Supplementary Information

A small change in the local atomic environment for a big improvement in single-atom catalysis

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1 Computational and Modelling Methods

1.1 Computational Details

Density functional theory (DFT) calculations were performed using the VASP code. Electronic exchange was described by the generalized gradient approximation (GGA) method, with the correlation described by the Perdew-Burke-Ernzerhof (PBE) functional.¹ Expanded Kohn-Sham wave functions in plane wave basis and the projector augmented wave (PAW) method were employed to describe valence and core electrons,^{2,3} respectively. The Brillouin zone was sampled through a $(3 \times 3 \times 1)$ Monkhorst-Pack k-point mesh.⁴ Water dissociation energy barriers were calculated using the climbing image nudged elastic band (Cl-NEB)⁵ method with at least six images generated between the initial and final configurations. The energy cutoff for all the calculations was set at 400 eV, with the force convergence criteria below 0.05 eV per Å. Zero-point energy and entropic corrections were applied using the data from Ref.⁶. Convergence tests with stricter criteria and spin-polarization were performed; no significant difference was found on the free energies and configurations. Solvation effect was neglected since previous studies showed that the solvation induced stabilization of adsorbates in NRR was only within ~0.1 eV.^{6,7} Previous studies with explicit solvation models on Ru found that their results have good agreement with the trends found from the less-expensive thermochemical calculations without kinetic barriers using the computational hydrogen electrode method.⁸ Therefore, the kinetic barriers for NRR were not computed due to the enormous computational cost overhead. The d-band centers were calculated as the average energy of the *d*-electrons of the Ru site.

1.2 Modeling Details

The Ru SAs/Cu_xO_y surfaces were modelled by placing a Ru atom on the four-layer surfaces, with the bottom two layers remained constrained. For each surface, different positions of Ru were tested; only

the most energetically favorable position of Ru was considered for further calculations. Stoichiometric Cu-terminated (111) surfaces were considered for all the Cu, Cu₂O, and CuO systems, with the reason that this is a favorable surface for Cu and its oxides.^{9–11} Our XRD experiments also indicate that our asprepared systems have the same predominant (111) surface (**Figure 2d**). For Cu₂O, both the Cu- and O-terminated (111), (110), and (100) were modelled for further comparisons. For the adsorption of N₂, an "end-on" configuration was found to be energetically more favorable than the "side-on" configuration (**Figure S14**). Therefore, the end-on configuration was used for further analysis in the free energy diagram. All of the optimized structural information can be found in our online database: https://github.com/NRRcat/database.

2 Experimental Methods

2.1 Chemicals

Ruthenium(III) chloride (RuCl₃, Ru content 45-55%), hydrogen peroxide solution (H₂O₂, reagent grade, 30 wt. %), sulfuric acid (H₂SO₄, 99.999%), hydrochloric acid solution (HCl 32 wt. % in H₂O), sodium hydroxide solution (NaOH, reagent grade, 10 M in H₂O), Nafion[®] perfluorinated membrane (Nafion[®] 115, thickness 0.005 in.), Nessler's reagent, and sodium borohydride powder (NaBH₄, reagent grade, \geq 98.0%) were purchased from Sigma-Aldrich. All chemicals were used without further purification. Argon gas (99.99%) and nitrogen gas (99.99%) were purchased from Coregas Australia, and all solutions were prepared with deionized water.

At first, the polymer electrolyte membrane Nafion[®] 115 was cleaned and treated by the following three main steps for removing organic material and activating the membrane. The pretreatment procedures include boiling in 3 wt% H₂O₂, for 60 min, followed by boiling for 60 min in deionized water. Then, the

membrane was boiled for 60 min in 0.5 M H_2SO_4 solution, followed by boiling for 60 min in deionized water. All of the treatment processes were performed at 80 °C

2.2 Synthesis and Characterization Methods

The copper oxides supported Ru SAs and Ru NPs were synthesized using a facile ultrasonic-assisted chemical reduction method. First, copper foams were pretreated by mild etching in HCl (32 wt. %) for 15 min, then rinsing thoroughly with ultrapure water, and dried at 80 °C overnight prior to use. Then, the obtained copper oxides were inserted in 100 ml RuCl₃ solutions with the concentrations of 2 mmol L^{-1} and 200 mmol L^{-1} . Subsequently, the above mixtures were placed in ultrasonic water bath with the temperature kept at 50 °C for 1 h; simultaneously, during this process, 100 ml NaBH₄ aqueous solutions (10 mM) were slowly added into the above mixtures. After aging for another 1 h at 50 °C, the resulting copper oxides supported Ru SAs and Ru NPs were taken out from solution and dried at room temperature overnight.

