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# **Electronic Supplementary Information**

# Conductive Co-based metal-organic framework nanowires: a competitive highrate anode towards advanced Li-ion capacitors

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#### **Experimental Section**

#### Materials synthesis

The electronic conductive Co<sub>3</sub>(HHTP)<sub>2</sub> was prepared by a facile solvothermal method. Typically, cobalt acetate tetrahydrate (100 mg) and 2, 3, 6, 7, 10, 11hexahydroxytriphenylene (HHTP) (70 mg) were added in 12 mL deionized (DI) water. After sonicated for 30 min, the solution was transferred into an oven at 85 °C for 24 h. Finally, the product was collected and washed with sufficient DI water and acetone, followed by dried at 85 °C for 24 h in vacuum.

Activated carbon spheres (denoted as ACS) were prepared by the inexpensive and readily available soluble starch. Firstly, 1 g of soluble starch was dissolved in 50 mL of DI water and stirred for 2 h in water bath at 100 °C. Then, the solution was transferred into a 50 mL of Teflon-lined autoclave and placed in an oven at 180 °C for 16 h. The generated carbon spheres (CS) were collected, washed thoroughly by water and ethanol, and dried at 60 °C in vacuum. The CS were pre-carbonized at 500 °C, and then activated using KOH with a mass ratio of 1 : 4 (CS : KOH) at 800 °C. After washed and dried thoroughly, the ACS was finally obtained.

## Material characterizations

The phase structure of the samples were studied by a BREKER-D8ADVANCE type X-ray diffractometer (Cu, K $\alpha$ ) with a scanning rate of 20° min<sup>-1</sup>. Fourier transformed infrared spectroscopy (FT-IR) was recorded on Nicolet iS50 instrument in transmission mode in the wavenumber range from 400 to 4000 cm<sup>-1</sup>. The morphology of the sample was expressed by field-emission scanning electron microscopy (FESEM, JEOL-6300F), and transmission electron microscopy (TEM) (JEOL JEM-2100). The Brunauer-Emmett-Teller (BET) surface area and pore size distribution data were collected by N<sub>2</sub> adsorption/desorption tests at 77 K using Quantachrome (NOVA 2000). X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo, Escalab 250xi spectrometer equipped with Al K*a* monochromatic X-ray source (1486.6 eV). The Raman spectra were recorded using a Renishaw1000B Raman spectrometer (with 633 nm laser excitation). The electronic conductivity measurement was conducted by a four-point probe meter (SDY-5, Guangzhou, China).

#### *Electrochemical measurements*

The Li-ion storage performance of the  $Co_3(HHTP)_2$  was investigated by half-cell configuration. The working electrode was fabricated by electroactive materials, acetylene black (AB) and carboxymethylcellulose sodium (CMC) with a mass ratio of 7 : 2 : 1, using the DI water as the dispersant. The slurry was coated on copper foil and dried under vacuum at 110 °C overnight. The mass loading was about 1 mg cm<sup>-2</sup>. The half-cell was assembled in a glove box (MIKROUNA) using LiPF<sub>6</sub>, polyethylene and Li metal were served as the electrolytes, separator and cathode, respectively. For the cathode electrode, ACS, AB, and polyvinylidene fluoride (PVDF) at a weight ratio of 8 : 1 : 1 in N-methyl-2-pyrrolidone (NMP) were mixed and coated on an Al foil. After dried at 110 °C in vacuum for 10 h, the ACS cathode electrode was transferred into glove box to fabricate half-cell configuration. The mass loading of ACS is around 1 mg cm<sup>-2</sup>. Finally, Li ion capacitor was also assembled with the Co<sub>3</sub>(HHTP)<sub>2</sub> anode and ACS cathode in the same electrolyte, and the optimized mass ratio of the cathode to

anode was 2.5 : 1.

