



Micro-doping tin-bismuth on modification of Co_3O_4 electrocatalyst and degradation of ammonia nitrogen

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ABSTRACT

Co_3O_4 has exhibited chlorine evolution reaction (CER) activity comparable to that of RuO_2 . However, it is plagued by relatively low catalytic activity and insufficient long-term stability. In the field of cobalt oxide doping, typically, a relatively large quantity of dopants is used to modulate its performance. In contrast, the exploration of doping with trace amounts of elements has been scarce. In this study, small amounts of Sn and Bi were introduced into the Co_3O_4 electrocatalyst. The impacts of different doping ratios on the morphology and catalytic performance of the catalyst were systematically investigated. Under specific proportion conditions, the co-doping of these two elements with cobalt tetroxide demonstrated a remarkable synergistic effect. Moreover, a mechanism for the improvement of catalyst performance, based on DFT calculations, was proposed. Subsequently, the ammonia-nitrogen degradation capacity and long-term stability of the modified catalyst were evaluated through ammonia-nitrogen degradation experiments. The degradation mechanism was further elucidated using free-radical scavenging experiments.

1. Introduction

As one of the most important electrochemical reactions, chlorine evolution reaction (CER) is widely used in disinfection and bleaching, wastewater treatment, chloro-alkali industry, and seawater antifouling. Among them, the chlorination evolution reaction is widely used to treat ammonia-nitrogen wastewater. The breakpoint chloride method can efficiently and selectively oxidize ammonia to nitrogen (N_2), the most common strategy for treating ammonia-containing wastewater. However, the application of breakpoint chlorination is greatly limited due to the high cost of chlorine and the difficulty of storage and transportation, so in situ CER in electrocatalytic systems (EC) has been widely developed. DSAs (Dimensionally Stable Anodes) based on ruthenium and iridium are considered to be the basis for the chlorine evolution reaction (CER) in many applications (Wang et al., 2021; Zhou et al., 2022; Liu et al., 2023).

However, DSAs are costly and have relatively poor CER selectivity in both dilute and neutral solutions. At the same time, the dissolution of RuO_2 will cause a decrease in the electrode surface active material content and the catalytic activity. Although various electrocatalysts, such as MOF-derived $\text{RuO}_2/\text{Co}_3\text{O}_4$ (Liu et al., 2017) RuO_2 @ TP,

atom-dispersed $\text{Ru}_1\text{-TiO}_x/\text{Ti}$, and Pt/CNT (Qiu et al., 2023; Lim et al., 2020; Yao et al., 2022) show excellent chlorine evolution selectivity, their demanding synthesis process, and high-cost limit their industrial applications (Al-Shareef et al., 1995). Therefore, it is urgent to develop new anodes with low cost, high activity, and high selectivity to achieve efficient chlorine evolution. In recent years, Co_3O_4 has attracted attention due to its low cost and the high redox potential (1.81 V) exhibited by Co^{3+} . In addition, $\text{Co}^{2+}/\text{Co}^{3+}$ in Co_3O_4 can rapidly oxidize Cl^- to Cl_2 , which opens up a new path for its application in chlorine evolution reactions. For example, Zhang et al. successfully synthesized a Co_3O_4 metal-organic framework material (ZIF-67) to achieve efficient chlorine evolution under neutral seawater conditions (Zhang et al., 2023). Wang et al. prepared a Co_3O_4 anode composed of nano-felt arrays (NBAs) on FTO substrates, which exhibited excellent chlorine evolution performance (Zhu et al., 2018). The iridium-cobalt mixed oxide electrode was also made for efficient chlorine evolution in dilute chloride solutions (Han et al., 2022). However, the catalytic activity of Co_3O_4 still needs to be improved (Zhang et al., 2024a, 2024b).

Studies have found that bimetal doping can effectively adjust the electronic band structure of the catalyst to affect the adsorption and activation of intermediates, effectively improve the surface structure

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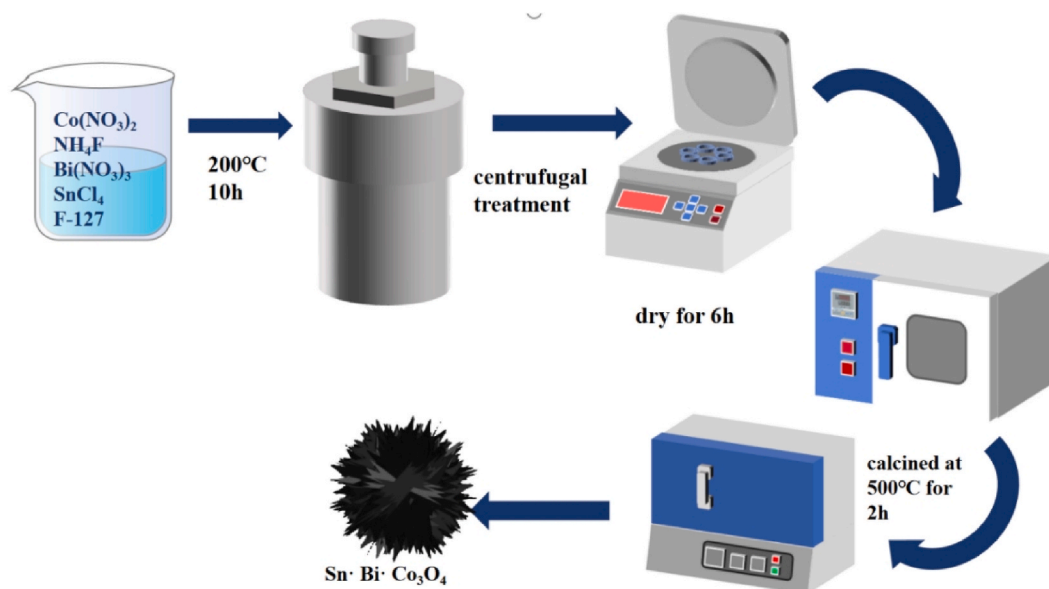


Fig. 1. Experimental flow chart.

and reaction path, and improve the physical properties of the material by inducing structural distortion and generating vacancies. It is considered to be the simplest and efficient method to improve the performance of the catalyst. It is reported that a $\text{Bi}_x\text{Ti}_{1-x}\text{O}_3$ functionalized heterojunction can effectively improve the generation efficiency of active chlorine at the anode in a dilute aqueous solution (Cho and Hoffmann, 2015). In addition, a Sb, Sn co-doped $\text{Sb}_2\text{O}_5\text{-Co}_3\text{O}_4/\text{Sn}$ electrode has also been demonstrated to enhance Cl^- enrichment by inducing the construction of Co (III) sites with strong electron deficit centers, thereby widening the potential difference between CER and OER reaction and promoting CER activity and selectivity at low Cl^- ion concentrations (Tian et al., 2024).

Most doping strategies aim to enhance chlorine evolution efficiency by constructing heterojunctions. In contrast, our research adopts a micro-doping strategy, which achieves similar performance enhancement in chlorine evolution by regulating charge distribution but operates through a different mechanism. The specific mechanism involves utilizing the abundant lone pair electrons in the outer electron orbit of Cl^- . Through strong interactions between these electrons and the vacancies in the outer orbit of transition metals, we construct Co(III) sites with strong electron-deficient centers on the Co_3O_4 anode to enhance Cl^- enrichment. This, in turn, effectively improves the CER activity and selectivity of Co_3O_4 (Zhang et al., 2022; Wang et al., 2023).

It is well-known that elements such as Sn (with an electronegativity value of 1.96) or Bi (with an electronegativity value of 1.90) have larger electronegativity values than Co (1.88). In this case, the electrons of Co may be induced to migrate towards Sn and Bi, potentially generating a strong electron-deficient (III) center.

To verify the above hypothesis, in this study, small amounts of Sn and Bi were co-doped into the Co_3O_4 electrocatalyst. The impacts of different doping ratios on the morphology and catalytic performance of the catalyst were thoroughly investigated.

An olive-like Sn, Bi co-doped Co_3O_4 catalyst was synthesized via the hydrothermal method. Its morphology, crystal structure, and surface state were characterized using SEM, XRD, and XPS. The electrochemical performance and chlorine evolution performance of the electrode were evaluated through electrochemical tests. The effects of different Sn and Bi doping levels on the properties of Co_3O_4 materials, as well as the performance of electrocatalytic CER for ammonia - nitrogen degradation, were meticulously studied (Shang et al., 2021).

2. Experimental methods and materials

2.1. Experimental materials

Reagents including concentrated sulfuric acid, starch, NaCl, KI, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, NaCl, KI, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, etc. were commercially available reagents and could be used without further purification. All the reagents used in this experiment were purchased from the Aladdin's company. Pure titanium plate was purchased from Sher Technology Co., Ltd.

2.2. Synthesis of anode

Preparation of electrodes mainly includes four steps: pretreatment of titanium matrix, preparation of active substances, preparation of coating solution, and preparation of electrode.

