

# Supplementary Information

## Bi-Doped $\text{Co}_3\text{O}_4$ Nanosheets for Nitrate to Ammonia with Near 100% Faradaic Efficiency

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## 1. Experimental

### 1.1 Materials

Ammonium chloride ( $\text{NH}_4\text{Cl}$ , 99.8%), sodium nitrite ( $\text{NaNO}_2$ ,  $\geq 99.0\%$ ), sodium sulfate ( $\text{Na}_2\text{SO}_4$ ,  $\geq 95\%$ ), cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.9%), bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 98%), N-(1-naphthyl) ethylene diamine dihydrochloride ( $\text{C}_{12}\text{H}_{14}\text{N}_2 \cdot 2\text{HCl}$ , 98%), Sulfanilamide ( $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$ , 99.5%), hydrochloric acid ( $\text{HCl}$ , 36%~38%), phosphoric acid ( $\text{H}_3\text{PO}_4$ , 99%), Salicylic acid ( $\text{C}_7\text{H}_6\text{O}_3$ , 99.5%), and Sodium hypochlorite ( $\text{NaClO}$ , 13%~18% effective chlorine) were obtained from Shanghai Macklin Biochemical Technology Co., Ltd. Ethanol ( $\text{C}_2\text{H}_6\text{O}$ , 99.7%) and sodium hydroxide ( $\text{NaOH}$ , AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium citrate dihydrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ , 99.0%) was provided by Tianjin Hengxing Chemical Reagent Co., Ltd. Sodium nitrate ( $\text{NaNO}_3$ , 99%) was obtained from Cheng Du Chron Chemicals Co., Ltd. All electrolyte solutions were prepared using deionized (DI) water ( $18.25 \text{ M}\Omega \cdot \text{cm}^{-1}$ ).

### 1.2 Synthesis of catalysts

#### 1.2.1 Synthesis of 0.25-BiO<sub>x</sub>-Co<sub>3</sub>O<sub>4</sub> NS

0.25-BiO<sub>x</sub>-Co<sub>3</sub>O<sub>4</sub> was obtained by co-precipitation followed by calcination. First, 1.5 mmol  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.5 mmol  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were added into 100 mL deionized (DI) water. With continuous stirring, 0.25 M  $\text{NaOH}$  with 0.05 M  $\text{Na}_2\text{CO}_3$  mixed solution was dropped in the above solution until the pH reached 9, obtaining the blue suspension. Next, the suspension was placed in a water bath at 90 °C for 6 hours. The resulting precipitate was washed three times with DI water and anhydrous ethanol and then dried overnight in a vacuum oven at 60 °C. The

obtained black solid was placed in the tubular furnace, where it was calcined at a heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  at  $350\text{ }^{\circ}\text{C}$  for 2 hours in high-purity argon gas. The powder obtained was named 0.25-BiO<sub>x</sub>-Co<sub>3</sub>O<sub>4</sub> NS.

### 1.2.2 Synthesis of 0.25-Bi-Co<sub>3</sub>O<sub>4</sub> NS catalysts

10mg 0.25-BiO<sub>x</sub>-Co<sub>3</sub>O<sub>4</sub> NS were dispersed in 960  $\mu\text{L}$  anhydrous ethanol and 40  $\mu\text{L}$  Nafion solution via the ultrasonic process for 20 minutes to obtain the uniform catalyst ink. The resultant catalyst ink was removed and dropped onto the carbon paper. After that, the catalyst loaded on carbon paper was reduced for 30 minutes at a potential of  $-0.4\text{ V}$  vs. RHE in 1 M NaOH, resulting in the final 0.25-Bi-Co<sub>3</sub>O<sub>4</sub> NS. For comparison, the other catalysts were prepared using the same methods as described above, except for varying Bi contents. The catalysts with precise atom proportions of the Bi/Co were named and detailed in Table S1.

### 1.3 Material characterization

X-ray diffraction (XRD) patterns were collected on a Smart Lab with a Cu K $\alpha$  radiation target (45 kV, 200 mA). Scanning electron microscopy (SEM) images were obtained from a TESCAN MIRA LMS instrument. Transmission electron microscopy (TEM) images, High-resolution TEM (HRTEM), and energy-dispersive X-ray spectroscopy (EDS) mappings were obtained on FEI Talos F200S operated at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were acquired by the Thermo Scientific K-Alpha radiation operating at ultrahigh vacuum. The Raman spectra were recorded with a Thermo Fisher Scientific DXR Raman spectrometer. A UV-1800 Spectrophotometer determined ultraviolet-visible (UV-Vis) absorbance. The electron spin resonance (ESR) spectra were collected by Bruker EMX plus-

