Electronic Supplementary Material

Synergistic coupling of carbon dioxide and nitrate for efficient electrosynthesis of urea using Cu-doped CeO_2 nanorods

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Faradaic Efficiencies Calculation

Faradaic efficiency serves as a quantitative measure of the selectivity of an electrochemical reaction, indicating the proportion of electrons utilized for the formation of a specific product. It is calculated using the following equation (1):

$$\textit{Faradaic efficiency(100\%)}= \frac{n_p \times n_e \times F}{Q} \times 100\% \quad (1)$$

In this equation, np represents the number of moles of the target product. The products considered in our study encompass urea, NH_3, CO, and H_2. The parameter ne denotes the number of electrons involved in the electrochemical process required to generate one mole of the specific product. Specifically, for urea synthesis, ne is 16, reflecting the complex multi - electron transfer process. In the case of NH_3 production, ne is 8, while for CO and H_2 formation, ne is 2. The Faraday constant, F, a fundamental physical constant, is defined as F=96485.3 C mol^{-1}, which relates the charge carried by one mole of electrons. The variable Q represents the total electric charge transferred during the entire reaction time. By measuring Q and knowing the values of np, ne, and F, we can accurately calculate the Faradaic efficiency, providing insights into the reaction's selectivity towards different products.

Product Yield Rates Calculation

The product yield rate is another important parameter that reflects the efficiency of product formation over time. It is calculated using equation (2):

$$R= (c \times V)/(t \times m) \quad (2)$$

Here, c represents the concentration of the product, which is measured in micrograms per milliliter (μg mL^{-1}). This parameter is determined through appropriate analytical techniques, such as spectroscopic methods or chromatographic analyses, depending on the nature of the product. The volume of the electrolyte, V, is maintained at a fixed value of 30 mL in our experimental setup to ensure the consistency of the reaction environment. The electrolysis time, t, is measured in hours (h), representing the duration for which the electrochemical reaction is allowed to proceed. Finally, m stands for the mass loading of the catalyst, expressed in milligrams (mg). The catalyst plays a vital role in facilitating the electrochemical reaction, and its mass loading can significantly influence the reaction rate and product yield. By using this equation, we can evaluate the productivity of the electrochemical system under different experimental conditions.

In conclusion, the accurate calculation of Faradaic efficiencies and product yield rates provides valuable information for optimizing electrochemical reactions and understanding the underlying reaction mechanisms.

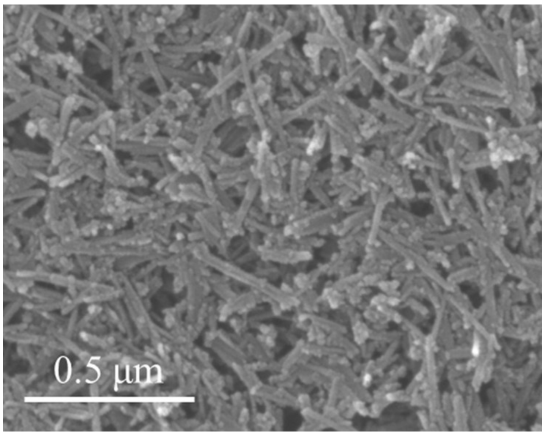

Fig. S1 SEM image of CeO_2.

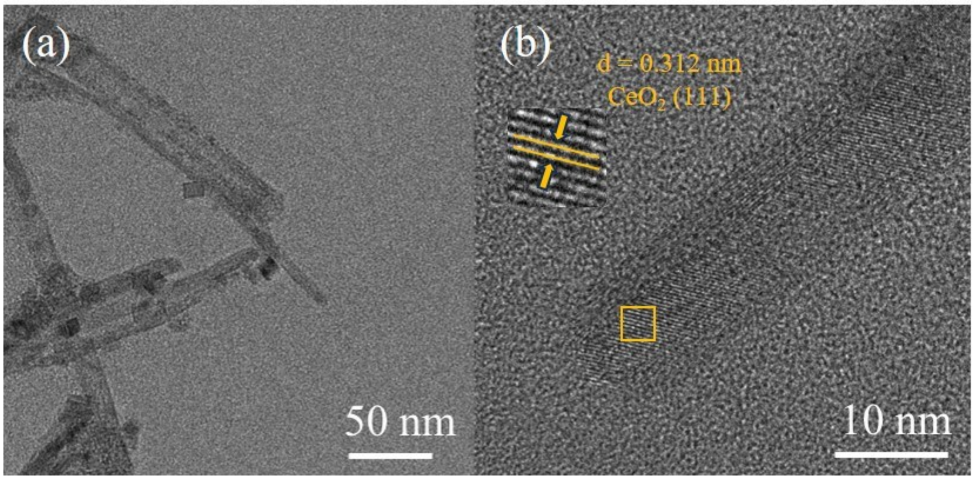

Fig. S2 TEM images of CeO_2.

