Supporting Information

Hierarchical Nanoporous Pd₁Ag₁ Alloy Enables Efficient
Electrocatalytic Nitrogen Reduction

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Experimental parts

Chemicals and materials: Palladium (Pd, China New Metal Materials Technology Co. Ltd., 99.99%), silver (Ag, China New Metal Materials Technology Co. Ltd., 99.99%), aluminum (Al, China New Metal Materials Technology Co. Ltd., 99.99%), nitric acid (HNO₃, Sinopharm Chemical Reagent Co. Ltd., 65.0~68.0%), sodium hydroxide (NaOH, Sinopharm Chemical Reagent Co. Ltd., 96.0%), Toray carbon paper (Toray TGP-H-060, Toray Industries Inc.), Nafion solution (5 wt%, Dupont), Potassium hydroxide (KOH, Sinopharm Chemical Reagent Co. Ltd., 85.0%), salicylic acid (C₇H₆O₃, Aladdin, 99.5%), sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O, Aladdin, 99.0%), sodium hydroxide (NaOH, Aladdin, 96.0%), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O, Aladdin, 99.0%), sodium hypochlorite solution (NaClO, MACKLIN reagent, available chlorine 4%), ammonium chloride (NH₄Cl, Sinopharm Chemical Reagent Co. Ltd., 99.5%), ethanol (C₂H₅OH, Sinopharm Chemical Reagent Co. Ltd., 99.7%), hydrazine hydrate (N₂H₄·H₂O, Sinopharm Chemical Reagent Co. Ltd., 85.0%), Nessler’s reagent (K₂[HgI₄], Tianjin Guangfu Fine Chemical Research Institute, analytically reagent), potassium sodium tartrate tetrahydrate (NaKC₄H₄O₆·4H₂O Tianjin Guangfu Technology development Co. Ltd., 99.0%) potassium chloride (KCl, Sinopharm Chemical Reagent Co. Ltd.). All chemicals were used without further purification. Electrolyte solutions were prepared with ultrapure water (UP H₂O) with a specific resistance of 18.2 MΩ·cm.

Material Characterizations: The crystal structures of products obtained at each step were confirmed by an X-ray diffractometer (XRD, Rigaku D/max 2500) using Cu Kα radiation (λ = 0.154598 nm). The morphologies of the samples were investigated by field emission scanning electron microscopy (SEM, Verios 460L) and transmission electron microscopy (TEM, Tecnai G2, Talos F200X, Titan Cubed Themis G2300) instruments equipped with energy
dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific) was utilized to analyze the surface chemistry composition of both two samples. The binding energies calibration was performed with reference of the C 1s main peak at 284.8 eV. Electrochemical experiments were carried out using CHI 760D electrochemical workstation (CH Instruments).

**Preparation of Pd\textsubscript{1}Ag\textsubscript{2}Al\textsubscript{97} ribbons.** Ternary Pd\textsubscript{1}Ag\textsubscript{2}Al\textsubscript{97} alloy was prepared by arc melting a mixture of Pd (99.99%), pure Ag (99.99%) and pure Al (99.99%) in an Ar atmosphere. Then the Pd\textsubscript{1}Ag\textsubscript{2}Al\textsubscript{97} ribbons with 20 were obtained by the melt spinning method.

**Preparation of nanoporous PdAg alloys.** The nanoporous PdAg alloys were obtained via two-step dealloying method. Firstly, 0.3 g of precursor ribbons was put into 200 mL of 2 M NaOH aqueous solution to remove partial of Al in the ribbons. The etching reaction was kept at 30 °C for around 5 h until no apparent bubbles were observed. The as-prepared Pd\textsubscript{1}Ag\textsubscript{2} alloy was washed with UP H\textsubscript{2}O for several times till the solution became neutral. After that, the second-step dealloying treatment was carried out by adding the as-prepared Pd\textsubscript{1}Ag\textsubscript{2} alloy into 100 mL of 0.1 M Fe(NO\textsubscript{3})\textsubscript{3}·9 H\textsubscript{2}O aqueous solution kept at 30 °C. After 2 h, nanoporous Pd\textsubscript{1}Ag\textsubscript{1} alloy was obtained. After washing process, the product was dried in vacuum oven at 60 °C for 12 hours for further structure characterization and electrocatalytic analysis. Nanoporous Pd\textsubscript{1}Ag\textsubscript{1} alloys were prepared with the same reaction conditions except the reaction times of the second-step dealloying were increased to 6 h. For comparison, nanoporous Pd\textsubscript{5}Ag\textsubscript{95} structure was fabricated by dealloying Pd\textsubscript{1}Ag\textsubscript{2}Al\textsubscript{97} ribbons in 1 M HNO\textsubscript{3} at 30 °C for 3 days. Nanoporous Pd structure was fabricated by dealloying Pd\textsubscript{5}Al\textsubscript{95} ribbons in 2 M NaOH at 30 °C for 5 h. Nanoporous Ag structure was fabricated by dealloying Ag\textsubscript{15}Al\textsubscript{85} ribbons in 2 M NaOH at 30 °C for 5 h.

