

Electronic Supplementary Information

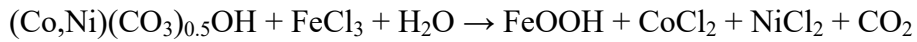
Experimental section

Materials: sodium nitrite (NaNO_2), ammonium chloride (NH_4Cl), sodium hydroxide (NaOH), sodium salicylate ($\text{C}_7\text{H}_5\text{NaO}_3$), trisodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), p-dimethylaminobenzaldehyde ($\text{C}_9\text{H}_{11}\text{NO}$), sodium nitroferricyanide dihydrate ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$), 0.8 wt% sulfamic acid solution ($\text{H}_3\text{NO}_3\text{S}$), sodium dihydrogen phosphate dihydrate (NaH_2PO_4), disodium hydrogen phosphate dodecahydrate (Na_2HPO_4) and sodium hypochlorite solution (NaClO) were purchased from Aladdin Ltd. (Shanghai, China). Iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), and urea were purchased from Chengdu Kelong Chemical Regent Co. Ltd. Sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and ethylalcohol ($\text{C}_2\text{H}_5\text{OH}$) were bought from Beijing Chemical Corporation. (China). chemical Ltd. in Chengdu. Carbon cloth (CC) was purchased from Qingyuan Metal Materials Co., Ltd (Xingtai, China). All reagents used in this work were analytical grade without further purification.

Preparation of $(\text{Co},\text{Ni})(\text{CO}_3)_{0.5}$ nanowire array on CC: All the chemicals in this work were of analytical grade and directly used after purchase without further purification. In a typical synthesis, 2.33 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 1.16 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 1.44 g of urea were dissolved in 80 mL deionized water under violent stirring for 20 min at room temperature. A piece of CC (2×4 cm) was immersed with concentrated HNO_3 solution for 2 h, and then cleaned with acetone, ethanol and deionized water for 10 min each. The solution was transferred into a 100 mL Teflon-lined autoclave and the cleaned CC substrate was immersed into the solution. The autoclave was sealed and maintained at 120°C for 6 h. After the autoclave cooling to room temperature naturally, as-obtained precursor was taken out, washed with ethanol and distilled water for several times, and dried at 70°C for 6 h.

Preparation of FeOOH nanotube arrays on CC: To convert into the FeOOH nanotube arrays, 3.24 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 300 mL deionized water with stirring for 30 min to form a yellow solution. Subsequently, the above CC grown with

(Co,Ni)(CO₃)_{0.5} precursor nanowire arrays were immersed in the solution and maintained at 50 °C for 6 h. An ion-exchange process in a hydrothermal system is an efficient strategy to obtain hollow nanoarchitecture materials based on the nanoscale Kirkendall effect due to the fast ion-exchange rate in the hydrothermal process. Based on the Kirkendall effect, the ionic transport rate from the crystals to the solution should be faster than that from the solution to the crystals. In our case, Ni²⁺ and Co²⁺ diffuse toward outward while Fe³⁺ diffuse toward inward through the formed layer. As the reaction proceeds, FeOOH nanotube arrays are formed ultimately. The reactions could be described by the following equation:



Characterizations: XRD data were acquired by a LabX XRD-6100 X-ray diffractometer with a Cu K α radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM measurements were carried out on a GeminiSEM 300 scanning electron microscope (ZEISS, Germany) at an accelerating voltage of 5 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer was measured on UV-Vis spectrophotometer. TEM image was obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV.

Electrochemical measurements: All electrochemical measurements were performed in a two-compartment cell separated by a treated Nafion 117 membrane using the CHI660E electrochemical workstation (Shanghai, Chenhua) with a standard three-electrode setup. To prevent the pH of the reaction medium from changing significantly during the reaction, phosphate buffer saline (PBS) was used as electrolyte and was prepared by mixing stock solutions of NaH₂PO₄ and Na₂HPO₄. Electrolyte solution was Ar-saturated 0.1 M PBS (pH = 7) with 0.1 M NO₃⁻, using FeOOH/CC (1.0 × 0.5 cm²) as the working electrode, a carbon rod as the counter electrode, and a Ag/AgCl as the reference electrode. All the potentials reported in our work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: E (RHE) = E (vs. Ag/AgCl) + 0.0591 × pH + 0.197 V

and the current density was normalized by the geometric surface area.

Determination of NH₃: Concentration of produced NH₃ was determined by spectrophotometry measurement with indophenol blue method (the obtained electrolyte was diluted 50 times).¹ In detail, 2 mL of the diluted catholyte was obtained from the cathodic chamber and mixed with 2 mL of a 1 M NaOH solution that contained salicylic acid and sodium citrate. Then, 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt% C₅FeN₆Na₂O were dropped in the collected electrolyte solution. After standing at room temperature for 2 h, the ultraviolet-visible absorption spectrum was measured. The concentration-absorbance curve was calibrated using the standard NH₄Cl solution with NH₃ concentrations of 0, 0.2, 0.5, 1.0, 2.0 and 5.0 μg mL⁻¹ in 0.1 M PBS. The absorbance at 655 nm was measured to quantify the NH₃ concentration using standard NH₄Cl solutions ($y = 0.4266x + 0.03451$, $R^2 = 0.999$).

Determination of N₂H₄: In this work, we used the method of Watt and Chrisp² to determine the concentration of produced N₂H₄. The chromogenic reagent was a mixed solution of 5.99 g C₉H₁₁NO, 30 mL HCl and 300 mL C₂H₅OH. In detail, 1 mL electrolyte was added into 1 mL prepared color reagent and stirred for 15 min in the dark. The absorbance at 455 nm was measured to quantify the N₂H₄ concentration with a standard curve of hydrazine ($y = 0.6691x + 0.07883$, $R^2 = 0.999$).

