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An electrochemiluminescent biosensor for glucose based on the electrochemiluminescence of luminol on the nafion/glucose oxidase/poly(nickel(II)tetrasulfophthalocyanine)/multi-walled carbon nanotubes modified electrode

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ABSTRACT

A poly(nickel(II) tetrasulfophthalocyanine)/multi-walled carbon nanotubes composite modified electrode (polyNiTSPc/MWNTs) was fabricated by electropolymerization of NiTSPc on MWNTs-modified glassy carbon electrode (GCE). The modified electrode was found to be able to greatly improve the emission of luminol electrochemiluminescence (ECL) in a solution containing hydrogen peroxide. Glucose oxidase (GOD) was immobilized on the surface of polyNiTSPc/MWNTs modified GC electrode by Nafion to establish an ECL glucose sensor. Under the optimum conditions, the linear response range of glucose was 1.0×10^{-6} to 1.0×10^{-4} mol L^{-1} with a detection limit of 8.0×10^{-8} mol L^{-1} (defined as the concentration that could be detected at the signal-to-noise ratio of 3). The ECL sensor showed an outstanding well reproducibility and long-term stability. The established method has been applied to determine the glucose concentrations in real serum samples with satisfactory results.

1. Introduction

Recently, the development of electrochemiluminescent (ECL) sensors has been paid more and more attention by the analysts since they not only retain the advantages of chemiluminescence (CL) sensor, such as excellent sensitivity, wide dynamic concentration response range, but also have some additional advantages [1–5]. For example, the applied potential to produce the CL reaction can be easily controlled, which can improve its selectivity. Furthermore, the generation of light in the vicinity of the electrode would improve the spatial control for sensitive detection of analyte [6,7]. Besides the widely used $Ru(bpy)_3^{2+}$-based ECL sensors [8,9], luminol-based ECL systems have also been developed to construct the ECL sensors because of its low oxidation potential, inexpensive reagent consumption and the high emission yields [10–16].

The luminol ECL intensity is directly proportional to the amount of luminol or hydrogen peroxide, and glucose can react with the dissolved oxygen to produce hydrogen peroxide in presence of glucose oxidase (GOD) [17], so a lot of ECL based glucose sensors have been developed [18–23]. Many efforts had been paid to develop more sensitive and durable glucose ECL sensors, such as using iron species in the clay to enhance the ECL intensity [18], using photo-cross-link polymer [19,20], sol–gel composite [21] or proactive membrane [22,23] to immobilize the GOD, and a lot of work still needs to be done.

Since the rediscovery of carbon nanotubes (CNT) in 1991 [24], intensive attention has been paid on the analytical application of CNT for its high aspect ratio, excellent electrical conductivity, good chemical stability and extremely high mechanical strength [25,26]. These remarkable mechanical and electrical properties endow them with a wide range of applications [27–32]. On the other hand, conducting polymer/CNTs composites have received great interests in recent years because the incorporation of CNTs into conducting polymers can lead to produce the new composite materials with individual properties of each component, and their synergistic effect would be useful in some particular applications [33]. Among the various conducting polymers, metallophthalocyanine has become the most attractive one because of its electrocatalytic property [34]. Ni-phthalocyanine, using as the electrocatalyst to prepare the modified electrodes has shown interesting electrocatalytic properties [35–39]. Nickel(II) tetrasulfophthalocyanine (NiTSPc) polymerized on the GCE can retain phthalocyanine's macrocycle structure, Ni atom can play as a role

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similar to that in $Ni(OH)_2$, which can catalyze ECL of luminol [39]. When it is immobilized on the electrode and used as the ECL sensor, the ECL sensitivity of the sensor can be greatly enhanced.

In our early study, we found that the presence of polyNiTSPc could catalyze the ECL of luminol, and the ECL intensity was increased with the thick of polyfilm, but if the film was too thick, it would block the charge transfer, and ECL intensity would not be enhanced anymore [39]. So if the charge transfer rate can be enhanced, the ECL behavior can be further improved. It is well known that MWNT can accelerate the electron transfer and can enhance ECL of luminol [46]. So the purpose of this study is to couple the catalyzing ability of NiTSPc with the charge transfer ability of MWNT to improve the performance of the luminol-based ECL sensor.

A polyNiTSPc/MWNT modified electrode has been fabricated by electropolymerization of NiTSPc on MWNT-modified glassy carbon electrode (GCE). GOD has been immobilized on the surface of the modified electrode to establish a glucose ECL sensor.

2. Experimental

2.1. Chemicals

Luminol, GOD (Aldrich Chem. Co., USA) and NiTSPc (Fluka, Switzerland,) were used as received without further purification. A stock solution of 1.0×10^{-3} mol L^{-1} luminol was prepared and stored at 4 °C. H_2O_2 working solution was prepared freshly daily from 30% (v/v) H_2O_2 (Bengbu, China Xinke Electrochemical Reagent Factory). Nafion (5 wt% aqueous alcoholic solution, Aldrich) was prepared as 0.1% by dilution with ethanol. The MWNT was obtained from Shenzhen Nanotech Port Co. Ltd. and purified according to the literature method [40]. Working solutions were made by dilution of these stock solutions. Serum samples were kindly provided by the Hospital of Fuzhou University (Fuzhou, China). Glucose concentration of the samples had been tested by sysmex CHEMIX-180 automated biochemistry analyzer (Tokyo, Japan, SYSMEX Corporation). All other reagents were of analytical grade or better, double-distilled water was used throughout the experiments.

2.2. Apparatus

ECL detection system consisted of a BPCL ultraweak luminescence analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China) and a CHI660a electrochemical analyzer (Shanghai Chenhua Instrument Co., China). A three-electrode system was used, a modified GCE (diameter 3 mm) was used as working electrode, platinum wire and Ag/AgCl (sat. KCl) were used as counter electrode and reference electrode, respectively. A commercial 5 mL cylindroid glass cell was used as an ECL cell, which was washed with 0.2 mol L^{-1} nitric acid and water in sequence before using.

2.3. Procedure

2.3.1. Fabrication of the modified electrode

The GCE was pretreated by polishing its surface with aqueous slurries of alumina powders (1.0 μm and 0.3 μm α-Al_2O_3) on polishing cloth and carefully rinsed with water to give a smooth and clean electrode surface. Followed by cyclic voltammetry (CV) scanning in 0.1 mol L^{-1} H_2SO_4 aqueous solution from −0.2 to 0.8 V at 0.05 V s^{-1} until a stable CV current obtained. 10 μL of the black suspension (which was prepared by dispersing the desired amount of purified MWNTs in N,N-dimethyl formamide (DMF) solution) was dropped on GCE surface and evaporated under an infrared lamp. PolyNiTSPc film was formed by using CV scanning in the range of 0.2–0.8 V (*versus* Ag/AgCl) with a scanning rate of 0.1 V s^{-1} in 0.20 mol/L NaOH solution containing 5.0×10^{-3} mol L^{-1} NiTSPc under argon deoxygenated conditions. After the electropolymerization, the electrode was rinsed with water, and transferred to the buffer solution for preservation. The thickness of the film can be controlled by varying the CV scanning times. Appropriate concentration of GOD mixed with Nafion was directly dropped onto the polyNiTSPc/MWNT/GCE surface and dried in the air. The established modified electrode was stored in buffer solution at 4 °C when it was not used.

2.3.2. Static ECL measurement

Luminol and glucose were mixed just before the experiment in borate buffer solution (pH 7.4). A potential from 0.0 to 0.80 V was applied to the working electrode and the ECL signal was recorded simultaneously. The emission at 0.50 V was used for the quantitative analysis.

