

GQDs/PEDOT Bilayer Films Modified Electrode as a Novel Electrochemical Sensing Platform for Rutin Detection

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Received: 4 August 2019 / Accepted: 16 September 2019 / Published: 29 October 2019

A glassy carbon electrode (GCE) modified with graphene quantum dots (GQDs) and poly (3, 4-ethylenedioxythiophene) (PEDOT) bilayer films (GQDs/PEDOT/GCE) was constructed and used as a novel electrochemical sensor for rutin detection. The GQDs/PEDOT/GCE sensor was fabricated by two-step electrodeposition and was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). Compared with individual GQDs/GCE and PEDOT/GCE, the current response of the composite electrode to rutin increased by about 10 times and 3 times respectively. The composite electrode exhibited a strong electrical response toward rutin redox due to the cooperative action of the large surface area of the GQDs which allowed strong analyte adsorption and the high electroconductivity of PEDOT. The current response of the GQDs/PEDOT/GCE electrochemical sensor was more linear at rutin concentrations between 0.05 μM and 10 μM and had a detection limit of 11 nM. The sensor also presented a high selectivity, high stability, and excellent recovery rate and could be used for the effective and reliable analysis of rutin in real samples.

Keywords: graphene quantum dots; poly (3, 4-ethylenedioxythiophene); electrodeposition; rutin; electrochemical sensors

1. INTRODUCTION

Rutin is a representative polyhydroxy flavone glycoside, and is the main active ingredient in many Chinese herbal medicines [1-2]. It is also widely used in the treatment of cardiovascular diseases in clinical practice [3], and some studies have shown that rutin has certain pharmacological functions such as anti-aging, anti-inflammatory, antibacterial, and antioxidant effects [4-5]. Thus, it is essential to develop a precise, sensitive, and durable method to achieve quantitative analysis of rutin. Due to the

electrochemical response properties of rutin, an increasing amount of attention has been paid to sensitive, simple, and rapid electrochemical analysis methods. Currently, the combination of highly conductive materials (such as metal nanomaterials, organic dyes, and ionic liquid) and carbon nanomaterials (such as SWCNT, MWCNT, graphene) with modified electrodes are commonly used for rutin detection. [6-12]. However, these highly conductive materials are expensive, have low biocompatibilities, are toxic, and are difficult to recycle. Therefore, environmentally-friendly modified materials with high conductivities should be prepared for the detection of rutin.

The application of GQDs in electrochemical sensors is ever-expanding due to their many attractive properties, including better surface group grafting through π - π conjugation, large surface areas, non-toxicity, excellent aqueous solubility, and excellent biocompatibility. However, GQDs may not be suitable for practical application as a single electrode material because of their slow heterogeneous electron transfer kinetics [13-14]. The combination of GQDs and other conductive materials to form an electrochemical sensor with an improved sensitivity and selectivity has been reported. Such materials include metal nanomaterials including gold nanorods, Cu nanoparticles, Fe₃O₄, and carbon nanomaterials such as MWCNTs, the conductive polymer polyaniline, chitosan, cyclodextrin, and so on [15-21].

Due to its good stability, good film formation, high conductivity, thermal stability, and good biological compatibility, PEDOT has been successfully used in solar cells, energy storage devices, supercapacitors, organic light-emitting diodes (OLEDs), and electrochemical sensors [22-30]. Thus, in this work, GQDs/PEDOT bilayer films were prepared on the surface of a GCE by a two-step electrodeposition method. The films were characterized by TEM, SEM, and CV. PEDOT were electrodeposited on the surface of GCE with uniformly dispersed spherical particles microstructures, and GQDs were uniformly attached to the surface of the PEDOT, which may significantly enhance the reproducibility and stability. In addition, these composite electrode materials showed higher redox current responses (I_p) toward the electrooxidation of rutin compared with the single materials, due to the synergistic effects of the high surface area and active sites of GQDs and high conductivity of PEDOT.

