Supporting Information

Fabrication of Cu nanoparticles@MOF via partial pyrolysis of hybrid dual-MOFs for high-efficiency electrocatalytic nitrate reduction

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Synthesis of etched samples of the HKUST-1/ZIF-8

200 mg of HKUST-1/ZIF-8 and 0.5 mL of HAc were added to 5 mL of methanol and stirred at room temperature for 30 min. The product was collected by centrifugation, washed with methanol several times, and dried at 80 °C overnight. It was

labeled as HKUST-1/ZIF-8-A, where A stands for acetic acid. 200 mg of HKUST-1/ZIF-8 and $NH_3 \cdot H_2O$ (0.5 mL) were added to 5 mL of methanol and stirred at room temperature for 30 minutes. The product was collected by centrifugation, washed with methanol several times, and dried at 80 ^oC overnight, denoted as HKUST-1/ZIF-8-B, where B stands for ammonia water.

Preparation of working electrode

The purchased PTFE-coated glassy carbon electrode with a diameter of 6 mm was used as the working electrode. 5 mg Cu@C/ZIF-8 was dispersed at 490 μL Deionized water and 490 μL in isopropyl alcohol, then 20 μL Nafion solution was added, followed by sonicating for 30 min. The above ink was dropped onto the pre-cleaned glassy carbon electrode and dried. The preparation methods of Cu NPs and ZIF-8-350 working electrodes were the same except for different samples.

Electrochemical measurements

The Nafion membrane was first boiled in water at 80 °C for 1 h, next in H_2O_2 and water at 80 °C for 1 h respectively, then 0.5 M H_2SO_4 for 3 h, and finally in water for 6 h before NO_3^-RR test. The electrochemical test was performed on the CHI660 electrochemical workstation with a three-electrode configuration, the glassy carbonelectrode was used as the working electrode, Ag/AgCl with saturated KCl was the reference electrode, and platinum mesh was the counter electrode. All testedpotentials were 95% IR compensation. The potentials were converted to RHE by the following formula: E (vs. RHE) = E (vs. Ag/AgCl) $^+$ 0.197 $^+$ 0.0591 × pH. Linear sweep voltammetry (LSV) testing was examined at ambient temperature with a scan

rate of 5 mV s^{-1}. The electrolyte used in the electrochemical test was 0.1 M KNO_3 and 0.1M $NaSO_4$.

Electrochemical active surface areas (ECSAs) measurements

Electrochemical active surface areas (ECSAs) were measured in the non-Faradaic region from −0.66 V to −0.56 V by cyclic voltammetry (CV) with different scanning rates (5~50 mV s^{-1}) in 0.1 M NaSO4 with 0.1 M KNO_3. Double-layer capacitances (Cdl) can be easily obtained by plotting the current density as a function of scan rate in CV curves. And the Cdl value is proportional to ECSA, meaning a higher Cdl represents a larger ECSA for these studied catalysts.

Determination of ammonia by UV-vis method

The concentration of NH_3 produced was determined by indophenol blue spectrophotometry. In detail, 2 mL aliquot of the solution was taken out of the cathode chamber of the H-type electrolytic cell. Then, add 2 mL of 1.0 M NaOH solution containing 5 wt.% salicylic acid and 5 wt.% sodium citrate, followed by the addition of 1 mL of 0.05 M NaClO and 0.2 mL of an aqueous solution of 1 wt.% $Na_2[Fe(NO)(CN)_5]$ $2H_2O$. After 2 h at room temperature, the UV-vis absorption spectrum was tested using a UV-2600i ultraviolet-visible spectrophotometer. The absorbance at a wavelength of 655 nm was used to determine the formation of indoxyl blue. Using standard NH_4Cl solutions with a range of concentrations to calibrate the concentration-absorbance curve

Determination of hydrazine

A mixture of p-(dimethylamino)benzalde hyde (5.99 g), 1.0 M HCl (30 mL) and ethanol (300 mL) was used as a color reagent. 5mL of electrolyte solution was extracted from the electrolytic cell, and then 5mL of color reagent was added and mixed uniformly. After the mixture solution was let stand for 10 min, the absorption intensity at a wavelength of 456 nm was recorded.

Determination of nitrite

A mixture of p-aminobenzenesulfonamide (4g), N-(1-Naphthyl) ethylenediamine dihydrochloride (0.2 g), ultrapure water (100 mL) and phosphoric acid (10 mL, ρ=1.70 g/mL) was used as a color reagent. 1.0 mL of the electrolyte was removed from the electrolytic cell and diluted to 5 mL to the detection range. Next, 0.1 mL of the color reagent was added into the aforementioned 5 mL solution and mixed uniformly. After the mixture solution was let stand for 20 min, the absorption intensity at a wavelength of 540 nm was recorded. The concentration-absorbance curve was calibrated using a series of standard sodium nitrite solutions.

