

## Electronic Supporting Information

### **Core-shell CuFeMnHCF@CuHCF: a high-rate and durable Prussian blue cathode for sodium-ion batteries**

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## Synthesis of Prussian blue analogue

CuFeMnHCF@CuHCF was synthesized via a co-precipitation method. The typical synthesis procedure is as follows: 5 mmol of  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$  was dissolved in 100 mL of deionized (DI) water to form Solution A. Separately, 4 mmol of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ , 1 mmol of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , and 5 mmol of sodium citrate were dissolved in 100 mL of DI water to form Solution B. In addition, 1 mmol of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in 20 mL of DI water to prepare Solution C. Subsequently, Solution B was dropwise added into Solution A at a flow rate of 10 mL/h using a peristaltic pump. After the completion of the dropwise addition of Solution B, Solution C was further titrated into Solution A. During the dropping process, the mixture was continuously stirred under an argon atmosphere for 12 h. After the reaction, the mixture was aged statically for 12 h, and the precipitate was collected by centrifugation. The obtained solid was washed several times with deionized water and ethanol, and then dried in a vacuum oven at 120 °C for 12 h. The final product was denoted as CuFeMnHCF@CuHCF.

For comparison, FeMnHCF was prepared using a similar procedure. For FeMnHCF, the  $\text{CuSO}_4$  solution was not involved in the synthesis, and the remaining steps were identical to those described above.

## Material characterization

The as-synthesized samples were characterized to elucidate their physicochemical properties. Their morphologies and microstructures were examined using scanning electron microscopy (SEM, ZEISS Sigma 360) and transmission electron microscopy (TEM, FEI Tecnai G2 F20). The crystalline phase was identified by X-ray diffraction (XRD) on a Bruker D8 Advance instrument with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ), scanning a  $2\theta$  range from  $5^\circ$  to  $80^\circ$ . The XRD data were analyzed by Rietveld refinement with GSAS software.<sup>1</sup> X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific) was employed to analyze the surface chemical composition and the valence states of Mn, Fe, and Cu. Raman spectra were acquired with a confocal laser micro-Raman spectrometer (HORIBA, Lab RAM HR Evolution). The contents of Na, Fe, Mn, and Cu were determined by inductively coupled plasma optical emission

spectroscopy (ICP-OES, Agilent 5800). Carbon, hydrogen, and nitrogen contents were measured using a VARIO EL III elemental analyzer. Thermogravimetric analysis (TGA, NETZSCH STA 449 F3) was performed from room temperature to 400 °C under N<sub>2</sub> atmosphere at a heating rate of 10 °C min<sup>-1</sup> to determine the water content.

## Reference

1. Larson, A. C. & Dreele, R. B. V. General structure analysis system (GSAS) (Report LAUR 86-748, Los Alamos National Laboratory, 2004).

## Electrochemical measurements

The electrochemical properties of the obtained FeMnHCF and CuMnHCF@CuHCF materials were tested by assembling CR2032 coin cells in an argon-protected glovebox (MIKROUNA, Model Super 1220/750/900, H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm). The cell assembly parameters are as follows: FeMnHCF or CuFeMnHCF@CuHCF were used as the working electrodes, metallic sodium as the counter electrode, the electrolyte was a 1.0 mol/L sodium perchlorate (NaClO<sub>4</sub>) solution in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (volume ratio 1:1:1) with the addition of 2 vol.% fluoroethylene carbonate (FEC), and Whatman glass fiber was employed as the separator. The preparation process of the working electrodes is as follows: First, the active material, Ketjen black (conductive agent), and polyvinylidene fluoride (PVDF, binder) were mixed at a mass ratio of 7:2:1, and dispersed in N-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry. Subsequently, the slurry was uniformly coated on aluminum foil and dried in a vacuum oven at 120°C for 12 h. Finally, the aluminum foil coated with active material was punched into 14 mm-diameter disks to obtain the working electrodes, with the active material loading mass of approximately 1 mg. For electrochemical measurements, galvanostatic charge-discharge testing, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) were performed using a Land battery testing system (China, Model CT4008TNn-5V10mA-164) and an electrochemical workstation (China, Model CHI660e), respectively. The cells were galvanostatically charged and discharged between 2.0 and 4.0 V at various current

densities. The capacity was calculated based on the mass of the active material in the electrode, excluding the mass of the conductive carbon (Ketjen black).