1) Titanium matrix pretreatment

First, the titanium plate was removed from oil and then etched with oxalic acid. The detailed operation steps are shown in the supporting information.

2) Preparation of active substances

Weighing 2.619g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and different amounts of $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 30 ml solution was prepared by weighing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ at the different ratio of Co: Sn: Bi, and added 0.4 g F-127 and ascorbic acid 0.11g, stirring for 30 min. After complete dissolution, the solution was transferred to the hydrothermal reaction system at 200 °C for 10 h, and the pressure during the hydrothermal reaction was about 0.176 MPa, the resulting solution was washed with ethanol, and the precipitate was collected by centrifugation. It was dried at 60 °C for 6 h and then annealed at 5 °C/min at 500 °C. The resulting materials were named Co_3O_4 , CB-501 (Co: Sn: Bi = 50: 0: 1), CS-501 (Co: Sn: Bi = 50: 1: 0), CSB-5011 (Co: Sn: Bi = 50: 1: 1), CSB-5031 (Co: Sn: Bi = 50: 3: 1), and CSB-5033 (Co: Sn: Bi = 50: 3: 3) respectively. The experimental process is shown in Fig. 1.

3) Preparation of electrode coating solution

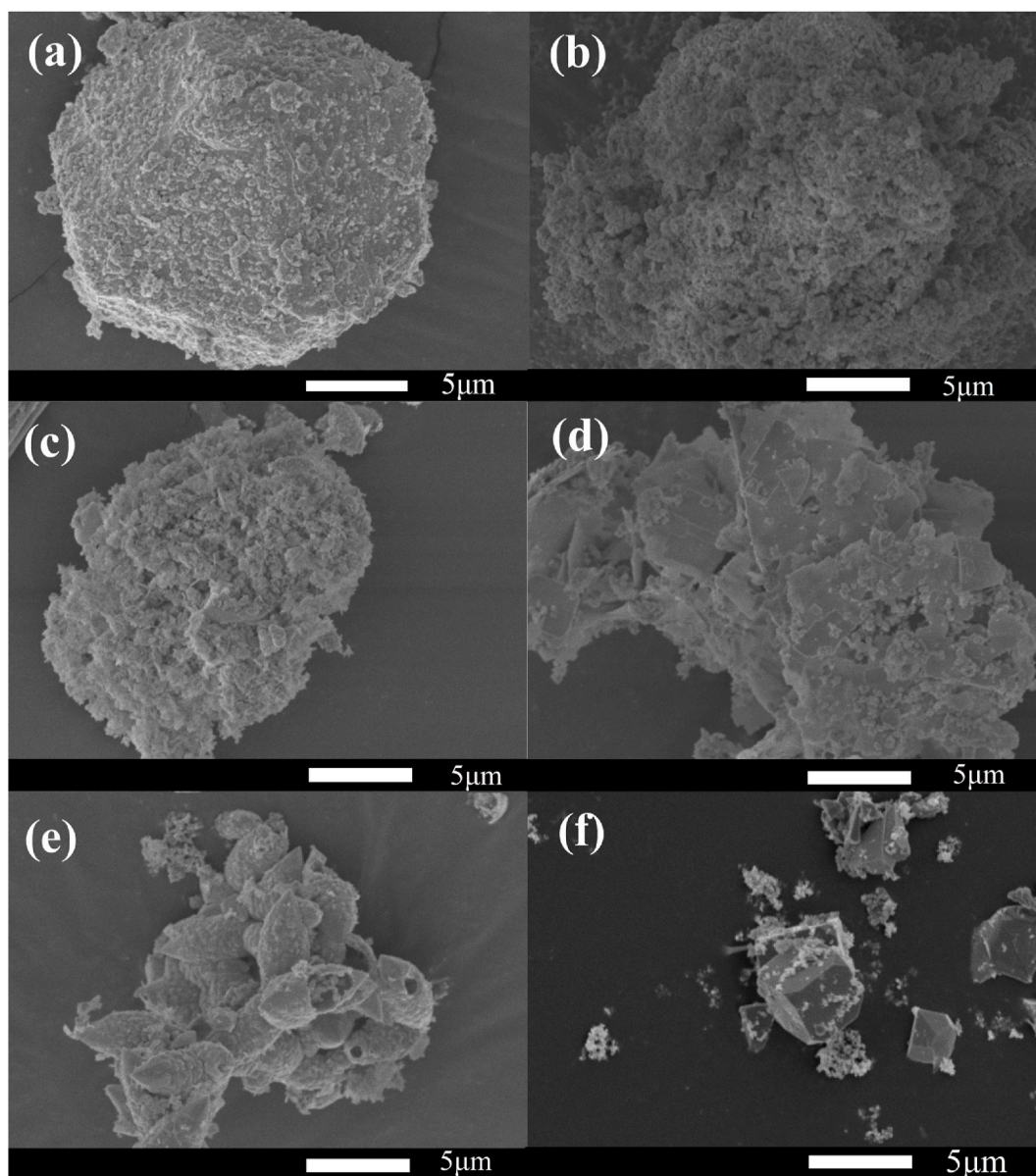


Fig. 2. SEM images of (a) Co₃O₄, (b) CB-501, (c) CSB-5031, (d) CSB-5033, (e) CB-5011, (f) CS-501.

According to the mass ratio of 8:1:1, take the active substance, polyvinylidene difluoride (PVDF), and acetylene black into the test tube, add the appropriate amount of *n*-methyl pyrrolidone, and ultrasonically to make it homogeneous until the test tube appears in black oily material, and then stop.

4) Preparation of the electrode

The pre-etched titanium plate was removed and dried, and the black oil material 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

The surface morphology and chemical composition of the electrodes were detected by a scanning electron microscope (SEM; JSM-6610LV) and combined with an energy dispersion X-ray spectroscopy system (EDS; Sigma 300). The crystal structure and the surface state were characterized by X-ray diffraction (XRD; Bruker D8-Advance) and X-ray

photoelectron spectroscopy (XPS; Thermo ESCALAB 250XI). Transmission electron microscope (TEM) test was carried out on JEOL JEM 2100F/F200. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was conducted on Agilent 7800 ICP-MS machine.

2.3.2. Electrochemical testing

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. Chronopotentiometry (CP) was used to assess electrode stability, the electrode was tested in 0.6 M NaCl solution at a current density of 10 mA/cm². The specific experimental steps are supplemented in the supporting information.

2.3.3. Evaluation of chlorine Separation efficiency

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.

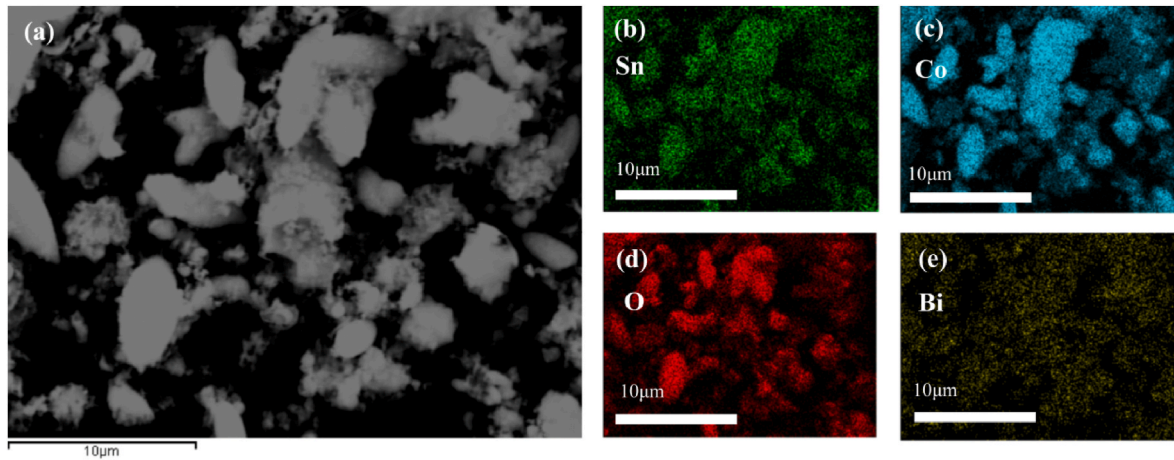


Fig. 3. (a–e) EDS of CB-5011.

Table 1

BET surface area and the adsorption average pore width of the material.

