Electronic Supplementary Information for

Urea synthesis via electrocatalytic C-N coupling of CO_2 and nitrate on oxygen-vacancy-rich Co_3O_4-CuO heterostructure nanowires

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Experimental section

Materials and chemicals

All the chemicals and reagents used in this study were of analytical grade and employed without undergoing any supplementary purification steps. Cu foam, acetone (C_3H_6O), KNO_3, potassium nitrate-^{15}N ($K^{15}NO_3$-^{15}N), $KHCO_3$, urea (CH_4N_2O), NH_4F, $Co(NO_3)_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, ethanol, and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of Co_3O_4-CuO/CF

Initially, a piece of Cu foam with area of 2×4 cm^2 was immersed in a 30 mL aqueous solution containing 5 mmol of $Co(NO_3)_2{\cdot}6H_2O$, 5 mmol of urea, 400 mg of NH_4F and 2 mmol of $CuCl_2{\cdot}2H_2O$. Subsequently, the mixture was poured into a 50 mL Teflon-lined reactor and heated to 120 °C for 12 h. Then, the precursor was rinsed with purified water and subsequently dried at a temperature of 50 °C within an oven. Ultimately, the Co_3O_4-CuO/CF was synthesized through calcination in air atmosphere at 300 °C for 60 min. For comparison, the CuO NWs were grown on Cu foam (CuO/CF) under the similar conditions without the addition of $Co(NO_3)_2{\cdot}6H_2O$. For comparison, the Co_3O_4 NWs were grown on Cu foam (Co_3O_4/CF) under the similar conditions without the addition of $CuCl_2{\cdot}2H_2O$.

Characterization

The morphology and microstructure of catalysts was examined using scanning electron microscopy (SEM, ZEISS Gemini 500) and transmission electron microscopy (TEM, JEOL JEM-2100F). The crystallographic properties were identified through X-ray diffraction equipment (XRD, X'Pert PRO MPD). The chemical composition and states of the catalysts were elucidated by X-ray photoelectron spectroscopy (XPS, ULVAC PHI Quantera). Electron paramagnetic resonance (EPR, Bruker EMX

PLUS) was employed to assess the presence of oxygen vacancies within the catalysts.

Electrochemical measurements

All electrochemical experiments were performed at room temperature using a three-electrode setup within a sealed H-cell on a CHI 760E electrochemical workstation. Co_3O_4-CuO/CF sample with dimensions of 1×1 cm^2 served as the working electrode. Meanwhile, an Ag/AgCl electrode and a carbon rod acted as the reference electrode and the counter electrode, respectively. Prior to the electrochemical experiments, the electrolyte solution (0.1 M KNO_3) was saturated with CO_2 for 30 min. In the process of co-reducing nitrate and CO_2, CO_2 was continuously introduced into the electrolyte at a flow rate of 20 mL min^{-1}. The individual CO_2RR tests were executed in a CO_2-saturated 50 mM $KHCO_3$ solution with a continuous CO_2 feed, while the NO_3RR tests were performed in an Ar-saturated 50 mM KNO_3 solution with persistent Ar supply. All potentials were normalized with the reversible hydrogen electrode ($E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + 0.197$). Gas chromatography was employed to identify the gaseous products, while colorimetric analysis using an ultraviolet-visible (UV-vis) spectrophotometer was utilized to quantify the liquid phase products.

Product quantification

The gaseous products (CO, CH_4, C_2H_4 and H_2) of the electrocatalytic co-reduction of CO_2 and NO_3^- were quantified by gas chromatograph. A thermal conductivity detector (TCD) was used to quantify H_2, and a flame ionization detector (FID) equipped with a methanator was used to quantify CO, CH_4, and C_2H_4. After elution of CO, CO_2 and CH_4, backwash non-methylalkanes. Non-methylalkanes are eluted as a peak. Carbon compounds are converted to methane using a methanator set at 272 ± 1 °C.

Determination of urea: Dilute the electrolyte after 40 microliters potentiostatic test to 1 mL with water, and then determine with diacetyl monoxime method.[1]

Reagent A: Mix 10 mL of concentrated phosphoric acid with 30 mL of concentrated sulfuric acid and 60 mL of ultra-pure water, and then dissolve 10 mg of ferric chloride in the above solution.

