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## Free radicals promote electrocatalytic nitrogen oxidation†

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In this work, we introduce hydroxyl radicals into the electrocatalytic nitrogen oxidation reaction (NOR) for the first time. Cobalt tetroxide (Co<sub>3</sub>O<sub>4</sub>) acts not only as an electrocatalyst, but also as a nanozyme (in combination with hydrogen peroxide producing <sup>•</sup>OH), and can be used as a high-efficiency nitrogen oxidation reaction (NOR) electrocatalyst for environmental nitrate synthesis. Co<sub>3</sub>O<sub>4</sub> + <sup>•</sup>OH shows an excellent nitrogen oxidation reaction (NOR) performance among Co<sub>3</sub>O<sub>4</sub> catalysts in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution. At an applied potential of 1.7 V vs. RHE, the HNO<sub>3</sub> yield of Co<sub>3</sub>O<sub>4</sub> + <sup>•</sup>OH reaches 89.35 μg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup>, which is up to 7 times higher than that of Co<sub>3</sub>O<sub>4</sub> (12.8 μg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup>) and the corresponding FE is 20.4%. The TOF of Co<sub>3</sub>O<sub>4</sub> + <sup>•</sup>OH at 1.7 V vs. RHE reaches 0.58 h<sup>-1</sup>, which is higher than that of Co<sub>3</sub>O<sub>4</sub> (0.083 h<sup>-1</sup>), demonstrating that free radicals greatly enhance the intrinsic activity. Density functional theory (DFT) demonstrates that <sup>•</sup>OH not only can drive nitrogen adsorption, but also can decrease the energy barrier (rate-determining step) of N<sub>2</sub> to N<sub>2</sub>OH\*, thus producing great NOR activity.

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## Introduction

Nitrate plays an important role in promoting social progress and economic development,<sup>1–5</sup> because it is a material for growing fertilizers and explosives.<sup>6–12</sup> Nowadays, the industrial production of nitric acid mainly adopts high temperature (400–600 °C) and high pressure (15–25 MPa) conditions, involving a multi-step reaction Ostwald process,<sup>13–15</sup> which is a high energy consumption and high emission production process.<sup>16–20</sup> The electrocatalytic nitrogen oxidation reaction (NOR) to produce nitrate is clean, pollution-free and environmentally friendly,<sup>21–23</sup> because the electrocatalytic NOR to produce nitrate only requires nitrogen and water in the environment as raw materials.<sup>24–26</sup> At the same time, it does not discharge polluting gases and waste liquids.<sup>27–29</sup> The electrocatalytic NOR to produce nitrate is very important to replace the Ostwald process with high energy consumption and high emission.<sup>25,30</sup>

There are great challenges in the production of nitrate in an aqueous medium by the electrocatalytic NOR.<sup>31–34</sup> The splitting of the strong N≡N bond requires an oxidation potential in which the oxygen evolution reaction (OER) occurs readily,<sup>35,36</sup> leading to

extremely low Faraday efficiency (FE) of the NOR<sup>37–39</sup> under ambient conditions. Therefore, it is ideal to find a catalytic system that promotes the NOR and inhibits the competing OER in neutral solution. In addition, it was previously reported that the adsorption of OH enhances the activity of the NOR, but the yield of nitrate was very low (<25 μg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup>) due to the weak adsorption of N<sub>2</sub> and a high energy barrier for the conversion of N<sub>2</sub> to N<sub>2</sub>OH\* (the rate-determining step). O<sub>2</sub><sup>•-</sup> radicals have been studied in the photocatalytic NOR, but no one has studied the role of free radicals in electrocatalytic nitrogen oxidation.<sup>9,35</sup>

