Electronic Supplementary Information

A Fluidized Electrocatalysis Approach for Ammonia Synthesis Using Oxygen Vacancy-Rich Co_3O_4 Nanoparticles

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Supplementary Tables and Figures

Table S1 The comparable results of our work and other recently reported NRR electrocatalysts.

Catalyst	System /Conditions	NH_3 Yield Rate	FE (%)	Detection method	Ref.
L-Co_3O_4-4.0	**0.1 M Na_2SO_4 (pH =10.5)**	**Fluidized electrocatalysis system 235.0 μg h^{-1} $mg_{cat.}^{-1}$ (-0.30 V *vs.* RHE) Catalyst-loading electrocatalysis system 49.6 μg h^{-1} mg^{-1} (-0.30 V *vs.* RHE)**	**20.7 (-0.20 V *vs.* RHE) 9.9 (-0.20 V *vs.* RHE)**	**Indophenol method**	**This work**
NiO NDs/G	0.1 M Na_2SO_4	18.6 μg h^{-1} mg^{-1} (-0.7 V *vs.* RHE)	7.8	Indophenol method	1
CuO/RGO	0.1 M Na_2SO_4	1.8×10^{-1} mol s^{-1} cm^{-2} (-0.75 V *vs.* RHE)	3.9	Indophenol method	2
CoO QD/RGO	0.1 M Na_2SO_4	21.5 μg h^{-1} mg^{-1} (-0.6 V *vs.* RHE)	8.3	Indophenol method	3
Mo_2C/C	0.5 M Li_2SO_4 (PH =2)	11.3 μg h^{-1} mg^{-1}_{Mo2C} (-0.3 V *vs.* RHE)	7.8	Nessler method	4
ZnO QDs/RGO	0.1 M Na_2SO_4	17.7 μg h^{-1} mg^{-1} (-0.65 V *vs.* RHE)	6.4	Indophenol method	5

SnO_2 QDs/RGO	0.1 M Na_2SO_4	25.6 μg h^{-1} mg^{-1} (-0.5 V *vs.* RHE)	7.1	Indophenol method	6
P-WO_3@TiO_2	0.1 M Na_2SO_4	6.54×10^{-10} mol s^{-1} cm^{-2} (-0.55 V *vs.* RHE)	17.5 (-0.35 V *vs.* RHE)	Indophenol method	7
Cr_2O_3 nanofiber	0.1 M HCl	28.13 μg h^{-1} mg^{-1} (-0.75 V *vs.* RHE)	8.56	Indophenol method	8
Bi_4O_{11}/CeO_2	0.1 M HCl (pH = 1)	23.21 μg h^{-1} $mg_{cat.}^{-1}$ (-0.2 V *vs.* RHE)	10.16	Indophenol method	9
Nb_2O_5/CP	0.1 M HCl	43.6 μg h^{-1} $mg_{cat.}^{-1}$ (-0.55 V vs. RHE)	9.26	Indophenol method	10
MXene ($Ti_3C_2T_x$)	0.5 M Li_2SO_4+ 0.1 M HCl (pH = 2)	4.72 μg h^{-1} cm^{-2} (-0.1 V *vs.* RHE)	5.78	Nessler method	11
$TiO_2/Ti_3C_2T_x$	0.1 M HCl	32.17 μg h^{-1} $mg_{cat.}^{-1}$ (-0.45 V *vs.* RHE)	16.07	Indophenol method	12
OVs-rich MoO_2	0.1 M HCl	12.20 μg h^{-1} mg^{-1} (-0.15 V vs. RHE)	8.2	Indophenol method	13
C-Ti_xO_y/C	0.1 M $LiClO_4$	14.8 μg h^{-1} $mg_{cat.}^{-1}$ (-0.4 V *vs.* RHE)	17.8	Indophenol method	14
Fe/Fe_3O_4	0.1 M PBS (pH = 7.2)	~0.19 μg cm^{-2} h^{-1} (~0.19 μg h^{-1} mg^{-1}) (-0.3 V vs. RHE)	8.29	Indophenol method	15
Zr-TiO_2	0.1 M KOH	8.90 μg h^{-1} cm^{-2} (8.90 μg h^{-1} mg^{-1}) (-0.45 V *vs.* RHE)	17.3	Indophenol method	16
Cu-CeO_2-3.9	0.1 M Na_2SO_4 (pH = 6.3)	5.3×10^{-10} mol s^{-1} cm^{-1} (13.3 μg h^{-1} mg^{-1}) (-0.1 V vs. RHE)	19.1	Indophenol method	17
MnO_x NA/TM	0.1 M Na_2SO_4	1.63×10^{-10} mol s^{-1} cm^{-2} (-0.5 V *vs.* RHE)	11.40	Indophenol method	18
α-Fe_2O_3 nanocubes	0.1 M KOH	35.55 μg h^{-1} $mg_{cat.}^{-1}$ (-0.5 V *vs.* RHE)	25.93 (0.0 V *vs.* RHE)	Indophenol method	19
SA-Ag/NC	0.1 M HCl	270.9 μg h^{-1} $mg_{cat.}^{-1}$ 69.4 mg h^{-1} mg_{Ag}^{-1} (-0.6 V *vs.* RHE)	21.9 (-0.65 V *vs.* RHE)	Indophenol method	20
Zn/Fe-N-C	0.1 M PBS	30.5 μg h^{-1} $mg_{cat.}^{-1}$ (-0.3 V *vs.* RHE)	26.5	Indophenol method	21
Au_1/C_3N_4	0.005 M H_2SO_4	1,305 μg h^{-1} mg^{-1}_{Au} (-0.1 V vs. RHE)	11.1	Indophenol method	22
Au@amorphous SnO_2 NPs	0.1 mol L^{-1} HCl	21.9 μg h^{-1} $mg_{cat.}^{-1}$ (-0.2 V vs. RHE)	15.3	Indophenol method	23

