Electronic Supplementary Information

Ambient ammonia production via electrocatalytic nitrate reduction catalyzed by flower-like CuCo$_2$O$_4$ electrocatalyst

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Experimental Section

Materials. Copper nitrate (Cu (NO$_3$)·3H$_2$O), cobalt nitrate (Co (NO$_3$)·6H$_2$O), anhydrous sodium sulfate (Na$_2$SO$_4$), methanol (CH$_3$OH), anhydrous ethanol (CH$_3$CH$_2$OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China), urea (CO (NH$_2$)$_2$) was purchased from Aladdin Chemical Reagent CO., Ltd. (China), potassium nitrate (KNO$_3$) was purchased from Shanghai Macklin Biochemical Technology CO., Ltd. (China), and carbon paper was purchased from Shanghai Hosen CO., Ltd. Deionized water was used in all experiments, and the chemicals were analytical grade and used directly without further purification.

Synthesis of CuCo$_2$O$_4$ catalyst. 2.0 mmol Cu(NO$_3$)·3H$_2$O and 4.0 mmol Co(NO$_3$)·6H$_2$O were dissolved in 20 mL CH$_3$OH and stirred to mix well. 10 mL CH$_3$OH containing 16.0 mmol CO (NH$_2$)$_2$ was slowly poured into the above solution and continued to stir for 30 min. The mixed solution was transferred to a 50 mL Teflon tank and reacted at 180℃ for 4 h. The collected precipitates were cleaned with deionized water and anhydrous ethanol respectively, and then dried overnight in an oven at 60℃. The obtained powder was calcined at 500℃ for 2 h in a Muff furnace

with a heating rate of 10°C min^{-1} to obtain $CuCo_2O_4$ powder.

Characterization. Scanning electron microscope (SEM) images and energy dispersive X-ray spectrum (EDS) images were obtained by field emission scanning electron microscope (FESEM SU8020). The powder X-ray diffraction (XRD) was obtained by X-ray diffractometer (Philips X-Pert Super). The Kα ray source was a Cu target (λ=0.15418nm).X-ray photoelectron spectroscopy (XPS) was obtained by X-ray spectrometer (ESCALAB 250Xi). The ^{1}H NMR (nuclear magnetic resonance) spectra were obtained using superconducting Fourier transform nuclear magnetic resonance spectrometer (Bruker Avance−400).

Electrochemical measurements. Electrocatalytic measurements were made in H-type cells separated by proton exchange membranes, using the CHI 660E electrochemical Workstation (CH Instruments, Inc.) to record the electrochemical reactions. 4.0 mg $CuCo_2O_4$ powder was added into anhydrous ethanol (200 μL) and Nafion solution (10 μL, 5wt%), and ultrasonic for 20 min to form uniform ink. The catalyst ink was evenly coated on carbon paper (effective area 1×1 cm^2) as working electrode, Ag/AgCl (3M) and Pt mesh were used as reference electrode and counter electrode respectively. The electrolyte (0.1 M Na_2SO_4 + 1.0 mM KNO_3) was evenly distributed to the cathode and anode chambers, and the volume of electrolyte in each chamber was 30mL. Linear sweep voltammetry (LSV) was performed at a rate of 10 mV s^{-1}. The constant potential was tested for 2 h at different potentials. In this work, all measured potentials (*vs.* Ag/AgCl) were transformed into the potentials *vs.* reversible hydrogen electrode (RHE) based on the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E°_{\text{Ag/AgCl}}$$

Determination of ammonia: Concentration of the produced ammonia was spectrophotometrically detected by the indophenol blue method. In detail，5 mL of sample was taken, and then diluted with 5 mL of deionized water. Subsequently, 100 μL of oxidizing solution (sodium hypochlorite (ρCl=4~4.9) and 0.75 M sodium hydroxide), 500 μL of colouring solution (0.4 M sodium salicylate and 0.32 M sodium hydroxide) and 100 μL of catalyst solution (0.1g $Na_2[Fe(CN)_5NO]\cdot2H_2O$

diluted to 10 mL with deionized water) were added respectively to the measured sample solution. After the placement of 1 h at room temperature, the absorbance measurements were performed at wavelength of 697.5 nm. The obtained calibration curve was used to calculate the ammonia concentration.

