

## Supporting Information

### Ni-loaded Co-NC Catalysts for Promoting Electrocatalytic Nitrate Reduction to Ammonia

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## Experimental measurement

Experimental measurements were performed in the workstation of CHI760E, used for three-electrode test system. Platinum wire as counter electrode, Ag/AgCl as reference electrode, 0.1 M KOH & 0.1 M KNO<sub>3</sub> as electrolyte. 10 mg of catalyst and 30 μL of Nafion solution (5 wt%) were dispersed in 970 μL of isopropanol and sonicated for 1 h to obtain a homogeneous suspension. Then, 20 μL of catalyst dispersion was dropped onto a smooth glassy carbon working electrode (effective area 0.196 cm<sup>2</sup>), which was naturally dried and used as the working electrode. All potentials obtained in the experiments were converted to reversible hydrogen electrodes (RHE).

Electrocatalytic NO<sub>3</sub>RR is conducted on a CHI760E electrochemical workstation. All electrochemical measurements were conducted on three-electron setup using a rotating ring-disk electrode (RDE). Platinum wire as counter electrode, Ag/AgCl as reference electrode, glassy carbon with catalyst dispersion as working electrode (effective area 0.196 cm<sup>2</sup>), 0.1 M KOH & 0.1 M KNO<sub>3</sub> as electrolyte. All potentials were recorded at the reversible hydrogen electrode (RHE). The potentials are expressed by the Nernst equation:

$$E \text{ (V vs. RHE)} = E \text{ (V vs. Ag/AgCl)} + 0.0591 \times \text{pH} + 0.197$$

Synthesis of the CoZn@ZIF Precursor. CoZn@ZIF precursor synthesized by solution-phase method. First, 0.119 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.2328 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in 10 mL deionized water. 3.628 g 2-methylimidazole was dissolved in 70 mL deionized water. After stirring for 1 h, the two solutions were rapidly mixed together. Then, the mixture was placed at room temperature overnight. Finally, the

resulting violet precipitates were collected filtration, washed with ethanol three times, and then dried under vacuum at 60°C overnight.

Synthesis of the NiCoZn@ZIF Precursor. First, 200 mg CoZn@ZIF precursor was dispersed in 25 mL of ethanol. Different amounts of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol; 0.2 mmol; 0.3mmol; 0.4 mmol) were dissolved in 12.5 mL of ethanol, respectively. To guarantee the equilibrium of Ni<sup>2+</sup> adsorption, the Ni<sup>2+</sup> solution was added dropwise to the CoZn@ZIF precursor solution by ultrasonication for 10 min, followed vigorous stirring for 1 h. Finally, the resulting violet precipitates were collected filtration, washed with ethanol three times, and then dried under vacuum at 60°C overnight.

Synthesis of the NiCo-NC Catalysts.

NiCo-NC catalysts were synthesized by pyrolysis of NiCoZn@ZIF powders in a tube furnace under Ar atmosphere at 900 °C for 2 h with a ramp rate of 5 °C min<sup>-1</sup>.

**Determination of NH<sub>3</sub>:** Determination by indophenol blue and spectrophotometry. Dissolve 5 g of sodium salicylate and 5 g of sodium tartrate in 100 mL of 1 M KOH as a colour developer (A), The colour developer (B) was then prepared by adding 5 mL of NaClO (14% active chlorine) to 100 mL of deionised water. Finally, 0.2 g of sodium nitrosferricyanide was dissolved in 20 mL of deionised water as colour developer C. Concentrations of 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 µg mL<sup>-1</sup> of ammonium chloride were prepared as standard solutions. Add 2 mL of standard solution to the test tube, then add 2 mL of colour developer A, 1ml of colour developer B and 0.2mL of colour developer C in that order, The mixed solution was shaken well. After standing for 1 hour, the mixed solution was transferred to a cuvette and detected

by UV-Vis spectrophotometer. UV-Vis absorption spectra were obtained from the absorbance at 655 nm. The concentration-absorbance curve (Figure S4) was obtained using a series of standard  $\text{NH}_4\text{Cl}$  solutions and fitted by linear regression:  $y=0.38645x+0.00755; R^2 = 0.9999$ .

