

## **Supplementary Material**

### **Effect of partial cation replacement on anode performance of sodium-ion batteries**

Shijiang He<sup>1, ‡</sup>, Zidong Wang<sup>2, ‡</sup>, Wenbo Qiu<sup>1</sup>, Huaping Zhao<sup>2</sup>, and Yong Lei<sup>2, †</sup>

<sup>1</sup>Institute of Nanochemistry and Nanobiology, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China

<sup>2</sup>Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, Ilmenau, 98693, Germany

<sup>†</sup> Correspondence to: Y Lei, [yong.lei@tu-ilmenau.de](mailto:yong.lei@tu-ilmenau.de)

<sup>‡</sup> These authors contributed equally to this work and should be considered as co-first authors.

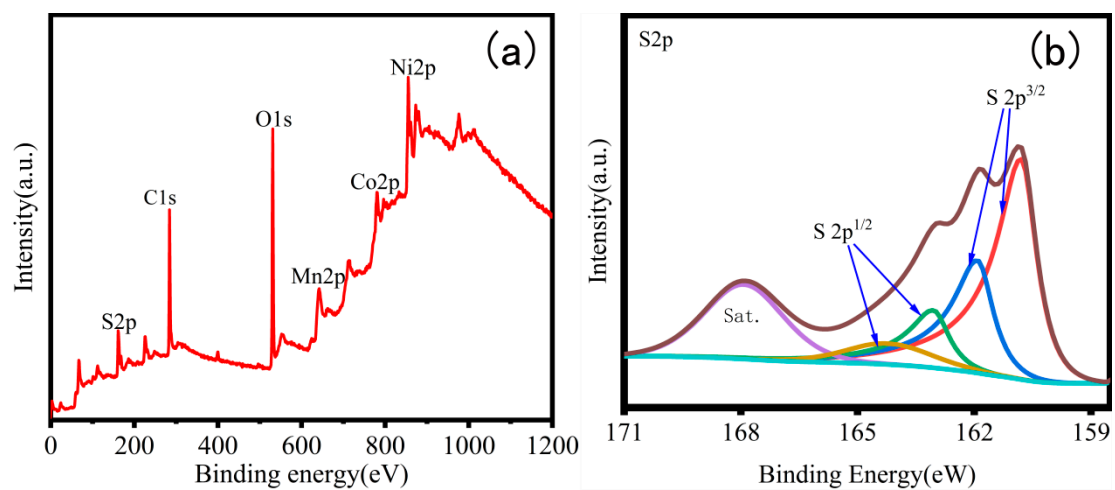
## **Instrumentation and Sample Analysis**

All materials were characterized by using scanning electron microscopy (SEM, Nova nano F7500, FEI, USA), Energy dispersive spectroscopy (EDS, OXFORD Xplore, OXFORD Instruments) was used to measure the elemental distribution of the material at an accelerating voltage of 15 kV. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA) transmission electron microscopy (TEM, JEOL, JEM-ARM200FTH) and X-ray diffraction (XRD, SmartLab, Rigaku, Japan). The TEM samples were prepared by drop-casting the composite from ethanol dispersions onto 200-mesh lacey carbon-coated copper grids and gold grids (Electron Microscope Sciences) drying at 60°C under vacuum conditions for 12 hours. X-ray diffractometer confirmed the crystal structure of the materials at a scanning speed of  $10^{\circ} \text{ min}^{-1}$  with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The chemical surface state and composition of the materials were characterized by X-ray photoelectron spectroscopy (XPS) with an Al K $\alpha$  exciting source ( $h\nu = 1486.6 \text{ eV}$ ) and corrected the C 1s peak at 284.8 eV before sample analysis.

