

Self-induce cobalt derive hollow structure Prussian blue as cathode for sodium-ion battery

Yu Luo, Jiayu Peng, Youwei Yan *

State Key Laboratory of Material Processing and Die & Mould Technology, School of
Materials Science and Engineering, Huazhong University of Science and Technology,
Wuhan, Hubei 430074, China.

* Corresponding Authors.

E-mail address: yanyw@hust.edu.cn

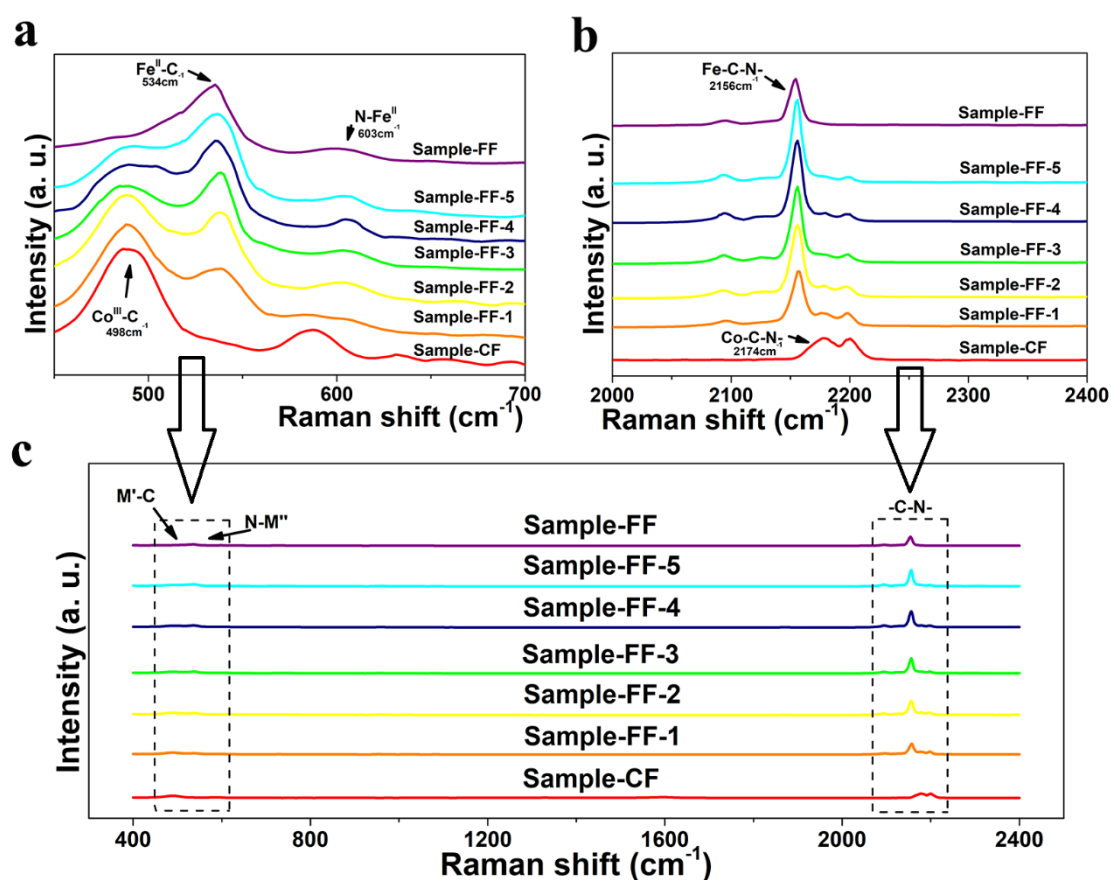


Figure S1. Ex situ Raman plots of the samples in different vibration interval ranges: (a) 400-700 cm⁻¹. (b) 2000-2400 cm⁻¹. (c) 400-2400 cm⁻¹.