The  $\text{NH}_3$  production rate is calculated as follows.

$$\text{NH}_3 \text{ yield} = (c \times V) / (t \times A) \quad (1)$$

$t$  is the electrochemical test time (h) and  $A$  is the effective geometric area of the working electrode ( $\text{cm}^2$ ). where  $c$  is the measured ammonia concentration and  $V$  is the volume (mL)

$$\text{FE} = 8F \times c \times V / 17 \times Q \quad (2)$$

where one  $\text{NH}_3$  molecule requires the production of 8 electrons,  $F$  is Faraday's constant and  $Q$  is the amount of electricity consumed in the electrochemical test.

**Determination of  $\text{NO}_2^-$ :** using indophenol blue and spectrophotometric methods.

To 50 mL of concentrated  $\text{HCl}$ , add 0.5 g of sulfa and fix with water to 100 mL. mix well to give colour developer A. Add 100 mg of naphthylenediamine hydrochloride to 50 mL of water and add water to 100 mL, mix well for colour developer B. The concentrations of 0, 0.1, 0.2, 0.4, 0.6, 0.8 and  $1.0 \mu\text{g mL}^{-1}$  sodium nitrite were prepared as standard solutions. Then, 4mL of the electrolytic solution was electrolyzed for a certain time and 1mL of colour developer A was added, shaken well and left for ten minutes. 100 $\mu\text{L}$  of colour developer B was then added to the above mixed solution, shaken well and left for twenty minutes, and the absorbance of the solution was measured at 540 nm by UV-Vis spectrophotometer. A series of standard  $\text{NaNO}_2$

solutions were used to obtain a concentration-absorbance curve (Figure S5), which was fitted by linear regression,  $y = 0.83521x + 0.01782$ ;  $R^2 = 0.9995$ .

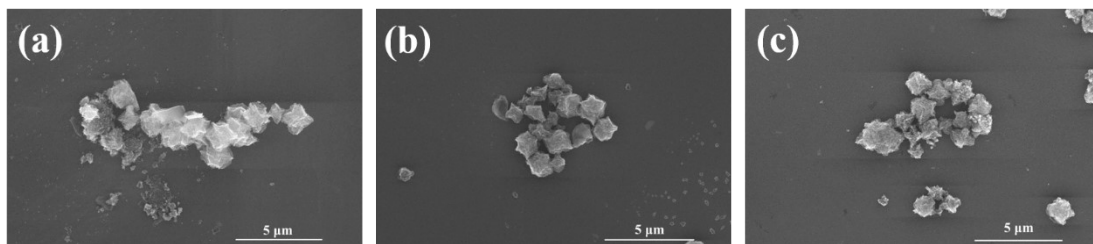
$$\text{NO}_2^- \text{ yield} = (c \times V) / (t \times A) \quad (1)$$

$t$  is the electrochemical test time (h) and  $A$  is the effective geometric area of the working electrode ( $\text{cm}^2$ ), where  $c$  is the measured ammonia concentration and  $V$  is the volume (mL).

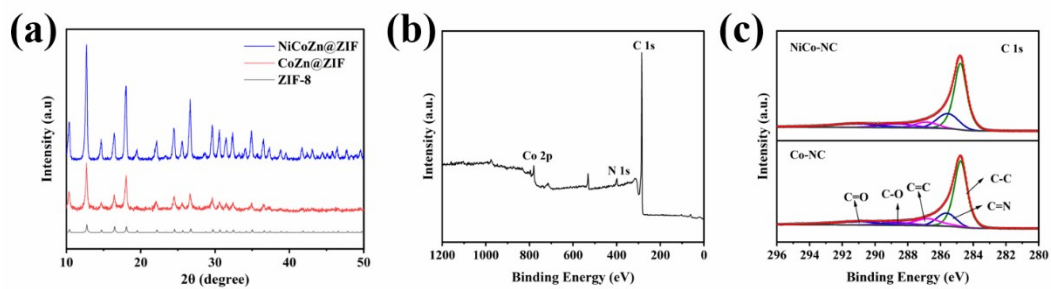
$$\text{FE} = 2F \times c \times V / 46 \times Q \quad (2)$$

where one  $\text{NO}_2^-$  molecule requires the production of 2 electrons,  $F$  is Faraday's constant and  $Q$  is the amount of electricity consumed in the electrochemical test.

