Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Electronic Supplementary Information

Cobalt Oxide and N-doped Carbon Nanosheets Derived from a Single Two-Dimensional Metal–Organic Framework Precursor and their Application in Flexible Asymmetric Supercapacitors

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Experimental

Material synthesis:

Preparation of 2D MOF on carbon cloth: an aqueous solution contains MIM (40 mL, 0.4 M) was quickly added into the aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ (40 mL, 50 mM), then a piece of clean CC substrate (2*5*0.036 cm^3, the upper side and back side protected with by polytetrafluoroethylene tape) was immersed into the mixture for 1 h. The CC was then taken out, cleaned with deionized water and vacuum dried overnight.

Preparation of CC@Co_3O_4: The CC@Co-MOF was firstly annealed in N_2 atmosphere at 500 ˚C for 1 h with a ramp rate of 1 °C min^{-1}, the temperature was then dropped to 350 ˚C at 5 °C min^{-1}, after which the samples were further annealed in air at 350 ˚C for 2 h. The mass loading of Co_3O_4 is ~0.25 mg cm^{-2}.

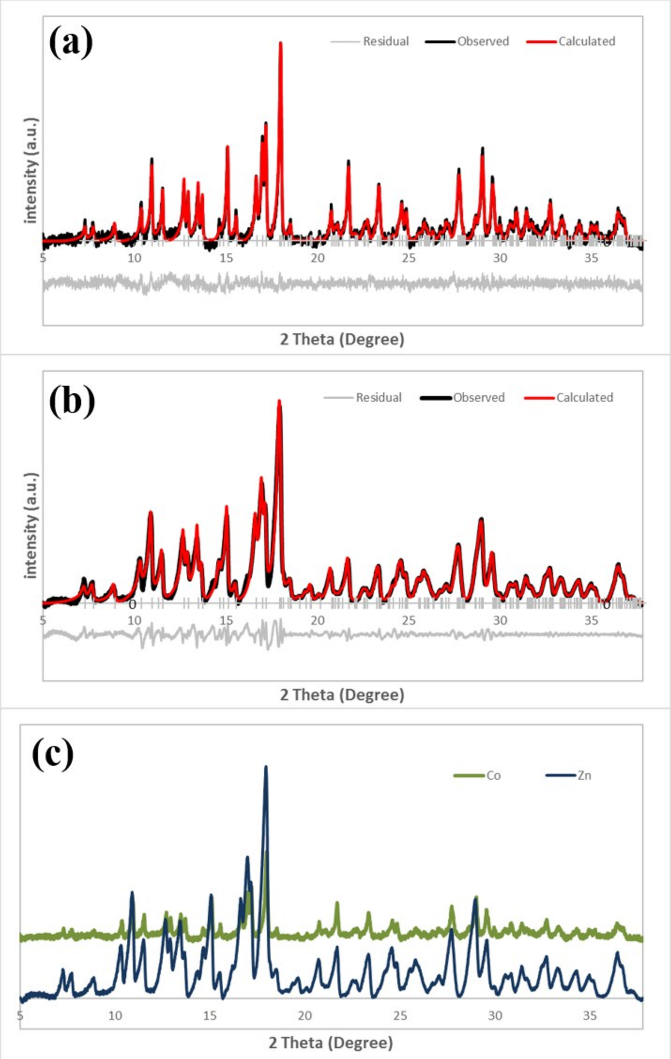
Preparation of CC@NC: The CC@Co-MOF was firstly annealed in N_2 atmosphere at 800 ˚C for 5 h with a ramp rate of 1 °C min^{-1}, the samples were then immersed in 1 M $FeCl_3$ solution for 6 h. After wash with deionized water, the samples were dried at 60 ˚C for 24 h. The mass loading of NC is ~0.4 mg cm^{-2}.

