

Electronic Supplementary Information

A heterostructure of 2D bimetallic metal-organic framework assembled on MXene for high-performance supercapacitors

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Experimental section

Synthesis of MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) nanosheets

1 g of MAX (Ti_3AlC_2) was added into 10 mL HF solution (40 wt%) and magnetically stirred for 24 h at room temperature. After that, the multilayered Mxene was collected by centrifugation, washed with distilled water and absolute ethanol repeatedly until the pH value of the supernatant reached 6, and dried in a vacuum oven at room temperature. To obtain MXene nanosheets, 0.1 g of multilayered Mxene was magnetically stirred in 5 mL of dimethyl sulfoxide (DMSO) for 24 h. Then, the suspension was diluted with deionized water and DMSO-intercalated MXene was harvested by centrifugation. Subsequently, the obtained powder was dispersed in 50 mL of deionized water and sonicated at room temperature for 6 h. The Mxene nanosheets were collected by centrifugation at 3500 rpm for 1 h, and dried in a vacuum oven at room temperature.

Preparation of NiCo-MOF/Mxene heterostructures

Typically, 10 mg Mxene nanosheets were ultrasonically dispersed into a mixed solution containing 2 mL ethanol, 2 mL deionized water and 30 mL N, N-dimethylformamide (DMF) at room temperature, and then 0.75 mmol (0.124g) terephthalic acid (PTA) was added under stirring. After PTA was completely dissolved, 0.5 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.118g) and 0.5 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.118g) were added, and then 0.8 mL triethylamine (TEA) was quickly injected into the above solution and stirred for 5 min. The mixture was continuously sonicated at room temperature for 4 h. The product was washed several times with ethanol by

centrifugation and dried in a vacuum oven at 60°C. The sample was denoted as NiCo-MOF/M₁₀. In addition, NiCo-MOF, NiCo-MOF/M₅, NiCo-MOF/M₁₅ and NiCo-MOF/M₂₀ were also prepared by the same experimental method, except adjusting the content of MXene to 0, 5, 15 and 20 mg, respectively.

Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku Ultimate IV diffractometer. Raman spectroscopy was obtained on a Renishaw inVia spectrometer. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) spectra were obtained from a field emission scanning electron microscope (FESEM, Hitachi S-4800). Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images, selected area electron diffraction (SAED) patterns and element mappings were obtained on a Tecnai G2 F20 transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha+ spectrometer with an Al source. The porosity of the sample was analyzed by N₂ physical adsorption (Micromeritics ASAP 2460). The multiple Brunauer-Emmert-Taylor (BET) method was used to determine the specific surface area, and the Barrett-Joyner-Halenda (BJH) method was used to measure the pore size distribution using the desorption branch of the isotherm.

Electrochemical evaluation

A three-electrode system was assembled to study the electrochemical performance of electrode materials, where platinum foil and saturated calomel electrode (SCE) acted

as counter electrode and reference electrode, respectively. Active material (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) were mixed with suitable amount of 1-methyl-2-pyrrolidone (NMP) to form a slurry, which was coated on a nickel foam (NF, 1 cm×1 cm) substrate to prepare the working electrode. Before use, the obtained electrode was pressed at 10 MPa and dried. The mass loading of active materials on working electrode was about 1.4 mg cm⁻². Cyclic voltammetry (CV), galvanostatic charge and discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were performed in 2 M KOH electrolyte by a CHI660E electrochemical workstation (Shanghai Chenhua). The specific capacitance (C , F g⁻¹) was calculated as follows:

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (S1)$$

where I (A) was the discharge current, Δt (s) was the discharge time, ΔV (V) was the charge/discharge potential, and m (g) was the mass of active materials.

