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Anodic electrochemiluminescent behavior of lucigenin on MWNT/GCE

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ABSTRACT

The electrochemiluminescent (ECL) behavior of lucigenin on a multiwall carbon nanotubes modified glassy carbon electrode (MWNT/GCE) during anodic scanning was studied. A strong and stable anodic ECL signal was found on MWNT modified electrode, which results from the oxidation reaction between lucigenin and the oxidation production of OH^-. The effects of electrode materials, pH and scan rate on the ECL intensity were studied, and the possible ECL mechanism was also proposed. Under the optimized conditions, the ECL intensity was found to be linear with concentration of lucigenin in the range of 5.0×10^{-7}–5.0×10^{-6} mol/L with a detection limit of 2.0×10^{-7} mol/L. Superoxide dimutase (SOD) was found to be able to inhibit this ECL system, based on which a sensitive ECL methods for detection of SOD had been established.

1. Introduction

Electrochemiluminescence (ECL) is a mean of converting electric energy into radioactive energy, which has the advantages of high sensitivity, high selectivity and well reproducibility. Three ECL compounds, ruthenium complexes, particularly tris(2,2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$), luminol and lucigenin (*N*,*N*-dimethyl- 9,9-biacridinium dinitrate) have been studied most widely [1,2]. However, for lucigenin, most studies concerning about property, mechanism and analytical applications were carried out at cathode potential in the presence of dissolved oxygen [3–7]. So far, just little attention has been paid to study ECL behavior of lucigenin at anode potential. Su found an anodic ECL in lucigenin/H_2O system during differential pulse voltammetry (DPV) scanning, but no ECL signal was found when cyclic voltammetry (CV) or linear sweep voltammetry (LSV) was performed [8]. Cui et al studied the lucigenin ECL in presence of tributylamine in ethanol solution at a polycrystalline gold electrode with CV scanning, they found that the electrode material had great effect on the behavior of the anodic ECL of lucigenin [9].

Carbon nanotubes (CNTs) had intrinsic properties, such as high surface area, high electrical conductivity, it had attracted considerable interest for development of electrochemical biosensor. The electronic properties of CNTs suggested that they have the ability to mediate the electron-transfer reactions and can be exploited as a mean of promoting the reactions in a wide range of bioactive species, edge-plane like sites occur at the ends and along the tube axis were likely to be the reason of CNTs' "electrocatalytic" properties [10,11]. A lot of ECL sensors based on CNTs modified electrodes had also been studied, the present of CNTs can enhance the ECL signals of luminol [12], $Ru(bpy)_3^{2+}$ [13] or lucigenin [14,15] system.

In this paper, the anodic ECL behaviors of lucigenin on multiwall carbon nanotubes (MWNTs) were explored under CV scanning, and an anodic ECL signal had been found on MWNT modified glassy carbon electrode (MWNT/GCE). The effects of various factors, such as dissolved oxygen, scan rates, pH on ECL signals were studied. Possible mechanism for the anodic lucigenin ECL was also proposed. Based on the fact that superoxide dimutase (SOD) could inhibit the ECL intensity of this ECL system, a sensitive and simple ECL method for determination of SOD could be developed.

2. Experimental

2.1. Apparatus and chemicals

ECL intensity versus potential was detected by a laboratory made system, which has been previously reported [16,17]. The MWNT was obtained from Shenzhen Nanotech Port Co. Ltd., China, and purified through flux with the following procedure: 1.5 g MWNT were suspended in 30 g concentrated nitric acid and refluxed for 5 h in an oil bath maintained at 140 °C. After washing with water and then dried at 100 °C over night, the solid was sonicated in chloroform and dried under the infrared lamp [18,19]. Lucigenin was obtained from Sigma Chemical Co. (USA). Other chemicals were analytical grade. The water used was double distilled water.

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2.2. Preparation of MWNT/GCE

The film was achieved by dropping 10 μL suspension (1 mg MWNT was dispersed in 10 mL of *N,N′*-dimethylfomamide (DMF) to give 0.1 mg/mL black suspension) onto the clean GCE surface and then evaporating the solvent under an infrared lamp. The modified GCE was used as the working electrode.

The electrodes modified by graphite or untreated MWNT (which had been used directly without further purification) were achieved with the same procedure.

2.3. Measurement of ECL

Required amount of lucigenin was added to a 10 mL volumetric flask and diluted with buffer solution. About 3 mL of this solution was transferred to the ECL cell. Then appropriate potential was applied on the newly prepared working electrode and ECL signal was measured simultaneously, the peak ECL intensity was used for calibration.

3. Results and discussion

3.1. Electrochemical and ECL behaviors of lucigenin during anodic scanning

The CV and ECL behaviors of lucigenin on different electrodes were studied during anodic potential scanning in the phosphate buffer solution (PBS, pH 10.0). As shown in Fig. 1A, on MWNT/GCE, the background current is much greater than that at bare GCE, which showed the "electrocatalytic" properties of MWNT, the increase of current was simply due to the intrinsic properties of the MWNTs film.

