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Crystallinity-Tuned Cu_3P Nanoparticles Constructed by Solvothermal Phosphidization of Metal-organic Frameworks for Electrocatalytic Nitrate Reduction to Ammonia

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Experiment section

Chemicals

Cupric (II) nitrate trihydrate ($Cu(NO_3)_2·3H_2O$, AR), white phosphorous (P_4,AR), ethanol(C_2H_5OH,AR,95%),benzene(C_6H_6,AR,99.5%),N,N-dimethylformamide (DMF,AR, 99.5%), 1,3,5-benzenetricarboxylic acid (BTC, CP, 98%), sulfuric acid (H_2SO_4, AR), hydrochloric acid (HCl, AR), phosphoric acid (H_3PO_4, AR), sulfamic acid (H_3NO_3S, AR), sulfanilamide ($C_6H_8N_2O_2S$, AR), potassium sodium tartrate tetrahydrate ($C_4H_4O_6KNa$, AR), N-(1-naphthyl) ethylenediamine dihydrochloride ($C_{12}H_{14}N_2·2HCl$, AR), maleic acid ($C_4H_4O_4$, AR), dimethyl sulfoxide-d6 (C_2D_6OS, 0.03% TMS), ammonium chloride-^{15}N ($^{15}NH_4Cl$, 99 at.%), potassium nitrate-^{15}N ($K^{15}NO_3$, AR), Nafion (5 wt %, Dupont) and nickel foam (thickness 1.5 mm) were used directly without further treatment.

Instrumentation

Scanning electron microscopy (SEM) images were taken with a ZEISS Sigma 300 scanning electron microscope. X–ray diffraction (XRD) patterns were measured on a Rigaku Smartlab9KW Diffraction System using a Cu Kα source (λ = 0.15406 nm). X–ray photoelectron spectroscopy (XPS) spectra were collected on a Shimadzu/Krayos AXIS UltrabDLD instrument using monochromatic Al Kα (hv = 1,486.6 eV) radiation. All binding energies were referenced to the C 1s peak at 284.8 eV. Ultraviolet–Visible (UV–vis) absorbance spectra were measured on a Shimadzu UV-2600. Avance NEO NMR spectrometer (400 MHz) was employed to ascertain the origin of ammonia.

The mechanism of NO_3^- reduction on different catalyst surfaces taken into account in this work involves intermediates including $*NO_3$, $*NO_2$, $*NO$, $*N$, $*NH$, $*NH_2$ and $*NH_3$, and the steps are as follows:

$$NO_3^-(l)+* \rightarrow *NO_3+e^- \tag{1}$$

$$*NO_3+2H^++2e^-\rightarrow *NO_2+H_2O \tag{2}$$

$$*NO_2+2H^++2e^-\rightarrow *NO+H_2O \tag{3}$$

$$*NO+2H^++2e^-\rightarrow *N+H_2O \tag{4}$$

$$*N+H^++e^-\rightarrow *NH \tag{5}$$

$$*NH+H^++e^-\rightarrow *NH_2 \tag{6}$$

$$*NH_2+H^++e^-\rightarrow *NH_3 \tag{7}$$

$$*NH_3 \rightarrow NH_3\,(g) + * \tag{8}$$

where the * represents the adsorption site.

Electrochemistry

The electrochemical NO_3RR was carried out in a standard H-type electrolytic cell controlled by a ParSTAT-MC electrochemical workstation. The cathode reaction chamber and the anode reaction chamber were separated by a Nafion 117 proton exchange membrane. The commercially available Nafion 117 membrane was pretreated with 5 wt% H_2O_2 for 1 h, water for 0.5 h, 1 M H_2SO_4 for 1 h and water for 0.5 h consecutively in an 80 °C water bath. The Cu-P was used as the working electrode (placed in cathode chamber), the SCE as the reference electrode (placed in cathode chamber), and the graphite electrode as the counter electrode (placed in anode chamber). The anolyte was 20 mL of 0.5 M K_2SO_4 aqueous solution, and the catholyte was 20 mL of 0.5 M K_2SO_4 and 50 ppm KNO_3 -N aqueous solution. Before each measurement, argon was purged into the electrolyte in both chamber for 0.5 h and magnetic stirring was turned on at the same time. The electrochemistry was carried out under Ar atmosphere and a Teflon-coated stir bar was used during the electrochemical experiments. The reported potentials are in the RHE scale, unless otherwise mentioned. The potentials are converted using Eq. 1.

