

Electronic Supplementary Information

Experimental section

Materials: NaH_2PO_2 was purchased from Aladdin Ltd. (Shanghai, China). $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Na_2SO_4 and HNO_3 were purchased from Chendu Chemical Corporation. CC was provided by Hongshan District, Wuhan Instrument Surgical Instruments business.

Synthesis of Fe_2O_3 NAs/CC

A typical procedure is described as follows: CC was carefully cleaned with concentrated HNO_3 to remove impurity of surface and attach hydroxyl on surface, and then deionized water and ethanol was used for several times to ensure the surface of the CC was well cleaned. A given amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.4 g) and Na_2SO_4 (0.24 g) was added in 35 mL aqueous, and then transferred to a 50 mL Teflon-lined stainless-steel autoclave. Afterwards, a piece of carbon cloth ($2.5\text{cm} \times 3\text{cm}$) was immersed into the solution and hydrothermally treated at 120°C for 4h and then cool down to room temperature. Finally, the Fe_2O_3 NAs/CC was obtained after annealing in Ar gas at 450°C for 3h with a heating rate of 3°C min^{-1} .

Synthesis of FeP NAs/CC

NaH_2PO_2 (1.0g) was put at the center of front zone in a two-zone furnace, while Fe_2O_3 NAs/CC was put at the center of back zone. The temperature of two zone were raised from $25\text{-}300^\circ\text{C}$ with a heating rate of 2°C min^{-1} and held at this temperature for 2 hours. After the conversion process, the furnace was allowed to cool down to room temperature under Ar. The loading for FeP was determined to be 0.9 mg/cm^2 .

Material characterization:

XRD data were collected on X-ray diffractometer (Philip Company, Pw1730) equipped with a Cu $K\alpha$ radiation ($\lambda=1.5418\text{ \AA}$). XPS data were collected on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. SEM measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20kV. TEM measurements were carried out on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV.

Electrochemical measurement: The FeP/CC electrodes were cut into $1 \times 1 \text{ cm}^2$ pieces and assembled in CR2025 coin cells configuration with sodium metal as counter electrodes in a glove box under argon atmosphere (O_2 and H_2O lower than 0.5 ppm). The electrolyte was 1M NaClO_4 dissolved in a mixture of polycarbonate (PC)/ethylene carbonate (EC) (1:1 by volume) with 5% fluoroethylene carbonate (FEC) by vol. as additive and a glass fiber was used as the separator. The batteries were cycled in the voltage range of 0.01-3.0 V on a battery testing system (Neware BTS-610) at room temperature ($25 \pm 2^\circ\text{C}$). Electrochemical impedance spectra (EIS) was measured on electrochemical workstation CHI660E (CH Instruments, China) in the frequency range from 100 kHz to 10 mHz with a voltage amplitude of 5 mV.

