Highly sensitive and selective detection of dopamine in the presence of ascorbic acid at graphene oxide modified electrode

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ABSTRACT

A graphene oxide (GO) modified glassy carbon electrode (GCE), namely GO/GCE was prepared by covalent coupling method, which was characterized by atomic force microscope (AFM), cyclic voltammetry (CV) and electrochemical impedance spectra (EIS). On this modified electrode, it is found that the electrochemistry of dopamine (DA) is greatly enhanced, while that of ascorbic acid (AA) is totally impressed, showing that the modified layer of GO has completely different impact on the electrochemical response of DA and AA. The probable mechanism to cause the different impact was proposed. GO/GCE was further applied as a biosensor for the determination of DA in the presence of with AA, and the results showed that the coexisted AA has no interference toward the electrochemistry of DA. The oxidation peak currents of DA present a good linear relationship with the concentrations in the range from 1.0 μM to 15.0 μM with a detection limit of 0.27 μM. The electrochemical parameters such as the electron transfer rate constant, catalytic rate constant, diffusion coefficient, and electron/proton transfer number of DA on GO/GCE were also studied.

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1. Introduction

Dopamine (DA) plays a significant role in the function of the central nervous, renal and hormonal system as an important neurotransmitter [1]. The DA biochemistry is believed to be related to several diseases such as Schizophrenia, Parkinsonism and Huntington [2]. The studies on the electrochemistry of DA are helpful for us to well understand its physiological functions and action mechanism in bodies [3]. Update, many electrochemical strategies have been designed and applied for the detection of DA in samples [4–6]. However, due to the non-reversibility of its electrochemical behaviors, as well as the fouling of the electrode surface by the oxidation products, poor results are often generated on the conventional electrodes [7]. Additionally, another common biological molecule of ascorbic acid (AA) that has higher concentration than DA in biological samples often interferes the accurate detection of DA because both of them have very close oxidation potentials [5,8,9]. Therefore, the selective and sensitive determination of DA in the presence of AA is still a major challenge in biological analysis. In order to realize this goal, numerous materials such as organic redox mediators [10], nanoparticles [11] and self-assembled monolayer [12] have been applied as modification layer to construct the highly selective and sensitive DA biosensor.

Recently, a new two-dimensional (2D) carbon material, graphene (GR) attracts much attention in fabricating electrochemical biosensors [13–16] because of its unique properties such as exceptional thermal and mechanical properties, large surface-to-volume ratio and high electrical conductivity. It has been reported that GR can provide a favorable micro-environment for enhancing the direct electron transfer of some redox enzymes such as glucose oxidase [17], cytochrome C [18] and hemoglobin [19]. DA has also been detected on graphene modified electrode. For example, Wang et al. [20] have reported that DA can be selectively determined on a graphene–chitosan nanocomposite modified electrode and the interference from AA can be completely eliminated by the modified layer. The similar result has also been obtained at a silanized graphene modified electrode [21]. However, on the most common preparation method of GR or its composite, i.e., through chemical reduction from graphene oxide (GO), a hazardous chemical of hydrazine is often used as the reductant. In addition, GR is hydrophobic and tend to form irreversible agglomerates or even restack to form graphite through strong π–π stacking or van der waals interaction [22]. All these disadvantages limit the practical application of GR in electrochemistry field.

Relatively, the precursor for preparing the chemically reduced graphene, GO shows good hydrophilicity and dispersibility in water because it contains a large number of hydrophilic functional groups, such as —OH, —COOH and epoxides on the basal plane and the sheet edge. Although the conductivity of GO is not as high as graphene, it is also regarded as a suitable candidate for biosensing analysis

due to its nano-scale effect, surface properties and strong affinity with biological molecules [23]. For example, based on its exclusive association with single-stranded DNA rather than double-stranded DNA, it has been exploited as fluorescent platform for DNA sensing analysis [24,25]. Additionally, it has also been applied as effective nanocarriers to construct electrochemical enzyme/protein biosensor [26] and immunosensor [27].

In this work, a GO modified glassy carbon electrode (GO/GCE) was prepared by covalent method, which was characterized by atomic force microscope (AFM) and electrochemical technologies. The electrochemical behaviors of DA and AA on the modified electrode were independently investigated, and the results show that the redox signal of DA is greatly promoted by the modified GO layer, but the electrochemical signal of AA is completely suppressed. Based on this feature, the modified electrode was applied as a highly selective biosensor for the detection of DA in the presence of AA. It is found that DA can be detected from $1.0 \mu M$ to $15.0 \mu M$ with the detection limit of $0.27 \mu M$ without any interference from AA. Also, the electrochemical parameters and electrochemical reaction mechanism of DA on GO/GCE were carefully investigated in this work. Compared with the DA biosensors based on the chemically reduced GR materials [8,20], the biosensor developed in this work is more environmentally friendly and easy to prepare rather than losing the performance of high selectivity and high sensitivity.

2. Experimental

2.1. Reagents and apparatus

Graphite and AA of analytical grade were obtained from Guangdong Xilong Chemical Co., Ltd (China). DA and Tris(hydroxymethyl)aminomethane (Tris) of analytical grades were purchased from Aladdin Reagent Co., Ltd (China). N-Hydroxy succinimide (NHS) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) were purchased from Shanghai Jingchun Reagent Co., Ltd (China). Hexaammineruthenium(III) chloride ($[Ru(NH_3)_6]^{3+}$) was purchased from ABCR GmbH & Co. KG (Germany). Phosphate buffer solution (PBS) was prepared by mixing $0.02 M$ NaCl and $0.05 M$ NaH_2PO_4–Na_2HPO_4. $0.04 M$ Britton–Robinson (B–R) buffer solutions with various pH values were used as the supporting electrolytes. All the other chemicals were of analytical reagent grade and were obtained commercially. Doubly distilled water (DDW) was used throughout experiments.

All the electrochemical measurements were carried out on a CHI 650C electrochemical analyzer (China) consisting of a traditional three-electrode system: a bare or GO modified GCE (GO/GCE) as the working electrode, an Ag/AgCl as auxiliary electrode and a Pt wire as counter electrode. AFM images were obtained with CSPM 5500 scanning probe microscope (China). The Raman spectroscopy was conducted on a Renishaw in Via plus Raman microscope (America).

