

Supporting Information

Copper Nanoparticle-embellished Zr-based Metal-Organic Framework for Electrocatalytic Hydrogen Evolution Reaction

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Experimental Section

➤ **Materials**

Zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), benzoic acid, 4-Aminobenzoic acid (ABA), sodium borohydride (NaBH_4), pyrene, bromine, 4-(methoxycarbonyl)phenyl)boronic acid, palladium tetrakis(triphenylphosphine), potassium carbonate, potassium hydroxide, hydrochloric acid, nitrobenzene, chloroform, THF, dioxane, N, N'-dimethylformamide (DMF), methanol, acetonitrile, acetone, dichloromethane, and diethyl ether were purchased from Merck. All the chemicals were used as received. Nanopure water was used for the experiments.

➤ **Synthesis of H_4TBAPy**

The ligand H_4TBAPy was synthesized according to the reported method.¹ Excess bromine was added to 100 mL of nitrobenzene and 46.5 g of pyrene (24 mmol) in a round-bottom flask. The mixture proceeded to react at 120 °C for 14 h to produce 1,3,6,8-tertrabromopyrene (C1).

2.85 g of the as-prepared C1 was taken in a round-bottom flask, 5 g (4-(methoxycarbonyl)phenyl)boronic acid, 0.1 g palladium tetrakis(triphenylphosphine), and 6 g potassium carbonate and 50 mL dioxane was added to it. The reaction mixture was stirred at 85 °C for 72 h. The resulting product was then added to an ice-cold, 3:1 solution of water and concentrated HCl. The organic component was extracted with chloroform and the product was re-crystallized in toluene to get 1,3,6,8-tetrakis(4-(methoxycarbonyl) phenyl) pyrene (C2).

1 g of C2 was taken in 100 mL of 5:2:2 mixture of THF, dioxane, and water, and 20 mL of concentrated NaOH aqueous solution was added to this, and the mixture was refluxed at 85 °C for 9–12 h. The residue was collected after removing the solvent and then dissolved in water. It was then stirred at room temperature for 2 h. The pH of the solution was adjusted to 2, and the yellow solid product was filtered, washed, and dried under vacuum.

➤ **Synthesis of NU-1000**

A reported procedure was followed for the synthesis of NU-1000.² 0.30 mmol of zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) (97 mg) was weighed into a 6-gram vial. 22.109 mmol of benzoic acid (2.7 g) was subsequently added to it. The solids were dissolved in 8 mL of DMF *via* sonication and were kept in an oven at 80 °C for 1 h. After 1 h, the solution was taken out of the oven and allowed to cool at room temperature. 40 mg of ligand (H_4TBApy) was added to the vial. The mixture was then sonicated until a homogenous yellow suspension was obtained and placed in an oven at 100°C for 24 h. The mother liquid was then decanted. The yellow powder obtained was washed three times with 10 mL of DMF over the course of 24 hours. The solid and liquid phases were separated by centrifugation at 8500 rpm for 5 minutes. The yellow solid was then re-suspended in 12 mL of DMF. 0.5 mL of 8M HCl was added to the solution and swirled, and it was placed in an oven at 100°C for 18 h. The mother liquid was decanted. The yellow powder was washed three times with 10 mL of DMF over the course of 24 h and then with 10 mL of acetone again over the course of 24 h. The sample was activated at 120 °C under a dynamic vacuum until a vacuum level of $\leq 0.002 \text{ mmHg mm}^{-1}$ was reached.

➤ **Synthesis of NU-1000-NH₂**

Amino (-NH₂) group was incorporated into the activated NU-1000 by solvent-assisted ligand incorporation (SALI).³ 0.021 mmol of NU-1000 was added to 3 mL of a 0.07 M solution of CFG (carboxylic acid-containing functional group) (0.21 mmol) in a polar solvent. For the amino (-NH₂) group, the incorporation of 4-aminobenzoic acid (4 ABA) and DMF was used as CFG and polar solvent, respectively. The reaction mixture was then sealed and heated at 60°C for 18-24 h with occasional swirling. The supernatant was decanted, and the obtained sample was soaked in fresh hot solvent, filtered, and washed sequentially with acetonitrile and dichloromethane (at 9500 rpm for 8 minutes). It was finally dried under the air.

➤ **Synthesis of Cu@NU-1000-NH₂**

Copper nanoparticles were incorporated into NU-1000-NH₂. 0.1 mmol of copper nitrate hydrate [$\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$] (18.75 mg) was dissolved in 15 mL of acetonitrile, to which 60 mg of

NU-1000 was added. The reagents were taken in a round bottom flask and stirred for 6 to 8 h at room temperature. The products were washed three times with acetonitrile (at 9500 rpm for 10 minutes). The washed product was finally dried under the air.

Cu(II)@NU-1000-NH₂ obtained was dissolved in acetonitrile and kept for stirring for 30 minutes at 0°C. 10 mg of sodium borohydride (NaBH₄) was dissolved in 5 mL of ice-cold methanol and added to the stirring solution through septa *via* syringe. The reaction was stopped after 5 to 10 minutes, and the products were washed three times with acetonitrile. The product was dried under the air.

➤ Electrocatalytic Hydrogen Evolution Reaction

The pristine MOF and Cu@MOF compounds have been applied for the water reduction study by using 0.5 M H₂SO₄ solution. Electrocatalytic studies were done with the conventional three-electrode system by using a graphite rod, saturated calomel electrode (SCE), and catalyst coated on carbon cloth as a counter, reference, and working electrode, respectively. The LSV polarization studies were carried out with a scan rate of 5 mV/sec, and all the polarization curves were 100 % iR corrected. The electrochemical impedance studies were carried out in the frequency range of 0.1 Hz to 100 kHz with an overpotential of 350 mV. All the electrodes have been fabricated *via* simple drop-casting methods, and the catalyst ink was prepared by mixing 3 mg of catalyst powder in a mixture of 750 µL of DI water, 200 µL of ethanol, and 50 µL of Nafion solution followed by ultrasonication for 15 minutes. 34.5 µL of as-prepared ink solution was drop-casted over the carbon previously washed with ethanol acetone mixture. The calculated catalytic loading was nearly 0.1 mg cm⁻².

