Electrochemiluminescent behavior of luminol on the glassy carbon electrode modified with CoTPP/MWNT composite film

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A B S T R A C T

A glassy carbon electrode (GCE) modified with cobalt(II) meso-tetraphenylporphrine/multiwall-carbon nanotube (CoTPP/MWNT) was applied to investigate the electrochemiluminescent (ECL) behavior of luminol. The ECL intensity of luminol was found to be increased greatly on this modified electrode. The presence of cobalt(II) meso-tetraphenylporphrine (CoTPP) can catalyze the reduction of oxygen on the electrode surface to produce $\text{HOO}^-$, which can increase the ECL intensity of luminol. Moreover, MWNT can provide the more effective area of the electrode, and can act as a promoter to enhance the electrochemical reaction. The proposed method enables a detection limit for luminol of $1.0 \times 10^{-8}$ mol/L in the neutral solution. Under the optimum condition, the enhanced ECL intensity of luminol by $\text{H}_2\text{O}_2$ had a linear relationship with the concentration of $\text{H}_2\text{O}_2$ in the range of $1.0 \times 10^{-7}$ to $8.0 \times 10^{-8}$ mol/L with the detection limit of $5.0 \times 10^{-9}$ mol/L.

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1. Introduction

Porphyrins and metalloporphyrins are a kind of functional dyes with some special chemical, photophysical and biological properties, which can be adsorbed strongly on graphite surfaces [1,2]. Metalloporphyrins have been used to modify electrodes by adsorption or electrodeposition, and these modified electrodes exhibit strong catalytic and electrocatalytic activity for many electrochemical reactions [3–5], such as the reduction of NO [6,7], $\text{O}_2$ [8], nitrite [9], norepinephrine [10], alcohols [11–13] and aldehydes [14]. Much literature about the applications of porphyrins or metalloporphyrins modified electrodes in electroanalytical chemistry has been reported [6–14]. However, no much attention has been paid to their application in electrochemiluminescence (ECL). Ci and coworkers [15] reported that the metalloporphyrin showed good catalytic function on the luminol chemiluminescence system. Nickel phthalocyanine polymer layer has been immobilized onto a glassy carbon electrode and used to catalyze the oxidation of luminol [16], based on which the ECL of luminol in the presence of hydrogen peroxide has been greatly enhanced.

The electronic properties of carbon nanotube suggested that it might have the ability to mediate electron-transfer reactions in solution [17], and the electronic properties of this material have been exploited as a means to promote the electron-transfer reaction of many bioactive species. More and more interests have been focused on the application of carbon nanotube in the research area of ECL [18–20].

The preparation of porphyrin-functionalized carbon nanotubes in solution has been reported [21]. It indicated that porphyrin molecules could be dissolved in SWNTs organic solutions and formed the solid SWNTs–porphyrin hybrid nano-material, but the application of porphyrin-functionalized carbon nanotubes has not been further studied. Sheu modified the MWNT with hemin and which has been applied for oxygen detection, they found that the present of hemin could catalyze the reduction of oxygen [22]. But till now, porphyrin–functionalized carbon nanotubes has not been applied for study of ECL. In this paper, cobalt(II) meso-tetraphenylporphrine (CoTPP) and MWNT were dissolved in DMF solution by sonicating, and the CoTPP/MWNT suspension was used to modify the glassy carbon electrode. It was found that the CoTPP/MWNT composite film modified glassy carbon electrode would greatly enhance the ECL of luminol and luminol/$\text{H}_2\text{O}_2$ system.

2. Experimental

2.1. Apparatus

ECL intensity versus potential was detected using a system made in our lab [23], consisting of a BPCL Ultra-Weak Chemiluminescence Analyzer controlled by a personal computer (Institute of Biophysics,
Fig. 1. Impedance (Nyquist) plots in the 5 mM K₃Fe(CN)₆–K₄Fe(CN)₆ and 0.1 M KCl system. (a) Bare GC electrode; (b) CoTPP modified GC electrode; (c) CoTPP/MWNT modified GC electrode.

