Supporting Information

Alloying Pd with Ru enables electroreduction of nitrate to ammonia with ~100% Faradaic efficiency over a wide potential window

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Methods

Chemicals

All the chemicals are at analytical grade and used without further purification. Nitric acid ($\text{HNO}_3$, 69%) was purchased from Honeywell. Sodium hydroxide ($\text{NaOH}$, 99%) was purchased from Schedelco. Palladium chloride ($\text{PdCl}_2$, ≥99.9%), Ruthenium(III) chloride trihydrate ($\text{RuCl}_3\cdot3\text{H}_2\text{O}$, ≥99.9%), potassium bicarbonate ($\text{KHCO}_3$, 99.7%), hydrochloric acid ($\text{HCl}$, 37%), potassium hydroxide ($\text{KOH}$, 90%), potassium nitrate ($\text{KNO}_3$, ≥99%), potassium nitrate-$^{15}\text{N}$ ($\text{K}^{15}\text{NO}_3$, ≥99%), nitrite Standard for IC (1000 mg/L nitrite in water), ammonium chloride ($\text{NH}_4\text{Cl}$, ≥99.5%), salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, ≥99%), sodium citrate tribasic dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7\cdot2\text{H}_2\text{O}$, ≥99%), sodium hypochlorite solution ($\text{NaClO}$, available chlorine 4.00-4.99%), sodium nitroferricyanide dihydrate ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O}\cdot2\text{H}_2\text{O}$, ≥99%), deuterium oxide ($\text{D}_2\text{O}$, 99.95%), dimethyl sulfoxide ($\text{DMSO}$, ≥99.9%), and Nafion™ 117 containing solution (~5% in a mixture of lower aliphatic alcohols and water) were purchased from Sigma-Aldrich. Hydrophilic carbon fiber paper (CFP, TGP-H-090) was purchased from Tianjin Annuohe New Energy Technology Co., Ltd. Nafion 117 membrane was purchased from The Fuel Cell Store. Deionized (DI) water of 18.2 MΩ·cm was used in all the experiments.

Preparation of $\text{Pd}_x\text{Ru}_y$, Pd and Ru nanocrystals (NCs)

$\text{Pd}_x\text{Ru}_y$ NCs were prepared via a co-electrodeposition process under galvanostatic current density of 20 mA cm$^{-2}$ for 20 min in a three-electrodes system, where a saturated calomel electrode, a platinum plate, and a 1×2 cm$^2$ hydrophilic CFP were used as the reference, counter, and working electrodes, respectively. CFP was sequentially ultrasonically pretreated in acetone, and ethanol, and then repeatedly rinsed with DI water. The deposition electrolyte (40 ml) consisted of 30 ml saturated 0.1 M $\text{KHCO}_3$ solution and 10 ml catalyst precursor solution. Among them, the catalyst precursor solution was composed of $\text{PdCl}_2$ and $\text{RuCl}_3\cdot3\text{H}_2\text{O}$ with different Pd/Ru molar ratios (9:1, 3:1, and 1:1), with the total metal ions of 0.2 mM. The solution was made transparent with HCl (37%) and brought to 10 ml with DI water. During the electroreduction process, CO$_2$ was continuously bubbled at a rate of 20 sccm. After the electrodeposition process, the obtained $\text{Pd}_x\text{Ru}_y$ NCs on CFP was rinsed repeatedly with DI water, and then dried at 60°C in a vacuum oven. The preparation of monometallic Pd and Ru NCs follows the same steps as the synthesis of $\text{Pd}_x\text{Ru}_y$ NCs, except that a single component of 0.2 mM $\text{PdCl}_2$ or $\text{RuCl}_3\cdot3\text{H}_2\text{O}$ was used in the catalyst precursor solution, respectively. By weighing the CFPs before and after electrodeposition, the loadings of $\text{Pd}_x\text{Ru}_y$ NCs, Pd, and Ru
deposited onto the CFPs were all about 1.6 mg cm$^{-2}$.

