Supporting information

$Na_4Fe_3(PO_4)_2(P_2O_7)$@C/$Ti_3C_2T_x$ Hybrid Cathode Materials with Enhanced Performances for Sodium-Ion Batteries

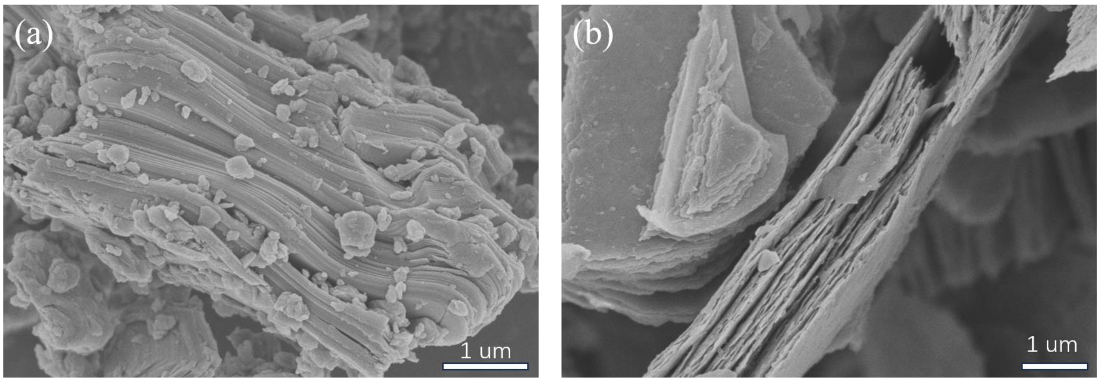

Figure S1 (a) SEM images of (a) Ti_3AlC_2 powders, and (b) $Ti_3C_2T_x$ powders.

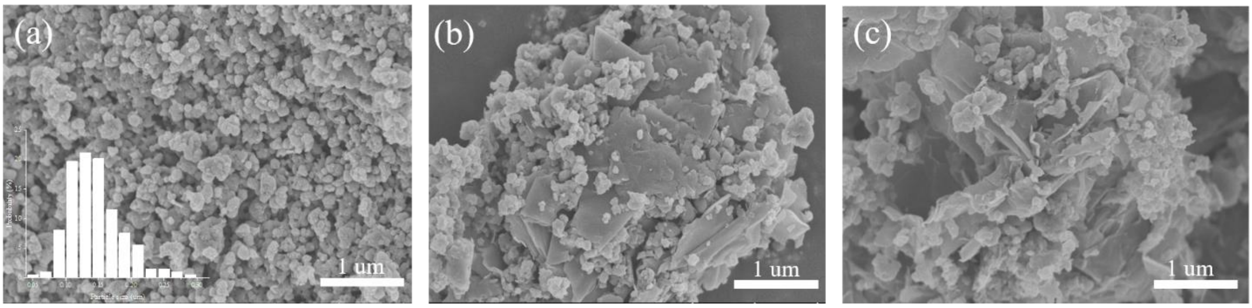

Figure S2 SEM images of (a) NFPP@C, (b)NFPP/MX, and (c) NFPP@MX.

