Electronic Supplementary Information

Nitrogen-rich MOF Derived Porous Co_3O_4/N-C Composite with Superior Performance in Lithium-Ion Batteries

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1. Experiment Section

1.1 Regents and equipment

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 CuKα radiation (λ=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).

1.2 Synthesis of N-rich MOFs

In a typical synthesis, A mixture of $Co(OAc)_2 \cdot 4H_2O$ (24.9 mg, 0.1 mmol), diimpym (21.8 mg, 0.1 mmol), and H_2npta (21.1g, 0.1 mmol) were placed into a 25 mL Teflon reactor in the presence of 2 mL methanol-water ($v:v$ = 1:1) and 50 μL 0.1 M NaOH, which was sealed and heated to 120 °C. The temperature was held for 3000 mins, and then the reactant mixture was cooled at a rate of 0.1 °C min^{-1} to room temperature, forming prismatic black crystals of **1** (yield, 70%). IR (solid KBr pellet): ν = 3121 (w), 1626 (m), 1585 (s), 1533(m), 1484 (m), 1348 (m), 1330 (m), 1313 (m), 1274 (w), 1231 (m), 1142 (w), 1102 (w), 1063 (s), 992 (m), 939 (w), 917 (w), 860 (m), 786 (m), 728 (s), 646 (s), 614 (m), 543 (w), 518 (w), 486 (m) cm^{-1}. Elemental analysis calcd (%) for $C_{18}H_{11}CoN_7O_6$: C 45.02, H 2.31, N 20.42; found: C 45.12, H 2.51, N 19.91.

1.3 Synthesis of porous Co_3O_4/N-C

Co_3O_4/N-C composite was synthesized via calcination of the obtained N-rich MOF at 500°C for 2 h in a N_2 condition with a slow heating rate of 0.5 °C·min^{-1}. The resulting powder was black in color.

1.4 Electrochemical measurements.

The working electrode was fabricated through squeezing a mixture of latex binderbinder

(LA132, 15%), Superconductive carbon black, and active materials, which the mixture weight ratio is 10: 20: 70. Then appropriate ethanol was added and stirred for 12h. Lithium was used as the reference and counter electrodes. 1 M $LiPF_6$ 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 $100 - 5000$ mA·g^{-1}. The cut-off potential for charge/discharge was set at 0.01 and 3.0 V (vs.Li$^+$/Li). All electrochemical measurements were performed at ambient temperature.
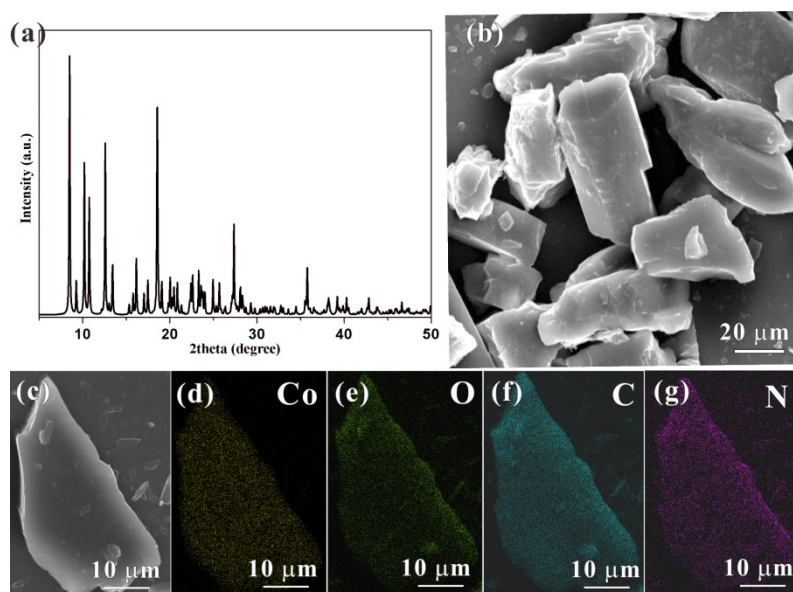
2. Experiment Results

