Research Article

Differential Electroanalysis of Dopamine in the Presence of a Large Excess of Ascorbic Acid at a Nickel Oxide Nanoparticle-Modified Glassy Carbon Electrode

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Electrochemical determination of dopamine (DA) in the presence of a large excess of ascorbic acid (AA) in their coexistence at a nickel oxide nanoparticle-modified preoxidized glassy carbon electrode ($\text{GC}_{\text{ox}}/\text{nano-NiO}_x$) is achieved. The $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode is prepared by electrodeposition of nickel nanoparticles (nano-Ni) onto an electrochemically activated glassy carbon (GC) electrode, and the thus prepared nano-Ni were subjected to electrochemical oxidation in alkaline medium for the formation of nickel oxide (NiO_x). Modified electrodes were electrochemically and morphologically characterized. The effect of loading level of nickel was investigated by changing the number of potential cycles for the deposition of nano-Ni, i.e., 1, 2, 5, and 10 potential cycles, in the potential range from 0 to -1.0 V vs. SCE. Also, the experimental and instrumental parameters were optimized. Experimental results showed that the modified electrode differentiates well the oxidation peaks of DA and AA enabling the electrochemical determination of DA in the presence of a large excess of AA. Remarkably, it is found that the oxidation current of DA is 2 times larger than that of AA even the concentration of AA is about 5 times larger than that of DA. The LOD and LOQ of DA were calculated and were found to equal 0.69 and 2.3 mM, respectively. This offers the advantage of simple and selective detection of DA free of the interference of AA in real samples.

1. Introduction

Dopamine (DA) is critical for medical treatment and clinical analysis. DA has long been of interest to neuroscientists and chemists because of its role as an essential neurotransmitter in the functionality of the central nervous, renal, hormonal, and cardiovascular systems [1]. Low level of DA in the mean central nervous system is the main cause of many neurological diseases (e.g., schizophrenia and Parkinson's disease) [2, 3]. A major problem for the detection of DA is the coexistence of many interfering compounds in biological systems. The most critical interferent of DA (typical concentration in vivo is 10^{-9} – 10^{-5} mol L⁻¹) is AA (typical concentration in vivo is 10^{-4} mol L⁻¹), which is a cofactor of multiple enzymes [4, 5]. AA is a vital vita-

min in the diet of humans, and it has been used for the prevention and treatment of common cold, mental illness, and other diseases [6]. To quantify DA coexisting with a large excess of AA, the major challenge is to achieve both high selectivity and sensitivity of the detection technique.

Many analytical techniques have been reported for the determination of DA and AA such as chromatographic methods, mass spectroscopy [7], spectrophotometry [8], and chemiluminescence [9]. However, these methods encounter some drawbacks such as long analysis time, high cost, and the requirement for sample modification. These disadvantages probably make them unsuitable for routine analysis. Electrochemical methods offer several merits such as simplicity, rapidity, high sensitivity and specificity, and ease of fabrication [10].

The simultaneous electrochemical detection of AA and DA faced several challenges as their peaks overlap due to their close redox potentials [11, 12]. AA is usually present in vivo at concentrations 100 to 1000 times larger than those of DA, resulting in an overlap of electrochemical responses and electrode fouling by oxidation products [10]. Thus, it is usually difficult to separate the responses of AA and DA at bare electrodes [13] such as GC, gold, and platinum electrodes. In recent years, several strategies to separate the electrochemical response of the two species while retaining the sensitivities have been introduced [14–23]. It includes the modification of gold and GC electrodes with either an organic or inorganic modifier. Modification with an organic modifier relies on the possible differentiation of the two redox peaks via controlling the electrode surface. For instance, controlling the surface charge could separate the two peaks based on the large difference in the dissociation constants of the two species; DA is positively charged ($pK_a = 8.9$) whereas AA is negatively charged ($pK_a = 4.2$) [14, 15] at a physiological pH. In this correspondence, Nafion- [16, 24, 25], clay- [26], and polymeric film- [27–29] modified electrodes have been reported to remove the interference of AA with DA [30]. However, the reported selectivity enhancement is not accompanied by a sensitivity improvement of DA detection [31, 32]. Accordingly, another strategy was developed by modification of an electrode with an electroactive material exhibiting preferential catalytic activity towards DA, such as ruthenium oxide pyrochlore [33], nickel hexacyanoferrate [34], carbon nanotube films (CNTs) [31] and metal nanoparticles [33–35].

