Journal of Electroanalytical Chemistry 823 (2018) 193–202

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Preparation and characterization of Fe-Ce co-doped Ti/TiO_2 NTs/PbO_2 nanocomposite electrodes for efficient electrocatalytic degradation of organic pollutants

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ARTICLE INFO

Keywords:
Pulse electrodeposition
Ti/TNTs/Fe-Ce-PbO_2 electrodes
Methylene blue
Electrochemical oxidation

ABSTRACT

To further improve the electrocatalytic activity and stability of PbO_2 electrode in refractory organic pollutants treatment, Fe and Ce co-doped Ti/TiO_2 nanotube (TNTs)/PbO_2 electrode was successfully synthesized by pulse electrodeposition. The morphology, crystallinity and elemental composition Ti/TNTs/Fe-Ce-PbO_2 electrodes were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impendence spectroscopy (EIS) were utilized to investigate the electrochemical performance of electrodes. Results showed that Ti/TNTs/Fe-Ce-PbO_2 electrodes (P) possessed finer grain size and higher specific surface than other three PbO_2-based electrodes. The electrochemical measurements showed that Ti/TNTs/Fe-Ce-PbO_2 electrodes (P) exhibited higher oxidation peak current, oxygen evolution potential and strong capability of ·OH generation than those of other three kinds of electrodes. The experiments on degradation of methylene blue (MB) also indicated that Ti/TNTs/Fe-Ce-PbO_2 electrodes (P) have higher chemical oxygen demand (COD) removal efficiency and instantaneous current efficiency (ICE) than the Ti/TNTs/Fe-Ce-PbO_2 electrodes (D). Meanwhile, high reusability and safety were achieved by Ti/TNTs/Fe-Ce-PbO_2 electrodes (P) when treating wastewater containing organic dyes.

1. Introduction

Contamination of freshwater caused by the organic pollutants and hazardous pollutants from the industrial production is known as a global issue. Especially, with the rapid development of synthetic dye technology, organic azo dyes have been widely used in several industries, such as textile, color paper and printing, and so on [1, 2]. The vast majority of colored wastewater has been discharged into the environment without sufficient treatment, which caused serious ecosystem problems in the past decade. Hence, the treatment of wastewater containing organic dyes is essential before discharge. Traditional various treatment strategies for the toxic of effluents containing azo dyes are inconvenient, as for example biological oxidation, chemical coagulation and activated carbon adsorption [3]. As a result, the development of the more efficient and feasibility method to completely remove the persistent organic dyes from wastewaters is essential. During the last two decades, electrochemical oxidation technology, which is regarded as an emerging method for the decontamination of various wastewater containing toxic or refractory organic pollutants, has attracted a great deal of attention because of its many distinctive advantages, such as high oxidation efficiency, easy control, environmental compatibility, and so on [4–10]. During the anodic oxidation process, the anode material as the core component is a crucial factor which strongly affects the efficiency of organic pollutant oxidation [11]. Therefore, it is very important to develop a novel electrode material with high catalytic activity and stability.

So far, various types of electrode materials [12] have been investigated to decompose the organics of wastewater, such as graphite [13], platinum [14], IrO_2 [15], RuO_2 [16], SnO_2 [17], PbO_2 [18], and boron-doped diamond (BDD) [19] electrodes. Among numerous types of electrodes, PbO_2 electrode has attracted a great deal of attention and investigations as one of the optimum metal oxide electrode materials

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https://doi.org/10.1016/j.jelechem.2018.06.007
Received 19 March 2018; Received in revised form 1 May 2018; Accepted 2 June 2018

because of its low electrical resistivity, low price, high corrosion-resistance, as well as high overpotential for the oxygen evolution reaction [20, 21]. However, it has some shortcomings which limit its further application, such as relatively large interface resistance, low catalyst activity and easily damaged [22]. Thus, the key point is to make a further improvement in the electrocatalytic performance and accelerate the practical applications of PbO_2 electrodes in electrochemical technologies for water treatment. More recently, the microstructure design of electrode substrate has attracted widely interests, and it has been confirmed that the nature of substrate material can further improve the electrochemical performances and stability of electrodes, especially for PbO_2 grew on the TiO_2 nanotube array template [23]. In addition, many studies also proved that the electrocatalytic ability and stability (chemical or mechanical) of PbO_2 electrode could be greatly improved by doping of some foreign materials into the oxide layer [24, 25]. The incorporation of foreign materials such as Co^{2+} [26, 27], Fe^{3+} [28, 29], F^- [30], rare earths ions [31] and Bi^{3+} [32, 33] into PbO_2 has been investigated, which has been proved to be beneficial to the improvement of the electrochemical performance. Direction current electrodeposition is the main preparation method of PbO_2 composite electrodes by adding some foreign elements into the deposition solution [34].

Recently, pulse electrodeposition has attracted more and more interest as a convenient method to control the density of materials and the size of the crystal particles, and to achieve a uniform morphology on the surface of the electrode. Compared with direct electrodeposition, pulse electrodeposition is helpful to control the structure and the properties of the produced deposits [35]. Therefore, the doped PbO_2 electrodes prepared by pulse electrodeposition possess more unique compositions and microstructures than that obtained by other electrodeposition methods [36–38].

In the present work, Fe and Ce co-doped PbO_2 electrode based on TNTs arrays was prepared by pulse electrodeposition. The subsequently morphology, crystalline structure, surface composition, electrochemical performances and stability were characterized. The electrocatalytic activities of Ti/TNTs/Fe-Ce-PbO_2 electrodes were further evaluated by degrading the methylene blue (MB) as the bio-refractory model organic pollutant. The COD and absorbance were recorded to investigate the removal process of MB.

