Coupling Cu with Au for enhanced electrocatalytic activity of nitrogen reduction reaction

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Experimental section

Ammonia determination

The absorbance of the produced NH\textsubscript{3} was spectrophotometrically quantitatively determined via indophenol blue method. In this method, ammonia reacted with phenol and hypochlorite in alkaline solution, sodium nitroferricyanide as the catalyst, producing blue-green indophenol blue dye for quantitative determination. In detail, the electrolyte (2 mL) after NRR test was mixed thoroughly with NaOH (2 mL) solution containing salicylic acid and sodium citrate, NaClO (1 mL, 0.05 mol L\textsuperscript{-1}) and \text{C}_\text{5}\text{FeN}_6\text{Na}_2\text{O} (0.2 mL, 1 wt%), then the mixed solution was preserved undisturbed for 2 h at room temperature. The absorbance of produced indophenol blue was measured by UV-Vis spectrophotometer at a wavelength of 655 nm. Meanwhile, the absorbance of the blank sample was subtracted for background correction. The calibration curve was obtained using a series of known concentrations of NH\textsubscript{4}\textsuperscript{+} as standard in 0.05 mol L\textsuperscript{-1} H\textsubscript{2}SO\textsubscript{4} solution. Then, the determined concentration of NH\textsubscript{4}\textsuperscript{+} could be calculated from the linear equation (\text{Absorbance} = 0.369 C_{NH_{4}^{+}} + 0.0233, R\textsuperscript{2} = 0.9999). The measurements of background solution were performed in all spectrum experiments.

Hydrazine determination

In an acidic environment, hydrazine (N\textsubscript{2}H\textsubscript{4}) could react with p-dimethylaminobenzaldehyde to produce yellow compounds with the absorption spectrum at a wavelength of 455 nm, which served as the basis for spectrophotometric determination of hydrazine. The preparation of the color reagent was as follows: p-dimethylaminobenzaldehyde (0.8 g) was dissolved in anhydrous ethanol (40.0 mL) and hydrochloric acid (12 mol L\textsuperscript{-1}, 4.0 mL) mixture solution. 5 mL electrolyte after 2 h electrolysis was added into as-obtained color reagent (5 mL) for 10 min at room temperature. Subsequently, the absorbance at 455 nm were measured.
by UV-Vis spectrophotometer. For background correction, 10 mL electrolyte before electrolysis was measured likewise.

**Faradic efficiency (FE) and NH₃ yield rate**

The faradic efficiency of NRR is the ratio of the amount of electric charge consumed for the production of NH₃ to the total amount of charge through the electrode during the electrolysis process. FE can be calculated according to the following formula:

\[
FE = 3 \times C_{NH_3} \times V_{electrolyte} \times F / (17 \times Q)
\]  \hspace{1cm} (1)

NH₃ yield rate formula as follows:

\[
\nu_{NH_3} = C_{NH_3} \times V_{electrolyte} / (t \times m_{cat})
\]  \hspace{1cm} (2)

Where constant 3 is the transfer electron number of produced NH₃, \( C_{NH_3} \) (μg mL⁻¹) is the concentration of produced NH₃, \( V_{electrolyte} \) (20 mL in our work) is the volume of the H₂SO₄ electrolyte, F (96485 C mol⁻¹) is the Faraday constant, constant 17 is the molar mass of NH₃, \( Q \) (C) is the normalized area of current and time after electrolysis, \( t \) (2 h) is the time for electrolysis and \( m_{cat} \) (3 μL × 0.5 mg mL⁻¹) is the loading mass of electrocatalyst.

