

# Constructing Well-dispersed Active Phase via Spontaneous Redox for Electrochemical Nitrate Reduction to Ammonia

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## Experimental section

### Materials

All chemical reagents used in this study were purchased from Aladdin (analytical grade).

### Synthesis of the electrocatalysts

**Synthesis of ZIF-67:** 1.98 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 80 mL of methanol and labeled as solution A; 4 g of 2-Methylimidazole was dissolved in 80 mL of methanol and labeled as solution B. Subsequently, solution B was slowly dropped into solution A with stirring for 24 h. The mixture was centrifuged with methanol for 6 times and vacuum-dried overnight. The final product underwent heat treatment in two stages, being held at 550 °C ( $2\text{ °C min}^{-1}$ ) for 1 h, and then at 950 °C ( $5\text{ °C min}^{-1}$ ) in an Ar environment for 3 h.

**Synthesis of Co/NCD@Co(OH)<sub>2</sub>:** 100 mg of Co-ZIF-67 was dispersed in 50 mL of 0.1 M  $\text{NaNO}_3$  solution by ultrasonication (100 W) for 30 mins. The resulting dispersion was heated at 100 °C with stirring for 2 hours. After cooling to room temperature, the dispersion was centrifuged with water three times and ethanol twice (The liquid supernatant from the first centrifugation was retained for inspecting the  $\text{NO}_2^-$  originated from the spontaneous redox between  $\text{NO}_3^-$  and metallic Co), and finally dried in a vacuum drying oven overnight.

**Synthesis of Co/NCD-A:** The Co/NCD@Co(OH)<sub>2</sub> was dispersed in 1 M nitric acid, and heated at 80 °C for 6 hours during stirring. Hereafter, the mixture was centrifuged 3 times with water and 3 times with ethanol, and dried overnight under vacuum.

**Synthesis of Co(OH)<sub>2</sub>:** 4.4 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 150 mL of deionized water and labeled as solution A; 10 g of NaOH was dissolved in 50 mL of deionized water and designated as solution B.

Subsequently, solution B was gradually dropped into solution A with continuous stirring for 2 h. Then, the resultant product was centrifuged and washed with water three times, followed by vacuum drying throughout the night.

### **Preparation of electrodes**

To prepare the catalyst-coated carbon paper (CP) electrode, taking Co/NCD@Co(OH)<sub>2</sub> as an example, 1 mg of Co/NCD@Co(OH)<sub>2</sub> powder dispersed in 0.7 mL ethanol solution and 0.3 mL deionized water with 20 μL of 5 wt % Nafion by ultrasonic treatment for 1 hours until the catalyst was evenly dispersed. The catalyst ink is uniformly dripped on one side of 1×1 cm<sup>2</sup> CP.

### **Electrochemical measurements**

A CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai, China) was used for electrochemical measurements. A platinum wire was used as a counter electrode, and a saturated mercurous chloride electrode (SCE) was used as a reference electrode. All the potentials were calibrated with respect to the reversible hydrogen electrode (RHE) according to the following equation:  $E_{\text{vs. RHE}} = E_{\text{vs. SCE}} + E_{\text{SCE}} + 0.059 \text{ pH}$ . The sweep speed of the linear sweep voltammetry (LSV) process is 5 mV/s. All current densities are normalized to the geometry area of the electrodes. Ar was used as carrier gas with a flow velocity of 20 sccm.

### **Quantification of products**

The FE of the gaseous products was monitored using online GC with flam ionization detector. The Ar was used as a carrier with a flow velocity of 20 sccm.

NH<sub>3</sub> and NO<sub>2</sub><sup>-</sup> were quantified by UV-Vis spectrophotometry and calibration curve plotted by different concentrations. For NH<sub>3</sub>, 0.1 mL electrolyte was diluted to 10 mL. Nessler's reagent (0.2 mL) was added to the above solution and shaken for 20 min. The absorbance at 420 nm was recorded for calculation. The calibration curve of NH<sub>3</sub> was plotted by the concentration of NH<sub>3</sub> standard solution (1, 3, 5, 7 and 9 μg/ml with the same content of Nessler's reagent) versus the absorbance at a wavelength of 420 nm. For NO<sub>2</sub><sup>-</sup>, the color-developing agent were prepared by 25 ml phosphoric acid, 10 g p-amino benzenesulfonamide, 0.5 g N-(1-naphthyl)-ethylenediamine dihydrochloride and 250 ml H<sub>2</sub>O. 0.05 mL electrolyte was mixed with 0.5 mL phosphoric acid for acidification and diluted to 10 mL with water. 0.2 mL of color-developing

agent was added and shaken for 20 min. The calibration curve was plotted using a nitrite standard solution (0.1, 0.5, 1, 2 and 3  $\mu\text{g/ml}$  with the same content of color-developing agent) and the absorbance at a wavelength of 540 nm. For the  $^1\text{H}$  NMR, a series of  $\text{NH}_4^+$  standard solutions (10, 50, 100, 150 and 200  $\mu\text{g/ml}$   $^{14}\text{NH}_4^+$ ) were prepared by 50 ml 0.5 M  $\text{Na}_2\text{SO}_4$  + 400 ppm maleic acid. 0.5 ml of the above  $\text{NH}_4^+$  standard solutions were mixed with 50  $\mu\text{l}$   $\text{D}_2\text{O}$  for  $^1\text{H}$  NMR (600 MHz) measurement after solvent suppression. The calibration curve was plotted by the peak ratio of  $\text{NH}_4^+$  to maleic acid. For quantification, 10 ml electrolyte was mixed with 15 ml of 0.5 M  $\text{H}_2\text{SO}_4$ , then the above mixture was diluted to 50 ml by 0.5 M  $\text{Na}_2\text{SO}_4$  with external standards of maleic acid (400 ppm). Subsequently, 0.5 ml of the above solution was abstracted and mixed with 50  $\mu\text{l}$   $\text{D}_2\text{O}$  for  $^1\text{H}$  NMR measurement after solvent suppression. The peak ratio of  $\text{NH}_4^+$  to maleic acid were recorded and the  $\text{NH}_4^+$  were quantified according to the calibration curve. An isotope-labeling experiment was conducted by using  $\text{Na}^{15}\text{NO}_3$  (98 atom%  $^{15}\text{N}$ ) as a nitrogen source.

