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Preparation of Co-TiO₂ Nanotube Array Electrode for the Electrocatalytic Degradation of Chlorine-Containing Wastewater

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Abstract. Shale gas fracturing flowback fluid is produced during shale gas exploitation, and its complex composition and high chloride content result in limited efficiency of conventional technology. In this work, the Co-TiO₂ nanotube array (Co-TiO₂ NTAs) electrode with high chlorine evolution activity was successfully prepared by electrodeposition for the treatment of containing chlorine PAM simulated wastewater. The internal morphology, crystal structure, and electrochemical characteristics of the nanotubes were analyzed by scanning electron microscopy, X-ray diffraction, energy dispersive spectrometry, and linear sweep voltammetry. The electrochemical catalytic oxidation activity toward chlorine evolution reaction and degradation against polyacrylamide (PAM) in chlorinecontaining wastewater were investigated. The results demonstrated that the chlorine evolution potential of the TiO2 NTAs electrode was decreased after loading 0.0333 mg/cm² of cobalt by bipolar pulse electrodeposition. The results showed that the removal rate of chemical oxygen demand (CODcr) was 62.7% and the yield of active chlorine (ACl) was 45.2 mg/L after 1 hour of electrolysis, which were attributed to the excellent catalytic performance of the novel electrodes for the degradation of polyacrylamide. Combined with the characterization results of GC-MS and IR, the degradation mechanism of PAM was briefly described. The results indicated that the novel Co-TiO₂ NTAs electrodes have a broad application prospect in electrochemical oxidation-catalytic degradation of high chlorine containing wastewater.

Keywords. Chlorine-containing wastewater, cobalt catalyst, electrochemical oxidation, TiO_2 nanotube

1. Introduction

Hydraulic fracturing is a promising technology, which often used to increase oil and gas production during shale gas development [1, 2]. Part of the wastewater inevitably returns to the surface, resulting in flowback fracturing shale gas wastewater (FFSGW), which

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usually contains high concentrations of potentially dangerous organic components (such as petroleum, polymers and surfactants) and inorganic components (such as heavy metals, solids and salts), causing serious harm to the ecological environment and human health [3-6]. The traditional biological and physical methods are limited by low efficiency and high cost, which can hardly meet the processing requirements [7, 8].

Electrochemical catalytic oxidation can produce strong oxidizing species (e.g., hydroxyl radicals and active chlorine) to remove organic pollutants; in addition, because it has the characteristics of convenient operation, low energy consumption, short time requirements and so on, it is drawing interests for the treatment of refractory wastewater [9, 10]. The effects of electrochemical catalytic oxidation depend on many factors, including electrode materials, operation conditions, and the nature of the wastewater [11]. FFSGW features high Cl⁻ concentrations, and the presence of Cl⁻ in the wastewater is not conducive to hydroxyl radicals. However, Cl⁻ can generate highly oxidizing active chlorine (e.g., Cl₂, HClO, and ClO⁻) to degrade organic matter during electrolysis (equations (1)-(3)). Da Moura et al. [12] demonstrated that a $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode for the electrochemical disinfection of actual effluent and confirmed that the active chlorine (ACl) is the main disinfectant active substance. Hong et al. ^[13] prepared a new pyrolusite particle electrode with good catalytic activity and found that it could increase the ACI concentration in the treatment of chlorine-containing sulfonated phenolic simulated wastewater. Therefore, the preparation of a new electrode for the highly efficient catalytic degradation of refractory organics in chlorine-containing wastewater is important.

$$2 Cl^- \to Cl_2 + 2 e^- \tag{1}$$

$$Cl_2 + H_2O \rightarrow HClO + HCl$$
 (2)

$$Cl0^{-} + organics \rightarrow CO_2 + H_2O + Cl^{-}$$
(3)