2.2. Preparation of GO/GCE

The water-soluble GO was prepared according to a modified Hummer's method using graphite powder as starting material [28]. Briefly, 1 g natural-flake graphite and $0.5 g$ $NaNO_3$ were reacted with 23 mL concentrated sulfuric acid in an ice bath for 30 min. Then, 3 g $KMnO_4$ was slowly added and went on reacting for 2 h. Afterwards, the mixture was heated to 35 °C and maintained for 30 min, followed by slow adding 46 mL water and going on reacting at 98 °C for 15 min to fully oxidize graphite. After cooling with water-bath, the reaction mixture was diluted with 140 mL water and 3 mL H_2O_2 (30%). After the mixture was purified by filter, multiple washing with 5% HCl and water, centrifugation and decanter, the precipitate was dialyzed for 7 days in DDW to

remove the residual acid until the pH was close to 7. Finally, the product was dried by vacuum overnight at room temperature. The homogeneous GO suspension ($1.0 mg mL^{-1}$) was obtained by dispersing 5 mg GO in 5 mL DDW with ultrasonication for 5 h.

Prior to modification with GO, a GCE was sequentially polished with $0.3 \mu m$ and $0.05 \mu m$ alumina slurries and rinsed with acetone, ethanol, and DDW under sonication for 2 min, in turn. Then the cleaned electrode was oxidized at +1.5 V for 15 s in an aqueous solution containing 2.5% $K_2Cr_2O_7$ and 10% HNO_3 to generate some active groups [29]. After rinsing with water, 10 μL PBS containing 5 mM EDC and 8 mM NHS was cast on the oxidized GCE for 5 h, and a rubber cap was fitted to prevent rapid evaporation. Subsequently 10 μL prepared GO suspension was cast on the surface of the activated GCE and dried naturally. Prior to use, the modified electrode was carefully rinsed with DDW to remove the loosely attached GO, and dried in an air stream. Thus the GO covalently modified GCE was prepared, which is denoted as GO/GCE.

2.3. Electrochemical measurements

Electrochemical characterization of GO/GCE was carried out in 1.0 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) mixture containing 0.1 M KCl with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The CV was scanned between −0.4 V and +0.6 V and the EIS was collected at a potential of +0.177 V in the frequency range of $0.01–10^4$ Hz with the voltage amplitude of 5 mV. The differential pulse voltammetry (DPV) was recorded within the potential range from 0 V to +0.7 V with a pulse amplitude 0.05 V, pulse width 0.05 s, pulse period 0.2 s in 0.04 M B–R buffer solution. Standard solution of DA and AA were prepared using DDW as solvent and stored under 4 °C. Electrochemical analysis of DA on GO/GCE was carried out in 0.04 M pH 5.0 B–R buffer solutions containing a certain amount of AA. After each measurement, the modified electrode was washed with water and scanned in blank B–R buffer solution until the electrochemical signals of DA were disappeared.

3. Results and discussion

3.1. Morphological and characterization of GO/GCE

The preparation of GO from graphite was characterized through Raman spectroscopy. As well known, Raman spectroscopy is a widely used tool to characterize carbon products due to increase in Raman intensities by the conjugated and double carbon—carbon bonds [30]. Fig. 1 shows the typical Raman spectra of graphite and
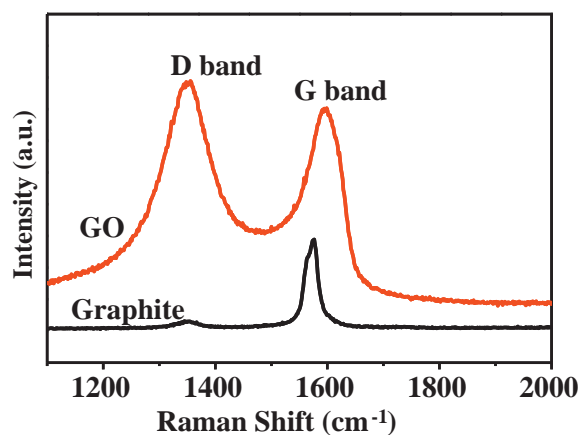

Fig. 1. The Raman spectra of graphite and GO. All of the spectra correspond to an exciting laser wavelength of 514 nm.
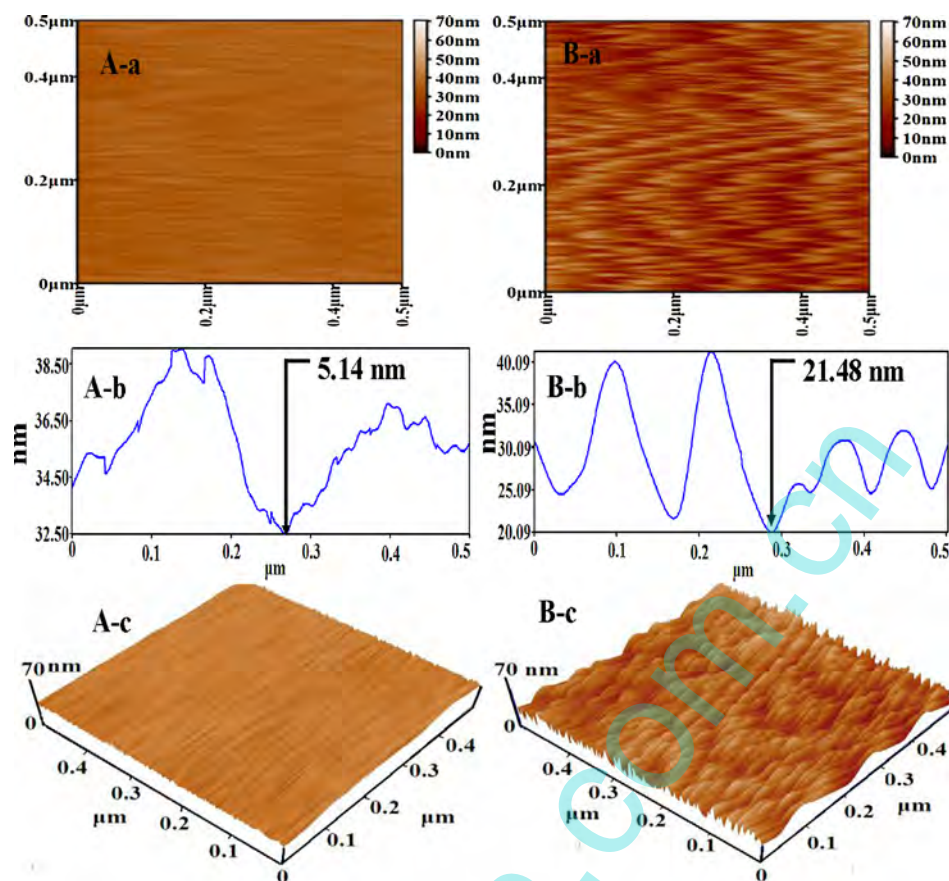
Fig. 2. AFM images of (a) topographic (b) three dimensional and (c) cross-sectional graph of bare GCE (A) and GO/GCE (B).