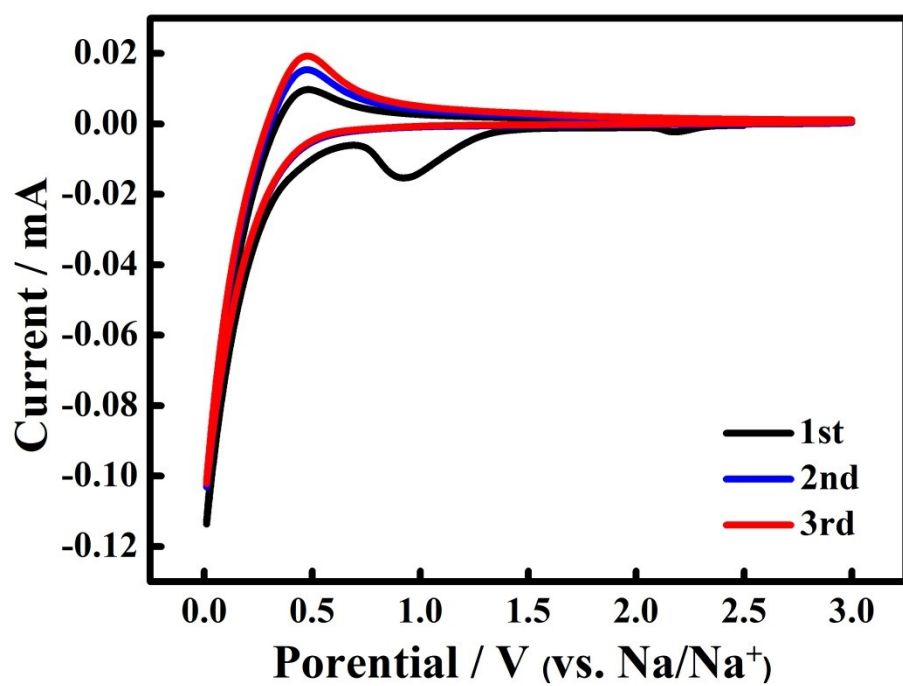


Fig. S1. CV curves of the bare carbon cloth at a rate scan of 0.2mV s⁻¹.

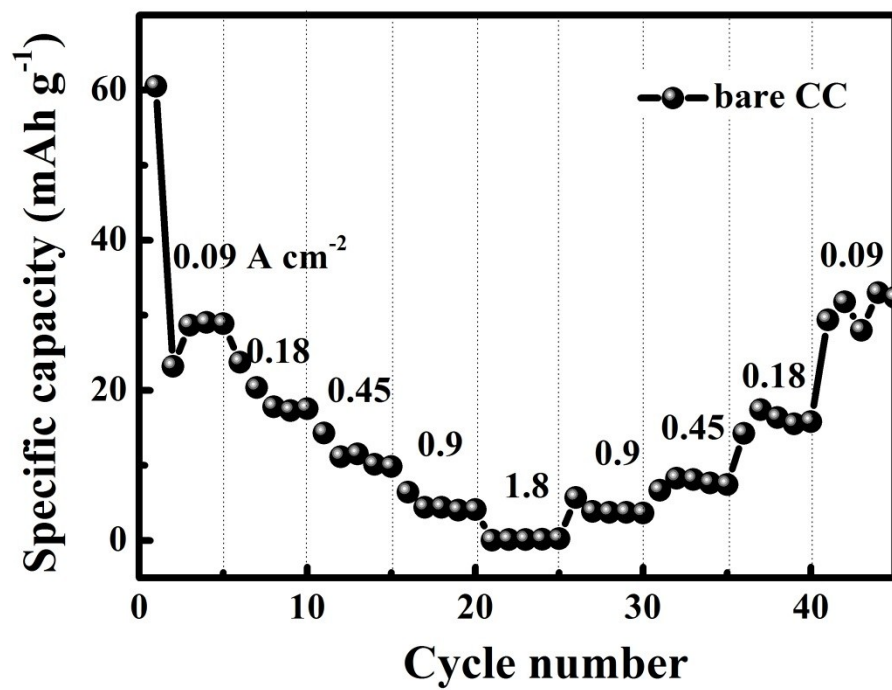


Fig. S2. Rate performance of bare CC.