Material	BET Surface Area (m ² /g)	Adsorption average pore width (nm)
Co ₃ O ₄	10	20
CB - 501	13	20
CSB - 5011	21	14
CSB - 5031	22	13
CSB - 5033	20	9

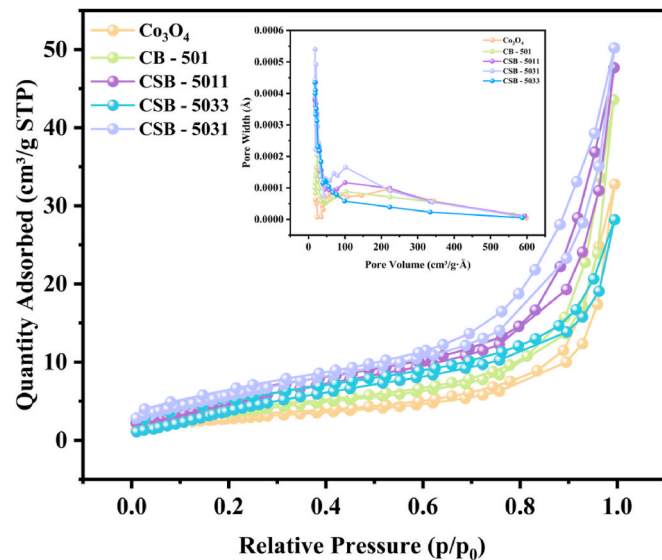
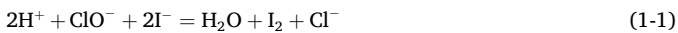


Fig. 4. BET and BJH pattern.



$$P_{\text{Cl}} = (C_1 \times V_1 \times 35.45) \div V_{\text{Cl}} \quad (2)$$

$$\text{CER}(\%) = (C_2 \times V_2 \times n \times F) \div (I_2 \times t_2) \quad (3)$$

The specific reaction equations are as above.

2.3.4. Methods for the detection of NH_4^+ concentrations

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 paper's supporting information.

The ammonia nitrogen concentration in the water sample was calculated as follows.

$$\rho_n = \left[\frac{A_s - A_b - a}{b \times V} \right] \times D \quad (4)$$

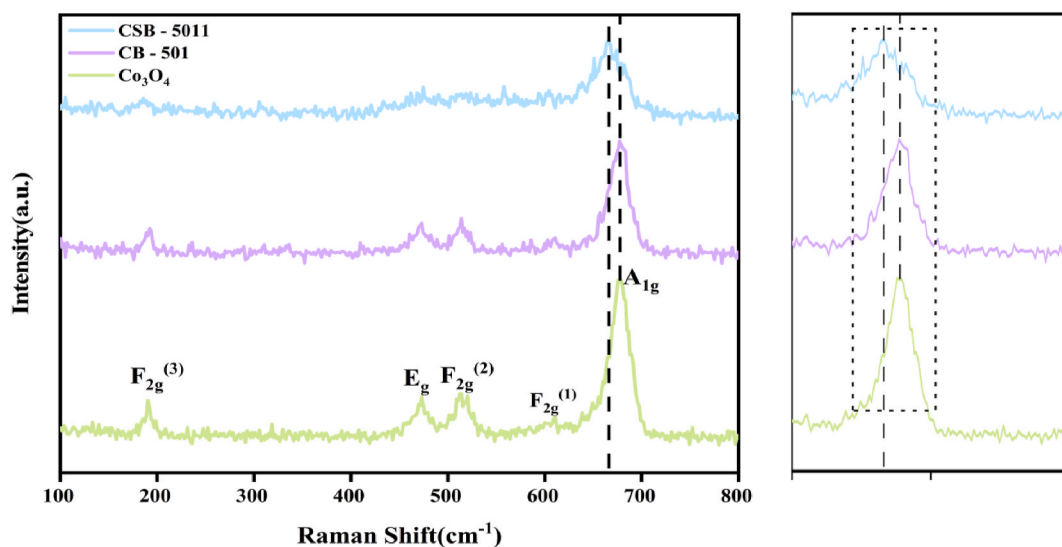
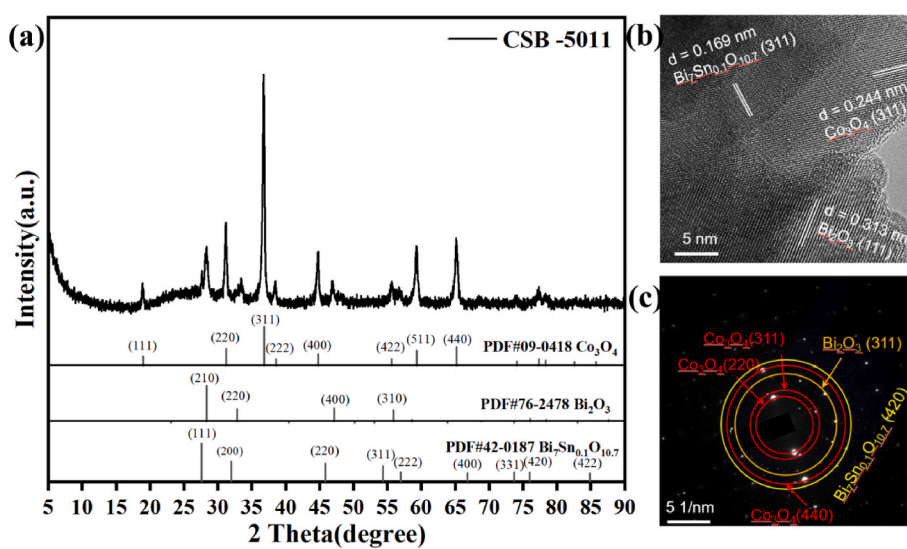
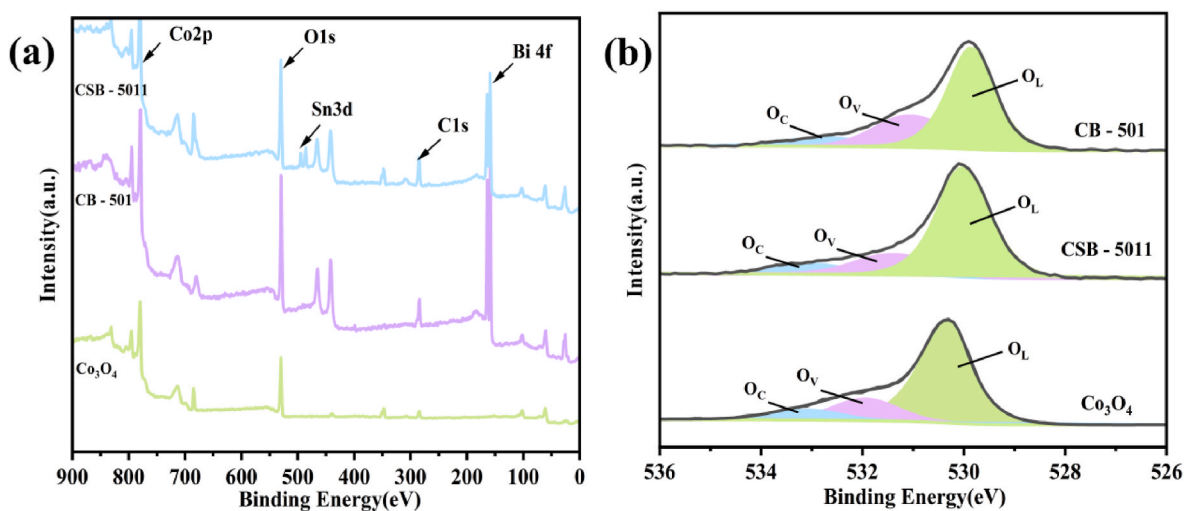
In Equation (4), ρ_n is the ammonia nitrogen concentration (mg/L) in the water sample to be tested, A_s is the absorbance of the sample, A_b is the absorbance of the blank experiment, a is the intercept of the calibration curve, b is the slope of the calibration curve, V is the volume of the water sample, and D is the dilution factor of the water sample.

3. Results and discussion

3.1. Structural features

Fig. 2(a–f) shows SEM images of the five materials. From Fig. 2(a), it can be seen that Co_3O_4 has a regular spherical structure. With the introduction of the Bi element, the surface of the CB-501 material appears dense and irregular small voids (Fig. 1(b)), SEM images show CSB-5031, CSB-5033, and CSB-5011 with sponge, sheet, and olive structures respectively (Fig. 2(c–e)), which indicates that different Sn and Bi doping ratios have a very significant effect on the microscopic morphology of Co_3O_4 materials. Fig. 2(f) is the SEM image of CS-501, and we can see that the material presents a cubic shape. EDS results (Fig. 3(a–e)) show that the Co, Sn, Bi, and O elements are uniformly distributed in CSB-5011.

In N_2 adsorption-desorption isotherm (Fig. 4 and Table 1), all materials present type IV isotherms and H_3 -type hysteresis rings, which means the material has mesoporous characteristics. In a certain range, with the addition of Sn and Bi elements, the specific surface area of the material increased significantly from 10 (m²/g) of the original Co_3O_4 material to 21(m²/g) of CSB - 5031 material. A larger specific surface area facilitates superior contact between the electrolyte and the electrode surface, while simultaneously exposing a greater number of active sites. In addition, the pore size of the material will also decrease with the addition of Sn and Bi elements, indicating that a porous structure is formed on the surface of the material, and the presence of more pores improves the permeability of the electrolyte solution, promoting the release of chlorine gas, and minimizing the bubble shielding effect. At the same time, it is worth noting that in CSB-5033, with the increase of specific surface area, the catalytic performance of the material does not improve significantly, which may be because when the molar ratio of Sn and Bi is too high, the surface catalytic active site Co (III) may be replaced, resulting in the decline of the catalytic performance of the

Fig. 5. Raman spectra of Co_3O_4 , CB-501, CSB-5011.Fig. 6. (a) The XRD patterns of CSB – 5011, (b–c) TEM images of Co_3O_4 doped by Sn and Bi.Fig. 7. (a) XPS of Co_3O_4 , CB-501, CSB-5011 Survey spectrum, (b) O 1s spectrum.