Reagent B: 0.5g diacetylmonoxime and 10 mg thiosemicarbazone were dissolved in ultra-pure water and diluted to 100 mL.

Diacetyl monoxime method: Add 2 mL of A and 1 mL of B to 1 mL of urea-containing solution and mix vigorously. The solution was then heated to 110 °C and kept at this temperature for 15 min. Cool to 25 °C. The color was developed by ultraviolet-visible spectrophotometer. Absorbance is recorded at 525 nm.

The concentration of ammonia was determined by UV-vis spectrophotometry and indophenol blue method.[2] Specifically, 2.0 mL 1 M sodium hydroxide aqueous solution containing 5% sodium citrate and 5% salicylic acid, 1.0 mL 0.05 M sodium hypochlorite aqueous solution and 0.2 mL sodium ferricyanide aqueous solution containing 1% mass fraction were successively added to 2.0 mL electrolyte obtained from the cathode chamber, and the above solutions were mixed evenly. The absorbance was measured at 662 nm after 2 h reaction in a dark environment.

The concentration of NO_2^- was determined by the N-(-1-naphthyl) ethylenediamine dihydrochloride method.[3] Specifically, 0.4 g sulfonamide, 0.02 g naphthylenediamine hydrochloride and 1 mL phosphoric acid were dissolved in 5 mL water as the chromogenic agent, and the diluted electrolyte of 5 mL was mixed with 0.1 mL chromogenic agent. After 20 min of chromogenic development, the chromogenic agent was developed by UV-vis at 540 nm.

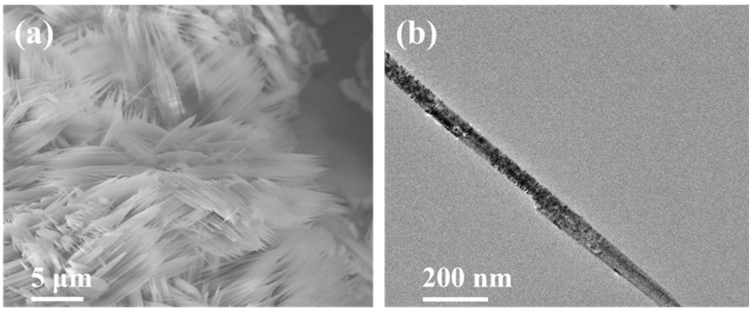


Fig. S1 SEM (a) and TEM (b) images of Co-Cu(OH)F/CF.

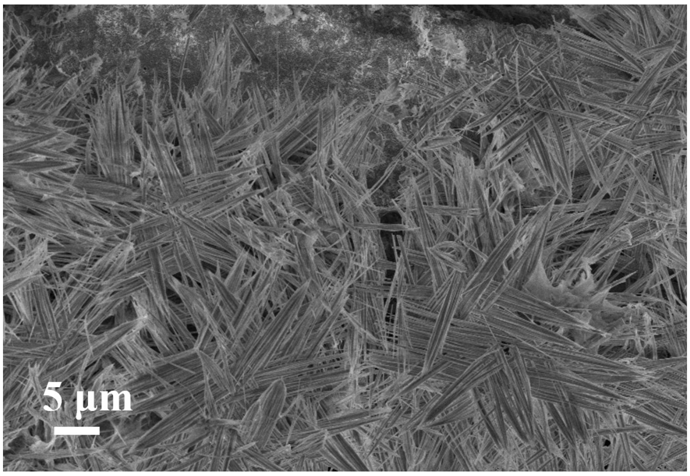


Fig. S2 SEM image of CuO/CF.

