Supplementary Information for

Revealing the Effect of Conductive Carbon Materials on the Sodium Storage Performance of Sodium Iron Sulfate

Wenqing Zhu,[+a, b] Zhiqiang Hao,[+b, c] Xiaoyan Shi,[b] Xunzhu Zhou,[b, c] Zhuo Yang,[b, c] Lingling Zhang,[b] Zongcheng Miao,[* a] Lin Li,[*b, c] and Shu-Lei Chou[* b, c]

a. School of Chemical and Environmental Engineering, Anhui Polytechnic University, Wuhu, Anhui 241000, China. E-mail: miaozongcheng@ahpu.edu.cn

b. Institute for Carbon Neutralization, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325035, China. E-mail: linli@wzu.edu.cn; chou@wzu.edu.cn

c. Wenzhou Key Laboratory of Sodium-Ion Batteries, Wenzhou University Technology Innovation Institute for Carbon Neutralization, Wenzhou, Zhejiang 325035, China.

+ These authors contributed equally to this work.

Experimental section

Synthesis of $Na_2Fe_2(SO_4)_3$@C

$FeSO_4 \cdot H_2O$ (Aladdin, 99.0%) was first annealed at 280 °C for 12 hours in an N_2 atmosphere to obtain anhydrous $FeSO_4$. The $Na_2Fe_2(SO_4)_3$@C (NFS@C) composites were synthesized through a low-temperature solid-state reaction method. Initially, a mixture was prepared by anhydrous Na_2SO_4 (Aladdin, 99.0%) and anhydrous $FeSO_4$ in a 1:2 molar ratio, along with different conductive carbons in a 7:1 mass ratio, such as Ketjen Black (Lion Corporation, EC-600JD), super p (Imerys, SUPER P-Li), acetylene black (Guangdong Canrd New Energy Technology Co., Ltd. Kappa 100), and conductive graphite KS6 (Imerys, KS-6). Finally, the mixture was homogeneously blended in a planetary ball mill under argon atmosphere at 800 rpm for 6 hours. Next, the precursor was transferred to a quartz tube filled with N_2 atmosphere and subjected to a sintering process at 350 ^{o}C for 24 h. Finally, these particles were ground in a mortar and pestle for 10 min to obtain the final sample NFS@C. The samples were labeled as NFS@KB, NFS@SP, NFS@AB, and NFS@G, according to the type of conductive carbon used.

Material characterization

The crystal structure of the NFS@C composites was examined using an Aeris Research Benchtop X-Ray Diffractometer from Malvern Panalytical equipped with a CuKα radiation source. The morphologies of the composites were characterized by field transmission scanning electron microscopy (FE-SEM, EVO 10) and transmission

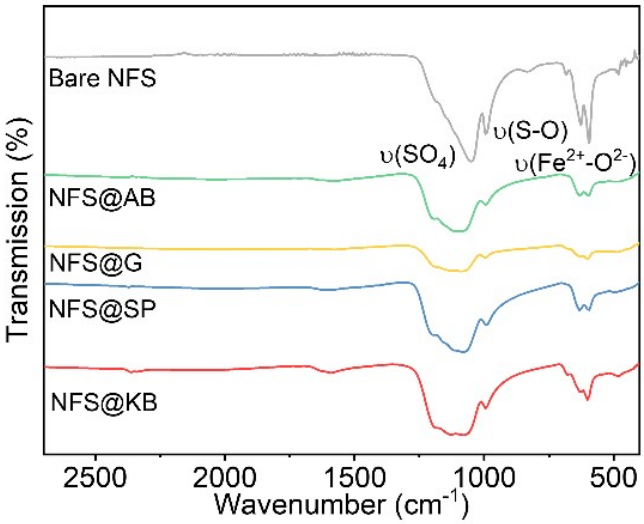
electron microscope (TEM, JEM-2100F). The specific surface area of $Na_2Fe_2(SO_4)_3$@C composite material was investigated using a nitrogen adsorption and desorption analysis with a surface area and pore size analyzer (V-Sorb 2802TP). Raman spectra (HORIBA XploRA PLUS) were collected in the range of 500-2500 cm^{-1} to characterize the carbon coating. The vibrational states of existing functional groups were examined via FT-IR (spectral resolution of 4 cm^{-1} on a SHIMADZU IRAffinity-1S). Thermogravimetric (TG) analysis was conducted using an Integrated Thermal Analyzer (ZCT-A), at a heating rate of 5 ^{o}C min^{-1}, from room temperature to 600 ^{o}C. X-ray photoelectron spectroscopy (XPS, PHI-5000 VPIII) was utilized to investigate the chemical states of Fe and C elements.

