

Supporting Information for

## Bio-derived Hierarchical Multicore–shell Fe<sub>2</sub>N-Nanoparticle-Impregnated N-doped Carbon Nanofiber Bundles: A Host Material for Lithium-/Potassium-ion Storage

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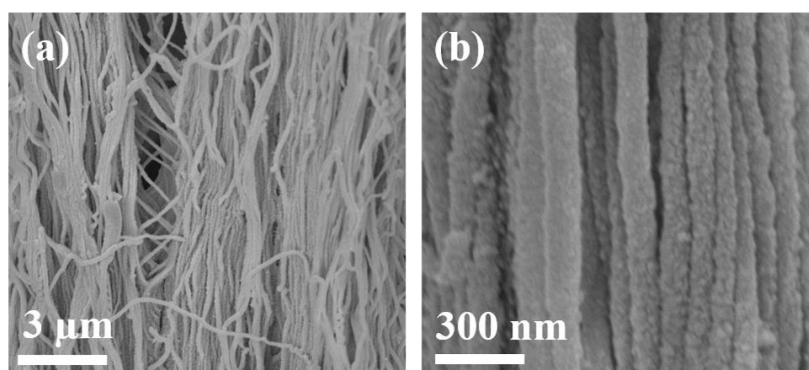
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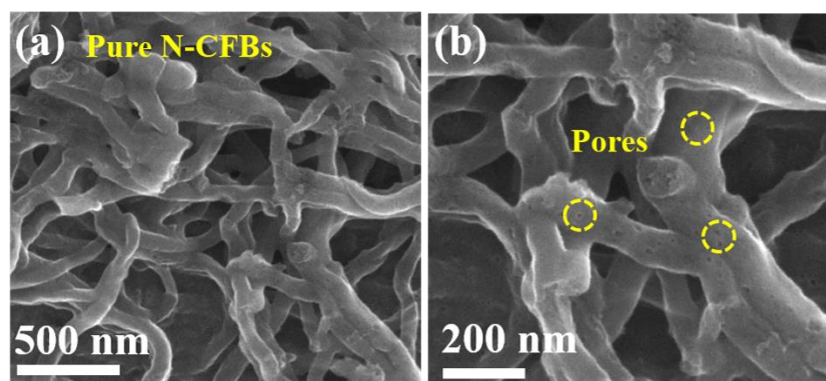
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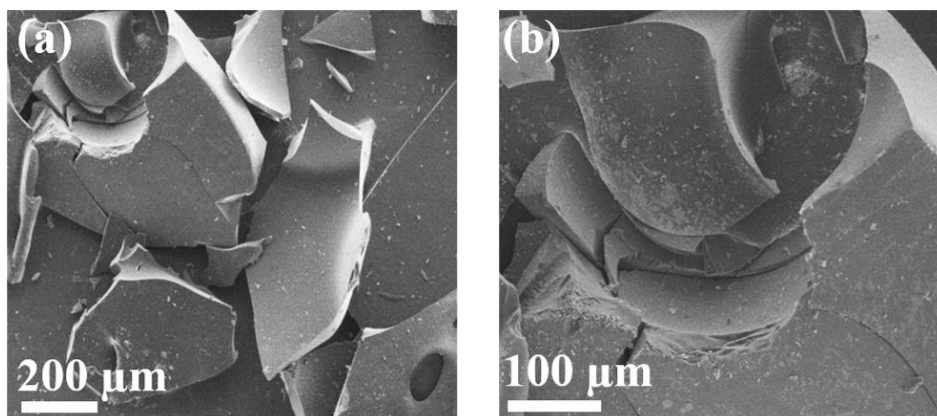
### Supporting Figures and Tables



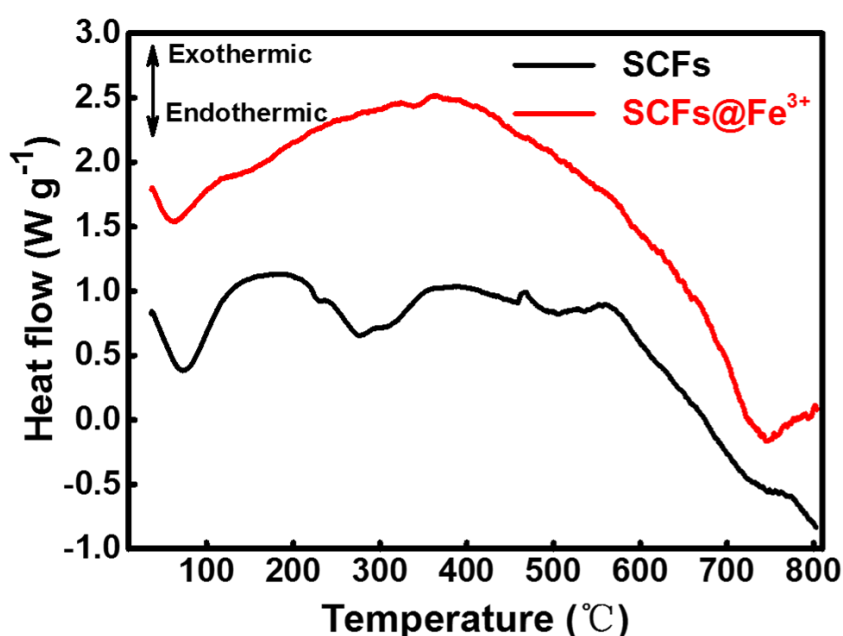
**Fig. S1** FESEM images of SCFs@Fe<sup>3+</sup> intermediates at different magnifications



**Fig. S2** FESEM images of pure N-CFBs

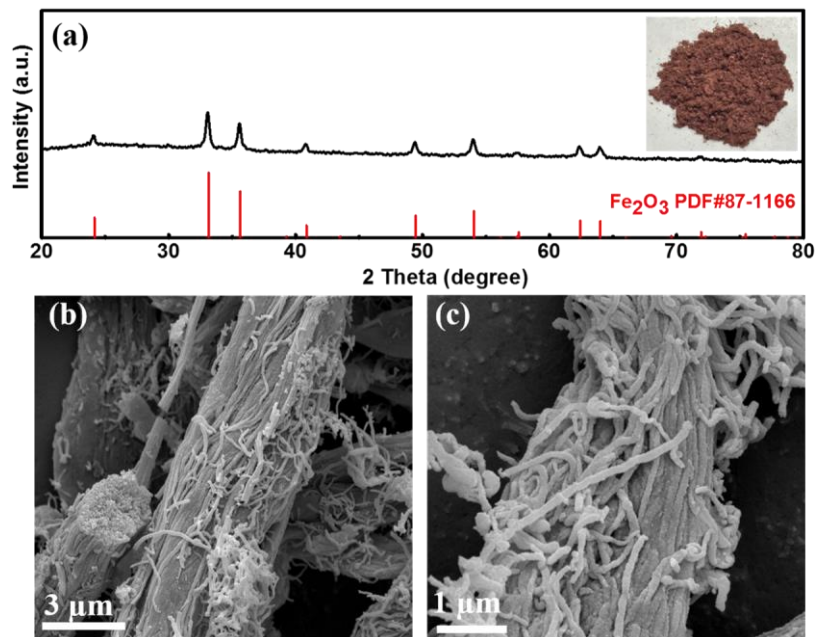


**Fig. S3** FESEM images of carbonized skin collagen fibers by directly calcining in  $\text{NH}_3$  atmosphere at  $500\text{ }^\circ\text{C}$

