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Electronic Supplementary Information

An Insight into the Pyrolysis Process of Metal-Organic Framework Templates/Precursors to Construct Metal Oxide Anode Materials for Lithium-Ion Batteries

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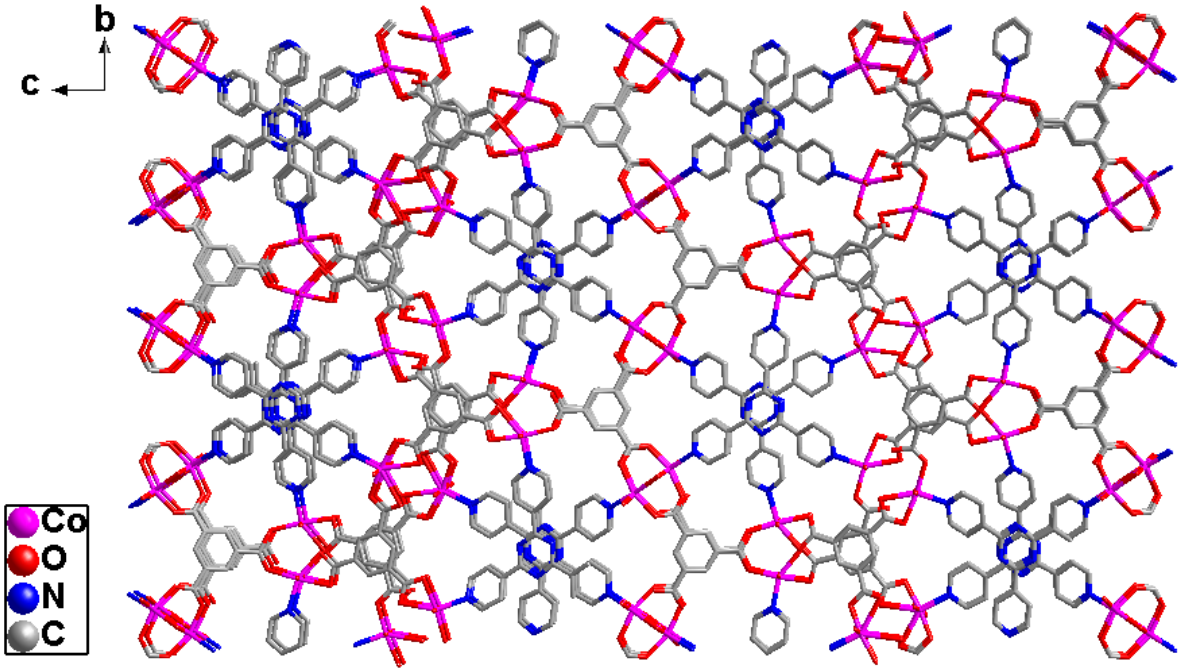

Fig.S1 The three dimensional (3D) framework of rod-like MOF.

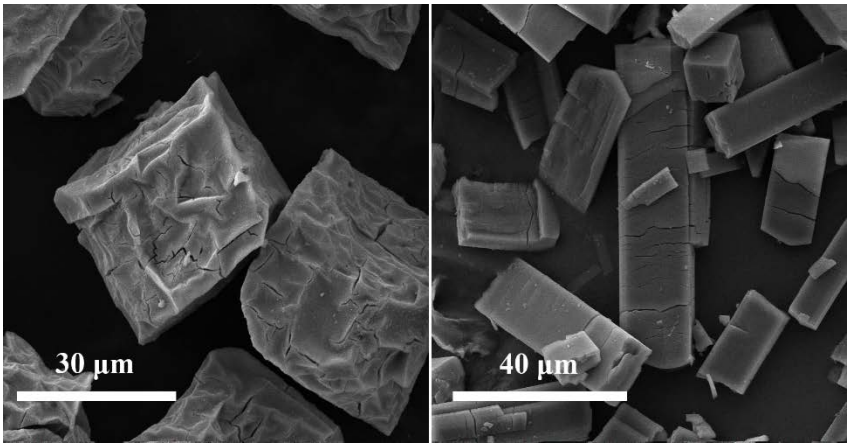

Fig. S2 The SEM images (low magnification) for the cube-like Co_3O_4 (left) and rod-like Co_3O_4 (right) samples.