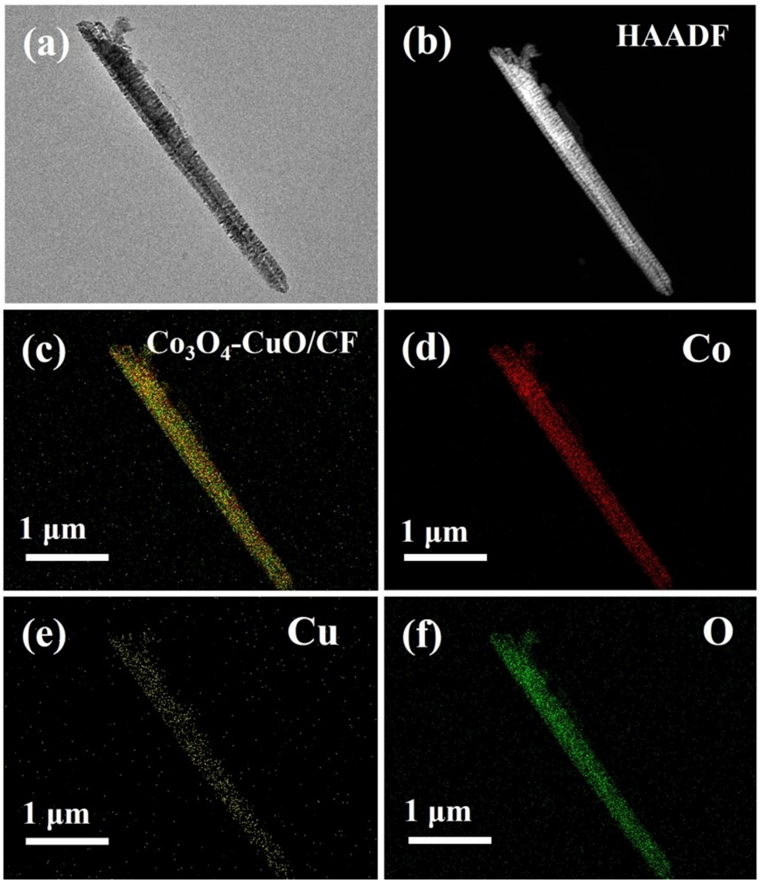
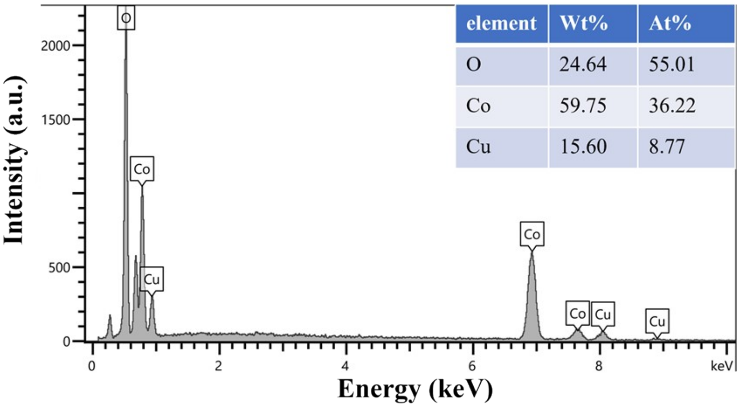


Fig. S3 TEM image (a) and EDS mapping images (b-f) of Co_3O_4-CuO-NW.



element	Wt%	At%
O	24.64	55.01
Co	59.75	36.22
Cu	15.60	8.77

Fig. S4 EDS spectrum of Co_3O_4-CuO NWs.

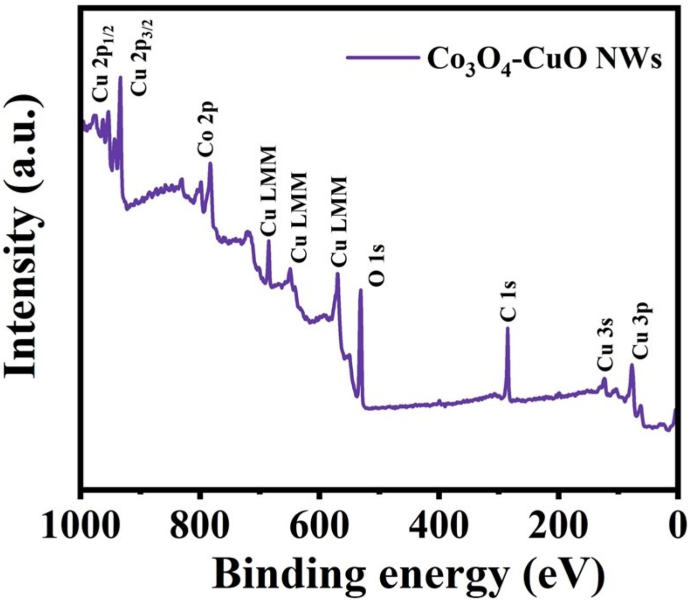


Fig. S5 XPS survey spectrum of Co_3O_4-CuO NWs.