$$E_{RH}E = E_{SCE} + 0.059*pH + 0.24 \qquad (1)$$

CV at different scan rates were performed in the non-Faradaic region to calculate the double layer capacitance (C_{dl}) and the electrochemical active surface area (ECSA) of the working electrode. Linear sweep voltammetry (LSV) was tested at a scan rate of 5 mV s^{-1} at -0.2 V – (-0.85) V. The electrochemical impedance spectroscopy (EIS) was carried out at a potential of -0.3 V, with the alternating voltage amplitude at 10 mV and the frequency range in 10^5 Hz - 1 Hz. The electrochemically active surface area (ECSA) was calculated based on the double-layer capacitance (C_{dl}) obtained from cyclic voltammetry (CV) measurements at various scan rates of 20, 40, 60, 80 and 100 mV s^{-1}. The ECSA of the working electrode was determined using Eq. 2:

$$ECSA = R_f S \qquad (2)$$

where S is the actual surface area of a smooth oxide electrode (taken as 1 cm^2 in this study), and Rf is the roughness factor of the working electrode. The roughness factor was estimated using the equation: $R_f = Cdl / 60\ \mu F\ cm^{-2}$, assuming a double-layer capacitance of 60 $\mu F\ cm^{-2}$ for a smooth oxide surface. The NO_3RR experiment was carried out by electrolysis at different voltages (-0.1 – 0.5 V with 0.1 V intervals) for 30 min each. After the reaction was completed, the electrolyte at the cathode chamber was taken to analyze the products. Experiments at each applied potential was repeated 3 times, and an average value was taken to reduce the error and reported. The durability test was carried out at -0.3 V using potentiostatic method for 30 min. After each cycle, the cathode electrolyte was collected, the working electrode was rinsed was water. Freshly prepared electrolyte was used for the next potentiostatic test. The durability test was carried out for a total of 8 cycles. Details of product detection and equations to calculate ammonia yield, selectivity and Faradaic efficiency are provided in the supporting information.

Assembly and Electrochemical Testing of Zinc-Nitrate Batteries

A zinc sheet (area: 1 × 2 cm^2) was employed as the negative electrode, while Cu_3P-a served as the positive electrode. Meanwhile, a typical H-type electrolytic cell was assembled, in which 20 mL of 1.0 M KOH was used as the electrolyte in the cathodic compartment, and 20 mL of a mixed solution containing 0.5 M K_2SO_4 and 0.1 M KNO_3 was used as the electrolyte in the anodic compartment. The two compartments were separated by a Nafion 117 membrane to prevent cross-contamination. Prior to measurements, all electrolyte solutions were prepared and diluted to the desired concentrations. Subsequently, polarization discharge curves were recorded at a scan rate of 5 mV s^{-1}, and constant current electrolysis tests were conducted at room temperature using a ParSTAT-MC electrochemical workstation.

The power density (P) of zinc-nitrate battery was determined by $P = I \times V$, where I and V are the discharge current density and voltage, respectively.

The electrochemical reactions in Zn-nitrate battery are presented as following:

Cathode reaction: $NO_3^- + 7H_2O + 8e^- \rightarrow NH_4OH + 9OH^-$

Anode reaction: $4Zn + 8OH^- \rightarrow 4ZnO + 4H_2O + 8e^-$

Overall reaction: $4Zn + NO_3^- + 3H_2O \rightarrow 4ZnO + NH_4OH + OH^-$

Product detection

The ammonia content in the product was measured by Nessler's reagent spectrophotometry. The 5 mL of the cathode electrolyte acquired after the potentiostatic measurement was diluted to the detection range, and 100 μL of potassium sodium tartrate solution (500 g L^{-1}) was added, followed by 100 μL of Nessler's reagent. The solution was left to stand for 10 min. The absorption intensity at the wavelength of 420 nm was detected using the ultra violet-visible spectroscopy (UV-vis). The NH_4Cl

crystal were dried at 110 °C for 2 h. A series of standard NH_4Cl solutions with known concentrations were prepared and were used to acquire the absorbance-concentration calibration curve, and the concentration of ammonia was calculated using the calibration curve.

