

Supporting information

Amino-functionalized metal-organic framework nanosheet array as battery-type electrode for advanced supercapattery

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Experimental section

Materials

Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-aminoterephthalic acid ($\text{NH}_2\text{-H}_2\text{BDC}$) polyvinylpyrrolidone (PVP) and activated carbon (AC) were purchased from Aladdin chemical Co. Ltd.. Nickel foam (NF) was purchased from Alfa aesar (Tianjin) chemical Co. Ltd. Absolute ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$), dimethylformamide (DMF), polyvinylidene fluoride (PVDF), acetylene black, potassium hydroxide (KOH) and poly(vinyl alcohol) (PVA) were purchased from Sinopharm. Platinum wire and saturated calomel electrode (SCE) were purchased from Chenhua (Shanghai).

Synthesis of Co-MOF nanosheets on nickel foam (Co-MOF NS/NF)

In a typical procedure, 250 mg $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added in 20 mL deionized water, while 71.4 mg $\text{NH}_2\text{-H}_2\text{BDC}$ and 250 mg PVP were dispersed in a mixture of 20 mL ethanol and 20 mL DMF. After stirring for 1 h, they were mixed uniformly and transferred into the autoclave (100 mL), where a piece of clean nickel foam (NF, 2×4 cm) was immersed in the solution. Subsequently, the autoclave was put into an oven for 24 h at 80 °C. Finally, the Co-MOF NS/NF sample was collected after washing with H_2O and $\text{C}_2\text{H}_5\text{OH}$ and drying at 60 °C for 12 h. For comparison, we also fabricated the bulk Co-MOF microplate on NF (Co-MOF MP/NF) when $\text{H}_2\text{BDC-NH}_2$ was replaced with H_2BDC .

Characterizations

The morphologies of samples were obtained from scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL, 2010F), respectively. FT-IR transmission spectrum was characterized by using a Nicolet 6700 IR spectrophotometer. The XRD patterns were recorded on X-ray Diffraction Spectrometry (XRD, BrukerD8 ADVANCE) with Cu K α radiation ($\lambda = 0.154178$ nm). X-ray photoelectron spectroscopy (XPS) data of the samples was collected on an Axis Ultra DLD system with a monochromatic Al K α radiation (1486.6 eV).

Electrochemical characterizations

Electrochemical performances of Co-MOF NS/NF and Co-MOF MP/NF electrodes were assessed with cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements in an electrochemical workstation (CHI660E) by employing a three-electrode system in 2 M KOH aqueous solution. The Co-MOF NS/NF (or Co-MOF MP/NF, 1×1 cm 2) was directly employed as the working electrode. A saturated calomel electrode (SCE) and platinum wire were used as reference electrode and auxiliary electrode. The electrochemical impedance spectra (EIS) of the electrodes were tested in the frequency range of 10 mHz–100 kHz at open circuit potential with 5 mV perturbation. The specific capacities (Q_s , C cm $^{-2}$) of electrode materials were calculated according to GCD data with following equation (1):

$$Q_s = \frac{I\Delta t}{S} \quad (1)$$

Where the I (A), Δt (s) and S (cm^2) are the constant discharge current, discharge time and geometric area of active material, respectively.

Furthermore, the supercapattery was constructed by using a two-electrode system, where the the Co-MOF NS/NF (or Co-MOF MP/NF) as positive electrode and active carbon covered on the NF as negative electrode. The energy density (E , mWh cm^{-2}), and power density (E , mW cm^{-2}) of the supercapattery device was calculated by the following equations:

$$E = I \int V dt \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

Where the I (mA cm^{-2}) represents the current density, V is voltage window and Δt is the discharge time.

