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Electrochemical preparation, characterization, and electrocatalytic studies of Nafion–ruthenium oxide modified glassy carbon electrode

Chien-Chieh Ti · S. Ashok Kumar · Shen-Ming Chen

Abstract Electrochemical synthesis of ruthenium oxide (RuOx) onto Nafion-coated glassy carbon (GC) electrode and naked GC electrode were carried out by using cyclic voltammetry. Electrochemical deposition of RuOx onto Nafion-coated electrode was monitored by in situ electrochemical quartz crystal microbalance (EQCM). Surface characterizations were performed by scanning electron microscope (SEM) and atomic force microscope (AFM). SEM and AFM images revealed that ruthenium oxide particles incorporated onto the Nafion polymer film. In addition, a GC electrode modified with ruthenium oxide–Nafion film (RuOx–Nf–GC) was shown excellent electrocatalytic activity towards dopamine (DA) and ascorbic acid (AA). The anodic peak current increases linearly over the concentration range of 50 μM–1.1 mM for DA with the correlation coefficient of 0.999, and the detection limit was found to be (S/N=3) 5 μM. Owing to the catalytic effect of the modified film towards DA, the modified electrode resolved the overlapped voltammetric responses of AA and DA into two well-defined voltammetric peaks with peak-to-peak separation about 300 mV. Here, RuOx–Nf–GC electrode employed for determination of DA in the presence of AA. This modified electrode showed good stability and antifouling properties.

Keywords Ruthenium oxide · Chemically modified electrode · Dopamine determination · Electrocatalysis · Nafion

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Introduction

Dopamine (DA) exists in the mammalian brain in the presence of several neurotransmitter amines, including ascorbic acid (AA) and uric acid. Recently, the identification and determination of DA with electrochemical procedures have attracted much attention. However, it is very difficult to determine DA by direct oxidation at bare electrodes because of the high overpotential and the fouling of electrode surface by its oxidation products [1–5]. Moreover, the oxidation waves of AA and DA occurred at nearly the same potential and overlapped, which results in poor selectivity and reproducibility. The ability to determine AA or DA selectively in the presence of each other has been a major goal of electroanalytical research. Various methods, mainly based on the chemical modification of traditional electrode materials, have been developed to resolve the problem [6–9]. The poor reproducibility of direct electrochemical oxidation of DA has led to interest in the use of various modified electrodes for the electrochemical determination of DA. For example, electrode surface modified with immobilized organic monolayers [10, 11], polymers film [12–17], carbon nanotubes [18, 19], surfactant [20], and quinone [21] have been used for detection of DA.

Recently, selective electrochemical determination of DA in the presence of ascorbic acid using sodium dodecyl sulfate micelles as masking agent [22], poly-chromotrope 2B modified glassy carbon (GC) electrode [23], poly(4-amino-1-1′-azobenzene-3,4′-disulfonic acid)-coated electrode [24], poly (p-nitrobenzenazo resorcinol)-modified GC electrode [25], nano-Au self-assembly GC electrode [26], Nafion–carbon-coated iron nanoparticles-chitosan composite film modified electrode [27], and PtAu hybrid film modified electrode [28] were reported.

Ruthenium dioxide carbon paste or mixed-oxidation state ruthenium oxide (RuOx)–ruthenium cyanide inorganic films on GC electrodes have been characterized and used as amperometric sensors for the detection of important organic molecules such as carbohydrates [29, 30], amino acids [31], alcohols [32, 33], inorganic ions, e.g. As (III) [34], and hydrazine compounds [35]. A Nafion (Nf)–ruthenium oxide pyrochlore chemically modified electrode was used for the selective determination of DA in the presence of a high concentration of ascorbic acid by square-wave voltammetry, and the linear range of DA detection was 0–20 μM [36]. Recently, ruthenium oxide-coated electrode for simultaneous detection of dopamine and ascorbic acid is also reported [37].

In this paper, we report electrochemically deposited RuOx film onto Nafion-modified electrode surface and its electrochemical properties. RuOx–Nf–GC electrode shows an excellent electrocatalytic activity towards oxidation of AA and DA when compared with RuOx–GC electrode and Nafion-modified GC electrode. The considerable peak separation between DA and AA at this modified electrode makes the possibilities for simultaneous determination of DA and AA. In addition, we used electrochemical quartz crystal microbalance (EQCM), scanning electron microscope (SEM), and atomic force microscope (AFM) to ascertain the deposition mechanism and surface morphology of the RuOx and Nafion–RuOx-coated electrode. This proposed method has wide dynamic range of detection, long-term stability, and antifouling properties.

Experimental

Apparatus

Electrochemical measurements were performed with CH Instruments (TX, USA) Model-400 potentiostat with conventional three-electrode cell. A Bioanalytical Systems glassy carbon and platinum wire are used as the working electrode and counter electrode, respectively. All the cell potentials were measured with respect to an Ag–AgCl [KCl (sat)] reference electrode. CH Instruments (TX, USA) Model-400A Time-Resolved Electrochemical Quartz Crystal Microbalance is used for mass measurements. The diameter of the quartz crystal was 13.7 mm, and the gold electrode diameter was 5 mm. Hitachi scientific instruments (London, UK) Model S-3000H Scanning Electron Microscope was used for surface image measurements. The AFM images were recorded with a Multimode Scanning Probe Microscope System operated in tapping mode using model CSPM4000 Instruments, Being Nano-instruments Ltd. (Beijing, China). The rotatable ring disk experiments were performed with CHI-750 potentiostat connected to a model AFMSRX analytical rotator purchased from Pine Instru-

ment Co. (Raleigh, NC, USA). All experiments were carried out at room temperature (25±2 °C).