In this work, we introduce hydroxyl radicals into the electrocatalytic NOR for the first time. Cobalt tetroxide (Co<sub>3</sub>O<sub>4</sub>) acts not only as an electrocatalyst, but also as a nanozyme (in combination with hydrogen peroxide producing <sup>•</sup>OH), and can be used as a high-efficiency NOR electrocatalyst for environmental nitrate synthesis. Co<sub>3</sub>O<sub>4</sub> + <sup>•</sup>OH shows an excellent NOR performance among Co<sub>3</sub>O<sub>4</sub> catalysts in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution. At an applied potential of 1.7 V vs. RHE, the NO<sub>3</sub><sup>-</sup> yield of Co<sub>3</sub>O<sub>4</sub> + <sup>•</sup>OH is 7 times higher than that of Co<sub>3</sub>O<sub>4</sub>. We use ultraviolet spectroscopy and ion chromatography to determine the concentration of nitrate produced. At the same time, we also conduct <sup>15</sup>N isotope labeling experiments by mass spectrometry to further determine the nitrogen source. The TOF of Co<sub>3</sub>O<sub>4</sub> + <sup>•</sup>OH is higher than that of Co<sub>3</sub>O<sub>4</sub>, demonstrating that free radicals can greatly enhance the intrinsic activity. It is the most active non-precious metal catalyst reported so far for the NOR process (Table S1†). This catalyst also demonstrates long-term electrochemical and structural stability, and the current density did not have a tendency to decrease even in a 50 h continuous test. Density functional theory (DFT) demonstrates that <sup>•</sup>OH not only can drive nitrogen adsorption, but also

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can further lower the energy barrier for the conversion of  $\text{N}_2$  to  $\text{N}_2\text{OH}^*$  (the rate-determining step), generating significant NOR activity.

## Results and discussion

### Preparation and characterization of catalysts

Here, we used a simple co-precipitation and subsequent annealing way to synthesize  $\text{Co}_3\text{O}_4$  NBs, as shown in Fig. 1a. A scanning electron microscope (SEM) and transmission electron microscope (TEM) were applied to detect the morphology of the catalyst. Firstly, highly uniform and small size (about 500 nm) Co–Co Prussian blue analogue (PBA) nanocubes (NCs)<sup>40</sup> were obtained by a co-precipitation strategy at room temperature (Fig. S1a†). From Fig. S1b,† we can know that the X-ray diffraction (XRD) of the Co–Co PBA corresponded well to crystalline  $\text{Co}_3[\text{Co}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$  (PDF#77-1161).<sup>41</sup> Secondly, the as-synthesized Co–Co PBA NCs were calcined at 350 °C in air for 2 h. Fig. 1b shows the XRD pattern of the catalyst, the peak of which matched greatly with the card of  $\text{Co}_3\text{O}_4$  (PDF#98-006-9366). After thermal treatment, the PBA NCs were transformed into concave  $\text{Co}_3\text{O}_4$  NBs, and the basic morphology remains the same, but the size is slightly smaller (Fig. 1c). As obviously shown in Fig. 1d and S2–S4,† the TEM energy-dispersive X-ray spectroscopy (TEM-EDX) and SEM-EDX elemental mapping images showed that Co and O elements are uniformly distributed on the catalyst. The high-resolution TEM (HRTEM, Fig. S5†) images demonstrated that the  $\text{Co}_3\text{O}_4$  NBs are uniform and the lattice spacing is 0.243 nm, which corresponds to the (311) face of the  $\text{Co}_3\text{O}_4$  NBs.

In addition, X-ray photoelectron spectroscopy (XPS) was used to study the valence electron states and electronic structures. As shown in Fig. S6,† the XPS survey spectrum shows that the  $\text{Co}_3\text{O}_4$  NBs are composed of Co and O elements. This result is consistent

with TEM-EDX and SEM-EDX spectroscopy. As obvious from Fig. S7a,† the Co 2p spectrum represented two main peaks, which belong to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub>, respectively.<sup>42</sup> The O 1s spectrum is composed of three species of oxygen, which can be attributed to the Co–O band, the defect sites (oxygen vacancies), and the absorbed oxygen, respectively (Fig. S7b†).<sup>43</sup> From Fig. S8,† we can apparently know that the Brunauer–Emmett–Teller (BET) surface area and the pore volume of  $\text{Co}_3\text{O}_4$  NBs are 51.06 m<sup>2</sup> g<sup>−1</sup> and 0.14 cm<sup>3</sup> g<sup>−1</sup>. This further indicates that  $\text{Co}_3\text{O}_4$  NBs with a porous structure were successfully synthesized.