$Ru@ZrO_2/NC$	0.1 M HCl	3.665 mg_{NH3} h^{-1} $mg_{Ru.}^{-1}$ (-0.21 V *vs.* RHE)	21 (-0.11 V *vs.* RHE)	Indophenol method	24
SA-Mo/NPC	0.1 M KOH	34.0 ± 3.6 μg_{NH3} h^{-1} $mg_{cat.}^{-1}$ (-0.3 V vs. RHE)	14.6 ±1.6	Nessler method	25
ISAS-Fe/NC	0.1 M PBS	62.9±2.7 μg h^{-1} $mg_{cat.}^{-1}$ (-0.4 V vs. RHE)	18.6 ±0.8	Indophenol method	26
Bi NS	0.5 M K_2SO_4 (pH = 3.5)	200 mmol g^{-1} h^{-1} 0.052 mmol cm^{-2} h^{-1} (3400 μg h^{-1} mg^{-1})	66	Nessler method	27
FL-BP NSs	0.01M HCl	31.37 μg h^{-1} mg^{-1} (-0.7 V *vs.* RHE)	5.07 (-0.6 V *vs.* RHE)	Indophenol method	28
VN NPs	0.05M H_2SO_4	3.3×10^{-10} mol s^{-1} cm^{-1} (40.4 μg h^{-1} mg^{-1}) (-0.1 V vs. RHE)	6.0	Nessler method	29
MBN	0.1 M Na_2SO_4	18.2 μg h^{-1} $mg_{cat.}^{-1}$ (-0.7 V *vs.* RHE)	5.5	Indophenol method	30
PCN	0.1 M HCl	8.09 μg h^{-1} $mg_{cat.}^{-1}$ (-0.2 V *vs.* RHE)	11.05	Indophenol method	31
B_4C/CPE	0.1 M HCl	26.57 μg h^{-1} $mg_{cat.}^{-1}$ (-0.75 V *vs.* RHE)	15.95	Indophenol method	32
TiC/C	0.1 M HCl	14.1 μg h^{-1} $mg_{cat.}^{-1}$ (-0.5 V *vs.* RHE)	5.8	Indophenol method	33
ZrS_2 NF-Vs	0.1 M HCl	30.72 μg h^{-1} $mg_{cat.}^{-1}$ (-0.35 V *vs.* RHE)	10.33 (-0.30 V *vs.* RHE)	Indophenol method	34
MoS_2	0.1 M Na_2SO_4	8.08×10^{-11} mol s^{-1} cm^{-1} (-0.6 V vs. RHE)	1.17	Indophenol method	35
CoS_2/NS-G	0.05 M H_2SO_4	25.0 μg h^{-1} $mg_{cat.}^{-1}$ (-0.2 V *vs.* RHE)	25.9 (-0.05 V *vs.* RHE)	Indophenol method	36
ZrB_2 nanocubes	0.5 M $LiClO_4$	37.7 μg h^{-1} mg^{-1} (-0.3 V *vs.* RHE)	18.2	Indophenol method	37
LaF_3	0.5 M $LiClO_4$	55.9 μg h^{-1} $mg_{cat.}^{-1}$ (-0.45 V *vs.* RHE)	16	Indophenol method	38
Pd_3Cu_1	1 M KOH	39.9 mg h^{-1} $mg_{cat.}^{-1}$ (-0.25 V *vs.* RHE)	1.56 (-0.05 V *vs.* RHE)	Nessler method	39
$Rh_{0.6}Ru_{0.4}$ NAs	0.1 M Na_2SO_4	57.75 μg h^{-1} $mg_{cat.}^{-1}$ (-0.2 V vs. RHE)	3.39	Indophenol method	40
PdCuIr	0.1 M Na_2SO_4	13.43 μg h^{-1} $mg_{cat.}^{-1}$ (-0.3 V vs. RHE)	5.29	Indophenol method	41

amorphous BiNi alloy	0.1 M Na_2SO_4	17.5 μg h^{-1} $mg_{cat.}^{-1}$ (-0.6 V vs. RHE)	13.8	Indophenol method	42
NPC	0.05 M H_2SO_4	1.40 mmol g^{-1} h^{-1} (23.8 μg h^{-1} mg^{-1}) (-0.9 V vs. RHE)	1.42	Nessler method	43
NPC-500	0.005 M H_2SO_4	1.31 mmol g^{-1} h^{-1} (22.3 μg h^{-1} mg^{-1}) (-0.4 V *vs.* RHE)	9.98	Indophenol method	44
CC-450	0.1 M Na_2SO_4 + 0.02 M H_2SO_4	15.8 μg cm^{-2} h^{-1} (-0.3 V *vs.* RHE)	6.92	Indophenol method	45
d-FG	0.1 M Na_2SO_4	9.3 μg h^{-1} $mg_{cat.}^{-1}$ (-0.7 V *vs.* RHE)	4.2	Indophenol method	46
Fe-N/C-CNTs	0.1 M KOH	34.83 μg h^{-1} $mg_{cat.}^{-1}$ (-0.2 V vs. RHE)	9.28	Indophenol method	47
BG	0.05 M H_2SO_4	9.8 μg cm^{-2} h^{-1} (11.0 μg h^{-1} mg^{-1}) (-0.5 V *vs.* RHE)	10.8	Indophenol method	48
BCN	0.1 M HCl	7.75 μg h^{-1} $mg_{cat.}^{-1}$ (-0.3 V *vs.* RHE)	13.79	Indophenol method	49
IrP_2@PNPC-NF	0.05 M H_2SO_4	94.0 μg h^{-1} $mg_{cat.}^{-1}$ (-0.3 V *vs.* RHE)	17.8 (-0.1 V *vs.* RHE)	Indophenol method	50

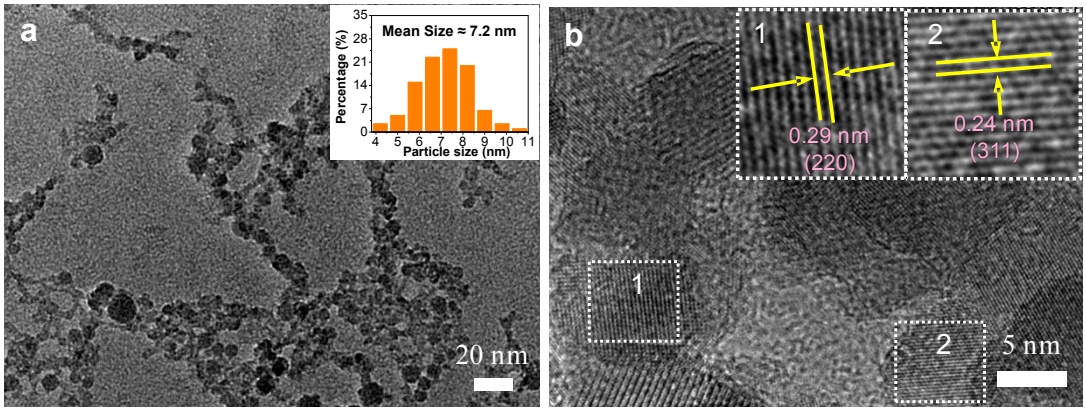

Fig. S1 (a) Low-magnification TEM image of L-Co_3O_4-7.2 and corresponding size distribution curve. (b) High-resolution TEM image of L-Co_3O_4-7.2 (inset of an individual nanoparticle).