**2.2. Chemicals**

Luminol was obtained from Sigma Chemical Co. (China) and used without further purification. The multiwall-carbon nanotube was obtained from Shenzhen Nanotech Port Co., Ltd., China. CoTPP was purchased from Sigma Chemical Co. (China). Other chemicals were analytical grade or better and double distilled water was used throughout. A working solution of H₂O₂ was prepared freshly daily from 30% (v/v) H₂O₂ (Xinke Electrochemical Reagent Factory, Bengbu, China). The concentration of stock solution of luminol is 1.0 × 10⁻³ mol/L and stored in the refrigerator. The stock standard solution was used to prepare working standard solutions daily by suitable dilution.

**2.3. Preparation of CoTPP/MWNT composite film-modified electrode**

To prepare a CoTPP/MWNT modified electrode, the GCE was pretreated before using by polishing its surface with aqueous slurries of alumina powders (average particle diameters: 1.0 μm and 0.05 μm Al₂O₃) on a polishing microcloth and then rinsed with water and sonicated in acetone. A typical solubilization procedure is as follows: MWNTs (5 mg) were added to 0.1 mmol/L solution of CoTPP in DMF (5 mL, spectral grade), and it was then sonicated (ultrasonic cleaner, Branson 5510) for 1 h at room temperature. The MWNTs were immobilized onto the glassy carbon electrode using DMF as the dispersing agent. The CoTPP molecules are adsorbed on the surface of MWNTs by spontaneous adsorption. The CoTPP/MWNT composite film-modified electrode was then prepared by dropping 10 μL of the above-mentioned suspension onto the surface of GC (5 mm i.d.) electrode surface and the solvent was evaporated using the infrared lamp. The same procedure was used for modification of GC electrode with MWNTs using DMF solution containing CoTPP without MWNT.

**3. Results and discussion**

**3.1. Electrochemical behavior of CoTPP/MWNT composite film-modified electrode**

Faradaic impedance spectroscopy is an effective method to probe the interfacial electron-transfer resistance at the modified...
electrode [24], the kinetics and diffusion characteristics of electron transfer can be extracted from the impedance spectra. Fig. 1 shows the Faradaic impedance spectra at the bare GC electrode, CoTPP/MWNT modified GC electrode and the CoTPP modified GC electrode, respectively. Point A (about 155 Ω) shows the ohmic resistance of the electrolyte solution. Curve a is the Nyquist plot of bare GC electrode, we can obtain a remarkable semicircle portion from it, and the electron-transfer resistance between the bare GC electrode and the solution is about 65 Ω. We can also obtain a semicircle in curve c and the diameter of the semicircle is bigger than curve a, the resistance between the CoTPP modified GC electrode and the solution is about 700 Ω, which means the porphyrin ring has lower conductivity and block the electron transfer. But the curve b represent a nearly straight line at higher frequencies, which means the electron-transfer resistance between the MWNT/CoTPP modified GC electrode and the solution is relative small and can be ignored, the reason for this phenomenon is that MWNT can greatly increase the electron transfer rate.

3.2. Cyclic voltammograms and ECL of luminol at different electrodes

Fig. 2 shows the cyclic voltammograms (CV) and the ECL behaviors of luminol solution at the different electrodes (pH 7.0). It can be known from Fig. 2(A) that the oxidation current obtained at the pure CoTPP modified electrode and bare electrode are different slightly, but the ECL intensity at the pure CoTPP modified electrode is about 2-fold as that at the bare electrode. Whereas, the oxidation current at the CoTPP/MWNT composite film-modified electrode was much greater than that at other electrodes, and the background current also increase greatly, which could be attributed to the electrocatalytic activity of MWNT and the more effective area of the electrode. If the dissolved oxygen was removed, no ECL could be observed on the electrodes, but the oxidation peak at about 0.5 V was remained and nearly unchanged. So the oxidation behavior of luminol on CoTPP/MWNT composite film-modified film can be express as following [25]:

\[
\text{LH}^- \rightarrow \text{LH}^* + e^- 
\]

The luminol anion, LH\(^-\), undergoes the electrooxidation to form the radical, LH\(^*\), and then LH\(^*\) reacts with dissolve oxygen to emit light.

We also found that addition of \(H_2O_2\) into the solution could enhance the ECL intensity of luminol, and the presence of CoTTP could enhance the ECL intensity of luminol/\(H_2O_2\) system.

3.3. Selection of reaction condition

3.3.1. Selection of buffer

It has been reported that the buffer solution has great effect on the ECL intensity of luminol [24]. In this study, phosphate buffer solution (PBS), borate and Britton–Robinson buffer solution (0.2 mol/L, pH 7.0) have been test to be used as the buffer solution, it was found that in PBS, the ECL intensity is higher than in the other solutions. The effect of pH value on the ECL intensity has also been studied, in acid solution, the system nearly has no ECL signals, but if the pH value is higher than 8.0, the background chemiluminescence (CL) intensity is stronger since the CL of luminol in basic solution is stronger and the present of Co complex can catalyze the CL of luminol system [26], which will bring interference to the ECL detection. In the pH range of 7.0–8.0, the background CL intensity is low, which can make the ECL detection with high sensitivity. So pH 7.0 phosphate buffer solution was selected in subsequent experiment.

3.3.2. Selection of electrochemical parameters

The linear sweep voltammetry (LSV), cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were selected to examine the effect of excitation waveform on the ECL signal. The results showed that cyclic voltammetry scanning in the potential range of 0–1.2 V (versus Ag/AgCl) could obtain the strongest ECL emission. The effect of scan rate on ECL was also investigated, and the results showed that the optimal scan rate for ECL was 100 mV/s.

The effect of scan rate on the oxidation peak current of luminol was also investigated. As shown in Fig. 3, the \(I_p\) was proportional to the square root of the scan rate over a range of 10–300 mV/s. The linear regression equation can be expressed as

\[
I_p \times 10^{-6} \text{ A} = -0.0228 + 22.26v^{1/2} \left[\text{V/s}\right]^{1/2}, \quad R = 0.9970
\]

where \(v\) is the scan rate; \(I_p\) means the peak current; \(R\) is the correlation coefficient. The result indicates that the electron transfer reaction is controlled by the diffusion of luminol.
3.4. Effect of amount of MWNT and CoTPP

ECL response of CoTPP/MWNT modified electrode to luminol in present of H2O2 is expected to be affected by the amount of MWNT and CoTPP on the electrode surface, which can be controlled by using the same volume (10 μL) of the suspensions with different concentration of MWNT and CoTPP. The relationship between the ECL intensity and the concentration of MWNT and CoTPP is shown in Fig. 4. Line a indicates that the ECL intensity of luminol is increased with the increment of MWNT which implies that higher MWNT concentration results in higher sensitivity. However, when the concentration of MWNTs reached 1 mg/mL, the ECL reached the maximum. Line b showed that the ECL reached the maximum when the concentration of CoTPP reached 0.1 mmol/L. But the excessive amount of MWNT and CoTPP deposited on the GC electrode would affect the electron transfer between the electrode and the reactant in solution. Therefore, 1 mg/mL of MWNT and 0.1 mmol/L of CoTPP were chosen in the subsequent experiment.

3.5. Reproducibility and stability of CoTPP/MWNT composite film-modified electrode

Fig. 5 shows the ECL emission of luminol from the CoTPP/MWNT composite film-modified electrode under continuous potential scanning for seven cycles. The relative standard deviation (R.S.D.) of the ECL intensity was lower than 1.0%, which suggested the good stability and the reproducibility of the modified method.

It is very important for a modified electrode to be stable for a prolonged time. The electrode was stored at 4 °C in a refrigerator, and then was used to detect 2 samples everyday. It was found that the response of the CoTPP/MWNT composite film-modified electrode retained 95.5% of its initial response after 7 days. Such stability is acceptable for most practical applications.

3.6. Linear response range and detection limit

Under the optimization condition, the ECL intensity was linear with the concentration of luminol in the range of 5.0 × 10⁻⁸ to 8.0 × 10⁻⁸ mol/L with the detection limit of 1.0 × 10⁻⁸ mol/L (defined as the concentration that could be detected at the signal-to-noise ratio of 3). The regression equation was

\[ I_{\text{ECL}} = -349.93 + 530.6 \times 10^3 C \quad (R = 0.9985) \]

The ECL intensity of luminol could be greatly enhanced by the H2O2. The result shows that the enhanced ECL intensity has good linear relationship with the concentration of H2O2 in the range of 1.0 × 10⁻⁸ to 7.0 × 10⁻⁷ mol/L with the detection limit of 5.0 × 10⁻⁹ mol/L (defined as the concentration that could be detected at the signal-to-noise ratio of 3). The regression equation was

\[ \Delta I_{\text{ECL}} = -296.1 + 606.42 \times 10^2 C \quad (R = 0.9987) \]

The relative standard deviation for 1.0 × 10⁻⁷ mol/L H2O2 was 3.5% (n = 8) at the same modified electrode.

3.7. Possible mechanism

The mechanism for the ECL reaction of luminol with H2O2 in neutral solution has been reported [27,28]. It was known that luminol was electrochemically oxidized to form an anion. Further oxidation of the resulting diazo compound in the presence of hydrogen peroxide would produce 3-aminophthalate in the excited state. Hydrogen peroxide can participate as the peroxide anion HOO• or as a superoxide radical O2•−. The electrocatalytic properties of Co porphyrins on O2 reduction have been studied and the pathways would be as follows ("Por" denotes porphyrin ligands) [29]:

\[
\begin{align*}
\text{Co(II)(Por)} + O_2 & \rightarrow \text{Co(III)(Por)} + O_2^- \\
\text{Co(II)(Por)} - O_2^{•−} + H^+ & \rightarrow \text{Co(III)(Por)} + \text{HO}_2^* \\
\text{Co(III)(Por)} + e^- & \rightarrow \text{Co(II)(Por)}
\end{align*}
\]

It was known that on the Co porphyrin modified electrode the dissolved O2 could be more easily transferred to O2•− and HOO•, which would enhance the ECL of luminol. On other hand, Co porphyrin would catalyze the oxidation of H2O2 to produce molecular oxygen and hydroxyl ion (in neutral pH) or water (in basic pH), so addition of H2O2 would greatly enhance the ECL of luminol [30]. In general, besides of the electrocatalytic properties of MWNT, the reason for the enhancement of ECL of luminol at the cobalt(II)-porphyrin/MWNT modified electrode is highly effective generation...
of lumino$^-$ and HO$_2$$^-$ (HO$^*$), the latter was from H$_2$O$_2$ and dissolved O$_2$ by the catalyzation of Co porphyrin.

4. Conclusions

A simple, fast and reproducible method was applied to immobilize cobalt(II)-porphyrin as electron transfer mediator on glassy carbon electrode modified with MWNTs, and this modified electrode has been applied to study the ECL of luminol and luminol/H$_2$O$_2$ system. The catalytic characters of CoTPP coupling with the electrocatalysis of the MWNT can greatly enhance the ECL intensity of the system. The porphyrin/MWNT composite film-modified electrode could be used for measurements of luminol with detection limit of $1.0 \times 10^{-8}$ mol/L, and H$_2$O$_2$ would greatly enhance the ECL of luminol in neutral solution. The reliability and stability of the electrodes offers a good possibility for determination of H$_2$O$_2$ with high sensitivity. Since H$_2$O$_2$ is the production of a series of enzyme reaction, so many ECL sensors can be further designed for detection of those substrates that can react with their corresponding enzymes to produce H$_2$O$_2$.

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