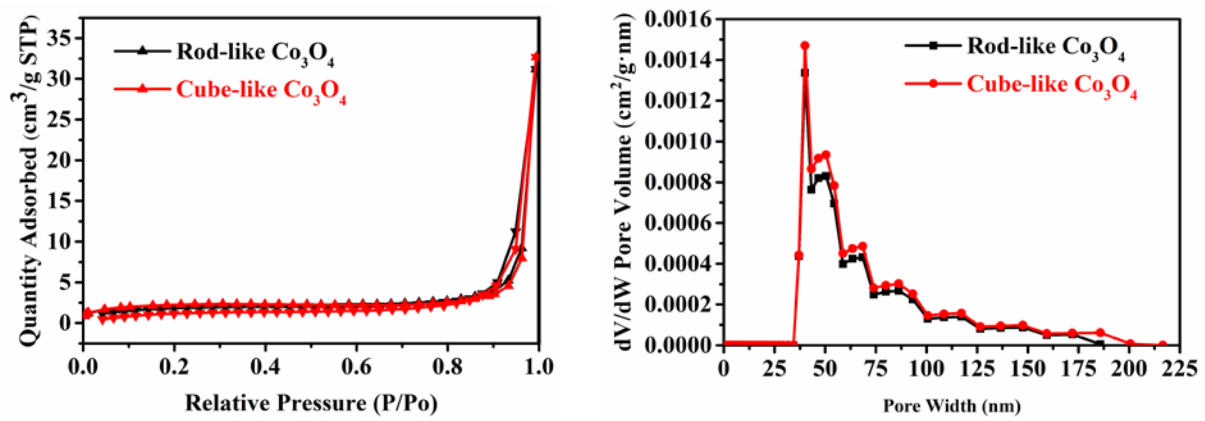

Fig S3 (a) Nitrogen sorption-desorption isotherms of rod-like Co_3O_4 and cube-like Co_3O_4 at 77 K. (b) The Pore-size distribution of rod-like Co_3O_4 and cube-like Co_3O_4.

Table S1. Crystal data and structure refinement parameters for rod-like MOF

Formula	$C_{72}H_{46}N_{12}O_{39}Co_6$
Mr (g mol^{-1})	2056.79
Space group	$P2_1/c$
Crystal system	monoclinic
a (Å)	7.2370(14)
b (Å)	18.371(4)
c (Å)	62.028(12)
α (°)	90
β (°)	92.02(3)
γ (°)	90
V ($Å^3$)	8242(3)
Z	4
F(000)	4144
D_c (gcm^{-3})	1.658
μ(mm^{-1})	1.282
Reflns collected/ Rint	36432/0.1433
Independent reflns	1172
Limiting indices	$-10 \leq h \leq 0$, $-25 \leq k \leq 25$, $-86 \leq l \leq 86$
GOF on F^2	1.057
R_1, wR_2 [$I>2\sigma(I)$][a]	0.2394 0.5551
R_1, wR_2 [all data][b]	0.2548 0.5615