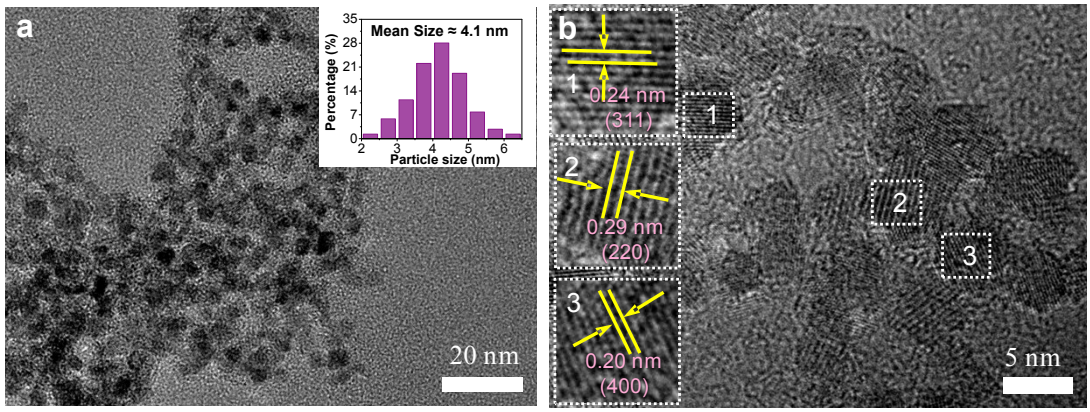

Fig. S2 (a) Low-magnification TEM image of C-Co_3O_4-4.1 and corresponding size distribution curve. (b) High-resolution TEM image of C-Co_3O_4-4.1 (inset of an individual nanoparticle).

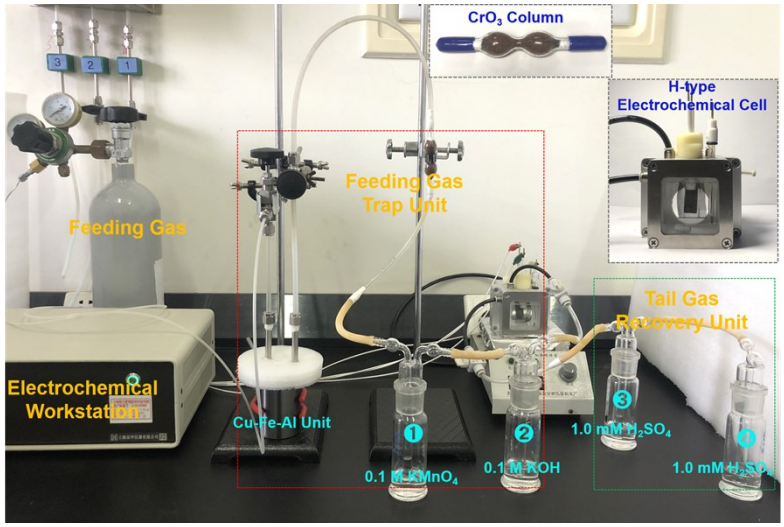

Fig. S3 Photograph of the electrochemical NRR experimental setup.

The electrochemical NRR experimental setup was constructed to eleminate the possible interferences of NH_3 and NO_x in the feeding gases based on previously reported protocol.[51-53] The Cu-Fe-Al catalyst (**Fig. S4**) was fabricated according to the reported methods.[54-56] Prior to each experiment, the Cu-Fe-Al catalyst was thermally treated at 300 ℃ for 2 h under 5% H_2/Ar stream. The treated Cu-Fe-Al catalyst was covered with a stainless-steel vessel which filled up with the mixed ethanol and liquid nitrogen. Moreover, a CrO_3 catalyst packed column (Dongguan Zhongtian Electronic Technology Co. LTD, China) was used to completely remove NO interference. In this purification system, any NO passed through this purification unit will be converted to water soluble NO_2, and then removed by the $KMnO_4$ and KOH before reaching the electrochemical cell.

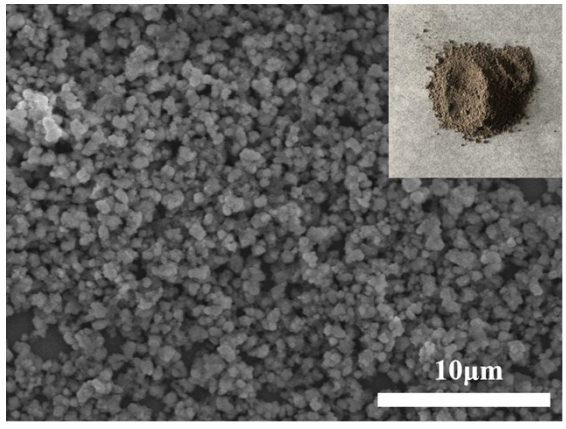

Fig. S4 SEM image and photograph (inset) of the Cu-Fe-Al catalyst.

