

Graphene Oxide Doped Poly(hydroxymethylated-3,4-ethylenedioxythiophene): Enhanced Sensitivity for Electrochemical Determination of Rutin and Ascorbic Acid*

Li-ping Wu^{a, b}, Long Zhang^b, Li-min Lu^{a**}, Xue-min Duan^b, Jing-kun Xu^{b**} and Tao Nie^a

^a College of Science, Jiangxi Agricultural University, Nanchang 330045, China

^b Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, China

Abstract A novel graphene oxide doped poly(hydroxymethylated-3,4-ethylenedioxythiophene) (PEDOT-MeOH/GO) composite film was synthesized and utilized as an efficient electrode material for simultaneous detection of rutin and ascorbic acid (AA). PEDOT-MeOH/GO films were synthesized on glassy carbon electrode (GCE) by a facile one-step electrochemical approach and were characterized by scanning electron microscopy, UV-Vis spectroscopy, FTIR spectra and electrochemical methods. Then the PEDOT-MeOH/GO/GCE was applied successfully in the simultaneous detection of rutin and AA. The results showed that the oxidation peak currents of rutin and AA obtained at the PEDOT-MeOH/GO/GCE were much higher than those at the traditional conducting polymer PEDOT/GO/GCE, PEDOT-MeOH/GCE, PEDOT/GCE and bare GCE. Under optimized conditions, the linear ranges for rutin and AA are 20 nmol/L–10 μ mol/L and 8 μ mol/L–1 mmol/L, respectively. The detection limit is 6 nmol/L for rutin and 2 μ mol/L for AA (S/N = 3), which are lower than those of the reported electrochemical sensors.

Keywords: Conducting polymer; Graphene oxide; Nanocomposites; Simultaneous determination; Electrochemical sensor.

INTRODUCTION

Conducting polymer composites have attracted much attention for a variety of applications because of their many features including low weight, low cost, corrosion resistance, and ease of processing and shaping^[1, 2]. To date, the combination of conducting polymer with carbon materials, such as fullerenes and carbon nanotubes has been widely studied because of their outstanding properties, such as electrochemical, thermal and mechanical properties^[3, 4]. However, different from the mentioned carbon materials, graphene oxide (GO) has created a new field of carbon-filled nanocomposites in recent years. GO, the oxidation form of graphene, bears two-dimensional plane and lots of functional groups, such as carboxyl, hydroxyl and epoxide, rendering it hydrophilic and dispersible in aqueous solutions^[5, 6]. This property, along with its abundance of negatively charged carboxyl groups, makes it an excellent dopant for the electropolymerization of polymer-based nanocomposites^[7].

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** Corresponding authors: Jing-kun Xu (徐景坤), E-mail: xujingkun@tsinghua.org.cn

Li-min Lu (卢丽敏), E-mail: lulimin816@hotmail.com

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Poly(3,4-ethylenedioxythiophene) (PEDOT), one of the conducting polymers among the various families, has been studied extensively because it combines a low oxidation potential and moderate bandgap with good stability in the oxidized state, high conductivity and highly transparent in thin, oxidized films^[8,9]. In comparison with other conducting polymers, PEDOT was found to be much more stable and able to retain its conductivity even after storage at high temperatures. Combining the advantageous features of PEDOT and GO, Si *et al.* reported a facile electrodeposition method to fabricate the GO doped PEDOT (PEDOT/GO) film for the simultaneous determination of hydroquinone (HQ) and catechol (CT) as an electrochemical sensor^[10]. The modified electrode showed enhanced electron transfer properties and good electrocatalytic activity to the redox reactions of HQ and CT. Liu *et al.* prepared PEDOT/GO nanocomposites *via* interface polymerization of EDOT in the presence of GO^[11]. It is found that such PEDOT/GO nanocomposites exhibit good catalytic activity toward the oxidation of nitrite and can be used as a sensor for detection of nitrite.

Although PEDOT-based nanocomposites have so many advantages, the poor water solubility of 3,4-ethylenedioxythiophene (EDOT) is a major disadvantage, which limits their further application in biosensors. Recent studies show that the poor aqueous solubility of EDOT can be improved by addition of an appropriate pendant side group onto the backbone^[12]. EDOT-MeOH is one of the derivatives of EDOT, which exhibits higher solubility in water than EDOT^[13]. Moreover, the resulting PEDOT-MeOH film was proven to display better biocompatibility^[14,15], higher conductivity^[16] and better electrochemical properties^[17–19]. To date, however, little work has been reported on the synthesis of PEDOT-MeOH/GO composites *via* a direct electrodeposition approach and the study of their electrochemical performances.

Rutin (3',4',5,7-tetrahydroxyflavone-3 β -D-rutinoside), as a kind of the most abundant bioactive flavonoid called as vitamin p, is widely present in multivitamin preparations and more than 70 herbal remedies. As a natural flavone derivative, rutin has a wide range of physiological activities including anti-inflammatory, hemostat, antibacterial, anti-tumor and anti-oxidant^[20–22]. Based on these properties, rutin is always used clinically as the therapeutic medicine^[23]. Ascorbic acid (AA), known as vitamin C, is a powerful water-soluble antioxidant. It plays a key role in protecting living cells against oxidative injury and has been used clinically for the treatment and prevention of scurvy, common cold, mental illness, cancer and AIDS^[24]. As to the efficacy, some works have claimed better results from the use of rutin in combination with AA than from rutin alone in pharmaceutical preparations. Furthermore, rutin and AA often present together in fruits, vegetables, teas and Chinese herbs^[25]. Therefore, developing a simple, sensitive and accurate analytical method for the simultaneous determination of rutin and AA is of great significance.

Up to now, a number of techniques such as spectrophotometry^[26], capillary electrophoresis^[27–29], high-performance liquid chromatography^[30] and electrochemical methods^[25,31], were employed for the determination of rutin and AA. Among these methods, electrochemical method is simple and sensitive. However, the sensitivity and selectivity of electrochemical method usually depends on the electrode material.

