

Fabrication and characterization of micro-band boron-doped diamond electrode for an application in adenosine phosphates sensor

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Abstract. Micro-band electrode was successfully fabricated by lamination method through sealing a piece of boron-doped diamond film inside a sandwich of two insulating plates, namely Teflon and silicon rubber as the gaskets. Characterization was performed using Raman and XPS spectra of the BDD film, while the fabricated micro-band was characterized by analyzing its SEM image. The electrode was examined for cyclic voltammetry of adenosine triphosphate solution, where an oxidation peak at +0.9 V vs. Ag/AgCl can be observed. The influence of scan rate and pH was also studied, in which pH 2 was selected as the optimum pH. The diffusion coefficient of 0.1 mM ATP at micro-band electrode was $3.84 \times 10^{-8} \text{ m}^2/\text{s}$, while the effective surface of the micro-band BDD electrode was $8.72 \times 10^{-14} \text{ m}^2$.

Keywords: micro-band electrode, boron-doped diamond, characterization, ATP, cyclic voltammetry

1. Introduction

Adenosine triphosphate (ATP) is clinically applied for the medication of progress wasting of muscles tissue (amyotrophia), intracerebral hemorrhage, a myocardial infarction and hepatitis. During the process of production and storage, ADP and AMP are often generated as impurities. Therefore, ATP, ADP and AMP determination is substantially significant for the product quality checking, production process monitoring, and clinical effectiveness evaluation of the ATP medicine [1, 2]. In this research, microelectrode was prepared for a detector in capillary electrophoresis in order to achieve an extremely fast scan rates and tiny areas that are necessary for high resistive media without considerable IR drops. The microelectrode is prepared from the cross section of boron-doped diamond (BDD) film, which generally provide around 5 μm thickness. Therefore, such type of electrode can be named as a micro-band electrode since the area of electrode can be considered as the band. Meanwhile, BDD exhibits interesting electrochemical properties, such as low and good stability of background current, a wide potential window in the aqueous media, high endurance towards deactivation, and highly stable for a long period [3-5]. Accordingly, modification of BDD as a micro-band is expected to provide a high performance of BDD microelectrode. Furthermore, electrochemistry of the micro-band electrode was examined for ATP detection.



2. Materials and methods

2.1. Apparatus and chemicals

Apparatus and chemicals used in this research were BDD, Teflon, silicon, platinum spiral, Ag/AgCl (saturated KCl), fused silica capillary, syringe, magnetic stirrer, stir bar, hotplate, ultrasonic bath, screw vial, cable, ATP, K_2HPO_4 , KH_2PO_4 , H_3PO_4 , CH_3COOH , H_3BO_4 , aqua bides, and methanol.

2.2. Fabrication of micro-band electrode

Micro-band electrode was prepared with lamination method. First, silicon substrate in BDD was chemically etched by the mixture of HF (48%) : HNO_3 (60%) 1:1 for 12 h [6]. Then, BDD was cut to 1 cm x 1 cm size, and insulated by Teflon and 1 cm x 1cm silicon rubber to form layers imitating a sandwich with 4 mm in width (figure 1). Stainless steel was applied to connect the electrode with electric current.

2.3. Procedure

Cyclic voltammetry of ATP in phosphate buffer solution (PBS) pH 6.8 with divers scan rates was performed at potential range of -1600 mV to 2000 mV (vs. Ag/AgCl). Influence of pH was investigated using Britton-Robinson buffer containing 0.04 M phosphoric acid, 0.04 M acetic acid, and 0.0404 M boric acid. NaOH was added to adjust the pH.

