

Supporting Information

Experimental Section

Materials: Hydrated cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; $\geq 98\%$), hydrated trisodium citrate (soft mold i.e. $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$; $\geq 99\%$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$; $\geq 98\%$), urea ($\text{CN}_2\text{H}_4\text{O}$, 99.0%), and sodium sulfide nonahydrate ($\text{NaS}_2 \cdot 9\text{H}_2\text{O}$, 98.0%) were purchased from Alfa-Aesar and directly used without purification. The carbon cloth was purchased from Japan Toray Company. Sodium nitrate (NaNO_3 , 99.0%), sodium nitrite (NaNO_2 , 99.0%), ammonium chloride (NH_4Cl), sodium hydroxide (NaOH), potassium hydroxide (KOH), 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 ($\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$), 0.8wt% sulfamic acid solution ($\text{H}_3\text{NO}_3\text{S}$), sodium dihydrogen phosphate dihydrate (NaH_2PO_4), disodium hydrogen phosphate dodecahydrate (Na_2HPO_4) and sodium hypochlorite solution (NaClO) were purchased from Aladdin Ltd. (Shanghai, China). Ultrapure water used throughout all experiments was purified through a Millipore system.

Synthesis of carbon paper @ CoS_2 octahedron: In a typical synthesis, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (1 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) and $\text{Na}_2\text{S}_2\text{O}_3$ (5 mmol) were dissolved in 75 mL of deionized water and stirred for 20 min to form a clear solution. A piece of a carbon paper (4 cm \times 1.5 cm) was annealed in air and carefully cleaned in an ultrasound bath with ethanol and DI water for 10 min each. The aqueous solution and the carbon paper were transferred to a Teflon-lined stainless-steel autoclave (100 mL) and maintained at 200° C for 12 h, and then cooled down to room temperature. The samples were rinsed several times with deionized water and ethanol with the assistance of ultrasonication, and dried at 80 ° C for 8 h.

Synthesis of carbon paper @ CoS_2 array: In a typical reaction, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (3 mmol)

and $\text{CN}_2\text{H}_4\text{O}$ (18 mmol) were dissolved in 60 mL of deionized water and stirred for 20 min to form a clear solution. A piece of a carbon paper (4 cm \times 1.5 cm) was annealed in air and carefully cleaned in an ultrasound bath with ethanol and DI water for 10 min each. The aqueous solution and the carbon paper were transferred to a Teflon-lined stainless-steel autoclave (100 mL) and maintained at 120° C for 8 h, and then cooled down to room temperature. The precursor sample was rinsed several times with deionized water and ethanol with the assistance of ultrasonication, and dried at 80 ° C for 8 h. Then, 10 mM $\text{NaS}_2\cdot 9\text{H}_2\text{O}$ was dissolved in 60 mL of deionized water and stirred for 20 min to form a clear solution. The aqueous solution and the precursor sample were transferred to a PPL lined hydrothermal autoclave (100 ml) and maintained at 220° C for 24 h. The samples were rinsed several times with deionized water and ethanol with the assistance of ultrasonication, and dried at 80 ° C for 8 h.

Characterizations: The crystallinity and composition of the synthesized samples were characterized by X-ray diffraction (XRD; Rigaku Co.) with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) and X-ray photoelectron spectroscopy (XPS; ESCALAB250Xi, Thermo Fisher Scientific). The morphological features and detailed structural information were conducted by field-emission scanning electron microscopy (FESEM; GeminiSEM, Zeiss), and transmission electron microscopy (TEM; JEOL JEM-2100F). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was carried out using a JEOL JEMARM200F STEM/TEM (resolution of 0.08 nm). The absorbance data of spectrophotometer were acquired on SHIMADZU UV-1800 UV-Vis spectrophotometer.

Electrochemical measurements: NO_3^- reduction experiments were carried out in a

two-compartment cell under ambient condition, which was separated by Nafion 117 membrane. The membrane was protonated by first boiling in ultrapure water for 1 h and treating in H₂O₂ (5 wt%) aqueous solution at 80 °C for another 1 h, respectively. And then, the membrane was treated in 0.5 M H₂SO₄ for 3 h at 80 °C and finally in water for 6 h. The electrochemical experiments were carried out with an electrochemical workstation (CHI 660E) using a three-electrode configuration with prepared electrodes, graphite rod and Ag/AgCl electrode (saturated KCl electrolyte) as working electrode, counter electrode and reference electrode, respectively. The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: $E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + 0.059 \times \text{pH} + 0.197 \text{ V}$ and the presented current density was normalized to the geometric surface area. For electrochemical NO₃⁻ reduction, chrono-amperometry tests were conducted in 1 M KOH solution with 0.1 M NO₃⁻.

Determination of NH₃: Owing to the large concentration of solution, the obtained reaction solutions were diluted 100 times. Specifically, 4 mL electrolyte was obtained from the cathodic chamber and mixed with 50 μL oxidizing solution containing NaClO (pCl = 4 ~ 4.9) and NaOH (0.75 M), 500 μL coloring solution containing 0.4 M C₇H₆O₃Na and 0.32 M NaOH, and 50 μL catalyst solution (1 wt% Na₂[Fe(CN)₅NO]) for 2 h. Absorbance measurements were performed at 654 nm. The concentration-absorbance curve was calibrated using standard NH₃ solution with a series of concentrations. The fitting curve ($y = 0.313x + 0.0313$, $R^2 = 0.999$) shows good linear relation of absorbance value with NH₃ concentration.

In addition, ^1H NMR spectroscopy (600 MHz) was also used to detect ammonia in the isotope-labelling measurement. The collected NH_3 sample was first diluted to the detection range and adjusted to pH 1.0 by adding 0.1 M HCl. Next, 0.5 ml of the sample solution was mixed with 0.1 ml DMSO-d_6 .

Determination of N_2H_4 : A mixed solution of 1.97 g $\text{C}_9\text{H}_{11}\text{NO}$, 10 mL concentrated HCl and 100 ml ethanol was used as a color reagent. Calibration curve was plotted as follows: firstly, preparing a series of N_2H_4 solutions of known concentration as standards; secondly, adding 4 mL color reagent to above N_2H_4 solution, separately, and standing 20 min at room temperature; finally, the absorbance of the resulting solution was measured at 460 nm.

Determination of NO_2^- : Owing to the large concentration of solution, the obtained reaction solutions were diluted 20 times. The NO_2^- concentration was analyzed using the Griess test.¹ The Griess reagent was prepared by dissolving 0.1 g N-(1-naphthyl) ethylenediamine dihydrochloride, 1.0 g sulfonamide and 2.94 mL H_3PO_4 in 50 mL deionized water. In a typical colorimetric assay, the 1.0 mL Griess reagent was mixed with the 1.0 mL nitrite-containing solution and 2.0 mL H_2O and allowed to react at room temperature for 10 min, in which sulfonamide reacts with NO_2^- to form a diazonium salt and then further reacts with amine to form an azo dye (magenta). The absorbance at 540 nm was measured to quantify the NO_2^- concentration with a standard curve of NO_2^- ($y = 0.53986x + 0.01177$, $R^2 = 0.999$).

Determination of FE and NH_3 yield: The FE for N_2 reduction was defined as the amount of electric charge used for synthesizing NH_3 divided the total charge passed

through the electrodes during the electrolysis. The total amount of NH_3 produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH_3 molecule, the FE could be calculated as follows:

$$\text{FE} = 8 \times F \times [\text{NH}_3] \times V / (17 \times Q) \times 100\% \quad (1)$$

NH_3 yield was calculated using the following equation:

$$\text{NH}_3 \text{ yield rate} = [\text{NH}_3] \times V / (s \times t) \quad (2)$$

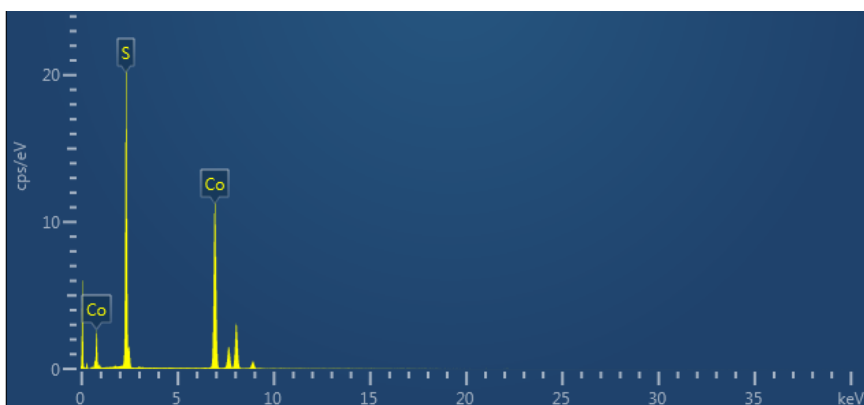
where F is the Faraday constant, $[\text{NH}_3]$ is the measured NH_3 concentration, V is the volume of the electrolyte in the cathodic chamber, Q is the total quantity of applied electricity; t is the reduction time; s is the electrode area.

