

# Modification of Carbon Paste Electrode with Conductive Polyglycine-nafion Composite Membrane and Multi-wall Carbon Nanotubes for the Determination of Dopamine

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Received: 5 December 2018 / Accepted: 21 January 2019 / Published: 10 March 2019

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In this work, a novel method was developed to fabricate modified carbon paste electrode (CPE) by a composition of conductive polyglycine-nafion membrane and multi-wall carbon nanotubes (MWCNTs) (Poly(gly)-nafion/MWCNTs/CPE). The conductive Poly(gly)-nafion composite membrane on MWCNTs/CPE was prepared by drop-coating and in situ electrochemical polymeric deposition. Electrochemical behaviors of the fabricated electrodes were studied using cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Compared with the bare CPE, Poly(gly)-nafion/MWCNTs/CPE exhibited more effective electrochemical catalytic performance for the determination of dopamine (DA). The oxidation peak current of LSV increased linearly with two concentration intervals of DA over the range of 0.1-3.0  $\mu\text{M}$  and 3.0-20.0  $\mu\text{M}$  in BRBS with pH 5.0 at Poly(gly)-nafion/MWCNTs/CPE, and the limit of detection (LOD) was 0.03  $\mu\text{M}$  (S/N=3). Finally, the proposed method was successfully applied to detect dopamine in human serum samples.

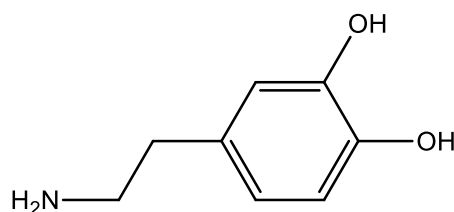
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**Keywords:** Carbon paste electrode, Multi-walled carbon nanotubes, Polyglycine, Nafion, Dopamine

## 1. INTRODUCTION

Dopamine (4-(2-Aminoethyl)benzene-1,2-diol, DA), an important neurotransmitter of the catecholamine family, is distributed throughout the human body, and plays an important role in the function of central nervous, endocrine, renal and cardiovascular systems [1, 2]. Its chemical structure is shown in Fig. 1. DA has been gaining increasing focus in the field of the clinical research. It has been proved that neurological disorders including Parkinson's disease [3], Schizophrenia [4] and Tourette's syndrome [5] are caused by the unusual level of dopamine. So, an accurate and sensitive method for the determination of DA is of great practical significance. Over recent decades, several traditional assay methods have been developed for the determination of DA, such as high-performance

liquid chromatography (HPLC) [6], capillary electrophoresis (CE) [7], and HPLC-Mass spectrometry (HPLC-MS) [8]. However, these developed methods require special instrumentation, long working time, tedious pretreatment and have high associated costs [2, 9]. Compared to these methods, electrochemical detection methods have many obvious advantages, such as high sensitivity, fast response, low cost, easy operation and real-time response [10, 11]. So, it has been used as an important analytical technique for the determination of electro-active species [12]. Although many studies on electrochemical detection methods for the detection of DA have been reported [13-18], developing simple, rapid, accurate, sensitive and low cost electrochemical methods based on modified electrodes for the determination of DA in the diagnosis of various diseases still need to be explored.



**Figure 1.** Chemical structure of dopamine.

Multi-walled Carbon nanotubes (MWCNTs) is a promising material for modifying electrode because of the unique structures and properties, such as good electrical conductivity, high electrocatalytic effect, strong adsorptive ability [19, 20]. Nafion, a cation-exchanger polymer and dispersant, is frequently used as a material for electrode modification [2, 21]. Nafion and MWCNTs modified glassy carbon electrodes (GCEs) have been used for DA detection [22, 23]. In recent years, conducting polymers have been largely explored owing to their combined properties of organic polymers and electronic properties of semiconductors [24]. Electrochemical polymerization is a well-known technique used to immobilize materials to the modified electrode surface, which can provide larger surface area by forming homogeneous film, and it is able to promote electron transfer rates through strong adherence of the polymer to the electrode surface [25]. Polyglycine (Poly(gly)), which has favorable electrocatalytic effects, can be obtained by electrochemical polymerized of glycine [26]. At present, some studies have reported on the electrochemical detection by Poly(gly) modified electrodes [27-29]. However, as far as we know, no research has been done about the preparation of Poly(gly)-nafion compound material on MWCNTs modified carbon paste electrode (CPE) and its application for electrochemical detection of DA.

