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Recent developments and advances in Ti/TiO_2-NTs/PbO_2 electrodes:A general Review of their controllable preparation and application in wastwater treatment

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ABSTRACT

Ti/TiO_2-NTs(nanotubes)/PbO_2 is a new composite electrode material,which has been considered as an optimal electrode material for electrochemical oxidation of organic contaminants in the aquatic environmentthat due to its its good physical and chemical properties,such as good electrocatalytic activity, high oxygen evolution potential, corrosion resistance, good stability, environmental friendliness and simple preparation. The fundamental research and practical application of Ti/TiO_2-NTs(nanotubes)/PbO_2 electrodes in the mineralization of organic pollutants have been well developed up to now. So this paper mainly reviews the preparation methods of Ti/TiO_2-NTs/PbO_2 electrodes and the structural characterization methods of electrode materials first. And then, the basic principle of electrocatalytic oxidation will be introduced in detail and the application of this electrodes in water treatment is going to be summarized systematically. Further, we also proposed the existing problems in recent research and the potential development direction of electrocatalytic water treatment technology in the future, which could provide reference for the follow-up research.

Key words: PbO_2; Ti /TiO_2-NTs electrodes; Electrochemical oxidation; Wastewater treatment

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1. Introduction

With the rapid development of modern economy and society, and the rise of petrochemical industry and pharmaceutical industry, refractory substances in industrial wastewater are increasing day by day. A large number of chemical substances are used and discharged into the natural environment[1]. The organic wastewater produced by people in daily life is also excessively discharged into the natural water body, resulting in the eutrophication of water body and other hazards. For these wastewater, although the traditional treatment methods have certain treatment effect, but for printing and dyeing, leather, paper and other wastewater containing high concentration, high toxicity and strong stability of organic pollutants, the limitations of these methods will be highlighted[2]. In addition, the traditional treatment method will produce a large number of harmful sludge, essy to cause secondary pollution. Therefore, it is difficult for traditional water treatment methods to meet the requirements of environmental protection[3]. In recent years, electrocatalytic technology has attracted the continuous attention of scholars at home and abroad for its effective treatment of refractory organic wastewater. Electrocatalysis technology can be carried out under normal temperature and pressure, and can easily control the reaction direction and rate effectively by changing the electric field at the solid-liquid interface[4]. The core of electrocatalysis technology lies in electrode materials. In electrocatalytic technology, the main reaction of pollutant degradation occurs in the anode region, which directly affects the degradation efficiency and mineralization degree of organic pollutants[5]. Currently, a wide variety of electrodes are applied in electrocatalytic oxidation technology, such as titanium electrode, graphite electrode, platinum electrode, RuO_2 electrode, glassy carbon electrode, PbO_2 electrode and BDD electrode, etc.[6]. As a typical representative of electrode materials, Ti matrix metal oxide electrode has been widely used in electrocatalytic water treatment due to its excellent characteristics. At present, there are many literatures on Ti matrix metal oxide electrode at home and abroad, among which PbO_2 has been paid more attention and applied in the field of electrocatalytic water treatment due to its high oxygen evolution potential, strong oxidation capacity, good corrosion resistance and relatively low price, etc.[7-9].However, practical application shows that PbO_2 electrode still has some problems: the coating adhesion is low, easy to fall off, the service life is unstable in the electrolysis process, and the catalytic performance of the electrode material is lower than that of Sb-SnO_2 and BDD electrode, etc.[10-15] Therefore, finding anode materials with good stability and high catalytic performance is the key to popularize electrochemical water treatment[10-15]. How to prepare TiO_2 modified nanometer electrode materials with excellent properties has become one of the active topics in the current material research, so it is of great scientific significance to conduct technical modification of titanium matrix to further improve the stability and catalysis of such electrodes[16].A new composite material Ti/TiO_2-NTs /PbO_2 was prepared by relevant researchers. This material formed a highly ordered layer of titanium dioxide nanotubes (TiO_2-NTs) with large specific surface area on the surface of titanium matrix, which enabled PbO_2 to be well supported on the titanium matrix, improved its electrocatalytic capacity and greatly improved the degradation rate of organic matters. Based on the latest research work at home and abroad and the latest research progress, the author will elaborate on the preparation method of Ti/ TiO_2-NTs /PbO_2 electrodes and the structural characterization methods of electrode materials. At the same time, the basic principle of electrocatalytic oxidation is introduced in detail and the application of this electrode in water treatment is summarized systematically.

