

## Supporting information

### **Synergetic Effects from a High-Entropy NASICON-type Cathode for Advanced Sodium-Ion Batteries**

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## Material preparation

All the experimental reagents were analytically pure and can be used directly without further purification. The high-entropy  $\text{Na}_3\text{V}_{1.5}(\text{CrMnFeMgAl})_{0.5}(\text{PO}_4)_3@\text{C}$  cathode material was synthesized by the following method. Typically, 12 mM  $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ , 3 mM  $\text{V}_2\text{O}_5$ , 8 mM citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) were weighed and placed in a beaker; 0.4 mM  $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  were also added into the beaker, respectively. Next, 30 mL of deionized water was added and stirred magnetically at 70 °C for 3 h to form a homogeneous solution. After that, the mixture was dried in an oven at 120 °C for 12 h to get a gel. Then, the product was ground into powder and heated at 300 °C for 4 h, then 800 °C for 10 h with a heating rate of 5 °C/min in a tube furnace with argon atmosphere. The simple  $\text{Na}_3\text{V}_2(\text{PO}_4)_3@\text{C}$  material was synthesized using the same method for meaningful comparison.

## Material characterizations

The structure of the prepared materials above was characterized by X-ray diffraction (Cu  $\text{K}\alpha$  radiation,  $\lambda=1.5418 \text{ \AA}$ ). The inductively coupled plasma-optical emission spectroscopy (ICP) was used to confirm the elements composition of samples. Scanning electron microscopy (SEM, JSM-7800F) and transmission electron microscopy (TEM, JEM-2100F) were carried out to explore the morphology and microstructure of samples. The mapping of energy-dispersive spectral elements was carried out in TEM mode. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALB250Xi instrument equipped with a monochromatic Al-K $\alpha$  source. Thermogravimetric analysis (TGA) of the samples was performed to test the carbon content of the sample surface.

## Electrochemical measurements

The slurry of the cathode was composed by mixing the HE-NVMP@C material, Super P, and polyvinylidene fluoride (PVDF) binder with a weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP) and stirred magnetically for 12 h. The stirred slurry was then

evenly coated onto the copper foil and dried in a vacuum oven at 80 °C for 12h. The coated copper foil was cut into electrodes with a diameter of 14 mm. Glass fiber (Grade GF/F, Whatman) and Na metal were used as a separator and counter electrodes, respectively, when assembled into a coin cell (CR2032) in a glovebox at Ar-atmosphere (both O<sub>2</sub> and H<sub>2</sub>O < 0.5 ppm). The battery performance was tested in 1 M NaClO<sub>4</sub> solution in a mixture (1:1, VOL%) of ethylene carbonate (EC) with 5% fluoroethylene carbonate (FEC). A cyclic voltammetry test was carried out through a BioLogic electrochemical workstation. The cycle performances of the cells were tested between 2.5 and 4.3 V (vs. Na/Na<sup>+</sup>) in the galvanostatic model on a battery test system (NEWARE). All electrochemical tests were carried out at room temperature.

### **Annotation**

The crystal structures in this paper (**Figure 1a** and **Figure 1c**) were drawn through VESTA [1].

The XRD Rietveld refinement results in this paper (**Figure 1b** and **Figure S2**) were drawn through EXPGUI[2]

1. K. Momma and F. Izumi, *Journal of Applied Crystallography*, 2011, **44**, 1272-1276.
2. B. H. Toby, *Journal of Applied Crystallography*, 2001, **34**, 210-213.

