

Electrochemical behavior of electrodeposited rutin film on a multi-wall carbon nanotubes modified glassy carbon electrode. Improvement of the electrochemical reversibility and its application as a hydrazine sensor

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Abstract By immobilizing rutin at the surface of a glassy carbon electrode (GCE) modified with multi-wall carbon nanotubes (MWCNT), a new modified electrode has been fabricated and its electrochemical behavior was investigated by cyclic voltammetry. Cyclic voltammograms of the resulting modified electrode show stable and a well defined redox couple with surface confined characteristics. The results show that the reversibility of rutin is significantly improved at a MWCNT modified GCE in comparison with GCE alone. The charge transfer coefficient, α , was calculated to be 0.4, and charge transfer rate constant, k_s , was 46.7 s^{-1} in pH 8, indicating great facilitation of the electron transfer between rutin and MWCNT deposited on the electrode surface. The rutin MWCNT (RMWCNT) modified GCE showed excellent mediation of hydrazine oxidation: a decrease in the overvoltage of hydrazine electrooxidation was observed as well as a dramatic increase in the peak current compared to that seen at a rutin modified GCE (RMGCE), activated GCE or bare GCE. Hydrazine was determined amperometrically at the surface of RMWCNT modified GCE in pH 8. Under the optimized conditions the calibration curve is linear in the concentration range 2.0–190.0 μM hydrazine. The detection limit and sensitivity are 0.61 μM and $0.0656 \mu\text{A } \mu\text{M}^{-1}$, respectively. Finally the kinetic parameters of the electron transfer coefficient, α , the heterogeneous rate constant of dependent to different potentials, $k'(E)$, and the standard heterogeneous rate constant, k^0 , for oxidation of hydrazine at the

RMWCNT surface were determined using various electrochemical methods. The advantages of this modified electrode for hydrazine determination are high sensitivity, excellent catalytic activity, short response time, wide linear range, and high exchange current density.

Keywords Electrocatalytic determination · Hydrazine · Multi-wall carbon nanotubes · Rutin · Voltammetric measurements

Introduction

Flavonoids are a large group of a polyphenolic compounds and widely distribute in fruits and vegetables [1]. Besides their important biological roles in plant pigmentation, flavonoids have gained tremendous interest over the past years because of their broad pharmacological activity and alleged anti-ageing properties, and their subsequent use in a great variety of health products [2, 3]. Rutin is one of a naturally occurring bioactive compounds, called vitamin P, which are present in substantial amount (0.5–1.5%) in plants [1]. It was formerly used in the treatment of diseases characterized by capillary bleeding with increased capillary fragility [4]. The literature on the electrochemistry and electrocatalytic affects of rutin is limited [5–10]. However, Zeng et al. investigated the voltammetric behavior and determination of rutin at a single-walled carbon nanotubes modified gold electrode [5]. Volikakis et al. [6], Bao et al. [7], He et al. [8], and Lin et al. [9] have reported determination of rutin using different modified electrode. Also, the preparation of a rutin embedded in lipid cast film at glassy carbon electrode and its use in the electrocatalysis

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of NADH [4] and ascorbic acid [10] was reported by Tang et al.

Carbon nanotubes are a kind of porous nanostructure material with properties such as high electrical conductivity, chemical stability, and high mechanical strength [11, 12]. The subtle electronic properties of carbon nanotubes suggest that they have the ability to promote electron transfer reaction when used as the electrode material in electrochemical reaction, which provides a new way in the electrode surface modification for designing new electrochemical sensors [13–17]. In the first part of this paper some of the electrochemical characteristics a rutin multi-walled carbon nanotubes (RMWCNT) modified glassy carbon electrode (GCE), which is prepared by the electrochemical deposition of the modifier (rutin) during the potential recycling at an multi-walled carbon nanotubes (MWCNT) modified GCE, was described. The electrochemical properties of RMWCNT modified electrode have been investigated and compared with those obtained for a rutin modified GCE (RMGCE) and a glassy carbon electrode modified with rutin embedded in lipid cast film [4]. The pH effect on electrochemical behavior, transfer coefficient, and the electron transfer rate constant of surface-immobilized rutin were also measured.

Hydrazine is an excellent reducing agent because of its industrial and pharmacological significance [18, 19] a highly sensitive method is required for its reliable measurement. In addition, electrooxidation of hydrazine is the basis of fuel cells, and hence is a reaction of practical importance, due to its high capacity and no contamination [20]. Unfortunately, because of the large overpotential of hydrazine at conventional electrodes, it is not well suited for quantitation via conventional electrochemical approaches. Accordingly, during the last decade, many efforts have been made to lower the oxidation potential of hydrazine, in order to facilitate its voltammetric and amperometric detection at various chemically modified electrodes [21–29]. Similarly to some other naturally occurring organic substances with an *o*-hydroquinone ring in their structure, that show the good electrocatalytic effect for hydrazine [26–29] it seems that the use of rutin, with an *o*-hydroquinone ring in its structure, as modified could be important and could yield some new information about the catalysis of hydrazine reaction. Accordingly, in the second part of this report the activity of the RMWCNT modified GCE toward the electrocatalytic oxidation of hydrazine and its use as an amperometric sensor for hydrazine determination is described. Also, the electrocatalytic oxidation of hydrazine at rutin modified GCE (RMGCE), activated and bare GCE was investigated and the results compared with those obtained at RMWCNT modified GCE.

Experimental

Chemicals

Rutin (3,3',4',5,7-pentahydroxyflavone-3-rutinoside) was purchased from Fluka and used without further purification. Hydrazine and dimethyl formamide (DMF) were obtained from Merck and used as received. The multi-wall carbon nanotubes (>95% purity, 10–20 nm diameter, 5–20 μm length) were obtained from Nanolab Inc (Brighton, MA). All other reagents were of analytical grade and used without further purification. The immobilizing solution of MWCNT was prepared by introducing 5 mg of MWCNT into 5 ml of DMF. All other solutions were prepared with doubly distilled water.