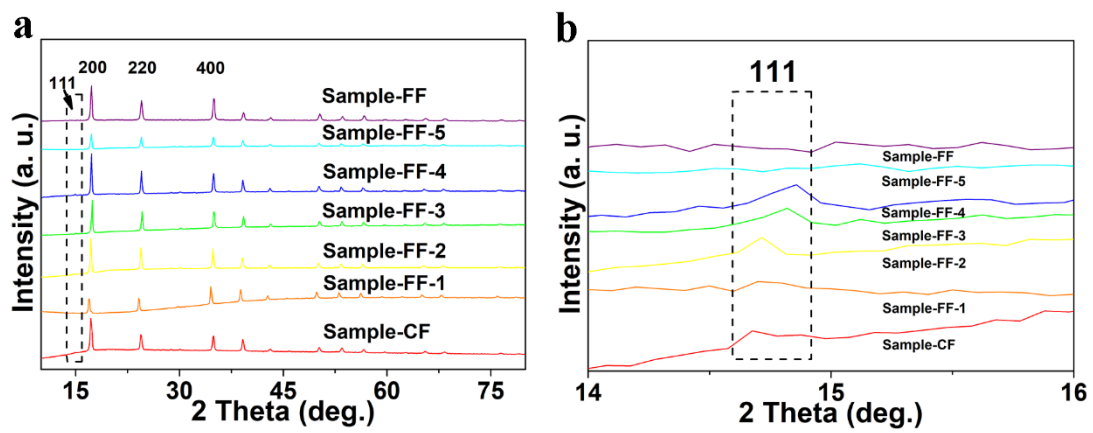


Figure S2. Ex XRD patterns of the samples in different interval ranges: (a) 10-80 degree. (b) 14-16 degree.

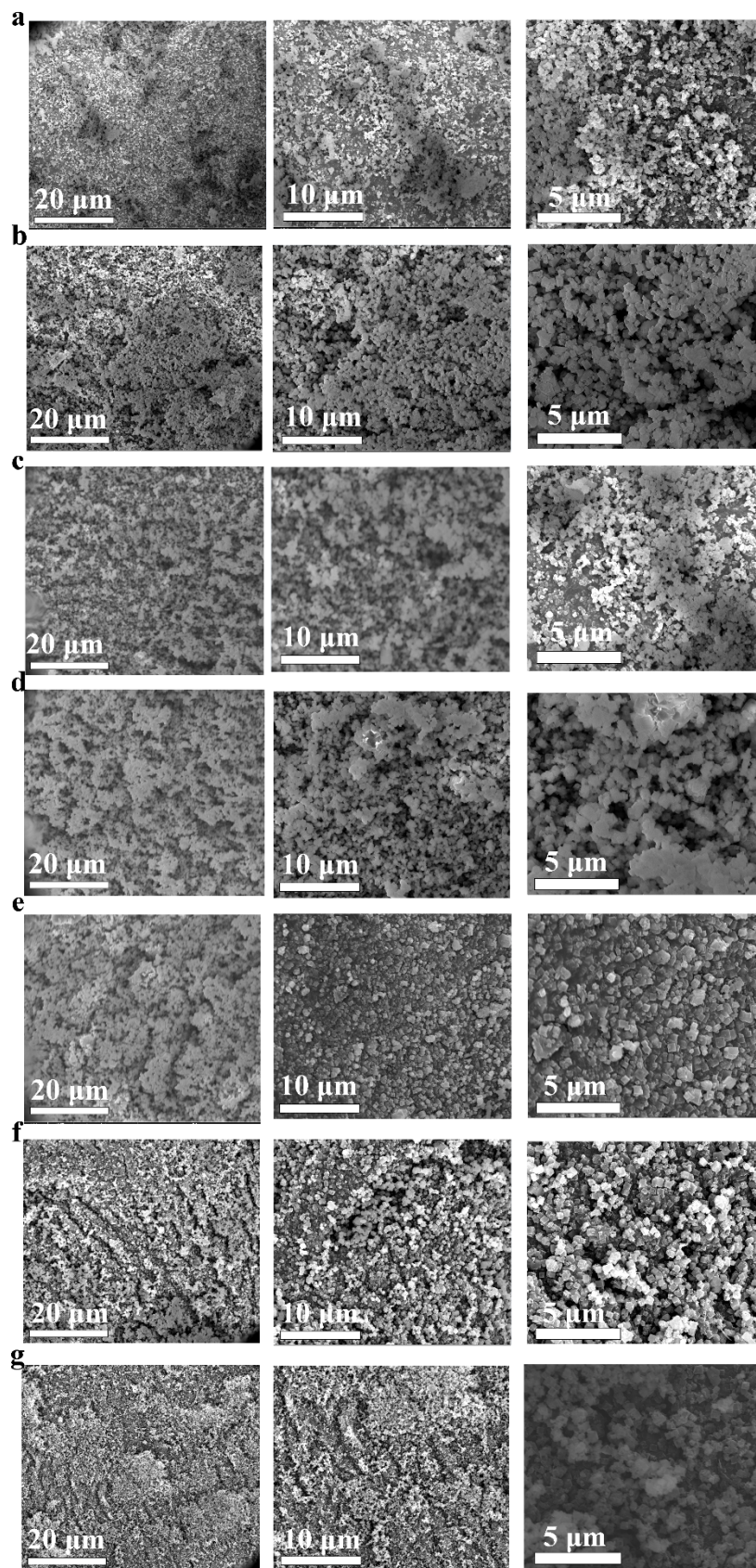


Figure S3. SEM images of (a) Sample-CF, (b) Sample-FF-1, (c) Sample-FF-2, (d) Sample-FF-3, (e) Sample-FF-4, (f) Sample-FF-5 and (g) Sample-FF.