To investigate the formation of free groups on the catalyst surface, a range of methods are used to detect oxygen species, including UV-vis, electron spin resonance (ESR) spectroscopy and fluorescence. Fig. 2a shows the process of generating reactive oxygen species including  $\cdot\text{OH}$  free radicals and  $\cdot\text{O}_2\text{H}$  free radicals by nanozymes. As shown in Fig. 2b, surface  $\text{Co}^{2+}$  species first catalyze the reduction of  $\text{H}_2\text{O}_2$  to  $\cdot\text{OH}$  radicals, and play a key role in the subsequent TMB oxidation discoloration and generation of  $\cdot\text{O}_2\text{H}$  radicals and  $\text{Co}^{3+}$  regeneration.<sup>44</sup> As displayed in Fig. 2c, the  $\text{Co}_3\text{O}_4 + \text{TMB} + \text{H}_2\text{O}_2$  group has a distinct absorption peak compared to the other groups, indicating that  $\text{Co}_3\text{O}_4$  has significant catalase-mimicking activities. At the same time, the obvious turquoise oxidation product (oxTMB) in the inset of Fig. 2c further indicates the great catalytic performance of  $\text{Co}_3\text{O}_4$ .<sup>45</sup> From Fig. 2d, we can know that the  $\text{Co}_3\text{O}_4/\text{H}_2\text{O}_2$  mixture yield  $\cdot\text{OH}$  was obtained by reacting with terephthalic acid (TA). Under these conditions, TA is oxidized by  $\cdot\text{OH}$  to form the fluorescent product TAOH. Fig. S9† depicts the effect of the mixture of  $\text{H}_2\text{O}_2$  and  $\text{Co}_3\text{O}_4$  on the adsorption spectrum of MB.  $\text{H}_2\text{O}_2/\text{Co}_3\text{O}_4$  promoted the formation of  $\cdot\text{OH}$  in the system, and the adsorption spectrum of MB +  $\text{H}_2\text{O}_2$  was significantly reduced. In addition, it was observed that  $\cdot\text{OH}$  and  $\cdot\text{O}_2\text{H}$  captured by DMPO agent had a pair of 1 : 2 : 2 : 1 and six resonance characteristic peaks (Fig. 2e and f),

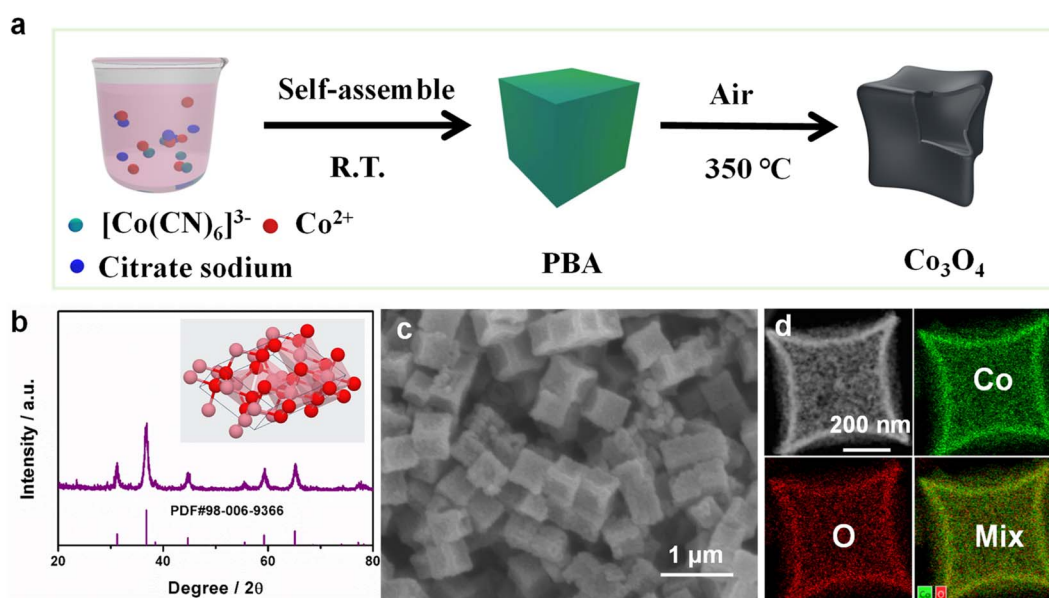


Fig. 1 (a) Schematic illustration of the formation of  $\text{Co}_3\text{O}_4$  NBs. (b) The X-ray diffraction (XRD) pattern of  $\text{Co}_3\text{O}_4$  NBs. (c) SEM image of  $\text{Co}_3\text{O}_4$  NBs. (d) TEM elemental mapping images of  $\text{Co}_3\text{O}_4$  NBs.