Herein, we for the first time report a facile one-step electrochemical approach to the synthesis of high quality PEDOT-MeOH/GO film on a glassy carbon electrode (GCE) by using GO and EDOT-MeOH as the starting materials. It is found that the PEDOT-MeOH/GO/GCE exhibited good electrochemical performance and good electrocatalytic activity to the redox reactions of rutin and AA. Thus, the prepared PEDOT-MeOH/GO was used for the simultaneous determination of rutin and AA as an electrochemical sensor. The proposed method possesses several advantages such as wide linear range, excellent repeatability and long-term stability, low cost, environmentally friendliness and simplicity.

EXPERIMENTAL

Reagents

Rutin and ascorbic acid were purchased from Aladdin and Bio Basic Inc, respectively. EDOT was purchased from Aldrich. EDOT-MeOH was synthesized by our research group. GO was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Rutin and ascorbic acid stock solutions (0.01 mol/L) prepared with absolute

ethyl alcohol and double-distilled deionized water were stored at 278–281 K. The supporting electrolyte was phosphate buffer solution (PBS) prepared with 0.1 mol/L NaH_2PO_4 and 0.1 mol/L Na_2HPO_4 . All reagents were analytically pure. All solutions were prepared by dissolving in double-distilled deionized water.

Apparatus

Scanning electron microscopy (SEM) analysis was performed using a Hitachi S-3000 N scanning electron microscope. The UV-Vis spectra were recorded on an Agilent 8453 UV-Vis spectrophotometer. Fourier transform infrared spectroscopy was obtained on a Bruker Vertex 70 Fourier spectrometer. The cyclic voltammetric measurements were carried out on a CHI 660D electrochemical workstation (Shanghai, China). A three-electrode cell (10 mL) was used with the modified glassy carbon electrode (GCE) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum foil electrode as the counter electrode. All potentials were measured and reported versus the SCE and all experiments were carried out at room temperature.

Preparation of PEDOT, PEDOT-MeOH, PEDOT/GO and PEDOT-MeOH/GO Modified GCEs

Before modification, the GCEs were polished to a mirror-like surface with 0.05 μm Al_2O_3 slurry, rinsed thoroughly with double distilled water, then washed successively with double distilled water, anhydrous ethanol and acetone in an ultrasonic bath, and dried under N_2 before use.

PEDOT film was electrochemically deposited on the GCE by cyclic voltammetry (CV) with potential scanning between -0.2 V and 1.2 V with a sweep rate of 100 mV/s at room temperature for 15 cycles in a fresh solution containing 0.01 mol/L EDOT + 0.02 mol/L LiClO_4 .

PEDOT-MeOH film was electrochemically deposited on the GCE by CV with potential scanning between -0.2 V and 1.2 V with a sweep rate of 100 mV/s at room temperature for 15 cycles in a fresh solution containing 0.01 mol/L EDOT-MeOH + 0.02 mol/L LiClO_4 .

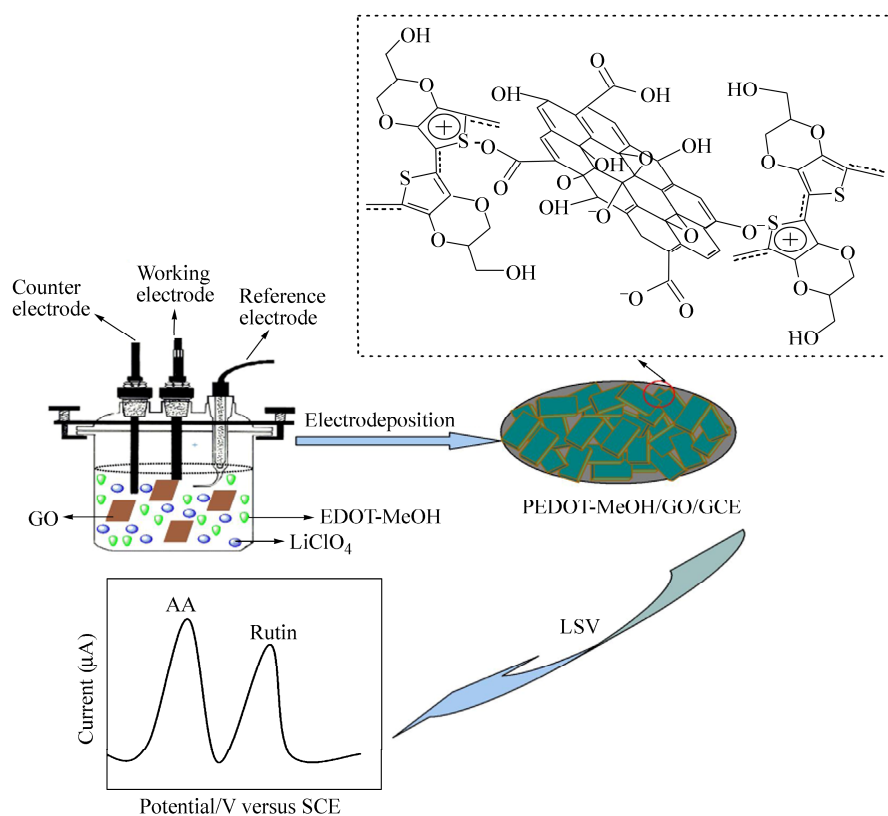
PEDOT/GO film was electrochemically deposited on the GCE by CV with potential scanning between -0.2 V and 1.2 V with a sweep rate of 100 mV/s at room temperature for 15 cycles in a fresh solution containing 0.01 mol/L EDOT + 1.0 mg/mL GO + 0.02 mol/L LiClO_4 .

PEDOT-MeOH/GO film was electrochemically deposited on the GCE by CV with potential scanning between -0.2 V and 1.2 V with a sweep rate of 100 mV/s at room temperature for 15 cycles in a fresh solution containing 0.01 mol/L EDOT-MeOH + 1.0 mg/mL GO + 0.02 mol/L LiClO_4 . After polymerization, the modified electrodes were rinsed with distilled water (shown in Scheme 1).

