

Simultaneous Voltammetric Determination of Dopamine and Ascorbic Acid Using Graphene Oxide/ Ionic Liquid-Modified Electrode

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Abstract

In this study, the surface of the glassy carbon electrode (GCE) is modified with the nanocomposite of graphene oxide (GO)/ ionic liquid (1-Butyl-3-methylimidazolium tetrafluoroborate; [BMIM]BF₄). The electrochemical behavior of ascorbic acid (AA) and dopamine (DA) at the surface of the modified glassy carbon electrode was studied using the differential pulse and cyclic voltammetric methods (DPV and CV). The results show good response sensitivity to AA and DA. The acceleration of the electron transfer rate and enhancement of the electroactive surface area is obtained due to a synergistic effect in the concurrent presence of GO and [BMIM]BF₄ at the surface of the electrode. The presence of GO caused to a higher specific surface of the electrode, and ionic liquid ([BMIM]BF₄) increased the ion conductivity and dispersibility in the modifier layer at the surface of the GCE. These results obtained in optimum conditions, show good peak separation for AA and DA (more than 300 mV), and the sub-micromolar detection limits for them. The obtained results in this work, make the modified GCE very effective in the manufacture of simple devices for the detection of AA and DA in human urine samples.

Keywords

Graphene oxide; Ionic liquid; Modified electrode; ascorbic Acid; Dopamine

1. INTRODUCTION

In recent years, the modification of electrodes using new modifiers and their application have been of substantial interest [1–6]. Specially, the detection of different samples using modified electrodes received many interests. For instance, modified carbon-based electrodes have been used for detection of paracetamol [7], rGO/ β -cyclodextrin- modified electrode has been applied in determination of catechol [8], TiO₂ nanoparticles modified carbon paste electrode has been prepared for detection of paracetamol in presence of Adrenaline [9], MWCNT-COOH/ covalent triazine framework -modified glassy carbon electrode has been used for determination of hydroquinone and Catechol [10], Ag decorated carbon nanosphere modified fluorine-doped tin oxide electrode has been prepared for determination of procaine [11], Fe₂O₃@Ni/Al-LDH modified electrode has been applied in sensing of mercury [12], AuNPs/graphene modified GCE has been prepared for determination of chlorzoxazone [13], MoO₃-graphitic carbon nitride sheets modified electrode has been applied for caffeine detection [14], laser-induced graphene modified electrode has been used for detection of hydrogen peroxide [15], La₂(MoO₄)₃ modified electrode has been prepared for detection of antibiotic drug [16], NiO nanocrystal modified electrodes has been used for 1,2-Benzenediol detection [17], Zn-mMOF/Cu ions modified glassy

carbon electrode has been prepared for detection of amoxicillin [18], pyrogallol red modified electrode has been applied for paracetamol detection [19], poly(p-coumaric acid) modified electrodes has been used for detection of cadmium and lead [20], different modified electrodes have been applied for illicit drugs detection [21], imprinted polymer/sol-gel/polyoxometalate/ reduced graphene oxide modified electrode has been used for detection of sumatriptan and paroxetine [22], pd nanoparticles modified electrode has been used for detection of direct yellow 50, carbendazim and caffeine [23], Au nanoparticles modified sensor has been used for As(III) detection [24], Fe₃O₄@polypyrrole-Pt core-shell nanoparticles modified electrode has been applied for sensing 6-mercaptopurine and 6-thioguanine [25], carbon black modified electrode has been used for detection of dissolved iron [26]. Among the biological compound, determination of neurotransmitters, e.g., dopamine (DA; a significant neurotransmitter) and ascorbic acid (AA; vitamin C) using modified electrodes, received many interests. An earnest drawback in detection of DA or AA is the lack of enough resolution between the anodic peaks of AA and coexisting DA at common solid electrodes. Various techniques have been used to prevail this disadvantage. The electrochemical response to DA was studied at a carbon black nanoparticles modified porous boron-doped diamond electrode [27], SU-8 modified carbon nanoglass electrodes

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[28], TiO₂/stainless steel modified electrode [29], cerium phosphate nanorods/rGO modified glassy carbon electrode [30], ZnO@MnO₂ nanocomposite modified carbon paste electrode [31] and Hydrogenated conical-tip carbon electrode [32]. On the other hand, CuCo₂O₄ rods [33], capsaicin/MWCNT [34], electropolymerized safranin [35], molecularly imprinted/MXene [36], and cetylpyridinium [37] were used as modifiers in preparation of modified electrode for determination of ascorbic acid.