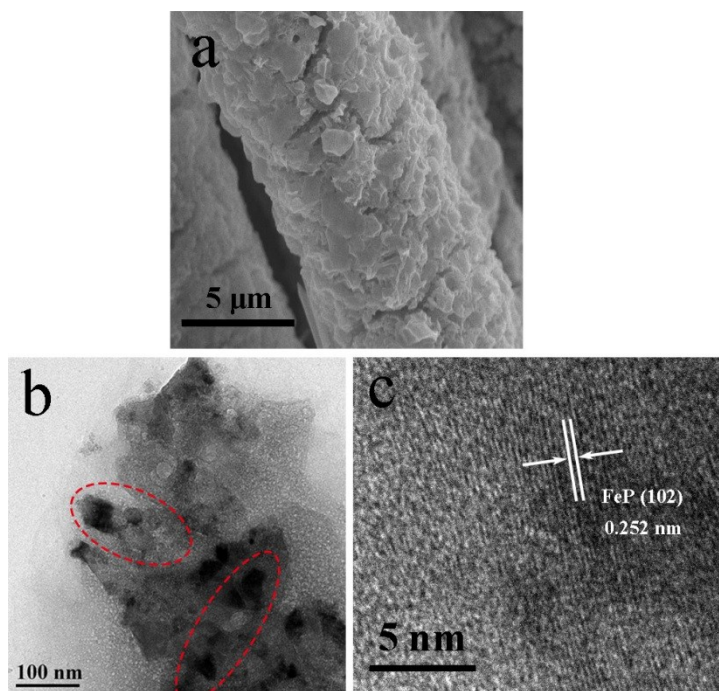


Fig. S3. SEM, TEM, and HRTEM images of FeP NAs/CC after long-term cycling test.
(a) SEM, (b) TEM, and (c) HRTEM.

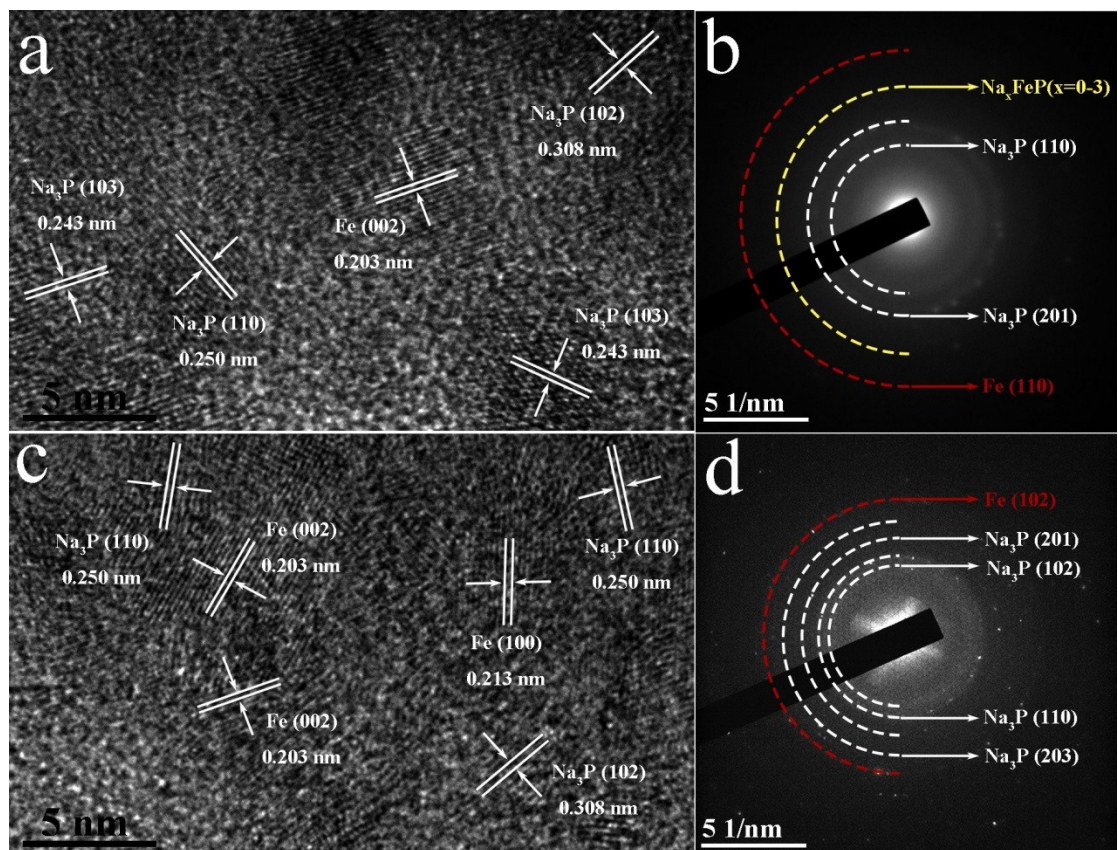


Fig. S4. HRTEM and SAED images of FeP NAs/CC electrode at different discharge stages in SIBs. (a,b) Initial discharge to 0.9 V, and (c,d) initial discharge to 0.01 V.