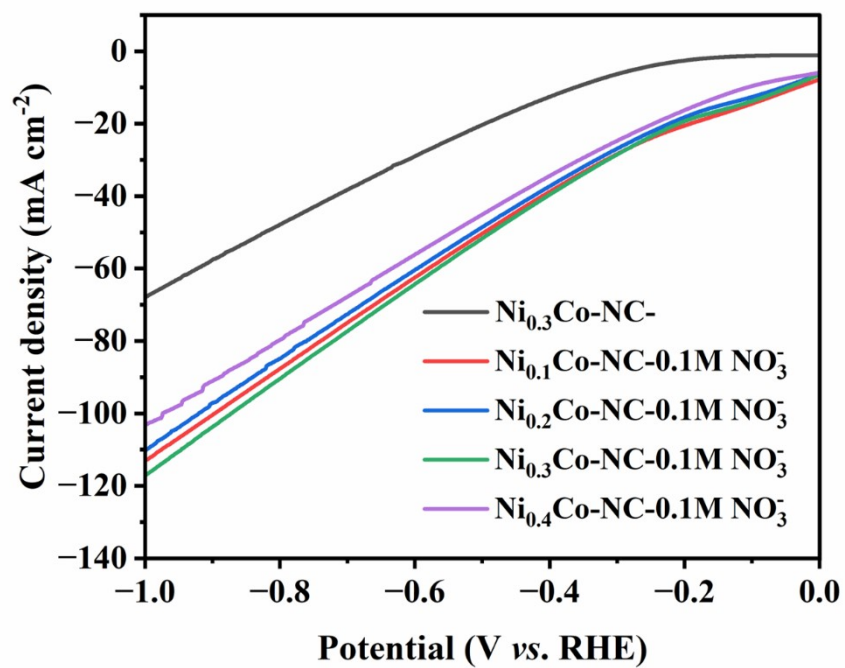
**Isotope labeling:** To find the source of ammonia, an isotopically labeled nitrate reduction experiment was conducted using 99atom%  $\text{K}^{15}\text{NO}_3$  as the feed N source. 0.1M  $\text{KOH}$  &  $\text{K}^{15}\text{NO}_3$  was used as electrolyte. After electroreduction, the obtained  $^{15}\text{NH}_4^+ - ^{15}\text{N}$  electrolyte was taken out, and the pH value was adjusted by 4 M  $\text{H}_2\text{SO}_4$  to a weak acid (PH=2). Further quantification with  $\text{DMSO-D}_6$  (deuterated dimethyl sulfoxide). 0.5ml  $^{15}\text{NH}_4^+ - ^{15}\text{N}$  solution was mixed with 50  $\mu\text{L}$   $\text{DMSO-D}_6$  for  $^1\text{H}$  NMR detection. The position of the peak is observed, a two-state peak of  $^{15}\text{NH}_4^+ - ^{15}\text{N}$  ( $\delta = 7.00$  and  $6.88$  ppm). Similarly, when  $\text{K}^{14}\text{NO}_3$  is used as the feed N source, the triplet peaks of  $^{14}\text{NH}_4^+ - ^{14}\text{N}$  ( $\delta = 7.03$ ,  $6.95$  and  $6.86$  ppm) are also detected by this method.



