

# A sensitive and reliable rutin electrochemical sensor based on palladium phthalocyanine-MWCNTs-Nafion nanocomposite

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**Abstract** Fabrication of multicomponent nanocomposites as electrode-modified materials is an effective strategy to design highly active electrochemical sensors. Here, we present a facile strategy to fabricate the palladium phthalocyanine-multiwalled carbon nanotube (PdPc-MWCNTs) nanocomposite for the sensitive detection of rutin. Results showed that the prepared nanocomposites exhibited excellent electrocatalytic activity toward rutin due to the synergetic effects of PdPc and MWCNTs (excellent electric conductivity and catalytic activity) and the homogeneous dispersibility of Nafion. Under the optimized conditions, the developed sensor exhibited a linear response range from 0.10 to 51  $\mu\text{M}$  for rutin with a low detectable limit of 75 nM and a fast response less than 3.0 s. The proposed method might offer a possibility for electrochemical analysis of rutin in Chinese medical analysis or serum monitoring owing to its low cost, simplicity, high sensitivity, good stability, and few interferences against common coexisting ions in real samples.

**Keywords** Nanocomposite · Palladium phthalocyanine · Multiwalled carbon nanotube · Rutin · Electrochemical

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## Introduction

Rutin (rutoside or quercetin-3-o-rutoside) as a kind of flavonoid glycoside compound is widely distributed in fruits and vegetables [1]. From a pharmacological and biochemical point of view, rutin has many properties and functions such as anti-hypertensive, anti-inflammatory, anti-bacterial, anticancer, anti-aging, and antioxidant [2–6]. Therefore, it has been used clinically as a therapeutic drug worldwide [7]. To date, various analytical methods have been developed for the determination of rutin, such as spectrophotometric analysis [8], capillary electrophoresis analysis [9], high-speed counter-current chromatography, and high-performance liquid chromatography [10]. However, some of these methods often require complicated preconcentration procedures and expensive instruments with mass use of organic solvents, which hamper their “in situ” application and make them inconvenient in practice. Considering that rutin is an electroactive flavonoid glycoside compound which can be easily subject to redox reaction on some kinds of working electrodes [1, 11, 12], the electrochemical method seems like a promising alternative due to its simplicity, sensitivity, low cost, and the possibility to construct portable devices for on-site determination of rutin [13–15].

In the electrochemical procedure, the crucial step is to fabricate suitable modified electrodes using excellent sensing materials to improve the electrochemical behaviors of analytes, such as sensitivity, stability, and anti-fouling ability. Different kinds of nanomaterials including carbon nanotubes, metal nanoparticles, and graphene have been proven to be excellent carriers to enhance response signals. Recently, phthalocyanine-based compounds [16], especially metallophthalocyanines (MPcs), have gradually caused concern due to their excellent thermal stability, chemical inertness, and conductivity [17]. It is a kind of two-dimensional 18-electron aromatic porphyrin synthetic analogs with a metal atom located at the central cavity.

Several MPc-based molecular materials have been exploited for the detection of some analytes based on the electrochemical method due to the presence of outstanding electrocatalytic metal centers [17–19]. However, MPcs have an obvious disadvantage of easily blocking the transfer of electrons between phthalocyanines and the electrode when being applied as electrocatalysts. One of the effective methods to solve this problem is designing the conjugation of nonsubstituted MPc complexes with carbon materials via  $\pi$ – $\pi$  interactions [19, 20]. For example, Wang fabricated cobalt phthalocyanine nanorods on graphene for the electrochemical detection of hydrogen peroxide and glucose sensing [20]. Except grapheme, multiwalled carbon nanotubes (MWCNTs) could also promote the direct electrochemistry of biomolecules, leading to the improved catalytic and sensing activity of MPc-CNTs [21–23].

Considering that palladium and its complexes are known to be excellent catalysts due to its nontoxic properties and superior catalytic activities toward many electrochemical reactions [24], it could be expected that the catalytic and sensing activity of the electrode modified with palladium(II) phthalocyanine complexes (PdPc) integrated with MWCNTs will be greatly enhanced. In addition, it is well known that Nafion can be used as a binder to stabilize the modified species on electrodes and as a permselective film to alleviate the interferences of anions; in this work, Nafion was used to disperse PdPc-CNTs and a novel electrochemical sensor was constructed based on PdPc-CNTs-Nafion film [25, 26]. A pair of well-defined quasi-reversible redox peaks of rutin was obtained with higher sensitivity, compared with those obtained based on only PdPc-Nafion- or MWCNTs-Nafion-modified electrode. To the best of our knowledge, this is the first time that the self-assembly of PdPc-MWCNT nanocomposite has been used as an electrode-modified material for electrochemical sensor. It might be an effective candidate for the detection of Chinese medical analysis or quality monitoring in real samples.

## Experimental

### Materials

Nafion (5.0 wt% ethanol solution) was obtained from Alfa Aesar. Palladium chloride was purchased from Aldrich. *O*-phthalic anhydride was obtained from Aladdin Biological Technology Co., Ltd. Urea, ammonium molybdate, and other reagents were of analytical grade from Tianjin kem'ou Chemical Reagent Co., Ltd. and used without further purification. Nafion was diluted to 0.1 wt% with double-distilled water in use. Phosphate buffer solution (PBS, pH 3.0) was prepared from  $\text{Na}_2\text{HPO}_4$  and  $\text{KH}_2\text{PO}_4$ . Glassy carbon electrode ( $d = 3.0$  mm) was purchased from Shanghai Chenhua Company.

