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SELECTIVE ELECTROCHEMICAL DETERMINATION OF DOPAMINE AT *p*-NITROANILINE FILM-HOLE MODIFIED GLASSY CARBON ELECTRODES

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ABSTRACT. Herein, we report determination of dopamine (DA) at modified glassy carbon electrode (GCE) with a film produced by reduction of diazonium generated from *p*-nitroaniline (PNA). Pores were created purposely by stripping pre-deposited gold nanoparticles (AuNPs) in the modifier film. The modified electrodes were characterized electrochemically by common redox probes: hydroquinone (HQ), hexacyanoferrate $[(Fe(CN)6)]^{3-}$ and hexamine ruthenium(III) $[Ru(NH3)6]^{3+}$. Comparison was made for the cyclic voltammetric and amperometric response of DA using the modified electrodes against the bare GCE in phosphate buffer solution (PBS) of pH 7.5. The bare and modified GCE showed a linear response to DA in the concentration range of 0.2-2.2 mM and 5-35 μM with detection limit of 0.015 mM and 0.6112 μM, respectively. The modified electrode showed high sensitivity, well selectivity, good anti-interference ability, durable stability and good electrode reproducibility for determining DA. The reported modified electrode is a promising sensor for use in electroanalysis of DA.

KEY WORDS: Diazonium, *p*-Nitroaniline, Gold nanoparticles, Dopamine, Ascorbic acid, Glassy carbon electrode

INTRODUCTION

Dopamine (DA) is a naturally occurring catecholamine that plays crucial role in the function of cardiovascular, central nervous, renal and hormonal systems and its anomalous concentration cause numerous problems like Parkinson's disease, neurological disorder, drug addiction and Schizophrenia [1-7]. Therefore, searching an appropriate method for sensitive determination of DA is of great importance in the biological diagnosis. Different pervious works have been reported for determination of DA. To mention some of them: chromatography [8, 9], spectrophotometry [10-12], fluorescence [13], chemiluminescence [14, 15], and electroanalysis [1-6, 16-19]. Electrochemical techniques have attracted great concern over other analytical methods as the analysis is fast, low in cost, high accuracy and low detection limit [1-7, 20]. However, electrochemical determination of DA has the challenge of eliminating interfering substances (such as ascorbic acid, uric acid and so on) that exist together with DA in biological fluids. Since these interfering molecules are electroactive and their redox reactions take place at similar potentials to that of DA at unmodified electrodes, results in overlapping of voltammetric response and thus poor selectivity [21-23]. As a result, modification of the electrode surface with suitable modifier is the interest of research in electroanalysis to improve sensitivity and selectivity.

DA at the physiological pH exists in its cationic form [1, 24]. Based on this property, to detect DA selectively in the presence of other electroactive ionic species different methods have been developed [25, 26]. Modification of the working electrode with substances like: metal and metal oxide nanoparticles [6, 27], carbon based materials [2, 5, 28], quantum dots (QDs) [3],

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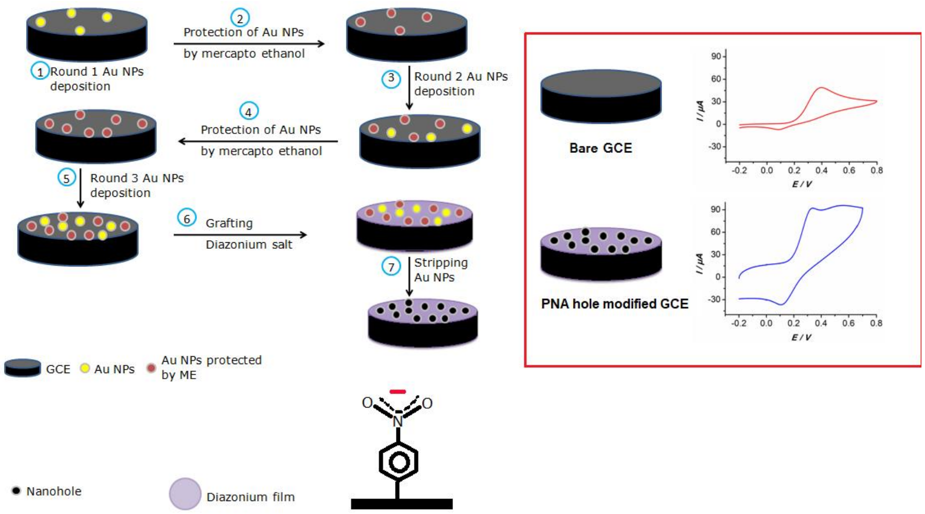
*Corresponding author. E-mail: tesfaye.refera@ju.edu.et polypyrrole [4, 29], and nanocomposite [30-33] showed very promising applications in the fabrication of biosensors for sensitive and selective detection of DA. To enhance the electrochemical signal for DA many of the sensors have used the catalytic properties of the modifiers. The modifiers also showed catalytic properties toward interferents for DA for example ascorbic acid (AA) and uric acid (UA), which would affect the detection of DA.