Figure S1. (a) XRD pattern of the N-rich MOF; (b) SEM image of N-rich MOF; (c) SEM image of a typical N-rich MOF structure; (d) Co elemental mapping; (e) O elemental mapping; (f) C elemental mapping; (g) N elemental mapping.
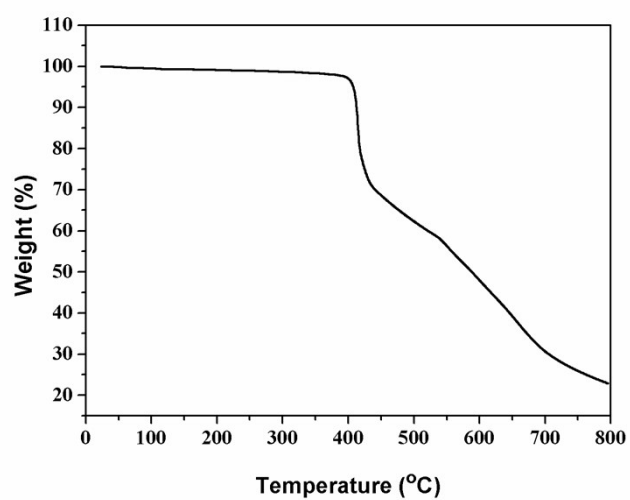

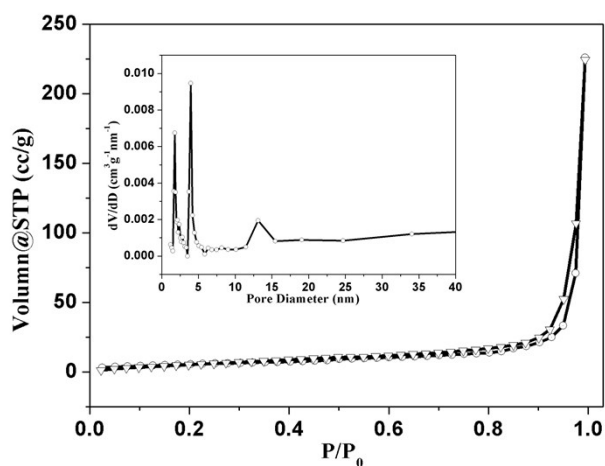Figure S2. TGA curve of sample, indicating that the sample was decomposed at 400 °C.

Figure S3. N$_2$ adsorption–desorption isotherms curves (77 K) of sample, inset is pore size distributions.
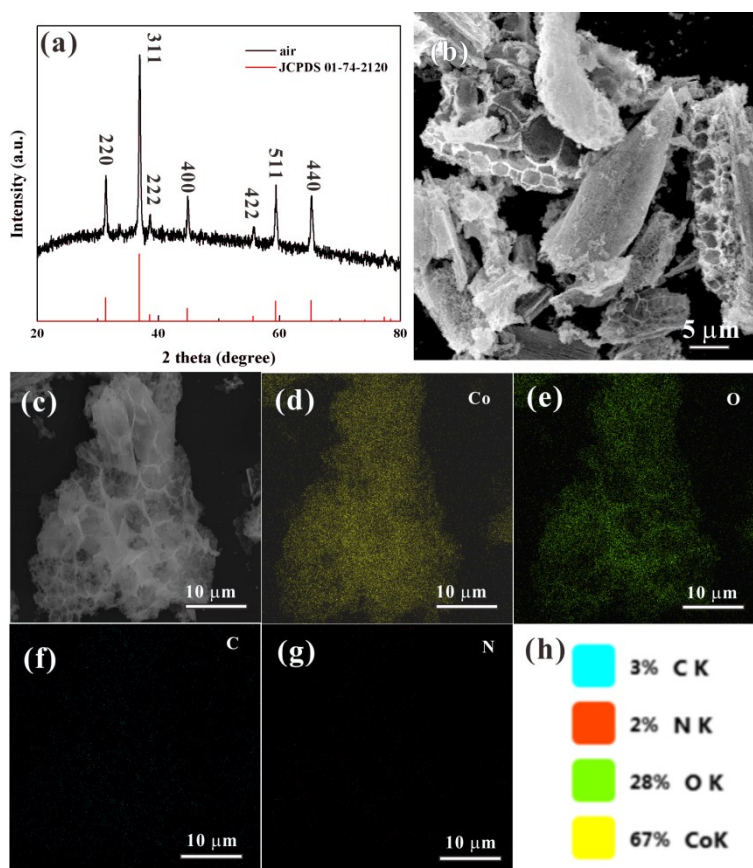