**Catalyst Characterizations**

The samples were confirmed by X-ray diffraction (XRD) using the Bruker D8 X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm). The structure and elemental composition were characterized by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive spectroscopy (EDS) elemental mapping using a JEOL 2100F microscope at an accelerating voltage of 200 kV. The chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Supra+ x-ray photoelectron spectroscopy. X-ray absorption fine spectroscopy (XAFS) experiments of the Ru K-edge and Pd K-edge were performed using a Si (311) monochromator crystal at the BL14B2 beamline at SPring-8, in Japan. The operando Fourier transform infrared spectroscopy (FTIR) tests were carried out jointly by the BRUKER-Fourier Transform Infrared Spectrometer-TENSOR27 and a CHI-760E electrochemical workstation using a customized cell, with a saturated Hg/HgO reference electrode and a Pt ring counter electrode in 1 M KOH.

**Electrochemical tests**

The electrochemical tests were performed using a typical three-electrodes system connected to the Solartron electrochemical workstation (England) in H-type cell. The Pd$_x$Ru$_y$/CFPs, Hg/HgO electrode (filled with 1 M KOH aqueous solution) and platinum plate were used as working, reference and counter electrodes, respectively. The H-type cell was separated by Nafion 117 membrane, which was pretreated with H$_2$O$_2$ (2%) and H$_2$SO$_4$ (0.5 M) at 80°C for 1 h, respectively. For the tests of eNO$_3^-$ RR, 1 M KOH aqueous solution (PH=14, determined by a Seven2Go pH Meter, Switzerland) was used as an electrolyte, with 50 ml each in the cathode and anode compartments. Different concentrations of KNO$_3$ were added into the cathode compartment for eNO$_3^-$RR. During the operation, Ar was continuously bubbled into the electrolyte in cathode compartment to shield the air interference, and the magnetic stirring was continued at a speed of 650 rpm. All potentials measured were referenced against reversible hydrogen electrode (RHE) by $E_{(V \text{ vs. RHE})} = E_{(V \text{ vs. Hg/HgO})} + 0.0591 \times \text{PH} + 0.098$. Note that the change in pH of the electrolyte during the reaction is negligible. The current density was normalized to the geometric electrode area (1 cm$^2$) and the potential was not iR compensated, unless otherwise specified. Before all formal testing, 50 cyclic voltammetry (CV) cycles (in the potential range of 0.3 to -0.7 V with a scan rate of
50 mV s\(^{-1}\)) were performed in 1 M KOH aqueous solution to allow sufficient structural evolution of the catalysts to a steady state. The electrochemically active surface area (ECSA) was evaluated by a double-layer capacitance method. The CV scans were conducted over a potential range of 0.53 to 0.55 V where no Faradaic current occurred, at different scan rates of 2, 4, 6, 8, and 10 mV s\(^{-1}\). Linear sweep voltammetry (LSV) was performed with a scanning rate of 5 mV s\(^{-1}\). Electrochemical impedance spectroscopy was measured at frequencies from 0.01 Hz to 100 kHz using an Autolab potentiostat (M204) under the applied potential of -0.2 V.

**Kinetic evaluation**

The electrochemical kinetic analysis of eNO\(_3^–\)RR was performed according to the Koutecký–Levich (K–L) equation:

\[
\frac{i}{i_m} = \frac{1}{i_k} + \frac{1}{0.2nF} \frac{D^{2/3}v^{-1/6}C\omega^{1/2}}
\]

Where \(i_m\) is the measured current density, mA cm\(^{-2}\); \(i_k\) is the kinetic current of eNO\(_3^–\)RR; \(n\) is the number of electrons transferred in the reaction; \(F\) is the Faraday constant of 96485.3383 C mol\(^{-1}\); \(D\) represents the effective diffusion coefficient of 0.1 M NO\(_3^–\) at 25°C, \(1.4\times10^{-5}\) cm\(^2\)s\(^{-1}\); \(v\) represents the kinematic viscosity of water at 25°C, \(1\times10^{-2}\) cm\(^2\)s\(^{-1}\); \(C\) is the concentration of NO\(_3^–\), mol L\(^{-1}\); \(\omega\) is the electrode rotation speed, rpm.

