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Electrochemical Sensing of Guanine and Adenine Based on the Boron-doped Carbon Nanotubes Modified Electrode

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基于 BCNTs/GC 电极的鸟嘌呤与腺嘌呤电化学行为及其同时检测

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摘要: 利用掺硼碳纳米管(BCNTs)/GC 电极研究了鸟嘌呤和腺嘌呤的电化学氧化行为. 与 GC 和 CNTs/GC 电极相比, BCNTs/GC 电极具有更强的电催化活性, 且响应电流明显增加. 两混合样品在 BCNTs/GC 电极上的氧化峰间隔较大, 可实现对鸟嘌呤和腺嘌呤的同时检测.

关键词: 掺硼碳纳米管; 鸟嘌呤; 腺嘌呤

中图分类号: O646

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鸟嘌呤(Guanine, G)和腺嘌呤(Adenine, A)是脱氧核糖核酸的重要组成部分, 在包括细胞能量转移和酶催化的信号传递等许多生物过程中都有重要作用^[1-2]. 鸟嘌呤和腺嘌呤的异常变化表明有机体内免疫系统的缺陷和突变, 因此鸟嘌呤和腺嘌呤的含量检测和分析非常重要. 已有文献报道嘌呤碱基的多种定量检测方法, 如荧光法^[3]、色谱法^[4]、电泳分离法^[5]和电化学法^[6]. 其中, 电化学法因操作简便, 灵敏性高和选择性好, 更适合嘌呤碱基的实际样品分析^[7]. 目前, 嘌呤碱基的电化学氧化检测已有广泛研究. Yang 等报道了基于 TiO₂-石墨烯纳米复合物的鸟嘌呤和腺嘌呤的电化学检测^[8]以及 β -环糊精/MWNTs 电极同时检测鸟嘌呤、腺嘌呤和胸腺嘧啶^[9]. Yin 等研究了石墨烯-Nafion 复合膜电极鸟嘌呤和腺嘌呤的电化学氧化及其同时检测^[10]. CdS 微球体电极电化学检测鸟嘌呤和腺嘌呤也取得了成功^[11]. 以上这些电极都增强了嘌呤碱基的氧化信号, 但电极制作复杂, 线性范围窄, 背景电流大. 据报道, 掺杂其它元素的碳纳米管(Carbon Nanotubes, CNTs)的物理化学性质会得到明显提高, 这归因于掺杂 CNTs 表面引入了更多的边缘位点和富氧基团^[12]. 作者课题组制备的硼掺杂的碳纳米管(B-doped Carbon Nano-

tubes, BCNTs)修饰电极对多巴胺^[13-14]、烟酰胺腺嘌呤二核苷酸(NADH)^[15]和过氧化氢^[16]具有更高的催化活性, 可提高电极与生物分子葡萄糖氧化酶(GOD)^[17]间的电子传递速率.

本文应用 BCNTs/GC 电极研究了鸟嘌呤和腺嘌呤的电化学氧化行为, 以期用于小牛胸腺 DNA 中鸟嘌呤和腺嘌呤的定量检测.

1 实验

1.1 仪器与试剂

CHI650D 电化学工作站(上海辰华), 磁力加热搅拌器 79-1(常州国华). 玻碳基底作电极, 饱和甘汞电极(SCE)和铂电极分别作为参比电极和辅助电极. 采用循环伏安法和差分脉冲伏安法在室温下测试, 脉冲幅度为 50 mV, 脉冲宽度为 50 ms, 背景溶液为磷酸盐缓冲溶液(PBS, pH 7.0, 0.1 mol·L⁻¹).

BCNTs 由 CNTs(~95%, 直径 20~30 nm, 深圳纳米技术)与 B₂O₃ 粉末经置换合成^[18]. CNTs 与 BCNTs 在浓缩的硫酸-硝酸混合溶液(3:1, by volume)中超声降解 3 h, 过滤, 二次蒸馏水洗涤, 60 °C 真空干燥. 将酸化处理的 BCNTs 及 CNTs 在二次蒸馏水中超声振荡 1 h, 形成黑色悬浮液(浓度 0.5 mg·mL⁻¹).

