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Facile Synthesis of Pd Nanoparticles-Graphene Oxide Hybrid and Its Application to the Electrochemical Determination of Rutin

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A Pd nanoparticles-graphene oxide (PdNPs/GO) hybrid as a highly sensitive sensing platform for determination of rutin was successfully prepared by a facile one-pot redox synthesis approach. Formation of PdNPs and loading onto the GO nanosheets were accomplished simultaneously by a redox reaction between H_2PdCl_4 and GO, without use of any additional reductants. Scanning electron microscopy (SEM) results demonstrated that PdNPs with an average size of 60 nm were distributed on the surface of GO nanosheets. Compared with the GO modified electrode, the PdNPs/GO modified electrode showed a better electrocatalytic activity toward the oxidation of rutin with larger peak current. Then the PdNPs/GO hybrid can be used as an enhanced sensing platform for the electrochemical determination of rutin. Under the optimal conditions, the anodic peak current was linear to the concentration of rutin in the range from 0.005 to 6 μM with the detection limit of 0.001 μM (S/N = 3). More importantly, the developed sensor can be used for the determination of rutin in medicine tablets with satisfactory results.

Keywords: Pd nanoparticles; Graphene oxide; Rutin; Electrochemical detection; Sensor

1. INTRODUCTION

Rutin is an important member of the flavonoid family. It has been widely distributed in plants and some plant leaves [1-2]. It has been reported that rutin has many physiological functions, including anti-inflammatory, anti-bacterial, anti-tumoral and anti-oxidant. In addition, rutin was also found to have the pharmacological actions, such as lowering blood pressure, diluting the blood and reducing the capillary permeability [3-5]. Until now, several analytical methods have been proposed for the determination of rutin, including capillary electrophoresis [6], chemiluminescence [7], high performance liquid chromatography [8] and electroanalysis [9]. Among them, electrochemical methods have gained considerable interest in recent years, owing to their simplicity, high sensitivity, good selectivity and low cost [10,11]. In this case, various modified electrodes have been used for the detection of rutin.

Noble metal NPs (such as Au, Pt and Pd) have the excellent electric and thermal conductivity, and can be acted as efficient catalysts for many chemical reactions [12-13]. They are usually used to construct various electrochemical sensing platforms due to their excellent properties. Compared with AuNPs and PtNPs, PdNPs have drawn much attention in electrochemical field because of their higher abundance, lower cost and good anti-poisoning property [14]. However, nanoscale metal particles with highly active centers tended to aggregate to minimize their total surface energy [15-16]. To solve this problem, different methods have been used to stabilize these NPs, for example, using capping agents to stabilize NPs [17], or immobilizing metal NPs onto specific supports [18-22].

Graphene oxide (GO), a representative derivate of graphene, has a large specific surface area with two-dimensional structure and numerous oxygen-containing groups such as hydroxyl, carbonyl and carboxyl groups on the basal planes and edges. These features enabled GO to be a promising support material for anchoring or binding various particles [23, 24]. More importantly, metal salts can be reduced by oxygen-functional groups of GO to form metal NPs, avoiding the usage of any toxic reducing reagent [25], and the strongly hydrophilic of GO can effectively prevent the aggregation of metal NPs. Based on these superiorities, GO was chosen as the supporting material to anchor PdNPs.

Herein, we described a simple, environmentally friendly and cost-effective strategy for dispersing PdNPs on the surface of GO by directly mixing GO with aqueous solutions of H_2PdCl_4. GO acted as both reducing agent and stabilizer, avoiding the use of additional reducing agent and toxic reagents. Further, this nanostructured material has been employed for the fabrication of electrochemical sensor for detection of rutin. The constructed sensor displayed fast electron transfer, prominent catalytic ability and excellent analytical performance to rutin with a wide linear range, a low detection limit and satisfactory recoveries.