GO. The Raman spectrum of the graphite displays a strong G band at 1575 cm^{-1} assigning to the E_{2g} phonon of C sp^2 atoms, and a very weak D band at 1348 cm^{-1} corresponding to the breathing mode of k-point phonons of A$_{1g}$ symmetry; whereas for GO, the G band is broadened and shift to more than about 1600 cm^{-1} due to the stress. In addition, the D band at 1348 cm^{-1} increases substantially, indicating the reduction in the plane sp^2 domains. This result clearly shows that the graphite has been successfully oxidized to GO.

The covalent immobilization process of GO on electro-oxidized GCE with the aid of EDC and NHS was characterized by AFM, and Fig. 2 shows the typical topographic (a), cross-sectional (b) and three dimensional (c) images of GCE without (A) and with (B) modification with GO in an area of 0.5 μm × 0.5 μm. It is observed that the bare GCE is relatively flat and smooth with the largest peak height of 5.14 nm (Fig. 2A). However on GO/GCE, lots of adjacent peaks with the average height of 21.48 nm are observed (Fig. 2B). This difference suggests that the material of GO has been modified on GCE surface. Furthermore, from the AFM results, it was obtained that the average roughness (R_a) of GO/GCE were determined to be 6.0 nm, which is obviously larger than that (1.13 nm) on bare GCE, indicating that GO had been anchored on GCE and improved the surface effect of the electrode interface.

The grafting of GCE with GO was further characterized by electrochemical methods. It is well known that GO contains rich —OH and —COOH and presents negative-charge characteristic, thus the electrode coated with GO should repel anionic species through electrostatic repulsion while attract cationic species through electrostatic attraction. Fig. 3A and C shows the CV results of 1.0 mM [Fe(CN)$_6$]$^{3-/4-}$ and 1.0 mM [Ru(NH$_3$)$_6$]$^{2+/3+}$ at bare (curve a) and

GO/GCE (curve b), respectively. It can be clearly found that a pair of well-defined redox peaks that correspond to the electron transfer of Fe^{II}/Fe^{III} couple appears at bare GCE (Fig. 3A, curve a). After modification of GCE with GO, the redox peaks of [Fe(CN)$_6$]$^{3-/4-}$ decrease significantly (Fig. 3A, curve b). In contrast, the electrochemical response of [Ru(NH$_3$)$_6$]$^{3+}$ ions show great enhancement on GO/GCE (Fig. 3C, curve b) in comparison with that on bare GCE (Fig. 3C, curve a). These different changes clearly testify that the negatively charged GO has been immobilized on GCE surface.

EIS is also a sensitive electrochemical technology to monitor the impedance variation of the electrode interface. From the EIS results showed in Fig. 3B, one could see that a small resistance value (R_{et}) of 495 Ω is estimated for bare GCE. However, on GO/GCE, the R_{et} value is sharply increased to 7321 Ω, which further suggests that GO has been successfully immobilized on GCE, and the electron transfer kinetic of [Fe(CN)$_6$]$^{3-/4-}$ on GO/GCE is inhibited by the GO layer. Furthermore, the coverage degree (θ) of the electrode surface was calculated through the increase extent of charge transfer resistance according to the following equation [31]:

$$\theta = 1 - \frac{R_{et}^{bare}}{R_{et}^{GO}} \tag{1}$$

where R_{et}^{bare} and R_{et}^{GO} are the charge-transfer resistance measured at bare GCE and GO/GCE, respectively. From the values of R_{et} on bare GCE and GO/GCE, the value of θ was then calculated to be 93.24% via Eq. (1), which clearly shows that GO has occupied most of the GCE surface by the developed covalent coupling method.
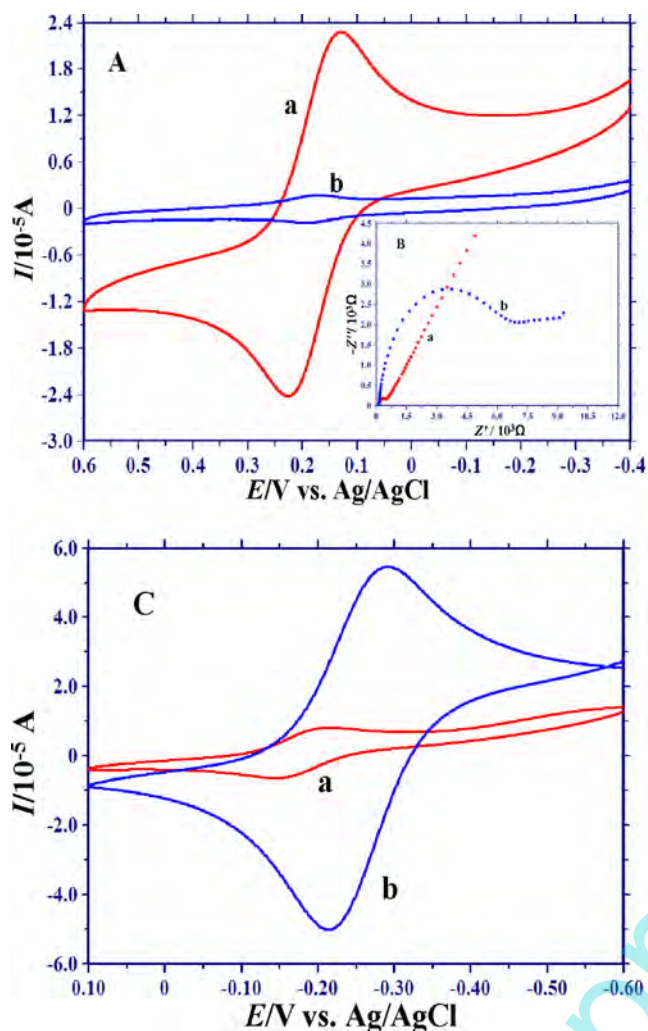
Fig. 3. Cyclic voltammograms (A) and electrochemical impedance spectroscopy (B) of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) with 0.1 M KCl on bare GCE (a) and GO/GCE (b); (C) shows the cyclic voltammograms of 1.0 mM $[Ru(NH_3)_6]^{3+}$ with 0.1 M Tris–HCl (pH 7.0) on bare GCE (a) and GO/GCE (b).