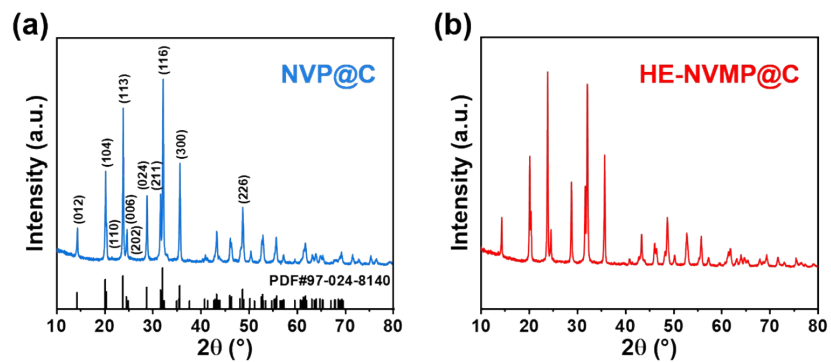


Figure S1. XRD patterns of (a) NVP@C and (b) HE-NVMP@C

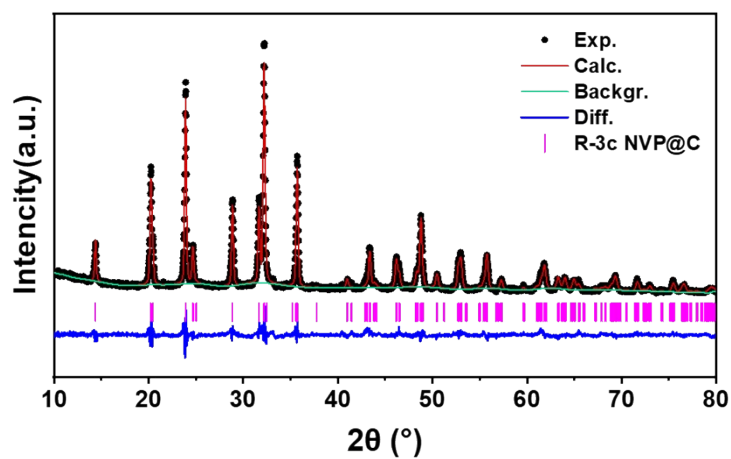


Figure S2. XRD pattern and Rietveld refinement result of the NVP@C.

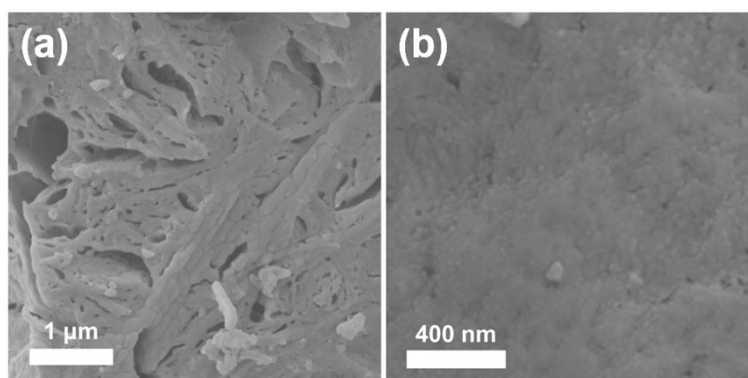


Figure S3. SEM images of the NVP@C sample: (a) Low and (b) High magnifications.

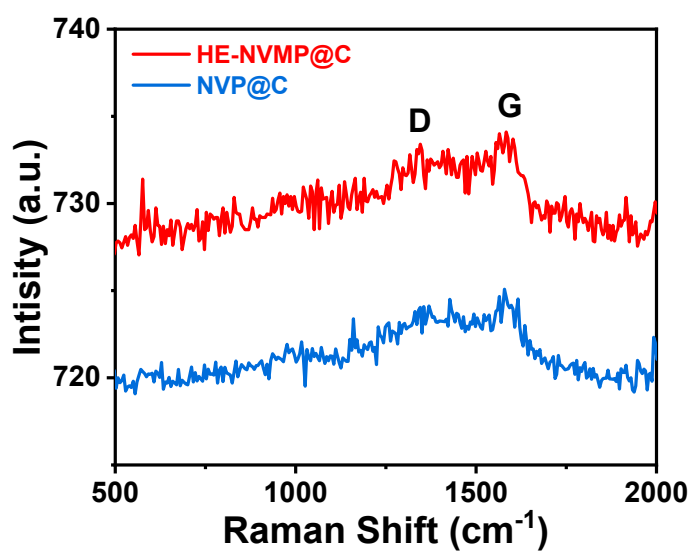


Figure S4. Raman spectra of the samples.

