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Regulating charge distribution of Cu$_3$PdN nanocrystals for nitrate electroreduction to ammonia†

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1. Experimental section

1.1 Chemicals and materials
Copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O), oleylamine, and 1-octadecene were purchased from Sigma-Aldrich. Palladium(II) acetylacetonate (Pd(acac)$_2$) was purchased from Alfa Aesar. Oleylamine and octadecene were degassed prior to used, and all other chemicals were used as received without further purification. All syntheses were carried out under Ar using standard Schlenk techniques, and the workup procedures were performed in air.

1.2 Synthesis of Cu$_3$PdN and Cu$_3$N
Cu(NO$_3$)$_2$·3H$_2$O (60 mg) and Pd(acac)$_2$ (25.2 mg) were dissolved in 7.5 mL of 1-octadecene and 2.5 mL of oleylamine. The solution was then transferred to a 100 mL three-necked round-bottom flask fitted with a condenser, thermometer adapter, thermometer, and rubber septum and was degassed under vacuum at 120 °C for 10 min. The flask was then filled with argon, heated to 240 °C, and kept at this temperature for 15 min. The flask was then removed from the heating mantle and allowed to cool to room temperature.$^1$ A solid was precipitated by adding 25 mL of ethanol and then centrifuging at 10000 rpm for 5 min. The product was washed three times by using a 1:1 toluene/ethanol mixture. By the same method, the Cu$_3$N nanoparticles were obtained without Pd(acac)$_2$.

1.3 Synthesis of Cu$_3$PdN-300/AC and Cu$_3$N-300/AC
The achieved Cu$_3$PdN (or Cu$_3$N) was dispersed in cyclohexane by ultrasonication to form a homogeneous solution. The obtained above dispersion was added in 50 mL carbon black (2 mg·mL$^{-1}$) dropwise with continuous ultrasonication and following stirring for 24 h. Subsequently, the achieved powder was washed with cyclohexane and ethanol, respectively. Then, the achieved powder was dried in a vacuum drying oven at 30 °C. The lastly, the achieved powder was annealed at 300 °C for 3 h at Ar atmosphere and named as Cu$_3$PdN-300/AC. By the same process, the Cu$_3$N-300/AC was obtained. In addition, other Cu$_3$PdN-200/AC, Cu$_3$PdN-400/AC and Cu$_3$PdN-500/AC samples at different annealing temperatures (such as 200 °C, 400 °C and 500 °C, respectively) were prepared by using the same method described above.
1.4 Characterization

The structure and morphology were characterized by X-ray powder diffraction (XRD, Rigaku Ultima IV), Transmission electron microscopy (TEM, Hitachi H-7700), high resolution TEM (HRTEM), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and elemental mapping by energy-dispersive X-ray spectrometry (EDS, JEOL JEM-2100F), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi). The metal contents in achieved product were detected by ICP-OES (Agilent 720). The products were determined by Nuclear magnetic resonance hydrogen spectrum (1H NMR, AVANCE 400).

2 Electrochemical measurements

2.1 Preparation of Cu₃PdN-300/AC (or Cu₃N-300/AC) electrode

Typically, 2 mg of Cu₃PdN-300/AC (or Cu₃N-300/AC) and 10 µL of Nafion (5wt%) were scattered in a mixture of 200 µL water and 100 µL anhydrous alcohol by ultrasonic treatment for 30 mins to form a homogeneous liquid. Then, 30 µL of suspension was added on carbon cloth (0.5×0.5 cm²) and dried at natural atmosphere, and the Cu₃PdN-300/AC (Cu₃N-300/AC) electrode. The preparation of the Cu₃PdN-300/CP (Cu₃N-300/AC/CP) electrode is the same as that of Cu₃PdN-300/AC electrode.

2.2 Electrochemical nitrate reduction experiment

Electrochemical measurements were tested by a CHI 660E electrochemical workstation. A typical H-type electrolytic cell separated by a membrane was employed. The catalyst located on carbon paper, saturated Ag/AgCl electrode and platinum wire respectively as the working electrode, reference electrode and counter electrode. The surface area of the working electrode was controlled with 0.25 cm². 1.0 g·L⁻¹ Na₂SO₄ solution (30 mL) was distributed to the cathode and anode compartment. NaNO₃ was added into the cathode compartment for NO₃⁻ reduction (containing 50 ppm nitrate-N). All potentials were recorded against the reversible hydrogen electrode (RHE). All the polarization curves were the steady lines after continuous cycles, and the current density was normalized to the geometric. The liner sweep voltammetry was performed at a rate of 10 mV·s⁻¹, and the potentiostatic test
was conducted at the different potential for 3 h at a stirring rate of ~300 rpm. For the stability test, the same piece of catalysts undergoes the above process eight times. The double-layer capacitance was evaluated at overpotential from -0.25 V to -0.35 V vs. RHE at different scan rate in 1.0 g·L⁻¹ Na₂SO₄ solution.

