Supporting Information

Realizing Efficient Ammonia Electrosynthesis Enabled by Metal Organic Frameworks derived CuCo-LDH

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1. Experimental Section

1.1 Preparation of CuCo-LDH

2.91 g cobalt nitrate and 3.30 g 2-methylimidazole were dissolved in 200 mL methanol, mixed and stirred for 30 minutes, then left undisturbed for 24 hours. After centrifugation and washing, the mixture was dried to obtain ZIF-67.

0.05 g ZIF-67 and 0.065 g $Cu(NO_3)_2$ were dissolved in 30 mL ethanol, mixed and transferred into a PTFE liner. The mixture was reacted at 120° C for 24 hours. After cooling to room temperature, it was centrifuged, washed, and dried overnight to obtain CuCo-LDH.

The copper source adjustment follows the CuCo-LDH preparation method described above, with the anhydrous copper nitrate replaced by copper acetate hydrate and copper chloride hydrate. The copper dosage adjustment is similar to the aforementioned method, but with the anhydrous copper nitrate quantity adjusted to 0 mg, 32 mg, and 96 mg (named as 0Cu, 32Cu, 96Cu). The preparation temperature adjustment mirrors the CuCo-LDH method, but with the temperature set at 100° C and 140° C. The preparation time adjustment is identical to the CuCo-LDH method, but with the preparation time adjusted to 18 h and 30 h.

1.2 Material Characterization

The morphology of the samples was characterized with field-emission scanning electron microscopy (FESEM, Tescan Mira4). Transmission electron microscopy (STEM) images were obtained on the FEI-TALOS-F200X microscope. X-ray diffraction (XRD) analysis was performed on a Smart Lab 9kw diffractometer equipped with a Cu Ka radiation source with a scanning 2θ of 10-80°, operated at 40 kV and 40 mA. Raman analysis were carried out on LabRAM HR 800 Raman Microscope using laser excitation at 532 nm. The surface characteristics of the samples were investigated using Thermo ESCALAB 250 X-ray photoelectron spectrometer (XPS). The mass fraction of the elements in the sample is measured by ICP (Thermo Kalpha).

1.3 Electrocatalysis test

The performance of the electrocatalysts for NO_3^- reduction was evaluated on a CHI660E electrochemical workstation with a three-electrode system in 0.1 M KOH + 0.1M KNO_3 solution. A glassy-carbon (GC) rotating disk electrode (RDE) (d = 6.0 mm) was used as working electrode while a graphite electrode and an HgO electrode were employed as counter and reference electrode, respectively. Before the measurement, the electrolyte was bubbled with Ar flow for 30 min, and continuous Ar flow was maintained during the measurement process. For the activity test, the catalyst sample (2 mg) was ultrasonically dispersed in a mixture of ethanol (0.6 mL), deionized water (0.38 mL) and Nafion (0.02 mL) to form a uniform suspension. A part of catalyst ink (0.020 mL) was then loaded onto the GC electrode, yielding an average mass loading of around 0.2 mg/cm^2.

1.4 UV-vis analysis

Different products, such as nitrite and ammonia, can be generated during the reduction of NO_3^-. The ion concentration of the pre- and post-test electrolytes was determined using an ultraviolet-visible (UV-vis) spectrophotometer. To ensure accurate measurements, the electrolytes were appropriately diluted to match the range of the calibration curves, which are listed below:

1. *Determination of nitrate-N*

4 mL electrolyte was extracted from the electrolytic cell, and adding 1 mL of 0.1 M HCl and 1 mL of 0.8 wt% sulfamic acid, and the resulting solution was diluted to a total volume of 50 mL to match the detection range. For measurement, approximately 5 mL of the uniformly mixed solution was placed in a cuvette, while another 5 mL of deionized water was used as the reference solution in a separate cuvette. The absorption of NO_3^- at wavelengths of 220 nm and 275 nm was then recorded by ultraviolet-visible spectrophotometer. A concentration-

absorbance (A_{220}-$2A_{275}$) curve was established using a series of standard nitrate solutions for calibration.