2. Preparation and properties of Ti/TiO_2-NTs /PbO_2

Preparation of Ti/ TiO_2-NTs /PbO_2 electrode this paper mainly introduces the step-by-step prep-

aration process, namely the preparation of TiO_2 -NTs intermediate layer and the preparation of Ti/ TiO_2-NTs /PbO_2 surface layer.

2.1 Preparation of TiO2-NTs intermediate layer

TiO_2 nanomaterials, as a new type of inorganic semiconductor material, have good electronic conductivity[17-19], especially tubular nano titanium dioxide, which has attracted more and more attention due to its controllable size and highly ordered characteristics. At present, the preparation methods of TiO_2 nanotubes mainly include template synthesis, anodic oxidation and hydrothermal synthesis [20].

2.1.1 Hydrothermal synthesis

Since Kasuga et al.[21] introduced the hydrothermal synthesis to prepare TiO_2 nanotubes, this method has been widely used. The preparation of TiO_2 nanotubes by this method is based on the principle that TiO_2 powder is used as titanium source in a high-pressure reaction kettle to conduct chemical reaction with concentrated alkali solution. Meanwhile, it is kept stirring at high temperature and taken out at room temperature after natural cooling. After pickling, washing and drying, TiO_2 nanotubes are obtained[22].Obviously, when TiO_2 nanotube array is prepared by hydrothermal synthesis, reaction time and temperature have very important influences on the morphology, structure and performance of nanotube array [23].

Liu et al.[24] prepared TiO_2 nanoarray on FTO substrate by simple hydrothermal synthesis. The results showed that with the increase of hydrothermal reaction temperature between 150-℃ and 180℃, the radial growth of nanotubes accelerated, and the surface density and voids of the whole array of nanotubes decreased. With the increase of hydrothermal reaction time, the nanotubes grow along the axial direction and the radial width is basically unchanged. Deng et al.[25] synthesized anatase TiO_2 nano powder by hydrothermal synthesis with $TiCl_4$ as titanium source and $NH_3 \cdot H_2O$ as pH value regulator. Zhang[26] successfully prepared TiO_2 nanotubes with exposed {001} crystal surface by hydrothermal synthesis using tetrabutyl titanate, KF, concentrated sulfuric acid and anhydrous ethanol as raw materials. Lv et al. [27] took $TiCl_4$ as the titanium source, extended the reaction time to 30h, and prepared highly oriented ultra-long diamond TiO_2 nanotube array by one-step hydrothermal synthesis, with a film thickness of up to 30 microns.As the preparation time of the traditional hydrothermal synthesis varies from a few hours to more than a few days after heating by oven, the application of this method in photoelectric catalysis is limited[28].In order to shorten the reaction time, Yang et al.[29] adopted microwave-assisted hydrothermal synthesis, which can speed up the heating rate in the crystallization process and provide higher reaction kinetics, and accelerate the formation of nanotubes, reducing the reaction time to 1-2h.

2.1.2 Template synthesis

The template synthesis method firstly prepares the template whose structure characteristics and size meet the requirements of TiO_2 nanotube formation, and then deposits TiO_2 onto the template. Finally, according to the properties of the template, the template is removed by calcining, acid or alkali dissolution, etc. to form the nanotube array. At present, the templates used to prepare TiO_2 nanotube array by template synthesis mainly include polymer templates, porous anodic alumina templates[30], metal templates, etc. Porous alumina templates have been widely used in the market due to their good properties such as uniform and neat distribution of deposition holes on the surface and electrochemical regulation of hole diameter and film thickness. Hoyer[31] deposited amorphous TiO_2 on a single crystal anodized alumina (AAO) template under nitrogen protection and applied voltage of 400mV, removed the template and dehydrated at high temperature to obtain anatase TiO_2 nanotube. Zhang[32] used AAO template to prepare large area of homogeneous and orderly TiO_2 nanotubes by direct current deposition method, and controlled reaction conditions, it was found that the array morphology and structure of the prepared nanotubes annealed at different temperatures all changed. Therefore, the temperature has a great influ-

ence on the formation of TiO_2 nanotubes. Nguyen et al.[33] used P123 as a soft template to form a water-based self-packaging system and prepared a series of anatase and diamond dual-crystal TiO_2 with a high specific surface area, providing a new basis for preparing mesoporous TiO_2 with adjustable dual-crystal structure from peroxytitanic acid by soft template method. Because the catalytic activity of one-dimensional and two-dimensional nanomaterials tends to weaken when organic pollution is degraded, Li[34] prepared three-dimensional TiO_2 nanotubes on ZnO template with TiO_2(P25) and NaOH as raw materials. The results showed that at the degradation rate of methylene blue could reach 98%, showing strong catalytic performance.