An asymmetric supercapacitor (ASC) device was assembled by using the NiCo-MOF/M₁₀ electrode as the positive electrode and an activated carbon (AC) as the negative electrode in 2 M KOH solution. To achieve the charge balance between the positive and negative electrodes, the optimal mass ratio of active materials on two electrodes was calculated by the following equation:

$$Q_- = m_- \times C_- \times \Delta V_- = m_+ \times C_+ \times \Delta V_+ = Q_+ \quad (S2)$$

where m (g), C (F g⁻¹) and ΔV (V) represented the mass of active materials, specific capacitance, and charge-discharge voltage of positive and negative electrodes, respectively. The energy density (E , Wh kg⁻¹) and power density (P , W kg⁻¹) of the

ASC device were calculated as follows:

$$E = \frac{C \times (\Delta V)^2}{2 \times 3.6} \quad (\text{S3})$$

$$P = \frac{3600 \times E}{\Delta t} \quad (\text{S4})$$

where C (F g^{-1}) was the specific capacitance, ΔV (V) was the operating voltage window, and Δt (s) was the time for full discharge of the ASC.

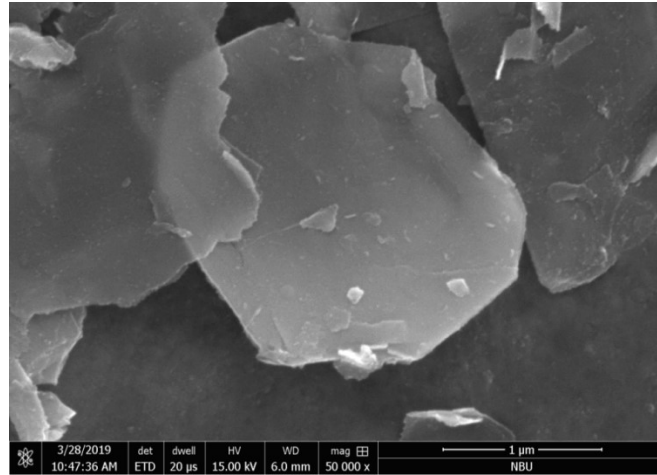


Fig. S1 SEM image of MXene nanosheets.

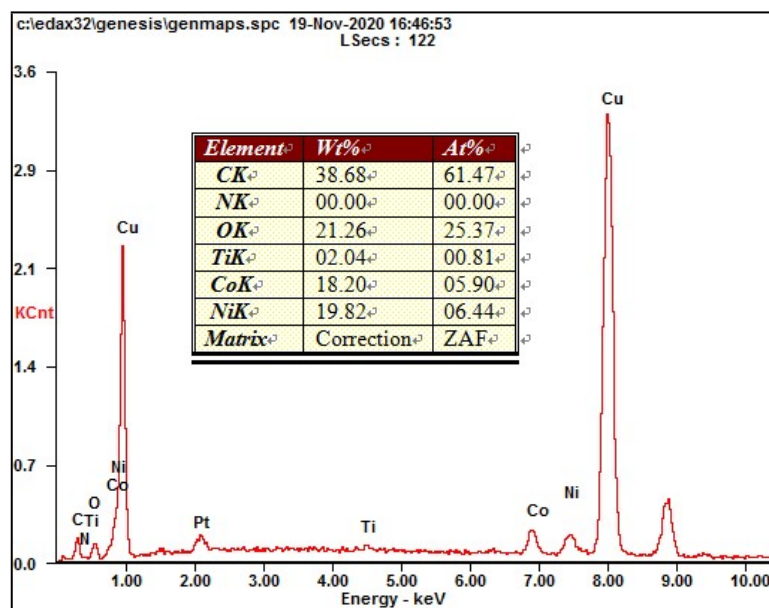


Fig. S2 EDS pattern of NiCo-MOF/M₁₀.

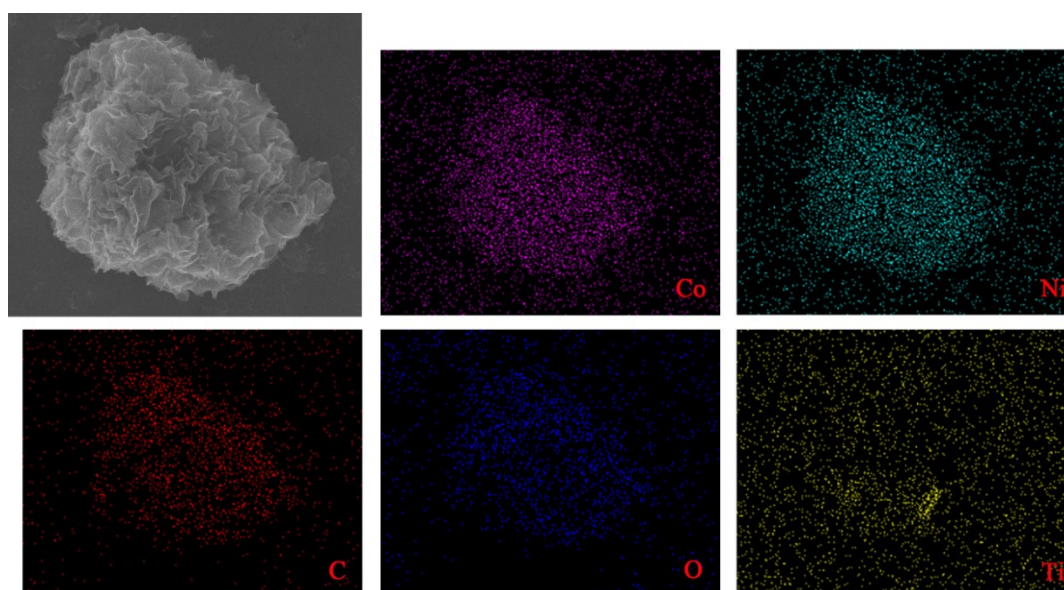


Fig. S3 EDS Mapping of NiCo-MOF/M₁₀.

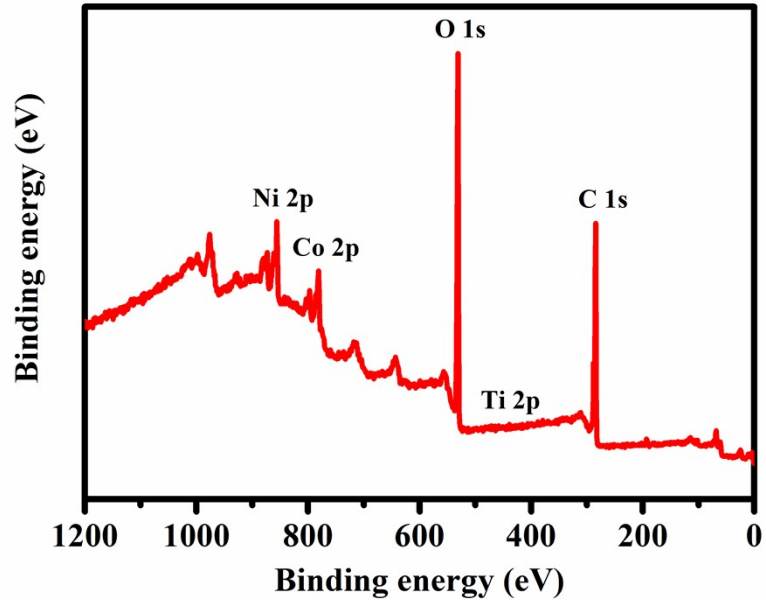


Fig. S4 XPS Survey spectrum of NiCo-MOF/M₁₀.