2. EXPERIMENTAL

2.1. Chemicals

Rutin and EDOT were obtained from Aladdin. Rutin stock solution was prepared with absolute ethanol and stored at 4–8 °C. Rutin tablets (20 mg) were purchased from Tianjin Lisheng pharmaceutical Co., Ltd. Lithium perchlorate (LiClO₄) and lauryl sodium sulfate (SDS) were obtained from Sinopharm Chemical Reagent Co., Ltd, (Shanghai, China). The electro polymerization of EDOT was performed in an aqueous solution containing 0.01 M EDOT (C. P. Sinopharm), 0.1 M LiClO₄ (A. R. Sinopharm) as the supporting electrolyte and 0.02 M sodium dodecyl sulfate (SDS, A. R. Sinopharm) as the surfactant. NaH₂PO₄ (0.1 M) and Na₂HPO₄ (0.1 M) solutions were used to prepare phosphate buffer solutions (PBS), and phosphoric acid was added to regulate the pH. Deionized water or ultrapure water were used throughout the experiments.

2.2 Instruments

TEM images were obtained using a JEM-F200 transmission electron microscope. SEM images were obtained on a JSM-6610LV scanning electron microscope (SEM, JEOL, Tokyo, Japan) at an accelerating voltage of 30 kV. Electrochemical measurements were carried out on a CHI660D electrochemical workstation (Shanghai, China). A three-electrode cell (5 mL) was used with a modified GCE as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum foil electrode as the counter electrode. Solid GQDs were obtained using a FD-1A-50 vacuum freeze drier from Beijing Biocool Experimental Instrument Co., Ltd (Beijing, China). Ultrapure water was obtained using a Millipore pure water machine.

