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## CoWO<sub>4</sub> nanoparticles with dual active sites for highly efficient ammonia synthesis†

Lian Duan,<sup>‡a</sup> Zhencong Huang,<sup>‡a</sup> Gen Chen,<sup>a</sup> Min Liu,<sup>id b</sup> Xiaohu Liu,<sup>c</sup> Renzhi Ma<sup>id \*d</sup> and Ning Zhang<sup>id \*a</sup>

The electrochemical reduction reaction of NO<sub>3</sub><sup>−</sup> (NO<sub>3</sub>RR) represents a promising green technology for ammonia (NH<sub>3</sub>) synthesis. Among various electrocatalysts, Co-based materials have demonstrated considerable potential for the NO<sub>3</sub>RR. However, the NH<sub>3</sub> production efficiency of Co-based materials is still limited due to challenges in the competitive hydrogen evolution reaction (HER) and hydrogenating oxynitride intermediates (\*NO<sub>x</sub>). In this study, tungsten (W) and cobalt (Co) elements are co-incorporated to form cobalt tungstate (CoWO<sub>4</sub>) nanoparticles with

### New concepts

Tungsten and cobalt elements are co-incorporated to form cobalt tungstate (CoWO<sub>4</sub>) nanoparticles, which feature bimetallic W and Co active sites. These nanoparticles are employed to optimize the hydrogenation of \*NO<sub>x</sub> and suppress hydrogen evolution reactions, thereby facilitating highly efficient NO<sub>3</sub><sup>−</sup> reduction to NH<sub>3</sub>. Theoretical calculations reveal that Co sites in CoWO<sub>4</sub> promote the adsorption and hydrogenation of \*NO<sub>x</sub> intermediates, while W sites inhibit the competing hydrogen evolution reaction (HER). These dual active sites work synergistically to enhance NH<sub>3</sub> production during NO<sub>3</sub><sup>−</sup> reduction. Guided by these computational insights, CoWO<sub>4</sub> nanoparticles are synthesized via a simple ion precipitation method, with sizes ranging from 10 to 30 nm. Electrochemical testing demonstrates that CoWO<sub>4</sub> nanoparticles achieve a high faradaic efficiency of 97.8 ± 1.5% and an NH<sub>3</sub> yield of 13.2 mg h<sup>−1</sup> cm<sup>−2</sup>, significantly outperforming the corresponding WO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> materials as well as most reported electrocatalysts. *In situ* Fourier transform infrared spectroscopy reveals the enhanced adsorption and hydrogenation of \*NO<sub>x</sub> intermediates and the suppression of the HER on CoWO<sub>4</sub>, which contributes to the high efficiency and selectivity toward NH<sub>3</sub>. This study presents a simple yet effective strategy for the design and synthesis of electrocatalytic materials by precisely tailoring active sites with distinct functions, which advances the development of highly efficient electrocatalysts for NH<sub>3</sub> production.

<sup>a</sup> School of Materials Science and Engineering, Central South University, Changsha, 410083, China. E-mail: nzhang@csu.edu.cn

<sup>b</sup> School of Physics and Electronics, Central South University, Changsha, 410083, China

<sup>c</sup> School of Chemical Engineering, Zhengzhou University, Zhengzhou, 450001, China

<sup>d</sup> Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, 305-0044, Japan.

E-mail: ma.renzhi@nims.go.jp

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‡ These authors contributed equally to this work.



Renzhi Ma

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dual active sites of Co<sup>2+</sup> and W<sup>6+</sup>, which are applied to optimize the hydrogenation of NO<sub>x</sub> and decrease the HER, thereby achieving a highly efficient NO<sub>3</sub>RR to NH<sub>3</sub>. Theoretical calculations indicate that the Co sites in CoWO<sub>4</sub> facilitate the adsorption and hydrogenation of \*NO<sub>x</sub> intermediates, while W sites suppress the competitive HER. These dual active sites work synergistically to enhance NH<sub>3</sub> production from the NO<sub>3</sub>RR. Inspired by these calculations, CoWO<sub>4</sub> nanoparticles are synthesized using a simple ion precipitation method, with sizes ranging from 10 to 30 nm. Electrochemical performance tests demonstrate that CoWO<sub>4</sub> nanoparticles exhibit a high faradaic efficiency of 97.8 ± 1.5% and an NH<sub>3</sub> yield of 13.2 mg h<sup>−1</sup> cm<sup>−2</sup>. *In situ* Fourier transform infrared spectroscopy characterizes the enhanced adsorption and hydrogenation behaviors of \*NO<sub>x</sub> as well as a minimized HER on CoWO<sub>4</sub>, which contributes to the high efficiency and selectivity to NH<sub>3</sub>. This work introduces CoWO<sub>4</sub> nanoparticles as an electrocatalytic material with dual active sites, contributing to the design of electrocatalysts for NH<sub>3</sub> synthesis.

# 1. Introduction

Ammonia ( $\text{NH}_3$ ) is essential for producing fertilizers and nitrogen compounds, largely *via* the Haber–Bosch process, which synthesizes  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$ .<sup>1</sup> Due to the high energy required to break the  $\text{N}\equiv\text{N}$  bond ( $941\text{ kJ mol}^{-1}$ ), this process requires extreme temperatures ( $400\text{--}600\text{ }^\circ\text{C}$ ) and pressures ( $200\text{--}300\text{ atm}$ ).<sup>2,3</sup> The required  $\text{H}_2$  comes from methane steam reforming, generating substantial  $\text{CO}_2$  emissions, contributing to environmental concerns.<sup>4,5</sup> Electrocatalytic synthesis offers an eco-friendly, energy-efficient method for  $\text{NH}_3$  production using renewable resources.<sup>6–8</sup> While the nitrogen reduction reaction (NRR) is promising, challenges such as the hydrogen evolution reaction (HER), low  $\text{N}_2$  solubility, and the high dissociation energy of the  $\text{N}\equiv\text{N}$  bond limit faradaic efficiency and  $\text{NH}_3$  yield.<sup>9,10</sup> Using nitrate ( $\text{NO}_3^-$ ) instead of  $\text{N}_2$  improves water solubility and reduces the energy required for bond dissociation, making it an ideal nitrogen source.<sup>11–13</sup> Moreover, the  $\text{NO}_3^-$  reduction reaction ( $\text{NO}_3\text{RR}$ ) can convert wastewater pollutants into  $\text{NH}_3$ , offering a strategy to balance the nitrogen cycle.<sup>14–16</sup> However, the  $\text{NO}_3\text{RR}$  is a complex, slow process requiring eight-electron transfer, and it generates by-products like  $\text{NO}_2^-$ ,  $\text{N}_2$ , and  $\text{H}_2$ .<sup>17,18</sup> Effective hydrogenation of adsorbed oxynitride intermediates ( $^*\text{NO}_x$ , *e.g.*,  $^*\text{NO}_3$  and  $^*\text{NO}_2$ ) and suppressed HER during the catalytic process are important to enhance the formation of  $\text{NH}_3$ .<sup>19,20</sup>

Transition metal-based oxide electrocatalytic materials, such as  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{MnO}_2$ , have been demonstrated to exhibit high hydrolysis dissociation activity and distinct electrocatalytic activity for the HER or oxygen evolution reaction (OER).<sup>21–24</sup> In the context of the  $\text{NO}_3\text{RR}$ , their remarkable hydrolysis dissociation capability provides substantial quantities of  $^*\text{H}$  for the hydrogenation of  $\text{NO}_x$  intermediates. Among them, Co based materials are promising electrocatalysts due to the strong electrostatic interaction of Co 3d electrons with  $\text{NO}_3^-$  as well as strong hydrolysis dissociation capability to provide  $^*\text{H}$  for hydrogenation of  $\text{NO}_x$  intermediates.<sup>25,26</sup> For example, Zhang *et al.* reported electron-deficient Co metal nanocrystals for improving both  $\text{NO}_3^-$  adsorption and  $^*\text{NH}$  hydrogenation to enhance the  $\text{NH}_3$  production in the  $\text{NO}_3\text{RR}$ .<sup>27</sup> Gu *et al.* designed ultrathin  $\text{CoO}_x$  nanosheets with abundant adsorbed oxygen species, which hampers the HER on cobalt oxide and leads to an enhanced  $\text{NO}_3\text{RR}$  activity.<sup>28</sup> Lu *et al.* synthesized a  $\text{Co}_3\text{O}_4$  nanosheet array with cobalt vacancies on carbon cloth, which exhibited a high faradaic efficiency.<sup>29</sup> However, competitive HER generally occurs intensively on most Co based materials within aqueous electroreduction systems, which hinders the selectivity of the  $\text{NO}_3\text{RR}$  and causes a decrease of  $\text{NH}_3$  production efficiency.

