Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 80 (9) 1161–1175 (2015)
JSCS–4788
UDC 547.475.2+543.55+544.6.076.32–033.5–039.6
Original scientific paper

Electrochemical determination of ascorbic acid at *p*-phenylenediamine film–holes modified glassy carbon electrodes

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(Received 4 November, revised 30 December 2014, accepted 19 January 2015)

Abstract: In this work, the determination of ascorbic acid (AA) at a glassy carbon electrode (GCE) modified with a perforated film produced by reduction of diazonium generated *in situ* from *p*-phenylenediamine (PD) is reported. Holes were intentionally created in the modifier film by stripping pre-deposited gold nanoparticles. The modified electrodes were electrochemically characterized using common redox probes: hydroquinone, ferrocyanide and hexaminеruthenium(III). The cyclic voltammetric and amperometric responses of AA using the modified electrodes were compared with those of a bare GCE. The bare GCE showed a linear response to AA in the concentration range of 5 mM to 45 mM with detection limit of 1.656 mM and the modified GCE showed a linear response to AA in the concentration range from 5 to 45 μM with detection limit of 0.123 μM. The effects of potential interferents on amperometric signal of AA at the modified GCE were examined and found to be minimal. The inter-electrode reproducibility, stability, and accuracy were determined. The modified electrode showed excellent inter-electrode reproducibility, accuracy and stability. The modified electrode reported is a promising candidate for use in the electro-analysis of AA.

Keywords: diazonium; *p*-phenyldiamine; gold nanoparticles; ascorbic acid; glassy carbon electrode.

INTRODUCTION

Ascorbic acid (AA) naturally occurs in a wide number of foods, such as fruits and vegetables. It is a water-soluble organic compound involved in many biological processes. It is known for its reductive properties that make it useful as an antioxidant agent in foods and drinks. Moreover, pharmaceuticals often contain AA as a supplementary source to human diets as a free-radical scavenger. It

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doi: 10.2298/JSC141104006O

has been used for the prevention and treatment of the common cold, mental illness, scurvy and cancer.[1] However, the intake of excess AA can lead to undesirable health effects, such as gastric irritation, excessive oxidative stress, diabetes mellitus, liver disease[2] and renal problems.[3] Excessive quantities of AA in food may result in the inhibition of the occurrence of natural processes and hence may contribute to taste deterioration.[4]

AA is a labile substance that easily degrades due to interaction with enzymes and atmospheric oxygen. Excessive heat, exposure to light, and interaction with heavy metal cations can accelerate the oxidation of AA.[5] Due to its susceptibility to oxidation, the analysis of the level of AA in foodstuffs and beverages helps to indicate their quality. Hence, the level of AA has to be carefully monitored to estimate the relative variation of AA from manufacture, storage up to consumption. For this reason, there is a necessity for an easy-to-use, inexpensive method for the detection of AA in food, beverages and pharmaceuticals.[6]

Many analytical methods have been reported in the literature for the determination of AA.[7,8] Electrochemical techniques are known to offer some benefits such as fast analysis, low cost, higher sensitivity and accuracy. However, the major problem frequently encountered in the electro-analysis of AA is the effect of interferents caused by substances with similar redox potentials at conventional electrodes, which results in poor selectivity. In the presence of co-existing oxidizable species, the determined amount of vitamin C could be overestimated.[9–12] Thus, it is difficult to detect specifically one substance in the presence of others substances in real biological samples at conventional electrodes. AA exists in the anionic form at physiological pH values. Based on this property; different techniques were developed to detect AA selectively. Modification of the working electrode with modifiers such as tetrabromo-*p*-benzoquinone,[13] electronically conductive anion exchange polymers based on polypyrrole[14] and polyaniline[15] showed promising applications in the fabrication of sensors for sensitive and selective detection of AA.

The most distinguishing feature of chemically modified electrodes is their modification by a selected substance that is coated onto the electrode surface thereby imparting certain desirable properties to the electrode. The use of nanomaterials for nanostructuring of an electrode surface has aroused the interest of analysts[16] because nanostructured materials can be tailored to improve the selectivity and sensitivity of sensors. Further investigation of these new materials in the fabrication chemically modified electrodes is required to exploit the systems.

In this work, a glassy carbon working electrode was modified with electronucleated gold nanoparticles and passivated with an organic film by grafting diazonium obtained from *p*-phenylenediamine. Holes were formed on the electrodeposited film by stripping the nucleated gold nanoparticles. Improvement in the

selectivity and sensitivity of the electrode surface modified using the developed method for the determination of AA was demonstrated.