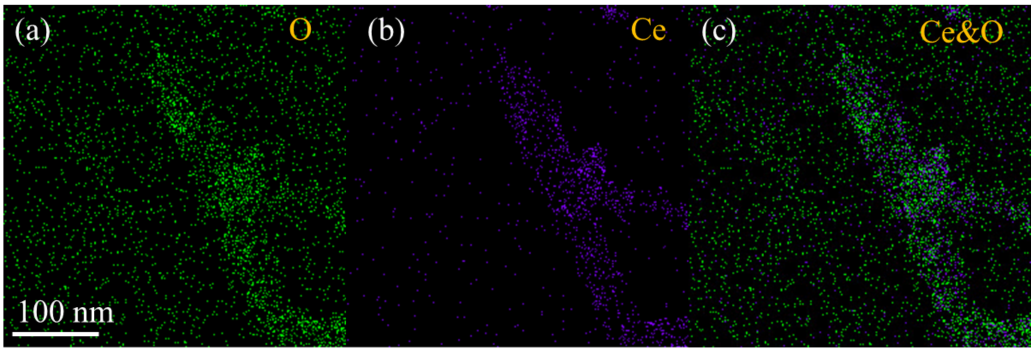

Fig. S3 EDS mapping images of CeO_2

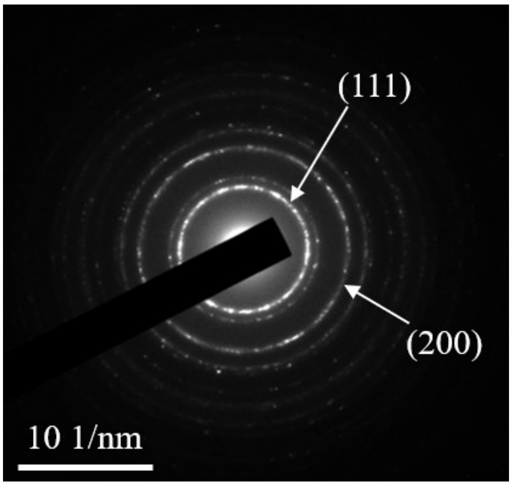

Fig. S4 The corresponding SAED pattern of the Cu-CeO$_2$ catalyst.

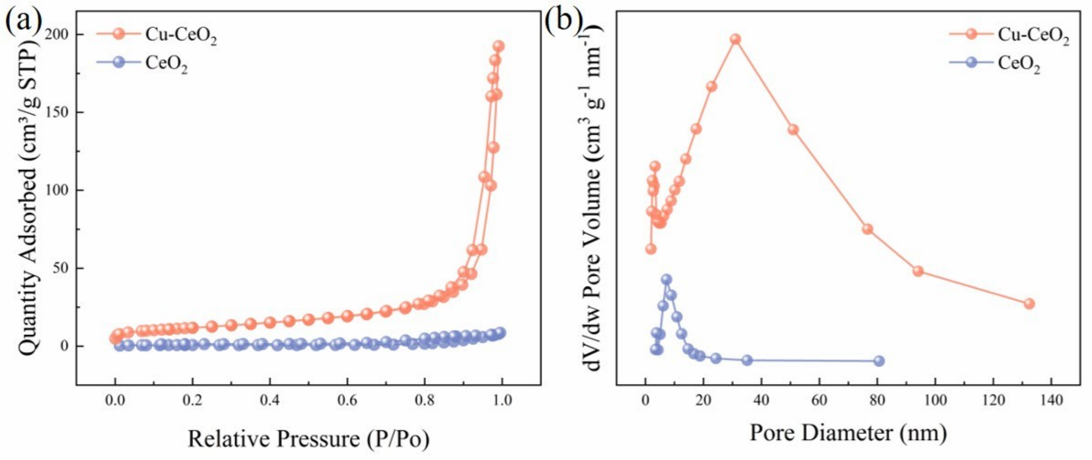

Fig. S5 Nitrogen adsorption-desorption isotherms (a) and the pore size distribution curves (b).