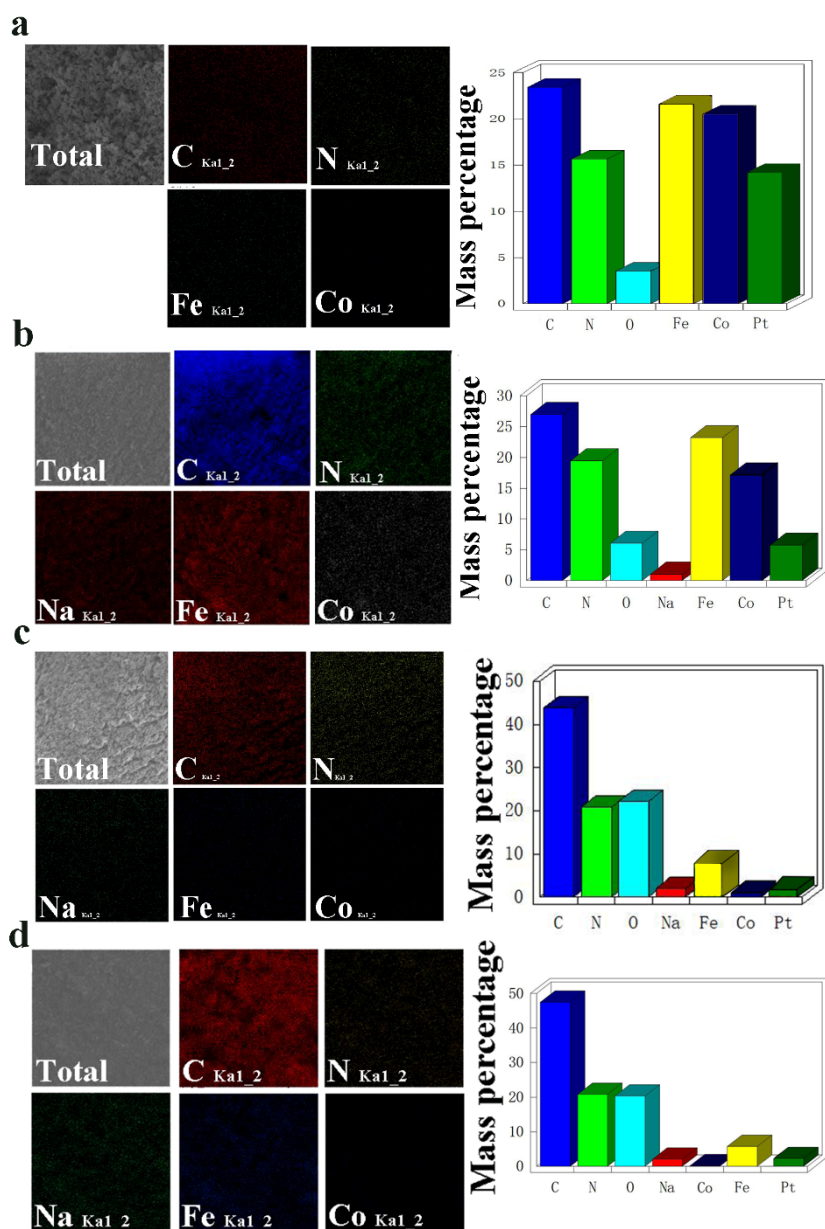


Figure S4. EDS analysis and the element mapping images of (a) Sample-CF, (b) Sample-FF-1, (c) Sample-FF-4 and (d) Sample-FF.

