Electronic Supplementary Information

Experimental section

Materials: Ni foam (NF) was provided by Shenzhen Green and Creative Environmental Science and Technology Co., Ltd. KOH, $Co(NO_3)_2 \cdot 6H_2O$, terephthalic acid ($C_8H_6O_4$) and N,N-dimethylformamide (DMF) were purchased from Chengdu Kelon Chemical Reagent Factory. Ethanol was bought from Tianjin Chemical Corporation. Activated carbon (AC) was bought from Fuzhou Yihuan Carbon Co. Ltd (China). All chemical regents were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of Co-MOF/NF and Co-MOF powder: Co-MOF/NF was prepared by simple one-step solvothermal process. A piece of NF $(2 \times 3 \text{ cm}^2)$ was treated with ethanol, HCl and deionized water by sonication sequentially for three times. Firstly, 1 mM Co(NO₃)₂·6H₂O (0.291 g) and 1 mM C₈H₆O₄ (0.166 g) were dissolved in 35 mL DMF to obtain a uniform solution. Subsequently, 5 mL ethanol was added slowly to the mixture solution under continuous stirring for 15 min. And then the abovementioned solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave where a piece of NF ($2 \times 3 \text{ cm}^2$) with a clean surface was immersed into the solution. The autoclave was sealed and maintained at 125 °C for 12 h in an electric oven to prepare Co-MOF/NF product. The weight increment of NF was calculated as 6.4 mg cm⁻² after hydrothermal process. For more reasonable research, Co-MOF-100/NF, Co-MOF-150/NF, and Co-MOF-175/NF were made by varying the hydrothermal temperature to 100, 150, and 175 °C, respectively, under otherwise identical experimental conditions used for preparing Co-MOF/NF. And Co-MOF-8/NF, Co-MOF-10/NF, Co-MOF-14/NF, and Co-MOF-16/NF were fabricated by varying the hydrothermal time to 8, 10, 14, and 16 h, respectively, under the same experimental conditions used for preparing Co-MOF/NF. The Co-MOF powder was prepared using the same experimental method except the absence of NF substrate.

Characterizations: The XRD patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). Scanning electron microscope (SEM) measurements were recorded on a JSM-7500F scanning electron microscope. X-ray photoelectron spectroscopy (XPS) data of the samples was collected on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Transmission electron microscopy (TEM) images were collected on a HITACHI H–8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. Infrared spectroscopy was collected on a Nicolet-6700 Fourier transform infrared (FTIR) spectrometer using the potassium bromide pellet method. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was performed on Thermo Scientific iCAP6300.

Electrochemical measurements: Electrochemical measurements were performed with a RST5000F electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd., Zhengzhou, China) in a three-electrode system. Co-MOF/NF was used as the working electrode, a platinum plate $(1.5 \times 1.5 \text{ cm}^2)$ and an Hg/HgO were used as the counter electrode and the reference electrode, respectively. Electrochemical performance were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests. CV tests were performed in the potential window of 0–0.8 V at the scan rates of 10, 20, 30, 40 and 50 mV s⁻¹, and GCD tests were conducted in the potential window of 0–0.5 V at the current densities of 2, 5, 10, 20, 30, 40, and 50 mA cm⁻². The EIS tests were carried out at the open-circuit potential with a frequency ranging from 100 KHz to 0.01 Hz. All the measurements were conducted in 2 M KOH electrolyte at room temperature (25 °C).

The calculation of accurate mass loading: ICP-MS analysis for Co-MOF powder scratched down from NF concludes that the atomic ratio of Ni/Co is roughly 1:10. The accurate mass for active materials of Co-MOF on Ni foam was calculated as follows. The weight increment (x mg) of NF can be directly weighted after the growth of Co-MOF. Co-MOF_{loading} = x mg × (MNi_{0.2}-Co₂(OH)₂C₈H₄O₄/MCo₂(OH)₂C₈H₄O₄) = x mg ×

(327.6/315.86) = 1.04x mg, where M is the molecular weight or atomic weight. For Co-MOF/NF electrode, the mass loading of Co-MOF is about 6.656 mg cm⁻².

Fabrication of asymmetric supercapacitor: The asymmetric supercapacitor (ASC) device was fabricated by using Co-MOF/NF ($1 \times 1 \text{ cm}^2$) as the positive electrode, activated carbon (AC) as the negative electrode, and non-woven fabrics as separator. The negative electrode was prepared by mixing AC, acetylene black, and polyvinylidene fluoride (PVDF, which was dissolved in N-methyl pyrrolidone with a concentration of 6 mg mL⁻¹) at the mass ratio of 8:1:1. The mixtures were ground adequately to form a slurry. Then, the slurry was uniformly pasted onto the surface of treated NF ($1 \times 1 \text{ cm}^2$) and dried at 70 °C for 12 h. The mass loading of AC was determined by Formula S3.

Areal capacitance calculation: Areal capacitances (F cm⁻²) were calculated from CV (C_{s1}) and GCD (C_{s2}) curves using Formula S1 and Formula S2, respectively, where I_1 (A) is the response current, ΔV (V) is the voltage window, v (V s⁻¹) is the scan rate, I_2 (A) is the constant current, Δt (s) is the discharging time, and S (cm²) is the geometrical area of the electrode.

$$C_{s1} = \frac{\int I_1 dV}{vS\Delta V}$$
 Formula S1
$$C_{s2} = \frac{I_2\Delta t}{S\Delta V}$$
 Formula S2

The determination for loading of AC on coated on NF:_The mass loading of AC was determined by balancing the charges between positive and negative electrodes $(q^+=q^-)$. The optimized mass ratio between two electrodes can be obtained from Formula S3, Where m^+ (g) is the mass loading, C_s^+ (F cm⁻²) and ΔV^+ (V) represent the specific capacitance and the potential window of positive electrode, respectively, and m^- , C_s^- and ΔV^- are the mass loading, specific capacitance and the potential window of negative electrode, respectively.

$$\frac{\mathrm{m}^{+}}{\mathrm{m}^{-}} = \frac{C^{-}\Delta V^{-}}{C^{+}\Delta V^{+}}$$
 Formula S3

The calculations for energy density and power density of the ASC devices: The

energy density (*E*) and power density (*P*) of assembled ASC devices were obtained from the GCD curves according to Formula S4 and Formula S5, respectively, where C_{s2} (F cm⁻²) is the areal specific capacitance from Formula S2, ΔV (V) is the voltage window, and *t* (s) is the discharging time of the fabricated ASC devices.

$$E = \frac{1}{2}C\Delta V^{2}$$
 Formula S4
$$P = \frac{E}{\Delta t}$$
 Formula S5



Fig. S1. (a) The XRD pattern and (b) SEM images of Co-MOF powder.



Fig. S2. (a) GCD curves for Co-MOF-100/NF, Co-MOF/NF, Co-MOF-150/NF, and Co-MOF-175/NF at 2 mA cm⁻² in 2 M KOH. (b) Area specific capacitance corresponding to panel (a). (c) GCD curves for Co-MOF-8/NF, Co-MOF-10/NF, Co-MOF/NF, Co-MOF-14/NF, and Co-MOF-16/NF at 2 mA cm⁻² in 2 M KOH. (d) Area specific capacitance corresponding to panel (c).



Fig. S3. (a) CV and (b) GCD curves of Co-MOF powder in 2 M KOH.



Fig. S4. (a) CV and (b) GCD curves of Co-MOF powder scratched down from NF in 2 M KOH.



Fig. S5. Areal capacitances versus current densities of Co-MOF powder and Co-MOF powder scratched down from NF.



Fig. S6. Cycling stability of Co-MOF/NF at a constant current density of 50 mA cm⁻².



Fig. S7. (a) XPS spectrum, (b) XRD pattern, and (c) SEM images of Co-MOF/NF after 10000 cycles GCD test at 50 mA cm⁻².



Fig. S8. (a) CV and (b) GCD curves for AC coated on NF in 2 M KOH.



Fig. S9. (a) CV and (b) GCD curves of Co-MOF powder//AC ASC device measured in 2 M KOH electrolyte.



Fig. S10. Cycling stability of Co-MOF/NF//AC device at a constant current density of 50 mA cm⁻².

Table S1. Comparison of specific capacitance between electrode materials prepared

 in this work and previous reports in alkaline solution.

Electrode	Current	Specific		
materials	density	capacitance	Electrolyte	References
	(j _s : mA cm ⁻²)	$(C_s: F cm^{-2})$		
Co-MOF/NF	j _s :2	C _s :13.6 C _m :2125 F g ⁻¹	2 М КОН	This work
Co-MOF	j _s :2	C _s :1.2	2 М КОН	H
powder		C _m :234 F g ⁻¹	_	
ZIF-67 -derived Co ₃ O ₄	j _m : 1.25 A g ⁻¹	C _s :5.6	3 М КОН	1
ZIF-67 -derived CoS	j _m : 1 A g ⁻¹	C _s :4.4	3 М КОН	2
2D-CMO	j _s :1	C _s :2.1	4 M KOH	3
carbon-L-950	$j_m: 0.1 \ A \ g^{-1}$	C _s :1.1 C _m :228 F g ⁻¹	6 M KOH	4
Co ₃ O ₄ /C NAs	j _s :1.0	C _s :1.3	3 M KOH	5
hierarchical Co ₃ O ₄ @PPy@ MnO ₂	j _s :1.2	C _s :1.1	1 M NaOH	6
Co ₃ O ₄ ANTAs	j _s :2.5	C _s :0.37	5 M KOH	7
core/shell Co ₃ O ₄ /NiO	$j_m: 2 \ A \ g^{-1}$	C _s :~1.35	2 М КОН	8
Co-LMOF	j_m : 1.0 A g^{-1}	$C_m:2474 \ F \ g^{-1}$	1 M KOH	9
Co-MOF (SNNU-80)	j _m : 1.0 A g ⁻¹	C _m :106 F g ⁻¹	1 M KOH	10
Co-BPDC		C_m :179.2 F g ⁻¹	0.5 M LiOH	11
Co-MOF films	j _m : 0.6 A g ⁻¹	C _m :206.8 F g ⁻¹	1 M LiOH	12
Ni-based MOF	j _m : 1 A g ⁻¹	C _m :726 F g ⁻¹	2 M KOH	13
accordion-like Ni-MOF	j _m : 1.4 A g ⁻¹	C _m :988 F g ⁻¹	3 М КОН	14
layer-structured Ni-MOF	j _m :0.5 A g ⁻¹	C _m :1127 F g ⁻¹	6 M KOH	15

 $j_{s}\!\!:$ areal current density; $j_{m}\!\!:$ mass current density

 $C_{s}\!\!:$ areal specific capacitance; $C_{m}\!\!:$ mass specific capacitance

Current density	Discharge time	Capacitance	Energy density	Power density
(mA cm ⁻²)	(s)	(F cm ⁻²)	(mWh cm ⁻²)	(mW cm ⁻²)
5.0	1550	4.84	1.72	4
10	611	3.82	1.36	8
20	256	3.20	1.14	16
30	151	2.83	1.01	24
40	102	2.55	0.91	32
50	74	2.31	0.82	40

Table S2. Various performance parameters for Co-MOF/NF//AC ASC device in 2 MKOH electrolyte.

Current density	Discharge time	Capacitance	Energy density	Power density
(mA cm ⁻²)	(s)	(F cm ⁻²)	(mWh cm ⁻²)	(mW cm ⁻²)
5.0	167	0.52	0.19	4
10	78	0.49	0.17	8
20	27	0.34	0.12	16
30	16	0.30	0.11	24
40	11	0.28	0.10	32
50	7	0.22	0.08	40

Table S3. Various performance parameters for Co-MOF powder//AC ASC device in2 M KOH electrolyte.

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