2. EXPERIMENTAL

2.1 Chemicals and reagents

Rutin was purchased from Aladdin and GO was purchased from Nanjing Xian Feng Nanomaterials Technology Co., Ltd. (Nanjing, China). Palladium chloride, disodium hydrogen phosphate (Na_2HPO_4), and sodium dihydrogen phosphate dehydrate (NaH_2PO_4) were purchased from Sinopharm chemical reagent Co. Ltd. Rutin stock solutions (0.01 M) were prepared with absolute ethyl alcohol and were stored at 278-281 K. Phosphate buffer solution (PBS, 0.1 M) was used as an electrolyte for all electrochemistry measurement. Double distilled water was used throughout the experiments. All other reagents were of analytical grade and were used without further purification.

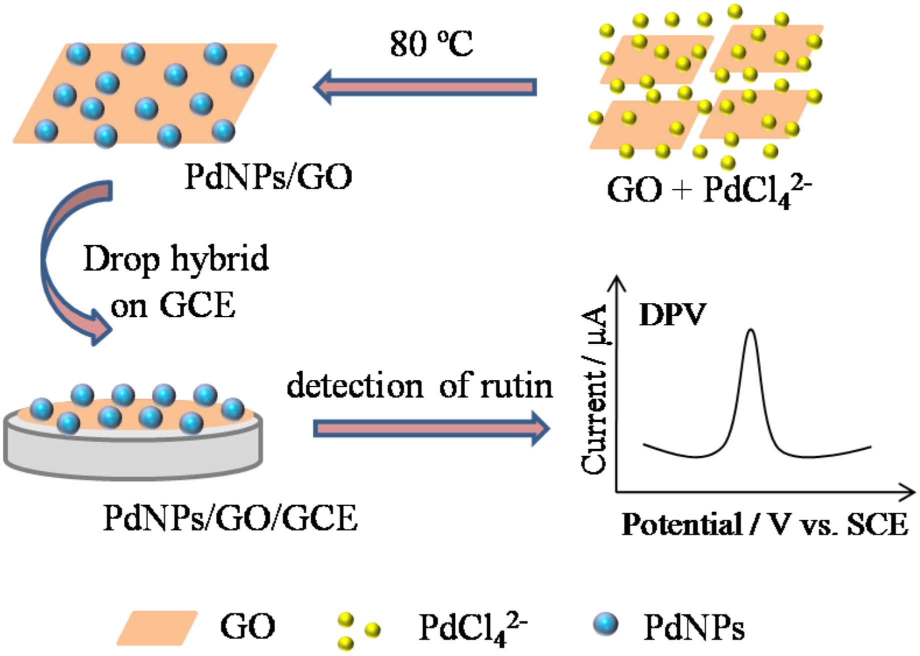
2.2 Apparatus

Scanning electron microscopy (SEM) analysis was performed by a Hitachi S-3000 N scanning electron microscope. The cyclic voltammetric (CV) and differential pulse voltammetry (DPV) measurements were operated on a CHI660D electrochemical workstation (Shanghai, China). A three-electrode cell (5 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.

2.3 Preparation of the PdNPs/GO modified GCE

4 mg GO were dispersed in 8 mL double distilled water for 1 h under ultrasonic agitation. Subsequently, 1 mL H_2PdCl_4 aqueous solution (5 mM) was added into the above stable GO aqueous, and the reaction mixture was stirred at 80°C for approximately 12 h. Then the resulting nanocomposite of PdNPs/GO was collected by centrifugation at 1000 × g for 5 min and washed with double distilled water. Finally, the precipitation was re-dispersed in 8 mL water and stored in 4 ºC for further use.

Prior to modification, the GCEs were polished with chamois leather containing 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. Then 5 μL of the PdNPs/GO suspension was dropped on the well-polished GCE and dried under the air. The obtained modified electrode was called PdNPs/GO/GCE (shown in scheme 1).



Scheme 1 The fabrication of PdNPs/GO/GCE for the detection of rutin.

3. RESULTS AND DISCUSSION

3.1 Surface morphologies of the GO and PdNPs/GO nanomaterials

The morphology and structure of the prepared GO and PdNPs/GO were characterized by SEM. As displayed in Fig. 1A, homogeneous, flexible and wrinkled sheets were observed on the surface of GO material. From Fig. 1B, we can clearly see that the uniform PdNPs were well dispersed on the surface of GO sheets. The results confirmed that PdNPs were successfully anchored on GO through the proposed simple one-step method. A possible mechanism for the formation of the PdNPs/GO nanocomposite can be ascribed to the redox reaction between GO and H_2PdCl_4.