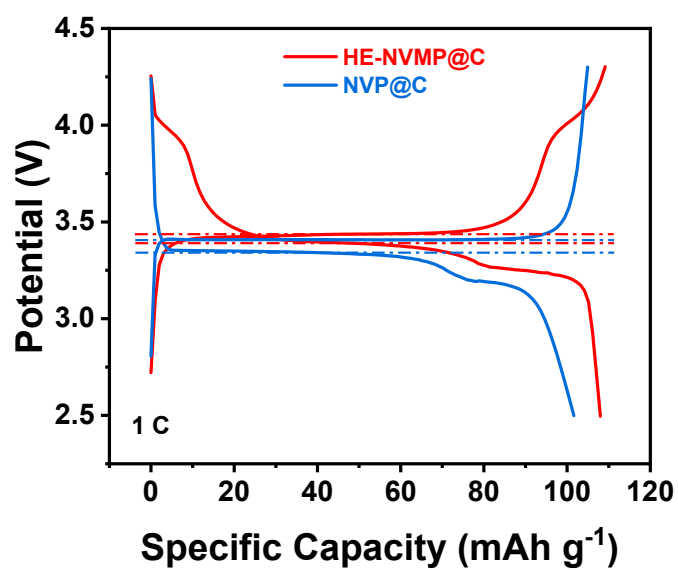
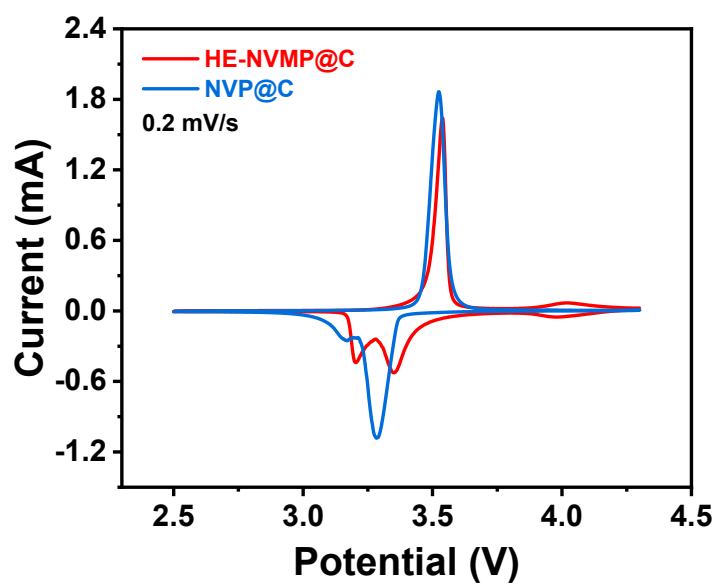
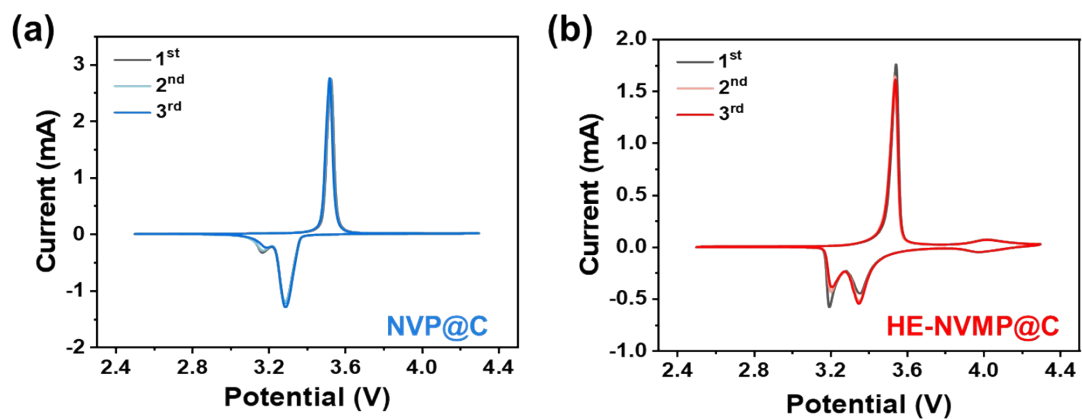


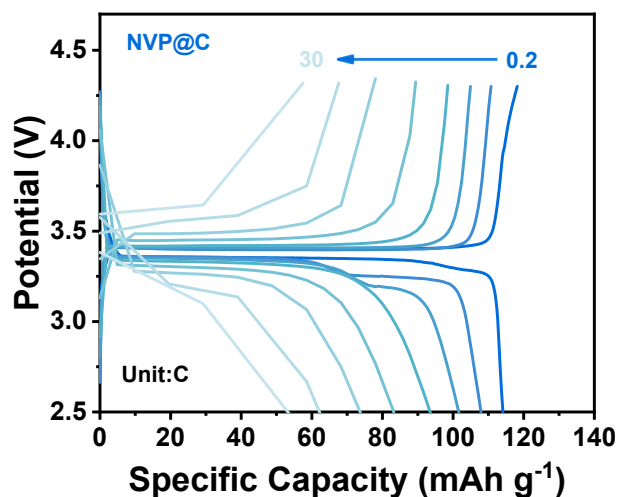
Figure S5. Charge/discharge curves of the samples at a rate of 1 C.



