# Supporting Information

## Enhanced Ammonia Selectivity on Electrochemical Nitrate Reduction: Cu-Ni Metal-Organic Frameworks with Tandem Active Sites for Cascade Catalysis

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# 1. Experimental Procedures

*Physical Characterization:*

PXRD patterns are measured on a PANalytical B.V. Empyrean having Cu Ka radiation (1.540598 Å) under 40 kV and 40 mA. SEM images are obtained on a HITACHI SU8000 microscope. High-resolution TEM is conducted on a JEOL JEM-2100F microscope. XPS spectra are measured on an ESCALAB 250 spectrometer using Al Ka excitation. The absorbance data of the spectrophotometer is measured on a UV-Vis spectrophotometer. A Bruker 400M NMR instrument is used to record 1H NMR spectra.

*Electrochemical measurements*

The electrochemical tests are conducted in a three-electrode cell under CHI 760e electrochemical station. Carbon cloth (CC), saturated calomel electrode (SCE), and graphite rod are serviced as working electrode, reference electrode, and counter electrode, respectively. Firstly, catalyst ink is obtained by mixing 4 mg catalysts, 1mg carbon black with 500 μL DMF, 475 μL ultrapure water, and 25 μL Nafion (0.5 wt% in ethanol). The mixture is well dispersed by ultrasonication for 1 h. Next, 30 μL catalyst ink is drop-casted onto the CC ($0.5 \times 0.5$ cm$^2$) in 2 times. Finally, the electrode is dried at 298 K. NRA electrochemical measurements are conducted in an H-cell. The electrolyte used for all nitrate reduction experiments is 0.1 M NaSO$_4$ with a concentration of 50 mM NO$_3^-$ (NaNO$_3$). Potentiostatic tests are conducted during NRA at different potentials under ambient conditions after 30 min of purging with Ar (99.999%). After 30 min of electroreduction, the ammonia and nitrite concentrations in the electrolyte are measured. Isotopic $^{15}$N labeling experiments are performed using Na$^{15}$NO$_3$ (99%-Cambridge Isotopes) as an isotopic nitrate source. The electrolyte used for the isotopic labeling experiments is 0.1 M NaSO$_4$ with 50 mM isotopically labeled sodium nitrate.

*Calculations of the NH$_3$ yield and Faradaic efficiency*

The nitrate reduction to ammonia Faradaic efficiency is calculated by eq.1.

$$FE_{NH_3} = \frac{n \times F \times c_{NH_3} \times V}{Q} \#eq.1$$

The nitrate reduction to ammonia yield rate is calculated by eq.2.

$$Yield_{NH_3} = \frac{c_{NH_3} \times V}{t \times A_{electrode}} \#eq.2$$

The nitrate reduction Faradaic efficiency is calculated by eq.3.

$$FE_{NO_2^-} = \frac{n \times F \times c_{NO_2^-} \times V}{Q} \#eq.3$$

where $c_{NH_3}$ is the concentration of NH$_3$(aq) (mol mL$^{-1}$), $V$ is the volume of the electrolyte (mL), $t$ is the electrolysis duration (h), the electrode is the geometric surface area of the working electrode (0.25 cm$^2$), n is the number of electrons transferred ($n = 8$ for nitrate reduction to ammonia and $n = 2$ for nitrate reduction to nitrite), $F$ is the Faraday constant (96485 C mol$^{-1}$), $c_{NO_2^-}$ is the concentration of NO$_2^-$ (mol mL$^{-1}$), $Q$ is the total charge passed during the electrolysis.

### *Product Detection*

The UV-Vis spectrophotometer is used to detect the ion concentration of electrolytes after dilution to an appropriate concentration to match the range of calibration curves. The specific detection methods are as follows:

*Detection of nitrite-N*

The color developer is configured as follows: 20 g of p-aminobenzenesulfonamide is added to a mixed solution of 250 mL of water and 50 mL of phosphoric acid, and then 1 g of N-(1-naphthyl)-ethylenediamine dihydrochloride is dissolved in the above solution. Finally, the above solution is transferred to a 500 mL volumetric flask and diluted to the mark. A certain amount of electrolyte is taken out from the electrolytic cell and diluted to 5 mL to the detection range. Next, 0.1 mL color reagent is added to the aforementioned 5 mL solution. After shaking and standing for 30 min, the absorbance is tested by UV-Vis spectrophotometry at a wavelength of 540 nm. The calibration curve can be obtained through different concentrations of NaNO$_2$ solutions and the corresponding absorbance.