Electrochemical characterization

The electrochemical properties of the NFS@C composites were performed in CR2032 coin half cells. The material powder was mixed with Ketjen Black and polyvinylidene fluoride (PVDF) binder (80:10:10 by weight) in N-methyl-2-pyrrolidone (NMP), and then the slurry was coated on an Al foil uniformly. The foil with active material was dried at 80 °C for 6 h in vacuum with a loading about 1.5-2 mg cm^{-2} and cut into circle electrode (diameter 10 mm). Sodium (Na) metal served as both the counter and reference electrode, while Glass fiber membranes (Whatman, GF/D) were utilized as separators. The electrolyte adopted was 1 M $NaClO_4$ in a mixture of EC/DEC (1:1 in volume) with an additional 2 wt% FEC. Concerning the fabrication of graphite electrode for the assembly of full cells, an 80% mixture of

Japanese carbon was combined with 10% super p and 10% Water-based adhesive (SA2) binder, subsequently applied as a coating on Al foil, and utilized as the anode in the coin cell architecture. All the coin cells were assembled inside a glove box filled with Ar gas, wherein the levels of O_2 and H_2O were meticulously regulated to remain below 0.1 ppm. Galvanostatic charge/discharge tests were conducted on a Neware test system (Neware Technology Limited) under various current densities. The voltage window between 2 and 4.5 V was selected. In addition, Cyclic Voltammetry (CV) tests were conducted on the CHI660E electrochemistry workstation with scan speeds ranging from 0.1 to 0.5 mV s^{-1}.

1



2

3 **Figure S1**. FT-infrared spectra of NFS@C composite materials and bare NFS.

4

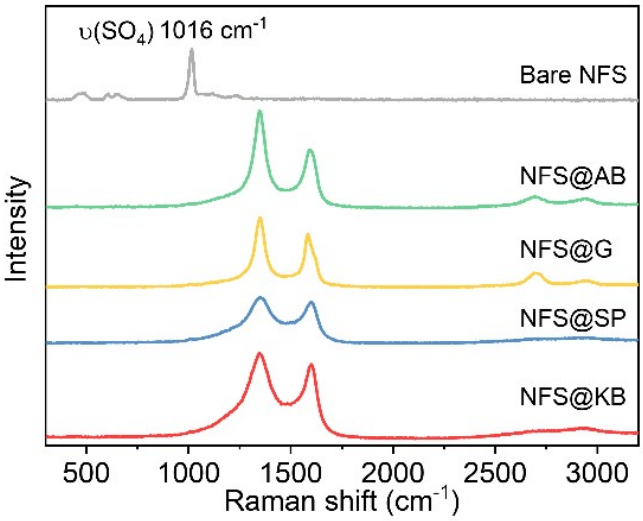


Figure S2. Raman spectrum of NFS@C composite materials and bare NFS.

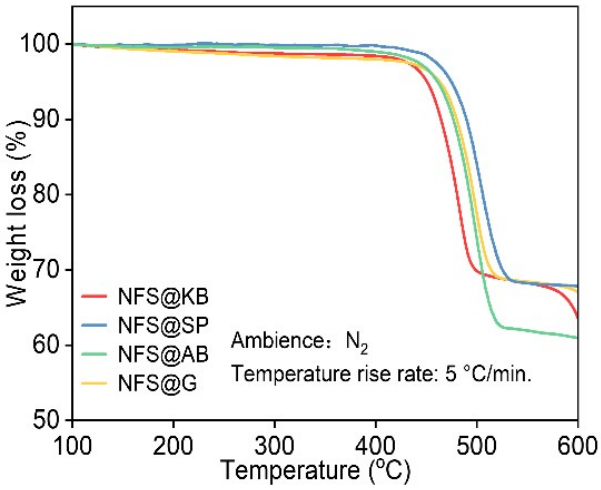


Figure S3. TG curve of NFS@C composite materials in N_2 atmosphere.

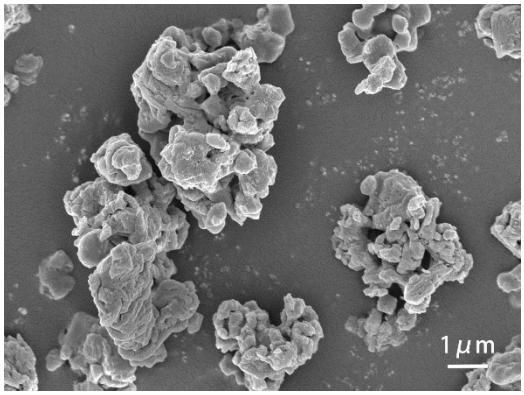


Figure S4. SEM image of bare NFS.

