

## Supporting Information

### Understanding air sensitivity and deterioration mechanism of

### $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ Cathode for Na-Ion Battery

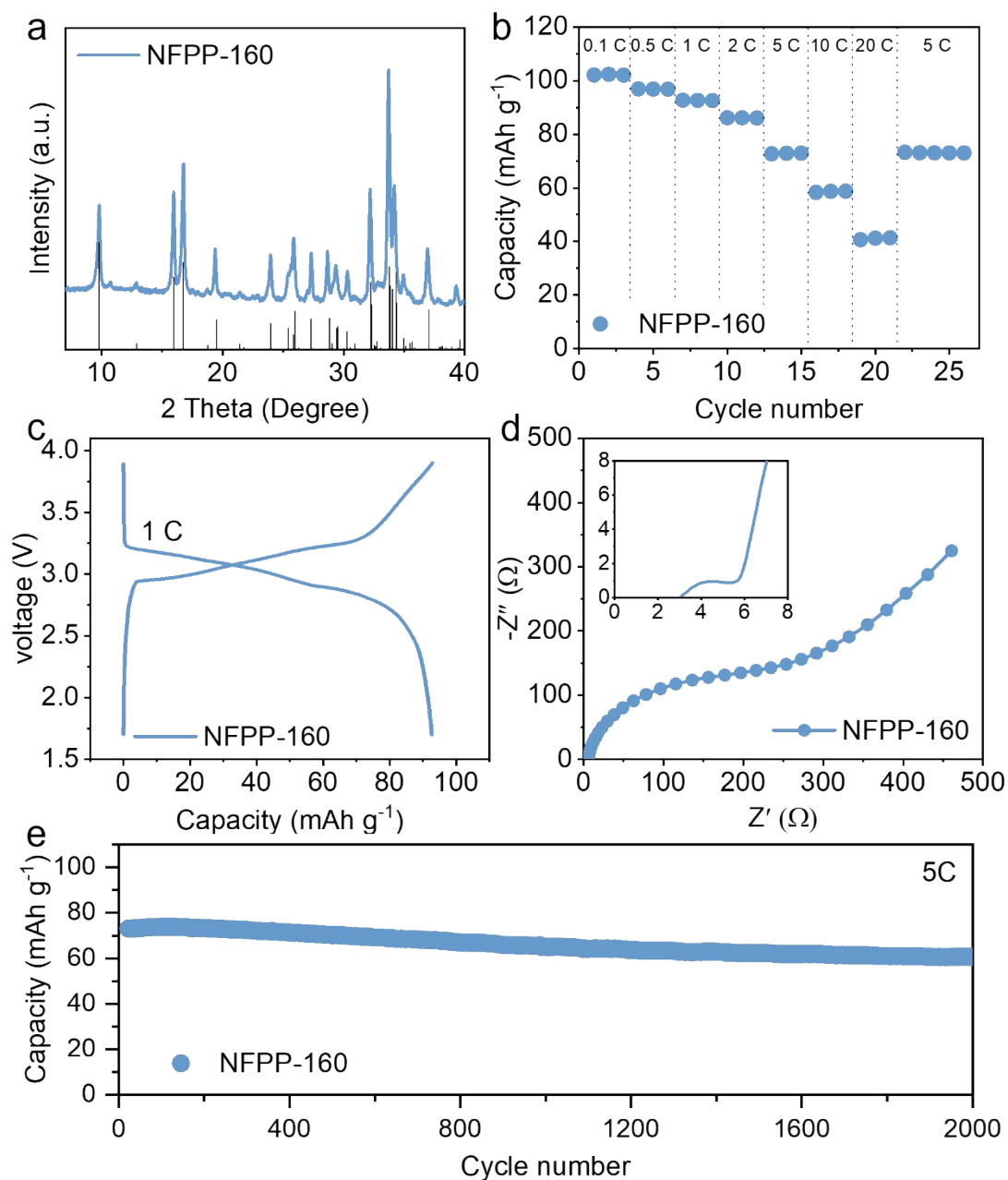
Xinyu Li,<sup>a</sup> Sheng Dai,<sup>a</sup> Qinlong Chen,<sup>a</sup> Hongyan Mao,<sup>a</sup> and Huilin Pan<sup>\*ab</sup>

<sup>a</sup>Department of Chemistry, Zhejiang University, Hangzhou, 310058, China

