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## Enhanced [Ru(bpy)<sub>3</sub>]<sup>2+</sup>-mediated Oxidation of Guanine Prompted by DHP

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# DHP 促进 $[\text{Ru}(\text{bpy})_3]^{2+}$ 介导鸟嘌呤的氧化

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**摘要:** 应用循环伏安法和微分脉冲伏安法研究了  $\text{ITO}$  电极上双十六烷基磷酸盐 (DHP) 和多壁碳纳米管 (MWNTs) 对  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $\text{bpy} = 2, 2$  联吡啶) 介导鸟嘌呤氧化的影响. 结果表明,  $[\text{Ru}(\text{bpy})_3]^{2+}$  能够介导鸟嘌呤氧化. 在  $0.01$  至  $0.15 \text{ mmol} \cdot \text{L}^{-1}$  DHP 浓度范围内,  $[\text{Ru}(\text{bpy})_3]^{2+}$  介导鸟嘌呤氧化峰电流随 DHP 浓度的增大而增大, 阳离子表面活性剂 HTAC 则起抑制作用. 讨论了 DHP 参与  $[\text{Ru}(\text{bpy})_3]^{2+}$  介导鸟嘌呤氧化的可能电极过程机理.

**关键词:** 多吡啶钌 (II) 配合物; 鸟嘌呤; 表面活性剂; 碳纳米管; 氧化

**中图分类号:** O646

**文献标识码:** A

鸟嘌呤在热解石墨电极<sup>[1-2]</sup>、玻碳电极<sup>[3]</sup>、碳糊电极<sup>[4]</sup>、金电极<sup>[5]</sup>和碳纳米管修饰电极<sup>[6-7]</sup>上反应的可逆性差, 其产物往往强吸附在电极表面<sup>[8-10]</sup>使反应速率下降. 多吡啶钌 (II) 配合物常被用作氧化还原媒质, 间接催化或介导鸟嘌呤的氧化<sup>[11]</sup>. Thorp 等<sup>[12-14]</sup>研究了  $[\text{Ru}(\text{bpy})_3]^{2+}$  对 DNA 及寡核苷酸中鸟嘌呤的间接电催化氧化.

碳纳米管 (CNTs) 修饰电极也已被用于鸟嘌呤<sup>[6-7]</sup>和次黄嘌呤<sup>[15]</sup>等生物分子的分析检测. 然而, CNTs 不溶于水 and 有机溶剂, 往往需加入表面活性剂分散 CNTs<sup>[16-17]</sup>. 双十六烷基磷酸 (DHP) 作为具有双疏水链的阴离子表面活性剂, 可以使 CNTs 分散于溶剂中. Rusling 和胡胜水等研究了 CNTs 修饰电极上或溶液中的表面活性剂参与的电极过程<sup>[18-19]</sup>, Thorp 等报导了  $[\text{Ru}(\text{bpy})_3]^{2+}$  对 DNA-CNTs 的间接电催化氧化<sup>[20]</sup>. 本文选择  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $\text{bpy} = 2, 2$  联吡啶) 介导鸟嘌呤氧化的体系, 探讨了  $\text{ITO}$  电极上 DHP 对鸟嘌呤氧化过程的影响.

## 1 实验部分

仪器: CH 160a 电化学工作站 (上海辰华仪器有限公司); PHS-3C 精密 pH 计 (上海雷磁); KQ 2200B

型超声波清洗器 (上海雷磁). 三电极系统: 工作电极为  $\text{ITO}$  (铟锡氧化物, 深圳南玻科技, 薄膜电阻  $20 \text{ cm}^{-2}$ , 经  $0.1 \text{ mmol} \cdot \text{L}^{-1} \text{K}_4[\text{Fe}(\text{CN})_6]$  /  $1.0 \text{ mol} \cdot \text{L}^{-1} \text{KCl}$  体系测定工作电极的有效面积为  $0.37 \text{ cm}^2$ <sup>[21]</sup>); 对电极为钛片; 参比电极为  $\text{Ag-AgCl}$  ( $50 \text{ mmol} \cdot \text{L}^{-1} \text{NaCl}$ , 文中所有电位都是相对于此参比电极). 支持电解质为  $10 \text{ mmol} \cdot \text{L}^{-1} \text{Tris} / 50 \text{ mmol} \cdot \text{L}^{-1} \text{NaCl}$  ( $\text{pH} = 7.2$ ) 缓冲溶液.

药品: 鸟嘌呤 (G, 上海伯奥生物科技有限公司), 含量 98.0%; 三羟甲基氨基甲烷 (Tris, 含量 99.0%); 多壁碳纳米管 (MWNTs, 中国科学院成都有机化学有限公司, 纯度 >95%, 外径 <8 nm, 长度约为 50  $\mu\text{m}$ ); 双十六烷基磷酸 (Fluka 公司), 十六烷基三甲基氯化铵 (HTAC, 天津市福晨化学试剂厂, 含量 98.0%); 其余试剂均为分析纯, 实验用水为二次蒸馏水.

除非特别说明, 微分脉冲伏安法的调制幅值为 50 mV, 阶跃电位 4 mV. 实验温度为  $25 \pm 1$ .

## 2 结果与讨论

### 2.1 DHP 促进 $[\text{Ru}(\text{bpy})_3]^{2+}$ 介导鸟嘌呤的氧化

图 1 示出  $[\text{Ru}(\text{bpy})_3]^{2+}$  在  $\text{ITO}$  电极上的微分

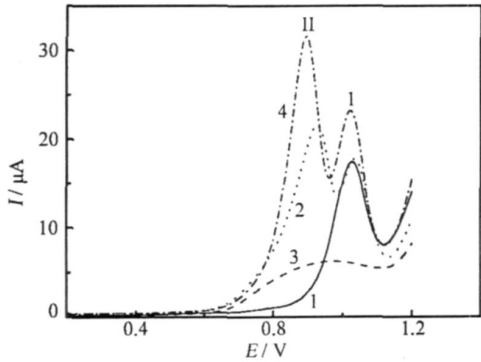


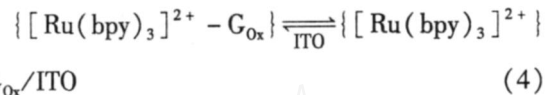
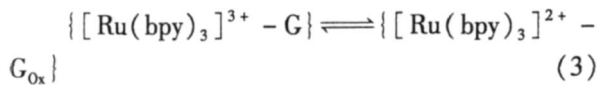
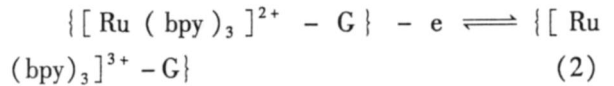
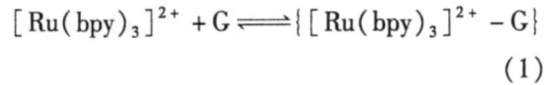
图 1 ITO电极在不同体系中的第 1次微分脉冲伏安曲线

1.  $0.10 \text{ mmol} \cdot \text{L}^{-1} [\text{Ru}(\text{bpy})_3]^{2+}$ , 2.  $0.10 \text{ mmol} \cdot \text{L}^{-1} [\text{Ru}(\text{bpy})_3]^{2+} / 0.10 \text{ mmol} \cdot \text{L}^{-1}$  鸟嘌呤, 3.  $0.10 \text{ mmol} \cdot \text{L}^{-1}$  鸟嘌呤, 4.  $0.10 \text{ mmol} \cdot \text{L}^{-1} [\text{Ru}(\text{bpy})_3]^{2+} / 0.10 \text{ mmol} \cdot \text{L}^{-1}$  鸟嘌呤  $/ 0.15 \text{ mmol} \cdot \text{L}^{-1}$  DHP

Fig 1 The 1<sup>st</sup> differential pulse voltammograms of  $0.10 \text{ mmol} \cdot \text{L}^{-1} [\text{Ru}(\text{bpy})_3]^{2+}$  on the ITO electrode in the absence (solid line 1) and presence of  $0.10 \text{ mmol} \cdot \text{L}^{-1}$  guanine (dot line 2) or  $0.10 \text{ mmol} \cdot \text{L}^{-1}$  guanine/ $0.15 \text{ mmol} \cdot \text{L}^{-1}$  DHP (dot-dash line 4) in contrast to  $0.10 \text{ mmol} \cdot \text{L}^{-1}$  guanine (dash line 3)

脉冲伏安 (曲线 1)。如图,在约  $1.024 \text{ V}$  电位处明显出现一个对应于  $[\text{Ru}(\text{bpy})_3]^{2+} \rightarrow [\text{Ru}(\text{bpy})_3]^{3+}$  的氧化峰 I 而当溶液加入  $0.10 \text{ mmol} \cdot \text{L}^{-1}$  鸟嘌呤时 (曲线 2),则在  $0.924 \text{ V}$  电位处还出现另一强氧化峰 II 对比单一鸟嘌呤在 ITO 电极上的氧化 (曲线 3),前者峰电流 (曲线 2 峰 II) 明显大于后者 (鸟嘌呤的直接氧化),而峰 I 电流则明显减小,这表明峰 I 可能为  $[\text{Ru}(\text{bpy})_3]^{2+}$  与鸟嘌呤作

用产生的氧化峰,或言之是  $[\text{Ru}(\text{bpy})_3]^{2+}$  介导鸟嘌呤氧化共同作用的结果. 反应初步设想如下: (G 和  $G_{ox}$  分别代表鸟嘌呤及其氧化产物):



然而,当向  $[\text{Ru}(\text{bpy})_3]^{2+}$  鸟嘌呤体系再加入  $0.15 \text{ mmol} \cdot \text{L}^{-1}$  DHP 时 (曲线 4),氧化峰 II 电流明显增大,且峰电位负移  $27 \text{ mV}$ ,由此可见适宜浓度的 DHP 也能明显地增强  $[\text{Ru}(\text{bpy})_3]^{2+}$  介导鸟嘌呤的氧化。

图 2a 示出,在  $0.01$  至  $0.15 \text{ mmol} \cdot \text{L}^{-1}$  DHP 浓度区间内,峰 II 电流随着 DHP 浓度的增大而增大,峰电位负移,表明 DHP 直接参与了  $[\text{Ru}(\text{bpy})_3]^{2+}$  介导鸟嘌呤的氧化. 相对地,当使用阳离子表面活性剂十六烷基三甲基氯化铵 (HTAC) 代替 DHP 时 (见图 2b),在  $0.01$  至  $0.15 \text{ mmol} \cdot \text{L}^{-1}$  HTAC 浓度区间内,氧化峰 II 峰电流随着 HTAC 浓度的增大而减小,电位正移,表明 HTAC 减弱了  $[\text{Ru}(\text{bpy})_3]^{2+}$  介导鸟嘌呤氧化. HTAC 浓度越大,抑制作用越强. 尽管 HTAC 含有疏水的十六烷基和甲基,易于与鸟嘌呤接近,但可能由于静电排斥而难于与  $[\text{Ru}(\text{bpy})_3]^{3+}$  结合,不能起到连

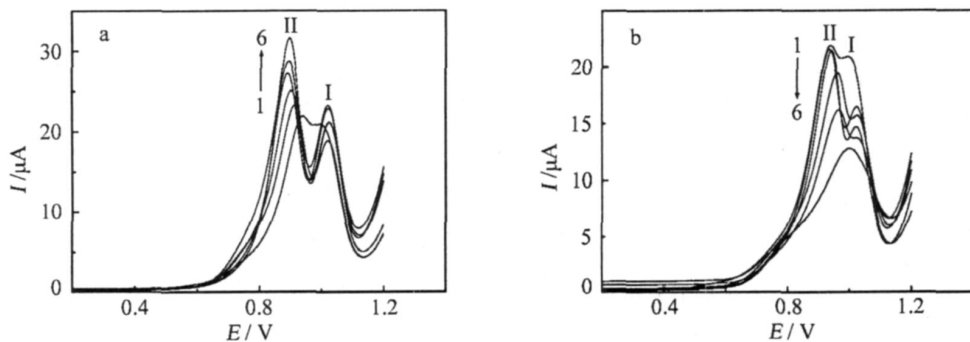


图 2 ITO 电极在含有不同浓度的 DHP (a) 和 HTAC (b) 的  $0.10 \text{ mmol} \cdot \text{L}^{-1} [\text{Ru}(\text{bpy})_3]^{2+} / 0.10 \text{ mmol} \cdot \text{L}^{-1}$  鸟嘌呤体系中的第 1 次微分脉冲伏安曲线

DHP (a) 或 HTAC (b) 浓度  $/ \text{mmol} \cdot \text{L}^{-1}$  (1~6):  $0, 0.01, 0.04, 0.08, 0.10, 0.15$

Fig 2 The 1<sup>st</sup> differential pulse voltammograms of  $0.10 \text{ mmol} \cdot \text{L}^{-1} [\text{Ru}(\text{bpy})_3]^{2+} / 0.10 \text{ mmol} \cdot \text{L}^{-1}$  guanine at the ITO electrode with presence of DHP (a) or HTAC (b)  $/ \text{mmol} \cdot \text{L}^{-1}$  (1~6):  $0, 0.01, 0.04, 0.08, 0.10, 0.15$

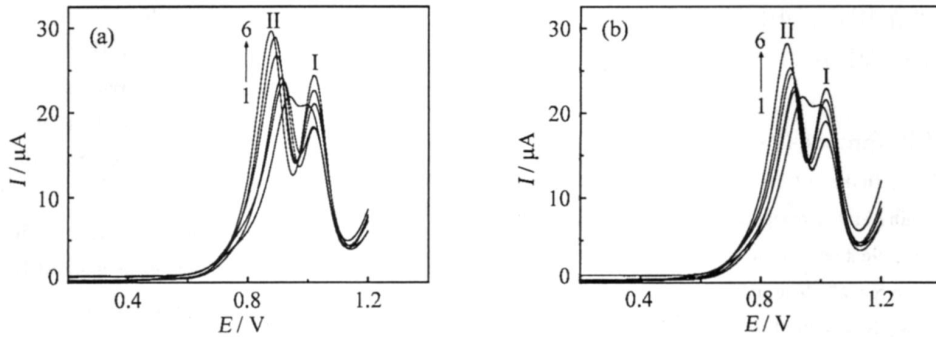
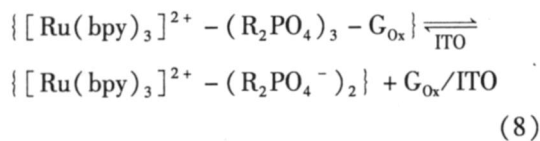
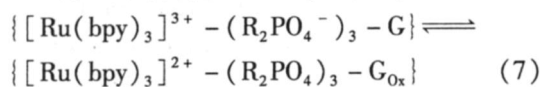
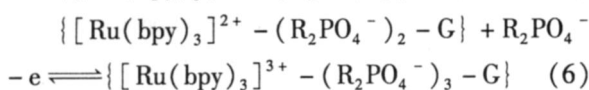
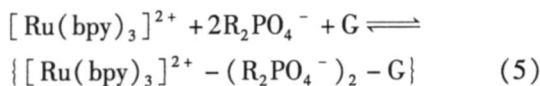


图 3 含有 5 mg · L<sup>-1</sup> (a)和 10 mg · L<sup>-1</sup> MWNTs(b)的 0.10 mmol · L<sup>-1</sup> [Ru(bpy)<sub>3</sub>]<sup>2+</sup> / 0.10 mmol · L<sup>-1</sup> 鸟嘌呤体系于不同 DHP浓度变化的第一次微分脉冲伏安曲线

DHP浓度 /mmol · L<sup>-1</sup> (1~6): 0, 0.02, 0.04, 0.08, 0.10, 0.15

Fig 3 The 1<sup>st</sup> differential pulse voltammograms of 0.1 mmol · L<sup>-1</sup> [Ru(bpy)<sub>3</sub>]<sup>2+</sup> / 0.10 mmol · L<sup>-1</sup> guanine system containing 5 mg · L<sup>-1</sup> (a), and 10 mg · L<sup>-1</sup> (b) MWNTs as a function of DHP concentrations /mmol · L<sup>-1</sup> (1~6): 0, 0.02, 0.04, 0.08, 0.10, 0.15

接媒质和反应底物间的传递作用. 当然, HTAC在 ITO 电极上的吸附也影响 [Ru(bpy)<sub>3</sub>]<sup>2+</sup> 在电极上的反应, 使氧化峰 II 电位正移. 此处设想, DHP 阴离子表面活性剂促进 [Ru(bpy)<sub>3</sub>]<sup>2+</sup> 介导鸟嘌呤氧化. 反应的可能途径如下 (R<sub>2</sub>PO<sub>4</sub><sup>-</sup> 代表 DHP 中阴离子部分):