EXPERIMENTAL

Chemicals

Ascorbic acid (99 %, Finkem), *p*-phenylenediamine (100 %, Aldrich), sodium nitrite (96 %, Wardle), potassium nitrate (99 %, Nice), potassium teterachloroaurate (99.99 %, Aldrich), 2-mercaptoethanol (100 %, Aldrich), hydrochloric acid, (37 %, Riedel-de Haen), sulfuric acid, (98 %, Merck), hydroquinone (99 %, KIRAN), potassium hexacyanoferrate(III) (97 %, Labmerk Chemicals), hexamineruthenium chloride(III), (98 %, Aldrich), potassium iodide (99 %, Nice), iodine resublimed (99.5 %, Nice), potassium chloride (99 %, Finkem), sodium citrate dihydrate (99 %, Finkem), citric acid (99 %, Wardle), sodium acetate trihydrate (99.8 %, Chem. Rein), glacial acetic acid (100 %, BDH Laboratory), potassium hydrogen phosphate (98 %, Finkem) and potassium dihydrogen phosphate (99 %, Nice) were of analytical grade and used as received. The vitamin C tablet 500 mg [Batch number 11202023, Ethiopian Pharmaceuticals] was purchased from a local drug store. Double distilled water was used to prepare all solutions.

Instrumentation

Cyclic voltammetry (CV) and amperometric experiments were performed using BASi Epsilion EC-Version 1.40.67 voltammetric analyzer (Bio-analytical Systems, USA) controlled with basic epsilon software. A conventional three-electrode setup was used with a glassy carbon electrode (3 mm diameter, BASi, MF 2012) as the working electrode and a platinum wire counter electrode (BASi, MW 1032). An Ag/AgCl electrode (BASi, MF 2079) served as the 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 the BASi C3 Cell stand at 500 rpm.

Methods

Electrode preparation. Prior to electrode modification, a bare glassy carbon electrode (GCE) was polished with polishing paper and then further polished to a mirror finish with alumina slurries (0.3 micron, BASi) and rinsed thoroughly with distilled water. The procedure reported by Soreta *et al.*[17] was used for electrochemical conditioning of the employed electrodes.

Fabrication of PD film–hole modified GCE. PD represents the aryldiazonium generated from *p*-phenylenediamine. Fabrication of the PD film–hole modified electrode was undertaken in several steps. The major steps were sequential electronucleation of gold nanoparticles (AuNPs) on the GCE (three rounds), grafting of a diazonium film from *p*-phenyldiamine (PD) on a GCE modified with AuNPs and stripping of the nucleated AuNPs.

i. Electrodeposition of AuNPs. Sequential electronucleation of gold nanoparticles on a GCE was performed following the procedure reported by Soreta *et al.*[18] Sequential electronucleation was used to increase the number of gold nanoparticles deposited on the GCE surface while preventing the growth of the already nucleated particles so that they remain in the nano-size range.

ii. Grafting of diazonium film generated from p*-phenylenediamine (modifier film).* The AuNPs-modified GCE was covered with *in situ* generated *p*-phenylenediamine diazonium cations based on literature information.[19,20] Briefly, 5 mL solution of 3 mmol L^{-1} *p*-phenylenediamine in 0.5 mol L^{-1} HCl and 5 mL of 3 mmol L^{-1} sodium nitrite in 0.5 mol L^{-1} HCl

were kept separately in an ice jacketed beaker for 1 h. Then, 2 mL of the $NaNO_2$ solution was added to 2 mL of the *p*-phenylenediamine solution under stirring at room temperature and CV was used to graft the phenylenediamine film onto the AuNPs nucleated GCE within potential window from 0.6 to –0.2 V at a scan rate of 0.1 V s^{-1} for 3 cycles. It was reported that an aryldiazonium film could be grafted on both carbon and gold particles surfaces.[21]

iii. Electrochemical formation of random holes on the modifier film. This is the only new step introduced in the fabrication of the modified electrode. After the modifier film had been grafted on the GCE on which gold nanoparticles were electronuclated in three rounds, the deposited AuNPs were stripped off by running three CV scans in the potential range of 0 to 1400 mV in 0.1 mol L^{-1} KCl. This step is used to create holes (could be in the nanometer diameter size) on the modifier film electrode. The size of the formed holes presumably reflected the size of the nanoparticle that was deposited on the surface of the GCE. An as such prepared modified electrode is refers to as a PD film–hole modified GCE.

Fabrication of a PD film modified GCE

This modified electrode is different from the PD film–hole modified electrode. The main difference is that gold nanoparticles were not deposited on the polished and electrochemically conditioned GCE and hence there was no AuNPs striping step. This electrode was prepared by just grafting the *in situ* prepared diazonium cation from *p*-phenylenediamine onto the bare GCE surface by running CV within a potential window from 0.6 to –0.2 V at a scan rate of 0.1 V s^{-1} for three scans.

