available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Electrochemical oxidation of rhodamine B by PbO₂/Sb-SnO₂/TiO₂ nanotube arrays electrode

Jia Wu ^a, Kai Zhu ^a, Hao Xu ^{b,*}, Wei Yan ^{b,#}^a Xi'an XD Switchgear Electric Co., Ltd., Xi'an 710049, Shaanxi, China^b Department of Environmental Science and Engineering, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China

ARTICLE INFO

Article history:

Received 19 November 2018

Accepted 4 March 2019

Published 5 June 2019

Keywords:

TiO₂ nanotube array

Electrochemical oxidation

Rhodamine B

Degradation mechanism

ABSTRACT

A PbO₂/Sb-SnO₂/TiO₂ nanotube array composite electrode was successfully synthesized and its electrochemical oxidation properties were investigated. Field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) results showed that the PbO₂ coating was composed of an α -PbO₂ inner layer and a β -PbO₂ outer layer. Accelerated life measurement indicated that the composite electrode had a lifetime of 815 h. Rhodamine B (RhB) was employed as a model pollutant to analyze the electrocatalytic activity of the electrode. The effects of initial RhB concentration, current density, initial pH, temperature, and chloride ion concentration on the electrochemical oxidation were investigated in detail. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) results suggested that the concentration of leached Pb²⁺ in the electrolyte during the electrocatalytic oxidation process can be neglected. Finally, the degradation mechanism during the electrocatalytic oxidation process was proposed based on the results of solid-phase micro-extraction-gas chromatography-mass spectrometry (SPME-GC-MS). The high electrocatalytic performance of the composite electrode makes it a promising anode for the treatment of organic pollutants in aqueous solution.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The treatment of textile wastewater has attracted much attention due to its toxicity and threat to the environment and human life [1]. Electrochemical oxidation has been regarded as an attractive approach because of its versatility, environmental compatibility, safety, automation, cost effectiveness, and energy efficiency [2–6]. Therefore, it has been widely used in the degradation of organic pollutants [7–9]. It is well known that the electrode materials play an important part in electrochemical

oxidation processes [10]. Numerous electrode materials including PbO₂ [11–13], SnO₂ [14,15], RuO₂ [16,17], IrO₂ [18,19], and boron-doped diamond (BDD) [20,21] have been extensively studied. Among these anode materials, PbO₂ has been regarded as a promising metal oxide electrode material due to its low cost, excellent conductivity, chemical stability, and high over-potential for the oxygen evolution reaction [22,23]. Many efforts have been devoted to improving the electrocatalytic activity and stability of PbO₂. Doping with metal or non-metal elements (Cu [24], Bi [25], Ce [26], Fe [27], F [28], etc.) or other

* Corresponding author. Tel: +86-15829780706; Fax: +86-29-82664731; E-mail: xuhao@xjtu.edu.cn

Corresponding author. E-mail: yanwei@xjtu.edu.cn

This work is supported by the National Natural Science Foundation of China (21507104) and Natural Science Basic Research Plan in Shaanxi Province of China (2017JM2015).

DOI: S1872-2067(19)63342-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 6, June 2019

compounds (TiO_2 [29], SnO_2 [30], ZrO_2 [31], Co_3O_4 [32], TiN [33], etc.) has been widely discussed in the last several years.

However, the application of PbO_2 electrodes faces the problem of electrochemical corrosion. Previous research showed that the introduction of an Sb-SnO_2 interlayer could increase the chemical stability and electrocatalytic activity of the anode [34]. Moreover, electrode substrate microstructure modification has also been demonstrated to be an efficient approach to enhance the stability and electrocatalytic properties [35]. Vertically oriented TiO_2 nanotube arrays (TiO_2 NTAs) are regarded as an effective microstructure modification due to their big specific surface area, high uniformity, and good hydrophilicity. It was found that the special TiO_2 NTA architecture could improve the loading of Sb-SnO_2 and thus enhance the electrocatalytic activity of a PbO_2 electrode [36]. Fabrication of an Sb-SnO_2 coating by electrodeposition can produce a more uniform and dense surface. However, the surface tension on TiO_2 NTAs should be suppressed during the electrodeposition process. In this study, an Sb-SnO_2 coating was prepared by a microwave method to decrease the surface tension.

Rhodamine B (RhB) has been widely used in many biotechnology applications and industrial processes, such as dye laser production, paper dyeing, flow cytometry, ELISA, and fluorescence microscopy. The treatment of RhB is difficult due to its high discharge quantity and because it is hard to biodegrade. To address the environmental influence of this pollutant, an electrochemical oxidation technique has been developed. However, the research towards the specific degradation process of RhB during electrocatalytic oxidation is still imperfect. Therefore, it is necessary to study the influencing factors and intermediate products of RhB in the electrochemical process.

Figure 1 shows the structure of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode. It was found that the TiO_2 NTAs served as a tubal template; the Sb-SnO_2 coating embedded in the TiO_2 NTAs acted as the interlayer and PbO_2 containing an $\alpha\text{-PbO}_2$ inner layer and a $\beta\text{-PbO}_2$ outer layer was employed as the catalytic surface layer. It was expected that this multilayer microstructure would significantly enhance the electrocatalytic activity. This paper is focused on the electrocatalytic properties and stability of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode for the treatment of textile wastewater. RhB was chosen as the model organic pollutant to investigate the electrocatalytic performance of the electrode. The removal of chemical oxygen demand (COD) and color was analyzed to study the decomposition of RhB. The influences of key operating variables such as

Fig. 1. The structure of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode.

initial concentration, current density, initial pH, temperature, and chloride ion concentration on the degradation efficiency were investigated in detail. The degradation kinetics and the energy efficiency of the electrode were evaluated during the electrocatalytic oxidation process. Moreover, the safety and stability of the electrode are also discussed. Finally, the degradation mechanism of RhB during electrochemical oxidation was proposed.