鸟嘌呤与腺嘌呤(加拿大 Bio Basic Inc 公司)分别溶于 $0.1 \text{ mol} \cdot \text{L}^{-1}$ NaOH 溶液. DNA 购自上海生物工程公司,无需纯化. 其它试剂均为分析纯,溶液均由二次蒸馏水配置.

1.2 电极制备

玻碳基底(GC, $\phi = 3 \text{ mm}$)用 1.0 和 $0.3 \text{ }\mu\text{m}$ 氧化铝粉末打磨至光滑镜面,用二次蒸馏水清洗. 在 $0.5 \text{ mol} \cdot \text{L}^{-1}$ H_2SO_4 溶液中进行循环伏安预处理直至图形稳定,电势范围为 $-0.15 \sim 1.0 \text{ V}$,扫描速率为 $50 \text{ mV} \cdot \text{s}^{-1}$. 然后取 $5 \text{ }\mu\text{L}$ BCNTs 的悬浮液滴于预处理后的 GC 基底,红外灯下干燥.

CNTs/GC 电极和 GC 电极同样按上述步骤处理.

1.3 DNA 样品处理

将小牛胸腺 DNA(dsDNA)溶液置于沸水中 15 min ,在冰浴中冷却得 ssDNA.

1.4 富集时间及富集电位

对 $10.0 \text{ }\mu\text{mol} \cdot \text{L}^{-1}$ 嘌呤碱基在 PBS($\text{pH } 7.0$, $0.1 \text{ mol} \cdot \text{L}^{-1}$) 中进行富集时间及富集电位优化. 在 $0 \sim 240 \text{ s}$ 内,富集时间增加,嘌呤碱基的氧化峰电流随之增大; $240 \sim 270 \text{ s}$,富集时间增加,峰电流增加缓慢,表明 240 s 时嘌呤碱基吸附量趋于饱和. 在 0.3 V 时,电流响应最大. 故富集时间与富集电位以 240 s 及 0.3 V 为宜.

2 结果与讨论

2.1 鸟嘌呤与腺嘌呤的循环伏安曲线

图 1 分别显示了 GC(a)、CNTs/GC(b)和 BCNTs/GC(c)电极在 $10.0 \text{ }\mu\text{mol} \cdot \text{L}^{-1}$ 鸟嘌呤(A)或 $10.0 \text{ }\mu\text{mol} \cdot \text{L}^{-1}$ 腺嘌呤(B)PBS($\text{pH } 7.0$, $0.1 \text{ mol} \cdot \text{L}^{-1}$)溶液的循环伏安曲线. 从图中可以看出,BCNTs/GC 电极的背景电流比 CNTs/GC 电极和 GC 电极的背景电流高,这主要是由于在 CNTs 中掺杂硼后使得碳纳米管的比表面积增大. 同时鸟嘌呤和腺嘌呤有很明显的氧化峰,而在阴极扫描中没有还原峰,这说明嘌呤碱基的氧化是不可逆的. 另外,在 GC 电极上嘌呤碱基的电氧化作用只有一个小凸起,而在 CNTs/GC 电极上嘌呤碱基的电氧化信号突然增强,这是由于 CNTs 能够提高嘌呤碱基与电极之间的电子传递. 相对于 CNTs/GC 和 GC 电极,BCNTs/GC 电极的峰电流明显增强很多,且鸟嘌呤和腺嘌呤的氧化电位负移,说明 BCNTs/GC

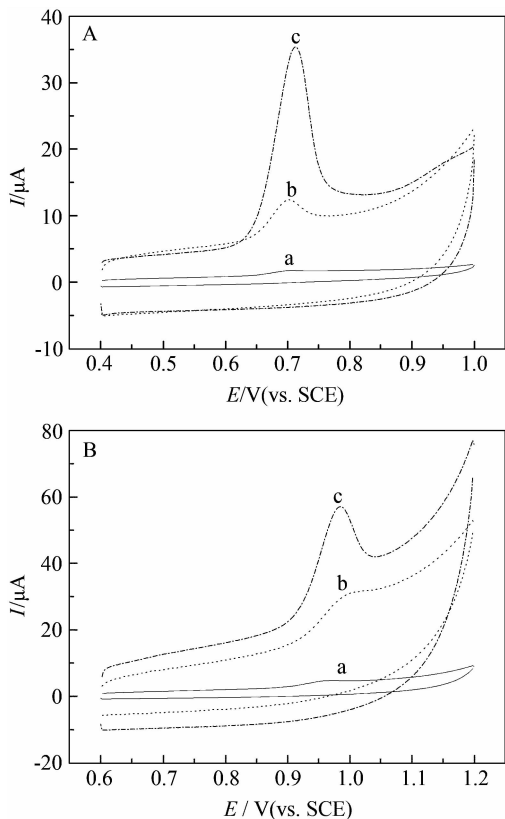


图 1 GC (a)、CNTs/GC (b)和 BCNTs/GC (c)电极在 $10 \text{ mol} \cdot \text{L}^{-1}$ 鸟嘌呤(A)和 $10 \text{ mol} \cdot \text{L}^{-1}$ 腺嘌呤(B) PBS 缓冲溶液($\text{pH } 7.0$, $0.1 \text{ mol} \cdot \text{L}^{-1}$)的循环伏安曲线(扫描速率 $50 \text{ mV} \cdot \text{s}^{-1}$)

Fig. 1 Cyclic voltammograms of the GC (a), CNTs/GC (b) and BCNTs/GC (c) electrodes in $10 \text{ mol} \cdot \text{L}^{-1}$ guanine (A) or adenine (B) PBS ($\text{pH } 7.0$, $0.1 \text{ mol} \cdot \text{L}^{-1}$) solutions (scan rate: $50 \text{ mV} \cdot \text{s}^{-1}$)

电极对嘌呤碱基的氧化有很好的电催化能力,这归因于 BCNTs 表面有较多边缘位点及含氧基团,更利于电子传递.

2.2 鸟嘌呤和腺嘌呤的电化学特征

图 2 是不同扫速下电极在鸟嘌呤(A)和腺嘌呤(B)的 PBS 缓冲溶液($\text{pH } 7.0$, $0.1 \text{ mol} \cdot \text{L}^{-1}$)中的循环伏安曲线. 由图可见,嘌呤碱基电流随扫速增加而增加,并呈线性关系(见插图). 鸟嘌呤和腺嘌呤的线性方程分别为 $I_{\text{pa}} = 0.2819 \nu + 6.642$ ($I_{\text{pa}}, \mu\text{A}$; $\nu, \text{mV} \cdot \text{s}^{-1}$; $R = 0.9912$) 和 $I_{\text{pa}}/\mu\text{A} = 0.1758 \nu + 7.371$ ($I_{\text{pa}}, \mu\text{A}$; $\nu, \text{mV} \cdot \text{s}^{-1}$; $R = 0.9945$),故该反应为表面控制反应.

图3示出鸟嘌呤(A)和腺嘌呤(B)在不同pH

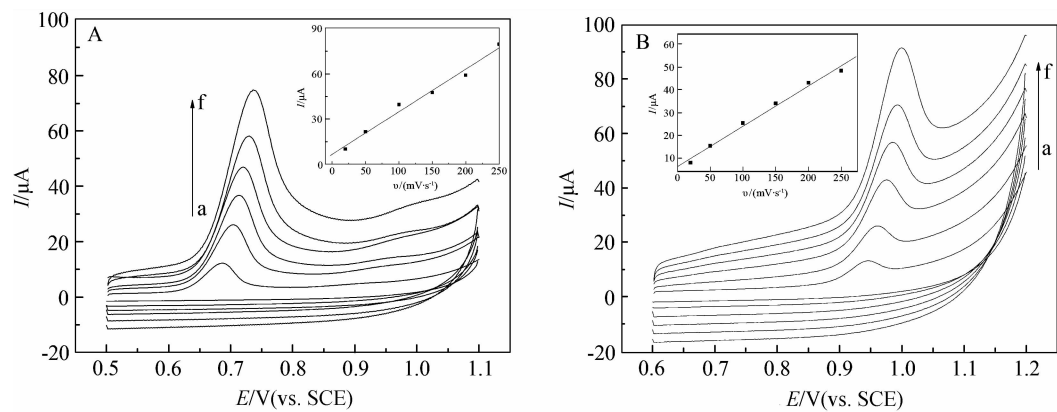


图2 BCNTs/GC 电极在 $10\text{ mol}\cdot\text{L}^{-1}$ 鸟嘌呤 (A) 和腺嘌呤(B) 的 PBS 缓冲溶液($\text{pH } 7.0, 0.1\text{ mol}\cdot\text{L}^{-1}$) 中的循环伏安曲线(A 和 B 中插图分别为鸟嘌呤、腺嘌呤氧化峰电流随扫描速率变化的曲线图)
扫描速率 $\nu(\text{a} \sim \text{f})/(\text{mV}\cdot\text{s}^{-1})$: 20, 50, 100, 150, 200, 250

Fig. 2 Cyclic voltammograms of the BCNTs/GC electrode in $10\text{ mol}\cdot\text{L}^{-1}$ guanine (A) or adenine (B) PBS ($\text{pH } 7.0, 0.1\text{ mol}\cdot\text{L}^{-1}$) solutions with different scan rates (the insets in A and B show the plots of the oxidation peak current vs. scan rate in guanine and adenine, respectively) $\nu(\text{a} \sim \text{f})/(\text{mV}\cdot\text{s}^{-1})$: 20, 50, 100, 150, 200, 250

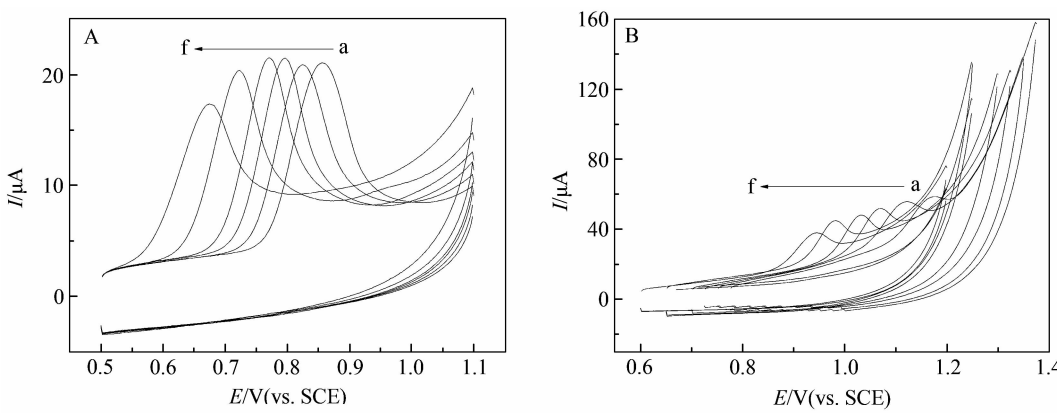


图3 鸟嘌呤(A)和腺嘌呤(B)在 BCNTs/GC 电极上不同 pH 值的 $0.1\text{ mol}\cdot\text{L}^{-1}$ PBS 缓冲溶液中的循环伏安曲线
 $\text{pH}(\text{a} \sim \text{f})$: 4.5, 5.0, 5.5, 6.0, 7.0, 8.0,扫描速率为 $50\text{ mV}\cdot\text{s}^{-1}$
Fig. 3 Cyclic voltammograms of guanine (A) and adenine (B) at the BCNTs/GC electrode in $0.1\text{ mol}\cdot\text{L}^{-1}$ PBS solutions with different pH values, $\text{pH}(\text{a} \sim \text{f})$: 4.5, 5.0, 5.5, 6.0, 7.0, 8.0, scan rate: $50\text{ mV}\cdot\text{s}^{-1}$

值缓冲液中的循环伏安曲线. 在 $\text{pH } 4.5 \sim 8.0$ 范围内,随着 pH 值增加,阳极峰电位负移,说明氢离子参与了电极反应. 鸟嘌呤和腺嘌呤的 pH 与 E_p 的线性方程(图 4)分别为 $E_p = 1.08 - 0.0513\text{ pH}$ ($E_p, \text{ V}; R = 0.9986$) 和 $E_p = 1.148 - 0.0604\text{ pH}$ ($E_p, \text{ V}; R = 0.9944$),斜率分别为 51.3 mV/pH 和 60.4 mV/pH ,与理论值 58.6 mV/pH 很接近^[30],说明嘌呤碱基的直接电化学氧化属于两个电子与两个质子参与的反应^[8].

2.3 鸟嘌呤和腺嘌呤的同时检测

图 5 为 BCNTs/GC(a) 和 CNTs/GC(b) 电极在 $10.0\text{ }\mu\text{mol}\cdot\text{L}^{-1}$ 鸟嘌呤和 $10.0\text{ mol}\cdot\text{L}^{-1}$ 腺嘌呤共存的 PBS 缓冲溶液($\text{pH } 7.0, 0.1\text{ mol}\cdot\text{L}^{-1}$) 中的循环伏安曲线. 可以看到,与 CNTs/GC 电极相比,BCNTs/GC 电极的嘌呤碱基的氧化峰电流明显增强,且鸟嘌呤与腺嘌呤的两氧化峰电位差达 300 mV ,足以清晰分开,故可能实现两者的同时测定.
图6 显示不同鸟嘌呤浓度的 PBS 缓冲溶液

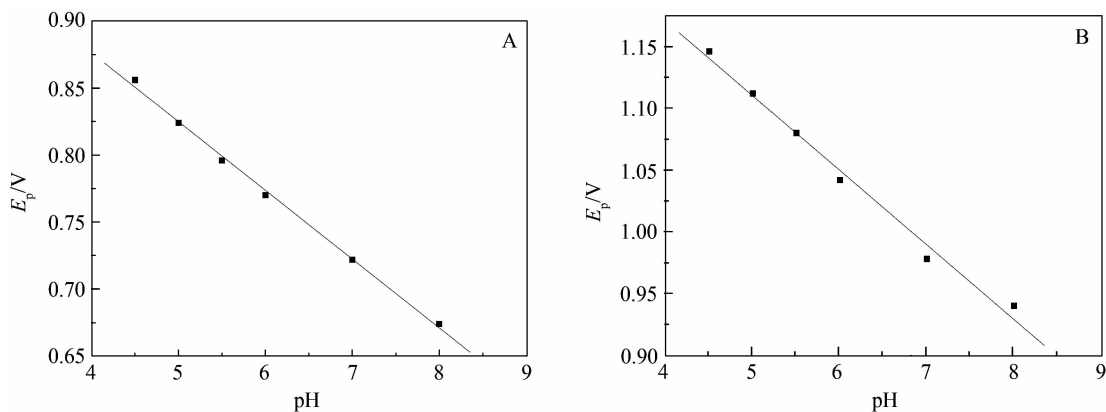


图 4 鸟嘌呤(A)和腺嘌呤(B)峰电位与溶液 pH 值之间的关系曲线

pH(a ~ f): 4.5, 5.0, 5.5, 6.0, 7.0, 8.0, 扫描速率 $50 \text{ mV} \cdot \text{s}^{-1}$

Fig. 4 The peak potentials of guanine (A) and adenine (B) at the BCNTs/GC electrode as a function of pH

pH(a ~ f): 4.5, 5.0, 5.5, 6.0, 7.0, 8.0, scan rate: $50 \text{ mV} \cdot \text{s}^{-1}$

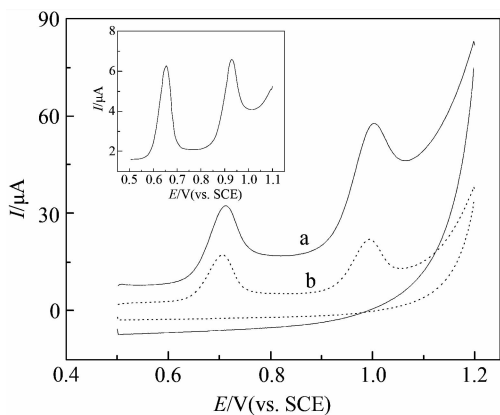


图 5 BCNTs/GC (a), CNTs/GC (b) 电极在 $10 \text{ mol} \cdot \text{L}^{-1}$ 鸟嘌呤和 $10 \text{ mol} \cdot \text{L}^{-1}$ 腺嘌呤共存的 PBS 缓冲溶液 ($\text{pH } 7.0, 0.1 \text{ mol} \cdot \text{L}^{-1}$) 中的循环伏安曲线 扫描速率为 $50 \text{ mV} \cdot \text{s}^{-1}$ (插图: BCNTs/GC 电极在 $3.0 \text{ mol} \cdot \text{L}^{-1}$ 鸟嘌呤和 $3.0 \text{ mol} \cdot \text{L}^{-1}$ 腺嘌呤共存的 PBS 缓冲溶液 ($\text{pH } 7.0, 0.1 \text{ mol} \cdot \text{L}^{-1}$) 中的微分脉冲伏安曲线)

Fig. 5 Cyclic voltammograms of the BCNTs/GC (a) and CNTs/GC (b) electrodes in $10.0 \text{ mol} \cdot \text{L}^{-1}$ guanine and $10.0 \text{ mol} \cdot \text{L}^{-1}$ adenine PBS ($\text{pH } 7.0, 0.1 \text{ mol} \cdot \text{L}^{-1}$) solution, scan rate: $50 \text{ mV} \cdot \text{s}^{-1}$ (the inset shows the differential pulse voltammetric response of $3.0 \text{ mol} \cdot \text{L}^{-1}$ guanine and $3.0 \text{ mol} \cdot \text{L}^{-1}$ adenine in $\text{pH } 7.0$ PBS solution at the BCNTs/GC electrode)

($\text{pH } 7.0, 0.1 \text{ mol} \cdot \text{L}^{-1}$) 中 BCNTs/GC 电极鸟嘌呤氧化峰电流-浓度关系曲线。可以看出,鸟嘌呤浓度增加,阳极峰电流随之增加,当鸟嘌呤浓度为 $40 \mu\text{mol} \cdot \text{L}^{-1}$ 时呈现稳定电流平台,线性回归方程为

$I_{\text{pa}} = 1.73 C + 0.9687$ ($I_{\text{pa}}, \mu\text{A}; C, \mu\text{mol} \cdot \text{L}^{-1}; R = 0.9941$)。图 7 显示不同腺嘌呤浓度的 PBS 缓冲溶液 ($\text{pH } 7.0, 0.1 \text{ mol} \cdot \text{L}^{-1}$) BCNTs/GC 电极腺嘌呤氧化峰电流-浓度关系曲线。腺嘌呤浓度增加,其峰电流随之增加,腺嘌呤浓度达 $20 \mu\text{mol} \cdot \text{L}^{-1}$ 时,其电流趋于稳定,其相关系数 $R = 0.9962$ 。鸟嘌呤和腺嘌呤的浓度检测下限分别是 $0.03 \mu\text{mol} \cdot \text{L}^{-1}$ 和 $0.1 \mu\text{mol} \cdot \text{L}^{-1}$ ($S/N = 3$)。上述检测方法可同时测定高浓度嘌呤碱基。

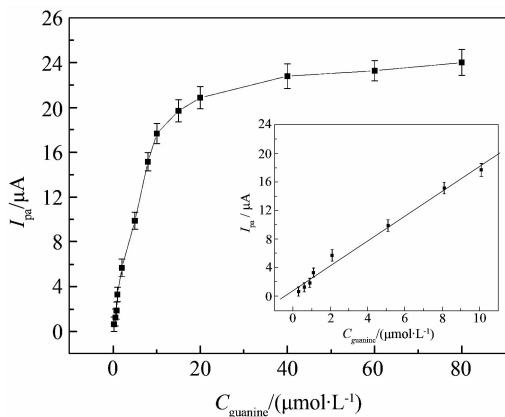


图 6 BCNTs/GC 电极上不同鸟嘌呤浓度的 PBS 缓冲溶液 ($\text{pH } 7.0, 0.1 \text{ mol} \cdot \text{L}^{-1}$) 中鸟嘌呤的氧化峰电流-浓度曲线 (插图: BCNTs/GC 电极的线性校正曲线)

Fig. 6 Calibration plots of the oxidation peak current versus concentration of guanine in PBS ($\text{pH } 7.0, 0.1 \text{ mol} \cdot \text{L}^{-1}$) solution (the inset shows the linear calibration curve obtained at the BCNTs/GG electrode)