Galvanostatic intermittent titration (GITT) measurement was used to evaluate the Na<sup>+</sup> diffusion coefficient ( $D$ ) of the FeMnHCF and CuFeMnHCF@CuHCF.  $D$  can be calculated by using Fick's second law as follows:

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

where  $V_M$ ,  $m_B$ ,  $M_B$ , and  $S$  are molar volume, mass, molar mass, and electrode area, respectively.  $\tau$  is the pulse time (s).  $\Delta E_s$  and  $\Delta E_\tau$  are the differences of voltage and time, respectively.

In-situ XRD measurements were performed using a custom-designed electrochemical cell compatible with a Bruker D8 Advance diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ). The cell was equipped with a beryllium (Be) window to allow X-ray transmission during electrochemical cycling. The working electrode was prepared by coating a slurry of active material (80 wt%), Super P (10 wt%), and PVDF (10 wt%) in NMP onto an Al foil, The counter electrode was a sodium metal disc, and the separator was a glass fiber membrane (Whatman GF/D). The electrolyte was 1 M NaPF<sub>6</sub> in a 1:1 volume ratio of EC/DEC. The cell was assembled in an argon-filled glovebox (O<sub>2</sub> < 0.1 ppm, H<sub>2</sub>O < 0.1 ppm).

Table S1. Crystallographic parameters of FeMnHCF obtained from XRD Rietveld refinement.

FeMnHCF, Monoclinic, space group P21/n, a = 10.590084 Å, b = 7.575208 Å, c = 7.390153 Å,  $\alpha = 90^\circ$ ,  $\beta = 92.0188^\circ$ ,  $\gamma = 90^\circ$ , V = 592.8535 Å<sup>3</sup>, weighted profile R-factor, Rwp=9.2 %.

Atom	X	Y	Z	Site	Occ
Na1	0.25775	0.44553	0.02722	4e	1.0000
Fe2	0.50000	0.00000	1.00000	2d	1.0000
Mn3	0.50000	0.50000	0.50000	2a	0.8000
Fe4	0.50000	0.50000	0.50000	2a	0.2000
N5	0.49939	0.31393	0.74298	4e	1.0000
N6	0.29412	0.50590	0.50582	4e	1.0000
N7	0.50173	0.26558	0.31835	4e	1.0000
C8	0.49796	0.19145	0.83494	4e	1.0000
C9	0.18931	0.49940	0.51831	4e	1.0000
C10	0.50246	0.16216	0.20308	4e	1.0000

Table S2. Crystallographic parameters of FeMnHCF@CuHCF obtained from XRD Rietveld refinement.

CuFeMnHCF (93.2 wt%) in CuFeMnHCF@CuHCF, Monoclinic, space group P21/n, a = 10.531471 Å, b = 7.540678 Å, c = 7.351224 Å, $\alpha = 90^\circ$ , $\beta = 91.9554^\circ$ , $\gamma = 90^\circ$ , V = 583.7932 Å <sup>3</sup> , weighted profile R-factor, Rwp= 8.7 %.					
Atom	X	Y	Z	Site	Occ
Na1	0.25775	0.44553	0.02722	4e	1.0000
Fe2	0.50000	0.00000	1.00000	2d	1.0000
Mn3	0.50000	0.50000	0.50000	2a	0.7900
Fe4	0.50000	0.50000	0.50000	2a	0.1900
Cu5	0.50000	0.50000	0.50000	2a	0.0200
N6	0.49939	0.31393	0.74298	4e	1.0000
N7	0.29412	0.50590	0.50582	4e	1.0000
N8	0.50173	0.26558	0.31835	4e	1.0000
C9	0.49796	0.19145	0.83494	4e	1.0000
C10	0.18931	0.49940	0.51831	4e	1.0000
C11	0.50246	0.16216	0.20308	4e	1.0000
CuHCF (6.8 wt%) in FeMnHCF@CuHCF, Cubic, space group Fm-3m, a = b = c = 9.986000 Å, $\alpha = \beta = \gamma = 90^\circ$ , V = 995.5965 Å <sup>3</sup> , weighted profile R-factor, Rwp=8.7 %.					
Atom	X	Y	Z	Site	Occ
Fe1	0.00000	0.00000	0.00000	4a	1.0000
Cu2	0.50000	0.00000	0.00000	4b	1.0000
Cu3	0.25000	0.25000	0.25000	8c	0.5000
C4	0.19600	0.00000	0.00000	24e	1.0000
N5	0.31200	0.00000	0.00000	24e	1.0000

Table S3. Summary of fitted EIS parameters for FeMnHCF and CuFeMnHCF@CuHCF.