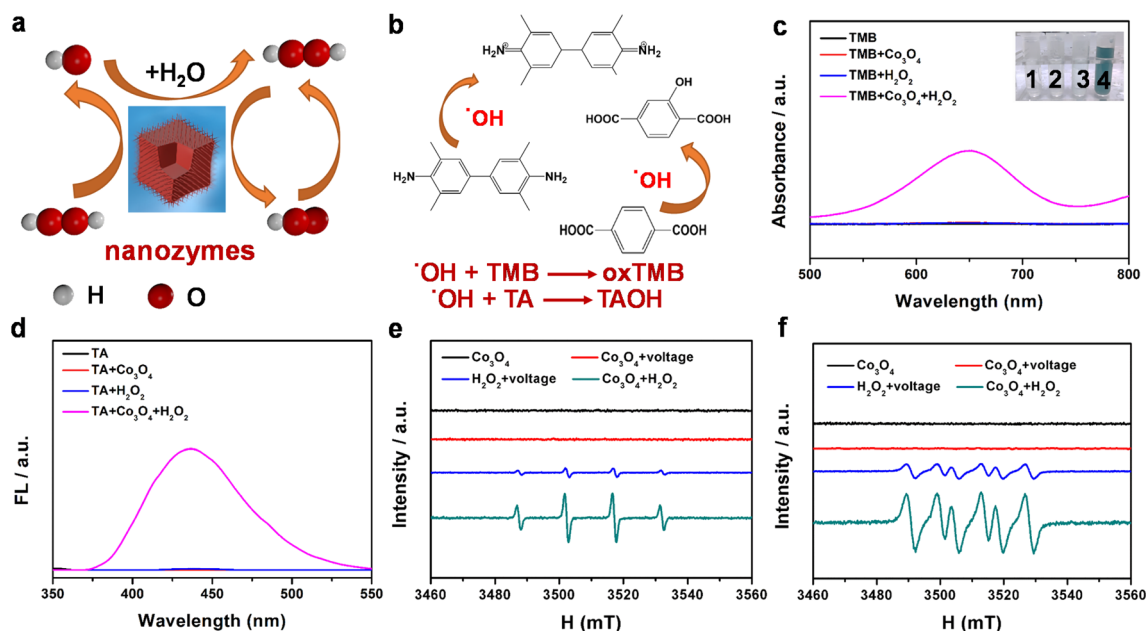


Fig. 2 (a) Process of generating reactive oxygen species by nanozymes. (b) Reaction of  $\cdot\text{OH}$  free radicals produced by nanozymes with TMB and TA. (c) The UV-vis spectra and visible color changes of TMB in various reaction systems: (1) TMB, (2) TMB +  $\text{Co}_3\text{O}_4$ , (3) TMB +  $\text{H}_2\text{O}_2$ , and (4) TMB +  $\text{Co}_3\text{O}_4$  +  $\text{H}_2\text{O}_2$ . (d) Probing  $\cdot\text{OH}$  formation through the fluorescence spectrum of the adduct of  $\cdot\text{OH}$  with TA. (e) Probing  $\cdot\text{OH}$  production through the electron spin resonance (ESR) spectrum of the adduct of  $\cdot\text{OH}$  with DMPO. (f) Probing  $\cdot\text{O}_2\text{H}$  production through the ESR spectrum of the adduct of  $\cdot\text{O}_2\text{H}$  with DMPO.

which also confirmed that  $\text{Co}_3\text{O}_4$  produced  $\cdot\text{OH}$  and  $\cdot\text{O}_2\text{H}$  during a catalytic reaction similar to peroxidase mimics.<sup>46</sup>

