Supporting Information

Significantly Enhanced Electrocatalytic N₂ Reduction to NH₃ by the Surface Selenization with Multiple Functions

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#Equal Contribution

Experimental Section

Materials. RuCl₃, Se, Li₂SO₄, NaOH, D₂O (99.9 atom%), DMSO (99.95%) and NaBH₄ were supplied by Aladdin (Shanghai, China). HCl was purchased from Far East Fine Chemicals (Yantai, China). NH₄Cl was obtained from Tianjin Bodi Chemical Co., Ltd. China. ¹⁵NH₄Cl (99 atom%) was supplied by Morai Chemical. All the chemicals were analytical-reagent grade and used without further purification.

Preparation of RuO₂/C. Specifically, a certain amount of Carbon (30 mg) and RuCl₃ were added into an agate mortar and grounded together for 30 minutes. Thereafter, 0.016 g of NaOH and 0.0152 g of NaBH₄ were added, after the ground for 30 minutes respectively. The resulting powder was centrifuged several times in a centrifuge until the solution pH = 7. The samples were then dried at 60 °C.

Preparation of RuO₂-Seₓ/C. 10 mg of the obtained RuO₂ powder was transferred into a magnetic boat and flattened. Then 100 mg of selenium powder is spread in another magnetic boat. Then magnetic boats were calcined at 250 °C, 300 °C and 350 °C for 2 h with a heating rate of 5 °C/min, respectively. After being cooled to room temperature, the resulting products were collected.
**Preparation of RuSe₂/C.** 10 mg of the obtained RuO₂ powder was transferred into a magnetic boat and flattened. Then 100 mg of selenium powder is spread in another magnetic boat. Then magnetic boats were calcined at 600 °C for 2 h with a heating rate of 5 °C/min, respectively. After being cooled to room temperature, the resulting products were collected.

**Preparation of C-Se:** 10 mg carbon was transferred into a magnetic boat and flattened. Then 100 mg of selenium powder is spread in another magnetic boat. Then magnetic boats were calcined at 300 °C for 2 h with a heating rate of 5 °C/min. After being cooled to room temperature, the resulting products were collected.

**Characterization.** X-ray diffraction (XRD) analysis at a scanning rate of 1° min⁻¹ in the 2θ ranges from 1 to 80° was used to examine the composition of the as-synthesized samples on X’Pert PRO MPD. Scanning electron microscopy (SEM) measurement was collected on Hitachi, S-4800 to investigate the structure and morphology of the samples. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were performed on JEM-2100UHR with operating at 200 kV. The X-ray photoelectron spectrum (XPS) was conducted using a VG ESCALABMK II spectrometer with AlKa (1486.6 eV) photon source. All the electrochemical performances of the as-synthesized samples were carried out on an electrochemical station (CHI 760E). The ¹H NMR spectrum was recorded on a Bruker 500 with Probe TXI at temperature of 25 °C using a 3 mm tube. The electrolyte after electrolysis was collected, lyophilized and further dissolved in 1M HCl solution (D₂O/H₂O mixed solution). The IC date were collected by an IC (863 Basic IC Plus. Metrohm, Switzerland) equipped with a Metrosep C Supp 4-250/4.0 column.

**Electrochemical measurements.** All electrochemical measurements were performed by using an electrochemical workstation (Shanghai Chenhua Instrument Corporation, China) and a two-compartment electrochemical cell, which was connected with a salt bridge. The RuO₂-Seₓ/C dropped on the carbon paper was used as a working electrode, carbon rod as an auxiliary electrode and the saturated calomel electrode (SCE) with a saturated KCl electrolyte as a reference electrode. All the gas used in this work is with a purity grade of 99.999 % and fully purified by the Cu impurity trap, then plunged into the electrolyte more than 30 min. The following equation was used to convert the potential reported in this work to the RHE scale: E(RHE)=E(SCE)+(0.244+0.059×pH)V. For the NRR test, the chronoamperometry experiments were conducted in N₂-saturated 0.1 M Li₂SO₄ solution (Notably, the Li₂SO₄ used was pretreated at 800 °C about 4 h in Ar.) with stirring at 450 rpm. For the preparation of the working electrode,
6 mg catalyst was first dispersed in 1.0 mL of absolute ethanol and 50 µL of Nafion solution (5.0 wt%) under ultrasonication for 5 min to form a homogeneous catalyst ink. After that, the as-prepared catalyst ink was completely loaded onto a commercial carbon paper with an area of 1.0×1.0 cm², then dried under ambient conditions for use.