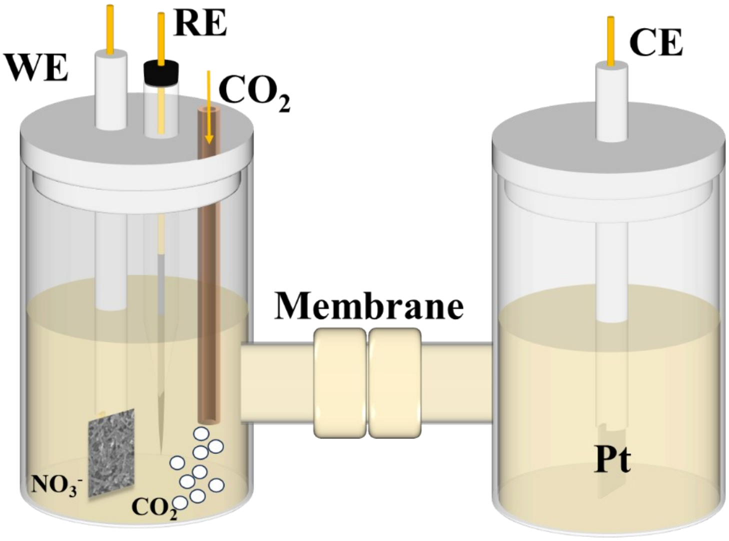

Fig. S6 Illustration of the three-electrode system in H-type cell.

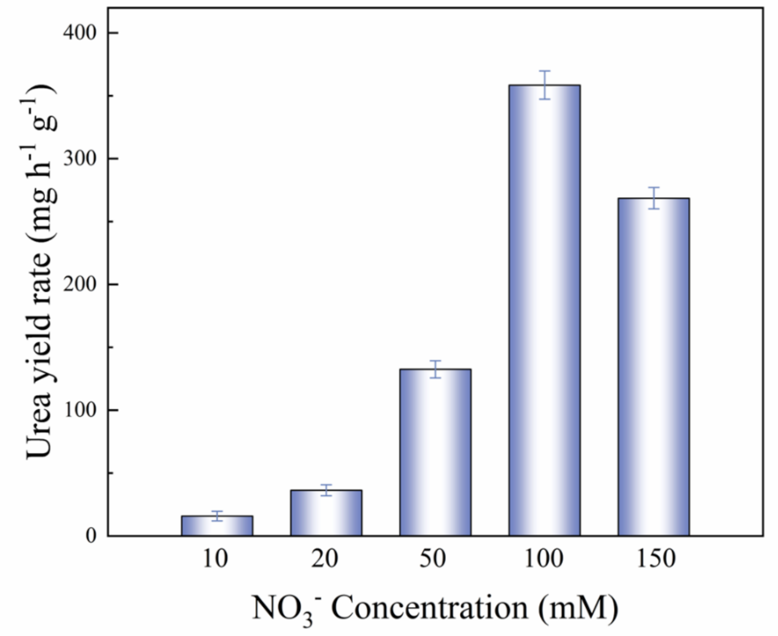

Fig. S7 The effect of different concentrations of nitrate on the yield of urea synthesis on Cu-CeO$_2$ catalyst.