### 2.2 DHP-MWNTs对 [Ru(bpy)<sub>3</sub>]<sup>2+</sup>介导鸟嘌呤氧化的影响

图 3 给出了在含有 MWNTs 的 [Ru(bpy)<sub>3</sub>]<sup>2+</sup> / 鸟嘌呤体系中不同 DHP 浓度下呈现的微分脉冲伏安曲线. 从图可见, 随 DHP 浓度的变化形状与不存在 MWNTs 的大体相似 (参见图 2). 图 4 表明, 在 0.01 ~ 0.15 mmol · L<sup>-1</sup> DHP 浓度范围内, 不管体系有无 MWNTs 存在, 峰 II 电流均随 DHP 浓度的增大而增大, 且其峰电位同时负移, 这可能是 MWNTs 的加入并没有改变 DHP 促进 [Ru(bpy)<sub>3</sub>]<sup>2+</sup> 介导鸟嘌呤氧化的主要反应途径. 尽管

DHP-MWNTs 也能促进 [Ru(bpy)<sub>3</sub>]<sup>2+</sup> 介导鸟嘌呤的氧化, 但其作用强度不如单纯 DHP, 表明 MWNTs 对 DHP 促进 [Ru(bpy)<sub>3</sub>]<sup>2+</sup> 介导鸟嘌呤的氧化并不能起增强作用.

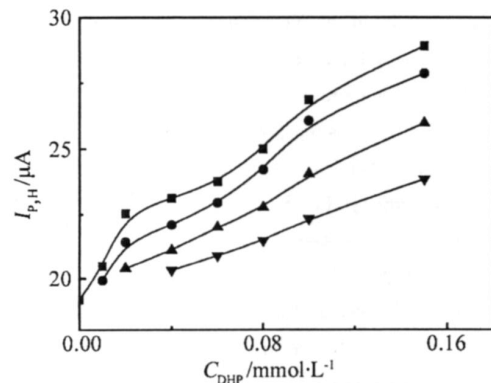


图 4 含有 MWNTs 的 0.10 mmol · L<sup>-1</sup> [Ru(bpy)<sub>3</sub>]<sup>2+</sup> / 0.10 mmol · L<sup>-1</sup> 鸟嘌呤体系氧化峰 (II) 电流随 DHP 浓度变化曲线

MWNTs 浓度 /mg · L<sup>-1</sup>: ( ) 0, ( ) 5, ( ) 10, ( ) 20

Fig 4 Plots of the peak II currents for 0.10 mmol · L<sup>-1</sup> [Ru(bpy)<sub>3</sub>]<sup>2+</sup> / 0.10 mmol · L<sup>-1</sup> guanine system as a function of DHP concentrations

MWNTs contents /mg · L<sup>-1</sup>: ( ) 0, ( ) 5, ( ) 10, and ( ) 20

### 3 结 论

[Ru(bpy)<sub>3</sub>]<sup>2+</sup> 能介导鸟嘌呤的氧化. 在合适

的 DHP 浓度范围内, DHP 能明显地促进了  $[\text{Ru}(\text{bpy})_3]^{2+}$  的介导作用.

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## Enhanced $[\text{Ru}(\text{bpy})_3]^{2+}$ - mediated Oxidation of Guanine Prompted by DHP

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**Abstract:** The effects of dihexadecyl phosphate (DHP) and multi-walled carbon nanotubes (MWNTs) on the oxidation of guanine mediated by  $[\text{Ru}(\text{bpy})_3]^{2+}$  on the PtO electrode have been investigated by cyclic voltammetry and differential pulse voltammetry. The results showed that  $[\text{Ru}(\text{bpy})_3]^{2+}$  can mediate the oxidation. In the range from 0.01 to 0.15  $\text{mmol} \cdot \text{L}^{-1}$ , peak currents for guanine oxidation mediated by  $[\text{Ru}(\text{bpy})_3]^{2+}$  increased with the rise of DHP concentrations. On the contrary, cationic surfactant HTAC has the ability to weaken the mediated oxidation of guanine. In addition, the oxidative mechanism of guanine mediated by  $[\text{Ru}(\text{bpy})_3]^{2+}$  with the participation of DHP is discussed.

**Key words:** polypyridyl ruthenium (II) complex; guanine; surfactant; carbon nanotubes; oxidation