Calculations of FE and NH₃ yield:

$$FE = (8 \times F \times [\text{NH}_3] \times V) / (M_{\text{NH}_3} \times Q) \times 100\%$$

$$\text{NH}_3 \text{ yield} = ([\text{NH}_3] \times V) / (t \times A)$$

Where F is the Faradic constant (96485 C mol⁻¹), [NH₃] is the measured NH₃ concentration, V is the volume of electrolyte (35 mL), M_{NH₃} is the molar mass of NH₃, Q is the total charge passing through the electrode; t is the electrolysis time and A is the geometric area of working electrode (0.5 × 0.5 cm²).

NO₂⁻ isotopic labelling experiment: The generated NH₃ was verified by an isotope-labelled tracer experiment using a 0.1 M ¹⁵NO₂⁻ as a N source. After 1 h of electroreduction at -1.0 V, the electrolyte (2 mL) in the cathodic chamber was neutralized by HCl aqueous solution (1.2 M). After that, the neutralized electrolyte

(500 μL) was mixed with deuterium oxide (D_2O , 50 μL). And the mixture was sealed into a nuclear magnetic resonance (NMR) tube (5 mm in diameter, 600 MHz) for further tests.

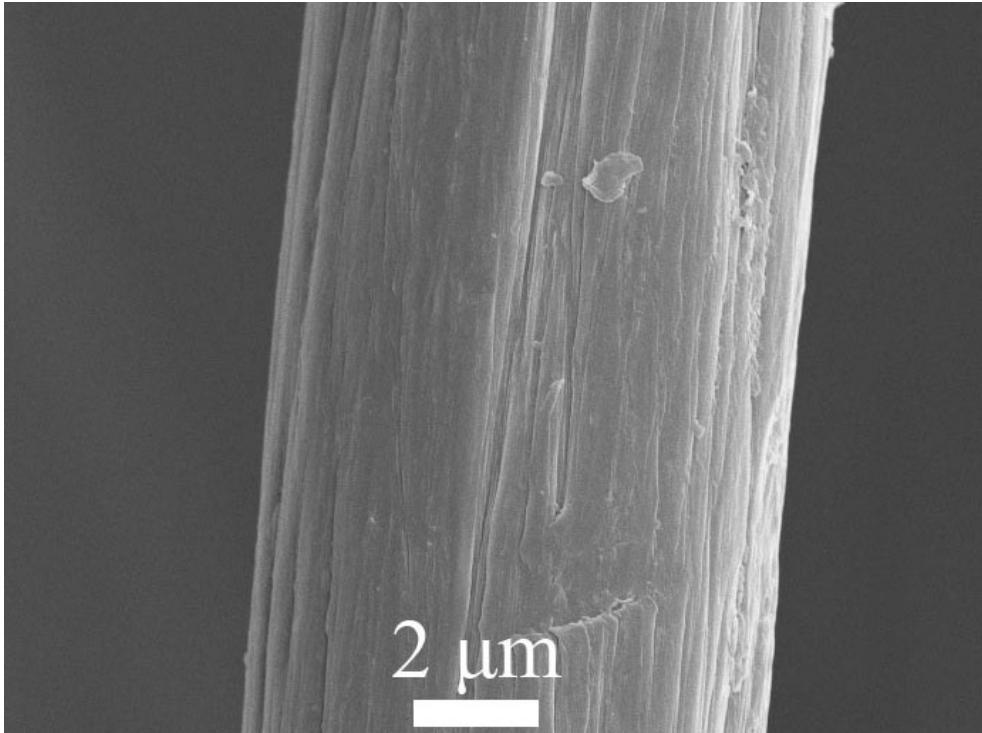


Fig. S1 SEM image of bare CC.

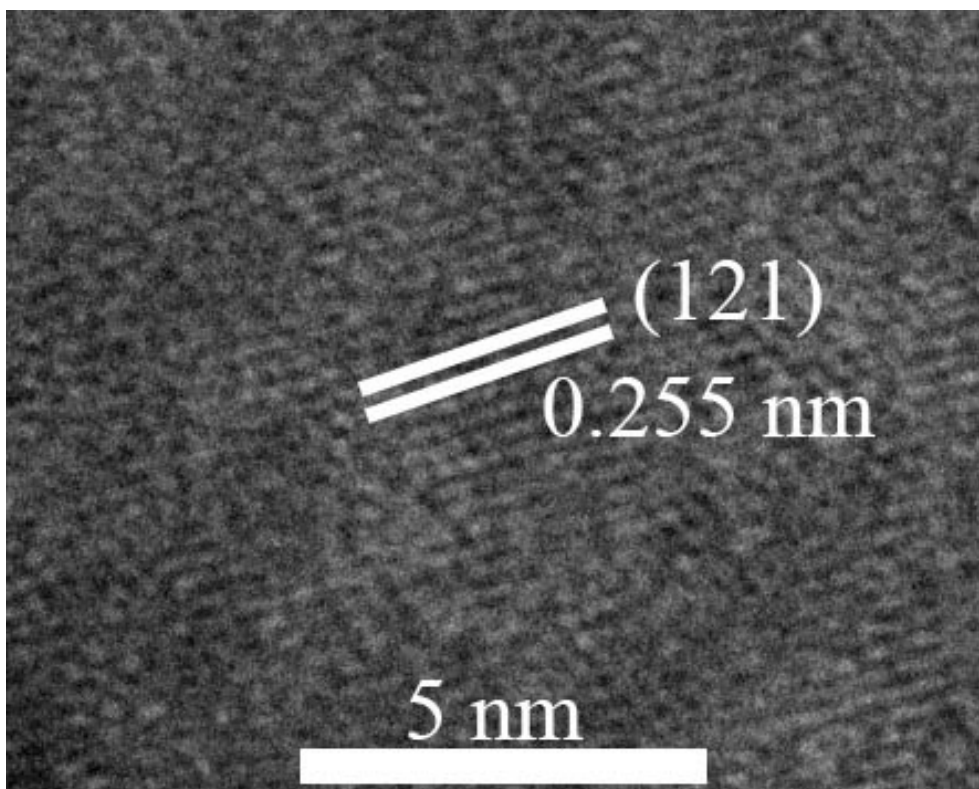


Fig. S2 HRTEM image of FeOOH.