3. Results and discussion

3.1. Electrode characterization

3.1.1. Formation of polyNiTSPc

The electropolymerization of NiTSPc was obtained by repetitive CV scanning in range of 0.2–0.8 V at a scan rate of 0.10 V s^{-1}, which resulted in the oxidation of Ni(II) ions to electrodeposit the corresponding electroactive polymers on the MWNT/GCE surface. Fig. 1 shows the typical CV curves recorded during the electropolymerization of NiTSPc on GCE and MWNT/GCE. It can be seen from Fig. 1A that a pair of reversible redox peaks appeared at E_c = 0.43 V and E_a = 0.55 V while in Fig. 1B appeared at E_c = 0.40 V and E_a = 0.52 V respectively. The area of polymer film on the MWNT/GCE is larger than that on the bare GCE, the reason for this maybe due to the presence of MWNT, which can increase the charge transfer rate, so more conductive polymer film has been deposited on the surface of the electrode.

3.1.2. Effect of amount of MWNTs attached on the electrode

ECL response of polyNiTSPc/MWNT/GCE to luminol is expected to be affected by the amount of MWNTs on the electrode surface. Fig. 2 shows the relationship between the ECL intensity and amount of MWNTs (represented as the MWNTs concentration of the suspension solution) on the modified electrode (the thickness of the polyNiTSPc is 80 cycles). With the increasing of MWNTs concentra-

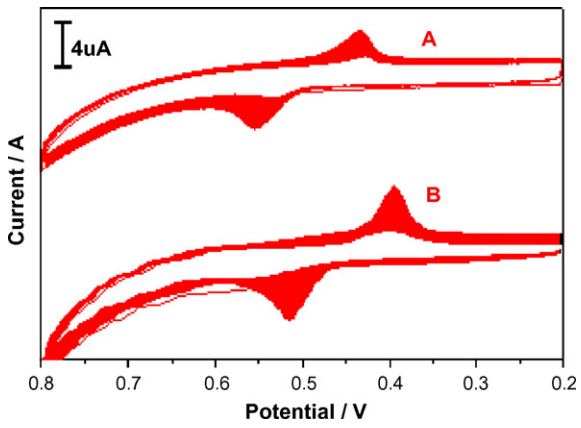

Fig. 1. CV curves of the electrodeposition of NiTSPc film on GCE (A) and MWNT/GCE (B) by consecutive potential cycling in a fresh solution containing 5.0×10^{-3} mol L^{-1} NiTSPc and 0.20 mol L^{-1} NaOH in the potential range of 0.20–0.80 V (*versus* Ag/AgCl) at a scan rate of 0.10 V s^{-1}.

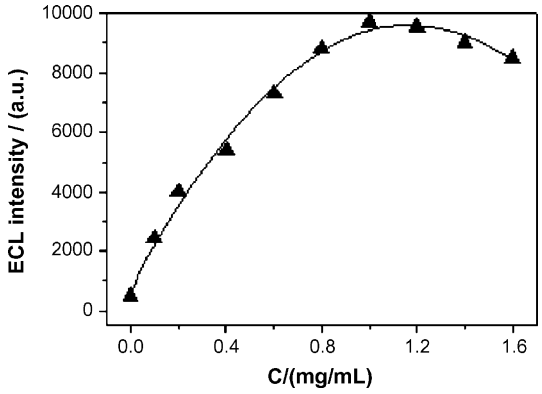

Fig. 2. Effect of MWNTs concentration on the ECL response of polyNiTSPc/MWNT modified electrode in borate buffer solution (pH 7.4) with 1.0×10^{-5} mol L^{-1} luminol and 8.0×10^{-4} mol L^{-1} H_2O_2.

tion, the ECL intensity of luminol enhances accordingly. When it is higher than 1 mg mL^{-1}, the ECL intensity decreases slightly. In this work, a moderate MWNTs concentration of 1 mg mL^{-1} was selected for the fabrication of polyNiTSPc/MWNT composite modified GCE.

3.1.3. Effect of NiTSPc film thickness

NiTSPc thickness can be easily controlled by the cycles of CV scanning during electropolymerization process. Fig. 3 shows the correlation between the thickness of the polymeric NiTSPc film and the ECL signal of luminol. The ECL intensity increases with the growing of the polymer film, but after 80 cycles of polymerizing scans the intensity tends towards constant. The ECL intensity obtained on the NiTSPc/MWNT modified GCE is about 10 times of that on MWNT modified electrode, indicating that the polymeric NiTSPc film can effectively enhance the ECL intensity of luminol.

3.1.4. Electro-oxidation and enhanced ECL of luminol on polyNiTSPc/MWNT/GCE

Fig. 4(I) (inset of Fig. 4) showed the CV curves of luminol on different electrodes in borate buffer solution (pH 7.4). On the bare GCE, only a small oxidation peak of luminol can be observed, while on MWNT modified electrode, the background current and the luminol oxidation peak current increase greatly. These results can be attributed to the large surface effect of the carbon nanotubes and the facilitation of electron-transfer by carbon nanotubes. Comparing curve C (for MWNT/GCE) with curve

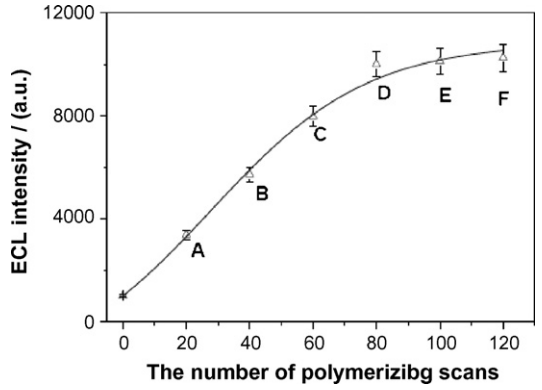

Fig. 3. ECL response of luminol on the different thickness polyNiTSPc/MWNT-modified GCE in borate buffer solution (pH 7.4) with 1.0×10^{-5} mol L^{-1} luminol and 8.0×10^{-4} mol L^{-1} H_2O_2. The polymers with different thickness were obtained by controlling the number of the electropolymerizing scans. A: 20 cycles, B: 40 cycles, C: 60 cycles, D: 80 cycles, E: 100 cycles, F: 120 cycles.

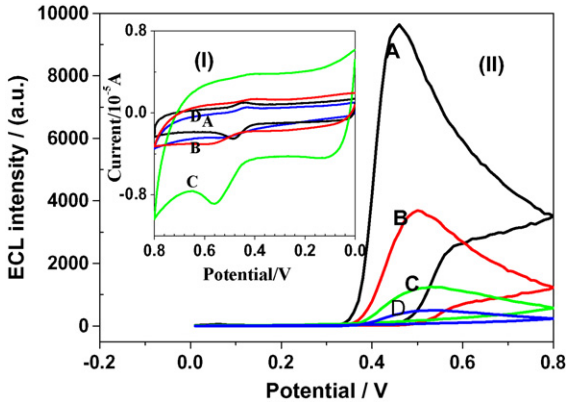

Fig. 4. ECL and CV (inset) response of luminol on the differentelectrodes in a borate buffer solution (pH 7.4) with 1.0×10^{-5} mol L^{-1} luminol and 8.0×10^{-4} mol L^{-1} H_2O_2. A: polyNiTSPc/MWNT/GCE; B: polyNiTSPc/GCE; C: MWNT/GCE; D: bare GCE.

A (for polyNiTSPc/MWNT/GCE) in Fig. 4(I), the background current reduces greatly if the polyNiTSPc has been deposited on the MWNT surface, the reason for this maybe due to the block of charge transfer by polyfilm.

