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Electrochemical detection of dopamine in the presence of ascorbic acid using PVP/graphene modified electrodes

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ABSTRACT

Graphene (GR) was synthesized through electrochemical reduction of graphene oxide and characterized by spectroscopic and electrochemical techniques. Polyvinylpyrrolidone (PVP)/graphene modified glassy carbon electrode (PVP/GR/GCE) was prepared and applied for the fabrication of dopamine (DA) sensors without the interference of ascorbic acid (AA). Compared to bare GCE, an increase of current signal was observed, demonstrating that PVP/GR/GCE exhibited favorable electron transfer kinetics and electrocatalytic activity towards the oxidation of dopamine. Furthermore, PVP/GR/GCE exhibited good ability to suppress the background current from large excess ascorbic acid. Amperometric response results show that the PVP based sensor displayed a wide linear range of 5×10^{-10} to 1.13×10^{-3} mol/L DA with a correlation coefficient of 0.9990 and a detection limit of 0.2 nM (S/N=3). The determination of dopamine in urine and human serum samples were studied.

1. Introduction

Dopamine (DA), as one of the important neurotransmitter, plays a significant role in the function of the central nervous, renal and hormonal systems [1]. The abnormal levels of DA may result in several diseases and neurological disorders such as schizophrenia, Parkinson's and Alzheimer's diseases [2–4]. Because of its electrochemical activity, dopamine detection attracts tremendous interest in electroanalysis [5–7]. However, there exist some challenges to measure DA under physiological conditions. The primary challenges are the very low levels of DA and the interference of coexisting ascorbic acid (AA) in organisms, which sharing a similar oxidation potential in electrochemical detection. Thus, it is desirable for diagnostic applications to develop a simple and rapid method for the determination of DA with high selectivity and sensitivity.

Graphene (GR), a flat monolayer of carbon atoms closely packed into a honeycomb two-dimensional model for carbon-based electronic materials as well as being a fundamental building block for fullerenes, carbon nanotubes and graphite, has been considered as a "rising-star" and attracted tremendous attention from scientific communities [8,9]. It has shown many intriguing properties, including high mobility of charge carriers [10,11], unique transport performance [12,13], high mechanical strength [14,15], and extremely high thermal conductivity [16,17]. Comparing to the commonly used carbon nanotubes, graphene has higher surface area, more excellent electrical conductivity and electron mobility at room temperature due to their unique two-dimensional nanostructure [18,19]. The high surface area is helpful in increasing the surface loading of the target molecules on the surface. The excellent conductivity and small band gap are favorable for conducting electrons from biomolecules [20]. Graphene-based chemical sensors can also have a much higher sensitivity because of the low electronic noise from thermal effect [21,22]. Furthermore, compared with carbon nanotubes, graphene can also be obtained easily by chemical conversion of the inexpensive graphite [23]. The special properties of graphene may provide insight to fabricate novel biosensors for virtual applications. Shang and co-workers [24] reported an electrochemical method on selective detection of dopamine by using multilayer graphene nanoflake films which were fabricated via chemical vapor deposition.

On the other hand, polyvinylpyrrolidone (PVP) as a neutral non-ionic and non-toxic macromolecule shows strong adsorption character to phenolic compounds, which is attributed to hydrogen bond between imide in the center of polymer and hydroxyl group in phenolic compounds. Unlike the electrostatic stabilization imparted by absorbed anions, steric or and depletion stabilization by the non-ionic yet largely hydrophilic polymer confers colloidal stability in water [25]. Also, compared to incomplete chemical

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reduction of polymer-protected graphene oxide single sheets [26], dropping PVP on the modified electrodes will not bear structure defects and discontinuities within their planar lattice [25]. Many reports have demonstrated that PVP has been used to fabricated glucose [27], alcohol [28], hydrazine [29], and AA [30] sensor.