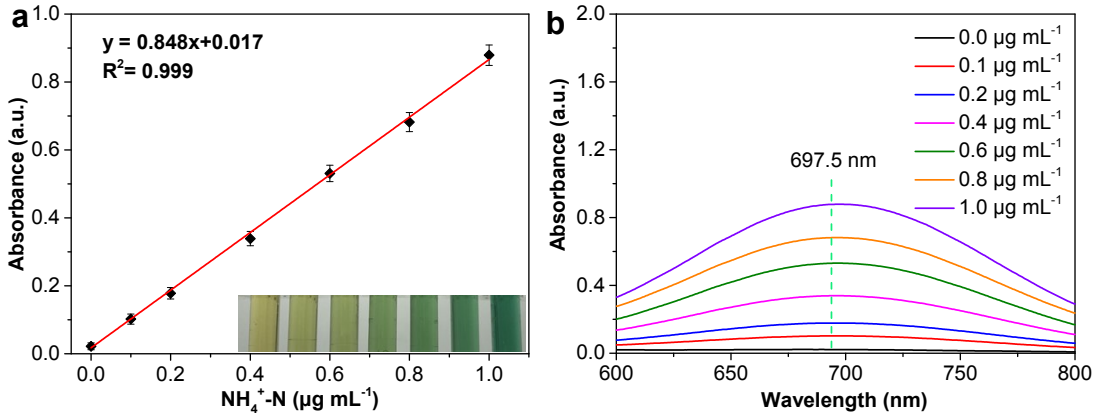

Fig. S5 (a) The calibration curve used for calculation of NH_4^+-N concentration. (b) UV-Vis absorption spectra of the indophenol blue indicator with various concentrations of NH_4^+-N (0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 μg mL^{-1}) after incubating for 1 h at room temperature.

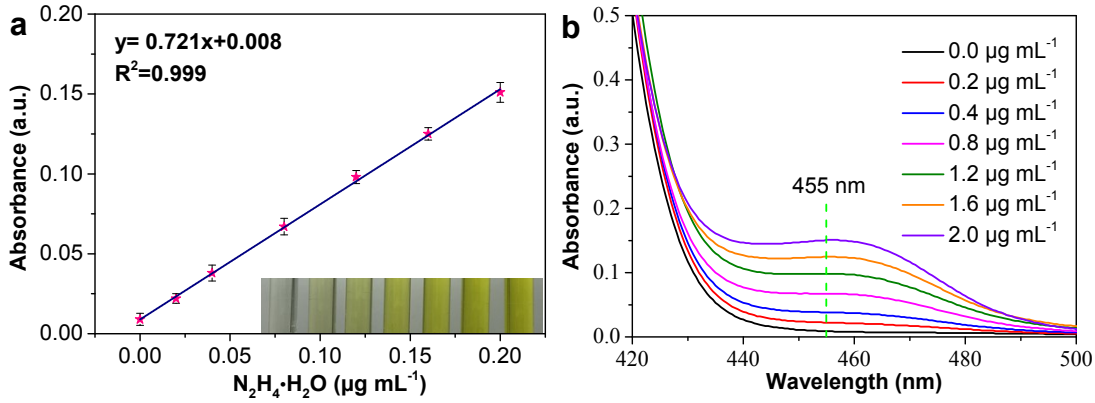

Fig. S6 (a) The calibration curve used for calculation of $N_2H_4 \cdot H_2O$ concentration. (b) UV-Vis absorption spectra with various concentrations of $N_2H_4 \cdot H_2O$ (0, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0 μg mL^{-1}) after incubating for 20 min at room temperature.

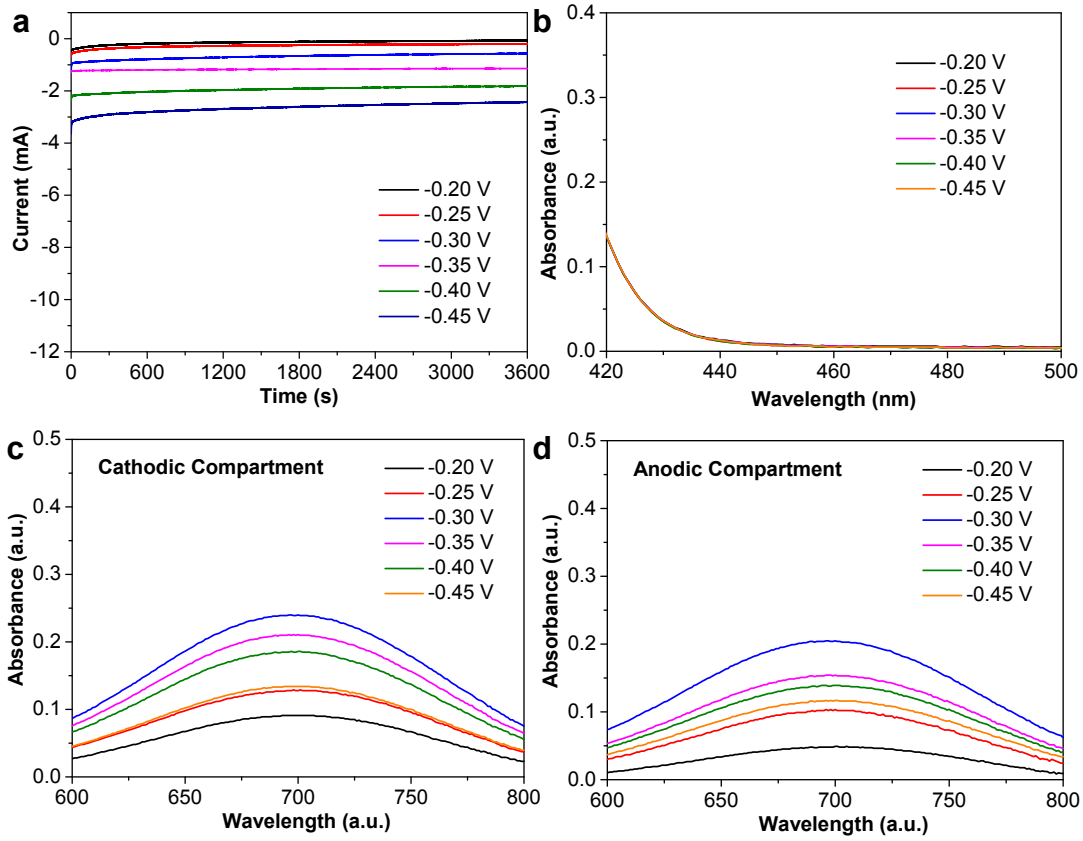

Fig. S7 (a) Time-dependent current density curves after NRR for 1 h in N_2-saturated 0.1 M Na_2SO_4 electrolyte at different potentials. UV-Vis absorption spectra of the corresponding collected samples (b) for the possible N_2H_4 detection and possible NH_3 detection from (c) cathodic compartment and (d) anodic compartment.