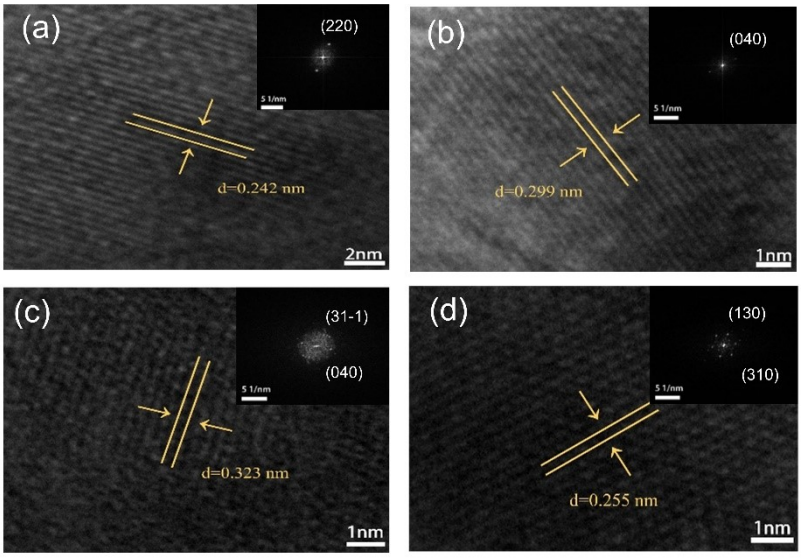


Figure S5. Enlarged lattice fringes of (a) NFS@KB, (b) NFS@SP, (c) NFS@AB, and (d) NFS@G, and the FFT image in the inset.

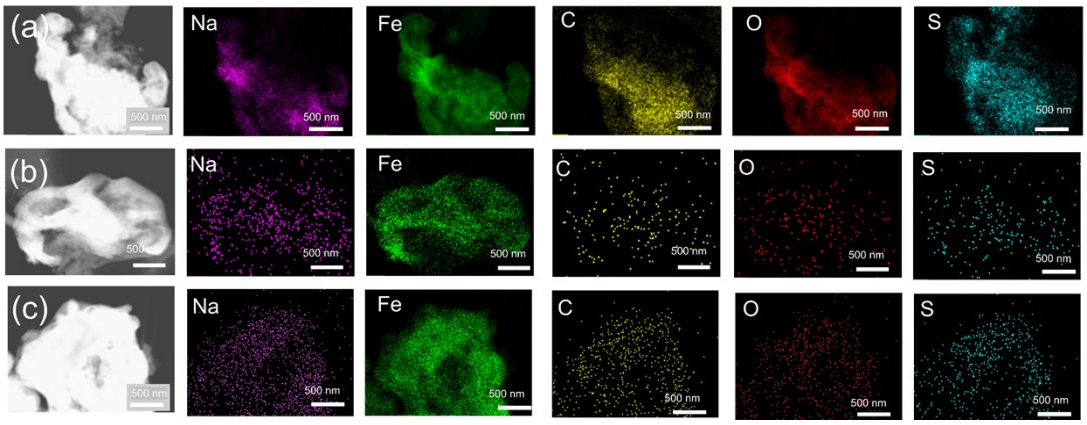


Figure S6. HAADF image and the corresponding Na, Fe, C, O, and S elemental mappings of (a) NFS@SP, (b) NFS@AB, and (c) NFS@G.

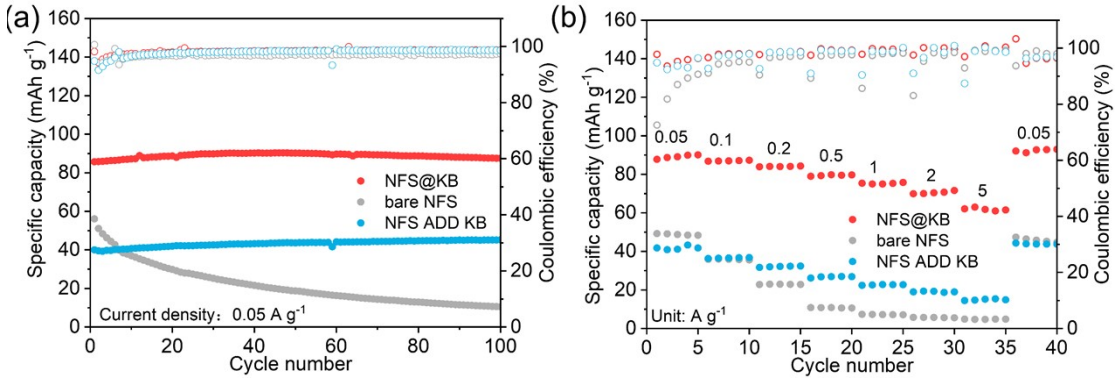


Figure S7. (a) Cycling performance at 0.05 A g^{-1} and (b) rate performance of NFS@KB, bare NFS and NFS ADD KB.