Here, we describe the fabrication of modified CPE with conductive Poly(gly)-nafion composite membrane and MWCNTs by drop-coating and in situ electrochemical polymeric deposition. The prepared Poly(gly)-nafion/MWCNTs/CPEs displayed fast electron transfer and prominent electrocatalytic ability to DA, and the oxidation current responses of DA by cyclic voltammetry (CV) were significantly increased at the modified electrodes. In addition, the Poly(gly)-nafion/MWCNTs/CPEs were also successfully employed to determine DA in human serum samples by linear sweep voltammetry (LSV) with satisfied simplicity, sensitivity, selectivity and repeatability.

## 2. EXPERIMENT

### 2.1. Apparatus and reagents

The electrochemical measurements were carried out on a CHI 830D electrochemical analyzer, which equipped with data processing software (Shanghai CH Instruments, Inc., Shanghai, China). A conventional three-electrode system, including a bare CPE or MWCNTs/CPE or Nafion/MWCNTs/CPE or Poly(gly)-nafion/MWCNTs/CPE as the working electrode (WE), an Ag/AgCl (sat. KCl) electrode as the reference electrode (RE), and a Pt wire as the counter electrode (CE) was employed for all the voltammetric experiments. The pH values were measured by a PHS-3C digital pH meter (INESA Scientific Instrument Co., Ltd, Shanghai, China).

Dopamine and glycine were obtained from Sigma-aldrich (Shanghai, China). Graphite powder, paraffin oil, acetic acid, boric acid and phosphoric acid were purchased from Sinopharm Chemical Reagent (Shanghai, China). Sodium hydroxide, dipotassium hydrogen phosphate and potassium dihydrogen phosphate were obtained from Tianjin Damao Chemical Reagent (Tianjin, China). Nafion (5% in ethanol, w/w) was acquired from Cool chemistry (Beijing, China). Multi-walled carbon nanotubes (>97% purity) with <math>2\mu\text{m}</math> length and 10~20 nm internal diameter were obtained from Nanotech Port Co., Ltd. (Shenzhen, China). All reagents were analytical grade and used as received otherwise specified statement. Ultra-pure water (Millipore, USA) was used for the formulation of all required solutions.

### 2.2. Fabrication of Poly(gly)-nafion/MWCNTs/CPEs modified CPE

The procedure for Poly(gly)-nafion/MWCNTs/CPE fabrication is depicted systematically in Scheme 1. In order to remove the impurities, MWCNTs were pretreated by stirring for 10 h in 3 M  $\text{HNO}_3$  at 60 °C, then filtered and rinsed to neutral pH value with water, followed by drying in a vacuum oven [30]. 0.2 g graphite powder and 100  $\mu\text{L}$  paraffin oil were mixed to a homogeneous paste in a mortar [31]. For the preparation of CPE, the resulting homogeneous paste was inserted into the bottom of a polyethylene tube (inside diameter = 3 mm), and polished carefully on a weighing paper [20]. According to the literature method [20, 26, 32], the MWCNTs were intercalated into the soft carbon paste of CPE with the aid of mechanical force and the action of chemical and physical absorption, by which the MWCNTs modified CPE (MWCNTs/CPE) was fabricated. Then, 10  $\mu\text{L}$  of Nafion solution (0.1% in ethanol, w/w) was dropped on the surface of the MWCNTs/CPE. After standing for 6 h at 25 °C, the Nafion and MWCNTs modified CPE (Nafion/MWCNTs/CPE) was fabricated. Next, the Nafion/MWCNTs/CPE was immersed in a solution containing 15 mM glycine, using 0.1 M PBS (pH 6.0) as supporting electrolyte, and cyclic scans were executed by applying 10 consecutive potential cycles at the potential range of -0.40 to +1.85 V (vs. Ag/AgCl), with initial potential of -0.40 V and scan rate of 100  $\text{mV}\cdot\text{s}^{-1}$  [26]. During this process, the conductive Poly(gly)membrane was formed on the surface of Nafion/MWCNTs/CPE by in situ electrochemical polymeric deposition. The fabricated Poly(gly)-nafion/MWCNTs/CPE was rinsed thoroughly with water after the electrochemical processing. All of the prepared electrodes were stored at 4 °C in refrigerator when not in use.



