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Electrocatalytic Oxidation of Hydrazine at Rutin Carbon Nanotubes Modified Electrode

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芦丁碳纳米管修饰玻碳电极电催化氧化胍的研究

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摘要: 应用循环伏安法研究了芦丁碳纳米管修饰玻碳电极(Rt-MWNT/GC)的电化学行为及其对胍的电催化氧化. 实验表明,该修饰电极能使胍的氧化电位降至260 mV附近,表现出良好的电催化作用. 安培法测得催化电流与胍浓度在 $2.5 \times 10^{-6} \sim 1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ 范围内呈线性关系,检出限 $5 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$.

关键词: 电分析; 电催化; 碳纳米管; 芦丁; 胍

中图分类号: O657.1

文献标识码: A

胍是一种强还原剂,被广泛应用于医药、化工、军事和航天等领域. 然而,胍对血液及神经系统有毒害,且毒性可长久蓄积,是公认的致癌物质^[1]. 因此,建立胍的高灵敏分析方法具有重要的意义. 关于胍的测定通常有分光光度法^[2-3], 化学发光法^[4], 色谱法以及电化学法^[5]. 在电化学法中,使用普通的碳电极,胍的氧化过电位较高,倘若采用金属铁氰化物及其它过渡金属络合物修饰的电极,均能不同程度地降低胍氧化的过电位,提高方法灵敏度^[6-9]. 咖啡酸、邻苯二酚紫和苏木精等含邻位羟基的有机化合物,在电极表面能发生可逆电催化氧化还原,也曾用于胍的电催化氧化^[10-11].

芦丁(Rutin, Rt)是一种常见的黄酮类化合物,其分子中B环上的邻苯二酚基团在一定条件下能发生可逆的电化学氧化还原,以其修饰的电极已被用于NADH和抗坏血酸等的电催化氧化^[12-13]. 碳纳米管(Carbon nanotube, CNT)具有降低化学物质氧化还原过电位并改善其氧化还原可逆性等优点^[14]. Zhao等^[15]研究了CNT粉末微电极对胍的电催化氧化,检出限为 $1 \mu\text{mol/L}$. Lawrence等^[16]指出,直接将电子媒介体吸附到CNT表面不会破坏CNT的 sp^2 结构,并能保留CNT的机械和电学特性.

本文将芦丁吸附在多壁碳纳米管(Multiwall

carbon nanotubes, MWNT)上,制备了芦丁碳纳米管修饰的玻碳(Glassy Carbon, GC)电极(Rt-MWNT/GC),应用循环伏安法研究了该修饰电极的电化学行为及其对胍的电催化氧化.

1 实验部分

1.1 仪器和试剂

CHI 660A 电化学工作站(上海辰华);三电极系统:工作电极为Rt-MWNT/GC电极,对电极为铂电极,参比电极为饱和甘汞电极;DL-180型超声仪(浙江象山石浦天电子仪器厂).

芦丁标准品(Sigma, USA);MWNT(直径:10~30 nm,纯度:95%,深圳纳米科技有限公司);磷酸盐缓冲溶液(PBS)由 $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ Na}_2\text{HPO}_4$ 和 $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ NaH}_2\text{PO}_4$ 按一定比例混合配制,其准确pH值由Orion SA-720离子计(美国Orion)测得. 其他试剂均为分析纯.

1.2 Rt-MWNT/GC 修饰电极

GC电极($d = 3 \text{ mm}$)用 Al_2O_3 粉抛光成镜面,依次用丙酮、蒸馏水超声清洗2 min. 取5 mg经酸处理的MWNT,加入5 mL二甲基甲酰胺,超声分散得到黑色悬浊液($1.0 \text{ mg} \cdot \text{mL}^{-1}$). 取 $10 \mu\text{L}$ 该悬浊液滴于GC电极表面,红外烤干,经蒸馏水淋洗后浸于芦丁储备液中30 s,水冲洗后于pH 7.0 PBS中,在-100~600 mV电位范围内,以25 mV

· s⁻¹扫速扫描 3 min 除去弱吸附的芦丁,即可制得 Rt-MWNT/GC 电极.