Characterization Techniques

Powder X-ray diffraction (PXRD) patterns were collected using a powder diffractometer (Bruker D8 Advance) equipped with Cu K_{α1} radiation ($\lambda = 1.5418 \text{ \AA}$) to analyze the phase purity of the materials. The morphology of the materials was examined using an FEI NOVA NANOSEM 450 field emission scanning electron microscope. IR Prestige-21 (Shimadzu) spectrometer was used to collect the FT-IR data in the range 4000-400 cm⁻¹ by making KBr pellets. UV-Vis diffuse reflectance spectroscopy was performed using a UV-3800 SHIMADZU

UV-Vis/NIR spectrometer. Inductively coupled plasma-mass spectrometry (ICP-MS) data were collected using iCAP RQ instrument from ThermoScientific. Nitrogen sorption studies were carried out on a Micromeritics 3Flex device at 77 K using Brunauer-Emmett-Teller (BET) method. The sample was degassed for 12 h at 65 °C before the experiment. Omicron X-ray photoelectron spectrometer equipped with Mg K α excitation source. GC-MS analysis was carried out using Shimadzu GC-2014 (Gas chromatograph) equipped with molecular sieve (5 Å) column (Chromatopack).

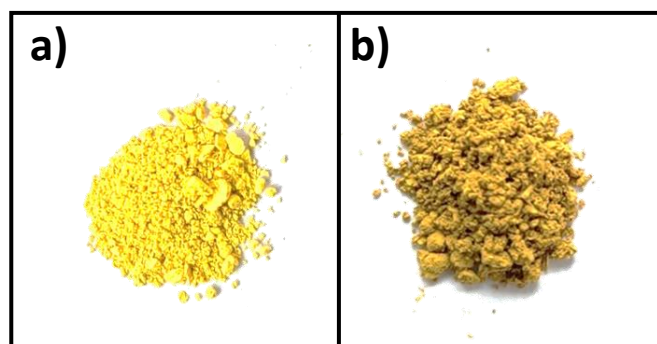


Figure S1. Photographs of a) NU-1000-NH₂, b) Cu@NU-1000-NH₂.

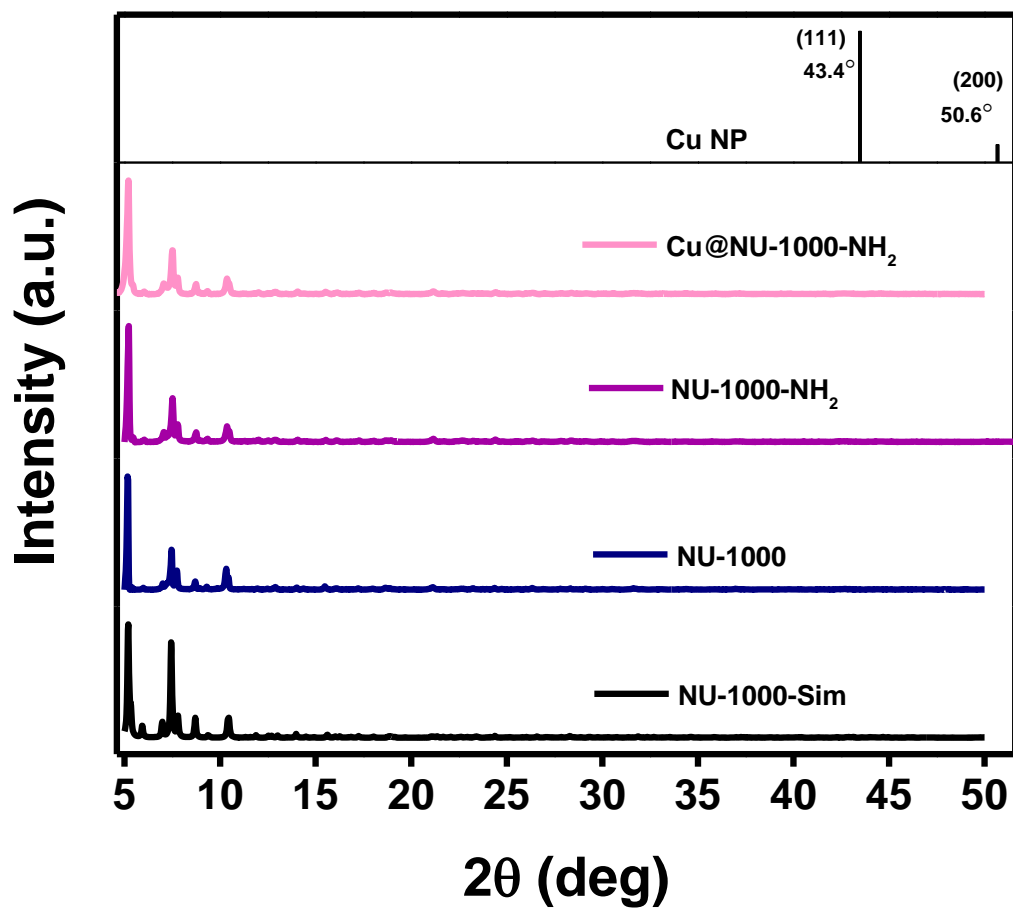


Figure S2. PXRD patterns of simulated NU-1000, as-synthesized NU-1000, NU-1000-NH₂, Cu@NU-1000-NH₂, and standard Cu NPs (JCPDS No: 003-1018).

