

Interfacial engineering of NaFePO₄/Na₂FePO₄F heterostructure cathode with enhanced kinetics for high-performance sodium-ion batteries

Biao-Yang Li¹, Lu-Lu Zhang¹(✉), Ze-Rong Deng¹, Yu-Jie Su², Xu-Heng Liu², Da-ping Qiu¹, Hua-Bin Sun², Bo Yan², Xue-Lin Yang^{1,2}(✉)

¹ Hubei Provincial Key Laboratory for Operation and Control of Cascaded Hydropower Station, College of Electrical Engineering & New Energy, China Three Gorges University, Yichang 443002, Hubei, China

² College of Materials and Chemical Engineering, China Three Gorges University, Yichang 443002, Hubei, China

Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94908999>

<https://www.sciopen.com/journal/1998-0124> on Jul. 6, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research*, **2025**, *18*, 94906990). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.

Research Article

Interfacial engineering of NaFePO₄/Na₂FePO₄F heterostructure cathode with enhanced kinetics for high-performance sodium-ion batteries

Biao-Yang Li¹, Lu-Lu Zhang^{1,*}, Ze-Rong Deng¹, Yu-Jie Su², Xu-Heng Liu², Da-ping Qiu¹, Hua-Bin Sun², Bo Yan², Xue-Lin Yang^{1,2,*}

¹Hubei Provincial Key Laboratory for Operation and Control of Cascaded Hydropower Station, College of Electrical Engineering & New Energy, China Three Gorges University, Yichang 443002, Hubei, China

²College of Materials and Chemical Engineering, China Three Gorges University, Yichang 443002, Hubei, China

Received: 9 January 2026; **Revised:** 17 June 2026; **Accepted:** 6 July 2026

✉ Address correspondence to Lu-Lu Zhang, luluzhang@ctgu.edu.cn; Xue-Lin Yang, xlyang@ctgu.edu.cn



Cite this article: *Nano Research*, 2026, 19, 94908999

<https://doi.org/10.26599/NR.2026.94908999>

Abstract

Sodium-ion batteries (SIBs) are promising for large-scale energy storage due to the abundance of sodium. Among potential cathodes, maricite NaFePO_4 (m-NFP) offers high theoretical capacity and low cost but is electrochemically inactive, while $\text{Na}_2\text{FePO}_4\text{F}$ (NFPF) possesses favorable Na^+ diffusion channels yet suffers from limited structural stability. To address these challenges, we develop a heterostructured NFP/NFPF composite coated with N, B-codoped carbon (NFP/F@C) via a facile solid-state method. The composite synergistically integrates the robust framework of m-NFP with the high ionic conductivity of NFPF through a well-defined heterointerface. Consequently, even at a high rate of 5C, the NFP/F@C cathode delivers a high discharge capacity of 63.9 mAh g^{-1} and outstanding cycling stability (94.2% capacity retention after 1000 cycles). Enhanced charge-transfer kinetics and Na^+ diffusion are confirmed by electrochemical analyses. *Ex situ* XRD reveals highly reversible structural evolution, contrasting with the irreversible amorphization of pristine m-NFP. DFT calculations further demonstrate that the heterointerface narrows the band gap to 0.22 eV and lowers the Na^+ migration barrier to 0.32 eV. A full cell paired with commercial hard carbon achieves a stable energy density of 215.3 Wh kg^{-1} , highlighting its practical viability. This work offers an effective interfacial-engineering strategy for designing high-performance, low-cost polyanionic cathodes for advanced SIBs.

Keywords: $\text{NaFePO}_4/\text{Na}_2\text{FePO}_4\text{F}$ heterostructure; interfacial engineering; kinetic enhancement; sodium-ion batteries; polyanionic cathode

1 Introduction

As the global energy structure transitions toward renewable sources, the large-scale integration of intermittent energy sources such as wind and solar has created a pressing need for cost-effective and safe energy storage technologies [1-3]. Sodium-ion batteries (SIBs) have emerged as a particularly attractive candidate for large-scale energy storage, given sodium's abundant reserves, wide distribution, and low cost [4-7]. As the core component determining the energy density, cycling stability, and rate capability of SIBs, cathode materials remain a focal point for performance optimization research. Significant efforts have been made in the modification of cathode materials for SIBs, including transition metal oxides, polyanionic compounds, Prussian blue analogs, and organic compounds [8-18]. Among various cathode materials for SIBs, maricite- NaFePO_4 (M-NFP) has attracted considerable research interest owing to its high theoretical specific capacity (155 mAh g^{-1}), excellent structural stability, and environmental benignity [19-22]. However, M-NFP possesses a structure consisting of edge-sharing FeO_6 octahedra and corner-sharing PO_4 tetrahedra that lacks continuous sodium-ion migration pathways, resulting in its characteristic electrochemical inactivity [23].

In recent years, researchers have significantly improved the electrochemical performance of M-NFP through various strategies, including electrospinning, high-energy ball milling, and structural design [24-27]. For instance, Fan et al. synthesized nanoscale NFP@C embedded in a 3D carbon network via electrospinning, in which the conductive framework facilitates efficient electron/ion transport,

resulting in a high reversible capacity of 145 mAh g⁻¹ at 0.2C and a notable rate capability of 61 mAh g⁻¹ even at 50C [24]. Mai et al. prepared structurally disordered M-NFP through 15 h of high-energy ball milling, in which the introduced defects significantly enhanced Na⁺ migration kinetics, leading to a high discharge capacity of 115 mAh g⁻¹ at 1C with 91.3% capacity retention after 800 cycles [25]. Wang et al. developed an ultrafine nanocluster-architected M-NFP via an amorphous-phase transformation strategy, in which the unique nanoarchitecture provided shortened ion diffusion pathways, thereby delivering a reversible capacity of 149.2 mAh g⁻¹ at 0.2C and maintaining 75.7 mAh g⁻¹ at 50C [26]. However, these strategies have inherent limitations. Nanoscale reduction lowers tapped density and energy density. Amorphization disrupts long-range order and fails to improve electronic conductivity. Both electrospinning and ball milling involve complex, high-cost processing. Recently, heterostructure strategies have emerged as a promising alternative, integrating the advantages of multiple phases and leveraging heterointerfaces for synergistic effects in ion transport, charge redistribution, and structural confinement [16-18].

In this work, we develop a heterostructured NFP/NFPF (Na₂FePO₄F) composite cathode via a facile solid-state synthesis route. By strategically introducing the NFPF phase with its favorable Na⁺ migration channel, the composite not only retains the structural stability of NFP but also establishes a well-defined heterointerface that significantly enhances electron and ion transport. Density functional theory (DFT) calculations confirm the underlying mechanism, showing a narrow band gap of 0.22

eV and a low Na^+ migration barrier of 0.32 eV. Benefiting from these favorable kinetics, the optimized composite cathode delivers a high discharge capacity of 63.9 mAh g^{-1} even at 5C and retains 94.2% of its capacity after 1000 cycles, demonstrating exceptional rate capability and long-term stability. Moreover, a full cell assembled with commercial hard carbon achieves an energy density of 215.3 Wh kg^{-1} , further confirming its practical viability. This work therefore demonstrates that heterostructure engineering between NFP and NFPF provides a viable and cost-effective strategy for developing high-performance cathodes for SIBs, offering a meaningful advance toward their practical implementation.

2 Experimental

2.1 Synthesis of the materials

First, Na_2CO_3 , $\text{FeC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed at a molar ratio of 0.5:1:1. Then, 0.35 g of citric acid, 0.175 g of urea, and NaBF_4 (added at 10%, 20%, and 30% of $\text{NH}_4\text{H}_2\text{PO}_4$'s molar amount) were incorporated into the mixture. The resulting mixture was ball-milled in anhydrous ethanol for 6 hours at a rotation speed of 400 rpm. After drying, the obtained powder was placed in a tube furnace for a two-step sequential calcination process based on the thermal decomposition behavior of the precursors. First, the sample was heated at 300 °C for 4 hours to remove small molecules (such as H_2O , NH_3 , and CO_2) originating from citric acid and urea, thereby preventing abrupt gas release and structural collapse. Subsequently, the temperature was ramped to 600 °C and held for 14 hours to promote the crystallization of the NFP and NFPF components, ensuring the formation of highly pure and well-crystallized

phases while avoiding excessive grain growth or decomposition. This two-step process yields the composite materials of NFP and NFPP, designated as NFP/F@C-1, NFP/F@C, and NFP/F@C-3). For comparison, NFP and NFPP materials (denoted as NFP@C and NFPP@C) were also prepared under the same process conditions.

2.2 Materials characterizations

The crystalline phases were analyzed by X-ray diffraction (XRD, SmartLab, Rigaku, Japan) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Chemical bonding and carbon structure were investigated using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, US). Morphological and microstructural characterization was conducted using field-emission scanning electron microscopy (FE-SEM, JSM-7500F, JEOL, Japan) and high-resolution transmission electron microscopy (HRTEM, F200, JEOL, Japan). with energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, UK). The carbon content and electronic conductivity of samples were determined by a carbon-sulfur analyzer (CS600, LECO, US) and a four-probe powder resistivity measurement system (FT-300I, Rico, China), respectively. The Raman spectra of all samples were recorded by a laser confocal Raman spectroscopy (Scientific DXR, Thermo, US). The Brunauer-Emmett-Teller (BET) specific surface area and pore structure were investigated by the N₂ isotherm adsorption and desorption measurement (Novatouch, Quantachrome, US).

2.3 Computational method

All the calculations was performed within the framework of the density functional theory (DFT) as implemented in the Vienna Ab initio Software Package

(VASP 5.4.4) code within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW) method [28-31]. The cutoff energy for the plane-wave basis set was set to 450 eV. The Brillouin zone of the surface unit cell was sampled by Monkhorst-Pack (MP) grids, with k-point mesh density of $2\pi \times 0.04 \text{ \AA}^{-1}$ for structures optimizations [32]. The convergence criterion for the electronic self-consistent iteration and force was set to 10^{-5} eV and $0.01 \text{ eV/\AA}$, respectively. The vacuum layer of $15 \text{ \AA}$ was introduced to avoid interactions between periodic images.

2.4 Electrode fabrication and electrochemical measurements

CR2025 coin cells were assembled to evaluate electrochemical performance. Cathode electrodes were prepared by casting a homogeneous slurry containing active material (NFP/F@C-1, NFP/F@C, NFP/F@C-3, NFP@C and NFPP@C), acetylene black, and PVDF binder (7:2:1 mass ratio) in N-methyl-2-pyrrolidone onto aluminum foil current collectors. The electrodes were vacuum-dried at 110°C for 6 hours and punched into 14 mm diameter disks. The typical mass loading of the active materials was controlled to be about 1.5 mg cm^{-2} . Cells were assembled in an Ar-filled glove box (Mikrouna Super 1220/750, $\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 1 \text{ ppm}$) using sodium metal anodes, glass microfiber separators (Whatman), and 1M NaClO_4 in EC: DMC: EMC (1:1:1 v/v) electrolyte with 2 vol.% fluoroethylene carbonate additive. Galvanostatic charge/discharge tests was performed between 1.5-4.5 V (vs. Na^+/Na) using a LAND CT2001A battery test system. Cyclic voltammetry (CV) in the voltage range of 1.5-4.5 V and electrochemical impedance spectroscopy (EIS) over a frequency range

from 0.01 Hz to 100 kHz of samples were conducted in the electrochemical workstation (CHI614C, China). All the electrochemical measurements were performed at room temperature (25 °C).