Apparatus

All electrochemical studies were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Eco Chemico Utrecht, Netherlands) equipped with a 663 VA stand three-electrode cell from Metrohm and a personal computer for data storage and processing. This configuration contains a rutin multi-wall carbon nanotubes (RMWCNT) modified glassy carbon working electrode (2 mm diameter), a platinum auxiliary electrode and an Ag/AgCl (sat.), KCl (3 M) served as the reference electrode. All potentials were reported with respect to this reference electrode. A Metrohm derive shaft to rotate working electrode was used in amperometric detection. The experiments were carried out inside a faraday cage at room temperature (25 ± 1 °C).

Preparation of rutin and RMWCNT modified glassy carbon electrode

The procedure of preparation of the working electrodes of rutin and RMWCNT modified GCEs are as follows. Prior to use, the working electrode was polished mechanically with 0.05 μm alumina powder to a mirror finish and then rinsed with doubly distilled water. Electrochemical activation of the electrodes was performed by continuous potential cycling from -1.1 to 1.6 V at a sweep rate of 100 mV s^{-1} in 0.1 M sodium bicarbonate solution until a stable voltammogram was obtained. After rinsing with doubly distilled water, the different modified electrodes were prepared subsequently as follow. For fabrication of RMGCE the activated GCE was placed in a 0.1 M phosphate buffer solution pH 3 containing 0.3 mM rutin and was modified by 16 cycles of potential sweep between 350 and 600 mV at 25 mV s^{-1} . Also, a 15 μl of DMF-MWCNT solution (1 mg/1 ml) was placed directly onto the activated GCE surface and dried at room temperature to

form a MWCNT at the GCE surface and preparation of the MWCNT modified GCE. The effective surface area of the MWCNT modified electrode was determined as 0.03 cm^2 from cyclic voltammograms of 0.1 M KNO_3 solution containing $4.0 \text{ mM K}_3[\text{Fe}(\text{CN})_6]$, at different scan rates. The RMWCNT modified GCE was prepared by immerse of MWCNT modified GCE in 0.3 mM rutin solution ($\text{pH } 3$) and using 16 cycles of potential sweep between 350 and 600 mV at 25 mV s^{-1} . Finally, the modified electrodes were rinsed thoroughly with water and placed in 0.5 M phosphate buffer solution ($\text{pH } 8$). Subsequently, the potential was scanned for 30 cycles at 25 mV s^{-1} over the range of 10 to 300 mV so as to obtain a stable redox response for the surface-immobilized films. The results show that the initial decay observed in all case for redox response, might be due to the release of modifiers (rutin) that are bound weakly to the surface and can be displaced somewhat easily.

Results and discussion

Electrochemical behavior of RMWCNT modified GCE

Figure 1 shows cyclic voltammograms of RMGCE (curve a) and RMWCNT modified GCE (curve b) in 0.5 M phosphate buffer solution ($\text{pH } 8$) at scan rates of 25 mV s^{-1} . As can be seen, for RMGCE a cyclic voltammogram with low peak currents ($0.2 \mu\text{A}$), high peak separation (about 80 mV) and low background currents was observed. However, a pair of well defined redox couple of rutin was observed at the RMWCNT modified GCE (Fig. 1, curve b) with high peak response ($2.8 \mu\text{A}$), low peak potential separation (35 mV) and relative high background currents, suggesting that the

reversibility of rutin is significantly improved. Thus, we concluded that MWCNT will increase the surface area of the modified electrode, so the background voltammetric response and capacitances of the MWCNT-coated surface is higher than that for the bare surface. In addition, this value of peak to peak separation is lower than the 49 mV that is reported for rutin embedded in lipid cast film (DPPC-rutin film) at GCE [4]. For a reversible surface redox process in which no reactants from the solution take place, the peak separation should be zero [30, 31]. The relatively small peak separations might arise due to non-ideal behavior caused by the effects of charge transfer and uncompensated ohmic drop [30, 31]. Also, the peak currents of the RMWCNT are higher than the DPPC-rutin film [4]. Compared to the bare and DPPC-rutin film GCE [4], and considering an increase of the conductive area due to the porous interfacial layer of the MWCNT modified electrode, it may be that an electron can penetrate through the conductive porous channels onto the electrode more easily, leading to higher sensitivity. Thus, MWCNT can be used as a new material for immobilizing and electron transfer reactions of rutin. Figure 2a illustrates the cyclic voltammograms of RMWCNT modified GCE in 0.5 M phosphate buffer solution ($\text{pH } 8$) as the supporting electrolyte at various scan rates. When the potential was scanned between 10 and 300 mV , a surface-immobilized redox couple with formal potential (E^0) value 167 mV was observed. In addition, the formal potential, E^0 , is almost independent of potential scan rate for sweep rates ranging from 10 mV to 100 mV s^{-1} , suggesting facile charge transfer kinetics over this range of sweep rate. The formal potential is obtained from equation $E^0 = E_{p,a} - \alpha(E_{p,a} - E_{p,c})$ [32] and considering $\alpha=0.4$ (see below). As shown in Fig. 2a, the ratio of anodic to cathodic peak currents obtained at various scan rates is almost constant. Furthermore, the anodic and cathodic currents increase linearly with scan rate in the whole of worked sweep rates (Fig. 2b). The peak to peak potential separation ($\Delta E_p = E_{p,a} - E_{p,c}$) is about 35 mV for sweep rates below 100 mV s^{-1} . At high scan rates, the separation between peak potentials increase with increasing scan rates (Fig. 3a) indicating the limitation arising from charge transfer kinetics. In otherwords, this is the range of which the reaction appears as quasireversible [33]. The transfer coefficient, α , and the apparent heterogeneous charge transfer rate constant, k_s , for electron transfer between the electrode and a surface confined redox couple can be evaluated in cyclic voltammetry from the variation of the anodic and cathodic peak potentials with the logarithm of scan rates, according to the method described by Laviron [31]. For high scan rates, theory predicts a linear dependence of E_p upon $\log \nu$, which can be used to extract the kinetic parameters of α and k_s from the slope and intercept of such plots, respectively. We found that for scan rates above 4 V s^{-1} the value of $E_{p,a}$ and $E_{p,c}$ were proportional to the $\log \nu$