Samples	$R_s(\Omega)$	$R_{ct}(\Omega)$	$R_{mt}(\Omega)$	$CPE_1$	$CPE_2$	$z$
FeMnHCF	14.0	782.8	787.1	0.8383	0.9343	0.0001501
CuFeMnCHF@CuHCF	8.3	521.5	520.8	0.8930	0.9571	0.0002662

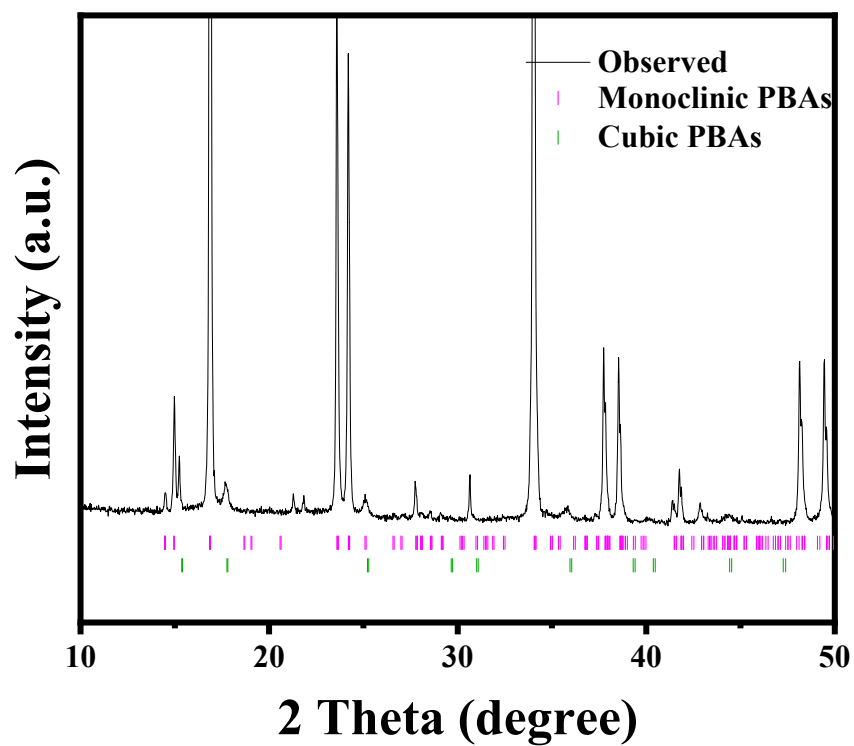


Fig. S1 Enlarged XRD pattern of CuFeMnHCF@CuHCF in the selected  $2\theta$  range

