



Low platinum loading Co_3O_4 electrode for highly efficient oxidation of ammonia in aqueous solution

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ABSTRACT

Chlorine-mediated electrochemical advanced oxidation (Cl-EAO) is an environmentally-friendly and promising ammonia removal technology to convert ammonia to N_2 and effectively reduce water pollution. The efficiency of ammonia removal in Cl-EAO hinges critically on the performance of the electrode materials. Currently, precious metal oxides are commonly used as electrode materials in the industry. However, their high cost limits their widespread application in ammonia treatment. Herein, Pt- Co_3O_4 catalyst with ultra-low content of Pt (1.67 wt%) is successfully synthesized, which performs superior CER activity and higher removal efficiency of ammonia. The favorable catalytic performance could be attributed to the increase in oxygen vacancy content and the strong metal-supported strong interaction (SMSI) between Pt and Co_3O_4 , which has been confirmed by XPS. Especially, the chlorine evolution efficiency of the Ti/Pt₃ % Co_3O_4 electrode was as high as 96 % in dilute chloride (<50 mM) solution at a current density of 10 mA/cm². Therefore, the Ti/Pt₃ % Co_3O_4 electrode has a broad application prospect as a new and efficient material for ammonia wastewater treatment.

1. Introduction

As human activities intensify, ammonia released from urban, agricultural, and industrial sources increasingly accumulates in natural water bodies. The excessive discharge of ammonia can trigger a cascade of environmental issues, including eutrophication, red tides, and algal blooms, posing significant threats to both the ecological environment and human health. Therefore, the efficient removal of ammonia pollutants is of utmost importance for safeguarding our environment and ecology.

Traditional methods for removing ammonia, including ion exchange [1,2], adsorption [3], and breakpoint chlorination [4–6], face technical challenges like low removal efficiency and the risk of secondary pollution due to inadequate treatment. To address these issues, recent years have seen the introduction of advanced oxidation techniques such as Fenton oxidation [7,8], ozone oxidation [9–12], electrocatalytic oxidation [13–15], and photocatalytic oxidation [16,17] for ammonia wastewater degradation. Among these, electrocatalytic oxidation technology (EOT) stands out for its high efficiency, stable and effective treatment results, and relatively lower operating costs. As early as 1980, Della et al. [18] proposed that electrochemical methods could efficiently eliminate ammonia and organic contaminants from domestic

wastewater. Similarly, Wang et al. [19] pointed out that electrochemical oxidation can convert ammonia into N_2 , thereby minimizing the accumulation of unwanted by-products in water. Consequently, EOT is widely recognized as one of the most environmentally responsible and promising techniques for ammonia wastewater treatment.

EOT utilizes electron transfer between the electrode material and the aqueous solution for the oxidative degradation of organic pollutants or inorganic substances, either directly or indirectly through redox reactions at the electrode (cathode or anode) [20]. However, the choice of electrode material significantly influences not only the type of active substance and its oxidizing potential but also the energy consumption and cost-efficiency of the process. Currently, DSA electrodes based on a titanium substrate coated with RuO_2 and IrO_2 are predominantly used in the industry, with RuO_2 content exceeding 20 mol% [21]. This high RuO_2 content contributes to their relatively high cost. Therefore, discovering alternative materials that offer both cost-effectiveness and excellent performance is crucial for the CER process in ammonia-containing wastewater treatment.

Co_3O_4 exhibits great potential as a CER electrocatalyst for purifying ammonia-containing wastewater, thanks to its low cost, exceptional Co (II)/Co(III) cycling capabilities, and the high redox potential ($E^0 = 1.81 \text{ V}$) of Co(III) [22]. As an illustration, Co_3O_4 nanowires, prepared by

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Bai et al. [23], demonstrated an impressive total nitrogen removal rate of 98.2 %, surpassing that of RuO₂ and Pt by 1.69 and 17.5 times, respectively. Nevertheless, there is still room for improvement in terms of CER selectivity and electrical conductivity of Co₃O₄.

Notably, the doping of noble metals serves as a highly effective technique to enhance the catalytic activity of Co₃O₄ [24]. Jiang et al. [25] incorporated Pt into Co₃O₄, resulting in an increased proportion of oxygen vacancies on the catalyst's surface, thereby significantly boosting its electrocatalytic activity. Separately, Ri Qiu et al. [26,27] discovered that Pt can effectively lower the overpotential for chlorine evolution. Additionally, Pt can be formed on the oxide surface by calcining the chloroplatinate precursor, and since Pt has good electrical conductivity, combining Co₃O₄ with Pt will increase the conductivity of Co₃O₄ [28]. Based on the above studies, we proposed a novel and highly efficient Ti/Pt-Co₃O₄ electrode for the oxidation of ammonia in wastewater. The electrode cleverly combines Pt and Co₃O₄, on the one hand, using Pt to reduce the chlorine evolution potential of Co₃O₄ and enhance its chlorine evolution activity; on the other hand, by introducing single-atom Pt, the content of oxygen vacancies on the surface of Co₃O₄ is effectively increased, thus further improving its catalytic activity.

Therefore, in this paper, a low-content Pt-loaded Co₃O₄ electrode was constructed. The scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray electron spectroscopy (XPS) were used to analyze morphology, crystal structure, and surface state of the Pt₃ %-Co₃O₄. Simultaneously, electrochemical tests were performed to evaluate the electrochemical performances of the Ti/Pt₃ %-Co₃O₄ electrode. In addition, the Ti/Pt₃ %-Co₃O₄ electrode was used for ammonia wastewater degradation, and the effects of current density, ammonia concentration, pH and supporting electrolyte on the ammonia degradation rate were investigated in detail. Finally, the stability of the Ti/Pt₃ %-Co₃O₄ electrode was investigated using the chronopotential method and ammonia degradation stability experiments, and the ammonia degradation mechanism was investigated by free radical scavenging experiments.

2. Experimental methods and materials

2.1. Materials

All reagents are analytical-grade, commercially available reagents and can be used without further purification. The sandblasted titanium plate was obtained from Shuer Technology Co., Ltd. and commercial ruthenium titanium plate (20 mm×20 mm×0.5 mm) was purchased from Hanston Technology Development Co., Ltd.

2.2. Electrode preparation method

The Ti/Pt-Co₃O₄ electrode was generated by the sol-gel method (Fig. 1).

2.2.1. Titanium substrate pretreatment

The sandblasted titanium plates (20 mm×20 mm×0.5 mm) were sonicated in acetone, ethanol and water for 30 min to remove the oil. After oil removal, the sandblasted titanium plates were etched in a 10 wt % boiling oxalic acid solution for 2 h. After etching, the plates were placed in anhydrous ethanol.

2.2.2. Preparation of coating solution by the sol-gel method

A solution of glycol citrate was obtained by dissolving 1.31 g of citric acid and 1.85 mL of ethylene glycol in a small amount of ethanol and dissolving by sonication. Then, 2.21 mmol Co(NO₃)₂·6H₂O and 0.0039 mmol H₂PtCl₆·xH₂O were dissolved in an amount of ethanol and the quantitative deionized water and HCl were added to give an orange mixed solution. An orange colored sol of Pt₃ %-Co₃O₄ was obtained by adding glycol citrate solution after sonication for 30 min and continuing sonication for 4 h. For comparison, samples of Pt_x %-Co₃O₄ (x = 0, 1.5, 100 %) were prepared using a similar method as a control.

2.2.3. Preparation of Ti/Pt-Co₃O₄, Ti/Co₃O₄ anode and Ti/Pt electrode

The sol was brushed onto the pretreated pure titanium plate, dried in an oven at 120 °C for 10 min, and then calcined at 350 °C for 15 min. The brushing process was repeated until 0.4 mg/cm² was reached, and finally Ti/Pt₃ %-Co₃O₄ electrode was prepared after annealing at 350 °C for 2 h. The Ti/Pt_{1.5} %-Co₃O₄ electrode, Ti/Co₃O₄ electrode and Ti/Pt electrode were prepared by the same procedure. Notably, the loading of the active substance on the electrode is calculated by the following Eq. (1):

$$M = \frac{(m_2 - m_1)}{S} \quad (1)$$

Where M is the weight of the load, m₁ is the mass before applying the coating, m₂ is the mass after the coating is completed and S is the electrode area.

2.3. Characterizations

The surface morphology and chemical composition of the Ti/Pt-Co₃O₄ electrode and the Ti/Co₃O₄ electrode were evaluated with the scanning electron microscopy (SEM, JSM-6610LV) and energy dispersive X-ray spectroscopy (EDS, Sigma 300). The crystal phase of the samples were detected with X-ray diffraction (XRD, Bruker D8-Advance) with Cu Kα radiation (40 kV, 250 mA) across a degree range of 10°-80°

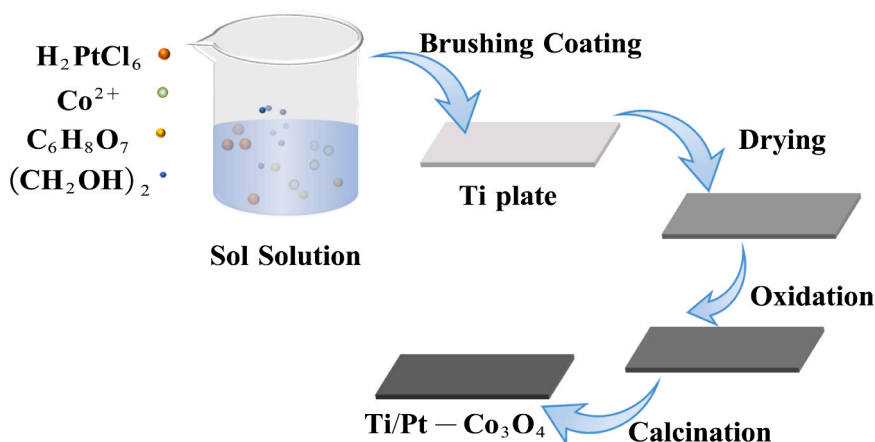


Fig. 1. Typical preparation flow chart of the Ti/Pt-Co₃O₄ electrode.

at a scan rate of 5°/min. Furthermore, the surface chemical state was determined by the X-ray photoelectron spectroscopy (XPS) with a Thermo Scientific K-Alpha⁺ X-ray photoelectron spectrometer.

