Preparation of electrochemically reduced graphene oxide/multi-wall carbon nanotubes hybrid film modified electrode, and its application to amperometric sensing of rutin

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Abstract. Through a facile electrochemical method, we prepared an electrochemically reduced graphene oxide (ERGO)/multi-wall carbon nanotubes (MWNTs) hybrid film modified glassy carbon electrode (GCE), and characterized it by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and x-ray diffraction (XRD). The experimental results demonstrated that ERGO-MWNTs/GCE exhibited excellent electrocatalytic activity toward rutin as evidenced by the significant enhancement of redox peak currents in comparison with a bare GCE, ERGO/GCE and MWNTs/GCE. This method has been applied for the direct determination of rutin in real samples with satisfactory results.

Keywords. Multi-wall carbon nanotubes; grapheme; rutin; electroanalysis

1. Introduction

Rutin is one of the most abundant bioactive flavonoid, also called rutoside. As a natural flavone derivative, rutin has many physiological activities, such as antioxidant, hemostat, anti-inflammatory, anti-tumor, and anti-bacterial.^{1–3} It is often used as a clinical drug to strengthen capillaries and helps in treating easy bruising or bleeding of the skin.⁴ Scientists have been increasingly paying more attention to the development of the sensitive, economical, convenient and efficient detection of rutin. Many techniques have been developed for the detection of rutin, such as capillary electrophoresis,⁵ chemiluminescence,⁶ flow injection analysis,⁷ high-performance liquid chromatography (HPLC)⁸ and spectrophotometry.⁹ Nevertheless, some of the above mentioned methods are time-consuming, costly, and need complicated pre-processing, as well as professional technicians. Electrochemical detection is characterized by low-cost instrumentation, small dimensions, high sensitivity, simplicity and on-site monitoring. Different modified electrodes have been developed for the determination of rutin because it is an electroactive compound.^{10,11} However, higher selective

and more sensitive electrochemical techniques for the detection of rutin should be developed.

Graphene (GR), as a novel two-dimensional material, has attracted tremendous attention due to its remarkable characteristics, such as high specific surface area, electrical conductivity, chemical stability and good biocompatibility. The application of graphene in the field of electrochemical sensing had been reviewed.¹² Graphene is hydrophobic. Especially, it tends to form irreversible agglomerates or even restacks to form graphite owing to strong π – π interaction and van der Waals interactions,¹³ which is a limit for its further application. In general, graphene can be large-scale synthesized by chemical reduction of graphene oxide (GO) using different kinds of reducing agents, such as sodium borohydride and hydrazine hydrate.^{14,15} Recently, by cyclic voltammetry (CV)¹⁶ and constant potential method,¹⁷ a simple, fast and green electrochemical reduction of GO was developed to prepare graphene, which is suitable for the graphene modified electrode.^{18,19}

On the nanoscale, carbon nanotubes (CNTs) have attracted tremendous interest since their discovery in 1991.²⁰ Recent studies implied that CNTs used as electrode material can provide strong electrocatalytic activity. For example, CNTs can accelerate electron transfer of various molecules on the surface of electrode

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and increase the available electroactive surface area of various electroactive substances.²¹ Graphene is provided with excess of $15,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ electron mobility at room temperature but has problem of its agglomerates property between individual graphene sheets, and results in lower conductivity. To overcome the above-mentioned disadvantages, intermingling of graphene nanosheets with other carbon based nanostructures has been proposed.²² The introduction of CNTs not only effectively inhibits the aggregation and restacking of graphene nanosheets, but also supplies a higher surface area and more electroactive interaction sites.²³

In this paper, we prepared ERGO-MWNTs/GCE by CV. Experiments revealed that the redox peak currents of rutin could be remarkably enhanced on ERGO-MWNTs/GCE. In addition, The ERGO-MWNTs hybrids modified electrode could effectively separate the overlapping voltammetric response of rutin and ascorbic acid (AA) into two well-defined voltammetric peaks, which suggested that the ERGO-MWNTs/GCE could be used to determine rutin in the presence of a certain concentration of AA.

