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# New capillary electrophoresis–electrochemiluminescence detection system equipped with an electrically heated $Ru(bpy)_3^{2+}$/ multi-wall-carbon-nanotube paste electrode

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## Abstract

A new capillary electrophoresis–electrochemiluminescence (ECL) detection system equipped with an electrically heated $Ru(bpy)_3^{2+}$/multi-wall-carbon-nanotube paste electrode ($Ru(bpy)_3^{2+}$/MWNTPE) was developed. $Ru(bpy)_3^{2+}$ was immobilized in the electrode by directly mixing with the multi-wallcarbon-nanotube paste (MWNTP). This modified electrode could be electrically heated and temperature of the electrode (Te) could be accurately controlled. Tri-*n*-propylamine (TPrA) was used as coreactant to investigate CE–ECL signals under different conditions. Compared with the conventional electrode at room temperature, the heated electrode has been shown to provide some advantages, such as higher sensitivity, lower RSD, and decreasing width of the peak. Furthermore, wider range of capillary-to-electrode distance and larger-area electrode are a benefit to CE–ECL. In addition, this system has been applied to separation and detection of acephate and dimethoate. The results indicated that the present CE–ECL system coupled with heated modified-electrode could provide high sensitivity, wide linear range, satisfying linear relationship and excellent reproducibility.

*Keywords:* Heated electrode; Immobilization; Electrochemiluminescence; Capillary electrophoresis; $Ru(bpy)_3^{2+}$

## 1. Introduction

Electrochemiluminescence (ECL), the chemiluminescence process produced directly or indirectly as a result of electrochemical reactions [1], has been a useful detection technique and applied to various fields, such as flow injection analysis [2], HPLC [3,4] and capillary electrophoresis (CE) [5–7], due to its inherent high detection sensitivity, low background noise and simple optical setup. Considering the high separating efficiency of CE and high detection sensitivity of ECL, the combination of CE with ECL would be a sensitive and efficient analytical technique. Among many ECL systems, luminol and $Ru(bpy)_3^{2+}$ ECL system were the most valuable in fundamental studies and commercial applications [8]. The first report of CE–ECL was a postcolumn luminol-based ECL detector for CE [9], however, the most recent CE–ECL systems were based on $Ru(bpy)_3^{2+}$ ECL due to the stability of $Ru(bpy)_3^{2+}$.

There are some modes for addition of $Ru(bpy)_3^{2+}$ in CE–ECL system, such as precolumn and postcolumn mode. With the postcolumn mode, the $Ru(bpy)_3^{2+}$ is directly added into the ECL detection cell [6,10], or is continuously delivered by pressure to the interface of capillary and electrode in the ECL cell [5,11,12]. The drawback associated with the first approach is the dilution of the solution by CE effluent, while the second approach needs complicated equipment. With the precolumn mode, $Ru(bpy)_3^{2+}$ is added to the separation buffer solution and converted to $Ru(bpy)_3^{3+}$ at the end of separation capillary [13–15]. In this way, the addition of $Ru(bpy)_3^{2+}$ into the separation buffer solution resulted in the variation of electrosmotic mobility. In addition, the $Ru(bpy)_3^{2+}$ would be adsorbed onto the silica wall of the capillary, which needed several hours to clean up the wall of capillary.

Since $Ru(bpy)_3^{2+}$ can be electrochemically regenerated, a very promising approach is the immobilization of $Ru(bpy)_3^{2+}$

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in the electrode to form solid-state ECL detector. Compared with the solution-phase $Ru(bpy)_3{}^{2+}$-ECL system, the immobilization of $Ru(bpy)_3{}^{2+}$ on a solid electrode surface shows several advantages, such as saving the expensive reagent, obtaining the high-reproducibility, simplifying the regenerable ECL-base sensor. In previous reports, $Ru(bpy)_3{}^{2+}$ was usually immobilized on various working electrodes, such as Pt disk electrode [16], glassy carbon electrode [17], and indium tin oxide (ITO) electrode [6,18], etc. These conventional modified electrodes should not be polished to avoid destroying the modified film. In the present paper, a $Ru(bpy)_3{}^{2+}$/multi-wall-carbon-nanotube paste electrode ($Ru(bpy)_3{}^{2+}$/MWNTPE) was developed. The $Ru(bpy)_3{}^{2+}$ was embedded into the multi-wall-carbon-nanotube paste (MWNTP) by simply mixing $Ru(bpy)_3{}^{2+}$ with the MWNTP. Compared with the conventional modified electrodes, the surface of $Ru(bpy)_3{}^{2+}$/MWNTPE could be easily renewed by polishing.

