Supporting Information

$Na_4Fe_7(PO_4)_6$: A zero-strain iron-based polyanionic cathode for sodium-ion batteries

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Experimental details

Material Preparation

$Na_4Fe_7(PO_4)_6$/C microspheres were prepared by a simple spray-dry method. Typically, stoichiometric amounts of 1.2481 g of $NaH_2PO_4 \cdot 2H_2O$, 0.4601 g of $NH_4H_2PO_4$, 5.656 g of $Fe(NO_3)_3 \cdot 9H_2O$ and 1.3075 g of $C_6H_8O_7 \cdot H_2O$ were dissolved in 30 mL of deionized water followed by vigorous stirring to form transparent solution. Then the final solution was spray-dried to form a solid precursor. Sebquently, the precursor was heated in Ar atmosphere at 600 °C for 12 h with a heating rate of 2 °C min^{-1} to obtain the $Na_4Fe_7(PO_4)_6$/C microspheres (denoted NFP/C).

Materials characterization

XRD measurements were performed on a Bruker AXS diffractometer (D8 Advance) using Cu Kα radiation at λ = 1.54 Å. The Rietveld refinement was carried out using the Palleysoftware. SEM test were carried out on a Histachi S-4800 scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Kratos XSAM800 Ultra Spectrometer. Raman spectroscopic analysis was performed with a Confocal Raman Microspectroscopy (Renishaw, UK) system utilizing a 514.5 nm incident radiation in the range from 400 to 2000 cm^{-1}. The calcination temperature was certified by TG, DTG and DTA at a heating rate of 10 °C min^{-1} in Ar atmosphere from 40 to 680 °C, and the carbon content was also determined by TG at 10 °C min^{-1} from 30 to 750 °C (TA 449 F3, USA). Fourier transformed infrared spectroscopy (FTIR) was performed on a Nicolet Avatar 360 FTIR (Thermo electro, USA).

Electrochemical measurements

The obtained NFP/C composite was mixed with Super P, and poly (vinylidene fluoride) (PVdF) in a mass ratio of 8:1:1, the mixture was dispersed in N-methyl-2-pyrrolidone (NMP) to form homogeneous slurry. Later, the slurry was pasted on Al foil and dried at 80 °C for 10 h in a vacuum oven. The electrode loading was about 1.5 mg cm^{-2}, and the electrode area was 1.44 cm^2. Electrochemical tests were performed using coin cells with the above electrode as cathode and Na metal as a counter electrode. The electrolyte was 1 mol L^{-1} $NaClO_4$ dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and Fluoroethylene carbonate (FEC) (1:1:0.05 by wt., Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd. China), and the separator was a microporous membrane (Celgard 2325). The coin cells (CR2032) were fabricated in an argon-filled glove box with water/oxygen content lower than 0.1 ppm and galvanostaticly charged/discharged with a CT2001A (Land Wuhan, China) battery tester. The charge/discharge capacities presented in this work were calculated on the mass of NFP. Cyclic voltammetric measurements were also conducted with the coin cell on a Corrtest 350Helectrochemical workstation (Correst, China).