2.4. Electrochemical test

All electrochemical tests were measured by the three-electrode system with the electrochemical workstation (CHI 660E, Chenhua). The working electrodes were Ti/Pt-Co₃O₄ electrode and Ti/Co₃O₄ electrode. The counter electrode was platinum electrode, the reference electrode was saturated calomel electrode (SCE). Different scanning speeds for CV operate in the possible range of 0.2 V vs. SCE to 0.6 V vs. SCE. In the potential range of 0.9 V vs. SCE to 1.6 V vs. SCE, LSV was conducted at scan rate of 10 mV/s. To compare the charge transfer resistance (R_{ct}) of the electrode in NaCl solution, EIS data were measured at an open circuit voltage from 0.1 Hz to 10⁴ Hz.

2.5. Evaluation of chlorine efficiency

The chlorine evolution performance test of the Ti/Pt-Co₃O₄ electrode (20 mm×20 mm×0.5 mm) and the Ti/Co₃O₄ electrode (20 mm×20 mm×0.5 mm) were carried out under the condition of 50 mM NaCl, with 10 mA/cm² current density, and the electrolysis time was 7 min. The effective chlorine content was detected by the iodometric method [29,30]. The chlorine evolution efficiency is calculated in Eq. (2) [31,32]:

$$\text{CER}(\%) = (C \times V \times n \times F) / (I \times t) \quad (2)$$

where C is the amount of free chlorine generated by electrolysis (mol/L), V is the volume of electrolyte (L), n is the number of electrons involved in CER (2 equiv mol⁻¹), F is the Faraday constant (96,485 C equiv.⁻¹), I is the current (A), and t is the electrolysis time (s).

2.6. Stability test

Approximately 25 h were spent testing the electrode stability in 2 M NaCl solution at a current density of 10 mA/cm².

2.7. Ammonia degradation

To further explore the practicability of a Ti/Pt-Co₃O₄ electrode and

the feasibility of wastewater treatment. The degradation of ammonia in dilute chloride was accomplished using the constructed electrode. In 50 mL (NH₄)₂SO₄ (1 g/L) solution containing 20 mM NaCl as a supporting electrolyte, ammonia was broken down at a current density of 10 mA/cm². The standard methods HJ 536–2009 visual spectrophotometer technique is used for the measurement of ammonium ions [22, 33].

In addition, ammonia removal follows a pseudo-zero-scale kinetic model. The kinetic model is shown in Eq. (3) [13]:

$$-\ln\left(\frac{[\text{NH}_4^+ - \text{N}]_t}{[\text{NH}_4^+ - \text{N}]_0}\right) = kt \quad (3)$$

Where k (min⁻¹) is the ammonia nitrogen removal rate constant. [NH₄⁺-N]₀ and [NH₄⁺-N]_t correspond, respectively, to the initial ammonia concentration and the concentration after a period of time.

3. Results and discussion

3.1. Structural characteristics

The surface morphology of the Pt₃%-Co₃O₄ and Co₃O₄ by SEM (Fig. 2 and Fig. S1). Fig. 2a, Fig. 2c and Fig. S1a show the surface morphology of the Ti/Pt₃%-Co₃O₄ electrode, the DSA electrode and the Ti/Co₃O₄ electrode, respectively. Due to the thermal stress during heat treatment, the electrodes showed obvious mud cracks [34]. In contrast, the coating cracks on the surface of the Ti/Pt₃%-Co₃O₄ electrode were not as dense as those of the DSA electrode, and the cracks were not coherent. In Fig. 2b and Fig. S2a, Pt in the Pt₃%-Co₃O₄ film is present on the surface of Co₃O₄ with an average size of 141.26 nm. In Fig. S1b and Fig. S2b, the average size of Co₃O₄ film is 67.27 nm.

In addition, the EDS images of Pt₃%-Co₃O₄ (Fig. 2d-g) showed that Pt, Co and O coexist in Pt₃%-Co₃O₄. The active metal can be uniformly dispersed on the carrier due to the strong interaction between the metal and the carrier [35]. In addition, ICP (Table S1) detected 1.67 wt% of Pt in Pt₃%-Co₃O₄. The EDS image of Co₃O₄ (Fig. S1c-e) showed that Co and O were uniformly distributed in Co₃O₄.

In Fig. 3a, the crystal structures of the Co₃O₄ and Pt₃%-Co₃O₄ were characterized by XRD. The diffraction peaks at 2θ of 19.0°, 31.3°, 36.8°, 38.5°, 44.8°, 55.7°, 59.4° and 65.2° separately correspond to the (111), (220), (311), (222), (400), (422), (511), (440) and (533) planes of the Co₃O₄ (PDF#42-1467) [36,37]. The diffraction peaks at 2θ=40.2°, 46.3° and 67.8°, corresponding to the (111), (200), and (220) planes of

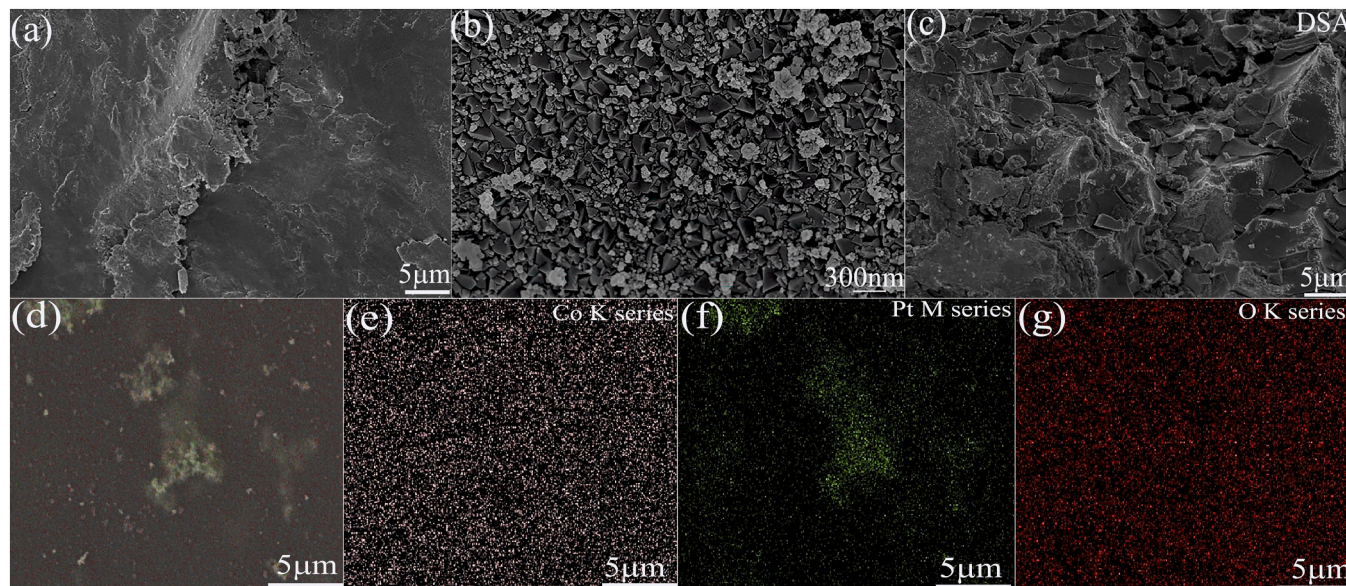


Fig. 2. (a) SEM image of Ti/Pt₃%-Co₃O₄, (b) SEM image of Pt₃%-Co₃O₄, (c) SEM image of DSA electrode, (d-g) Mapping images of Pt₃%-Co₃O₄.