RESULTS AND DISCUSSION

Fabrication and Characterization of PEDOT, PEDOT-MeOH, PEDOT/GO and PEDOT-MeOH/GO Films

The PEDOT (a), PEDOT/GO (b), PEDOT-MeOH (c) and PEDOT-MeOH/GO (d) films were electropolymerized onto the GCEs by CV. As can be seen from Fig. 1, the CVs of EDOT and EDOT-MeOH show characteristic features as other conducting polymers, such as polythiophene and polypyrrole, during the potentiodynamic synthesis. As the CV scan continues, a polymer film is formed on the surface of GCE. The increase in the redox wave currents implies that the amounts of polymer on the electrode are increasing. The CVs of GCE in GO + EDOT aqueous solution and GO + EDOT-MeOH aqueous solution are shown in Fig. 1(b) and Fig. 1(d), respectively. The trend of the CVs in GO + EDOT solution and GO + EDOT-MeOH solution were similar to those in EDOT and EDOT-MeOH. While the difference between these electropolymerization processes is the current response, the polymerization current densities recorded during the backward potential scan for PEDOT/GO composite films or PEDOT-MeOH/GO composite films were larger than those of pure PEDOT film or PEDOT-MeOH film.



Scheme 1 The fabrication of PEDOT-MeOH/GO modified GCE for simultaneous detection of rutin and AA

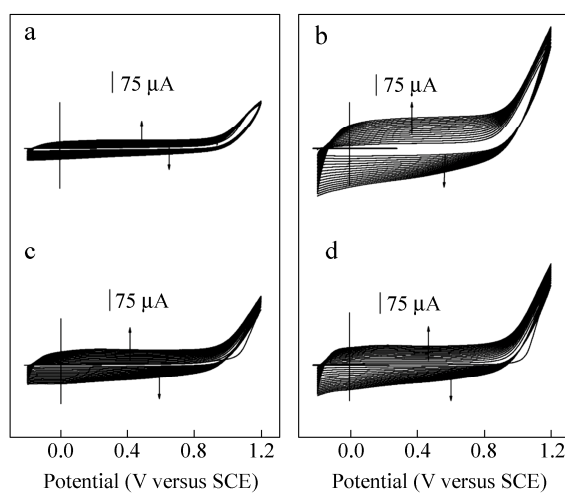


Fig. 1 CVs of GCE in 0.01 mol/L EDOT (a), 0.01 mol/L EDOT + 1 mg/mL GO (b), 0.01 mol/L EDOT-MeOH (c) and 0.01 mol/L EDOT-MeOH + 1 mg/mL GO (d) at a sweep rate of 100 mV/s in the potential range between -0.2 V and 1.2 V

The morphological characters of the as-synthesized PEDOT, PEDOT-MeOH, PEDOT/GO and PEDOT-MeOH/GO films electropolymerized on ITO glasses were investigated by SEM. As shown in Fig. 2(a) and Fig. 2(c), the PEDOT film and PEDOT-MeOH film grow regularly and present twisty structure. After doped with GO, the PEDOT/GO and PEDOT-MeOH/GO composite films (Figs. 2b and 2d) show high roughness and

loose structure formed by wrinkled paper-like sheets. There is no doubt that such open structure of the composite films can promote the diffusion of the ions or target analytes from the electrolyte to the electrode surface. And the well-combination of GO with PEDOT and PEDOT-MeOH may provide a large surface area for the design of the electrochemical sensor.

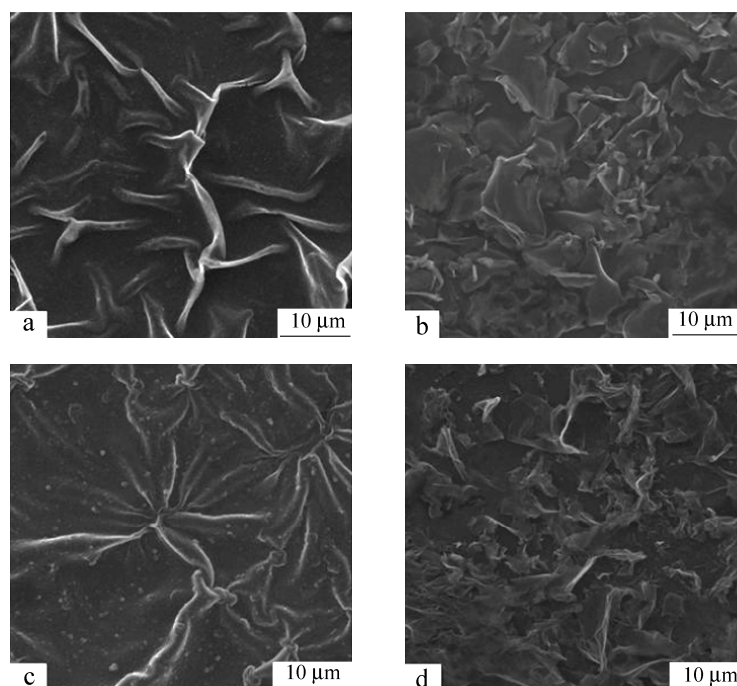


Fig. 2 SEM images of PEDOT (a), PEDOT/GO (b), PEDOT-MeOH (c) and PEDOT-MeOH/GO (d)

FTIR spectra of GO, PEDOT, PEDOT/GO, PEDOT-MeOH and PEDOT-MeOH/GO composites are shown in Fig. 3. In the GO spectrum (a), the peak at 3430 cm^{-1} corresponds to the O—H bond, the peak at 1625 cm^{-1} corresponds to the C=C bond and peaks at 1731 , 1388 , 1221 and 1053 cm^{-1} are ascribed to oxygen-based functional groups such as C=O carbonyl, C—O carboxy, C—O epoxide/ether and C—O alkoxy/alkoxide, respectively^[32]. In the PEDOT spectrum (b), the peaks at 1303 , 1522 and 1388 cm^{-1} are attributed to the stretching modes of C=C and C—C in the thiophene ring. The vibration modes of the C—S bond in the thiophene ring can be seen at 982 , 831 and 610 cm^{-1} . The bands at 1217 cm^{-1} and 1070 cm^{-1} are assigned to the stretching modes of the ethylenedioxy group^[33, 34]. Compared with PEDOT, the peak at 1303 cm^{-1} shifts to 1289 cm^{-1} in the FTIR spectrum of PEDOT/GO (c). In addition, new bands appear at 1733 cm^{-1} and 3400 cm^{-1} which are derived from the C=O carbonyl stretching and O—H bond of GO in the polymer chains. In the PEDOT-MeOH spectrum (d), the peaks at 1304 , 1522 and 1388 cm^{-1} are attributed to the stretching modes of C=C and C—C in the thiophene ring. The vibration modes of the C—S bond in the thiophene ring can be seen at 989 , 837 and 609 cm^{-1} . The bands at 1211 cm^{-1} and 1077 cm^{-1} are assigned to the stretching modes of the ethylenedioxy group. Compared with PEDOT-MeOH, the peak at 1304 cm^{-1} shifts to 1309 cm^{-1} in the FTIR spectrum of PEDOT-MeOH/GO (e). In addition, new bands appear at 1733 cm^{-1} and 3400 cm^{-1} which are derived from the C=O carbonyl stretching and O—H bond of GO in the polymer chains.

