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Nafion covered core–shell structured Fe_3O_4@graphene nanospheres modified electrode for highly selective detection of dopamine

Wuxiang Zhang [a], Jianzhong Zheng [a], Jiangu Shi [a], Zhongqiu Lin [a], Qitong Huang [a], Hanqiang Zhang [a], Chan Wei [a], Jianhua Chen [a,b], Shirong Hu [a,b,c,*], Aiyou Hao [c]

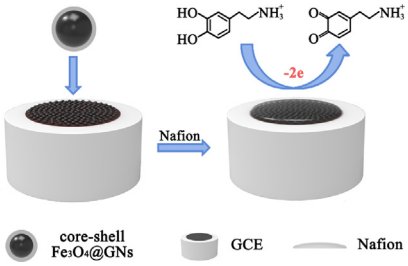
[a] College of Chemistry and Environment, Minnan Normal University, Zhangzhou 363000, PR China
[b] Fujian Province University Key Laboratory of Analytical Science, Minnan Normal University, Zhangzhou 363000, PR China
[c] School of Chemistry & Chemical Engineering, Shandong University, Jinan 250100, PR China

HIGHLIGHTS

- The sensor based on Fe_3O_4@graphene nanospheres was prepared for the first time.
- The biosensor shows a wide linear range and a lower detection limit of 0.007 μM.
- This method was successfully applied to detection of DA in real samples.

GRAPHICAL ABSTRACT

Schematic illustration of the reaction mechanism of Fe_3O_4@GNs/Nafion with DA.



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ABSTRACT

Nafion covered core–shell structured Fe_3O_4@graphene nanospheres (GNs) modified glassy carbon electrode (GCE) was successfully prepared and used for selective detection dopamine. Firstly, the characterizations of hydro-thermal synthesized Fe_3O_4@GNs were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. Then Fe_3O_4@GNs/Nafion modified electrode exhibited excellent electrocatalytic activity toward the oxidations of dopamine (DA). The interference test showed that the coexisted ascorbic acid (AA) and uric acid (UA) had no electrochemical interference toward DA. Under the optimum conditions, the broad linear relationship was obtained in the experimental concentration from 0.020 μM to 130.0 μM with the detection limit (S/N = 3) of 0.007 μM. Furthermore, the core–shell structured Fe_3O_4@GNs/Nafion/GCE was applied to the determination of DA in real samples and satisfactory results were got, which could provide a promising platform to develop excellent biosensor for detecting DA.

1. Introduction

Dopamine (3,4-dihydroxyphenyl ethylamine, DA), acting as one of the neurotransmitters of inotropic synapses, plays an important role in several physiological activity such as mood, behavior and movement [1]. In addition, it is involved in many processes of vital movement like cardiovascular systems, physiological functions and action mechanism in bodies [2]. Recently, various instrumental methods have been used for sensitive detection of DA. Compared with previously reported methods, electrochemical method has been developed and extensively applied in the determination of biomarkers due to its excellent properties such as operator-simplicity, short-time, cost-effective and highly sensitive [3–6]. However, ascorbic acid (AA) and uric acid (UA),

* Corresponding author at: College of Chemistry and Environment, Minnan Normal University, Zhangzhou 363000, PR China. Tel.: +86 596 2528075; fax: +86 596 2528075.
E-mail address: Hushirong6666@163.com (S. Hu).

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the electroactive species, usually coexist with DA in the central nervous system and both of them have very close oxidation potentials, so selective detection of DA is still a challenge in biological analysis [7–10]. Therefore, it is essential to rapid and selective for determination of DA without interferences.

Thus far, carbon nanomaterials are considered as ideal candidate in the fabrication of electrochemical and biosensors [11–13]. Many carbon nanomaterials, such as carbon quantum dots [14], single-walled carbon nanotubes [15], multi-walled carbon nanotubes [16–18], carbon nanofiber [19], functionalized graphene [20–24] have been studied. Among of them, graphene exhibits a significant potential for sensor application. Graphene, which is a two-dimensional monolayer of graphite, has recently received tremendous attention because of its extraordinary properties [25–27]. However, many unique properties of graphene can be realized after integrated into more complex assemblies for improving its versatility. Currently, graphene/metal oxides have been widely reported. Metal oxides are active and durable electrocatalysts for biosensors, among which InO_2, RuO_2 and SnO_2 are also used as the electrochemical study [28,29]. However, the high cost and element scarcity greatly hindered the widespread use of these noble-metal oxide catalysts. Compared to noble-metal oxide, Fe_3O_4 has attracted growing interest in recent years, due to its inexpensive prices, distinguished magnetic and electrochemical properties, which is widely utilized in various fields [30].