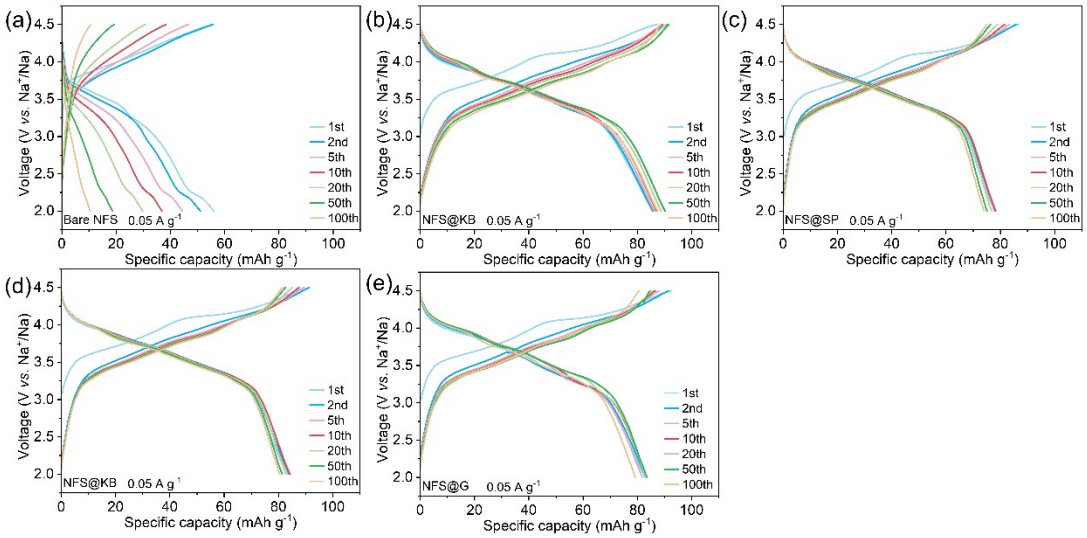


Figure S8. The select charge/discharge curves of (a) Bare NFS, (b) NFS@KB, (c) NFS@SP, (d) NFS@AB, and (e) NFS@G.

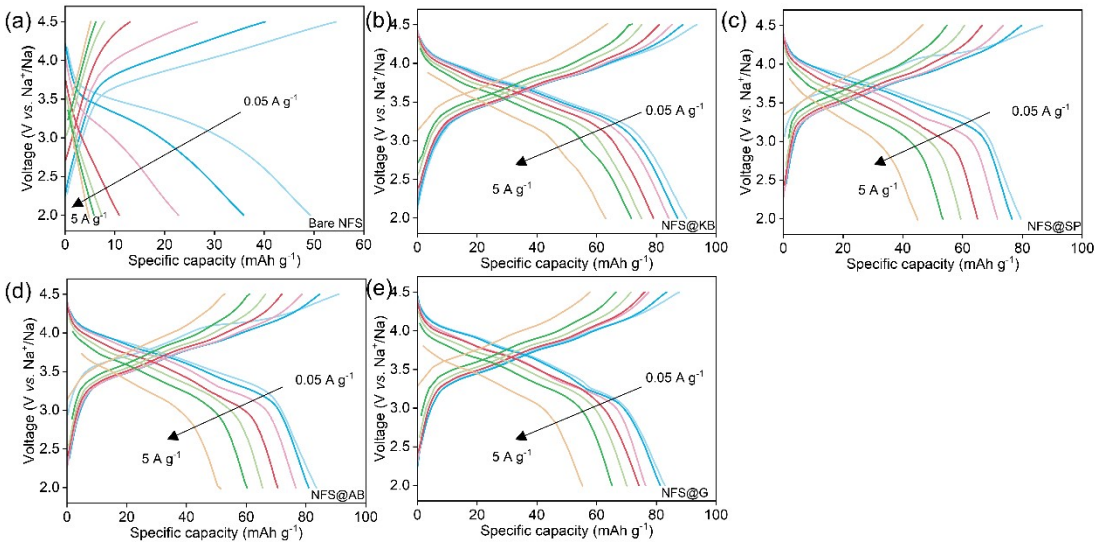


Figure S9. Charge/discharge curves of (a) bare NFS, (b) NFS@KB, (c) NFS@SP, (d) NFS@AB, and (e) NFS@G at different current densities.