Electrochemical characterization of the modified GCEs

The prepared modified electrodes were electrochemically characterized by CV using common redox probes: hydroquinone, hexamineruthenium chloride $Ru(NH_3)_6Cl_3$ and ferrocyanide $K_3Fe(CN)_6$. The selection of the redox probes was intentional so that hydroquinone represented molecular probes, while hexamineruthenium chloride $Ru(NH_3)_6Cl_3$ represented cationic probes and ferrocyanide $K_3Fe(CN)_6$ anionic probes in aqueous solution. The voltammetric signals of these probes at the modified GCEs were compared to the signals of those of the bare GCE.

Preparation of AA solutions

A 2 mmol L^{-1} stock solution of AA was prepared in 0.1 mol L^{-1} acetate buffer solution (pH 5) and AA solutions of other concentrations were prepared by appropriate dilution of the stock solution in acetate buffer (pH 5).

Real sample solutions, preparation and analysis

For real sample analysis, orange fruit, which was obtained from a local market in Jimma, Ethiopia, and vitamin C tablets, purchased from local drug stores in Jimma, Ethiopia, were used. Fresh orange juice was obtained by squeezing orange fruit into a glass beaker. Then, after filtering the juice through a filter paper to remove the fiber and pulp, 1 mL was diluted with 5 mL of 0.1 mol L^{-1} sodium acetate buffer (pH 5). Vitamin C tablet solution was prepared according to a literature procedure.[22] Briefly a weighed tablet was crushed with a pestle and mortar, and the powder dissolved in 20 mL of distilled water and then 10 mL of 1 mol L^{-1} H_2SO_4 was added. From this solution, 9.3 mL were taken and diluted with 20 mL sodium acetate buffer. The concentration of AA in orange fruit and vitamin C tablet was determined by standard iodimetric titration. Amperometric analysis was performed three times at 0.237 V at the PD film–hole modified GCE and average results of the three measurements were taken. Concentration of AA was determined by the standard addition method.

Study of the effect of pH on the oxidation peak current of AA

Effect of pH of the supporting electrolyte (buffer) on oxidation peak current of AA was studied within range 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, 0.1 mol L^{-1} acetate buffer was used within range of 4.5 to 6 and 0.1 mol L^{-1} phosphate buffer of was used within the range 6 .5 to 8.5. Dilute NaOH or HCl were used to adjust the pH of the buffer solutions.

RESULTS AND DISCUSSION

Electrode fabrication

Grafting of a PD film onto a GCE. In situ generated diazonium from *p*-phenylenediamine was electrochemically grafted onto a GCE surface and the resulting film was electrochemically characterized using common redox probes. The CV of the PD film grafted onto a bare GCE is shown in Fig. 1A. A broad, irreversible cathodic peak was observed in the first cycle. In the subsequent scans, the reduction peak current decreases due to the insulation effect of the grafted surface film.

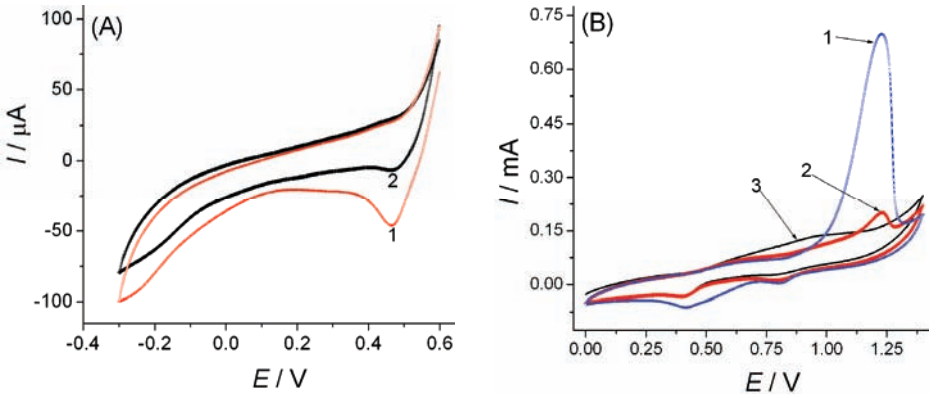

Fig. 1. A) CVs of the grafting of a diazonium film from 3 mmol L^{-1} *p*- phenylenediamine in 0.5 mol L^{-1} HCl at a bare GCE in 2 cycles (1 and 2 representing first and second cycles, respectively); B) CVs for the striping of the electronucleated gold nanoparticles from a GCE surface in 0.1 mol L^{-1} KCl in 3 cycles (1, 2 and 3 representing first, second and third cycles, respectively). In all cases, the scan rate was 100 mV s^{-1}.

Electronucleation of gold nanoparticles and stripping of the particles

Gold nanoparticles were sequentially electronucleated from a solution of 0.1 mmol L^{-1} $KAuCl_4$ in 0.5 mol L^{-1} H_2SO_4 following the procedure reported by Soreta *et al.*[18] The nucleation of gold nanoparticles was confirmed by linear a voltammetric scan from 1.4 to 0 V, when the characteristic gold oxide reduction peak appeared at 0.953 V. After three rounds of gold nanoparticles electronucleation, the electrode was passivated by electro-grafting of diazonium *in situ* generated from *p*-phenylenediamine. Pores on the modifier film were intentionally

created by stripping the deposited Au NPs by running three CV scans in the potential range of 0 to 1400 mV in 0.1 mol L^{-1} KCl (Fig. 1B). As depicted Fig. 1B, the anodic peaks at around 1.2 V, associated with gold stripping, decreased as the number of scans increases. The gold was stripped by electro-oxidation due to the presence of excess chloride that encourages the oxidation of gold to form its water-soluble chlorocomplex.

Electrochemical characterization of the modified GCEs

CV of hydroquinone (HQ). The CV of HQ at the bare GCE and at the PD film–hole modified GCE are depicted in Fig. 2, curves a and b, respectively. The anodic peak currents are comparable for the two electrodes except the peak current was slightly higher and the peak potential slightly shifted anodically at the modified electrode. When the voltammogram of hydroquinone on the PD film modified GCE (Fig. 2, curve c), was compared with the two former cases, the following differences were registered, *i.e.*, the anodic peak current was lower and shifted to a higher anodic potential. However, the modified PD–film could not prevent hydroquinone from interacting with the electrode. Hydroquinone is a molecular redox probe and diffusion of the probe towards the electrode surface was not very influenced by the surface charge of the electrodes that was developed due to the presence of modifier molecules on the GCE, *i.e.*, the modifier film does not effectively block the approach of hydroquinone to the electrode.

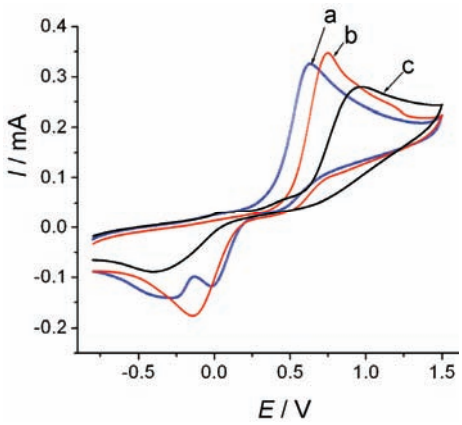

Fig. 2. CV of 10 mmol L^{-1} HQ in 0.1 mol L^{-1} $NaClO_4$ at: a) bare GCE, b) PD film–hole modified GCE and c) PD film modified GCE. The scan rate was100 mV s^{-1} in all cases.

CV of hexaminеruthenium(III)

The CVs of $Ru(NH_3)_6Cl_3$ at the bare and the modified GCEs are depicted in Fig. 3. Electrochemical response of $Ru(NH_3)_6Cl_3$ was significantly suppressed at the PD film–hole modified GCE (Fig. 3, curve c) relative to that at the bare GCE (Fig. 3, curve a). At the PD film modified GCE, redox peak of $Ru(NH_3)_6^{3+}$ was significantly diminished (Fig. 3, curve b). From the voltammograms, it was

concluded that the modified electrodes were positively charged as the signal for the cationic redox probe was significantly diminished due to its repulsion from the surface of the electrode.

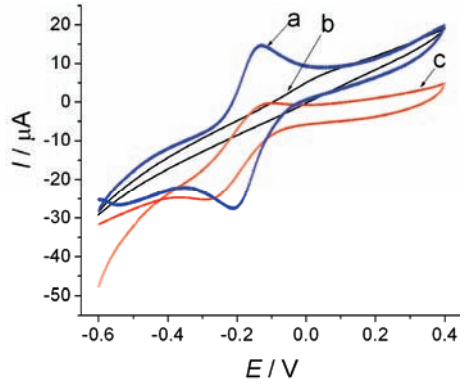

Fig. 3. CVs of 10 mmol L^{-1} $Ru(NH_3)_6Cl_3$ in 0.1 mol L^{-1} KNO_3 at: a) bare GCE, b) PD film modified GCE and c) PD film–hole modified GCE. The scan rate was 50 mV s^{-1} in all cases.

