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Fe single-atom-regulated carbon nanofibers for high-performance lithium/sodium ion battery anode

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How to cite this article: Xue, C.; Zhang, Y.; Zhang, Y.; Wang, L.; Zhou, N.; Zhang, G.; Geng, Q.; Zheng, Y.; Li, X.; Liu, B.; Li, Q. Fe single-atom-regulated carbon nanofibers for high-performance lithium/sodium ion battery anode. *Energy Mater.* 2025, 5, 500113. <https://dx.doi.org/10.20517/energymater.2024.283>

Received: 11 Dec 2024 **First Decision:** 15 Jan 2025 **Revised:** 2 Mar 2025 **Accepted:** 20 Mar 2025 **Published:** 26 May 2025

Academic Editor: Jiazhao Wang **Copy Editor:** Ping Zhang **Production Editor:** Ping Zhang

Abstract

Carbon-based materials, commonly used as commercial anodes in lithium/sodium ion batteries, nevertheless suffer from sluggish kinetic properties. Constructing electrode materials with one-dimensional nanostructures that offer convenient ion/electron transport pathways can improve Li⁺/Na⁺ storage behavior. Recently, metal single-atom doping has also emerged as an effective strategy to enhance storage kinetics. However, it remains challenging to construct one-dimensional carbon materials doped with metal single atoms using simple methods to achieve outstanding Li⁺/Na⁺ storage performance. Herein, three-dimensional intertwined short carbon nanofibers (SCNFs) coupled with single atomic iron dopants were tailored through a hydrothermal strategy followed by high-temperature carbonization free from strong acids etching metals. In the SCNFs, only a trace amount of Fe (0.37 at.%) was introduced; the nitrogen-coordinated Fe single atoms and the nanofibers-intertwined structure



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promoted Li-ion adsorption, improved diffusion kinetics, and enhanced conductivity, thereby facilitating Li⁺/Na⁺ storage capacity. Acting as an anode in lithium/sodium batteries, SCNFs demonstrated an outstanding electrochemical performance. After assembling lithium ion batteries, the optimal Fe-N-C-2 exhibited a high reversible capacity of 903.4 mAh g⁻¹ at 50 mA g⁻¹ with retention of 518.7 mAh g⁻¹ at 1.0 A g⁻¹. For sodium-ion storage, Fe-N-C-2 preserved excellent high-rate cyclic stability, maintaining 152.6 mAh g⁻¹ after 500 cycles at 0.5 A g⁻¹. Moreover, the hydrothermal method is simple and convenient for large-scale preparation. Our strategy offers a heuristic perspective on the controllable design of nitrogen-coordinated atomic metals for energy storage applications.

Keywords: Single atom, iron doping, carbon nanofibers, sodium storage, lithium storage

INTRODUCTION

Carbon materials were considered as an encouraging alternative to anodes for commercialization due to their non-toxic, environmentally benign properties and high abundance^[1-3]. Nevertheless, they still suffered from the bottlenecks of sluggish lithium/sodium storage kinetics and low reversible capacity^[4,5].

Lots of strategies have been developed to probe high-capacity and highly reversible anode porous carbon materials, such as doping various non-metallic atoms (B, N, P and S), adjusting pore configuration, and designing structure and morphology^[6]. Wang *et al.* reported that nitrogen-doped carbon nanofibers, benefiting from the improving wettability and conductivity, worked as anode materials to enhance the rate performance and reversible capacity^[7]. Liu *et al.* reported that large layer spacing (0.40 nm) amorphous carbon nanotubes with B, N heteroatomic active sites showed excellent sodium ion diffusion kinetics and capacitor storage behavior^[8]. Theoretical studies have revealed that single-atom metal doping can effectively lower the energy barrier in relation to the specific relation^[9-11]. Atomic metal doping carbons with M-N-C (M stands for metal elements) coordination structure can modify the electronic structure and enhance the active sites which have been extensively studied for boosting effective catalytic activity. In recent years, this metal single atom doping carbons (SACs) design was introduced into lithium/sodium/potassium ion batteries, metal batteries and lithium-ion capacitors. For example, high content of single atomic Copper (26.3 wt%) on a carbon micro cuboid substrate, through coordination with phosphorus atoms, can adjust the Na storage mechanism and retain Na in an ionic state^[12]. Similarly, in the nitrogen-doped carbon material, Co single atoms embedded can efficiently lower the nucleation energy barrier and simultaneously accelerate the deposition kinetics of K^[13]. The dopants of Ni-single atoms in N, P co-doped hard carbon accommodate the composition of the interface layer formed from solid electrolyte, thus maintaining the state of Ni-single atoms-modified N, P co-doped hard carbon (Ni-NPC)^[14]. Single Zn atom (0.73 wt%)-doping hard carbon can yield a local electric field favoring the Na⁺ transfer. Also, the introduction of single Zn atoms allows the establishment of a robust and inorganic-rich solid-electrolyte layer by fastening the decomposition of NaPF₆, thereby reaching a high capacity (443 mAh g⁻¹) under low-temperature conditions^[15]. It can be found that single atoms design can really provide more active sites than conventional doping, and also can improve diffusion kinetics, and enhance conductivity. Meanwhile, the low dosage of single atoms also contributes to economic efficiency. As single metal atoms-doping carbon materials via M-N-C coordination structure can deliver excellent lithium/sodium storage performance, this design concept deserves more intensive study to reveal the underlying mechanism.

Carbon materials with one-dimensional (1D) nanostructure favor rapid axial electron transport and radial ion diffusion^[16]. In addition, more 1D porous carbon materials have a large specific surface area and can avoid the agglomeration problem of single metal atoms doping carbon nanomaterials. One-dimensional carbon with single metal atoms-doping was also developed using an electro-spun method^[17]. For example,

the dopants of Cu atoms into carbon nanofibers via electrospinning can enhance the diffusion kinetics of Li^+ , while serving as sites for Li^+ storage^[18]. Single atomic iron-decorated carbon nanofibers were also prepared by electrospinning for kinetically accelerated Li^+ storage. Although various SAC materials have been produced using this method, the process of preparing SACs from precursors was complicated. Subsequent processing often requires the use of strong corrosive and toxic chemical agents such as HF or HCl, which, when used to produce 1D single-atom doped carbon, usually incur high costs^[19-21]. Therefore, there is great urgency in exploring a convenient and reliable route for the production of 1D single-atom-doped carbon.