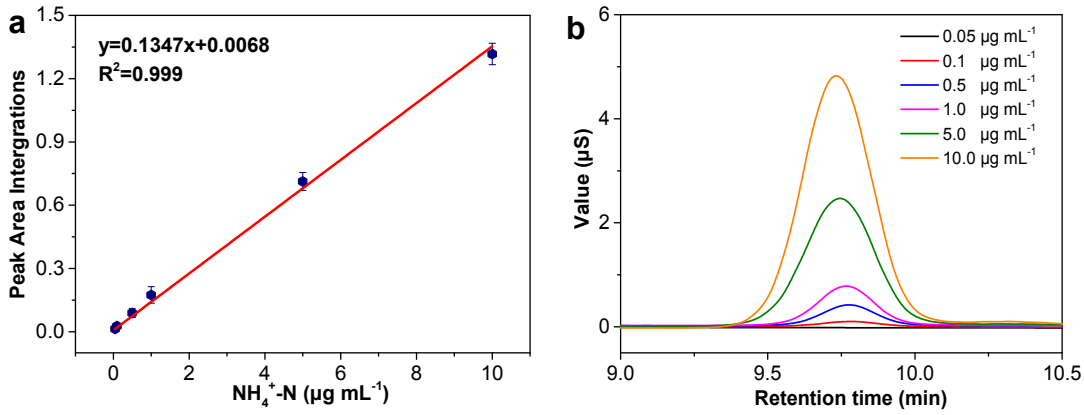

Fig. S8 (a) The calibration curve of NH_4^+-N peak area (retention time of ~9.8 min) used for calculation of NH_4^+-N concentration detected by the ion chromatograph. (b) The corresponding ion chromatograph spectra with various concentrations of NH_4^+-N (0.05, 0.1, 0.5, 1.0, 5.0, 10.0 μg mL^{-1}) in 0.1 M Na_2SO_4.

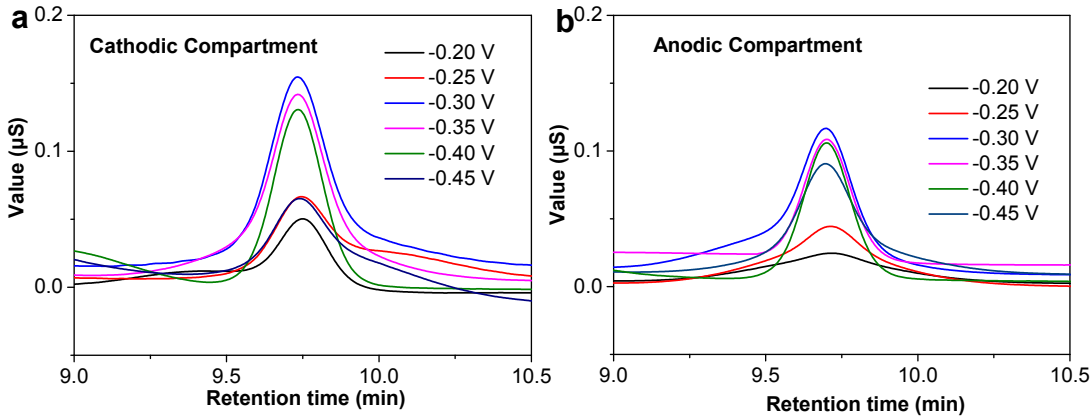

Fig. S9 Ion chromatograph spectra of collected samples for possible NH_3 detection from (a) cathodic compartment and (b) anodic compartment after NRR for 1 h in N_2-saturated 0.1 M Na_2SO_4 electrolyte at different potentials.

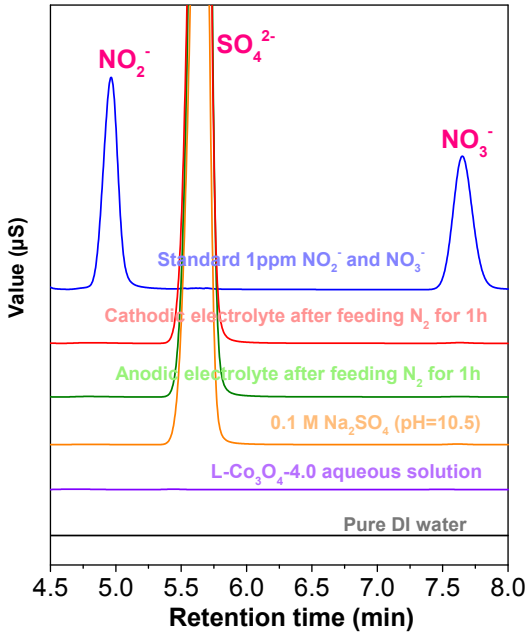

Fig. S10 Ion chromatograph spectra of the standard solution (1.0 ppm NO_2^- and 1.0 ppm NO_3^-) and the collected samples under various conditions.

