

Supporting Information

Active Hydrogen Tuning by Copper-Cobalt Bimetal Catalysts for Boosting Ammonia Electrosynthesis from Simulated Waster Water

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Experimental section

1.1 Chemicals and materials

Copper (II) nitrate hexahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Macklin, 98%) and potassium hydroxide (KOH, Macklin, 95%), Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aladdin Ltd, 99%), 1,3,5-tricarboxylate (H_3BTC , Aladdin Ltd, 98%), N, N-Dimethylformamide (DMF, Aladdin Ltd, 99.5%), Potassium nitrate (KNO_3 , Aladdin Ltd, 99%), Deuterium oxide (D_2O , Aladdin Ltd), Potassium nitrate (K^{15}NO_3 , Shanghai Nature Sci Co), Hydrochloric acid (HCl, Aladdin Ltd, 37%). Nafion 117 membranes were obtained from DuPont. All the reagents were used without further purification. Deionized water was used for all experiments.

1.2 Catalyst synthesis

A modified MOF-template (CuCo-BTC, BTC = benzene-1,3,5-tricarboxylate) method is used to prepare CuCo catalysts with different Cu: Co molar ratios.

Synthesis of $\text{Cu}_5\text{Co}_5\text{-BTC}$ Firstly, 1.208 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (5 mmol), 1.455 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5 mmol) and 1.40 g H_3BTC are sealed into a 100 mL Teflon-lined hydrothermal synthesis autoclave and heated to 140 °C for 24 h with 40 mL DMF and 10 mL ethanol. After cooling the autoclave, the precipitate is filtered and washed with deionized water and ethanol several times to remove impurities and excess DMF. Then, the powder is dried at 60 °C in a vacuum oven overnight. Similarly, the different molar ratios of CuCo-BTC were prepared following the above steps, only changing the molar ratio of Cu: Co (9:1, 7:3, 3:7, 1:9).

Synthesis of Cu-BTC and Co-BTC Only 2.4016 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (10mmol) or 2.9103 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are used for Cu-BTC or Co-BTC.

Synthesis of various $\text{Cu}_x\text{-Co}_y$ nanocomposites The $\text{Cu}_5\text{Co}_5\text{-BTC}$ are grounded into powder and calcinated at 400 °C under H_2/Ar stream for 2 h to finally obtain $\text{Cu}_5\text{-Co}_5$ catalyst. In addition, other control samples (pure Cu, $\text{Cu}_9\text{-Co}_1$, $\text{Cu}_7\text{-Co}_3$, $\text{Cu}_3\text{-Co}_7$, $\text{Cu}_1\text{-Co}_9$ and pure Co) are prepared by calcinating according to CuCo-BTC precursors.

Synthesis of Cu_5Co_5 alloy The Cu_5Co_5 alloy is synthesized through a NaBH_4 reduction and calcination method.³⁴ Firstly, 1.208 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (5 mmol) and 1.455 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5 mmol) are ultrasonically dispersed in 70 mL ethylene glycol. Then, 0.25 M NaBH_4 (30mL) is slowly added to the solution. After stirring for 1 hour, the precipitate is filtered with deionized water and ethanol several times. The powder is dried at 60 °C in a vacuum oven overnight and then

calcinated at 400 °C under H₂/Ar stream for 2 h to finally obtain Cu₅Co₅ alloy.

1.3. Electrochemical measurements

NO₃RR experiments were carried out in a H-type cell separated by a Nafion 117 membrane using an electrochemical workstation (CHI 760E). The Nafion 117 membrane was first pretreated with the H₂O₂ aqueous solution, the deionized water and the H₂SO₄ aqueous solution at 80 °C for an hour. The cathode (i.e. the working electrode) was fabricated by spray-coating a catalyst ink (10 mg of catalyst powders and 40 μL of Nafion binder uniformly dispersed in 960 μL of ethanol) on a carbon paper (CP, TGP-H-060). The mass loading of the catalyst on CP was 1 mg cm⁻². The reference electrode is Ag/AgCl and platinum foil is the counter electrode. 30 mL mixed 1.0 M KOH with 0.1 M KNO₃ solution was the catholyte and 30 mL pure 1.0 M KOH solution was anolyte. Ar gas (10 sccm) is continuously pumped into the cathode chamber during the reaction to eliminate the interference of impurity gases and detect the generated gases. All potentials were calibrated to the reversible hydrogen electrode (RHE) reference by $E(\text{RHE}) = E(\text{V vs. Ag/AgCl}) + 0.197 + 0.0591 \times \text{pH}$ (pH = 14).

NO₃RR experiments were carried out in a flow cell separated by a Nafion 117 membrane in an electrochemical workstation (Autolab PGSTAT204). The cathode (i.e. the working electrode) was fabricated by spray-coating a catalyst ink (5 mg of catalyst powders and 20 μL of Nafion binder uniformly dispersed in 480 μL of ethanol) on a carbon paper (Sigracet 39BB). The mass loading of the catalyst on CP is 1 mg cm⁻².

All LSV curves were performed with a scanning rate of 10 mV s⁻¹ from 0.5 V to -1.0 V vs. RHE. Chronoamperometry tests were carried out at different given potentials under continuous stirring (500 rpm). After the reaction for 1 hour, the obtained cathodic electrolyte solution was collected for the following detection of different liquid products. Fresh electrolyte solutions were always used for each run. All the electrolytes were stored in the fridge before the detection. Cyclic voltammetry (CV) was managed at different scan rates to test electrochemical double-layer capacitance (C_{dl}). EIS tests were performed in the range of 100000 Hz ~ 0.1 Hz. Tafel slopes were determined according to the Tafel plots. ¹⁵N isotopic labeling experiments were used to determine the N source of the detected NH₄⁺ through ¹H NMR spectroscopy. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used to capture the instable hydrogen radical to form the DMPO-H adduct to generate EPR spectra. In EPR experiments, 3 ml electrolyte was mixed with 100 μL DMPO. The constant current electrolysis

was carried out for 10 min in the H-type cell under -0.6 V. EPR measurement was performed by 100G-18KG/EMX-8/2.7 spectrometer operating at a frequency near 9.5 GHz, sweep width of 200 G and power of 20 mW.

