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Determination of Epinephrine using a Novel Sensitive Electrochemiluminescence Sensor based on ZnO Nanoparticles Modified Pencil Graphite Electrode

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The accurate determination of epinephrine is important for medical application. In the paper, a novel electrochemiluminescence (ECL) sensor, ZnO nanoparticles modified pencil graphite electrode (ZnO/PGE) was fabricated by self-prepared ZnO and low-cost 2B pencil graphite. The ZnO/PGEs showed excellent electrochemiluminescence performances and the possible electrochemiluminescence mechanism of ZnO/PGEs was also discussed. The effects of experimental parameters such as scanning rate, pH, concentrations of persulfate and reproducibility on ECL intensity have been investigated. Under the optimum condition, the ECL intensity of ZnO/PGE decreased linearly with concentrations of epinephrine over the wide range from 8×10^{-10} to 2×10^{-7} mol L^{-1}, with detection limit of 1×10^{-10} mol L^{-1} (S/N=3). The results showed that this novel sensor was successfully applied for the analysis of epinephrine in drug samples with satisfactory results.

Keywords: Pencil graphite electrode, ZnO, Electrochemiluminescence, Epinephrine

1. INTRODUCTION

Epinephrine (Ep) is an important catecholamine neurotransmitter released by the adrenal glands. It has a critical role in human central nervous system[1, 2], and it is responsible for many life phenomena like exciting the heart muscle, raising blood pressure, and quickly relieving symptoms[3, 4]. Many illnesses are related to the change of its concentrations in blood level [5]. Medically, it has been used as a kind common healthcare medicine and used in the treatment of sepsis, anaphylaxis, hypertension, bronchial asthma and other diseases [6]. For this reason, it is essential to develop rapid and sensitive detection methods for detecting epinephrine. Many current techniques such as capillary electrophoresis [7] fluorescence [8], chemiluminescence [9], high-performance liquid chromatography [10, 11]and electrochemical method[12-14] are used in detecting epinephrine. However, conventional methods for

detecting epinephrine are complicated, time-consuming, labor-intensive and expensive. Electrochemiluminescence (ECL) is a detection method that combines electrochemical reaction with chemical reaction. Due to its simple operation, low background signal, low reagent consumption, good stability, high sensitivity and controllability, the electrochemiluminescence method has been developed into an important detection method for analytical chemistry [15-17].

Recently, semiconductor nanoparticles have attracted extensive attentiondue to its size-dependent electronic and optical properties, semiconductor [18, 19]. Among the variety of semiconductor nanomaterials, Zinc oxide nanoparticles (ZnONPs) is a high-quality semiconductor material show very interesting features, such as good biocompatibility, high chemical stability and fast electron transfer kinetic functions[20,21]. It has been widely used for solar cells [22], electrochemical sensors [23] and optoelectronic devices [24]. However, there is rarely application in electrochemiluminescence. Liu et al found ZnO quantum dots dotted carbon nanotube (ZnO@CNT) showed excellent ECL characteristics, and ZnO@CNT was used to detection of PSA [25]. Geng et al reported the ECL behaviors of ZnO, ZnO/ZnSe and ZnO/ZnS core/shell nanostructures in aqueous system they achieved enhanced ECL intensity and a reasonably good stability [26]. Nevertheless, the ECL of ZnO in application fields need more in depth studied. In this work, electrochemiluminescence sensor based on the zinc oxide nanoparticles was developed for quickly detecting epinephrine.

Compared with other carbon-based electrodes used in electrochemiluminescence analytical tools such as glassy carbon electrodes[27], carbon fiber electrodes[28], carbon paste electrodes[29], pencil graphite electrodes (PGEs) possess the advantages like low cost, commercial availability, disposable, low technology and easy of modification, good mechanical rigidity, extremely inexpensive [30, 31]. Due to these advantages pencil graphite electrodes (PGEs) have widely used in analytical chemistry [32-34].