2. Experimental

2.1. Fabrication of $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode

The $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode was fabricated on the basis of our previous research [37]. Anodization was performed at 50 V for 1 h in the electrolyte (0.3 wt% NH_4F + 3 vol% H_2O + ethylene glycol). The as-prepared TiO_2 NTAs electrode was annealed in atmosphere at 500 °C for 2 h. Then, Sb and Sn were deposited onto the TiO_2 NTAs by a microwave method, and the Sb-SnO_2 layer was formed by annealing at 500 °C for 1 h. Finally, the PbO_2 coating was fabricated by electrodeposition with an inner layer ($\alpha\text{-PbO}_2$) and an outer layer ($\beta\text{-PbO}_2$). The electrodeposition process was conducted in a two-electrode system under a current of 10 $\text{mA}\cdot\text{cm}^{-2}$. The $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$ layers were prepared by electrodeposition at 40 °C for 30 min and 65 °C for 120 min, respectively.

2.2. Electrode characterization

Field-emission scanning electron microscopy (FE-SEM) was performed on a JEOL JSM-6700F instrument equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. X-ray diffraction (XRD) patterns were obtained from an X'pert PRO MRD diffractometer ($\text{Cu K}\alpha$ source; $\lambda = 0.15416$ nm) with a scanning angle (2θ) range of 10°–80°.

The electrochemical properties of the as-prepared $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode were investigated on an electrochemical workstation (CHI 660D, Chenhua). The traditional three-electrode configuration, in which a saturated Ag/AgCl electrode was the reference electrode, a Pt sheet was the counter electrode, and the as-synthesized $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode was the working electrode, was used. Linear sweep voltammetry (LSV) measurement was conducted in 0.5 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 aqueous solutions at a scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$. Accelerated life measurement was carried out to investigate the lifetime of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode in 0.5 $\text{mol}\cdot\text{L}^{-1}$ H_2SO_4 aqueous solutions with a current density of 0.5 $\text{A}\cdot\text{cm}^{-2}$. In this process, the electrode was supposed to be deactivated when the cell potential was higher than 10 V. Cyclic voltammetry (CV) experiments were conducted in RhB solutions at a scan rate of 20 $\text{mV}\cdot\text{s}^{-1}$ (reference electrode: Ag/AgCl ; counter electrode: Cu sheet; working electrode: $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode).

2.3. Electrocatalytic oxidation process

Electrochemical oxidation was conducted using the

Fig. 2. The schematic diagram of the electrocatalytic degradation experiment.

two-electrode configuration, as shown in Fig. 2. The $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode was used as the anode and a copper sheet was employed as the cathode. The volume of the electrolyte solutions was 200 mL. A UV-visible spectrophotometer (UV2600A, Unico, Shanghai) was employed to measure the absorbance spectra of RhB and the maximum absorption peak of RhB was at 554 nm. COD was measured using a water quality tester (ET99722 Lovibond). The color removal efficiency (η) and COD removal of RhB were determined according to equations (1) and (2):

$$\eta = (A_0 - A_t)/A_0 \times 100\% \quad (1)$$

$$\text{COD removal efficiency} = (\text{COD}_0 - \text{COD}_t)/\text{COD}_0 \times 100\% \quad (2)$$

where A_0 and A_t were the absorbance values of RhB at 554 nm before electrolysis and after an electrolysis time t , respectively; COD_0 and COD_t were the chemical oxygen demands at time 0 and t , respectively.

The average energy demand per gram of RhB (EC_p , $\text{kWh}\cdot\text{gRhB}^{-1}$) and the energy consumption per COD (EC_{COD} ,

$\text{kWh}\cdot\text{gCOD}^{-1}$) were calculated using equations (3) and (4):

$$\text{EC}_p = (5 \times U \times I \times t)/[18 \times V \times (C_0 - C_t)] \quad (3)$$

$$\text{EC}_{\text{COD}} = (5 \times U \times I \times t)/[18 \times V \times (\text{COD}_0 - \text{COD}_t)] \quad (4)$$

where U is the cell voltage (V), I is the current (A), t is the electrolysis time (s), V is the volume of the electrolyte, and 5/18 is the conversion coefficient of J to kWh.

A solid-phase micro-extraction-gas chromatography-mass spectrometry (SPME-GC-MS) technique was used to determine the intermediates in the electrocatalytic degradation process. The samples that were adsorbed on the SPME syringe were automatically injected into a TRACE GC Ultra (Thermo/Finnigan, Milan, Italy) gas chromatograph and a TraceISQ (Thermo/Finnigan, Milan, Italy) mass spectrometric detector. The injection port was set to splitless mode and kept at 260 °C. The oven temperature was maintained at 60 °C for 3 min and then ramped to 280 °C at 10 °C $\cdot\text{min}^{-1}$. The flow was set to continuous flow mode with a carrier gas (He, 99.999%) rate of 1 mL $\cdot\text{min}^{-1}$. The ion source temperature and interface temperature were maintained at 230 °C and 280 °C, respectively.

