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Fabrication of a hydrophobic SDBS-PbO$_2$ anode for electrochemical degradation of nitrobenzene in aqueous solution

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ABSTRACT

In present work, a hydrophobic PbO$_2$ electrode modified by sodium dodecyl benzene sulfonate (SDBS-PbO$_2$) was fabricated using electrodeposition method. The effect of SDBS concentration in electroplating bath on the surface morphology, structure, electrochemical properties, hydrophilicity, •OH generation ability and stability of SDBS-PbO$_2$ electrodes was studied using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), water contact angle, fluorescence probe technique, and accelerated life test, respectively. Results showed that SDBS modification not only increased the electro-catalytic activity, but also prolonged the service life of PbO$_2$ electrode. The electrode prepared from the electroplating bath containing 10 mg/L SDBS (SDBS-PbO$_2$-10 mg/L) showed the highest electrocatalytic activity and the longest service life. The electrochemical degradation of nitrobenzene (NB) in simulated wastewater was used to evaluate the potential application of SDBS-PbO$_2$ electrodes for wastewater treatment. The highest NB removal efficiency and total organic carbon (TOC) removal efficiency of 89.35% and 52.62% were both obtained by SDBS-PbO$_2$-10 mg/L anode. Thus, the SDBS-PbO$_2$-10 mg/L anode was used to systematically investigate the effects of applied current density, initial NB concentration, temperature, and pH value on the reaction kinetics and mineralization current efficiency (MCE) of NB degradation. It was found that the increase of applied current density and the reduction of initial NB concentration exerted a prominent effect on the degradation of NB, but caused the decrease of MCE, while high temperature and low pH value improved both NB degradation rate and MCE. These results show that the SDBS-PbO$_2$-10 mg/L electrode may become a promising anode for organic pollutant degradation.

1. Introduction

Nitrobenzene (NB), an essential material in the synthesis of many products including polymers, dyes, pharmaceuticals, pesticides, explosives, herbicides and synthetic rubbers [1], has been listed as a priority pollutant in many countries due to its high toxicity, tendency to accumulate in the environment, and hard biological degradation [2–4]. Statistics have shown that approximately 10, 000 tonnes of NB is released into the water annually through various pathways, such as wastewater discharge, industry leaks and sudden environmental pollution events [5], which will inevitably cause great harm to the environment. Hence, it is necessary to develop an effective technology for the removal of NB from wastewater. Recently, many treatment technologies have been developed for the aqueous NB treatment, such as adsorption [4], photocatalysis [6], microelectrolysis [7], electrochemical reduction [8], electrochemical oxidation [9] and biological processes [5]. Among these methods, the electrochemical oxidation processes have attracted lots of attentions due to its high mineralization efficiency, easy control, versatility, mild reaction conditions and environmental compatibility [10,11].

The efficiency of electrochemical oxidation processes depends strongly on the anode material [10,12], which determines the •OH radicals generation rate on the surface of the anode. A vast variety of electrodes have been used in electrochemical oxidation processes for organic pollutants degradation, including boron-doped diamond, noble metals, graphite, carbon and various dimensionally stable anode such as PbO$_2$, SnO$_2$, IrO$_2$ and RuO$_2$ [13]. Among

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these anodes, PbO_2 electrode has been illustrated to be a superior metal oxide anode due to its advantages of relatively high oxygen evolution overpotential, high chemical stability in corrosive media, low cost and easy preparation [14]. However, it has been shown in previous studies that the application of PbO_2 anode is stilled limited due to its shortcoming of low current efficiency. Also, its service life should be further improved for application [14,15]. Thus, researchers have taken a great deal of efforts to improve its electrocatalytic activity and service lifetime, including adopting new substrates [16,17], adding intermediate layer (SnO_2-Sb, MnO_2) between substrate and oxidation layer, and doping metal oxides [18] or metallic ions (Bi^{3+}, Co^{2+}, La, $[Fe(CN)_6]^{3-}$, F^-, Ce^{3+}, Al^{3+}) [14,19–23] into β-PbO_2 active layer. Our previous studies have also confirmed that the electro-catalytic activity and stability of PbO_2 anode were markedly improved by introducing carbon nanotubes (CNTs) into active layer [24]. CNTs energetically enhanced the electron transport rate between PbO_2 electrode and organic pollutants on account of its high electrical conductivity and high surface area, but the doping of CNTs was greatly restricted by its poor dispersibility in acid solution. The surfactant can improve the dispersion of CNTs in aqueous solution because its charged groups (hydrophilic heads) attract to water and their alkyl chains (hydrophobic tails) adsorb on the surfaces of CNTs. Therefore, sodium dodecyl benzene sulfonate (SDBS), a common anion surfactant, was introduced into the electroplating bath. Consequently, more CNTs were doped into the β-PbO_2 active layer by the synergetic action of SDBS. However, it is well known that the surfactant can affect the structure and properties of coatings, which has been widely applied in electrochemistry fields to improve the property of electrode/solution interface [25], so the amount of introduced SDBS into electroplating bath may greatly influence the electrochemical activity and stability of PbO_2 electrode. Nevertheless, in our previous study, in order to decrease the complexity of research system, the effect of SDBS on the electro-catalytic oxidation capacity of PbO_2 anode wasn't discussed in detail.