3 Results and discussion

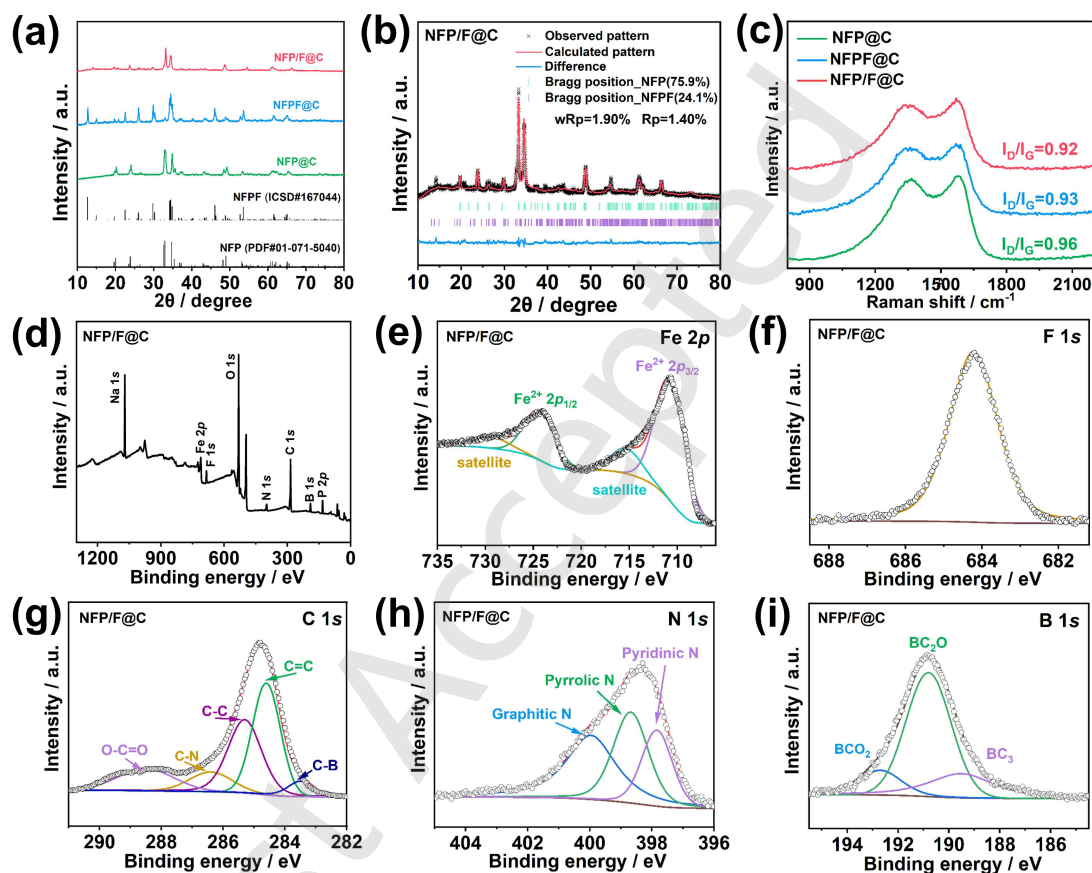


Fig. 1. (a) XRD patterns of samples, (b) Rietveld refinement results of NFP/F@C, (c) Raman spectra of samples, (d) X-ray photoelectron spectroscopy (XPS) full spectra of NFP/F@C, and (e-i) high-resolution XPS spectra of Fe 2p, F 1s, C 1s, N 1s, and B 1s for NFP/F@C, respectively.

The XRD patterns of the five samples (NFP@C, NFPF@C, NFP/F@C-1, NFP/F@C, and NFP/F@C-3) are displayed in Fig. 1(a) and Fig. S1(a). The major diffraction peaks of NFP@C correspond well to the standard NFP phase (orthorhombic, *Pnma* space group; PDF#01-071-5040), while those of NFPF@C match the standard NFPF phase (orthorhombic, *Pbcn* space group; ICSD#167044). In

the three composite samples (NFP/F@C-1, NFP/F@C, and NFP/F@C-3), the dominant diffraction peaks remain consistent with the NFP phase. Notably, a distinct peak observed around 12.8° in all three composites can be assigned to the (020) plane of the NFPP phase. The intensity of this peak progressively increases with higher NFPP content, confirming the successful formation of a NFP/NFPP heterocomposite structure. To quantify the phase ratios in the composites, Rietveld refinement was performed on the XRD data. The refinement results are reliable, as indicated by the low R_{wp} and R_p values (both below 2%) for all samples. Specifically, the phase proportions of NFP in the NFP/F@C-1, NFP/F@C, and NFP/F@C-3 composites were determined to be 93.1%, 75.9%, and 44.2%, respectively, with corresponding NFPP contents of 6.9%, 24.1%, and 55.8% (Fig. 1(b) and Fig. S1(b, c)). These results clearly demonstrate the successful synthesis of a heterocomposite with precisely tunable phase composition.

Raman spectroscopy was employed to investigate the carbon structure in the samples (Fig. 1(c)). All spectra exhibit two characteristic peaks located at approximately 1360 cm^{-1} and 1590 cm^{-1} , corresponding to the D band (disordered carbon) and G band (graphitic carbon), respectively [33, 34]. Although the intensity ratio of the D to G band (I_D/I_G) of the three samples are relatively close (0.96 for NFP/C, 0.93 for NFPP/C, and 0.92 for NFP/F@C) and the carbon content of NFP/F@C (4.28 wt.%) is lower than that of NFP/C (4.61 wt.%) and NFPP/C (4.43 wt.%) (Table S1), the composite NFP/F@C demonstrates the highest electronic conductivity ($3.26 \times 10^{-5}\text{ S cm}^{-1}$) among the series. This enhancement is attributed to its

slightly higher graphitization degree, as reflected by the lowest I_D/I_G value, suggesting that the composite structure effectively preserves favorable carbon ordering and promotes more efficient electron transport, thereby contributing to improved electrode kinetic.

The chemical states and surface composition of the NFP/F@C composite were investigated by XPS (Figs. 1d-i). To gain deeper insight into the distribution of elements, XPS depth profiling was also performed (Fig. S2). The high-resolution Fe 2p spectrum (Fig. 1e) exhibits characteristic peaks at 711.2 eV (Fe 2p_{3/2}) and 724.7 eV (Fe 2p_{1/2}), along with their satellite features, confirming that Fe predominantly exists in the +2 oxidation state [35, 36]. The Fe 2p depth profile (Fig. S2(b)) shows that the Fe signal is relatively weak at the surface and gradually increases with sputtering time. The F 1s spectrum (Fig. 1(f)) clearly shows a characteristic peak at around 684.2 eV, corresponding to Fe-F bonds in NFPF. With increasing sputtering depth, the F signal follows the same trend as Fe, and the peaks at 684.2 eV and 686.6 eV (assigned to Fe-F and P-F bonds, respectively) become more apparent (Fig. S2c). These observed trends for Fe and F are attributed to the shielding effect of the surface carbon coating layer. Deconvolution of the C 1s spectrum (Fig. 1(g)) reveals five components at binding energies of approximately 283.5, 284.7, 285.3, 286.2, and 288.5 eV, assigned to C-B, C=C, C-C, C-N, and O-C=O bonds, respectively [37, 38]. C element originates from both citric acid and urea, while N originates solely from urea. The C signal is strong at the surface and gradually decreases with sputtering depth (Fig. S2(d)), confirming successful carbon coating. The N 1s spectrum (Fig. 1(h)) can be

fitted with four peaks corresponding to pyridinic N (398.5 eV), pyrrolic N (399.5 eV), and graphitic N (401.0 eV). The defect-associated pyridinic and pyrrolic N species are known to facilitate Na^+ migration and provide additional active sites for sodium storage [39, 40]. The N 1s depth profiles (Fig. S2(e)) show that N follows the same trend as C, indicating that N is distributed throughout the carbon layer with a relatively higher concentration near the surface. The presence of B originates from the decomposition of NaBF_4 . During the high-temperature solid-state reaction, NaBF_4 decomposes into active B and F species. B species are incorporated into the carbon coating layer, while F species participate in the formation of the NFPP phase. The B 1s spectrum (Fig. 1(i)) displays three components assigned to BC_3 (189.5 eV), BC_2O (190.8 eV), and BCO_2 (192.7 eV) configurations. The B 1s depth profile (Fig. S2(f)) reveals that the B signal is weak at the outermost surface but increases after sputtering for 25 s and remains stable at 50 s, indicating that B is primarily distributed beneath the surface carbon layer. This phenomenon can be explained by the thermal decomposition behavior of NaBF_4 . Upon heating, NaBF_4 decomposes into NaF and highly volatile BF_3 . NaF participates in the formation of NFPP, while BF_3 readily escapes from the surface. Consequently, B is preferentially retained beneath the surface carbon layer rather than on the outer surface. The incorporation of N and B into carbon layer is beneficial for enhancing electronic conductivity [41-44].

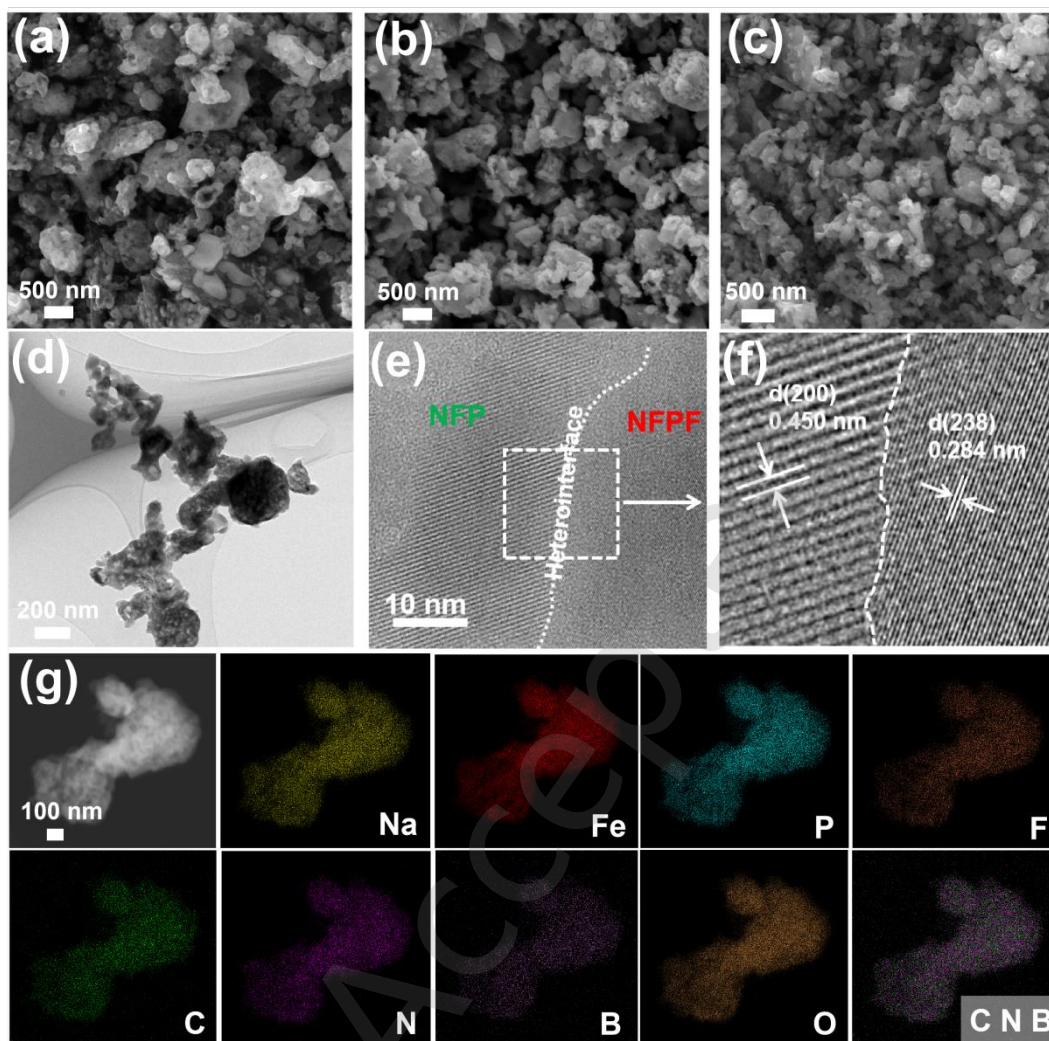


Fig. 2. (a-c) SEM images of NFP@C, NFPF@C, and NFP/F@C, respectively, (d) TEM image of NFP/F@C, (e) HRTEM image of NFP/F@C, (f) corresponding magnified image of the area indicated in (e), and (g) HAADF image and corresponding EDS elemental mapping images of NFP/F@C.

