



Promotion of nitrate reduction reaction activity by $\text{Co}_3\text{O}_4@\text{MoS}_2$ Particle-Support system

Yanli Zhang, Jiuqing Xiong, Shihai Yan^{*}, Bingping Liu^{*}

College of Chemistry and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao, 266109, China

ARTICLE INFO

Keywords:

Electrochemical nitrate reduction reaction
 $\text{Co}_3\text{O}_4@\text{MoS}_2$
 Particle-support system
 Synergistic effect
 Density functional theory

ABSTRACT

Electrochemical reduction of nitrate to NH_3 is a very promising alternative reaction to the Haber-Bosch process, and it is necessary to develop the efficient electrocatalysts. In this study, a particle-support mode Co_3O_4 catalyst was synthesized with ZIF-67 as the precursor, and then dispersed on MoS_2 nanoflowers by hydrothermal method. The Co_3O_4 is anchored to MoS_2 by forming Co-S coordination bond. Furthermore, the particle-supported Co_3O_4 exhibits better performance than Co_3O_4 alone, as is manifested by higher Faradaic efficiencies and NH_3 yield rate at -0.64 V (52.69% vs 32.03%; $4539.61\text{ }\mu\text{g h}^{-1}\text{ mg}_{\text{cat}}^{-1}$ vs $2048.63\text{ }\mu\text{g h}^{-1}\text{ mg}_{\text{cat}}^{-1}$), lower energy barriers (0.96 eV vs 1.19 eV), and better electronic conductivity (Bandwidth: 0.581 eV vs 0.613 eV). In addition, this research provides an effective solution to solve the aggregation problem of metal oxide nanoparticles.

1. Introduction

Ammonia is the basis of modern agriculture, heavy industry, pharmaceutical industry, and fertilizer production [1,2]. In addition, it has made outstanding contributions to the growth and development of animals and plants, and is considered as a renewable carbon-free hydrogen-rich energy carrier with high hydrogen content of 17.7 wt% [3–6]. With the development of society, the demand for ammonia has increased sharply. A large proportion of NH_3 is fabricated via the traditional Haber-Bosch process with the nitrogen and hydrogen as the raw materials under the harsh conditions with high temperature (400 – 500 °C) and pressure (150 – 300 atm) [7–9], and the process consumes about 1–3% of annual global energy and generates huge CO_2 emission [10]. Beyond that, it has a poor energy efficiency with the low conversion constrained by thermodynamics and requiring large centralized infrastructure [11].

More recently, electrochemical nitrogen reduction reaction (eNRR) has been paid extensive attention [12] due to its simplicity, safety, and environmental friendship in contrast with other alternative methods, such as photocatalysis [13] and enzymatic catalysis [14]. In eNRR, nitrogen reacts with water to generate ammonia by a certain voltage under mild conditions [15]. However, the high dissociation energy of $\text{N}\equiv\text{N}$ (941 kJ mol^{-1}) and the competitive reaction of hydrogen evolution reaction (HER) lead to lower generation rate of ammonia and lower faraday efficiency (FE%), which is not suitable for industrial production

[4,12,16]. Compared with eNRR, electrochemical nitrate reduction reaction (e NO_3RR) avoids the above shortcomings effectively and attracted extensive attention. In nitrate ions (NO_3^-), dissociation energy of N-O bond is 204 kJ mol^{-1} only and NO_3^- is very soluble in water, both of which strongly promote the reduction from NO_3^- to NH_3 and the rate is distinctly larger than that of NRR reaction [17,18]. In addition, the raw material of NO_3^- exists widely in the environment as a pollutant, produced by chemical and agricultural industries [19,20]. Therefore, the conversion of NO_3^- into NH_3 can not only solve environmental pollutants, but also obtain ammonia resources, which is of great research value.

So far, several groups have reported cobalt-based oxides as cathode catalysts for e NO_3RR because of Co_3O_4 is one of the spinel oxides with flexible ionic arrangement and multivalent structure [3,17,21,22,39–41]. The results demonstrate that Co_3O_4 is indeed active for e NO_3RR , but with a low ammonia yield ($283\text{ }\mu\text{g mg}^{-1}\text{ h}^{-1}$) [23,24]. Co_3O_4 nanoparticles are prone to aggregation due to its high surface energy [25], the most common solution is to disperse the nanoparticles on a template. For example, Zhou et al. used the template method to disperse Co_3O_4 nanoparticles onto TiO_2 nanosheets. It was pointed out that the supports could affect or even dominate the catalytic activity and selectivity of the nanoparticles because atomic geometry and electronic structure of the active site at the interface of nanoparticles and support could be regulated [26]. Therefore, a support-like composite might effectively solve the aggregation problem of Co_3O_4 nanoparticles by

^{*} Corresponding authors.

E-mail addresses: shyan@qau.edu.cn (S. Yan), bpiliu@qau.edu.cn (B. Liu).

<https://doi.org/10.1016/j.jelechem.2023.117702>

Received 20 June 2023; Received in revised form 21 July 2023; Accepted 3 August 2023

Available online 7 August 2023

1572-6657/© 2023 Elsevier B.V. All rights reserved.

increasing the specific surface area to add more active sites, while the electron transfer between the carrier and nanoparticles enhances the electrical conductivity of Co_3O_4 , thus improves the activity of the reaction center. Molybdenum disulfide (MoS_2) has been widely reported in NRR for its high chemical stability and large specific surface area, where the base of 2H- MoS_2 has a large numbers of sulfur atoms that can bond with transition metals to form coordination bonds covering the surface [27,28,42], and its flower morphology provides a good platform for later loading. The structure of MoS_2 nanoflower has a larger loading area than TiO_2 nanosheet. The Co_3O_4 anchored on MoS_2 nanoflowers ($\text{Co}_3\text{O}_4@/\text{MoS}_2$) is expected to be synergistic effect of Co_3O_4 and MoS_2 to improve the efficiency of eNO_3RR .

The support of MoS_2 nanoflowers in $\text{Co}_3\text{O}_4@/\text{MoS}_2$ composite can promote the electron transfer and prevent the aggregation of Co_3O_4 nanoparticles. The Co_3O_4 nanoparticles are synthesized by pyrolysis of zeolitic imidazolate frameworks (ZIFs) precursor to reduce the size. The $\text{Co}_3\text{O}_4@/\text{MoS}_2$ catalyst exhibits outstanding catalytic performance for eNO_3RR with the NH_3 yield rate of $4539.61 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and the Faradaic efficiency (FE) of 52.69% at -0.64 V . To explore the reaction mechanism and the catalytic principle, the density functional theory (DFT) calculations are performed for NO_3^- reduction to NH_3 on the active site of the catalysts. It is elucidated that the improved performance comes from the synergistic effect of Co_3O_4 and MoS_2 , as well as better electronic conductivity of $\text{Co}_3\text{O}_4@/\text{MoS}_2$ with lower energy barriers (0.96 eV).

2. Experimental section and computational method

2.1. Materials

Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), isopropanol, sodium hydroxide (NaOH), sodium nitroferrocyanide ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$), potassium nitrate (KNO_3), sulfonamide were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Methanol, thiourea ($\text{CH}_4\text{N}_2\text{S}$), sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$), sodium hypochlorite (NaClO), anhydrous sodium sulfate (Na_2SO_4) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd., Tianjin BASF Chemical Co., Ltd., Tianjin Bodi Chemical Co., Ltd., Tianjin Yongda Chemical Reagent Co., Ltd., and Tianjin Dingshengxin Chemical Co., Ltd. respectively. Hexaammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$), 2-Methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$), Nafion (5 wt%) were purchased from Shanghai Silver Iodine Chemical Co., Ltd., Shanghai McLean Biochemical Technology Co., Ltd., and Aladdin Ltd.(China) respectively. Salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$) and ethanol were purchased from Laiyang Kangde Chemical Co., Ltd.(China). Phosphoric acid (H_3PO_4) was bought from Beijing Chemical Industry Co., Ltd (China). N-(1-naphthyl) ethylenediamine dihydrochloride was purchased from Tianjin Aopuseng Chemical Co., Ltd.

2.2. Catalyst synthesis

2.2.1. Synthesis of Co_3O_4 nanoparticles

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 2-Methylimidazole were dissolved in the binary mixture of 40 mL methanol and 40 mL water, then ultrasonic oscillated for 10 mins. The mixture was allowed to stand overnight at room temperature for precipitation reaction and the purple precipitate was collected by centrifugation followed by washing several times with methanol. Finally, the dried sample was obtained under vacuum as the precursor of Co_3O_4 Nanoparticles and named as ZIF-67 (a metal-organic framework material). The ZIF-67 precursor was placed in the furnace and heated to 500°C for 10 h with the heating rate of $2^\circ\text{C}/\text{min}$ to prepare Co_3O_4 nanoparticles [43].

2.2.2. Synthesis of MoS_2 nanoflowers

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and $\text{CH}_4\text{N}_2\text{S}$ were dissolved in 40 mL ultrapure water, and stirred for 1 h. The resulting solution moved into a Teflon-

equipped stainless-steel autoclave and heated at 220°C for 18 h. The product was collected by centrifugation and washed several times with ethanol. Then, the MoS_2 catalyst were obtained by drying overnight in a vacuum oven at 60°C [44,45].

2.2.3. Synthesis of $\text{Co}_3\text{O}_4@/\text{MoS}_2$

A solution of the same steps as the above 2.2.2 to make MoS_2 nanoflowers, mixed with Co_3O_4 nanoparticles (100 mg /150 mg /200 mg), and then stirred for 0.5 h. The mixed solution was moved into a Teflon-equipped stainless-steel autoclave for heating, washing, and drying under the same conditions as the step of 2.2.2. Then got the $\text{Co}_3\text{O}_4@/\text{MoS}_2$ catalyst.