2. Characterizations

The structures of the catalysts were observed by SEM (SU-8020) and TEM (FEI F30) equipped with energy-dispersive X-ray spectroscopy. The valence states of elements on the surface of catalysts were verified by XPS (ESCALAB 250Xi) and taking C 1s of 284.8 eV as the internal reference. X-ray powder diffraction (XRD) for powder analysis was carried out with an Ultima IV utilizing Cu K α radiation ($\lambda = 1.54178$ Å). Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on Agilent 720ES. The ultraviolet-visible (UV-Vis) absorbance spectra were measured on a UV-2600 spectrometer. The isotope labeling experiments were measured by ^1H NMR measurement (Bruker 600-MHz system). Operando attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) was performed on an iZ10 FT-IR spectrometer. The Si single crystal was used as the substrate for the working electrode to ensure we could get enough IR signals. Operando Raman spectra are measured by Invia Reflex confocal microscope using a 785 nm laser source.

3 Determination of products

The ultraviolet-visible (UV-Vis) spectrophotometer was used to detect the ion concentration of pre- and post-test electrolytes after diluting to appropriate concentrations to match the range of calibration curves. The specific detection methods are as follows.

Determination of NH_3 The amount of NH_3 in the solution was determined by colorimetry using the indophenol blue method. The three reagents required for the indophenol blue method are in the following.

Solution A: 100 mL 1 M NaOH solution containing 5 g potassium sodium tartrate-salicylic acid.

Solution B: 100 mL 0.05 M NaClO_4 .

Solution C: 100 mL nitroferricyanide solution (1 wt%).

Then, 2 mL solution A, 1 mL solution B and 0.2 mL solution C are mixed uniformly with a certain amount of diluted electrolyte and then stand for 2 h in lightproof conditions. The absorption intensity at a wavelength of 655 nm is recorded. The concentration-absorbance curve is calibrated through a series of standard NH_4Cl solutions.

Determination of NO_2^- The color reagent is as follows, 50 mL ultrapure water contains 4 g p-aminobenzenesulfonamide, 0.2 g N-(1-Naphthyl) ethylenediamine dihydrochloride and 10 mL phosphoric acid. Then, 0.2 mL color reagent is mixed with a certain amount of diluted electrolyte and then stand for 20 min in lightproof conditions. The absorption intensity at a wavelength of 540 nm is recorded. The concentration-absorbance curve is calibrated through a series of standard KNO_3 solutions.

Determination of N_2H_4 The color reagent is as follows, 25 mL ethanol and 2 mL concentration of concentrated HCl are mixed with 0.5 g pdimethylaminobenzaldehyde. Then, the 0.5 mL color reagent are mixed with a certain amount of diluted electrolyte and stands for 10 min in lightproof conditions. The absorption intensity at a wavelength of 460 nm is recorded. The concentration-absorbance curve is calibrated through a series of standard N_2H_4 solutions.

4. Calculation of the FE and yield rate

$$\text{FE}(\text{NH}_3) = (8F \times c_{\text{NH}_3} \times V) / (M_{\text{NH}_3} \times Q) \quad (1)$$

$$\text{Yield}(\text{NH}_3) = (c_{\text{NH}_3} \times V) / (M_{\text{NH}_3} \times t \times S) \quad (2)$$

where c_{NH_3} is the mass concentration of NH_3 in the electrolyte, V is the volume of electrolyte in the cathode compartment (30 mL), M_{NH_3} is the molar mass of NH_3 , t is the electrolysis time (3600 s), S is the geometric area of working electrode (1 cm^2), F is the Faradaic constant (96485 C mol^{-1}), Q is the total charge passing the electrode.

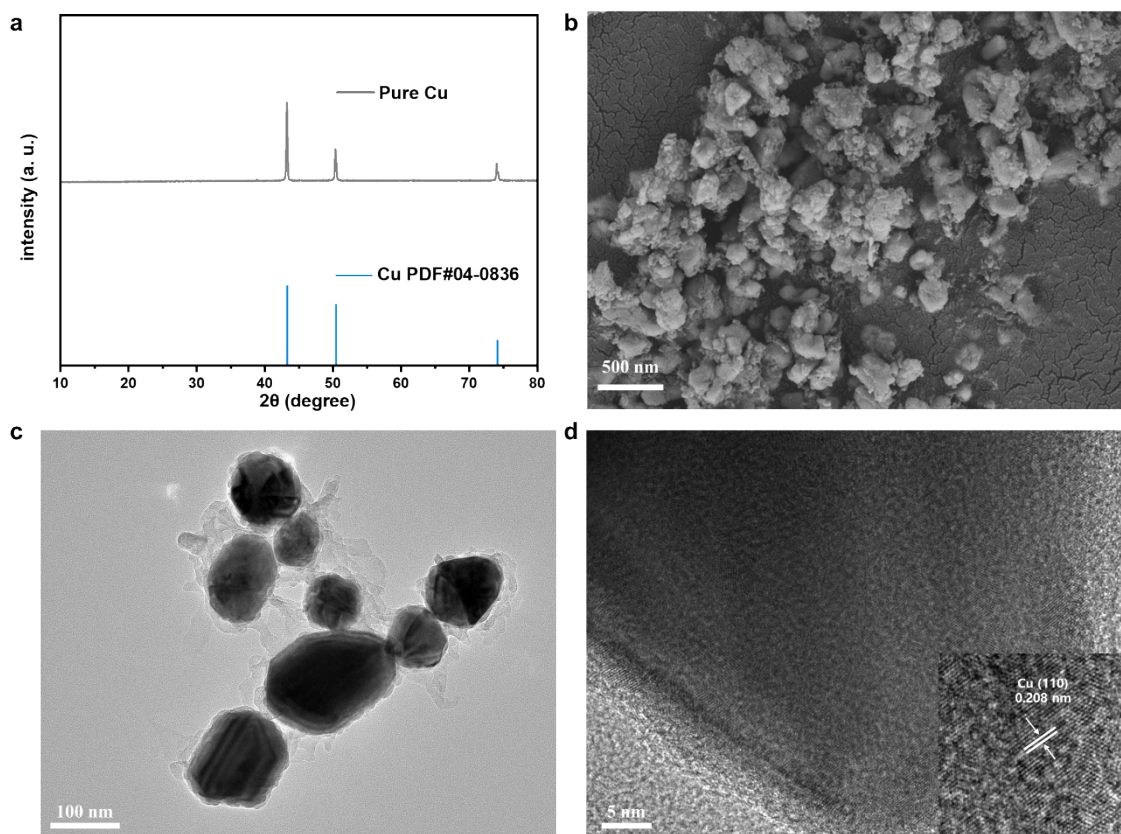


Fig. S1 Characterization of the pure Cu catalyst. (a) XRD patterns. (b) SEM image. (c) TEM image. (d) HRTEM image.