CV of hexacyanoferrate

The CVs of $K_3Fe(CN)_6$ at the modified GCEs (Fig. 4, curves a and b) were compared to that at the bare GCE (Fig. 4, curve c). The redox peaks for the modified GCEs were significantly higher than that for the bare GCE. Comparing the CV response of $K_3Fe(CN)_6$ at the PD film–hole modified GCE (Fig 4, curve a) to that at the PD film GCE (Fig 4, curve b), the redox peak current of the probe at the modified GCE was found to be higher. From this observation, it was concluded that the modification imparted a positive charge on the surface of the organic film and hence the ferrocyanide approached the electrode surface not only by diffusion, but also by electrostatic interaction between the positively charged PD film and the negatively charged ferricyanide. The presence of holes on the PD film–hole modified GCE could be responsible for the extra enhancement for the ferrocyanide signal due to the three-dimension diffusion of the anionic redox probes towards nanoelectrodes. The produced holes could change diffusion of

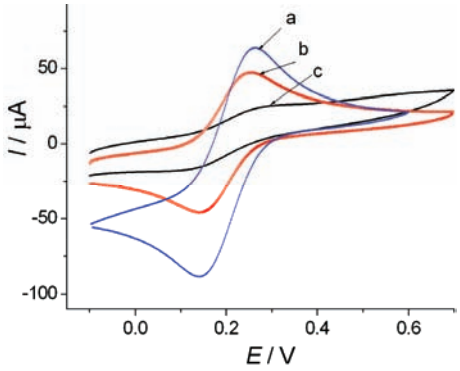

Fig. 4. CV of 10 mmol L^{-1} $K_3Fe(CN)_6$ in 0.1 mol L^{-1} KCl at: a) the PD film-hole modified GCE, b) the PD film modified GCE and c) the bare GCE. The scan rate was 50 mV s^{-1} in all cases.

ions from planar to three dimensional.[23,24] Compton and his coworkers[25] demonstrated that modifying an electrode with porous layers of a conducting material could affect voltammetric peaks because of a change in the mass-transport mode from planar diffusion to one with a thin-layer character.

The observation from the studied redox probes indicated that the modified PD–film was positively charged and repelled $Ru(NH_3)_6^{3+}$ but strongly attracted the $Fe(CN)_6^{3-}$ probe. From this, it was decided to use the modified electrode for electro-analysis of the negatively charged analyte. The advantage could be two-fold: enhancement in the signal of the analyte and improvement in the selectivity as cationic interferents would not approach the modified electrode surface. With this in mind, the PD film–hole modified GCE was used for the electro-analysis of AA.

CV of ascorbic acid (AA) at the PD film–hole modified GCE

The CV curves of AA at the bare GCE and the PD film–hole modified GCE over a wide range of potentials are depicted in Fig. 5. It is clearly presented that the oxidation peak current of AA is enhanced and shifted to a lower potential at the PD film–hole modified GCE relative to those at the bare GCE. The electro oxidation of AA at a bare GCE generally occurs at a relatively high oxidation potential, indicating a slow electron transfer rate.[26]

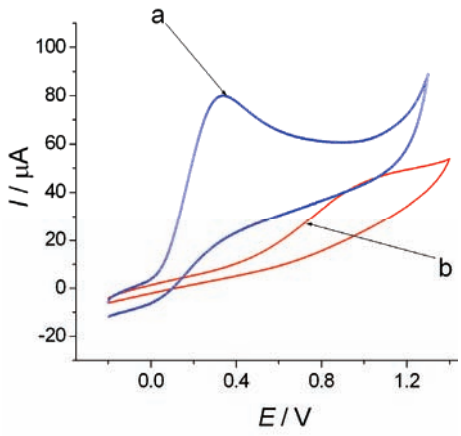

Fig. 5. CVs of 2 mmol L^{-1} AA in 0.1 mol L^{-1} acetate buffer (pH 5) at: a) PD film–hole modified GCE and b) bare GCE; in all cases scan rate 100 mV s^{-1}.

The oxidation of AA ($C_6H_8O_6$) involves a two-electron and two-proton irreversible reaction to produce dehydroascorbic acid ($C_6H_6O_6$).[27] From the voltammograms, the oxidation potential of AA is close to 0.8 and 0.237 V for bare and PD film–hole modified GCE, respectively. These potentials for were selected for the amperometric determination of AA at the studied electrodes.

Effect of the pH of the supporting electrolyte on the electro-analysis of AA

The pH of the electrolyte is one of the important parameters that could influence the response of the electrode in the analysis of AA. The pH is an important parameter that controls the surface charge of the modifier film and the state in which AA could be available in the solution. The pH of the supporting electrolyte was varied within the range of 2 to 8.5 to study the effect of pH on oxidation peak current of AA at the PD film–hole modified GCE.

Oxidation peak current of AA was found to increase as the pH was changed from pH 2 to 5 (Fig. 6, curve a). A further increase in pH of the buffer led to a decrease in the response of AA. This observation is in agreement with the proposed interaction model. In the pH range in which the modifier film can be made positive film and the AA in its anionic form, the interaction of the modified GCE surface with AA enhances the redox signal. At higher pH conditions, the film might develop a negative charge (due to adsorption free hydroxyl ions) and cause the anionic form of AA to be repelled. Thus, pH 5 is the condition that favors the formation of cationic film and anionic form of AA. Hence, a pH value of 5 was selected as optimum condition for the electro-analysis of AA at the PD film–hole modified GCE. For the sake of comparison, similar study on the effect of pH on the oxidation peak current of AA at bare GCE was conducted. The oxidation peak current for AA consistently decreased with increasing pH (Fig. 6, curve b). A comparison of the two results clearly demonstrated the difference in surface property between the modified and the unmodified GCE.