2. Experimental

2.1. Materials

All chemical reagents were supplied by Alfa Aesar and used as received without further purification. All solutions were prepared using deionized water.

2.2. Preparation of Ti/TNTs matrices

A Ti foil (1 cm × 3 cm × 0.5 mm, 99.7%) was used as a substrate for the formation of vertically-aligned TNTs. The TNTs were prepared by anodic oxidation as described in our previous work [39]. After anodization, the obtained Ti/TNTs were cleaned in the deionized water by ultrasonic. The cleaned TNTs were air-dried and then annealed to induce crystallization in a muffle furnace, where the annealing was conducted in air at 500 °C for 120 min. In order to increase their conductivity, the prepared TNTs were electrochemically reduced in 1 M $(NH_4)_2SO_4$ as described in a ref. [40].

2.3. Preparation of Ti/TNTs/Fe-Ce-PbO_2 electrodes

The surface layer of Fe, Ce and PbO_2 on the Ti/TNTs were achieved in the prepared nanotubes substrates by electrodeposition method in a three-electrode system (the Ti/TiO_2NTs as a working electrode, platinum foil as a counter electrode and the saturated calomel electrode as a reference electrode). The composition of electrodeposition solution was: 0.5 mol L^{-1} Pb $(NO_3)_2$, 0.1 mol L^{-1} HNO_3, 0.02 mol L^{-1} Fe $(NO_3)_3{\cdot}9H_2O$ and 0.01 mol L^{-1} Ce $(NO_3)_3{\cdot}9H_2O$ [24, 27, 45]. The parameters of the pulse electrodeposition were negative pulse (−50 mA cm^{-2}, 1 ms), positive pulse (+50 mA cm^{-2}, 10 ms), current off-time (1000 ms) and the deposition processes were carried out at 60 °C for 45 min. The obtained electrode was marked as Ti/TNTs/Fe-Ce-PbO_2 electrode (P). For comparison purposes, the direct electrodeposition was also carried out at 60 °C for 45 min, and the current density was controlled at 50 mA cm^{-2}, which was marked as Ti/TNTs/Fe-Ce-PbO_2 electrode (D). When the Ti/TNTs/Fe-PbO_2 electrodes (P) was prepared by the same pulse electrodeposition procedures of the preparation of the Ti/TNTs/Fe-Ce-PbO_2 electrode (P), 0.02 mol L^{-1} Fe $(NO_3)_3{\cdot}9H_2O$ was added into the electrodeposition solution (0.5 mol L^{-1} Pb $(NO_3)_2$, 0.1 mol L^{-1} HNO_3). A similar methodology was followed for the preparation of the Ti/TNTs/PbO_2 electrodes (P), but no Fe $(NO_3)_3{\cdot}9H_2O$ was added into the electrodeposition solution. The approximate thicknesses of all PbO_2 deposit are 16 μm.

2.4. Characterization of Ti/TNTs/Fe-Ce-PbO_2 electrodes

A SEM (Netherlands FEI Sirion-200) was employed to investigate and analyze the structure of the prepared samples, including Ti/TNTs, Ti/TNTs/Fe-Ce-PbO_2 electrodes. The XRD analysis were recorded with a Japan MXPAHF X-ray diffractometer equipped with graphite monochromatized Cu Kα irradiation (λ = 0.154056 nm), employing a scanning rate of $0.02°/s^1$ in the 2θ range of 10–70°. XPS were taken on a Thermo ESCALAB 250 X-ray photoelectron spectrometer with Al Kα radiation (1486.60 eV, 150 W) to analyze the element state of the electrodes.

2.5. Electrochemical experiments

Electrochemical behaviors of Ti/TNTs, Ti/TNTs/Fe-PbO_2 (P), Ti/TNTs/Fe-Ce-PbO_2 (P) and Ti/TNTs/Fe-Ce-PbO_2 (D) electrodes (1 cm × 1 cm) were measured with a standard three-electrode cell using Autolab PGSTAT302N electrochemical analysis system. The platinum was used as the counter electrode and saturated calomel electrode (SCE) was the reference electrode. The measurement of CV was conducted in 0.1 mol L^{-1} Na_2SO_4 solution at a scan rate of 50 mV s^{-1}. The steady-state polarization curves were conducted in 0.2 mol L^{-1} Na_2SO_4 solution at a scan rate of 10 mV s^{-1}. EIS measurements were made at a measurement potential of open-circuit potential in 0.2 mol L^{-1} Na_2SO_4 solution, the frequencies swept from 1×10^5 Hz to 0.1 Hz with an applied sine wave of 20 mV amplitude [41]. The stability tests were performed by anodic polarization at 1 A cm^{-2} in 2 mol L^{-1} H_2SO_4 solution at 60 °C.

During the experiments, the absorbance of MB with different electrolytic times was analyzed by the UV/visible analysis Spectrophotometer (UV-3600 plus, SHIMADZU). The chemical oxygen demand (COD) was determined by a 5B-1F COD reactor and a spectrophotometer (Lianhua Tech Co., China). The COD removal efficiency (η) was calculated as follow,

$$\eta = \frac{COD_0 - COD_t}{COD_0} \times 100\% \tag{1}$$

where COD_0 is the COD of initial concentration and COD_t is the COD at given time t.

The instantaneous current efficiency (ICE) of Ti/TNTs/Fe-Ce-PbO_2 electrodes (1 cm × 3 cm) for different conditions was another evaluation of the electrocatalytic ability and was calculated as [42].

$$ICE = \frac{[(COD)_t - (COD)_t + \Delta t]FV}{8I\Delta I} \tag{2}$$

where COD_t and $COD_{t+\Delta t}$ are the COD at time t and t + Δ t ($g{\cdot}O_2\ L^{-1}$), respectively; F is the Faraday constant (96,487 C mol^{-1}); V is the