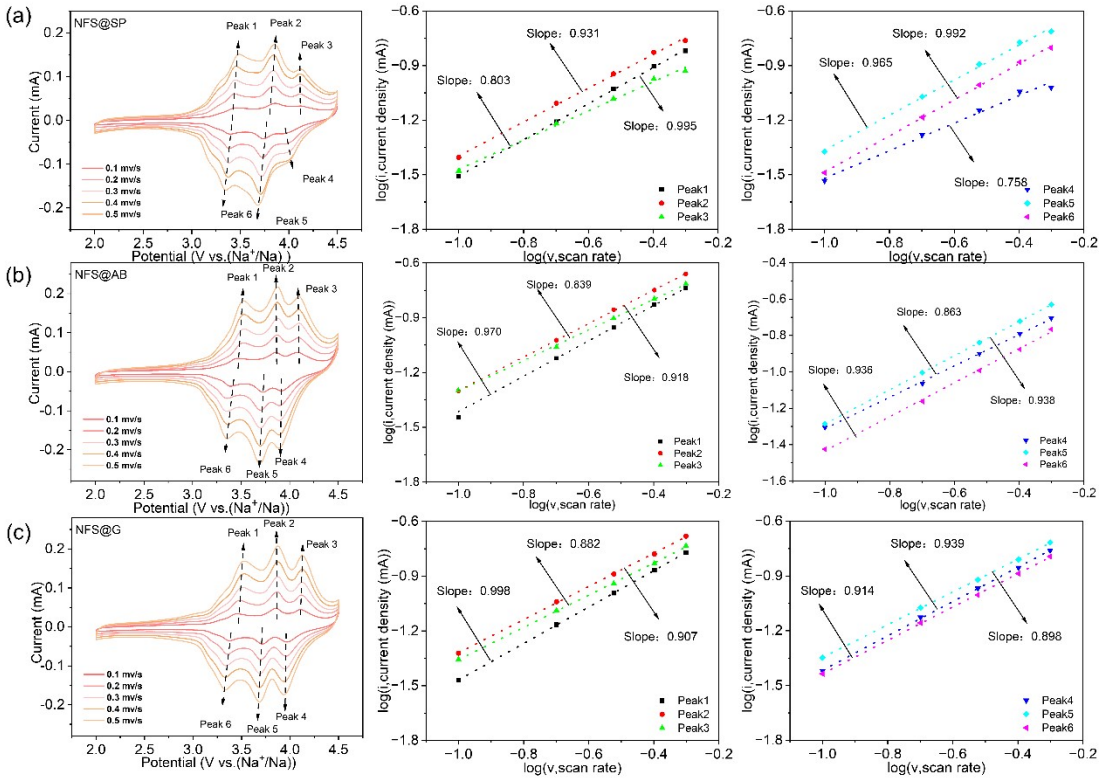


Figure S10. CV curve of NFS@C from 0.1 mV s^{-1} to 0.5 mV s^{-1}, The relevant b-values determination for the anodic and cathodic peaks of corresponding (a) NFS@SP, (b) NFS@AB and (c) NFS@G.

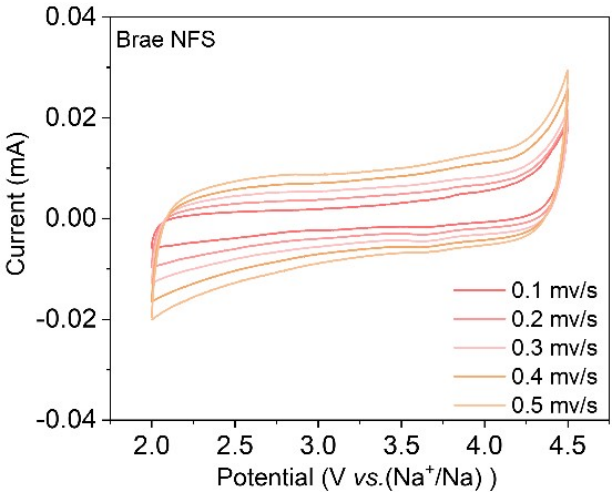


Figure S11. CV curve of bare NFS from 0.1 mV s^{-1} to 0.5 mV s^{-1}.