Fig. 4(II) shows the ECL response of luminol on the different electrodes. The light emission on the bare GC electrode was quite small, on MWNT/GCE and polyNiTSPc/GCE, the ECL intensity increases about 2 and 8 times respectively. And on polyNiTSPc/MWNT/GC modified electrode, the maximum ECL intensity was about 21.3 times of that at the bare electrode, which means such kind of modification can combine the merits of both compounds.

3.2. Development of an ECL sensor for glucose

3.2.1. Principle of the ECL sensor

The principle of this ECL sensor can be shown in Fig. 5. On the surface of GCE, a MWNT layer had been modified. And the nickel complex was attached to the electrode surface through an O–Ni^{II} [41,42]. GOD was fixed on this modified electrode with the help of Nafion. Glucose reacts with the dissolved oxygen in the presence of GOD and produce gluconolactone and H_2O_2 [43]. The oxidation product of luminol at the surface of the electrode reacts with H_2O_2 to produce ECL. The adsorbed Ni(II)Pc took part in the catalytic oxidation of luminol and H_2O_2 generated in the reaction [39]. When the electrode potential was more positive than the redox potential of Ni(II)/Ni(III) (about 0.45 V), the oxidation production Ni(III) of Ni(II) would catalyze the oxidation of luminol (which also appeared

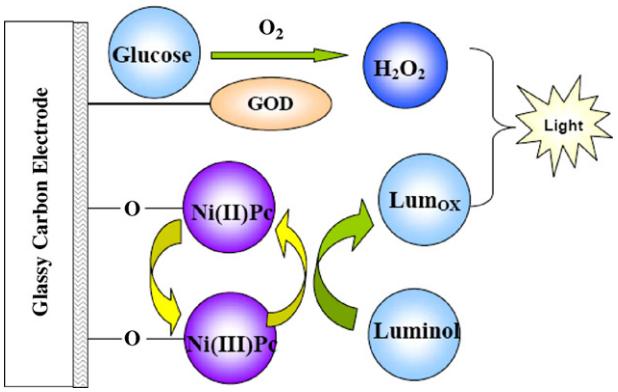

Fig. 5. The principle of the ECL biosensor. The marked layer on the surface of the GCE is MWNT. Lum_{OX} means the oxidation production of luminol.

at about 0.45 V) and H_2O_2, and itself would be reduced to Ni(II), which shows the redox cycling of Ni ion.

3.2.2. Effect of nafion on the sensor performance

Nafion, as a cation-exchange polymer, has been widely used for modification of electrode and for construction of biosensors and chemical sensor [44]. GOD can be firmly immobilized in the Nafion film and its activity can be ratained [45]. Moreover, the oxidation product of luminol is an anion, which can be adsorbed strongly onto the surface of the modified electrode without Nafion coating, which will affect the reaction between GOD and glucose. In addition, some interferences, such as ascorbic acid and uric acid were anions in the studied pH value, the presence of Nafion film will block off these anions.

3.2.3. Effect of pH on the ECL

It is well known that ECL reaction of luminol is more efficient in alkaline media, but the optimum pH condition for the activity of GOD was usually below neutral pH. Therefore, in this study, the effect of pH value on the enhanced ECL intensity (ΔI_{ECL}) was investigated in the range of 5.0-9.0. The results showed that ΔI_{ECL} would increase with the increase in pH in the range of 5.0–7.0, and remain constant in the range of 7.0–8.0, after that the ECL intensity would decrease with the increase in pH value. Considering that 7.4 is the physiological pH value, it has been chosen in this study.

3.2.4. Effect of luminol concentration on the ECL sensor

The concentration of the luminol also affects ΔI_{ECL}. Fig. 6 shows the relationship between ΔI_{ECL} and luminol concentration. The enhanced ECL intensity was increased with the increasing of luminol concentration, but if the concentration were higher than 1.0×10^{-5} mol L^{-1}, the ΔI_{ECL} would not increase anymore. Higher luminol concentration would cause more fouling on the electrode surface, so in this study 1.0×10^{-5} mol L^{-1} was chosen as the optimized concentration of luminol.

