Supporting information

Construction of cationic porphyrin organic polymers with different catalytic centers for electrocatalytic small molecule activation

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Experimental section

Electrochemistry

The electrode preparation and testing methods of HER and OER

All the electrochemical measurements were performed on a CHI660E electrochemical work station with a standard three-electrode system. The modified glassy carbon electrode (GCE, 3 mm, 0.071 cm^2) was used as the working electrode, while the Hg/HgO electrode and graphite rod served as the reference electrode and counter electrode, respectively. All the potentials in this report were versus the reversible hydrogen electrode (RHE) unless otherwise noted, according to the equation:

E(RHE) = E (Hg/HgO) + (0.098 + 0.059 pH) V.

The catalyst ink was prepared according to the following proportions: 5 mg catalyst powders, 500 μL ethanol and 500 μL distilled water, 100 μL 5 wt% Nafion solution. Then the suspension was vigorously sonicated for 30 min. For fabricating the working electrode, 8 μL of the as-prepared homogeneous ink was carefully dropcast onto the polished mirror-like GCE (catalyst loading: ~0.51 mg/cm^2) and it was allowed to dry in air at room temperature. The scan rates were 5 mV s^{-1} for linear sweep voltammetry.

The electrochemical impedance spectroscopy (EIS) represents the change in impedance of the electrode system as a function of frequency, which was carried out at the potential corresponding to 10 mA·cm^{-2} in a range of 0.01-100 kHz.

The electrode preparation and testing methods of NO_2^-RR

The electrocatalytic activity of various catalysts for NO_2^- Reduction was measured at 298 K using a CHI660E electrochemical workstation. All tests were conducted in a standard three-electrode system using a typical H-type electrolytic cell with a Nafion 115 proton exchange membrane. The three-electrode cell configuration included a working electrode (catalyst-supported carbon paper

(CP), a reference electrode (Hg/HgO), and a counter electrode (Pt column). The total current density was normalized to the geometric area of the working electrode. To prepare the ink solution, adding catalyst (5 mg) and carbon black (CB) (2.5 mg) in a mixed solvent of ethanol, water, and 5 wt% Nafion (7.5/2.5/1 v/v/v, 220 μL). After mixing, the catalyst ink was uniformly dispersed using ultrasonic treatment for 1 h. The 8 μL well-dispersed samples were then evenly dropped onto 0.5 × 0.5 cm^2 CP, dried at room temperature. The loading capacity of catalyst on CP is 0.75 mg cm^{-2}. For nitrite reduction, 25 mL 0.1 M KOH solution containing 0.15 M $NaNO_2$ was added into the cathode and 25 mL 0.1 M KOH solution was added into the anode compartment. The catalysts were subjected to a constant potential test at various voltages for 60 min.

Calculation the faradaic efficiency of NO_2^-RR and NH_3 yield

The FE of NH_3 production is defined as the theoretic charge required for NH_3 conversion (q) against the total amount of charge through the electrode during electrolysis (Q). Assuming that n electrons are required to synthesize one molecule of NH_3 (n = 6 for NO_2^- reduction), the FE formula can be calculated using Eq. (1). The formation rate of NH_3 ($r(NH_3)$) is calculated by Eq. (2). The unit of r (NH_3) is μg h^{-1} mg$_{cat}^{-1}$.

$$FE(NH_3) = \frac{q}{Q} = \frac{96500 \times n \times \frac{[NH_3] \times v}{17}}{1000000 \times \int idt} \qquad \text{(eq 1)}$$

$$\mathrm{r}(NH_3) = \frac{[NH_3] \times v}{\mathrm{t} \times M_{\mathrm{cat}}} \qquad \text{(eq 2)}$$

^{15}N isotopic labeling experiment

The NH_3 generation was determined by ^{1}H NMR (600 MHz) with deuterium dimethyl sulfoxide (DMSO-d6) as the internal standard. The equipment and procedure used in the isotopic labelling experiment were the same as in the electrolytic experiment above, except that the re-actants in the electrolyte were changed from $NaNO_2$ to isotopically labelled $^{15}NO_2^-$. After electrocatalytic reaction, 10 mL of electrolyte was transferred and its pH was adjusted to 1.0 ~ 2.0 by 1.0 M H_2SO_4 solution. Then this solution was concentrated to 1 mL. Afterwards, 100 μL of DMSO-d6 was added to above electrolyte for ^{1}H NMR test.

