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# **Supplementary Information**

## Preparation and application of the high-performance sodium-ion

## battery cathode material Na<sub>3.6</sub>Fe<sub>2.6</sub>(PO<sub>4</sub>)<sub>1.6</sub>P<sub>2</sub>O<sub>7</sub>@CNT

### with coated dual-carbon.

Binghan Dai<sup>a,c</sup>, Tianming Lu<sup>a,c</sup>, Jinhan Teng<sup>a</sup>, Junjie Huang<sup>a</sup>, Enmin Li<sup>a</sup>, Kaibo Zhang<sup>a</sup>, QiangWang<sup>a</sup>, Dongdong Yin<sup>a</sup>, Sicheng Liu<sup>a</sup>, Luyu Lei<sup>a</sup>, Xin Tang<sup>a,c,\*</sup>, Jing Li<sup>a,b,c,\*</sup> <sup>a</sup> State Key Laboratory of Environment-Friendly Energy Material, School of Materials and Chemistry, Engineering Research Center of Biomass Materials (Ministry of Education), Southwest University of Science and Technology, Mianyang 621010, PR China.

<sup>b</sup> Sichuan Qing Yan Super Energy Capacitor Technology Co., Ltd, Suining 629201, P R China.

<sup>c</sup> Chengdu Nacheng New Energy Technology Co., Ltd., Chengdu 610041, P R China

\* Corresponding Authors.

E-mail: taxi42175@163.com (Xin Tang)

xy13787103391@126.com

(Jing Li)

#### **Material Synthesis**

Synthesis of 1.38-NFPP: 271.48 g FePO<sub>4</sub>, 143.92 g FeC<sub>2</sub>O<sub>4</sub> $\bowtie$ 2H<sub>2</sub>O, 320.38 g Na<sub>2</sub>HPO<sub>4</sub> $\bowtie$ 2H<sub>2</sub>O, 130 g C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> $\bowtie$ H<sub>2</sub>O were mixed with 2700 mL ultrapure water. The slurry was obtained by grinding at 3000 rpm for 1 h in a sand-mill, and then the slurry was spray-drying (inlet air temperature 220 °C, outlet air temperature 105 °C) to obtain a powder precursor. Finally, the precursor was sintered at 300 °C for 3 h and 500 °C for 15 h under argon atmosphere at a heating rate of 2 °C/min to obtain dual-carbon coated Na<sub>3.6</sub>Fe<sub>2.6</sub>(PO<sub>4</sub>)<sub>1.6</sub>P<sub>2</sub>O<sub>7</sub> (denoted as 1.38-NFPP).

Synthesis of 1.38-NFPP@SP: 271.48 g FePO<sub>4</sub>, 143.92 g FeC<sub>2</sub>O<sub>4</sub> $\bowtie$ 2H<sub>2</sub>O, 320.38 g Na<sub>2</sub>HPO<sub>4</sub> $\bowtie$ 2H<sub>2</sub>O, 110 g C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> $\bowtie$ H<sub>2</sub>O, and 20 g SP were mixed with 2700 mL ultrapure water. The slurry was obtained by grinding at 3000 rpm for 1 h in a sand-mill, and then the slurry was spray-drying (inlet air temperature 220 °C, outlet air temperature 105 °C) to obtain a powder precursor. Finally, the precursor was sintered at 300 °C for 3 h and 500 °C for 15 h under argon atmosphere at a heating rate of 2 °C/min to obtain dual-carbon coated Na<sub>3.6</sub>Fe<sub>2.6</sub>(PO<sub>4</sub>)<sub>1.6</sub>P<sub>2</sub>O<sub>7</sub>@SP (denoted as 1.38-NFPP@SP).



Fig. S1. Rietveld refinements of (a) 1.38-NFPP; (b) 1.38-NFPP@SP.



**Fig. S2.** XPS spectra of Fe 2p of (a) 1.38-NFPP; (b) 1.38-NFPP@SP; (c) C 1s of 1.38-NFPP@SP.



**Fig. S3** The particle size distribution curves of 1.38-NFPP, 1.38-NFPP@SP and 1.38-NFPP@CNT.



**Fig. S4.** Nitrogen adsorption/desorption isotherms and pore size distribution curves of (a) 1.38-NFPP; (b) 1.38-NFPP@SP; (c) 1.38-NFPP@CNT.



Fig. S5. SEM image of (a-c) 1.38-NFPP; (d-f) 1.38-NFPP@SP.



Fig. S6. SEM image of 1.38-NFPP@CNT precursor.



Fig. S7. The  $dQ_m/dV$  curves of 1.38-NFPP, 1.38-NFPP@SP and 1.38-NFPP@CNT at 0.1C.