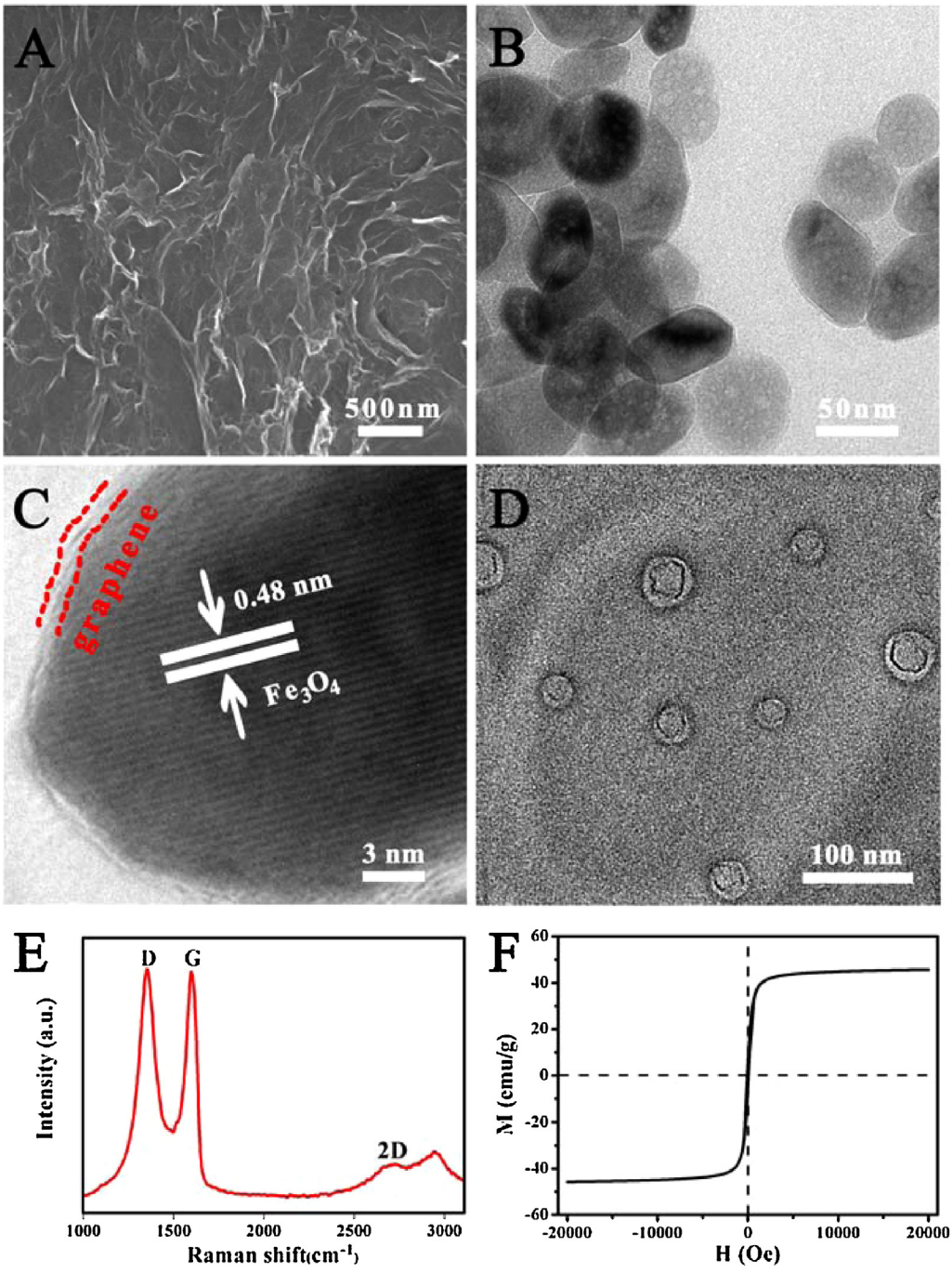

Fig. 1. (A) SEM image of graphene oxide. (B) TEM image of core–shell Fe_3O_4@GNs. (C) HRTEM image of Fe_3O_4@GNs. (D) TEM image of a hollow structure of graphene after the treatment of HCl. (E) Raman spectrum of core–shell Fe_3O_4@GNs. (F) Magnetization curve of core–shell Fe_3O_4@GNs measured at 300 K.