Synthesis of 5,10,15,20-tetrakis(4-aminophenyl porphyrin)-H_2TAPP

H_2TAPP was prepared with modifications to previous reports.[1] The solution of 4-nitrobenzaldehyde (5.5 g, 36.5 mmol) and acetic anhydride (6.5 mL, 63.5 mol) in propionic acid (150 mL) was heated to 120 °C under reflux. Freshly distilled pyrrole (2.5 mL) was slowly added via syringe. The reaction was stirred for 1.5 hours at 140 °C, and upon cooling, the mixture was refrigerated overnight. The resulting black precipitate was filtrated, washed with methanol, and deionized (DI) water (50/50). Next, the dark solid was dissolved in pyridine (120 mL) and refluxed for 1 hour. The mixture was cooled to room temperature and refrigerated overnight. The purple precipitate,5,10,15,20-tetrakis(4-nitrophenyl porphyrin), H_2TNPP was obtained by filtration and washed sequentially with dichloromethane and acetone until the washings were clear, and the sample was vacuum dried overnight.

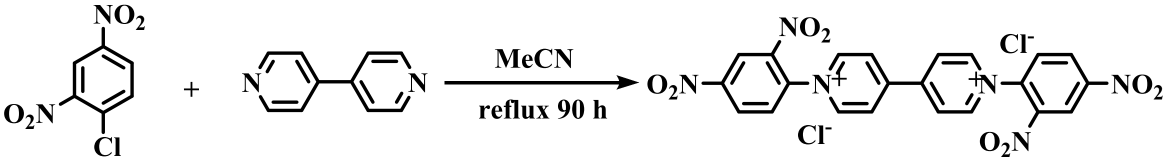
A solution of H_2TNPP (1.5 g) in concentrated HCl (20 mL) was placed in a round bottom flask. A solution of $SnCl_2 \cdot 2H_2O$ (10 g ,44 mmol) in concentrated HCl was quickly added to the flask. The temperature was increased to 75 °C, and the mixture was stirred for 1.5 hour. The solution was then cooled to room temperature and refrigerated overnight. The green solution was diluted with 600 mL of DI water, and ammonia was added to reach a pH of 7–8. The crude was then filtered and washed with DI water and vacuum-dried overnight. The crude solid was placed in a Soxhlet extractor in chloroform (250 mL) for 48 hours. After complete Soxhlet extraction, dichloromethane and ethanol were used as eluents, the column was packed with silica gel, and the main color band was collected, and the purple solid was obtained as H_2TAPP.

Synthesis of metalloporphyrins, (M-TAPP, where M = Co, Ni, Cu)

H_2TAPP (100 mg, 0.148 mmol) was dissolved in 30 mL of DMF: $CHCl_3$=2:1 mixed solution, then cobalt acetate (105 mg, 0.593 mmol) was dissolved in methanol and added to the above solution. and the resulting mixture was refluxed at 80 °C for 24 h. After cooling to room temperature, the purplish-red solid was obtained by filtration, and then the solid obtained was washed with water (3×15 mL) and dichloromethane (3×15 mL) sequentially. Finally, the obtained solid was dried under vacuum at 80 °C for 12 h to obtain the product CoTAPP.

The syntheses of CuTAPP and NiTAPP were similar to that of CoTAPP, and only the cobalt acetate was replaced by copper acetate or nickel acetate.

Synthesis of 1,1'-Bis-(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride (MV)



2, 4-dinitrochlorobenzene (14.0 g, 70 mmol) and 4, 4'-bipyridine (3.2 g, 20 mmol) were individually dissolved in acetonitrile (100 mL) and then mixed and refluxed (72 hours). A yellow powder precipitated, which was filtered and washed several times with acetonitrile and acetone[2].

