Electronic Supporting Information

Surface defect-regulated PdCu/TiO$_{2-x}$ promoting efficient electrocatalytic nitrogen reduction

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Experimental Section

NH$_3$ quantification

The quantitative detection of NH$_3$ concentration in solution was based on indiophenol blue coloration method.$^{1,2}$ Specifically, 2 mL cathode electrolyte and 2 mL absorption solution were collected, then 2mL chromogenic reagent containing salicylic acid (5 wt%), sodium citrate (5 wt%) and 1 mol/L NaOH solution was added, followed by adding 1mL NaClO solution (0.05 mol/L). and finally, 200 µL sodium nitroferricyanide solution (1 wt%) was added and then shaken slightly. The absorbance data of the UV-vis absorption spectra were measured on the UV-1800 spectrophotometer after standing the mixed solution in the dark and reacting for 2 h at room temperature. To further quantitative calculation, the absorbance (Abs, a.u.) of a series of standard NH$_4$Cl solutions (c, µg mL$^{-1}$) with specified concentrations at λ = 655 nm were recorded in advance. The NH$_4^+$ standard curve in 0.1 mol/L HCl is $y = 0.361x + 0.036$ ($R^2 = 0.999$).

N$_2$H$_4$ quantification

The quantitative detection of N$_2$H$_4$ concentration in solution was based on the method of Watt and Chrisp.$^{3,4}$ A mixture of 5.99 g C$_9$H$_{11}$NO, 30 mL hydrochloric acid and 300 mL ethanol was used as an indicator. Afterward, 2 mL cathode electrolyte and 2 mL absorption solution were collected, followed by adding 2 mL of indicator into above solutions, respectively. The corresponding absorbance at λ = 455 nm were measured after at 10 min at room temperature Similarly, The N$_2$H$_4$ standard curve in 0.1 mol/L HCl was measured in advance, and the curve is $y = 0.730x + 0.022$ ($R^2 = 0.999$).
**15N isotope labeling experiment**

When $^{15}\text{N}_2$ (99%, Shanghai Aladdin Biochemical Technology Co., LTD.) was used as the only feed gas, the produced $\text{NH}_3$ was determined by $^1\text{H}$ NMR spectra, using to further verify the N source of the produced $\text{NH}_3$. Before the electrochemical measurement, $^{15}\text{N}_2$ was immersed in the electrolyte for 1h until saturation. 500 $\mu$L of the electrolyte after electrolysis at $-0.1$ V vs. RHE was collected and 50 $\mu$L of DMSO-D6 was added, and then determined by a $^1\text{H}$ NMR spectrometer. Furthermore, the same procedure was used to detect $^{14}\text{NH}_3$ produced, apart from $^{14}\text{N}_2$ (99.999 %) as the feed gas.

**Computational criterion**

The $\text{NH}_3$ yield rate was calculated as follows equation:

$$\text{NH}_3 \text{ yield rate} = \frac{c(\text{NH}_4^+) \times V}{m_{\text{cat}} \times t}$$

where $c(\text{NH}_4^+)$ is the concentration of $\text{NH}_4^+$ determined by indophenol blue method, quantitatively. $V$ is the volume of the electrolyte, $m_{\text{cat}}$ is the mass of the catalyst and $t$ is the reduction time.

The Faradaic efficiency was estimated by the ratio of the charge consumed for $\text{NH}_3$ production to the total charge passing through the circuit. It was calculated according to following equation:

$$\text{FE} = \frac{3 \times F \times c(\text{NH}_4^+) \times V}{17 \times Q}$$

where $F$ is the Faraday constant ($96485$ C mol$^{-1}$), $c(\text{NH}_4^+)$ is the concentration of $\text{NH}_4^+$ determined by indophenol blue method, quantitatively. $V$ is the volume of the electrolyte and $Q$ is the quantity of applied electricity.
Fig. S1. SEM images of pristine TiO$_2$ and TiO$_{2-x}$-$T$ ($T = 200, 400, 600$). (a) SEM image of TiO$_2$; (b) SEM image of TiO$_{2-x}$-200; (c) SEM image of TiO$_{2-x}$-400; (d) SEM image of TiO$_{2-x}$-600.