3.2.5. Calibration curve for glucose

A calibration curve was obtained for determination of glucose in aqueous solution under the optimal conditions. As shown in Fig. 7, the ECL intensity was linear with the concentration of glucose in the range of 1.0×10^{-6} to 1.0×10^{-4} mol L^{-1}. The linear regression equation was

$$\log \Delta I_{ECL} = 1.10 \log \left(\frac{C_{glucose}}{\text{mol L}^{-1}} \right) + 8.26 \quad (R = 0.9942)$$

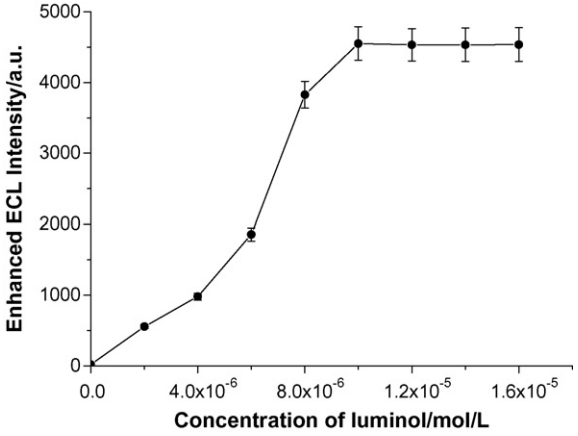

Fig. 6. Effect of the luminol concentration on the enhanced ECL intensity [glucose] = 6.0×10^{-5} mol L^{-1}; borate buffer: pH 7.4.

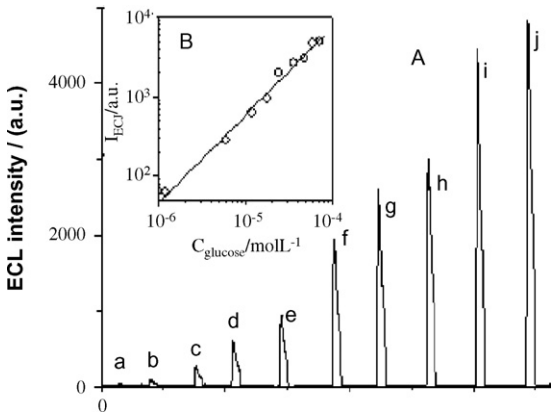

Fig. 7. The calibration curve for glucose [luminol] = 1.0×10^{-5} mol L^{-1}, Borate buffer: pH 7.4. A: ECL curves with various glucose concentration: (a) 0.0; (b) 1.2×10^{-6}; (c) 6.0×10^{-6}; (d) 1.2×10^{-5}; (e) 1.8×10^{-5}; (f) 2.4×10^{-5}; (g) 3.6×10^{-5}; (h) 4.8×10^{-5}; (i) 6×10^{-5}; (j) 7.2×10^{-5} mol L^{-1}. B: linear relationship between ECL intensity and glucose concentration.

where ΔI_{ECL} is the enhanced ECL intensity, $C_{glucose}$ is the concentration of glucose, R is the regression coefficient. The detection limit (defined as the concentration that could be detected at the signal-to-noise ration of 3) was 8.0×10^{-8} mol L^{-1}. The relative standard deviation for 5.0×10^{-6} mol L^{-1} glucose was 1.2%. Compared with the glucose ECL sensor prepared early in our laboratory [46,47] or different enzyme immobilized methods [48–50], the ECL sensor established in this study has lower detection limits and large linear response range. But the method for sensor establishment was a little more complicated in this study.

3.2.6. Interference studies

Some species that commonly existed and possibly interfered with determination of glucose in biological samples were tested. Increasing amounts of foreign species were added into the solution containing 6.0×10^{-5} mol L^{-1} of glucose. A foreign specie was considered not to interfere if it caused a relative error <5% during the measurement of the glucose sample. It was found that 5 times of sucrose, fructose, 7 times of lactose, maltose, 8 times of phenylformic acid and 15 times of uric acid and 17 times of ascorbic acid, 5 times of Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+} and 0.05 times of Co^{2+} has no interference with the determination of glucose.