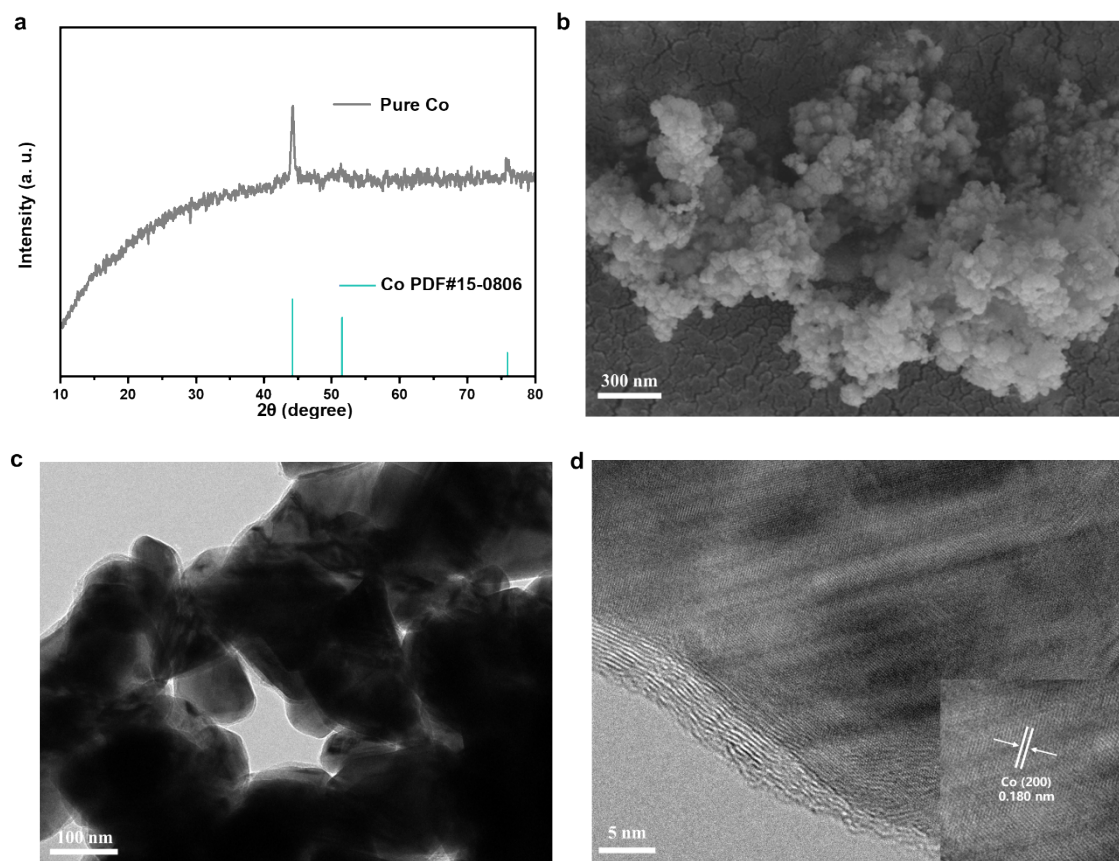


Fig. S2 Characterization of the pure Co catalyst. (a) XRD patterns. (b) SEM image. (c) TEM image. (d) HRTEM image.