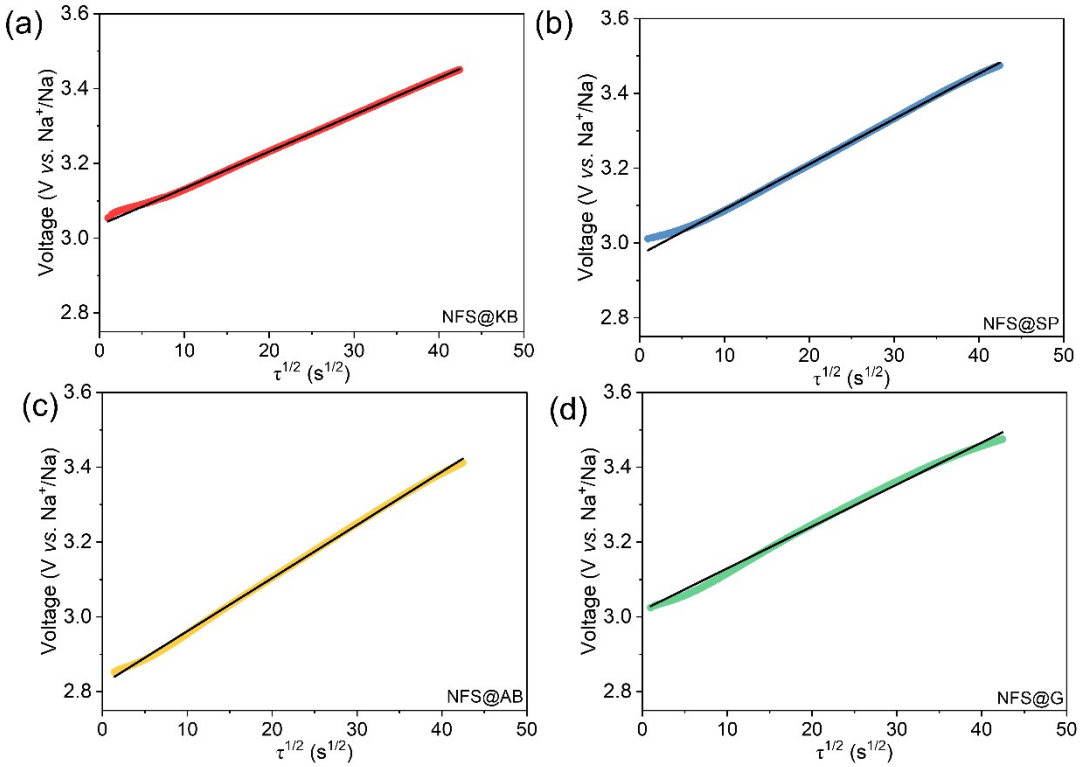


Figure S12. Linear relationship of voltage vs. $\sqrt{\tau}$ in GITT of (a) NFS@KB, (b) NFS@SP, (c) NFS@AB, and (d) NFS@G.

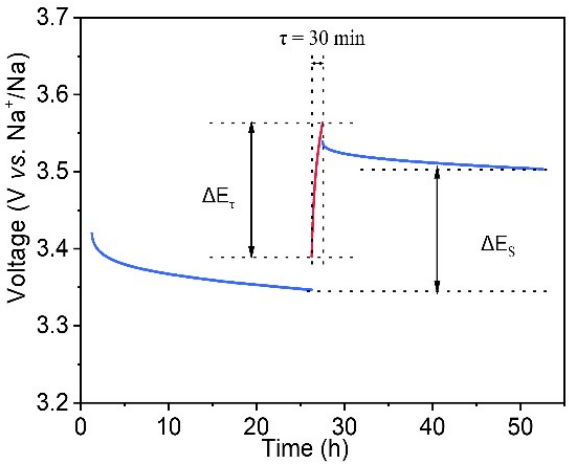


Figure S13. The time versus voltage curve for a single titration.