### Preparation of PdPc-MWCNTs

Prior to the preparation, MWCNTs were refluxed in the nitric acid at 120 °C to obtain carboxylated MWCNTs. Then, the carboxylated MWCNTs were separated by centrifugation and repeatedly washed with double-distilled water until the pH of the resulted MWCNT solution became neutral. PdPc was obtained via solid-phase synthesis as follows. In brief, 3.34 g of *o*-phthalic anhydride, 8.13 g of urea, 1.0 g of palladium chloride, and 0.25 g of ammonium molybdate were mixed and grinded thoroughly. Then, the previous mixture was transferred to the autoclave and heated at 453.50 K for 4 h in the oven. The resulted solid was purified and recrystallized by concentrated sulfuric acid (98%) and double-distilled water. The obtained precipitate PdPc was washed with water until the pH value of the supernatant was neutral. The sample was dried in a vacuum oven at room temperature for 12 h. PdPc-MWCNTs were prepared by adding 750  $\mu\text{L}$  of PdPc sulfuric acid solution (50 mg/mL) to 0.1 g of MWCNTs dropwise, followed by stirring the mixture to form a smooth dough with a glass bar. Then, the as-prepared mixture was diluted by water and PdPc-MWCNTs were crystallized, in which the resulted solution was washed with double-distilled water several times until its pH became neutral and dried in a vacuum oven at room temperature.

### Fabrication of modified GCEs

Before modification, the surface of glassy carbon electrode (GCE) was polished with 1.0, 0.3, and 0.05  $\mu\text{m}$  aluminum oxide paste successively and then ultrasonically washed with 1:1  $\text{HNO}_3$ , absolute ethanol, and distilled water, respectively. The cleaned GCE was dried with high-purity nitrogen stream. Of PdPc-MWCNTs, 1.0 mg was added into 1.0 mL of 0.1 wt% Nafion solution, and this solution was ultrasonicated for 30 min to form a stable suspension (1 mg/mL). Nine microliters of the solution was cast onto the surface of GCE to obtain PdPc-MWCNTs-Nafion-modified electrode, which was marked as PdPc-MWCNTs-Nafion/GCE. For comparison, PdPc-Nafion/GCE and MWCNTs-Nafion/GCE were prepared using a similar procedure. To investigate the influence of Nafion, the PdPc-MWCNTs/GCE was also prepared by a similar procedure except that 0.1 wt% of Nafion was replaced by double-distilled water.

### Characterization

Scanning electron microscopy (SEM) images were collected on a JSM-7001F scanning electron microscope equipped with an X-ray energy-dispersive spectrum (EDX) at an accelerating voltage of 20 kV. Raman spectra were recorded on Renishaw RM-1000. X-ray photoelectron spectroscopy (XPS) was performed using Thermo Scientific Escalab 250Xi equipped with 150 W monochromatized Al  $K_{\alpha}$  radiation ( $h\nu = 1486.6$  eV),

where all peaks were referred to the signature C1s peak for adventitious carbon at 284.8 eV. UV-visible spectroscopy was collected on a Shimadzu UV-2600 spectrophotometer. All electrochemical experiments were carried out on a CHI660D electrochemical workstation (CHI, Shanghai). A three-electrode setup was used in the experiment with GCE as the working electrode, with saturated Ag/AgCl electrode as the reference electrode and platinum wire as the counter electrode.

## Results and discussion

### Characterization of PdPc-MWCNT composite

The morphology of PdPc was characterized by TEM. As shown in Fig. S1a, PdPc presents a typical columnar morphology with a length of about 3  $\mu\text{m}$  in length [27]. Compared with PdPc, SEM observation of the PdPc-MWCNTs showed that PdPcs combined with MWCNTs were in a disordered fashion (Fig. 1a). The existence of Pd was confirmed by the EDX spectra (Fig. 1b). These results clearly indicate the successful synthesis of PdPc-MWCNTs by a facile solid-phase method.

XPS spectra were used to further determine the composition of the composite. In the close-up view of the Pd3d region of PdPc-MWCNTs (Fig. 2a), two peaks for Pd3d<sub>5/2</sub> and Pd3d<sub>3/2</sub> were observed at 338.7 and 344.1 eV, respectively, which could be assigned to the binding energy of Pd(II) in the phthalocyanine complexes [28]. In the close-up view of the C1s (Fig. 2b) and N1s (Fig. 2c) regions, the photoelectron peak of C1s for PdPc-MWCNT composite was greatly enhanced and the N1s peak for PdPc-MWCNT composite was suppressed compared to those peaks from PdPc. These changes revealed the donation of electron and thereby the redistribution of the charge density between the phthalocyanine ring and MWCNTs. Meanwhile, the conjugation

of PdPc and MWCNTs could be further investigated by Raman spectra and UV-vis absorption spectra with PdPc and MWCNTs as controls. The structure of carbon materials can be characterized by Raman spectra. In the Raman spectrum of MWCNTs (Fig. 3), two characteristic peaks appeared, one is the D band located at 1325  $\text{cm}^{-1}$ , corresponding to  $\text{sp}^2$  domains isolated by oxidized carbon atoms, and the other is the G band at around 1565  $\text{cm}^{-1}$ , common to all  $\text{sp}^2$  carbon forms [29]. In addition, the two bands appear in the Raman spectrum of the PdPc-CNT hybrid again, and the Raman spectrum of the PdPc-CNT hybrid shows almost the same signals as those coming from PdPc, confirming the existence of both precursors in the as-prepared hybrid. Besides, the characteristic vibrational bands of PdPc located at 1519 and 1448  $\text{cm}^{-1}$ , were assigned to C $\alpha$ N $\alpha$ -pyrrole and isoindole ring [28]. The D band of MWCNTs shifted from 1325 to 1334  $\text{cm}^{-1}$  and G band from 1535 to 1575  $\text{cm}^{-1}$  in the PdPc-MWCNT composite, which could be attributed to  $\pi$ - $\pi$  interactions between PdPc and the MWCNTs. In UV-vis absorption spectra, MPc usually exhibits characteristic electronic absorption in the visible and near infrared region (Q-band at 600–800 nm) and near ultraviolet region (B-band at 300–400 nm), both arising from  $\pi \rightarrow \pi^*$  transition [30, 31]. As shown in Fig. S2, the Q-band and B-band of PdPc located at 630 and 305 nm were slightly red shifted to 635 and 320 nm for PdPc-MWCNTs, respectively. These previous results clearly indicate the conjugation of PdPc and MWCNTs via strong  $\pi$ - $\pi$  interactions and thereby the relocation of the electrons from MWCNTs to the phthalocyanine groups of PdPc [32], which was expected to improve the catalytic and sensing activity of the electrode for rutin detection. This is also in accord with Raman spectra.