Calculation of the yield rate, and Faradaic efficiency

The yield rate of electrocatalytic NO3−-NH3 was defined according to Eq. (1):

$$\gamma_{NH_3} = (C_{NH_3} \times V) \div (t \times m_{cat.}) \quad (1)$$

The content of the by-product NO_2^- is calculated similarly, except that CNH_3 is replaced by C. The Faradaic efficiency of the electrocatalytic $NO_3^- - NH_3$ was defined from the electric charge consumed for synthesizing ammonia and total charge passed through the electrode according to Eq. (2):

$$FE_{NH_3} = (8 \times F \times C\mathrm{NH3} \times V)/(17 \times Q) \quad (2)$$

The Faradaic efficiency of electrocatalytic NO_3^-–NO_2^- was defined from the electric charge consumed for synthesizing ammonia and total charge passed throughthe electrode according to Eq. (3):

$$FE_{NO2^-} = (2 \times F \times CNO_2^- \times V)/(46 \times Q) \quad (3)$$

where CNH_3 is the concentration of NH3(aq), V is the volume of electrolyte in the cathode compartment (70 mL), t is the electrolysis time (2 h), C is the generated concentration of ammonia or nitrite, F is the Faradaic constant (96485 C mol^{-1}), Q is the total charge passing the electrode, and mcat. is the loading mass of catalysts.

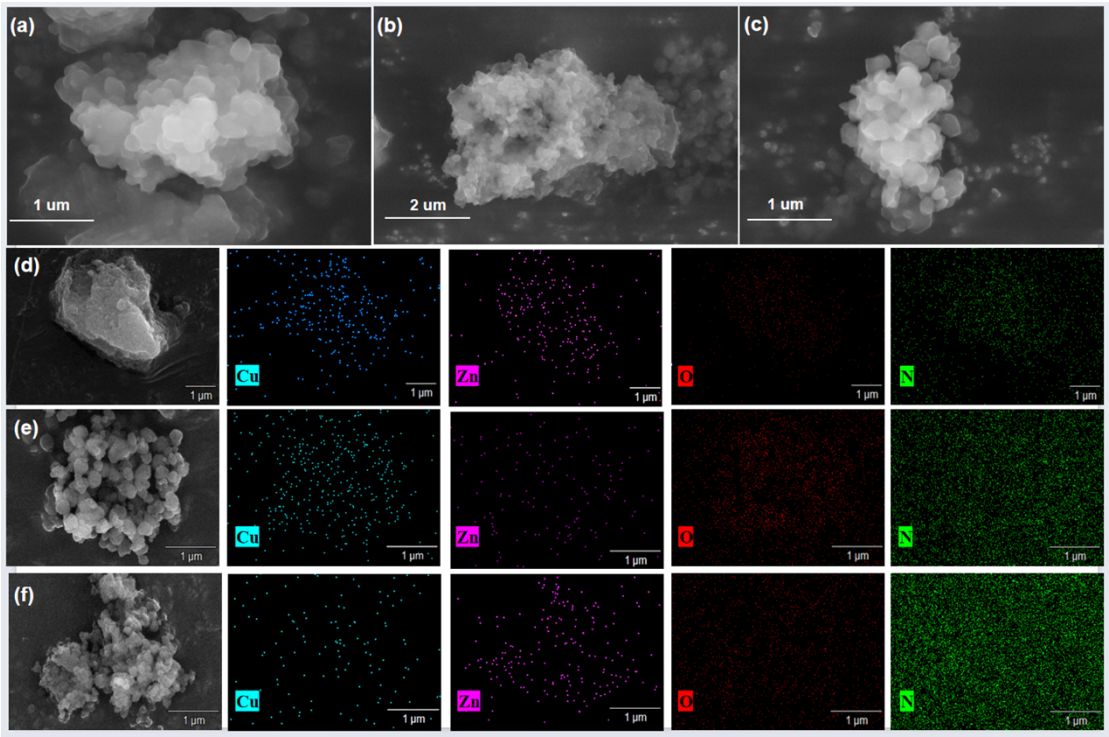

Fig. S1. SEM images of (a) HKUST-1/ZIF-8, (b) HKUST-1/ZIF-8-A and (c) HKUST-1/ZIF-8-B; EDS elemental mapping images of (d) HKUST-1/ZIF-8, (e) HKUST-1/ZIF-8-A and (f) HKUST-1/ZIF-8-B.

