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Non-precious $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode based electrocatalytic nitrate reduction: Preparation, performance and mechanism

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1 **Abstract**

2 The presence of high nitrate (NO_3^-) concentration in natural water constitutes a serious issue to the
3 environment and human health. Therefore, the development of low-cost, stable non-precious metal
4 catalysts is imminent for efficient NO_3^- reduction. In this study, we prepared a Co_3O_4 - TiO_2/Ti
5 cathode via combining sol-gel and calcination methods and evaluated its performance for
6 electrocatalytic NO_3^- reduction. The dispersion of the Co_3O_4 catalyst particles was improved by the
7 addition of PVP to the coating liquid. The presence of anatase could effectively stabilize Co_3O_4 and
8 prevent the releasing of toxic Co ions into the solution. The Co_3O_4 - TiO_2/Ti cathode with the
9 optimized performance for NO_3^- reduction could be prepared by four times coating at calcination
10 temperature of 500°C . The electrocatalytic reduction of NO_3^- was negligibly impacted by solution
11 pH in the range of 3.0-9.0, while it could be facilitated by elevating the current density from 2.5 to
12 25 mA cm^2 . Ammonium ions were the main final NO_3^- reduction product, and the presence of Cl^-
13 was capable to oxidize ammonium ions to N_2 due to the electrochemical production of reactive
14 chlorine species. The electrochemical analyses, scavenging experiments and density functional
15 theory calculations collectively confirm that NO_3^- reduction was mainly induced by the
16 Co^{2+} - Co^{3+} - Co^{2+} redox process instead of being directly resulted from the electrons generated at the
17 cathode. Unlike noble metal (e.g., Pd and Ag) based catalytic reaction systems, in the present Co_3O_4
18 mediated electrocatalytic reaction process, atomic H^* would more favorably turn to H_2 by
19 Heyrovsky and Tafel routes and therefore contributed marginally to the NO_3^- reduction. Generally,
20 this study provided a new paradigm for designing the stable and cost-effective cathode for NO_3^-
21 reduction.

22

23 **Keywords:** Nitrate reduction; Electrocatalysis; Co_3O_4 - TiO_2/Ti cathode; $\text{Co}^{3+}/\text{Co}^{2+}$ redox couple;

24 Non-precious catalyst

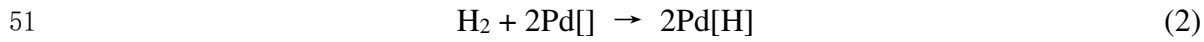
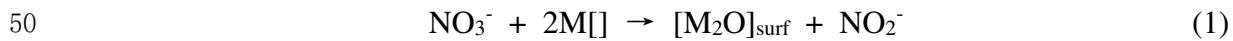
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26 **1. Introduction**

27 In water, nitrate (NO_3^-) is considered an underlying hazardous material that is derived from
28 various sources including the feedlot runoff, the excessive use of nitrogen fertilizer and natural
29 degradation of pollutants [1]. The presence of NO_3^- in drinking water can cause serious health
30 problems such as the cancers, liver damage and blue baby syndrome due to its transformation
31 product, i.e. nitrite anions (NO_2^-) [2]. To diminish this potential health risk, the concentration limit
32 for NO_3^- in drinking water is set at 10 and 11.3 ppm by the United States EPA and the European
33 Drinking Water Directive, respectively [3,4]. In this regard, the removal technologies of NO_3^- are
34 imperious demands in populated regions.

35 Physicochemical treatments such as electro dialysis, ion exchange and reverse osmosis are the
36 most common technologies for NO_3^- removal from water [5], but the post-treatments are still needed
37 to address the concentrated solutions produced in these methods. Although biological denitrification
38 can gradually convert NO_3^- to N_2 [6], it is a time-consuming process and its performance is strongly
39 impacted by the variable conditions, such as dissolved oxygen and temperature. Recently, zero valent
40 metals (e.g. iron [7], aluminum [8], and magnesium [9]) based stoichiometrically chemical reduction
41 of NO_3^- has been increasingly explored. Unfortunately, the flexibility of this strategy is greatly
42 confined by the formation of inert oxide surface, deteriorating the electron transfer efficiency, and
43 the inevitable production of secondary solid sludge. More recently, some catalytic hydrogenation
44 processes with the combined noble/promoting metals (e.g., Pd/Cu and Pd/Fe) have been proposed for
45 NO_3^- reduction [10,11]. In these processes, the reduction of NO_3^- is mainly initiated by promoter
46 metal (Eq. (1)) with the formation of NO_2^- , and the subsequent reduction process is gradually
47 achieved by the noble metal activated hydrogen (Eq. (2)) [12]. However, catalytic hydrogenation

48 reduction requires H₂ as a reducing agent or electron donor, and there are safety hazards in the
49 transport and use of H₂, which greatly limits its industrial application potential [13].



52 Considering the advantages of self-produced hydrogen, environmental compatibility and
53 ambient operating conditions, electrocatalysis has been regarded as a promising method for
54 denitrification [14], in which the reduction of NO₃⁻ can be obtained by either a direct or an indirect
55 pathway at the cathode surface. Direct reduction of NO₃⁻ is initiated by the electron tunneling or
56 generation of chemisorbed complex between the NO₃⁻ and cathode whereas in the indirect pathway,
57 NO₃⁻ is reduced by a surface-adsorbed atom H^{*}, which is produced from the reduction of protons by
58 electron via the Volmer process [15]. Specially, Pd-based catalysts have recently been distinguished
59 mainly because of their potential to electrochemically reduce oxyanion contaminants in water in
60 which the indirect reduction mediated by atomic H^{*} plays a leading role compared to the direct
61 electron transfer from the cathode to NO₃⁻ [16]. Nevertheless, considering the extremely expensive
62 price of Pd, the research significance of the Pd-based catalyst is obviously theoretical but not
63 practical. Additionally, despite the fact that the indirect reduction mechanism of NO₃⁻ has been well
64 explored in electrochemical noble metal-based process, the targeted strategies to develop some
65 specific catalysts for the direct reduction of NO₃⁻ is sparsely reported.

66 The cost-effective cobalt oxide (Co₃O₄) is a typical p-type metal oxide, which exhibits a
67 normal spinel structure with Co²⁺ ions in tetrahedral interstices and Co³⁺ ions in octahedral
68 interstices. During the recent decades, Co₃O₄ has been demonstrated to own strong catalytic
69 reduction activity and thus extensively used in electrochemical hydrogen evolution reaction [17] and

70 reduction of CO₂ [18] and NO_x [19]. Recently, Su et al. [20] reported that the pure Co₃O₄ loaded
71 onto the titanium substrate by thermal sintering could also electrocatalytically reduce NO₃⁻ in the
72 water. However, the Co₃O₄-mediated electrochemical mechanism of NO₃⁻ reduction has remained
73 unclear. Moreover, it is known that the biologically toxic cobalt ion probably causes human
74 carcinogen, and the discharge standard of cobalt ions in industrial wastewater is 1 mg L⁻¹ based on
75 GB/T 25467-2010 of China. Therefore, efforts should be made to improve the stability of the
76 cobalt-based catalyst and prevent its leaching from the substrate and leaking into the water. To this
77 end, we prepared a novel cathode, Co₃O₄-TiO₂/Ti, by combining sol-gel and calcination methods,
78 which seems to be promising for remarkably facilitate the electrocatalytic reduction of NO₃⁻. The
79 effects of electrode preparation factors (calcination temperature and coating times) and operation
80 parameters (pH, current density and chloride ions concentration) on NO₃⁻ reduction were also
81 investigated. In addition, based on the characterization of the prepared catalysts using XRD, SEM,
82 HRTEM, EDS elemental mapping and XPS, we tried to relate the results to the catalytic activity.
83 Furthermore, electrochemical analyses, radical scavenging experiments and density functional theory
84 calculations were utilized to inspect the possible NO₃⁻ reduction mechanisms.

85

86 **2. Experimental section**

87 **2.1. Reagents and materials**

88 Titanium (Ti) plate (99.99% purity, thickness 1.0 mm) and IrO₂-RuO₂/Ti plate were purchased
89 from Yunxuan Metallic Materials Co. Ltd. Potassium iodide (KI, >99%), mercuric iodide red (HgI₂, >
90 99.5%), potassium sodium tartrate tetrahydrate (NaKC₄H₄O₆·4H₂O, > 99%), sulfamic acid
91 (NH₂SO₃H, > 99%), sulfanilamide (C₆H₈N₂O₂S, > 99%), titanium butoxide (C₁₆H₃₆O₄Ti), cobalt

92 hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, > 99%), sodium chloride (NaCl , > 99.5%), sodium pyrophosphate
93 ($\text{Na}_4\text{P}_2\text{O}_7$, > 99%), cobaltic oxide (Co_2O_3 , > 99%), sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$, > 99%), ethanol
94 (95%), hexadecyl trimethyl ammonium bromide ($\text{C}_{19}\text{H}_{42}\text{BrN}$, TBA, > 99%), polyvinyl pyrrolidone
95 K30 ($(\text{C}_6\text{H}_9\text{NO})_n$, PVP), ammonium chloride (NH_4Cl , 99.8%), potassium nitrate (KNO_3 , > 99.5%),
96 sodium nitrite (NaNO_2 , > 99%), H_2SO_4 (95%–98%), HCl (36%-38%), NaOH (>96%) were provided
97 by Sinopharm Chemical Reagent Co. Ltd., China. All the reagents were analytical grade and used
98 without further purification. All working solutions were prepared using ultrapure water (18.2 M Ω cm
99 resistivity). The experiments were done triplicate.

100 **2.2. Preparation of the working cathode**

101 The substrate of electrode was Ti plate with size of 2.5 × 5.0 cm. The Ti plate was first
102 polished with 300-mesh emery paper and then boiled in 20% sulfuric acid for 40 min. Next, the Ti
103 plate was cleaned by ultrapure water, sonicated for 15 min, and dried for use. To synthesize the
104 typical $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode, 0.5 mL titanium butoxide, 0.1 mL hydrochloric acid and 0.15 mL
105 ultrapure water were dissolved in 8.5 mL ethyl alcohol. Then, 0.5 g PVP was added and stirred
106 vigorously for 0.5 h. Subsequently, 2.69 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 M) was added and stirred to obtain a
107 purplish red liquid. The prepared sol-gel was pasted to the both faces of the pretreated Ti plates using
108 a brush. The painted Ti plate was dried at 100 °C for 10 min. Then it was sintered at 500 °C for 2 h in
109 a muffle oven to remove all organic substances with the formation of the oxide. The above
110 procedures were repeated 4 times and the electrode films were annealed for 6 h at 500 °C in the last
111 time. Other different kinds of cathodes were prepared with the same process with that for the
112 $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) cathode. Furthermore, the coating times (2, 4, 6 and 8) and the
113 calcination temperatures (300 °C, 400 °C, 500 °C, 600 °C and 700 °C) were adjusted to optimize the

114 preparation factors.