3.2. Different electrochemistry of DA and AA on GO/GCE

Fig. 4A shows the electrochemical behaviors of DA at bare GCE (curve a) and GO/GCE (curve b). It is observed that a pair of redox peaks is appeared at +0.375 V and +0.141 V, respectively, which is in accordance with the electrochemical behaviors of DA in previous reports [8,32,33]. When GO/GCE was used, the redox peaks were significantly increased, suggesting that the GO film is very effective for enhancing the electrochemistry of DA. However for AA, a completely opposite change in electrochemistry was observed, i.e., the characteristic oxidation peak of AA at +0.2 V appeared on bare GCE (curve a, Fig. 4B) is totally disappeared when GO/GCE was used (curve b, Fig. 4B). We think that this difference might be caused by the following reasons: (1) Under the measured acidity (pH 5.0), DA ($pK_a = 8.9$) and AA ($pK_a = 4.2$) are positively and negatively charged [34], respectively; thus, the protonated DA is easily permeated into and accumulated within the anionic GO layer on the electrode interface, which resulted in a large redox response; In contrast, the negatively charged AA molecules are inhibited to approach the electrode surface by the GO film because of the existence of electrostatic repulsion between them. (2) It has been reported that the GO has some unoxidized aromatic rings with rich delocalized π electrons, which make the material owning strong ability to interact with the substances of phthalocyanine [35], single-stranded DNA
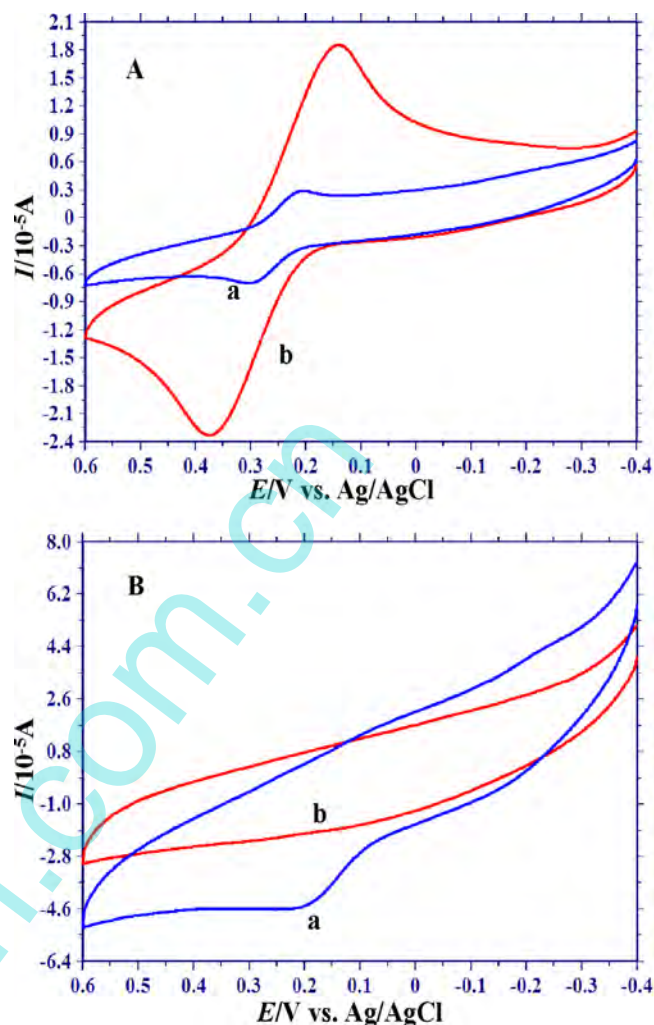
Fig. 4. CVs of 0.1 mM DA (A) and 0.1 mM AA (B) on bare GCE (a) and GO/GCE (b) in 0.04 M B–R buffer solutions with pH 5.0.

[36] and multiwalled carbon nanotubes [37] through π–π staking mode. As compared with AA, DA has a special aromatic ring, therefore the interaction and electron communication between GO and DA can be further strengthened via π–π stacking force. Summarily, the different electrochemical response of DA and AA on GO/GCE observed in this work can be explained by the following principles (as illustrated in Fig. 5): The positively charged aromatic DA molecules can easily approach the sensing interface of GO/GCE through π–π stacking and/or electrostatic attraction with the GO,
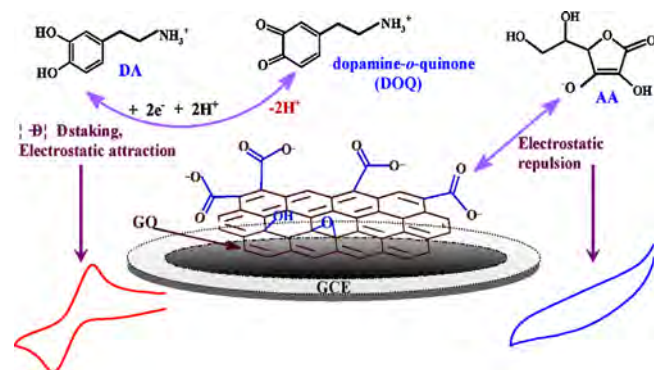

Fig. 5. Proposed different the electrochemistry of DA and AA on GO/GCE.
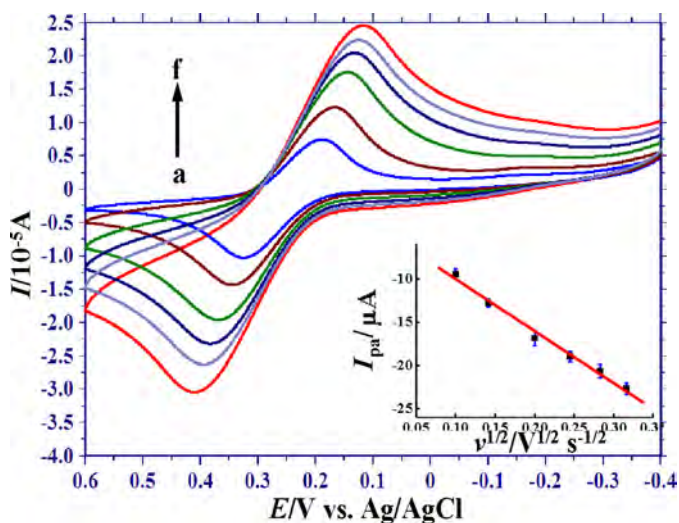
Fig. 6. CVs of 0.1 mM DA at GO/GCE at 0.04 M B–R buffer solutions with pH 5.0 at different scan rate: 0.01 V s^{-1} (a), 0.02 V s^{-1} (b), 0.04 V s^{-1} (c), 0.06 V s^{-1} (d), 0.08 V s^{-1} (e), 0.10 V s^{-1} (f).

and produce large electrochemical response. However, the π–π stacking force between AA and GO is absent because AA has not aromatic ring, and even more the electrostatic repulsion between the modified GO film and AA prevents the approaching of AA toward the transducer interface, leading to the complete disappearance of its electrochemical signal. It is also necessary to pointed out that, as compared with the previously reported graphene-based DA biosensors [20,21,38], the biosensor presented in this work has the following merits: (1) the GO is much more convenient and safe to prepare, and the obtained GO is more stable than the graphene materials; (2) The covalent modification of GO/GCE make the DA biosensor having the better stability and reproducibility than those fabricated through physical adsorption of graphene-related materials.

