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Improved electrochemical performance of boron-doped diamond electrode depending on the structure of titanium substrate

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ABSTRACT

This work is focused on the role of porous titanium (Ti) substrate on the electrochemical performance of boron-doped diamond (BDD) films. BDD film deposited on porous Ti substrate combines the excellent property of porous Ti and BDD film, porous Ti endows the film three-dimensional (3D) porous performance and enhances the surface area of BDD electrode. The effective electrochemical surface area of 3D-Ti/BDD electrode is 8.37 cm^2 cm^{-2}, 3.2 times as much as that of conventional plate BDD electrode while smaller electron transfer resistance (31.3 Ω cm^2) for $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple on 3D-Ti/BDD electrode is obtained compared to 128.3 Ω cm^2. 3D-Ti/BDD electrode presents higher response current and the degradation of aspirin reveals that corresponding kinetic constant for plate and 3D-Ti/BDD electrode is 0.185 h^{-1} and 0.367 h^{-1}, respectively. Moreover, porous BDD electrode owns higher stability analyzing by accelerated life tests, 25% higher than plate BDD electrode. The enhancement of electrocatalytic activity and stability is essentially attributed to porous structure of Ti substrate.

1. Introduction

Boron-doped diamond (BDD) [1–3] is considered as an excellent electrode material that exhibits well physical and chemical properties, which include high wide potential window, low background current, high stability in various solution and extraordinarily well resistance to corrosion. These superior features endow BDD electrode with potential widely electrochemical applications, such as wastewater treatment [4,5], electrosynthesis [6,7] and electrochemical sensors [8,9]. Especially, BDD electrode has been considered as optimal electrode material for electrochemical oxidation. The degradation of different pollutants has been studied on BDD electrode including phenols [10], surfactants [11], antibiotics and medical intermediate [12,13], pesticides [14], pigment and dyes [15], and so on.

Through completed mineralization of pollutants on BDD electrode could be realized while keeping higher current efficiency [16,17] compared to traditional DSA electrodes, the reduce of current efficiency appears when the electrochemical process is limited by the mass transfer of the species under the situation of low concentration of pollutant. The side reaction of oxygen evolution reaction happens sharply at high current density and reduces the efficiency when oxidation of organic pollutants is adopted as main reaction. On the other hand, the large scale application of BDD is restricted by the economy and stability of the substrate materials and it is necessary to develop efficient electrode materials. Generally, the efficiency of the process is related to the nature and structure of electrode material. Porous electrode [18,19] with large surface area, which would provide more active sites and contracts for electrochemical reaction compared to the conventional two dimensional electrode, becomes a feasible condition and has been an attractive research content in the development of electrode materials. The application of porous electrodes in the fields of energy storage, sensors and water treatment has been widely studied.

Many researchers have focused on the construction of porous BDD film electrode. One approach to produce porous electrode is to etch BDD film by plasma [20–22], stream activation [23] or thermal treatment [24]. Highly order honeycomb diamond structures have been obtained after oxygen plasma treatment through a porous alumina membrane by Honda [21], while the capacitance values of 1.97 mF cm^{-2} and the surface area 10.5 times larger compared to the flat surface; Ohashi [23] has adopted a stream activation process to prepare BDD electrode with porous microstructure, while the electrochemical active surface area is up to 20 times than pristine BDD electrode. Complex or multistep treatments are usually required for above methods, accompanied with poor feasibility in economy and industry application. Normally, BDD films are deposited on substrate materials, and the porous substrate becomes another approach, such as porous silicon [25], silicon nanowires [26], carbon fiber [27] and nanotubes [28,29]. Luo has prepared BDD nanorod forest electrode on Si NWs [26], exhibiting improved sensitivity and selectivity for biomolecule detection. Teepee nanostructured BDD/CNTs have been produced by Zanin [28] with the double-layer capacitance values ~450 times greater than those for flat BDD electrode. However,

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the substrates above restrict the application of the electrodes as a result of poor conductivity, low mechanical stability or not suitable for large scale.

The ideal substrate should withstand the harsh CVD growth conditions and own the features of high porosity, mechanical stability and electrical conductivity. Meanwhile, porous titanium [30,31] obtained by power metallurgy technique (P/M) with diverse porosity and interconnected structure would be a novel substrate material, which would be beneficial to improve the catalytic activity of Ti/BDD electrode, owing to its high surface area and rough factor. Especially, its low density and high strength would obviously improve the industrial feasibility of Ti/BDD. Hence, porous Ti/BDD film electrode would exhibit excellent application as a promising electrode material in the future, where porous Ti provides more active sites for BDD films. The influence of parameters (pressure, methane concentration, temperature) on the quality of diamond on porous Ti substrate has been investigated by Braga [30,32]. However, the relationship between the porous Ti structure and performance of BDD film has not been systematically studied.

In this paper, BDD films are deposited on three-dimensional porous titanium substrate by hot filament chemical vapor deposition (HFCVD) technique. The morphology, phase composition and quality are characterized. The effect of the porous Ti substrate on the performance of BDD film is investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Chronocoulometry is adopted to determine the effective electrochemical surface area of the electrodes. Electrochemical response of aspirin on different electrodes from chronoamperometric experiments is to examine the electrochemical activity. The electrochemical degradation of aspirin is conducted to investigate the oxidation ability. The stability of the electrodes is characterized by accelerated life tests.

2. Experimental

2.1. Preparation of Ti/BDD electrodes

The BDD film electrodes were prepared by HFCVD technique on plate and porous (porosity of 27%) titanium substrates. Before the deposition, the substrates were boiled in the mixed solution of concentrated HCl and H_2O (the volume ratio is 1:2) for 15 min to clean the surfaces, and cleaned ultrasonically in deionized water for 5 min. Then, they were pre-treated in a suspension of diamond powder for 30 min. At last, ultrasonically clean was conducted in acetone, ethanol, and deionized water in sequence for 5 min and the substrates were dried in nitrogen. 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 as the boron source and the amount of boron doping level was adjusted by $B(OCH_3)_3/H_2$ flow rate, corresponding flow rate was 3 sccm. The total gas flux is kept at 300 sccm and CH_4 1.0 vol.% for all experiments while the substrate temperature was kept at 750 ± 20 °C and the deposition time was 7 h.

2.2. Characterization of Ti/BDD electrodes

The film crystallinity and phase composition of Ti/BDD films were analyzed by X-ray diffraction (XRD) using a Rigaku D/Max 2550 diffractometer (Japan) with Cu-Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM, SU8020, HITACHI, Japan) was employed to investigate the surface morphology and quality of the BDD films.

2.3. Electrochemical measurements

Electrochemical properties were tested on PARSTAT 2273 electrochemical work station (Princeton Applied Research, USA) using a conventional three-electrode cell system. Porous and plate Ti/BDD electrodes (geometric area of 1.0 cm^2) were employed as working electrodes, Ti/RuO_2–TiO_2–SnO_2 electrode as the counter electrode, and KCl-saturated calomel electrode (SCE) as the reference electrode. All the potentials were referred to SCE. The current densities were calculated based on the geometric area of BDD electrodes in the present study. EIS was conducted in 10 mM $K_3[Fe(CN)_6]$ + 10 mM $K_4[Fe(CN)_6]$ + 1.0 M KCl solution with the frequency range from 10 kHz to 50 mHz with amplitude of 5 mV. The electrochemical effective surface areas of electrodes were measured as earlier literature [18] using $K_3Fe(CN)_6$ as model complex (the diffusion coefficient of $K_3[Fe(CN)_6]$ is 7.6×10^{-6} cm^2 s^{-1} [33]).

2.4. Electrochemical degradation

Anodic oxidation of aspirin (100 mg L^{-1}) was carried out in a single compartment cell without diaphragm. Ti/BDD electrodes were used as the anodes and the cathode was a Ti/RuO_2–TiO_2–SnO_2 net with the electrode gap of 10 mm. The supporting electrolyte was 0.5 mol L^{-1} Na_2SO_4. The current density was controlled at 30 mA cm^{-2} based on the geometric area using an 8511C potentiostat/galvanostat. The contaminant concentration was quantified by high performance liquid chromatography (HPLC) (Shimadzu Prominence LC-20A HPLC, Japan). COD (Chemical Oxygen Demand) value of the solution was measured by COD analyzer.

2.5. Accelerated life tests

Accelerated life tests were conducted to evaluate the stability of different Ti/BDD electrodes. The electrochemical tests were conducted in 3 mol L^{-1} H_2SO_4 solution and operation temperature was 25 °C. Ti/BDD electrodes were used as working electrodes, Ti/RuO_2–TiO_2–SnO_2 net as a counter electrode. The service life was denoted the time when the electrode deactivated completely.

3. Results and discussions

3.1. Characteristics of Ti/BDD electrodes

Fig. 1a and b shows the SEM images of the porous Ti substrate before and after the deposition of BDD film, respectively. The SEM images reveal that porous Ti consists of holes and internal cannel, which presents three-dimensional porous structure. After the deposition, porous Ti substrate is uniformly continuous covered by BDD films, without voids or cracks on the surface, named 3D-Ti/BDD electrode. Fig. 1c and d presents the SEM image of plate and 3D-Ti/BDD film electrodes, respectively. Both of the samples show well-faceted crystal with the crystal size being in range of 1–2 μm while porous Ti substrate is covered by the BDD film, including the inner holes, keeping the structure of three dimensional porous. Therefore, it could be believed that the introduction of porous Ti substrate material improves the surface area of the film electrode compared to the traditionally two-dimensional plate electrode.

The phase composition and crystal structure are characterized by XRD, as shown in Fig. 2. The typical diffraction peaks of both electrodes are observed at 2θ = 43.9° and 75.2°, which are assigned to the (111), (220) facet of diamond composition. And the values of I (111)/I (220) are all greater than the standard value, indicating that the BDD films have preferred orientation with (111) facet. The sharp peaks at 2θ = 43.9° suggests that both of the films exhibit well crystallinity. In addition, due to the high activity of metal Ti to reaction gases under diamond deposition conditions, TiC peaks in the patterns demonstrate the existence of TiC interlayer, which is accordance with the previous report [34]. Hence, 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.