On the other hand, tungsten (W) based oxide materials such as  $\text{WO}_3$  are regarded as a prospective electrocatalyst for the  $\text{NO}_3\text{RR}$  due to its low cost, strong electronegativity, and excellent electrochemical stability.<sup>30,31</sup> Prior research indicates that the 5d electron orbital of W exhibited an exceptionally robust adsorption capacity for reactive hydrogen, impeding the desorption of  $^*\text{H}$  and contributing to the suboptimal HER.<sup>32</sup> From the perspective of electrocatalytic  $\text{NO}_3\text{RR}$ , a stronger  $^*\text{H}$

adsorption capacity and low tendency for the HER are favourable for achieving efficient  $\text{NH}_3$  production.<sup>33,34</sup> However, for pristine  $\text{WO}_3$  materials, the too sluggish HER resulting from strong  $^*\text{H}$  adsorption introduces a high energy barrier for hydrogenation of  $^*\text{NO}_x$ , thereby restricting its involvement in the hydrogenation process and causing the excessive formation of  $\text{NO}_2^-$ . Therefore, it is essential to maintain a balanced state for  $\text{NO}_x$  hydrogenation and the HER.

In this work, tungsten oxides and cobalt oxides are co-incorporated to form cobalt tungstate ( $\text{CoWO}_4$ ) with bimetallic Co–W dual active sites to optimize the hydrogenation of  $^*\text{NO}_x$  intermediates and decrease the HER process to enhance the electrochemical  $\text{NO}_3\text{RR}$  to  $\text{NH}_3$ . Density functional theory (DFT) calculations predict that Co sites in  $\text{CoWO}_4$  benefit the adsorption and hydrogenation of  $\text{NO}_x$  intermediates, while W sites decrease water dissociation and the HER, which exhibits a synergistic high efficiency in electrocatalytic reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$ . Inspired by DFT calculations, the  $\text{CoWO}_4$  nanoparticles are synthesized via a one-step precipitation method.  $\text{CoWO}_4$  exhibits excellent  $\text{NO}_3\text{RR}$  performance across a broad potential range, spanning from  $-0.2$  to  $-0.7\text{ V}$  *versus* the reversible hydrogen electrode (*vs.* RHE). At a potential of  $-0.4\text{ V}$ , the maximum Faraday efficiency (FE) of  $\text{NH}_3$  generation on  $\text{CoWO}_4$  is  $97.8 \pm 1.5\%$ , which is significantly higher than that of  $\text{WO}_3$  ( $60.1 \pm 5.8\%$ ) and  $\text{Co}_3\text{O}_4$  ( $83.9 \pm 5.1\%$ ). *In situ* Fourier-transform infrared (FT-IR) spectroscopy further confirms that  $\text{CoWO}_4$  not only enhances the hydrogenation of  $^*\text{NO}_x$  intermediates but also minimizes the HER, thus facilitating efficient  $\text{NO}_3\text{RR}$  to produce  $\text{NH}_3$ . This work offers an effective strategy to engineer high performance  $\text{NO}_3\text{RR}$  electrocatalysts based on bimetallic oxides.

## 2. Experimental

### 2.1 Synthesis of $\text{CoWO}_4$ nanoparticles

$\text{CoWO}_4$  nanoparticles were synthesized by an ion precipitation method. In a typical procedure,  $1.455\text{ g}$  of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $5\text{ mmol}$ ) and  $1.649\text{ g}$  of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  ( $5\text{ mmol}$ ) were added into  $60\text{ mL}$  deionized water. Then, the solution was mixed and heated to  $70\text{ }^\circ\text{C}$  for 3 hours with constant stirring. The resulting suspension and precipitate were subjected to washing with deionized water and ethanol, followed by several rounds of centrifugation. Finally, the  $\text{CoWO}_4$  powder was obtained through oven drying.

### 2.2 Synthesis of $\text{WO}_3$ and $\text{Co}_3\text{O}_4$ nanoparticles

In the preparation of  $\text{Co}_3\text{O}_4$  nanoparticles,  $20\text{ mL}$  of  $0.5\text{ M}$   $\text{Na}_2\text{CO}_3$  was added dropwise to the solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  ( $0.291\text{ g}$  dissolved in  $20\text{ mL}$  deionized water) under constant stirring. In order to synthesize  $\text{WO}_3$  nanoparticles,  $20\text{ mL}$  of  $0.1\text{ M}$   $\text{HCl}$  was added dropwise to a solution of sodium tungstate ( $0.329\text{ g}$  dissolved in  $20\text{ mL}$  deionized water) under constant stirring. Subsequently, the mixed solution was subjected to a series of washes with deionized water and ethanol, followed by several rounds of centrifugation. The precipitate obtained following drying was subjected to calcination in a muffle furnace at  $500\text{ }^\circ\text{C}$  in air for a period of two hours,

resulting in the formation of  $\text{Co}_3\text{O}_4$  and  $\text{WO}_3$  nanoparticles, respectively.

Details on the electrocatalytic performance tests, DFT computations, characterizations,  $\text{NH}_3$  and  $\text{NO}_2^-$  quantification, faradaic efficiency and yield rate calculations, and *in situ* measurements are described in the ESI.†

### 3. Results and discussion

#### 3.1 Theoretical calculations

DFT calculations were initially employed to investigate the adsorption properties of  $^*\text{NO}_x$  intermediates and  $^*\text{H}_2\text{O}$  species over the surface of  $\text{WO}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CoWO}_4$ . The (001) surfaces of  $\text{WO}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CoWO}_4$  were constructed for calculations (Fig. 1a), and additional DFT computational details could be found in the ESI.† As illustrated in Fig. 1b, the adsorption energies of  $^*\text{NO}_3$  and  $^*\text{NO}_2$  on  $\text{WO}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CoWO}_4$  surfaces were initially investigated. From the calculated values in Fig. 1c, it can be observed that the adsorption energies of  $^*\text{NO}_3$  on the surfaces of the catalysts are 0.55, −0.75, and −0.86 eV for  $\text{WO}_3$ ,  $\text{CoWO}_4$ , and  $\text{Co}_3\text{O}_4$ , respectively. And we also investigated the adsorption energies of  $^*\text{NO}_3$  on the Co and W sites of  $\text{CoWO}_4$  and electron transfer between active sites and  $\text{NO}_3^-$  (Fig. S1, ESI†). The adsorption of  $^*\text{NO}_3$  is more favourable at the Co sites than at the W sites, suggesting that the  $\text{NO}_3\text{RR}$  is more likely to occur at the Co sites. And the adsorption energies of  $^*\text{NO}_2$  on the surfaces of catalysts are −0.45, −1.63, and −2.07 eV for  $\text{WO}_3$ ,  $\text{CoWO}_4$ , and  $\text{Co}_3\text{O}_4$ , respectively. The  $^*\text{NO}_2$  is thus more easily adsorbed on  $\text{Co}_3\text{O}_4$  and  $\text{CoWO}_4$ .

