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Effect of Ultrasound on Electrochemiluminescence of Tris(2,2'-bipiridine)ruthenium with Various Co-reactants

超音波照射下における種々の共反応物を用いたルテニウム錯体の電気化学発光挙動の検討

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1. Introduction

The application of ultrasound to electrochemical processes is currently attracting an amount of interest on account of a number of advantages, such as increasing of the mass transport, activation or cleaning of the electrode surface [1]. The improvement of determination efficiency of several chemical species by ultrasound depends of physical process of mass transport and chemical reaction of cavitation. However, there is little investigation for the analysis each effects in detail.

Electrochemiluminescence (ECL) is a process where the species generated at electrodes undergo electron transfer reactions to form the excited state that emits light. Tris(2,2'-bipyridine)-ruthenium ($Ru(bpy)_3^{2+}$) is the most widely used ECL emitter among various ECL systems because which have a highly ECL efficiency. The ECL of $Ru(bpy)_3^{2+}$ / tripropylamine (TPA) has been well investigated and the mechanism was described as follows;

Scheme 1

$$TPA \rightarrow TPA^{\bullet+} + e^- \quad (1)$$
$$TPA^{\bullet+} \rightarrow TPA^{\bullet} + H^+ \quad (2)$$
$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^- \quad (3)$$
$$Ru(bpy)_3^{3+} + TPA^{\bullet} \rightarrow {}^*Ru(bpy)_3^{2+} + \text{products} \quad (4)$$
$${}^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\upsilon \quad (5)$$

It can be shown in **Scheme 1**, the typically ECL phenomenon is generally caused by radical species which is generated by the electrode reaction (eqn. (1)) and following chemical reaction (eqn. (2)). Hence, the ECL can remotely detect the some radical species. In addition, ECL is strongly dependence of mass transport of $Ru(bpy)_3^{2+}$ and TPA, the physically direct condition of solution can be analyzed. In this work, an attempt is made to discuss the dependence of light intensity under ultrasound irradiation, the physical and chemical process of ultrasound was considered by a comparison study of the effects of ultrasound irradiation on $Ru(bpy)_3^{2+}$ ECL with various co-reactant.

2. Experimental

An ultrasonic ECL cell used in this study was fabricated from a Tefron cylinders, which is schematically shown in **Figure 1**. An ITO, an Ag/AgCl electrode and a Pt wire were used as working, reference and counter electrode, respectively. The ultrasonic transducer was an ultrasonic homogenizer (TAITEC, Saitama, Japan) with working frequency of 20 kHz, and the maximum output power of 50 W. The light emitting from the electrode surface was measured with a H7468-1 photomultiplier tube (PMT, Hamamatsu photonics, Shizuoka, Japan).

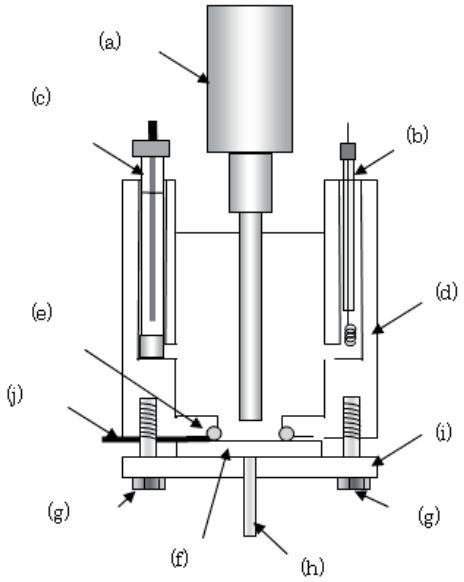

Figure 1. Schematic diagram of the ultrasonic ECL cell. (a) ultrasonic transducer, (b) Pt counter electrode, (c) Ag/AgCl reference electrode, (d) Teflon blocks, (e) o-ring, (f) ITO working electrode, (g) screws, (h) optical fiber, (i) Teflon plate and (j) cupper foil.

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3. Results and discussion

First, $Ru(bpy)_3^{2+}$ / TPA was used as a model ECL system and the effect of ultrasound irradiation. **Fig. 2** depicts the ECL-potential curves at an ITO electrode for 0.50 mM $Ru(bpy)_3^{2+}$ and 0.50 mM TPA with potential sweep technique. At stationary condition, maximum light emission signal was observed at +1.2 V vs. Ag/AgCl (Fig. 2 (B)). Under the ultrasound irradiation, ECL intensity was found to be increased ca. 3-fold. The increasing of ECL intensity was caused with the increasing of generation of electrochemical active species at electrode surface by ultrasonic irradiation.

Besides TPA, the other co-reactants, such as MP and CAF were also investigated in $Ru(bpy)_3^{2+}$ based ECL system. The dependence of ultrasound output power on the normalized ECL intensity (I_{ECL}/I_{ECL}^0) for each co-reactant was shown in **Fig. 3**. I_{ECL}/I_{ECL}^0 is defined as the ration of ECL intensity under ultrasound irradiation (I_{ECL}) to that observed in the stationary condition (I_{ECL}^0). The ECL signals significantly increased with increasing ultrasonic output power in TPA system, whereas only slight increasing was observed in MP system. We suppose the ECL mechanism of $Ru(bpy)_3^{2+}$ / MP system is thus proposed;

Scheme 2

$$MP \rightarrow R^{\bullet} + H^+ + e^- \quad (6)$$

$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^- \quad (3)$$

$$Ru(bpy)_3^{3+} + R^{\bullet} \rightarrow {}^*Ru(bpy)_3^{2+} + \text{products} \quad (7)$$

$${}^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\upsilon \quad (5)$$

The lower enhancement factor in $Ru(bpy)_3^{2+}$ / MP system could be due to the slow electron transfer process of MP and the lower catalytic efficiency in homogeneous reaction (eqn. 6 and 7). In opposite to these co-reactants, the ECL signal in $Ru(bpy)_3^{2+}$ / CAF system was found to be suppressed greatly under the ultrasound irradiation. This ECL generation mechanism at stationary condition was proposed as follows;

Scheme 3

$$CAF \rightarrow CAF^{\bullet} + H^+ + e^- \quad (8)$$

$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^- \quad (3)$$

$$Ru(bpy)_3^{3+} + CAF^{\bullet} \rightarrow {}^*Ru(bpy)_3^{2+} + \text{products} \quad (9)$$

$${}^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{2+} + h\upsilon \quad (5)$$

Scheme 3 is similar to each $Ru(bpy)_3^{2+}$ / TPA or MP ECL systems, however, it is thought that the quenching reaction of ECL that contribute the decreasing of ECL intensity, especially in the presence of ultrasound irradiation, can be involved (**Scheme 4**).

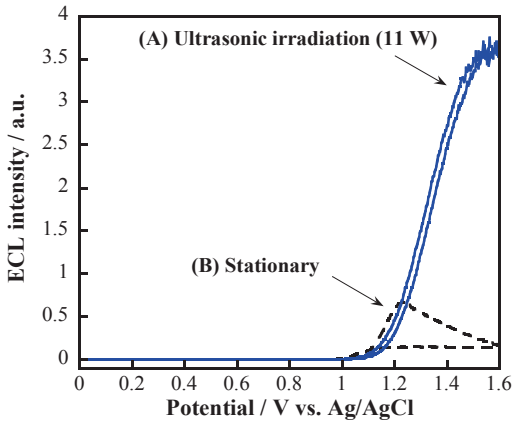

Fig. 2 ECL responses for 0.50 mM $Ru(bpy)_3^{2+}$ and 0.50 mM TPA in 0.1 M phosphate buffer solution (pH 9.0) at ITO electrode. (A) with sonication (solid line) and (B) stationary condition, respectively.

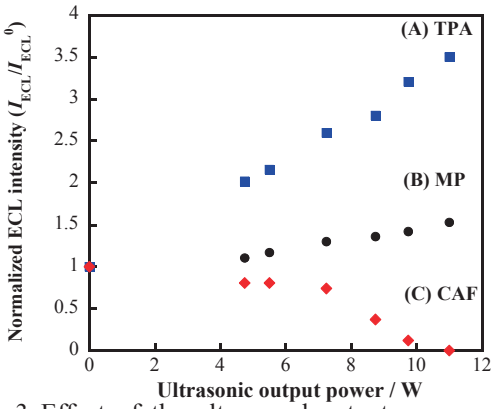

Fig. 3 Effect of the ultrasound output power on ECL enhancement factor (I_{ECL}/I_{ECL}^0) in $Ru(bpy)_3^{2+}$ based ECL systems using (A) TPA, (B) MP and CAF as co-reactants, respectively.

Scheme 4

$${}^*Ru(bpy)_3^{2+} + CAF \rightarrow [Ru(bpy)_3^{+} \cdots CAF^-] \quad (10)$$

$$\leftrightarrow Ru(bpy)_3^{2+} + CAF \quad (11)$$

The ultrasound irradiation gave rise to an effective collision frequency between ${}^*Ru(bpy)_3^{2+}$ and CAF and resulted in the drop of ECL intensity.

The effect of ultrasound irradiation on ECL behavior of $Ru(bpy)_3^{2+}$ / TPA, MP and CAF systems in this ultrasound ECL cell should be mainly due to the increasing of mass transport as physical process, because it was confirmed that the oxidants such as hydroxyl radical induced by ultrasonic cavitation was not significantly evidenced in the cell. These oxidants are effectively generated at 500 kHz ultrasonic field, and now we have been studying the chemical effect induced in the ultrasonic field for $Ru(bpy)_3^{2+}$ ECL systems.

References

1. R.G. Compton, F.M. Matysik: Electroanalysis **8** (1996) 218.

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