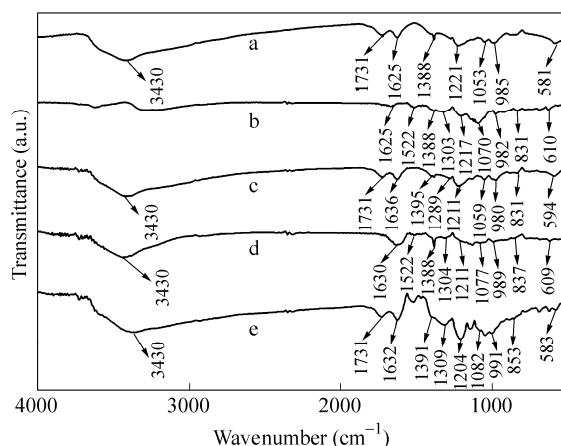


Fig. 3 FTIR spectra of GO (a), PEDOT (b), PEDOT/GO (c), PEDOT-MeOH (d) and PEDOT-MeOH/GO (e)

The structural characterization of PEDOT (a), PEDOT/GO (b), PEDOT-MeOH (c) and PEDOT-MeOH/GO (d) were further monitored by UV-Vis spectrum. It could be observed in Fig. 4 that all of the curves present absorption peaks near 370 nm, which may be attributed to π - π^* transitions in the benzenoid units of the polymer chain^[35]. While PEDOT (a), PEDOT/GO (b), PEDOT-MeOH (c) and PEDOT-MeOH/GO (d) exhibit broad absorbances at 724, 791, 785 and 821 nm, respectively, which are the feature typically seen in the partially doped (oxidized) state of PEDOT^[36]. All the two PEDOT bands in the PEDOT/GO and PEDOT-MeOH bands in PEDOT-MeOH/GO are shifted due to the interaction of polymer chain and GO sheets.

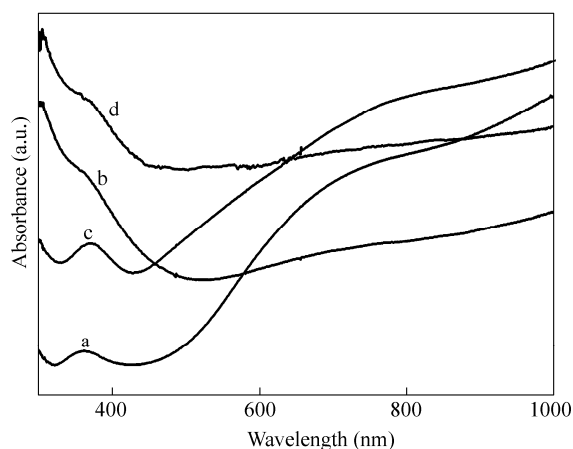


Fig. 4 UV-Vis spectra of PEDOT (a), PEDOT/GO (b), PEDOT-MeOH (c) and PEDOT-MeOH/GO (d)

Electrochemical Characterization of the Modified Electrodes

CV of ferricyanide system is a valuable and convenient tool to characterize the modified electrode. Figure 5 shows the CVs of different electrodes in 5.0 mmol/L $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (1:1) containing 0.1 mol/L KCl at a scan rate of 50 mV/s. The bare GCE (a) shows a pair of quasi-reversible peaks. The redox peak currents increase obviously after PEDOT (b) and PEDOT-MeOH (c) deposition onto the surface of GCE, indicating that the conducting polymer films could accelerate the electron transfer between the electrochemical probe $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and the GCE. As for PEDOT/GO/GCE (d) and PEDOT-MeOH/GO/GCE (e), the peak currents are higher than those of PEDOT/GCE (b) and PEDOT-MeOH/GCE (c), respectively. The reason might be that such open structure of the polymer/GO films can promote the faster ion diffusion/migration from the electrolyte to the electrode surface. Moreover, the well-dispersed sheets and well-combination of GO with polymer may lead to a large surface area of the conducting polymer/GO modified electrode^[10].

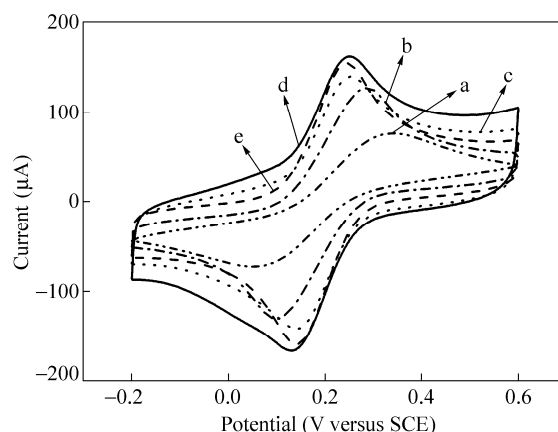


Fig. 5 CVs of bare GCE (a), PEDOT/GCE (b), PEDOT-MeOH/GCE (c), PEDOT/GO/GCE (d) and PEDOT-MeOH/GO (e) in 5.0 mmol/L $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1/1) containing 0.1 mol/L KCl at a scan rate of 50 mV/s

