Supporting Information

Metal-organic Framework-derived Co-NC Catalyst for Electrocatalytic Reduction of Nitrate to Ammonia

Zhuofan Wu^a, Haiding Zhu^{a,c}, Zi Wang^a, Yiming Sun^a, Meibing Jia^a, Xiaoxin Meng^a, Yushan Li^b, Lifen Liu^a, Anmin Liu

^a, Xuefeng Ren^{a,*}

^a School of Chemical Engineering, Ocean and Life Sciences, Dalian University of Technology,

Panjin 124221, China.

E-mail: renxuefeng@dlut.edu.cn

^b Panjin Institute of Industrial Technology, Dalian University of Technology, Panjin 124221, Liaoning, China.

^c Department of Chemistry, Tsinghua University, Beijing, 100084 China.

Marerials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), 2-Methylimidazole (C₈H₁₅BrN₂), Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), Potassium hydroxide (KOH), Potassium nitrate (KNO₃), Sodium salicylate (C₇H₅O₃Na), Potassium sodium tartrate (NaKC₄H₄O₆), sodium hypochlorite (NaClO), Sodium nitroprusside (C₅H₄FeN₆Na₂O₃), Sulfonamides (C₆H₈N₂O₂S), 4-Dimethylaminobenzaldehyde (C₉H₁₁NO), were obtained from Aladdin. Methanol was obtained from Damao. Nafion was obtained from Sigma-Aldrich. Naphthalene ethylenediamine hydrochloride (CHN₂·2HCl) Sulfamic acid (NH₂SO₃H) were obtained from Macklin.

Product detection

Detection of NH₄⁺: The indophenol blue method was used to measure the ammonia content in the solution. 5 g of C₇H₅O₃Na and 5 g of KOH tartrate were dissolved in 100 mL of 1 M KOH to prepare reagent A. 4.5 mL of sodium NaClO (with an effective chlorine content of 6%–14%) was added to 100 mL of deionized water to prepare solution B. 0.25 g of Na₂[Fe(CN)₅NO]·2H₂O was dissolved in 25 mL of deionized water to prepare solution C. A specific volume of the electrolyte was diluted to 2 mL, followed by the sequential addition of 2 mL of solution A, 1 mL of solution B, and 200 µL of solution C. The mixture was allowed to stand for 1 hour. The absorbance spectrum of the solution was measured at a wavelength of 655 nm. This absorbance value was then used to refer to a standard curve for quantification.

Detection of NO₂⁻: The Griess method was used to detect the content of NO₂⁻ in the solution. Dissolve 0.5 g of C₆H₈N₂O₂S in 50 mL of HCl, and then dilute to 100 mL with water. After thorough mixing, this solution will serve as reagent A. 0.1 g of C₁₂H₁₄N₂ was dissolved in 50 mL water and diluted to 100 mL to prepare solution B. To determine the concentration of nitrite, take a specified volume of the electrolyte solution and dilute it to 4 mL. Add 1 mL of reagent A to this solution, let it stand for 10 minutes, then introduce 100 µL of reagent B. After thorough mixing, allow the mixture to stand for an additional 20 minutes. The absorbance of the solution was measured at 540 nm. Use this absorbance value to interpolate the concentration of nitrite (NO₂⁻) in the electrolyte solution by a standard curve.

Detection of N₂H₄: The Watt and Chrisp method was used to detect the content of N₂H₄ in the solution. 4.0 g of C₉H₁₁NO was dissolved in a solution composed of 20 mL of concentrated hydrochloric acid and 200 mL of C₂H₅OH to prepare the color reagent. Dilute a specified volume of the electrolyte solution to 5 mL, then add 5 mL of the prepared color reagent and allow it to stand for 20 minutes. Finally, measure the absorbance of the solution at 458 nm using a UV-visible spectrophotometer.

Isotope Labeling Experiment: To identify the source of ammonia, isotopic labeling experiment was conducted using 99 atom% K¹⁵NO₃ as the nitrogen feed source. A 0.1 M KOH and K¹⁵NO₃ mixture was used as the electrolyte. After electroreduction, the resulting ¹⁵NH₄⁺-¹⁵N electrolyte was extracted, the pH of the electrolyte was subsequently adjusted to approximately 2.0, which corresponded to a weakly acidic condition,

by the addition of 4 M sulfuric acid (H₂SO₄). The electrolyte was then further analyzed by ¹H NMR spectroscopy. A 0.5 mL aliquot of the ¹⁵NH₄+-¹⁵N solution was mixed with 50 μ L of DMSO-D₆ for NMR analysis.

Calculation formula

The NH₃ yield is calculated as follow.

$$Y_{\rm NH_3} = \frac{C_{\rm NH3} \times V}{M_{\rm NH_3} \times t \times m_{\rm cat}} \#$$

$$FE_{NH_{3}} = \frac{8F \times (C_{NH3} \times V)}{M_{NH_{3}} \times Q}$$
$$FE_{NO_{2}^{-}} = \frac{2F \times (C_{NO_{2}^{-}} \times V)}{M_{NO_{2}^{-}} \times Q} \#$$

Where c represents the mass concentration, M represents the molar mass, V is 75 mL, t signifies the reaction duration (1 hour), m_{cat} corresponds to the mass of the catalyst loading, F is the Faraday constant (96485 C/mol), and Q indicates the total charge transferred via the electrode.

Sample	Particle size (nm)
ZnCo@ZIF	810
Co-NC-600	720
Co-NC-700	600
Co-NC-800	560
Co-NC-900	480
Co-NC-1000	360

Table S1 The particle size data of Co-NC calcined at different conditons

Table S2 The BET data of Co-NC calcined at different conditons

Sample	$S_{BET} (m^2 g^{-1})$	$V_{pore}(cm^3g^{-1})$	Pore diameter (nm)
Co-NC-600	34.864	0.031	1.192
Co-NC-700	297.610	0.138	1.191
Co-NC-800	575.152	0.271	1.195
Co-NC-900	742.480	0.437	1.191
Co-NC-1000	603.247	0.408	1.364



Fig. S1 SEM image of Co-NC catalysts pyrolyzed at different temperature. (a) Co-NC-600, (b) Co-NC-700, (c) Co-NC-800, (d) Co-NC-1000



Fig. S2 SEM images of (a) ZIF-8 and (b) NC





Fig S4 *i-t* test with different applied potentials of Co-NC-900



Fig. S5 (a) UV-vis absorption of standard NH₄⁺ solutions; (b) standard curve for calculating NH₄⁺ concentration





Fig. S7 (a) UV-vis absorption of standard NO₂⁻ solutions; (b) standard curve for calculating NO₂⁻ concentration



Fig. S8 (a) UV-vis absorption of standard N_2H_4 solutions with different concentrations; (b) standard curve for calculating N_2H_4 concentration



S9



Fig. S10 LSV curves of Co-NC catalysts pyrolyzed at different temperature. (a) Co-NC-600, (b) Co-NC-700, (c) Co-NC-800, (d) Co-NC-1000



Fig. S11 i-t curves of comparison of Co-NC pyrolyzed at different temperatures of 600°C-1000°C



Fig. S12 *i-t* tests corresponding to cycle stability tests of Co-NC-900 at -0.5 V (vs. RHE)



Fig. S13 SEM image of Co-NC-900 after electrochemical tests (a) after 24 h long-term *i-t* test, (b) after 5 cycle experiments



Fig. S14 (a) *i-t* curves at -0.5 V (vs. RHE), (b) UV-vis spectrum of samples without NO₃⁻ and without catalyst.