DA (pK_a = 8.87) exists in its cationic form whereas AA (pK_a = 4.10) exists in its anionic form at physiological pH 7.4 [1], it could be possible to differentiate the two species using electrochemically charged electrode. Since *p*-nitroaniline (PNA) film modified glassy carbon electrode (GCE) surface exists in anionic form, attractive electrostatic interactions can occur with the positively charged DA. Interference from AA can be excluded from the electrode surface through electrostatic repulsion with the negatively charged electrode surface at physiological pH. Thus, PNA film-hole modified GCE based sensor could be a promising tool for sensitive and selective detection of DA.

In this work, the working electrode from GCE was modified with electronucleated Au NPs and passivated with grafted diazonium film obtained from *p*-nitroaniline (PNA). Holes were formed by stripping the pre-nucleated Au NPs on the electrodeposited film (Scheme 1). We have demonstrated the improvement in sensitivity and selectivity for determination of DA using the electrode surface modification method.



Scheme 1. Schematic representation of the electrode modification strategy employed.

EXPERIMENTAL

Chemicals

Potassium teterachloroaurate [99.99%, Aldrich], sodium nitrite [96%, Wardle], potassium hexacyanoferrate [99%, BDH Laboratory], hydrochloric acid, [37%, Riedel-De Haen], sulfuric acid, [98%, Riedel-De Haen], 2-mercaptoethanol [100% Aldrich], *p*-nitroaniline [99%, Kiran], hydroquinone [99%, Kiran], hexamine ruthenium(III) chloride [98%, Aldrich], potassium dihydrogen phosphate [99%, Nice], potassium hydrogen phosphate [98 %, FINKEM], potassium chloride [99%, FINKEM], dopaminehydrochloride injection [Chandra Bhagat

Pharma] were of analytical grade reagents and used as received. Distilled water was used throughout the experiment to prepare aqueous solutions.

Instrumentation

In this study, BASi Epsilion EC-Version 1.40.67 voltammetric analyzer (Bio-analytical Systems, USA) controlled with the Basic epsilon software version was used to run cyclic voltammetry (CV) and amperometric experiments. The electrochemical cell consists of a three-electrode setup: GCE (3 mm diameter, BASi MF 2012) as working electrode, a platinum wire as a counter electrode (BASi, MW 1032) and an Ag/AgCl electrode (BASi, MF 2079) as a reference electrode. All potentials were reported with respect to this reference electrode. For stirring the electrolytes in the cell, a small magnetic bar was used in BASi C3 Cell stand at 500 rms.

Electrode preparation

The bare GCE was polished preceding the electrode modification procedure. First it was polished with a polishing paper. Then, it was further polished to a mirror finishing with alumina slurries (0.3 µm, BASi) and rinsed carefully with distilled water. The procedure reported by Soreta *et al.* [34, 35] was used for electrochemical conditioning of the electrodes used.

Fabrication of the PNA film-hole modified GCE

Fabrication of the PNA film-hole modified electrode was undertaken in several steps. The fabrication procedure is almost the same to that of the report by Olana *et al.* [35] except the *p*-phenyldiamine film was replaced by the PNA film. Briefly, the major steps were sequential electronucleation of gold nano particles (AuNPs) on GCE (three rounds), grafting of diazonium film from PNA on GCE modified with AuNPs and stripping of the nucleated AuNPs (Scheme 1).

Electrodeposition of AuNPs

Sequential electronucleation of AuNPs on GCE was carried out following the procedure reported by Soreta *et al.* [36] Three sequential electronucleation steps were used to increase the number density of the nucleated AuNPs on a GCE surface while preventing the growth of the already nucleated particles so that they remain in nano size range.