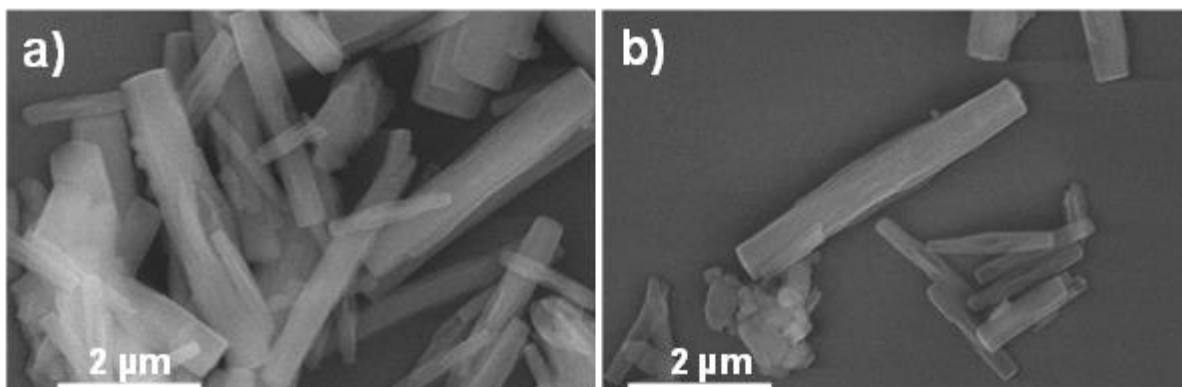


Figure S3. SEM images of a) NU-1000-NH₂ and b) Cu@NU-1000-NH₂.

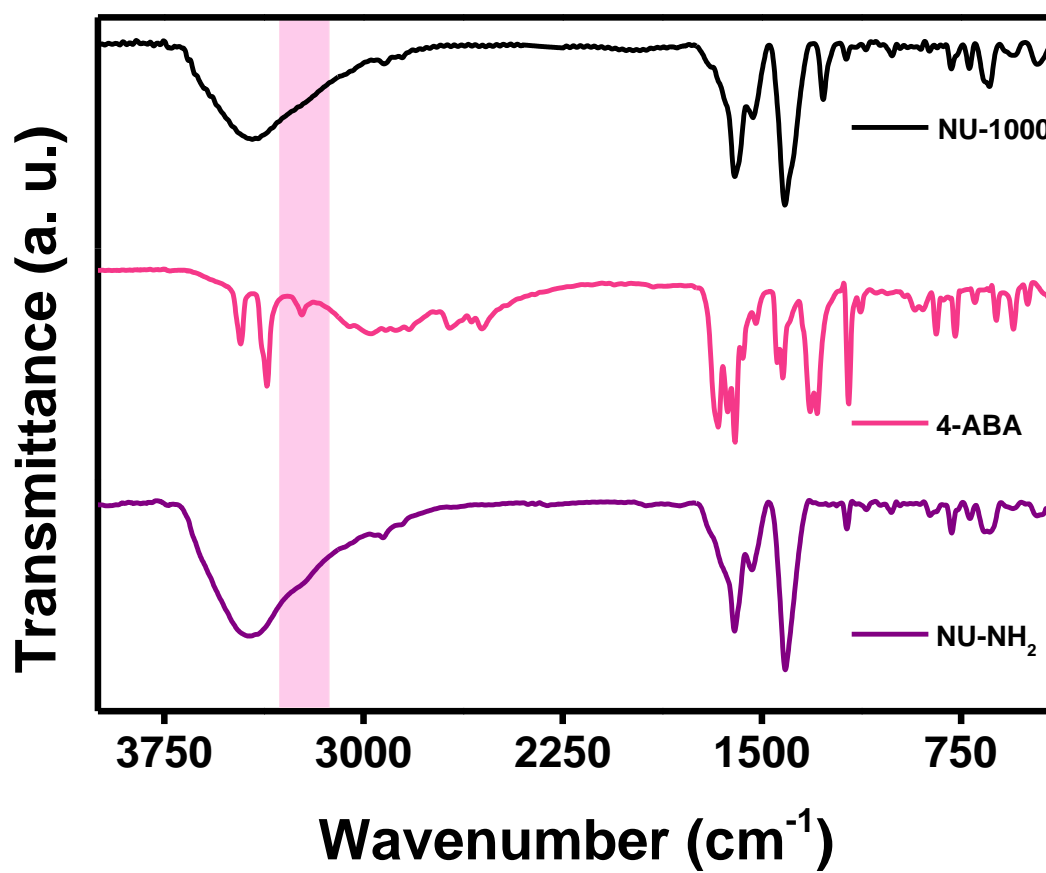


Figure S4. FT-IR spectra of NU-1000, ABA, and NU-1000-NH₂.

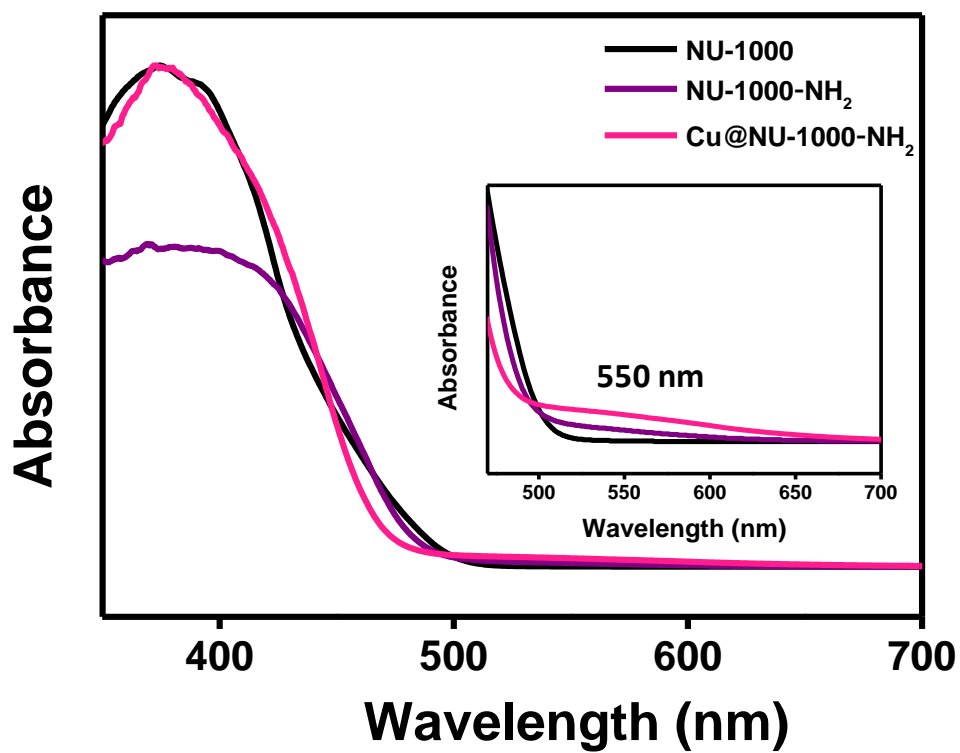


Figure S5. UV-Visible diffuse reflectance spectrum of NU-1000, NU-1000-NH₂, and Cu@NU-1000-NH₂.

