Electronic Supplementary Information

Experimental section

Materials: Sodium Tungstate Dihydrate (Na₂WO₄·2H₂O), Nickel foam (NF), Cobalt chloride hexahydrate (CoCl₂·6H₂O), acetone (C₃H₆O), anhydrous ethanol (C₂H₆O), ammonium chloride (NH₄Cl), sodium hydroxide (NaOH), salicylic acid (C₇H₆O₃), sodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O), p–dimethylaminobenzaldehyde (C₉H₁₁NO), and sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O) were purchased from Chengdu Kelong Ltd.

Preparation of CoWO₄/NF: Typically, 0.65974 g of Na₂WO₄·2H₂O and 0.47586 g of CoCl₂·6H₂O were dissolved in 30 mL of deionized water, respectively, and stirred for one hour. Finally, the solution was transferred to a 100 ml sealed Teflon-lined stainless steel autoclave. Subsequently, the nickel foam (NF) was ultrasonically cleaned with acetone, ethanol, and deionized water for 10 min in turn and dried in air. And the cleaned NF was placed in the solution in an autoclave. Then the autoclave was kept at 150 °C for 6 h, 12 h and 18 h, respectively. After the autoclave cooled down to room temperature, the catalysts were was taken out and washed with water and ethanol several times, and subsequently dried at 60 °C for overnight. The catalysts CoWO₄/NF-6, CoWO₄/NF-12, and CoWO₄/NF-18 were obtained.

Characterizations: The crystal structure of the prepared material was determined using an X–ray diffractometer with Cu Kα radiation (DX–2700B). Microstructural observations were performed on a field–emission scanning electron microscopy (FEI Insect F50) and an atomic resolution scanning transmission electron microscopy (FEI Talos F200S Super). XPS measurements were carried out with Thermo Fischer ESCALAB Xi⁺. The absorbance data were measured via an Ultraviolet–visible (UV– Vis) spectrophotometer (Shimazu UV–2600). EPR spectra were recorded on a Brüker EMX spectrometer at room temperature. In situ mass spectrometry was conducted on a Linglu mass spectrometer (QAS100, China). DEMS was conducted on a mass spectrometer (Linglu QAS100) to in situ analysis of produced intermediates and products.

Electrochemical measurements: All electrochemical measurements were carried out in an H–shaped electrochemical cell separated by Nafion 117 membrane using CHI 760E electrochemical workstation (Chenhua, Shanghai). The area of the working electrode immersed in the electrolyte is 0.25 cm^{-2} . LSV was performed in Ar–saturated 0.5 M Na₂SO₄ with 0.1 M NaNO₂ at a scan rate of 5 mV s⁻¹. All potentials reported in this work were converted to a reversible hydrogen electrode (RHE) scale, and current densities were normalized to the geometric surface area. All experiments were carried out at room temperature (25 °C).

DEMS was conducted using an in-situ mass spectrometer (Linglu QAS100) combined with an electrochemical workstation. A small electrolytic cell with a volume of 2 mL was used, and the electrolyte was bubbled with high-purity Ar gas for 30 min to remove O_2 and N_2 . The CoWO₄ nanosheet (25 µg) was loaded on a planar conductive film (a dedicated film for in situ detection) to serve as the working electrode. A Pt wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. In situ mass spectrometry was performed simultaneously with LSV tests at a scanning rate of 5 mV·s⁻¹ to detect products and intermediates.

Determination of NH₃: The NH₃ concentration in the electrolyte was determined (the obtained electrolyte was diluted 20 times) by the indophenol blue method. Specifically, 2 mL of electrolyte collected after electrolysis was mixed with 2 mL of coloring solution (1 M NaOH containing 5% salicylic acid and 5% sodium citrate),

and 1 mL of oxidizing solution (0.05 M NaClO). Then 0.2 mL oxidation solution (0.05 M NaClO) mL catalyst solution (1 wt% C₅FeN₆Na₂O 2H₂O) was dropped into the collected solution. After standing in the dark for 2 h, the concentration of NH₃ was determined by UV–Vis at a specific wavelength of 655 nm. The concentration–absorbance curve was calibrated using the standard NH₄Cl solution with known concentrations of 0.0, 0.25, 0.5, 1.0, 1.5, 2.0, and 2.5 μ g mL⁻¹ in 0.5 M Na₂SO₄. The fitting curve (y = 0.41822x + 0.04157, R² = 0.9999) shows good linear relation of absorbance value with NH₃ concentration.

Determination of NH₃ yield and FE:

The NH_3 FE is estimated from the charge consumed for NO_2^- reduction and the total charge passed through the electrode:

$$FE = 6 \times F \times V \times [NH_3] / (Q \times 17) \times 100\%$$

The yield rate of NH₃ (aq) is calculated:

$$NH_3$$
 yield = V × $[NH_3] / (A × t × 17)$

Where $[NH_3]$ is the concentration of NH_3 (aq), F is the Faradaic constant (96485 C mol⁻¹), V is the volume of electrolyte in the anode compartment (45 mL), Q is the total charge passing the electrode, t is the electrolysis time, and A is the geometric surface area.

DFT calculation details: First–principles calculations with spin–polarized were performed based on density functional theory (DFT) implemented in the VASP package.¹ The interaction between valence electrons and ionic core were expanded using the projector augmented wave (PAW)²approach with cutoff of 500 eV and 400

eV for bulk and slab model, respectively. Perdew–Burke–Ernzerhof functional (PBE) with semi–empirical corrections of DFT-D3 was adopted to describe exchangecorrelation functional effect³ based on general gradient approximation (GGA). CoWO₄(111) slab with the thickness of the vacuum region is >15 Å was built. Hubbard U model was implemented with an effective U = 4.5 eV for both Co 3d and W 5d orbitals.⁴ The Brillouin zone was sampled by $3 \times 2 \times 1$ special k-points using the Monkhorst Pack scheme for structural configuration optimizations.⁵ The force convergence thresholds are 0.02 eV/Å and the total energy is less than 1E–5 eV, respectively.



Fig. S1. SEM images of the CoWO₄/NF-6.



Fig. S2. SEM images of the CoWO₄/NF–18.



Fig. S3. XPS survey spectra of (a) CoWO₄/NF–6, (b) CoWO₄/NF–12, and (c) CoWO₄/NF–18.



Fig. S4. XPS spectra of CoWO₄/NF–6 in the (a) Co 2p, (b) W 4f, and (c) O 1s region.



Fig. S5. XPS spectra of $CoWO_4/NF-18$ in the (a) Co 2p, (b) W 4f, and (c) O 1s region.



Fig. S6. EPR spectrum of CoWO₄/NF–6 and CoWO₄/NF–18.



Fig. S7. (a) UV–Vis spectra and (b) corresponding calibration curves were used to calculate NH₄⁺.



Fig. S8. (a) Chronoamperometry curves and (b) corres-ponding UV–Vis spectra of CoWO₄/NF–12 from -0.4 V to -0.8 V.



Fig. S9. CV curves of (a) CoWO₄/NF–6, (b) CoWO₄/NF–12, and (c) CoWO₄/NF–18 at different scan rates (20–100 mV s⁻¹)



Fig. S10. (a) C_{d1} and (b) ECSA of CoWO₄/NF–6, CoWO₄/NF–12, and CoWO₄/NF–18.



Fig. S11. Nyquist plots for CoWO₄/NF–6, CoWO₄/NF–12, and CoWO₄/NF–18.



Fig. S12. H_2 yield and FE of after NO_2 ⁻RR electrolysis at various potentials.



Fig. S13. NH₃ yield and FE of CoWO₄/NF were evaluated during alternating cycling tests.



Fig. S14. (a) UV–Vis spectra and (b) amounts of electrogenerated NH₃ under different operating conditions.



Fig. S15. ¹H NMR spectrum of the electrolyte after ${}^{15}NO_2{}^-$ electroreduction. The generated NH₃ was verified by isotopic labelling experiment using 0.1 M Na₂SO₄ and 0.1 M Na¹⁵NO₂ as electrolyte. After 5 h of chronoamperometry test at -0.7 V vs RHE, the pH of the post-electrolysis electrolyte was adjusted to 2 with concentrated HCl. Then, the electrolyte (500 µL) was mixed with D₂O (50 µL) for further ¹H NMR detection. ¹H NMR spectra were collected on Bruker AVANCE NEO 400MHz spectrometer at the ambient temperature.



Fig. S16. (a) LSV curves of CoWO₄/GC tested in 0.5 M Na₂SO₄ solution containing 0.1 M NaNO₂ or not. (b) NH₃ yield and FE of CoWO₄/NF and CoWO₄/GC at -0.7 V.



Fig. S17. (a) Chronoamperometry curves and (b) corresponding UV–Vis absorption spectra of $CoWO_4/NF-12$ for electrochemical catalytic production of NH₃ during cycling tests in 0.5 M Na_2SO_4 with 0.1 M NO_2^- at -0.7 V.



Fig. S18. LSV curves before and after the stability test.



Fig. S19. EIS of CoWO₄/NF-12 before and after the stability test.



Fig. S20. SEM images of CoWO₄/NF-12 after long-term electrolysis.



Fig. S21. (a) XPS survey spectrum. High–resolution XPS spectra of (b) Co 2p, (c) W 4f, and (d) O 1s of CoWO₄/NF–12 after long–term electrolysis.



Fig. S22. Atomic structure of $CoWO_4$ (111) slab model with various terminated surfaces.



Fig. S23. Different adsorption sites for *NO₂ over CoWO₄ (111) surface.



Fig. S24. PDOS of $CoWO_4$ (111) with NO_2^- adsorption.



Fig. S25. The optimized configurations of reaction intermediates of $NO_2^{-}RR$ on $CoWO_4$ (111).



Fig. S26. Free energy diagram and corresponding atomic structure of HER processing on

different sites of CoWO₄ (111).

Catalyst	Electrolyte	Potential (V vs RHE)	FE (%)	NH3 yield rate	Refs.
CoWO4/NF	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	- 0.7 V	95.2	18.856 mg h ⁻¹ cm ⁻²	This work
MoS ₂	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	-0.8V	93.52	8.99 mg h ⁻¹ cm ⁻²	6
Mo ₁ –ZrO ₂	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	-0.7V	94.83	$5.897 \text{ mg h}^{-1} \text{ cm}^{-2}$	7
Nb-NiO	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	-0.6V	92.4	$3.4085 \text{ mg h}^{-1} \text{ cm}^{-2}$	8
L—Pd	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	-0.8V	95.2	$8.6955 \text{ mg h}^{-1} \text{ cm}^{-2}$	9
NiMoO4	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	-0.8V	94.49 ± 0.42	$\begin{array}{c} 18.09 \pm 0.22 \\ mg \ h^{-1} \ cm^{-2} \end{array}$	10
Cu ₁ /Mo ₂ C	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	-0.6V	91.5	$8.024 \text{ mg h}^{-1} \text{ cm}^{-2}$	11
MoO ₂	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	-0.8V	94.5 ± 0.2	$\begin{array}{c} 8.68 \pm 0.19 \\ mg \ h^{-1} \ cm^{-2} \end{array}$	12
u–Cu	0.5 M Na ₂ SO ₄ (0.1 M NaNO ₂)	-0.7V	94.7	$8.4065 \text{ mg h}^{-1} \text{ cm}^{-2}$	13
Cu ₃ P NA/CF	0.1 M PBS (0.1 M NaNO ₂)	-0.5V	91.2± 2.5	1626.6 μg h ⁻¹ cm ⁻²	14
CoFe–NC	0.1M PBS (0.1 M NaNO ₂)	-0.7V	94.5	$3.44 \text{ mg h}^{-1} \text{ cm}^{-2}$	15
Ag	0.1 M NaOH (0.1 M NaNO ₂)	-0.7V	90	$5.7 \text{ mg h}^{-1} \text{ cm}^{-2}$	16
WO ₂ /W	0.1 M NaOH (0.1 M NaNO ₂)	-0.9V	94.32 ± 1.15	$\begin{array}{c} 14964.25\pm826.06\\ \mu gh^{-1}cm^{-2} \end{array}$	17

Table S1. Comparison of catalytic performance of $CoWO_4/NF$ with other reported NO_2 -RR electrocatalysts.

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