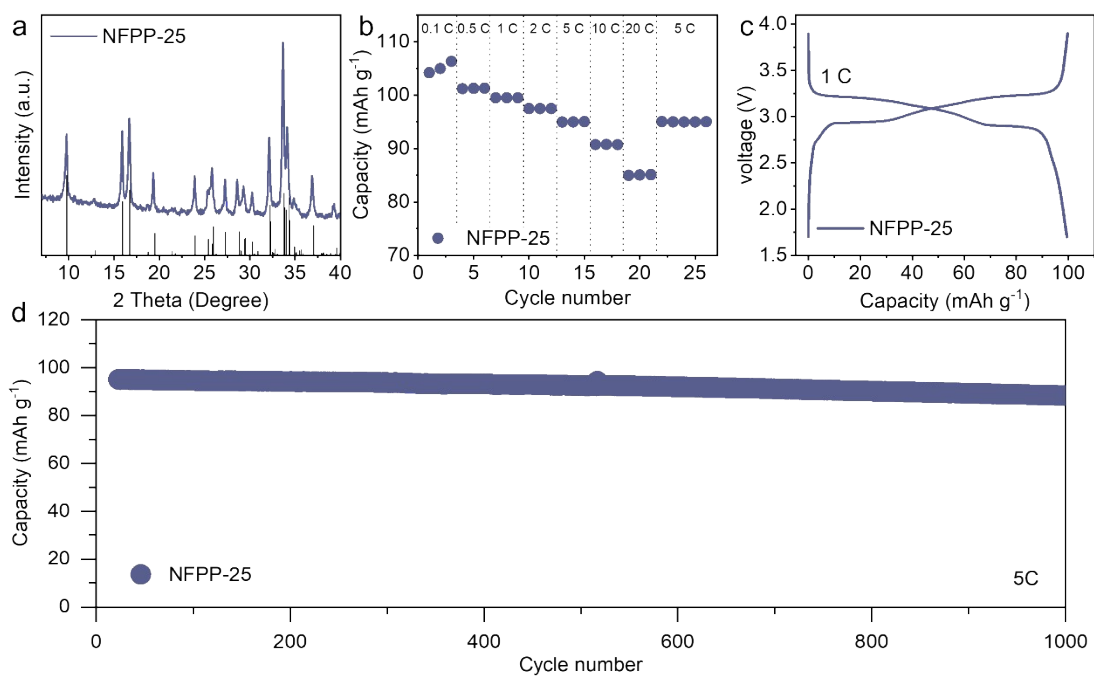
<sup>b</sup>State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou,

310012, China

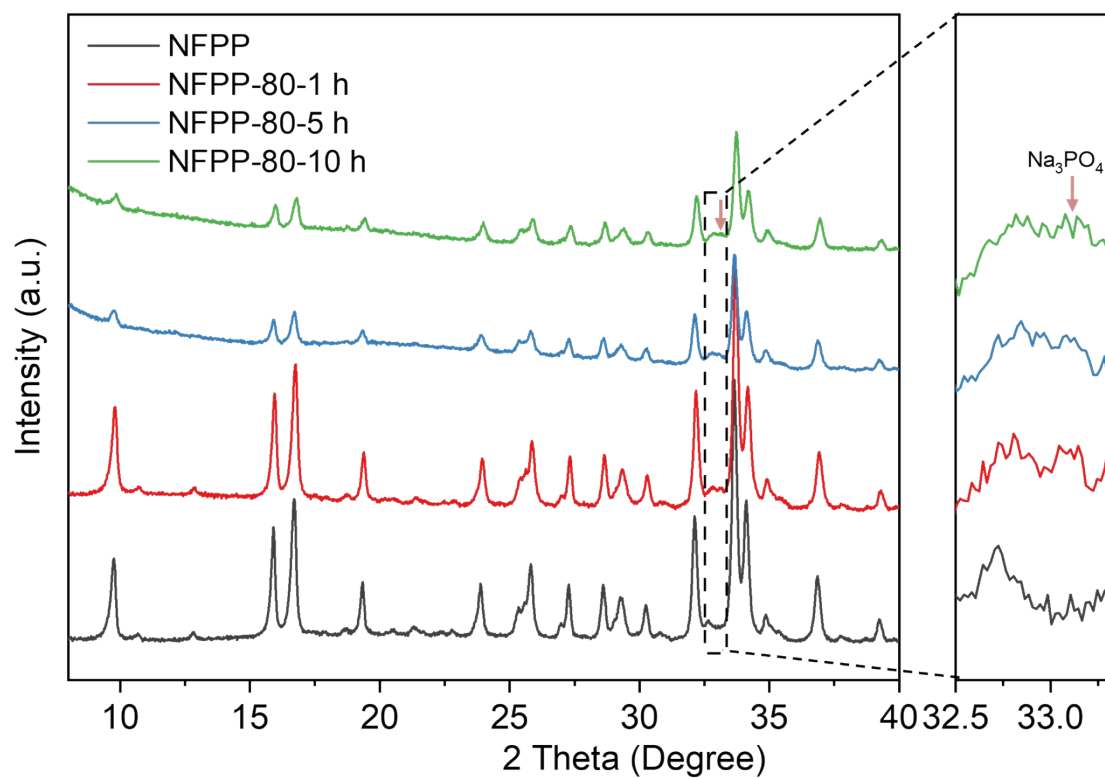
\*Corresponding authors: Huilin Pan (panhuilin@zju.edu.cn)