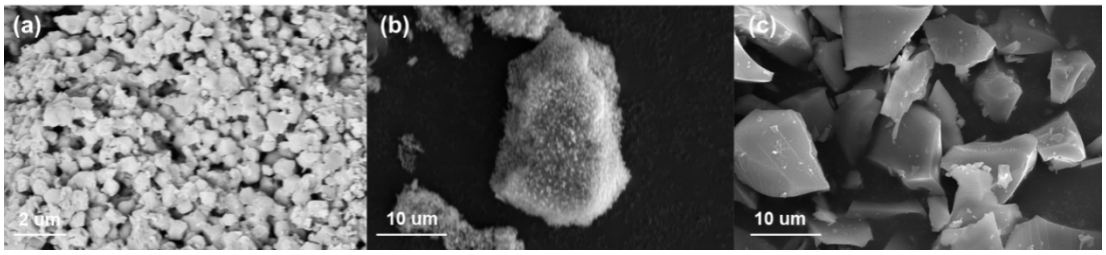

Fig. S2. SEM images of (a) ZIF-8-350, (b) Cu NPs, (c) Cu@C/ZIF-8.

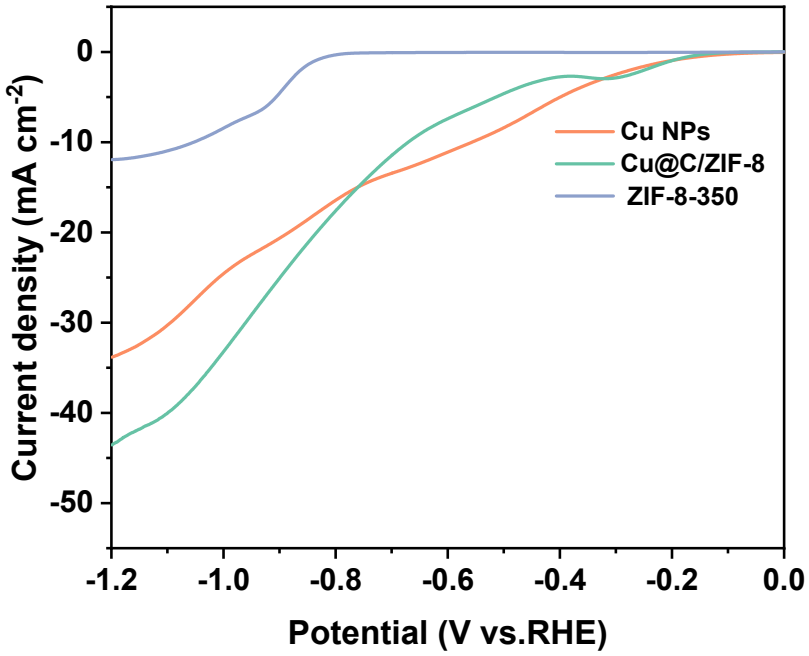

Fig. S3. LSV curves of different catalysts.

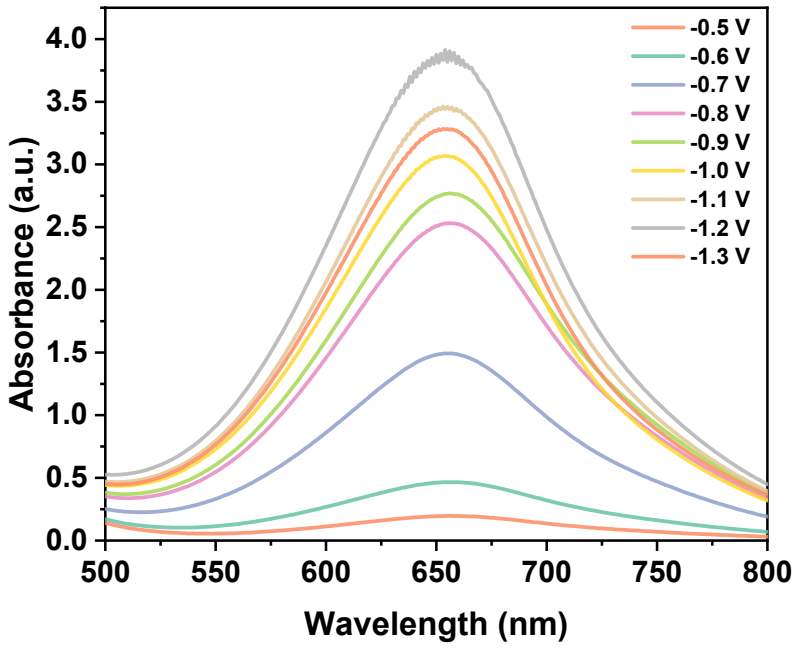

Fig. S4. UV-visible absorption spectra of Cu@C/ZIF-8 at different potentials.