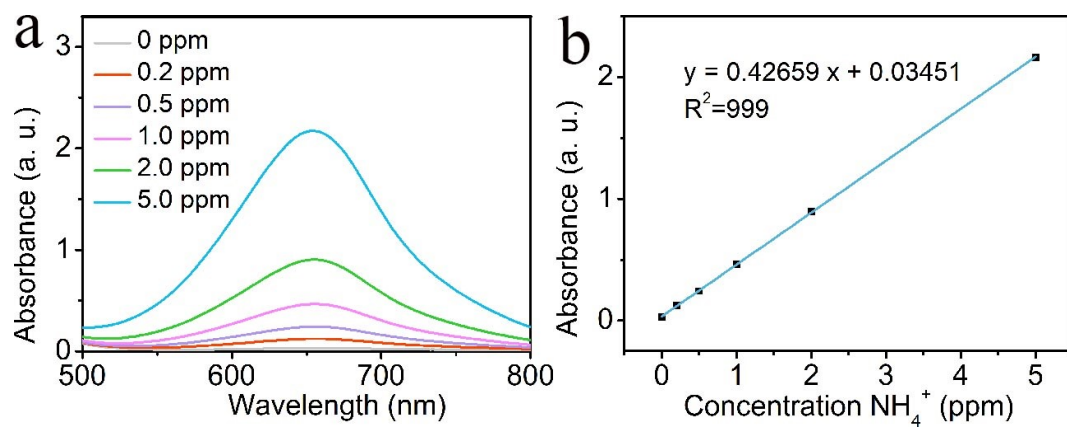


Fig. S3 (a) UV-Vis absorption spectra of indophenol assays kept with different concentrations of NH_4^+ after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_4^+ concentration.

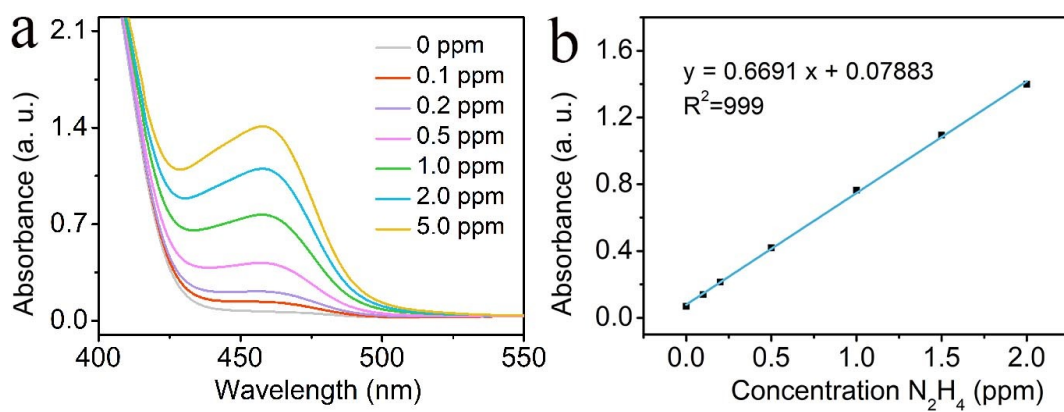


Fig. S4 (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentration.

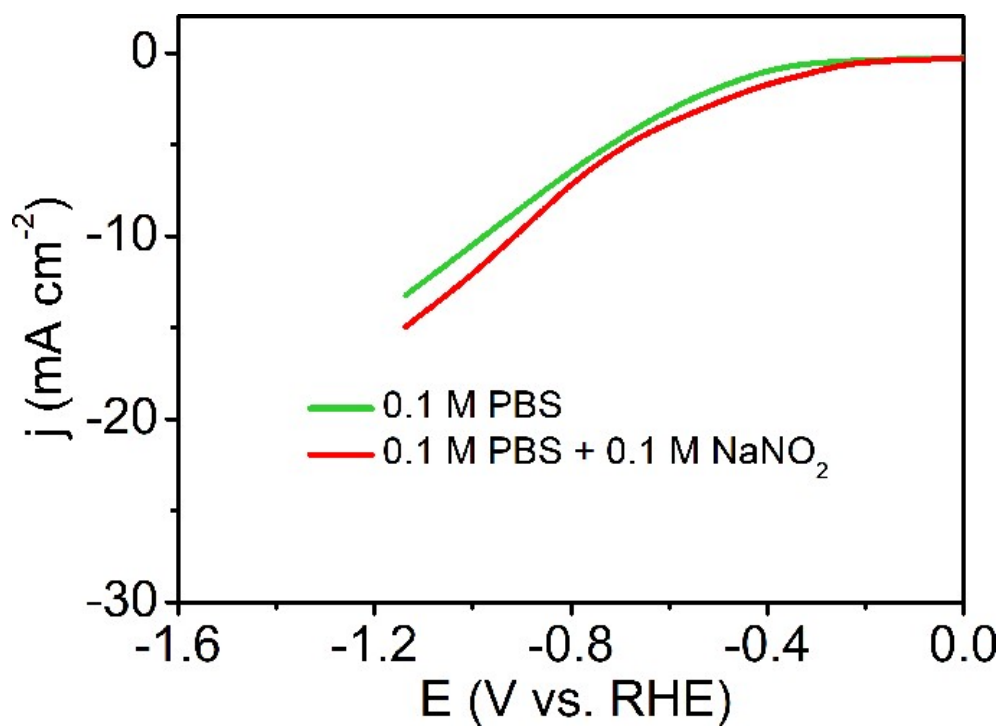


Fig. S5 LSV curves of bare CC in 0.1 M PBS with and without 0.1 M NO₂⁻.