*Detection of ammonium-N*

Preparation of Nessler's reagent: First, 16.0 g of sodium hydroxide (NaOH) is dissolved in 50 mL ultrapure water. Then, 7.0 g of potassium iodide (KI) and 10.0 g of mercury iodide (HgI$_2$) are also dissolved in ultrapure water. The above solution is gradually added to the 50 mL sodium hydroxide solution under strong agitation. Finally, the mixture is diluted to 100 mL with ultrapure water.

Preparation of sodium potassium tartrate solution ($\rho$=0.5 g mL$^{-1}$): First, 50.0 g of sodium potassium tartrate (KNaC$_4$H$_6$O$_6$ • 4H$_2$O) is dissolved in 50 mL ultrapure water. Then the solution is diluted to 100 mL.

A certain amount of electrolyte is taken out from the electrolytic cell and diluted to 5 mL to the detection range. 0.1 mL of sodium potassium tartrate solution and 0.1 mL of Nessler's reagent are added to the above-mentioned 5 mL solution. After shaking and standing for 30 min, the absorbance is tested by UV-Vis spectrophotometry at a wavelength of 420 nm. The calibration curve can be obtained through different concentrations of NH$_4$Cl solutions and the corresponding absorbance.

### [15]N Isotope Labeling Experiments

The isotopic labeling nitrate reduction experiments are carried out using the aforementioned electrochemical nitrate reduction methods. After 30 min of electroreduction, the pH of the electrolyte in the cathodic chamber is adjusted to 2 by 1 M HCl. After that, the adjusted electrolyte (800 μL) is mixed with deuterium oxide (D$_2$O, 200 μL). And the mixture is sealed into a nuclear magnetic resonance (NMR) tube for further tests.

### Turn over frequency calculation

TOF calculation: The TOF values were estimated based on our previous report [1], resulting in the following formula:

$$TOF = \frac{Number\ of\ total\ ammonia\ turnover\ /\ cm^2}{Number\ of\ active\ sites\ /\ cm^2} \#eq.4$$

The number of total ammonia turnovers was calculated from the current density and the Faraday efficiency by the following equation:

$$Number\ of\ NH_3 = \left(J\frac{mA}{cm^2}\right)\left(FE_{NH_3}\right)\left(\frac{1\ C\ s^{-1}}{1000\ mA}\right)\left(\frac{1\ mol\ e^-}{96485.3\ C}\right)\left(\frac{1\ mol\ NH_3}{8\ mol\ e^-}\right)\left(\frac{6.022*10^{23}\ NH_3\ molecules}{1\ mol\ NH_3}\right) eq.5$$

The number of active sites was regarded as the number of surface sites, and calculated by the following formula:

$$Number\ of\ active\ sites = \left(\frac{Number\ of\ metal\ sites\ /\ unit\ cell}{\dfrac{Volume}{unit\ cell}}\right)^{\frac{2}{3}} \#eq.6$$

Finally, the plot of current density can be converted into a TOF plot according to the following formula:

$$TOF = \frac{(Number\ of\ NH_3)*|J|}{Number\ of\ active\ sites*A_{ECSA}} \#eq.7$$

The $A_{ECSA}$ is the electrochemical active surface area, which can be calculated from the following formula, where specific capacitance is $C_{dl}$, and 40 μF cm$^{-2}$ is a constant to convert capacitance to $A_{ECSA}$:

$$A_{ECSA} = \frac{specific\ capacitance}{40\ \mu F\ cm^{-2}\ per\ cm_{ECSA}^2} \#eq.8$$

### Theoretical simulation.

All the calculations are performed using Quantum ESPRESSO[2, 3]. To investigate the electrocatalytic mechanism of the $Ni_xCu_{3-x}(HITP)_2$, $Ni_{1.5}Cu_{1.5}(HITP)_2$ slab is established. MOF models in this work are built using BURAI. PBE under the GGA[4] with PAW[5] pseudopotentials from Pslibrary 1.0.0 is used for SCF calculations[6]. An electronic convergence threshold of 1E-6 eV is set during SCF cycles, and Broyden–Fletcher–Goldfarb–Shanno (BFGS) is chosen for ionic dynamics optimization. A 50 Ry kinetic energy cut-off for wavefunctions and a 500 Ry kinetic energy cut-off for charge density and potential are employed. The reaction free energy is calculated by