### Electrocatalytic performance for the NOR

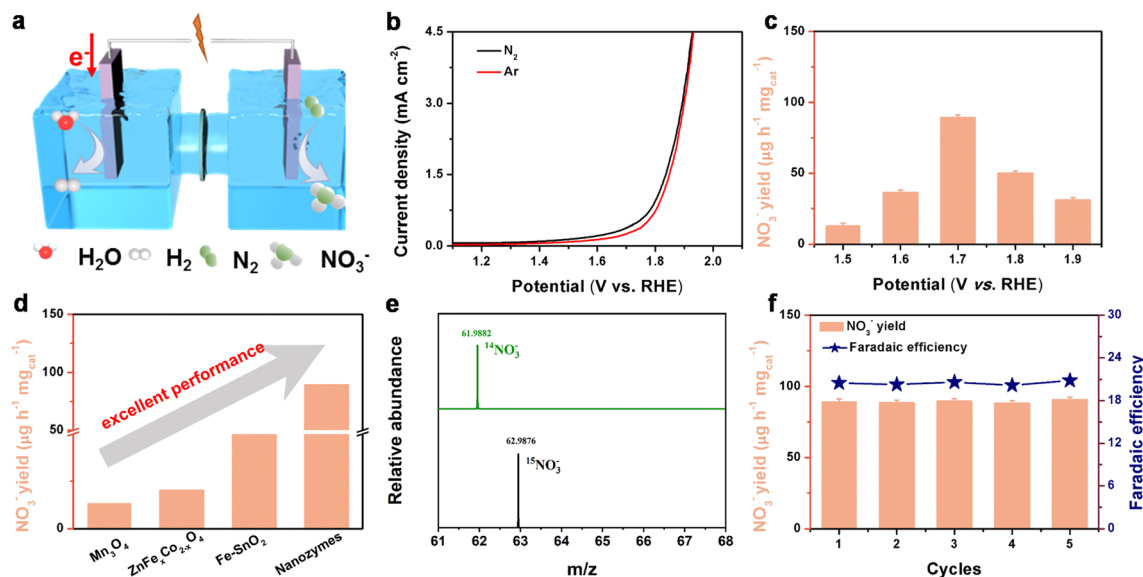
To evaluate the electrocatalytic NOR activity of nanozymes under ambient conditions, a series of electrochemical tests were performed in 0.1 M  $\text{Na}_2\text{SO}_4$  solution with  $\text{H}_2\text{O}_2$  (the contrast experiment is to test in 0.1 M  $\text{Na}_2\text{SO}_4$  without adding  $\text{H}_2\text{O}_2$  (Fig. S11†)). Before the test, the third exclusion measurement was conducted on  $\text{H}_2\text{O}_2$ , and no nitrogenous substances such as ammonia were found, so as to exclude the source of N in  $\text{H}_2\text{O}_2$  (Fig. S12†). A  $\text{Co}_3\text{O}_4/\text{H}_2\text{O}_2$  mixture could produce  $\cdot\text{OH}$  in the electrolyte. Fig. 3a shows a schematic diagram of the electrocatalytic NOR, while Fig. S10† displays a picture of the actual device tested. The linear sweep voltammetry (LSV) curves of  $\text{Co}_3\text{O}_4$  +  $\cdot\text{OH}$  showed an obvious enhancement under a  $\text{N}_2$ -saturated electrolyte compared to an Ar-saturated sample, indicating the possible electro-oxidation of  $\text{N}_2$  (Fig. 3b). Then, the possible oxidation product of nitrate was measured and quantified based on the standard method by using ultraviolet-visible (UV-Vis) spectrophotometry (Fig. S13 and S14†) and anion chromatography (Fig. S15†). From 1.5 to 1.9 V vs. RHE, the yield of nitrate and FEs displayed a volcanic shaped curve (Fig. 3c and S16†). At an applied potential of 1.7 V vs. RHE, the  $\text{NO}_3^-$  yield of nanozymes reaches  $89.35 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ , which is up to 7 times higher than that of  $\text{Co}_3\text{O}_4$  ( $12.8 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ ) without  $\text{H}_2\text{O}_2$ . The FE reached 20.4% and 1.23% at 1.7 V vs. RHE for nanozymes and  $\text{Co}_3\text{O}_4$  NBs, respectively (Fig. S17†). It is the most effective non-precious metal catalyst reported so far for the NOR process (Fig. 3d and Table S1†). As shown in Fig. S18,† we can know that

the TOF of the nanozymes catalyst at 1.7 V vs. RHE reaches  $0.58 \text{ h}^{-1}$ , which is better than that of  $\text{Co}_3\text{O}_4$  ( $0.083 \text{ h}^{-1}$ ), demonstrating that the nanozyme has a great intrinsic activity.

