

## Selective Determination of Epinephrine in the Presence of Ascorbic Acid and Dopamine at Silver Doped Polyglycine Modified Electrode

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A silver doped polyglycine modified electrode was prepared by cyclic voltammetry. The electrochemical behavior of epinephrine at the modified electrode was studied. A novel method for determination of epinephrine using cyclic voltammetry was established. In pH=4.0 phosphate buffer solution, epinephrine gave an anodic peak at the modified electrode which can eliminate the interference of ascorbic acid and dopamine to the epinephrine determination. The peak potentials were  $E_{pa}=0.399V$  and  $E_{pc}=0.375V$  (vs Ag/AgCl). The anodic peak current versus the concentration of epinephrine showed a linear relations over the range of  $5.60 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1} \sim 1.00 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$  with a correlation coefficient as follows:  $i_{pa}=3.53 \times 10^{-6} + 0.079c(\text{mol} \cdot \text{L}^{-1})$ ,  $R=0.9979$ ; The detection limit was  $1.10 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ . The recovery was 96.7%~ 104.3%. The methods have been applied to injection sample analysis, and the results were in good agreement with the standard values.

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**Keywords:** Polyglycine, Epinephrine, Silver, Selective determination

### 1. INTRODUCTION

Epinephrine (EP) is one of the most important neurotransmitters in mammalian central nervous systems, and exists in the nervous tissue and body fluids. EP controls the nervous system in its performance for a series of biological reactions and nervous chemical processes [1]. Many diseases are related to changes of the EP concentration in mammals. It also serves as a chemical mediator, transmitting the nerve impulse to different organs. Medically, EP has been used as a common emergency health care medicine [2]. Also, low levels of EP have been found in patients with

Parkinson's disease [3]. Quantitative determination of EP is a significant thing in developing nerve physiology, diagnosis and controlling medicine [4]. Till date, the ability to detect EP with high selectivity and sensitivity is still a major target of electroanalytical research [5, 6]. The main problem of measuring this monoamine in vivo is the very low EP concentration and the large excesses of interfering substances, such as ascorbic acid (AA) and dopamine (DA). Unfortunately, at most solid electrodes, AA and DA are oxidized at a potential close to that of EP, resulting in an overlapping voltammetric response. In order to resolve this problem, one of the most common routes is to use a modified electrode, which can eliminate to the EP determination [7, 8]. In this study, a novel electrochemical sensor was fabricated with silver doped polyglycine modified glassy carbon electrodes (Ag-PGly/GCE), and its electrochemical properties were investigated. The results show that the silver can obviously improve conductivity, selective and sensitivity.

## 2. EXPERIMENTAL PART

### 2.1. Reagent and Chemicals

Epinephrine and glycine and L-ascorbic acid were purchased from National Institute for the Control of Pharmaceutical and Biological Products. Dopamine was purchased from Sigma. Phosphate buffer solutions (PBS) were prepared by mixing  $\text{KH}_2\text{PO}_4$  and  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , which were purchased from Beijing Chemical Reagent Company. All other chemicals not mentioned here were of analytical reagent grade and were used as received. Double distilled water was used throughout.

