

## Electronic Supplementary Information

### Experimental Section

**Materials:** Sodium nitrate ( $\text{NaNO}_3$ , 99.9%), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), sodium hydroxide ( $\text{NaOH}$ ), ethanol ( $\text{C}_2\text{H}_6\text{O}$ , 99.9%), 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 ( $\text{C}_5\text{FeN}_6\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$ ) and sodium hypochlorite solution ( $\text{NaClO}$ ) were purchased from Aladdin Co., Ltd. (Shanghai, China). Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), hydrochloric acid ( $\text{HCl}$ ), 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). Cobalt chloride nitrate hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) were purchased from Chengdu Kelong Chemical Regent Co. Ltd. Titanium plate (thickness is 0.2 mm) was purchased from Qingyuan Metal Materials Co., Ltd (Xingtai, China). All reagents used in this work were analytical grade without further purification.

**Preparation of Co foam/TP:** The Co foam/TP was synthesized via a constant current electrodeposition of  $-2.0 \text{ A cm}^{-2}$  for 70 s. Firstly, Ti plate ( $1.0 \text{ cm} \times 1.2 \text{ cm}$ ) was ultrasonically washed with  $\text{HCl}$  (3.0 M), ethanol, and ultrapure water to remove surface oxide and oil. The cleaned TP was subsequently masked by Teflon tape, leaving an exposed area of  $1.0 \text{ cm}^2$ , which was then used as working electrode for electrodeposition. A saturated calomel electrode (SCE) and Pt foil were then used as reference and counter electrode. The electrodeposition was carried out in the electrolyte containing 0.2 M  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and 2.0 M  $\text{NH}_4\text{Cl}$ . The formed Co foam/TP were thoroughly rinsed with UP water and kept under UP water for  $\sim 1 \text{ h}$  to completely remove residual traces of electrolyte (particularly  $\text{NH}_4^+$  ions).

**Preparation of Co film/TP:** For the control sample, Co film/TP was prepared as followed. Firstly, Co powder was scraped off the electrodeposited Co foam/TP for removal of the 3D porous foam structure. Then, Co powder was mixed with isopropanol

and 5 wt% Nafion to form the catalyst ink by 30 min ultrasonication. Finally, the Co film/TP was obtained by dropping the prepared ink onto a cleaned TP ( $0.5 \times 0.5 \text{ cm}^2$ ) with a loading mass of about  $2.36 \text{ mg cm}^{-2}$ .

**Characterizations:** XRD data were acquired from a LabX XRD-6100 X-ray diffractometer with a Cu  $K\alpha$  radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM images were collected on a GeminiSEM 300 scanning electron microscopy (ZEISS, Germany) at an accelerating voltage of 5 kV. TEM images were acquired on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 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 (SHIMADZU UV-2700). Gaseous products from nitrate reduction reaction were determined by gas chromatography (GC) with SHIMADZU GC-2014 gas chromatograph.

**Electrochemical measurements:** All electrochemical measurements were carried on the CHI660E electrochemical workstation (Shanghai, Chenhua) using a standard three-electrode setup. Electrolyte solution was Ar-saturated of 0.1 M NaOH with 0.1 M  $\text{NO}_3^-$ , using Co foam/TP, Co film/TP, or TP as working electrode, a graphite rod as the counter electrode, and a Hg/HgO as the reference electrode. We use an H-type electrolytic cell separated by a Nafion 117 membrane which was protonated by boiling in ultrapure water,  $\text{H}_2\text{O}_2$  (5%) aqueous solution and 0.5 M  $\text{H}_2\text{SO}_4$  at 80 °C for another 2 h, respectively. Unless otherwise specified, the potentials reported in our work were converted to reversible hydrogen electrode via calibration with the following equation:  $E (\text{RHE}) = E (\text{Hg/HgO}) + (0.098 + 0.0591 \times \text{pH}) \text{ V}$  and the presented current density was normalized to the geometric surface area.

**Determination of  $\text{NH}_3$ :** The  $\text{NH}_3$  concentration in the solution was determined by colorimetry using the indophenol blue method.<sup>1</sup> In detail, 2.0 mL of the solution after reaction (the obtained electrolyte was diluted 40 times), and 2.0 mL of 1.0 M NaOH

coloring solution containing 5% salicylic acid and 5% sodium citrate. Then, 1.0 mL oxidizing solution of 0.05 M NaClO and 0.2 mL catalyst solution of  $C_5FeN_6Na_2O$  (1 wt%) were added to the above solution. After standing in the dark for 2 h, the UV-vis absorption spectra were measured. The concentration of  $NH_3$  was identified using the absorbance at a wavelength of 655 nm. The concentration-absorbance curve was calibrated using the standard  $NH_4Cl$  solution with  $NH_3$  concentrations of 0.0, 0.2, 0.5, 1.0, 2.0, and 5.0 ppm in 0.1 M NaOH solution. The fitting curve ( $y = 0.41893 x + 0.04851$ ,  $R^2 = 0.9999$ ) shows good linear relation of absorbance value with  $NH_3$  concentration.

**Determination of  $N_2H_4$ :** The  $N_2H_4$  was estimated by the Watt and Chrisp method.<sup>2</sup> The color reagent was a solution of 18.15 mg  $mL^{-1}$  of  $C_9H_{11}NO$  in the mixed solvent of HCl and  $C_2H_5OH$  (V/V: 1/10). In detail, 2.0 mL electrolyte was added into 2.0 mL color reagent for 15 min under stirring. The absorbance of such solution was measured to quantify the hydrazine yields by the standard curve of hydrazine ( $y = 0.68594 x + 0.04767$ ,  $R^2 = 0.9997$ ).