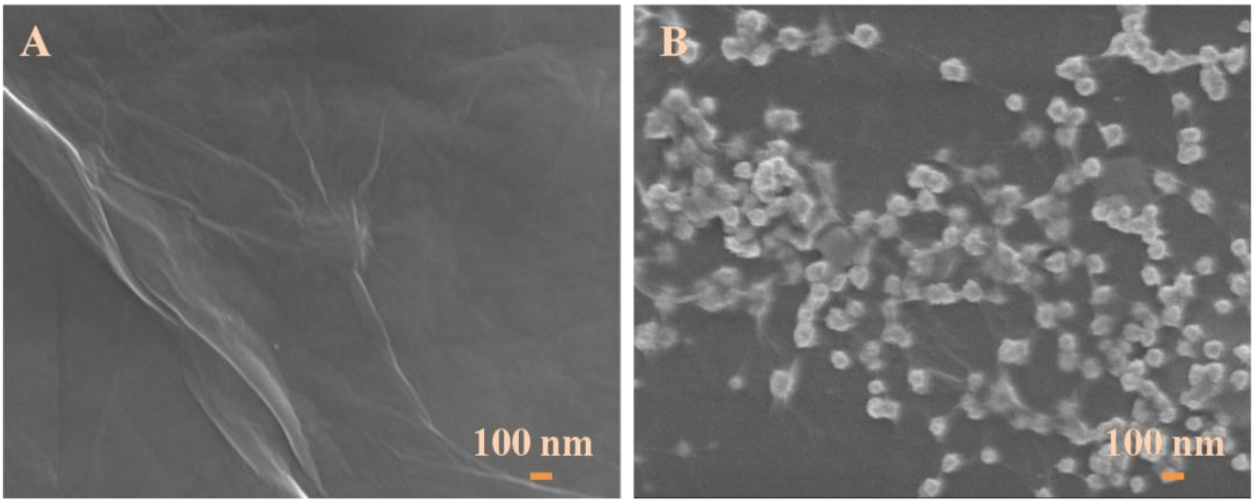


Figure 1. SEM images of GO (A) and PdNPs/GO (B).

3.2 Electrocatalytic behaviors of modified electrodes

The electrochemical behavior of 20 μM rutin on bare GCE (a), GO/GCE (b) and PdNPs/GO/GCE (c) was examined using cyclic voltammetry (CV) in PBS and the results were shown in Fig. 2. From Fig. 2a, it revealed that rutin exhibited a quasi-reversible redox behavior with low peak currents at the bare GCE, demonstrating that the redox activity of rutin was very low on bare GCE. When using GO/GCE (b), a higher current response for the rutin oxidation was observed (b) compared with the bare GCE, which was ascribed to the interaction between the oxygen-containing groups on GO and rutin. Notably, PdNPs/GO/GCE (c) displayed the largest current value, which could be attributed to the high conductivity of PdNPs and the large effective surface area of PdNPs/GO. The greatly improved electrocatalytic activity of rutin at the PdNPs/GO/GCE enabled PdNPs/GO to be an efficient electrochemical sensing material for rutin detection.

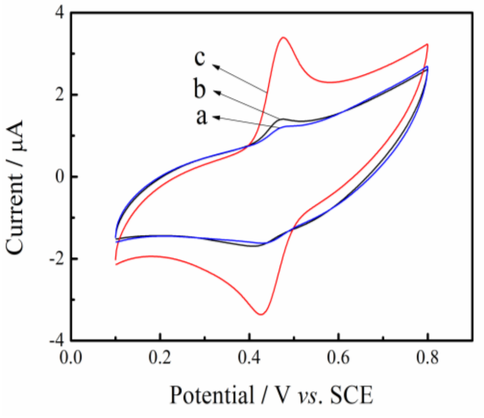


Figure 2. Cyclic voltammograms of bare GCE (a), GO/GCE (b) and PdNPs/GO/GCE (c) in 0.1 M PBS (pH 4.0) containing 20 μM rutin. Scan rate: 50 mV s^{-1}.