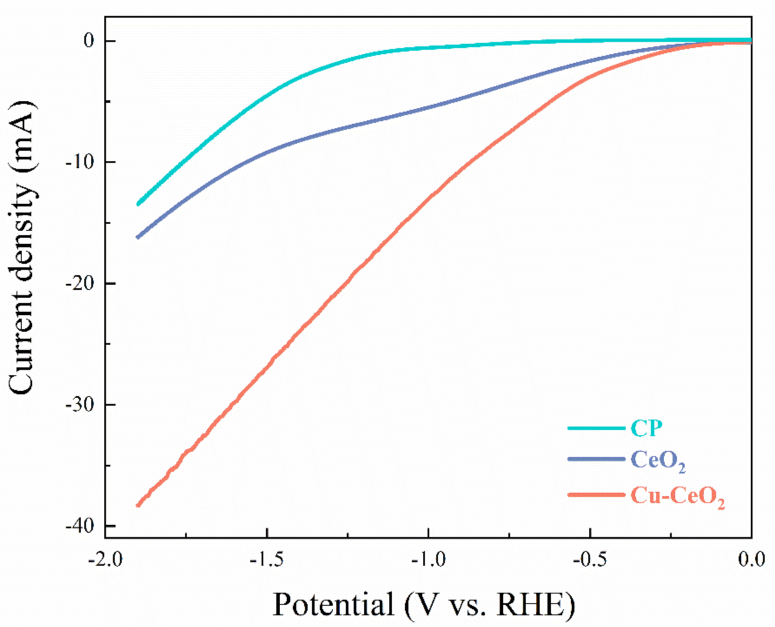

Fig. S8 LSV curves over CP, CeO$_2$ and Cu-CeO$_2$ in CO$_2$-saturated 0.1 M KNO$_3$ and 0.1 M KHCO$_3$ electrolytes.

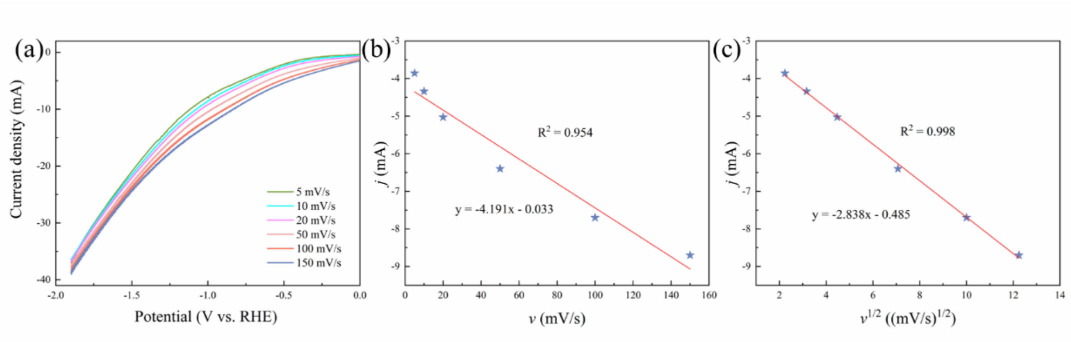

Fig. S9 (a) Linear sweep voltammetry (LSV) curves at different scan rates. (b) Relationship between current density and scan rate, and (c) relationship between current density and the square root of scan rate (both at a potential of -0.7 V vs. RHE).

To evaluate capacitive current interference, LSV measurements spanning 5 to 150 mV/s were conducted. As shown in Fig. S9(a), the consistent LSV curve shapes across scan rates indicate stable reaction kinetics. Critical analysis at -0.7 V vs. RHE reveals a linear j-v relationship ($j = -4.191v - 0.033$, $R^2 = 0.954$; Fig. S9(b)), deviating from ideal capacitive behavior (requiring strict $j \propto v$ proportionality). Conversely, the j-$v^{1/2}$ plot demonstrates a robust linear correlation ($j = -2.838v^{1/2} - 0.485$, $R^2 = 0.998$; Fig. S9(c)), characteristic of diffusion-controlled Faradaic processes. This confirms that the measured currents predominantly originate from Faradaic CO_2/nitrate reduction for urea synthesis.

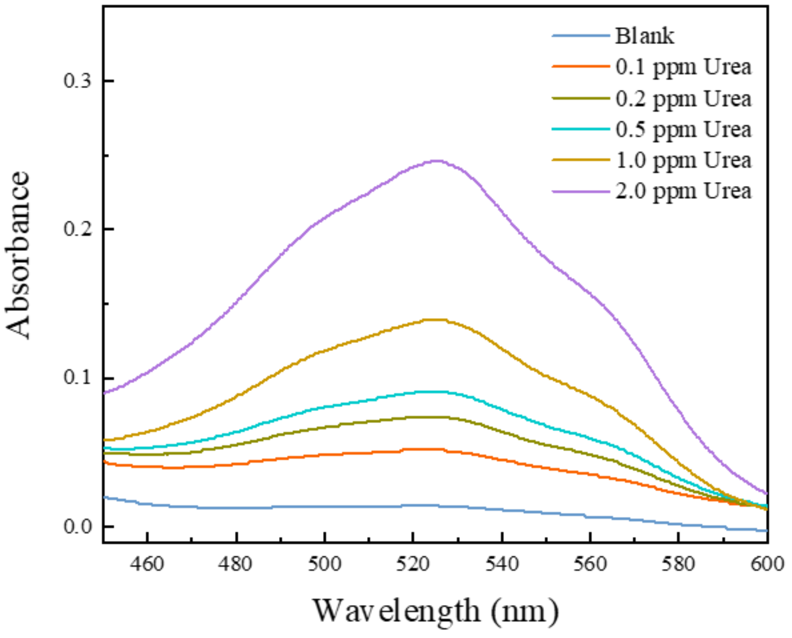

Fig. S10 UV-vis absorption spectra for different urea concentrations.