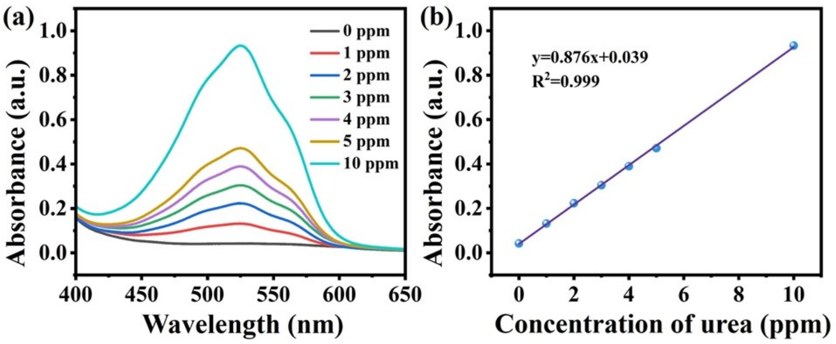


Fig. S6 UV-vis spectra and calibration curves for urea quantification.

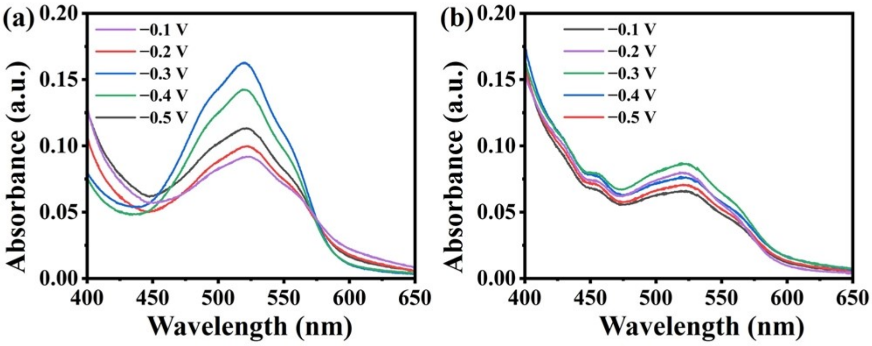


Fig. S7 UV-vis spectra (a) Co_3O_4-CuO/CF and (b) CuO/CF at different potentials for 1 h CO_2-saturated 0.1 M KNO_3.

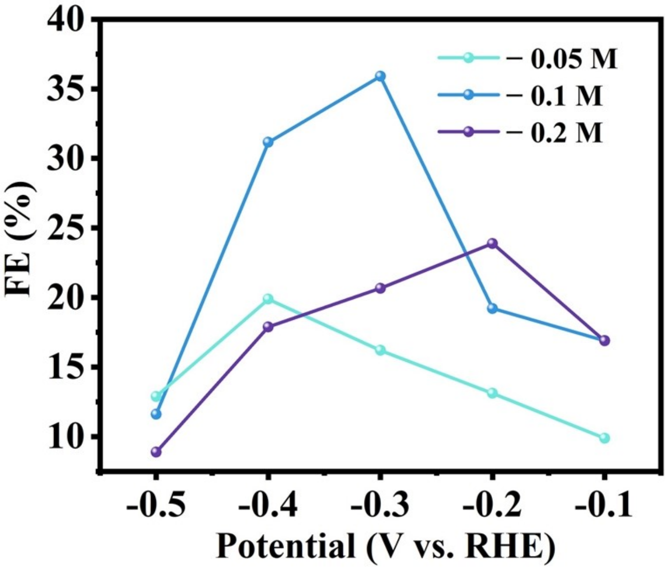


Fig. S8 Faraday efficiency of urea formation at different concentrations of NO_3^- (0.05, 0.1 and 0.2 M) over Co_3O_4-CuO/CF.