The concentration of nitrate was determined as follows. First, dilute 5 mL of the cathode electrolyte to the detection range. Then, 100 μL of 1 M HCl solution and 20 μL of 0.8 wt% Sulfamic acid solution was added to the analyte. After 20 min, the absorption intensities at 220 nm (A_{220}) and 275 nm (A_{275}) were acquired using UV-vis. The absorbance intensity (A) is calculated according to the formula

$$A = A_{220} - 2\,A_{275}. \qquad \text{(R 2)}$$

The absorbance-concentration calibration curve was acquired using the KNO_3 aqueous solution with known concentration.

The isotope labeled $K^{15}NO_3$ was used as a nitrogen source to verify the source of nitrogen. The anolyte was 20 mL of 0.5 M K_2SO_4 solution, and the catholyte was 20 mL of 0.5 M K_2SO_4 and 50 ppm $K^{15}NO_3$-N solution. After electroreduction at -0.3 V (Vs. RHE) for 1800 s, the electrolyte was removed to adjust the pH to neutral (= 7), and then maleic acid was added (the final mixed solution content was 0.4 mg mL^{-1}). Finally, 0.5 mL of the mixed solution, 50 μL of 4 M H_2SO_4 and 50 μL of DMSO-d_6 were transferred to the NMR tube.

Equations

The calculation of ammonia production from electrocatalytic nitrate synthesis is as (E 3)

$$\mathbf{Yield_{NH_3}} = \frac{\mathbf{c_{NH_3} \times V}}{\mathbf{t \times s}} \qquad \text{(E 3)}$$

Where $c_{NH_3}$is the mass concentration of NH_3, V is the volume of the cathode electrolyte, t is the reaction time, S is the surface area of the working electrode immersed in the electrolyte (1 cm^2).

The selectivity of NH_3 product is calculated as (E 4)

$$\boldsymbol{Selectivity} = \frac{c_{NH_3}}{\Delta_{c_{NO_3^-}}} \times \boldsymbol{100\%} \qquad \text{(E 4)}$$

Where $\Delta_{c_{NO_3^-}}$ is the difference in mass concentration of nitrate before and after electrolysis.

The Faradaic efficiency of electrocatalytic nitrate reduction to ammonia is calculated as (E 5)

$$\boldsymbol{FE_{NH_3}} = \frac{\boldsymbol{8F \times c_{NH_3} \times V \times 10^{-6}}}{\boldsymbol{M_{NH_3} \times Q}} \times \mathbf{100\%} \qquad \text{(E5)}$$

Where F is the Faraday constant 96485 (C mol^{-1}), V is the volume of the cathode electrolyte (20 mL), $M_{NH_3}$is the molar mass of NH_3 (g mol^{-1}), and Q is the total charge consumed.

Arrhenius plots of NO_3RR and NO_2RR

$$k = Ae^{-\frac{E_a}{RT}} \qquad \text{(E 6)}$$

where k is the reaction rate constant, A is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature in Kelvin.

XRD crystallinity calculation

The crystallinity of the sample was estimated based on the integrated area of the diffraction peaks and the total diffracted intensity from the X-ray diffraction (XRD) pattern. Specifically, the total area under the XRD curve (A_{total}) was first obtained by integrating the entire pattern after baseline correction. Subsequently, individual crystalline diffraction peaks were fitted and integrated to determine their respective areas. The sum of these fitted peak areas ($A_{crystalline}$) represents the contribution from the crystalline regions.

The degree of crystallinity (Xc) was then calculated using the following equation:

$$X_C = \frac{A_{\mathbf{crystalline}}}{A_{\mathbf{total}}} \times 100\% \qquad \text{(E 7)}$$

Table S1. The amounts of reagents used in the synthesis of Cu_3P

	Cu-MOF (g)	P_4 (g)	DMF (mL)
Cu_3P-H	0.1	0.15	30
Cu_3P-L	0.1	0.25	30
Cu_3P-a	0.1	0.35	30

2. ICP-OES

Table S2. Element contents of Cu-P

		Mass		Mass ratio (Cu:P)	Atomic ratio (Cu:P)
		Cu (mg)	P (mg)		
Cu_3P-H	ICP-OES	0.780414	0.107828	7.24	3.53
	XPS			5.09	2.48
Cu_3P-L	ICP-OES	0.191551	0.388345	2.54	1.24
	XPS			3.43	1.49
Cu_3P-a	ICP-OES	0.08673	0.47989	0.18	0.09
	XPS			0.16	0.08
Cu_3P-a after cycle	XPS			0.21	0.11