In our work, a ZnO modified pencil graphite electrode (ZnO/PGE) was made and ECL properties of ZnO/PGEs were investigated. And the related electrochemiluminescence mechanism of ZnO was also discussed. We developed a new method for determining epinephrine based on ECL quenching of ZnO/PGE when epinephrine was added in the solution. The novel method for determination of epinephrine in drug samples with satisfactory results is proposed.

2. EXPERIMENTAL

2.1 Materials and apparatus

Materials

Sodium hydroxide, potassium persulfate, urea and zinc nitrate hexahydratewere purchased from Xilong chemical co., LTD. Epinephrine (Ep) was purchased from Sinopharm Chemical Reagent Co. LTD (Shanghai, China). Epinephrine tartrate injection was purchased from Yuanda pharmaceutical Co. LTD. The clinical epinephrine samples were provided by local hospital. All reagents and solvents were analytical-reagent grade and used without further purification, distilled water was used in all assays and solutions.

Apparatus

The ECLmeasurements were conducted on a MPI-E analyzer equipped with a PMT (Xi'an Remax Electronic Science Tech. Co., Ltd., China) and thevoltage of the PMT (photo-multiplier tube) was set at 600 V. X-raypowder diffraction (XRD) patterns were obtained from DX-2700 (Dandong China).Scanning electron microscopy (SEM) photographs were obtained from S-4800 (Hitachi, Tokyo, Japan). All experiments were carried out with the working bare PGE or ZnO /PGE, a platinum foil counter electrode, and an Ag/AgCl (3 mol L^{-1}KCl) electrode reference electrode.

2.2 Synthesis of ZnO nanoparticles

ZnO nanoparticles were prepared according to following step: Briefly, urea and zinc nitrate hexahydrate (the molar ratio is 3:1) are added into a 50 mL beaker, enough water was added until the mixture was completely dissolved. Then, the obtained solution was reacted at 100 °C for 90 min in a stirred reactor. The resulting suspension including white precipitate was filtered, the precipitate was washed three times with distilled water. Finally the precipitate was dried in a vacuum drier at 60 °C for 5 h to obtain the ZnO nanoparticles.

2.3 Fabrication of PGE and ZnO /PGE

A commercially available 2B pencil with a diameter of 2 mm was used in this study. After removing of the outer packing of the pencil and get a total length of 1.5 cm pencil graphite, Electrical contact with the pencil graphite was obtained by winding copper wire around the pencil graphite, then this pencil graphite was inserted into a glass tube. The ends of the glass tube was fixed with glue. Firstly, the PGE was polished on a flint paper and a fine grit sandpaper. Then, the PGE was polished by 0.3 ìm and 0.05 ìm Al_2O_3 powder, and cleaned by ethanol and double-distilled water in an ultrasonic bath. 40 mg ZnO nanoparticles were added to 2 mL double distilled water, and the resulting solution was sonicating for 30 min. The surface of bare PGE was covered with 5 µL above ZnO nanoparticles suspension, and then dried in the air to get the ZnO/PGE.

2.4 ECL detection

ECL measurements were obtained in phosphate buffer solution (PBS, 0.1mol L^{-1}, pH 9.0) prepared from NaH_2PO_4 and Na_2HPO_4 containing 0.01 mol L^{-1} $K_2S_2O_8$. Cyclic voltammetry with a voltage range from 0 to –1.6 V have been used to investigate the ECL behaviour of ZnO/PGE in the buffer solutions and the scan rate was set at 0.1 V s^{-1}.

3. RESULTS AND DISCUSSION

3.1 Characterization ofZnO nanoparticles

SEM photographs were selected to characterize the morphology of ZnO nanoparticles, as shown in Fig. 1. It exhibited a relatively uniform spheres with average diameter of 75 nm. X-ray diffraction (XRD) measurement was performed to elucidate the crystalline phases of ZnO nanoparticles. Fig. 2A showed the XRD pattern of ZnO nanoparticles. All of the diffraction peaks were consistent with ZnO standard patterns (JCPDS: 36-1451, Fig. 2B), and the prominent characteristic peaks at 31.82°, 34.46°, 36.44°, 47.48°, 56.38°, 62.65°, 66.14°, 67.91°, 69.04°, 72.34° and 76.77°, respectively corresponding to the crystal plane with (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202). This result confirms that ZnO nanoparticles exhibited high phase purity.