3.2.7. Reproducibility and stability of Nafion/GOD/polyNiTSPc/MWNT/GC electrode

It is important to study the stability and the reproducibility of the enzyme electrode response for practical applications. Fig. 8 shows the ECL response of the sensor in 10 different solutions containing 6.0×10^{-5} mol L^{-1} glucose and 1.0×10^{-5} mol L^{-1} luminol, the RSD was 5.0% (n = 10). The long-term stability of the established sensor had also been studied, the sensor was used to detect 6.0×10^{-5} mol L^{-1} glucose 10 times/day, the ECL response of 6.0×10^{-5} mol L^{-1} glucose only found to be decreased 7.8% and 10% after two weeks and two months, respectively. Such reproducibility and stability could be acceptable for most practical applications.

In spite of Nafion film, small amount of oxidized products of luminol can be adsorbed on the electrode surface after many times of application, which can be removed easily through successive scanning (10 circles) in the buffer solution in potential range of −1.0 to 1.0 V. The modified electrode can be applied for at least 10 times determination without any obvious decrease in reproducibility.

Table 1
Glucose content and recovery in serum samples (diluted 1:100).

Sample	Detected[a] (mmol/L)	Reference[b] (mmol/L)	RSD (%)	Added (mmol/L)	Found[a] (mmol/L)	Recovery (%)
1	4.82	4.93	1.05	2.00	6.91	105
2	4.02	3.95	1.36	2.00	5.98	98
3	5.13	5.28	1.31	2.00	7.18	103
4	6.98	6.95	1.71	2.00	8.89	96

[a] Average of 5 times of determination.
[b] Determined by sysmex CHEMIX-180.

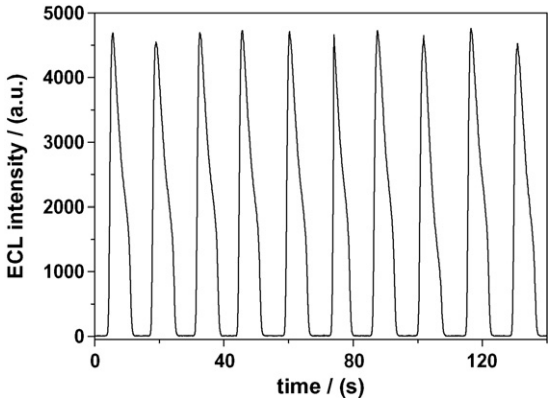

Fig. 8. The reproducibility of ECL on Nafion/GOD/polyNiTSPc/MWNT/GCE [luminol] = 1.0×10^{-5} mol L^{-1}, [glucose] = 6.0×10^{-5} mol L^{-1}; borate buffer: pH 7.4.

3.2.8. Application of the biosensors for determination of glucose in human serum samples

The proposed method has been applied to evaluate glucose content in serum samples. Before determination, the samples were diluted by buffer solution to the appropriate concentration. Under the optimum condition, the ECL of the samples had been tested, the results are shown in Table 1. These values obtained are consistent with the reference values. The recovery values ranged from 96% to 105%, which indicates that the sensor can be used clinically.

4. Conclusions

The oxidation of luminol could be catalyzed by the polyNiTSPc/MWNT-modified glassy carbon electrode, and the modified electrode could effectively enhance the luminol ECL. Based on which, an ECL biosensors have been successfully developed for detection of glucose by immobilizing GOD on the polyNiTSPc/MWNT/GC modified electrode. The proposed biosensor shows good response for glucose in the range of 1×10^{-6} to 1×10^{-4} mol L^{-1} with a detection limit of 8.0×10^{-8} mol L^{-1}. The response of the biosensor was very fast and achieved the maximum intensity within 10 s.

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