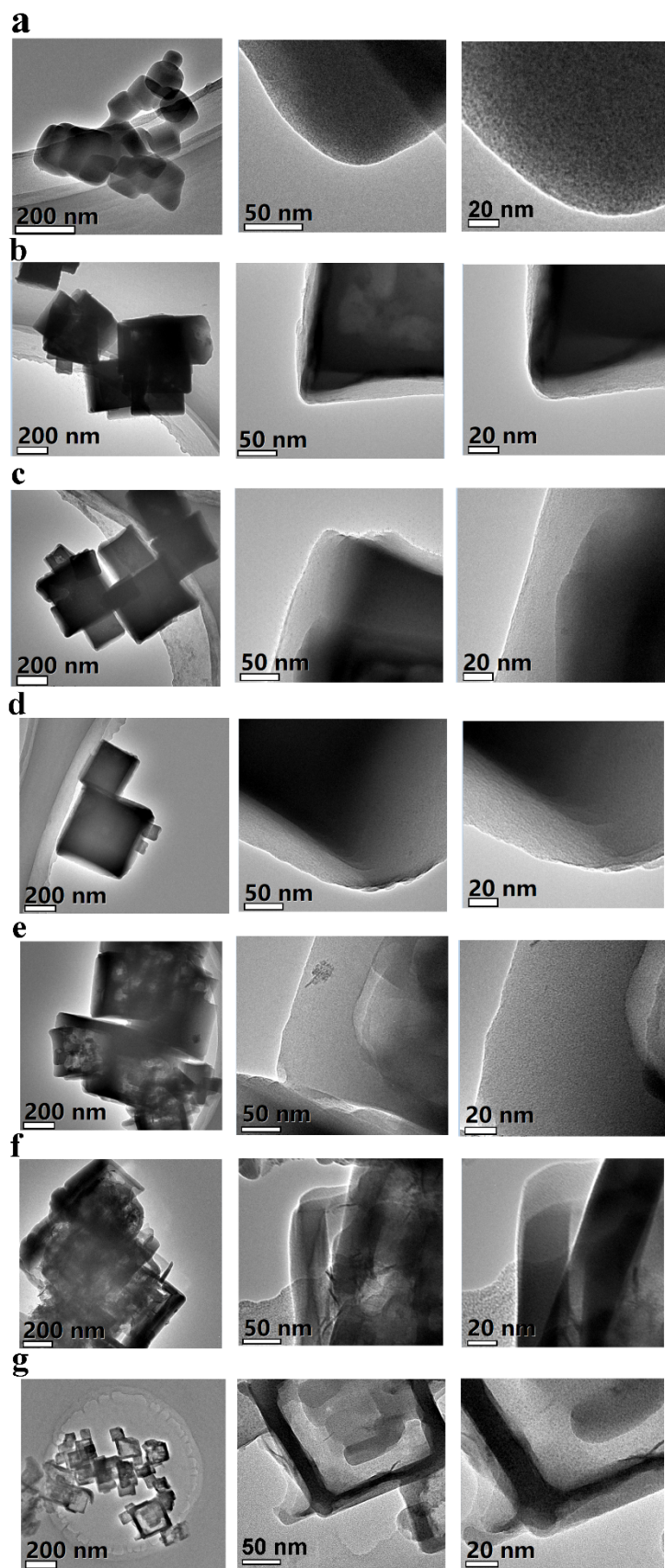


Figure S5. TEM images of (a) Sample-CF, (b) Sample-FF-1, (c) Sample-FF-2, (d) Sample-FF-3, (e) Sample-FF-4, (f) Sample-FF-5 and (g) Sample-FF.