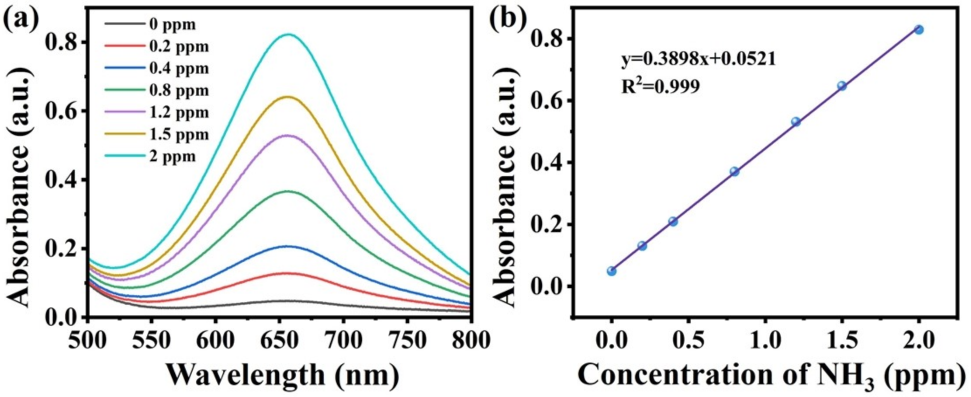


Fig. S9 UV-vis spectra and calibration curves for NH_3 quantification.

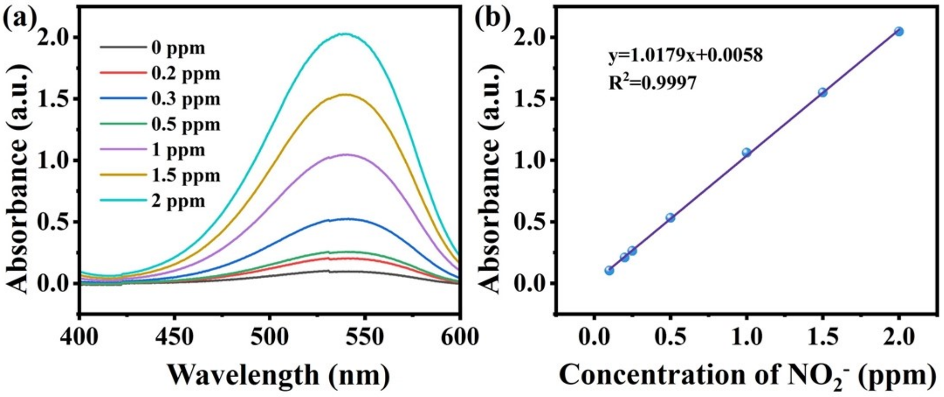


Fig. S10 UV-vis spectra and calibration curves for NO_2^- quantification.

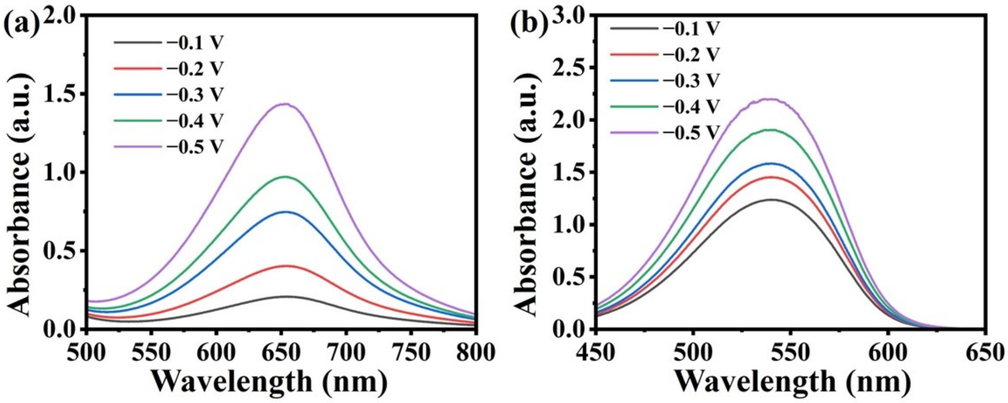


Fig. S11 The UV-vis spectra of electrolysis solutions at different potentials for the detection of (a) NH_4^+ and (b) NO_2^- over Co_3O_4-CuO/CF.