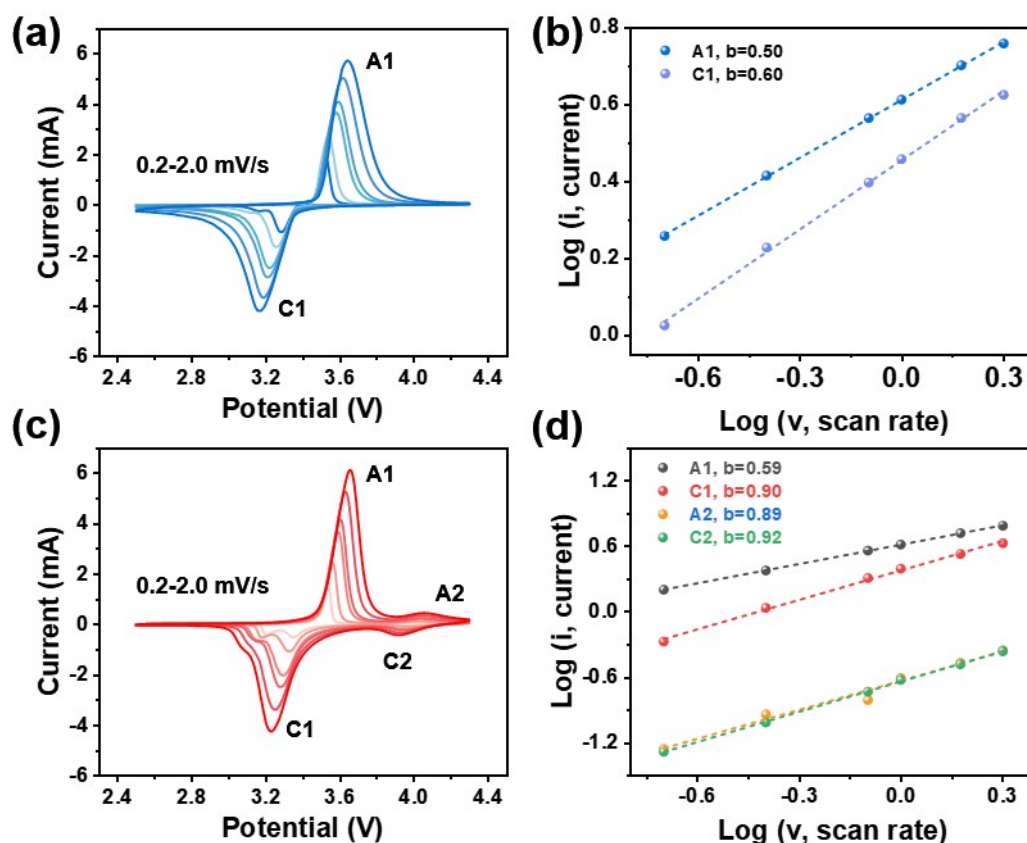
**Figure S6.** CV curves of the cathodes at a scan rate of 0.2 mV/s.