2 结果与讨论

2.1 Rt-MWNT/GC 电极循环伏安曲线

图 1 是在 pH 7.0 的 0.1 mol · L⁻¹ PBS 中,不同扫速下 Rt-MWNT/GC 电极上的循环伏安曲线.由图可见,当扫速为 25 mV · s⁻¹时,在 262 mV 处出现一对氧化还原峰;在 5 ~ 100 mV · s⁻¹的扫速范围内,峰电位几乎不随扫速变化,而峰电流则随着扫速的增加线性增加,表明该电极反应受表面反应过程控制.根据芦丁分子的结构,可推断该氧化还原峰是芦丁分子结构中 B 环上 3',4' 位邻羟基氧化/还原产生的,乃为两电子、两质子的可逆过程^[12].氧化还原峰电位差 (ΔE_p) 小于 50 mV,表明电极表面发生了较快的电子传递.但当扫速超过 400 mV · s⁻¹时, ΔE_p 增至 100 mV,电子传递受阻.据 Laviron 理论,计算出该电极反应的表现电子转移常数 $k_s = 2.9 \text{ s}^{-1}$,电子转移系数 $\alpha = 0.53$.

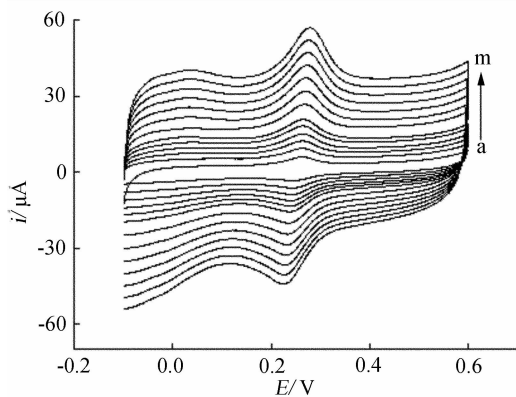


图 1 Rt-MWNT/GC 电极于 pH 7.0 PBS 中不同扫速下的循环伏安曲线

Fig. 1 Cyclic voltammograms of the Rt-MWNT/GC electrode in 0.1 mol · L⁻¹ PBS (pH 7.0) at different scan rates

scan rate (a ~ m)/mV · s⁻¹: 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100

2.2 Rt-MWNT/GC 电极电催化氧化肼

图 2 示明,在 pH 7.0 PBS 中, -100 ~ 1000 mV 范围内,不论溶液中含或不含肼,GC 电极 (a, b) 的循环伏安曲线均无氧化还原峰出现,只存在背景电流;而在 Rt-MWNT/GC 电极上,当溶液中加入肼后,其伏安曲线 (c, d) 的阳极支电流急增,符

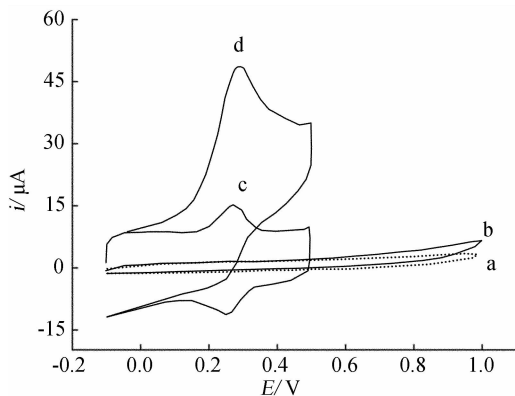


图 2 GC (a, b) 与 Rt-MWNT/GC (c, d) 电极在含 (b, d) 或不含 (a, c) 肼的 PBS (pH 7.0) 中的循环伏安曲线

Fig. 2 Cyclic voltammograms of the GC (a, b) and Rt-MWNT/GC (c, d) electrode in pH 7.0 PBS with absence (a, c) or presence (b, d) of hydrazine

合典型的电催化特征,肼的氧化电位降低至 262 mV.

2.3 肼电催化条件优化

实验表明,在 MWNT/GC 电极浸泡于 $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ 芦丁溶液,从 3 s 增至 60 s 时间范围内,该电极伏安扫描的芦丁氧化还原峰电流不断增大,对肼的催化电流也随之增加,但如浸入时间超过 30 s,则其峰电流即随着扫描次数的增加而逐渐降低,这可能是由于芦丁吸附达到量饱和之后,又会逐渐解吸.本实验在制作 Rt-MWNT/GC 电极时,选取的吸附时间为 30 s.

在 pH 4.2 ~ 9.1 的 PBS 中, Rt-MWNT/GC 电极的循环伏安扫描曲线表明:芦丁氧化还原峰的式量电位 $E^{0'}$ 随着 pH 值增大负移,线性方程: $E^{0'} = 628.6 - 57.8 \text{ pH}$ ($r = 0.994$). pH < 7.0 时,氧化还原峰电流基本不变;而当 pH > 7.0 时,峰电流逐渐减小,此时,芦丁难以发生得失质子的氧化还原(芦丁 $\text{p}K_a \approx 7.1$ ^[17]),或因荷负电的芦丁与荷负电 MWNT 之间的相互排斥作用致使部分芦丁解吸. Rt-MWNT/GC 电极在中性条件下对肼的电催化效果最好,这可能是由于溶液中的肼以中性分子形式存在的缘故.

在含有不同浓度肼的 pH 7.0 PBS 中, Rt-MWNT/GC 电极的循环伏安曲线如图 3 所示.由图可见,当肼浓度从 $4.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ 增至 $1.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$,其电催化氧化电流线性增加,据此可建立肼的定量测定方法.

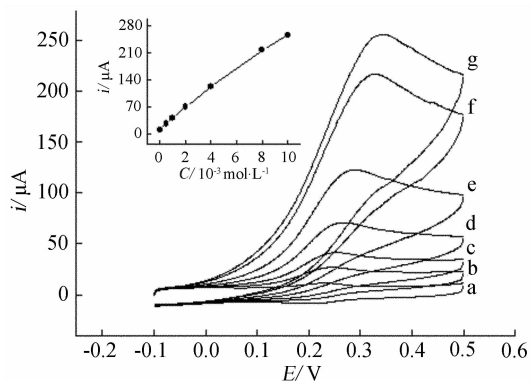


图 3 在含不同浓度肼的 PBS (pH 7.0) 中 Rt-MWNT/GC 电极的循环伏安曲线

Fig. 3 Cyclic voltammograms of the Rt-MWNT/GC electrode in PBS (pH 7.0) containing 4.0×10^{-5} (a), 5.0×10^{-4} (b), 1.0×10^{-3} (c), 2.0×10^{-3} (d), 4.0×10^{-3} (e), 8.0×10^{-3} (f) and 1.0×10^{-2} (g) mol · L⁻¹ of hydrazine

2.4 安培法测定肼

图 4 给出 Rt-MWNT/GC 电极在 260 mV 极化电位下, pH 7.0 PBS 中连续 6 次加入 2.5×10^{-6} mol · L⁻¹ 肼 (A) 和连续 7 次加入 2.5×10^{-5} mol · L⁻¹ 肼 (B) 的安培响应曲线. 由图可见, 随着肼的连续加入, 阳极电流逐渐增加, 且在体系肼浓度为 2.5×10^{-6} mol · L⁻¹ ~ 1.0×10^{-4} mol · L⁻¹ 范围内呈线性关系, 灵敏度 46 mA · L · mol⁻¹, 检出限 5×10^{-7} mol · L⁻¹, 响应时间约 2 s. 如将 Rt-MWNT/GC 电极浸于 pH 7.0 PBS 底液和含 1.0×10^{-3} mol · L⁻¹ 肼的溶液中, 6 次重复测得其氧化电流的相对标准偏差 (RSD) 分别为 3.2% 和 3.7%. 表 1 列出了 Rt-MWNT/GC 电极与其他醌-氢醌类物质修饰电极对肼电催化氧化的性能参数, 表明 Rt-MWNT/GC 电极具有较好电催化性质.