Fig. 1B showed that no ECL signal was found on bare GC electrode, but an obvious ECL peak could be observed at 1.4 V on MWNT/GCE. If the solution contains no lucigenin, no ECL signal could be found, so this ECL signal was resulted from lucigenin, and the present of MWNT was a key point.

3.2. Effect of different electrode materials on ECL

Fig. 2 shows the ECL intensities of lucigenin on the different electrodes under anodic scanning. It can be seen from Fig. 2 that on graphite modified GCE, weak ECL signals can be detected. If the MWNT was not pre-treated by the procedure shown in Section 2.1 before modification, the ECL signal was relative lower. It has been reported that the edge-plane sites and tube ends are reactive sites for graphite or carbon nanotube modified electrodes [10,11]. As graphite contains only a little "reactive sites", so the ECL signals observed on the graphite modified GCE were weak. In our early study [20], it showed that the end of the MWNT tubes would become open after acidic treatment, so compared with untreated MWNT, the pre-treated MWNT tubes would contain much more "reactive sites", and which would cause stronger ECL intensity.

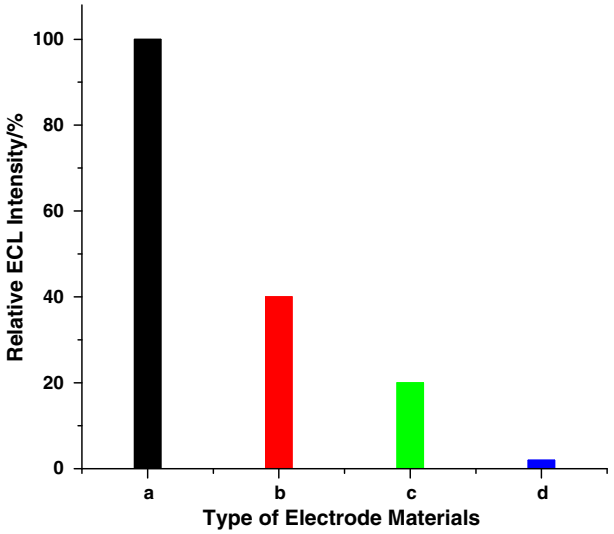

Fig. 2. Effect of electrode materials on ECL intensity (a) treated MWNT modified GCE; (b) untreated MWNT modified GCE; (c) graphite modified GCE and (d) bare GCE.

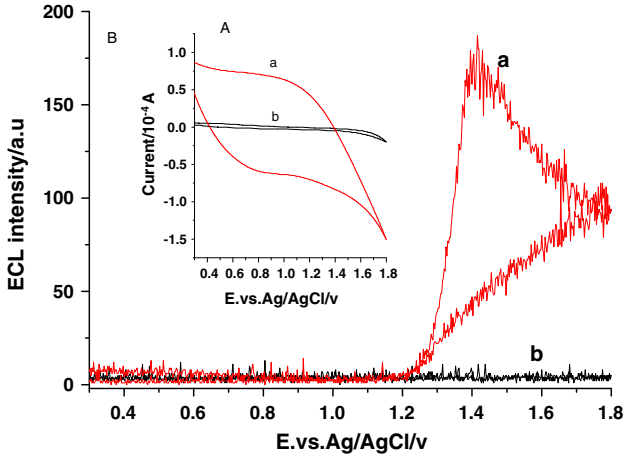

Fig. 1. (A) The CV curves and (B) ECL curves of 2.0×10^{-6} mol/L lucigenin in PBS (pH 10.0) on different electrodes. (a) bare GCE; (b) MWNT/GCE.

3.3. Selection of electrochemical parameters

The CV, LSV, square wave voltammetry (SWV) and DPV scanning modes were selected to examine the effect of excitation waveform on the ECL signal. The result showed that the ECL could be detected with each mode, but the most stable ECL signal could be obtained by using CV, so CV was selected for the subsequent studies.

The effect of scan rate on the ECL intensity was also investigated, the results showed that with the increasing of scan rate, the ECL intensity increased and reached the maximum emission at 50 mV/s. But if the scan rate was higher than that, the emission intensity decreases. Therefore, 50 mV/s was used for subsequent experiment.

3.4. Effect of pH value on the ECL intensity

The effect of pH on anodic ECL intensity of lucigenin had been studied, and the results showed that in acidic solution or neutral solution, nearly no ECL signals could be observed, but the ECL intensity increased greatly with the increasing of pH. Since chemiluminescence (CL) of lucigenin was also affected by pH, the CL increases greatly in strong base solution, which would cause interference for ECL measurement. Therefore pH 10.0 was chosen in this study.

3.5. Linear response range and detection limit of lucigenin

It is found that the ECL intensity is dependent on the concentration of lucigenin. As shown in Fig. 3, the ECL intensity was linear with the lucigenin concentration in the range of 5.0×10^{-7}–5.0×10^{-6} mol/L with a detection limit of 5.0×10^{-7} mol/L (defined as S/N = 3).