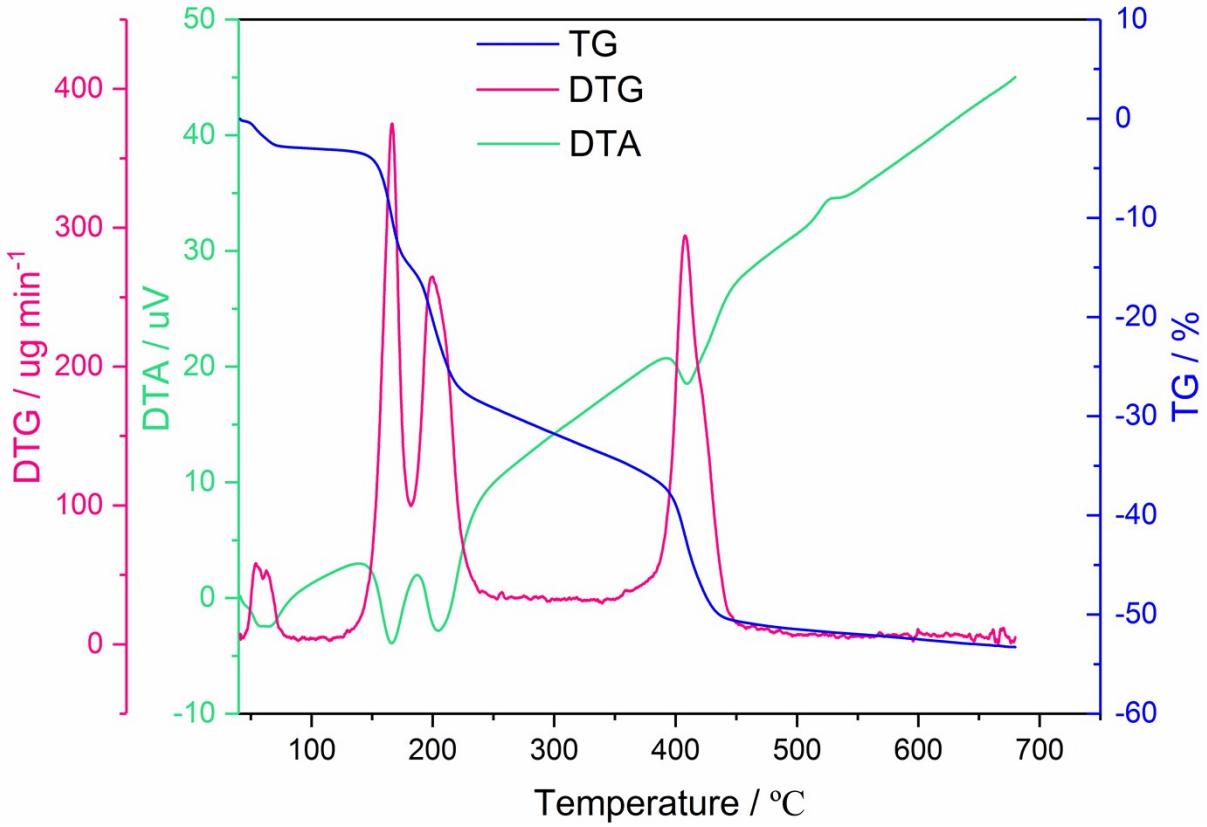

Fig. S1 Thermogravimetric Analysis (TG) and Differential Thermal Analysis (DTA) of raw materials in Ar atmosphere.

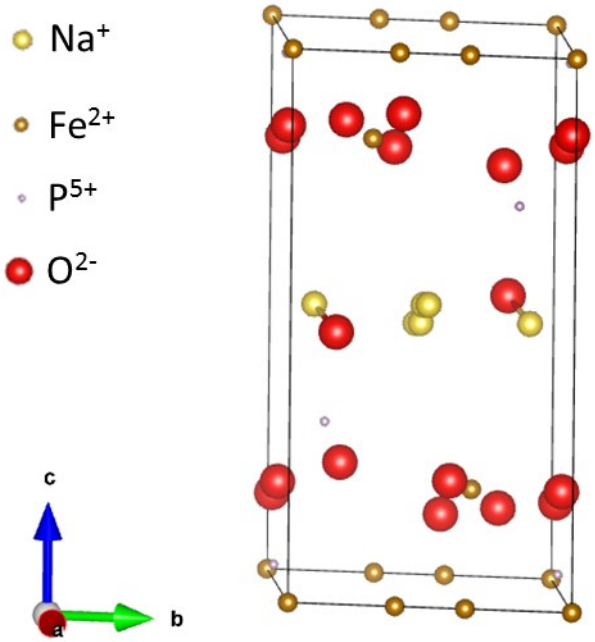

Fig. S2 Structure view of $Na_4Fe_7(PO_4)_6$ along the *a* axis.

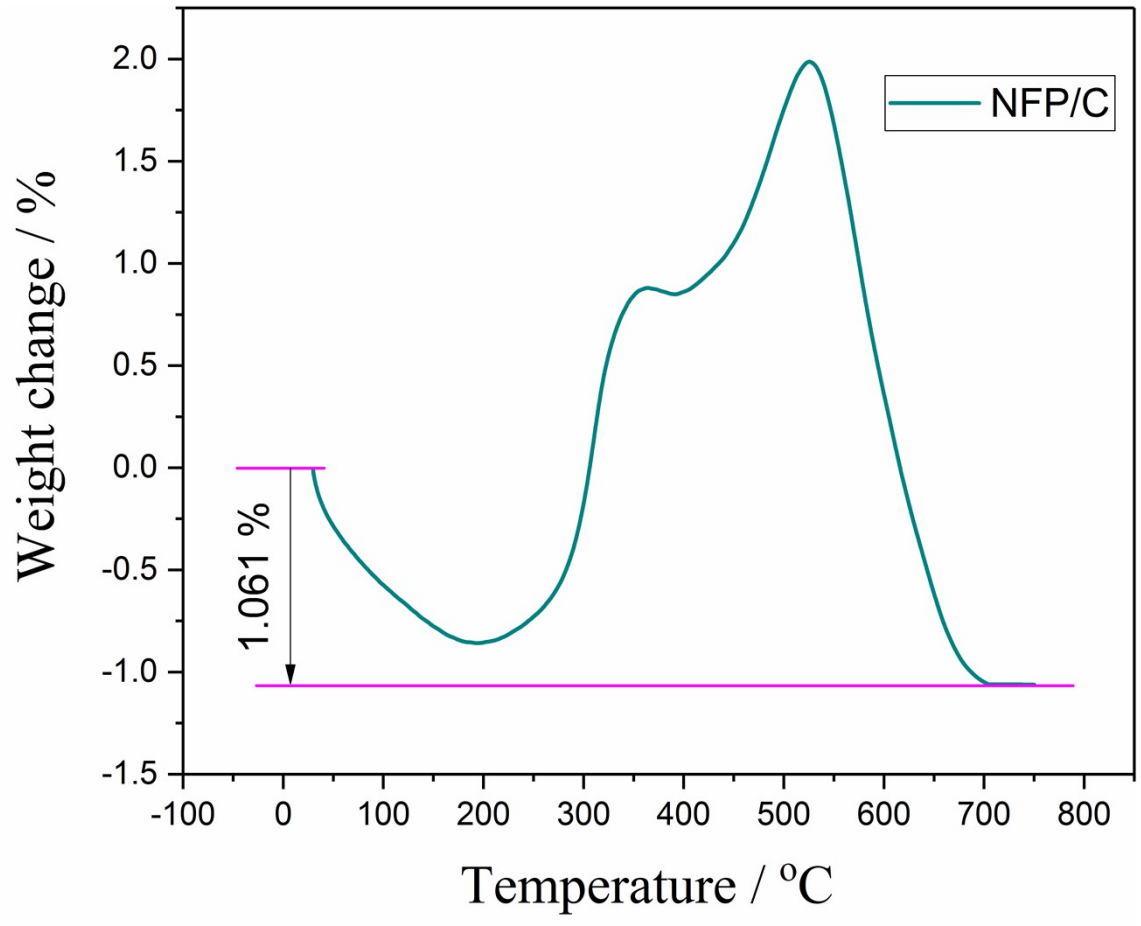

Fig. S3 Thermogravimetric Analysis (TG) of final NFP/C in air.