**Scheme 1.** Schematic illustration of Poly(gly)-nafion/MWCNTs/CPE fabrication

### 2.3. Electrochemical measurements

Stock solution of DA was prepared in Britton-Robinson buffer solution (BRBS) with pH 5.0. DA solutions with different concentration were prepared by placing required quantity of the stock solution into a 10 mL volumetric flask and diluting it with BRBS. The  $\text{N}_2$  saturated buffer was used to remove dissolved oxygen present in the electrolyte solution. For electrochemical characterization of the modified CPEs, CV from -0.3 to +0.7 V (vs. Ag/AgCl), with initial potential of -0.3 V, was carried out in 0.1 M KCl containing  $2.0 \times 10^{-4}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  at scan rate of  $50 \text{ mv} \cdot \text{s}^{-1}$ . Additionally, CV from +0.1 to +0.8 V (vs. Ag/AgCl), with initial potential of +0.1 V, was carried out in  $1.0 \times 10^{-5}$  M DA at the Poly(gly)-nafion/MWCNTs/CPE in BRBS with different pH values (pH 2.0-6.0) at scan rate of  $50 \text{ mv} \cdot \text{s}^{-1}$  for investigating the influence of supporting electrolyte solution and pH. LSV was carried out by applying potential from +0.05 to +0.7 V (vs. Ag/AgCl) with initial potential of +0.05 V at scan rate of  $50 \text{ mv} \cdot \text{s}^{-1}$  in BRBS with pH 5.0 for the electrochemical detection of DA.

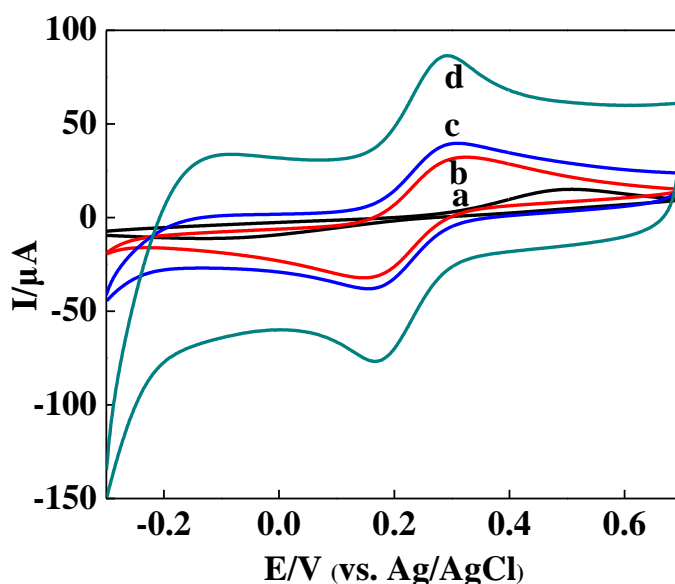
All electrochemical measurements were performed at room temperature.

## 3. RESULTS and DISCUSSION

### 3.1 Electrochemical characterization of the modified CPEs

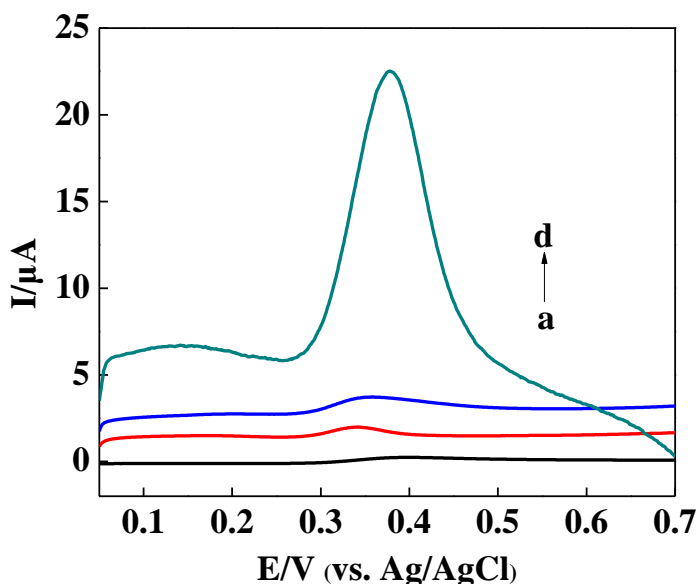
First, the redox probe of  $\text{K}_3\text{Fe}(\text{CN})_6$  (0.1 M KCl as supporting electrolyte) had been used to explore the electrochemical performance of the modified CPEs. As shown in Fig.2, a pair of redox peaks of  $\text{K}_3\text{Fe}(\text{CN})_6$  were observed at bare CPE (a), MWCNTs/CPE (b), Nafion/MWCNTs/CPE (c) and Poly(gly)-nafion/MWCNTs/CPE (d) in  $2.0 \times 10^{-4}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  (0.1 M KCl), respectively. By comparing the CV curves, it was found that the peak current ratios ( $I_{\text{pc}}/I_{\text{pa}}$ ) of bare CPE,