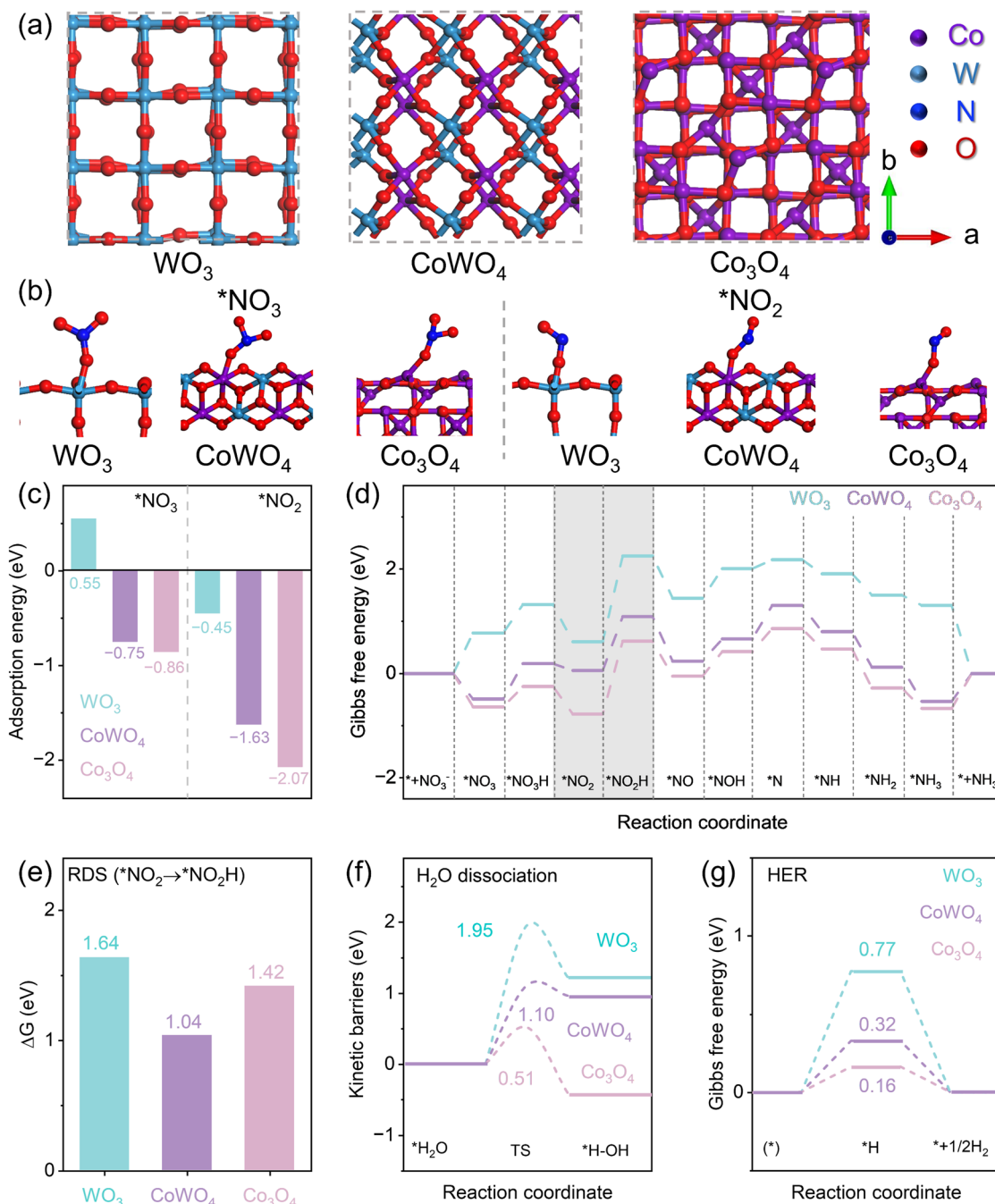
Subsequently, the Gibbs free energy for each reaction step on these catalyst surfaces was calculated to examine the effect of  $^*\text{NO}_x$  adsorption on the reaction pathway of the  $\text{NO}_3\text{RR}$  (atomic models are shown in Fig. S2–S4, ESI†). We considered that the reaction pathways from  $\text{NO}_3^-$  to  $\text{NH}_3$  are as follows:  $(^+\text{NO}_3^-) \rightarrow ^*\text{NO}_3 \rightarrow ^*\text{NO}_3\text{H} \rightarrow ^*\text{NO}_2 \rightarrow ^*\text{NO}_2\text{H} \rightarrow ^*\text{NO} \rightarrow ^*\text{NOH} \rightarrow ^*\text{N} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$ .<sup>35</sup> As presented in Fig. 1d, the results of the calculated Gibbs free energies demonstrate that the formation of  $^*\text{NO}_3$  intermediates on the  $\text{CoWO}_4$  and  $\text{Co}_3\text{O}_4$  surfaces exhibits a negative free energy, indicating that  $\text{CoWO}_4$  and  $\text{Co}_3\text{O}_4$  have a strong adsorption capacity for  $\text{NO}_3^-$ . Furthermore, the maximum reaction Gibbs free energy change ( $\Delta G_{\text{max}}$ ) of the  $\text{NO}_3\text{RR}$  on  $\text{WO}_3$ ,  $\text{CoWO}_4$ , and  $\text{Co}_3\text{O}_4$  occurs in the step of  $^*\text{NO}_2$  to  $^*\text{NO}_2\text{H}$ , suggesting that the hydrogenation of  $^*\text{NO}_2$  is the rate-determining step (RDS) of the reaction. Fig. 1e illustrates the  $\Delta G_{\text{max}}$  of the hydrogenation of  $^*\text{NO}_2$  to  $^*\text{NO}_2\text{H}$  on  $\text{WO}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{CoWO}_4$ , which are 1.64, 1.42 and 1.04 eV, respectively. It is evident that the  $\text{CoWO}_4$  lowers the reaction energy barrier of the RDS, which is favourable to the  $^*\text{NO}_2$  hydrogenation process.

The  $\text{H}_2\text{O}$  dissociation process on  $\text{WO}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CoWO}_4$  is also investigated (Fig. S5–S8, ESI†). Fig. S5 (ESI†) shows that the stronger adsorption of  $^*\text{H}$  and  $\text{H}_2\text{O}$  occurs more easily on the W sites than on the Co sites in  $\text{CoWO}_4$ , indicating that the hydrolysis process occurs predominantly on the W sites. The calculation results of the  $\text{H}_2\text{O}$  dissociation process in Fig. 1f demonstrate that the hydrolysis barrier on  $\text{CoWO}_4$  is lower than

that on  $\text{WO}_3$ , but higher than that on  $\text{Co}_3\text{O}_4$ . Furthermore, the HER process on the catalyst is also investigated (Fig. S9, ESI†). The results demonstrate that  $\text{Co}_3\text{O}_4$  has notable activity for the HER, while the HER process on  $\text{WO}_3$  and  $\text{CoWO}_4$  is relatively slow (Fig. 1g). The above DFT calculations indicate that the  $\text{CoWO}_4$  material exhibits favourable adsorption of  $^*\text{NO}_x$  and an efficient RDS for the conversion of  $^*\text{NO}_2$  to  $^*\text{NO}_2\text{H}$  in comparison with  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ . Additionally, it possesses a relatively minimized hydrolysis and HER process, which together make  $\text{CoWO}_4$  have a potentially exceptional ability to reduce  $\text{NO}_3^-$  to  $\text{NH}_3$ .

#### 3.2 Characterization analysis

Inspired by the theoretical calculations, we synthesized  $\text{CoWO}_4$  nanoparticles using  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as raw materials through a straightforward one-step precipitation method, followed by drying at 60 °C (Fig. S10, ESI†). Fig. 2a presents the X-ray diffraction (XRD) pattern of the synthesized  $\text{WO}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CoWO}_4$ . The XRD pattern indicates that the diffraction peaks of the prepared  $\text{CoWO}_4$  correspond well with monoclinic  $\text{CoWO}_4$  (JCPDS No. 15-0867), confirming the successful synthesis of monoclinic-phase  $\text{CoWO}_4$  with a  $P2_1/a$  space group. And the XRD patterns of the synthesized pure  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$  correspond well with monoclinic  $\text{WO}_3$  (JCPDS No. 71-2141) and cubic  $\text{Co}_3\text{O}_4$  (JCPDS No. 73-1701), respectively. The morphologies of the above synthesized catalysts were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HR-TEM).  $\text{CoWO}_4$  exhibits a particle morphology (Fig. 2b and c), which are in an aggregated state of irregular nanoparticles with a size of about 20–30 nm. And  $\text{CoWO}_4$  has a more uniform and smaller nanoparticle morphology. Fig. 2d and Fig. S11 (ESI†) show the TEM images of  $\text{CoWO}_4$ , revealing that the nanoparticles are approximately 20 nm in size and exhibit an irregular shape. The HR-TEM image of  $\text{CoWO}_4$  in Fig. 2e shows a crystalline region with an interplanar spacing of 0.46 nm, corresponding to the (001) plane of monoclinic  $\text{CoWO}_4$ . Additionally, Fig. 2f presents the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of  $\text{CoWO}_4$  along with the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping images, illustrating the uniform distribution of W, Co, and O elements throughout the  $\text{CoWO}_4$  nanoparticles. Fig. 2g illustrates the microscopic atomic structure model of  $\text{CoWO}_4$ , wherein alternating Co and W are discernible. To clarify the physical nature of the prepared  $\text{CoWO}_4$  catalyst, we conducted the IR and Raman characterization of the catalysts. According to the IR and Raman profiles, the as-prepared  $\text{CoWO}_4$  is monophasic (Fig. S12, ESI†). The SEM images of  $\text{WO}_3$  in Fig. 2h and Fig. S13 (ESI†) show that  $\text{WO}_3$  displays a significantly larger irregular nanoparticle morphology, with sizes around 200–300 nm. TEM images of  $\text{WO}_3$  (Fig. 2i and Fig. S14, ESI†) reveal that the nanoparticles are larger, with sizes around 200–300 nm, consistent with the SEM results. The HR-TEM image in Fig. S14 (ESI†) demonstrates that the entire  $\text{WO}_3$  lattice exhibits a highly ordered rectangular array, characterized by alternating atomic arrangements. The further magnified HR-TEM image shows