Grafting of diazonium film generated from PNA (modifier film)

The AuNPs modified GCE was covered with the *in situ* prepared PNA diazonium based on the literature information [37]. Briefly, 100 mL of 3 mmol L^{-1} PNA in 0.5 mol L^{-1} HCl and 10 mL of 0.1 mol L^{-1} $NaNO_2$ were kept separately in an ice jacketed beaker for 1 h. Then 400 µL of 0.1 mol L^{-1} $NaNO_2$ was added to 20 mL of 3 mmol L^{-1} PNA in 0.5 mol L^{-1} HCl under stirring at room temperature and CV was used to graft nitrophenyl film on AuNPs nucleated GCE from potential window of 0.0 V to -0.8 V at a scan rate of 0.1 Vs^{-1} for 3 cycles. It has been reported that the aryldiazonium film can be grafted both on the carbon and gold particles surfaces [38].

Electrochemical formation of random hole on the modifier film

This procedure is similar to what we have reported before [35] on *p*-phenyldiamine film. First, AuNPs were pre-electronuclated in three rounds as described in before. Then, the modifier film was grafted on the GCE as described before. Finally, the deposited AuNPs were stripped off by running three cycles CV in a potential range of 0 to 1400 mV in 0.1 mol L^{-1} KCl. This step is used to create holes (in nanometer diameter size) on the modifier film electrode. The size of the holes formed presumably equals the size of the nanoparticles that was pre-deposited on the surface of the GCE. The as such prepared modified electrode is refers to as PNA film-hole modified GCE.

Fabrication of the PNA film modified GCE

This modified electrode is different from the PNA film-hole modified electrode. The main difference is that AuNPs were not deposited on the polished and electrochemically conditioned GCE and hence there is no AuNPs striping step. This electrode is prepared just by grafting the *in situ* prepared PNA diazonium on the bare GCE surface by running CV within potential window of 0.0 V to -0.8 V at a scan rate of 0.1 V/s for 3 cycles.

Electrochemical characterization of the modified GCEs

The prepared modified electrodes were electrochemically characterized by CV using common redox probes: hydroquinone (HQ), hexamine ruthenium chloride ($Ru(NH_3)_6Cl_3$) and potassium hexacyanoferrate ($K_3[Fe(CN)_6]$). The selection of the redox probes was based on criteria where the HQ to represent molecular probes, while the $Ru(NH_3)_6Cl_3$ to represent cationic probes and $K_3[Fe(CN)_6]$ to represent anionic probes in aqueous solution. The voltammetric signals of these probes at the modified GCEs were compared to the signals of the bare GCE.

Preparation of DA solutions

DA solution (2 mmol L^{-1}) was prepared in 0.1 mol L^{-1} PBS (pH 7.5) and other dilute standard solutions of DA were prepared by appropriate dilution of stock solutions in PBS (pH 7.5).

Preparation of solutions of interferents

For interference study, solutions of 0.2 mol L^{-1} each of ascorbic acid (AA), uric acid (UA), citric acid (CA), glucose (GLU) and tartaric acid (TA) were prepared in 0.1 mol L^{-1} PBS (pH 7.5). Interference study was done amperometrically at 0.25 V at the PNA film-hole modified GCE.

Study of the effect of pH on oxidation of DA

Effect of pH of the supporting electrolyte (buffer) on oxidation of DA was studied with the range of 2 to 9. Citrate buffer of 0.1 mol L^{-1} was used to study effect of pH within the range of 2 to 4, acetate buffer of 0.1 mol L^{-1} was used within range of 4.5 to 6 and PBS 0.1 mol L^{-1} was used within the ranges of 6.5 to 9.

RESULTS AND DISCUSSION

Grafting PNA film onto a GCE

PNA film was grafted on bare GCE from *in situ* generated diazonium and characterized electrochemically using the three redox probes. Figure 1A shows CV of the PNA film grafted onto a bare GCE. A broad, irreversible cathodic peak was observed in the first scan. The reduction peak current decreased in the subsequent scans, indicating monolayer coverage of PNA films on the electrodes surface.

