

Electronic Supplementary Information

Ambient Electrosynthesis of Urea with Nitrate and Carbon Dioxide over CuRu Alloying Catalyst

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1. Experimental Section

1.1. Chemicals and materials

Bacterial cellulose (BC) pellicle was obtained from Guilin Qihong Technology Co., Ltd., China. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and KNO_3 were purchased from China Sinopharm Chemical Reagent Co., Ltd. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, KNO_2 , NH_4Cl , sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99.0%), salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, 99.5%), NaOH (96.0%), sodium nitroferricyanide (III) dihydrate ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$, 99.0%), NaClO (available chlorine $\geq 5.0\%$), urea amidohydrolase, p-aminobenzenesulfonamide ($\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$, 95.0%), N-(1-naphthyl)ethylenediamine dihydrochloride ($\text{C}_{10}\text{H}_7\text{NHC}_2\text{H}_4\text{NH}_2 \cdot 2\text{HCl}$, 95.0%) and H_3PO_4 ($\geq 85\%$) were purchased from Aladdin (China). Commercial carbon cloth (CP, HCP331) was purchased from Shanghai Hesun Electric Co., Ltd.

1.2. Synthesis of Cu-CBC, CuRu-CBC and Ru-CBC

Bacterial cellulose (BC) was firstly frozen directly with liquid nitrogen, and then freeze-dried at $-75\text{ }^\circ\text{C}$ for 48 h. 1.0 g of pretreated BC, 1.0 mmol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 1.0 mmol of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were added to a beaker containing 200 mL of deionised water and macerated for 12 h. After washing with deionised water and freeze-drying, the products underwent heating to $360\text{ }^\circ\text{C}$ at a rate of $2\text{ }^\circ\text{C}/\text{min}$ for 2 h, followed by further heating to $700\text{ }^\circ\text{C}$ at a rate of $5\text{ }^\circ\text{C}/\text{min}$ for 3 h under an Ar atmosphere. Finally, the products were collected at room temperature. The CuRu alloy nanoparticles (denoted as CuRu-CBC) were obtained. As for Cu-CBC and Ru-CBC samples, the process of preparation was similar to that of CuRu-CBC. Specifically, for Cu-CBC (or

Ru-CBC), 1.0 g of pre-treated BC and 1.5 mmol of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (or 1.5 mmol of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$) were added to a beaker containing 200 mL of deionized water and macerated for 12 h. The subsequent preparation process was consistent with that for CuRu-CBC sample. The obtained samples were denoted as Cu-CBC (or Ru-CBC).

1.3. Material characterization

Powder X-ray diffraction (XRD) analysis was conducted on a PANalytical X'Pert diffractometer equipped with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) characterization were carried out on a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh-vacuum (UHV) chambers. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HR-TEM) images and scanning electron microscopy (SEM) elemental mapping were obtained with JEOL 2010, and a FEI Tecnai G2 F20, respectively. All UV-Vis absorption spectra were obtained by using a UV-Vis spectrophotometer (Shimadzu UV-2700). The specific surface area and pore size distribution of samples were analyzed by the automated gas sorption analyser (Micromeritics, ASAP2460).

1.4. Electrochemical measurements

Electrochemical measurements were performed at an electrochemical workstation (CH Instruments, Shanghai, China) with an H-type electrolytic cell separated by a Nafion 211 membrane. A three-electrode system equipped with CO_2 gas flow system was used. The working electrode was prepared as follows: 5 mg of catalyst sample was mixed with 980 μL of anhydrous ethanol and 20 μL of 5.0 wt.%

Nafion solution. The mixture was sonicated for 30 minutes to form a homogeneous catalyst ink. Subsequently, 200 μL of the catalyst ink was evenly deposited onto a 1×1 cm commercial carbon cloth and dried at room temperature. A 1×1 cm Pt mesh and Ag/AgCl (saturated KCl) electrodes served as the counter and reference electrodes, respectively. Before the activity test, CO_2 gas (99.99% purity) was bubbled through a 50 mL electrolyte solution of 0.1 M KNO_3 for 30 minutes to remove dissolved air. During the experiment, CO_2 gas was continuously supplied to the cathode chamber at a flow rate of 5 mL/min. The electrolyte in the cathode chamber was stirred at 400 rpm throughout the measurement. Potentials in this study were referenced to the reversible hydrogen electrode (RHE) scale, calculated using the following equation:

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

where $E_{\text{Ag/AgCl}}$ is the equilibrium potential under standard conditions, and $E^{\circ}_{\text{Ag/AgCl}} = 0.197 \text{ V}_{\text{vs. RHE}}$ at 25 $^{\circ}\text{C}$.

1.5 Determination of ammonia

The concentration of ammonia produced was detected using the indophenol blue method. Specifically, 1 mL of cathode electrolyte was taken and diluted to 10 mL with deionized water. Subsequently, the following solutions were prepared: Solution A comprised 10 g of sodium citrate, 10 g of salicylic acid, 50 mL of water, and 55 mL of 2 M NaOH, adjusted to 200 mL with water. Solution B consisted of 5 g of sodium nitrite ferrocyanide and 50 mL of water, mixed well. Solution C was prepared by mixing 5 mL of sodium hypochlorite stock solution with 45 mL of 2 M NaOH. To measure the ammonia concentration, 500 μL of Solution A, followed by 100 μL each

of Solutions B and C, were sequentially added to the sample. The absorbance at 697.5 nm was then measured using a UV-Vis spectrophotometer, and the ammonia concentration was determined using a calibration curve. The equation for calculating the NH₃ yield is as follows:

$$R(\text{NH}_3)(\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}) = \frac{c(\text{NH}_4^+ - \text{N})(\mu\text{g mL}^{-1}) \times V(\text{mL}) \times 17}{t(\text{h}) \times m(\text{mg}) \times 14}$$

where $c(\text{NH}_4^+ - \text{N})$ is the measured mass concentration of $\text{NH}_4^+ - \text{N}$; V is the electrolyte solution volume; t is the reaction time; 14 is the molar mass of $\text{NH}_4^+ - \text{N}$ atom; 17 is the molar mass of NH_3 molecules; m was the mass of catalysts.