On the other hand, metal nanoparticles, compared with their counterpart, are excellent electrode materials for potential applications in electroanalysis due to their unique structure and good electrical conductivity [36]. Several nanoparticles (NPs) have been used in this correspondence such as gold [37], silver [38], and platinum [39] as well as metal oxides such as ZnO [40], MnO₂ [41], CuO [42] and NiO [43].

The purpose of this work is to investigate the electroanalysis of DA in the presence of overly abundant AA at the GC electrode modified with nano-NiO_x by cyclic and square wave voltammetries. Experimental conditions were optimized for achieving the largest peak separation for the oxidation potential of DA and AA along with the largest possible sensitivity. It has been reported that nickel oxide electrocatalyzes the oxidation of hydroxyl compounds [44]. Thus, it is expected that nano-NiO_x will help in the differentiation of responses of DA and AA (hydroxyl compounds). Moreover, oxidized glassy carbon (GC_{ox}) has been reported to separate electrochemical responses of both species based on the generation of various groups. Some of these groups are anionic groups, and thus, it can repel anionic analytes, as AA is under pH of 7, and attract cationic analytes, as DA is under pH of 7 [45]. Thus, the deposition of nano-NiO_x at GC_{ox} is promising for the selective analysis of the two species in their coexistence.

2. Materials and Methods

2.1. Materials and Reagents. All chemicals were used as received without further purification. AA and DA were pur-

chased from Sigma Chemical Co. (USA). Stock solutions of DA and AA were prepared prior to experiments by dissolving a suitable amount of reagents in deionized water. Appropriate concentrations of analytes are prepared by dilution.

2.2. Apparatus and Electrodes. Electrochemical measurements have been performed on Gamry Instruments (potentiostat/galvanostat/ZRA model Reference 600™). Voltammetric experiments were realized using a conventional electrochemical cell with three electrodes, where the modified glassy carbon electrode (GC_{ox}/nano-NiO_x) was used as the working electrode and the saturated calomel electrode (SCE) as the reference electrode. The auxiliary electrode was a platinum wire. The GC electrode (1 mm in diameter) was polished to get a mirror shine using polishing papers of two grades (3000 and 2000) and then cleaned thoroughly with deionized water.

2.3. Fabrication of the GC_{ox}/Nano-NiO_x Electrode. GC was oxidized in 0.5 M H₂SO₄ by potential cycling from -0.2 to 2 V at a scan rate of 100 mV s⁻¹. This oxidized GC was denoted as GC_{ox} throughout. GC modification with NiO_x was achieved as follows: nickel was electrodeposited from a Watts bath (0.02 M NiSO₄ · 6H₂O + 0.03 M NiCl₂ · 6H₂O + 0.03 M H₃BO₃) of pH 5.8 [46] by cycling the potential in the range from 0 to -1.0 V vs. SCE at a scan rate of 50 mV s⁻¹ and at 25°C. Then, the thus modified electrode was subjected to several potential cycles in 0.5 M NaOH for oxidizing the deposited nickel (Scheme 1).

2.4. Instrumentation. Morphological characterization of the bare and modified GC electrodes was investigated by scanning electron microscopy (SEM, JSM-7600F Field Emissions Scanning Electron Microscope). Chemical composition was probed by Energy-Dispersive X-ray (EDX, Inca Oxford Instrument), and crystallographic orientation was examined using X-ray diffraction (XRD, D8 Discover Bruker using 2-theta from 5 to 90 degrees with 2 degrees per minute scan speed).

3. Results and Discussion

3.1. Surface Characterization. Typical EDX, SEM, and XRD micrographs obtained on the surface of the bare GC, GC_{ox}, and GC_{ox}/nano-NiO_x electrodes are presented in Figures 1–3, respectively. The elemental analysis of the GC_{ox}/NiO_x electrode is probed by EDX (Figure 1). The extracted data from this figure are shown in Table 1. The GC_{ox} (Figure 1(b)) exhibits a significant increase in the oxygen signal compared with the bare GC (Figure 1(a)). This observation is clear evidence for the oxidation of GC as previously reported [47–49] after being subjected to electro-oxidation. In Figures 1(a) and 1(d), the nickel signal appeared as evidence for the deposition of Ni on GC_{ox}. Also, in Figure 1(d), the oxygen signal increased compared with that shown in Figure 1(c), denoting the formation of NiO_x on GC_{ox}. These results are in line with morphological features seen in SEM (Figure 2). The smooth surface of the bare GC (Figure 2(a)) becomes roughened (Figure 2(b)) with electrochemical oxidation of GC. The GC_{ox} contains a few flakes on the surface (Figure 2(b)). Figure 2(c) shows the

SCHEME 1: Steps of fabrication of the $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode.