Chemicals

Ruthenium chloride, Nafion, and dopamine hydrochloride were purchased from Sigma–Aldrich (St. Louis, MO, USA). Other chemicals were of analytical grades and used without further purification. Ascorbic acid, potassium nitrate, sodium dihydrogen phosphate, and sodium acetate were received from E-Merck (Darmstadt, Germany). Sodium hydroxide and sulfuric acid were purchased from Wako pure chemicals (Osaka, Japan) and used without purification. The aqueous solutions were prepared by using doubly distilled deionized water, and before each experiment, the solutions were deoxygenated by purging with pre-purified nitrogen gas. The Vitaminc C tablets (Ascorbic acid, 500 mg, CBC Biotechnological and Pharmaceutical Co., Ltd.) were purchased from a local drug store in Taipei, Taiwan.

Modification of the electrode surface

The surface of the GC electrode was polished with alumina suspension (0.05 μm) on a micro cloth polishing pad, rinsed with water, and sonicated for 5 min in distilled water. The 20 μL of 5% alcoholic Nafion solution was cast onto the GC-working electrode surface and dried to get the film by hot air blowing method. The film thickness was calculated by assuming a density of 1.58 g/cm^2 for the wet Na^+ form or a Nafion dry density of 1.98 g/cm^2 [38]. Typically, the thickness of a film obtained by casting 20 μL of a 5% Nafion solution on to the surface was estimated as 150±10 nm.

The electrochemical deposition of the RuOx film onto Nafion-modified electrode was accomplished by potentiodynamic cycling between preset potential limits of −0.3 and 1.0 V at 100 mVs^{-1} in supporting electrolyte (0.1 M KNO_3) aqueous solution containing 1 mM $RuCl_3$. Thereafter, the electrode was rinsed with deionized water and used for investigation of electrochemical properties. The amount of immobilized material at the electrode surface after potentiodynamic experiments were controlled by the number of potential cycles, and the surface concentration (Γ) was determined from the charge under the voltammetric peak of the Ru(II/III) redox process.

Results and discussions

Electrode modification and its electrochemical properties

Figure 1 shows the repetitive cyclic voltammograms (CVs) of the RuOx films deposition onto Nafion-modified GC
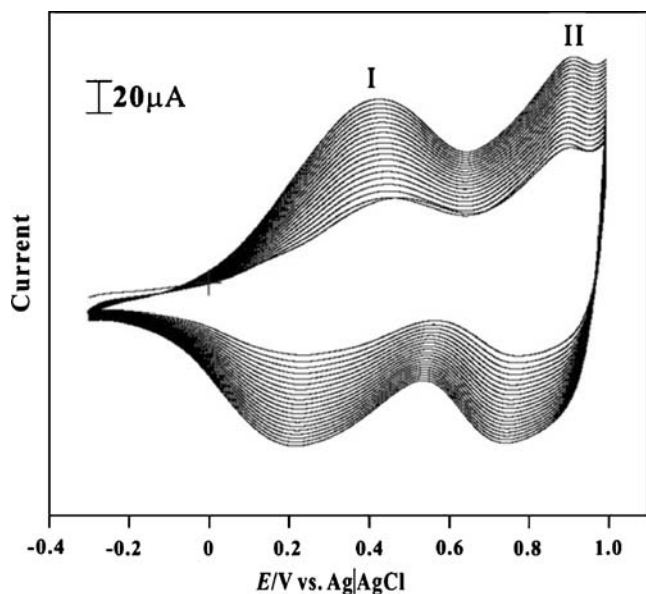
Fig. 1 CVs of RuOx·nH₂O film growth on Nafion-coated GC electrode in 1 mM RuCl₃·xH₂O and 0.1 M KNO₃. (pH 2), Scan rate 0.1 V/s

Fig. 2 A CVs of RuOx–Nf–GC in 0.1 M KNO₃ (pH 2) with various scan rates (a–j) 20–200 mV/s. *Inset* (a) shows the plot of the I_{pc} and I_{pa} vs. the scan rate. (b) Shows the plot of the log I_{pc} vs. the log of scan rate

electrode from RuCl₃ in an aqueous solution containing 0.1 M KNO₃. Two reversible redox couples (I and II) were characterized with the formal potentials occurring at about 0.33 and 0.84 V (vs. Ag|AgCl), and the ascribed electrode reactions are presented in [39–41]. The electrochemical properties of RuOx–Nf–GC electrode were investigated in 0.1 M KNO₃ solution.

CVs were recorded using RuOx–Nf–GC electrode in 0.1 M KNO₃ at different scan rate as shown in Fig. 2. The peak-to-peak separation (ΔE_p) for two redox couples was estimated as 10 mV at low scan rate (10 mV/s). The inset of Fig. 2a shows the plots of I_{pa} and I_{pc} vs. the scan rate that illustrate a close linear dependence of peak currents with the scan rate and that the ratio of I_{pa}/I_{pc} value was close to unity. The slope of the plot of log (I_p) versus log(υ) is 0.93 with a correlation coefficient of 0.999, which is close to the theoretical slope of 1 for thin layer voltammetry (Fig. 2b). The relationship between the peak current and scan rate can be related as follows [42, 43]:

$$I_p = n^2F^2\upsilon A\Gamma_0 / 4RT \tag{1}$$

Where, Γ_0, υ, A, and I_p represents the surface coverage, the scan rate, the electrode area (0.0707 cm²), and the peak current, respectively. The surface concentration (Γ) of peak I and II were estimated to be 1.0×10^{-8} and 1.07×10^{-10} mol/cm², respectively. The above results indicated that the redox process was surface-confined on GC electrode, confirming the immobilized state of the RuOx films [42–44]. To ascertain the effect of pH, the voltammetric response of RuOx–Nf–GC electrode was recorded in
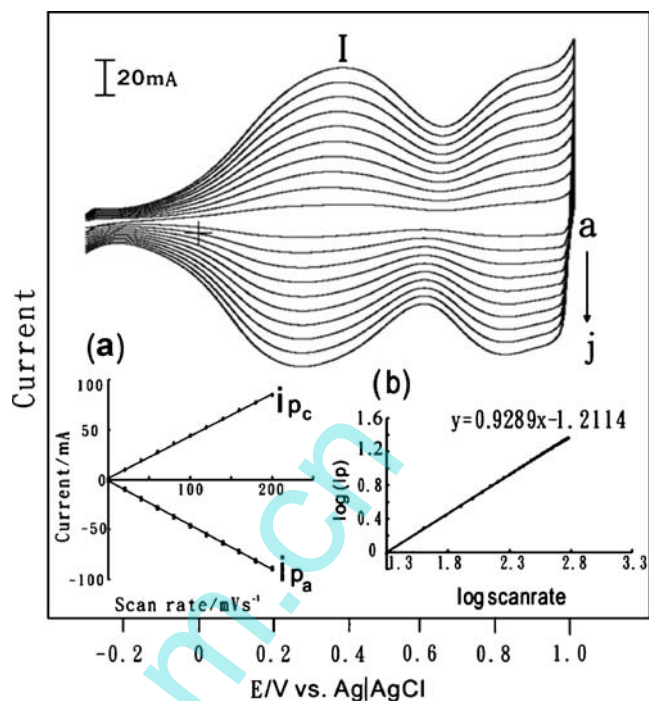
solutions of different pH in the range of 1–6. As can be seen in Fig. 3, the $E^{0\prime}$ of redox couples were pH dependent with a slope of −49 mV per pH for RuOx redox couple (Inset, Fig. 3), which are very close to the anticipated
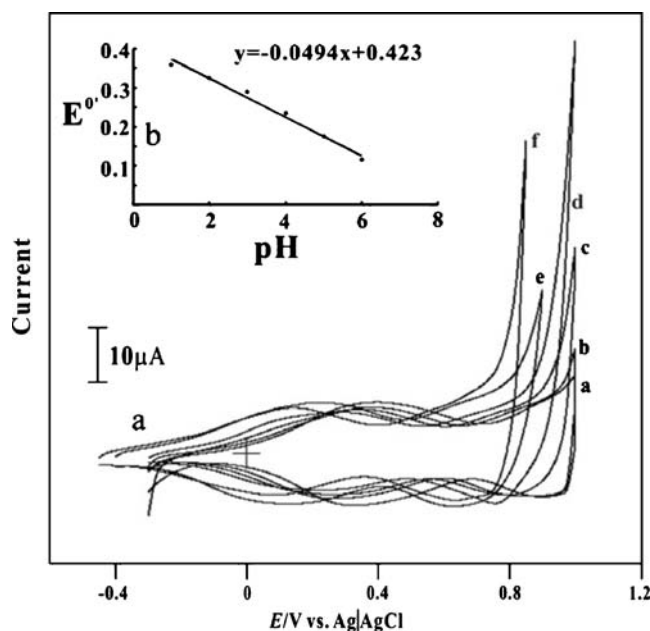

Fig. 3 (a) CVs for RuOx–Nf–GC at different pH values (a) 1.0 (b) 2.0 (c) 3.0, (d) 4.0, (e) 5.0, and (f) 6.0. (b) *Inset figure* shows E⁰′ as a function of pH at scan rate of 0.1 V/s

Nernstian value of −59 mV for electrochemical processes involving the same number of protons and electrons [45].

In situ EQCM studies

Figure 4a and b demonstrates the growth of the RuOx film onto the Nafion-coated gold quartz crystal electrode and the resulting change in the frequency of the quartz crystal. The RuOx films were deposited from the 1 mM Ru^{3+} ions in 0.1 M KNO$_3$ by scanning over the potential range between -0.25 and 0.9 V.

The voltammetric peak current in Fig. 4a and the frequency decrease (or the mass increase) in Fig. 4b are found consistent with the growth of a RuOx film on Nafion-coated gold quartz crystal electrode. The EQCM results showed that the deposition of the RuOx film occurred at a potential of 0.9 V in the first positive scan, but the major deposition occurred between the potential range of 0.2 and 0.9 V (vs. Ag|AgCl). The electrochemical deposition mechanism of RuOx film has been reported on bare Au-coated quartz crystal [39]. In this paper, we studied the RuOx deposition onto Nafion film-modified Au-coated quartz crystal electrode. In this experiment, the changes in the mass at the quartz crystal were calculated from the changes in frequency using the Sauerbrey Equation [46, 47].

$$\text{Change in mass}(\Delta f) = -\left(2f_0^2/A\sqrt{\mu\rho}\right)\Delta m \quad (2)$$

Where, Δf is the observed change in frequency, A is the area of the gold disk-coated quartz crystal (=0.196 cm^2), ρ is the density of the crystal (2.648 g/cm^3), μ is the shear modulus of the crystal (2.947×10^{11} dyn cm^{-2}), and f$_o$ is the oscillation frequency of the crystal (8 MHz). A frequency change of 1 Hz is equivalent to a change in mass of 1.4 ng. RuOx film deposition of about 45 ng was observed for one cycle on the Nafion-coated gold electrode, and a total of about 182 ng of RuOx film was deposited after the first five cyclic voltammetric scans (Inset, Fig. 4a). Based on EQCM results, RuOx film deposition was observed mainly in the potential range between 0.2 to 0.9 V, this range was confirmed by EQCM measurements. Nafion layer on Au quartz crystal electrode enhanced electrochemical deposition of RuOx and the oxide particles firmly attached onto the electrode surface. The amount of deposition is higher in the case of Nafion-modified Au quartz crystal electrode than unmodified quartz crystal, which was confirmed by control experiments. In control experiments, RuOx film deposition was carried out onto bare Au quartz crystal, and

