

Rod-Like Fe, Bi Co-doped Co_3O_4 as an Efficient Electrocatalyst for Chlorine Evolution Reaction and Ammonia-Nitrogen-Oxidation in Water

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Chlorine evolution reaction (CER) using dimensionally stable anode (DSA) materials are widely used in the chlor-alkali industry. However, they still have problems such as high preparation cost, limited selectivity, the titanium substrate being easy to passivate,^[2] and the electrode active material being easy to dissolve. Co_3O_4 , a nonprecious metal material, has shown good catalytic potential in promoting the CER reaction, which has broad application prospects as a CER electrocatalyst. In this paper, a

highly regular Rod-like Fe, Bi co-doped Co_3O_4 electrocatalyst was prepared. Compared with pure Co_3O_4 , the material had a larger electrochemical-specific surface area, lower charge transfer resistance, and better catalytic performance. In a 0.6 M NaCl solution, at a current density of 20 mA/cm^2 , it achieves a current efficiency of 91.8% and degrades ammonia nitrogen with an efficiency of 82%.

1. Introduction

The chlorine evolution reaction (CER) is one of the most important electrochemical reactions widely used in disinfection bleaching, wastewater treatment, chlor-alkali industry, and marine antifouling. Currently, the most common chlorine evolution catalyst is a dimensionally stable anode (DSA) composed of RuO_2 and IrO_2 . However, DSAs are expensive, and their CER selectivity is relatively poor in dilute and neutral solutions.^[1–3] Moreover, the dissolution of RuO_2 can cause a decline in the content of active substances on the electrode surface and a decrease in catalytic activity. Various advanced electrocatalysts have been successfully developed, such as CoSbO_x prepared by Lewis et al. through magnetron sputtering, which exhibits excellent catalytic performance with a current efficiency of up to 97%, and good stability after 250 h of stability test,^[4] and MOF-derived $\text{RuO}_2/\text{Co}_3\text{O}_4$,^[5] but their stringent synthesis process and high cost hinder its industrial application. Hence, there is an urgent need to develop cost-effective, highly active, and selective non-noble metal-based anodes for efficient chlorine evolution reactions.^[6]

At the same time, with the increasing frequency of human activities, the accumulation of ammonia nitrogen in natural water bodies has resulted in a series of environmental problems,^[7] such as eutrophication and harmful algal blooms. Electrochemical treatment technology (ETO) has gained increasing importance as a promising wastewater treatment method, noted for its high efficiency, stability, and low cost. Because of

its low cost of preparation, excellent Co(II)/Co(III) cycle characteristics, and high oxidation–reduction potential ($E_0 = 1.81$ V) of Co(III), it makes it possible to replace DSA electrode as a CER electrocatalyst for purifying ammonia nitrogen wastewater. It is noteworthy that doping noble metals is an effective strategy to enhance Co_3O_4 activity. Our research group has successfully prepared a Ti/Pt- Co_3O_4 electrode for ammonia nitrogen oxidation treatment in wastewater.^[8] To further reduce the cost, a noodle linear Fe, Bi co-doped Co_3O_4 catalyst was prepared by hydrothermal method, and SEM, XRD, and XPS analyzed its morphology, crystal structure, and surface state. Meanwhile, the electrochemical and chlorine evolution properties of the electrode were evaluated by electrochemical tests. The effects of Fe and Bi doping on the properties of Co_3O_4 materials and the performance of electrocatalytic CER were investigated. Meanwhile, ammonia nitrogen degradation experiments were carried out to explore the practical application potential of the materials in treating wastewater containing ammonia nitrogen.

2. Experimental Methods and Materials

2.1. Experimental Materials

In experiments, solutions were prepared using distilled water, the reagents used in the experiments included: concentrated sulfuric acid, starch, NaCl, KI, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and F-127(polyether) are commercially available reagents of analytical grade and used without further purification. All the reagents used in this experiment were purchased from Aladdin's. Titanium plates were purchased from Shure Technologies Co., LTD.

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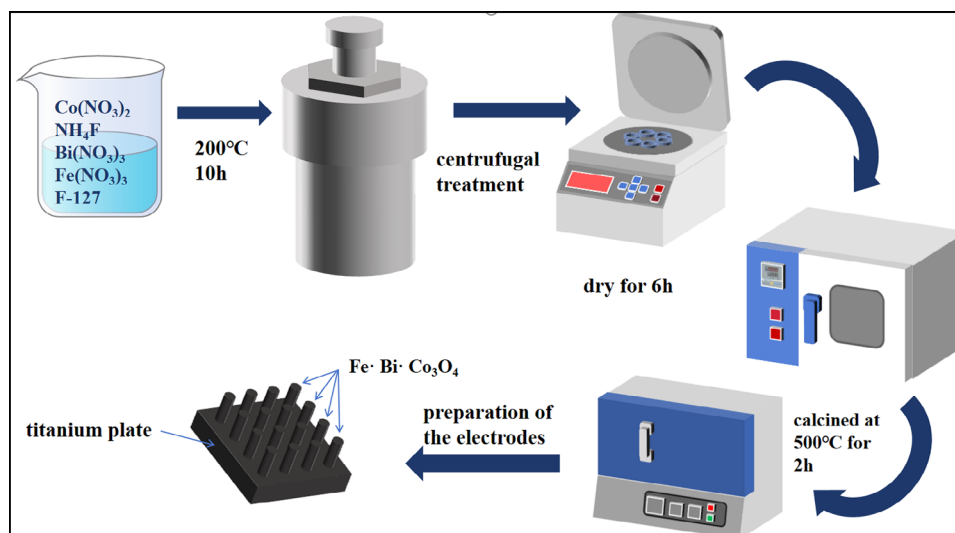


Figure 1. Experimental flow chart.

2.2. Synthesis of Anode

The preparation of electrodes mainly includes three steps: pretreatment of titanium matrix, electrode coating solution preparation, and electrode preparation.

2.2.1. Pretreatment of Titanium Matrix

Oil removal: the titanium plate was placed in acetone, ethanol, and water solution, and sonicated for 30 min to remove oil.