This work is related to the voltammetric simultaneous detection of DA and AA at the surface of the modified glassy carbon electrode using the suspended nanocomposite containing graphene oxide (GO) and ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄). Preliminary, the reaction mechanism is studied using cyclic voltammetry (CV) in the various scan rates of potential and pHs. The differential pulse voltammetric (DPV) method has been developed for the simultaneous determination of trace amounts of DA and AA in the mixture solutions. Very good resolution between the voltammetric responses of these species and acceptable accuracies with sub-micromolar detection limits were obtained.

2. EXPERIMENTAL

2.1. Chemicals

Graphene oxide (> 98 wt%, D > 50 μm, 1-2 layers) was purchased from Nanostructured & Amorphous Materials (USA). The ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) was purchased from Sigma-Aldrich with a purity higher than 98 %. A 5% Nafion solution (Aldrich, EW, 1100, dissolved in lower aliphatic alcohol and water) was used to dispersing of Graphene oxide. Spectroscopic mineral oil (Nujol) and Graphite powder (20 μm) were purchased from Merck. All the other chemicals were analytical reagent grade, purchased from Merck. Using doubly distilled deionized water, all aqueous solutions were made up.

Stock solutions of DA and AA were freshly made up and purged with pure nitrogen gas (99.999%, Roham Gas Company) for 2 min for voltammetric studies. During the voltammetric analysis, nitrogen gas was passed over the surface of the test solutions in order to avoid the entrance of oxygen into the solution. In order to study the recovery for the determination of dopamine, the sample of fresh human serum was filtered and diluted using the buffer solution.

2.2. Apparatus

A digital pH/mV/ion meter (CyberScan model 2500, Eutech Instruments) was used in order to make up the buffered solutions. A common three-

electrode system was applied with a saturated Calomel reference electrode, a platinum wire as a counter electrode, and a glassy carbon working electrode (GCE, bare or modified, diameter = 2 mm). Voltammetric measurements were performed using a computerized potentiostat/galvanostat Autolab model 302 (Eco Chemie Utrecht, the Netherlands) controlled with General Purpose Electrochemical System (GPES) software.

2.3. Preparation of modified electrode

Before the modification step, the GCE was polished with alumina slurry (0.1 μm) on a polishing cloth, rinsed thoroughly with water, sonicated in water for 60 s, and air dried. 1.0 mg GO or GO/Nafion was dispersed in 1.0 mL of doubly distilled water, and in order to obtain the homogenous suspensions, ultrasonicated for 15 min. The dispersion of GO/Nafion/[BMIM]BF₄ was prepared by simple addition to the ionic liquid 1-Butyl-3-methylimidazolium tetrafluoroborate in a 1 wt.% proportion following the method described previously by Fukushima [38]. With this procedure, the modifier materials are weighed and manually mixed in an agate mortar for 15 minutes. Afterward, the mixtures were ultrasonicated during 1 hour at room temperature to better disperse the graphene oxide. For the preparation of the modified GCEs, using a micropipette, 2 μL of different prepared suspensions (GO, GO/Nafion, and GO/Nafion/[BMIM]BF₄) was applied directly onto a well-polished glassy carbon electrode and left to dry at room temperature.