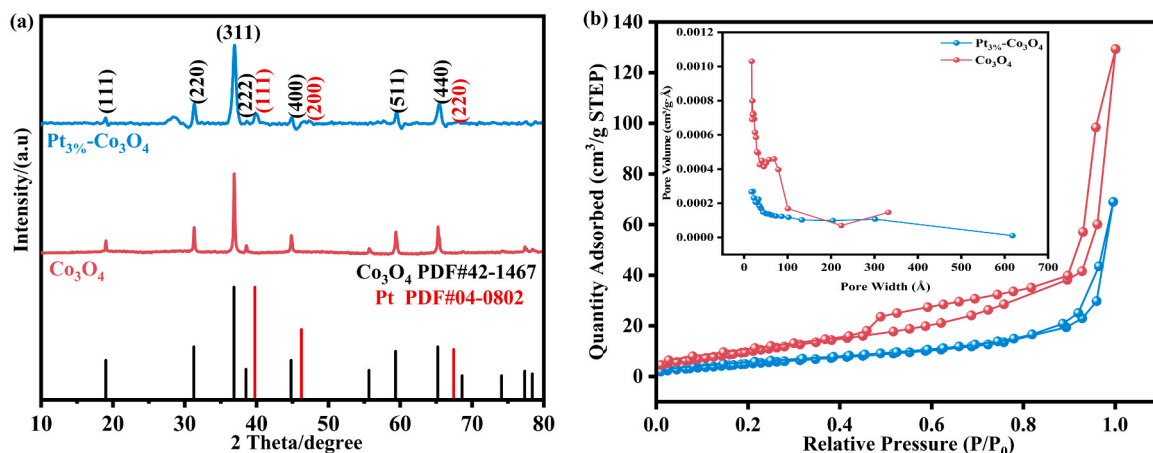


Fig. 3. (a) XRD, (b) N_2 adsorption-desorption isotherms and pore size distributions of Co_3O_4 and $Pt_3\%-Co_3O_4$.

the Pt (PDF#04–0802)[38–40]. The diffraction peaks of Pt and Co_3O_4 can be observed in the XRD pattern of $Pt_3\%-Co_3O_4$, which confirms that $Pt_3\%-Co_3O_4$ prepared in this paper are composites of Pt and Co_3O_4 . In addition, the crystalline size of the resulting samples was calculated based on the half-peak width of Scherrer's formula at $2\theta=36.8^\circ$ (Table S2). The results show that at $2\theta=36.8^\circ$, the grain size of $Pt_3\%-Co_3O_4$ decreases compared to Co_3O_4 .

The specific surface area and pore size of $Pt_3\%-Co_3O_4$ and Co_3O_4 were evaluated by the N_2 adsorption-desorption curves and pore size distribution plots (Fig. 4b). In Table S2, the specific surface areas of $Pt_3\%-Co_3O_4$ and Co_3O_4 were $21.48\text{ m}^2/\text{g}$ and $41.42\text{ m}^2/\text{g}$, and the pore diameters were 19.86 nm and 19.32 nm , respectively. Notably, the

introduction of Pt resulted in the specific surface area of $Pt_3\%-Co_3O_4$ being slightly smaller than that of Co_3O_4 , probably due to the fact that the Pt nanoparticles blocked some of the pores.

The surface states of the Co_3O_4 and $Pt_3\%-Co_3O_4$ were investigated by XPS (Fig. 4). The full-range scanning spectra of Co_3O_4 and $Pt_3\%-Co_3O_4$ are shown in Fig. 4a, where $Pt_3\%-Co_3O_4$ is made up of the elements Pt, Co, and O, while Co_3O_4 is made up of the elements Co and O. The C 1 s peak in the spectrum is due to the addition of carbon-based additives.

Fig. 4b shows high-resolution O 1 s spectra. The O 1 s signal is mainly composed of lattice oxygen (530.03 eV , O_L), oxygen vacancies (531.40 eV , O_V) and chemisorbed and dissociated oxygen species of O_2^- , O^{2-} , O^- and OH^- (533.07 eV , O_C). In addition, the O_V of $Pt_3\%-Co_3O_4$

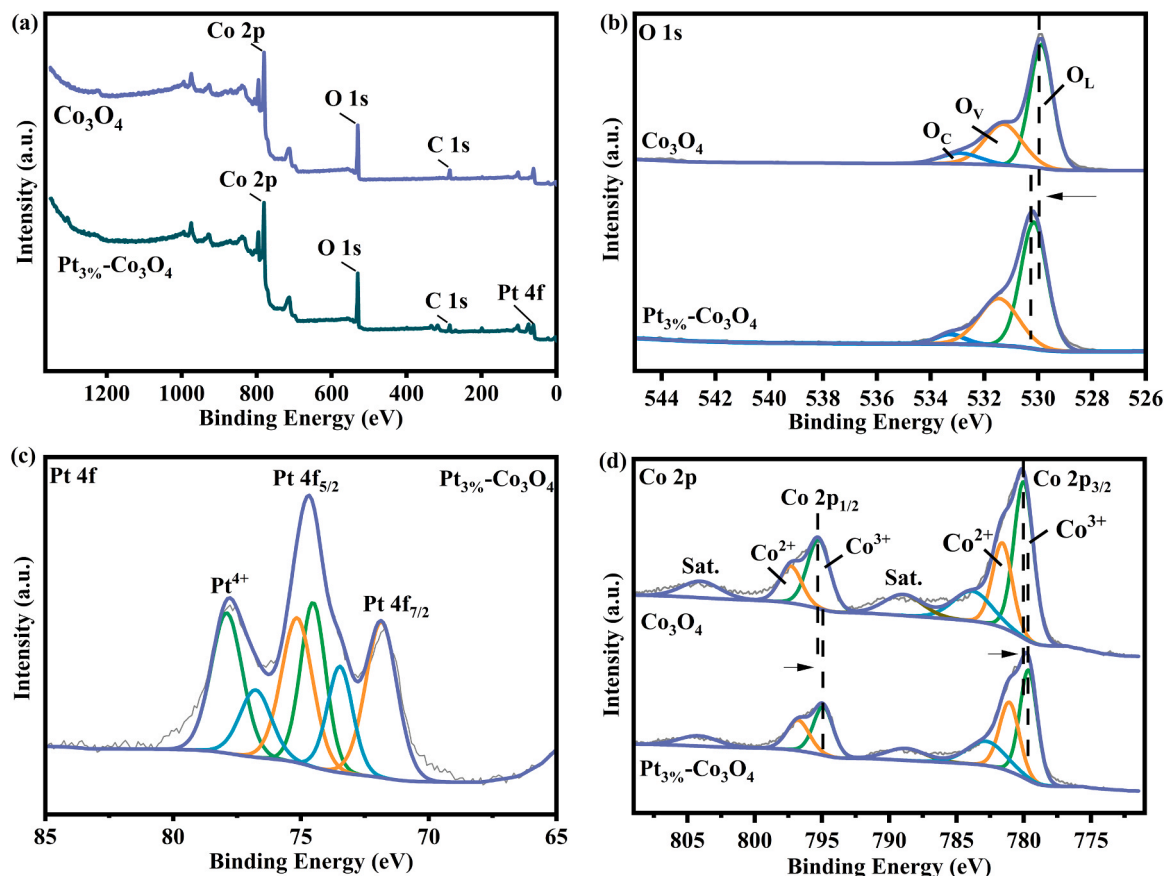


Fig. 4. XPS spectra of Co_3O_4 and $Pt_3\%-Co_3O_4$: (a) survey spectrum, (b) O 1s, (c) Pt 4f, (d) Co 2p.

was 32.16 % while that of Co_3O_4 was 31.74 % (Table 1)[41–43]. Compared to Co_3O_4 , $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ has more surface oxygen vacancies. This phenomenon is attributed to the interaction between Pt and Co_3O_4 support promotes the formation of oxygen vacancies. The Pt sites, which had high occupied electronic states, exhibited a strong affinity for the 3d orbital of adjacent Co atoms, resulting in significant electron transfer from Pt to Co, ultimately, increasing the proportion of oxygen vacancies present on the catalysts surface[25].

Fig. 4c shows the fitted peaks of high-resolution Pt 4f. The fitted peaks located at 71.6 eV and 74.7 eV are assigned to metallic Pt 4f_{7/2} and Pt 4f_{5/2} peaks, respectively. The peak positioned at 77.7 eV is attributed to Pt⁴⁺, which is caused by the inevitable surface oxidation [39,44,45].

The XPS spectra of high-resolution Co 2p are shown in Fig. 4d. Two sets of peaks in Co 2p_{1/2} and Co 2p_{3/2} are 797.05 eV and 795.07 eV, 781.33 eV and 779.82 eV, corresponding to Co²⁺ and Co³⁺, respectively. Sat. is satellite peak. The weak peaks on the left of the two main peaks correspond to the satellite peaks of Co²⁺ and Co³⁺, respectively. The contents of Co³⁺ and Co²⁺ are presented in Table 1, with 64.81 % Co³⁺ in $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ compared to 58.55 % Co³⁺ in Co_3O_4 , the ratio of Co³⁺/Co²⁺ in $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ is greater than in Co_3O_4 [25,46,47].

In addition, compared with the binding energy (BE) values of Co²⁺ and Co³⁺ in Co_3O_4 , the BE values of Co²⁺ and Co³⁺ in $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ exist negative shift. It can be observed that after the introduction of Pt, the Co 2p spectrum is shifted towards the low binding energy end, which is due to the strong metal-supported strong interaction (SMSI) between Pt and Co_3O_4 [47,48].

3.2. Electrochemical test

The chlorine evolution performance of the Ti/Pt- Co_3O_4 electrode and Ti/ Co_3O_4 electrode were investigated by electrochemical measurements.

Fig. 5a shows the LSV curves for the Ti/Pt- Co_3O_4 electrode and the Ti/ Co_3O_4 electrode in solutions of sodium chloride. The current density of each electrode increased with the increase in potential. This indicates that a good CER response was obtained for the samples[49]. The LSV curve of the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode shows the maximum slope, indicating the best electrocatalytic performance of the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode. Notably, the catalytic activity of each electrode is ranked as follows: Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ (23.76 mA/cm² @1.20 V) > Ti/ $\text{Pt}_{1.5}\%-\text{Co}_3\text{O}_4$ (9.15 mA/cm² @1.20 V) > Ti/ Co_3O_4 (8.5 mA/cm² @1.20 V) > Ti/Pt (6.61 mA/cm² @1.20 V) (Table S3). Therefore, the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode exhibits good catalytic performance.

