

Electrochemiluminescence of tris(2,2'-bipyridine)ruthenium with Various Coreactants under Ultrasound Irradiation

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Abstract

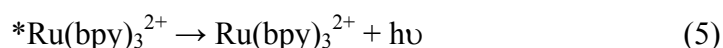
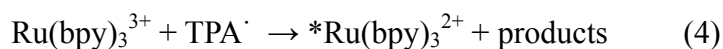
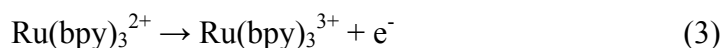
Electrochemiluminescence (ECL) of tris(2,2'-bipyridine)ruthenium, $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of various coreactants, such as tripropylamine (TPA), oxalate ion ($\text{C}_2\text{O}_4^{2-}$), ascorbic acid (H_2A) and dehydroascorbic acid (DHA), were investigated under ultrasound irradiation. In sono-ECL experiments, an indium-thin-oxide (ITO) was used as working electrode, and a titanium tipped sonic horn probe (diameter 2 mm) which operated at a frequency of 20 kHz was set in the front of the ITO electrode. Under the ultrasound irradiation, ECL signals were found to be significantly enhanced when TPA and $\text{C}_2\text{O}_4^{2-}$ were used as coreactants, only slightly enhanced in $\text{Ru}(\text{bpy})_3^{2+}/\text{DHA}$ system, but total quenched in $\text{Ru}(\text{bpy})_3^{2+}/\text{H}_2\text{A}$ system. The difference of $\text{Ru}(\text{bpy})_3^{2+}$ ECL behaviors for various co-reactant could be due to the different kinetics of catalytic reactions associated in ECL schemes. ECL quenching effect observed in $\text{Ru}(\text{bpy})_3^{2+}/\text{H}_2\text{A}$ system was suggested to be due to electron transfer (ET) route between the excited state $^*\text{Ru}(\text{bpy})_3^{2+}$ and ascorbate anion HA^- diffused from the bulk solution, where the diffusional HA^- species served as electron donor. The effect becomes more pronounced upon sonication because the effective collision frequency between $^*\text{Ru}(\text{bpy})_3^{2+}$ and HA^- would be significantly increased by the enhanced mass transport effect of ultrasound.

Keywords: Electrochemiluminescence; tris(2,2'-bipyridine)ruthenium; Ultrasound irradiation; Coreactant, ECL quenching

1. Introduction

Electrochemiluminescence (ECL), also known as electrogenerated chemiluminescence is a process where the species generated at electrodes undergo electron transfer reactions to form the excited state that emits light [1]. Because it does not need an excitation light source like fluorometry, ECL provides the advantages of simple instrumentation and low background signal, and the technique has been received considerably attention in the field of analytical chemistry [2-4]. Tris(2,2'-bipyridine)ruthenium ($\text{Ru}(\text{bpy})_3^{2+}$) is the most widely used ECL emitter among various ECL systems because this complex is capable of producing ECL with various coreactants, such as tripropylamine (TPA), oxalate ion ($\text{C}_2\text{O}_4^{2-}$) [5,6], peroxydisulfate [7,8], and ascorbic acid [9-11]. $\text{Ru}(\text{bpy})_3^{2+}$ based ECL system can emit light at room temperature in both aqueous and non-aqueous solutions with relatively higher ECL efficiency. The ECL reaction of $\text{Ru}(\text{bpy})_3^{2+}$ with TPA has been well investigated by many workers [3,12,13]. Scheme 1 describes the general ECL mechanism where the oxidation of TPA generates a strongly reducing specie of $\text{TPA}\cdot$ [3]. This oxidation can be via a catalytic route where the electrogenerated $\text{Ru}(\text{bpy})_3^{3+}$ (in equation (3)) reacts with $\text{TPA}\cdot$ to produce the excited state of $\text{Ru}(\text{bpy})_3^{2+}$ at the electrode surface.

Scheme 1



Although $\text{Ru}(\text{bpy})_3^{2+}$ is regenerated in this scheme (itself is not consumed in whole ECL reaction), it suffers from the problems that the working electrode easily becomes fouled with time, and the ECL intensity does not keep continuously in stationary condition.

The application of ultrasound to electrochemical processes (sonoelectrochemistry) is currently attracting amount of interest due to a number of advantages, such as increasing of the mass transport and activation or keeping the electrode surface to be clean [14,15]. The influence of ultrasonic irradiation on the ECL of in $\text{Ru}(\text{bpy})_3^{2+} / \text{C}_2\text{O}_4^{2-}$ system was first reported by Walton et. al., and both enhanced ECL emission signal and improved reproducibility were achieved in their experiments [16]. It can be shown in Scheme 1, the mechanism of $\text{Ru}(\text{bpy})_3^{2+}$ ECL is very complicated, accompanying with a series of the electrode reaction (E reaction) and following some homogeneous chemical reactions (C reaction), which is considered to be effected by ultrasound irradiation. In order to obtain the information concerning the nature of the species producing light, the comparison study of the influences of ultrasound irradiation on $\text{Ru}(\text{bpy})_3^{2+}$ ECL with various coreactants (TPA, $\text{C}_2\text{O}_4^{2-}$, DHA and H_2A) were described in this work.