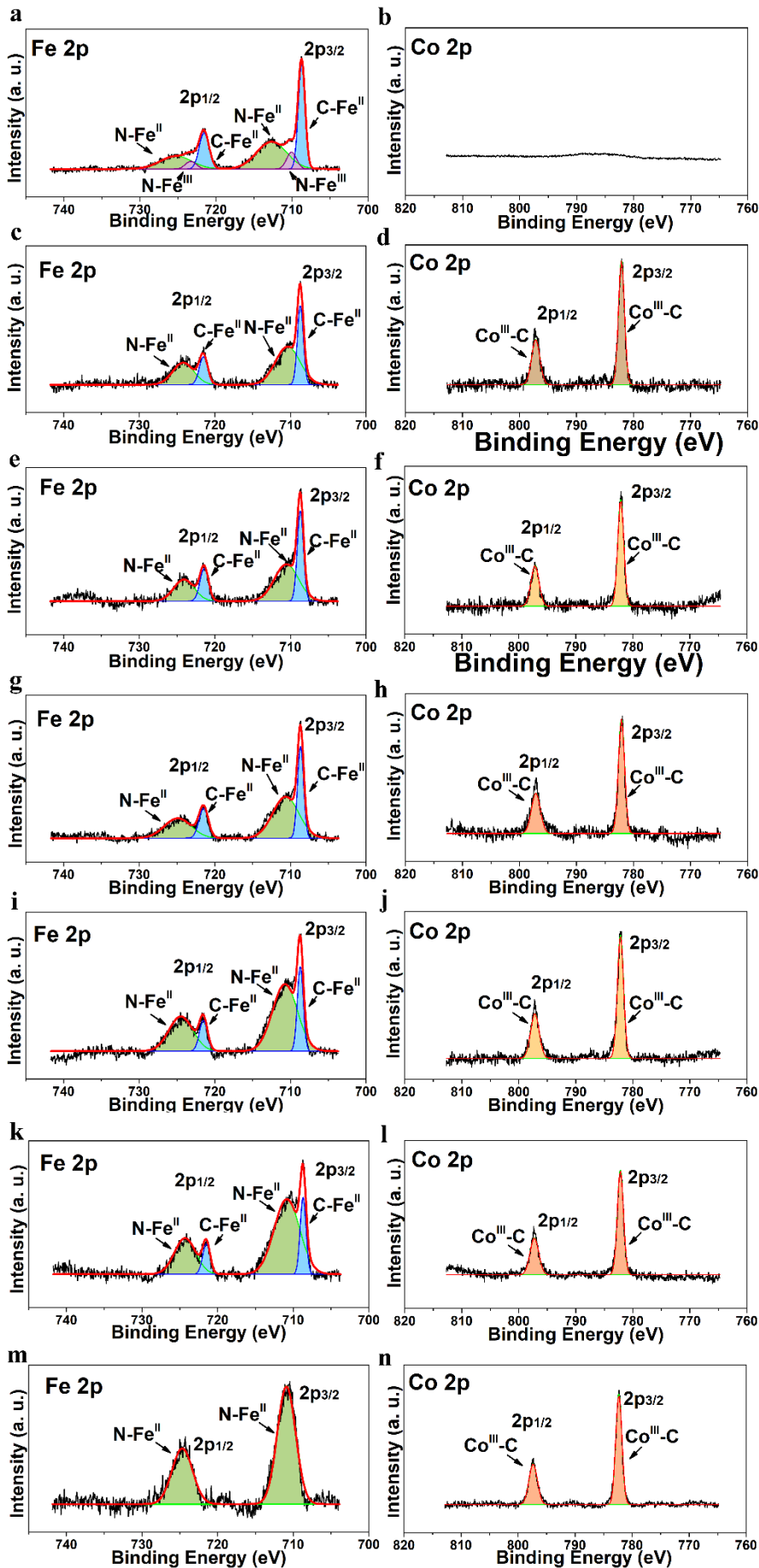


Figure S6. Ex situ XPS results of (a, b) Sample-CF, (c, d) Sample-FF-1, (e, f) Sample-FF-2, (g, h) Sample-FF-3, (i, j) Sample-FF-4, (k, l) Sample-FF-5 and (m, n) Sample-FF.

a							
Quantify By		Components					
Sample-CF							
Component	BE [eV]	FWHM [eV]	RSF	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]
Fe 2p	710.46	0.00	2.96	2.7	0.38	10.1	1.30
Co 2p	782.31	0.00	3.59	3.3	0.51	13.0	1.78
N 1s	398.71	0.00	0.48	17.5	0.45	16.2	0.55
C 1s	284.96	0.00	0.28	76.4	0.68	60.6	1.58

b							
Quantify By		Components					
Sample-FF							
Component	BE [eV]	FWHM [eV]	RSF	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]
Co 2p	803.17	0.00	3.59	0.0	0.06	0.1	0.22
N 1s	397.97	0.00	0.48	22.4	0.55	21.1	0.67
C 1s	285.02	0.00	0.28	72.2	0.68	58.5	1.34
Fe 2p	708.77	0.00	2.96	5.4	0.54	20.3	1.70

c							
Quantify By		Components					
Sample-PB							
Component	BE [eV]	FWHM [eV]	RSF	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]
Fe 2p	708.70	0.00	2.96	7.2	0.61	25.9	1.75
Co 2p	805.40	0.00	3.59	0.0	0.07	0.1	0.25
N 1s	397.95	0.00	0.48	21.8	0.66	19.5	0.73
C 1s	285.00	0.00	0.28	70.9	0.80	54.4	1.40

Figure S7. XPS element mass content test: (a) Sample-CF. (b) Sample-FF. (c) Sample-PB.