2. *Determination of nitrite-N*

Mix 4 g of p-aminobenzenesulfonamide, 0.2 g of N-(1-Naphthyl) ethylenediamine dihydrochloridee and 10 mL of phosphoric acid (ρ = 1.70 g/mL) and dilute with ultrapure water to 100 mL was obtained to prepare the color reagent. Taking 1 mL of tested electrolyte and adding 9 mL of untested electrolyte, 1 mL of color reagent, stand for 20 minutes. For measurement, above uniformly mixed solution was placed in a cuvette, while another 5 mL of deionized water served as reference solution in a separate cuvette. The absorption of NO_2^- at wavelength of 540 nm was then recorded by ultraviolet-visible spectrophotometer. To establish a concentration-absorbance curve, a series of standard nitrite solutions were employed for calibration.

3. *Determination of ammonia-N*

Typically, the chromogenic agents were prepared as the follows: C, 1 g sodium nitroferricyanide dehydrate was dissolved into 100 mL H_2O; A, 6.4 g sodium salicylate and 1.3 g NaOH were dissolved into 100 mL H_2O; B, 7.5 mL sodium hypochlorite solution and 3.1 g NaOH were dissolved into 100 mL H_2O. The reaction electrolyte with a certain volume were extracted and then diluted to a final volume of 4 mL. Afterwards, 0.32 mL C solution was added, followed by the addition of 2.4 mL A and 0.8 mL B solution. The absorbance of ammonia was measured during 500 ~ 800 nm by ultraviolet-visible spectrophotometer. The ammonia concentration was calculated based on the standard calibration curve. The absorption of NH_4^+ at a wavelength of 655 nm was then recorded. To establish a concentration-absorbance curve, a series of standard nitrate solutions were employed for calibration.

1.5 Products calculation

Calculations of NH_3 yield (r_{NH3}) and NH_3 Faraday Efficiency (FE):

$$r_{NH_3} = \frac{n \times V}{t \times A}$$

$$FE = \frac{n \times F \times c \times V}{M \times Q} \times 100\%$$

Where F is the Faraday constant (96485 C/mol), c represents the measured NH_3 concentration, V denotes the volume of the electrolyte (80 mL), M is the molecular mass of NH_3, Q is the total applied charge (C), t is the test time (0.5 h), A is the geometric area of the working electrode (0.2826 cm^2).

1.6 The adsorption capacity of NO_3^-

To determine the adsorption capacity of NO_3^-, 50 mg of catalyst was added to 25 mL of 0.1M KOH + 0.1 M KNO_3 solution and stirred for three days. The solution was filtered and separated using a 0.45 μm microporous membrane filter. Calculate the adsorption capacity using the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

q_e is the adsorption capacity ($g/g_{cat.}$), C_0 represents the initial concentration of NO_3^- (g/mL), C_e is the measured concentration of NO_3^- after the adsorption (g/mL), V is the volume of the electrolyte (mL), m means the mass of the catalyst (g).

1.7 In situ differential electrochemical mass spectrometry (DEMS) analysis

A solution containing 0.1 M of NO_3^-, 0.1 M KOH was continuously circulated through a peristaltic pump-driven electrochemical cell. To eliminate interference from other components in the air, Ar was continuously injected. To establish a stable baseline, LSV tests were conducted from 0.2 to -1 V *vs.* RHE at a scan rate of 5 mV/s. The differential mass signals appeared as gaseous products formed on the electrode surface, and returned to baseline once the electrochemical LSV process concluded. To mitigate any potential accidental errors, three successive LSV tests were performed under identical conditions.