We experimentally demonstrate the importance of various sources of pollution and show how to remove unstable nitrogenous compounds present in  $\text{N}_2$  gas and how to make isotopic measurements with  $^{15}\text{N}_2$  gas to reduce pollution. In order to examine the N sources of the product in the NOR of nanozymes, some control experiments were performed (Fig. S19†), including experiments with a pure carbon paper (CP) electrode in 0.1 M  $\text{Na}_2\text{SO}_4$  solution at 1.7 V vs. RHE, a nanozyme electrode in 0.1 M  $\text{Na}_2\text{SO}_4$  solution at an open circuit and an electrode in an Ar-saturated electrolyte after electrolysis for 10 h. In order to exclude other possible contamination, the active test resulted in  $\text{NO}_3^-$  levels comparable to the control test. These sources include Nafion, which is used in some  $\text{N}_2$  oxidation experiments as a separation membrane or electrolyte (Fig. S20†).  $\text{NO}_3^-$  was not detected in these experiments, which ensured that the N source of  $\text{NO}_3^-$  came from the NOR of the nanozymes. Meanwhile, a  $^{15}\text{N}$  isotopic labeling experiment was also performed to examine the N source of  $\text{NO}_3^-$  detected. Here, we present such a rigorous procedure to reliably detect the electrooxidation of  $\text{N}_2$  to  $\text{NO}_3^-$  by using  $^{15}\text{N}_2$ . In the  $^{15}\text{N}_2$ -saturated electrolyte experiment,  $^{15}\text{NO}_3^-$  was obtained with a molecular weight of 62.9884, compared with 61.988 for  $^{14}\text{NO}_3^-$  in the  $^{14}\text{N}_2$ -saturated electrolyte (Fig. 3e). These results suggest that the detected  $\text{NO}_3^-$  was completely derived from the electrochemical oxidation of  $\text{N}_2$ . To further quantify the yield of  $\text{NO}_3^-$ , ion chromatography was used. It is found that the  $\text{NO}_3^-$  yield calculated by ion chromatography is close to the  $\text{NO}_3^-$  yield calculated by the colorimetric method (Fig. S20†).





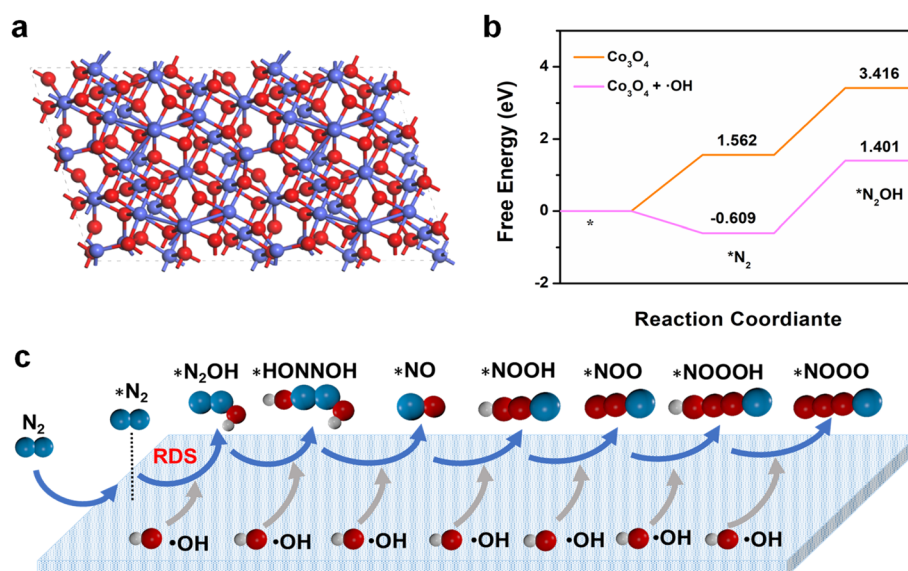


**Fig. 3** (a) Schematic diagram of  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$  for  $\text{NO}_3^-$  production. (b) Linear sweep voltammetric (LSV) curves of  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$  in  $\text{N}_2$ - and Ar-saturated 0.1 M  $\text{Na}_2\text{SO}_4$  solutions. (c)  $\text{NO}_3^-$  production of  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$  at various potentials in  $\text{N}_2$ -saturated 0.1 M  $\text{Na}_2\text{SO}_4$  electrolytes. (d) Comparison of  $\text{NO}_3^-$  production of  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$  with different reported non-noble metal catalysts for the NOR. (e) MS spectra of both  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  generated from the NOR tests (at 1.7 V vs. RHE) used as a  $\text{N}_2$  source with  $^{14}\text{N}_2$  or  $^{15}\text{N}_2$ . (f) Recycling measurement of  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$  at 1.7 V vs. RHE.

