performance in potassium storage. Figure 3A shows the cyclic voltammetry (CV) curves of the Se@N-HCNS with the voltage window of 0.5 ~ 3.0 V at a scan rate of 0.1 mV s\(^{-1}\). During the first potassiation process, two peaks at 0.81 and 1.52 V indicate the conversion reaction of Se to K\(_2\)Se is two-step progress. In the subsequent anodic scan, there are two corresponding peaks at 1.60 and 1.92 V, demonstrating the reversible two-step reaction of K\(_2\)Se and Se. The initial irreversible capacity is due to the decomposition of electrolyte and the formation of solid electrolyte interphase (SEI) on the interface of the electrode. After the initial cycle, the CV curves are almost overlapped, indicating excellent cycling performance of the Se@N-HCNS cathode. Figure 3B displays the potassium storage behaviors of the

![Figure 3](image)

**FIGURE 3** Electrochemical evaluation of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC electrodes as cathodes in K-Se batteries. (A) CV curves of Se@N-HCNS. (B) Cycle performance at 0.1 A g\(^{-1}\). (C,D) The galvanostatic charge–discharge curves and rate capacity performance of three electrodes at 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 A g\(^{-1}\). (E) Long cycling performance at high rates of 1.0 A g\(^{-1}\).
Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC at 0.1 A g\(^{-1}\). The Se@N-HCNS cathode delivers a higher reversible specific capacity of 542 mAh g\(^{-1}\) after 100 cycles. In cases of the Se@N-MCNS and the Se@N-MC, they only deliver reversible capacities of 296 and 169 mAh g\(^{-1}\), respectively. Figure S12 shows the specific capacity of the N-HCNS at 0.1 A g\(^{-1}\) in the voltage window of 0.5–3.0 V. It displays a low capacity of 60 mAh g\(^{-1}\) after 500 cycles, which indicates that the reversible capacity contributed by the N-HCNS is negligible.

Figure 3C compares the rate performance of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC. The Se@N-HCNS shows the best rate capacity among the three samples. It delivers unprecedented specific capacities of 610, 561, 501, 458, 400, and 337 mAh g\(^{-1}\) at 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 A g\(^{-1}\), respectively, much higher than those of the Se@N-MCNS and the Se@N-MC. The rational design of porous structure and defect in the Se@N-HCNS lead to the improved potassium storage performance. Figure 3D shows the charge/discharge curves of different current densities of the Se@N-HCNS cathode. It keeps stable voltage plateau at 5.0 A g\(^{-1}\), showing the outstanding kinetic during the charge/discharge process. Figure 3E demonstrates the ultra-long cycle performance of the Se@N-HCNS cathode. After 2000 cycles, the charge capacity maintains 260 mAh g\(^{-1}\), and the Coulombic efficiency keeps ~100%. Figure S13 shows the specific capacity of the Se@N-HCNS at a large current density, it keeps 245 mAh g\(^{-1}\) after 800 cycles even at 2 A g\(^{-1}\), showing an outstanding confinement effect of Se phase. Table S3 compares the cycle performance and rate capacity of the Se@N-HCNS with other Se-based electrodes reported in literature. The Se@N-HCNS demonstrates superior electrochemical performance among these cathode materials. Figure S14 shows the Ragone plot of the N-HCNS electrode and other cathode electrodes which describes the relation between energy density and power density. The N-HCNS delivers a higher energy density and power density because of the superior rate performance.