Electrochemical tests were conducted at room temperature. GCD and CV tests were performed on an IVIUM electrochemical workstation (The Netherlands). The rate performance and cycling tests are carried out on 8-channel Land Test System (CT2001A, Wuhan Jinnuo Electronic Co., Ltd., China). For galvanostatic intermittent titration technique (GITT) analysis, the duration time for each applied galvanostatic current and rest was 200 and 150 s. The Li<sup>+</sup> diffusion coefficient ( $D_{Li}$ ) values can be calculated according to the following equation:<sup>1</sup>

$$D_{Li} = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B S}\right) \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \qquad \tau = \frac{L^2}{D_{Li}} \qquad (1)$$

where  $m_B$ ,  $M_B$ , and  $V_m$  is the practical mass, molecular weight, and molar volume of Co<sub>3</sub>(HHTP)<sub>2</sub>, respectively.  $\tau$  is the time for an applied galvanostatic current; *S* and *L* is the contact area and thickness of the electrode; and  $\Delta E_s$  and  $\Delta E_{\tau}$  are the quasi-equilibrium potential and the change of cell voltage *E* during the current pulse, respectively. The energy density (*E*) of the LICs can be achieved according to the following equation:<sup>2</sup>

$$\mathbf{E} = \int_{t_1}^{t_2} IV(t) dt \qquad (2)$$

The power density (P) of the LIC device can be achieved by the energy density (E) and discharging time (t) according to the following equation:

$$\mathbf{P} = \frac{E}{t} \tag{3}$$



Fig. S1 XRD pattern of the  $Co_3(HHTP)_2$ .



Fig. S2 XPS spectra of Co<sub>3</sub>(HHTP)<sub>2</sub>.



Fig. S3 High resolution XPS spectra: (a) C 1s and (b) O 1s of Co<sub>3</sub>(HHTP)<sub>2</sub>.



Fig. S4 (a)  $N_2$  adsorption/desorption isotherms and (b) pore size distributions of the  $Co_3(HHTP)_2$ .



Fig. S5 (a) FESEM, (b) TEM and (c) HRTEM image of the 1D  $Co_3$ (HHTP)<sub>2</sub> nanowires after the initial lithiation.

FESEM image shows that 1D  $Co_3(HHTP)_2$  NW structure is still preserved, but coated with layer-like structure, which is also observed in TEM image. The layer-like structure may be associated with the SEI formed during the lithiation process.



Fig. S6 High resolution XPS spectra: (a) Co 2p, (b) C 1s, and (c) O 1s of Co<sub>3</sub>(HHTP)<sub>2</sub> after cycling.

The high-resolution Co 2p spectrum (Fig. S6a) exhibits characteristic peaks of Co  $2p_{1/2}$  and Co  $2p_{3/2}$ , as well as other two shake-up satellites at 803 and 786.5 eV, indicating that the state of Co in the Co<sub>3</sub>(HHTP)<sub>2</sub> NWs is divalent. The core level photoelectron spectrum of C 1 s exhibits a slight shift (Fig. S6b), indicating that Li<sup>+</sup> can enter the benzene ring, which is attested by the cathode peak at 0.6 V in the CV curves (Fig. 2a). Meanwhile, the variation of O 1 s spectrum (Fig. S6c) is also associated with the charge-discharge cycles.<sup>3-4</sup>