3. Results and discussion

3.1. Electrode characterization

Electrode characterization through SEM, XRD, LSV, and accelerated life was conducted to investigate the surface morphology, crystalline structure, oxygen evolution potential, and stability of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode. It was found that highly ordered TiO_2 NTAs were formed on the Ti substrate. Moreover, the TiO_2 NTA surface was completely covered by the Sb-SnO₂ coating after Sb and Sn were deposited using microwaves, as shown in the right corner of Fig. 3a. The XRD pattern reveals that the TiO_2 NTAs electrode exhibits the diffraction peaks of anatase TiO_2 . It is clear that no peaks cor-

Fig. 3. (a) FE-SEM images of pure TiO_2 NTAs and $\text{Sb-SnO}_2/\text{TiO}_2$ NTAs; (b) FE-SEM images of $\alpha\text{-PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs and $\beta\text{-PbO}_2/\alpha\text{-PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs; (c) XRD profiles of TiO_2 NTAs and $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs; (d) LSV and accelerated life curves of $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs; (e) CV curve of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode in RhB solution (RhB concentration: 100 $\text{mg}\cdot\text{L}^{-1}$; supporting electrolyte: 0.1 $\text{mol}\cdot\text{L}^{-1}$ Na_2SO_4 ; room temperature).

responding to TiO_2 were detected after deposition of Sb and Sn, suggesting better coverage of the Sb-SnO₂ coating. This is in accord with the SEM results. Fig. 3b shows the surface morphology of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs. The PbO_2 coatings contain an inner layer ($\alpha\text{-PbO}_2$) and an outer layer ($\beta\text{-PbO}_2$). It was observed that $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$ exhibit spicules and a hill-like surface, respectively. In this composite electrode, the TiO_2 NTAs served as a tubal template, the Sb-SnO₂ coating embedded in the TiO_2 NTAs acted as an interlayer to enhance the electrocatalytic activity and electrochemical stability of the PbO_2 coating, the $\alpha\text{-PbO}_2$ inner layer was applied to provide better contact between the particles for its compact structure, and the $\beta\text{-PbO}_2$ outer layer was employed as the catalytic surface layer to enhance the electrocatalytic activity and service lifetime. This well-aligned multilayer microstructure could enhance the effective area and loading amount, which was expected to result in better electrocatalytic activity during the oxidation reactions of organic dye molecules.

The characteristic reflections of $\beta\text{-PbO}_2$ in the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs were detected in the XRD results and there were no other diffraction peaks. The corresponding plane of $\beta\text{-PbO}_2$ is clearly shown in Fig. 3c. This phenomenon indicates that the outer layer is thoroughly covered by a thick $\beta\text{-PbO}_2$ layer. According to the Debye-Scherrer equation, the average grain size of $\beta\text{-PbO}_2$ is 14.7 nm, which is smaller than the reported size (29.1 nm) resulting from the one-step electrodeposited method [38]. This may be attributed to the introduction of the inner $\alpha\text{-PbO}_2$ layer. The compact structure of the $\alpha\text{-PbO}_2$ layer may affect the growth of $\beta\text{-PbO}_2$ and thus decrease the grain size.

The oxygen evolution potential of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode is 1.7 V (vs. Ag/AgCl), as shown in the inset of Fig. 3d. Moreover, it was also observed that the electrode exhibits a lifetime of 815 h under a current density of 0.5 A·cm⁻² in 0.5 mol·L⁻¹ H₂SO₄ aqueous solutions. SEM of the deactivated $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode is also shown in Fig. S1 (see the Supporting Information). It was observed that the coating fell off from the substrate, resulting in the deactivation of the electrode. Moreover, we found two plateaus in the accelerated life curve. The first plateau and the second plateau were

attributed to the anti-corrosion of the PbO_2 coating and the generation of a solid solution by PbO_2 and Sb-SnO₂, respectively. The EDS result in Fig. S2 further demonstrates the formation of a solid solution by PbO_2 and Sb-SnO₂. Fig. 3e shows the CV curve of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode in a RhB solution. The CV curve shows that one oxidation peak corresponding to RhB oxidation appears at 1.26 V (vs. Ag/AgCl). There is no reduction peak in the CV curve, which suggests that the RhB oxidation is an irreversible reaction. It should be noted that water is not electrolyzed during this process because the voltage is lower than the water decomposition voltage.

3.2. Influence of current density

The current density plays a significant role in the electrocatalytic oxidation process. Current density values ranging from 20 to 60 mA·cm⁻² were applied to evaluate its effect on the electrochemical degradation of RhB. Fig. 4 shows the relationships between color and COD removal efficiency and electrolysis time for different current densities. It was found that the color removal of RhB increased from 67.7% to 99.8% when the current density increased from 20 to 60 mA·cm⁻² after 120 min. COD removal efficiency also increased from 42.5% to 77.2%. This can be attributed to the higher yields of strong oxidation free radicals. The active radicals will attack the chromophoric structure of RhB, which is then mineralized to small molecules. The experimental results show that 99.7% of color is removed after 180 min of electrolysis at 40 mA·cm⁻², and only 80.2% of COD is removed under the same conditions. The probable reason is that the chromophore of RhB is destroyed to form the soluble organic intermediates that made a contribution to the COD. Fig. S3a shows the kinetics of RhB electrochemical degradation at different current densities. It should be noted that the reaction can be divided into two stages and both of them obey pseudo-first-order kinetics. This can be attributed to the competition between the intermediates and RhB molecules during the electrolysis process. The amount of RhB molecules decreases with the degradation time. However, the species of the intermediates increase with increases in electrolysis time. Different intermediates had different degra-

Fig. 4. The effect of current density on (a) RhB removal efficiency with time and (b) COD removal efficiency with time on $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode (initial pH: 7; initial RhB concentration: 100 mg·L⁻¹; supporting electrolyte: 0.1 mol·L⁻¹ Na₂SO₄; room temperature).

