

Electronic Supplementary Information

High efficient urea anodizing to promote electrochemical nitrogen reduction process

Ying Hou,^a Ning Deng,^c Fengyun Han,^c Xuan Kuang^{*a} and Xiaodong Zheng^{*b}

^aSchool of Chemistry and Chemical Engineering, University of Jinan, Key Laboratory of Interfacial Reaction & Sensing Analysis in Universities of Shandong, Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, Jinan 250022, P. R. China.

E-mail: chm_kuangx@ujn.edu.cn

^bJinan Fruit Research Institute, All China Federation of Supply & Marketing Cooperatives, Jinan 250014, China.

E-mail: zhxd1106@163.com

^cShandong Institute for Product Quality Inspection, Jinan 250102, China.

Experimental section

Reagents: All solutions were prepared using deionized (DI) water. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, sodium dihydrogen phosphate, urea, hydrochloric acid, potassium phosphate monobasic, dibasic sodium phosphate, sodium sulfate, potassium hydroxide, fluoroboric acid were obtained from Aladdin, Shanghai. Ethanol, dimethyl sulfoxide, N,N-dimethylacetamide were purchased from Tianjin Fuyu Fine Chemical Co, Ltd. All the chemicals were of analytical grade and not purified unless otherwise specified. Before measurements, Nickel foam (NiF) ($5 \text{ mm} \times 10 \text{ mm}$) was immersed in dilute hydrochloric acid, sonicated for 5 min, and rinsed with deionized water and anhydrous ethanol. Highly pure N_2 and Ar (99.999%) gases were used for the electrochemical measurements.

Characterization: Scanning electron microscopy (SEM) images were obtained on an FEI QUANTA FEG250 scanning electron microscope at an accelerating voltage of 15.0 kV, which were carried out on a Hitachi S-4800. XRD patterns were acquired by a Bruker SMART APEX diffractometer using $\text{Cu-K}\alpha$ radiation X-ray source ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 30 mA. Fourier transform infrared (FT-IR) spectroscopy was recorded by using a Nicolet iS50 spectrometer. UV/vis absorption spectra of samples were tested in a 1 cm quartz cell with a UV-2550 UV/visible spectrophotometer (Shimadzu Company). The fluorescence spectra were performed on an RF-5301pc luminescence spectrometer (Shimadzu Company) under excitation wavelengths at 270 nm. XPS measurements were obtained at an ESCALABMK II X-ray photoelectron spectrometer with $\text{Al-K}\alpha$ X-ray excitation. Electrochemical measurements were carried out at CHI 660E (Shanghai Chenhua).

Preparation of CDs: The CDs were prepared by using 3 g (16.7 mmol) sorbitol, 1 g (7.2 mmol) sodium dihydrogen phosphate which was dissolved in 8 ml deionized water. The mixture solutions were heated in a microwave at 750 W for 120 s. Then the fresh CDs solution was obtained. The brownish and thick solution was on dialysis for three days in a 500-1000 Da cellulose dialysis bag.

Synthesis of H_6L : H_6TDPAT {2,4,6-tris(3,5-dicarboxylphenylamino)1,3,5-triazine} was prepared according to the literature.¹ 5-aminoisophthalic acid (15.2 g, 0.084 mol), NaOH (5.36 g, 0.134 mol), and NaHCO_3 (8.74 g, 0.104 mol) were added to 140 mL H_2O . The mixture was stirred at 0 °C for 30 min, with the dropwise addition of cyanuric chloride (3.68 g, 0.02 mol) dissolved in 1,4-dioxane (70 mL). The mixture was heated at 100 °C for 24 h. The resulting solution was adjusted to pH=2 using HCl solution. The solid was collected by filtration, rinsed several times

with distilled water, and dried to give H₆TDPAT.

Synthesis of catalysts: Cu-MOF/NiF catalyst was synthesized by the electrochemical method. 0.060 g (0.098 mmol) of the ligand was dissolved in 4 mL of DMA, 4 mL of DMSO, 200 μ L of H₂O, 1.8 mL of HBF₄ with gently vibrate. 0.328 g (1.36 mmol) of Cu(NO₃)₂·3H₂O was added to the mixture solution and ultrasound to clarification. Nickel foam (NiF) (5 mm \times 10 mm) was immersed in dilute hydrochloric acid, sonicated for 5 min, and rinsed with deionized water and anhydrous ethanol. The electrodeposition was processed in a one-chamber electrolysis cell with the mixture solution as an electrolyte, NiF as a working electrode separately, the platinum plate as a counter electrode, the Ag/AgCl (4 M KCl) electrode as reference electrode at a voltage -1.2 V for 10 minutes.

