



A novel tris(2,2'-bipyridine)ruthenium(II)/tripropylamine cathodic electrochemiluminescence in acetonitrile for the indirect determination of hydrogen peroxide

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ABSTRACT

A novel tris(2,2'-bipyridine)ruthenium(II) ($\text{Ru}(\text{bpy})_3^{2+}$) cathodic electrochemiluminescence (ECL) was generated at -0.78 V at the Pt electrode in acetonitrile (ACN), which suggested that the cathodic ECL differed from conventional cathodic ECL. It was found that tripropylamine (TPrA) could enhance this cathodic ECL and the linear range (log–log plot) was $0.2 \mu\text{M}$ – 0.2 mM. In addition, hydrogen peroxide (H_2O_2) could inhibit the cathodic ECL and was indirectly detected with the linear range of 27 – $540 \mu\text{M}$. The RSD ($n = 12$) of the ECL intensity in the presence of $135 \mu\text{M}$ H_2O_2 was 0.87% . This method was also demonstrated for the fast determination of H_2O_2 in disinfectant sample and satisfactory results were obtained.

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1. Introduction

Tris(2,2'-bipyridine)ruthenium(II) ($\text{Ru}(\text{bpy})_3^{2+}$) electrochemiluminescence (ECL) has been a powerful tool in analytical chemistry because of its high sensitivity, wide linear range, simplicity, and good stability [1]. There are two detection modes for the different analytes including enhanced ECL detection (direct detection) and inhibition ECL detection (indirect detection). Concerning the direct detection mode, oxalate ($\text{C}_2\text{O}_4^{2-}$) [2,3] and nitrogen-containing compounds [4–8] can be directly detected by the oxidative-reduction type ECL. In addition, hydrogen peroxide (H_2O_2) [9] and peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$) [10] can be directly determined by the reductive-oxidation type ECL. Regarding the indirect detection mode, some inorganic compounds [11] and organic acids [12,13] can be indirectly detected based on their inhibition of $\text{Ru}(\text{bpy})_3^{2+}$ /tripropylamine (TPrA) or $\text{Ru}(\text{bpy})_3^{2+}/\text{C}_2\text{O}_4^{2-}$ ECL system.

In general, the two ECL detection modes are usually carried out in aqueous solution. However, the applied potential is either much more positive (>1.05 V vs. SCE) or negative (<-1.25 V vs. SCE), and

thus the influence of water is inevitable. Concerning anodic ECL, oxygen evolution occurs easily, resulting in decreased ECL intensity. In addition, the most often used Pt electrode needs reactivation [14]. Regarding cathodic ECL, some particular electrodes such as oxide-covered tantalum electrode [15] or bismuth electrode [16] were used because of the very negative potential of $\text{Ru}(\text{bpy})_3^{2+}$ reduction, where hydrogen evolution occurs at conventional metal electrode.

In order to eliminate the influence of water, ECL could be generated in organic solution such as acetonitrile (ACN). Bard's group [17] first demonstrated the $\text{Ru}(\text{bpy})_3^{2+}/\text{S}_2\text{O}_8^{2-}$ cathodic ECL in ACN. Here, a novel $\text{Ru}(\text{bpy})_3^{2+}$ cathodic ECL was demonstrated at the Pt electrode at -0.78 V in ACN. It was found that $\text{S}_2\text{O}_8^{2-}$ could not enhance this cathodic ECL, while TPrA could, which indicated that the cathodic ECL differed from the conventional cathodic ECL. In addition, H_2O_2 could inhibit this cathodic ECL. There are a lot of reports about the detection of H_2O_2 by direct ECL detection [18–22]. The first sensing application of quantum dot ECL was demonstrated to detect H_2O_2 by Ju's group [18]. Cui et al. [22] presented a H_2O_2 sensor based on the ECL of luminol-reduced gold nanoparticles. However, among these ECL detection methods, few reports were used to detect H_2O_2 in real sample. In our study, H_2O_2 was simply and indirectly detected based on its inhibition of the cathodic ECL with good reproducibility. In addition, this method was applied for the fast determination of H_2O_2 in disinfectant sample.

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2. Experimental

2.1. Chemicals and solutions

Tris(2,2'-bipyridine)ruthenium(II) dichloride hexahydrate ($\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$) and tripropylamine (TPrA) were purchased from Aldrich (Milwaukee, WI, USA) and used without further purification. Tetrabutylammonium perchlorate (TBAP, electrochemical grade) was obtained from Fluka (Milwaukee, WI, USA). Acetonitrile (ACN), acetic acid (HAc), sodium acetate (NaAc), and aqueous hydrogen peroxide (H_2O_2) (30%) were purchased from Beijing Chemical Factory. H_2O_2 disinfectant sample (2.5–3.5%) was obtained from Hebei Jianjing medical and chemical factory. All the reagents and chemicals were of analytical reagent grade. ACN-based media containing 40 mM TBAP, 1 M HAc, and 20 mM NaAc was used as buffer solution. All solutions were prepared with ACN.

2.2. Instrumentation

Cyclic voltammograms were performed with a CH Instrument model 800 voltammetric analyzer (Austin, TX, USA) using a 500 μm Pt disc working electrode (or a 3 mm GC electrode), a platinum coil counter electrode (CE), and a Ag pseudo-reference electrode in a poly(dimethylsiloxane) (PDMS) detection cell sealed by a modified plastic sample vial with three holes for the three electrode, respectively. The corresponding ECL signals were measured with a photomultiplier tube (PMT, Xi'an Remex Electronic Science Tech Co., Ltd., Xi'an, China) installed under the PDMS detection cell. Unless mentioned otherwise, the Pt electrode was used as the working electrode and all potentials were referenced to Ag pseudo-reference electrode. According to the literature [9], the CE was isolated by a porous ceramic tip and a glass capillary filled with ACN-based media containing 40 mM TBAP, 1 M HAc, and 20 mM NaAc. It needed to be emphasized that cathodic ECL was generated when CE was not isolated (called exposed CE), otherwise there was no cathodic ECL.

3. Results and discussion

3.1. Cathodic ECL in ACN

One of the most attractive features of $\text{Ru}(\text{bpy})_3^{2+}$ ECL in ACN is that there is no influence of water on the ECL intensity. However, $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ was often used instead of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in ACN because Cl^- was easily oxidized preceding the oxidation of $\text{Ru}(\text{bpy})_3^{2+}$ and its oxidation influenced the ECL intensity [23,24]. Moreover, the preparation of $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ needed recrystallization and dryness [25–28]. We reported a strong $\text{Ru}(\text{bpy})_3\text{Cl}_2/\text{TPrA}$ anodic ECL system in ACN by inhibiting the oxidation of Cl^- using acetate buffer without $\text{Ru}(\text{bpy})_3(\text{ClO}_4)_2$ [29]. Not only was the influence of water eliminated, but also the Pt electrode reactivation, necessary for aqueous ECL system, was not needed. In addition, a cathodic ECL was observed at -0.78 V.

Fig. 1 shows the cyclic voltammograms (Fig. 1A) and their corresponding ECL curves (Fig. 1B) of 2 mM $\text{Ru}(\text{bpy})_3^{2+}$ in ACN with exposed (solid line) and isolated (dotted line) CE. From Fig. 1A, we can see that there was no obvious change in the cyclic voltammograms whether the CE was isolated or not. With the potential scanned negatively, a broad reductive peak could be observed between 0.4 and -0.65 V, which was attributed to the reduction of oxygen (no peak when saturated with N_2 , not shown). When it was more negative than -0.65 V, there was an increasing reductive current and a corresponding cathodic ECL was observed at about -0.78 V with exposed CE (Fig. 1B, solid line). According to the literature [24], $\text{Ru}(\text{bpy})_3^{2+}$ was reduced at about -1.33 V

