Electrochemiluminescence of Tris(2,2′-bipyridine)ruthenium(II)/Tri-n-propylamine with an Electric Contactless Power Transfer System

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An electrochemiluminescence (ECL) analytical device was developed using an electric contactless power transfer system. A mutually induced electromotive voltage was generated by wrapping an enameled wire around a commercial contactless charger. There was no electrical contact between the power supply and the electrochemical cell. For the tris(2,2′-bipyridine)ruthenium(II) (Ru(bpy)32+)/tri-n-propylamine system, a weak ECL signal was observed. When an inexpensive rectifier diode was introduced between the coil and the working electrode, the ECL intensity detection sensitivity increased by more than 100 times. The relationship between the waveform of the applied voltage and the ECL response was clarified, and the optimum conditions were determined. The intensity of the induced electromotive voltage was easily controlled by changing the number of turns in the coil. The proposed method is a safe, simple, and inexpensive technique without electrical contact.

Keywords: Electric contactless power transfer, mutually induced voltage, electrochemiluminescence, tris(2,2-bipyridine)-ruthenium(II), tri-n-propylamine, rectifier diode

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Introduction

The electric contactless power transfer technology used in electromagnetic induction has attracted attention for applications in daily life. This technology has been widely applied in contactless power supplies for electronic devices such as smartphones, toothbrushes, and prototype electric vehicles. The core of the system is two inexpensive coils. Magnetic flux is generated through power distribution to the primary coil as a transmitter, and electromotive force into the secondary coil (receiver) is induced by electromagnetic induction from the transmitter. The induced current provides an electric contactless power supply, which is a safe and straightforward system. The induced voltage difference (ΔE) is sometimes called the induced voltage difference (ΔV). The induced voltage is proportional to the number of coil turns (N), magnetic flux (Φ), and Itrans, as described by

\[ \Delta E = -M \times \frac{dI_{\text{trans}}}{dt}, \]  

(1)

where \( M \) is the mutual inductance (H = V \times s/A in SI base units) between the transmitter coil and receiver coil, and \( I_{\text{trans}} \) is the current through the transmitter coil. The mutual induction is proportional to the number of coil turns (N), magnetic flux (Φ), and Itrans, as described by

\[ M = \frac{N \Phi}{I_{\text{trans}}}. \]  

(2)

The induction voltage is proportional to the number of coil turns and the magnetic flux change

\[ \Delta E = -N \Phi \times \frac{dI_{\text{trans}}}{dt}. \]  

(3)

In principle, a high-frequency magnetic flux change is required for a high induced voltage. Therefore, complex electrical control is needed in a contactless power supply unit, the system produces complex signals, and the results must be analyzed carefully. Thus, the applications of this method in analytical chemistry are quite limited.

Electrochemiluminescence (ECL) is light emitted from excited species in heterogeneous electrochemical reactions. It has attracted significant attention because of its high sensitivity, low background signal, reproducibility, and reasonable temporal and spatial control. Some groups have recently applied the electric contactless power transfer technique to ECL measurements. In these studies, luminol was selected as an ECL emitter to determine hydrogen peroxide using a simple procedure. To the best of our knowledge, there have been no reports concerning the use of other ECL emitters with this technique. ECL of the tris(2,2′-bipyridine)ruthenium complex (Ru(bpy)32+) can be observed in aqueous solutions for the determination of several coreactants, such as amines, vitamins, pesticides, and DNA. The ECL technique can be used with coreactant systems for analytical detection in environmental, clinical, forensic, and biomedical applications. However, when Ru(bpy)32+ is used as an ECL emitter, it requires a higher potential than the luminol system. Therefore, it is necessary to increase the number of receiver coil turns and change the magnetic flux density (Eqs. (1) - (3)), which complicates the measurement system. Also, Ru(bpy)32+ has reversible electrochemical activity.
Electrochemically generated Ru(bpy)$_3^{3+}$ is reduced to Ru(bpy)$_3^{2+}$ through an electrode reaction under a sinusoidal induction voltage without generation of the excited state (*Ru(bpy)$_3^{2+}$). Therefore, it is not easy to achieve continuous luminescence to detect analytes using the electric contactless power transfer technique.

In this study, we developed a method combining Ru(bpy)$_3^{2+}$ as an ECL emitter with an electric contactless power-transfer system. A commercially available electric contactless toothbrush charger was used as the transmitter coil, and an enamel wire was wound around the charger to act as a receiver coil. This simple and inexpensive system provides a high mutual induced voltage, which can be controlled by adjusting the number of coil turns. Only weak ECL was measured when a typical Ru(bpy)$_3^{2+}$ coreactant, tri-$n$-propylamine (TPA), was used. After introducing a suitable rectifier diode to the system, ECL was efficiently observed and the ECL mechanism under the mutually induced voltage was characterized. The proposed method is simple, cost effective, and sensitive for the analysis of TPA.

Experimental

Reagents and chemicals

Tris(2,2′-bipyridine)ruthenium(II) chloride [Ru(bpy)$_3$]Cl$_2$ hexahydrate was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used without further purification. TPA was purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan). A stock solution (100 mM) was prepared in ultrapure water and stored at 4°C when not in use. Phosphate-buffered saline (PBS, 0.1 M) was selected as the buffer solution because it did not affect the ECL reactions. The PBS was prepared by mixing known volumes and concentrations of disodium hydrogen phosphate and potassium dihydrogen phosphate (Nacalai Tesque, Inc., Kyoto, Japan). The pH was adjusted with phosphoric acid or an aqueous solution of sodium hydroxide. Working standard solutions were prepared by precise dilution of the stock solution with PBS. All other reagents were of analytical grade and purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Ultrapure water (resistivity > 18.2 MΩ·cm) was obtained using a Milli-Q water purification system (Millipore, Billerica, MA).

Apparatus for the ECL measurement system with electric contactless power transfer

Figure 1(A) shows a circuit diagram of the ECL measurement system with electric contactless power transfer. A commercially available automatic toothbrush charger (Oral-B; Braun GmbH, Kronberg, Germany) was used as the transmitter coil (37.8 kHz, 0.9 W). A mutually induced voltage was obtained by wrapping enameled wire in a coil around the charger. The number of coil turns was used to control the magnitude of the induced voltage. After introducing a suitable rectifier diode to the system, ECL was efficiently observed and the ECL mechanism under the mutually induced voltage was characterized. The proposed method is simple, cost effective, and sensitive for the analysis of TPA.
electrode was mounted 3 mm from the bottom of the electrochemical cell, and at an accurate standardized distance from the photon counter. Light emission from the working electrode was measured by a multi-pixel photon counter (MPPC) module (C13365-3050SA; Hamamatsu Photonics, Shizuoka, Japan), which was set opposite to the working electrode. Photomultiplier tubes have been widely used for light detection in ECL measurements; however, the output signal from a photomultiplier tube is frequently affected by the ambient magnetic field. Consequently, we used a MPPC as the light detector in the present study. Before the measurements, the working electrode was carefully polished using aluminum powder ($\phi = 0.30 \mu m$) and then sonicated in an ultrasonic cleaner (47 kHz, 30 W; Branson Ultrasonics, Danbury, CT). The output ECL signal from the MPPC module was collected into an AIO-160802AY-USB AD/DA converter (Contec Co. Ltd., Osaka, Japan).

**Results and Discussion**

**ECL behavior of Ru(bpy)$_3^{2+}$/TPA in the electric contactless power transfer system**

First, the ECL behavior of Ru(bpy)$_3^{2+}$/TPA in the electric contactless power transfer system was evaluated. Figure 2 (A, a) shows the waveform of the mutually induced voltage from a receiver coil with 15 turns of enameled wire in a system without a diode. The power supply unit was turned on and off every 10 s. A bipolar AC voltage was applied to the circuit while the power supply was continuously on. The frequency of the mutually induced voltage was 37.8 kHz, which corresponded to the frequency of the transmitter coil. The output ECL signal from the MPPC module was collected into an AIO-160802AY-USB AD/DA converter (Contec Co. Ltd., Osaka, Japan).

The applied voltage was rectified by introducing a Schottky barrier diode in the system. A type 1N5817 rectifier diode (ON Semiconductor Corp., Phoenix, AZ) was inserted in the circuit between the working electrode and the receiver coil, and the cathodic voltage was rectified to the diode (Fig. 2 (B, a)). When a voltage was applied to the ECL measurement, a clear ECL response was observed in the presence of TPA (Fig. 2 (B, b)).

![Voltage-time profiles (a) and the corresponding ECL profiles (b) for 0.10 mM Ru(bpy)$_3^{2+}$ and 0.10 mM TPA with the electric contactless power transfer system in the absence of a diode (A) and the presence of a diode (B). The black lines in (b) are the ECL responses without TPA addition.](image)

The electrochemical oxidation of TPA was believed to occur at +0.8 V (Eq. (4)) and generate the reducing species TPA· at the electrode surface (Eq. (5)). Simultaneously, Ru(bpy)$_3^{3+}$ was electrochemically generated at +1.2 V (Eq. (6)). The light-emitting species of the excited state of *Ru(bpy)$_3^{2+}$ was produced by an electron transfer reaction between Ru(bpy)$_3^{3+}$ and TPA· (Eqs. (7) and (8)). The ECL intensities are essentially dependent on the concentrations of intermediates (Ru(bpy)$_3^{3+}$ and TPA·) at the electrode surface. However, these chemical species are readily reduced through electrode reactions to reductants at lower electrode potentials. Under the electric contactless power transfer technique, both the anodic and cathodic voltages were provided to the working electrode. The intermediate chemical species were deactivated without electron transfer through the subsequent chemical reaction (Eq. (7)). Therefore, only weak ECL was observed.

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The ECL intensity was more than 100-times that obtained without the rectifier diode. On the other hand, a clear ECL response could not be measured when another wireless charger for a smartphone was used as a transmitter. It was assumed that the charger had a circuit particular and did not have a simple sinusoidal current. These results suggest that the efficiency of the TPA determination could be improved by connecting a rectifier diode to the solution with the toothbrush charger.

Optimization of the ECL response for Ru(bpy)₃²⁺/TPA with the electric contactless power transfer system

To optimize the conditions for the ECL measurement, the effect of the mutually induced voltage was investigated. Figure 3 (a) shows the dependence of the induced voltage on the number of turns of the enameled wire. The mutually induced voltage increased with increases in the number of turns in the receiver loop. Simultaneously, the minimum induced voltage (baseline) also increased. To confirm the role of the diode in the system, we studied the effect on the mutually induced voltage without a diode. In this case, the mutually induced voltage increased proportionally with increases in the number of coil turns (Fig. S1). However, the minimum mutually induced voltage (baseline) did not increase. These results could be attributed to the features of the diode used in this experiment and the rectification effect. A plot of the maximum mutually induced voltage (Eₘₐₓ) against the number of coil turns (Fig. 3 (b)) showed that the applied Eₘₐₓ increased proportionally with the number of receiver coil turns. This meant that the applied voltage could be easily controlled by changing the number of coil turns. The Eₘₐₓ for 0.10 mM Ru(bpy)₃⁺ and 0.10 mM TPA with different numbers of turns in the receiver coil are shown in Fig. 3 (c). Weak ECL was observed with 10 turns in the receiver coil. The applied Eₘₐₓ was equivalent to ca. +1.5 V with 10 turns in the coil (Fig. 3(b)). In this case, the voltage was insufficient for the ECL reaction to proceed. Clear ECL responses were observed with more than 10 turns in the coil. However, the ECL intensity decreased when there were more than 20 turns in the coil. The Eₘₐₓ with 20 turns in the coil was greater than +3.0 V, and this might contaminate the electrode surface. Interference from competitive reactions occurred because of the generation of hydroxyl ions and hydroxyl radicals through hydrolysis. The ECL intensities are plotted against the number of turns in the receiver coil in Fig. 3 (d). In the system without a diode, no ECL was observed for any number of coil turns of the enameled wire. Because the highest ECL intensity was detected with 15 turns in the coil, this was selected as the optimum number of coil turns.

Determination of TPA by the proposed ECL measurement system

ECL responses were measured using the electric contactless power...
transfer technique were recorded for 0.10 mM Ru(bpy)_3^{2+} in 0.1 M PBS with different TPA concentrations (Fig. 4). A linear relationship was observed between 0 and 100 μM with a good determination coefficient ($r^2 = 0.991$). The TPA detection limit was approximately 2.0 μM (290 ng/mL) with a residual standard deviation of three. The proposed method was confirmed for other antitussive drugs, such as methoxyphenamine, and is expected to be applied to the unique detection methods for pharmaceutical analysis. Furthermore, because the proposed technique can be carried out without an electrical contact, this method could be used safely in analytical chemistry.

Conclusions

In conclusion, a simple ECL measurement system using the electric contactless power-transfer technique was developed for Ru(bpy)_3^{2+}/TPA. The ECL improved on the incorporation of a rectifier diode in the system. In the electric contactless power transfer system, the applied voltage intensity could be easily controlled by changing the number of receiver coil turns. The ECL measurement conditions were optimized, and quantitative analysis of TPA was performed with a good linear relationship. The electric contactless power transfer technique eliminates electric shock because there is no electrical contact between the power supply unit and the electrodes. In principle, the receiving coil only needs to be a loop of enameled wire, so it was proposed as an inexpensive analytical technique combined with a commercially available transmitter. The analytical device was expected to be a simple detection method that could be detect by merely “placing” it on the transmitter. Consequently, it is expected to be a safe and inexpensive analytical platform for on-site detection and education.

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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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