Electrochemical in-situ Raman spectroscopy measurements: In-situ Raman measurements were carried out on an XploRA PLUS Raman spectrometer (Horiba Jobin Yvon) equipped with a $50\times$ objective and a 638 nm He-Ne laser. All spectra were recorded by using a commercial three-electrode spectro-electrochemical cell (Gaussian-Union Ltd.Co). The as prepared materials, Ag/AgCl (3.0 M KCl), and Pt slice were employed as the working, reference, and counter electrode, respectively. The Ar-saturated 1M KOH with 0.1 M NaNO_3 was used as electrolyte. The signal acquisition duration was 10 s and the filter was 20%.

Electrochemical ATR-FTIR spectroscopy measurements: The in situ electrochemical ATR-FTIR measurements were carried out on a Nicolet iS50 FT-IR spectrometer equipped with a liquid nitrogen-cooled MCT-A detector. The Si prism loaded with catalyst, platinum plate, and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. The 1 M KOH was used as electrolyte. In this work, catalyst suspensions were dropped on the Au film modified Si prism. Before catalyst loading, the Au film was deposited directly on the Si prism by a

chemical deposition method. First, the Si prism was polished with a slurry of 100 nm Al₂O₃ and sonicated in acetone and deionized water. Next, the Si prism was soaked in a piranha solution (3:1 volumetric ratio of 98% H₂SO₄ and 30% H₂O₂) for 30 min and washed by deionized water for several times in order to removal organic contaminants. Following, the reflecting plane of the Si prism was dried with a nitrogen gas flow. Then, the reflecting surface was immersed in a mixture of the Au plating solution (5.75 mM NaAuCl₄ • 2H₂O + 0.025 M NH₄Cl + 0.075 M Na₂SO₃ + 0.025 M Na₂S₂O₃ + 0.026 M NaOH) and a 2 wt % HF solution at 60 for 5 min. After deposition, the Au film was rinsed with deionized water and dried by nitrogen gas flow. In situ ATR-FTIR spectra were recorded during stepping the working electrode potential.

Computational Details: All the calculations were implemented in the VASP package by employing density functional theory (DFT) with spin-polarized Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.^{2,3} The cutoff energy of plane-wave basis set is 400 eV, and the (2×2×1), (2×3×1) and (3×3×1) grid sampling was used for Brillouin zone integration of CoS₂ (100), (110) and (111) slabs, respectively. The DFT+U method was adopted to describe the Co 3*d* electrons with an effective U value of 2 eV.^{4,5} The convergence criteria of energy and force for structural optimization were set to 1×10⁻⁵ eV and 0.02 eV/Å, respectively. All the slabs were repeated periodically with a 20 Å vacuum layer between the images in the direction of the surface normal. The free energies of the reaction intermediates were obtained by $\Delta G = \Delta E_{\text{ads}} + \Delta ZPE - T\Delta S$, where ΔE_{ads} is the adsorption energy, ZPE is the zero point energy and S is the entropy at 298 K. The values of ($\Delta ZPE - T\Delta S$) were obtained through the post-processing tool for VASP code (VASPKIT).



Element	k factor	wt%	wt% Sigma	Atomic %
S	0.991	48.36	0.12	66.24
Co	1.211	51.64	0.12	33.76
Total:		100.00		100.00

Fig. S1. EDS spectrum and corresponding atomic ratio for CoS₂ OC.

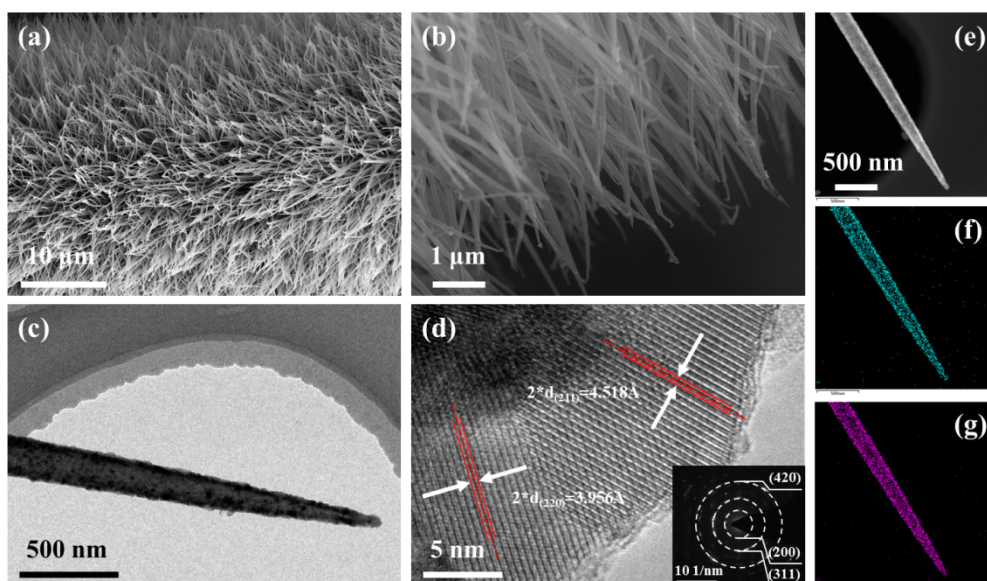


Fig. S2. (a,b) SEM images of carbon paper@CoS₂ nanowire. (c) TEM image of one single CoS₂ nanowire. (d) HRTEM image of CoS₂ nanowire. Bottom-right inset in (d) is the corresponding SAED pattern. (e) STEM image and (f,g) corresponding element mappings of Co and S.

CoS₂ nanowire arrays (CoS₂ NW) on carbon paper (CC) were also fabricated for comparison by two-step hydrothermal reaction. **Fig. S2** shows the SEM, TEM, HRTEM, SEAD and EDS mapping of the CoS₂ NW sample. Clearly, the slim CoS₂ with pointed tips are homogeneously aligned on carbon paper, forming an uniform nanoarray on a large scale, as shown in **Fig. S2a** and **b**. The nanowire morphology was confirmed by TEM image (**Fig. S2c**). The single nanowire has porous and rough structure, composed of nanocrystallites with size of 10 to 20 nm. HRTEM image of the CoS₂ NW in **Fig. S2d** reveals well-resolved lattice distance of 2.259 and 1.978 Å, which are well corresponded to the (211) and (220) planes of cattierite-type CoS₂. **Fig. S2e-g** show the STEM image and corresponding EDS mapping of one CoS₂ NW, also presenting an uniform distribution of Co and S elements.

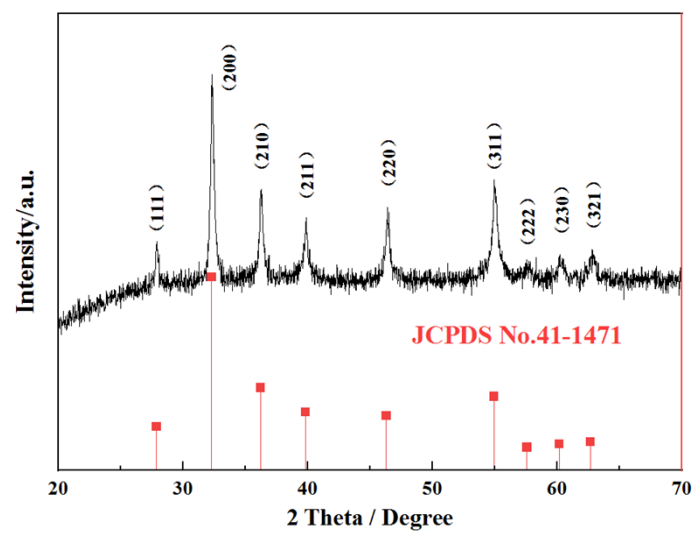
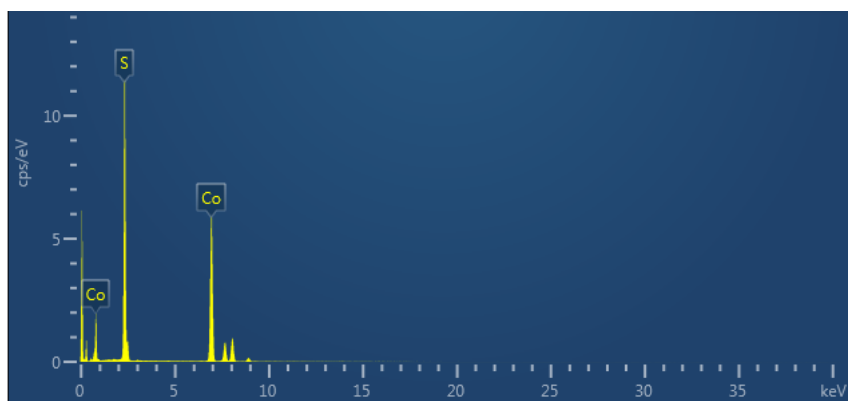


Fig. S3. XRD pattern of CoS₂ NW.