Acid etching: After oil removal, the titanium plate was placed in a 10 wt % boiling oxalic acid solution and etched for 2 h. After etching, the titanium plate was cleaned with deionized water for 5–10 min. Afterward, it was dried thoroughly and kept in absolute ethanol for utilization.

2.2.2. Preparation of Active Substance

$\text{Co}(\text{NO}_3)_2$ (2.619 g) $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.106 g) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.148 g) were dissolved in water to give a 30 mL solution. F-127 (polyether) 0.4 g and NH_4F 0.37 g were added and stirred for 30 min. After complete dissolution, the solution was transferred to a hydrothermal reactor, and then the hydrothermal reaction was performed for 10 h at 200 °C. The resulting solution was washed with ethanol and the residue was collected by centrifugation. They were dried at 60 °C for 6 h, followed by annealing at 500 °C for 2 h in a muffle furnace at a heating rate of 5 °C/min to give material CFB-5011. The pure Co_3O_4 was prepared with the same procedure from $\text{Co}(\text{NO}_3)_2$ without $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. The experimental procedure is shown in Figure 1.

2.2.3. Preparation of electrode coating solution

According to the mass ratio of 8:1:1, take the active substance (CFB-5011 or Co_3O_4), polyvinylidene difluoride (PVDF), and acetylene black into the test tube, add the appropriate amount of

n-methyl pyrrolidone, and ultrasonic to make it homogeneous until the test tube appears in black oily material, and then stop.

2.2.4. Preparation of the Electrode

The pre-etched titanium plate was removed and dried, and the black oil was uniformly coated on the titanium plate with a brush, about 0.1 g/cm², and finally dried at 60 °C for 12 h.

2.3. Experimental Analysis Methods

2.3.1. Structural Characterization

Surface morphology and chemical composition of the electrodes were scrutinized using scanning electron microscopy (SEM, JSM-6610LV) with low magnification observation and high magnification observation with an integrated energy-dispersive X-ray spectroscopy system (EDS) on a ZEISS Sigma 300 machine. The crystal structure and surface state were characterized through X-ray diffraction (XRD, Bruker D8-Advance) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI). Specific components of the CFB-5011 test were carried out on a transmission electron microscope of JEOL Jem 2100F/ F200(TEM).

2.3.2. Electrochemical Test

All electrochemical tests were performed on an electrochemical workstation (CHI 660E, Chenhua). The electrochemical properties of the anode were measured by cyclic voltammetry (CV), linear cyclic voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) using a three-electrode system. The Pt electrode was used as the counter electrode and the standard hydrogen electrode (RHE) was used as a reference electrode. The working electrodes were CFB-5011 and Co_3O_4 electrodes. The distance between the working and counter electrodes was approximately 1 cm. The CV was scanned at different scan rates at potentials

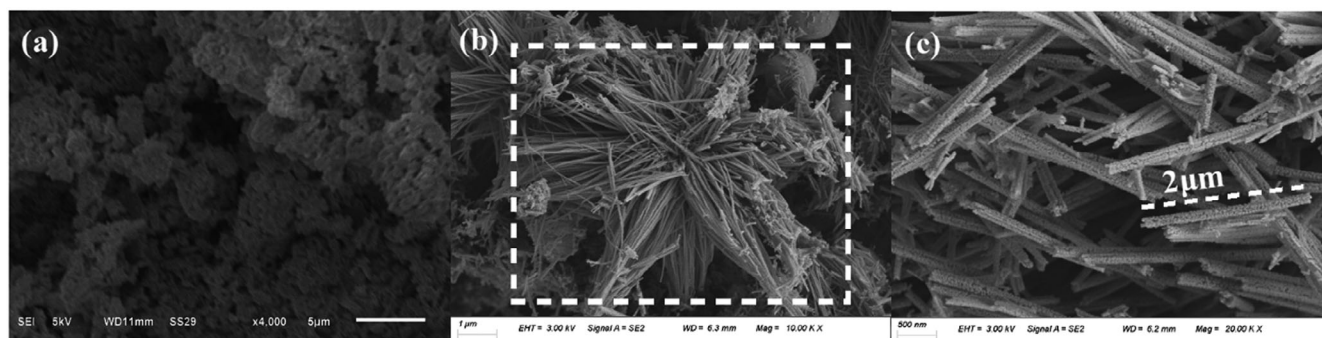


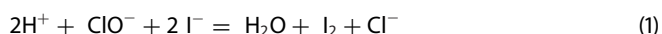
Figure 2. SEM image of (a) Co_3O_4 , (b–c) CFB-5011.

Sample	$S_{\text{BET}}(\text{m}^2\cdot\text{g}^{-1})$	Pore Volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Average Pore Size ($\text{\AA}$)	The Type of Absorption and Desorption curve	Hysteresis Loop Type
Co_3O_4	10.1133	0.050670	199.149	III	H_3
CFB-5011	43.4911	0.195153	189.048	III	H_3

ranging from 1.03 V versus RHE to 1.13 V versus RHE. The LSV was tested at a scan rate of 5 mV/s at potentials ranging from 1.425 V versus RHE to 1.675 V versus RHE. NaCl and NaNO_3 aqueous solutions were used as electrolytes to determine the selectivity of CER and OER. NaNO_3 solution was used to detect oxygen evolution at neutral pH, and NaCl solution was used to detect chlorine evolution.^[9]

2.3.3. Chlorine Evolution Efficiency Evaluation

In this paper, the indirect iodometric method is used to detect the amount of effective chlorine produced to determine the current efficiency. Specific procedures are shown in the Experimental section of the Supporting Information.^[10] The specific reaction equation is as below.^[11]



$$P_{\text{Cl}} = (C_1 \times V_1 \times 35.45) \div V_{\text{Cl}} \quad (3)$$

$$\text{CER} (\%) = (C_2 \times V_2 \times n \times F) \div (I_2 \times t_2) \quad (4)$$

2.3.4. Detection Method of NH_4^+ Concentration

The detection method of NH_4^+ concentration refers to the national standard HJ 535–2009 visible spectrophotometry, and the specific experimental procedures are provided in the Supporting Information of the paper.

