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High-Sensitivity Electrochemical Detection of Chlorogenic Acid Based on Pt@r-GO@MWCNTs Ternary Nanocomposites Modified Electrodes

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Abstract

This work reports an electrochemical sensor for high-sensitivity electrochemical determination of chlorogenic acid. The electrochemical sensor was mainly fabricated from Pt@r-GO@MWCNTs ternary nanocomposites prepared by one-pot method, and the modified material structure was characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) techniques. The electrochemical behavior of chlorogenic acid on Pt@r-GO@MWCNTs/GCE was investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Due to the excellent electrical conductivity and catalytic properties of Pt@r-GO@MWCNTs nanocomposites, compared with bare GCE, Pt@r-GO@MWCNTs/GCE showed stronger electrochemical response signals towards chlorogenic acid. In a 0.1 M PBS buffer solution at pH 6.0 with an enrichment potential of -0.1 V and an enrichment time of 150 s, the linear range of Pt@r-GO@MWCNTs/GCE for the detection of chlorogenic acid was 0.005 ~ 2 μM and 2 ~ 20 μM, and the limit of detection (LOD) was 0.001 μM. In addition, the sensor also has good selectivity, reproducibility, and stability and has been successfully used for the detection of chlorogenic acid in real serum samples with satisfactory results.

Keywords: Electrochemical sensor; Chlorogenic acid; Selectivity; Real sample detection; Nanocompasite.
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1. Introduction

Chlorogenic acid (CGA), a naturally occurring phenolic acid, also called 5-O-caffeoylquinic acid, is a needle-like crystal hemihydrate that is soluble in ethanol and slightly soluble in water. Chlorogenic acid is found in the seeds, roots, stems, and leaves of plants. a needle-like crystal hemihydrate that is soluble in ethanol and slightly soluble in water.[1-6] Clinical studies have shown that CGA has various effects. As a small molecule, chlorogenic acid can cross the blood-brain barrier and induce the differentiation of tumor cells, thus transforming them into healthy cells. And it has a wide range of antibacterial effects, beneficial to the gallbladder, hemostasis, increasing white blood cells, and antiviral effects, and can be used clinically for the treatment of respiratory infections, anti-inflammatory and antipyretic, cooling the blood, dissipating heat, *etc*.[7-13] In addition, CGA has a promising effect on the regulation of blood glucose in patients with type II diabetes mellitus.[12,13] Therefore, high-sensitivity detection of CGA has attracted the interest of all scientists**.**

Nowadays, various methods have been established for the detection of CGA, including high-performance liquid chromatography,[14-16] capillary electrophoresis,[17-19] and nuclear magnetic resonance spectroscopy.[20] Although the above methods have good accuracy and high sensitivity for the detection of CGA,[21-24] they also have various drawbacks, such as expensive instruments, time-consuming sample processing, and the difficulty of performing rapid detection. Compared

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with the above detection methods, electrochemical detection methods have the advantages of simple instrumentation, low cost, convenient operation, and rapid detection. Therefore, electrochemical detection based on various electrode modification materials can provide a new method for the determination of CGA.

MWCNTs and graphene have attracted the attention of the scientific community due to their stable physicochemical properties, good electrical conductivity, and lower cost.[25,26] They have been widely used as excellent electrode modification materials in the construction of various electrochemical sensors.[27-37]

Pt nanoparticles (Pt NPs) are another widely used electrode modification material,[38,39] and in order to achieve good sensing performance, various conductive carbon materials,[40-44] such as carbon black,[45-49] carbon nanofibres, porous carbon, carbon nanotubes,[50-52] and graphene, can be combined with PtNPs in order to prevent nanoparticle agglomeration.[53-57]
In this work, we synthesized a new ternary nanocomposite using multi-walled carbon nanotubes (MWCNTs), reduced graphene oxide (r-GO) and platinum nanoparticles (Pt NPs) and modified this nanocomposite onto GCE to construct an electrochemical sensor for the detection of chlorogenic acid. Under the optimal detection conditions, the detection of chlorogenic acid by Pt@r-GO@MWCNTs/GCE presented a wide linear range and a low detection limit.