3. RESULTS AND DISCUSSION

3.1. Cyclic and differential pulse voltammetry studies

The potential application of GO/Nafion/[BMIM]BF₄ composite at the surface of GCE as an electrochemical sensing film for DA and AA was examined using cyclic and differential pulse voltammetry. The results of the cyclic voltammetric studies of 0.1mM DA and AA in acetate buffer solutions with pH 5.0 on the surface of different electrodes are shown in Figure 1. The cyclic voltammogram at the bare GCE shows a totally irreversible process for the oxidation of AA at approximately 320 mV with an anodic peak current of 10 μA. These results showed that the presence of GO alone at the surface of the GCE (GO/GCE) has an efficient effect on decreasing the overpotential of the anodic oxidation of AA (about 210 mV) and improving its anodic peak current to 24.1 μA. The reason may originate in the large surface area created by the presence of graphene oxide and the enhancement of the kinetics of the electron transfer process on the GO/GCE surface. On the other hand, by the addition of Nafion into

the modifier film at the surface of GCE (GO/Nafion/GCE), a slight enhancement in the voltammetric responses for AA is observed, because of the effect of Nafion in better dispersion of graphene oxide at the surface of modified electrode. A better catalytic effect on the electrochemical oxidation of AA is observed on the surface of GO/Nafion/[BMIM]BF₄/GCE. By using this electrode, the peak current of AA increased to more than 200% (about 57.0 μ A). In fact, ascorbic acid (pK_a of 4.17) can exist mainly as ascorbate (anionic form) in the buffered electrolyte with pH 5.0, and therefore has an effective electrostatic interaction (attraction) with cationic sites of ionic liquid at the surface of the modified GCE. The effect of ionic liquids, as a new class of CNT dispersant [39], with many different technological applications and their ability to disperse the carbon nanotubes and among their main advantages [40]. Furthermore, the enhancement of the electroactive surface area and acceleration of the electron transfer rate is obtained due to a synergistic combination of GO such as a high specific surface with the advantages of ionic liquid like ion conductivity and dispersability [41]. As can be seen in Figure 1B, at the surface of the bare GCE a quasi-reversible process (with an anodic peak potential of 420 mV and peak current of 11.4 μ A) for DA is obtained. These results showed that the presence of graphene oxide at the surface of the GCE (GO/GCE) has an efficient

effect on increasing the anodic peak current to 49.0 μ A and the corresponding peak potential has appeared in 380 mV. On the other hand, by the addition of Nafion into the modifier film at the surface of GCE (GO/Nafion/GCE), because of the effect of Nafion in better dispersion of graphene oxide at the surface of GCE, a slight enhancement in the voltammetric responses for DA is observed. By using the GO/Nafion/[BMIM]BF₄/GCE, the peak current of DA increased to about 61.0 μ A due to improving the dispersability of graphene oxide and film conductivity at the surface of the prepared electrode.

The electrochemical behavior of DA and AA at the surfaces of the modified GCEs is better described in the mixture solutions. Figure 2 illustrates the cyclic and differential pulse voltammograms of 0.1mM AA and DA in 0.1 M acetate buffer solution (pH 5.0) at the surface of four prepared electrodes, bare GCE, GO/GCE, GO/Nafion/GCE, and GO/Nafion/[BMIM]BF₄/GCE.

As can be seen in Figure 2 at the bare GCE, the voltammograms of the anodic oxidation of DA and AA overlap with each other and therefore this electrode isn't suitable for the simultaneous voltammetric detection of DA and AA in mixture samples. But the responses of these biomolecules are much different at the modified GCEs. The results of the voltammetric studies of DA and AA in 0.1 M acetate buffer solution with pH 5.0 revealed that the presence By using