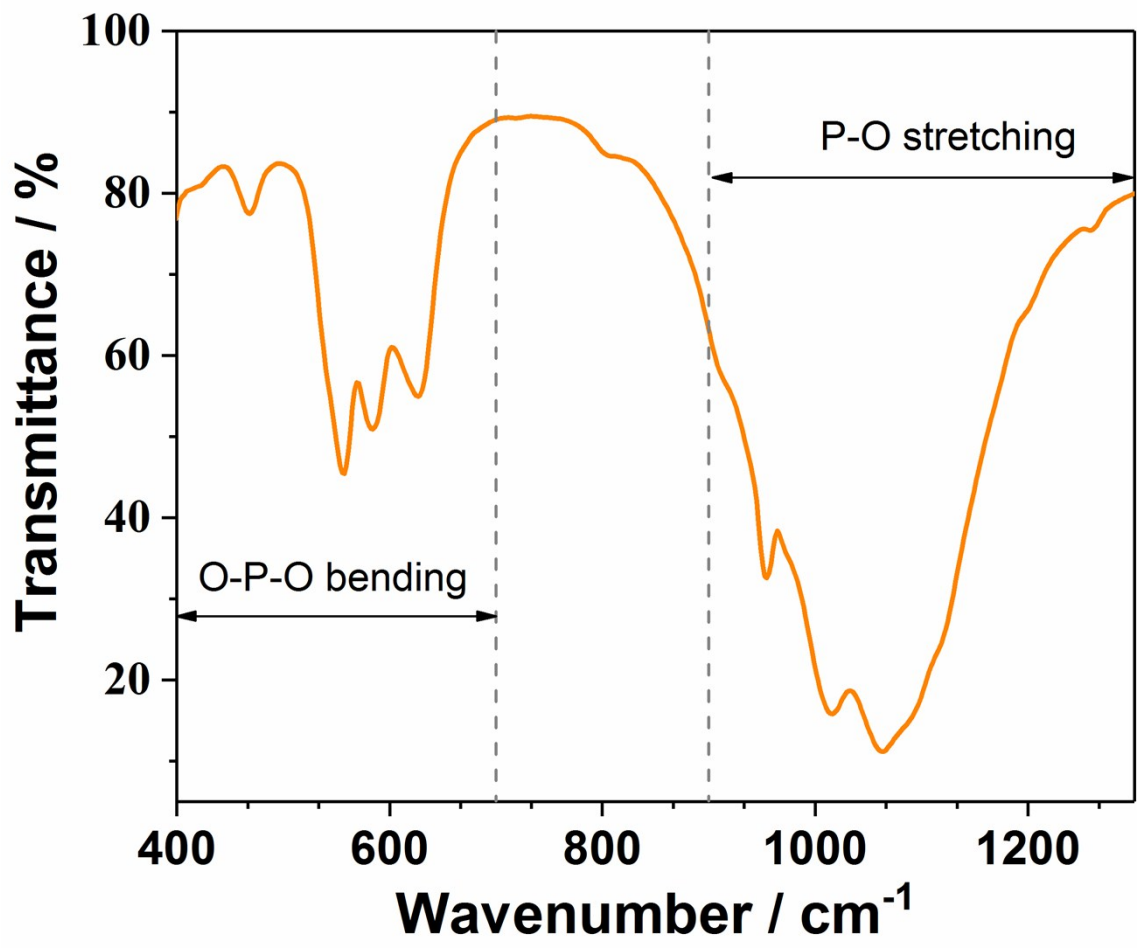

Fig. S4 The FTIR specrum of NFP/C showing various bands stemming from PO_4 tetrahedra.