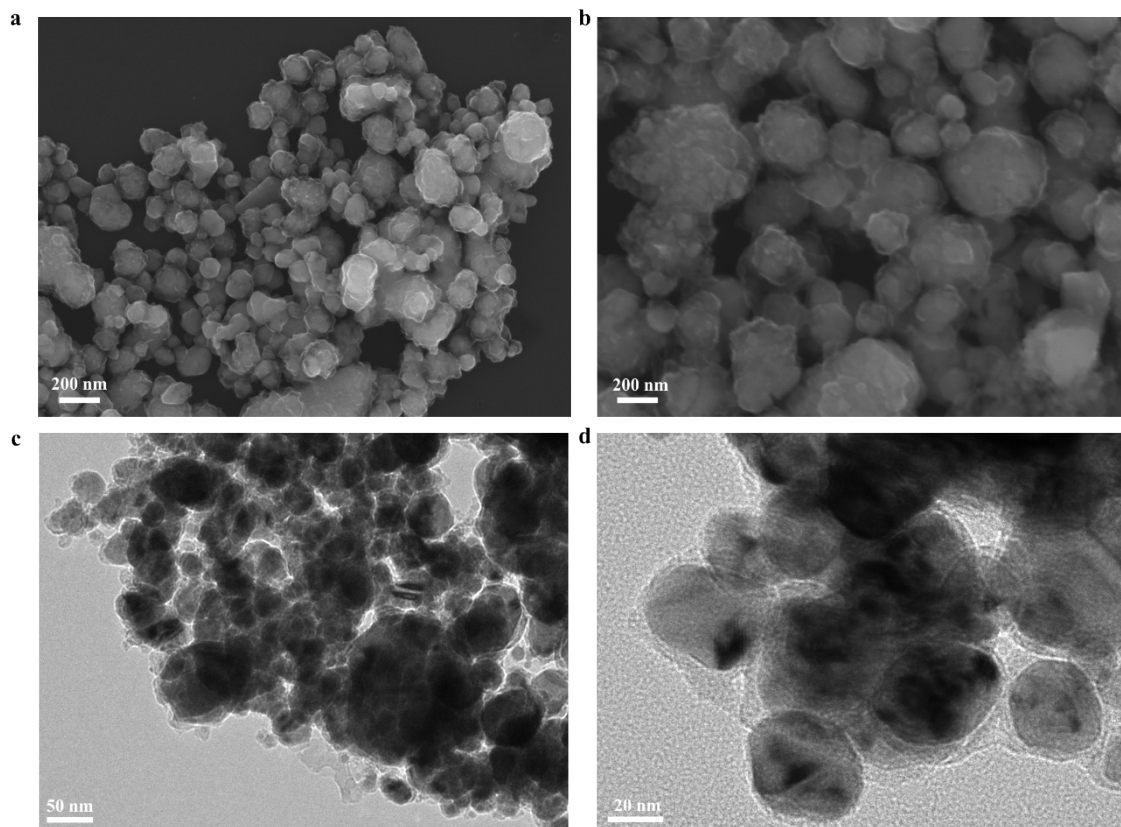


Fig. S3 Characterization of the $\text{Cu}_5\text{-Co}_5$ catalyst. (a-b) SEM images. (c-d) TEM images.

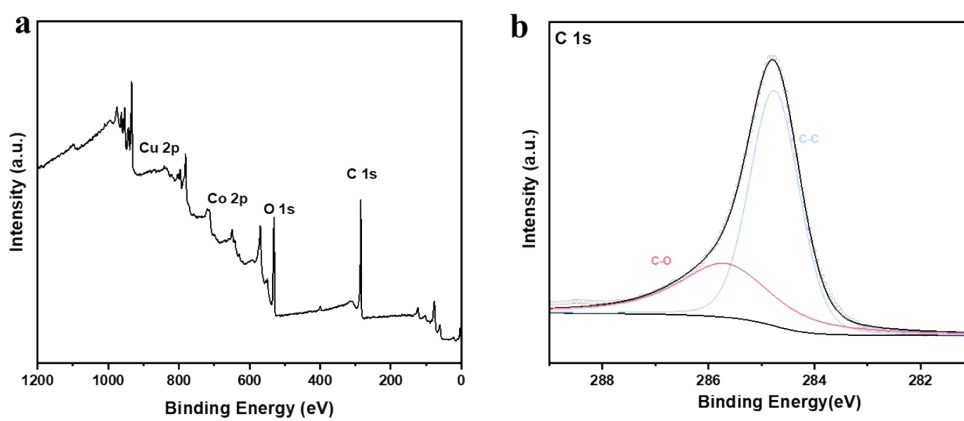


Fig. S4 (a) X-ray photoelectron spectroscopy of the $\text{Cu}_5\text{-Co}_5$ catalyst. (b) High-resolution of C 1s spectrum of the $\text{Cu}_5\text{-Co}_5$ catalyst.

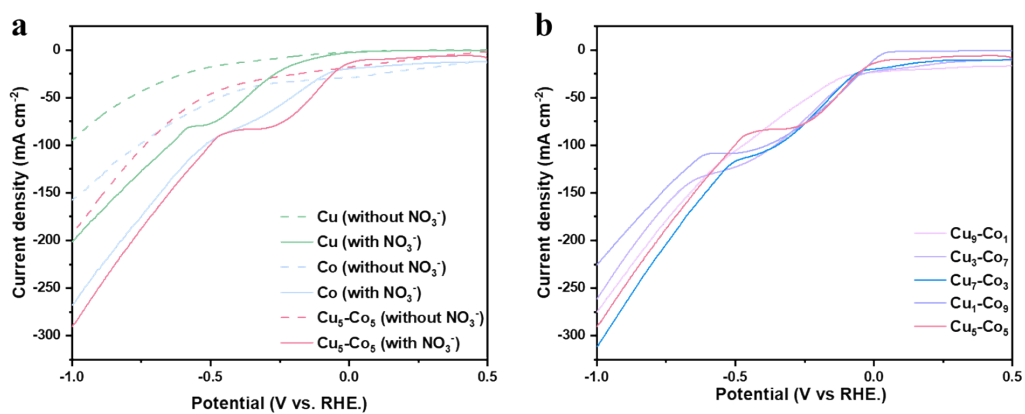


Fig. S5 LSV curves of (a) Cu₅-Co₅, pure Cu and Co in 1 M KOH electrolyte with and without NO₃⁻.
 (b) Various ratios of Cu_x-Co_y catalysts in 1 M KOH electrolyte with 0.1 M NO₃⁻.