2. Experimental

2.1 Chemicals

Tris(2,2'-bipyridine)ruthenium(II) chloride [$\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$] was purchased from Aldrich. Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) was purchased from Nacalai Tesque (Kyoto, Japan). Tripropylamine (TPA), dehydroascorbic acid (DHA) and L-ascorbic acid (H_2A) were of analytical grade purchased from Wako Co. (Osaka, Japan) and were used as received. Phosphate buffer solution (PBS) was prepared by equimolar amount of disodium

hydrogenphosphate (Na_2HPO_4) and potassium dihydrogenphosphate (KH_2PO_4). The appropriate pH of the buffer was adjusted with orthophosphoric acid or sodium hydroxide. All solutions were with distilled water purified by a WS200 distillation system (Yamato Scientific Co., Tokyo, Japan).

2.2 Apparatus

Cyclic voltammetry and the potential control in ECL measurements were conducted with a model 660 CHI electrochemical analyzer (CH Instruments, Austin, TX, USA). An ultrasonic ECL cell used in this study was fabricated from a Teflon cylinders (60 mm in diameter), which is schematically shown in Fig. 1. The transparent working electrode was made from indium tin oxide (ITO) coated glass (Aldrich, $7.5 \Omega/\text{cm}$). It was cut into size of 60 mm \times 15 mm, and was laid horizontally and sandwiched between two cylinders by screw thread. There is a hole with 3-mm diameter at the bottom of the cell, and the electrode surface was exposed to the solution with a silicone O-ring (5-mm bore diameter). An Ag/AgCl (3 M KCl) electrode and a Pt wire were used as reference and counter electrodes, respectively. In order to minimize ultrasonic field perturbations the two electrodes were placed in the separated chambers, as shown in Fig.1. 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 sonic probe with a 2-mm diameter titanium tip is positioned “face-on” the ITO electrode (Fig. 1). The distance between the immersion horn and the working electrode is variable between 0 and 30 mm. The light emitting from the electrode surface was measured with a H7468-1 photomultiplier tube (PMT) module (Hamamatsu Photonics, Shizuoka, Japan) via an optical fiber which was positioned opposite to the ultrasonic transducer.

The PMT module was controlled by a notebook computer and a laboratory-written software package via RS-232C interface. The program was developed by Microsoft Visual Basic 6.0. All ECL measurements were conducted in a light proof box.

Photoluminescence spectra were obtained with a RF-5300PC fluorescence spectrometer (Shimadzu Co., Kyoto, Japan). A quartz cuvette cell with 1 cm path length was used.

3. Results and discussion

3.1 ECL of $\text{Ru}(\text{bpy})_3^{2+}$ / TPA system in the presence of ultrasound irradiation

First, $\text{Ru}(\text{bpy})_3^{2+}$ /TPA was used as a model ECL system and the effect of ultrasound irradiation on both electrochemical and ECL behavior were investigated. From the results of cyclic voltammograms in 0.50 mM $\text{Ru}(\text{bpy})_3^{2+}$ in 0.1 M PBS (pH=8.8), a pair of redox peak of $\text{Ru}(\text{bpy})_3^{2+}$ was observed around +1.2 V vs. Ag/AgCl. When amount of TPA was added in the solution, the anodic peak current increased dramatically while the cathodic current decreased due to the catalytic reactions between $\text{Ru}(\text{bpy})_3^{2+}$ and TPA as was described in Scheme 1. Figure 2 depicts the ECL-potential profiles at an ITO electrode for 0.50 mM $\text{Ru}(\text{bpy})_3^{2+}$ and 0.50 mM TPA. At stationary condition, maximum light emission signal was observed at +1.2 V vs. Ag/AgCl (dotted line in Fig. 2). When the electrode potential was scanned to more positive region, the light intensity decreased due to the depletion of the electrochemically active substance at the electrode surface. Under the ultrasound irradiation (with output power of 10 W), ECL intensity was found to be increased ca. 5-fold. The chemical effect induced in the ultrasonic field was examined by Wiessler reaction using potassium iodide as a chemical dosimeter [17]. It was confirmed that the oxidants such as hydroxyl radical induced by ultrasonic

cavitation was not significantly evidenced in the cell, and the enhanced ECL signal should be mainly due to the increasing of mass transport in electrochemical systems. Figure 3 compares the reproducibility of ECL signals generated by a pulse potential mode (potential step from 0 to 1.5 V vs. Ag/AgCl with pulse width of 5 s) in Ru(bpy)₃²⁺/TPA system, measured with and without ultrasound irradiation. Under stationary condition, the ECL signal decayed greatly (ca. 70%) after 40 repeated measurements owing to the electrode fouling. With ultrasound irradiation, however, both reproducibility and sensitivity were significantly improved. The major benefit of ultrasound can be due to the mass transport enhancement, as well as the cleaning effect of ultrasound.

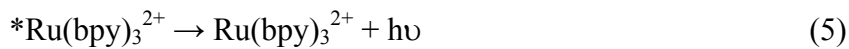
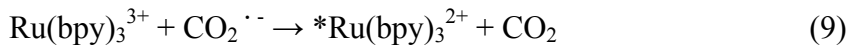
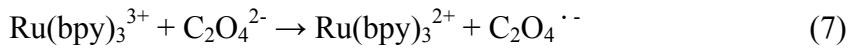
3.2 Effect of ultrasound irradiation on Ru(bpy)₃²⁺ ECL with the other coreactants

Besides TPA, the other coreactants, such as C₂O₄²⁻, DHA and H₂A were also investigated in Ru(bpy)₃²⁺ based ECL system. Figure 4(A) shows the linear sweep voltammograms of 0.5 mM Ru(bpy)₃²⁺ at a carbon fiber microdisc electrode (ϕ 10 μ m) in 0.1 M PBS (pH=8.8), and the a steady-state current corresponding to the oxidation of Ru(bpy)₃²⁺ was observed at the potential region above +1.1 V vs. Ag/AgCl. The dotted lines represent the voltammetric responses of 10 mM of each coreactant. After addition 10 mM of TPA (B), C₂O₄²⁻ (C), DHA (D) and H₂A (E) to this solution, the oxidation currents of Ru(bpy)₃²⁺ were increased due to the catalytic homogeneous process between electrochemically generated Ru(bpy)₃³⁺ and coreactants. Because the voltammograms were measured in the presence of excess coreactants (20-fold concentration of Ru(bpy)₃²⁺), their concentration can be considered constant and the kinetic information about these systems can be evaluated by comparing the variation of the catalytic efficiency, defined as the ratio of i_s/i_s^0 [18-20]. Here, i_s^0 is the steady-state

current of $\text{Ru}(\text{bpy})_3^{2+}$ only, while i_s is the oxidation current of $\text{Ru}(\text{bpy})_3^{2+}$ in the presence of coreactant. From the voltammetric data in Fig.4, the catalytic efficiency were estimated as 5.76, 5.78, 1.65 and 3.98 for the systems of $\text{Ru}(\text{bpy})_3^{2+}/\text{TPA}$, $\text{Ru}(\text{bpy})_3^{2+}/\text{C}_2\text{O}_4^{2-}$, $\text{Ru}(\text{bpy})_3^{2+}/\text{DHA}$, and $\text{Ru}(\text{bpy})_3^{2+}/\text{H}_2\text{A}$, respectively. Lower catalytic efficiency in $\text{Ru}(\text{bpy})_3^{2+}/\text{DHA}$ system may be due to the lower electrochemical activity of DHA.

With the addition of these coreactants, light generations can be observed in a sono-ECL cell when $\text{Ru}(\text{bpy})_3^{2+}$ was oxidized at ITO electrode. ECL of $\text{Ru}(\text{bpy})_3^{2+}/\text{TPA}$ system has been described in Scheme 1. The ECL using $\text{C}_2\text{O}_4^{2-}$ as coreactant was proposed by Bard et al as is shown in Scheme 2 [18].

Scheme 2

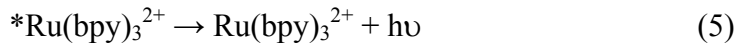
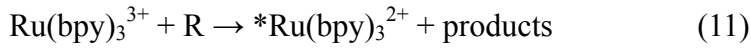
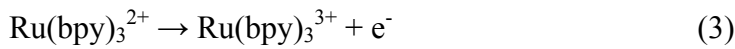


the oxidation of oxalate produces a strong reducing agent, $\text{CO}_2^{\cdot -}$, which can inject an electron into the LUMO of an oxidized $\text{Ru}(\text{bpy})_3^{3+}$ to produce an excited state $\text{*Ru}(\text{bpy})_3^{2+}$ that then emits light.

Until now, there have been few studies regarding the ECL reaction using DHA as coreactant. DHA is oxidized form of H_2A . The commercial DHA would be hydrated in aqueous solution to yield its hydration product, HDHA (hydrated bicyclic hemiketal)

[14, 21]. The anodic current observed around +0.42 V in Fig.4 (D) can be associated with the further oxidation of HDHA or DHA at a carbon fiber electrode. As the oxidation current was significantly less than the corresponding oxidative wave for H₂A, it is assumed that kinetics of the electron transfer is slow for the electrochemical oxidation of DHA or HDHA. The oxidation mechanism seems complicated, involving a series of decomposition process and the generation of some the unstable intermediates [22, 23]. We suppose that the intermediates (R) are probably reaction with Ru(bpy)₃³⁺ to produce *Ru(bpy)₃²⁺ at the electrode surface and the ECL mechanism is thus proposed as follows.

Scheme 3



The dependent of ultrasound output power on the electrolytic enhancement factor (i/i^0) as well as the ECL enhancement factor ($I_{\text{ecl}}/I_{\text{ecl}}^0$) for each coreactant were shown in Fig. 5. The electrolytic enhancement factor (i/i^0) is defined as the ratio of oxidation current density under ultrasound irradiation (i) to that observed in the stationary condition (i^0), while the ECL enhancement factor ($I_{\text{ecl}}/I_{\text{ecl}}^0$) is defined as the ratio of ECL intensity under ultrasound irradiation (I_{ecl}) to that observed in the stationary condition (I_{ecl}^0). The data in Fig.5 (A) indicate that the electrolytic enhancement factor (i/i^0) increased with the increasing of ultrasound output power, indicating that the electrolytic efficiencies were increased due to the accelerating mass transport by

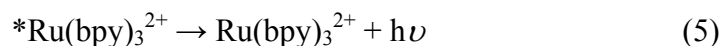
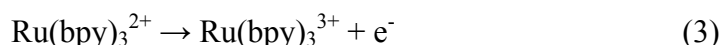
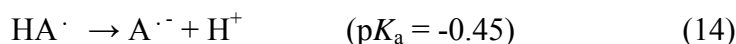
ultrasound. The difference in values of (i/i^0) can be caused by the different kinetic behavior (catalytic efficiency) of these coreactants involved in the heterogeneous or the homogenous oxidation reactions in scheme 1-3. The ECL enhancement factor $(I_{\text{ecl}}/I_{\text{ecl}}^0)$ of $\text{Ru}(\text{bpy})_3^{2+}$ was also strongly influenced by ultrasound irradiation, depending on the what coreactant was used. It can be seen in Fig.5 (B), the ECL signals increased with increasing of ultrasonic output power in $\text{Ru}(\text{bpy})_3^{2+}/\text{TPA}$ and $\text{Ru}(\text{bpy})_3^{2+}/\text{C}_2\text{O}_4^{2-}$ systems, only slight enhancement was observed in $\text{Ru}(\text{bpy})_3^{2+}/\text{DHA}$ system. The level of ECL enhancement in steady state is believed to be dependent on the catalytic efficiency of $\text{Ru}(\text{bpy})_3^{2+}$ with the intermediates of coreactant [24]. The lower enhancement factor in $\text{Ru}(\text{bpy})_3^{2+}/\text{DHA}$ system could be due to the slow electron transfer process of DHA and the lower catalytic efficiency in homogeneous reactions. The dependence of ECL enhancement factor $(I_{\text{ecl}}/I_{\text{ecl}}^0)$ on the catalytic current values obtained in steady states is shown in Fig. 6. The $(I_{\text{ecl}}/I_{\text{ecl}}^0)$ values vary linearly with catalytic current density in the systems of $\text{Ru}(\text{bpy})_3^{2+}/\text{TPA}$ and $\text{Ru}(\text{bpy})_3^{2+}/\text{DHA}$, whereas it is proportional to the square of the current density in $\text{Ru}(\text{bpy})_3^{2+}/\text{C}_2\text{O}_4^{2-}$ system. Here, the catalytic current density is defined as the oxidation current density subtracted from that contributed by $\text{Ru}(\text{bpy})_3^{2+}$ background. Theses results are in accordance with the theoretical treatment in steady state ECL reactions, proposed by Malins and Bard, respectively [16, 18]. In opposite to theses coreactants, the ECL signal in $\text{Ru}(\text{bpy})_3^{2+}/\text{H}_2\text{A}$ system was found to be suppressed greatly under the ultrasound irradiation. Apparently, some other reactions that contribute the decrease of ECL intensity, especially in the presence of ultrasound irradiation, can be involved.

3.3. Sonication induced ECL quenching in $\text{Ru}(\text{bpy})_3^{2+}/\text{H}_2\text{A}$ system

Regarding the ECL mechanism of $\text{Ru}(\text{bpy})_3^{2+}/\text{H}_2\text{A}$ system, there were different reaction

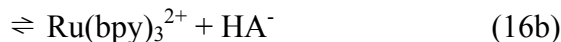
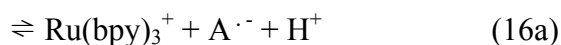
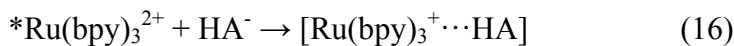
routes proposed by M. Sato and M. Zorzi, respectively [9,10]. We investigated and proposed the ECL mechanism as follows,

Scheme 4



At pH 8.8, H₂A was dissociated to form ascorbate monoanion (HA⁻) according to the reported pK_a values (pK_{a1} = 4.17, pK_{a2} = 11.57) [14]. In first electron transfer step, HA⁻ was oxidized to the ascorbate radical (HA[·]). Since HA[·] is a very strong acid (pK_a = -0.45)[25], it subsequently underwent a rapid decomposition, which led to the formation of a highly reducing species of ascorbate anion radical (A^{·-}). *Ru(bpy)₃²⁺ is thought to be produced by the energetic electron transfer between electrochemically generated Ru(bpy)₃³⁺ and A^{·-}. In our previous study, the ECL intensity was confirmed to be linearly proportional to the concentration of H₂A from 0 to 1 mM [11].

Under the ultrasound irradiation, some side reactions contributing the decrease of the ECL intensity should be taken into account. It was reported that photoluminescence of Ru(bpy)₃²⁺ can be significantly quenched by some coexisting reducing reagents [26]. Similarly, the ultrasound induced ECL quenching effect could be interpreted in terms of electron transfer (ET) route (16), where the diffusional HA⁻ species from the bulk solution served as electron donor.



This means that $*\text{Ru}(\text{bpy})_3^{2+}$ species generated at the electrode surface might be scavenged by HA^- diffused from the bulk solution. The accelerated mass transfer rate by ultrasound gave rise to an effective collision frequency between $*\text{Ru}(\text{bpy})_3^{2+}$ and HA^- and resulted in the drop of ECL intensity. The intermediate state, $[\text{Ru}(\text{bpy})_3^+ \cdots \text{HA}^{\cdot-}]$ was assumed to be formed in diffusional control process. Once the intermediate state was formed, both the decomposition reaction (16a) and the back electron transfer reaction (16b) could occur.

The ET route (16) the presence of H_2A was further examined in photoluminescence experiment. The fluorescence intensity of $10 \mu\text{M}$ $\text{Ru}(\text{bpy})_3^{2+}$ at 620 nm was found to be quenched by the addition of H_2A in a concentration range of 0 – 100 mM in 0.1 M PBS (pH 8.8), and the dependence of H_2A concentration on emission intensity obeyed the Stern-Volmer equation [27]. It thus suggested that equation (15) played a predominant role in ECL reaction at stationary condition, while the excited state $*\text{Ru}(\text{bpy})_3^{2+}$ would be scavenged by HA^- diffused from the bulk solution under ultrasound irradiation, owing to the ET quenching route.

4. Conclusions

The effect of ultrasound irradiation on $\text{Ru}(\text{bpy})_3^{2+}$ based ECL in the presence of different coreactants was studied. It was found that the ECL signals significantly increased using TPA, $\text{C}_2\text{O}_4^{2-}$ as coreactant. Only slight enhancement of was observed in $\text{Ru}(\text{bpy})_3^{2+}/\text{DHA}$ system. On the other hand, however, the ECL signal was found to be

suppressed greatly in Ru(bpy)₃²⁺/H₂A system. As the level of ECL enhancement upon ultrasound irradiation is believed to be dependent on the homogeneous chemiluminescence routes, the kinetic processes in the subsequent chemical reactions as well as the ET process in quenching reactions in Ru(bpy)₃²⁺/H₂A system were proposed in this study.

5. Acknowledgements

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Figure captions

Fig. 1. The cell designed for sono-ECL measurement.

Fig. 2. ECL responses for 0.5 mM $\text{Ru}(\text{bpy})_3^{2+}$ and 0.5 mM TPA in 0.1 M PBS (pH 8.8) at ITO electrode. Dotted line: without sonication; solid line: with sonication. Potential scan rate was 100 mV/s.

Fig. 3. Repetitive ECL measurements by pulse potential mode. The potential was stepped from 0 to +1.5 V with pulse width of 5 s. The other conditions were the same as in Fig. 2.

Fig. 4. Linear sweep voltammograms of 0.5 mM $\text{Ru}(\text{bpy})_3^{2+}$ system at carbon fiber ultramicroelectrode ($\phi 10 \mu\text{m}$) (A) in PBS (pH=8.8), and the voltammograms in the presence 10 mM each of TPA (B), $\text{C}_2\text{O}_4^{2-}$ (C), DHA(D) and H_2A (E), respectively. The dotted lines represent the voltammetric responses of each coreactant in PBS. The scan rate was 10 mV/s.

Fig. 5. Effect of the ultrasound output power on (A) current enhancement factor (i/i^0) and (B) ECL enhancement factor ($I_{\text{ecl}}/I_{\text{ecl}}^0$) in $\text{Ru}(\text{bpy})_3^{2+}$ based ECL systems using TPA(\blacktriangle), $\text{C}_2\text{O}_4^{2-}$ (\blacksquare), DHA(\bullet) and H_2A (\blacklozenge) as coreactants, respectively. The ECL measurement conditions were the same as in Fig.2, whereas the electrolytic solutions were the same as in Fig.4.

Fig. 6. Relationship between ECL enhancement factor ($I_{\text{ecl}}/I_{\text{ecl}}^0$) and catalytic current in $\text{Ru}(\text{bpy})_3^{2+}$ based ECL system when TPA(\blacktriangle), $\text{C}_2\text{O}_4^{2-}$ (\blacksquare), DHA(\bullet) and H_2A (\blacklozenge) were used as coreactants, respectively. The other conditions were the same as in Fig. 5. Inset: plot of square of catalytic current vs. $I_{\text{ecl}}/I_{\text{ecl}}^0$.

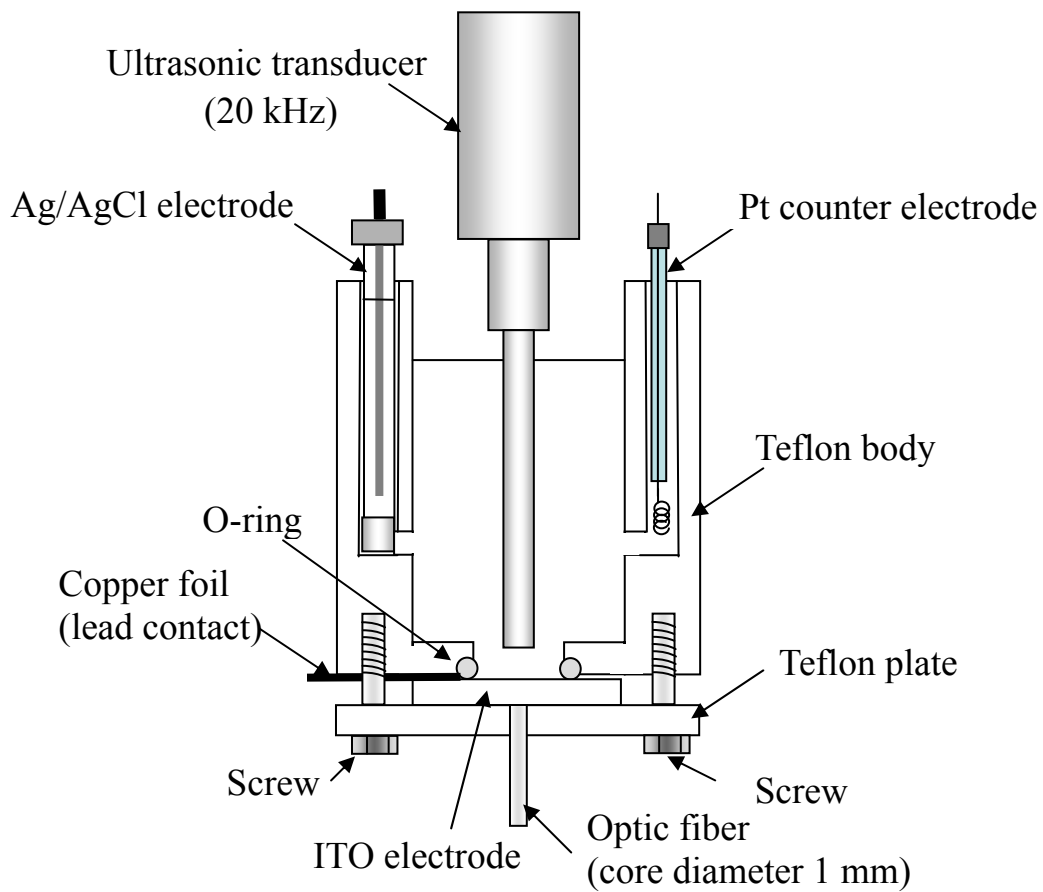


Fig. 1. F. Takahashi

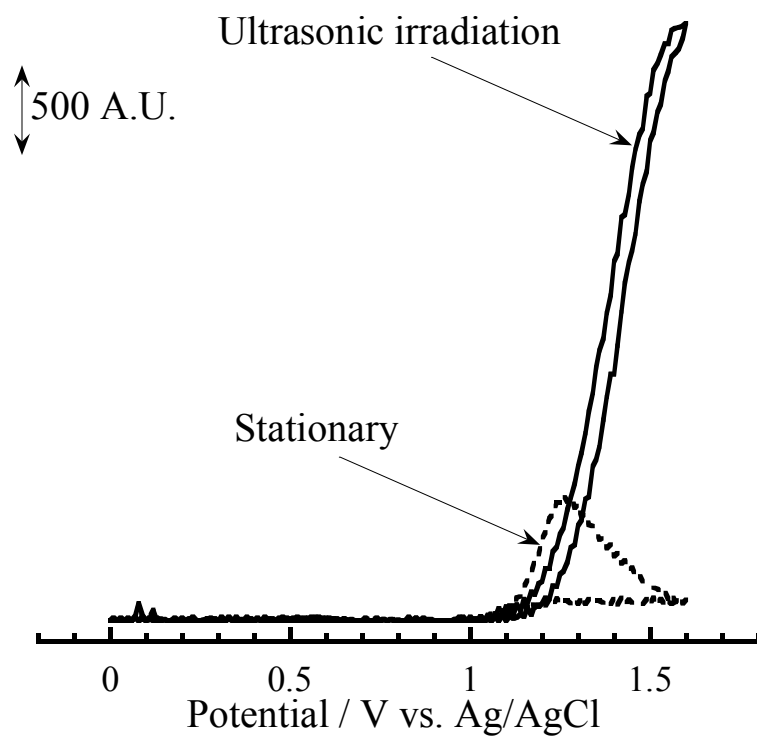


Fig. 2. F. Takahashi

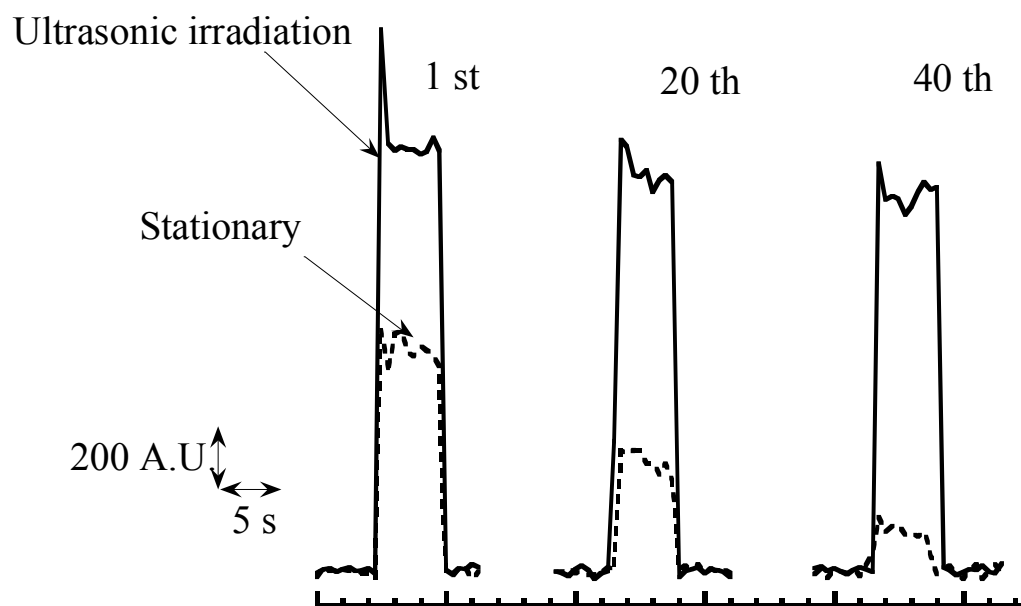
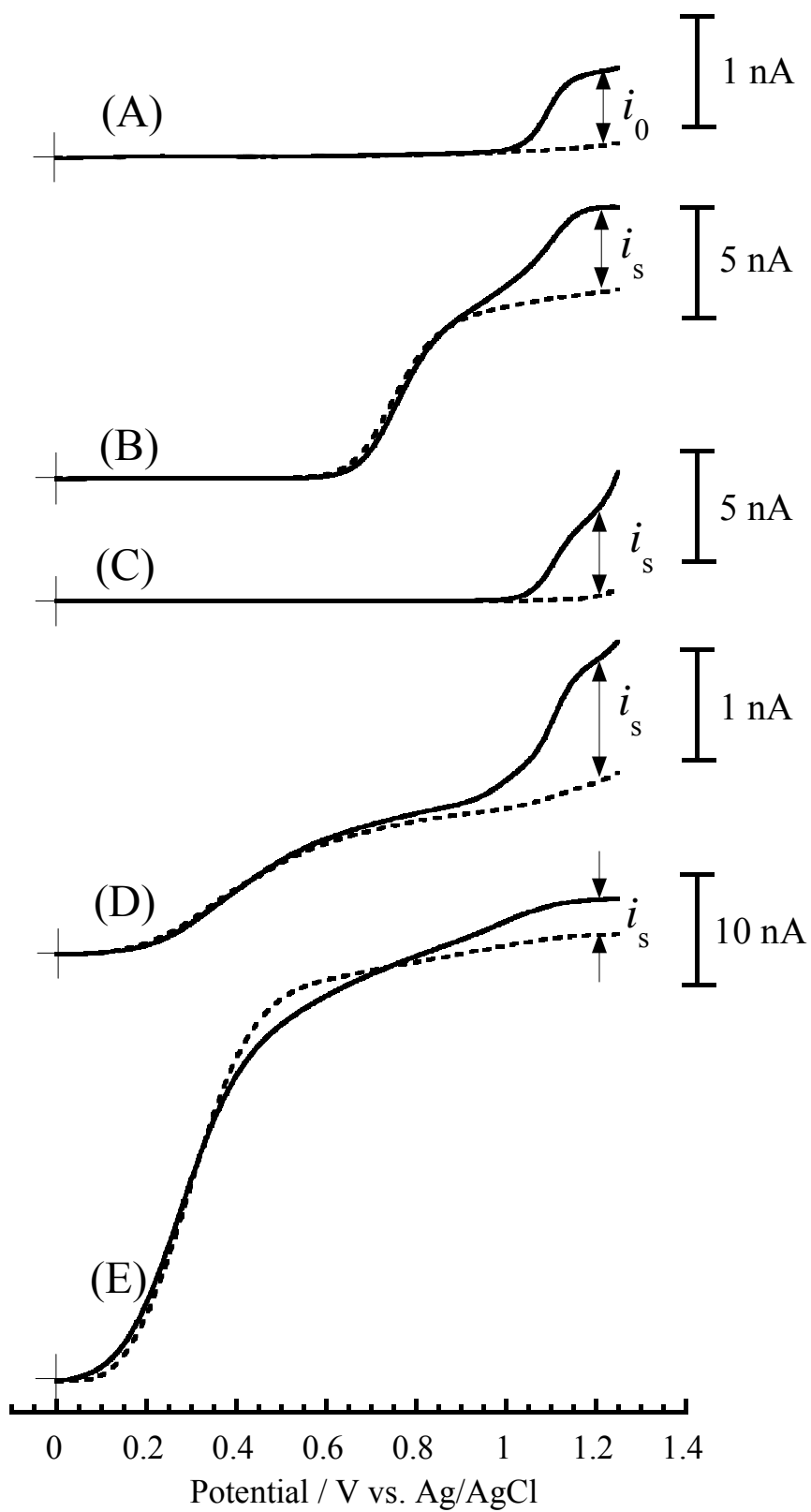