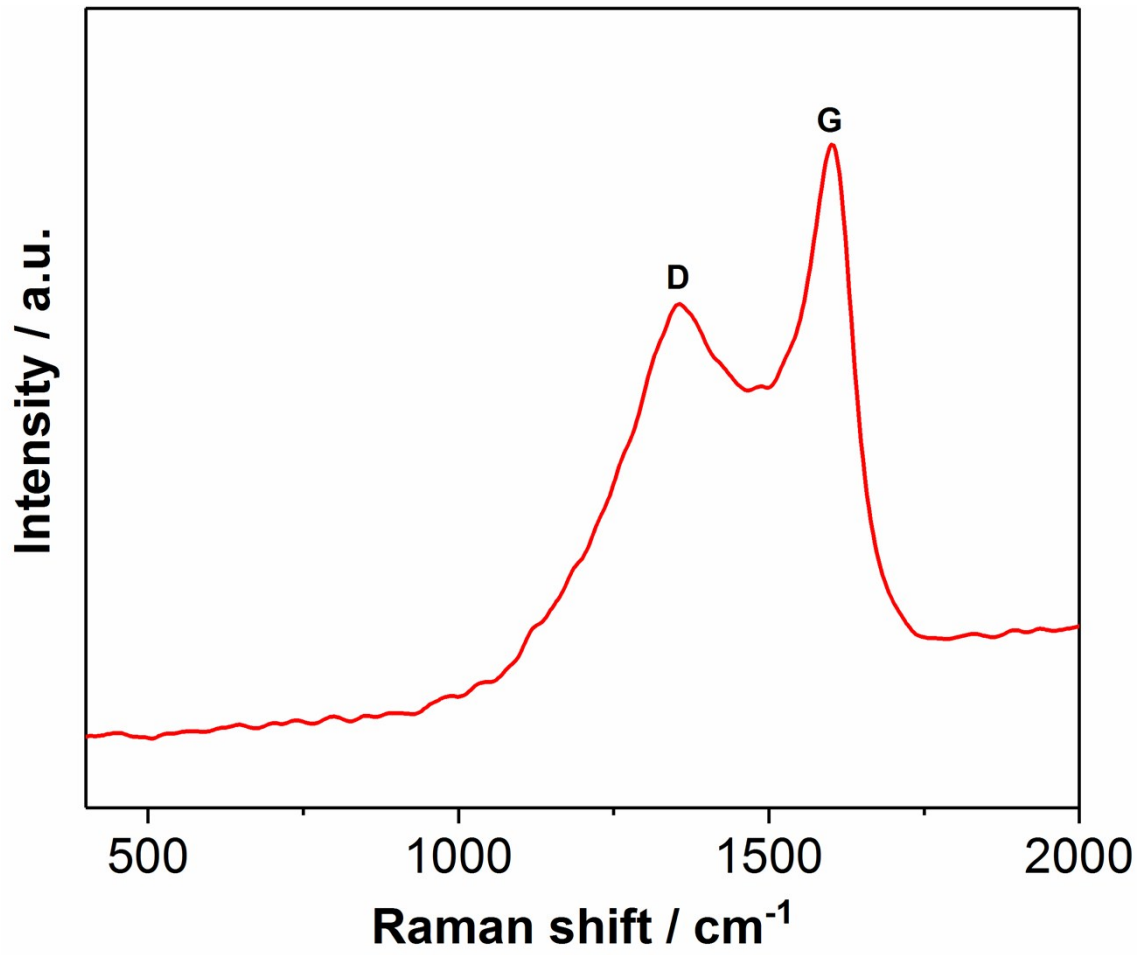

Fig. S5 The Raman spectrum of NFP/C showing the information of carbon coating.

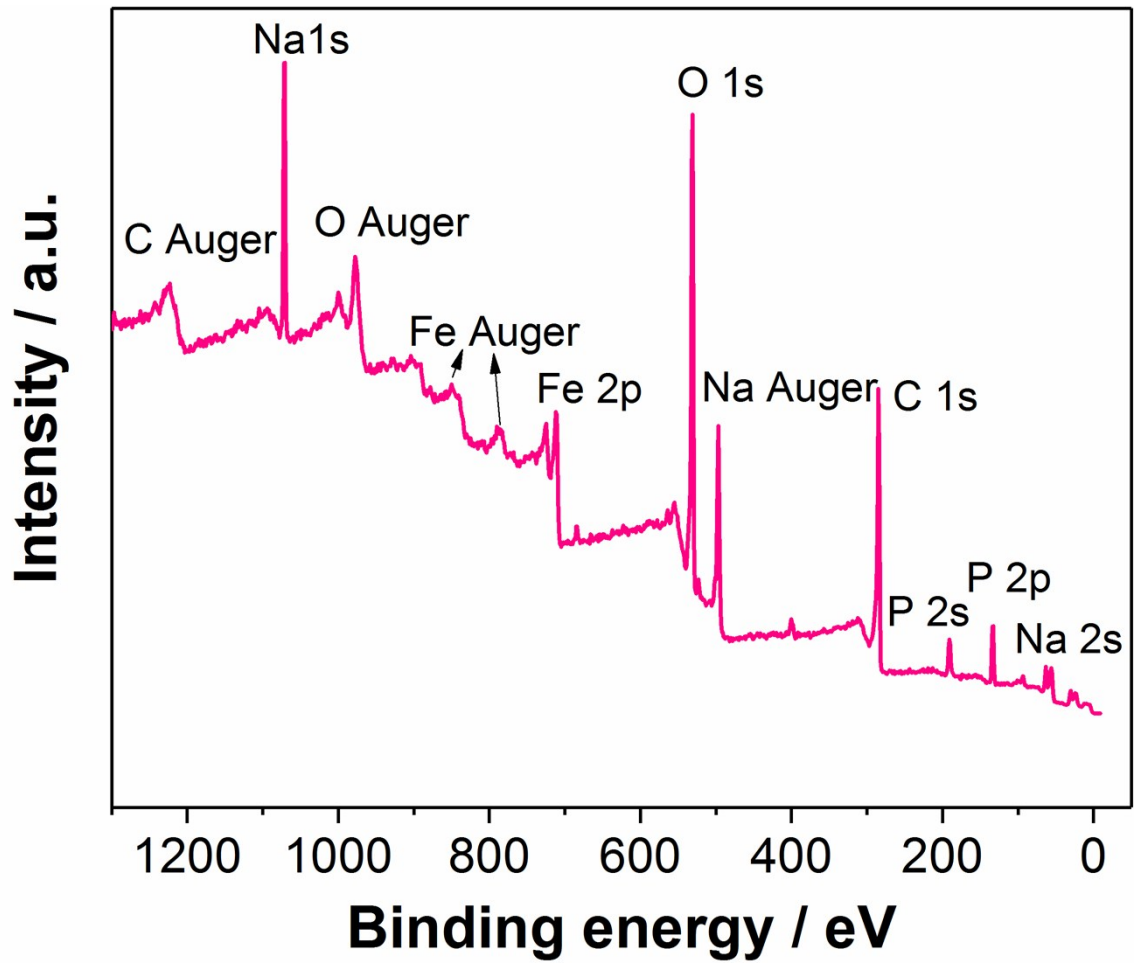

Fig. S6 The full X-ray photoelectron spectroscopy (XPS) spectrum of NFP/C.