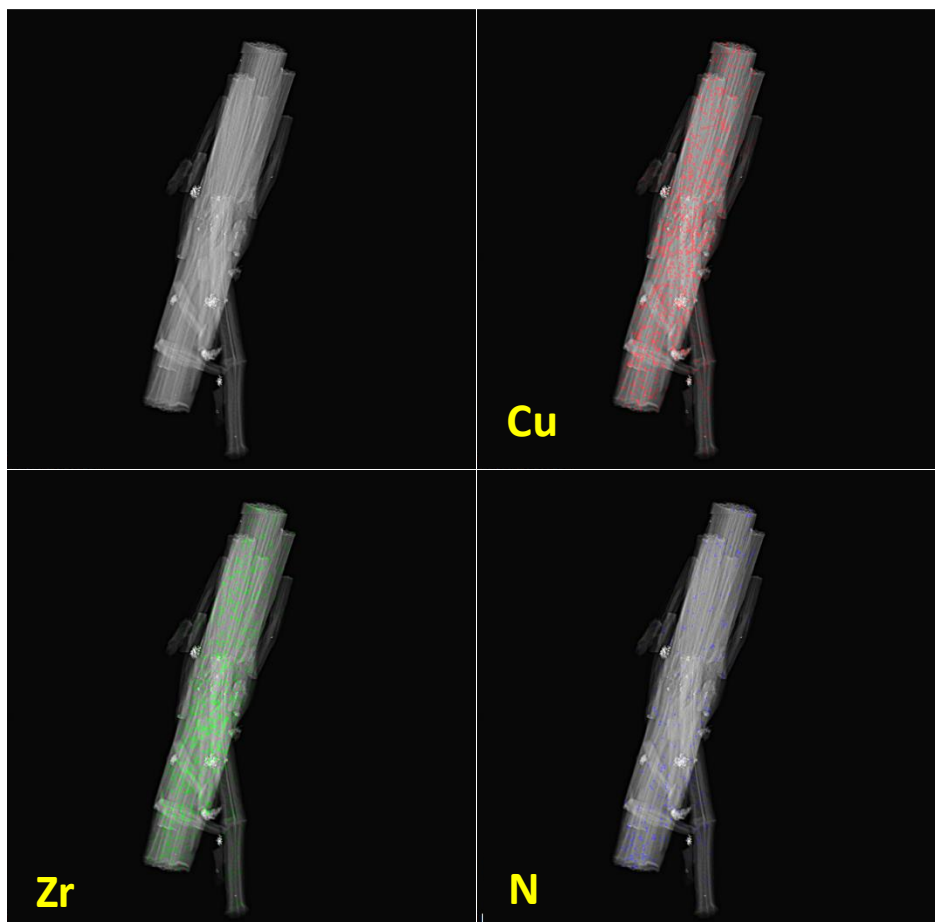


Figure S6. TEM-EDS elemental mapping images of Cu@NU-1000-NH₂.

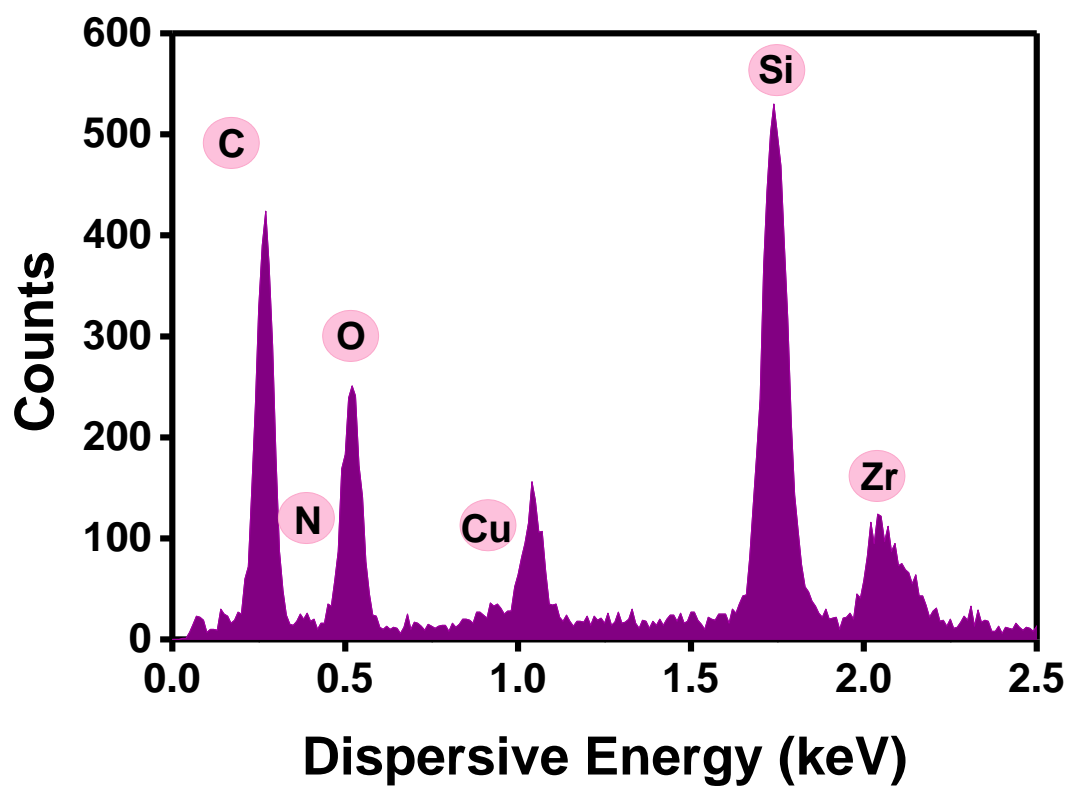


Figure S7. SEM-EDS spectrum of Cu@NU-1000-NH₂.