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## **1.4 Electrochemical measurements**

All electrochemical tests were conducted using the CHI660 workstation at room temperature in a H-type electrolytic cell. 1 M NaOH with 0.5 M NaNO<sub>3</sub> was used as the electrolyte in the cathode chamber and the cell environment was maintained in an Ar gas atmosphere. In this paper, all potentials have been converted to the potentials relative to the reversible hydrogen electrode. Before the electrochemical reduction of nitrates, cyclic voltammetry (CV) scans and linear sweep voltammetry (LSV) were performed at a scan rate of 10 mV s<sup>-1</sup>. Then a chronoamperometric test was conducted at a potential for 1 h in fresh electrolyte.

The double-layer capacitance ( $C_{dl}$ ) was obtained by performing CV curves in the non-faradaic potential region to estimate electrochemically active surface area (ECSA). The CV measurements of Bi, Co<sub>3</sub>O<sub>4</sub> NS, and 0.25-Bi-Co<sub>3</sub>O<sub>4</sub> NS were conducted at different scan rates from 20 to 100 mV s<sup>-1</sup> in 1 M NaOH containing 0.5 M NaNO<sub>3</sub>. By plotting the  $\Delta j$  (one-half of the differences in current density) against the scan rates, the linear slopes were the  $C_{dl}$  for different catalysts.

## **1.5 Determination of products**

### **1.5.1 Determination of ammonia**

The electrolyte products were detected using a UV-Vis spectrophotometer, after being diluted to the appropriate concentration. The amounts of NH<sub>3</sub> were measured by colorimetry using the indophenol blue method. First, the color reagents were prepared, including 1 M NaOH solution containing 5 wt.% salicylic acid and 5 wt.% sodium citrate, 1 wt.% sodium

nitroprusside solution, and 2 M NaOH solution containing 4 M NaClO. To obtain the amount of  $\text{NH}_3$  in the electrolyte after  $\text{NO}_3\text{-RR}$ , 1 mL electrolyte was extracted from the cathode chamber, mixed with an equal volume of 0.5 M  $\text{H}_2\text{SO}_4$ , and diluted to the detectable concentration range. Subsequently, the diluted electrolyte was added 1 mL, 0.1 mL, and 0.1 mL of the color reagents. The absorption intensity at the wavelength of 657 nm was recorded after standing for 1 h in the dark. The concentration-absorbance curve was calibrated using a series of standard ammonium chloride solutions.

### **1.5.2 Determination of nitrite**

The colorimetric reaction of Griess reagent with nitrite was utilized to determine the concentration of nitrite. To prepare the colorimetric reagent, 8 g of sulfanilamide, 0.4 g of N-(1-naphthyl) ethylenediamine dihydrochloride, and 20 mL of phosphoric acid were sequentially added to 100 mL of water and the volume was adjusted to 200 mL. The mixed solution should be stored at 2~5 °C in the dark. To obtain the concentration of nitrite in the electrolyte, 1 mL of electrolyte from the cathode chamber was diluted to a detectable concentration range, and 0.2 mL of the Griess reagent was added. The solution was left in the dark for 20 minutes before the absorbance was measured using a UV-Vis spectrophotometer. The concentration-absorbance curve was calibrated using a series of standard sodium nitrite solutions.

### **1.6 Calculation of yield rate and FE of product.**

The production rate of  $\text{NH}_3$  was calculated using the following equation:

$$r_{\text{NH}_3} = \frac{c_{\text{NH}_3} \times V \times 10^{-3}}{14 \times t \times A}$$

where  $r_{\text{NH}_3}$  is the yield rate of  $\text{NH}_3$  ( $\text{mmol h}^{-1} \text{cm}^{-2}$ ),  $c_{\text{NH}_3}$  is the detected concentration of  $\text{NH}_3\text{-N}$ , ( $\mu\text{g mL}^{-1}$ ),  $V$  is the volume of the electrolyte (mL),  $t$  is the reaction time (h), and  $A$  is the geometric area of the working electrode ( $\text{cm}^2$ ).

The FE of ammonia was calculated with the following equation:

$$\text{FE}_{\text{NH}_3} = \frac{8 \times F \times c_{\text{NH}_3} \times V \times 10^{-6}}{14 \times Q} \times 100\%$$

where  $F$  is Faraday constant ( $96500 \text{ C mol}^{-1}$ ),  $Q$  is the total charge during the reaction (C).