2. Experimental

2.1 Reagents and solutions

AA and rutin were purchased from National Institute for the Control of Pharmaceutical and Biological Products, China. Phosphate buffer solution (PBS) was prepared by mixing 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 at different ratios to adjust the pH value of 4.0. The Rutin Tablets and Compound Rutin Tablets were commercially available, and the labeled amount of rutin is 20 mg/tablet. Spectral graphite (about 30 μm , Shanghai Colloid Chemical Plant, China) used to synthesize GO, was obtained from Shanghai Carbon Co., Ltd. The multi-wall carbon nanotubes (diameter: 10–20 nm, length: 1–2 μm , purity > 95%) were obtained from Shenzhen Nanotech Port Co., Ltd. China. Nafion (wt. 5%) was purchased from Sigma. All the other chemicals used in this study were all of analytical grade. All experiments were completed in a supporting electrolyte of PBS (0.1 M, pH 4.0) at room temperature ($25 \pm 1^\circ\text{C}$).

2.2 Apparatus

CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd. Shanghai, China) was performed for all the electrochemical measurements. A

conventional three-electrode system was used, including a bare GCE ($d = 3 \text{ mm}$) or ERGO-MWNTs/GCE as working electrode, an Ag/AgCl (3 M) as reference electrode and a platinum wire electrode as auxiliary electrode. The morphology of the modified films was characterized using SEM (SEM, Hitachi S-4800 field emission scanning electron microscope (<http://www.hitachi-hita.com>)). All the pH values were measured with a PHS-3C precision pH meter (Leici Devices Factory of Shanghai, China), which was calibrated with standard buffer solution every day.

2.3 Preparation of ERGO-MWNTs/GCE

Firstly, GO was synthesized from spectral graphite by a modified Hummers' method.²⁴ Secondly, the pretreated GCE and the acidified MWNTs were obtained according to our previous report,²⁵ and then, in 10.0 mL 0.1% (w/w) Nafion methanol solution, adequate amount of GO and MWNTs were sonicated together for 30 min. to get 0.5 mg mL^{-1} GO-MWNTs homogeneous solution. Subsequently, 5.0 μL GO-MWNTs suspension was coated on the pretreated GCE evenly and dried at room temperature to get GO-MWNTs/GCE. Finally, in 0.1 M NaH_2PO_4 solution, the GO-MWNTs/GCE was reduced at a potential range of -1.6 – 0 V at 80 mV s^{-1} for 10 min. After reduction, the electrode surface was rinsed with ethanol and double-distilled water in turn, and dried with N_2 to achieve ERGO-MWNTs/GCE. GO/GCE, GRGO/GCE and MWNTs/GCE were prepared in a similar procedure.

2.4 Experimental procedure for electrochemical analysis

Before each measurement, the three-electrode system was installed in a blank solution, and cycled successively for three times at the potential of -0.2 – 0.8 V (vs. Ag/AgCl). The quantitative determination of rutin was achieved by measuring the oxidation peak current after background subtraction using differential pulse voltammetry (DPV). Five tablets of Compound Rutin Tablets or Rutin Tablets was ground into powder in an agate mortar, respectively. And then the average weight of one tablet was accurately weighed and dissolved in 10 mL ethanol. After ultrasonic dissolving for an hour, the mixtures were filtrated. In order to fit into the linear range of the proposed method, appropriate amount of the filtrate was diluted by a factor of 1/10,000 (v/v) with 0.1 M PBS (pH 4.0) for the measurement. The dilution process can actually help decreasing the matrix effect in real samples.

3. Results and discussion

3.1 Characterization of modified electrode

As shown in figure 1, the morphologies of different electrodes were characterized by SEM. The bare GCE presented a uniform and smooth surface (figure 1a). An obvious homogeneous membrane appeared on the ERGO/GCE (figure 1b), and the thin layer of ERGO sheets displayed a typical crumpled and folded structure. The morphology of the MWNTs/GCE (figure 1c) showed a network-like structure. Compared to the MWNTs/GCE, nanocomposite film of ERGO-MWNTs (figure 1d) exhibited the long tortuous network of MWNTs covered with the thin ERGO sheets completely, implying that ERGO and MWNTs evenly mixed together. The results may be the π - π stacking interaction between the hydrophobic regions of ERGO and the side walls of MWNTs, which avoided the aggregation of ERGO and kept the ERGO-MWNTs dispersing stably for long time.

The FTIR spectra for the pristine MWNTs, GO, GO-MWNTs and ERGO-MWNTs were shown in figure 2. C=O band characteristic of ketone/quinone on MWNTs was observed at $\sim 1635\text{ cm}^{-1}$, and the band of $\sim 1197\text{ cm}^{-1}$ was most probably due to the C-O stretching deformation vibration (figure 2a).²⁶ The spectrum of GO displayed three broad and intense peaks centered at around $\sim 1050\text{ cm}^{-1}$, $\sim 1623\text{ cm}^{-1}$ and $\sim 1735\text{ cm}^{-1}$

Figure 2. FTIR spectra of (a) MWNTs, (b) GO, (c) GO-MWNTs and (d) ERGO-MWNTs.

(figure 2b), while the band at $\sim 1050\text{ cm}^{-1}$ could be due to the C-O stretching mode of epoxy or alkoxy, and C=O in carboxylic acid and carbonyl moieties ($\nu(\text{carbonyl})$) at 1735 cm^{-1} ; C=C at $\sim 1623\text{ cm}^{-1}$ assigned to skeletal vibrations of unoxidized graphitic domains or contribution from the stretching deformation vibration of intercalated water.¹⁷ Interestingly, the spectra of GO-MWNTs hybrid material exhibited all the characteristic peaks of GO and MWNTs despite the lower peak intensity (figure 2c). Apparently, these peaks appeared due to the co-existence of GO along

Figure 1. SEM images of different electrodes: (a) bare GCE, (b) ERGO/GCE, (c) MWNTs/GCE and (d) ERGO-MWNTs/GCE.

with MWNTs in the hybrid. As the GO was electrochemically reduced (figure 2d), the adsorption bands of C=O in carboxylic acid and carbonyl moieties at $\sim 1735\text{ cm}^{-1}$ disappeared; the peak of C–O stretching mode of epoxy or alkoxy at $\sim 1050\text{ cm}^{-1}$ and the peak at $\sim 1623\text{ cm}^{-1}$ were considerably decreased, which confirmed the successful conversion of GO into ERGO.¹⁷

XRD could further support the characterization of GO and ERGO. XRD patterns of the GO and ERGO were recorded in figure 3. The feature diffraction peak of GO appeared at 10.1° (002) as the AB stacking order was observed in graphite oxide with layer-to-layer distance (d -spacing) of 0.849 nm. After the GO was electrochemically reduced, the diffraction peak of ERGO was at 26.4° , similar to the reported results.²⁷

3.2 Electrochemical reduction of GO-MWNTs

Figure 4 shows the electrochemical reduction of GO-MWNTs film at the potential range from 0 V to -1.6 V in 0.1 M NaH_2PO_4 . It can be seen that during the first cycle, a large cathodic peak appeared at -1.15 V due to the reduction of oxygen functional groups such as hydroxyl, epoxy and carboxyl groups residing on the surface of GO,²⁸ which proved the electrochemical reduction of GO to form ERGO-MWNTs.

3.3 Voltammetric behaviour of rutin at different electrodes

Figure 5 demonstrated CVs responses of the 8.0×10^{-5} M rutin at different electrodes in PBS (pH 4.0). It was found that the oxidation peak current (i_{pa}) of rutin at the ERGO/GCE (c) and MWNTs/GCE (d) were obviously higher than that of at the GO/GCE (b),

Figure 3. X-ray diffraction patterns of the (a) ERGO (b) and pristine GO.

