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聚茜素红-多壁碳纳米管复合膜修饰电极的研制及叶酸含量测定

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摘要: 采用电聚合方法将茜素红(AR)非共价修饰到多壁碳纳米管(MWCNTs)上, 制得了 PAR/MWCNTs/GC 电极, 该电极对叶酸(FA)具有良好的电催化作用. 结果表明, 在最佳实验条件下, 在 -0.63 V 处叶酸还原峰电流与浓度 ($1.25 \times 10^{-6} \sim 4.00 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) 呈现良好线性关系, 相关系数 0.9985. 用标准加入法检测了回收率, 其值达 92.0% ~ 103.0%. 该电极制作简单, 有良好的稳定性.

关键词: 叶酸; 多壁碳纳米管; 茜素红

中图分类号: O646

文献标识码: A

水溶性 B 族维生素叶酸 (N-[对-[(2-氨基-4-羟基-6-蝶啶基)甲氨基]苯甲酰基]-L-谷氨酸, FA, 图 1) 是维持生物体正常生命过程所必需的一类有机物质^[1], 以及人体细胞生长和分裂所必需的物质之一, 主要参与核酸合成和促进氨基酸合成蛋白质^[2]. 因此, 研发一种简捷准确的分析方法对药物和食品中叶酸的检测极为重要. 目前, 叶酸测定有高效液相色谱法^[3]、化学发光法^[4]、荧光分析法^[5]、毛细管电泳法^[6]和电化学方法^[1-2, 7]. 其中, 电化学方法无需借助衍生过程, 灵敏快速.

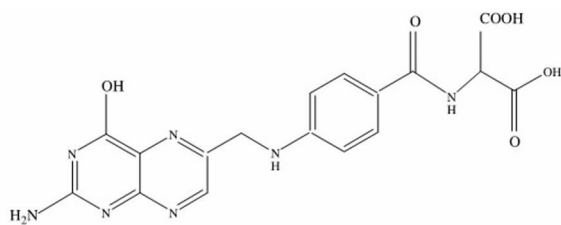


Fig. 1 The structure of folic acid

独特的管状分子结构的多壁碳纳米管有较高的比表面积和表面活性^[8-9]. 茜素红(AR)是一种羟基蒽醌类染料, 含有大的共轭芳香环, 通过 π - π 键作用可在 MWCNTs 侧壁有一定程度的吸附, 并可改变电极表面聚合成膜的电化学性质.

基于此, 本文将茜素红电聚合于多壁碳纳米管(MWCNTs)表面, 制得聚茜素红/MWCNTs 复合膜修饰电极, 与单独的 MWCNTs 修饰电极^[2]相比, 该电极对叶酸(FA)有更佳的电催化性能和更高的稳定性, 为叶酸的检测提供了一种更可行的方法.

1 实验

1.1 仪器与试剂

CHI 650 电化学工作站(美国, CHI), HI 221 型数字酸度计(意大利, HANA).

叶酸(Aladdin)标准储备液: $4.9 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ 叶酸 + $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ NaOH}$ (4 °C 冷藏). MWCNTs^[10]: 浓硝酸回流处理, 长度 μm 级, 直径 10 ~ 50 nm, 德国马尔堡大学化学系材料科学中心. 其他试剂均为分析纯, 溶液由二次蒸馏水配置.

1.2 修饰电极

将玻碳电极(GC)经 1.0、0.3、0.05 $\mu\text{m} \text{ Al}_2\text{O}_3$ 粉抛光, 硝酸(1:1)、无水乙醇和二次蒸馏水分别超声清洗 3 min, 晾干, 备用.

将 1 mg MWCNTs 置于 2 mL DMF 中超声 30 min 可得到黑色悬浮液. 取 6 μL 该悬浮液滴于 GC 基底表面, 红外灯烘干即得 MWCNTs/GC 电极.

将 MWCNTs/GC 电极置于 $0.025 \text{ mol} \cdot \text{L}^{-1} \text{ PBS}$ (pH 6.9) + $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ KNO}_3$ + $1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ 茜素红体系中, -1.4 ~ 1.8 V 电位范围以 $100 \text{ mV} \cdot \text{s}^{-1}$ 循

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环扫描 15 周,经二次蒸馏水淋洗,即得 PAR/MC-NTs/GC 电极.