Fig. 4 a Consecutive CVs of RuOx film deposition on Nafion-coated gold electrode. Scan rate=0.02 V/s. b Change in EQCM frequency recorded concurrent with the first five consecutive cyclic voltammograms between of -0.25 and 0.95 V. Inset plot shows the total mass change versus the scan cycle
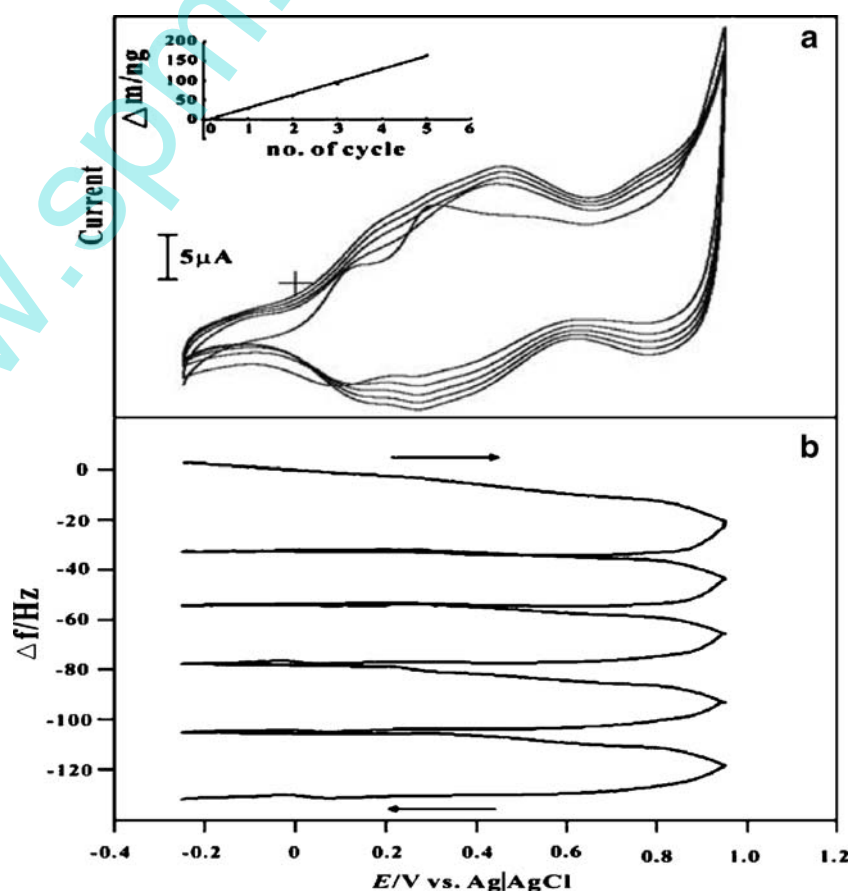
the mass was found to be 42 ng. This experimental result suggested that higher amount of RuOx particles were strongly attached onto negatively charged Nafion layer.

Surface characterizations

Figure 5a shows SEM image of Nafion-coated electrode; it seems like a thin film uniformly covered the electrode surface. Figure 5b shows surface morphologies of the RuOx film on Nafion-coated electrode. The ruthenium oxide thin film prepared by CV had highly porous microstructure with fractal-like agglomerates of fine particles. It was found that RuOx deposition does change the surface morphology of the Nafion-coated electrode. Thicknesses of the Nafion and RuOx–Nafion films were found to be 150 and 224 nm, respectively (Fig. 5c and d), which is confirmed by AFM images.

Voltammetric behavior of DA

Figure 6a shows the CVs of DA at the bare GC electrode (curve a′) and the RuOx–Nf–GC-modified electrode (curve a–i) in 0.1 M KNO$_3$ solution. At bare GC, DA shows irreversible electrochemical behavior with ΔE_p, $\left(\Delta E_p = E_{pa} - E_{pc}\right)$ was 350 mV at a scan rate of 10 mV/s. However, a well-defined redox wave of DA is observed at the RuO–

Nf–GC-modified electrode with ΔE_p (100 mV), the oxidation peak potential shifts negatively to 0.57 V, the reduction peak potential shifts positively to 0.47 V, and the overpotential of DA at the RuOx–Nf–GC electrode decreased. Furthermore, the peak current increases significantly. These results indicated that RuOx–Nf–GC electrode could accelerate the rate of electron transfer of DA by a mediation mechanism, which is in agreement with earlier reports [36, 37].

Cyclic voltammetry of DA at a RuO–Nf–GC-modified electrode shows that the oxidation current is linearly dependent on the concentration in the range of 50 μM– 1.1 mM with a correlation coefficient of 0.999 (Inset, Fig. 6a). The detection limit, taken as the concentration that produces a signal equal to three times the standard deviation of the blank signal calculated from the calibration graph, was 5 μM. A DA concentration level of 500 μM was used to examine the reproducibility of the RuOx–Nf– GC electrode. The relative standard deviation of ten determinations was 3.5%, which showed that the RuOx– Nf–GC electrode has a good reproducibility.