Electrocatalytic Behaviors of Rutin and AA on Modified Electrodes

The electrochemical behaviors of 50 $\mu\text{mol/L}$ rutin and 0.5 mmol/L AA at bare GCE (a), PEDOT (b), PEDOT/GO (c), PEDOT-MeOH (d) and PEDOT-MeOH/GO (e) modified GCEs in 0.1 mol/L PBS (pH 4.0) were investigated by CVs, and the results are shown in Fig. 6. At the bare GCE, a broad oxidation peak at 0.54 V was observed which was derived from the simultaneous oxidation of rutin and AA. It is obvious that the individual rutin and AA cannot be separated at the bare GCE. In contrast, two oxidation peaks, corresponding to the electrochemical oxidation of rutin and AA, were observed on other modified electrodes. The order of the oxidation peak currents of rutin and AA on these electrodes is as follows: PEDOT-MeOH/GO/GCE > PEDOT-MeOH/GCE > PEDOT/GO/GCE > PEDOT/GCE > bare GCE, which implies that the electrochemical oxidation behavior of rutin and AA on the bare GCE is improved significantly by PEDOT-MeOH, PEDOT and GO. The enhancement effect may be due to the large surface area and high adsorption capability of GO, and good electrochemical properties, good electrocatalytic properties of PEDOT-MeOH and PEDOT. This result further confirms that the PEDOT-MeOH/GO/GCE has excellent electrocatalytic properties for the oxidation and sensitive detection of rutin and AA.

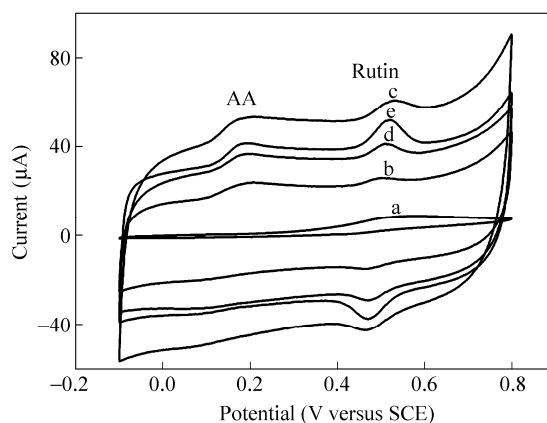


Fig. 6 CVs of 50 $\mu\text{mol/L}$ rutin and 0.5 mmol/L AA at bare (a), PEDOT (b), PEDOT/GO (c), PEDOT-MeOH (d) and PEDOT-MeOH/GO (e) modified GCEs in 0.1 mol/L PBS (pH 4.0)

Influence of pH Values

The effect of pH value on the determination of rutin and AA in the mixture at PEDOT-MeOH/GO/GCE was carefully investigated by linear sweep voltammograms (LSV) in a wider pH range (pH 2.0–7.0). It can be seen from Fig. 7, all the peak potentials for the oxidation of rutin and AA shifted negatively with higher pH value, indicating that protons took part in their electrode reaction processes. Furthermore, the relationship between the anodic peak potential and the pH value of rutin and AA was as following: $E_p = -0.051 \text{ pH} + 0.65$ ($R^2 = 0.9921$) and $E_p = -0.048 \text{ pH} + 0.35$ ($R^2 = 0.9932$) (Fig. 7b). Slope values obtained from the above equations for rutin and AA were 0.051 and 0.048 V/pH which were close to the anticipated Nernstian value (0.059 V/pH) for two electrons/two protons reactions.

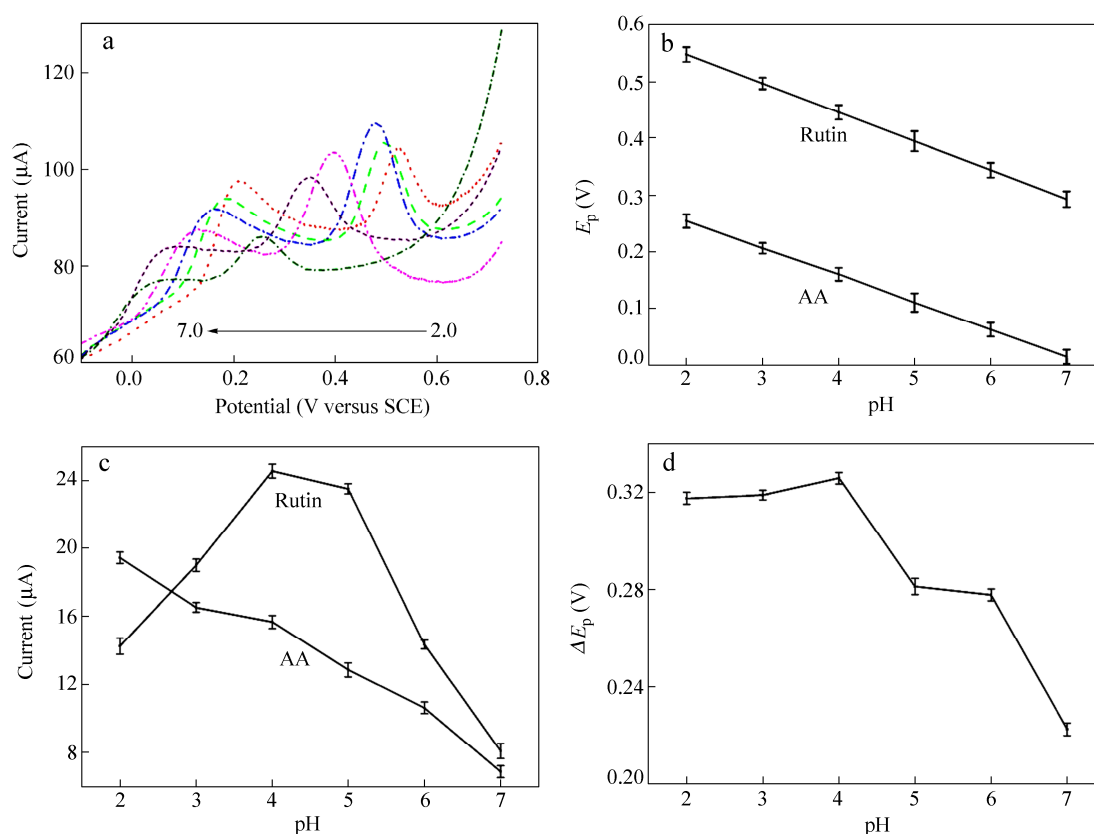


Fig. 7 (a) LSVs of 50 $\mu\text{mol/L}$ rutin and 0.5 mmol/L AA at different pH values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0) in PBS at PEDOT-MeOH/GO/GCE (Scan rate: 50 mV/s); (b) the influences of pH on oxidation peak potential of rutin and AA; (c) the influences of pH on the oxidation peak current of rutin and AA and (d) the influences of pH on the separation of peak potentials of rutin and AA

Moreover, it can be seen from Fig. 7(c) that the peak current of AA decreases with a higher pH value. The anodic peak current of rutin increases with an increasing in the solution pH until it reaches 4 and then decreases when the pH exceeds 4. Figure 7(d) shows the effect of pH on the separation of peak potentials. The maximum separation of peak potentials for rutin and AA is observed at pH 4.0. In order to obtain high sensitivity and selectivity, pH 4.0 was selected as an optimum pH value for the determination of rutin and AA in their mixture.