SEM images (Figs. 2(a-c)) show irregular particle morphologies for all samples. Compared to NFP@C and NFPF@C, the composite NFP/F@C exhibits reduced agglomeration and a more uniform particle size distribution, with typical dimensions around 200 nm (Fig. 2(d)). HRTEM images (Figs. 2(e, f)) clearly reveal two distinct crystalline regions with different lattice spacings of 0.450 nm for the (200) plane of

NFP (left), and 0.284 nm for the (238) plane of NFPP (right). Notably, the lattice fringes of NFP appear less sharp than those of NFPP, owing to its higher susceptibility to electron beam irradiation. This differential beam sensitivity provides additional strong evidence that the two regions are intrinsically distinct crystalline phases. To further confirm that the heterostructure is not accidental, other region of the sample was examined. As shown in Figs. S3a-b, two distinct crystalline regions with different lattice spacings of 0.269 nm for to the NFP (121) plane (left) and 0.261 nm for corresponding to the NFPP (211) plane (right) are observed. Consistent with the previous observation, the lattice fringes of NFP again appear less sharp than those of NFPP. The consistency of these HRTEM images across different regions confirm that the NFP/F@C composite is indeed a heterostructured material consisting of NFP and NFPP phases. Additionally, the SAED patterns of NFP/F@C (Figs. S3d and S3e) corresponding to NFP and NFPP further verify the formation of the heterostructure. Moreover, Fig. S3(c) clearly shows that the NFP/F@C particles are uniformly encapsulated by a thin amorphous carbon layer, which contributes to the structural integrity during cycling. EDS elemental mapping images (Fig. 2(g)) demonstrates homogeneous distribution of all constituent elements (Na, Fe, P, F, C, N, B, and O) throughout the NFP/F@C composite. The overlaid map highlights the spatial colocalization of C, N, and B, which, in conjunction with XPS analysis, confirms the formation of an N, B-codoped carbon coating on the particle surface. This conductive and structurally integrated coating facilitates electron transport and enhances interfacial stability, collectively supporting the outstanding sodium storage

performance of the NFP/F@C composite.

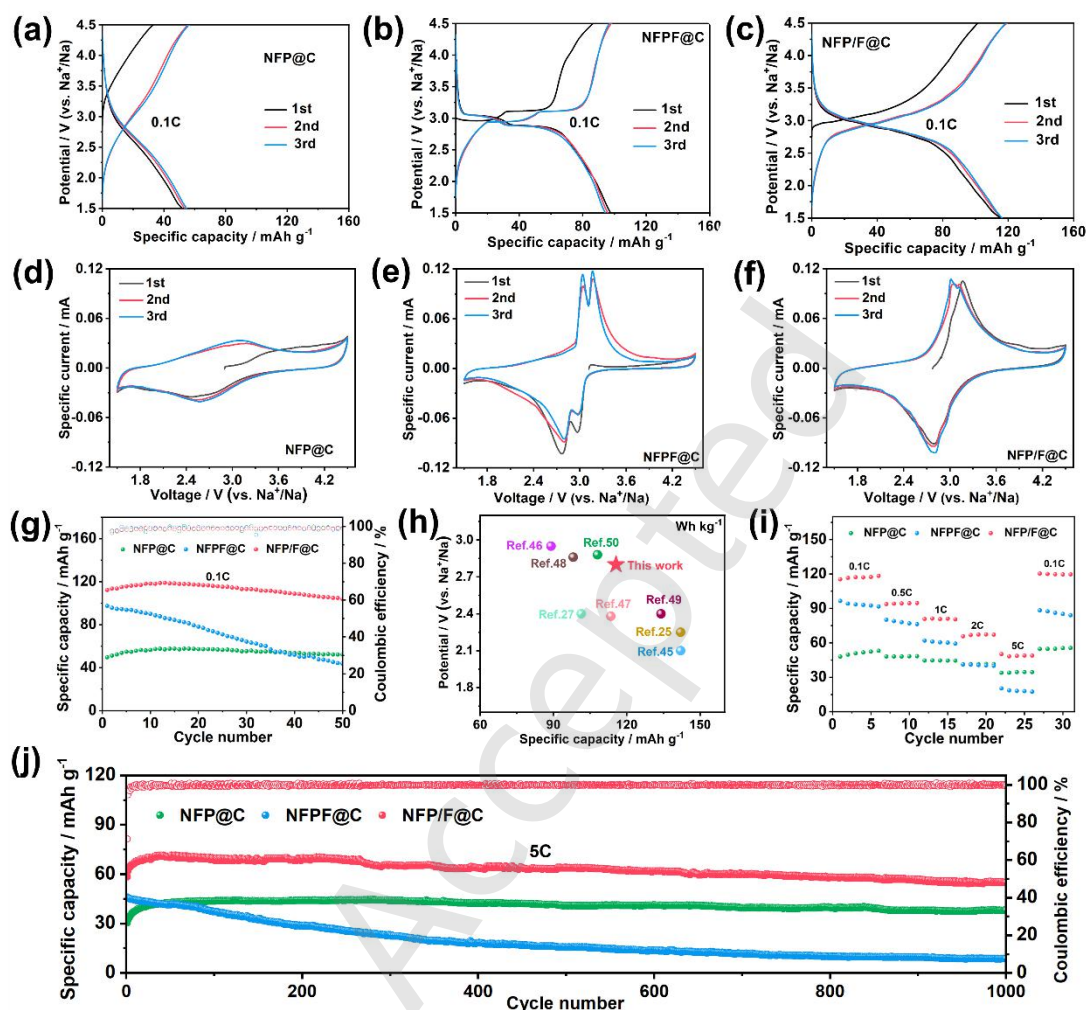


Fig. 3. Electrochemical performance of samples: (a-c) charge-discharge profiles at 0.1C, (d-f) CV curves recorded at a scan rate of 0.1 mV s⁻¹, (g) cycling performance at 0.1C, (h) comparison of energy density between the present composite and representative iron-based polyanionic cathode materials [25, 27, 45-50], (i) rate performance, and (j) long-term cycling performance at a high rate of 5C.

Galvanostatic charge-discharge (GCD) tests were conducted to evaluate the specific capacity and cycling performance of the synthesized samples. The initial charge-discharge profiles at 0.1C are presented in Figs. 3(a-c) and S4(a, c). NFP@C shows no distinct voltage plateau, while NFPF@C exhibits two characteristic plateaus

near 3.1/2.8 V and 3.0/3.2 V, consistent with its known redox behavior [45, 51]. In contrast, all composite samples effectively integrate the structural stability of NFP with the well-defined redox activity of NFPF. As the NFPF content increases, the associated plateaus become more pronounced, confirming successful integration of both phases, which is consistent with the cyclic voltammetry (CV) profiles shown in Figs. 3(d-f) and S4(b, d). Compared to NFP/C, the three composites (NFP/F@C-1, NFP/F@C and NFP/F@C-3) deliver improved initial discharge capacities (60.0, 115.6, and 95.1 mAh g⁻¹, respectively), along with elevated median discharge voltages (Table S2). Notably, the optimized composite NFP/F@C exhibits a median discharge voltage of 2.80 V, significantly exceeding that of NFP/C (2.43 V). The elevation in operating voltage, combined with the improved specific capacity (115.6 mAh g⁻¹), substantially boosts the energy output of the NFP/F@C electrode, which achieves a calculated energy density of approximately 323.7 Wh kg⁻¹, markedly higher than that of NFP/C (ca. 120.5 Wh kg⁻¹). After 50 cycles at 0.1C (Fig. 3(g)), NFP/C retains only 43.8 mAh g⁻¹, whereas NFP/F@C maintains a capacity of 103.8 mAh g⁻¹, demonstrating markedly improved cycling stability. It should be noted that there remains a gap between the experimental capacity of NFP/F@C and its theoretical value. Pristine M-NFP is inherently inactive, and our work aims to activate it by leveraging the favorable Na⁺ diffusion channels provided by NFPF. However, NFPF itself has a relatively low theoretical capacity of 124 mAh g⁻¹, while NFP offers a higher theoretical capacity of 155 mAh g⁻¹. In NFP/F@C, the NFPF phase accounts for approximately 24.1% (as determined by Rietveld refinement shown in Fig. 1b), so

the overall theoretical capacity of the heterostructure is inevitably lower than that of pure NFP. Additionally, during cycling, a portion of the NFP phase may remain inactive or not be fully utilized, contributing to the capacity gap. This incomplete activation could result from factors such as particle isolation, limited ionic/electronic conductivity, or kinetic barriers at the heterointerface. Electrode polarization and interfacial resistance under operating conditions may further influence the practical capacity. Nonetheless, the elevated median voltage, increased capacity, and improved cycling stability exhibited by the NFP/F@C cathode establish a critical foundation for achieving high performance in practical full-cell configurations, as will be quantitatively demonstrated in the subsequent full-cell analysis section. These results underscore the strong competitiveness of NFP/F@C among iron-based polyanionic cathodes (Fig. 3(h)) and highlight the essential role of heterointerface engineering in balancing high capacity, elevated voltage, and long-term cyclability.

The rate capabilities of the five samples are evaluated under current densities ranging from 0.1 to 5C (Figs. 3(i) and S4(f)). As anticipated, the discharge specific capacities of all samples decrease with increasing current density, reflecting a Na^+ insertion/extraction process governed by solid-state diffusion. Among them, NFP/F@C delivers the highest average discharge capacities at each rate (118.2, 94.3, 80.7, 67.2, and 49.6 mAh g^{-1} at 0.1, 0.5, 1, 2, and 5C, respectively). When the current density is returned to 0.1C, the capacity returns to 117.6 mAh g^{-1} , indicating excellent electrochemical reversibility. Long-term cycling performance is presented in Figs. 3(j) and S4(g). The average discharge capacities of NFP@C and NFPF@C are 40.2 and

17.8 mAh g⁻¹, respectively, while the composite samples NFP/F@C-1 and NFP/F@C-3 exhibit 37.3 and 33.6 mAh g⁻¹. In contrast, the optimally phase-balanced NFP/F@C delivers a higher average discharge capacity of 63.9 mAh g⁻¹ at 5C, retaining 94.2% of its capacity after 1000 cycles. Under the same conditions, NFP/F@C-3 retains only 38.6%, highlighting the detrimental effect of excessive NFPF content on long-term structural stability. Even at a high loading of approximately 4 mg cm⁻², the NFP/F@C delivers an initial discharge capacity of 109.8 mAh g⁻¹ at 0.1C and an average capacity of 55.4 mAh g⁻¹ at 5C, which are higher than those of the lower-loading NFP@C and NFPF@C electrodes under the same measurement conditions (Fig. S5). These results collectively demonstrate that while NFPF contributes to higher specific capacities, an excessive proportion compromises cycling durability due to its inherent structural instability. The superior performance of NFP/F@C stems from a synergistic interplay between NFP and an optimal amount of NFPF, enabled by a well-defined heterointerface that effectively balances high capacity with structural durability, thus achieving high-rate capability and long-cycle sodium storage.