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \qquad\qquad eq.9$$

where $\Delta E$ is the total energy difference between reactants and products, $\Delta ZPE$ is the zero-point energy correction, and $\Delta S$ is the vibrational entropy change at finite temperature $T$. The free energy corrections of adsorbates are estimated by Atomic Simulation Environment (ASE, a set of tools and Python modules)[7]. The enthalpy and entropy of the ideal gas molecule are taken from the standard thermodynamic Tables. Notably, a vacuum slab of 15 Å is applied along the c-axes to reduce the unwanted interactions during the free energy calculation.

## 2. Result and Discussion
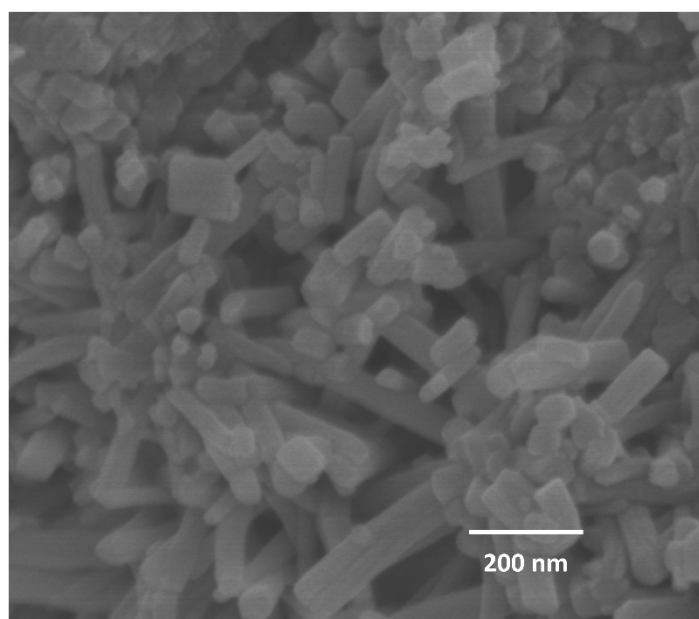


**Figure S1.** SEM image of $Ni_3(HITP)_2$.
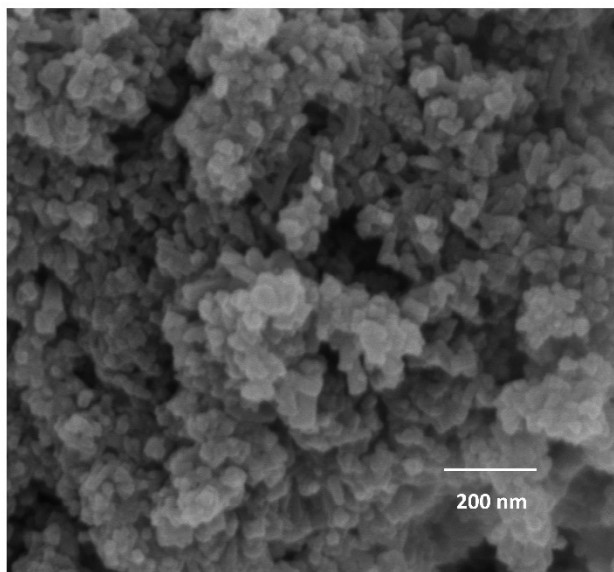
**Figure S2.** SEM image of $Ni_{2.4}Cu_{0.6}(HITP)_2$
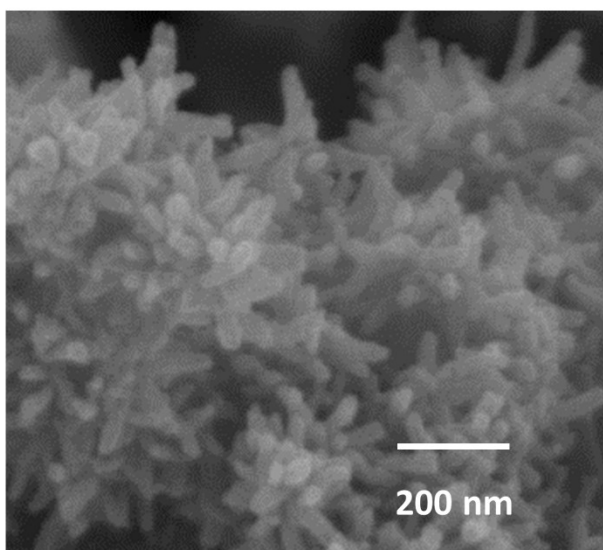