2.3. Characterization of samples

The morphology and microstructure of all prepared samples were analyzed by scanning electron microscopy (SEM, ZEISS Gemini SEM 300). The crystal structure of the catalyst was characterized by X-ray diffraction (XRD, Rigaku Smart Lab SE). The composition and state of the catalyst surface were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The concentration of NH_3 was measured using a UV-3900 spectrophotometer.

2.4. Preparation of the working electrode

3 mg of catalyst and 20 μL of Nafion solution were dispersed into 500 μL of isopropanol and were ultrasonicated for 1 h to form a uniform ink. Then 40 μL of ink was evenly dropped on the glassy carbon electrode with a loading of 0.23 mg cm^{-2} to prepare the working electrode and the thickness is almost unmeasurable due to the thin layer on the GC surface.

2.5. Electrochemical measurements

Electrochemical measurements were performed in an H-type electrolytic cell with a standard three-electrode system separated by a nafion 117 membrane. In this system, the catalyst was supported on a glassy carbon electrode as the working electrode, a graphite rod and a saturated Ag/AgCl electrode as the counter and reference electrodes, respectively. All potentials in this paper were measured by saturated Ag/AgCl and converted to the reversible hydrogen electrode potential by E (vs. RHE) = E (vs. Ag/AgCl) + 0.61 as the reference scalar. The performance test of eNO_3RR was carried out in the electrolyte (30 mL) of 0.1 M Na_2SO_4 and 0.2 M KNO_3 . Before the test, Ar gas was introduced into the cathodic electrolytic cell for 15 min to remove the residual air in the system, and then Ar was continued to be introduced and reacted at an external potential for 1 h. After the test is completed, the electrolyte is collected and disposed of as waste liquid to avoid contamination.

2.6. Determination of NH_3

The concentration of NH_3 was determined by UV-Vis spectrophotometer using a modified indophenol blue method. Take 2 mL of the reacted catholyte and add 1 mL of 0.05 M NaClO , 2 mL of a mixture of 1 M NaOH containing 5 wt% salicylic acid and 5 wt% sodium citrate, and 0.2 mL of 1 wt% $\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$ (sodium nitroferrocyanide). Then, the absorbance at 665 nm was measured by UV-Vis spectrophotometer after standing at room temperature for 2 h. And concentration-absorbance curves were drawn using a series of standard ammonium chloride solutions.

2.7. Determination of NO_2

Firstly, 0.1 g of N-(1-naphthyl) ethylenediamine dihydrochloride, 1 g of sulfonamide and 2.94 mL of H_3PO_4 in 50 mL H_2O and mixed thoroughly as the color reagent. Take 1 mL of the reacted catholyte and add 1 mL color reagent, 2 mL H_2O to stand for 10 min, and the absorption

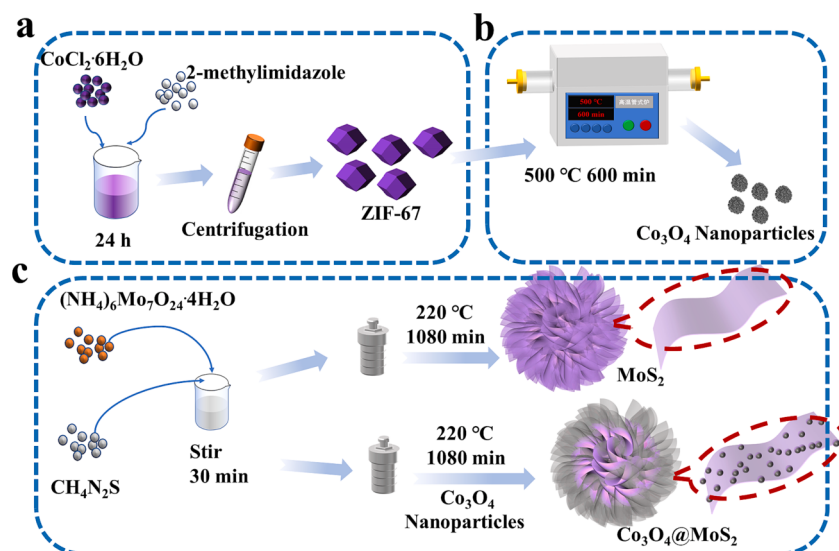


Fig. 1. Schematic diagrams to illustrate the synthesis of (a) ZIF-67, (b) Co_3O_4 nanoparticles, (c) MoS_2 and $\text{Co}_3\text{O}_4@\text{MoS}_2$.

intensity at a wavelength of 540 nm is recorded by UV-Vis absorption spectra.

2.8. Calculation of the NH_3 yield and faradic efficiency (FE)

The FE calculation formula for electrocatalytic NO_3^- - NH_3 conversion is calculated as follows:

$$FE_{\text{NH}_3} = \frac{8 \times F \times C_{\text{NH}_3} \times V}{17 \times Q}$$

where F is the Faraday constant, C_{NH_3} is the measured NH_3 concentration, V is the volume of catholyte, and Q is the total charge.

The formula for calculating the yield of NH_3 is as follows:

$$\text{Yield}_{\text{NH}_3} = \frac{C_{\text{NH}_3} \times V}{t \times m_{\text{cat}}}$$

where t is the time of the electrocatalytic reaction and m is the catalyst loading.

2.9. Computational details

Density functional theory (DFT) calculations were performed using the first-principle computational simulation package (VASP 5.4.4) developed by Hafner's group [29,30]. The generalized gradient

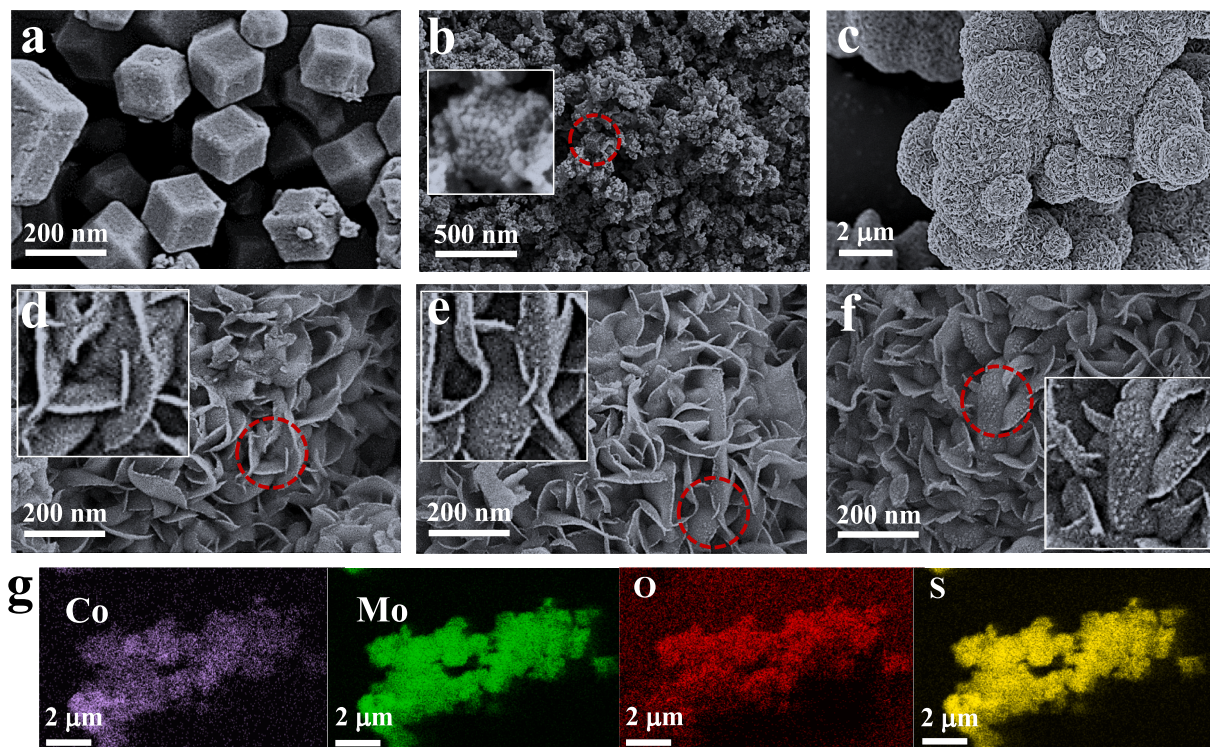


Fig. 2. SEM of (a) ZIF-67, (b) Co_3O_4 nanoparticles, (c) MoS_2 , (d-f) Co_3O_4 nanoparticles loadings of 100 mg (Co to Mo is 6:13), 150 mg (Co to Mo is 9:13), and 200 mg (Co to Mo is 12:13) in $\text{Co}_3\text{O}_4@\text{MoS}_2$, respectively. (g) EDX mapping images of $\text{Co}_3\text{O}_4@\text{MoS}_2$ with the ratio of Co to Mo is 9:13.