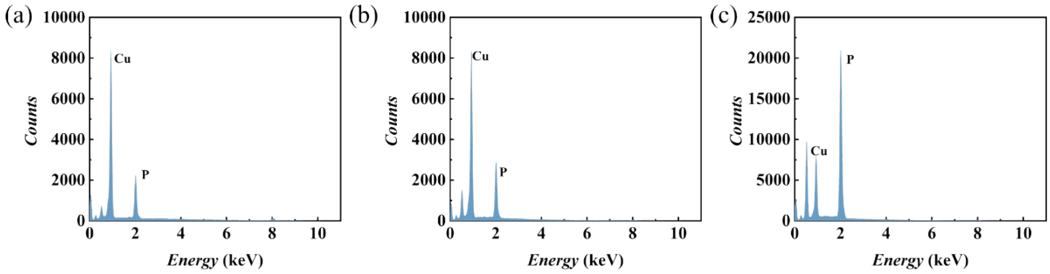

Fig. S1. EDX spectrum of Cu_3P-H (a), Cu_3P-L (b) and Cu_3P-a(c).

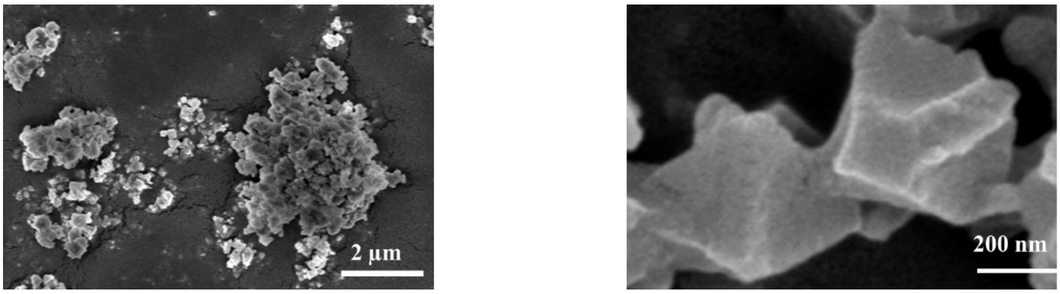

Fig. S2 SEM of Cu-BTC MOF

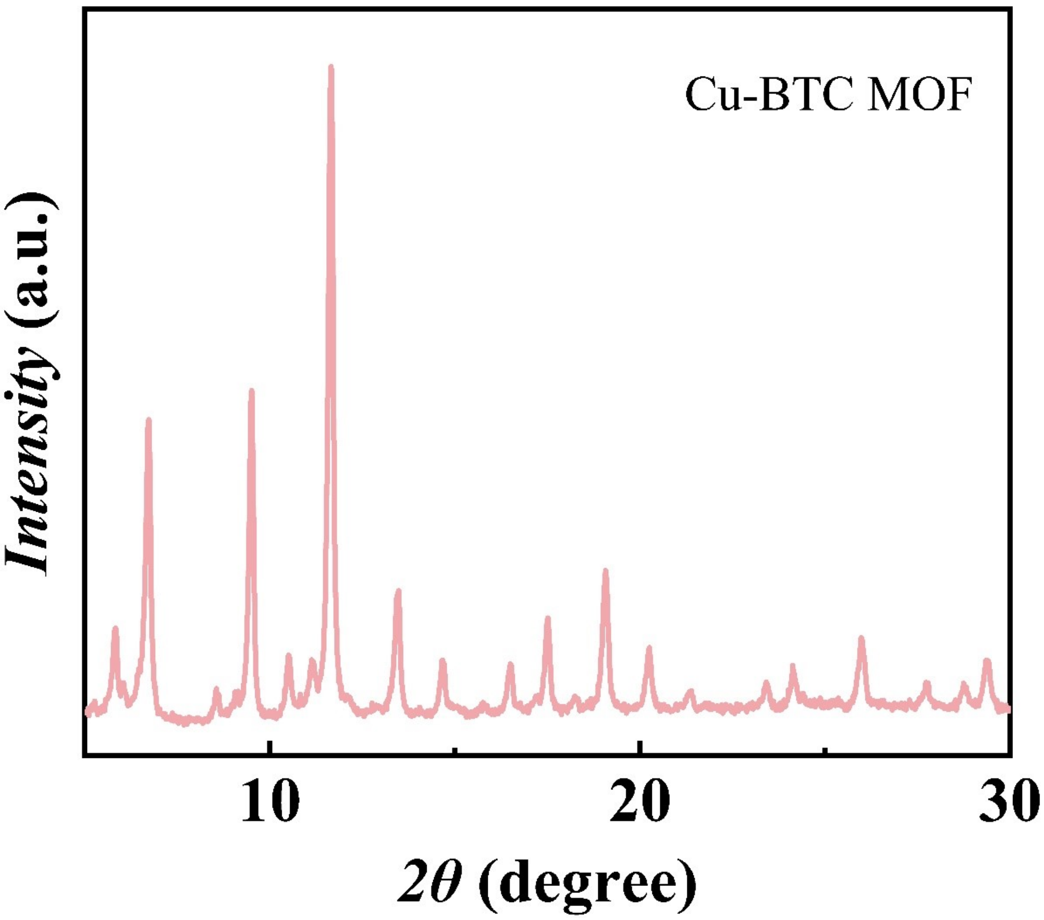

Fig. S3 XRD patterns of Cu-BTC MOF

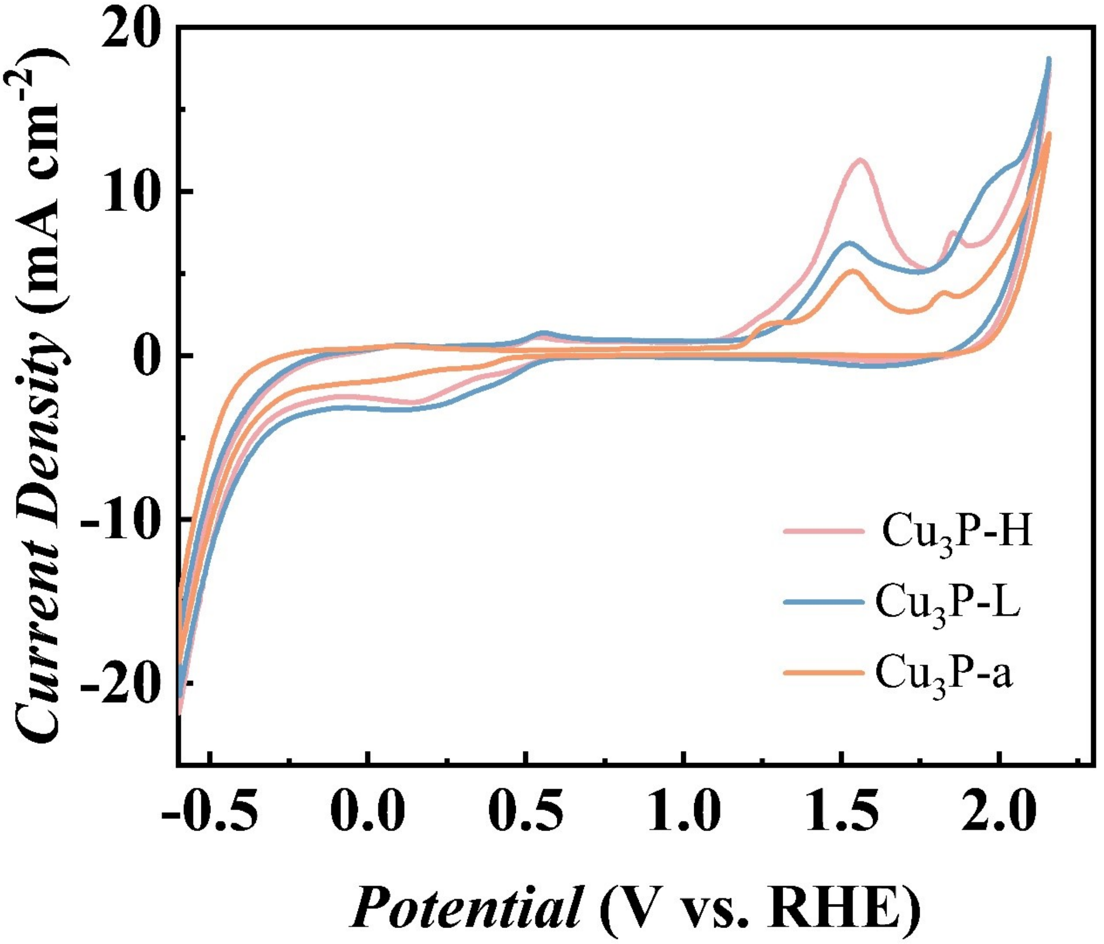