Fig. 1 Cyclic voltammograms of RMGCE (a) and RMWCNT modified GCE (b) in 0.5 M phosphate buffer solution ($\text{pH } 8$) at scan rate of 25 mV s^{-1}

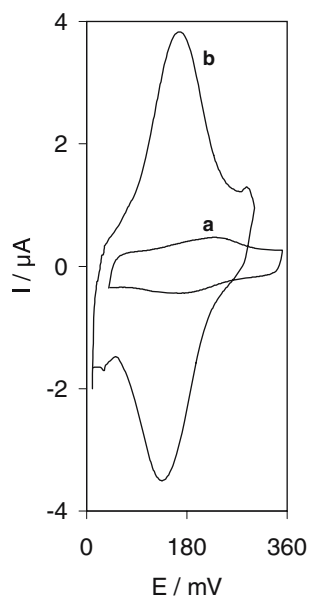
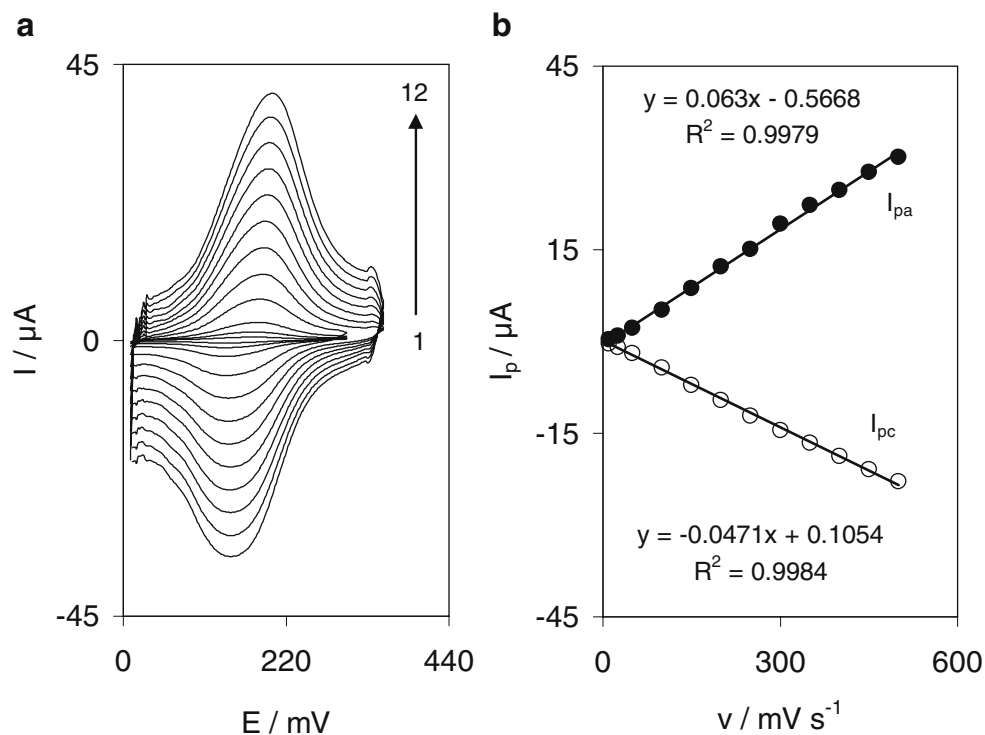


Fig. 2 (a) Cyclic voltammograms of RMWCNT modified GCE in different scan rates. The numbers of 1–12 correspond to 10, 25, 50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 mV s^{-1} sweep rates, respectively. (b) Dependence of peak currents on the scan rate



(Fig. 3b). Although in the present case the values of k_s and α were pH dependent, using this plots at pH 8 the value of 46.7 s^{-1} and 0.4 were obtained for these kinetic parameters. This value of k_s is significantly higher than those previously reported for electrodes modified by some other compounds with catechol ring [28, 34–36]. Such a difference seems to be due to the high ability of MWCNT to promote electrons between rutin and the electrode surface.

Electrocatalytic properties of RMWCNT modified GCE for oxidation of hydrazine

One of the objectives of this work was the development of a modified electrode capable of the electrocatalytic oxidation of hydrazine. In order to test the potential electrocatalytic oxidation of different modified electrodes, the cyclic voltammetric response of RMWCNT modified GCE, RMGCE and activated GCE were obtained in the absence and presence of 1.0 mM hydrazine, and the voltammograms are presented in Fig. 4. At the RMWCNT modified electrode, the oxidation of hydrazine gave rise to a typical electrocatalytic response at 160 mV, with an anodic peak current that was greatly enhanced over that observed for the modified electrode alone and with virtually no current on the cathodic sweep (Fig. 4, curve b). The peak potential value of 160 mV is very close to that of the surface confined mediator anodic peak potential in the absence of hydrazine (Fig. 4, curve a). Cyclic voltammogram RMGCE in the absence of hydrazine is shown in Fig. 4, curve c. Under the same experimental conditions, the oxidation of