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$

Table S2 Selected bond lengths (nm) for rod-like MOF

Co(1)-O(26)	2.036(11)	Co(4)-O(17)	2.014(8)
Co(1)-O(25)	2.049(11)	Co(4)-O(20)	2.057(9)
Co(1)-O(8)	2.093(11)	Co(4)-O(32)	2.099(11)
Co(1)-N(3)	2.101(9)	Co(4)-N(9)#2	2.104(9)
Co(1)-O(2)	2.157(8)	Co(4)-O(34)	2.189(9)
Co(1)-O(1)	2.386(9)	Co(4)-O(33)	2.206(11)
Co(2)-O(27)	2.028(9)	Co(5)-O(35)	2.025(9)
Co(2)-O(5)#1	2.035(10)	Co(5)-O(36)	2.029(9)
Co(2)-O(9)	2.095(9)	Co(5)-O(23)	2.066(8)
Co(2)-O(28)	2.105(10)	Co(5)-O(11)#3	2.080(8)
Co(2)-N(8)	2.139(10)	Co(5)-N(2)#4	2.125(11)
Co(3)-O(19)	2.028(9)	Co(6)-O(30)	2.004(8)
Co(3)-O(18)	2.044(10)	Co(6)-O(13)	2.051(8)
Co(3)-N(1)	2.088(11)	Co(6)-O(29)	2.051(9)
Co(3)-O(31)	2.126(10)	Co(6)-N(7)#5	2.136(11)
Co(3)-O(33)	2.204(9)	Co(6)-O(3)#5	2.155(9)
Co(3)-O(34)	2.249(11)	Co(6)-O(4)#5	2.234(9)
Co(3)-Co(4)	2.963(2)		

#1 x,y-1,z #2 x-1,-y+1/2,z+1/2 #3 -x,y+1/2,-z+1/2 #4 -x,y-1/2,-z+1/2 #5 -x,-y+1,-z

Table S3 Selected angles (°) for rod-like MOF

O(26)-Co(1)-O(25)	174.9(4)	O(17)-Co(4)-O(20)	159.4(4)
O(26)-Co(1)-O(8)	93.8(4)	O(17)-Co(4)-O(32)	93.3(5)
O(25)-Co(1)-O(8)	85.1(4)	O(20)-Co(4)-O(32)	101.8(6)
O(26)-Co(1)-N(3)	93.3(4)	O(17)-Co(4)-N(9)#2	99.2(4)
O(25)-Co(1)-N(3)	91.7(4)	O(20)-Co(4)-N(9)#2	94.1(4)
O(8)-Co(1)-N(3)	93.3(4)	O(32)-Co(4)-N(9)#2	92.4(5)
O(26)-Co(1)-O(2)	90.1(3)	O(17)-Co(4)-O(34)	84.7(4)
O(25)-Co(1)-O(2)	90.3(4)	O(20)-Co(4)-O(34)	82.0(3)
O(8)-Co(1)-O(2)	171.6(3)	O(32)-Co(4)-O(34)	87.8(5)
N(3)-Co(1)-O(2)	93.8(4)	N(9)#2-Co(4)-O(34)	176.0(4)
O(26)-Co(1)-O(1)	84.9(3)	O(17)-Co(4)-O(33)	82.4(4)
O(25)-Co(1)-O(1)	91.1(3)	O(20)-Co(4)-O(33)	83.7(4)
O(8)-Co(1)-O(1)	116.0(3)	O(32)-Co(4)-O(33)	173.3(6)
N(3)-Co(1)-O(1)	150.7(4)	N(9)#2-Co(4)-O(33)	83.3(4)
O(2)-Co(1)-O(1)	57.1(3)	O(34)-Co(4)-O(33)	96.8(4)
O(27)-Co(2)-O(5)#1	94.9(4)	O(35)-Co(5)-O(36)	175.2(4)
O(27)-Co(2)-O(9)	91.5(4)	O(35)-Co(5)-O(23)	90.6(4)
O(5)#1-Co(2)-O(9)	170.5(4)	O(36)-Co(5)-O(23)	90.4(4)
O(27)-Co(2)-O(28)	177.7(4)	O(35)-Co(5)-O(11)#3	87.7(4)
O(5)#1-Co(2)-O(28)	82.9(4)	O(36)-Co(5)-O(11)#3	90.8(4)
O(9)-Co(2)-O(28)	90.5(4)	O(23)-Co(5)-O(11)#3	173.7(4)
O(27)-Co(2)-N(8)	93.6(4)	O(35)-Co(5)-N(2)#4	91.0(5)
O(5)#1-Co(2)-N(8)	92.8(4)	O(36)-Co(5)-N(2)#4	93.5(4)
O(9)-Co(2)-N(8)	93.8(4)	O(23)-Co(5)-N(2)#4	92.5(4)
O(28)-Co(2)-N(8)	87.4(4)	O(11)#3-Co(5)-N(2)#4	93.6(4)
O(19)-Co(3)-O(18)	159.5(4)	O(30)-Co(6)-O(13)	91.7(4)
O(19)-Co(3)-N(1)	97.2(4)	O(30)-Co(6)-O(29)	175.4(3)
O(18)-Co(3)-N(1)	95.7(5)	O(13)-Co(6)-O(29)	92.5(4)
O(19)-Co(3)-O(31)	96.8(4)	O(30)-Co(6)-N(7)#5	89.8(4)
O(18)-Co(3)-O(31)	98.4(4)	O(13)-Co(6)-N(7)#5	91.1(4)
N(1)-Co(3)-O(31)	92.7(5)	O(29)-Co(6)-N(7)#5	92.0(4)