115 **2.3. Electrocatalytic reduction of NO₃⁻**

116 A DC potentiostat (GPS-3030D, Gwinstek, China) was utilized as the power supply for
117 electrochemical experiments. The electrocatalytic NO₃⁻ reduction experiments were carried out in a
118 150 mL electrolytic cell at room temperature (25 °C). If not specially mentioned, the volume of the
119 working solution was 100 mL, NO₃⁻ concentration was 50 mg L⁻¹, and 0.1 M Na₂SO₄ was used as
120 supporting electrolyte to maintain the conductivity of the solution. The solution pH was adjusted
121 using concentrated NaOH and H₂SO₄. The 12.5 cm² Co₃O₄-TiO₂-PVP electrodes were used as
122 cathode and 12.5 cm² IrO₂-RuO₂/Ti electrodes were used as anode. The distance between the
123 electrodes was 2 cm. The typical electrochemical experiment was conducted at current density of 10
124 mA cm⁻². All experiments were repeated at least twice.

125 **2.4. Physicochemical characterizations and DFT calculation**

126 The crystalline nature of the surface of Co₃O₄-TiO₂/Ti cathode was examined by X-ray
127 diffraction (XRD) measurement and the 2θ values acquired within the range of 10° to 80° using a
128 Bruker D2 PHASER X-ray diffractometer that uses Cu K_α radiation. The morphology of the
129 cathode surface was depicted by a scanning electron microscopy (SEM, FEI QUANTA FEG250) and
130 high-resolution transmission electron microscope (HRTEM, JEM-2100F). The X-ray photoelectron
131 spectroscopy (XPS) was obtained using a Thermo Fisher ESCALAB 250Xi system with Al K_α as an
132 X-ray source. C 1s peak at 284.8 eV from residual carbon was conducted to correct the binding
133 energy of other elements. The details of DFT calculation were provided in the supplementary
134 material.

135 2.5. Electrochemical characterizations

136 All electrochemical measurements were performed on an electrochemical station (PGSTAT
137 302N, Metrohm). A standard three-electrode system was used in which the working electrode was a
138 home made $\text{Co}_3\text{O}_4\text{-TiO}_2\text{-Ti}$ cathode, the counter electrode was a platinum plate, and the reference
139 electrode was a saturated calomel electrode (SCE). The effective working area of the working and
140 counter electrodes was 12.5 cm^2 . The electrolyte for linear sweep voltammetry (LSV) and cyclic
141 voltammetry (CV) tests was composed of $0.1 \text{ M Na}_2\text{SO}_4$ solution with or without $50 \text{ mg L}^{-1} \text{ NO}_3^-$.
142 CV tests were recorded between 0.0 V and -1.5 V/SCE at a scan rate of 20 mV s^{-1} . Electrochemical
143 impedance spectroscopy (EIS) measurements were operated in $0.1 \text{ M Na}_2\text{SO}_4$ solution using the
144 frequency ranged from 10^5 to 10^{-2} Hz and the amplitude of the potential of 10 mV .

145 2.6. Chemical analyses

146 The concentrations of NO_3^- , NO_2^- and NH_4^+ were determined with a UV-vis spectrophotometer
147 as it has been depicted in detail in the previous literature [21]. The residual NO_3^- ratio ($R_{\text{NO}_3^-}$), the
148 generated NO_2^- ratio ($S_{\text{NO}_2^-}$), the generated NH_4^+ ratio, ($S_{\text{NO}_4^+}$), the total nitrogen (TN) removal
149 efficiency, (R_{TN}) and N_2 selectivity (S_{N_2}), were calculated by the following equations:

$$150 \quad R_{\text{NO}_3^-}(\%) = \frac{[\text{NO}_3^-]_t}{[\text{NO}_3^-]_0} \times 100 \quad (3)$$

$$151 \quad S_{\text{NO}_2^-}(\%) = \frac{[\text{NO}_2^-]_t}{[\text{NO}_3^-]_0} \times 100 \quad (4)$$

$$152 \quad S_{\text{NH}_4^+}(\%) = \frac{[\text{NH}_4^+]_t}{[\text{NO}_3^-]_0} \times 100 \quad (5)$$

$$153 \quad R_{\text{TN}} = 1 - R_{\text{NO}_3^-} - S_{\text{NO}_2^-} - S_{\text{NH}_4^+} \quad (6)$$

$$154 \quad S_{\text{N}_2}(\%) = \frac{R_{\text{TN}}}{1 - R_{\text{NO}_3^-}} \times 100 \quad (7)$$

155 where $[\text{NO}_3^-]_0$ is the initial concentration of NO_3^- and $[\text{NO}_3^-]_t$, $[\text{NO}_2^-]_t$ and $[\text{NH}_4^+]_t$ are the
156 concentrations of NO_3^- , NO_2^- and NH_4^+ at time t .

157

158 **3. Results and discussion**

159 **3.1. Catalytic NO₃⁻ reduction by different cathodes**

160 The comparative NO₃⁻ reduction process efficiency at different cathodes was depicted in Fig. 1.
161 As shown in Fig. 1(a), the NO₃⁻ removal efficiency of TiO₂/Ti cathode was only 45% at current
162 density of 10 mA cm⁻² after 120 min. However, as for Co₃O₄-TiO₂/Ti (without PVP) cathode, NO₃⁻
163 removal efficiency suddenly became twice that of TiO₂/Ti cathode, reaching approximately 80%.
164 Moreover, with the introduction of the dispersant PVP, the removal efficiency of NO₃⁻ was further
165 increased to 89%. Although the addition of TiO₂ resulted in a slight decrease (nearly 6%) in the
166 removal efficiency of NO₃⁻ compared to Co₃O₄/Ti cathode, the release of Co ions into the aqueous
167 solution was remarkably inhibited, probably due to the stabilization effect of TiO₂ (see Fig. 1(b)). In
168 the case of Co₃O₄/Ti cathode, the leaching of Co ions (Co²⁺/Co³⁺) reached 0.2 mg L⁻¹ after 120 min,
169 while Co ions were barely detected for both the Co₃O₄-TiO₂/Ti and Co₃O₄-TiO₂/Ti (without PVP)
170 cathodes. Recently, many non-precious catalysts for NO₃⁻ reduction have been developed as the
171 alternatives to conventional noble Pd catalyst. As shown in Table S1, the Co₃O₄-TiO₂/Ti cathode
172 exhibits significantly superior NO₃⁻ reduction activity over other non-precious electrodes.

173

174

<Fig. 1>

175

176 As shown in Fig. 1(c), the profiles of ammonium (NH₄⁺) formation as a function of electrolysis
177 time have similar trends with those of NO₃⁻ removal in the above reaction systems. The amount of
178 NH₄⁺ formed in the case of Co₃O₄/Ti cathode was larger than those of Co₃O₄-TiO₂/Ti and

179 $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) cathodes. In addition, among all the cathodes tested, the TiO_2/Ti
180 produced the lowest amount of NH_4^+ , due to its inferior performance for NO_3^- reduction. During
181 NO_3^- reduction process, the toxic intermediate NO_2^- was negligibly detected in the cases of
182 $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$, $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) and $\text{Co}_3\text{O}_4/\text{Ti}$ cathodes, while a significant amount
183 (around 1%) of NO_3^- was transformed into NO_2^- when using TiO_2/Ti as the cathode. Although NO_3^-
184 reduction efficiency of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode was slightly lower than that of $\text{Co}_3\text{O}_4/\text{Ti}$ cathode, the
185 TN removal efficiency and N_2 selectivity for the former were comparable to that of the latter as
186 shown in Fig. S1. Besides, the TN removal efficiency and N_2 selectivity of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without
187 PVP) and TiO_2/Ti cathodes were much lower than those of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode.

188 Fig. 2 shows the XRD pattern of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode calcinated at the temperature of 500
189 °C. A comparison was performed between the obtained XRD data and standard patterns of various
190 cobalt oxide and titanium oxide structures including cubic phase Co_3O_4 (PDF#42-1467), Ti
191 (PDF#44-1294), anatase TiO_2 (PDF#21-1272), and rutile TiO_2 (PDF#21-1276). It is observed that all
192 the detectable peaks agree well with standard cubic phase Co_3O_4 , anatase TiO_2 , and rutile TiO_2 . And
193 the main characteristic peaks of Co_3O_4 are at $2\theta = 31.3^\circ, 36.9^\circ, 38.6^\circ, 44.8^\circ, 59.4^\circ, 65.2^\circ, 77.3^\circ$,
194 which correspond to (220), (311), (222), (400), (511), (440), and (533) planes, respectively. This
195 shows that the main components of the as-prepared cathode were the target catalyst Co_3O_4 and the
196 dispersant carrier TiO_2 .

197

198

<Figs. 2>

199

200 SEM images (Fig. 3) illustrate the morphology of as-prepared catalysts. Figs. 3(a)-(c)

201 correspond to $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$, $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP), and $\text{Co}_3\text{O}_4/\text{Ti}$ cathodes, respectively. It
202 can be clearly seen that Co_3O_4 particles on $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode were small and uniform, whereas
203 that on $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) and $\text{Co}_3\text{O}_4/\text{Ti}$ cathodes were apparently agglomerated and
204 represented in the forms of disordered nanotubes and irregular aggregates, respectively, showing the
205 successful role of PVP as surface dispersant by mixing PVP and metal-salt precursor solution [22].
206 Figs. 3(d)-(h) provide the EDS maps of Co and Ti elements at the above three cathodes. Obviously,
207 the presence of PVP could effectively improve the uniformity of Co and Ti distribution on the
208 surface of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode, which was therefore better than that of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without
209 PVP) cathode. As for $\text{Co}_3\text{O}_4/\text{Ti}$ cathode, the aggregation of Co element was more pronounced in
210 comparison with the other two cathodes, indicating the worst distribution of Co_3O_4 on $\text{Co}_3\text{O}_4/\text{Ti}$
211 cathode. The electrocatalytic property could be improved by using PVP as surface stabilizer and
212 growth modifier since it could effectively alleviate the agglomeration of the catalysts and enhance
213 the relative population of stable clusters during the synthesis of nanoparticles (NPs), thereby more
214 active sites are exposed at the cathode surface. [23-24] Therefore, it can be concluded that both the
215 TiO_2 and the PVP dispersant could evidently promote the distribution and stability of Co_3O_4 on the
216 Ti plate, which will expose more active sites and inhibit the leaching of catalyst from the electrode
217 surface. This may explain the superior catalytic performance and stability of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode
218 over $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) and $\text{Co}_3\text{O}_4/\text{Ti}$ cathodes as shown in the Fig. 1. HRTEM images of
219 $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ in Fig. 4(a) presents dark Co_3O_4 species with a 10–50 nm diameter. The primarily
220 exposed crystal planes of as-synthesized Co_3O_4 are (311) with the lattice spacing (d) of 0.244 nm
221 (Fig. 4(b)), which is consistent with the XRD patterns.

222

223 <Figs. 3 and 4>

224

225 **3.2. Preparation parameters**

226 **3.2.1. Effect of coating times**

227 The Co ions concentration of 0, 0.5, 1.0, and 2.0 M with 4 coating times was investigated. The
228 NO_3^- concentration decay kinetics and LSV curves (Fig. S2) demonstrate that 1.0 M was compatible.
229 In this section, the studied number of coating times was 2, 4, 6, and 8 with Co ions concentration of
230 1.0 M, which was represented as 2- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$, 4- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$, 6- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ and
231 8- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes, respectively. Although, as shown in Fig. S3, the coating times negligibly
232 affected the morphology of the electrode surface, too many or too few coating times were not
233 conducive to NO_3^- reduction. The NO_3^- removal efficiencies for 2- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$, 4- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$,
234 6- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ and 8- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes were 80%, 89%, 64% and 61%, respectively, within
235 120 min. Thus, the optimum number of coating times was 4. As illustrated in Fig. 5(b),
236 4- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode has the largest response current intensity. And the trend of response current
237 intensity at the same voltage was consistent with the NO_3^- reduction trend of Fig. 5(a). The above
238 experimental and LSV results can be explained by the fact that when the number of coating times
239 was below 4, insufficient Co loadings may not afford enough active sites for NO_3^- reduction. In
240 contrast, when the number of coating times was more than 4, the catalyst coating on the Ti plate was
241 thick, which probably deteriorated the electron transfer, and the increased potential would exacerbate
242 the occurrence of hydrogen evolution side reactions, therefore led to a decrease in NO_3^- reduction
243 efficiency.