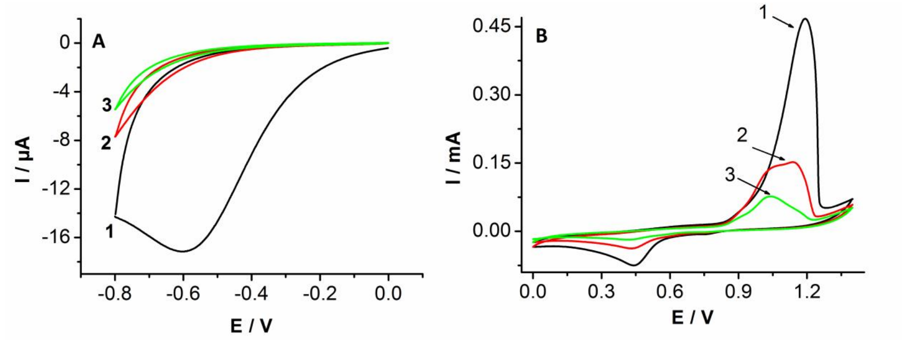


Figure 1. (A) CVs of grafting of a diazonium film from 3 mmol L^{-1} *p*-nitroaniline on bare GCE; (B) CVs for the stripping of electroneucleated AuNPs from a GCE surface in 0.1 mol L^{-1} KCl for 3 cycles (1, 2, 3 represent first, second and third cycles); scan rate 100 mVs^{-1}.

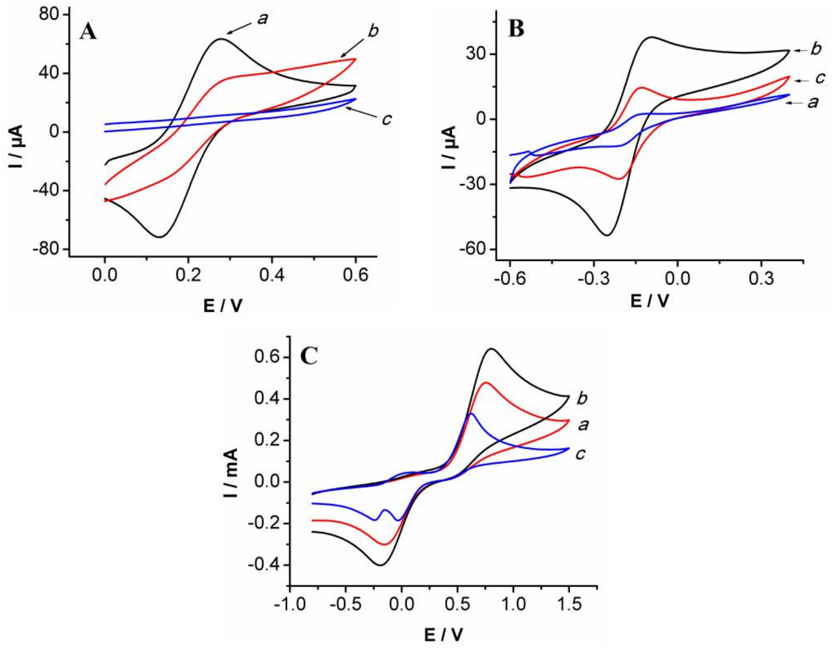


Figure 2. CV of 10 mmol L^{-1} Fe(CN)$_6^{3-}$ in 0.1 mol L^{-1} KCl (A), 10 mmol L^{-1} Ru(NH$_3$)$_6^{3+}$ in 0.1 mol L^{-1} KNO$_3$ (B) and 10 mmol L^{-1} HQ in 0.1 mol L^{-1} NaClO$_4$ (C) at (a) bare GCE, (b) PNA film-hole modified GCE and (c) PNA film modified GCE; scan rate 50 mVs^{-1}.

Electronucleation of AuNPs and stripping of the particles

Following the procedure reported by Soreta *et al.* [36] AuNPs were electronucleated sequentially in three rounds on bare GCE. Linear voltammetric scan from 1.4 to 0 V in 0.5 mol

L^{-1} H_2SO_4 was run to confirm the nucleation of AuNPs. The characteristic gold oxide reduction peak appeared at 0.97 V to confirm the deposition of gold on the GCE. After three rounds of AuNPs electronucleation, the electrode was passivated by electro-grafting *in situ* produced diazonium from PNA. Pores on the modifier film were deliberately created [34] by stripping the deposited AuNPs by running three CV scans in the potential range of 0 to 1400 mV in 0.1 mol L^{-1} KCl (Figure 1B). As shown in Figure 1B, the magnitude of the oxidation peak current (for gold stripping) decreases in subsequent cycles indicating removal of the deposited AuNPs. Due to the presence of excess chloride in the solution, the stripping of electronucleated gold by electro-oxidation is encouraged as the stripped gold forms its water-soluble chlorocomplex [35].