The electron transfer efficiencies of the Ti/Pt- Co_3O_4 electrode and the Ti/ Co_3O_4 electrode during the CER process were examined through EIS, as depicted in Fig. 5b. Specifically, Fig. 5b reveals that the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode exhibits the smallest charge transfer resistance (R_{ct}) when compared to the Ti/ Co_3O_4 electrode. This observation signifies that the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode possesses the quickest charge transfer rate, facilitating rapid electron transfer at the interface between the electrocatalyst and the electrolyte. This rapid electron transfer is intricately linked to the electrode's superior CER activity. Consequently, the integration of Pt into the pure Co_3O_4 catalyst enhances the electrocatalytic reaction of Co_3O_4 , primarily due to the SMSI-induced electron transfer mechanism between Pt and the Co_3O_4 carrier.

Additionally, in Fig. S3a, the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode shows the highest feed current and the largest voltammetric charge in 2 M NaCl solution, indicating the strongest chlorine evolution activity. During the

positive scanning process, the current density increased rapidly when the voltage exceeded 1.0 V vs. SCE, which indicated the initiation of a vigorous chlorine evolution reaction[50]. During negative potential scanning, a distinct reduction peak was observed at 0.9 V vs. SCE, which was attributed to the reduction of chlorine (Fig. S3a)[51]. Notably, CV experiments were performed in 2 M NaCl and 2 M NaNO_3 solutions at a scan rate of 100 mV/s (Fig. S3b). The CV curves varied considerably in the two different electrolytes. In 2 M NaCl solution, the feed current and voltammetric charge increased significantly, which indicated that the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode had better chlorine evolution activity and selectivity.

The electrochemical surface area (ECSA) of the Ti/Pt- Co_3O_4 and Ti/ Co_3O_4 electrodes was compared to their intrinsic activity by electrochemical double layer capacitance (C_{dl}). Fig. 6a–c present the cyclic voltammetry (CV) plots of the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$, Ti/ $\text{Pt}_{1.5}\%-\text{Co}_3\text{O}_4$, and Ti/ Co_3O_4 electrodes across various scan rates. Notably, the CV plots exhibited nearly ideal rectangular curves, suggestive of a pronounced double-electric-layer capacitance effect.

Notably, the ECSA was proportional to the C_{dl} [52]. In Fig. 6d, the values size of C_{dl} is Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ (10.8 mF/cm²) > Ti/ $\text{Pt}_{1.5}\%-\text{Co}_3\text{O}_4$ (8.3 mF/cm²) > Ti/ Co_3O_4 (3.9 mF/cm²). Table. S4 shows that the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode exhibits the largest ECSA value of 720 cm²; the ECSA value of the Ti/ $\text{Pt}_{1.5}\%-\text{Co}_3\text{O}_4$ electrode is 553 cm², while the Ti/ Co_3O_4 electrode has the least ECSA value, just 260 cm². Additionally, we also analyze the ECSA-normalized CER performance of these electrodes (Table. S4). As we can see, the ECSA-normalized electrochemical activities follow the sequence: Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ (0.132 mA/cm² @1.20 V) > Ti/ Co_3O_4 (0.130 mA/cm² @1.20 V) with those of normalized via geometric area. Therefore, the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode exhibits good electrochemical activities.

Fig. S4a presents the results of chronopotentiometry conducted to assess the stability of the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode. Notably, after 25 h test, the electrode exhibited minimal fluctuations in potential, indicating its good stability. Furthermore, as shown in Fig. S4b–d, the CV curves obtained before and after the stability test closely overlap, and the SEM images reveal minimal morphological changes. These observations collectively confirm the good stability of the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode. Finally, CVs before and after electrolysis were tested in ammonia-free and chlorine-free solutions. In Fig. S5, the CV plots show a rectangular shape.

In summary, the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode shows excellent chlorine evolution performance, a high electrochemical surface area and low charge transfer resistance.

3.3. Evaluation of chlorine evolution efficiency of the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode

Fig. 7a illustrates the chlorine evolution efficiency of Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$, Ti/ Co_3O_4 , and commercial DSA in dilute chloride solutions. Notably, the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode demonstrates a remarkable chlorine evolution efficiency of 96 % in diluted chloride, surpassing both the Ti/ Co_3O_4 electrode and commercial DSA in terms of chlorine evolution performance.

Fig. 7b explores the impact of varying current densities on the concentration of effective chlorine generated through electrolysis. It becomes evident that as the current density rises, the current efficiency initially increases but subsequently declines. This trend primarily results from the oxygen evolution side reaction and current losses encountered at higher anode potentials [20,53]. Additionally, Fig. S6 delves into the effective chlorine content and current efficiency of the Ti/ $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ electrode at different times. It is observed that the effective chlorine content gradually increases with time, while the current efficiency attains a stable value before gradually decaying with the passage of time.

Table 1

XPS results for the O 1s and Co 2p of $\text{Pt}_3\%-\text{Co}_3\text{O}_4$ and Co_3O_4 (atom%).

Sample	O _L	O _V	O _C	Co ³⁺	Co ²⁺
$\text{Pt}_3\%-\text{Co}_3\text{O}_4$	62.65 %	32.16 %	5.18 %	64.81 %	35.09 %
Co_3O_4	59.50 %	31.74 %	8.76 %	58.55 %	41.45 %

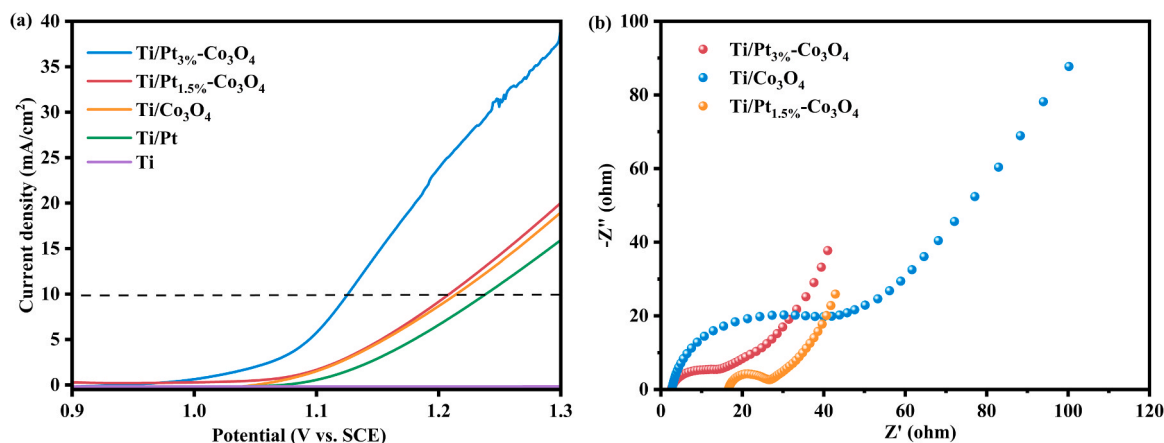


Fig. 5. (a) LSV plots of Ti/Pt-Co₃O₄ electrode, Ti/Co₃O₄ electrode, Ti/Pt electrode and pure titanium plate, (b) Nyquist plot.