**Figure S3.** SEM image of $Ni_{0.6}Cu_{2.4}(HITP)_2$
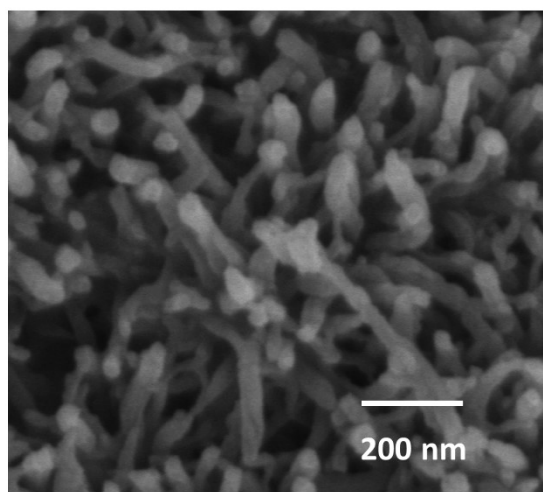
**Figure S4.** SEM image of $Cu_3(HITP)_2$
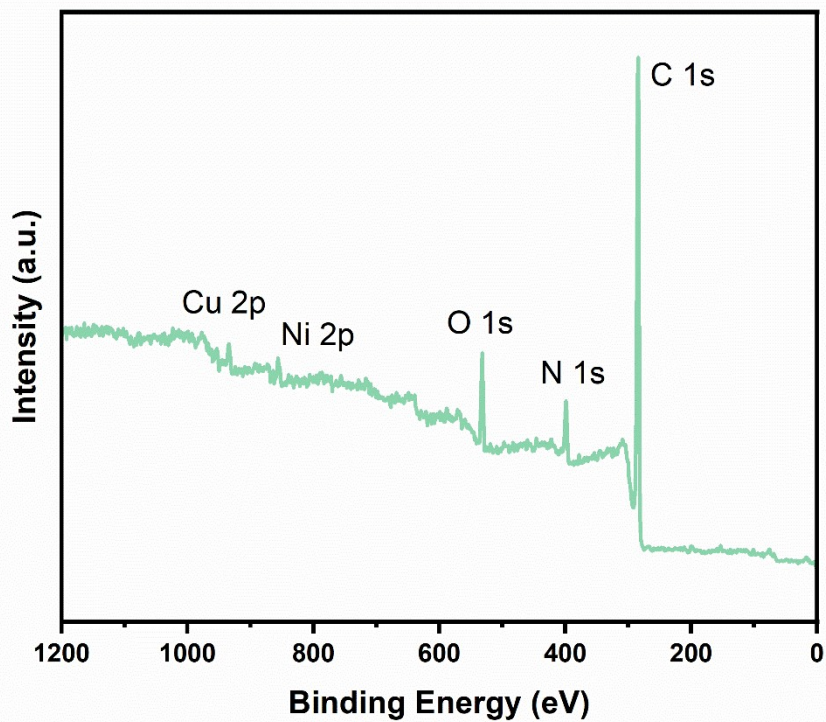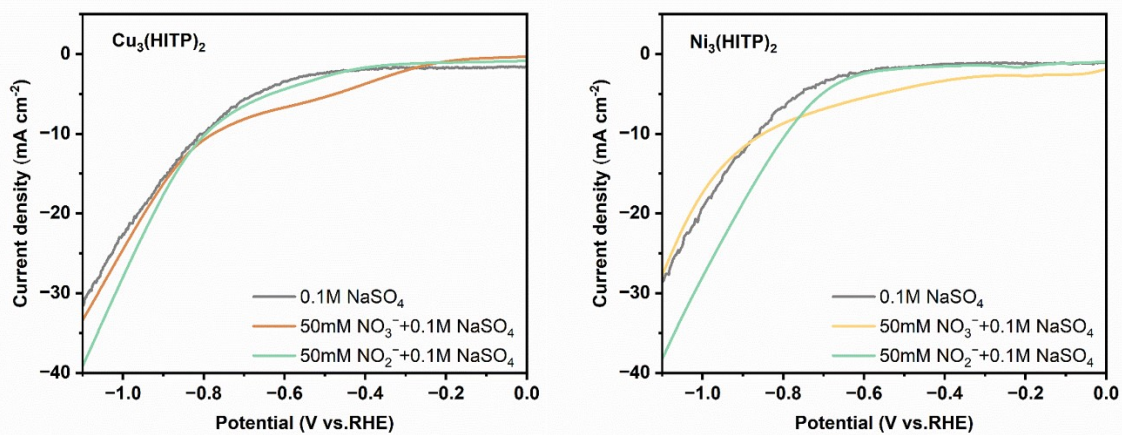
**Figure S5.** XPS survey spectrum of $Ni_{1.5}Cu_{1.5}(HITP)_2$.