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Herein, we designed a novel core–shell structured Fe_3O_4@GNs composite by a simple hydro-thermal synthesized reaction. The biosensor platform, constructed by Fe_3O_4@GNs coupling with Nafion on the modified electrode and applied it as dopamine sensor. It was found that DA can be detected from 0.020 μM to 130.0 μM with the detection limit of 0.007 μM (S/N = 3). In addition, the Fe_3O_4@GNs/Nafion/GCE was successfully applied in the determination of dopamine (DA) in the practical samples.

2. Experimental

2.1. Reagents and instrumentation

Graphite powder, sodium nitrate, potassium permanganate, hydrochloric acid, sulfuric acid, barium chloride, hydrogen peroxide (30%), phosphate buffer solution, dopamine, uric acid and ascorbic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Iron(III) chloride anhydrous (98%) and Nafion were obtained from Sigma–Aldrich. Real samples (human serum and urine) were provided from Zhangzhou hospital. All other reagents were analytical reagents. All aqueous solutions were prepared using ultrapure water (18 MΩ cm) from a Milli-Q system (Millipore).

2.2. Apparatus

Scanning electron microscopy (SEM) was conducted on Hitachi S-4800. Transmission electron microscope (TEM) was conducted on FEI Tecnai G2 S-TWIN and the accelerating voltage was 200 kV. Raman spectroscopy was measured on Renishaw inVia plus using 633 nm laser excitation. The magnetic property of magnetite material was carried on PPMS-9 (quantum design). CHI 104 glassy carbon electrode (3 mm) was used as the working electrode. All electrochemical measurements were performed on a CHI650E electrochemical workstation (ChenHua Instruments Co., Shanghai, China).

2.3. Synthesis of core–shell structured Fe_3O_4@GNs materials

Firstly, graphene oxide (GO) was synthesized by oxidation of graphite using Hummers' method [31]. Briefly, graphite power (1.0 g) was stirred with concentrated sulfuric acid (23 mL at 0 °C) in a 1000 mL round bottom flask. Then, $NaNO_3$ (0.5 g) and $KMnO_4$ (3.0 g) were slowly added to the suspension and keep the temperature constant at (0 ± 1) °C. Subsequently, stirred and heated to 35 ± 3 °C for 30 min, then water (23 mL) was added and stirred at 98 °C for 15 min, following by adding water (140 mL) and 30% H_2O_2 (2 mL) to end the reaction. Thereafter, the product was collected by filtration and washing (5% HCl and water, 3 times each). After that, NaAc (3.0 g) and a suitable amount of graphene oxide solution were added into the homogeneous solution of $FeCl_3$ (1.0 g) and dissolved in diethylene glycol (20 mL). Then, ultrasonic for 30 min was employed to disperse the mixture and transferred to a teflon-lined stainless-steel autoclave with 200 °C for 6 h. Finally, the black products were obtained and washed several times with water and ethanol and then dried at 80 °C.

2.4. Modification of electrodes

Firstly, the glassy carbon electrode was polished to a mirror-like finish with 1.0, 0.3 and 0.05 μm alumina powder, respectively and thoroughly cleaned before use. Then, 6.0 μL of Fe_3O_4@GNs solution was cast on the clean surface of the working electrode, and dried in 50 °C. The purchased Nafion solution (5.0%) was diluted to 0.5% by ethanol, then 5 μL of 0.5% Nafion solution was added to the surface of the dried Fe_3O_4@GNs modified electrode and evaporated it at room temperature.

3. Results and discussion

3.1. Characterization of core–shell structured Fe_3O_4@GNs composite

Firstly, the sheet structured graphene oxide with wrinkle (Fig. 1A) was prepared. Then the Fe_3O_4@GNs (Fig. 1B) was synthesized by hydro-thermal synthesis reaction with a uniform size of 70 nm. High-resolution transmission electron microscopy (HRTEM) image (Fig. 1C) demonstrated a typical Fe_3O_4 nanoparticle with a well-crystalline measures at 0.48 nm, which corresponding to the (1 1 1) plane of Fe_3O_4 [32]. This structure of Fe_3O_4 was tightly enwrapped by graphene sheets and interconnected by graphene networks. Additionally, after the treatment of HCl, a hollow structure of graphene was observed (Fig. 1D), indicting the core–shell structure of the Fe_3O_4@GNs was successfully synthesized. Raman spectroscopy (Fig. 1E) confirmed that the shell of above product was graphene, as to the strong G band 1605 cm^{-1}, D band 1355 cm^{-1} and weak 2D band 2730 cm^{-1}. The G peak was associated with first-order scattering of the E_{2g} mode for sp^2 hybridized carbon domain, and the D and 2D peaks were assigned to the structural defect [33]. Furthermore, the ratio of I_D and I_G was 0.84, which indicated the highly disordered carbon structure and the partial reduction of graphene oxide [34]. The magnetic saturation value was 43.155 emu g^{-1}, which demonstrated the good magnetic properties of core–shell Fe_3O_4@GNs (hysteresis loops in Fig. 1F).

3.2. Cyclic voltammetric behavior of DA on the Fe_3O_4@GNs/Nafion/GCE

In order to evaluate the electrochemical properties of the Fe_3O_4@GNs/Nafion composite film, cyclic voltammograms (CV) of DA at different electrodes were studied. As illustrated in Fig. S1, graphene nanosphere wrapped Fe_3O_4 in the cores showed superior stability, specificity, higher repeatability, tailorability properties and synergistic effect in both the incorporated metal oxide cores and shells. A possible reaction mechanism was discussed that the Fe_3O_4 possessed of a strong electrochemical activity as it was a conductor and the Fe^{2+} and Fe^{3+} disorderly arrangement in octahedral sites. The electronics rapidly transferred between two oxidation states of iron when applied voltage to the gate electrode, produced unbound electrons can be divert to the shell structure of graphene nanosphere. A strong synergistic coupling effect between the Fe_3O_4 crystals and graphene nanosphere could provide a homogenous environment for an electrochemical catalysis.

The positively charged aromatic DA molecules can easily approach to the surface of Fe_3O_4@GNs/Nafion/GCE through π–π stacking and electrostatic attraction. The Nafion film, cation-exchanger polymer, on the electrode's surface not only could protect the modified electrode and enhance storage time, but also repele electronegative AA and UA toward working electrode to improve the selectivity of DA [35–37]. Therefore, Fe_3O_4@GNs/Nafion can be used to electrochemical biosensor for the selective detection of DA at lower concentration.

3.3. Electrochemical parameters of DA on the Fe_3O_4@GNs/Nafion/GCE

In order to better ascertain electrochemical behaviors on the Fe_3O_4@GNs/Nafion/GCE, electrochemical parameters of DA biosensor were further investigated. In the following experiments, scan rate of DA (CV of 0.05 mM DA) was shown in Fig. S2. The oxidation peak currents (I_{pa}) increased linearly with the square root of scan rate ($v^{1/2}$) in the range of 0.01–0.25 V s^{-1}, the

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regression equation of DA was I_{pa} (μA) = −82.93 $v^{1/2}$ ($v^{1/2}$ $s^{-1/2}$) + 4.960 (R = 0.9964), which could indicate that the electro-redox of DA on Fe_3O_4@GNs/Nafion/GCE was a typical diffusion controlled process. The diffusion coefficient (D) of DA could be estimated for a reversible process according the Randles–Sevcik formula:

$$I_{pa} = (2.69 \times 10^5) n^{3/2} A C_0 D^{1/2} v^{1/2} \quad (1)$$

where A was the electrode area, v was the scan rate, n was electron transfer number. C_0 and D were the molar concentration and diffusion coefficient of DA, respectively. The value of the diffusion coefficient (D) was calculated to be 9.42×10^{-4} cm^2 s^{-1}.