Determination of NO_3^-: Take 2 mL electrolyte and dilute it with 8 mL deionized water. Then add 200 μL 1 M HCl and 20 μL 0.8wt% sulfamic acid solution to the above solution and shake well. The absorbance was measured at 220 nm and 275 nm. The final absorbance is calculated using the following formula: $A=A_{220nm}-2A_{275nm}$. The obtained calibration curve was used to calculate the nitrate concentration.

Determination of NO_2^-: 20 g of p-aminobenzenesulfonamide was 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 was dissolved in the above solution. Finally, the above solution was transferred to a 500 mL volumetric flask and diluted to the mark. Boric acid saturated solution was used to adjust the pH of electrolyte to weak acid. 1.0 mL electrolyte was taken out from the electrolytic cell and diluted to 5 mL with 3 mL boric acid saturated solution and 1 mL H_2O. Next, 0.1 mL color reagent was added into the above mentioned 5 mL solution. After shaking and standing for 20 minutes, the absorbance measurements were performed at wavelength of 540 nm. The obtained calibration curve was used to calculate the nitrite concentration.

Calculations.

The equation of NH_3 yield rate:

$$R(NH_3)(\mu g\ h^{-1}\ cm^{-2}) = \frac{C(NH_4^+ - N)(\mu g\ mL^{-1}) \times V(mL) \times 17}{t(h) \times 14}$$

where R (NH_3) is the ammonia yield rate; C (NH_4^+-N) is the measured mass concentration of NH_4^+-N; V is the electrolyte solution volume; t is the reaction time; 14 is the molar mass of NH_4^+-N atom; 17 is the molar mass of NH_3 molecules.

The equation of Faradaic efficiency:

$$FE(NH_3)(\%) = \frac{8 \times n(NH_3)(mol) \times F}{Q} \times 100\%$$

where F is the Faradaic constant (96485.34); Q is the total charge during the NtRR.

The equation of NO_2^- yield rate:

$$R(NO_2^-)(\mu g\ h^{-1}\ cm^{-2}) = \frac{C(NO_2^- - N)(\mu g\ mL^{-1}) \times V(mL) \times 46}{t(h)\ \times 14}$$

where R (NO_2^-) is the ammonia yield rate; C (NO_2^-−N) is the measured mass concentration of NO_2^-−N; V is the electrolyte solution volume; t is the reaction time; 14 is the molar mass of NO_2^-−N atom; 46 is the molar mass of NO_2^- molecules.

The equation of Faradaic efficiency:

$$FE(NO_2^-)(\%) = \frac{2 \times n(NO_2^-)(mol) \times F}{Q} \times 100\%$$

where F is the Faradaic constant (96485.34); Q is the total charge during the NtRR.

$^{15}N_2$ isotope labelling experiments. The ^{15}N isotopic labeling experiments was conducted using $K^{15}NO_3$ (99 atom % ^{15}N) as electrolyte in 0.1 M Na_2SO_4 with identical experimental procedure as that of $Na^{14}NO_3$ experiments. The ^1H NMR (nuclear magnetic resonance) spectra were obtained using superconducting Fourier transform nuclear magnetic resonance spectrometer (Bruker Avance-400).