The obtained absorbance and \( Q \) value on Au₁Cu₁/GCE at -0.2 V were used for sample calculation. Sample data:

<table>
<thead>
<tr>
<th>Potential</th>
<th>Abs-1</th>
<th>Abs-2</th>
<th>Abs-3</th>
<th>Q</th>
<th>( C_{NH_3} )-1</th>
<th>( C_{NH_3} )-2</th>
<th>( C_{NH_3} )-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.2 V</td>
<td>0.0319</td>
<td>0.0320</td>
<td>0.0317</td>
<td>0.0144</td>
<td>0.0233</td>
<td>0.0236</td>
<td>0.0228</td>
</tr>
</tbody>
</table>

For example, after 2 h electrolysis on Au₁Cu₁/GCE at -0.2 V, the obtained absorbance by three successive measurements with indophenol blue method at the wavelength of 655 nm are 0.0319, 0.0320, and 0.0317, respectively. Based on the linear equation for NH₄⁺ determination (Absorbance = 0.369 \( C_{NH_4^+} \) + 0.0233, \( R^2 = 0.9999 \)), we can calculate the produced NH₄⁺ concentration (0.0233 μg mL⁻¹, 0.0236 μg mL⁻¹ and 0.0228 μg mL⁻¹). Therefore, we can obtain corresponding FE through formula (1):

\[
FE = 3 \times C_{NH_4^+} \times V_{electrolyte} \times F / (17 \times Q)
\]

\[
= 3 \times 0.0233 \text{ μg mL}^{-1} \times 20 \text{ mL} \times 96485 \text{ C mol}^{-1} / (17 \text{ g mol}^{-1} \times 0.0144 \text{ C}) \times 10^{-4} \%
\]

\[
= 55.10\%
\]

Similarly, \( \nu_{NH_3} = C_{NH_3} \times V_{electrolyte} / (t \times m_{cat}) \)

\[
= 0.0233 \text{ μg mL}^{-1} \times 20 \text{ mL} / (2 \text{ h} \times 3 \text{ μL} \times 0.5 \text{ mg mL}^{-1})
\]

\[
= 155.33 \text{ μg h}^{-1} \text{ mg}_{cat}^{-1}
\]

So, we can calculate the NH₃ yield rate and corresponding FE at different potentials through the obtained NH₄⁺ concentration and \( Q \) value.
**Fig. S1** (a) UV-Vis spectra of indophenol blue method with multiple known NH$_4^+$ concentrations after incubated for 2 h at room temperature. (b) Calibration curve is used to calculate the produced NH$_4^+$ concentration after 2h electrolysis in 0.05 mol L$^{-1}$ H$_2$SO$_4$ electrolyte.

**Fig. S2** UV-Vis spectra of the electrolyte after electrolysis for 2 h on Au$_1$Cu$_1$/GCE at different potentials stained with the indicator for N$_2$H$_4$·H$_2$O.

**Fig. S3** UV-Vis spectra of the electrolyte after 2 h electrolysis stained with indophenol indicator.
**Fig. S4** (a, b) HAADF-STEM image and EDX mapping images of Au$_3$Cu$_1$ (a) and Au$_1$Cu$_3$ (b) nanowires.

**Fig. S5** (a-c) TEM images of Au$_1$Ag$_1$, Au$_1$Pd$_1$ and Au$_1$Ru$_1$ nanowires, respectively. (d) XRD patterns of Au$_1$Ag$_1$, Au$_1$Pd$_1$ and Au$_1$Ru$_1$ nanowires, respectively. (e-h) XPS spectra of Au 4f region (Au 4f$_{7/2}$ and Au 4f$_{5/2}$) (e), Ag 2p region (Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$) (f), Pd 3d region (Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$) (g), and Ru 3p region (Ru 3p$_{3/2}$ and Ru 3p$_{1/2}$) (h) of Au$_1$Ag$_1$, Au$_1$Pd$_1$ and Au$_1$Ru$_1$ nanowires.

**Fig. S6** (a) Cycling tests on Au$_1$Cu$_1$/GCE at -0.2 V; (b) corresponding UV-Vis spectra of the electrolytes after 2 h electrolysis stained with indophenol indicator.
Table S1. Comparison of the electrocatalytic NRR activity of Au$_{1}$Cu$_{1}$ nanocatalyst with other reported NRR catalysts under ambient condition.