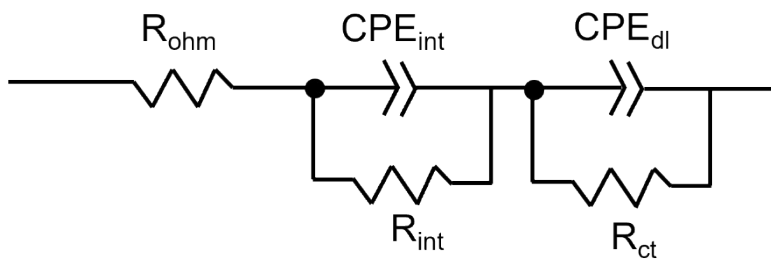
**Fig. S1** (a) X-ray diffraction patterns of NFPP-160. (b-e) Electrochemical performance of NFPP-160 in Na||NFPP half cells. (b) Rate performance. (c) Charge-discharge profiles at 1 C at the 3<sup>rd</sup> cycle. (d) EIS profiles at 5 C at the 1<sup>st</sup> cycle. (e) Long-term cycling performance at 5 C.



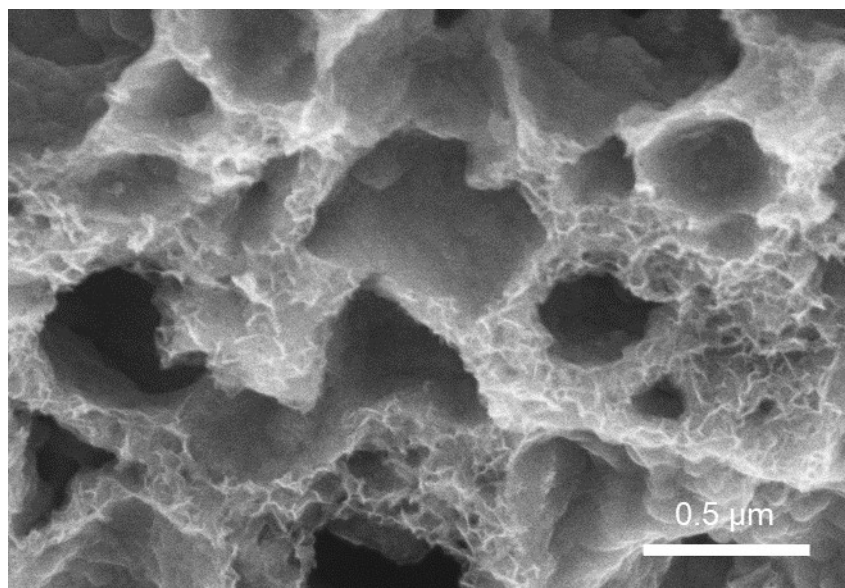
**Fig. S2** (a) X-ray diffraction patterns of NFPP-25. (b-d) Electrochemical performance of NFPP-25 in Na||NFPP half cells. (b) Rate performance. (c) Charge-discharge profiles at 1 C at the 3<sup>rd</sup> cycle. (d) Long-term cycling performance at 5 C.