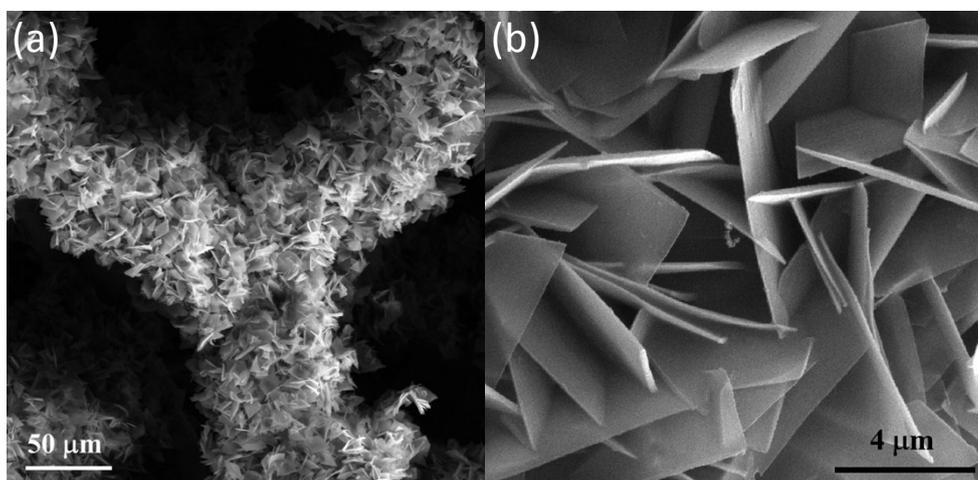


Fig. S1 The SEM images of $\text{NH}_2\text{-Co-MOF-NS/NF}$.

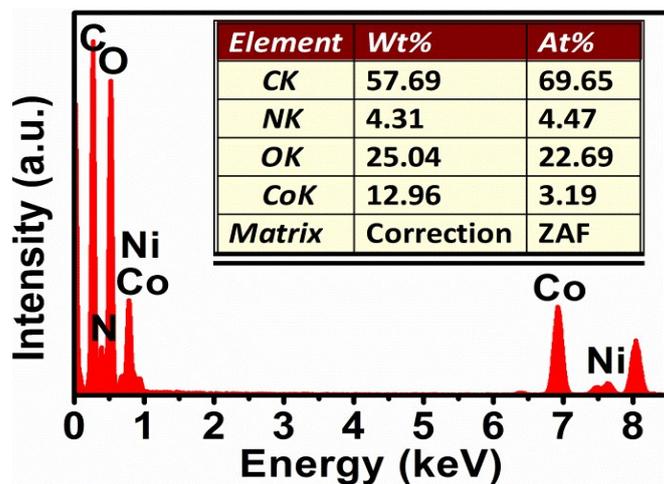


Fig. S2 The EDS spectrum of NH₂-Co-MOF-NS/NF.

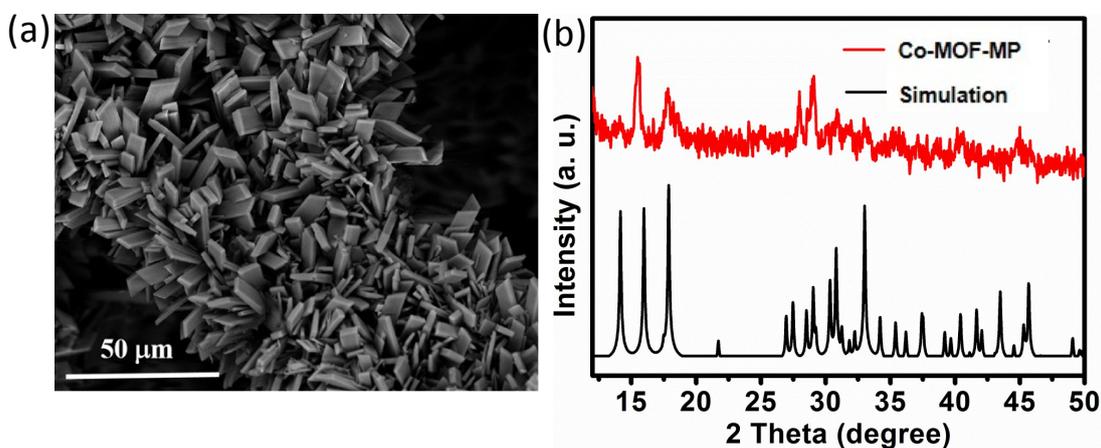


Fig. S3 The SEM image and XRD pattern of Co-MOF-MP/NF.