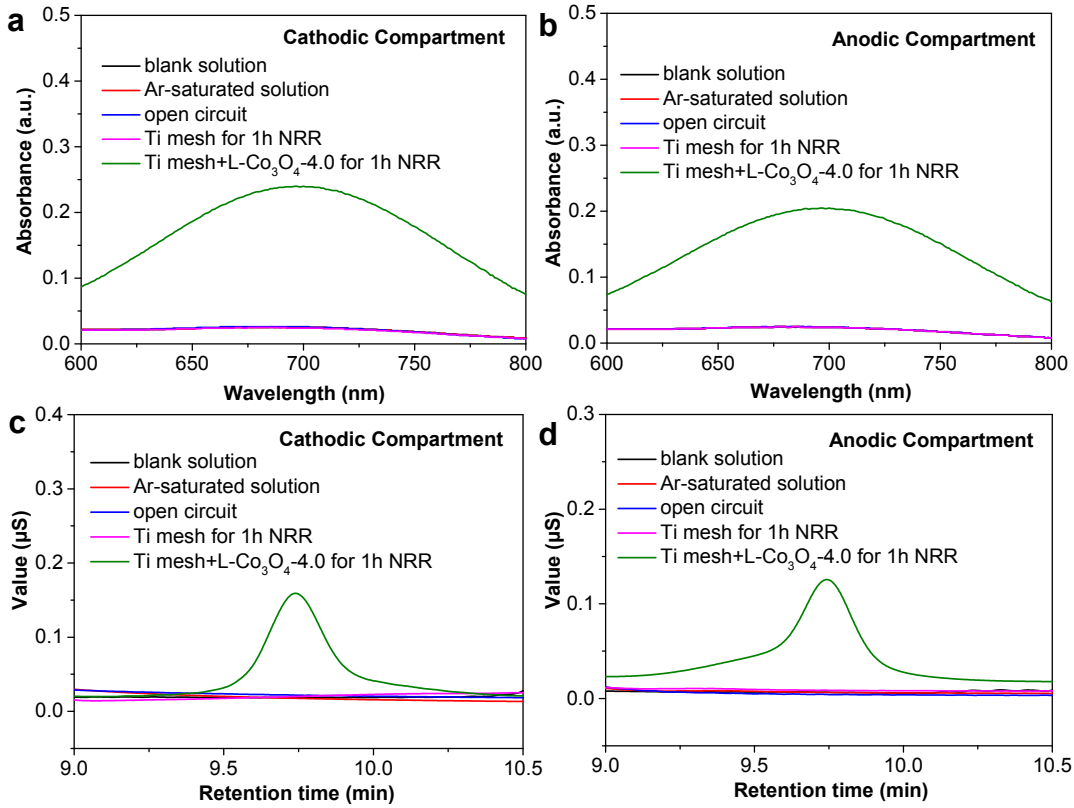

Fig. S11 UV-Vis absorption spectra of collected solution samples from (a) cathodic compartment and (b) anodic compartment under different control conditions. Ion chromatograph spectra of collected solution samples from (c) cathodic compartment and (d) anodic compartment under different control conditions.

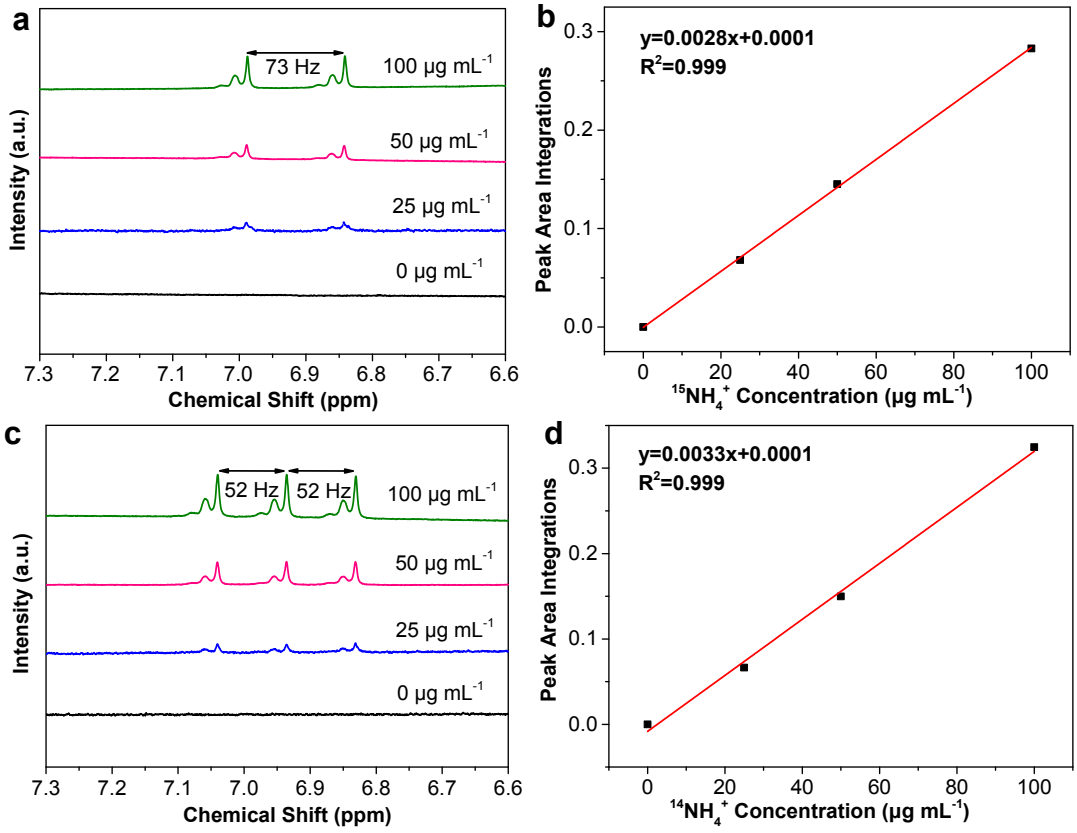

Fig. S12 (a, c) ^{1}H NMR spectra of the $^{15}NH_4^+$ and $^{14}NH_4^+$ standards with different concentrations. (b, d) Corresponding $^{15}NH_4^+$ and $^{14}NH_4^+$ calibration curves constructed by plotting the integrated ^{1}H NMR signal (7.00 ppm for $^{15}NH_4^+$ and 6.97 ppm for $^{14}NH_4^+$) against the standard concentration.

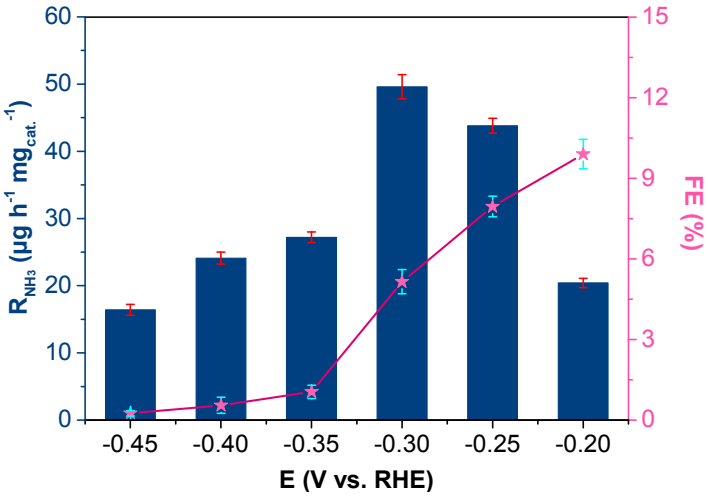

Fig. S13 Dependence of R_{NH_3} and FE of L-Co_3O_4-4.0/CC electrocatalyst at different applied potentials in N_2-saturated 0.1 M Na_2SO_4 electrolyte using conventional catalyst-loading electrocatalysis system.

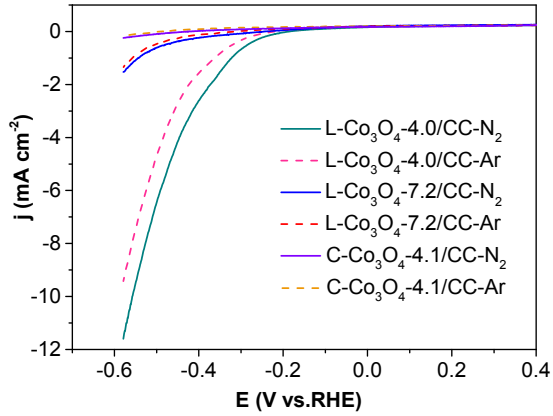

Fig. S14 The comparison results of of LSV curves for three Co_3O_4/CC in N_2- and Ar-saturated electrolytes.

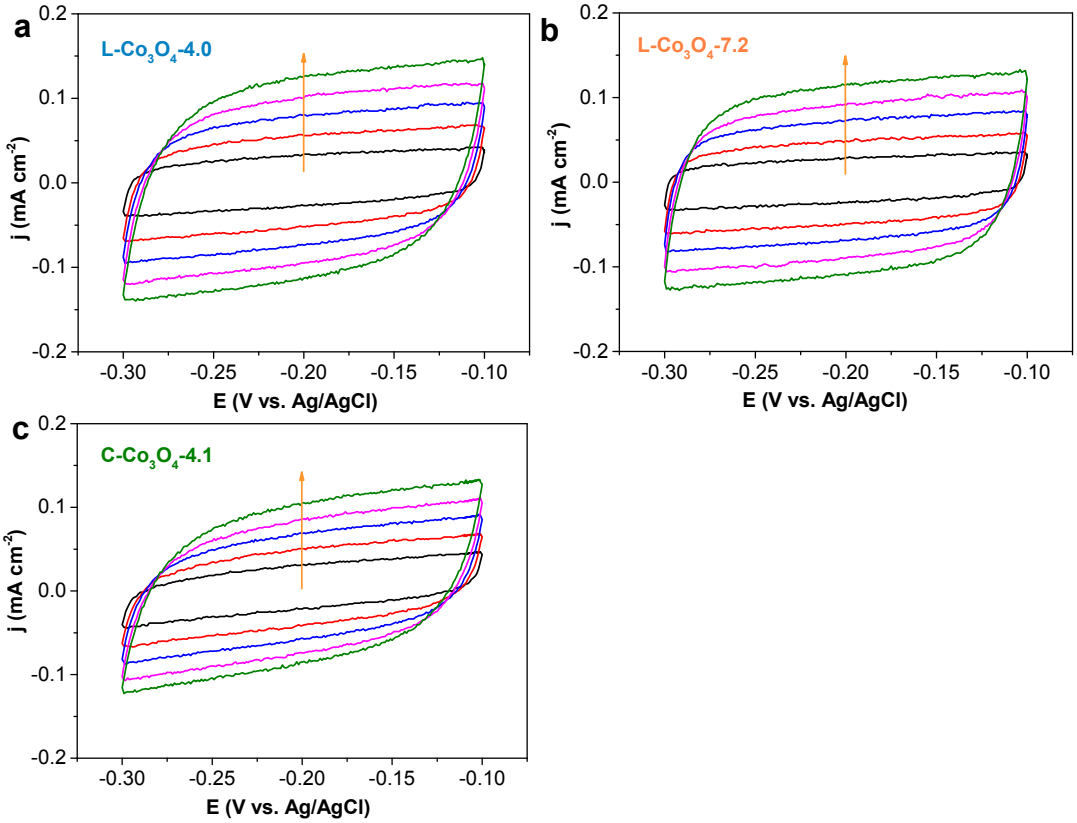

Fig. S15 Cyclic voltammetry curves of (a) L-Co_3O_4-4.0, (b) L- Co_3O_4-7.2 and (c) C-Co_3O_4-4.1 with various scan rates (25, 50, 75, 100, 125 mV s^{-1}) in the region of - 0.10 to - 0.30 V (*vs.* Ag/AgCl).

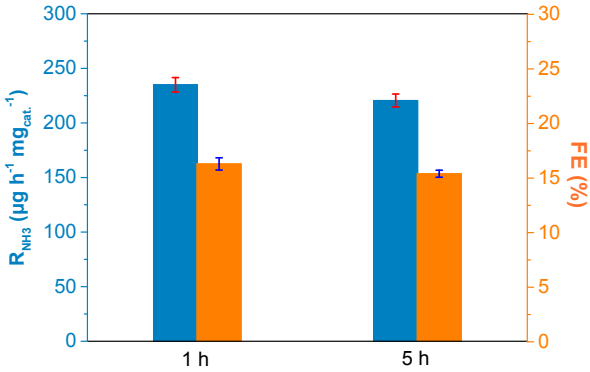

Fig. S16 The comparison results of NH_3 yield rate and FE for L-Co_3O_4-4.0 in the fluidized electrocatalysis system after 1 h and 5 h of NRR, respectively.