Electrochemical characterization of the modified GCEs

CV of $Fe(CN)_6^{3-}$

The CV of $Fe(CN)_6^{3-}$ at modified and bare GCE is shown in Figure 2A. The redox peak of $Fe(CN)_6^{3-}$ significantly suppressed at PNA film-hole modified GCE (Figure 2A, b) relative to the bare GCE (Figure 2A, a). This is due to repulsion effect between negatively charged PNA film and negatively charged $Fe(CN)_6^{3-}$. At PNA film modified GCE redox peak of $Fe(CN)_6^{3-}$ totally suppressed because GCE is insulated by PNA film (Figure 2A, c).

CV of $Ru(NH_3)_6^{3+}$

The CV of $Ru(NH_3)_6^{3+}$ at modified and bare GCEs is illustrated in Figure 2B. Redox peak of $Ru(NH_3)_6^{3+}$ enhanced at PNA film modified GCE (Figure 2B, c) relative to that of the bare GCE (Figure 2B, a); which could be associated with the effect of negatively charged nitro film towards the cationic probe. Comparing the redox peak currents of $Ru(NH_3)_6^{3+}$ at PNA film-hole modified GCE (Figure 2B, b) to that of PNA film modified GCE (Figure 2B, c), it was found to be higher in the former case. The following conclusions were drawn based on the observations. The $Ru(NH_3)_6^{3+}$ approached the negatively charged electrode surface not only by diffusion but also by electrostatic interaction between the negatively charged PNA film and the positively charged $Ru(NH_3)_6^{3+}$. The presence of holes on the PNA film hole modified GCE have further enhanced the $Ru(NH_3)_6^{3+}$ signal due to change in diffusion mode of the cationic redox probes towards nanoelectrodes. The change in the mode of transport of ions at the hole modified film electrode could be from planar to three dimensional diffusion [35].

This study indicated that the modified PNA film was negatively charged and repelled $Fe(CN)_6^{3-}$ but strongly attracted the $Ru(NH_3)_6^{3+}$ probe. Therefore, we decided to utilize this surface interaction behaviour to develop PNA film hole modified electrode for electro-analysis of the positively charged DA at physiological pH. Because it was observed that the signal of the cationic probe significantly enhanced while anionic probe suppressed, the selectivity for cationic analyte could be improved in the presence of anionic interferents.

CV of HQ

Figure 2C shows CV of HQ at PNA film-hole modified, PNA film modified and bare GCE. HQ is a neutral redox probe and its electrochemical response is not affected by both positive and negative charged films formed on the electrodes [35]. But at PNA film-hole modified GCE, the redox peaks were enhanced (Figure 2C, b) relative to bare and PNA film modified GCE due to 3D diffusion to modified electrode. On the contrary at PNA film modified GCE, its redox peak suppressed (Figure 2C, c) because PNA film formed on electrode reduces active areas of the electrode.

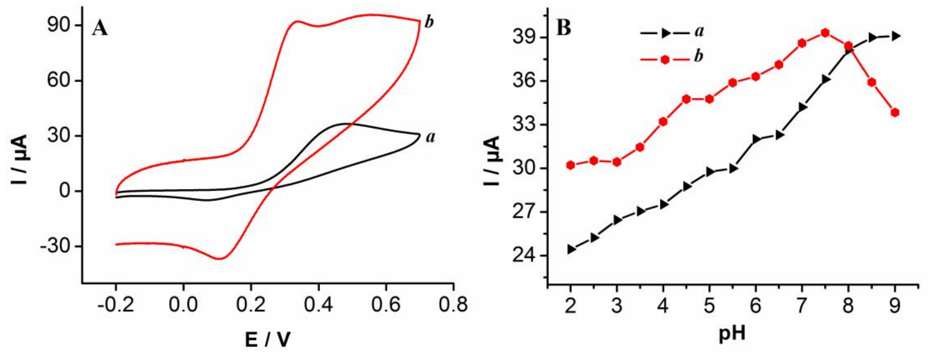
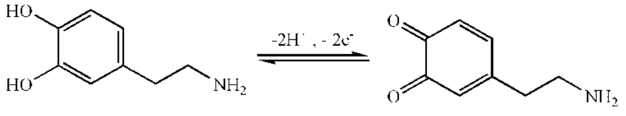


Figure 3. (A) CVs of 2 mmol L^{-1} DA in 0.1 mol L^{-1} PBS (pH 7.5) and (B) plot of oxidation peak current of 2 mmol L^{-1} DA vs pH at (a) bare GCE and (b) PNA film-hole modified GCE, scan rate: 100 mVs^{-1}.

CV of DA

Figure 3A depicts the CV curves of DA at the PNA film-hole modified GCE and the bare GCE. The electrochemical oxidation of DA is depicted in Scheme 2 [3]. The oxidation peak current of DA enhanced and shifted to a lower potential at PNA film-hole modified GCE relative to at bare GCE, which is attributed to 3D diffusion of ions toward the modified electrode and electrostatic interaction between positively charged DA and negatively charged PNA film. Therefore, PNA film-hole modified GCE was used for electroanalysis of DA. From the voltammograms, the oxidation potential of DA is 0.5 V and 0.3 V at bare and PNA film-hole modified GCE, respectively. These potentials were selected for the amperometric determination of DA at the studied electrodes.



Scheme 2. The two protons, two-electron redox process of DA.

Effect of pH on oxidation of DA

The pH of the electrolyte is one of the important parameters that could influence the response of the electrode in the analysis of DA. Effect of pH of the supporting electrolyte (buffer) on oxidation of DA was studied in the range of 2 to 9. As shown in Figure 3B oxidation peak current of DA increase from low to high pH; which shows oxidation of DA is favorable at high pH than at low pH due to proton transfer involved in oxidation of DA [39]. Therefore, 0.1 mol L^{-1} PBS of pH 7.5 was used as supporting electrolyte for electroanalysis of DA in this study.

Amperometric response of DA

Figure 4 displays amperometric response of DA at bare GCE and PNA film-hole modified GCE. Amperometric measurement was carried out through successive addition of DA into a continuously stirred 0.1 mol L^{-1} PBS (pH 7.5) at applied potential of 0.5 V and 0.3 V at bare and PNA film-hole modified GCE, respectively. A linear relationship between oxidation peak current and concentration of DA was observed in the range from 2.0×10^{-4} to 2.2×10^{-3} mol L^{-1} and 5×10^{-6} to 3.5×10^{-5} mol L^{-1} with a coefficient of 0.998 and 0.999 at bare and PNA film-hole modified GCE, respectively, demonstrating good relationship between oxidation peak current and concentration. The limit of detection (LOD) at bare and at PNA film-hole modified GCE were 0.015 mmol L^{-1} and 0.61 µmol L^{-1}, respectively. The current values were the average of three measurements for each concentration. These experimental results show that PNA film-hole modified GCE has potential application as a good electrochemical sensor for the determination of DA.

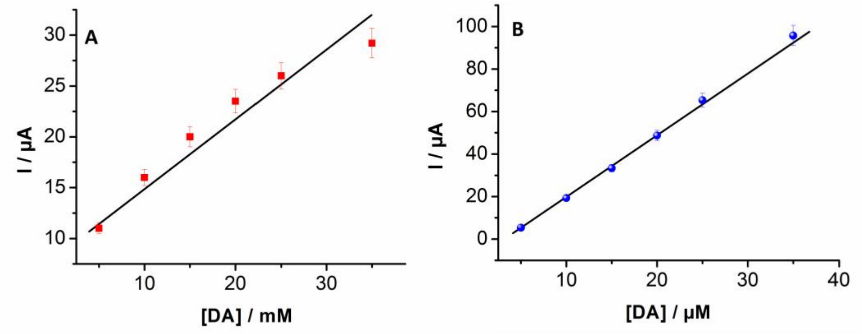


Figure 4. Calibration curve of amperometric response of DA at (A) bare GCE at 0.5 V and (B) PNA film-hole modified GCEs at 0.3 V.