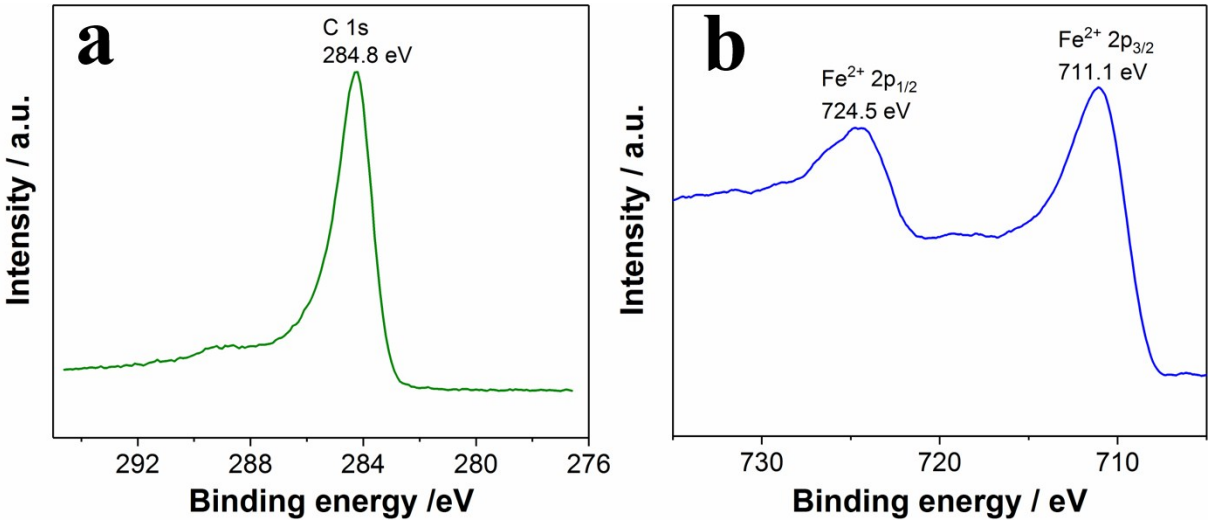

Fig. S7 The XPS spectra of (a) C 1s and (b) Fe 2p of the NFP/C.