Synthesis of M-MV

MTAPP (0.5 mmol) and 2 eq MV were dissolved in 2 mL 1,4-Dioxane in a reaction kettle. The kettle was kept in the oven for 72 hours at 120 °C. The solids were collected by centrifugation and respectively washed several times with tetrahydrofuran, dioxane and ethanol, respectively. Then dried in a vacuum oven at 100°C for 24 h.

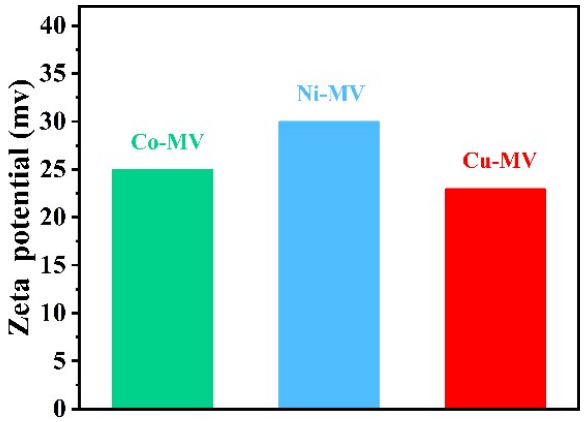


Fig. S1. The Zeta potential of M-MV.

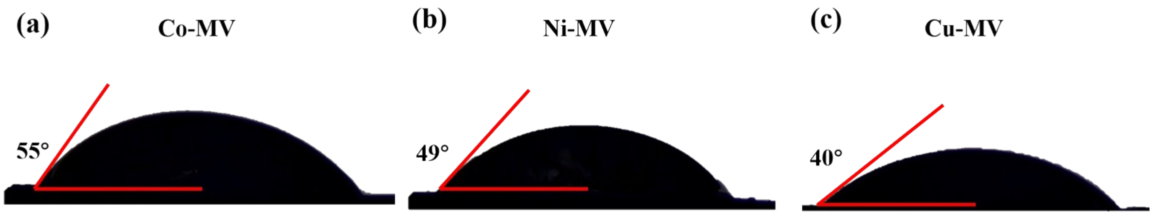


Fig. S2. Water contact angles of (a) Co-MV, (b) Ni-MV and (c) Cu-MV.

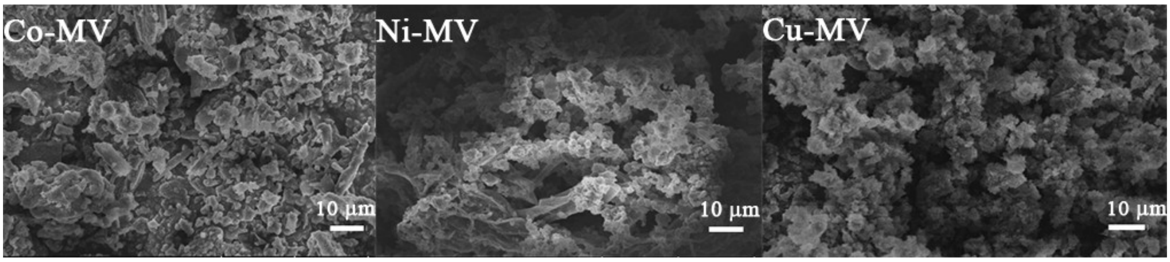


Fig. S3. SEM micrographs of Co-MV, Ni-MV and Cu-MV.

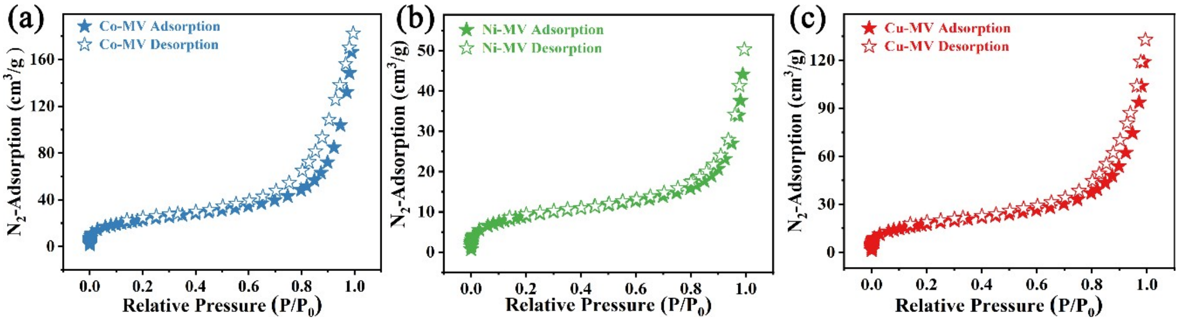


Fig. S4. N_2 adsorption isotherms of (a)Co-MV, (b)Ni-MV and (c)Cu-MV.