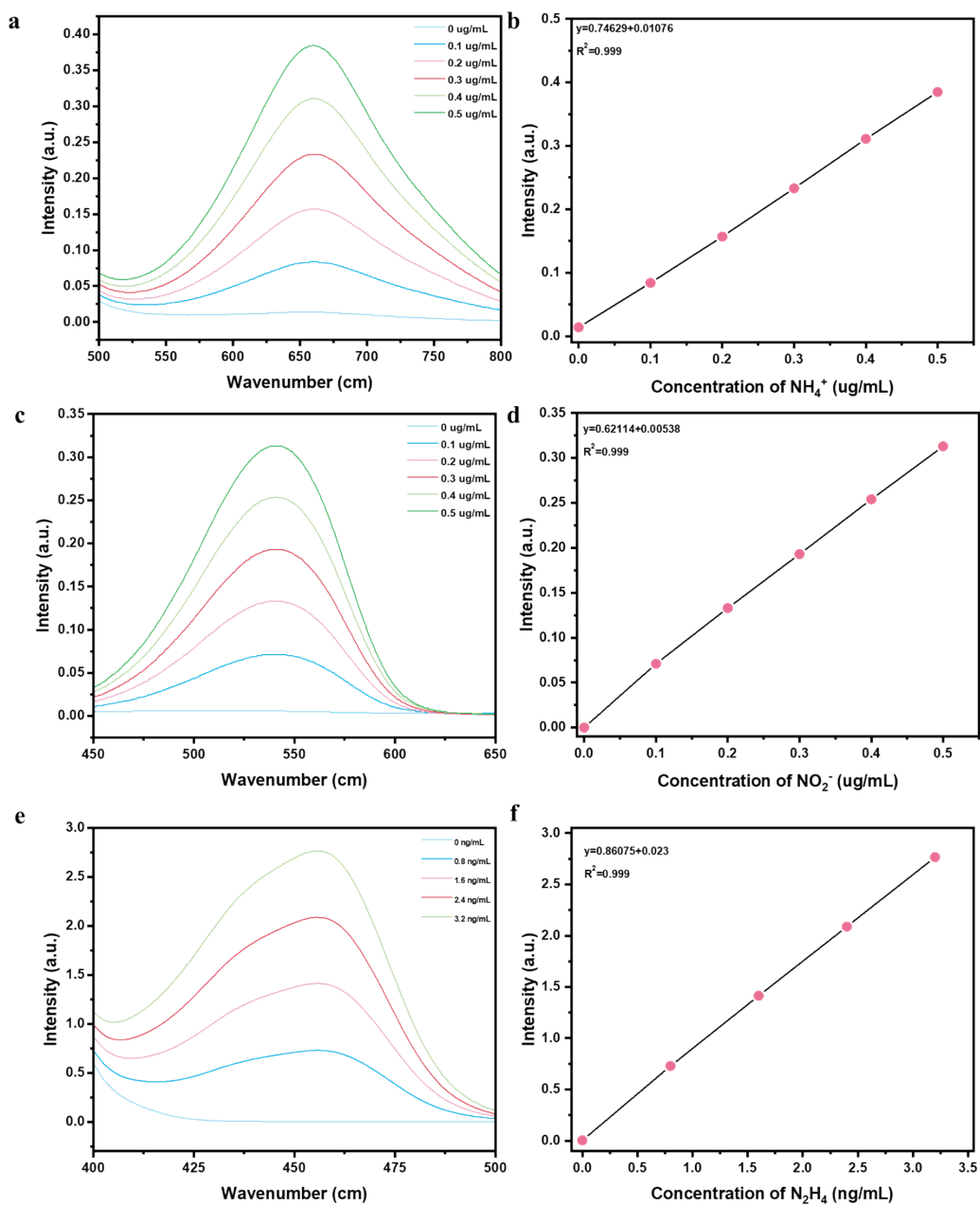


Fig. S6 The quantification of NH_3 , NO_2^- , and N_2H_4 . (a) UV-vis absorption spectra of NH_3 . (b) The linear standard curve for the calculation of NH_3 . (c) UV-vis absorption spectra of NO_2^- . (d) The linear standard curve for the calculation of NO_2^- . (e) UV-vis absorption spectra of N_2H_4 . (f) The linear standard curve for the calculation of N_2H_4 .

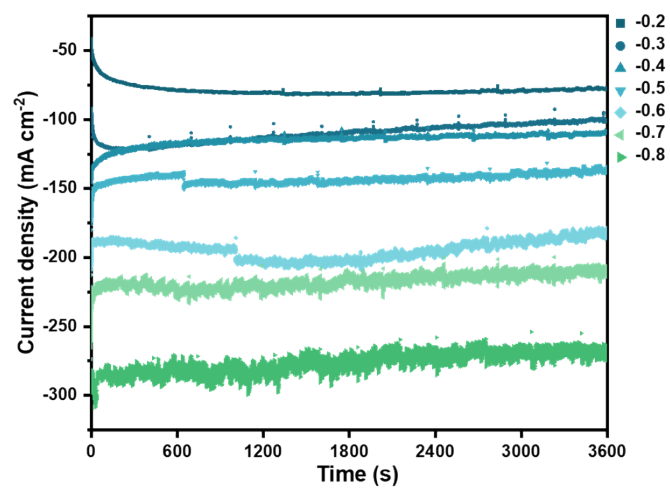


Fig. S7 Chronoamperometry curves of the Cu₅-Co₅ catalyst at different potentials.

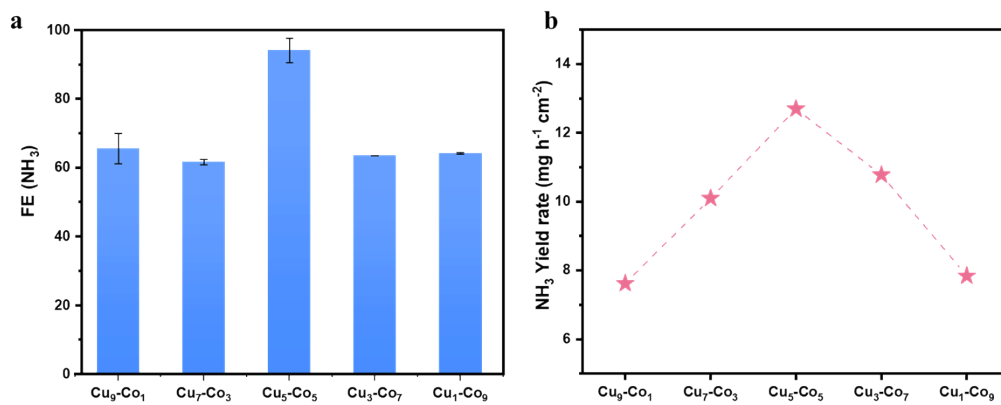


Fig. S8 (a) FE_{NH_3} of different ratio Cu_x-Co_y catalysts. (b) The NH_3 yield rate of different ratio Cu_x-Co_y catalysts.

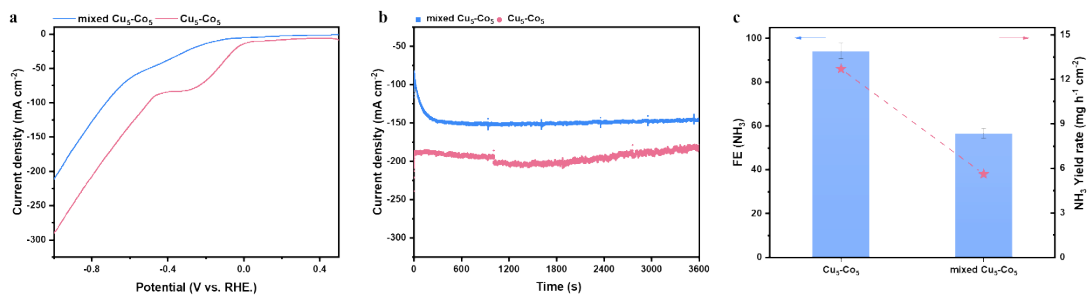


Fig. S9 (a) LSV curves of the Cu₅-Co₅ and mixed Cu₅-Co₅. (b) Chronoamperometry curves of the Cu₅-Co₅ and mixed Cu₅-Co₅ under -0.6 V. (c) NH₃ FEs and yield rates of Cu₅-Co₅ and mixed Cu₅-Co₅ under -0.6 V.