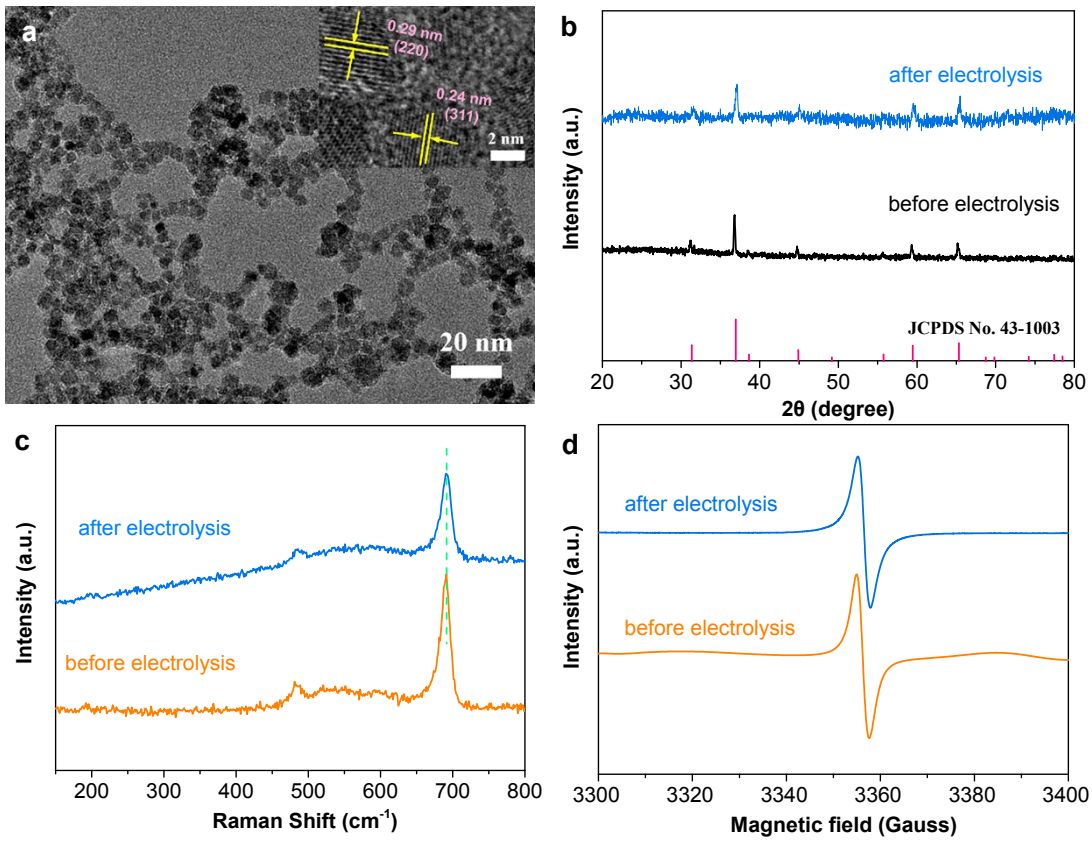

Fig. S17 (a) TEM image and inset HRTEM image of L-Co_3O_4-4.0 after 5 h of NRR electrolysis. (b) XRD patterns (c) Raman spectra and (d) EPR spectra of the L-Co_3O_4-4.0 before and after 5 h of NRR.

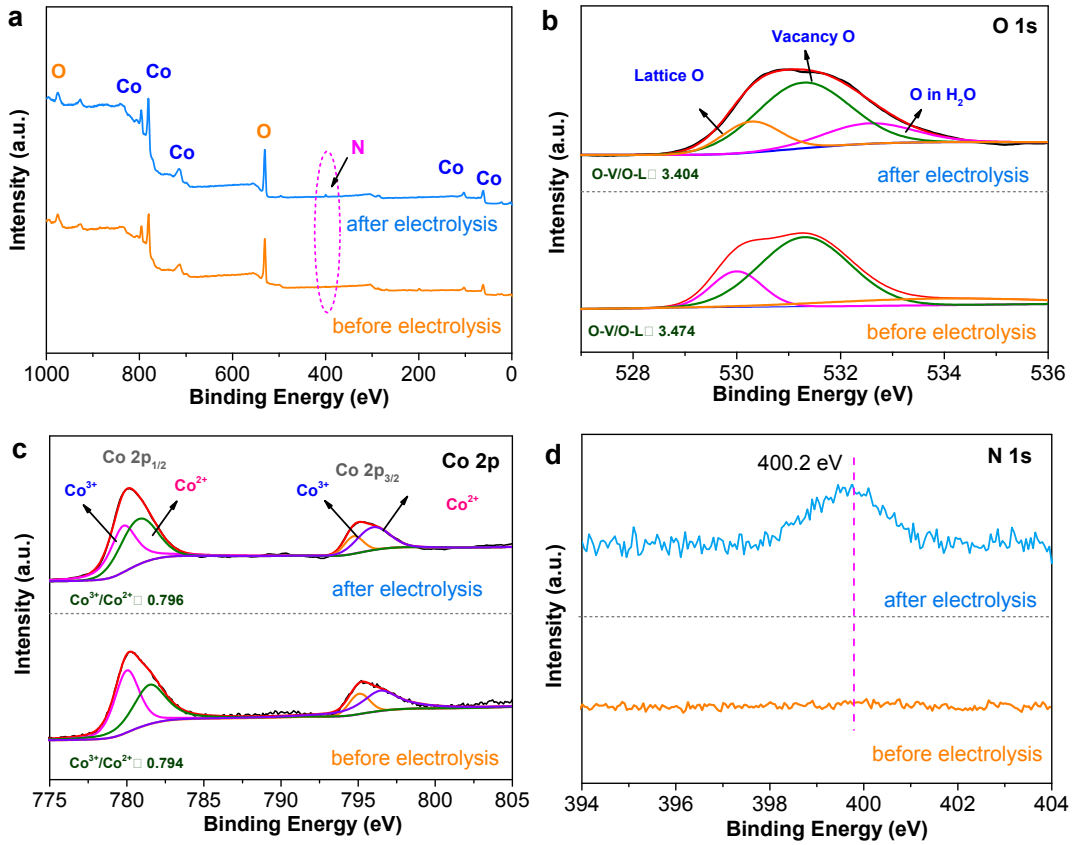

Fig. S18 (a) The surface survey XPS spectra. (b) High-resolution O 1s XPS spectra, (c) High-resolution Co 2p XPS spectra and (d) High-resolution N 1s XPS of the L-Co_3O_4-4.0 before and after 5 h of NRR.

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