Supplementary Tables and Figures
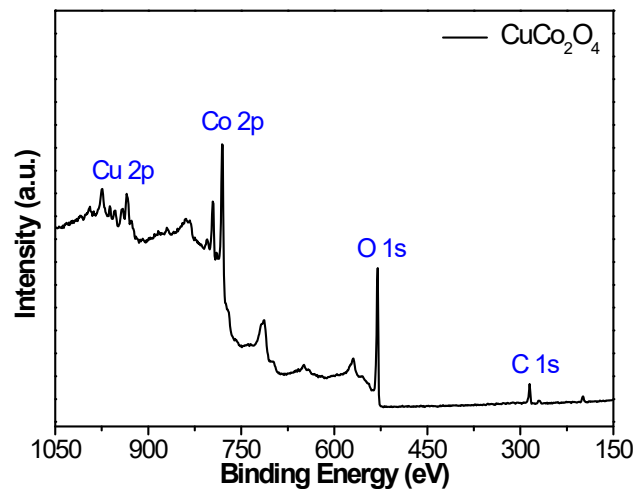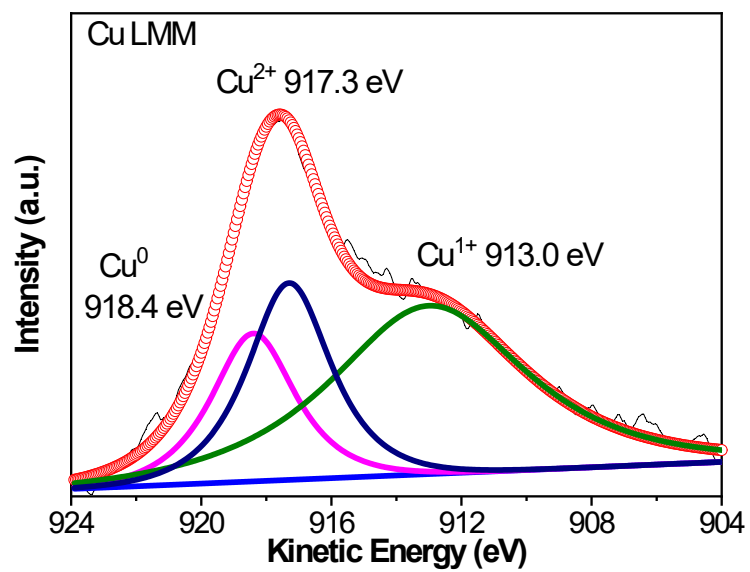

Fig. S1 Surface survey XPS spectrum of CuCo$_2$O$_4$.

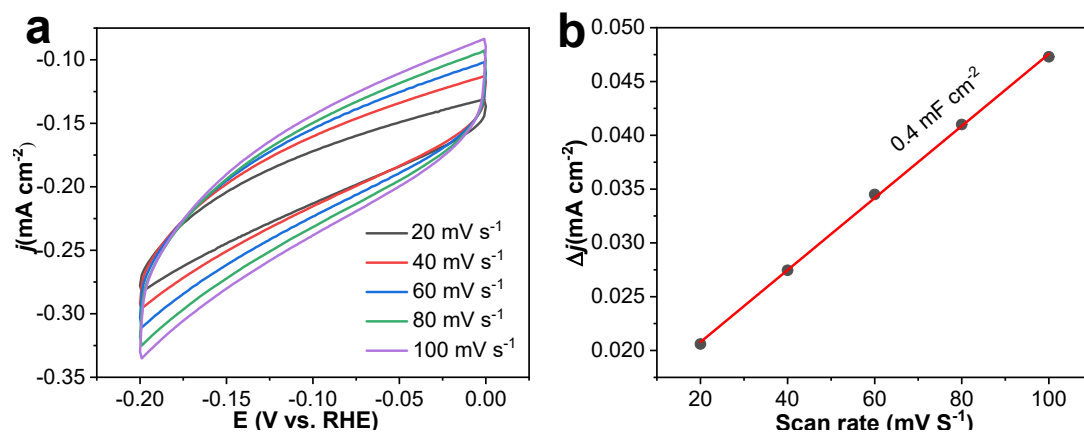**Fig. S2** Cu *LMM* XPS spectrum of CuCo$_2$O$_4$.