**Figure S6.** LSV curves of a) $Cu_3(HITP)_2$ and b) $Ni_3(HITP)_2$ MOF in 0.1 M $Na_2SO_4$ solution with and without 50 mM $KNO_3$.
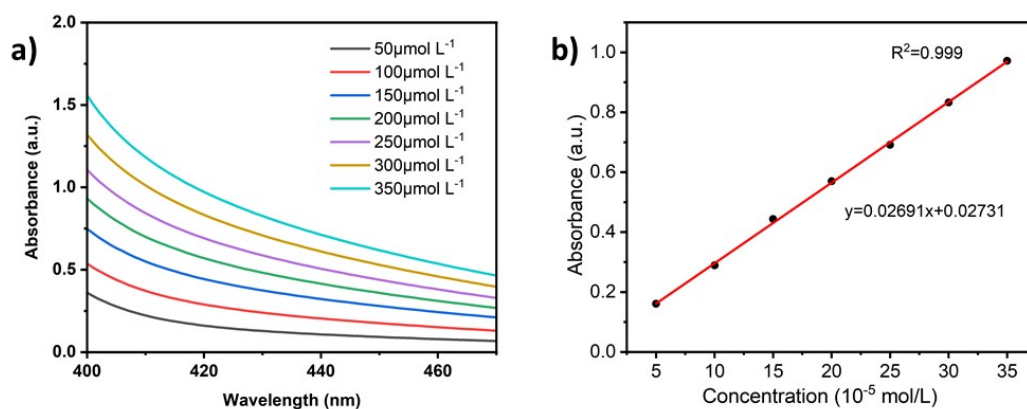
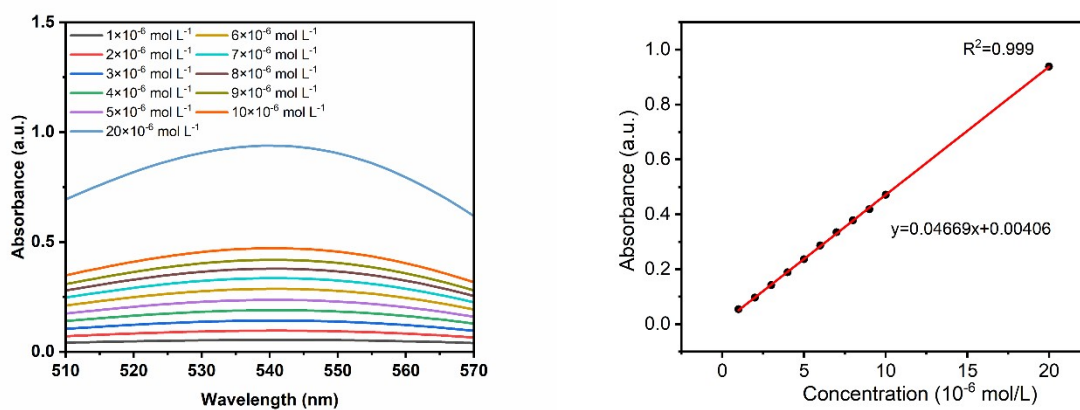**Figure S7.** a) The UV-Vis adsorption curves and b) calibration curves of ammonium-N with good linearity.