2. Supplementary Figures

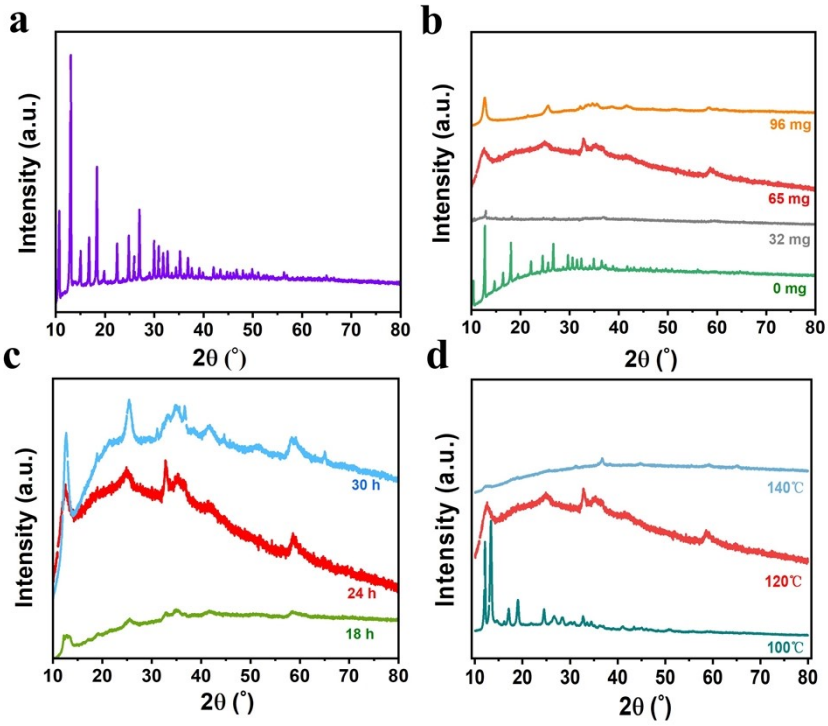

Figure S1. XRD pattern the ZIF-67, obtained samples with varied reactive time, varied $Cu(NO_3)_2$ addition, varied reactive temperature.

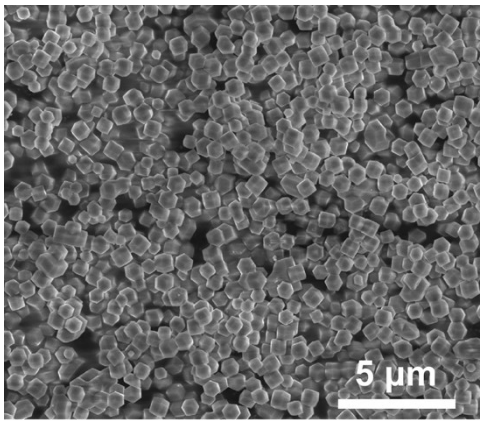

Figure S2. SEM images of the ZIF-67 samples.

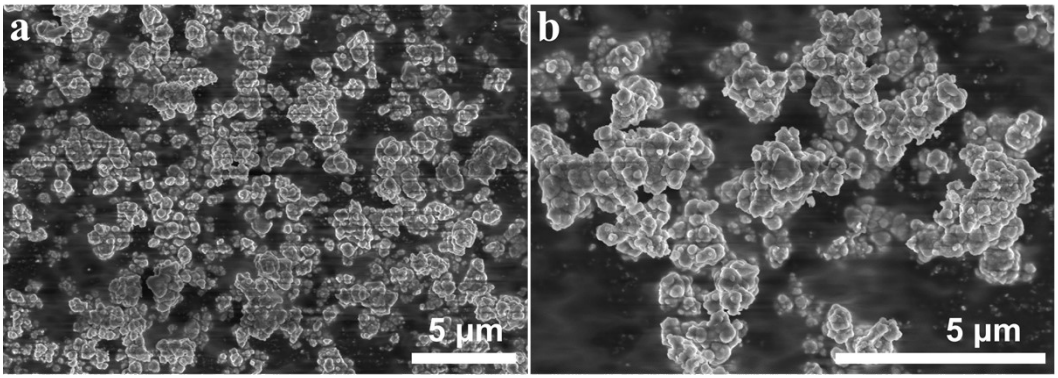

Figure S3. SEM images of the compared Cu free LDH samples.