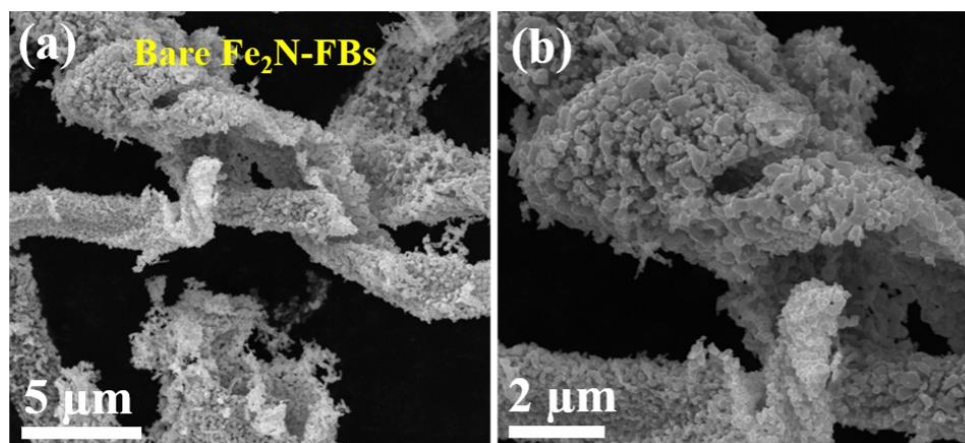


**Fig. S4** Differential scanning calorimetry (DSC) curves of native skin collagen fibers (SCFs) and  $\text{Fe}^{3+}$ -immobilized SCFs ( $\text{SCFs@Fe}^{3+}$ ) in Ar atmosphere at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$

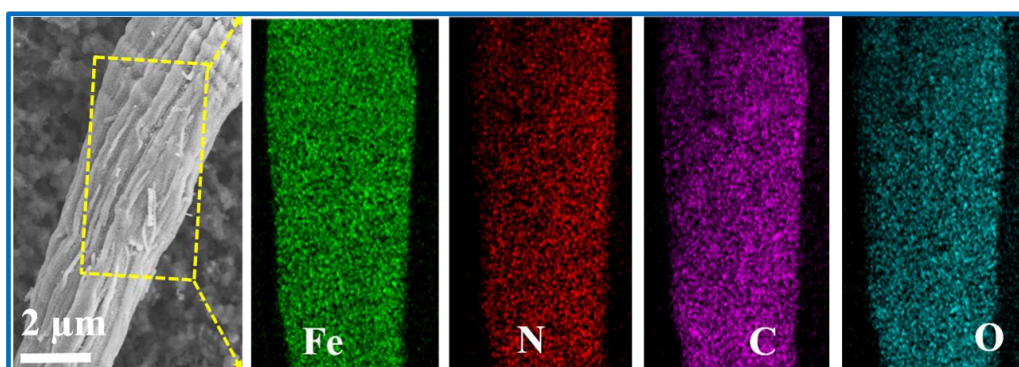
As shown in **Fig. S4**, the  $\text{Fe}^{3+}$ -immobilized skin collagen fibers ( $\text{SCFs@Fe}^{3+}$ ) show remarkably enhanced thermal stability with a higher decomposition temperature ( $\approx 370\text{ }^\circ\text{C}$ ) than that of pristine SCFs ( $\approx 175\text{ }^\circ\text{C}$ ). This result further confirms that the complexing interaction of SCFs with iron salts is indeed able to increase the degree of cross-linking between the collagen macromolecules, as well as significantly improving the thermal shrinkage temperature of SCFs.



**Fig. S5** a XRD pattern and b, c FESEM images of  $\text{Fe}_2\text{O}_3$  prepared by calcinating the SCFs@ $\text{Fe}^{3+}$  in air. The inset in a is a photograph of the resultant  $\text{Fe}_2\text{O}_3$  powder