The equation of Faradic efficiency:

$$\text{FE} (\%) = \frac{8 \times n (\text{NH}_3)(\text{mol}) \times F}{Q} \times 100\%$$

where F is the Faradic constant (96485.34); Q is the total charge during the electrolysis period.

1.6 Determination of urea

Urea was detected by urease decomposition method¹. The procedure involved taking 1 mL of the reacted cathode chamber electrolyte and adding 200 μL of urease solution (5 mg/mL) and 8.8 mL of deionized water. The mixture was heated at 37°C for 40 minutes. Subsequently, the concentration of ammonia was detected using the indophenol-orchid colorimetry method and recorded as C1. As a control, another 1 mL of the reacted cathode chamber electrolyte without urease was taken, and 9 mL of deionized water was added. The concentration of ammonia in this solution was also determined using the same experimental procedure and noted as C2. Since urease

decomposes 1 molecule of urea into 2 molecules of NH₃, the final concentration of urea was calculated as (C1 –C2)/2. The final yield of urea was determined using the following equation:

$$R(\text{urea})(\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}) = \frac{\frac{C1 - C2}{2} (\mu\text{g mL}^{-1}) \times V (\text{mL}) \times 60}{t (\text{h}) \times m (\text{mg}) \times 14}$$

Where C1,C2 represent the concentration of ammonia in the two tests, respectively; V is the electrolyte solution volume; t is the reaction time; 14 is the molar mass of NH₄⁺-Natom; 60 is the molar mass of urea molecules; m was the mass of catalyts.

The equation of Faradic efficiency:

$$\text{FE (\%)} = \frac{16 \times n (\text{urea})(\text{mol}) \times F}{Q} \times 100\%$$

where F is the Faradic constant (96485.34); Q is the total charge during the electrolysis period.

1.7Determination of nitrite-N

The color developer was prepared as follows: In a 500 mL beaker, 250 mL of water and 50 mL of phosphoric acid were combined. To this solution, 20 g of p-aminobenzene sulfonamide and 1 g of N-(1-naphthyl)-ethylenediamine dihydrochloride were dissolved. The solution was then transferred to a 500 mL volumetric flask and diluted to the mark with deionized water. For the analysis, 5 mL of the sample solution was taken and diluted to 10 mL with deionized water. Subsequently, 200 μL of the prepared color-developing reagent was added to the diluted sample. After 30 minutes, the absorbance at a wavelength of 540 nm was measured using a UV-visible spectrophotometer. The concentration of NO₂⁻ was determined by reference to a standard curve for NO₂⁻. The equation of NO₂⁻ yield:

$$R(\text{NO}_2^-)(\mu\text{g h}^{-1} \text{ mg}_{\text{cat}}^{-1}) = \frac{c(\text{NO}_2^- - \text{N})(\mu\text{g mL}^{-1}) \times V(\text{mL}) \times 46}{t(\text{h}) \times m(\text{mg}) \times 14}$$

where $c(\text{NO}_2^- - \text{N})$ is the measured mass concentration of $\text{NO}_2^- - \text{N}$; V is the electrolyte solution volume; t is the reaction time; 14 is the molar mass of $\text{NO}_2^- - \text{N}$ atom; 46 is the molar mass of NO_2^- molecules; m was the mass of catalysts.

The equation of Faradic efficiency:

$$\text{FE} (\%) = \frac{2 \times n(\text{NO}_2^-)(\text{mol}) \times F}{Q} \times 100\%$$

where F is the Faradic constant (96485.34); Q is the total charge during the electrolysis period.

1.8 Determination of CO and H₂

The amounts of CO and H₂ were quantitatively analyzed by gas chromatography (GC9790 Plus, Zhejiang Fuli Analytical Instruments Co., Ltd, China) measurements.

H₂ and CO standard curves were obtained using the external standard method. The equation of Faradic efficiency:

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

where F is the Faradic constant (96485.34); Q is the total charge during the electrolysis period; n is the amount of substance of H₂ or CO.

1.9 *In-situ* DEMS measurements

The intermediate products formed during the synthesis of urea were detected by online DEMS measurement. The Ag/AgCl and Pt wire electrodes were used as reference and counter electrodes, respectively. The working electrode was a mixture of ink containing 1 mg CuRu-CBC, 200 μL ethanol and 20 μL naphthol added dropwise to a 0.5*0.5 cm gold foil paper. The mass signals were collected during

electrochemical urea synthesis at -0.55 V (vs RHE) with 0.1 M KNO_3 as the electrolyte under continuous injection of CO_2 gas. The photo of the experimental instrument is shown in **Fig. S16**.