Fig. S8. The charge and discharge curves of (a) 1.38-NFPP; (b) 1.38-NFPP@SP; (c) 1.38-NFPP@CNT at various rates.



**Fig. S9.** The XRD patterns of 1.38-NFPP@CNT electrodes after charging and discharging at different rates.



**Fig. S10.** The XRD comparison patterns of 1.38-NFPP@CNT electrodes before and after 10000 cycles at 50 C.



Fig. S11. SEM comparison image of 1.38-NFPP@CNT electrodes (a-b) before and(c-d)after10000cyclesat50C.



**Fig. S12.** Single period diagram during (a) charging; (b) discharging of 1.38-NFPP@CNT at 0.1 C.

The calculation equation of  $D_{Na}{}^{+} \, is \, as \, follows:^{1,\,2}$ 

$$D_{Na^{+}} = \frac{4}{\pi\tau} \left(\frac{mV_{\rm m}}{MA}\right)^2 \left(\frac{\Delta E_{\rm s}}{\Delta E_{\tau}}\right)^2 \left(\tau \ll \frac{L^2}{D_{Na^{+}}}\right)$$

In the formula,  $\tau \cdot m \cdot V_m \cdot M \cdot \Delta E_s \cdot \Delta E_\tau$  represent the relaxation time, the mass of the electrode active material, the molar volume of the material, the relative molecular mass, the area of the electrode material (diameter 14 mm), the voltage difference caused by the adjacent two relaxations, and the voltage difference before and after the relaxation current, respectively.



Fig. S13. (a) EIS; (b) Liner patterns of Z' vs  $\omega^{-1/2}$  of 1.38-NFPP, 1.38-NFPP@SP and 1.38-NFPP@CNT.

The electrochemical impedance spectroscopy (EIS) of 1.38-NFPP, 1.38-NFPP@SP and 1.38-NFPP@CNT is shown in Fig. S13a (the equivalent circuit is in the illustration section). The high frequency region of the Nyquist curve is semi-circular, which represents the charge transfer impedance ( $R_{ct}$ ) between the electrode material and the electrolyte interface. The low-frequency region presents a straight line, which is related to the Walburg impedance ( $Z_w$ ) of Na<sup>+</sup> diffusion in the electrode material. The calculation equation of  $D_{Na^+}$  is as follows:<sup>3,4</sup>

$$Z' = R_o + R_{ct} + \sigma \omega^{-1/2}$$

$$D_{Na^{+}} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$

In the formula, R, T, A, n, F, C,  $\sigma$  represent the gas constant, the Kelvin temperature at room temperature, the electrode material area (diameter of 14 mm), the number of electrons transferred in the reaction, the Faraday constant, the Na<sup>+</sup> bulk concentration, and the Warburg impedance factor (the slope of the curve in Fig. S13b), respectively.



**Fig. S14.** (a) CV curves at various scan rates; (b) Linear relationship of log(i) and log(v); (c) Contribution ratio of the capacitive and diffusion-controlled charge versus scan rate of 1.38-NFPP@CNT.

The charge storage in the electrochemical process consists of two parts: the pseudocapacitance of the Faraday process and the double-layer capacitance of the non-Faraday process. Usually, in the multi-sweep CV test, the relationship between the peak current (*i*) and the sweep speed (v) is satisfied:<sup>5</sup>

$$i=a v^{b} >> \log(i)=b\log v + \log a$$

1.38-NFPP@CNT multi-sweep CV curve (Fig. S14a) is fitted to calculate the b value, and the fitting result is shown in Fig. S14b. When the b value is 0.5, the charge storage is mainly realized by the diffusion process. When the b value is 1, it shows that the pseudocapacitance mechanism dominates the charge storage.

The contribution of pseudocapacitance of 1.38-NFPP@CNT in charge storage is calculated by the following formula:<sup>6</sup>

$$i(V) = k_1 v + k_2 v^{1/2} >> i(V) / v^{1/2} = k_1 / v^{1/2} + k_2$$

In the formula,  $k_1v$  is the diffusion control current, and  $k_2 v^{1/2}$  is the capacitance contribution current. Therefore, the ratio of diffusion control to capacitance contribution can be obtained by the slope of the curve and its intercept in the longitudinal axis (Fig. S14c).



**Fig. S15.** CV curves at various scan rate of (a) 1.38-NFPP; (c) 1.38-NFPP@SP; Contribution ratio of the capacitive and diffusion-controlled charge versus scan rate of (b) 1.38-NFPP; (d) 1.38-NFPP@SP.