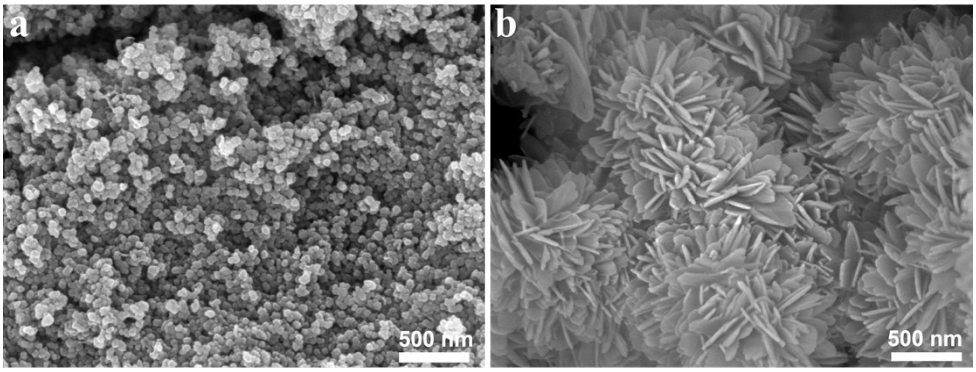

Figure S4. SEM images of the obtained samples by addition of 32 mg and 96 mg $Cu(NO_3)_2$.

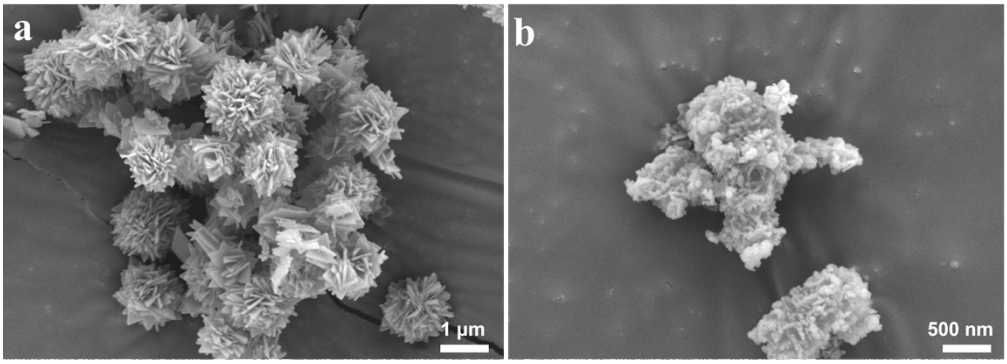

Figure S5. SEM images of the samples prepared at (a) 100°C and (a) 140°C.

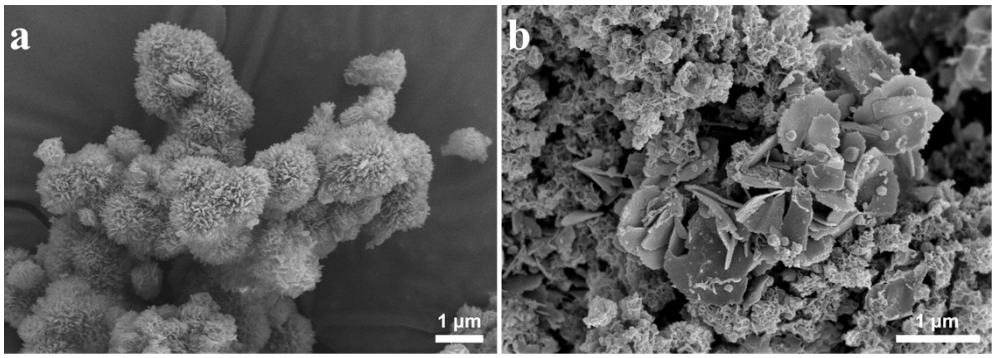

Figure S6. SEM images of the samples prepared by (a) 18 h and (a) 30 h.

Table S1. Fitting results of the Cu LMM spectrum of CuCo-LDH (65 mg $Cu(NO_3)_2$).