In the present work, by combining the unique electronic properties of graphene with the above-mentioned excellent properties of PVP, the PVP/graphene modified glassy carbon electrode (GCE) exhibited favorable electron transfer kinetics and electrocatalytic activity towards the oxidation of DA. Complete peak separation between DA and AA was observed at the PVP/graphene modified GCE. Furthermore, the selective determination of DA was confirmed in an excess amount of AA at the PVP/graphene modified GCE, and DA can be detected with good sensitivity and selectivity.

2. Experimental

2.1. Chemicals

Graphite power (99%, 40 nm), AA, polyvinylpyrrolidone and dopamine hydrochloride were purchased from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China, http://www.aladdin-reagent.net). 0.1 M phosphate buffer solution (PBS, pH 7.4) was used as the supporting electrolyte [20]. All other reagents were of analytical grade. All aqueous solutions were prepared with deionized water.

2.2. Apparatus and measurements

Electrochemical measurements were performed on a CHI660D electrochemical workstation (Shanghai, China, http://chi.instrument.com.cn) with conventional three-electrode cell. A bare glassy carbon (GC) electrode or the modified electrode was used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and counter electrodes, respectively. The CV experiments were carried out in a quiescent solution at 50 mV s^{-1} in an electrochemical cell with 0.1 M PBS (pH 7.4). Current-time experiments were measured in 10.0 mL 0.1 M PBS (pH 7.4); the potential was set at 0.4 V. The electrochemical impedance spectroscopy (EIS) measurements were performed in a 0.1 M KCl solution containing 5 mM $K_3[Fe(CN)_6]$ and the results were plotted in the form of complex plane diagrams (Nyquist plots) with a frequency range from 0.5 Hz to 100 kHz. The amplitude of the applied sine wave potential is 5 mV. The surface morphologies of the electrochemical reduced GR were evaluated by atomic force microscope (AFM, Agilent 5500, USA) images.

2.3. Preparation of graphene oxide

Graphene oxide (GO) was prepared with the modified Hummers method [31,32]. Typically, 1.0 g graphite powder was added into 36 mL concentrated H_2SO_4 and stirred for 1 h. Then 12 mL fuming HNO_3 was slowly added to the mixture under ice-cooling and stirring. After cooling down, 5 g $KMnO_4$ was slowly added under ice-cooling and stirring. The mixed slurry was stirred at room temperature for 12 h. After that, 120 mL deionized (DI) water was slowly added into the reacted slurry and stirred for 2 h; then 6 mL 30% H_2O_2 was added, and the slurry immediately turned into a bright yellow solution with bubbling. The resultant solution was stirred for 2 h and then allowed to settle down for 24 h; after that, the supernatant was decanted. The resultant yellow slurry was centrifuged and then washed in 250 mL DI water with 1 mL HCl (37%) and 10 mL 3% H_2O_2 added. After stirring for 2 h, the solution was centrifuged and then washed again. This process was repeated three times. After that, the yellow slurry was further washed with 120 mL DI water until the pH of the washing solution increased to neutral (ca.6.7). The remaining dark-yellow solid was lyophilized for 48 h and ground to a fine powder. Before the modification step, a total of 10 mg GO was mixed with 20 mL DI water and ultrasonicated for 3 h. The resultant homogeneous yellow-brown GO solution (0.5 mg mL^{-1}) can be stable for months due to the negatively charged surface of GO.

2.4. Fabrication of the modified electrode

The glassy carbon electrode (3 mm diameter) was polished to a mirror-like surface with 1.0 and 0.3 μL alumina slurry and washed thoroughly with ultrapure water. Afterwards, a 5 μL of 0.5 mg mL^{-1} graphene oxidation (GO) was dropped to fully cover the surface of the polished electrode and dried under an infrared lamp for 30 min. 30 minutes later, the GO-modified electrode was put into 0.1 M PBS (pH 5.0) for cyclic voltammograms scanning 5 cycles in a potential range from 0.0 to −1.5 V. After that, the surface of GR-modified electrode was washed carefully with ultrapure water. At last, drop 5 μL 1% PVP on the GR modified electrode to fabricate PVP/GR/GCE. The GR/GCE was also fabricated as above. Prior to modify electrodes, the preparation conditions were optimized. And results showed that 0.5 mg mL^{-1} oxidation graphene, 5 μL 1% PVP was reasonable and optimal for the detection of dopamine.