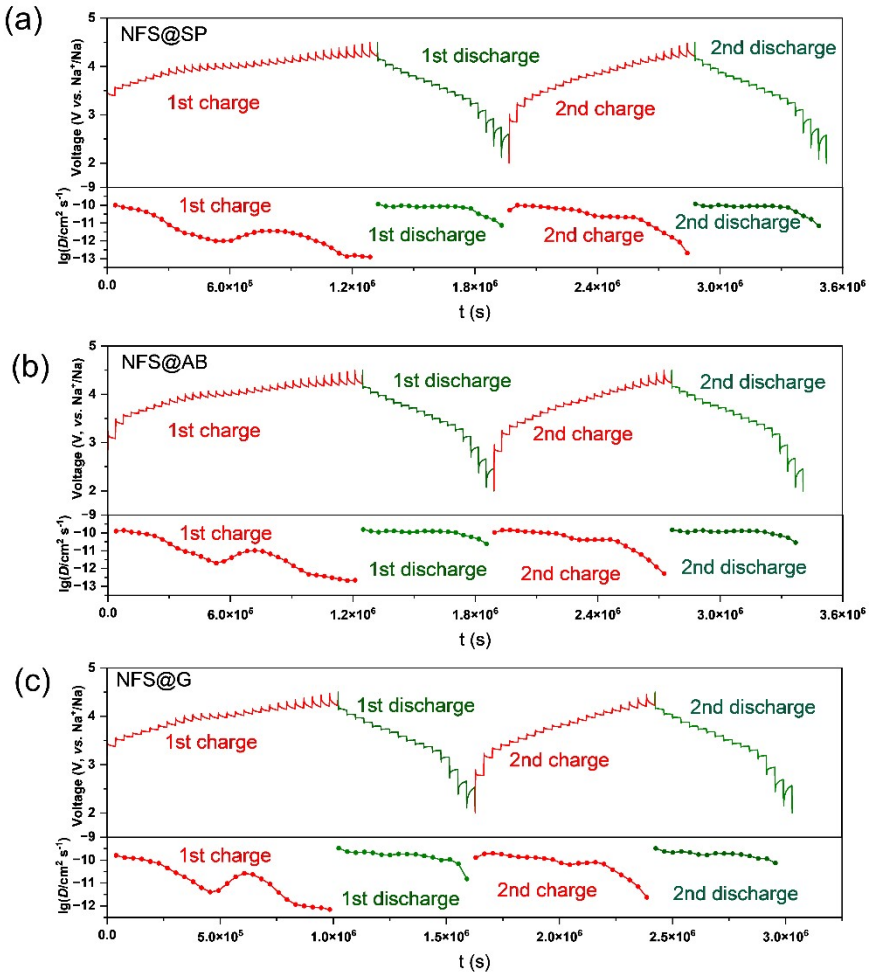


Figure S14. Galvanostatic intermittent titration technique (GITT) curves of (a) NFS@SP, (b) NFS@AB, and (c) NFS@G material for the charge and discharge process.

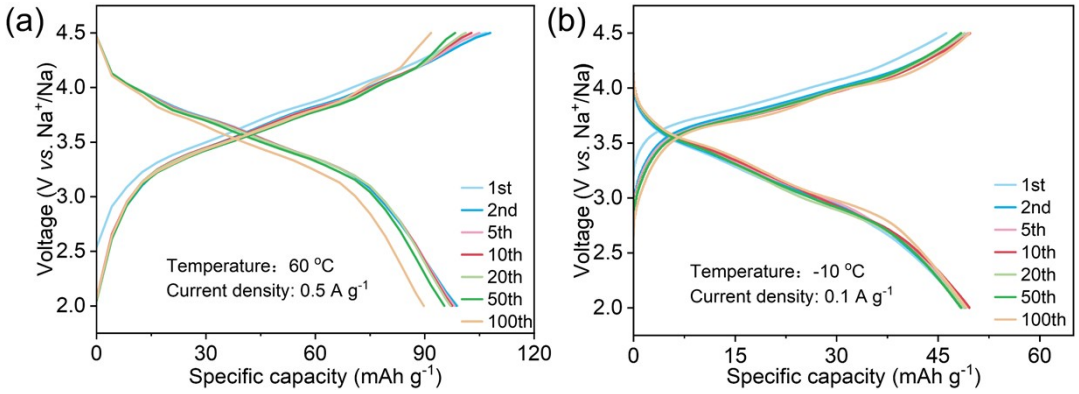


Figure S15. (a) The select charge/discharge curves for NFS@KB at 0.5 A g^{-1} at 60 °C, (b) the select charge/discharge curves for NFS@KB at -10 °C at 0.1 A g^{-1}.