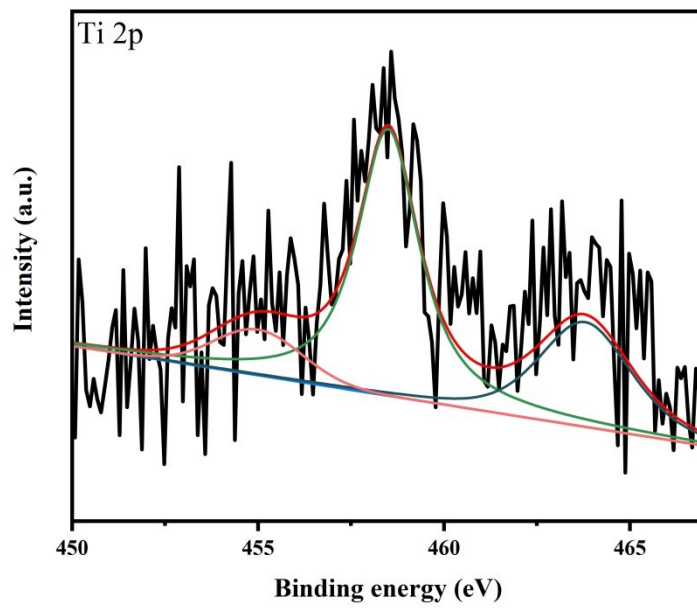


Fig. S5 High-resolution Ti 2p spectrum of NiCo-MOF/M₁₀.

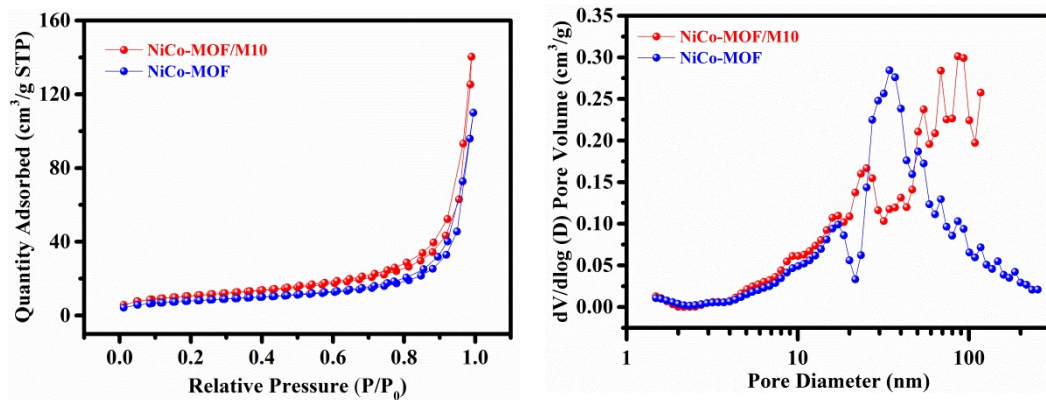


Fig. S6 (a) Nitrogen adsorption–desorption isotherms and (b) pore size distribution curves of NiCo-MOF and NiCo-MOF/M₁₀.

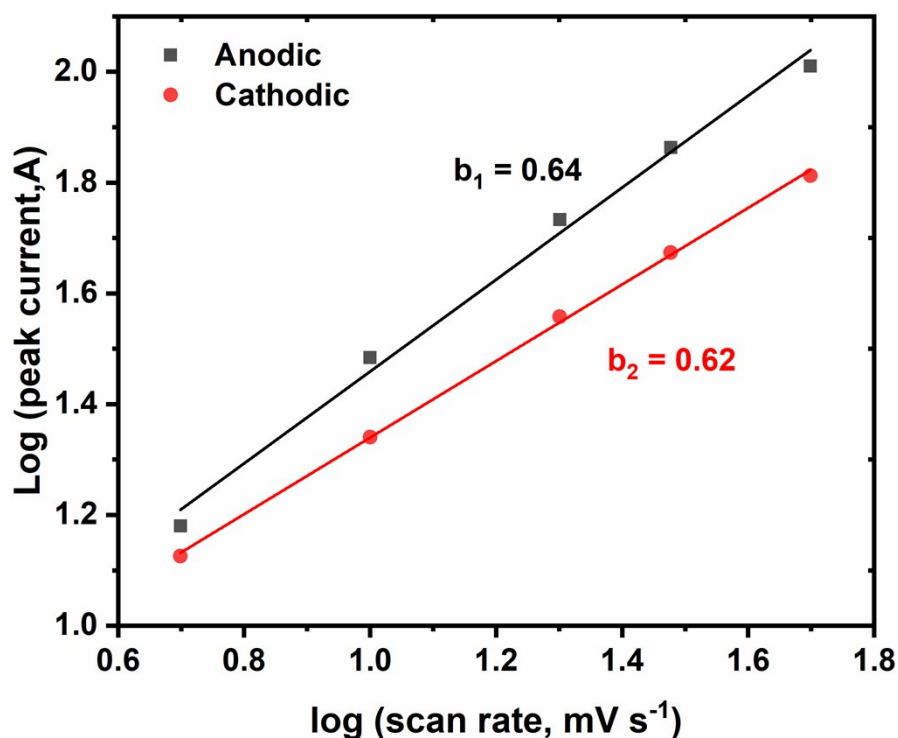


Fig. S7 Logarithm of peak currents of as a function of logarithm of scan rates.