Fig.S3 (a) CV curves of different sweep speeds in non-faradic current range and (b) calculated ECSA values.
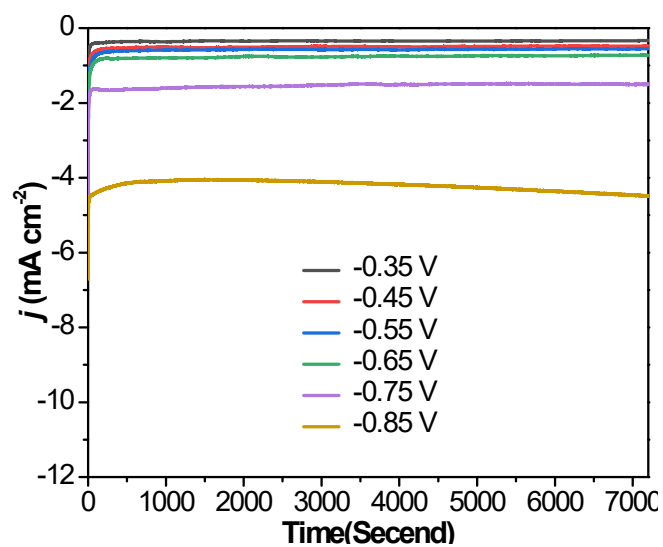
Fig. S4 Chronoamperometry curves of $CuCo_2O_4$ catalyst obtained at different applied potentials in 0.1 M Na_2SO_4 + 1.0 mM KNO_3 solution.
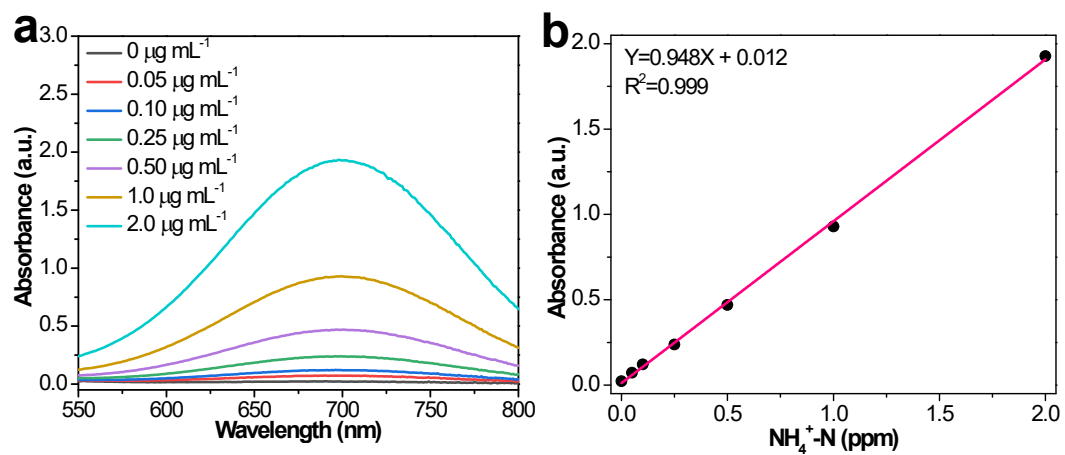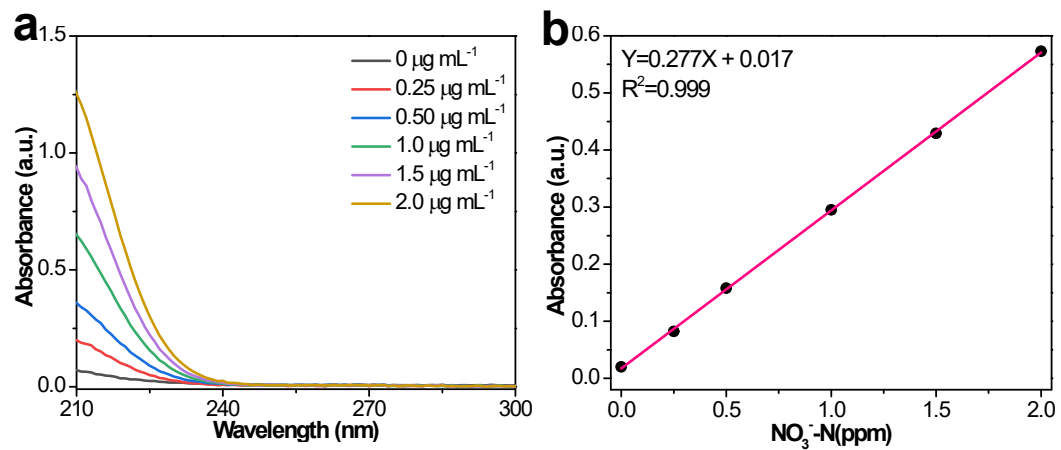
Fig. S5 (a) UV-Vis absorption spectra of various NH_4^+-N concentrations. (b) The calibration curve used for calculation of NH_4^+-N concentration.