**Electrode preparation and Electrochemical NRR measurements:** 2 mg of PdAg alloy, 2 mg of activated carbon and 200 μL of 0.5 % Nafion solution were dispersed into 200 μL of absolute ethanol and ultrasonicated for 30 min to form a uniform electrocatalyst ink. Then, 40 μL of the electrocatalyst ink was uniformly dispersed onto a carbon paper with an area of 1×1 cm\textsuperscript{2}. The carbon paper electrode was dried naturally under ambient conditions. The NRR experiments were conducted via a similar procedure as our reported work (ref. 54 in main text).

**Determination of ammonia and hydrazine products:** Concentrations of produced NH\textsubscript{3} were spectrophotometrically determined by the Nessler’s reagent and indophenol blue methods. The concentration of hydrazine in the electrolyte was determined by the method of Watt and Chrisep. The tested conditions were the same as our previous reported work (ref. 54 in main text).
Calculation of faradaic efficiency: After 6-h electrolysis, the concentrations of NH₄⁺ product were calculated based on the calibration curves. The Faradaic efficiencies of liquid products were calculated as follows:

\[
FE = \frac{n \times M \times V \times F}{Q} \times 100
\]

Where, \( n \) is the number of electrons transferred to produce a given product (for NH₃, \( n=3 \)), \( M \) is the concentration of the liquid product in the electrolyte sample (mol/L), \( V \) is the total volume of electrolyte and gathering solution, \( Q \) the total number of electrons measured during this reaction period.
**Fig. S1.** XRD patterns of the Pd$_{1}$Ag$_{2}$Al$_{97}$ precursor alloy.
Fig. S2. SEM images of PdAg alloy obtained by dealloying of Pd$_2$Ag$_{97}$ precursor alloy in NaOH solution.
**Fig. S3.** TEM images of PdAg alloy obtained by dealloying of Pd$_2$Ag$_{10}$Al$_{97}$ precursor alloy in NaOH solution.
Fig. S4. EDS of PdAg alloy obtained by dealloying of Pd$_{4}$Ag$_{2}$Al$_{97}$ precursor alloy in NaOH solution. The composition of the obtained alloy is confirmed to be Pd$_{4}$Ag$_{2}$.
Fig. S5. EDS of PdAg alloy obtained by dealloying of Pd$_3$Ag$_2$ alloy in Fe(NO$_3$)$_3$·9 H$_2$O solution for 2 hours. The composition of the obtained alloy is confirmed to be Pd$_3$Ag$_2$. 

Atomic %: 
Pd: 43.16 
Ag: 47.64 
Al: 9.21
Fig. S6. SEM images of Pd$_1$Ag$_1$ alloy.
Fig. S7. EDS of PdAg alloy obtained by dealloying of Pd$_3$Ag$_2$ alloy in Fe(NO$_3$)$_3$·9H$_2$O solution for 6 hours. The composition of the obtained alloy is confirmed to be Pd$_3$Ag$_2$. 

Atomic %:  
Pd: 64.14  
Ag: 25.73  
Al: 10.13
Fig. S8. SEM image of Pd$_3$Ag$_1$ composites.
Fig. S9. TEM image of Pd$_3$Ag$_5$ composites.
Fig. S10. XRD patterns of Pd$_1$Ag$_2$, Pd$_1$Ag$_3$, and Pd$_3$Ag$_1$ alloys.
Fig. S11. SEM images of the obtained product via one-step dealloying of the precursor alloy in HNO₃ solution.
Fig. S12. XRD of the obtained product via one-step dealloying of the precursor alloy in HNO₃ solution.
Fig. S13. EDS of PdAg alloy obtained by dealloying of precursor alloy in HNO$_3$ solution for 3 days. The composition of the obtained alloy is confirmed to be Pd$_5$Ag$_1$. 

Atomic %: 
Pd: 52.58
Ag: 12.65
Al: 34.77
Fig. S14. XPS patterns of Pd$_{1}$Ag$_{2}$ and Pd$_{3}$Ag$_{1}$ alloys relative to those of nanoporous Pd and Ag.
Fig. S15. SEM images of nanoporous Pd.
Fig. S16. SEM images of nanoporous Ag.
Fig. S17. Time-dependent current density curves obtained at -0.2 V vs RHE.
Fig. S18. (a) UV-Vis curves of Nessler reagent solutions after keeping in darkness for 25 min at room temperature, (b) calibration curve used for the estimation of NH$_4^+$ concentration. This figure was published in our previous work (ref. 54 in the main text).
Fig. S19. (a) UV-Vis curves of indophenol blue methods after keeping in darkness for 2 h at room temperature, (b) calibration curve used for the estimation of NH$_4^+$ concentration. This figure was published in our previous work (ref. 54 in the main text).
Fig. S20. Calibration curve used for the estimation of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ concentration. This figure was published in our previous work (ref. 54 in the main text).
Fig. S21. Corresponding NH$_3$ yield rates and Faradaic efficiencies of samples at -0.2 V vs. RHE with 6-hour electrolysis. The yields of NH$_3$ products were quantified via Nessler's reagent method in this Figure.
Fig. S22. (a, b) UV-Vis spectra of the electrolytes mixed with indophenol indicator for 2 hours. The electrolytes were obtained at small applied potentials with 6 hours electrolysis. (c) Corresponding NH₃ yield rates obtained from PdAg alloys.
Fig. S23. Time-dependent current density curves at the corresponding potentials.
Fig. S24. NH$_3$ yield rates and Faradaic efficiencies of the Pd$_{1}$Ag$_{1}$ alloy at different applied potentials. The yields of NH$_3$ products were quantified via Nessler's reagent method in this Figure.
Fig. S25. Corresponding NH$_3$ product yields and faradaic efficiency for each consecutive electrocatalysis cycle. The yields of NH$_3$ products were quantified via indophenol blue method in this Figure.
Fig. S26. Corresponding NH₃ product yields and faradaic efficiency for each consecutive electrocatalysis cycle. The yields of NH₃ products were quantified via indophenol blue method in this figure.
Fig. S27. SEM images of Pd$_x$Ag$_{1-x}$ alloy after stability test.
Fig. S28. The electrochemical impedance spectra of the Pd$_3$Ag$_1$ (blue), Pd$_1$Ag$_2$ (red) and Pd$_1$Ag$_1$ (black) in 1 M KOH.
Table S1. The atomic ratios of the obtained PdAg alloys determined by ICP-MS measurement.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Atomic ratios of Pd/Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_2$Ag$_1$</td>
<td>1:2.1</td>
</tr>
<tr>
<td>Pd$_3$Ag$_1$</td>
<td>0.95:1</td>
</tr>
<tr>
<td>Pd$_3$Ag$_1$</td>
<td>2.5:1</td>
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</table>

Table S2. Comparison of NH$_3$ production rates for the Pd$_3$Ag$_1$ alloy with other alloy catalysts under ambient conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Potential (V vs. RHE)</th>
<th>NH$_3$ yield rate</th>
<th>Electrolyte</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoporous Pd$_3$Ag$_1$</td>
<td>-0.2</td>
<td>23.9 μg h$^{-1}$ mg$_{cat.}^{-1}$</td>
<td>1 M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>Bimodal nanoporous Pd$_3$Cu$_1$ alloy</td>
<td>-0.25</td>
<td>39.9 μg h$^{-1}$ mg$_{cat.}^{-1}$</td>
<td>1 M KOH</td>
<td>Nano Energy 2019, 58, 834–841</td>
</tr>
<tr>
<td>PdRu tripods</td>
<td>-0.2</td>
<td>37.23 μg h$^{-1}$ mg$_{cat.}^{-1}$</td>
<td>0.1 M KOH</td>
<td>J. Mater. Chem. A 2019, 7, 801–805</td>
</tr>
<tr>
<td>Pd-Ru BPNs</td>
<td>-0.1</td>
<td>25.92 μg h$^{-1}$ mg$_{cat.}^{-1}$</td>
<td>0.1 M HCl</td>
<td>ACS Sustainable Chem. Eng. 2019, 7, 2400–2405</td>
</tr>
<tr>
<td>PdCuIr-LS</td>
<td>-0.3</td>
<td>13.43 μg h$^{-1}$ mg$_{cat.}^{-1}$</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>J. Mater. Chem. A 2019, 7, 3190–3196.</td>
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<tr>
<td>Ag nanosheet</td>
<td>-0.6</td>
<td>$4.62 \times 10^{-11}$ mol s$^{-1}$ cm$^{-2}$</td>
<td>0.1 M HCl</td>
<td>Chem. Commun. 2018, 54, 11427-11430.</td>
</tr>
<tr>
<td>(BD-Ag/AF)</td>
<td>-0.6</td>
<td>$2.07 \times 10^{-11}$ mol s$^{-1}$ cm$^{-2}$</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Inorg. Chem. 2018, 57, 14692–14697.</td>
</tr>
<tr>
<td>Pd nanoparticles</td>
<td>0.1</td>
<td>4.5 μg h$^{-1}$ mg$_{Pd}^{-1}$</td>
<td>0.1 M PBS</td>
<td>Nat. Commun. 2018, 9, 1795.</td>
</tr>
<tr>
<td>Pd$<em>{0.2}$Cu$</em>{0.8}$/rGO</td>
<td>-0.2</td>
<td>2.80 μg h$^{-1}$ mg$_{cat.}^{-1}$</td>
<td>0.1 M KOH</td>
<td>Adv. Energy Mater. 2018, 8, 1800124.</td>
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