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Investigation of boron-doped diamond on porous Ti for electrochemical oxidation of acetaminophen pharmaceutical drug

Yapeng He [a], Yujie Dong [b], Weimin Huang [a,*], Xuqing Tang [a], Honghong Liu [a], Haibo Lin [a], Hongdong Li [c]

[a] College of Chemistry, Jilin University, Changchun 130012, China
[b] Emergency Department, China–Japan Union Hospital of Jilin University, Changchun 130033, China
[c] State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

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ABSTRACT

The electrochemical oxidation of acetaminophen, a kind of potentially dangerous pharmaceutical compound, is conducted on planar and porous Ti/boron-doped diamond (BDD) electrodes to investigate the effect of electrode structure on the electrochemical oxidation behavior. Oxidative peak corresponding to the electron transfer of acetaminophen could be observed around 0.90 V (versus saturated calomel electrode, SCE) on BDD electrodes. The current response from a chronoamperometric curve is proportionally linear in the concentration range from 0 to 3 mmol L^{-1} and higher response slope could be obtained on porous Ti/BDD electrode. Complete mineralization can be realized on Ti/BDD electrodes while porous Ti/BDD presents higher COD removal rate and current efficiency compared with planar BDD. The decay kinetics of acetaminophen on BDD electrodes follows a pseudo-first-order behavior, and the corresponding apparent rate constants are 0.208 and 0.344 h^{-1} for planar and porous Ti/BDD electrodes at 30 mA cm^{-2}. From the detection of hydroxyl radicals, higher generation rate and amount can be obtained on porous Ti/BDD electrode. The enhancement for electrochemical oxidation is related to the porous structure of porous Ti/BDD electrode, which provides more active sites for hydroxyl radicals (•OH) generation. The discrepancy between the COD removal and amount of •OH could be explained by the utilization rate of •OH.

1. Introduction

Pharmaceutical compounds have emerged as a novel class of water contaminants [1,2] and been detected in the surface, ground and even drinking water. Among the pharmaceutical compounds, non-steroidal anti-inflammatory drugs (NSAIDs) are paid more attention due to the large consumption [3] for therapeutic purposes, such as anti-inflammatory, analgesic or antipyretic. Despite environmental problems caused by the extensive usage of these types of drugs, their consumption is unlikely to be restricted since they are beneficial to humankind. The presence of these contaminants has grown a raising concern for the public as they would present potential hazard for human health even at trace level [4].

To eliminate pharmaceutical compounds in the aquatic environment, various treatment methods, such as biological method [5] and physical and chemical remediation technology [6–9] have been extensively investigated to remove some pharmaceutical drugs, including ibuprofen, ketoprofen, paracetamol, diclofenac and aspirin. Especially, because of the features of versatility, environmental compatibility and potential cost effectiveness for the degradation process, electrochemical oxidation [10–12] has shown a promising result in the removal of pharmaceutical pollutants. The procedure allows the electrochemical incineration of pollutants by the hydroxyl radicals (•OH) [13] generating on the electrode surface. As we all known, the electrode material [14,15], as a key part of the electrolysis process, plays an important role in the electrochemical oxidation. Different electrodes are adopted to eliminate the NSAIDs in the aquatic environment, such as platinum, PbO_2, SnO_2, and BDD electrodes. The comparison of different electrodes on the electrochemical degradation of different pollutants has been conducted by various researchers [16–18]. Among the electrode materials, BDD electrode [19,20] is considered as the best known material for electrochemical oxidation due to its excellent physical and chemical properties, which include high wide potential window, high stability in various solution and extraordinarily well resistance to corrosion. Especially, the superior features of high oxygen evolution potential and high stability endow the BDD electrode with potential widely electrochemical application in wastewater treatment, and the degradation of different pollutants has been widely studied on BDD electrodes accompanying with its kinetics. Meanwhile, the effect of the characteristics of the BDD electrode, including surface termination and roughness, sp^3/sp^2 ratio, boron content [21] and so on [22], transfer performance [23] of the species and the parameters in the process [24] on the electrochemical oxidation are studied.

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* Corresponding author.
E-mail address: huangwm@jlu.edu.cn (W. Huang).

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On the other hand, compared with planar electrode, porous electrode can provide higher surface area and more abundant active sites for electrochemical reaction [25–27]. Many researches involving the fabrication and application of porous electrodes have been reported. Chai et al. [28] have fabricated three-dimensional ordered macroporous PbO_2 electrodes for recalcitrant pollutant incineration with apparent rate constant 2.4 times that with flat-PbO_2 and the material would be a good alternative anode for wastewater remediation. Another metal oxide with porous structure [25,29,30] is also adopted to enhance the electrochemical performance for pollutant elimination. Nevertheless, despite the effort to prepare a BDD electrode with porous structure [31–33], the application of porous BDD electrodes into the pollutants decomposition is rarely reported.

Therefore, electrochemical oxidation of acetaminophen, a representative anti-inflammatory drug, is carried out on planar and porous Ti/BDD electrodes in the present investigation. The oxidation behavior of acetaminophen on the BDD electrode is evaluated by linear sweep scan and chronoamperometry to investigate the relationship between the electron transfer behavior and structure of BDD electrodes. The effectiveness of planar and porous Ti/BDD for the degradation behavior of acetaminophen is studied under a galvanostatic model, accompanying with the generation ability of free hydroxyl radicals and the utilization rate.

