-Supplementary Information

**Boosting Electrochemical Nitrogen Reduction to Ammonia with High Efficiency using LiNb$_3$O$_8$ Electro catalyst in Neutral Media**

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1. Determination of NH$_4^+$

The concentration of NH$_4^+$ was quantitatively determined by Indophenol blue colorimetry.

Preparation of chromogenic agent: 2 mL of 5wt% sodium citrate dehydrate-salicylic acid solution, 1 mL of sodium hypochlorite solution (0.05M), 0.2 mL of sodium nitroferricyanide dihydrate aqueous solution (1 wt%).

After 2 h of electrolysis, 2.0 mL of cathode electrolyte was mixed and slightly shaken with the above chromogen solution added in turn. After the reaction of mixed solution for 2 h, the curves were scanned in an ultraviolet spectrophotometer with the non-electrolytic electrolyte as blank contrast. The concentration of NH$_4^+$ can be obtained by substituting the absorbance at the wavelength of 655 nm into the standard working curve of NH$_4^+$.  

Standard working curve of NH$_4^+$: The linear relationship between the absorbance and NH$_4^+$ concentration can be obtained by measuring the absorbance curves corresponding to the standard ammonia solutions with different concentration gradients. The fitting curve (y =0.4437x+0.0014, \( R^2=0.9996 \)) shows good linear relation of absorbance value with NH$_4^+$ concentration, as shown in Fig.S9. The standard curves and fitting curve in acidic and alkaline electrolytes were tested in the same way, and the results are shown in Fig.S10.

The standard curve and fitting curve of the Nessler reagent used for control are shown in Fig.S11.

2. Determination of N$_2$H$_4$

The concentration of N$_2$H$_4$ was quantitatively determined by Watt and Chrisp method.

Preparation of chromogenic agent: 2mL of P-dimethylamino-benzaldehyde solution (0.2998 g p-dimethylamino-benzaldehyde powder, 15 mL of ethanol and 1.5 mL of concentrated hydrochloric acid).

After 2 h of electrolysis, 2.0 mL of cathodic electrolyte was mixed
with 2 ml of chromogenic solution and slightly shaken. Then the mixture reacted for 20 min, the curves were scanned in an ultraviolet spectrophotometer and pure water was used as blank contrast. The concentration of N$_2$H$_4$ can be obtained by subbing the absorbance at the wavelength of 455 nm into the N$_2$H$_4$ standard working curve.

Standard working curve of N$_2$H$_4$: The linear relationship between the absorbance and N$_2$H$_4$ concentration can be obtained by measuring the absorbance curves corresponding to the standard N$_2$H$_4$ solutions with different concentration gradients. The fitting curve ($y = 0.9843x + 0.0151$, $R^2 = 1$) shows good linear relation of absorbance value with N$_2$H$_4$ concentration, as is shown in Fig.S12.

3. Calculation of ammonia yield rate and faradaic efficiency

Ammonia yield rate ($r_{NH_3}$) is calculated by the formula:

$$r_{NH_3} = \frac{[NH_4^+] \times V}{t \times m_{cat}}$$

Faradaic efficiency (FE) is calculated by the formula:

$$FE = \frac{3F \times m_{NH_3}}{17 \times Q}$$

Where [NH$_4^+$] is the concentration of ammonia in the electrolyte ($\mu$g·mL$^{-1}$); $V$ represents the volume of the electrolyte(mL); $t$ is the reduction time (h); $m_{cat}$ is the loaded mass of catalyst on carbon paper ($\mu$g). F is the Faraday constant (96485 C/mol); Q is the amount of electricity consumed in the electrolysis process (C); $m_{NH_3}$ is the quality of the ammonia.

4. Calculation of ECSA

The electrochemical double-layer capacitance ($C_{dl}$) of the materials was measured to determine their electrochemical surface area (ECSA) using the cyclic voltammetry curves (CVs) in no faradic processes between 0.5 V vs. RHE and 0.6 V vs. RHE with diverse scan rates of 10, 20, 30, 50, 70, and 90 mV/s, respectively. The plotted current
density current density differences (Δ\( j/2 \)) at 0.55 V vs. RHE have a linear relationship with different scan rates and its slope is twice the \( C_{dl} \). The specific capacitance for a flat surface is generally found to be in the range of 20~60 \( \mu F \ cm^{-2} \), and we plug in 40 \( \mu F \ cm^{-2} \) in the following calculation.