MWCNTs/CPE, Nafion/MWCNTs/CPE and Poly(gly)-nafion/MWCNTs/CPE were 0.42, 0.83, 0.92 and 1.03, respectively. The redox peak currents were also obviously increased, and Poly(gly)-nafion/MWCNTs modified CPE (curve d) showed the highest responses. These indicated that Poly(gly)-nafion/MWCNTs/CPE can promote electron transfer reaction better than other CPEs do [33]. Moreover, the peak separation was slightly decreased to 118 mV at Poly(gly)-nafion/MWCNTs/CPE compared to 144 mV for Nafion/MWCNTs/CPE, which may due to the electrostatic attraction between  $[\text{Fe}(\text{CN})_6]^{3-}$  and Poly(gly) surface [26, 29]. These behaviors suggesting that the Poly(gly) surface is more positively charged and Poly(gly)-nafion/MWCNTs/CPE has remarkable efficient electrocatalytic activity.



**Figure 2.** CV curves of bare CPE (a), MWCNTs/CPE (b), Nafion/MWCNTs/CPE (c) and Poly(gly)-nafion/MWCNTs/CPE (d) in  $2.0 \times 10^{-4}$  M  $\text{K}_3\text{Fe}(\text{CN})_6$  (0.1 M KCl), scan rate:  $50 \text{ mV} \cdot \text{s}^{-1}$ .

Then, the electrochemical behaviors of DA were investigated in BRBS with pH 5.0 at the different CPEs by LSV. Fig. 3 showed LSV responses of bare CPE (a), MWCNTs/CPE (b), Nafion/MWCNTs/CPE (c) and Poly(gly)-nafion/MWCNTs/CPE (d) in BRBS with pH 5.0 containing  $2.0 \times 10^{-6}$  M DA at a scan rate of  $50 \text{ mV} \cdot \text{s}^{-1}$ . Although all the electrodes exhibited electrochemical responses for DA, the oxidation response signals of the DA were relatively low at bare CPE ( $0.24 \mu\text{A}$ ), MWCNTs/CPE ( $0.99 \mu\text{A}$ ) and Nafion/MWCNTs/CPE ( $1.72 \mu\text{A}$ ). On the contrary, the oxidation response signal of DA at Poly(gly)-nafion/MWCNTs/CPE was greatly enhanced, and the oxidation peak appeared at 0.38 V with the peak current of  $15.84 \mu\text{A}$ . Such a phenomenon can be attributed to the synergistic electrocatalytic effect of conducting Poly(gly) on Nafion/MWCNTs/CPE surface [28, 34]. Therefore, poly (Gly)-Nafion/MWCNTs/CPE has the potential to be used effectively for the sensitive determination of DA.



**Figure 3.** LSV curves of bare CPE (a), MWCNTs/CPE (b), Nafion/MWCNTs/CPE (c) and Poly(gly)-nafion/MWCNTs/CPE (d) in BRBS with pH 5.0 containing  $2.0 \times 10^{-6}$  M DA, scan rate: 50 mV/s.