FIGURE 1: EDX analysis of bare GC (a), GC_{ox} (b), $\text{GC}_{\text{ox}}/\text{Ni}$ (c), and $\text{GC}_{\text{ox}}/\text{NiO}_x$ (d).

FIGURE 2: SEM images of bare GC (a), GC_{ox} (b), GC_{ox}/Ni (c), and GC_{ox}/NiO_x (d) electrodes.

FIGURE 3: XRD analysis of bare GC (a), GC_{ox} (b), GC_{ox}/Ni (c), and GC_{ox}/NiO_x (d) electrodes.

formation of a granular overlayer of the deposited Ni nanoparticles by small density and size and diverse geometric structure. Upon oxidation of Ni, the nano- NiO_x electrodeposited on GC_{ox} becomes denser and larger, as shown in (Figure 2(d)).

X-ray diffraction (XRD) is a powerful nondestructive technique for characterizing crystalline materials. The XRD

patterns recorded from the bare GC, GC_{ox} , GC_{ox}/Ni , and GC_{ox}/NiO_x are shown in Figure 3. The sharp peak located at around 19° corresponds to the (002) diffraction of the carbon substrate [50]. In pattern d, diffraction peaks at 37.77° , 43.43° , 63.51° , 76.24° , and 79.45° correspond to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes, respectively, and characteristics of cubic crystalline NiO_x [51, 52] are

TABLE 1: Surface composition of GC, GC_{ox}, GC_{ox}/Ni, and GC_{ox}/NiO_x electrodes.

Electrode	Elements	Atomic content (at.%)	Weight content (wt.%)
GC	C K	97.7	96.89
	O K	2.35	3.11
GC _{ox}	C K	92.7	90.56
	O K	7.28	9.44
GC _{ox} /Ni	C K	91.6	85.16
	O K	6.87	8.38
GC _{ox} /NiO _x	Ni K	1.58	6.46
	C K	76.2	70.54
GC _{ox} /NiO _x	O K	23.8	29.29
	Ni K	0.04	0.17

shown indicating the successful fabrication of nano-NiO_x-modified electrode.

3.2. Electrochemical Characterization of the Nanostructure

3.2.1. Cyclic Voltammetric Studies. Figure 4 shows a series of cyclic voltammograms obtained from bare GC (curve 1), GC_{ox} (curve 2), GC_{ox}/nano-Ni (curve 3), and GC_{ox}/nano-NiO_x (curve 4) electrodes in 0.1 M NaOH solution at a scan rate of 100 mV s⁻¹. The cyclic voltammograms at bare GC (curve 1) show no redox peak current in the potential region examined, but the GC_{ox} electrode (curve 2) shows an increase in the current due to the fact that the surface area of the GC electrode increases as a result of oxidation, consistent with the SEM shown in Figure 2(b). In curve 3 obtained from GC_{ox}/nano-Ni, the Ni/NiO_x redox couple is revealed; the redox couple is represented by the following equation:

Oxidation peak at 0.55 V corresponds to the oxidation of nickel to Ni²⁺, and subsequently Ni(OH)₂ is oxidized to NiOOH, as represented in Eq. 2 [53]

However, in this case, the response is obscured by the large background current of GC_{ox}. In curve 4, the redox response obtained after oxidation in NaOH is enhanced; the oxidation peak is negatively shifted and revealed at 0.47 V, along with the increase in oxygen evolution, which started at 0.6 V [53]. The oxidation peak is coupled with a redox one appearing at ca. 0.3 V. The electroactive areas of GC_{ox}/Ni and GC_{ox}/NiO_x electrodes were estimated from the charge consumed in the oxidation peak taking into consideration the fact that the formation of one monolayer of Ni(OH)₂ consumes 514 μC cm⁻² [54]. The electroactive areas of GC_{ox}/nano-Ni and GC_{ox}/nano-NiO_x electrodes were estimated to be 2.1 and 1.6 cm², respectively.