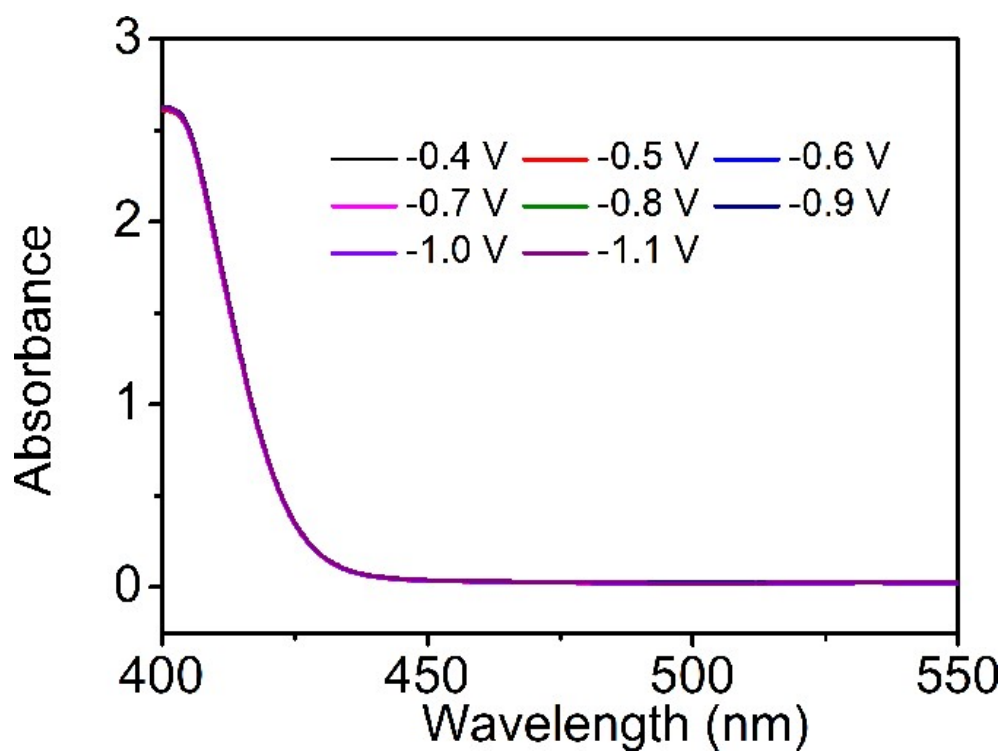


Fig. S6 UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp for the calculation of N_2H_4 concentration.

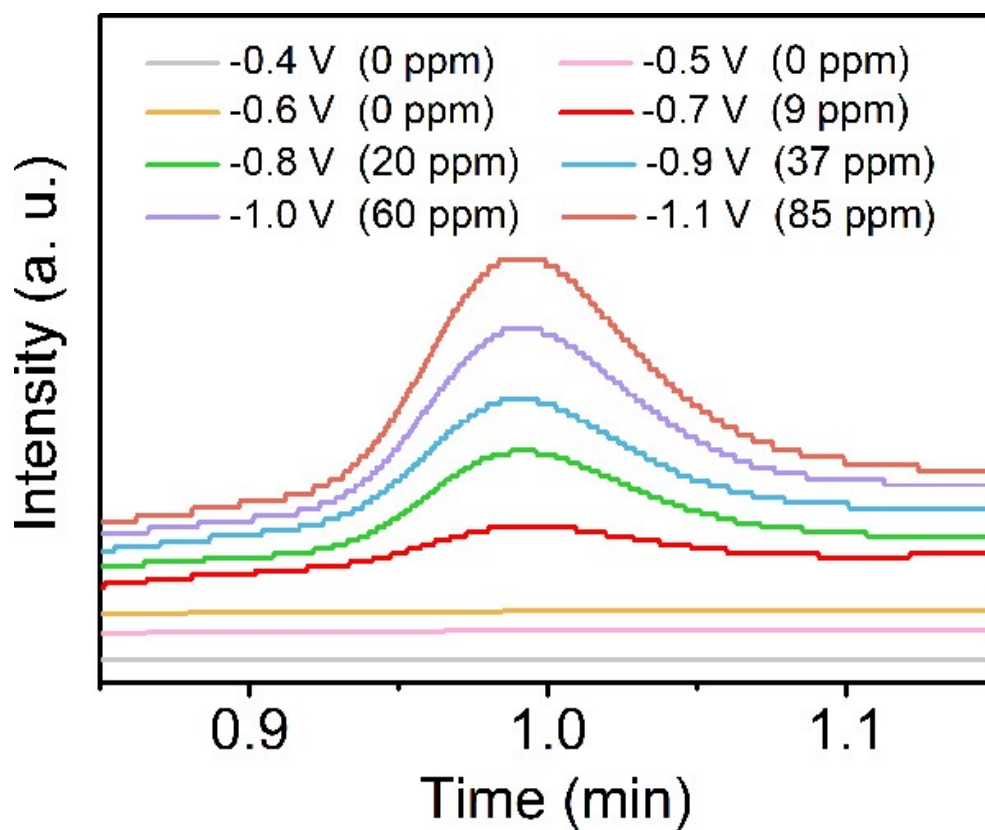


Fig. S7 Chromatograph curves of FeOOH NTA/CC in 0.1 M PBS with 0.1 M NO_2^- .