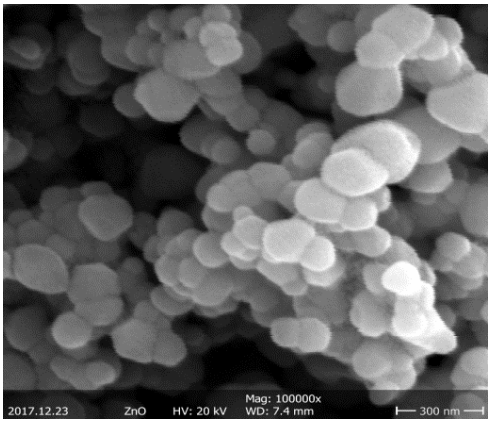


Figure 1.SEM image of ZnO nanoparticles

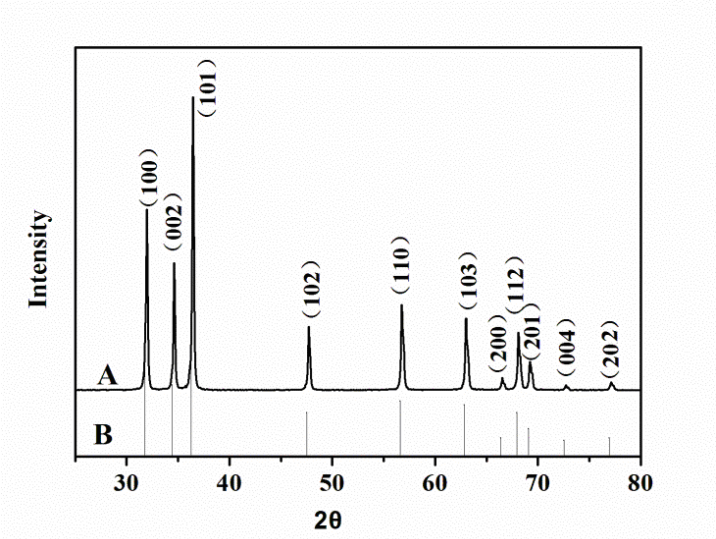


Figure 2. XRD pattern of ZnO nanoparticles

3.2 ECL behavior of ZnO nanoparticles

ECL behavior of bare PGE, ZnO/PGE and influence of epinephrine were studied in 0.1 mol L^{-1} phosphate buffer solution with persulfate as a coreactive agent. As shown in Fig 3, there was no ECL background signal at bare PGE (Fig 3a), when ZnO nanoparticles were dropt on the PGE, obvious ECL signal was detected at ZnO/PGE (Fig 3c). It proved that the ECL intensity was produced from ZnO on surface of the pencil graphite electrode [25]. The ECL intensity decreased rapidly when 4×10^{-9}mol L^{-1} epinephrine was added into the solution (Fig 3b). According to this principle we developed a new method for determining epinephrine based on ECL quenching of ZnO/PGE.

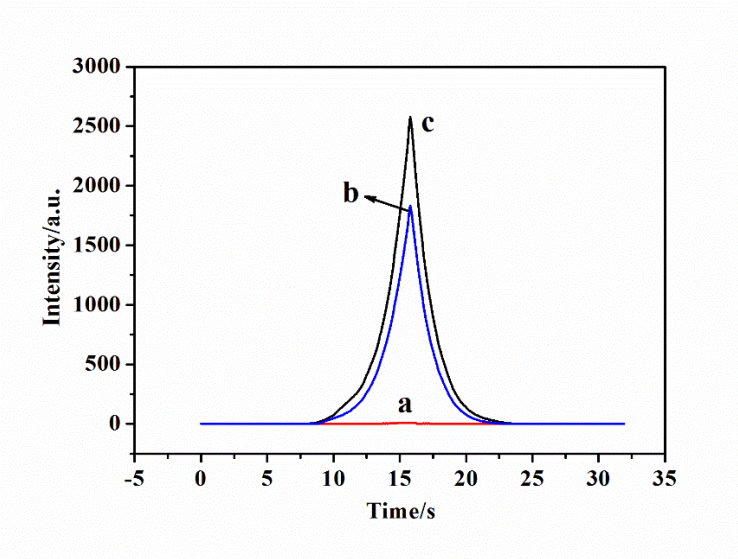


Figure 3. ECL curves of bare PGE (a), ZnO/PGE (c),4 × 10^{-9}mol L^{-1} epinephrine and ZnO/PGE (b); Solution: 0.1 mol L^{-1} PBS (pH 9.0)containing 0.01mol L^{-1} $K_2S_2O_8$.Scanning rate: 0.1Vs^{-1}.

The possible ECL mechanism was also discussed according to previous literatures [25, 35]. In such a mechanism, ZnO nanoparticles immobilized on the surface of the PGE were reduced to $ZnO^{\bullet-}$ (equation 1) when the potential was scanned to negative, and persulfate used as a co-reactive agent was reduced to oxidant radical $SO_4^{\bullet-}$ (equation 2) when $S_2O_8^{2-}$ got an electron. The excited state ZnO (ZnO*) was produced through electron transfer by the negatively charged $ZnO^{\bullet-}$ react with $SO_4^{\bullet-}$(equation 3). The ECL was produced by the release of a photon (equation 4) when ZnO* returned to its ground state. The possible ECL mechanism was exliained as follows:

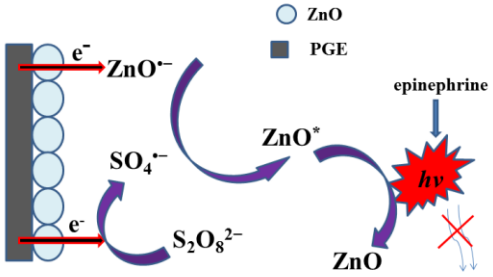
$$ZnO + e^- \rightarrow ZnO^{\bullet-} \quad (1)$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\bullet-} \quad (2)$$

$$ZnO^{\bullet-} + SO_4^{\bullet-} \rightarrow ZnO^* + SO_4^{2-} \quad (3)$$

$$ZnO^* \rightarrow ZnO + h\nu \quad (4)$$

The epinephrine was oxidation to corresponding oquinone when epinephrine was added to the solution, the strong oxidant radical $SO_4^{*-}$was consume, leading to significantly decrease of ECL [36].The schematic representation of the reaction process was listed in scheme 1.



Scheme 1. Possible reaction mechanism

3.3 Effect of scan rate on ECL

Different scanning rates on ECL of ZnO/PGE were discussed from 0.01V s^{-1} to 0.5 V s^{-1}. The results were listed in Fig.4. ECL intensity gradually increased with the increase of scanning rate, the possible reason may be the rapid formation of ZnO* on the surface of PGE. However, ECL intensity became unstable when the scanning rates were more than 0.1 V s^{-1}, taking the sensitivity and stability into consideration, 0.1 V s^{-1} was chosen for the entire experiment.