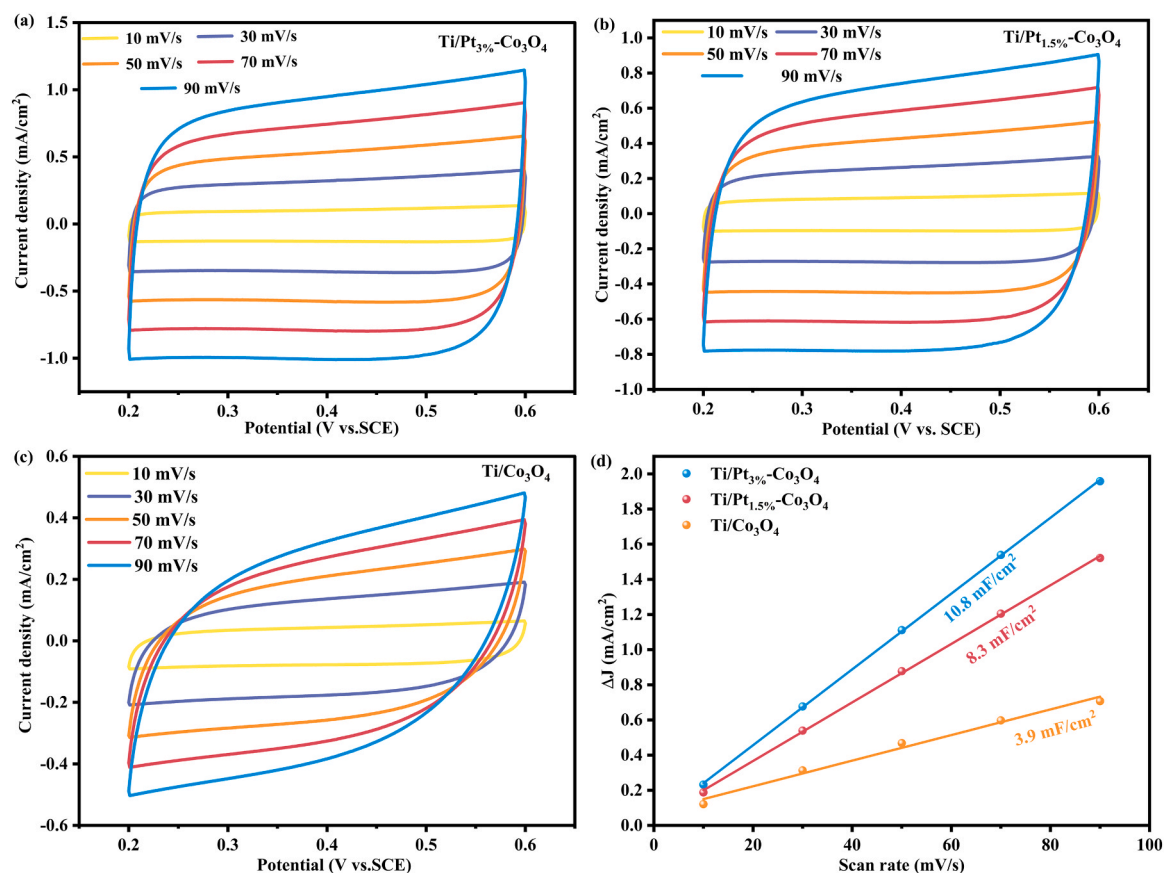


Fig. 6. (a) Ti/Pt_{3%}-Co₃O₄ electrode, (b) Ti/Pt_{1.5%}-Co₃O₄ electrode, (c) CV curves of Ti/Co₃O₄ electrode at different scan rates, (d) C_{dl} at the potential of 0.4 V vs. SCE.

3.4. Ti/Pt_{3%}-Co₃O₄ electrode for ammonia degradation in diluted chloride

3.4.1. Influencing factors of ammonia degradation

Given the exceptional CER activity and robust stability demonstrated by the Ti/Pt_{3%}-Co₃O₄ electrode in dilute chloride solutions, it was used for ammonia wastewater degradation. Through a comprehensive electrochemical ammonia oxidation experiment, the influence of various environmental factors, including the type of electrode, concentration of ammonia solution, electrolyte, current density, and pH, on the removal efficiency of ammonia was meticulously investigated.

Fig. 8a illustrate the influence of electrode materials on the removal efficiency of wastewater containing ammonia. As time elapses, it becomes evident that the removal efficiency of various electrodes increase. Concurrently, the concentrations of NH₄⁺-N and Cl⁻ decrease in tandem with the breakdown of ammonia, thereby affecting the current efficiency. Notably, the Ti/Pt_{3%}-Co₃O₄ electrode exhibits the most superior removal efficiency and kinetic constant during the same reaction time, significantly surpassing both the DSA electrode and the Ti/Co₃O₄ electrode. In Fig. S7a, The kinetic constant of Ti/Pt_{3%}-Co₃O₄ electrode was 0.0092 min⁻¹, which was significantly larger than that of commercial DSA electrode (0.0068 min⁻¹) and Ti/Co₃O₄ electrode (0.0079 min⁻¹).

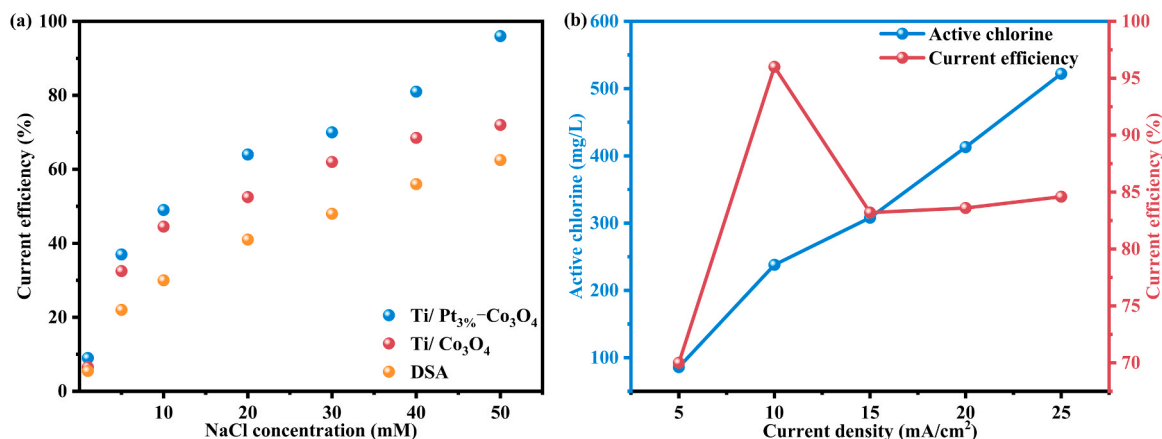


Fig. 7. (a) CER efficiencies of the Ti/Pt₃%-Co₃O₄, Ti/Co₃O₄, and DSA electrode in various concentrations of NaCl aqueous solutions (current density = 10 mA/cm²), (b) CER efficiencies and active chlorine levels of Ti/Pt₃%-Co₃O₄ electrode in various current densities (electrolyte concentration=50 mM NaCl).

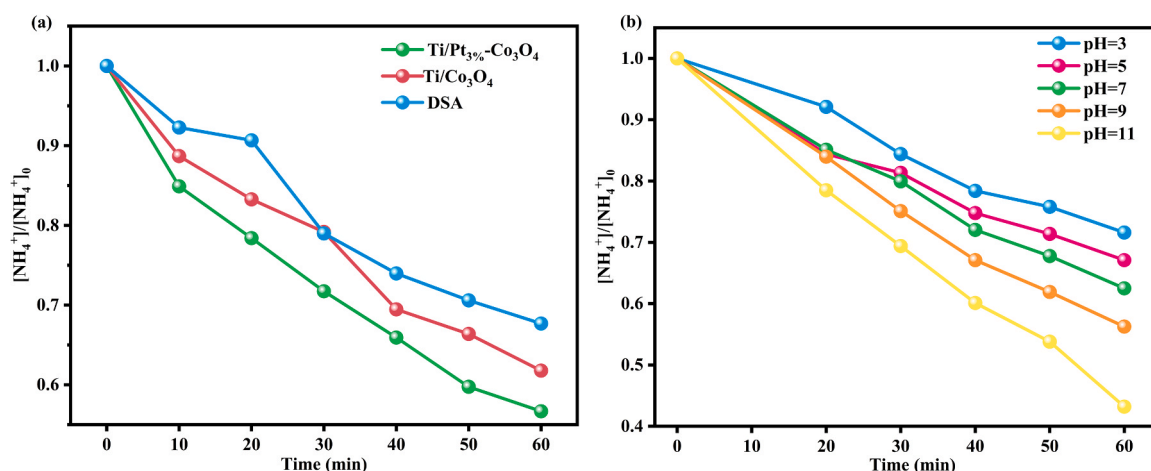


Fig. 8. Time courses of ammonia degradation by the Ti/Pt₃%-Co₃O₄ electrode under the different conditions: (a) electrodes, (b) pH. Operating condition: Surface area=20 mm×20 mm, T=25 °C, current density=10 mA/cm², t= 60 min, V=50 mL, 1 g/L (NH₄)₂SO₄+20 mM NaCl.

The removal efficiency of ammonia is also influenced by the pH level of the solution. As depicted in Fig. 8b, we evaluated the removal capabilities of ammonia-containing wastewaters under different pH conditions. In this study, the pH of the ammonia solution was adjusted using diluted sulfuric acid and sodium hydroxide. As clearly shown in Fig. 8b and Fig. S7b, the removal efficiency and kinetic constant of ammonia significantly increases with an increase in pH. The fastest removal efficiency and the largest kinetic constant (0.014 min⁻¹) of the ammonia were observed at pH = 11 (Fig. S7b). However, considering that the experiment is conducted in a semi-closed setting, it is noteworthy that, under neutral or alkaline conditions, the molecular state of NH₃ in the solution exhibits greater susceptibility to oxidation than the ammonium ion. During the ammonia degradation process, sodium chloride solution serves as the supporting electrolyte, and chlorine gas will be continuously generated on the electrode surface. The varying pH of the solution influences the ratio of chlorine gas, hypochlorite ions, and hypochlorous acid, thereby affecting the rate of ammonia degradation. Previous studies by T. David Waite et al. [54,55] have demonstrated that ammonia oxidation is more efficient under weak alkaline conditions, which helps minimize the escape of chlorine and minimizes environmental pollution. However, excessively high pH levels can lead to increased side reactions, such as the formation of ClO₃⁻, which can reduce the reaction rate [56]. Therefore, to ensure an efficient removal efficiency of ammonia, a pH range of 7–9 is recommended for investigation. In this study, a pH of 7 was chosen for the experiments.