**Fig. 1** (a) The atomic models of the (001) surface for WO<sub>3</sub>, CoWO<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub>. (b) The adsorption configurations of \*NO<sub>3</sub> and \*NO<sub>2</sub> intermediates on WO<sub>3</sub>, CoWO<sub>4</sub>, and Co<sub>3</sub>O<sub>4</sub> surfaces. (c) The adsorption energies of \*NO<sub>3</sub> and \*NO<sub>2</sub> intermediates. (d) Reaction Gibbs free energies for different reaction intermediates and (e) the reaction Gibbs free energy changes (ΔG) of the RDS on the W site of WO<sub>3</sub>, the Co site of CoWO<sub>4</sub>, and the Co site of Co<sub>3</sub>O<sub>4</sub>. (f) Energy barrier of the H<sub>2</sub>O dissociation process and (g) the reaction Gibbs free energy of the HER on the W site of WO<sub>3</sub>, the W site of CoWO<sub>4</sub>, and the Co site of Co<sub>3</sub>O<sub>4</sub>.

that the atomic spacing in the transverse and longitudinal directions is 0.38 nm and 0.37 nm, respectively, corresponding to the (002) and (020) planes of monoclinic WO<sub>3</sub>. In contrast, Fig. 2j and Fig. S13 (ESI<sup>†</sup>) show that Co<sub>3</sub>O<sub>4</sub> appears as agglomerated nanoparticles with sizes ranging from about 30 to 60 nm. The TEM images of Co<sub>3</sub>O<sub>4</sub> display a relatively uniform nanoparticle morphology with an average size of approximately 40 nm (Fig. 2k and Fig. S14, ESI<sup>†</sup>). Fig. S14 (ESI<sup>†</sup>) reveals that

Co<sub>3</sub>O<sub>4</sub> has good crystallinity, and the further magnified HR-TEM image shows an interplanar spacing of 0.24 nm, corresponding to the (311) plane of cubic Co<sub>3</sub>O<sub>4</sub>. The aforementioned study validates the successful synthesis of CoWO<sub>4</sub>, WO<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub> nanoparticles.

In order to further understand the composition of the catalyst, X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure spectroscopy (XAFS) were used to

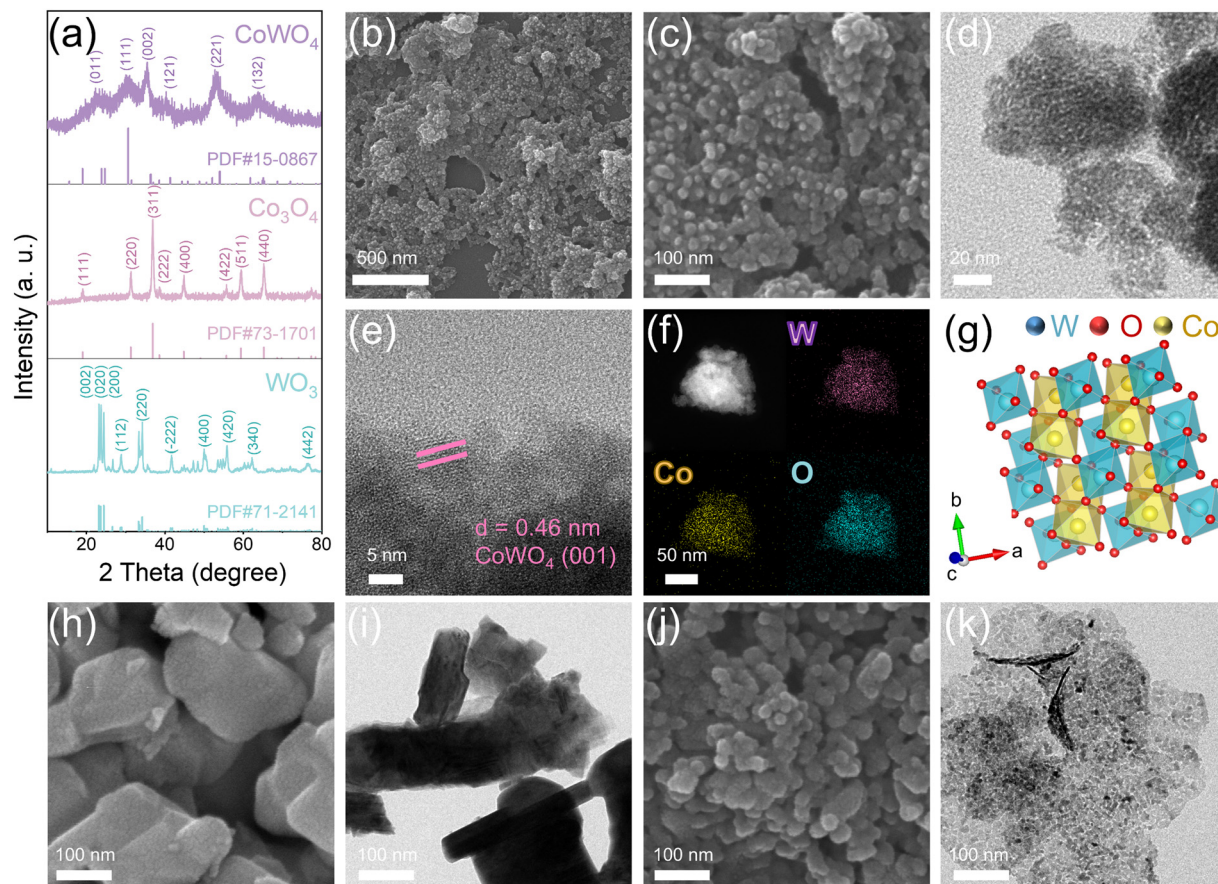


Fig. 2 (a) XRD patterns of  $\text{CoWO}_4$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{WO}_3$ ; (b) and (c) SEM images of  $\text{CoWO}_4$ ; (d) TEM image of  $\text{CoWO}_4$ ; (e) HR-TEM image of  $\text{CoWO}_4$ ; (f) HAADF-STEM image of  $\text{CoWO}_4$  and the corresponding EDS elemental maps of W, Co, and O; (g) microscopic atomic structure modeling of  $\text{CoWO}_4$ ; (h) and (i) SEM and TEM images of  $\text{WO}_3$ ; (j) and (k) SEM and TEM images of  $\text{Co}_3\text{O}_4$ .

analyze the surface chemistry and valence state of the materials. All XPS spectra were calibrated by the C 1s peak of adventitious carbon at 284.8 eV. Fig. S15 (ESI<sup>†</sup>) shows the full XPS spectra of  $\text{CoWO}_4$ ,  $\text{WO}_3$ , and  $\text{Co}_3\text{O}_4$ . The XPS full spectrum of  $\text{CoWO}_4$  reveals the presence of characteristic peaks corresponding to the W, Co, O, and C elements. The carbon comes from the environments during the measurements. The absence of additional impurity peaks suggests that no additional impurity elements were introduced into the prepared samples. Fig. 3a–c show the high-resolution XPS spectra of W 4f, Co 2p and O 1s for  $\text{CoWO}_4$ , respectively. As shown in Fig. 3a, the XPS spectrum of W 4f shows two different split spin-orbit peaks, located at 35.2 and 37.4 eV, which correspond to a pair of typical characteristic peaks of W–O bonds ( $\text{W}^{6+} 4f_{7/2}$  and  $\text{W}^{6+} 4f_{5/2}$ ).<sup>36,37</sup> The XPS spectrum of Co 2p in Fig. 3b can be divided into spin-orbit peaks and satellite peaks, and the spin-orbit peaks can be divided into Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> regions; among them, the pair of peaks at 782.5 and 798.2 eV correspond to  $\text{Co}^{2+}$ , while the pair of peaks at 780.6 and 796.8 eV correspond to  $\text{Co}^{3+}$ , which is consistent with the reports in the literature.<sup>38</sup> Additionally, the two peaks at 787.1 and 803.3 eV are the satellite peaks of Co 2p.<sup>39</sup> In the high-resolution XPS spectrum of O 1s, as shown in Fig. 3c, the O 1s spectrum can be divided into three sub-peaks at 530.3, 531.4,

and 532.9 eV, corresponding to lattice oxygen (OL, M–O bond), defect oxygen (OD) and adsorbed oxygen (OA), respectively.<sup>39,40</sup> The corresponding Fourier transform magnitudes in the *R* space of the W L<sub>3</sub>-edge demonstrates the presence of W–O bonds in  $\text{WO}_3$  and  $\text{CoWO}_4$  (Fig. 3d).<sup>41</sup> In addition, the high-resolution XPS spectra of  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$  are also characterized, which are consistent with the typical  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$  materials (Fig. S16, ESI<sup>†</sup>).<sup>42–45</sup> The above results prove the successful synthesis of  $\text{CoWO}_4$ ,  $\text{WO}_3$ , and  $\text{Co}_3\text{O}_4$ .