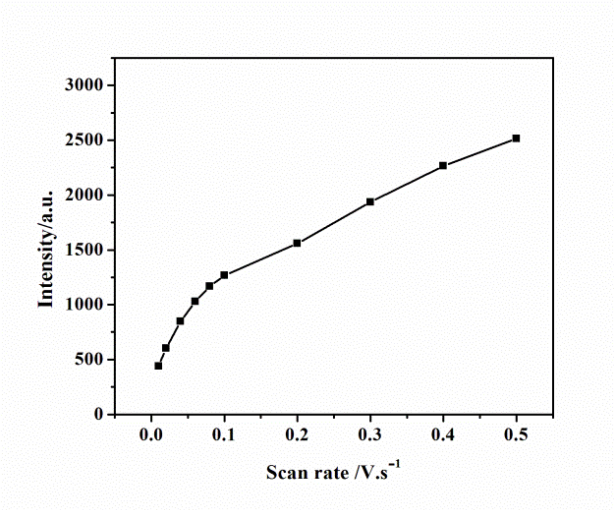


Figure 4. Effect of scan rates on ECL; Solution: 0.1 mol L^{-1} PBS (pH 9.0)containing 0.01mol L^{-1} $K_2S_2O_8$ and 4×10^{-9}mol L^{-1}epinephrine

3.4 Effect of the concentrations of persulfate

The concentrations of persulfate on determination of epinephrine were studied. Fig. 5 depicted the quenching effect of epinephrine. The ECL intensity quenching effect increased with the increasing concentrations of persulfate and then decreased when concentrations of persulfate were above 0.01

mol/L. The possible reason is attributed to epinephrine react with surplus persulfate when too much persulfate was added [29]. Therefore 0.01 mol/L persulfate was selected in this study.

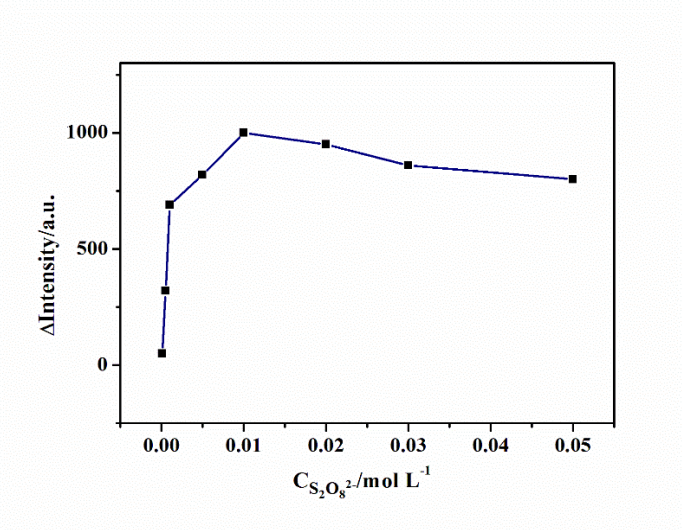


Figure 5. Effect of the concentration of persulfate; Solution: 0.1 mol/L PBS (pH 9.0) containing various concentrations of $K_2S_2O_8$ and 4×10^{-9}mol L^{-1} epinephrine. Scanning rate: 0.1 V/s.

3.5 Effect of pH on ECL

In most cases, the solution pH was an important factor influencing the ECL intensity of the sensor [31]. The effects of different pH on ECL were investigated (Fig.6). The luminous quenching effect increased gradually with increasing pH in the range from 3.00 to 9.00 when 4×10^{-9}mol L^{-1} epinephrine was added, the probable reason was that ZnO nanoparticles were unstable under acidic conditions [36]. The ECL arrived at its maximum at pH 9.0. While pH was greater than 9.0, the ECL quenching intensity decreased slightly. Hence, the pH 9.0 was chosen in this study.

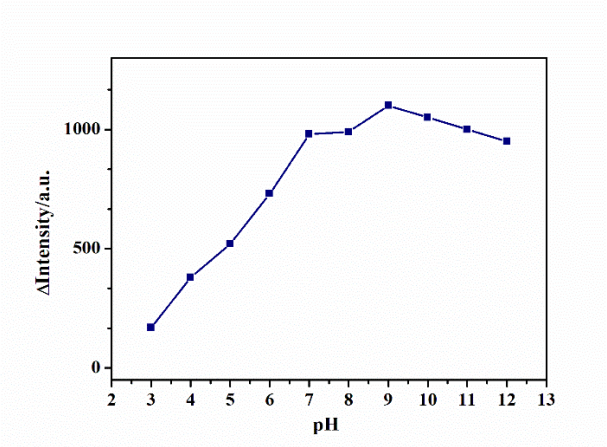


Figure 6. Effect of the pH; Solution: 0.1 mol/L PBS containing 0.01 mol/L $K_2S_2O_8$. and 4×10^{-9}mol L^{-1} epinephrine Scanning rate: 0.1 V/s.

3.6 Standard curve and linear range

Under the optimum conditions, as described previously, a linear relationship between the ECL intensity and log concentrations of epinephrine was observed from 8×10^{-10} to 2×10^{-7}mol L^{-1}, the detection limit was 1×10^{-10} mol L^{-1}, inset was the plots of ECL peak intensity versus logarithm of epinephrine concentration. The calibration plot of ECL intensity vs. log concentration (mol/L) was described by the following equation: Y= −727.87logC − 4036.08, with R= 0.9989.

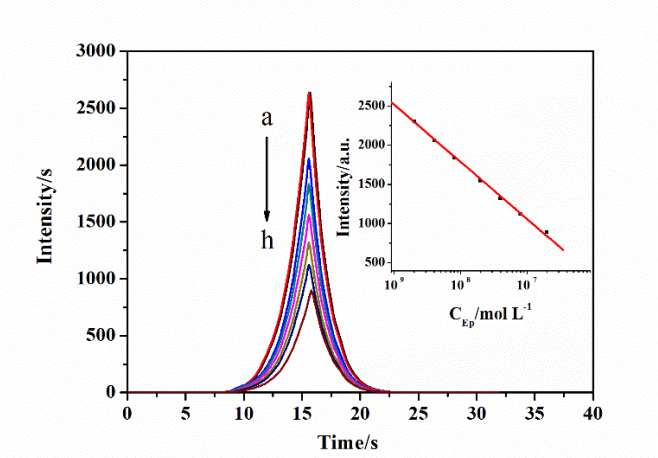


Figure 7.ECL intensity for detection of epinephrine with different concentrations; Solution: 0.1 mol L^{-1} PBS (pH 9.0) containing 0.01 mol L^{-1} $K_2S_2O_8$. Scanning rate: 0.1 V/s. (a), 8×10^{-10} mol L^{-1}; (b), 2×10^{-9} mol L^{-1}, (c), 4×10^{-9}mol L^{-1}; (d), 8×10^{-9} mol L^{-1}; (e), 2×10^{-8}mol L^{-1}; (f), 4×10^{-8}mol L^{-1}; (g), 8×10^{-8} mol L^{-1}, (h), 2×10^{-7} mol L^{-1}

We compared the linear range and LOD of the ZnO/PGE with other analytical methods for determination of epinephrine, as summarized in Table 1. It is clear that the proposed ECL sensor showed a wider linear range and the lowest detection limits than many published reports.

Table 1 Comparison with other epinephrine sensors

Methods	Linear range (mol·L^{-1})	LOD	Ref.
Fluorescence	1×10^{-8}–2×10^{-5}	6.8×10^{-9}	[37]
Chemiluminescence	1×10^{-7}– 7.060×10^{-3}	1.1×10^{-9}	[38]
Electrochemicalsensor	1×10^{-7} – 2.50×10^{-4}	1.0×10^{-8}	[39]
Electrochemicalsensor	9.0×10^{-8} – 1.0×10^{-4}	7.6×10^{-8}	[6]
electrochemical biosensor	5×10^{-7} – 7×10^{-4}	2.6×10^{-8}	[40]
Electrochemicalsensor	2×10^{-7} – 7.5×10^{-5}	1×10^{-7}	[41]
ECL	8×10^{-10} – 2×10^{-7}	1×10^{-10}	our work

3.7 Reproducibility and stability

The reproducibility of ZnO/PGE was discussed, as shown in Fig. 8. The modified electrode was tested 7-times successive measurements towards determination of epinephrine. The sensor

reproducibility of the modified electrode in 4×10^{-9} mol·L^{-1} each epinephrine gave a relative standard deviations of 1.95%, indicate that theZnO/PGE had good reproducibility. In addition, the stability of the ZnO/PGE was also investigated over a period of 7 days and no significant changes were observed indicated that the fabricated ZnO/PGE could be used for the detection of epinephrine.