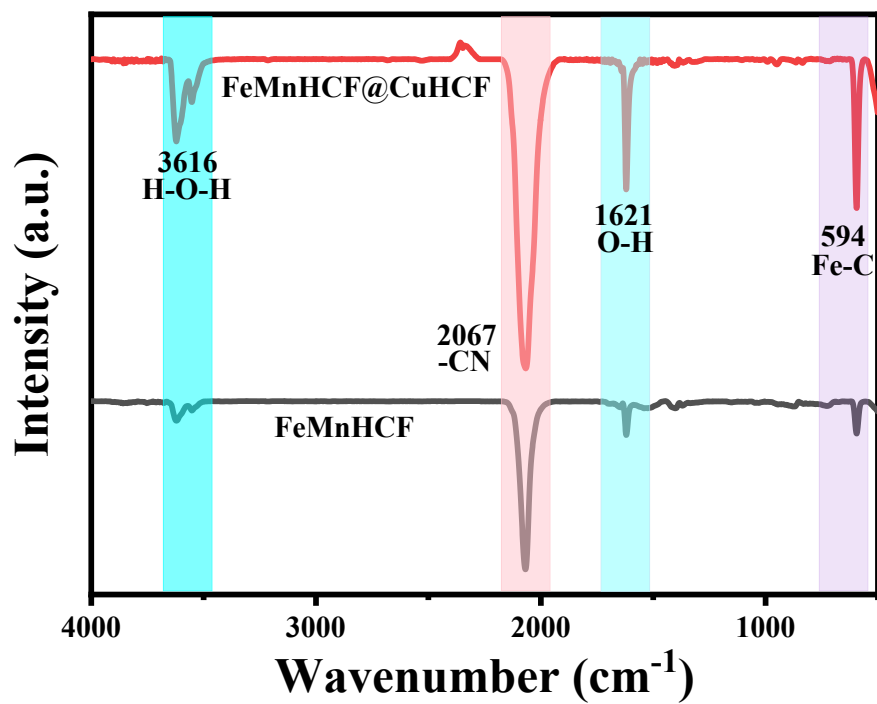


Fig. S2 FTIR spectra of FeMnHCF and CuFeMnHCF@CuHCF

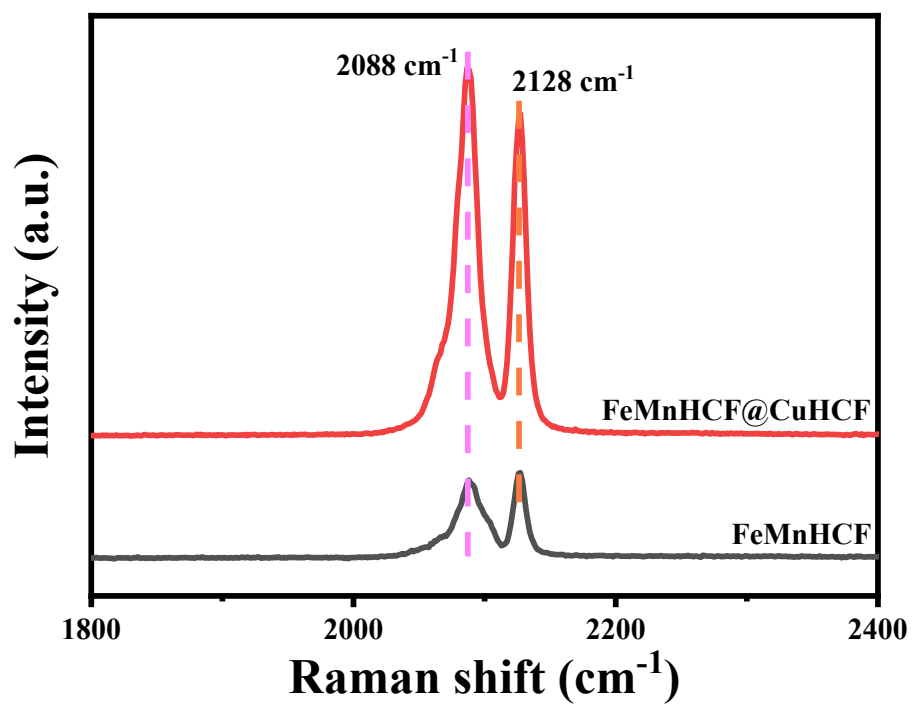


