## Electronic Supplementary Information

# Foam-like CoO@N,S-codoped carbon composition derived from a well-designed N,S-rich Co-MOF for lithium-ion battery

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#### **Reagents and instruments**

All starting materials were purchased from Sigma-Aldrich and used without any purification. The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Bruker D8 diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.5418 Å) at room temperature. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (Hitachi SU-8010 field emission SEM), and transmission electron microscopy (FEI Tecnai G20). All TEM samples were prepared by depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid. Thermogravimentric analysis (TGA) was carried on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The gas sorption isotherms were measured on an autosorp-IQ instrument from Quantachrome Instruments Corporation (Boynton Beach, Florida USA). IR spectra were recorded on a PerkinElmer Spectrum Two in the frequency range of 4000-400 cm<sup>-1</sup>. The diffuse-reflectance spectra were recorded on a UV/Vis spectrophotometer (Evolution 220, ISA-220 accessory, Thermo Scientific) using a built-in 10 mm silicon photodiode with a 60 mm Spectralon sphere.

### Synthesis of [Co(dmimpym)(tdc)(H<sub>2</sub>O)·H<sub>2</sub>O]<sub>n</sub> (1)

A mixture of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 mmol, 291 mg), 4,6-di(2-methyl-imidazol-1-yl)pyrimidine (1 mmol, 234 mg), and 2,5-thiophenedicarboxylic acid (1 mmol, 172 mg) was suspended in 20 mL MeOH-H<sub>2</sub>O (v:v =1:1) in the presence of 200  $\mu$ L 0.1 M NaOH aqueous solution. Such mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 120 °C for 3 days. After cooling to the room temperature, purple block crystals were isolated by filtration, washed with EtOH and dried in air. Yield: 55 % (based on Co). Elemental analysis calcd (%) for (C<sub>18</sub>H<sub>18</sub>CoN<sub>6</sub>O<sub>6</sub>S): C 42.78, H 3.59, N 16.63; found: C 42.58, H 3.66, N 16.24. Selected IR peaks (cm<sup>-1</sup>): 1580 (m), 1353 (s), 1294 (s), 1175 (w), 997 (w), 752 (s), 669 (m), 500 (s).

#### Synthesis of foam-like CoO/N, S-C

CoO/N, S-C composite was synthesized via calcination of the obtained MOF precursors at 550 °C for 2 h in a Ar condition with a slow heating rate of 5 °C·min<sup>-1</sup>. The resulting powder was black in color.

#### **Electrochemical measurements**

The working electrode was fabricated through squeezing a mixture of binder (Polyacrylic acid, 50%), superconductive carbon black, and active materials, which the mixture weight ratio is 10: 20: 70. The average mass of active materials is about 0.4 mg and the areal mass loading of the active material is  $0.8 \text{ mg/cm}^2$ . Lithium was used as the reference and counter electrodes. 1 M LiPF<sub>6</sub> electrolyte dissolved in a mixture, which is composed with dimethyl carbonate (DMC), ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (volume ratio of 1:1:1). The LAND-CT2001A instrument was used to measure the cycle life and electrochemical capacity of the working electrode by the galvanostatic method at the charge and discharge current density of 100 - 1200 mA  $\cdot$ g<sup>-1</sup>. The cut-off potential for charge/discharge was set at 0.01 and 3.0 V (vs. Li<sup>+</sup>/Li). All electrochemical measurements were performed at ambient temperature.

Empirical formula	C <sub>18</sub> H <sub>18</sub> CoN <sub>6</sub> O <sub>6</sub> S
Formula weight	505.37
Temperature/K	298.15
Crystal system	orthorhombic
Space group	Pna2 <sub>1</sub>
a/Å	10.5854(16)
b/Å	12.2457(18)
c/Å	16.403(2)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	2126.2(5)
Ζ	4
$\rho_{calc}g/cm^3$	1.579
μ/mm <sup>-1</sup>	0.954
F(000)	1036.0
Radiation	MoKα ( $\lambda$ = 0.71073)
$2\Theta$ range for data collection/°	5.086 to 49.996
Index ranges	$-9 \le h \le 12, -14 \le k \le 13, -18 \le l \le 19$
Reflections collected	9476
Independent reflections	$3646 [R_{int} = 0.0234, R_{sigma} = 0.0409]$
Data/restraints/parameters	3646/1/293
Goodness-of-fit on F <sup>2</sup>	1.031
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0294, wR_2 = 0.0761$
Final R indexes [all data]	$R_1 = 0.0339, wR_2 = 0.0789$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.47/-0.33
Flack parameter	-0.009(8)

 Table S1. Crystal data collection and structure refinement.