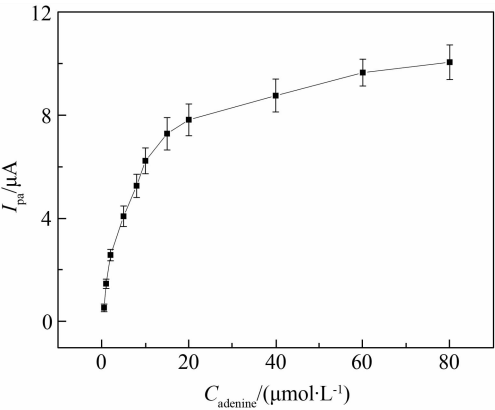


图7 BCNTs/GC 电极上不同腺嘌呤浓度的 PBS 缓冲溶液 (pH 7.0, 0.1 mol·L⁻¹) 中腺嘌呤的氧化峰电流-浓度曲线

Fig.7 Calibration plots of the oxidation peak current versus different concentration of adenine in PBS (pH 7.0, 0.1 mol·L⁻¹) solution

2.4 电极重现性及稳定性

BCNTs/GC 电极在 20 μmol·L⁻¹ 鸟嘌呤与 20 μmol·L⁻¹ 腺嘌呤的共存混合溶液中连续测试 10 次, 相对标准偏差 (RSD) 分别为 (3.58 ± 0.04) % 和 (2.26 ± 0.05) %。该电极保存 3 周后, 鸟嘌呤和腺嘌呤的氧化峰电流相对标准偏差分别为 (2.89 ± 0.03) % 和 (3.56 ± 0.04) %。

2.5 实际样品检测

使用 BCNTs/GC 电极检测热变性的 DNA 中的嘌呤碱基含量。按传统方法将 50.0 μmol·L⁻¹ 热变性 DNA 加入到 5 mL PBS 缓冲溶液中, 检测其中的嘌呤碱基浓度。而后加入 10.0 μmol·L⁻¹ 鸟嘌呤及 10.0 μmol·L⁻¹ 腺嘌呤, 再检测其中的嘌呤碱基, 据线性回归方程可以计算出 DNA 中的嘌呤碱基的浓度。得鸟嘌呤与腺嘌呤浓度分别为 28.0% 与 21.8% (by mole), (G + C)/(A + T) = 0.81 与理论值 0.77^[19] 比较接近, 因此本方法可用于实际检测。

3 结 论

BCNTs/GC 电极表面鸟嘌呤和腺嘌呤的电化学氧化电流大大提高, 这归因于 BCNTs 表面有更多的边缘位点和功能基团。两种嘌呤碱基的阳极峰间距较大, 可实现同时检测, 检测下限分别为 0.03 μmol·L⁻¹ 和 0.1 μmol·L⁻¹ (S/N = 3)。实际检测 DNA 中鸟嘌呤与腺嘌呤的浓度分别为

28.0% 与 21.8% (by mole), (G + C)/(A + T) = 0.81 与理论值 0.77 比较接近, 因此本方法可用于实际检测。

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Electrochemical Sensing of Guanine and Adenine Based on the Boron-Doped Carbon Nanotubes Modified Electrode

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Abstract: In the present paper, the boron-doped carbon nanotubes (BCNTs) modified glassy carbon (GC) electrode was simply fabricated, and the electrochemical oxidation behaviors of guanine and adenine at the BCNTs/GC electrode were investigated. Compared with the bare GC and CNTs/GC electrodes, the BCNTs-modified electrode exhibited extraordinary electrocatalytic activity towards the oxidations of guanine and adenine as indicated by the obvious increase in current responses. Moreover, the peak separation between guanine and adenine was large enough for their potential recognition in mixture without any separation or pretreatment. Therefore, the simultaneous determination of guanine and adenine was successfully achieved. The BCNTs/GC electrode showed high sensitivity, wide linear ranges and low detection limits for the electrochemical determination of guanine and adenine. The possibility of the BCNTs/GC electrode for the determination of guanine and adenine in calf thymus DNA has also been evaluated. The BCNTs/GC electrode has advantages of excellent catalytic activity, selectivity and simplicity, which plays a potential role in the development of the related DNA analysis.

Key words: boron-doped carbon nanotubes; guanine; adenine