An Autolab rotating electrode (RDE) with a diameter of 0.3 cm deposited with 5 µL of the prepared homogeneous catalyst ink was used as the working electrode. The homogeneous catalyst ink was prepared as 10 mg of the catalyst powder scraped off from Pd\(_x\)Ru\(_y\)/CFPs was dispersed in 1 mL of ethanol solution containing 120 µL of Nafion 117 solution, followed by sonication of the mixed solution for 1 h. LSV measurements were performed in 1 M KOH aqueous solution (50 ml) with 0.1 M KNO\(_3\) at different rotation speeds (400, 625, 900 and 1600 rpm) with a scan rate of 5 mV s\(^{-1}\). Ar was continuously bubbled into the electrolyte to remove dissolved O\(_2\) and N\(_2\).

**Determination of N-containning species**

Determination of NH\(_3\). As-produced NH\(_3\) was spectrophotometrically determined by the indophenol blue method with modification. First, a certain amount of post-reaction electrolyte was collected and diluted to the detection range of NH\(_3\) with 1 M KOH, and took 2 ml of the diluted electrolyte into an 8 ml glass vial. Then 2 ml of 1 M NaOH solution containing 5 wt% C\(_5\)FeN\(_6\)Na\(_2\)O\(_2\)H\(_2\)O and 5 wt% C\(_6\)H\(_3\)Na\(_3\)O\(_7\)2H\(_2\)O was added, followed by addition of 1 ml of 0.05 M NaClO solution and 0.2 ml of 1 wt% C\(_5\)FeN\(_6\)Na\(_2\)O\(_2\)H\(_2\)O aqueous solution. After keeping at room temperature for 2 h for the
sufficient colour reaction, the absorption spectrum of the resulting solution was measured using an UV–vis spectrophotometer (Shimadzu UV-2700i). The absorbance at ~655 nm was used to determine the concentration of NH₃. The concentration–absorbance curve was calibrated using a series of standard NH₄Cl solutions (0, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 µg ml⁻¹) in 1 M KOH electrolyte.

Determination of NO₂⁻. The produced NO₂⁻ was quantified by ion chromatogram instrument (930 compact IC Flex, Metrohm). Different concentrations of nitrite Standard solution for IC (0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 µg ml⁻¹) were used to build the area-concentration calibration curve of NO₂⁻. A certain amount of post-reaction electrolyte was collected and diluted 100 times with deionized water, and took 12 ml of the diluted electrolyte for detection.

Determination of NO₃⁻. Reactant NO₃⁻ was also quantified by ion chromatogram instrument. The calibration curve was built using a series of standard KNO₃ solutions (0, 0.01, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 mM). The detection process was consistent with that of NO₂⁻.

N isotope labelling experiments

The ¹H magnetic resonance (NMR) spectroscopy was collected on a Bruker Avance III HD 800 MHz (18.8 T) standard-bore NMR spectrometer. Specifically, the collected post-reaction electrolyte was first diluted to the detection range of NH₃ and the PH was adjusted to 2 with HCl. Next, 0.4 ml of the sample solution was mixed with 0.1 ml of D₂O and 0.1 ml of DMSO aqueous solution (10 ppm) in an NMR tube (Ø, 5 mm), where DMSO serves as internal standard. The test was conducted with water suppression by using the pre-saturation technique.

¹H NMR spectroscopy was also used to quantify the ¹⁵NH₄⁺ yield rate after eNO₃⁻RR in 1 M KOH with different ¹⁵NO₃⁻ concentrations at -0.3 V. The calibration curves with defined ¹⁵NH₄Cl concentrations were constructed as standards. Specifically, (1) a series of ¹⁵NH₄Cl solutions with known concentrations (0.5, 1, 2.5, 5, 10 mM) were prepared in 1 M NaOH as standards; (2) The standard solutions were adjust to pH 2.0 by adding HCl; (3) 30 mL of the above standard solutions were mixed with 0.012 g maleic acid; (4) 50 µL of D₂O was added in 0.5 mL above mixed solutions for the NMR detection.

Calculation of average NH₃ FE (FE₉₃) and NO₂⁻ FE (FE₉₂⁻), NH₃ yield rate (Y₉₃) and NH₃ partial current density (j₉₃)

The average FE₉₃ was calculated as follows:

\[
FE_{NH₃} = \frac{8F \times C_{NH₃} \times V}{Q}
\]
Where \( C_{\text{NH}_3} \) is the detected concentration of \( \text{NH}_3 \) (M), \( V \) is the volume of the electrolyte (0.05 L), and \( Q \) is the total charge passed through the working electrode (C).