hydrazine at a RMGCE and activated GCE show irreversible waves with peak potentials at approximately 236 mV (curve d) and 580 mV (curve e), respectively, while at the bare GCE no current was observed in the presence of hydrazine (curve f). These results are in agreement with the facts reported in the literature that hydrazine catalytic oxidation is observed on DPPC-rutin modified GCE [4] and GCE after special pretreatment of the surface [37]. However, as can be seen, RMGCE and activated GCE show anodic peaks at more positive potentials and with low peak currents, with respect to RMWCNT modified GCE. Considering the porous interfacial layer of the MWCNT-modified GCE, in all probability an electron can penetrate through the conductive porous channels onto the electrode more easily and lead to higher response. Figure 5 shows the dependence of the voltammetric response of RMWCNT modified GCE on hydrazine concentration in different pH values (pH 6–8). As can be seen in Fig. 5a, inset d, the half wave peak potential, $E_{P/2}$, of electrocatalytic oxidation of hydrazine was pH dependent with a slope of -75.5 mV per unit of pH, which based on relation between $E_{P/2}$ and pH (Eq. (1)) [33] is very close to the anticipated Nernstian value -74 mV for a four electron, five proton process.

$$\begin{aligned}
 E_{P/2} &= E_{P/2}^{pH=0} - 2.303(mRT/nF)pH \\
 &= E_{P/2}^{pH=0} - (0.0592m/n)pH
 \end{aligned}
 \quad (1)$$

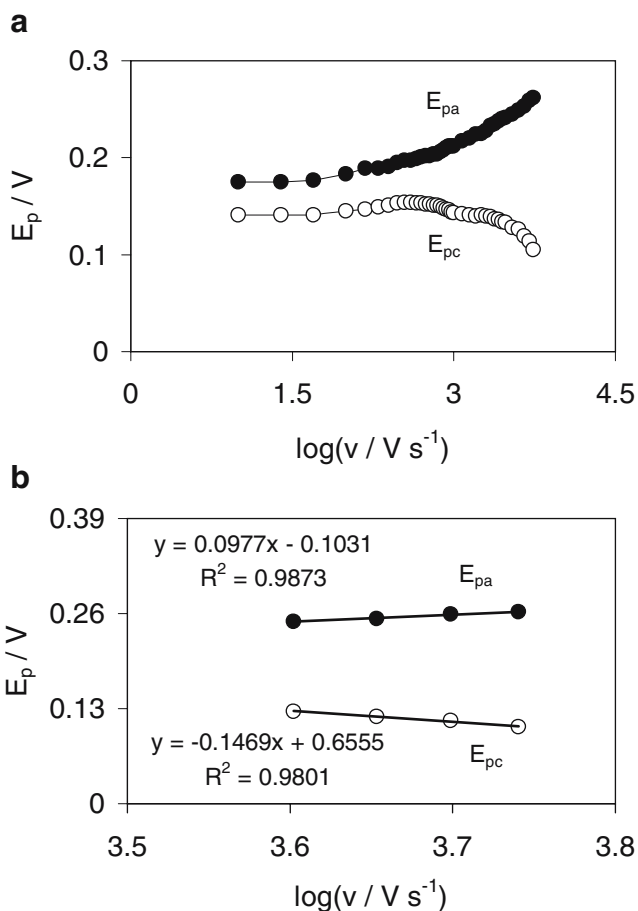


Fig. 3 (a) Experimental variation of the peak potentials versus the logarithm of the scan rate for a RMWCNT modified GCE in 0.5 M phosphate buffer solution (pH 8). (b) Magnification of the same plot for high scan rates

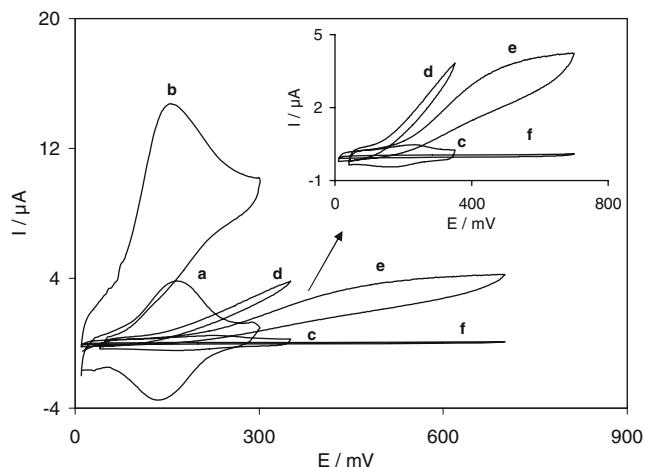


Fig. 4 Cyclic voltammograms of RMWCNT modified GCE in 0.5 M phosphate buffer solution (pH 8) at scan rate of 25 mV s⁻¹ in (a) absence and (b) presence of 1.0 mM hydrazine. (c) as (a) and (d) as (b) for an RMGCE. (e) and (f) as (b) for activated and bare GCE