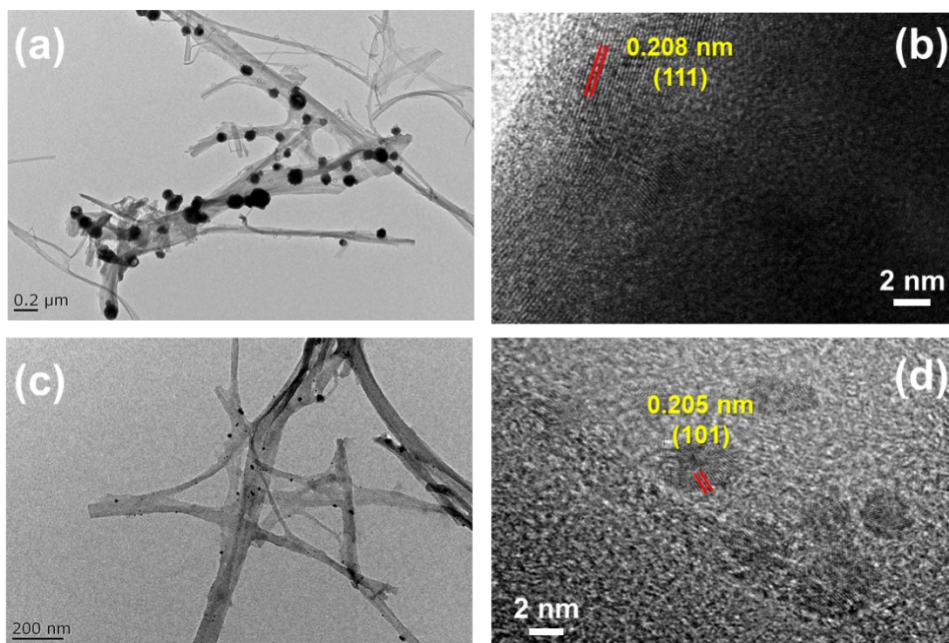


Fig. S1. (a) TEM and (b) HR-TEM images of Cu-CBC; (c) TEM and (d) HR-TEM images of Ru-CBC.

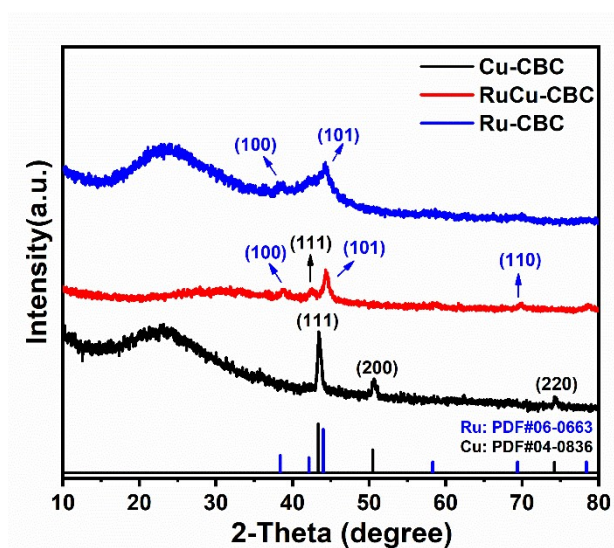


Fig. S2. XRD spectra of Cu-CBC, CuRu-CBC and Ru-CBC samples.

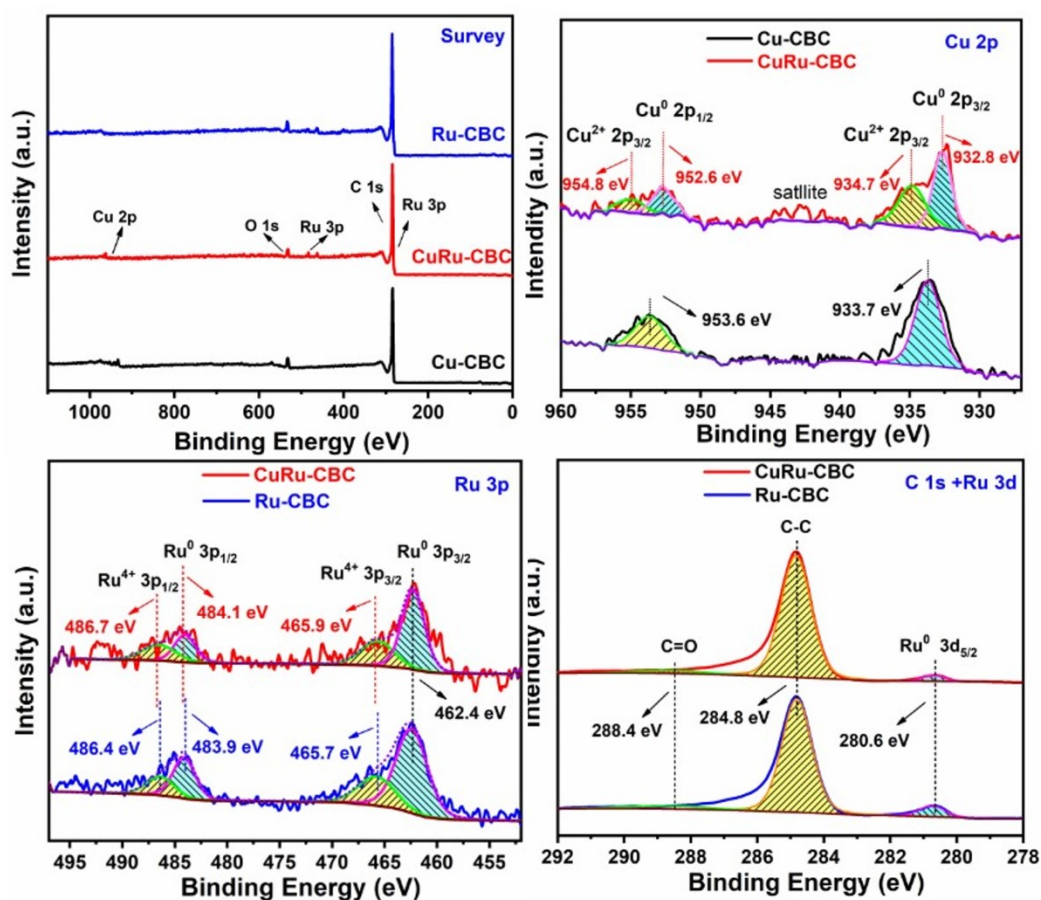


Fig. S3. (a) The surface survey XPS spectra of Cu-CBC, Ru-CBC and CuRu-CBC; The high-resolution XPS spectra of (b) Cu 2p, (c) Ru 3p and (d) C 1s + Ru 3d.