Electrochemical investigations of ascorbic acid

Since AA is the major interferent in the voltammetric measurement of DA, its voltammetric behavior at the

Fig. 5 SEM images of a Nafion film, b RuOx–Nf film, and AFM images of c Nafion film and d RuOx–Nf film

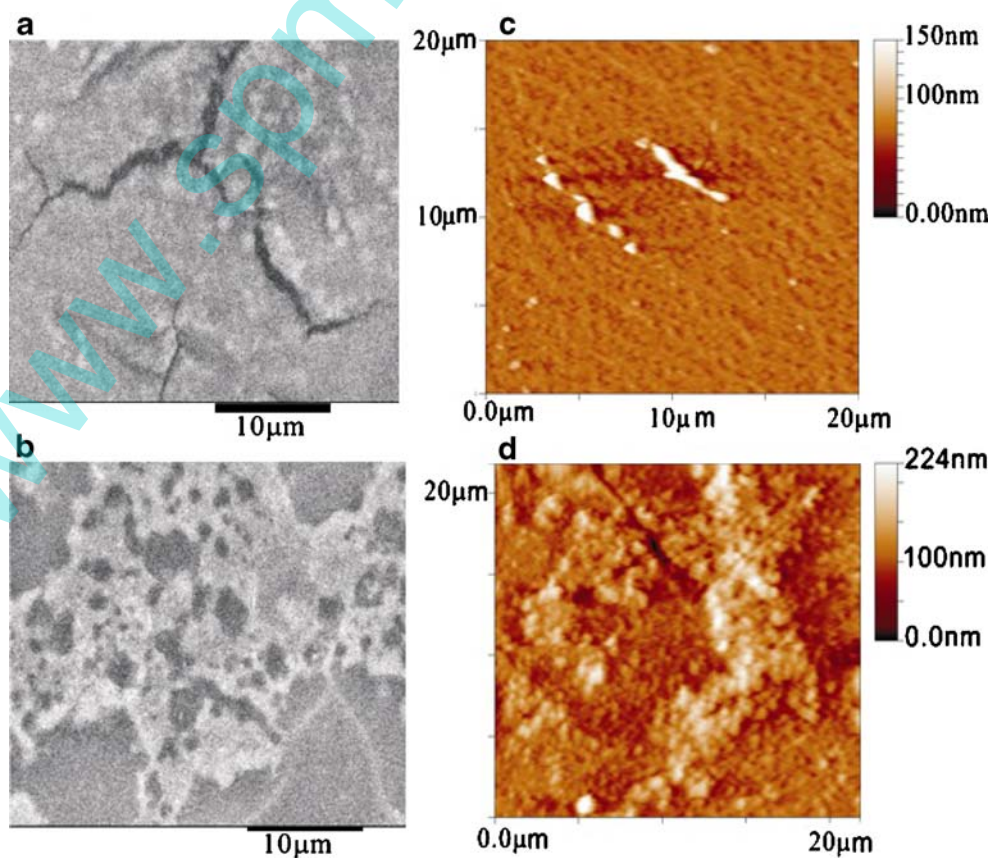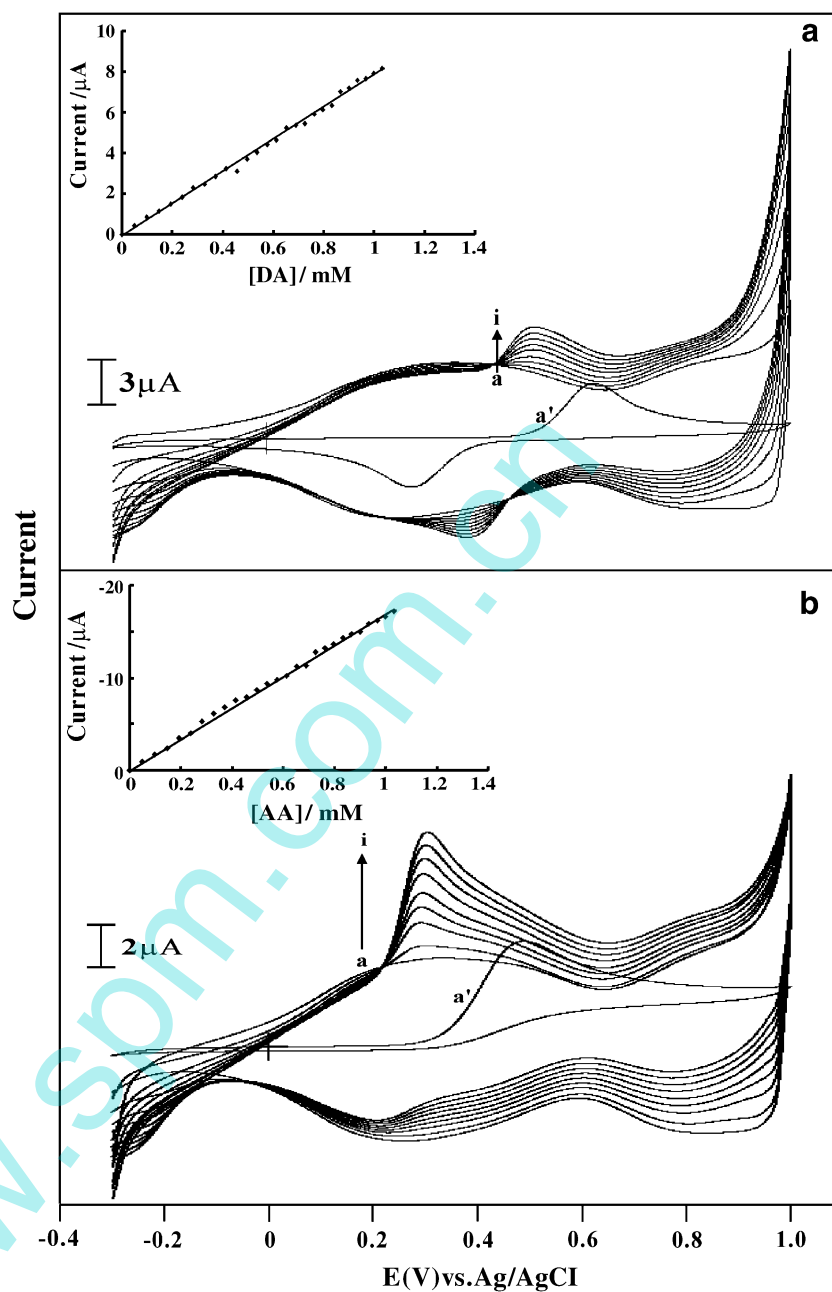**Fig. 6 a** CVs of RuOx–Nf–GC in 0.1 M KNO$_3$ solution with various concentrations of DA (*a*) 0.0, (*b*) 50, (*c*) 100, (*d*) 150, (*e*) 200, (*f*) 250, (*g*) 300, (*h*)350, (*i*) 400 μM, and (*a'*) Bare GC with 400 μM [DA]. *Inset* figure shows the plot of the I_{pa} vs. [DA]. **b** [AA] = (*a*) 0.0, (*b*) 50, (*c*) 100, (*d*) 150, (*e*) 200, (*f*) 250, (*g*) 300, (*h*) 350, (*i*) 400 μM, and (*a'*) bare GC with 400 μM [AA]. Scan rate=10 mV/s. *Inset* figure shows the plot of the I_{pa} vs. [AA]

RuOx–Nf–GC-modified electrode was studied. Figure 6b shows the CVs of AA at bare GC electrode (curve a′) and the RuOx–Nf–GC-modified electrode (curve a–i). Oxidation of AA at bare electrode is generally believed to be totally irreversible and requires high overpotential and also, no reproducible electrode response is obtained due to fouling of the electrode surface by the adsorption of the oxidized product of AA [15, 25].

Above results suggested that RuOx–Nf–GC electrode can be applied to the detection of AA. Cyclic voltammetry was employed in this experiment, and the oxidation peak current of AA was used as the analytical signal. Results indicated that there was a linear relationship between the oxidation peak current of AA and its concentration over the range from 50 μM to 1.1 mM (Inset, Fig. 6b). The detection limit for AA was found to be 4 μM.

Simultaneous detection of DA and AA

Figure 7a shows the CVs obtained for DA and AA coexisting at bare GC and modified electrodes. As shown in curve a, bare electrode cannot separate the voltammetric signals of DA and AA. A single broad voltammetric signal of DA and AA was observed. The fouling of the electrode surface by the oxidation products results in a single voltammetric peak for both DA and AA. Therefore, it is
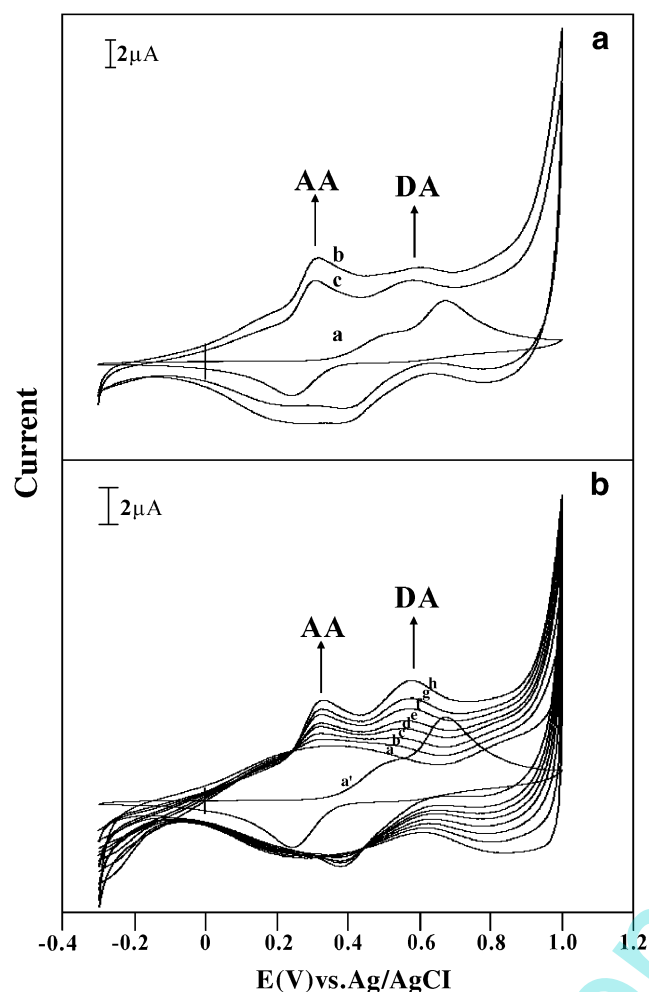
Fig. 7 a CVs were recorded in 0.1 M KNO$_3$ solution containing 400 μM [DA] and 400 μM [AA] using (a) bare GC electrode, (b) RuOx–Nf, and (c) RuOx-modified electrodes. b Simultaneous measurements of DA and AA at RuOx–Nf–GC, [DA] = [AA] = (a) 0.0, (b) 50, (c) 100, (d) 150, (e) 200, (f) 250, (g) 300, (h) 350, and (a') bare GC with [DA] = [AA] = 350 μM

presence of AA is possible at the RuOx–Nf–GC-modified electrode. The voltammetric signals of DA and AA remained unchanged in the subsequent sweeps, indicating that the RuOx–Nf–GC-modified electrode does not undergo surface fouling. Furthermore, the separation between the CV oxidative peaks of DA and AA is large (300 mV); thus, the simultaneous determination of DA and AA or the selective determination of DA in the presence of AA is feasible at the RuOx–Nf–GC-modified electrode. RuOx–Nf–GC electrode showed higher electrocatalytic response towards AA and DA than RuOx–GC electrode (Fig. 7a curve c). This improvement may be due to the high loading of RuOx on Nafion surface. Moreover, the RuOx–Nf–GC electrode showed wide linear range (50 μM–1.1 mM) and lower detection limit (5 μM) for determination of DA which is much better than the only RuOx-modified electrodes [36, 37]. The improvement in the detection of DA was achieved by high loading of RuOx catalyst on Nafion-modified electrode. This study further proved that the application of Nafion in this film modified electrode.