2.3.5. Stability Test

Chronopotentiometry (CP) was used to assess electrode stability, electrode was tested in 0.6 M NaCl solution at a current density of $10 \text{ mA}/\text{cm}^2$

3. Result and Discussion

3.1. Structural Features

Figure 2(a–c) shows scanning electron microscope images of the prepared materials. Figure 2(a) shows that Co_3O_4 has an irregular spherical structure with low magnification observation (JSM-6610LV), and Figure 2(b,c) shows the microscope images of the CFB-5011 with high magnification observation (ZEISS Sigma 300). It can be seen that CFB-5011 presents an obvious rod-like nanorod structure with a uniform length distribution of about $2 \mu\text{m}$. Figure 2(b) demonstrates that numerous small rod-like structures spontaneously assemble into lily-like formations. In addition, to further explore the specific components of CFB-5011, a transmission electron microscope experiment was carried out, and the experimental results are shown in Figure S2. The (311) crystal plane of Co_3O_4 and (111) crystal plane of BiFeO_3 appear in CFB-5011, indicating that these two crystals do exist in CFB-5011.

The results of the specific surface area and pore size of the material via BET tests are shown in Table 1. We can see that the specific surface area of the CFB-5011 reaches $43.4911 \text{ m}^2\cdot\text{g}^{-1}$ significantly higher than that of Co_3O_4 , while the pore size is slightly reduced. A higher specific surface area means a larger contact area between the catalyst and the solution, leading to a higher mass transfer rate and more exposed active sites.^[12] At the same time, a smaller pore size can also better overcome the effect of bubble-shielding.^[10]

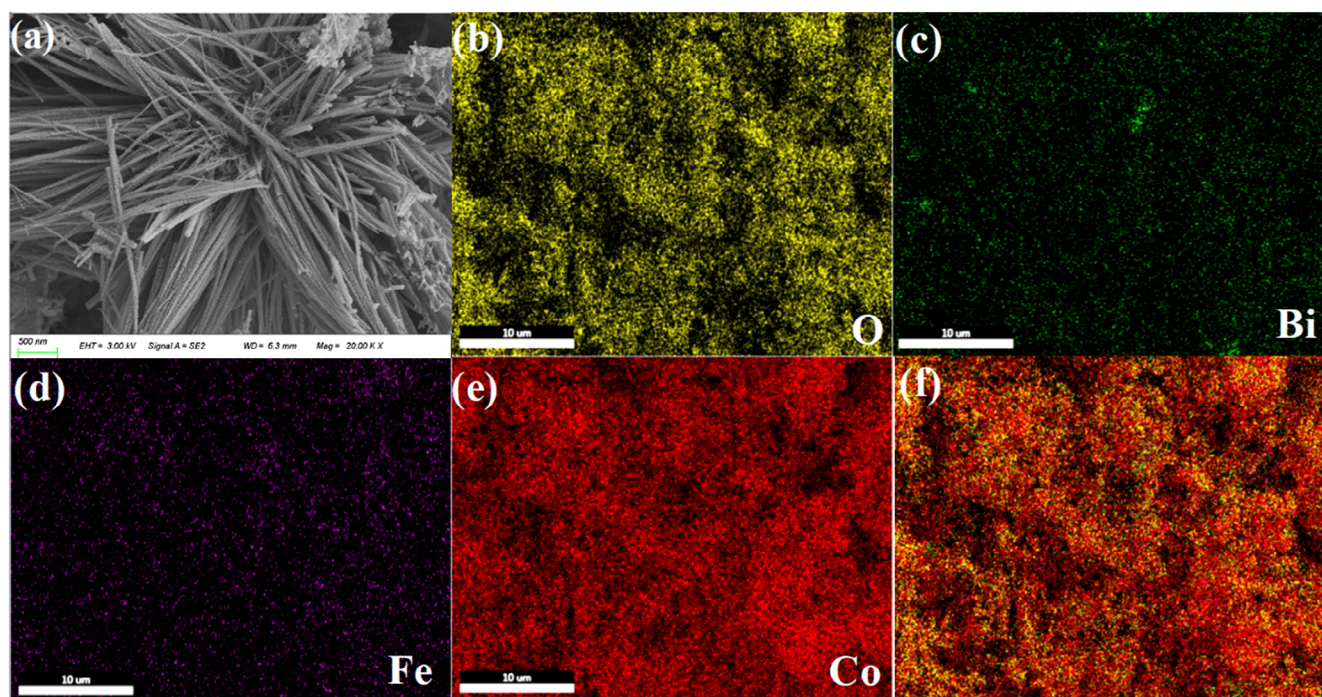


Figure 3. (a–f) The EDS of CFB-5011.

By analyzing the isotherm and pore size distribution of nitrogen adsorption and desorption in Figure S1, the specific surface area and pore size of different samples are evaluated. It is worth noting that all samples show typical type III adsorption and desorption curves, and obvious H₃ type post-adsorption hysteresis rings also appear, which indicates that the samples have mesoporous characteristics.

The BET surface area, pore size, pore volume, adsorption and desorption curves, and hysteresis loop type of Co₃O₄ and CFB-5011 are shown in Table 1 below.

Figure 3 shows the EDS image of CFB-5011. Figure 3(b–e) illustrates that Bi Fe was successfully introduced into the material. Figure 3(f) shows that Co, Fe, Bi, and O elements are uniformly distributed in CFB-5011.