The catalytic reaction of DA also can be calculated by chronoamperometry experiment using the potential step technique. As shown in Fig. S3. The chronoamperometry response in 0.1 M PBS in absence (curve a) and presence of 0.1 mM DA (curve b) on the Fe_3O_4@GNs/Nafion/GCE. The apparent catalytic rate constant (k_{cat}) was determined by the following equation [38]:

$$\frac{I_{cat}}{I_L} = (\pi k_{cat} C_0 t)^{1/2} \quad (2)$$

where I_L was the limiting current in the absence of DA, I_{cat} was the catalytic current of the Fe_3O_4@GNs/Nafion/GCE in the presence of DA (0.1 mM), C_0 was the concentration of DA and t was time elapsed. A linear regression equation between I_{cat}/I_L with $t^{1/2}$ was obtained: I_{cat}/I_L = 4.81 $t^{1/2}/(t^{1/2}/s^{1/2})$ − 1.605 (inset of Fig. S3). Thus, the apparent catalytic rate constant (k_{cat}) of DA on the Fe_3O_4@GNs/Nafion/GCE was estimated to be 7.36×10^4 M^{-1} s^{-1}. The result of diffusion coefficient (D) and catalytic rate constant (k_{cat}) of DA were obviously larger than that reported in literatures [38–40]. It illustrated that the higher catalytic capacity to promote electrochemical oxidation of DA at the Fe_3O_4@GNs/Nafion/GCE.

3.4. Effect of pH

The effect of pH values of the Fe_3O_4@GNs/Nafion electrode were also investigated, the results was shown in Fig. 2. As we know, DA is unstable in alkaline solution. Therefore, at pH higher than 8.5 was not tested and pH of 7.0 was chosen in the whole experiments. The oxidation peak potential shifted negatively with the increase of pH value, which indicated that protons were involved in the electrode reaction as pH increased ranging from 5.5 to 8.5. The potentials of DA followed the linear regression equations with pH: E_{pa}/V = −0.068 pH + 0.7649 (R = 0.9922) (inset of Fig. 2). The slope was approximate with the theoretical value −59.0 mV/pH of Nernstian, indicated that the electrochemical redox of DA should be a two electrons and two protons process.

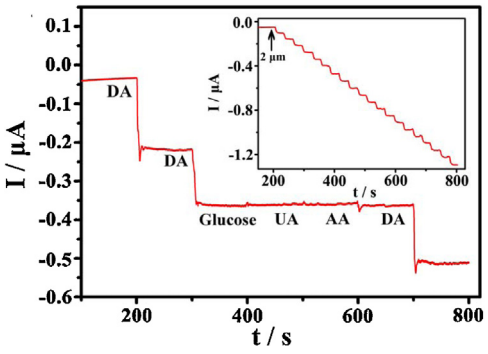

Fig. 3. Amperometric responses of Fe_3O_4@GNs/Nafion/GCE in sequential addition of 0.01 mM DA, 0.5 mM of various interfering species and 0.01 mM of DA in 0.1 M PBS with pH 7.0. Inset is current–time plot addition each of 2 μM DA in the interferes conditions.

3.5. Interference study

In order to evaluate the selectivity of sensor, the amperometric response of various foreign species was investigated. 0.01 mM DA, 0.5 mM glucose, UA and AA were added to the solution in turn. As illustrated (Fig. 3), glucose, UA and AA had not interfered when present in 50 folds excess. The inset of Fig. 3 shows the current–time plot on successive dropped with the same concentration of dopamine under present in 50 folds UA and AA. In addition, other influences from common co-existing substances were also investigated, such as NaCl, K_2SO_4, $CaCl_2$ solutions (300 folds), lysine, cysteine, and glucose solutions (100 folds). The oxidation peak potential and current of DA were observed almost constantly. The results indicated an excellent selectivity of Fe_3O_4@GNs/Nafion modified electrode.

3.6. Calibration plot and limit of detection

Differential pulse voltammetry (DPV) technology was used for quantitative detection of DA because of the sensitivity of DPV was higher than the CV. The oxidation peak current (I_{pa}) of DA increased with its concentration in the range from 0.020 μM to 130.0 μM (Fig. 4), with the linear regression equations: I_{pa}(μA) = −0.3969, C(μM) = −17.36 (R = 0.9979). The limit of detection was estimated to be 0.007 μM based on S/N of 3 and the relative standard derivation (RSD, n = 5) was less than 2.8%. In comparison to the previous reports, designed Fe_3O_4@GNs/Nafion/GCE