2. Experimental section

2.1 Chemicals and reagents

Chlorogenic acid was purchased from Shanghai Aladdin Biochemical Co. MWCNTs were purchased from Fung Nano Materials Technology Co. Human serum was purchased from Beijing Hua Yue Yang Biotechnology Co. GO was purchased from Nanjing Xianfeng Nano Co. Chloroplatinic acid hexahydrate (H_2PtCl_6 $6H_2O$) was purchased from Beijing Bailing Wei Technology Co. The reagents used in the experiments were analytically pure. 1.0 mM chlorogenic acid was dissolved in 50 mL of ethanol and diluted to 100 mL with evaporated water. Phosphate buffer solution (PBS, 0.1 M) was made by mixing potassium dihydrogen sulfate (KH_2PO_4, 0.1 M) with dipotassium hydrogen phosphate (K_2HPO_4, 0.1 M) and potassium chloride (KCl, 0.1M). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions were used to adjust the pH of the solution. Human blood serum samples were diluted 1:50 v/v with PBS buffer solution pH 6.0.

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2.2 Synthesis of Pt@r-GO@MWCNTs nanocomposites and preparation of Pt@r-GO@MWCNTs/GCE

The Pt@r-GO@MWCNTs ternary nanocomposites were prepared by a simple one-pot method, and the structures of the materials and electrode preparation are shown in Fig. 1. Firstly, 30 mg of monolayer graphene oxide and 30 mg of MWCNT were added to 30 mL of distilled water and ultrasonically mixed for 30 min at room temperature. Then, under stirring conditions, 500 μL of a solution with a concentration of 60 mM of H_2PtCl_6 and 10 mL of a solution with a concentration of 0.05 g/mL of $NaBH_4$ were added, and the reaction was vigorously stirred for 30 min. Finally, the reaction was carried out with a volume of the clean Pt@r-GO@MWCNTs ternary nanocomposites obtained by centrifugal washing three times (centrifugation speed of 8000 rpm for 3 min) with a mixture of ethanol and distilled water in the ratio of 1:1.[58]

The glassy carbon electrode needs to be pretreated before the electrode preparation for the specific process. The prepared Pt@r-GO@MWCNTs/GCE nanocomposites were added to a mixture of 2 mL of ethanol and 6 mL of distilled water, and ultrasonically mixed homogeneously. 5 μL of Pt@r-GO@MWCNTs suspension was added dropwise to the surface of the pre-treated glassy carbon electrode, and Pt@r-GO@MWCNTs/GCE was obtained by drying at room temperature.[47]

2.3 Instruments and Methods

All electrochemical voltammetric tests were performed on an electrochemical workstation (CHI 660B, Shanghai Chenhua Instrument Co., Ltd.), which consists of a three-electrode system, i.e., a bare GCE (3 mm in diameter) or modified electrode was used as the working electrode, a platinum wire electrode was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The surface morphology of the materials was characterized by field emission scanning electron microscopy (FE-SEM; Zeiss Ultra 55, Germany). A pH meter (PHS-3C, Shanghai Leizi Instrument Factory) was used to adjust the pH of the buffer solution. A 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) solution containing 0.1 M KCl was used as an electrochemical probe to reflect the state of modification of the electrode surface.

3. Results and discussion

3.1 The choice of materials for sensor preparation

MWCNTs and graphene nanomaterials have the advantages of a large surface area, good electrical conductivity and a fast electron transfer rate, which can effectively increase the catalytic activity of electrochemical sensors and improve their sensitivity. They are thus widely used in the field of electrochemical sensors. Platinum nanoparticles (Pt NPs) are another widely used electrically modified material with a promising role in catalysis. Pt NPs are usually loaded in carbon nanofibres and applied in electrocatalytic reactions. To achieve good sensing performance, various conductive carbon materials can be used in combination with Pt NPs to prevent