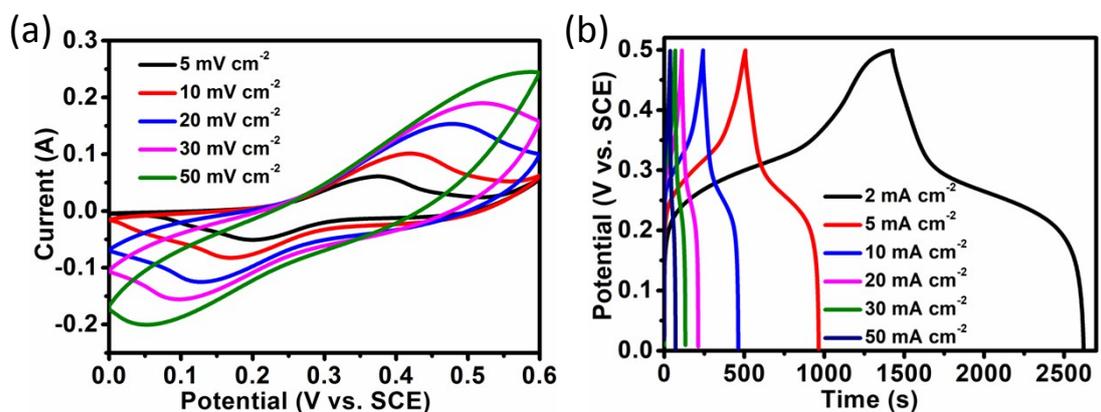


Fig. S4 The CV and GCD curves of Co-MOF-MP/NF electrode.

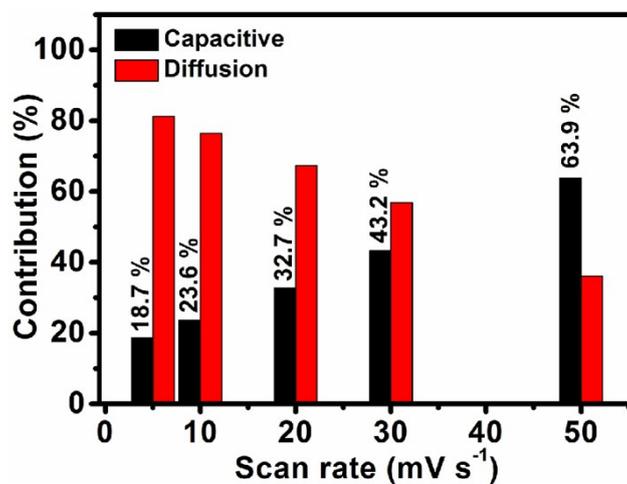


Fig. S5 The charge storage of $\text{NH}_2\text{-Co-MOF-NS/NF}$ electrode at different scan rates.