Electrochemical impedance spectroscopy (EIS) is an effective tool to evaluate the process kinetics and interfacial properties of the modified electrodes. The typical Nyquist plot of EIS includes a semicircle and a linear portion, which correspond to the electron transfer-limited process and the

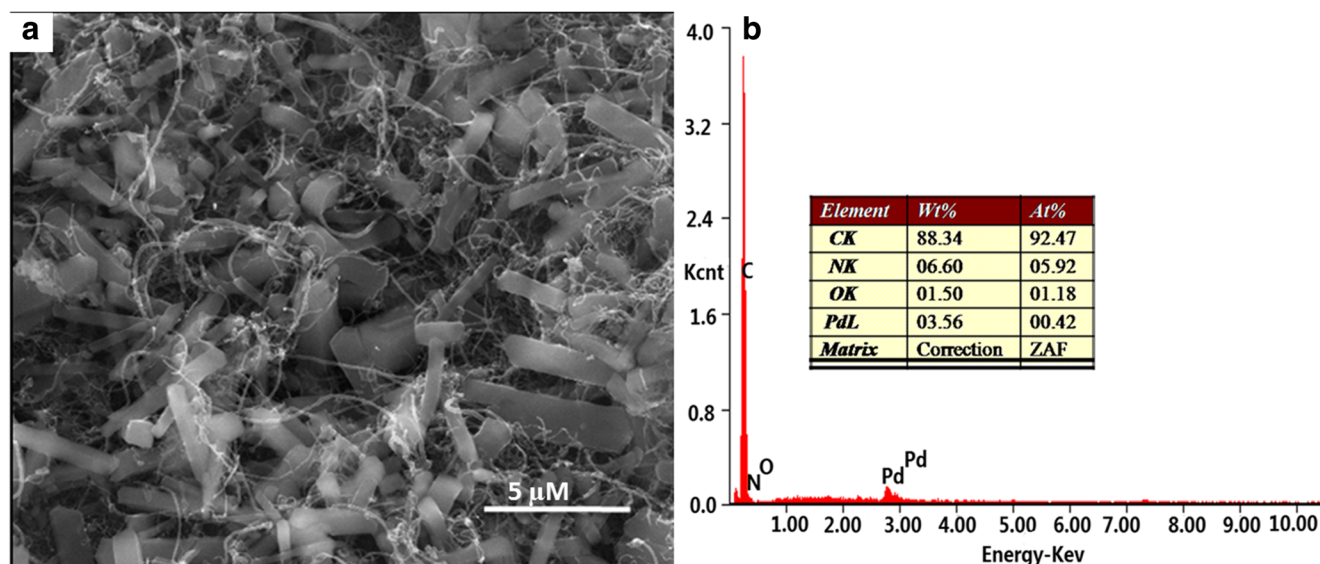
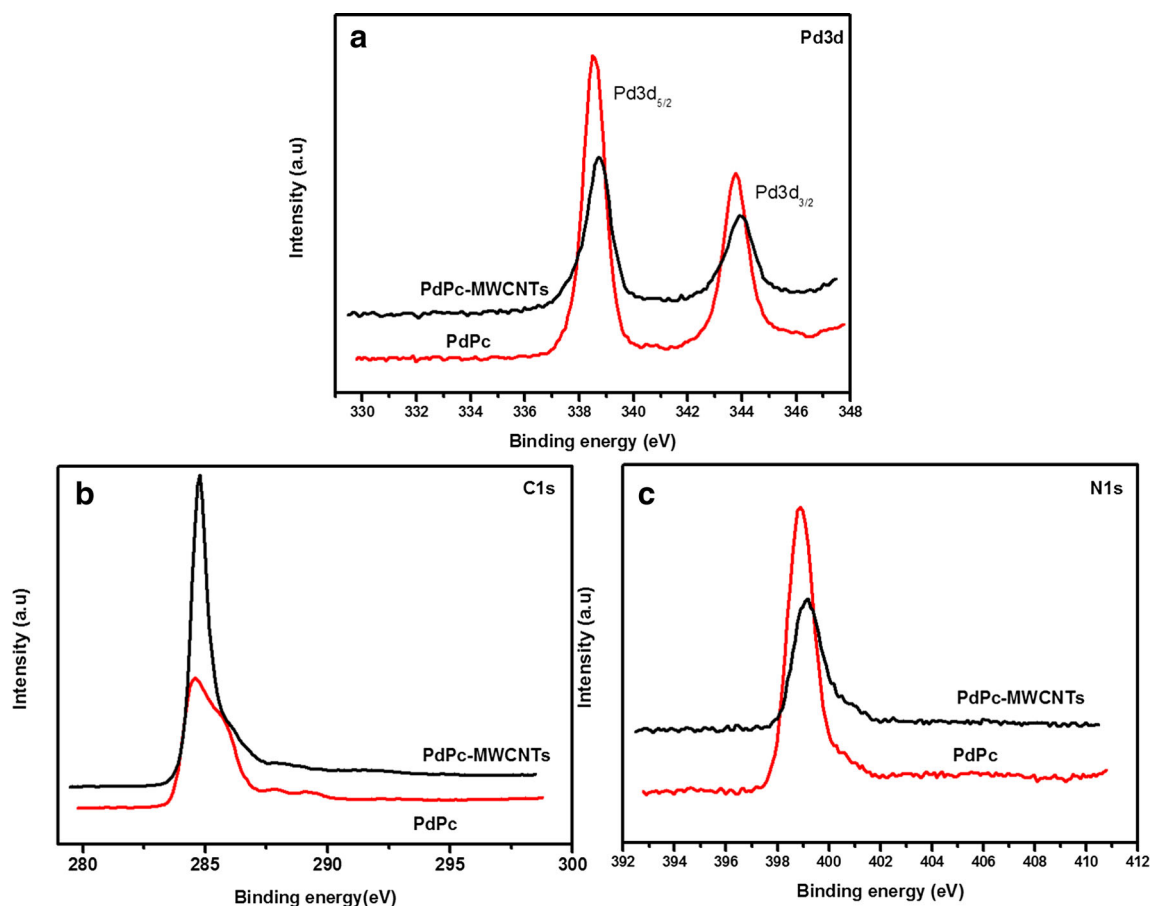