Fig. S3 Raman spectra of FeMnHCF and CuFeMnHCF@CuHCF

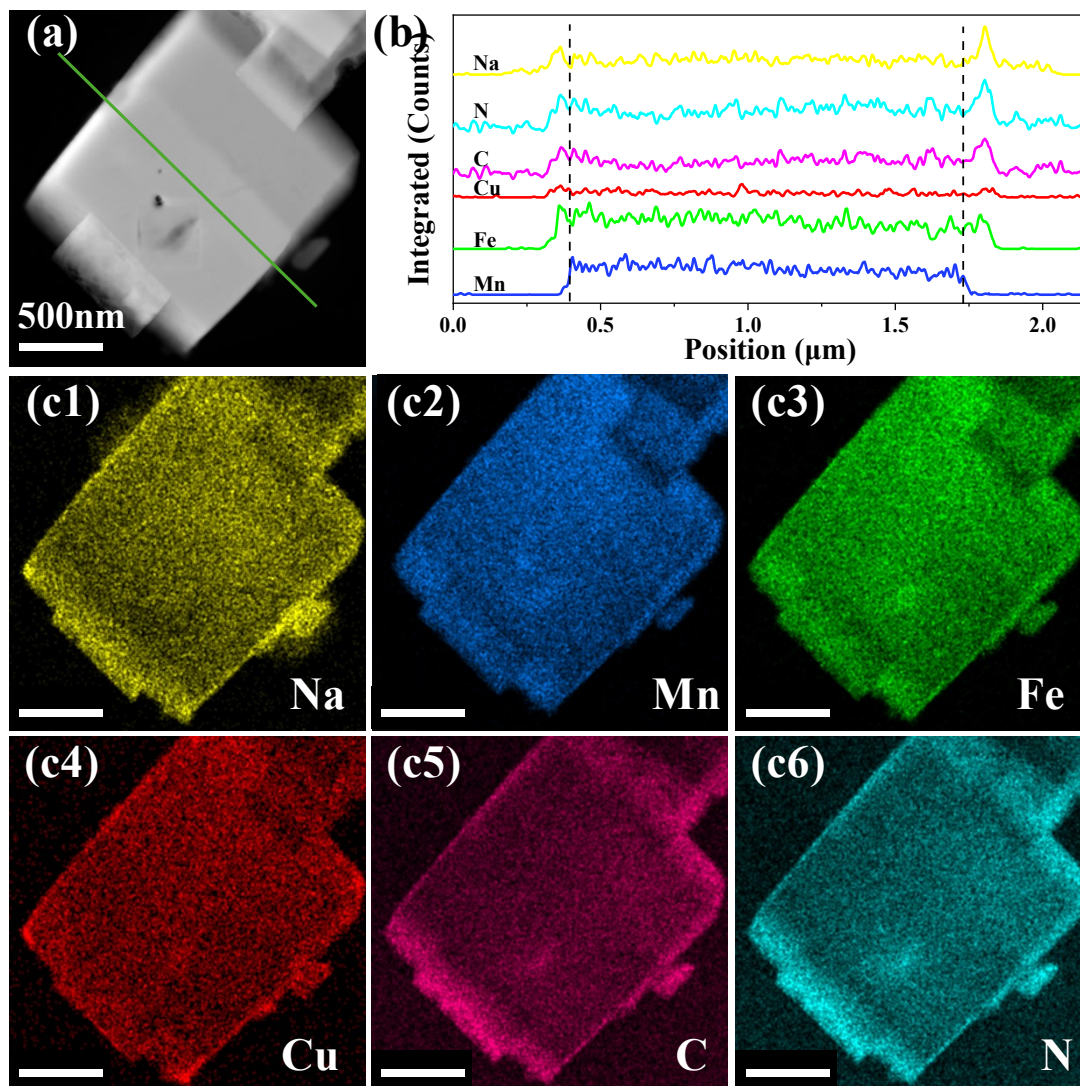


Fig. S4 TEM image (a), EDS maps (c) and the line-scan profile (b) of CuFeMnHCF@CuHCF