Table S1. ICP result

Sample ID	Sample-FF		Sample-PB	
	Na	Fe	Na	Fe
Mean	1.587	5.166	0.547	2.2
Units	mg/L	mg/L	mg/L	mg/L

EA result

Sample ID	Sample-FF		Sample-PB	
	C	N	C	N
Weight ratio	20.535	23.958	17.744	20.701

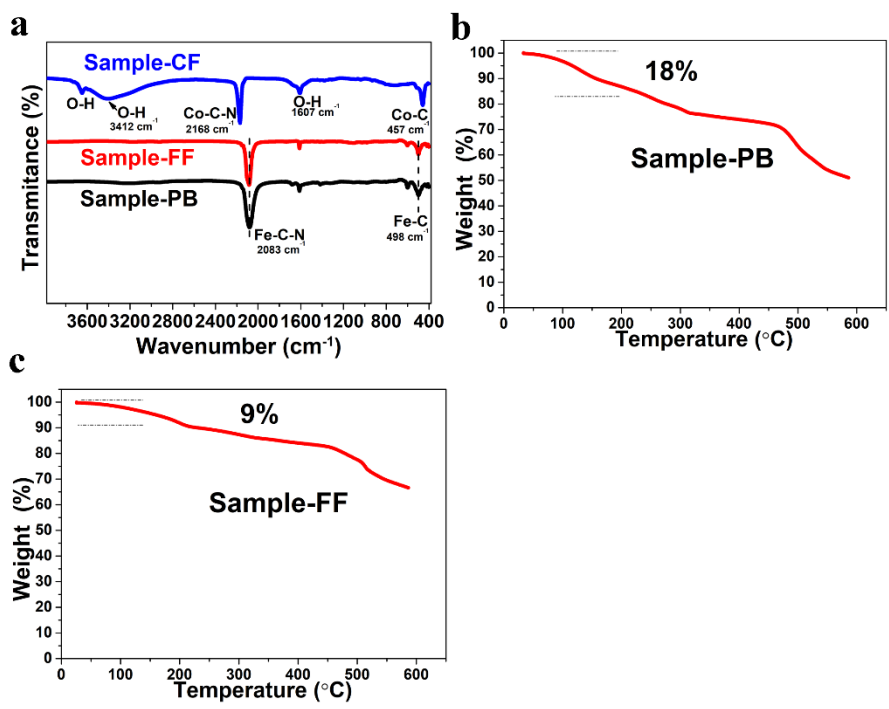


Figure S8. TG curves of (a) Sample-FF and (b) Sample-PB.