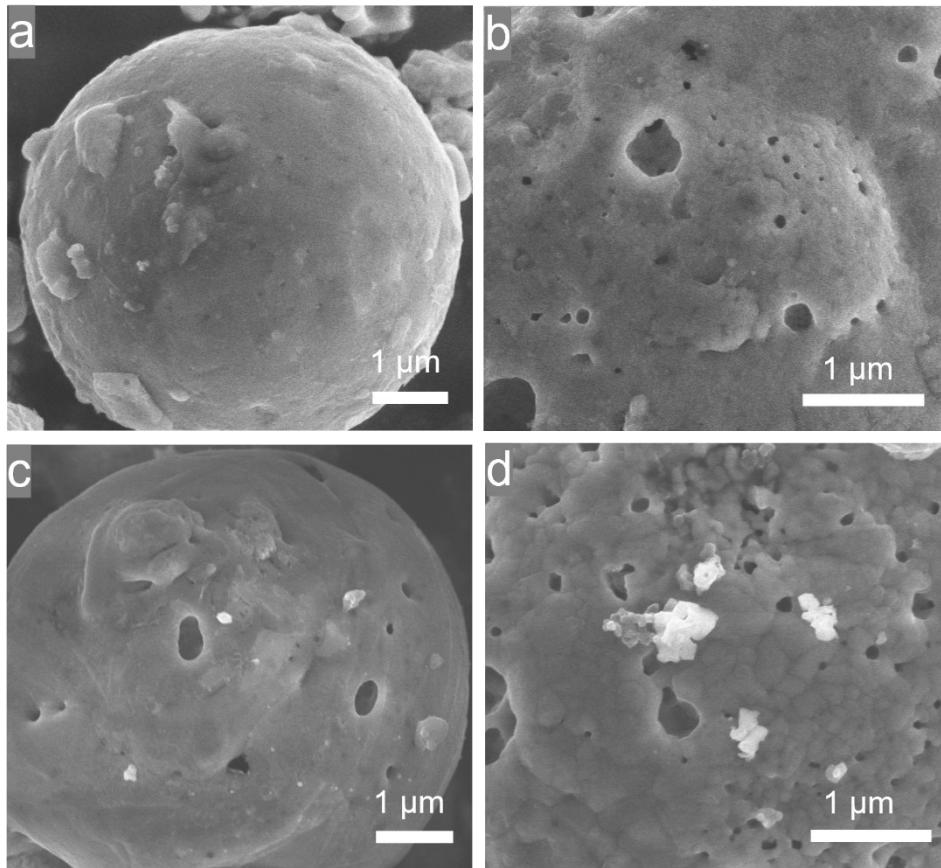
**Fig. S3** XRD patterns of pristine NFPP, NFPP-80-1h, NFPP-80-5 h and NFPP-80-10 h.