Herein, single atomic iron nitrogen-doped carbon materials with 3D cross-linked structure composed of 1D nanorods were obtained by a simple hydrothermal strategy, and a series of structural characterizations were carried out. The experimental results show that iron atoms are uniformly distributed in nitrogen-doped carbon thereby affording isolated atoms. Also, the Fe-N-C sample is further applied to lithium ion/sodium ion batteries (SIBs) and demonstrates excellent lithium/sodium storage performance. Furthermore, the first-principle calculations provide evident proof for an optimized adsorption route and a reduced energy barrier responsible for rapid migration of Li ions favoring the resulting electrochemical property. This single-atom-regulated carbon nanofiber design can also be used in other energy storage systems, such as potassium ion storage and lithium-sulfur batteries.

EXPERIMENTAL

Preparation of Fe-N-C

First, phenol (0.40 g), benzimidazole (0.20 g), cetyl trimethyl ammonium bromide (CTAB) (0.3 g), melamine (0.4 g), 3,5-diaminobenzoic acid (0.10 g), various amounts of iron acetylacetonate (0.02, 0.06 and 0.10 g) and formaldehyde (1.8 mL) are added into 50 mL deionized water. After thorough dissolving, the solution underwent stirring overnight at a temperature of 60 °C. Afterward, the mixture was poured into a 100 mL autoclave and subjected to 200 °C heat in a furnace for a full day. Eventually, the monolithic sample is formed and collected for further use after drying at 80 °C. The above bulk precursor is calcined directly under ammonia gas and at 800 °C with a duration of 2 h. Afterward, the carbonization is performed to obtain short rodlike Fe/N co-doped carbon material. According to the amounts of Fe precursors of 0, 0.02, 0.06 and 0.10 g, the resulting carbon samples are marked as N-C, Fe-N-C-1, Fe-N-C-2, and Fe-N-C-3, respectively.

Characterization

X-ray Diffraction (XRD, Bruker AXS D8), Scanning Electron Microscopy (SEM, Carl Zeiss), Transmission Electron Microscopy (TEM, JEOL 2100Plus), X-ray Photoelectron Spectroscopy (XPS, AXIS ULTRA) and Raman spectra (Renishaw inVia) are adopted for chemical components and structure analysis. Physical adsorption data are collected by an Autosorb-IQ-MP-C. High-Angle Annular Dark Field (HAADF) images are captured on a Titan Themis G2 operated at 300 kV. Fe K-edge spectra are recorded via the photoemission station located at beamline BL10B within the National Synchrotron Radiation Research Center (NSR) Centre (Hefei, China).

Electrochemical measurements

Each sample that underwent electrochemical testing was assembled using 2032-type coin cells. The mixture of polyvinylidene fluoride (PVDF), the active material, and Super-P was thoroughly ground at a proportion of 8:1:1 by mass in N-methyl-2-pyrrolidone (NMP), followed by pasting on copper foil and heating for 12 h. Finally, it was cut into round slices to prepare the electrodes, where the active material loading (areal density) was 1.35 and 1.40 mg cm^{-2} for N-C and Fe-N-C, respectively. The pure lithium sheet as the counter electrode was fully immersed into the electrolyte of 1M LiPF_6 according to the recipe prepared by dispersing

LiPF₆ into the mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) as the volume ratio of 5:3:2 (vol.%). Similarly, for the SIB test, the active material loading (areal density) was 1.45 and 1.50 mg cm⁻² for N-C and Fe-N-C, respectively. The counter electrode was replaced as a pure Na sheet and fully immersed in 1 M NaPF₆ solvated in the solvent composed of EC and DEC with an equal volume fraction. The electrochemical performance tests were performed on a Neware-CT4008 battery system. In addition, Cyclic voltammetry (CV) was performed using a CHI660D workstation. Electrochemical impedance spectroscopy (EIS) was carried out at Energylab XM.

Theoretical calculations

In order to evidence the role of single atomic iron atoms in N-doped carbon, theoretical calculations on the optional chemical adsorption and energy barrier of Li ion transport are given using Vienna Ab initio Simulation Package (VASP). All the Density Functional Theory (DFT) calculations are achieved referring to the Generalized Gradient Approximation (GGA) derived by the Perdew-Burke-Ernzerhof (PBE) formulation^[22-24]. The ionic cores coupled with valence electrons are discussed in the context of the Projector Augmented-Wave (PAW) potentials, which are constructed on a plane wave basis set with a kinetic energy threshold of 450 eV^[25]. Moreover, the Gaussian smearing method is employed to examine partial occupancies of the Kohn-Sham orbitals with an accuracy of 0.05 eV^[26]. If the value of energy fluctuations is below 10⁻⁵ eV, the self-consistent state is established. As the value of the force changes is less than 0.05 eV/Å, a geometry optimization reaches the convergent state. Subsequently, the DFT-D3 approach by Grimme is implemented to deal with dispersion interactions^[27]. Furthermore, it is necessary to set the vacuum spacing perpendicular to the plane at 15 Å. Meanwhile, Monkhorst-Pack grids are outlined with 3 × 3 × 2 at the Brillouin zone where the Climbing Image-Nudged Elastic Band methods are adopted to evaluate the migration barriers of Li ions.

