Supporting Information

Connection of Ru Nanoparticles with Rich Defects Enables Enhanced Electrochemical Reduction of Nitrogen

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Experimental section

Chemicals

Ruthenium(III) chloride hydrate (RuCl₃·xH₂O), ammonium chloride (NH₄Cl), sodium borohydride (NaBH₄), sodium hydroxide (NaOH), potassium hydroxide (KOH), polyvinylpyrrolidone (PVP, Mw=29000), sodium hypochlorite solution (NaClO), tri-sodium citrate dihydrate (C₆H₅Na₃O₂·2H₂O), salicylic acid (C₇H₆O₃) were purchased from Aladdin Chemistry Co. Ltd. Sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O) was purchased from Sinopharm Chemical Reagent Co. Ltd. Nafion solution was purchased from Sigma Aldrich. Water used in all experiments was ultrapure (Millipore, 18.2 MΩ).

Synthesis of dispersed Ru nanoparticles

In a typical synthesis, 0.06 mmol of $RuCl_3 \cdot xH_2O$ and 100 mg of PVP were dissolved in 10 mL of DI water. Then, 1 mL of 100 mM NaBH₄ was added, and the total volume of the solution was adjusted to 15 mL with water. The homogeneous black solution was transferred to a 25 mL Teflon-lined stainless-steel autoclave and heated at 160 °C for 4 h. The black product was centrifuged at 10000 rpm for 5 min and washed with water/acetone for three times. The centrifuged sample was dried in a vacuum drying oven for 24 hours to get the dispersed Ru nanoparticles.

Synthesis of connected Ru nanoparticles

In a typical synthesis, the dispersed Ru nanoparticles was heated to 550 °C with a heating rate of 10 °C min⁻¹ in a tube furnace, and kept at 550 °C for 1 h. After the tube furnace cooled to room temperature, the connected Ru nanoparticles were obtained.

Electrochemical measurements

Electrochemical measurements were performed in a three-electrode system at an electrochemical station (CHI660E). Typically, 4.0 mg of catalysts and 30 μ L of Nafion solution (5 wt%) were dispersed in 1 mL ethanol by sonication for 1 h. Then 10 μ L of the dispersion was loaded onto a glassy carbon electrode with the diameter of 5 mm. The mass loadings of dispersed Ru nanoparticles and connected Ru nanoparticles were calculated to be 0.198 mg cm⁻². Graphite rod and Ag/AgCl electrodes were used as counter electrode and reference electrode, respectively. All

potentials were converted to the RHE reference by $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.95$ V. The N₂ electrochemical reduction was conducted in N₂-saturated 0.1 M KOH solution at room temperature. After purging N₂ into the solution for 30 min, controlled electrolysis was conducted at applied potentials for 1 h. Cu UPD and stripping was measured by LSV with a scan rate of 5 mV s⁻¹ in 0.1 M H₂SO₄ in the presence of 2 mM CuSO₄. The double-layer capacitance (C_{dl}) was obtained by plotting the capacitive currents, which were associated with double-layer charging, with different scan rates.

Determination of ammonia

Concentration of ammonia was detected by the indophenol blue method. In detail, 2 mL of NaOH solution (1 M) containing salicylic acid (5 wt%) and sodium citrate (5 wt%) were added into 2 mL of electrolytes, after which 1 mL of NaClO (0.05 M) and 0.2 mL of $C_5FeN_6Na_2O$ (1 wt%) were added. The concentration of indophenol blue was measured using the absorption spectrum at the wavelength of 655 nm. The concentration-absorbance curve was calibrated using standard ammonia chloride solution.

The calculation method for Faradaic efficiency

The Faradaic efficiency for NH₃ production was obtained as follow:

$$FE = C_{NH3} \times V \times N \times F/Q$$

Where Q is the quantity of electric charge, N is the number of electrons transferred for NH₃ formation, F is the Faraday constant, C_{NH3} is the measured NH₃ concentration, and V is the volume of electrolytes.

Instrumentations

TEM images were taken using a FEITecnai G2 F20 transmission electron microscope at an acceleration voltage of 100 kV. XRD patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu K α radiation (λ =1.54178 Å). XPS and UPS measurements were performed on a Thermo ESCALAB 250XI X-ray photoelectron spectrometer with an exciting source of Mg K α =1253.6 eV. The absorbance data were measured on UV-vis spectrophotometer (Agilent Technologies, Cary 60). The concentration of the NH₄⁺ was obtained on an ion chromatography (MetrohmECO IC 881).

The calculation details on the work function values

Work function = E_f *vs vacuum level* = $hv - E_{cutoff}$

Where hv was the total energy of photon, E_{cutoff} was the secondary cutoff edge of the UPS spectra.



Figure S1. TEM image of dispersed Ru nanoparticles.



Figure S2. The particle size histogram of dispersed Ru nanoparticles.



Figure S3. HRTEM image of dispersed Ru nanoparticles.



Figure S4. HRTEM image of Ru nanoparticles at different annealing temperatures. (a) unannealed; (b) 100 °C; (c) 300 °C; (d) 550 °C.



Figure S5. XPS spectra of Ru 3p for dispersed Ru nanoparticles and connected Ru nanoparticles.



Figure S6. (a) UV-vis curves and (b) concentration-absorbance curve of NH_3 ions solution with a series of standard concentration. The standard curve showed good linear relation of absorbance with NH_4^+ concentration.



Figure S7. LSV curves of connected Ru nanoparticles and dispersed Ru nanoparticles.



Figure S8. The yield rates of NH₃ production with dispersed Ru nanoparticles and dispersed Ru nanoparticles without washing. (b) The yield rate of NH₃ production over the connected Ru nanoparticles treated with PVP solution. The slightly decreased yield rate indicated the blocked active sites by PVP were negligible.



Figure S9. Faradaic efficiency for NH_3/H_2 production using connected Ru nanoparticles.



Figure S10. Ion chromatograms of NH_4^+ with different concentrations in 0.1 M KOH solution.



Figure S11. Yield rate of NH_3 production using connected Ru nanoparticles in Ar/N_2 -saturated electrolytes.



Figure S12. CV curves of (a) connected Ru nanoparticles and (b) dispersed Ru nanoparticles.

Potential	Yield rate (μg_{NH3} cm ⁻² h ⁻¹)	FE (%)
-0.3 V vs RHE	19.1	4.4
-0.25 V vs RHE	20.7	5.3
-0.2 V vs RHE	21.8	6.1
-0.15 V vs RHE	21.4	5.8
-0.1 V vs RHE	29.3	7

Table S1. Yield rate and FE of NH_3 production at different potentials over connected Ru nanoparticles in N₂-saturated electrolytes.

Catalyst	Potential	Yield rate F	FE	Ref.
		(µg _{NH3} mg _{cat.} ⁻¹ h ⁻¹)	(%)	
Ru SAs/N-C	–0.2 V vs RHE	120.9	29.6	Adv. Mater. 2018,1803498
N-doped porous carbon	–0.9 V vs RHE	23.8	-	ACS Catal. 2018,8,2,1186-1191
AuCu/ZIF-8	-0.2 V vs RHE	63.9	14.2	J. Mater. Chem. A 2020,8,18,8868-8874
Co ₃ O ₄ @CNT	-0.49 V vs RHE	27.16 ± 2.22	3.86	Electrochim. Acta 2021,367,137421
Pd ₃ B	-0.2 V vs RHE	59.05 ± 2.27	21.52	Adv. Mater. 2021,33,2007733
MnO ₂	-0.5 V vs RHE	25.3	6.7	Small 2020,1907091
P-mRh/NF	-0.4 V vs RHE	32.57	40.86	Nanoscale 2021,13,32,13809
This work	-0.1 V vs RHE	148.0	7	

Table S2. Comparison of the N_2 electrochemical reduction activity for connected Ru nanoparticles and other catalysts.