Quenching of the Electrochemiluminescence of Tris(2,2'-bipyridine)-ruthenium(II) by Sodium Diphenylamine-4-sulfonate

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Efficient quenching electrochemiluminescence (ECL) of the tris(2,2'-bipyridine)ruthenium(II)/tripropylamine (Ru(bpy)₃²⁺/TPrA) system by a novel quencher, sodium diphenylamine-4-sulfonate (SDS), has been investigated. The quenching behaviors can be observed with a 100-fold excess of SDS over Ru(bpy)₃²⁺. The mechanism of quenching is believed to involve energy transfer from the excited-state Ru(bpy)₃^{2+*} to the dimer of SDS, which was formed after the electrochemical oxidation of SDS at the electrode surface. Photoluminescence experiments coupled with bulk electrolysis support formation of the SDS dimer upon electrochemical oxidation.

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Introduction

The electrochemiluminescence (ECL) of tris(2,2'-bipyridyl)-ruthenium(II) (Ru(bpy)₃²⁺) as well as principles and applications have been well documented in the literature.¹⁻³ It has been demonstrated that a power detection method provides high sensitivity with low background *via* the generation of an optical signal on an electrode surface. In comparison with other luminescence detectors, ECL detection offers versatility, a simplified optical setup, and good temporal and spatial control;³ moreover, because the ECL reaction only occurs close to the surface of an electrode, the sample requirement is quite small.

Quenching ECL of the tris(2,2'-bipyridine)ruthenium(II)/tripropylamine (TPrA) system has been studied quite extensively in terms of the mechanism and applications.⁴⁻¹³ McCall *et al.*^{10,11} reported on the inhibition of Ru(bpy)₃²⁺/TPrA ECL by phenol, substituted phenols, hydroquinones, catechols, and benzoquinones, and suggested a quenching mechanism involving benzoquinone derivatives formed at the electrode surface that quenches ECL *via* energy transfer. Li *et al.*^{12,13} observed the ECL of Ru(bpy)₃²⁺/TPrA inhibited by adrenaline, gallic acid, phenols, and anilines, and made a quantitative detection of adrenaline and gallic acid based on this inhibition. Zheng *et al.*¹⁴ reported a highly efficient quenching of coreactant by phenolic compounds *via* interception of the ECL intermediate radicals by the quencher. In a recent report, Cao *et al.*¹⁵ observed the quenching behavior of ferrocene, and proposed a potential application to quantitative DNA detection. The study of quenched ECL of Ru(bpy)₃²⁺ is of great interest to further understand the ECL mechanism and to increase the analytical applications of the ECL method.

Sodium diphenylamine-4-sulfonate (SDS) was first studied as a chemical indicator by Sarver *et al.*¹⁶ in 1931. SDS can complex with many metal ions to form various color compounds. Thus, it is widely used in chemical analysis as a sensitive indicator to

determine the concentration of many metal ions, especially in iron analysis. In the current work, we studied the quenching behavior of SDS to the ECL of the Ru(bpy)₃²⁺/TPrA system with an attempt to expand on this earlier work. To develop analytically important sensors, we were interested in testing other SDS derivatives for both ECL activity and their effect on the ECL excited state to propose a potential method that can detect these species for environmental monitoring.

Experimental

Reagents and chemicals

Tris(2,2'-bipyridyl)ruthenium(II) chloride and tripropylamine (TPrA) were purchased from Alfa Aesar Chemical Reagent Co., Ltd. (Tianjin) and used as received. Sodium diphenylamine-4-sulfonate was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai) and used as received. Other chemicals were of analytical reagent grade. All solutions were prepared with water treated with a Ya Rong triple-distilled water system (Shanghai). The ECL solution, containing 0.15 M phosphate buffer and 0.05 M TPrA, was adjusted with concentrated NaOH or phosphoric acid to pH 7.5 before use. Nitrogen (99.999%) was used for air-free experiments, and a constant flow of nitrogen was maintained over the solutions during the measurements. In the present work, all the measurements were nitrogen-saturated.

Electrochemical and ECL measurement

Cyclic voltammetry (CV) was performed with a Model CHI660C electrochemical analyzer (Chenhua Inc., Shanghai). A 3.0-mm diameter glassy carbon electrode (GCE) was employed as a working electrode. An Ag/AgCl/saturated KCl reference electrode and a Pt wire counter electrode were separated from the working electrode by a glass capillary. The working electrode was polished with 0.05 μm γ-Al₂O₃ powder to obtain a mirror surface, then sonicated and thoroughly rinsed with deionized water. Before each experiment, the working electrode was subjected to repeat scanning in the potential ranges of -0.5 to 1.5 V

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Fig. 1 ECL intensity-potential curves at the glassy carbon electrode in 0.15 M phosphate buffer (pH 7.5) containing 0.05 M TPrA in the absence (a) and presence of 100 μM SDS (b). The $\text{Ru}(\text{bpy})_3^{2+}$ concentration is 1.0 μM and the scan rate is 0.1 V/s.

in a 0.1 mol/L phosphate buffered solution until reproducible voltammograms were obtained. ECL generation and detection were performed on a Model MPI-E ECL analyzer system (Xi'an Remax Electronic Science & Technology Co. Ltd., Xi'an, China); and the voltage of the PMT was set at 600 V. The fluorescence spectra were acquired on a Model F-4500 photospetrometer (Hitachi, Japan); and the voltage of the PMT was set at 700 V. The widths of both the excitation slit and the emission slit were set to 5 nm. All experiments were carried out at ambient room temperature ($\sim 25^\circ\text{C}$).

Results and Discussion

ECL of $\text{Ru}(\text{bpy})_3^{2+}$ quenched by sodium diphenylamine-4-sulfonate

As shown in Fig. 1a, a typical ECL intensity-potential curve for the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system with 1.0 μM $\text{Ru}(\text{bpy})_3^{2+}$ and 0.05 M TPrA is presented. Two ECL peaks were observed while sweeping the potential from 0 to 1.5 V. The first peak began to appear at about 0.85 V, and reached the maximum at about 0.95 V. This peak can be described as follow:^{17,18}

The second peak started at about 1.05 V and reached the maximum at 1.2 V. ECL at this potential is attributed to direct oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ on the electrode to generate $\text{Ru}(\text{bpy})_3^{3+}$, which further reacted with the $\text{TPrA}^{\cdot+}$ radical species to generate $\text{Ru}(\text{bpy})_3^{2+*}$,¹⁹ and can be explained as follows:

Fig. 2 ECL intensity versus the quencher concentration for SDS at 1.2 V on a glassy carbon electrode in 0.15 M phosphate buffer (pH 7.5) containing 0.05 M TPrA. The $\text{Ru}(\text{bpy})_3^{2+}$ concentration was 1.0 μM and the scan rate was 0.1 V/s.

Fig. 3 Stern-Volmer ECL quenching curve for 1.0 μM $\text{Ru}(\text{bpy})_3^{2+}$ by SDS at 1.2 V on a glassy carbon electrode in 0.15 M phosphate buffer (pH 7.5) containing 0.05 M TPrA. The scan rate was 0.1 V/s.

The curve as shown in Fig. 1b describes the ECL of $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system in the presence of 100 μM SDS. About 72% of ECL at 1.2 V was quenched; meanwhile, the intensity of the ECL at 0.95 V decreased to 9% of that in the absence of SDS. In order to determine the effect of the quencher concentration, 1.0 μM $\text{Ru}(\text{bpy})_3^{2+}$ with different concentrations of SDS 1.2 V was investigated. The emission intensity was a function of the SDS concentration, as shown in Fig. 2. The quenching behavior can be described by the Stern-Volmer equation,

$$I_0/I = 1 + K_{\text{SV}}[\text{Q}], \quad (9)$$

where I_0 and I define the emission intensities in the absence and presence of the quencher, respectively. The Stern-Volmer constant, K_{SV} , represents the efficiency of quenching. From the Stern-Volmer plot shown in Fig. 3, the value of K_{SV} for the quenching of $\text{Ru}(\text{bpy})_3^{2+}$ ECL by SDS was calculated to be $2.5 \times 10^4 \text{ M}^{-1}$, and the extent of errors using the standard deviation was 7%.

Mechanism discussion

Figure 4a shows cyclic voltammograms (CV) of a mixed solution at a GC electrode. In the presence of 10 μM $\text{Ru}(\text{bpy})_3^{2+}$

Fig. 4 Potential-current curves at a glassy electrode in 0.15 M phosphate buffer (pH 7.5) containing 0.05 M TPrA in the absence (a) and presence of 1.0 mM SDS (b). The $\text{Ru}(\text{bpy})_3^{2+}$ concentration was 10 μM and the scan rate was 0.1 V/s.

Fig. 5 Fluorescence spectra of $\text{Ru}(\text{bpy})_3^{2+}$ in 0.15 M phosphate buffer (pH 7.5) containing 0.05 M TPrA and 0.01 M SDS ($\lambda_{\text{ex}} = 452 \text{ nm}$). The potential was stepped to +1.5 V to effectively oxidize $\text{Ru}(\text{bpy})_3^{2+}$, TPrA, and SDS. Bulk electrolysis was performed for 3 h with samples taken at 60-min intervals. The spectra reported above are for the following times: (a) no electrolysis, (b) 1, (c) 2, (d) 3 h.

and 0.05 M TPrA, a scan was made between 0 and 1.5 V, with a current increase beginning at 0.7 V and reaching its peak potential at about 1.1 V, signaling the direct oxidation of TPrA.¹⁸ Compared without SDS in the mixed solution (Fig. 4a), a new oxidative peak was observed at about 0.67 V in the presence of SDS. This peak can be attributed to the oxidation of SDS. A similar result was observed in a CH_3CN medium.²⁰ In addition, the authors in this paper proposed that diphenylamine can undergo a fast single-electron process, generating a cationic free radical following a chemical reaction that produce a dimer of diphenylamine. After many cycles, these dimers can further polymerize, producing a high polymer. In our system, we only scanned the mixed solution one time; therefore, the dimer of SDS may be produced, but no high polymer. The process of forming the dimer may be described as Scheme 1.^{20,21}

As shown in Fig. 5, bulk electrolysis coupled with fluorescence detection was used to probe the nature of products formed during electrolysis. The signal decreased with increasing time of electrolysis, indicating that a product of SDS is directly responsible for the luminescence signal and ECL quenching.¹⁰

Conclusions

SDS can efficiently quench the ECL of $\text{Ru}(\text{bpy})_3^{2+}$ /TPrA system. The differences between the ECL and photoluminescence data suggest that these types of interactions could be very important in probing energy- and electron-transfer processes of $\text{Ru}(\text{bpy})_3^{2+}$ sensitizers in solution and at charged interfaces. In addition, ECL quenching may find use in environmental analyses of SDS and its derivatives as well as in biotechnology and pharmaceutical applications, like the description in a previous report.²²

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