The average \( \text{FE}_{\text{NO}_2^-} \) was calculated as follows:

\[
\text{FE}_{\text{NO}_2^-} = \frac{2F \times C_{\text{NO}_2^-} \times V}{Q}
\]

Where \( C_{\text{NO}_2^-} \) is the detected concentration of \( \text{NO}_2^- \) (M).

The average \( \text{NH}_3 \) yield rate was calculated as follows:

\[
\text{Y}_{\text{NH}_3} = \frac{C_{\text{NH}_3} \times V}{A \times t}
\]

Where \( A \) is the electrode geometric area, and \( t \) is the electrolysis time (h).

The \( j_{\text{NH}_3} \) was calculated as follows:

\[
\dot{j}_{\text{NH}_3} = \frac{Q \times \text{FE}_{\text{NH}_3}}{A \times t}
\]

**Density functional theory (DFT) calculations**

All the calculations were performed using density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP).\(^3\)\(^4\) The ion-electron interactions were treated with the projected augmented wave (PAW) pseudopotentials,\(^5\) and the plane-wave basis set was cut off at 400 eV. The general gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) was used to describe the exchange-correlation.\(^6\) All structures were fully relaxed by the conjugate gradient method until the force component on each unfixed atom was less than 0.01 eV/Å, and the convergence criterion of total energy in the self-consistent field method was set to \( 10^{-5} \) eV.

Closed-packed Pd(111), Ru(0001), and Pd\(_3\)Ru(111) slab models with four layers of atoms were used in our simulations to represent the dominant surfaces of Pd, Ru, and Pd\(_{74}\)Ru\(_{26}\) nanocrystals, respectively. The bottom two layers of atoms in the slab models were fixed during structure relaxations. The optimized lattice constants are \( a = b = c = 3.936 \) Å, \( \alpha = \beta = \gamma = 90^\circ \) for Pd; \( a = b = 2.717 \) Å, \( c = 4.292 \) Å, \( \alpha = \beta = 90^\circ, \gamma = 120^\circ \) for Ru; and \( a = b = c = 3.898 \) Å, \( \alpha = \beta = \gamma = 90^\circ \) for Pd\(_3\)Ru.

The thickness of vacuum in the slab models is larger than 15 Å to make sure that there is no superficial interaction between different slabs. The sizes of slab supercells are larger than 10 Å, and the k-point grid used for the Brillouin-zone integration was \( 3 \times 3 \times 1 \) sampled by the Monkhorst-Pack scheme.\(^7\) The
adsorption free energies of reaction intermediates were calculated by using the computational hydrogen electrode (CHE) model developed by Nørskov et al.⁸
Figure S1. TEM image of PdRu NCs synthesized by the co-electrodeposition of Pd and Ru (the ratio of precursor Pd and Ru ions is 3:1) without CO$_2$ assistance.

Figure S2. Structure characterization of Ru NCs. (a) TEM image. (b) HRTEM image. (c) The corresponding fast Fourier-transform (FFT) pattern of the selected area with the red dashed square in (b).

Figure S3. Structure characterization of Pd NCs. (a) TEM image. (b) HRTEM image. (c) The corresponding fast Fourier-transform (FFT) pattern of the selected area with the red dashed square in (b).
Figure S4. XRD patterns of Pd$_{90}$Ru$_{10}$, Pd$_{74}$Ru$_{26}$ and Pd$_{57}$Ru$_{43}$ NCs.

Figure S5. (a) EDS elemental mapping images of Pd$_{74}$Ru$_{26}$ NCs. (b) The corresponding EDS spectrum with the calculated atomic ratio of Pd and Ru.

Figure S6. (a) Scanning TEM image of Pd$_{90}$Ru$_{10}$ NCs and the corresponding EDS elemental mapping images.
Figure S7. (a) EDS elemental mapping images of Pd$_{90}$Ru$_{10}$ NCs. (b) The corresponding EDS spectrum with the calculated atomic ratio of Pd and Ru.