To improve the performance of the catalyst, the carbon dots doped composite catalyst Cu-MOF@CDs/NiF was synthesized by a one-step method. 0.136 mmol of copper(II) nitrate hydrate (0.328 g), 0.098 mmol the ligand (0.060 g) and the above fresh carbon dots (CDs) were dissolved in 4 mL of DMA, 4 mL of DMSO, 200 μ L of H₂O, 1.8 mL of HBF₄ in the electrolysis cell. The NiF (5 mm \times 10 mm) was immersed in dilute hydrochloric acid, sonicated for 5 min, and rinsed with deionized water and anhydrous ethanol. The electrodeposition process is the same as the synthesis of Cu-MOF/NiF.

The as-prepared catalyst Cu-MOF@CDs/NiF was washed with ethanol and activated at 350 $^{\circ}$ C for 2 h at tube furnace with a heating rate of 5 $^{\circ}$ C min⁻¹. The new catalyst was made successfully after the tube furnace was cooled to room temperature at a rate of 2 $^{\circ}$ C min⁻¹, which was named CuO/Cu₂O@CDs-CN/NiF. The heating process was carried out in air atmosphere.

Electroreduction of N₂ to NH₃ (NRR): The reduction of nitrogen fixation to ammonia was performed in a gas-tight two-compartment electrochemical cell (Fig. S1a) at room temperature. A piece of Nafion 115 membrane was used to divide the cell. Before the reduction, the Nafion 115 membrane was heated at 80 $^{\circ}$ C for 1 h at H₂O₂ (5%) and then pretreated in H₂SO₄ solution (0.5 M) at 80 $^{\circ}$ C for another hour.

A traditional three-electrode system was used to measure the electrochemistry process of NRR at CH Shanghai Instruments 760E workstation. The platinum plate as a counter electrode was put in one compartment. The Ag/AgCl (4 M KCl) electrode as a reference electrode and catalyst as a working electrode were put in another compartment. Pure N₂ gas was continued through into the cathodic compartment to make sure that the entire cathode was surrounded by N₂ gas bubbles during the entire process. All potentials were calculated to the RHE scale via calibration. For the rigor of the experiment, the electrochemistry process of NRR was tested in 0.5 M KOH, 1.0 M Na₂SO₄ and phosphate buffer saline solution (PBS) (PH=7) to select the most

suitable electrolyte. The linear sweep voltammetry was scanned at a rate of 5 mV s^{-1} . The NRR activity of an electrode was evaluated using controlled potential electrolysis in an electrolyte for 2 h at room temperature. After the reduction, the electrolyte and gas absorption liquid were both collected and analyzed by chromogenic reactions for qualitative measurements. The applied potentials were iR-compensated, and the reported current densities were normalized to geometric surface areas.

Determination of the produced ammonia: The produced ammonia in the 0.5 M KOH, 1.0 M Na_2SO_4 and PBS (PH=7) were quantitatively determined using the indophenol blue method.² Typically, 2 mL of the electrolyte after the potentiostat test was taken out. Afterward, 2 mL of NaOH (1 M) solution containing salicylic acid (5 wt%) and sodium citrate (5 wt%), 1 mL of NaClO solution (0.05M) and 0.2 mL of sodium nitroferricyanide solution (1 wt%) were added subsequently. The mixture solution was reacted to 2 h. The absorption spectra of the resulting solution were acquired with an ultraviolet-visible (UV-vis) spectrophotometer. The concentration of indophenol blue was measured according to the absorbance at a wavelength of 657 nm. The standard curve method was used to quantify the produced NH_3 . The calibration curves were built using a series of standard NH_4Cl solutions in the presence of 0.5 M KOH, 1.0 M Na_2SO_4 and PBS solution (PH=7), respectively (Fig. S2) to examine the effects of different pH values. The measurements with the background solutions (no NH_3) were measured for all reduction process, and the background peak was calibrated by the measured peaks of NRR experiments to calculate the rate of NH_3 and the Faradaic efficiencies.