Characterization:

Samples were characterized using Scanning Electron Microscopy (SEM, Zeiss, 2.0-20.0 kV), Transmission Electron Microscopy (TEM, JEOL-2100F), X-Ray Diffraction (XRD, Bruker D8 diffractometer), Raman scattering spectra (LABRAM-HR Raman spectrometer, excited with 514.5 nm Arþ laser), and X-ray Photoelectron Spectroscopy (XPS, AXIS Ultra). The mass of electrode materials was also recorded by an AX/MX/UMX Balance (METTLER TOLEDO, maximum=5.1 g; delta= 0.001 mg).

Electrochemical measurement:

Electrochemical measurements were conducted using Solartron 1470E at room temperature. For three-electrode system tests, CC@Co_3O_4 or CC@NC was directly used as the working electrode without any metal support or other current collector. A Pt plate and a Hg/HgO were used as the counter electrode and the reference electrode, respectively. KOH (2M) was used as the electrolyte. The polymer electrolyte was obtained by dissolving PVA (6 g) into H_2O (40 mL) at 85 °C and then mixed with KOH (20 mL, 6 M) solution. To assemble the solid-state device, the two electrodes were immersed into the gel electrolyte and left under ambient condition to remove the unnecessary water before being assembled face-to-face. The polymer electrolyte serves as both the electrolyte and the separator. After the electrolyte was solidified, a flexible quasi-solid-state device can be attained. The capacity of the electrode was calculated by $C=I\Delta t/A\Delta V$, where I is the discharge current, Δt is the discharge time, and A is active materials' mass or electrode area, ΔV is the voltage drop upon discharge. The energy density (E) and power density (P) of the full cell were calculated by: $E=\int IV(t)dt/B$, $P=E/\Delta t$, where I is the discharge current, V(t) is the discharge voltage at t, dt is time differential and B is the total mass of active materials or the whole electrodes' mass. EIS measurements were conducted by applying an AC voltage with 5 mV amplitude in a frequency range from 0.1 Hz to 100 kHz at open circuit potential, and the results were fitted using Z-view software (detailed process is: open the data, using Instant Fit, choose and set parameters for Equivalent Circuits, then Run Simulation).



(d)

Component	Co ZIF	Zn ZIF
a / Å	24.093(9)	24.094(22)
b / Å	16.969(7)	16.985(15)
c / Å	19.733(8)	19.751(18)
α / °	90	90
β / °	90	90
γ / °	90	90
V / Å3	8067(6)	8083 (13)
Space group	Cmce	
Observations	3573	
Rp / %	0.55	2.2
wRp / %	0.7	3.17
Rp' / %	19.62	9.16
wRp' / %	15.33	10.31
χ2	1.33	4.26

Fig. S1. (a) Pawley refinement of Co-MOF (background removed). (b) Pawley refinement of Zn-MOF (background removed). (c) XRD patterns of prepared Co-MOF and Zn-MOF, confirming the same crystal structure. (d) Table of Pawley Refinement Details.

Data collected from X-ray powder diffraction was analysed using Pawley refinement in Topas program. The large background was manually removed and the prepared Co-MOF was confirmed to have the same crystal structure as the prepared Zn-MOF (space group of Cmce). The lattice parameters of the Co-MOF was determined with *a* = 24.093(9) Å, *b* = 16.969(7) Å and *c* = 19.733(8) Å. The unit cell is slightly smaller than the Zn-MOF.