**Ammonia quantification.** The produced NH₃ was quantitatively determined using the indophenol blue method.¹ Typically, 1 mL of the sample solution was first pipetted from the post-electrolysis electrolyte. Afterward, 1 mL of a 1M NaOH solution containing salicylic acid (5 wt%) and sodium citrate (5 wt%) was added, and 0.5 mL of NaClO solution (0.05 M) and 0.1 mL of sodium nitroferricyanide solution (1 wt%) were added subsequently. After 2 h, the absorption spectra of the resulting solution were acquired with an ultraviolet-visible (UV-vis) spectrophotometer (BioTek Synergy H1 Hybrid Multi-Mode Reader). The formed indophenol blue was measured by absorbance at λ = 654 nm. The concentration (NH₄⁺) absorbance curve used for estimation of NH₃ amount was calibrated using standard NH₄Cl solution with NH₄⁺ concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 µg mL⁻¹ in 0.1 M Li₂SO₄. The fitting curve (y=0.509x+0.04065, R²=0.999) showed a good linear relation between the NH₄⁺ concentration and absorbance.

**¹⁵N₂ isotope labelling experiments.** The produced NH₃ was detected by the ¹H NMR. ¹⁵N₂ (99%, provided by the Shanghai Aladdin Biochemical Technology Co., Ltd) was used to further verify the N-source of NH₃ produced. All the gases were purified by the Cu impurity trap. Before the electrolysis, the Ar was plunged into the electrolyte about 1 h, then ¹⁵N₂ was plunged into the electrolyte to saturation. The electrolyte after electrolysis at -0.1 (V vs. RHE) was collected, lyophilized and further dissolved in the solution of 1 M HCl, D₂O and H₂O. Then the ¹⁵NH₃ produced was detected by the ¹H NMR spectrum (Bruker 500). The procedure that detected ¹⁴NH₃ produced was the same except the ¹⁴N₂ (99.999%) was used. The standard curves was calibrated by using a series of concentrations of NH₄Cl And the fitting curves are y=0.034x+0.004, R²=0.999 and y=0.036x-0.002, R²=0.998.

**Determination of hydrazine.** The hydrazine present in the electrolyte was estimated by the method of Watt and Chrisp.² A mixture of para-(dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. The calibration curve was plotted as follow: First, preparing a series of reference solutions, by pipetting suitable volumes of the hydrazine hydrate-nitrogen 0.1 M HCl solution in colorimetric tubes; Second, making up to 5 mL with 0.1 M HCl solution; Third, adding 5 mL above prepared color reagent and stirring 10 min at room temperature; Fourth, the absorbance
of the resulting solution was measured at 455 nm, and the obtained calibration curve (y=1.184x+0.02371, \( R^2 = 0.999 \)) was used to calculate the hydrazine concentration.

**Calculation of the Faradaic efficiency and the yield rate.** The faradaic efficiency for \( N_2 \) reduction was defined as the amount of electric charge used for synthesizing \( NH_3 \) divided the total charge passed through the electrodes during the electrolysis. The total amount of \( NH_3 \) produced was measured using colorimetric methods. Assuming three electrons were needed to produce one \( NH_3 \) molecule, the FE could be calculated as follows:

Faradaic efficiency (FE,%) = \( \frac{3F \times C_{NH_4^+} \times V}{17Q} \times 100\% \)

The \( NH_3 \) yield was calculated using the following equation:

\( NH_3 \) yield = \( \frac{C_{NH_4^+} \times V}{t \times A} \)

where \( F \) is the faraday constant, \( C_{NH_4^+} \) is the measured concentration of \( NH_4^+ \), \( V \) is the electrolyte volume, \( Q \) is the sum of electric charge recorded by electrochemical workstation, 17 is the molarmass of \( NH_4^+ \) atom, \( t \) is the reaction time, and \( A \) is the geometric area of the cathode (1 cm\(^2\)).

**Calculation Setup.** DFT calculations were performed in the Vienna ab initio simulation package (VASP). A spin-polarized GGA PBE functional, all-electron plane-wave basis sets with an energy cutoff of 520 eV, and a projector augmented wave (PAW) method were adopted. RuO\(_2\) and RuO\(_2\)-Se\(_x\) are simulated using a surface model of \( p \) (2 \( \times \) 2) unit cell periodicity. A (3 \( \times \) 3 \( \times \) 1) Monkhorst-Pack mesh was used for the Brillouin-zone integrations to be sampled. The conjugate gradient algorithm was used in the optimization. The convergence threshold was set \( 1 \times 10^{-4} \) eV in total energy and 0.05 eV/ Å in force on each atom.

The adsorption energy change (\( \Delta E_{ads} \)) was determined as follows:

\( \Delta E_{ads} = E_{total} - E_{sur} - E_{mol} \)

where \( E_{total} \) is the total energy for the adsorption state, \( E_{sur} \) is the energy of pure surface, \( E_{mol} \) is the energy of molecule.