The yield-rate of  $\text{NH}_3$  was calculated as follow:

$$v_{\text{NH}_3} = \frac{c_{\text{NH}_3} \times V}{M_{\text{NH}_3} \times t \times S}$$

The FE of  $\text{NH}_3$  was calculated as follow:

$$FE_{\text{NH}_3} = \left( \frac{c_{\text{NH}_3} \times V \times 8 \times F}{M_{\text{NH}_3} \times Q} \right) \times 100\%$$

The FE of  $\text{NH}_2$  was calculated as follow:

$$FE_{\text{NO}_2^-} = \left( \frac{c_{\text{NO}_2^-} \times V \times 8 \times F}{M_{\text{NO}_2^-} \times Q} \right) \times 100\%$$

The partial current density of  $\text{NH}_3$  was calculated as follow:

$$J_{\text{NH}_3} = \frac{v_{\text{NH}_3} \times 3600 \times 8}{F}$$

Where C and M are the concentration and the mole mass of  $\text{NH}_3$  or  $\text{NO}_2^-$ , respectively; V is the volume of electrolyte; Q is the charge consumed during the chronoamperometric test; F is the Faradaic constant; t is the time of chronoamperometric test, S is the loading geometric area of the electrode.

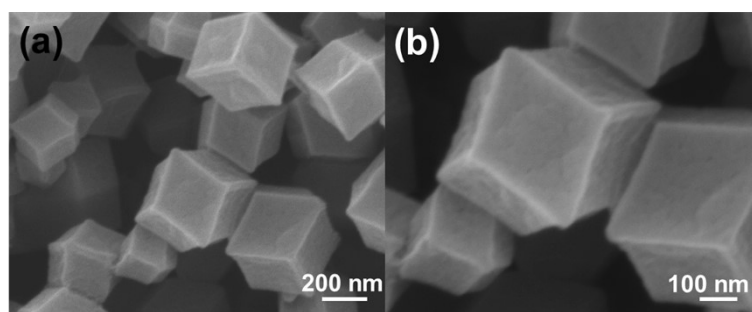


Figure S1 SEM image of ZIF-67 dodecahedrons.

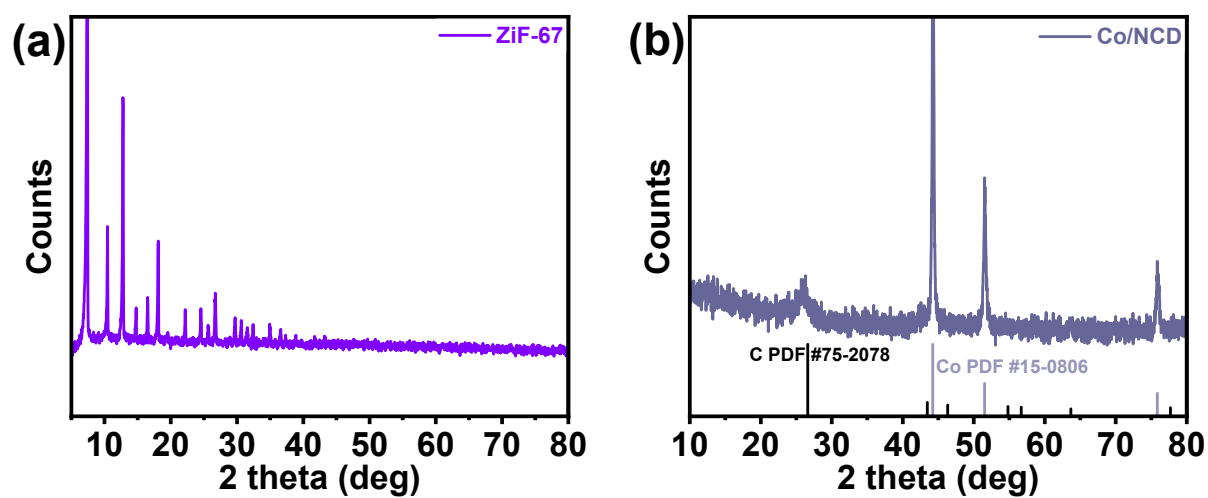


Figure S2 XRD patterns of (a) ZIF-67 dodecahedrons and (b) Co/NCD.

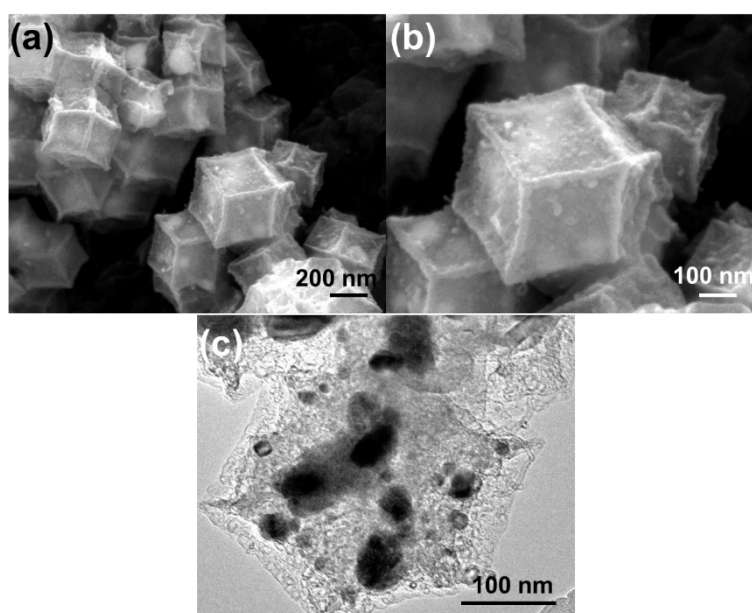


Figure S3 (a, b) SEM and (c) TEM images of Co/NCD.

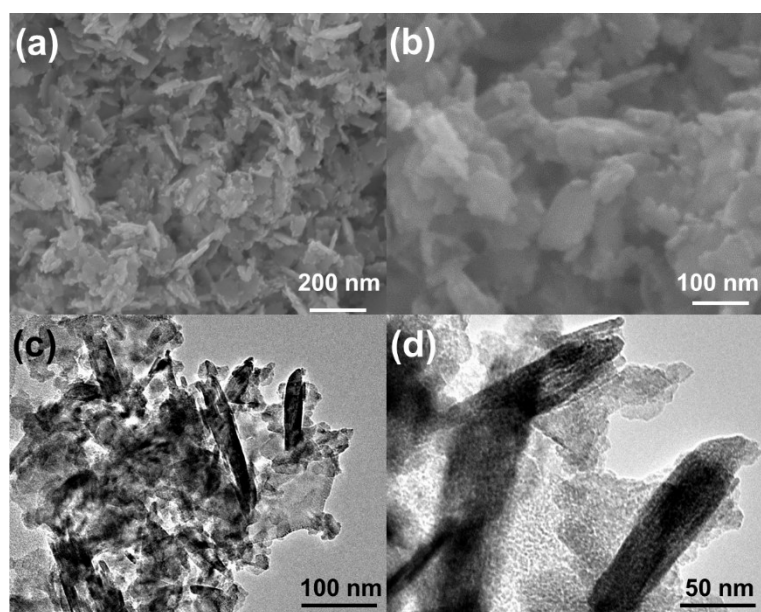


Figure S4 (a, b) SEM and (c, d) TEM images of  $\text{Co}(\text{OH})_2$ .