Fig. 3. F. Takahashi



F. Takahashi

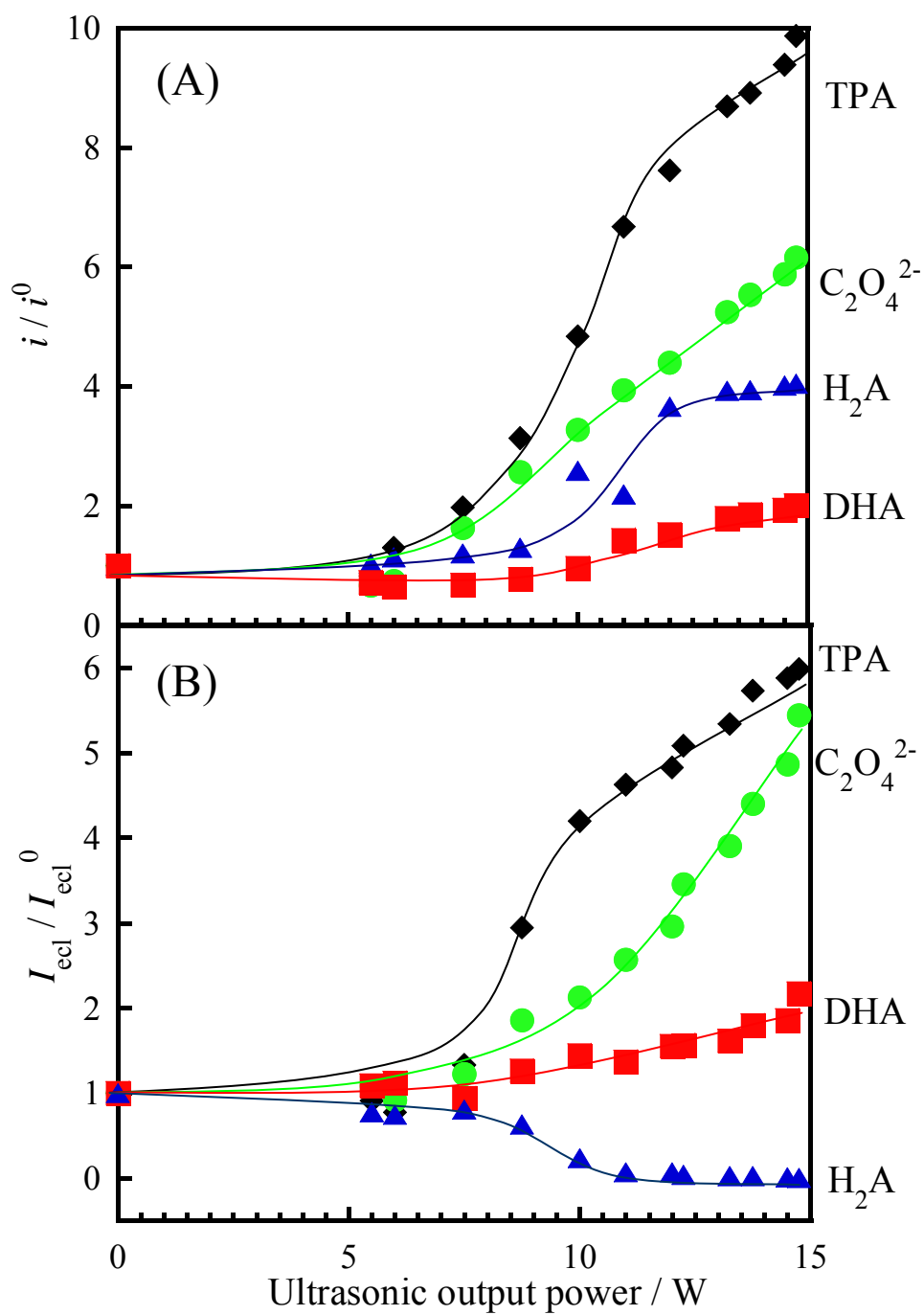


Fig. 5. F. Takahashi

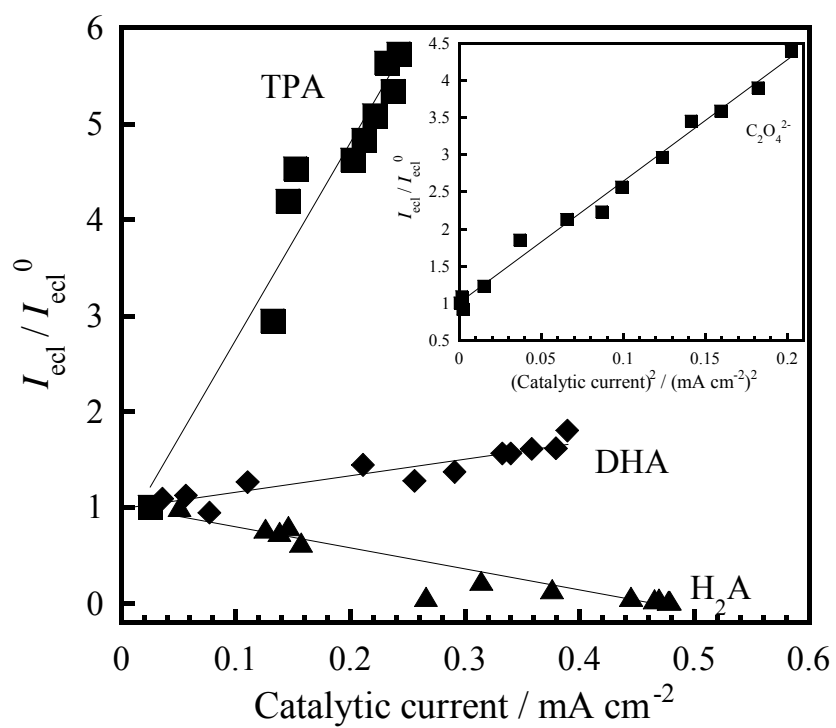


Fig. 6. F. Takahashi