Fig. S4 CV of the Cu_3P in 0.5 M K_2SO_4 and KNO_3-50 ppm N at 10 mV s^{-1}

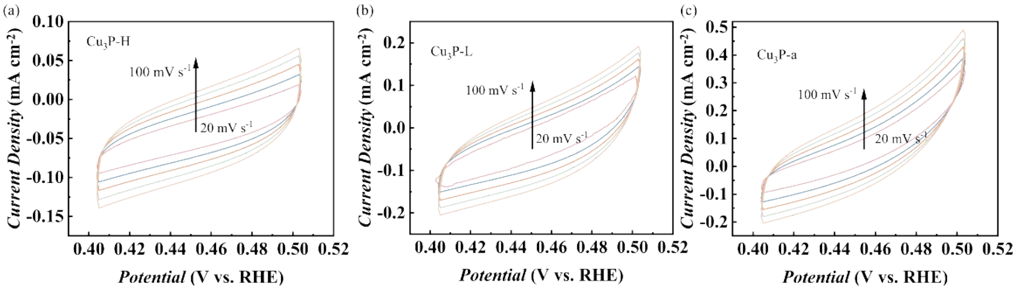

Fig. S5. CV for the determination of the double-layer capacitance of different samples at different scan rates (20 - 100 mV s^{-1}) in the potential region from 0.4 to 0.5 V *vs.* RHE. (a) Cu_3P-H (b) Cu_3P-L and (c) Cu_3P-a.