Figure S8. (a) EDS elemental mapping images of Pd$_{57}$Ru$_{43}$ NCs. (b) The corresponding EDS spectrum with the calculated atomic ratio of Pd and Ru.
Figure S9. XPS survey spectra of Pd, Pd$_{74}$Ru$_{26}$ and Ru NCs.

Figure S10. Pd K-edge EXAFS spectra in R space and fitting for Pd$_{57}$Ru$_{43}$ (a), Pd$_{74}$Ru$_{26}$ (b), and Pd$_{90}$Ru$_{10}$ (c), as well as EXAFS oscillation functions and fitting at the Pd K-edge of Pd$_{57}$Ru$_{43}$ (d), Pd$_{74}$Ru$_{26}$ (e), and Pd$_{90}$Ru$_{10}$ (f).
Figure S11. CV curves obtained on the Pd NCs (a), Ru NCs (b), and Pd$_{74}$Ru$_{26}$ NCs (c) at the scan rate of 2, 4, 6, 8 and 10 mV s$^{-1}$, respectively.

Figure S12. LSV curves (80% iR corrected) at different rotation rates and corresponding electron transfer numbers at different potentials for Pd (a) and Ru (b) on RDE in 1 M KOH with 0.1 M NO$_3^-$.

Figure S13. Koutecký-Levich plots of different potentials on Pd (a), Ru (b) and Pd$_{74}$Ru$_{26}$ (c).
Figure S14. LSV curves (80% iR corrected) of Pd$_{74}$Ru$_{26}$ at 1 M KOH with different NO$_3^-$ concentrations (a), and the corresponding $\lg(-j)$-$\lg(C)$ plots fitted at 0.1 V (b).

A quasi-first-order reaction kinetics relationship between current density and NO$_3^-$ concentrations on Pd$_{74}$Ru$_{26}$ at -0.1 V is obtained. This indicates that eNO$_3^-$ RR on Pd$_{74}$Ru$_{26}$ driven by this potential is only related to the adsorption of NO$_3^-$'. It is only limited by the mass transfer rate of NO$_3^-$ to the catalytic site caused by the concentration difference, and is not subject to the kinetic constraints of the intermediate reaction steps. This is because the adsorbed NO$_3^-$ on the catalytic site can quickly undergo a direct 8-electron transfer reaction and be converted into NH$_3$, as analyzed for the Koutecký-Levich plots.

Figure S15. LSV curves of Pd, Ru and Pd$_{74}$Ru$_{26}$ NCs in a purely protic medium (1 M NaOH+H$_2$O+0.1 M KNO$_3^-$) and a purely deuterium medium (1 M NaOD+D$_2$O+0.1 M KNO$_3^-$).
Figure S16. The i-t curves of Pd (a) at applied potentials from -0.3 to -0.5 V, Ru (b) at applied potentials from 0.1 to -0.5 V, and Pd$_7$Ru$_{26}$ (c) at applied potentials from 0.1 to -0.5 V in 1 M KOH with 32.3 mM NO$_3^-$.

The i-t curves show that Pd$_7$Ru$_{26}$ consistently exhibits higher current density than Ru and Pd at each applied potential, indicating its superior eNO$_3^-$RR activity. The current density of Pd$_7$Ru$_{26}$ decreased over time at relatively high potentials of -0.4 and -0.5 V, which is due to the gradual consumption of NO$_3^-$ in the electrolyte. This is also an indication of the good electrochemical response of Pd$_7$Ru$_{26}$ to NO$_3^-$.

Figure S17. (a) Absorbance UV-vis spectra of standard NH$_4$Cl with different concentrations in 1 M KOH solution. (b) The corresponding linear fitting calibration curve for the determination of NH$_4$Cl, the inset is the optical images of the NH$_4$Cl standards stained with indophenol blue indicator. Error bars denote the standard deviations of absorbance from three independent tests.
Figure S18. The ion chromatogram spectra for the standard NO$_2^-$ (a), and the corresponding linear fitting calibration curves (b). The ion chromatogram spectra for the standard NO$_3^-$ (c), and the corresponding linear fitting calibration curves (d).