The template method is simple to prepare, but its disadvantage is that the morphology of the generated nanotubes depends on the template pores used. In addition, during the separation process of the template and nanotubes, the morphology of the nanotubes may be easily destroyed due to operation or other reasons, so the reproducibility is relatively poor.

2.1.3 Anodic Oxidation

Anodic oxidation process is after pretreatment of the anode materials (mostly titanium plate), add fluoride ion electrolyte, with Pt and Cu, graphite, the material such as stainless steel as cathode, the anode oxidation corrosion orderly system of titanium dioxide nanotube structure, is one of the main method in the preparation of TiO_2 nanotube arrays[23]. Liu[35] prepared TiO_2 /Ti by anodic oxidation method and studied the kinetics and degradation mechanism of OG degraded by photoelectric oxidation.

Wang[36] used anodic oxidation method to prepare TiO_2 nanotube by using titanium plate as anode and red copper plate as cathode and using constant voltage dc power supply to provide applied voltage. It was found that the diameter of nanotube was affected by voltage. Liu et al.[37] studied the influence of anodic oxidation preparation process on the formation of TiO_2 nanotubes, and the study showed that the nanotubes obtained at different voltages have the characteristics of bamboo structure. The results show that there is a good linear relationship between the oxidation voltage and the average diameter of nanotubes. In addition, oxidation time, electrolyte solution composition, temperature and other experimental conditions have certain effects on the morphology, length and diameter of TiO_2 nanotubes, which are also research hotspots in recent years[23].The research results of Zou[38] showed that the critical anodic oxidation time of the nanotube array was 5min, and the length of the nanotube increased with the extension of the oxidation time. When the oxidation time increased to 2h, the nanotube did not increase. Du [39] compared the effects of three electrolytic liquid systems on the morphology of nanotube arrays, and the results showed that nanotube arrays with different aspect ratios were prepared by three different electrolytic liquid systems. According to previous research results, a highly ordered and uniform TiO_2 nanotube array can be obtained in an organic system. Li et al. [40] studied the effect of temperature on the nanotube array and found that temperature mainly affected the growth rate of TiO_2 nanotube, and the length of nanotube increased rapidly with the increase of temperature. On the other hand, temperature has a great impact on the surface morphology of the array. It can be found that when the temperature is 0℃, the nanopores on the top of the nanotube are uniform and orderly without any impurities, but the surface impurities increase with the increase of temperature, which are mainly caused by the tearing of the top nanotube under the action of electric field [41].

Studies have shown that most studies [42] used primary anodizing method to prepare TiO2 nanotubes by anodizing. In this way, although nanotube arrays can be obtained, the regularity of nanotubes is not very good. So Lin [43] number of anodic oxidation of nanotube arrays is studied, the influence of willow embankment[37], Xiao[44] and Xie[45] secondary anodic oxidation was studied and an anodic oxidation preparation of TiO_2 nanotubes, and the results show that an anodic oxidation was prepared by TiO_2 nanotube arrays to relatively uneven surface, has the floc, and improved secondary anodic oxidation method can produce surface level off,

the orderliness of TiO_2 nanotube arrays, and showed higher catalytic efficiency [43 -45].

2.2 Preparation of Ti/ TiO2-NTs/PbO2 surface layer

The Ti/TiO_2-NTs/PbO_2 electrode material is a novel composite material for surface modification of titanium matrix. The purpose is to load the nanoparticles PbO_2 onto the surface of a titanium substrate having TiO_2 nanotubes. This not only solves the problems of poor mechanical strength, brittleness and easy detachment of PbO_2 electrode, but also has a large specific surface area, a large number of active sites and a strong directional electron transport capability, and its special structure makes TiO_2-NT have photoelectrocatalytic oxidation. Strong ability to degrade organic pollutants[46]. Among them, Duan et al.[47] showed that TiO_2-NTs improved the catalytic activity of PbO_2 electrode. P-NP is better than PbO_2/SnO2-Sb_2O_3/Ti on PbO^2/TiO_2 -NTs/Ti electrode surface. The surface of the electrode is more prone to oxidation. After degradation by electrocatalytic oxidation for 120 min, the degradation rate of p-NP can reach 97.8%, which is obviously higher than the degradation rate of PbO_2 /SnO_2-Sb_2O_3 /Ti electrode is 87.6%. Therefore, PbO_2/TiO_2-NTs/Ti electrode materials have great research significance in water treatment. At present, there are many researches on the modification of titanium dioxide at home and abroad, but the research methods of PbO_2 loaded Ti/TiO_2-NTs electrode have not been uniformly discussed. The author will do the preparation method of PbO_2 loaded Ti/TiO_2-NTs electrode. A more detailed summary.