Fig. 1 SEM of PdPc-MWCNTs (a). EDX spectrum of PdPc-MWCNTs (b)



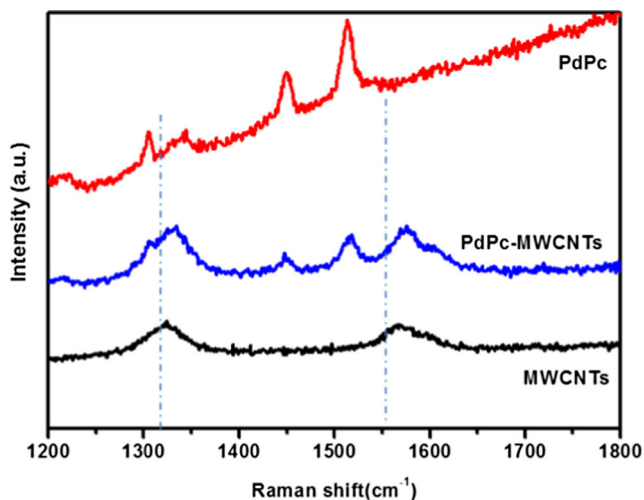
**Fig. 2** XPS spectra of PdPc and PdPc-MWCNTs: high-resolution XPS spectrum of Pd3d (a), C1s (b), and N1s (c)

diffusion-limited process, respectively. Figure S3 shows the impedance plot of PdPc-MWCNTs-Nafion/GCE and bare GCE in 0.1-M KCl solution containing 5.0 mM  $K_3[Fe(CN)_6]$ /5.0 mM  $K_4[Fe(CN)_6]$ . A remarkable decrease in the semicircle diameter was observed using PdPc-MWCNTs-Nafion/GCE compared to bare GCE, possibly resulting from the facilitated electron transfer based on PdPc-

MWCNT composite. Hence, it can be concluded that PdPc-MWCNTs-Nafion/GCE greatly contributed to accelerate the transfer of electrons [33].

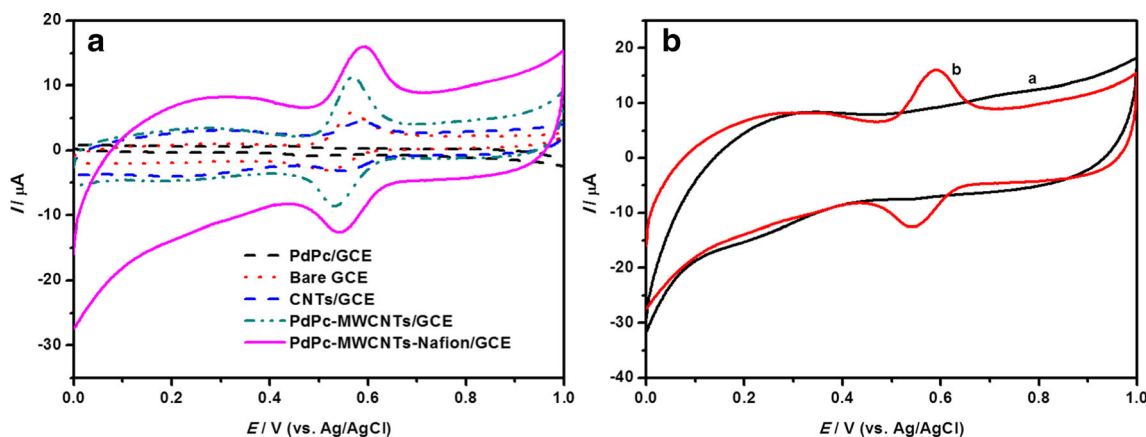
#### Electrochemical rutin detection based on PdPc-MWCNTs-Nafion/GCE

The electrochemical behavior of rutin (0.1 mM) was studied by cyclic voltammograms (CVs) on different electrodes, such as bare GCE, PdPc/GCE, CNTs/GCE, PdPc-MWCNTs/GCE, and PdPc-MWCNTs-Nafion/GCE. As shown in Fig. 4 A, a pair of redox peaks with different levels appeared on different types of electrodes, indicating that electrochemical reaction of rutin was realized on different electrodes. The redox peak current at the PdPc-MWCNTs-Nafion/GCE was higher than that at the bare GCE, PdPc/GCE, MWCNTs/GCE, and PdPc-MWCNTs, which meant that the PdPc-MWCNT nanocomposite can greatly improve the electrochemical activity of rutin. The extraordinarily electrocatalytic activity may be attributed to not only the synergetic electrocatalytic activity of PdPc and MWCNTs but also the excellent conductivity and homogeneous dispersibility of Nafion toward the nanocomposites. Figure 4b shows the CVs of PBS solution (pH 3) in the