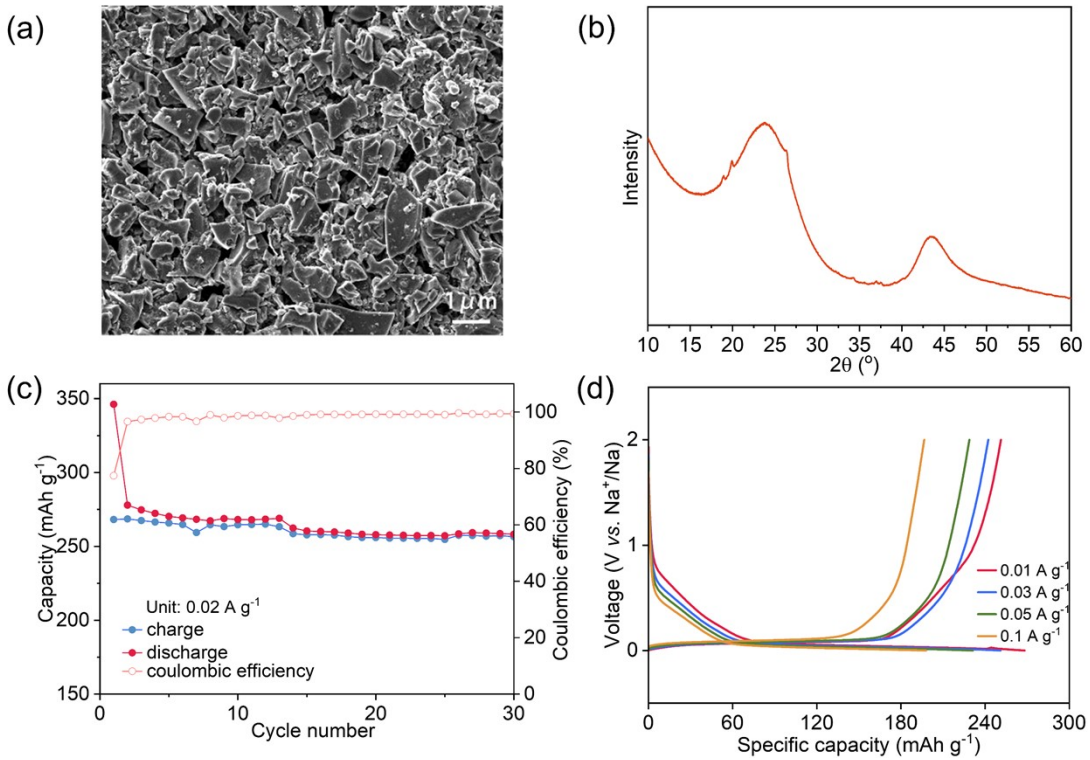


Figure S16. (a) SEM, (b) XRD, (c) cycling properties, and (d) rate performance of commercially available hard carbon.

Table S1. Mass loadings of polyanionic cathode materials in reported literatures.

Cathode materials	Active material loading	Reference
$Na_2FeP_2O_7$	1.5-3.5 mg cm^{-2}	1
$Na_4Fe_3(PO_4)_2(P_2O_7)$@C	~2.5 mg cm^{-2}	2
$Na_4Fe_3(PO_4)_2(P_2O_7)$@C@rGO	~2.5 mg cm^{-2}	2
$Na_2MnP_2O_7$	1.6±0.1 mg cm^{-2}	3
$Na_2Fe(SO_4)_2$@rGO/C	~1.5 mg cm^{-2}	4
$Na_2Fe_2(SO_4)_3$@C	~1.6 mg cm^{-2}	5
$Na_2Fe_2(SO_4)_3$@C@GO	~1.6 mg cm^{-2}	5
$Na_3V_2(PO_4)_3$	3.2-3.3 mg cm^{-2}	6
$Na_2Mn_2(SO_4)_3$	~2.2 mg cm^{-2}	7
$NaFePO_4$@C	~2.5 mg cm^{-2}	8
$Na_2Fe_2(SO_4)_3$@KB	1.5-2.0 mg cm^{-2}	This work

References

1. H. Kim, R. A. Shakoor, C. Park, S. Y. Lim, J.-S. Kim, Y. N. Jo, W. Cho, K. Miyasaka, R. Kahraman, Y. Jung and J. W. Choi, *Adv. Funct. Mater.*, 2013, **23**, 1147-1155.
2. J. Gao, Y. Tian, Y. Mei, L. Ni, H. Wang, H. Liu, W. Deng, G. Zou, H. Hou and X. Ji, *Chem. Eng. J.*, 2023, **458**, 141385.
3. H. Li, X. Chen, T. Jin, W. Bao, Z. Zhang and L. Jiao, *Energy Stor. Mater.*, 2018, **16,** 383-390.
4. G. Yao, X. X. Zhang, Y. L. Yan, J. Y. Zhang, K. M. Song, J. Shi, L. W. Mi, J. Y. Zheng, X. M. Feng and W. H. Chen , *J Energy chem.*, 2020, **50**, 387-394.
5. M. Chen, D. Cortie, Z. Hu, H. Jin, S. Wang, Q. Gu, W. Hua, E. Wang, W. Lai, L. Chen, S. -L. Chou, X. -L. Wang and S. -X. Dou, *Adv. Energy Mater.*, 2018, **8**, 1800944.
6. Y. Liu, X. Wu, A. Moeez, Z. Peng, Y. Xia, D. Zhao, J. Liu and W. Li, *Adv. Energy Mater.*, 2022, **13**, 2203283.
7. B. awaz and M. O. Ullah, *J. Mater. Sci.: Mater. Electron.*, 2021, **32**, 14509-14518.
8. Y. Liu, N. Zhang, F. Wang, X. Liu, L. Jiao and L.-Z. Fan, *Adv. Funct. Mater.*, 2018, **28**, 1801917.