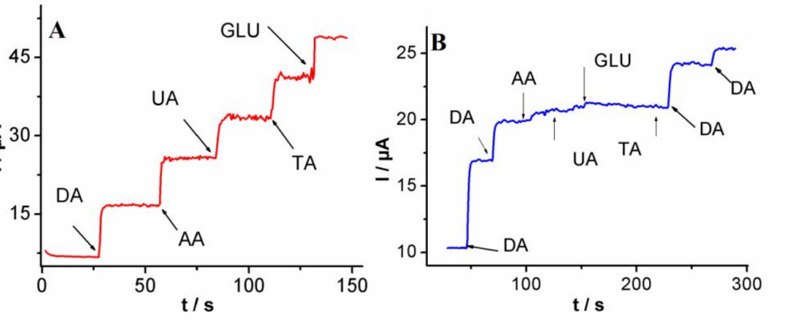


Figure 5. Amperometric responses of (A) 1 mmol L^{-1} DA and interfering species at bare GCE at 0.5 V and (B) 1 mmol L^{-1} DA and 200-fold excesses of interfering species at PNA film-holes modified GCE at 0.3 V.

Interferent study

The major sources of interference in DA determination are common coexisting species in biological fluids which lead to overlap with redox peak current of dopamine. The effect of ascorbic acid (AA), uric acid (UA), glucose (GLU) and tartaric acid (TA) on the amperometric peak response of 1 mmol L^{-1} of DA was examined (Figure 5). At bare GCE, 1 mmol L^{-1} of each of these interferents found to give amperometric response the same as 1 mmol L^{-1} DA but it was observed that 200-fold concentrations of these interferents found to have no major influence on the amperometric peak response of 1 mmol L^{-1} DA at PNA film-hole modified GCE. This is due to attraction of DA and repulsion of negative substance by the PNA film.

Stability and reproducibility of PNA film-hole modified GCE

Five PNA film-hole modified GCEs were fabricated in different days under the same preparing conditions and the peak current of 2 mmol L^{-1} DA was measured at each electrodes. The relative standard deviation of peak current of these result was 5.3% (n = 5), showing good reproducibility of the PNA film-hole modified GCE. PNA film-hole modified GCE was prepared according to the optimized condition and stored in 0.1 mmol L^{-1} PBS (pH 7.5) solution and the stability of modified electrode was tested on 28 days at 2 mmol L^{-1} DA; the peak current of DA retained 97% of its initial current response. The result showed that PNA film-hole modified GCE has a good stability and long life.

Table 1. Comparison of the analytical performance of the proposed dopamine sensor with previously reported dopamine sensors.

Sensor	Method	LOD (µM)	Ref
Co(II) complex and multi-walled carbon nanotubes modified GCE	Amp	1.76	[5]
Ni-doped V_2O_5 nanoplates modified GCE	Amp	0.028	[6]
AuNPs tryptophan-grapheme modified GCE	DPV	0.056	[7]
Carbon nanotubes/alizarin red S–poly(vinylferrocene) modified GCE	DPV	0.2	[20]
Carbon nanotubes/alizarin red S–poly(vinylferrocene) modified GCE	Amp	2.5	[20]
Reduced graphene oxide - palladium nanoparticles composite modified GCE	LSV	0.233	[33]
Au-NPs/polyaniline modified GCE	Amp	0.8	[40]
Graphene-bismuth nanocomposite film modified GCE	Amp	0.35	[32]
Multi-wall carbon nanotubes modified GCE	DPV	0.67	[41]
Graphene-AuNPs modified GCE	DPV	1.86	[42]
Graphene modified GCE	DPV	2.64	[43]
p-Nitroaniline film-holes modified GCE	Amp	0.611	This work

LSV – linear sweep voltammetry, DPV – differential pulse voltammetry, Amp – Amperometry.

The proposed sensor is selective and sensitive for DA detection when compared with other techniques (Table 1) by excluding anionic impurities from the electrode surface through electrostatic repulsion. Significantly lower detection limits were achieved with these modified electrodes that could be used as sensitive amperometric detector for lower concentration detection of DA.

CONCLUSION

In this work fabrication of PNA film-hole modified GCE and its electrochemical characterization was studied. Application of the modified electrode was demonstrated with amperometric determination of DA. The PNA film-hole modified GCE was found to have good characteristics for selective determination of DA. The electrode modification strategy used here could be used as a means of selective determination of other cationic electroactive substances where the anionic species may interfere.

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