574.1Species	Binding energy (eV)	Relative content (%)
Cu^+	570.4	16
Cu^{2+}	574.1	84

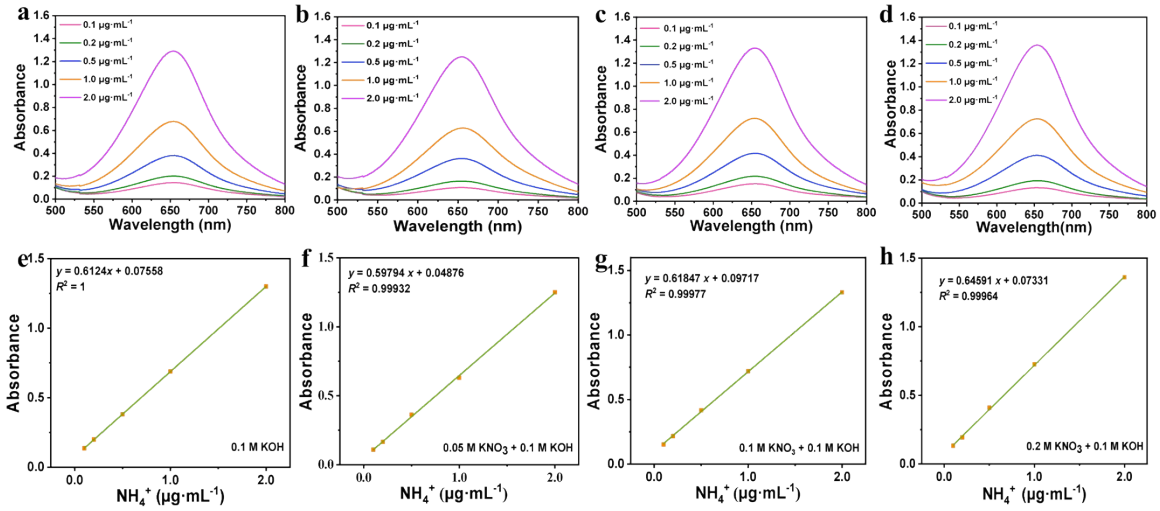

Figure S7. Standard curve of NH_4^+ in the 0.1 M KOH, 0.1 M KOH + 0.05 M KNO_3 , 0.1 M KOH + 0.1 M KNO_3, 0.1 M KOH + 0.2 M KNO_3.

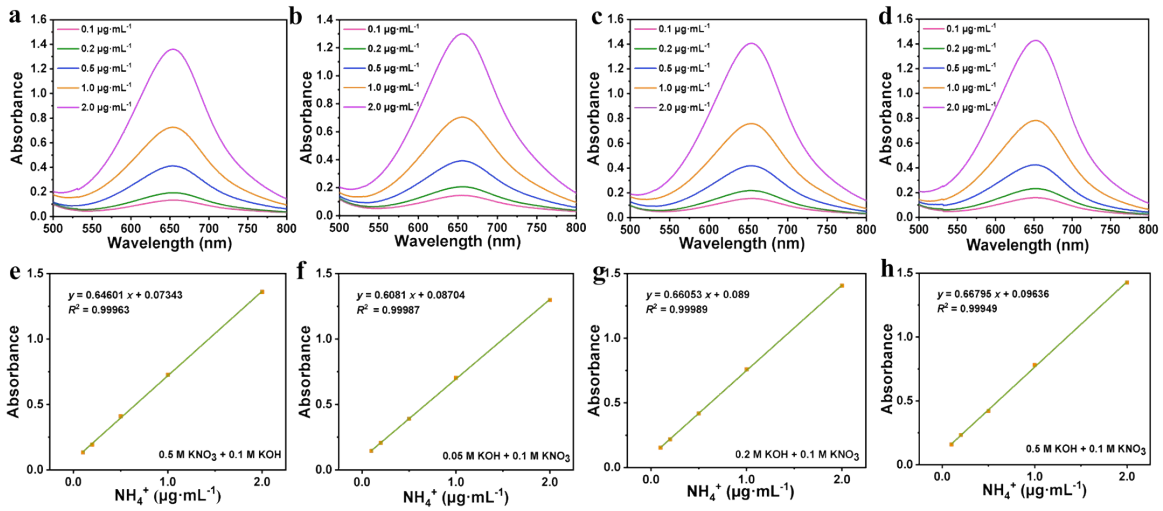

Figure S8. Standard curve of NH_4^+ in the 0.1 M KOH + 0.5 M KNO_3, 0.05 M KOH + 0.1 M KNO_3, 0.2 M KOH + 0.1 M KNO_3, 0.5 M KOH + 0.1 M KNO_3.