**Fig. S6** FESEM images of bare  $\text{Fe}_2\text{N}$ -FBs



**Fig. S7** SEM-EDS mapping images of the  $\text{Fe}_2\text{N}$ @N-CFBs

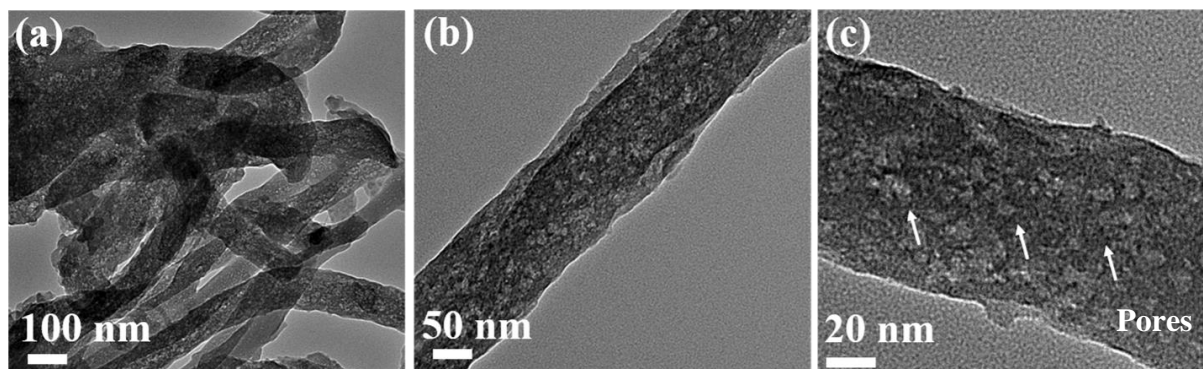


Fig. S8 TEM images of pure N-CFBs

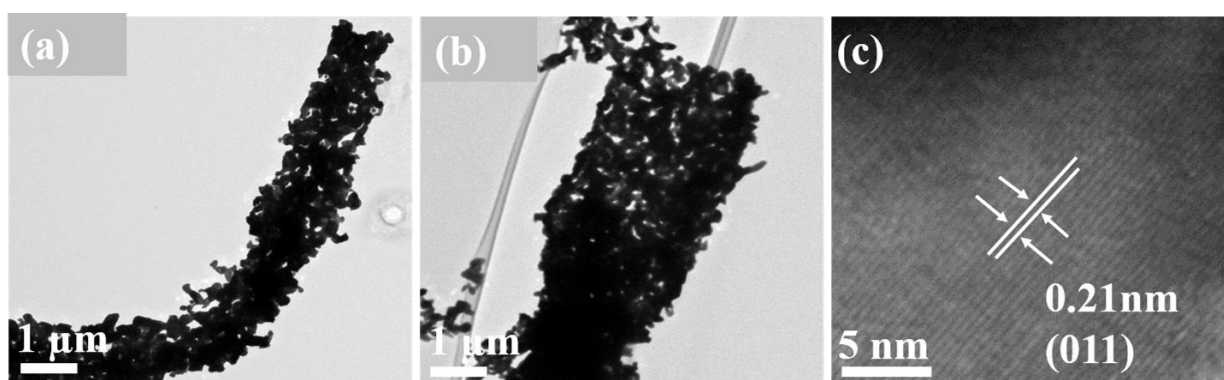


Fig. S9 TEM images of bare Fe<sub>2</sub>N-FBs

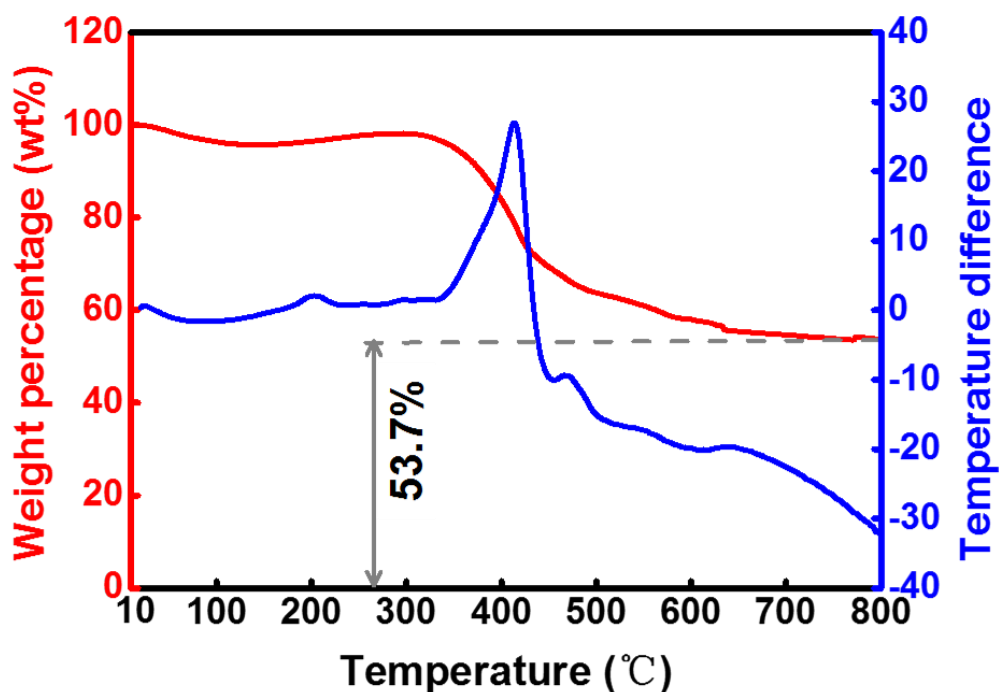


Fig. S10 TGA and differential thermogravimetry (DTG) curves of Fe<sub>2</sub>N@N-CFBs collected in air atmosphere at a heating rate of 10 °C min<sup>-1</sup>

As shown in Fig. S10, the weight loss below 200 °C is mainly due to the loss of absorbed gaseous molecules. An obvious weight increase between 200 and 300 °C is related to the oxidation of

external  $\text{Fe}_2\text{N}$ . The sharp decrease in weight between 350 and 400 °C is mainly associated with the burning of N-CFBs. A relatively slow weight loss between 400 and 700 °C is attributed to two processes, the combustion of N-CFBs and oxidation of  $\text{Fe}_2\text{N}$ , in which the transformation from  $\text{Fe}_2\text{N}$  to  $\text{Fe}_2\text{O}_3$  gives a weight increase of 27%. Considering that the Fe:N ratio is 2:0.84, we assume the  $\text{Fe}_2\text{N}_{0.84}$  content is  $x$ , and therefore, the weight content of  $\text{Fe}_2\text{N}_{0.84}$  can be calculated using the following formula:

$$x \times \frac{112}{112 + 14 \times 0.84} = 53.7\% \times \frac{112}{160}$$

Thus, the  $\text{Fe}_2\text{N}$  content is 41.5%.