Fig. S6 (a) UV-Vis absorption spectra of various NO_3^--N concentrations. (b) The calibration curve used for calculation of NO_3^--N concentrations.
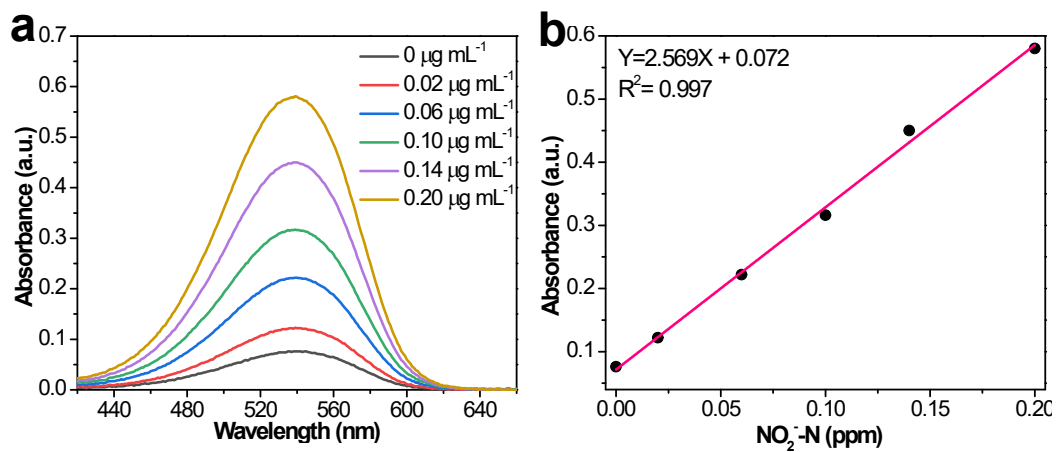
Fig. S7 (a) UV-Vis absorption spectra of various NO_2^--N concentrations. (b) The calibration curve used for calculation of NO_2^--N concentrations.
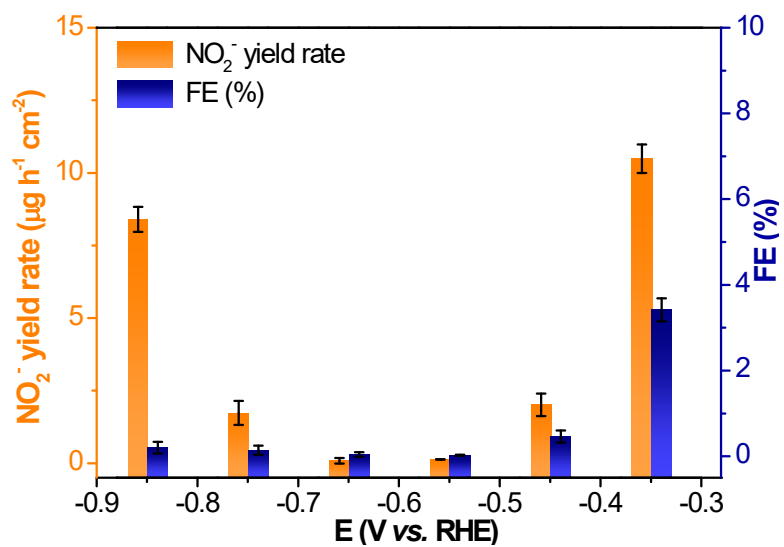