For these reasons, in this study, the SDBS modified PbO_2 (SDBS-PbO_2) electrodes used for electro-catalysis oxidation were prepared by electrodeposition method. The optimum addition amount of SDBS in electroplating solution was investigated through structure characterizations and electrochemical measurements. The SDBS-PbO_2 electrodes were used as anode in electrochemical oxidation of NB, and the effects of some operation variables, such as applied current density, initial NB concentration, temperature and pH value, on electrochemical mineralization of NB were also explored.

2. Experimental section

2.1. Materials

Pure titanium sheets were purchased from Jinkai Co., Baoji, China. All chemicals used in the experiments were analytical purity and were used as received without any further purification. All solutions were prepared using ultrapure water (resistivity = 18.2 MΩ cm at 25 °C) obtained from a Millipore water system.

2.2. Electrode preparation

In this study, the PbO_2 electrodes were prepared following these steps. Firstly, the titanium substrates were pretreated through polishing, ultrasonic cleaning in acetone and ultrapure water, and etching in 15% oxalic solution. Secondly, the SnO_2-Sb_2O_3 bottom layers were prepared by the method of thermal decomposition. Then, the α-PbO_2 intermediate layers were electroplated in alkaline electrolyte consisting of 3.5 mol/L NaOH and 0.1 mol/L PbO. Finally, the β-PbO_2 active layers were electroplated in acidic electrolyte consisting of 0.5 mol/L $Pb(NO_3)_2$, 0.05 mol/L NaF and 1.0 mol/L HNO_3. When the SDBS-PbO_2 electrodes were prepared, 5 mg/L, 10 mg/L, 20 mg/L or 50 mg/L SDBS was added into acidic electrolyte, and the obtained electrodes were denoted as SDBS-PbO_2-5 mg/L, SDBS-PbO_2-10 mg/L, SDBS-PbO_2-20 mg/L and SDBS-PbO_2-50 mg/L, respectively. Other details can be found in our previous study [26].

2.3. Characterization and performance tests

The surface morphology of the prepared electrodes was observed by scanning electron microscopy (SEM; Hitachi S-570, Japan). The phase structure of electrodes was examined by X-ray diffraction (XRD) on a D-max/3C X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation source (45 kV, 30 mA), where the samples were exposed to X-ray with a scan rate of 16°/min from 10° to 90°. X-ray photoelectron spectrometry (XPS) analysis was performed on an ESCALAB250XI (USA) spectroscope equipped with Al Kα radiation to ascertain the surface chemical states of coatings.

Cyclic voltammetry (CV) tests were performed using an electrochemical workstation (Versas TAT3, USA) with the conventional three-electrode system. The tested PbO_2 electrode, platinum sheet and saturated calomel electrode were used as working electrode, counter electrode and reference electrode, respectively.

The •OH radicals generation levels of electrodes were determined with terephthalic acid trapping and fluorescence spectrophotometer according to the literature [27]. Terephthalic acid readily reacts with •OH radicals to form 2-hydroxy terephthalic acid, which has a characteristic fluorescence signal around 425 nm. The fluorescence intensity of 2-hydroxy terephthalic acid can be used to estimate the production amount of •OH radicals. The electrolysis was performed at a current density of 30 mA/cm^2 at 30 °C in 200 mL of aqueous solution containing 0.5 mmol/L terephthalic acid, 0.5 g/L NaOH and 0.25 mol/L Na_2SO_4. Samples were drawn from the reactor every 5 min and diluted 10 times with ultrapure water, then measured on a fluorescence spectrophotometer (Cary EclipseG9800A, Agilent). Fluorescence spectra were recorded in the range of 370–520 nm, using an excitation wavelength of 315 nm.

To reduce the test time, the accelerated life tests were conducted at a high applied current density of 1 A/cm^2 with a three-electrode system, the tested electrode was used working electrode, and the Pt sheet and saturated Ag/AgCl electrode were used as counter and reference electrodes, respectively. The electrolyte was 2 mol/L H_2SO_4 and the temperature was about 60 °C. During the tests, the anode potential was monitored periodically. The electrolysis time when the anode potential increased to 10 V was regarded as the lifetime of electrode.

2.4. Electrochemical oxidation of NB

The degradation experiments of NB were carried out in a plexiglass vessel using batch process. The prepared SDBS-PbO_2 electrode or pure PbO_2 electrode (3 cm × 5 cm) was used as the anode and a stainless steel sheet with the same area was used as the cathode. The volume of NB solution was 200 mL, and 0.05 mol/L Na_2SO_4 was added to the solution as supporting electrolyte. The effect of main operational variables including applied current density (10–50 mA/cm^2), initial NB concentration (10–90 mg/L), temperature (20–40 °C) and pH value (3–12) were investigated. The pH value was adjusted by H_2SO_4 or NaOH, and the constant current was provided by a DC-power supply. All experiments were conducted in triplicate in order to ensure accurate data acquisition, and the error bars in figures represented the standard deviation from the mean values. The concentrations of NB were quantified using high performance liquid chromatography (CTO-6A,