3 Determination of ion concentration

The ultraviolet-visible (UV-Vis) spectrophotometer was used to detect the ion concentration of pre- and post-test electrolytes after diluting to appropriate concentration to match the range of calibration curves. The specific detection methods are as follow:

3.1 Determination of nitrate-N

Firstly, 1.0 ml electrolyte was taken out from the electrolytic cell and diluted to 5 ml to the detection range. Then, 0.1 mL 1 M HCl and 0.01 ml 0.8 wt% sulfamic acid solution were added into the aforementioned solution. The absorption spectrum was measured using an ultraviolet-visible spectrophotometer and the absorption intensities at a wavelength of 220 nm and 275 nm were recorded. The final absorption value was calculated by this equation: \( A = A_{220nm} - 2A_{275nm} \). The concentration-absorbance curve was calibrated using a series of standard potassium nitrate solutions and the potassium nitrate crystal was dried at 105 ~ 110 °C for 2h in advance.

3.2 Determination of nitrite-N

The color developer was configured as follows: p-aminobenzenesulfonamide (20 g) was added to a mixed solution of 250 mL of ultrapure water and 50 mL of phosphoric acid (\( \rho = 1.70 \text{ g·mL}^{-1} \)), and then N-(1-Naphthyl)ethylenediamine dihydrochloride (1.0 g) was dissolved in the above solution. Finally, the above solution was transferred to a 500 mL volumetric flask and diluted to the mark. 1.0 mL electrolyte was taken out from the electrolytic cell and diluted to 5 mL to detection range. Next, 0.1 mL color reagent was added into the aforementioned 5 mL solution. After shaking and standing for 20 minutes, the absorbance was tested by UV-Vis spectrophotometry at a wavelength of 540 nm. The concentration-absorbance curve was calibrated using a series of standard sodium nitrite solutions.

3.3 Determination of ammonia-N
The produced ammonia was spectrophotometrically determined by the indophenol blue method. Typically, 1.0 mL electrolyte was taken out from the electrolytic cell and diluted to 5 mL to the detection range. Afterwards, 2 mL of 1.0 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate was added, followed by 1 ml NaClO solution (0.05 M) and 0.2 mL of an aqueous solution of sodium nitroferricyanide (1 wt%) were added. After standing at room temperature for 2h, the UV-Vis absorption spectrum was collected at a wave-length of 655 nm. The concentration-absorbance curve was calibrated by using standard NH₄Cl solution for a series of concentrations. The concentration-absorbance curve was calibrated can be obtained through different concentrations of NH₄Cl solutions and the NH₄Cl chloride crystal was dried at 105 °C for 2 h in advance.

3.4 Calculation of the yield, selectivity, and Faradaic efficiency

The potential (versus saturated Ag/AgCl) was converted to RHE using the following equations:

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0592 \, \text{pH} + E^0_{\text{Ag/AgCl}} \]

The conversion of NO₃⁻ was calculated using the equations:

\[ C_{\text{NO}_3^-} = \Delta C_{\text{NO}_3^-} / C_0 \times 100\% \]

The selectivity of the product calculated using the equations:

\[ S_{\text{NO}_2^-} = C_{\text{NO}_2^-} / \Delta C_{\text{NO}_3^-} \times 100\% \]
\[ S_{\text{NH}_3} = C_{\text{NH}_3} / \Delta C_{\text{NO}_3^-} \times 100\% \]

The yield rate of NH₃ was calculated using the equations:

\[ Y_{\text{NH}_3} = (C_{\text{NH}_3} \times V) / (t \times m_{\text{cat}}) \]

The Faradaic efficiency was calculated using the equations:

\[ \text{FE}_i = (n_i \times z_i \times F) / Q \times 100\% \]