Fig. S8 NO_2^- yield rate and faradaic efficiency of $CuCo_2O_4$ catalyst obtained at different potentials for 2 h NtRR measurement.
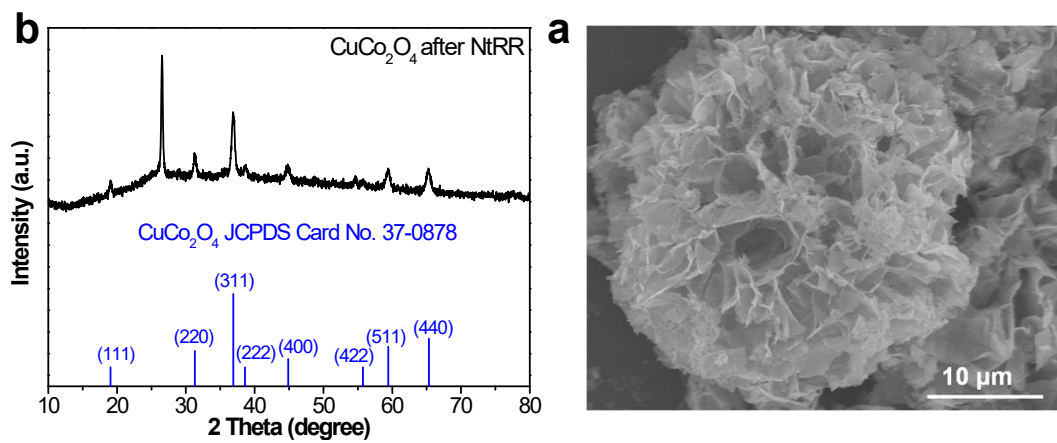
Fig. S9 (a) XRD pattern and (b) SEM image of the CuCo$_2$O$_4$ catalyst after durability test.
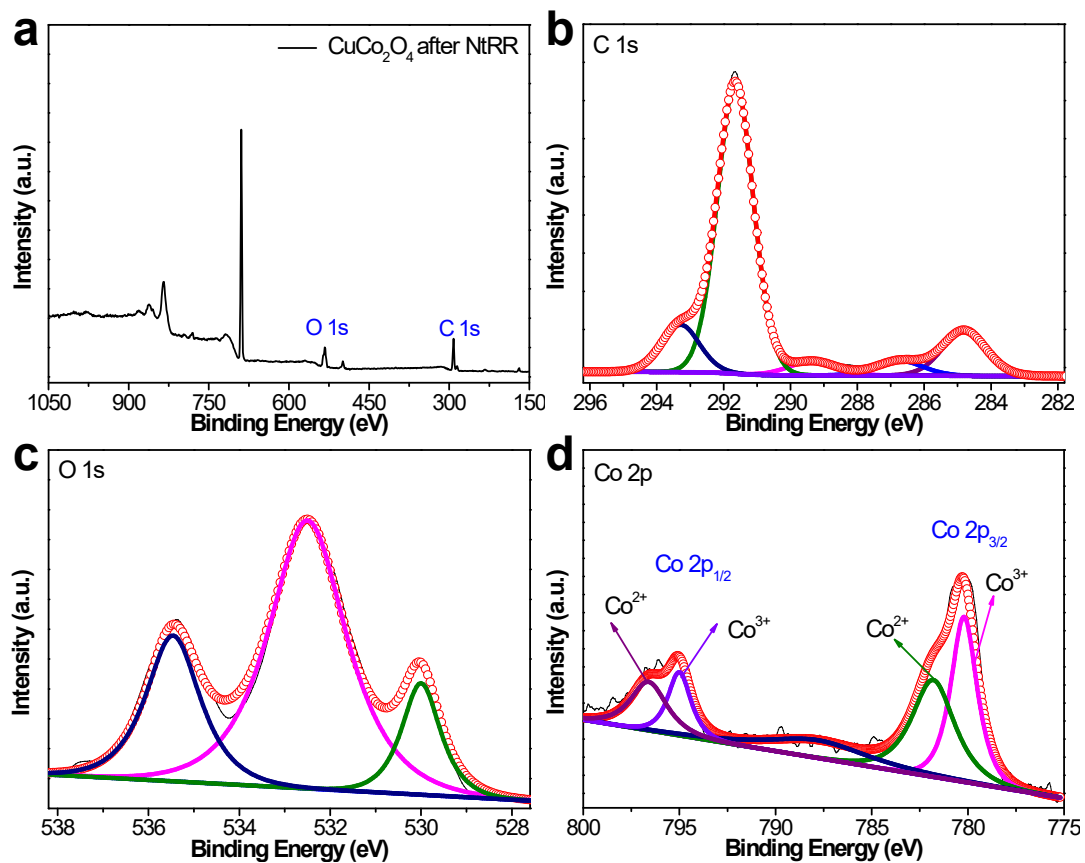
Fig. S10 (a) Surface survey XPS spectrum of CuCo$_2$O$_4$. High-resolution XPS spectra of (b) Cu *1s*, (c) O *1s* and (c) Co *2p* of CuCo$_2$O$_4$ after NtRR.
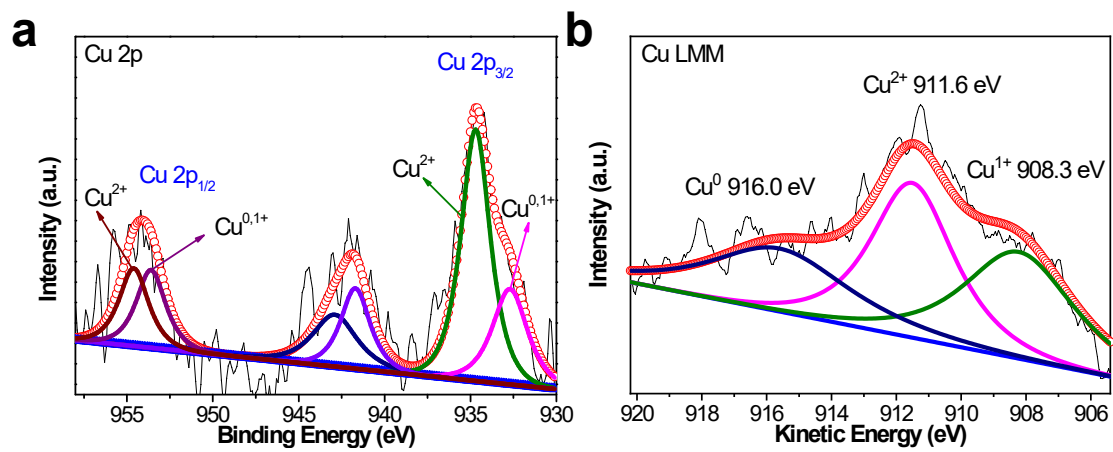
Fig. S11 High-resolution XPS spectra of (a) Cu *2p* and (b) Cu *LMM* of CuCo$_2$O$_4$ after NtRR.

Fig. S12. Photograph of the pH value of cathodic electrolyte for two replicated tests after 2 h NtRR at -0.85 V *vs.* RHE.

Table S1. The adsorption energy of various intermediates.

Sample	Adsorption energy (eV)
$CuCo_2O_4$-NO_3	-2.15
$CuCo_2O_4$-NO_2	-2.64
$CuCo_2O_4$-NO	-2.53
$CuCo_2O_4$-NOH	-2.28
$CuCo_2O_4$-NH_2OH	-2.50
$CuCo_2O_4$-NH_3	-0.96