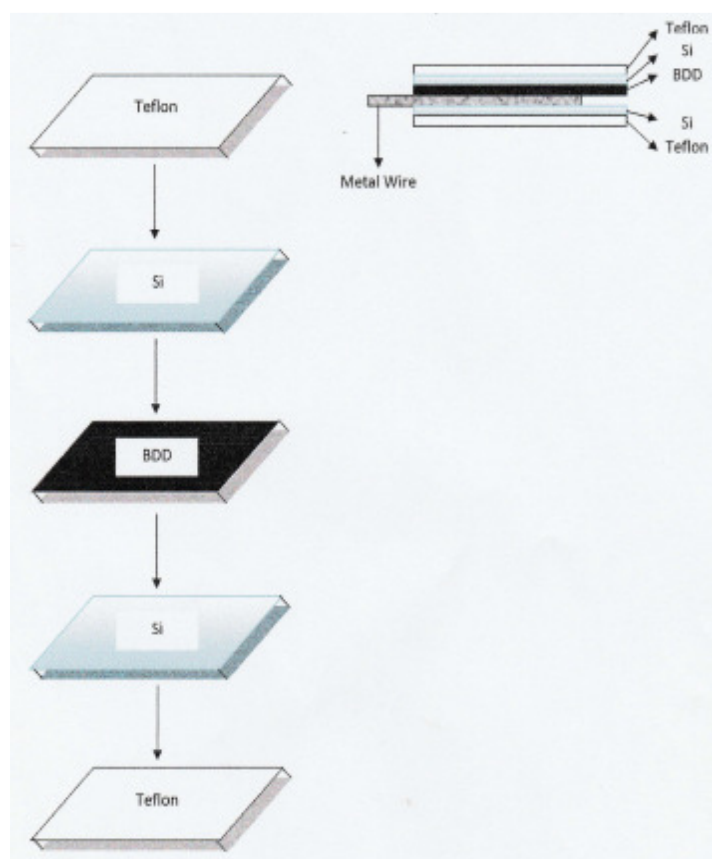


Figure 1. Longitudinal section of micro-band electrode

3. Results and discussion

3.1. Characterization of micro-band boron-doped diamond electrode

Characterization of BDD micro-band was performed by Raman and XPS spectroscopy as well as SEM method. Raman spectroscopy (figure 2a) provided the information concerning carbon phase, such as amorph, graphite, diamond, indicated by a peak at 1332 cm^{-1} attributed to diamond with C-C structure in sp^3 hybridization and a peak at 500 cm^{-1} suggested the presence of the disordered diamond formed due to the influence of the boron doping. Furthermore, XPS spectra (figure 2b) displays a C ($1s$) peak in hybridization sp^3 with a binding energy at 284.5 eV and an O($1s$) peak at binding energy of 532.5 eV resulted from the bonding between O and H [2]. In addition, SEM image (figure 3c) shows that the BDD film in the micro-band electrode with a $10\text{ }\mu\text{m}$ thickness.

3.2. Electrochemistry of ATP at BDD micro-band electrode

Cyclic voltammetry was performed for 0.1 mM ATP in PBS pH 6.8. A peak at $+0.6\text{ V}$ was observed in figure 3a. High resistive backgrounds of cyclic voltammograms were mainly consist of radial diffusion in which the voltammetric response is directly match towards the electrode length and is rather insensitive against width, was identified due to delamination defects. Then, $+0.9\text{ V}$ vs Ag/AgCl was selected as the optimum detection potential for adenosine, because when the oxidation process was applied at exactly $+0.6\text{ V}$, the result suggested that the process was just started at that potential and not all species could be oxidated. In figure 3b, cyclic voltammetry was performed with various scan rates from 25 mV/s to 250 mV/s , and the linear correlation of current and square root of scan rate was obtained, therefore the detection of adenosine triphosphates using micro-band electrodes can be performed as per Randles-Sevcik equation and depends on mass transfer only.

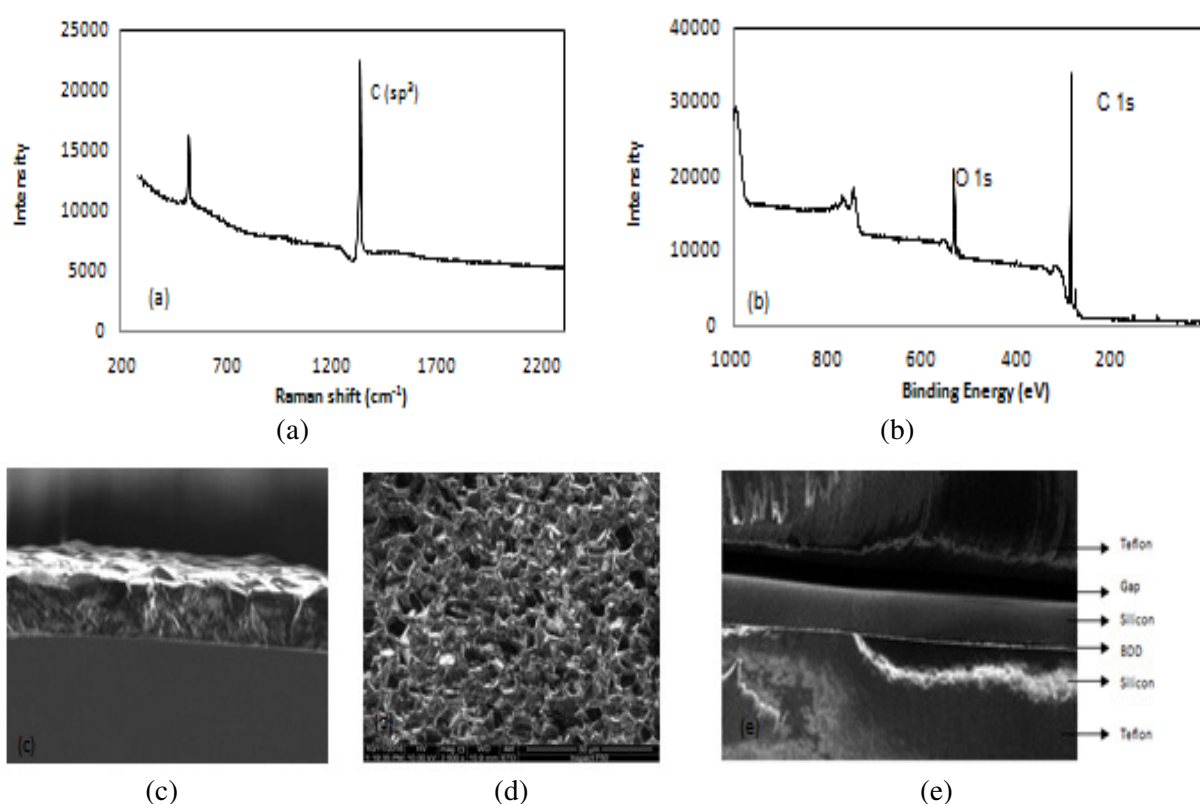


Figure 2. (a) Raman and (b) XPS spectra of BDD as well as the SEM image of micro-band electrode in (c) longitudinal section, (d) surface, (e) layer

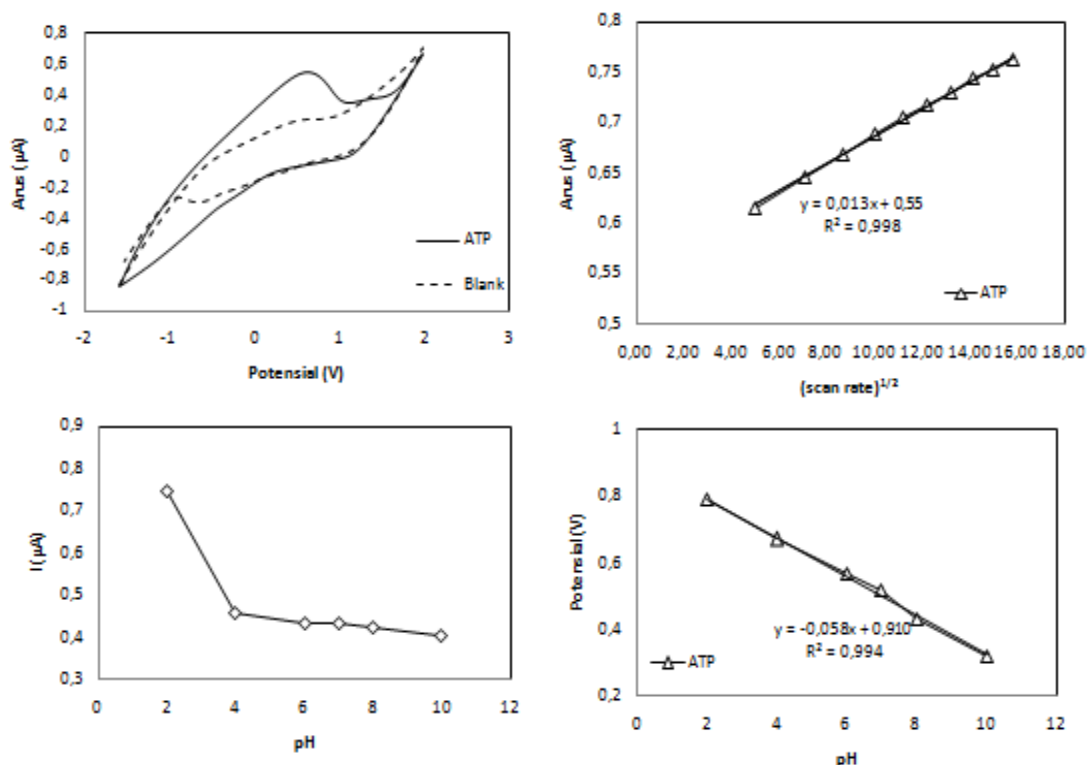


Figure 3. (a) Cyclic voltammograms of blank and ATP (b) plot I vs. (scan rate)^{1/2}, (c) plot I vs. pH in ATP, (d) plot pH vs. potential in ATP

Influence of pH was investigated using Britton-Robinson buffer as universal buffer from pH 2 to 10. A mixture containing 0.04 M H_3BO_3 , 0.04 M H_3PO_4 and 0.04 M CH_3COOH titrated to the desired pH with 0.2 M NaOH . In figure 3c, it was discovered that the highest current response was pH 2 in acid solution due to more phosphate groups with more negative charges are available in ATP. In figure 3d, the determination of adenosine triphosphate was conducted as per Nernst equation, at 25°C; the slope of the pH electrode was close to -59 mV/pH units, indicated that the oxidation and reduction in half reaction occurred at the same amount of electrons. When PBS pH 6.8 and Britton-Robinson buffer pH 2 was applied, the same responses in the reaction was observed, i.e the higher response of current in potential range from +0.6 V to +0.8 V due to the same ionic strength.

Diffusion defined as the net motion of molecules or atoms from a high chemical potential to a low chemical potential one. Diffusion will keep continue until all the species are uniformly dispersed and reached the equilibrium, although there was no gradient concentration. Diffusion velocity is influenced by temperature, particle size, and viscosity. Investigation of diffusion coefficient for 0.1 mM ATP in Britton-Robinson buffer pH 2 with micro-band BDD electrode was performed using Cottrell equation, which conducted by amperometry at +0.9 V along 5 minutes. Diffusion coefficient of this process was $3.84 \times 10^{-8} \text{ m}^2/\text{s}$ and the effective surface of the micro-band BDD electrode was $8.72 \times 10^{-14} \text{ m}^2$.

4. Conclusions

Micro-band electrode was successfully fabricated by lamination method through sealing boron doped-diamonds inside a sandwich of two insulating plates, namely Teflon and silicon. The thickness was about 10 μm and delivered the ideal condition for the surface of BDD. Under voltammetry experiment, +0.9 V vs. Ag/AgCl was selected as optimum detection potential for adenosine. Additionally, the calculation result demonstrated that this electrode follows the theory of Randles-Sevcik and Nernst equation, with pH 2 as the optimum pH. Furthermore, the diffusion coefficient of 0.1 mM ATP at micro-

band electrode was $3.84 \times 10^{-8} \text{ m}^2/\text{s}$ and the effective surface of the micro-band BDD electrode was $8.72 \times 10^{-14} \text{ m}^2$.

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