Determination of the produced hydrazine: The concentration of the produced hydrazine in the 0.5 M KOH, 1.0 M Na_2SO_4 and PBS solution (PH=7) was determined according to the Watt and Chrisp method.³ The spectrophotometric method of p-dimethylaminobenzaldehyde (PDAB) to solutions of N_2H_4 was carried out (Fig. S3). In both cases, 5 mL of the electrolyte solution and 5 mL of the coloring solution (4 g of PDAB dissolved in 20 mL of concentrated hydrochloric acid and 200 mL of ethanol) were well mixed. The resulting solution was reacted for 15 min, and its absorbance was measured using a UV-vis spectrophotometer at a wavelength of 456 nm. Standard hydrazine monohydrate solutions at a series of concentrations in 0.5 M KOH, 1.0 M Na_2SO_4 and 0.1 M PBS solution (PH=7) were prepared to build the calibration curves and quantify the produced hydrazine. The color development method was consistent with the above.

Calculation of the rate of ammonia formation and the Faradaic efficiency: To determine the electrochemical surface area (ECSA), the electrochemical double-layer capacitance (C_{dl}) of the materials were tested. At the potential of 0.85 and 0.95 vs. RHE, cyclic voltammograms (CVs) were scanned against different rates. The plotted current density had a linear relationship with the scan rate, in which the slope was twice the C_{dl} . The ECSA was calculated as below:

$$A_{\text{ECSA}} = C_{\text{dl of material}} (\text{mF/cm}^2) / 40 \mu\text{F cm}^{-2} \text{ per cm}_{\text{ECSA}}^2 \quad (1)$$

The yield rate of ammonia formation and faradaic efficiency can be calculated through the follows:

$$r_{\text{NH}_3} = (17 c_{\text{NH}_3} \times V) / (t \times A_{\text{ECSA}}) \quad (2)$$

$$\text{FE (\%)} = (3F \times c_{\text{NH}_3} \times V) / Q \quad (3)$$

where r_{NH_3} is the rate of ammonia formation ($\mu\text{g h}^{-1}\text{cm}^{-2}$), c_{NH_3} is the measured NH_3 concentration, V is the volume of the electrolyte (30 ml), t is the time of collection, A_{ECSA} is calculated using Eqs. (1), F is the faraday constant ($96,485 \text{ C mol}^{-1}$), and Q is the total charge passed through the electrode. Q is obtained through mathematical integral.

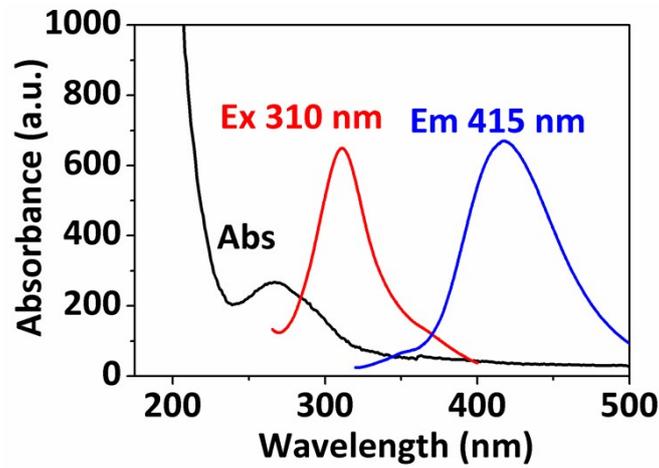


Figure S1. UV-vis absorption spectrum of CDs (black line), fluorescence excitation spectra of CDs (red line) and fluorescence emission spectra of CDs (blue line).

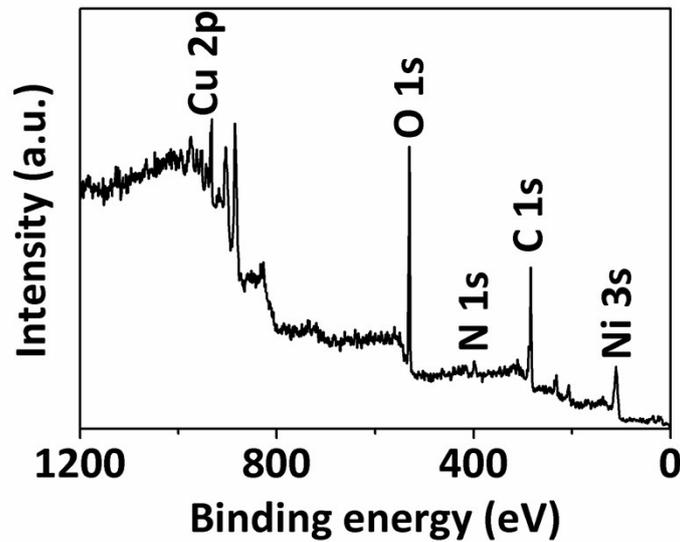


Figure S2. Overall XPS spectrum for CuO/Cu₂O@CDs-CN/NiF.