Element	k factor	wt%	wt% Sigma	Atomic %
S	0.991	50.10	0.12	64.86
Co	1.211	49.90	0.12	35.14
Total:		100.00		100.00

Fig. S4. EDS spectra of CoS₂ NW illustrating the presence of S and Co.

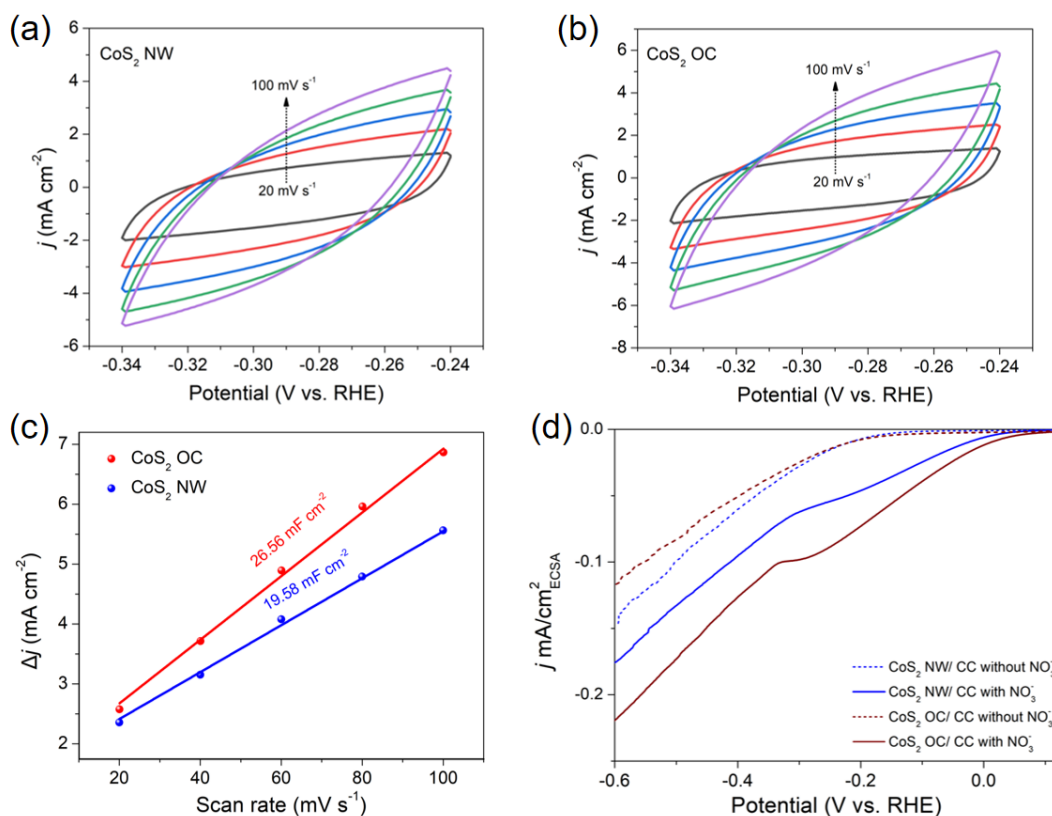


Fig. S5. CVs of (a) CoS₂ NW/CC and (b) CoS₂ OC/CC with various scan rates (20-100 mV s⁻¹). (c) The capacitive current densities as a function of scan rates for CoS₂ NW/CC and CoS₂ OC/CC. (d) ECSA-normalized LSV curves.

For the calculation of ECSA, 40 μF cm⁻² is assumed as a moderate value of the specific capacitance for a flat surface. ECSA of the catalysts was calculated according to the following equation: $ECSA = C_{dl}/40\mu F\ cm^{-2}\ per\ cm^2_{ECSA}$. Our results show that the the current density of the octahedral CoS₂ nanocrystal (CoS₂ OC) is also significantly higher than that nanowire CoS₂ (CoS₂ NW) using ECSA approach when adding NO₃⁻, see Fig. S5.

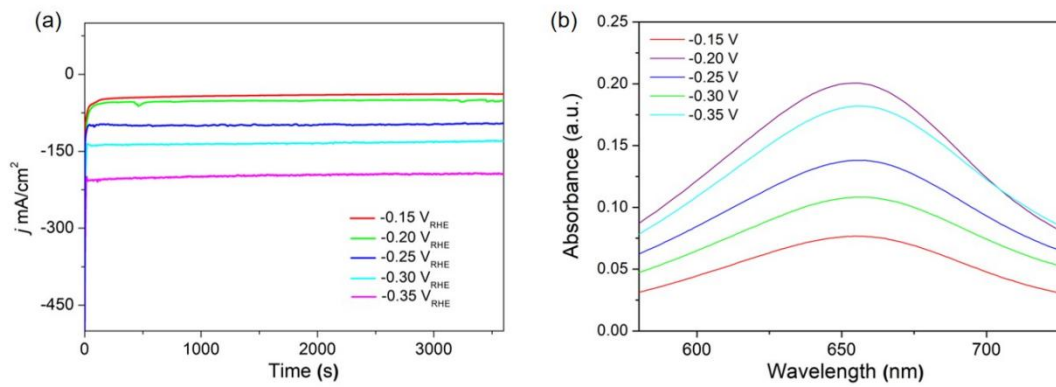


Fig. S6. (a) Chronoamperometry curves and (b) corresponding UV-Vis absorption spectra.

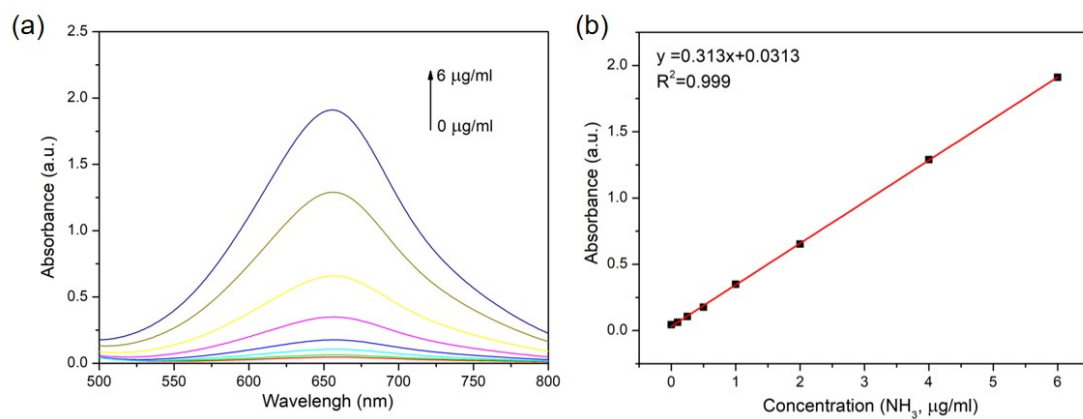


Fig. S7. (a) UV-vis absorption spectra of indophenol assays with NH_3 concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_3 concentration.

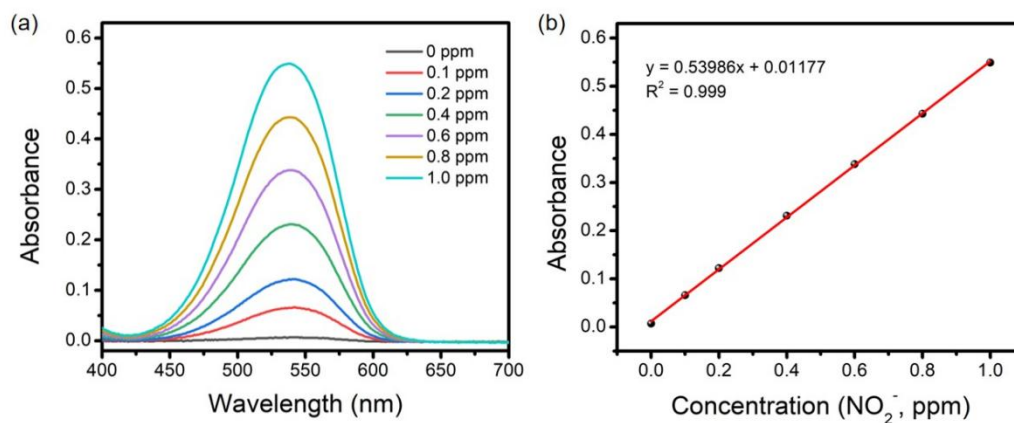


Fig. S8. (a) UV-Vis absorption spectra of different NO_2^- concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for estimation of NO_2^- concentration.