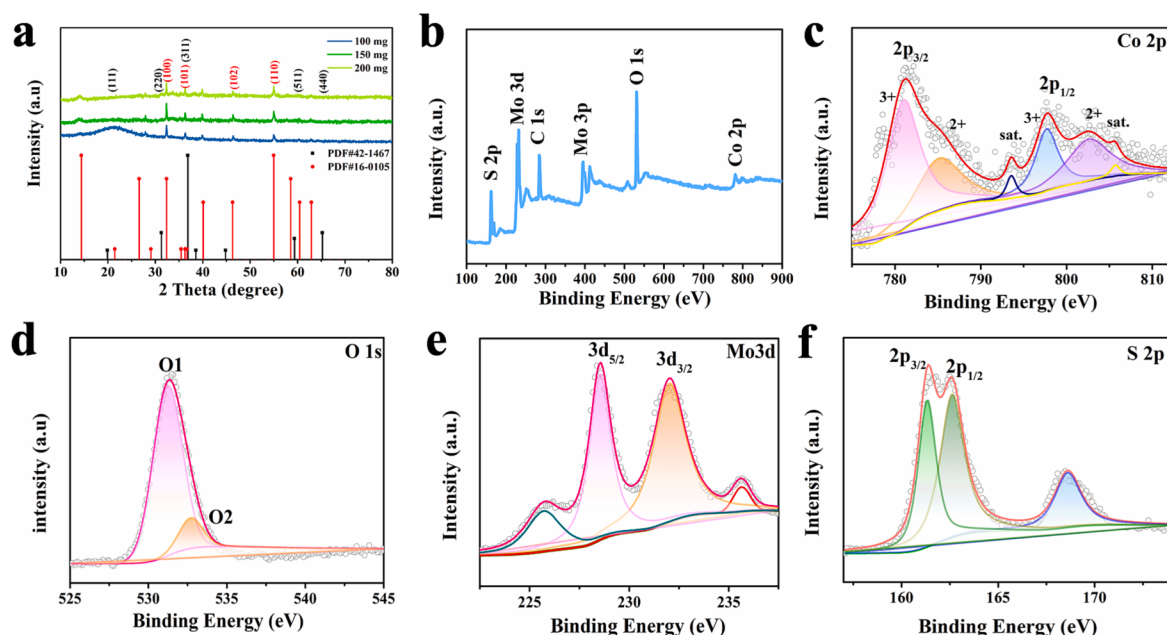


Fig. 3. XRD patterns of (a) Co_3O_4 nanoparticles loadings of 100 mg (Co to Mo is 6:13), 150 mg (Co to Mo is 9:13), and 200 mg (Co to Mo is 12:13) in $\text{Co}_3\text{O}_4/\text{MoS}_2$. The XPS of $\text{Co}_3\text{O}_4/\text{MoS}_2$ (Co to Mo is 9:13) measured spectra are (b) full spectrum, (c) Co 2p, (d) O 1s, (e) Mo 3d, (f) S 2p.

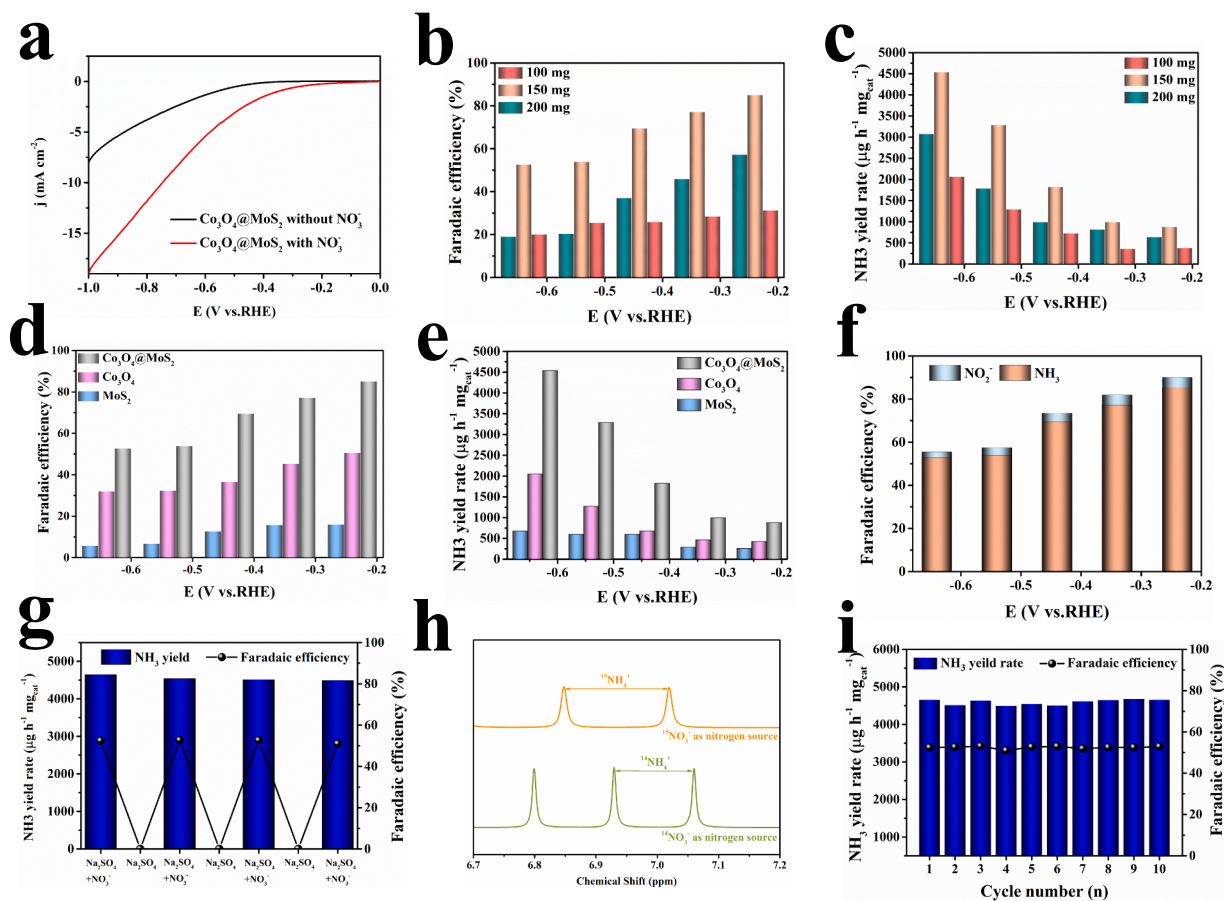


Fig. 4. (a) LSV of the Co_3O_4 nanoparticles loadings of $\text{Co}_3\text{O}_4/\text{MoS}_2$ are 150 mg (Co to Mo is 6:13) with and without NO_3^- . The Co_3O_4 nanoparticles loadings of $\text{Co}_3\text{O}_4/\text{MoS}_2$ are 100 mg (Co to Mo is 6:13), 150 mg (Co to Mo is 9:13), 200 mg (Co to Mo is 12:13) of (b) NH_3 Faradaic efficiency and (c) NH_3 yield rate, respectively. The (d) Faradaic efficiency and (e) NH_3 yield rate of MoS_2 , Co_3O_4 , $\text{Co}_3\text{O}_4/\text{MoS}_2$ (Co to Mo is 9:13). (f) The distribution of products NO_2^- and NH_3 between -0.24 and -0.64 V for $\text{Co}_3\text{O}_4/\text{MoS}_2$ (Co to Mo is 9:13). (g) NH_3 yield rate and Faradaic efficiency in alternating cycles between with and without NO_3^- electrolyte of $\text{Co}_3\text{O}_4/\text{MoS}_2$ (Co to Mo is 9:13) at -0.64 V. (h) ^1H nuclear magnetic resonance (NMR) spectrum of the electrolyte after eNO_3RR on $\text{Co}_3\text{O}_4/\text{MoS}_2$ (Co to Mo is 9:13) at -0.64 V with $^{15}\text{NO}_3^-$ and $^{14}\text{NO}_3^-$ as nitrogen sources. (i) 10-cycle test of $\text{Co}_3\text{O}_4/\text{MoS}_2$ (Co to Mo is 9:13) at -0.64 V.

approximation of the Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation functional and the pseudo-potential determination by Projector-Augmented-Wave (PAW) were used to optimize the structure and calculate the electronic energy [31,32]. A $(3 \times 3 \times 1)$ Monkhorst-Pack k-point grid was employed to sample at the Brillouin zone gamma points. At the same time, the cutoff energy was set to 500 eV and the self-consistent calculation was performed with a total energy of 10^{-5} eV and a force of -0.05 eV/Å per atom. The DFT-D2 method was also employed to approximate the van der Waals interaction and the adsorption energy of each intermediate on the catalyst [33]. The Gibbs free energy is determined by using a standard vibrational correction for entropy, calculated as $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the electron energy difference, ΔZPE is the zero-point correction energy, T is the reaction temperature (298.15 K), and ΔS is the entropy change.

3. Results and discussion

3.1. Synthesis and characterizations of electrocatalysts

The composite of $\text{Co}_3\text{O}_4/\text{MoS}_2$ was prepared following the scheme shown in Fig. 1. Firstly, the metal-organic frameworks precursor of ZIF-67 was obtained by precipitation reaction shown in Fig. 1a. Then, ZIF-67 was calcined at 500 °C for 10 h to obtain Co_3O_4 nanoparticles (Fig. 1b), which was dispersed into the reactants to prepare the $\text{Co}_3\text{O}_4/\text{MoS}_2$ composite by hydrothermal method shown in Fig. 1c. The morphologies of all the samples were characterized by scanning electron microscopy (SEM) (Fig. 2), including ZIF-67, Co_3O_4 nanoparticles, MoS_2 , and $\text{Co}_3\text{O}_4/\text{MoS}_2$.