### 3.3 Catalytic performance analysis

Subsequently, the electrochemical  $\text{NO}_3\text{RR}$  performance of the synthesized catalysts was investigated in an alkaline electrolyte (1 M NaOH + 0.1 M  $\text{NaNO}_3$ ) using a typical H-type electrolytic cell. The linear sweep voltammetry (LSV) curves of the catalysts were recorded under controlled conditions. As shown in Fig. 4a, the addition of  $\text{NO}_3^-$  to the electrolyte led to a significant increase in current density in all three catalysts, indicating that  $\text{NO}_3^-$  actively participated in the reduction reaction, and the  $\text{NO}_3\text{RR}$  occurred in the solution system.  $\text{CoWO}_4$  exhibits the highest current density compared to  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ . Additionally,  $\text{CoWO}_4$  shows a significant increase in current density compared to the electrolyte without  $\text{NO}_3^-$  (Fig. S17, ESI<sup>†</sup>), indicating its superior catalytic

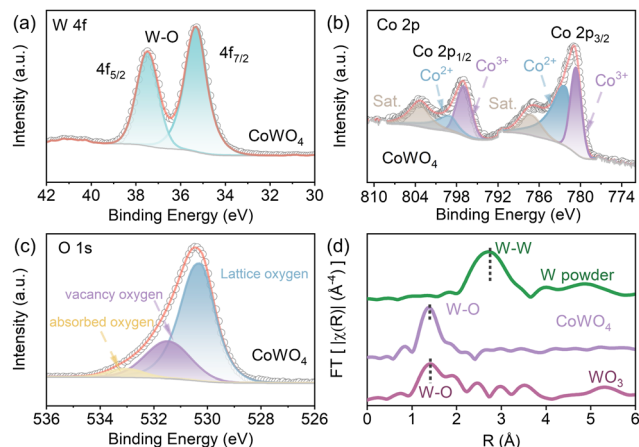


Fig. 3 High resolution XPS spectra of (a) W 4f, (b) Co 2p, and (c) O 1s for CoWO<sub>4</sub>. (d) Fourier transform magnitudes in *R* space of the W L<sub>3</sub>-edge for WO<sub>3</sub>, CoWO<sub>4</sub>, and W powder.

activity for the NO<sub>3</sub>RR. And the Tafel slopes are fitted according to the LSV curves during the NO<sub>3</sub>RR process (Fig. 4b). CoWO<sub>4</sub> has

the lowest Tafel slope (310.9 mV dec<sup>-1</sup>) during the NO<sub>3</sub>RR, which is much lower than those of WO<sub>3</sub> (443.1 mV dec<sup>-1</sup>) and Co<sub>3</sub>O<sub>4</sub> (345.1 mV dec<sup>-1</sup>), suggesting that the CoWO<sub>4</sub> surface has faster NO<sub>3</sub>RR kinetics.

Then, we investigated the selectivity of electrochemical NO<sub>3</sub>RR at different potentials. The concentrations of NH<sub>3</sub> and NO<sub>2</sub><sup>-</sup> in the electrolyte were detected by indoxyl blue colorimetry (Fig. S18, ESI†). The faradaic efficiencies of NH<sub>3</sub> at varying potentials were determined through chronoamperometry and UV-visible absorbance measurements (Fig. S19, ESI†). According to the LSV curves of the catalysts, a suitable voltage range (−0.2 to −0.7 V vs. RHE) was selected to perform chronoamperometric (CA) electrolysis tests on the catalysts to more comprehensively evaluate the NO<sub>3</sub>RR performance of the catalysts. Fig. S19a–c (ESI†) show the CA curves of CoWO<sub>4</sub>, WO<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub> at different potentials. It can be seen that the current of the electrolysis reaction improves with the increase of the applied voltage. CoWO<sub>4</sub> shows the highest reaction current at each applied voltage, indicating that it has a relatively superior NO<sub>3</sub>RR activity to WO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>. After the electrolysis experiment, the electrolyte in the cathode chamber

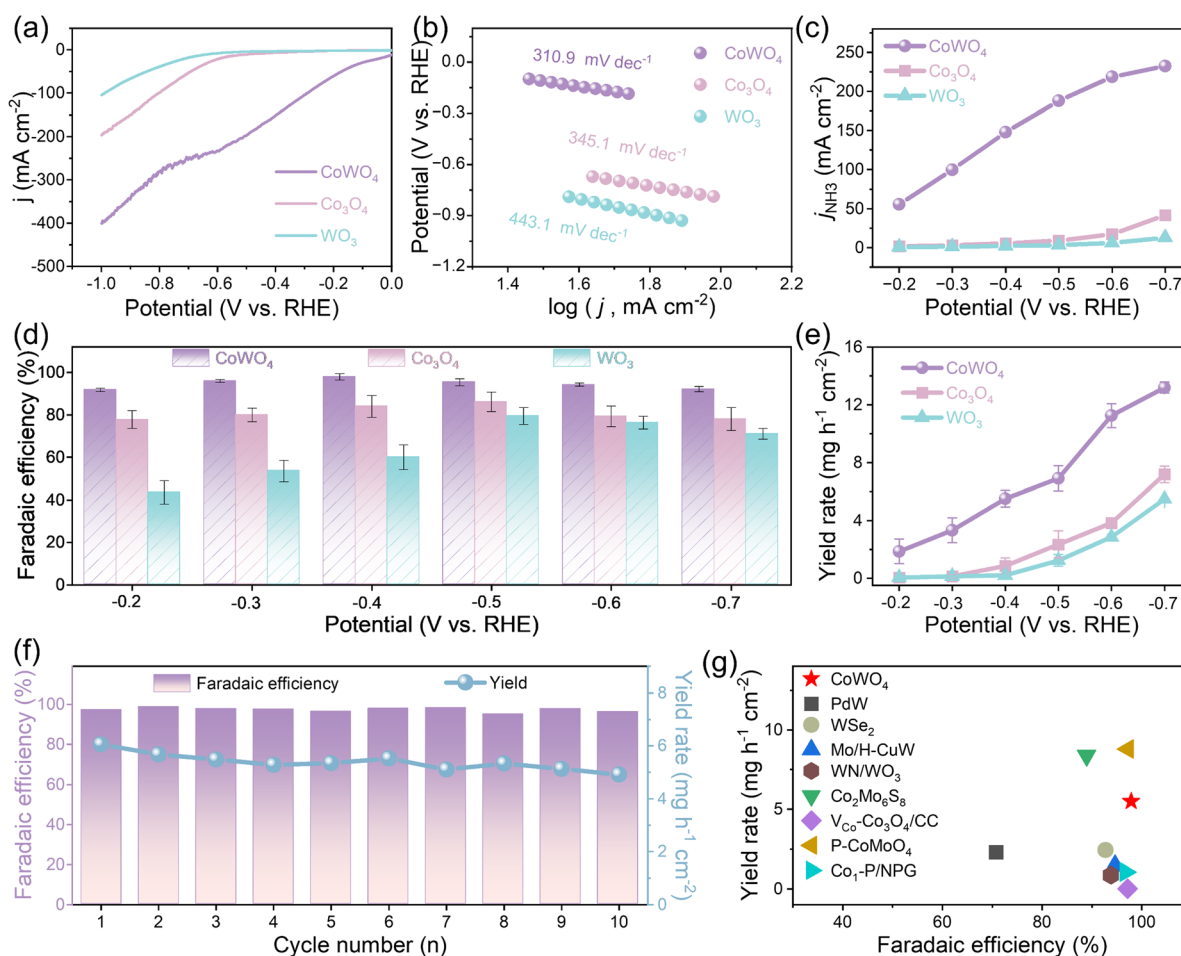


Fig. 4 (a) LSV curves of CoWO<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, and WO<sub>3</sub> during the NO<sub>3</sub>RR. (b) The Tafel slope derived from LSV during the NO<sub>3</sub>RR. (c) Partial current density of NH<sub>3</sub> production under different potentials. (d) Faraday efficiencies of NH<sub>3</sub> production under different potentials. (e) Yield rate of NH<sub>3</sub> at different potentials. (f) FE and NH<sub>3</sub> yields during the cycling stability test. (g) The comparison of CoWO<sub>4</sub> with other reported catalysts.