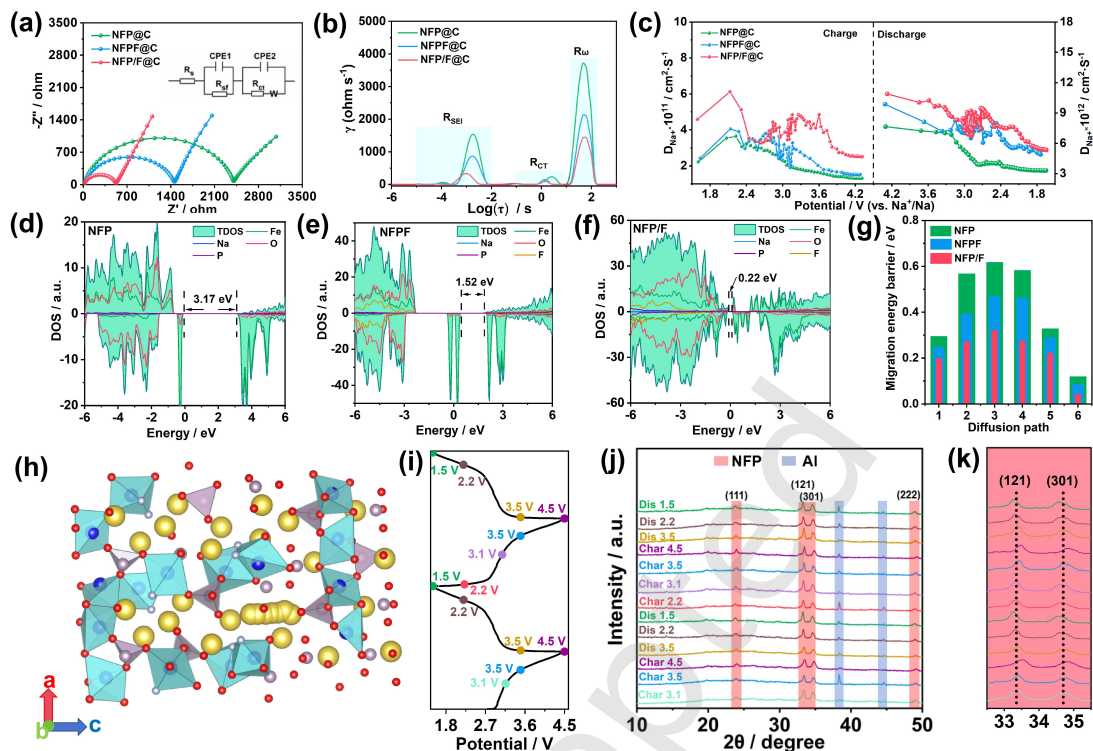


Fig. 4. Electrochemical kinetic performance of samples: (a) EIS spectra and fitted equivalent circuit of three samples, (b) DRT curves of three samples according to AC impedance plots, (c) Na⁺ diffusion coefficients during charge and discharge process. (d-f) Calculated density of states (DOS) for NFP, NFPF, and the NFP/F species, respectively. (g) Energy barrier along the migration paths. (h) Optimized migration paths of Na⁺ ions in NFP/F species. (i) Charge/discharge profile of the NFP/F@C cathode at 0.1C between 1.5 and 4.5 V, and (j-k) *ex situ* XRD patterns of NFP/F@C collected at selected states during the first two cycles.

Electrochemical impedance spectroscopy (EIS) and galvanostatic intermittent titration technique (GITT) measurements were performed to investigate the electrode kinetics of the three samples. As shown in Fig. 4(a), the EIS spectra of all electrodes consist of a small high-frequency intercept, a well-defined semicircle in the medium-frequency range, and a low-frequency inclined line. The semicircle reflects the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface [52]. Fitted

with the equivalent circuit model “R(Q(RW))(QR)” (Fig. 4(a)), the R_{ct} value of NFP/F@C is 527.3 Ω , markedly lower than those of NFP/C (2401.8 Ω), NFPF/C (1454.7 Ω), NFP/F@C-1 (741.6 Ω), and NFP/F@C-3 (1680.4 Ω) (Figs. 4(a), S6(a), and Table S3), indicating significantly accelerated charge-transfer kinetics. This improvement is attributed to the conductive heterointerface formed between NFP and NFPF, which facilitates efficient Na^+ transport. Distribution of relaxation times (DRT) analysis derived from EIS data at open-circuit voltage (OCV) further distinguishes the kinetic characteristics of the three electrodes (Fig. 4(b)). For the composite electrode, the reduced peak intensities in the τ_1 and τ_2 regions suggest decreased resistance associated with the solid-electrolyte interphase (R_{SEI}) [53]. Meanwhile, the attenuated τ_3 peak corresponds to the decreased R_{ct} , reflecting enhanced redox kinetics. The well-preserved intensity and position of the τ_4 peak, related to ion diffusion (Warburg impedance, R_w), suggest sustained fast ionic diffusion in NFP/F@C. Consistently, the plots of Z' versus $\omega^{-1/2}$ (Fig. S6(b)) exhibit a smaller slope for NFP/F@C, indicating lower diffusion resistance. The corresponding Na^+ diffusion coefficients, calculated using equation (Table S3) [54]

$$D = \frac{R^2 T^2}{2 A^2 n^4 F^2 C^2 \sigma^2} \quad (1)$$

where D is the diffusion coefficient of Na^+ , R is the gas constant, T is the absolute temperature, A is the effective area of the electrode, n is the number of electrons transferred, F is the Faraday constant, C is the Na^+ concentration in electrolyte, and σ is the Warburg factor. It confirm that NFP/F@C possesses the highest value ($5.17 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) among the samples, further clarifying the origin of its superior

sodium-storage performance.

GITT measurements were performed to evaluate the Na⁺ diffusion kinetics of the three representative samples (Fig. 4(c)). Key parameters used in the analysis are defined as follows: Na⁺ diffusion coefficient (D , cm² s⁻¹), pulse duration (τ , s), active material mass (m_B , g), molar volume (V_M , cm³ mol⁻¹), molar mass (M_B , g mol⁻¹), effective electrode area (S , cm²), steady-state voltage change per titration step (ΔE_S), and total voltage change during galvanostatic pulse (ΔE_τ). The Na⁺ diffusion coefficients were calculated according to equations [54, 55]

$$D = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2 \quad (2)$$

where τ (s), m_B (g), V_M (cm³ mol⁻¹), M_B (g mol⁻¹) and S (cm²) are the pulse time, active mass, molar volume, molecular weight and effective area of the electrode, respectively. ΔE_S and ΔE_τ represent the change of the steady-state voltage at a single titration and the total change of voltage during constant current pulse, respectively.

As shown in Fig. 4(c), NFP/F@C exhibits consistently higher D values than both NFP@C and NFPF@C throughout the charge-discharge process, in full agreement with the EIS analysis. These results collectively confirm that the NFP/NFPF heterointerface plays a decisive role in enhancing cycling stability and enabling exceptional rate performance.

To investigate the beneficial effect of the heterointerface on electronic conductivity and Na⁺ diffusion kinetics, density functional theory (DFT) calculations were performed to analyze the density of states (DOS) and Na⁺ migration energy barriers of NFP, NFPF, and the NFP/F composite. To elucidate the

beneficial role of the heterointerface in enhancing electronic conductivity and Na^+ diffusion kinetics, density functional theory (DFT) calculations were conducted to analyze the density of states (DOS) and Na^+ migration energy barriers of NFP, NFPP, and the NFP/F species. As shown in Figs. 4(d-f), the calculated band gaps for pristine NFP and NFPP are 3.17 eV and 1.52 eV, respectively, whereas the NFP/F species exhibits a significantly reduced band gap of only 0.22 eV. This narrowing indicates that interfacial coupling effectively optimizes the electronic structure of NFP, lowering the energy required for electron excitation and thereby enhancing charge-transport efficiency. The energy barrier profiles and optimized Na^+ migration pathways are presented in Figs. 4(g-h) and Fig. S7. Fig. 4h illustrates the optimized migration path of Na^+ ions in the NFP/NFPP composite, which is a cross-interface atomic trajectory from the NFP side to the NFPP side, rather than an intragranular pathway within a single phase. The Na^+ migration barrier in the NFP/F heterostructure is only 0.32 eV, which is substantially lower than those in pristine NFP (0.62 eV) and NFPP (0.51 eV). Obviously, the heterointerface itself serves as a fast percolation channel. Na^+ ions migrate slowly within the NFP or NFPP bulk domains with their intrinsic barriers (0.62 eV and 0.51 eV, respectively). However, once they reach the interfacial region, they can enter the low-barrier cross-interface pathway (0.32 eV). Thus, the enhanced kinetics arise not from lowering the intrinsic barriers of the bulk phases, but from constructing a low-barrier interfacial percolation network that provides an alternative fast pathway to bypass the slow bulk regions. This mechanism explains how the engineered heterointerface facilitates Na^+ transport, providing a

theoretical foundation for the superior electrochemical performance of the NFP/F heterostructure.

To elucidate the structural evolution of the NFP/F@C composite during electrochemical cycling, *ex situ* XRD analysis was conducted at selected charge and discharge states. As illustrated in Fig. 5(a), the electrode was cycled at 0.1C between 1.5 and 4.5 V, with XRD patterns collected at 13 distinct voltage points during the first and second cycles (Figs. 4(i-k)). Although the characteristic NFPP peak near 12.8° was not detected, likely due to its low content and limited crystallinity, well-defined reversible structural changes were observed in the NFP phase. Specifically, the diffraction peaks at 33.1° and 34.7° , corresponding to the (220) and (222) planes of NFP, systematically shifted toward higher angles during Na^{+} extraction (charging) and reversibly returned toward lower angles during Na^{+} insertion (discharging). This highly reproducible shift pattern over consecutive cycles confirms exceptional reversibility of the Na^{+} extraction/insertion process. Such behavior fundamentally differs from the irreversible amorphization reported for m-NFP (which converts to amorphous FePO_4) [56, 57], underscoring the crucial role of the NFP/NFPP heterointerface in maintaining structural integrity and enabling highly reversible sodium storage.