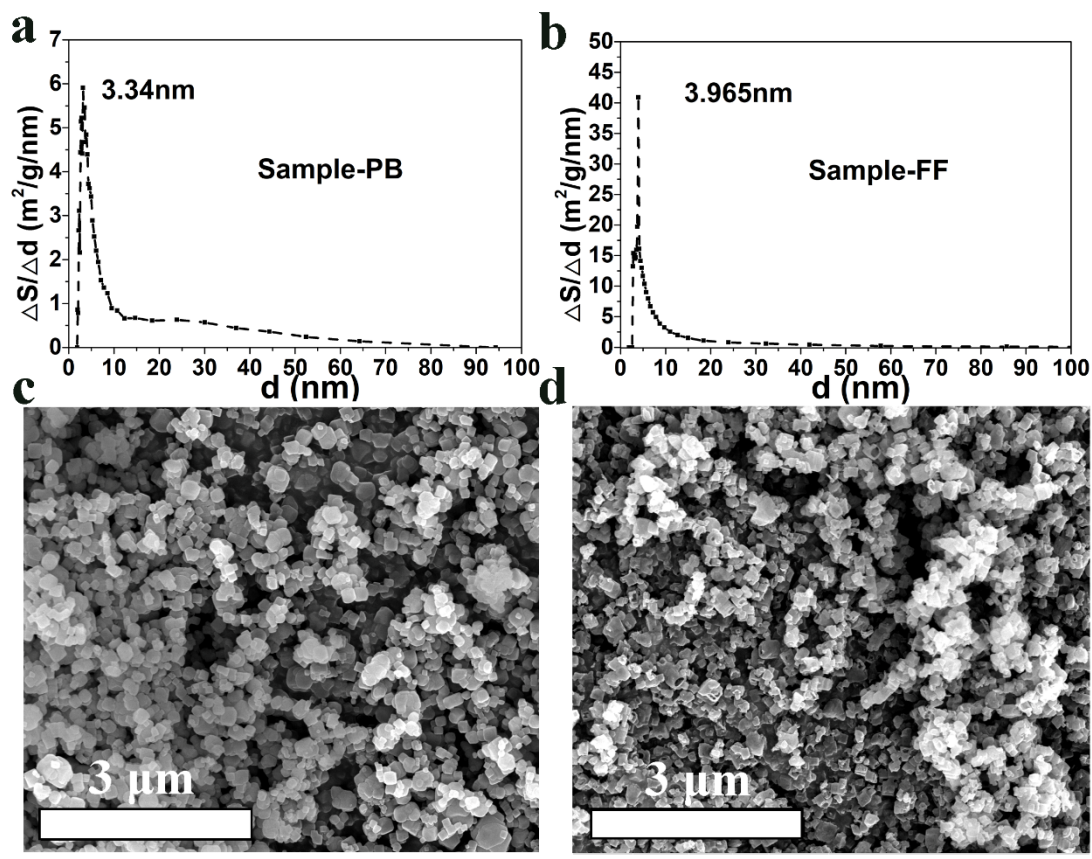


Figure S9. (a) The BJH pore-size distribution plot the Sample-PB. (b) The BJH pore-size distribution plot the Sample-FF. (c) The HR-FESEM image of the Sample-PB. (d) The HR-

FESEM image of the Sample-FF.

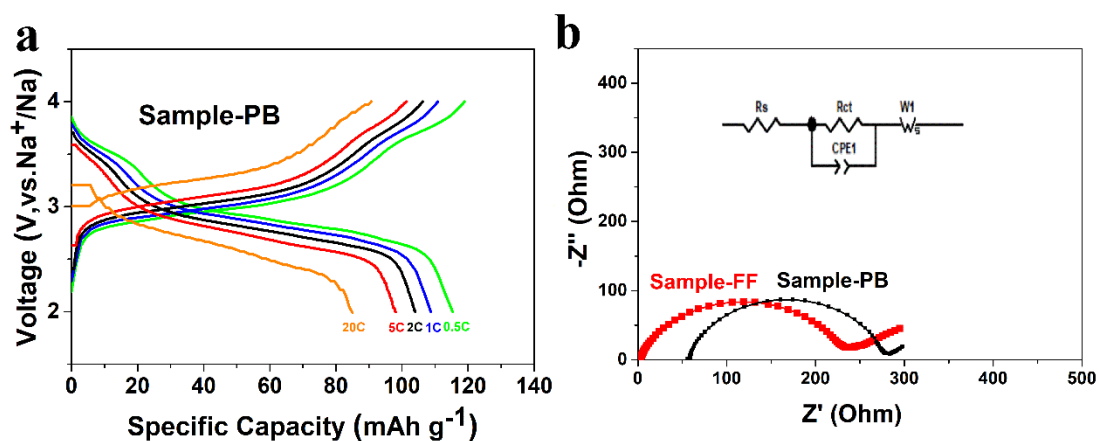


Figure S10. (a) charge/discharge curves of the Sample-PB at various current densities. (b) EIS plot and fitted result of both the samples.

