三种碳基电极材料的电化学性质对比研究

周艳丽^{1,*} 只金芳² 张向飞¹ 徐茂田^{1,*}¹ 商丘师范学院化学系, 河南 商丘 476000;² 中国科学院理化技术研究所, 中国科学院光化学转换与功能材料重点实验室, 北京 100190)

摘要: 对硼掺杂纳米金刚石(BDND), 硼掺杂微米金刚石(BDMD)和玻碳(GC)电极的电化学性质做了对比研究. 利用扫描电子显微镜表征了 BDMD 和 BDND 电极, 其表面粒子大小分别为 1–5 μm 和 20–100 nm. 利用 Raman 光谱对两种金刚石薄膜的成分进行了表征, 结果表明利用热丝化学气相沉积法得到了高质量的 BDND 和 BDMD 薄膜. 采用 0.5 mol·L⁻¹ H₂SO₄ 溶液测定了三种电极的电化学窗口, BDND 和 BDMD 电极的电化学窗口分别为 3.3 和 3.0 V, 远比 GC 电极(2.5 V)的要宽. [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻溶液的循环伏安和交流阻抗测定表明, 在 BDND、BDMD 和 GC 电极上的峰间距(ΔE_p)分别为 73、92 和 112 mV, 且其电子传递电阻(R_{ct})分别为 (98±5)、(260±19)和 (400±25) Ω . 我们也研究了 0.1 mmol·L⁻¹ 双酚 A 在三种电极上的电化学氧化行为. 上述的电化学测定结果表明, 两种金刚石电极均比 GC 电极表现出了更宽的电化学窗口、更好的电化学可逆性质、更快的电子传递速度和更高的电化学稳定性, 更为重要的是与 BDMD 相比 BDND 的电化学性质有进一步的提高.

关键词: 电化学性质; 硼掺杂纳米金刚石; 硼掺杂微米金刚石; 玻碳; 电极

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Comparative Study of Electrochemical Performances of Three Carbon-Based Electrode Materials

ZHOU Yan-Li^{1,*} ZHI Jin-Fang² ZHANG Xiang-Fei¹ XU Mao-Tian^{1,*}¹Department of Chemistry, Shangqiu Normal University, Shangqiu 476000, Henan Province, P. R. China;²Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China)

Abstract: The electrochemical properties of three carbon-based electrodes including boron-doped nanocrystalline diamond (BDND), boron-doped microcrystalline diamond (BDMD), and glassy carbon (GC) were compared. We used scanning electron microscopy to characterize the two diamond electrodes and the grain sizes of the BDMD and BDND films were 1–5 μm and 20–100 nm, respectively. The phase composition was characterized by Raman spectroscopy and high-quality BDMD and BDND films were formed by hot-filament chemical vapor deposition. Cyclic voltammograms for 0.5 mol·L⁻¹ H₂SO₄ showed that the potential windows for the BDND and BDMD electrodes were 3.3 and 3.0 V, respectively. The potential windows were much wider than that of the GC electrode (2.5 V). The cyclic voltammograms and Nyquist plots of the impedance measurements for [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ show peak to peak separations (ΔE_p) of 73, 92, and 112 mV and electron transfer resistances (R_{ct}) of (98±5), (260±19), and (400±25) Ω for the BDND, BDMD, and GC electrodes, respectively. We also investigated the oxidation of 0.1 mmol·L⁻¹ bisphenol A (BPA) on the three carbon-based electrodes. The above-mentioned electrochemical results reveal that the two diamond electrodes have wider potential windows, better reversibility, faster electron transfer, and higher stability than the GC electrode. Additionally, the BDND electrode shows better electrochemical properties than the BDMD electrode.

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*Corresponding authors. ZHOU Yan-Li, Email: zhouyanli@mails.gucas.ac.cn. XU Mao-Tian, Email: xumaotian@sqnc.edu.cn; Tel: +86-370-2595685.

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Key Words: Electrochemical property; Boron-doped nanocrystalline diamond; Boron-doped microcrystalline diamond; Glassy carbon; Electrode

Carbon materials, such as graphite, glassy carbon (GC), carbon black, carbon nanotubes, and vapor-deposited carbon films have been widely used in electroanalytical chemistry^[1–2]. The often-cited advantages of carbon electrodes include low cost, wide potential window, relatively inert electrochemistry, and electrocatalytic activity for a variety of redox reactions^[3–7]. Boron-doped diamond (BDD) prepared by chemical vapor deposition (CVD) is a relatively new carbon electrode material. BDD electrodes have a unique combination of electrochemical properties, for example, wide electrochemical potential window, low and stable background current, and high resistance to deactivation by fouling^[8–12].

Depending on growth parameters, such as vapor pressure, temperature, and substrate seeding, CVD growth of BDD can produce two types of films, which are generally classified according to the crystal grain size as microcrystalline (BDMD, grain size in micrometer range) and nanocrystalline (BDND, grain sizes below 100 nm) films^[13]. In addition to the smoother surface, BDND electrodes have more sp^2 -bonded carbon phase on grain boundaries than BDMD electrodes. It has demonstrated that the electrochemical properties are influenced mainly by morphological features, non-diamond impurity content (sp^2 -bonded carbon), and surface chemistry^[14–17]. In a recent study, the effect of the sp^2 -bonded nondiamond carbon impurity on the response of BDD thin-film electrodes was reported and the results indicated the incorporated sp^2 -bonded carbon in BDND electrodes can provide charge carriers and pathways of high carrier mobility^[18–19].

In this paper, the basic electrochemical properties of BDND electrodes were systematically compared with BDMD and GC (complete sp^2 -bonded carbon) electrodes. The comparison of stability for the above three electrodes was also studied by the detection of bisphenol A (BPA), which usually fouls the conventional electrode surfaces after electrochemical oxidation.

1 Experimental

BPA was supplied by Wako (Japan). Trimethyl borate was purchased from Sigma-Aldrich (USA). All other chemicals were of analytical grade, and water was obtained from a Millipore M-Q purification system ($>18\text{ M}\Omega\cdot\text{cm}$). The phosphate buffer solution (PBS) was prepared with KH_2PO_4 and K_2HPO_4 .

BDMD and BDND thin films were prepared by hot-filament CVD on silicon (100) wafers. Prior to deposition, Si substrates were abraded with 1 μm diamond powder, and then ultra-sonically cleaned successively in acetone and in distilled water for 1 min. Acetone and hydrogen were used as a carbon source and carrier gas, respectively. Trimethyl borate dissolved in the acetone was used as boron source at a B/C molar ratio of 0.5%. The experimental conditions were as follows: the diameter and length of Ta filament were 0.6 mm and 14 cm, respectively;

filament-substrate distance was 6 mm, T_{fil} was $(2100\pm200)^\circ\text{C}$, T_{sub} was $850\text{--}950^\circ\text{C}$, acetone flow rate was $50\text{ mL}\cdot\text{min}^{-1}$, and H_2 flow rate was $200\text{ mL}\cdot\text{min}^{-1}$. After 7 h growth, BDMD and BDND thin films were obtained under the similar condition except that the vapor pressure was 1.7 and 0.7 kPa, respectively. The surface morphologies and phase composition of the two diamond films were evaluated by scanning electron microscopy (SEM, Hitachi S-4300, Japan) and Raman spectroscopy (Renishaw 1000, England) using a He-Ne laser (632.8 nm) as an excitation source, respectively.

The electrochemical measurements were performed in a three-electrode cell system using a 263A Potentiostat/Galvanostat with a FRD 100 frequency response detector (Princeton, USA). Diamond electrodes were sonicated successively in 2-propanol and distilled water before use. GC electrodes were polished with 4.0, 1.0, and 0.01 μm alumina powder in succession, rinsed thoroughly with distilled water between each polishing step, and then sonicated in acetone and distilled water in succession. The planar working electrodes were mounted on the bottom of the glass cell by use of a silicone O-ring with an exposed area of 0.07 cm^2 . Platinum wire and Ag/AgCl (saturated KCl) electrode were used as auxiliary electrode and reference electrode, respectively. The electrolyte solutions were purged with high-purity N_2 gas for 15 min to reduce the level of oxygen dissolved before each electrochemical measurement.

2 Results and discussion

2.1 Characterization of as-deposited BDD films

Fig.1 shows the SEM images obtained from the as-deposited BDMD and BDND films. Uniform BDD films were deposited after growth for 7 h, and the grain sizes of BDMD and BDND films are 1–5 μm and 20–100 nm, respectively. There are four features in the Raman spectrum of the BDMD film as shown in Fig.2a. The 1332 cm^{-1} diamond peak widens, decreases in intensity, and shifts to a lower wavenumber (1313 cm^{-1}) according to the Raman result of conductive diamond. Broad peaks at 500 and 1200 cm^{-1} and a secondary feature around 1000 cm^{-1} are associated with Fano effect due to the doped boron^[17]. In Fig.2b, the Raman of BDND film has some change with that of the BDMD films. Firstly, a shoulder peak around 1150 cm^{-1} is often used as a signature for nanocrystalline diamond and is attributed to a surface phonon mode of diamond^[20]. Secondly, the signal with a maximum at 1540 cm^{-1} is assigned to disordered sp^2 -bonded carbon in the grain boundaries, and the signal is weak indicating the low proportion of sp^2 -bonded carbon^[21]. The characterization of the above surface morphologies and phase composition demonstrated that high-quality BDMD and BDND films have formed by hot-filament CVD.

2.2 Comparison of electrochemical potential window

The surfaces of as-grown diamond electrodes that have been

Fig.1 SEM images of the as-deposited BDMD (A) and BDND (B) films

Fig.2 Raman spectra of the as-deposited BDMD (a) and BDND (b) films

cooled to room temperature under atomic hydrogen are terminated with hydrogen. Due to the hydrophobic surfaces, electrode reactions that involve adsorbed intermediates may be strongly inhibited on diamond. Thus, the rate of water electrolysis is negligible in a very wide potential range on the two diamond electrodes. Fig.3 shows a cyclic voltammogram for different electrodes in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$ electrolyte. The potential windows for BDND and BDMD electrodes are 3.3 and 3.0 V, respectively. The potential windows are greatly wider than that of GC electrode (2.5 V). Also, as shown in Fig.3, the current for both diamond electrodes is significantly less than that for GC electrode. In contrast, potential window of the BDND electrode is improved compared to that of BDMD electrode. However, the mechanistic cause of this overpotential at BDND electrode is currently unknown. A low background current and wide work-

Fig.3 Cyclic voltammograms for water electrolysis at the three carbon-based electrodes

(a) BDND, (b) BDMD, (c) GC; supporting electrolyte: $0.5 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$; scan rate: $200 \text{ mV} \cdot \text{s}^{-1}$

ing potential window at BDND electrode is very similar to what has been reported for nitrogen-incorporated nanocrystalline diamond and carbon film consisting sp^2/sp^3 mixed bonds^[22–24].

2.3 Comparison of electrochemical behavior for redox species

$[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ is an excellent redox system for probing the electronic properties, surface cleanliness, and surface structure of electrodes, particularly carbon-based electrodes. As shown in Fig.4, the cyclic voltammograms for $0.5 \text{ mmol} \cdot \text{L}^{-1} [\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{PBS}$ and Nyquist plots of impedance measurements for $10 \text{ mmol} \cdot \text{L}^{-1} [\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{KCl}$ were performed at the above three electrodes. In Fig.4A, well-defined and symmetric CV curves of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ on the three electrodes were obtained, indicating nearly reversible or quasi-reversible electron transfer kinetics for the electrode interfaces. The anodic peak current of 11.1, 7.76, and $6.06 \mu\text{A}$ and the separation of peak to peak (ΔE_p) of 73, 92, and 112 mV were obtained at the BDND, BDMD, and GC electrodes, respectively. In Fig.4B, the profiles showed a semicircular portion at high frequencies corresponding to the electron transfer limited process and a linear part at low frequencies to the diffusion process. The electron transfer resistance, R_{et} , is equal to the semicircle diameter. Thus, the R_{et} could be estimated to be (98 ± 5) , (260 ± 19) , and $(400 \pm 25) \Omega$ for the BDND, BDMD, and GC electrodes, respectively. These facts suggest that the reversibility of electrode reaction becomes better and electron transfer is faster at diamond electrodes than GC electrode. In comparison with BDMD electrode, BDND electrode shows superior electron transfer properties due to the increased sp^2 -bonded carbon phase on grain boundaries of BDND films which may provide charge carries and high carrier mobility pathways. Bennett *et al.*^[19] also studied the effect of sp^2 -bonded non-diamond impurity on the electrochemical properties of diamond electrodes and as a result, the peak separation of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ decreases with increasing of sp^2 -bonded carbon. Clearly, the sp^2 carbon sites on the grain boundaries can have a profound impact on the electrode-reaction kinetics for redox sys-

Fig.4 (A) Cyclic voltammograms of $0.5 \text{ mmol} \cdot \text{L}^{-1} [\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in $0.1 \text{ mol} \cdot \text{L}^{-1}$ PBS (pH 7.0) and (B) Nyquist plots of $10 \text{ mmol} \cdot \text{L}^{-1} [\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in $0.1 \text{ mol} \cdot \text{L}^{-1}$ KCl by applying an ac voltage with 10 mV amplitude in a frequency range from 10 kHz to 0.1 Hz under open-circuit potential conditions obtained at the three carbon-based electrodes (a) BDND, (b) BDMD, (c) GC

tems.

2.4 Comparison of electrochemical stability

BPA, as an environmental endocrine disrupter, can be used as

Fig.5 Cyclic voltammograms of $0.1 \text{ mmol} \cdot \text{L}^{-1}$ BPA at the three carbon-based electrodes

(a) BDND, (b) BDMD, (c) GC; (1) first sweep, (2) second sweep, (3) third sweep; supporting electrolyte: $0.1 \text{ mol} \cdot \text{L}^{-1}$ PBS (pH 7.0); scan rate: $50 \text{ mV} \cdot \text{s}^{-1}$

model compounds for examining electrode stability due to strong adsorption of the reaction product and intermediate product^[25–26]. Fig.5 shows the cyclic voltammograms for three times sweeps in $0.1 \text{ mmol} \cdot \text{L}^{-1}$ BPA solution at the above three electrodes. A well-defined cyclic voltammogram was obtained with a peak potential at 1.2 V and the peak current of second and third sweeps has a slight decrease on the two diamond electrodes. As mentioned above, the BDND electrode showed a bigger peak current than BDMD electrode. At GC electrode, BPA oxidation results in a distinct deactivation, indicating that the GC surface is blocked due to the strong adsorption of the oxidation reaction products. Diamond electrodes, even though belonging to the carbon family, are inert with respect to adsorption. The result demonstrates that the diamond electrodes, especially BDND electrode, possess the promising features for analytical applications.

3 Conclusions

Both BDND and BDMD electrodes showed wider potential window, faster electron transfer, and better reversibility of electrode reaction than the GC electrodes. Importantly, compared to the BDMD electrode, the BDND electrode demonstrated superior electrochemical properties ascribed to the incorporated sp^2 -bonded carbon as charge transfer mediators and flat surface. The oxidation of BPA was detected on the two diamond electrodes with a very low background current, unlike the case of GC, which is known to be vulnerable to deactivation and fouling due to the strong adsorption of the oxidation products. Besides electroanalytical application, the BDND thin film with the outstanding electrochemical properties, inherent biocompatibility and flat surface, have the potential to be used to amperometric biosensors.

