Phosphorus-doped potassium peroxyniobate electrocatalyst with enriched oxygen vacancy boosts electrocatalytic nitrogen reduction to ammonia

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Supplementary experimental details

Working electrode preparation process

Toray TGP-H-060 carbon paper was used for pretreatment: the carbon paper was uniformly cut into 1 cm \times 1.3 cm size and cleaned by ultrasonic with 1 M HCl, ethanol and water for 20 min in turn, then dried in an oven at 80 °C. After being removed, the carbon paper was soaked in deionized water for storage. 2.5 mg catalyst powder were accurately weighed and the catalyst was dispersed with a ratio of 60 µL deionized water, 180 µL anhydrous ethanol, 10 µL Nafion solution. After ultrasonic treatment for 1 h, the dispersed and uniform catalyst suspension was finally obtained. After treatment, the carbon paper is clamped on the electrode clip of the replaceable piece, so that the exposed carbon paper is 1 cm \times 1 cm in size. 10 µL of the catalyst suspension were removed with a pipette gun of an appropriate range, evenly spread on carbon paper (Catalyst load is 0.1 mg/cm²) and baked under an infrared lamp for 1 h to dry^[1].

H-type electrolytic cell installation process

Firstly, the Nafion membrane was pretreated: it was cut into 2 cm \times 2 cm size, so that it could completely block the port between the two electrode chambers of H-type electrolytic cell. The cut Nafion membrane was treated with 5% H₂O₂, deionized water, 0.5 M H₂SO₄ and deionized water for 1 h respectively at 80 °C. Then, it was soaked in deionized water after treatment^[2]. When installing the electrolytic cell, the pretreated Nafion membrane is placed in the middle of the opening of the two electrode chambers, then clamped, so that the opening can be completely blocked by the membrane, to ensure that no liquid leakage from the opening after installing the electrolyte.

The detection of NH₃

The NH₃ was detected by indophenol blue method, and the chromogenic agent was prepared for later use. 1 M NaOH was prepared, 5 wt% salicylic acid and 5 wt% sodium citrate were added as solution A. 0.05 M NaClO was prepared as solution B. Prepare 1 wt% C₅FeN₆Na₂O·2H₂O solution as solution C. 2 mL of electrolyte in the cathode chamber after electrolysis was taken, and 2 mL of solution A, 1 mL of solution B and 0.2 mL of solution C were added. Two hours later, the mixture solution was detected by UV-vis spectrophotometer. The absorbance at 655 nm could be used to calculate the concentration of NH₄⁺ by the measured standard curve shown in **Fig. S9**.^[3]

The ammonia yield and Faradaic efficiency were calculated from the results of electrochemical test combined with the ammonia yield determined by the indophenol blue indicator method. Here is the NRR performance calculation formula^[4]:

$$r = \frac{c \cdot V}{t \cdot m}$$
(1-1)
$$FE = \frac{3F \cdot c \cdot V}{17Q}$$
(1-2)

where c is the concentration of NH_4^+ in the electrolyte (µg/mL); V is the volume of electrolytic liquid (mL); t is the electrolyte time (h); m is the overall mass loading of electrocatalyst (mg); F is the Faradaic constant (C·mol⁻¹); Q is the total charge (C) in the electrolysis process.

The detection of N₂H₄

The Watt-Chrisp method was used to detect the concentration of N_2H_4 . 5.99 g of p-dimethylaminobenzaldehyde, 30 mL of 12 M HCl and 300 mL of anhydrous ethanol were mixed uniformly as the chromogenic agent. 2 mL of the cathode chamber electrolyte after electrolysis was taken, and added 2 mL of the above color developing agent. 20 min later, the mixture solution was detected by UV-vis spectrophotometer. The absorbance at 455 nm could be used to calculate the concentration of N_2H_4 by the measured standard curve shown in **Fig. S17**^[5]:

The detection of NO₂⁻

The chromogenic agent was prepared as follows: 1mL of phosphoric acid, 0.4 g of sulphanilic acid and 0.02 g of ethylenediamine hydrochloride were added into 5 mL of deionized water, completely dissolved, and then transferred it to a 100 mL volumetric flask with constant volume. 1 mL of the cathode chamber electrolyte after electrolysis was taken, and added 4 mL of the above chromogenic agent. After 30 min in the dark, the mixed solution was detected by UV-vis spectrophotometer. The absorbance at 540 nm could be used to calculate the concentration of NO₂⁻ by the measured standard curve shown in **Fig. S11**. ^[6]

The detection of NO₃⁻

The concentration of NO₃⁻ was directly detected by UV spectrophotometry. 5 mL of electrolyte in the cathode chamber after electrolysis was taken, and directly detected by UV-vis spectrometer. The absorbance at 210 nm was subtracted from that at 275 nm, and the difference obtained can be used to calculate the concentration of NO_3 ⁻ through standard curve shown in Fig. S12.