Table 1Parameters during electrochemical RhB degradation over PbO₂/Sb-SnO₂/TiO₂ NTAs electrode at different current densities ($t = 120$ min).

Current density (mA·cm ⁻²)	$\eta/\%$	$k_1 \times 10^3/\text{min}^{-1}$	R_1^2	$k_2 \times 10^3/\text{min}^{-1}$	R_2^2	COD removal efficiency/%	$k_{\text{COD}} \times 10^3/\text{min}^{-1}$	R_{COD}^2	$\text{EC}_p/\text{kWh}\cdot\text{gRhB}^{-1}$	$\text{EC}_{\text{COD}}/\text{kWh}\cdot\text{gCOD}^{-1}$
20	67.7	9.14	0.994	15.5	0.996	42.5	5.36	0.970	0.235	0.225
30	75.6	11.7	0.990	22.2	0.995	49.5	6.57	0.965	0.352	0.293
40	92.0	21.4	0.977	58.1	0.999	66.0	9.59	0.988	0.480	0.340
50	95.2	23.6	0.984	84.4	0.947	72.1	10.7	0.984	0.627	0.420
60	99.8	48.3	0.992	40.7	0.901	77.2	12.2	0.987	0.832	0.664

dation rates and the overall degradation rate was determined by all of the kinds of molecules in the solutions. Therefore, two different stages occur during the electrochemical degradation process. Table 1 displays the pseudo-first-order rate constants (k_1 , k_2) in different stages. It was observed that k_1 increased with increasing current density in the range of 20–60 mA·cm⁻². However, the value of k_2 decreased when the current density was 60 mA·cm⁻², which can be ascribed to the low substrate concentration. From Fig. 4a, we found that the removal efficiency reached 94.1% at 60 min. This implies that the number of degradable substances is very low in the solutions. The low substrate concentration leads to a decrease in the degradation rate. Moreover, COD removal also follows pseudo-first-order kinetics and the rate constant (k_{COD}) increases with the current density. The k_{COD} value increased from 5.36×10^{-3} to $12.2 \times 10^{-3} \text{ min}^{-1}$, which implies that RhB degradation efficiency increases with the current density. The EC_p and EC_{COD} at 120 min are listed in Table 1 towards investigation of the energy consumption. It was found that EC_p and EC_{COD} increase with the current density. These results show that higher current densities are beneficial for RhB removal. However, high current densities result in high energy consumption. Therefore, it is not necessary to employ an excessively high current density.

3.3. Effect of initial RhB concentration

It is necessary to investigate the influence of initial dye concentration on the electrochemical oxidation process because practical wastewater contains various concentrations of RhB. As shown in Fig. 5, it can be found that the color removal effi-

ciency and COD removal both decrease with increasing initial concentration. According to the literature [39], the electrocatalytic oxidation process is controlled by mass transfer. At low concentrations, the electrochemical process is faster than diffusion. RhB molecules can be totally degraded on the electrode surface. Nevertheless, active free radicals generated on the electrode surface are insufficient for pollutant degradation with increasing concentration. With an increase in concentration, more organic substances are transferred to the electrode surface. However, the amount of hydroxyl radicals produced on the electrode was not enough for readily degrading pollutants. Therefore, color removal efficiency decreases with increases in initial concentration. It should be noted that COD removal efficiency is very close when the concentration is 80 and 100 mg·L⁻¹. This phenomenon may be caused by the deficiency of active free radicals. It is assumed that too many intermediates are accumulated on the electrode surface during the electrochemical oxidation. COD removal is limited by the amount of active free radicals. Table S1 shows the apparent kinetic coefficients of initial concentration, which were obtained from Fig. S4a. The value of k_2 significantly decreases with increasing RhB concentration, which further confirms that the electrocatalytic process is determined by mass transfer. Moreover, Fig. S4a shows a negative relationship between EC_p and electrolysis time, which indicates that electrochemical oxidation consumes less energy for high-concentration wastewater than for low-concentration wastewater. This result reveals that a high concentration of RhB is not favorable for its degradation. However, it is worthy to note that the electrocatalytic oxidation technique exhibits promise for application in the treatment of

Fig. 5. The influence of initial RhB concentration on (a) RhB removal efficiency with time and (b) COD removal efficiency with time on PbO₂/Sb-SnO₂/TiO₂ NTAs electrode (initial pH: 7; current density: 40 mA·cm⁻²; supporting electrolyte: 0.1 mol·L⁻¹ Na₂SO₄; room temperature).

Fig. 6. The effect of initial pH on (a) RhB removal efficiency with time and (b) COD removal efficiency with time on $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode (current density: $40 \text{ mA}\cdot\text{cm}^{-2}$; initial RhB concentration: $100 \text{ mg}\cdot\text{L}^{-1}$; supporting electrolyte: $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ Na}_2\text{SO}_4$; room temperature).

high-concentration wastewater due to its low energy consumption.