3.3 Influence of pH values

Fig. 3A showed the influence of pH on the response of 20 μM rutin. It can be observed that the anodic peak current of rutin increased with the increase of pH value when it reached 3.0, and it decreased as the pH increased further. The maximum anodic current was obtained at a pH value of 4.0. Then, pH 4.0 was chosen as the optimal pH for detection in the subsequent experiments.

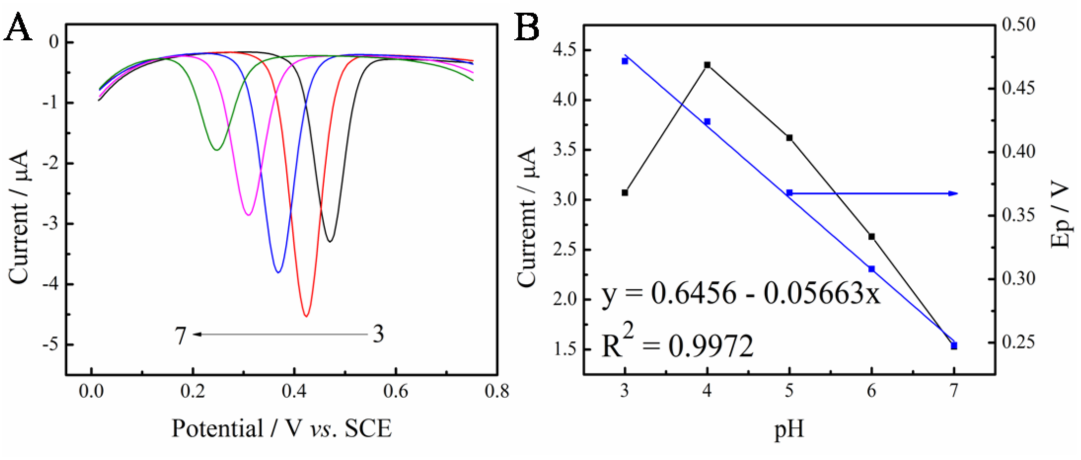


Figure 3. (A) Differential pulse voltammetry of 20 μM rutin at different pH values (3.0, 4.0, 5.0, 6.0, 7.0) in PBS at PdNPs/GO/GCE. (B) The influences of pH on the oxidative peak current of 20 μM rutin.

Moreover, with increasing the pH value from 3.0 to 7.0, the anodic peak shifted negatively, which demonstrated that the proton had taken part in the reduction and oxidation process of rutin (shown in Fig. 3B). The anodic peak potential was linear to pH, where the linear regression equation was E_{pa} (V) = - 0.05663 pH + 0.6456 (R^2 = 0.9972). The slope of the equation (56.63 mV pH^{-1}) was approximately close to the theoretical value of 58.5 mV pH^{-1}, indicating that the electro-chemical reaction involved equal numbers of proton-transfer and electron-transfer [26].

3.4. Influence of scan rate

The influence of scan rate on the electrochemical response of 20 μM rutin in 0.1 M PBS (pH 4.0) at PdNPs/GO/GCE was studied by CV (Fig. 4A). The anodic peak currents (Ipa) and cathodic peak currents (Ipc) increased gradually along with the increase of the scan rate. In the range of 10-500 mV s^{-1}, both the logarithm of reversible oxidation peak currents (log I_{pa}) and reversible reduction peak currents (log I_{pc}) were linearly correlated to the scan rates (Fig. 4B). The linear relationship can be expressed in the following equations: log I_{pa} = 0.7069 log$v$ - 0.6833 (R^2 = 0.9998) and log I_{pc} = - 0.6864 log$v$ + 0.7505 (R^2 = 0.9981). These results indicated that the oxidation of rutin followed a predominantly diffusion-controlled electron transfer process occurring at PdNPs/GO/GCE.