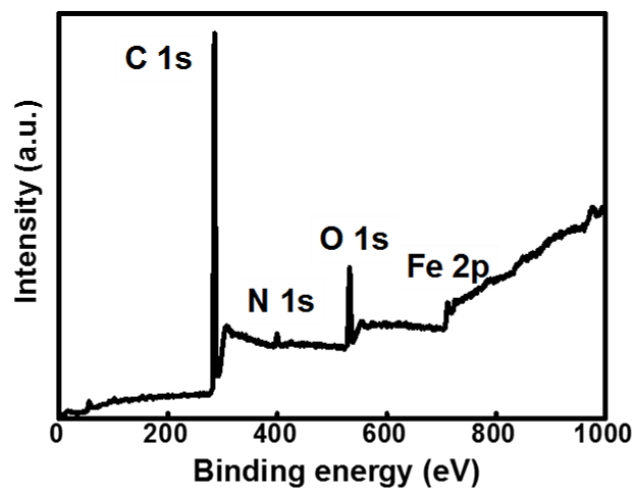


Fig. S11 XPS survey scan of  $\text{Fe}_2\text{N}@$ N-CFBs

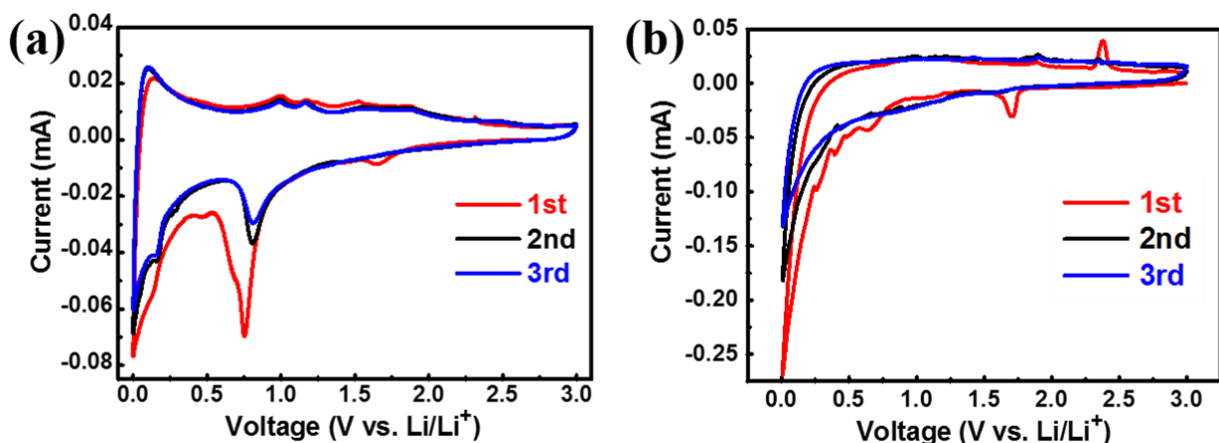
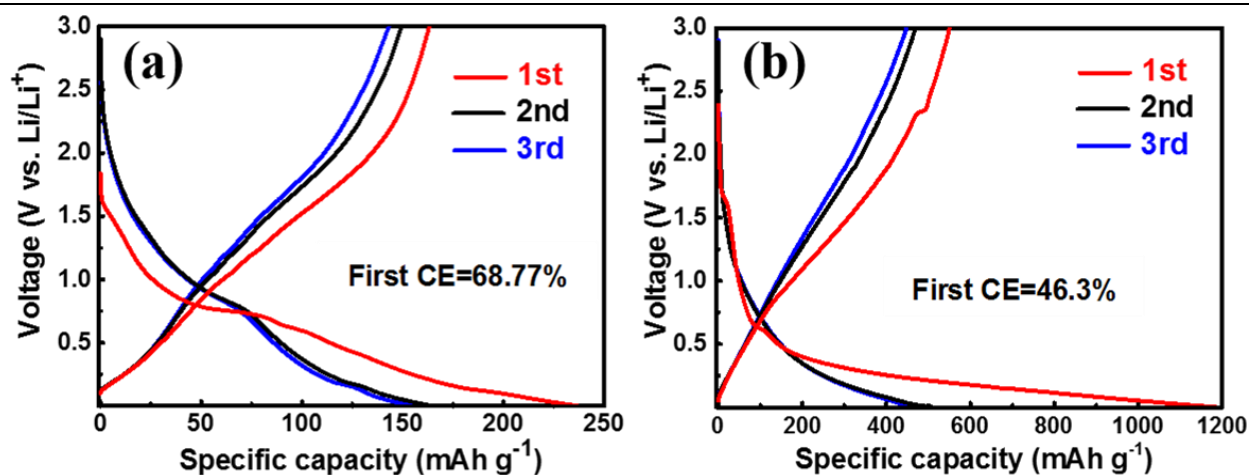
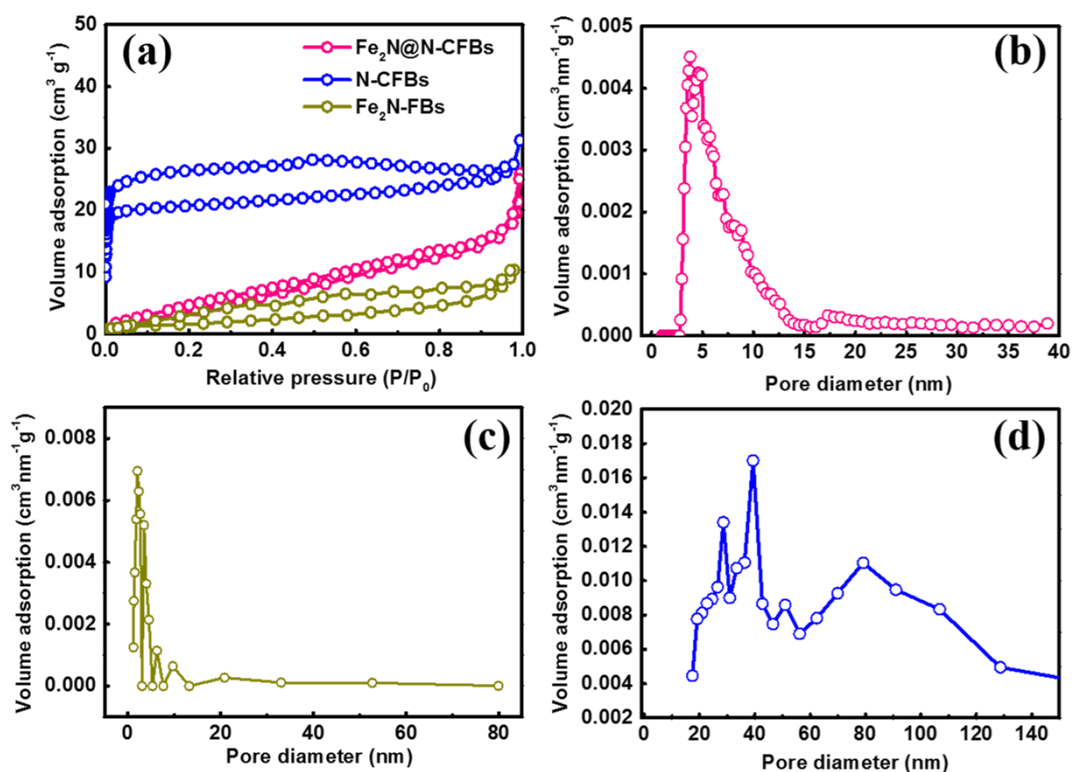


Fig. S12 CV curves of **a** bare  $\text{Fe}_2\text{N}$ -FBs and **b** pure N-CFBs at a scan rate of  $0.1 \text{ mV s}^{-1}$



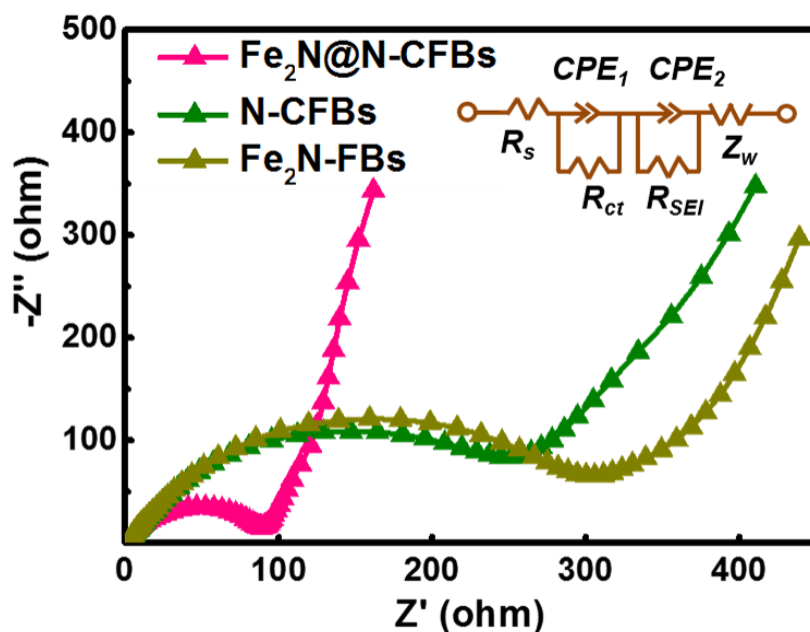
**Fig. S13** Discharge-charge curves of **a** bare Fe<sub>2</sub>N-FBs and **b** pure N-CFBs at the current density of 0.1 A g<sup>-1</sup>



**Fig. S14 a** N<sub>2</sub> sorption/desorption isotherm of the Fe<sub>2</sub>N@N-CFBs, Fe<sub>2</sub>N-FBs, and pure N-CFBs electrodes. **b-d** Pore size distribution of the Fe<sub>2</sub>N@N-CFBs, Fe<sub>2</sub>N-FBs, and pure N-CFBs electrode