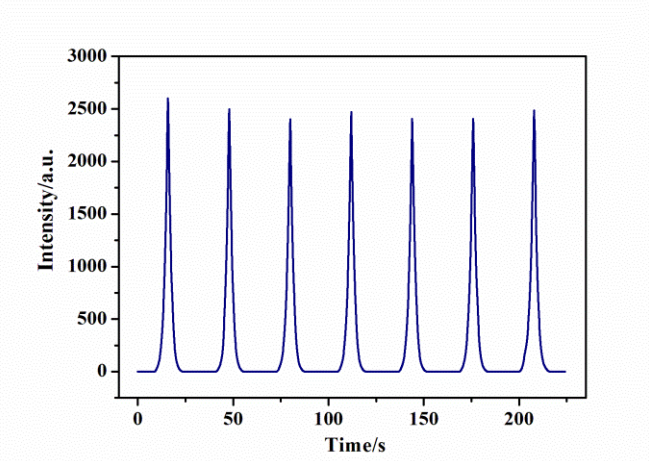


Figure 8. ECL stability of ZnO/PGE with epinephrine; Solution: 0.1 mol L^{-1} PBS (pH 9.0) containing 0.01 mol L^{-1} $K_2S_2O_8$ and 4×10^{-9} mol L^{-1} epinephrine. Scanning rate: 0.1 V/s.

3.8 Analytical application

Standard addition method with real samples was used to assess the analytical applicability of ZnO/PGE. Epinephrine tartrate injection samples purchased from a local pharmacy was diluted to 2×10^{-6}mol/L using PBS (pH 7.0).The detection results were listed in Tab. 2. It was found that the recovery for each sample changed between 97% and 105%. These results confirmed that the proposed ECL sensor was sensitive and reliable enough for the determination of epinephrine in real pharmaceutical samples.

Table 2. Determination of epinephrine in injection (n = 3)

NO.	Ep samples ($\times10^{-8}$mol·L^{-1})	Add Ep ($\times10^{-8}$mol L^{-1})	Found ($\times10^{-8}$mol L^{-1})	Recovery (%)	Average recovery（%）
1	3.29	4.00	7.17	97	
2	4.08	4.00	8.12	101	101
3	3.64	4.00	7.84	105	

3.9 Interference study

The influences of potential interfering substances on the determination of epinephrine were investigated. A change on the signal of ±5% caused by the maximum concentration of potential interfering substance was defined as tolerance limit. In this work, the measurements were performed at the concentration of 4×10^{-9} mol L^{-1} epinephrine with increasing concentrations of the possible interfering

ingredients. No interfering effects were found in 1000-fold Na^+, Br^-, NO_3^-, K^+, Cl^-, SO_4^{2-}, 100-fold ethanol and soluble starch, 50-fold I^- and NO_2^- were not found interfering effect, while there was interference for 10-fold glucose, this is because of the reducing property of glucose.

4. CONCLUSIONS

In the present study, a ZnO nanoparticles modified pencil graphite electrode (ZnO/PGE) was fabricated. A novel sensitive method for determination of epinephrine was developed and the ECL performances of ZnO/PGE were investigated. Various influences (pH, scan rates, concentration of persulfate) on ECL were studied. The new method reflected high advantages of wide linear range (from 8×10^{-10} mol L^{-1} to 2×10^{-7} mol L^{-1}) and high sensitivity with a low detection limit (1×10^{-10}mol L^{-1}). In addition, the ECL of ZnO/PGE was highly stable and stability. This method showed fine applicability for the detection of epinephrine in Epinephrine tartrate injection samples with a recovery of 97% to 105%. The ZnO/PGE will hopefully be of good application to further sensor development.

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