The production rate of nitrite was calculated using the following equation:

$$r_{\text{NO}_2^-} = \frac{c_{\text{NO}_2^-} \times V \times 10^{-3}}{14 \times t \times A}$$

where  $r_{\text{NO}_2^-}$  is the yield rate of  $\text{NO}_2^-$  ( $\text{mmol h}^{-1} \text{cm}^{-2}$ ),  $c_{\text{NO}_2^-}$  is the detected  $\text{NO}_2^-$ -N concentration ( $\mu\text{g mL}^{-1}$ ).

The FE of nitrite was calculated with the following equation:

$$\text{FE}_{\text{NO}_2^-} = \frac{1 \times F \times c_{\text{NO}_2^-} \times V \times 10^{-6}}{14 \times Q} \times 100\%$$

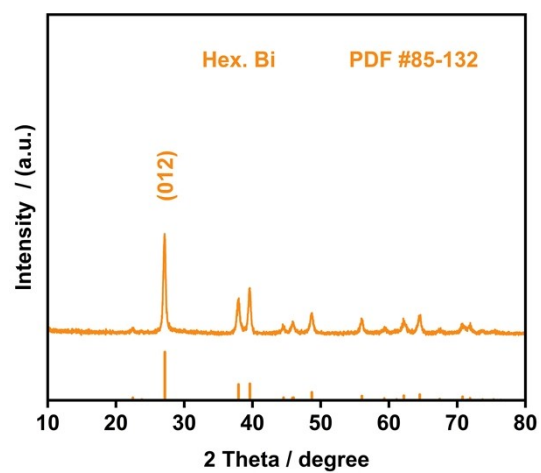


Fig. S1 XRD pattern of pure Bi.

