Journal of Environmental Chemical Engineering 4 (2016) 2807–2815

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

A comparative study on electrochemical oxidation of bisphenol A by boron-doped diamond anode and modified SnO_2-Sb anodes: Influencing parameters and reaction pathways

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ARTICLE INFO

Article history:
Received 3 February 2016
Received in revised form 1 May 2016
Accepted 28 May 2016
Available online 28 May 2016

Keywords:
Boron doped diamond
Antimony doped tin dioxide
Supporting electrolyte
Byproducts
Pathway

ABSTRACT

In this study, electrochemical oxidation of bisphenol A (BPA) was investigated using BDD anode and two types of modified SnO_2-Sb anodes, TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT. The influences of solution pH (3, 7 and 11) and the type of supporting electrolyte (0.05 M Na_2SO_4 and 0.1 M NaCl) on the electrocatalytic activity of the three anodes were investigated. The anodes exhibited remarkably different behavior for BPA oxidation, due to their different surface morphology, oxygen evolution potential and ability in the hydroxyl radical generation. Both BDD and the modified SnO_2-Sb anodes could degraded BPA effectively in 0.05 M Na_2SO_4 at pH 3 and 7. However, in 0.1 M NaCl, TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT showed better electrocatalytic activity for BPA oxidation than BDD with less Cl loss and ClO_3^- generation. On the contrary, a considerable amount of chlorinated intermediates and polymer byproducts were observed with BDD, resulting in its ineffective TOC removal (46.8%). It indicates that the modified SnO_2-Sb anodes are more environmentally benign for the treatment of wastewater containing chloride ion. LC–MS/MS and ion chromatography revealed the aromatic intermediates and aliphatic acids produced during BPA oxidation. Finally, the reaction pathways of BPA oxidation in Na_2SO_4 and NaCl supporting electrolytes are proposed.

1. Introduction

Bisphenol A (BPA) serves as an important chemical in polymer industry and has been widely used as a monomer for the production of epoxy resins and polycarbonate resins. However, it is also known as an important endocrine disrupter which has been found in natural environment and treated effluents due to its extensive usage [1]. The exposure of BPA may affects the human health by its estrogenic activity even in very low concentration levels [2,3]. The byproducts of BPA generated during the treatment process may also exhibit high endocrine-disrupting effect [4]. Therefore, it is important to achieve completely degradation of BPA to final products such as CO_2, water or the environmentally benign products which are non-toxic and biodegradable [5].

To date, various techniques have been employed for the removal of aqueous BPA such as biological treatment [6], adsorption [7], wet oxidation [8] and advanced oxidation processes (AOPs) [9,10]. In recent years, electrochemical oxidation has emerged as a promising method for the removal or alleviation of aqueous BPA contaminants [11,12]. However, anode material is crucial to the success of this application [13]. Boron doped diamond (BDD) has been verified to be a very attractive anode material for the removal of organic pollutants through direct anodic oxidation due to its notably high oxygen evolution potential (OEP) [14–18]. Moreover, BDD has the advantage of high physical and electrochemical stability comparing with other electrodes [19–22], which is an important factor for its successful commercialization. Commercial BDD anodes have been reported for the total removal of various phenolic compounds, such as phenol [23], 4-nitrophenol [24], 4-chlorophenol [25] and bisphenol A [26,27]. However, the high fabrication cost of BDD material is prohibitive for its scale-up applications [28].

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http://dx.doi.org/10.1016/j.jece.2016.05.034
2213-3437/

Apart from BDD anode, antimony doped tin dioxide (SnO_2-Sb) is another type of anode material with high OEP. However, it has the problem of short service life which inhibits its commercial applications [29–31]. A lot of attempts have been made to overcome this problem. Two types of modified SnO_2-Sb electrodes (TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT) have been fabricated in our recent studies, which exhibit enhanced electrocatalytic activity and improved service lifetime than the conventional Ti/SnO_2-Sb fabricated by thermochemical decomposition [32,33]. Thus, from the viewpoint of practical application, a comparative study on these novel SnO_2-Sb anodes with the commercial BDD anode would be meaningful to provide some insights into their electrocatalytic performance and potential as alternative anode materials to BDD in the treatment of recalcitrant organic pollutants.

In this work, BPA was used as the target pollutant for the comparative study on the electrocatalytic performance of commercial BDD anode and two types of modified SnO_2-Sb anodes (TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT) fabricated in laboratory. Their surface morphology, oxygen evolution potential and ability for hydroxyl radical ($HO^{\bullet}$) generation of the anodes were characterized. The influences of operating parameters including the solution pH (3, 7 and 11) and the type of supporting electrolyte (0.05 M Na_2SO_4 and 0.1 M NaCl) on the electrocatalytic activity of the anodes were investigated. The aromatic intermediates and aliphatic acid intermediates of BPA oxidation were also analyzed to elucidate the reaction pathways and related mechanisms.