Figure 4 shows the XRD spectrum image of the material. CFB-5011 has a typical diffraction peak at 2θ of 18.99°, 31.27°, 36.92°, 38.55°, 44.81°, 55.65°, 59.35°, 65.63°, and 77.07°. They are associated with the crystal planes of (111), (220), (311), (222), (400), (422), (511), (440), and (533) of Co₃O₄ (PDF#74–2120).^[13] At the same time, iron and bismuth form Bi(FeO₃) crystals, corresponding to 110 and 211 crystal planes when 2θ is 22.29° 31.67°.^[14,15] Combined with the subsequent XPS analysis, iron exists in divalent and trivalent forms.^[16]

Studying the surface state of the material through XPS spectroscopy. Strong Co 2p, Bi 4f, O 1 s, and Fe 2p peaks were observed in the XPS spectrum of CFB-5011 (Figure 5a).^[17] Figure 5 b shows the fine spectra of O 1 s for these two materials, and the peak at 531.5 eV in the map is due to oxygen vacancy, which increases significantly in intensity after the introduction of Fe, this may be related to the change of the valence of the iron element in the lattice. More oxygen vacancies can effectively optimize charge transport, adjust electronic structure, and

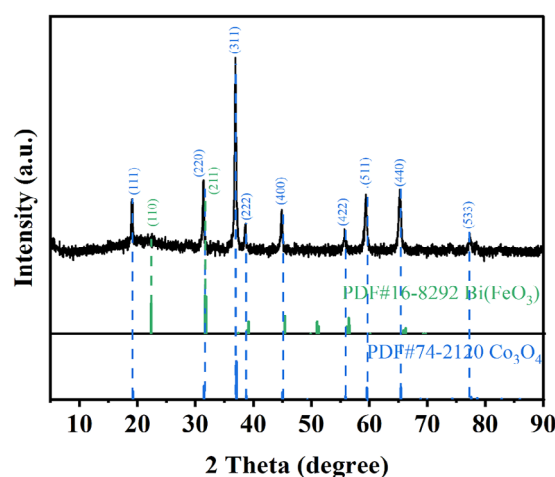


Figure 4. XRD patterns of CFB-5011.

enhance reactant adsorption and product desorption. This may also be one of the reasons for the improved catalytic activity of CFB-5011.^[18] Figure 6(a) shows the Co 2p fine spectra of CFB-5011 and Co₃O₄, respectively.^[19] The Co (III) and Co (II) contents in Co₃O₄ before and after doping were compared by Co 2P_{3/2} XPS spectra, it was found that the ratio of Co (III) /Co (II) decreased significantly after the introduction of Fe. Fe exists in the material in divalent and trivalent forms, and divalent Fe and trivalent cobalt have similar extra-nuclear electron arrangements. From Figure 6(a), we can also find that the content of trivalent Co decreases with the introduction of Fe, the same phenomenon was not observed when Bi was introduced into Co₃O₄ alone, so the decrease in Co (III) /Co (II) ratio after the simultaneous introduction of Fe and Bi should be attributed to Fe possibly

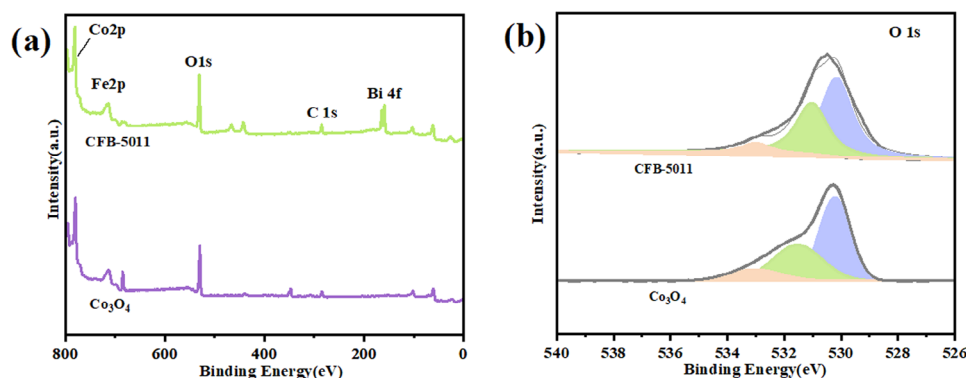


Figure 5. (a) XPS of Co_3O_4 , CFB-5011 survey spectrum, (b) O 1 s spectrum.

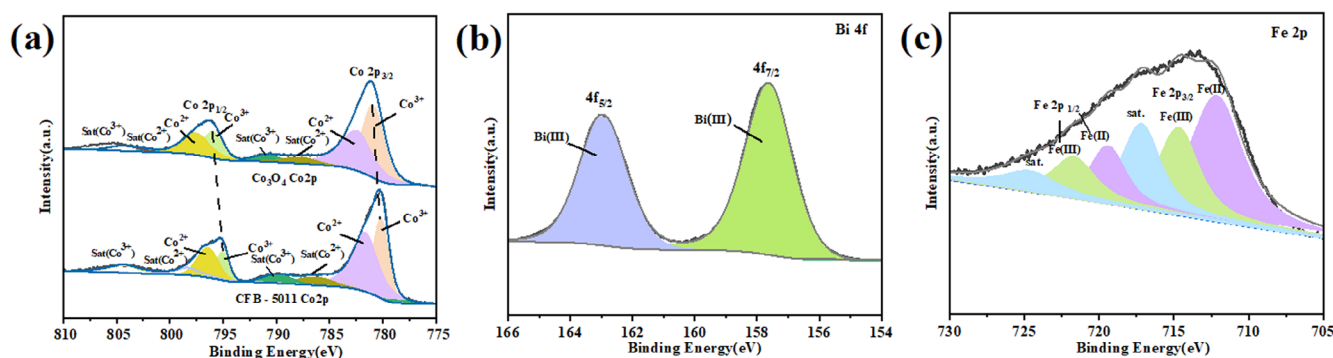


Figure 6. XPS of Co_3O_4 , CFB-5011: (a) Co 2p, (b) Bi 4f, and (c) Fe 2p.

occupying the place of Co (III) in the tetrahedral structure.^[20] At the same time, it can be seen that with the doping of Bi and Fe elements, the binding energy of Co (III) decreased, indicating that Bi and Fe elements may have a strong electron-withdrawing effect, leading to the generation of electron-deficient centers, which is in favor of the enrichment of Cl^- , and further facilitating the CER activity and selectivity of the electrocatalyst.