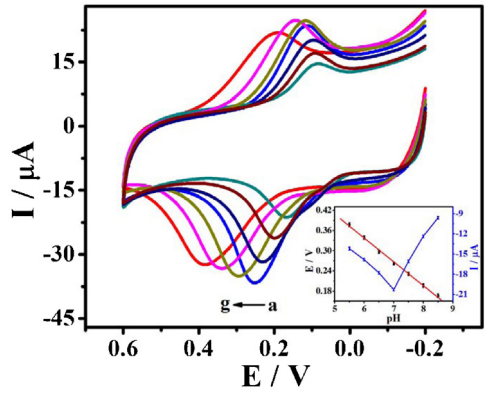

Fig. 2. CV of 0.1 mM DA on the Fe_3O_4@GNs/Nafion/GCE in 0.1 M PBS at different pH (a → g: 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5) (scan rate: 0.1 V s^{-1}). Inset: the plots of I_{pa} (B) and E_{pa} (A) with pH values.

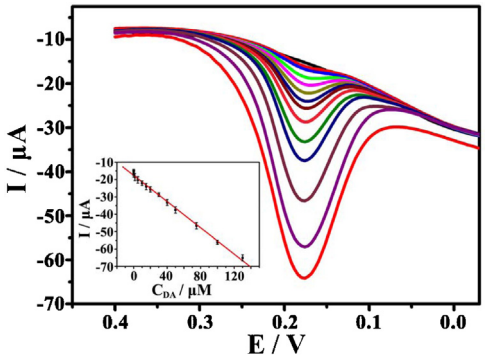

Fig. 4. DPV for different concentrations of DA (a → l: 0, 0.02, 0.05, 1, 5, 10, 15, 20, 30, 40, 50, 75, 100, 130 μM) on the Fe_3O_4@GNs/Nafion/GCE in 0.1 M PBS with pH 7.0 (scan rate: 0.1 V s^{-1}). Inset: The relationship of the I_{pa} with the concentration of DA.

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Table 1
Determination of DA levels in real samples using the Fe_3O_4@GNs/Nafion/GCE and DPV in 0.1 M PBS (pH 7.0).

Sample	Detected (μM)	Add (μM)	Found (μM)	Recovery (%)	RSD (%)
Serum 1	0.19	5	5.3 ± 0.8	100.6	1.5
		10	10.1 ± 1.3	99.3	1.7
		15	15.5 ± 1.4	101.2	2.1
Serum 2	0.23	5	4.9 ± 1.1	98.6	1.6
		10	10.4 ± 1.6	102.5	2.4
		15	15.5 ± 1.4	101.2	1.8
Urine	1.2	5	5.2 ± 1.9	102.3	2.6
		10	10.3 ± 1.5	98.4	2.3
		15	16.5 ± 1.3	100.8	1.9

exhibited wide linear range and a lower detection limit (shown in Table S1). In addition, the biosensor could keep its activity for at least a month.

3.7. Reproducibility and stability of the modified electrode

In order to verify the practical performance of the Fe_3O_4@GNs/Nafion/GCE, DPV quantificationally evaluated a certain amount of DA solution via the standard addition approach. As shown in Table S2, the recovery ranged from 99.18% to 101.15% and relative standard derivation (RSD, $n = 5$) was <2.0%. The recovery and RSD are acceptable, indicating the high accuracy and high precision properties of this method, which could be used for the determination of DA.

3.8. Application of the method to real samples

For the further evaluation of the applicability of the method, real samples were analyzed by the standard addition method. 2 mL of the real samples was diluted to 5 mL with 0.1 mM PBS solutions. Then the diluted samples were spiked with certain amounts of DA and detected. The recovery of the spiked samples ranged between 98.4% and 102.5% ($n = 6$) (Table 1). The experimental results verify the feasibility and effectiveness of this method.

4. Conclusions

In summary, based on the special properties of the core–shell structured nanosphere Fe_3O_4@GNs/Nafion modified electrode, an electrochemical sensor for highly sensitive and selective determination of DA in the presence of large excess of AA and UA was designed, which successfully used for the detection of DA in real practical application. The modified Fe_3O_4@GNs/Nafion/GCE greatly catalyzes redox of DA and the linear relationship was obtained in a range from 0.020 μM to 130.0 μM with the limit of detection as 0.007 μM (3 S/N). In addition to the good properties of high selectivity, sensitivity, accuracy and reproducibility, this method could provide a simple and suitable for the quantitative determination of micromole level of DA for clinical.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.aca.2014.10.032.

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