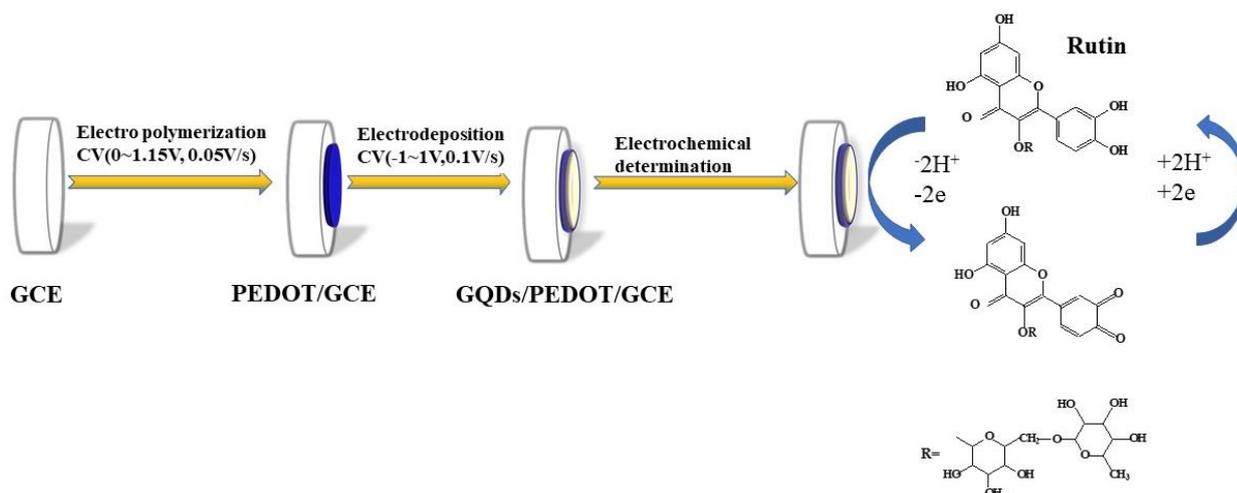
2.3 GQDs synthesis

GQDs were prepared by directly pyrolyzing citric acid (CA) according to a previously-reported bottom-up method [31]. First, 2 g of citric acid was placed into a small beaker and heated to 200 °C on an electric heating mantle until the CA was converted from a solid to a liquid. At this point, the heating was immediately stopped, and the liquid gradually changed from colorless to yellow. Thereafter, 50 mL of a 0.25 mol/L NaOH solution was added dropwise to the above solution, and stirred continuously for about 30 minutes. The pH of the solution was adjusted to 6.8 – 7 using 0.25 mol/L NaOH solution. The solution was dialyzed for 2 days with a dialysis bag (MWCO: 3500 Da), and then lyophilized to obtain GQDs solids, which were stored in a refrigerator at 4 °C. A certain amount of GQDs was dissolved in water to prepare a 2 mg/ml solution to modify the electrode.

2.4 Preparation of GQDs/PEDOT composite modified GCE

The GCE was sequentially polished using polishing cloths with Al₂O₃ particle sizes of 0.3 μm and 0.05 μm, followed by successive sonication in deionized water and ultrapure water, and then drying in air. CV scans were performed in a 5 μM potassium ferricyanide (0.1 M KCl) solution at a 50 mV s⁻¹ scan rate between -0.1 V and 0.5 V. The redox peak potential difference reached the requirement below 80 mV.

As shown in Scheme 1, the PEDOT film was electrodeposited on the surface of the GCE prepared by the CV method in a 0.01 M EDOT solution at a scan rate of 50 mV s⁻¹ from 0 V to +1.15 V vs. SCE for 30 cycles. After drying at room temperature in a clean environment, the GQDs were electrodeposited on the surface of PEDOT/GCE by the CV method in a 2 mg/mL GQDs solution at a scan rate of 100 mV s⁻¹ from -1 V to +1 V vs. SCE for 50 cycles. The modified electrode was allowed to naturally dry at room temperature.



Scheme 1. Schematic illustration of the fabrication of GQDs/PEDOT/GCE and the electrochemical detection of rutin.

2.4. Electrochemical measurements

The GQDs/PEDOT/GCE was immersed into 20 mL of a buffer solution (pH 3.0) containing a certain amount of rutin for detection. CV was performed within a potential range from 0 to 0.8 V at a scan rate of 50 mV s^{-1} . The Differential Pulse Voltammetry (DPV) was recorded within a potential range of 0.3 to 0.7 V. The pulse amplitude, pulse width, and pulse period for the DPV were 0.05 V, 0.05 s, and 0.2 s, respectively, and the quiet time was 2 s. Impedance measurements were performed by EIS in $5 \mu\text{M}$ of $[\text{Fe}(\text{CN})_6]^{4-/3-}$ containing 0.1 M KCl solution.

2.5 Sample Preparation

10 pieces of rutin tablets were ground into fine powder, and then precise amounts of powder were dissolved in 50 mL absolute ethanol. The supernatant was sonicated for 10 min and diluted to the desired concentration with a buffer solution (pH 3.0) prior to measurements.

3. RESULTS AND DISCUSSION

3.1. Sensor characterization

The morphology of GQDs was analyzed by TEM, as shown in Figure 1. The maximum and minimum lateral diameters of the GQDs were 7.0 nm and 3.3 nm, respectively, and the diameters were mainly distributed from 4 - 6 nm (4.6 nm average diameter), indicating that the GQDs were relatively uniform in diameter and monodisperse.

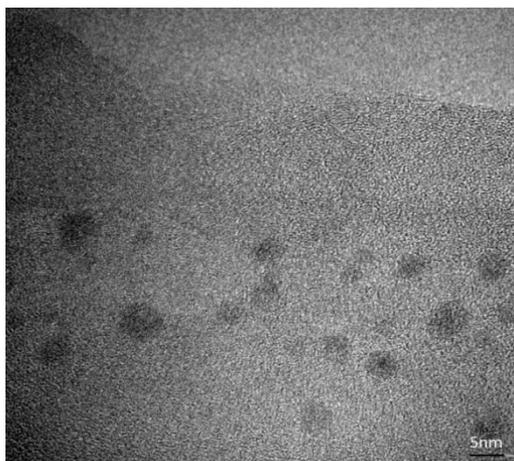


Figure 1. TEM image of GQDs.