In recent years, ordered TiO_2 nanotubes (NTAs) that are electrochemically synthesized directly on Ti surface have attracted considerable attention in photoelectrochemical, electrochemical energy storage, and electrocatalysis [14-20]. With the unique structure and highly special surface area of in situ erected TiO_2 NTAs, the effective area of the electrochemical reduction of TiO_2 NTAs and considered that their excellent electrochemical properties are suitable for supercapacitors, photocatalysis, and lithium batteries. Chen et al. [22] found that hydrogenated TiO_2 nanoscale materials exhibit stable photovoltaic catalytic activity and the ability to oxidize organic molecules in water. Qian et al. [23] found that the flow-through sequential adsorption and electrochemical degradation (SAED) based on TiO_2 NTAs as an electrochemical anode material has some shortcomings, such as low conductivity, poor electrocatalytic ability, and short lifetime.

Related studies show that the electrochemical performance of TiO_2 NTAs electrode modified with metal particles or metal oxides can be significantly improved [24-28]. Co spinel (densely packed cubic lattice of oxygen particles and metal ions) is a promising electrode material, and its oxide exhibits good catalytic activity in lithium batteries [29]. Yan et al. [30] prepared a cobalt–nickel electrode by electrodeposition for the electrolysis treatment of urea and found that the electrode has good application potential in wastewater treatment. some works shed light that cobalt-based catalysts electrode can improve the chlorine evolution reaction and show their potential application in water treatment [31-33]. Thus, in the electrochemical treatment of chlorine-containing FFSGW, in order to improve the production of active chlorine, a new type of Co-TiO₂ NTAs electrode appeared in our mind.

Polyacrylamide (PAM) as a drag reducer is the most important source of organic matter in FFSGW. PAM is a linear polymer that is biodegradable. Upon formation, the long-chain polymer becomes converted into a short-chain low-molecular substance and appears in pressure-return liquid, which increases the CODcr of the FFSGW. Therefore, PAM was chosen as the processing object in this study.

Herein, in this work, a $Co-TiO_2$ NTAs electrode was prepared for the degradation of chlorine-containing PAM simulated wastewater and the electrode performance and the degradation mechanism of PAM were investigated.

2. Materials and Methods

2.1. Experiment Materials

Industrial titanium plates (98% thickness=0.5 mm) were purchased from Hongwang.co (Shenzheng, China) and graphite plate electrode were purchased from Pingdingshanlvlin.co (China). Cation PAM (AN934SH) was obtained from SNF (France). All the chemical reagents (analytical grade) used in the experiment were provided by Kelong (Chengdu, China).

2.2. Pretreatment of Twice Oxidation TiO₂ NTAs Electrode

The schematic for preparing the Co-TiO₂ NTA electrode is illustrated as follows. The Ti plate was polished with SiC sand paper (600, 800, 1200, 2000, and 3000 mesh) until the surface was smooth and then washed with petroleum ether in ultrasound cleaner. A 20 % oxalic acid solution was used to etch the Ti plate at 80°C for 20 min and then ultrasonically cleaned in DI water for 10 min before drying. With the Ti plate as the anode and the double graphite plate as the cathode, TiO₂ NTAs were prepared by primary anode oxidation of the Ti plate in 2 wt% H₂O and ethylene glycol (EG) electrolyte with 0.25 wt% NH₄F for 6 h at 42 V. After primary anodization, the TiO₂ NTAs were subjected to a second anodization in 5 wt% H₃PO₄/EG electrolyte for 1 h at 42 V. After being rinsed with ethanol, the TiO₂ NTAs were crystallized into anatase by annealing in a muffle furnace at 350 °C for 1 h.

2.3. Preparation of Co-TiO₂ NTAs Electrode

Before the modification of TiO₂, the TiO₂ NTAs were cathodized in 0.1 M Na₂SO₄ solution for 10 s. The electrodeposition of cobalt was carried out in a water bath composed of 0.025 g $C_{12}H_{25}SO_3Na$, 7 g $CoSO_4 \cdot 7H_2O$, 7.5 g NaCl, 5 g H_3BO_4 , and 23.5 g deionized water. Then, TiO₂ NTAs served as the cathode and two graphite plate as the anodes. The Co-TiO₂ NTA electrode was prepared by cathodic deposition using three current conditions (direct current (DC), unipolar pulse current (UPC), and bipolar pulse current (BPC)), in a water bath at 40°C for 20 s with magnetic stirring. The operating

parameters of each current are shown in Table 1. BPC deposition was applied for 10 s to 60 s, and different loads of Co-TiO₂ electrodes ($0.0157-0.533 \text{ mg/cm}^2$) were prepared. The final Co-TiO₂ NTA electrodes containing Co loadings of 0, 0.0157, 0.0333, 0.0514, and 0.533 mg/cm^2 respectively.

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Current	Positive pulse (duty cycle, %)	Negative pulse (duty cycle, %)	Potential (vs. Ag/AgCl)	Frequency (kHz)
DC	/	/	-0.85V	0
UPC	/	30%	-0.85V	1
BPC	70%	30%	-0.85V	1

Table 1. The operating parameters of DC, UPC and BPC.

2.4. Electrolysis Experiment

The electrolysis reactor support was a 250 mL beaker. The conditions of electrolysis were as follows: Co-TiO₂ NTA electrode as anode, graphite plate as cathode, distance between plates of 4 cm, electrode effective area of 60 cm², initial pH of 5, chloride ion concentration of 20,000 mg/L, PAM concentration of 500 mg/L, current density of 7 mA/cm², and electrolytic volume of 200 mL. During electrolysis, a modified method for determining the CODcr for samples with high salinity was used in the experiment. The ACl concentration was measured using the N, N-diethyl-1, 4-phenylenediamine sulfate spectrophotometric method (Standard methods for examination of water and wastewater).

2.5. Analytical Methods

The morphology of the TiO_2 NTAs electrode was observed on an SEM (FEI Inspect F50) by EDS operated at an acceleration voltage of 500 kV. The crystal structure of the TiO_2 NTAs electrode was obtained by XRD (PANalytical, Netherlands). The chlorine evolution potential (ClEP) of Co-TiO₂ NTAs electrode was measured by linear sweep voltammetry (LSV). The samples were separated by solid phase extraction (SPE), and the intermediate products of PAM electrolysis reaction were determined by GC-MS (GCMS-QP2010Plus, SHIMADZU). The change of substance in electrolysis was analyzed by IR spectrometry.

3. Results and Discussion

3.1. Characteristics of the Co-TiO₂ NTAs Electrode

Figure 1 illustrates a typical SEM morphology of TiO_2 NTAs after 6 hours of primary oxidation and 1 hour of secondary oxidation. During the oxidation process, a dense oxide film layer formed on the surface of the plate to generate highly ordered and uniformly arranged TiO_2 NTAs with a length of approximately 17 µm (Figure 1b). A sample of ripple structures generated in the tube body after secondary oxidation in Figures 1c and 1d, while the only primary oxidation TiO_2 NTAs was smooth in Figure 1). The stability of the connection layer between the bottom of the TiO_2 NTAs and the Ti matrix was the key to electrode life and conductivity. Yang et al. [34] found that the organic electrolyte of phosphoric acid can strengthen the bottom structure of the nanotubes and make it

adhere firmly. The connection area between the nanotubes and the Ti matrix indicated that the bonding force between the nanotubes bundles was strengthened. The results imply the TiO_2 NTAs can effectively resist deformation under the action of external forces.



Figure 1. Scanning electron microscopy (SEM) cross images of pure TiO_2 NTAs without modification. (a): primary oxidation for 6 hours; (b) and (c): secondary oxidation NTAs; (d): bottom of secondary oxidation NTAs.