2.3 Electrochemical Measurements

Prior to N₂ reduction tests, Nafion 115 membranes were heat-treated in sequence by 5% H₂O₂, 0.5 M H₂SO₄ and deionized water for 1 h. After being rinsed in water thoroughly, the membranes were immersed in deionized water for future use. Electrochemical measurements were performed using an Autolab/PGSTAT302 Potentiostat–Galvanostat (Metrohm Autolab BV, Netherlands), with a gas-tight two-compartment electrochemical cell separated by a piece of Nafion 115 membrane at room temperature. A piece of Pt gauze was used as counter electrode, and the Ag/AgCl/sat. KCl (4 M) was employed as reference electrode. All the potentials in this work were calculated to a RHE scale based on the Nernst equation ($E_{RHE} = E_{Ag/Ag/Cl} + 0.059 \times pH + 0.205$) (noted that 0.205 will be different if another KCl concentration is selected).

LSV tests were performed in N₂- and Ar-saturated solutions at a scan rate of 5 mV s⁻¹. All LSV curves were steady-state ones after the working electrodes were scanned for several times. The current density was normalized to the geometrical area. Potentiostatic tests were performed at different potentials ranging from 0.05 to -0.6 V vs. RHE for 1 h at room temperature (~25 °C). Prior to each electrolysis, the work electrode was reduced at a low applied potential (-0.1 V vs. RHE) for 30 min. 1 M NaOH solution was used as electrolyte, and it was pre-saturated with N₂ by introducing a pure N₂ gas stream for 1 h. During each electrolysis, the electrolyte was continuously bubbled with a constant N₂ flow with stirring by a magnetic stirrer at ~150 rpm.

Quantitative analysis of the produced NH₃ in the electrolyte was performed by an ionselective electrode meter (Orion Star A214 Benchtop pH/ISE Meter; Thermo Scientific). A colorimetric method using Nessler's reagent for NH₃ detection was also performed to further examine the reliability of the former method, and the test solutions were measured as the absorbance at 420 nm by a UV-vis spectrometer (PerkinElmer Lambda 950).

The calculation of FE of NH_3 was based on [Eq. (1)]:

$$FE = \frac{3 \times F \times c \times V}{17 \times Q} \qquad [Eq. (1)]$$

where F is the Faraday constant, V is the total volume of electrolyte in cathodic compartment, Q is the total charge passed through the electrochemical system, and c is the calculated concentration of NH₃.

NH₃ yield was also obtained according to [Eq. (2)]:

$$NH_3 \text{ yield} = \frac{c \times V}{t \times A} \qquad [Eq. (2)]$$

where *t* is the reaction time, *A* is the surface area of working electrode, *V* is the total electrolyte volume in cathodic compartment, and *c* is the concentration of NH_3 .



3 Additional Results and Discussion

Figure S1. Calculated free energy pathways of NRR on (a) Ru SAs/Cu(111) and (b) Ru SAs/CuO(111). The NH_3^* will be protonated and form NH_4^+ in solution (not shown). Insets show the optimized

adsorption geometries of the reactants. Brown, red, green, blue, and white spheres represent Cu, O, Ru, N, and H, respectively.



Figure S2. Free energy diagram of the initial pathways with a Langmuir-Hinshelwood (LH) mechanism.

Brown, red, green, blue, and white spheres represent Cu, O, Ru, N, and H, respectively.



Figure S3. Low-magnification SEM image of the as-synthesized Ru SAs/Cu_xO_y.



Figure S4. TEM image of the as-synthesized Ru SAs/Cu_xO_y.



Figure S5. HRTEM image of the as-synthesized Ru SAs/Cu_xO_y.



Figure S6. EDS analysis of the as-synthesized Ru SAs/Cu $_xO_y$.



Figure S7. EXAFS spectra of the as-synthesized Ru SAs/Cu $_xO_y$ and Ru NPs.

Electrocatalysis. The electrocatalytic NRR tests were performed in an H-type cell separated by a Nafion 115 membrane, and the schematic diagram of the NRR experimental set-up is shown in **Figure S8.** All potentials were converted to the RHE scale and current densities were normalized to the geometric surface area. Given that the impurities from catalysts, the Nafion dispersed liquid, and the ambient environment may contribute to the production of ammonia, the investigation of the source of ammonia is of great importance. Firstly, the measurement of linear sweep voltammetry (LSV) curves for Ru SAs/Cu_xO_v in Ar- or N₂-saturated electrolyte was performed. As shown in Figure S9, a higher current density in N₂-saturated electrolyte was observed compared to that of Ar-saturated electrolyte when the applied potential was less negative than -0.07 V vs. RHE. It can be inferred that the additional reduction reaction may occur as the introduction of N2 feed gas. However, the current density in N₂-saturated electrolyte was found to be very close to that of Ar-saturated electrolyte when the applied potential was more negative than -0.07 V vs. RHE. This was probably due to the fact that HER was dominant at high applied potentials, and the evoluted H₂ will occupy the active sites of Ru SAs/Cu_xO_v and thus block the mass transfer of N₂ molecules from the electrolyte to the surface of the active sites of the used catalyst.