Figure 6(b) shows the Bi 4f fine spectrum of CFB-5011, indicating that Bi elements exist in the form of Bi(III), and Figure 6(c) shows the Fe 2p fine spectrum of CFB-5011, indicating that Fe exists in the material in the form of both Fe(II) and Fe(III).

3.2. Electrochemical Test

Figure 7 shows the LSV curve of the material in 0.6 M sodium chloride solution. An LSV test was used to evaluate the catalytic performance of the electrode that was obtained. To explore the catalytic ability of CFB-5011, Co_3O_4 , DSA, and bare Ti electrodes were used to compare with CFB-5011. Under the same current density, the catalytic performance between different electrodes was judged by comparing the level of electrode potential. When the current density was 10 mA/cm^2 , the CFB-5011 electrode had the lowest potential, indicating it had the best catalytic activity. At the same time, when the electrode potential was 1.65 V, the current density of the CFB-5011 electrode was about 20.8 mA/cm^2 , while that of the DSA electrode was only 5.93 mA/cm^2 . It is worth noting that the current density of the

bare titanium matrix electrode is just about 0.32 mA/cm^2 , indicating that there is almost no chlorine evolution reaction at this potential.^[21]

The Tafel slope is frequently employed to investigate the kinetics of the CER process, where a lower Tafel slope value signifies a more gradual increase in overpotential, indicating a better catalytic activity of the catalyst.^[22] As shown in Figure 7(b), the image shows that the minimum Tafel slope of the CFB-5011 electrode is just 88 mV/dec but the Tafel slope of the Co_3O_4 electrode reaches up to 102 mV/dec, indicating that Fe, Bi doping can effectively improve the catalytic activity of Co_3O_4 .^[23]

As a competing reaction of CER, the OER reaction often proceeds simultaneously with the CER reaction. Therefore, to ensure the current efficiency in the electrolytic process, the CER anode should have good selectivity. The selectivity of the chlorine evolution reaction is usually compared by judging the current density of CER and OER at the same potential using linear sweep voltammetry. Figure 7(c) demonstrates that in the same potential, the CFB-5011 electrode exhibits higher current density in a 0.6 M NaCl solution than the DSA electrode but lower current density than the DSA electrode in a 0.6 M $\text{Na}(\text{NO}_3)_3$. Thus, the CFB-5011 electrode exhibits better chlorine evolution selectivity than the DSA electrode.

Figure 8 shows the CV diagram of the prepared electrode at different sweep speeds, which is generally similar to a rectangle and presents an ideal rectangular CV curve, indicating that the material has good stability in this potential range and

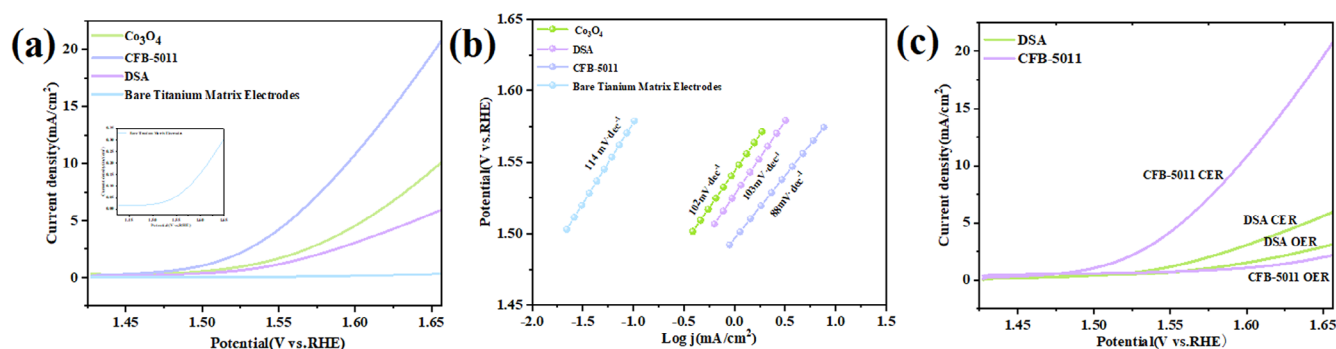


Figure 7. (a) LSV images of the Co₃O₄, CFB-5011 electrodes, (b) Tafel slope test images of the Co₃O₄, CFB-5011 electrodes, and (c) selectivity of Co₃O₄, CFB-5011 electrodes.

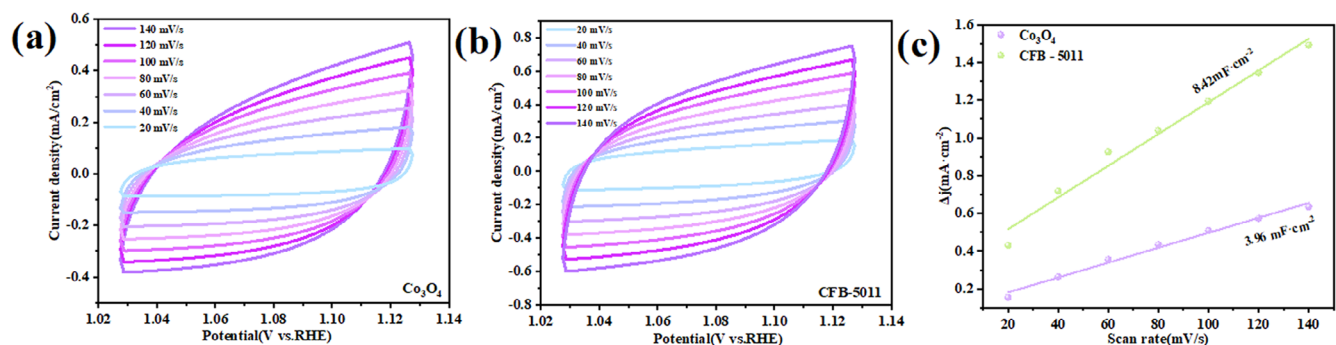


Figure 8. (a) The CV of Co₃O₄ electrode in 0.6 M NaCl solution, (b) the CV of CFB-5011 electrode in 0.6 M NaCl solution, and (c) the C_{dl} of Co₃O₄, CFB-5011 electrodes.