1.3 测试方法

由 GC 或化学修饰 GC (PAR/MWCNTs/GC、MWCNTs/GC) 电极为工作电极、旋状铂丝为对电极、Ag/AgCl(饱和 KCl) 为参比电极组成三电极系统,在叶酸的磷酸盐缓冲溶液(PBS, pH 6.6) 中,以 $100 \text{ mV} \cdot \text{s}^{-1}$ 在氮气气氛中进行循环伏安扫描.

2 结果与讨论

2.1 茜素红的聚合

图 2 为 MWCNTs/GC 电极茜素红电聚合曲线. 由图 2 可知,在 0.5 V 处有一氧化峰,在 -0.5 V 呈现一对氧化还原峰,随电聚合周期增加,其峰电流逐增,表明茜素红已电聚合于电极表面,且其膜厚度与聚合周期有关.

2.2 修饰电极的电化学性能

PAR/MWCNTs/GC、MWCNTs/GC 电极在 $3.95 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ 叶酸溶液的循环伏安曲线如图 3 所示. 从图 3 中可以看出,在 -0.4 ~ 0.8 V 之间,GC 电极 (a) 叶酸无氧化还原峰;MWCNTs/GC 电极 (b) 叶酸有一对可逆的氧化还原峰 (-0.42 V 和 -0.47 V) 和一不可逆的还原峰 (-0.62 V); 而 PAR/MWCNTs/GC 电极 (c) 有两对可逆的氧化还原峰 (-0.42 V 和 -0.46 V, -0.54 V 和 -0.64 V). 显然 PAR/MWCNTs/GC 电极叶酸的还原峰的稳定性更显著、峰电流激增,即叶酸电催化性能更佳. 这归因于复合膜的多壁碳纳米管增大电极的有效表面,形成的 π 电子密度较高的纳米量级的聚合膜.

2.3 实验条件优化

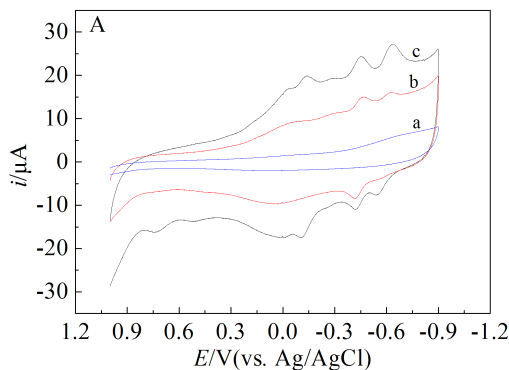


图 3 GC(a)、MWCNTs/GC(b)、PAR/MWCNTs/GC(c, c': $0.1 \text{ mol} \cdot \text{L}^{-1}$ PBS) 在 $3.95 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ FA + $0.1 \text{ mol} \cdot \text{L}^{-1}$ PBS (pH = 6.6) 的循环伏安曲线

Fig. 3 CVs at bare GC (a), MWCNTs/GC (b), and PAR/MWCNTs/GC (c, c': $0.1 \text{ mol} \cdot \text{L}^{-1}$ PBS) electrodes in $3.95 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ FA + $0.1 \text{ mol} \cdot \text{L}^{-1}$ PBS (pH = 6.6)

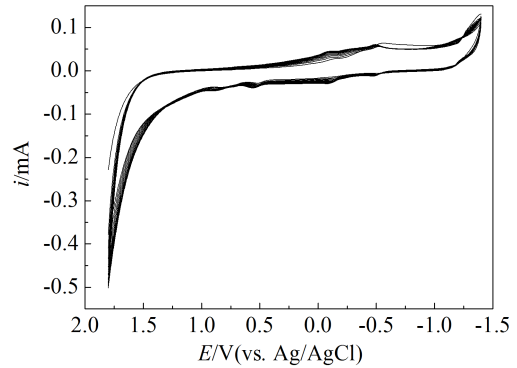


图 2 MWCNTs/GC 电极茜素红的电聚合曲线

Fig. 2 CVs of electropolymerization of alizarin red on MWCNTs/GC electrode

1) MWCNTs 用量

MWCNTs 用量从 $2 \mu\text{L}$ 增至 $12 \mu\text{L}$, 初始叶酸峰电流逐增, $6 \mu\text{L}$ 用量其峰电流达到最大, 随之其峰值又下降, 故选取 $6 \mu\text{L}$ 为最佳用量.

2) 茜素红电聚合周期

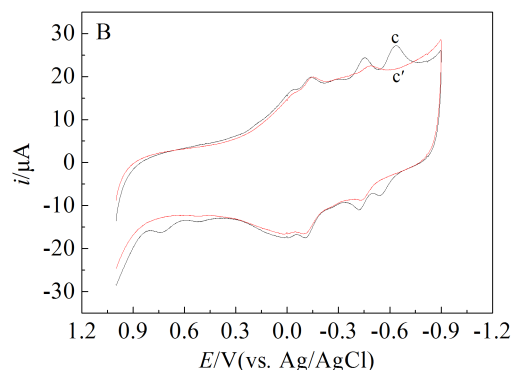
图 4 给出茜素红电聚合周期与叶酸峰电流曲线. 结果表明, 随电聚合周期增加, 其峰电流增大, 电聚合 15 周期电极峰电流最大, 而后其峰电流激增, 故选取电聚合 15 周期为宜.

3) 底液 pH 值

图 5 给出 PAR/MWCNTs/GC 电极在不同 pH 磷酸盐缓冲溶液叶酸还原峰电流-pH 值曲线. pH = 6.6 时, 其峰形好, 峰电流最大, 故选取 pH = 6.6 的 PBS 底液.

2.4 扫描速率

图 6 是 PAR/MWCNTs/GC 电极的叶酸峰电



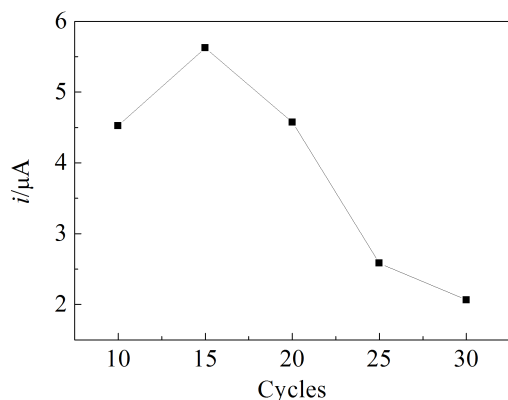


图 4 茜素红电聚合周期与叶酸峰电流曲线
Fig. 4 Peak current of folic acid as a function of electropolymerization cycle of alizarin red

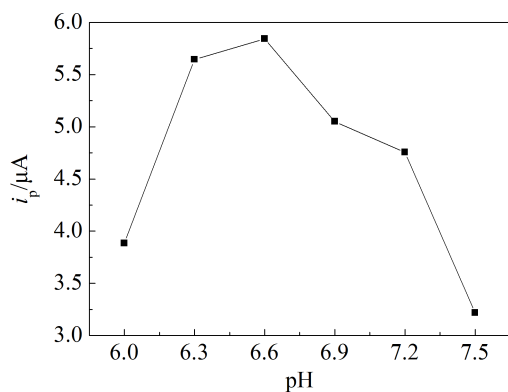


图 5 底液 pH 值-叶酸峰电流曲线
Fig. 5 Peak current of folic acid versus pH of PBS curve

流-扫描速率曲线. 在 $20 \sim 280 \text{ mV} \cdot \text{s}^{-1}$ 扫描速率范围, 扫描速率增大, 叶酸氧化还原峰电流不断增大, 且峰电流与扫描速率呈线性关系, 其线性方程 $i_p (\mu A) = 0.07689 + 0.0322 v (\text{mV} \cdot \text{s}^{-1})$, 该电极过程受吸附控制.

2.5 线性范围和检出限

图 7 为 PAR/MWCNTs/GC 电极的叶酸峰电流与浓度 ($1.25 \times 10^{-6} \sim 4.00 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) 曲线. 可以看出, 线性关系良好. 其线性方程为 $i_p (\mu A) = 0.37047 + 0.09735c (\mu \text{mol} \cdot \text{L}^{-1})$, $R = 0.9985$, 检出限为 $7.20 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$.

2.6 加标回收率

用标准加入法检测叶酸回收率, 如表 1 所示. 结果表明, 该法测定叶酸的回收率为 $92.0\% \sim 103.0\%$, 满足测试要求.

2.7 电极的稳定性和重现性

在含有叶酸的 PBS ($\text{pH} = 6.6$) 中, 以

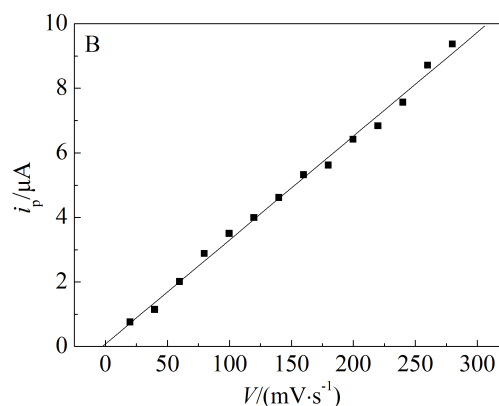
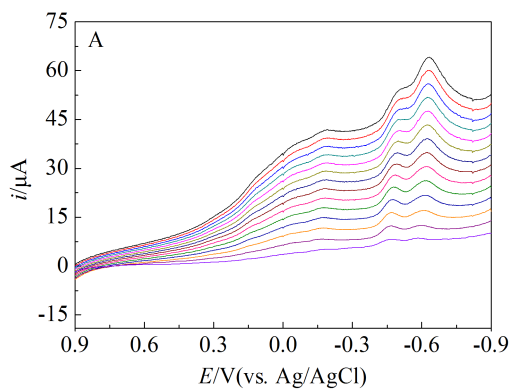


图 6 不同扫速(从内向外: $20 \sim 280 \text{ mV} \cdot \text{s}^{-1}$)下 PAR/MWCNTs/GC 电极的循环伏安曲线(A)和叶酸峰电流-扫描速率曲线(B)

Fig. 6 CVs of PAR/MWCNTs/GC electrode at different rates (A, from inner to outer: $20 \sim 280 \text{ mV} \cdot \text{s}^{-1}$, and the peak current of folic acid (i_p)-scan rate(V) curve(B)

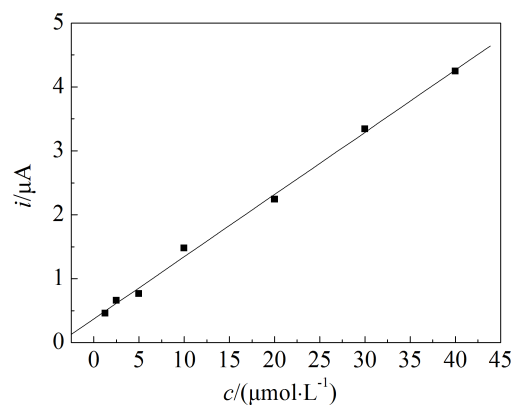


图 7 PAR/MWCNTs/GC 电极的叶酸峰电流与浓度曲线
Fig. 7 The peak current-concentration of folic acid curve obtained with PAR/MWCNTs/GC electrode

PAR/MWCNTs/GC 电极连续循环扫描 20 周期, 其还原电流仅下降 6% 初始值. 同一电极 5 次重复测定, 其还原峰电流值基本不变, RSD 为 2.3%, 表明

表 1 回收率实验结果

Tab. 1 Results of test for recovery ratio

Added/ ($10^{-5} \text{ mol} \cdot \text{L}^{-1}$)	Determined/ ($10^{-5} \text{ mol} \cdot \text{L}^{-1}$)	Recovery ratio/%	Average/%
0.80	0.82	103.0	97.0
1.30	1.20	92.0	
2.50	2.30	92.0	
3.50	3.50	100.0	

该电极具有良好的稳定性和重现性。

3 结论

研制了 PAR/MWCNTs/GC 电极, 在 PBS(pH = 6.6) 溶液中, 叶酸的还原峰电流与浓度 ($1.25 \times 10^{-6} \sim 4.00 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) 呈良好线性关系, 相关系数 0.9985。该方法灵敏、准确, 且电极制作简单、稳定性好, 为叶酸检测提供了一种更可行的方法。

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Determination of Folic Acid by Composite Film Electrode Modified with Poly-Alizarin Red and Multi-walled Carbon Nanotubes

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Abstract: The novel modified electrode was fabricated by electropolymerizing alizarin red onto the surface of multi-walled carbon nanotubes on glassy carbon electrode surface, which exhibited good electrocatalytic activity for folic acid. The experimental results showed that the reduction peak current of folic acid at -0.63 V was linear to its concentration over the range of $1.25 \times 10^{-6} \sim 4.00 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ in the optimized experimental conditions ($R = 0.9985$). Test for recovery was carried out by standard addition method, and the recovery ratios were in the range of 92.0% ~ 103.0%. The modified electrode was prepared simply with excellent stability, which provides a new feasible method for determination of folic acid.

Key words: poly-alizarin red; multi-walled carbon nanotubes; folic acid