Supporting Information

Interface-Engineered Co₃O₄ Nano-Islands on Cu Substrate for High-Efficiency Electrocatalytic Nitrate-to-Ammonia Conversion

Tong Xu^{a,1}, Zhenxiao Wang^{a,1}, Hongyang Zhu^a, Ziwei Zhang^a, Yangping Zhang^{a,*}, Danhong Shang^a, Linzhi Zhai^a, Tongyi Yang^a, Mengnan Wang^{b,*}, Fu Yang^{a,*}

a School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, PR China.

b Department of Chemical Engineering, Swansea University, Swansea, SA1 8EN, UK.

¹ These authors equally contribute to this work.

*Corresponding author: <u>fuyang@just.edu.cn;</u> <u>ypzhang@just.edu.cn;</u> <u>mengnan.wang@swansea.ac.uk</u>

Text S1. Chemicals and reagents

Reagents used in this experiment: Cupric nitrate trihydrate (99%, Cu(NO)₃·3H₂O), Cobaltous acetate(AR, (CH₂COO)₂Co), Trimesic acid (98%, H₃BTC), Dopamine hydrochloride (98%, C₈H₁₂ClNO₂) from Annergy Chemical, Potassium sulfate (99%, K₂SO₄), N, N-dimethylformamide (99.9%, DMF), potassium nitrate (AR, KNO₃), salicylic acid (99%, C₇H₆O₃), Sodium hydroxide (AR, NaOH), Sodium citrate (99%, C₆H₅Na₃O₇), and Sodium nitroferrocyanide dihydrate (AR, Na₂[Fe(CN)₅NO]·2H₂O) were purchased from Shanghai Siene Chemical Technology Co., LTD., and anhydrous ethanol (C₂H₅OH) was purchased from Shanghai Titan Technology Co., LTD. Nafion® (5 wt%) was purchased from Beijing Keyi Scientific Instrument Co., LTD. Sodium hypochlorite solution (NaClO, 8-10.0%) was purchased from Tianjin Huadong Reagent Factory. Ammonium chloride (NH₄Cl) purchased from Shanghai McLean Biochemical Co., LTD. All tests were performed using deionized water purified by the Millipore system.

Text S2. Synthesis of catalysts

Preparation of Cu-BTC precursor

Firstly, 21.5 mmol of copper nitrate trihydrate was weighed into a beaker, and 125 ml of DMF, ethanol and deionized water were added at a ratio of 1:1:1. Let sit for 20 minutes. Subsequently, 11.9 mmol tripolycaproic acid was added to the above solution, and the solution was kept at 75°C for 24 hours after ultrasound for 30 minutes. After cooling to room temperature, the solid product Cu-BTC was obtained by centrifugation. The resulting solid was washed three times with DMF and dried for 48 hours under vacuum at 25 degrees Celsius to obtain the Cu-BTC precursor.

The synthesis of targeted catalyst

Firstly, AB solution is prepared: Solution A: take 1 gram of the Cu-BTC precursor in a beaker, add 100 ml of anhydrous ethanol, and stir well; B solution: Take 0.2g of dopamine into a beaker, add 50 ml of anhydrous ethanol, and stir well. Then, slowly add solution A to solution B. After mixing evenly, 1mmol cobalt acetate was slowly added, stirring for 12 hours, and then the solution was centrifuged to obtain a solid product, washed with ethanol 3 times, and left for 12 hours at 70°C. Get the Cu-BTC@Co precursor. Finally, calcined under argon atmosphere at 500°C for 2 hours, C/Cu@Co₃O₄ was obtained.

The synthesis of other comparative catalysts

Catalyst C/Cu: The Cu-BTC precursor mentioned above was directly calcined at 500 °C in an argon atmosphere for 2 hours and then ground to prepare catalyst C/Cu;

Catalyst C/Cu@C: The Cu-BTC was modified with PDA according to the above modified strategy without addition of Co precursor. After the precursor Cu-BTC was coated with dopamine, the obtained material was directly calcined in an argon atmosphere for 2 hours to obtain the catalyst C/Cu@C.

Text S3. Characterization Information

The surface microstructure and morphology were determined by field emission scanning electron microscopy (FESEM, Zeiss Merlin). The microstructure of the samples was observed by transmission electron microscope (TEM, JEM-2010 EX, 200 kV), and the element mapping analysis was performed. The crystal phase of the sample was identified by X-ray diffractometer (Shimadzu XRD-6000 type Cu-kα radiation

source). X-ray photoelectron spectroscopy (XPS) was recorded on the PHI 5000 Versa Probe X-ray photoelectron spectrometer (ULVAC-PHI, Kanagawa, Japan) equipped with Al-K α radiation (1486.6 eV). Finally, the electron binding energy of the sample was modified with the binding energy of C1s (284.8 eV).