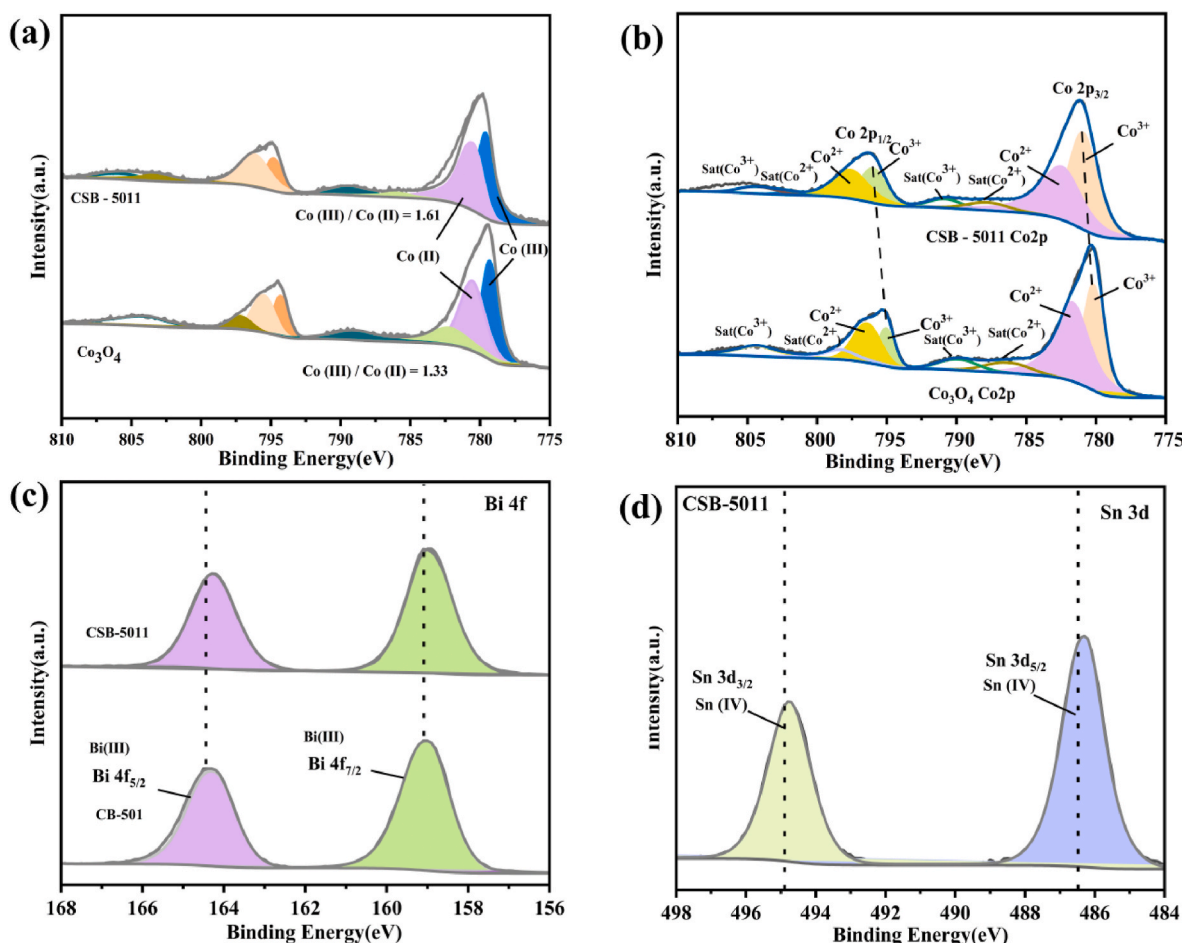


Fig. 8. (a) The ratio of Co(III) to Co(II) in CSB-5011 and Co_3O_4 , XPS of the materials: (b) Co 2p, (c) Bi 4f, (d) Sn 3d.

material.

Fig. 5 shows Raman spectra of the material, showing five vibrational peaks ($A_{1g} + E_g + 3F_{2g}$) in the range of $100\text{--}2000\text{ cm}^{-1}$ Raman shifts. It is worth noting that the positions of the Raman peaks of $F_{2g}^{(3)}$ and A_{1g} of CB-5011 both shift to lower frequencies (redshift) and the peak intensity of A_{1g} decreases, indicating a slight change in the electron configuration of Co after the introduction of Bi and Sn. The above results verified the successful introduction of Bi and Sn into Co_3O_4 . Based on the Raman spectra, it can be found that the spectral half-peak width of CSB-5011 is larger than that of the other two materials. A larger half-peak width implies a smaller particle size, lower crystallinity, and the presence of more defects and impurities in the crystal. In contrast, the variation in the half-peak width of CB-501 compared to Co_3O_4 is insignificant. Incorporating the subsequent XPS and XRD tests, we hypothesize that the Sn element might have entered Co_3O_4 in the form of Sn(IV). At the same time, the lower crystallinity and the existence of more defects in the crystal have a certain positive influence on the catalytic performance of the material.

Fig. 6 shows the XRD pattern of the material CSB-5011, which is mainly composed of Co_3O_4 , Bi_2O_3 , and $\text{Bi}_7\text{Sn}_{0.1}\text{O}_{10.7}$ (Wang et al., 2022a). The XRD pattern shows that only a tiny amount of Sn binds Bi to form $\text{Bi}_7\text{Sn}_{0.1}\text{O}_{10.7}$, at the same time, the Raman spectrum of the material CB-5011 was observed to be redshifted, the intensity of the A_{1g} peak was reduced, and the presence of Sn element in EDS indicated that Sn was likely to be doped into the crystal lattice of Co_3O_4 (Chen et al., 2017; Jiang et al., 2020).

Fig. 6 (b) is the transmission electron microscope (TEM) image of CSB-5011. According to the structure and morphology of the transmission electron microscope image, more understanding of CSB-5011

has been obtained. The plane spacing of the lattice stripes of the material is 0.169, 0.244, and 0.313 nm, corresponding to the (311) crystal plane of $\text{Bi}_7\text{Sn}_{0.1}\text{O}_{10.7}$, the (311) crystal plane of Co_3O_4 , and the (111) crystal plane of Bi_2O_3 respectively. The crystalline nature of CSB-5011 was further confirmed by the corresponding SAED profile (Fig. 6 (c)). In addition, since only short and disordered lattice stripes can be seen from Fig. 6 (b), it further indicates that the lattice defects within the CSB-5011 crystal are serious.

XPS spectroscopy can be used to study the surface states of materials. Strong peaks such as Co 2p, Bi 4f, O1s, and Sn 3d can be observed in the XPS spectrum of CB - 5011 (Fig. 7 (a)). Fig. 7 (b) shows the O1s spectra of the three materials. The spectra with a peak at 530 eV are due to lattice oxygen, as can be seen from the above table, with the doping of Sn and Bi, the proportion of O_V in CSB-5011 increases, and more O_V can effectively change the energy band structure of metal oxides, reduce the adsorption energy of reactants on the catalyst surface, thus reducing the reaction energy barrier and promoting molecular activation. This may also be one of the reasons for the improved catalytic performance of CSB-5011 (Correa-Baena et al., 2016; Haverkamp et al., 2011). By comparing the content of Co (III) and Co (II) in Co_3O_4 before and after doping in Fig. 8 (a), it is found that after the simultaneous introduction of Sn and Bi, the ratio of Co (III)/Co (II) increased slightly, from 1.33 to 1.61.

However, the same phenomenon was not observed when Bi was introduced into Co_3O_4 alone. Since the ratio of Co (III)/Co (II) remained the same after Bi was introduced alone, after both Sn and Bi were introduced, the decreases in the Co (III)/Co (II) ratio should be attributed to Sn possibly occupying the Co (II) position.