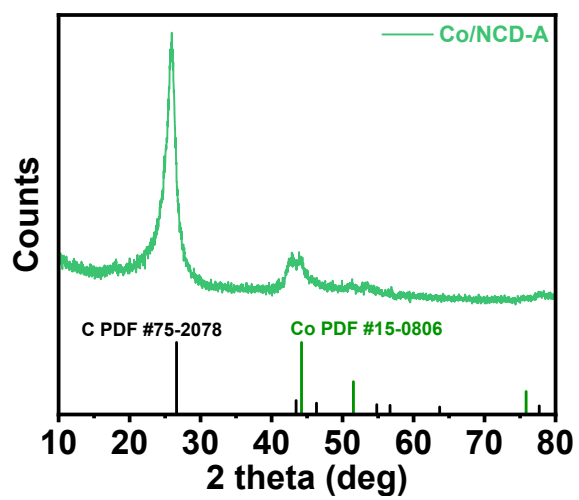
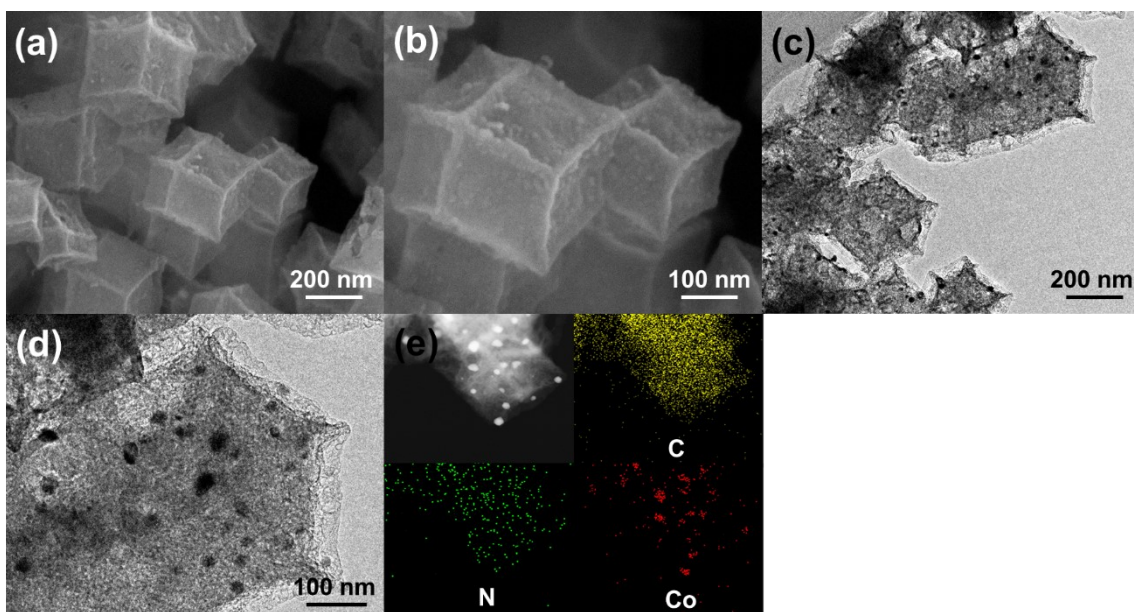
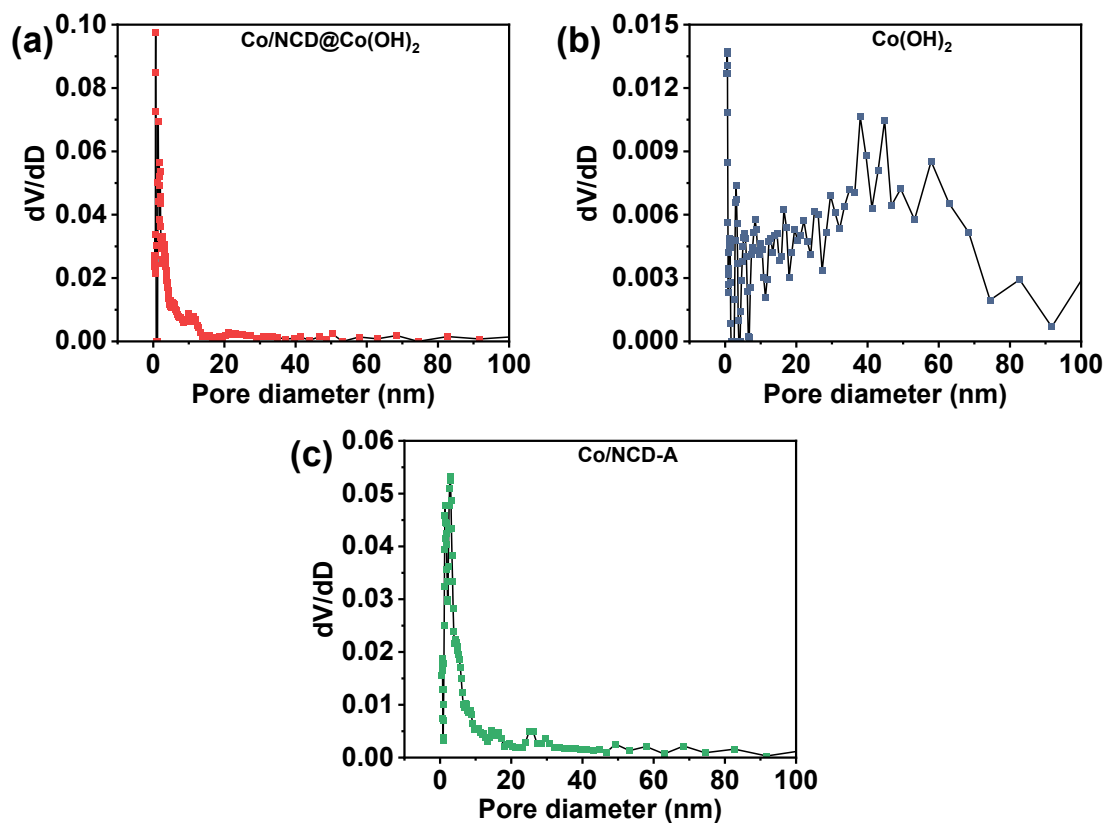


Figure S5 XRD pattern of Co/NCD-A.



