Electronic Supplementary Information

Experimental section

Materials: GO, ruthenium chloride (RuCl₃), sodium monophosphate (NaH₂PO₂), ammonium chloride (NH₄Cl), hydrazine hydrate (N₂H₄·H₂O), salicylic acid (C₇H₆O₃), sodium citrate (C₆H₅Na₃O₇), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol (CH₃CH₂OH), and carbon paper (CP) were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), sodium nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system.

*Preparation of Ru*₂*P-rGO:* Similar Ru₂*P-rGO* was reported.¹ 20 mg RuCl₃·3H₂O was dissolved in 30 mL homogeneous GO aqueous dispersion (1mg/ml) under stirring for about 2 h. After that, the solution was transferred to a 50 mL Teflon-sealed autoclave and heated at 160 °C for 12 h. The resulting black mixture was freeze-dried, and the black powder (Ru(III)/rGO) was collected. Then, the black powder and 2.0 g NaH₂PO₂ (weight ratio: 1:45) were grounded to form homogeneous powder. The powder was then annealed at 600 °C for 2 h under Ar atmosphere. After cooled to room temperature, the black products were collected, washed by centrifugation with deionized water several times to remove the residue of reactants. Finally, the product was freeze-dried. In addition, Ru-rGO was also prepared through annealing Ru(III)/rGO at 600 °C for 2 h under Ar/H₂ atmosphere (volume ratio = 9:1) atmosphere without adding NaH₂PO₂.

*Preparation of Ru*₂*P-rGO/CP electrode:* 10 mg Ru₂*P-rGO* powders and 40 μ L of Nafion solution (5 wt%) were dispersed in 960 μ L mixed solution contain 720 μ L ethanol and 240 μ L H₂O by 2 h sonication to form a homogeneous ink. Then, 10 μ L Ru₂*P-rGO* was loaded on a CP with area of 1 x 1 cm² and dried under ambient condition.

Characterizations: X-ray diffraction (XRD) analysis was performed using a LabX XRD-6100 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) at 40 kV and 40

mA. Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer were measured on SHIMADZU UV-2700 ultraviolet-visible (UV-Vis) spectrophotometer.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) using a standard three-electrode system using Ru₂P-rGO/CP as the working electrode, graphite rod as the counter electrode, and saturated Ag/AgCl electrode as the reference electrode. The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.059 × pH + 0.197 V. All experiments were carried out at room temperature. For electrochemical N₂ reduction, chrono-amperometry tests were conducted in N₂-saturated 0.1 M HCl solution (the HCl electrolyte was purged with N₂ for 0.5 h before the measurement).

Determination of NH₃: The produced NH₃ was spectrophotometrically determined by the indophenol blue method.² In detail, 2 mL electrolyte was taken from the cathodic chamber, and then 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. Subsequently, 1 mL of 0.05 M NaClO and 0.2 mL of 1% C₅FeN₆Na₂O·2H₂O were add into the above solution. After standing at room temperature for 2 h, UV-Vis absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curve was calibrated using standard NH₄⁺ solution with a serious of concentrations. The fitting curve (y = 0.40534x + 0.06591, R² = 0.999) shows good linear relation of absorbance value with NH₄⁺ concentration.

Determination of N_2H_4 : N_2H_4 in the electrolyte was estimated by the method of Watt and Chrisp.³ The mixture solution of 5.99 g C₉H₁₁NO, 30 mL HCl and 300 mL

ethanol was used as a color reagent. Typically, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL above prepared color reagent 10 min at room temperature. Moreover, the absorbance of the resulting solution was measured at a wavelength of 455 nm. The obtained calibration curve of N_2H_4 is y = 0.4925x + 0.1276, R² = 0.999.

Calculations of NH₃ yield rate and FE: NH₃ yield rate was calculated using the following equation:

NH₃ yield =
$$[NH_4^+] \times V/(m_{cat.} \times t)$$

FE was calculated according to following equation:

$$FE = 3 \times F \times [NH_4^+] \times V/(18 \times Q)$$

Where $[NH_4^+]$ is the measured NH_4^+ concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; $m_{cat.}$ is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of applied electricity.

Details of Density Functional Theory (DFT) Calculations: All calculations were performed on standard DFT by using Vienna ab initio Simulation Package (5.4.4 VASP) incorporating the projector augmented wave (PAW) scheme.⁴ All electron exchange correlation functional was treated through the generalized gradient approximation (GGA) with the revised Perdew-Burke-Ernzerhof using a cutoff energy 450 eV.⁵ For the analysis of structural and electronic properties of the defects, the Brillouin zone was sampled using a $3 \times 3 \times 1$ k-point grid generated within the Monkhorst–Pack. A vacuum space exceeds 20 Å was employed to avoid the interaction between two periodic units. The atomic position was fully relaxed until the maximum force on each atom was less than -0.02 eV/A and 10⁻⁵ eV. And thermal and zero point energy (ZPE) corrections were calculated over Γ points.⁶ The van der Waals interaction has been considered using the DFT-D3 scheme.⁷



Fig. S1. (a) UV-Vis absorption spectra of indophenol assays with NH_{4^+} concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH_{4^+} concentrations.



Fig. S2. (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.