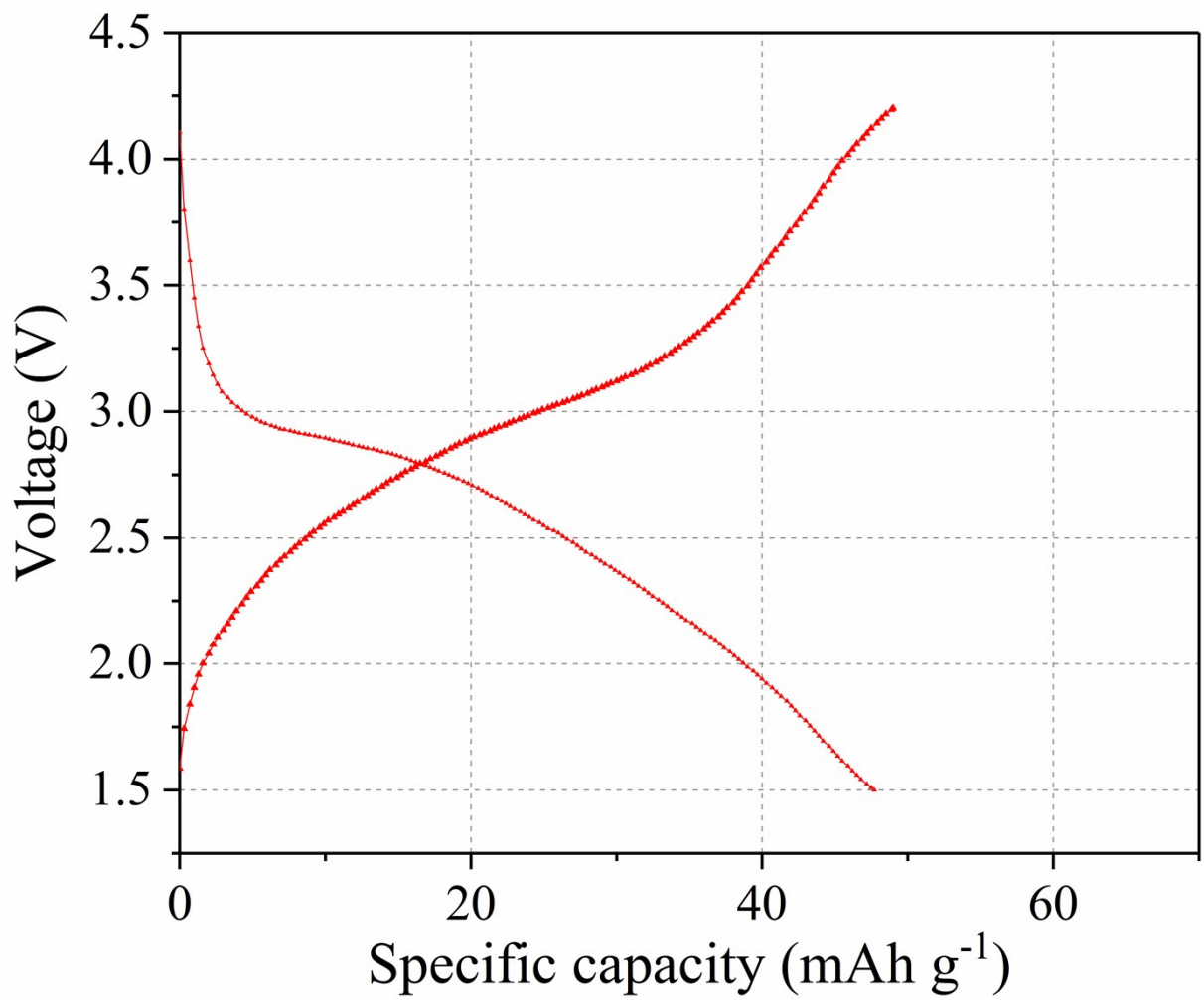

Fig. S8 The galvanostatic charge/discharge profiles at a current density of 200 mA g^{-1}.

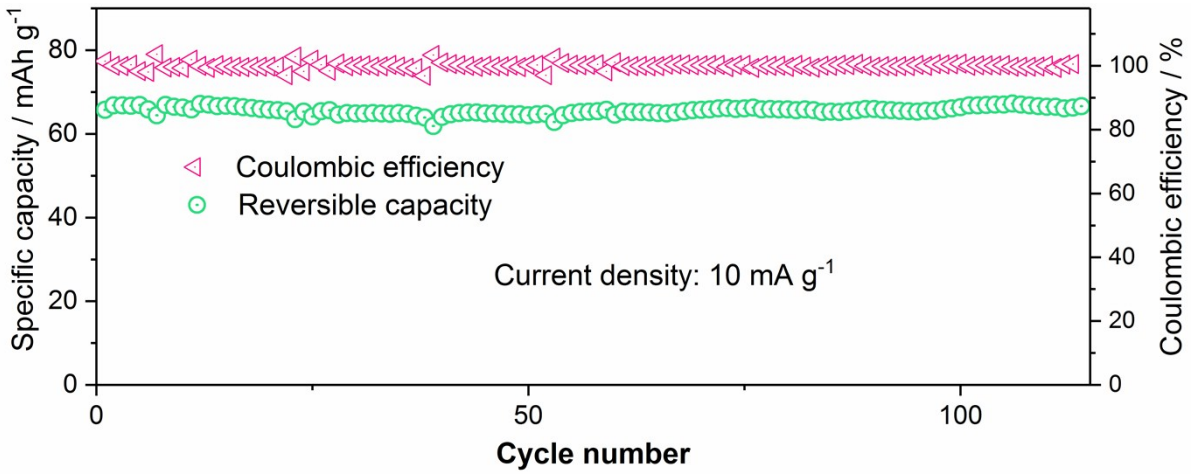

Fig. S9 Cycling performance of NFP/C electrode at 10 mA g^{-1}.