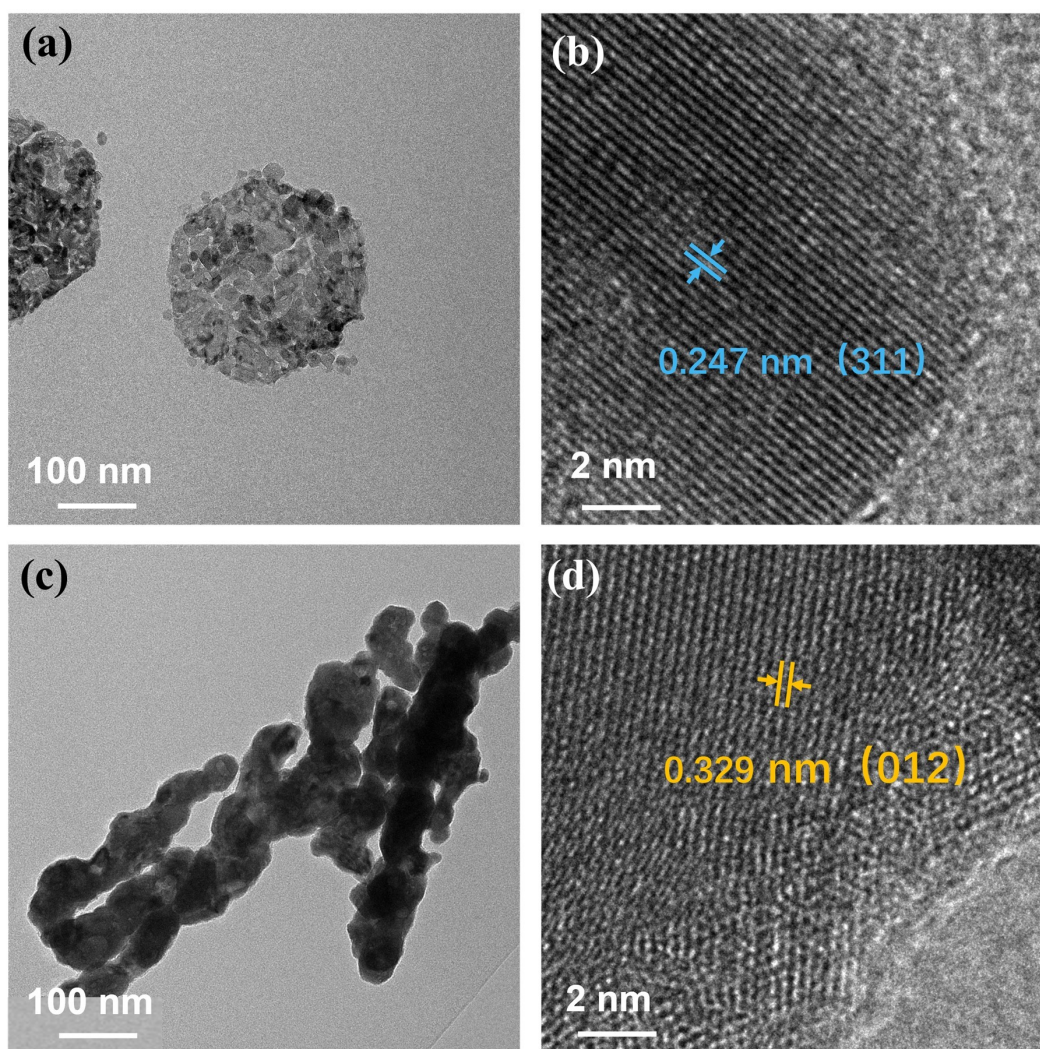


Fig. S2 (a)-(b) TEM and HRTEM images of  $\text{Co}_3\text{O}_4$  NS. (c)-(d) TEM and HRTEM images of

Bi.

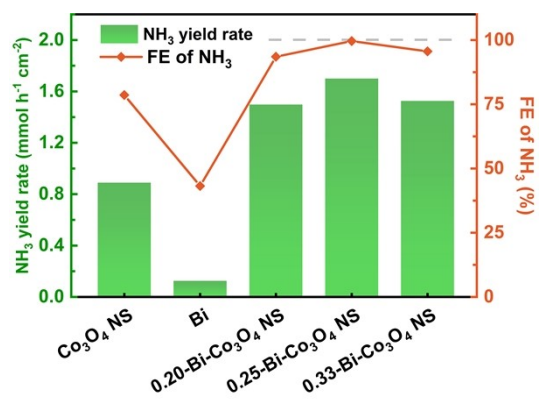


Fig. S3 Yield rate and FE of NH<sub>3</sub> at -0.6V vs. RHE in 1 M NaOH with 0.5 M NaNO<sub>3</sub>.