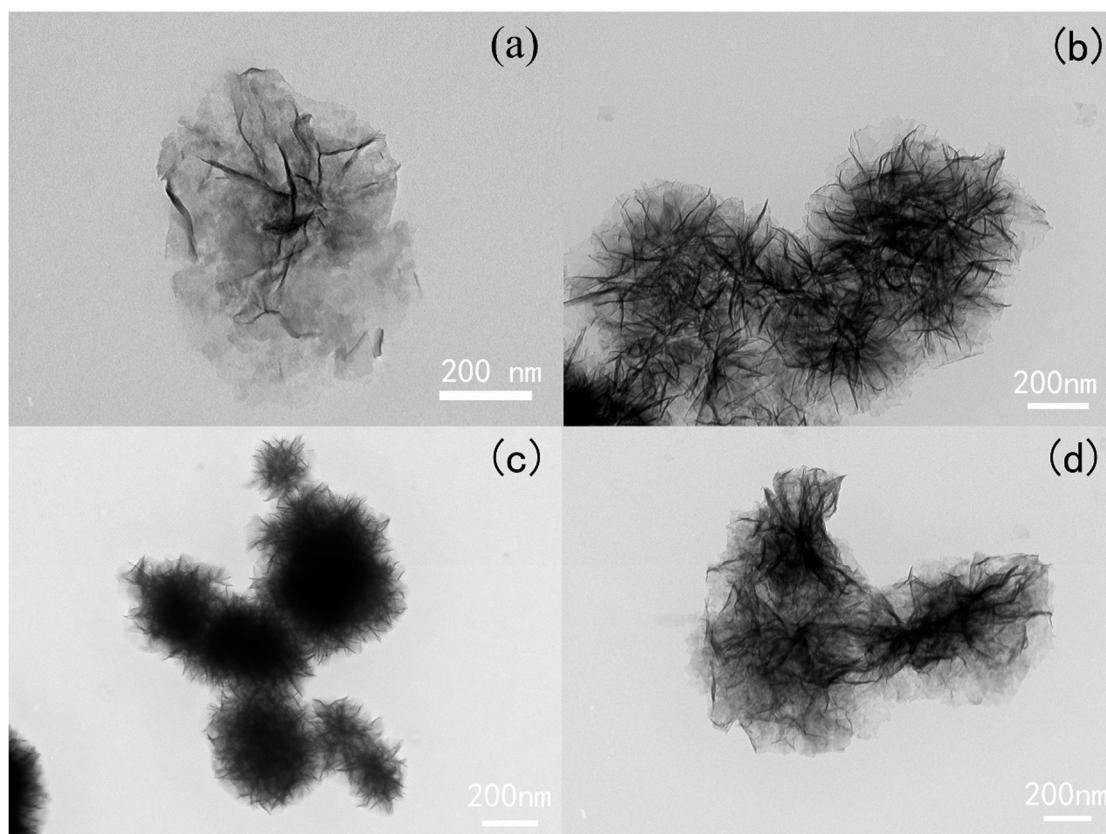
## **Electrochemical measurement**

Anodes were prepared using the coating method. The mixture was formulated by combining the active substance, Super P, with sodium carboxymethyl cellulose in a mass ratio of 7:2:1. The mixed slurry is applied to the copper foil and a vacuum drying is carried out at 80 °C for 12 hours. The dried, coated copper foil is then cut into circular discs 12 mm in diameter and the mass loading of the electrodes is determined using a microbalance with a resolution of 0.1  $\mu\text{g}$  (Sartorius SE2). The active mass load of these electrodes ranges from 1.0-2.0 mg. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were collected using a multi-channel electrochemical analyzer (VMP3). CV values were measured at different potential scanning rates in the range of 0.01 to 3 V. EIS was completed in the frequency range of 0.01 to 100 kHz. The specific capacity of the electrode is calculated by determining the ratio of NCMS-10 to the total load mass of copper foil. The coin-type half cell (CR2032) uses self-made Na metal foil as the counter electrode and is assembled in a glove box filled with argon gas.