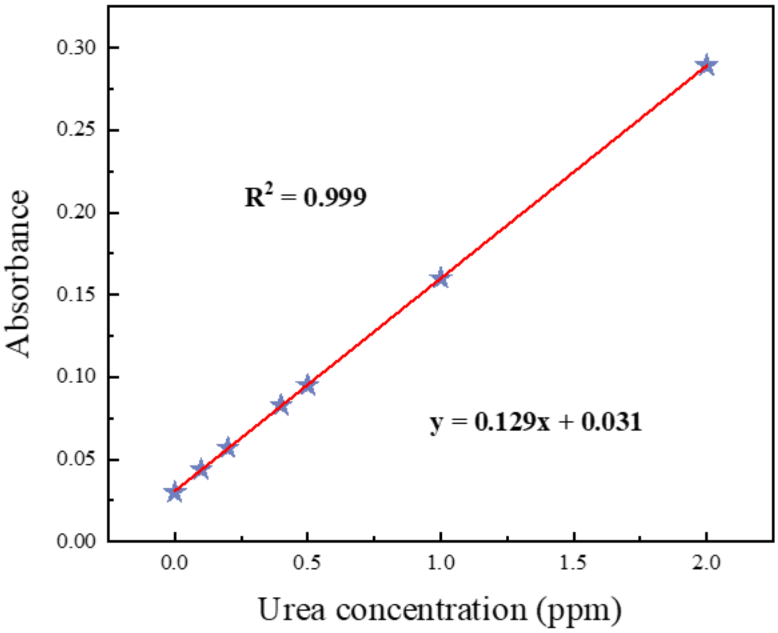

Fig. S11 Calibration curve for urea analysis.

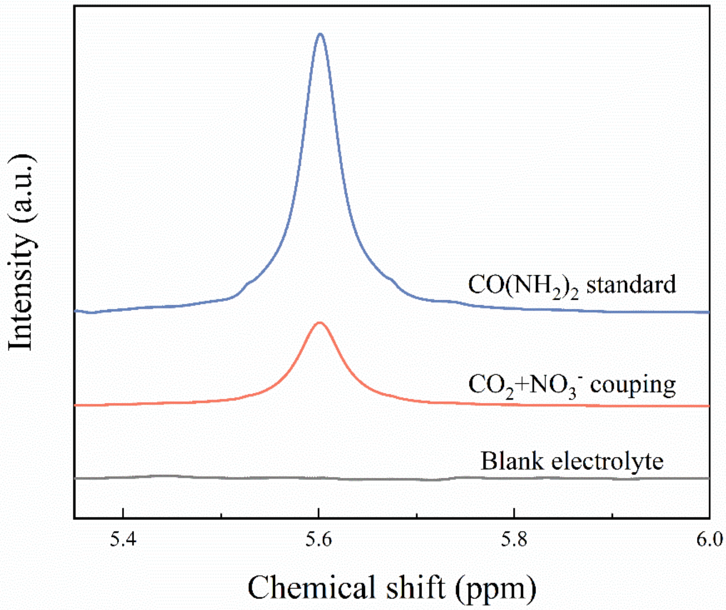

Fig. S12 ^{1}H NMR spectra of electrolytes after electrolysis.