**Figure S8.** a) The UV-Vis adsorption curves and b) calibration curves of nitrite-N with good linearity.
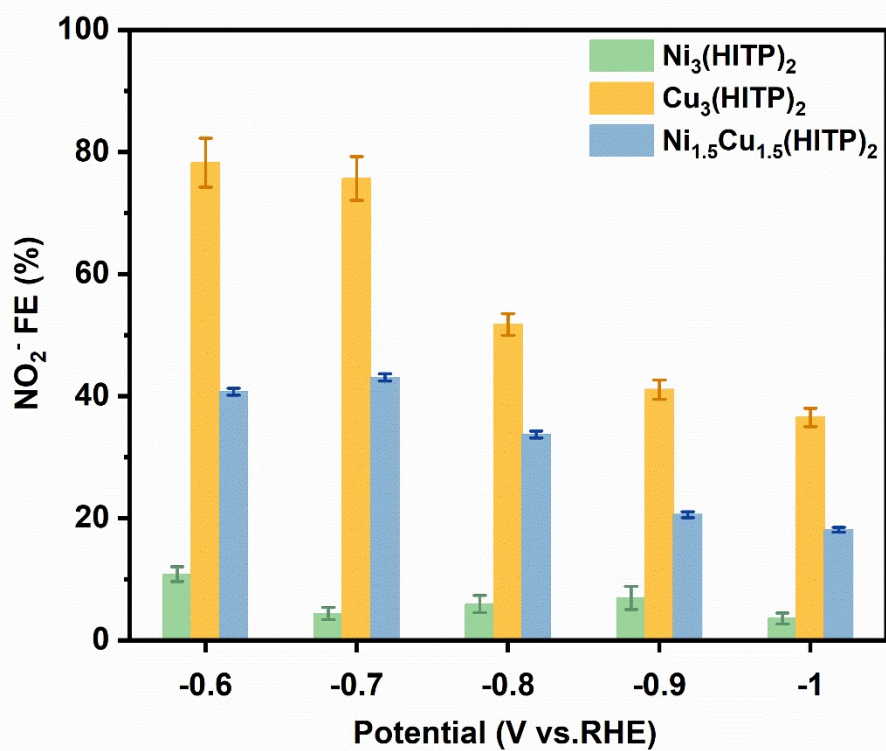
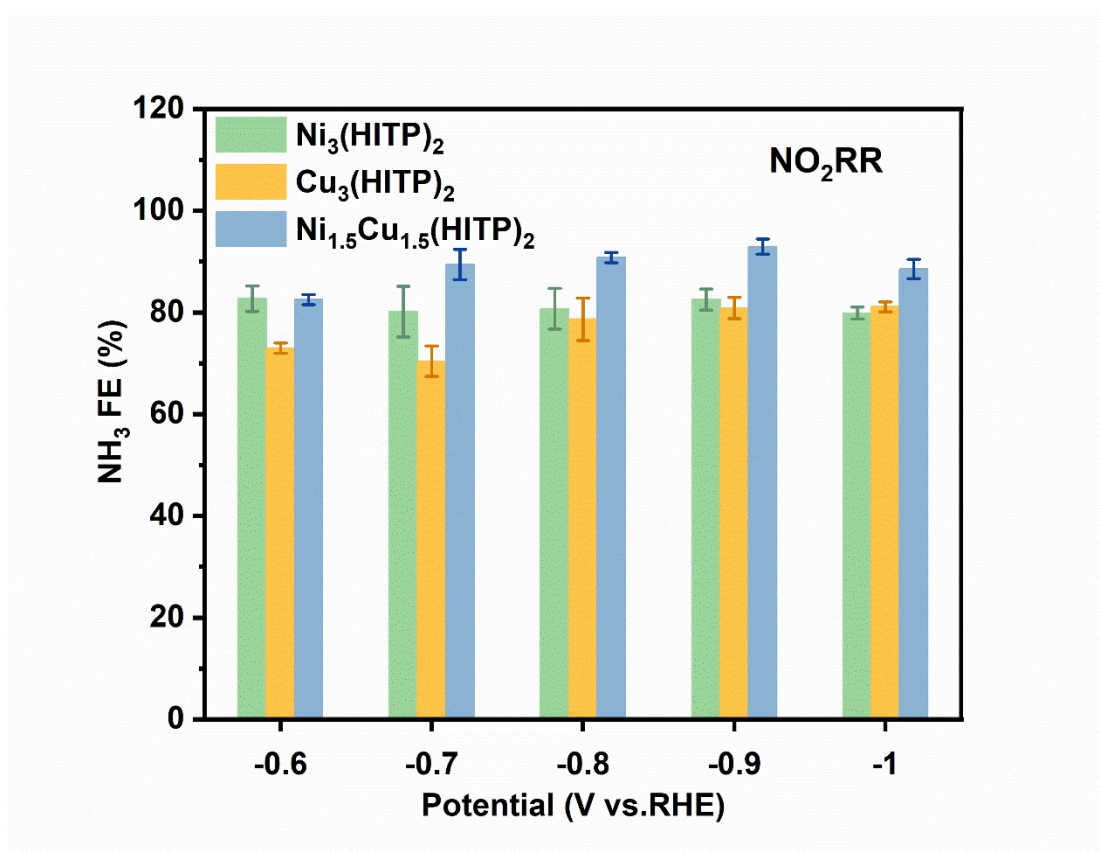**Figure S9.** $NO_2^-$ FE of the three MOFs in NRA