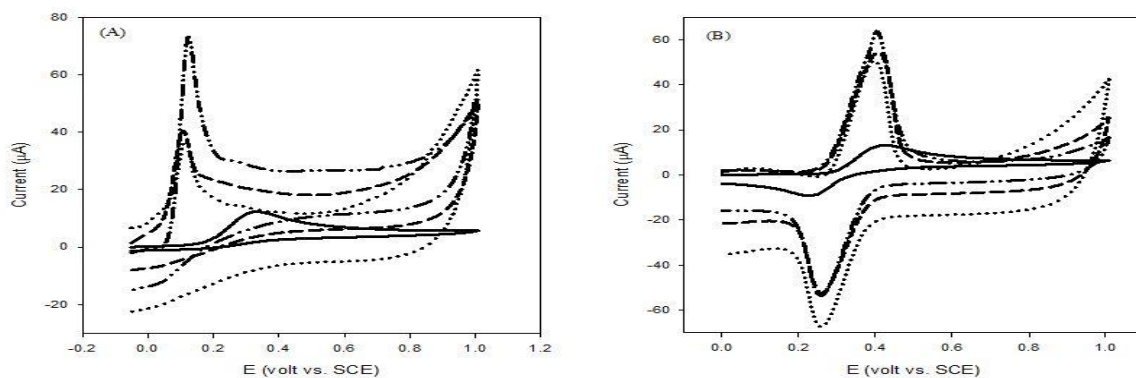


Fig. 1. Cyclic voltammograms for (A) 0.1mM AA and (B) 0.1mM DA in acetate buffer solution (0.1 M, pH = 5.0) at the surface of four prepared electrodes: bare GCE (—), GO/GCE (.....), GO/Nafion/GCE (— — —) and GO/Nafion/[BMIM]BF₄/GCE (— · — · —). Sweep rate was 100 mV s⁻¹.

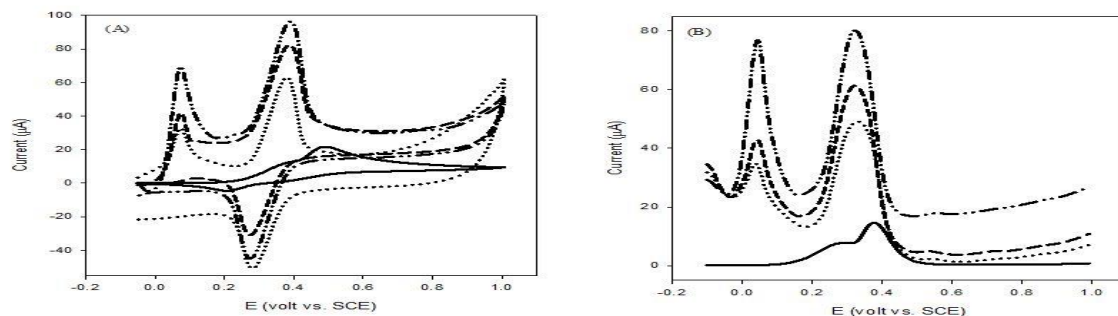


Fig. 2. CV (A) and DPV (B) responses for a mixture of 0.1mM AA and 0.1mM DA in acetate buffer solution (0.1M, pH = 5.0) at the surface of the bare GCE (—), GO/GCE (.....), GO/Nafion/GCE (— — —) and GO/Nafion/[BMIM]BF₄/GCE (— · — · —). Sweep rate was 100 mV s⁻¹ and Pulse amplitude was 50 mV.

GO/Nafion/GCE electrode, a slight improvement in anodic peak currents is resulted. On the other hand, at the surface of GO/Nafion/[BMIM]BF₄/GCE the peak currents of DA and AA extremely increased, which can be described with the synergic effect of GO and ionic liquid [BMIM]BF₄. The resulting resolution between the anodic peaks of DA and AA in these studies (315 mV) is more desirable than other reported voltammetric sensors. The peak resolution for DA and AA about 218 mV is obtained at the platinum nanoparticles/graphene/GCE [42], about 200 mV at the titanium nitride-reduced graphene oxide modified electrode [43], about 150 mV at the Au-polydopamine nanospheres modified electrode [44] and about 166 mV at the NiO/graphene oxide modified electrode [45]. Modification of electrode with CeO₂/reduced graphene oxide resulted in a peak resolution of 190 mV for the simultaneous detection of DA and AA [46]. In comparison to the previous reports, by using the modified electrode in this work (GO/Nafion/[BMIM]BF₄/GCE) the decay of anodic current between the differential pulse voltammetric waves of DA and AA is observed close to the capacitive background current, significantly causes to decrease the overlapping of the voltammetric responses of DA and AA, and possesses more desirable accuracy in the simultaneous determination of these compounds in mixture samples. In fact, the presence of graphene oxide together with ionic liquid can improve the catalytic effect of the modifier film at the surface of GCE in the electro-oxidation of AA, leading to improve the peak current and decreasing the corresponding anodic overpotential.