2.2.1 Spin coating method[48-49]

Also known as thermal decomposition. Firstly, Ti/ TiO_2-NTs substrate needs to be polished and corroded, etc., and then the intermediate layer is uniformly coated with $Pb(NO_3)_2$ aqueous solution, which is then dried in an oven at 120 ℃ for 20 min, and then transferred to a muffle furnace at 500 ℃ for 20min. After repeated sample feeding, the electrode material of PbO_2 active layer is prepared. Liu et al.[50] coated saturated $Pb(NO_3)_2$ solution containing N-butanol after substrate pretreatment, and then put it into an oven with a temperature set at 80 ℃ and kept the reaction until 10 min. After that, the temperature was set to 500℃ for thermal decomposition for 10 min. Studies have shown that the electrode prepared by spinning coating method has good electro-catalytic performance, and a large amount of OH• will be produced in the process of degrading the target pollutant phenol, and the cell voltage is significantly reduced in the experiment.

2.2.2 Compression Molding[51]

Compression molding is prepared by mixing P-bO_2 powder with inert binder under high pressure. Cao et al.[52] mixed a small amount of FDPF-1 organic adhesive into the prepared β-PbO_2 powder, and shaped the mixed powder tablet under the pressure of 20MPa.The degradation of nitrobenzene and alizarin red wastewater by electrocatalytic degradation of the obtained electrode plates was found to be the best for the β-PbO_2 electrode prepared by Compression molding, and the problem of coating shedding was completely solved, and it had good corrosion resistance. Relaxation, etc.[53] doped lanthanum and activated carbon prepared by high compression slice method and polytetrafluoroethylene (PTFE), a new type of lead dioxide electrode, and its catalytic organic dyes wastewater treatment was studied, the study found that high molding method of electrode corrosion resistance is strong, high degradation rate of methylene blue, compared with ordinary method of lead dioxide electrode, the dye with good decolorization and removal of COD has obvious advantages, at the same time, the research shows that the electrode in electrolysis chlorine organic wastewater has good application prospect.

2.2.3 Electrodeposition method

The selected substrate is the anode, and materials such as stainless steel or titanium plate are used as the cathode. Under the action of direct current, Pb ions in the electrolyte are oxidized or reduced by gaining and losing elec-

trons, and PbO_2 nanoparticles or thin films are precipitated on the anode.Yang[54] prepared high-performance PbO_2-TiO_2 nanocomposite electrode under the condition of pulse electrodeposition with pulse frequency of 10 Hz, deposition current density of 0.05 A/cm^2 and duty cycle ratio of 0.2. Li[55], Wang[56], Yao[57] such as high-performance titanium base prepared by electrodeposition method respectively lead dioxide electrode, Li[56] and nodules in the actual preparation of production in large surface roughness, catalytic activity and stability improvement, the first screening of Mn^{2+} and Ni^{2+}, Al^{3+} three kinds of ions on the doping modification of catalytic oxidation of phenol waste water action to improve the performance of the electrode.Pr-PbO_2 was deposited into TiO_2-NTs by pulsed electrodeposition method[58] to prepare Pr-PbO_2/TiO_2-NTs/Ti electrode. The electrocatalytic degradation of methylene blue showed that the electrode had good electrocatalytic ability, and the degradation rate of methylene blue reached 98% in 120 min.Similarly, Chen [59] also doped CeO_2 and $Ce(NO_3)_2$ in the electrolyte to improve the catalytic performance of Ti/ PbO_2-TiO_2 anode. The results showed that the electrocatalytic activity of Ti/ PbO_2-TiO_2 plus CeO_2 electrode was good, and its electrolytic life also increased. According to the latest research trends, the doping of some oxides or ionic elements on Ti/PbO_2-TiO_2 matrix can greatly improve the photoelectric catalytic performance of the electrode, which plays a good role in promoting the application of this kind of electrode in the actual electrocatalytic water treatment technology and widens its application scope. Therefore, doping on Ti/PbO_2-TiO_2 matrix is a research hotspot at present. Sahar Boukhchina[60] obtained Ti/ TiO_2-NTs /PbO_2 electrode with electrolyte of 0.5M $Pb(NO_3)_2$,0.5 M HNO_3 and 0.04M NaF by using a three-electrode system, and used to treat pharmaceutical pollutants. Wang et al. [61] also prepared Ti/ TiO_2-NTs electrode by anodic oxidation method, and prepared Ti/ TiO_2-NTs electrode by pulse electrodeposition method and direct current electrodeposition method respectively. After comparing the degradation ability of methylene blue, it was found that the degradation rate of methylene blue obtained by pulse electrodeposition method was higher than that obtained by direct current electrodeposition method. This is the same as the research results of Wang[62], indicating that the catalytic performance of PbO_2 loaded on the substrate by pulse electrodeposition is better than that by direct current electrodeposition.