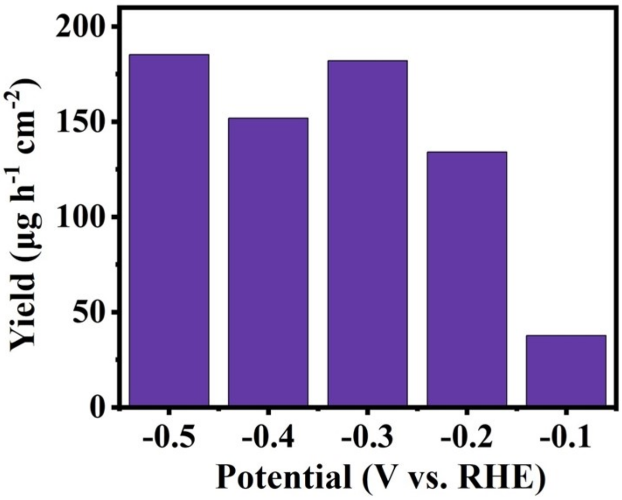


Fig. S12 The NH_4^+ yields of Co_3O_4-CuO/CF at different potentials.

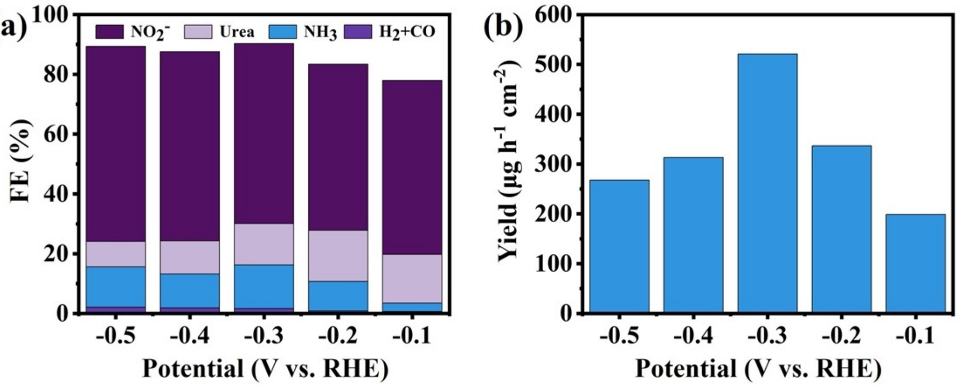


Fig. S13 The FE (a) and yield (b) of urea formation at different potentials over CuO/CF.

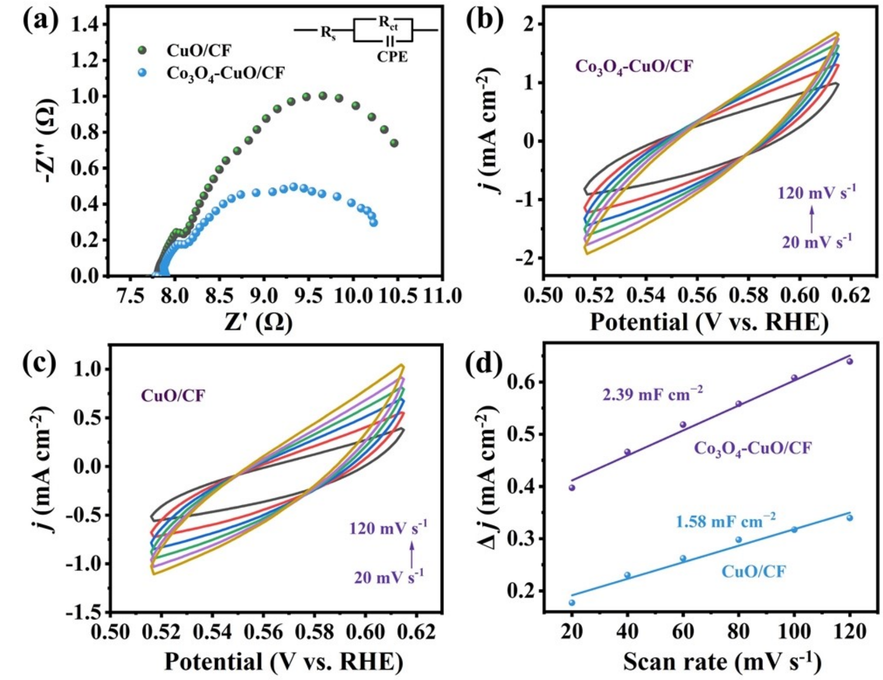


Fig. S14 (a) EIS spectra of CuO/CF and Co_3O_4-CuO/CF. CV curves of (b) Co_3O_4-CuO/CF and (c) CuO/CF at various scan rates, and (d) the corresponding capacitances.

