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博 士 学 位 论 文

基于纳米修饰电极及三原色原理的
固相电致化学发光研究

Solid-state Electrochemiluminescence Study Based on
Nanomaterial Modified Electrodes and Tri-color System

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摘要

自从联吡啶钌电致化学发光的现象 (ECL) 被发现以来, ECL 的分析方法就引起了人们极大的兴趣。由于该方法具有检测背景低、灵敏度高、线性范围宽等特点, 被广泛应用于常规分析检测、生化检测和环境监测的研究中。本论文在固相 ECL 研究的基础上, 结合三原色原理, 针对 ECL 研究中存在的问题提出了解决的方法。

本论文共五章。

第一章, 文献综述, 主要介绍 ECL 的基本原理及发展概况。

第二章, 建立在电极表面修饰金纳米颗粒的方法, 并研究了修饰过程中金纳米颗粒的生长机理。实验中, 首先在玻碳电极上修饰了规整的金纳米颗粒, 然后采用自组装技术, 利用羧基和氨基的缩合反应, 将发光试剂二(2, 2' - 二联吡啶)(5-氨基-1, 10-邻菲咯啉)合钌固定在电极表面。并将该修饰电极应用于阴极化过程的 ECL 研究。该修饰电极的制成解决了基于自组装技术的固相 ECL 研究中线性、稳定性和需要贵金属电极等问题。该修饰电极应用于阴极化过程的 ECL 研究的实验结果表明, 电极具有良好的稳定性和线性范围区间, 对过硫酸根离子的检测限可达 10^{-5} M。

第三章, 以聚苯乙烯球为载体, 建立了简单的一锅反应法, 将 9, 10 - 二苯基蒽掺杂于聚苯乙烯球中 (DPA@PS)。使用 NaFion 离子交换膜将 DPA@PS 修饰于电极表面, 并应用于固相 ECL 研究中。虽然掺杂在聚苯乙烯球中的 DPA 仍会受到氧猝灭的影响, 但该修饰电极仍具有良好的发光性能。实验证明, 聚苯乙烯球可做为一个载体平台, 将有机 ECL 染料应用于水相 ECL 研究中, 从而拓宽发光试剂的选择和应用范围。

第四章, 基于固相 ECL 及三原色原理, 构建了 ECL 比色传感器。通过与稳定的绿色背景光复合, 该传感器将传统的联吡啶钌红色 ECL 强度信息转化为更容易记忆和辨认的颜色信息。由于 ECL 强度与分析物的浓度相关, 实验中将该传感器应用于三丙基胺、赖氨酸以及多巴胺的检测, 获得了较好的效果。由于该传感器的修饰电极可以产生很强的 ECL, 因此只需使用商业化的电荷耦合器件

(CCD) 就可以检测发光信息, 从而简化传统的 ECL 检测系统。实验证明利用基于双色系统的 ECL 比色传感器可应用于快速半定量的检测中。

第五章, 将三原色原理的光学编码概念引入到 ECL 的研究中。通过合成异硫氰根荧光素与联吡啶钌共掺杂的纳米二氧化硅编码球, 并固定编码球中联吡啶钌的浓度, 从而使不同编码球在相同的条件下产生相同强度的红色 ECL。由于不同的编码球中异硫氰根荧光素的浓度不一, 因此在外界光激发下, 不同的编码球会产生不同的绿色荧光强度。由于固定强度的红光和不同强度的绿光复合后会产生不同的颜色, 实现对 ECL 的编码。本章的研究为解决 ECL 分析通量低的问题, 提供了一种较好的解决方案。

关键词: 电致化学发光 固相电致化学发光 三原色

Abstract

Since the first report of Tris(2,2'-bipyridyl) ruthenium(II) ($\text{Ru}(\text{bpy})_3^{2+}$) electrogenerated chemiluminescence (ECL), $\text{Ru}(\text{bpy})_3^{2+}$ ECL has been received great attention and applied in many fields including daily analysis, bioassay and environmental monitoring, due to its low back ground noise, high sensitivity and wide linear range. In this dissertation, the research works are focus on the resolution to part of the problems related to the present ECL approaches, based on the principle of solid-state ECL and red-green-blue (RGB) tri-color system.

This dissertation includes five chapters.

In Chapter I, the mechanism and developments of ECL have been briefly reviewed.

In Chapter II, a direct modification method for gold nanoparticles (AuNPs) onto an electrode surface was developed. The growth mechanism of AuNPs was discussed. Based on the developed method, an AuNPs modified glassy carbon electrode (AuNPs@GCE) was prepared, and then modified with $\text{Ru}(\text{bpy})_2(\text{phen-NH}_2)^{2+}$ (Ru-AuNPs@GCE) using self-assembly method. Ru-AuNPs@GCE was applied in cathodic ECL. The results indicated that Ru-AuNPs@GCE presented good ECL performance. The detection limit with 10^{-5} M for $\text{S}_2\text{O}_8^{2-}$ was obtained.

In Chapter III, polystyrene beads (PS) were selected as the carrier of 9,10-biphenylanthrance (DPA). DPA was successfully doped in PS beads (DPA@PS) by a one-pot synthesis method. DPA@PS was then modified on a glassy carbon electrode (DPA@PS@GCE) with NaFion ethanol solution. The modified GCE was used as a working electrode in solid-state-ECL study. Although the ECL of DPA was still affected by the oxygen quenching, the ECL result showed that DPA@PS@GCE had good performance, and proved that PS might be a good platform to apply organic ECL reagents in aqueous ECL systems.

In Chapter IV, a colorimetric ECL sensor was fabricated based on the principle of

solid-state ECL and RGB tri-color system. In the sensing system, the change of ECL intensity was varied into color change, as a result, it is much easier for a person to recognize and remember. Since the ECL intensity was related to the analyte concentration, the sensor was applied to the analysis of tripropylamine, proline and dopamine. Because the sensor emit strong ECL enough to be captured by a commercial CCD camera, the detection system of the sensor became very simple compared to the traditional approach. As a result, the sensor might be applied in fast and semi-quantitative analysis.

In Chapter V, the concept of optical coding based on RGB tri-color system was introduced into ECL study. The ECL coding beads were synthesized by doping $\text{Ru}(\text{bpy})_3^{2+}$ and fluorescein isothiocyanate (FITC) in silica nanoparticles (Ru-FITC@SiNPs). The concentration of $\text{Ru}(\text{bpy})_3^{2+}$ in the beads was kept at constant, but the concentration of FITC was varied. Consequently, the red ECL intensity of different beads kept the same under the same experimental conditions, however, the green fluorescence (FL) intensity of FITC was different. It indicated that the ratio of $I_{\text{ECL}}/I_{\text{FL}}$ was different for different kinds of beads. As a result, the bead color observed would be different and related to FITC concentration. It means that the ECL was successfully coded. This study provided a way to resolve the problem that had been mentioned by Mark M. Richter.

Key words: Electrogenerated Chemiluminescence; Solid-state Electrogenerated Chemiluminescence; Tri-color.

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