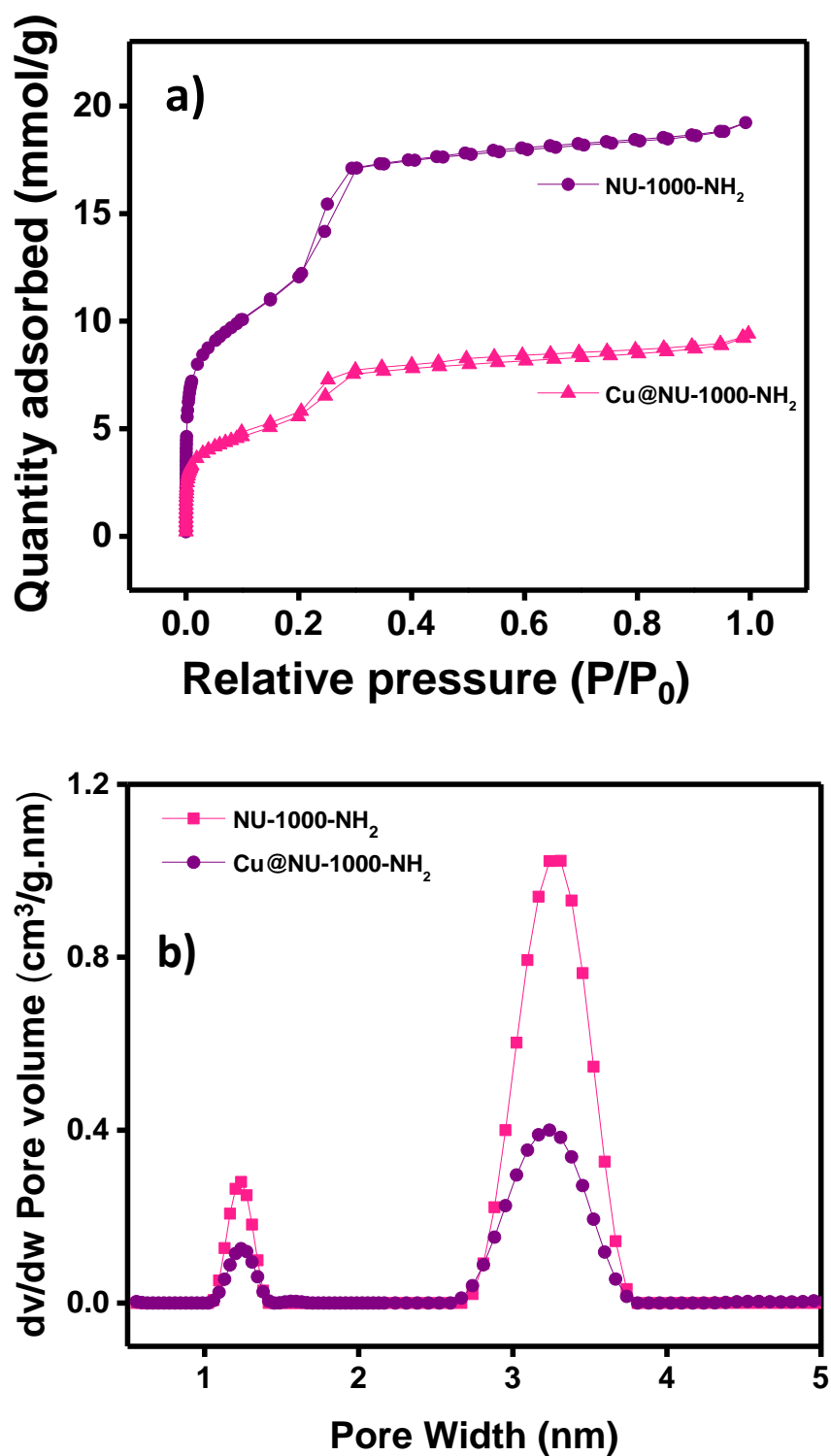


Figure S8. a) Nitrogen adsorption-desorption isotherms at 77 K. b) DFT pore size distribution plots of NU-1000-NH₂ and Cu@ NU-1000-NH₂.

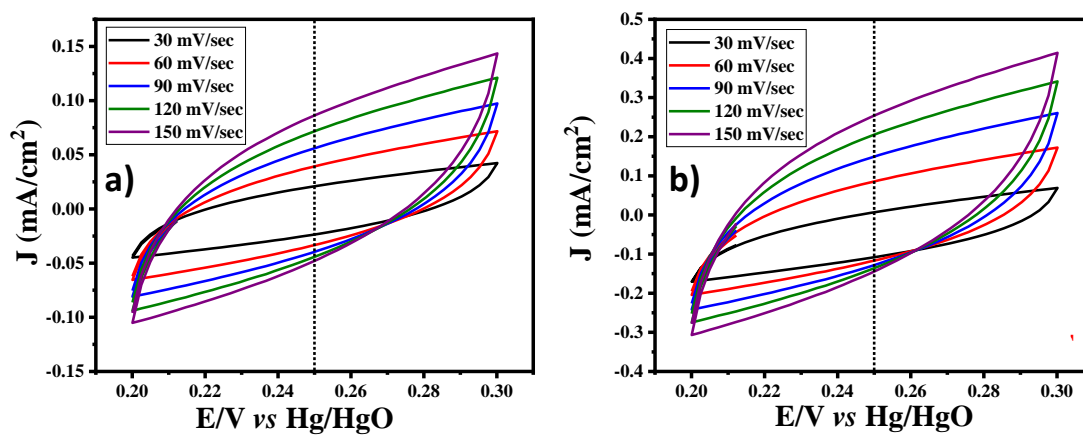


Figure S9. a) and b) C_{dl} curves of Cu@NU-1000- NH₂ and pristine NU-1000-NH₂ acquired at different scan rates in the non-Faradaic region, respectively.