3. Results and discussion

3.1. Characterization of the PVP/GR/GCE

The morphologies of graphene oxides, graphene were examined by AFM. Fig. 1 shows the typical AFM images of graphene oxide (a) and electrochemically reduced graphene (b) on the electrode surface, respectively. From Fig. 1, the graphene oxide and the electrochemically reduced graphene film all show a clear flake-like shape with a thickness of ca.1–1.5 nm. The thickness of GO film and the coverage remains nearly the same after electrochemical reduction. However, the sheets seem to be fractured after electrochemical treatment.

To further confirm that the graphene oxide was reduced through the electrochemical routine, the EIS is used as an efficient tool for studying the interface properties of the modified electrodes. The electron-transfer resistance (R_{et}) at the electrode surface is equal to the semicircle diameter of the Nyquist plots and can be used to describe the interface properties of the electrode. Fig. 2 shows the results for the Nyquist plots on bare GCE, GO/GCE, GR/GCE and PVP/GR/GCE. For the bare GCE, the R_{et} was 26.5 ± 0.5 Ω. After modifying GO, the R_{et} (486.2 ± 1.0 Ω), which was reflected by the appearance of substantial increase in the semicircular part of the spectrum, increased due to the blocking effect of GO in the charge transfer process. This is probably because the negative charges of carboxylic groups on the GO surface limit the access of $[Fe(CN)_6^{3-/4-}]$ to the electrode surface [33]. For the GR/GCE, the R_{et} decreased to 126.2 ± 0.5 Ω, the lower electron-transfer resistance on the GR/GCE indicated that the negatively charged groups of GO were effectively reduced after the electrochemical reduction step and the GR films were formed on the surface of GCE. When PVP was modified onto the surface of GR/GCE, the R_{et} of PVP/GR/GCE was significantly increased which demonstrated that the PVP film was successfully immobilized onto the GR/GCE surface.

Fig. 3 shows the cyclic voltammograms (CVs) of the GCE (a), GR/GCE (b), and PVP/GR/GCE (c) in 1 mM DA with a scan rate of 50 mV s^{-1}. The oxidation peak current of DA on GR/GCE is larger than that on bare glassy electrode, which can be ascribed to the

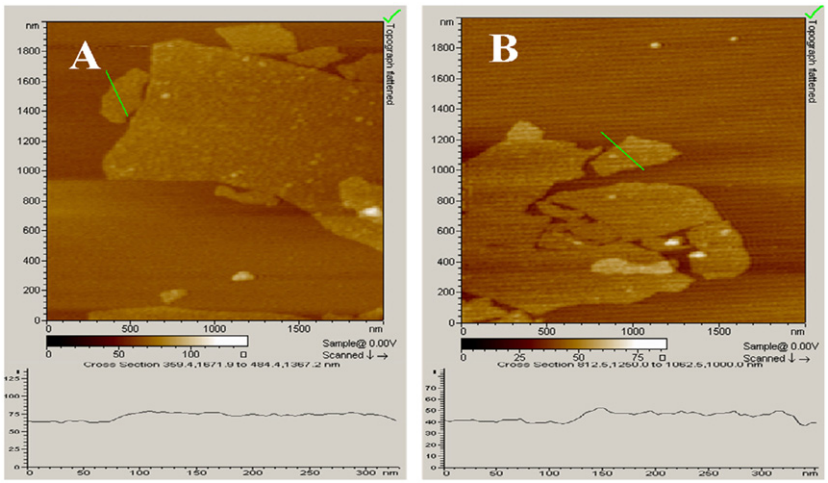

Fig. 1. AFM images of GO (A) and electrochemically reduced GR (B).