To reveal charge storage mechanism of the NiCo-MOF/M₁₀ electrode, CV curves at different scan rates are analyzed. The relationship between current (i) and scan rate (v) can be expressed by following equation.

$$i = av^b \quad (S5)$$

The electrochemical energy storage is classified into two different processes depending on the b -values. When $b=1$, it means that the charge storage is capacitive, while $b=0.5$, it means that charge storage is diffusion-controlled. By linear fitting $\log(i)$ vs. $\log(v)$, b -values are obtained from the slopes of the fitted lines. The b values are 0.62 and 0.64 for the cathodic and anodic processes (Fig. S7), indicating that both processes contribute to the current response.

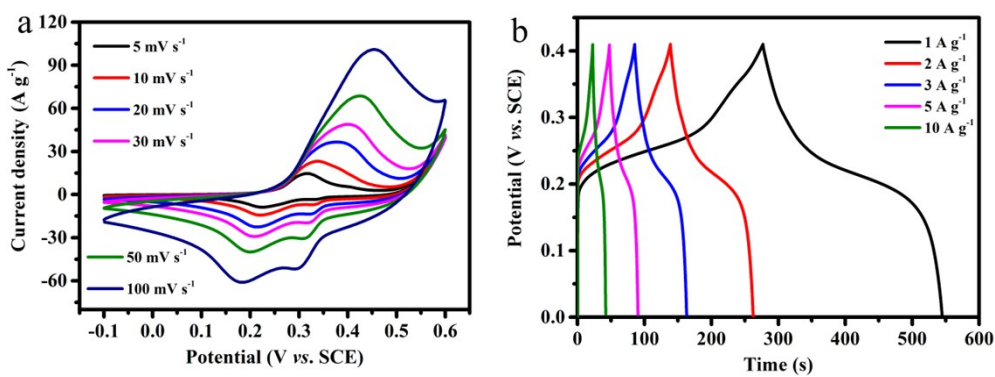


Fig. S8 (a) CV and (b) GCD curves of NiCo-MOF.

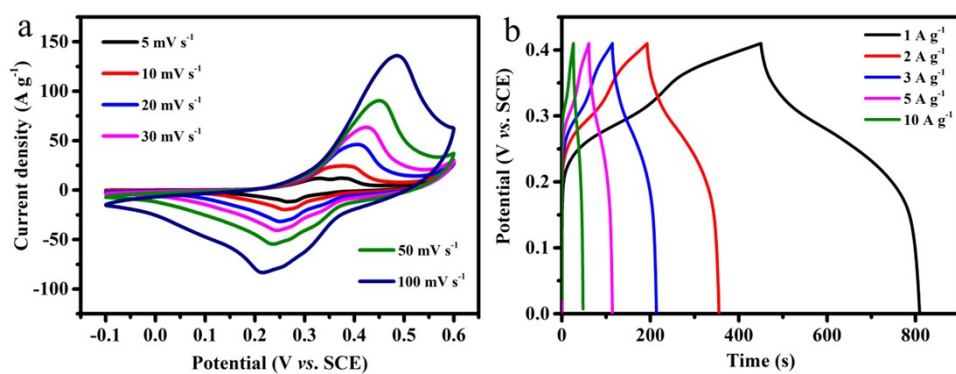


Fig. S9 (a) CV and (b) GCD curves of NiCo-MOF/M₅.