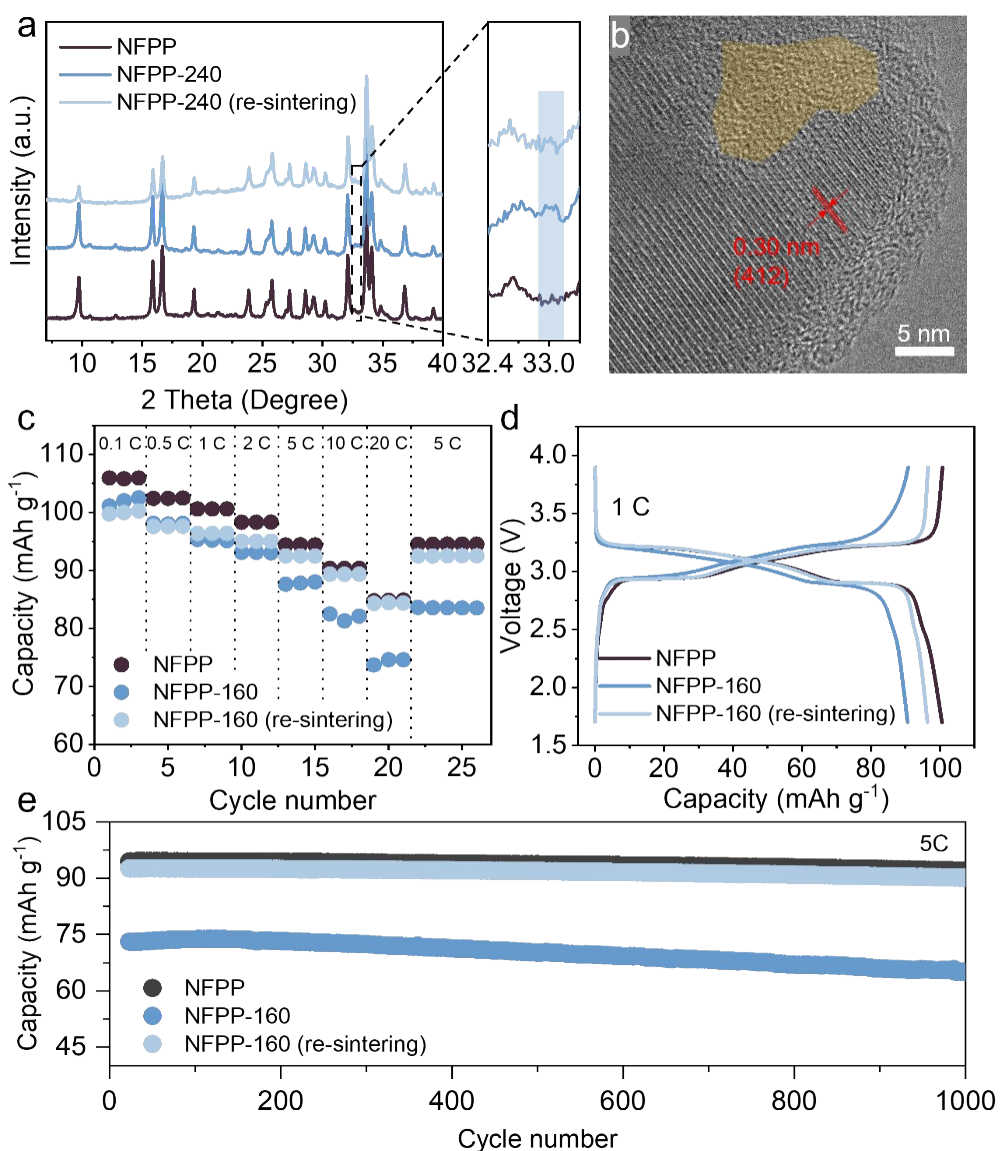
**Fig. S4** The proposed equivalent circuit for Na||NFPP half cell. Constant phase element (CPE) is used in the model in place of a capacitor to compensate for non-ideal behavior of electrode.  $R_{int}/CPE_{int}$  is the interphase contact resistance and its related capacitance in the cathode electrode bulk.  $R_{ct}/CPE_{dl}$  is the charge-transfer resistance and its related capacitance.