Our previous researches showed that the ECL intensity was dependent on the temperature, because temperature could affect the electrochemical reaction rate, diffusion and convection [19,20]. However, no attention has been paid to ECL coupled with CE at elevated temperature of the electrode. Different techniques of heating can be used to elevate the temperature of electrode, such as laser beam [21] or focused microwave radiation [22]. Whereas, the required complex experimental setups, and the temperature of the bulk solution would be elevated by these conventional heating techniques. Recently, the heated electrode has been introduced and developed, which the electrode body itself could be subjected to direct electrical heating. In particular, this technique can increase the temperatures in a thin hot solution layer near to the surface of electrode, but keep the bulk solution at room temperature. Gründler and co-workers [23–27] have designed a series of hot electrodes and applied them in many electrochemical applications. Baranski [28] also introduced a kind of hot-disk electrode, and pointed out that the heat-generating waveform does not electrically interfere with normal electroanalytical measurements. Their work indicates that there are several advantages of heated electrodes for the electroanalytical work, such as simple equipment, enhancing the sensitivity and minimizing the fouling effects. As electrochemical reaction is the key course for ECL, the application of the heated electrode in ECL detection offers many advantages. Chen and co-workers [20] first introduced an ECL detection system equipped with an electrically controlled heating cylindrical microelectrode and gained the lower detection limit and the better reproducibility for ECL of $Ru(bpy)_3{}^{2+}$-oxalate.

In the present paper, for the first time, we applied an novel electrically heated $Ru(bpy)_3{}^{2+}$/MWNTPE in CE with end-column $Ru(bpy)_3{}^{2+}$-ECL system. The $Ru(bpy)_3{}^{2+}$ was embedded in the MWNTP, and the analytes would react with the electrochemically generated $Ru(bpy)_3{}^{3+}$ and emit light when they were exiting out of capillary. The $Ru(bpy)_3{}^{2+}$/MWNTPE could be renewed easily by polishing the surface of electrode, and the temperature of electrode (Te) could be elevated by electrical heating, while the temperature of bulk solution remain unchanged. TPrA was used as coreactant to investigate the effects of electrode temperature on the behaviors of the CE–ECL system equipped with an electrically heated $Ru(bpy)_3{}^{2+}$/MWNTPE. In addition, the separation and determination of acephate and dimethoate were performed to evaluate the feasibility and reliability of this system.

## 2. Experimental

### 2.1. Reagents

$Ru(bpy)_3Cl_2 \cdot 6H_2O$ was obtained from Sigma (St. Louis, MO, USA) and used as received. TPrA, graphite powder and mineral oil were purchased from Aldrich (Milwaukee, WI, USA). Other reagents and chemicals were all commercially available and of analytical reagent grade. The ferricyanide/ferrocyanide solution ($5 \times 10^{-3}$ mol/L) was prepared in 0.05 mol/L KCl. The concentration of stock solution of TPrA, acephate and dimethoate were $1.0 \times 10^{-3}$ mol/L, and the stock solution was stored in amber bottle at 4 °C in the refrigerator. The working standard solutions were prepared daily by diluting with buffer just before use. All other chemicals were of analytical regent grade. Before use, all samples and buffer solutions were filtered through 0.22 μm cellulose acetate filters (Xinya Purification Material Factory, Shanghai, China), and sonicated for 3 min to degas. All the water used was purified in a Milli-Q water purification system (Millipore, Milford, MA, USA).

### 2.2. Apparatus

A laboratory-built CE–ECL system equipped with an electrically heated $Ru(bpy)_3{}^{2+}$/MWNTPE was used throughout the study. The overall setup includes three sub-units shown in Fig. 1: a CE separation system, an ECL detection unit and a heating device.

CE separations in an open tubular fused-silica capillary (25 μm I.D., 375 μm O.D. and 40 cm length, Yongnian Optical Conductive Fiber Factory, Hebei, China) was driven by a high-voltage power supply (Nucleus Institute, Shanghai, China), which was applied at the injection end with the detection cell held at ground potential through the separation capillary guide. The 3 mm-length polyimide layer coating on the outlet of capillary was removed for avoiding photon absorption.

An ECL cell (20 mm × 20 mm × 20 mm) with three-electrode system was placed directly at the top of a photomultiplier tube (PMT) and was fixed in a dark detection chamber. The $Ru(bpy)_3{}^{2+}$/MWNTPE was used as the working electrode, and placed in parallel. The working electrode could be electrical heated and the temperature of surface on electrodes could be controlled accurately. The counter electrode was made of a platinum wire (99.99%). The reference electrode was Ag/AgCl in saturated KCl. Different from the CE–electrochemical detection system, of which the oxidation current is measured, in this CE–ECL system the corresponding ECL intensity is not affected by the separation electric field [29,30]. Hence, a wall-jet configuration was adopted and the end of the capillary was placed directly in the ECL cell without decoupler. The capillary and the working electrode were aligned, and the distance of capillary-to-electrode was