3.3. Electrochemical parameters of DA on GO/GCE

In order to better understand the electrochemical mechanism of DA on GO/GCE, some electrochemical parameters of DA on the modified electrode were further investigated. Fig. 6 shows the CVs of DA at GO/GCE at different scan rate (v). It is observed that the electrochemical response of DA varies accordingly with the changes of v. The oxidation peak currents (I_{pa}) show good linear relationship with the square root of scan rate ($v^{1/2}$) with the equation of $I_{pa}/\mu A = -59.830\, v^{1/2}/(V^{1/2}\, s^{-1/2}) - 4.069$ ($r = 0.9946$) (inset of Fig. 6), suggesting that the diffusion process in bulk solution is a controlling factor to impact the electrochemical response of DA [39].

The electro-transfer kinetic parameters such as the electron transfer coefficient (α) and the standard electron transfer rate constant (k_s) of DA on the modified electrode were also investigated according to the following Laviron's equations [40]:

$$E_{pa} = \frac{E^{0'} + 2.3RT}{(1-\alpha)nF \log v} \tag{2}$$

$$E_{pc} = \frac{E^{0'} - 2.3RT}{anF \log v} \tag{3}$$

$$\log k_s = \alpha \log(1-\alpha) + (1-\alpha)\log \alpha - \log\left(\frac{RT}{nFv}\right) - \frac{(1-\alpha)anF\,\Delta E_p}{2.3RT} \tag{4}$$

where n represents the number of electron transferred in reaction, and the other symbols have their usual meanings.

The linear relationships between the oxidation peak potential (E_{pa}) and reduction peak potential (E_{pc}) with the logarithm values of v ($\log v$) were established to be $E_{pa}/V = 0.08232 \log v/(V\,s^{-1}) + 0.48663$ ($r = 0.9953$) and $E_{pc}/V = -0.07223 \log v/(V\,s^{-1}) + 0.04435$ ($r = 0.9996$), respectively. Then according to Eqs. (2) and (3), the values of α and n were calculated to be 0.53 and 2.2, respectively. Furthermore, based on Eq. (4), the average value of k_s was calculated to be 1.59 s^{-1}, which is larger than those reported in the previous literatures [41,42], showing that the modified electrode in this work has higher catalytic capacity to promote electron transfer kinetics of DA.

The catalytic reaction of DA on the surface of GO/GCE was also studied by chronoamperometry using the potential step technique. Fig. 7 shows the chronoamperometry response on the supporting electrolyte (B–R buffer) in absence (curve a) and presence of 0.1 mM DA (curve b) on GO/GCE. The catalytic rate constant (k_{cat}) for electron communication between DA and the mediator of GO was determined by the following equation [43]:

$$\frac{I_{cat}}{I_L} = (\pi k_{cat} C_0 t)^{1/2} \tag{5}$$

where I_{cat} is the catalytic current of the GO/GCE in the presence of DA, I_L is the limiting current in the absence of DA, and C_0 and t are the substrate concentration and time elapsed, respectively. Inset A in Fig. 7 shows the plot of I_{cat}/I_L versus $t^{1/2}$ in a small time range, which is found to well obey the linear relationship of Eq. (5). Thus, for the given concentration of DA (0.1 mM), the value of k_{cat} was calculated to be 6.80×10^2 M^{-1} s^{-1}, which is obviously larger than that reported in literatures [44,45], further suggesting that the material of GO has significantly catalytic action toward the redox of DA.

In addition, the diffusion coefficient (D) of DA in the system was determined according to the following Cottrell's law [46]:

$$I_{cat} = nFAD^{1/2}C_0\pi^{-1/2}t^{-1/2} \tag{6}$$

where A the electrode area, and the other symbols are the same with the aforementioned equations. The plot of I_{cat} versus the inverse square root of time elapsed ($t^{-1/2}$) is displayed in Inset B of Fig. 7. Then, from the slope of the plot, the value of the diffusion coefficient was calculated to be $2.26(\pm0.01) \times 10^{-6}$ cm^2 s^{-1}, which is consistent with the values reported in the literature [34,47,48].
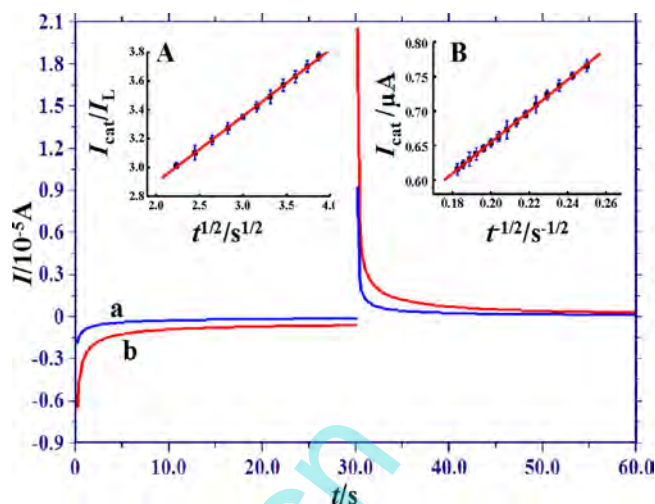

Fig. 7. Chronoamperometry response on GO/GCE in the absence (a) and presence (b) of 0.1 mM DA in 0.04 M B–R buffer solutions (pH 5.0). Inset A and B show plots of I_{cat}/I_L vs. $t^{1/2}$ and I_{cat} vs. $t^{-1/2}$, respectively.
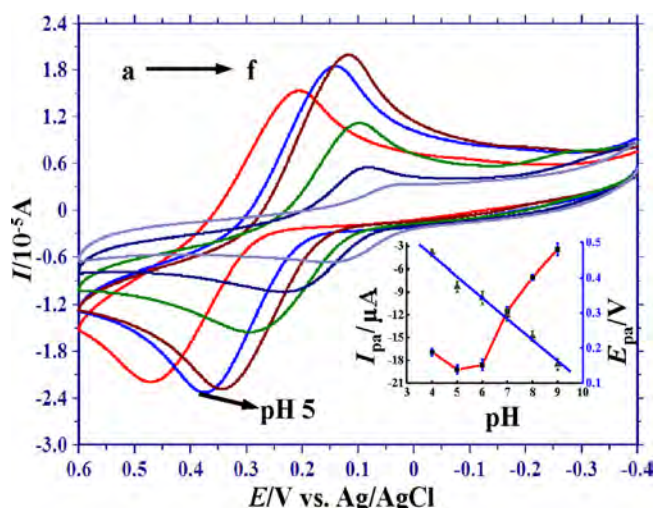
Fig. 8. CVs of 0.1 mM DA on GO/GCE in 0.04 M B–R buffer solutions with various pH values (a–f): 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0; Inset: plots of I_{pa} and E_{pa} vs. pH values.