**Fig. S5** SEM image of NFPP-25 °C water sample.

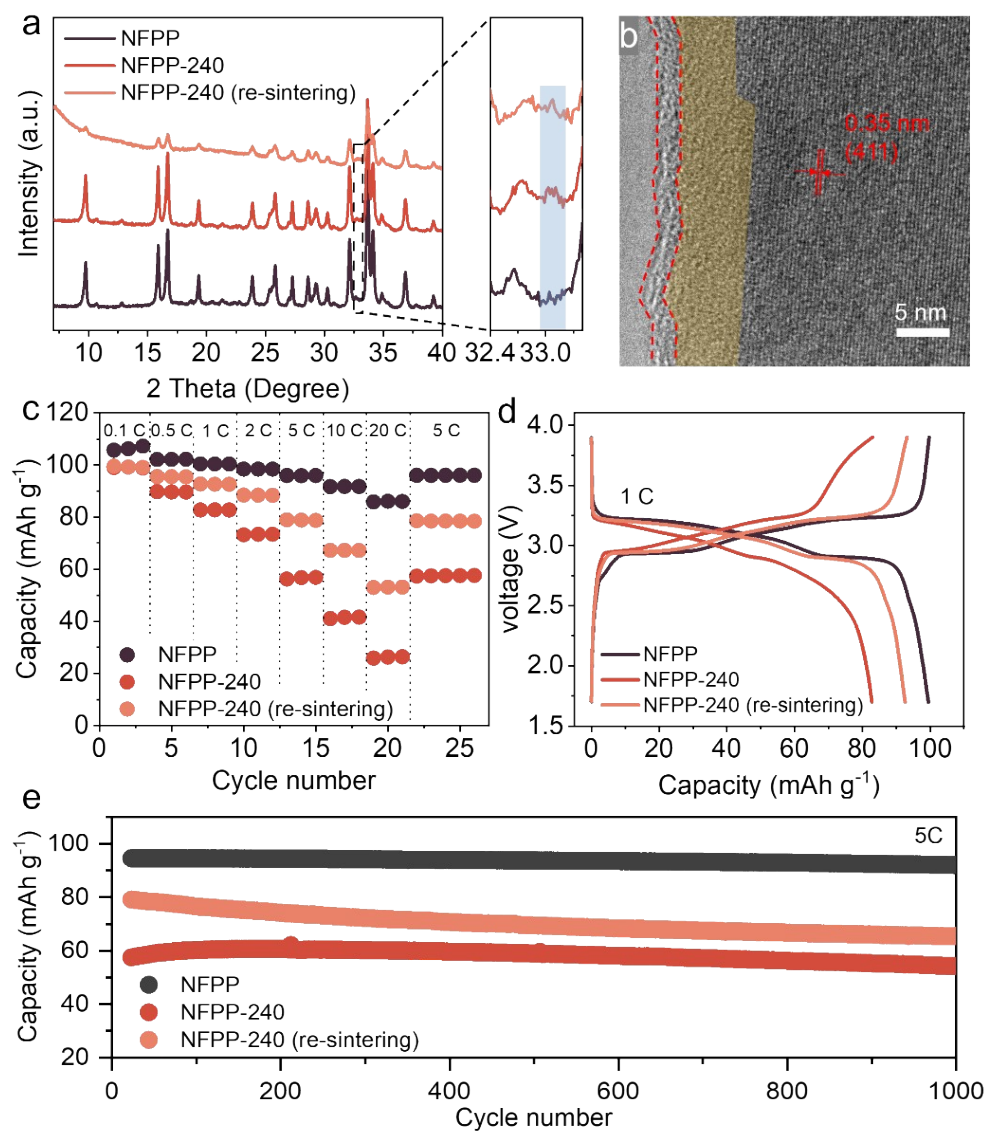


**Fig. S6** SEM images of re-sintering sample; (a-b) NFPP-80 (re-sintering); (c-d) NFPP-240 (re-sintering).



**Fig. S7** (a) XRD patterns of NFPP, NFPP-160 and NFPP-160 (re-sintering). (b) HRTEM image of NFPP-160 (re-sintering). (c-e) Electrochemical performance of NFPP-160 sample before and after re-sintering in half cells: (c) Rate performance. (d) Charge and discharge profiles at 1 C at the 3<sup>rd</sup> cycle. (e) Cycling performance at 5 C.





**Fig. S8** (a) XRD patterns of NFPP, NFPP-240 and NFPP-240 (re-sintering). (b) HRTEM image of NFPP-240 (re-sintering). (c-e) Electrochemical performance of NFPP-240 sample before and after re-sintering in half cells: (c) Rate performance. (d) Charge and discharge profiles at 1 C at the 3<sup>rd</sup> cycle. (e) Cycling performance at 5 C.

**Table S1** EIS analysis results. The Ohmic resistance ( $R_{\text{ohm}}$ ), interface resistance ( $R_{\text{int}}$ ) and charge-transfer resistance ( $R_{\text{ct}}$ ) of NFPP samples exposed in air at different temperatures at 5 C at the 1<sup>st</sup> cycle.

Sample	$R_{\text{ohm}}$ ( $\Omega$ )	$R_{\text{int}}$ ( $\Omega$ )	$R_{\text{ct}}$ ( $\Omega$ )
NFPP	3.250	1.160	0.9302
NFPP-80	2.948	1.992	229.3
NFPP-160	3.053	2.661	277.0
NFPP-240	2.854	2.137	356.9

**Table S2** ICP-MS raw data of the filtrate.

Samples	Concentration of Na element (ng mL <sup>-1</sup> )	Concentration of Fe element (ng mL <sup>-1</sup> )	Concentration of P element (ng mL <sup>-1</sup> )
Blank	406.68	0.15	<0.000
NFPP-25 °C water	298279.16	61489.65	191410.62
NFPP-80 °C water	448190.25	201249.98	368744.97

The results have all undergone background correction and the volume of the filtrate is 10 mL. We can determine the total amounts of Na, Fe, and P elements in the filtrate, as summarizing in Table S3.

**Table S3** Total amounts of Na, Fe, P elements in the filtrate.

Samples	Na (mmol)	Fe (mmol)	P (mmol)
NFPP-25 °C water	0.1295	0.01098	0.06175
NFPP-80 °C water	0.1947	0.03594	0.1189

The total amounts of Na, Fe, P elements in 150 mg NFPP are 0.9615 mmol, 0.7212 mmol, and 0.9615 mmol, respectively. Dividing the data in Table S3 by the total content of the corresponding element in the NFPP gives the percentage of element extraction.