**Figure S6** SEM and TEM images of Co/NCD-A; HAADF-STEM image and corresponding elemental mapping of Co/NCD-A.



**Figure S7** Pore diameter distributions of (a)  $\text{Co/NCD@Co(OH)}_2$ , (b)  $\text{Co(OH)}_2$  and (c)  $\text{Co/NCD-A}$ .

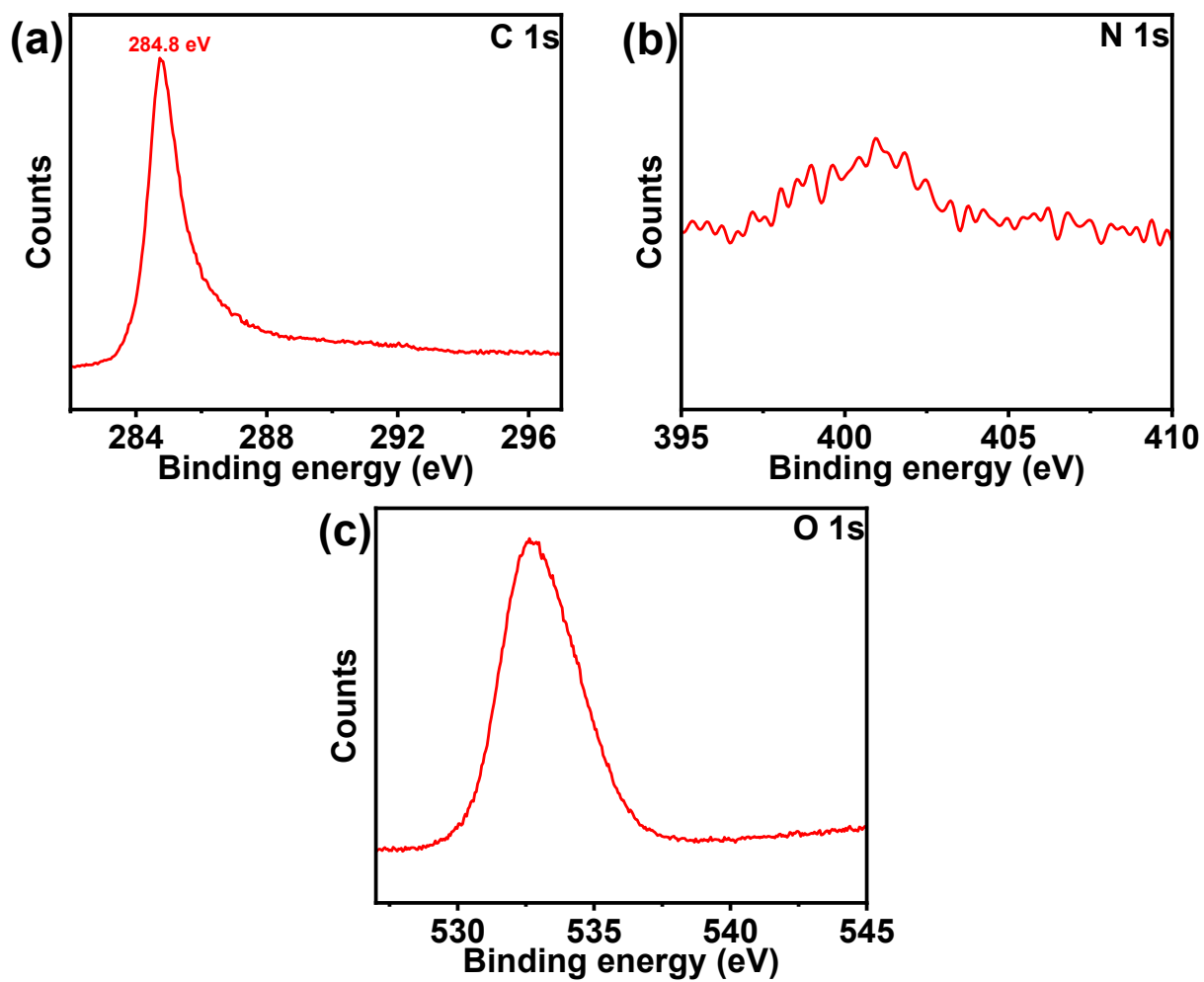


Figure S8 C 1s, N 1s and O 1s spectra of Co/NCD@Co(OH)<sub>2</sub>.