In this work, the effect of the pH values of the supporting electrolyte (B–R buffer) on the electrochemical behaviors of DA were also investigated, and the results are showed in Fig. 8. It is found that the redox peak potentials shift to more negative values as pH increased over a range from 4.0 to 9.0, and the oxidation peak potentials present a linear relationship with the pH values, $E_{pa}/V = 0.695 - 0.059$ pH ($r = 0.9910$) (inset of Fig. 8). Since E_p can be expressed as (at 25 °C):

$$E_p = E^0 - \left(\frac{m}{n}\right) 0.059 \text{pH} \tag{7}$$

where E^0 is the standard potential, and m the number of protons transferred, the value of m/n was then obtained to be 1 from the slope of the relationship of E_p–pH. This also means that the number of protons involved in the electrode reaction is two, which is well in accordance with the classical electrochemical characteristic of DA [7,38].

On the other hand, from Fig. 8 it can be seen that the acidity of the buffer also has significant effect on the peak currents of DA. As showed in the inset of Fig. 8, the oxidation peak currents (I_{pa}) increase with the decrease the pH values until it reaches 5.0 and then decrease when the pH value is further decreased. So, pH 5.0 of B–R buffer was chose as the optimal acidity in this experiment.

3.4. Electrochemical determination of DA in the presence of AA

The initial studies in this work have shown that the electrochemistry of AA can be totally eliminated by the modification film of GO, but the electrochemistry of DA can be significantly promoted. Based on this feature, the GO/GCE was utilized as a sensor for the highly selective and sensitive determination of DA coexisted with AA. Fig. 9 shows the CVs of 0.1 mM DA in the presence of increasing amounts (0.1–1.5 mM) of AA. It can be clearly observed that with the increase of the amount of AA, the redox signals are almost constant, suggesting that the co-existed AA in a wide concentration range has no impact on the electrochemical response of DA on GO/GCE.

Because differential pulse voltammetry (DPV) commonly has the higher sensitivity than the CV technology, the DPV technology was applied for the quantitative detection of DA in the presence of AA. The corresponding results are showed in Fig. 10. As seen, in the presence of 0.1 mM AA, also only a well-defined oxidation peak corresponding to the electro-oxidation of DA is observed, and the peak currents enhance gradually with the adding of DA. The oxidation
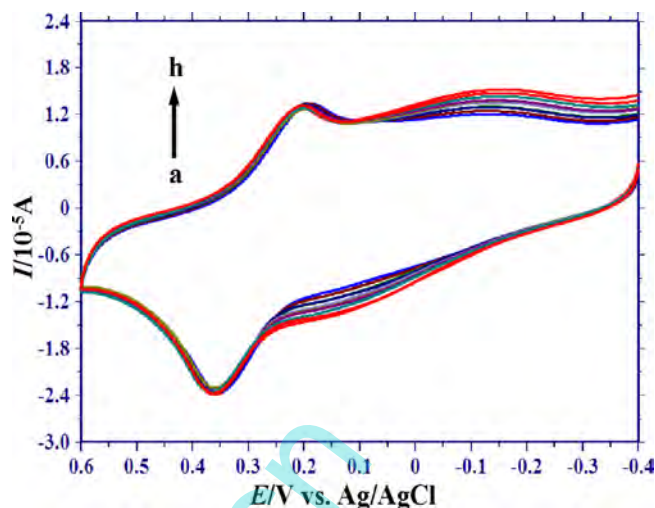
peak currents (I_{pa}) show a good linear relationship with the concentrations of DA (C_{DA}) ranging from 1.0 μM to 15.0 μM. The linear equation is $I_{pa}/\mu A = -0.5545 C_{DA}/\mu M - 5.4316$ ($r = 0.9980$) (curve a in inset of Fig. 10), which is very close to the case in the absence of AA (curve a in inset of Fig. 10), further showing that the co-existed AA has no effect for the detection of DA. Moreover, based on 3σ (where σ is the standard deviation of a blank solution, $n = 6$), the limit of detection (LOD) was estimated to be 0.27 μM. The comparison of the proposed method with other electrochemical methods reported for the determination of DA is summarized in Table 1 [8,9,38,39], showing that the developed sensor also has high sensitivity for the determination of DA.

3.5. Reproducibility and stability of the modified electrode

The reproducibility and stability of the modified electrode was also evaluated in these sensing studies. Five GO modified electrodes were made and their current responses to 0.1 mM DA were investigated. The relative standard deviation (RSD) was found to be 3.5%, indicating excellent reproducibility of the sensor prepared.
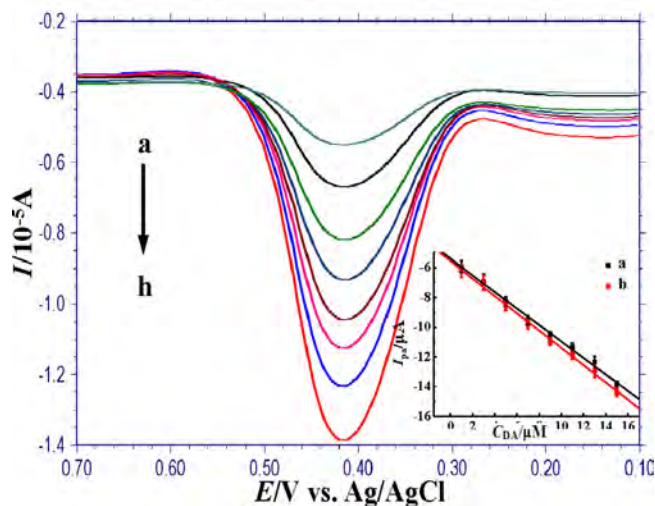

Fig. 9. Effects of increasing concentrations (a–h: 0.1–1.5 mM) of AA on the CVs of 0.1 mM DA in 0.04 M B–R buffer on GO/GCE.

Fig. 10. DPVs of 1.0 μM (a), 3.0 μM (b), 5.0 μM (c), 7.0 μM (d), 9.0 μM (e), 11.0 μM (f), 13.0 μM (g), 15.0 μM (h) of DA in the presence of 0.1 mM AA on GO/GCE in 0.04 M B–R buffer solutions with pH 5.0. Inset: plots of I_{pa} vs. C_{DA} in the presence (a) and absence (b) of AA.

Table 1
Comparison of some characteristics of the different graphene-based electrodes for the determination of DA.

Electrode	Electrolyte	Methods	Linear range (μM)	Detection limit (μM)	Refs.
Graphene/GCE	PBS (pH 7.0)	DPV	4–100	2.64	[8]
Graphene–Au nano particles/GCE	PBS (pH 6.0)	DPV	5–1000	1.86	[9]
Graphene/GCE	PBS (pH 7.0)	DPV	2.5–100	0.5	[38]
TiO_2–graphene/GCE	PBS (pH 7.0)	DPV	5–200	2	[39]
GO/GCE	B–R (pH 5.0)	DPV	1.0–15	0.27	This work

The stability of the GO/GCE was checked in two weeks. After measurements GO/GCE was stored in a B–R buffer. Before subsequent measurement the GO/GCE was only washed with water. In two weeks, the current responses of 0.1 mM DA decreased by less than 5% of the initial response, indicating that the GO/GCE was stable for electrochemical application.