3.2. The effect of pH and sweep rate

Another effect that must be optimized is pH of the electrolyte solution. Therefore, the redox behavior of the DA and AA at the surface of the finally modified GCE (GO/Nafion/[BMIM]BF₄/GCE) in the mixture solution of these compounds with various pHs was studied and these results are shown in Table 1. These results revealed that the best peak resolution between DA and AA has resulted in pH 5.0. Therefore, the buffered solution with pH 5.0 was applied as supporting electrolyte in all voltammetric studies.

The results of cyclic voltammetric experiments at different potential scan rates revealed that the anodic peak currents (*I*_{p,a}) of DA and AA increase linearly with increasing the square root of the scan

rate ($v^{1/2}$) in the range of 25–250 mVs⁻¹. These results corroborate the diffusion-controlled anodic oxidation of DA and AA at the surface of the prepared GO/Nafion/[BMIM]BF₄/GCE.

Table 1. Results of cyclic voltammetric studies of 0.1mM DA and 0.1mM AA in mixture solutions with different pH at the surface of GO/Nafion/[BMIM]BF₄/GCE

pH	AA		DA		ΔE_p
	<i>I</i> _{p,a} (μA)	<i>E</i> _{p,a} (mV)	<i>I</i> _{p,a} (μA)	<i>E</i> _{p,a} (mV)	
3.0	52.6	129	58.4	407	278
4.0	51.9	115	57.1	392	277
5.0	57.1	72	60.1	387	315
6.0	49.6	71	49.8	301	230
7.0	43.8	73	48.3	239	166

3.3. Analytical characterization

The modified GCE in this work (GO/Nafion/[BMIM]BF₄/GCE) and the DPV method was used as useful method with low detection limits for detections of DA and AA in a wide range of their concentrations. Figure 3 shows some of these obtained DPV responses. A linear range is obtained by drawing the anodic peak currents versus the concentration, that is 2.0×10^{-7} to 1.0×10^{-4} M for AA and DA (Figure 4). A slope of 0.056982 μA/μM ($R^2 = 0.9981$) has resulted for DA, and a slope of 0.044323 μA/μM ($R^2 = 0.9933$) has been obtained for AA. The respective detection limits ($S/N = 3$) were 1.0×10^{-7} M for DA and AA. On the basis of ten replicates, the relative standard deviations (R.S.D.) of these slopes for DA and AA were obtained 3.3 and 3.0% respectively, and based on twelve measurements in a period of three months, were less than 3.2% for both DA and AA. So, the prepared GO/Nafion/[BMIM]BF₄/GCE E in this work was revealed to be very stable.

The waves obtained in solutions including 5×10^{-5} M DA and nine different concentrations of AA in the range of 4.0×10^{-7} to 1.0×10^{-4} M are represented in Figure 5A. The DPVs obtained in solutions containing 5.0×10^{-5} M AA and different concentrations of DA from 4.0×10^{-7} to 1.0×10^{-4} M are shown in Figure 5B. The resulting linear ranges and detection limits were very similar to the experiments in solutions containing only DA or AA. In the presence of 5×10^{-5} M DA, the calibration curve slope for AA was 0.043733 μA/μM ($R^2 = 0.9959$), which was about 98.7% of the resulting slope value of the separate AA solutions. This slope for DA, in the presence of 5.0×10^{-5} M AA was 0.056841 μA/μM ($R^2 = 0.9965$).

