Supporting Information

Metal-organic frameworks derived Cu nanoparticles binder-free monolithic electrodes with multiple support structures for electrocatalytic nitrate reduction to ammonia

Yingying Wang, § Yue Cao, § Yan Hai, Xinyan Wang, Senda Su, Wenming Ding, Zhenyu Liu, Xiaoman Li, and Min Luo*

State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, School of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, Ningxia 750021, P. R. China

§These authors contributed equally to this work.

E-mail: luominjy@nxu.edu.cn
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1. Experimental section

1.1 Determination of NO₃⁻-N

First, remove 1 mL electrolyte from the electrolytic cell and dilute it to 50 mL to the detection range. Afterwards, 1 mL 1 M HCl and 1 mL 0.8 wt% H₃NO₃S solution were added to the above solution. The absorbance was detected by UV-Vis spectrophotometry after 60 minutes at a wavelength of 220 nm and 275 nm. The final absorbance of NO₃⁻ can be calculated as following: 

\[ A = A_{220\ nm} - 2A_{275\ nm} \]

The calibration curve can be acquired through different concentrations of KNO₃ solutions and corresponding absorbance. The fitting curve \( y = 0.23994x + 0.02701, R^2 = 0.9991 \) exhibits great linear relation of absorbance value with NO₃⁻-N concentration.

![Figure S1](image)

Figure S1. (a) UV-Vis absorption curves of NO₃⁻-N. (b) Calibration curve used to estimate the concentrations of NO₃⁻-N.

1.2 Determination of NO₂⁻-N

A mixture of p-aminobenzenesulfonamide (5 g), HCl (50 mL), and ultrapure water (450 mL) were used as a color reagent. 1 mL electrolyte was extracted from the electrolytic cell and diluted to 100 mL to detection range. 1 mL mixed solution of p-aminobenzenesulfonamide and HCl and 1 mL N-(1-Naphthyl) ethylenediamine dihydrochloride (1 g/L) were added into the above solution and mixed uniformity. After standing at room temperature for 60 min, the absorbance was recorded at a wavelength of 540 nm. The concentration-absorbance curve was calibrated using the standard KNO₂ with different NO₂⁻-N concentrations. The fitting curve \( y = 3.4212x + 0.0001026, R^2 = 0.9998 \) exhibits great linear relation of absorbance value with NO₂⁻-N concentration.
1.3 Determination of NH$_3$-N

The Nessler’s reagent was employed as the color reagent for the determination of NH$_3$-N. Firstly, 1 mL electrolyte was extracted from the cathodic chamber and diluted to 100 mL to detection range. Then, 1 mL of potassium sodium tartrate solution and 1 mL Nessler’s reagent were subsequently added into the above solution and mixed uniformly. After standing at room temperature for 20 min, the absorbance was recorded at a wavelength of 420 nm. The concentration-absorbance curve was calibrated using the standard NH$_4$Cl with different NH$_4$⁻-N concentrations. The fitting curve ($y = 0.1521x + 0.010$, $R^2 = 0.999$) exhibits great linear relation of absorbance value with NO$_4$⁻-N concentration.

1.4 Calculations of FE, NH$_3$ yield, selectivity and conversion rate

$$FE = \left(8 \times F \times C_{NH_3} \times V \right) + \left( M_{NH_3} \times Q \right) \times 100\%$$

$$NH_3 \text{ yield} = \left( C_{NH_3} \times V \right) \div \left( M_{NH_3} \times t \times S \right)$$
\[ S_{NH_3} = C_{NH_3} \div \Delta C_{NO_3} \times 100\% \]

\[ Conversion = \Delta C_{NO_3} \div C_0 \times 100\% \]

Where \( F \) is the Faradic constant (96485 C mol\(^{-1}\)), \( C_{NH_3} \) is the measured NH\(_3\) concentration, \( V \) is the volume of electrolyte in the anode compartment (120 mL), \( M_{NH_3} \) is the molar mass of NH\(_3\), \( Q \) is the total quantity of applied electricity, \( t \) is the electrolysis time (1 h), \( S \) is the loaded area of catalyst (1 cm\(^{-2}\)), \( C_0 \) is the initial concentration of NO\(_3\)^{-}, and \( \Delta C_{NO_3} \) is the concentration difference of NO\(_3\)^{-} before and after electrolysis.

