

Detection of Bio-chemical by Boron-doped Diamond Electrode

붕소가 도핑된 다이아몬드 전극을 이용한 생체화학물질의 검출

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Abstract

Selective, highly stable determination of epinephrine(adrenalin) was achieved in cyclic voltammetric measurement carried out at electrochemically treated conductive boron-doped diamond electrode. Boron-doped diamond electrodes were prepared on single crystal Si wafers by microwave plasma chemical vapor deposition and B_2O_3 was dissolved in acetone/methanol(9:1) mixture solution so that the B/C weight ratio ca. 10^4 ppm. Epinephrine is a kind of catecholamines, which secreted from adrenal marrow cells. The serious problem to detection of epinephrine is the interference phenomena of electroactive constituent, including AA.

In this study, electrochemical treatment of BDD was carried out to discriminate between epinephrine and AA responses. Experimental results showed that the peak potential of AA oxidation shift to the positive direction and the oxidation peak of epinephrine was unchanged. The effect of electrochemical treatment was maintained up to 40hrs.

Key Words : Boron-doped diamond electrode, Epinephrine, Ascorbic acid, interference.

1. Introduction

Polycrystalline chemical vapor-deposited(CVD) diamond films that are highly boron are metallic conductors. Boron-doped diamond exhibits several superior electrochemical properties that are significantly different from those of other carbon allotropes, e.g., glassy carbon(GC), pyrolytic graphite(PG), and highly oriented pyrolytic graphite(HOPG), which have been widely used as electrode materials for many years. BDD has received attention from electrochemists only in the past few years and no reports are published in our country. Its

attractive features include a wide electrochemical potential window in aqueous media, very low capacitance, and extreme electrochemical stability. In addition, diamond electrodes have recently been found to show high resistance to deactivation, via fouling, and insensitivity to dissolved oxygen. These properties make diamond a promising material for electroanalytical applications. GC and HOPG are composed almost exclusively depend on several factors, including surface preparation, microstructure, and the presence of carbon-oxygen functional groups.

Epinephrine, which is a component of neural transmission medium, takes effect on the transmission of nerve impulse. Many life phenomena are related to the concentration of epinephrine in blood. Medically, epinephrine has been used as a common emergency healthcare medicine. Therefore, the detection and determina

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-tion of epinephrine has attracted much attention of the scientist in life science and medicine. Previous techniques for the determination of epinephrine have been primarily based upon cation exchange, HPLC, CE, FIA, fluorimetry and sensors. However, the previous techniques suffered either tedious process or low sensitivity. A convenient method for direct determination of epinephrine is strongly desired. In detecting epinephrine, a serious source of interference is the presence of electroactive constituent, including ascorbic acid at a typical concentration of 10^{-4} M. For the most unmodified electrode materials, the voltammetric responses for these two species overlap, necessitating the use of electrode modification for selective epinephrine measurements.

In this work, we have found that it is possible to achieve high selectivity for epinephrine in the presence of ascorbic acid solution after a simple electrochemical pretreatment of the diamond electrode.

2. Experimental

2.1 Synthesis of conducting diamond films.

The boron-doped diamond thin films were grown on n-Si(100) substrate, which had been polished by 0.5 μ m diamond powder (Type Micron+SND, De Beers). Microwave plasma chemical vapor deposition (CVD) method was adopted by using commercial microwave plasma reactor (ASTeX Corp., Woburn, MA, USA). A 9:1 (v/v) mixture of acetone (Guaranteed, Koso Chemical Co., Ltd.) and methanol (Guaranteed, Nacalai Tesque) (volume ratio) was used as the carbon source. B₂O₃ (Extra pure, Wako Chemical Co., Ltd) was used as the boron source. We dissolved B₂O₃ in this mixture solution so that the B/C weight ratio was ca. 10^2 ppm. 99.99% H₂ gas was used as the carrier gas, which carries carbon source into chamber. The H₂ flow rate was controlled at 532sccm (standard cubic centimeters per minute) and the carbon source flow rate was 10sccm with a mass flow controller. The total pressure was fixed 100

Torr. Diamond film deposition was carried out using a microwave power of 4000W. Raman spectroscopy was carried out using an Ar⁺ laser (wave length = 514.5nm) in a Renishaw Raman imaging microscope system (Renishaw System 2000). Surface morphology was observed by laser microscope (KEYENCE Co., Ltd., Model no. VF-7510), which magnification was 2500.

2.2 Electrochemical measurements.

L(-)-epinephrine (AROS), L(+)-ascorbic acid and concd HClO₄ (Aldrich), were used as received. All other reagents were analytical reagent grade. All solutions were prepared in milli-Q water (Millipore).