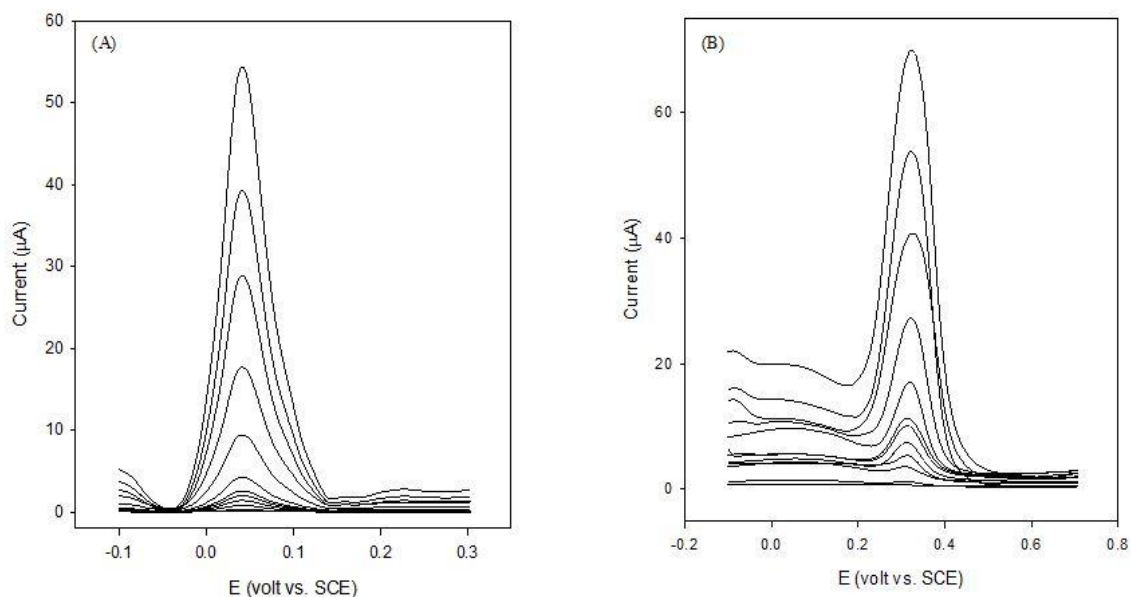


Fig. 3. DPVs at the surface of GO/Nafion/[BMIM]BF₄/GCE in buffered solution of pH 5.0 containing (A) 0.0, 0.0008, 0.002, 0.004, 0.006, 0.008, 0.02, 0.04, 0.06, 0.08 and 0.1mM AA and (B) 0.0, 0.0002, 0.0004, 0.0006, 0.0008, 0.002, 0.004, 0.006, 0.008, 0.02, 0.04, 0.06, 0.08 and 0.1mM DA (down to up). Pulse amplitude: 50 mV.

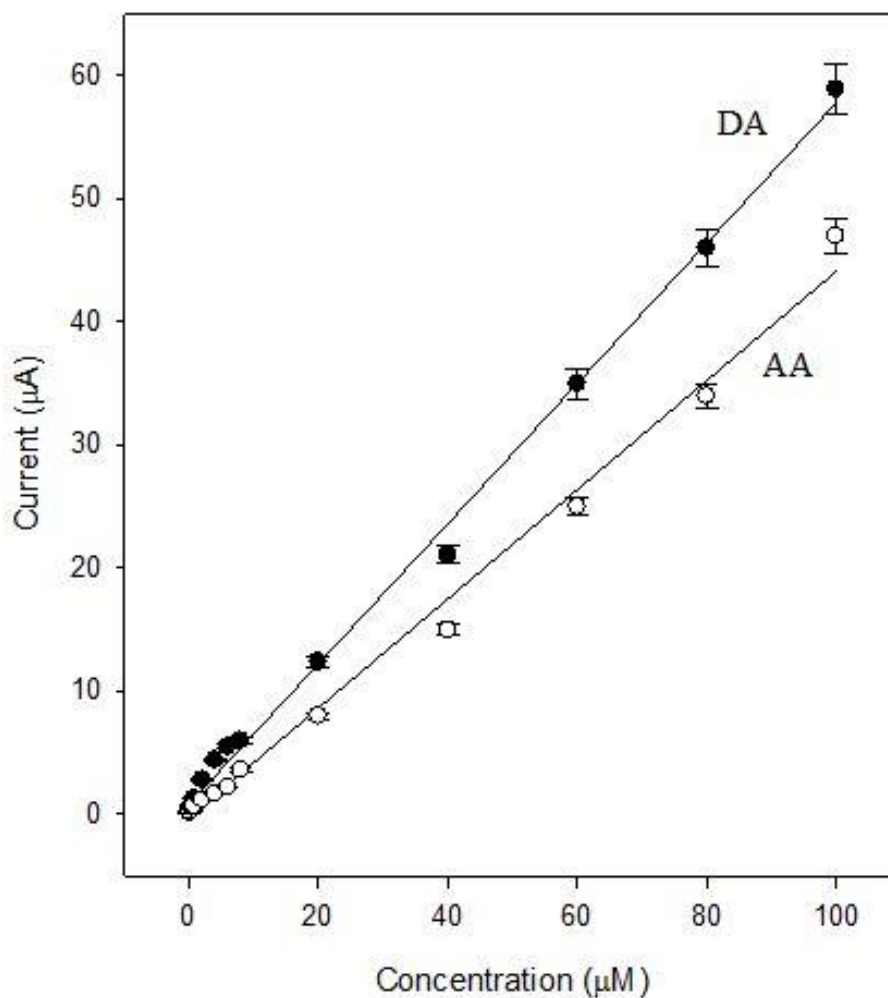


Fig. 4. Anodic peak current at the surface of GO/Nafion/[BMIM]BF₄/GCE versus DA and AA concentration in the range of 0.2 to 100.0 µM.

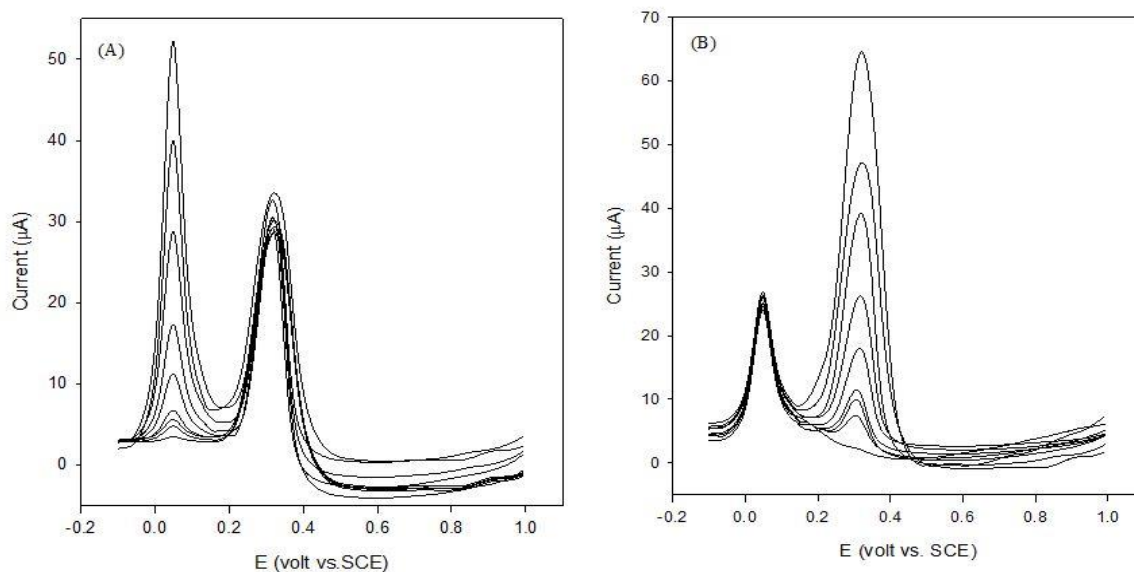


Fig. 5. DPVs at the surface of GO/Nafion/[BMIM]BF₄/GCE in buffered solution of pH 5.0 containing (A) 0.05 mM DA (constant) and various concentrations of AA: 0.0004, 0.004, 0.006, 0.008, 0.02, 0.04, 0.06, 0.08 and 0.1 mM. (B) 0.05 mM AA (constant) and various concentrations of DA: 0.0004, 0.004, 0.006, 0.008, 0.02, 0.04, 0.06, 0.08 and 0.1 mM. Pulse amplitude: 50 mV.