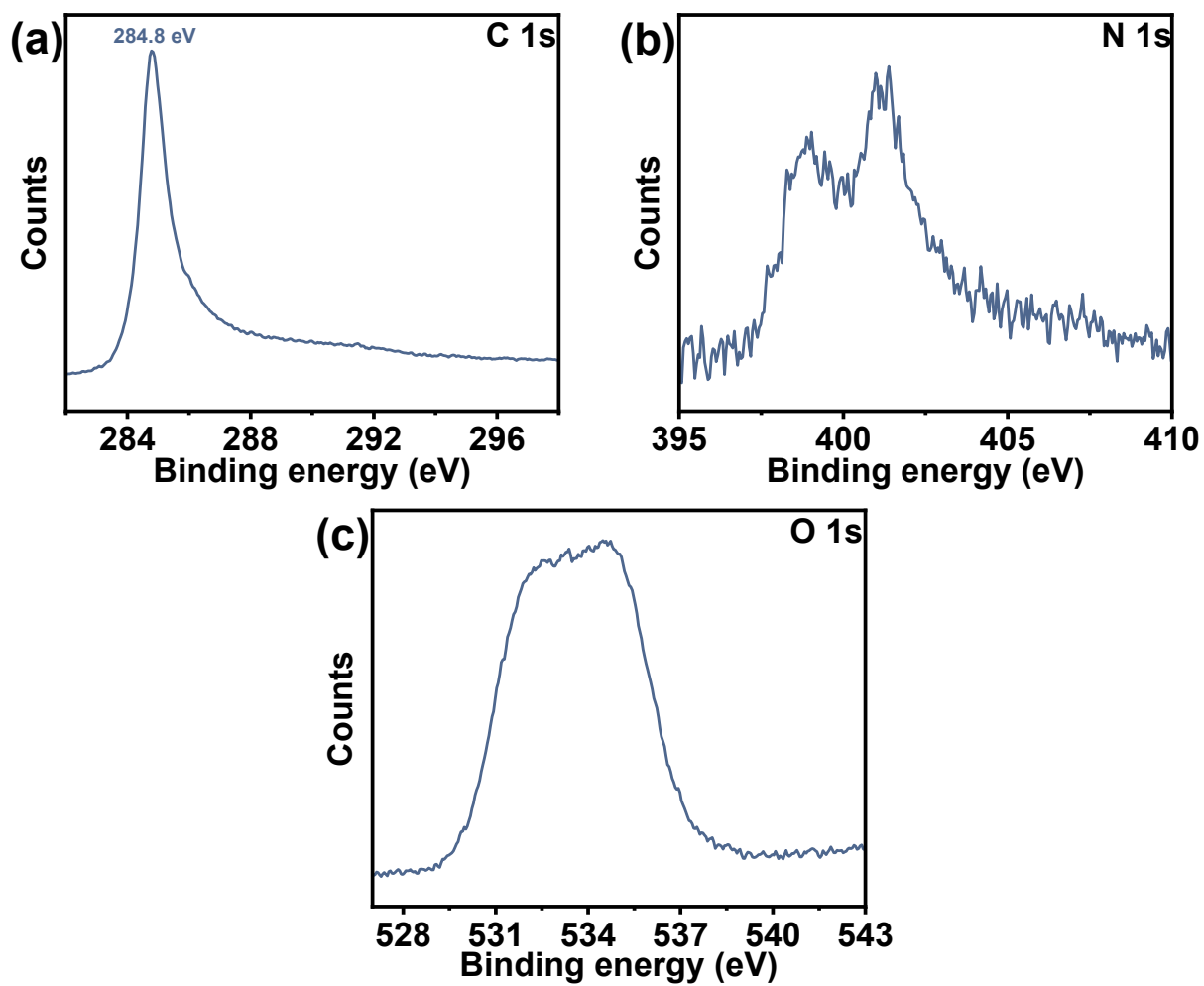
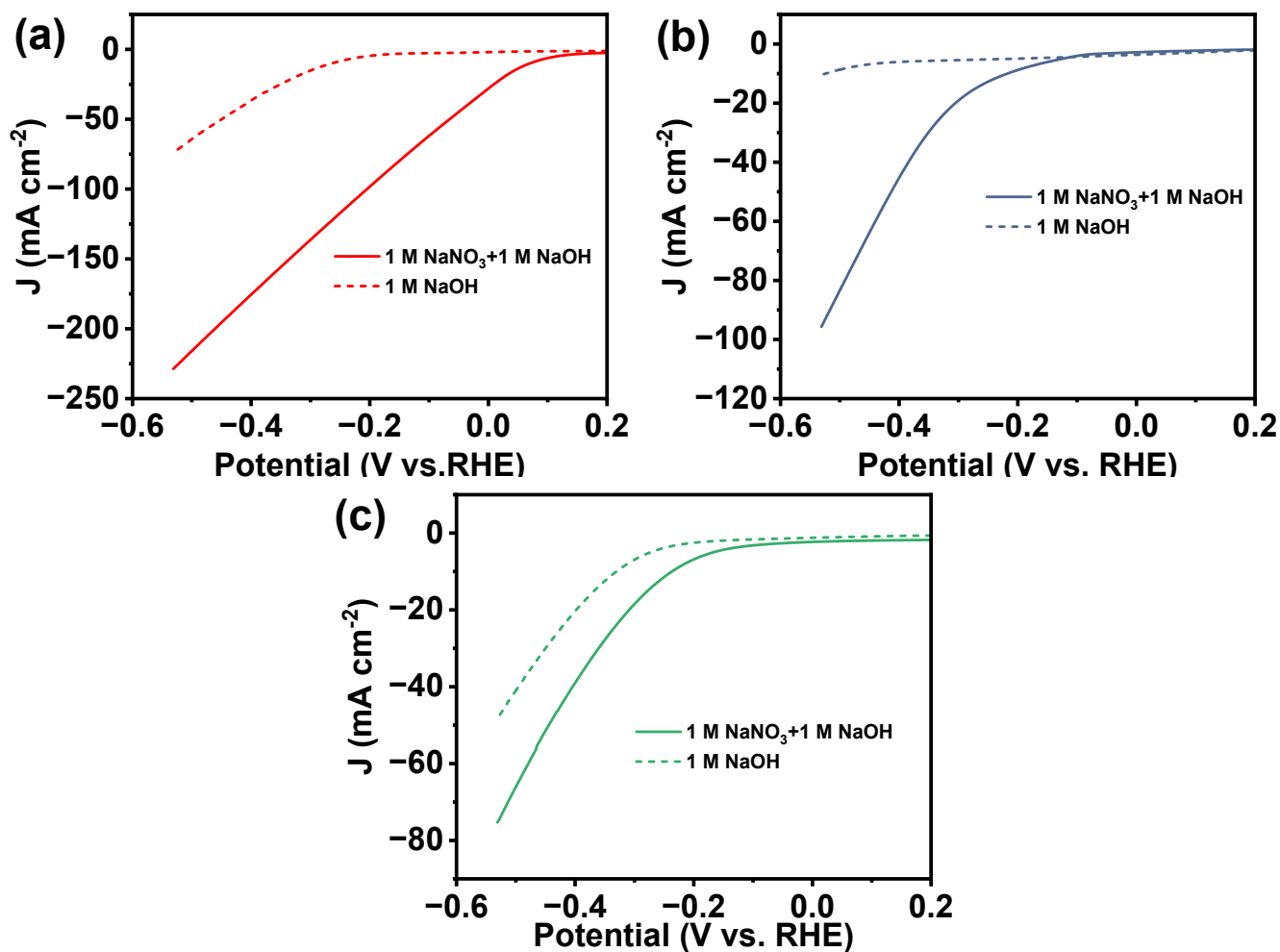
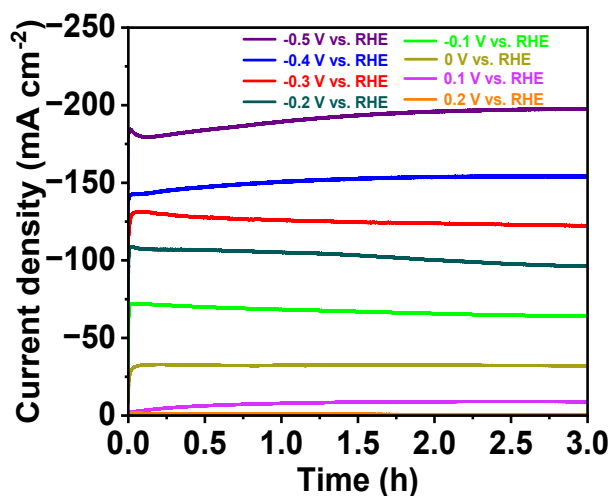


Figure S9 C 1s, N 1s and O 1s spectra of  $\text{Co(OH)}_2$ .