3.4. Effect of initial pH

Initial pH can affect coexisting ions or the morphology of organic matter; thus, it is an important factor when evaluating the electrocatalytic oxidation. The effect of initial pH on the electrochemical oxidation is shown in Fig. 6. It can be observed that the maximum color removal of RhB was obtained under neutral conditions ($\text{pH} = 7$, $\eta = 99.7\%$, COD removal efficiency = 80.2%). When the pH was 2, 7, and 11, the corresponding color removal efficiencies were 75.2%, 92.0%, and 66.8%, respectively ($t = 120 \text{ min}$). The different forms of RhB at different pH levels may affect the generation of active radicals. It can be observed that acidic conditions ($\text{pH} = 2$) and alkaline conditions ($\text{pH} = 11$) are not favorable for the electrochemical degradation. Fig. S5a shows that the degradation at different pH levels follows pseudo-first-order kinetics. The values of k_1 , k_2 , and k_{COD} in Table 2 further prove that degradation in neutral conditions is better than in acidic or alkaline conditions. As shown in Fig. S5b, when the pH was 2, 7, and 11, the corresponding EC_p was 0.564, 0.480, and $0.632 \text{ kWh}\cdot\text{gRhB}^{-1}$, respectively. From Fig. S5b, we learned that the lowest EC_p was acquired in neutral conditions. Both acidic and alkaline conditions could enhance the energy consumption. These results indicate that the electrocatalytic degradation can work well in a wide pH range and the best degradation efficiency can be obtained in neutral conditions. Therefore, pH adjustment is not necessary during the RhB degradation process.

Table 2

Parameters during electrochemical RhB degradation over $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode at different initial pH.

Initial pH	$k_1 \times 10^3 / \text{min}^{-1}$	R_1^2	$k_2 \times 10^3 / \text{min}^{-1}$	R_2^2	$k_{\text{COD}} \times 10^3 / \text{min}^{-1}$	R_{COD}^2
2	12.3	0.997	17.3	0.993	3.77	0.965
7	21.4	0.977	58.1	0.999	9.59	0.988
11	8.98	0.986	11.3	0.999	4.21	0.953

3.5. Influence of temperature

The effect of temperature on electrochemical degradation was investigated because the temperature is of importance for oxidation reactions. As shown in Fig. 7, it was observed that a low temperature is beneficial for electrolysis. The color removal efficiency of RhB decreased from 99.8% to 72.2% and COD removal efficiency decreased from 65.7% to 52.1% when the temperature was increased from 0°C to 30°C after 100 min. We employed pseudo-first-order kinetics to simulate the kinetic reaction (Fig. S6a). The data listed in Table S2 show that the value of k_1 slightly changes with the temperature. However, the value of k_2 dramatically decreases with increases in temperature, which reveals that a low temperature can improve RhB degradation. When the temperature was 0, 10, 20, and 30°C , the corresponding k_{COD} was 11.2, 9.19, 8.54, and 6.39 min^{-1} . The change of the k_{COD} implies that a low temperature can enhance the performance of the electrochemical oxidation. The probable reason is that the rates of side reactions such as the hydrogen evolution reaction and the oxygen evolution reaction may increase with the temperature, thus decreasing the efficiency of the electrocatalytic oxidation process. The relationship between EC_p and time is also shown in Fig. S6b. It can be observed that EC_p first decreased and then increased with time when the temperature was 0 or 10°C . However, EC_p increased with time when the temperature was 20 or 30°C . This phenomenon can be explained by the relationship between $U \times t$ and η according to equation (3). From the above results, we speculate that a low temperature can accelerate the electrocatalytic oxidation because the rates of side reactions (hydrogen evolution reaction and oxygen evolution reaction) increase with increasing temperature. The enhanced side reactions result in decreasing degradation efficiency. However, we need to consume extra energy to change the temperature, which increases the cost of degradation. Therefore, room temperature is the best choice for us for the electrocatalytic oxidation process.

3.6. Effect of chloride ion concentration

Fig. 7. The effect of temperature on (a) RhB removal efficiency with time and (b) COD removal efficiency with time on PbO₂/Sb-SnO₂/TiO₂ NTAs electrode (initial pH: 7; current density: 40 mA·cm⁻²; initial RhB concentration: 100 mg·L⁻¹; supporting electrolyte: 0.1 mol·L⁻¹ Na₂SO₄).

It is necessary to investigate the influence of chloride ions on electrochemical oxidation because wastewater usually contains chloride ions. The degradation efficiency (η and COD removal efficiency) significantly increases with the addition of chloride ions, as shown in Fig. 8. A higher concentration of chloride ions leads to a faster electrocatalytic oxidation process. It is well known that chloride ions can be oxidized to active chlorine on an electrode surface during electrolysis. The enhanced degradation efficiency can be attributed to the strong oxidizability of active chlorine. The molecular structure of RhB can be destroyed owing to the strong oxidizability, thus improving the RhB removal efficiency. The dynamics simulation is displayed in Fig. S7, from which we found that k_1 and k_2 increase with the chloride ion concentration. The kinetic constants of RhB degradation listed in Table S3 further confirm that the addition of chloride ions is helpful to the electrocatalytic degradation process. When the concentration of chloride ions was 1, 5, and 10 mmol·L⁻¹, the corresponding k_{COD} was 13.6, 78.1, and 99.9 min⁻¹, respectively. From these results, we speculate that the addition of chloride ions can improve the RhB removal efficiency due to the generation of active chlorine.

It should be noted that the color and COD removal efficiencies have positive relationships with the concentration of chloride ions. Moreover, it was observed that E_{CP} decreases with the addition of chloride ions, which can be attributed to the enhanced removal efficiency. Therefore, we conclude that the removal efficiency increases with an increase in chloride ion concentration. However, halogenated by-products may be generated due to the addition of chloride ions; thus, it is worth weighing whether to add the chloride ions.