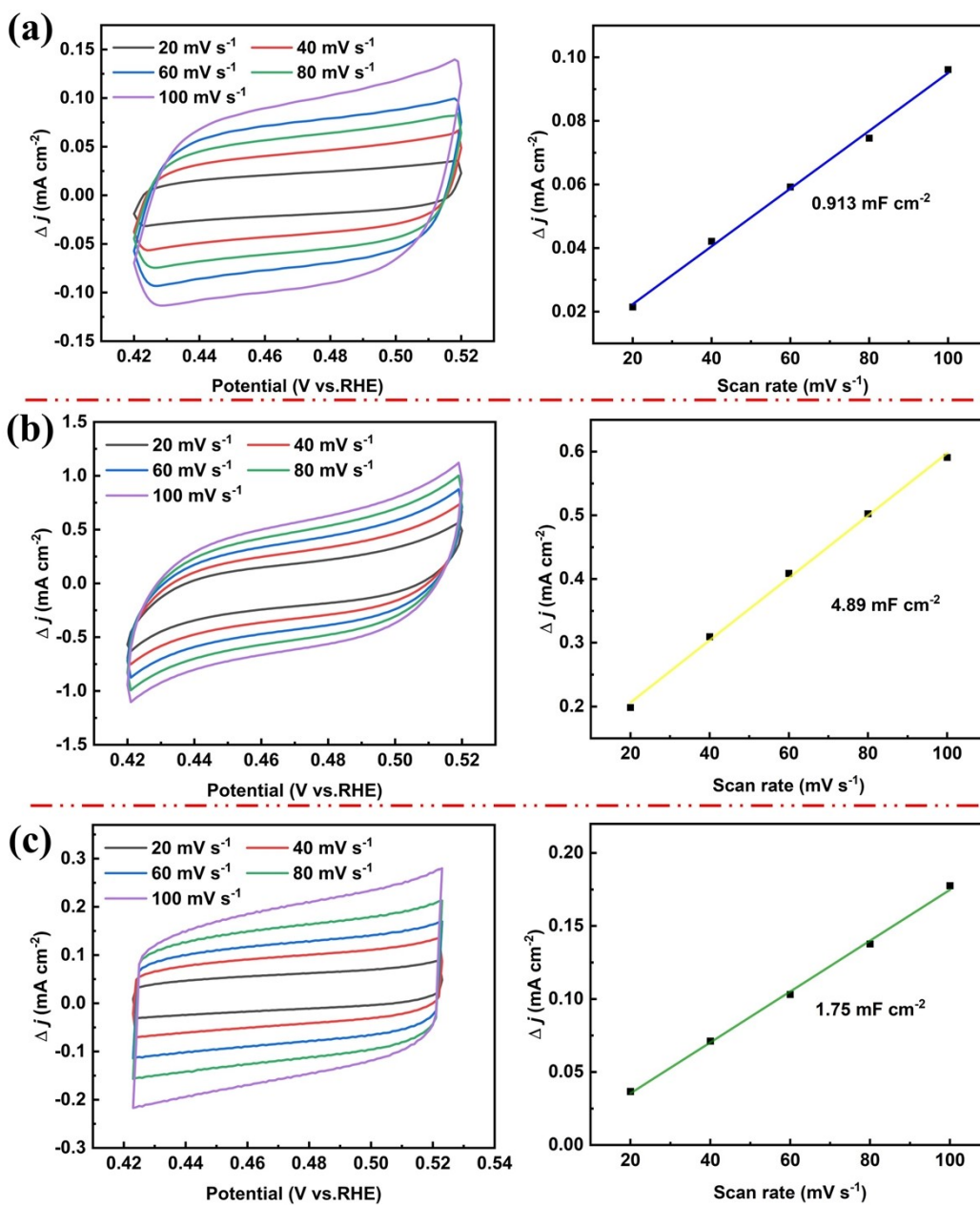


Fig. S4 CV curves in different scan rates and the  $C_{dl}$  of (a)  $\text{Co}_3\text{O}_4$  NS, (b) Bi, and (c) 0.25-Bi-

$\text{Co}_3\text{O}_4$  NS.

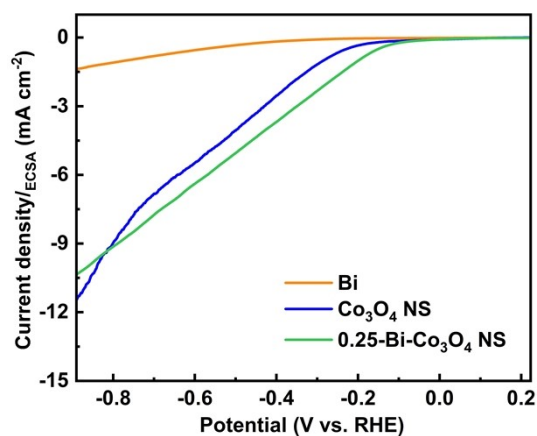


Fig. S5 ECSA normalized LSV curves of three catalysts.

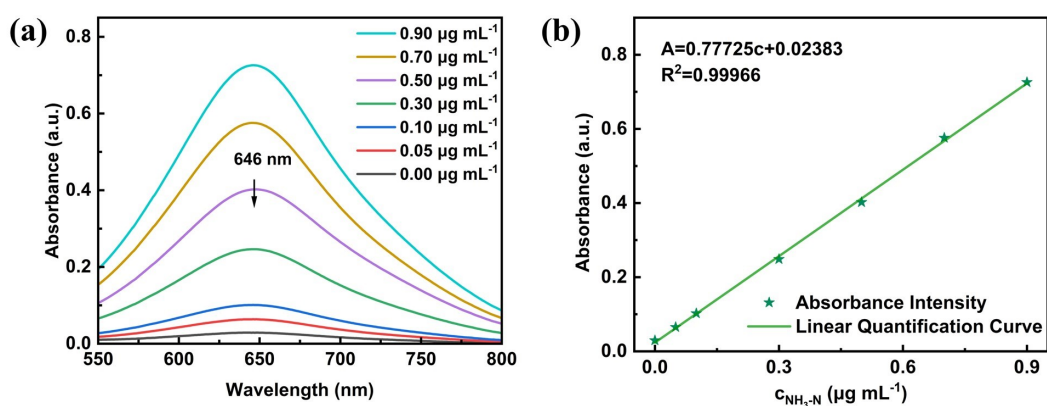


Fig. S6 (a) The UV-vis absorption spectra of a series of standard ammonium chloride solutions. (b) The A-C standard curve of  $\text{NH}_3\text{-N}$  quantification.

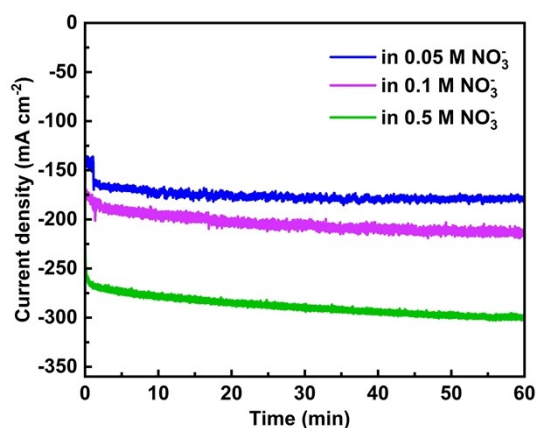


Fig. S7 The chronoamperometric tests of 0.25-Bi- $\text{Co}_3\text{O}_4$  NS in 1 M NaOH with different concentrations of  $\text{NO}_3^-$ .