Fig. S2. Raman spectra of pristine TiO$_2$ and TiO$_{2-x}$-400.
Fig. S3. SEM images of Pd$_1$Cu$_1$/TiO$_2$ and Pd$_1$Cu$_1$/TiO$_{2-x}$-T ($T = 200, 400, 600$). (a) SEM image of Pd$_1$Cu$_1$/TiO$_2$; (b) SEM image of Pd$_1$Cu$_1$/TiO$_{2-x}$-200; (c) SEM image of Pd$_1$Cu$_1$/TiO$_{2-x}$-400; (d) SEM image of Pd$_1$Cu$_1$/TiO$_{2-x}$-600.
Fig. S4. (a) TEM image of Pd₁Cu₁/TiO₂; (b) TEM image of Pd₁Cu₁/TiO₂ₓ-200. (c) TEM image of Pd₁Cu₁/TiO₂ₓ-400; (d) TEM image of Pd₁Cu₁/TiO₂ₓ-600.
Fig. S5. TEM images of Pd$_x$Cu$_y$/TiO$_{2-x}$-400. (a) TEM image of Pd/TiO$_{2-x}$-400; (b) TEM image of Pd$_2$Cu$_1$/TiO$_{2-x}$-400; (c) TEM image of Pd$_1$Cu$_2$/TiO$_{2-x}$-400; (d) TEM image of Cu/TiO$_{2-x}$-400.
**Fig. S6.** (a, b) TEM and HRTEM images of Rutile Pd\textsubscript{1}Cu\textsubscript{1}/TiO\textsubscript{2-x}-400; (c, d) TEM and HRTEM images of P25 Pd\textsubscript{1}Cu\textsubscript{1}/TiO\textsubscript{2-x}-400.

**Fig. S7.** XRD patterns of a series of different crystal phases (a) XRD patterns of rutile phase series; (b) XRD patterns of P25 series.
Fig. S8. Schematic diagram of a H-type electrolytic cell with a three-electrode system.

Fig. S9. Quantitative determination of NH$_3$ concentration based on indophenol blue method. (a) UV-vis absorption spectra of NH$_4^+$ standard solutions with specified concentrations; (b) NH$_4^+$ Standard curve in 0.1 mol/L HCl of specified concentrations.
Fig. S10. Quantitative determination of \( \text{N}_2\text{H}_4 \) concentration. (a) UV-vis absorption spectra of \( \text{N}_2\text{H}_4 \) standard solutions with specified concentrations; (b) \( \text{N}_2\text{H}_4 \) Standard curve in 0.1 mol/L HCl of specified concentrations.

Fig. S11. (a) UV-vis absorption spectra of electrolytes in cathode chamber after chronoamperometry test of \( \text{Pd}_1\text{Cu}_1/\text{TiO}_{2-x}-400 \) catalyst in the potential range of 0—0.5 V vs. RHE. (b) UV-vis absorption spectra of absorption solutions after chronoamperometry test of \( \text{Pd}_1\text{Cu}_1/\text{TiO}_{2-x}-400 \) catalyst in the potential range of 0—0.5 V vs. RHE.
Fig. S12. Comparison of the NRR performance of the Pd$_1$Cu$_1$/TiO$_{2-x}$-400 catalyst with other palladium-based catalysts and their alloy catalysts reported to date under ambient conditions.

Fig. S13. The N$_2$H$_4$ UV-vis absorption spectra of electrolytes at different potentials.

Fig. S14. Chronoamperometry stability test of 20 h in 0.1 mol/L HCl under ambient conditions.
Fig. S15. (a) Electrocatalytic NRR performance of the Pd$_1$Cu$_1$/TiO$_{2-x}$-200; (b) Electrocatalytic NRR performance of the Pd$_1$Cu$_1$/TiO$_{2-x}$-600.

Fig. S16. EPR spectra of pristine TiO$_2$, Rutile TiO$_{2-x}$-400, P25 TiO$_{2-x}$-400, and TiO$_{2-x}$-400.
Fig. S17. (a) Electrocatalytic NRR performance of the pristine Pd/TiO$_{2-x}$-400; (b) Electrocatalytic NRR performance of the Pd$_2$Cu$_1$/TiO$_{2-x}$-400; (c) Electrocatalytic NRR performance of the Pd$_1$Cu$_2$/TiO$_{2-x}$-400; (d) Electrocatalytic NRR performance of the Cu/TiO$_{2-x}$-400.

Fig. S18. NH$_3$ yield rate of the Pd$_x$Cu$_y$/TiO$_{2-x}$-400 of various metal mole ratios.
Fig. S19. Full high-resolution XPS spectra of (a) Pd/TiO$_2$; (b) Cu/TiO$_2$; (c) Pd$_x$Cu$_{1-x}$/TiO$_2$; (d) Pd$_1$Cu$_{1}$/TiO$_2$.$-$400.