The modified electrodes were examined for the electrochemical behaviour of DA and AA, and data are shown in Figure 5, i.e., at bare GC (1, 2), GC_{ox} (3), GC_{ox}/nano-Ni (4) and GC_{ox}/nano-NiO_x (5) electrodes in PBs (pH 6.0) (curve 1) containing 0.25 mM DA + 1.0 mM AA (2–5). At bare GC, the electrochemical responses of DA and AA are overlapping, as well as at GC_{ox}, albeit the response to DA is enhanced and the one of AA is diminished. At GC_{ox}/nano-Ni (curve 4) and GC_{ox}/nano-NiO_x (curve 5), the oxidation peaks of DA and AA are differentiated with the larger response obtained at the latter. It has been reported that NiO_x rather than metallic nickel is the appropriate electrocatalyst for the oxidation of hydroxyl compounds [44].

The effect of loading of nano-NiO_x on the electrochemical response of DA and AA is shown in Figure 6 in which CVs obtained from GC_{ox}/nano-NiO_x electrodes, prepared by different potential cycles, in PBs (pH = 6.0) containing 0.25 mM DA + 1.0 mM AA are shown. The effect on both separation of the peak potential of DA and AA and the sensitivity is not that large. The largest separation of peak potentials and the large current response for DA along with a smaller response for AA are obtained from GC_{ox}/nano-NiO_x prepared by two potential cycles. This helps in the simultaneous analysis of the two species, knowing that AA is always in larger concentration than DA in real samples [4, 5]. Hence, the loading prepared by two potential cycles will be used hereafter as the optimum one.

The effect of pH on the electrochemical response of DA and AA at the GC_{ox}/nano-NiO_x electrode in phosphate buffer solutions of different pH at a scan rate of 100 mV s⁻¹ was examined. Oxidation of DA (Equations (3)–(5)) and AA (Equation (6)) involves the release of two protons; thus, it is expected to be dependent on the pH of the electrolyte. According to literature [55], it is proposed that dopamine oxidation leads to the formation of dopamine quinone (B), which subsequently undergoes an intramolecular cyclization to form leucodopaminechrome (C). The leucodopaminechrome is further oxidized to form dopaminochrome (D).

The anodic peak potentials were strongly dependent on pH (Figure 7), suggesting the participation of H⁺ in the

FIGURE 4: CVs obtained from bare GC (1), GC_{ox} (2), $\text{GC}_{\text{ox}}/\text{nano-Ni}$ (3), and $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ (4) electrodes in 0.1 M NaOH solution. Scan rate: 100 mV s^{-1} .

FIGURE 5: CVs obtained from bare GC (1, 2), GC_{ox} (3), $\text{GC}_{\text{ox}}/\text{nano-Ni}$ (4), and $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ (5) electrodes in PBs (pH 6.0) (1) containing 0.25 mM DA + 1.0 mM AA (2–5). $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ was prepared using two potential cycles as mentioned in Materials and Methods. Scan rate: 100 mV s^{-1} .

oxidation processes. As shown in Figure 7, the effect of pH is significant on both the peak potential and peak current of DA. Regarding AA, the significant effect is on its peak potential but not peak current. The optimum pH shows the largest separation of peak potential of DA, and the current response is obtained at pH 6 (curve 3). Therefore, PBs of pH 6.0 were selected for all subsequent electrochemical studies of DA and AA. At pH larger than 6, the two peaks of DA and AA oxidation overlap. The linear regression equations are given by

$$\begin{aligned} E_{\text{pa}}(\text{V}) &= -0.051\text{pH} + 0.514 \quad R^2 = 0.994 (\text{for DA}), \\ E_{\text{pa}}(\text{V}) &= -0.041\text{pH} + 0.288 \quad R^2 = 0.872 (\text{for AA}). \end{aligned} \quad (7)$$

The slopes of the linear variations of peak potentials with pH were -51 mV/pH and -41 mV/pH for DA and AA, respectively. The correlation coefficient in the case of AA is smaller than one, probably because in the case of AA ($\text{pK}_a = 4.2$) at pH larger than 4, the oxidation is little bit retarded [56]; i.e., cyclic voltammetric curves in Figure 7 are for AA while it is protonated and nonprotonated. Also, it has been reported that the response to the electrode fouling occurs due to oxidation products of DA [10]. In the case of DA ($\text{pK}_{a1} = 8.9$ and $\text{pK}_{a2} = 10.6$), it is nonprotonated in the studied pH range [14, 15, 57], so the electrochemical behaviour shows ideal pH dependence, and the correlation coefficient in this case equals almost one. Negative slopes showed that deprotonation was involved in the oxidation process, which was facilitated at

FIGURE 6: CVs obtained from the $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode in PBs (pH = 6.0) containing 0.25 mM DA + 1.0 mM AA. The $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode was prepared by one (1), two (2), five (3) and ten (4) potential cycles. Scan rate: 100 mV s^{-1} .