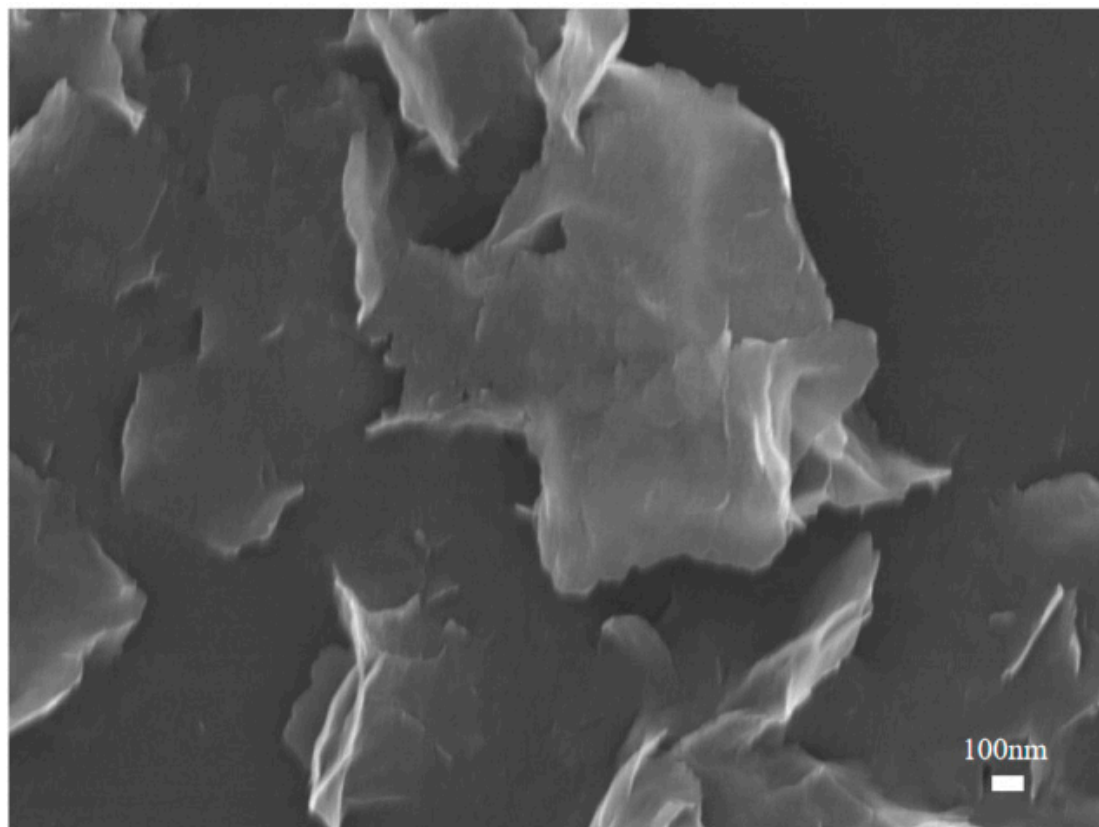
Add 1 M NaPF<sub>6</sub> electrolyte to ethylene glycol dimethyl ether (DME) to permeate the anode electrode, then add a glass fibre separator, and then add Na foil. Remove the crimped battery from the glove box and conduct electrochemical performance testing on the Maccor Series 4000 battery testing system with a voltage range of 0.01 V to 3.0 V.