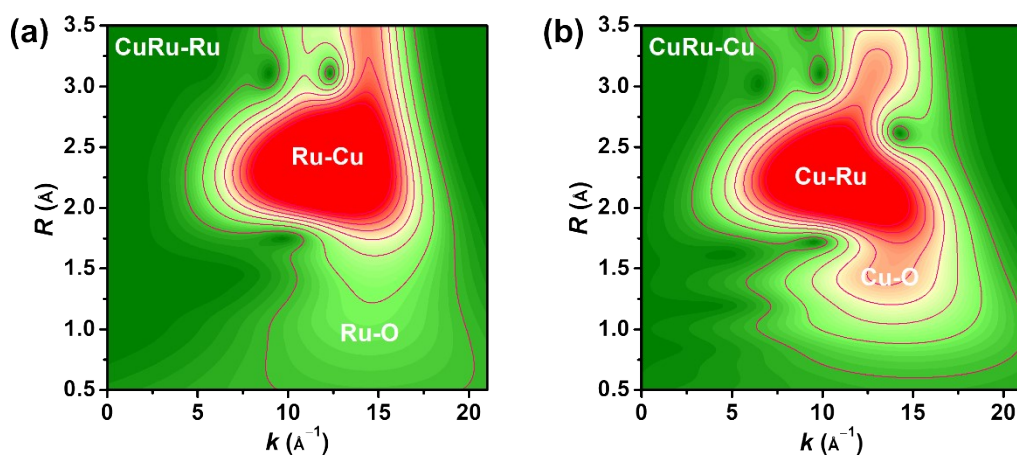


Fig. S4. Wavelet transform of (a) Ru *K*-edge and (b) Cu *K*-edge EXAFS spectra from CuRu-CBC samples.

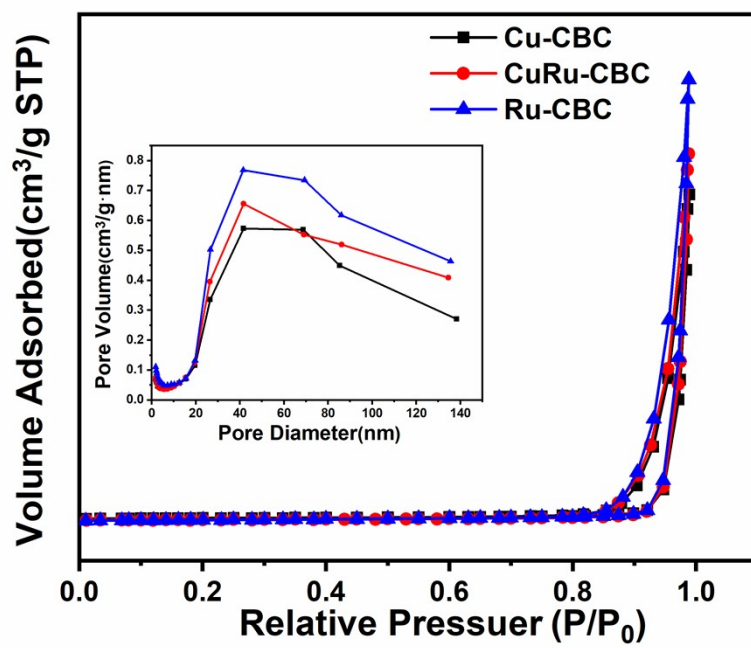


Fig. S5. N_2 adsorption-desorption isotherms for Cu-CBC, CuRu-CBC and Ru-CBC (inset shows the corresponding pore size distribution curves).

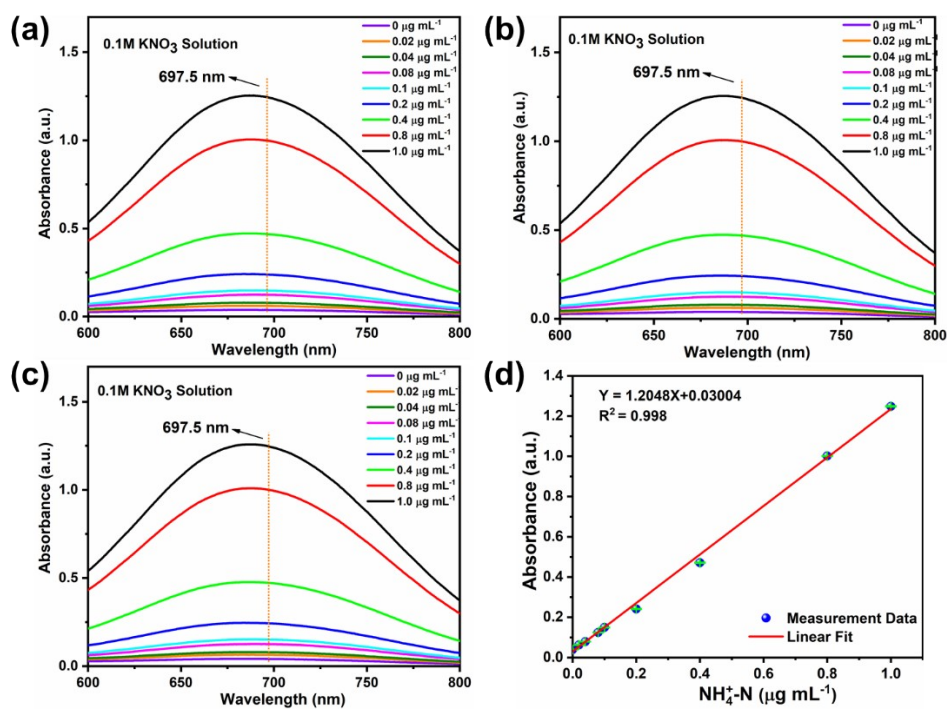


Fig. S6. (a)-(c) UV-Vis absorption spectra of various $\text{NH}_4^+\text{-N}$ concentrations for three repeated experiments. (d) Calibration curve used for estimation of $\text{NH}_4^+\text{-N}$ concentration.