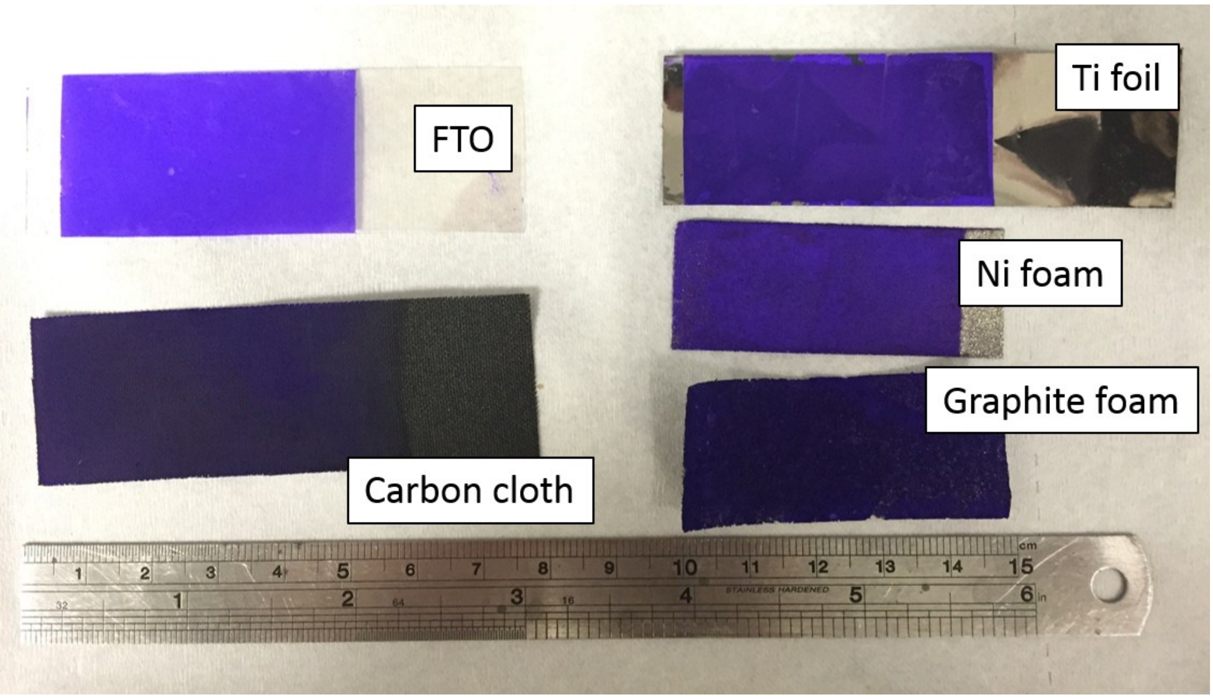


Fig. S2. Digital image of 2D MOF grown directly on different flexible conductive substrates.

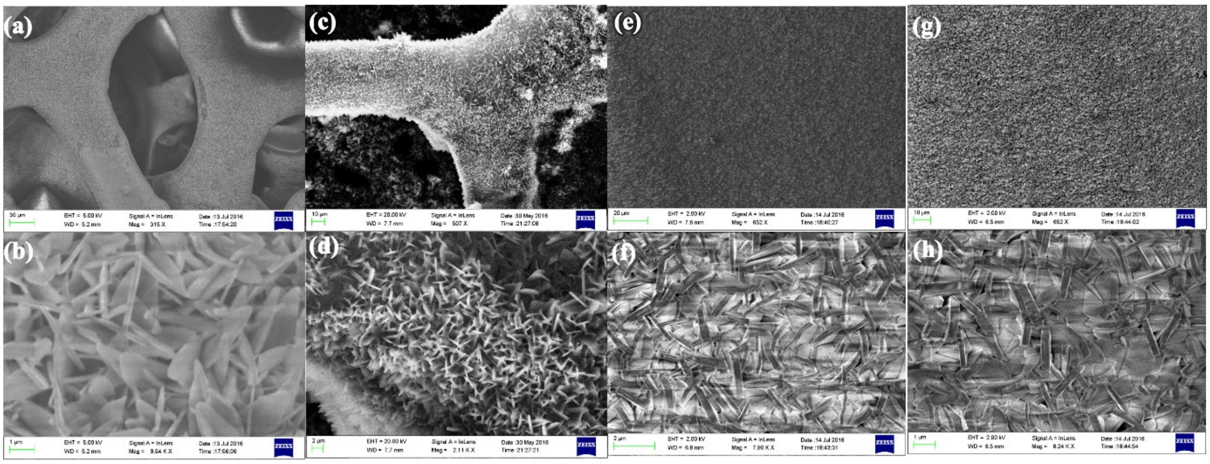


Fig. S3. SEM images of 2D MOF grown on (a, b) nickel foam, (c, d) graphite foam, (e, f) FTO, (g, h) Ti foil.

