1 **Preparation and Characterization of Vertically Columnar Boron**
2 **Doped Diamond Array Electrode**

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ABSTRACT: A vertically columnar boron doped diamond (BDD) array electrode was fabricated by microwave plasma chemical vapor deposition. Observed by scanning electron microscopy, the fabricated samples were structured with aligned columns whose diameter and height was 8 μm and 12 μm , respectively, and the minimum interval of neighboring columns was 2 μm . The results of electrochemistry measurement showed that the columnar BDD array electrode possessed high oxygen evolution potential and low background current. Besides that, comparing with flat BDD electrode, the columnar BDD array electrode showed higher electrochemical activity (due to its inner active surface being up to 4.25 cm^2), lower impedance of electric double layer, and especially enhanced electrical response signal (2.12 $\mu\text{A}/\mu\text{M}$, 4 times of flat BDD in glucose detection as a sample). These excellent performances may open the door for the BDD materials to be applied in wide areas including electrochemical detection, electrochemistry degradation, electrochemical synthesis, and so on.

Key Words: BDD Array Electrode; Electrochemical Activity; Electrical Response Signal

1. Introduction

Electrochemistry, an important part of physical chemistry, is widely involved in the fields of metal industry, environmental science, energy science, imageology, electronics, biology, medical science and so on.[1] Electrode materials play an important role in electrochemical oxidation by influencing the effectiveness of oxidation, degradation pathways, and reaction mechanisms. Different electrode materials (including graphite electrode, glassy carbon electrode, metal electrodes and metal oxide electrodes) have been examined to improve the effectiveness of oxidation and current efficiency.[2] Comparing with these traditional electrode, boron doped diamond (BDD) electrodes obtain following advantages[3-8]: wide electrochemical working potential window in aqueous electrolyte; high mechanical strength and corrosion resistance (even anodic polarization in acidic solution); high resistance to deactivation and long term response stability; and low and stable electric double layer capacitor and voltammetric background current. Therefore, BDD electrode has been investigated extensively in treatment of toxic refractory organic wastewater,[9-19] detection of organic compounds and metal ions,[20-28] electrosynthesis of organic and inorganic substances.[29-31] However, most studied BDD electrodes are flat with low special surface area and less activity reaction site. Thus they can not meet the requirements of those applications in sensitivity, efficiency and selectivity.[32,33]

To find the methods of improving their performance, the electrochemical process mechanism of organics on BDD electrode was analyzed. The widely acknowledged mechanism considers that organics oxidation and oxygen evolution are carried out

through intermediate hydroxyl radicals (produced by water discharge) adsorbed on BDD electrode surface. This mechanism reveals the efficiency of electrocatalytic reaction can be improved by the following methods: increasing the reaction site (area) to promote the quantity of $\cdot\text{OH}$ on electrode surface; increasing the contact between reactant and electrode, and improving products fast release from electrode surface to accelerate electrocatalytic reaction. According to the above analysis, many researches focused on increase of the reaction site (area) by etching BDD film with diamond powder as covering film,[34] or depositing BDD on substrates with special micro-structure.[35] In these studies a large increase of reaction site is obtained. However, above mentioned methods always ignore that Warburg impedance (mass transfer resistance) will increase with the morphological nonuniformities of the surface, roughness and porosity.[36] The efficiency of electrochemistry will reduce with the increase of Warburg impedance.

As mentioned above, the nonuniform structure leads to increase of Warburg impedance. Obviously, a BDD electrode with aligned array structure may solve this contradiction. It can improve the reaction rate not only by increasing the reaction site and electron transfer rate, but also by building a smooth way for the transfer of reactant to electrode surface and products to solution. The aligned array structure can inhibit the increasing of Warburg impedance taken from the three-dimensional structure. However, no report with respect to this topic has been published up to now.

In this work, a vertically aligned BDD electrode was fabricated by depositing BDD onto vertically aligned Si columns. Both its reaction sites and Warburg impedance

were evaluated by electrochemical impedance spectroscopy (EIS). Enhanced electrical response signal (glucose detection as a sample) proved that the columnar BDD array electrode performed a higher electrochemical activity and efficiency comparing with flat BDD electrode, successfully.