Determination of TOF

The TOF value with respect to J_{geo} was calculated according to the following equation:

$$TOF = \left(\frac{\text{total hydrogen turnovers/cm}^2}{\text{number of active sites}} \right)$$

The number of total oxygen turnovers,

$$\text{Hydrogen turnover} = (j \text{ mA/cm}^2) \left(\frac{1 \text{ C/s}}{1000 \text{ mA}} \right) \left(\frac{1 \text{ mol } e^-}{96485.3 \text{ C}} \right) \left(\frac{1 \text{ mol}}{2 e^-} \right) \left(\frac{6.023 \times 10^{23} \text{ molecules of } H_2}{1 \text{ mol of } H_2} \right)$$

The number of total hydrogen turnovers was calculated from the current density extracted from the LSV polarization curve.

According to this, the number of total oxygen turnovers for 0.1 mg of catalyst loading would be

$$TON_{(\eta = 150 \text{ mV})} (\text{Cu@MOF}) = (9.25 \text{ mA/cm}^2) \left(\frac{1 \text{ C/s}}{1000 \text{ mA}} \right) \left(\frac{1 \text{ mol } e^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol}}{2 e^-} \right) \left(\frac{6.023 \times 10^{23} \text{ molecules of } H_2}{1 \text{ mol of } H_2} \right) = 2.88 \times 10^{16}$$

$$TON_{(\eta = 300 \text{ mV})} (\text{Cu@MOF}) = (35.9 \text{ mA/cm}^2) \left(\frac{1 \text{ C/s}}{1000 \text{ mA}} \right) \left(\frac{1 \text{ mol } e^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol}}{2 e^-} \right) \left(\frac{6.023 \times 10^{23} \text{ molecules of } H_2}{1 \text{ mol of } H_2} \right) = 11.17 \times 10^{16}$$

$$TON_{(\eta = 450 \text{ mV})} (\text{Cu@MOF}) = (126.4 \text{ mA/cm}^2) \left(\frac{1 \text{ C/s}}{1000 \text{ mA}} \right) \left(\frac{1 \text{ mol } e^-}{96485 \text{ C}} \right) \left(\frac{1 \text{ mol}}{2 e^-} \right) \left(\frac{6.023 \times 10^{23} \text{ molecules of } H_2}{1 \text{ mol of } H_2} \right) = 39.39 \times 10^{16}$$

Using the number of total hydrogen turnovers, active site density, and electrochemically active surface area; we converted the current density from the LSV polarization curve into TOF, as:

$$TOF = \left(\frac{\text{total hydrogen turnovers/cm}^2}{\text{active sites}} \right)$$

$$TOF (\text{Cu@MOF}) = \left(\frac{\text{total hydrogen turnovers/cm}^2}{\text{number of active sites}} \right) = \left(\frac{2.88 \times 10^{16}}{2.52 \times 10^{17} \times 0.058} \right) = 1.97 \text{ sec}^{-1} (150 \text{ mV})$$

$$TOF (\text{Cu@MOF}) = \left(\frac{\text{total hydrogen turnovers/cm}^2}{\text{number of active sites}} \right) = \left(\frac{11.17 \times 10^{16}}{2.52 \times 10^{17} \times 0.058} \right) = 7.64 \text{ sec}^{-1} (300 \text{ mV})$$

$$TOF (\text{Cu@MOF}) = \left(\frac{\text{total hydrogen turnovers/cm}^2}{\text{number of active sites}} \right) = \left(\frac{39.39 \times 10^{16}}{2.52 \times 10^{17} \times 0.058} \right) = 26.94 \text{ sec}^{-1} (450 \text{ mV})$$

From the ICP-OES data:

10^6 μL of solution contains 12.13 mg of Cu

1 μL solution contains = $12.13/10^6$ mg of Cu

34.5 μL solution contains = $12.13*34.5/10^6$ mg of Cu = 0.000418 mg = 0.000000418 gm of Cu

63 gm Cu contain 6.023×10^{23} number of Cu

$0.000000418 = (6.023 \times 10^{23} * 0.000000418) / 63 = 2.52 \times 10^{17}$

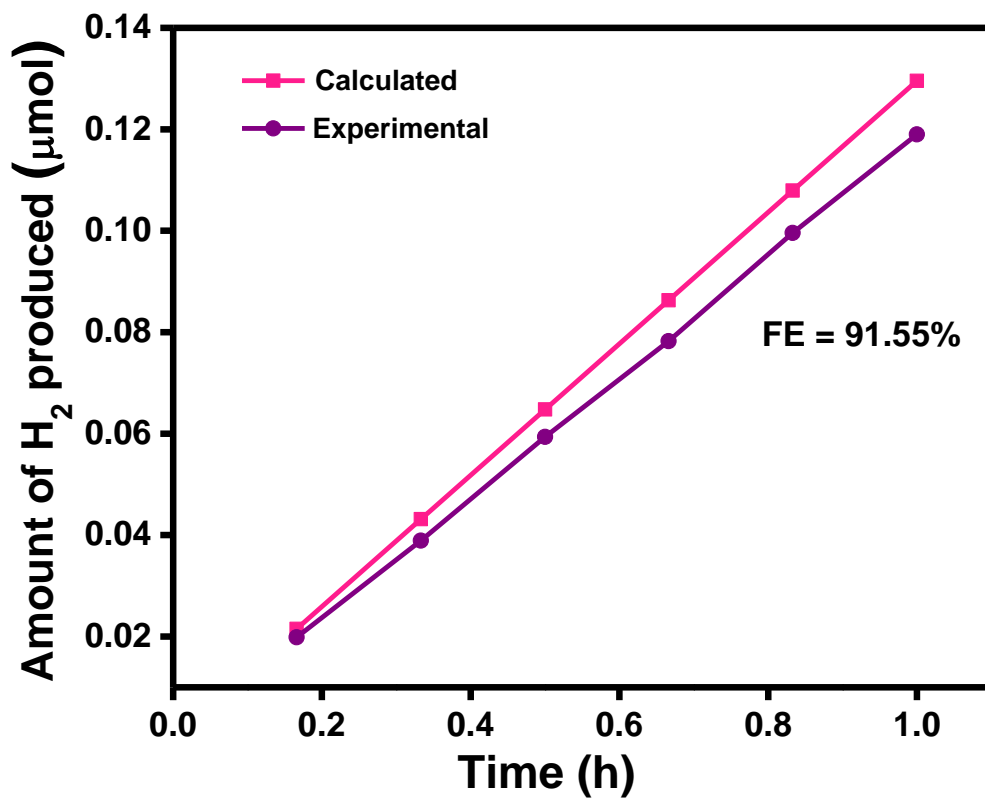


Figure S10. Amount of gas produced experimentally by applying constant potential.

Table S1. Comparative HER data for Cu-based catalysts.

No.	Catalysts	Electrolyte	Over potential (mV) @ 10 mAcm ⁻²	Stability	References
1	Cu(0)-PEDA/SiO ₂	0.5 M H ₂ SO ₄	200	2 h	5
2	CuNP/CNFs	0.5 M H ₂ SO ₄	580	10 h	6
3	Cu _{2-x} Te/hyd	0.5 M H ₂ SO ₄	347	12 h	7
4	Cu(poly)-polished	1 M KOH	320 (5 mA cm ⁻²)	--	8
5	MCNTs@Cu@MoS ₂	1 M H ₂ SO ₄	225 mV	--	9
6	Cu@CoFe	1 M KOH	171	24 h	10
7	NP-1	18 M H ₂ SO ₄	450	2000 cycles	11
8	NC-1	18 M H ₂ SO ₄	760	2000 cycles	11
9	Cu/Cu ₂ O	0.5 M PBS	217	8 h	12
10	Cu-BTC	0.5 M H ₂ SO ₄	270	12 h	13
11	Cu-MOF/ CeO ₂	1M NaOH	145.9	1000 cycles	14
12	HKUST-1 electrodeposited	0.5M H ₂ SO ₄	590	12	15
13	HKUST-1 hydrothermal	0.5M H ₂ SO ₄	660	11	15
14	Cu@NU-1000-NH₂	0.5 M H₂SO₄	158	45 h	This wok

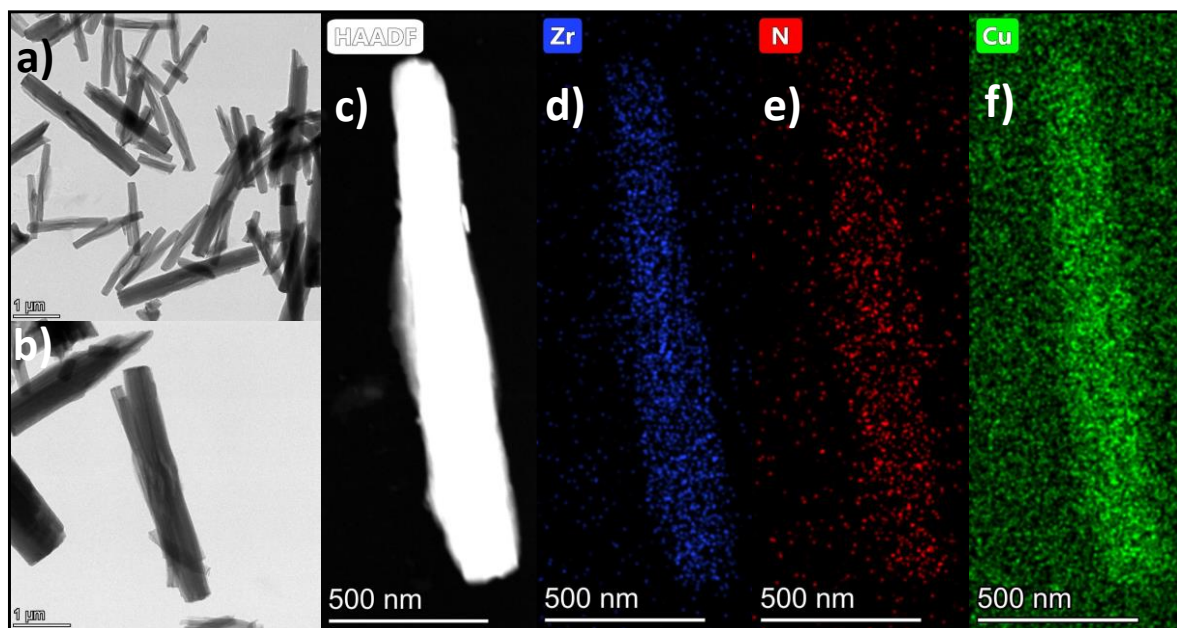


Figure S11. a) and b) HR-TEM images of Cu@NU-1000-NH₂ after catalysis, c-f) elemental analysis using TEM-EDS.