The surface morphology of the PEDOT film and GQDs/PEDOT/GCE were investigated by SEM. When PEDOT was deposited on the surface of the electrode (Fig. 2A), it had a uniformly dispersed spherical particles microstructure. When the GQDs were deposited, the surface of the PEDOT was covered with the GQDs (Fig. 2B), and the particles could still be observed, indicating that the GQDs were successfully deposited on the surface of the PEDOT/GCE. This morphology may help enhance the current response due to a larger reaction surface with the analyte.

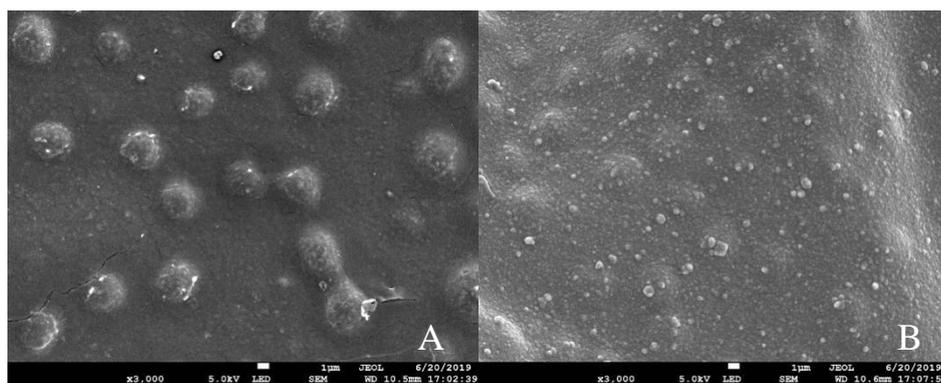


Figure 2. SEM image of PEDOT film (A) and GQDs/PEDOT composite films (B).

EIS is an efficient analytical method to monitor the modification procedure of the electrode surface. The Nyquist plots of different electrodes including bare GCE, GQDs/GCE, PEDOT/GCE, and GQD/PEDOT/GCE are given in Fig. 3. By comparing the plots, it can be seen that the semicircle portion at higher frequencies for GQD/GCE was similar to the bare GCE. According to previous reports, GQDs have a low electroconductivity due to slow heterogeneous electron transfer kinetics [13-14]. This may explain why the GQDs showed a low conductivity. However, when the GQDs were electrodeposited on the PEDOT/GCE surface, the Nyquist plot was nearly a straight line, and the semicircle portion was smaller than either of the two single materials. This suggests that combining GQDs with PEDOT greatly

improved the electron transfer performance. This may be attributed to the good electrical conductivity of PEDOT and the strong adsorption of analytes due to the high surface area of the GQDs. Therefore, the novel composite electrochemical sensor had a higher electrocatalytic performance.

The use of combined PEDOT and GQDs for electrochemical sensing is rarely reported. It has been reported that a mixed solution of GQDs and PEDOT was electrodeposited on GCE as an electrocatalyst to investigate the electrocatalytic performance of a redox reaction. In this paper, the GQDs/PEDOT/GCE electrode was prepared by electrodeposition of GQD on the PEDOT/GCE surface as electrocatalysts for specific analyte detection, indicating that this sensor was novel and practical.