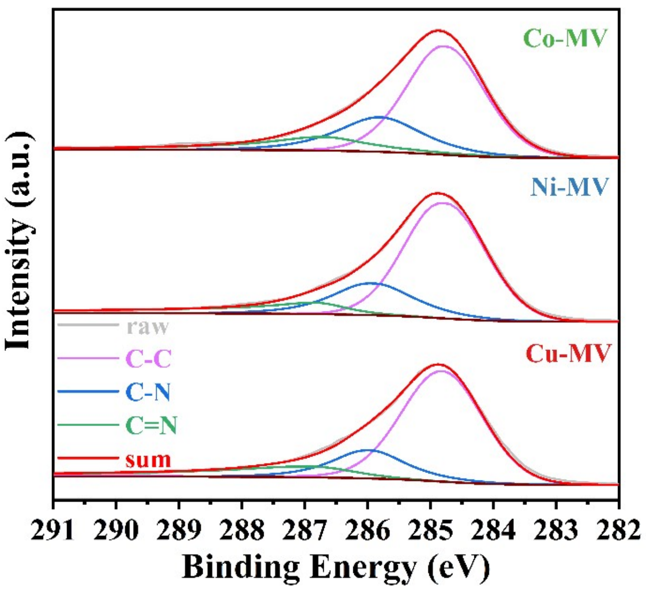


Fig. S5. C 1s XPS spectra of Co-MV, Ni-MV and Cu-MV.