RESULTS AND DISCUSSION

The details of the carbon precursor synthesis are demonstrated in [Figure 1A](#). The Fe-N-C-2 is composed of intertwined nanorods with a radius of about 30 nm and a length of about 1 μm (referring to [Figure 1B and C](#)). Likewise, the content of iron precursor has no effect on the final morphology [[Supplementary Figure 1](#)], which suggests that the doping amounts have negligible effects on their morphology. In fact, the 1D short-rod structure can provide a favorable pathway for fast ion transport. The elements involved are evenly decorated on the surface of nanorods, referring to the (HAADF) energy dispersive X-ray spectroscopy (EDS) mapping [[Figure 1D](#)]; the good uniformity of element distribution can prevent localized polarization during the charging and discharging processes, enhancing the cycle stability of the battery. Further analysis of the atomic structure of the porous nanorods is characterized by HAADF-scanning transmission electron microscopy (STEM) [[Figure 1E](#)], which demonstrates that there are many bright spots densely (marked with red circles) arranged on the Fe-N-C-2 sample indicating the homogeneous distribution of single atomic iron atoms, which increases the material's surface area and reactivity, thereby improving the efficiency of electrochemical reactions.

Relevant XRD patterns and Raman spectra of these samples are further demonstrated in [Figure 2A and B](#). The XRD patterns show two main characteristic peaks located at ~43° and ~24° assigned as the (100) and (002) planes of the graphite, respectively. The D and G bands of carbon materials are detected according to Raman spectra showing two peaks located at 1,345 and 1,585 cm⁻¹, respectively^[28,29]. The I_D/I_G (area ratios) for the Fe-N-C-2 sample is 1.23, which is somewhat larger than the rest including N-C (1.08), Fe-N-C-1 (1.11) and Fe-N-C-3 (1.18), indicating more defects/vacancies emerging from the Fe-N-C-2 samples. In this regard, the dopants of iron atoms into the N-doped carbon material cause more disordered structures. The elemental components of all the samples are further identified by XPS. The Fe contents of the four materials

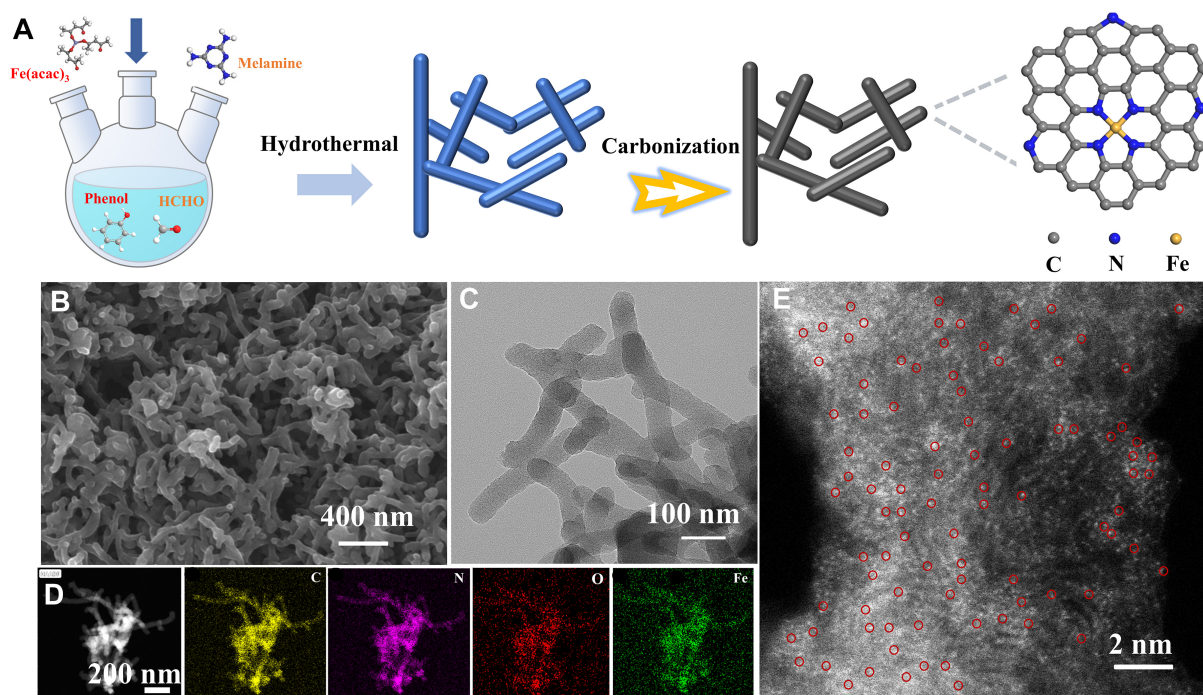


Figure 1. Synthesis and morphological characteristics of the Fe-N-C. (A) Schematic illustration of the fabrication procedures of the Fe-N-C; (B-D) Characterizations of Fe-N-C. (B) SEM images, (C) TEM images, (D) EDS elemental mappings and (E) HAADF-STEM image of Fe-N-C-2; the red circle represents single Fe atom. SEM: Scanning electron microscopy; TEM: transmission electron microscopy; EDS: energy dispersive X-ray spectroscopy; HAADF-STEM: high-angle annular dark field- scanning transmission electron microscopy.