Fig. S3. UV-Vis absorption spectra of the electrolyte stained with indophenol indicator after charging at -0.05 V for 2 h under different electrochemical conditions.



Fig. S4. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 2 h electrolysis in N_2 atmosphere at -0.05 V.



Fig. S5. (a) Time-dependent current density curves of Ru_2P -rGO/CP at -0.05 V for continuous cycles. (b) UV-Vis absorption spectra of the electrolytes stained with NH_3 color agent for continuous cycles.



Fig. S6 Photographs of pH test papers in 0.1 M HCl before and after 24 h electrolysis.



Fig. S7. (a) Time-dependent current density curves for Ru_2P -rGO/CP at different potentials in 0.1 M Na₂SO₄. (b) UV-Vis absorption spectra of the 0.1 M Na₂SO₄ electrolytes stained with indophenol indicator after electrolysis at a series of potentials. (c) NH₃ yields and FEs at a series of potentials.



Fig. S8. Calculated energy profiles for NRR catalyzed by Ru₂P-rGO: (a) distal, (b) alternating mechanisms.

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.
Ru ₂ P-rGO	0.1 M HCl	32.8 μ g h ⁻¹ mg ⁻¹ _{cat.}	13.04	This work
Ru NPs	0.01 M HCl	$0.55 \ \mu g \ h^{-1} \ cm^{-2}$	5.4	8
α-Au/CeO _x -RGO	0.1 M HCl	8.31 μ g h ⁻¹ mg ⁻¹ _{cat.}	10.1	9
TA-reduced Au/TiO ₂	0.1 M HCl	21.4 $\mu g h^{-1} m g^{-1}{}_{cat.}$	8.11	10
Au ₁ on N-doped porous noble carbon	0.1 M HCl	$2.32 \ \mu g \ h^{-1} cm^{-2}$	12.3	11
Au flowers	0.1 M HCl	$25.57 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	6.05	12
AuHNCs	0.5 M LiClO ₄	$3.9 \ \mu g \ h^{-1} \ cm^{-2}$	30.2	13
Pd/C	0.1 M PBS	4.5 μ g h ⁻¹ mg ⁻¹ _{cat.}	8.2	14
Pd ₃ Cu ₁ alloy	1 М КОН	39.9 μ g h ⁻¹ mg ⁻¹ _{cat.}	1.56	15
Pd _{0.2} Cu _{0.8} -rGO	0.1 M KOH	$2.8 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	0.6	16
PdRu tripods	0.1 M KOH	37.23 μ g h ⁻¹ mg ⁻¹ _{cat.}	1.85	17

Table S1. Comparison of electrocatalytic N_2 reduction performance for Ru_2P -rGOwith other aqueous-based noble-metal electrocatalysts under ambient conditions.

References

- T. Liu, S. Wang, Q. Zhang, L. Chen, W. Hu and C. Li, *Chem. Commun.*, 2018, 54, 3343–3346.
- 2 D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, **12**, 836–841.
- 3 G. W. Watt and J. D. Chrisp, Anal. Chem., 1952, 24, 2006–2008.
- 4 G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- 5 J.P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 6 L.M. Azofra, N. Li, D.R. MacFarlane and C. Sun, *Energy Environ. Sci.*, 2016,
 9, 2545–2549.
- W. Zhao, J. Zhang, X. Zhu, M. Zhang, J. Tang, M. Tan and Y. Wang, *Appl. Catal. B: Environ.*, 2014, 144, 468–477.
- 8 D. Wang, L. M. Azofra, M. Harb, L. Cavallo, X. Zhang, B. H. R. Suryanto and D. R. MacFarlane, *ChemSusChem*, 2018, 11, 3416–3422.
- 9 S. Li, D. Bao, M. Shi, B. Wulan, J. Yan and Q. Jiang, *Adv. Mater.*, 2017, 29, 1700001.
- M. Shi, D. Bao, B. Wulan, Y. Li, Y. Zhang, J. Yan and Q. Jiang, *Adv. Mater.*, 2017, 29, 1606550.
- Q. Qin, T. Heil, M. Antonietti and M. Oschatz, *Small Methods*, 2018, 2, 1800202.
- 12 Z. Wang, Y. Li, H. Yu, Y. Yu, H. Xue, X. Li, H. Wang and L. Wang, *ChemSusChem*, 2018, **11**, 3480–3485.
- M. Nazemi, S. R. Panikkanvalappil and M. A. El-Sayed, *Nano Energy*, 2018, 49, 316–323.
- J. Wang, L. Yu, L. Hu, G. Chen, H. Xin and X. Feng, *Nat. Comm.*, 2018, 9, 1795.
- 15 F. Panga, Z. Wanga, K. Zhang, J. He, W. Zhang, C. Guob, Y. Ding, *Nano Energy*, 2019, **58**, 834–841.

- M. Shi, D. Bao, S. Li, B. Wulan, J.-M. Yan and Q. Jiang, *Adv. Energy Mater.*, 2018, 8, 1800124.
- H. Wang, Y. Li, C. Li, K. Deng, Z. Wang, Y. Xu, X. Li, H. Xue and L. Wang,
 J. Mater. Chem. A, 2019, 7, 801–805.