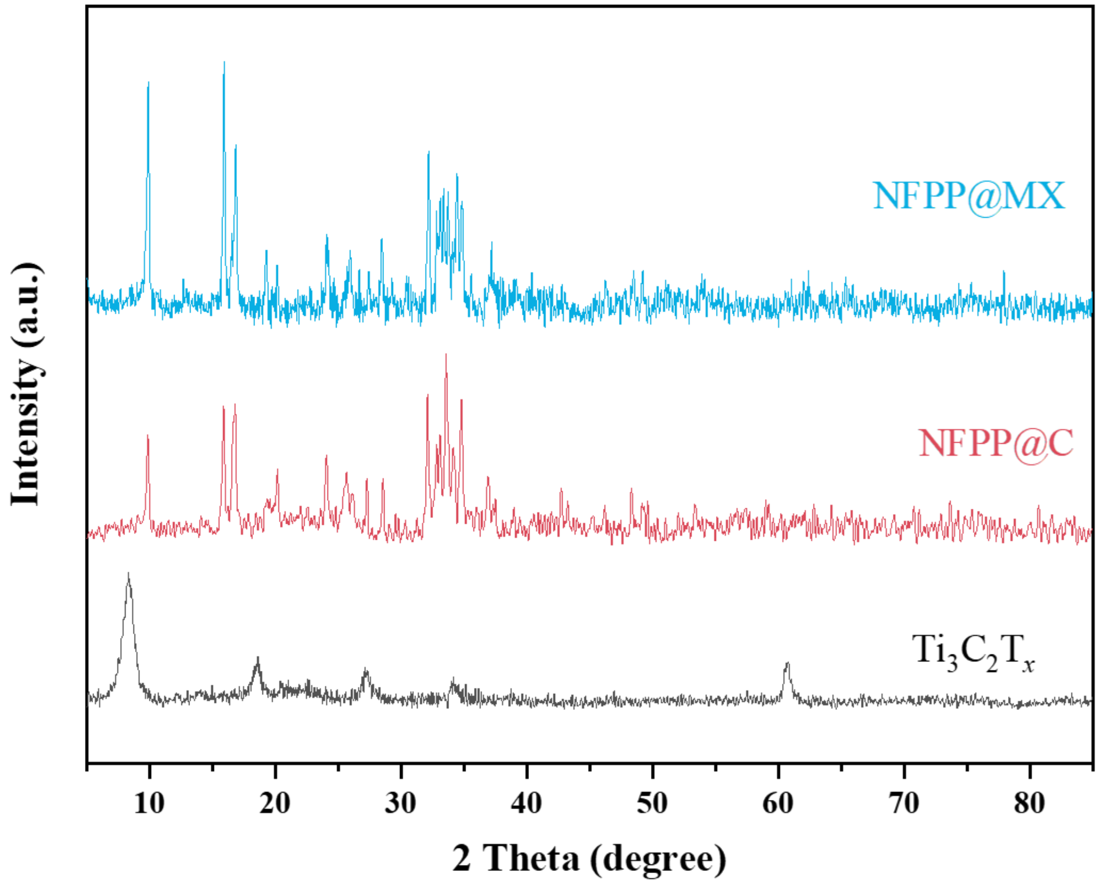

Figure S3 XRD patterns of $Ti_3C_2T_x$, NFPP@C and NFPP@MX.

