EXPERIMENTAL SECTION

Materials

Commercially available WO₃ Powder was purchased from Sigma Aldrich (Product Number: 95410). NaBH₄ was purchased from Tokyo Chemical Industry Co., Ltd (TCI). Ethanol used in all experiments was purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

Synthesis of WO_{3-x}

In brief, 1.0 g of bulk WO₃ powder was initially dissolved into 200 mL of ethanol/water mixtures with ethanol volume fractions of 50%. Then the dispersion was centrifuged at 3000rpm for 30 min to remove aggregates, and the supernatant was dried to obtained WO₃ nanosheets. To synthesize the defective WO₃, 50 mg WO₃ obtained by ultrasound and 50 mg NaBH₄ were mixed and fully ground. Then the mixture was calcining at 300°C with a heating rate 5°C/min in N₂ atmosphere for 1h. After cooling to room temperature, the obtained dark-blue powder was collected and washed for several times with ethanol and deionized water. Finally, the product was dried at 60°C for 3h.

Preparation of Au/WO_{3-x} hybrids

The synthesized WO_{3-x} (10 mg) was dispersed in distilled water (50 mL). Then, in dark environment, an amount of HAuCl₄ (20 mM) was added dropwise with constant stirring at room temperature for 6h. Finally, the sample is collected and dried at 60°C.

Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterizations were performed with a JEM-2100. XRD patterns were recorded using a Y-2000 X-ray Diffractometer with Cu Kα radiation. X-ray photoemission spectroscopy (XPS) was performed using ESCLAB 280. The electron paramagnetic resonance spectroscopy (EPR) was carried out using a BRUKER EMX plus-9.5/12/P/L

electron spin spectrometer at room temperature. The absorbance data were measured with an UV-vis-NIR spectrophotometer (UV-vis DRS, Cary 500).

Preparations of the working electrodes

First, 5mg catalyst was dispersed in 5mL deionized water containing 50 μ L Nafion, and homogeneous suspension after sonication is formed. Then the carbon paper electrode was prepared by drop-coating the suspension on a piece of carbon paper (1×1 cm²) with a total mass loading of 0.5mg/cm², which is used as working electrode for electrochemical test. (Fig. S8).

Electrocatalytic measurements

The NRR experiments were carried out in a two-compartment electrochemical cell separated by Nafion 211 membrane under ambient condition. The electrochemical experiments were carried out with an electrochemical workstation (CHI 660E) using a three-electrode configuration. We used Pt foil and Ag/AgCl electrode as working electrode, counter electrode and reference electrode, respectively. All potentials were converted to reversible hydrogen electrode (RHE) scale via by E (vs RHE) =E (vs Ag/AgCl) +0.197V+0.0591×pH. The N₂ electrochemical reduction was conducted in N₂-saturated 0.1 M KOH solution at 25 °C under atmospheric pressure. Pure N₂ (99.999% purity) was continuously fed to the cathodic compartment during the experiments. Then nitrogen flow and ammonia blown out were absorbed by 0.1M HCl, which can avoid ammonia loss by N₂ blowing during the experiments.

Determination of NH₃

The concentration of produced ammonia was spectrophotometrically determined by the indophenol blue method. In detail, 2 mL electrolyte was taken from the electrochemical reaction vessel and 2 mL of 1 M NaOH solution containing 5wt% salicylic acid and 5wt% sodium citrate was added into this solution, respectively. And Then, 1 mL of 0.05 M NaClO and 0.2 mL of 1wt% C₅FeN₆Na₂O·2H₂O were added into the above solution. After standing at room temperature for 2 hours in dark environment, the UV-Vis absorption spectrum was measured. The concentrationabsorbance curves were calibrated using standard ammonia chloride solution with a serious of concentrations.

Determination of N₂H₄

The N₂H₄ in the electrolyte was estimated using the Watt and Chrisp method. The mixture of para- (dimethylamino) benzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. In detail, 5 mL electrolyte was taken from the electrochemical reaction vessel and added into 5 mL above prepared color reagent and stirring 15 min at room temperature. The UV-Vis absorption spectrum was measured, and the concentration-absorbance curves were calibrated using standard N₂H₄ ·H₂O solution with a serious of concentrations.

Calculation of the Faradaic efficiency and the yield rate

The ammonia yield rate (v) and faradic efficiency (FE) were calculated using the following equation:

$$v_{NH3} = \frac{C_{NH3} \times V}{t \times m}$$

$$FE = \frac{3F \times C_{NH3} \times V}{17Q}$$

where F was the Faraday constant (96485 C/mol e⁻¹). C_{NH3} was the NH₃ concentration, V was the electrolyte volume, t and m are the reduction reaction time and the catalyst mass, respectively.

Computational details

The first-principles calculations based on density functional theory were performed by using the Dmol3 with Perdew-Burke-Ernzerhof exchange-correlation function. A density functional semi-core pseudopotential method was used for core electrons of W and Au atoms, and all-electron method was used for core electrons of the O and N atoms. A double-numeric quality basis set with polarization functions (DNP) basis set version 4.4 and an orbital cutoff of 4.9Å were used. At the same time, 2*2*1 k-points meshes were used for the Brillouin zone sampling, and the distance between two adjacent monolayers was larger than 15Å to avoid the layer–layer interaction. Moreover, the tolerances of energy, gradient and displacement convergence were 1.0×10^{-5} hartree (Ha), 2.0×10^{-3} Ha/Å and 5.0×10^{-3} Å, respectively. The lattice constants of the optimized pristine unit cells of W₁₀O₂₉(100) are a=12.18 Å, b=3.81 Å, c=23.83 Å (Fig. S15).