Fig. S16. (a) The initial three cycles charge-discharge curve at 20 mA  $g^{-1}$ ; (b) Cycle performance at 100 mA  $g^{-1}$  of Hard Carbon.



Fig. S17. The rate performance from 1~30 C of 1.38-NFPP//HC.



Fig. S18. (a) The cycling stability at 1 C; (b) The charge-discharge curves with differentcyclenumbersof1.38-NFPP//HC.

| Sample        | Lattice parameters/Å |        |         | Volume/Å | <b>Reliability factors</b>   |                              |
|---------------|----------------------|--------|---------|----------|------------------------------|------------------------------|
|               | a                    | b      | c       | 3        | <i>R<sub>p</sub></i> /%      | <i>R<sub>wp</sub></i> /%     |
| 1.38-NFPP     | 18.0729              | 6.5421 | 10.6660 | 1261.1   | <i>R</i> <sub>p</sub> =8.17% | <i>R<sub>wp</sub></i> =9.88% |
| 1.38-NFPP@SP  | 18.0740              | 6.5348 | 10.6760 | 1260.9   | <i>R</i> <sub>p</sub> =8.20% | <i>R<sub>wp</sub></i> =9.91% |
| 1.38-NFPP@CNT | 18.0875              | 6.5358 | 10.6643 | 1260.7   | <i>R</i> <sub>p</sub> =8.53% | <i>R<sub>wp</sub></i> =9.98% |

**Table S1.** Parameters of 1.38-NFPP, 1.38-NFPP@SP and 1.38-NFPP@CNT byRietveld Refinement.

 Table S2. The performance comparison table of 1.38-NFPP@CNT with the previously

 reported NFPP electrode.<sup>7-11</sup>

| Sample        | Specific capacity   | Cycle performance  | Mass loadings               | Ref       |
|---------------|---|--|-----------------------------|-----------|
| 1.38-NFPP@CNT | 114.8 mAh g <sup>-1</sup> at 0.1 C<br>89.1 mAh g <sup>-1</sup> at 50 C  | 99.8% after 200<br>cycles at 1 C<br>89.3% after 10000<br>cycles at 50 C  | 1.8~2.8 mg cm <sup>-2</sup> | This work |
| NFPP@C@rGO    | 111.7 mAh g <sup>-1</sup> at 0.05C<br>80.7 mAh g <sup>-1</sup> at 20 C  | 87.1% after 2000<br>cycles at 2 C<br>91.7% after 10000<br>cycles at 20 C | ~2.5 mg cm <sup>-2</sup>    | [7]       |
| NFPP3         | 110.9 mAh g <sup>-1</sup> at 0.2C<br>51.9 mAh g <sup>-1</sup> at 100 C  | ~100% after 500<br>cycles at 1 C<br>~100% after 10000<br>cycles at 10 C  | ~1.5 mg cm <sup>-2</sup>    | [8]       |
| NFPP-E        | 113.0 mAh g <sup>-1</sup> at 0.5 C<br>80.3 mAh g <sup>-1</sup> at 20 C  | 85.0% after 200<br>cycles at 0.2 C<br>69.1% after 4500<br>cycles at 20 C | ~2.0 mg cm <sup>-2</sup>    | [9]       |
| Ni6-NFPP@C-N  | 128.4 mAh g <sup>-1</sup> at 0.05 C<br>62.5 mAh g <sup>-1</sup> at 50 C | 95.3% after 500<br>cycles at 10 C<br>82.9% after 3000<br>cycles at 10 C  | 1.3~1.9 mg cm <sup>-2</sup> | [10]      |
| NCM111        | 122.3 mAh g <sup>-1</sup> at 0.1 C<br>62.5 mAh g <sup>-1</sup> at 50 C  | 98.2% after 100<br>cycles at 1 C<br>78.4% after 14000<br>cycles at 50 C  | 1.0~1.5 mg cm <sup>-2</sup> | [11]      |

| Sample        | $R_{ct}(\Omega)$ | $D_{Na}^{+}$ (cm <sup>2</sup> s <sup>-1</sup> ) |
|---------------|------------------|---|
| 1.38-NFPP     | 506.2            | 8.70×10 <sup>-12</sup>                          |
| 1.38-NFPP@SP  | 229.3            | 1.04×10 <sup>-11</sup>                          |
| 1.38-NFPP@CNT | 133.7            | 1.28×10 <sup>-11</sup>                          |

**Table S3.** R<sub>ct</sub> values and Sodium-Ion Diffusion Coefficients calculated of 1.38-NFPP,1.38-NFPP@SP and 1.38-NFPP@CNT before cycling.

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