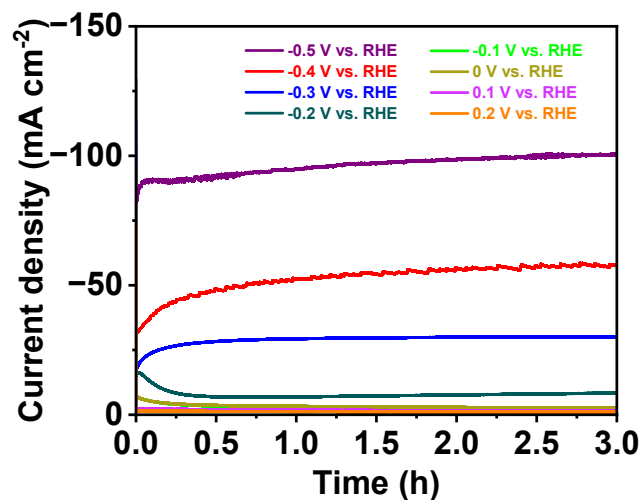




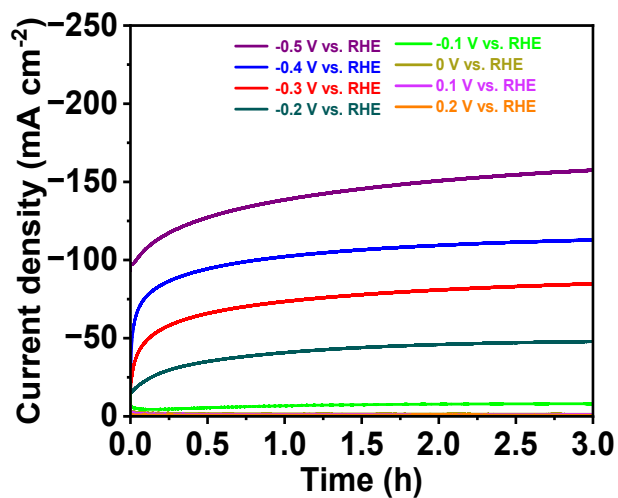
**Figure S10** LSV curves of (a) Co/NCD@Co(OH)<sub>2</sub>, (b) Co(OH)<sub>2</sub> and (c) Co/NCD-A with and without NO<sub>3</sub><sup>-</sup> in electrolyte.



**Figure S11** Chronoamperometric curves of Co/NCD@Co(OH)<sub>2</sub> at various potentials in 100 ml electrolyte containing 1.0 M NaNO<sub>3</sub> and 1.0 M NaOH.



**Figure S12** Chronoamperometric curves of Co/NCD-A at various potentials in 100 ml electrolyte containing 1.0 M NaNO<sub>3</sub> and 1.0 M NaOH.



**Figure S13** Chronoamperometric curves of Co(OH)<sub>2</sub> at various potentials in 100 ml electrolyte containing 1.0 M NaNO<sub>3</sub> and 1.0 M NaOH.

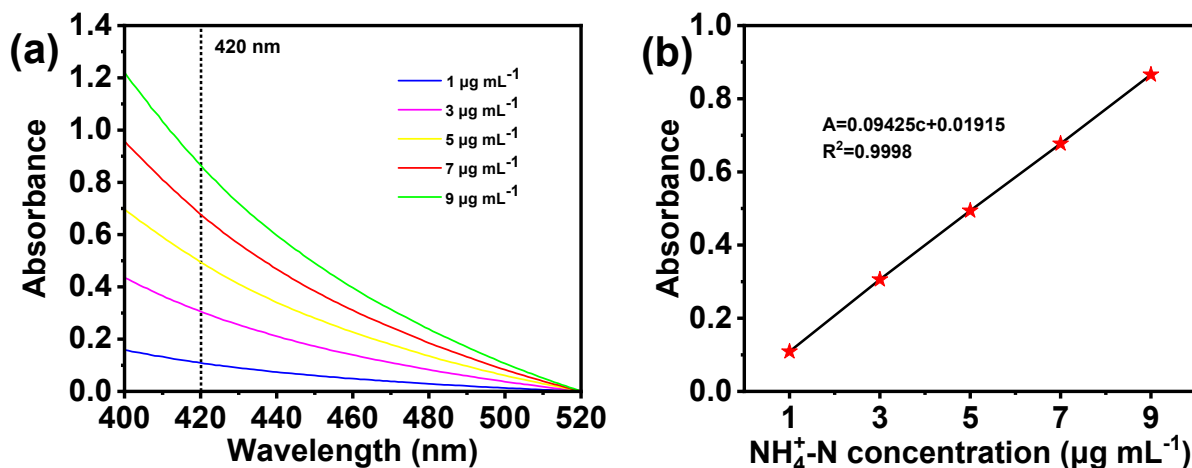


Figure S14 (a) UV-Vis spectra of various  $\text{NH}_3$  concentrations and (b) calibration curve used for estimating concentrations of  $\text{NH}_3$ .

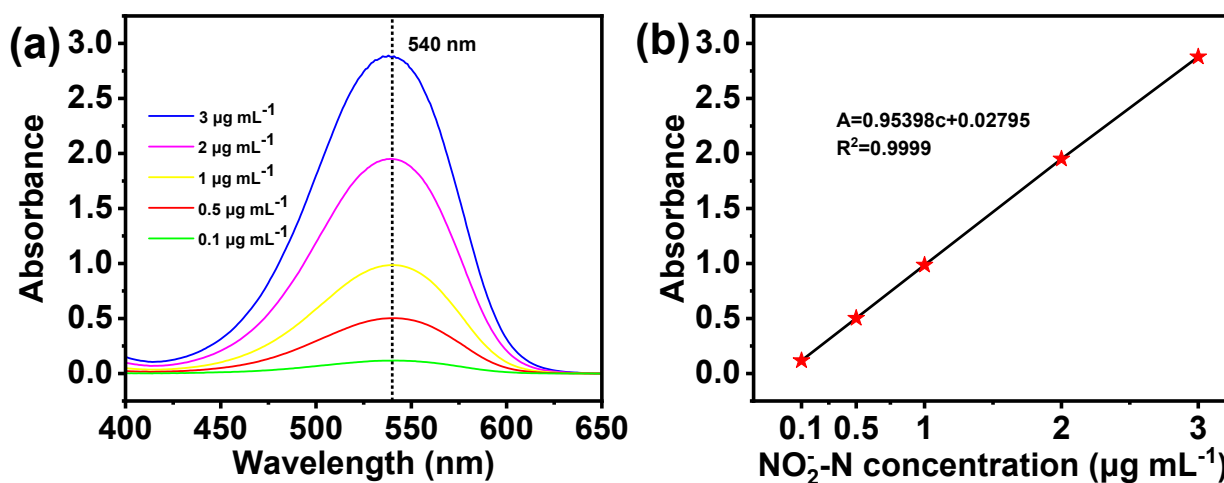


Figure S15 (a) UV-Vis spectra of various  $\text{NO}_2^-$  concentrations and (b) calibration curve used for estimating concentrations of  $\text{NO}_2^-$ .