2. Experimental

2.1. Materials

Acetaminophen and terephthalic acid were obtained from Aladdin Co., China. All the other reagents such as Na_2SO_4 and H_2SO_4 were purchased from Beijing Chemical Works, China with purity level >98%. All of the chemicals were of reagent grade and used without further purification. All solutions were prepared with deionized water with a resistivity of 18.25 MΩ cm.

2.2. Preparation of planar and porous Ti/BDD electrodes

The BDD film electrodes were prepared on planar and porous titanium substrates (purity 99.9%, 20 mm × 10 mm × 1 mm) by the hot filament chemical vapor deposition (HFCVD) method. The mixture of CH_4 and H_2 was used as the gas source while $B(OCH_3)_3$ liquid taken out by bubbling H_2 gas was used as the boron source. The total gas flux was kept at 300 sccm for all experiments with 1.0 vol% CH_4.

2.3. Electrochemical measurement and degradation experiments

Cyclic voltammograms were measured on a PARSTAT 2273 electrochemical work station (Princeton Applied Research, USA) using a conventional three-electrode cell system. Ti/BDD electrodes (10 mm × 10 mm × 1 mm) were used as the anodes, respectively. A Pt gauze electrode with a geometric size of 20 mm × 20 mm was used as the counter electrode, and KCl-saturated calomel electrode (SCE) as the reference electrode. All the potentials were referred to SCE. Anodic oxidation of acetaminophen on planar and porous Ti/BDD electrodes was conducted in a single compartment cell without diaphragm. The cathode was a $Ti/RuO_2–TiO_2–SnO_2$ net with the electrode gap of 10 mm. Na_2SO_4 with concentration of 0.5 M was used as supporting electrolyte and not optimized. The current density was controlled using an 8511C potentiostat/galvanostat.

2.4. Analytical methods

During the experiment, the samples were drawn at different time intervals and the degradation of acetaminophen molecule was monitored by a UV–Vis spectrophotometer (Shimadzu UV-2450, Japan). The value of chemical oxygen demand (COD) was measured with a chemical oxygen demand analyzer. The concentration of acetaminophen was determined by high performance liquid chromatography (HPLC) (Shimadzu Prominence LC-20A HPLC, Japan) equipped with an Inertsil ODS-SP, C18 column (4.6 × 150 mm), 5 μm. Acetonitrile:water (30:70) filtered with a 0.2 μm filter was used as mobile phase at a slow rate of 0.6 ml L^{-1}. Terephthalic acid was used as a spin trap for the detection of •OH using a fluorescence spectrometer (FluoroMax-4, Horiba, France). The values of current efficiency (CE) on different electrodes are calculated by the following equation:

$$CE = \frac{COD_0 - COD_{\Delta t}}{I\ \Delta t \times 8000} FV \times 100\%$$

where COD_0 and $COD_{\Delta t}$ are the values of COD (mg L^{-1}) at 0 and Δt, respectively; I is the electrolysis current (A); Δt is the electrolysis time (s); F is Faraday's constant, 96,500 (C mol^{-1}) and V is the volume of solution (L).

3. Results and discussion

3.1. Preparation and characterization of BDD electrodes

Fig. 1a and b presents the SEM images of the planar and porous Ti substrates without the deposition of BDD film, respectively. The SEM images suggest that the porous Ti substrate consists of holes and internal channel, which presents a three-dimensional porous structure. After the deposition, the BDD films cover the Ti substrates continuously on the Ti surface as shown in Fig. 1c and d. Both of the samples show well-faceted crystal with the crystal size in the range of 1–2 μm. On the other hand, the porous Ti substrate is uniformly continuous covered by the BDD film after the deposition without cracks on the surface, keeping the structure of three dimensional porous. As a case of BDD film on porous Ti substrate, not only the outer surface of the three-dimensional porous Ti substrate is deposited by BDD films, but also the deep surface while keeping well quality. It could be believed that BDD films deposited on the porous Ti substrate under the condition exhibits a porous structure. Since the porous structure of BDD films would enhance the surface area of the electrode [26], it is reasonable that a porous Ti/BDD electrode with more active sites would contribute to enhancing the electrochemical performance of the BDD electrode.

The phase composition and crystal structure are characterized by XRD, as shown in the insert of Fig. 2. The typical diffraction peaks of both electrodes are observed at $2\theta = 43.9°$ and 75.2°, which are assigned to the (111) and (220) facet of diamond phase. Meanwhile, the values of I (111)/I (220) are all greater than the standard value, indicating that the BDD films have preferred orientation with the (111) facet. The sharp peaks at $2\theta = 43.9°$ suggest that both of the films exhibit well crystallinity. In addition, due to the high activity of metal Ti to the reaction gases, TiC peaks in the patterns demonstrate the existence of a TiC interlayer under diamond deposition condition, which is in accordance with the previous report about the preparation of Ti/BDD [34]. In conclusion, BDD films deposited on porous Ti substrate keep the analogous crystal size, phase composition and well quality as plate BDD while expanding the specific surface area of the BDD electrode.

Fig. 2 also displays the steady-state polarization curves obtained on different BDD electrodes in 0.5 M H_2SO_4 aqueous solution with the scan rate of 2 mV s^{-1}. As an important parameter for anode material in electrochemical oxidation, the oxygen evolution potential (OEP) for planar and porous Ti/BDD electrodes is 2.4 V. According to the previous theory [13] about the electrode material for electrochemical oxidation, the BDD electrode with high OEP will reduce the opportunity for oxygen evolution and increase the effectiveness for electrochemical oxidation of pollutants in comparing with DSA anodes. At the same time, due to the expanding of surface area, porous Ti/BDD electrode exhibits higher current density than planar Ti/BDD at constant potential, which further