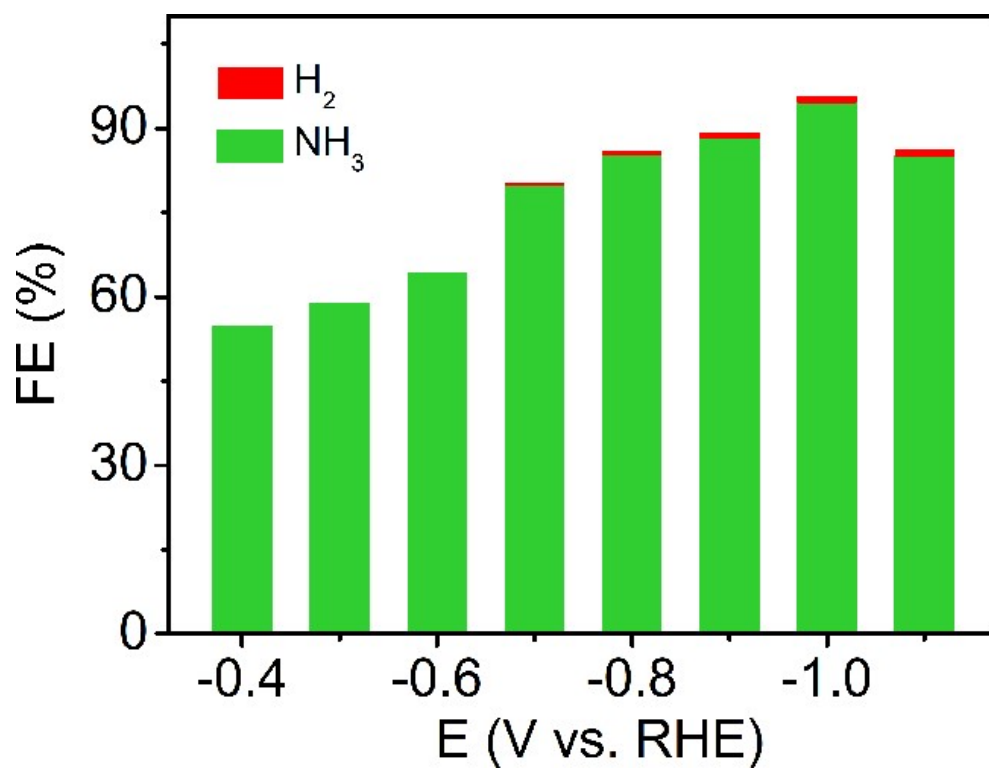


Fig. S8 The FEs of H₂ and NH₃.

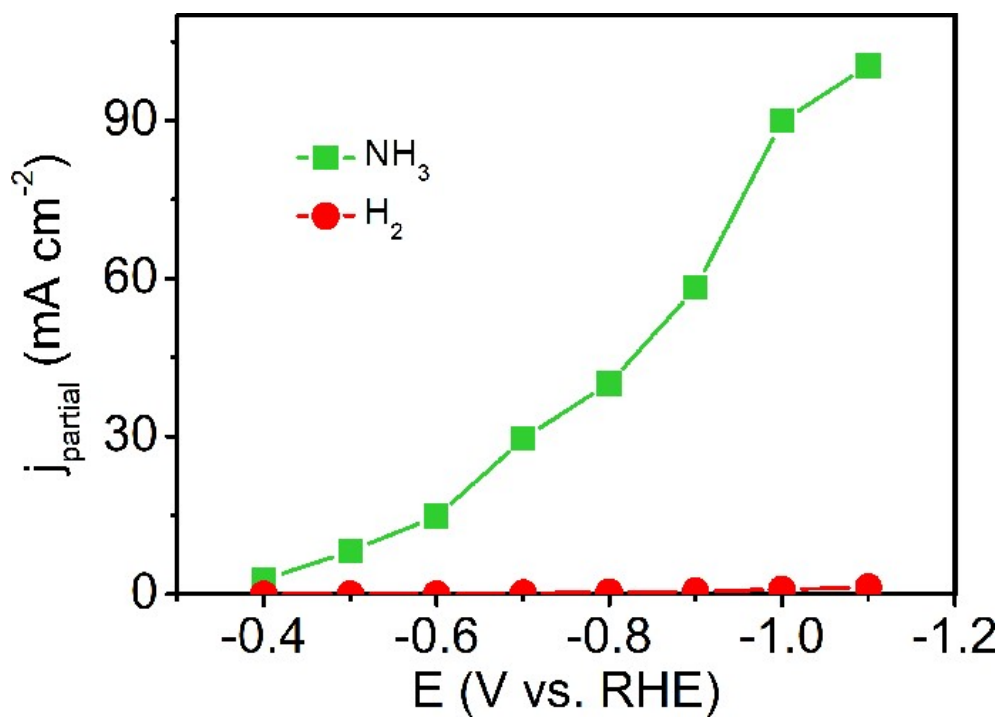


Fig. S9 Comparison of potential-dependant partial current density for different products on FeOOH NTA/CC with the total current density.