**Figure S1.** CoZn@ZIF with different Ni loadings of (a) 0.1 mmol; (b) 0.2 mmol; (c) 0.4 mmol

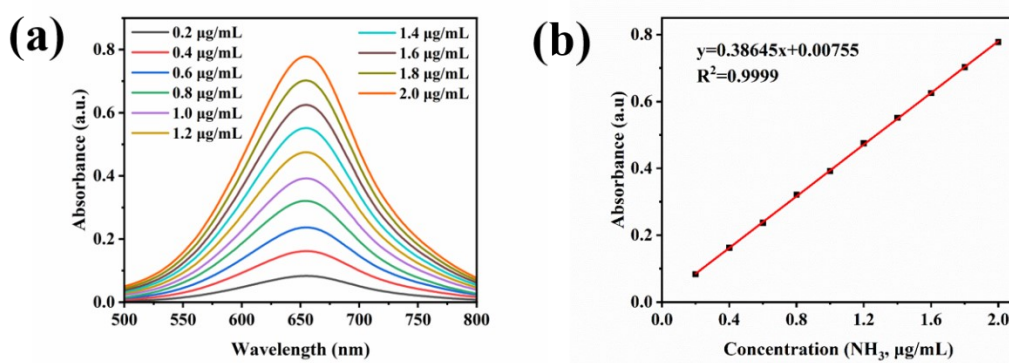


**Figure S2.** (a) XRD spectra of CoZn@ZIF; ZIF-8 and NiCoZn@ZIF; (b) XPS survey spectra of Co-NC; (c) XPS spectra of C 1s for NiCo-NC and Co-NC.

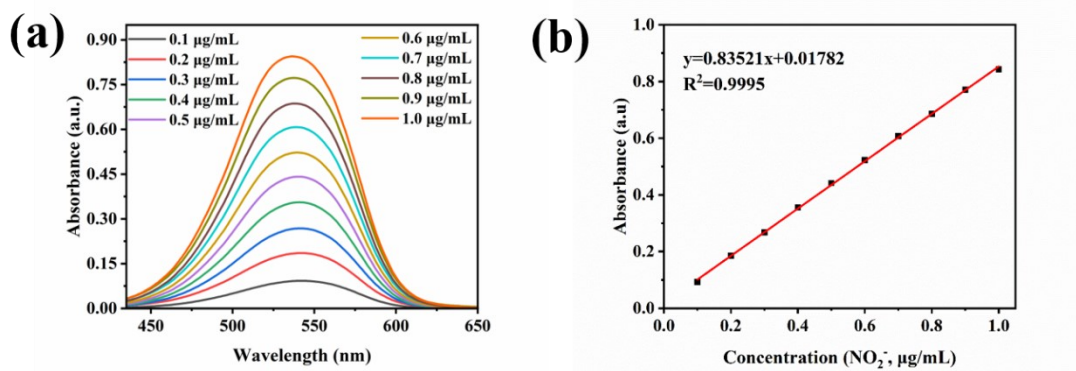


**Figure S3.** LSV curves of different Ni loadings in electrolytes containing 0.1 M KOH & 0.1M KNO<sub>3</sub>.

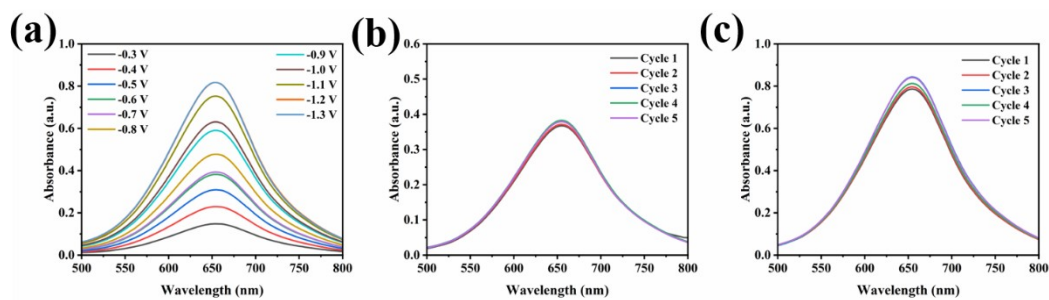




**Figure S4.** Plotting of standard curve of  $\text{NH}_3$  in 0.1 M KOH &  $\text{KNO}_3$  solution.



**Figure S5.** Plotting of standard curve of  $\text{NO}_2^-$  in 0.1 M KOH& $\text{KNO}_3$  solution



**Figure S6.** (a) UV-Vis absorption spectra of  $\text{NH}_4^+$  of NiCo-NC at different potentials (dilute eightfold); (b)(c) UV-Vis Stability tests with five cycles at applied potentials of -0.6V and -1.1V, respectively(dilute eightfold).

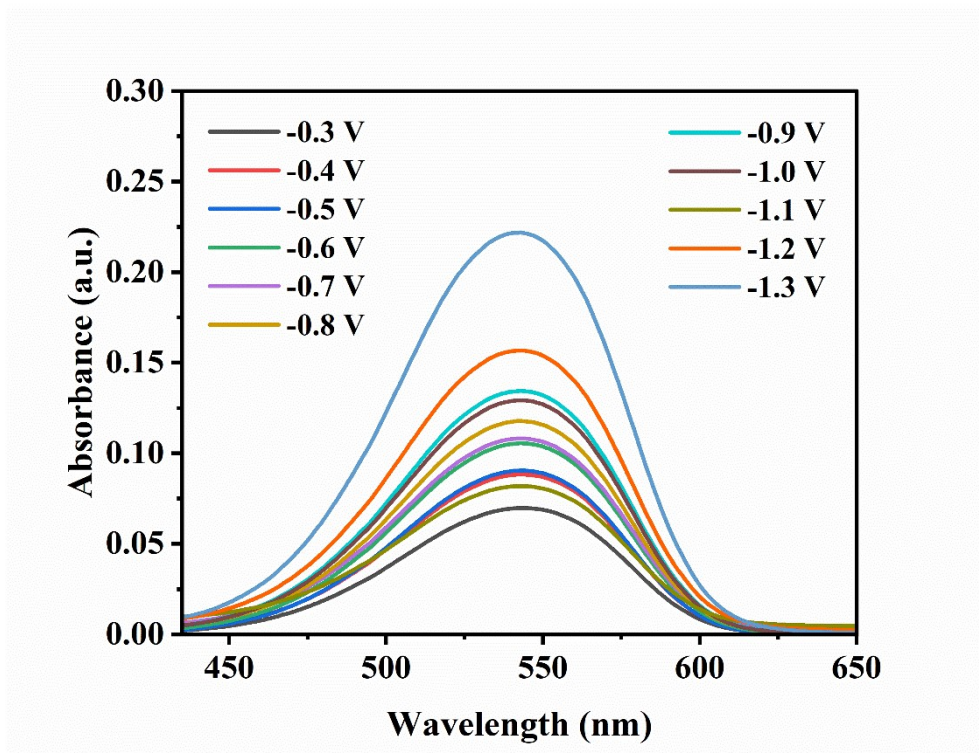


Figure S7. UV-Vis absorption spectra of produced  $\text{NO}_2^-$  (dilute eightfold).

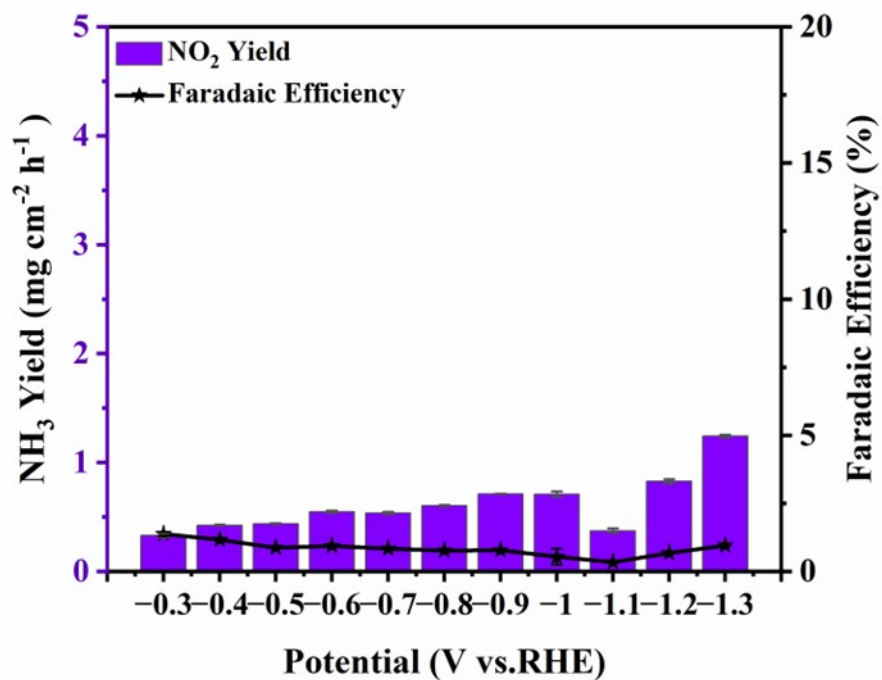


Figure S8. Ni loaded Co-NC-nitrite yield and FE.