Fig. S20. (a) NH$_4^+$ Standard curve in 0.1 mol/L LiCl of specified concentrations; (b) NH$_4^+$ Standard curve in 0.1 mol/L KHCO$_3$ of specified concentrations.
**Table S1** Details for synthesis of PdCu/TiO$_{2-\times}$-400 electrocatalysts with various metal molar ratios.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PdCl$_2$ (µL, 5 mg mL$^{-1}$)</th>
<th>CuCl$_2$-2H$_2$O (µL, 5 mg mL$^{-1}$)</th>
<th>TiO$_{2-\times}$-400 (mg)</th>
<th>NaBH$_4$ solution (10 mg mL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/TiO$_{2-\times}$-400</td>
<td>510</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd$_2$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>340</td>
<td>164</td>
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<tr>
<td>Pd$_2$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>256</td>
<td>246</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>Pd$_2$Cu$<em>2$/TiO$</em>{2-\times}$-400</td>
<td>170</td>
<td>328</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu/TiO$_{2-\times}$-400</td>
<td>0</td>
<td>492</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table S2** Details for synthesis of Pd$_1$Cu$_1$/TiO$_{2-\times}$-400 electrocatalysts with various metal loadings.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PdCl$_2$ (µL, 5 mg mL$^{-1}$)</th>
<th>CuCl$_2$-2H$_2$O (µL, 5 mg mL$^{-1}$)</th>
<th>TiO$_{2-\times}$-400 (mg)</th>
<th>NaBH$_4$ solution (10 mg mL$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>128</td>
<td>123</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>256</td>
<td>246</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>384</td>
<td>369</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>4 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>512</td>
<td>492</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>640</td>
<td>615</td>
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</tr>
</tbody>
</table>

**Table S3** Weight quantifications of PdCu/TiO$_{2-\times}$-400 with various metal molar ratios based on ICP-MS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading (wt%)</th>
<th>Loading (wt%)</th>
<th>Molar ratio</th>
<th>Practical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/TiO$_{2-\times}$-400</td>
<td>2.26</td>
<td>0.00</td>
<td>/</td>
<td>Pd/TiO$_{2-\times}$-400</td>
</tr>
<tr>
<td>Pd$_2$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>1.91</td>
<td>0.58</td>
<td>1.98:1</td>
<td>Pd$_{1.91}$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
</tr>
<tr>
<td>Pd$_2$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>1.38</td>
<td>0.75</td>
<td>1.10:1</td>
<td>Pd$_{1.10}$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
</tr>
<tr>
<td>Pd$_2$Cu$<em>2$/TiO$</em>{2-\times}$-400</td>
<td>0.93</td>
<td>1.16</td>
<td>0.48:1</td>
<td>Pd$_{0.48}$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
</tr>
<tr>
<td>Cu/TiO$_{2-\times}$-400</td>
<td>0.00</td>
<td>2.07</td>
<td>/</td>
<td>Cu/TiO$_{2-\times}$-400</td>
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</tbody>
</table>