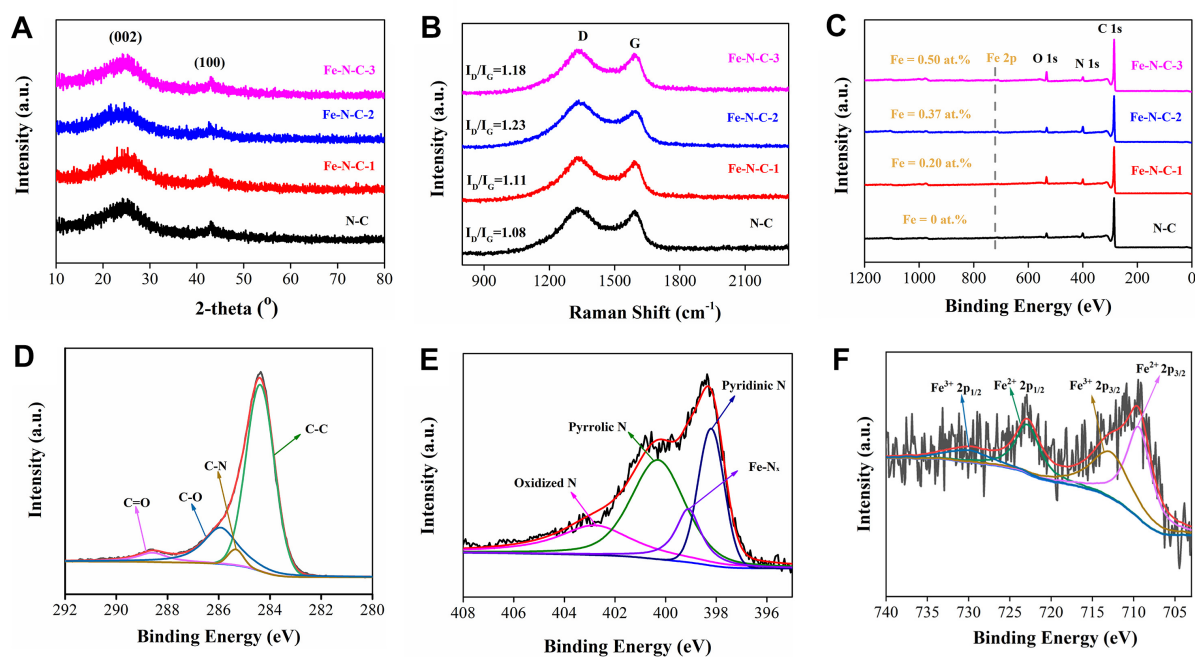


Figure 2. Structural characterizations of the N-C and Fe-N-C. XRD pattern (A); Raman spectrum (B) and XPS survey scan (C) of the N-C and Fe-N-C; (D) High-resolution C 1s spectrum; (E) high-resolution N 1s spectrum and (F) high-resolution Fe 2p spectrum for Fe-N-C-2. XRD: X-ray diffraction; XPS: X-ray photoelectron spectroscopy.

are 0 at.%, 0.20 at.%, 0.37 at.% and 0.50 at.% [Figure 2C], respectively, which are consistent with the initial amounts of iron acetylacetonate added. Furthermore, we carried out the Inductively Coupled Plasma (ICP) to examine the content of iron in these samples [Supplementary Table 1]. The Fe contents of the four materials are 0 at.%, 0.44 at.%, 1.18 at.% and 2.03 at.%, respectively. Moreover, the EDS, XPS and ICP analyses showed that the trend of Fe content was consistent and relatively low. Furthermore, the C1s spectrum of Fe-N-C-2 at 285.5 eV (C-N) demonstrates the successful doping of nitrogen [Figure 2D]. The N1s spectra [Figure 2E] of Fe-N-C-2 are fitted as pyridinic N (398.2 eV), Fe-N_x (399.1 eV), pyrrolic N (400.3 eV) and oxidized N (402.7 eV) in Figure 2E^[30,31]. The high-resolution nitrogen spectrum of N-C is provided in Supplementary Figure 2. The pyridinic-N and pyrrolic-N with robust redox reactions can increase the electrochemical activity and conductivity of inert carbon, thereby increasing Li⁺/Na⁺ storage capacity. The oxidized-N can improve the electrode's wettability and promote Li⁺/Na⁺ desolvation, improving charge transfer efficiency. Fe-N_x is believed to be favorable for the improvement of electrochemical performance^[32]. Also, the Fe 2p spectrum [Figure 2F] of Fe-N-C-2 can be resolved into 725.0 eV (Fe³⁺2p_{1/2}), 723.8 eV (Fe²⁺2p_{1/2}), 714.7 eV (Fe³⁺2p_{3/2}) and 710.4 eV (Fe²⁺2p_{3/2})^[33]. The emergence of the Fe-N bond reflects that iron atoms should be stabilized by the coordination of N atoms^[34]. The further N₂ adsorption-desorption isotherm of the N-C and Fe-N-C-2 is shown in Supplementary Figure 3. The specific surface areas of N-C and Fe-N-C-2 are 941.1 m² g⁻¹ and 745.8 m² g⁻¹, respectively. In this respect, large surface area guarantees facile access to more active sites, thus improving electrochemical performance^[22].

To further reveal Fe species incorporated in Fe-N-C-2 nanorods, X-ray absorption spectroscopy (XAS) was also performed. In the normalized X-ray Absorption Near Edge Structure (XANES), the position of absorption threshold of Fe-N-C-2 nanorods is higher than Fe foil [Figure 3A], but smaller than that of Fe₂O₃, representing that Fe species in Fe-N-C-2 nanorods remains between Fe⁰ and Fe³⁺, denoted as Fe^{δ+} (0 < δ < 3)^[33,35]. In Figure 3B, the Fourier Transform Extended X-ray Absorption Fine Structure (FT-EXAFS) spectrum of Fe-N-C-2 nanorods shows a single prominent peak at 1.5 Å, which agrees well with the Fe-N coordination^[36,37]. However, the peak typically attributed to Fe-Fe interactions is absent. These results further confirm the atomic distributions of Fe species in Fe-N-C-2, which is consistent with the HAADF-STEM observation above. According to fitting results of the EXAFS in K-space, the length of Fe-N bond is about 2.0 Å and therefore the coordination mode of iron atoms in the Fe-N-C-2 sample is ascribed to the Fe-N₄ structure [Figure 3C]. Furthermore, the analysis based on EXAFS wavelet transform was performed to elucidate the structure information of Fe-N-C-2 associated with coordination environment through K-edge. There is a lack of signals associated with the Fe-Fe bond (~8.3 Å⁻¹) with the exception of a single signal at 4.7 Å⁻¹, which is also attributed to the Fe-N bond [Figure 3D]^[37,38].

