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 ($C_7H_6O_3$, Aladdin, 99.5%), sodium citrate dehydrate ($C_6H_5Na_3O_7\cdot2H_2O$, Aladdin, 99.0%), sodium hydroxide (NaOH, Aladdin, 96.0%), sodium nitroferricyanide dihydrate ($C_5FeN_6Na_2O\cdot2H_2O$, Aladdin, 99.0%), sodium hypochlorite solution (NaClO, MACKLIN reagent, available chlorine 4%), ammonium chloride (NH₄Cl, Sinopharm Chemical Reagent Co. Ltd., 99.5%), ethanol (C_2H_5OH , Sinopharm Chemical Reagent Co. Ltd., 99.7%), hydrazine hydrate (N_2H_4 H_2O , Sinopharm Chemical Reagent Co. Ltd., 85.0%), Nessler's reagent ($K_2[HgI_4]$, Tianjin Guangfu Fine Chemical Research Institute, analytically reagent), potassium sodium tartrate tetrahydrate ($NaKC_4H_4O_6\cdot4H_2O$ Tianjin Guangfu Technoligy 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 H_2O) with a specific resistance of 18.2 MΩ·cm.

Material Characterizations: The crystal structures of products obtained at each step were confirmed by an Xray diffractometer (XRD, Rigaku D/max 2500) using Cu K α 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 1*s* main peak at 284.8 eV. Electrochemical experiments were carried out using CHI 760D electrochemical workstation (CH Instruments).

Preparation of Pd₁Ag₂Al₉₇ ribbons. Ternary Pd₁Ag₂Al₉₇ 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 Pd₁Ag₂Al₉₇ 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 Pd₁Ag₂ alloy was washed with UP H₂O for several times till the solution became neutral. After that, the second-step dealloying treatment was carried out by adding the as-prepared Pd₁Ag₂ alloy into 100 mL of 0.1 M Fe(NO₃)₃.9 H₂O aqueous solution kept at 30 °C. After 2 h, nanoporous Pd₁Ag₁ 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 Pd₃Ag₁ alloys were prepared with the same reaction conditions except the reaction times of the second-step dealloying Pd₁Ag₂Al₉₇ ribbons in 1 M HNO₃ at 30 °C for 3 days. Nanoporous Pd structure was fabricated by dealloying Pd₅Al₉₅ 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 μ L of 0.5 % Nafion solution were dispersed into 200 μ L of absolute ethanol and ultrasonicated for 30 min to form a uniform electrocatalyst ink. Then, 40 μ L of the electrocatalyst ink was uniformly dispersed onto a carbon paper with an area of 1×1 cm². 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 NH₃ 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 Chrisp. 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 NH_3 , 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 solutoin, Q the total number of electrons measured during this reaction period.



Fig. S1. XRD patterns of the $Pd_1Ag_2Al_{97}$ precursor alloy.



Fig. S2. SEM images of PdAg alloy obtianed by dealloying of $Pd_1Ag_2Al_{97}$ precursor alloy in NaOH solution.



Fig. S3. TEM images of PdAg alloy obtianed by dealloying of $Pd_1Ag_2Al_{97}$ precursor alloy in NaOH solution.



Fig. S4. EDS of PdAg alloy obtianed by dealloying of $Pd_1Ag_2Al_{97}$ precursor alloy in NaOH solution. The composition of the obtained alloy is confirmed to be Pd_1Ag_2 .



Fig. S5. EDS of PdAg alloy obtianed by dealloying of Pd_1Ag_2 alloy in $Fe(NO_3)_3 \cdot 9 H_2O$ solution for 2 hours. The composition of the obtained alloy is confirmed to be Pd_1Ag_1 .



Fig. S6. SEM images of Pd_1Ag_1 alloy.



Fig. S7. EDS of PdAg alloy obtianed by dealloying of Pd_1Ag_2 alloy in $Fe(NO_3)_3 \cdot 9 H_2O$ solution for 6 hours. The composition of the obtained alloy is confirmed to be Pd_3Ag_1 .



Fig. S8. SEM image of Pd_3Ag_1 composites.



Fig. S9. TEM image of Pd_3Ag_1 composites.



Fig. S10. XRD patterns of Pd_1Ag_2 , Pd_1Ag_1 and Pd_3Ag_1 alloys.



Fig. S11. SEM images of the obtianed product via one-step dealloying of the precursor alloy in HNO_3 solution.



Fig. S12. XRD of the obtianed product via one-step dealloying of the precursor alloy in HNO_3 solution.



Fig. S13. EDS of PdAg alloy obtianed by dealloying of precursor alloy in HNO_3 solution for 3 days. The composition of the obtained alloy is confirmed to be Pd_5Ag_1 .



Fig. S14. XPS patterns of Pd_1Ag_2 and Pd_3Ag_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 N_2H_4 · H_2O 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_1Ag_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 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. S27. SEM images of Pd_1Ag_1 alloy after stability test.



Fig. S28. The electrochemical impedance spectra of the Pd_3Ag_1 (blue), Pd_1Ag_2 (red) and Pd_1Ag_1 (black) in 1 M KOH.

Table S1. The atomic ratios of the obtained PdAg alloys determined by ICP-MS measurement.

Catalysts	Atomic ratios of Pd/Ag
Pd ₁ Ag ₂	1:2.1
Pd ₁ Ag ₁	0.95;1
Pd ₃ Ag ₁	2.5:1

Table S2.	Comparison	of NH ₃	production	rates	for the	e Pd ₁ Ag ₁	alloy	with	other	alloy	catalysts	under	ambient
conditions													

Catalyst	Potential	NH ₃ yield rate	Electrolyte	Reference
	(V vs. RHE)			
Nanoporous Pd ₁ Ag ₁	-0.2	23.9	1 M KOH	This work
		μ g h ⁻¹ mg _{cat.} ⁻¹		
Bimodal		39.9		Nano Energy
nanoporous Pd ₃ Cu ₁	-0.25	µg h⁻¹ mg _{cat.} ⁻¹	1 M KOH	2019, 58, 834–841
alloy				
PdRu tripods	-0.2	37.23	0.1 M KOH	J. Mater. Chem. A
		μ g h ⁻¹ mg _{cat.} ⁻¹		2019 , 7, 801–805
Pd-Ru BPNs	-0.1	25.92	0.1 M HCl	ACS Sustainable Chem.
		μ g h ⁻¹ mg _{cat.} ⁻¹		Eng. 2019 , 7, 2400–2405
PdCulr-LS	-0.3	13.43	0.1 M	J. Mater. Chem. A
		$\mu g h^{-1} m g_{cat.}^{-1}$	Na_2SO_4	2019, 7, 3190–3196.
Ag nanosheet	-0.6	4.62 × 10 ⁻¹¹	0.1 M HCl	Chem. Commun.
		mol s ⁻¹ cm ⁻²		2018, 54, 11427-11430.
(BD-Ag/AF)	-0.6	2.07 × 10 ⁻¹¹	0.1 M	Inorg. Chem.
		mol s ⁻¹ cm ⁻²	Na_2SO_4	2018, 57, 14692–14697.
Pd nanoparticles	0.1	4.5	0.1 M PBS	Nat. Commun.
		µg h ⁻¹ mg _{Pd} ⁻¹		2018, 9, 1795.
Pd _{0.2} Cu _{0.8} /rGO	-0.2	2.80	0.1 M KOH	Adv. Energy Mater.
		$\mu g h^{-1} m g_{cat.}^{-1}$		2018, 8, 1800124.