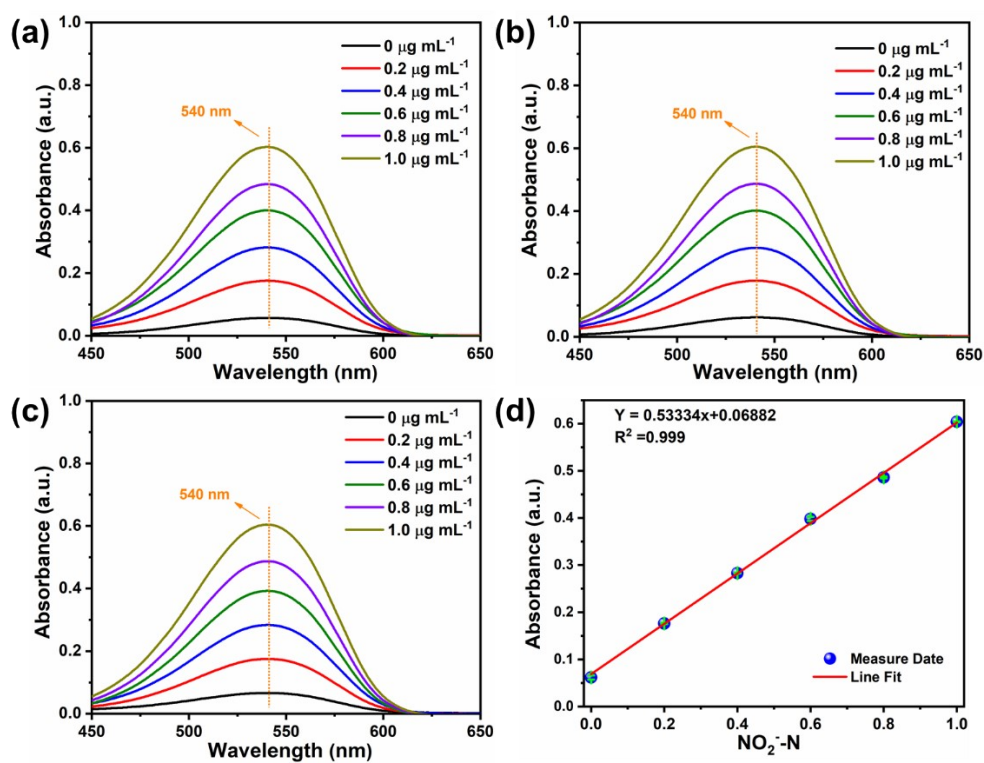


Fig. S7. (a)-(c) UV-Vis absorption spectra of various NO_2^- -N concentrations for three repeated experiments. (d) Calibration curve used for estimation of NO_2^- -N concentration.

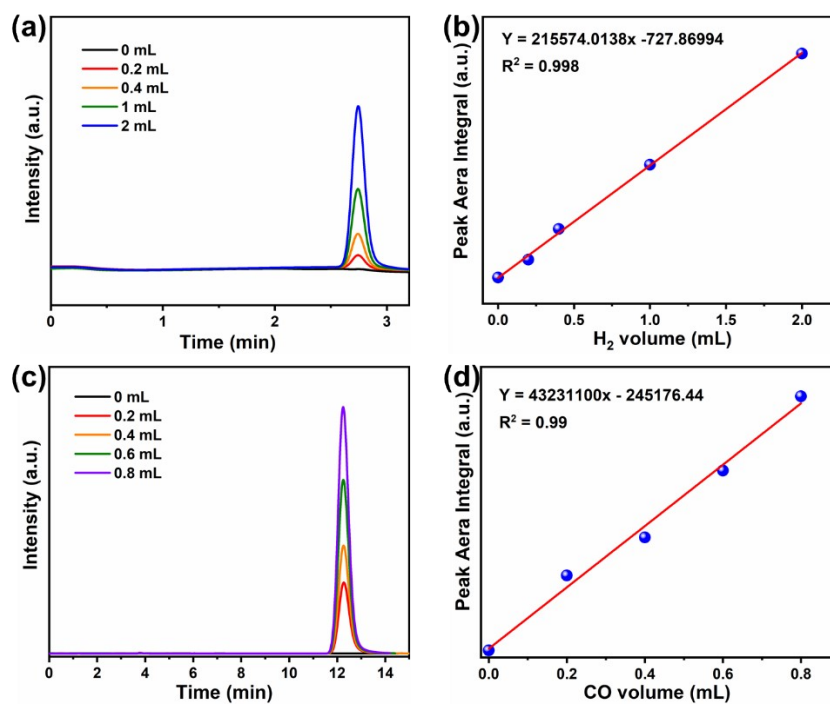


Fig. S8. (a) Chromatograms of the CO standards and (b) Corresponding calibration curve. (C) Chromatograms of the H₂ standards and (d) Corresponding calibration curve.