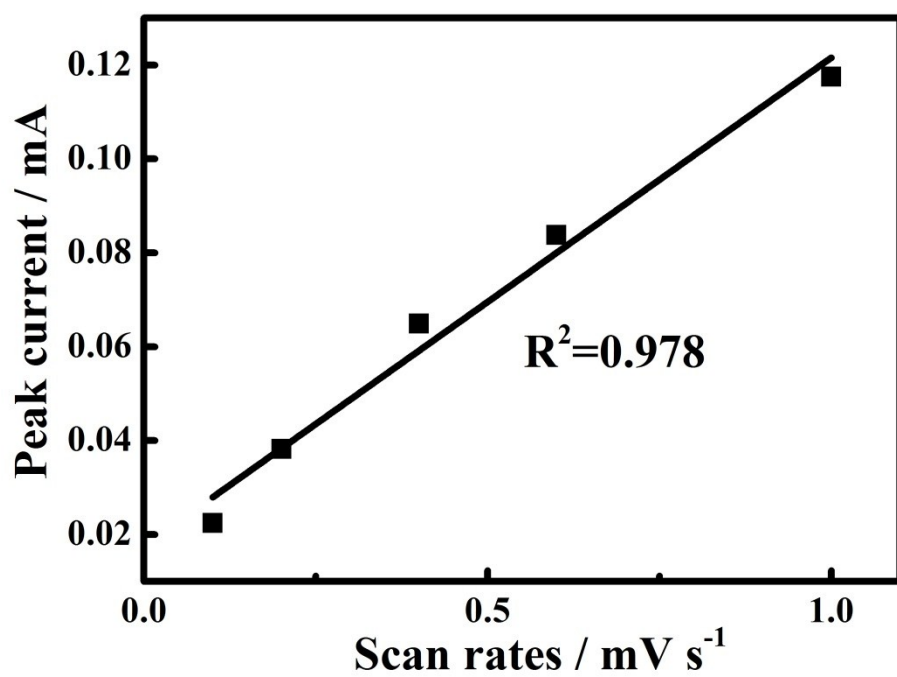


Fig. S5. Relationship between the oxidation peak current and scanning rates.