The ECSA of LNO/CP can then be calculated as following:

\[
ECSA = \frac{0.24 \ mF \ cm^{-2}}{40 \ \mu F \ cm^{-2}} = 6.0 \ cm_{ECSA}^2
\]
Fig. S1. Raman spectrum of LNO.
Fig.S2. FTIR spectrum of LNO.
Fig. S3. EIS Nyquist plots of Li$_2$CO$_3$, Nb$_2$O$_5$ and LNO.
Fig. S4. (a) UV-vis absorption spectra using Nessler reagent assays. (b) NH₃ yield rate and FE of LNO after NRR electrolysis using Nessler reagent assays and Indophenol assays.
Fig.S5. (a) UV-vis absorption spectra in different electrolyte (0.05M H$_2$SO$_4$ , 0.1M Na$_2$SO$_4$, 0.1M KOH). (b) NH$_3$ yield rate and FE of LNO after NRR electrolysis in different electrolyte.
Fig. S6. (a) Cyclic voltammetry curves and (b) Plots of current density differences ($\Delta j/2$) at 0.55V with different scan rates of Nb$_2$O$_5$/CP. (c) Cyclic voltammetry curves and (d) Plots of current density differences ($\Delta j/2$) at 0.55V with different scan rates of Li$_2$CO$_3$/CP. (e) Cyclic voltammetry curves and (f) Plots of current density differences ($\Delta j/2$) at 0.55V with different scan rates of LNO/CP.
Fig. S7. (a) UV-vis absorption spectra using different catalyst (Nb$_2$O$_5$, Li$_2$CO$_3$, LNO). (b) NH$_3$ yield rate and FE after NRR electrolysis using different catalyst (Nb$_2$O$_5$, Li$_2$CO$_3$, LNO).
Fig. S8. Contact angles for blank CP, Li$_2$CO$_3$/CP, Nb$_2$O$_5$/CP and LNO/CP.
Fig. S9. (a) UV-vis absorption spectra of Indophenol assays with NH$_3$ in 0.1 M Na$_2$SO$_4$ after incubated for 2h under ambient conditions. (b) Calibration curve used for calculation of NH$_3$ concentration.
Fig. S10. (a) UV-vis absorption spectra of Indophenol assays with NH$_3$ in 0.05 M H$_2$SO$_4$ after incubated for 2h under ambient conditions. (b) Calibration curve used for calculation of NH$_3$ concentration. (c) UV-vis absorption spectra of Indophenol assays with NH$_3$ in 0.1 M KOH after incubated for 2h under ambient conditions. (d) Calibration curve used for calculation of NH$_3$ concentration.
Fig. S11. (a) UV-vis absorption spectra of Nessler reagent assays with NH$_3$ in 0.1 M Na$_2$SO$_4$ after incubated for 2h under ambient conditions. (b) Calibration curve used for calculation of NH$_3$ concentration.
Fig. S12: (a) UV-vis absorption spectra of various N\textsubscript{2}H\textsubscript{4} concentrations stained with C\textsubscript{9}H\textsubscript{11}NO indicator after incubated for 15 min under ambient conditions. (b) Calibration curve used for calculation of N\textsubscript{2}H\textsubscript{4} concentration.
Table S1. Comparison of the NRR electrocatalytic performance of LNO and other previously reported NRR electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH₃ yield rate</th>
<th>FE</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>LiNb₃O₈</td>
<td>0.1M Na₂SO₄</td>
<td>7.85</td>
<td>82.83</td>
<td>Our work</td>
</tr>
<tr>
<td>Ru-ZIF-8</td>
<td>0.1M KOH</td>
<td>16.68</td>
<td>14.23</td>
<td>[1]</td>
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<tr>
<td>Pd</td>
<td>0.1M PBS</td>
<td>4.5</td>
<td>8.20</td>
<td>[2]</td>
</tr>
<tr>
<td>Au/Ni</td>
<td>0.05M H₂SO₄</td>
<td>7.4</td>
<td>67.8</td>
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<tr>
<td>Fe₃₉-N-C</td>
<td>0.1M KOH</td>
<td>7.48</td>
<td>56.55</td>
<td>[4]</td>
</tr>
<tr>
<td>C18@Fe₂P</td>
<td>0.1M Na₂SO₄</td>
<td>1.80×10⁻¹⁰mol·s⁻¹·cm²</td>
<td>11.22</td>
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</tr>
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<td>MoS₂ NDs/rGO</td>
<td>0.1M Na₂SO₄</td>
<td>16.41</td>
<td>27.93</td>
<td>[6]</td>
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<tr>
<td>FeMo@NC</td>
<td>1.0M KOH</td>
<td>14.95</td>
<td>41.70</td>
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<td>Ti₃C₂Tx MXene</td>
<td>0.05M H₂SO₄</td>
<td>21.9</td>
<td>25.44</td>
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<tr>
<td>Co-N/S-N</td>
<td>0.05M Na₂SO₄</td>
<td>15.7</td>
<td>25.90</td>
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<td>NiO/G</td>
<td>0.1M Na₂SO₄</td>
<td>18.6</td>
<td>7.8</td>
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<td>CN/N</td>
<td>0.1M HCl</td>
<td>2.9</td>
<td>62.1</td>
<td>[11]</td>
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<tr>
<td>BiVO₄</td>
<td>0.2M Na₂SO₄</td>
<td>8.6</td>
<td>10.40</td>
<td>[12]</td>
</tr>
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</table>
Reference: