



Fabrication of porous boron-doped diamond electrodes by catalytic etching under hydrogen–argon plasma

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ABSTRACT

Porous boron-doped diamond (BDD) was prepared by hydrogen–argon plasma etching using electrodeposited Ni nanoparticles as a catalyst. The etching process and formation mechanism of porous BDD were investigated by changing the etching time from 30 s to 300 s. Pores were produced due to the C atoms around Ni nanoparticles are easy to react with hydrogen plasma and form methane. With the increase of etching time, the pore size increased, the pore density decreased, and the pore depth first increased and then maintained unchanged. The sp²-bonded graphitic carbons existing on the surface of BDD increase with increasing etching time due to the increase of surface area. No preferential etching was observed due to the high energy of argon plasma. The electrochemical behaviors of the pristine and porous BDD electrodes were characterized by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS). The results showed that the porous BDD electrode exhibited high specific capacitance, which is attributed to its high electrical conductivity and large specific surface area. The highest specific capacitance of porous BDD electrode is 9.55 mF cm⁻², which is 22 times higher than that of pristine BDD electrode. The specific capacitance retention of the porous BDD electrode reduced to 98.2% of the initial capacitance after 500 cycles and then increased to 120.0% after 10,000 cycles. For the first 500 cycles, the reduction of capacitance can be attributed to the dissolution of Ni nanoparticles that attached on the porous BDD surface or buried in the shallow layer. The capacitance increase after 10,000 cycles is due to the better contact of the electrolytic solution with the residual Ni with the increase of cycle number.

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1. Introduction

Conductive boron-doped diamond (BDD) is a promising electrodes material that exhibits a wide potential window, a low back ground current, high chemical stability and well biocompatibility [1,2]. These outstanding properties enable BDD electrodes to be applied broadly, for example in wastewater treatment [3–6], biological and chemical sensors [7–10], fuel cells [11] and supercapacitors [12]. Large active surface area of BDD electrode can increase reaction efficiency and is an attractive feature for such electrochemical applications [13]. Porous BDD electrodes are of practical importance when they are used as catalyst supports and

substrates for electrochemical reactions due to their large surface area.

Various methods have been developed to fabricate porous BDD electrodes. Honda et al. succeeded in fabricating porous BDD films with honeycomb structures by oxygen plasma etching through porous alumina masks [14–16]. The porous BDD electrode exhibited a wide electrochemical potential window and a double layer capacitance of 1.97 mF cm⁻². Ohashi et al. reported catalytic roughening of BDD electrodes by Ni, Co and Pt particles in hydrogen atmosphere [12]. The specific surface area of the roughened BDD was enhanced nearly 15 times than that of pristine BDD electrode. Oxidative activation etching of BDD electrodes with steam or CO₂ is another commonly method to prepare porous BDD electrodes [17–19]. Ohashi et al. prepared porous BDD electrodes with columnar structures by steam activation etching [17]. The steam-activated BDD electrodes possess a wider potential window and

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larger electrochemically active surface area up to 20 times than the pristine BDD electrodes. Zhang et al. further investigated the steam-activation and CO₂ activation processes of BDD electrodes with different crystal orientation [18,19]. They found that CO₂ activation leads to preferential {100} etching, whereas steam-activation results in preferential {111}c etching. Recently, a two-step thermal treatment method was developed to fabricate porous BDD electrodes with dense pores of several tens to several hundred nanometer sizes by Kondo et al. [20]. The potential window of the prepared porous BDD electrodes remained wide at ca. 3 V and the double layer capacitance of 140 μF cm⁻² was obtained. Terashima et al. reported a simple technique, which involves maskless reactive ion etching (RIE) with oxygen plasma, for the formation of diamond whiskers on highly boron-doped diamond films [21].

These methods are effective for the fabrication of porous BDD electrodes with a large specific surface area. However, the etching effect of BDD electrodes is inhomogeneous because the etching level is dependent on the crystal orientation and the BDD prepared by CVD is usually polycrystalline with several crystal orientations. In addition, for practical applications, the method used to fabricate porous BDD should be simple and fast. In this study, we have proposed a fast, effective and isotropic etching method to fabricate porous BDD electrodes. The BDD films were etched by hydrogen–argon plasma with Ni nanoparticles as a catalyst. The Ni nanoparticles are electrodeposited on BDD films. Dense pores were formed on the BDD surfaces after etching for several seconds. The BDD etching process and mechanism were discussed. The electrochemical properties of the porous BDD electrode were investigated with cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS).

2. Experimental details

2.1. Preparation of porous BDD electrodes

Boron-doped polycrystalline diamond film was deposited on Ta substrate (1 × 2 cm²) by electron-assisted hot filament chemical vapor deposition (CVD). Methane (CH₄) was used as the carbon source. Trimethyl borate (B(OCH₃)₃) was dissolved in ethanol and used as the source of boron. The ethanol-B(OCH₃)₃ solution was introduced with high purity hydrogen gas. The boron level expressed as the [B]/[C] atomic ratio was 0.1% w/w. The substrate temperature was maintained at 1000 °C during the deposition process. After the deposition, the sample was cooled down to room temperature and the BDD film was peeled off the Ta substrate automatically due to the large gap between their expansion coefficients. The typical self-standing BDD film thickness was approximately 160 μm after 50 h deposition.

The etching technique consists of two steps: Ni catalyst electrodeposition and catalytic etching by hydrogen plasma. Firstly, Ni nanoparticles were fabricated by an electrodeposition process on the surface of the BDD film using a two-electrode system. A Pt sheet of 1 cm² and BDD film were used as the cathode and anode, respectively. The interelectrode distance was 1 cm. The deposition was performed using square wave potentials with a high of 0 V and a low of -1.5 V. The frequency and offset of the square wave were 500 Hz and -750 mV, respectively. The electrodeposition process lasted for 20 min. The electrolyte was composed of 0.1 M NaH₂PO₄ and 2 mM Ni(NO₃)₂. The experiments were carried out in an electrolytic cell with ultrasonic wave (50 W) irradiation at a temperature of 25 ± 2 °C. After the electrodeposition process, the obtained Ni coated BDD (Ni/BDD) was washed carefully with redistilled water and then dried with N₂ at room temperature. Secondly, Ni/BDD was etched in a dc arc plasma jet CVD system, which usually dedicated to diamond growth. A mixture of hydrogen and argon

in the ration of 1/1 (v/v) was introduced into the reactor. The operating pressure was 3 kPa, the sample temperature is about 800 °C, and the plasma power was 7 kW. To obtain a fundamental insight into the etching process, the etching time was varied from 30 s to 300 s.

For comparison, a BDD film without Ni nanoparticles was also etched for 300 s with hydrogen–argon plasma, and a BDD film with Ni nanoparticles was etched in argon plasma without hydrogen for 300 s.

2.2. Characterization

Surface and cross-sectional morphologies of the BDD were observed by a field emission-scanning electron microscope (FE-SEM; Merlin Compact, Zeiss, German). The microstructure was characterized by Raman spectroscopy (Raman, Thermo Scientific, DXR) using a YAG laser (excitation wavelength 532 nm) as the excitation source. The crystallization was characterized by X-ray diffraction (XRD, Rigaku). The resistivity of the pristine BDD measured by a four point resistivity system was ca. 1.0 Ω cm. The residual nickel was tested by X-Ray photoelectron spectrometer (XPS, Thermo Fisher) and energy dispersive spectrometer (EDS, Hitach S4800). Electrochemical measurements were performed using a CHI660E (Shanghai Chenhua) electrochemical work station with a conventional three-electrode configuration. A Ag/AgCl electrode served as the reference and a platinum sheet was used as the counter electrode. Pristine or porous BDD was used as the working electrode. The exposed geometric electrode area was 1.0 cm², and all currents are normalized to this area. The BDD working electrodes were rinsed with ultrapure water prior to use. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and AC electrochemical impedance spectroscopy (EIS) measurements were conducted to characterize the electrochemical performances of the BDD electrodes. All measurements were carried out at room temperature (25 ± 2 °C) in 0.1 M Na₂SO₄ solution deoxygenated by nitrogen gas.

3. Results and discussions

The surfaces of pristine BDD film and Ni nanoparticle coated BDD film were characterized by FE-SEM. The pristine BDD film consists of randomly oriented crystallites with {111} and {100} planes as the exposed facets, as shown in Fig. 1a–c. The crystallographic plane can be identified by the contrast as well as the geometry in the FE-SEM images. The {111} planes display darker contrast and triangular shapes with 90° and 120° angles; while the {100} planes appear brighter contrast and square surfaces [19,20,22]. The Ni nanoparticles were dispersed on the BDD films by electrodeposition (Fig. 1d–f). Most of the nanoparticles have diameters of about 10 nm. There are also bigger Ni deposits with a size of 100–150 nm.

The Ni/BDD films were etched in hydrogen–argon plasma for various times (30, 120 and 300 s) and their FE-SEM images were shown in Fig. 2. As shown in Fig. 2a–c, the shapes of larger crystallites can still be observed and those of small grains disappeared after 30 s of etching. The crystal faces of {111} and {100} become difficult to recognize, which indicated that the etching is isotropic to the two kinds of planes. The images under high magnification show that porous BDD films with dense nanopores on the BDD surfaces are obtained (Fig. 2b and c). The nanopores are round holes with diameters from 10 to 100 nm. With the etching time increasing to 120 s, the surfaces of etched BDD become flatter and the outlines of crystal grains are dimly visible (Fig. 2d). The reason is that the grain boundaries are concave and more difficult to etch than the convex grain center due to the shadow effect of ions bombardment. Fig. 2e and f presents the detail with enlarged scale of Fig. 2d. It is found that the diameter of nanopores increases and the

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