ZIF-67 exhibits a rhombic dodecahedron morphology with a uniform particle size of 100 nm (Fig. 2a). After calcination, Co_3O_4 nanoparticles maintained the original dodecahedron framework with a diameter of 40 nm (Fig. 2b). When MoS_2 was prepared (Fig. 2c), different amount of Co_3O_4 nanoparticles were dispersed into the raw materials, including 100 mg (Co to Mo is 6:13), 150 mg (Co to Mo is 9:13) and 200 mg (Co to Mo is 12:13), and the results were shown in Fig. 2d to Fig. 2f, respectively. The uniform dispersion of the Co_3O_4 nanoparticles on MoS_2 nanoflowers should contribute to the synthesis method using ZIFs as precursors, as effectively reduces the aggregation of particles. The energy dispersive X-ray spectroscopy (EDX) mapping of $\text{Co}_3\text{O}_4/\text{MoS}_2$ composites (Fig. 2g) demonstrated the uniform distribution of Co, Mo, O, and S elements.

To further illustrate the crystal structure of $\text{Co}_3\text{O}_4/\text{MoS}_2$, the powder X-ray diffraction (XRD) spectra are measured for three different $\text{Co}_3\text{O}_4/\text{MoS}_2$ composites (Fig. 3a). The distinct characteristic peaks at 19.9° , 31.3° , 36.8° , 59.3° , and 68.6° can be assigned to (111), (220), (311), (511), and (440) crystallographic planes of Co_3O_4 (PDF no. 42-1467), as demonstrates that the Co_3O_4 particles are synthesized successfully. The additional peaks at 32.3° , 39.8° , 46.2° , and 54.9° in the XRD pattern of the composite are attributed to (100), (101), (102), and (110) crystal faces of CoMoS (PDF no.16-0105), as indicates the formation of Co-S bond. Therefore, the Co_3O_4 nanoparticles is successfully

anchored on MoS_2 nanoflower support by Co-S coordination bond.

The chemical composition and oxidation state of the surface of $\text{Co}_3\text{O}_4/\text{MoS}_2$ are measured by X-ray photoelectron spectroscopy (XPS). In Fig. 3b, the peaks at 162.08, 232.08, 284.08, 395.08, 534.08, and 781.08 eV in the full spectra correspond to S 2p, Mo 3d, C 1s, Mo 3p, O 1s, and Co 2p, respectively, indicating the presence of Co, O, Mo, S. This is consistent with the elemental results measured by SEM elemental maps (Fig. 2g). As shown in Fig. 3c, the Co 2p spectrum can be fitted with two spin-orbit doublets for Co^{2+} (785.13 and 802.69 eV) and Co^{3+} (780.96 and 797.68 eV). The two peaks in the O 1s spectra (Fig. 3d) at the binding energies of 531.24 and 532.70 eV correspond to metal-oxygen bonds and hydroxyl groups. Similarly, the Mo 3d spectrum (shown in Fig. 3e) can be fitted with two spin-orbit doublets for the Mo $3d_{3/2}$ (232.02 eV) and Mo $3d_{5/2}$ (228.54 eV) orbitals of the tetravalent molybdenum ion. The two peaks measured in the spectrum of S 2p are S $2p_{3/2}$ and S $2p_{1/2}$ orbitals at 161.33 and 162.62 eV (Fig. 3), respectively. In addition, the unlabeled peaks in the XPS spectrum are the satellite peaks. The above description proves the successful fabrication of $\text{Co}_3\text{O}_4/\text{MoS}_2$ without any impurities.

3.2. eNO_3RR performance of the electrocatalysts

To study the catalytic activity of $\text{Co}_3\text{O}_4/\text{MoS}_2$ for eNO_3RR , the linear sweep voltammetry (LSV) measurements are carried out firstly in Na_2SO_4 solution in the absence and presence of NO_3^- , respectively (Fig. 4a). As the potential is more negative than -0.24 V, the current density of $\text{Co}_3\text{O}_4/\text{MoS}_2$ in the presence of NO_3^- is significantly higher than that in the absence of NO_3^- . It demonstrates that the eNO_3RR occurs on $\text{Co}_3\text{O}_4/\text{MoS}_2$ as the potential is lower than -0.24 V. The synthesized NH_3 in the electrolyte are measured by UV-Vis spectrophotometry after maintaining a certain potential. Firstly, the voltage selected for testing is based on the results of LSV, the polarization curves are tested with $\text{Co}_3\text{O}_4/\text{MoS}_2$ as a catalyst and exhibit the eNO_3RR activity in the negative potential lower than -0.24 V. Then the catalytic performance is tested with the voltage range of -0.94 V to -0.24 V (Fig. S3a). It can be seen that the Faradaic efficiency gradually decreased due to the accumulation of catalyst surface charge and the effect of hydrogen evolution reaction (HER) occupied more active sites at higher negative voltages [36]. The absorbance in UV-Vis spectra becomes higher with the increase of voltage (Figs. S3b and c), as means the yield of ammonia increases. The higher rate of NH_3 is due to the fact that a larger negative potential exerts a greater thermodynamic driving force for the reaction than a lower potential does. Considering the optimal voltage and FE changes, the voltage from -0.64 V to -0.24 V is selected to test the catalyst performance (Fig. S4). According to the measured NH_3 concentrations, the yield and FE of $\text{Co}_3\text{O}_4/\text{MoS}_2$ with three different Co_3O_4 loadings (100 mg, 150 mg, and 200 mg) are shown in Figs. 4b and 4c. The loading of Co_3O_4 has a major effect on the activity of the $\text{Co}_3\text{O}_4/\text{MoS}_2$ catalyst and the catalytic performance is the highest when the loading of Co_3O_4 is 150 mg. Moreover, the effect of electrical potential is explored. At the optimum potential, the NH_3 yield rate reaches

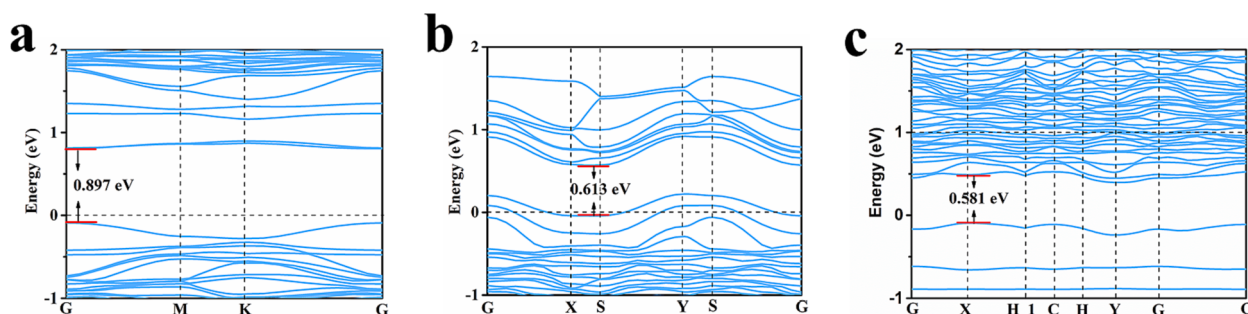


Fig. 5. Band diagram of (a) MoS_2 , (b) Co_3O_4 , (c) $\text{Co}_3\text{O}_4/\text{MoS}_2$.

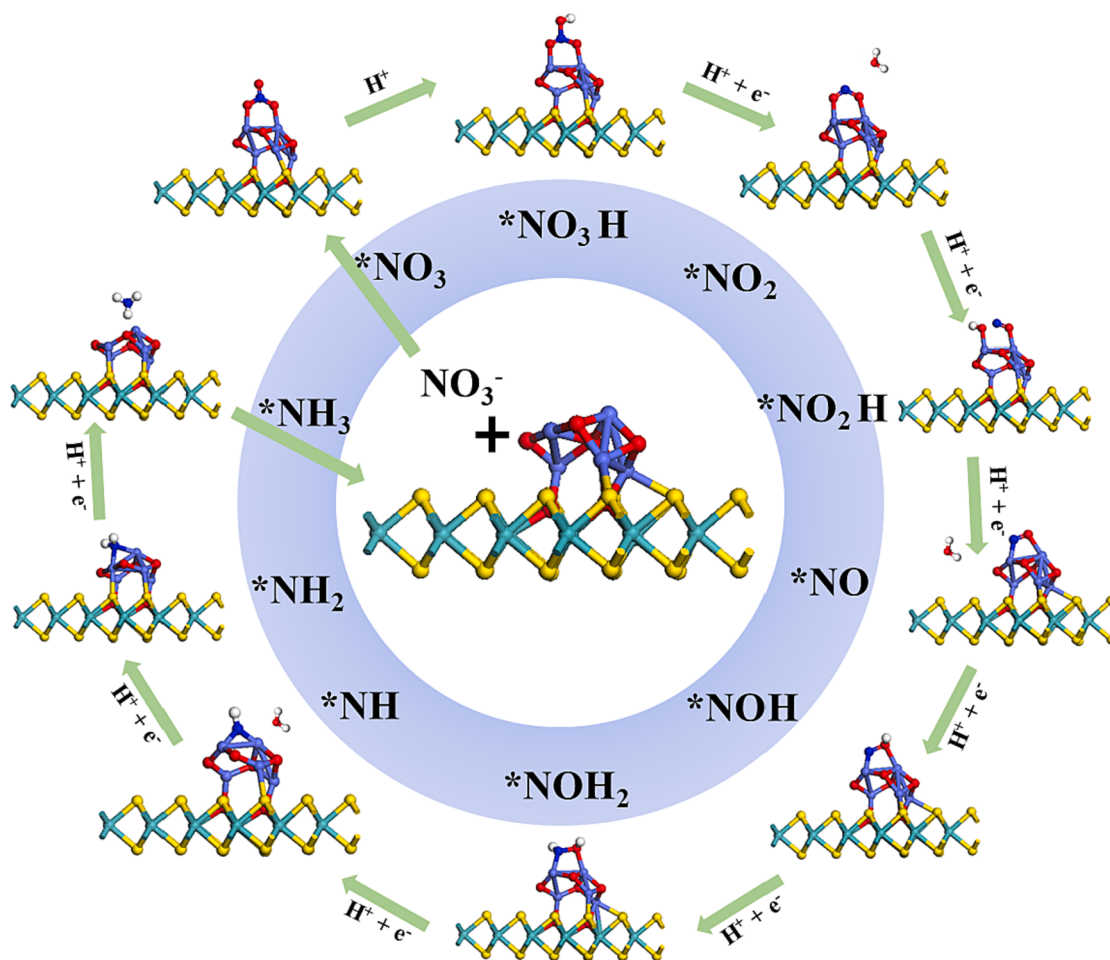


Fig. 6. Intermediates of all optimized structures of the $\text{Co}_3\text{O}_4@\text{MoS}_2$ eNO_3RR reaction process (atomic colors represent: yellow, S; green, Mo; blue, N; red, O; purple, Co; white, H).