244

245 <Fig. 5>

246

247 3.2.2. Effect of calcination temperature

248 In this section, the effect of calcination temperatures on the performance of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$
249 cathode was investigated. The as-prepared cathodes sintered at 300 °C, 400 °C, 500 °C, 600 °C and
250 700 °C were marked as 300- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$, 400- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$, 500- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$,
251 600- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ and 700- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$, respectively. Fig. 6(a) shows that there were significant
252 differences in NO_3^- reduction efficiency between the cathodes sintered at different temperatures. The
253 optimum NO_3^- removal efficiency was observed for the cathode calcination in the temperature range
254 of 300-500 °C, e.g., approximately 89% for 500- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode. A moderate NO_3^- removal
255 efficiency was obtained for 600- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode (67%) while the 700- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode
256 had the marginal NO_3^- removal efficiency, approximately 34%. The variation trend of response
257 current intensity observed from the LSV measurements (Fig. 6(b)) was in good accordance with that
258 of the cathodes for NO_3^- removal, which confirmed the best performance of the
259 500- $\text{Co}_3\text{O}_4\text{-TiO}_2\text{-PVP}$ cathode.

260

261 <Fig. 6>

262

263 As shown in Fig. 2, the main characteristic peaks of Co_3O_4 in XRD spectra for $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$
264 cathode became narrower and sharper as the calcination temperature increased in the range of 300
265 -700 °C. According to the previous studies, complete conversion of Co_3O_4 can be achieved in the
266 sol-gel and calcination process when the temperature exceeds 270 °C [20]. Better crystallinity

267 structure of Co_3O_4 could be obtained at higher calcination temperatures. Nevertheless, Ti plate has
268 some problems when being sintered at relatively high temperature. Specially, as demonstrated in the
269 previous literature [20], the conductivity of Ti plate was greatly reduced when the calcination
270 temperature reached $600\text{ }^\circ\text{C}$. Besides, the phase structure, composition, and crystallinity of TiO_2 are
271 of great influence on its electrocatalytic activity and electrochemical properties [25]. Therefore, XRD
272 was also used to analyze the changes of TiO_2 phase on the cathodes sintered at various temperatures.
273 It can be seen from the XRD patterns presented in Fig. 2 that the calcination temperature
274 significantly impacted the crystallization and phase structures of surface catalysts on $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$
275 cathode. For $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes sintered at the temperature of $300\text{-}500\text{ }^\circ\text{C}$, except the
276 diffraction peaks of Ti substrate and Co_3O_4 , two broad peaks at $2\theta = 53.9^\circ$ and 76.0° can be attributed
277 to the (105) and (301) plane diffraction, respectively, of anatase TiO_2 . However, as for
278 $600\text{-Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode, small peaks at $2\theta = 27.4^\circ, 36.1^\circ, 54.3^\circ, 56.6^\circ, 69.0^\circ,$ and 69.8° correspond
279 to (110), (101), (211), (220), (301), and (112) plane diffraction, respectively, of rutile. Notably, the
280 intensity of rutile diffraction peaks of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode increases sharply at the calcination
281 temperature of $700\text{ }^\circ\text{C}$. This suggests the occurrence of phase transformation of anatase to rutile
282 when elevating the calcination temperature from 300 to $600\text{ }^\circ\text{C}$, which was even more pronounced
283 for $700\text{ }^\circ\text{C}$. Furthermore, with the calcination temperature increase to $600\text{ }^\circ\text{C}$ and $700\text{ }^\circ\text{C}$, the crystal
284 turned to aggregation, which was probably responsible for the decrease of NO_3^- reduction efficiency
285 (Fig. S4). Based on these results, it can be concluded that the phase transformation of TiO_2 began to
286 take place at the calcination temperature above $500\text{ }^\circ\text{C}$. When calcination temperature reaches $600\text{ }^\circ\text{C}$,
287 the rutile phase even became the prevalent phase of the composite. This was consistent with the
288 results in the previous literature papers [26].

289 Based on the EIS measurements, the Nyquist plots of various $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes sintered
290 at various temperatures are provided in Fig. 6(c). The radius of semicircle was related with the
291 charge transfer resistance and the sample with smaller arc radius indicates faster interfacial electron
292 transfer [27]. The calcination temperature exerts a significant effect on the electrochemical properties
293 of the electrodes. In this study, when the calcination temperature was increased from 300 to 500 °C,
294 the radius of the arc did not appear, indicating that the charge transfer resistance was small. However,
295 when the calcination temperature rose to 600 °C, the arc radius appeared, suggesting the fact that
296 increasing calcination temperature caused an increase in impedance for $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode. And
297 the charge transfer resistance of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode obtained at the calcination temperature of
298 700 °C was larger than that of 600 °C. The change of EIS results indicates that the phase
299 transformation of anatase to rutile with elevating calcination temperature could inhibit the charge
300 transfer within the cathode, which adverse to NO_3^- reduction [28]. This can be ascribed to the higher
301 electric resistance of rutile than that of anatase [28].

302 Therefore, the relatively low NO_3^- reduction efficiencies for 600- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ and
303 700- $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes could be explained by the increase in the charge transfer resistance of
304 $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode prepared at a high calcination temperature. Consequently, appreciable
305 $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes could be obtained at the calcination temperature of 300-500 °C, in which
306 cobalt precursor could be completely transformed to Co_3O_4 and the relatively low charge transfer
307 resistance could be also ensured.

308

309 **3.3. Effect of electrochemical reaction parameters**

310 **3.3.1. Effect of solution pH and current density**

311 As illustrated in Fig. 7, the effect of solution pH (3.0–9.0) on NO_3^- reduction was evaluated in
312 this section. Figs. 7 (a) and 7(b) show the reduction curves of NO_3^- over time and the final solution
313 pH for different initial pH values. Contrarily to the previous studies [29], Fig. 7(a) shows that
314 different pH conditions did not play significant role on NO_3^- reduction efficiency over the
315 electrolysis time. This indicates that $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode prepared in this study has a wide
316 working pH range and can be potentially used to treat the NO_3^- containing wastewaters in a relatively
317 large pH range. Besides, Fig. 7(b) shows that, regardless of the initial pH, the pH value was
318 significantly increased after 120 min reaction. For example, after 2 h of nitrate reduction, the solution
319 pH increased from 3.0, 5.0, 7.0 and 9.0 to 9.0, 10.6, 10.9 and 11.0, respectively. The explanation for
320 this pH variation will be discussed in the following section 3.4.

321

322

<Fig. 7>

323

324 On the other hand, the reduction efficiency of NO_3^- was significantly enhanced with the
325 increase of current density from 2.5 to 10 mA cm^{-2} (Fig. 8(a)). However, when the current density
326 was increased from 10 to 25 mA cm^{-2} , the removal efficiency of NO_3^- was not greatly improved. Fig.
327 S5 shows that the reduction of 50 mg L^{-1} NO_3^- followed a zero-order kinetic trend at the current
328 density of 2.5 and 5 mA cm^{-2} with the rate constant increased from 0.190 ($R^2 = 0.99$) to 0.440 ($R^2 =$
329 0.98) min^{-1} (indicating a charge controlled kinetic stage) while a first-order kinetic trend was
330 observed at the current densities of 10 and 25 mA cm^{-2} (indicating a mass controlled kinetic stage)
331 with the rate constant of 0.018 ($R^2 = 0.99$) and 0.027 ($R^2 = 0.99$) min^{-1} , respectively. As the current
332 density was increased from 10 to 25 mA cm^{-2} , more energy was used to generate hydrogen bubble,

333 so that the increase in the NO_3^- removal efficiency was not significant as expected. There is a good
334 correspondence between the amount of NH_4^+ produced and the amount of NO_3^- reduced as shown on
335 Fig. 8(b). Low current density leads to lower energy consumption, but in actual use, it is necessary to
336 seek the balance between the energy saving and the NO_3^- treatment requirements to gain the highly
337 appreciable treatment performance.

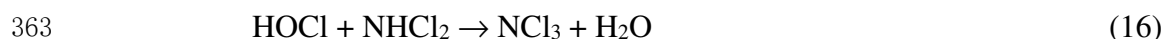
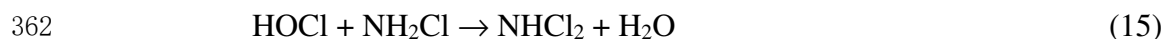
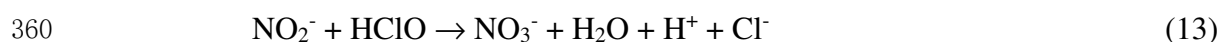
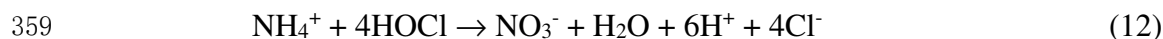
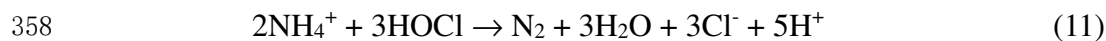
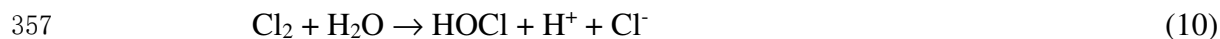
338

339 <Fig. 8>

340

341 3.3.2. Effect of chlorine concentration

342 As can be seen in Fig. S1, the main product of the electrocatalytic reduction of NO_3^- was NH_4^+ ,
343 which is also a contaminant that needed to be removed. The removal of NH_3 is primarily takes place
344 through direct oxidation on the anode surface and indirect oxidation mediated by active chlorine in
345 the solution bulk. In the direct oxidation process, the NH_3 is first adsorbed on the surface of the
346 anode and subsequently oxidized to N_2 , as shown in Eq. (8) [30]. However, NH_4^+ cannot be oxidized
347 directly at the anode. Hence it is necessary to adjust the solution pH to reach the pK_a of the
348 $\text{NH}_4^+/\text{NH}_3$ acid-base pair (i.e., $\text{pH} > 9.25$). [32] In addition to the direct oxidation of NH_3 on the
349 anode, the generated active chlorine species (Eqs. (9) and (10)) at the anode could also be involved
350 in the oxidative transformation of NH_4^+ to nitrogen gas (Eq. (11)) or NO_3^- (Eqs. (12)) as well as the
351 oxidation of NO_2^- to NO_3^- (Eq. (13)) in the homogeneous solution, so-called indirect (or mediated)
352 oxidation [30]. Furthermore, HOCl reacts also on NH_3 to form chloramines (Eqs. (14)-(16)).
353 Compared with direct ammonia oxidation, the chlorine-mediated ammonia oxidation is much more
354 efficient and feasible due to the abundant presence of chloride ion in wastewaters.