The effects of supported electrolyte types on the removal efficiency of ammonia were examined in Fig. 9a using sodium chloride and sodium sulfate as supporting electrolytes. It is clear that when sodium chloride solution is used as a supporting electrolyte, the efficiency of ammonia removal is significantly faster than when sodium sulfate is used as a supporting electrolyte. This shows that sodium chloride solution has a strong promoting effect on the oxidative degradation of ammonia. This is due to the production of chlorine radicals (Cl•, ClO•, Cl₂••) and reactive chlorine species (Cl₂, HClO, and ClO⁻) by sodium chloride during electrolysis, which promotes the oxidative degradation of ammonia. Therefore, sodium chloride was chosen as the supporting electrolyte in other ammonia oxidation experiments. Fig. 9b and Fig. S8a examine the effect of ammonia removal at different NaCl concentrations. The removal efficiency and kinetic constant of ammonia increased with a steady increase in NaCl content. In Fig. S8a, the kinetic constant was 0.021 min⁻¹ when the concentration of the supporting electrolyte NaCl reached 40 mM. This is mainly due to the fact that the higher the concentration of NaCl, the more chlorine radicals and active chlorine species are generated, and these active substances react with ammonium ions to promote the removal of ammonia.

During the actual wastewater treatment process, the amount of ammonia in water fluctuates, necessitating an investigation into how the initial quantity of ammonia impacts its removal efficiency. As depicted in Fig. 10a, with the increase in ammonia concentration, the change curve of ammonia concentration is linear and keeps parallel, indicating

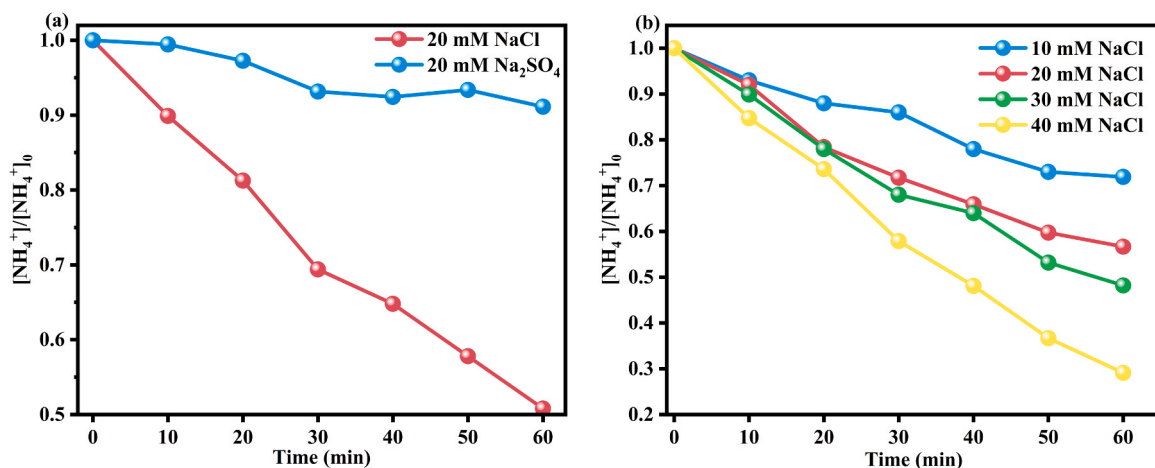


Fig. 9. Time courses of ammonia degradation by the Ti/Pt₃%-Co₃O₄ electrode under the different conditions: (a) supporting electrolytes, (b) supporting electrolytes concentration. Operating condition: Surface area=20 mm×20 mm, T=25 °C, current density=10 mA/cm², t= 60 min, V=50 mL, 1 g/L (NH₄)₂SO₄.

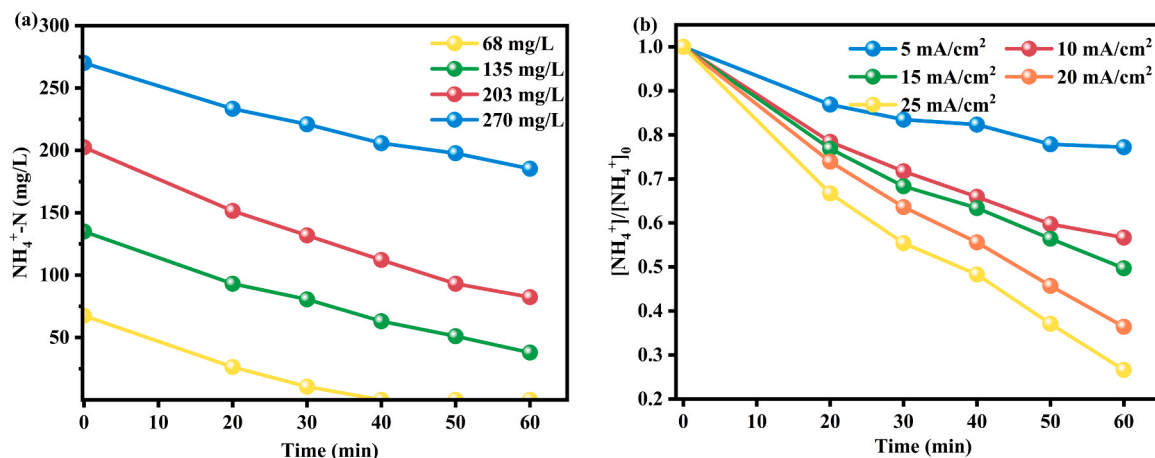


Fig. 10. Time courses of ammonia degradation by the Ti/Pt₃%-Co₃O₄ electrode under the different conditions: (a) ammonia concentration, (b) current density. Operating condition: Surface area=20 mm×20 mm, T=25 °C, t=60 min, V=50 mL, 1 g/L (NH₄)₂SO₄+20 mM NaCl.

that the effect of electrochemical oxidation of ammonia wastewater has little to do with the initial concentration of ammonia.

The investigations in Fig. 10b and Fig. S8b explored the influence of current density on ammonia removal efficiency. The removal efficiency

and kinetic constants of ammonia increased with increasing current density. Notably, at a current density of 5 mA/cm², the rate of ammonia removal was maintained at a low level and the kinetic constant was only 0.0042 min⁻¹; a higher level of ammonia removal was achieved at a

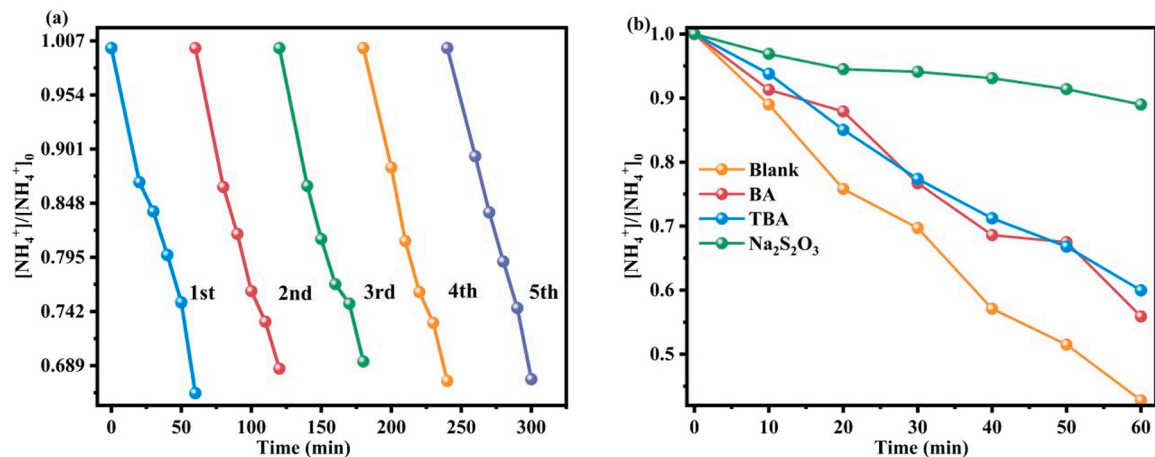


Fig. 11. (a) Stability of Ti/Pt₃%-Co₃O₄ electrode during ammonia degradation tests, (b) The mechanism of ammonia degradation by the Ti/Pt₃%-Co₃O₄ electrode in the different scavengers.

current density of 25 mA/cm² with a kinetic constant of 0.021 min⁻¹. While an elevated current density and the subsequent increase in solution surface temperature can, to some extent, enhance the electrode reaction at the surface, selecting an excessively high current density is not advisable. This is due to increased oxygen evolution side reactions at higher current densities[20].

3.4.2. Ammonia degradation stability and its mechanism

The stability of the Ti/Pt₃%-Co₃O₄ electrode can be further evaluated through repeated ammonia electrolysis tests. As evident from Fig. 11a, the removal efficiency of the ammonia maintains a high level even after five consecutive repetitions of the test, demonstrating the good stability of the Ti/Pt₃%-Co₃O₄ electrode.

During the electrolysis of aqueous sodium chloride solutions, various oxidants are generated, including free chlorine species (Cl₂, HOCl, and OCl⁻) as well as •OH, Cl•, and Cl₂•⁻ radicals [15,57]. We chose tert-butanol (TBA), Na₂S₂O₃ and benzoic acid (BA) as scavengers to elucidate the ammonia oxidation mechanism, and the results are shown in Fig. 11b. It has been reported that BA can only burst •OH and Cl•, while TBA can burst •OH, Cl• and ClO•, and Na₂S₂O₃ can burst •OH, Cl• and ClO• and other free radicals and reactive chlorine species[58]. Notably, the addition of BA and TBA to the reaction system caused a slight but not significant inhibition in ammonia removal efficiency. However, when Na₂S₂O₃ was added, a significant inhibition in ammonia removal efficiency was observed. Consequently, in the Ti/Pt₃%-Co₃O₄ electrode system, the oxidants for ammonia degradation are chlorine radicals and active chlorine species.