**Fig. 3** Raman spectra of CNTs, PdPc, and PdPc-MWCNTs





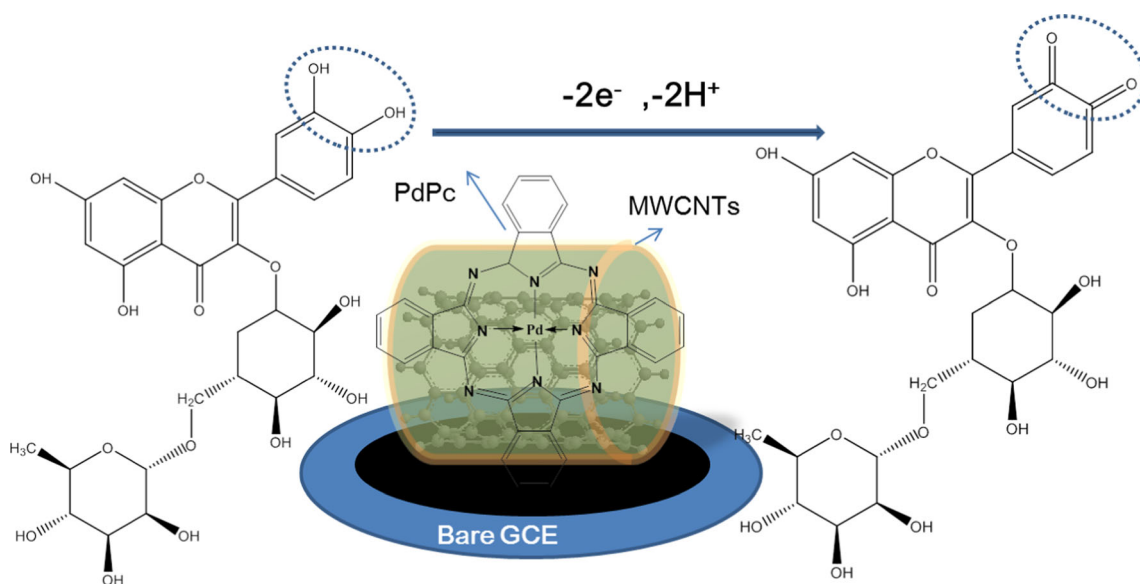
**Fig. 4** **a** CVs on different types of electrodes in the presence of 0.1 mM rutin at 50 mV/s. **b** CVs on PdPc-MWCNTs-Nafion/GCE in *a* 0.1 M PBS (pH = 3.0) and *b* 0.1 M PBS (pH = 3.0) containing 0.1 mM rutin

absence (a) and presence (b) of rutin (0.1 mM) on PdPc-MWCNTs-Nafion/GCE. Without rutin, no redox peak was observed; for comparison, a pair of redox peaks appeared at 0.60 and 0.55 V in the presence of rutin. The anodic peak current ( $I_{pa}$ ) and cathodic peak current ( $I_{pc}$ ) were recorded as 15.8 and  $-12.8 \mu\text{A}$ , respectively. The ratio of redox peak current ( $I_{pa}/I_{pc}$ ) was calculated to be 1.23 with  $\Delta E_p$  as 50 mV, indicating that the reversibility of rutin was considerably improved compared with bare GCE. That is to say, the combination of PdPc and MWCNTs played an important role in facilitating the electron transfer processes, improving the reversibility, and enhancing the sensitivity for rutin; this was in accordance with the EIS. Therefore, an electroanalytical method was developed for the sensitive detection of rutin based on PdPc-MWCNTs-Nafion/GCE and a schematic representation is shown in Fig. 5.

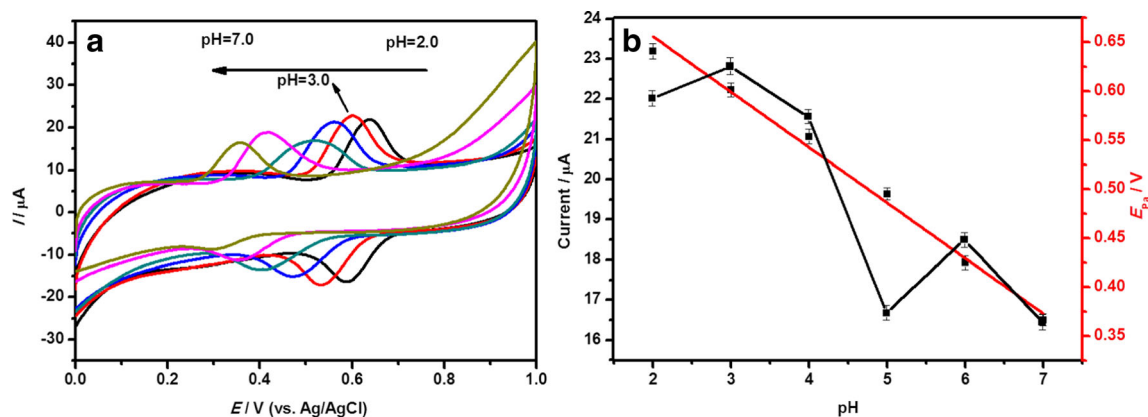
**Optimization of electrode preparation conditions and rutin detection conditions**