4. Conclusion

A GCE interface covalently anchored with GO film (GO/GCE) was prepared and applied as DA sensing platform in this work. The electrochemical experiments show that the GO film has absolutely different effect on the electrochemistry of DA and AA, i.e., the redox signals of DA on GO/GCE is greatly enhanced as compared with bare GCE, while the electrochemical response of AA on GO/GCE is completely shielded. The possible mechanism to cause this difference was proposed. The electrochemical parameters such as electron transfer rate constant (k_s), the diffusion coefficient (D), and catalytic rate constant (k_{cat}) of DA on GO/GCE were investigated. Furthermore, based on the different response of DA and AA on GO/GCE, the modified electrode was applied as a sensor for the determination of DA in the presence with AA, and the results show that the coexisted AA has not any effect for the determination of DA, suggesting that the interference of AA to the determination of DA can be completely precluded by the sensor. Although similar results have been reported on graphene or its composite modified electrode [8,20,38], the biosensor developed in this work is more environmentally friendly and easy to prepare but without losing high selectivity and high sensitivity, which make it having more promising in the real application.

Acknowledgements

References

[1] R. Zhang, G.D. Jin, D. Chen, X.Y. Hu, Simultaneous electrochemical determination of dopamine, ascorbic acid and uric acid using poly(acid chrome blue K) modified glassy carbon electrode, Sensors and Actuators B 138 (2009) 174–181.

[2] S. Reyes, Y. Fu, K.L. Double, V. Cottam, L.H. Thompson, D. Kirik, G. Paxinos, C. Watson, H.M. Cooper, G.M. Halliday, Trophic factors differentiate dopamine neurons vulnerable to Parkinson's disease, Neurobiology of Aging 34 (2013) 873–886.

[3] J.M. Zen, P.J. Chen, A selective voltammetric method for uric acid and dopamine detection using clay-modified electrodes, Analytical Chemistry 69 (1997) 5087–5093.

[4] C.L. Sun, H.H. Lee, J.M. Yang, C.C. Wu, The simultaneous electrochemical detection of ascorbic acid dopamine, and uric acid using graphene/size-selected Pt nanocomposites, Biosensors & Bioelectronics 26 (2011) 3450–3455.

[5] Y. Mao, Y. Bao, S.Y. Gan, F.H. Li, L. Niu, Electrochemical sensor for dopamine based on a novel graphene-molecular imprinted polymers composite recognition element, Biosensors & Bioelectronics 28 (2011) 291–297.

[6] S. Alwarappan, K.S.A. Butcher, D.K.Y. Wong, Evaluation of hydrogenated physically small carbon electrodes in resisting fouling during voltammetric detection of dopamine, Sensors and Actuators B 128 (2007) 299–305.

[7] C.Y. Deng, J.H. Chen, M.D. Wang, C.H. Xiao, Z. Nie, S.Z. Yao, A novel and simple strategy for selective and sensitive determination of dopamine based on the boron-doped carbon nanotubes modified electrode, Biosensors & Bioelectronics 24 (2009) 2091–2094.

[8] Y.R. Kim, S. Bong, Y.J. Kang, Y. Yang, R.K. Mahajan, J.S. Kim, H. Kim, Electrochemical detection of dopamine in the presence of ascorbic acid using graphene modified electrodes, Biosensors & Bioelectronics 25 (2010) 2366–2369.

[9] J. Li, J. Yang, Z.J. Yang, Y.F. Li, S.H. Yu, Q. Xu, X.Y. Hu, Graphene–Au nanoparticles nanocomposite film for selective electrochemical determination of dopamine, Analytical Methods 4 (2012) 1725–1728.

[10] J.H. Chen, J. Zhang, X.H. Lin, H.Y. Wan, S.B. Zhang, Electrocatalytic oxidation and determination of dopamine in the presence of ascorbic acid and uric acid at a poly (4-(2-pyridylazo)-resorcinol) modified glassy carbon electrode, Electroanalysis 19 (2007) 612–615.

[11] F.H. Li, J. Chai, H.F. Yang, D.X. Han, L. Niu, Synthesis of Pt/ionic liquid/graphene nanocomposite and its simultaneous determination of ascorbic acid and dopamine, Talanta 81 (2010) 1063–1068.

[12] Y.Z. Zhang, Y. Pan, S. Su, L.P. Zhang, S.P. Li, M.W. Shao, A novel functionalized single-wall carbon nanotube modified electrode and its application in determination of dopamine and uric acid in the presence of high concentrations of ascorbic acid, Electroanalysis 19 (2007) 1695–1701.

[13] S. Alwarappan, A. Erdem, C. Liu, C.Z. Li, Probing the electrochemical properties of graphene nanosheets for biosensing applications, Journal of Physical Chemistry C 113 (2009) 8853–8857.

[14] S. Alwarappan, C. Liu, A. Kumar, C.Z. Li, Enzyme-doped graphene nanosheets for enhanced glucose biosensing, Journal of Physical Chemistry C 114 (2010) 12920–12924.

[15] S. Alwarappan, S. Boyapalle, A. Kumar, C.Z. Li, S. Mohapatra, Comparative study of single- few-, and multilayered graphene toward enzyme conjugation and electrochemical response, Journal of Physical Chemistry C 116 (2012) 6556–6559.

[16] S. Alwarappan, R.K. Joshi, M.K. Ram, A. Kumar, Electron transfer mechanism of cytochrome c at graphene electrode, Applied Physics Letters 96 (2010) 263702.

[17] C.S. Shan, H.F. Yang, J.F. Song, D.X. Han, A. Ivaska, L. Niu, Direct electrochemistry of glucose oxidase and biosensing for glucose based on graphene, Analytical Chemistry 81 (2009) 2378–2382.

[18] J.F. Wu, M.Q. Xu, G.C. Zhao, Graphene-based modified electrode for the direct electron transfer of cytochrome C and biosensing, Electrochemistry Communications 12 (2010) 175–177.

[19] K.P. Liu, J.J. Zhang, G.H. Yang, C.M. Wang, J.J. Zhu, Direct electrochemistry and electrocatalysis of hemoglobin based on poly (diallyldimethylammonium chloride) functionalized graphene sheets/room temperature ionic liquid composite film, Electrochemistry Communications 12 (2010) 402–405.

[20] Y. Wang, Y.M. Li, L.H. Tang, J. Lu, J.H. Li, Application of graphene-modified electrode for selective detection of dopamine, Electrochemistry Communications 11 (2009) 889–892.