$4539.61 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and the FE is 52.69% with the Co_3O_4 loading of 150 mg at -0.64 V. As the potential increases, the FE of $\text{Co}_3\text{O}_4@\text{MoS}_2$ increases continuously, and the maximum value is 85.05% at the optimum potential of -0.24 V. Compared to Co_3O_4 and MoS_2 , $\text{Co}_3\text{O}_4@\text{MoS}_2$ exhibits excellent NH_3 yield rate and FE under the same test conditions (as shown in Figs. 4d and 4e), implying that the combination of Co_3O_4 and MoS_2 can accelerate the process of eNO_3RR . And $\text{Co}_3\text{O}_4@\text{MoS}_2$ showed a combination of performance as good as most of the material previously reported (Table S1). $\text{Co}_3\text{O}_4@\text{MoS}_2$ shows such a superior performance because the combination of Co_3O_4 and MoS_2 reduces the bandwidth, improves electronic conductivity and surface chemical active sites, which will be discussed in the theoretical calculations. The FE and NH_3 yield rate at the optimum potentials of Co_3O_4 and MoS_2 are 50.67% and 16% at -0.24 V, $2048.63 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and $675.01 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ at -0.64 V, respectively. The above observations indicate that the performance exhibited by $\text{Co}_3\text{O}_4@\text{MoS}_2$ varies with the amount of Co_3O_4 on the composite. So, it can be speculated that the active site of eNO_3RR in the $\text{Co}_3\text{O}_4@\text{MoS}_2$ composite should populate on the Co atom.

In order to investigate the selectivity of the $\text{Co}_3\text{O}_4@\text{MoS}_2$ catalyst, the main byproduct of NO_2^- has been detected and calculated by UV–Vis (Fig. S5). As shown in Fig. 4f, the FE of NO_2^- starts from an onset potential of 5% and then gradually decreases to about 2%. This trend is the same as the conversion of NO_3^- to NH_3 , suggesting that the synthesis of NH_3 is followed by the formation of NO_2^- at each applied potential. And the yield rate of NO_2^- increases distinctly after -0.44 V (Fig. S5c), but the overall concentration of NO_2^- was still at a low level. In addition, the presence of N_2H_4 was hardly observed in the electrolyte after electrolysis at the applied voltage (Fig. S6). In general, the byproducts are negligible

compared to the FE and yield rate of NH_3 , which indicates that $\text{Co}_3\text{O}_4@\text{MoS}_2$ has excellent selectivity for the conversion from NO_3^- to NH_3 .

Subsequently, it is proceeded to electrolysis for a total of 7 cycles in 0.1 M Na_2SO_4 (with and without NO_3^-) at -0.64 V (Fig. 4g) to confirm the origin of NH_3 . The NH_3 was obtained only in the electrolyte with NO_3^- and the performance remained stable after the alternating test. Furthermore, the ^{15}N isotopic labeling experiments also confirmed the origin of NH_3 . As shown in Fig. 4h, the proton nuclear magnetic resonance (^1H NMR) spectra show only double characteristic peaks of $^{15}\text{NH}_4^+$ and triple characteristic peaks of $^{14}\text{NH}_4^+$ when $^{15}\text{NO}_3^-$ and $^{14}\text{NO}_3^-$ are used as raw materials. The above results indicated that NO_3^- is the only nitrogen source for NH_3 synthesis rather than others.

The stability of the catalyst is another vital factor to evaluate the practical application in eNO_3RR . As shown in Fig. S7a, the current density at -0.64 V has been measured for 24 h. The curve has no obvious fluctuations and the overall trend is relatively stable. In general, the current density exhibits good stability over 24 h, indicating the stable conductivity and durability of the catalyst. Furthermore, the NH_3 yield rate and FE at -0.64 V were test for 10 cycles as shown in Fig. 4i. It can be seen that the NH_3 yield rate and FE fluctuate slightly and remain above $4588 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and 52%, respectively. As shown in Figs. S7b and S7c, the current density and absorbance almost keep constant during the 10-cycle test. Importantly, SEM images (Fig. S7d) reveal that $\text{Co}_3\text{O}_4@\text{MoS}_2$ with Co_3O_4 loadings of 150 mg still maintains its nano-flower and the presence of the loadings was also clearly visible after the eNO_3RR experiment. Therefore, the conclusion can be drawn that the catalyst has excellent activity and stability with bright future in

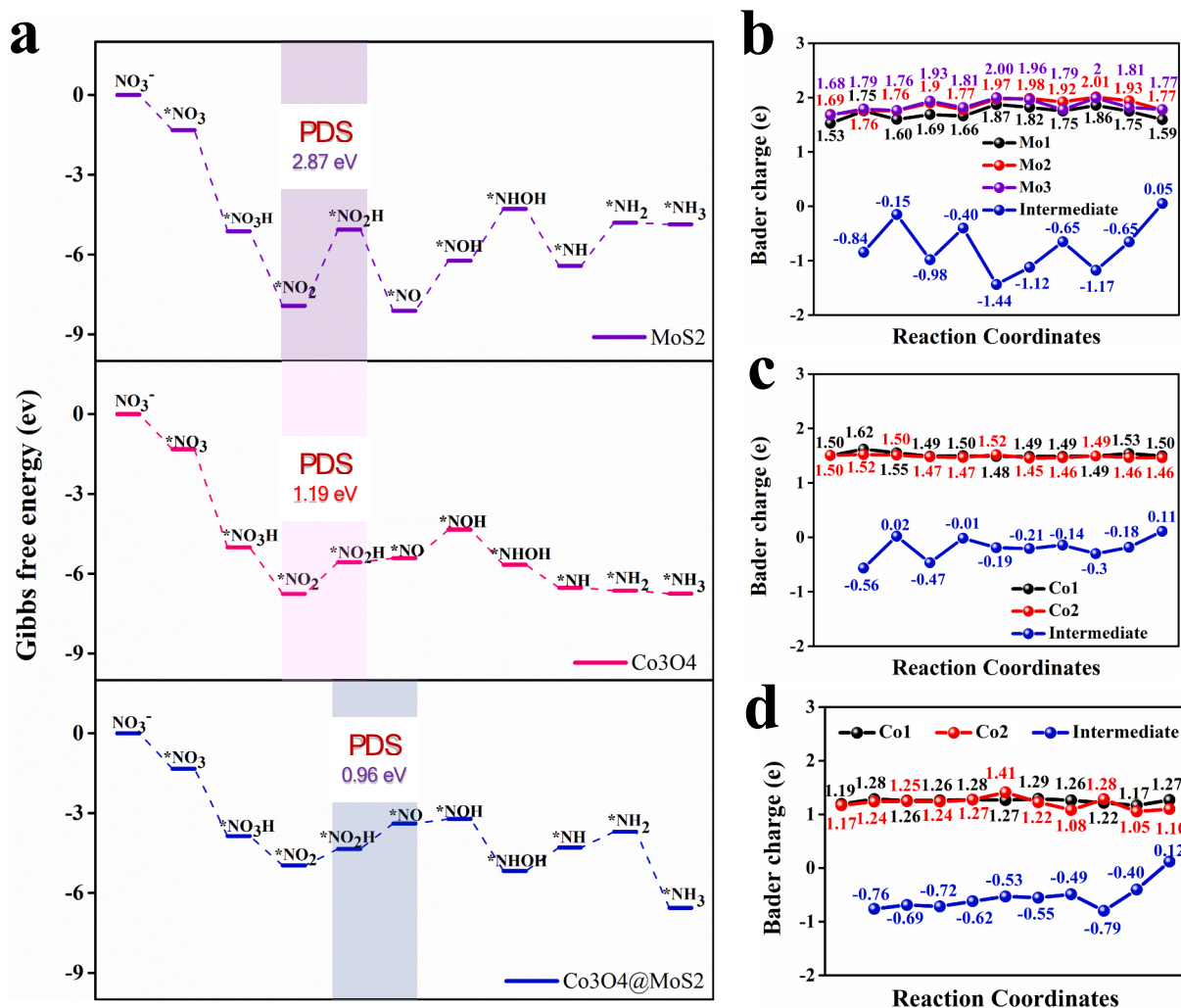


Fig. 7. (a) Free energy changes in each step of the reaction processes of MoS₂, Co₃O₄, and Co₃O₄@MoS₂. The calculated Bader charges of the active site and intermediate on (b) MoS₂, (c) Co₃O₄, and (d) Co₃O₄@MoS₂.

commercial application.