364 Chloride ions are widely presented in drinking water and industrial water. For instance, the
 365 concentration of chloride ions in the bulk drug manufacturing industrial wastewater and zinc refinery
 366 wastewater reached 3119 and 10000 mg L⁻¹, respectively [35]. Considering the role of chloride ions
 367 in oxidation of NH₄⁺, various concentrations of chloride ions were added to the solution in order to
 368 study its effect. As shown in Fig. 9(a), the NO₃⁻ removal efficiency was almost unaffected by the
 369 presence of chloride ions. But, as the concentration of chloride ions increased from 0 to 2000 mg L⁻¹,
 370 the formation of NH₄⁺ progressively decreased (Fig. 9(b)). For instance, when the concentration of
 371 chloride ions increased to 2000 mg L⁻¹, the generated NH₄⁺ ions ratio initially slightly increased to 7%
 372 within 40 min but then gradually decreased to approximately 0 after 100 min reaction time. Besides,
 373 it appears from Fig. 9(c) that the formation of NO₂⁻ could be deteriorated with increasing chloride
 374 ions concentration from 0 to 2000 mg L⁻¹, with the highest NO₂⁻ generation of 0.47%. It can also be
 375 seen from Fig. S6 that the TN removal efficiency and N₂ selectivity of Co₃O₄-TiO₂/Ti cathode
 376 increased with the increase of chloride ions concentration. When the chloride ions concentration

377 reached 2000 mg L⁻¹, the TN removal efficiency and N₂ selectivity reached 82% and 100%,
378 respectively.

379

380

<Fig. 9>

381

382 NH₄⁺ formation curves plotted in Fig. 9(d) clearly show that its amount formed at Co₃O₄/Ti
383 cathode (49%) was about twice of that formed at Co₃O₄-TiO₂/Ti cathode (24%) after 120 min
384 reaction at the same chloride ions concentration of 1000 mg L⁻¹. Fig. S6 shows that the TN removal
385 efficiency and N₂ selectivity for Co₃O₄-TiO₂/Ti cathode were 60% and 71%, respectively, while the
386 corresponding values for Co₃O₄/Ti cathode were 42% and 46%, respectively. The difference in NT
387 removal efficiency between Co₃O₄-TiO₂/Ti and Co₃O₄/Ti cathodes in the presence of chloride ions
388 was much larger than in the chloride-free cases as observed in Fig. S1. The indirect oxidation
389 mechanism of NH₄⁺ was similar to the intensively studied breakpoint chlorination [31]. First, the
390 NH₄⁺ reacts with the active chlorine (HOCl or OCl⁻ depending to the solution the pH) to produce
391 intermediate products such as monochloramine, dichloramine and tri-chloramine, and were finally
392 oxidized to N₂ [32]. It is worth noting that the oxidation process of the NH₄⁺ began to occur only
393 when active chlorine/ammonia mole ratio reaches 1.5 [33]. Specially, Ding et al. [34] found that
394 higher active chlorine/ammonia mole ratio (>5) brought about 100% removal of NH₄⁺, while less
395 efficient removal efficiencies (nearly 50%) were achieved with lower mole ratio (< 2). Thus, it can
396 be inferred that electrochemical ammonia oxidation in these reaction systems was closely related
397 with the active chlorine/ammonia mole ratio. As demonstrated in Fig. 1, the efficiency of NO₃⁻
398 reduction to NH₄⁺ with Co₃O₄/Ti cathode was higher than that with Co₃O₄-TiO₂/Ti cathode. This

399 would result in less mole ratio of active chlorine/ammonia in the former case compared with that in
400 the latter case. Therefore, as shown in Fig. 9(d), the indirect oxidation of ammonia was more
401 favorable for the $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode mediated electrochemical system.

402

403 **3.4. The NO_3^- removal mechanism**

404 **3.4.1 Direct reduction**

405 Electrochemical reduction of NO_3^- is a complex process involving a range of intermediates and
406 broad valence changes (from +5 to -3). The process mainly includes direct reduction and indirect
407 reduction. Direct reduction is mainly achieved by electrons and H^+ , and indirect reduction is mainly
408 caused by atomic H^* [35]. This mechanism was verified in the present electrochemical reaction
409 system by CV tests as depicted in Fig. 10(a). When $50 \text{ mg L}^{-1} \text{ NO}_3^-$ was added to the reaction
410 solution, the peak current density of -2.4 and -4.0 mA cm^{-2} appeared at the potential of -0.9 and -1.2
411 V/SCE , respectively, at TiO_2/Ti cathode. These reduction peaks can be attributed to the electron
412 transfer from the cathode to NO_3^- because no peak was observed in the absence of NO_3^- . Thus, it is
413 rational that approximately 45% NO_3^- was reduced at TiO_2/Ti cathode (Fig. 1(a)). According to the
414 previous studies [36], these two reduction peaks correspond to the reduction of NO_3^- to NO_2^- and the
415 formation of NH_4^+ , respectively. Furthermore, single reduction peak does not mean single electron
416 transfer [37]. In contrast, the peaks were completely disappeared in the case of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$
417 cathode, regardless of the presence or absence of NO_3^- . Notably, the experimental results presented
418 in Fig. 1 show that the NO_3^- reduction efficiency was greatly increased in the presence of Co_3O_4 .
419 Therefore, the disappearance of the reduction peak was not ascribed to the poor catalytic activity of
420 the Co_3O_4 toward the electrocatalytic reduction of NO_3^- . This peculiar phenomenon just became a

421 breakthrough point to understand the mechanism of the NO_3^- electrocatalytic reduction by Co_3O_4 . It
422 is known that two processes, i.e., heterogeneous charge transfer and diffusional mass transport,
423 mainly determine the shape of the CV curve [38]. The CV curve can reflect the heterogeneous charge
424 transfer from the electrode to electroactive species. However, it fails to reflect the charge transfer and
425 valence change inside the electrode. Co_3O_4 contains Co^{2+} ions in tetrahedral interstices and Co^{3+} ions
426 in octahedral interstices. Thus, it can be inferred that NO_3^- probably did not directly receive electrons
427 from the cathode via the circuit, but from the "electron porter" of the structural Co^{2+} ions. This
428 proposition can be validated by the density functional theory (DFT) calculation results, which can be
429 seen in Fig. 11. Co_3O_4 (222) was selected considering XRD detection and NO_3^- reduction
430 experiments. The DFT calculation results show that the O atom in NO_3^- and the Co atom on the
431 surface of Co_3O_4 (222) are thermodynamically favorably bonded with the required energy of -9.04
432 eV. Besides, the differential charge density distribution indicates that electrons can transfer from the
433 Co atoms on the surface of Co_3O_4 (222) to NO_3^- . Differential charge density analysis further showed
434 that the O atoms in NO_3^- obtained 0.41, 0.65, and 0.57 electrons, respectively, and the N atoms lost
435 0.82 electrons, and a total of 0.81 electrons were transferred from the Co atom to NO_3^- .

436 In order to further confirm this, the electrochemical reduction of NO_3^- at $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$
437 cathode was investigated at different cathode potentials, and the experimental results are shown in
438 Fig. 10(b). Nearly no NO_3^- was removed at the applied potential of -0.5 and -0.7 V/SCE within 120
439 min. The NO_3^- removal efficiency of 36% and 40% were attained at -1.0 and -1.2 V/SCE,
440 respectively. Besides, NO_3^- removal efficiency finally raised to 98% after 120 min electrolysis when
441 the applied potential was further decreased to -1.3 V/SCE. However, the NO_3^- reduction efficiency
442 was decreased to approximately 94% when further decreasing the cathode potential to -1.5 V/SCE.

443 This can be attributed to the enhancement of hydrogen evolution reaction at this potential and the
444 hindrance of hydrogen bubbles to the electron transfer at the cathode surface [39]. The strong
445 dependence of NO_3^- reduction on the cathode potential corresponding to reduction peaks of CV curve
446 is in agreement with the literature [40]. This confirms the above conjecture that electrons were
447 transferred from the power source to the cathode surface through a circuit, in which Co^{3+} was
448 reduced to Co^{2+} via accepting an electron. Then nitrogen-containing contaminants, such as NO_3^- ,
449 receive the electrons from the structural Co^{2+} ions. This particular reaction process cannot be directly
450 detected by CV test, explaining the disappearance of the reduction peak in Fig. 10(a) and the strong
451 voltage-dependent phenomenon in Fig. 10(b).

452

453

<Fig. 10>

454

455 In the above process, the ratio $\text{Co}^{2+}/\text{Co}^{3+}$ would definitely change. To further confirm this
456 statement, XPS analysis was used. The XPS wide-survey scan of Co(2p) is illustrated in Fig. 10(c).
457 The peaks at 780 and 795 eV (binding energy) should be assigned to Co(2p_{3/2}) and Co(2p_{1/2}),
458 respectively [41]. The Co (2p_{3/2})/Co (2p_{1/2}) ratio value of almost 2:1 was consistent with the previous
459 literature report [42]. The peaks of Co^{2+} were located at 781.5 and 796.6 eV, while the peaks at 780
460 and 794.8 eV should be assigned to Co^{3+} [43, 44]. Besides, the peaks at 786.8 and 804 eV were
461 attributed to the shake-up satellite peaks of Co^{2+} [45]. Moreover, the $\text{Co}^{2+}/\text{Co}^{3+}$ ratios of the pristine
462 and used $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes were calculated as 1.49 and 0.42, respectively, which indicated the
463 transformation of Co^{2+} to Co^{3+} during the electrochemical NO_3^- reduction process. This confirms the
464 electrochemical redox cycle $\text{Co}^{2+}\text{-Co}^{3+}\text{-Co}^{2+}$ and the electron transfer from Co^{2+} to NO_3^- during the

465 electrocatalytic NO_3^- reduction process.

466

467

<Fig. 11>

468

469 **3.4.2. Indirect reduction**

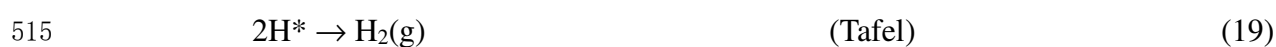
470 In the indirect pathway, electrons from the cathode could produce surface-adsorbed atomic H^*
471 via the reduction of protons, which is known as Volmer process [15]. Here, we employed CV
472 technique to qualitatively detect the formed H^* during the electrochemical reaction process, which
473 has been well introduced by Jiang et al. [46] and Liu et al. [47]. First, the cathode was repeatedly
474 scanned for activation in a potential range of -0.20 to 0.90 V/SCE in 0.1 M Na_2SO_4 electrolyte at
475 sweep rate of 100 mV s^{-1} . Electrochemical analysis did not start until a stable CV curve was obtained
476 [46]. As shown in Fig. 10(d), the starting potential was set from -1.20 to -1.35 V/SCE and the
477 termination potential was 0.45 V/SCE. As reported in the previous study involving C-Pd cathode for
478 nitrate reduction [46]; the lower the starting potential, the stronger the corresponding oxidation peak.
479 And the oxidation peaks of molecular hydrogen and atomic H^* were located at -0.80 to -0.60 V/SCE
480 and -0.10 to -0.00 V/SCE, respectively. Fig. 10(d) shows that at different initial potentials, reduction
481 peaks were observed at the potentials from -0.6 to -0.1 V/SCE, corresponding to the oxidation of
482 molecular H_2 and H^* , respectively. After adding 10 mM TBA, the intensity of the oxidation peak
483 corresponding to atomic H^* immediately weakened. This markedly suppressed the availability of the
484 formed H^* for the NO_3^- reduction.