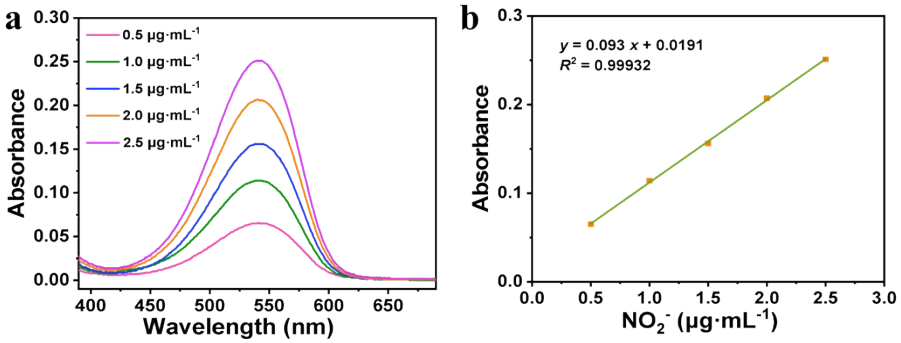

Figure S9. Standard curve of NO_2^-.

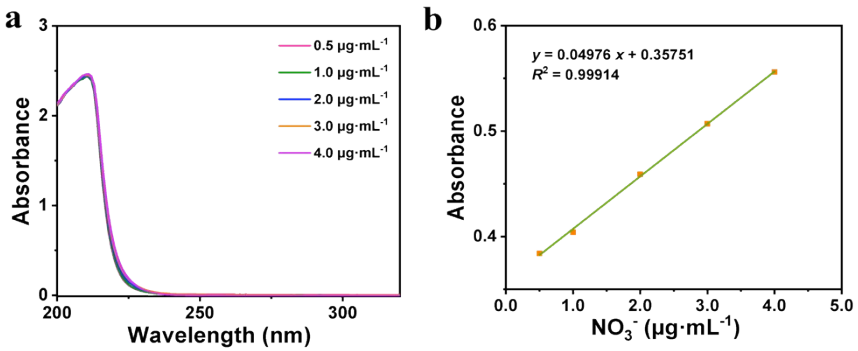

Figure S10. Standard curve of NO_3^-.

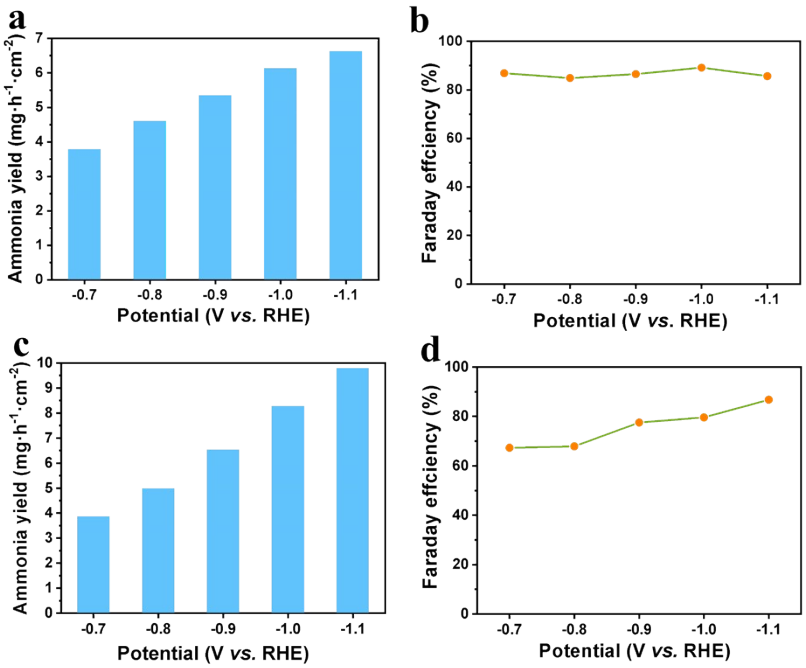

Figure S11. (a) NH_3 yield rates and (b) FE over 32Cu; (c) NH_3 yield rates and (d) FE over 96Cu in 0.1 M KOH with 0.1M KNO_3 at each given potential.