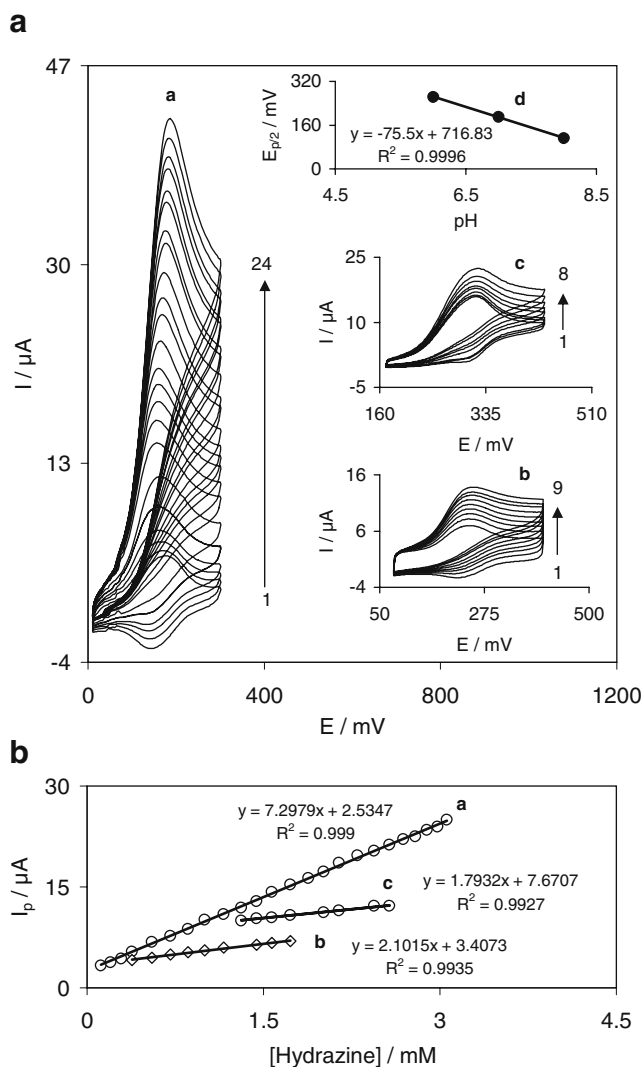


Fig. 5 (a) Cyclic voltammograms of RMWCNT modified GCE in 0.5 M phosphate buffer solution containing various concentrations of hydrazine at 25 mV s⁻¹ and at different pH. **a**) pH 8 in range 0.12–3.06 mM, **b**) pH 7 in range 0.38–1.73 mM and **c**) pH 6 in range 1.31–2.57 mM hydrazine. Inset **d** shows the variation of half wave potential, $E_{p/2}$, versus pH. **(b)** Effect of pH on the calibration curves of the electrocatalytic oxidation of hydrazine at RMWCNT modified GCE. **(a)** pH 8 in the linear range of 0.12–3.06 mM, **(b)** pH 7 in linear range 0.38–1.73 mM and **(c)** pH 6 in linear range 1.31–2.57 mM hydrazine

Here *m* and *n* are the number of protons and electrons in the redox reaction of hydrazine, respectively, and all other symbols have their conventional meanings. Consequently, for the whole range of $pH < pK_a^{N_2H_5^+}$, the electrode process corresponds to the following reaction.



Figure 5b shows the calibration plots of hydrazine catalytic oxidation at the modified electrode obtained at various solution pH. As can be ascertained from these curves for pH values lower than about the pK_a of protonated hydrazine ($pK_a^{N_2H_5^+} = 8.1$) [38], a decrease in

the sensitivity, slope of the calibration plots, and linear range is observed. Indeed, at this range of pH, hydrazine will be present in its protonated form and is then repulsed to some extent from the electrode surface during the anodic change of potential, which might be responsible for the observed effect. Approaching, pH to pK_a , the uncharged form of the substrate predominates, thus it appears as an increase in the sensitivity and linear range. Although the slopes of the calibration plots increase with increasing pH, the changes are not dramatic for pH value above 8. In addition, the linear range of calibration plots remained virtually unchanged. These results suggest a more effective interaction of hydrazine with the rutin film at slightly basic pH with respect to the neutral or acidic pH.

Cyclic voltammograms of a solution contains 1.0 mM hydrazine, in 0.5 M phosphate buffer (pH 8) using a RMWCNT modified GCE scanned at different scan rates are shown in Fig. 6a. As can be seen in the inset of Fig. 6a, the electrocatalytic peak currents increased linearly with the square root of scan rate. This result shows that the overall electrochemical oxidation of hydrazine at this electrode might be controlled by the diffusion of hydrazine from solution to the redox sites of the surface attached rutin. The points of linear sweep voltammograms Fig. 6a, show the rising part of voltammograms which is known as Tafel region and is affected by electron transfer kinetic between hydrazine and surface attached rutin, assuming the deprotonation of hydrazine as a sufficiently fast step. In this condition, the number of electrons involved in the rate determining step, n_α , and exchange current density, j_0 , can be estimated from the slope and intercept of Tafel plots [33]. Figure 6b shows the Tafel plots were drawn, derived from points of the Tafel region of the linear sweep voltammograms in Fig. 6a. The results of polarization studied for electrooxidation of hydrazine show that at whole of potential sweep rates, the Tafel slopes are in the range of 0.0107–0.0115 mV^{-1} (Fig. 6b). Assuming an average charge transfer coefficient of $\alpha=0.33$, the value obtained for the average of Tafel slope of different plots, agrees well with the involvement of one electron in the rate determining step of the electron transfer process. Also, the average value obtained for the exchange current density for hydrazine at the RMWCNT modified GCE was found to be $10.76 \mu\text{A cm}^{-2}$. This value is significantly higher than those reported for electrocatalytic reaction of hydrazine at coumestan and catechin films that are $0.4 \mu\text{A cm}^{-2}$ [27] and $0.8 \mu\text{A cm}^{-2}$ [28], respectively. Probably this improvement is due to the fact that MWCNT is highly permeable porous film and electrolytes can penetrate through the film and gain access to the interior surface [39]. Also, according to the approach of Andrieux and Saveant and using Fig. 2 in ref. [40], the average value of heterogeneous rate constant of hydrazine reaction at a