The crystal structure of TiO₂ NTAs changes from amorphous to anatase and rutile at 350°C (Figure 2). The diffraction peaks at 25.304°, 37.793°, 48.037°, 54.323°, and 69.01° can be attributed to the (101), (004), (200), (211), and (301) of the anatase phase. Second oxidation doesn't affect the crystal structure of TiO₂ NTAs. The produced by electrooxidation were amorphous and had poor stability. The heat treatment process rendered the TiO₂ atoms in the nanotubes arrange orderly, formed a stable crystal structure, and improved the electrocatalytic and electrical conductivity of the TiO₂ NTAs [35]. The TiO₂ phase includes three types crystal structure, anatase, brookite, and rutile. The rutile crystal structure of TiO₂ structure is the most stable [36]. However, the formation of rutile phase requires increasing the calcination temperature of TiO₂, which may cause the surface of TiO₂ NTAs to crack or fracture, thus destroying its overall structure. Anatase phase has good catalytic activity, and the sharp XRD diffraction peak indicates that the prepared TiO₂ NTAs electrode has a highly crystalline anatase structure.



Figure 2. X-ray diffraction patterns of TiO₂ NTAs. (a): no heated; (b): annealed at 350°C.

The electrocatalytic oxidation capacity and stability of the TiO_2 NTAs electrode are expected to be improved by introducing Co nanoparticles. Electrodeposition is accomplished by the charge exchange of metal ions at the interface of the electrode and the solution; thus, selecting different load currents has an important influence on the deposition effect. The morphology of the Co-TiO₂ NTA electrode prepared by different load currents of DC, UPC, and BPC is shown in Figure 3.



Figure 3. Effect of different electrodeposit current on morphology.

The prepared TiO₂ NTAs is 17 μ m in length. Thus, exchanging the materials inside and outside the tube when Co was loaded took time, and the deposition effect was affected by mass transfer. The specific process was as follows: (1) the Co²⁺ in the electrolyte moved to the inner wall of the nanotubes, and the electrons were reduced to elemental Co deposition on the inner wall surface; (2) the concentration of Co²⁺ in the nanotubes gradually reduced because of the mass transfer efficiency, and a hydrogen evolution reaction occurred; (3) the H₂ generated in the nanotubes was difficult to discharge in time, which affected the deposition of cobalt.

When the DC was the power source, a large amount of H₂ generated in the nanotubes hindered the deposition of Co and deoxidized the TiO_2 . The conductivity of the TiO_2 was enhanced. Thus, the solid-liquid two-phase electron transporting portion was gradually transferred from the inner wall of the tube bottom to the nozzle. Finally, Co was covered with scales on the surface of the nanotube, and the nanotube nozzle was completely blocked. At the instant of switching on, the pulse current would provide a higher current density than DC, allowing the Co²⁺ ions to be deposited on the nanotubes in the form of impact, resulting in a tighter and purer deposited layer. Scanning electron micrographs of the Co-TiO₂ NTAs electrode prepared by UPC show that Co was uniformly distributed on the surface of the nanotubes, but the diameter of the Co crystal particles was much larger than that of the nanotubes and cannot be deposited in the tubes. Thus, the overall deposition efficiency was limited. The main reason was that the UPC had an on-off process, which would produce a capacitive effect. The TiO₂ NTAs electrode had good capacitance performance, and some current was consumed during the charging and discharging of the capacitor. Therefore, the current density distribution on the surface of the whole plate was not uniform, which caused the uneven thickness distribution of the deposited layer. The BPC applied a positive pulse after the negative pulse, and the convexly loaded Co was dissolved to some extent during the positive pulse. Hence, the entire plating surface was even and flat. At the same time, the positive pulse could also oxidize and remove the H_2 generated by the negative pulse, which was beneficial to the deposition of Co in the nanotubes. Therefore, the BPC load of Co was deposited along the edge of the tube, and the structure was dense.

The electrocatalytic oxidation capacity of Co-TiO₂ NTAs electrode can be described by chlorine evolution potential (CIEP). LSV was used to analyze the three types of Co-TiO₂ NTAs electrode prepared by loading current. As shown in Figure 4, These electrocatalytic properties presented a low overpotential for chlorine evolution. The best CER performance was observed for BPC. Compared with DC and UPC loads, BPC can load Co into nanotubes under the condition of ensuring the porosity of nanotubes. Therefore, the Co-TiO₂ NTAs electrode prepared by BPC exhibits better electrocatalytic activity in terms of chlorine evolution performance.