of the electrolytic cell was collected and diluted to an appropriate concentration to determine the  $\text{NH}_3$  content by the indophenol blue method. Fig. S19d–f (ESI†) shows the UV-visible absorption spectra of  $\text{CoWO}_4$ ,  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ , respectively. The  $\text{FE}_{\text{NH}_3}$  can be calculated using the reaction current and the corresponding absorbance. The partial current density, FEs and yield rates of  $\text{NH}_3$  under different potentials are also shown in Fig. 4c–e. It shows that the partial current density ( $j_{\text{NH}_3}$ ) of  $\text{CoWO}_4$  for  $\text{NH}_3$  generation is significantly better than that of  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ . In addition, Fig. 4d illustrates the FE of the catalyst for  $\text{NH}_3$  generation at various potentials. It can be seen that, with the increase of the applied potential, the FE firstly increases and then decreases, and the FE of all catalysts shows a volcano diagram trend.  $\text{CoWO}_4$  shows superior selectivity and  $\text{FE}_{\text{NH}_3}$  at all potentials compared to  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ . The FE at all test potentials exceeds 91.7% for  $\text{CoWO}_4$ , which is much higher than those of  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ . Among them, at a potential of  $-0.4$  V vs. RHE, the maximum FE of  $\text{NH}_3$  generation on  $\text{CoWO}_4$  can reach  $97.8 \pm 1.5\%$ , which is much higher than those on  $\text{WO}_3$  ( $60.1 \pm 5.8\%$ ) and  $\text{Co}_3\text{O}_4$  ( $83.9 \pm 5.1\%$ ). Based on the high selectivity and current density for  $\text{NH}_3$  generation,  $\text{CoWO}_4$  can also show a significantly higher  $\text{NH}_3$  yield, where the yield is  $5.5 \pm 0.6$   $\text{mg h}^{-1} \text{cm}^{-2}$  at  $-0.4$  V. The maximum  $\text{NH}_3$  yield reaches  $13.2$   $\text{mg h}^{-1} \text{cm}^{-2}$  at  $-0.7$  V and the FE is 92.1% at this time, which is much higher than those of  $\text{WO}_3$  ( $5.4$   $\text{mg h}^{-1} \text{cm}^{-2}$ ) and  $\text{Co}_3\text{O}_4$  ( $7.1$   $\text{mg h}^{-1} \text{cm}^{-2}$ ). The above results suggest that  $\text{CoWO}_4$  has obviously enhanced  $\text{NO}_3\text{RR}$  performance than  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ . To double check the production of  $\text{NH}_3$  from  $\text{CoWO}_4$ , Nessler's test was employed to determine the production rate of  $\text{NH}_3$ . The comparable results obtained using Nessler's reagent are shown in Fig. S20 (ESI†), confirming the great reliability of the detection results of the indophenol blue method.

The  $\text{NO}_3\text{RR}$  performances of  $\text{CoWO}_4$  in low-concentration  $\text{NO}_3^-$  (100, 50, 20, and 10 mM) electrolytes were also studied. Fig. S21a (ESI†) shows the LSV curves obtained in electrolytes with different  $\text{NO}_3^-$  concentrations. As the  $\text{NO}_3^-$  concentration in the electrolyte decreases, the current response of the LSV obtained also gradually decreases, showing that the  $\text{NO}_3\text{RR}$  activity decreases accordingly. Subsequently, their  $\text{NO}_3\text{RR}$  selectivity and efficiency were studied at a voltage of  $-0.4$  V. Fig. S21b and c (ESI†) show the corresponding chronoamperometric curves and UV curves of the solution after the reaction. The  $i$ - $t$  curve during the reaction also shows a gradually decreasing trend with decreasing  $\text{NO}_3^-$  concentration. As shown in Fig. S21d (ESI†),  $\text{CoWO}_4$  can exhibit  $\text{FE}_{\text{NH}_3}$  values of 97.9%, 94.8% and 91.8% under the electrolysis conditions of 100 mM, 50 mM and 20 mM  $\text{NO}_3^-$  concentrations, respectively. Even in the electrolyte with an extremely low  $\text{NO}_3^-$  concentration (10 mM), its FE of the  $\text{NO}_3\text{RR}$  to synthesize  $\text{NH}_3$  is 83.4%. So,  $\text{CoWO}_4$  has relatively excellent  $\text{NO}_3\text{RR}$  activity under low  $\text{NO}_3^-$  concentration electrolyte conditions. The as-prepared  $\text{CoWO}_4$  materials have potential application prospects in electrocatalytic synthesis of  $\text{NH}_3$  from wastewater.

In order to exclude the interference of other nitrogen sources that may exist in the experiment and ensure that the

$\text{NH}_3$  produced in the experiment comes from  $\text{NO}_3^-$  in the electrolyte rather than other pollutants, a blank control experiment without  $\text{NO}_3^-$  electrolyte and without applied voltage was carried out. Fig. S22 (ESI†) shows the UV curves obtained by detecting the electrolyte under a series of different experimental conditions. Obviously, under the conditions of electrolyte without  $\text{NO}_3^-$  and electrolyte with  $\text{NO}_3^-$  without applied voltage, obvious adsorption peaks are difficult to detect in the UV curve, indicating that there is no  $\text{NH}_3$  produced in the electrolyte. The results show that negligible amounts of  $\text{NH}_3$  are detected in the absence of  $\text{NO}_3^-$  or without applying a voltage. However, when  $\text{NO}_3^-$  is present and a voltage is applied, a significant  $\text{NH}_3$  yield and FE are achieved. The above results indicate that there is no contamination from any other nitrogen source during the experiment, ensuring that the  $\text{NH}_3$  in the solution is produced from electrolytic reduction of  $\text{NO}_3^-$  in the electrolyte.

To assess the stability of the  $\text{CoWO}_4$  catalyst, both cyclic electrolysis and long-term continuous electrolysis tests were carried out at a potential of  $-0.4$  V. During the cyclic electrolysis test, the electrolyte was collected every 30 minutes for colorimetric analysis. After each cycle, the electrolytic cell was cleaned, and the electrolyte was replaced before the next cycle. The chronoamperometric curves for each cycle and the corresponding UV spectra of the electrolyte are shown in Fig. S23 (ESI†). A slight decrease in current density is observed after the first cycle, but the electrolysis current remained stable in subsequent cycles. No significant decrease is detected during the cyclic test, and the corresponding UV spectra show minimal variation. As shown in Fig. 4f, after 10 cycles, the FE and  $\text{NH}_3$  yield of  $\text{CoWO}_4$  remain stable, with the FE exceeding 96% and the  $\text{NH}_3$  yield maintained at approximately  $5.5$   $\text{mg h}^{-1} \text{cm}^{-2}$ , indicating excellent stability. Additionally, a 21-hour continuous electrolysis test was performed (Fig. S24, ESI†), without replacing the electrolyte or electrodes. The electrolyte was periodically collected for colorimetric analysis, and its UV spectra were recorded (Fig. S25, ESI†). The  $i$ - $t$  curve in Fig. S23 (ESI†) shows stable current throughout the electrolysis, with no significant fluctuations in current density. The corresponding FE of  $\text{NH}_3$  remains consistent throughout the test. After 21 hours, the FE is still above 88.9%. The slight decline in FE may be due to the gradual depletion of  $\text{NO}_3^-$  in the electrolyte over time. These results demonstrate the excellent electrocatalytic stability of  $\text{CoWO}_4$  for the  $\text{NO}_3\text{RR}$ . Furthermore, ITO conductive glass was employed as the substrate for catalyst loading to test the XRD patterns of the catalyst before and after the electrochemical reaction (Fig. S26, ESI†). The results reveal that there is no shift in peak positions or the appearance of new peaks after the reaction, except for a reduction in the intensity of the  $\text{CoWO}_4$  diffraction signal, which is likely due to catalyst detachment from the ITO substrate during the electrochemical test. The structural characterizations and the corresponding EDS elemental maps of  $\text{CoWO}_4$  after reduction are shown in Fig. S27 and S28 (ESI†). The above results suggest that  $\text{CoWO}_4$  exhibits excellent durability and stability for the  $\text{NO}_3\text{RR}$  to produce  $\text{NH}_3$ . Furthermore, the electrocatalytic performance of  $\text{CoWO}_4$  is benchmarked against other

previously reported catalysts (Fig. 4g and Table S1, ESI†), revealing that CoWO<sub>4</sub> nanoparticles exhibit a relatively superior FE and excellent NH<sub>3</sub> yield, outperforming most reported Co- and W-based catalysts.<sup>19,29,46–51</sup>