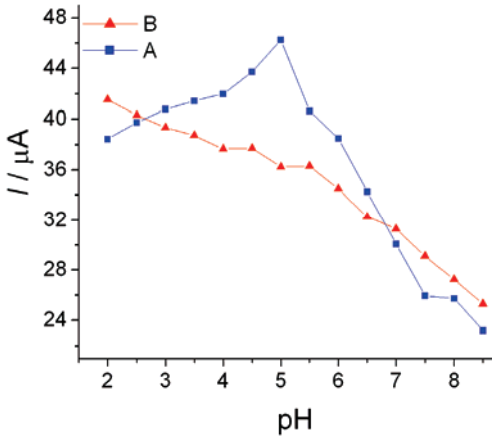

Fig. 6. Oxidation peak current of 2 mol L^{-1} AA in different pH supporting electrolytes at: a) the PD film–hole modified GCE and b) the bare GCE.

Amperometric determination of AA

In this work, amperometric measurements were performed and the results compared for the determination of AA at the two electrodes, *i.e.*, the PD film––hole modified GCE and the bare GCE. For the PD film–hole modified GCE, the

amperometric measurement was performed at 0.237 V while for bare the GCE, it was at 0.8 V (the potential at which the highest oxidation peak current was observed). The amperometric response of both the modified and the bare GCE, for successive additions of AA, increased stepwise with increasing concentration of AA in 0.1 mol L^{-1} acetate buffer (pH 5). The bare GCE showed a linear response to AA in the concentration range from 5 to 45 mmol L^{-1} with detection limit of 1.656 mmol L^{-1} and a correlation coefficient of 0.995 (Fig. 7A). The PD film–hole modified GCE showed a linear response to AA in the concentration range from 5 to 45 μmol L^{-1} with a detection limit of 0.123 μmol L^{-1} and a correlation coefficient of 0.998 (Fig. 7B). The average of three measurements for each concentration was calculated to plot the calibrations curves. The limit of detection ($LOD = 3\sigma$/slope) at the bare GCE and the PD film–hole modified GCE were 1.656 mmol L^{-1} and 0.123 μmol L^{-1}, respectively. The PD film–hole modified GCE had improved characteristics, such as, detection of a lower concentration of AA and better reproducibility of the signal for the studied concentrations. Thus, the observed attributes are encouraging for the potential application of the modified electrode as an electrochemical sensor for the determination of AA.

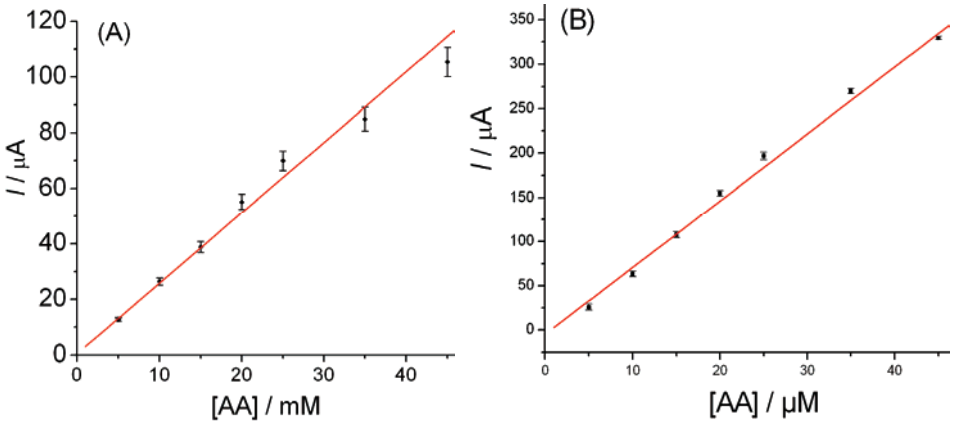

Fig. 7. Amperometric calibration curve for determination of AA in acetate buffer (pH 5) at: A) bare GCE; B) PD film–hole modified GCE.

Effect of interferents

The influence of compounds, such as caffeine (CAF), starch (STA), which could coexist in the pharmaceutical dosages, vitamin C, glucose (GLU), citric acid (CA) and tartaric acid (TA), which may co-exist in fruit juices,[28–30] and compounds such as GLU, dopamine (DA) and uric acid (UA), which co-exist in human fluid,[31] may interfere with the determination of AA. Amperometric signal for AA in the presence of the above possible interfering substances was studied at a fixed concentration of 1 mmol L^{-1} AA and 1 mmol L^{-1} each interferent at

the bare GCE at 0.8 V (Fig. 8A). For the PD film–hole modified GCE, amperemetric signal of AA in the presence of the above possible interfering substances was studied at a fixed concentration of 1 mmol L^{-1} AA and 200-fold excesses of interfering species at 0.237 V (Fig. 8B and C).