¹⁵N₂ Isotope Labeling Experiments

 $^{15}N_2$ was used as feed gas, the electrolyte was electrolyzed for 2 h and then removed. The PH was adjusted to be 2~3 with sulfuric acid. Last it was concentrated to 5 mL. 0.9 mL of the concentrated electrolyte was taken and 0.1 mL of heavy water was added for ¹H NMR test. The concentration of 15NH⁴⁺ can be calculated by the standard curve shown in Fig. S13.



Fig. S1. Schematic diagram of gas-solid reaction device.



Fig. S2. SEM image of KNO catalyst.



Fig. S3. TEM image of P-KNO catalyst.



Fig.S4. (a) TEM and (b) HRTEM images of KNO catalyst.



Fig. S5. Contact angle images of (a) KNO and (b) P-KNO.



Fig. S6. (a) Full XPS survey spectrum of P-KNO and KNO; (b) High-resolution XPS spectrum of O 1s for KNO and P-KNO.



Fig. S7. ESR of the as-prepared P-KNO and KNO.



Fig. S8. The three-electrode gas tight two-compartment system.



Fig. S9. (a) UV-Vis absorption spectra of various NH_4^+ -N concentrations and (b) corresponding calibration curves for the colorimetric NH_4^+ -N assay using the indophenol blue method in 0.1 M Na₂SO₄.



Fig. S10. (a) Chronoamperometric results and (b) UV-vis spectra of 0.1 M Na_2SO_4 electrolyte (after cycling stability test at -0.45 V_{RHE} for 2 h) after incubated with NH_3 color agent.



Fig. S11. (a) UV-vis absorption spectra of various NO_2^- concentrations after incubated for 30 min at room temperature; (b) Calibration curve used for estimation of NO_2^- ; (c) Absorbance curves of NO_2^- under three situations.



Fig. S12. (a) UV-vis absorption spectra of various NO_3^- concentrations; (b) Calibration curve used for estimation of NO_3^- ; (c) Absorbance curves of NO_3^- under three situations.



Fig. S13. (a) ¹H NMR spectra of various ¹⁵NH₄⁺-N concentrations and (b) corresponding calibration curves for ¹⁵NH₄⁺-N assay.



Fig. S14. LSV of the KNO and P-KNO in $N_2\mbox{-saturated}\ 0.1$ M $Na_2SO_4.$



Fig. S15. (a) UV-vis spectra and (b) NH_3 yield rate and FE of P-KNO and KNO after electrolysis at -0.45V_{RHE}.



Fig. S16. UV-vis spectra of electrolytes colored with indicator for $N_2H_4{\cdot}H_2O$ after

electrolysis over P-KNO at -0.45 $V_{\text{RHE}}.$



Fig. S17. (a) UV-Vis absorption spectra of various N_2H_4 concentrations and (b) Calibration curve for the colorimetric N_2H_4 assay using dimethylaminobenzaldehyde reagent in 0.1 M Na₂SO₄.

Table S3. Comparison of different transition metal-based NRR electrocatalysts

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.
P-KNO	0.1 M Na ₂ SO ₄	23.01 μ g h ⁻¹ mg _{cat.} ⁻¹	39.77	Our work
OV-TiO ₂ @C/Cu	0.1 M Na ₂ SO ₄	16.1 $\mu g h^{-1} m g_{cat.}^{-1}$	6.04	[7]
Porous Fe ₃ O ₄	0.1 M Na ₂ SO ₄	$12.09 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	34.38	[8]
nanosheets				
Mn–N–C SAC	0.1 M NaOH	21.43 μ g h ⁻¹ mg _{cat.} ⁻¹	32.02	[9]
Fe–SAs/NSDG	0.1 M KOH	28.89 μ g h ⁻¹ mg _{cat.} ⁻¹	23.7	[10]
BiOCl@Ti ₃ C ₂ T _x	0.1 M HCl	$4.06 \ \mu g \ h^{-1} \ cm^{-2}$	11.98	[3]
Zn nanosheets	0.5 M LiClO ₄	25.3 μ g h ⁻¹ mg _{cat.} ⁻¹	11.7	[2]
Sn _{SC} /C	0.1 M Na ₂ SO ₄	$17.28 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	22.76	[11]
BN QDs@CoP/CC	0.1 M Na ₂ SO ₄	$5.39 \times 10^{-10} \text{ mol}$	10.34	[12]
		$s^{-1}cm^{-2}$		
BTO@KTO	0.25 M LiClO ₄	$32.02 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	12.71	[13]
hollow Cr ₂ O ₃	0.1 M Na ₂ SO ₄	$2.72 \ \mu g \cdot h^{-1} \cdot cm^{-2}$	5.31	[14]
Mo ₂ C-MoO ₂	0.1 M Na ₂ SO ₄	13.94 μ g h ⁻¹ mg _{cat.} ⁻¹	12.72	[15]
NiO-NFs	0.1 M Na ₂ SO ₄	$16.16 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	9.17	[16]
СоТРР	0.1 M HCl	$15.18 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	11.43	[17]

under ambient condition.

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