The electrochemical measurements were carried out in a single compartment, three-electrode cell. A saturated calomel electrode (SCE) was used as the reference electrode, and Pt was used as the count electrode. All of the electrochemical measurements were taken using a WBCS 3000 measurement system (Wonatech Co.) and X-Y plotter. For the type of electrochemical pretreatment that was used for most of the measurement, the diamond electrodes were immersed in 0.1M KOH, and a potential of +2.6V vs. SCE was supplied for 75min. Using a more stringent electrochemical pretreatment, the diamond electrodes were subjected to three potential sweeps at 0.1V/s between +4 and -4V vs SCE, and then the potential was held for 1 min at +4V in 0.1M KOH solution.

3. Results and discussion

Fig. 1 is the microscope images of boron-doped diamond film, which deposited for 10hrs. The microwave-deposited polycrystalline boron-doped films were continuous and well faced, i.e., only planar were observed. The Raman spectra of the 10^2 ppm doped films exhibited a sharp peak at 1334cm^{-1} with a full width at half maximum of 7cm^{-1} , which is consistent with the literature. These results indicate that this film is of high quality. The resistivity of boron-doped diamond film was approximately 250 Ω cm.



Fig. 1. Scanning electron micrograph of the semiconducting boron-doped diamond thin film.

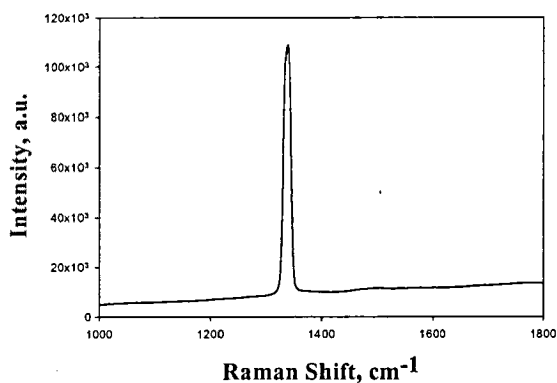


Fig. 2. Raman spectrum of the semiconducting boron-doped diamond thin film.

The shape of the voltammograms for epinephrine oxidation, obtained at both as-grown (untreated) diamond electrode and after treatment are typical of an electrochemically irreversible process (Fig. 3A). The oxidation process for AA is even more electrochemically irreversible (Fig. 3B). For epinephrine oxidation on as-deposited diamond electrodes, the anodic peak ($E_{p,a}$) was $+0.8 \pm 0.01$ V vs. SCE, with a shift of only 70 ± 10 mV after treatment. For ascorbic acid oxidation at the untreated diamond electrode $E_{p,a}$ was 1.03 ± 0.01 V vs. SCE. After treatment, the $E_{p,a}$ value shifted to 1.23 ± 0.01 V vs. SCE.

The extreme difference in electrochemical behavior of epinephrine and ascorbic acid as a result of the oxidation pretreatment is surprising. Two possible explanations are as follows. First,

nondiamond carbon impurities (sp^2 carbon) can be electrochemically oxidized, either removing them or rendering them inactive, thereby suppressing their contribution to the electrochemical response. It was already reported that dioxygen reduction in acid solution at conductive diamond electrodes was suppressed by polarization at relatively positive potentials in alkaline electrolytes. In present case, oxidized diamond surface acquires surface dipoles as a result of introducing oxygen-containing functional groups, which then electrostatically repel both anions and neutral molecules with strong dipoles.

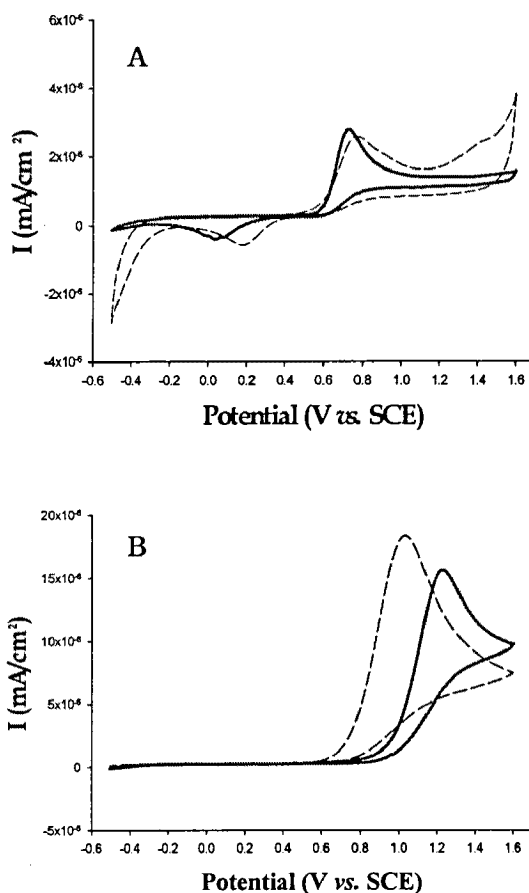


Fig. 3. Cyclic voltammograms for (A) 0.1 mM epinephrine and (B) 1 mM ascorbic acid at untreated (dashed lines) and electrochemically treated (solid lines) diamond electrodes in 0.1 M $HClO_4$ solution. Sweep rate, 20 mV/s

Cyclic voltammograms obtained at a diamond thin film electrode for a solution containing both epinephrine and ascorbic acid in 0.1M HClO₄ are shown in Fig. 4. The curve obtained before treatment exhibited a single broad peak, while that for the treated diamond electrode exhibited two anodic peaks (epinephrine at +0.8V and ascorbic acid 1.2V vs SCE). For the untreated electrode, the single broad peak can be attributed to epinephrine oxidation, while the ascorbic acid oxidation peak is presumed to be absent due to the catalytic regeneration of epinephrine, which is a well-known process occurring on unmodified carbon electrode. On the treated diamond electrode, due to the significant repulsion of ascorbic acid, the contribution from this catalytic chemical reaction appears to be strongly suppressed.

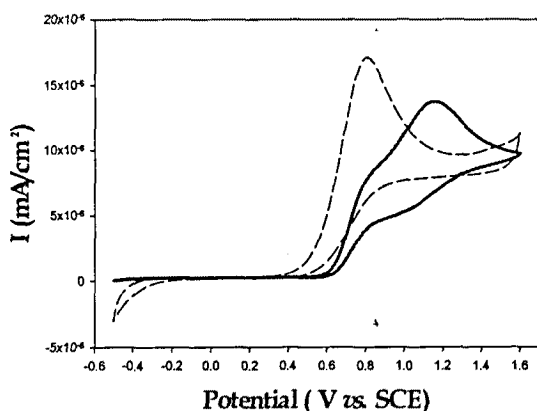


Fig. 4. Cyclic voltammograms for a 0.1M HClO₄ solution containing 0.1mM epinephrine and 1mM ascorbic acid at untreated (dashed line) and treated (solid line) diamond electrode. Sweep rate, 20mV/s.

4. Conclusion

In this work, we have showed that epinephrine and ascorbic acid can be selectively determined in acidic media using an electrochemically pretreated diamond electrode.

The unique features of the treated diamond electrode include very high sensitivity, remarkably good long-term stability, very good selectivity, insensitivity to oxygen, and ease of preparation. We are currently in the process of attempting to obtain more clear peak separation and detect very low concentration of epinephrine.

References

- [1] J. C. Argus, C. C. Hayman, *Science*, **241**, 913 (1988)
- [2] K. Hirabayashi, Y. Hirose, *Diamond Relat. mater.*, **5**, 48, 1996.
- [3] E. Popa, H. Notsu, T. Miwa, D. A. Tryk and Akira Fujishima, *Electrochemical and Solid-State Letter*, **2**, 49, 1999.
- [4] E. Danielson, J. H. Golden, E. W. McFarland, C. M. Reaves, W. H. Weinberg, *Science*, **270** 273, 1995.
- [5] M. Yanagisawa, L. Jiang, D. A. Tryk, K. Hashimoto, A. Fujishima, *Diamond Relat. mater.*, **8**, 2059i-2063, 1996.
- [6] K. Hayashi, S. Yamanaka, H. Okushi, K. Kajimura, *Diamond Relat. mater.*, **5**, 1002, 1996.
- [7] A. Sakhariva, L. Nyikos, Y. Pleskov, *Electrochemical Acta*, **37**, 973, 1992.
- [8] G.M. Swain, R. Ramesham, *Anal. Chem.* **65**, 345, 1993.
- [9] N. Lee, A. Badzian, *Diamond Relat. Mater.*, **6**, 130, 1997.
- [10] K. Hayashi, S. Yamanaka, H. Okushi, K. Kajimura, *appl. Phys. Lett.*, **68**, 1220, 1996.
- [11] W. B. Nowall and W. G. Kuhr, *Anal. Chem.*, **67**, 3583, 1995
- [12] P.M. Kovach, M. R. Deakin, and R. M. Wightman, *J. Phys. Chem.*, **90**, 4612, 1986
- [13] Y. Einaga, G. S. Kim, S. G. Park, A. Fujishima, *Diamond and Related Materials*, **10**, 3-7, 306-311, 2001
- [14] Y. Einaga, G. S. Kim, K. Ohnishi, S. G. Park, A. Fujishima, *Materials Science & Eng., B*, **8**, 1-3, 19-23, 2001