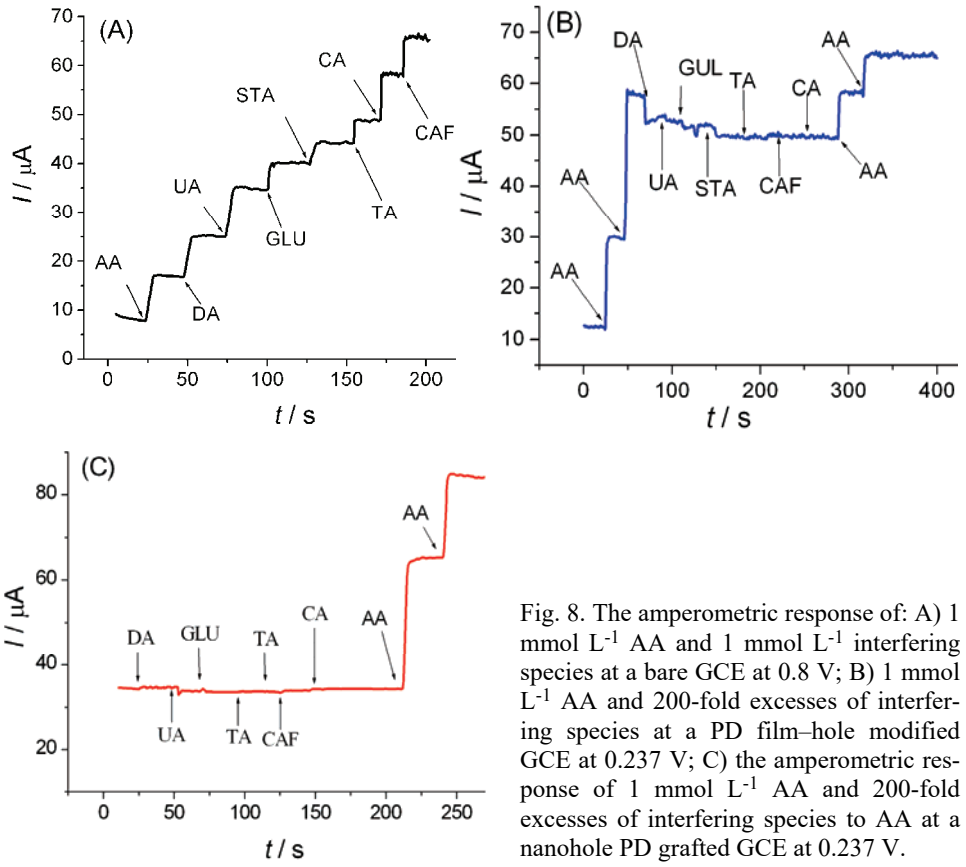

Fig. 8. The amperometric response of: A) 1 mmol L^{-1} AA and 1 mmol L^{-1} interfering species at a bare GCE at 0.8 V; B) 1 mmol L^{-1} AA and 200-fold excesses of interfering species at a PD film–hole modified GCE at 0.237 V; C) the amperometric response of 1 mmol L^{-1} AA and 200-fold excesses of interfering species to AA at a nanohole PD grafted GCE at 0.237 V.

As can be seen from Fig. 8, the influence of even very high concentrations of the studied potential interferents on the amperometric response of AA at the PD film–hole modified GCE was found to be minimal. This could be due to a lowering of the oxidation potential of AA at the modified electrode compared to at the bare GCE and the repulsion by the modifier film of species, such as DA, that are available in cationic form.

Inter-electrode reproducibility and stability tests

The inter-electrode reproducibility was investigated for PD film–hole modified GCE by preparing five electrodes under the same conditions. Amperometric measurement at 0.237 V for 2 mmol L^{-1} AA at five different electrodes, prepared

with the same electrode modification strategy, was used to estimate the reproducibility. The reproducibility expressed by the relative standard deviation was found to be 5.18 % (n = 5) for PD film–hole modified GCE, thereby showing the good reproducibility of the modified electrode.

The stability of the PD film–hole modified electrode was studied by comparing the current response of a freshly prepared PD film–hole modified GCE with the response of electrodes after storage for 28 days in 0.1 mol L^{-1} acetate buffer (pH 5) at room temperature. For 2 mmol L^{-1} AA, the modified electrodes retained 98 % of the initial current response. The result showed that the PD film––hole modified GCE has a good stability and long life.