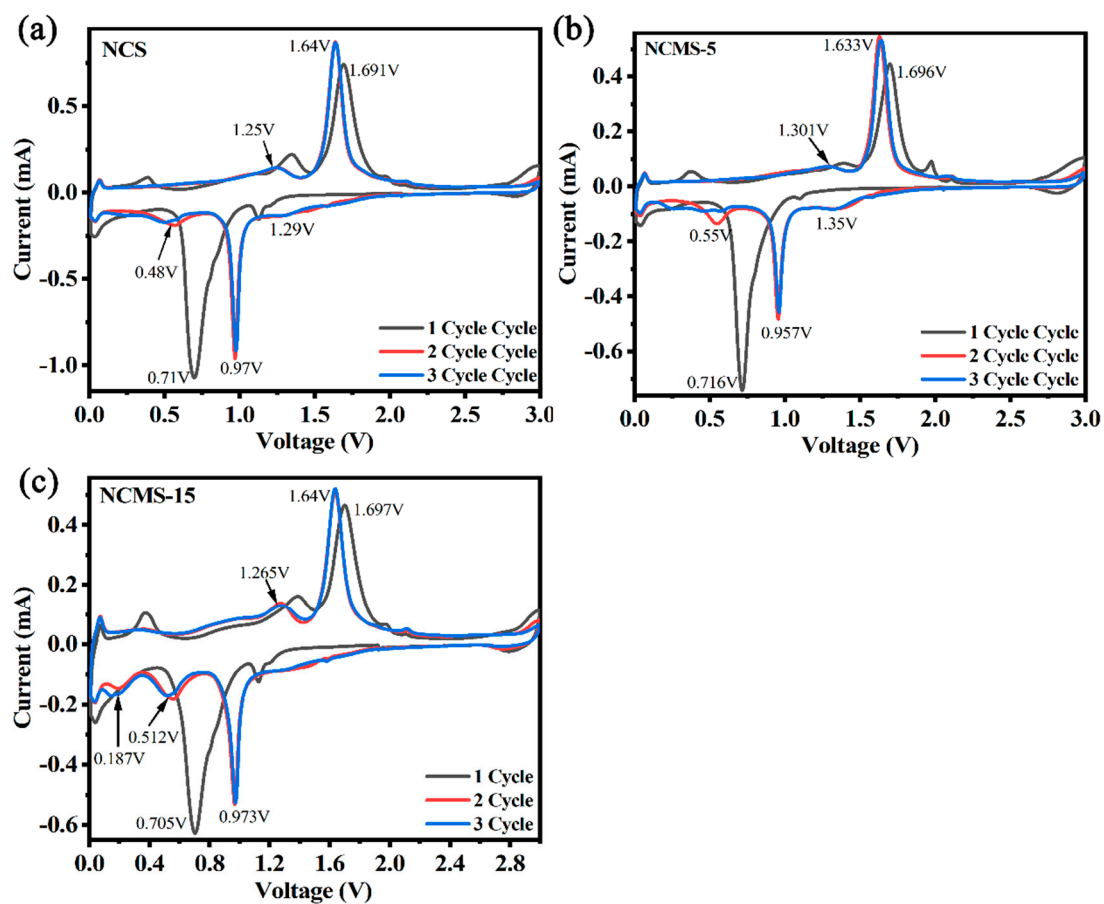
**Figure S1.** XPS full spectra of NCMS-10 sample. (a) Survey spectrum, (b) S 2p



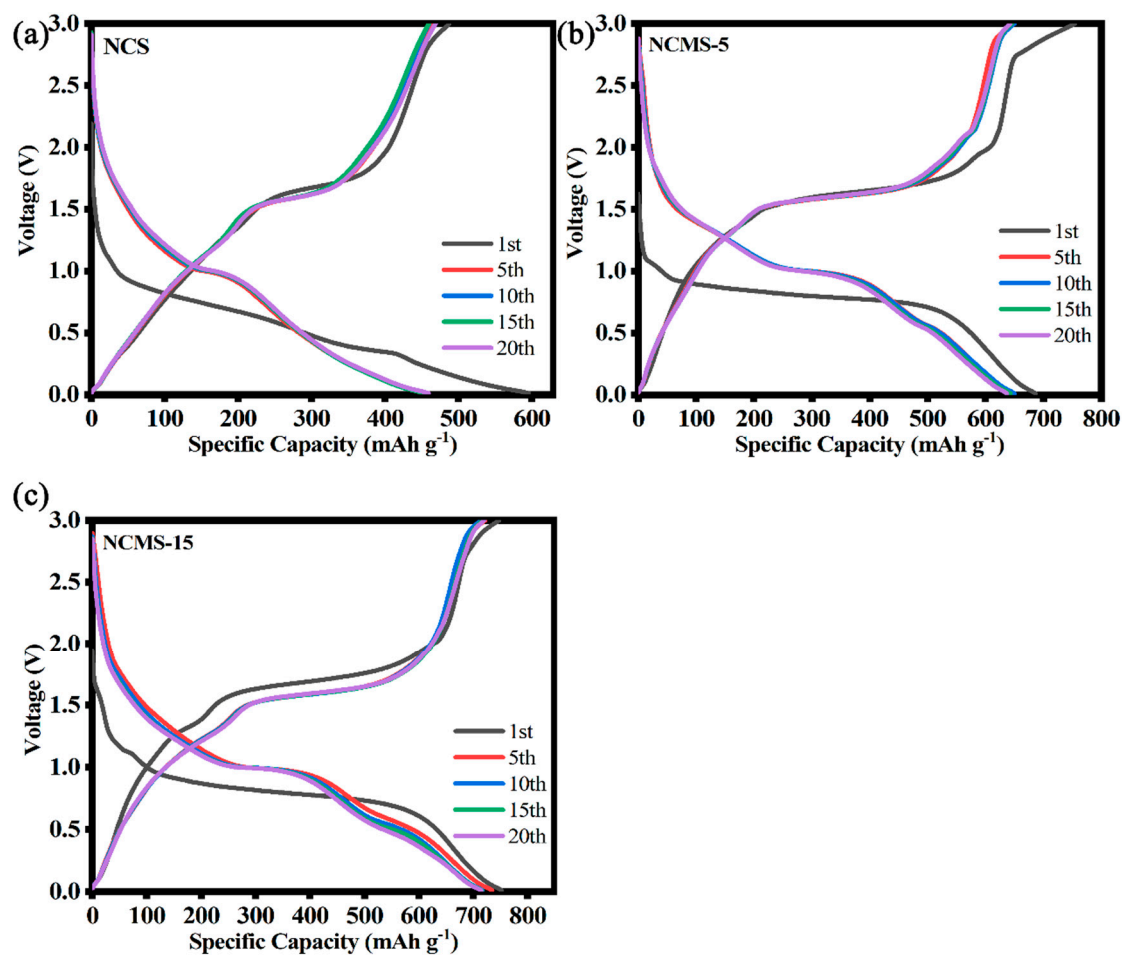
**Figure S2.** (a-d) TEM images of NCS, NCMS-5, NCMS-10 and NCMS-15 precursors, respectively.