2. Experimental

2.1 Preparation of columnar BDD array electrode

The Si column array (as the substrate of BDD) was obtained by micro electro mechanical systems (MEMS) techniques.[37] Firstly, SiO₂ film was grown on Si wafer (p-type, 111 plane) by thermally oxidation. Successively, a layer of photoresist was sputtered on the surface of the oxide layer. Subsequently, standard photolithography and microfabrication were performed. The diameter of Si columns and their spacing could be controlled by using various templates. Both the diameter and the spacing of the template used in this work were 5 μm. After photolithography, the unexposed photoresist layer was dissolved with the developer. Following, inductively coupled plasma (ICP) etching was performed to etch SiO₂ layer and Si substrate by C₄F₈ and SF₆-C₄F₈ vicissitudinary, respectively. After removing residual SiO₂, Si column array substrate was obtained.

A microwave plasma chemical vapor deposition (MPCVD) process was used to deposit BDD on the Si column array substrate (Fig. 1). A mixture of CH₄ and H₂ was used as the source gas, wherein the content of CH₄ was varied between 0.5 and 4%. B₂H₆ diluted in H₂ (100 ppm) was employed as a boron doping agent. During the deposition process, the total flow rate, chamber pressure, substrate temperature and

deposition duration was 100 sccm, 6 kPa, 500 °C and 6 h, respectively. As a comparison, flat BDD electrode was prepared by depositing BDD on a flat Si substrate under the same conditions.

2.2 Characterization

The general morphology of columnar BDD array electrode was characterized by field emission scanning electron microscopy (FESEM; Hitachi S-4800). Raman spectrum was obtained from Renishaw Micro-Raman System 2000 Spectrometer operated at He-Ne laser excitation (wavelengths 623.8 nm; laser power 35 mW) with a beam spot size of about 2 μm. X-ray diffraction (XRD) was used to identify the crystal of columnar BDD array electrode.

Electrochemical experiments were performed on an electrochemical workstation (CH Instruments 650B) at room temperature in a conventional three-electrode electrochemical cell (5 cm of depth and 3 cm of diameter). Columnar BDD array electrode was acted as the working electrode with geometric area 0.725 cm². A platinum foil and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The electrochemical redox properties were obtained by the cyclic voltammetry (CV) test in 0.1 M KCl solution containing 1 mM Fe(CN)₆^{3-/4-}. The EIS was carried out in 0.1 M KCl solution containing 0.1 mM Fe(CN)₆^{3-/4-}. Then the potential window was tested by CV in 0.5 M H₂SO₄ solution at a scan rate of 100 mV·s⁻¹. Finally, amperometric response to glucose was carried out in 0.1 M Na₂SO₄ solution with 1 mL glucose solution (50 μM) addition every time. All these tests were conducted on flat BDD electrode for comparison.

3. Results and discussion

3.1 Characterization of columnar BDD array electrode

Raman spectra is very sensitive to the presence of defects and widely used to determine the chemical composition and construction of carbonaceous materials.[38] BDD material could be evaluated according to the intensity ratio of sp^3 and sp^2 hybrid peaks and the full width half maximum (FWHM) of the sp^3 hybrid peak. As shown in Fig. 2 (a), the characteristic peak of diamond (sp^3 hybrid peak) was at 1333 cm^{-1} , and there was a broadband peak of sp^2 band in the range of $1400\text{-}1600\text{ cm}^{-1}$. The sharp peak sp^3 hybridization with low Raman cross-sectional scattering coefficients ($9\times 10^{-7}\text{ cm}^{-1}/\text{sr}$) was much stronger than the peak of sp^2 and amorphous carbon hybrid with a high Raman cross-sectional scattering coefficients ($500\times 10^{-7}\text{ cm}^{-1}/\text{sr}$). [39] Very low content of sp^2 hybridized graphite and amorphous carbon was in BDD electrode. In addition, FWHM of columnar BDD was relatively narrow (13.5 cm^{-1}) in the range of $5\text{-}25\text{ cm}^{-1}$. [40] It indicated almost no lattice defects in columnar BDD.

XRD analysis was a non-destructive method to test the crystal structure of materials. Fig. 2 (b) was the XRD pattern of columnar BDD. According to the standard XRD pattern of diamond,[41] the diffraction peak at 44° , 75.4° and 91.5° was corresponding to (111), (220) and (311) plane of diamond, respectively. The stronger diffraction peak at 44° proved that the diamond (111) was dominant growth direction in both of columnar BDD and flat BDD.