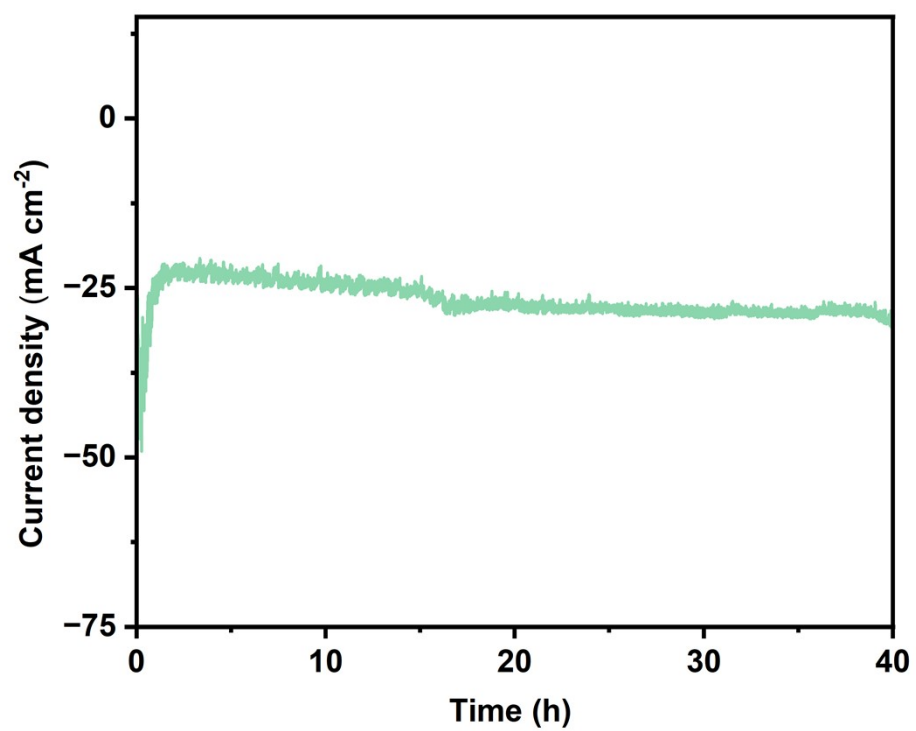**Figure S10.** NH$_3$ FE of the three MOFs in NO$_2$RR