Fig. 8 shows the fine spectrum of Co 2p. It is worth noting that the

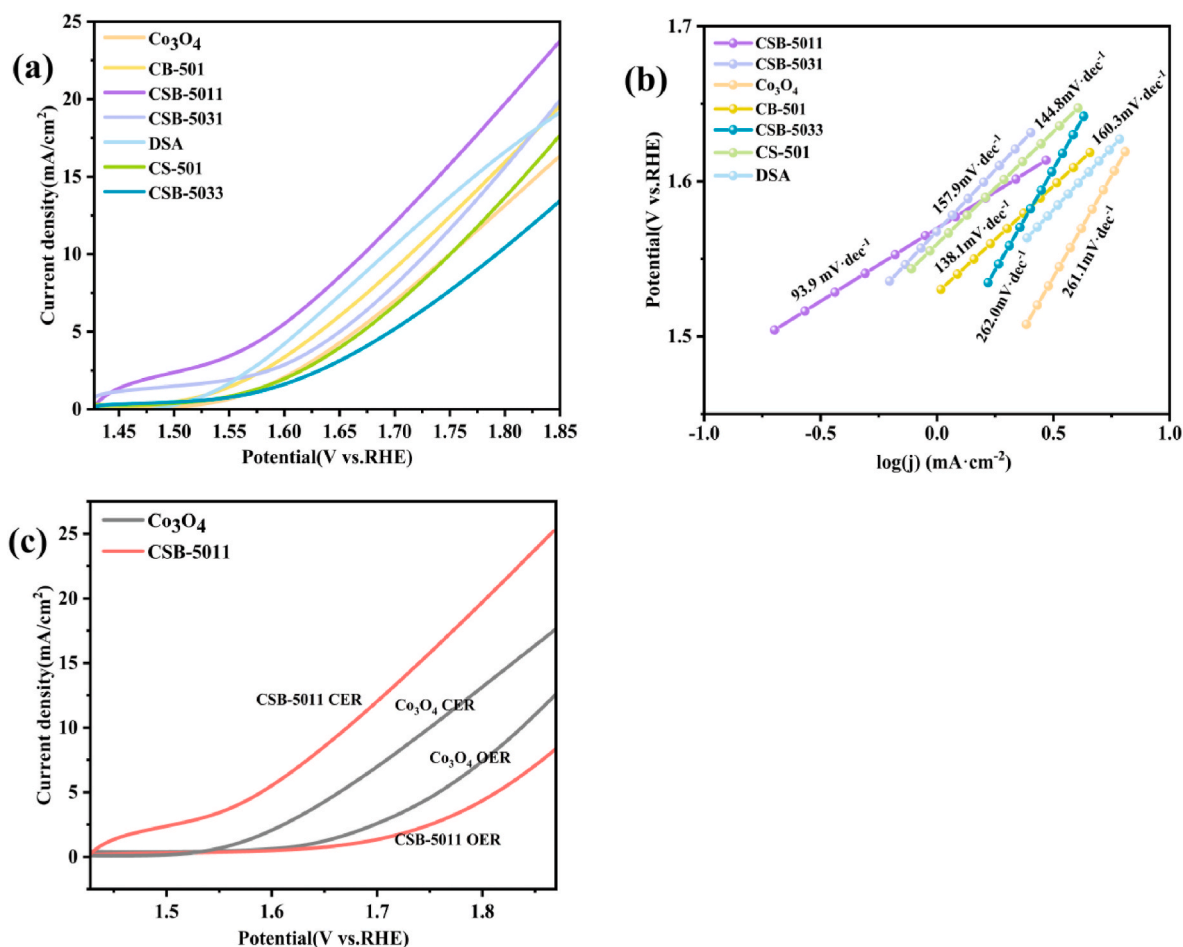


Fig. 9. (a) The LSV of Co₃O₄, CB - 501, CS-501, CSB - 5011, CSB - 5031, DSA and CSB - 5033 electrodes in 0.6M NaCl (b) Tafel slope of Co₃O₄, CB - 501, CS-501, CSB - 5031, DSA and CSB - 5033, DSA electrodes, (c) The LSV of Co₃O₄ and CSB - 5011 in 0.6M NaCl solution and 0.6M NaNO₃.

XPS spectrum of Co₃O₄ changes with the introduction of Sn and Bi elements. The binding energies of the Co 2p_{1/2} and Co 2p_{3/2} orbitals of CB - 501 significantly increase from 794.6eV to 779.6eV–795.3eV and 780.4eV, respectively, indicating that the electron cloud around Co (III) in Co₃O₄ moves toward Bi, as a result, the Co (III) with an electron-deficient center is formed.

Thus, it is speculated that Sn and Bi have a synergistic effect on the construction of the electron-deficient center, so the mechanism of the enhancement of the catalytic performance of the CER reaction of the material can be summarized as follows: introduction of highly electronegative Sn and Bi elements into Co₃O₄ can synergistically induce the construction of a strong electron-deficient center at the Co (III) site, resulting in enhanced binding between Co (III) and Cl⁻, leading to improved CER activity and selectivity (Wang et al., 2022b).

3.2. Electrochemical testing

Fig. 9 (a) is the LSV curve of the material in 0.6 M sodium chloride solution, the LSV test evaluates the catalytic performance of the prepared electrode, and the catalytic performance of the prepared electrode is judged by comparing the electrode potential under the same current density, and the LSV curve can be found in the case of a current density of 10 mA/cm². CSB - 5011 has the lowest potential compared to the other four materials, indicating that it has the best activity in the chlorine evolution reaction (Zhang et al., 2019).

The lower the Tafel slope value, the slower the rise of the overpotential, and the smaller the Tafel slope indicates that the catalyst has better catalytic activity. As shown in Fig. 9 (b), the image shows that the

minimum Tafel slope of the CSB-5011 electrode is 93.9 mV·dec⁻¹, the Tafel slope of the Co₃O₄ electrode is 261.1 mV·dec⁻¹, indicating that the doping of Sn and Bi can effectively improve the CER reactivity of Co₃O₄ (Zhang et al., 2023; Qiu et al., 2022). It is worth noting that the Tafel slope of the DSA electrode is 160.3 mV·dec⁻¹, which is much higher than 93.9 mV·dec⁻¹, indicating that CSB-5011 can show much better catalytic performance than the DSA electrode under certain conditions.

The OER reaction often occurs in the electrochemical process at the same time as a competing reaction of CER, so to ensure the current efficiency in the electrolysis process, the CER anode should have good selectivity, and the LSV curves are now measured in chlorine-containing and chlorine-free solutions using the blank Co₃O₄ electrode as a reference. Fig. 9 (c) shows that the electrocatalytic activity of the CSB-5011 electrode in 0.6 M NaCl is higher than that of the Co₃O₄ electrode. In comparison, the electrocatalytic activity in 0.6 M NaNO₃ is lower than that of the blank Co₃O₄ electrode. Therefore, the CSB-5011 electrode exhibits better selectivity for chlorine evolution than Co₃O₄ (Ha et al., 2019).

Fig. 10 shows the CV diagram of the prepared electrode at different sweep speeds. It is generally similar to a rectangle and shows an ideal rectangular CV curve, which indicates that the material has good stability in this potential range and is not prone to redox reaction.

The electrochemical surface area (ECSA) is mainly used to evaluate the relationship between a material's specific surface area and its electrocatalytic performance. It is calculated as shown in (5) (Chi et al., 2021; Hu et al., 2021).