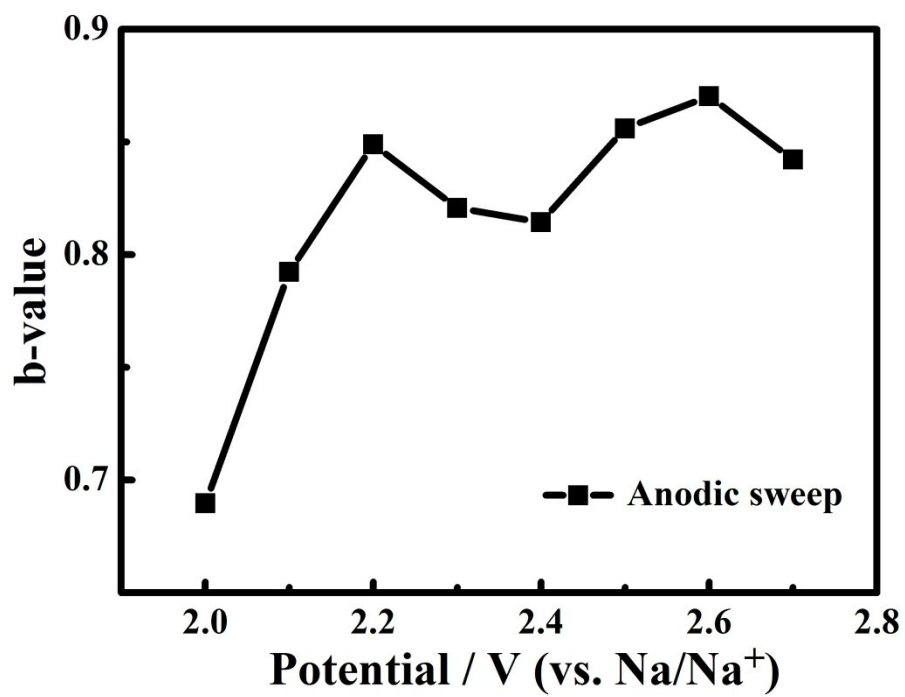


Fig. S6. b-values for electrode as a function of potential for anodic sweeps.

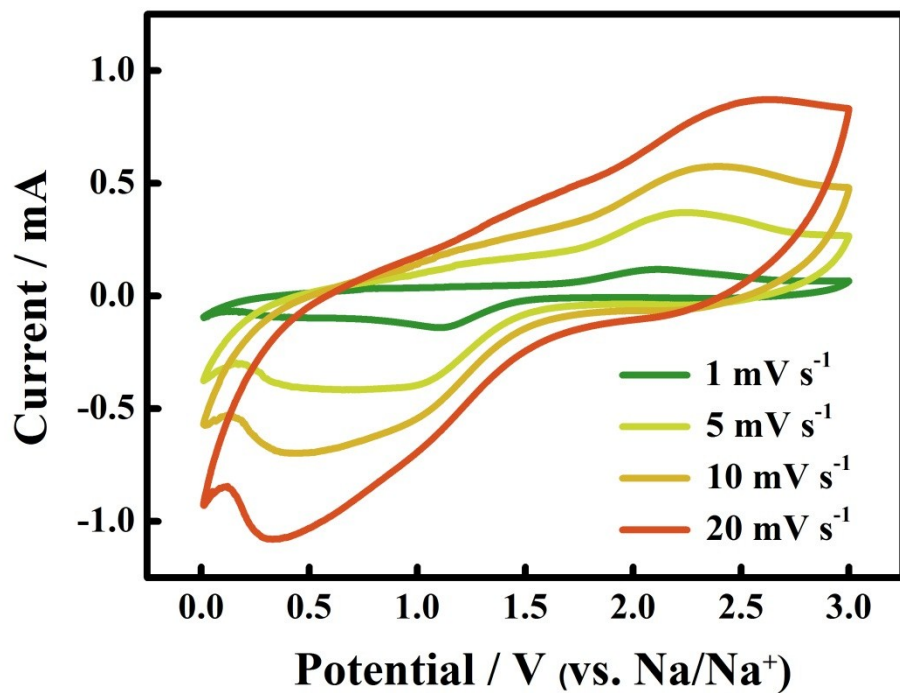


Fig. S7. CV curves of FeP NAs/CC electrode at different scan rates (1-20 mV s⁻¹).

Table S1. Electrochemical performance of FeP NAs/CC and reported FeP anode in sodium-ion batteries.

Nanostructures	Current density (A g⁻¹)	Capacity (mAh g⁻¹)	Cycle number	Ref.
FeP NAs/CC	0.2	548	100	This work
	0.1	766	-	
	2	110	500	
Hollow FeP@carbon nanocomposite	0.1	436	100	1
	1.6	237	50	
CNT@FeP@C	0.1	415	100	2
	0.2	391	-	
	0.5	295	500	
	0.8	313	-	
FeP/graphite	0.05	240	70	3
FeP particle	0.05	321	60	4
FeP ₄	0.089	1100	30	5
C-FeP	0.1	184	200	6
FeP@rGO	0.1	388	250	7

References

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