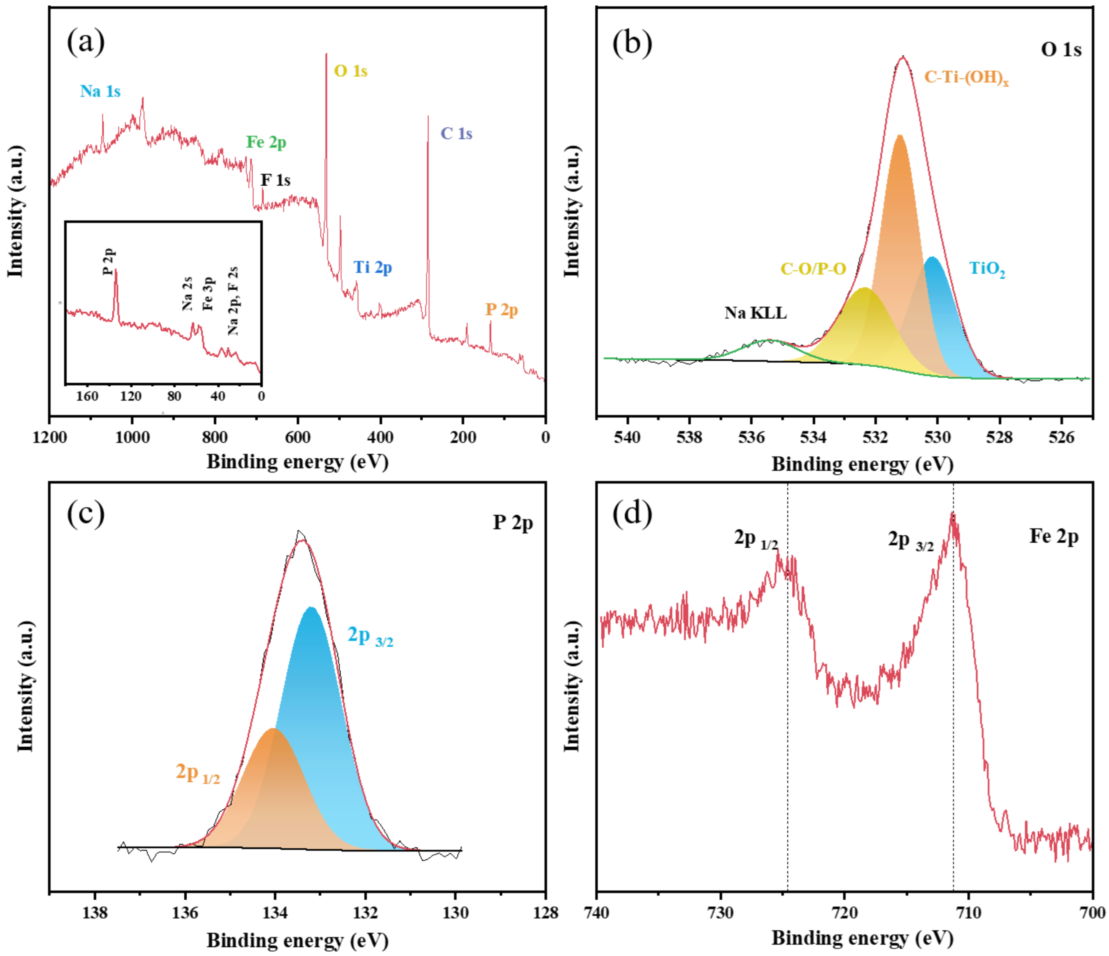

Figure S4 (a) Full XPS spectrum of NFPP@MX composite and corresponding XPS spectra of (b) O 1s region, (c) P 1s region, (d) Fe 2p region.

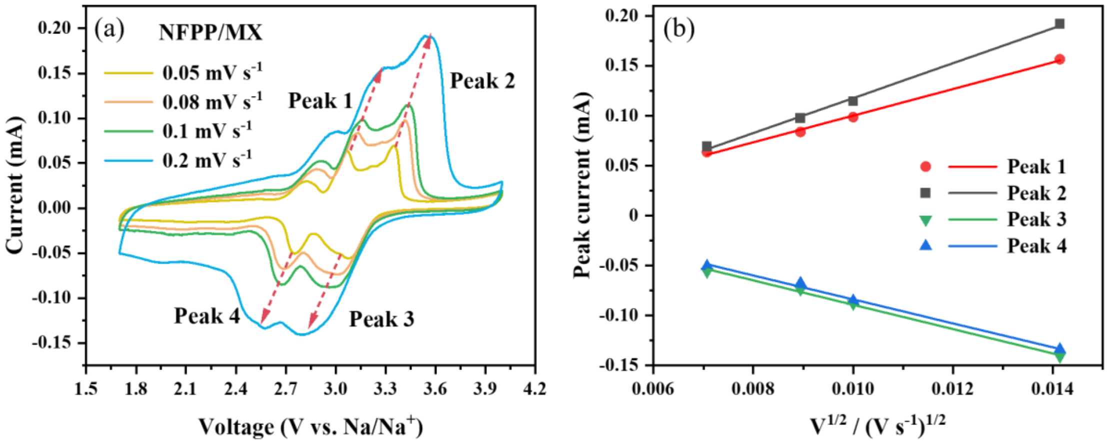

Figure S5 CV curves of (a) NFPP/MX cathodes at various scanning rates (0.05, 0.08, 0.1, and 0.2 mV s-1) and (b) corresponding relationships between i_{p} and $\nu_{1/2}$.

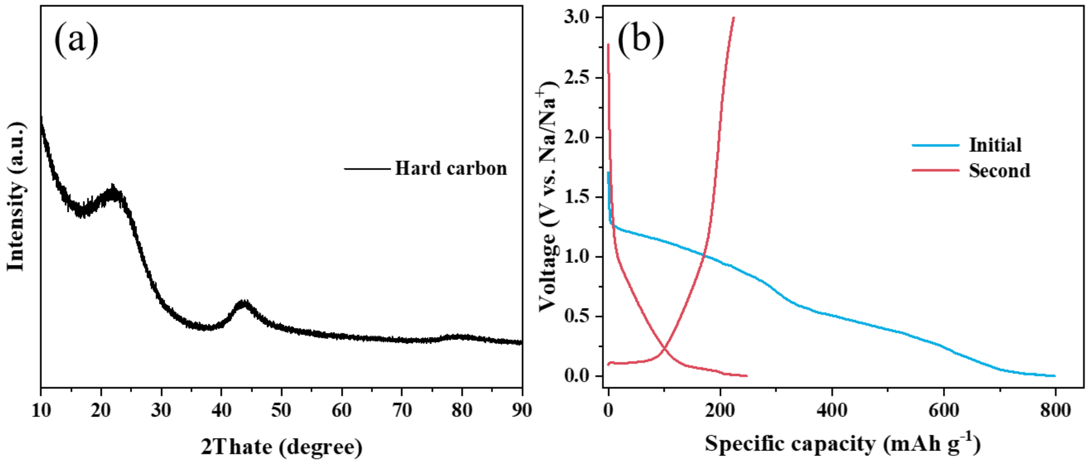

Figure S6 (a) XRD pattern for CHC sample, (b) charge/discharge curves of CHC//Na half cells at 50 mA g^{-1}.