Figure 4. Electrochemical reduction of GO-MWNTs hybrid for 14 cycles in 0.1 M NaH_2PO_4 (pH 4.7); scan rate 80 mV s^{-1} .

GO-MWNTs/GCE (e) and GCE (f). Compared to the ERGO/GCE and MWNTs/GCE, the redox peak currents at the ERGO-MWNTs/GCE (a) were remarkably higher. The experimental results might be attributed to the synergistic effect of the 3D nano-structured ERGO-MWNTs, including its large specific surface area and remarkable electric conductivity. The optimal ERGO-MWNTs/GCE showed the highest capacitive current value over the other control systems. It is related to the successful conversion of GO into ERGO. The excellent sp^2 hybridized structure of ERGO contributes to the high capacitive nature, which promotes the electron gain and loss of ions during charging/discharging.²⁹ In addition, this capacitance behaviour can be explained by that ERGO provides a high electrical conductivity and high specific surface area, allowing rapid and effective electron and ion transport.^{30,31}

3.4 Effect of scan rate on the response of rutin at ERGO-MWNTs/GCE

Figure 6a showed the CVs of 8.0×10^{-5} M rutin at the ERGO-MWNTs/GCE. In the range of $20\text{--}300\text{ mV s}^{-1}$, the redox peak current enhanced gradually along with the increase of the scan rate. The linear relationship of the anodic peak current and the scan rate (v) is corresponding to a regression equation: $i_{\text{pa}} = 0.0391v + 1.7356$ (i_{pa} : μA , v : mV s^{-1} , $r = 0.9978$) (figure 6b), which implied that the system presented features corresponding to an adsorption-controlled process of rutin at the ERGO-MWNTs/GCE. According to the reported paper,³² the adsorption of rutin on ERGO-MWNTs/GCE includes chemisorbed and physisorbed rutin is moieties. Concerned about the chemisorption, it may be that rutin is immobilized

Figure 5. CVs of (a) ERGO-MWNTs/GCE, (b) GO/GCE, (c) ERGO/GCE, (d) MWNTs/GCE, (e) GO-MWNTs/GCE and (f) GCE in 0.1 M PBS (pH 4.0) containing 8.0×10^{-5} M rutin with a scan rate of 80 mV s^{-1} .

Figure 6. (a) CVs of 8.0×10^{-5} M rutin solution on the ERGO-MWNTs/GCE at different scan rates (a–g: 20, 60, 100, 160, 200, 240, 300 mV s^{-1}) in 0.1 M PBS (pH = 4.0); (b) plots of the oxidation peak current versus the scan rate.

on the ERGO-MWNTs/GCE surface due to -COOH, -OH, and -O₂H surface functional groups. As far as physisorption is concerned, it may be that rutin is physically adsorbed on the ERGO-MWNTs/GCE surface through some interactions, such as hydrophobic effects, van der Waals forces, $\pi\pi$ bonds, electrostatic action and hydrogen bonds. However, different mechanisms may act simultaneously; the prediction of rutin adsorption on ERGO-MWNTs/GCE is not straightforward.³³ They need more detailed and thorough studies. According to the equation: $i_{pa} = n^2 F^2 v A \Gamma_0^* / 4RT = nFQv/4RT$,³⁴ n was calculated to be $1.88 \approx 2$, which suggested that the oxidation process of rutin involved two electrons transfer. In addition, when the scan rate rose, the redox peak potentials shifted with the increasing peak-to-peak separation, which demonstrated that the electrode reaction gradually became more irreversible.

The ERGO-MWNTs/GCE can be used for the determination of rutin for 40 cycles (the current relative error <10%). After each measurement, the three-electrode system was installed in a blank solution, and then magnetically stirred for 5 min. Subsequently, the cyclic voltammetry scan was repeated successively until the redox peaks of rutin didn't appear for renewing the electrode.