Influence of the Concentration of GO

In order to achieve high sensitivity, the concentration of GO suspension was explored. Figure 8 shows the changes of the peak current with different concentrations of GO, while the concentration of EDOT-MeOH was fixed to 0.01 mol/L . As can be seen from Fig. 8, the oxidation peak currents of rutin and AA increased

remarkably with the concentration of GO suspension from 0.25 mg/mL to 1.0 mg/mL, and then gradually decreased when further improving the amount of GO. The reason might be that GO possesses high accumulation efficiency and contains large number of oxygen-containing functional groups. Therefore, a small amount of GO will notably enhance the oxidation response. However, the GO sheet incorporated into the polymer film becomes compact when the amount is high, accompanied by decreased electric conductivity of PEDOT-MeOH. Apparently, the oxidation peak current decreased. Therefore, a concentration of 1.0 mg/mL GO was chosen to modify GCE for the simultaneous detection of rutin and AA.

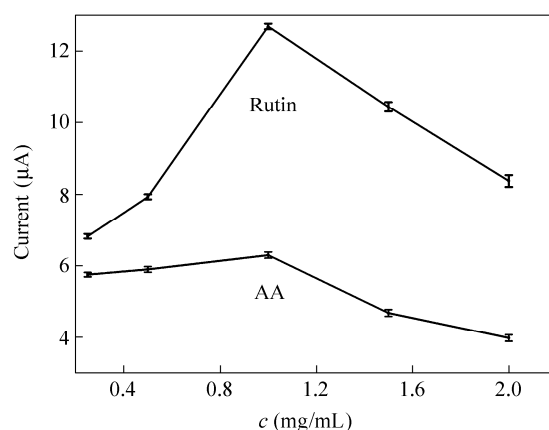


Fig. 8 Influence of the concentration of GO on the electrochemical response of 50 μmol/L rutin and 0.5 mmol/L AA

Influence of Scan Rate

The effect of scan rate on the oxidation of rutin and AA was investigated individually at PEDOT-MeOH/GO/GCE. The CVs obtained for rutin and AA at PEDOT-MeOH/GO/GCE in PBS (pH 4.0) at scan rates from 10 mV/s to 200 mV/s are shown in Fig. 9. As shown in Fig. 9, the redox peak currents for rutin and AA increased with increasing the sweep rates. Plots of the anodic peak currents intensified linearly as the scanning rate increased from 10 mV/s to 200 mV/s, which displayed the electrode reactions of rutin and AA were adsorption-controlled processes, according to the following equations: $I_{pa} (\mu A) = 4.710 + 0.662 V (mV/s)$ ($R^2 = 0.999$), $I_{pc} (\mu A) = -2.778 - 0.595 V (mV/s)$ ($R^2 = 0.999$) and $I_{pa} (\mu A) = 5.590 + 0.538 V (mV/s)$ ($R^2 = 0.999$), respectively.

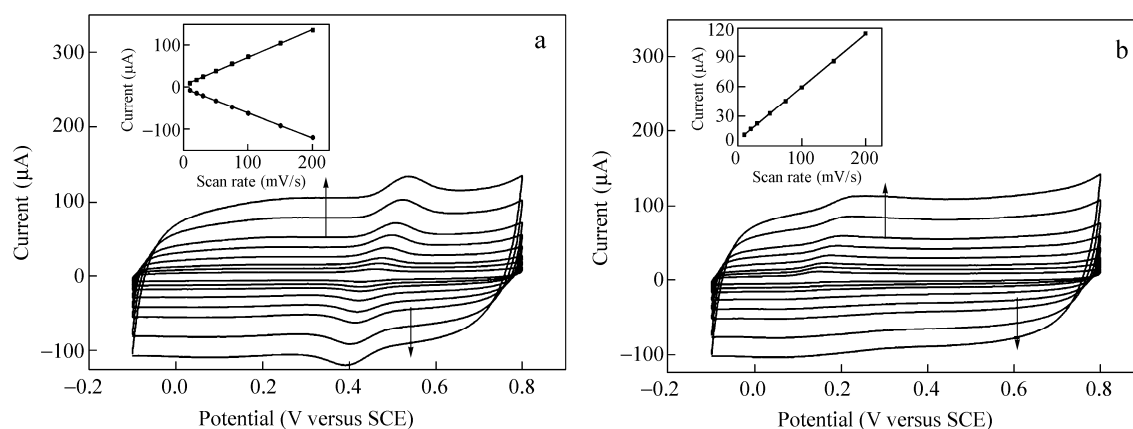


Fig. 9 (a) CVs of 50 μmol/L rutin at PEDOT-MeOH/GO/GCE at different scan rates of: 10, 20, 30, 50, 75, 100, 150, 200 mV/s; Inset: plots of redox peak current versus potential scan rates; (b) CVs of 0.5 mmol/L AA at PEDOT-MeOH/GO/GCE at different scan rates of: 10, 20, 30, 50, 75, 100, 150, 200 mV/s; Inset: plots of redox peak current versus potential scan rates

Simultaneous Determination of Rutin and AA Using PEDOT-MeOH/GO/GCE and PEDOT/GO/GCE, Respectively

LSV was performed to investigate the relationship between the peak current and concentration of rutin and AA. The individual determination of rutin or AA in their mixtures was performed when the concentration of one species changed while another as a constant. As can be seen in Fig. 10(a), under the optimal conditions, the oxidation peak current was linear with the concentration of rutin ranging from 20 nmol/L to 10 μ mol/L. The regression equation was $I (\mu\text{A}) = 1.07 C (\mu\text{mol/L}) + 0.43$ ($R^2 = 0.9941$) and the detection limit was 6 nmol/L ($S/N = 3$). Similarly, as shown in Fig. 10(b), the oxidation peak current of AA increased with its concentration from 8 μ mol/L to 1 mmol/L. A linear equation $I (\mu\text{A}) = 17.39 C (\text{mmol/L}) - 0.12$ ($R^2 = 0.9991$) was obtained and the detection limit was 2 μ mol/L ($S/N = 3$).