The next attempt was taken to detect DA and AA simultaneously by using the RuOx–Nf–GC-modified electrode using CV. Figure 7b represents the CVs recorded at different concentrations of DA and AA. The oxidative peak current for DA was increased linearly with the increase in DA concentration. Furthermore, the peak current of AA also increased with respect to the solution concentration. Thus, it is confirmed that the responses of DA and AA at the RuOx–Nf–GC-modified electrode are independent.

Using differential pulse voltammetry, the effect of AA on the linear range and detection limit of DA at RuOx–Nf–GC-modified electrode was investigated. Figure 8 (curve a–

impossible to use the bare electrode for the voltammetric determination of DA in the presence of AA. Moreover, the RuOx–Nf–GC-modified electrode resolved the mixed voltammetric signals into two well-defined voltammetric peaks (curve b). Two well-defined oxidation peaks are observed at 0.318 and 0.609 V corresponding to the oxidations of AA and DA, respectively (curve b). RuOx–Nafion-modified electrode showed electrocatalytic activities towards DA and AA. This dual behavior may arise due to the hydrophilic and hydrophobic nature of the RuOx–Nafion film [48–50]. According to the earlier literature reports [36, 37], RuOx film can separate interfering AA signal peak from DA peak. Reduced regions on RuOx–Nafion may act as sites for oxidation of DA. Oxidized regions of RuOx–Nafion film could catalyze the oxidation of ascorbate anions. AA is readily oxidized well before the oxidation potential of DA is reached. Thus, the precise determination of DA in the
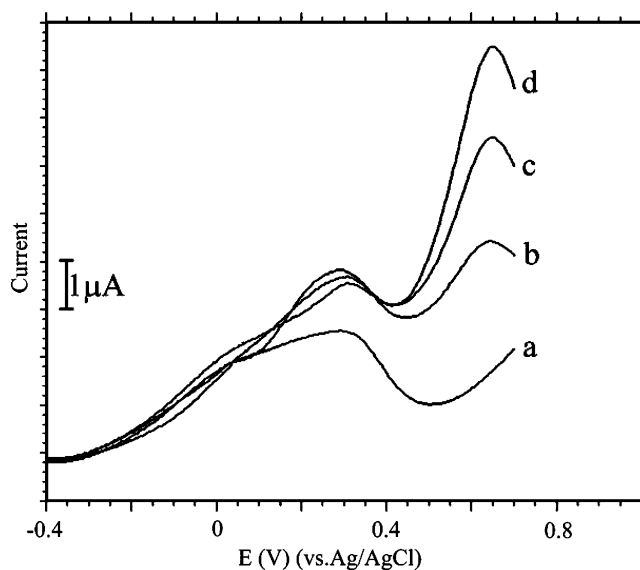

Fig. 8 Differential pulse voltammograms recorded in 0.1 M KNO$_3$ containing (a) 0.0 μM AA and DA, (b) 300 μM AA and 300 μM DA, (c) 300 μM AA and 400 μM DA and (d) 300 μM AA and 500 μM DA at RuOx–Nf–GC-film-modified electrode

Table 1 Results for the determination of ascorbic acid in pharmaceuticals

Vitamin C tablet samples	Labeled value (mg)	Proposed method[a] (mg)	RSD (%)
Sample 1	500	498.573	2.1
Sample 2	500	498.761	1.6
Sample 3	500	499.241	2.8

[a] Average of three replicate determinations

b) shows the voltammograms in the absence and presences of equal molar concentration of AA and DA. As seen in voltammograms, two well-defined oxidation peaks were observed for AA (0.291 V) and DA (0.645 V) at RuOx–Nf–GC electrode. Further, we increased only the concentration of DA (curve c–d); the catalytic peak currents were increased with respect to DA concentrations. There is no considerable change at the oxidation peak of AA which is indicated that AA is not interfering at this modified electrode. Also, the electrode responds linearly with respect to added DA concentrations as shown in Fig. 8c,d. We observed that linear range and detection limit were similar as we found in cyclic voltammetry. From this experiment, we have concluded that DA can be measured in the presence of AA at RuOx–Nf–GC-modified electrode.

In order to confirm the applicability of the proposed method, we have tested the method for the determination of ascorbic acid in Vitamin C tablets. An accurately weighed portion of finely powdered sample obtained from three tablets, equivalent to about 100 mg of ascorbic acid, was transferred to a 25-mL standard flask and dissolved in double distilled water and diluted to 25 mL. A 0.5-mL portion of extract was diluted with 10 mL of 0.1 M KNO₃ in a voltammetric cell, and catalytic current was measured at RuOx–Nf–GC-modified electrode. The obtained results for three tablet samples are given in Table 1. As seen in Table 1, the precision and reliability of the method is good. We have analyzed the spiked known amount of DA in vitamin C tablet solutions, and the mixed solutions are investigated under the identical condition used for simultaneous determination of AA and DA. As seen in Table 2, our proposed method can be applied for determination of dopamine and ascorbic acid in real samples accurately.

Table 2 Determination of dopamine in ascorbic acid tablet samples

Pharmaceutical samples	Added (μg/mL)	Found[a] (μg/mL)	RSD (%)	Recovery (%)
Sample 1	10	10.14	2.43	101.4
Sample 2	10	10.27	1.94	102.7
Sample 3	10	10.51	2.81	105.1