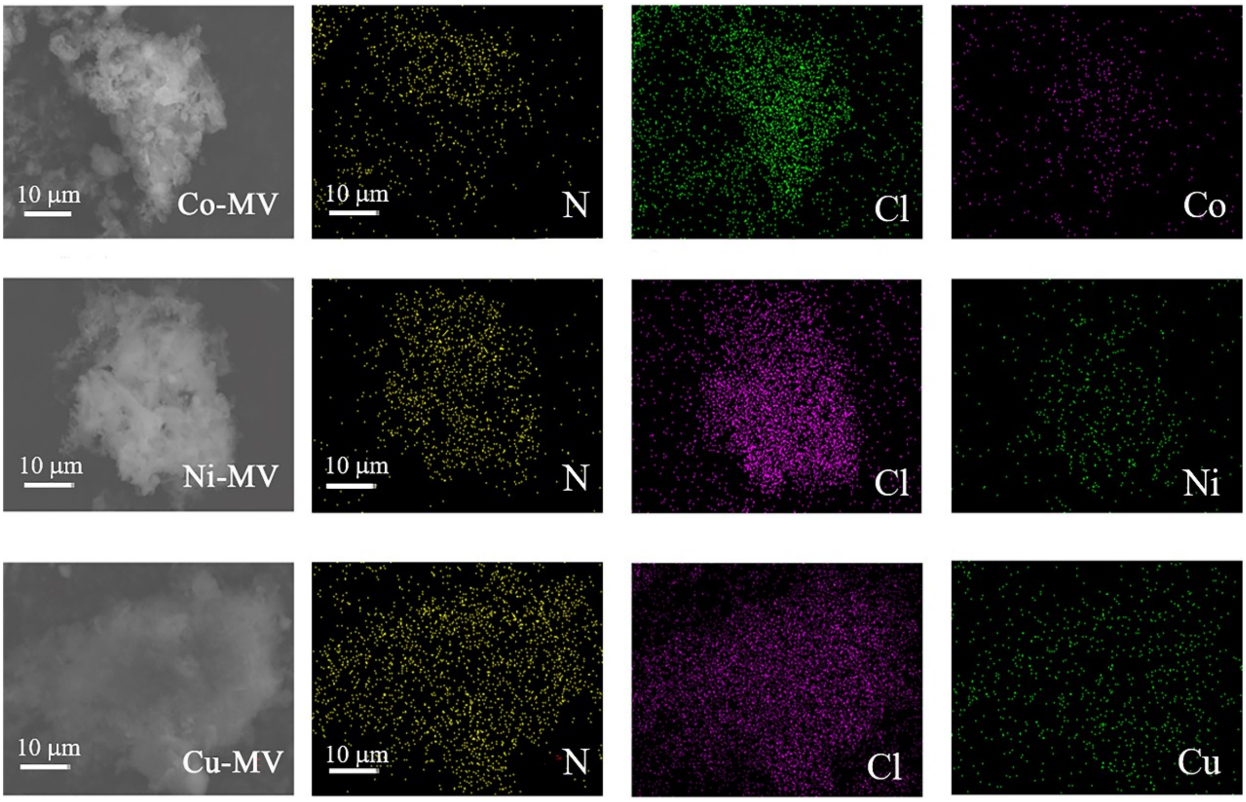


Fig. S6. SEM image and the corresponding elemental mapping images of Co-MV, Ni-MV and Cu-MV.

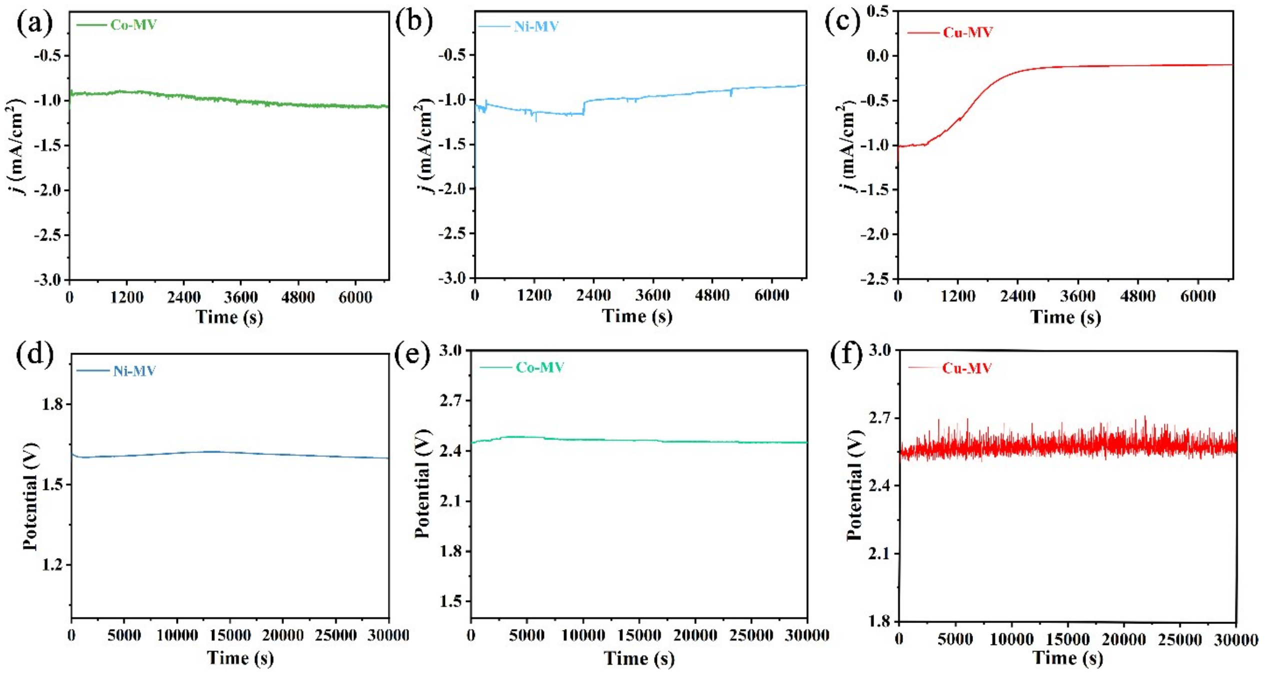


Fig. S7. HER chronoamperometry curve of (a) Co-MV, (b) Ni-MV and (c) Cu-MV; OER chronopotentiometry curve of (d) Ni-MV, (e) Co-MV and (f) Cu-MV.