3. Technology for morphology and electrochemical analysis of Ti/TiO_2-NTs/PbO_2 electrodes

3.1 Morphology and structure characterization method

Electrocatalytic reactions are heterogeneous reactions that occur between two phases (solid and liquid). Therefore, the surface morphology and structure of the electrode, as well as the crystallization, will have a significant impact on the electrocatalytic reactions. The same electrocatalytic reaction will have different reaction results in different electrode materials, and the degradation ability of organic compounds will also be reflected differently. Therefore, it is very important to study the internal relationship between the structure of electrode materials and electrocatalytic mechanism. Therefore, the author will mainly introduce several common methods to study the characterization of electrode morphology, composition and structure.

(1) Scanning electron microscopy (SEM) The principle of SEM is to use electron microscope to scan the thin electron beam on the surface of the sample, and then enlarge the image according to the principle of television, and then the surface morphology of the detected electrode materials can be clearly seen on the screen.

(2) Transmission electron microscope (TEM) TEM is different from SEM in that it projects a beam of accelerated and concentrated electrons onto a sample. The electrons collide with the atoms in the sample and change direction, resulting in solid angular scattering. The result-

ting light and dark images are then aggregated and displayed on the imaging device. Thus, the internal structure of the electrode material can be seen by TEM.

(3) X-ray diffraction (XRD) By conducting X-ray diffraction on electrode materials and analyzing their diffraction patterns, the research means to obtain the information of the composition of the material and the structure or morphology of atoms or molecules inside the material. XRD can be used to analyze and identify the phase of the electrode coating, and the grain size can be estimated according to Scherrer formula.

(4) X-ray photoelectron spectroscopy (XPS) XPS is one of the most advanced and useful techniques for the characterization of electrode materials. The principle is to use X-ray radiation sample, so that atoms or molecules of inner or valence electrons excited out. XPS can provide elemental analysis of electrode surface, as well as qualitative and quantitative information of element oxidation state in surface compounds.

3.2 Electrochemical analysis method

The electrochemical analysis method can analyze the intrinsic relationship between the electrocatalytic activity and the structure of the electrode and provide convincing basic data for the study of electrocatalytic mechanism. Electrochemical analysis methods are often performed at electrochemical workstations in three-electrode systems.

(1) cyclic voltammetry (CV) is a common electrochemical analysis method. The method is to control the motor potential at different rates, with time to the triangular waveform once or repeatedly scanning. The obtained current-potential curves can be used to determine the range of oxidation potential and reduction potential in the motor reaction, as well as the reversibility of the motor reaction, the possibility of intermediates, phase boundary adsorption or new phase formation.

(2) linear polarization curve method (LSV) the so-called polarization phenomenon refers to a state of deviation from equilibrium. The electrochemical polarization of the electrode is the electrode polarization phenomenon caused by the slowest electrochemical reaction step reflecting the loss of electrons on the surface of the electrode The polarization curve shows the relationship between electrode potential and polarization current or polarization current density. It can react electrode material oxygen evolution potential, oxygen evolution potential is high, electrode material electrocatalytic performance is good, and vice versa.