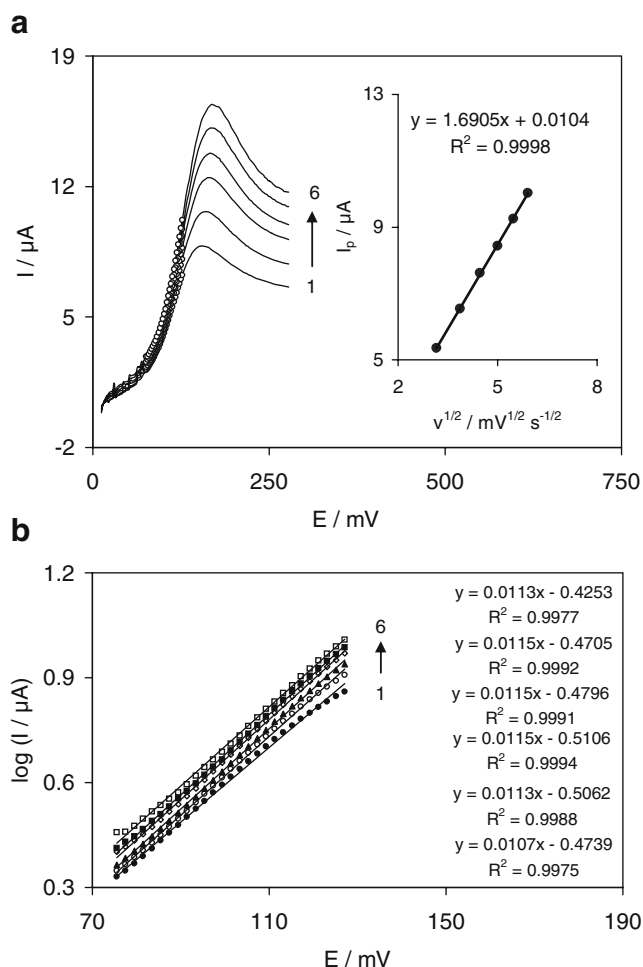


Fig. 6 Linear sweep voltammograms of RMWCNT modified GCE in 0.5 M phosphate buffer solution (pH 8) containing 1.0 mM hydrazine at different scan rates. The numbers 1 to 6 correspond to 10, 15, 20, 25, 30, and 35 mV s^{-1} sweep rates, respectively. The points are the data used in the Tafel plots. Inset shows the variation of the electrocatalytic current versus the square root of scan rate. (b) Tafel plots derived from linear sweep voltammograms shown in (a). The equations from bottom to top correspond to curves 1–6, respectively

RMWCNT modified electrode surface was calculated to be $1.12 \times 10^{-3} \text{ cm s}^{-1}$.

Amperometric studies of electrocatalytic oxidation of hydrazine at a RMWCNT modified electrode

Amperometry under stirred conditions has a much higher current sensitivity than cyclic voltammetry and it can be used to estimate the lower limit of detection of hydrazine. Amperograms obtained for different concentrations of hydrazine at potential step 220 mV and under conditions rotation speed 2000 rpm of RMWCNT modified electrode, are depicted in Fig. 7a. This figure is shown amperograms in the concentration ranges 0.0–29.5 μM (curve a), 29.5–86.1 μM (curve b), and 86.1–367.3 μM (curve c)

hydrazine. As shown in Fig. 7a (curve a), during the addition of even 2.0 μM hydrazine, a well-defined responses is observed. For each addition of hydrazine within a response time less than 2 s, a sharp rise in the current was observed. The plot of current versus hydrazine concentration is shown in Fig. 7b. The calibration plot was linear for a wide concentration range 2.0–190.0 μM hydrazine (Fig. 7b, inset) and has a slope of 0.0656 μA μM⁻¹ (sensitivity). At higher concentrations, there appears to be a deviation of the linear response, due most probably to the kinetic limitation. The lower detection limit, C_m, was obtained using the equation C_m = 3s_{bl}/m, where s_{bl} is the standard deviation of the blank response (μA) and m is the

slope of the calibration plots (0.0656 μA μM⁻¹). In this experiment, s_{bl}=0.0134 μA was obtained from the data of 18 replicate measurements on the blank solution and from the analysis of the data; we estimate that the limit of detection of hydrazine is on order of 0.61 μM. In Table 1, analytical parameters of electrocatalytic determination of hydrazine in this work are compared with the corresponding values previously reported for some modified electrodes [23–29, 41, 42]. As can be seen the proposed modified electrode shows somewhat similar (or worse), in some cases, or superior, in most cases, the previously reported modified electrodes.

The amperometric response of 10.0 μM of hydrazine on over 4000 s period (not shown) is indicated that after an initial decrease of current, the response of RMWCNT modified GCE remains almost stable throughout the experiment, indicates no inhabitation effect of hydrazine and their oxidation product for the modified electrode surface. Thus RMWCNT modified GCE was found to exhibit fast response time, high sensitivity, good detection limit, and wide linear range for hydrazine determination.

RMWCNT modified rotating disk electrode measurements in hydrazine solution

In order to elucidate the kinetics of electrocatalytic oxidation of hydrazine at a RMWCNT modified rotating disk GCE, RDE measurements were performed with different rotation speeds in 0.5 M phosphate buffer (pH 8) containing various different concentration of hydrazine. The results for a 1.5 mM solution of hydrazine are shown in Fig. 8a. The plots of currents measured at 100 mV versus ω^{1/2} (Levich plots), for different concentrations of hydrazine, are shown in Fig. 8b. The clear lack of linearity immediately suggests that the reaction is limited by kinetics of reaction between hydrazine and electrodeposited rutin at the modified electrode surface. In such cases, the Koutecky-Levich plots (plots of Γ⁻¹ versus ω^{-1/2}) can be used to determine transfer coefficient, α, heterogeneous rate constant, k', and standard heterogeneous rate constant, k⁰, of the reaction of hydrazine at a RMWCNT modified electrode surface [33]. Figure 8c shows the Koutecky-Levich plots using the data of Fig. 8b, and in this case, well-behaved linear responses are obtained. The Koutecky-Levich equation is formulated as Eq. (3) [33].

$$I^{-1} = (nFAk'C)^{-1} + (0.62nFA\nu^{-1/6}D^{2/3}\omega^{1/2}C)^{-1} \quad (3)$$

where ν is the kinematic viscosity (cm² s⁻¹), ω is the angular frequency of rotation (rad s⁻¹) and all other parameters have their conventional meanings. From the intercept of these plots, which were obtained by the measured currents at a potential of 100 mV, the mean value

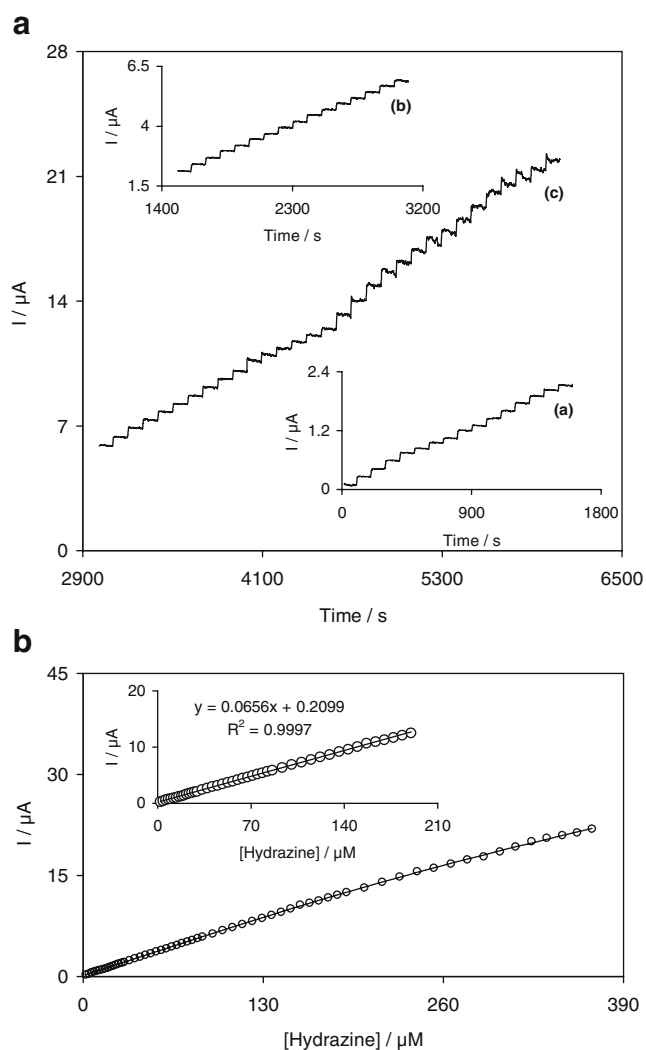


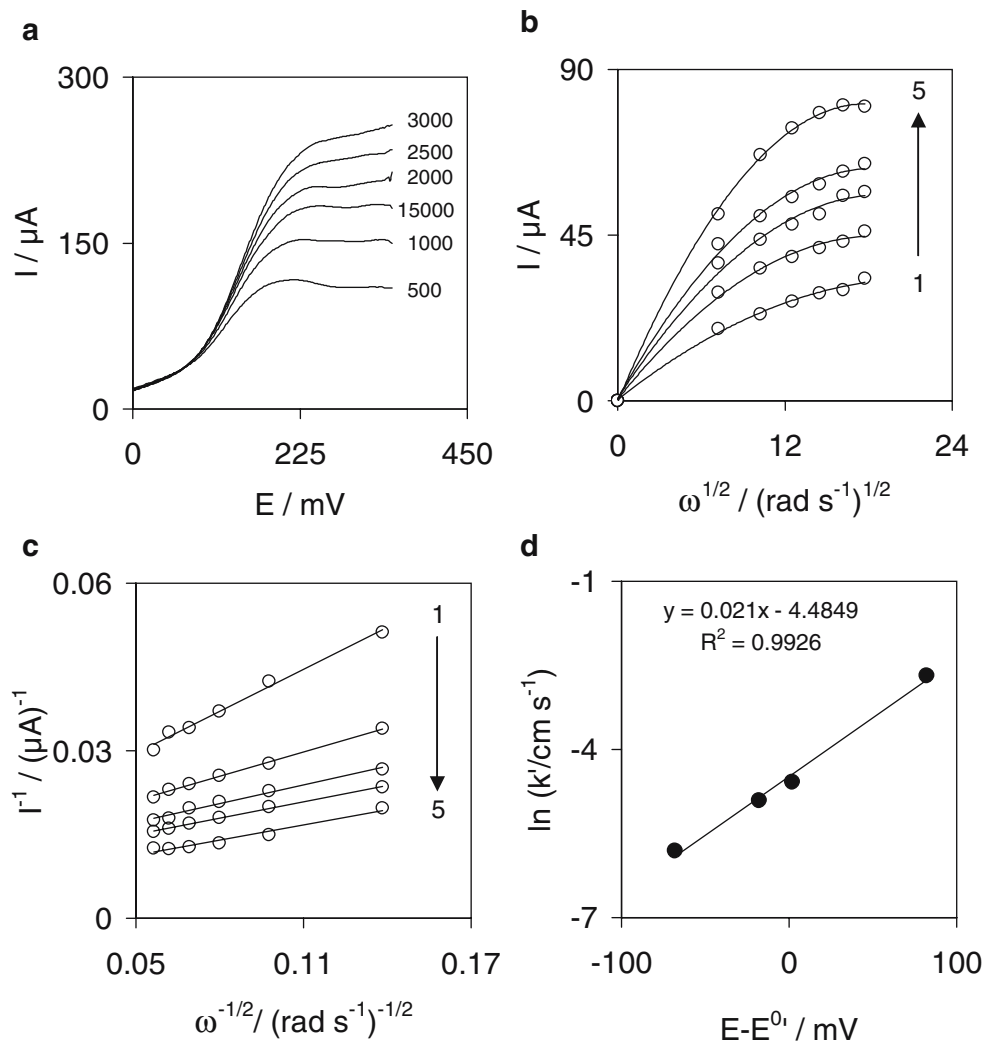
Fig. 7 (a) Amperograms of RMWCNT modified GCE kept in 220 mV in 10 ml, 0.5 M phosphate buffer solution (pH 8) for various successive additions of 2.0 mM hydrazine. Additions: (a) 15 addition of 10 μl, (b) 15 addition of 20 μl to (a) and (c) 15 addition of 40 μl and 15 addition of 80 μl to (b). (b) Variation of amperometric current versus hydrazine concentration in the range of 2.0–378.0 μM. Inset shows the calibration plot for the range of 2.0–190.0 μM hydrazine