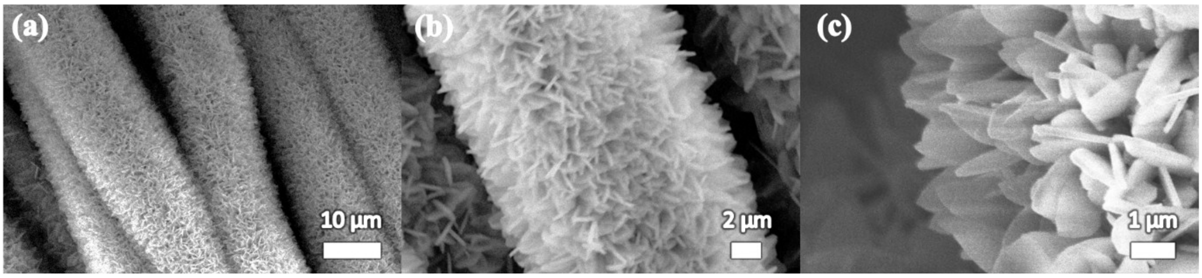


Fig. S4. SEM images of 2D MOF grown on carbon cloth.

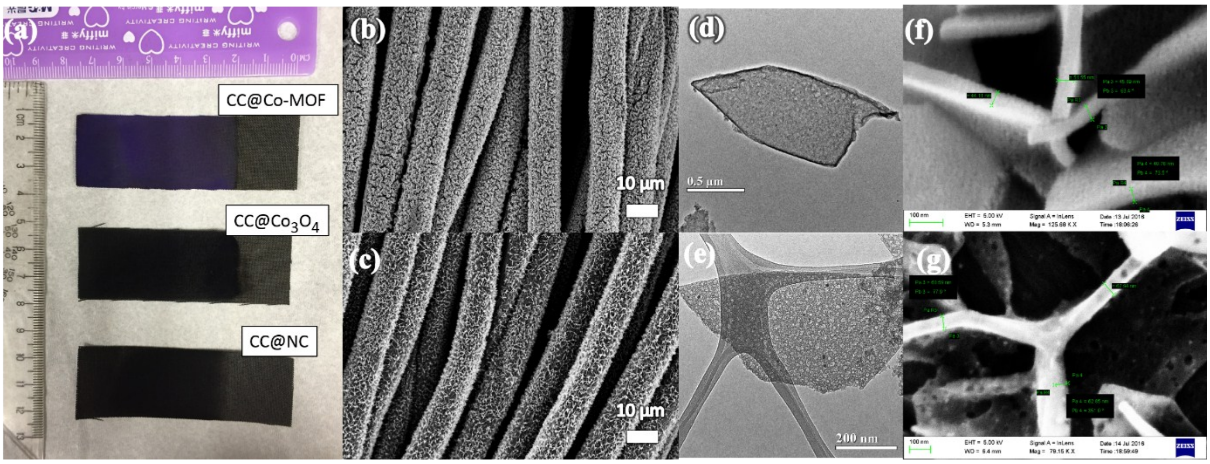


Fig. S5. (a) Images of 2D MOF and the thus derived electrodes (Co_3O_4 and N-doped carbon) grown directly on carbon cloth. (b) Large scale SEM image of CC@Co_3O_4. (c) Large scale SEM image of CC@NC. (d) Typical TEM image of a 2D Co_3O_4 nanosheet. (e) Typical TEM image of a 2D NC nanosheet. (f) Top view of 2D Co_3O_4 nanosheets. (g) Top view of 2D NC nanosheets.