**Table S4** Weight quantifications of Pd$_1$Cu$_1$/TiO$_{2-\times}$-400 with various metal loadings based on ICP-MS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading (wt%)</th>
<th>Loading (wt%)</th>
<th>Molar ratio</th>
<th>Practical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>0.38</td>
<td>0.66</td>
<td>1.03:1</td>
<td>1.04 wt%-Pd$_{1.03}$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
</tr>
<tr>
<td>2 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>1.38</td>
<td>0.75</td>
<td>1.10:1</td>
<td>2.13 wt%-Pd$_{1.10}$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
</tr>
<tr>
<td>3 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>1.31</td>
<td>2.26</td>
<td>1.03:1</td>
<td>3.57 wt%-Pd$_{1.03}$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
</tr>
<tr>
<td>4 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>1.56</td>
<td>2.66</td>
<td>1.02:1</td>
<td>4.23 wt%-Pd$_{1.02}$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
</tr>
<tr>
<td>5 wt%-Pd$_1$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
<td>1.90</td>
<td>3.35</td>
<td>1.05:1</td>
<td>5.25 wt%-Pd$_{1.05}$Cu$<em>1$/TiO$</em>{2-\times}$-400</td>
</tr>
</tbody>
</table>
Table S5 Comparison of the NRR performance of the Pd$_{1}$Cu$_{1}$/TiO$_{2}$-x-400 catalyst with other palladium-based catalysts and their alloy catalysts reported to date under ambient conditions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Potential (V vs. RHE)</th>
<th>NH$<em>3$ yield rate (mmol g$</em>{cat}$ h$^{-1}$)</th>
<th>Faradaic efficiency (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$<em>{1}$Cu$</em>{1}$/TiO$_{2}$-x-400</td>
<td>0.1 M HCl</td>
<td>-0.10</td>
<td>8.51</td>
<td>49.09</td>
<td>This work</td>
</tr>
<tr>
<td>Pd-TA</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.45</td>
<td>1.42</td>
<td>9.49</td>
<td>5</td>
</tr>
<tr>
<td>Pd/C</td>
<td>0.1 M PBS</td>
<td>-0.05</td>
<td>0.26</td>
<td>8.20</td>
<td>6</td>
</tr>
<tr>
<td>Pd/C</td>
<td>0.1 M HCl</td>
<td>-0.05</td>
<td>0.28</td>
<td>0.15</td>
<td>7</td>
</tr>
<tr>
<td>PdPb/C</td>
<td>0.1 M HCl</td>
<td>-0.05</td>
<td>2.22</td>
<td>1.19</td>
<td>7</td>
</tr>
<tr>
<td>PdO/Pd/CNTs</td>
<td>0.1 M NaOH</td>
<td>0.10</td>
<td>1.07</td>
<td>11.50</td>
<td>8</td>
</tr>
<tr>
<td>PdP$_2$rGO</td>
<td>0.5 M LiClO$_4$</td>
<td>-0.10</td>
<td>1.78</td>
<td>12.56</td>
<td>9</td>
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<tr>
<td>nanoporous Pd$_{1}$Bi</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>-0.20</td>
<td>3.47</td>
<td>21.52</td>
<td>10</td>
</tr>
<tr>
<td>np-PdH$_{0.43}$</td>
<td>0.1 M PBS</td>
<td>-0.15</td>
<td>1.20</td>
<td>43.6</td>
<td>11</td>
</tr>
<tr>
<td>Pd$<em>{0.2}$Cu$</em>{0.8}$/rGO</td>
<td>0.1 M KOH</td>
<td>-0.20</td>
<td>0.16</td>
<td>3.00</td>
<td>12</td>
</tr>
<tr>
<td>Nanoporous Pd$<em>{3}$Cu$</em>{1}$</td>
<td>1 M KOH</td>
<td>-0.25</td>
<td>2.35</td>
<td>0.60</td>
<td>13</td>
</tr>
<tr>
<td>RhCu-BUNNs</td>
<td>0.1 M KOH</td>
<td>-0.20</td>
<td>5.59</td>
<td>1.50</td>
<td>14</td>
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<tr>
<td>mAu$_3$Pd/NF</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.10</td>
<td>1.41</td>
<td>18.16</td>
<td>15</td>
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<tr>
<td>BCC PdCu</td>
<td>0.5 M LiCl</td>
<td>-0.10</td>
<td>2.10</td>
<td>11.50</td>
<td>16</td>
</tr>
<tr>
<td>AuPdP NWs</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>-0.30</td>
<td>1.10</td>
<td>15.44</td>
<td>17</td>
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<tr>
<td>PdRu TP$_s$</td>
<td>0.1 M KOH</td>
<td>-0.20</td>
<td>2.19</td>
<td>1.85</td>
<td>18</td>
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<tr>
<td>PdZn/NHCP</td>
<td>0.1 M PBS</td>
<td>-0.20</td>
<td>0.31</td>
<td>16.9</td>
<td>19</td>
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<tr>
<td>BCC OV-PdCu-2</td>
<td>0.1 M Li$_2$SO$_4$</td>
<td>0.00</td>
<td>3.27</td>
<td>15.6</td>
<td>20</td>
</tr>
</tbody>
</table>
References

1. Z. Geng, Y. Liu, X. Kong, P. Li, K. Li, Z. Liu, J. Du, M. Shu, R. Si and J. Zeng, Achieving a record-high yield rate of 120.9 $\mu$g NH$_3$ mg$^{-1}$ h$^{-1}$ for N$_2$ electrochemical reduction over Ru single-atom catalysts, Adv. Mater., 2018, 30, 1803498.


16. W. Tong, B. L. Huang, P. T. Wang, L. G. Li, Q. Shao and X. Q. Huang, Crystal-phase-engineered PdCu electrocatalyst for enhanced ammonia synthesis, Angew. Chem. Int. Ed., 2020, 59, 2649-