**Figure S3.** SEM images of Ni-Co precursor without Mn addition.

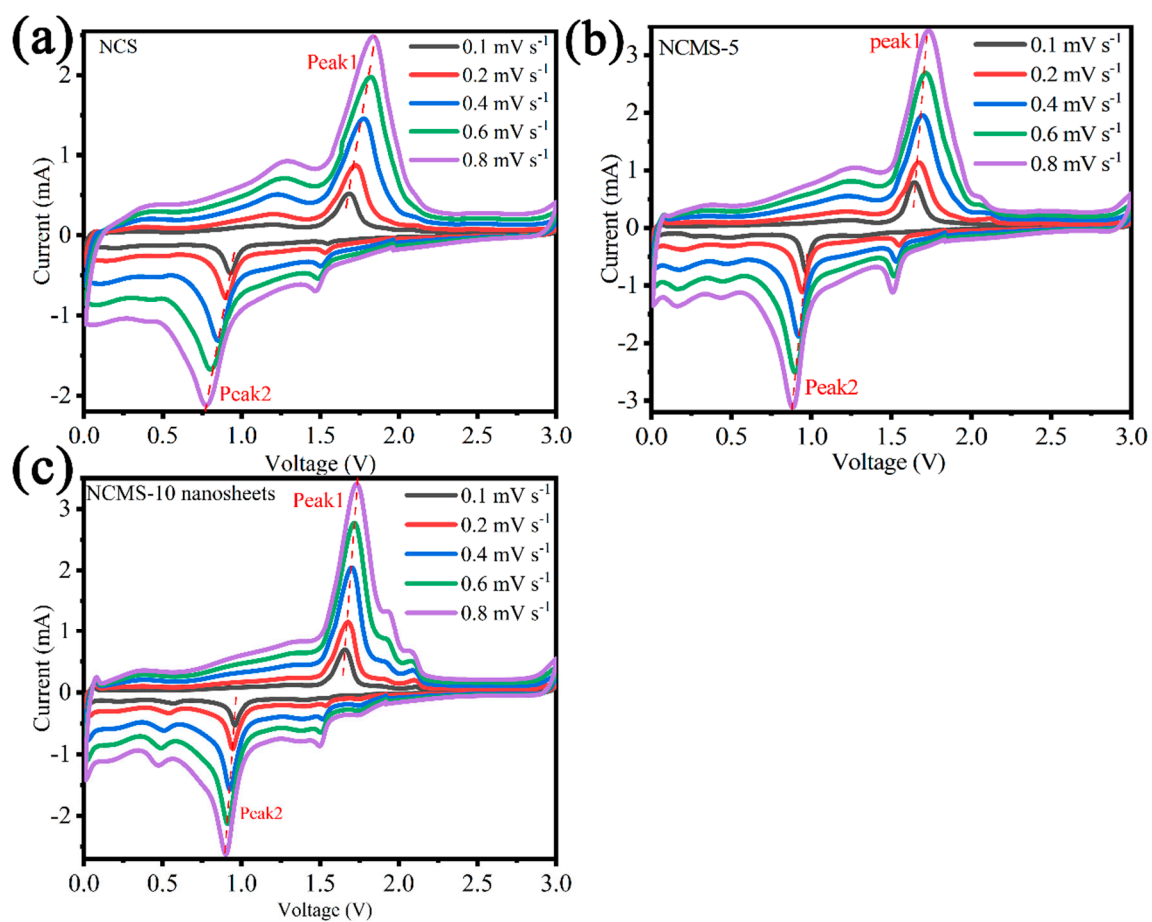


**Figure S4.** CV curves of (a) NCS, (b) NCMS-5 and (c) NCMS-15 at  $0.1 \text{ mV s}^{-1}$ .



**Figure S5.** Charge/discharge profiles at different cycles of (a) NCS, (b) NCMS-5 and (c) NCMS-15 at 0.3 A g<sup>-1</sup>.





**Figure S6.** CV curves of (a) NCS, (b) NCMS-5 and (c) NCMS-15 at different scanning rates, respectively.

**Table S1.** Performance comparison between this work and existing studies.

Material	ICE	Capacity (mAh g <sup>-1</sup> )	Rate performance (mAh g <sup>-1</sup> )	Reference
ZnS-NC@C	75.6%	475 (0.1 A g <sup>-1</sup> )	188.6 (2 A g <sup>-1</sup> )	[1]
SnS <sub>2</sub> /FeS <sub>2</sub> /rGO	65%	763.4 (0.1 A g <sup>-1</sup> )	405.3 (2 A g <sup>-1</sup> )	[2]
Co <sub>9</sub> S <sub>8</sub> /WS <sub>2</sub> @NC	81.7%	465 (0.1 A g <sup>-1</sup> )	359 (5 A g <sup>-1</sup> )	[3]
CuS nanocables	96.03%	534.6 (0.1 A g <sup>-1</sup> )	254.7 (15 A g <sup>-1</sup> )	[4]
FeS <sub>8</sub> @NS-C	73.2%	601.2 (0.1 A g <sup>-1</sup> )	387.2 (5 A g <sup>-1</sup> )	[5]
NCMS-10	97.98%	662.58 (0.3 A g <sup>-1</sup> )	583 (8 A g <sup>-1</sup> )	This work

## Reference

1. Cheng, A.; Hu, Y.N.; Yue, M.; Fu, J.X.; Wu, H.M.; Wang, S.Q.; Liu, J.W. Hollow N, C-co-doped carbon-coated ZnS nanospheres derived from metal organic framework (ZIF-8) with improved lithium and sodium storage performance. *J Phys-Mater* **2021**, *4*, 044003.
2. Chen, Y.; Liu, H.B.; Guo, X.L.; Zhu, S.P.; Zhao, Y.; Iikubo, S.; Ma, T.L. Bimetallic Sulfide SnS/FeS Nanosheets as High-Performance Anode Materials for Sodium-Ion Batteries. *Acs Appl Mater Inter* **2021**, *13*, 39248-39256.
3. Fu, L.K.; Kang, C.X.; Xiong, W.Q.; Tian, P.F.; Cao, S.Y.; Wan, S.Y.; Chen, H.Y.; Zhou, C.B.; Liu, Q.M. WS nanosheets@ZIF-67-derived N-doped carbon composite as sodium ion battery anode with superior rate capability. *J Colloid Interf Sci* **2021**, *595*, 59-68.
4. Zhang, L.F.; Hu, Y.; Liu, Y.; Bai, J.X.; Ruan, H.; Guo, S.W. Tunable CuS nanocables with hierarchical nanosheet-assembly for ultrafast and long-cycle life sodium-ion storage. *Ceram Int* **2021**, *47*, 14138-14145.
5. Zhao, C.Y.; Fan, R.Z.; Dai, J.J.; Dong, Y.T.; Wu, J.; Gao, J.K.; Cai, Y.R. Cu triggered phase transitions in FeS@NS-C anode: A neglected factor affecting the electrochemical performance of sodium storage. *Appl Surf Sci* **2023**, *609*, 155407