does not easily undergo redox reactions. Electrochemical surface area (ECSA) is mainly used to evaluate the relationship between the specific surface area of a material and the electrocatalytic performance, and the calculation method is shown in Equation (5):^[24]

$$\text{ECSA} = (C_{\text{dl}} \div C_s) \times S \quad (5)$$

C_s is the capacitance value corresponding to the ideal electrode with a smooth surface, which is 60 μF/cm², C_{dl} is the capacitance of the electric double layer (mF/cm²); S is the area of the electrode (cm²). Figure 8(c) shows that the C_{dl} value of the CFB-5011 electrode is 8.42 mF/cm², and the C_{dl} value of the Co₃O₄ electrode is 3.96 mF/cm². The C_{dl} of the CFB-5011 electrode is greater than that of the Co₃O₄ electrode.^[25] The electrochemical active area (ECSA) is proportional to C_{dl}. Therefore, the ECSA of the CFB-5011 electrode is larger than that of Co₃O₄. The larger electrochemical active area (ECSA) means that the effective surface area on the electrode surface can participate in the electrochemical reaction is larger, and the reaction rate and the current density can be greater in the electrochemical reaction.

Figure 9(a) shows Nyquist plots of Co₃O₄, CFB-5011 electrodes in 0.6 M NaCl.^[22] Compared to the Co₃O₄ anode the CFB-5011 anode exhibits lower charge transfer resistance and higher charge transfer efficiency.^[26]

The exact resistance values and the corresponding potentials are shown in Table S2.

3.3. Assessment of the Electrodes' capacity for Chlorine Evolution Efficiency

The chlorine evolution efficiency was tested at different current densities to explore the electrochemical properties of the fabricated electrodes. In Figure 9(b), compared to the other electrodes, at the current densities of 5, 10, and 20 mA/cm², the electrode of CFB-5011 has a higher current efficiency. At a current density of 20 mA/cm², the current efficiency reaches 91.8% much higher than the DSA electrode (78.9%) and the bare titanium matrix electrode (74.1%).

3.4. Stability Testing of the CFB-5011 Electrode

Chronoamperometry is a significant approach for assessing the stability of electrodes. The CFB-5011 electrode underwent a 24-h testing period in a solution of 0.6 M NaCl, with a current density of 10 mA/cm². Figure 9(c) shows that during the first 15 h, the electrode voltage was relatively stable, only rising slowly. However, from about 15 h onwards, as the electrolysis continued, the ion concentration in the solution decreased and bubbles were generated on the electrode surface, resulting in a rapid rise of the electrode potential, which was one of the reasons for the fluctuations. The electrolyte was replaced at about 21 h, and the potential decreased accordingly. Until the end of the 24-h stability test, due to the electrode surface being in the electrical oxidation/reduction state for a long time, a small part of the active substance on the electrode was reconstructed or shed,

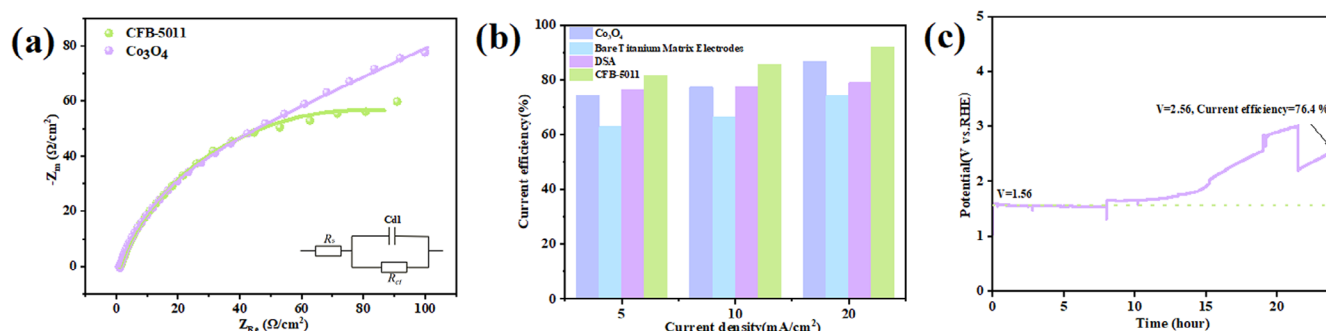


Figure 9. (a) Nyquist plots of Co_3O_4 , CFB-5011 electrodes in 0.6 M NaCl, (b) CER current efficiencies of Co_3O_4 and, CFB-5011 electrodes in various current densities, (c) stability testing of the CFB-5011 electrode.

resulting in a small increase in the electrode potential. Finally, the chlorine evolution performance test was carried out, and it was discovered that the current efficiency could remain at 76.4%. This suggests that the CFB-5011 electrode possesses excellent long-term stability.

4. The CFB-5011 Electrode Used for Ammonia Nitrogen Degradation in Dilute Chloride

Ammonia oxidation mainly includes direct and indirect pathways. Direct oxidation predominantly takes place in alkaline or neutral solutions, and the reaction is as follows.



In acidic circumstances, the direct oxidation process of ammonia nitrogen is hard to proceed since ammonia nitrogen mainly exists in the form of NH_4^+ at this time, and it is readily attached to the surface of the anode, thereby impeding its oxidation reaction. Moreover, the direct oxidation route is restricted by the rate of electron transfer, leading to a prolonged kinetic process and a relatively poor oxidation efficiency for ammonia nitrogen.^[27] Additionally, in acidic conditions, the main product of ammonia nitrogen oxidation is nitrate instead of nitrogen gas, which not only fails to achieve harmless treatment but may also cause secondary pollution issues in the environment.^[28]

The indirect oxidation pathway refers to the oxidation of ammonia nitrogen by reactive chlorine or chlorine radical radicals generated by the electrolysis process.