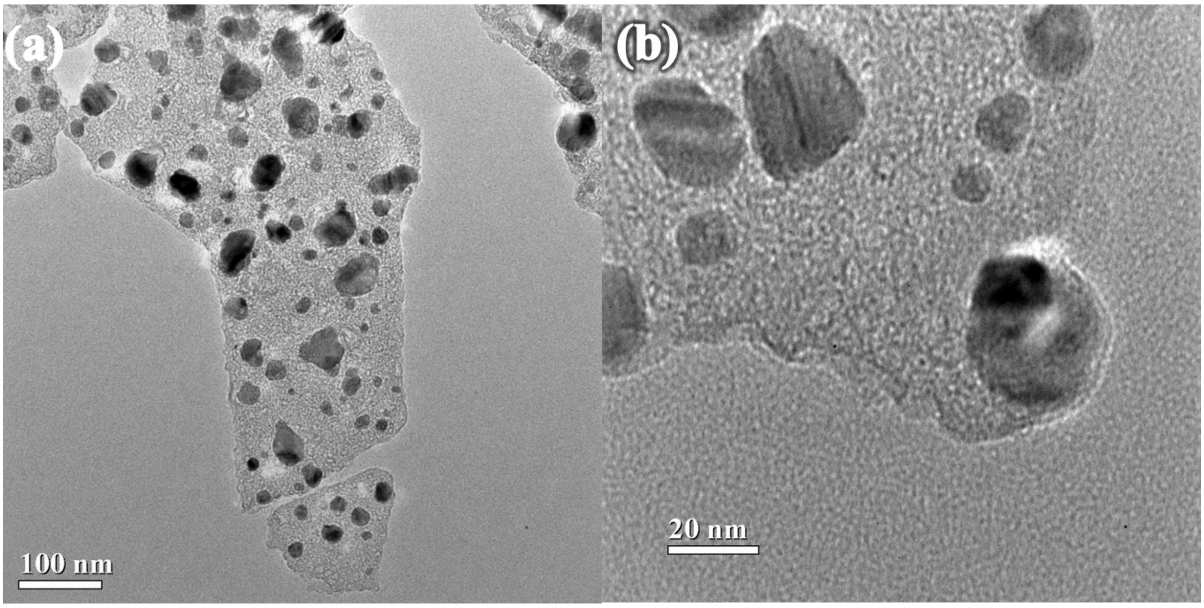


Fig. S6. SEM image of 2D MOF after annealing in N_2 at 800 °C without $FeCl_3$ etching.

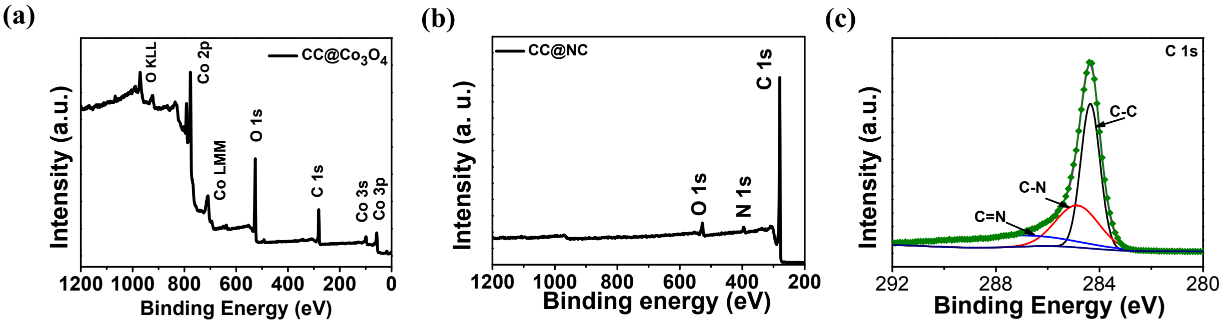


Fig. S7. Wide survey XPS spectra of (a) CC@Co_3O_4 and (b) CC@NC. (C) C 1s spectra in CC@NC.