Figure S4. (a) XRD pattern of Co$_3$O$_4$ obtained by Co-MOF calcinated in air atmosphere; (b) the corresponding SEM image; (c) SEM image of a typical Co$_3$O$_4$ structure; (d) Co elemental mapping; (e) O elemental mapping; (f) C elemental mapping; (g) N elemental mapping; (g) atomic ratios of different elements.
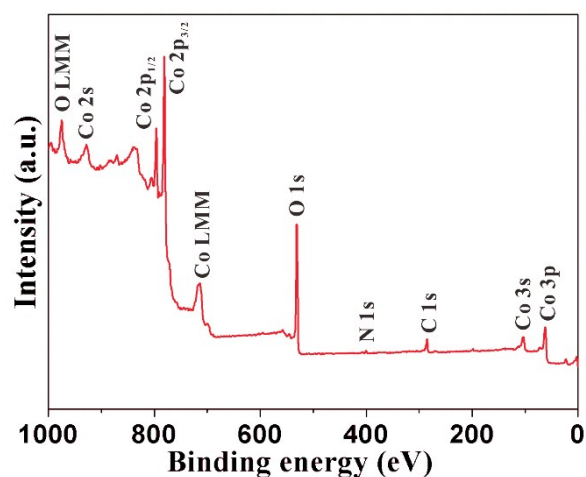
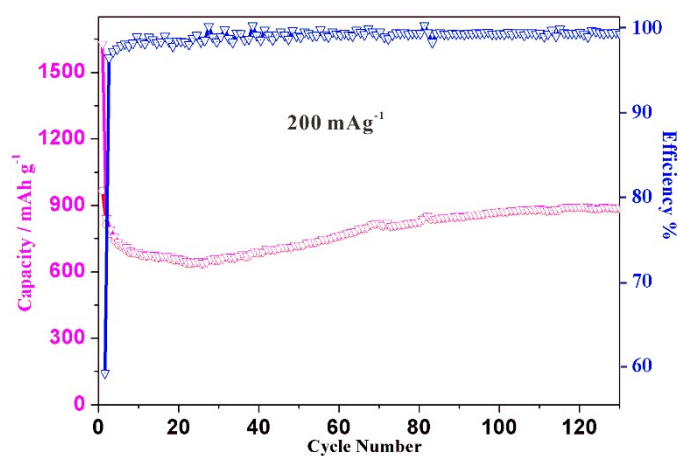Figure S5. Typical survey scanned XPS spectrum of sample.

Figure S6. Cycle performance and corresponding coulomic efficiency curves of sample tested at current density of 200 mA·g^{-1}.

Table S1 Comparison of the LIB performance for different electrodes.

Active material	Charging rate (mA·g^{-1})	Capacity retention (Capacity in mAh·g^{-1})	Cycle No
This work	200	883	130
Co$_3$O$_4$ nanowires [1]	111	700	20
Co$_3$O$_4$ cages [2]	178	670	50
Co$_3$O$_4$/NRGO [3]	100	910	100
Co$_3$O$_4$/GO [4]	50	1004	50
Co$_3$O$_4$ nanoparticles/N-C [5]	100	892	100