Fig. 3 was the SEM images of samples. Fig. 3 (a) showed the array of silicon columns was continuous and uniform. Fig. 3 (b) exhibited that both the diameter of Si

columns and their spacing were 5 μm . The inset of Fig. 3 (b) displayed the height of Si columns was 10 μm , and Si columns were parallel to each other.

After BDD deposited on Si with columnar array, the array structure was preserved very well (Fig. 3 (d)). In addition, the high magnifications image (Fig. 3 (e)) showed that the size of BDD crystal was in the range from 0.5 μm to 1 μm and no obvious cracks and hydrogen etching spots could be observed on their surface. The diameter and height of the columns as well as the spacing between each columns were 8 μm , 12 μm and 2 μm (seen from Fig. 3 (f) and inset Fig. 3 (e)), respectively. Compared with flat BDD electrode showed in Fig. 3 (c), columnar BDD array electrode exhibited a larger specific surface area which increased for the side wall of the columns. Therefore, the active surface would increase with the increasing of specific surface area. It would be verified in the following electrochemical performance test.

3.2 Cyclic voltammetry and electrochemical impedance spectroscopy

The active electrochemical performance on columnar BDD array electrode was investigated to evaluation the correlation between area increase and electrochemical properties. CV of columnar BDD array electrode and flat BDD electrode were measured and the result was shown in Fig. 4 (a). Comparing with flat BDD electrode, the oxidation and reduction peaks of the $\text{Fe}(\text{CN})_6^{3-/4-}$ on the CV curve of columnar BDD array electrode were symmetrical with a smaller ΔE_p (oxidation peak potential minus the reduction peak potential) of 257 mV. Columnar BDD array electrode exhibited larger oxidation peak current. The small ΔE_p and increase of redox peak current indicated a fast electron transfer rate and higher redox efficiency on columnar

BDD array electrode compared with flat BDD electrode. In order to clarify the factors that resulted in the increased redox efficiency of columnar BDD array electrode, CV tests at a range of scan rates and electrochemical impedance were carried out and the results were displayed in Fig. 4 (b~d). A range of the oxidation and reduction peak currents (i_p) were showed in Fig. 4 (b). A good linear relationship between peak current (i_p) and scan rate ($v^{1/2}$) was obtained (Fig. 4 (c)). It suggested that the reaction of the electroactive substance on the electrode was diffusion controlled. The liner line of i_p versus $v^{1/2}$ could be described by the following equation.[42]

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} c v^{1/2}$$

Where i_p is the peak current (A), A is the inner active surface area of electrode (cm^2), c the concentration of $\text{Fe}(\text{CN})_6^{3-/4-}$ in the bulk of the solution (mM), n is the number of exchanged electrons ($n = 1$), v is the scan rate ($\text{V} \cdot \text{s}^{-1}$), and D is the diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-/4-}$ ($\text{cm}^2 \cdot \text{s}^{-1}$). According to the equation, the slope of the line was $2.69 \times 10^5 n^{3/2} A D^{1/2} c$. Calculated using the slope of the line and the diffusion coefficient of $0.63 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ for $\text{Fe}(\text{CN})_6^{3-/4-}$, [42] the inner active surface area of columnar BDD array electrode was 4.25 cm^2 (its outer active surface area was 0.725 cm^2), while the inner active surface area of flat BDD electrode was 2.64 cm^2 . The electrochemical active surface area of the electrode could be signified by the area ratio ($S_{\text{in}} / S_{\text{out}}$). The $S_{\text{in}} / S_{\text{out}}$ of columnar BDD array electrode was 5.86 (1.6 times of flat BDD electrode). The active surface enhancement was provided from the vertical side of the columns on columnar BDD array electrode, which was consistent with the discussion of Fig. 3 (c) and Fig. 3 (e).