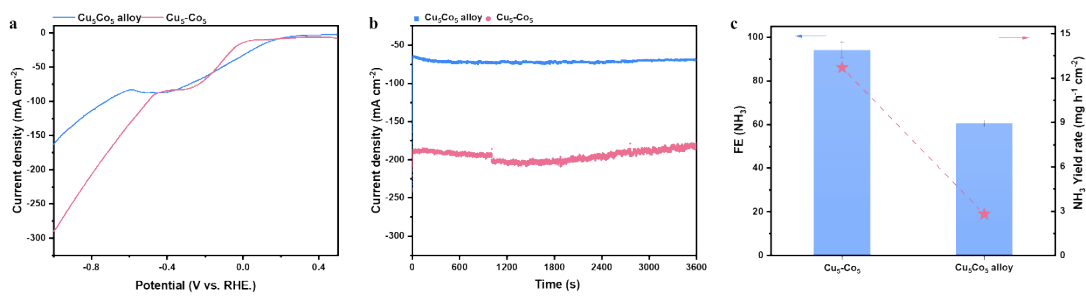


Fig. S10 (a) LSV curves of the $\text{Cu}_5\text{-Co}_5$ and Cu_5Co_5 alloy. (b) Chronoamperometry curves of the $\text{Cu}_5\text{-Co}_5$ and Cu_5Co_5 alloy under -0.6 V . (c) NH_3 FEs and yield rates of $\text{Cu}_5\text{-Co}_5$ and Cu_5Co_5 alloy catalysts under -0.6 V .

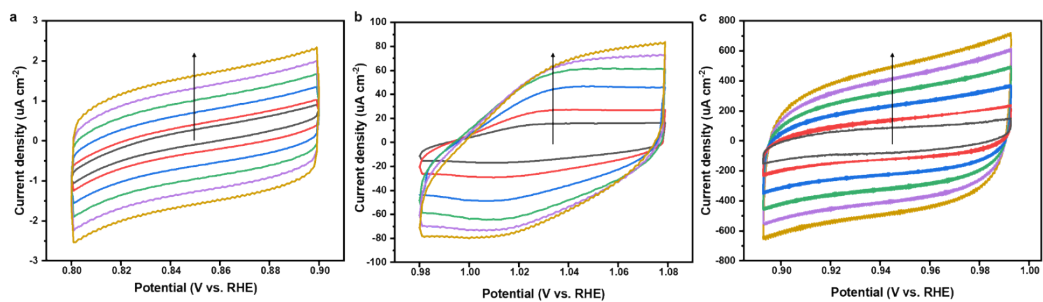


Fig. S11 ECSA measurements of (a) Cu, (b) Co, (c) Cu₅-Co₅. The cyclic voltammetry profiles were measured at the sweep rates of 10, 20, 40, 60, 80, 100 mV/s individually.

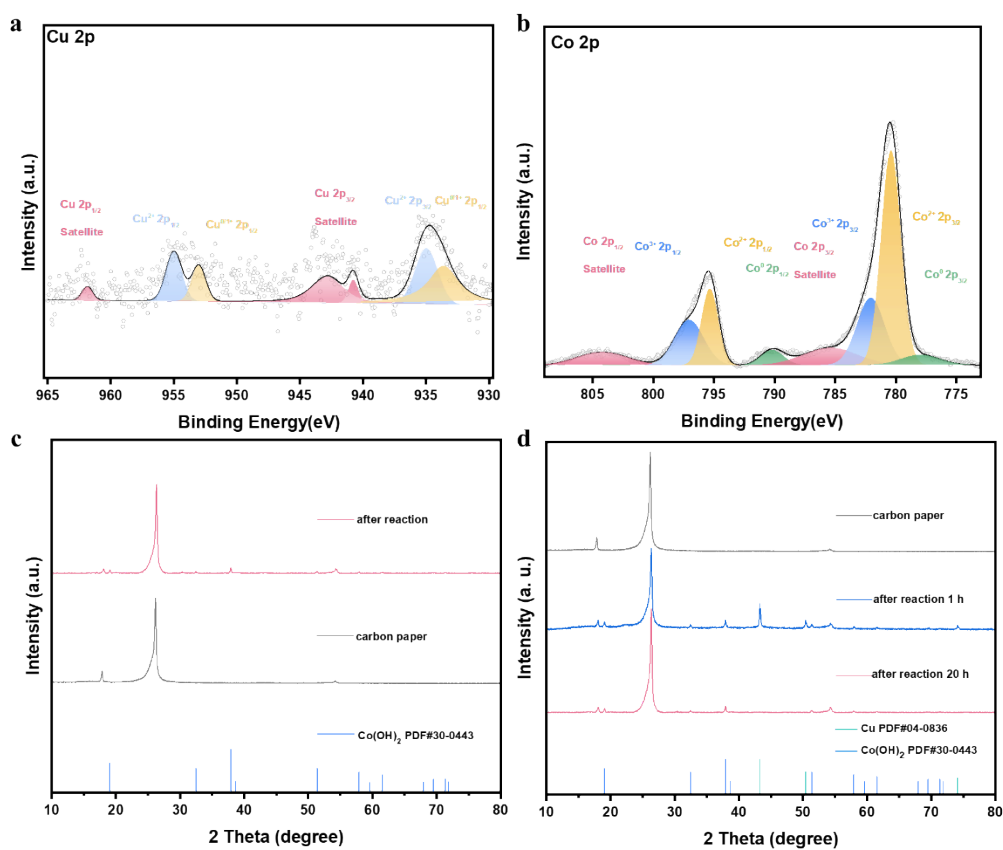


Fig. S12 High-resolution of XPS peaks of the catalyst after cycles stability testing (a) Cu 2p, (b) Co 2p. (c) XRD patterns of the Cu₅-Co₅catalyst after NO₃RR stability test. (d) XRD patterns of the Cu₅-Co₅ catalyst after reaction 1 h and 20 h.