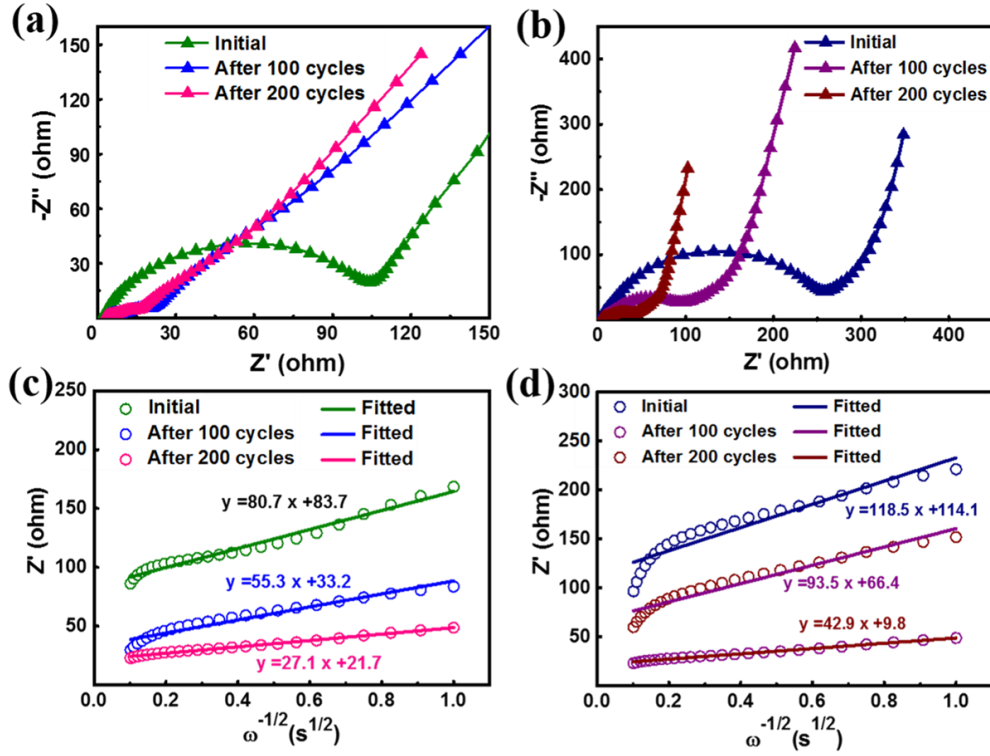
As shown in **Fig. S14a**, the Brunauer-Emmett-Teller (BET) specific surface of the Fe<sub>2</sub>N@N-CFBs measured here is 20.8 m<sup>2</sup> g<sup>-1</sup>, much higher than that of Fe<sub>2</sub>N-FBs (6.8 m<sup>2</sup> g<sup>-1</sup>), but significantly lower than the value for pure N-CFBs (57.2 m<sup>2</sup> g<sup>-1</sup>). Pore size distribution demonstrates that mesopores dominate in the Fe<sub>2</sub>N@N-CFBs and Fe<sub>2</sub>N-FBs electrodes evidently, whereas a significant amount of macro-pores are observed in the pure N-CFBs electrode, as displayed in **Fig. S14b-d**. The presence of macro-pores is resulted from the removal of Fe<sub>2</sub>N nanoparticles. The much higher surface area of pure N-CFBs could result in lower ICE because of the inevitable surficial chemisorption of Li ions into the pores as well as defect sites of carbon fibers, which is likely to

cause more irreversible lithium-ion consumption. Whilst electrode materials with small surface area, for instance,  $6.8 \text{ m}^2 \text{ g}^{-1}$  for  $\text{Fe}_2\text{N}$ -FBs, is unfavored for the rapid transportation of Li ions and the wettability of electrolyte to the electrode surface, the  $\text{Fe}_2\text{N}@\text{N}$ -CFBs with an appropriate surface area of  $20.8 \text{ m}^2 \text{ g}^{-1}$  is able to provide sufficient active sites for surface chemisorption as well as rapid electrolyte and Li ion diffusion passages, and thus achieving a relatively high ICE of 73.5%.



**Fig. S15** EIS spectra of  $\text{Fe}_2\text{N}$ -FBs and  $\text{Fe}_2\text{N}@\text{N}$ -CFBs with the equivalent circuit in the inset

As shown above, the EIS profiles for both the  $\text{Fe}_2\text{N}@\text{N}$ -CFBs and  $\text{Fe}_2\text{N}$ -FBs electrodes show a compressed semicircle from the high to medium frequency range of each spectrum and an inclined line in the low-frequency range. The diameter of the compressed semicircle is ascribed to the charge transfer resistance ( $R_{ct}$ ) for these electrodes, and the inclined line is considered to be related to the Warburg impedance ( $Z_w$ ). In the equivalent circuit,  $R_s$  represents the Ohmic resistance of the electrode system, including the electrolyte and the cell components.  $R_{SEI}$  is the resistance due to the SEI.  $R_{ct}$  represents the resistance related to charge transfer, and the constant phase element (CPE) reflects the double-layer capacitance.  $Z_w$  represents the Warburg impedance, which is attributed to the Li-ion diffusion in the solid. Apparently, the ohmic resistance ( $R_s$ ) values of the two electrodes are almost the same, but the  $\text{Fe}_2\text{N}@\text{N}$ -CFBs one exhibits a lower  $R_{ct}$  of  $\approx 90 \Omega$ . This implies that the  $\text{Fe}_2\text{N}@\text{N}$ -CFBs features better electrical contact and a faster charge transfer reaction for Li-ion insertion/extraction compared with the bare  $\text{Fe}_2\text{N}$ -FBs.



**Fig. S16** Electrochemical impedance spectra of (a) Fe<sub>2</sub>N@N-CFBs and (b) bare Fe<sub>2</sub>N-FBs collected during the cycling test at 0.2 A g<sup>-1</sup>; The corresponding linear fitted curves of Z' versus ω<sup>-1/2</sup> of the fresh (c) Fe<sub>2</sub>N@N-CFBs and (d) Fe<sub>2</sub>N-FBs electrodes and after the 100<sup>th</sup> and 200<sup>th</sup> cycles..

Figure S16 presents the EIS curves of Fe<sub>2</sub>N@N-CFBs and Fe<sub>2</sub>N-FBs electrodes after different numbers of cycles at 0.2 A g<sup>-1</sup>. As seen in **Fig. S16a**, the  $R_{ct}$  for Fe<sub>2</sub>N@N-CFBs dramatically decreases to 30 and 25 Ω after 100 and 200 cycles, respectively. Note that the reduction in  $R_{ct}$  for the Fe<sub>2</sub>N@N-CFBs is more significant than that for the bare Fe<sub>2</sub>N-FBs (100 Ω and 50 Ω, **Fig. S16b**), confirming that the Fe<sub>2</sub>N NPs encapsulated in the highly electrically conducting 1D N-doped carbon nanofiber framework are capable of greatly enhanced rapid electron transfer during the Li<sup>+</sup> insertion/extraction process. In addition, the lithium-ion diffusion coefficient ( $D_{Li}$ , cm<sup>2</sup> s<sup>-1</sup>) can be calculated from the inclined lines in the Warburg region using Eqs. S1 and S2 [S1, S2]:

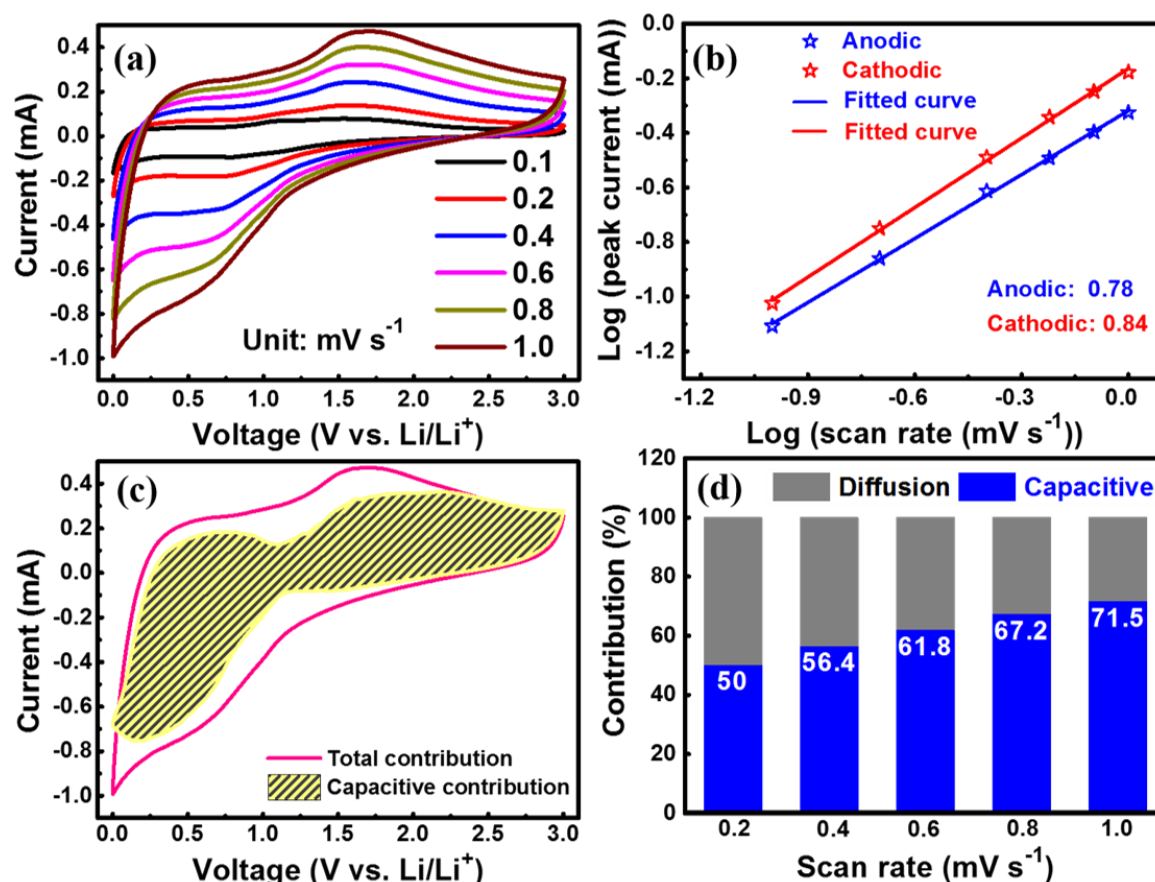
$$Z' = R + \sigma\omega^{-1/2} \quad (S1)$$