3 | DISCUSSION

To investigate the kinetics process of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC, the CV measurements at various sweep rates from 0.1 to 5 mV s\(^{-1}\) were performed. In Figure 4A–C, a pair of peaks shown at cathodic and anodic scans represent the sequential reversible reactions between Se and K\(_2\)Se. The integral capacity is divided into the diffusion and adsorption dominant process, which can be calculated by the equation: \(i = av^b\). The value of \(a\) and \(b\) are the adjustable parameters, and \(v\) is scan rate. The closer the \(b\) value gets to 1, the greater the ratio of capacitive electrochemical behavior. As shown in Figure 4D, the value of \(b\) for the cathodic scan is 0.89, which is higher than that of the anodic (0.83), indicating that the transfer process of Se to K\(_2\)Se is faster than K\(_2\)Se to Se. The \(b\)-values of the Se@N-MCNS and the Se@N-MC for cathodic scan are both 0.83, and the fitted \(b\) value for anodic scan are 0.78 and 0.77, respectively (Figure 4E, F). Compared to the Se@N-HCNS, the lower \(b\)-values of the Se@N-MCNS and the Se@N-MC indicate the sluggish kinetics of K-ions during charge/discharge. Figure 4G shows the capacitive contributions for three electrodes at various sweep rates. As the sweep rate increases, the capacitive charge contributions get higher. The Se@N-HCNS shows the highest proportion of capacitive contribution at all scan rates. The Galvanostatic Intermittent Titration Technique (GITT) was employed to measure the K-ion diffusion coefficient \((D)\) of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC. The value of \(D\) as a function of voltage was obtained according to the calculation in Figure S15. Compared to the other two electrodes, a smallest overpotential and a highest value of \(D\) (Figure 4H, I) are observed for the Se@N-HCNS, indicating fastest reaction kinetics.

Figure S16A shows the galvanostatic charge–discharge curves of the Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC at 0.1 A g\(^{-1}\). The polarization voltages of three electrodes are 0.45, 0.84, and 1.02 V, respectively. The Se@N-HCNS electrode appears higher discharge voltage platforms and less polarization, implying higher energy density and faster reactive kinetics. Figure S16B displays the energy density of the three electrodes at various current densities. The Se@N-HCNS shows much higher energy density at different current density (0.1 ~ 5 A g\(^{-1}\)), indicating that the advantages of the unique electrode design. Figure 5A–C compare the differential capacity curves of first cycle of three electrodes. It reveals that the three electrodes show different cathode peaks of the differential capacity plots. The Se@N-HCNS, the Se@N-MCNS, and the Se@N-MC show two peaks (1.68 and 1.03 V), three peaks (1.53, 1.11, and 0.80 V), and one peak (0.84 V), respectively. Figure 5D,E shows the K\(_2\)Se\(_5\) and K\(_2\)Se phases of the Se@N-HCNS, which corresponding to the peaks at 1.68 and 1.03 V of the Se@N-HCNS, respectively. Figure 5F–H show the K\(_2\)Se\(_5\), K\(_2\)Se\(_2\), and K\(_2\)Se phases, which are distributed to the peaks at 1.53, 1.11, and 0.80 V of the Se@N-MCNS, respectively. The appearance of the K\(_2\)Se\(_5\) is mainly due to the long-chain Se filling in the mesoporous larger than 5 nm, which is showed in Figure 5F. The single peak at 0.84 V of the Se@N-MC corresponds to the direct formation of K\(_2\)Se, as shown in Figure 4I. This result indicates that there are different discharge processes of three electrodes.
Figure S17 show the Ex-situ Raman spectra of the Se@N-HCNS during cycling. In Figure S17A, the D- and G-band of three stages are nearly no change, corresponding to the minor change of graphitization during charging and discharging. When discharged to 0.5 V, the peak of Se (254 cm\(^{-1}\)) vanished, indicating Se completely transfer to K\(_2\)Se. When charged to 3.0 V, the peak of Se appeared at 248 cm\(^{-1}\) with a blue shift (Figure S17B), corresponding to the product of shorter chain-like Sen.52 The electrochemical impedance spectrum during cycles of three electrodes are shown in Figure S18. The charge-transfer resistance (R\(_{ct}\)) after the first cycle of Se@N-HCNS is 103 \(\Omega\), which is smaller than those of the Se@N-MCNS (159 \(\Omega\)) and the Se@N-MC (218 \(\Omega\)). After five cycles, the R\(_{ct}\) of the Se@N-HCNS is 795 \(\Omega\), which is smaller than those of the Se@N-MCNS (911 \(\Omega\)) and the Se@N-MC (1500 \(\Omega\)). Those results reveal the faster electrochemical kinetics of K\(^+\) of the N-HCNS, leading to the excellent rate capability.