Figure S10 shows the LSV curves for Ru SAs/Cu_xO_y, Ru NPs/Cu_xO_y, and Cu_xO_y in the presence of continuous N₂ bubbling. It can be clearly seen that Cu_xO_y exhibited a much lower onset potential than those of Ru SAs/Cu_xO_y and Ru NPs/Cu_xO_y. Moreover, the current densities of Cu_xO_y were the lowest among these three catalysts at all potentials. All these results suggested that Cu_xO_y was inert towards HER compared to that of Ru SAs/Cu_xO_y and Ru NPs/Cu_xO_y, and this characteristic makde Cu_xO_y an ideal support for NRR catalysts. In addition, the current densities for Ru SAs/Cu_xO_y were much lower than those of Ru NPs/Cu_xO_y, which was probably due to the fact that the bulk Ru supported on Cu_xO_y had a higher HER activity than the single Ru sites.



Figure S8. Experimental apparatus for the electrocatalytic NRR.



Figure S9. LSV curves for Ru SAs/Cu_xO_y in Ar- or N₂-saturated electrolyte.



Figure S10. LSV curves for Ru SAs/Cu_xO_y, Ru NPs/Cu_xO_y, and Cu_xO_y electrodes in a N₂ saturated 0.5 M NaOH electrolyte.



Figure S11. (a) Electrocatalytic NRR tests in the presence of continuous N_2 and Ar bubbling for 10 h. (b) A consecutive electrocatalytic NRR test at the potential of 0.05 V vs. RHE in the presence of continuous N_2 bubbling.



Figure S12. Chronoamperometry results for Ru SAs/ Cu_xO_y based NRR at the corresponding potentials.



Figure S13. Chronoamperometry results for Ru SAs/Cu_xO_y based NRR at -0.10 and -0.20 V *vs*. RHE for 8 h.



Figure S14. Calculated binding free energies of N_2 respectively with the configurations of "side-on" and "end-on" on the three Ru SAs/Cu_xO_y(111). Brown, red, green, and blue spheres represent Cu, O, Ru, and N, respectively.

Table S1. Calculated binding energy	v of the Ru SA on	$Cu_xO_y(111).$
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	Cu-terminated Cu ₂ O(111)	Cu-terminated CuO(111)	Cu(111)
Ru Binding Energy	-5.97 eV	-5.64 eV	-3.16 eV

Table S2. Calculated *d*-band centres of Ru SAs at other Cu_2O facets. The energy at Fermi level is used as the reference.

	O-terminated		O-terminated	Cu-terminated	O-terminated
	(111)	(110)	(110)	(100)	(100)
<i>d</i> -band centre	-0.87 eV	-0.42 eV	-1.38 eV	-0.79 eV	-2.06 eV

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Potential (V vs. RHE)
This Study	1 M NaOH	42.4 $\mu g h^{-1} m g_{cat}^{-1}$	14.1	0.05
Ru SAs/g- $C_3N_4^{12}$	0.5 M NaOH	$23 \ \mu g \ h^{-1} \ m g_{cat}{}^{-1}$	8.3	0.05
Ru/NC ¹³	0.1 M HCl	$3.67 \text{ mg } h^{-1} \text{ mg}_{Ru}^{-1}$	7.5	-0.21
Au SAs-NDPCs ¹⁴	0.1 M HCl	$2.32 \ \mu g \ h^{-1} \ cm^{-2}$	12.3	-0.20
$Au_1/C_3N_4^{15}$	$0.005 \text{ M} \text{ H}_2\text{SO}_4$	$1.31~\mu gh^{-1}m g_{Au}{}^{-1}$	11.1	-0.10
SA-Mo/NPC ¹⁶	0.1 M KOH	$34.0 \ g \ h^{-1} \ m g_{cat}{}^{-1}$	14.6	-0.45
ISAS-Fe/NC ¹⁷	0.1 M PBS	$62.9~gh^{-1}mg_{cat}{}^{-1}$	18.6	-0.40
FePc/C ¹⁸	0.1 M Na ₂ SO ₄	$10.25 \ \mu g \ h^{-1} \ m g_{cat}{}^{-1}$	10.5	-0.30
Fe-N/C-CNTs ¹⁹	0.1 M KOH	34.83 $\mu g h^{-1} m g_{cat}^{-1}$	9.3	-0.20
Fe-MoS ₂ ²⁰	0.1 M KCl	97.5 μg h ⁻¹ cm ⁻²	31.6	-0.20
$Fe-(O-C_2)_4^{21}$	0.1 M KOH	32.1 $\mu g h^{-1} m g_{cat}^{-1}$	29.3	-0.10
Ni _x -N-C-700-3h ²²	0.5 M LiClO ₄	115 μg cm ⁻² h ⁻¹	21±1.9%	-0.80
CSA/NPC ²³	0.05 M Na ₂ SO ₄	0.86 µmol cm ⁻² h ⁻¹	10.5%	-0.20

Table S3. Summary of typical heterogeneous single atom catalysts for NRR at mild conditions reported

 in very recent years.

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