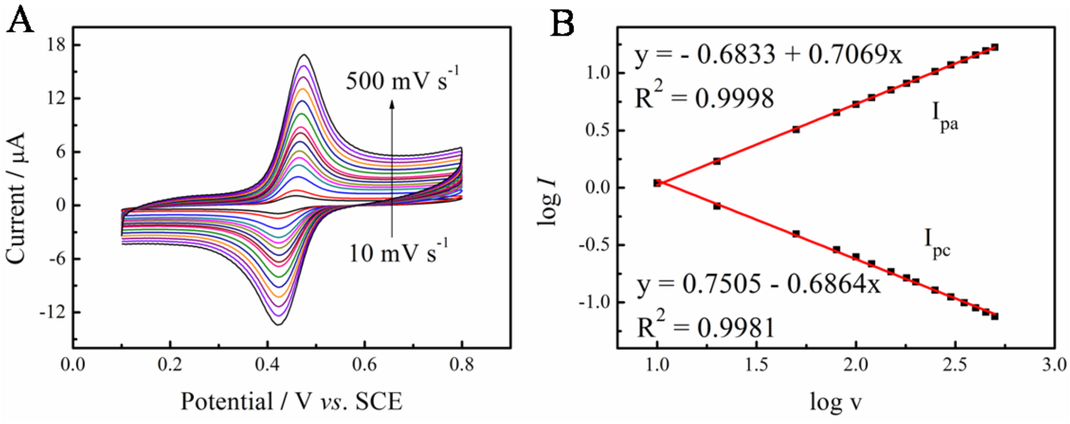


Figure 4. CVs of 20 μM rutin at PdNPs/GO/GCE in 0.1 M PBS (pH 4.0) at different scan rate (A); plots of the logarithm of reversible oxidation peak currents (log I_{pa}) and reversible reduction peak currents (log I_{pc}) against the logarithm of scan rates (log v) (B) Scan rate (mV s^{-1}): 10, 20, 50, 80, 100, 120, 150, 180, 200, 250, 300, 350, 400, 450 and 500.

3.5. Electrochemical determination of rutin

Fig. 5A shows the differential pulse voltammetry (DPV) of rutin with the concentration ranging from 0.005 μM to 5 μM under optimized experimental conditions. The linear regression equation can be expressed as Ipa = - 0.0829 + 0.8706 c, with a correlation coefficient of 0.9973 (Fig.5B). The detection limit was evaluated to be 0.001 μM (based on S/N = 3). The comparison of PdNPs/GO/GCE with other electrodes for the rutin determination was summarized in Table 1 [27-34]. It can be observed that the PdNPs/GO/GCE offered reasonable linear range for rutin detection and the detection limit was lower than some of previous reports. These results indicated that PdNPs/GO/GCE was an excellent platform for the detection of rutin. The superior performance of the prepared sensor might be due to the high surface area and excellent electrocatalytic activity of PdNPs/GO nanocomposite.

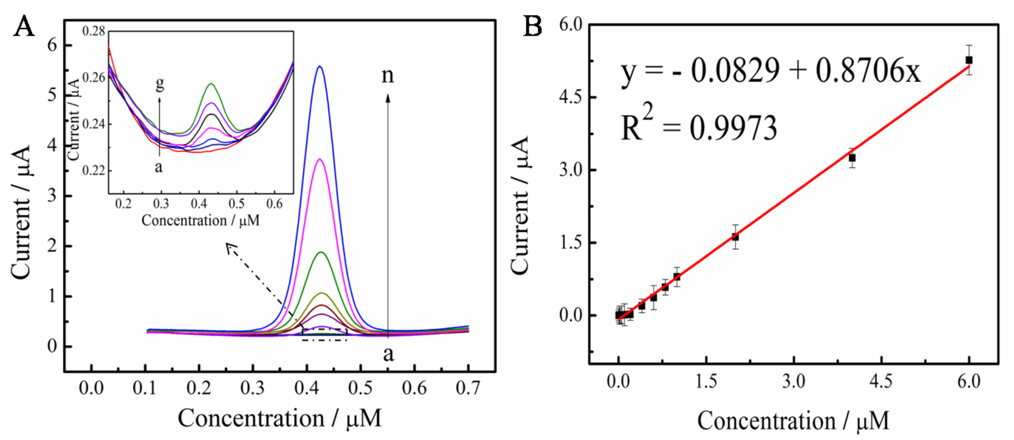


Figure 5. DPV of different concentrations of rutin (0, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 4 and 6 μM) at PdNPs/GO/GCE in 0.1 M PBS (pH 5.0). Inset: *i vs. c* rutin plots. Pulse amplitude: 50 mV, pulse width: 0.2 s, pulse increment: 4 mV.