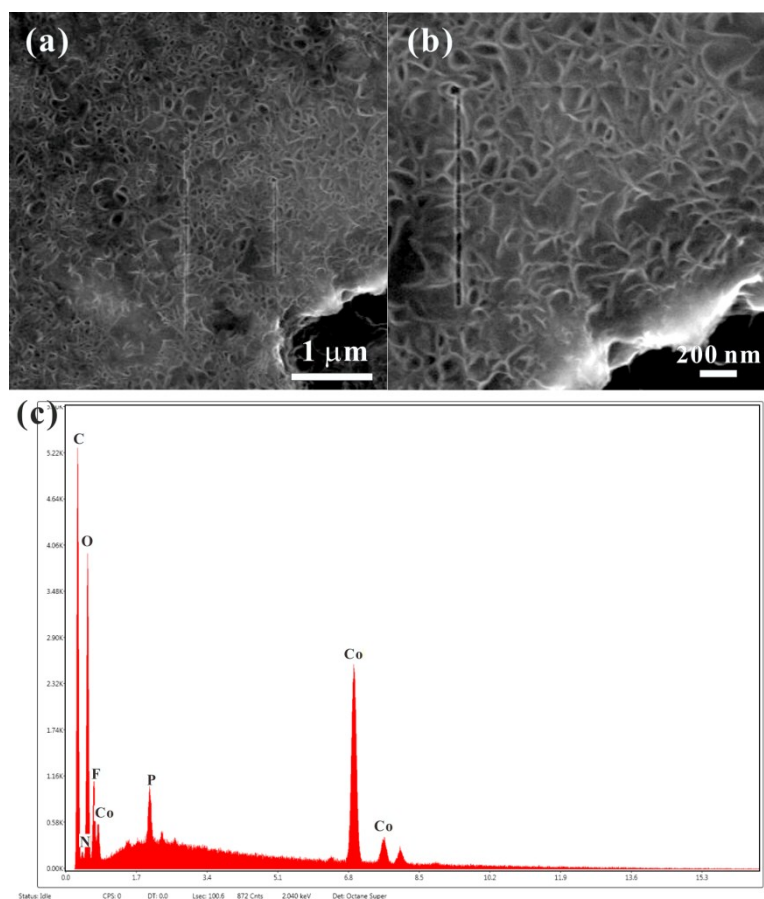Figure S7. (a-b) SEM image of Co_3O_4/N-C structure after lithium insertion/extraction process at different magnification; (c) the corresponding EDS spectrum.
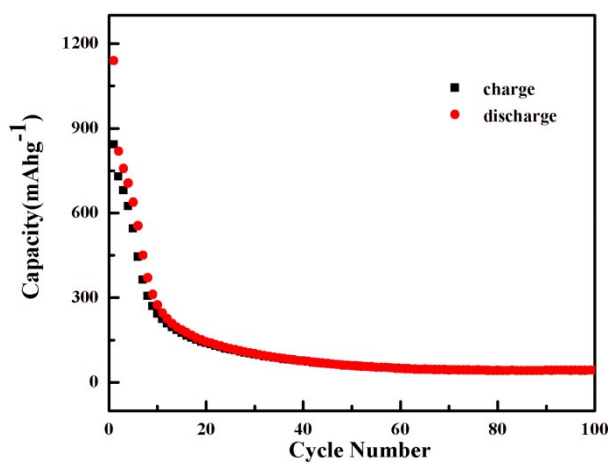

Figure S8. Cycle performance of sample obtained by Co-MOF calcinated in air atmosphere at current density of 1000 mA·g^{-1} between 0.01 and 3 V over 100 cycles.
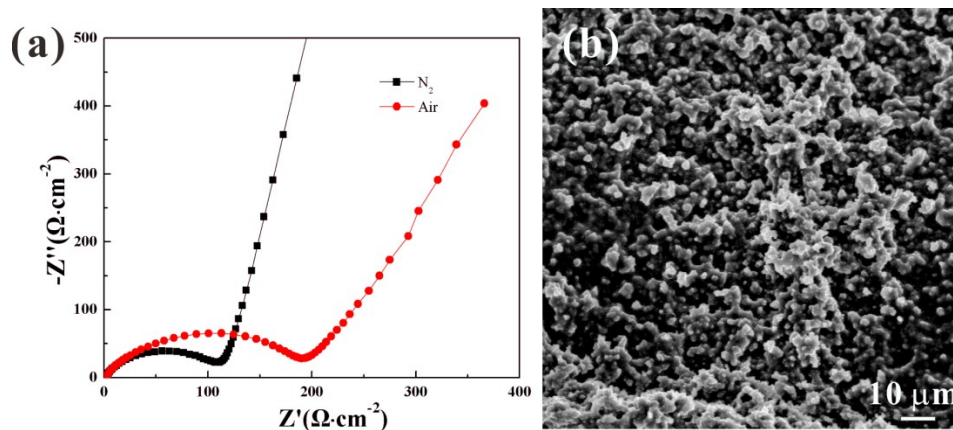
Figure. S9. (a) Impedance spectra of samples obtained by Co-MOF calcinated in nitrogen and air atmosphere; (b) SEM image of sample obtained by Co-MOF calcinated in air atmosphere after lithium insertion/extraction process.

3. References:

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