3.5 Effect of pH on the response of rutin at the ERGO-MWNTs/GCE

Figure 7 shows the effect of different pH on the response of 8.0×10^{-5} M rutin. When the pH changed from 3.0 to 9.0, the anodic peak moved to the negative direction. There was a linear relationship between

Figure 7. (a) Influence of solution pH on voltammograms of 8.0×10^{-5} M rutin with a scan rate of 80 mV s^{-1} . 0.1 M phosphate buffer solution pH (a $\rightarrow$ g): 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0; (b) The linear relationship of E_{pa} versus pH.

the anodic peak potential and the pH value as follows: $E_{pa}/V = 0.635 - 0.061\text{pH}$ ($r = 0.9946$). According to the slope of 61 mV pH^{-1} , it could be deduced that the number of electron and proton transferred were equal in the electrochemical reaction. With the increase in pH, the peak current increased until at about pH 4.0, and then decreased. But when the pH was over 8.0, the anodic peak became very small. These experimental phenomena were related to the proton involved in the electrochemical reaction. When pH exceeded 7.0, the electrostatic repulsion occurred between the ERGO-MWNTs and rutin with negative charges. Therefore, acidic solution of pH 4.0 was selected for the determination of rutin.

3.6 Calibration curve

As DPV has a higher current sensitivity and better resolution from background current than CV, it was used for the determination of rutin. Figure 8 displayed the DPV of the different concentration of rutin at the ERGO-MWNTs/GCE. The experimental results showed that i_{pa} was linear with the concentration of rutin in the ranges of $0.06\text{--}1.0 \mu\text{M}$ and $1.0\text{--}20.0 \mu\text{M}$ (figure 8). The regression equations were: $i_{pa}/\mu\text{A} = 13.139C_{\text{rutin}}/\mu\text{M} + 0.4599$ ($r = 0.9973$) for the range of $0.06\text{--}1.0 \mu\text{M}$ and $i_{pa}/\mu\text{A} = 1.985C_{\text{rutin}}/\mu\text{M} + 12.624$ ($r = 0.9989$) for the range of $1.0\text{--}20.0 \mu\text{M}$. The lowest detection concentration of rutin was $0.04 \mu\text{M}$.

The repeatability and stability are the vital properties for the modified electrode, which should be studied for analytical measurement. The same ERGO-MWNTs/GCE was used for five successive

measurements, and then the relative standard deviation (RSD) of the peak current was 6.3% for $1.0 \times 10^{-5} \text{ M}$ rutin. Moreover, five freshly prepared ERGO-MWNTs/GCEs were used to measure $1.0 \times 10^{-5} \text{ M}$ rutin in the same condition, and then a RSD of 9.2% was obtained. These results revealed that the ERGO-MWNTs/GCE was highly repeatable. The stability of the ERGO-MWNTs/GCE was investigated by determining the steady-state response current of $1.0 \times 10^{-5} \text{ M}$ rutin every day after preparation, the RSD of steady-state response current was 6.0%. When it was not in use, the sensor was stored in 0.1 M PBS (pH 7.0) at 4°C . The experimental results showed that the steady-state response current only decreased by 14% after 7 days, indicating that the ERGO-MWNTs/GCE electrode was considerably stable.

3.7 Interference studies

The influence of potential coexistent interference compounds were examined by this proposed method. A fixed amount of $2.0 \times 10^{-5} \text{ M}$ rutin was mixed with various foreign species. The results demonstrated that glucose, K^+ , Cl^- and SO_4^{2-} were 500 times more than that of rutin, aminoacetic acid 200 times, Zn^{2+} , Ca^{2+} and Mg^{2+} 50 times, no observable interference was observed in the electrochemical response of rutin according to the relative error $< \pm 10\%$.

Ascorbic acid (AA) is an electroactive substance, and always coexists in the Compound Rutin Tablets. At conventional electrodes, the oxidation peak potential of AA is very close to that of rutin, implying a poor selectivity for the measurement of AA and rutin in real samples.