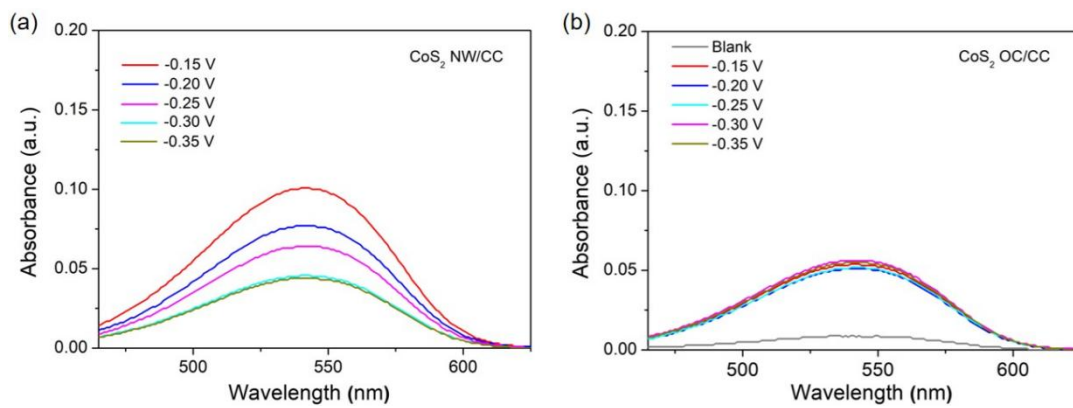


Fig. S9. (a,b) UV-Vis absorption spectrum of NO_2^- concentrations on CoS_2 NW/CC and CoS_2 OC/CC, respectively.

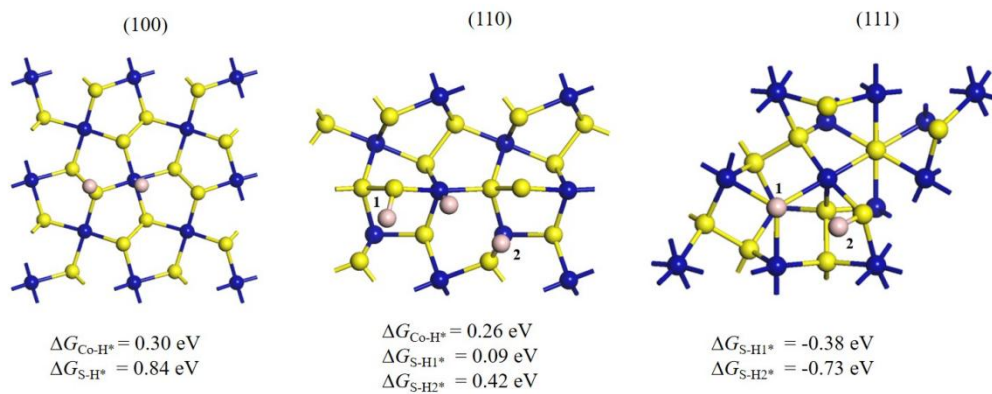


Fig. S10. Free energies of HER on CoS₂ (100), (110) and (111) surfaces. Co, blue; S, yellow; H, pink.

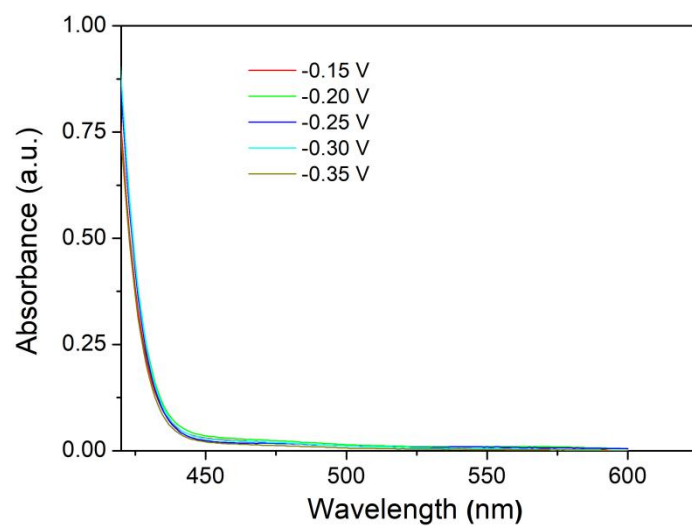


Fig. S11. UV-Vis absorption spectrum at different electrode potentials after electrocatalysis for 1h.

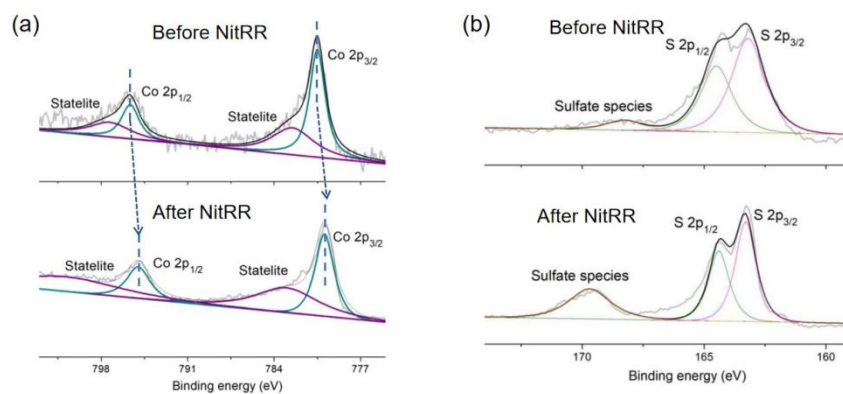


Fig. S12. (a) XPS spectrum in Co 2p region before and after NO₃RR (b) XPS spectrum in S 2p region before and after NO₃RR.

Alternatively, the chemical state informations on CoS₂ OC/CC before and after NO₃RR were further confirmed by X-ray photoelectron spectroscopy (XPS). **Fig. S12a** shows that the two main peaks at 780.46 and 795.62 eV can be assigned to the characteristic peaks of Co 2p_{3/2} and Co 2p_{1/2}, respectively, which can be ascribed to the Co²⁺.^{6,7} After NO₃RR, these two main peaks are slightly shifted to 779.98 and 795.11 eV, suggesting that a small amount of Co³⁺ appear. For S 2p, it exhibits binding energy located at 163.18, 164.44, and 168.5 eV, of which the first two can be ascribed to S 2p_{3/2} and S 2p_{1/2} peaks of Co-S bonds and last peak located at 168.5 eV might be ascribed to S-O bonding, see **Fig. S12b**.^[6] After NO₃RR, the intensity of S-O bonding is obviously increased, suggesting that more oxygen-containing species is formed. Thus, it is inferred that the formation of Co³⁺ after NO₃RR could be attributed to the coverage of oxygen-containing species on catalyst surface due to its stronger electronegativity. Finally, Co⁰ is not detectable by XPS in CoS₂ OC after NO₃RR, indicating that the CoS₂ OC catalyst is stability during reduction process.