$$D = (R^2T^2)/(2A^2n^4F^4C^2\sigma^2) \quad (S2)$$

In these equations,  $\omega$  is the angular frequency,  $R$  is the universal gas constant,  $T$  is the absolute temperature,  $A$  is the active surface area of the electrode,  $n$  is the number of electrons,  $F$  is the Faraday constant, and  $C$  is the concentration of lithium ions.  $\sigma$  is the Warburg factor which could be calculated from the gradient of the oblique line  $Z' - \omega^{-1/2}$  ( $\omega = 2\pi f$ ) in the low-frequency region. As displayed in **Fig. S16c-d**, the slope of the straight lines for both the Fe<sub>2</sub>N@N-CFBs and the Fe<sub>2</sub>N-FBs have remarkably decreased after cycling, although the Fe<sub>2</sub>N@N-CFBs exhibits a rather lower slope than that of the bare Fe<sub>2</sub>N-FBs, indicating its faster Li<sup>+</sup> diffusion process. The calculated  $D_{Li}$  of Fe<sub>2</sub>N@N-CFBs after 200 cycles is  $1.60 \times 10^{-17}$  cm<sup>2</sup> s<sup>-1</sup>, which is over 2.5 times that of Fe<sub>2</sub>N-FBs ( $6.36 \times 10^{-18}$  cm<sup>2</sup> s<sup>-1</sup>). Such high performance for Fe<sub>2</sub>N@N-CFBs could be ascribed to the SCF-derived oxygen-containing carbon nanofiber backbone together with the



nitrogen heteroatom doping. These factors significantly boost the electrical conductivity and the surface wettability of electrode, which allows efficient contact of the embedded Fe<sub>2</sub>N NPs with the electrolyte, and results in faster electrode/electrolyte interface kinetics.



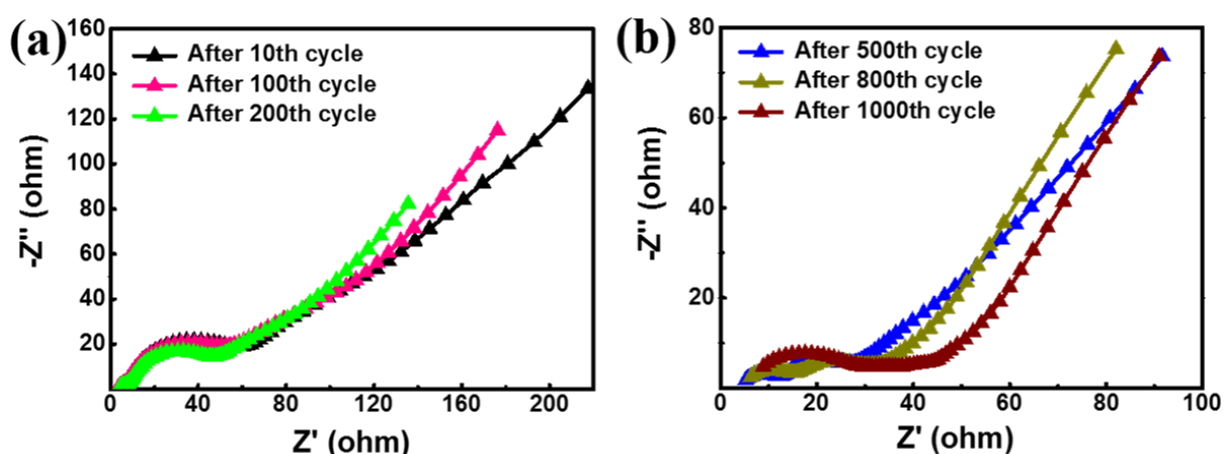
**Fig. S17** **a** CV curves of Fe<sub>2</sub>N@N-CFBs at different scan rates from 0.1 to 1.0 mV s<sup>-1</sup>. **b** Plots of peak current versus the corresponding scan rate; **c** The CV curve at 1.0 mV s<sup>-1</sup> with an estimated capacitive contribution in the yellow-shaded region. **d** The capacitive contribution ratio at various scan rates

The capacitive behavior was characterized by CV measurements at varied scan rates from 0.1 to 1.0 mV s<sup>-1</sup>. In **Fig. S17a**, the CV curves of Fe<sub>2</sub>N@N-CFBs electrode show a well-preserved shape along with steadily enhanced redox peaks as the scan rate increases from 0.1 to 1.0 mV s<sup>-1</sup>. The peak currents ( $i$ ) in different CV curves obey a power-law relationship with the scan rate ( $v$ ) according to the following equation [S3, S4]:  $i = av^b$ , where  $a$  and  $b$  are parameters. By plotting  $\log(i)$  versus  $\log(v)$ , the  $b$  value can be obtained from the slope of the profile. Specifically, the  $b$  value of 1 suggests a surface diffusion process (capacitor-type), while 0.5 reveals a totally diffusion-controlled behavior (battery-type). The plots for both the anodic and the cathodic peaks are shown in **Fig. S17b**. At scan rates ranging from 0.1 to 1.0 mV s<sup>-1</sup>, the  $b$  values of the anodic and cathodic peaks are 0.78 and 0.84, respectively, which implies that the charge storage of Fe<sub>2</sub>N@N-CFBs is mostly dominated by capacitive behavior. Thus, to further determine the potential regions where the capacitive contributions occur in the CV plots, the current is divided into capacitive effect and diffusion behavior through Eqs. S3 and S4 [S5]:

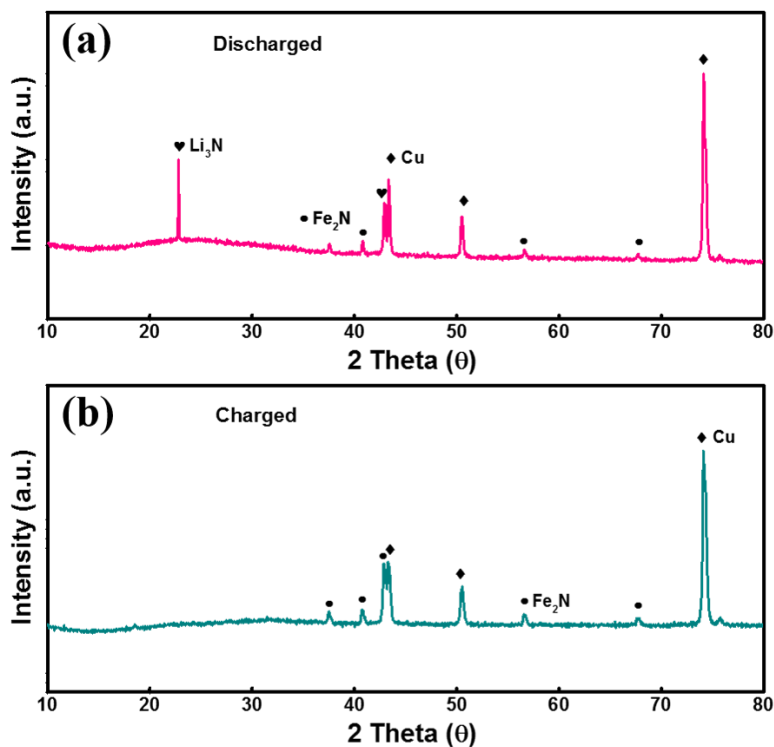
$$i = k_1v + k_2v^{1/2} \quad (\text{S3})$$

$$i(V)/v^{1/2} = k_1v^{1/2} + k_2 \quad (\text{S4})$$

Accordingly, the portion of the current from surface capacitance and diffusion contributions can be differentiated by determining both the  $k_1$  and  $k_2$  constants. Figure S17c shows the original CV curve of the total current and the calculated CV curve of the capacitive current (yellow-shaded section). Based on the integration of the CV curve, over 71% of the total charge storage of Fe<sub>2</sub>N@N-CFBs electrode is capacitive at the scan rate of 1.0 mV s<sup>-1</sup>. The percentages at other scan rates were also calculated as shown in **Fig. S17d**, and it displays that the capacitive capacity contribution of Fe<sub>2</sub>N@N-CFBs electrode is gradually improving from 50 to 71.5% with the increase of scan rates from 0.2 to 1.0 mV s<sup>-1</sup>. Hence, the well-defined capacitive behavior for the Fe<sub>2</sub>N@N-CFBs electrode is attributed to the unique 1D hierarchically ordered fibrous framework that is organized from numerous staggered N-doped carbon nanofibers with uniformly dispersed Fe<sub>2</sub>N NPs, which not only provides sufficient active sites for surface electrochemical reaction, but also creates direct and continuous transport pathways in both the radial and axial directions for Li ion diffusion, thereby enhancing the high-rate Li-ion storage capability.

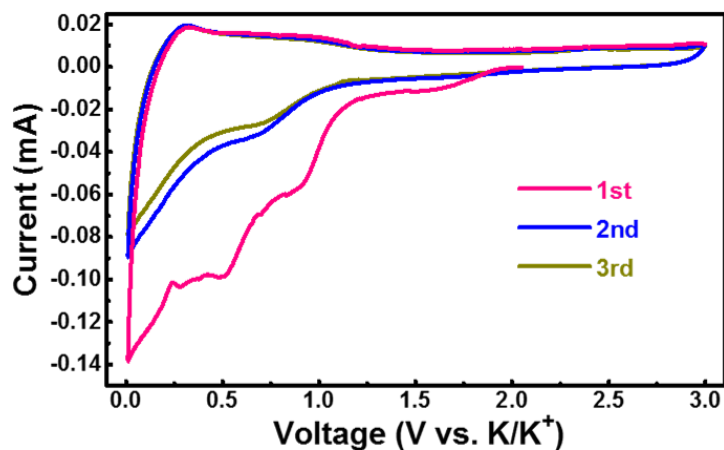


**Fig. S18 a, b** Electrochemical impedance spectra of Fe<sub>2</sub>N@N-CFBs electrode collected during the cycling test at 1.0 A g<sup>-1</sup>

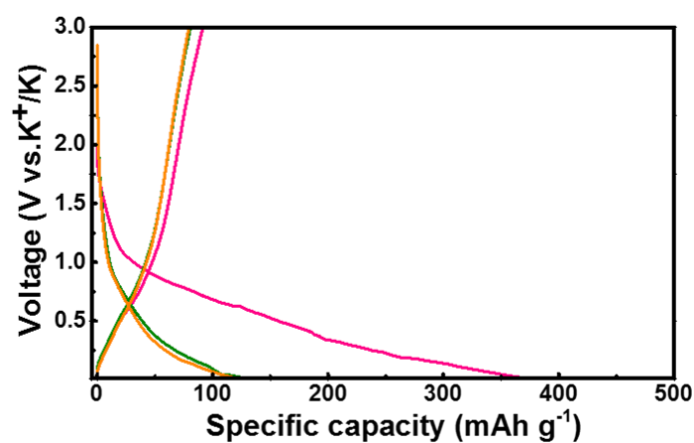


**Fig. S19** Ex-situ XRD patterns of the  $\text{Fe}_2\text{N}@N\text{-CFBs}$  electrode after **a** discharging and **b** charging at  $50 \text{ mA g}^{-1}$  in the voltage range of 0.01–3.0 V

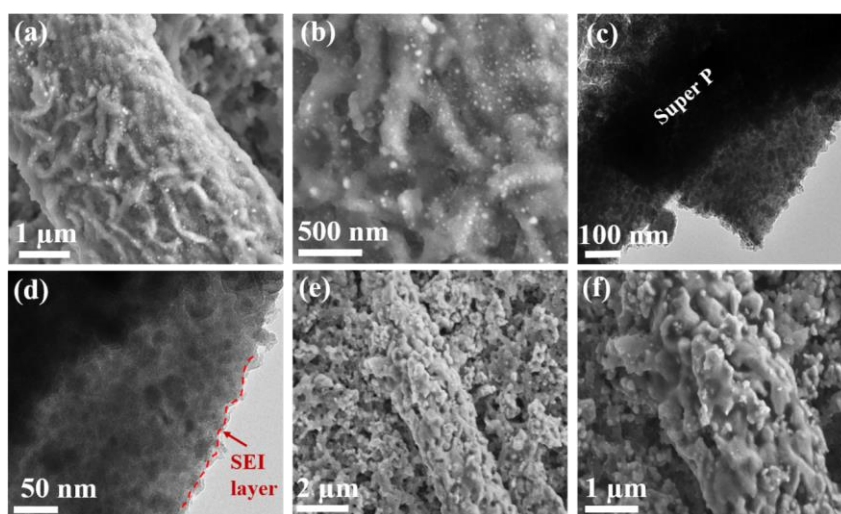
As shown in **Fig. S19**, from the XRD patterns, we observed metallic Cu, crystalline  $\text{Li}_3\text{N}$ , and  $\text{Fe}_2\text{N}$ . The strong signal of Cu comes from the current collector of copper foil. Peaks assigned to  $\text{Li}_3\text{N}$  confirms the formation of crystal products after discharging, consistent with the TEM results (**Fig. 5c1-c3**). After charging, all the peaks assigning to  $\text{Li}_3\text{N}$  disappeared, with only crystal  $\text{Fe}_2\text{N}$  and Cu detected, demonstrating that  $\text{Fe}_2\text{N}$  could react with  $\text{Li}^+$  reversibly by generating  $\text{Li}_3\text{N}$  during charging/discharging process. It should be mentioned that the expected metallic Fe is not probed whilst  $\text{Fe}_2\text{N}$  crystal is still observable after discharging. The possible reason for the missing of Fe peaks could be due to the formation of small size Fe nanoparticles which shows low peak intensity. Also limited by our testing condition, the ex-situ XRD was carried out without protection, making it possible to form an amorphous oxidation layer on the surface of iron before testing, and thus could further lower the peak intensity and resulting in the burial of iron peaks underneath the strong Cu peaks. The detectable  $\text{Fe}_2\text{N}$  after discharging suggests incomplete conversion of  $\text{Fe}_2\text{N}$ , consistent with our argument of delayed wettability of electrolyte to the inner  $\text{Fe}_2\text{N}$  nanoparticles.