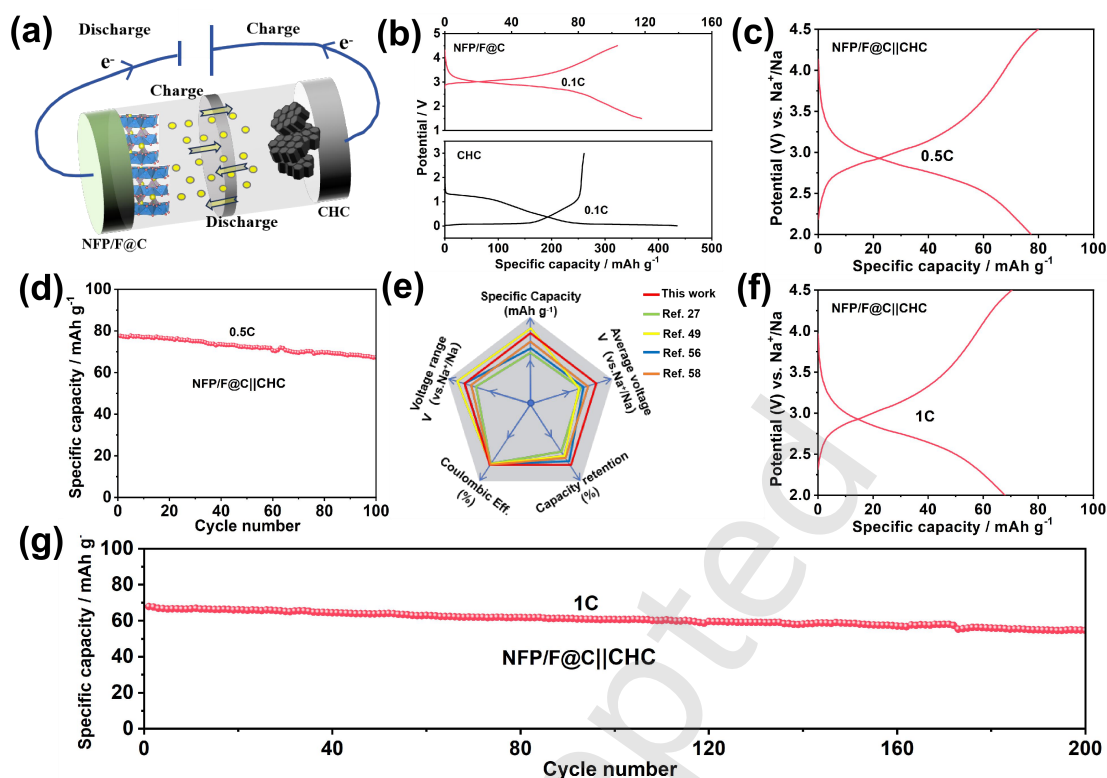


Fig. 5. (a) Schematic diagram of the working principle of the CHC||NFP/F@C full cell. (b) Initial charge-discharge profiles of the NFP/F@C cathode and CHC anode at 0.1C. (c) Initial charge-discharge profiles of the CHC||NFP/F@C full cell at 0.5C. (d) Cycling performance of the CHC||NFP/F@C full cell at 0.5C. (e) Radar-chart comparison of the CHC||NFP/F@C full cell performance with other NFP-based full cells [27, 49, 56, 58]. (f) Initial charge-discharge profiles of the CHC||NFP/F@C full cell at 1C. (g) Cycling performance of the CHC||NFP/F@C full cell at 1C.

To assess the practical viability of NFP/F@C, a full cell was assembled using NFP/F@C as the cathode and commercial hard carbon (CHC) as the anode, with the N/P ratio controlled between 1.1:1 and 1.3:1. Fig. 5(a) schematically illustrates the configuration of the CHC||NFP/F@C full cell, which operates via a rocking-chair mechanism based on reversible Na⁺ shuttling between the electrodes. The initial charge-discharge profiles at 0.1C (Fig. 5(b)) show that the NFP/F@C cathode delivers

a first discharge capacity of 117.8 mAh g⁻¹, while the CHC anode exhibits a first capacity of 260.5 mAh g⁻¹, confirming good sodium-storage capability for both electrodes. When cycled at 0.5C (based on cathode mass) between 2.0 and 4.5 V, the full cell delivers an initial discharge capacity of 77.6 mAh g⁻¹ and retains 86.7% of its capacity after 100 cycles (Figs. 5(c, d)), corresponding to an energy density of 215.3 Wh kg⁻¹. Performance comparison using a radar chart (Fig. 5(e)) reveals that the full cell exhibits an average voltage of 2.8 V and overall superior metrics among reported NFP-based full cells. Moreover, at 1C, it achieves an initial discharge capacity of 67.9 mAh g⁻¹ and maintains 80.6% capacity retention after 200 cycles (Figs. 5(f, g)). These results collectively demonstrate that NFP/F@C is a promising cathode candidate with practical potential for SIBs.

4 Conclusions

In this work, a heterostructured NFP/NFPF (NFP/F@C) composite cathode was successfully synthesized via a solid-state method. The composite integrates the structural stability of NFP with the high ionic conductivity of NFPF through a well-defined heterointerface, which was systematically confirmed by XRD, TEM, and elemental mapping. Electrochemical evaluations demonstrate that the optimized NFP/F@C delivers a high reversible capacity of 115.6 mAh g⁻¹ and an energy density of 323.7 Wh kg⁻¹ at 0.1C, along with outstanding rate capability (49.6 mAh g⁻¹ at 5C) and remarkable cycling stability (94.2% capacity retention after 1000 cycles at 5C). Kinetic analysis based on EIS and GITT reveals significantly reduced charge-transfer resistance and enhanced Na⁺ diffusion kinetics in the composite. DFT calculations

provide theoretical insight, showing that the heterointerface effectively narrows the band gap (0.22 eV) and lowers the Na⁺ migration barrier (0.32 eV), thereby promoting both electronic and ionic transport. *Ex situ* XRD further verifies the highly reversible structural evolution during cycling, distinct from the irreversible amorphization observed in conventional m-NFP. Moreover, a full cell assembled with commercial hard carbon anode achieves a stable energy density of 215.3 Wh kg⁻¹, underscoring its practical feasibility. This study highlights the critical role of heterointerface engineering in balancing capacity, stability, and kinetics, offering a cost-effective and scalable strategy for developing high-performance polyanionic cathodes for sodium-ion batteries.

Acknowledgements

This work was financially supported by the Joint Funds of the Hubei Natural Science Foundation Innovation and Development (No. 2022CFD034), the National Natural Science Foundation of China (No. 52572239, 52072217, 22509113, and 52402278), and the Hubei Natural Science Foundation Innovation Group Project (No. 2022CFA020).

Electronic Supplementary Material: Supplementary material (additional material and electrochemical characterization data).

References

- [1] Erdogan, S.; Pata, U. K.; Solarin, S. A. Towards carbon-neutral world: The effect of renewable energy investments and technologies in G7 countries. *Renew. Sust. Energy Rev.* **2023**, 186, 113683.

- [2] Badawi M, N.; Agrawal, N.; Luqman, M.; Ramesh, S.; Ramesh, K.; Khan, M.; Adil, S. F. Developments and challenges in batteries, and hydrogen as a future fuel, and storage and carrier devices. *Int. J. Hydrogen Energy* **2025**, 105, 1242-1260.
- [3] Wu, Y.; Zhong, X.; Wang, X.; Yang, Y.; Wang, Z. L. Hybrid energy cell for simultaneously harvesting wind, solar, and chemical energies. *Nano Research* **2014**, 7, 1631-1639.
- [4] Wang, Y.; Zhang, X.; Wang, X.; Zhong, J.; Yu, J.; Liu, T. Overcoming sluggish kinetics in $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ via synergistic Zr doping and iron defect engineering for high-performance sodium-ion batteries. *ACS Applied Materials & Interfaces* **2025**, 17, 56205-56216.
- [5] Wang, X.; Ma, L.; Yan, W.; Zhang, X.; Han, J.; Yu, W.; Liu, T. High-valence Mo doping enables phase-stable, fast-transport $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathodes for high-performance sodium-ion batteries. *Nano Energy* **2026**, 150, 111754.
- [6] Liu, Q.; Hu, Z.; Chen, M.; Zou, C.; Jin, H.; Wang, S.; Chou, S. L.; Dou, S. X. Recent progress of layered transition metal oxide cathodes for sodium - ion batteries. *Small* **2019**, 15, 1805381.
- [7] Vaalma, C.; Buchholz, D.; Weil, M.; Passerini, S. A cost and resource analysis of sodium-ion batteries. *Nature reviews materials* **2018**, 3, 1-11.
- [8] Gao, H.; Zeng, J.; Sun, Z.; Jiang, X.; Wang, X. Advances in layered transition metal oxide cathodes for sodium-ion batteries. *Materials Today Energy* **2024**, 42, 101551.
- [9] Wang, Y.; Wang, X.; Li, X.; Yu, R.; Chen, M.; Tang, K.; Zhang, X. The novel

- P3-type layered $\text{Na}_{0.65}\text{Mn}_{0.75}\text{Ni}_{0.25}\text{O}_2$ oxides doped by non-metallic elements for high performance sodium-ion batteries. *Chemical Engineering Journal* **2019**, 360, 139-147.
- [10]Zhang, L.-L.; Liu, J.; Wei, C.; Sun, P.-P.; Gao, L.; Ding, X.-K.; Liang, G.; Yang, X.-L.; Huang, Y.-H. N/P-dual-doped carbon-coated $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{O}_2\text{F}$ microspheres as a high-performance cathode material for sodium-ion batteries. *ACS Applied Materials & Interfaces* **2019**, 12, 3670-3680.
- [11]Deng, Z. R.; Zhang, L. L.; Pei, F.; Liu, W.; Sun, C.; Sun, H. B.; Ding, X. K.; Yang, X. L. Achieving high rate and long cycle performance of $\text{Na}_2\text{FePO}_4\text{F}$ cathode through co - modification of Ti doping and carbon coating. *Small* **2024**, 20, 2400149.
- [12]Chen, Z.-Y.; Fu, X.-Y.; Zhang, L.-L.; Yan, B.; Yang, X.-L. High-performance Fe-based Prussian blue cathode material for enhancing the activity of low-spin Fe by Cu doping. *ACS Applied Materials & Interfaces* **2022**, 14, 5506-5513.
- [13]Fu, X. Y.; Zhang, L. L.; Chen, Z. Y.; Xu, Y.; Wu, J.; Wang, C. C.; Ding, X. K.; Yang, X. L.; Lu, J. Achieving a superior Na storage performance of Fe - based Prussian blue cathode by coating perylene tetracarboxylic dianhydride amine. *Carbon Energy* **2024**, 6, e446.
- [14]Wei, C.; Fu, X.-Y.; Zhang, L.-L.; Liu, J.; Sun, P.-P.; Gao, L.; Chang, K.-J.; Yang, X.-L. Structural regulated nickel hexacyanoferrate with superior sodium storage performance by K-doping. *Chemical Engineering Journal* **2021**, 421, 127760.
- [15]Zhou, M.; Zhou, X.; Li, L.; Chen, X.; Qiao, Z.; Chou, S. Emerging high voltage

V^{4+}/V^{5+} redox reactions in $Na_3V_2(PO_4)_3$ -based cathodes for sodium-ion batteries.

Chemical Science **2024**, *15*, 8651-8663.

[16]La, C.; Lv, Y.; Dai, S.; Hao, S.; Peng, J.; Zhao, J.; Huang, C.; Xue, L.; Zhang, W.;

Huang, Y. Biphasic interactions between $Na_4Fe_3(PO_4)_2P_2O_7$ and $Na_3V_2(PO_4)_3$ to achieve ultra-long lifespan cathode material for sodium-ion batteries. *Chemical Engineering Journal* **2025**, *519*, 164736.