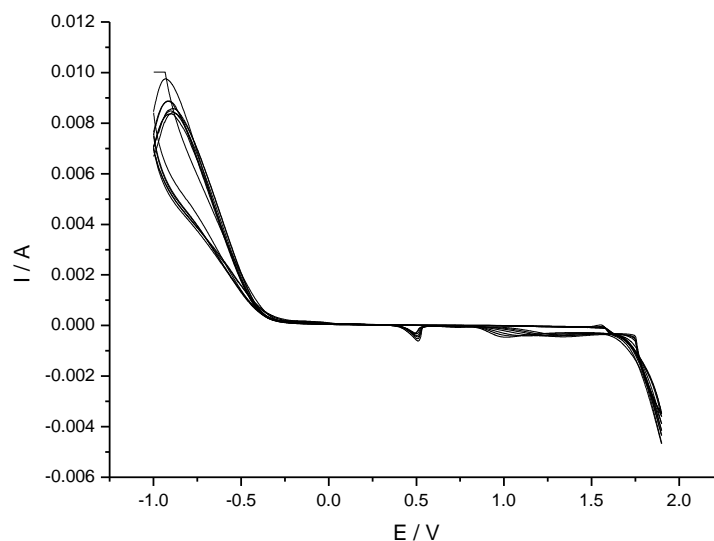
### 2.2 Apparatus

Electrochemical experiments were performed with an electrochemical work station-CHI660C (CH Instruments, Shanghai Chenhua Instrument Corporation, China). A conventional three-electrode system was used throughout. The working electrode was a bare or a polyglycine film-modified GCE (3.8mm in diameter), the auxiliary electrode was a Pt electrode and a silver electrode was employed as reference electrode. PHS-3B (Shanghai Precision Scientific Instrument Co.,Ltd, China), KQ-100 ultrasonic cleaner (Kunshan Ultrasonic Instrument Factory, China).

### 2.3 Electrode preparation and modification

The bare glassy carbon electrode (GCE) was polished before each experiment with gold sand paper and  $0.05\mu\text{m}$  alumina powder respectively, rinsed thoroughly with doubly distilled water between each polishing step, then washed successively with 1:1 nitric acid, ethanol and doubly distilled water in ultrasonic bath, and dried in air. The Ag-PGly/GCE was obtained by cyclic voltammetric (CV) in the

potential range between -1.0 V and 1.9 V for 7 cycles at a scan rate of  $100 \text{ mV}\cdot\text{s}^{-1}$  (Fig.1). The silver doped glycine modified solution was made up of  $0.01 \text{ mol}\cdot\text{L}^{-1} \text{AgNO}_3$ , nitric acid and water (1:1, V/V),  $0.05 \text{ mol}\cdot\text{L}^{-1} \text{KNO}_3$ ,  $0.01 \text{ mol}\cdot\text{L}^{-1}$  glycine and double distilled water. Then the Ag-PGly/GCE was treated in PBS (pH 4.0) by repetitive scanning in the potential range between 0V and 0.9 V at a scan rate of  $80 \text{ mV}\cdot\text{s}^{-1}$  by scanning and rinsed with doubly distilled water.



**Figure 1.** Cyclic voltammetric curves of metal-silver and glycine in polymerization process Scan rate:  $100 \text{ mV}\cdot\text{s}^{-1}$

#### 2.4 Determination of epinephrine

Under optimal conditions, a series of different concentrations of EP were investigated by CV in PBS solution (pH4.0). A three-electrode system was used, including a Ag-PGly/GCE as working electrode, a platinum electrode as counter electrode, and Ag/ AgCl ( $1 \text{ mol}\cdot\text{L}^{-1} \text{KCl}$ ) as reference electrode. Cyclic voltammograms (CVs) of EP were recorded. The glassy carbon electrode was restored by repetitive scanning under optimal conditions until no record. The GME was dried with filter paper and was used again.

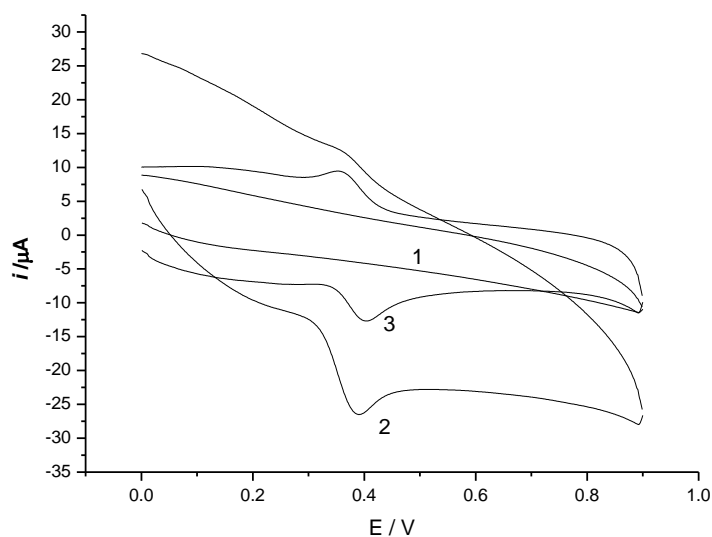
### 3. RESULTS AND DISCUSSION

#### 3.1 The optimization of electrochemical polymerization

The electrochemical polymerization of silver doped polyglycine at electrode is an electrochemistry process and is shown in Fig.1. Electrochemical behaviors of the Ag-PGly/GCE are affected by polymerization conditions, such as potential range, scanning rate and cycle, and the