485 Figs. 10(e) and (f) show LSV curves and NO_3^- reduction results, respectively, after the addition
486 of 10 mM TBA. As illustrated in Fig. 10(e), the current intensity was significantly enhanced after the

487 addition of 5 and 50 mg L⁻¹ NO₃⁻. However, the current intensity was decreased as TBA was added,
488 which was more pronounced at higher TBA concentration. In addition, as shown in Fig. 10(f),
489 increasing TBA concentration could gradually inhibit the NO₃⁻ removal efficiency. When TBA
490 concentration was 0.2 mM, the NO₃⁻ removal efficiency was decreased by approximately 10%, and it
491 was further decreased by 18% at TBA concentration of 1 mM. But negligible difference in the NO₃⁻
492 reduction efficiency between 1 and 10 mM TBA was observed, suggesting nearly complete hindering
493 of the contribution of the formed H* to NO₃⁻ reduction when TBA concentration was 1 mM.
494 Therefore, we can reasonably speculate that approximately 18% NO₃⁻ reduction proceeded via the
495 indirect pathway mediated by the atomic H* during the electrocatalytic reduction of NO₃⁻ process.

496 Atomic H* would accordingly be generated first by Volmer mechanism (Eq. (17)), which can
497 explain the increase of solution pH observed for the Co₃O₄-TiO₂-PVP cathode. In some noble metal
498 catalysts (e.g., Pd and Ag)-based reaction systems, atomic H* would be favorably preserved for NO₃⁻
499 reduction [12]. As a result, after the addition of 1 mM and 10 mM TBA in the Pd-mediated process,
500 the NO₃⁻ removal rate constant was reduced by 38% and 81%, respectively, which fully demonstrates
501 the importance of atomic H* for NO₃⁻ reduction. For Pd-based catalysts, the high efficiency of the
502 use of protons to generate atomic H* at low overpotentials (Eq. (17)) and the strong adsorption of
503 atomic H* to Pd atoms make Eqs. (18) and (19) difficult to occur [47, 48]. Even if atomic H* is
504 converted to H₂, Pd atoms can cleave H₂ and regenerate atomic H* (this mechanism belongs to
505 catalytic reduction) [12]. Through such electrocatalytic reduction processes, the indirect reduction of
506 NO₃⁻ by Pd-based catalysts is dominant. In contrast, in present Co₃O₄-based electrochemical system,
507 the produced H* was inclined to transform to H₂ by Heyrovsky and Tafel routes (Eqs. (17)-(19)) [15].
508 Consequently, as for Co₃O₄-TiO₂-PVP cathode, the indirect reduction mediated by atomic H*

509 accounted for only 18% of NO_3^- reduction. Thus, the role of atomic H^* in the electrocatalytic
 510 reduction of NO_3^- at the $\text{Co}_3\text{O}_4\text{-TiO}_2\text{-PVP}$ electrode was secondary, while the direct electron transfer
 511 was mainly responsible for NO_3^- reduction. In view of this, future research should focus on
 512 improving the atomic H^* adsorption capacity of non-precious metal catalysts.

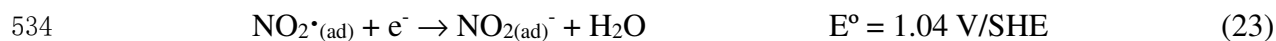
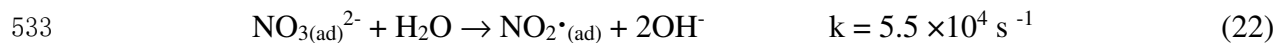
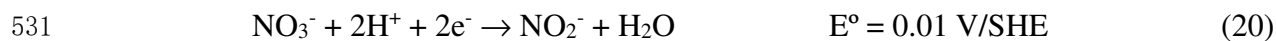


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517 **3.4.3. Proposed reaction pathway**

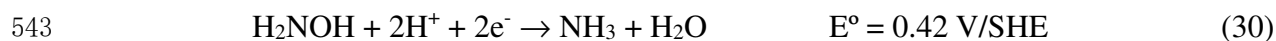
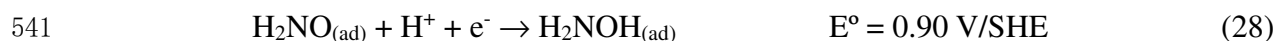
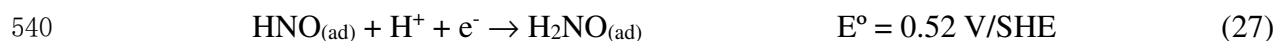
518 It was observed from Fig. 1 that the NH_4^+ concentration gradually increased over the reaction
 519 time for all cathodes containing Co_3O_4 catalyst as it was the main product of electrocatalytic NO_3^-
 520 reduction, while NO_2^- was the minor intermediate product at a relatively low concentration.
 521 According to the aforementioned discussion and the experimental results, there are two main
 522 pathways (i.e., Co-mediated direct reduction and atomic H^* -mediated indirect reduction) responsible
 523 for the electrocatalytic reduction of NO_3^- by the Co_3O_4 bearing cathodes investigated in this study.

524 It is known that the reduction of NO_3^- to NO_2^- (Eq. (20)) is the kinetically rate-determining step
 525 for the electrocatalytic reduction of NO_3^- . This step actually consists of the reactions set presented
 526 through Eqs. (21)-(23) which is known as an electrochemical-chemical-electrochemical path [35].
 527 The elementary electron transfer reactions lead to the generation of $\text{NO}_3^{2-}_{(\text{ad})}$ and $\text{NO}_2^-_{(\text{ad})}$, which
 528 are adsorbed short-lived intermediates. Then, $\text{NO}_2^-_{(\text{ad})}$ converts to an unstable dianion radical,
 529 namely $\text{NO}_2^{2-}_{(\text{ad})}$, by direct electron transfer (Eq. (24)), which would quickly hydrolyzes to form
 530 $\text{NO}_{(\text{ad})}$ (Eq. (25)) [35]:



537 According to the previous studies, the stepwise reduction of $\text{NO}_{(\text{ad})}$ eventually forms NH_4^+ ,

538 which is regarded as an electrochemical-electrochemical path, as depicted in Eqs. (26)-(31) [49]:



545 The direct electron transfers in above reactions are mostly single electron transfer processes.

546 The above experimental results demonstrated that the redox process $\text{Co}^{2+} \text{--} \text{Co}^{3+} \text{--} \text{Co}^{2+}$ accelerates the

547 electron transfer during NO_3^- reduction. The source of electrons for NO_3^- reduction is directly

548 derived from Co^{2+} instead of the cathode through the circuit. Co^{2+} gives an electron to NO_3^- or its

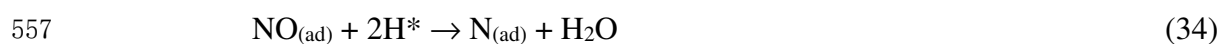
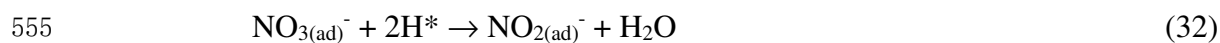
549 daughter intermediates with the formation of Co^{3+} , and then Co^{3+} would transform to Co^{2+} via

550 obtaining an electron from the cathode surface. Thus, during the whole reaction, Co_3O_4 mainly acts

551 as an electron shuttle rather than a reducing agent. Moreover, H^+ is consumed in many NO_3^-

552 reduction steps, which is consistent with the pH variation as shown in Fig. 7(b).

553 At the same time, due to the strong reducibility of atomic hydrogen ($E^{\circ}_{(H^+/H)} = -2.31$ V/SHE)
554 [49], the indirect reduction path of NO_3^- can not be ignored. Atomic H^* involved in Eqs. (32)-(37).



561

562 **4. Conclusions**

563 A novel $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode was synthesized for removal of NO_3^- from water by its
564 electrocatalytic reduction of. It was proved that adding a certain amount of PVP in the coating liquid
565 could improve the dispersibility of the catalyst and therefore promote the electrocatalytic reduction
566 of NO_3^- . More importantly, the release of toxic Co ions into the solution was almost completely
567 prohibited during the NO_3^- reduction process due to the stabilization effect of TiO_2 . The introduction
568 of a certain amount of chloride ions into the electrolyte significantly increased the N_2 selectivity and
569 total nitrogen removal efficiency. When the concentration of chloride ions reached 2000 mg L^{-1} ,
570 almost no NH_4^+ was detected after 100 min of electrolysis. The electrocatalytic mechanism of NO_3^-
571 reduction consisted of direct reduction and indirect reduction, which are mediated by the
572 $\text{Co}^{2+}\text{-Co}^{3+}\text{-Co}^{2+}$ redox cycle and atomic H^* , respectively. Notably, the former route played a
573 superior role in NO_3^- reduction over the latter one. Generally, considering the abundant chloride ions
574 in industrial/municipal wastewaters, the developed $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode in this study might be a

575 promising alternative for the electrocatalytic treatment of aqueous effluents loaded with NO_3^- .

576

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FIGURE CAPTIONS

Figure 1. NO_3^- concentration decay kinetics (a), and evolution of concentration of Co (b), NH_4^+ (c) and NO_2^- (d) during electrolysis time. Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2} .

Figure 2. XRD patterns of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes calcined at 300°C , 400°C , 500°C , 600°C and 700°C . The locations of the characteristic peaks for Co_3O_4 (C), Ti substrate (Ti), anatase (A), and rutile (R) are represented by the vertical dashed lines.

Figure 3. SEM images of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (a), $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) (b) and $\text{Co}_3\text{O}_4/\text{Ti}$ (c) cathodes. Elemental mapping of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (d,e), $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) (f,g) $\text{Co}_3\text{O}_4/\text{Ti}$ (h) cathodes. Elemental mapping: (d–h) correspond to Co, Ti, Co, Ti and Co maps, respectively.

Figure 4. HRTEM images of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$.

Figure 5. NO_3^- concentration decay kinetics (a) and LSV curves (b) for different coating times. Experimental conditions: (a) $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2} , (b) $0.1 \text{ M SO}_4^- + 50 \text{ mg L}^{-1} \text{ NO}_3^-$ solution, scan rate: 100 mV s^{-1} .

Figure 6. NO_3^- concentration decay kinetics at different calcination temperature (a) under experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2} , LSV curves at different calcination temperature (b) in $0.1 \text{ M SO}_4^- + 50 \text{ mg L}^{-1} \text{ NO}_3^-$ solution at a scan rate of 100 mV s^{-1} and (c) EIS Nyquist plots of the cathodes at different calcination temperature by applying an impedance amplitude of 10 mV with the frequency range from 10^5 to 10^{-2} Hz .

Figure 7. NO_3^- concentration decay kinetics at different pH (a) and Final solution pH for various initial pH after 120 min reaction (b). Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, current density = 10 mA cm^{-2} .

Figure 8. NO_3^- concentration decay kinetics (a) and NH_4^+ generation (b) at different current density. Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$.

Figure 9. Effect of Cl^- concentration on NO_3^- decay kinetics (a), NH_4^+ generation (b), NO_2^- generation (c) with $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode, and NH_4^+ generation with $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ and $\text{Co}_3\text{O}_4/\text{Ti}$ cathodes (d). Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2} .