The first charge/discharge capacity related to Fe-N-C-2 is up to 1,769.0/921.7 mA h g⁻¹, definitely higher than that of N-C (826.0/340.2 mA h g⁻¹), Fe-N-C-1 (1,670.0/857.5 mA h g⁻¹) and Fe-N-C-3 (1,499.5/815.7 mA h g⁻¹) [Figure 4A]. The low coulomb efficiency of these samples is mainly attributed to the high specific surface area leading to the formation of solid electrolyte interface (SEI) films^[39]. Although the coulombic efficiency of Fe-N-C-2 is higher than that of N-C, it is still relatively low, largely due to the high specific surface area [Supplementary Figure 3]. However, improvements in initial efficiency can be achieved through pre-lithiation, electrolyte optimization, and binder adjustments^[40]. CV cycles at 0.1 mV s⁻¹ demonstrate an obvious reduction peak at 0.59 V related to SEI film formation, referring to Supplementary Figure 4. The Fe-N-C-2 offers the best cycle stability (903.4 mA h g⁻¹ after undergoing 50 cycles at 50 mA g⁻¹) [Figure 4B]. Referring to the rate performance of the samples [Figure 4C], the discharge capacity of the Fe-N-C-2 maintains 518.7 mA h g⁻¹ at 1 A g⁻¹, much larger than those of the N-C (160.4 mA h g⁻¹), Fe-N-C-1 (444.7 mA h g⁻¹) and Fe-N-C-3 (386.8 mA h g⁻¹). Lithium storage dynamic analysis is further discussed by the EIS measurements [Supplementary Figure 5]^[23,41]. The charge-transfer resistance (R_{ct} =

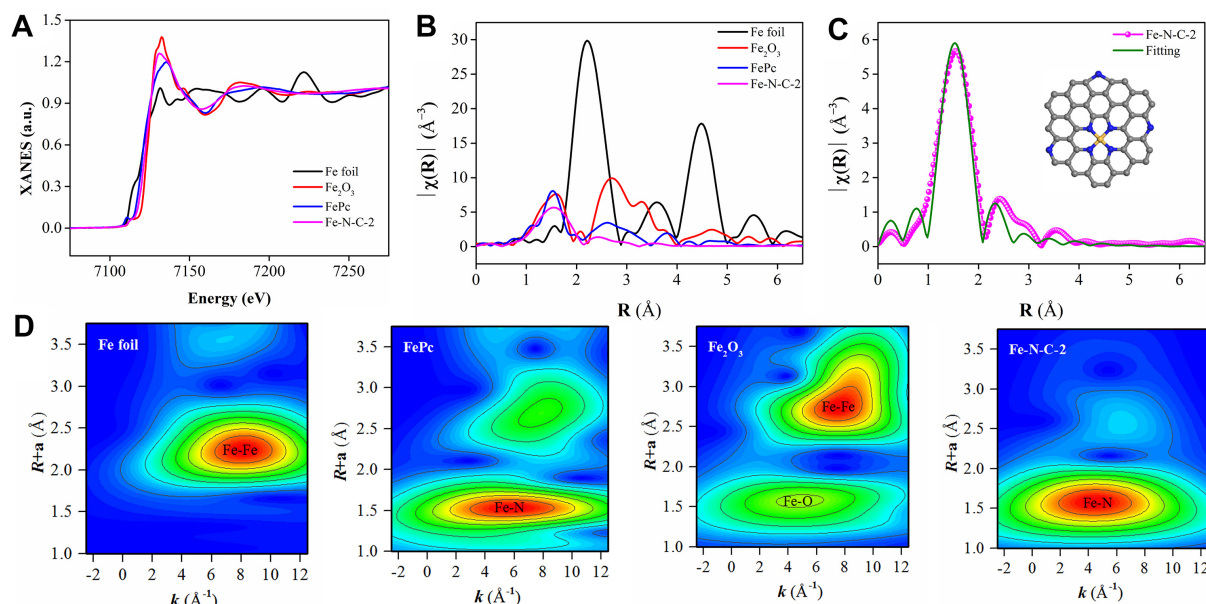


Figure 3. (A) Fe K-edge XANES spectra; (B) k³-weighted $\chi(R)$ function of EXAFS spectra; and (C) EXAFS fitting curve of Fe-N-C-2; (D) WT patterns of Fe foil, FePc, Fe₂O₃ and Fe-N-C-2. XANES: X-ray absorption near edge structure; EXAFS: extended X-ray absorption fine structure; WT: wavelet transform.

38.9 Ω) of Fe-N-C-2 is smaller than that of N-C ($R_{ct} = 126.0 \Omega$), Fe-N-C-1 ($R_{ct} = 57.1 \Omega$) and Fe-N-C-3 ($R_{ct} = 87.5 \Omega$). Furthermore, the diffusion coefficient of Li-ion (D_{Li^+}) in Fe-N-C-2 ($9.04 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) is obviously larger in comparison with those of N-C ($3.58 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$), Fe-N-C-1 ($8.18 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) and Fe-N-C-3 ($7.47 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) [Figure 4D]. Moreover, the capacity of the Fe-N-C-2 remains at 553.0 mA h g⁻¹ after 500 cycles at 500 mA g⁻¹ and is much higher than that of N-C (186.4 mA h g⁻¹), Fe-N-C-1 (433.2 mA h g⁻¹) and Fe-N-C-3 (159.1 mA h g⁻¹) [Figure 4E]. The large specific surface area of the Fe-N-C-3 [Supplementary Figure 3], which leads to a high loading amount, causes agglomeration [Supplementary Figure 6], preventing Fe from existing in a single-atom form. The SEM images of the Fe-N-C-2 and Fe-N-C-3 electrodes were further investigated after the 0th, 5th, 200th, and 500th cycles [Supplementary Figures 7 and 8]; the SEI film of Fe-N-C-2 is thinner than that of Fe-N-C-3, and its structure is more stable. Consequently, its kinetics are poorer compared to those of Fe-N-C-2 [Supplementary Figure 9 and Supplementary Table 2]. Therefore, the results validate that iron atoms can significantly enhance the activity of carbon materials and thus speed up the dynamics of the lithium-ion diffusion, thereby improving the resulting electrochemical properties. In addition, as the number of iron atoms doped continuously increases, it is more likely to form nanoparticles due to the aggregation of the neighboring single iron atoms while exposed to carbonization process at high temperatures and therefore lowering the storage activity for lithium^[12]. In this sense, compared to iron nanoparticles, iron atoms coordinated with N atoms can significantly enhance the lithium storage performance of materials, which can be ascribed to the interaction at the atomic scale^[22].