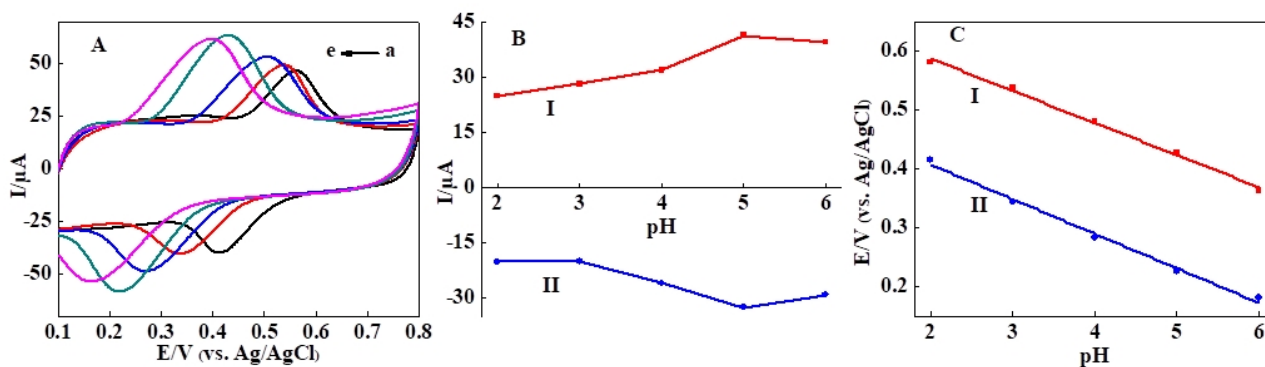
### 3.2 Influence of supporting electrolyte solution and pH

The LSV responses of DA in different supporting electrolyte solutions such as 0.1 M sodium acetate-acetic acid buffer solution, 0.1 M sodium citrate-citric acid buffer solution, 0.1 M phosphate buffer solution, and Britton-Robinson buffer solution (BRBS) were investigated at Poly(gly)-nafion/MWCNTs/CPE. And after comparison, we found that the well-defined LSV response with stable oxidation peak and high peak current of DA was obtained in BRBS. So, BRBS was chosen as supporting electrolyte solution.

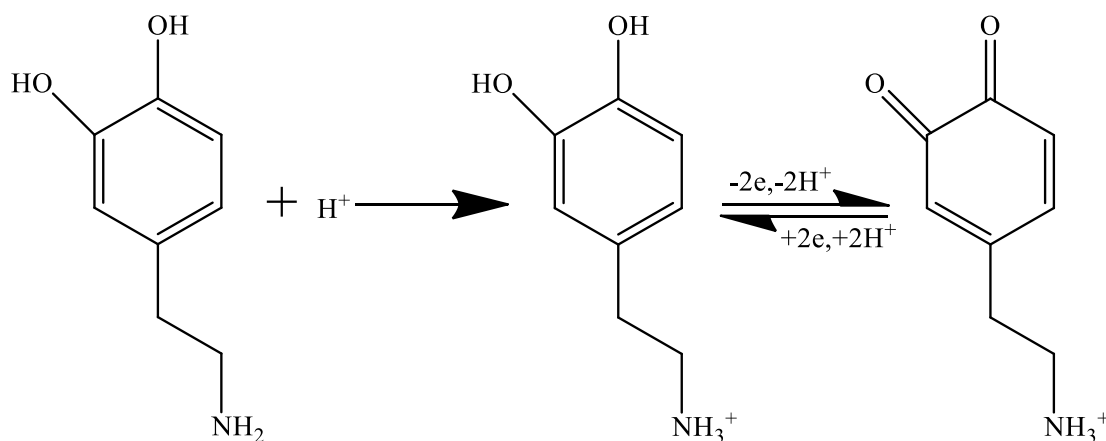
According to the literature, BRBS could be used below pH 6.0 but could not be used above pH 6.0 because of interaction between borate and the *o*-dihydroxy moiety of the catecholamines [35]. To achieve the optimization condition for the electrochemical detection, we examined the influence of supporting electrolyte solution pH by CV. As shown in Fig. 4A, CV curve of  $1.0 \times 10^{-5}$  M DA was recorded in BRBS with various pH values over the range between 2.0 and 6.0. Fig. 4B and Fig. 4C show the influence of supporting electrolyte solution pH on the peak current responses and peak potential. It can be seen that the anodic peak current ( $I_{pa}$ ) increased firstly and then decreased, and the maximum of  $I_{pa}$  was observed in pH 5.0 (Fig. 4B I). The change rule of the cathode peak current ( $I_{pc}$ ) was consistent with that of  $I_{pa}$  (Fig. 4BII). Hence, the BRBS with pH 5.0 was selected in the following experiments to achieve higher sensitivity.