As shown in Figure 10, during the electrolysis process, Cl^- ions are rapidly adsorbed to the surface of the anode under the action of electrostatic force. Then, they lose one electron under the oxidation of the anode, transforming into $\text{Cl}\cdot$ free radicals. These adsorbed $\text{Cl}\cdot$ free radicals combine or pair with Cl^- ions adsorbed on the anode surface to form Cl_2 molecules. Cl_2 then reacts with water in the solution to further form HClO or ClO^- . Meanwhile, $\text{HO}\cdot$ free radicals are generated on the anode surface, with some of them reacting with Cl^- ions in the solution to regenerate $\text{Cl}\cdot$, while the remaining $\text{HO}\cdot$ react with HClO or ClO^- to form $\text{ClO}\cdot$.

During this process, $\text{Cl}\cdot$ and $\text{ClO}\cdot$ react with ammonia to form $\text{NH}_2\cdot$. $\text{NH}_2\cdot$ mainly reacts with active chlorine to form NH_2Cl .

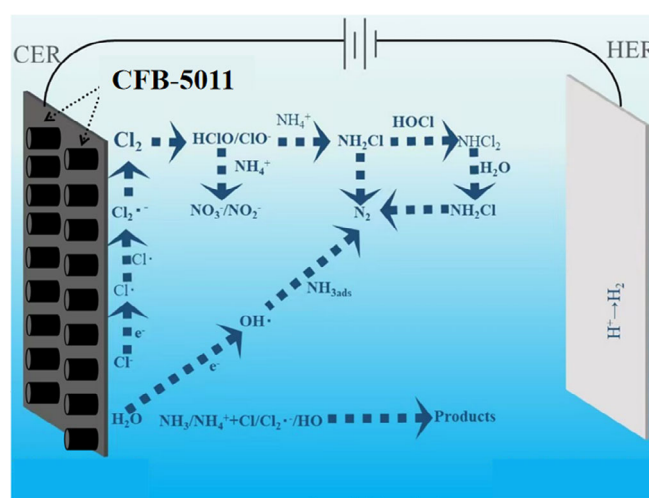
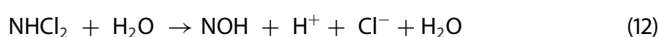
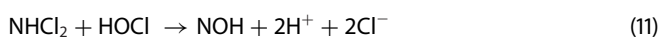
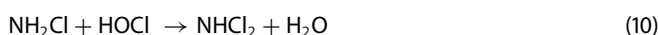
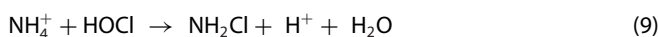


Figure 10. Schematic representation of the ammonia nitrogen degradation process.

NH_2Cl then reacts with $\text{Cl}\cdot$ or $\text{ClO}\cdot$ to form $\text{NHCl}\cdot$, and $\text{NHCl}\cdot$ reacts with active chlorine to form NHCl_2 . Finally, NH_2Cl and NHCl_2 react with NOH in the solution to form N_2 through a series of transformation processes. Therefore, the generation rate of active chlorine and chlorine free radicals is the controlling step in the ammonia nitrogen degradation process. The reactions that occurred were as follows:

Oxidation of reactive chlorine species:



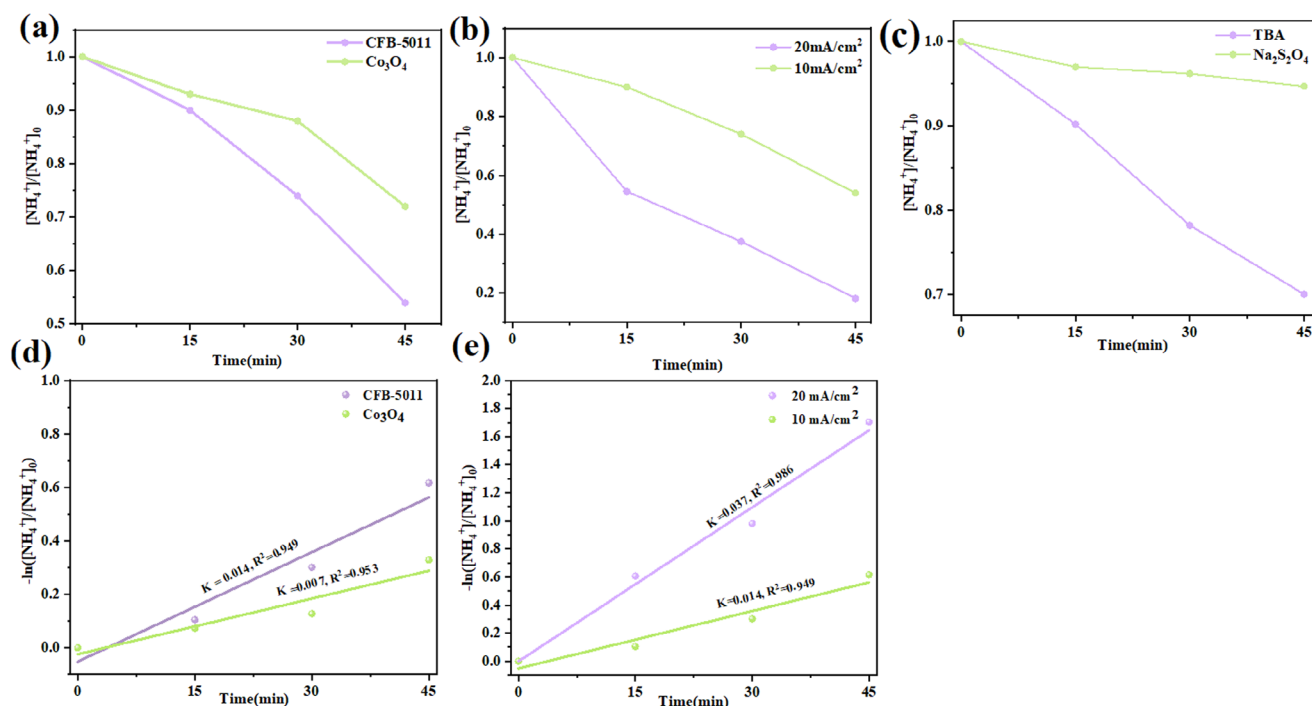
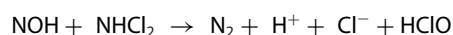
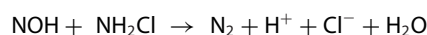
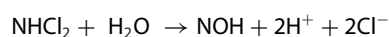
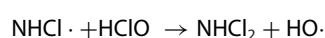
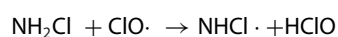
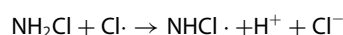
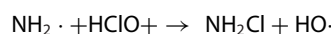
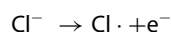