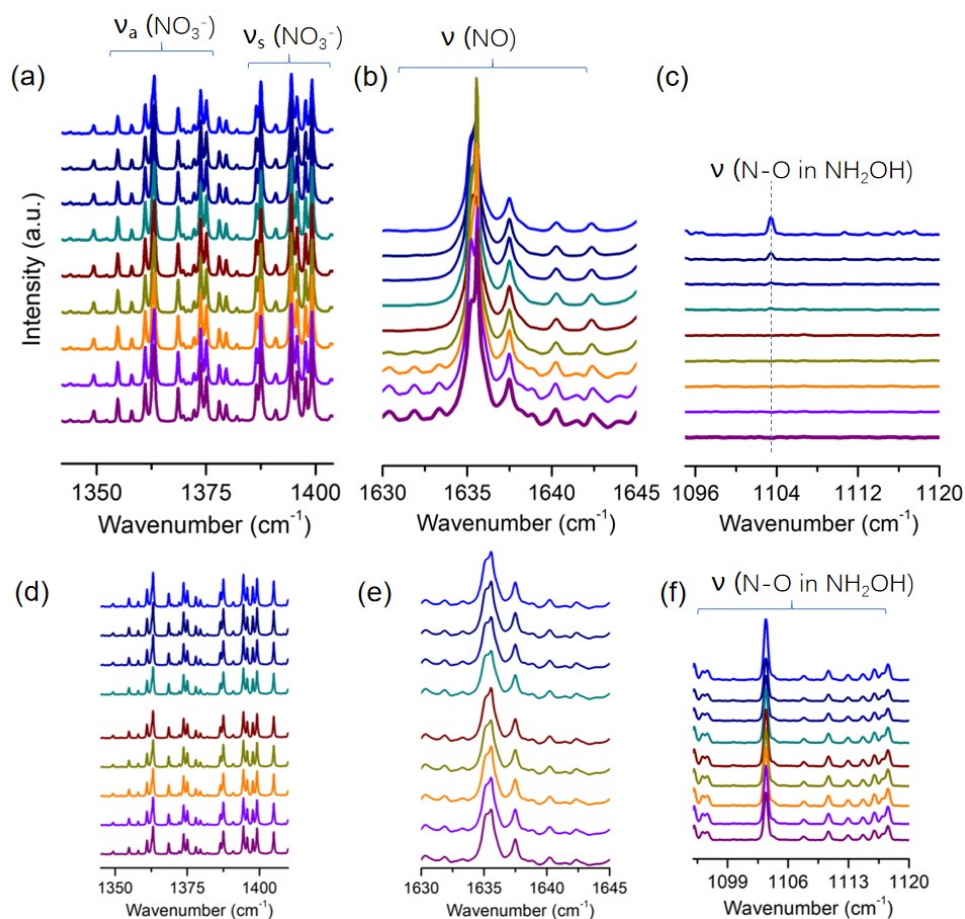


Fig. S13. In situ ATR-FTIR spectra of (a-c) CoS₂ OC and (d-f) CoS₂ NW.

The absorption bands at 1393 and 1364 cm⁻¹ were ascribed respectively to N-O symmetric and asymmetric stretching vibration of NO₃⁻,^[8] see **Fig. S13a and d**. The absorption band of adsorbed *NO is detected at 1636 cm⁻¹,^[8] see **Fig. S13b and e**. **Fig. S13c** shows that on CoS₂ OC/CC the -N-O- stretching vibration of another hydroxylamine (NH₂OH) intermediate appears at lower electrode potential around 1110 cm⁻¹ and then disappears as applied potential increases;^[8] however, on CoS₂ NW/CC it has existed at all given electrode potentials, see **Fig. S13f**.

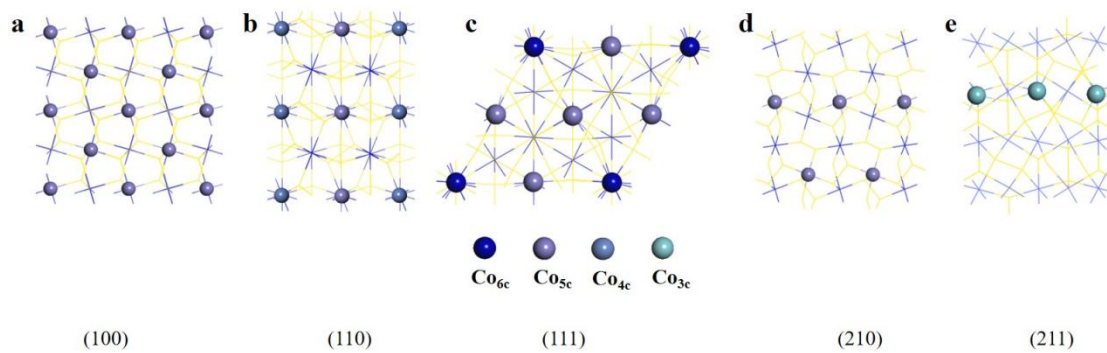


Fig. S14. The top view of atom configurations on CoS₂ (100), (110), (111), (210) and (211) surfaces, respectively.

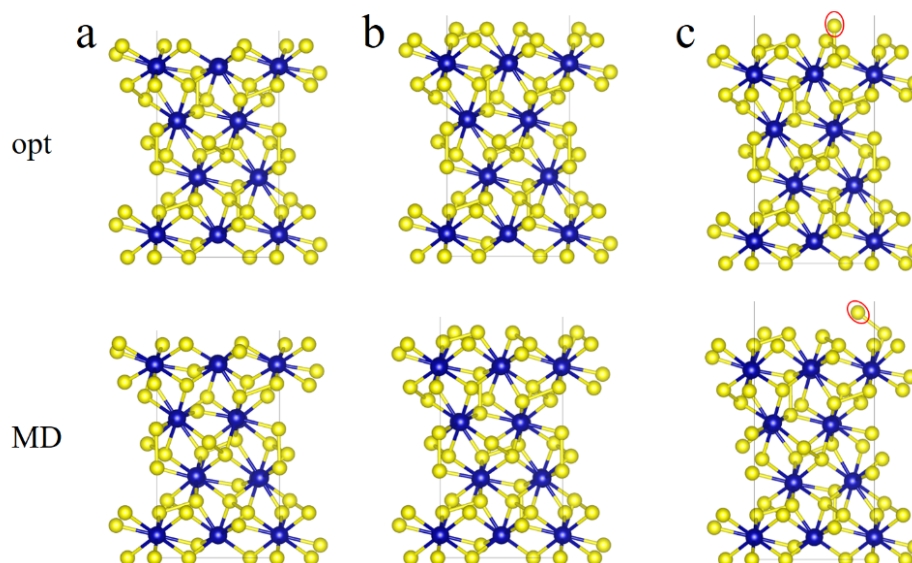


Fig. S15. The optimized and MD structures of (a) stoichiometry surface, (b) 3S surface and (c) 4S surface.

Two sulfur-rich surface models were checked for CoS_2 (111), namely (111)-3S and (111)-4S surfaces. We employed ab initio molecular dynamics (AIMD) to explore their stability under room temperature. After 10 ps simulation at 300K, atomic structures of stoichiometry and 3S surfaces underwent very tiny changes, which means that stoichiometry and 3S surfaces are reasonably stable at room temperature (**Fig. S15**). Notably, there is a reconstruction of S atoms on 4S surfaces, see **Fig. S15c**.

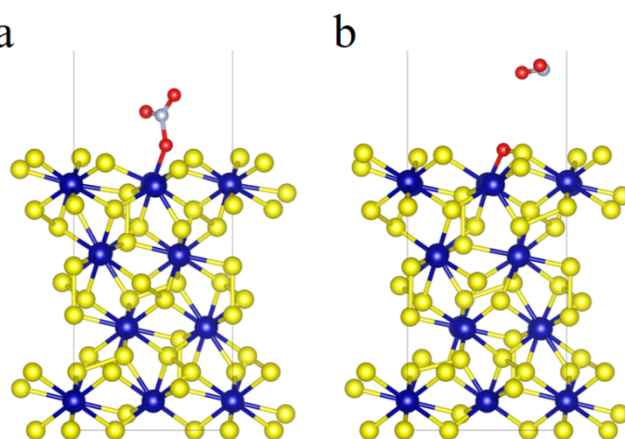


Fig. S16. AIMD structures of NO₃* on CoS₂ (111) stoichiometry facets, (a) 0 ps, (b) 0.4 ps.

When the NO₃* molecule was placed at a high height from the (111) stoichiometry facet, it could not dissociate during geometry optimization (**Fig. S16a**). However, the NO₃* molecule would spontaneously dissociate during the AIMD simulation at 300K, which the NO₃* molecule would dissociate into O* and NO₂ within 0.4 ps (**Fig. S16b**) meaning a metastable state. We have further employed CI-NEB method to identify saddle-point structures for the NO₃* → NO* + 2O* dissociation steps. The barriers of NO₃* → O* + NO₂* and NO₂* → O* + NO* on CoS₂ (111) stoichiometry facets are 0.24 eV and 0.25 eV, respectively (**Fig. S17a** and **Fig. S18**), meaning that the NO₃* → NO* + 2O* dissociation steps could occur under room temperature. However, the barrier of NO₃* → O* + NO₂* on (111)-3S facet is 0.18 eV, and the NO₂* → O* + NO_(g) is higher barrier with 0.93 eV (**Fig. S17b** and **Fig. S19**). It suggests that the CoS₂ (111) stoichiometry facet is the actual catalytic surface due to the lower activation energy from *NO₂ to *O + *NO.