(3) electrochemical impedance spectra of the electrode system can be obtained by a set of frequency response function values measured by alternating current impedance method (EIS) at a series of different angular frequencies. According to the measured EIS spectra, can determine the equivalent circuit or EIS mathematical model, which can analyze the dynamic process and mechanism of the electrode system contains the equivalent circuit can estimate the dynamic parameters of the motor system, such as electric double layer capacitor electrode, the resistance of the charge transfer process, diffusion and mass transfer process parameters, etc.

Generally, electrode materials are used for electrocatalysis in practical studies, and the basic data indexes required are obtained by using the electrode morphology analysis and electrochemical analysis methods described above. See Table 1 for details.

Table 1 Common characterization methods for PbO_2-TiO_2-NTs/Ti electrode performance

Index	Characterization method	Function
Microscopic appearance	SEM，TEM	Observe the fine morphology of the electrode surface layer and the distribution inside the coating

Index	Characterization method	Function
Crystal structure	XRD XPS	Perform phase identification on the electrode surface layer to understand the crystal structure of the motor
Elemental composition	EDS	According to the peak position, peak shape and peak intensity of each element of the spectrum, the chemical composition of the electrode surface and the proportion of each component are quantitatively analyzed.
Oxygen evolution potential	LCV CV	The oxygen evolution potential can be directly obtained by linear spirometry or cyclic voltammogram
Solution resistance, charge transfer resistance, etc.	EIS	By electrochemical impedance spectroscopy, the best equivalent circuit fitting parameters, the composition of the reaction equivalent circuit and then the catalytic process of the circuit

4. Research progress of Ti/TiO2-NTs/PbO2 in electrocatalytic toxic wastewater treatment

4.1 Basic principle of electrocatalysis

The basic principle of electrocatalytic oxidation treatment is REDOX reaction. In the electrolytic cell, the reaction is carried out at the electrode/ solution interface through the action of the applied electric field, and the organic matter is degraded directly on the anode or the strongly oxidizing substances such as hydroxyl radical (OH•) [63], Cl_2[64] and H_2O_2[65] are produced to degrade the organic matter. The degradation pathways can be divided into direct oxidation stage and indirect oxidation stage.

(1) Direct oxidation stage

It is the direct catalytic oxidation of organic pollutants on the surface of the anode, the conversion of large molecular organic matters into non -toxic small molecular organic matters or direct mineralization into CO_2 and H_2O.The specific reaction is: metal anode material reacts with hydroxyl radicals formed by H_2O or •OH to form high-priced oxides, as shown in equations (1) ~ (2) :

$MO_x+H_2O\rightarrow MO_x[\bullet OH]+H^++e^-$ （1）

$MO_x[\bullet OH]\rightarrow MO_{x+1}+H^++e^-$ （2）

Organic pollutants R in wastewater react with high-priced oxides generated above, and organic pollutants are degraded, as shown in equations (3) ~ (4) :

$R+MO_x[\bullet OH]_y\rightarrow CO_2+MO_x+yH^++e^-$ （3）

$R+MO_{x+1}\rightarrow MO_x+RO$ （4）

(2) Indirect oxidation stage

It is the use of the active substances produced in the electrolysis process: hydroxyl radical OH•, Cl_2, HClO, H_2O_2 and other intermediates to react with organic pollutants in the water to achieve the purpose of degradation of pollutants [66].

$MO_x+H_2O\rightarrow MOx[\bullet OH]+H^++e^-$ (5)

$R+MO_x[\bullet OH]_y\rightarrow CO_2+MO_x+yH^++e-$ (6)

When Cl^- is present in the solution, the following reactions will occur under certain conditions [67-69]:

$2Cl^-\rightarrow Cl_2+2e^-$ (7)

$Cl_2+H_2O\leftrightarrow HClO+Cl^-+H^+$ (8)

$HClO\leftrightarrow ClO^-+H^+$ (9)

When the pH value reaches 3, the active substance in the solution is Cl_2. When the pH value is 3-8, the main performance of Cl is HClO. When the pH value reaches above 8, the active substance in the solution is ClO[70-73].

In addition, other researchers believe that the anode can produce O_3, which can effectively degrade organic matter in solution Thanos et al. [74] found that O_3 can be produced on the lead electrode by the following reaction:

$3H_2O\rightarrow O_3(g)+6e^-+6H^+$ (10)

$O_2+H_2O\rightarrow O_3(aq)+2e^-+2H^+$ (11)

Ozone has a strong oxidation ability, can oxidize cyanide and organic compounds, such as phenol.