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

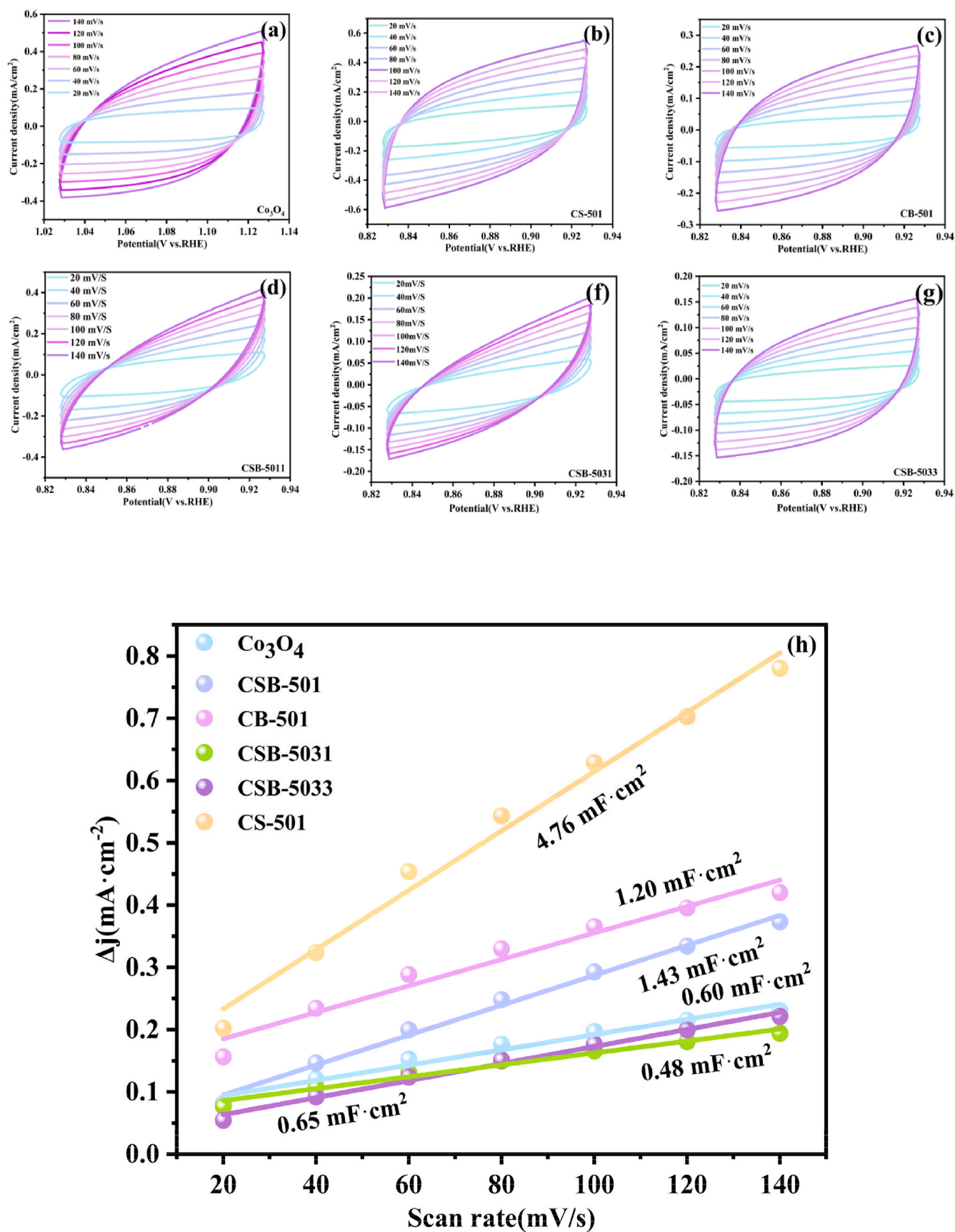


Fig. 10. (a–g) The CV of Co_3O_4 , CB - 501, CS-501, CSB - 5011, CSB - 5031 and CSB - 5033, electrodes in 0.6 M NaCl solution, (h) The C_{dl} of Co_3O_4 , CB - 501, CS-501, CSB - 5011, CS-501, CSB - 5031 and CSB - 5033 electrodes.

Table 2The O_L, O_V, O_C XPS results of Co₃O₄ doped with different molar ratios of Sn, Bi.

Sample	Co ₃ O ₄	CB-501	CSB-5011
O _L	76 %	64 %	68 %
O _V	14 %	35 %	26 %
O _C	10 %	5 %	6 %

where Cs is the capacitance value corresponding to the ideal electrode with a smooth surface, the value is 60 $\mu\text{F}/\text{cm}^2$. Cdl is the capacitance value of the electric double layer (mF/cm^2); S is the area of the electrode (cm^2).

As can be seen from Fig. 10, the Cdl value of the CB-501 electrode is 1.20 mF/cm^2 , the Cdl value of the CSB-5011 electrode is 1.43 mF/cm^2 , while the Cdl value of the Co₃O₄ electrode is 0.60 mF/cm^2 , the Cdl of the electrode that doped Sn, Bi elements is larger than the Co₃O₄ electrode. Because the electrochemical active area (ECSA) is proportional to Cdl. Thus, the ECSA of the CB-501, CSB-5011 electrode is greater than the ECSA of the Co₃O₄ (Pu et al., 2014).

Fig. 11 (a) shows the prepared material's Nyquist plot, which characterizes the electron transport efficiency of the prepared material as an anode during the CER process by electrochemical impedance spectroscopy (EIS). Table 3 shows that the R_{ct} of CSB-5011 is also smaller, the smaller R_{ct} means a smoother charge transfer process, higher electrode reactivity, and smaller interface resistance, which means a higher charge transfer efficiency (Cheng et al., 2022).

The exact resistance values are shown in Table 3 below:

Based on the analysis of the results of the electrochemical tests above, the CSB-5011 electrode has the highest current density and the lowest Tafel slope at the same electrode potential, so it is considered to have the best catalytic activity. C_{dl} was used to evaluate the electrochemically active area (ECSA) at the contact between the electrolyte and the electrode surface. The C_{dl} value of the CSB-5011 electrode was second only to CS-501, indicating that the ECSA value of the CSB-5011 electrode was also larger. In the Nyquist diagram of the electrode, the CSB - 5011 anode exhibits a lower charge transfer resistance which is

Table 3

Exact resistance values of electrodes.

Samples	Co ₃ O ₄	CB-501	CSB-5011	CSB-5031	CSB-5033	CS-501
Rs(Ω)	1.959	1.553	2.415	0.915	0.283	2.09
Cdl($\mu\text{F}.\text{cm}^2$)	541.6	989.3	4798	1564	2807	1731
nd	0.842	0.787	0.789	0.801	0.855	0.766
Rct(Ω)	542.8	425.3	146.2	103.1	130.4	1317

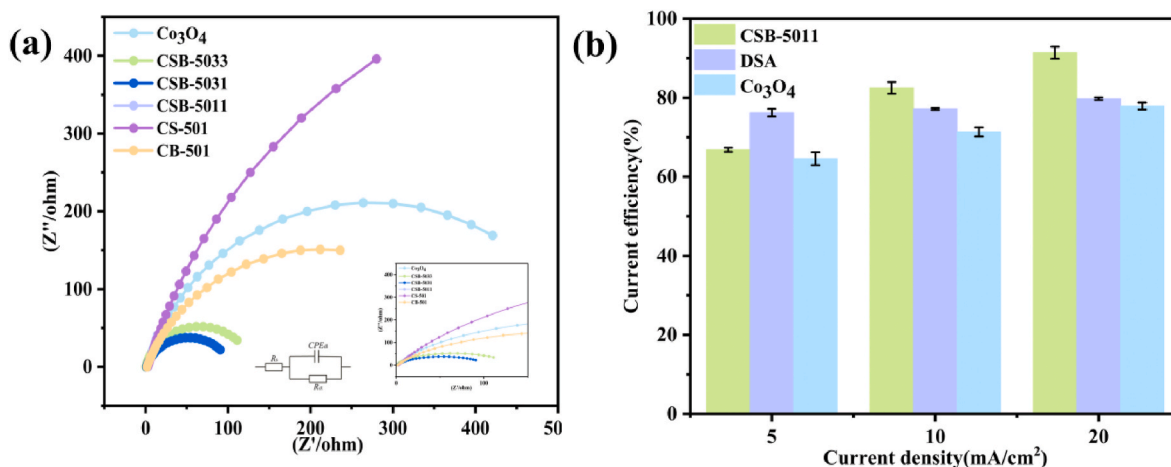


Fig. 11. (a) Nyquist plots of Co₃O₄, CB-501, CS-501, CB-5011, CSB-5031, and CSB-5033 electrodes in 0.6 M NaCl, (b) CER current efficiencies of Co₃O₄ and CSB-5011 electrodes in various current densities.

also an important factor in the improvement of its electrocatalytic performance (Chen et al., 2022).

3.3. Evaluation of chlorine separation efficiency of electrodes

To explore the electrochemical performance of the prepared electrode, current efficiency tests were carried out at different current densities and concentrations of sodium chloride solution. In Fig. 11 (b), at current densities of 5, 10, and 20 mA/cm^2 , the CSB-5011 electrode has a higher current efficiency compared to the Co₃O₄ electrode and the DSA electrode. At a current density of 20 mA/cm^2 , the current efficiency is 92 %. However, when the current density is low (5 mA/cm^2), DSA electrode has a higher current efficiency than CSB-5011. When the current density increases, the current efficiency of CSB-5011 increases significantly.

The solution with 0.01M, 0.1M, 0.6M, and 3M sodium chloride concentrations was carried out the current efficiency test, respectively. The experimental results are shown in Table 4 below.

It was found that as the ion concentration in the electrolyte decreased, the current efficiency decreased significantly. These results indicate that the chlorine evolution performance of the CSB-5011 electrode in chloride solution is not ideal, so it does not have obvious advantages in the application of dilute chloride solution, which is also one of the reasons for the unsatisfactory degradation rate of dark ammonia nitrogen of the electrode. When the NaCl concentration was further increased, the chlorination efficiency did not change significantly, even at concentrations approximating seawater ($\approx 0.6\text{M}$) or up to 3M. This may be because the effect of the conductivity on the formation of free

Table 4

Current efficiency in different concentrations of sodium chloride solutions.