Figure S19. ECSA-normalized total current density (a) and NH$_3$ partial current density ($j_{\text{NH}_3}$) (b) of Pd, Ru and Pd$_{74}$Ru$_{26}$. 
Figure S20. The i-t curves (a) of Pd\textsubscript{74}Ru\textsubscript{26} at -0.3 V in 1 M KOH without NO\textsubscript{3}\textsuperscript{-}, with 32.3 mM \textsuperscript{14}NO\textsubscript{3}\textsuperscript{-} and with 32.3 mM \textsuperscript{15}NO\textsubscript{3}\textsuperscript{-}, respectively, and the corresponding NH\textsubscript{3} yields (b) in the post-reaction electrolyte.

Figure S21. (a) \textsuperscript{1}HNMR spectra of \textsuperscript{15}NH\textsubscript{4}\textsuperscript{+} with different concentrations. (b) The corresponding linear fitting calibration curve for \textsuperscript{15}NH\textsubscript{4}\textsuperscript{+} obtained from the intensity of two NMR peaks. (c) Comparison of the \textsuperscript{15}NH\textsubscript{4}\textsuperscript{+} yield rate quantified by the \textsuperscript{1}H NMR and UV-vis spectra.

Figure S22. NH\textsubscript{3} yield rates of Pd\textsubscript{74}Ru\textsubscript{26}/CFP and bare CFP electrodes at different potentials in 1 M KOH with 32.3 mM NO\textsubscript{3}\textsuperscript{-}.
Figure S23. Time-dependent concentration ratios of NO$_3^-$–N, NH$_3$–N, and NO$_2^-$–N in the electrolyte during a continuous eNO$_3^-$RR at -0.3 V in a simulated industrial wastewater containing 1 M KOH and 32.3 mM NO$_3^-$.

Figure S24. Comparison of NH$_3$ production performance of Pd$_{74}$Ru$_{26}$ NCs and other reported advanced eNO$_3^-$RR catalysts at different NO$_3^-$ concentration, with references.

Figure S25. XRD patterns of Pd$_{74}$Ru$_{26}$ after the long-term chronopotentiometry (CP) test.
Figure S26. TEM mapping images of Pd$_{74}$Ru$_{26}$ after the long-term chronopotentiometry (CP) test.

Figure S27. HRTEM image of Pd$_{74}$Ru$_{26}$ after the long-term chronopotentiometry (CP) test, and the corresponding FFT pattern (inset) of the selected area with the red dashed square.

Figure S28. High-resolution Pd 3d XPS spectrum (a), and Ru 3p XPS spectrum (b) of Pd$_{74}$Ru$_{26}$ before/after the CP test.

Figure S29. Optimized adsorption configurations of each intermediate on Pd(111), Ru(001) and Pd$_{74}$Ru$_{26}$(111) surfaces along the HER steps (a) and eNO$_3$RR steps (b) (top view).
Figure S30. Free energy diagram of each intermediate state on Pd(111) surface along different eNO$_3^-$ RR pathways calculated at 0 V vs. RHE.

Figure S31. Free energy diagram of each intermediate state on Ru(001) surface along different eNO$_3^-$ RR pathways calculated at 0 V vs. RHE.
Figure S32. Free energy diagram of each intermediate state on Pd$_{74}$Ru$_{26}$(111) surface along different eNO$_3$ RR pathways calculated at 0 V vs. RHE.

Table S1. Atomic ratios of Pd and Ru elements in Pd$_x$Ru$_y$ bimetallic NCs obtained by ICP-OES.

<table>
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<tr>
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<th>Pd$<em>{90}$Ru$</em>{10}$</th>
<th>Pd$<em>{74}$Ru$</em>{26}$</th>
<th>Pd$<em>{57}$Ru$</em>{43}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd: Ru atomic ratio</td>
<td>92.32: 7.68</td>
<td>69.44: 30.56</td>
<td>54.1: 45.9</td>
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Table S2. Surface metal elemental ratio calculated from XPS spectra of Pd$_{74}$Ru$_{26}$ NCs before and after reaction.