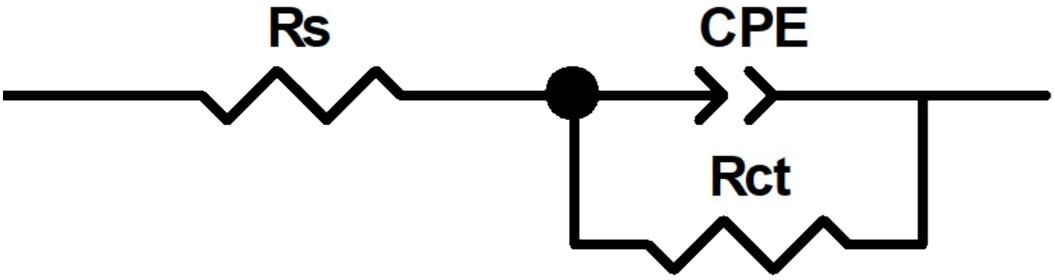

Fig. S6. The fitted equivalent circuit of EIS

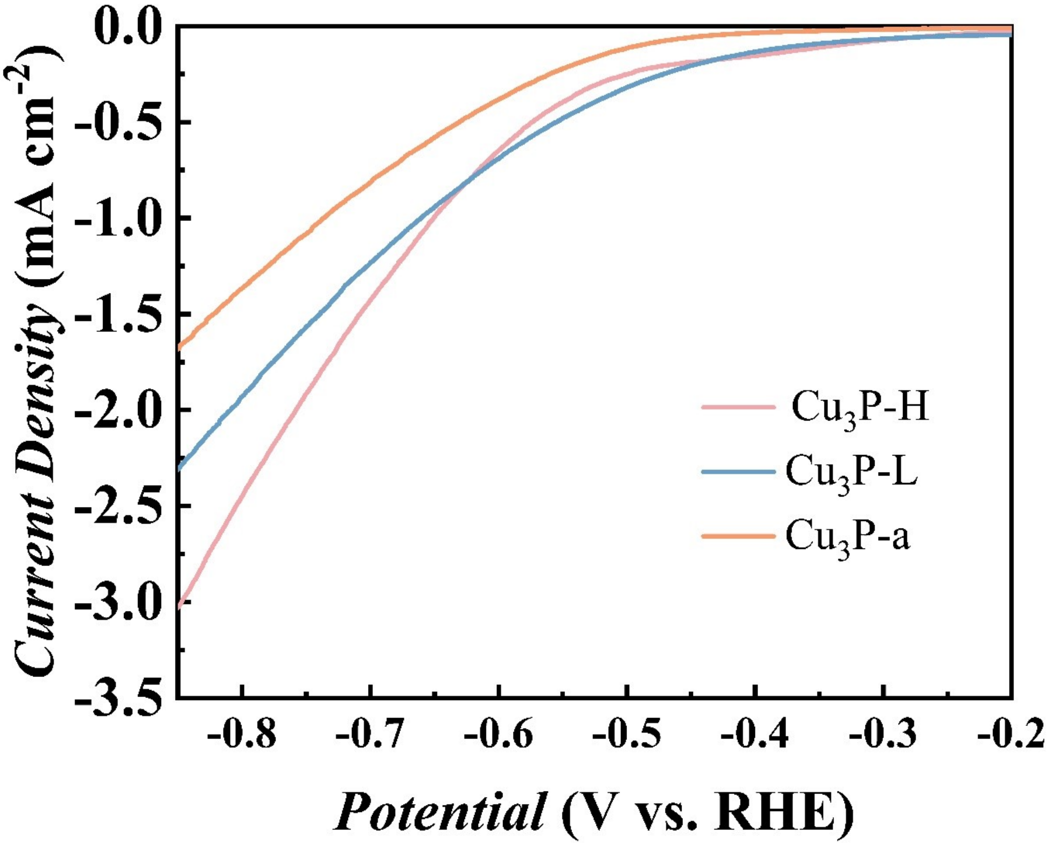

Fig.S7. LSV curves of Cu_3P-H, Cu_3P-L, and Cu_3P-a normalized by ECSA in 0.5 M K_2SO_4 with 50 ppm KNO_3-N.