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>electrolyte</th>
<th>FE(%)</th>
<th>NH$_3$ yield rate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$<em>{1}$Cu$</em>{1}$/GCE</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>54.96</td>
<td>154.91 µg h$^{-1}$ mg$_{cat}$$^{-1}$</td>
<td>This work</td>
</tr>
<tr>
<td>PdCu/rGO</td>
<td>0.1 M KOH</td>
<td>0.6</td>
<td>2.8 µg h$^{-1}$ mg$_{cat}$$^{-1}$</td>
<td>1</td>
</tr>
<tr>
<td>Pd-Co/CuO</td>
<td>0.1 M KOH</td>
<td>2.16</td>
<td>10.04 µg h$^{-1}$ mg$_{cat}$$^{-1}$</td>
<td>2</td>
</tr>
<tr>
<td>PdRu nanorod</td>
<td>0.1 M HCl</td>
<td>2.4</td>
<td>34.2 µg h$^{-1}$ mg$_{cat}$$^{-1}$</td>
<td>3</td>
</tr>
<tr>
<td>Ag nanosheet</td>
<td>0.1 M HCl</td>
<td>4.8</td>
<td>4.62×10$^{-11}$ mol s$^{-1}$ cm$^{-2}$</td>
<td>4</td>
</tr>
<tr>
<td>AuAg@ZIF</td>
<td>THF-based electrolyte</td>
<td>18</td>
<td>0.61 µg h$^{-1}$ cm$^{-2}$</td>
<td>5</td>
</tr>
<tr>
<td>TA-reduced Au/TiO$_2$</td>
<td>0.1 M HCl</td>
<td>8.11</td>
<td>21.4 µg h$^{-1}$ mg$_{cat}$$^{-1}$</td>
<td>6</td>
</tr>
<tr>
<td>THH Au NRs</td>
<td>0.1 M KOH</td>
<td>4.1</td>
<td>1.648 mg h$^{-1}$ cm$^{-2}$</td>
<td>7</td>
</tr>
<tr>
<td>pAu/NF</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>13.36</td>
<td>9.42 µg h$^{-1}$ cm$^{-2}$</td>
<td>8</td>
</tr>
<tr>
<td>Au/C$_3$N$_4$</td>
<td>5 mM H$_2$SO$_4$</td>
<td>11.1</td>
<td>1,305 µg h$^{-1}$ mg$_{Au}$$^{-1}$</td>
<td>9</td>
</tr>
<tr>
<td>Au/CoO$_x$</td>
<td>0.1 M HCl</td>
<td>10.1</td>
<td>37.3 µmol h$^{-1}$ mg$_{Au}$$^{-1}$</td>
<td>10</td>
</tr>
<tr>
<td>AuHNCs/ITO</td>
<td>0.5 M LiClO$_4$</td>
<td>30.2</td>
<td>3.9 µg cm$^{-2}$ h$^{-1}$</td>
<td>11</td>
</tr>
<tr>
<td>Au flowers</td>
<td>0.1 M HCl</td>
<td>6.05</td>
<td>25.57 µg h$^{-1}$ mg$_{cat}$$^{-1}$</td>
<td>12</td>
</tr>
<tr>
<td>Ru SAs/N-C</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>29.6</td>
<td>120.9 µg h$^{-1}$ mg$_{cat}$$^{-1}$</td>
<td>13</td>
</tr>
<tr>
<td>Ru NPs</td>
<td>0.01 M HCl</td>
<td>5.4</td>
<td>21.4 mg h$^{-1}$ m$^{-2}$</td>
<td>14</td>
</tr>
<tr>
<td>Ru@ZrO$_2$/NC</td>
<td>0.01 M HCl</td>
<td>21</td>
<td>3.665 mg$<em>{mom}$ h$^{-1}$ mg$</em>{Ru}$</td>
<td>15</td>
</tr>
<tr>
<td>Bi/carbon black</td>
<td>pH 3.5, 1.0 M K$^+$</td>
<td>66</td>
<td>200 mmol NH$_3$ g$^{-1}$ h$^{-1}$</td>
<td>16</td>
</tr>
</tbody>
</table>

References