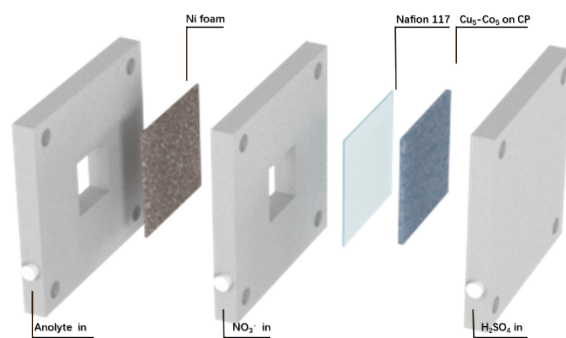


Fig. S13 Schematic illustration of the flow cell equipped with acid capture chamber.

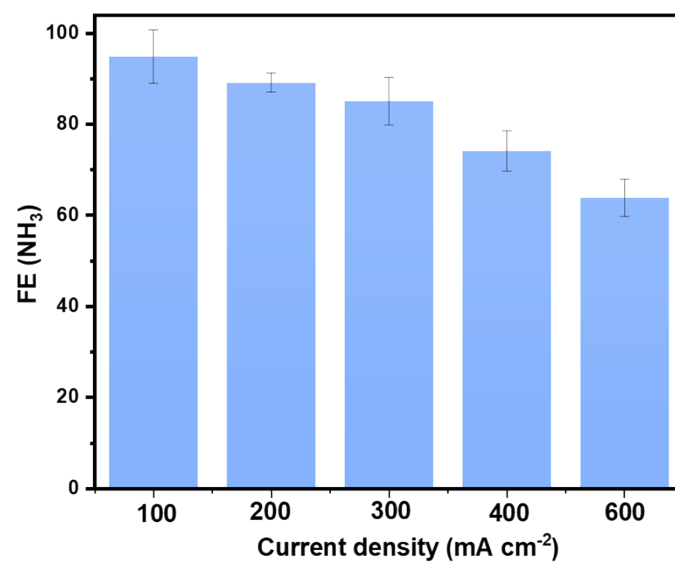


Fig. S14 FE_{NH_3} of the $\text{Cu}_5\text{-Co}_5$ catalyst in the flow cell under different current densities.

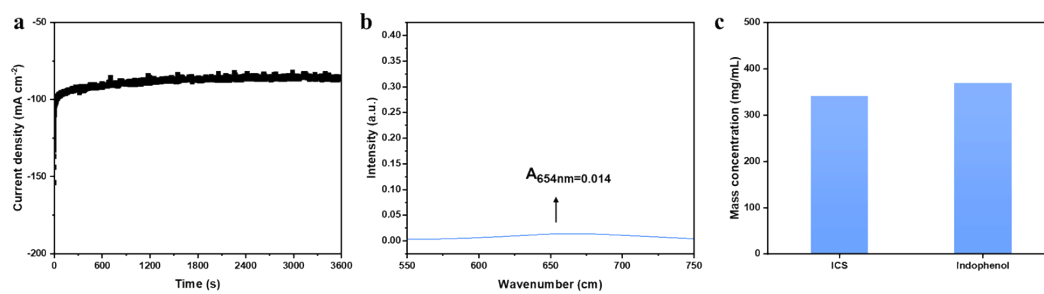


Fig. S15 (a) Potential-time curve of the Cu₅-Co₅ catalyst in 1 M KOH without NO₃⁻. (b) UV-vis absorption spectra of NH₄⁺ from the electrolyte after reaction in 1 M KOH without NO₃⁻. (c) Comparison of ion chromatography and indophenol methods.

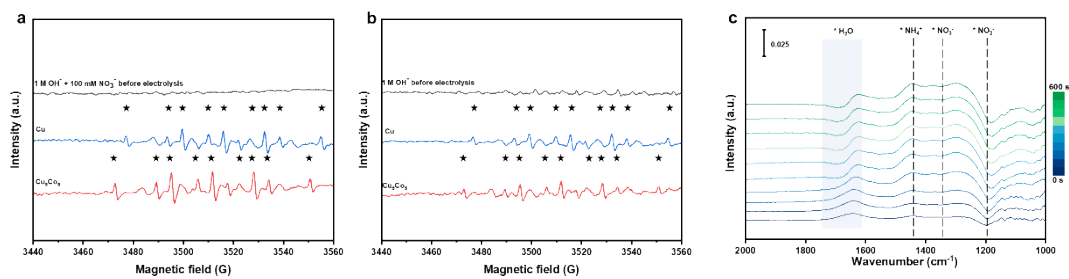


Fig. S16 (a) EPR spectra of the Cu₅-Co₅ and Cu catalysts (collected after 10 min electrolysis at -0.6 V in 1 M KOH with NO₃⁻). (b) EPR spectra of the Cu₅-Co₅ and Cu catalysts (collected after 10 min electrolysis at -0.6 V in 1 M KOH without NO₃⁻). (c) Time-dependent *in-situ* ATR-SEIRAS spectrums of NO₃RR on the Cu₅-Co₅ catalyst.