[17]Kong, L.Y.; Li, Z.Q.; Liu, H.X.; Li, X.Y.; Zhu, Y.F.; Li, J.Y.; Tan, P.; Yang, M.;

Mao, J.F.; Pang, W.K. High energy density heterostructured sodium layered oxide cathodes enabled by mechanical-chemical coupling effect. *Angewandte Chemie International Edition* **2025**, *64*, e202517300.

[18]Ma, X.; Pan, Z.; Wu, X.; Shen, P.K. $Na_4Fe_3(PO_4)_2(P_2O_7)@NaFePO_4@C$

core-double-shell architectures on carbon cloth: A high-rate, ultrastable, and flexible cathode for sodium ion batteries. *Chemical Engineering Journal* **2019**, *365*, 132-141.

[19]Ahsan, Z.; Cai, Z.; Wang, S.; Moin, M.; Wang, H.; Liu, D.; Ma, Y.; Song, G.;

Wen, C. Recent development of phosphate based polyanion cathode materials for sodium - ion batteries. *Advanced Energy Materials* **2024**, *14*, 2400373.

[20]Gao, Y.; Zhang, H.; Liu, X. H.; Yang, Z.; He, X. X.; Li, L.; Qiao, Y.; Chou, S. L.

Low - cost polyanion - type sulfate cathode for sodium - ion battery. *Advanced Energy Materials* **2021**, *11*, 2101751.

[21]Niu, Y.; Zhang, Y.; Xu, M. A review on pyrophosphate framework cathode

materials for sodium-ion batteries. *Journal of Materials Chemistry A* **2019**, *7*,

15006-15025.

- [22] Liao, H.; Zhang, Z.; Zheng, Y.; Gao, Y. NaFePO₄ for sodium-ion batteries: Mechanism, synthesis and optimization strategies toward commercialization. *Energy Storage Materials* **2024**, *65*, 103157.
- [23] Guo, S.-P.; Li, J.-C.; Xu, Q.-T.; Ma, Z.; Xue, H.-G. Recent achievements on polyanion-type compounds for sodium-ion batteries: syntheses, crystal chemistry and electrochemical performance. *Journal of Power Sources* **2017**, *361*, 285-299.
- [24] Liu, Y.; Zhang, N.; Wang, F.; Liu, X.; Jiao, L.; Fan, L. Z. Approaching the downsizing limit of maricite NaFePO₄ toward high - performance cathode for sodium - ion batteries. *Advanced Functional Materials* **2018**, *28*, 1801917.
- [25] Xiong, F.; An, Q.; Xia, L.; Zhao, Y.; Mai, L.; Tao, H.; Yue, Y. Revealing the atomistic origin of the disorder-enhanced Na-storage performance in NaFePO₄ battery cathode. *Nano Energy* **2019**, *57*, 608-615.
- [26] Liu, B.; Zhang, Q.; Li, L.; Zhang, L.; Jin, Z.; Wang, C.; Su, Z. Achieving highly electrochemically active maricite NaFePO₄ with ultrafine NaFePO₄@C subunits for high rate and low temperature sodium-ion batteries. *Chemical Engineering Journal* **2021**, *405*, 126689.
- [27] Zhao, L.; Yu, L.; Wan, G.; Ahmad, N.; Ma, X.; Tao, Z.; Zhang, G. Co - manipulation of ultrafine nanostructure and uniform carbon layer activates maricite - structured NaFePO₄ as a high - performance cathode for sodium - ion batteries. *Small Science* **2023**, *3*, 2300122.
- [28] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made

simple. *Physical review letters* **1996**, 77, 3865.

- [29]Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Physical review B* **1999**, 59, 7413.
- [30]Blöchl, P. E. Projector augmented-wave method. *Physical review B* **1994**, 50, 17953.
- [31]Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical review b* **1999**, 59, 1758.
- [32]Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Physical review B* **1976**, 13, 5188.
- [33]Yang, G.; Ding, B.; Wang, J.; Nie, P.; Dou, H.; Zhang, X. Excellent cycling stability and superior rate capability of a graphene–amorphous FePO₄ porous nanowire hybrid as a cathode material for sodium ion batteries. *Nanoscale* **2016**, 8, 8495-8499.
- [34]Zhang, J.; Zhang, W.; He, T.; Amiin, I. S.; Kou, Z.; Li, J.; Mu, S. Smart reconstruction of dual-carbon decorated MnO for anode with high-capacity and ultralong-life lithium storage properties. *Carbon* **2017**, 115, 95-104.
- [35]Ma, X.; Wu, X.; Shen, P. Rational design of Na₄Fe₃(PO₄)₂(P₂O₇) nanoparticles embedded in graphene: toward fast sodium storage through the pseudocapacitive effect. *ACS Applied Energy Materials* **2018**, 1, 6268-6278.
- [36]Ren, X.; Turcheniuk, K.; Lewis, D.; Fu, W.; Magasinski, A.; Schauer, M. W.; Yushin, G. Iron phosphate coated flexible carbon nanotube fabric as a

multifunctional cathode for Na⁺ ion batteries. *Small* **2018**, *14*, 1703425.

- [37] Yi, G.-d.; Fan, C.-l.; Hu, Z.; Zhang, W.-h.; Han, S.-c.; Liu, J.-s. Construction of high performance N-doped Na₃V₂(PO₄)₂F₃/C cathode assisting by plasma enhanced chemical vapor deposition for sodium-ion batteries. *Electrochimica Acta* **2021**, *383*, 138370.
- [38] Jiang, Y.; Yang, Y.; Xu, R.; Cheng, X.; Huang, H.; Shi, P.; Yao, Y.; Yang, H.; Li, D.; Zhou, X. Ultrafast potassium storage in F-induced ultra-high edge-defective carbon nanosheets. *ACS nano* **2021**, *15*, 10217-10227.
- [39] Zhang, H.; Hasa, I.; Buchholz, D.; Qin, B.; Passerini, S. Effects of nitrogen doping on the structure and performance of carbon coated Na₃V₂(PO₄)₃ cathodes for sodium-ion batteries. *Carbon* **2017**, *124*, 334-341.
- [40] Zhang, L.-L.; Ma, D.; Li, T.; Liu, J.; Ding, X.-K.; Huang, Y.-H.; Yang, X.-L. Polydopamine-derived nitrogen-doped carbon-covered Na₃V₂(PO₄)₂F₃ cathode material for high-performance Na-ion batteries. *ACS Applied Materials & Interfaces* **2018**, *10*, 36851-36859.
- [41] Zhao, Y.; Yang, L.; Chen, S.; Wang, X.; Ma, Y.; Wu, Q.; Jiang, Y.; Qian, W.; Hu, Z. Can boron and nitrogen co-doping improve oxygen reduction reaction activity of carbon nanotubes? *Journal of the American Chemical Society* **2013**, *135*, 1201-1204.
- [42] Jo, G.; Shanmugam, S. Single-step synthetic approach for boron-doped carbons as a non-precious catalyst for oxygen reduction in alkaline medium. *Electrochemistry communications* **2012**, *25*, 101-104.

- [43] Ozaki, J.-i.; Kimura, N.; Anahara, T.; Oya, A. Preparation and oxygen reduction activity of BN-doped carbons. *Carbon* **2007**, *45*, 1847-1853.
- [44] Kwon, T.; Nishihara, H.; Itoi, H.; Yang, Q.-H.; Kyotani, T. Enhancement mechanism of electrochemical capacitance in nitrogen-/boron-doped carbons with uniform straight nanochannels. *Langmuir* **2009**, *25*, 11961-11968.
- [45] Rahman, M. M.; Sultana, I.; Mateti, S.; Liu, J.; Sharma, N.; Chen, Y. Maricite NaFePO₄/C/graphene: a novel hybrid cathode for sodium-ion batteries. *Journal of Materials Chemistry A* **2017**, *5*, 16616-16621.
- [46] Langrock, A.; Xu, Y.; Liu, Y.; Ehrman, S.; Manivannan, A.; Wang, C. Carbon coated hollow Na₂FePO₄F spheres for Na-ion battery cathodes. *Journal of Power Sources* **2013**, *223*, 62-67.
- [47] Guo, Z.; Yao, X.; Tian, H.; Cai, Y.; Su, Z. Effect of Zn-doping on the electrochemical performance of NaFePO₄/C cathode material for lithium ion battery. *International Journal of Electrochemical Science* **2021**, *16*, 210758.
- [48] Zhang, X.; Du, K.; Hu, G.; Peng, Z.; Cao, Y. Improved sodium storage in Na₂FePO₄F via N-Doped carbon coating. *Industrial & Engineering Chemistry Research* **2025**, *64*, 20671-20678.
- [49] Lu, X.; Liu, X.; Li, Y.; Wang, C.; Zhang, P.; Shi, P.; Xu, S.; Lyu, Y.; Zhu, C. Easy approach of highly electrochemical-active maricite NaFePO₄ cathode for low cost and high rate sodium-ion batteries. *Applied Physics Letters* **2023**, *123*.
- [50] Ko, J. S.; Doan-Nguyen, V. V.; Kim, H.-S.; Petrissans, X.; DeBlock, R. H.; Choi, C. S.; Long, J. W.; Dunn, B. S. High-rate capability of Na₂FePO₄F nanoparticles

by enhancing surface carbon functionality for Na-ion batteries. *Journal of Materials Chemistry A* **2017**, *5*, 18707-18715.

- [51]Jiang, S.; Wang, Y.; Ge, H.; Yu, B.; Wang, T.; Wang, T.; Wang, H.; Qu, X.; Zuo, H.; Zhao, Z. Trace Cu doping enabled high rate and long cycle life sodium iron phosphate cathode for sodium-ion batteries. *ACS nano* **2025**, *19*, 1499-1508.
- [52]Pi, Y.; Gan, Z.; Yan, M.; Pei, C.; Yu, H.; Ge, Y.; An, Q.; Mai, L. Insight into pre-sodiation in $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}@$ hard carbon full cells for promoting the development of sodium-ion battery. *Chemical Engineering Journal* **2021**, *413*, 127565.
- [53]Chen, J.; Quattrocchi, E.; Ciucci, F.; Chen, Y. Charging processes in lithium-oxygen batteries unraveled through the lens of the distribution of relaxation times. *Chem* **2023**, *9*, 2267-2281.
- [54]Zhang, L.-L.; Chen, Z.-Y.; Fu, X.-Y.; Yan, B.; Tao, H.-C.; Yang, X.-L. Effect of Zn-substitution induced structural regulation on sodium storage performance of Fe-based Prussian blue. *Chemical Engineering Journal* **2022**, *433*, 133739.
- [55]Zhang, L. L.; Wei, C.; Fu, X. Y.; Chen, Z. Y.; Yan, B.; Sun, P. P.; Chang, K. J.; Yang, X. L. Ternary Ni - based Prussian blue analogue with superior sodium storage performance induced by synergistic effect of Co and Fe. *Carbon Energy* **2021**, *3*, 827-839.
- [56]Ma, X.; Xia, J.; Wu, X.; Pan, Z.; Shen, P. K. Remarkable enhancement in the electrochemical activity of maricite NaFePO_4 on high-surface-area carbon cloth for sodium-ion batteries. *Carbon* **2019**, *146*, 78-87.