In summary, within the ammonia degradation system utilizing sodium chloride as the supporting electrolyte, the electrolysis process gives rise to reactive species such as •OH and Cl•. Subsequently, HClO and ClO⁻ are formed, which then interact with ammonium ions to produce NH₂Cl, NHCl₂, and NOH in sequence. Ultimately, these reactions culminate in the generation of N₂.

4. Conclusion

In summary, a low-content Pt-loaded Co₃O₄ electrode was successfully synthesized using sol-gel method. The electrode exhibited superior chlorine evolution activity and higher ammonia degradation capability than the commercial DSA electrode and Ti/Co₃O₄ electrode. The chlorine evolution efficiency was as high as 96 % at a current density of 10 mA/cm² in dilute chloride solution. This good catalytic performance could be attributed to the increased oxygen vacancy content and the SMSI between Pt and Co₃O₄. In addition, the effects of electrode materials, ammonia solution concentration, supporting electrolyte, current density, and pH on the ammonia removal efficiency were explored. Therefore, in this paper, a low-cost and efficient CER catalyst was prepared to rapidly oxidize ammonia to N₂.

CRediT authorship contribution statement

Ran Zhang: Writing – original draft, Investigation. **Quan Chen:** Investigation. **KeXuan Wu:** Investigation. **Ting Peng:** Investigation. **Jing Cao:** Writing – review & editing.

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.

Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.113252.

References

- [1] W. Zhang, R. Fu, L. Wang, J. Zhu, J. Feng, W. Yan, Rapid removal of ammonia nitrogen in low-concentration from wastewater by amorphous sodium titanate nano-particles, *Sci. Total Environ.* 668 (2019) 815–824.
- [2] M.A.B. Puzan, M.H. Puteh, A. Yuzir, M.H.D. Othman, R. Abdul Wahab, M. Zainal Abideen, Optimizing ammonia removal from landfill leachate using natural and synthetic zeolite through statically designed experiment, *Arab J. Sci. Eng.* 45 (5) (2019) 3657–3669.
- [3] M. Yamaguchi, T. Ichikawa, H. Miyaoka, T. Zhang, H. Miyaoka, Y. Kojima, Proton-based solid acids for ammonia absorption in ammonia water, *Int. J. Hydrogen Energ.* 45 (41) (2020) 22189–22194.
- [4] D. Stéfán, N. Erdélyi, B. Izsák, G. Záray, M. Vargha, Formation of chlorination by-products in drinking water treatment plants using breakpoint chlorination, *Microchem. J.* 149 (2019) 104008.
- [5] X. Zhang, P. Ren, J. Zhou, J. Li, Z. Li, D. Wang, Formation of disinfection byproducts in an ammonia-polluted source water with UV/chlorine treatment followed by post-chlorination: a pilot-scale study, *Environ. Technol. Innov.* 26 (2022) 102266.
- [6] C.T.Ja.R.L. Valentine, Reaction scheme for the chlorination of ammoniacal water, *Environ. Sci. Technol.* 26 (3) (1992) 577–586.
- [7] J. Cao, R. Wang, H. Zhu, S. Cao, Z. Duan, Effect of Fenton pre-oxidation on the physicochemical properties of sludge-based biochar and its adsorption mechanisms for ammonia nitrogen removal, *J. Environ. Chem. Eng.* 11 (5) (2023) 110689.
- [8] Q. Zhang, S. Chen, H. Wang, A surface plasmon-enhanced nanozyme-based fenton process for visible-light-driven aqueous ammonia oxidation, *Green Chem.* 20 (17) (2018) 4067–4074.
- [9] Z. Zhang, H. Ai, M.-L. Fu, Y.-b Hu, J. Liu, Y. Ji, V. Vasudevan, B. Yuan, Oxygen vacancies enhancing performance of Mg-Co-Ce oxide composite for the selective catalytic ozonation of ammonia in water, *J. Hazard. Mater.* 436 (2022) 129000.
- [10] P. Anggo Krisbiantoro, T. Togawa, L. Mahardiani, H. Aihara, R. Otomo, Y. Kamiya, The role of cobalt oxide or magnesium oxide in ozonation of ammonia nitrogen in water, *Appl. Catal. A* 596 (2020) 117515.
- [11] J.Ha.H. Bader, Ozonation of water: kinetics of oxidation of ammonia by ozone and hydroxyl radicals, *Environ. Sci. Technol.* 12 (1978) 79–84.
- [12] P.C. Singer, W.B. Zilli, Ozonation of ammonia in wastewater, *Water Res* 9 (2) (1975) 127–134.
- [13] J. Chen, H. Shi, J. Lu, Electrochemical treatment of ammonia in wastewater by RuO₂-IrO₂-TiO₂/Ti electrodes, *J. Appl. Electrochem.* 37 (10) (2007) 1137–1144.
- [14] Y. Yang, J. Shin, J.T. Jasper, M.R. Hoffmann, Multilayer heterojunction anodes for saline wastewater treatment: design strategies and reactive species generation mechanisms, *Environ. Sci. Technol.* 50 (16) (2016) 8780–8787.
- [15] Y. Yang, L.C. Kao, Y. Liu, K. Sun, H. Yu, J. Guo, S.Y.H. Liou, M.R. Hoffmann, Cobalt-doped black TiO₂ nanotube array as a stable anode for oxygen evolution and electrochemical wastewater treatment, *ACS Catal.* 8 (5) (2018) 4278–4287.
- [16] Z. Zheng, J.H.K. Man, I.M.C. Lo, Integrating reactive chlorine species generation with H₂ evolution in a multifunctional photoelectrochemical system for low operational carbon emissions saline sewage treatment, *Environ. Sci. Technol.* 56 (22) (2022) 16156–16166.
- [17] Y. Liu, R. Mao, J. Hao, K. Wang, K. Hu, Y. Cui, X. Zhao, Efficient oxidation of ammonium to nitrogen gas via accelerated ClO• generation at TiO₂/Ru-IrO₂ bifacial electrode in a UV-driven photoelectrochemical system, *Chem. Eng. J.* 463 (2023) 124999.
- [18] A.A.M. Della Monica, A. Ceglie, An electrochemical sewage treatment process, *J. Appl. Electrochem.* 10 (1980) 527–533.
- [19] Z. Ye, R. Shen, X. Zhou, J. Yao, J. Wang, The research of steady-state electrochemical kinetics of effective and selective conversion of total nitrogen to N₂, *Environ. Sci. Pollut. Res.* 26 (22) (2019) 22971–22978.
- [20] W. Ji, Y. Xiong, Y. Wang, T.C. Zhang, S. Yuan, Multilayered TNAs/SnO₂/PPy/β-PbO₂ anode achieving boosted electrocatalytic oxidation of As(III), *J. Hazard. Mater.* 430 (2022) 128449.
- [21] M. Hu, T. Yu, K. Tan, A. Zhou, L. Luo, S. Yin, Ultralow Ru loading RuO₂-TiO₂ with strong oxide-support interaction for efficient chlorine evolution and ammonia-nitrogen-elimination, *Chem. Eng. J.* 465 (2023) 143001.
- [22] L. Tian, X.-Y. Xia, L.-J. Zhou, L.-L. Zheng, Q.-J. Xing, L.-S. Zhang, J.-P. Zou, Z.-Q. Liu, Enhanced chlorine enrichment via electron-deficient centers of Co(III) for efficient electrochlorination and ammonia removal, *Appl. Catal., B* 340 (2024) 123260.
- [23] Y. Zhang, W. Tang, J. Bai, J. Li, J. Wang, T. Zhou, X. Guan, B. Zhou, Highly efficient removal of total nitrogen and dissolved organic compound in waste reverse osmosis concentrate mediated by chlorine radical on 3D Co₃O₄ nanowires anode, *J. Hazard. Mater.* 424 (2022) 127662.
- [24] Z. Zhang, G. Tan, A. Kumar, H. Liu, X. Yang, W. Gao, L. Bai, H. Chang, Y. Kuang, Y. Li, X. Sun, First-principles study of oxygen evolution on Co₃O₄ with short-range ordered Ir doping, *Mol. Catal.* 535 (2023) 112852.
- [25] Z. Jiang, X. Feng, J. Deng, C. He, M. Douthwaite, Y. Yu, J. Liu, Z. Hao, Z. Zhao, Atomic-scale insights into the low-temperature oxidation of methanol over a single-atom Pt₁-Co₃O₄ catalyst, *Adv. Funct. Mater.* 29 (31) (2019) 1902041.