Figure 10. Cyclic voltammograms of NO_3^- reduction (a) at TiO_2/Ti and $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes (scan rate: 20 mV s^{-1}); Effect of cathode potential on NO_3^- concentration decay kinetics (b) at $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode (Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2}); XPS spectra of Co 2p for fresh and used $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (c); Cyclic voltammograms obtained with $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode (d) in 0.1 M SO_4^- in the presence (dotted line) and absence (full line) of 10 mM TBA ; LSV curves of different electrolyte (e); and concentration decay kinetics of NO_3^- at $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode (f) with various TBA concentrations (Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2}).

Figure 11. (a) Adsorption configuration of NO_3^- on Co_3O_4 (222) surface and corresponding adsorption energy, (b) Differential charge density distribution of NO_3^- on Co_3O_4 (222) surface. Electron accumulation and electron deletion are represented by yellow and blue, respectively.

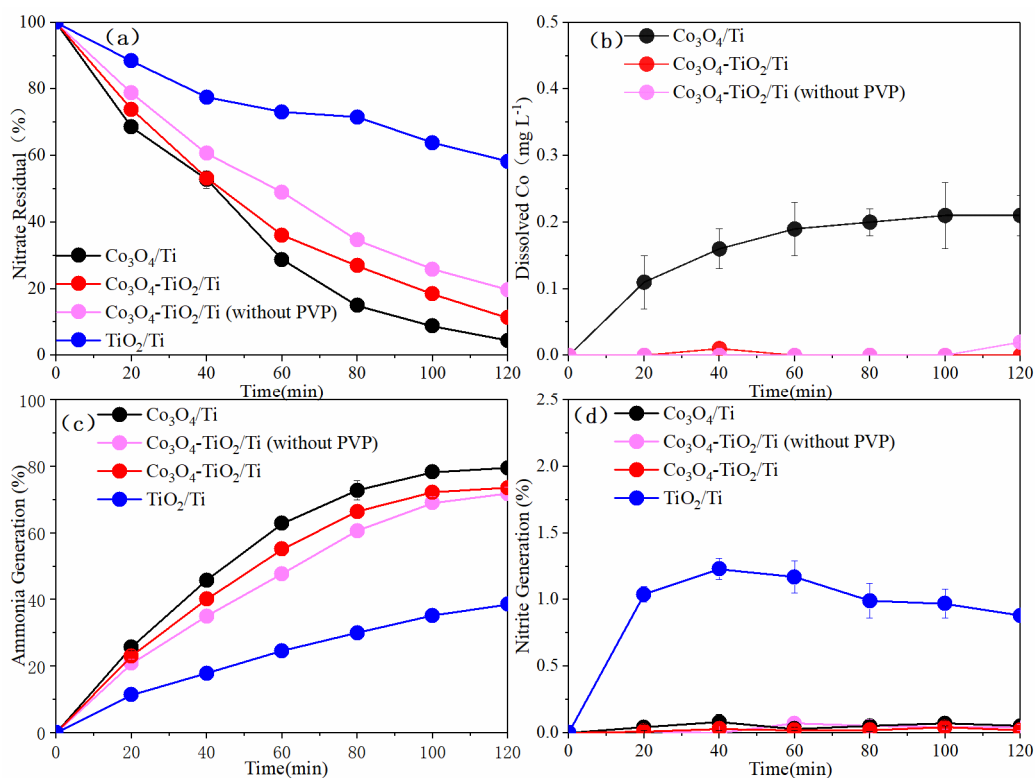


Figure 1

NO₃⁻ concentration decay kinetics (a), and evolution of concentration of Co (b), NH₄⁺ (c) and NO₂⁻ (d) during electrolysis time. Experimental conditions: [NO₃⁻]₀ = 50 mg L⁻¹, pH = 7.0, current density = 10 mA cm⁻².

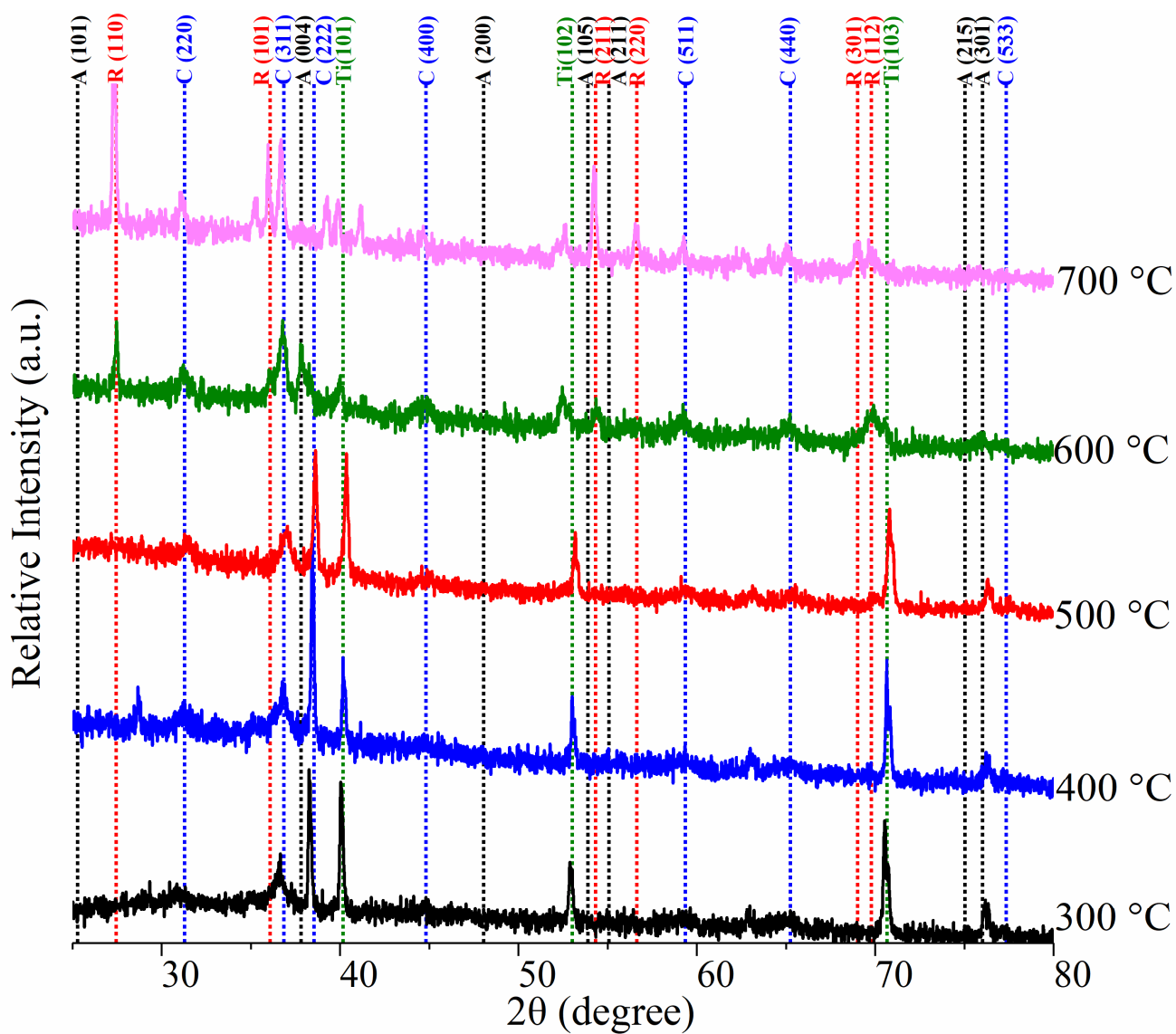


Figure 2

XRD patterns of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathodes calcined at 300 °C, 400 °C, 500 °C, 600 °C and 700 °C. The locations of the characteristic peaks for Co_3O_4 (C), Ti substrate (Ti), anatase (A), and rutile (R) are represented by the vertical dashed lines.

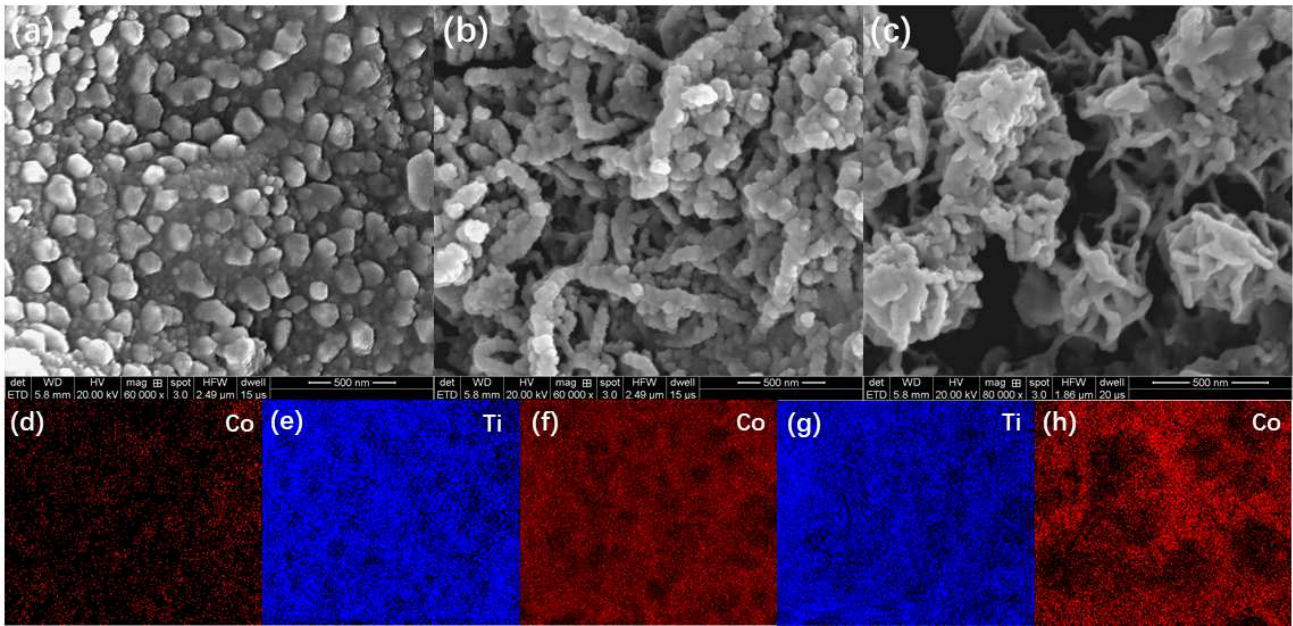


Figure 3

SEM images of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (a), (b) $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) (b) and $\text{Co}_3\text{O}_4/\text{Ti}$ (c) cathodes. Elemental mapping of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (d,e), $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ (without PVP) (f,g) $\text{Co}_3\text{O}_4/\text{Ti}$ (h) cathodes. Elemental mapping: (d–h) correspond to Co, Ti, Co, Ti and Co maps, respectively.