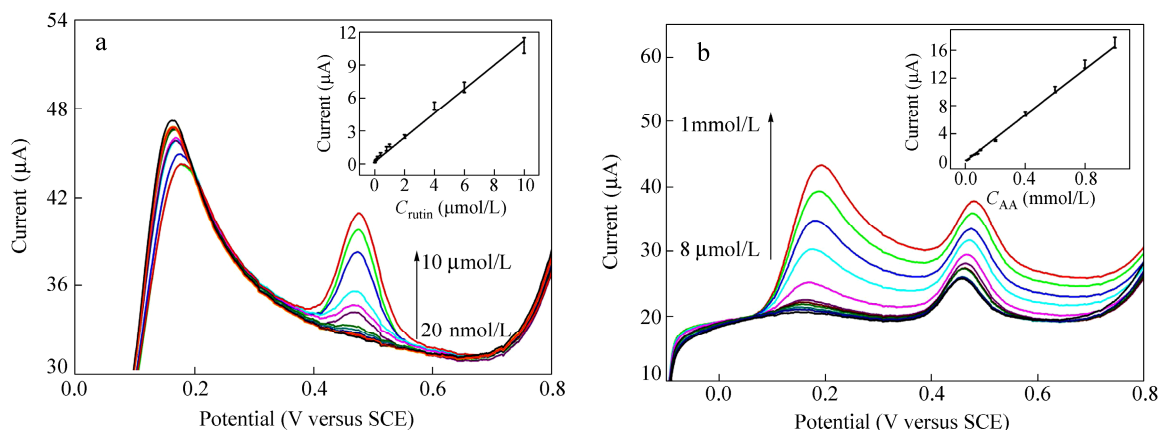


Fig. 10 (a) LSVs obtained at PEDOT-MeOH/GO/GCE in 0.1 mol/L PBS (pH 4.0) containing 0.5 mmol/L AA in the presence of different concentrations of rutin: 20 nmol/L, 60 nmol/L, 80 nmol/L, 0.1 μ mol/L, 0.2 μ mol/L, 0.4 μ mol/L, 0.8 μ mol/L, 1 μ mol/L, 2 μ mol/L, 4 μ mol/L, 6 μ mol/L and 10 μ mol/L; Inset: calibration plots of the oxidation peak current versus different concentrations of rutin. (b) LSVs obtained at PEDOT-MeOH/GO/GCE in 0.1 mol/L PBS (pH 4.0) containing 50 μ mol/L rutin in the presence of different concentrations of AA: 8 μ mol/L, 20 μ mol/L, 40 μ mol/L, 60 μ mol/L, 80 μ mol/L, 0.1 mmol/L, 0.2 mmol/L, 0.4 mmol/L, 0.6 mmol/L, 0.8 mmol/L and 1 mmol/L; Inset: calibration plots of the oxidation peak current versus concentration of AA

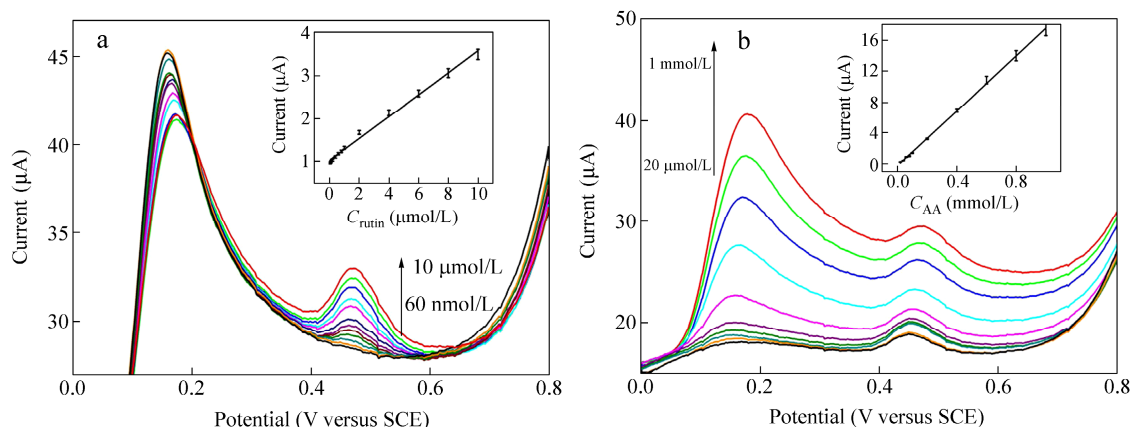


Fig. 11 (a) LSVs obtained at PEDOT/GO/GCE in 0.1 mol/L PBS (pH 4.0) containing 0.5 mmol/L AA in the presence of different concentrations of rutin: 60 nmol/L, 0.1 μ mol/L, 0.2 μ mol/L, 0.4 μ mol/L, 0.6 μ mol/L, 0.8 μ mol/L, 1 μ mol/L, 2 μ mol/L, 4 μ mol/L, 6 μ mol/L, 8 μ mol/L and 10 μ mol/L; Inset: calibration plots of the oxidation peak current versus concentration of rutin; (b) LSVs obtained at PEDOT/GO/GCE in 0.1 mol/L PBS (pH 4.0) containing 50 μ mol/L rutin in the presence of different concentrations of AA: 20 μ mol/L, 40 μ mol/L, 60 μ mol/L, 80 μ mol/L, 0.1 mmol/L, 0.2 mmol/L, 0.4 mmol/L, 0.6 mmol/L, 0.8 mmol/L and 1 mmol/L; Inset: calibration plots of the oxidation peak current versus concentration of AA

In addition, the oxidation peak current of rutin at the PEDOT/GO/GCE increased linearly with the increase in the rutin concentration from 60 nmol/L to 10 μ mol/L (Fig. 11a) and the corresponding linear function was I (μ A) = 0.25 C (μ mol/L) + 1.03 (R^2 = 0.9935). The detection limit was found to be 20 nmol/L (S/N = 3). Similarly, as shown in Fig. 11(b), the oxidation peak current of AA increased with its concentration from 20 μ mol/L to 1 mmol/L and the corresponding linear function was I (μ A) = 17.93 C (mmol/L) – 0.31 (R^2 = 0.9992). The detection limit was found to be 6 μ mol/L (S/N = 3). Table 1 gives the comparison of some of the analytical parameters obtained for rutin and AA in this study with other previous literatures. It can be observed that the proposed electrodes display good superiority in terms of linear ranges and limits of detection.