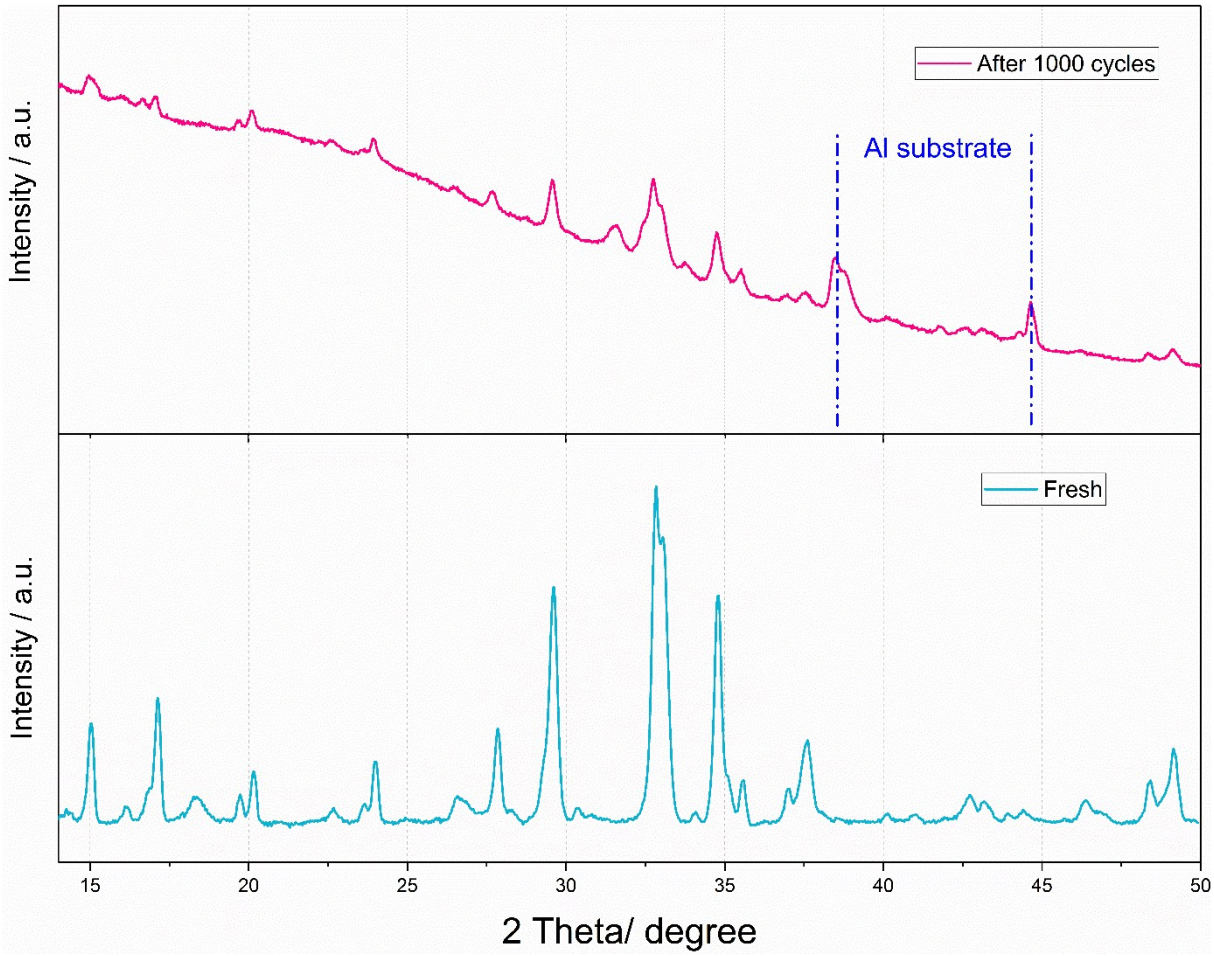

Fig. S10 XRD pattern of NFP/C after cycling test (comparing with the initial pattern).

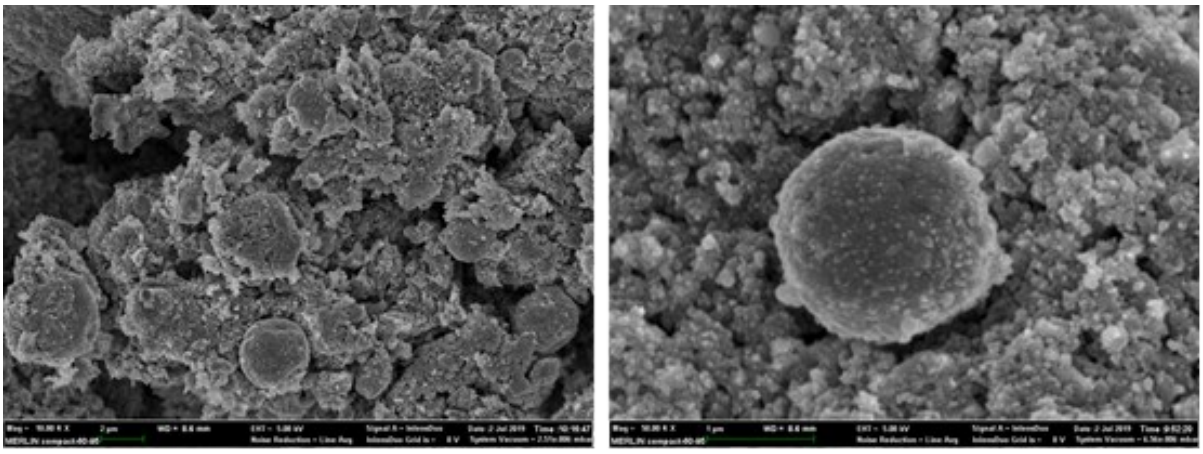

Fig. S11 SEM images of the $Na_4Fe_7(PO_4)_6$/C electrode after 500 cycles.