1.5 Electrochemical in-situ ATR-FTIR test

The glassy carbon electrode supported by catalyst was used as the working electrode. 0.1 M Na\(_2\)SO\(_4\) with 50 ppm NO\(_3\)^{-}-N was adopted as the electrolyte. The in-situ ATR-FTIR spectra were collected during LSV test from 0 to −1.5 V vs. Ag/AgCl with a scan rate of 2 mV/s. Each reflectance spectrum was collected with a time resolution of 60 s at a spectral resolution of 4 cm\(^{-1}\). Then, all of the spectra were transformed into absorbance spectra.

2. Result and discussion
Figure S4. (a) XRD patterns of the Cu-BTC, Cu-BTEC and Cu-BDC. (b) CV curves of Cu-BTC in the reduction process during the last few cycles. (c) High-resolution XPS spectra for Cu 2p of the Cu-BTC-Cu, Cu-BTEC-Cu, and Cu-BDC-Cu.

Figure S5. SEM images of the (a, d) Cu-BTC-Cu, (b, e) Cu-BTEC-Cu, and (c, f) Cu-BDC-Cu.
Figure S6. Experimental equipment schematic diagram for electrocatalytic NRA

Figure S7. (a) LSV curves of Cu-BTEC-Cu and Cu-BDC-Cu at 0.05 M Na$_2$SO$_4$ and 0.05 M Na$_2$SO$_4$+750 mg/L NO$_3$⁻-N.

Figure S8. CV curves of (a) Cu-BTC-Cu, (b) Cu-BTEC-Cu, and (c) Cu-BDC-Cu under different scan rates from 20 to 120 mV s$^{-1}$. 

Figure S9. CV curves of Cu-BTC-Cu-5 and Cu-BTC-Cu-15 under different scan rates from 20 to 100 mV s$^{-1}$. 

Figure S10. Activity and selectivity of Cu-BTC-Cu, Cu-BTEC-Cu, and Cu-BDC-Cu towards nitrite reduction.
Figure S9. CV curves of (a) Cu-BTC-Cu-5, (b) Cu-BTEC-Cu-15, and (c) Cu-BDC-Cu-30 under different scan rates from 20 to 100 mV s\(^{-1}\). (d) The fitted linear relationship between current density and the scan rate for the Cu-BTC-Cu-5, Cu-BTEC-Cu-15, and Cu-BDC-Cu-30.

Figure S10. Characterizations of the Cu-BTC-Cu participates in electrocatalytic nitrate reduction before and after (Cu-BTC-Cu-Before and Cu-BTC-Cu-After): (a) High-resolution XPS spectra for Cu 2p, (b) XRD patterns, and (c, d) SEM images.

The standard curve is prepared by external standard method using NH\(_4\)Cl as standard solution. (Figure S11 a and b)
Figure S11. The NH$_4^+$ detection of (a) standard spectra and (b) fitting curve by ion chromatography.

Figure S12. NH$_3$ yields and FE of the Cu-BTC-Cu at different potentials by the Nessler’s color reagent and ion chromatography.

Figure S13. NH$_3$ yields and FE of the Cu-BTC-Cu at different concentrations of NO$_3^-$-N.
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Figure S15. The electrochemical impedance spectroscopy of Cu-BTC-Cu, Cu-BTEC-Cu, and Cu-BDC-Cu.

Table S1 Comparison of ammonia synthesis from nitrate reduction over Cu-BTC-Cu and other reported catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH$_3$ yield (μg h$^{-1}$ cm$^{-2}$)</th>
<th>Ref.</th>
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<tr>
<td>Cu-BTC-Cu</td>
<td>0.05 M K$_2$SO$_4$/750 mg L$^{-1}$ NO$_3^-$-N</td>
<td>4009.3</td>
<td>This work</td>
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<td>Cu@Th-BPYDC</td>
<td>1 M KOH/1400 mg L$^{-1}$ NO$_3^-$-N</td>
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<td>BCN-Cu 10</td>
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<td>FeS$_2$/RGO</td>
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<td>3</td>
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<td>WSe$_{2-x}$</td>
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<tr>
<td>MnO$_{2-x}$</td>
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<tr>
<td>BCN@Ni</td>
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<tr>
<td>Material</td>
<td>Solution Composition</td>
<td>Result</td>
<td>Source</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----------------------------------------------------------</td>
<td>--------</td>
<td>--------</td>
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<td>Pd/TiO$_2$</td>
<td>1 M LiCl/3500 mg L$^{-1}$ NO$_3^-$-N</td>
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<td>BP</td>
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<td>Co$_3$O$_4$-Mn$_2$</td>
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<td>Fe-MoS$_2$</td>
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<td>MoO$_2$-C NBF</td>
<td>1 M KOH/1400 mg L$^{-1}$ NO$_3^-$-N</td>
<td>1857.7</td>
<td>12</td>
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</table>
References:


