



Electrogenerated chemiluminescence method for the determination of riboflavin at an ionic liquid modified gold electrode

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ARTICLE INFO

Article history:

Received 11 March 2010
Received in revised form 27 August 2010
Accepted 29 September 2010

Keywords:

Electrogenerated chemiluminescence
Riboflavin
Lucigenin
Room temperature ionic liquids

ABSTRACT

A highly sensitive electrogenerated chemiluminescence (ECL) method for the determination of riboflavin was developed based on the enhancement of ECL intensity of lucigenin at room temperature ionic liquids (RTILs) modified gold electrode. RTILs modified gold electrode exhibited excellent electrochemical and ECL property to lucigenin system and the ECL intensity of lucigenin was greatly enhanced by riboflavin. The characterization of the RTILs modified electrode and the attractive performance of the sensitive ECL method for the determination of riboflavin were investigated. Under the optimized conditions, the ECL intensity was directly proportional to the concentration of riboflavin in the range from 5.0×10^{-10} g/mL to 1.0×10^{-8} g/mL with the detection limit of 1×10^{-10} g/mL. The method has been applied to the determination of riboflavin in the pharmaceutical preparations with satisfactory recovery from 96% to 101%. This work demonstrates that the incorporation of ECL method with RTILs modified electrode is a promising strategy for the determination of organic compounds with high sensitivity and good reproducibility.

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1. Introduction

Riboflavin (vitamin B₂) is the water-soluble B-group vitamin and is essential in the diet for the metabolism of amino acids and for the maintenance of body cell. Riboflavin deficiency is associated with eye lesions, skin disorders and cellular growth. The determination of riboflavin has appeared especially attractive and a variety of techniques have been utilized to the determination of riboflavin such as fluorescence [1], electrochemistry [2], HPLC [3], chemiluminescence (CL) [4,5] and electrogenerated chemiluminescence techniques [6,7]. Electrogenerated chemiluminescence (also called electrochemiluminescence and abbreviated ECL) involves the generation of species at electrode surfaces that then undergo electron-transfer reactions to form excited states that emit light [8]. ECL technique has been received considerable attention during the past several decades due to simplified optical setup, very low background signal, and good temporal and spatial control [9]. An ECL method for the determination of riboflavin was reported based on the enhancement ECL of riboflavin at poly(lyminol)-modified sensor in the alkaline solution. A detection limit for riboflavin was 8.3×10^{-8} M [7]. However, this method suffered from the unstable ECL signal due to the photochemical reaction and the instability of riboflavin in alkaline solution. Our group has developed

an ECL method for the determination of riboflavin based on the enhancement effect of riboflavin on the lucigenin ECL at a platinum electrode in a neutral aqueous solution [6]. Despite this, to develop sensitive and reproductive method for the determination of riboflavin is also the goal of analyst.

ECL usually occurs at the surface of electrode or in the solution adjacent to the electrode, therefore adjusting the position of electrode or changing the material of electrode can always improve the behavior of ECL system [10]. Recently, room temperature ionic liquids (RTILs) have attracted intensive interest in electrochemistry because of their unique chemical and physical properties such as high chemical and thermal stabilities, a relatively wide potential window and high ionic conductivity [11]. At RTILs modified electrode, good conductivity and good microenvironment have been obtained for the determination of H₂O₂, oxygen, or trichloroacetic acid [12–16]. The effect of room temperature ionic liquids on ECL has also been exploited recently. RTILs has been used both as supporting electrolytes, as additives to aqueous solvents in ECL detection method [17,18], as binder for ECL carbon paste electrode [19–21] and as additives to modify electrode [22]. For example, ionic liquids have been used as electrolytes for the turn-on time of electroluminescent devices based on the iridium complex [17] and as additives in aqueous solvents for detection of tris(2,2'-bipyridyl)ruthenium(II) (Ru(bpy)₃²⁺) by the an enhanced ECL efficiency [18]. Chen et al. reported an electrochemiluminescent sensor for methamphetamine hydrochloride based on multiwall carbon nanotube/ionic liquid composite electrode [22]. Coupling of

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multiwall carbon nanotubes with ionic liquid facilitate the transfer of electrons, and improve the electrochemical character and enlarge the active surface area at the present composite electrode. When $\text{Ru}(\text{bpy})_3^{2+}$ is immobilized in this composite electrode, which display high sensitivity and good stability and reproducibility.

Lucigenin (N, N'-dimethyl-9, 9'-biacridinium dinitrate) is one kind of acridinium ester and numerous studies concerning the mechanism of lucigenin chemiluminescence have been carried out since it is reported in 1935 by Gleu and Petsch [23]. As ECL is advantageous over CL, the ECL of lucigenin has been investigated in aqueous and non-aqueous media at different electrodes and the mechanism of ECL has also been discussed [7,24–32]. Unfortunately, only few papers on ECL of lucigenin in aqueous media have been reported and few analytical applications involving ECL of lucigenin have been proposed due to its low sensitivity and the poor analytical reproducibility [6]. To our best knowledge, the ECL of lucigenin and its application at RTILs modified electrode have not been reported.

In the present work, a highly sensitive ECL method for the determination of riboflavin was developed based on the enhancement of riboflavin on the ECL intensity of lucigenin at RTILs modified gold electrode. The characterization of the RTILs modified electrode and the attractive performance of the sensitive ECL method for the determination of riboflavin are investigated in connection with the determination of riboflavin in the pharmaceutical preparations.

2. Material and methods

2.1. Chemical reagents and apparatus

Lucigenin (nitrate salt) was purchased from Sigma (USA) and used without further purification. A 1.00×10^{-4} g/mL stock standard solution of riboflavin was prepared by dissolving 10.0 mg riboflavin (Shanghai Third Chemical Reagent Company, China) in 100 mL of 0.10 M acetic acid, and stored in brown bottles in order to avoid light decomposition. The lucigenin and riboflavin working solutions were prepared by appropriate dilution with 0.010 M KCl solution.

Nafion (perfluorinated ion-exchange resin, 5 wt% solution in a mixture of lower aliphatic alcohols and water) was obtained from Sigma (USA) and used as received. Room temperature ionic liquids (RTILs) 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM- PF_6) was obtained from Lanzhou Institute of Chemical Physics (China). All other reagents were of analytical grade, and Millipore Milli-Q water ($18 \Omega\text{M cm}^{-1}$) was used throughout.

The experimental setup for ECL measurements was same as in Ref. [7]. A three-electrode system, including a RTILs modified gold electrode or gold electrode as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (Sat. KCl) electrode as the reference electrode, was used.

2.2. Preparation of modified electrode

A gold disk electrode ($\varphi = 2$ mm) was pretreated according to Ref. [33]. Subsequently, Nafion-BMIM- PF_6 mixture solution was prepared by mixing equal volume of Nafion and BMIM- PF_6 and sonicating for 30 min until a homogeneous solution obtained. Then, 2 μL of the mixture was drop-cast on the surface of the cleaned gold electrode with a microsyringe, and dried at room temperature to acquire RTILs modified gold electrode.

2.3. ECL measurement

The ECL measurement was performed at a constant potential of -0.70 V in 2.5 mL of 0.010 M KCl containing 2.0 μM lucigenin

and different concentrations of riboflavin. The concentration of riboflavin was quantified by an enhanced ECL intensity ($\Delta I = I_s - I_0$), where I_s was the ECL intensity of lucigenin with riboflavin (sample) and I_0 was the blank ECL intensity of lucigenin without riboflavin. All experiments were carried out at room temperature. The ECL peak intensity was recorded to quantify the concentration of riboflavin.

2.4. Determination of riboflavin in pharmaceutical preparations

10 tablets of riboflavin from Shanxi YunPeng pharmaceutical Co., Ltd. were accurately weighed, then ground to fine powder. A tablet sample equivalent to approximately 5 mg riboflavin was weighed accurately, and then dissolved in 100 mL of 0.10 M acetic acid. 10 injections of riboflavin were mixed. An injection sample from Shanxi YunPeng pharmaceutical Co., Ltd., which was equivalent to about 5 mg of riboflavin, was diluted into 100 mL with 0.10 M acetic acid. When the level of riboflavin was over the calibration ranges, samples were appropriately diluted with 0.010 M KCl prior to the assay. To avoid strong photolysis of riboflavin, all the sample solutions should be protected from blazing light during the experiment. The determination procedures of the samples were the same as that of riboflavin standard solution described in the above ECL measurement.

3. Results and discussion

3.1. ECL behaviors of lucigenin at RTILs modified gold electrode

The electrochemical and ECL behaviors of lucigenin were investigated both at bare gold electrode and RTILs modified gold electrode. BMIM- PF_6 was used as an example of hydrophobic RTILs. Fig. 1A shows ECL curves of 2.0 μM lucigenin at bare gold electrode and at RTILs modified gold electrode. From Fig. 1A, it can be seen that when an applied potential was scanned from 0 to -1.0 V, two ECL peaks of lucigenin appeared at ca. -0.33 V and -0.64 V on bare gold electrode (line a) and at ca. -0.33 V and -0.65 V on RTILs modified gold electrode (line b), respectively. A weak ECL intensity of lucigenin was observed at the bare gold electrode while a great ECL intensity appeared at the RTILs modified gold electrode. This indicates that riboflavin strongly enhanced the ECL of lucigenin. Xu et al. [18] thought that the change of the polarity of the electrode surface in addition of ionic liquids may results in an increase of ECL intensity. Li et al. [20] thought that MCM-41-modified carbon paste electrode had more open structures to allow faster diffusion of $\text{Ru}(\text{bpy})_3^{2+}$ and that the ionic liquid also acted as a conducting bridge to connect tripropylamine with $\text{Ru}(\text{bpy})_3^{2+}$ sites immobilized in the electrode, resulting in a higher ECL intensity compared with the MCM-41-modified traditional carbon paste electrode. The electrochemical behavior of lucigenin at bare gold electrode and at RTILs modified gold electrode in the absence of oxygen was examined in order to illustrate the reason of the increase of ECL intensity. The results were shown in Fig. 1B. From Fig. 1B, it can be seen that the reduction peak current at RTILs modified gold electrode is greatly increased compared with that at bare gold electrode. However, the potential has no significant shift. The lack of potential shift implies that BMIM- PF_6 does not bind strongly with lucigenin, which is further confirmed by the following reproducibility experiment. In conclusion, the increase of current is maybe the reason that BMIM- PF_6 , increasing the diffusion rate of lucigenin, leads to a dramatic rise in the lucigenin redox current and then to the enhancement in the ECL intensity. Additionally, BMIM- PF_6 , as hydrophobic ionic liquid, can increase in the ECL efficiency of lucigenin ECL on the electrode surface.

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