Text S4. Electrochemical Measurement

Electrochemical measurements are performed at room temperature on the CHI-760E electrochemical station using a standard three-electrode sealed H-cell. The working electrode is carbon cloth (CC), the reference electrode is Ag/AgCl, and the electrode is graphite rod. 50mL 0.1M H₂SO₄ and 0.1M HNO₃ are used as electrolyte in the cathode chamber. The carbon cloth is soaked in concentrated HNO₃ for 24 h, then washed with deionized water and dried at 60°C. In order to minimize the error caused by ammonia contamination, the Nafion 117 membrane is ultrasonic treated in 1M H₂SO₄ for 10 minutes before any electrochemical tests are performed. Preparation of the working electrode: 4 mg of electric catalyst powder and 50µL 5% Nafion solution were dispersed into 950µL anhydrous ethanol, and ultrasonic action was performed for 30 min to form a uniform electric catalyst ink. Then, 100µL of electrocatalyst ink is loaded onto a carbon cloth with an area of 1×1 cm². All potentials in the experiment were based on reversible hydrogen electrodes, and linear sweep voltammetry (LSV) measurements were performed at a sweep rate of 5mV·s⁻¹ based on Nernst equation (E_{RHE} = $E_{Ag/AgCl}$ + 0.059 × pH + 0.198).

Text S5. EXPERIMENTAL SECTION

Determination of NH3:

Ammonium concentration was determined using the indophenol blue method. A 2 mL aliquot of the diluted electrolyte was mixed with 2 mL of 1 M NaOH solution containing 5 wt% sodium citrate and 5 wt% salicylic acid. Subsequently, 1 mL of 0.05 M NaClO solution and 0.2 mL of 1 wt% aqueous C₃FeN₆Na₂O were added. The mixture was left to react in the dark for 2 hours, after which the absorbance was measured at 655 nm. Calibration curves were constructed using standard NH₄Cl solutions of known concentrations.

Determination of NO₂⁻:

The Griess reagent method was employed to measure nitrite concentration. To 5 mL of

the diluted electrolyte, 0.1 mL of Griess reagent was added. The mixture was allowed to stand at room temperature for 30 minutes, and the absorbance was recorded at 540 nm. Calibration curves were prepared using KNO₂ solutions. The Griess reagent was prepared by dissolving 4 g of p-aminobenzenesulfonamide,0.2g of N-(1-naphthyl)-ethylenediamine dihydrochloride, and 10 mL of phosphoric acid in 50 mL of deionized water.

Determination of NO₃-:

For nitrate determination, 0.2 mL of 1 M HCl and 0.02 mL of 0.8 wt% sulfamic acid solution were added to 5 mL of the diluted electrolyte. The absorbance was measured at 220 nm, and calibration curves were established using KNO₃ solutions.

Calculation of Product Yield and Faradaic Efficiency:

The yields of NH₃ (Y_{NH_3}) , NO₂⁻ ($Y_{NO_2^-}$) and NO₃⁻ ($Y_{NO_3^-}$)were calculated using the following equations:

$$Y = \frac{C \times V}{t \times m}$$

Where C represent the concentrations of NH_3 , NO_2^- and NO_3^- after electrolysis, respectively, V is the volume of the electrolyte (50 mL), t is the reaction time (1 hour), and m is the mass of the catalyst loaded on the electrode.

The Faradaic efficiency (FE) for NH₃, NO₂⁻ and NO₃⁻ was calculated as follows:

$$FE = \frac{n \times F \times C \times V}{M \times Q}$$

Where n is the number of electrons required to produce a molecule of NH_3 , NO_2^- and NO_3^- , F is Faraday's constant (96485 C·mol⁻¹), M is the relative molecular mass, and Q is the total charge passed through the electrode during electrolysis.

The nitrate removal efficiency was determined using:

$$Conversion = (C_0 - C_t)/C_0 \times 100\%$$

Where C_0 is the initial nitrate concentration and C_t is the concentration after reaction time t.

The selectivity for NH₃, NO₂⁻ and NO₃⁻ was calculated as:

Selectivity=
$$C/(C_0-C_t) \times 100\%$$

Where C represents the concentration of NH₃, NO₂⁻ and NO₃⁻ produced.

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Fig. S3. (A) Nitrogen adsorption and desorption isotherms, (B) pore size distribution curves of catalysts Cu-BTC, C/Cu, C/Cu@C and C/Cu@Co₃O₄.

Fig. S4. XRD patterns of catalysts Cu-BTC and C/Cu@C.

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Fig. S6. X-ray photoelectron spectroscopy (XPS) spectra of catalyst C/Cu@C: O 1s.

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Fig. S9. The calibration curve of indoxyl blue method was determined with different concentrations of NH₄Cl solution as the standard. (A) The UV-vis curves of different concentrations of NH₃ were darkened by adding color developer for two hours. (B) Calibration curve for NH₃ concentration measurement. The linear relationship between absorbance and NH₃ concentration was determined by UV-vis spectrophotometry at a wavelength of $665nm(y=0.09892x+0.0467, R^2=0.9999)$.

Fig. S10. (A) UV-visible curve after 20 min of NO_3^- culture at different concentrations, (B) determination of NO_3^- Calibration curve of concentrations. The absorbance at 220 nm was measured with a UV-vis spectrophotometer and the fitting curve showed a good linear correlation between absorbance and NO_3^- concentration (y = 0.04226x + 0.00095, R^2 =0.999).