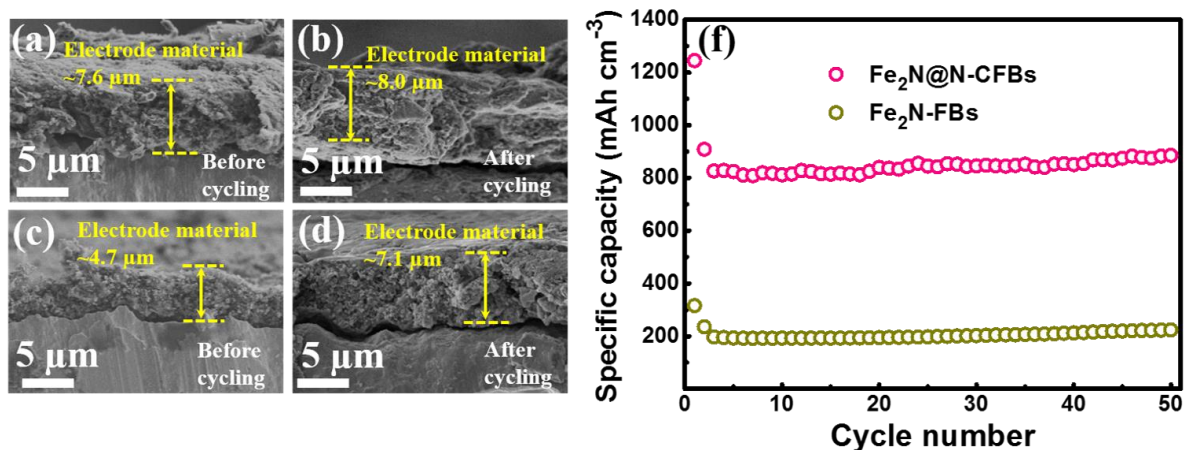
**Fig. S20** CV curves of bare Fe<sub>2</sub>N-FBs electrode at a scan rate of 0.1 mV s<sup>-1</sup> in the first three cycles for PIBs



**Fig. S21** Discharge-charge curves of bare Fe<sub>2</sub>N-FBs electrode at the current density of 25 mA g<sup>-1</sup> in the first three cycles for PIBs



**Fig. S22** a, b FESEM images and c, d TEM images of Fe<sub>2</sub>N@N-CFBs electrode after 100 cycles at 0.5 A g<sup>-1</sup>; e, f FESEM images of Fe<sub>2</sub>N-FBs electrode after 100 cycles at 0.5 A g<sup>-1</sup>



**Fig. S23** FESEM images of cross-section of the **a, b** Fe<sub>2</sub>N@N-CFBs and **c, d** Fe<sub>2</sub>N-FBs electrodes before and after 50 cycles at 0.2 A g<sup>-1</sup>. **f** The volumetric capacities of Fe<sub>2</sub>N@N-CFBs and Fe<sub>2</sub>N-FBs during cycling at a current density of 262 mA cm<sup>-3</sup>

**Table S1** Comparison of the electrochemical performance of previously reported metal nitride-based LIB anode materials with our work.

Electrode materials	Current density (A g <sup>-1</sup> )	2 <sup>nd</sup> cycle capacity (mAh g <sup>-1</sup> )	Cycle number	Capacity retention (vs. 2 <sup>nd</sup> cycle capacity)	References
<b>Multicore-shell</b>	<b>1.0</b>	<b>402</b>	<b>1000</b>	<b>144.3%</b>	<b>This work</b>
<b>Fe<sub>2</sub>N@N-CFBs</b>	<b>2.0</b>	<b>321</b>	<b>1000</b>	<b>130.8%</b>	
Fe <sub>3</sub> N@C	0.1	540	500	68.5%	[S6]
FeN/N-rG-O	0.1	510	100	78.1%	[S7]
Sn <sub>3</sub> N <sub>4</sub>	0.2	≈800	50	46.3%	[S8]
CrN	1.218	≈1050	200	68.9%	[S9]
Fe <sub>2</sub> N@C-RGO	0.1	≈810	100	93.9%	[S10]
3D Ni <sub>3</sub> N nanosheets	0.423	≈510	50	113.7%	[S11]
Porous Fe <sub>2</sub> N@C	0.1	618	50	107.0%	[S12]
	10.0	391	2000	85.0%	
TiN-900	0.335	567	100	93.0%	[S13]
	1.675	288	100	93.0%	
MoN <sub>x</sub> film	0.1	≈900	100	77.3%	[S14]
	(μA cm <sup>-2</sup> )				
Fe <sub>2</sub> N/carbon textile	1.0	≈820	681	83.0%	[S15]
	6.0	≈310	300	77.4%	
Mn <sub>3</sub> N <sub>2</sub>	0.08	579	110	80.0%	[S16]
	0.16	500	300	75.1%	
VN	0.1	455	100	114.3%	[S17]
	1.0	341	250	75.0%	
Cu <sub>3</sub> N	1.0	270	140	120.0%	[S18]

**Table S2** Comparison of the electrochemical performance of the state-of-art electrode for PIBs with our work

Electrode materials	Current density (mA g <sup>-1</sup> )	2 <sup>nd</sup> cycle capacity (mAh g <sup>-1</sup> )	Cycle number	Capacity retention (vs. 2 <sup>nd</sup> cycle capacity)	References
<b>Multicore-shell Fe<sub>2</sub>N@N-CFBs</b>	<b>200</b>	<b>≈125</b>	<b>100</b>	<b>82.6%</b>	<b>This work</b>
F-doped graphene foam	500	≈250	200	66.4%	[S19]
N-doped graphene	100	≈260	100	80.7%	[S20]
Amorphous ordered mesoporous carbon	200	≈270	200	73.0%	[S21]
VN quantum dot@N-doped carbon microsheets	100	≈325	100	76.9%	[S22]
Bamboo-like MnS <sub>2</sub> /N-doped-C	100	≈350	200	60.6%	[S23]
Pure MnS <sub>2</sub>	100	≈320	200	47.5%	
FeP	100	≈180	300	27.8%	[S24]
Zn@nanoporous carbon network	100	≈260	100	80.8%	[S25]
N-doped porous carbon derived from MOFs	2000	≈320	2000	72.2%	[S26]
Hard carbon	100	≈275	50	90.5%	[S27]
CoP/N,P-codoped porous carbon sheets	100	≈200	1000	63.5%	[S28]
CoSe <sub>2</sub> @N-doped CNTs	200	≈350	100	81.4%	[S29]

### Supplementary References

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