Table 1. The comparison of the fabricated sensor with reported electrochemical methods for the detection of rutin and AA

Electrode	Linear range (μ mol/L)		Determination limit (μ mol/L)		Reference
	rutin	AA	rutin	AA	
AuNPs/en/MWNTs/GCE ^a	0.048–0.96	–	0.032	–	[37]
SWCNTs/CILE ^b	0.1–800	–	0.07	–	[38]
PAA-MWCNTs/SPCE ^c	–	100–1000	–	49.8	[39]
SGNF/IL/CS/GCE ^d	–	30–350	–	14.8	[40]
MWCNTs-CHIT/ABPE ^e	0.02–10	1–400	0.01	0.8	[1]
PEDOT/GO/GCE	0.06–10	20–1000	0.02	6	This work
PEDOT-MeOH/GO/GCE	0.02–10	8–1000	0.006	2	This work

^a Gold nanoparticles/ethylenediamine/MWNTs/GCE;

^b SWCNTs/carbon ionic liquid electrode (CILE);

^c Polyacrylic acid-MWCNTs/ screen printed carbon electrode (SPCE);

^d Stacked graphene platelet nanofibers/ionic liquids/chitosan /GCE;

^e MWCNTs-chitosan/ acetylene black paste electrode (ABPE)

Reproducibility, Stability and Selectivity of the PEDOT-MeOH/GO/GCE

The reproducibility of PEDOT-MeOH/GO/GCE was examined by a series of 10 successive CV measurements for 50 μ mol/L rutin and 0.5 mmol/L AA (Fig. 12). The relative standard deviation (RSD) values of the anodic peak current were 0.88% for rutin and 1.33% for AA, indicating that the modified electrode had good reproducibility. For evaluating the long-term stability of the PEDOT-MeOH/GO/GCE, it was stored in the air at room temperature and used for monitoring 50 μ mol/L rutin and 0.5 mmol/L AA daily over a period of 4 weeks. The test results showed that there was no significant change of the current responses, indicating the PEDOT-MeOH/GO/GCE was quite stable. Possible interferences for the detection of rutin and AA at the PEDOT-MeOH/GO/GCE were investigated by adding various foreign species into a fixed amount of 10 μ mol/L rutin and 0.1 mmol/L AA. A relative error of 5% was considered tolerable. The results showed that most of the ions, as Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Al^{3+} in a 100-fold concentration, citric acid and amino acids in a 50-fold concentration,

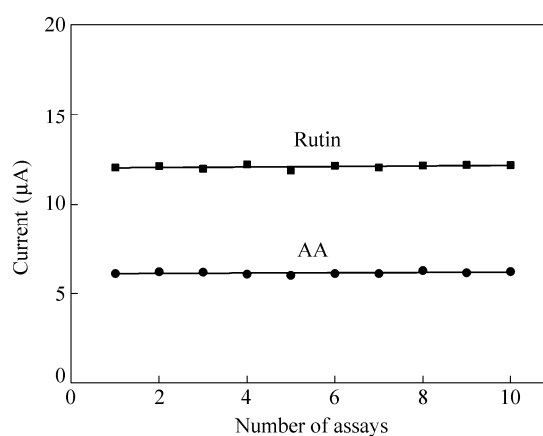


Fig. 12 The repeatability of the current response of the PEDOT-MeOH/GO/GCE in 0.1 mol/L PBS (pH 4.0) containing 50 μ mol/L rutin and 0.5 mmol/L AA for 10 successive assays

hesperidin, tangeretin, naringin and quercetin in a 100-fold concentration had no effect on the detection of rutin and AA.

Practical Sample Analysis

The analytical applicability of the PEDOT-MeOH/GO modified GCE for determination of rutin and AA was evaluated in urine samples. The urine samples were diluted 500 times with 0.1 mol/L PBS (pH 4.0) before the measurement to fit the calibration curve. Rutin and AA in urine samples were determined by the standard addition method to prevent any matrix influence. The analytical results are presented in Table 2. The obtained results showed that the recoveries were satisfactory. Thus, the modified electrodes can be successfully applied for the detection of rutin and AA in real sample analysis.

Table 2. Determination of rutin and AA in urine samples

Sample	Ingredient	Added ($\mu\text{mol/L}$)	Found ($\mu\text{mol/L}$)	Recovery (%)
1	rutin	10	9.96	99.6%
	AA	300	319	106.3%
2	rutin	30	30.18	100.6%
	AA	500	505.6	101.1%
3	rutin	50	48.57	97.14%
	AA	1000	998.6	99.86%

CONCLUSIONS

We have demonstrated a fast, green, effective and one-step electrochemical method to synthesize a novel PEDOT-MeOH/GO film using GO and EDOT-MeOH as the starting materials. The PEDOT-MeOH/GO film was used as a new electrode material for the fabrication of electrochemical sensor for simultaneous determination of rutin and AA. This novel composite film combines the advantages of PEDOT-MeOH and GO, exhibiting large surface area, high electrical conductivity, excellent catalytic activity as well as high adsorption capability. Wide linear concentration ranges, low detection limits and excellent reproducibility and stability were achieved on the sensor based on the PEDOT-MeOH/GO/GCE. The analytical performance of this method has been evaluated for simultaneous detection of rutin and AA in real samples and satisfying results were achieved.

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