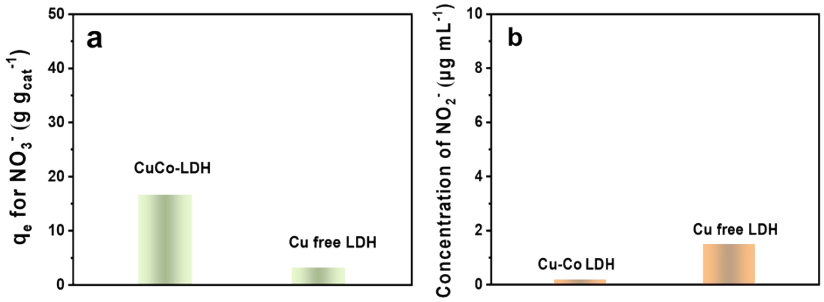

Figure S12. (a) Adsorption capacities of CuCo LDH and Cu-free LDH for NO_3^-; (b) Concentration of NO_2^- of CuCo LDH and Cu-free LDH for NO_3^- after testing 0.5 h at -0.9 V *vs.* RHE.

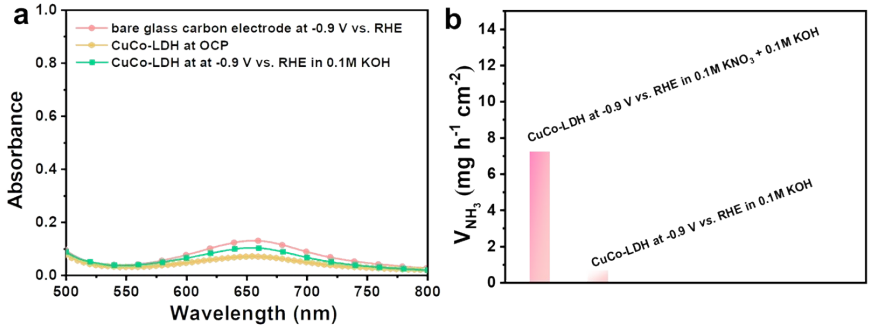

Figure S13. (a) UV-vis spectra of electrolyte after reacting for 0.5 h over bare glass carbon electrode at -0.9 V *vs.* RHE, CuCo-LDH at open circuit potential, CuCo-LDH at -0.9 V *vs.* RHE in 0.1 M KOH; (b) NH_3 yield rates over CuCo-LDH in 0.1 M KOH with or without 0.1 M KNO_3 at -0.9 V *vs.* RHE.

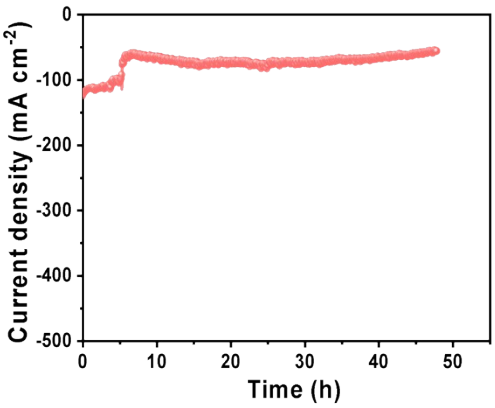

Figure S14. Long-time stability measurement of CuCo-LDH at -0.9 V *vs.* RHE.