In addition, the FEs of the byproducts (such as NO<sub>2</sub><sup>−</sup>, N<sub>2</sub> and H<sub>2</sub>) that may appear during the NO<sub>3</sub>RR are also calculated. It can be seen that NH<sub>3</sub> and NO<sub>2</sub><sup>−</sup> are the main nitrogen-containing products. Fig. S29a–c (ESI†) show the corresponding UV curves for the detected NO<sub>2</sub><sup>−</sup>. According to the gas chromatograph detection results in Fig. S28d–f (ESI†), there is no N<sub>2</sub> detected during the reaction, and only a small amount of H<sub>2</sub> is detected. Fig. 5a–c show the main products of the NO<sub>3</sub>RR of CoWO<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and WO<sub>3</sub>, respectively. As the applied voltage increases, NO<sub>2</sub><sup>−</sup> is gradually converted and consumed, and the HER becomes increasingly intense. It is clearly seen that CoWO<sub>4</sub> generates fewer by-products of NO<sub>2</sub><sup>−</sup> than WO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>, which is attributed to its more favorable hydrogenation ability as predicted by DFT calculations. Meanwhile, the HER process in CoWO<sub>4</sub> is obviously decreased in comparison with WO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>, which is well consistent with the DFT calculation results. Therefore, in comparison to WO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>, CoWO<sub>4</sub> demonstrates a decreased HER process and a high NO<sub>x</sub> hydrogenation ability, which together contribute to its superior capability to reduce NO<sub>3</sub><sup>−</sup> to NH<sub>3</sub>.

To deeply evaluate the intrinsic activity of these catalysts, kinetic electrochemical impedance spectroscopy (EIS) and electrochemically active surface area (ECSA) tests were conducted. Fig. 5d shows the fitted EIS of CoWO<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, and WO<sub>3</sub>. The inset in the figure shows the fitting model, which includes the charge transfer resistance (*R*<sub>ct</sub>), solution resistance (*R*<sub>s</sub>) and a constant phase element (CPE). From the further enlarged EIS

graph, it can be seen that the *R*<sub>s</sub> values of the three catalysts are very close. CoWO<sub>4</sub> has a significantly smaller charge transfer impedance (7.91 Ω). So, compared with WO<sub>3</sub> (303.80 Ω) and Co<sub>3</sub>O<sub>4</sub> (194.00 Ω), CoWO<sub>4</sub> has a higher mass transfer rate during the NO<sub>3</sub>RR and is more conducive to the reaction. The resistance values of the EIS fitted by the three catalysts are shown in Fig. S30 (ESI†) and the inserted table. Moreover, the non-polarized cyclic voltammetry (CV) curves of these catalysts were recorded at different scan rates in the potential range of 0.75–0.85 V vs. RHE, and the ECSA was evaluated by the double layer capacitance (*C*<sub>dl</sub>) method (Fig. 5e and Fig. S31, ESI†). Fig. 5e shows the *C*<sub>dl</sub> value calculated from the current density difference  $\Delta j$  at the midpoint of the measurement point interval in the CV curve and the scan rate fitting. The *C*<sub>dl</sub> values of WO<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> and CoWO<sub>4</sub> are 0.099, 0.161 and 0.166 mF cm<sup>−2</sup>, respectively. Obviously, CoWO<sub>4</sub> has the highest *C*<sub>dl</sub> value, which indicates that it has the largest active surface area and more abundant active sites. Furthermore, to assess the intrinsic activities of these catalysts, we normalized the LSV curves by ECSA (Fig. 5f). In comparison, CoWO<sub>4</sub> continues to demonstrate the highest activity for the NO<sub>3</sub>RR, suggesting that its enhanced catalytic performance is primarily due to the intrinsic activity of CoWO<sub>4</sub> itself.

### 3.4 Catalytic mechanism analysis

To verify the catalytic process, *in situ* FT-IR spectroscopy was applied to identify the reaction intermediates generated during the electrocatalytic reaction and their adsorption changes. Fig. 6a–c show the *in situ* infrared spectra of CoWO<sub>4</sub>, WO<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub> for the NO<sub>3</sub>RR at different applied potentials, respectively. The initial peak observed at 1210 cm<sup>−1</sup> is indicative of the formation of \*NO<sub>2</sub> (O–N–O) intermediates.<sup>52–54</sup>

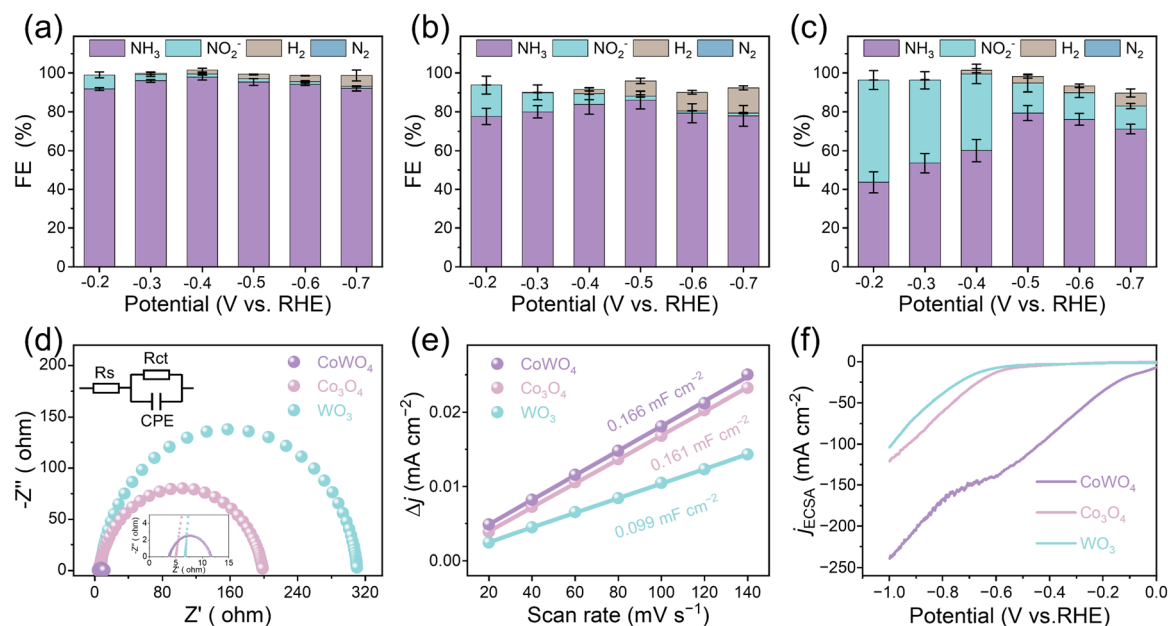


Fig. 5 (a)–(c) FEs of different products (NH<sub>3</sub>, NO<sub>2</sub><sup>−</sup>, H<sub>2</sub>, and N<sub>2</sub>) during NO<sub>3</sub>RR electrolysis at various potentials for (a) CoWO<sub>4</sub>, (b) Co<sub>3</sub>O<sub>4</sub>, and (c) WO<sub>3</sub>. (d) The electrochemical impedance spectra of CoWO<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, and WO<sub>3</sub> (the inset shows the fitted equivalent circuit model). (e) The electrochemical active surface areas. (f) LSV curves normalized by ECSA of CoWO<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, and WO<sub>3</sub>.