Table 1 Comparison of analytical parameters of several modified electrodes for hydrazine determination

Modifier	Electrode	Method	Linear range (μM)	Detection limit (μM)	Sensitivity ($\mu\text{A } \mu\text{M}^{-1}$)	Ref.
Rhodium	CFME ¹	Amperometry	5.0–1000.0	0.62	0.00263	[23]
Palladium hexacyanoferrate	Aluminum	Amperometry	390–10000	4.6	0.1188	[24]
A salophen derivatives	GCE ²	Cyclic voltammetry	10–400	1.6	0.017	[25]
Chlorogenic acid	GCE	Chronoamperometry	50–3000	–	0.0054	[26]
A coumestan derivatives	CPE ³	Differential pulse voltammetry	1–40 40–400	0.66	6.1 3.0	[27]
Catechin	GCE	Amperometry	2.0–58.4 58.4–237.2	0.16	0.0084 0.0052	[28]
Cobalt phthalocyanine	GCE	Chronoamperometry	5000–21000	–	0.00049	[29]
Pyrocatechol violet	GCE	Amperometry	5.0–500.0	4.2	–	[41]
Caffeic acid	GCE	Amperometry	2.5–1000	0.4	3.16	[42]
Rutin	MWCNT GCE ⁴	Amperometry	2.0–190.0	0.61	0.0656	This work

¹ Carbon fiber microelectrode² Glassy carbon electrode³ Carbon paste electrode⁴ Multi-wall carbon nanotubes modified glassy carbon electrode

Fig. 8 (a) Voltammograms of a RMWCNT modified glassy carbon RDE in 0.5 M phosphate buffer solution (pH 8), containing 1.5 mM hydrazine at various rotation rates indicated for each voltammogram. (b) Levich plots constructed from RDE voltammograms of solutions with different concentrations of hydrazine. The number of 1 to 5 correspond to 1.5, 2.0, 2.5, 3.0 and 4.0 mM hydrazine and using currents for $E_{\text{disk}} = 100$ mV. (c) Koutecky–Levich plots obtained from Levich plots shown in (b). (d) Plot of the $\ln k'$ versus $E - E^{0'}$. E and $E^{0'}$ are the potentials which were considered for obtaining the Koutecky–Levich plots and the formal potential of rutin in worked conditions (pH 8)



of k' was found to be $3.01 \times 10^{-3} \text{ cm s}^{-1}$. This value of k' is in good agreement with that obtained by cyclic voltammetry in the previous section. Also, the mean values of k' , for different concentration of hydrazine, dependent on potentials 150, 170 and 250 mV were found to be 7.35×10^{-3} , 1.03×10^{-2} , and $6.83 \times 10^{-2} \text{ cm s}^{-1}$, respectively. As seen, the heterogeneous rate constant, k' , of electro-oxidation of hydrazine at the modified electrode surface is strongly potential dependent and increases with increasing the potential which is considered for obtaining the Koutecky-Levich plot. The k^0 and α can be calculated according to Eq. (4) [33].

$$k'(E) = k' = k^0 \exp \left[n_{\alpha} (1 - \alpha) F (E - E^{0'}) / RT \right] \quad (4)$$

where E and $E^{0'}$ are the potentials which are considered for obtaining the Koutecky-Levich plot and the formal potential of rutin, respectively. Figure 8d shows the plots of $\ln k'$ versus $E - E^{0'}$. According to Eq. (4) the values of k^0 and α can be determined from the intercept and the slope of Fig. 8d, respectively. The value of k^0 was found to be $1.13 \times 10^{-3} \text{ cm s}^{-1}$. Also, the slope of 0.021 mV^{-1} was obtained, indicating that one electron process was involved in the rate determining step, $n_{\alpha} = 1$, assuming a charge transfer coefficient of $\alpha = 0.46$. This α value is higher than 0.33 that was obtained from Tafel plots in the previous section.

Conclusion

Electrochemical behavior of a rutin multi-wall carbon nanotube (RMWCNT) modified GCE and a rutin modified GCE (RMGCE) shows that using MWCNT in the modified electrode structure, the reversibility of rutin and its electrocatalytic activity toward hydrazine oxidation are significantly improved. The RMWCNT modified electrode offers a marked decrease in the overvoltage and an increase in peak current for the hydrazine oxidation and it was used for fast amperometric detection of hydrazine at low potentials. The values $1.13 \times 10^{-2} \text{ cm s}^{-1}$ and 0.46 were obtained for the standard heterogeneous rate constant, k^0 , and transfer coefficient, α , respectively, between the deposited rutin layer and hydrazine. The overall number of electrons involved in the catalytic oxidation of hydrazine and the number of electron involved in rate determining step were obtained as 4 and 1, respectively. The electrocatalytic oxidation of hydrazine at the modified electrode is strongly dependent on hydrazine solution pH.

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