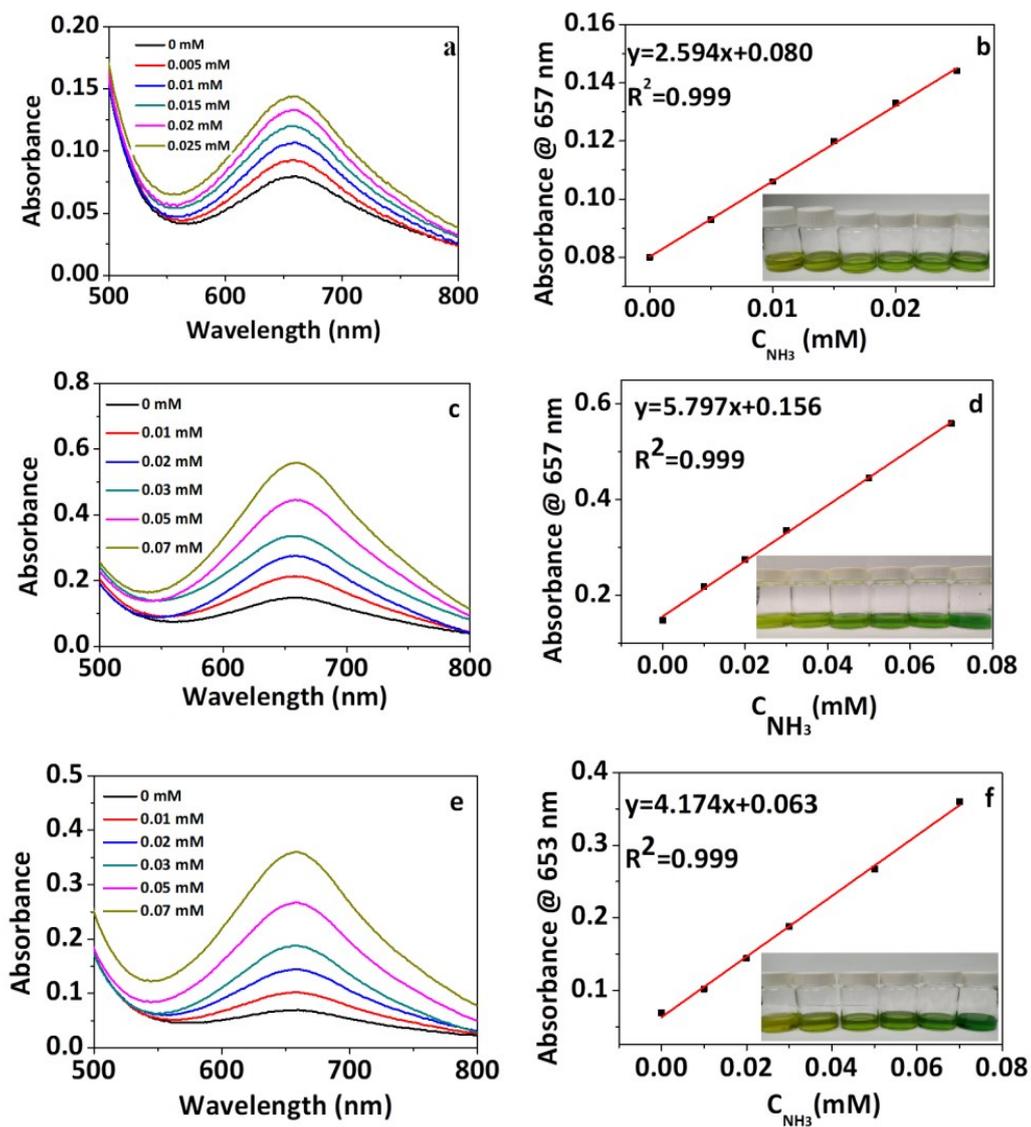


Figure S3. NH_3 quantification. The UV-Vis absorption spectra and corresponding calibration curves for the colorimetric NH_3 assay using the indophenol blue method in different background solutions: a, b 0.5 M KOH, c, d 0.1 M PBS (pH=7), and e, f 0.1 M Na_2SO_4 . The error bars correspond to the standard deviations of multiple measurements. The insert in b, d, f is the solution after using the indophenol blue method.