To further validate the advantages of Fe-N-C material in improving battery electrochemical properties, the optimal Fe-N-C-2 working as an anode material in SIBs was also evaluated. Fe-N-C-2 was assembled as the anode material in the first cycle, which can deliver higher capacities of 393.6/299.1 mA h g⁻¹ compared to the N-C sample (299.9/135.0 mA h g⁻¹) at 50 mA g⁻¹ as given in Figure 5A. In the first cycle, the reduction peaks of N-C and Fe-N-C-2 at 0.57 V in the CV curve are related to the formation of SEI film as shown in Supplementary Figure 10^[12]. The easier it is to form SEI film, the lower the coulomb efficiency. Fe-N-C-2

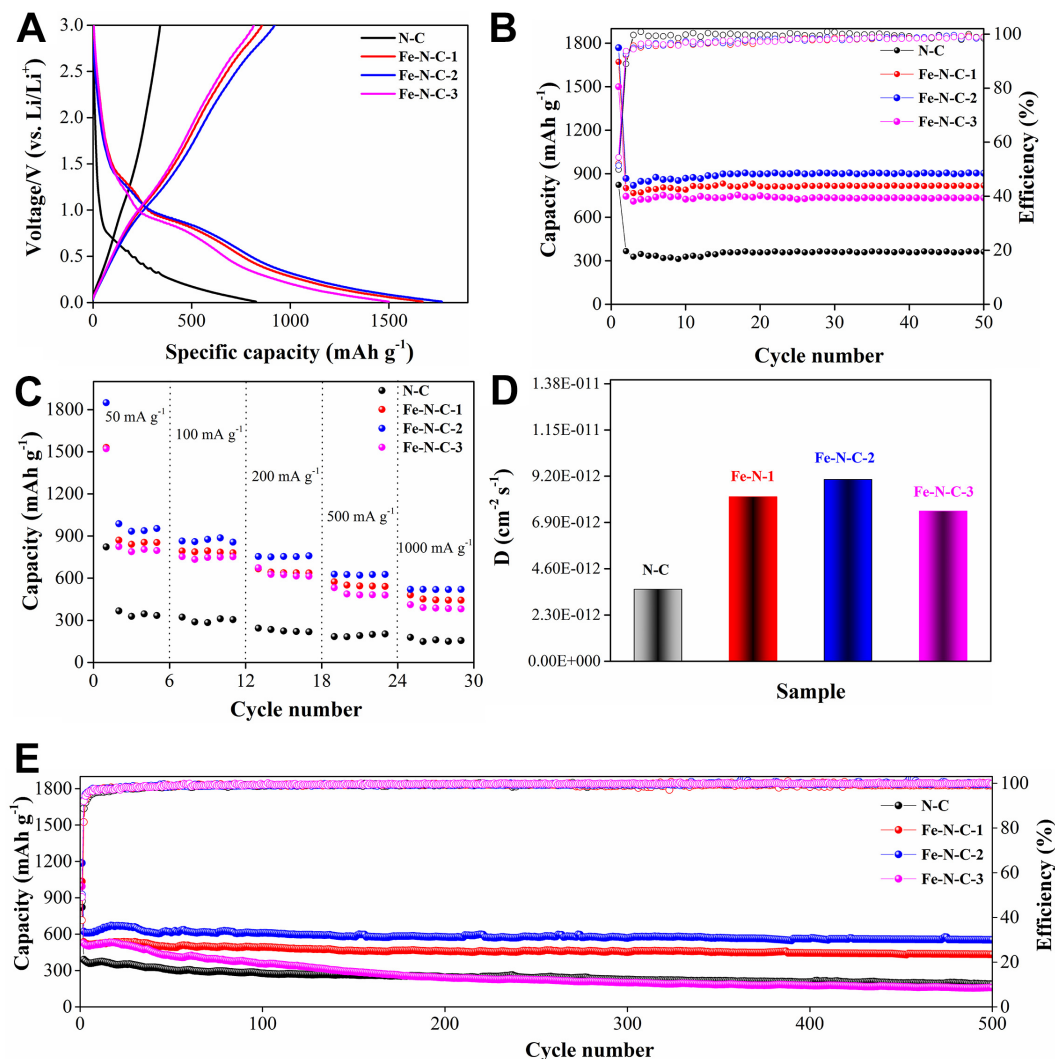


Figure 4. (A) Initial galvanostatic discharge/charge curves at 50 mA g⁻¹; (B) Cycling at 50 mA g⁻¹; (C) Rate, (D) Diffusion coefficients obtained from EIS spectra and (E) Cycling at 500 mA g⁻¹ of samples. EIS: Electrochemical impedance spectroscopy.

shows a higher first-cycle Coulombic efficiency compared to N-C. In addition, the capacity delivered by Fe-N-C-2 remains at 216.1 mAh g⁻¹ after 100 cycles, which is remarkably higher than N-C (165.1 mAh g⁻¹) [Figure 5B]. The rate capability of N-C and Fe-N-C-2 at varying current densities (50–1000 mA g⁻¹) is displayed in Figure 5C. Even at a current density of 1000 mA g⁻¹, Fe-N-C-2 maintains a capacity of 145.8 mA h g⁻¹ showing superior performance compared to the N-C sample (105.8 mA h g⁻¹). As for the N-C and Fe-N-C-2 after 500 cycles as demonstrated in Figure 5D, the capacity of N-C and Fe-N-C-2 can retain at 101.0 and 152.6 mAh g⁻¹, respectively. Compared to previous reports [Supplementary Table 3], the specific capacity of this carbon nanofiber is not the highest, but the Fe content is really much lower. By optimizing experimental conditions and refining the local structure of our materials, the energy storage performance may be further improved. Thus, the single iron atom coordinated with nitrogen atoms can efficiently enhance the electrochemical performance when compared with the untouched carbon materials.