The stability of catalysts is not only a vital factor for practical applications, but also critical to evaluate the NOR activity. As shown in Fig. S22 and S23,<sup>†</sup> this catalyst also demonstrates long-term electrochemical and structural stability, and the current density did not have a tendency to decrease even in a 50 h continuous test. Besides, it can be seen from Fig. 3f that the  $\text{NO}_3^-$  yield rate and FE show slight fluctuations for 5 reduplicate tests at 1.7 V (vs. RHE). Most importantly, the results of the cycling experiments clearly show that the nanozyme catalyst exhibits no appreciable decline in the  $\text{NO}_3^-$  yield and FEs after the five

continuous cycles. Furthermore, it is distinct from the SEM (Fig. S24a<sup>†</sup>) and TEM images (Fig. S24b<sup>†</sup>) that the catalyst maintains the original structure after stability testing. XRD and XPS (Fig. S25 and S26<sup>†</sup>) analysis showed that the position and intensity of peaks did not change significantly compared with the initial results, which further indicated that the stability of the catalyst was impressive.

DFT was used to explore the specific mechanisms of  $\cdot\text{OH}$  free radicals in the NOR process. At first, the  $\text{N}_2$  adsorption capacity of catalysts was studied using the  $\text{N}_2$  Temperature Programmed



**Fig. 4** (a) The top and side views of  $\text{Co}_3\text{O}_4$ . (b) Reaction free energy diagram of the  $\text{N}_2$  electrooxidation process on  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$ . (c) Simplistic mechanism of  $\text{NO}_3^-$  production on the surface of catalysts.



Desorption ( $\text{N}_2$ -TPD) way. We can see in Fig. S26† that the high signal of chemisorption of nanozyme indicates that the adsorption of  $\text{N}_2$  is higher. From Fig. 4a, we can know the structural model of  $\text{Co}_3\text{O}_4$ . Subsequently, the energy barriers for the conversion of  $\text{N}_2$  to  $\text{N}_2\text{OH}^*$  (the rate-determining step) can be obtained from Fig. 4b. And it was found that the introduction of the  $\cdot\text{OH}$  free radical ( $\text{Co}_3\text{O}_4/\text{H}_2\text{O}_2$  system) decreases the energy barrier substantially and accelerates the reaction (Fig. S28 and S29†). Fig. 4c depicts the entire path diagram of the electrocatalytic NOR. Nitrogen molecules are first absorbed and oxidized to form  $^*\text{NNOH}$  intermediates.  $\text{N}\equiv\text{N}$  key fracture occurred in the second step (the rate-determining step), which is suitable for  $^*\text{N}_2\text{OH}$ . The  $^*\text{N}$  intermediate formed evolves into  $^*\text{NO}$ . The  $^*\text{NO}$  intermediate is continuously combined with  $\cdot\text{OH}$  in the electrolyte, and the final nitrate product is formed. DFT demonstrates that  $\cdot\text{OH}$  not only can drive nitrogen adsorption, but also can further decrease the energy barrier for the conversion of  $\text{N}_2$  to  $\text{N}_2\text{OH}^*$  (the rate-determining step), leading to great NOR activity.

## Conclusions

In short, we introduce hydroxyl radicals into the electrocatalytic NOR for the first time.  $\text{Co}_3\text{O}_4$  acts not only as an electrocatalyst, but also as a nanozyme (in combination with hydrogen peroxide producing  $\cdot\text{OH}$ ), and can be used as an efficient NOR electrocatalyst for environmental nitrate synthesis.  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$  shows an excellent NOR performance among  $\text{Co}_3\text{O}_4$  catalysts in 0.1 M  $\text{Na}_2\text{SO}_4$  solution. At an applied potential of 1.7 V vs. RHE, the  $\text{NO}_3^-$  yield of  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$  reaches  $89.35 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ , which is 7 times that of  $\text{Co}_3\text{O}_4$  ( $12.8 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ ) and the corresponding FE is 20.4%. We use ultraviolet spectroscopy and ion chromatography to determine the concentration of nitrate produced. At the same time, we also conduct  $^{15}\text{N}$  isotope labeling experiments by mass spectrometry to further determine the nitrogen source. It is the most effective non-precious metal catalyst reported so far for the NOR process. This catalyst also demonstrates long-term electrochemical and structural stability, and the current density did not have a tendency to decrease even in a 50 h continuous test. The TOF of the  $\text{Co}_3\text{O}_4 + \cdot\text{OH}$  catalyst at 1.7 V vs. RHE reaches  $0.58 \text{ h}^{-1}$ , which is better than that of  $\text{Co}_3\text{O}_4$  ( $0.083 \text{ h}^{-1}$ ), demonstrating that free radicals can greatly enhance the intrinsic activity of catalysts. DFT demonstrates that  $\cdot\text{OH}$  not only can drive nitrogen adsorption, but also can decrease the energy barrier (rate-determining step) of  $\text{N}_2$  to  $\text{N}_2\text{OH}^*$ , thus producing great NOR activity. Therefore, the next direction of development is that an electric Fenton can be used to generate more free radicals to promote the NOR.