*Effect of solution pH*

Aiming to propose the mechanism of rutin oxidation on PdPc-MWCNTs-Nafion/GCE, the effect of pH on the electrochemical response of 0.1 mM rutin was investigated when the pH of PBS was ranged from 2.0 to 7.0. As clearly seen in Fig. 6a, the highest oxidation peak appeared when the solution pH was 3.0, after that, the peak current decreased when the pH was higher than 3.0. Furthermore, the effect of pH on the electrochemical behaviors of rutin was also investigated and is shown in Fig. 6b. It is found that the redox peak potentials shifted to more negative values as the pH increased over a range

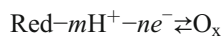


**Fig. 5** A schematic representation of the typical electrooxidation of rutin on PdPc-MWCNTs-Nafion/GCE



**Fig. 6** **a** CVs of 0.1 mM rutin on PdPc-MWCNTs-Nafion/GCE in 0.1 M PBS with various pH values (2.0–7.0) 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0. **b** Plots of  $I_{pa}$  and  $E_{pa}$  vs. pH values. Error bars showed the standard deviation of three experiments

from 2.0 to 7.0; this indicates the participation of protons in the electron transfer reaction of rutin. The oxidation reaction can be explained as follows:



where Red is the rutin,  $\text{O}_x$  is the corresponding oxidized product,  $m$  stands for the number of protons, and  $n$  is the electrons in the reaction. Since  $E_p$  can be expressed as (at 25 °C)

$$E_p = E_0 - \frac{m}{n} 0.059 \text{ pH}$$

where  $E_0$  is the standard potential and  $E_p$  (Red, pH = 0) is the anodic peak potential for Red at pH 0. The oxidation peak potentials presented a linear relationship with the pH increased as follows,  $E_{pa}/\text{V} = 0.769 (\pm 0.013) - 0.0567 (\pm 0.0026) \text{ pH}$  ( $R^2 = 0.991$ ). From the slope value of the previous equations, it could be concluded that  $E_p$  was pH dependent with a slope close to 59 mV, which indicates that the number of electrons and protons involved in the reaction

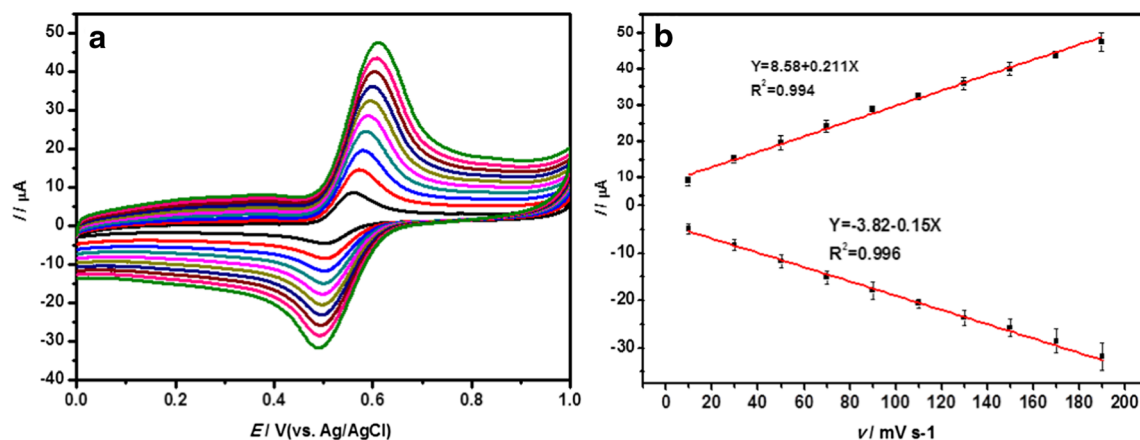
mechanisms is the same. Thus, the electrode reaction of rutin redox was two electrons accompanied by two proton processes [34].

#### Effect of the deposition amounts of PdPc-MWCNTs-Nafion solution

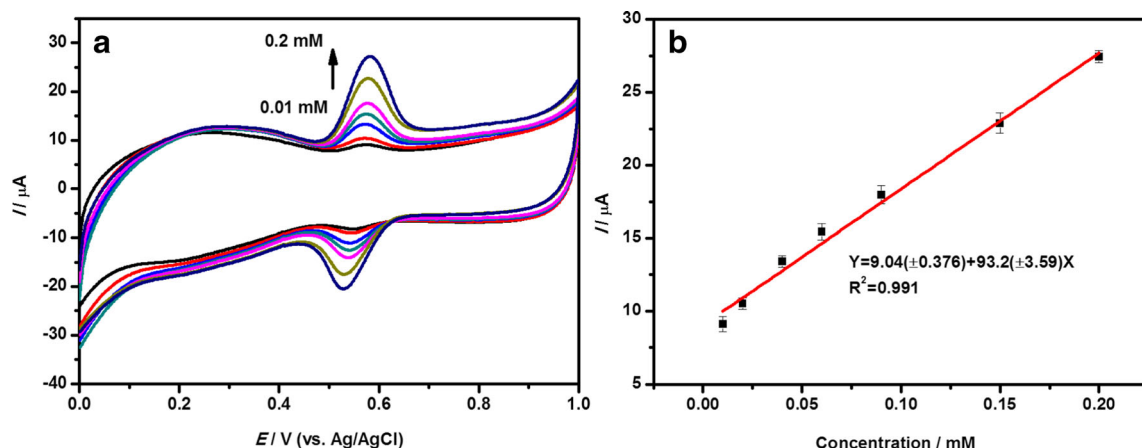
As shown in Fig. S4, the oxidation peak current increased as the deposition amount increased from 3.0 to 9.0  $\mu\text{L}$ ; afterward, the peak current decreased with further increasing the deposition amount. The reason may be that too many PdPc-MWCNTs would block the charge transfer between the composites and the solution, which was not favorable to the electrocatalytic oxidation of rutin. Thus, 9.0  $\mu\text{L}$  was selected as the optimal deposition amount in the experiments.