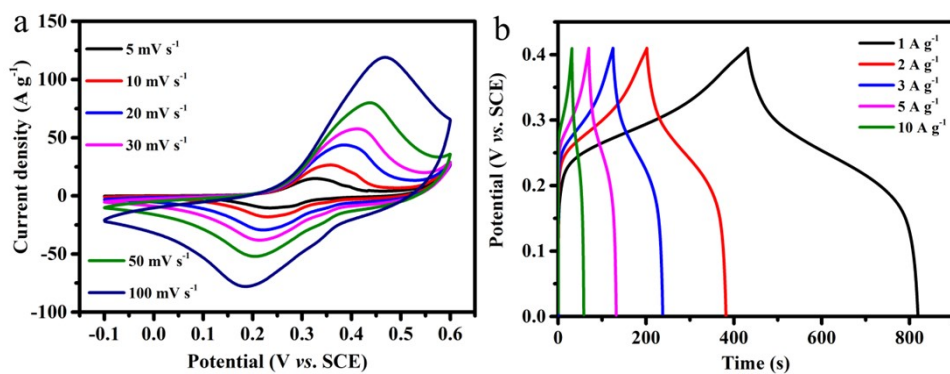


Fig.S10 (a) CV and (b) GCD curves of NiCo-MOF/M₁₅.

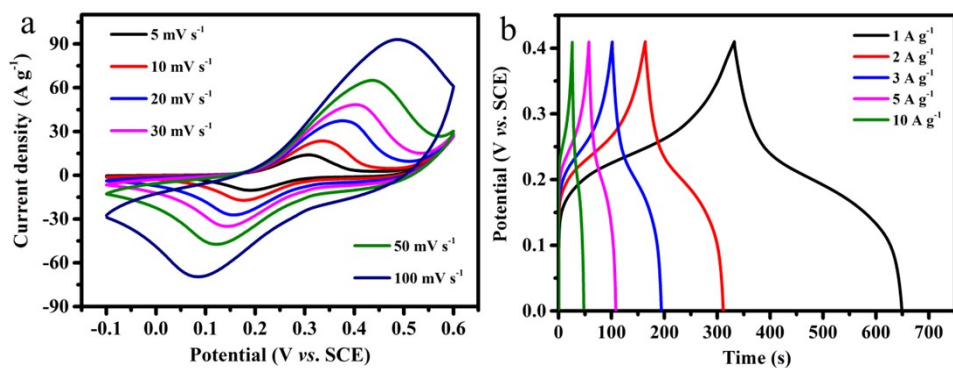


Fig. S11 (a) CV and (b) GCD curves of NiCo-MOF/M₂₀.

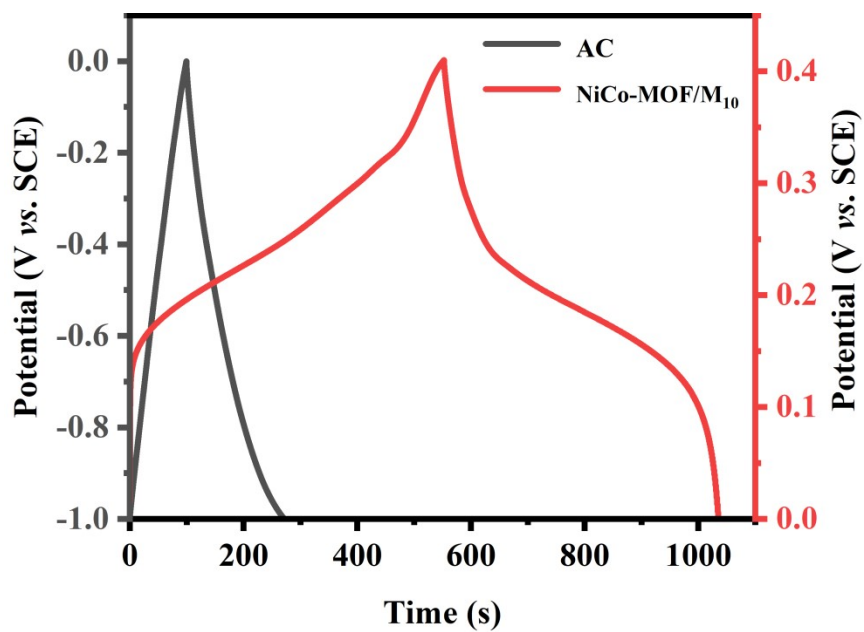


Fig. S12 GCD curves of individual NiCo-MOF/M₁₀ and AC at 1 A g⁻¹.