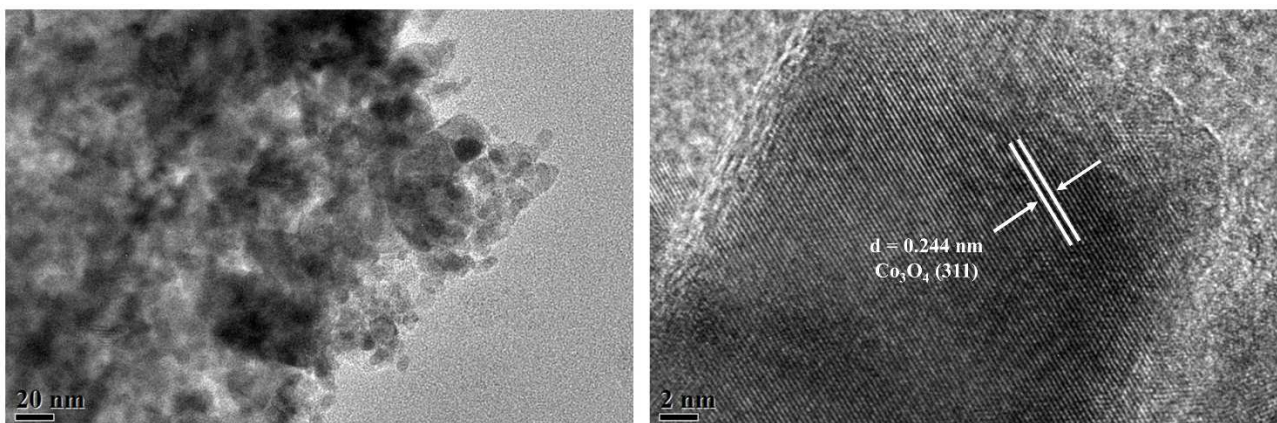


Figure 4

HRTEM images of $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$.

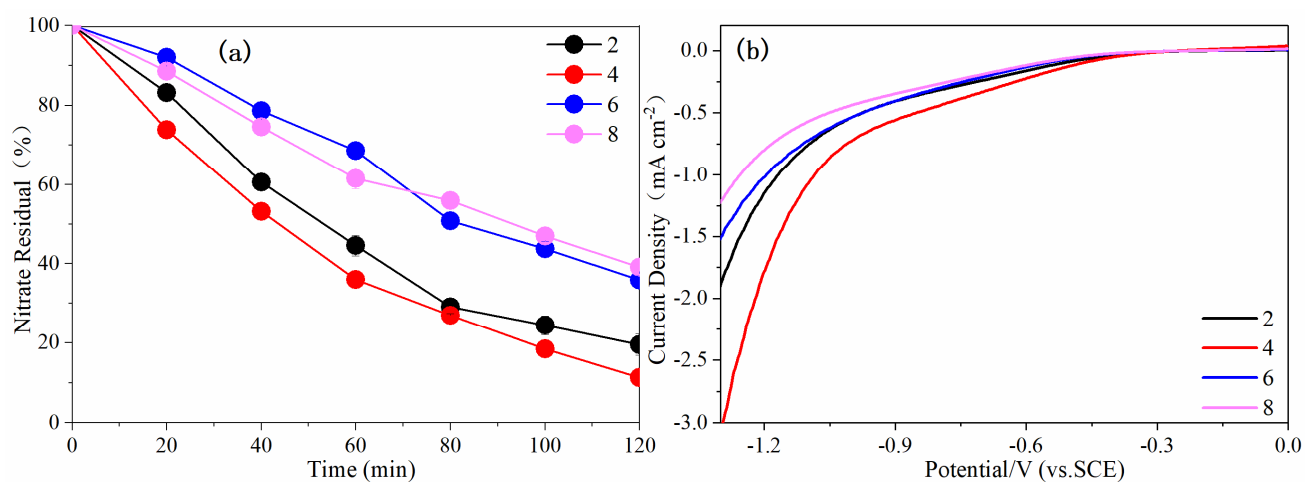


Figure 5.

NO_3^- concentration decay kinetics (a) and LSV curves (b) for different coating times.

Experimental conditions: (a) $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2} , (b) $0.1 \text{ M SO}_4^- + 50 \text{ mg L}^{-1} \text{ NO}_3^-$ solution, scan rate: 100 mV s^{-1}).

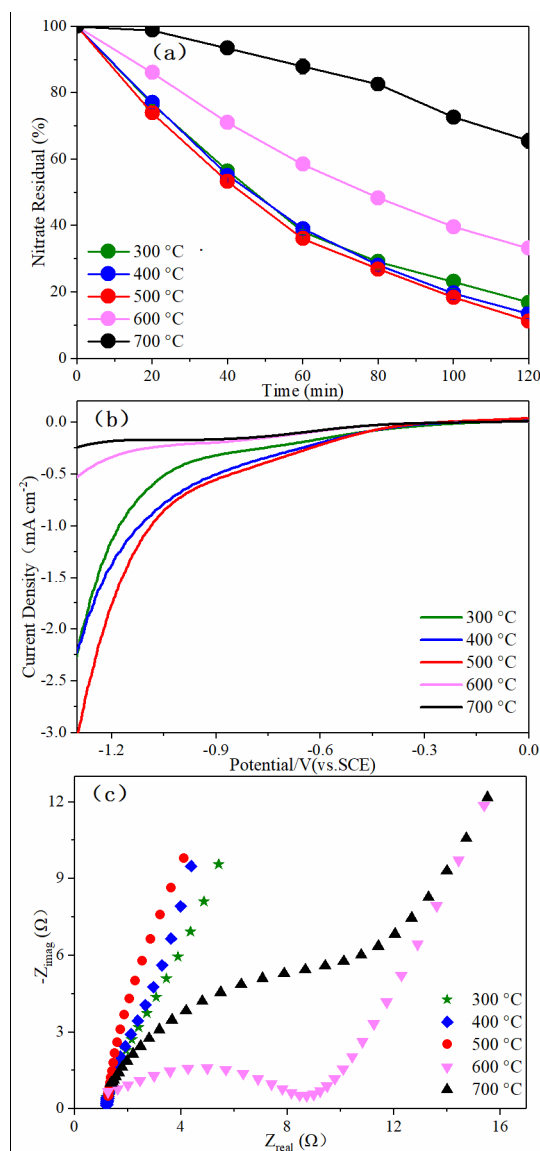


Figure 6

NO_3^- concentration decay kinetics at different calcination temperature (a) under experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2}), LSV curves at different calcination temperature (b) in $0.1 \text{ M SO}_4^- + 50 \text{ mg L}^{-1} \text{ NO}_3^-$ solution at a scan rate of 100 mV s^{-1} and (c) EIS Nyquist plots of the cathodes at different calcination temperature by applying an impedance amplitude of 10 mV with the frequency range from 10^5 to 10^{-2} Hz .

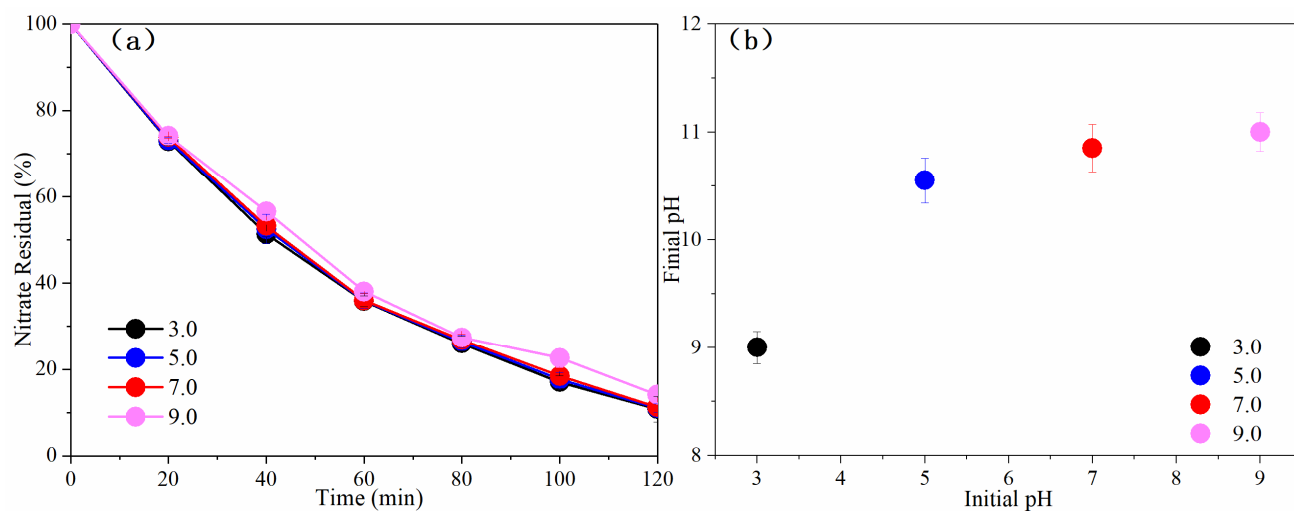


Figure 7

Figure 7. NO_3^- concentration decay kinetics at different pH (a) and Final solution pH for various initial pH after 120 min reaction (b). Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, current density = 10 mA cm^{-2} .

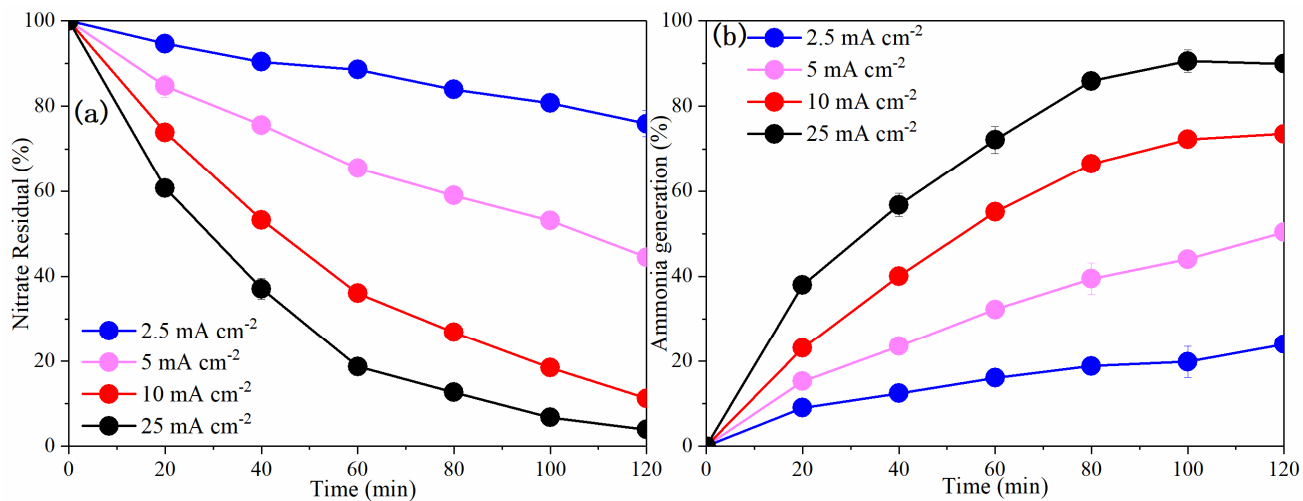


Figure 8

NO_3^- concentration decay kinetics (a) and NH_4^+ generation (b) at different current density.

Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$.