Besides, as shown in Fig. 4B and Fig. 4C, we found that both the peak current and the peak potential of DA are strongly dependent on pH value from pH 2.0-6.0. And the anodic peak potential ( $E_{pa}$ ) and cathode peak potential ( $E_{pc}$ ) shifted negatively with the increase of pH values. All these demonstrating that the proton took part in the oxidation reaction process of DA directly [28]. The

linear relationships were established between  $E_{pa}/E_{pc}$  and pH values of supporting electrolyte solution. The linear regression equations for  $E_{pa}$  and  $E_{pc}$  were  $E_{pa} (V)=0.697-0.0546 \text{ pH}$ ,  $R^2=0.9952$  (Fig. 4C I) and  $E_{pc} (V)=0.525-0.0588 \text{ pH}$ ,  $R^2=0.9911$  (Fig. 4CII), respectively. And the slope ( $dE_p/dpH$ ) value was found to be  $-54.6\text{mV/pH}$  ( $E_{pa}$ ) and  $-58.8 \text{ mV/pH}$  ( $E_{pc}$ ), respectively, which were close to the anticipated Nernstian value of  $-59 \text{ mV/pH}$  and in agreement with the literature reports [36-38]. This indicates that the electrochemical process of DA involves the same number of protons and electrons. Therefore, we supposed that the oxidation-reduction of DA at Poly(gly)-nafion/MWCNTs/CPE was involves  $2e^-/2H^+$  transfer processes as shown in Scheme 2, which was consistent with the literature [18, 39].



**Figure 4.** (A) CV curves of  $1.0 \times 10^{-5} \text{ M}$  DA at the Poly(gly)-nafion/MWCNTs/CPE in different pH values of BRBS ( a→e: pH values of 2.0-6.0), scan rate: 50 mV/s. (B) Influence of supporting electrolyte solution pH values on the anodic peak current ( $I_{pa}$ ) (I) and cathode peak current ( $I_{pc}$ ) (II) response of DA at Poly(gly)-nafion/MWCNTs/CPE. (C) The plots of anodic peak potential ( $E_{pa}$ ) (I) and cathode peak potential ( $E_{pc}$ ) (II) of DA versus various pH values.

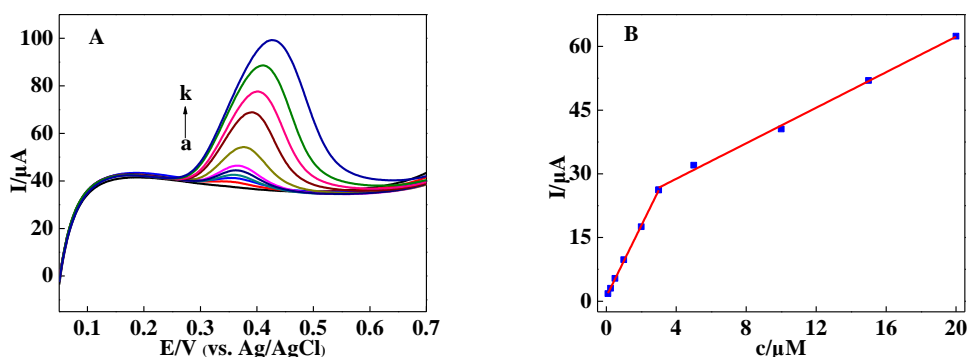


**Scheme 2.** The oxidation-reduction mechanism for DA at Poly(gly)-nafion/MWCNTs/CPE.

### 3.3 Calibration curve and detection limit

The quantitative analysis of DA at Poly(gly)-nafion/MWCNTs/CPE was carried out under

optimum experimental condition by LSV. As presented in Fig. 5A, the oxidation peak currents were enhanced gradually with the increase of DA concentration. The peak currents and the concentrations showed good linear relationships with two concentration intervals of DA over the range of 0.1-3.0  $\mu\text{M}$  and 3.0-20.0  $\mu\text{M}$  (Fig. 5B). The linear regression equations were  $I_p (\mu\text{A})=8.359c (\mu\text{M})+1.068$  ( $R^2=0.9993$ ) and  $I_p (\mu\text{A})=2.092c (\mu\text{M})+20.454$  ( $R^2=0.9965$ ), and the limit of detection (LOD) for DA was obtained as 0.03  $\mu\text{M}$  according to a signal-to-noise ratio of 3 ( $S/N=3$ ).



**Figure 5.** (A) LSV curves of different concentrations of DA (a: bg, b→k: 0.1-20.0  $\mu\text{M}$ ) at Poly(gly)-nafion/MWCNTs/CPE in BRBS with pH 5.0, scan rate: 50 mV/s. (B) The corresponding calibration plot of peak current and the concentration of DA.