In Fig. 4 (d), the Nyquist plots of EIS showed a semicircle and a linear region, the semicircle at high frequencies corresponds to an electron-transfer-limited process, and the linear portion at low frequencies corresponds to a diffusion-limited process. Under the hybrid process, when AC signal went through the electrode, Faraday impedance of the electrode was more complex. Electric double layer and Warburg impedance were in high and low frequency part respectively. Reaction on electrode converted from electrochemical control to diffusion control with the frequency decreasing. Here the equivalent circuit of electrode could be indicated as C(RW).[43] Results of calculation from EIS showed that electric double layer capacitance and charge transfer resistance of columnar BDD array electrode was an order of magnitude lower than that of flat BDD. It implied that the activity of electrons on columnar BDD array electrode was higher than that on flat BDD electrode. The calculated similar Warburg impedance from EIS indicated that diffusion resistance of reactants to the electrode did not increase with the construction of the microstructure. So the columnar BDD array electrode performed a high electrochemical activity.

CV measurement was used to characterize the electrochemical properties of columnar BDD array electrode. Flat BDD electrode was also used as a control. In Fig. 5 (a), the working potential window for columnar BDD array electrode remained wide in 0.5 M H_2SO_4 at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$. Current of oxygen evolution on columnar BDD array electrode was larger than that of flat BDD electrode. The stronger oxygen evolution reaction on the surface of the electrode was resulted from the larger active surface and the higher electron activity of the electrode mentioned

above. In addition, columnar BDD array electrode also had low background current (inset of Fig. 5 (a)). And the oxygen evolution potential on columnar BDD array electrode did not decline, compared to that of flat BDD electrode. In Fig. 5 (b) the amperometric response to 50 μM glucose increased successively on different electrodes was detected in 0.01 M Na_2SO_4 under 2 V (vs. SCE) potential. As expected, the electrical response signal to glucose solution (50 μM) on columnar BDD array electrode (about 106 μA) was larger than that of flat BDD electrode (about 27.8 μA). There was higher sensitivity (2.12 $\mu\text{A}/\mu\text{M}$) on columnar BDD array electrode than it (0.556 $\mu\text{A}/\mu\text{M}$) on flat BDD electrode. The electrical response increased to 4 times.

4. Conclusions

A vertically aligned columnar BDD array electrode was prepared. The columnar BDD array electrode exhibited high oxygen evolution potential and low background current, higher electrochemical active specific surface area and low Warburg impedance. Especially, enhanced electrical response signal (4 times of flat BDD electrode) was exhibited in glucose detection as sample. Hence, the columnar BDD array electrode was proved to perform a high electrochemical activity and efficiency successfully. The attractive performance indicated that columnar BDD array electrode was promising for applications in the field of electrochemical detection, electrochemical degradation and electrochemical synthesis.

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338

339 Figure Captions:

340 Figure 1

341 Schematic diagram of fabrication process of columnar BDD array electrodes.

342 Figure 2

343 Raman spectrum (a) and XRD pattern (b) of the columnar BDD array electrode.

344 Figure 3

345 The SEM images of silicon column array (a ,b), flat BDD electrode (c) and BDD
346 array (d ~ f). The inset of (b) and (e) is a profile of silicon column array and columnar
347 BDD, respectively.

348 Figure 4

349 (a) CV curves of samples in 0.1 M KCl solution containing 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at a
350 scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$; (b) CV analysis of columnar BDD array electrode in 0.1 M
351 KCl solution containing 1 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at a range of scan rate from $50 \text{ mV}\cdot\text{s}^{-1}$ to
352 $500 \text{ mV}\cdot\text{s}^{-1}$; (c) Plots of anode peak current and cathode peak current vs. the square
353 root of scan rate; (d) The Nyquist plots of EIS in 0.1 M KCl solution containing 0.1
354 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ at 0.3 V to columnar BDD array electrode and flat BDD electrode.

355 Figure 5

356 (a) CV behavior of columnar BDD array electrode at a scan rate of $100 \text{ mV}\cdot\text{s}^{-1}$ in 0.5
357 M H_2SO_4 ; (b) Amperometric response of columnar BDD array electrode at an applied
358 potential of 2 V (vs. SCE) to the successive increase of 50 μM glucose; electrolyte: 5
359 mL of 0.01 M Na_2SO_4 ; The inset of (a) is the partial enlargement drawing of (a); In all
360 the figures, the flat BDD electrode is as control.

Figure 1

Figure 2a)

Figure 2b)

Figure 3

Figure 4a)

Figure 4b)

Figure 4c)

Figure 4d)

Figure 5a)

Figure 5b)