The free energy change (\( \Delta G \)) for adsorptions were determined as follows:

\( \Delta G = E_{total} - E_{sur} + \Delta E_{ZPE} - T\Delta S \)

where \( E_{total} \) is the total energy for the adsorption state, \( E_{sur} \) is the energy of pure surface, \( \Delta E_{ZPE} \) is the
zero-point energy change and $\Delta S$ is the entropy change.
Figure S1. The XRD pattern of RuSe$_2$/C catalyst.
**Figure S2.** TEM image of (a) precursor RuO$_2$/C, (b) RuO$_2$-Se$_{0.06}$/C and (c) RuO$_2$-Se$_{0.64}$/C.
Figure S3. XPS spectra of (a) Ru 3d, (b) O 1s and (c) Se 3d signals in RuO$_2$-Se$_{0.18}$/C.
Figure S4. XPS spectra of (a) Ru 3d, (b) O 1s and (c) Se 3d signals in RuO$_2$-Se$_{0.06}$/C.
Figure S5. XPS spectra of (a) Ru 3d, (b) O 1s and (c) Se 3d signals in RuO$_2$-Se$_{0.64}$/C.
Figure S6. (a) The UV-Vis absorption spectra of indophenol assays with NH$_3$ after incubated for 2 h at room temperature. (b) Corresponding calibration curves for the colorimetric NH$_3$ assay in 0.1 M Li$_2$SO$_4$. 

NH$_3$ Standard Curve

$y = 0.509x + 0.04065$

$R^2 = 0.999$
**Figure S7.** (a) Ion chromatogram analysis for the NH$_4^+$.
(b) Calibration curve used for estimation of NH$_4^+$. 

![Ion chromatogram analysis for the NH$_4^+$](image1)

![Calibration curve used for estimation of NH$_4^+$](image2)
Figure S8. (a) Calibration curves for determination of $^{14}\text{NH}_4^+$. (b) Calibration curves for determination of $^{15}\text{NH}_4^+$. 
Figure S9. (a) The UV-Vis absorption spectra of indophenol assays with N\textsubscript{2}H\textsubscript{4} after incubated for 10 min at room temperature. (b) Corresponding calibration curves for the colorimetric N\textsubscript{2}H\textsubscript{4} assay in 0.1 M Li\textsubscript{2}SO\textsubscript{4}.
Figure S10. UV-Vis spectra of the electrolyte before and after electrolysis at -0.1 V (vs. RHE).
Figure S11. (a) Ion chromatogram analysis for the NH$_4^+$ of RuO$_2$-Se$_{0.18}$/C. (b) The NH$_4^+$ yield and FE detected by ion chromatography.
Figure S12. Comparison of the FE and NH₃ yield using different feeding gases for the NRR at -0.1 V (vs. RHE).
Figure S13. UV-Vis absorption spectra of the electrolyte stained with indophenol indicator before and after electrolysis at -0.1 V (vs. RHE).
Figure S14. Control tests in 0.1 M Li$_2$SO$_4$ solution at -0.1 V (vs. RHE).
Figure S15. (a) The $^1$H-NMR spectrum of electrolyte that electrolysis in $^{14}$N$_2$-saturated condition. (b) The $^1$H-NMR spectrum of electrolyte that electrolysis $^{15}$N$_2$-saturated condition.
**Figure S16.** Comparative tests of different catalysts in 0.1 M Li$_2$SO$_4$ solution at -0.1 V (vs. RHE).
Figure S17. (a) LSV curves of catalysts in three N$_2$-saturated solutions with a scan rate of 5 mV s$^{-1}$. (b) Chronoamperometry curves at various potentials in three N$_2$-saturated solutions. (c) NH$_3$ yield and FE at -0.1 V (vs. RHE) in three solutions.
Figure S18. (a) The UV-Vis absorption spectra of indophenol assays with NH$_3$ in 0.1 M KOH after incubated for 2 h at room temperature. (b) Corresponding calibration curves for the colorimetric NH$_3$ assay in 0.1 M KOH.
Figure S19. (a) The UV-Vis absorption spectra of indophenol assays with NH$_3$ in 0.1 M HCl after incubated for 2 h at room temperature. (b) Corresponding calibration curves for the colorimetric NH$_3$ assay in 0.1 M HCl.
Figure S20. LSV curves of RuO₂/C, RuO₂-Se₀.₀₆/C, RuO₂-Se₀.₁₈/C and RuO₂-Se₀.₆₄/C catalysts in 0.1 M Li₂SO₄ solution with a scan rate of 5 mV s⁻¹.
Figure S21. Electrochemical impedance spectroscopy (EIS) of RuO$_2$/C, RuO$_2$-Se$_{0.06}$/C, RuO$_2$-Se$_{0.18}$/C, RuO$_2$-Se$_{0.64}$/C.
Figure S22. Time-dependent current density curves of RuO$_2$-Se$_{0.18}$/C with 1 h for each cycle in N$_2$-saturated 0.1 M Li$_2$SO$_4$. 
Figure S23. NH$_3$ yield and FE after charging at -0.1 V vs. RHE for 1h and 50 h.
Figure S24. (a) The TEM image and (b) HRTEM image of RuO$_2$-Se$_{0.18}$/C catalyst after NRR.
Figure S25. The XRD pattern of RuO$_2$-Se$_{0.18}$/C catalyst before and after NRR.
Figure S26. XPS spectra of (a) Ru 3d, (b) O 1s and (c) Se 3d signals in RuO$_2$-Se$_{0.18}$/C after time-dependent current density test.
Figure S27. PDOS of active Ru atoms on RuO$_2$-Se$_{0.18}$ and RuO$_2$ upon (a) $^\ast$N$_2$ adsorption and (b) $^\ast$NH$_3$ adsorption.
Figure S28. The reaction path carried out around the optimized geometry of the RuO$_2$ intermediate. Color code: pink, H; red, O; blue, N; gray, Ru.
**Figure S29.** The reaction path carried out around the optimized geometry of the RuO$_2$-Se$_{0.18}$ intermediate. Color code: pink, H; red, O; blue, N; gray, Ru; green, Se.
Figure S30. The reaction path carried out around the optimized geometry of the RuO$_2$-Se$_{0.06}$ intermediate. Color code: pink, H; red, O; blue, N; gray, Ru; green, Se.
Figure S31. The reaction path carried out around the optimized geometry of the RuO$_2$-Se$_{0.64}$ intermediate. Color code: pink, H; red, O; blue, N; gray, Ru; green, Se.
Table S1. The comparable results of our work and other recently reported NRR catalysts at the following potentials.