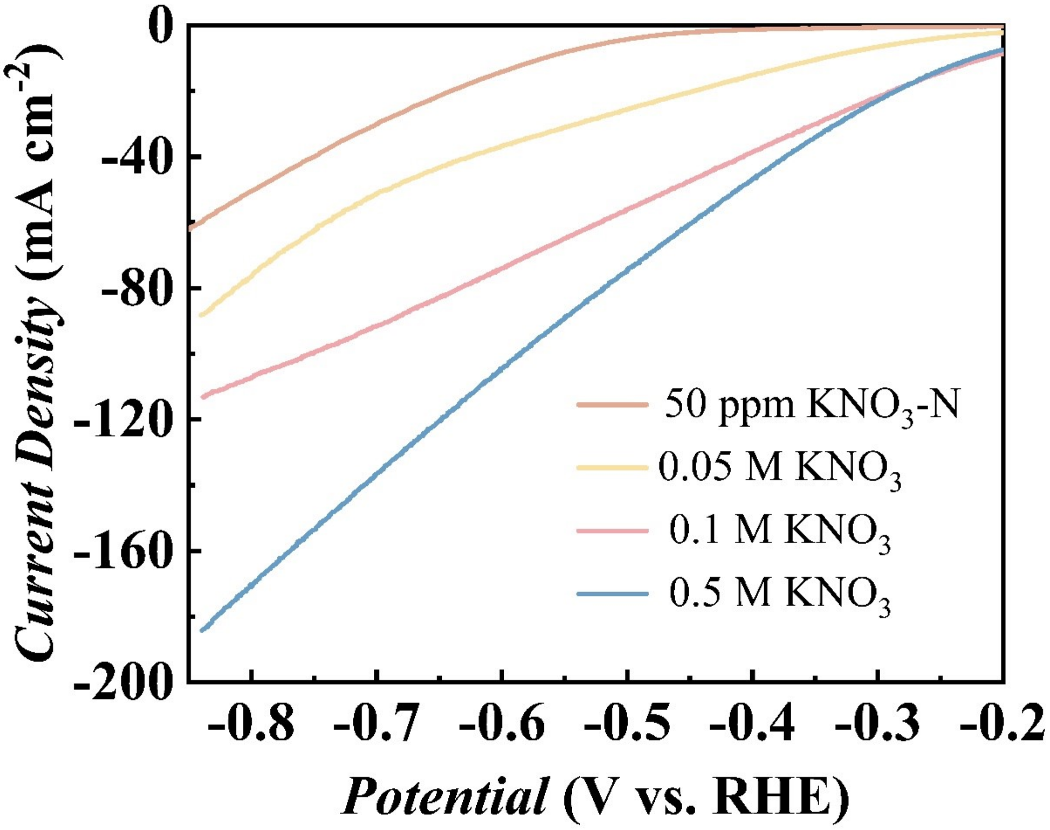

Fig.S8 LSVcurves of the Cu_3P-a for the NO_3RR. The measurements were conducted in 0.5 M K_2SO_4 electrolyte containing various concentrations of KNO_3 (50 ppm-N, 0.05 M, 0.1 M, and 0.5 M KNO_3)