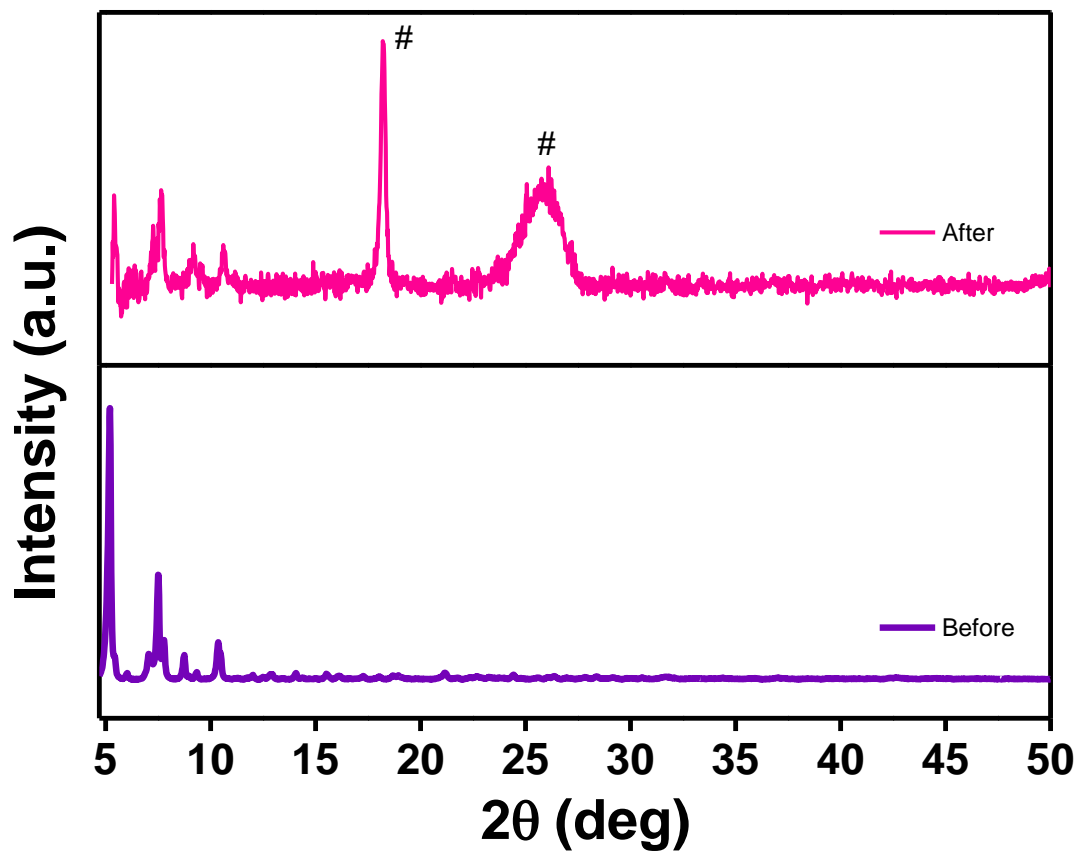


Figure S12. PXRD plot of Cu@NU-1000-NH₂ after catalysis. (The peaks marked in hash (#) come from carbon cloth).¹⁶

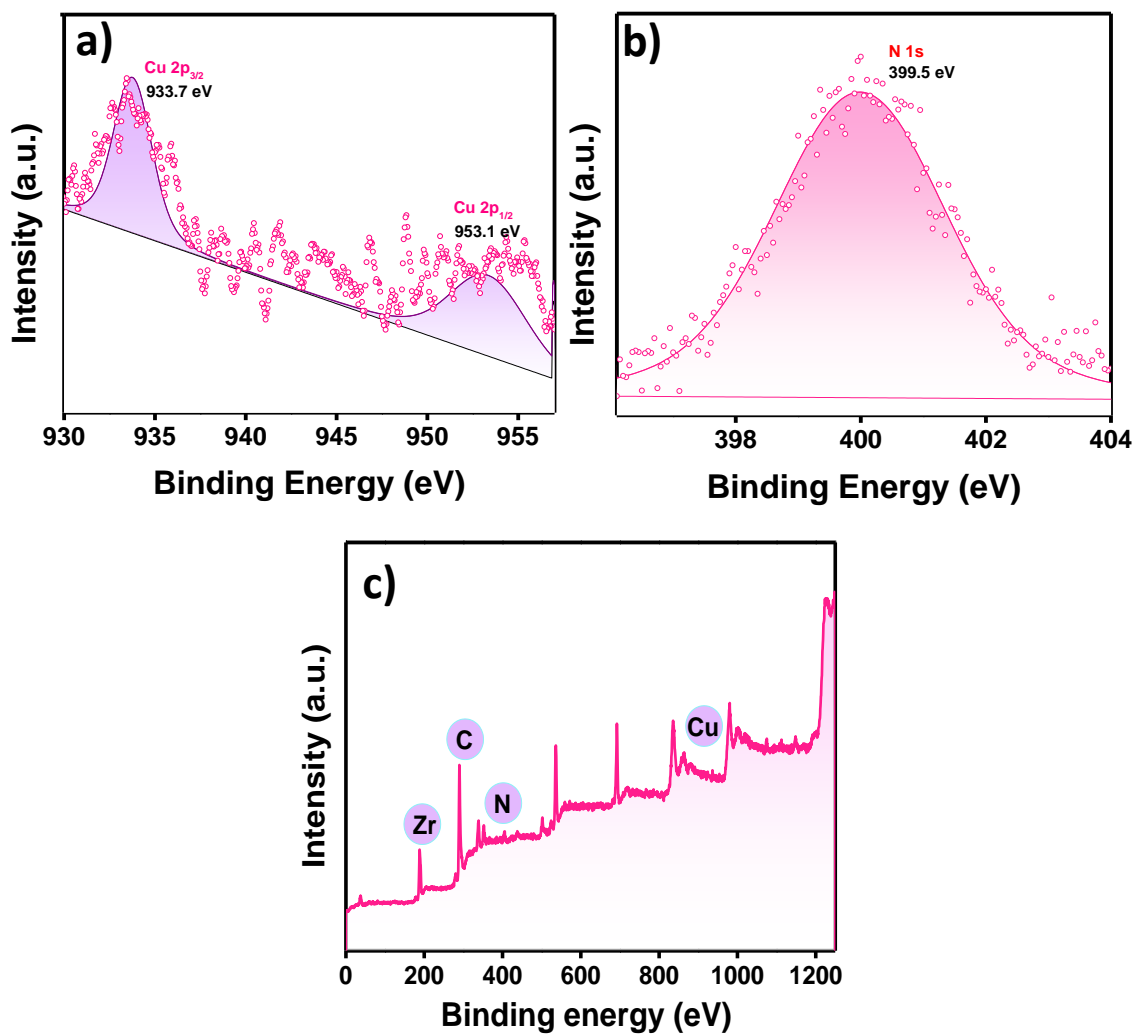


Figure S13. High-resolution XPS spectra a) Cu 2p, b) N 1s of Cu@NU-1000-NH₂ after catalysis.

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