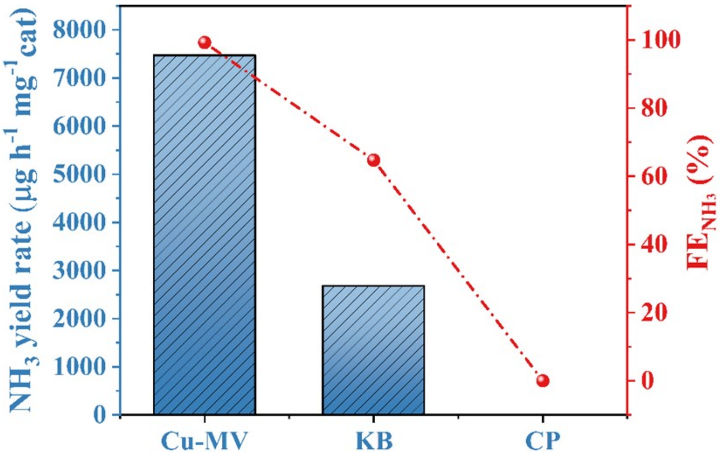


Fig. S8. Comparison NH$_3$ yield rates with Cu-MV, KB, and CP at –0.55 V vs RHE.

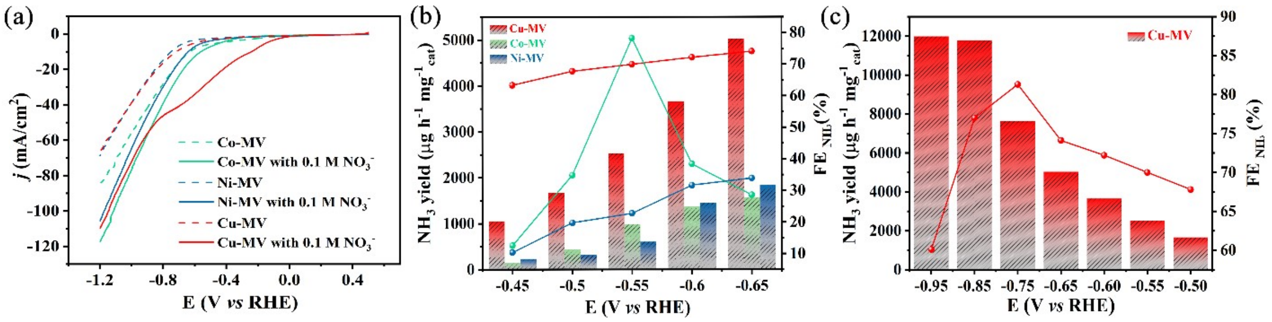


Fig. S9. (a) LSV curves in 0.1 M KOH solution with and without 0.1 M NO_3^- of Co-MV, Ni-MV, and Cu-MV, (b) The comparison of electrocatalytic performance of Cu-MV, Co-MV and Ni-MV for NO_3^-RR, (c) The NH_3 yield rate and FE_{NH3} at different applied potentials ranging of Cu-MV.

Table S1. ICP-AES results for the metal content in M-MV.

Catalysts	Content wt%	
	Experimental value	Theoretical value
Co-MV	3.8%	4.5%
Ni-MV	3.8%	4.5%
Cu-MV	4.6%	4.8%

Table S2. The resistance parameters obtained from Randles equivalent circuit fitting.

Catalysts	Catalysis	Rs (Ω)	Rct (Ω)
Co-MV	HER	13.3	85.5
	OER	10.4	74.9
Ni-MV	HER	22.63	108.5
	OER	10.3	47.3
Cu-MV	HER	28.05	288.5
	OER	11.83	146.2

References

1. Y. Chen, R. Luo, Q. Xu, J. Jiang, X. Zhou and H. Ji, *ACS Sustain. Chem. Eng.*, 2018, **6**, 1074-1082.
2. S. M. Beladi-Mousavi, J. Klein, B. Khezri, L. Walder and M. Pumera, *ACS Nano*, 2020, **14**, 3434-3441.