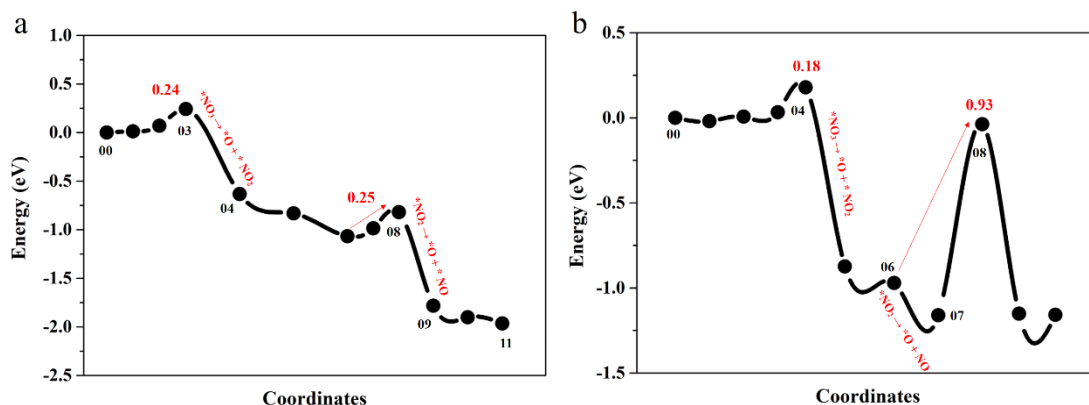


Fig. S17. Calculated energy profile of NO₃* → NO* + 2O* on (111) facets, (a)

stoichiometry CoS_2 , (b) (111)-3S surface.

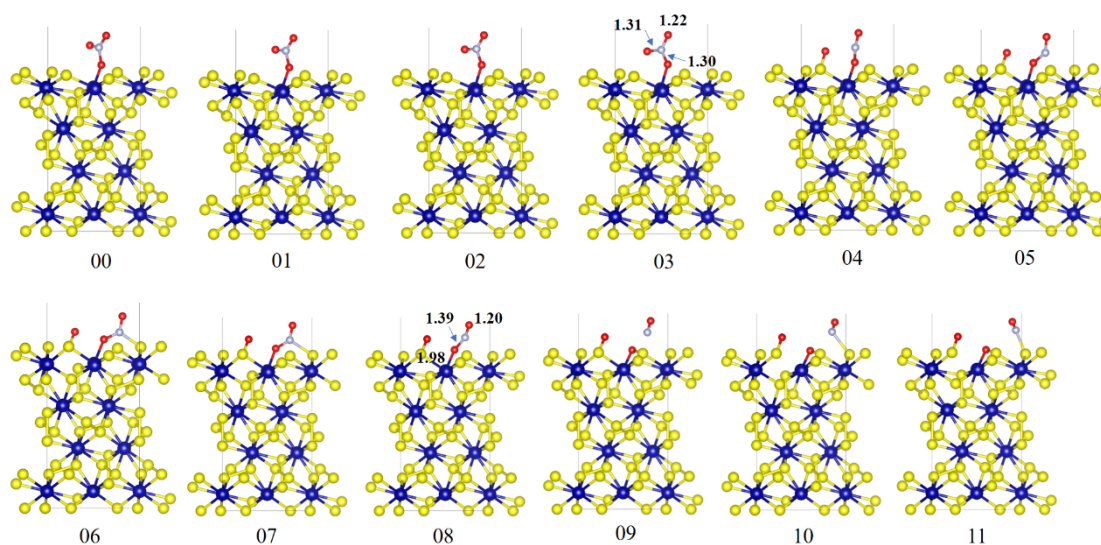


Fig. S18. The corresponding structures of $\text{NO}_3^* \rightarrow \text{NO}^* + 2\text{O}^*$ steps on (111) stoichiometry CoS_2 .

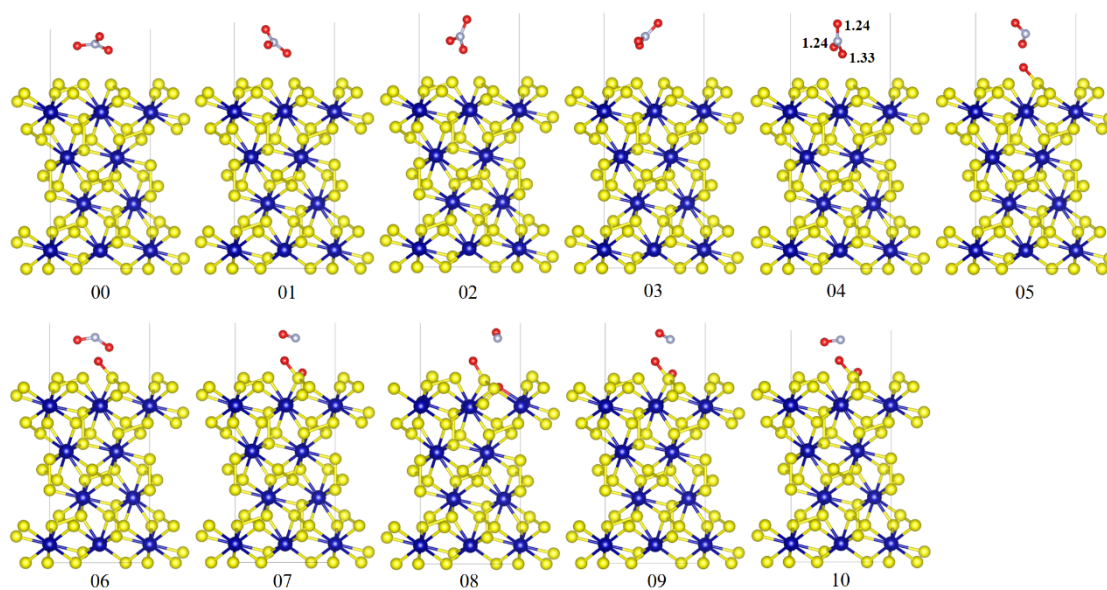


Fig. S19. The corresponding structures of $\text{NO}_3^* \rightarrow \text{NO}^* + 2\text{O}^*$ steps on (111)-3S surface.

The dissociation barriers of NO_3^* on (110) and (100) surfaces have been calculated, see **Fig. S20-22**. The barriers of $\text{NO}_3^* \rightarrow \text{O}^* + \text{NO}_2^*$ on (110) and (100) surfaces are 2.06 and 1.34 eV (**Fig. S20-22**), respectively, which means that the $\text{NO}_3^* \rightarrow \text{O}^* + \text{NO}_2^*$ steps are hard to occur on these two surfaces. Hence, the study of subsequent $\text{NO}_2^* \rightarrow \text{O}^* + \text{NO}^*$ steps has been omitted.

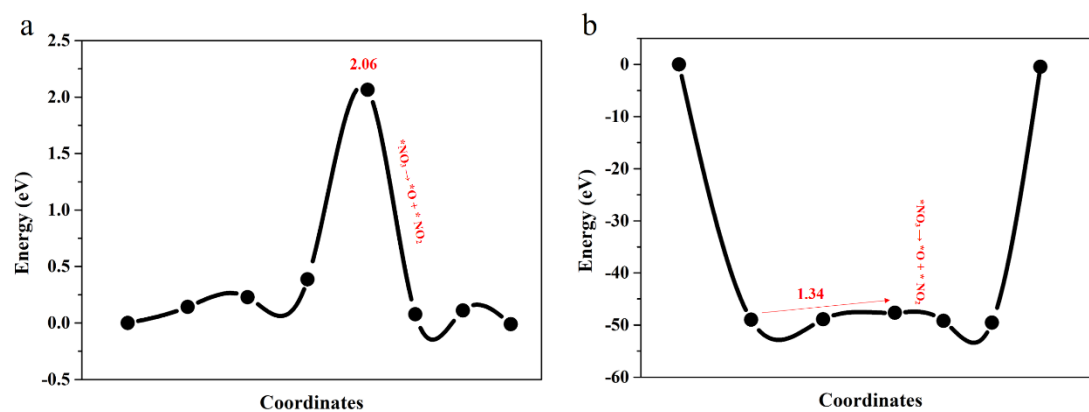


Fig. S20. Calculated energy profile of NO_3^* dissociation of (a) (110) surface and (b) (100) surface.