### 3.4 Reproducibility and stability of Poly(gly)-nafion/MWCNTs/CPE

In order to examine the reproducibility of Poly(gly)-nafion/MWCNTs/CPE, five electrodes were prepared under the same conditions and used for the detection of  $2.0 \times 10^{-6}$  M DA in BRBS with pH 5.0 by LSV. The RSD of the LSV current responses were found to be 4.9 % for DA, confirming that the presented fabrication method of Poly(gly)-nafion/MWCNTs/CPE was highly repeatable. The long-term stability was also evaluated by performing a detection for DA about every 2 days at five Poly(gly)-nafion/MWCNTs/CPEs by LSV. It was observed that the electrodes retained about 87 % of its initial LSV current response after 10 days. The results indicate a good stability of Poly(gly)-nafion/MWCNTs/CPE.

### 3.5 Comparison of proposed electrode with literature electrodes

To demonstrate the advantage of the proposed electrode for the determination of DA, the analytical performances have been compared with other previously reported modified electrodes and listed in Table 1. It was noticed that Poly(gly)-nafion/MWCNTs/CPE shows favorable analytical performance in terms of wide linear range and low detection limit over other electrodes. Therefore, Poly(gly)-nafion/MWCNTs/CPE is suitable for the detection of DA.



**Table 1.** Comparison with other modified electrode for determination of DA.

Electrode	Method	Linear range ( $\mu\text{M}$ )	LOD ( $\mu\text{M}$ )	Ref.
AuNPs/Trp-GR/GCE	DPV	0.5-411	0.056	[13]
Py-PBA/GCE	DPV	0.05-10	0.033	[14]
AuNP/Gr/OPPy-MIP/GCE	DPV	0.5-8	0.1	[15]
Iron(III) Doped Zeolite/CPE	DPV	0.1-200	0.05	[16]
TCPP-Sa/CPE	SWV	0.4-10	0.1	[17]
Graphene nanowalls/Ta	DPV	0.2-10 10-40	0.04	[18]
GQD/SPE	DPV	0.1-1000	0.05	[40]
PPy-MWCNTs/GCE	DPV	0.62-100	0.06	[41]
Co <sub>3</sub> O <sub>4</sub> /rGO/CTAB/CPE	DPV	8.2-76	2.8	[42]
Poly(gly)-nafion/MWCNTs/CPE	LSV	0.1-3.0 3.0-20	0.03	This work

### 3.6 Analytical applications

In order to verify the reliability of the developed method for analysis of DA in real biological samples, Poly(gly)-nafion/MWCNTs/CPE was applied for determination of DA in human serums. Human blood obtained from healthy volunteers in Henan University of Science and Technology First Affiliated Hospital was centrifuged at 3500 rpm for 30 min to separate serum. The human serum was diluted 10 times with BRBS (pH 5.0) without any pretreatment. Then, the samples were spiked with known amounts of DA and measured by LSV as described before. Each sample was measured five times under the optimized conditions. As shown in Table 2, the quantitative recoveries rates for DA was 92.4% to 100.2% ( $\text{RSD} \leq 4.1\%$ ). These results indicate that the proposed method could be effectively used for the determination of DA in complicated biological samples.

**Table 2.** Analytical results for DA in human serum samples (n=5).

Method	Added/( $\mu\text{M}$ )	Determined/( $\mu\text{M}$ )	Recovery/%	RSD/%
LSV	5	4.62	92.4	4.1
	10	9.92	99.2	2.9
	15	15.03	100.2	3.3

## 4. CONCLUSION

At the present work, a rapid, accurate and sensitive modified electrode for the determination of DA was readily fabricated based on a composition of conductive Poly(gly)-nafion membrane and MWCNTs modified CPE. The obtained Poly(gly)-nafion/MWCNTs/CPE displays excellent electrochemical catalytic properties and favorable analytical performance towards DA. What's more, the test results of DA at Poly(gly)-nafion/MWCNTs/CPE in mixture solution formed by human serum

sample demonstrates the high selectivity. Therefore, the developed sensor is feasible for DA detection in practical biological samples.

#### ACKNOWLEDGEMENTS

This work was supported by programs for Science & Technology Innovation teams in Universities of Henan Province (#18IRTSTHN026) and Outstanding Youth of Science & Technology Innovation in Henan Province (#184100510006).

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