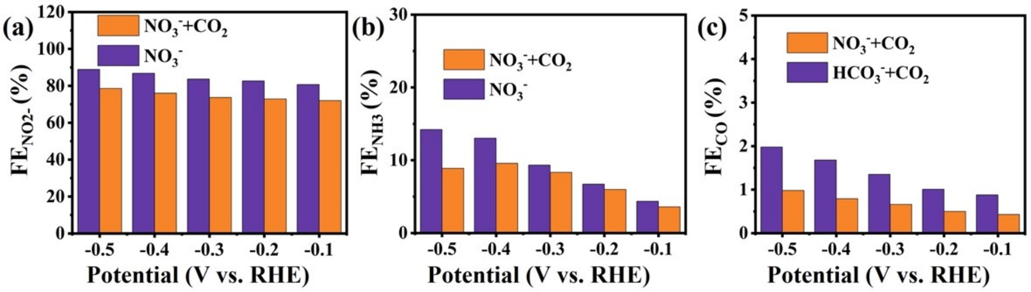


Fig. S15 (a) FE values of formation of NO_2^- for CuO/CF in CO_2-saturated 0.1 M KNO_3 solution and 0.1 M KNO_3 solution. (b) FE values of the formation of NH_3 for CuO/CF in CO_2-saturated 0.1 M KNO_3 solution and 0.1 M KNO_3 solution. (c) FE values of the formation of CO for CuO/CF in CO_2-saturated 0.1 M KNO_3 solution and CO_2-saturated 0.1 M $KHCO_3$ solution.

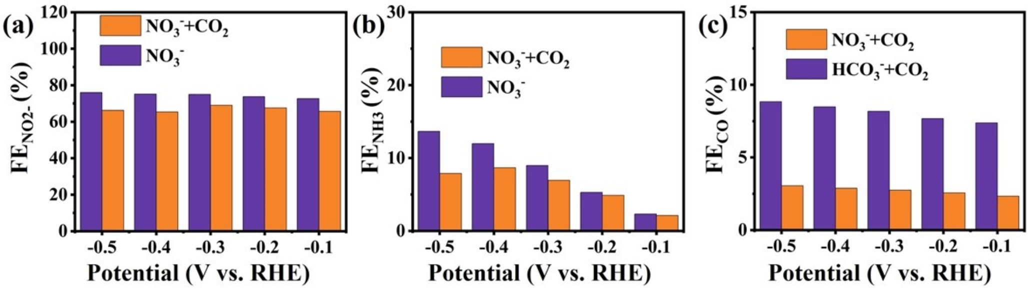


Fig. S16 (a) FE values of formation of NO_2^- for Co_3O_4/CF in CO_2-saturated 0.1 M KNO_3 solution and 0.1 M KNO_3 solution. (b) FE values of the formation of NH_3 for Co_3O_4/CF in CO_2-saturated 0.1 M KNO_3 solution and 0.1 M KNO_3 solution. (c) FE values of the formation of CO for Co_3O_4/CF in CO_2-saturated 0.1 M KNO_3 solution and CO_2-saturated 0.1 M $KHCO_3$ solution.

Table S1. Electrocatalytic urea synthesis from N–integrated CO_2 reduction.

N-source	**Catalyst**	**Urea Yield**	**FE_{urea} (%)**	**Ref**
NO_3^-	**Co_3O_4-CuO/CF**	**1.12 mg cm^{-2} h^{-1}**	**35.89**	**This Work**
	Co–O–C	2704.2 μg h^{-1} mg^{-1}	31.4	4
	Cu-HATNA	1.46 g h^{-1} g^{-1}	32.3	5
	Ti-DHTP	348.0 μg h^{-1} cm^{-2}	21.75	6
	Co_3O_4	3361 μg h^{-1} mg^{-1}	26.3	7
	Cu@Zn	7.29 μmol cm^{-2} h^{-1}	9.28	8
	AuPd	204.2 μg h^{-1} mg^{-1}	15.6	9
	Vo–InOOH	592.5 μg h^{-1} mg^{-1}	51	10
NO_2^-	AuCu nanofibers	3,88.6 mg h^{-1} mg^{-1}	24.7	11
	Cu−TiO_2	20.8 μmol h^{-1}	43.1	12
N_2	CuIII−HHTP	7.780 mmol h^{-1} g^{-1}	23.09	13
	PdCu/TiO_2	3.36 mmol g^{-1} h^{-1}	8.92	14

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