3.3. Mechanisms study for eNO₃RR

To reveal the essence of excellent performance in nitrate reduction, the reaction mechanism has been studied employing the DFT calculations. The structures of Co₃O₄, MoS₂, and Co₃O₄@MoS₂ are designed based on the characterization results using metal atoms as active sites (Fig. S8). It is found that new Co-S bonds are formed between Co₃O₄ and MoS₂ during the Co₃O₄@MoS₂ structural optimization, which is consistent with the XRD results. The energy bands of three catalysts are calculated and presented in Fig. 5. It can be clearly seen that the energy band of MoS₂, Co₃O₄, and Co₃O₄@MoS₂ is 0.897, 0.613, and 0.581 eV, respectively. Therefore, Co₃O₄@MoS₂ has better electronic conductivity than its individual materials, which also provides better electron transfer for eNO₃RR process.

The reduction of nitrate to ammonia is accompanied by the transfer of eight proton-coupled-electrons and the overall pathway of the reaction can be described by the following equation:

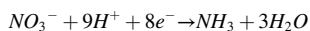


Fig. 6 and Fig. S9 show the minimum energy pathway for the reduction of nitrate to NH₃ at the active site. The first step of the reaction is the adsorption of nitrate. To avoid the influence of negatively charged NO₃⁻ on the calculated results, a thermodynamic cycle from NO₃⁻ to NO₃

(NO₃(l) → HNO₃(l) → HNO₃(g) → NO₃(g)) has been adapted (Fig. S10) [34]. Taking into account the changes in entropy and enthalpy during liquid to gaseous conversion from NO₃ to NO₃, an energy of 0.75 eV has been used to correct the free energy of NO₃ [34,35]. The formula for calculating the Gibbs free energy in solution before nitrate adsorption is as follows:

$$\Delta G_{\text{NO}_3} = E(^*\text{NO}_3) + \frac{1}{2}E(\text{H}_2) - E(^*) - E(\text{HNO}_3) + 0.75\text{eV}$$

where $E(^*\text{NO}_3)$ is the energy of NO₃ adsorbed on the catalyst system, $E(\text{H}_2)$ refers to the energy of gaseous H₂ molecule, $E(^*)$ denotes the energy of the catalyst alone, and $E(\text{HNO}_3)$ is the energy of HNO₃ molecule. Then, the Gibbs free energies of each elementary step for the complete processes of MoS₂, Co₃O₄, and Co₃O₄@MoS₂ are calculated by the pathway: $^*\text{NO}_3 \rightarrow ^*\text{NO}_3\text{H} \rightarrow ^*\text{NO}_2 \rightarrow ^*\text{NO}_2\text{H} \rightarrow ^*\text{NO} \rightarrow ^*\text{NOH} \rightarrow ^*\text{NHOH} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3 \rightarrow \text{NH}_3(\text{g})$ [34].

The variations of the Gibbs free energy and the charge in each elementary step along the reaction pathway of NO₃⁻ electroreduction to ammonia on MoS₂, Co₃O₄, and Co₃O₄@MoS₂ catalysts are collected in Fig. 7. It can be observed clearly that the elementary steps of NO₃⁻ adsorption, the proton-electron pair combination, and the first dehydration are all exothermic processes. This is in accordance with the results reported recently [37,38]. The subsequent hydrogenation of $^*\text{NO}_2$ to produce $^*\text{NO}_2\text{H}$ is endothermic distinctly. The Gibbs free energy is enhanced by 2.87 eV when the conversion from $^*\text{NO}_2$ to $^*\text{NO}_2\text{H}$ occurs

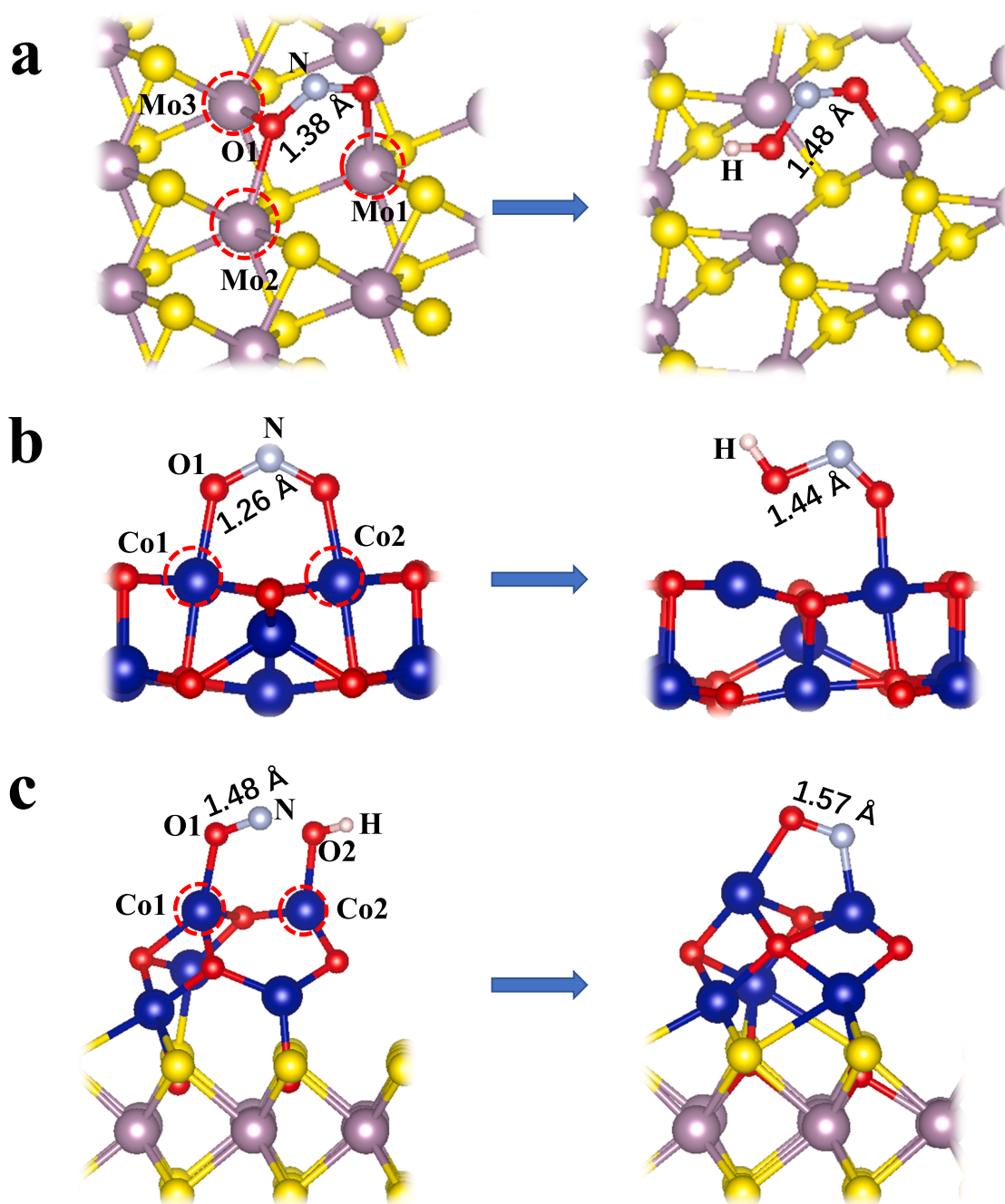


Fig. 8. The structural model changes at PDS for (a) Co_3O_4 , (b) MoS_2 and (c) $\text{Co}_3\text{O}_4/\text{MoS}_2$ (atomic colors represent: yellow, S; purple, Mo; gray, N; red, O; blue, Co; white, H).

on MoS_2 surface, accompanied by significant electron transfer ($0.58 e$) between the intermediate and the catalyst. It is taken as the potential determining step (PDS). As the catalyst varies from MoS_2 to Co_3O_4 , the Gibbs free energy is raised by 1.19 eV and the transferred electron is $0.46 e$. It also corresponds to the PDS. While for the $\text{Co}_3\text{O}_4/\text{MoS}_2$ composite, the variation of Gibbs free energy for this hydrogenation is 0.62 eV and transferred electron is $0.1 e$. While the Gibbs free energy of the subsequent formation of $^*\text{NO}$ ($^*\text{NO}_2\text{H} \rightarrow ^*\text{NO}$) increases distinctly by 0.96 eV , which is taken as the PDS.