In comparison, the vibration peak of  $\text{WO}_3$  at  $1210\text{ cm}^{-1}$  exhibits a downward shift, while the vibration peaks of  $\text{CoWO}_4$  and  $\text{Co}_3\text{O}_4$  display an upward shift. This suggests that  $^*\text{NO}_2$  can be accumulated on the surface of  $\text{CoWO}_4$  and  $\text{Co}_3\text{O}_4$ , while it displays a tendency of desorption onto the surface of  $\text{WO}_3$ . This result indicates that  $\text{WO}_3$  exhibits poor adsorption of  $\text{NO}_2^-$  and leads to more by-products of  $\text{NO}_2^-$ , while  $\text{NO}_2^-$  is strongly adsorbed and exhibits enhanced  $\text{NO}_3\text{RR}$  activity on the surfaces of  $\text{CoWO}_4$  and  $\text{Co}_3\text{O}_4$ . The lower peak at  $1460\text{ cm}^{-1}$  and the upper peak at  $1585\text{ cm}^{-1}$  can be ascribed to the stretching vibration of N–H in the  $^*\text{NH}_3$  intermediate, which suggests that  $^*\text{NH}_3$  is desorbed and produced  $\text{NH}_3$  and  $^*\text{NH}$  species.<sup>55</sup> Compared to  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$ , these N–H vibration peaks of  $\text{CoWO}_4$  are notably stronger, indicating the presence of significant  $\text{NO}_3\text{RR}$  processes on their surfaces. It can be clearly seen that  $\text{CoWO}_4$  is able to enhance the hydrogenation of  $\text{NO}_x$  intermediates, which is consistent with DFT calculations. Furthermore, the downward absorption band observed near  $1650\text{ cm}^{-1}$  is attributed to the H–O–H bending vibration of  $\text{H}_2\text{O}$ , which reflects the dissociation of  $\text{H}_2\text{O}$  on the catalyst surface.<sup>56</sup> The H–O–H peak is nearly absent in  $\text{WO}_3$ , indicating its limited hydrolysis performance, which hinders hydrogenation leading to formation of the byproduct  $\text{NO}_2^-$ . In comparison, the H–O–H peak in  $\text{CoWO}_4$  exhibits a low intensity

compared to  $\text{Co}_3\text{O}_4$ , demonstrating minimized hydrolytic performance, and the HER is suppressed to some extent, which contributes to its high selectivity to  $\text{NH}_3$ . Consequently, a reaction mechanism for the  $\text{NO}_3\text{RR}$  over  $\text{CoWO}_4$  catalysts was proposed (Fig. 6d).  $\text{CoWO}_4$  not only enhances the adsorption and hydrogenation of  $^*\text{NO}_x$  intermediates but also minimizes the HER, thus facilitating a highly efficient and selective  $\text{NO}_3\text{RR}$  to produce  $\text{NH}_3$ .

## 4. Conclusions

In conclusion,  $\text{CoWO}_4$  nanoparticles with Co–W dual sites have been developed to enhance the hydrogenation of  $^*\text{NO}_x$  intermediates and decrease the competitive HER to significantly enhance the  $\text{NO}_3\text{RR}$  for  $\text{NH}_3$  production. Theoretical DFT calculations suggest that the Co sites in  $\text{CoWO}_4$  facilitate the adsorption of  $\text{NO}_x$  intermediates, while the W sites decrease the HER. These two sites work synergistically to promote  $\text{NH}_3$  formation. As predicted by DFT calculations, we synthesize pure phase  $\text{CoWO}_4$  nanoparticles by a facile ion precipitation method. The electrochemical tests demonstrate that  $\text{CoWO}_4$  exhibits enhanced  $\text{NO}_3\text{RR}$  performance across a broader potential range (approximately  $-0.2$  to  $-0.7\text{ V}$  vs. RHE), with a faradaic efficiency

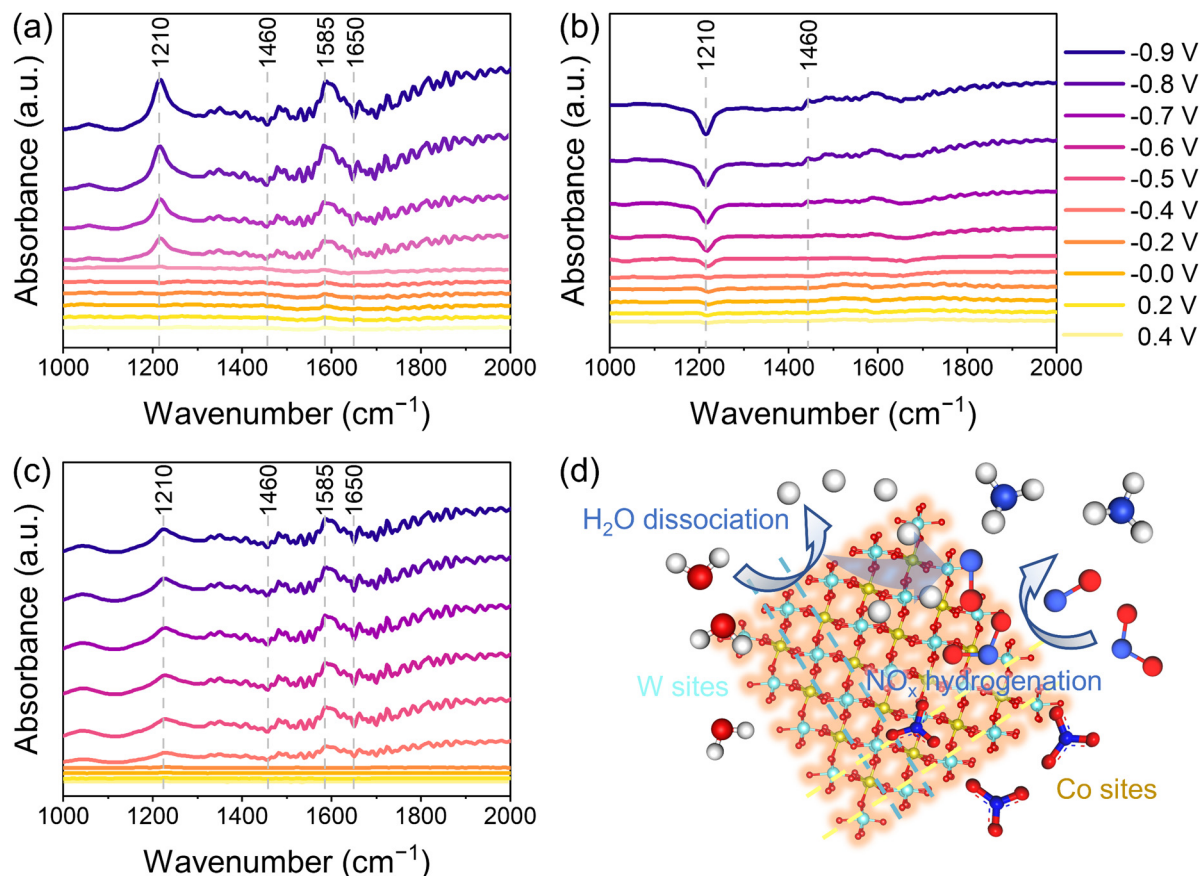


Fig. 6 *In situ* FT-IR spectra of (a)  $\text{CoWO}_4$ , (b)  $\text{WO}_3$ , and (c)  $\text{Co}_3\text{O}_4$  at different applied potentials. (d) Proposed catalytic reaction mechanism for  $\text{NH}_3$  formation on  $\text{CoWO}_4$ .

exceeding 91.7% at all test potentials, which is much higher than those of  $\text{WO}_3$  and  $\text{Co}_3\text{O}_4$  materials. Especially, the maximum FE of  $\text{NH}_3$  generation on  $\text{CoWO}_4$  is  $97.8 \pm 1.5\%$  at a potential of  $-0.4$  V, which is significantly higher than that of  $\text{WO}_3$  ( $60.1 \pm 5.8\%$ ) and  $\text{Co}_3\text{O}_4$  ( $83.9 \pm 5.1\%$ ). At a potential of  $-0.7$  V, the maximum yield of  $\text{NH}_3$  reaches  $13.2 \text{ mg h}^{-1} \text{ cm}^{-2}$ . *In situ* FT-IR spectroscopy provides further evidence for the enhanced adsorption and hydrogenation behaviors of  $\text{*NO}_x$  on  $\text{CoWO}_4$  as well as decreased HER, which aligns well with the DFT calculation results. This study introduces a novel and efficient strategy for designing effective  $\text{NO}_3\text{RR}$  electrocatalysts to synthesize  $\text{NH}_3$ .

## Data availability

The authors declare that all data in this manuscript are available upon reasonable request.

## Conflicts of interest

The authors declare no conflicts of interest.

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