Figure 8. DPV of different concentrations of rutin (a→k): 0, 0.06, 0.08, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 20.0 μM ; insert is the calibration curve of i_{pa} vs. C_{rutin} .

Figure 9. Cyclic voltammograms of the mixed solution of (a) 1.0×10^{-4} M AA and 2.0×10^{-5} M rutin, (b) 2.0×10^{-5} M rutin, (c) 1.0×10^{-4} M AA, (d) and 0.1 M phosphate buffer solution (pH 4.0) on the ERGO-MWNTs/GCE.

So, it is significant to develop more sensitive, selective and simple techniques for the segregative measurement of AA and rutin. Figure 9 displayed the CVs of the mixture of 2.0×10^{-5} M rutin and 1.0×10^{-4} M AA (a), 2.0×10^{-5} M rutin (b), 1.0×10^{-4} M AA (c) and without AA and rutin (d) in 0.1 M PBS (pH 4.0) at a ERGO-MWNTs/GCE. Figure 9c displayed an obvious anodic peak of AA at 0.117 V. Figure 9a showed two anodic peaks at around 0.117 V and 0.467 V, which were attributed to the oxidation of AA and rutin with a 0.350 V separation of both peaks, indicating broad enough separation for the simultaneous electrochemical determinations of rutin and AA in the mixed solution. In addition, in the presence of 1.0×10^{-4} M AA, the redox peak currents of rutin were almost not changed (figure 9a), which suggested that the ERGO-MWNTs/GCE could eliminate the interference of AA for the determination of rutin.

3.8 Analysis of real samples

In order to examine the practicability of the proposed method, the content of rutin in Compound Rutin Tablets and Rutin Tablets were analyzed. The total value of rutin

were obtained to be 19.1 ± 0.23 mg and 18.3 ± 0.61 mg per tablet for the Compound Rutin Tablets and Rutin Tablets, respectively (the labeled quantity of Rutin was 20 mg per tablet), which was calculated by multiplying the examined value and the diluted factor. In order to evaluate the correctness of the determination results, the standard addition method was employed to determine the rutin sample spiked with suitable rutin. The experimental results were listed in table 1. In order to verify the accuracy of the proposed method, HPLC was used to determine the contents of rutin in real samples. By using HPLC, the contents of rutin were 19.3 ± 0.49 mg and 20.0 ± 0.25 mg per tablet for the Compound Rutin Tablets and Rutin Tablets, respectively, which were in agreement with the results obtained by the proposed electrochemical method. The experimental results indicated that the proposed electrochemical method could be efficiently used for Rutin determination in real samples.

4. Conclusions

In this paper, an ERGO-MWNTs/GCE was fabricated conveniently and firmly. Under the optimum condition, the ERGO-MWNTs/GCE provided excellent sensitivity and selectivity towards rutin. The anodic peak current was proportional to the rutin concentration in the ranges of $0.06\text{--}1.0\text{ }\mu\text{M}$ and $1.0\text{--}20.0\text{ }\mu\text{M}$ with the detection limit of $0.04\text{ }\mu\text{M}$. The coexisting substance of AA declared no interference to the determination of rutin. The proposed method was further applied to the determination of rutin in the Compound Rutin Tablet and Rutin Tablet samples with satisfactory results.

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Table 1. Determination results for rutin in Compound Rutin Tablets* and Rutin Tablets*.

Sample	Detected (mg/tablet)	Spiked (10^{-7} M)	Found (10^{-7} M)	Average recovery (%)	RSD of recovery (%)
Compound Rutin Tablets ^a	19.3 ± 0.49	0.8	0.8 ± 0.10	100.0	6.0
		8.0	9.1 ± 0.05	113.7	4.5
Rutin Tablets ^a	18.3 ± 0.61	0.8	0.76 ± 0.22	95.0	3.2
		8.0	8.2 ± 0.62	102.5	5.4

^aDilution factor: 1/10,000.

*Number of samples assayed: 5.

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