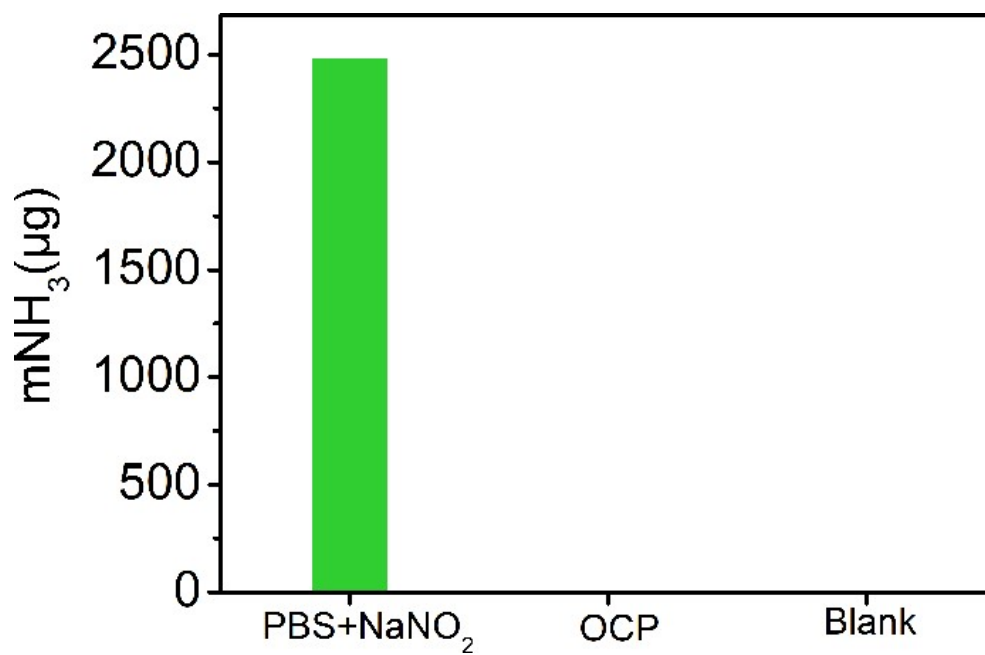


Fig. S10 Comparison of NH₃ concentration under different conditions.

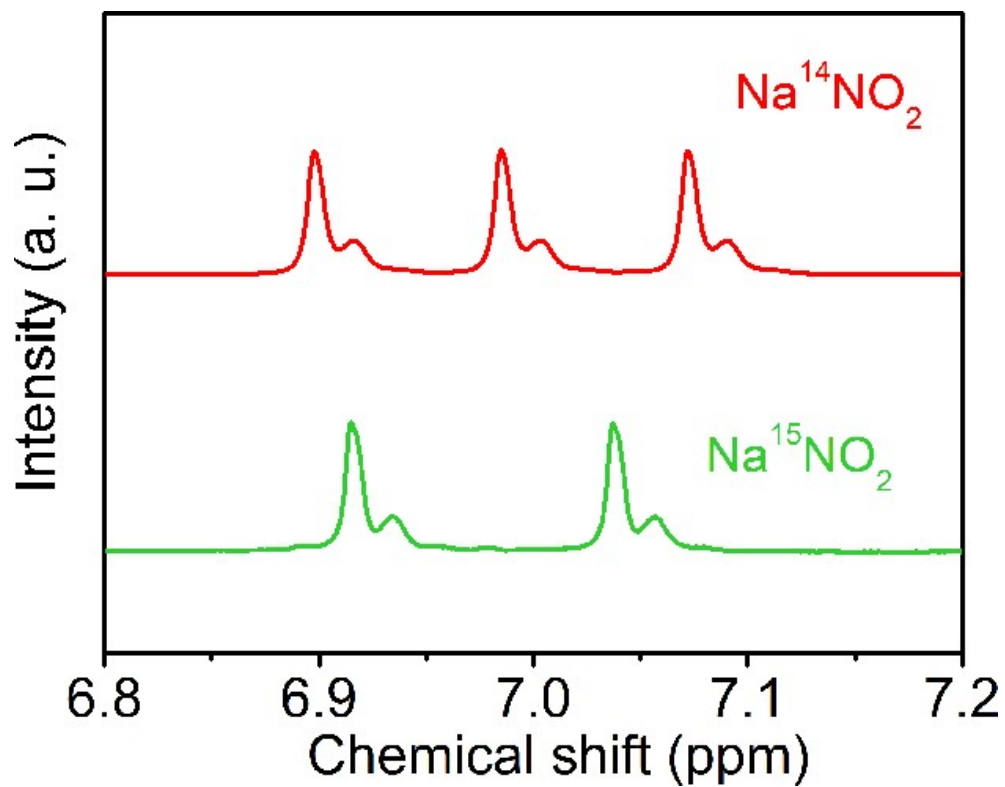


Fig. S11 ^1H NMR spectra for the post-electrolysis electrolyte with $\text{Na}^{15}\text{NO}_2$ and $\text{Na}^{14}\text{NO}_2$ as the nitrogen resources.

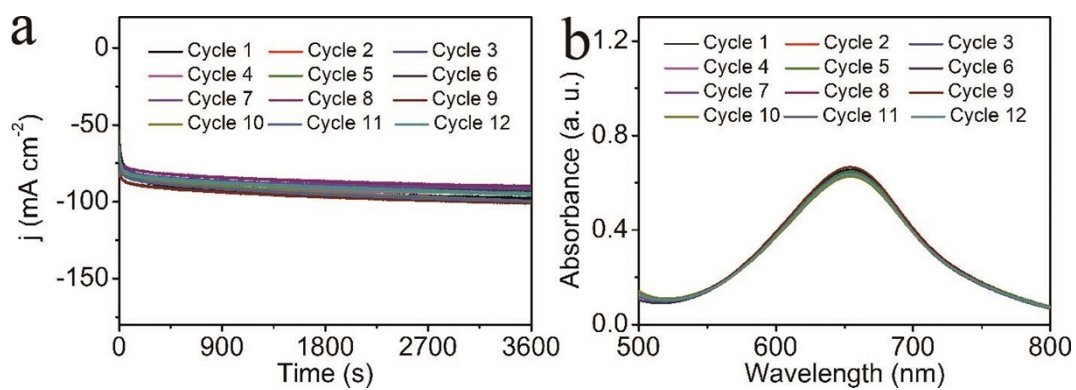


Fig. S12 Chronoamperometry curves of recycling tests at -1.0 V in 0.1 M PBS with 0.1 M NO_2^- for FeOOH NTA/CC. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after recycling tests for NO_2RR at -1.0 V in 0.1 M PBS with 0.1 M NO_2^- .

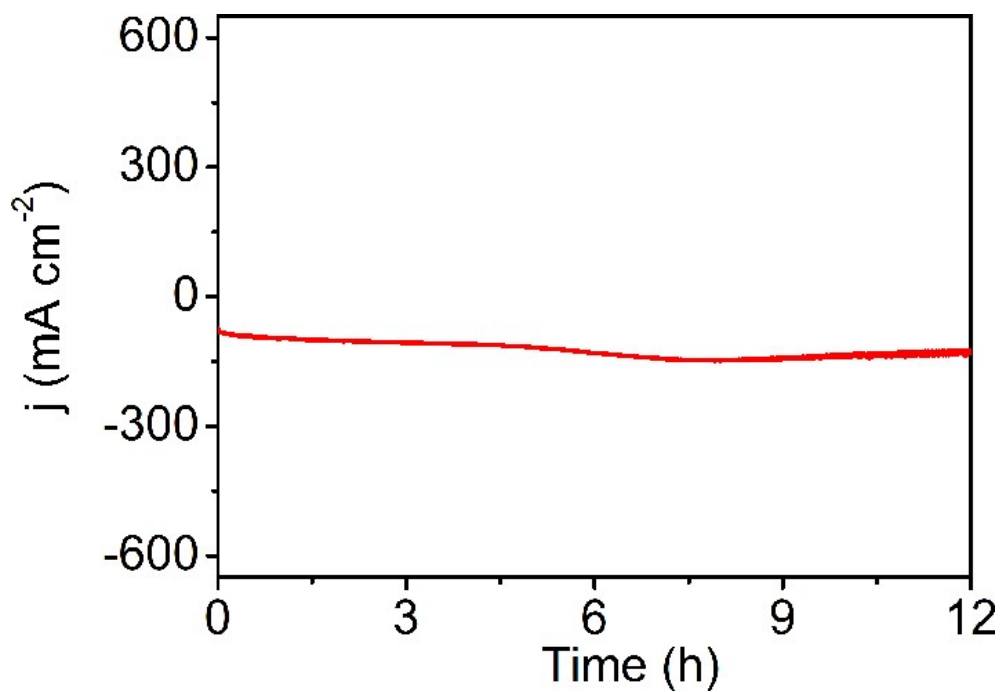


Fig. S13 Long-term stability tests for continuous generation of NH_3 on FeOOH NTA/CC.

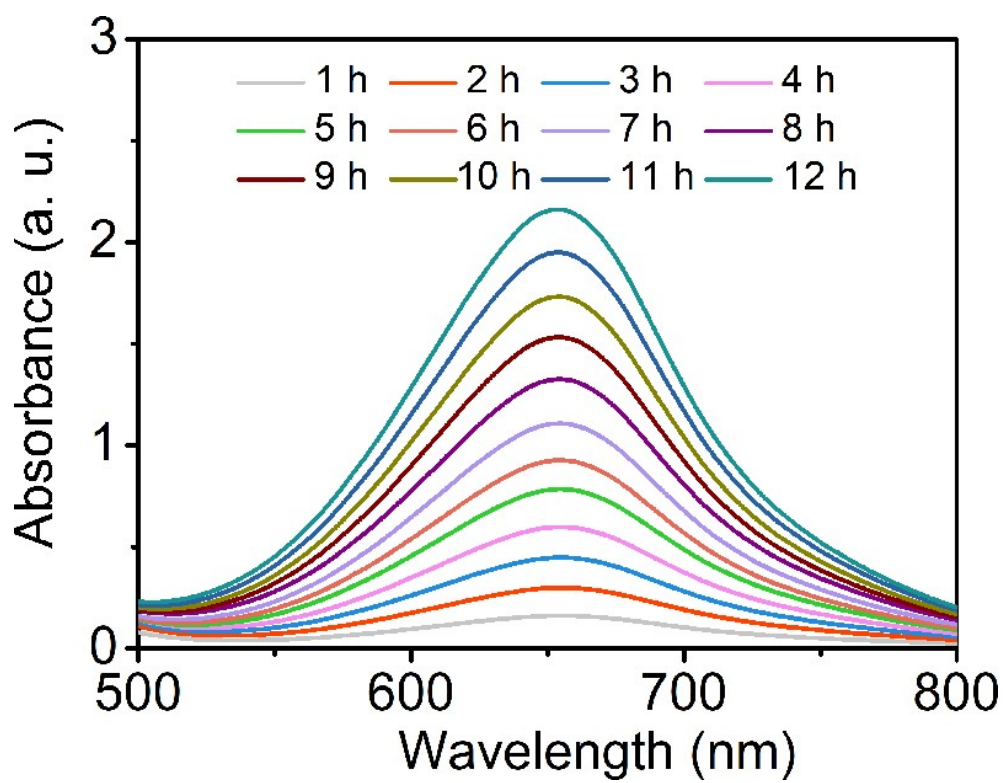


Fig. S14 UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after 12 h electrolysis on FeOOH NTA/CC at -1.0 V.

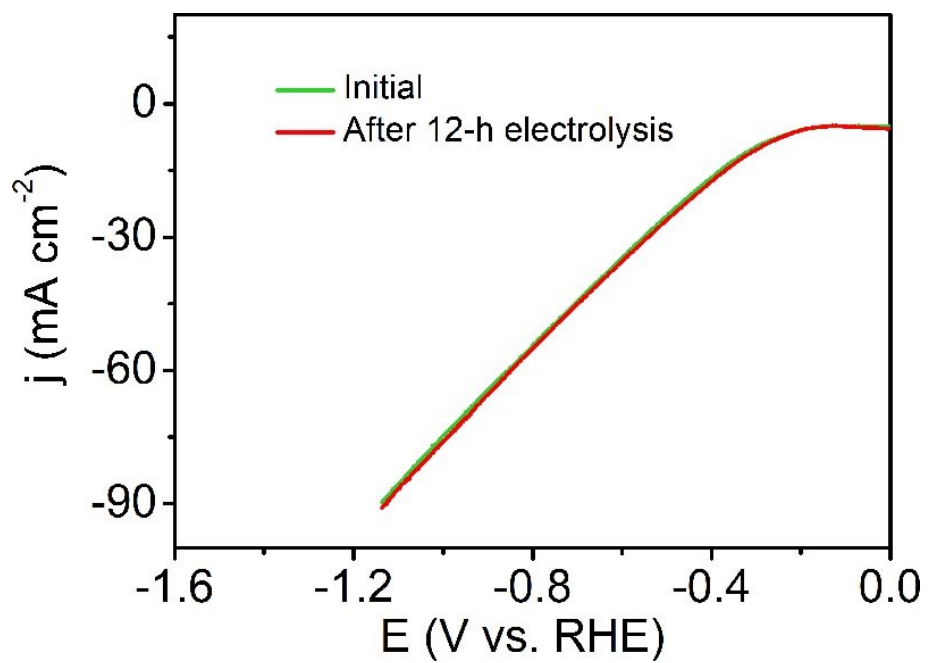


Fig. S15 LSV curves of FeOOH NTA/CC before and after 12-h electrolysis.

Table S1. Comparison of catalytic performance of FeOOH NA/CC with other reported NO₂RR electrocatalysts.

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.
FeOOH NTA/CC	0.1 M PBS (0.1 M NO ₂ ⁻)	11937 μg h ⁻¹ cm ⁻²	94.7	This work
Ni-NSA-V _{Ni}	0.2 M Na ₂ SO ₄ (200 ppm NaNO ₂)	235.98 μmol h ⁻¹ cm ⁻²	88.9	3
MnO ₂ nanoarrays	0.1 M Na ₂ SO ₄ (NaNO ₂)	3.09 × 10 ⁻¹¹ mol s ⁻¹ cm ⁻²	6	4
Cobalt-tripeptide complex	1.0 M MOPS buffer (1.0 M NaNO ₂)	3.01 × 10 ⁻¹⁰ mol s ⁻¹ cm ⁻²	90±3	5
Poly-NiTRP complex	0.1 M NaClO ₄ (NaNO ₂)	1.1 mM	-	6
Cu phthalocyanine complexes	0.1 M KOH (NaNO ₂)	-	78	7
[Co(DIM)Br ₂] ⁺ (Carbon rod working electrode)	0.1 M solution of NaNO ₂	-	88	8
Oxo-MoS _x	0.1 M nitrite in 0.2 M citric acid (pH=5)	-	13.5	9
Hemin-pyrolitic graphite electrode	0.1 M phosphate buffer solutions with NaNO ₂ (acidic media)	-	-	10
Cu _x Ir _{1-x} Nanoalloy	0.1 M phosphate buffer (100 mg L ⁻¹)	-	-	11
Rh/Al ₂ O ₃	25 mM phosphate buffer (50 mM NO ₂ ⁻)	-	-	12
FeN ₅ H ₂	1.0 M MOPS	-	18	13

	(1.0 M NaNO ₂)			
Cu ₈₀ Ni ₂₀	1.0 M NaOH (20 mM NaNO ₂)	-	87.6	14

Table S2. pH value of FeOOH NA/CC before and after electrolysis.

electrolytic time (h)	0	1	12
pH	7.0	7.4	12.3

References

- 1 D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, **12**, 836–841.
- 2 G. W. Watt and J. D. Chrisp, *Anal. Chem.*, 1952, **24**, 2006–2008.
- 3 C. Wang, W. Zhou, Z. Sun, Y. Wang, B. Zhang and Y. Yu, *J. Mater. Chem. A*, 2021, **9**, 239–243.
- 4 R. Wang, Z. Wang, X. Xiang, R. Zhang, X. Shi and X. Sun, *Chem. Commun.*, 2018, **54**, 10340–10342.
- 5 Y. Guo, J. R. Stroka, B. Kandemir, C. E. Dickerson and K. L. Bren, *J. Am. Chem. Soc.*, 2018, **140**, 16888–16892.
- 6 P. Dreyse, M. Isaacs, K. Calfumán, C. Cáceres, A. Aliaga, M. J. Aguirre and D. Villagra, *Electrochim. Acta*, 2011, **56**, 5230–5237.
- 7 N. Chebotareva and T. Nyokong, *J. Appl. Electrochem.*, 1997, **27**, 975–981.
- 8 S. Xu, H. Y. Kwon, D. C. Ashley, C. H. Chen, E. Jakubikova and J. M. Smith, *Inorg. Chem.*, 2019, **58**, 9443–9451.
- 9 D. He, Y. Li, H. Ooka, Y. K. Go, F. Jin, S. H. Kim and R. Nakamura, *J. Am. Chem. Soc.*, 2018, **140**, 2012–2015.
- 10 M. Duca, S. Khamseh, S. C. S. Lai and M. T. M. Koper, *Langmuir*, 2010, **26**, 12418–12424.
- 11 H. Li, C. Yan, H. Guo, K. Y. Shin, S. M. Humphrey, C. J. Werth and G. Henkelman, *ACS Catal.*, 2020, **10**, 7915–7921.
- 12 C. A. Clark, C. P. Reddy, H. Xu, K. N. Heck, G. Luo and T. P. Senftle, *ACS Catal.*, 2020, **10**, 494–509.
- 13 J. R. Stroka, B. Kandemir, E. M. Matson and K. L. Bren, *ACS Catal.*, 2020, **10**, 13968–13972.
- 14 L. Mattarozzi, S. Cattarin, N. Comisso, P. Guerriero, Marco Musiani, L. Vázquez-Gómez and E. Verlato, *Electrochim. Acta*, 2013, **89**, 488–496.