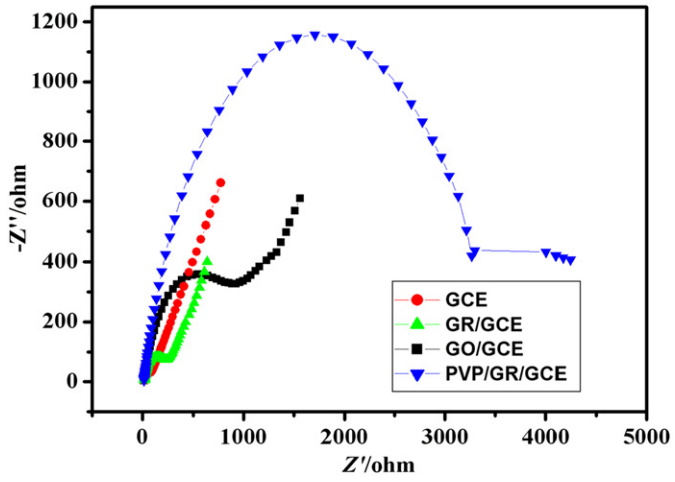

Fig. 2. Nyquist plots of 5 mM $K_3[Fe(CN)_6]$ at bare GCE (red), GO/GCE (black), GR/GCE (green) and PVP/GR/GCE (blue). The frequency range is from 0.5 Hz to 100 kHz. The ac amplitude of 5 mV was applied. (For interpretation of the references to color in this legend, the reader is referred to the web version of this article.)

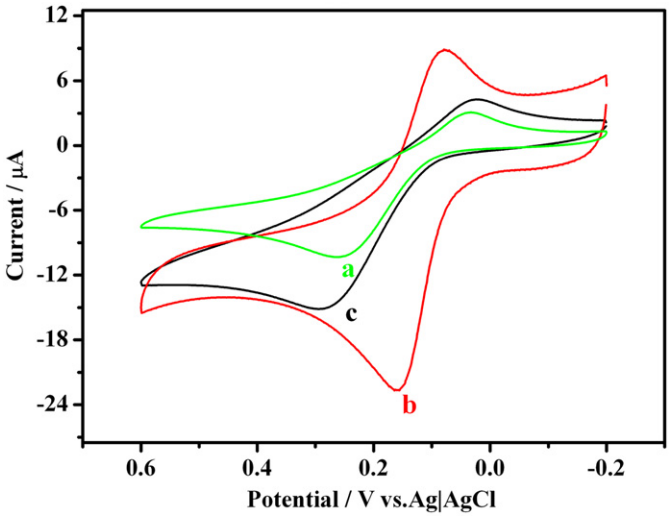

Fig. 3. Cyclic voltammograms of GCE (a), GR/GCE (b) and PVP/GR/GCE (c) in 0.1 M phosphate buffer solution (pH 7.4) containing 1 mM DA. Scan rate: 50 mV s^{-1}.

electrocatalytic activity of graphene[34]. In contrast, the PVP/GR/GCE shows a smaller oxidation peak current compared to GR/GCE. This can be explained by the insulation effect of PVP, which interrupts the electron transfer. Whatever, the oxidation peak current of PVP/GR/GCE is larger than that of bare GCE, suggesting that direct electron transfer was realized on PVP/GR/GCE. After each experiment, the PVP/GR/GCE was removed into 0.1 M PBS (pH 7.4) for CV scan.

3.2. *Optimization of the general procedures*

To further improve the performance of the DA sensor, several factors such as the concentration of GO and PVP and the pH were optimized. The concentration of GO controlled the thickness of graphene films, which had a profound influence upon electrochemical response. The effect of the GO concentration on the oxidation peak currents of dopamine was studied by cyclic voltammetric (Fig. 4A). The oxidation peak currents increased rapidly upon raising the concentration of GO from 0.3 to 0.5 mg/mL and then decreased above to 0.5 mg/mL. It indicated that the mass transfer of dopamine was hindered while the concentration of GO was above 0.5 mg/mL, due to the high thickness and density of graphene film. Therefore, the GO concentration of 0.5 mg/mL was chosen in this work.