Co1—O1	2.115 (3)	Co1—N6 <sup>ii</sup>	2.174 (3)
Co1—O2	2.287 (3)	O4—Co1 <sup>iii</sup>	2.040 (3)
Co1—O4 <sup>i</sup>	2.039 (3)	Co1—N1	2.115 (4)
O1—Co1—O2	59.86 (11)	O4 <sup>i</sup> —Co1—N1	97.07 (14)
01—Co1—N1	103.50 (13)	O4 <sup>i</sup> —Co1—N6 <sup>ii</sup>	88.07 (12)
O1—Co1—N6 <sup>ii</sup>	96.93 (13)	N1—Co1—O2	163.33 (12)
04 <sup>i</sup> —Co1—O1	158.38 (12)	N1—Co1—N6 <sup>ii</sup>	94.17 (13)
O4 <sup>i</sup> —Co1—O2	99.58 (12)	N6 <sup>ii</sup> —Co1—O2	87.40 (12)
Symmetry codes: (i) $-x+1/2$ , $y-1/2$ , $z+1/2$ ; (ii) $-x+3/2$ , $y-1/2$ , $z-1/2$ ; (iii) $-x+1/2$ , $y+1/2$ , $z-1/2$ ; (iv) $-x+3/2$ , $y+1/2$ , $z+1/2$ .			

Table S2. Selected bond lengths (Å ) and angles (°).

Figure S1: The IR spectrum of 1.



Figure S2: The UV-Vis spectrum of 1 in the solid state.



Figure S3. Compared PXRD patterns of 1.



Figure S4. Element mapping of 1 in the solid state.



Figure S5. TGA curve of 1 in the solid state.



Figure S6. N<sub>2</sub> adsorption/desorption isotherms and BJH pore size distribution of FCNSC.



Figure S7. EDX of CoO/N,S-C sample.



Table S3 the atom % content of elements in CoO/N, S-C according to EDX and

XPS	results.
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Elements	Со	0	С	N	S
EDX (atom%)	24.48	40.48	24.90	6.61	3.53
XPS (atom%)	23.78	38.24	27.22	6.99	3.76

		Capacity retention	
Active material	Charging rate	(Capacity in	Cycle No
	$(mA \cdot g^{-1})$	$mAh \cdot g^{-1}$ )	
This work	1000	887	200
CoO <sup>[1]</sup>	60	893	60
CoO nanonets <sup>[2]</sup>	1000	637	200
CoO/C <sup>[3]</sup>	1400	855	100
CoO/N-C <sup>[4]</sup>	100	598	50
Carbon-decorated	100	800	70
CoO <sup>[5]</sup>			
ultra-small CoO/C	70	642	50
nanocomposite <sup>[6]</sup>			
Pomegranate-like	89	1244	120
CoO@NC			
microspheres <sup>[7]</sup>			

Table S4 Comparison of the LIB performances for different electrodes.

Figure S8. Voltage profile of CoO/N,S-C sample at current different densities between 0.01 and 3 V.



Figure S9. Cycling performance of three different samples at 1 A·g<sup>-1</sup>.



Figure S10. Optical photograph and SEM image of (a-c) the electrode film before the cycle test, (d-f) the electrode film after the cycle test.



Figure S11. SEM image and Element mapping of FCNSC electrode after 200 cycle at a current density of 1 A g<sup>-1</sup>.



Figure S12. XPS of Co2p (a), O1s (b), C1s (c), N1s (d) and S2p (e) after cycling.



#### **References:**

- 1. M. V. Reddy, G. Prithvi, K. P. Loh, B. V. R. Chowdari, ACS Appl. Mater. Interfaces, 2014, 6, 680-690.
- X. Zhou, Y. Zhong, M. Yang, Q. Zhang, J. Wei, Z. Zhou, ACS Appl. Mater. Interfaces, 2015, 7, 12022-12029.
- 3. J. H. Kim, Y. C. Kang, Nanoscale 2014, 6, 4789-4795.
- K. Xie, P. Wu, Y. Zhou, Y. Ye, H. Wang, Y. Tang, Y. Zhou, T. Lu, ACS Appl. Mater. Interfaces, 2014, 6, 10602-10607.
- S. Xiong, J. S. Chen, X. W. Lou, H. C. Zeng, Adv. Funct. Mater., 2012, 22, 861-871.
- S. Chu, C. Yang, X. Xia, J. Wang, Y. Hou, X. Su, New J. Chem., 2016, 40, 2722-2729.
- 7. G. Liu, J. Shao, J. Mater. Chem. A, 2017, 5, 9801-9806.