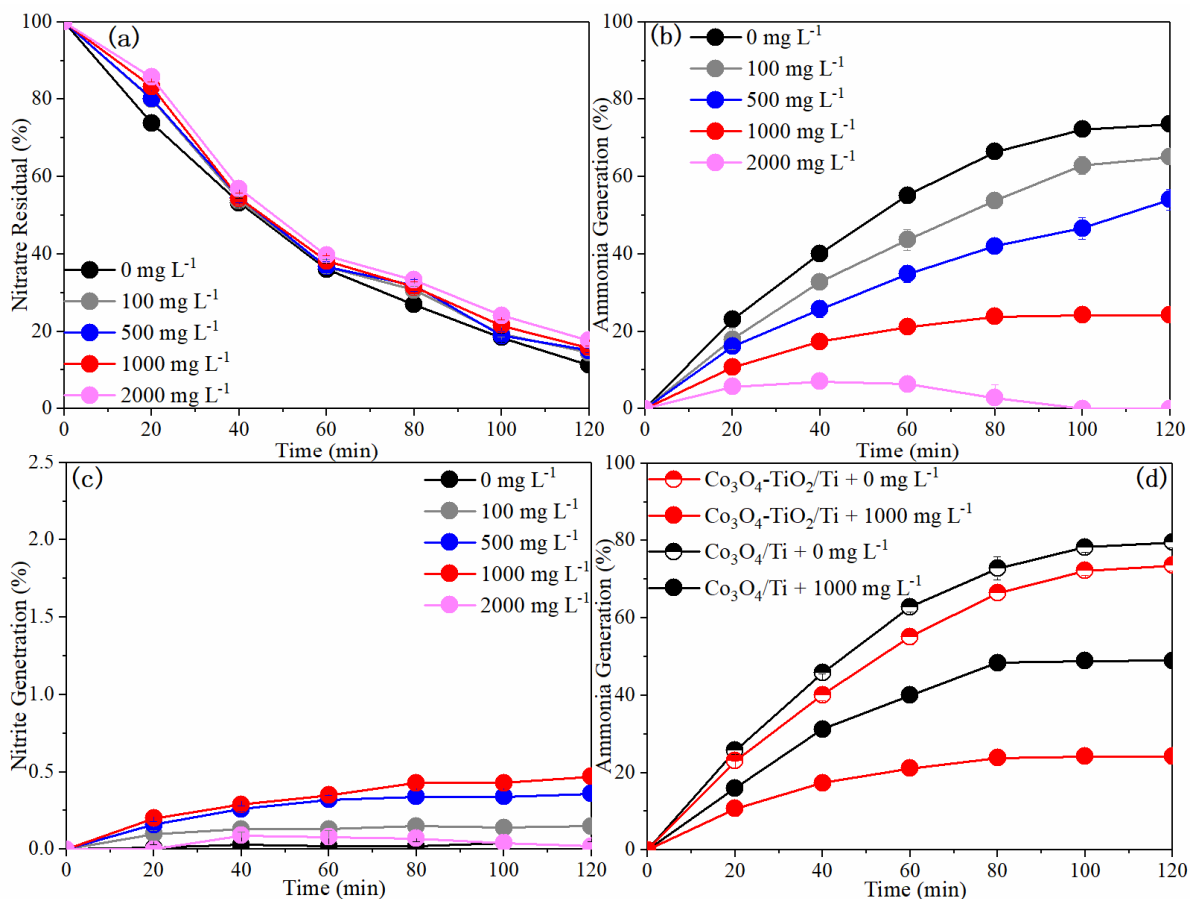


Figure 9

Figure 9. Effect of Cl^- concentration on NO_3^- decay kinetics (a), NH_4^+ generation (b), NO_2^- generation (c) with $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ cathode, and NH_4^+ generation with $\text{Co}_3\text{O}_4\text{-TiO}_2/\text{Ti}$ and $\text{Co}_3\text{O}_4/\text{Ti}$ cathodes (d). Experimental conditions: $[\text{NO}_3^-]_0 = 50 \text{ mg L}^{-1}$, $\text{pH} = 7.0$, current density = 10 mA cm^{-2} .

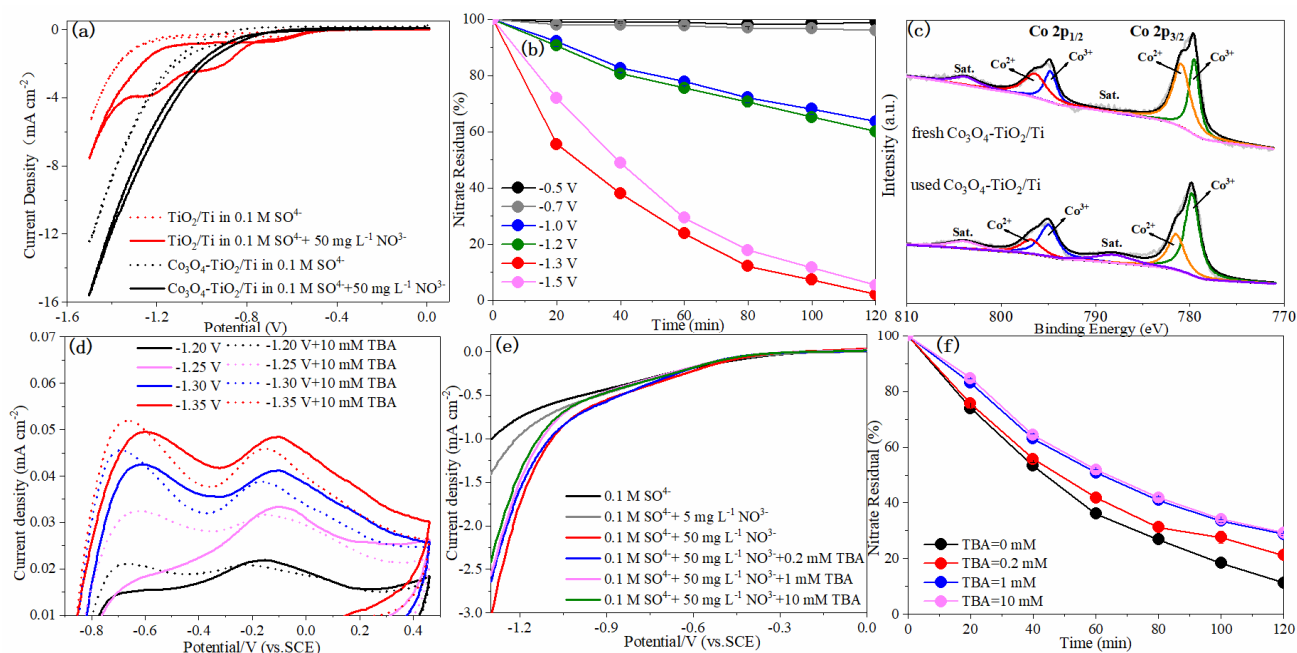


Figure 10

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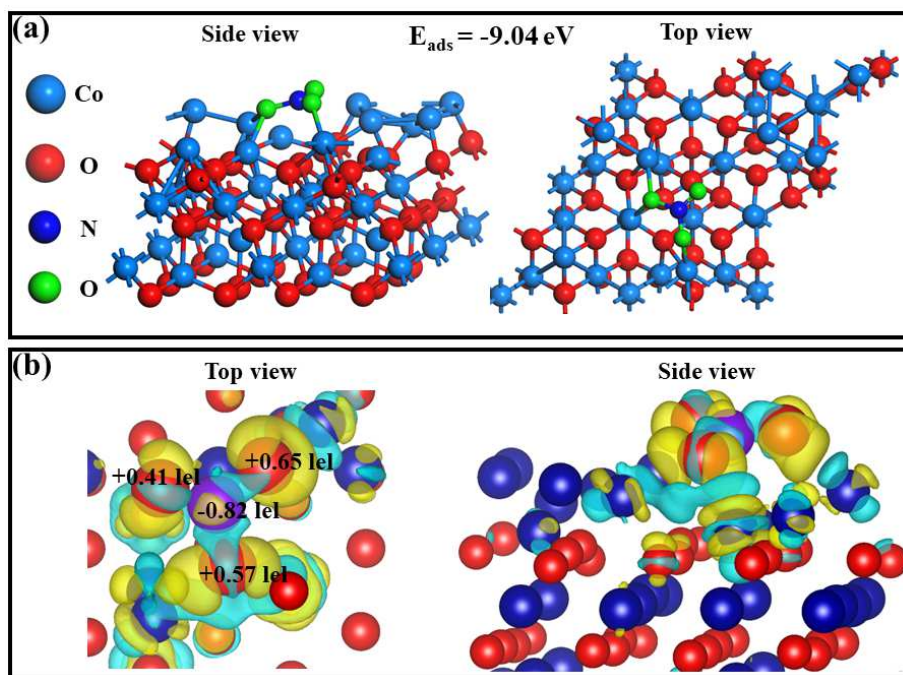
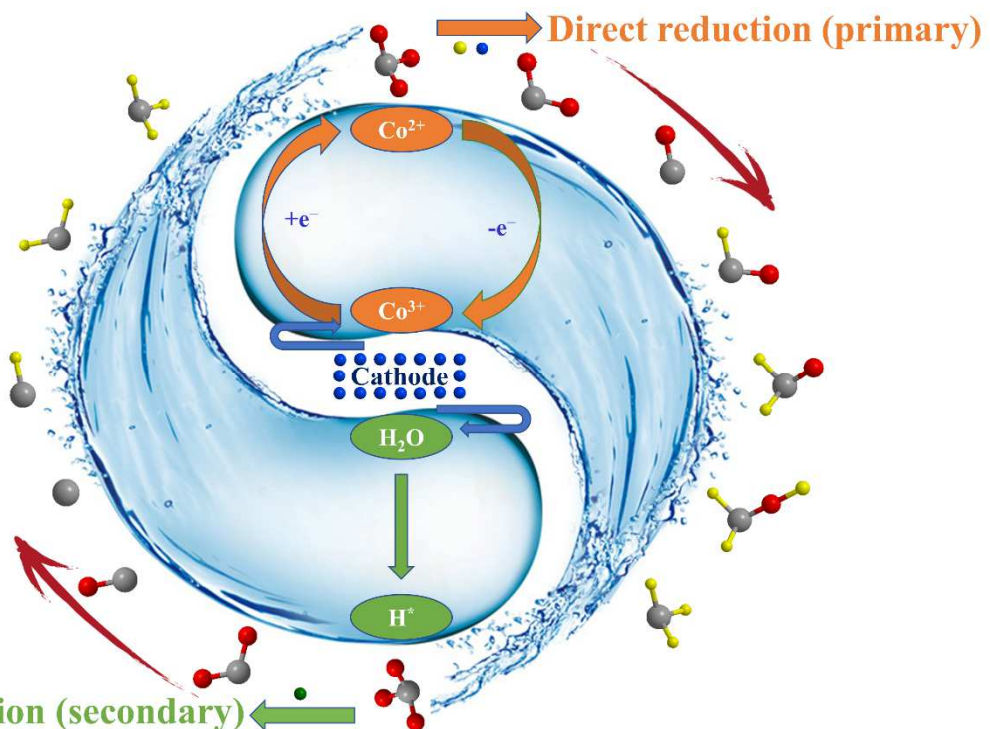


Figure 11

- (a) Adsorption configuration of NO_3^- on Co_3O_4 (222) surface and corresponding adsorption energy,
 (b) Differential charge density distribution of NO_3^- on Co_3O_4 (222) surface, electron accumulation and electron deletion are represented by yellow and blue, respectively.

Graphical abstract

- N
- O
- H/H⁺
- H⁺
- e⁻



Indirect reduction (secondary)