

## Supporting Information

### Experimental and theoretical section

**Materials:** Cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\geq 99.0\%$ ), Ammonium fluoride ( $\text{NH}_4\text{F}$ ,  $\geq 99.0\%$ ), Urea ( $\text{H}_2\text{NCONH}_2$ ,  $\geq 99.0\%$ ), Sodium nitrate ( $\text{NaNO}_3$ , 99.99%), Sodium hydroxide ( $\text{NaOH}$ , 97.00%), Sodium hypochlorite ( $\text{NaClO}$ ), Sodium nitroferricyanide dihydrate ( $\text{Na}_2[\text{Fe}(\text{NO})(\text{CN})_5]_2\text{H}_2\text{O}$ , 99.98%), ammonium chloride ( $\text{NH}_4\text{Cl}$ , 99.5%), sulfamic acid (99.999%), Para (dimethylamino) benzaldehyde ( $p\text{-C}_9\text{H}_{11}\text{NO}$ ), N-(1-naphthyl) ethylenediamine dihydrochloride, sulfonamide (98%), phosphoric acid ( $\text{H}_3\text{PO}_4$ , 99%), and sodium sulfate ( $\text{Na}_2\text{SO}_4$ , 99.999%) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. The water used in the experiments was from a microporous purification system and the resistivity was  $18.25 \text{ M}\Omega \text{ cm}^{-1}$ .

**Carbon cloth pretreatment:** The carbon cloths (CC) were infiltrated in  $\text{HNO}_3$  solution at  $85^\circ\text{C}$  for 3 h and washed with distilled water.

A series of measurements of concentrations of relevant substances. The concentration of a series of related substances in electrolytes was determined by UV-Vis spectrophotometry. To dilute the large electrolyte concentration a certain number of times within the detection limit. The specific detection methods are as follows :

Preparation of color-developing agent

**Colorant:** Weigh 2.5 g  $\text{C}_7\text{H}_6\text{O}_3$  and 2.5 g  $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$  into a beaker, add 50 mL ultra-pure water, dissolve until the solid powder disappears, then weigh 1.8 g  $\text{NaOH}$  into the solution, mix well with ultrasound, transfer to a glass bottle covered with tin foil, and store in the refrigerator away from light.

**Oxidizing agent:** Measure 0.64 mL 4 wt%  $\text{NaClO}$  solution into a beaker, add 20 mL ultra-pure water, mix well, transfer to a glass covered with tin foil and store in the refrigerator away from light.

**Catalyst:** Weigh 0.1 g sodium isopropyl, dissolve ultrasonic into 10 mL ultra-pure deionized water, ultrasonic mix well, transfer to a glass bottle covered with tin foil, and store in the refrigerator away from light.

#### Determination of $\text{NH}_4^+$ :

First, a certain amount of electrolyte is removed from the cathode tank with a pipette gun and diluted to 4.0 mL. Then, A mixture of 50  $\mu\text{L}$  oxidizer ( $\text{NaClO}$  4wt%) and 0.75 M  $\text{NaOH}$ , 500  $\mu\text{L}$  colorant (0.40 M  $\text{C}_7\text{H}_5\text{O}_3\text{Na}$  and 0.32 M  $\text{NaOH}$ ), and 50  $\mu\text{L}$  catalyst (1.0 wt%  $\text{Na}_2[\text{Fe}(\text{CN})_5] \text{NO} \cdot \text{H}_2\text{O}$ ) was prepared is accordingly added to the diluted electrolyte and mixed well. The absorbance intensity of the above solution was recorded at 665 nm wavelength after being kept in the dark for 1.0 h. The relevant concentration-absorbance curves were recorded from a series of  $\text{NH}_4\text{Cl}$  solutions with known standard concentrations. The fitted curves were  $y = 0.400x - 0.0194$ ,  $R^2 = 0.998$ .

#### Determination of $\text{NO}_3^-$ :

First, a certain amount of electrolyte is taken from the cathode tank and diluted to 5.0 mL. Then, add 100  $\mu\text{L}$  of 1.0 M  $\text{HCl}$  and 10  $\mu\text{L}$  of 0.8 wt% sulfamic acid solution, mix evenly, hide from light for 15 min, and remove. The UV spectrum was measured and the absorbance intensity of the above solution was recorded at 220 and 275 nm

wavelengths. The final absorbance value is obtained by the following equation:  $A = A_{220\text{nm}} - 2A_{275\text{nm}}$ . The relevant concentration-absorbance curves were recorded from a series of  $\text{NaNO}_3$  solutions with known standard concentrations, and the fitted curves were  $y = 0.250x + 0.00123$ ,  $R^2 = 0.999$ .

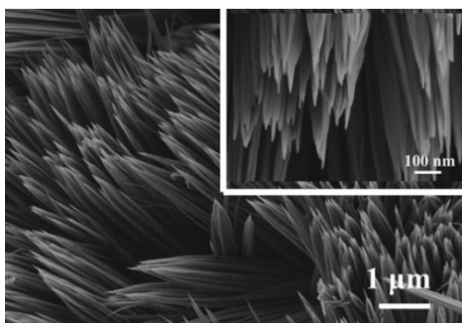
**Determination of  $\text{NO}_2^-$ :**

Remove 500 mL electrolyte from the cathode pool, dilute to 5.0 mL, add 100  $\mu\text{L}$  color developer (containing 4.0 g  $\text{C}_6\text{H}_4\text{SO}_2\text{N}_2\text{H}_4$ , 0.20 g  $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{N}_2$ , 10 mL  $\text{H}_3\text{PO}_4$  ( $\rho = 1.70 \text{ g mL}^{-1}$ ) and 50 mL  $\text{H}_2\text{O}$ ), mix well, and remove after 15 min of dark color development. The corresponding concentration-absorbance curve was recorded by a series of  $\text{NaNO}_2$  solutions with known standard concentrations. The fitting curve was  $y = 0.990x + 0.00695$ ,  $R^2 = 0.999$

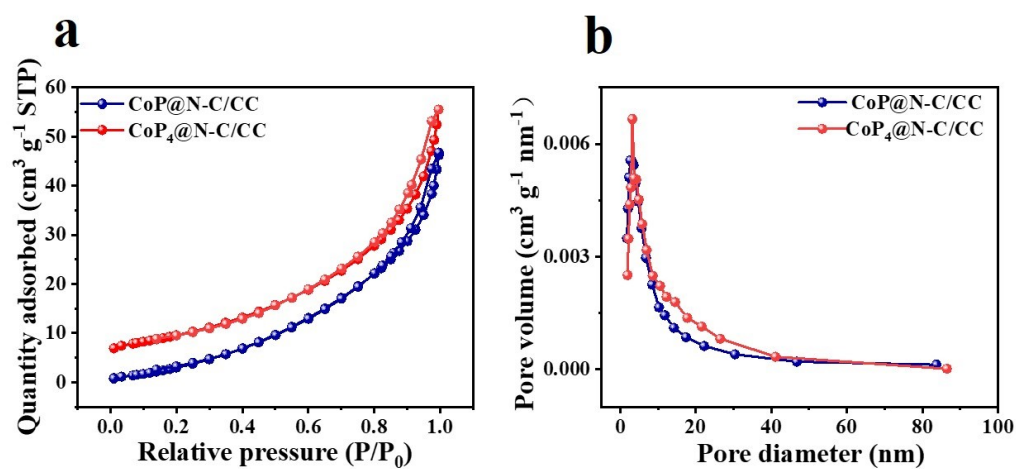
**Determination of  $\text{N}_2\text{H}_4$ :**

Remove 2.0 mL electrolyte from the cathode electrolytic cell, add 2.0 mL color developer (containing 6.0 g p- $\text{C}_9\text{H}_{11}\text{NO}$ , 10 mL  $\text{HCl}$ , and 300 mL  $\text{C}_2\text{H}_5\text{OH}$ ), hide from light for 15 min, and then perform UV-visible spectrum test. The absorbance intensity of the above solution was recorded after 15 minutes at 455 nm wavelength. The relevant concentration-absorbance curves were recorded from a series of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  solutions with known standard concentrations. The fitted curves were  $y = 0.329x + 0.0764$ ,  $R^2 = 0.997$

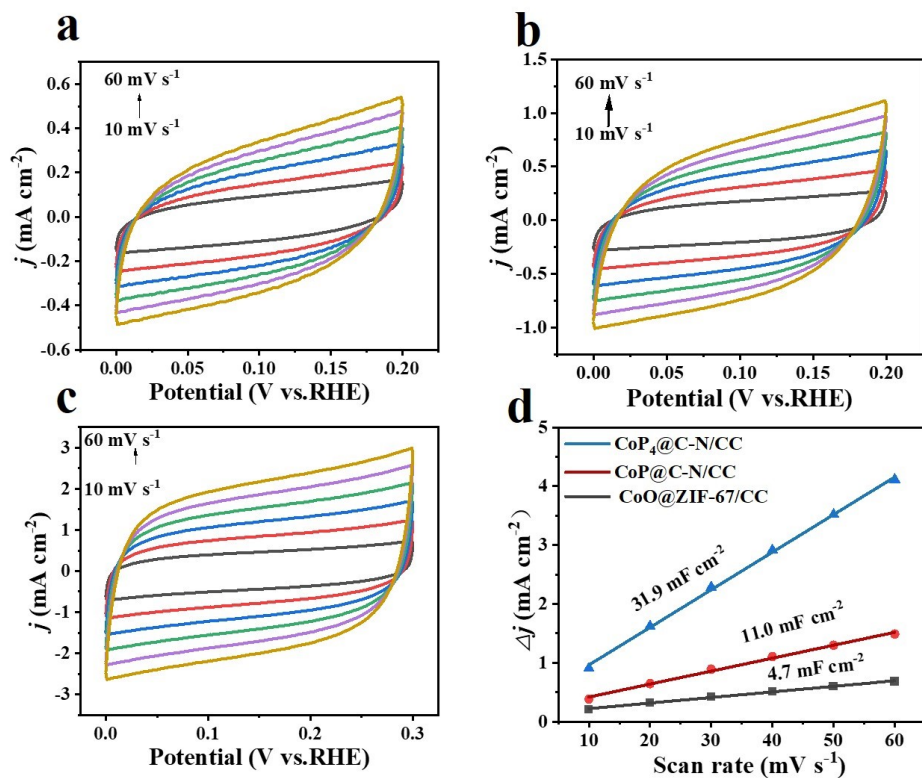
## Figures



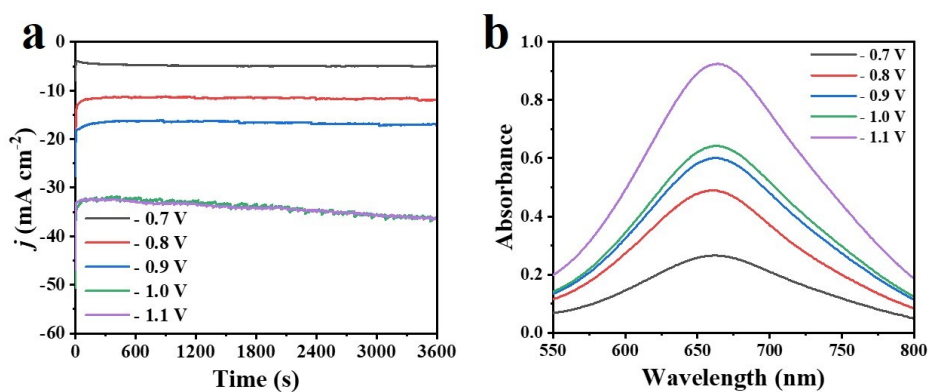
**Fig. S1.** SEM images of Co(OH)F/CC.



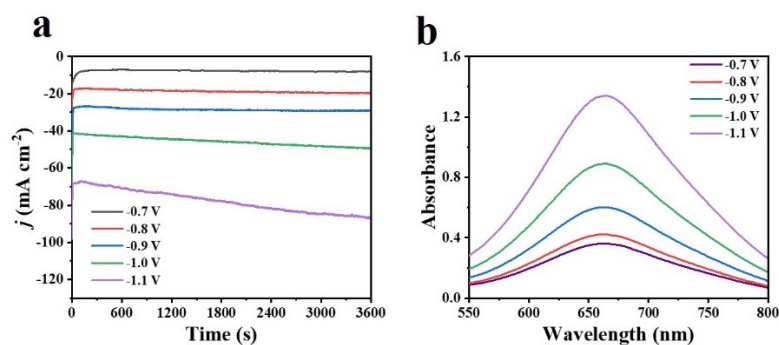
**Fig. S2.** (a)  $\text{N}_2$  sorption isotherms of CoP@N-C/CC and CoP<sub>4</sub>@N-C/CC (b) pore-size distribution of CoP@N-C/CC and CoP<sub>4</sub>@N-C/CC.



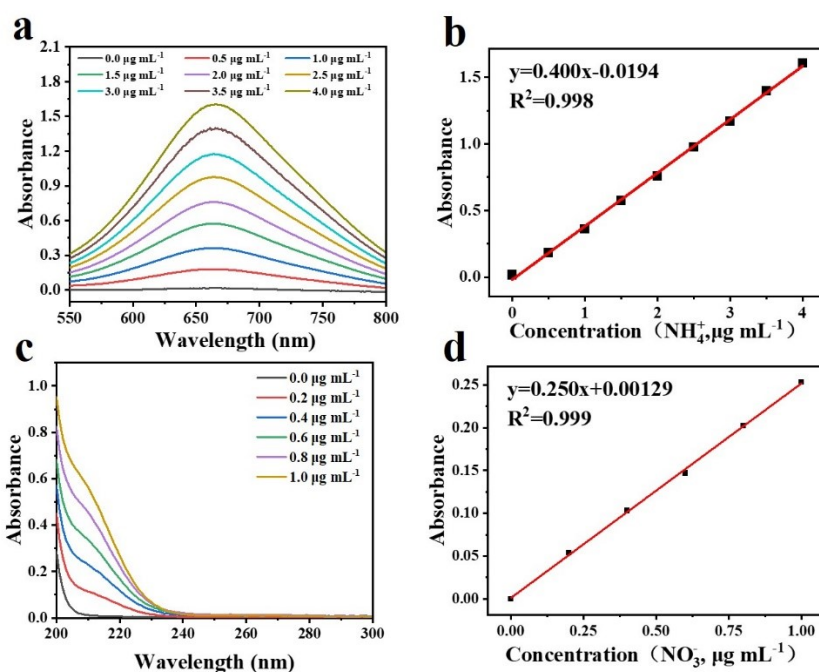
**Fig. S3.** (a)-(c) The CV curves of CoO@ZIF-67/CC, CoP@N-C/CC, and CoP<sub>4</sub>@N-C/CC rhombic dodecahedrons at a scan rate of 10 to 60 mV s<sup>-1</sup> in 0.1 M KOH. (d) The linear relationship between the current density difference ( $\Delta j$ ) and the sweep speed of CoO@ZIF-67/CC, CoP@N-C/CC, and CoP<sub>4</sub>@N-C/CC.



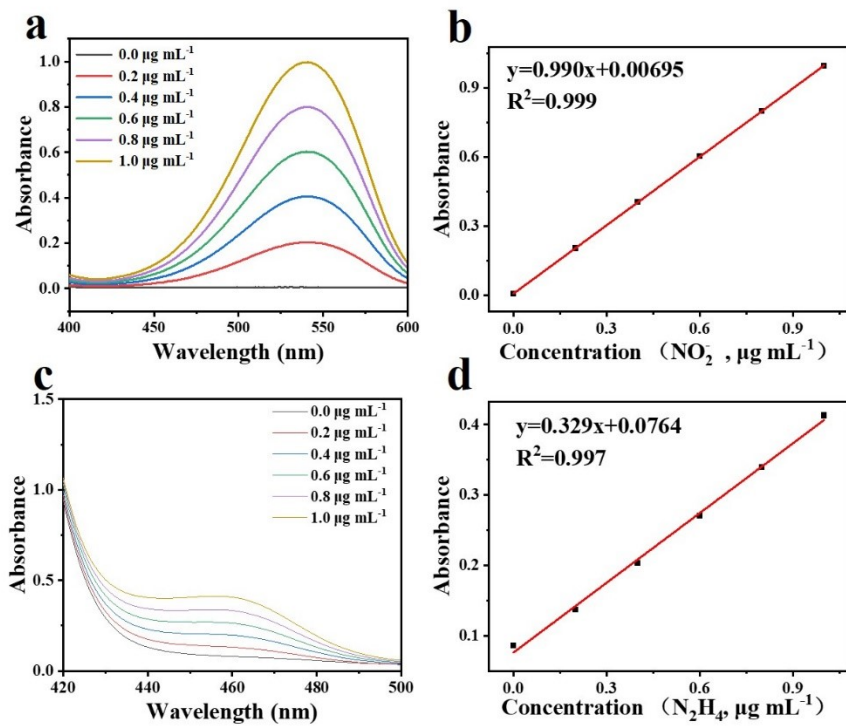
**Fig. S4.** CoO@ZIF-67 (a) Chronocurrent determination at a specific potential, (b) The UV-vis absorption spectra of NH<sub>4</sub><sup>+</sup>.



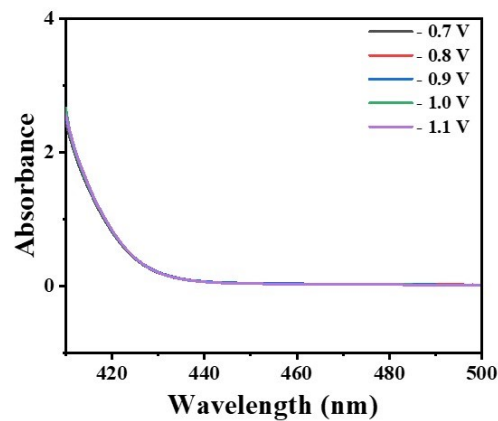
**Fig. S5.** CoP@N-C (a) Chronocurrent determination at a specific potential, (b) The UV-vis absorption spectra of  $\text{NH}_4^+$ .



**Fig. S6.** (a) UV-Vis absorption spectra with  $\text{NH}_4^+$  ions in 0.1 M  $\text{Na}_2\text{SO}_4$  after incubation for 60 min at room temperature. (b) Calibration curve used for calculation of  $\text{NH}_4^+$  concentrations. (c) UV-Vis absorption spectra with  $\text{NO}_3^-$  ions in 0.1 M  $\text{Na}_2\text{SO}_4$  after incubation for 15 min at room temperature. (d) Calibration curve used for calculation of  $\text{NO}_3^-$  concentrations.



**Fig. S7.** (a) UV-Vis absorption spectra with  $\text{NO}_2^-$  ions in  $0.1 \text{ M Na}_2\text{SO}_4$  after incubation for 25 min at room temperature. (b) Calibration curve used for calculation of  $\text{NO}_2^-$  concentrations. (c) UV-Vis absorption spectra with  $\text{N}_2\text{H}_4$  ions in  $0.1 \text{ M Na}_2\text{SO}_4$  after incubation for 20 min at room temperature. (d) Calibration curve used for calculation of  $\text{N}_2\text{H}_4$  concentrations.



**Fig. S8.**  $\text{CoP}_4@\text{N-C}$  The UV-vis absorption spectra of  $\text{N}_2\text{H}_4$ .

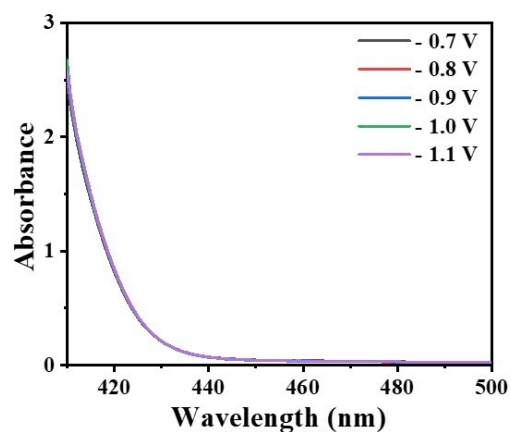


Fig. S9. CoP@ZIF-67 The UV-vis absorption spectra of  $N_2H_4$ .

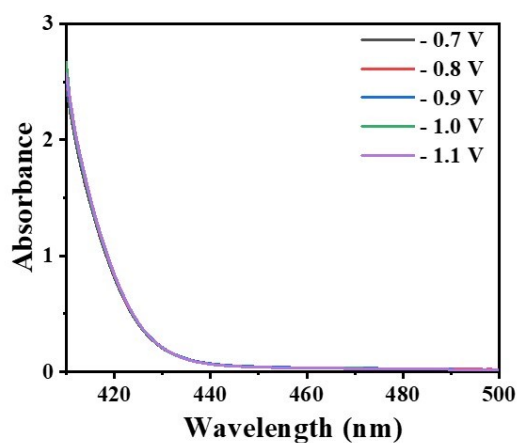


Fig. S10. CoO@ZIF-67 The UV-vis absorption spectra of  $N_2H_4$ .

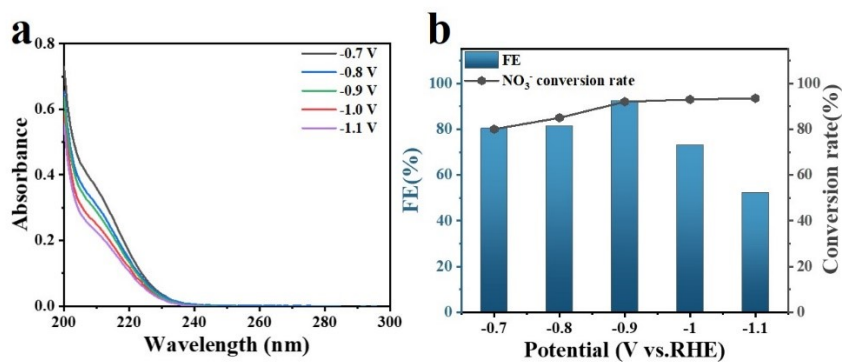


Fig. S11. (a) CoP<sub>4</sub>@N-C The UV-vis absorption spectra of  $NO_3^-$ ; (b) FE and  $NO_3^-$  conversion rate of CoP<sub>4</sub>@N-C/CC.

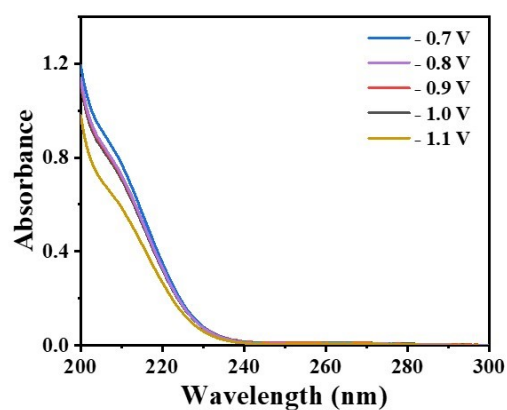


Fig. S12.  $\text{CoP@N-C}$  The UV-vis absorption spectra of  $\text{NO}_3^-$ .

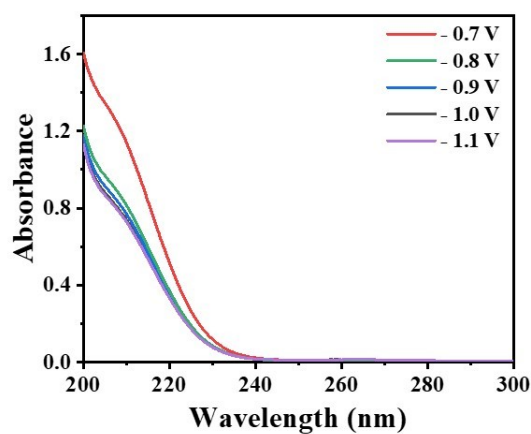


Fig. S13.  $\text{CoO@ZIF-67}$  The UV-vis absorption spectra of  $\text{NO}_3^-$ .

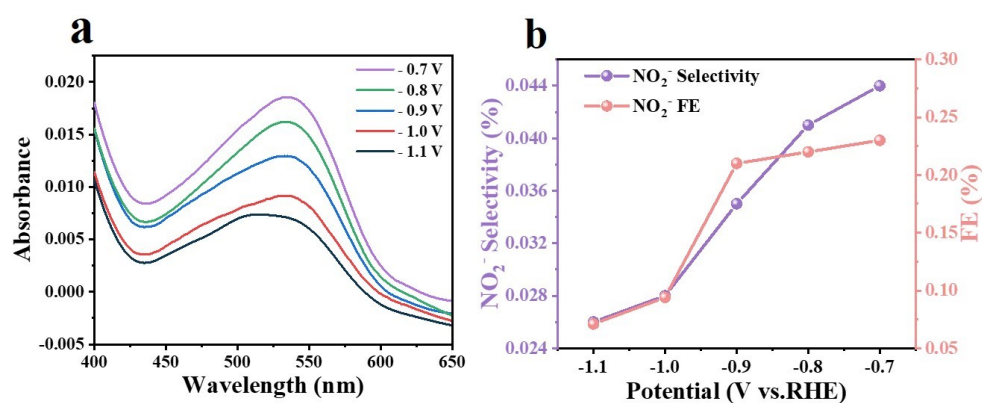
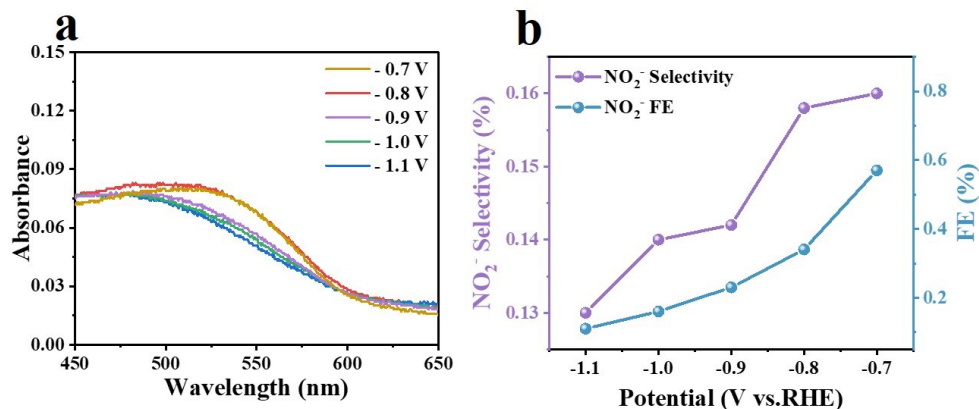
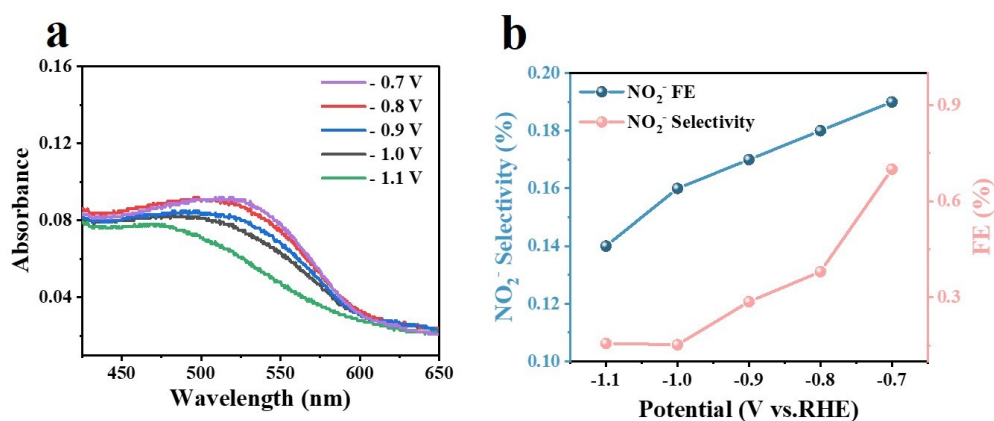


Fig. S14.  $\text{CoP}_4@N-C$  (a) The UV-vis absorption spectra of  $\text{NO}_2^-$ , (b)  $\text{NO}_2^-$  selectivity and FE.

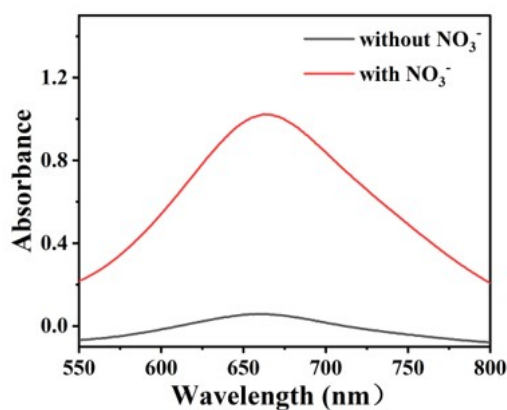




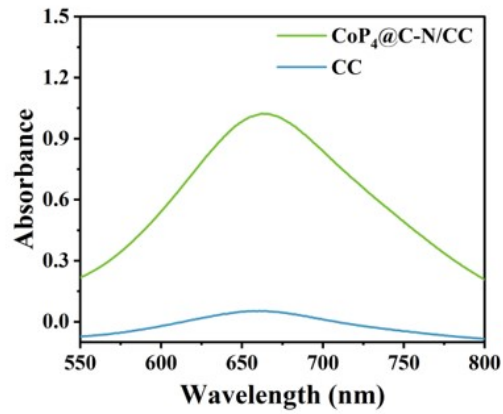
**Fig. S15.** CoP@N-C (a) The UV-vis absorption spectra of  $\text{NO}_2^-$ , (b)  $\text{NO}_2^-$  selectivity and FE.



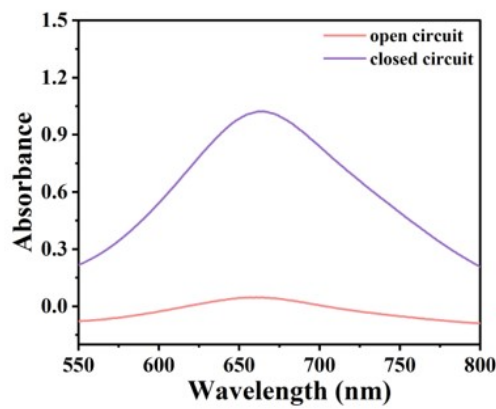
**Fig. S16.** CoO@ZIF-67 (a) The UV-vis absorption spectra of  $\text{NO}_2^-$ , (b)  $\text{NO}_2^-$  selectivity and FE.



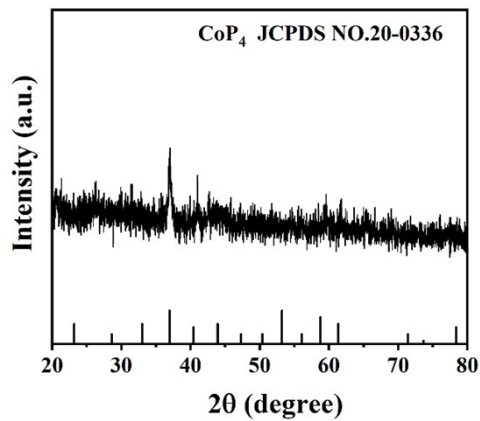
**Fig. S17.** The UV-vis absorption spectra of  $\text{NH}_4^+$  with  $\text{NO}_3^-$  and without  $\text{NO}_3^-$ .



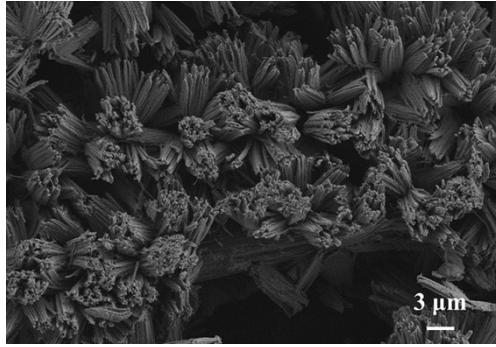
**Fig. S18.** The UV-vis absorption spectra of  $\text{NH}_4^+$  over  $\text{CoP}_4@\text{N-C/CC}$  and CC.



**Fig. S19.** The UV-vis absorption spectra of  $\text{NH}_4^+$  with open circuit and closed circuit.



**Fig. S20.** XRD pattern of  $\text{CoP}_4@\text{N-C/CC}$  after long-time stability test.



**Fig. S21.** SEM pattern of CoP<sub>4</sub>@N-C/CC after long-time stability test.

**Table S1.** Comparison of different electrocatalysts reported in NO<sub>3</sub><sup>-</sup>RR under ambient conditions.

<b>Catalyst</b>	<b>Electrolyte</b>	<b>NH<sub>3</sub> yield rate</b>	<b>FE(%)</b>	<b>Ref.</b>
CoO@ZIF-67/CC	0.1 M Na <sub>2</sub> SO <sub>4</sub>	423.35 μmol h <sup>-1</sup> cm <sup>-2</sup>	49.6%	This work
CoP@N-C/CC	0.1 M Na <sub>2</sub> SO <sub>4</sub>	466.05 μmol h <sup>-1</sup> cm <sup>-2</sup>	75.8%	This work
CoP <sub>4</sub> @N-C/CC	0.1 M Na <sub>2</sub> SO <sub>4</sub>	610.20 μmol h <sup>-1</sup> cm <sup>-2</sup>	92.3%	This work
Fe <sub>2</sub> O <sub>3</sub> NRs/CC	0.5 M Na <sub>2</sub> SO <sub>4</sub>	328.17 μmol h <sup>-1</sup> cm <sup>-2</sup>	/	1
Cu@Cu <sub>2</sub> O	0.1M Na <sub>2</sub> SO <sub>4</sub>	326.7 μmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	80.6%	2
Cu <sub>x</sub> Co <sub>y</sub> HHTP	0.5 M Na <sub>2</sub> SO <sub>4</sub>	299.9 μmol h <sup>-1</sup> cm <sup>-2</sup>	96.4%	3
30Cu-Co <sub>3</sub> O <sub>4</sub>	0.1 M KOH	0.584 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	92.4%	4
La <sub>2</sub> Cu <sub>0.8</sub> Co <sub>0.2</sub> O <sub>4</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	0.0699 mmol·h <sup>-1</sup> <sup>1</sup> ·mg <sup>-1</sup>	99.7%	5
Au–Cu NWs/CF	0.1M Na <sub>2</sub> SO <sub>4</sub>	5336.0 μg h <sup>-1</sup> cm <sup>-2</sup>	84.1%	6

## References:

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