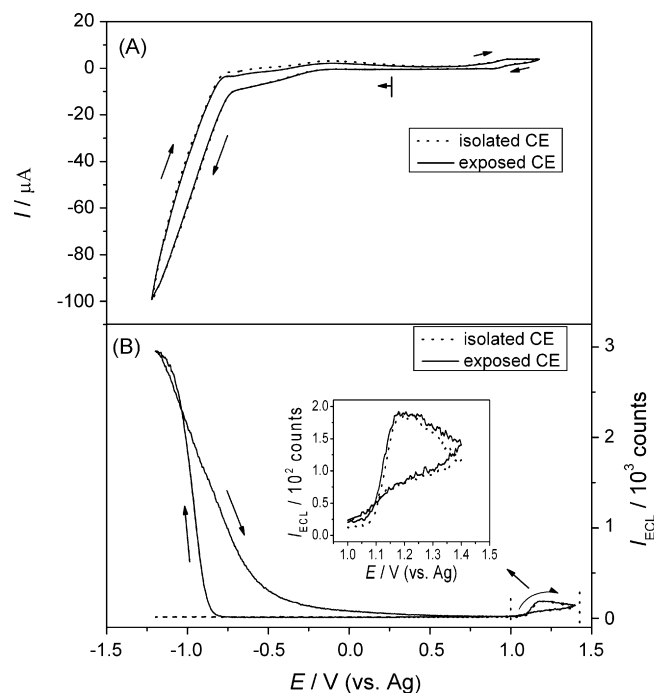


Fig. 1. Cyclic voltammograms (A) and their corresponding ECL curves (B) of 2 mM $\text{Ru}(\text{bpy})_3^{2+}$ in ACN with exposed (solid line) and isolated CE (dotted line). Buffer solution, 40 mM TBAP + 1 M HAc + 20 mM NaAc in ACN; scan rate, 0.1 V/s; PMT voltage, 600 V.

vs. Ag pseudo-reference electrode in ACN, which suggested that $\text{Ru}(\text{bpy})_3^+$ could not be generated. In addition, the cathodic ECL could not be enhanced by $\text{S}_2\text{O}_8^{2-}$, proving that $\text{Ru}(\text{bpy})_3^+$ was not generated. Therefore, this cathodic ECL is different from conventional cathodic ECL. When the potential was scanned positively, $\text{Ru}(\text{bpy})_3^{2+}$ started to oxidize at about 1.0 V and reached the maximum oxidation peak around 1.18 V, and a corresponding anodic ECL similar to the conventional anodic ECL in aqueous solution could be observed.

Dong's group [30] reported a novel cathodic ECL at a glassy carbon electrode (GC) at -0.4 V (vs. Ag/AgCl) in aqueous solution, which was caused by the reduction of oxygen. Choi and Bard [9] also investigated this cathodic ECL and they considered that the counter electrode reaction was another important factor for the cathodic ECL besides the reduction of oxygen.

When the CE was isolated by a porous ceramic tip, the cathodic ECL disappeared but the anodic ECL had no change in our study (Fig. 1B, dotted line). Therefore, the CE reaction also contributed to the cathodic ECL. In addition, the cathodic ECL did not disappear but increased after the solution was saturated with N_2 , which suggested oxygen did not contribute to the cathodic ECL. Here, oxygen only quenched the ECL, which accords with the literature [24]. The ECL behaviour of $\text{Ru}(\text{bpy})_3^{2+}$ at GC electrode was also investigated in ACN (supporting information, Figure SI-1) and the result showed that oxygen was easily reduced and a cathodic ECL was generated. In addition, both the reduction of oxygen and CE reaction were dispensable to generate the cathodic ECL at the GC electrode.

It was noted that homoconjugation, heteroconjugation, and ion-pair often take place in ACN, which might be another reason to generate the cathodic ECL [29,31–33]. When only TBAP was used as supporting electrolyte, the cathodic ECL was not generated, and there was still no cathodic ECL while HAc was added. The adding of NaAc was indispensable to produce the cathodic ECL. However, the mechanism was not clear.

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