	0.01M	0.1M	0.6M	3M
CSB-5011	47.3 %	67.4 %	82.1 %	88.4 %
Co ₃ O ₄	42.7 %	62.1 %	71.7 %	83.6 %
DSA	66.7 %	74.2 %	77.4 %	84.1 %

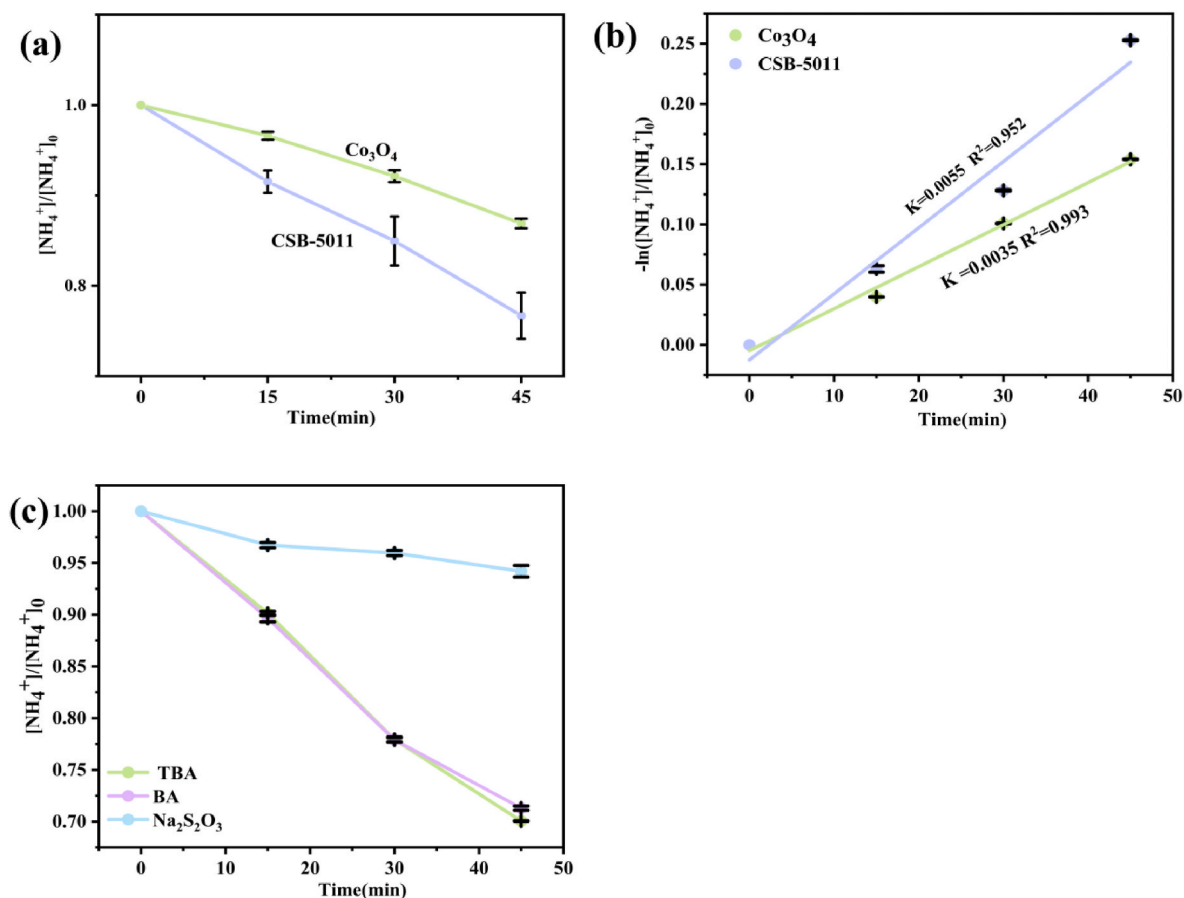


Fig. 12. (a) Ammonia degradation efficiency of Co_3O_4 and CSB - 5011 for 45 min, (b) Kinetic study of ammonia nitrogen removal with different electrodes, (c) Mechanism of ammonia nitrogen degradation by CSB-5011 electrodes in different scavengers.

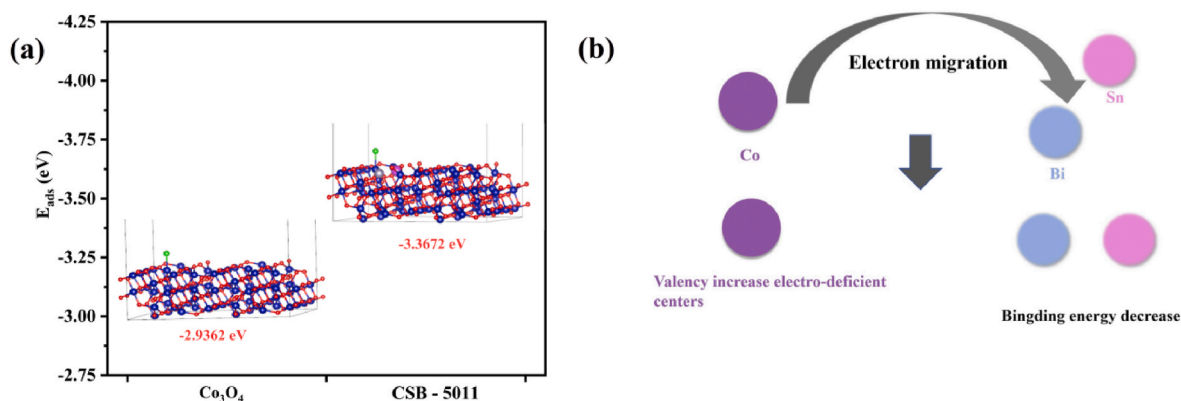


Fig. 13. (a) Adsorption of the energy between Cl^- and the structural Co(III) in the Co_3O_4 and CSB-5011 electrodes, (b) Schematic diagram of charge transfer.

chlorine during electrolysis becomes negligible after the chloride concentration reaches 0.6M. In other words, excess chloride ions no longer react with electrons, so the concentration of free chloride no longer increases with increasing sodium chloride concentration. Alternatively, the reactive surface of the electrode may be limited or the decomposition of free chlorine may have occurred at the cathode. Combined with the above electrochemical test results, compared with the DSA electrode, the current efficiency and selectivity are greatly improved under the current density of 10 mA/cm^2 in 0.6M sodium chloride solution. However, it is worth noting that the current of CSB-5011 is greatly affected by chloride ion concentration, and the current efficiency is significantly reduced in extremely dilute sodium chloride solution.

4. CSB-5011 electrodes used for ammonia nitrogen degradation in dilute chlorides

The effect of different electrode materials on the removal efficiency of ammonia nitrogen was studied, and the mechanism of ammonia nitrogen degradation was discussed (Lima et al., 2009). 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

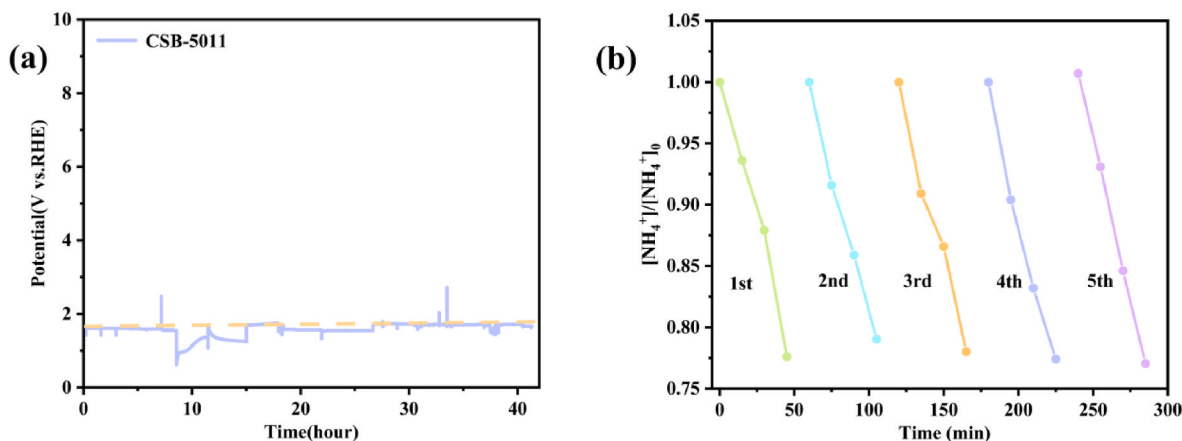


Fig. 14. (a) Cell voltage with time in the stability test of CB-5011 electrodes (b) Stability of the CSB-5011 electrodes in ammonia degradation tests.

Table 5
ICP-MS decomposition results.

	Co($\mu\text{g/L}$)	Sn($\mu\text{g/L}$)	Bi($\mu\text{g/L}$)
Before stability test	0	0	0
After stability test	72.356	22.218	267.714

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 electron transfer rate restricts the direct oxidation route, leading to a prolonged kinetic process and a relatively poor oxidation efficiency for ammonia nitrogen (Zöllig et al., 2015). Additionally, in acidic conditions, the main product of ammonia nitrogen oxidation is nitrate instead of nitrogen gas, which may cause secondary pollution issues in the environment. Therefore, all ammonia degradation tests were performed under neutral conditions (Lima et al., 2009).

The indirect oxidation pathway refers to the oxidation of ammonia nitrogen by reactive chlorine or chlorine radical radicals generated by the electrolysis process. The specific reaction equation and schematic diagram can be seen in the supporting information.

In addition, ammonia nitrogen removal follows a pseudo-zero-order kinetic model, which is shown in Equation 7

$$-\ln\left(\frac{[\text{NH}_4^+]}{[\text{NH}_4^+]_0}\right) = kt \quad (7)$$

Where k (min^{-1}) is the ammonia removal rate constant, $[\text{NH}_4^+]$ is the initial ammonia nitrogen concentration, and $[\text{NH}_4^+]_0$ is the ammonia nitrogen concentration after a period of electrolysis.