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Fig. S12. (A) I-T curves of catalyst Cu-BTC at different voltages. (B) UV-visible spectra of electrolyte in the cathode chamber stained with indiophol indicator. (C) NH₃ yield and Faradaic efficiency of catalyst Cu-BTC at different potentials.

Fig. S13. (A) I-T curves of catalyst C/Cu at different voltages. (B) UV-visible spectra of electrolyte in the cathode chamber stained with indiophol indicator. (C) NH₃ yield and Faradaic efficiency of catalyst C/Cu at different potentials.

Fig. S14. (A) I-T curves of catalyst C/Cu@C at different voltages. (B) UV-visible spectra of electrolyte in the cathode chamber stained with indiophol indicator. (C) NH₃

yield and Faradaic efficiency of catalyst C/Cu@C at different potentials.

Fig. S15. Comparison of the electrocatalytic NO₃RR performances of $C/Cu@Co_3O_4$ with other extensively reported electrocatalysts.

Fig. S16. (A) XRD patterns of C/Cu@Co₃O₄ catalyst before and after reaction. X-ray photoelectron spectroscopy (XPS) spectra of catalysts C/Cu@Co₃O₄ after reaction: (B) Co 2p (C) Cu 2p (D) C 1s (E) N 1s (F) O 1s.

Fig. S17. Concentration variation of NO₃⁻, NO₂⁻, NH₄⁺ during the dynamic electrolysis process (0-12 h) in the presence of catalysts (A) C/Cu@Co₃O₄ (B) Cu-BTC (C) C/Cu (D) C/Cu@C and 100 ppm NO₃⁻ reactants.

Fig. S18. Electrolytes after 1 h of reaction under different conditions, e.g. pure carbon cloth, blank control, KNO₃, and an open-circuit potential of -1.0 V vs.RHE. (A) UV-vis absorption spectra and (B) corresponding NH₃ yields, (C) 1H-NMR spectra of NO₃RR at -1.0 V vs. RHE by C/Cu@Co₃O₄ using ¹⁴NO₃⁻ and ¹⁵NO₃⁻ as the nitrogen source.

Fig. S19. The adsorption curves of NO_3^- n the presence of the various catalysts: (A) UV-vis spectra; (B) Concentration variation of NO_3^- in the presence of different catalysts.

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Catalyst	NH ₃ Yield Rate	FE (%)	Ref.
C/Cu@Co ₃ O ₄	57.4 mg h ⁻¹ mg _{cat} ⁻¹	98.4	This Work
Cu/NC	32.3 mg h ⁻¹ mg _{cat} ⁻¹	100	[1]
Cu SA/NC	7.48 mg h ⁻¹ mg _{cat} ⁻¹	100	[2]
LaSrNiCoMnFeCuO ₃ PNTs	1.657 mg h ⁻¹ mg _{cat} ⁻¹	100	[3]
MoO ₂ /C	4.8385 mg h ⁻¹ mg _{cat} ⁻¹	30	[4]
Cu-NSs	$0.39 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$	99.7	[5]
Mo ₁ Fe _{1.5} /CNF	37.84 mg h ⁻¹ mg _{cat} ⁻¹	99.3	[6]
Fe/Cu-HNG	18.36 mg h ⁻¹ mg _{cat} ⁻¹	92.51	[7]
Cu ₅ Co ₅ /OMC	0.2896 mg h ⁻¹ mg _{cat} ⁻¹	<80	[8]
Meso-PdN NCs	3.7604 mg h ⁻¹ mg _{cat} ⁻¹	96.1	[9]
Geminal-Co	30 mg h ⁻¹ mg _{cat} ⁻¹	95.7	[10]
FeCo	17.2 mg h ⁻¹ mg _{cat} ⁻¹	90.3	[11]
PdCuRu alloy MSs	8.518 mg h ⁻¹ mg _{cat} ⁻¹	95	[12]
FeNC-Ce	20.9692 mg h ⁻¹ mg _{cat} ⁻¹	89.3	[13]
Fe-rGO	47.815 mg h ⁻¹ mg _{cat} ⁻¹	96.51	[14]
SACs	0.628 mg h ⁻¹ mg _{cat} ⁻¹	97	[15]
SnO ₂ -δ	17.27 mg h ⁻¹ mg _{cat} ⁻¹	95.67	[16]
CuCo/NC	9.1108 mg h ⁻¹ mg _{cat} ⁻¹	95.1	[17]
Pyridinic N-dominated graphene	0.0411 mg h ⁻¹ mg _{cat} ⁻¹	62.9	[18]
BiNPs	3.40 mg h ⁻¹ mg _{cat} ⁻¹	66	[19]
Ru SAs/N-C	0.129 mg h ⁻¹ mg _{cat} ⁻¹	29.6	[20]
COFs	0.1253 mg h ⁻¹ mg _{cat} ⁻¹	45.43	[21]

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