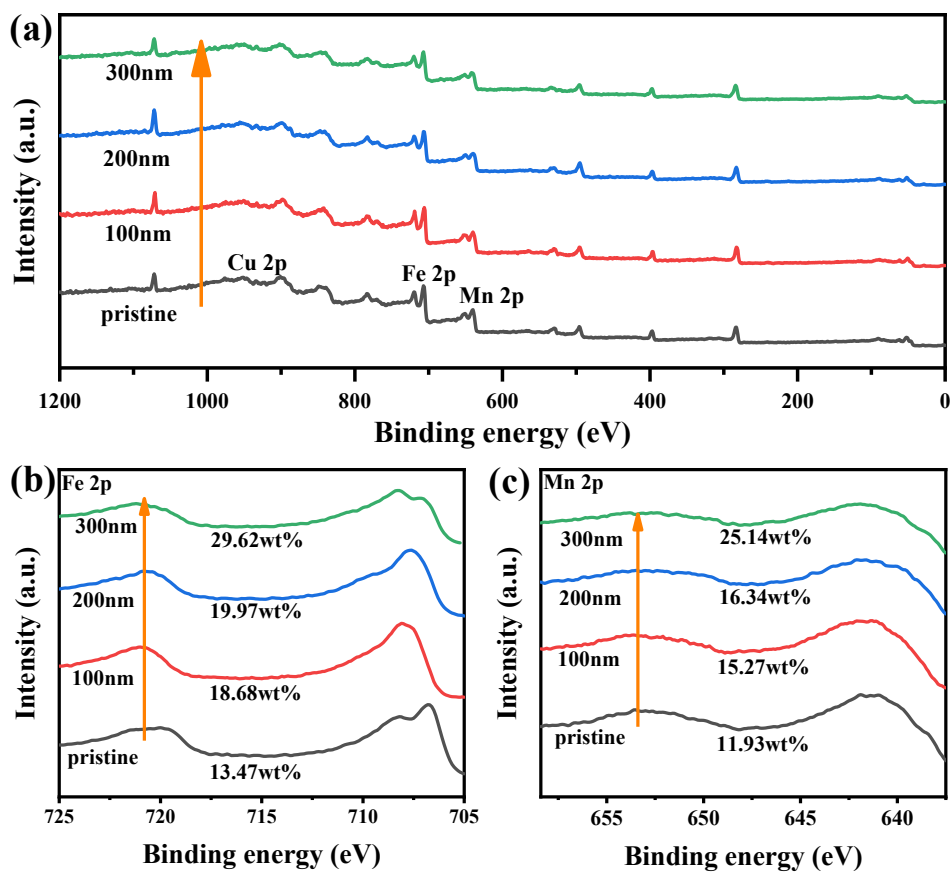


Fig. S5 Depth-profiling XPS spectra of CuFeMnHCF@CuHCF as a function of argon sputtering time: (a) Full survey, (b) Fe 2p, and (c) Mn 2p.

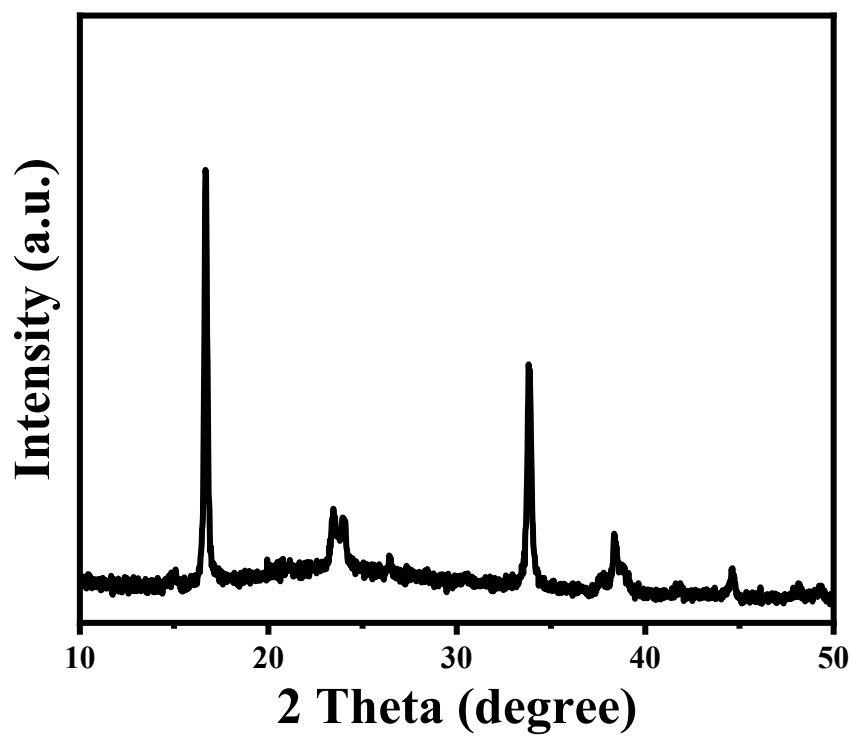


Fig. S6 XRD pattern of CuFeMnHCF@CuHCF after 150 cycles

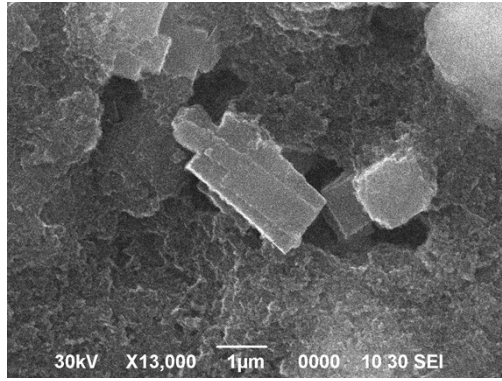


Fig. S7 SEM image of CuFeMnHCF@CuHCF after 150 cycles