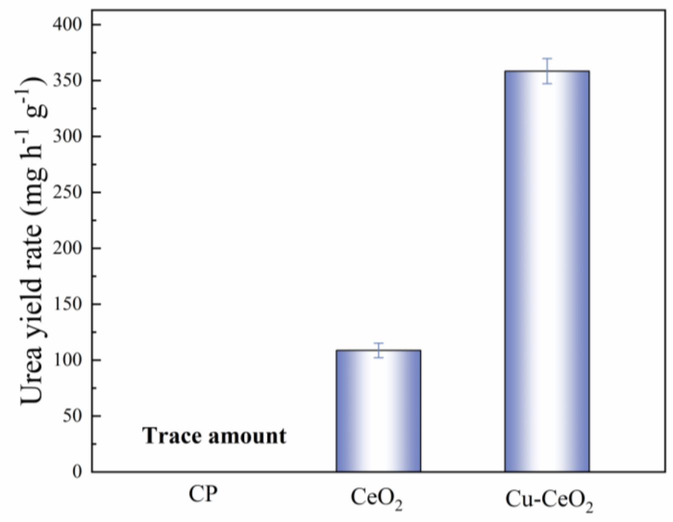

Fig. S13 Urea yield of CP, CeO$_2$ and Cu-CeO$_2$ at -0.7 V vs. RHE.

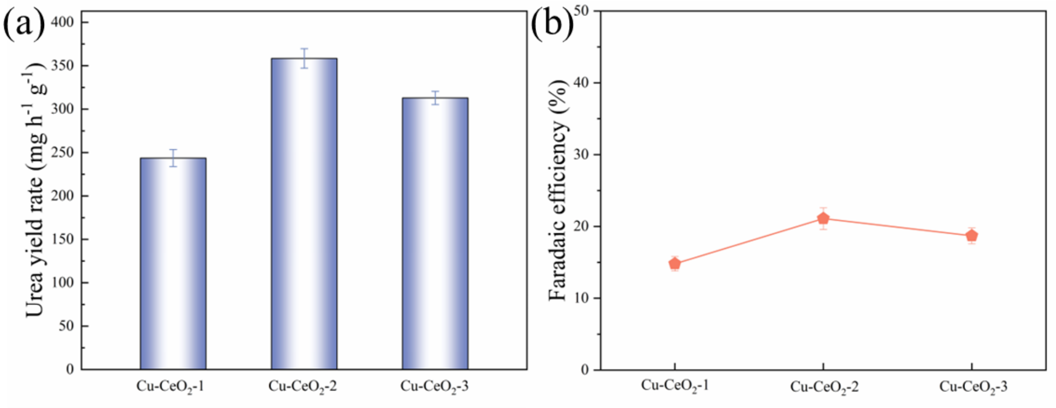

Fig. S14 Urea yield (a) and Faraday efficiency (b) of Cu-CeO$_2$-1, Cu-CeO$_2$-2 and Cu-CeO$_2$-3.

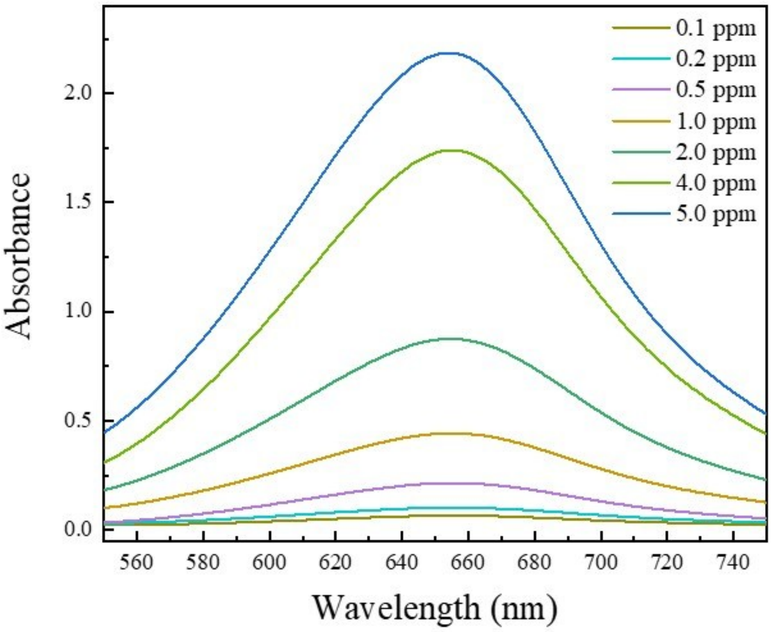

Fig. S15 UV-vis absorption spectra for different NH_3 concentrations.