- [26] Y. Xue, J. Zhao, R. Qiu, J. Zheng, C. Lin, B. Ma, P. Wang, In situ glass antifouling using Pt nanoparticle coating for periodic electrolysis of seawater, *Appl. Surf. Sci.* 357 (2015) 60–68.
- [27] V.C. Pinto, P.J. Sousa, E.M.F. Vieira, L.M. Gonçalves, G. Minas, Antibiofouling strategy for optical sensors by chlorine generation using low-cost, transparent and highly efficient electrodes based on platinum nanoparticles coated oxide, *Chem. Eng. J.* 404 (2021) 126479.
- [28] W. Yang, X. Wang, Y. Yan, X. Ding, Co_3O_4 nanofibers compounded with Pt/C as efficient bifunctional electrocatalysts for rechargeable Zn-air battery, *J. Mater. Sci.: Mater. Electron.* 34 (10) (2023) 871.
- [29] Y. Wang, Y. Xue, C. Zhang, Rational surface and interfacial engineering of $\text{IrO}_2/\text{TiO}_2$ nanosheet arrays toward high-performance chlorine evolution electrocatalysis and practical environmental remediation, *Small* 17 (17) (2021) e2006587.
- [30] I.A. Moreno-Hernandez, B.S. Brunschwig, N.S. Lewis, Crystalline nickel, cobalt, and manganese antimonates as electrocatalysts for the chlorine evolution reaction, *Energy Environ. Sci.* 12 (4) (2019) 1241–1248.
- [31] H.W. Lim, D.K. Cho, J.H. Park, S.G. Ji, Y.J. Ahn, J.Y. Kim, C.W. Lee, Rational design of dimensionally stable anodes for active chlorine generation, *ACS Catal.* 11 (20) (2021) 12423–12432.
- [32] S. Chen, Y. Zheng, S. Wang, X. Chen, $\text{Ti}/\text{RuO}_2\text{-Sb}_2\text{O}_5\text{-SnO}_2$ electrodes for chlorine evolution from seawater, *Chem. Eng. J.* 172 (1) (2011) 47–51.
- [33] S. Wang, X. Huang, L. Pei, X. Zhu, S. Zhu, Y. Liu, Z. Ye, Synergistic removal of ammonia nitrogen by UV photo-electrocatalytic process: Heterogeneous reaction pathways and mechanism, *J. Clean. Prod.* 384 (2023) 135515.
- [34] H. Qi, L. Wang, W. Sun, Z. Yang, X. Chen, J. Yu, W. Wu, G. Liu, Preparation of $\text{Ti}/\text{IrRuSnSbOx}$ electrodes by a hydrosol process for efficient and stable chlorine evolution reaction, *Ind. Eng. Chem. Res.* 62 (29) (2023) 11517–11526.
- [35] C. Gai, H. Song, X. Liu, F. Li, M. Xiao, T. Huang, H. Gai, Nitrogen doping carbon deriving from ionic liquid anchoring Ru coated on P-zeolite as high activity and stability catalyst for the catalytic wet air oxidation of highly concentrated ammonia, *Mol. Catal.* 515 (2021) 111941.
- [36] Y. Wang, Y.-Q. Zhu, Z. Xie, S.-M. Xu, M. Xu, Z. Li, L. Ma, R. Ge, H. Zhou, Z. Li, X. Kong, L. Zheng, J. Zhou, H. Duan, Efficient electrocatalytic oxidation of glycerol via promoted OH^* generation over single-atom-bismuth-doped spinel Co_3O_4 , *ACS Catal.* 12 (19) (2022) 12432–12443.
- [37] Y. Su, K. Fu, Y. Zheng, N. Ji, C. Song, D. Ma, X. Lu, R. Han, Q. Liu, Catalytic oxidation of dichloromethane over Pt-Co/HZSM-5 catalyst: synergistic effect of single-atom Pt, Co_3O_4 , and HZSM-5, *Appl. Catal. B* 288 (2021) 119980.
- [38] G.P.V.C.H. Comninellis*, Characterization of DSA| oxygen evolving electrodes: choice of a coating, *J. Appl. Electrochem.* 21 (1991) 335–345.
- [39] M. Gu, Q. Jia, Y. Zhu, L. Xu, Y. Tang, In situ growth of ultrafine Pt nanoparticles onto hierarchical $\text{Co}_3(\text{O})_4$ nanosheet-assembled microflowers for efficient electrocatalytic hydrogen evolution, *Chemistry* 26 (66) (2020) 15103–15108.
- [40] M. Wu, F. Gui, X. Lu, Z. Yan, F. Chen, Y. Jiang, X. Luo, W. Chen, Achieving a high long-term stability for room temperature CO-sensitive Pt-SnO₂ composite nanoceramics through two strategies, *Mater. Sci. Eng. B-Adv.* 286 (2022) 116070.
- [41] X. Shi, J. Li, X. Zhang, J. Guo, MOF derived NiCo-LDH hollow structure for oxygen evolution reaction, *J. Phys. Chem. Solids* 172 (2023) 111051.
- [42] M. Cui, L. Wei, S.-J. Park, S. Kim, Electrochemical behaviors of binder-free CoFe-layered double-hydroxide-decorated hexagonal-flower-like NiCo_2O_4 as electrode for supercapacitors, *J. Alloy. Compd.* 940 (2023) 168875.
- [43] X. Zhang, D. Wu, X. Liu, Y. Qiu, Z. Liu, H. Xie, J. Duan, B. Hou, Efficient electrocatalytic chlorine evolution under neutral seawater conditions enabled by highly dispersed Co_3O_4 catalysts on porous carbon, *Appl. Catal., B* 330 (2023) 122594.
- [44] Z. Zhao, H. Liu, W. Gao, W. Xue, Z. Liu, J. Huang, X. Pan, Y. Huang, Surface-engineered PtNi-O nanostructure with record-high performance for electrocatalytic hydrogen evolution reaction, *J. Am. Chem. Soc.* 140 (29) (2018) 9046–9050.
- [45] L.S. Bezerra, G. Maia, Developing efficient catalysts for the OER and ORR using a combination of Co, Ni, and Pt oxides along with graphene nanoribbons and NiCo_2O_4 , *J. Mater. Chem. A* 8 (34) (2020) 17691–17705.
- [46] J. Zhao, T. Hu, J. Wang, Y. Wang, J. Zhang, B. Lv, W. Zhang, J. Jia, Strain effect induced Pd nanoparticles decorated Pd^{2+} -doped Co_3O_4 nanosheets for efficient electrocatalytic ethanol oxidation and oxygen reduction reactions, *Mol. Catal.* 556 (2024) 113902.
- [47] M. Zhang, S. Zou, S. Mo, J. Zhong, D. Chen, Q. Ren, M. Fu, P. Chen, D. Ye, Enhancement of catalytic toluene combustion over Pt- Co_3O_4 catalyst through in-situ metal-organic template conversion, *Chemosphere* 262 (2021) 127738.
- [48] L. Jin, B. Liu, M.E. Louis, G. Li, J. He, Highly crystalline mesoporous titania loaded with monodispersed gold nanoparticles: controllable metal-support interaction in porous materials, *ACS Appl. Mater. Interfaces* 12 (8) (2020) 9617–9627.
- [49] H. Wang, J. Li, D. Zhang, G. Wang, P. Wang, Morphology regulation and application of nano cobalt oxide (Co_3O_4) electrocatalysts for chlorine evolution toward marine anti-biofouling, *J. Colloid Interface Sci.* 628 (2022) 794–806.
- [50] F. Zhang, X. Gu, S. Zheng, H. Yuan, J. Li, X. Wang, Highly catalytic flexible RuO_2 on carbon fiber cloth network for boosting chlorine evolution reaction, *Electrochim. Acta* 307 (2019) 385–392.
- [51] L. Cai, Y. Liu, J. Zhang, Q. Jia, J. Guan, H. Sun, Y. Yu, Y. Huang, Unveiling the geometric site dependent activity of spinel Co_3O_4 for electrocatalytic chlorine evolution reaction, *J. Energy Chem.* 92 (2024) 95–103.
- [52] X. Zhu, P. Wang, Z. Wang, Y. Liu, Z. Zheng, Q. Zhang, X. Zhang, Y. Dai, M.-H. Whangbo, B. Huang, Co_3O_4 nanobelt arrays assembled with ultrathin nanosheets as highly efficient and stable electrocatalysts for the chlorine evolution reaction, *J. Mater. Chem. A* 6 (26) (2018) 12718–12723.
- [53] H. Ha, K. Jin, S. Park, K.G. Lee, K.H. Cho, H. Seo, H.Y. Ahn, Y.H. Lee, K.T. Nam, Highly selective active chlorine generation electrocatalyzed by Co_3O_4 nanoparticles: mechanistic investigation through in situ electrokinetic and spectroscopic analyses, *J. Phys. Chem. Lett.* 10 (6) (2019) 1226–1233.
- [54] C. Zhang, Y. Jiang, Y. Li, Z. Hu, L. Zhou, M. Zhou, Three-dimensional electrochemical process for wastewater treatment: a general review, *Chem. Eng. J.* 228 (2013) 455–467.
- [55] C. Zhang, D. He, J. Ma, T.D. Waite, Active chlorine mediated ammonia oxidation revisited: Reaction mechanism, kinetic modelling and implications, *Water Res.* 145 (2018) 220–230.
- [56] V.-A. Thai, T.-B. Nguyen, C.P. Huang, X.-T. Bui, R.-a. Doong, C.-W. Chen, C.-D. Dong, Graphene quantum dots (GQDs) decorated zeolitic imidazole framework-67 (ZIF67) electrode for the in-situ oxidation of ciprofloxacin in water, *Environ. Technol. Innov.* 30 (2023) 103039.
- [57] Y. Yang, M.R. Hoffmann, Synthesis and stabilization of blue-black TiO_2 nanotube arrays for electrochemical oxidant generation and wastewater treatment, *Environ. Sci. Technol.* 50 (21) (2016) 11888–11894.
- [58] Q. Li, G.-h. Liu, L. Qi, H. Wang, G. Xian, Chlorine-mediated electrochemical advanced oxidation process for ammonia removal: Mechanisms, characteristics and expectation, *Sci. Total Environ.* 896 (2023) 165169.