## Experimental

### Reagents and materials

Cobalt acetate ( $(\text{H}_3\text{CO}_2)_2\text{Co}$ , Shanghai Macklin Biochemical Technology Co., Ltd, China, 98%). Sodium citrate dihydrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ , Shanghai Aladdin Biochemical Technology Co., Ltd, China, 99%). Sodium fluoride ( $\text{K}_3[\text{Co}(\text{CN})_6]$ , Shanghai Aladdin Biochemical Technology Co., Ltd, China, 99%). Sodium sulfate ( $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , 99%) were purchased from Aladdin. Nafion solution

(5%) was purchased from Sigma Aldrich. Ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) was purchased from Sinopharm Chemical Reagent Co., Ltd. Ultrapure water (Millipore Milli-Q grade) with a resistivity of  $18.2 \text{ M}\Omega$  was used in all the experiments.

### Preparation of Co-Co PBA NCs

In a typical synthesis, 0.6 mmol of cobalt acetate and 0.9 mmol of sodium citrate were dissolved in 20 mL of deionized (DI) water to form solution A. At the same time, 0.4 mmol of potassium hexacyanocobaltate(III) was dissolved in 20 mL of DI water to form solution B. Then, solutions A and B were mixed together under magnetic stirring for 1 min. The obtained mixed solution was aged for 12 h at room temperature. Then, the obtained black gelatinous solutions were collected by centrifugation at 8000 rpm for 3 min, and washed 3 times with DI and ethanol. Finally, the precipitates were dried at  $70^\circ\text{C}$  overnight.

### Preparation of $\text{Co}_3\text{O}_4$ NBs

The as-prepared PBA NCs were annealed at  $350^\circ\text{C}$  for 2 h with a heating temperature rate of  $2^\circ\text{C min}^{-1}$  in air.

### Materials characterization

X-ray diffraction (XRD) analysis was used to examine the composition of the as-synthesized samples on an X'Pert PRO MPD. Scanning electron microscopy (SEM) measurement was collected on a Hitachi, S-8200 to investigate the structure and morphology of the samples. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) measurements were performed on a JEM-2100UHR operating at 200 kV. Electron spin resonance (ESR) was performed using a German Bruker A-300 and a magnetic field strength (0-9500) Gauss. The  $^1\text{H}$  NMR spectrum was obtained on a Bruker 500 with a Probe TXI at room temperature of  $25^\circ\text{C}$  using a 3 mm tube. The electrolyte after electrolysis was collected, lyophilized and further dissolved in 1.0 M HCl solution ( $\text{D}_2\text{O}/\text{H}_2\text{O}$  mixed solution). The IC data were collected by using an IC (863 Basic IC Plus, Metrohm, Switzerland) equipped with a Metrosep C Supp 4-250/4.0 column.  $\text{N}_2$ -TPD of  $\text{N}_2$  experiments was conducted on a Quantachrome Chem BET Pulsar TPR/TPD.

### Electrochemical measurements

All the electrochemical performances of the as-synthesized samples were determined on an electrochemical workstation (CHI 760E). A typical H-type electrolytic cell divided by a proton-exchange membrane (Nafion 117) was used. Except for special instructions, all potentials were recorded against the RHE. The potentials against the saturated calomel electrode ( $\text{Ag}/\text{AgCl}$ ) were translated to those against the RHE using the following equation:  $E(\text{vs. RHE}) = E(\text{vs. Ag}/\text{AgCl}) + 0.197 + 0.059 \times \text{pH}$ . All the polarization curves were steady lines after many cycles and the current density was normalized to the geometric surface area.

## Author contributions

L. W. and J. L. supervised the research. J. L. conceived the research. J. L. and Z. W. designed the experiments. Z. W.



performed most of the experiments and data analysis. Z. W., J. L. and H. Z. prepared the electrodes and helped with electrochemical measurements. W. X. helped analyze physical characterization data. J. L. and Z. L. helped answer some questions. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

The authors declare no competing financial interests.

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