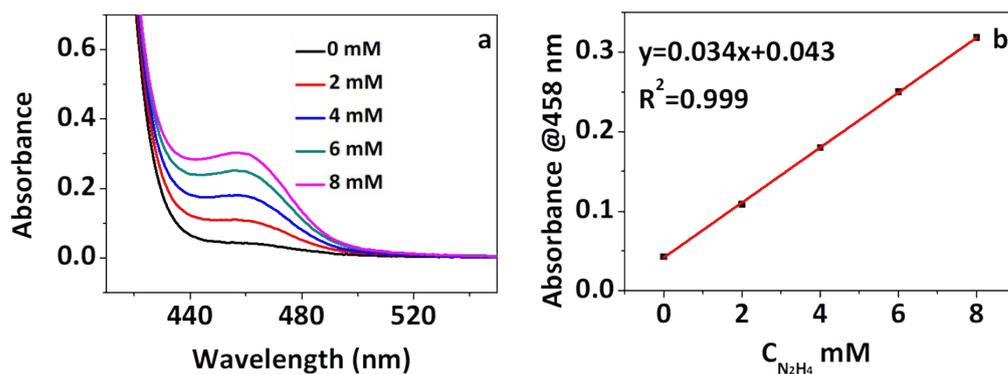


Figure S4. a The UV-Vis absorption spectra and b corresponding calibration curves for the colorimetric N_2H_4 assay in 0.1 M Na_2SO_4 . The error bars correspond to the standard deviations of multiple measurements.

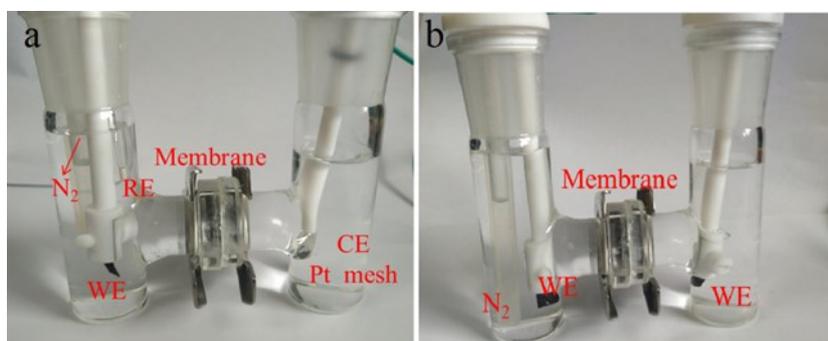


Figure S5, Photograph of the two-compartment electrochemical cell used for the NRR electrolysis without urea (a) and with urea (b).

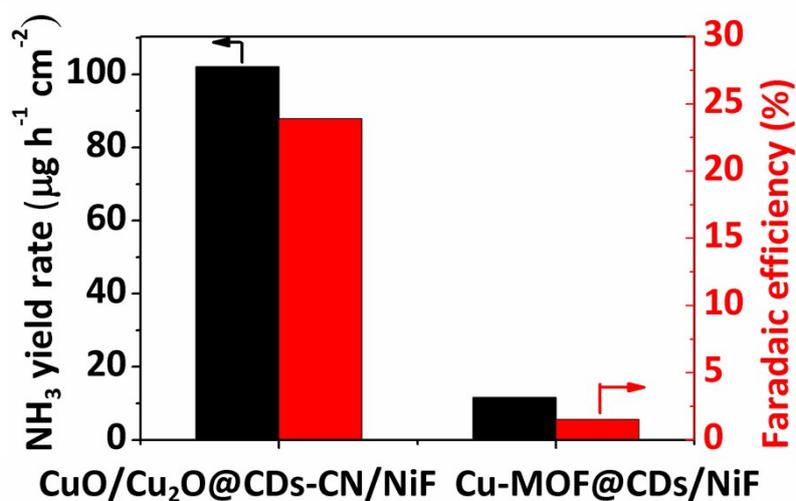


Figure S6. NH_3 yield rates and FE in 1.0 M Na_2SO_4 with 0.5 M urea of $CuO/Cu_2O@CDs-CN/NiF$ and $Cu-MOF@CDs/NiF$ at 0.4 V.