4.2 Application of Ti/TiO2-NTs/PbO2 to electrochemical oxidation in wastewater treatment

Due to its strong catalytic activity and chemical inertia, Ti/TiO_2-NTts /PbO_2 electrode is now widely used in the experimental study of wastewater degradation of refractory organic substances, such as phenolic substances, dyes, pesticides, and the treatment of chemical wastewater and other practical refractory organic wastewater.

4.2.1 Degradation of model wastewater

(1) Wastewaters containing Phenols

Phenolic compounds are mainly used in pesticide, dye plastics, paint, petrochemical and pharmaceutical industries. Therefore, waste water from these industries contains a large number of phenolic substances that are difficult to degrade. Phenolic substances do great harm to environmental quality and human health and safety.

Duan et al.[47] studied the electrocatalytic degradation of target pollutant p-np (p-nitrophenol) by PbO_2/ TiO_2-NTs/Ti electrode. The results showed that the degradation rate of p-np by PbO_2/ TiO_2-NTs/Ti electrode prepared by anodic oxidation was 97.8% after 120 min of electrolysis. Hong [75] evaluated the catalytic activity of the β- PbO_2/ TiO_2-NTs/Ti electrode by electrocatalytic degradation of phenol. The experimental results showed that the electrodeposition of β- PbO_2/ TiO_2-NTs/Ti improved the electrocatalytic activity of the electrode, and the degradation of phenol reached 83% in the electrolysis for 180min, while the degradation of phenol by pure TiO_2-NTs/Ti only reached 27.4 %.

(2) Wastewaters containing dyes

Nowadays, with the development of economy, synthetic dyes are widely used in textile, cosmetics, leather and other major industries. Data show that the printing and dyeing processes adopted by printing and dyeing enterprises consume 100 ~ 200 m^3 of pure water per 1 t of products, 80% ~ 90% of which become waste water because they cannot be recycled [76].The composition of dye wastewater is complex, the content of organic pollutants is high, and the amount of water is large. Among them, azo dyes, which are the most widely used ones, are difficult to degrade and do great harm to biology.

Dayanne [77] studied the effect of electrocatalytic oxidation of acidic blue-113 wastewater by Pb/PbO_2, Ti/Pt, PbO_2/TiO_2-NTs/Ti electrode. The results showed that under the same experimental conditions, PbO_2/TiO_2-NTs/Ti electrode could better degrade the acidic Blue-113 wastewater, and the chroma and COD degradation rate could reach 98% and 92.5% respectively. Moreover, compared with Pb/PbO_2, Ti/Pt, PbO_2/TiO_2-NTs/Ti electrode has higher current efficiency and lower energy consumption. Wu[77] used the prepared PbO_2/Sb-SnO_2 /TiO_2NTs/Ti electrode to treat simulated rhodamine B wastewater, and investigated the effects of different initial concentrations of rhodamine B, initial pH, temperature and chloride ion concentration on electrocatalysis. Yang [54] also used PbO_2-TiO_2 nanocomposite electrode to study the photoelectric catalytic degradation performance of rhodamine B on dye, and pointed out that the degradation rate of rhodamine B and COD was in line with the first-order reaction kinetics model. The results showed that rhodamine B's uv-visible spectral absorption decreased gradually with the progress of photophotocatalytic degradation, and the solution color became lighter and colorless gradually. After continuous degradation for 90 min, the ultraviolet absorption of rhodamine B at 553 nm basically disappeared. After degradation of rhodamine B to 75 min, rhodamine B removal rate and COD removal rate of PbO_2/TiO_2-NTs /Ti electrode were 98.2% and 71.8% respectively. Wang[61] used pulsed electrodeposition of Co- PbO_2/ TiO_2-NTs/Ti electrode to electrocatalyze the degradation of methylene blue, an organic pollutant. 0.2mol/LNa_2SO_4 was added as an applied electrolyte. Under the condition of pH=3, current density of 50mA/cm^2 and solution containing 30mg/L methylene blue, the degradation rate of methylene blue reached 100% and COD degradation rate reached 74% after 2 hours of electrolysis. Meanwhile, Wang

also electrocatalyzed methylene blue with PbO_2/ TiO_2-NTs/Ti electrode under the same conditions, and found that the electrocatalysis effect of Co- PbO_2/ TiO_2-NTs/Ti electrode was better. Obviously, combining other active elements on PbO_2/ TiO_2-NTs/Ti electrode can improve the electrocatalytic ability.