In order to find an optimal modified quantity of PVP, the effect of the PVP concentration on the electrocatalysis of DA was studied in Fig. 4B. It can be seen that the oxidation peak currents of DA increased from 0.5% to 1% and decreased from 1% to 1.5%. It reached a maximum at 1%. PVP shows strong adsorption character to phenolic compounds, which is attributed to hydrogen bond between imide in the center of PVP and hydroxyl group in phenolic compounds, thus, the oxidation peak currents increased with the PVP concentration raising. However, higher concentration led to higher thickness and density of PVP film, which hinderer the mass transfer of dopamine. Therefore, we chose 1% as the optimal concentration for PVP.

Furthermore, the effect of the pH of PBS on the electrochemical response of dopamine at PVP/Graphene/GCE was examined by cyclic voltammetric as shown in Fig. 4C. The results showed that the oxidation peak currents of DA increased as the pH changing from 6.2 to 7.4, and then decreased from 7.4 to 7.6, the oxidation peak current reached a maximum at pH=7.4. In addition, pH=7.4 is a physical suitable pH value which can meet the demand of practical application better. Therefore, considering the sensitivity, 0.1 M phosphate buffer solution (pH=7.4) as supporting electrolyte is chosen for the electrochemical experiments.

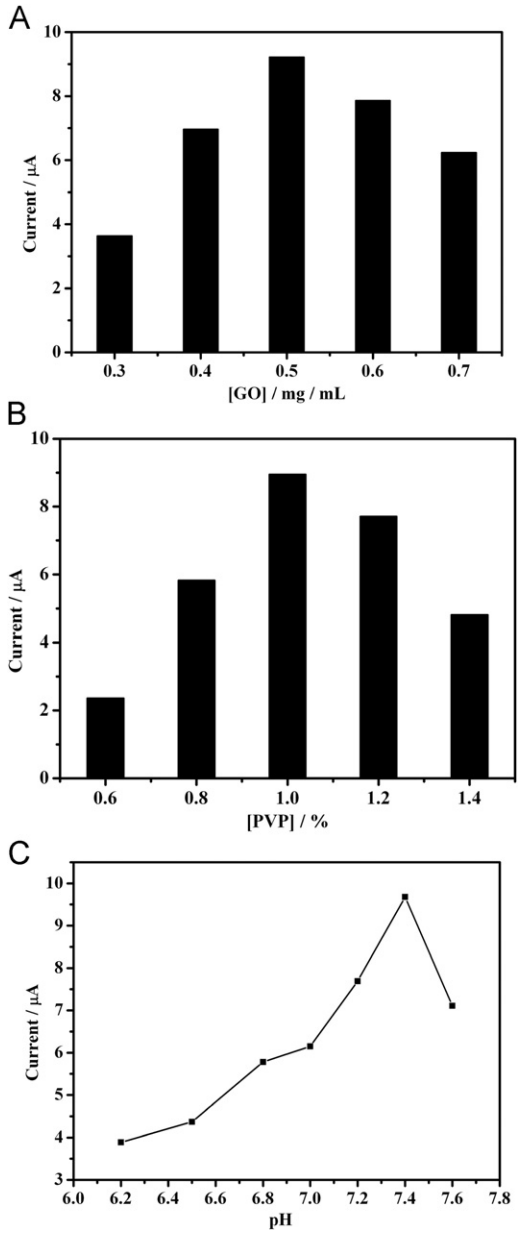

Fig. 4. (A) Effect of the concentration of GO; (B) Effect of the concentration of PVP; (C) Effect of pH on the peak currents of PVP/GR/GCE in 1 mM DA. Scan rate: 50 mV s^{-1}.