An electrolyte with an ammonia nitrogen concentration of 100 mg/L was prepared to test the efficiency of ammonia nitrogen removal. As

shown in Fig. 12 (a), compared with the Co_3O_4 electrode, the ammonia nitrogen removal rate of the CSB-5011 electrode was significantly improved under the same conditions. Besides as shown in Fig. 12 (b), the dynamic constants of CSB-5011 are 0.0055min^{-1} , while those of Co_3O_4 are only 0.0048min^{-1} , indicating a significant improvement. Various oxidants are generated during the electrolysis of aqueous sodium chloride solutions, including free chlorine (Cl_2 , HOCl , and OCl^-), $\cdot\text{OH}$, $\text{Cl}\cdot$, and Cl_2 radicals. Tert-butyl alcohol (TBA), $\text{Na}_2\text{S}_2\text{O}_3$, and benzoic acid (BA) were selected as scavengers to elucidate the ammonia oxidation mechanism. It has been reported that BA can only quench $\cdot\text{OH}$ and $\text{Cl}\cdot$, while TBA can quench $\cdot\text{OH}$, $\text{Cl}\cdot$ and $\text{ClO}\cdot$, and $\text{Na}_2\text{S}_2\text{O}_3$ can quench $\cdot\text{OH}$, $\text{Cl}\cdot$ and $\text{ClO}\cdot$ free radicals and reactive chlorine species. As shown in Fig. 12 (c) BA and TBA in the reaction system do not significantly inhibit the ammonia removal rate. But, when $\text{Na}_2\text{S}_2\text{O}_3$ was added, the ammonia removal rate was significantly inhibited. This suggests that the oxidants for ammonia degradation in the CSB-5011 electrode system are chlorine radicals and reactive chlorine species (Chen et al., 2017).

5. Enhanced enrichment mechanism of Cl^- at Co(III)

In general, as the electron density around the atom decreases, the absorption and scattering effects of the atom on the X-ray photoelectron spectroscopy (XPS) photon will decrease accordingly, leading to an increase in the binding energy. As shown in Fig. 8 (b), the binding energy of Co (III) in CSB-5011 does grow slightly compared to Co_3O_4 , indicating that the electron cloud around Co (III) moves toward Bi and Sn, leading to the formation of electron-deficient Co (III).

To better understand the mechanism of Sn and Bi elements in improving the catalytic performance of Co_3O_4 , XPS analysis of the Bi element in CB-501 and the comparison of the Sn element in CSB-5011 with the standard binding energy were also performed. The binding

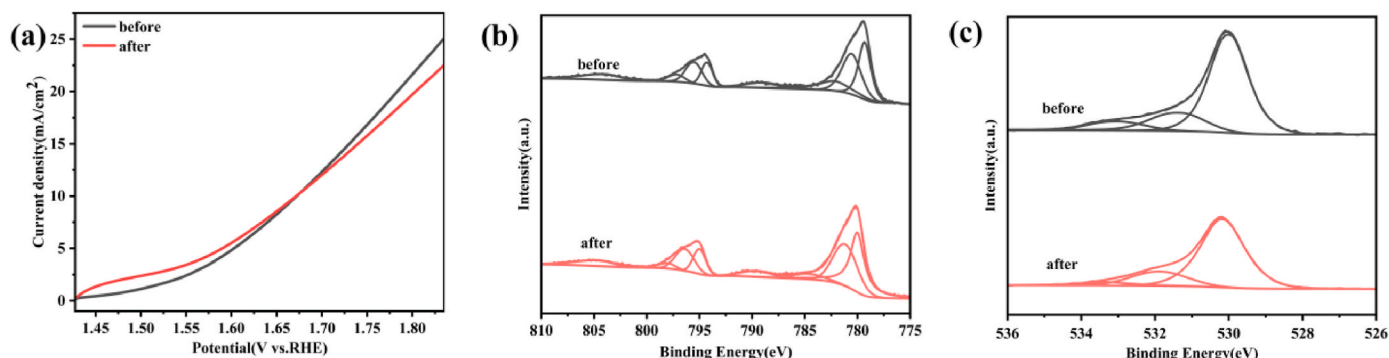


Fig. 15. (a) LSV images before and after stability testing, (b-c) XPS comparison of Co and O elements in CSB-5011 before and after stability test.

energies of Co 2p_{1/2} and Co 2p_{3/2} orbitals of Co₃O₄ are unchanged before and after Sn doping alone, indicating that no electron transfer occurs between Co and Sn. But as shown in Fig. 8(d) above, where the vertical black line represents the standard binding energy of the tetravalent Sn element, it can be found that the binding energy of CSB-5011 shifts slightly to lower values, indicating that indeed some of the electrons are transferred to Sn. Besides, we find that the binding energies of Bi4f_{7/2} and 4f_{5/2} orbitals are slightly increased compared with those of Co₃O₄, Sn, and Bi-doped alone, indicating that the charge density around Bi atoms in the crystal increases, which indirectly proves that Sn and Bi atoms have a synergistic electron-absorbing effect. The specific charge transfer processes are shown in Fig. 13(b).

As can be seen from Table 2, with the doping of Sn and Bi, the proportion of O_v in CSB-5011 increases, and more O_v can effectively change the energy band structure of metal oxides, reduce the adsorption energy of reactants on the catalyst surface, thus reducing the reaction energy barrier and promoting molecular activation. This may also be one of the reasons for the improved catalytic performance of CSB-5011.

At the same time, because the Eads values between Co (III) and Cl[−] are much higher than those at other sites, it is suggested that Co (III) is the key site for Cl[−] enrichment and activation. In this study, the results of adsorption energy (Eads) between Co (III) and Cl[−] before and after Co₃O₄ doping were calculated by density functional theory (DFT). As shown in Fig. 13 (a), in Co₃O₄ the Eads between Co (III) and Cl[−] was only −2.9362 eV, after introducing Sn and Bi elements, it increased significantly to −3.3672 eV. It can be seen that after doping with two elements, tin and bismuth, the binding energy between the crystal plane (113) and chloride ions increases by 0.431 eV. This indicates that the doped cobalt tetroxide crystal is more likely to bind with the chloride ions in the solution, which may accelerate the subsequent chlorine evolution process. The detailed description of the computational simulation is provided in the supporting materials.

6. Long-term stability tests of materials

The stability test was re-conducted by timing potential analysis (CP) in 0.6M NaCl and a mixed solution of ammonium sulfate with a nitrogen content of 1 g/L. As shown in Fig. 14, there was no significant increase in electrode potential after 42 h of continuous testing. In addition, repeated ammonia degradation experiments, as an important means to evaluate the electrode life, can maintain a high removal efficiency of ammonia nitrogen and ammonia nitrogen after five consecutive repeated experiments, which indicates that the CSB-5011 electrode has excellent long-term stability.

After the stability test, the dissolved Co, Sn, and Bi contents were 72.356(μg/L), 22.218(μg/L), and 267.714(μg/L) respectively which were analyzed by ICP-MS (Table 5).

LSV test was used to evaluate the structural integrity, as shown in Fig. 15 (a) after the stability tests, the current density decreased slightly compared to that before testing, but it remained in the high range. In addition, Fig. 15(b–c) shows that the XPS spectra of O1s and Co2p are consistent in terms of peak area, intensity, and binding energy before and after the test, so we inferred that there was no significant exfoliation or reconstruction of the electrode surface. In addition, the surface of the electrode material after testing was characterized by SEM. As can be seen from Fig. S2, the surface of the material remained intact after the stability test, and there was no crack or local shedding, which maintained excellent structural integrity.

7. Conclusion

In this paper, a very low content Sn, Bi-doped Co₃O₄ electrode was prepared by hydrothermal method, which showed superior chlorine evolution activity than the commercial DSA electrode. When the current density was 10 mA/cm² in 0.6M sodium chloride solution, the chlorination efficiency reached 82.1 %, much higher than 77.4 % of

commercial DSA electrodes. This good catalytic performance may be attributed to increased oxygen vacancy content and the electron-withdrawing effect between Sn and Bi. Considering the electronegativity of the elements. In the EC system using the CSB-5011 electrode, 100 mg/L nitro-containing solution could be partially mineralized to N₂ within 45 min. It may effectively overcome the shortcomings of the current mainstream ammonia nitrogen treatment methods. Although its ammonia degradation capacity is slightly lower than commercial DSA electrodes, the huge cost difference makes it a great application potential.

CRedit authorship contribution statement

KeXuan Wu: Writing – review & editing, Writing – original draft, Visualization, Data curation, Conceptualization. **Jing Cao:** Writing – review & editing, Writing – original draft, Software, Resources, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Ran Zhang:** Writing – review & editing, Methodology, Investigation. **Yong Pei:** Software. **Ting Peng:** Resources, Conceptualization. **Ge Chen:** Conceptualization.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2025.121366>.

Data availability

Data will be made available on request.

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