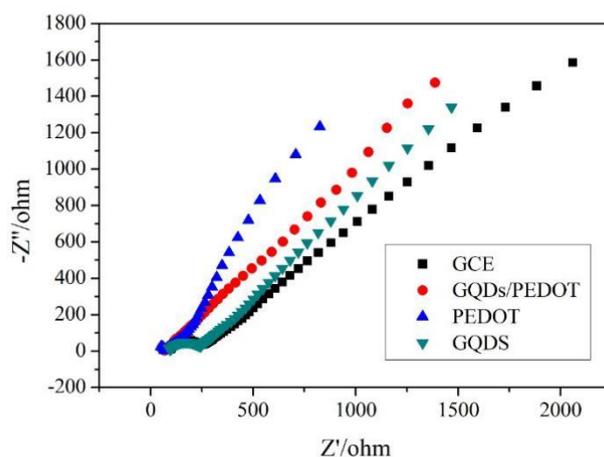


Figure 3. EIS spectra of bare GCE, PEDOT/GCE, GQDs/GCE, and GQDs/PEDOT/GCE.

3.2 Electrochemical detection of rutin

Fig. 4 depicts the CV curves of various electrodes in 0.1 M PBS (pH 3.0) containing 10 μ M rutin, and shows that the redox peak currents of the bare GCE were weak due to the slow electron transfer. After modification with GQDs, the reduction peak current increased slightly, which is consistent with the EIS result. Relative to the GQDs/GCE and PEDOT/GCE, the electrocatalytic activity of the GCE modified with a GQDs/PEDOT bilayer films dramatically increased. This electrochemical sensor increased the detection current for the same rutin concentration by about 10 times and 3 times compared with the single GQDs/GCE and PEDOT/GCE, respectively, which suggests an excellent synergetic effect of PEDOT and GQDs.

According to the literature [10,12], the redox reaction of rutin on the surface of the electrode was mainly due to the rutin structure containing an ortho-diphenol structure. This was oxidized to 3',4'-diquinone, which was then reduced to rutin during the reverse scan.

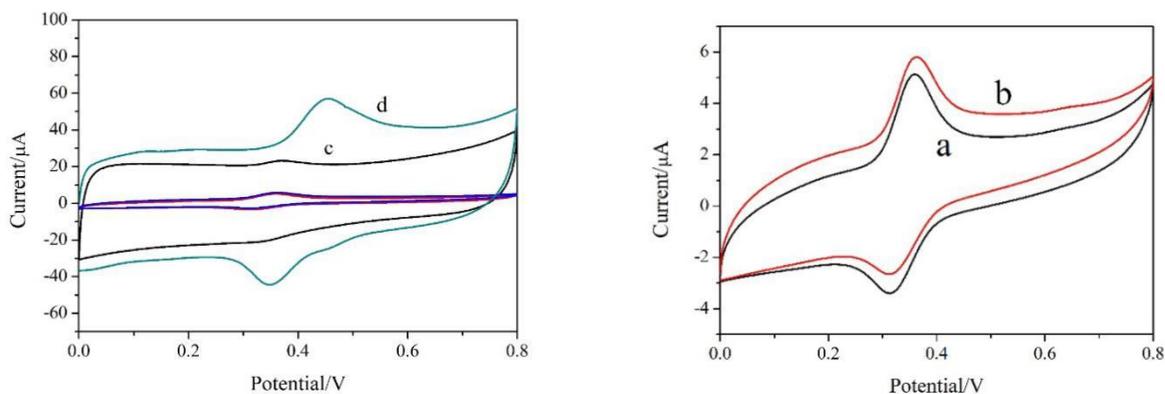


Figure 4. CV behaviors of rutin (10 μM) in buffer solution (pH = 3.0) on the bare GCE (a), GQDs/GCE (b), PEDOT/GCE (c), and GQDs/PEDOT/GCE (d).