concentration of modified solution. The results showed that the biggest peak currents of EP were obtained on the polymer membrane which was fabricated with the potential range of -1.0~1.9V and the peak currents increased with the sum of the scan cycles and almost reached constant after seven cycles, indicating that a uniform membrane was formed on the surface of the electrode. The results also showed that the solution of  $0.01 \text{ mol}\cdot\text{L}^{-1}$  silver nitrate,  $0.01 \text{ mol}\cdot\text{L}^{-1}$  glycine and  $0.05 \text{ mol}\cdot\text{L}^{-1}$  potassium nitrate.

### 3.2 Electrochemical behaviors of EP on the Ag-PGly/GCE



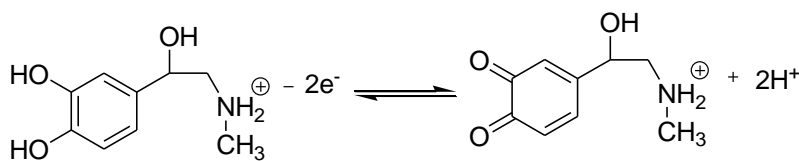
**Figure 2.** Cyclic voltammetric curves of EP at GCE (1), PGly/GCE (2), Ag-PGly/GCE (2) PBS (pH4.0), scan rate:  $100 \text{ mV}\cdot\text{s}^{-1}$ .

Fig. 2 shows the CVs of  $5.0\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  EP in PBS (pH 4.0) at GCE, PGly /GCE and Ag-PGly /GCE. The results showed that very faint electrochemical responses of EP were obtained on the bare GCE (curve 1), and on the PGly/GCE, a pair of anodic peak current ( $i_{pa}$ ) and cathodic peak current ( $i_{pc}$ ) were  $-3.58 \mu\text{A}$  and  $3.58 \mu\text{A}$ , respectively (curve 2). When the membrane of PGly was doped silver particles (curve 3), the  $i_{pa}$  and  $i_{pc}$  of EP increased to  $-5.42 \mu\text{A}$  and  $5.38\mu\text{A}$ . They almost were 1.5 times of that on the PGly/GCE. The results showed Ag-PGly has excellent electrocatalytic activity to EP

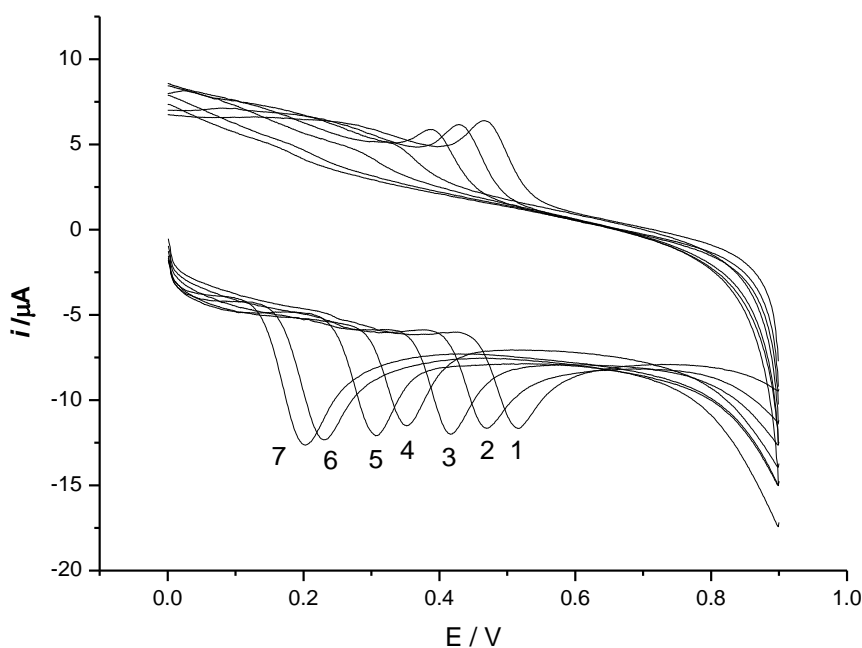
### 3.3 Optimization of the experimental conditions

The pH value of PBS: 1, 2.2; 2, 3.0; 3, 4.0; 4, 5.0; 5, 6.0; 6, 7.0; 7, 8.0

The effect of the medium's pH on the electrochemical signal was analyzed. Fig.3 shows the important influence of pH on the redox reaction of EP at the Ag-PGly /GME. As we can see, with increasing pH value of the solution the redox peak negatively shifted, based on  $[E_p^{\square} = (E_{pa} + E_{pc})/2]$ , the equation was  $E_p^{\square} = 0.64 - 0.058\text{pH}$ ,  $R = 0.9977$ .