3.7. The safety and stability of PbO₂/Sb-SnO₂/TiO₂ NTAs electrode

SEM and EDS of the PbO₂/Sb-SnO₂/TiO₂ NTAs electrode after the degradation experiment were performed to evaluate its stability, as shown in Fig. 9. It was found that the morphology of the electrode slightly changes and some particles are adsorbed on the surface. EDS measurement indicated that the adsorbed particles may come from the sodium sulfate or organic matter in the electrolyte. This result shows that the electrode has strong stability and is promising for application in wastewater

Fig. 8. The effect of chloride ion concentration on (a) RhB removal efficiency with time and (b) COD removal efficiency with time on PbO₂/Sb-SnO₂/TiO₂ NTAs electrode (initial pH: 7; current density: 40 mA·cm⁻²; initial RhB concentration: 100 mg·L⁻¹; room temperature).

Fig. 9. SEM and EDS of $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode after electrolysis of 20 h.

Table 3

The concentrations of leached Pb^{2+} under different current densities after electrolysis.

Current density ($\text{mA}\cdot\text{cm}^{-2}$)	Concentration of $\text{Pb}^{2+}/(\text{mg}\cdot\text{L}^{-1})$
20	not detected
30	not detected
40	not detected
50	0.0037
60	0.0133

treatment.

Safety of the electrode is very important [40]. Therefore, the risk of secondary water pollution should be carefully considered due to Pb^{2+} leaching from the anode. An ICPE technique was employed to investigate the concentration of leached Pb^{2+} at different current densities after electrolysis, as listed in Table 3. It was observed that the concentration of leached Pb^{2+} cannot be detected because of its detectable limit when the current density is below $40 \text{ mA}\cdot\text{cm}^{-2}$. Little Pb^{2+} was detected when the current density was increased to 50 or $60 \text{ mA}\cdot\text{cm}^{-2}$. The concentrations of leached Pb^{2+} listed in Table 3 meet the national standard for the wastewater discharge guideline (GB8978-2015). This result reveals that the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode is safe for electrochemical degradation and the risk of secondary water pollution caused by Pb^{2+} can be ignored. Moreover, our previous research also showed that a modified PbO_2 electrode exhibits strong stability [33,41,42]. However, it should be noted that the optimal current density should be controlled at below $40 \text{ mA}\cdot\text{cm}^{-2}$ in practical wastewater treatment due to the high energy consumption.

3.8. Degradation mechanism of RhB

Fig. S8 shows the GC-MS spectrogram and Table S4 shows the identified intermediates for the electrocatalytic oxidation at different degradation times. Based on the identified intermediates obtained by the SPME-GC-MS technique, a possible pathway for the electrochemical degradation of RhB was proposed,

as shown in Fig. 10. As the electrocatalytic degradation proceeds, various new intermediate products can be detected at different times. According to Table S4, it was found that benzene rings and poly-heterocyclic compounds are detected during the first 20 min, which can be attributed to the destruction of the conjugated chromophoric structure. Then, some long chain esters or ketone compounds are generated with increasing degradation time due to the oxidation of active free radicals. Moreover, smaller carboxylic acids or esters further form as the electrochemical oxidation proceeds and the contents of these intermediates decrease with the degradation time. Finally, most of them eventually degrade to CO_2 and H_2O at the end of the process due to the destruction of the reactive species. In summary, the degradation process undergoes the following stages: destruction of the conjugated chromophoric structure to form benzene rings or poly-heterocyclic compounds, opening of rings to generate long chain esters or ketones, destruction of longer chains by reactive species to produce smaller molecules (carboxylic acids or esters), and finally mineralization to CO_2 and H_2O .

4. Conclusions

The current work revealed that a $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode with a multilayer microstructure can be successfully employed for the electrochemical degradation of RhB. SEM, XRD, and electrochemical measurements were carried out to understand the morphology, structure, and electrochemical performance of the electrode. Moreover, the influences of key operating parameters (initial RhB concentration, current density, initial pH, temperature, and chloride ion concentration) on RhB removal were systematically investigated to evaluate the electrocatalytic activity of the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode. It was found that RhB removal (η and COD removal efficiency) increases with increasing current density and chloride ion concentration. In contrast, RhB removal increases with decreasing initial RhB concentration and temperature. It should be noted that neutral conditions are helpful to electrochemical oxidation. Moreover, we also observed that the

Fig. 10. Proposed mechanism of electrochemical oxidation of RhB on $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode.

$\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode exhibits high safety and stability. The risk of secondary water pollution caused by Pb^{2+} can be neglected. SPME-GC-MS results suggested that the conjugated chromophoric structure of the RhB molecule is destroyed by active free radicals during the initial stage. Then, the intermediate products are gradually oxidized to form small esters, ketones, and other small organic compounds and finally mineralized. In summary, the $\text{PbO}_2/\text{Sb-SnO}_2/\text{TiO}_2$ NTAs electrode exhibits enhanced stability and electrocatalytic activity in the electrochemical degradation process and has a potential application in wastewater treatment.

Acknowledgments

The authors gratefully acknowledge the financial supports from the National Natural Science Foundation of China (Grant

No. 21507104) and Natural Science Basic Research Plan in Shaanxi Province of China (Program No. 2017JM2015).

References

- [1] D. M. de Araújo, C. Sáez, C. A. Martínez-Huitle, P. Cañizares, M. A. Rodrigo, *Appl. Catal. B*, **2015**, 166–167, 454–459.
- [2] W. Wu, Z. H. Huang, T. T. Lim, *Appl. Catal. A*, **2014**, 480, 58–78.
- [3] M. G. Tavares, L. V. A. da Silva, A. M. S. Solano, J. Tonholo, C. A. Martínez-Huitle, C. L. P. S. Zanta, *Chem. Eng. J.*, **2012**, 204–206, 141–150.
- [4] E. Petrucci, D. Montanaro, *Chem. Eng. J.*, **2011**, 174, 612–618.
- [5] W. Fu, K. Wang, X. Lv, H. Fu, X. Dong, L. Chen, X. Zhang, G. Jiang, *Chin. J. Catal.*, **2018**, 39, 693–700.
- [6] J. Li, Q. Zhuang, P. Xu, D. Zhang, L. Wei, D. Yuan, *Chin. J. Catal.*, **2018**, 39, 1403–1410.
- [7] M. Panizza, G. Cerisola, *Chem. Rev.*, **2009**, 109, 6541–6569.