References

- McCreery, R. L. *Chem. Rev.*, **2008**, *108*: 2646
- Wang, Y. R.; Hu, P.; Liang, Q. L.; Luo, G. A.; Wang, Y. M. *Chin. J. Anal. Chem.*, **2008**, *36*: 1011 [王月荣, 胡坪, 梁琼麟, 罗国安, 王义明. *分析化学*, **2008**, *36*: 1011]
- Chen, P. H.; Fryling, M. A.; McCreery, R. L. *Anal. Chem.*, **1995**, *67*: 3115
- Wang, J.; Musameh, M.; Mo, J. W. *Anal. Chem.*, **2006**, *78*: 7044
- Hermans, A.; Seipel, A. T.; Miller, C. E.; Wightman, R. M. *Langmuir*, **2006**, *22*: 1964
- Lü, Y. F.; Yin, Y. J.; Wu, P.; Cai, C. X. *Acta Phys. -Chim. Sin.*, **2007**, *23*: 5 [吕亚芬, 印亚静, 吴萍, 蔡称心. *物理化学学报*, **2007**, *23*: 5]
- Zhang, B.; Adams, K. L.; Luber, S. J.; Eves, D. J.; Heien, M.; Ewing, A. G. *Anal. Chem.*, **2008**, *80*: 1394
- Zhi, J. F.; Tian, R. H. *Prog. Chem.*, **2005**, *17*: 55 [只金芳, 田如海. *化学进展*, **2005**, *17*: 55]
- Granger, M. C.; Witek, M.; Xu, J.; Wang, J.; Hupert, M.; Hanks, A.; Koppang, M. D.; Butler, J. E.; Lucazeau, G.; Mermoux, M.;

- Strojek, J. W.; Swain, G. M. *Anal. Chem.*, **2000**, **72**: 3793
- 10 Tatsuma, T.; Mori, H.; Fujishima, A. *Anal. Chem.*, **2000**, **72**: 2919
- 11 Compton, R. G.; Foord, J. S.; Marken, F. *Electroanalysis*, **2003**, **15**: 1349
- 12 Swain, G. M.; Ramesham, R. *Anal. Chem.*, **1993**, **65**: 345
- 13 Zhou, Y. L.; Zhi, J. F.; Zou, Y. S.; Zhang, W. J.; Lee, S. T. *Anal. Chem.*, **2008**, **80**: 4141
- 14 Wilson, N. R.; Clewes, S. L.; Newton, M. E.; Unwin, P. R.; MacPherson, J. V. *J. Phys. Chem. B*, **2006**, **110**: 5639
- 15 Barnard, A. S.; Sternberg, M. *J. Phys. Chem. B*, **2006**, **110**: 19307
- 16 Zhang, Y.; Yoshihara, S.; Shirakashi, T.; Kyomen, T. *Diamond Relat. Mater.*, **2005**, **14**: 213
- 17 Fischer, A. E.; Show, Y.; Swain, G. M. *Anal. Chem.*, **2004**, **76**: 2553
- 18 Duo, I.; Fujishima, A.; Comninellis, C. *Electrochem. Commun.*, **2003**, **5**: 695
- 19 Bennett, J. A.; Wang, J.; Show, Y.; Swain, G. M. *J. Electrochem. Soc.*, **2004**, **151**: E306
- 20 Show, Y.; Witek, M. A.; Sonthalia, P.; Swain, G. M. *Chem. Mater.*, **2003**, **15**: 879
- 21 Praver, S.; Nugent, K. W.; Jamieson, D. N.; Orwa, J. O.; Bursill, L. A.; Peng, J. L. *Chem. Phys. Lett.*, **2000**, **332**: 93
- 22 Chen, Q.; Gruen, D. M.; Krauss, A. R.; Corrigan, T. D.; Witek, M.; Swain, G. M. *J. Electrochem. Soc.*, **2001**, **148**: E44
- 23 Niwa, O.; Jia, J.; Sato, Y.; Kato, D.; Kurita, R.; Maruyama, K.; Suzuki, K.; Hirono, S. *J. Am. Chem. Soc.*, **2006**, **128**: 7144
- 24 Jia, J.; Kato, D.; Kurita, R.; Sato, Y.; Maruyama, K.; Suzuki, K.; Hirono, S.; Ando, T.; Niwa, O. *Anal. Chem.*, **2007**, **79**: 98
- 25 Yin, H.; Zhou, Y.; Ai, S. *J. Electroanal. Chem.*, **2009**, **626**: 80
- 26 D'Antuono, A.; Dall'Orto, V. C.; Lo Balbo, A.; Sobral, S.; Rezzano, I. *J. Agric. Food Chem.*, **2001**, **49**: 1098