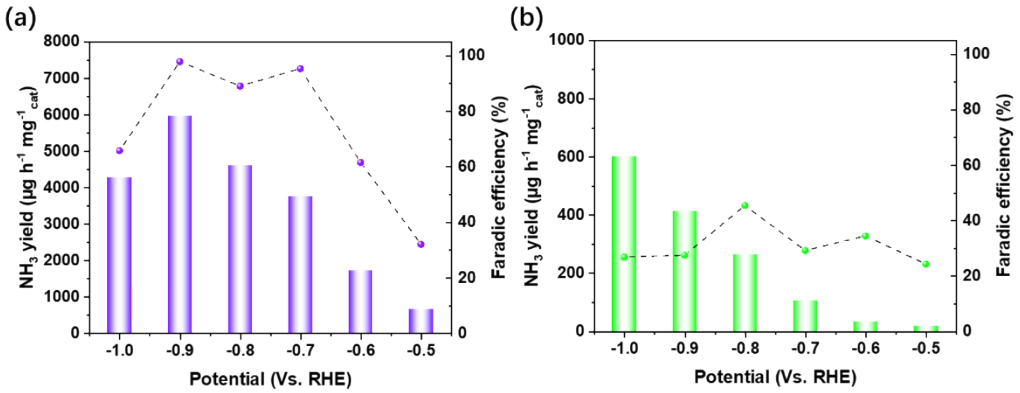

Fig. S5. (a) Ammonium yield and Faraday efficiency of Cu NPs and (b) ZIF-8-350 at different potentials.

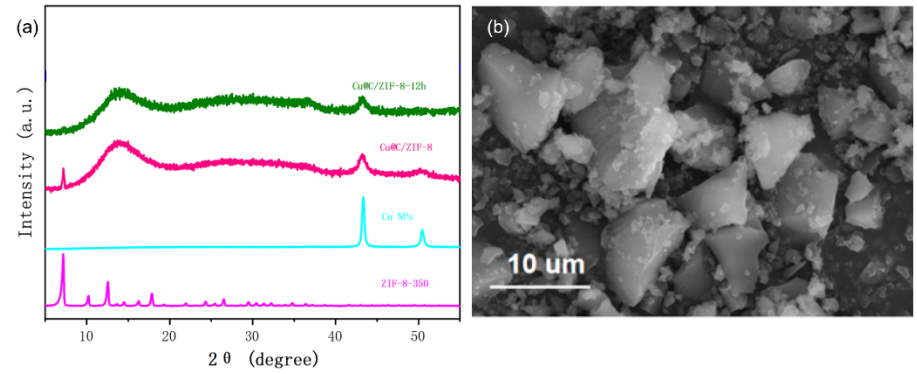

Fig. S6. (a) XRD and (b) SEM patterns of Cu@C/ZIF-8 after 12 h electrolysis.

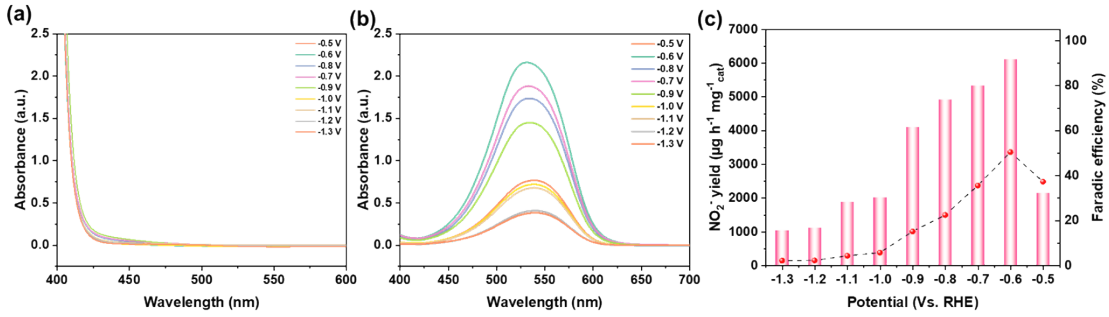

Fig. S7. Determination of Cu@C/ZIF-8 byproducts: (a) UV-vis absorption spectra of N_2H_4 and (b) NO_2^-; (c) NO_2^- yield and Faraday efficiency at -0.5V ~ -1.3 V *vs.* RHE.