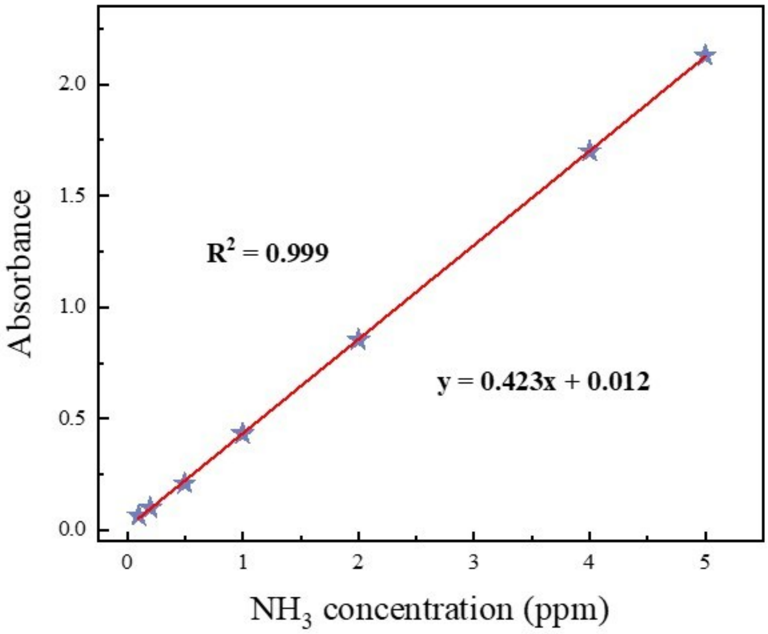

Fig. S16 Calibration curve for NH_3 analysis.

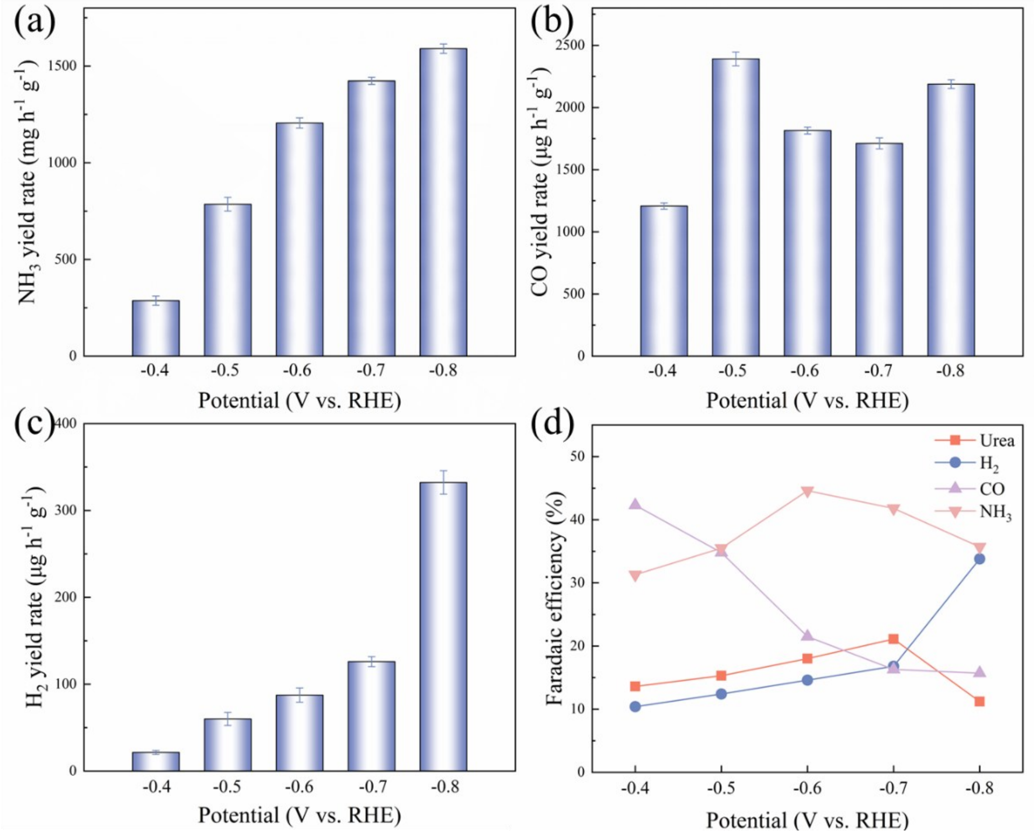

Fig. S17 The yield rates of Cu-CeO$_2$ for (a) NH$_3$, (b) CO, and (c) H$_2$. The Faradaic efficiency of Cu-CeO$_2$ electrocatalytic products (d).