<table>
<thead>
<tr>
<th></th>
<th>Before reaction</th>
<th>After reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd (at%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd$^0$</td>
<td>57.32</td>
<td>53.09</td>
</tr>
<tr>
<td>Pd$^{2+}$</td>
<td>16.86</td>
<td>22.51</td>
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<tr>
<td>Ru (at%)</td>
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<tr>
<td>Ru$^0$</td>
<td>17.76</td>
<td>15.42</td>
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<tr>
<td>Ru$^{4+}$</td>
<td>8.06</td>
<td>8.98</td>
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Table S3. Structural parameters of Pd foil, Pd$_{57}$Ru$_{43}$, Pd$_{74}$Ru$_{26}$, and Pd$_{90}$Ru$_{10}$ extracted from the EXAFS fitting. Multi ($k_1$, $k_2$, $k_3$)-weighted is carried out, the fitting range is $3 < k < 14$ Å$^{-1}$, $1 < R < 3$ Å, and $S_0^2$ =0.895. $S_0^2$ represents the amplitude reduction factor, determined through the fitting of the Pd foil; CN is the coordination number; R is the interatomic distance (the bond length between Pd central atoms and surrounding coordination atoms); $\sigma^2$ is the Debye-Waller factor; $\Delta E_0$ is edge energy shift; The R factor evaluates the quality of the fitting.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter path</th>
<th>CN</th>
<th>R(Å)</th>
<th>$\sigma^2$ (Å²)</th>
<th>$\Delta E_0$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd foil</td>
<td>Pd-Pd</td>
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<td>2.759±0.003</td>
<td>0.0056±0.0004</td>
<td>-3.7±0.6</td>
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<tr>
<td>Pd$<em>{74}$Ru$</em>{43}$</td>
<td>Pd-Pd/Ru</td>
<td>10.2±0.7</td>
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<td>0.0071±0.0005</td>
<td>6.1±0.5</td>
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<tr>
<td>Pd$<em>{74}$Ru$</em>{26}$</td>
<td>Pd-Pd/Ru</td>
<td>10.5±0.8</td>
<td>2.744±0.004</td>
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<td>7.6±0.5</td>
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<tr>
<td>Pd$<em>{90}$Ru$</em>{10}$</td>
<td>Pd-Pd/Ru</td>
<td>9.8±0.8</td>
<td>2.754±0.004</td>
<td>0.0068±0.0005</td>
<td>-5.1±0.6</td>
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Table S4. Estimated ECSAs of Pd, Ru and Pd$_{74}$Ru$_{26}$ NCs. The ECSA was determined by: ECSA = $C_{dl}/C_s$, where $C_{dl}$ is the double layer capacitance and $C_s$ is the specific capacitance of the sample. The specific capacitance for a flat surface is generally found to be in the range of 20-60 μF cm$^{-2}$. In this study, the specific capacitance is assumed to be $C_s = 40$ μF cm$^{-2}$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\text{NO}_3^-$ concentration (mM)</th>
<th>Applied potential (V vs. RHE)</th>
<th>NH$_3$ FE (%)</th>
<th>NH$_3$ yield rate (mg h$^{-1}$ cm$^{-2}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Fe-CO$_3$ LDH</td>
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<td>1.261</td>
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<td>Au$_1$Cu</td>
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<td>Pd-ND$_8$/Zr-MOF</td>
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<td>85.9</td>
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</tr>
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<td>2.58</td>
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<td>Cu-NSs</td>
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<td>99.7</td>
<td>0.39</td>
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<td>Cu(B)-2</td>
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<td>0.798</td>
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<td>a-RuO$_2$</td>
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<td>19</td>
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<td>-0.3</td>
<td>99.8</td>
<td>9.231</td>
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Table S5. Comparison of performance of Pd$_{74}$Ru$_{26}$ NCs and other reported advanced electrocatalysts for NH$_3$ production via eNO$_3$-RR.
<table>
<thead>
<tr>
<th>Material</th>
<th>Symbol</th>
<th>Current Density</th>
<th>Overpotential</th>
<th>Selectivity</th>
<th>Activity</th>
<th>Ref.</th>
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<td>PA-RhCu cNCs</td>
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<td>-0.05</td>
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<td>-0.5</td>
<td>98.6</td>
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<td>Rh NFs</td>
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<td>Cu-doped Fe₃O₄</td>
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<td>ISAA In–Pd</td>
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<td>Zn/Cu-2.3</td>
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<td>Fe/Ni₃P</td>
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</table>
<pre><code>                                                             | 100              | 0.9           | ~100        | 42.98   | 31  |
</code></pre>

Reference


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