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Electrochemiluminescence of lucigenin/tributylamine system in ethanol solution

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Abstract

The electrogenerated chemiluminescence (ECL) behavior of lucigenin in the presence of tributylamine (TBA) or other amines in ethanol solution at a polycrystalline gold electrode was studied under conventional cyclic voltammetric conditions. An anodic ECL peak (ECL-1 at 0.91 V vs. SCE) with two shoulders (S_1 at 0.52 V and S_2 at 1.19 V) and their counter-peaks (ECL-2 at 0.66 V, S_3 at 0.33 V, and S_4 at 1.07 V) during reversal potential scan were found in the lucigenin/TBA system. The effects of various factors such as media, material of electrode, concentration of lucigenin and TBA, atmosphere, electrolytes, and potential scan rate on ECL peaks were examined. The emitter of all ECL peaks was identified as *N*-methylacridone (NMA) by analyzing the ECL spectra. The mechanism for these ECL peaks is proposed to be due to the reactions of lucigenin with the free radical reductant such as $Bu_3N^{\bullet}$ and $Bu_2NH^{\bullet}$ electrogenerated by TBA at different potentials.

Keywords: Electrochemiluminescence; Lucigenin; Tributylamine

1. Introduction

Lucigenin (*N*,*N*′-dimethyl-9,9′-biacridinium dinitrate) is an important electrogenerated chemiluminescence (ECL) reagent. Numerous studies [1–8] concerning property, mechanism and analytical applications of lucigenin CL have been carried out since it was reported [9]. The lucigenin ECL was mainly studied at negative potential in the presence of the dissolved oxygen. In the ECL reactions, the species lucigenin radicals electro-reduced by lucigenin reacted with the dissolved oxygen [10] or the species $O_2^{\bullet-}$ electro-reduced by the dissolved oxygen [11–15] to give rise to light emission. A new ECL peak of lucigenin at a glassy carbon electrode when platinum nanoparticles were dispersed in alkaline aqueous solutions was found in the hydrogen-evolution potential region by use of conventional cyclic voltammetry (CV) when platinum nanoparticles were dispersed in alkaline aqueous solutions. The $H_{ads}Pt^0$ formed by reduction of H_2O during the hydrogen-evolution process in the presence of nano-Pt reacted with the dissolved oxygen to generate $O_2^{\bullet-}$, which followed by the reaction with lucigenin to generate light emission [16]. Besides, an anodic peak could be obtained in the lucigenin/H_2O system. The species $O_2^{\bullet-}$ and fresh atomic oxygen [O] generated by electro-oxidation of H_2O could react with lucigenin to emit light [17]. In previous work [11–17], the lucigenin ECL was initiated by the electrogenerated radicals such as lucigenin radicals electro-reduced by lucigenin, or $O_2^{\bullet-}$, fresh atomic oxygen [O], and $H_{ads}Pt^0$ electrogenerated by the dissolved oxygen or H_2O. However, the initiation of the lucigenin ECL has not been reported by other reactants than lucigenin, oxygen, and H_2O.

In ($Ru(bpy)_3{}^{2+}$)/tripropylamine (TPA) system, TPA could be electro-oxidized to $Pr_3N^{\bullet}$, which was a very activated free radical reductant and could react with $Ru(bpy)_3{}^{3+}$ or $Ru(bpy)_3{}^{2+}$ to yield light emission [18–22]. Papadopoulos et al. studied the photo- and radiochemiluminescence of lucigenin with photo- or radiooxygenated amines in 1999 [23]. *N*,*N*′-dimethyl-9,9′-biacrylidene (DBA) was considered as the primary emitter. Therefore, it was deduced that the radicals electro-oxidized by amines might induce the lucigenin ECL.

In this paper, the ECL behaviors of lucigenin with TBA and other amines were explored under cyclic voltammetric conditions. An anodic ECL peak with two shoulders and their counter-peaks during reversal potential scan were found in the lucigenin/TBA system. The effects of various factors such as

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media, material of electrode, concentration of lucigenin and TBA, atmosphere, electrolytes, and potential scan rate on ECL peaks were examined. Possible mechanism for each ECL peak has been proposed based on the experiments above.

2. Experimental

2.1. Apparatus and procedures

2.1.1. ECL and EC measurements

The ECL and electrochemistry (EC) detections were performed with a homemade ECL–EC system, which contained a model CHI730B electrochemical work station (Chenhua Inc., Shanghai, China), an H-type electrochemical cell (homemade), a model IFFM-D CL analyzer (Ruimai Electronic Technology Co., Ltd., Xi'an, China) and a computer. During the measurements, the potential was applied to the working electrode via the electrochemical work station, and ECL signal was generated.

The H-type ECL cell with a gold working electrode (6.0 mm × 7.0 mm), a platinum wire auxiliary electrode, and a silver quasi-reference electrode (AgQRE) was constructed as described previously [24,25]. The AgQRE was used due to simplicity for cell construction and quick potential response. Although the potential of the AgQRE was found to be essentially stable during an experiment, the difference between the AgQRE and the saturated calomel electrode (SCE), $\Delta E = E_{\mathrm{AgQRE}} - E_{\mathrm{SCE}}$ in different solutions was measured for potential calibration. The H-type ECL cell was separated into working compartment and auxiliary compartment by a piece of porous glass filter, which was used to prevent solution mixing.

Before measurement, the working electrode was polished carefully with a 4000 P silicon carbide abrasive paper and chamois leather, rinsed with ethanol, and dried with filter paper. Then, the electrode was cycled between −0.2 and 1.0 V (vs. SCE) in 0.5 mol/L sulfuric acid at a scan rate of 100 mV/s. This potential cycling has been continued until a reproducible voltammogram for gold oxide formation/reduction was obtained, indicating a clean surface of gold electrode was obtained. The electrode was again rinsed with redistilled water and cleaned in absolute ethanol in an ultrasonic bath.

A 2.5 mL portion of working solution contained 1.0×10^{-4} mol/L lucigenin and 1.0×10^{-2} mol/L amine was added to the working compartment of the H-type ECL cell and an appropriate amount of blank solution without lucigenin was transferred into the auxiliary compartment. If not mentioned additionally, 0.10 mol/L $NaClO_4$ was used as an electrolyte. Before each measurement, the working solution was preserved in the cell for about 10 min in order to avoid the influence of weak CL from the reaction between lucigenin and amine. To provide nitrogen atmosphere condition, nitrogen was bubbled through the solutions for 10 min in both compartments of the cell, and the gas flow was maintained over the solution during experiments. When the potential was applied to the working electrode, ECL was generated. The curves of ECL intensity vs. applied potential (I_{ECL}–E) and the curves of current vs. applied potential (i.e. CV) were recorded simultaneously.

2.1.2. Optical measurements

The ECL spectra of this system were measured on a model F-7000 Fluorescence Spectrophotometer (Hitachi, Japan) with the excitation light source being turned off. UV–vis spectra were measured on a model UV-5401 PC Spectrophotometer (Shimadzu, Japan).

For the measurement of the ECL spectra of the peaks at different potentials under CV conditions, the time needed for recording an ECL spectrum was about 2 s, and the adopted potential ranges for the measurement of ECL-1 and ECL-2 were 0.89–0.93 and 0.68–0.64 V, respectively. In these potential ranges, the ECL intensity did not change significantly with the potential.

All experiments were carried out at ambient room temperature.

2.2. Chemicals and solutions

Absolute ethanol (>99.9%, GR) was purchased from YongHua Fine Chemistry Co., Ltd. (Jiangsu, China). Lucigenin and tetrabutyl ammonium perchlorate ($TBAClO_4$, >99%, electrochemical grade) were obtained from Fluka Chemie AG (Switzerland). Sodium perchlorate (analytical grade) was purchased from Beijing Reagents (Beijing, China). Tetrabutyl ammonium tetrafluoroborate ($TBABF_4$, Zhejiang, China) was purified by recrystallization for three times from ethyl acetate and then dried in a vacuum oven at 85–100 °C. Tributylamine (TBA) and tripropylamine (TPA) (GR) were purchased from ACROS Organics (New Jersey, USA). Triethylamine (TEA), triethanolamine, ethylenediamine, diethylamine, *n*-propylamine, *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline, phenylamine, cyclohexylamine, *N*,*N*-dimethylformamide (DMF), and hexamethylene tetramine (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Amino acids were purchased from Kangda Reagent (Shanghai, China). Oxygen and nitrogen used during experiments were highly purified nitrogen (>99.999%) and oxygen (>99.99%).

A 1.0×10^{-3} mol/L stock solution of lucigenin was prepared by dissolving lucigenin in absolute ethanol. 0.10 mol/L stock solutions of amines such as TBA, TPA, and TEA, etc. were prepared by dissolving the amines in absolute ethanol. Working solutions of the reagents were prepared by diluting the stock solutions with ethanol.

3. Results and discussion

3.1. Cyclic voltammogram and ECL of lucigenin/TBA system in ethanol solution

The cyclic voltammogram (CV) and I_{ECL}–E curve of the lucigenin/TBA system in an air saturated ethanol solution are shown in Fig. 1. In the CV (a), three anodic peaks (cvp1, cvp2, cvp3) were found at 0.51, 0.83, and 1.25 V (vs. SCE), respectively. Cvp1 and cvp2 could not be obtained in the solution without TBA, indicating that they were related to the oxidation of TBA. Cvp3 could also be observed in the solution without lucigenin and TBA as shown in Fig. 1 and the inset. Therefore, it was not

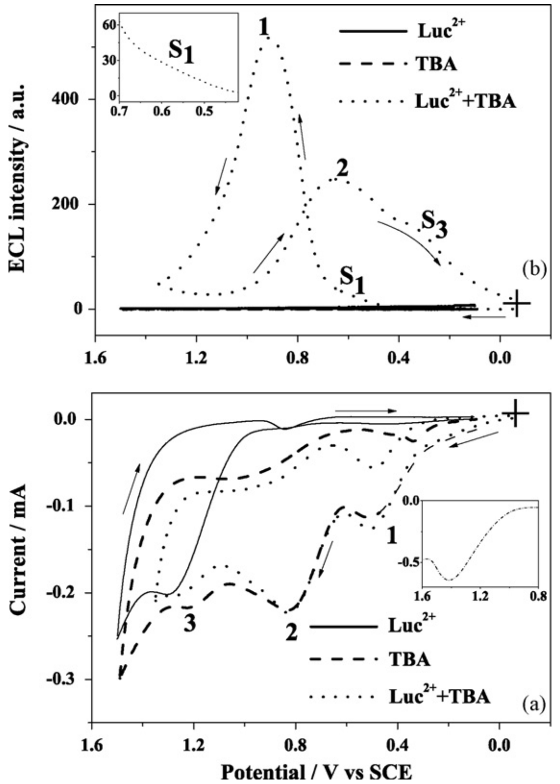

Fig. 1. CV (a) and I_{ECL}–E curves (b) of lucigenin/TBA system in EtOH solution. Scan rate: 20 mV/s. Dot line: 1.0×10^{-4} mol/L lucigenin, 1.0×10^{-2} mol/L TBA, 0.10 mol/L $NaClO_4$. Solid line: 1.0×10^{-4} mol/L lucigenin, 0.10 mol/L $NaClO_4$. Dash line: 1.0×10^{-2} mol/L TBA, 0.10 mol/L $NaClO_4$. Inset in (a) shows the CV curve of the blank ethanol solution without lucigenin and TBA from 0.8 V to 1.6 V. 0.10 mol/L $TBAClO_4$ was used as the electrolyte. Inset in (b) shows the enlarged I_{ECL}–E curves from 0.42 V to 0.70 V. If not mentioned additionally, all high voltages applied to the PMT in the ECL experiments were maintained at −400 V.

related to lucigenin and TBA. In our previous work, the peak was considered as the electro-oxidation of ethanol, which was also reported in the literature [26].

In I_{ECL}–E curve (Fig. 1(b)), corresponding to cvp1 and cvp2, ECL-1 (0.91 V vs. SCE) with a shoulder S_1 (0.52 V) was obtained. On the reverse scan from 1.35 V, ECL-2 and a shoulder S_3 were found at 0.66 and 0.33 V, respectively.

S_1 and ECL-1 were related to cvp1 and cvp2 and could not be observed in the solution without either TBA or lucigenin. Therefore, we concluded that TBA and lucigenin were both necessary species in the ECL process. The formation mechanism of these peaks will be discussed later.

It was reported that weak CL emission could be observed when lucigenin was mixed with some amines [6]. However, under the ECL experimental conditions, no CL signals could be detected. Actually, the intensity of ECL was about 2–3 orders higher than the CL intensity.

3.2. CV and ECL behaviors of lucigenin/TBA system under a nitrogen and an air atmosphere

To decreases the amount of dissolved oxygen, nitrogen is bubbled. Fig. 2 shows the CVs and I_{ECL}–E curves of lucigenin/TBA in ethanol solution under a nitrogen atmosphere. Compared with the CV peaks and ECL peaks under an air atmosphere, the intensity of ECL-1 and ECL-2 decreased under a nitrogen atmosphere. These results indicate that ECL-1 and ECL-2 were dependent on oxygen. The CV peaks did not change significantly.

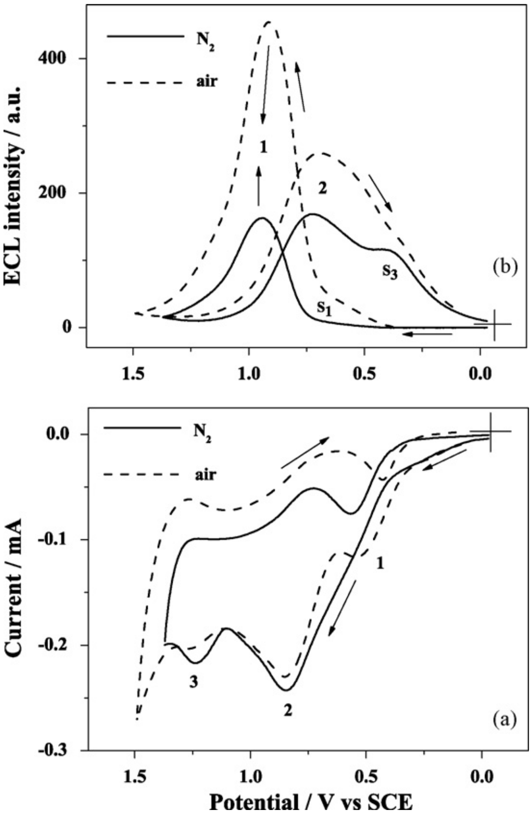

Fig. 2. CV (a) and I_{ECL}–E curves (b) of lucigenin/TBA system in N_2 and air saturated EtOH solution. Scan rate: 20 mV/s. Lucigenin: 1.0×10^{-4} mol/L, TBA: 1.0×10^{-2} mol/L, $NaClO_4$: 0.10 mol/L. Solid line: N_2 saturated solution. Dash line: air saturated solution.

3.3. Effect of supporting electrolyte

CVs and I_{ECL}–E curves of lucigenin/TBA system in ethanol solution containing various electrolytes such as $TBAClO_4$, $TBABF_4$, and $NaClO_4$, respectively, are shown in Fig. 3. Cvp1 almost vanished when $TBABF_4$ was used as a supporting electrolyte. As a result, S_1 was also vanished in such chemical conditions. ECL-1 and ECL-2 could be obtained in all tested electrolytes.

3.4. Effect of electrode material

CVs and I_{ECL}–E curves of lucigenin/TBA system in ethanol solution at glass carbon (GC) and platinum (Pt) electrodes are shown in Fig. 4. Cvp1 was difficult to be observed at GC and Pt electrodes. Cvp2 could be obtained at all the tested electrodes. In I_{ECL}–E curves, S_1 could not be obtained at GC and Pt electrodes as it was related to cvp1. Thus, the gold electrode played an important role in the formation of cvp1 and S_1.

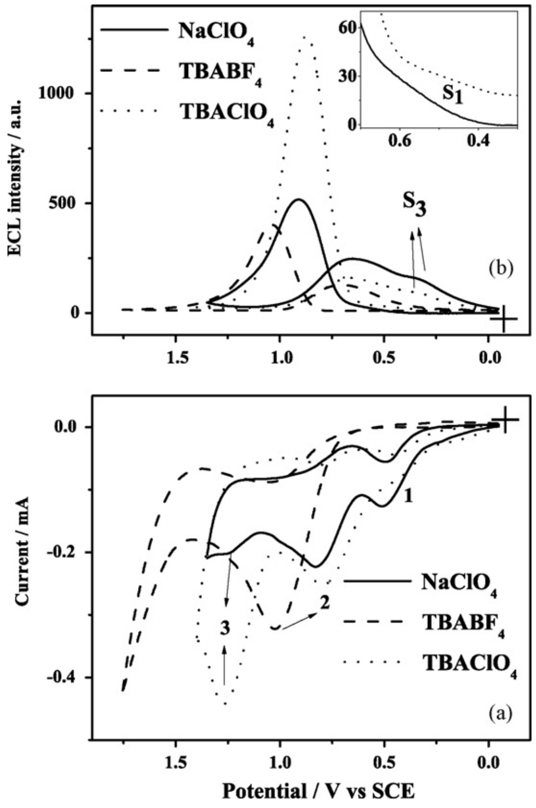

Fig. 3. CV (a) and I_{ECL}–E curves (b) of lucigenin/TBA system in EtOH solution with various electrolytes. Scan rate: 20 mV/s. Lucigenin: 1.0×10^{-4} mol/L, TBA: 1.0×10^{-2} mol/L. Solid line: $NaClO_4$: 0.10 mol/L. Dash line: 0.10 mol/L $TBABF_4$, Dot line: 0.10 mol/L $TBAClO_4$.

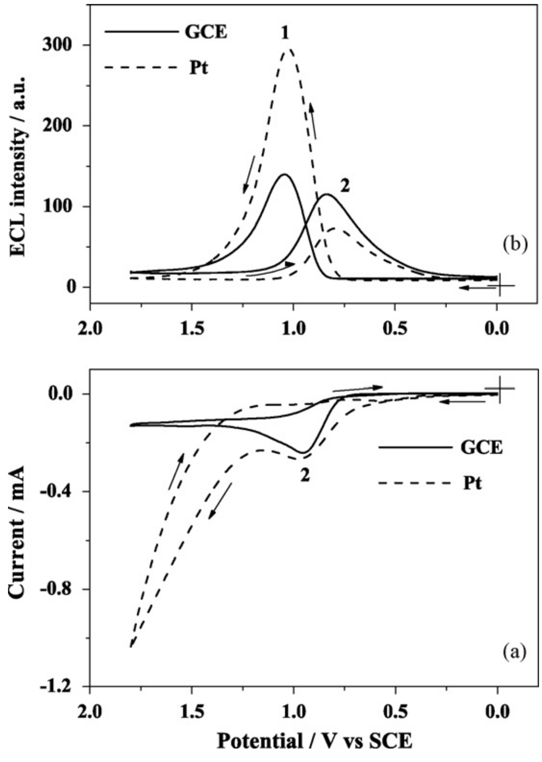

Fig. 4. CV (a) and I_{ECL}–E curves (b) of lucigenin/TBA system at a GC (solid line) and a Pt (dash line) electrode. Scan rate: 20 mV/s. Lucigenin: 1.0×10^{-4} mol/L, TBA: 1.0×10^{-2} mol/L. $NaClO_4$: 0.10 mol/L.

It was reported [27,28] that oxyanions such as ClO_4^- could be specifically adsorbed at Au electrode and played a major role in the initial stages of oxidation of the metal. Burke and Lyons [29] proposed that premonolayer oxidation might occur at the gold electrode and the product could catalyze the oxidation of TPA at a more negative potential. Our experimental results suggested that cvp1 was related to TBA and only occurred at Au electrode in the solution containing ClO_4^-. As the trialkylamines had the similar physicochemical and electrochemical properties [30], we deduced that Au electrode could be oxidized to form a premonolayer in the presence of ClO_4^-, which also catalyzed the electro-oxidation of TBA. Therefore, cvp1 was the catalyzed electro-oxidation of TBA. However, the oxidation current of gold could hardly be observed in this case. We presumed that the amount of the anodic oxide was too little to cover all the gold surface. Therefore, only a small part of TBA was oxidized by virtue of the catalysis of the oxide films. Most of TBA was directly oxidized to form the cvp2 on the gold surface because it was only related to TBA, just as for the direct oxidation of TPA described in the literature [22].

3.5. Cyclic voltammogram and ECL of lucigenin/TBA system in DMSO solution

CVs and I_{ECL}–E curves of lucigenin/TBA system in DMSO solution are shown in Fig. 5. S_1 could not be found in DMSO

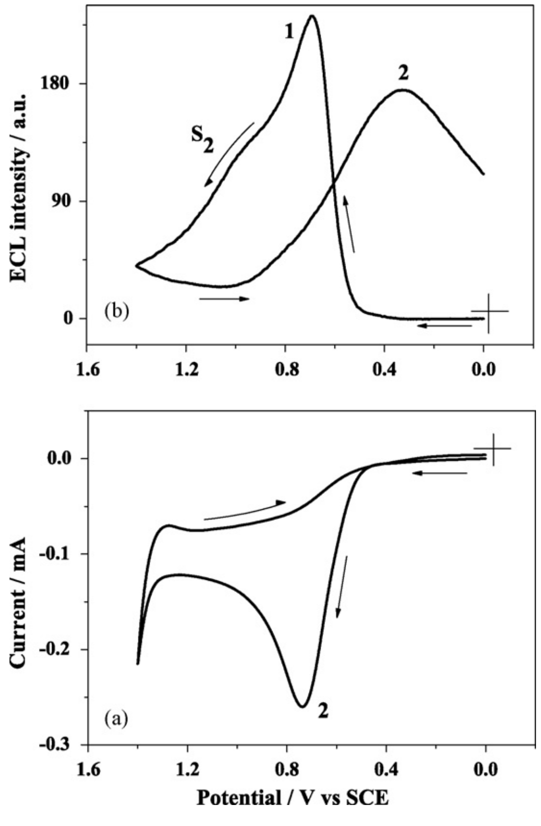

Fig. 5. CV (a) and I_{ECL}–E curves (b) of lucigenin/TBA system in DMSO solution. Scan rate: 20 mV/s. Lucigenin: 1.0×10^{-4} mol/L, TBA: saturated DMSO solution ($<1.0 \times 10^{-2}$ mol/L). $NaClO_4$: 0.10 mol/L.

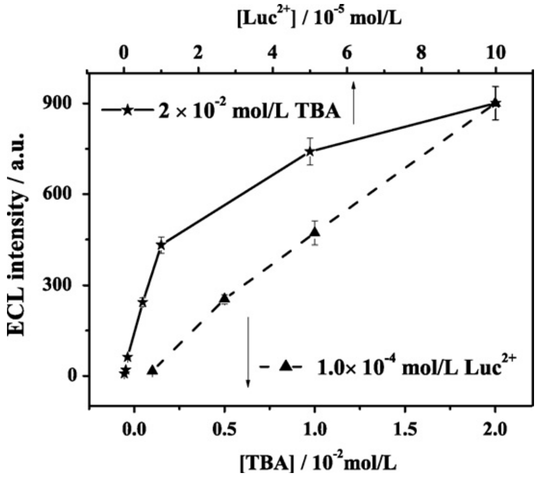

Fig. 6. The relationship between ECL intensity and TBA/lucigenin concentration. Scan rate: 20 mV/s. $NaClO_4$: 0.10 mol/L. triangle: 1.0×10^{-4} mol/L lucigenin, pentagon: 2.0×10^{-2} mol/L TBA.

solution as for cvp1 disappeared. It might be due to the premonolayer oxidation process was hard to proceed in such a chemical condition, or corresponded to the overlapping between cvp1 and cvp2. In order to clarify this, further researches should be done. Besides, a shoulder named as S_2 emerged at the potential more positive than ECL-1.

3.6. Effect of tributylamine and lucigenin concentration

The effect of TBA and lucigenin concentration on the ECL behavior was tested. There was no light emission when the concentration of either TBA or lucigenin was zero and the intensity of ECL-1 and ECL-2 increased with an increase in either TBA or lucigenin concentration, showing that ECL-1 and ECL-2 depended on TBA and lucigenin. Fig. 6 shows the correlation between ECL-1 intensity and the concentration of TBA and lucigenin.

When the concentration of lucigenin was chosen as 5.0×10^{-6} mol/L, the shoulder S_2 (1.19 V) obtained in DMSO solution could also be observed here with its counter-peak S_4 (1.07 V) at Au electrode as shown in Fig. 7(a). The shoulders could also be obtained at GC and Pt electrode (Fig. 7(b)), just as for the Au electrode. The results revealed that S_2 and S_4 were not related to either the solvent or the material of electrode.

3.7. ECL spectra of various peaks

The ECL spectra of ECL-1 and ECL-2 were analyzed under the same experimental conditions as for Fig. 1, as shown in Fig. 8. The results showed that the maximum emission of the ECL peaks was at about 442 nm, which corresponded to the light emission of *N*-methylacridone (NMA) [3]. Therefore, it was concluded that both the ECL peaks were initiated by the lucigenin reaction.

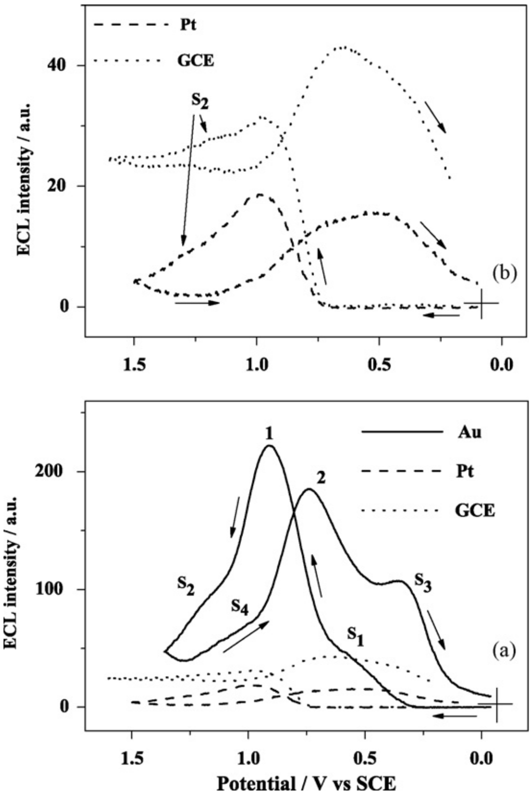

Fig. 7. I_{ECL}–E curves of lucigenin/TBA system at a gold (solid line), a Pt (dash line) and a GC (dot line) electrode. Scan rate: 20 mV/s. Lucigenin: 5.0×10^{-6} mol/L, $NaClO_4$: 0.10 mol/L. (b) shows the enlarged I_{ECL}–E curves at a Pt and a GC electrode.

3.8. ECL between different amines and lucigenin

Various amines were used as the reactant instead of TBA in the ECL system as shown in Table 1. It was found that the ECL intensity decreased either as the length of aliphatic substituents decreased, i.e. TBA > TPA > TEA, or as the number of aliphatic chains decreased, i.e. TEA > diethylamine > *n*-propylamine. Furthermore, it should be pointed out that the ECL

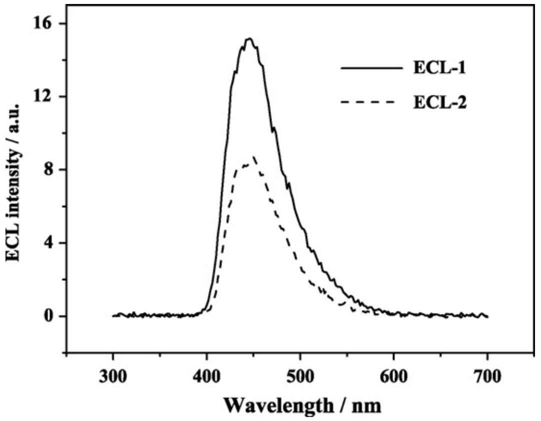

Fig. 8. The spectra of ECL-1 and ECL-2 under Fig. 1 experimental conditions. Lucigenin: 1.0×10^{-4} mol/L, TBA: 1.0×10^{-2} mol/L, $NaClO_4$: 0.10 mol/L. ECL-1: 0.89–0.93 V, ECL-2: 0.68–0.64 V.

Table 1
Lucigenin ECL in the presence of various compounds

Compounds	ECL intensity (a.u.)	Compounds	ECL intensity (a.u.)
TBA	472 ± 39	*n*-Propylamine	0.4 ± 0.1
TPA	430 ± 30	Triethanolamine	6.6 ± 0.5
TEA	129 ± 15	*N*,*N*-dimethylaniline	ND
Proline	ND	*N*,*N*-diethylaniline	ND
Alanine	ND	Phenylamine	ND
Arginine	ND	Cyclohexylamine	ND
Cysteine	ND	Hexamethylene tetramine	ND
Ethylenediamine	11 ± 1	DMF	ND
Diethylamine	1.2 ± 0.3		

peak of diethylamine emerged at ca. 1.22 V, which was very close to the potential of S_2.

3.9. Mechanism of ECL of lucigenin/TBA system

The ECL spectra demonstrated that the emitter of ECL-1 and ECL-2 was NMA. Therefore, both the ECL peaks were initiated by the reactions of lucigenin with species electrogenerated at different potentials.

Cvp2 was due to the direct electro-oxidation of TBA and initiated the emission of ECL-1. S_1 was involved in electrochemical process cvp1. In Section 3.4 we concluded that cvp1 was the catalyzed oxidation peak of TBA. Thus, S_1 might undergo the same process with ECL-1. In the $(Ru(bpy)_3{}^{2+})$/TPA system, the electro-oxidation of TPA was studied intensively and reasonable mechanism has been proposed [18–22]. The species $Pr_3N^{\bullet}$ generated by the electro-oxidation of TPA was a free radical reductant. As a trialkylamine, TBA might have the similar electrochemical and physicochemical properties to TPA [30] and the electrogenerated species $Bu_3N^{\bullet}$ might reduce the lucigenin to $Luc^{\bullet+}$, which further generated chemiluminescence in the presence of oxygen. Thus, we proposed the process of cvp2 and ECL-1 as in Scheme 1. Cvp1 and S_1 might proceed as in Scheme 1 as well with the catalysis of the Au premonolayer.

S_2 could be observed at all the tested electrodes in EtOH solution, and also occurred in DMSO solution. It was reported that dipropylamine, the electro-oxidation product of TPA, could also be electro-oxidized to form free radical reductant $Pr_2N^{\bullet}$ [19]. The radical might also be able to reduce lucigenin to generate chemiluminescence in the presence of oxygen. In Section 3.8, we also mentioned that the ECL peak potential of diethylamine/lucigenin system was very close to the value of S_2. Therefore, S_2 might correspond to the ECL process between dibutylamine and lucigenin.

ECL-1:

$$\mathrm{Bu_3N - e \rightarrow Bu_3N^{\bullet+}}$$

$$\mathrm{Bu_3N^{\bullet+} \xrightarrow{-H^+} Bu_2N^{\bullet}CHCH_2CH_2CH_3}$$

$$\mathrm{Bu_2N^{\bullet}CHCH_2CH_2CH_3 + Luc^{2+} \rightarrow Luc^{\bullet+} + Bu_2N^{+}CHCH_2CH_2CH_3}$$

$$\mathrm{Bu_2N^{\bullet}CHCH_2CH_2CH_3 + O_2 \rightarrow O_2^{\bullet-} + Bu_2N^{+}CHCH_2CH_2CH_3}$$

$$\mathrm{Luc^{\bullet+} + O_2^{\bullet-} \rightarrow Luc(OO) \rightarrow NMA^* + NMA}$$

$$\mathrm{NMA^* \rightarrow NMA} + h\nu$$

Scheme 1.

$$\mathrm{Bu_2NH - e \rightarrow Bu_2NH^{\bullet+}}$$

$$\mathrm{Bu_2NH^{\bullet+} \xrightarrow{-H^+} BuNH^{\bullet}CHCH_2CH_2CH_3}$$

$$\mathrm{BuNH^{\bullet}CHCH_2CH_2CH_3 + Luc^{2+} \rightarrow Luc^{\bullet+} + BuNH^{+}CHCH_2CH_2CH_3}$$

$$\mathrm{BuNH^{\bullet}CHCH_2CH_2CH_3 + O_2 \rightarrow O_2^{\bullet-} + BuNH^{+}CHCH_2CH_2CH_3}$$

$$\mathrm{Luc^{\bullet+} + O_2^{\bullet-} \rightarrow Luc(OO) \rightarrow NMA^* + NMA}$$

$$\mathrm{NMA^* \rightarrow NMA} + h\nu$$

Route-2 corresponding to DBA (A):

$$\mathrm{Bu_2N^{\bullet}CHCH_2CH_2CH_3 + Luc^{2+} \rightarrow Luc^{\bullet+} + Bu_2N^{+}CHCH_2CH_2CH_3}$$

$$\mathrm{Bu_2N^{\bullet}CHCH_2CH_2CH_3 + Luc^{\bullet+} \rightarrow DBA(A) + Bu_2N^{+}CHCH_2CH_2CH_3}$$

$$\mathrm{DBA(A) + Luc^{2+} \xrightarrow{O_2} Luc(OO) \rightarrow NMA^* + NMA}$$

$$\mathrm{NMA^* \rightarrow NMA} + h\nu$$

Scheme 2.

In our previous work [11], we found that lucigenin could be reduced to DBA in EtOH solution at ca. −0.39 V ($E_{Luc^{2+}/DBA} = -0.39$ V vs. SCE), and the value of $E^0_{Pr_2N^+CHCH_2CH_3/Pr_3N^{\bullet}}$ was reported to be about −1.7 V vs. Ag/AgCl [20]. Thus, the process that $Pr_3N^{\bullet}$ reacted with Luc^{2+} was thermodynamically feasible. As trialkylamines had the similar physicochemical and electrochemical properties [30], we concluded that radical $Bu_3N^{\bullet}$ generated in Eq. (2) reduced lucigenin to DBA was thermodynamically feasible. DBA had two structures and the unstable form DBA (A) could react with lucigenin and initiate chemiluminescence in the presence of oxygen [31]. Therefore, S_2 could also proceed through this route.

The two routes of S_2 are proposed as in Scheme 2.

We have proposed that the ECL counter-peaks might be observed as long as one of the ECL reactants was the intermediate species during continuous electrochemical reactions [32]. In the E-E/C reaction mechanism, accumulation and consumption model could explain the appearance of counter-peaks. It was believed that ECL-2 was the counter-peak of ECL-1. In our experiments, $Bu_3N^{\bullet}$ was generated during the electro-oxidation of TBA and could be further electro-oxidized to $Bu_2NH^{\bullet}$ as reported [19]. At lower potential than the cvp2, $Bu_3N^{\bullet}$ was accumulated and initiated the ECL-1. The accumulation was the dominant effect and the ECL intensity increased during this process. When higher potential was applied, $Bu_3N^{\bullet}$ was further oxidized. Thus, the $Bu_3N^{\bullet}$ was consumed and the ECL intensity decreased. In this case, the consumption effect dominated the process. On the reversal scan, the consumption decreased and the accumulation increased with the decrease of the potential. The reaction rate of $Bu_3N^{\bullet}$ with Luc^{2+} increased and the ECL intensity first increased and then decreased owing to the decrease of $Bu_3N^\bullet$ with the further decrease of the potential, leading to the formation of ECL-2. ECL-2, S_3, and S_4 always emerged and changed with ECL-1, S_1, and S_2 under all the tested conditions. Hence, we concluded that ECL-2, S_3, and S_4 were the counter-peaks of ECL-1, S_1, and S_2, respectively.

4. Conclusion

In the lucigenin/TBA system, the ECL behavior was studied. An anodic ECL peak with two shoulders was found. ECL-1 and S_1 were supposed to be the light emission of lucigenin with the species electrogenerated from TBA. The further reaction of intermediates such as dibutylamine and DBA with lucigenin may lead to the formation of S_2. ECL-2, S_3 and S_4 were determined as the counter-peak of ECL-1, S_1 and S_2, respectively, and followed the same ECL mechanism as their counter-peak. Moreover, ECL behaviors of lucigenin in the presence of other amines such as TPA and TEA were also examined. The results show that ECL also could occur. The present work provides a new way to design the lucigenin ECL reaction, which may be found the applications in the future.

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