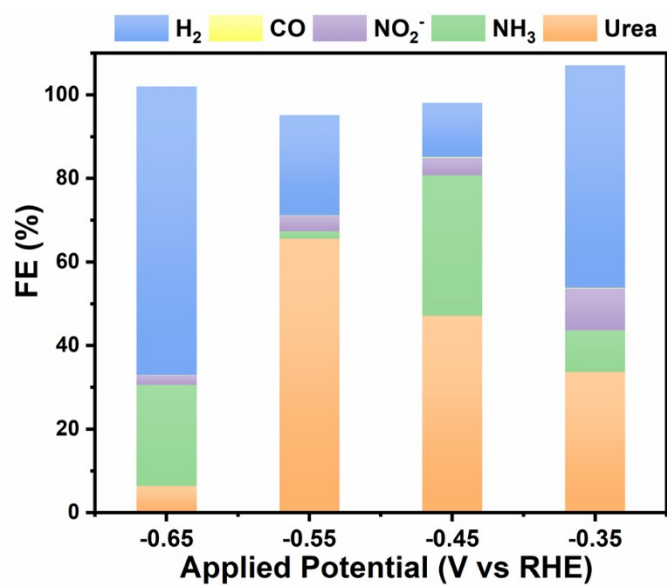


Fig. S9. FEs of all products distribution for CuRu-CBC at various potentials.

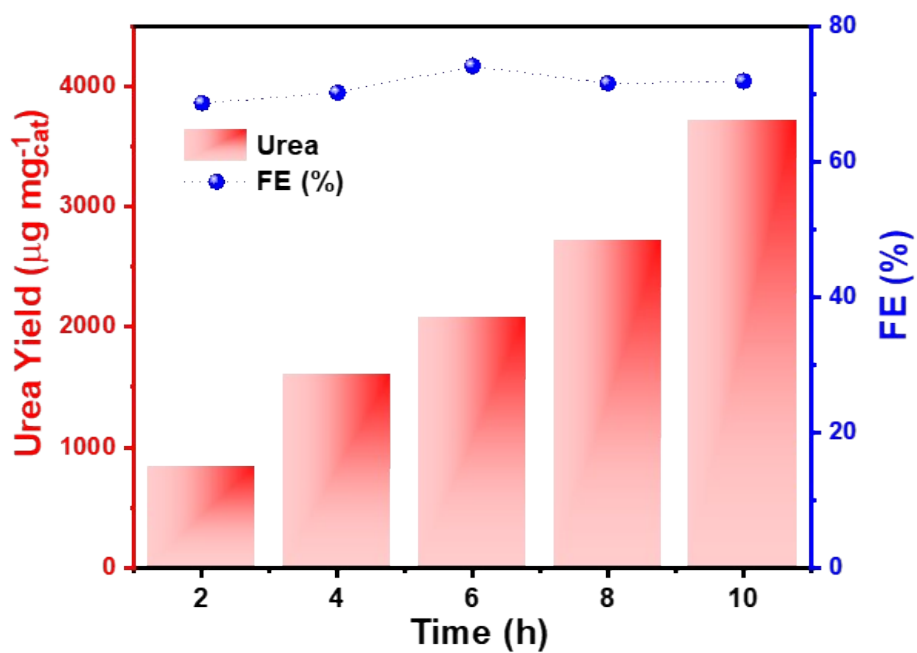


Fig. S10. The urea yield and FE for urea production over CuRu-CBC toward electrochemical coupling NO₃⁻ reaction time at -0.55 V (vs. RHE).

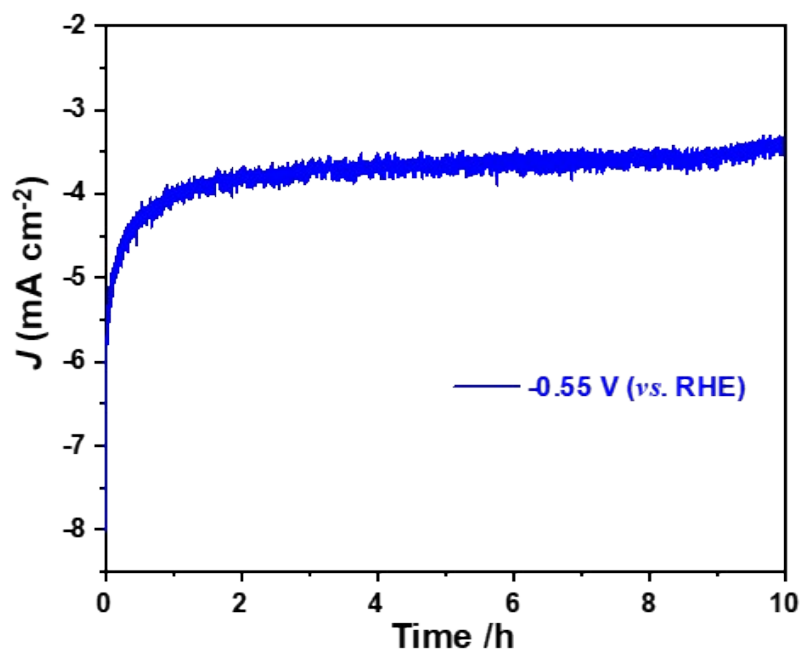


Fig. S11. Stability test of CuRu-CBC at -0.55 V (vs. RHE).

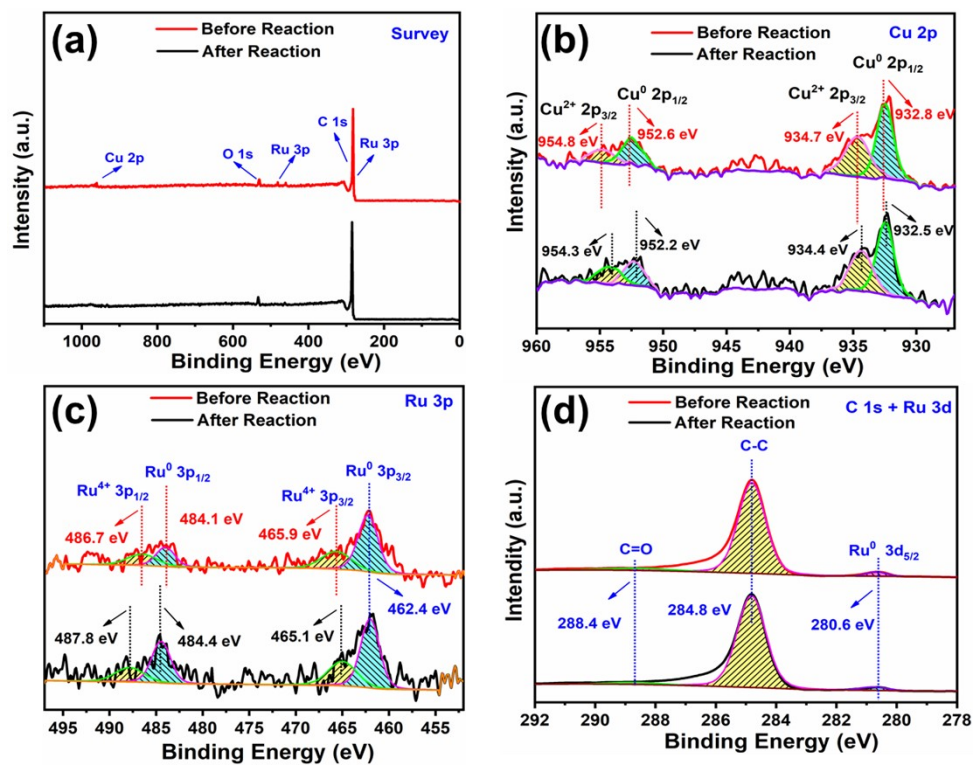


Fig. S12. The high-resolution XPS spectra of (b) Cu 2p, (c) Ru 3p and (d) C 1s + Ru 3d before and after reaction.

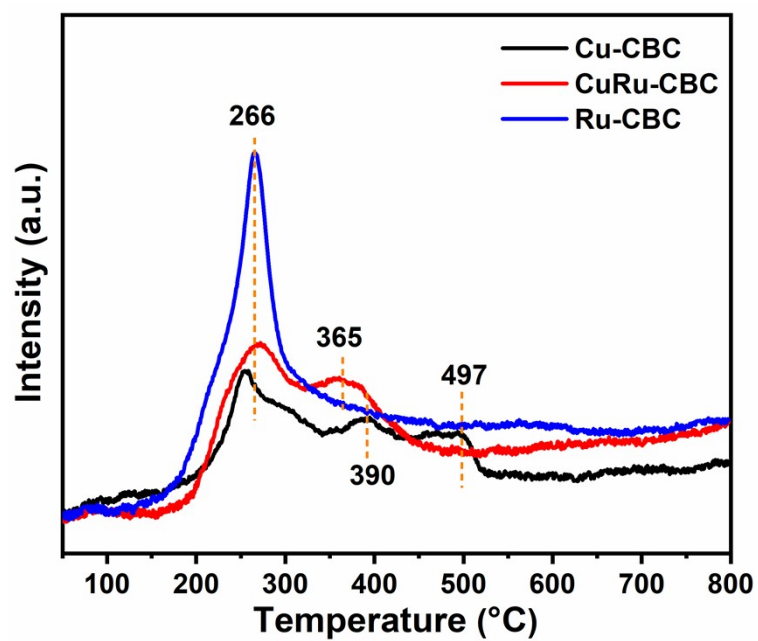


Fig. S13. CO₂-TPD spectra of Cu-CBC, CuRu-CBC and Ru-CBC.

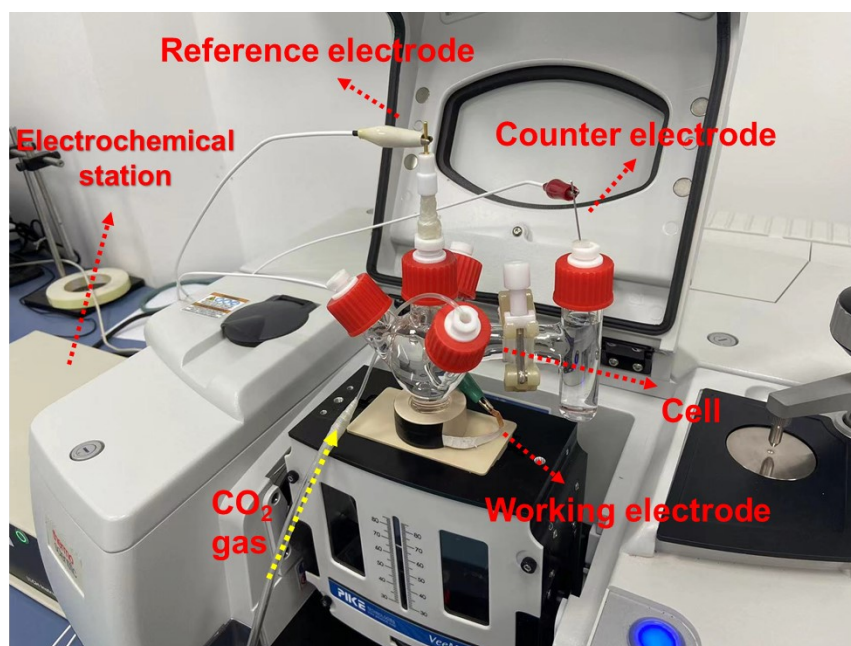


Fig. S14. The experimental setup for the *in-situ* ATR-SEIRAS measurements.

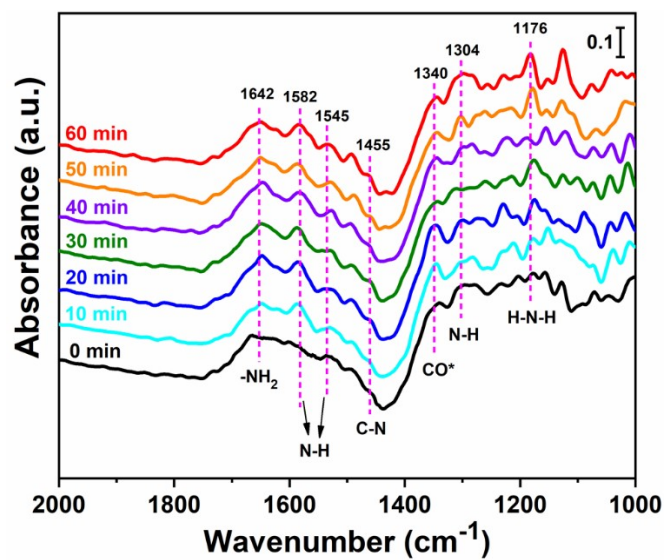


Fig. S15. *In-situ* ATR-SEIRAS spectra of CuRu-CBC at -0.55 V (vs. RHE) over a 60 min time period.

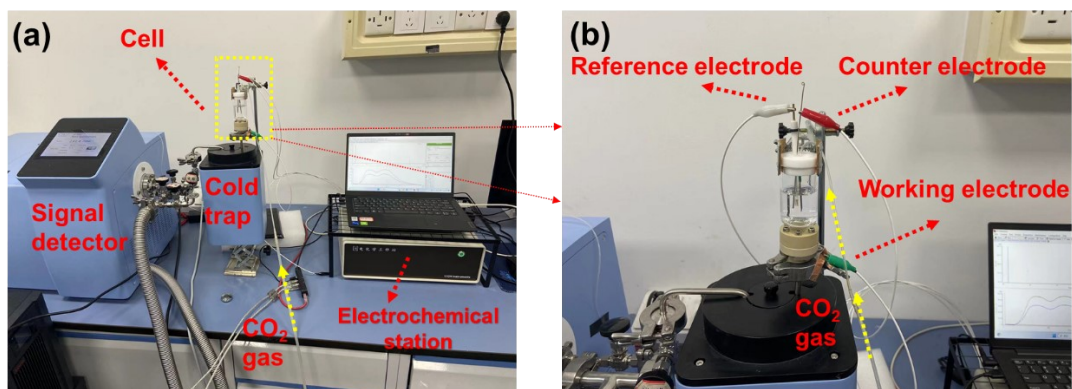


Fig. S16. Photograph of (a) differential electrochemical mass spectrometer and (b) DEMS cell.

Table. S1. Physicochemical properties of the prepared CuRu-CBC, Cu-CBC and Ru-CBC catalysts

Entry	Catalysis	Cu wt.%	Ru wt.%
1	Cu-CBC	3.43	0
2	CuRu-CBC	2.54	1.73
3	Ru-CBC	0	4.49

Table. S2. Comparison of electrocatalytic performance of CuRu-CBC toward urea synthesis with previously reported catalysts

Catalyst	Eleetrolyte	Potential (V vs RHE)	Yield rate ($\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$)	FE (%)	Ref.
In(OH) ₃ -S	0.1 M NaNO ₃ +CO ₂	-0.4	533.1	53.4	2
F-CNT-300	0.1 M KNO ₃ +CO ₂	-0.65	381.6	18	3
V _O -InOOH	0.1 M KNO ₃ +CO ₂	-0.5	92.5	51	4
CoRuN ₆	0.1 M KNO ₃ +CO ₂	-0.6	538.8	25.31	5
Cu/ZnO	0.1 M KNO ₃ +CO ₂	-0.3	192	37.4	6
Single-atom	0.1 M KNO ₃	-1.5	265.6 ± 13.3	26.4	7

Co/TiO ₂	+0.1 M PBS+CO ₂				
Graphene- In ₂ O ₃	0.1 M KNO ₃ + 0.1 M KHCO ₃ +CO ₂	-0.35	357.47	10.46	8
CuWO ₄	0.1 M KNO ₃ +CO ₂	-0.2	98.5 ± 3.2	70.1 ± 2.4	9
Ru-Pd/WO ₃ /MXene	0.5 M NaNO ₃ /NaHCO ₃ + N ₂ +CO ₂	-0.6	227	23.7	10
Bi ₂ Se ₃	0.1 M KNO ₃ +CO ₂	-0.4	276	32	11
CuRu-CBC	0.1 M KNO₃ + CO₂	-0.55	394.85 ± 16.19	68.94 ± 3.05	This work

Table. S3. Physicochemical properties of CuRu-CBC catalysts before and after reaction

Entry	Catalysis	Cu wt.%	Ru wt.%
1	CuRu-CBC(Fresh)	2.54	1.73
2	CuRu-CBC(Used)	2.52	1.66

Notes and references

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- 2 C. Lv, et al., *Nat. Sustain.*, 2021, **4**, 868-876.
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- 10 B. Govindan, et al., *ACS Sustain. Chem. Engin.*, 2024, **12**, 8174-8187.
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