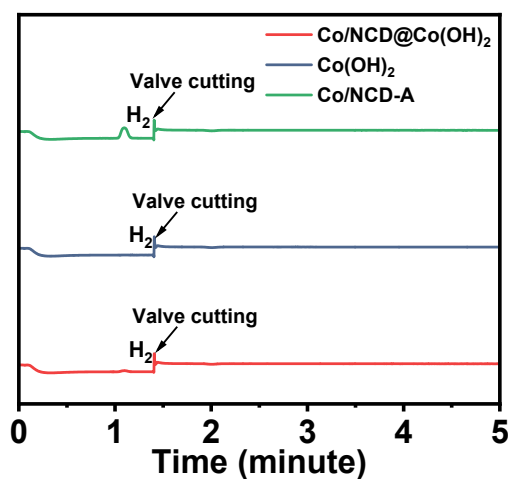


Figure S16 Chromatograms for Co/NCD@Co(OH)<sub>2</sub>, Co(OH)<sub>2</sub> and Co/NCD-A.

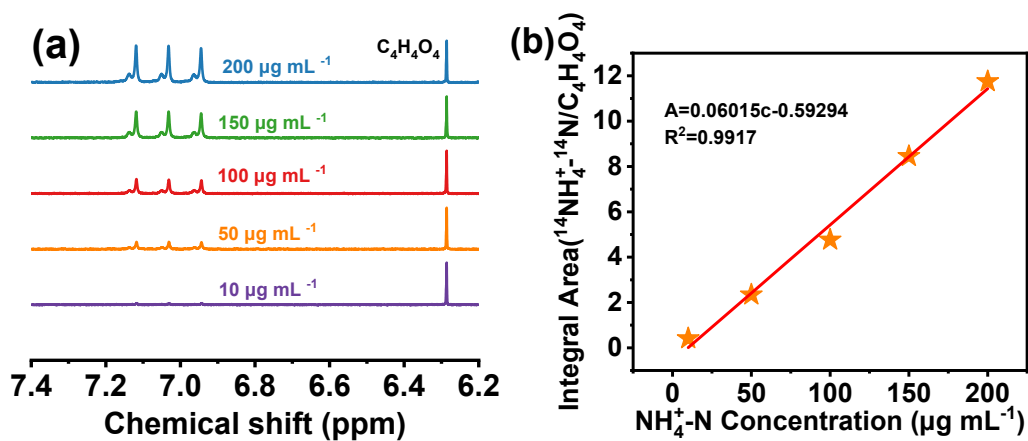
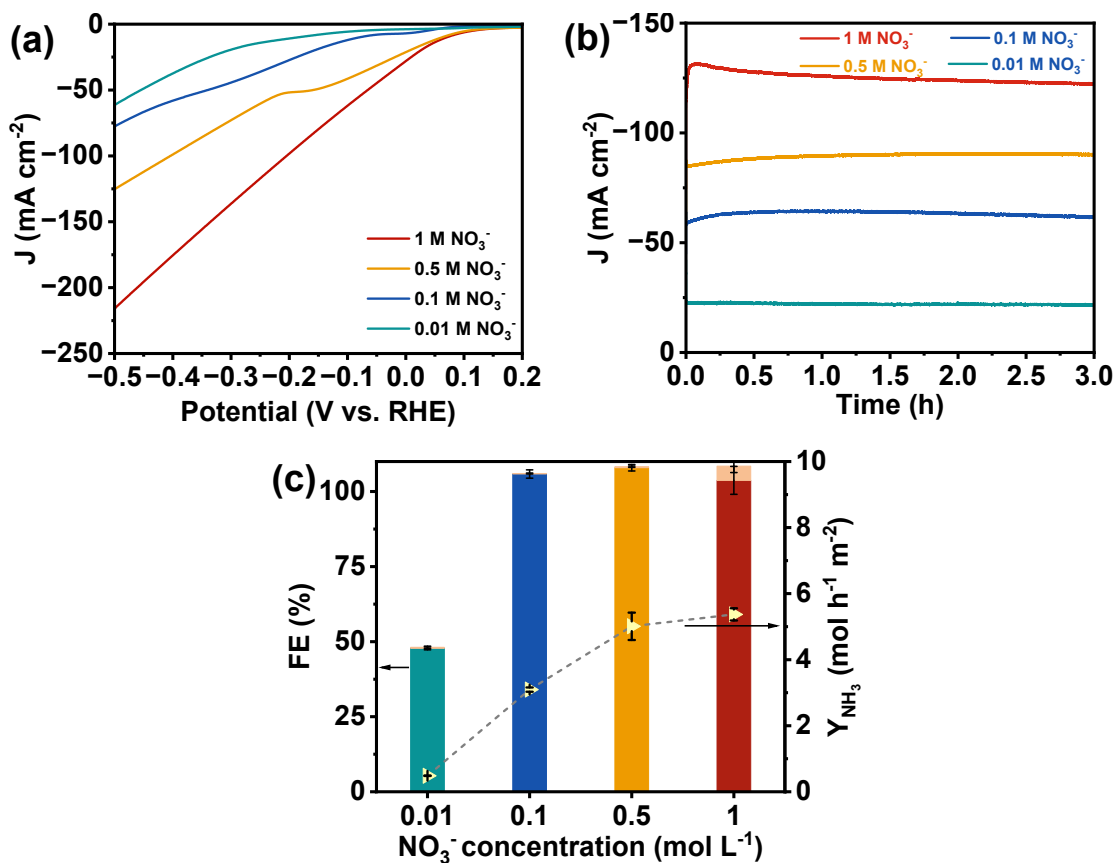
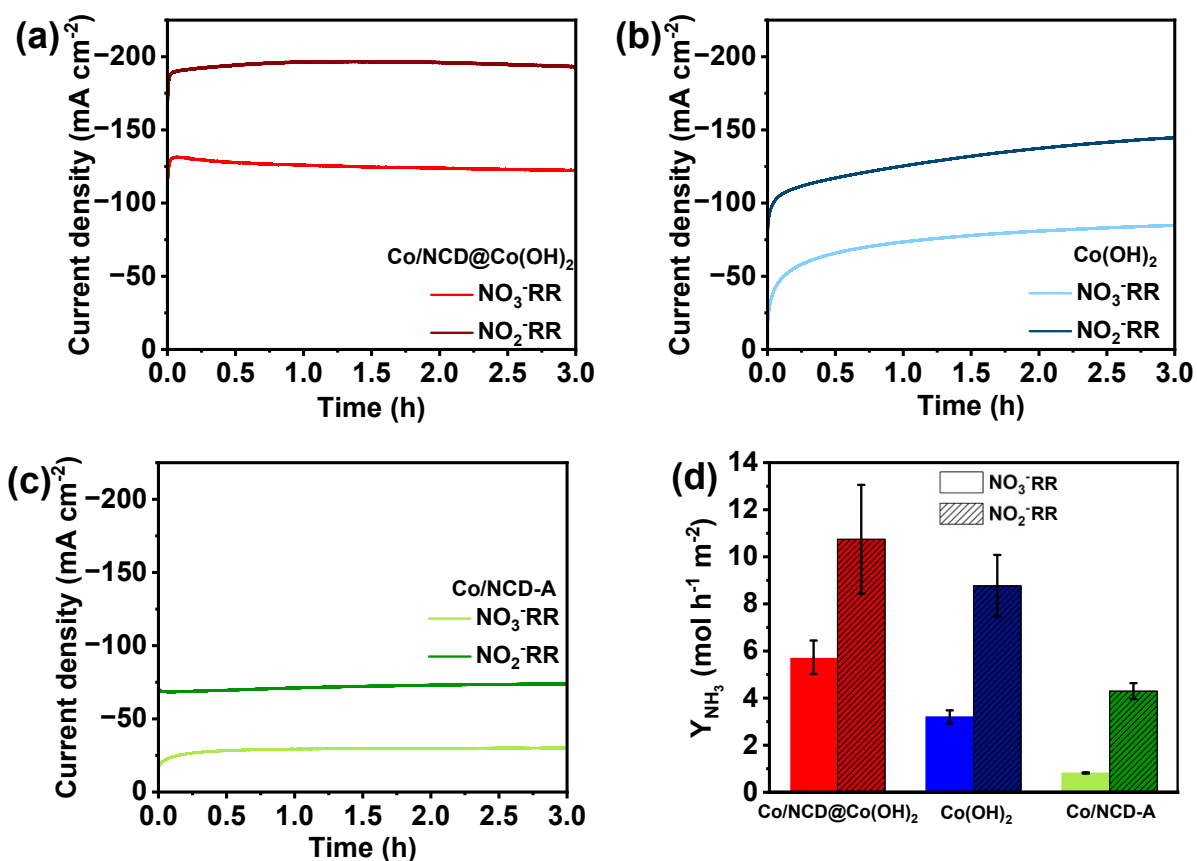