Materials	Capacity	Discharge rate	Referenc e
Co <sub>3</sub> (HHTP) <sub>2</sub>	715 mAh g <sup>-1</sup>	0.1 A g <sup>-1</sup>	This work
Cobalt 1,3,5-benzenetricarboxylate MOF	845 mAh g <sup>-1</sup>	0.1 A g <sup>-1</sup>	5
Cobalt 1,4-benzenedicarboxylate [Co <sub>2</sub> (OH) <sub>2</sub> BDC]	1107 mAh g <sup>-1</sup>	0.1 A g <sup>-1</sup>	4
$Zn_4O(1,3,5$ -benzenetribenzoate) <sub>2</sub>	105 mAh g <sup>-1</sup>	0.05 A g <sup>-1</sup>	6
Manganese 2,3,5,6- tetrafluoroterephthalatic acid and 4,4'- bipyridine [Mn-(tfbdc)(4,4'-bpy)(H <sub>2</sub> O) <sub>2</sub> ]	390 mAh $g^{-1}$ , after fourth cycle	0.05 A g <sup>-1</sup>	7
Nickel 3,3',5,5'-tetramethyl-4,4'- bipyrazole [Ni-Me <sub>4</sub> bpz]	140 mAh g <sup>-1</sup>	0.05 A g <sup>-1</sup>	8
Nickel 2,3,5,6-tetrafluoroterephthalatic acid and 4,4'-bipyridine $[Ni(4,4'-byy)(tfbdc)(H_2O)_2]$	406 mAh g <sup>-1</sup>	0.05 A g <sup>-1</sup>	9
Manganese 1,4-Naphtalenedicarboxylic acid [Mn <sub>2</sub> (NDC) <sub>2</sub> (DMF) <sub>2</sub> ]	696.4 mAh g <sup>-1</sup>	0.1 A g <sup>-1</sup>	10
Cadmium 1,4-Naphtalenedicarboxylic acid $[Cd_2(NDC)_2(DMF)_2]$	517.6 mAh g <sup>-1</sup>	0.1 A g <sup>-1</sup>	10
Ferrum/Cobalt/Nickel 2,5- dihydroxyterephthalic acid	670 mAh g <sup>-1</sup>	0.1 A g <sup>-1</sup>	11
Nickel terephthalic acid	229 mAh g <sup>-1</sup>	0.5 A g <sup>-1</sup>	12

Table S1 Comparison of the  $Co_3(HHTP)_2$  NWs with previous reported MOF-based anode materials for Li-ion storage.



**Fig. S7** Electrochemical performance of the HHTP: (a) galvanostatic discharge/charge profiles, (b) cycling performance at a current density of 0.5 A g<sup>-1</sup>.



Fig. S8 EIS of the  $Co_3(HHTP)_2$  electrode, (b) EIS of HHTP electrode.



Fig. S9 Cycling stability of the Co<sub>3</sub>(HHTP)<sub>2</sub> anode.



Fig. S10 (a, b) FESEM images and (c, d) TEM images of the 1D Co<sub>3</sub>(HHTP)<sub>2</sub> NWs after 2000 cycles.

As seen from the FESEM and TEM images, no obvious NWs can be observed, may be ascribed to the collapse of NW structures during continues charge/discharge process.



Fig. S11 The linear relationship between the voltage and  $\tau^{1/2}$  for Co<sub>3</sub>(HHTP)<sub>2</sub> anode during (a) discharge and (b) charge process.

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**Fig. S12** FESEM images of the as-synthesized (a) CS and (b) ACS, (c, d) TEM images of the ACS.



Fig. S13 (a) XRD, (b) Raman spectra, (c)  $N_2$  adsorption/desorption isotherms, and (d) pore size distribution of the ACS.



**Fig. S14** Electrochemical performance of the ACS electrode: (a) CV curves from 5 to 100 mV s<sup>-1</sup>, (b) GCD curves, (c) capacities at different current densities, and (d) cycling performance at a current density of 1 A g<sup>-1</sup>.



Fig. S15 (a) CV and (b) GCD curves of the fabricated LICs with the anode to cathode

mass ratio of 1 : 2.0, 1 : 2.5, 1 : 3.0, and 1 : 5.0.



Fig. S16 Specific capacitances at different current densities of the fabricated LICs.



Fig. S17 Rate performance of the  $Co_3(HHTP)_2//ACS$  cell at different current densities from 0.1 to 0.2, 0.5, 1, 2, and 3 A g<sup>-1</sup>.



Fig. S18 EIS of  $Co_3(HHTP)_2//ACS$  cell before and after 2000 cycles.

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