Fig. S1. Schematic illustration of the preparation of Au/WO_{3-x}.



Fig. S2. (a) TEM images of Au/WO_{3-x} hybrid. (b) HRTEM image of Au/WO_{3-x}.



Fig. S3. HRTEM images of Au/WO₃ hybrid.



Fig. S4. XRD pattern of pristine WO₃.



Fig. S5. XPS survey spectrum of WO_{3-x} and Au/WO_{3-x} .



Fig. S6. High-resolution W 4f XPS of WO₃.



Fig. S7. UV–Vis-NIR absorbance spectra of WO₃ and WO_{3-x}.

The change in colour and light absorbance of sample can further identify the presence of defects. As depicted in Fig. S7, the colour of WO_{3-x} is altered from yellowish of WO₃ to deep blue due to the presence of oxygen vacancies.¹ Compared with pristine WO₃, WO_{3-x} sample enabled remarkable near-infrared light harvesting, which can be considered to the emergence of defect states below the conduction band minimum (CBM),^{2, 3} providing the evidence that the as-prepared WO_{3-x} contains a large number of oxygen vacancies.



Fig. S8. H-type cell reactor for NRR.



Fig. S9. (a) UV-Vis absorption curves of indophenol assays after in darkness for 2 hours at room temperature. (b) A calibration curve used to estimate the concentrations of NH⁴⁺ ions.



Fig. S10. (a) UV-Vis absorption curves of indophenol assays after in darkness for 2 hours at room temperature. (b) A calibration curve used to estimate the concentrations of NH_4^+ ions.



Fig. S11. (a) UV-Vis absorption spectra of various N_2H_4 concentration after incubated for 10 min at room temperature. (b) calibration curve used for estimation of N_2H_4 concentration.



Fig. S12. UV-Vis absorption spectra of the electrolytes stained with indicator after NRR electrolysis at a series of potentials.



Fig. S13. UV-Vis absorption spectra of the electrolytes stained with $p-C_9H_{11}NO$ indicator after NRR electrolysis at a series of potentials.



Fig. S14. The ¹H NMR spectra for ¹⁵NH₄⁺ standard sample (blue curve) and ¹⁵NH₄⁺ obtained from the NRR using ¹⁵N₂ as the feeding gas (yellow curve).



Fig. S15. 28h durability test for Au/WO_{3-x} catalyst at -0.2V versus RHE.



Fig. S16. Optimized structure of $W_{10}O_{29}$, the lattice constants are a=12.18 Å, b=3.81 Å, c=23.83 Å.



Fig. S17. Optimized structure of $W_{10}O_{29}$ (a), N_2 - $W_{10}O_{29}$ (b), $Au/W_{10}O_{29}$ (c) and N_2 - $Au/W_{10}O_{29}$ (d).

Catalyst	$Yield(\mu g \cdot h^{-1} \cdot mg^{-1})$	FE(%)	Potential (vs. RHE)	Literature source
Au/WO _{3-x}	23.15	14.72	-0.2V	This work
Au nanorods	$1.648 \mu g \cdot h^{-1} \cdot cm^{-2}$	4.02	-0.2V	Advanced materials
				2017, 29 (3), 1604799
Au-CeOx/RGO	8.3	10.1	-0.2V	Advanced materials 2017,
				29 (33), 1700001
Au/TiO ₂	21.4	8.11	-0.2V	Advanced materials 2017,
				29 (17), 1606550
porous Au film on Ni	$9.42 \mu g \cdot h^{-1} \cdot cm^{-2}$	13.36	-0.2V	Small 2019, 15, 1804769
foam (pAu/NF)				
PdRu tripods	37.23	1.85	-0.2V	J. Mater. Chem. A, 2019, 7,
				801-805
Fe ₂ O ₃ nanorods	15.9	0.94	-0.8V	ChemCatChem 2018, 10
				(20), 4530-4535
S-doped carbon	19.07	7.47	-0.7V	Small Methods 2018,
nanosphere				1800251
TiO ₂ -rGO	15.13	3.3	-0.9V	Journal of Materials
				Chemistry A 2018, 6 (36),
				17303-17306
Bi ₄ V ₂ O ₁₁ /CeO ₂ hybrid	23.21	10.16	-0.2V	Angewandte Chemie
				International Edition 2018,
				57 (21), 6073-6076
Polymeric carbon	8.09	11.59	-0.2V	Angewandte Chemie 2018,
nitride (PCN)				130 (32), 10403-10407
Pd/C catalyst	4.5	8.2	0.1V	Nature communications
				2018, 9 (1), 1795
MoS ₂ Nanoflower	29.28	8.34	-0.4V	Advanced Energy Materials
				2018, 8 (30), 1801357
Mo ₂ C/C	11.3	7.8	-0.3V	Advanced materials 2018,
				30 (46), 1803694
MoO ₃ nanosheets	29.43	1.9	-0.5V	Journal of Materials
				Chemistry A 2018, 6 (27),
				12974-12977
γ -Fe ₂ O ₃	0.212	1.9		ACS Sustainable Chemistry
				& Engineering 2017, 5 (11),
				10986-10995

Table S1. Comparison of the electrocatalytic N_2 reduction performance for Au/WO_{3-x} with other catalysts under ambient conditions.

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