- [57] Han, L.; Liao, S.; Zhang, S.; Chen, K.; Chen, X.; Li, M.; Li, Q.; Ai, X.; Cao, Y.; Fang, Y. Unlocking electrochemical potential: amorphous NaFePO₄ as a high-capacity and cycle-stable cathode material for advanced sodium-ion batteries. *Science China Materials* **2025**, 68, 1109-1116.
- [58] Wang, H.; An, J.; Zhao, W.; Yu, B.; Li, Y.; Hu, J.; Jiang, S.; Gu, Q.; Zhu, J.; Zhu, H. Constructing heterotransition metal ligand field clusters with a compact spatial structure for maintaining unimpeded sodium-ion migration. *ACS nano* **2025**, 19, 34966-34980.

Electronic Supplementary Material

Interfacial engineering of $\text{NaFePO}_4/\text{Na}_2\text{FePO}_4\text{F}$ heterostructure cathode with enhanced kinetics for high-performance sodium-ion batteries

Biao-Yang Li¹, Lu-Lu Zhang^{1,*}, Ze-Rong Deng¹, Yu-Jie Su², Xu-Heng Liu², Da-ping Qiu¹, Hua-Bin Sun², Bo Yan², Xue-Lin Yang^{1,2,*}

¹Hubei Provincial Key Laboratory for Operation and Control of Cascaded Hydropower Station, College of Electrical Engineering & New Energy, China Three Gorges University, Yichang 443002, Hubei, China

²College of Materials and Chemical Engineering, China Three Gorges University, Yichang 443002, Hubei, China

✉ Address correspondence to Lu-Lu Zhang, luluzhang@ctgu.edu.cn; Xue-Lin Yang, xlyang@ctgu.edu.cn

Supporting information to <https://doi.org/10.26599/NR.2026.94908999>

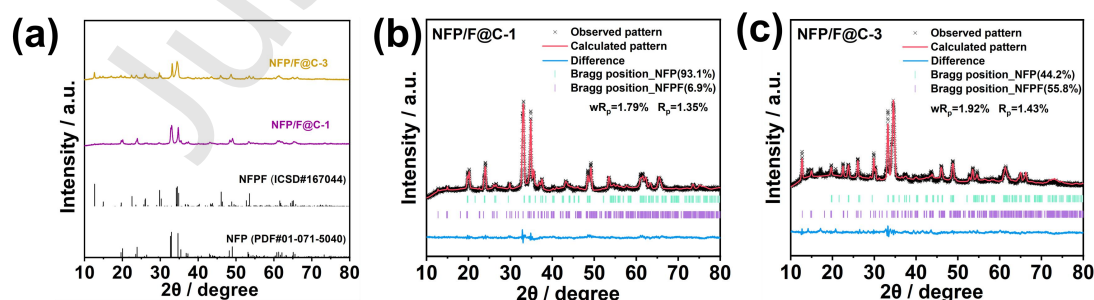


Fig. S1. (a) XRD patterns of samples, and (b, c) Rietveld refinement results of the NFP/F@C-1 and NFP/F@C-3.

Table S1. Carbon content and electronic conductivity of three samples.

Sample	Carbon content (%)	Electronic conductivity (S cm ⁻¹)
NFP@C	4.61	1.61×10 ⁻⁵
NFPF@C	4.43	2.98×10 ⁻⁶
NFP/F@C	4.28	3.26×10 ⁻⁵

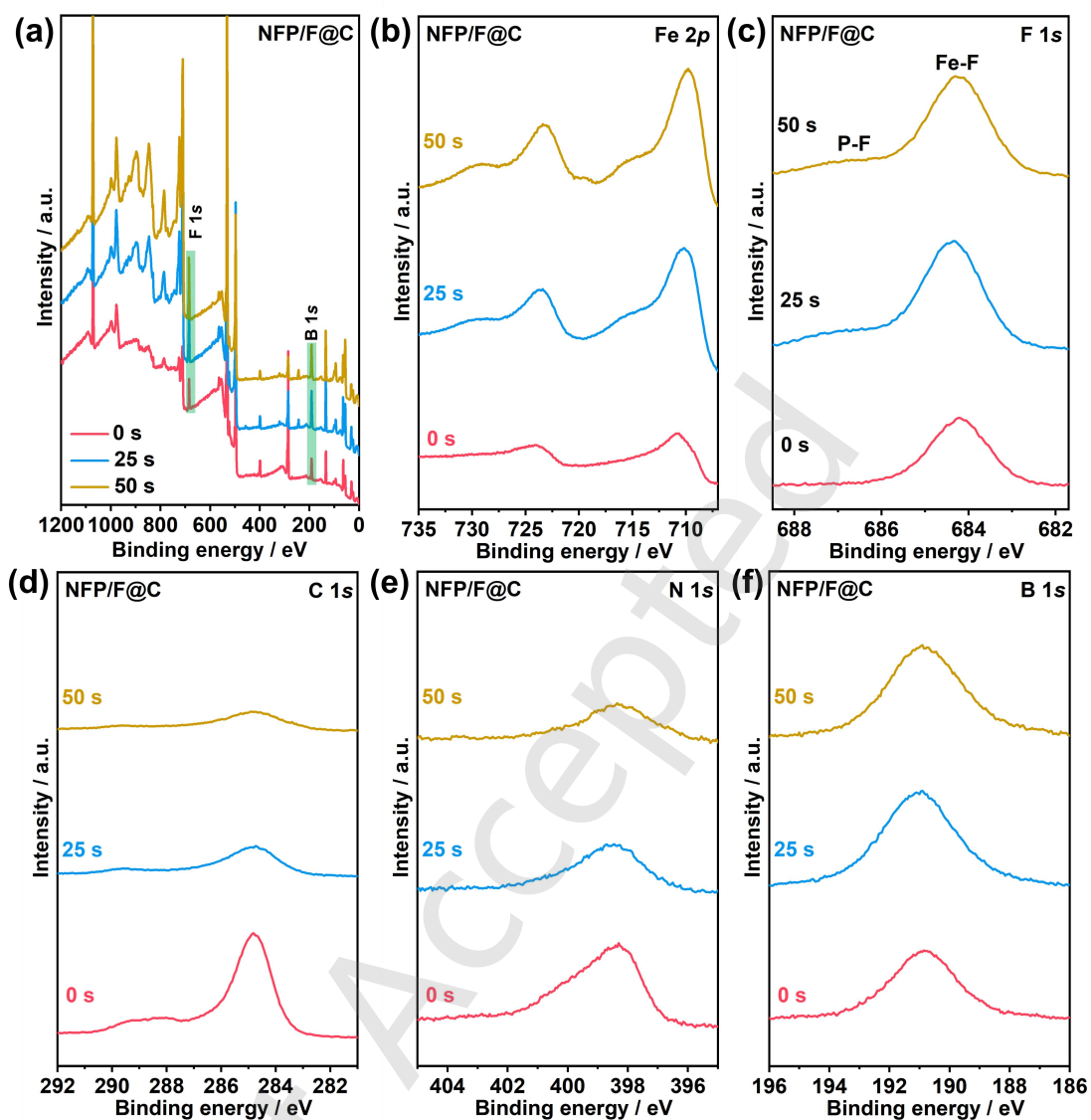


Fig. S2. (a) XPS survey spectra, and (b-f) high-resolution Fe 2p, F 1s, C 1s, N 1s and B 1s spectra of NFP/F@C after different sputtering time.

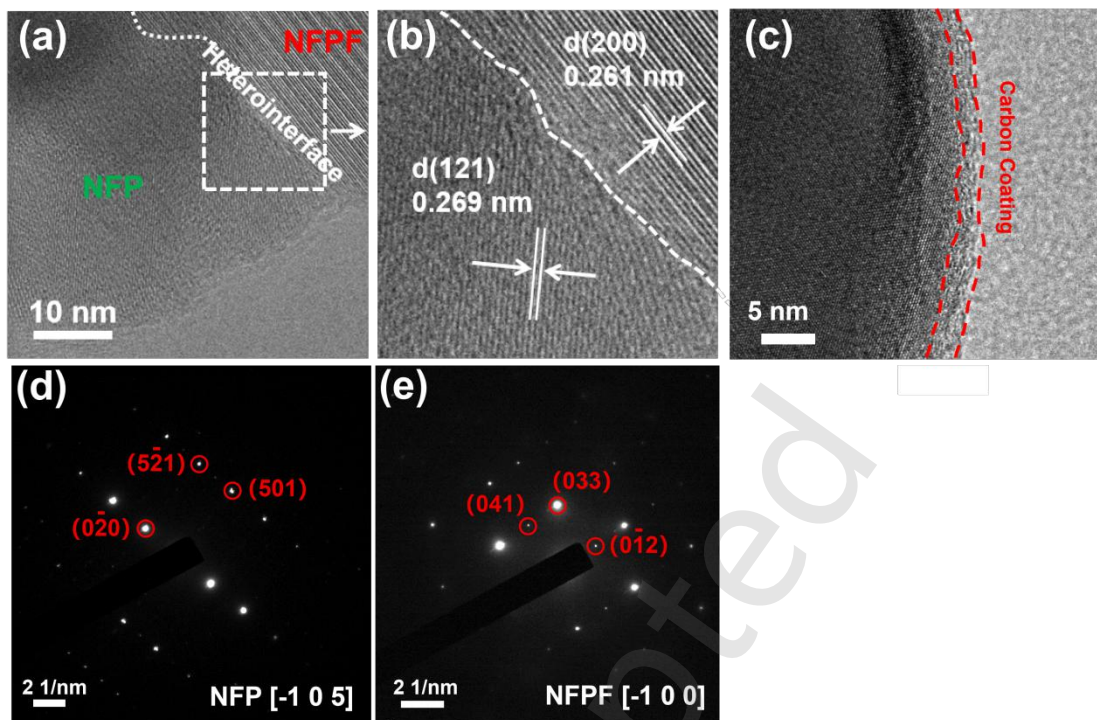


Fig. S3. (a) HRTEM image of NFP/F@C, (b) corresponding magnified image of the area indicated in (a), (c) HRTEM image of NFP/F@C, and (d-e) SAED patterns of NFP/F@C.

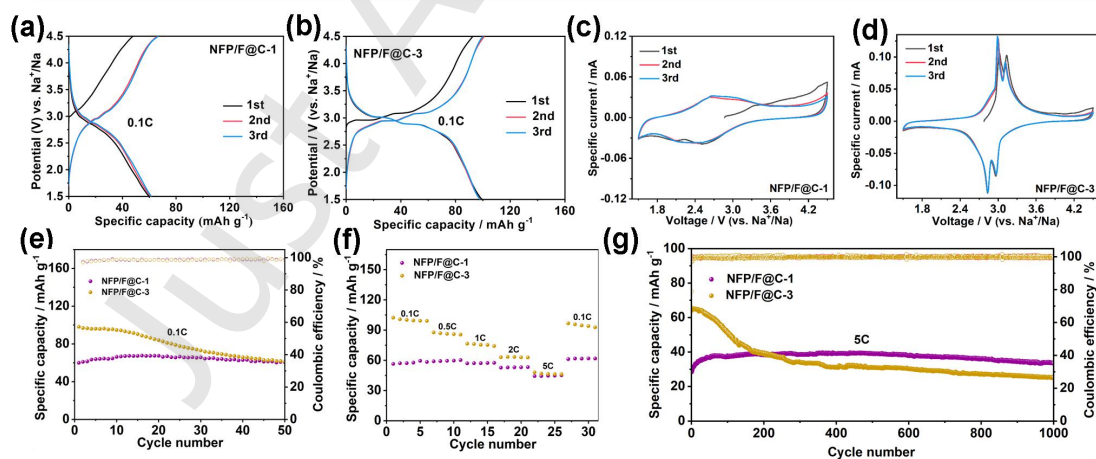


Fig. S4. Electrochemical performance of NFP/F@C-1 and NFP/F@C-3: (a, b) Charge/discharge profiles at 0.1C, (c, d) CV curves recorded at a scan rate of 0.1 mV s⁻¹, (e) cycling performance at 0.1C, (f) rate performance, (g) long-term cycling performance at a high rate of 5C.