Comparison of the PD film–hole modified GCE with previously reported methods

The detection limit of the PD film hole modified GCE is compared in Table I with those of previously reported modified electrodes. As can be seen from Table I, the electrode modification strategy reported herein resulted in an electrode with a better detection limit than most of those previously reported.

TABLE I. Comparison of the modified electrode with previously reported modified electrodes for the determination of ascorbic acid

Electrode	Detection limit μM	Ref.
Bi_2O_2 microparticles modified GCE	8.1	32
Tiron modified GCE	1.79	33
GCE modified with carbon-spheres (linear range 2–300 μM)	0.60	34
GCE modified with a nickel(II)-bis(1,10-phenanthroline) complex (linear range 10–630 μM)	4.0	35
Quaternized carbon nanotubes/ionic liquid–polyaniline composite film modified GCE (linear range 20 nM–4 μM)	0.25	36
Nitrogen doped porous carbon nanopolyhedra (linear range 80–2000 μM)	0.74	37
Graphene modified GCE (linear range 10.0–1000 μM)	1.20	38
Gold electrode modified with a flower-like gold nanostructure (linear range 60–500 μM)	10	39
Over oxidized *p*-aminophenol polymer film on GCE	1.0	40
GCE modified with poly(ethylene oxide)	50	41
Methionine modified carbon paste electrode	5.0	42
Electropolymerized aniline on GCEs	1.0	15
PD film–hole modified GCE	0.123	This work

Real sample analysis

To demonstrate the applicability of the PD film–hole modified GCE for real sample analysis, orange fruit and vitamin C tablet samples were analyzed (Table II). The bulk concentration of AA was first determined by titration. The concentration of AA obtained in orange fruit and vitamin tablet were 23.33±0.01 mg per

100 mL and 504.97±0.03 mg per tablet, respectively. Then the AA was determined by amperometry using PD film–hole modified GCE. The relative error for PD film–hole modified GCE was 0.04 % for the determination of AA in orange and 0.37 % for the determination of AA in vitamin C tablet. The data presented clearly showed that the method reported herein is accurate.

Table II Accuracy test for the modified electrode against the standard titration method

Working electrode	Concentration of AA, mean ± *SD*, *n* = 3 for each sample	
	In orange fruit, mg/100mL	In vitamin C tablet, mg/tablet
PD film–hole modified GCE	23.34±0.17	506.87±0.39
Standard titration method	23.33±0.01	504.97±0.03

CONCLUSIONS

In this work, the fabrication and electrochemical characterization of PD film–hole modified GCE was reported. The modified GCE was demonstrated for the amperometric determination of AA. The PD film–hole modified GCE was found to have very good selectivity towards AA and high sensitivity for the determination of AA and could be applied in different matrices. The electrode modification strategy could be used as a means for the selective determination of anionic analytes in the presence of cationic interfering species. Further study is required to understand fully the reported surface modification strategy and to explore different modifying films and other important analytes.

Acknowledgements. We would like to acknowledge the Department of Chemistry, Jimma University, Ethiopia, for providing the laboratory facilities. Financial support from Jimma University School of Graduate Studies is also acknowledged.

ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ОДРЕЂИВАЊЕ АСКОРБИНСКЕ КИСЕЛИНЕ НА ЕЛЕКТРОДИ ОД СТАКЛАСТОГ УГЉЕНИКА МОДИФИКОВАНОЈ ПЕРФОРИРАНИМ ФИЛМОМ *p*-ФЕНИЛЕНДИАМИНА

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У раду је приказано одређивање аскорбинске киселине (АА) на електроди од стакластог угљеника која је модификована перфорираним филмом формираним редукцијом диазонијум јона генерисаним *in situ* из *p*-фенилендиамина. Перфорације филма постигнуте су растварањем претходно исталожених наночестица злата. Модификоване електроде су електрохемијски карактерисане коришћењем уобичајених редокс реакција хидрохинона, јона гвожђе(II)-цијанида и јона рутенијум(II)-хексамина. Струје оксидације АА одређене цикличном волтаметријом и хроноамперометријом на модификованим електродама су упоређене са струјама на немодификованој електроди од стакластог угљеника. Немодификована електрода је показала линеаран одговор у опсегу концентрација АА од 5 до 45 mM уз границу детекције од 1,656 mM, док је модификована електрода показала линеаран одговор у опсегу концентрација АА од 5 до 45 μM уз границу детекције од 0,123 μM. На модификованој електроди је испитан утицај суп-

станци које могу да ометају амперометријски сигнал АА и нађено је да је он минималан. Такође је утврђено да су репродуктивност самих модификованих електрода, њихова стабилност и тачност одлични. Модификована електрода приказана у овом раду има потенцијалну примену за електроаналитичко одређивање АА.

(Примљено 4. новембра, ревидирано 30. децембра 2014, прихваћено 19. јануара 2015)

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