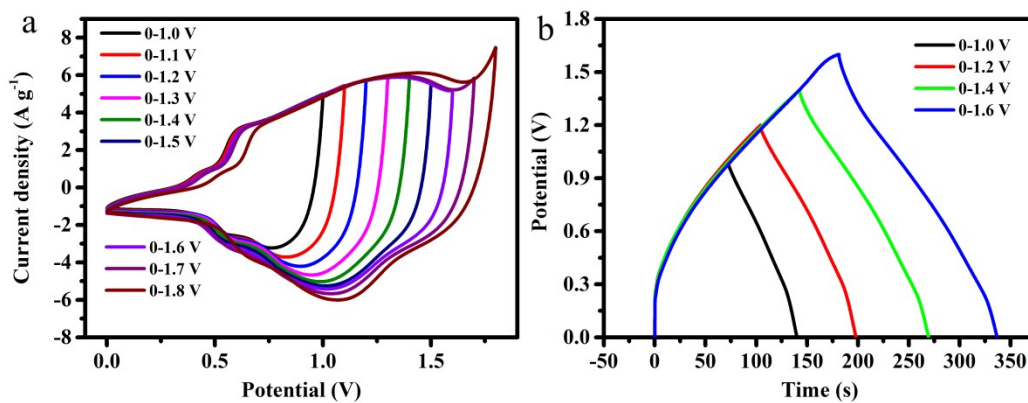


Fig. S13 (a) CV and (b) GCD curves of NiCo-MOF/M₁₀//AC.

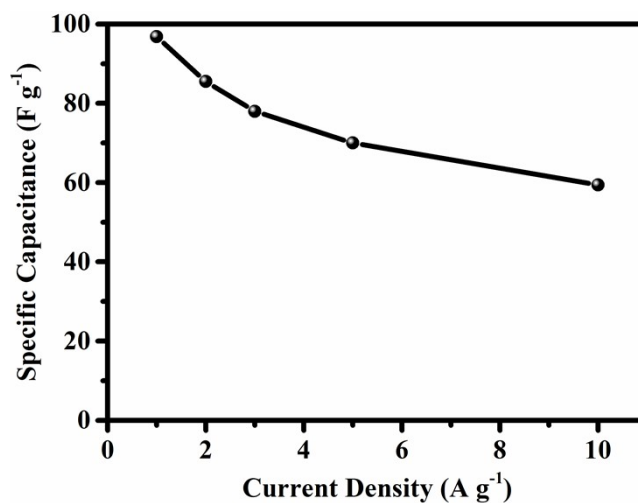


Fig. S14 The specific capacitances of NiCo-MOF/M₁₀//AC at different current densities.

Table S1 Comparison of electrochemical performance of this work with representative MOF or MXene based electrode materials reported in literature.

Electrode materials	Specific capacitance	Current density	Refs
NiCo-MOF/M₁₀	1176.8 F g⁻¹	1 A g⁻¹	This work
NiCo-MOF/AB-5	916.1 F g ⁻¹	1 A g ⁻¹	1
NiCo-MOF/MWCNT	1010.0 F g ⁻¹	0.5 A g ⁻¹	2
NiCo-MOF@PNTs	1109.0 F g ⁻¹	0.5 A g ⁻¹	3
NiCo-MOF NSHS	1126.7 F g ⁻¹	0.5 A g ⁻¹	4
NiCo-MOF BPDC	990.7 F g ⁻¹	1 A g ⁻¹	5
MXene/MPFs	326.1 F g ⁻¹	0.1 A g ⁻¹	6
Ti ₃ C ₂ /Ni-Co-Al-LDH	748.2 F g ⁻¹	1 A g ⁻¹	7

References

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