The geometrical structures of the PDS from $^*\text{NO}_2$ to $^*\text{NO}_2\text{H}$ are optimised (Fig. 8). The generation of O1-H bond on MoS_2 is followed by the broken of both Mo2-O1 and Mo3-O1 bonds, the elongation of N-O1 bond from $1.38 \text{ \AA}$ to $1.48 \text{ \AA}$ (Fig. 8a), as well as the charge variation from $-0.87 e$ on O1 to $-0.20 e$ on O1H group. The strong interaction

between Mo and O1 leads to the immersion of O1 (in the plane of sulfurs) and the bulging of N, as is disadvantageous structurally to the subsequent combination of proton-electron pair. Similarly, the formation of O1-H bond on Co_3O_4 is accompanied by the Co1-O1 bond broken, the N-O1 bond extension from $1.26 \text{ \AA}$ to $1.44 \text{ \AA}$ (Fig. 8b), and the increase of charges from $-0.51 e$ on O1 to $-0.09 e$ on O1H group. It indicates the weakening of both Co1-O1 and N-O1 interactions. In addition, the O1 stands on the surface of Co_3O_4 , as favors the following combination of next proton-electron pair and the consequent dehydration reaction. In the $^*\text{NO}_2\text{H} \rightarrow ^*\text{NO}$ process on $\text{Co}_3\text{O}_4/\text{MoS}_2$, more obvious structural changes are observed: the broken of Co2-O2 bond, the departure of dissociated OH group, the formation of Co2-N bond, and the extension of N-O bond from $1.48 \text{ \AA}$ to $1.57 \text{ \AA}$ and the Co1-O1 bond extension from $1.97 \text{ \AA}$ to $2.11 \text{ \AA}$ (Fig. 8c). The O replaces N as the most

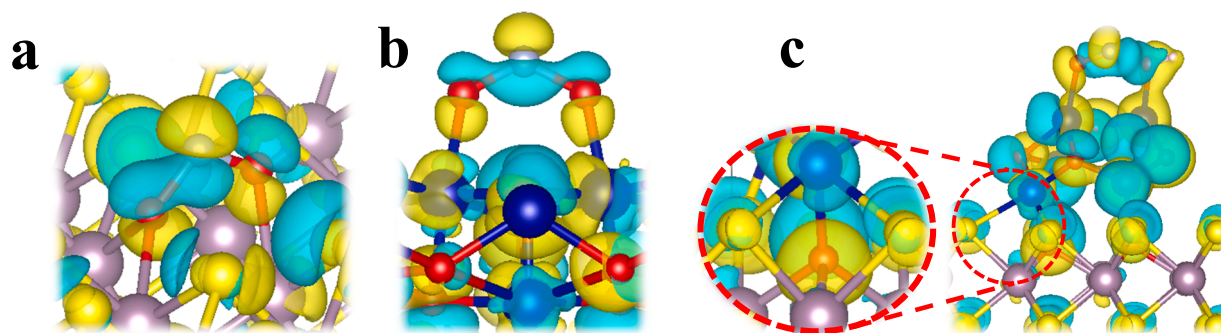


Fig. 9. The charge density difference of (a) MoS_2 , (b) Co_3O_4 , and (c) $\text{Co}_3\text{O}_4@\text{MoS}_2$ (atomic colors represent: yellow, S; purple, Mo; gray, N; red, O; blue, Co; white, H. Electron density cloud color: yellow, charge accumulation: blue, charge depletion).

exposed atom, facilitating the next step of hydrogenation. During the $^*\text{NO}_2\text{H} \rightarrow ^*\text{NO}$ process on $\text{Co}_3\text{O}_4@\text{MoS}_2$, MoS_2 transfers $0.35 e$ to Co_3O_4 and the intermediate. There are more charge accumulation compared to those on the independent Co_3O_4 . In addition, in the O1-N group on $\text{Co}_3\text{O}_4@\text{MoS}_2$, the charge on O1 decreases by $0.04 e$ while the N charge increases by $0.34 e$, indicating that the Co2-N interaction increases while the Co1-O1-N coupling decreases, which facilitates the next step of deoxygenation. In contrast, the charge on O1 and N in the O1-N group on the independent Co_3O_4 increases by $0.27 e$ and $0.01 e$ respectively, and the enhanced interaction between Co2-O1 is not conducive to the next step of deoxygenation. Therefore, MoS_2 in $\text{Co}_3\text{O}_4@\text{MoS}_2$ does not directly participate in the reaction as an active site but also plays a non-negligible role.

The charge density differences of the PDS step on three catalysts are represented in Fig. 9. With MoS_2 as a catalyst, the charge depletion between O1-N and the accumulation between Mo-O1 observed in Fig. 9a indicate that more electrons populate on O1, as is in accordance with the former discussion about the charges. Fig. 9b shows distinct charge depletion between O-N and charge accumulation between Co-O, which implies that the Co_3O_4 cluster can serve as a nitrate-activated center. In the case of $\text{Co}_3\text{O}_4@\text{MoS}_2$ (Fig. 9c), the oxygen atom accumulates a large charge, which makes deoxygenation easier, as the energy accumulation after the oxygen hydrogenation step leads to the breaking of the N-O bond. Furthermore, the electron depletion and accumulation of $\text{Co}_3\text{O}_4@\text{MoS}_2$ locate mainly on Co_3O_4 , as indicates that the immediate active site of the reaction is on Co_3O_4 . The charge distribution on the surface of Co and S atoms also reflects the new Co-S bond as a bridge for charge transfer between MoS_2 and Co_3O_4 , which corresponds to the previous charge transfer situation, further demonstrating the synergistic role played by MoS_2 in the catalyst. It attributes to the lower energy barrier of $\text{Co}_3\text{O}_4@\text{MoS}_2$ as compared to those of Co_3O_4 and MoS_2 . The theoretical results show that the catalytic performance of $\text{Co}_3\text{O}_4@\text{MoS}_2$ is significantly improved, which is in consistent with the experimental results.

4. Conclusion

The use of ZIF-67 as a precursor to synthesize Co_3O_4 effectively reduces the volume of nanoparticles, then the use of MoS_2 as a support solves the problem of nanoparticle aggregation and provides a synergistic effect for the formation and coordination of S-Co to enhance the activity of the catalyst. Experiments show that $\text{Co}_3\text{O}_4@\text{MoS}_2$ has good catalytic activity, selectivity, and stability. It shows excellent FE and NH_3 yield rate of 52.69% and $4539.61 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ at -0.64 V , as is significantly improved as compare with those of Co_3O_4 . DFT calculations show that $\text{Co}_3\text{O}_4@\text{MoS}_2$ has lower energy barrier and smaller bandwidth than those of Co_3O_4 and MoS_2 , proving that the $\text{Co}_3\text{O}_4@\text{MoS}_2$ has better performance for e NO_3RR than Co_3O_4 and MoS_2 . This study proposes an effective solution to the problem of metal oxide

nanoparticle aggregation, and future research needs to carry out for nitrate reduction tests in the protection of resources and environment.

CRediT authorship contribution statement

Yanli Zhang: Writing – original draft, Investigation. **Jiuqing Xiong:** Validation, Data curation. **Shihai Yan:** Supervision, Funding acquisition, Writing – review & editing. **Bingping Liu:** Conceptualization, Methodology, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21203227), Natural Science Foundation of Shandong Province (Grant No. ZR2016BM33), the Research Foundation for Talented Scholars of Qingdao Agricultural University (No. 6631120039 & 6631113335), National College Student Innovation and Entrepreneurship Training Program (S202010435041), and the open fund of the state key laboratory of molecular reaction dynamics in DICP, CAS. The authors would like to thank Zhao Baobao from Shiyanjia Lab (www.shiyanjia.com) for the XPS analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jelechem.2023.117702>.

References

- [1] N.a. Cao, G. Zheng, Aqueous electrocatalytic N_2 reduction under ambient conditions, *Nano Res.* 11 (6) (2018) 2992–3008.
- [2] Y. Huang, D.D. Babu, Z. Peng, Y. Wang, Atomic Modulation, Structural Design, and Systematic Optimization for Efficient Electrochemical Nitrogen Reduction, *Adv. Sci.* 7 (4) (2020) 1902390.
- [3] Q. Liu, L. Xie, J. Liang, Y. Ren, Y. Wang, L. Zhang, L. Yue, T. Li, Y. Luo, N.a. Li, B. o. Tang, Y. Liu, S. Gao, A.A. Alshehri, I. Shakir, P.O. Agboola, Q. Kong, Q. Wang, D. Ma, X. Sun, Ambient Ammonia Synthesis via Electrochemical Reduction of Nitrate Enabled by NiCo_2O_4 Nanowire Array, *Small* 18 (13) (2022) e2106961.
- [4] J.i. Li, Y. Zhang, C. Liu, L. Zheng, E. Petit, K. Qi, Y. Zhang, H. Wu, W. Wang, A. Tiberj, X. Wang, M. Chhowalla, L. Lajaunie, R. Yu, D. Voiry, 3.4% Solar-to-Ammonia Efficiency from Nitrate Using Fe Single Atomic Catalyst Supported on MoS_2 Nanosheets, *Adv. Funct. Mater.* 32 (18) (2022) 2108316.
- [5] V. Smil, Detonator of the population explosion, *Nature* 400 (6743) (1999) 415.
- [6] T. Wu, X. Zhu, Z. Xing, S. Mou, C. Li, Y. Qiao, Q. Liu, Y. Luo, X. Shi, Y. Zhang, X. Sun, Greatly Improving Electrochemical N_2 Reduction over TiO_2 Nanoparticles by Iron Doping, *Angew. Chem. Int. Ed.* 58 (51) (2019) 18449–18453.