3.3 Effect of pH

Protons participate in the electrochemical reaction of organic compounds and significantly affect the reaction rate. Thus, the influence of solution pH on the electrochemical behavior of rutin was also studied, as shown in Fig.5A. The results showed that the effect of pH on the detection of rutin by GQDs/PEDOT/GCE was studied using CV, with pH values ranging from 2.0 to 5.0. the oxidation peak current of rutin decreased as the pH increased, reaching a maximum at a pH of 3.0, so this value was chosen for detection, which is consistent with the previous reports[8]. The results show that protons participated in the electrochemical reaction of rutin on the surface of the modified electrode, and the acidic environment was more conducive to the transfer of electrons, which is consistent with previous reports [10]. There is a good linear relationship between potential and pH which can be expressed as: $E_{pa} \text{ (V)} = -0.0492\text{pH} + 0.638$ ($R^2 = 0.9971$) (Fig. 5B). The slope of this linear equation was 49.2 mV/pH, which is close to the ideal value of 59 mV/pH, indicating that the electrochemical process of rutin detection was a reaction involving the equal participation of protons and electrons.

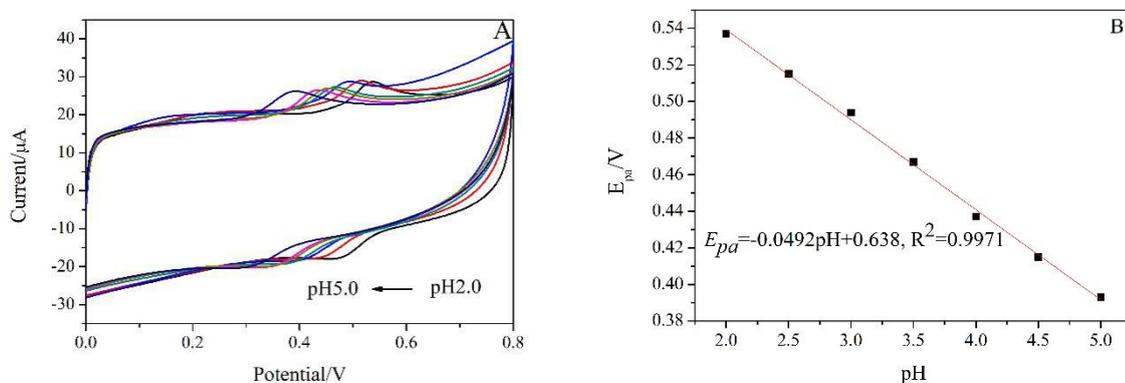


Figure 5. (A) CVs of 1 μM rutin on GQDs/PEDOT/GCE in a buffer solution with pH values ranging from 2.0 to 5.0 at a scan rate of 0.05 mV s^{-1} . (B) Plots of the anodic peak potential against pH.

3.4 Effect of scan rates

Fig. 6 shows the effect of scanning rate on the electrochemical detection of rutin. The figure shows that the oxidation peak current (I_{pa}) increased with the scanning speed from 0.05 - 0.35 $V s^{-1}$, which shows a good linear relationship ($I_{pa}(\mu A)=10.328v+5.602$, $R^2 = 0.9926$). This indicates that this reaction is an adsorption-controlled process. Furthermore, the linear regression equation between the anode peak potential (E_{pa}) and Napierian logarithm of the scan rate ($\ln v$) was examined and expressed as $E_{pa} = 0.0261\ln v + 0.5546$ ($R^2=0.9918$). Based on Laviron's theory [33], the slope of the line of E_{pa} can be expressed as RT/anF ,

$$E_{pa} = E^0 + \frac{RT}{anF} \ln \left(\frac{RTK_s}{anF} \right) + \frac{RT}{anF} \ln v$$

With a charge transfer coefficient of 0.5, the number of transferred electrons n was calculated to be approximately 2, indicating that the electrochemical reaction of rutin on the modified electrode involves two electrons and two protons due to the oxidation of the *o*-diphenol structure in rutin.