3.3. Application for selective determination of DA

The major challenge encountered with the detection of DA is the interference from AA, because the oxidation potential of DA and AA are very close at conventional unmodified electrodes, resulting in the overlap of voltammetric responses [35]. What's more, the oxidation product of DA can catalyze the oxidation of AA, leading to the electrode fouling with poor selectivity and reproducibility [36]. Therefore, it becomes a major goal to selectively detect dopamine in the presence of ascorbic acid [37]. Fig. 5 depicts the interference of AA and uric acid (UA) on PVP/GR/GCE by the means of current-time response method under applied potential 0.4 V. Results show that the injection of 1 mM AA to 0.1 M PBS did not cause any current response on the modified electrode, while the successive addition of 1 mM DA can result in a clear current step, which means there is a negligible interference from AA. This is because that PVP do not only show strong adsorption character to phenolic compounds in DA but also weak the π–π interactions

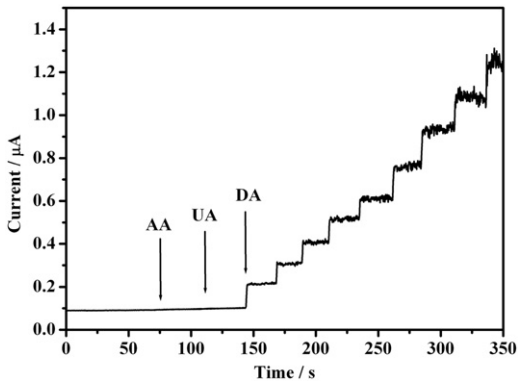

Fig. 5. Amperometric response of PVP/GR/GCE with successive addition of 1 mM AA, UA and DA at an applied potential of +0.4 V.

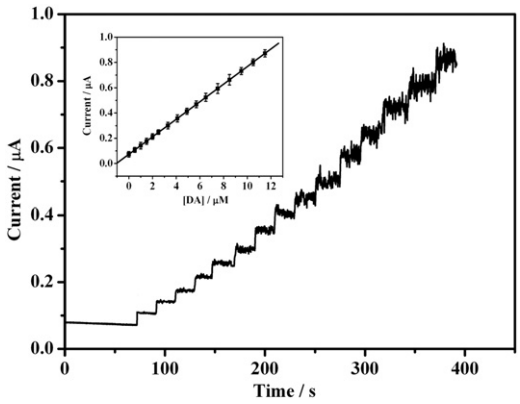

Fig. 6. Amperometric response of PVP/GR/GCE to the successive addition of 1 mM DA in the 0.1 M PBS (pH 7.4) in the presence of 1 mM AA at an applied potential of +0.4 V. Inset: linear relationship between the reduction peak current and the concentration of DA.

Table 1
Recovery tests for DA determination in urine and human serum samples.

Samples (%)	No.	Amounts of added DA (μM)	Amounts of found DA (μM)	Recovery
Urine	1	200.0	195.8	97.9
	2	200.0	204.06	101.2
	3	200.0	203.2	101.4
Serum	1	100.0	98.0	98.7
	2	100.0	96.0	96.4
	3	100.0	104.0	104.0

All samples were analyzed using standard addition method (n=3).

between hexenoic acid-lactone in AA molecules and graphene plane. As we know, UA also coexists with DA in biological systems and its concentration is much higher than that of DA. We examined the influence of UA on the signals of DA and found that no interference occurred with the addition of 1 mM UA in the presence of DA. In addition, other influences from common co-existing substances were also investigated. No interference occurred in the presence of substances as following: 150-fold glucose, 100-fold tartaric acid, 150-fold citric acid, 800-fold sodium chloride and 1000-fold potassium nitrate.

To further confirm that PVP/GR/GCE was able to determine the DA selectively, current-time responses (Fig. 6) were obtained by successive addition of 1 mM DA under applied potential 0.4 V in the presence of 1 mM AA and UA. The modified electrode responded rapidly to the change of dopamine levels, when 0.5 μM DA was

Table 2
The comparison of the results for the determination of DA using different electrodes.