**Scheme 1.** The mechanism of EP

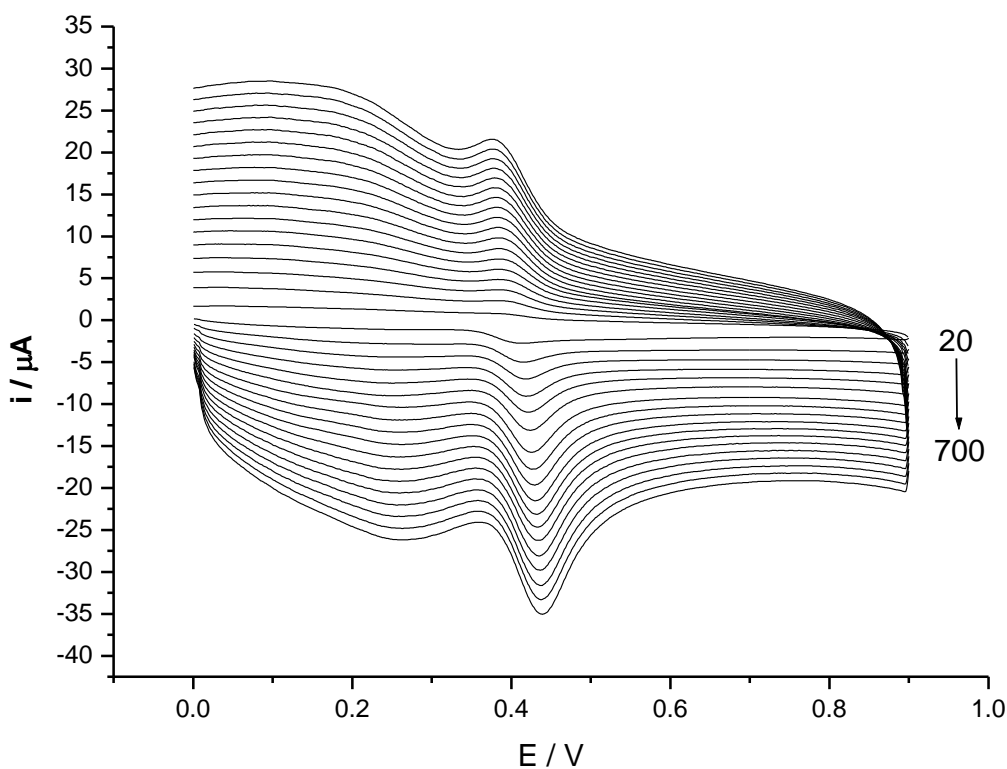


**Figure 3.** CVs of  $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  EP on Ag-PGly/GCE at scan rate  $140 \text{ mV} \cdot \text{s}^{-1}$  in PBS with different pH from 2.2 to 8.0.

According to the Nernst equation, the slope of  $-58 \text{ mV} \cdot \text{pH}^{-1}$  reveals that the proportion of the electron and proton involved in the reactions is 1: 1. Therefore, a mechanism for the EP oxidation can be proposed in Scheme 1. This is in agreement with the previous report [9, 10].

The pH of EP solutions were changed from pH 2.2 to 8.0, and potential was 0.0~0.9V. The redox peak currents increased till pH 4.0, indicating that the redox reactions involve the protons. Thus, in this study pH 4.0 was chosen.