#### Effect of the scan rates

Figure 7 shows the CVs of 0.1 mM rutin at different scan rates on the PdPc-CNTs-Nafion/GCE under the



**Fig. 7** **a** CVs of 0.1 mM rutin (0.1 M PBS, pH = 3.0) at different scan rates (0.01–0.19  $\text{V s}^{-1}$ ) on the PdPc-MWCNTs-Nafion/GCE. **b** Plot of peak current versus scan rate. Error bars showed the standard deviation of three experiments

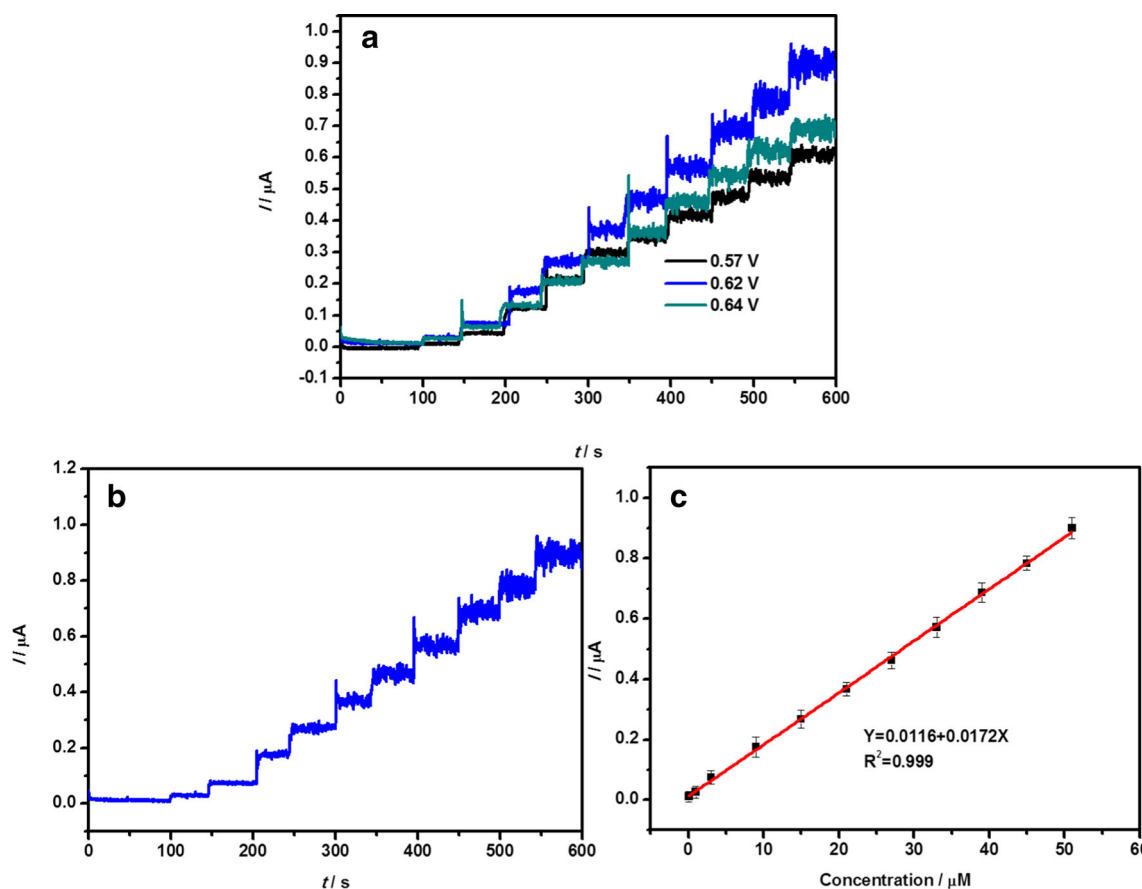


**Fig. 8** **a** CV curves of various concentrations of rutin in 0.1 M PBS (pH = 3.0) on the PdPc-MWCNTs-Nafion/GCE, scan rate of 50 mV s<sup>-1</sup>. **b** Plots of peak current versus concentrations. Error bars showed the standard deviation of three experiments

optimal conditions. The peak currents increased with increasing the scan rates. Figure 7b shows that the redox peak currents ( $I_p$ ) were linearly related to the scan rates, indicating an adsorption-controlled electrode process on the PdPc-MWCNTs-Nafion/GCE [15].

**Selective and sensitive determination of rutin and the stability of the PdPc-MWCNTs-Nafion/GCE**

Considering that coexistence of AA in biological fluids would cause severe interference, which often leads to poor selectivity



**Fig. 9** **a** Amperometric current responses of successive addition of rutin in PBS solution at different potentials on the PdPc-MWCNTs-Nafion/GCE. **b** Amperometric current responses of successive addition of rutin

in PBS solution at 0.62 V on the PdPc-MWCNTs-Nafion/GCE. **c** Plot of current vs. rutin concentration at 0.62 V. Error bars showed the standard deviation of three experiments

**Table 1** Merits of comparable electrochemical sensor for determination of rutin

Electrode	LOD (nmol L <sup>-1</sup> )	Linear range (μmol L <sup>-1</sup> )	Reference
Chitosan/graphene/GCE	–	0.5–10.4	[35]
Molecularly imprinted multiwall carbon nanotube paste electrode	50	0.08–1.4	[36]
Pyridinium-based ionic liquid-modified carbon paste electrode	358	0.5–100	[37]
Ionic liquid-modified carbon ceramic electrode	90	0.3–100	[38]
SWCNT-modified carbon ionic liquid electrode	70	0.1–800	[39]
CeO <sub>2</sub> -modified gold electrode	200	0.5–500	[40]
PdPc-MWCNTs-Nafion/GCE	75	0.1–51	This work

and sensitivity for rutin detection, therefore, it is essential to separate the overlapping signals of rutin and AA from each other. Figure S5 shows the CVs of different kinds of solution in 0.1 M PBS at pH = 3.0 on the PdPc-MWCNTs-Nafion/GCE, suggesting that this proposed method has excellent selectivity toward determination of rutin in the presence of AA.