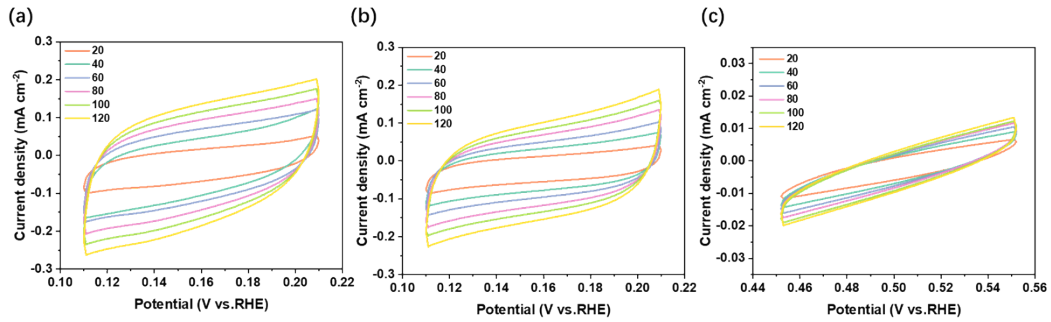

Fig. S8. Double layer capacitance for different catalysts: (a) CV diagram of Cu@C/ZIF-8, (b) Cu NPs and (c) ZIF-8-350.

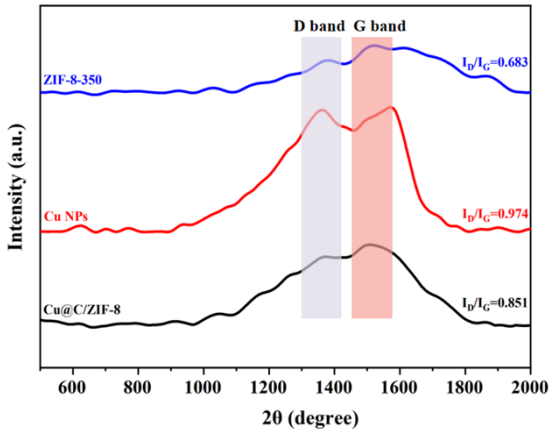

Fig. S9. Raman spectra of ZIF-8-350, Cu NPs and Cu@C/ZIF-8.

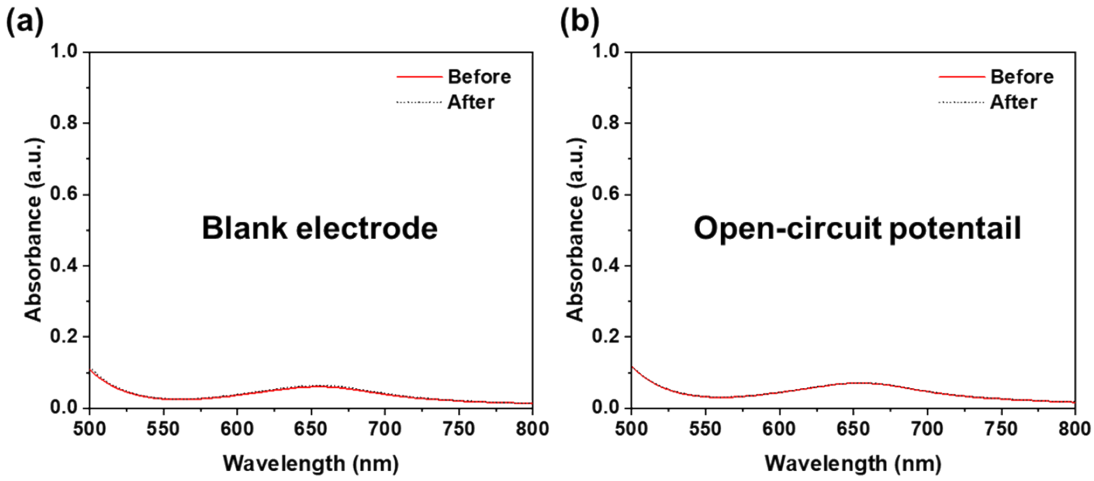

Fig. S10. UV-vis absorption spectra of (a) blank electrode and (b) reaction at open-circuit potential before and after reaction for 2 h.