Figure 4. Effect of different electrodeposit current on chlorine evolution potential.



Figure 5. EDS spectrum of BPC.

An elemental analysis was carried out by using EDS on the side of the nanotubes to further investigate the loading of cobalt inside the Co-TiO₂ NTAs electrode under BPC. Figure 5 shows the EDS profile of the Co-TiO₂ NTA electrode prepared by BPC. The atomic percentages were 3.34%, 68.6%, and 22%, for elements Co, Ti and O. The results mean that Co had been successfully loaded into the nanotubes.

The electrocatalytic activity of the Co-TiO₂ NTAs electrode was evaluated through the degradation of PAM-simulated wastewater. The electrocatalytic degradation of PAM are shown in Figure 6. The formed TiO₂ NTAs without Co exhibited weak catalytic activity toward degrading PAM. An obvious electrocatalytic performance was observed as the Co content was increased. This result indicates that the doped Co oxide plays a key role in the electrocatalytic activity of the electrode. However, the influence of the doped amount of Co on the electrocatalytic activity showed a non-monotonic behavior. The Co-TiO₂ NTAs electrode had the best removal rate of PAM when the cobalt loading was 0.0333 mg/cm². The COD removal rate started to decrease as the amount of cobalt loaded was increased. The reason was that the high loading reduced the porosity of the nanotubes, blocked the surface of the nanopores on the surface of the TiO_2 nanotubes, and reduced the effective electrolysis area of the electrodes. At the same time, electrochemical corrosion occurred during electrolysis, which affected the degradation performance of the Co-TiO₂ NTAs electrode. Therefore, the prepared Co-TiO₂ NTAs electrode is a promising material in the field of electrochemical degradation of chlorine-containing organic wastewater.



Figure 6. CODcr removal efficiency at different doping amounts of Cobalt.

3.2. Electrochemical Oxidation of PAM Simulated Wastewater by Co-TiO₂ NTAs Electrode

The Co-TiO₂ NTAs electrode was used to treat the PAM-simulated wastewater to confirm its performance in the 2D electrode system.



Figure 7. Infrared spectra PAM wastewater before and after treatment.

The time evolution of the IR spectra of PAM during degradation is displayed in Figure 7. In the wastewater, the characteristic absorption peak at approximately 3400 cm⁻¹ can be attributed to the structures of $-NH_2$, and 615 cm⁻¹ is the out-of-plane rocking vibration peak of $-NH_2$. These characteristic peaks show the functional group to prove the presence of organic substances with amide groups in the water sample. The absorption peak at 1100 cm⁻¹ is a C-N stretching vibration peak. After 60 min of electrolysis, the structures of C-N and $-NH_2$ nearly disappeared. Therefore, we could

infer that the Co-TiO₂ NTAs electrode has strong catalytic oxidation ability and effectively destroys the amide group of PAM.

Table 2. Electrolytic products of $Co-TiO_2$ NTAs electrode 2D electrolytic systems by GC-MS at 60 and 90 min.

Chemical name (60 min)	Molecular formula	Peak area (%)	Chemical name (90 min)	Molecular formula	Peak area (%)
Chloroform	CHC13	70.95	Chloroform	CHCl3	63.45
Dichloroacetonitrile	C2HCl2N	15.79	Dichloroacetonitrile	C2HCl2N	31.75
2-Methylpropionitrile	C8H12N4	13.26	2-Methylpropionitrile	C8H12N4	4.80

Table 2 displays that the results of GC-MS measurements. CHCl₃, C₂HCl₂N, and $C_8H_{12}N_4$ were produced in the 2D electrode system of the Co-TiO₂ NTAs electrode. The two-dimensional electrolysis system could rapidly break the high-polymer PAM to form small molecular substances, and the content of small molecules in the system increased with the extension of electrolysis time. We considered that the Co-TiO₂ NTAs electrode has good catalytic performance, which can generate a large amount of ACl in the electrolysis process and rapidly degrade organic matter. The discovery of several chlorinated organics indicating that the active chlorine failed to completely degrade some organic substances during the electrolysis process but formed a chlorinated organic by-product. We could infer that polyacrylamide is catalytically oxidatively degraded into small molecular intermediates, and then some intermediate products and active chlorine are formed by substitution, addition, and so on to form various chlorinated organic compounds in the electrolysis process.