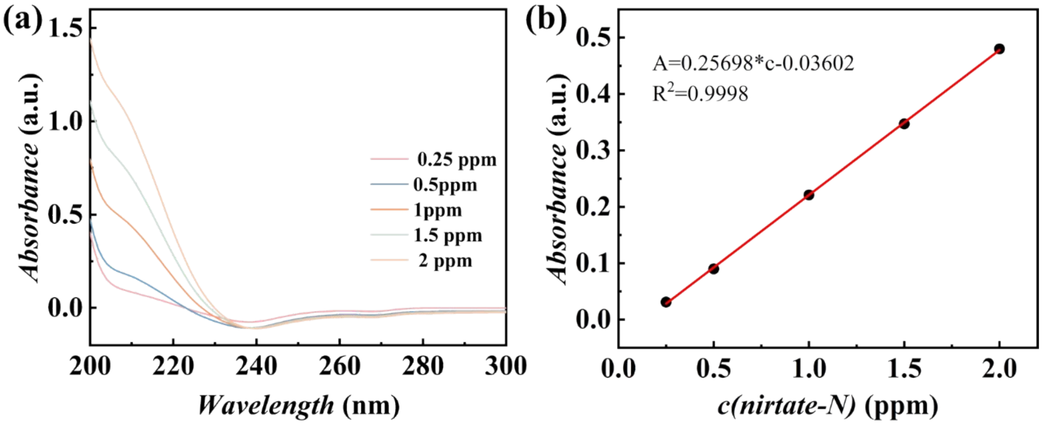

Fig. S9. UV-vis spectroscopy measurements of the concentration of nitrate. (a) UV-vis absorption spectra of solutions with different nitrate concentrations. (b) Calibration curve for NO_3^-colorimetric determination. The post-catalyzed electrolyte was diluted to ensure that the NO_3^-concentration in the test solution is within the linear range of the calibration curve.

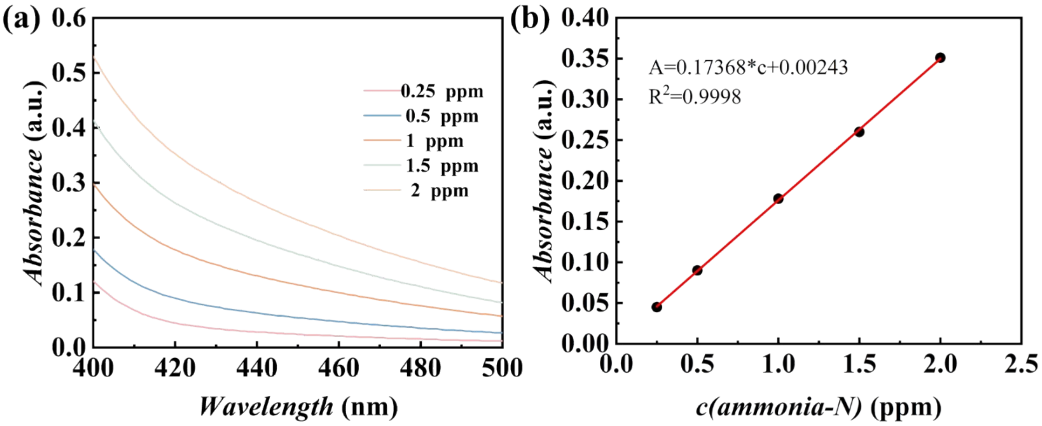

Fig. S10. UV-vis spectroscopy measurements of the concentration of ammonium with Nessler's reagent. (a) UV-vis absorption spectra of solutions with different ammonium concentrations. (b) Calibration curve for NH_3 colorimetric determination using Nessler's reagent. The post-catalyzed electrolyte was diluted to ensure that the ammonia concentration in the test solution is within the linear range of the calibration curve.