2. Experimental

2.1. Chemicals and materials

All of the chemicals are of or above analytical grade and used without further purification. Bishphenol A, Na_2SO_4, NaCl, dimethyl sulfoxide (DMSO) and 2,4-dintrophenylhydrazine were purchased from Sigma-Aldrich. Pure acetonitrile (LC–MS grade), NaOH pellet and HCl were purchased from Merck. All the solutions used in the experiments were prepared through Milli-Q water.

Nb/BDD anode with a coating thickness of 5 μm and boron doping concentration of 2500 ppm was purchased from NeoCoat Co., Switzerland. Two modified SnO_2-Sb electrodes, TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT, were fabricated through pulse electrodeposition method. The fabrication processes of the modified SnO_2-Sb anodes are indicated in the Supplemental Information (Fig. S1). Both TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT show polycrystalline SnO_2 with diffraction peaks at $2\theta = 26.8$, 34.1°, 38.2°, 52.1°, 55.1°, 65.0° and 66.2° (Fig. S2). The presence of Ti substrate and TiO_2 is also observed with TiO_2-NTs/SnO_2-Sb-PTFE by EDS (Table S1) and XRD (Fig. S2).

2.2. Electrode characterization

The surface morphologies of the three electrodes were characterized through field emission scanning electron microscopy (FESEM, JEOL-7660F). Linear sweep voltammetry (LSV) experiments were conducted to measure the oxygen evolution potential of the electrodes using an electrochemical workstation (PGSTAT 302N, Autolab) equipped with a three-electrode cell in 0.5 M Na_2SO_4 electrolyte. The counter electrode and reference electrode were platinum and Ag/AgCl electrode, respectively. A scan range of 0 V–3.0 V and a scan rate of 50 mV s^{-1} were applied. The chlorine evolution potential of the electrodes were also examined through LSV in 3 M NaCl electrolyte and a scan range of 0 V–2.0 V, meanwhile other conditions were kept the same.

2.3. Bulk electrolysis of bisphenol A

The electrocatalytic activities of BDD, TiO_2-NTs/SnO_2-Sb-PTFE and Ti/SnO_2-Sb/SnO_2-Sb-CNT anodes were investigated through 6-h electrolysis of BPA synthetic wastewater in a 200 ml single-compartment cell. Synthetic wastewater containing 100 mg L^{-1} BPA was prepared in 0.05 M Na_2SO_4. The influence of pH on the electrocatalytic performance was investigated by adjusting the initial solution pH to 3, 7 and 11 using 0.5 M H_2SO_4 or 1 M NaOH. The influence of the type of supporting electrolyte was also investigated by comparing the electrochemical oxidation of 100 mg L^{-1} BPA in 0.1 M NaCl and 0.05 M Na_2SO_4 at pH 7. The current applied is 0.16 A and the nominal area of the electrodes is 8 cm^2. Platinum electrode with the same surface area was used as the cathode with 1-cm distance from the anode.

The aliquot solutions were drawn for analysis at 1-h interval. The elctrocatalytic performances of the electrodes were evaluated by determining the BPA concentration and total organic carbon (TOC) of the synthetic wastewater. TOC was measured using a TOC analyzer (TOC-L/CPH, Shimadzu). BPA concentrations were determined by high-performance liquid chromatography (HPLC, PerkinElmer Series 200) equipped with a reverse-phase C18 column (Hypersil Gold, Thermo Scientific). The mobile phase used was acetonitrile/water (40/60, v/v) with a flow rate of 1 ml L^{-1}, and the signal was acquired through a UV detector at 220 nm wavelength. Mineralization byproducts of formic acid, acetic acid, oxalic acid as well as chloride ion, chlorate ion and sulfate ion of the synthetic wastewater were quantified through ion chromatography (IC, Thermo Scientific Dionex ICS-2100). Other intermediates during electrochemical oxidation of BPA were verified by liquid chromatography tandem mass spectrometry (LC–MS/MS, Agilent 6460 Triple Quadrupole LC/MS System). The operation specifics of LC–MS/MS are described in the Supporting Information.

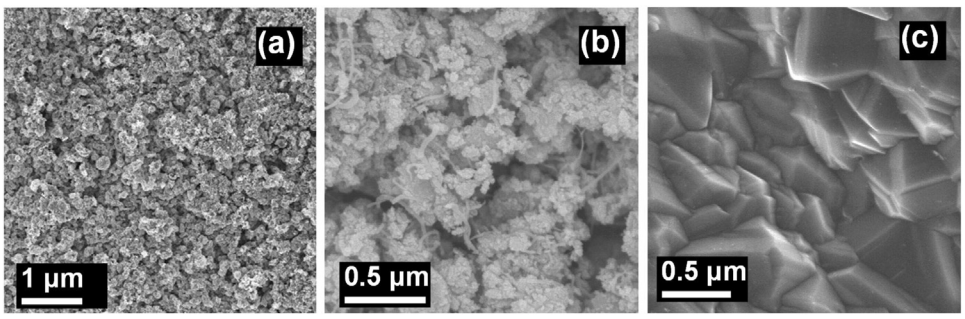

Fig. 1. FESEM images of (a) TiO_2-NTs/SnO_2-Sb-PTFE, (b) Ti/SnO_2-Sb/SnO_2-Sb-CNT and (c) BDD anodes.