FIGURE 7: CVs obtained from the $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode in PBs containing 0.25 mM DA + 1.0 mM AA. pH: 3.47 (1), 4.72 (2), 6.00 (3), 7.42 (4) and 8.10 (5). Scan rate: 100 mV s^{-1} . Inset: dependence of the anodic peak potential on the pH of the solution.

higher pH values. Near Nernstian slopes indicated the equal numbers of electrons and protons in the charge-transfer step at the surface of the modified electrode [58].

3.2.2. Electroanalysis of DA and AA

(1) *Selectivity.* The selectivity of the $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode for the determination of DA and AA was examined by measur-

ing the CVs of 1 mM AA in the presence of different concentrations of DA. As it can be seen in Figure 8, the oxidation peak current of AA is constant irrespective of the concentration of DA. Thus, it can be utilized in selective determination of DA in the presence of AA under the present conditions.

(2) *Effect of Scan Rate.* The effect of scan rate on the peak currents of DA and AA oxidation is shown in Figure 9.

FIGURE 8: CVs obtained from the $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode in PBs (pH = 6.0) containing (a, b, c) 1.0 mM AA and different concentrations of DA: (a) 0.125, (b) 0.25 and (c) 0.375 mM. Scan rate: 100 mV s^{-1} .

FIGURE 9: CVs of (a) 0.25 mM of DA and (b) 1 mM of AA at the $\text{GC}_{\text{ox}}/\text{NiO}_x$ electrode in 0.1 M PBs (pH 6.0) at various scan rates from 20 to 600 mV s^{-1} .

Relations between the scan rate and the peak current for DA and AA are shown in Figure 10.

A good linear relationship between the peak current of AA and square root of scan rate (Figure 10(a)) indicates the diffusion process. For DA, the relation ($i_{\text{pa}} - \nu^{1/2}$) is not linear. The relation ($i_{\text{pa}} - \nu$) for DA (data are not shown) gives a linear relation indicating a surface-confined process.

Also, the linear response of the anodic peak current versus scan rate ($\log i_{\text{pa}} - \log \nu$ plot) is illustrated in Figure 10(b) in which the slope of $\log i_{\text{pa}}$ versus $\log \nu$ is calculated to be 0.83 ($R^2 = 0.992$) for DA and 0.52 ($R^2 = 0.997$) for AA. A slope value close to 0.5 indicates a diffusion-

controlled reaction, and a value equals 1 indicates an adsorption reaction. A value between 0.5 and 1.0 indicates a mixing diffusion and adsorption reaction [59], but diffusion control is more dominant. In the present case, the slope of DA 0.83 is very close to the theoretical value of 1 for adsorption-controlled processes. Also, the slope of AA 0.52 indicates that oxidation of AA is a diffusion-controlled process.

3.2.3. Square Wave Voltammetry. A square wave voltammetric (SWV) method is utilized for the selective determination of DA and AA. SWV offers excellent discrimination against double-layer charging current, and accordingly it has high sensitivity [60]. Under the optimum conditions of instrumental parameters: step potential (2 mV), square wave

FIGURE 10: (a) $i_{pa} - v^{0.5}$ plot for DA and AA at the GC_{ox}/NiO_x electrode. (b) $\log i_{pa} - \log v$ plot for DA and AA at the GC_{ox}/NiO_x electrode.