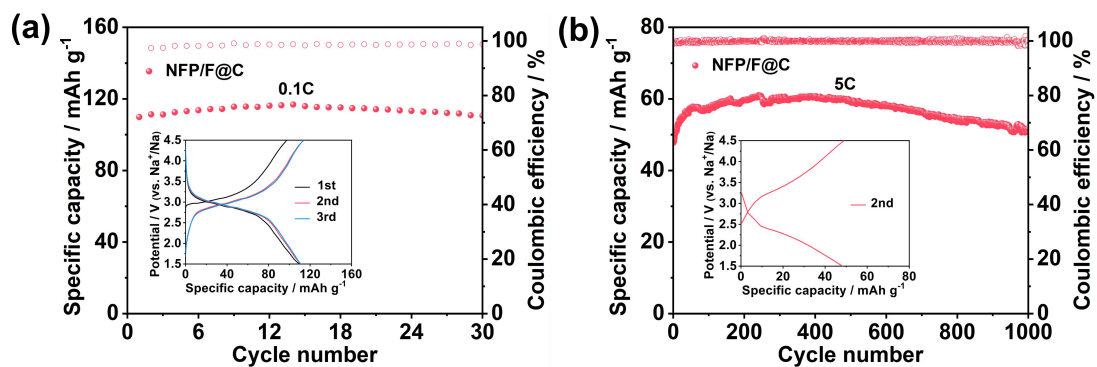


Fig. S5 (a) Cycling performance at 0.1C of NFP/F@C, (b) long-term cycling performance at 5C of NFP/F@C. The insets are the corresponding charge/discharge curves.

Table S2 The median discharge voltage during the first cycle at 0.1 C.

Sample	Median discharge voltage (V)
NFP@C	2.43
NFPF@C	2.87
NFP/F@C-1	2.62
NFP/F@C	2.80
NFP/F@C-3	2.88

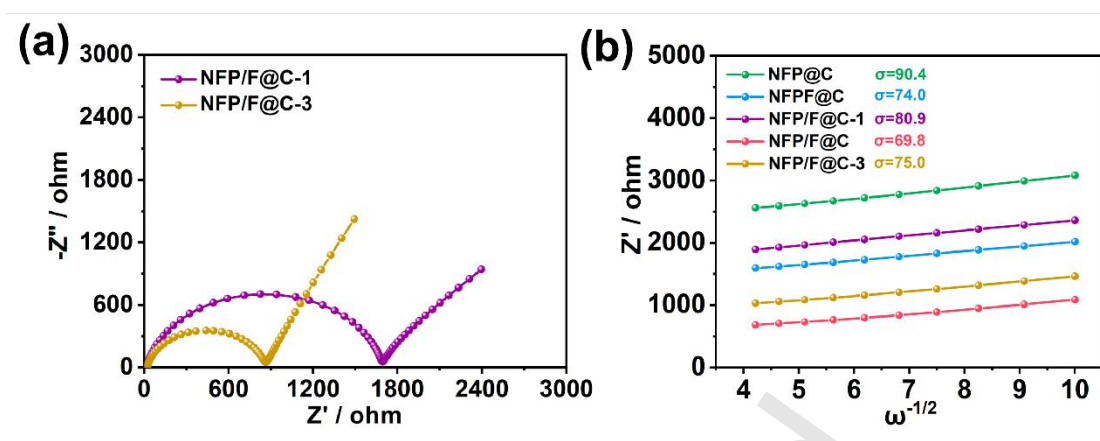


Fig. S6. (a) Nyquist plots of the NFP/F@C-1 and NFP/F@C-3, (b) relationship lines between Z' and $\omega^{-1/2}$ in the low-frequency region.

Table S3 Charge-transfer resistance (R_{ct}) and Na^+ diffusion coefficient (D_{Na^+}) obtained from EIS analysis for the five samples.

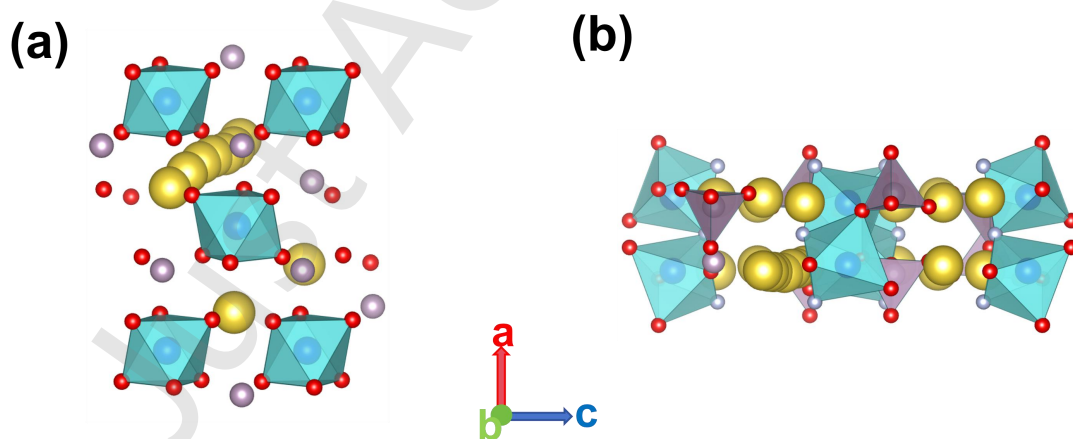
Sample	R_{ct} (Ω)	D_{Na^+} ($\text{cm}^2 \text{ s}^{-1}$)
NFP@C	2401.8	3.08×10^{-12}
NFPF@C	1454.7	4.60×10^{-12}
NFP/F@C-1	741.6	3.85×10^{-12}
NFP/F@C	527.3	5.17×10^{-12}
NFP/F@C-3	1680.4	4.47×10^{-12}

Table S4 Comparison of energy density of the NFP/F@C composite with representative iron-based polyanionic cathode materials at 0.1C ^[1-8].

Sample	Potential (V)	Specific capacity (mAh g ⁻¹)	Energy density (Wh kg ⁻¹)	Ref.
NaFePO ₄ /C/graphene	2.10	142.0	298.2	1
NFP-1.8	2.40	101.4	243.4	2
C/Na ₂ FePO ₄ F	2.95	89.0	262.6	3
NaFe _{0.97} Zn _{0.03} PO ₄ /C	2.38	113.5	270.1	4
NFPF-PAN	2.86	98.1	284.5	5
NFP-15	2.25	142.0	319.5	6
NaFePO ₄ /C	2.40	134.0	321.6	7
NFPF-rGO	2.88	108.0	319	8
NFP/F@C	2.80	115.6	323.7	This work

Table S5 Comparison of CHC||NFP/F@C with other NFP-based full cells [2, 7, 9, 10].

Sample	Average voltage (V)	Specific capacity (mAh g ⁻¹)	Energy density (Wh kg ⁻¹)	Capacity retention (%)	Voltage range (V)	Coulombic eff. (%)	Ref.
NFP-1.8	1.99	62.3 (0.5C)	124.0	90.6% (0.5C/250)	0.6-3.6	98.0	2
NaFePO ₄ /C	2.58	112.8 (0.5C)	291.0	84.5% (5C/500)	0.5-4.5	99.5	7
NFP@C-eCC	1.96	129 (20 mA g ⁻¹)	252.8	98.0% (50 mA g ⁻¹ /100)	0.5-3.5	85.5	9
NFMP-0.05	2.50	72.0 (0.5C)	180.0	86.5% (0.1C/100)	1.5-4.2	93.4	10
NFP/F@C	2.80	77.6 (0.5C)	215.3	80.6% (1C/200)	2.0-4.5	96.7	This work

**Fig. S7.** Optimized migration paths of Na⁺ in species: (a) NFP, and (b) NFPP .

References:

- [1] Rahman, M. M.; Sultana, I.; Mateti, S.; Liu, J.; Sharma, N.; Chen, Y. Maricite $\text{NaFePO}_4/\text{C}/\text{graphene}$: a novel hybrid cathode for sodium-ion batteries. *Journal of Materials Chemistry A* **2017**, 5, 16616-16621.
- [2] Zhao, L.; Yu, L.; Wan, G.; Ahmad, N.; Ma, X.; Tao, Z.; Zhang, G. Co - manipulation of ultrafine nanostructure and uniform carbon layer activates maricite - structured NaFePO_4 as a high - performance cathode for sodium - ion batteries. *Small Science* **2023**, 3.
- [3] Langrock, A.; Xu, Y.; Liu, Y.; Ehrman, S.; Manivannan, A.; Wang, C. Carbon coated hollow $\text{Na}_2\text{FePO}_4\text{F}$ spheres for Na-ion battery cathodes. *Journal of Power Sources* **2013**, 223, 62-67.
- [4] Guo, Z.; Yao, X.; Tian, H.; Cai, Y.; Su, Z. Effect of Zn-doping on the electrochemical performance of NaFePO_4/C cathode material for lithium ion battery. *International Journal of Electrochemical Science* **2021**, 16.
- [5] Zhang, X.; Du, K.; Hu, G.; Peng, Z.; Cao, Y. Improved sodium storage in $\text{Na}_2\text{FePO}_4\text{F}$ via N-Doped carbon coating. *Industrial & Engineering Chemistry Research* **2025**, 64, 20671-20678.
- [6] Xiong, F.; An, Q.; Xia, L.; Zhao, Y.; Mai, L.; Tao, H.; Yue, Y. Revealing the atomistic origin of the disorder-enhanced Na-storage performance in NaFePO_4 battery cathode. *Nano Energy* **2019**, 57, 608-615.
- [7] Lu, X.; Liu, X.; Li, Y.; Wang, C.; Zhang, P.; Shi, P.; Xu, S.; Lyu, Y.; Zhu, C. Easy approach of highly electrochemical-active maricite NaFePO_4 cathode for

low cost and high rate sodium-ion batteries. *Applied Physics Letters* **2023**, *123*.

- [8] Ko, J. S.; Doan-Nguyen, Vicky V. T.; Kim, H.-S.; Petrissans, X.; DeBlock, R. H.; Choi, C. S.; Long, J. W.; Dunn, B. S. High-rate capability of Na₂FePO₄F nanoparticles by enhancing surface carbon functionality for Na-ion batteries. *Journal of Materials Chemistry A* **2017**, *5*, 18707-18715.
- [9] Ma, X.; Xia, J.; Wu, X.; Pan, Z.; Shen, P. K. Remarkable enhancement in the electrochemical activity of maricite NaFePO₄ on high-surface-area carbon cloth for sodium-ion batteries. *Carbon* **2019**, *146*, 78-87.
- [10] Wang, H.; An, J.; Zhao, W.; Yu, B.; Li, Y.; Hu, J.; Jiang, S.; Gu, Q.; Zhu, J.; Zhu, H.; Sun, J.; Zhou, L.; Peng, S.; Wu, Y.; Xia, H.; Chen, M. Constructing heterotransition metal ligand field clusters with a compact spatial structure for maintaining unimpeded sodium-ion migration. *ACS Nano* **2025**, *19*, 34966-34980.