Note S1 Carbon content calculation process

The chemical formula is as follows:

$$C+O_2=CO_2 \quad (S1)$$

$$Na_4Fe_3(PO_4)_2P_2O_7+3/4O_2=4/3Na_3Fe_2(PO_4)_3+1/6Fe_2O_3 \quad (S2)$$

Assuming the mass of the composite is 1 g and the carbon content is x (base on mass), then the composite is $(1-x)Na_4Fe_3(PO_4)_2P_2O_7@xC$. After calcination, the mass increase part is the mass of O_2 react with $Na_4Fe_3(PO_4)_2P_2O_7$ which can be written as

$$m(3/4O_2) = (1-x) *M(3/4O_2)/M(Na_4Fe_3(PO_4)_2P_2O_7) \quad (S3)$$

Considering the mass loss part is x, so 4.1 wt.% = x - m(3/4O_2) and x = 5.9 wt% is obtained.

Table S1. The calculated diffusion coefficients of the Na^+ ions (D) of NFPP@C, NFPP/MX, and NFPP@MX.

Samples	NFPP@C (D cm^2 s^{-1})	NPP/MX (D cm^2 s^{-1})	NFPP@MX (D cm^2 s^{-1})
Peak 1	3.35×10^{-12}	5.25×10^{-12}	8.09×10^{-12}
Peak 2	8.74×10^{-12}	9.04×10^{-12}	1.79×10^{-11}
Peak 3	3.43×10^{-12}	4.40×10^{-12}	8.81×10^{-12}
Peak 4	4.40×10^{-12}	4.25×10^{-12}	9.70×10^{-12}

Table S2. Simulation results of the EIS spectra of three electrodes.

Sample	NFPP@C	NFPP/MX	NFPP@MX
R_s (Ω)	2.059	3.98	3.476
R_{ct} (Ω)	2235	1505	1292

Table S3. Comparison of cathode materials for Na-ion batteries.

Cathode material	Specific capacity at 0.2C (mAh g^{-1})	Capacity retention	Specific capacity at 10C (mAh g^{-1})	References
NFPP@MX	107.2	85.2% (1000 cycles ,1C)	60.4	This work
NFPP/C-500	99	89% (300 cycles , 0.5C)	78	[1]
NVOPF/$Ti_3C_2T_x$	111	83.3% (400 cycles , 5C)	83	[2]
FNV-2	110	98.66% (600 cycles , 2C)	103	[3]
NVTP-NS3	162.71	73.1% (500 cycles, 2C)	78.18	[4]
$Na_{6.88}V_{2.81}(P_2O_7)_4$	59.8(0.1C)	94.5% (500 cycles 0.5C)	46.1	[5]
NFPP@MCNTs	107.1	96% (1200 cycles 2C)	82.1	[6]

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2. Yue, L.; Wang, J.; Li, M.; Qin, J.; Cao, M. Conductive $Ti_3C_2T_x$ networks to optimize $Na_3V_2O_2(PO_4)_2F$ cathodes for improved rate capability and low-temperature operation. *Dalton Transactions* **2023**, *52*, 4717-4727.
3. Kadam, S.; Kate, R.; Chothe, U.; Chalwadi, P.; Shingare, J.; Kulkarni, M.; Kalubarme, R.; Kale, B. Highly Stable MWCNT@NVP Composite as a Cathode Material for Na-Ion Batteries. *ACS Applied Materials & Interfaces* **2023**, *15*, 34651-34661.
4. Zhu, Y.; Song, K.; Shen, S.; Liu, Z.; Xu, J.; Yang, L.; Zhao, L. Realizing efficient sodium storage property with NASICON-type $Na_2VTi(PO_4)_3$ modified by nitrogen and sulfur dual-doped carbon layer for sodium ion batteries. *Journal of Alloys and Compounds* **2021**, *856*, 157992.
5. Li, J.; Wang, R.; Zhao, W.; Hou, X.; Paillard, E.; Ning, D.; Li, C.; Wang, J.; Xiao, Y.; Winter, M.; et al. A high-voltage symmetric sodium ion battery using sodium vanadium pyrophosphate with superior power density and long lifespan. *Journal of Power Sources* **2021**, *507*, 230183.
6. Cao, Y.; Xia, X.; Liu, Y.; Wang, N.; Zhang, J.; Zhao, D.; Xia, Y. Scalable synthesizing nanospherical $Na_4Fe_3(PO_4)_2(P_2O_7)$ growing on MCNTs as a high-performance cathode material for sodium-ion batteries. *Journal of Power Sources* **2020**, *461*, 228130.