Electrode	Detection method	Linear range (μM)	Detection limit (μM)	References
Carbon nanotube-modified pyrolytic graphite	DPV	0.5–10	0.1	[40]
MWNT-modified graphite	DPV	0.5–10	0.1	[41]
SDS-MWNT-modified GC	DPV	20–200	3.75	[42]
Carbon nanotubes-ionic liquid gel modified GC	DPV	1–10	0.1	[43]
Graphene-Chi-modified GC	DPV	5–200	-	[19]
Graphene-modified GC	DPV	4–100	2.64	[44]
Fe_3O_4 nanoparticles modified GC	I–T	0.15–400	0.03	[45]
Fullerene-C_{60} coated gold electrode	DPV	0.001–5	0.00026	[46]
Overoxidized polypyrrole modified GC	DPV	0.3–10	0.05	[47]
Gold nanoparticles modified indium tix oxide electrode	DPV	0.001–500	0.0005	[48]
Graphene-PVP-modified GC	I–T			This work

Table 3
The comparison of the results for the determination of DA using different analytical parameters.

Methods	Limit of detection (μM)	Linear range (μM)	References
Capillary electrophoresis	0.00034	0.05–2.00	[49]
Chemiluminescence	0.023	0.08–5.0	[50]
LC/MS/MS	0.016	0.07–6.53	[51]
HPLC	26	0.196–52.2	[52]
Electrochemistry	0.0002	0.0005–1130	This work

added in 0.1 M PBS (pH 7.4); a clear current step can be observed, indicating a high sensitivity of the DA sensor. The current changes in a good linear relationship with the successive additions of 1 mM DA, the calibration curve was shown in the insert, displaying a linear response to dopamine (inset, Fig. 6; linear regression equation: I (μA)=72.71+69.47c_{DA} (μM), R=0.9990). Experiments demonstrate that a wide linear range of PVP/GR/GCE can be obtained from 5×10^{-10} to 1.130×10^{-3} mol/L, Furthermore, the linear range is wider than some other dopamine biosensors based on graphene-modified electrodes reported previously[20,38]. The detection limit of PVP/GR/GCE is 0.2 nM (S/N=3). And it is better than that of previously reported work based on graphene [39]. The relative standard deviations are 1.79% for PVP/GR/GCE.

3.4. Stability, reproducibility of PVP/GR/GCE

The stability and reproducibility of the PVP/GR/GCE were investigated by the measurement of the response to the PBS solution containing 1 mM DA. The relative standard deviation (RSD) of the oxidation peak currents by 10 successive measurements was 1.93%. The fabrication reproducibility was estimated at 5 modified electrodes that were prepared under the same condition, and the RSD was 2.16%. When the electrode was kept at 4 °C for 10 days, the peak currents remained more than 90.1% of their initial values. The above results revealed the good stability and reproducibility of PVP/GR/GCE due to the firm combination and adsorption properties of PVP on the electrode surface.

3.5. Sample analysis

In order to evaluate the applicability of the proposed method to the determination of DA in real samples, the utility of the developed method was tested by determining DA in urine and human serum samples. The results are summarized in Table 1. The accepted recoveries indicated that the presence of AA, UA and some other substances, such as glucose and sodium chloride did not interfere with the determination of DA. It implies a promising application of PVP/GR in direct determination of DA in real samples.

The comparison of the results for determination of DA by different modified electrodes and different analytical parameters in the literature were given in Tables 2 and 3 The proposed electrode system resulted in a better detection limit, higher sensitivity and selectivity of DA, which implies a promising feature for the applicability of the modified electrode for the direct determination of DA in real samples.

4. Conclusions

Combining the unique electronic properties of graphene with the excellent properties of PVP, PVP/GR modified film was constructed on the surface of GCE conveniently and firmly. Under the optimum condition, PVP/GR/GCE showed excellent sensitivity and selectivity towards DA. Besides, the modified electrode can also eliminate the interference of ascorbic acid and uric acid effectively. The PVP/GR film is expected to be an ideal electrode modification material for electrochemically detection of DA. Sample analysis indicates that such a modified electrode can offer great promise for its sensing applications, and more relative works are in progress.

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