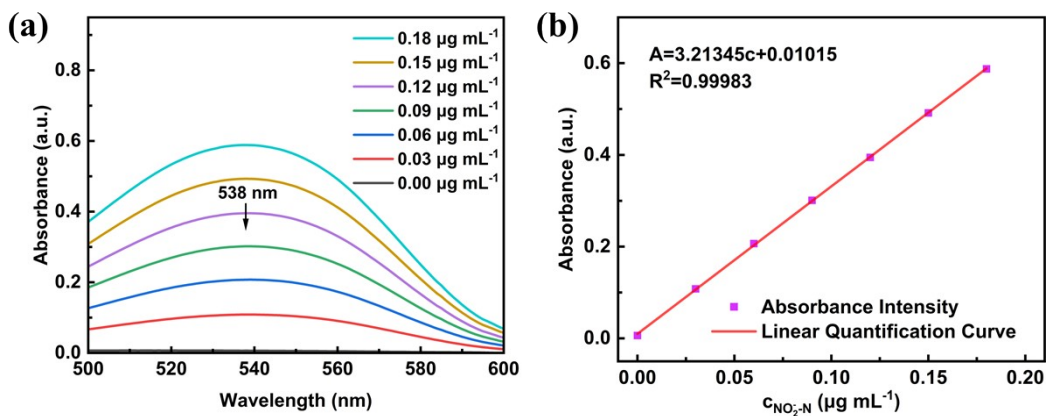


Fig. S8 (a) The UV-vis absorption spectra of a series of standard sodium nitrite solutions. (b)

The A-C standard curve of  $\text{NO}_2^-$ -N quantification.

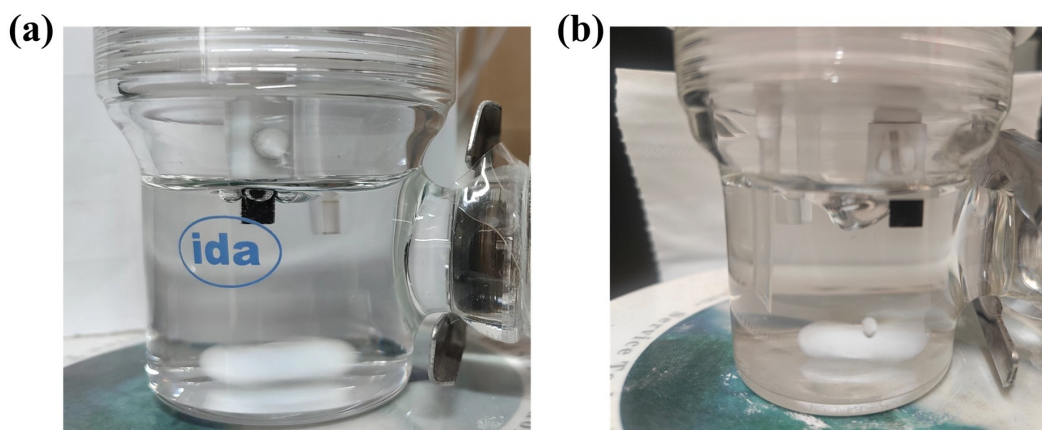


Fig. S9 The generation of  $\text{H}_2$  on (a)  $\text{Co}_3\text{O}_4$  NS and (b) 0.25-Bi- $\text{Co}_3\text{O}_4$  NS.