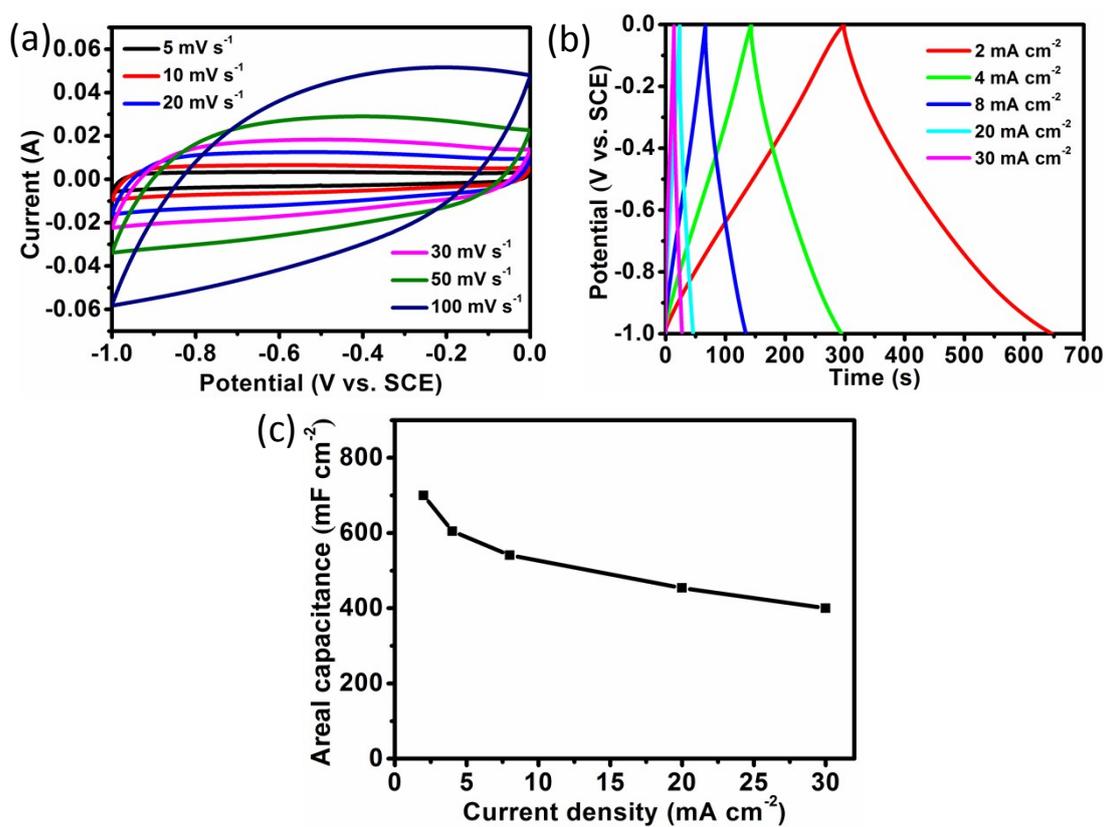


Fig. S6 The electrochemical performances of AC electrode in three-electrode system.

Table S1. Comparison of NH₂-Co-MOF-NS/NF with other reported electrode materials in capacitive performance.

Electrodes	Q _s (C cm ⁻² /mAh cm ⁻²) C _s (F cm ⁻²) C _m (F g ⁻¹)	Current density	Potential range	Electrolyte	Ref.
Co-MOF NS/NF	6.7 C cm ⁻² /1861 □μAh cm ⁻² /13.4 F cm ⁻²	2 mA cm ⁻²	0-0.5 V vs. SCE	3 M KOH	This work
Co-MOF powder	1.2 F cm ⁻²	2 mA cm ⁻²	0-0.5 V vs. SCE	2 M KOH	32
Co-Mn MOF	1.318 F cm ⁻²	1 mA cm ⁻²	0-0.35 V vs. Ag/AgCl	2 M KOH	33
MOF-derived Ni-Zn-Co-S	1.11 mAh cm ⁻²	10 mA cm ⁻²	0-0.53 V vs. Hg/HgO	3 M KOH	34
Co ₃ O ₄ ANTAs	0.37 F cm ⁻²	2.5 mA cm ⁻²	-0.1-0.45 V vs. Ag/AgCl/KCl	5 M KOH	35
PANI-ZIF-67-CC	2146 mF cm ⁻²	10 mV s ⁻¹	-0.2-1.0 V vs. Ag/AgCl	3 M KCl	36
layer-structured Ni-MOF	1127 F g ⁻¹	0.5 A g ⁻¹	0-0.35 V vs. SCE	6 M KOH	37
accordion-like Ni-MOF	988 F g ⁻¹	1.4 A g ⁻¹	0-0.43 V vs. Hg/HgO	3 M KOH	38
Co-MOF (SNNU-80)	106 F g ⁻¹	1.0 A g ⁻¹	0-0.4 V vs. SCE	1 M KOH	39