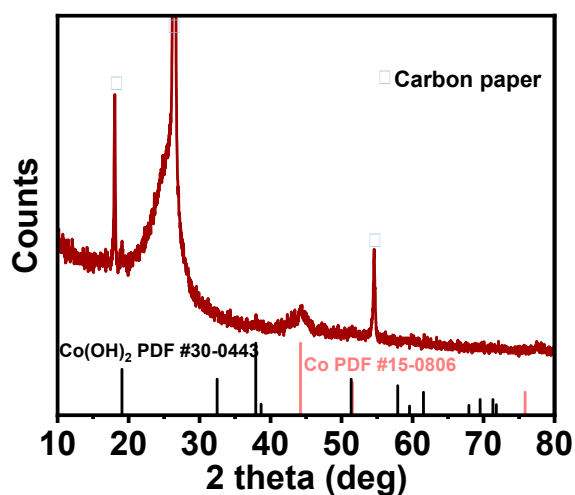
Figure S17 (a) <sup>1</sup>H NMR spectra (600 MHz) of standard samples of (<sup>14</sup>NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; (b) The standard curve of integral area (<sup>14</sup>NH<sub>4</sub><sup>+</sup>-<sup>14</sup>N/C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) against <sup>14</sup>NH<sub>4</sub><sup>+</sup>-<sup>14</sup>N concentration.



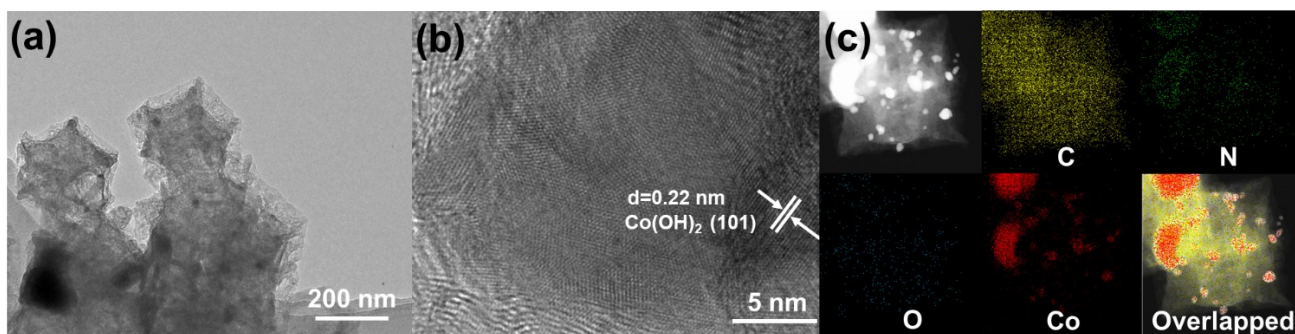
**Figure S18** (a) LSV curves and (b) chronoamperometric curves of Co/NCD@Co(OH)<sub>2</sub> performed in electrolyte with different concentration of NO<sub>3</sub><sup>-</sup> at -0.3 V vs. RHE.; (c) Corresponding FE and Y<sub>NH<sub>3</sub></sub>.



**Figure S19** Chronoamperometric curves of (a)  $\text{Co/NCD@Co(OH)}_2$ , (b)  $\text{Co/NCD-A}$  and (c)  $\text{Co(OH)}_2$  in 1 M NaOH + 1 M  $\text{NaNO}_3$ /1 M NaOH + 1 M  $\text{NaNO}_2$  at -0.3 V vs. RHE.; (d) Corresponding  $\text{NH}_3$  yield-rate.



**Figure S20** XRD pattern of  $\text{Co/NCD@Co(OH)}_2$  after durability testing



**Figure S21** (a) TEM images of Co/NCD@Co(OH)<sub>2</sub> after NO<sub>3</sub><sup>-</sup>RR; (b) HR-TEM images of Co/NCD@Co(OH)<sub>2</sub> after NO<sub>3</sub><sup>-</sup>RR; (c) HAADF-STEM image and corresponding elemental mapping of Co/NCD@Co(OH)<sub>2</sub> after NO<sub>3</sub><sup>-</sup>RR.