Electronic Supplementary Information

Determination of products

Detection of nitrate-N. [1] In order to adjust the absorbance to match the range of calibration curves, the electrolytes were diluted 12.5 times. Then, 0.1 mL 1 M HCl and 0.01 mL 0.8 wt.% NH$_2$SO$_3$H solution were added into 5 mL of diluted electrolyte. After 10 min, the absorption spectrum was recorded at wavelength of 220 nm and 275 nm. The final absorbance was confirmed by the following formula: $A = A_{220\text{nm}} - 2A_{275\text{nm}}$. The calibration curve of nitrate is measured by different concentrations of KNO$_3$.

Detection of nitrite-N. [1] First, 400 mg C$_6$H$_8$N$_2$O$_2$S, 20 mg C$_{12}$H$_{14}$N$_2$·2HCl and 1 mL H$_3$PO$_4$ was dissolved in the 5 mL water to form color developer. Then, 0.1 mL color developer was added into 5 mL of electrolytes which was diluted 20 times. When 20 min later, the absorbance was tested by UV-Vis spectrum and recorded at wavelength of 540 nm. The calibration curve of nitrate is measured by different concentrations of NaNO$_2$.

Detection of ammonium-N. [1] Nessler's reagent was used as color reagent for ammonium-N. A little of post-tested electrolyte was taken out and diluted 20 times. Then, 0.1 mL Nessler's reagent and 0.1 mL of 0.5 g/L C$_4$H$_6$O$_6$KNa·4H$_2$O was added to 5 mL diluted electrolyte., and the mixture was left for 20 min. The wavelength of ammonium-N at 420 nm was confirmed using UV-Vis spectrum. And the calibration curve of nitrate is measured by different concentrations of NH$_4$Cl.
**Isotope Labeling Experiments.**

The isotope labeling nitrate reduction experiment was performed using K$^{15}$NO$_3$ as N-source to confirm source of N in ammonia. The electrolyte contained 0.5 M K$_2$SO$_4$ and 50 ppm K$^{15}$NO$_3$-$^{15}$N was added into electrolytic cell as the reactant. Then, the pH value of the cathode electrolyte was adjusted to 1~2 by 4 M H$_2$SO$_4$ after electrocatalytic procedure in order to confirm that the N-source is nitrate reduction. The standard reference material used is K$^{15}$NO$_3$ and $^{15}$NH$_4$Cl.

**Calculation of yield, selectivity and Faradaic efficiency:** The calculation source of all results is provided by the absorbancemeasured by the UV-Vis spectrophotometer.

The result of yield is obtained by Eq. 1:

$$Yield_{NH_3} = (c_{NH_3} \times V)/(t \times m)$$  \hspace{1cm} (1)

The result of conversion rate is obtained by Eq. 2:

$$Conversion_{NO_3^-} = \frac{\Delta c_{NO_3^-}}{c_0} \times 100\%$$  \hspace{1cm} (2)

The result of NO$_2^-$ selectivity is obtained by Eq. 3:

$$Selectivity = \frac{c_{NO_2^-}}{\Delta c_{NO_3^-}} \times 100\%$$  \hspace{1cm} (3)

The result of NH$_3$ selectivity is obtained by Eq. 4:

$$Selectivity = \frac{c_{NH_3}}{\Delta c_{NO_3^-}} \times 100\%$$  \hspace{1cm} (4)

The Faradaic efficiency (FE) of nitrate reduction was obtained by Eq 5:

$$FE = \frac{(8F \times c_{NH_3} \times V)/(M_{NH_3} \times Q)}{(8F \times c_0 \times V)/(M_{NH_3} \times Q)}$$  \hspace{1cm} (5)

Here, $c_{NH_3}$ is the mass concentration of NH$_3$ in the cathode electrolyte after the test, V is the volume of electrolyte in the cathode, $M_{NH_3}$ is the molar mass of NH$_3$, t is the electrocatalytic time, m is the mass of the catalyst on the working electrode, $\Delta c_{NO_3^-}$ is the difference in the concentration of nitrate in the catholyte before and after electrocatalytic, $c_0$ is the actual concentration of nitrate in the conFig.d electrolyte, c is the concentration of nitrite or ammonia.
in the catholyte after electrolysis, \( F \) is the Faradaic constant (96485 C mol\(^{-1}\)), \( Q \) is the total charge pass electrode during the electrochemical process.

**Fig. S1** (a) SEM image and (b) TEM image of CuO NPs.

**Fig. S2** Cu 2p XPS spectrum of \( dr \)-Cu NPs.

**Fig. S3** SEM image of \( dr \)-Cu NPs.
Fig. S4. The electrocatalytic reduction of nitrate to ammonia in an H-type electrolytic cell.

Fig. S5 (a) The absorbance of different NaNO$_3$ concentration ranging from 0.2 μg mL$^{-1}$ to 4.0 μg mL$^{-1}$ (b) The concentration-absorbance calibration curves of nitrate-N.

Fig. S6 (a) The absorbance of different NaNO$_2$ concentration ranging from 0.01 μg mL$^{-1}$ to 0.2 μg mL$^{-1}$ (b) The concentration-absorbance calibration curves of nitrite-N.
**Fig. S7** (a) The absorbance of different NH$_4$Cl concentration ranging from 0.2 μg mL$^{-1}$ to 2 μg mL$^{-1}$ (b) The concentration-absorbance calibration curves of ammonium-N.