amplitude (25 mV), and frequency (25 Hz), the SWVs of both AA and DA in their coexistence are recorded at the $GC_{ox}/nano-NiO_x$ electrode and shown in Figure 11. The oxidation peaks of DA and AA are clearly observed at about 0.2 and 0.02 V, respectively. The linear calibration curves for both species were obtained in PBs (pH 6.0) over a wide concentration range and shown as an inset. Analytical parameters for simultaneous determination of DA and AA at the $GC_{ox}/nano-NiO_x$ electrode are summarized in Table 2. As can be seen, the sensitivity (slope) of DA is very large compared with that of AA, even the concentration of AA is larger. The high sensitivity is due to the preconcentration of the DA cations at the electrode. The linear relation with correlation

coefficients around 0.980 and 0.987 for DA and AA, respectively, and a limit of detection of $0.69 \mu M$ for DA and $18 \mu M$ for AA are obtained. The LOD and LOQ were calculated from the calibration curve using the equations $LOD = 3 S/N$ and $LOQ = 10 S/N$, where S is the standard deviation and N is the slope of the regression line. The comparison of this method with other reported electrochemical methods is given in Table 3. It can be seen that the GC_{ox}/NiO_x exhibited a wider linear range with lower detection limit in comparison with other relevant reported results.

3.2.4. Simultaneous Determination of DA in the Presence of a Large Excess of AA. Based on the above results, the difference

FIGURE 11: SWVs obtained from the $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode in PBs (pH 6.0) containing different concentrations of AA (1.16, 2.32, 3.48, 4.64, and 5.8 mM) and DA (0.08, 0.17, 0.26, 0.35 and 0.44 mM). Square wave amplitude: 25 mV; frequency: 25 Hz; step potential: 2 mV. The electrode potential was scanned from -0.5 V to 0.5 V. The inset shows the calibration curves for DA and AA.

TABLE 2: Parameters of the electroanalytical determination of DA and AA using SWV.

Parameter	DA	AA
Optimum buffer	Phosphate	Phosphate
Optimum pH	6.00	6.00
Measured potential (mV)	200	30
Scan rate (mV s^{-1})	100	100
Linear concentration range (μM)	80.0–800	1160–11600
Slope ($\mu\text{A cm}^{-2}/\mu\text{M}$)	0.329	0.062
Correlation coefficient (R^2)	0.9808	0.9879
Standard deviation (SD) ($n = 7$) (mM)	0.005	0.026
Relative standard deviation (%)	0.48	0.29
LOD (μM)	0.69	18
LOQ (μM)	2.3	62

in the oxidation peak potentials for DA and AA at the $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ electrode is large enough for the separation and simultaneous determination of DA in the presence of high levels of AA in a mixture. The SWV response of DA and AA in their coexistence is shown in Figure 12. The oxidation peak currents of these species increase with their concentrations, indicating the stable and efficient electrocatalytic activity of the modified electrode. Calibra-

tion plots extracted from this figure are shown as an inset. For both species, a calibration curve with two slopes was obtained. The correlation coefficient values in all cases are larger than 0.97.

3.3. Study of Interference. The influences of some possible species on the determination of DA and AA at the $\text{GC}_{\text{ox}}/\text{nano-NiO}_x$ -modified electrode are examined. To investigate the selectivity of the proposed method, various interfering chemicals including amino acids (glycine and tryptophan), urea, oxalate, and catechol were added to the sample solution containing 0.25 mM DA and 1 mM AA at optimum conditions. As can be seen in Figure 13, i_{pa} in the absence (reference) of interferences and in the presence of glycine, urea, potassium oxalate, and tryptophan is almost the same, and catechol exhibits the increased catalytic current of DA compared to other substances. This could be attributed to its similar structure to that of DA, which is a type of catecholamine, 3,4-dihydroxyphenyl (catechol) [66], indicating that this method for detecting DA and AA is of high selectivity.

3.4. Real Sample Analysis. In order to evaluate the applicability of the proposed method for the determination of DA and AA in real samples, the concentrations of the two species were detected separately and in their coexistence. For the analysis of DA and AA separately, real samples of DA-HCl

TABLE 3: Comparison of analytical parameters for the detection of DA and AA at GC_{ox}/nano-NiO_x with other modified electrodes.

Materials	Technique	Analyte	Linear range (μM)	LOD (μM)	Sensitivity ($\mu\text{A cm}^{-2}/\mu\text{M}$)	Reference
OMC/Nafion/GCE ^a	DPV	DA	1–90	0.5	4.76	[61]
		AA	40–800	20	0.496	
Ni@poly-1,5 DAN/GC ^b	SWV	DA	100–500	0.011	0.583	[62]
		AA	100–500	0.0	0.751	
PEDOT-modified Ni/Si MCP ^c	DPV	DA	12–48	1.5	5.40	[63]
		AA	20–1400	10	0.539	
Ni-Meso-PANI/GCE ^d	DPV	DA	10–300	6.9	3.78	[64]
		AA	10–300	7.1	2.71	
Bi/BiVO ₄	PEC ^e	DA	0.05–100	0.008	0.199	[65]
		AA	0.2–118	0.09	0.194	
GC _{ox} /nano-NiO _x	SWV	DA	80.0–800	0.69	0.329	This work
		AA	1160–11600	18	0.062	

^aOrdered mesoporous carbon (OMC)/Nafion composite film; ^bNickel nanoparticles dispersed at poly(1,5-diaminonaphthalene); ^cNi/silicon microchannel plate (Ni/Si MCP) electrode modified with poly(3,4-ethylenedioxythiophene) (PEDOT); ^dTransition metal ion-exchanged mesoporous polyaniline; ^ePhotoelectrochemical.

FIGURE 12: (a) SWVs obtained from the GC_{ox}/nano-NiO_x electrode in PBs (pH 6.0) containing different concentrations of AA (0.5, 1, 1.5, 2, 2.5, 3, and 3.5 mM) and DA (1.5, 3, 4.5, 6, 7.5, 9 and 10.5 μM). Square wave amplitude: 25 mV; frequency: 25 Hz; step potential: 2 mV. The electrode potential was scanned from -0.5 V to 0.5 V. Panels (b) and (c) are the calibration plots for DA and AA, respectively.

FIGURE 13: Effect of interferences on DA and AA detection. The concentration of DA, AA, tryptophan, and other interferences is 0.25 mM, 1 mM, 0.05 mM and 0.50 mM, respectively.

TABLE 4: Electroanalytical determination of AA and DA in real samples with comparison to the UV-Vis approach.

Sample		Proposed method ^a (mM)	Proposed method ^a (mM)	Recovery ^b (%)	UV-visible method (mM)
Vitamin C	AA	—	1.35 ± 0.05	—	1.325 ± 0.05
	AA	1.50	2.85 ± 0.05	100	—
	AA	3	4.29 ± 0.12	98	—
DA-HCL	DA	—	0.0505 ± 0.001	—	0.0523 ± 0.0001
	DA	0.75	0.85 ± 0.01	106	—
	DA	1.25	1.27 ± 0.017	97	—

^aAverage of seven determinations; ^bmean ± SD ($n = 7$).

TABLE 5: Simultaneous electroanalytical determination of mixed DA-HCl and vitamin C real samples.

Sample	Added		Found ^a		Recovery ^b (%)	
	DA-HCL (μ M)	Vitamin C (mM)	DA-HCL (μ M)	Vitamin C (mM)	DA-HCL	Vitamin C
1	3.15	6.3	3.30	6.17	104 ± 0.18	97.9 ± 0.11
2	4.46	10.5	4.38	10.4	98 ± 0.07	99 ± 0.09
3	15.75	21	15.72	21	99 ± 0.06	100 ± 0.03

^aAverage of seven determinations; ^bmean ± SD ($n = 7$).

and vitamin C were used. The results are presented in Table 4. As shown in this table, the recovery is overall between 97% and 106% which is acceptable in this case. The proposed method results were also compared to those of the UV-visible method to confirm that there are no significant differences between these two methods, suggesting that the present method exhibits high selectivity and sensitivity to

detect DA and AA. Also, both DA-HCl and vitamin C were mixed and studied by adding different concentrations of vitamin C and DA-HCl (Table 5). The results again proved that the proposed method is accurate and the recovery is in the range of 97.9% and 104%, confirming the suitability of the present method for the analysis of DA in real samples containing a large excess of AA.

4. Conclusions

A simple and rapid electrochemical method to detect DA in the presence of a large excess of AA at the GC_{ox}/nano-NiO_x electrode is investigated. The modified electrode shows excellent electroanalytical activity towards the oxidation of DA in the presence of excess AA in PBs (pH 6.0) enabling the electrochemical determination of DA and AA using SWV in their simultaneous coexistence. The SWV of DA in the presence of excess AA indicates that the detection limit of DA on the GC_{ox}/nano-NiO_x can be 0.69 μ M, which is much lower than that of AA (18.49 μ M). It thus appears that the GC_{ox}/nano-NiO_x acts as an excellent electrode for detecting DA in an AA-dominating real sample.

Data Availability

The generated or analysed data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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