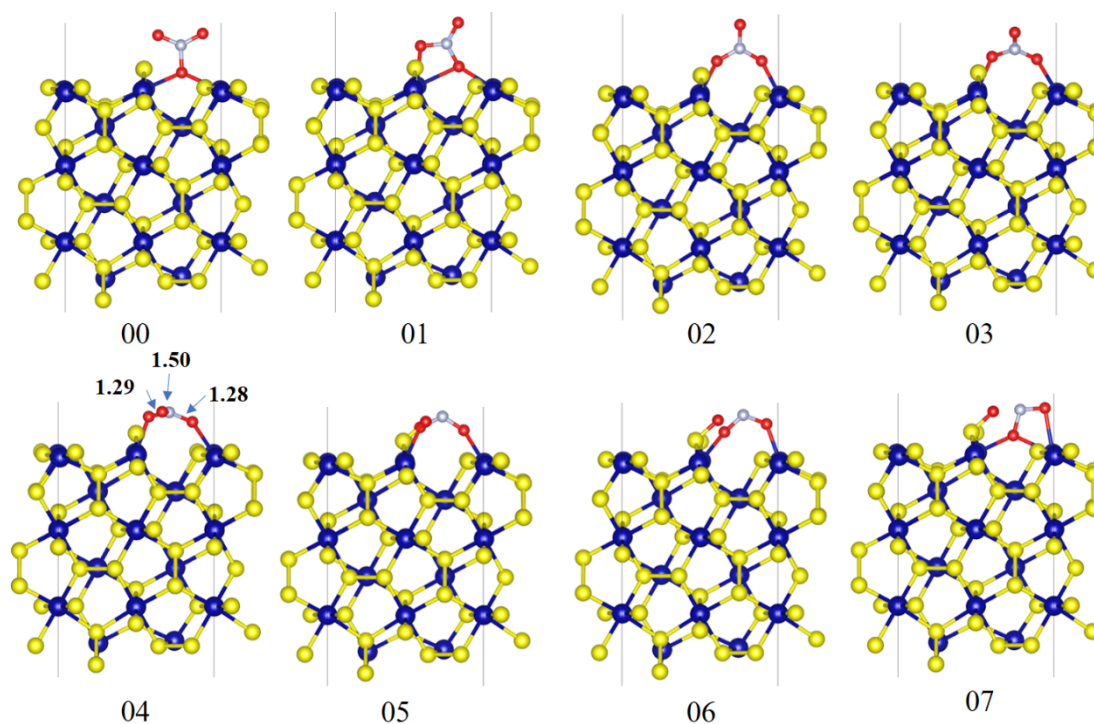


Fig. S21. The corresponding structures of NO_3^* dissociation on (110) surface.

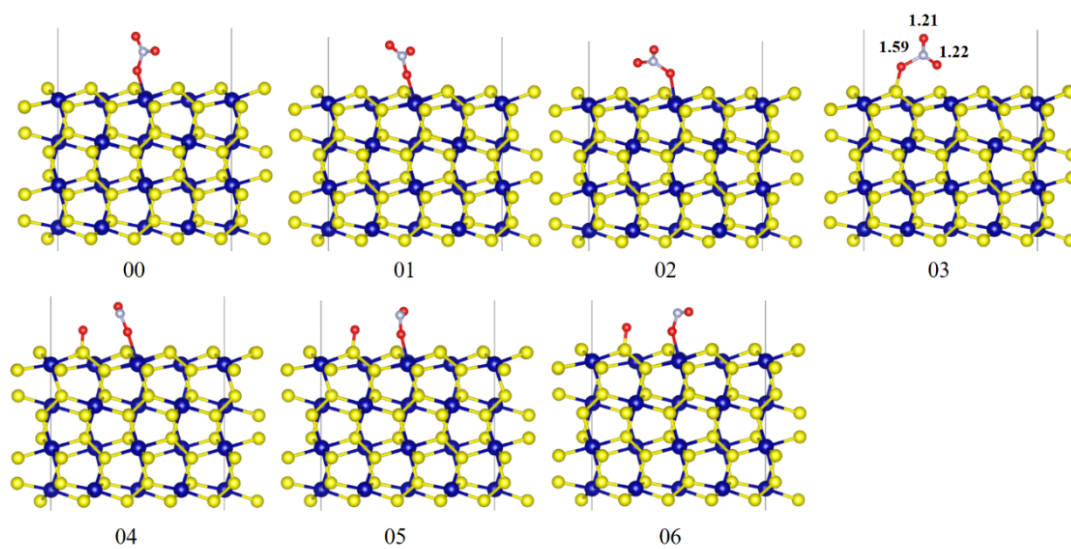


Fig. S22. The corresponding structures of NO_3^* dissociation on (100) surface.

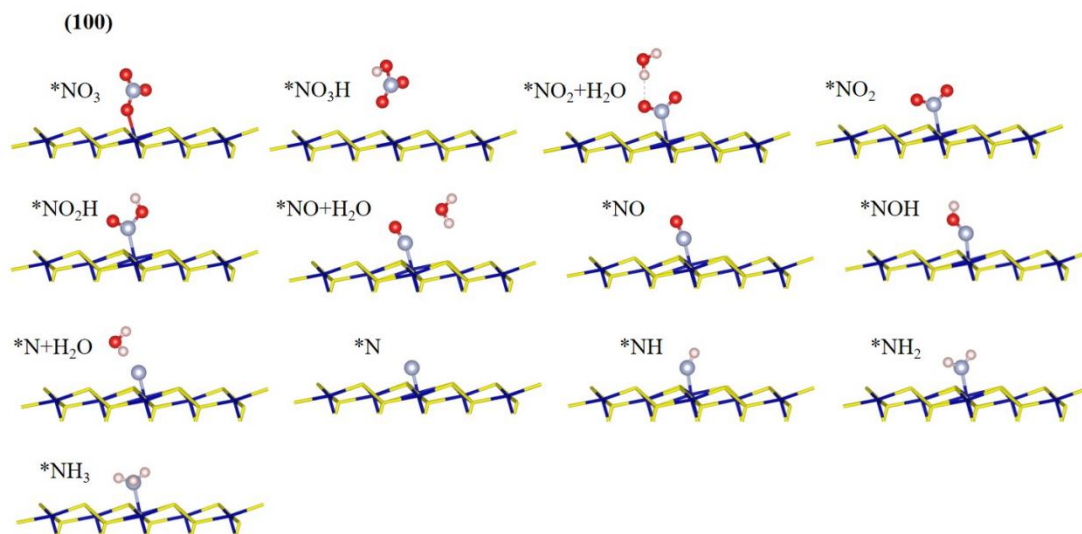


Fig. S23. The atom configurations of NO₃RR process on CoS₂ (100) surface. Co, blue; S, yellow; H, pink; N, grey; O, red.

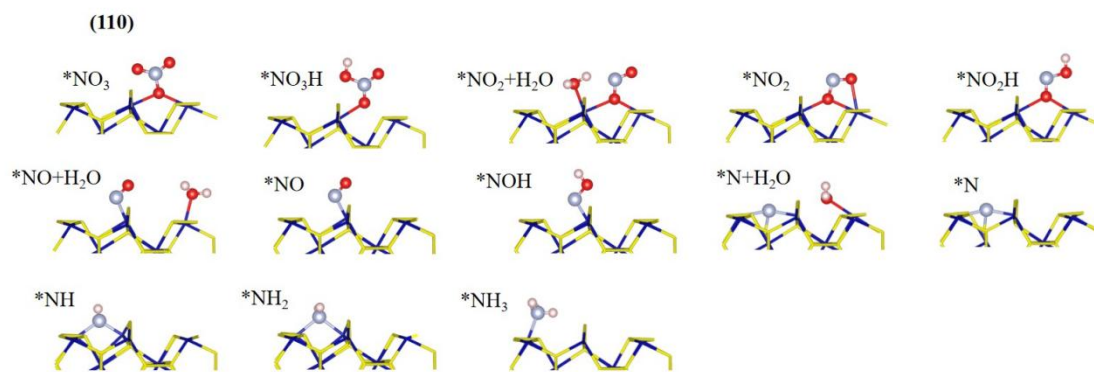


Fig. S24. The atom configurations of NO₃RR process on CoS₂ (110) surface.

(111)

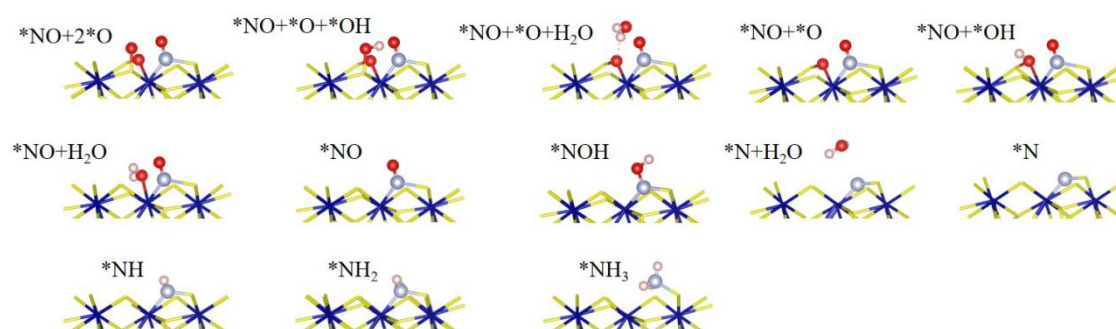


Fig. S25. The atom configurations of NO₃RR process on CoS₂ (111) surface.