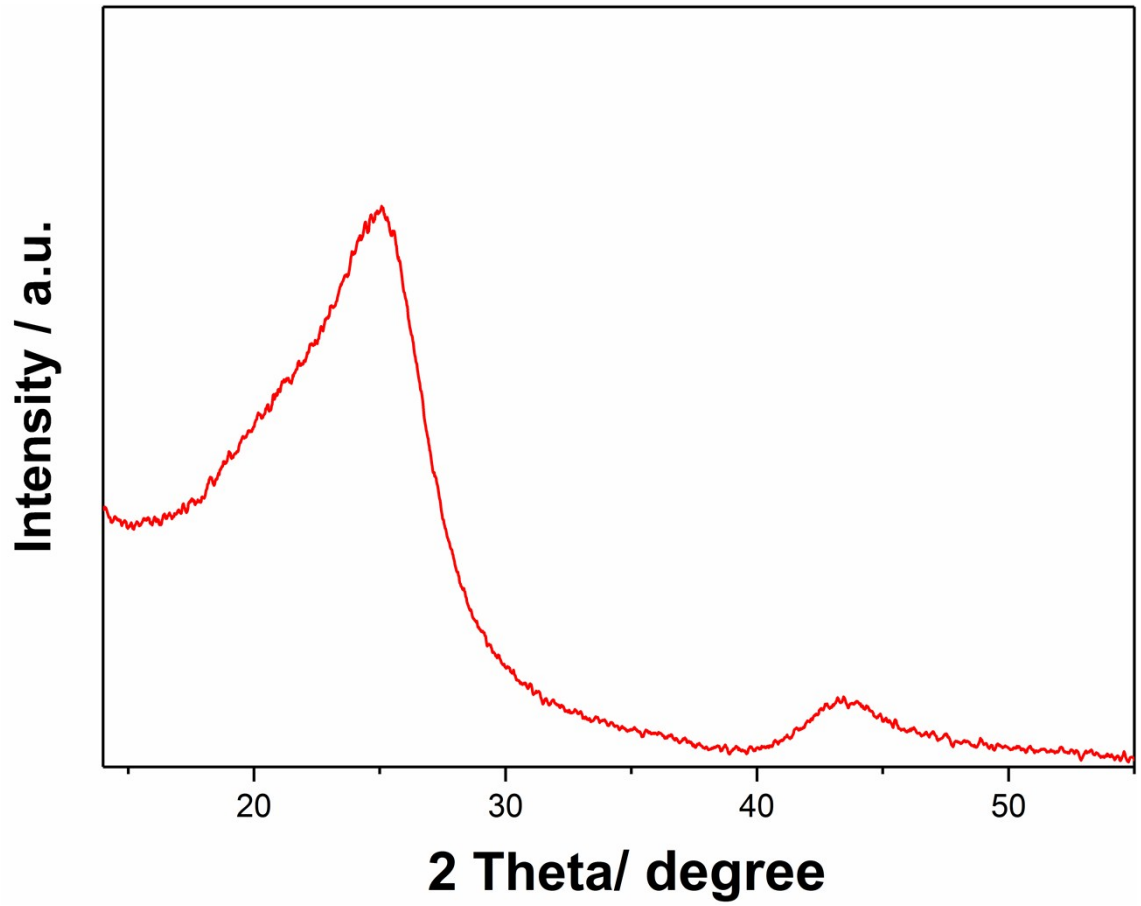

Fig. S12 XRD pattern of super P.

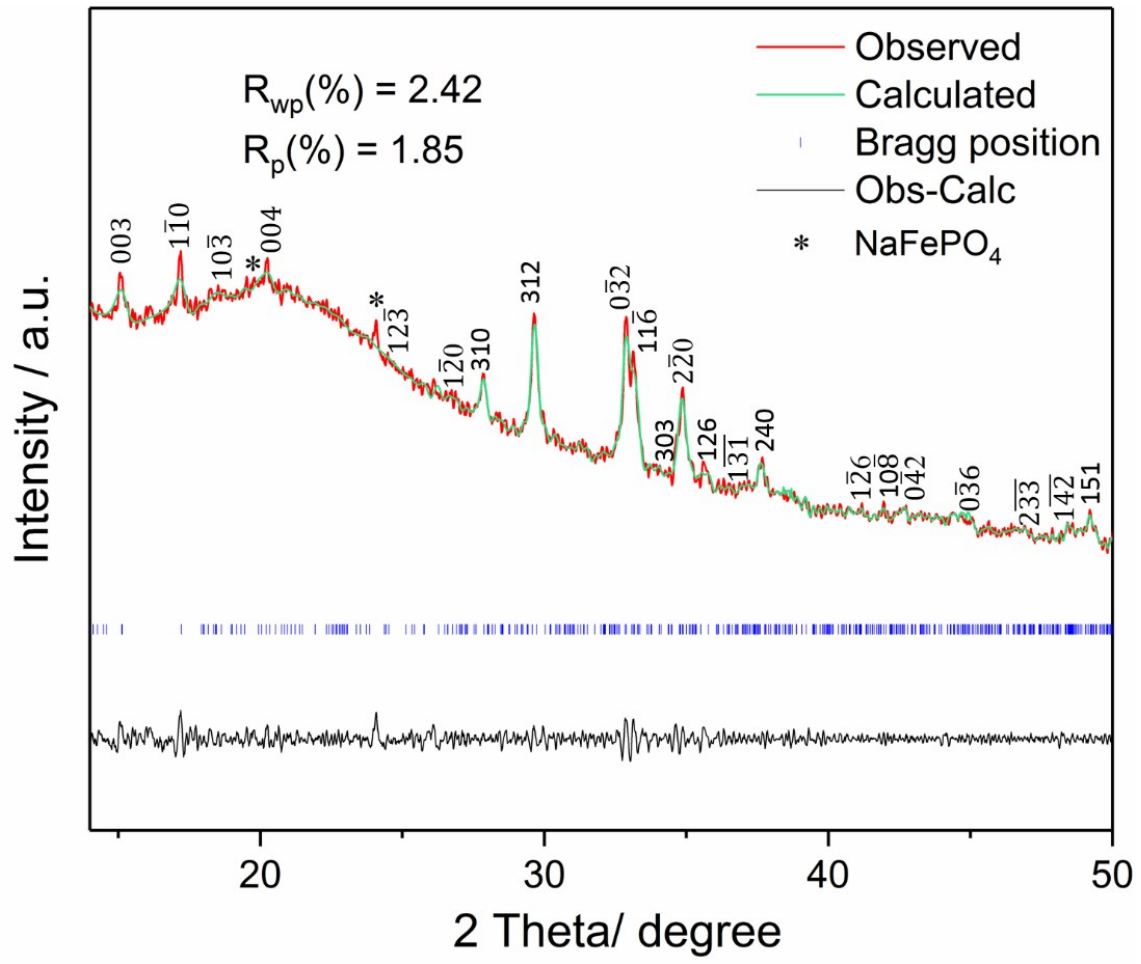

Fig. S13 Rietveld refinement of X-ray diffraction patterns of NFP/C at 4.2 V. (Desodiation state).