**Determination of  $NO_2^-$ :** The  $NO_2^-$  concentration was quantitatively determined by Griess method.<sup>3</sup> Firstly, 1.0 mL of deionized water, 1.0 mL of sample solution, and 2.0 mL of Griess reagent were sequentially added to a 10.0 mL of centrifuge tube. The absorbance at 540 nm was then measured by a UV-vis spectrophotometer after 15 min of dark incubation. The concentration-absorption spectra were calibrated using standard  $NaNO_2$  solution with different concentration ( $y = 0.22429 x + 0.03511$ ,  $R^2 = 0.9999$ ).

**Determination of  $N_2$  and  $H_2$ :**  $N_2$  and  $H_2$  were quantified by GC with SHIMADZU GC-2014 gas chromatograph. A GC run was initiated per 1200 s. Argon (99.999%) was used as the carrier gas. A flame ionization detector with a thermal conductivity detector (TCD) was used to quantify  $H_2$  and  $N_2$ . The electrolyzer outlet was introduced into a condenser before being vented directly into the gas sampling loop of the gas chromatograph.

### Calculations of the $n_{\text{NH}_3}$ , FE and $\text{NH}_3$ yield:

The amount of  $\text{NH}_3$  ( $n_{\text{NH}_3}$ ) was calculated by the following equation:

$$n_{\text{NH}_3} = [\text{NH}_3] \times V$$

FE of  $\text{NH}_3$  formation was calculated by the following equation:

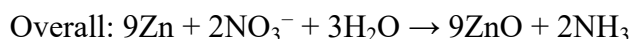
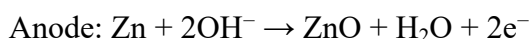
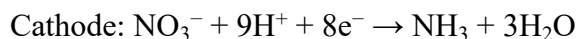
$$\text{FE} = (8 \times F \times [\text{NH}_3] \times V) / (M_{\text{NH}_3} \times Q) \times 100\%$$

$\text{NH}_3$  yield rate is calculated using the following equation:

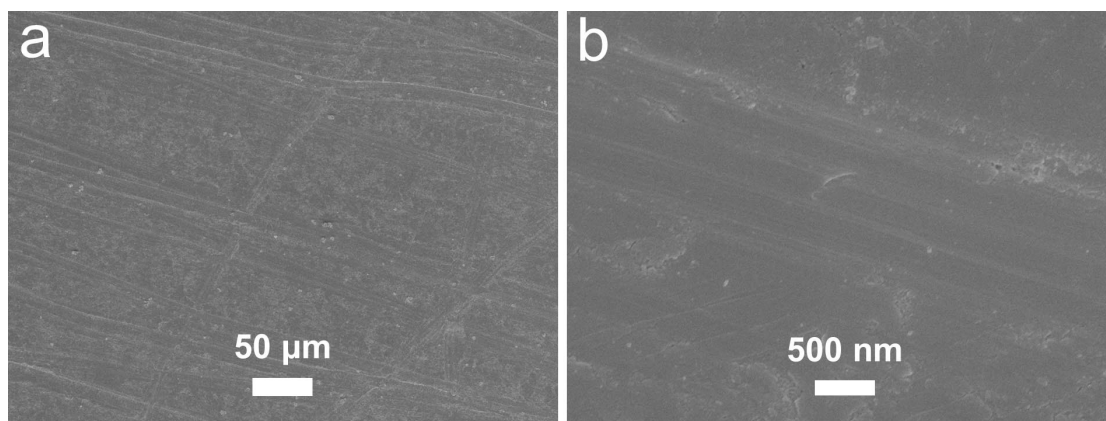
$$\text{NH}_3 \text{ yield} = ([\text{NH}_3] \times V) / (M_{\text{NH}_3} \times t \times A)$$

Where F is the Faradic constant ( $96485 \text{ C mol}^{-1}$ ),  $[\text{NH}_3]$  is the  $\text{NH}_3$  concentration, V is the volume of electrolyte in the anode compartment (40 mL),  $M_{\text{NH}_3}$  is the molar mass of  $\text{NH}_3$  molecule, Q is the total quantity of applied electricity; t is the electrolysis time (1 h) and A is the geometric area of working electrode ( $0.5 \times 0.5 \text{ cm}^2$ ).

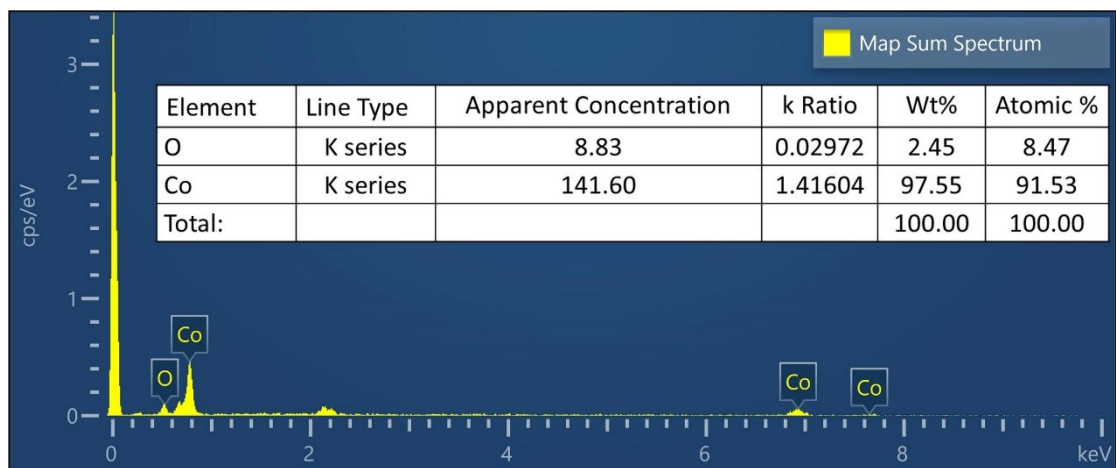
**Zn- $\text{NO}_3^-$  battery:** Co foam/TP was employed as the cathode to perform the e $\text{NO}_3^-$ RR in a cathodic electrolyte (0.1 M NaOH with 0.1 M  $\text{NO}_3^-$ ). A polished Zn plate was set in an anodic electrolyte (1.0 M KOH), and a bipolar membrane was employed to separate the two different electrolytes. During the battery discharge process, electrochemical  $\text{NO}_3^-$  reduction occurs on Co foam/TP, and Zn converts to ZnO. The electrochemical reactions on each electrode can be described as follows:



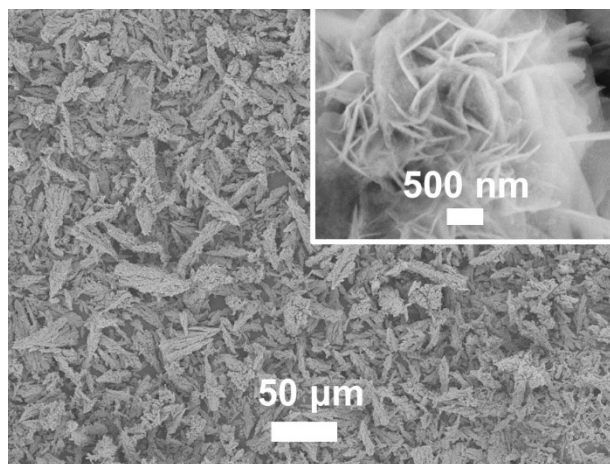
The  $\text{NH}_3$  yield is quantified by using colorimetric methods. Power density is calculated using equation ( $P = U \times I$ ) from the results of polarization data.



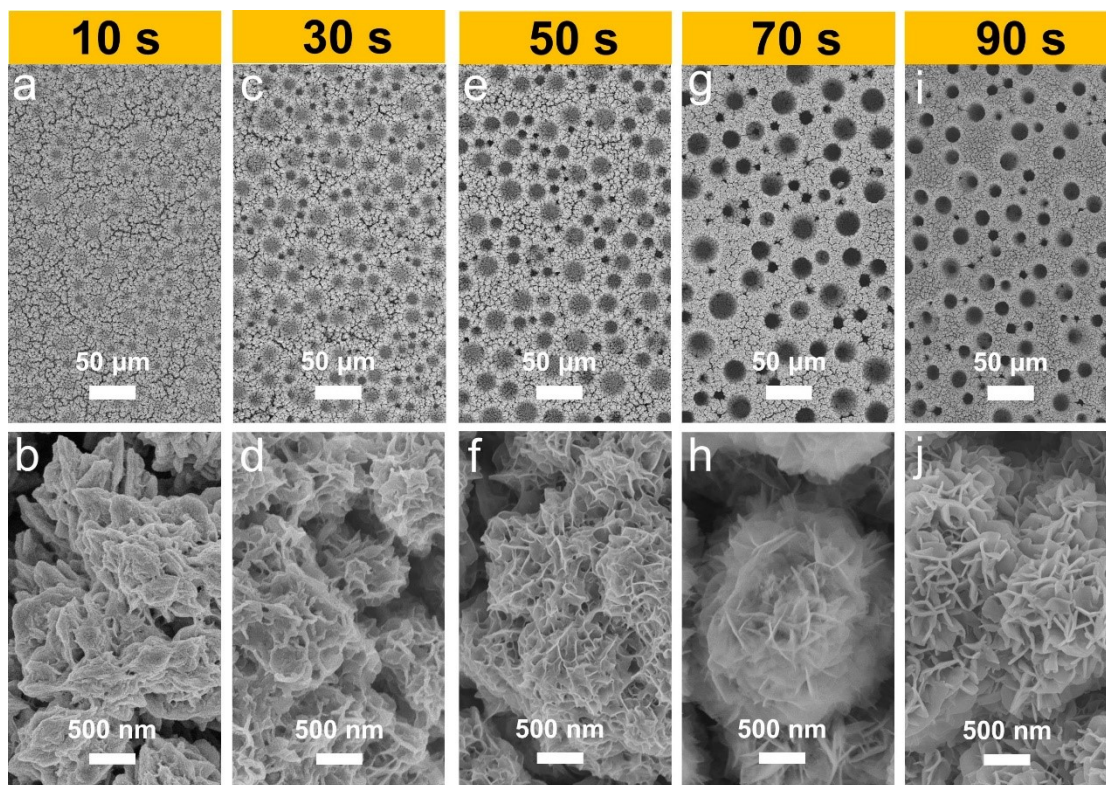
**Fig. S1.** (a) Low- and (b) high-magnification SEM images of bare TP.



**Fig. S2.** EDX spectrum of Co foam/TP.

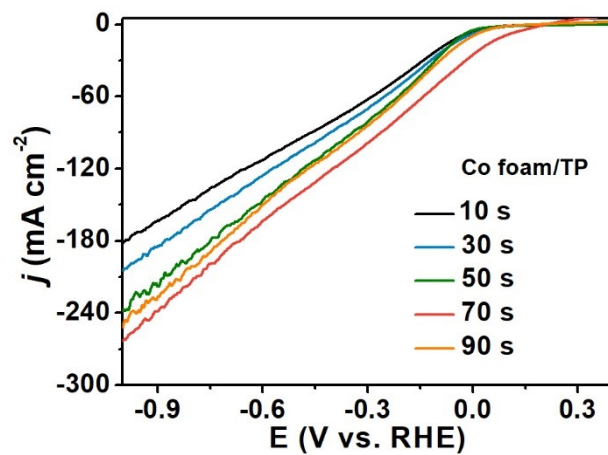


**Fig. S3.** Low- and high-magnification SEM images of Co film/TP.

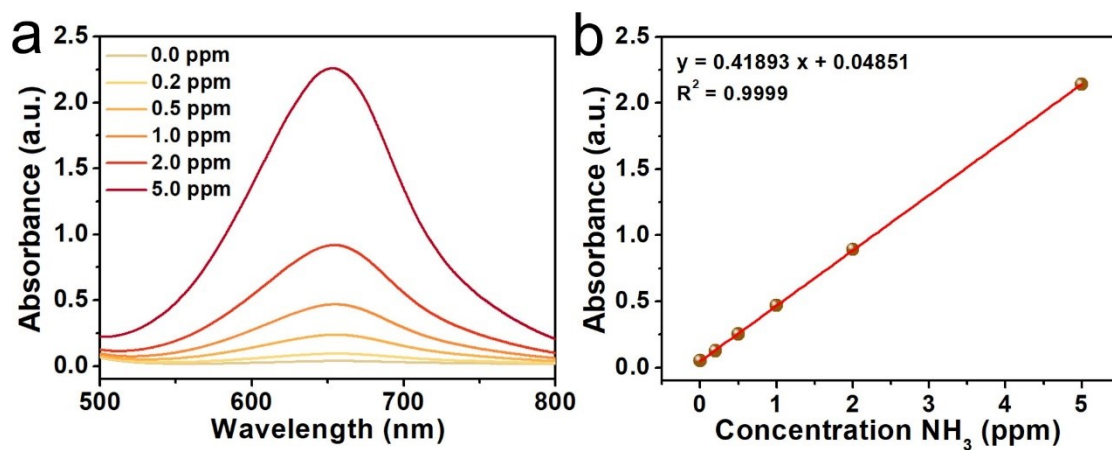


**Fig. S4.** Low- and high-magnification SEM images of Co foam/TP with different deposition times (10-90 s).

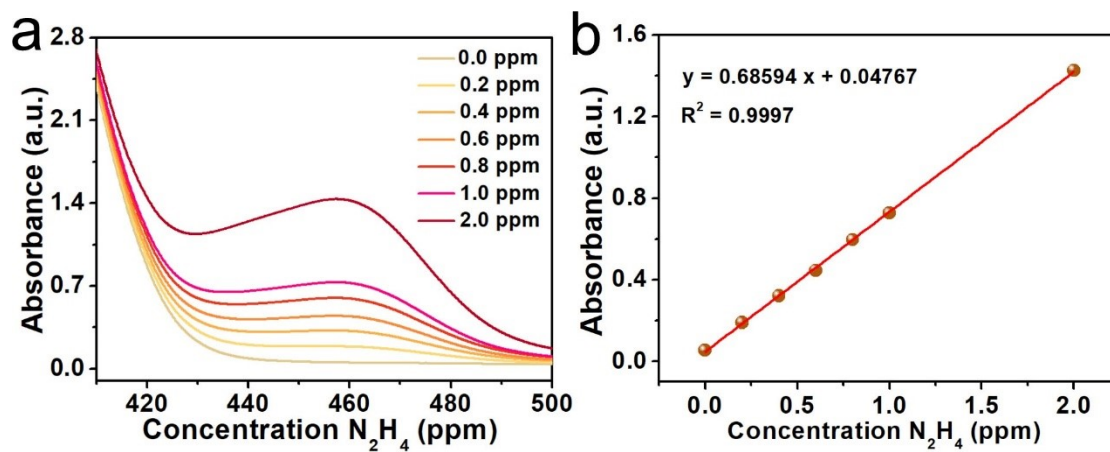




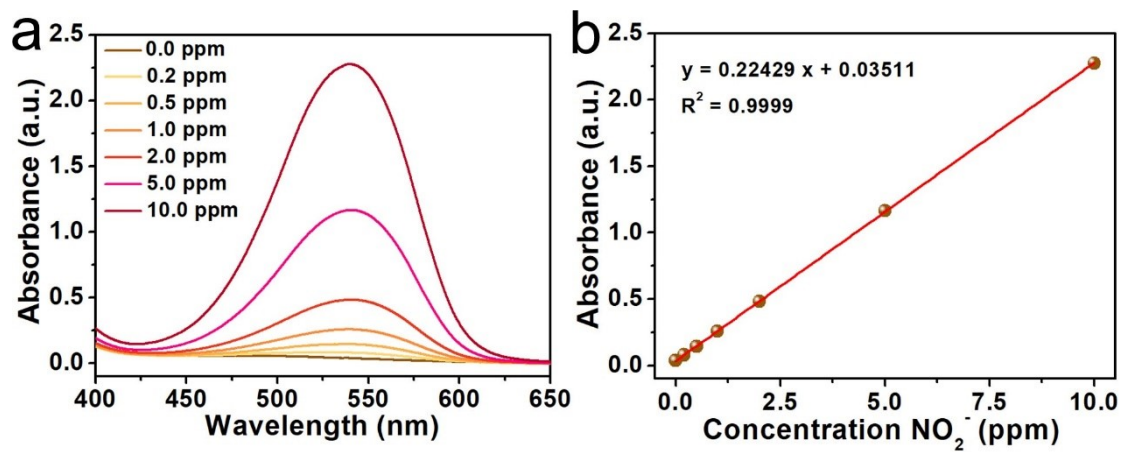
**Fig. S5.** LSV curves of the Co foam/TP with different deposition times (10-90 s) in 0.1 M NaOH with 0.1 M NO<sub>3</sub><sup>-</sup>.



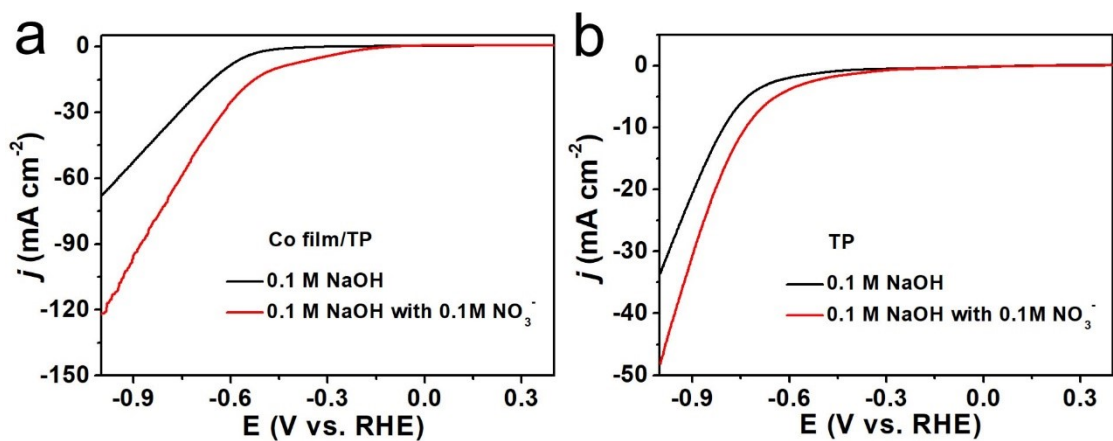
**Fig. S6.** (a) UV-vis absorption spectra and (b) corresponding calibration curve for the calculation of NH<sub>3</sub> concentration.



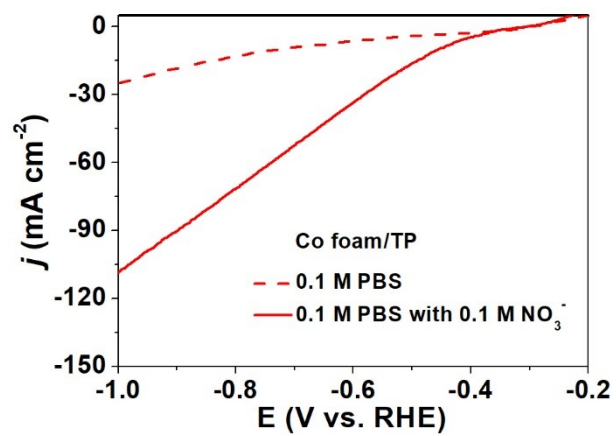
**Fig. S7.** (a) UV-vis absorption spectra and (b) corresponding calibration curve for the calculation of  $N_2H_4$  concentration.



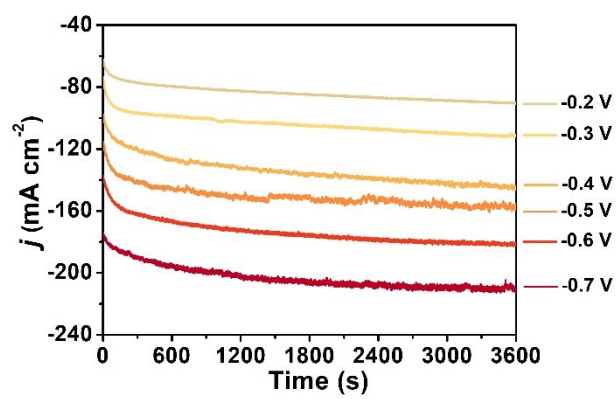
**Fig. S8.** (a) UV-vis absorption spectra and (b) corresponding calibration curve for the calculation of  $\text{NO}_2^-$  concentration.



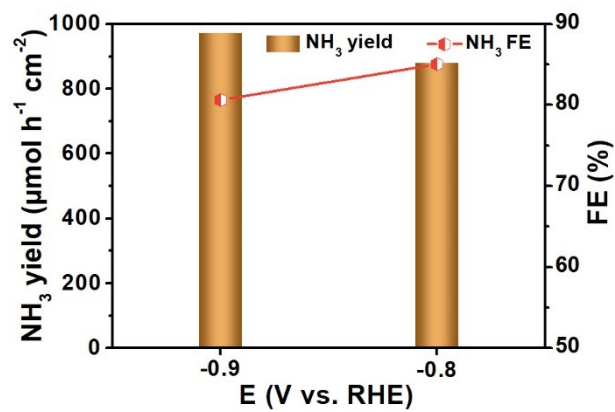
**Fig. S9.** LSV curves of (a) Co film/TP and (b) bare TP in 0.1 M NaOH with/without 0.1 M NO<sub>3</sub><sup>-</sup>.



**Fig. S10.** LSV curves of Co foam/TP in 0.1 M PBS without and with 0.1 M NO<sub>3</sub><sup>-</sup>.

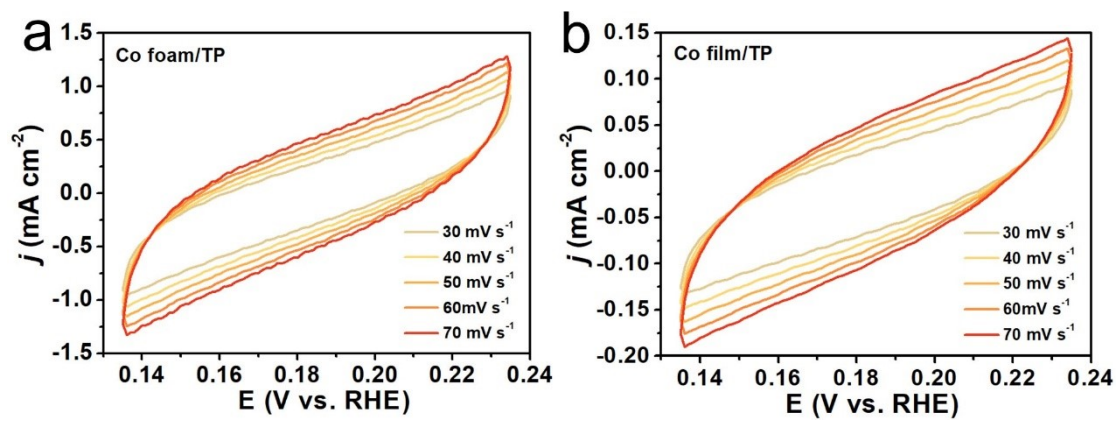


**Fig. S11.** Chronoamperometry curves at a potential range from  $-0.2$  V to  $-0.7$  V.

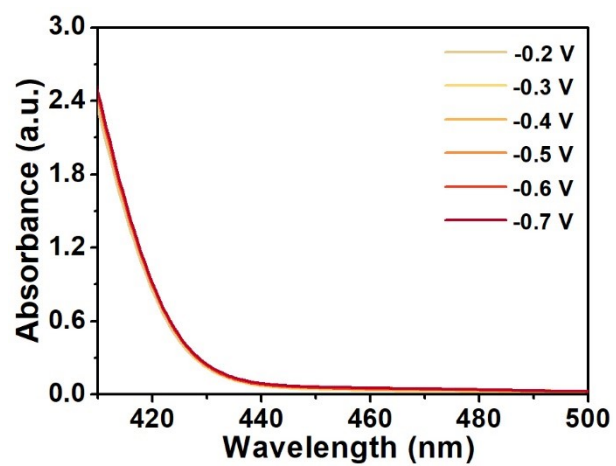


**Fig. S12.** NH<sub>3</sub> yields and FEs at -0.8 V and -0.9 V.

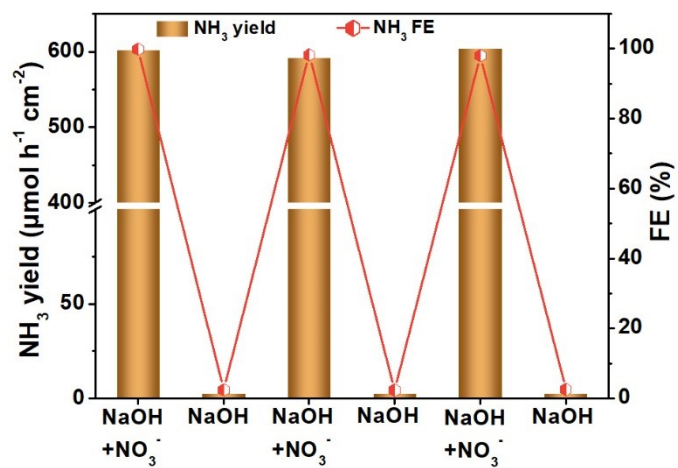




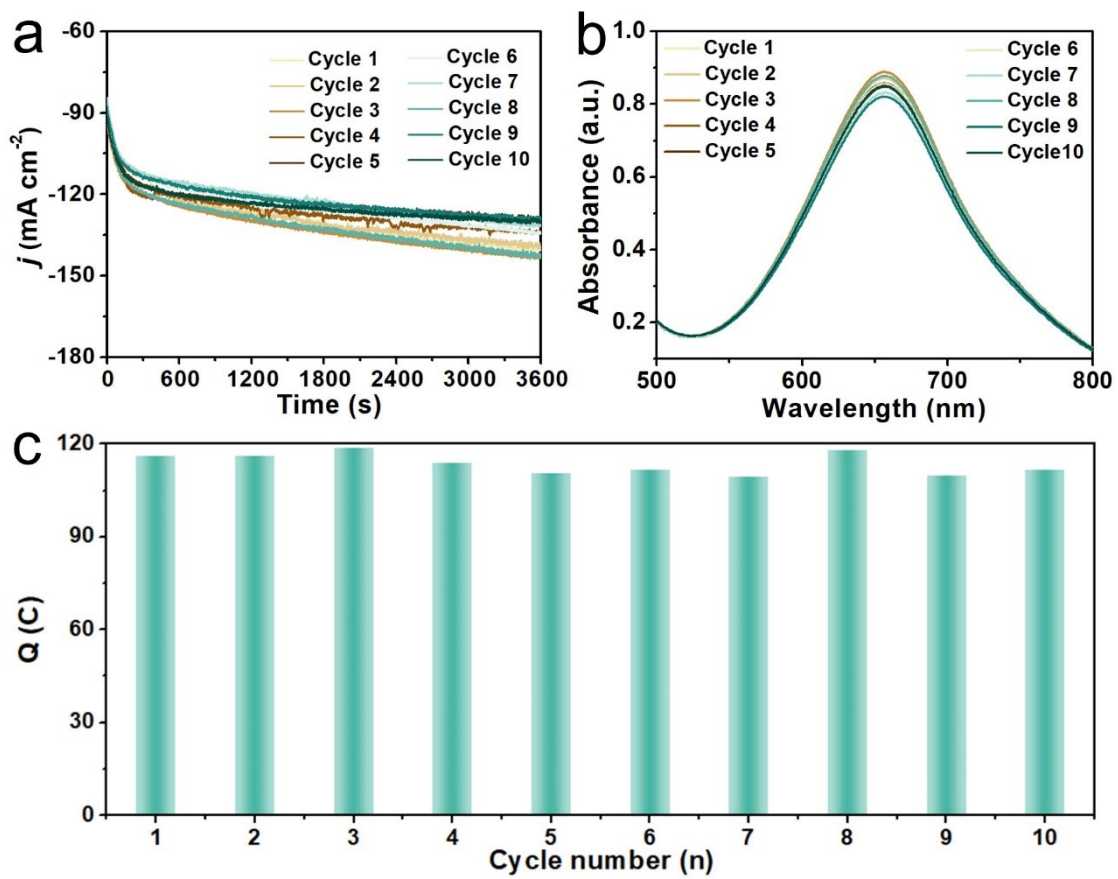
**Fig. S13.** Cyclic voltammetry curves for (a) Co foam/TP and (b) Co film/TP in the double layer region at different scan rates of 30, 40, 50, 60, and 70 mV s<sup>-1</sup>.



**Fig. S14.** UV-vis absorption spectra of  $N_2H_4$  detection.



**Fig. S15.** NH<sub>3</sub> yields and FEs during the alternating cycle tests between NO<sub>3</sub><sup>-</sup>-containing and NO<sub>3</sub><sup>-</sup>-free 0.1 M NaOH at -0.4 V.



**Fig. S16.** (a) Chronoamperometry curves, (b) corresponding UV-vis spectra of Co foam/TP for generated  $\text{NH}_3$ , and (c) Q values during recycling tests at  $-0.4$  V.

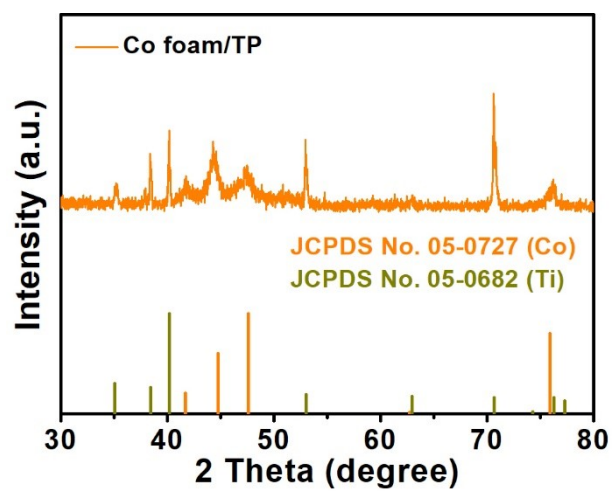
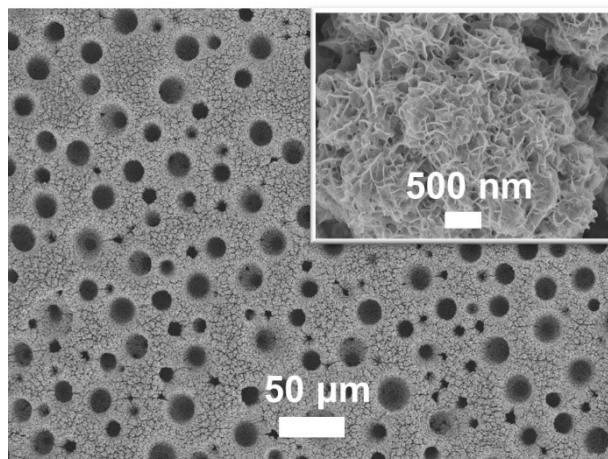
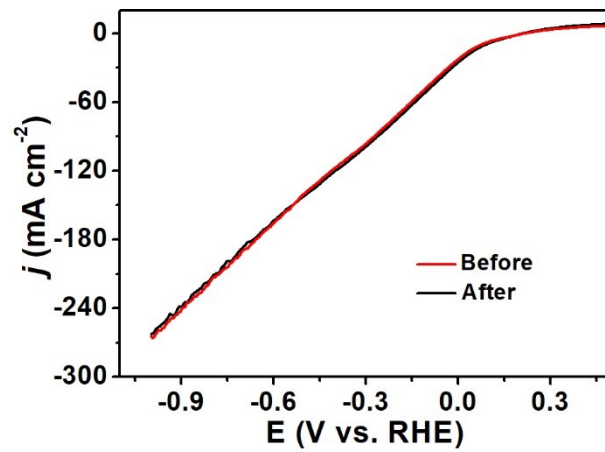


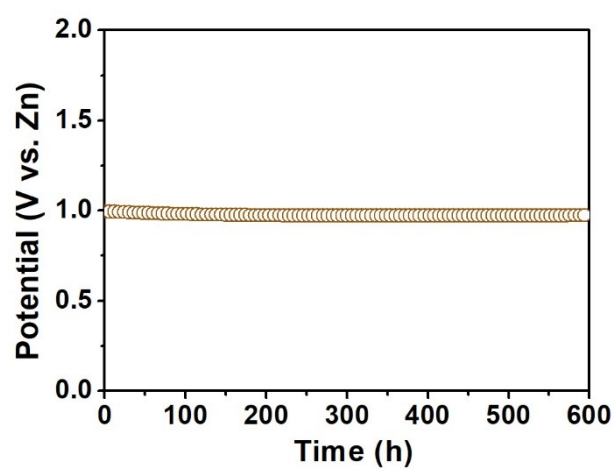
Fig. S17. XRD pattern of Co foam/TP after stability test.



**Fig. S18.** Low- and high-magnification SEM images for Co foam/TP after stability test.

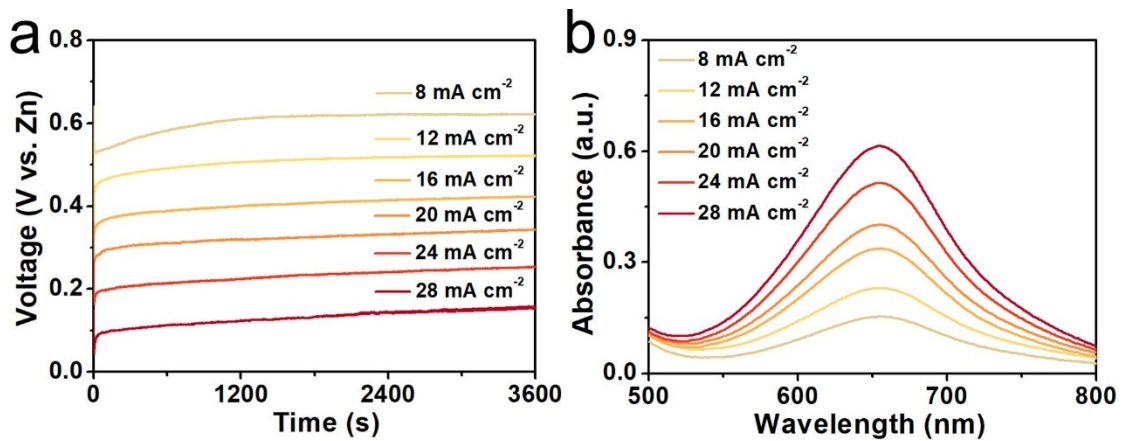


**Fig. S19.** LSV curves of Co foam/TP in 0.1 M NaOH with 0.1 M NO<sub>3</sub><sup>-</sup> before and after stability test.



**Fig. S20.** Open circuit voltage of the assembled Zn-NO<sub>3</sub><sup>-</sup> battery.





**Fig. S21.** (a) Chronopotentiometry curves of Co foam/TP-based Zn-NO<sub>3</sub><sup>-</sup> battery system and (b) corresponding UV-vis absorption spectra for electrogenerated NH<sub>3</sub>.

**Table S1.** Comparison of the catalytic performances of Co foam/TP with other reported  $eNO_3^-RR$  Co-based catalysts.

Catalyst	Electrolyte	Potential (V vs. RHE)	NH <sub>3</sub> yield ( $\mu\text{mol h}^{-1} \text{cm}^{-2}$ )	FE (%)	Ref.
Co foam/TP	0.1 M NaOH (0.1 M NaNO <sub>3</sub> )	-0.40	600.6	96.5	This work
Co/Ti	0.05 M Na <sub>2</sub> SO <sub>4</sub> (1.615 mM NaNO <sub>3</sub> )	/	/	62.0	4
Co@NC	0.1 M NaOH (0.1 M NaNO <sub>3</sub> )	-0.50	503.3	96.0	5
Co <sub>3</sub> O <sub>4</sub> /Co	0.1 M Na <sub>2</sub> SO <sub>4</sub> (1000 ppm NaNO <sub>3</sub> )	-0.80	260.6	88.7	6
CoO NC/Graphene	1.0 M NaOH (1.0 M KNO <sub>3</sub> )	-0.72	/	97.8	7
Co/CoO NSA	0.1 M Na <sub>2</sub> SO <sub>4</sub> (3.23 mM NaNO <sub>3</sub> )	-0.65	194.5	93.8	8
Co <sub>2</sub> B@Co <sub>3</sub> O <sub>4</sub> /TM	0.1 M NaOH (0.1 M NaNO <sub>3</sub> )	-0.70	301.8	97.0	9
Co <sub>3</sub> O <sub>4</sub> @NiO	0.5 M Na <sub>2</sub> SO <sub>4</sub> (3.23 mM NaNO <sub>3</sub> )	-0.70	69.0	55.0	10
CoO@NCNT/GP	0.1 M NaOH (0.1 M NaNO <sub>3</sub> )	-0.60	531.8	93.8	11
Fe-Co <sub>3</sub> O <sub>4</sub> /TM	0.1 M PBS (50 mM NaNO <sub>3</sub> )	-0.70	36.7	95.5	12
CoTiO <sub>3-x</sub>	0.1 M NaOH (0.1 M NaNO <sub>3</sub> )	-1.0	858.0	92.6	13
Co-NCNT	0.1 M NaOH (0.1 M NaNO <sub>3</sub> )	-0.60	352.7	92.0	14
PP-Co	0.1 M NaOH (0.1 M NaNO <sub>3</sub> )	-0.60	1100.0	90.1	15
Co@CC	0.1 M NaOH (0.1 M NaNO <sub>3</sub> )	-0.80	600.0	93.4	16

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