Table 1. Comparison with other electrodes for the determination of rutin.

Modified electrodes	Linear range (μM)	Detection limit (μM)	References
Nafion-GO-IL/CILE	0.08-100	0.016	[27]
GR/CILE	0.07-100	0.024	[28]
[a]Fc-S/AuNPs/GR-Chit/GCE	0.04-100	0.01	[29]
[b]MIP-MWNPE	0.08-1.4 and 2.0-160	0.05	[30]
[c]PABSA/GCE	0.25-10	0.1	[31]
Fe_2O_3/RGO/GCE	0.015-18	0.0098	[32]
PtNP/rGO/GCE	0.05-10	0.01	[33]
IL/MWCNTs/CPE	0.03-1.5	0.01	[34]
PdNPs/GO/GCE	0.005-6	0.001	This work

[a] Fc-S: Ferrocene benzyne derivative/gold nanoparticles;
[b] MIP-MWNPE: molecularly imprinted polymer-multiwall carbon nanotube paste electrode;
[c] PABSA: Poly(p-aminobenzene sulfonic acid).

3.6. Interference

The interferential experiment of PdNPs/GO/GCE was tested towards the detection of rutin in the presence of different concentrations of interferents. These results demonstrated that 100-fold of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, 50-fold of ascorbic acid, glucose, citrate and 10-fold of shikonin did not interfere with the oxidation signal of 0.5 μM rutin (peak current change < 6%), indicating the proposed method has excellent selectivity toward rutin.

3.7. Reproducibility and stability of the PdNPs/GO/GCE

The reproducibility of the modified electrode was estimated by determining 1 μM rutin with five modified electrodes prepared independently. Five measurements from the batch resulted in a relative standard deviation of 4.63%, revealing this method had excellent reproducibility.

The stability of the PdNPs/GO/GCE was also investigated. It was kept in the air at room temperature and used for measuring1 μM rutin daily over a period of 2 weeks. The eligible decrease of the response current (less than 5%) was observed, which showed long-term stability of the PdNPs/GO film on the GCE surface.

3.8. Sample Determination

For verifying the practicality and reliability of the developed method, PdNPs/GO/GCE was applied to detect rutin in the compound rutin tablet samples in PBS (4.0). The drug tablets were ground and dissolved in ethanol. And the resulting solution was properly diluted with 0.1 M PBS (pH 4.0) to prepare the sample solutions. The samples were detected by a standard addition method. The results were listed in Table 2. The recoveries of rutin were in the range from 95.75 to 104.43%, revealing that the proposed method has good accuracy and satisfactory repeatability.

Table 2. Results for the determination of rutin in compound tablet samples.

samples	Specified (μM)	Detected (μM)	Added (μM)	Total found (μM)	Recovery (%)
1	3.02	3.01	1.00	4.06	101.25
2	3.02	2.98	2.00	5.21	104.62
3	3.02	3.06	3.00	6.02	99.34
4	3.02	3.03	4.00	6.78	96.44
5	3.02	2.99	5.00	8.16	102.12

4. CONCLUSION

In this paper, a green one-step method was successfully developed for the synthesis of a new type of PdNPs/GO hybrid. The PdNPs/GO nanocomposite modified electrode showed excellent electrochemical properties and excellent electrocatalytic activity toward the oxidation of rutin, which was designed as electrochemical sensor for the detection of rutin. The fabricated PdNPs/GO/GCE showed a low detection limit of 0.001 μM and a wide linear range from 0.005 to 6 μM. In addition, the modified electrode also exhibited good stability, acceptable reproducibility, and excellent anti-interference capability. This proposed method can be used for the detection of rutin in medicines.

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