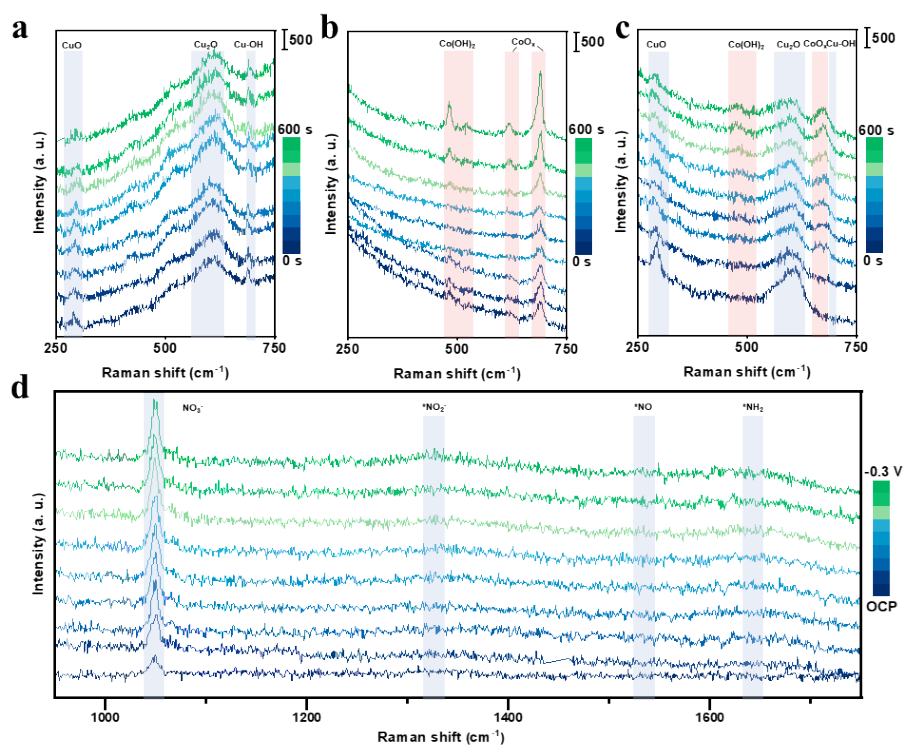


Fig. S17 *In-situ* Raman spectra measured under 0 V of (a) Cu, (b) Co and (c) Cu₅-Co₅. (d) *In-situ* Raman spectra between of the Cu₅-Co₅ catalyst under different potentials.

Table S1 ICP-OES results of the Cu₅-Cu₅ catalyst.

| Catalyst | Cu: Co |
|----------------------------------|---------------|
| Cu ₅ -Co ₅ | 55: 45 |

Table S2 The series resistances (R_s) and charge-transfer resistances (R_{ct}) for Cu₅-Co₅, Cu and Co.

| Catalysts | R_s ($\Omega \text{ cm}^{-2}$) | R_{ct} ($\Omega \text{ cm}^{-2}$) |
|----------------------------------|---|--|
| Cu ₅ -Co ₅ | 1.76 | 10.45 |
| Cu | 2.34 | 14.36 |
| Co | 2.18 | 21.43 |

Tabel S3 Comparison of the electrocatalytic NO₃RR performances of the Cu₅-Co₅ catalyst with other recently reported electrocatalysts.

| | Catalysts | Electrolyte | FE (%) | Yield rate (mg h ⁻¹ cm ⁻²) | Ref. |
|----|---------------------------------------|--|--------|---|------------------|
| 1 | Cu ₅ -Co ₅ | 1 M KOH + 0.1 M NO ₃ ⁻ | 94.8 | 30.9 | This work |
| 2 | Cu/Cu ₂ O | 0.5 M Na ₂ SO ₄ + 200 ppm NO ₃ ⁻ | 95.8 | 4.3 | [15] |
| 3 | pCuO-5 | 0.05 M H ₂ SO ₄ + 0.05 M NO ₃ ⁻ | 89.0 | 8.8 | [16] |
| 4 | Sn-FeS ₂ | 1 M KOH + 0.1 M NO ₃ ⁻ | 96.7 | 15.8 | [22] |
| 5 | Ru ₁ Cu ₁₀ /rGO | 1 M KOH + 0.1 M NO ₃ ⁻ | 98.0 | 6.5 | [23] |
| 6 | Cu/a-CeO _x | 1 M KOH + 0.05 M NO ₃ ⁻ | 98.7 | 10.3 | [24] |
| 7 | Cu-OMS-1 | 0.5 M Na ₂ SO ₄ + 0.05 M NO ₃ ⁻ | 97.0 | 11.8 | [25] |
| 8 | Cu/Co-Cu ₂ O | 0.1 M KOH + 0.05 M NO ₃ ⁻ | 98.1 | 3.8 | [33] |
| 9 | FeB ₂ | 1 M KOH + 0.1 M NO ₃ ⁻ | 96.8 | 25.5 | [39] |
| 10 | Co ₃ CuN | 0.5 M KOH + 2000 ppm NO ₃ ⁻ | 97.6 | 7.6 | [45] |
| 11 | Cu ₄₉ Fe ₁ | 0.1 M K ₂ SO ₄ + 200 ppm NO ₃ ⁻ | 94.5 | 4.0 | [46] |
| 12 | Cu-PTCDA | 1 M PBS + 500 ppm NO ₃ ⁻ | 77.0 | 0.4 | [47] |
| 13 | Fe-N/P-C | 0.1 M KOH + 0.1 M NO ₃ ⁻ | 90.3 | 9.0 | [49] |
| 14 | Ru&Cu/Cu ₂ O | 1 M KOH + 0.1 M NO ₃ ⁻ | 95.0 | 23.8 | [50] |
| 15 | Co+Bi@Cu | 0.1 M Na ₂ SO ₄ + 0.05 M NO ₃ ⁻ | 99.5 | 5.4 | [51] |
| 16 | Ni-BO _x -NF | 0.1 M Na ₂ SO ₄ + 0.5 M NO ₃ ⁻ | 94.0 | 19.2 | [52] |
| 17 | Fe/Ni ₂ P | 0.2 M K ₂ SO ₄ + 0.05 M NO ₃ ⁻ | 94.0 | 4.2 | [53] |
| 18 | TiO _{2-x} | 0.5 M Na ₂ SO ₄ + 50 ppm NO ₃ ⁻ | 85.0 | 0.04 | [54] |
| 19 | Zr-TiON | 0.5 M Na ₂ SO ₄ + 0.05 M NO ₃ ⁻ | 94.3 | 4.3 | [55] |
| 20 | RuFe NFs | 0.5 M Na ₂ SO ₄ + 0.1 M NO ₃ ⁻ | 92.9 | 7.7 | [56] |