Figure 11. (a) Ammonia nitrogen degradation efficiency of Co_3O_4 , CFB-5011 electrodes, (b) ammonia degradation efficiency of CFB-5011 electrodes at different current densities, (c) explanation of ammonia degradation mechanism, (d) ammonia nitrogen removal rate constants for different electrodes, and (e) ammonia removal rate constants at different current densities.



Chlorine radical oxidation:



In addition, ammonia nitrogen removal follows a pseudo-zero-order kinetic model, as shown in Equation (24).

$$-\ln\left(\frac{[\text{NH}_4^+]_t}{[\text{NH}_4^+]_0}\right) = kt \quad (24)$$

where k (min^{-1}) is the ammonia removal rate constants, $[\text{NH}_4^+]_0$ is the initial ammonia nitrogen concentration, and $[\text{NH}_4^+]_t$ is the ammonia nitrogen concentration after a period of electrolysis. The electrode working environment was tested under neutral conditions to simulate the realistic electrocatalytic oxidation of ammonia nitrogen.^[29] The Co_3O_4 and CFB-5011 electrodes were tested in 60 mM sodium chloride solution to investigate their ability to catalyze ammonia nitrogen degradation by CER reaction in dilute chloride solution. It was found that the current efficiency of the CFB-5011 electrode reached 70.6% under the condition of a current density of 10 mA/cm^2 . In comparison, the current efficiency of the Co_3O_4 electrode was only 62.1% under the same condition. The electrode has a good ability to degrade ammonia nitrogen wastewater. Therefore, the effect of different electrode materials and current density on the removal efficiency of ammonia nitrogen was studied, and the mechanism of ammonia nitrogen degradation was discussed.

Ammonium chloride solution with a nitrogen content of 100 mg/L was prepared as the electrolyte. As shown in Figure 11(a), under a current density of 10 mA/cm^2 , the degradation rate of the CFB-5011 electrode reached 54%, significantly higher than that of the Co_3O_4 electrode (28%). At the same time, the removal efficiency of ammonia nitrogen at a current density of 20 mA/cm^2 was explored, as shown in

Figure 11(b). After 45 min of electrolysis, the concentration of ammonia nitrogen in the solution was detected by spectrophotometry, and the concentration of ammonia nitrogen in the solution was reduced to 18 mg/L after treatment. As shown in Figure 11(d),(e), the CFB-5011 electrode has better ammonia nitrogen removal efficiency and a larger kinetic constant than the Co_3O_4 electrode, and its kinetic constant is 0.014 min^{-1} , which is significantly higher than 0.007 min^{-1} of the Co_3O_4 electrode. At the same time, with the increase of current density, the ammonia nitrogen removal rate maintains a high level. The kinetic constant also reached 0.037 min^{-1} . Although the experiment proved that higher current density and the consequent increase of surface temperature could increase the reaction on the electrode surface to a certain extent, it was worth noting that too high current density was not desirable, because the side reaction of oxygen evolution would also increase.

During the electrolysis of aqueous sodium chloride solutions, a diverse array of oxidants is generated, comprising free chlorine species such as Cl_2 , HOCl , and OCl^- , in addition to radicals like $\cdot\text{OH}$, $\text{Cl}\cdot$, and $\text{Cl}_2\cdot^-$. The mechanism of ammonia removal was elucidated by free radical scavenging experiments using tert-butyl alcohol (TBA) and $\text{Na}_2\text{S}_2\text{O}_4$ as scavengers. TBA can quench $\cdot\text{OH}$, $\text{Cl}\cdot$, and $\text{ClO}\cdot$, while $\text{Na}_2\text{S}_2\text{O}_4$ can quench $\cdot\text{OH}$, $\text{Cl}\cdot$, and $\text{ClO}\cdot$ and other free radicals as well as reactive chlorine species.^[20] The experimental results are shown in Figure 11(c). In the system with TBA, the ammonia nitrogen removal efficiency of the material is not affected. Still, after $\text{Na}_2\text{S}_2\text{O}_4$ is added, the ammonia nitrogen removal efficiency is significantly reduced, indicating that in this electrode system, free radicals and reactive chlorine species serve as the oxidizing agents for the degradation of ammonia nitrogen.

5. Conclusion

In summary, using the hydrothermal method to synthesize Co_3O_4 with high CER activity and selectivity, the experimental results and characterization results show that $\text{Bi}(\text{FeO}_3)$ is complexed with Co_3O_4 , while another part of Fe enters the tetrahedral Co (II) site of Co_3O_4 . In the current efficiency test, CFB-5011 was compared with Co_3O_4 , bare titanium electrode, and DSA electrode. It was found that the current efficiency of CFB-5011 (85.6%) was much higher than that of bare titanium electrodes (66.3%) under the condition of 10 mA/cm^2 . And it was slightly higher than DSA (77.4%) and Co_3O_4 (77.2%). In addition, CFB-5011 can achieve the highest current density at the same electrode potential in the LSV test. After the subsequent ammonia degradation test, it was found that at the current density of 20 mA/cm^2 , after 45 min of electrolysis, ammonia degradation of chlorine could reach 82%, reflecting the practical application potential of CFB-5011. Finally, the mechanism of ammonia degradation was explored by free radical scavenging experiments. This study provides a new design idea for the construction of electrode materials with high activity and selectivity.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Active chlorine · Ammonia nitrogen degradation · Chlorine evolution reaction · Electrocatalysis

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