To fully consider the reaction kinetics, CV measurements for Fe-N-C-2 [Figure 5E] are conducted to calculate the contribution originating from surface capacitive through^[41]

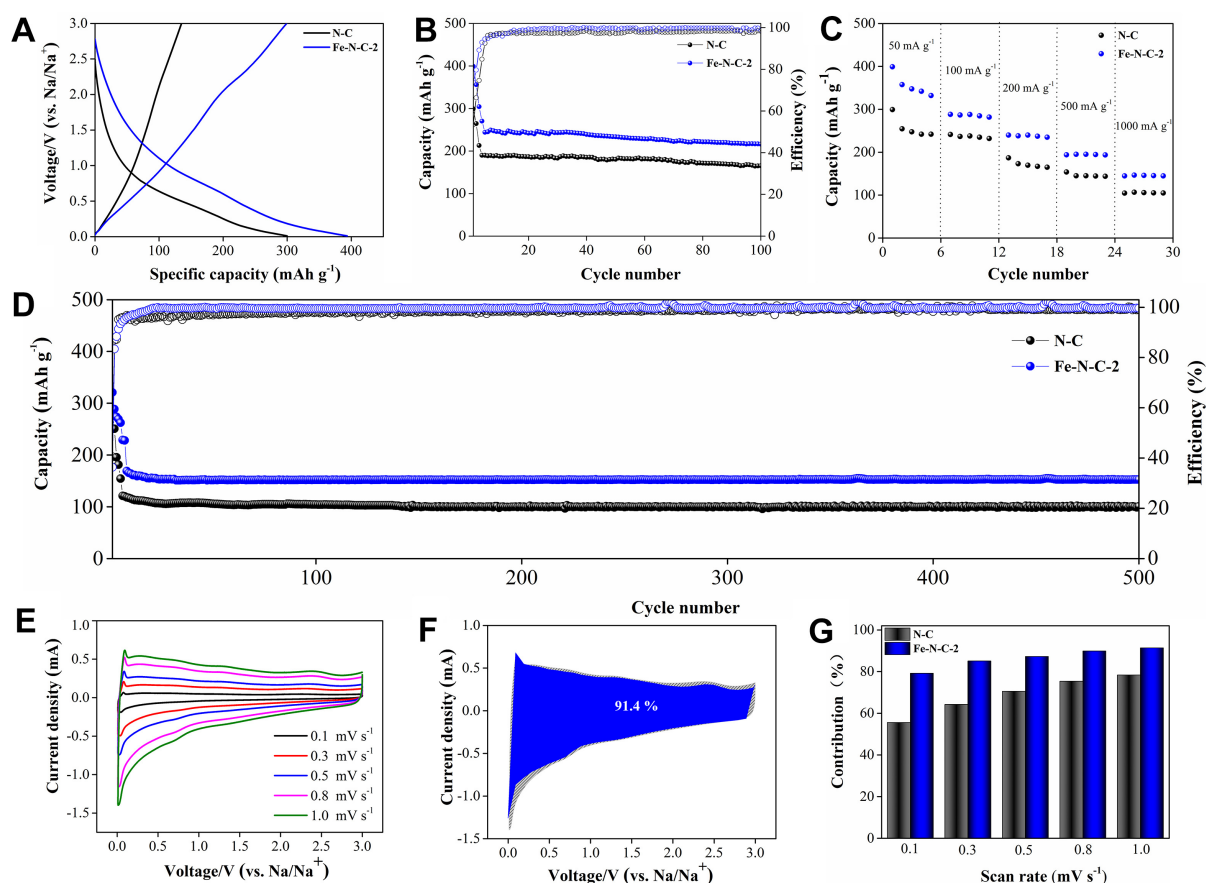


Figure 5. (A) Initial galvanostatic discharge/charge profiles (50 mA g⁻¹); (B) Cycling stability (50 mA g⁻¹); (C) Rate capability and (D) Cycling stability of N-C and Fe-N-C-2 (500 mA g⁻¹); (E) CV curves of the Fe-N-C-2 at multiple sweep rates; (F and G) respectively corresponding to quantitative analysis of capacitive contribution of the Fe-N-C-2 at 1.0 mV s⁻¹ and capacitive contribution of the N-C and Fe-N-C-2 at multiple sweep rates. CV: Cyclic voltammetry.

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2 \quad (1)$$

The pseudo-capacitance contribution rate of Fe-N-C-2 was up to 91.4% [Figure 5F]. The detailed results of the capacitive effects for the N-C sample are provided in Supplementary Figure 11. The capacitive contributions of Fe-N-C-2 at 0.1, 0.3, 0.5, 0.8 and 1.0 mV s⁻¹ account for 79.2%, 85.1%, 87.3%, 89.9% and 91.4%, respectively, affording higher ratios than those of the N-C sample at the same scan rates [Figure 5G]. The pseudo-capacitance effects of Fe-N-C-2 on the surface capacitance control process are predominant and are conducive to improving sodium storage performance at high rates^[22].

Herein, DFT were performed to uncover the mechanism underlying intrinsically related to the adsorption energy of Li ions on the atomic scale concerning the Fe-N-C-2. From the EXAFS spectra, we have confirmed that the structure is Fe-N₄-C, which is a structurally stable coordination. For N-C, we chose pyridine nitrogen as the model. Firstly, the adsorption energy of Li ions of N-C and Fe-N-C-2 was provided, referring to [Figure 6A and B]. The negative adsorption energy emerging in the two structural models indicates that the two samples are beneficial for adsorbing Li ions. Moreover, the adsorption energy of Fe-N-C-2 (-1.928 eV) to Li ion is higher than the -3.033 eV of N-C, implying the appropriate adsorption energy in the case of Fe-N-C-2 structural model facilitates the adsorption and desorption process of Li ions thereby offering superior electrochemical performance^[22,42]. This argument is further validated by the