Table 2. Analysis of AA and DA in human urine samples (n = 10) using the GO/Nafion/[BMIM]BF₄/GCE.

Sample	Species	Detected (µM)	Added (µM)	Found (µM)	Recovery (%)
Urine 1	AA	-	150.0	149.1	99.4
	DA	-	25.0	25.2	100.8
Urine 2	AA	-	175.0	178.2	101.8
	DA	-	40.0	40.9	102.3
Urine 3	AA	-	200.0	197.1	98.6
	DA	-	45.0	44.1	98.0
Urine 4	AA	-	160.0	165.0	103.1
	DA	-	30.0	29.8	99.3

R.S.D. was less than 3.3% for ten replicates in the spiked range of DA and AA.

The GO/Nafion/[BMIM]BF₄-modified GCE and DPV method were applied for the simultaneous detection of DA and AA in human urine samples in order to estimate the reliability of this method. Only diluted urine samples were added into the electrochemical cell, in order to avoid the interferences of the real samples matrix and fit into the linear ranges of AA and DA. Buffered solutions of pH 5.0 were used to dilute the urine samples before detection. To ascertain the accuracy of the results, real samples were analyzed by the method of standard addition. The results are shown in Table 2. The obtained recovery of the spiked samples is in ranged from 98.0% to 103.1% and demonstrated that the GO/Nafion/[BMIM]BF₄-modified GCE was sensitive and reliable enough for the detection of DA and AA in these samples

4.CONCLUSION

The GO/Nafion/[BMIM]BF₄-modified GCE prepared in the present work can improve the selectivity and the peak resolution between DA

and AA. In this work, the application of voltammetric methods and GO/Nafion/[BMIM]BF₄-modified GCE results in an acceptable resolution of more than 300 mV for anodic oxidation waves of AA and DA, the enhancement of anodic peak currents, which were approximately 6.0 times higher than them at the bare GCE, and make it very efficient for simultaneous detection of these compounds. The appropriate sensitivity, selectivity, and sub-micromolar detection limit (0.1 µM for DA and AA) together with a wide linear range indicate the prepared GO/Nafion/[BMIM]BF₄/GCE is very useful in the manufacture of accessible tools for the simultaneous detection of DA and AA in clinical samples.

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اندازه‌گیری ولتامتری همزمان دوپامین و آسکوربیک اسید با استفاده از الکتروود اصلاح‌شده با گرافن اکسید/ مایع یونی

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چکیده

سطح الکتروود کربن شیشه‌ای با استفاده از نانوکامپوزیت حاوی گرافن اکسید و مایع یونی ۱-بوتیل-۳-متیل ایمیدازولیوم تترا فلئوروبورات اصلاح شد. رفتار الکتروشیمیایی دوپامین و آسکوربیک اسید در سطح الکتروود تهیه شده با استفاده از روش ولتامتری چرخه‌ای و پالس تفاضلی مطالعه شد. نتایج نشان دهنده افزایش مساحت سطح الکتروود فعال و تسریع فرایند انتقال الکترون بوده است که به دلیل ترکیب اثر سینرژیک گرافن اکسید مانند سطح ویژه زیاد و مزایای مایع یونی نظیر هدایت یونی و قابلیت پخش همگن می باشد. نتایج حاصل در شرایط بهینه نشان دهنده جدایی بسیار خوب پیکهای آندی دوپامین و آسکوربیک اسید (بیشتر از ۳۰۰ میلی ولت) و حدود تشخیص زیر میکرومولار (۰/۱ میکرومولار) برای دو ماده است. استفاده از الکتروود کربن شیشه‌ای اصلاح شده در این پژوهش جهت آنالیز دو ماده در نمونه حقیقی ادرار انسانی موفقیت آمیز بوده است.

کلید واژه‌ها

گرافن اکسید؛ مایع یونی؛ الکتروود اصلاح شده؛ آسکوربیک اسید؛ دوپامین.