(3) Wastewaters containing pharmaceuticals

The composition of pharmaceutical wastewater is complex, and the drug components and their related metabolites are discharged into the natural water environment, which will have a serious toxic effect on the water. Boukhchina S [60] used PbO_2/TiO_2-NTs/Ti electrodes prepared by different methods to study the effect of electrocatalytic oxidation on degradation of target pollutant ampicillin.Studies have found that by spin coating method of TiO_2-NTs and electrodeposition method doped PbO_2 nanoparticles obtained by the PbO_2/TiO_2-NTs/Ti electrode electric catalytic activity is stronger, in 300 min, the COD degradation rate of 64%, ampicillin can complete degradation in the space of an hour, and ampicillin pseudo-first-order kinetics model of degradation and the anode oxidation TiO_2-NTs and electrodeposition method doped PbO_2 nanoparticles preparation of Ti/TiO_2-NTs /PbO_2 electrode degradation effect is relatively poor, and ampicillin degradation accords with zero order kinetics model. Boukhchina analyzed the intermediate products of ampicillin degradation by high performance liquid chromatography, and proposed the degradation mechanism of ampicillin based on previous research results.

Chen[79] electrocatalyzed nitrobenzene with PbO_2/SnO_2-Sb/TiO_2-NTs/Ti electrode, and kinetic analysis showed that the degradation process of nitrobenzene by the electrode was in line with the pseudo-first-order kinetic model. After 6 hours of electrolysis, the COD degradation rate reached 100%, and it was found by GC-MS that the intermediate products containing nitro groups in the solution disappeared. Therefore, through the conversion of intermediate products, the authors reasonably proposed the degradation mechanism of the two nitrobenzene. This has very important reference significance to the future research work.

4.2.2 Degradation of real wastewater

In addition to the above simulated wastewater, Ti/TiO_2-NTs/PbO_2 electrode has also been studied in actual wastewater. Yin[80] applied Ti/Ti O_2-NTs/SnO_2-Sb/PbO_2, a new type of TiO^2 nannanotube modified electrode, to the electrocatalytic oxidation treatment of membrane concentrated water from the tailwater of a sewage plant in a concentrated chemical area. The influences of electrolysis time, current density and pH value on COD removal rate were investigated. The results showed that, with the increase of current density, COD degradation rate significantly increased, electrolysis 1 h, COD degradation rate reached 55%. Li[81] used Ti/TiO_2-NTs/PbO_2 electrode to treat coal chemical wastewater. After 120 min degradation, the removal rate of COD and total phenol by the electrode was 16.13% and 35.48%, respectively, which had good removal effect on refractory phenolic substances.

5. Conclusions and prospects

Ti/TiO_2-NTs/PbO_2 electrode has a good application prospect in the treatment of refractory organic wastewater due to its excellent electrochemical performance and strong degradation ability of organic pollutants. However, at present, the research on Ti/TiO_2-NTs/PbO_2 electrode is only limited to the laboratory, which is quite different from the actual industrial demand. Therefore, it is necessary to promote industry-university-research cooperation among universities, research institutes and enterprises, which will quickly bring cheap and practical electro-catalytic materials to the market, thus accelerating the process of large-scale production. Based on the current research on electrodes, the author puts forward the following two prospects:

(1) develop the preparation technology of Ti/Ti O_2-NTs/PbO_2 electrode with large area. At present, the preparation of Ti/TiO_2-NTs/PbO_2 elec-

trode is still in the stage of small area experimental laboratories mainly in universities. Therefore, through technical reform or independent research and development, the preparation equipment and process of Ti/TiO_2-NTs /PbO_2 electrode with intended area is developed, and the formation of large area Ti/TiO_2-NTs /PbO_2 electrode is a major breakthrough to realize its industrial application.

(2) further improve the electrocatalytic performance and stability of Ti/TiO_2-NTs/PbO_2 electrode. Although Ti/TiO_2-NTs/PbO_2 electrode has a good ability to degrade organic matter, it can be found that in the later stage of electrocatalytic reaction, with the decrease of organic matter concentration and the influence of mass transfer process, the current efficiency will decline, which will reduce the degradation rate of organic matter and correspondingly increase the energy consumption. At present, the focus of the current research on electrode materials lies in the synthesis of materials with controllable morphology and reasonable surface doping of rare earth metal elements, which will further improve the electrocatalytic activity and stability of the electrode, improve the overall current efficiency and solve the problem of large energy consumption.

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