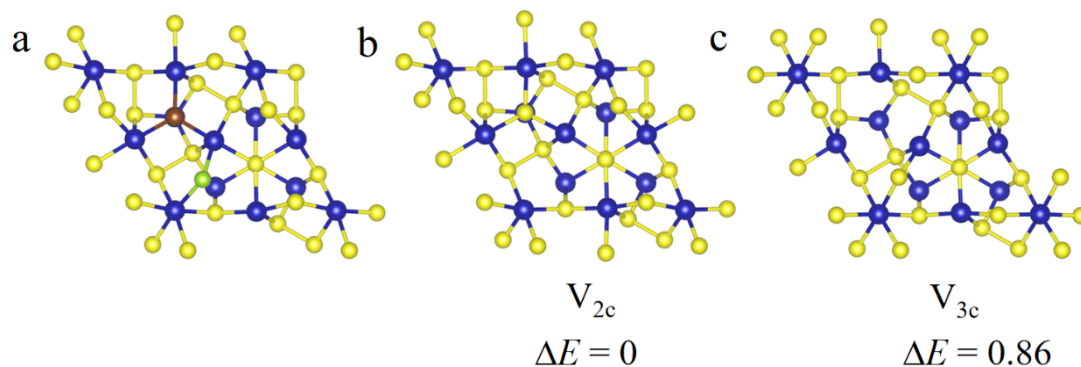


Fig. S26. The optimized structures of (111) facets, (a) stoichiometry, (b) V_{2c} , (b) V_{3c} . The green and brown atoms are two-coordinated and three-coordinated S atoms, respectively.

The (111) stoichiometry facets were selected to study defect impact on NO_3RR reaction. There exist two-coordinated and three-coordinated S atoms on (111) stoichiometry facets, which corresponding defects are designated as V_{2c} and V_{3c} . The V_{2c} is more easily formed than V_{3c} (Fig. S26) due to the lower formation energy (ΔE). The NO_3^* molecule on the (111)- V_{2c} facets still did not dissociate after a 10 ps simulation at 300K (Fig. S27), indicating that S defects are not conducive to the dissociation of the NO_3^* molecule. However, on the $\text{CoS}_2(111)$ surface without S defects, the NO_3 molecule has already spontaneously dissociated. Our in situ Raman and infrared spectroscopy results show that surface NO_3^* is readily converted. Therefore, we are inclined to believe that the Co active sites without S defects are the primary catalytic sites in our material.

Subsequently, the reaction free energy (ΔG) is also calculated to identify the rate-determining step (RDS). As for (111)- V_{2c} facets with S vacancy (Fig. S28), the first hydrogenation step ($^*\text{NO}_3 \rightarrow ^*\text{NO}_3\text{H}$) is the RDS with $\Delta G = 0.44$ eV, and this ΔG value is smaller than that of (111) stoichiometry facets. So, it indicates that preparing CoS_2 catalyst with S vacancies could also be a promising material for NO_3RR .

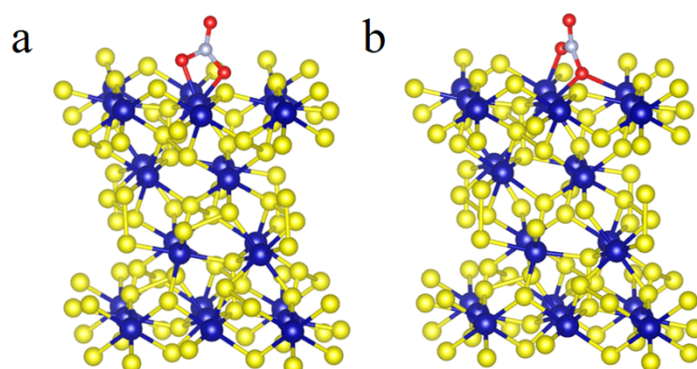


Fig. S27. AIMD structures of NO_3^* on (111)- V_{2c} facets, (a) 0 ps, (b) 10 ps.

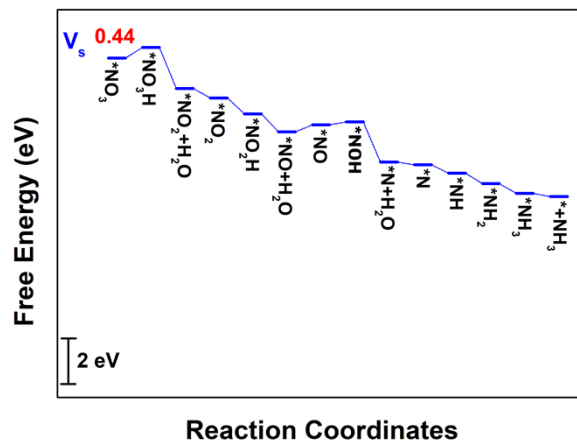


Fig. S28. Free energy diagrams of NO₃RR reaction on (111)-V_{2c} facets.

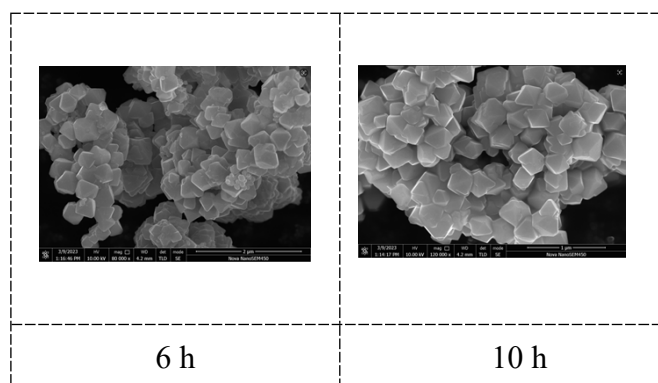


Fig. S29. The morphological changes of CoS₂ OC after different electrolysis times for NO₃RR.

We found that CoS₂ OC exhibits partial agglomeration (Fig. S29), but its performance remains stable. This suggests that the CoS₂ OC may have some resistance to agglomeration or that agglomeration has little impact on its performance.

Table S1. Comparison of the catalytic performances of CoS₂ OC with reported Co-based NO₃RR catalysts at ambient conditions.

Catalyst	Electrolyte	NH ₃ yield rate ($\mu\text{mol h}^{-1} \text{cm}^{-2}$ @V vs. RHE)	FE (%@V vs. RHE)	Ref.
CoS ₂ OC	1 M KOH (0.1 M NO ₃ ⁻)	588 @ -0.35V	97.5 @ -0.25V	This work
Co@TiO ₂ /TP	0.1 M PBS (0.1 M NO ₃ ⁻)	800 @ -0.40V	96.7 @ -0.70V	[9]
Co-P/TP	0.2 M PBS (200 ppm NO ₃ ⁻)	24.47 @ -0.6	93.6 @ -0.3	[10]
Co ₂ AlO ₄ /CC	0.1 M PBS (0.1 M NO ₃ ⁻)	464.7 @ -0.9	92.6 @ -0.7	[11]
Co/CoO NSA	0.1 M Na ₂ SO ₄ (200 ppm NO ₃ ⁻)	194.46 @ -0.65	93.8 @ -0.65	[12]
ZnCo ₂ O ₄ NSA/CC	0.1 M NaOH (0.1 M NO ₃ ⁻)	634.74 @ -0.8	98.33 @ -0.6	[13]
CoTiO _{3-x} /CP	1 M KOH (0.1 M NO ₃ ⁻)	858 @ -1.0	92.6 @ -1.0	[14]
NiCo ₂ O ₄ /CC	0.1 M NaOH (0.1 M NO ₃ ⁻)	973.2 @ -0.6	99 @ -0.3	[15]
CoP NAs/CFC	1 M NaOH (1 M NO ₃ ⁻)	956 @ -0.3	100 @ -0.3	[16]
CuCo	1 M KOH (0.1 M NO ₃ ⁻)	4800 @ -0.2	100 @ -0.2	[8]
Mn-Co ₃ O ₄	0.5 M K ₂ SO ₄ (0.1 M NO ₃ ⁻)	2058 @ -1.2	99.5 @ -1.2	[17]
Fe ₃ C NPs@NCF	0.1 M NaOH (0.1 M NO ₃ ⁻)	466 @ -0.8	96.9 @ -0.8	[18]
Cu nanosheets	0.1 M KOH (10 mM KNO ₃)	21.67 @ -0.15 V	99.7 @ -0.15 V	[19]

FeCo ₂ O ₄	0.1 M NaOH (20 mM NaNO ₃)	277.1 @ -0.5V	95.9	[20]
Cu ₅₀ Ni ₅₀	1 M KOH (100 mM NO ₃ ⁻)	80.7 @ -0.15	82.0 @ -0.15	[21]
Fe ₃ O ₄ /PC	0.1 M NaOH (0.1 M NO ₃ ⁻)	394.8 @ -0.4	91.6 @ -0.4	[22]

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