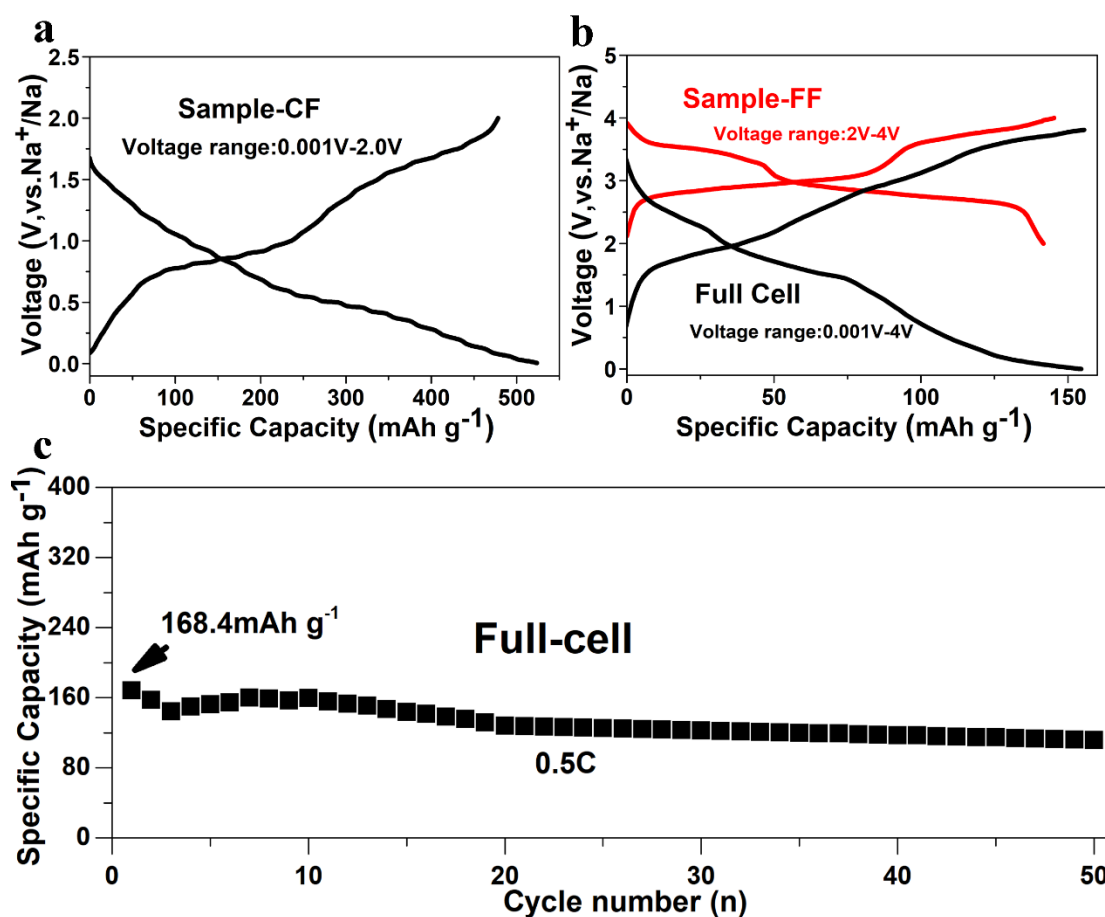


Figure S11. (a) Electrochemical charge and discharge plots of the Sample-CF at a current density of 100 mA g⁻¹. (b) The Sample-FF/the Sample-CF full-cell charge and discharge plots at a current density of 0.5C, 1 C=170 mA g⁻¹. (c) Full-cell electrochemical cycling performance at a current density of 0.5C, 1 C=170 mA g⁻¹.

title	Precursors	additive name	Need additive	Structures	Applications	Specific capacity	Year
Frontispiece: Synthesis of Monocrystalline Nanoframes of Prussian Blue Analogues by Controlled Preferential Etching	Ni-Fe cube	HCl	YES	Ni-Fe yolk@frame structure	Na+/Li+ storage	less than 100 mAh/g at 1C	2016
Potassium ions stabilized hollow Mn-based prussian blue analogue nanocubes as cathode for high performance sodium ions battery	Mn-Fe cube	sodium citrate assisted	YES	Mn-Fe Box	Na+ storage	128 mAh/g at 50mA/g	2020
Hierarchical sodium-rich Prussian blue hollow nanospheres as high-performance cathode for sodium-ion batteries	Fe-Fe cube	ascorbic acid, and NaCl	YES	hollow sphere	Na+ storage	142 mAh/g at 0.1C	2018
Metal-organic-framework-derived hollow polyhedrons of prussian	Co-Fe cube	cetyltrimethylammonium bromide	YES	CoHCF hollow dodecahedrons	Na+ storage	32.7–50 Wh/kg	2019
Hierarchical Hollow Prussian Blue Rods Synthesized via Self-Sacrifice Template as Cathode for High Performance Sodium Ion Battery	MnO2 nanosheet	tetramethylammonium hydroxide	YES	hollow rod-like structure	Na+ storage	117.3 mAh/g at 1C	2018
A Chemical Precipitation Method Preparing Hollow-Core-Shell Heterostructures Based on the Prussian Blue Analogs as Cathode for Sodium-Ion Batteries	PBA cube	3.0 g of PVP (K30, MW ≈ 40 000) and 4.38 g of sodium citrate	YES	hollow structure	Na+ storage	123 mA h/g at 1C	2018
This work	Fe-Co cube	NO	NO	hollow cube	Na+ storage	133.6mAh/g at 1C	

Figure S12. Comparison of other reported work and this work.

The calculation process of the exact formula:

The Sample-FF:



The formula changes into $\text{Na}_{x_1}\text{Fe}_1[\text{Fe}(\text{CN})_6]_{y_1}$

1. $x_1:(y_1+1) = (1.587/23) : (5.166/56)$ -----atom ratio
2. $x_1+2=4y_1$ -----electron balance

Result: $x_1=1.38, y_1=0.845$.

Water content:



$$18\delta : (157.03 + 18\delta) = 9 : 100 \quad \text{-----weight ratio}$$

Result: $\delta=0.86$

The Sample-PB:



The formula changes into $\text{Na}_{x_2}\text{Fe}_1[\text{Fe}(\text{CN})_6]_{y_2}$

3. $x_2:(y_2+1) = (0.547/23) : (2.2/56)$ -----atom ratio
4. $x_2+2=4y_2$ -----electron balance

Result: $x_2=1.07, y_2=0.768$.

Water content:



$$18\delta:(143.51+18\delta)=18:100$$

-----weight ratio

Result: $\delta=1.75$