[21] S.F. Hou, M.L. Kasner, S.J. Su, K. Patel, R. Cuellari, Highly sensitive and selective dopamine biosensor fabricated with silanized graphene, Journal of Physical Chemistry C 114 (2010) 14915–14921.

[22] Y. Si, E.T. Samulski, Synthesis of water soluble graphene, Nano Letters 8 (2008) 1679–1682.

[23] D. Li, M.B. Muller, S. Gilje, R.B. Kaner, G.G. Wallace, Processable aqueous dispersions of graphene nanosheets, Nature Nano 3 (2008) 101–105.

[24] S.J. He, B. Song, D. Li, C.F. Zhu, W.P. Qi, Y.Q. Wen, L.H. Wang, S.P. Song, H.P. Fang, C.H. Fan, A graphene nanoprobe for rapid sensitive, and multicolor fluorescent DNA analysis, Advanced Functional Materials 20 (2010) 453–459.

[25] F. Li, Y. Huang, Q. Yang, Z.T. Zhong, D. Li, L. Wang, S.P. Song, C. Fan, A graphene-enhanced molecular beacon for homogeneous DNA detection, Nanoscale 2 (2010) 1021–1026.

[26] L.L. Zhang, H.H. Cheng, H.M. Zhang, L.T. Qu, Direct electrochemistry and electrocatalysis of horseradish peroxidase immobilized in graphene oxide—Nafion nanocomposite film, Electrochimica Acta 65 (2012) 122–126.

[27] D. Du, L.M. Wang, Y.Y. Shao, J. Wang, M.H. Engelhard, Y.H. Lin, Functionalized graphene oxide as a nanocarrier in a multienzyme labeling amplification strategy for ultrasensitive electrochemical immunoassay of phosphorylated p53 (S392), Analytical Chemistry 83 (2011) 746–752.

[28] W.S. Hummers, R.E. Offeman, Preparation of graphitic oxide, Journal of American Chemical Society 80 (1958) 1339.

[29] G.Y. Xu, K. Jiao, J.S. Fan, W. Sun, Electrochemical detection of specific gene related to CaMV35S using methylene blue and ethylenediamine modified glassy carbon electrode, Acta Chimica Slovaca 53 (2006) 486–491.

[30] K.P. Liu, J.P. Wei, C.M. Wang, Sensitive detection of rutin based on β-cyclodextrin@chemically reduced graphene/Nafion composite film, Electrochimica Acta 56 (2011) 5189–5194.

[31] M.A. Wilson, A. Pohorille, L.R. Pratt, Molecular dynamics of the water liquid–vapor interface, Journal of Physical Chemistry 91 (1987) 4873–4878.

[32] S.K. Kim, S.R. Bae, M.S. Ahmed, J.M. You, S.W. Jeon, Selective determination of serotonin on poly(3,4-ethylenedioxy pyrrole)-single-walled carbon nanotube-modified glassy carbon electrodes, Bulletin of the Korean Chemical Society 32 (2011) 1215–1220.

[33] Y.X. Sun, F.W. Sheng, Simultaneous determination of dopamine and ascorbic acid at a triazole self-assembled monolayer-modified gold electrode, Microchimica Acta 154 (2006) 115–121.

[34] A.A. Ensafi, M. Taei, T. Khayamian, A. Arabzadeh, Highly selective determination of ascorbic acid, dopamine, and uric acid by differential pulse voltammetry using poly(sulfonazo III) modified glassy carbon electrode, Sensors and Actuators B 147 (2010) 213–221.

[35] X.Q. Zhang, Y.Y. Feng, S.D. Tang, W. Feng, Preparation of a graphene oxide-phthalocyanine hybrid through strong π–π interactions, Carbon 48 (2010) 211–216.

[36] W.D. Pu, L. Zhang, C.Z. Huang, Graphene oxide as a nano-platform for ATP detection based on aptamer chemistry, Analytical Methods 4 (2012) 1662–1666.

[37] C. Zhang, L. Ren, X.Y. Wang, T.X. Liu, Graphene oxide-assisted dispersion of pristine multiwalled carbon nanotubes in aqueous media, Journal of Physical Chemistry C 114 (2010) 11435–11440.

[38] X.Y. Ma, M.Y. Chao, Z.X. Wang, Electrochemical detection of dopamine in the presence of epinephrine, uric acid and ascorbic acid using a graphene-modified electrode, Analytical Methods 4 (2012) 1687–1692.

[39] Y. Fan, H.T. Lu, J.H. Liu, C.P. Yang, Q.S. Jing, Y.X. Zhang, X.K. Yang, K.J. Huang, Hydrothermal preparation and electrochemical sensing properties of TiO_2–graphene nanocomposite, Colloids and Surfaces B 83 (2011) 78–82.

[40] E. Laviron, General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems, Journal of Electroanalytical Chemistry 101 (1979) 19–28.

[41] S.M. Ghoreishi, M. Behpour, M.H.M. Fard, Electrochemical methods for simultaneous determination of trace amounts of dopamine and uric acid using a carbon paste electrode incorporated with multi-wall carbon nanotubes and modified with α-cyclodextrine, Journal of Solid State Electrochemistry 16 (2012) 179–189.

[42] W. Sun, X.Z. Wang, Y.H. Wang, X.M. Ju, L. Xu, G.J. Li, Z.F. Sun, Application of graphene–SnO_2 nanocomposite modified electrode for the sensitive electrochemical detection of dopamine, Electrochimica Acta 87 (2013) 317–322.

[43] Z. Galus, Fundamentals of Electrochemical Analysis, Ellis Horwood, New York, 1976.

[44] H. Razmi, A. Azadbakht, Electrochemical characteristics of dopamine oxidation at palladium hexacyanoferrate film, electroless plated on aluminum electrode, Electrochimica Acta 50 (2005) 2193–2201.

[45] X.X. Wang, N.J. Yang, Q.J. Wan, X. Wang, Catalytic capability of poly(malachite green) films based electrochemical sensor for oxidation of dopamine, Sensors and Actuators B 128 (2007) 83–90.

[46] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, second ed., Wiley, New York, 2001.

[47] M. Mazloum Ardakani, H. Beitollahi, B. Ganjipour, H. Naeimi, M. Nejati, Electrochemical and catalytic investigations of dopamine and uric acid by modified carbon nanotube paste electrode, Bioelectrochemistry 75 (2009) 1–8.

[48] M.M. Ardakani, H. Beitollahi, M.K. Amini, F. Mirkhalaf, B.F. Mirjalili, A. Akbaria, Application of 2-(3,4-dihydroxyphenyl)-1,3-dithialone self-assembled monolayer on gold electrode as a nanosensor for electrocatalytic determination of dopamine and uric acid, Analyst 136 (2011) 1965–1970.

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