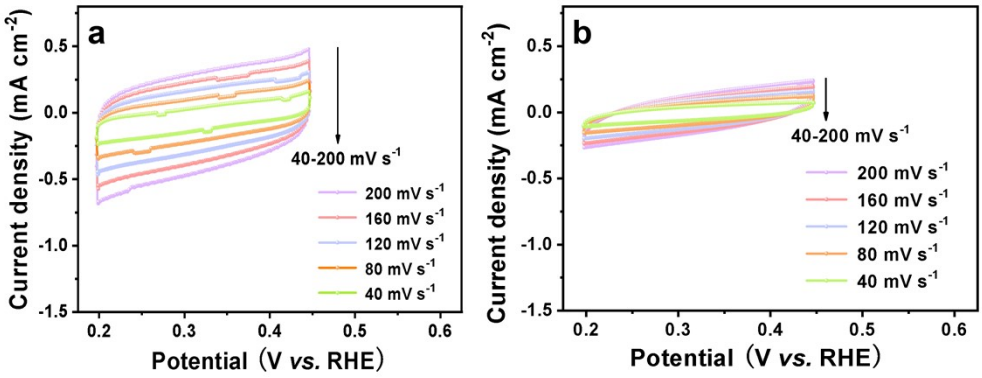

Figure S15. Cyclic voltammetry (CV) could be carried out to probe the electrochemical double layer capacitance of various samples at non-Faradaic overpotentials as the means for estimating the effective electrode surface areas. Accordingly, a series of CV measurements in 0.1 M KOH with 0.1 M KNO_3 of (a) CuCo-LDH and (b) Cu free LDH samples were performed at various scan rates (40, 800,120mV s^{-1}, etc.) in 0.2 - 0.45 V *vs.* RHE region , and the sweep segments of the measurements were set to 40 to ensure consistency.

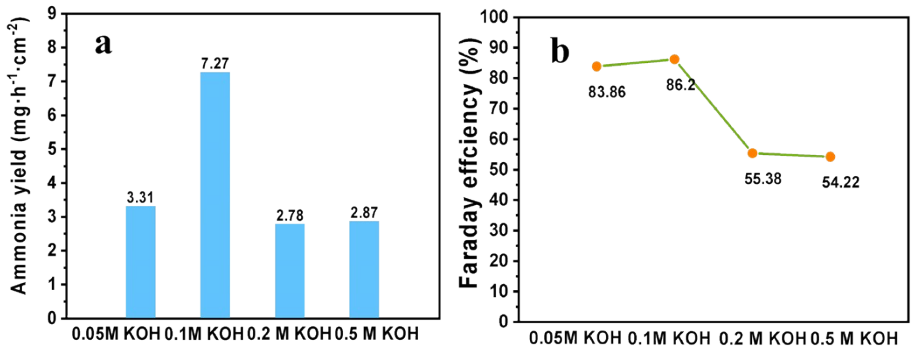

Figure S16. (a) NH_3 yield rates and (b) FE of CuCo-LDH at -0.9 V *vs.* RHE in the 0.05 M KOH + 0.1 M KNO_3, 0.1 M KOH + 0.1 M KNO_3, 0.2 M KOH + 0.1 M KNO_3, 0. 5 M KOH + 0.1 M KNO_3.

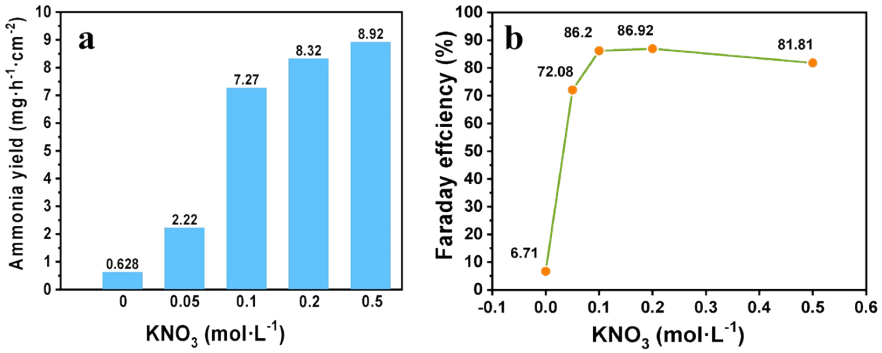

Figure S17. (a) NH_3 yield rates and (b) FE of CuCo-LDH at -0.9 V *vs.* RHE in the 0.1 M KOH, 0.1 M KOH + 0.05 M KNO_3, 0.1 M KOH + 0.1 M KNO_3, 0.1 M KOH + 0.2 M KNO_3, 0.1 M KOH + 0.5 M KNO_3.