As is shown in Fig.4, the oxidation potentials of EP move to positive direction and the redox peak currents increased with the scan rates ranging from 20 to 700  $\text{mV}\cdot\text{s}^{-1}$ . The liner regression equations of the  $i_{\text{pa}}$  and  $i_{\text{pc}}$  of the scan rates are expressed as  $i_{\text{pa}} (\text{A}) = -1.33 \times 10^{-6} - 1.76 \times 10^{-6}v (\text{mV})$ ,  $R=0.9968$ ;  $i_{\text{pc}} (\text{A}) = 7.19 \times 10^{-8} + 1.75 \times 10^{-8}v (\text{mV})$ ,  $R=0.9964$ , respectively, indicating that the electrochemical behaviors of EP on the Ag-PGly/GCE is an adsorption process. If the Ag-PGly/GCE was taken out from solution of EP, we can found that the redox peak currents still exist after scanning in blank PBS solution, but with scanning time after time it decreased sharply until disappear completely. It also may be ascribed to an adsorption process of electrochemical behaviors of EP on the Ag-PGly/GCE. However, the symmetry of potential becomes worse with the scan rates ranging after 100  $\text{mV}\cdot\text{s}^{-1}$ . Therefore, 100  $\text{mV}\cdot\text{s}^{-1}$  were used as the scan rate.



**Figure 4.** CVs of EP on Ag-PGly/GCE in the buffer of PBS ( $0.1 \text{ mol}\cdot\text{L}^{-1}$  pH 4.0) at different scan rates from 20 to 700  $\text{mV}\cdot\text{s}^{-1}$ .

### 3.4 Linear range and detection limit

To quantitatively detect EP, the concentrations of EP were varied from  $3.85 \times 10^{-7} \text{ mol}\cdot\text{L}^{-1}$  to  $1.09 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ . The peak potentials of EP remained unchanged, and the oxidation peak currents of

EP showed a linear relation versus EP concentration in the range of  $5.60 \times 10^{-7} \sim 1.00 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$  with a correlation coefficient as follows:  $i_{pa} = 3.53 \times 10^{-6} + 0.079c \text{ (mol} \cdot \text{L}^{-1})$ ,  $R = 0.9979$ ; The detection limit was  $1.10 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ .

### 3.5 Tolerance of foreign substances

AA and DA often coexist with EP in physiological fluids and possess close oxidation potentials to EP at a bare electrode. In this study, it was found that the above problem could be resolved by using the Ag-PGly/GCE. Thus, it provides a possible method for the selective determination of EP in the mixture solution containing EP and AA and DA.

If a foreign species caused a relative error of less than  $\pm 5\%$  during the determination of  $5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$  EP, it was considered no interference. No interference has been found when including up to  $1 \text{ mmol} \cdot \text{L}^{-1}$  of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\beta$ -alanine,  $0.1 \text{ mmol} \cdot \text{L}^{-1}$  of glucose and tartaric acid.

## 3. APPLICATIONS

The present method was used to the determination of EP in three kinds of EP injection. The pharmaceutical injections were diluted in the capacity of 50ml brown volumetric flask separately. An aliquot of diluted EP was mixed with a certain amount of the AA, DA ( $C_{AA}/C_{EP} = 1000$ ,  $C_{DA}/C_{EP} = 2$ ), and further diluted with PBS (pH 4.0) in another capacity of 50ml brown volumetric flask. EP in these preparations was determined by CV using the Ag-PGly/GCE respectively. The recoveries were calculated according to the oxidation peak currents. These results in table 1 show that the novel Ag-PGly/GCE is a potential tool for the selective determination of EP in the presence of AA and DA.

**Table 1.** Determination results of EP (n=6)

| Sample | EP sample<br>( $\times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) | EP standard<br>( $\times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) | Total EP<br>( $\times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) | Recovery<br>% |
|--------|---|---|--|---------------|
| 1      | 3.08  | 3.00  | 5.98   | 96.7          |
| 2      | 2.98  | 3.00  | 5.95   | 99.0          |
| 3      | 3.02  | 3.00  | 6.15   | 104.3         |

## 4. CONCLUSIONS

Voltammetric behavior of EP was investigated at silver doped polyglycine modified GCE by CV. The Ag-PGly/GCE showed electrocatalytic action for the redox of EP characterized by the

enhancement of the peak current and the redox of peak potential. The proposed method is a better method for the analytical determination of EP because it is simple, fast, and it has sufficient precision, accuracy, and sensitivity. The developed sensor has been successfully applied for the voltammetric determination of EP in injection samples.

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