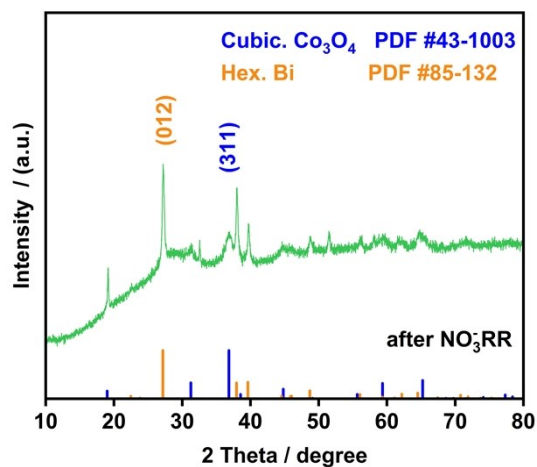
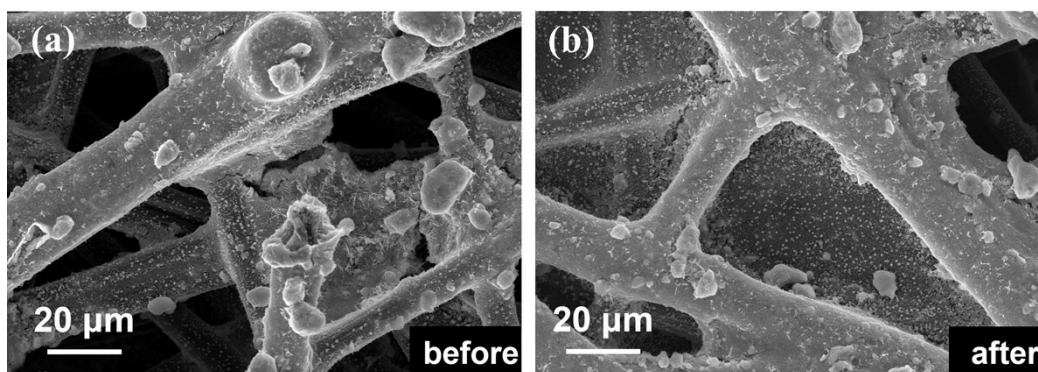


Fig. S10 XRD pattern of 0.25-Bi- $\text{Co}_3\text{O}_4$  NS after  $\text{NO}_3^-$ -RR.



Element	Atomic (%)	Wt (%)
Co	39.37	39.40
O	47.17	12.82
Bi	13.46	47.78

Element	Atomic (%)	Wt (%)
Co	49.54	41.06
O	32.93	7.41
Bi	17.53	51.53

Fig. S11 SEM of 0.25-Bi-Co<sub>3</sub>O<sub>4</sub> NS (a) before and (b) after NO<sub>3</sub><sup>-</sup>RR.

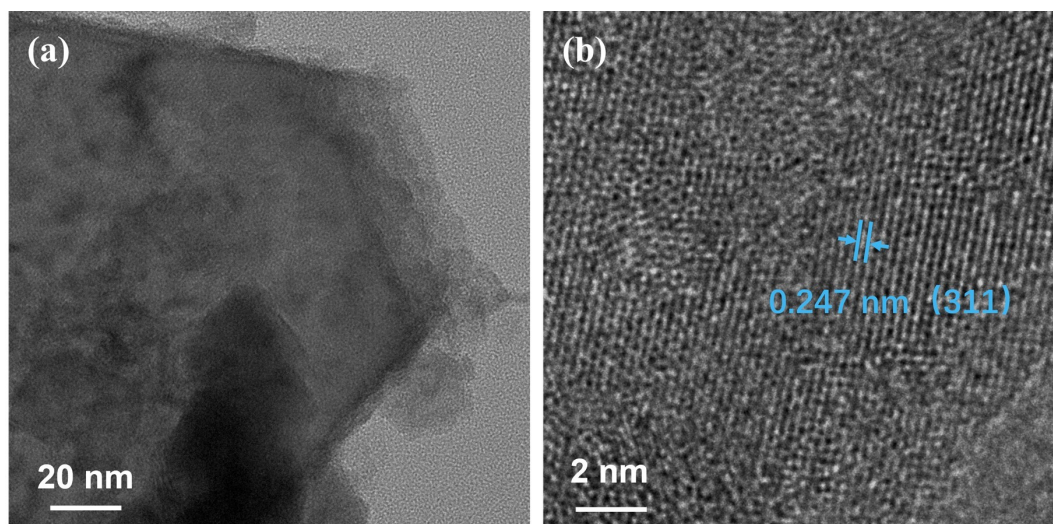


Fig. S12 (a) TEM image, (b) HRTEM image of 0.25-Bi-Co<sub>3</sub>O<sub>4</sub> NS after NO<sub>3</sub><sup>-</sup>RR.