<table>
<thead>
<tr>
<th>Process</th>
<th>Catalyst</th>
<th>Conditions</th>
<th>Yield rate (μg h(^{-1}) cm(^{-2}))</th>
<th>Faradaic efficiency (%)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Electrocatalysis</td>
<td>RuO(_2)/C</td>
<td>0.1M Li(_2)SO(_4) -0.1 V</td>
<td>1.6</td>
<td>10.45</td>
<td>This work</td>
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<td></td>
<td>RuO(<em>2)-Se(</em>{0.06})/C</td>
<td>0.1M Li(_2)SO(_4) -0.1 V</td>
<td>1.85</td>
<td>12.25</td>
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<td>RuO(<em>2)-Se(</em>{0.18})/C</td>
<td>0.1M Li(_2)SO(_4) -0.1 V</td>
<td>12.97</td>
<td>26.01</td>
<td>This work</td>
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<tr>
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<td>RuO(<em>2)-Se(</em>{0.64})/C</td>
<td>0.1M Li(_2)SO(_4) -0.1 V</td>
<td>3.25</td>
<td>14.43</td>
<td>This work</td>
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<tr>
<td></td>
<td>Ti(_3)C(_2)</td>
<td>0.1M KOH -0.1 V</td>
<td>0.5</td>
<td>21.3</td>
<td>3</td>
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<td>RO-Cu(_3)P/CFC</td>
<td>0.1M Na(_2)SO(_4) -0.1 V</td>
<td>4.7</td>
<td>12.3</td>
<td>4</td>
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<td>FL-Sb</td>
<td>0.1M KOH -0.1 V</td>
<td>1.84</td>
<td>6.2</td>
<td>5</td>
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<td>MoS(_2)</td>
<td>0.1M KOH -0.1 V</td>
<td>8.35</td>
<td>16.1</td>
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<td>E(_{ex})-COF/NC</td>
<td>0.1M KOH -0.1 V</td>
<td>7.1</td>
<td>34.9</td>
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<td>NV-W(_2)N(_3)</td>
<td>0.1M KOH -0.1 V</td>
<td>0.94</td>
<td>10.1</td>
<td>8</td>
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<td>Fe(_{SA})-N-C</td>
<td>0.1M KOH -0.1 V</td>
<td>5.8</td>
<td>26.3</td>
<td>9</td>
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<td>Haber-Bosch method</td>
<td>Fe/Ru-based catalysts</td>
<td>350<del>550 °C, 200</del>300 atm</td>
<td>~20 % (N(_2) conversion rate)</td>
<td>-----</td>
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<tr>
<td>Biocatalysis</td>
<td>CdS:MoFe, N(_2)</td>
<td>-----</td>
<td>321.3 μg mg MoFe(^{-1}) h(^{-1})</td>
<td>-----</td>
<td>11</td>
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References