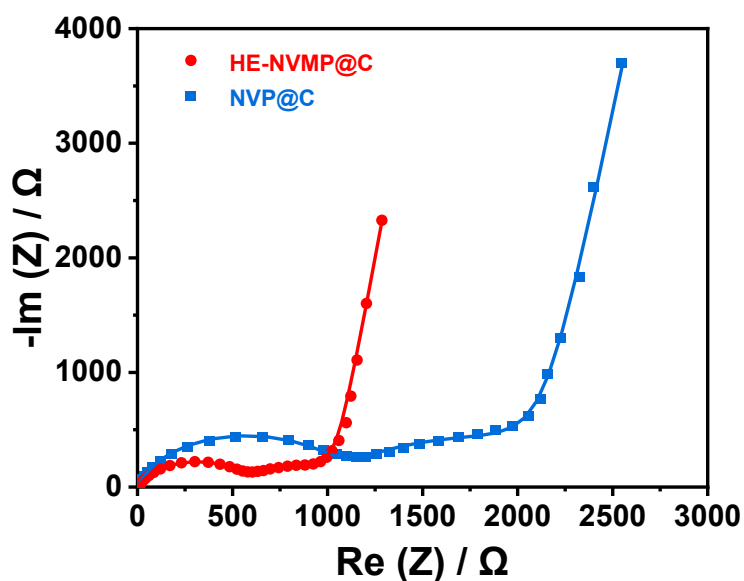
**Figure S7.** The initial three CV curves of the cathodes at a scan rate of 0.2 mV/s.



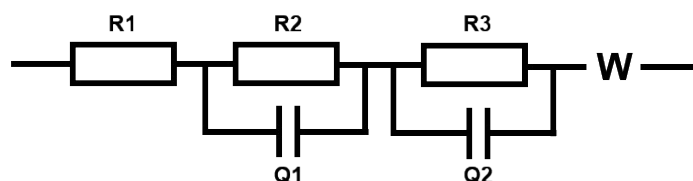
**Figure S8.** Charge/discharge curves of the NVP@C cathode at 0.2, 0.5, 1, 2, 5, 10, 20, and 30 C, respectively.



**Figure S9.** CV curves of (a) NVP@C and (c) HE-NVMP@C cathodes at various scan rates. The log (peak current) vs. log (scan rate) plots of (b) NVP@C and (d) HE-NVMP@C cathodes at different charge/discharge states.



**Figure S10.** The EIS spectra of the samples before cycling test.



**Figure S11.** The equivalent circuit diagram for impedance fitting.

R1 represents the internal resistance of the battery, including the resistance of the collector, electrolyte, active material, etc.; R2 and R3 represent the SEI resistance and the interfacial transfer resistance; Q1 and Q2 are the corresponding double-electric-layer capacitance, respectively; W represents the Warburg impedance, which is the diffusion impedance of sodium ions in the active material.



**Table S1.** Detailed structure information of HE-NVMP@C from Rietveld refinement from the X-ray powder diffraction pattern.

Na<sub>3</sub>V<sub>1.5</sub>(CrMnFeMgAl)<sub>0.5</sub>(PO<sub>4</sub>)<sub>3</sub>@C sample. Crystal phase: rhombohedral, R-3c; a = b = 8.7295 Å, c = 21.8269 Å, V= 1440.47 Å<sup>3</sup>, R<sub>wp</sub>=9.20%, R<sub>p</sub>=7.00%.

Atom	x	y	z	Occupancy	Wyckoff Position
Na1	0.3333	0.6667	0.1667	1.073	6b
Na2	0.6667	0.9697	0.0833	0.810	18e
V	0.3333	0.6667	0.0196	0.746	12c
Cr	0.3333	0.6667	0.0196	0.0471	12c
Mn	0.3333	0.6667	0.0196	0.0468	12c
Fe	0.3333	0.6667	0.0196	0.0472	12c
Mg	0.3333	0.6667	0.0196	0.0417	12c
Al	0.3333	0.1667	0.0196	0.0365	12c
O1	0.1459	0.4982	0.0782	1.002	36f
O2	0.5492	0.8473	-0.0252	1.062	36f
P	-0.0410	0.3333	0.0833	0.9867	18e

**Table S2.** Detailed structure information of NVP@C from Rietveld refinement from the X-ray powder diffraction pattern.

Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>@C sample. Crystal phase: rhombohedral, R-3c; a = b = 8.7435 Å, c = 21.7563 Å, V= 1440.42 Å<sup>3</sup>, R<sub>wp</sub>=9.0%, R<sub>p</sub>=7.00%

Atom	x	y	z	Occupancy	Wyckoff Position
Na1	0.3333	0.6667	0.1667	0.844	6b
Na2	0.6667	0.9681	0.0833	0.7735	18e
V	0.3333	0.6667	0.0194	0.9994	12c
O1	0.1355	0.4930	0.7827	1.0111	36f
O2	0.5538	0.8519	-0.2674	1.0068	36f
P	-0.0426	0.3333	0.0833	0.9800	18e