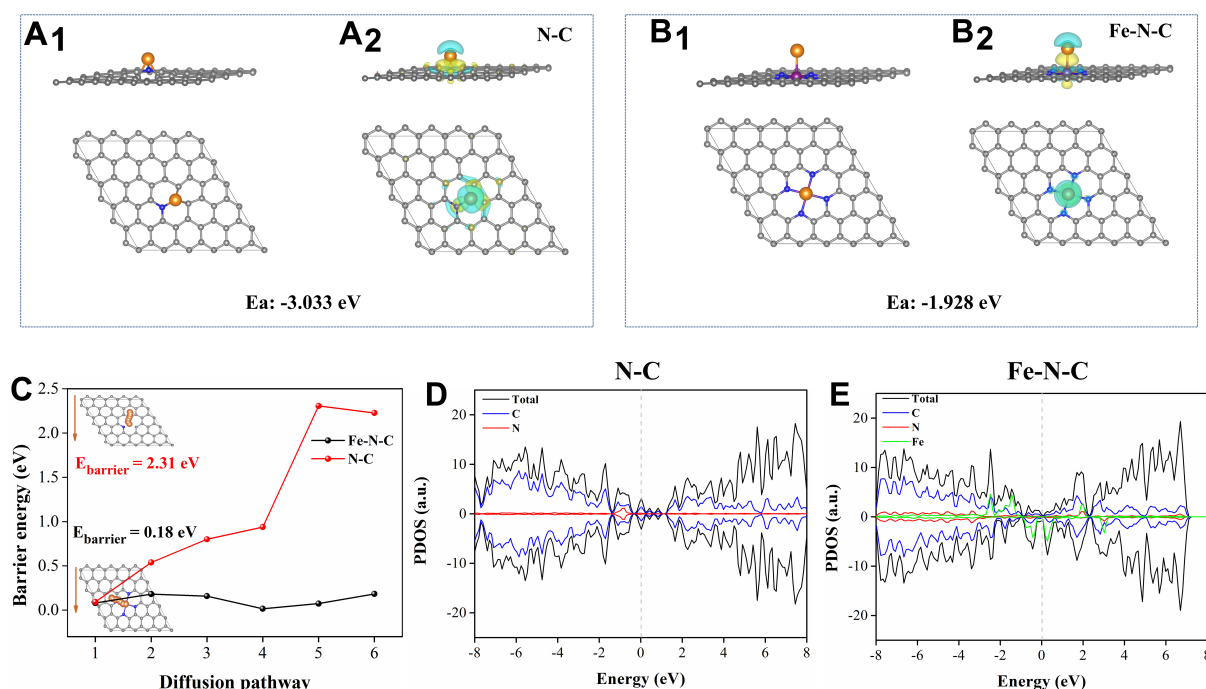


Figure 6. Various perspectives of a single Li atom adsorbed on N-C (A1) and Fe-N-C-2 (B1); (A2 and B2) The associated differences in charge density. The regions of charge gain and loss are depicted in yellow and cyan. (N, C, Li, and Fe atoms are depicted as blue, gray, pink, and purple balls); (C) Energy barrier, pathway of N-C and Fe-N-C-2. (G) The calculated density of states of (D) N-C and (E) Fe-N-C-2.

computational results of the diffusion barrier of Li ions across the N-C and Fe-N-C-2 samples, according to Figure 6C. Both N-C and Fe-N-C spread vertically along the carbon plane (Figure 6C, with an arrow). The diffusion energy barrier (0.18 eV) in the case of the Fe-N-C-2 sample is definitely less than that of the N-C sample (2.31 eV), addressing the faster movement of Li^+ in Fe-N-C-2 compared to the N-C sample and thus improving the rate performance. The partial density of states (PDOS) results of N-C and Fe-N-C-2 demonstrate that there is a 0.203 eV band gap in the N-C electronic structure [Figure 6D and E], while the structural gap is filled in Fe-N-C-2 sample indicating the improved electrical conductivity. Moreover, different from the symmetric structure between the spin up and spin down curve in the N-C sample, the additional peaks in spin down curve of the Fe-N-C-2 confirm the emergence of unpaired electrons, thus favoring the improvement of electrical conductivity.

CONCLUSIONS

In summary, highly dispersed single iron atoms stabilized by N atoms of N-doped short carbon nanorods are successfully prepared from their precursors of phenolic-resin counterparts utilizing an easy hydrothermal procedure. In lithium ion batteries, the resulting Fe-N-C-2 can deliver a significant reversible capacity ($553.0 \text{ mA h g}^{-1}$ after 500 cycles) and high-rate performance ($518.7 \text{ mA h g}^{-1}$ at a rate of 1000 mA g^{-1}). Furthermore, the Fe-N-C-2 sample is also employed as an anode material in SIBs and shows excellent electrochemical properties ($152.6 \text{ mA h g}^{-1}$ following 500 cycles at a rate of 500 mA g^{-1}). The enhanced Li^+/Na^+ storage originates from highly dispersed iron atoms anchored on the carbon skeleton and the exceptional construction composed of the intertwined short carbon nanorods. Moreover, the results based on DFT calculation reveal that the tetra-coordination of FeN_4 can efficiently reduce the energy barrier and boost the Li/Na ion adsorption thus achieving superb electrochemical performance. The facile preparation of single-atom iron catalysts provides a simple and reliable strategy for highly efficient energy

storage.

DECLARATIONS

Authors' contributions

Developed the concepts for the study and performed the fundamental characterization, such as XPS and Raman: Xue, C.; Wang, L.; Zhou, N.; Zhang, G.

Electrochemical performance testing of lithium-ion batteries: Zhang, Y.; Zhang, Y.; Li, X.

Electrochemical performance test of sodium ion batteries: Geng, Q.; Zheng, Y.; Li, Q.

Helped to conduct the physical adsorption instrument and Fe K-edge (XANES) spectra and analysis: Liu, B.

Engaged in analyzing the data and composing the final version of the paper: Xue, C.; Li, X.; Liu, B.; Li, Q.

Experiment supervisor: Li, Q.

The data was analyzed by all authors, who also took part in the discussions.

Availability of data and materials

Some results of supporting the study are presented in the [Supplementary Materials](#). Other raw data and materials that support the findings of this study are available from the corresponding author upon reasonable request.

Financial support and sponsorship

This study received financial backing from the National Natural Science Foundation of China (NSFC: 52003129), Basic Research Projects for the Pilot Project of Integrating Science and Education and Industry of Qilu University of Technology (Shandong Academy of Sciences) (2023PY029). Natural Science Foundation of Henan (Grant No. 252300420493), the Key scientific research projects of colleges and universities in Henan Province (Grant No. 24B110016).

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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