- [7] G. Soloveichik, Electrochemical synthesis of ammonia as a potential alternative to the Haber-Bosch process, *Nat. Catal.* 2 (2019) 377–380.
- [8] B. Suryanto, H.L. Du, D. Wang, J. Chen, A.N. Simonov, D.R. MacFarlane, Challenges and prospects in the catalysis of electroreduction of nitrogen to ammonia, *Nat. Catal.* 2 (2019) 290–296.
- [9] C. Guo, J. Ran, A. Vasileff, S.-Z. Qiao, Rational design of electrocatalysts and photo (electro) catalysts for nitrogen reduction to ammonia (NH₃) under ambient conditions, *Energ. Environ. Sci.* 11 (1) (2018) 45–56.
- [10] Y. Wan, J. Xu, R. Lv, Heterogeneous electrocatalysts design for nitrogen reduction reaction under ambient conditions, *Mater. Today* 27 (2019) 69–90.
- [11] J. Wen, H. Chang, T. Huang, M. Hossain, Z. Liu, H. Sun, Y. Zhu, Y. Chen, Q. Huang, Y. Wu, A simple synthesis of Co₃O₄@CNT to boost electrochemical nitrogen fixation, *Electrochim. Acta* 367 (2021).
- [12] T. Mou, J. Long, T. Frauenheim, J. Xiao, Advances in Electrochemical Ammonia Synthesis Beyond the Use of Nitrogen Gas as a Source, *ChemPlusChem* 86 (8) (2021) 1211–1224.
- [13] Z. Ning, J. Abdul, D. Chen, S. Liu, Y. Gao, Refining Defect States in W₁₈O₄₉ by Mo Doping: A Strategy for Tuning N-2 Activation towards Solar-Driven Nitrogen Fixation, *J. Am. Chem. Soc.* 140 (2018) 9434–9443.
- [14] M.A. Kaczmarek, A. Malhotra, B. GA, A. Timmins, S.P. Devissier, Nitrogen Reduction to Ammonia on a Biomimetic Mononuclear Iron Centre: Insights into the Nitrogenase Enzyme Wiley-Blackwell Online Open 24 2018 1 11.
- [15] Y. Luo, G.-F. Chen, L.i. Ding, X. Chen, L.-X. Ding, H. Wang, Efficient Electrocatalytic N₂ Fixation with MXene under Ambient Conditions, *Joule* 3 (1) (2019) 279–289.
- [16] L. Zeng, X. Li, S. Chen, J. Wen, F. Rahmati, J. van der Zalm, A. Chen, Highly boosted gas diffusion for enhanced electrocatalytic reduction of N₂ to NH₃ on 3D hollow Co–MoS₂ nanostructures, *Nanoscale* 12 (10) (2020) 6029–6036.
- [17] J. Li, D. Zhao, L. Zhang, L. Yue, Y. Luo, Q. Liu, N.a. Li, A.A. Alshehri, M.S. Hamdy, Q. Li, X. Sun, A FeCo₂O₄ nanowire array enabled electrochemical nitrate conversion to ammonia, *Chem. Commun. (Camb)* 58 (28) (2022) 4480–4483.
- [18] Z. Li, G. Wen, J. Liang, T. Li, Y. Luo, Q. Kong, X. Shi, A.M. Asiri, Q. Liu, X. Sun, High-efficiency nitrate electroreduction to ammonia on electrodeposited cobalt–phosphorus alloy film, *Chem. Commun.* 57 (76) (2021) 9720–9723.
- [19] P. Song, G. Huang, Y. Hong, C. An, X. Xin, P. Zhang, A biophysiological perspective on enhanced nitrate removal from decentralized domestic sewage using gravitational-flow multi-soil-layering systems, *Chemosphere* 240 (2020), 124868.
- [20] J.O. Lundberg, E. Weitzberg, J.A. Cole, N. Benjamin, Nitrate, bacteria and human health, *Nat. Rev. Microbiol.* 2 (7) (2004) 593–602.
- [21] P. Huang, T. Fan, X. Ma, J. Zhang, Y. Zhang, Z. Chen, X. Yi, 3D flower-like zinc cobaltite for electrocatalytic reduction of nitrate to ammonia under ambient conditions, *ChemSusChem* 15 (2022) e202102049.
- [22] J. Gao, B.o. Jiang, C. Ni, Y. Qi, X. Bi, Enhanced reduction of nitrate by noble metal-free electrocatalysis on P doped three-dimensional Co₃O₄ cathode: mechanism exploration from both experimental and DFT studies, *Chem. Eng. J.* 382 (2020), 123034.
- [23] C. Li, K. Li, C. Chen, Q. Tang, T. Sun, J. Jia, Electrochemical removal of nitrate using a nanosheet structured Co₃O₄/Ti cathode: effects of temperature, current and pH adjusting, *Sep. Purif. Technol.* 237 (2020), 116485.
- [24] Y. Gong, J. Wu, M. Kitano, J. Wang, T.-N. Ye, J. Li, Y. Kobayashi, K. Kishida, H. Abe, Y. Niwa, H. Yang, T. Tada, H. Hosono, Ternary intermetallic LaCoSi as a catalyst for N₂ activation, *Nat. Catal.* 1 (3) (2018) 178–185.
- [25] L. Zhou, S. Cao, L. Zhang, G. Xiang, J. Wang, X. Zeng, J. Chen, Facet effect of Co₃O₄ nanocatalysts on the catalytic decomposition of ammonium perchlorate, *J. Hazard. Mater.* 392 (2020), 122358.
- [26] L.-Y. Zhou, S.-B. Cao, L.-L. Zhang, G. Xiang, X.-F. Zeng, J.-F. Chen, Promotion of the Co₃O₄/TiO₂ Interface on Catalytic Decomposition of Ammonium Perchlorate, *ACS Appl. Mater. Interfaces* 14 (2) (2022) 3476–3484.
- [27] B.H.R. Suryanto, D. Wang, L.M. Azofra, M. Harb, L. Cavallo, R. Jalili, D.R. G. Mitchell, M. Chatti, D.R. MacFarlane, MoS₂ polymorphic engineering enhances selectivity in the electrochemical reduction of nitrogen to ammonia, *ACS Energy Lett.* 4 (2) (2019) 430–435.
- [28] M.I. Ahmed, L.J. Arachchige, Z. Su, D.B. Hibbert, C. Sun, C. Zhao, Nitrogenase-Inspired Atomically Dispersed Fe–S–C Linkages for Improved Electrochemical Reduction of Dinitrogen to Ammonia, *ACS Catal.* 12 (2) (2022) 1443–1451.
- [29] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set - ScienceDirect, *Comput. Mater. Sci.* 6 (1) (1996) 15–50.
- [30] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M. C. Payne, First-principles simulation: ideas, illustrations and the CASTEP code, *J. Phys.: Condens. Matter* 14 (2002), 2717–2744.
- [31] P.E. Blöchl, Projector Augmented-Wave Method, *Phys. Rev. B* 50 (24) (1994) 17953–17979.
- [32] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. 77, 3865 (1996)], *Phys. Rev. Lett.* 78 (7) (1997).
- [33] S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, *J. Comput. Chem.* 27 (15) (2006) 1787–1799.
- [34] T. Hu, C. Wang, M. Wang, C.M. Li, C. Guo, Theoretical Insights into Superior Nitrate Reduction to Ammonia Performance of Copper Catalysts, *ACS Catal.* 11 (23) (2021) 14417–14427.
- [35] J.-X. Liu, D. Richards, N. Singh, B.R. Goldsmith, Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals, *ACS Catal.* 9 (8) (2019) 7052–7064.
- [36] W. Nie, X. Wang, Z. Wang, Y. Gao, R. Chen, Y. Liu, C. Li, F. Fan, Identifying the Role of the Local Charge Density on the Hydrogen Evolution Reaction of the Photoelectrode, *J. Phys. Chem. Lett.* 12 (44) (2021) 10829–10836.
- [37] W.-J. Sun, L.-X. Li, H.-Y. Zhang, J.-H. He, J.-M. Lu, A Bioinspired Iron-Centered Electrocatalyst for Selective Catalytic Reduction of Nitrate to Ammonia, *ACS Sustain. Chem. Eng.* 10 (18) (2022) 5958–5965.
- [38] S. Wang, H. Gao, L. Li, K.S. Hui, D.A. Dinh, S. Wu, S. Kumar, F. Chen, Z. Shao, K. N. Hui, High-throughput identification of highly active and selective single-atom catalysts for electrochemical ammonia synthesis through nitrate reduction, *Nano Energy* 100 (2022), 107517.
- [39] Z. Deng, C. Ma, Z. Li, Y. Luo, L. Zhang, S. Sun, Q. Liu, J. Du, Q. Lu, B. Zheng, X. Sun, High-Efficiency Electrochemical Nitrate Reduction to Ammonia on a Co₃O₄ Nanoarray Catalyst with Cobalt Vacancies, *ACS Appl. Mater. Interfaces* 14 (2022) 46595–46602.
- [40] X. Fan, C. Ma, D. Zhao, Z. Deng, L. Zhang, Y. Wang, Y. Luo, D. Zheng, T. Li, J. Zhang, S. Sun, Q. Lu, X. Sun, Unveiling selective nitrate reduction to ammonia with Co₃O₄ nanosheets/TiO₂ nanobelt heterostructure catalyst, *J. Colloid Interface Sci.* 630 (2023) 714–720.
- [41] D.i. Liu, L. Qiao, Y. Chen, P. Zhou, J. Feng, C.C. Leong, K.W. Ng, S. Peng, S. Wang, W.F. Ip, H. Pan, Electrocatalytic reduction of nitrate to ammonia on low-cost manganese-incorporated Co₃O₄ nanotubes, *Appl Catal B* 324 (2023), 122293.
- [42] B. Fang, J. Yao, X. Zhang, L. Ma, Y. Ye, J. Tang, G. Zou, J. Zhang, L. Jiang, Y. Sun, A large scaled-up monocrystalline 3R MoS₂ electrocatalyst for efficient nitrogen reduction reactions, *New J. Chem.* 45 (5) (2021) 2488–2495.
- [43] S. Luo, X. Li, B. Zhang, Z. Luo, M. Luo, MOF-Derived Co₃O₄@NC with Core-Shell Structures for N₂ Electrochemical Reduction under Ambient Conditions, *ACS Appl. Mater. Interfaces* 11 (2019) 26891–26897.
- [44] C. Ma, D.a. Liu, Y. Zhang, J. Yong Lee, J. Tian, B. Liu, S. Yan, MOF-derived Fe₂O₃@MoS₂: An efficient electrocatalyst for ammonia synthesis under mild conditions, *Chem. Eng. J.* 430 (2022), 132694.
- [45] C. Ma, N. Zhai, B. Liu, S. Yan, Defected MoS₂: An efficient electrochemical nitrogen reduction catalyst under mild conditions, *Electrochim. Acta* 370 (2021), 137695.