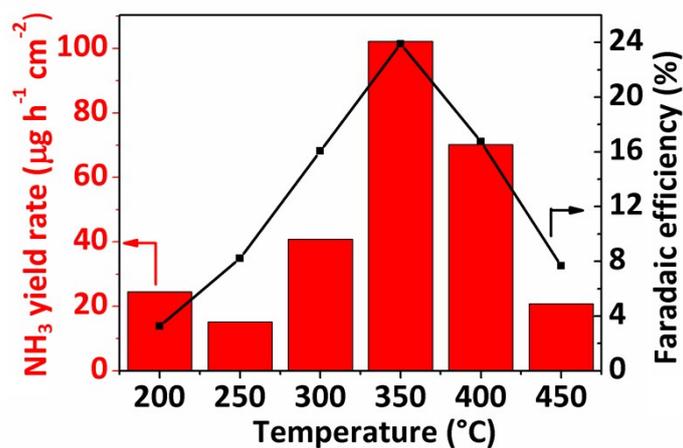


Figure S7. NH₃ yield rates and FE at different temperatures in 1.0 M Na₂SO₄ with 0.5 M urea of CuO/Cu₂O@CDs-CN/NiF at 0.4 V.

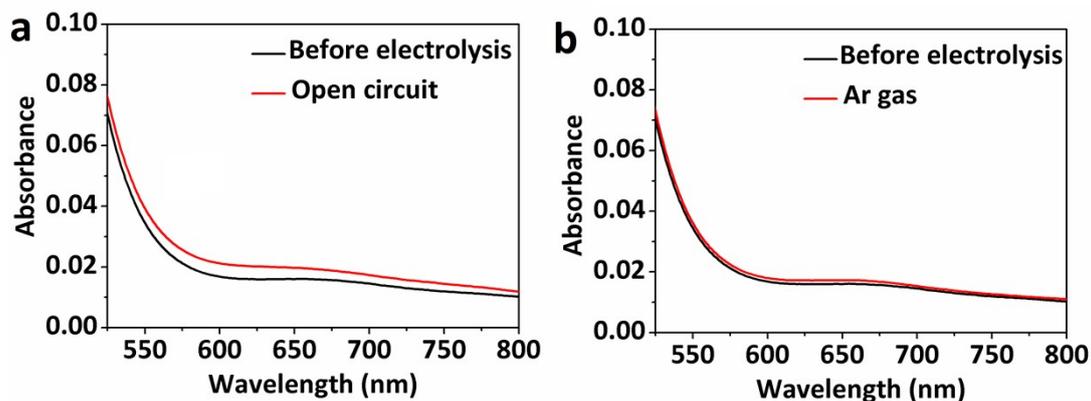


Figure S8. (a) UV-Vis spectra of electrolyte at open circuit condition for 2 h using bare NiF and of the blank electrolyte, (b) UV-Vis spectra of electrolyte at -0.1 V for 2 h under Ar-saturated atmosphere using CuO/Cu₂O@CDs-CN/NiF and of the blank electrolyte.

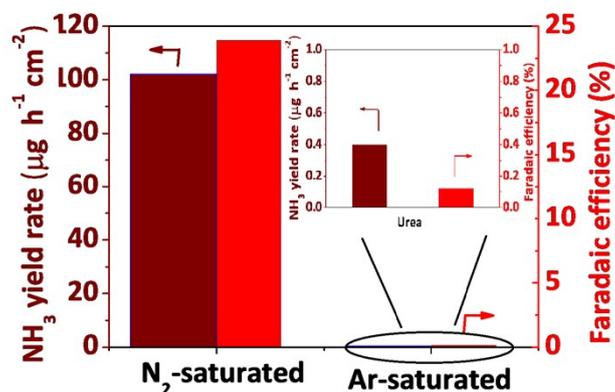


Figure S9. Cathodic NH₃ yield rates and FE with CuO/Cu₂O@CDs-CN/NiF in N₂-saturated and Ar-saturated Na₂SO₄ electrolyte at 0.4 V with urea in anode. Inset is an enlarged view of NH₃ yield rates and FE in Ar-saturated electrolyte.

References

- 1 B. Y. Li, Z. J. Zhang, Y. Li, K. X. Yao, Y. H. Zhu, Z. Y. Deng, F. Yang, X. J. Zhou, G. H. Li, H. H. Wu, N. Nijjem, Y. J. Chabal, Z. P. Lai, Y. Han, Z. Shi, S. H. Feng and J. Li, *Angew. Chem.*, 2012, 1412-1415.
- 2 P. L. Searle, *Analyst*, 1984, **109**, 549–568 .
- 3 G. W. Watt and J. D. Chrisp, *Anal. Chem.*, 1952, **24**, 2006–2008.