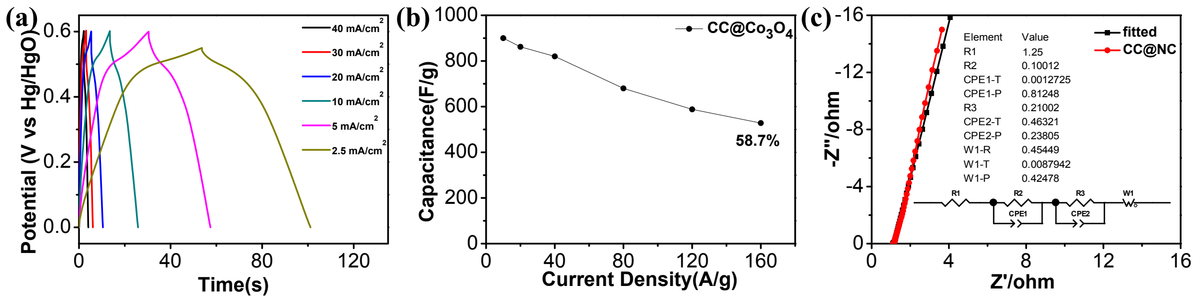


Fig. S8. (a) Charge-discharge curves, (b) rate property, and (c) EIS results of CC@Co_3O_4 and (b) CC@NC.

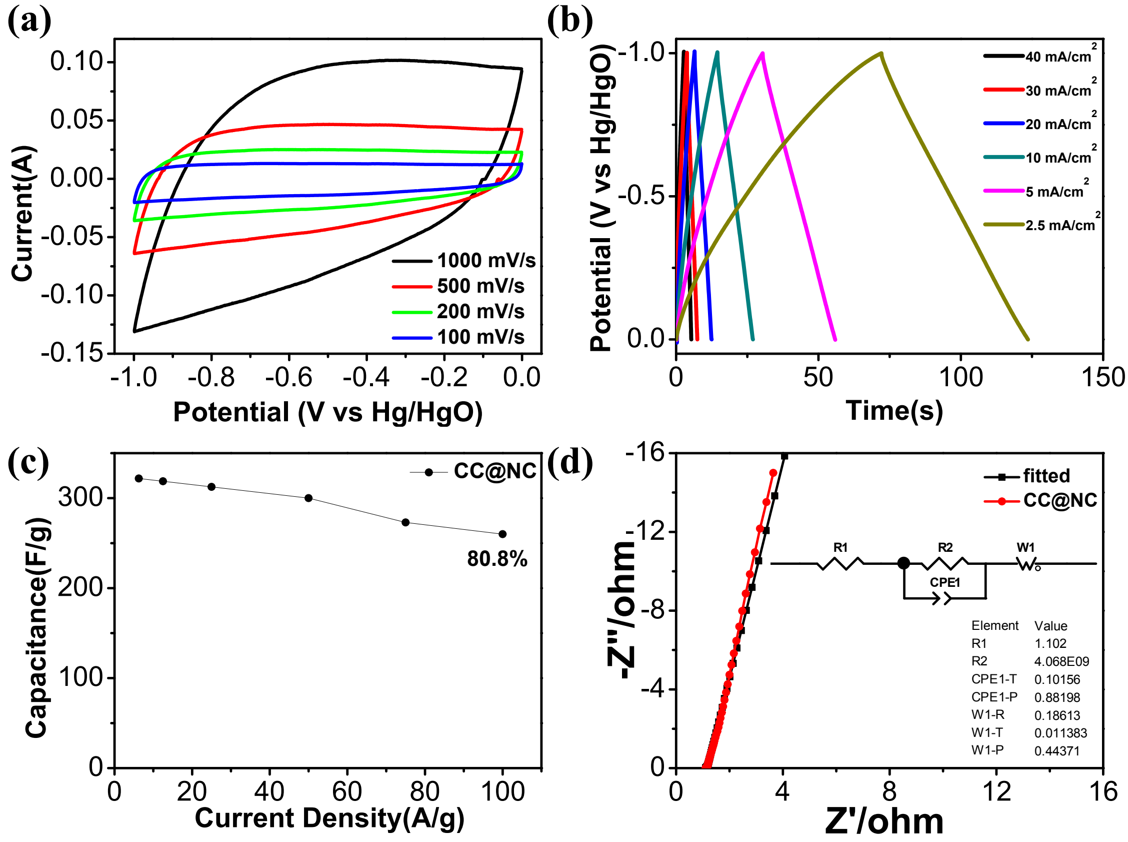


Fig. S9. (a) CV curves at high scan rates, (b) charge-discharge curves, (c) rate property, and (d) EIS results of CC@NC.