Where \( E^0_{\text{Ag/AgCl}} = 0.197 \, \text{V} \), \( C_0 \) is the initial concentration of NO₃⁻, \( C_{\text{NH}_3} \) is the measured NH₃ concentration (mol·L⁻¹), \( V \) is the electrolyte volume of cathode cell, \( t \) is the electrolysis time, \( m_{\text{cat}} \) is the mass of catalyst, \( n_i \) is the amount of product i (mol), \( z_i \) is the number of electrons transferred to product i, \( F \) is the Faradaic
constant ($96,485 \text{ C mol}^{-1}$), $Q$ is the total charge (C) passing the electrolytic cell.
**Fig. S1** TEM image of Cu₃PdN.
Fig. S2 TEM image of Cu$_3$N nanoparticles.
Fig. S3 LSV curves of (A) Cu$_3$PdN-200/AC, (B) Cu$_3$PdN-300/AC, (C) Cu$_3$PdN-400/AC and (D) Cu$_3$PdN-500/AC in Na$_2$SO$_4$ with and without 50 ppm NO$_3^-$.
Fig. S4 (A) TEM image and (B) XRD pattern of commercial Pd/C.
**Fig. S5** Comparison of electrocatalytic activities of Cu$_3$PdN-300/AC and commercial Pd/C in Na$_2$SO$_4$ with and without 50 ppm NO$_3^-$.
Fig. S6 The $i$-$t$ curves of (A) Cu$_3$N-300/AC, (B) Cu$_3$PdN-300/AC and (C) Pd/C at different potential.
Fig. S7 (A) The UV-Vis absorption spectra of NH₄Cl solutions with different concentrations, (B) the standard calibration curve for the determination of ammonia; (C) The UV-Vis absorption spectra of KNO₃ solutions with different concentrations, (D) the standard calibration curve for the determination of NO₃⁻-N; (E) The UV-Vis absorption spectra of KNO₂ solutions with different concentrations, (F) the standard calibration curve for the determination of NO₂⁻-N.
Fig. S8 Faradaic efficiency and selectivity of ammonia and conversion rate of nitrate over Cu₃PdN-300/AC and commercial Pd/C.
Fig. S9 (A) The Tafel slope of Cu$_3$PdN-300/AC, Cu$_3$N-300/AC and Pd/C in Na$_2$SO$_4$ with NaNO$_3$, (B) Nyquist curves for Cu$_3$PdN-300/AC, Cu$_3$N-300/AC and Pd/C.
Fig. S10 The CV curves of (A) Cu$_3$N-300/AC and (B) Cu$_3$PdN-300/AC at different scan rates.
Fig. S11 Standard calibration curve of $^{15}$NH$_4^+$. 

$^{15}$NH$_4^+$. $^{15}$N/C$_2$H$_4$O$_4$

$y = 0.04976x - 0.5814$

$R^2 = 0.9966$
Fig. S12 $^1$H NMR spectra of the standard $^{14}$NH$_4^+$ solutions with different concentrations.
Fig. S13 Standard calibration curve of $^{14}$NH$_4^+$. 
Table S1. Comparison of ammonium synthesis from nitrate electroreduction over Cu3PdN-300/AC with other reported catalysis.

<table>
<thead>
<tr>
<th>Catalysis</th>
<th>Electrolyte</th>
<th>Yield rate of NH₃</th>
<th>S NH₃</th>
<th>FE NH₃</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃PdN-300/AC</td>
<td>50 ppm NO₃⁻ + 1.0 g L⁻¹ Na₂SO₄</td>
<td>0.10 mmol h⁻¹ mg⁻¹ cat</td>
<td>76.3%</td>
<td>77.3%</td>
<td>This work</td>
</tr>
<tr>
<td>Co₃O₄/Ti mesh</td>
<td>100 g L⁻¹ KNO₃ + 0.1 M K₂SO₄</td>
<td>0.854 mmol h⁻¹ mg⁻¹ cat</td>
<td>33.6%</td>
<td>1.23%</td>
<td>2</td>
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<tr>
<td>Co₃O₄@NiO</td>
<td>200 ppm NO₃⁻ + 0.5 M Na₂SO₄</td>
<td>0.00693 mmol h⁻¹ mg⁻¹ cat</td>
<td>62.29%</td>
<td>54.97%</td>
<td>3</td>
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<tr>
<td>PdMoCu₀.₅</td>
<td>0.1 M KNO₃⁻ + 1 M KOH</td>
<td>0.254 mmol h⁻¹ mg⁻¹ cat</td>
<td>-</td>
<td>56.95%</td>
<td>4</td>
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<tr>
<td>Pd₀.₆₄Cu₀.₆₆</td>
<td>0.8 mM NO₃⁻ + 0.01 M NaClO₄</td>
<td>0.0002 mmol h⁻¹ mg⁻¹ cat</td>
<td>49.0%</td>
<td>-</td>
<td>5</td>
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<tr>
<td>Pd₁₀₅₋Cu₂₅/₅₀CeO₂</td>
<td>0.8 mM NO₃⁻ + 0.05 M Na₂SO₄</td>
<td>0.0019 mmol h⁻¹ mg⁻¹ cat</td>
<td>37.0%</td>
<td>-</td>
<td>6</td>
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<tr>
<td>CuPd@DCLMCS/CNTs</td>
<td>100 mg L⁻¹ NO₃⁻ + 0.1 M Na₂SO₄</td>
<td>-</td>
<td>5%</td>
<td>36%</td>
<td>7</td>
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<tr>
<td>PdCu@OMC</td>
<td>8 mM NO₃⁻ + 0.1 M Na₂SO₄</td>
<td>0.0053 mmol h⁻¹ mg⁻¹ cat</td>
<td>24.5%</td>
<td>-</td>
<td>8</td>
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<tr>
<td>Pd-Cu/γAl₂O₃</td>
<td>50 ppm NO₃⁻</td>
<td>0.0091 mmol h⁻¹ mg⁻¹ cat</td>
<td>19.6%</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Pd-Cu/SS</td>
<td>0.6 mM NO₃⁻ + 0.01 M NaClO₄</td>
<td>-</td>
<td>6%</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>BDD</td>
<td>50 ppm NO₃⁻ + 0.1 g L⁻¹ Na₂SO₄</td>
<td>-</td>
<td>8.9%</td>
<td>42%</td>
<td>11</td>
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<tr>
<td>CuO-Co₃O₄/Ti</td>
<td>100 mg L⁻¹ NO₃⁻ + 0.05 M Na₂SO₄</td>
<td>-</td>
<td>44%</td>
<td>54.5%</td>
<td>12</td>
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<tr>
<td>FeN-NC-140</td>
<td>1.6 mM NO₃⁻ + 0.1 M Na₂SO₄</td>
<td>0.0001/0.00004 mmol h⁻¹ mg⁻¹ cat</td>
<td>&lt;10.0%</td>
<td>-</td>
<td>13</td>
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<tr>
<td>Cu/rGO/GP</td>
<td>20 mM NO₃⁻ + 20 mM NaCl</td>
<td>0.0145 mmol h⁻¹ mg⁻¹ cat</td>
<td>19.4%</td>
<td>-</td>
<td>14</td>
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<tr>
<td>FeO₀@Fe₃O₄</td>
<td>0.8 mM NO₃⁻ + 0.4 M NaCl</td>
<td>0.0009 mmol h⁻¹ mg⁻¹ cat</td>
<td>&lt;20%</td>
<td>-</td>
<td>15</td>
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<tr>
<td>CuOₓ</td>
<td>50 ppm NO₃⁻ + 0.1 M KOH</td>
<td>0.024 mmol h⁻¹ mg⁻¹ cat</td>
<td>-</td>
<td>74.18%</td>
<td>16</td>
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<tr>
<td>Blended Sn₀.₄Pd₀.₃/SS</td>
<td>0.008 M NaNO₃ + 0.1 M HClO₄</td>
<td>0.0013 mmol h⁻¹ mg⁻¹ cat</td>
<td>14%</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>Ni-Feoyo@Fe₃O₄</td>
<td>50 ppm NO₃⁻ + 10 mM NaCl</td>
<td>-</td>
<td>10.4%</td>
<td>-</td>
<td>18</td>
</tr>
<tr>
<td>CL-Fe@C</td>
<td>1.6 mM NO₃⁻ + 0.1 M Na₂SO₄</td>
<td>0.0007/0.00018 mmol h⁻¹ mg⁻¹ cat</td>
<td>58%</td>
<td>-</td>
<td>19</td>
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<tr>
<td>Fe SAC</td>
<td>0.5 M KNO₃⁻ + 0.1 M K₂SO₄</td>
<td>0.46 mmol h⁻¹ mg⁻¹ cat</td>
<td>69%</td>
<td>75%</td>
<td>20</td>
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</table>
References

Author contributions: