Electronic Supplementary Information

Materials: Cobalt nitrate ($Co(NO_3)_2·6H_2O$, AR, 99.0%)，sodium nitrate ($NaNO_3$, AR, 99.0%), sodium nitrite ($NaNO_2$, AR, 99.0%), sodium sulfate (Na_2SO_4, AR, 99.0%), ammonium chloride (NH_4Cl, AR, 99.5%), sodium hydroxide (NaOH, AR, 97%), sodium salicylate ($C_7H_5NaO_3$, AR, 99.5%), trisodium citrate dihydrate ($C_6H_5Na_3O_7·2H_2O$, AR, 99.0%), p-dimethylaminobenzaldehyde ($C_9H_{11}NO$, AR, 99.0%), sodium nitroferricyanide dihydrate ($C_5FeN_6Na_2O·2H_2O$, AR, 99.0%) and sodium hypochlorite solution (NaClO, available chlorine ≥ 5.0%) were purchased from Aladdin Ltd. (Shanghai, China). Sulfuric acid (H_2SO_4, ~98%), hydrogen peroxide (H_2O_2, 30%), hydrochloric acid (HCl, ~37%), hydrazine monohydrate ($N_2H_4·H_2O$, 98%) and anhydrous ethyl alcohol (C_2H_5OH, 95%) were bought from Beijing Chemical Corporation (Chengdu, China). Carbon cloth (CC) was provided by Hongshan District, Wuhan instruments business. All chemicals were used as received without further purification. The ultrapure water used throughout all experiments was purified through a Millipore system.

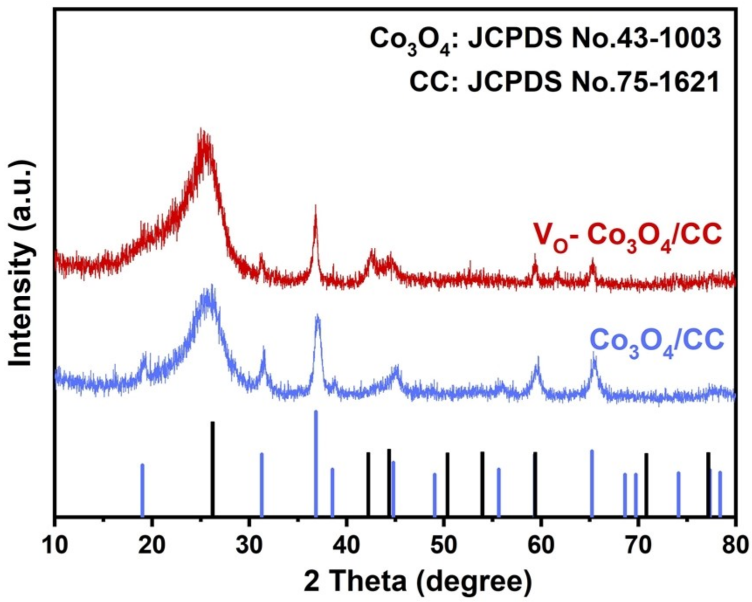

Fig. S1. XRD patterns of V_O-Co_3O_4/CC and Co_3O_4/CC.

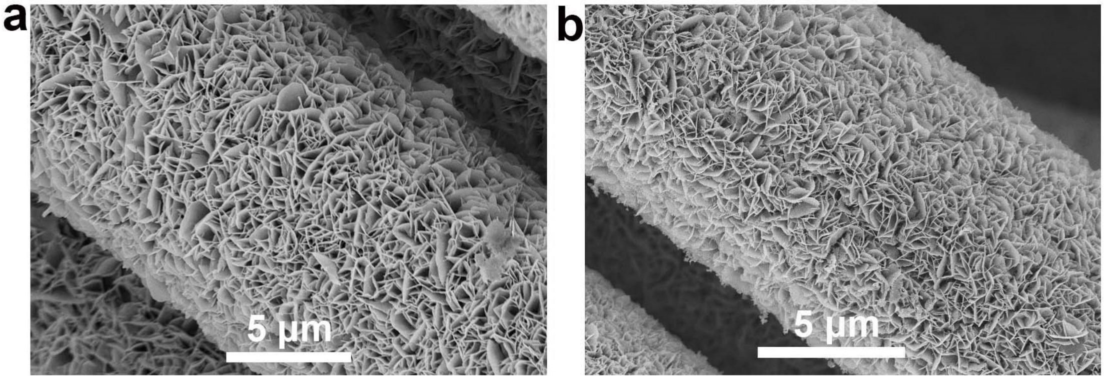

Fig. S2. SEM images of (a) Co_3O_4/CC and (b) V_O-Co_3O_4/CC.

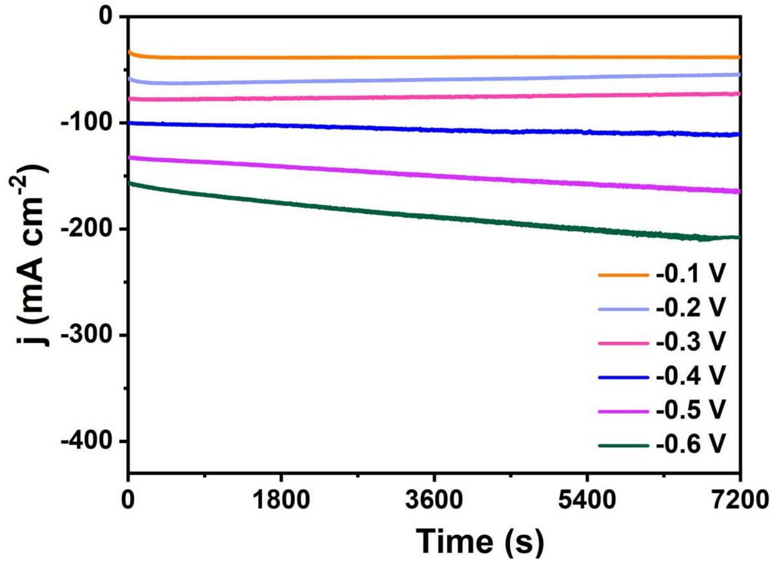

Fig. S3. Chronoamperometry curves of V_O-Co_3O_4/CC at different potentials in 0.1 M NaOH with 0.1 M NO_3^-.

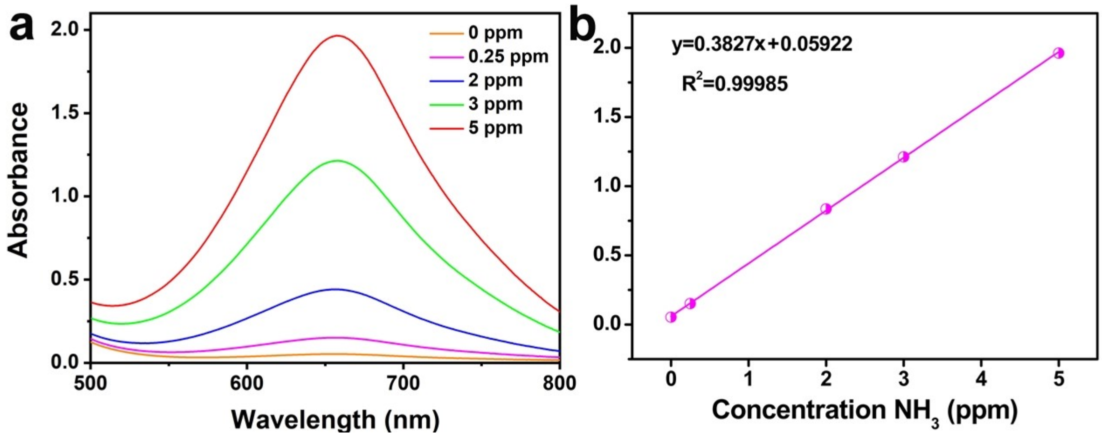

Fig. S4. (a) UV-vis absorption spectra and corresponding (b) calibration curve used for NH_3 quantification.

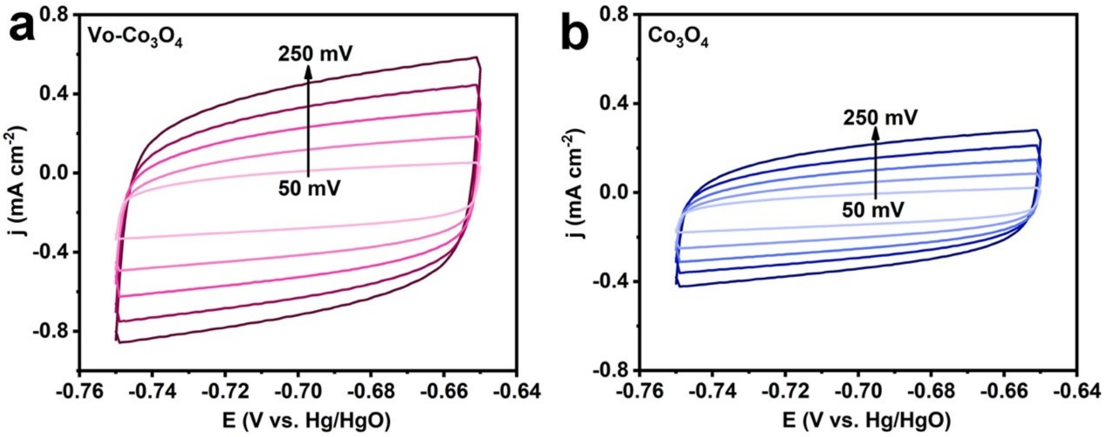

Fig. S5. Cyclic voltammograms of (a) Vo-Co_3O_4/CC and (b) Co_3O_4/CC at different scanning rates for double layer capacitance calculation.

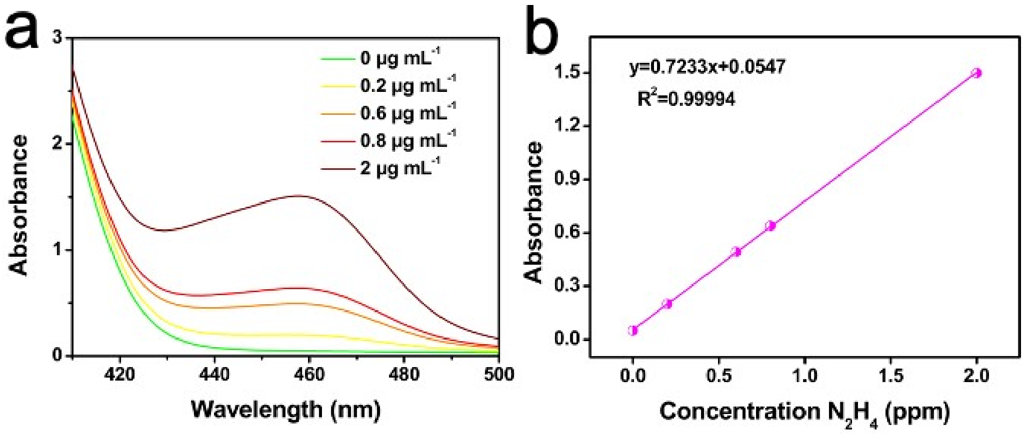

Fig. S6. (a) UV-vis spectra and corresponding (b) calibration curve used for N_2H_4 quantification.

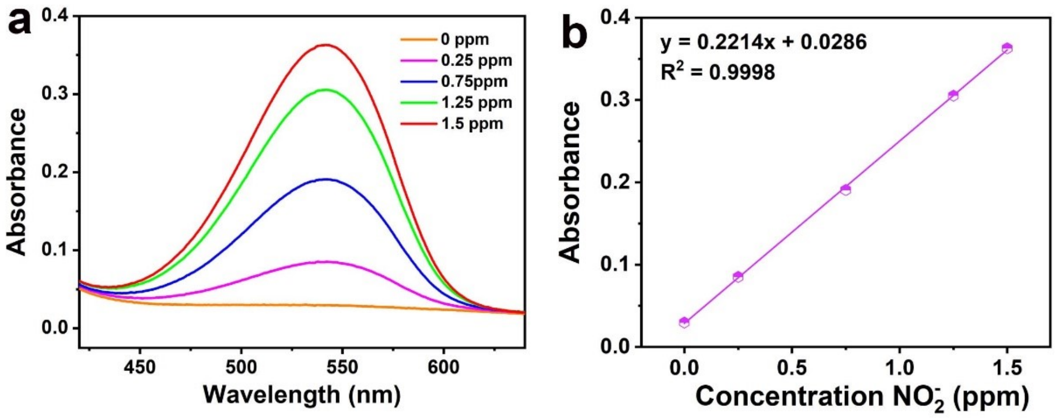

Fig. S7. (a) UV-vis spectra and corresponding (b) calibration curve used for NO_2^- quantification.

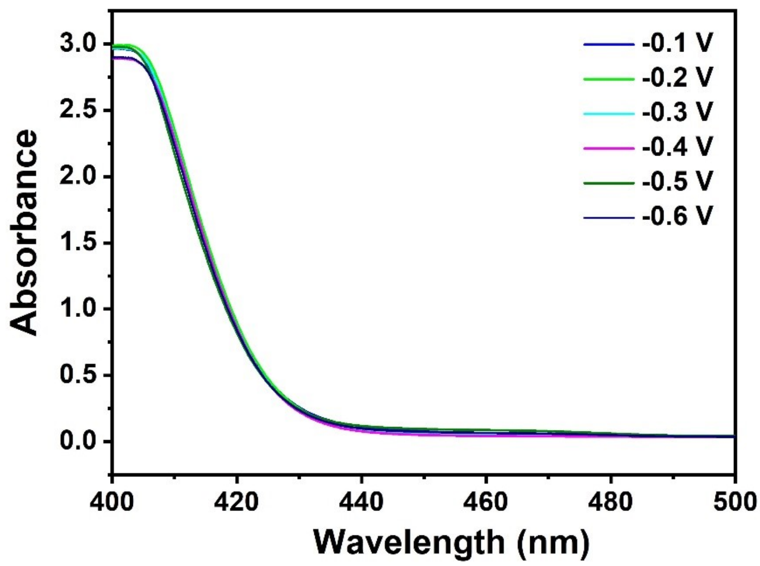

Fig. S8. UV-vis spectra of the electrolytes estimated by the method of Watt and Chrisp after electrolysis at each given potential for N_2H_4 detection.

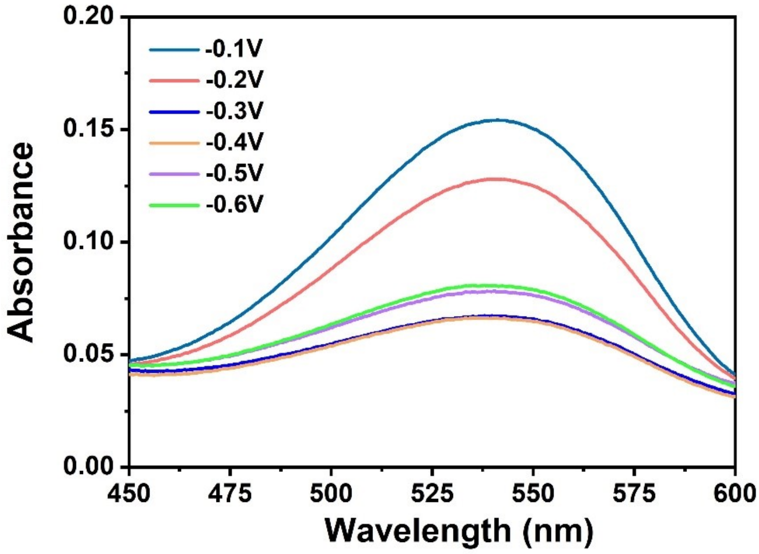

Fig. S9. UV-vis spectra of the electrolytes after electrolysis colored with Griess reagent for NO_2^- detection.

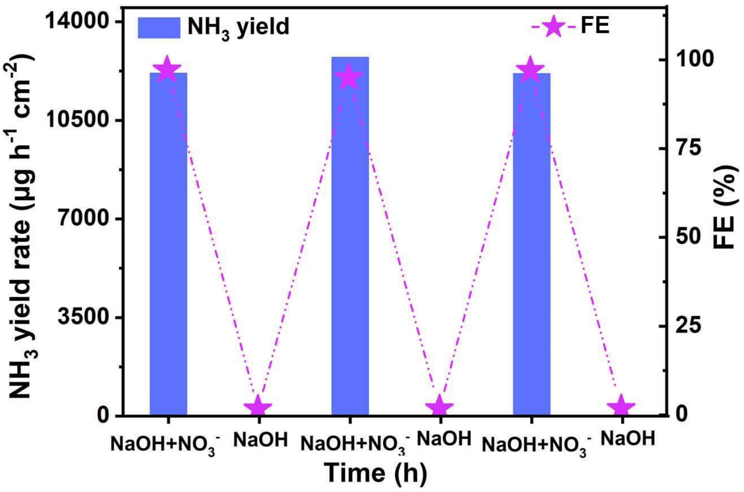

Fig. S10. NH_3 yields and FEs of V_O-Co_3O_4/CC for alternating cycle tests between NO_3^--containing and NO_3^--free 0.1 M NaOH at −0.5 V.

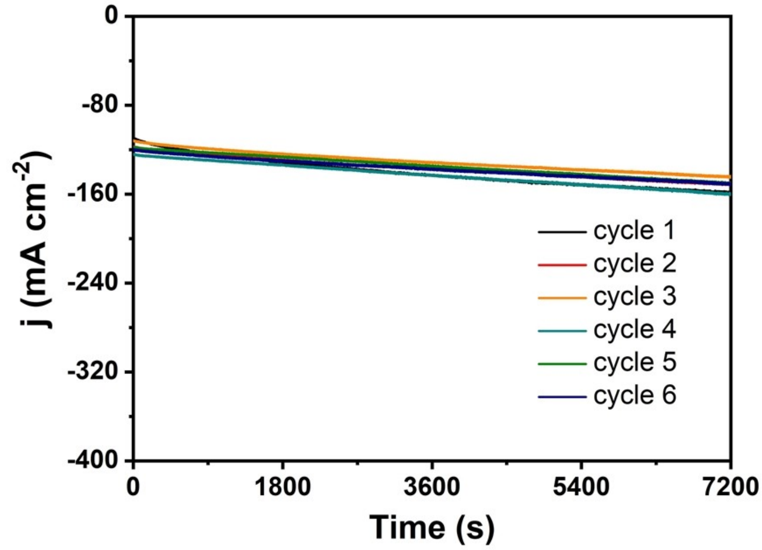

Fig. S11. Chronoamperometry curves for V_O-CO_3O_4/CC during consecutive cycling tests toward NO_3RR at –0.5 V in 0.1 M NaOH with 0.1 M NO_3^-.

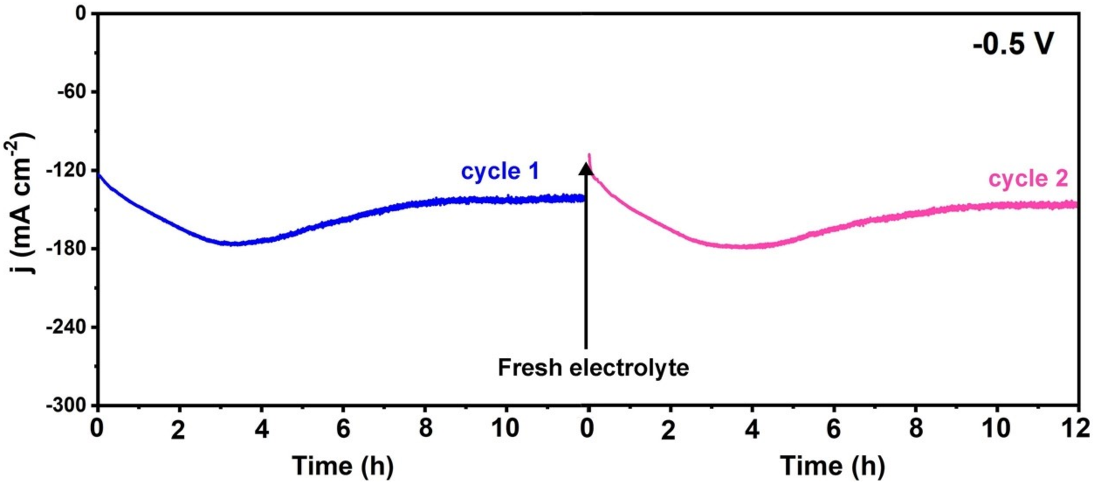

Fig. S12. Long-term stability test of V_O-Co_3O_4/CC at –0.5 V for two cycles.

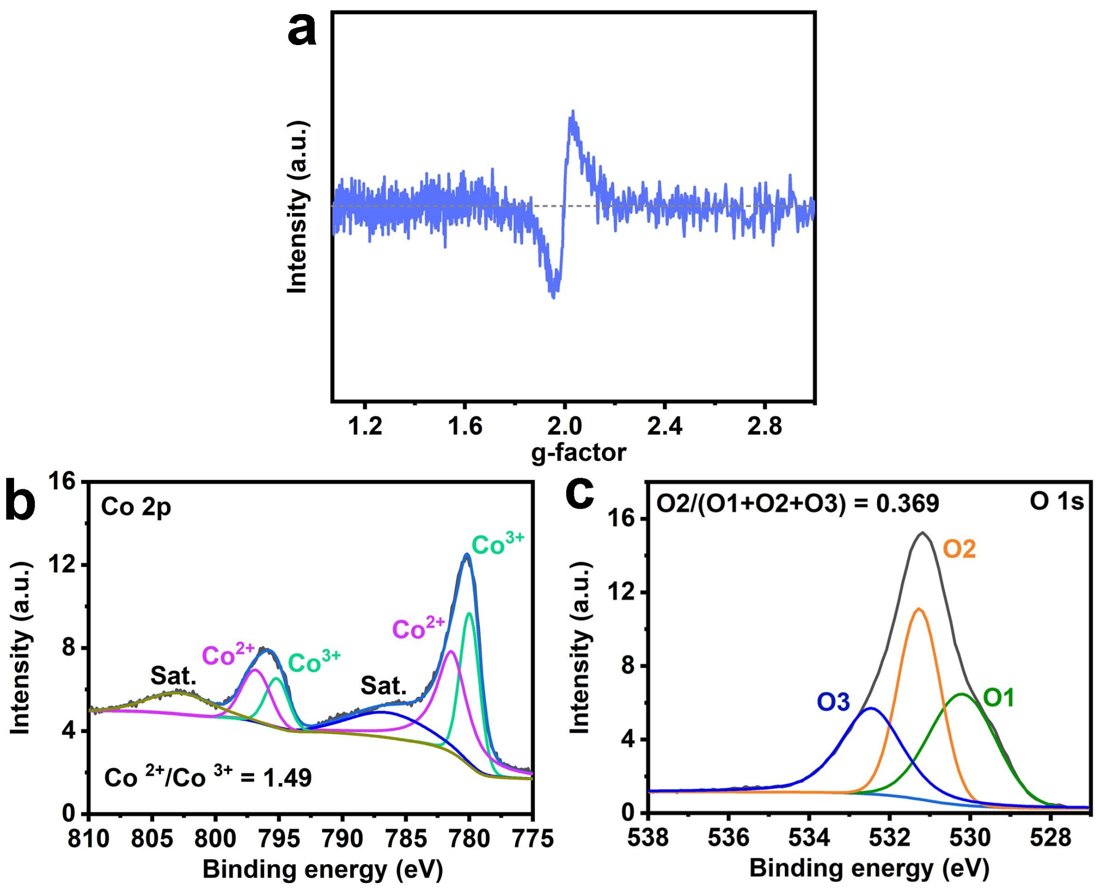

Fig. S13. (a) EPR spectrum and (b, c) XPS spectra of V_O-Co_3O_4/CC after 12-h electrolysis.

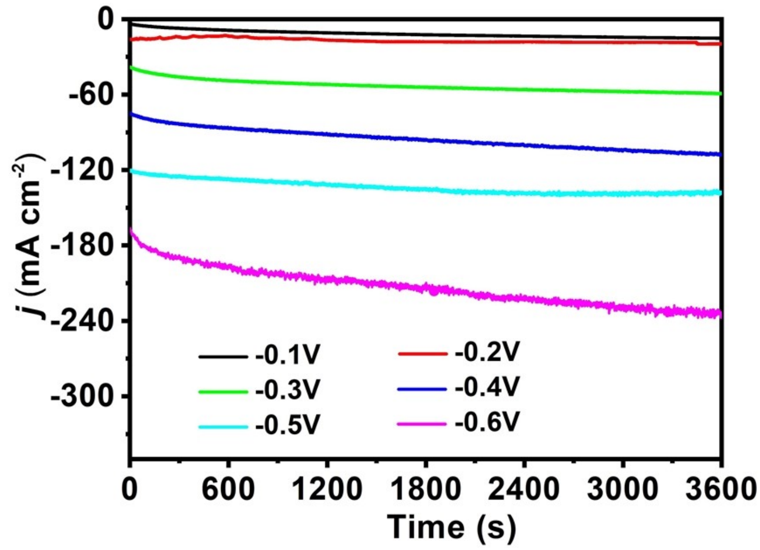

Fig. S14. Chronoamperometry curves of V_O-Co_3O_4/CC at different potentials in alkaline wastewater.

Table S1. Comparison of catalytic performances comparison of V_O-Co_3O_4/CC with other reported NO_3RR electrocatalysts.

Catalyst	Electrolyte	Performance	Ref.
V_O-Co_3O_4/CC	0.1 M NaOH (0.1 M NO_3^-)	NH_3 yield rate: 12,157 μg h^{-1} cm^{-2} FE_{NH3}: 96.9 %	This work
TiO_{2-x}	0.5 M Na_2SO_4 (50 ppm NO_3^-)	NH_3 yield rate: 850 μg h^{-1} cm^{-2} FE_{NH3}: 85.0 %	1
PTCDA/O-Cu	0.1 M PBS (500 ppm NO_3^-)	NH_3 yield rate: 436 ± 85 μg h^{-1} cm^{-2} FE_{NH3}: 85.9 %	2
Co/CoO NSA	3.28 mM Na_2SO_4 (200 ppm NO_3^-)	NH_3 yield rate: 3305 μg h^{-1} cm^{-1} FE_{NH3}: 93.8 %	3
Co_3O_4@NiO HNTs	0.5 M Na_2SO_4 (200 ppm NO_3^-)	NH_3 yield rate: 6.93 mmol h^{-1} g^{-1} FE_{NH3}: 54.97 %	4
NiPc complex	0.1 M KOH, in the presence of NO_3^-	NH_3 yield rate: n/a FE_{NH3}:85 %	5
Cu nanosheets	1 M KOH	NH_3 yield rate: 390.1 μg h^{-1} mg^{-1} FE_{NH3}:99.7 %	6
$Cu_{50}Ni_{50}$	1 M KOH (10 mM KNO_3)	NH_3 yield rate: n/a FE_{NH3}:84 ± 2 %	7
Ti/GC	KOH (~0.1 to 0.6 M NO_3^-)	NH_3 yield rate: n/a FE_{NH3}:82 %	8
NTEs	NaCl (0.65 mM $NaNO_3$)	NH_3 yield rate: n/a FE_{NH3}:5.6 %	9
CoO@NCNT/GP	0.1 M NaOH (0.1 M NO_3^-)	NH_3 yield rate: 9041.6 ± 370.7 μg h^{-1} cm^{-2} FE_{NH3}: 93.8 ± 1.5 %	10
$ZnCo_2O_4$	0.1 M KOH (0.1 M NO_3^-)	NH_3 yield rate: 2100 μg h^{-1} mg^{-1} FE_{NH3}:95.4 %	11
PP-Co	0.1 M NaOH (0.1 M NO_3^-)	NH_3 yield rate: 1.1 mmol μg h^{-1} mg^{-1} FE_{NH3}:90.1 %	12
$Co_{0.5}Cu_{0.5}$	1 M KOH (50 mM KNO_3)	NH_3 yield rate: n/a FE_{NH3}:95 %	13
Co_2AlO_4	0.1 M PBS (0.1 M NO_3^-)	NH_3 yield rate: 7.9 mg h^{-1} cm^{-2} FE_{NH3}:92.6 %	14

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