We further performed the DFT calculations of the relative adsorption energies by discharging product K\(_2\)Se on the defected carbon lattice. DFT results demonstrate that the Se@N-HCNS outperforms the other two samples in capacity performance. The high-resolution N 1 s spectra of XPS show that the type of nitrogen species of the N-HCNS is mostly pyrrole nitrogen (N-5) and pyridine nitrogen (N-6). The other two samples (N-MCNS and N-MC) occupy with the graphite nitrogen (N-Q). Figure 6A–C show the
optimized adsorption sites of K$_2$Se on N-Q, edge N-5 and N-6. The adsorption energy of nitrogen-doping structures inside the plane have summarized in previous work.$^{54}$

The results demonstrate that the edge-nitrogen doping structure (N-5 and N-6) have the K$_2$Se adsorption energy of $-4.17$ and $-3.00$ eV, while the N-Q structure only has the adsorption energy to K$_2$Se of $-1.00$ eV, leading to a weak interaction force and low capacity. The high polar adsorption to K$_2$Se of N-5 and N-6 could restrain the K$_2$Se and activate the conversion of polyselenide, enhancing the cycle performance in K-Se batteries. Moreover, we calculated the charge density difference to analyze the bonding situation of absorbed K$_2$Se. As shown in Figure 6D–I, the increased electron charge between the K$_2$Se molecule and carbon matrix indicated injected electrons on conjugate p-orbit of carbon and nitrogen atom from K$_2$Se molecule. More electrons transfer to p-orbit of C atom in the conjugate system between p-orbit of N atom and extended pi bond of a hexatomic ring in N-5 and N-6 structures, which is beneficial to migration of charge carrier.$^{54}$ It is reasonable that the N-HCNS with high N-5 and N-6 structures has stronger adsorption to K$_2$Se. Figure S19A–C show the optimized adsorption sites of K$_2$Se on the N-Q/N-Q, edge N-6/N-6, and edge N-5/N-5 structures. The adsorption energies of three structures are $-0.88$, $-3.13$, and $-3.77$ eV, respectively. The result shows that the adsorption energies of edge N-6/N-6, edge N-5/N-5 are lower than those of edge N-5 and edge N-6, indicating electron delocalization with higher density of edge nitrogen. Figure S18D–I show the electron density differences of N-Q/N-Q (Figure S19D,G), edge N-6/N-6 (Figure S19E,H), edge N-5/N-5 (Figure S19F,I) structures. The delocalization effect of charge in N-5/N-5 structures implies that the charge

**Figure 5** (A–C) The differential capacity plots at first discharge and corresponding HAADF-STEM image of (D and E) the Se@N-HCNS, (F–H) the Se@N-MCNS, and (I) the Se@N-MC at specific voltages.
transfer from the discharge product to carbon atoms. The charge density assembles around the pyridinic and pyrrolic N sites in edge N-5 and edge N-6 structures and transfer to carbon atoms in N-Q structures on account of p electrons (N-Q atoms) participating in delocalization pi bond (C atoms). The calculations mentioned above are strong evidence of the benefit of rich-N-5/N-6 structures to K-Se batteries. Therefore, the excellent electrochemical property of the Se@N-HCNS could attribute to the doping of the edge N-5 and N-6 atoms.

4 CONCLUSIONS

In summary, we design and synthesis nitrogen-doped porous carbon nanosheets (N-HCNS) as an effective host to chemical binding and physical confinement Se. The obtained Se@ N-HCNS shows unprecedented potassium storage performance in terms of high reversible capacity (337 mAh g\(^{-1}\) at 5.0 A g\(^{-1}\)) and long cycle life (260 mAh g\(^{-1}\) at 1.0 A g\(^{-1}\) after 2000 cycles). The abundant micropores and hierarchical architecture of the N-HCNS host accommodates the volume expansion during Se potassiation, and meanwhile offers highly electronic/ionic conductive network for efficient mass/charge transportation. The chemical bonding between Se and carbon matrix acts as an anchor to strongly immobilize the Se species against their shuttling behaviors. More importantly, the high content of nitrogen-doping in the N-HCNS provides more active sites and enhances the utilization efficiency of active Se. The GITT electrochemical measurement verifies higher diffusion kinetics of the Se@N-HCNS compared to the other two samples, which can be further confirmed by DFT calculation. The optimization design of 3D hierarchical carbon-based skeleton with high contents of N-6 and N-5 could enhance the adsorption energy to K\(_2\)Se and lower the potential barrier of diffusing. This approach offers a new route to design multifunctional Se immobilizer with highly chemical bonding and physical confinement capabilities for rapid charge/discharge process, holding a great promise in promoting the practical application of alkali ion-chalcogen batteries.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

ORCID
Yan Yu https://orcid.org/0000-0002-3685-7773

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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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