Figure 8a illustrates the CODcr removal efficiency of PAM-simulated wastewater treated with the Co-TiO₂ NTAs electrode. The maximum removal rate was 62.7% after 60 minutes of electrolysis. TiO₂ is a typical non-active electrode with high oxygen evolution potential. Adding TiO₂ to the electrode material can increase the concentration of high oxidation potential hydroxyl radical in the electrolysis process [37]. Therefore, the in-situ growth of TiO₂ NTAs can produce a large number of hydroxyl radicals that can oxidize organic compounds without selectivity. When the electrolyte contains a large amount of Cl⁻, Cl⁻ is not conducive to the action of hydroxyl radicals on organic compounds. However, chloride ions can generate active chlorine during electrolysis. Strong oxidizing active chlorine can oxidize and degrade organic pollutants, playing a key role in the degradation of organic matter. As mentioned above, the Co-TiO₂ NTAs electrode has a low chlorine evolution potential, which can generate the active chlorine oxidation degradation of organic matter. The high CODcr removal efficiency of the Co-TiO₂ NTAs electrode can be explained as follows:

PAM chain scission mainly formed small molecular substances containing amide groups and alcohols. The amide group was dehydrated to form a cyanide organic substance, and a highly stable dichloroacetonitrile and 2-methylpropionitrile formed under the action of active chlorine. Alcohols undergo a substitution reaction to form chloroform. Finally, under the synergy of \cdot OH, the organic matter was completely oxidatively degraded to form inorganic substances such as CO₂, H₂O, NO₃⁻. Therefore, given these characteristics, the Co-TiO₂ NTAs electrode has good performance to treat PAM.

Figure 8b shows the change trend of ACl in the reaction system with the time of electrolysis. As the time of electrolysis increases, the concentration of ACl increases rapidly in the first 50 minutes and then tends to be flat, which may be caused by the

consumption of ACl by \cdot OH. The results argue that the Co-TiO₂ NTAs electrode performed well in the ACl electrolysis test. Evidently, the 2D electrode system with the Co-TiO₂ NTAs electrode produced additional ACl. Li et al. [38] believed Co could form corrosion-resistant oxides and hydroxides distributed in the form of a network on the surface of the TiO₂ NTAs electrode and become a new catalytic site. Thus, the Co-TiO₂ NTAs electrode features good electrocatalytic properties and can produce a large number of active chlorines.

Since ACl can react with NH_4^+ to generate chloramine with lower reactivity, NH_4^+ (30mM) was added into the system to quench ACl in order to determine the main active substance in the reaction system. As shown in (Figure 8a), the degradation rate of PAM was only 30.2%, which was greatly reduced after adding NH_4^+ . This phenomenon proved that ACl plays an important role in the degradation of PAM in the presence of Cl⁻.



Figure 8. Effect of the Co-TiO₂ NTAs electrode. (a): COD_{Cr} removal efficiency; (b): ACl concentration.

4. Conclusion

We have successfully prepared a novel type of Co-TiO₂ NTAs electrode with a high ACl yield by bipolar pulse deposition current. EDS and SEM results showed that TiO₂ NTAs were loaded by Co nanoparticles. The Co-TiO₂ NTAs electrodes were proven to be effective in electrochemical oxidation in the treatment of chlorine-containing PAM-simulated wastewater. After 60 minutes of electrolysis, the ACl concentration and CODcr removal for the 2D electrode system packed with the Co-TiO₂ NTAs electrode reached 45.2 mg/L (ACl) and 62.7% (CODcr removal), correspondingly. The developed Co-TiO₂ NTAs electrode is promising for treating chlorine-containing flowback fracturing shale gas wastewater.

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