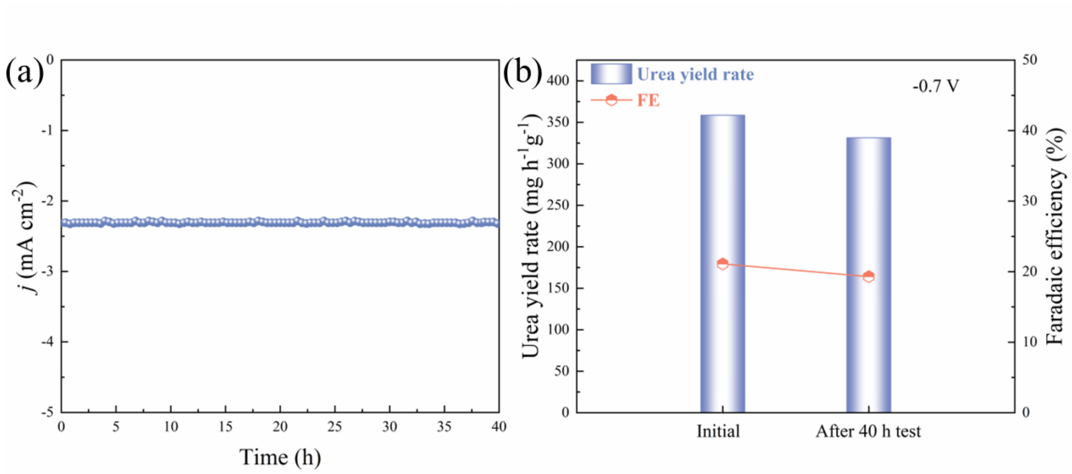

Fig. S18 Long-term stability tests (a) and performance evaluation (b) of Cu-CeO$_2$ at -0.7 V versus RHE.

Table S1 The Cu and Ce content in different catalysts determined by ICP-OES.

Catalysts	Element	Weight (g)	Volume (mL)	Dilution factor	Reported concentration (mg/L)	Element content (%)
Cu-CeO_2-1	Cu	0.0351	50	50	1.2947	9.22
Cu-CeO_2-2	Cu	0.0446	50	50	2.2694	12.72
Cu-CeO_2-3	Cu	0.0479	50	50	2.7833	14.53
Cu-CeO_2-1	Ce	0.0351	50	50	2.3682	67.47
Cu-CeO_2-2	Ce	0.0446	50	50	2.9201	65.47
Cu-CeO_2-3	Ce	0.0479	50	50	3.0434	63.54

Table S2 S_{BET}, pore volume and average pore size of catalysts.

Catalysts	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore size (nm)
CeO_2	2.61	0.298	20.18
Cu-CeO_2	41.0	0.013	29.05

Table S3 The copper and cerium content in the electrolyte after long-term electrolysis was measured using the ICP-MS method.

Catalysts	Element	Weight (g)	Volume (mL)	Dilution factor	Reported concentration (mg/L)
Cu-CeO_2	Cu	1	10	1	0.0080
Cu-CeO_2	Ce	1	10	1	0.0606

Table S4 Comparative analysis of electrocatalytic urea synthesis performances with latest studies.

Catalysts	Applied potential (V vs. RHE)	Electrolyte	Urea yields mg h^{-1} g^{-1}	Urea FEs %	Ref.
Cu-CeO_2	-0.7	0.1 M KNO_3 + 0.1 M $KHCO_3$	358.5	21.1	This work
XC72R-AuPd	-0.5	0.075 M $KHCO_3$ + 0.025 M KNO_3	204.2	15.6	[1]
PdCu/TiO_2	-0.4	0.1 M $KHCO_3$	201.8	8.92	[2]
Cu-CeO_2/MXene	-0.8	0.1 M $KHCO_3$ + 50 mM KNO_3	505.1	6.30	[3]
Ru-CeO_2	-0.7	0.1 M $KHCO_3$ + 50 mM KNO_3	1213.2	20.10	[4]
Cu_1Au_8@CeO_2	-0.94	0.1 M KNO_3	813.6	45.20	[5]
$FeNi_3$/NC	-0.9	0.1 M KNO_3	496.5	16.58	[6]
Graphene-In_2O_3	-0.35	0.1 M $KHCO_3$ + 0.1 M KNO_3	357.47	10.46	[7]

References

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