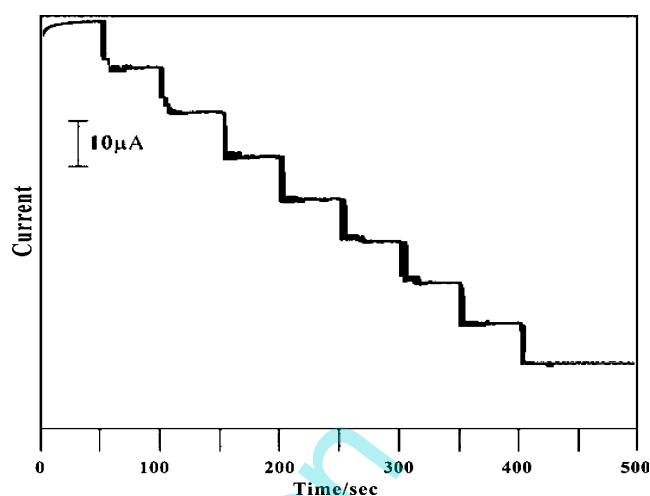[a] Average of three replicate determinations

Fig. 9 Amperometric current-time curves for eight successive addition of 50 μM DA into 0.1 M KNO₃ at RuOx–Nf–GC-film-modified electrode. Electrode rotation speed ~600 rpm and applied potential +600 mV (vs. Ag/AgCl)

Amperometric determination of DA

The catalytic oxidation of DA at RuOx–Nf–GC-modified electrode was carried out using amperometric technique in stirred solutions using an applied potential of 0.6 V to assure that all the mediator is quickly oxidized on the electrode surface. A typical amperogram is displayed in Fig. 9. A linear dynamic range was found between 50 μM–1.1 mM (r=0.999). The detection limit was 5 μM. The response is fast (10 s) and reproducible (3.9%, n=8). The reproducibility was evaluated from the slope of three calibration plots performed with different modified electrodes. The stability was evaluated carrying out calibration
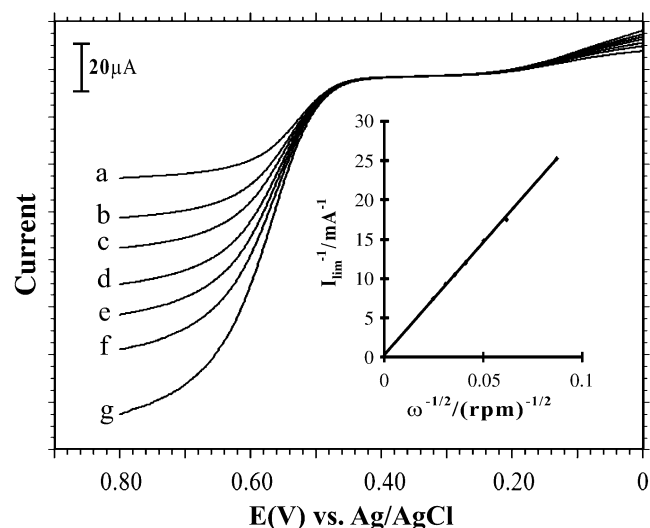

Fig. 10 RDE voltammograms of RuOx–Nf film adsorbed on a GC disk electrode in an aqueous 0.1 M KNO₃ solution with [DA] 350 μM and rotation rate (a) 200, (b) 400, (c) 600, (d) 900, (e) 1,200, (f) 1,600, and (g) 2500 rpm. Scan rate=0.015 V/s. *Inset* figure shows plots of I^{-1}_{lim} vs. $\omega^{-1/2}$

experiments after different periods of time and keeping the modified electrode in 0.1 M KNO$_3$ when not in use. The stable and reproducible results are obtained and 10% loss in peak current observed after a month. Nonetheless, the electrode modification is very simple and rapid; thus, the modified electrode can be easily prepared. To study the reproducibility of the sensor and reliability of fabrication procedure, seven times GC electrode was modified with RuOx–Nf film independently. CVs of modified electrodes were recorded in buffer solution. The relative standard deviation (RSD) value of measured anodic peak currents was 2.7%. Furthermore, the seven electrodes showed acceptable reproducibility with RSD of about 3.1% for the current determination of 400 μM DA.

Rotatable disk electrode studies

Figure 10 shows the RDE voltammograms of 350 μM DA present in 0.1 M KNO$_3$ solution at different rotation rates with the RuOx–Nf-film-modified glassy carbon disk electrode [51, 52]. The RDE data were analyzed using the Koutecky–Levich Equation [42, 53], and plotted as I^{-1}_{lim} vs. $\omega^{-1/2}$, as shown in the inset of Fig. 10.

$$1/I = 1/Ik + 1/I_{lim} \quad (3)$$

Where

$$I_{lim} = 0.62nFAD^{2/3}\omega^{1/2}\gamma^{-1/6}C^*0 \quad (4)$$

The parameter I is the measured limiting current of the disk, ω is the rotation rate, D and C_0 are the diffusion coefficient and the bulk concentration of DA, respectively, and γ is the kinematic viscosity of water in the experimental rotating rates. The surface coverage, Γ, was estimated to be 5×10^{-8} mol/cm^2 of the RuOx in Nafion film from the chronocoulometry charge. If we assume that the film undergoes a mediated reaction mechanism, then the rate constant of the chemical reaction, k, can be estimated to be an average value of $k = 2.1 \times 10^3 M^{-1}s^{-1}$.

Conclusions

Cyclic voltammetry was used to electrodeposit thin films of RuOx onto Nafion film. The as-formed thin RuOx–Nf layers exhibited high specific electrocatalytic activities towards AA and DA. The RuOx–Nf-modified electrode offers marked electrocatalytic effect for the oxidation of DA than only RuOx-coated electrode; this behavior may be due to higher loading of RuOx particles on Nafion-film-coated electrode. The wide linear range for DA detection was observed in this method than the previously

reported [36]. Cyclic voltammetry combined with EQCM were used to study the growth mechanism of the RuOx–Nf films. The result indicates that the redox process was confined to the surface confirming the immobilized state of the RuOx–Nf. The ease of preparation of the ruthenium microparticles dispersed in Nafion film results the good temporal stability and reproducibility, and the low detection limits justify the potential interest of this electrode as an electrochemical sensor for the determination of DA in the presences of AA.

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