**Figure S11.** The chronoamperometric curve of $Ni_{1.5}Cu_{1.5}(HITP)_2$.
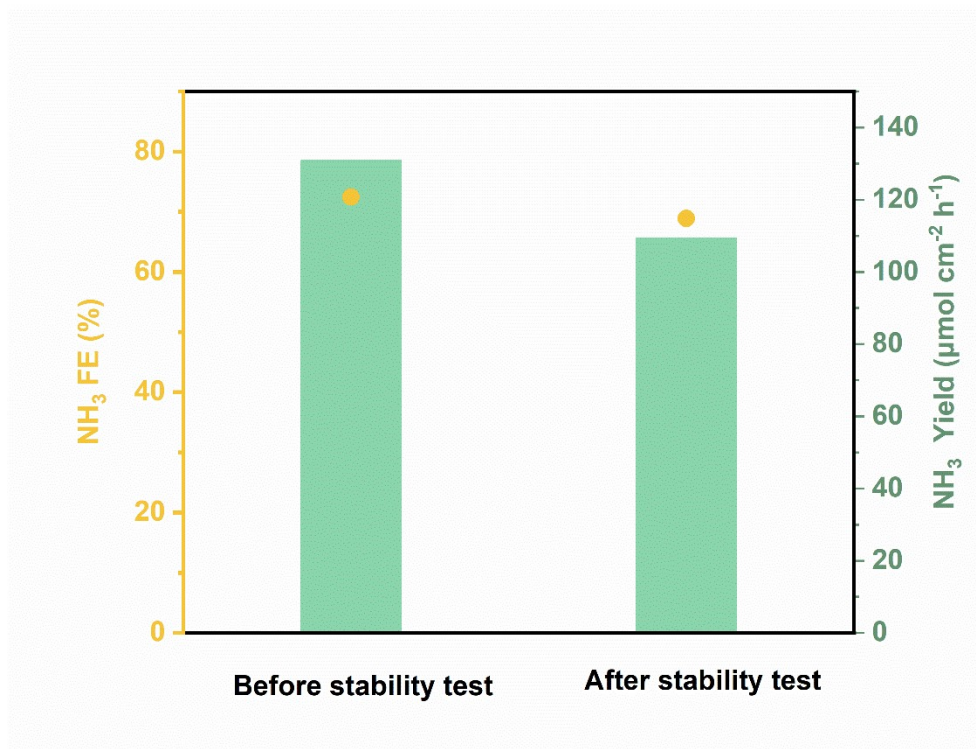
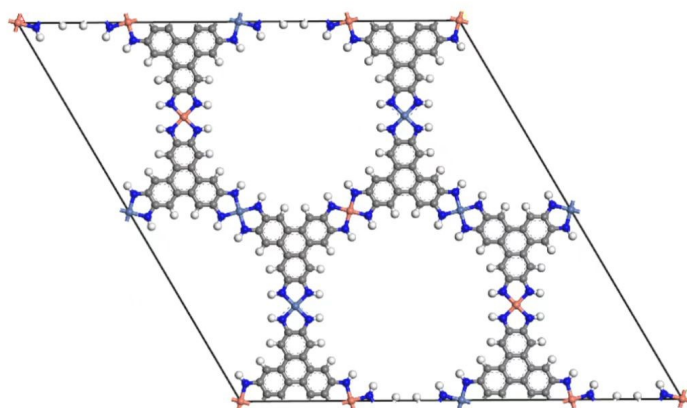**Figure S12.** NH$_3$ FE and yield before and after 40h of stability test.



**Figure S13.** Simulated structure of Ni$_{1.5}$Cu$_{1.5}$(HITP)$_2$

**Table S1.** Mass Ratio of Metal Salts for the Synthesis of MOFs

| Sample Name | $Ni(CH_3COOH)_2 \cdot 4H_2O$ (mg) | $Cu(NO_3)_2 \cdot 3H_2O$ (mg) |
|:---:|:---:|:---:|
| $Ni_3(HITP)_2$ | 13.94 | 0.00 |
| $Ni_{2.4}Cu_{0.6}(HITP)_2$ | 11.15 | 2.71 |
| $Ni_{1.8}Cu_{1.2}(HITP)_2$ | 8.36 | 5.42 |
| $Ni_{1.5}Cu_{1.5}(HITP)_2$ | 6.97 | 6.76 |
| $Ni_{1.2}Cu_{1.8}(HITP)_2$ | 5.58 | 8.13 |
| $Ni_{0.6}Cu_{2.4}(HITP)_2$ | 2.79 | 10.82 |
| $Cu_3(HITP)_2$ | 0.00 | 13.53 |

$Ni(CH_3COOH)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$, as Ni and Cu sources, were added to the reaction in a certain proportion (4:1 for $Ni_{2.4}Cu_{0.6}(HITP)_2$; 3:2 for $Ni_{1.8}Cu_{1.2}(HITP)_2$; 1:1 for $Ni_{1.5}Cu_{1.5}(HITP)_2$; 2:3 for $Ni_{1.2}Cu_{1.8}(HITP)_2$ and 1:4 for $Ni_{0.6}Cu_{2.4}(HITP)_2$).

# Reference

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