- [8] C. A. Martinez-Huitle, E. Brillas, *Appl. Catal. B*, **2009**, 87, 105–145.
- [9] I. Sires, E. Brillas, M. A. Oturan, M. A. Rodrigo, M. Panizza, *Environ. Sci. Pollut. Res.*, **2014**, 21, 8336–8367.
- [10] P. S. Patel, N. Bandre, A. Saraf, J. P. Ruparelia, *Procedia Eng.*, **2013**, 51, 430–435.
- [11] Q. Dai, Y. Xia, S. Chen, M. Weng, J. Chen, J. Wang, J. Chen, *Chem. Eng. J.*, **2014**, 245, 359–366.
- [12] A. Mukimin, H. Vistanty, N. Zen, *Chem. Eng. J.*, **2015**, 259, 430–437.
- [13] H. Lin, J. Niu, J. Xu, Y. Li, Y. Pan, *Electrochim. Acta*, **2013**, 97, 167–174.
- [14] Y. Duan, Y. Chen, Q. Wen, T.G. Duan, *J. Electroanal. Chem.*, **2016**, 768, 81–88.
- [15] Y. H. Cui, Y. J. Feng, Z. Q. Liu, *Electrochim. Acta*, **2009**, 54, 4903–4909.
- [16] L. A. Naslund, C. M. Sanchez-Sanchez, A. S. Ingason, J. Backstrom, E. Herrero, J. Rosen, S. Holmin, *J. Phys. Chem. C*, **2013**, 117, 6126–6135.
- [17] L. Du, J. Wu, C. W. Hu, *Electrochim. Acta*, **2012**, 68, 69–73.
- [18] A. Kapalka, S. Fierro, Z. Frontistis, A. Katsaounis, S. Neodo, O. Frey, N. de Rooij, K. M. Udert, C. Comninellis, *Electrochim. Acta*, **2011**, 56, 1361–1365.
- [19] H. Li, Q. N. Yu, B. Yang, Z. J. Li, L. C. Lei, *J. Electroanal. Chem.*, **2015**, 738, 14–19.
- [20] J.R. Sun, H.Y. Lu, L.L. Du, H.B. Lin, H.D. Li, *Appl. Surf. Sci.*, **2011**, 257, 6667–6671.
- [21] N. R. Stradiotto, K. E. Toghill, L. Xiao, A. Moshar, R. G. Compton, *Electroanalysis*, **2010**, 21, 2627–2633.
- [22] J. M. Aquino, R. C. Rocha-Filho, L. A. M. Ruotolo, N. Bocchi, S. R. Biaggio, *Chem. Eng. J.*, **2014**, 251, 138–145.
- [23] C. Tan, B. Xiang, Y. J. Li, J. W. Fang, M. Huang, *Chem. Eng. J.*, **2011**, 166, 15–21.
- [24] H. Xu, D. Shao, Q. Zhang, H. Yang, Y. Wei, *RSC Adv.*, **2014**, 4, 25011–25017.
- [25] L. Chang, Y. Zhou, X. Duan, W. Liu, D. Xu, *J. Taiwan Inst. Chem. Eng.*, **2014**, 45, 1338–1346.
- [26] X. Duan, Y. Zhao, W. Liu, L. Chang, X. Li, *J. Taiwan Inst. Chem. Eng.*, **2014**, 45, 2975–2985.
- [27] L. S. Andrade, L. A. M. Ruotolo, R. C. Rocha-Filho, N. Bocchi, S. R. Biaggio, J. Iniesta, V. Garcia-Garcia, V. Montiel, *Chemosphere*, **2007**, 66, 2035–2043.
- [28] J. Cao, H. Zhao, F. Cao, J. Zhang, C. Cao, *Electrochim. Acta*, **2009**, 54, 2595–2602.
- [29] Y. W. Yao, Y. Li, L. H. Cui, N. C. Yu, H. S. Dong, *J. Electrochem. Soc.*, **2015**, 162, E7–E12.
- [30] Z. Q. He, C. X. Huang, Q. Wang, Z. Jiang, J. M. Chen, S. Song, *Int. J. Electrochem. Sci.*, **2011**, 6, 4341–4354.
- [31] Y. Yao, C. Zhao, M. Zhao, X. Wang, *J. Hazard. Mater.*, **2013**, 263, 726–734.
- [32] J. Zhao, C. Zhu, J. Lu, C. Hu, S. Peng, T. Chen, *Electrochim. Acta*, **2014**, 118, 169–175.
- [33] X. Li, H. Xu, W. Yan, *J. Electrochem. Soc.*, **2016**, 163, D592–D602.
- [34] C. Zhong, K. Wei, W. Han, L. Wang, X. Sun, J. Li, *J. Electroanal. Chem.*, **2013**, 705, 68–74.
- [35] X. Cui, G. Zhao, Y. Lei, H. Li, P. Li, M. Liu, *Mater. Chem. Phys.*, **2009**, 113, 314–321.
- [36] Q. Wang, T. Jin, Z. Hu, L. Zhou, M. Zhou, *Sep. Purif. Technol.*, **2013**, 102, 180–186.
- [37] J. Wu, H. Xu, Y. Wei, *RSC Adv.*, **2015**, 5, 19284–19293.
- [38] Y. Chen, H. Li, W. Liu, Y. Tu, Y. Zhang, W. Han, L. Wang, *Chemosphere*, **2014**, 113, 48–55.