O(19)-Co(3)-O(33)	84.4(4)	O(30)-Co(6)-O(3)#5	85.3(3)
O(18)-Co(3)-O(33)	83.3(4)	O(13)-Co(6)-O(3)#5	173.9(4)
N(1)-Co(3)-O(33)	177.6(4)	O(29)-Co(6)-O(3)#5	90.3(3)
O(31)-Co(3)-O(33)	85.3(4)	N(7)#5-Co(6)-O(3)#5	94.3(4)
O(19)-Co(3)-O(34)	82.8(4)	O(30)-Co(6)-O(4)#5	86.2(4)
O(18)-Co(3)-O(34)	82.1(4)	O(13)-Co(6)-O(4)#5	114.3(4)
N(1)-Co(3)-O(34)	86.9(5)	O(29)-Co(6)-O(4)#5	90.4(4)
O(31)-Co(3)-O(34)	179.4(4)	N(7)#5-Co(6)-O(4)#5	154.4(4)
O(33)-Co(3)-O(34)	95.1(3)	O(3)#5-Co(6)-O(4)#5	60.2(4)

#1 x,y-1,z #2 x-1,-y+1/2,z+1/2 #3 -x,y+1/2,-z+1/2 #4 -x,y-1/2,-z+1/2 #5 -x,-y+1,-z

Table S4. Comparison of LIBs performances of different Co_3O_4-based anodes.

Electrode materials	Current density	Specific capacity / mAh g^{-1}	Cycling number	Ref.
Cube-like Co_3O_4	100 mA g^{-1}	936.2	500	This work
bowknot-like Co_3O_4	2 C	751.3	150	1
Co_3O_4-$CoFe_2O_4$	100 mA g^{-1}	940	80	2
Co/Co_3O_4@N-C	100 mA g^{-1}	903	100	3
MWCNTs/Co_3O_4	100 mA g^{-1}	813	100	4
Co_3O_4 hollow dodecahedra	100 mA g^{-1}	1115	50	5
Hollow Co_3O_4 parallelepipeds	100 mA g^{-1}	780	100	6

1. H. Du, C. Yuan, K. Huang, W. Wang, K. Zhang and B. Geng, *J. Mater. Chem. A*, 2017, **5**, 5342-5350.
2. M. Zhong, D.-H. Yang, L.-J. Kong, W. Shuang, Y.-H. Zhang and X.-H. Bu, *Dalton Trans.*, 2017, **46**, 15947-15953.
3. J. Qiu, M. Yu, Z. Zhang, X. Cai and G. Guo, *J. Alloys Compd*., 2019, **775**, 366-371.
4. G. Huang, F. Zhang, X. Du, Y. Qin, D. Yin and L. Wang, *ACS Nano*, 2015, **9**, 1592-1599.
5. Y. Han, M. Zhao, L. Dong, J. Feng, Y. Wang, D. Li and X. Li, *J. Mater. Chem. A*, 2015, **3**, 22542-22546.
6. R. Wu, X. Qian, X. Rui, H. Liu, B. Yadian, K. Zhou, J. Wei, Q. Yan, X.-Q. Feng, Y. Long, L. Wang and Y. Huang, *Small*, **2014**, 10, 1932-1938