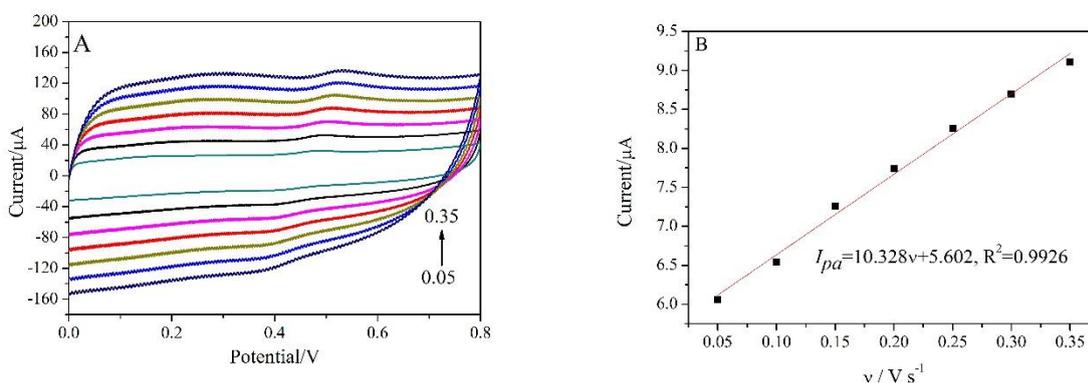


Figure 6. (A) CVs of GQDs/PEDOT/GCE in 0.1 M PBS (pH = 3.0) in the presence of 1 μM rutin at scan rates ranging from 0.05 to 0.35 $V s^{-1}$. (B) The linear relationship between the peak currents and scan rates.

3.5. Electrochemical detection of rutin

GQDs/PEDOT/GCE was also used for rutin detection using DPV. As shown in Fig. 7A and B, the oxidation peak current of rutin (I_{pa}) on GQDs/PEDOT/GCE increased with the rutin concentration from 0.05 μM to 10 μM , and the corresponding linear function was $I(\mu A) = 4.255C + 18.297$ ($R^2 = 0.9956$), which showed a good linear relationship. The detection limit was 11 nM ($S/N = 3$). This sensor has a wide linear range and lower detection limit mainly because the modified electrode combines the strong adsorption and high conductivity of the individual materials.

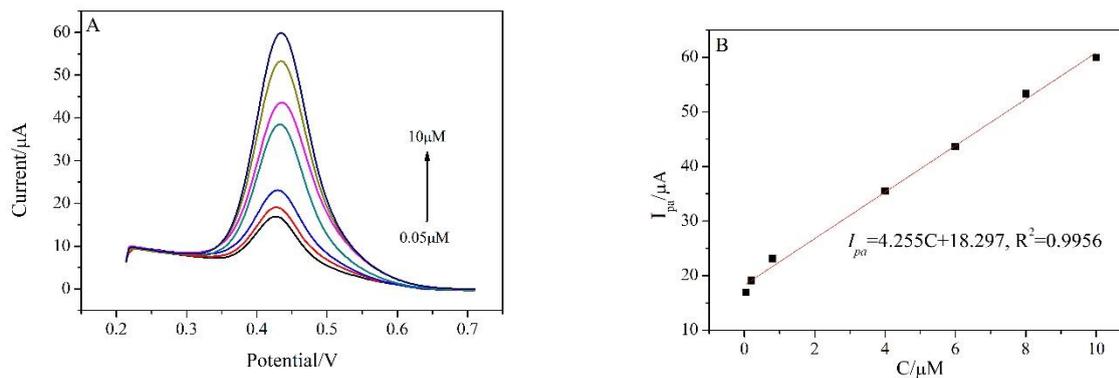


Figure 7. (A) DPV of GQDs/PEDOT/GCE at various rutin concentrations (0.05 μM , 0.2 μM , 0.8 μM , 4 μM , 6 μM , 8 μM , and 10 μM) in a buffer solution (pH = 3.0). (B) Corresponding linear calibration curve of peak current vs. rutin concentration.

Table 1 compares the analytical performance of GQDs/PEDOT/GCE with other rutin sensors, including detection methods, detection limits and linear ranges. It can be seen that the fabricated sensor provided a reasonable linear range and a preferable detection limit for rutin compared with others reported in the literature.

Table 1. Comparison of the fabricated sensor with reported electrochemical methods for the detection of rutin.

Electrode	Method	Linear range (μM)	Detection limit (nM)	reference
MWCNTs/ β -CD	CV	0.4~1000	200	[9]
SMWCNT-PEDOT-IL	LSV	1.0~14	77	[34]
PEDOT-MeOH/ GO/GCE	LSV	0.020–10	2	[11]
PPO/AuNPs/FDU-15/GCE	Chronoamperometry	1.5 -28	510	[35]
GS/GCE	DPV	0.01-1250	3.2	[6]
GO/IL/GCE	SWV	0.03-1.0	10	[36]
GQDs/PEDOT/GCE	DPV	0.05-10	11	This work

3.6 Reproducibility , repeatability and stability

The reproducibility and stability of the GQDs/PEDOT/GCE was also studied. Five modified electrodes were prepared using an identical method and used to detect rutin. The RSD of the sensor response to rutin was 2.8% for peak currents in a 1 μM rutin solution, indicating that the electrode had

an acceptable reproducibility.. Each modified electrode was used for detection 8 times continuously, and the RSD was 1.6%, demonstrating the good repeatability of the electrode. After storing at 4 °C for four weeks, the current response of the sensors to 1 μM rutin was maintained at 92.4% of its initial value, suggesting that the modified electrode had good long-term stability. The good reproducibility, repeatability, and stability of the GQDs/PEDOT/GCE may be related to the stability of GQDs and PEDOT, the strong binding between PEDOT and GQDs, and the low solubility of the prepared bilayer membrane in water.

3.7 Interfering substances

CV was used to investigate the selectivity of the sensor to rutin by mixing it with 100 times concentrations of inorganic ions (Na^+ , K^+ , Cl^- , NO_3^- , Ca^{2+} , Zn^{2+} , Mg^{2+} , and SO_4^{2-}) and 50 times concentrations of organic matter (glucose, urea, ascorbic acid, and dopamine) as interfering substances. It was found that these substances had little effect on the peak current of rutin ($\text{RSD} < \pm 3\%$), indicating that the electrochemical sensor has good anti-interference ability for the determination of rutin.

3.8 Determination of rutin tablets

The performance of the electrochemical sensor based on GQDs/PEDOT/GCE for the detection of rutin was evaluated using rutin tablets shown in Table 2. The concentration of rutin in the sample solution was calculated according to a standard curve. Rutin standard was added at 80%, 100%, and 120% of the sample concentration in solution, and the recovery rate was calculated. The results in Table 1 show that the recoveries were greater than 90%, and the RSD values were less than 4%, indicating that this sensor is accurate and reliable for the detection of rutin in real samples.

Table 2. Determination of rutin in tablets (n = 3).

Original/ μM	Added/ μM	Found/ μM	Recovery/%	RSD/%
	0.24	0.52 \pm 0.023	90.67	3.55
0.30	0.30	0.59 \pm 0.040	97.22	1.83
	0.36	0.65 \pm 0.014	97.91	3.18

4. CONCLUSIONS

In this paper, a new electrochemical sensor based on a GCE modified with GQDs and PEDOT bilayer films was successfully constructed and used for the detection of rutin. This sensor significantly

improved the current response to rutin due to the synergistic effect of the strong adsorption of GQDs and high conductivity of PEDOT. Due to its wide linear range, good stability, excellent reproducibility, and high selectivity and recovery rate, the electrochemical sensor may be used to detect rutin in traditional Chinese medicines or other actual samples.

ACKNOWLEDGEMENTS

We are grateful to the Key Science and Technology program of Shanxi Province (20140311007-5).

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