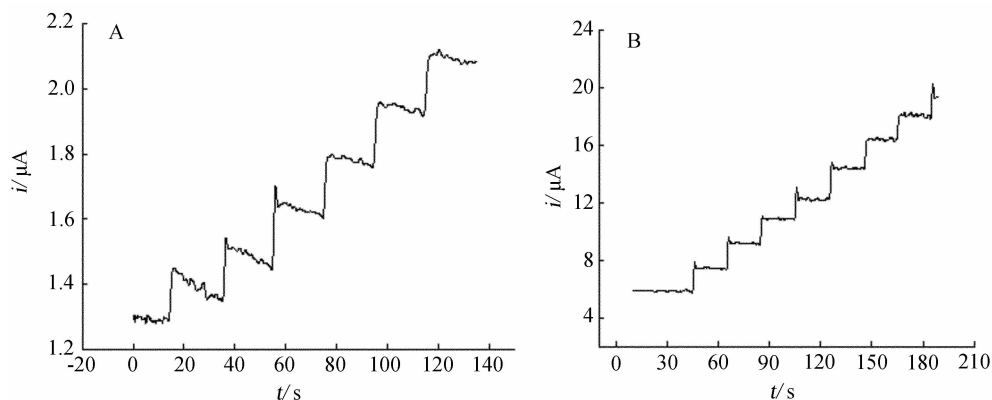


图 4 Rt-MWNT/GC 电极于 PBS 中连续加入 2.5×10^{-6} mol · L⁻¹ (A) 或 2.5×10^{-5} mol · L⁻¹ (B) 肼的安培响应

Fig. 4 Amperometric response of the Rt-MWNT/GC electrodes in PBS by successive addition of 2.5×10^{-6} mol · L⁻¹ (A) or 2.5×10^{-5} mol · L⁻¹ (B) hydrazine

表 1 不同电极电催化氧化肼的参数比较

Tab. 1 Comparison of the electrocatalytic oxidation parameters for hydrazine at various electrodes

Electrode	E_p /mV	Sensitivity/ $\mu A \cdot L \cdot mmol^{-1}$	Linear range/ $\mu mol \cdot L^{-1}$	Detection limit/ $\mu mol \cdot L^{-1}$	Reference
Pyrocatechol violet/GCE	240		5 ~ 40	4.2	[11]
Hematoxylin/MWNT/GCE	203	21	2 ~ 122.8	0.7	[18]
Catechols/MWNT/GCE	180	4	2.5 ~ 5.0	0.2	[19]
Coumestan/CPE	320		1 ~ 40 and 40 ~ 400	1.6	[20]
Rt-MWNT/GCE	262	46	2.5 ~ 100	0.5	This work

3 结 论

Rt-MWNT/GC 电极可在较低氧化电位下用于肼的安培测定,线性范围 $2.5 \times 10^{-6} \sim 1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$,检出限 $5 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$. 有望用于含肼样品的定量测定.

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Electrocatalytic Oxidation of Hydrazine at Rutin Carbon Nanotubes Modified Electrode

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Abstract: The electrochemical behavior and electrocatalytic oxidation of hydrazine on rutin multiwall carbon nanotubes modified glassy carbon electrode were studied by cyclic voltammetry. The experimental results indicated that the electrode exhibits good electrocatalytic activity to hydrazine at a reduced oxidation potential of 262 mV. The amperometric response of the modified electrode showed linear increase after successive addition of hydrazine in the concentration range of $2.5 \times 10^{-6} \sim 1.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ with a detection limit of $5 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$.

Key words: electroanalysis; electrocatalysis; carbon nanotubes; rutin; hydrazine