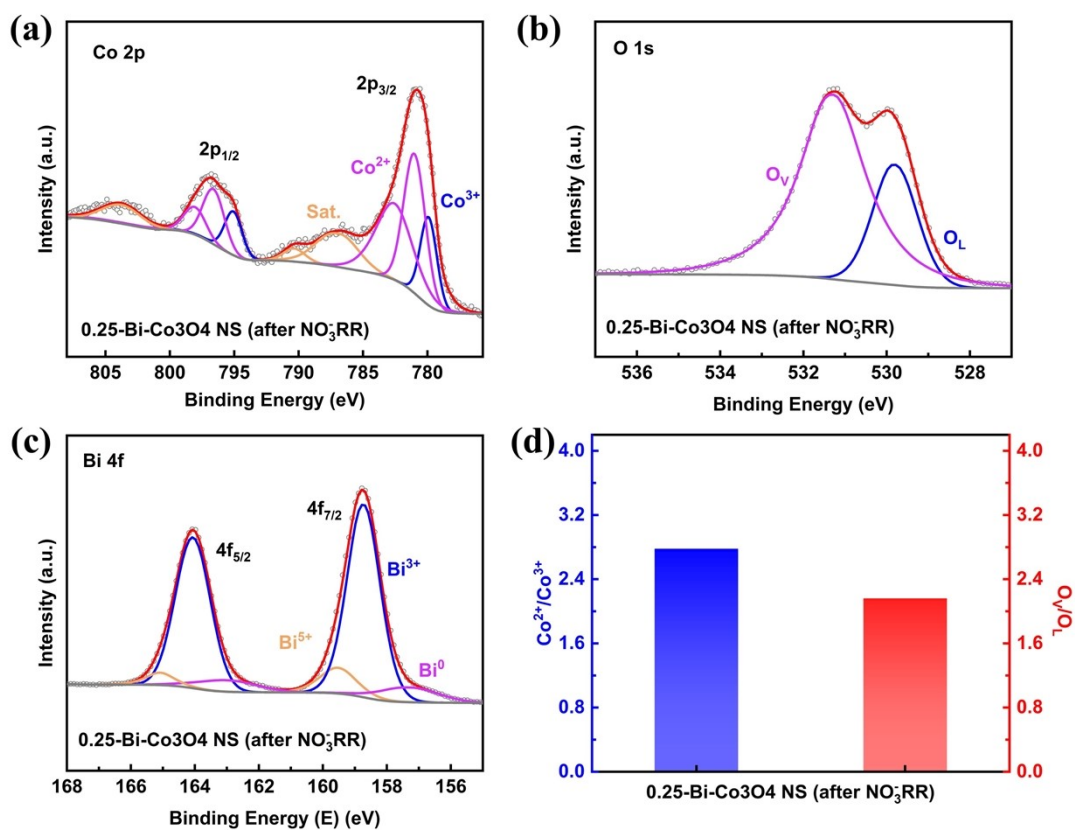


Fig. S13 (a)-(c) XPS spectra of Co 2p, O 1s and Bi 4f for 0.25-Bi-Co<sub>3</sub>O<sub>4</sub> NS after NO<sub>3</sub><sup>-</sup>RR. (d)

The ratios of O<sub>V</sub>/O<sub>L</sub> and Co<sup>2+</sup>/Co<sup>3+</sup> for 0.25-Bi-Co<sub>3</sub>O<sub>4</sub> NS after NO<sub>3</sub><sup>-</sup>RR.

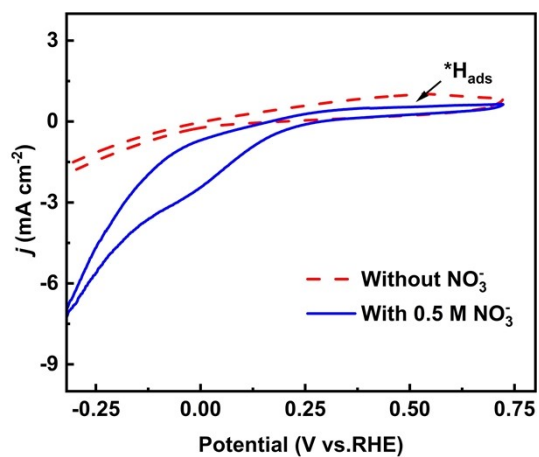


Fig. S14 CV curves in a wide potential range of Co<sub>3</sub>O<sub>4</sub> NS.

Table S1 The atom contents of Co and Bi in the catalysts.

	Co contents	Bi contents
	at.%	at.%
Co <sub>3</sub> O <sub>4</sub> NS	100	0
Bi	0	100
0.2-Bi-Co <sub>3</sub> O <sub>4</sub> NS	80	20
<b>0.25-Bi-Co<sub>3</sub>O<sub>4</sub> NS</b>	75	25
0.33-Bi-Co <sub>3</sub> O <sub>4</sub> NS	67	33