Graphical Abstract

Chin. J. Catal., 2019, 40: 917–927 doi: S1872-2067(19)63342-5

Electrochemical oxidation of rhodamine B by PbO₂/Sb-SnO₂/TiO₂ nanotube arrays electrode

Jia Wu, Kai Zhu, Hao Xu*, Wei Yan*

Xi'an XD Switchgear Electric Co., Ltd.; Xi'an Jiaotong University

A stable PbO₂/Sb-SnO₂/TiO₂ nanotube arrays electrode was prepared and applied to the removal of RhB from aqueous solution under various operating parameters. The multilayer composite electrode exhibited excellent electrocatalytic activity for RhB removal and the optimal operation conditions were determined. Moreover, the degradation mechanism during the electrocatalytic oxidation process was proposed on the basis of solid-phase micro-extraction-gas chromatography-mass spectrometry.

- [39] C. A. Martínezhuitle, S. Ferro, *Chem. Soc. Rev.*, **2006**, 35, 1324–1340.
- [40] L. Yang, Z. Chen, D. Cui, X. Luo, B. Liang, L. Yang, T. Liu, A. Wang, S. Luo, *Chem. Eng. J.*, **2019**, 359, 894–901.
- [41] H. Xu, W. Guo, J. Wu, J. Feng, H. Yang, W. Yan, *RSC Adv.*, **2016**, 6, 7610–7617.
- [42] H. Xu, Q. Yuan, D. Shao, H. Yang, J. Liang, J. Feng, W. Yan, *J. Hazard. Mater.*, **2015**, 286, 509–516.

PbO₂/Sb-SnO₂/TiO₂纳米管阵列电极电化学氧化降解罗丹明B

武佳^a, 朱凯^a, 徐浩^{b,*}, 延卫^{b,#}

^a西安西电开关电气有限公司, 陕西西安710049

^b西安交通大学环境科学与工程系, 动力工程多相流国家重点实验室, 陕西西安710049

摘要: 罗丹明B(RhB)在印染废水中广泛存在, 具有难降解和易积累等特点, 严重威胁生态系统和人类健康, 因此寻找一种高效、清洁、经济的处理方法引起人们的广泛关注. 电化学氧化法因其操作简单、环境友好等特点而广泛应用于难处理废水或有毒废水的降解, 但过多的能源消耗限制了其进一步应用. 在电化学氧化过程中, 电极材料的选择是影响电催化性能的重要因素之一, 目前的电极材料主要有硼掺杂金刚石电极、IrO₂电极、RuO₂电极和PbO₂电极等. 在这些电极材料中, PbO₂电极因价格低廉、导电性良好、化学稳定性好及析氧电位高等优点而成为具有潜力的电极材料之一. 近年来, 为了提高PbO₂电极的电催化活性和稳定性, 研究者对其进行了一系列掺杂改性, 如Cu, Bi, Ce, Fe和F等金属或非金属掺杂, 以及TiO₂, SnO₂, ZrO₂, Co₃O₄和TiN等其他化合物复合等.

相比于传统的PbO₂电极基底Ti, TiO₂纳米管阵列具有高度有序、垂直取向、表面积大及亲水性良好等优势, 这些特性可使其成为一个更好的载体, 关于其做基底负载电催化活性层的研究引起了人们的广泛关注. 本文以TiO₂纳米管阵列作为基底, 通过微波法沉积Sb-SnO₂中间层, 电沉积法沉积PbO₂表层(含 α -PbO₂内层和 β -PbO₂外层), 制得一种复合DSA阳极材料, 并将其用于处理RhB废水. 通过扫描电镜(FE-SEM)、X射线衍射(XRD)和电化学测试等手段对该复合电极进行了表征, 系统探讨了RhB初始浓度、电流密度、pH值、温度和氯离子浓度等因素对电化学氧化降解过程的影响, 并对电极稳定性及RhB降解机理进行了深入研究.

SEM和XRD结果表明, PbO₂/Sb-SnO₂/TiO₂纳米管阵列电极表面涂层覆盖紧密, 电化学测试结果表明该电极寿命达815 h. RhB电化学氧化实验结果发现, RhB降解过程遵循准一级动力学模型, 且高的电流密度、中性环境、低温和氯离子的添加均有利于其降解, 但电流密度过高以及人工降温均会造成能耗过大, 而氯离子的加入会带来潜在的二次污染, 故在实际应用中需根据实际情况进行调节. 此外, 通过系统研究不同参数的影响, 发现该复合电极对外界环境具有较强的适应性及催化能力, 而降解机理的提出有利于我们更好地研究降解过程中变化. 综上可知, 该复合电极较强的稳定性及催化活性使其在电化学氧化降解废水中具有较大潜在应用前景.

关键词: TiO₂纳米管阵列; 电化学氧化; 罗丹明B; 降解机理

收稿日期: 2018-11-19. 接受日期: 2019-03-04. 出版日期: 2019-06-05.

*通讯联系人. 电话: 15829780706; 传真: (029)82664731; 电子信箱: xuhao@xjtu.edu.cn

#通讯联系人. 电子信箱: yanwei@xjtu.edu.cn

基金来源: 国家自然科学基金(21507104); 陕西省自然科学基金基础研究计划(2017JM2015).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).