Figure 8a shows the CVs of different concentrations of rutin in PBS (0.1 M, pH 3.0) on the PdPc-MWCNTs-Nafion/GCE at a scan rate of 50 mV s<sup>-1</sup>. The wave shape of all the curves was similar, but the area of the curves became larger with increasing the concentration of rutin, which suggested that the oxidation peak at about 0.60 V was caused by the oxidation of rutin at the PdPc-MWCNTs-Nafion/GCE. Figure 8b shows that the catalytic current was proportional to the concentration of rutin within the range from 0.01 to 0.2 mM.

To improve the performance of the sensor, the effect of detection potential on the amperometric response was systematically studied. As shown in Fig. 9a, the maximum response with a good signal/noise ratio was observed at 0.62 V. Therefore, 0.62 V was selected as the optimal detection potential in subsequent experiments. Figure 9b displays the *i*-*t* plots of successive addition of rutin into a stirring solution of 0.1 M PBS (pH 3.0) at 0.62 V on the PdPc-MWCNTs-Nafion/GCE. The reduction current rapidly increased to reach a steady state within 3.0 s after addition of rutin. It may be attributed to the synergistic effect of PdPc and MWCNTs, which provided an excellent conductive pathway to transfer electrons. As shown in Fig. 9c, the response current was proportional to the concentration of rutin over the range from 0.1 to 51 μM with a correlation coefficient of 0.999. The linear regression equation is expressed as  $I = 0.012(\pm 0.003) + 0.01720(\pm 0.00014)C_{\mu\text{M}}$ . The sensitivity was found to be 0.764 μA μM<sup>-1</sup> cm<sup>-2</sup>. Moreover, the limit of detection (LOD) was 75 nM at the signal to noise of 3. The comparison of the

analytical performance of PdPc-MWCNTs-Nafion/GCE with other rutin sensors is presented in Table 1. It can be seen that the fabricated electrode offered a reasonable linear range and a preferable detection limit for rutin compared to the reported literature. The response of rutin in real samples containing common coexisting ions on PdPc-MWCNTs-Nafion/GCE was investigated (Fig. S6). The results show that the common coexisting ions tested have no obvious interference on the determination of rutin. Besides the common existing ions, the variations of peak current of L-cysteine, L-glutamic acid, uric acid, sucrose, and ethanol were smaller than 5%. Quercetin has some influence of peak current, but it is not the coexisting substance in drug tablets, so the prepared sensor is acceptable for rutin determination [15].

The stability of PdPc-MWCNTs-Nafion/GCE was estimated in PBS containing 3 μM rutin at 0.62 V. As shown in Fig. S7, there was a stable amperometric response after being run for 2000 s. After the electrochemical measurement, the sensor was rinsed with double-distilled water and stored at 4 °C; 7 days later, the response current of rutin behaved the same as before. Meanwhile, the repeatability of PdPc-MWCNTs-Nafion-modified GCE was examined by measuring the responses of the mixture of 0.05, 0.09, and 0.10 mM rutin in PBS (0.1 M, pH 3.0) for ten successive measurements. The relative standard deviation (RSD) was 3.0, 3.8, and 2.5% respectively. To evaluate the possible applications of the proposed method, recovery experiments were carried out by spiking the standard rutin solution in PBS containing bovine serum protein using the standard addition method (Table 2). The recovery was 95–103%; therefore, the previous results clearly indicated that the proposed electrochemical sensor based on PdPc-MWCNTs-Nafion composite possessed good stability, acceptable reproducibility, and applicability.

**Table 2** Recovery results for rutin in bovine serum.

Added (μM)	Found (μM)	Recovery (%)
10	9.54	95.4
20	20.3	101
30	30.8	103

**Table 3** Determination of rutin in tablets by the proposed method (*n* = 3).

No.	Added (μM)	Expected (μM)	Found (μM)	Recovery (%)
1	0	10	9.81	98.1
2	5	15	14.8	98.7
3	10	20	20.2	101

Each tablet contains 20 mg



In order to fit into the linear range of the method, rutin tablet samples (20 mg tablet<sup>-1</sup>) for the detection were accurately diluted with the supporting electrolyte. The determination of rutin was conducted by the proposed method. Recovery experiments were carried out by spiking standard rutin solution in the sample containing 10 μM rutin, which was extracted previously and diluted by 0.1 M PBS (pH 6.0) using the standard addition method. As can be seen in Table 3, the results were satisfactory with the recovery 98–101%, which indicated clearly that this new proposed method exhibited good applicability.

## Conclusion

In summary, an electrochemical sensor based on PdPc-CNTs-Nafion composite was successfully fabricated for the sensitive detection of rutin. The developed sensor exhibited excellent electrocatalytic activity toward rutin due to the synergetic effects of PdPc and CNTs (excellent electric conductivity and catalytic activity) and the homogeneous dispersibility of Nafion toward the nanocomposites. The proposed approach has wide linear range, good stability, and acceptable reproducibility, and common coexisting ions were found to have no interference on the determination of rutin, which will probably bring widespread applications in Chinese medical analysis or quality monitoring in real samples.

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