**Fig. S8** (a) TEM image and (b) HAADF-SEM image of $dr$-Cu NPs after electrocatalytic nitrate reduction testing.

**Fig. S9** SEM image of $df$-Cu NPs.
Fig. S10 LSV curves of $df$-Cu NPs and $dr$-Cu NPs in 0.5 M K$_2$SO$_4$ with 50 ppm KNO$_3$-N.

Fig. S11 LSV curves of $dr$-Cu NPs in 50 ppm KNO$_3$-N with and without 50 ppm SCN$^-$. 

Fig. S12 The $^1$H NMR spectra (600 MHz) of $^{15}$NH$_4^+$ with different $^{15}$NH$_4^+_1^{15}$N concentration. The proton signal of maleic acid appears at $\delta = 6.31$ ppm. The $^1$H NMR spectra of $^{15}$NH$_4^+$ showed double peaks at $\delta = 7.10$ and 6.98 ppm.
Fig. S13 (a) CV curves of \( dr\)-Cu NPs, (b) Plots of the current density versus the scan rate for \( dr\)-Cu NPs, (C) CV curves of \( df\)-Cu NPs with various scan rates from 20 to 100 mV s\(^{-1}\) and (d) Plots of the current density versus the scan rate for \( df\)-Cu NPs.

Fig. S14 EIS of \( dr\)-Cu NPs and \( df\)-Cu NPs.
Table S1 The comparisons of NO$_3$RR performance for the $dr$-Cu NPs and some other reported electrocatalysts.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Electrolyte</th>
<th>NO$_3^-$ conversion</th>
<th>Ammonia Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$dr$-Cu NPs</td>
<td>50 ppm NO$_3^-$-N + 0.5 M K$_2$SO$_4$</td>
<td>93.26%</td>
<td>81.99%</td>
<td>This work</td>
</tr>
<tr>
<td>Fe</td>
<td>50 ppm NO$_3^-$-N + 0.5 g/L Na$_2$SO$_4$</td>
<td>91%</td>
<td>28%</td>
<td>[2]</td>
</tr>
<tr>
<td>Pd-Fe foam</td>
<td>50 ppm NO$_3^-$-N + 413 ppm K$_2$HCO$_3$ + 172 ppm CaSO$_4$</td>
<td>39.8%</td>
<td>92%</td>
<td>[3]</td>
</tr>
<tr>
<td>Fe (20%)@N-C</td>
<td>50 ppm NO$_3^-$-N + 50 mM Na$_2$SO$_4$</td>
<td>83.0%</td>
<td>&lt;75%</td>
<td>[4]</td>
</tr>
<tr>
<td>Cu/Ti + Cu/AC</td>
<td>50 ppm NO$_3^-$-N</td>
<td>96.05%</td>
<td>62.64%</td>
<td>[5]</td>
</tr>
<tr>
<td>Cu/Ti</td>
<td>50 ppm NO$_3^-$-N +0.5 mg/L Na$_2$SO$_4$</td>
<td>71.8%</td>
<td>N.A.</td>
<td>[6]</td>
</tr>
<tr>
<td>Ni-Fe@Fe$_3$O$_4$</td>
<td>50 ppm NO$_3^-$-N + 10 mM NaCl</td>
<td>90.2%</td>
<td>10.4%</td>
<td>[7]</td>
</tr>
<tr>
<td>BDD</td>
<td>50 ppm NO$_3^-$-N + 0.1 g/L Na$_2$SO$_4$</td>
<td>42%</td>
<td>8.9%</td>
<td>[8]</td>
</tr>
<tr>
<td>Pd–Cu/γAl$_2$O$_3$</td>
<td>50 ppm NO$_3^-$-N</td>
<td>100%</td>
<td>19.6%</td>
<td>[9]</td>
</tr>
<tr>
<td>Pd$<em>{0.4}$Cu$</em>{0.6}$</td>
<td>50 ppm NaNO$_3$</td>
<td>N. A.</td>
<td>49%</td>
<td>[10]</td>
</tr>
<tr>
<td>Co$_3$O$_4$-TiO$_2$/Ti</td>
<td>50 ppm NO$_3^-$ + 0.1 M Na$_2$SO$_4$ + PVP + 1000 ppm Cl$^-$</td>
<td>89%</td>
<td>24%</td>
<td>[11]</td>
</tr>
<tr>
<td>Cu/Ni/20-min</td>
<td>50 ppm NO$_3^-$-N + 0.1 M K$_2$SO$_4$</td>
<td>97.2%</td>
<td>66.6%</td>
<td>[12]</td>
</tr>
<tr>
<td>Ni-TNTA</td>
<td>50 ppm NO$_3^-$-N</td>
<td>89.6%</td>
<td>N.A.</td>
<td>[13]</td>
</tr>
<tr>
<td>Pt nanoparticle</td>
<td>50 ppm NO$_3^-$-N</td>
<td>35%</td>
<td>N.A.</td>
<td>[14]</td>
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</table>
References