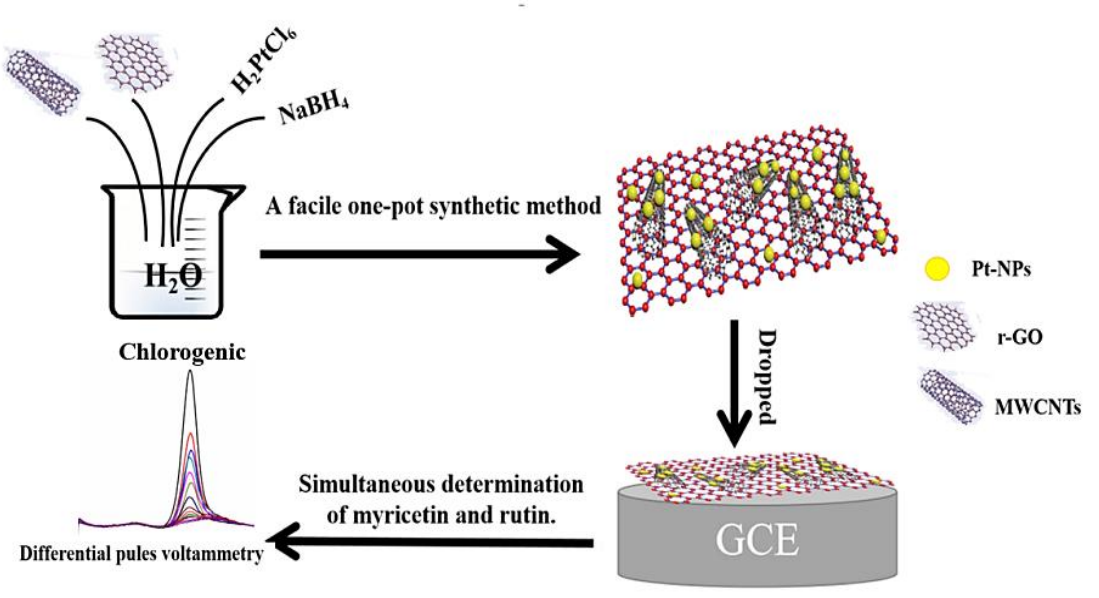

Fig. 1 Synthesis of Pt@r-GO@MWCNTs nanocomposites and preparation of Pt@r-GO@MWCNTs/GCE.

nanoparticle agglomeration. In addition, carbon-based nanomaterials modified electrodes have a solid-phase extraction effect and strong drug adsorption capacity. Therefore, in this study, Pt@r-GO@MWCNTs nanocomposites were synthesised using a simple one-pot method and constructed into electrochemical sensors for sensitive detection of chlorogenic acid.

3.2 Morphology and characterization of nanocomposites

The SEM is an instrument for characterising the morphology, particle size and dimensions of nanomaterials and is generally used for the characterisation of nanomaterials. In addition, SEMs are often equipped with EDS for analysing the elemental composition and proportions of the material. Therefore, SEM to characterize the morphology of Pt@r-GO@MWCNTs nanocomposites. As shown in Figs. 2(A) and (B), we can observe a large number of Pt nanoparticles loaded on carbon nanotubes and graphene sheets. The peaks of C, O and Pt elements can be observed on Fig. 3, with the percentage of 85.27 wt%, 12.50 wt% and 2.23 wt%, respectively. (The carrier of Pt@r-GO@MWCNTs nanocomposites is silicon wafer). Combined with SEM and EDS images, it can be proved that the Pt@r-GO@MWCNTs nanocomposites were successfully prepared. The electrochemical surface area of the different modified materials was calculated from the Randle-Sevcik equation: $Ip = 2.69 \times 10^5 AD^{1/2} n^{3/2} \upsilon^{1/2} C$.[34] Where A is the electrochemical surface area of the electrode, n is the number of electrons involved in the redox reaction, D is the diffusion coefficient of the molecule in the solution (6.67×10^6 cm^{-2} s^{-1} for ferricyanide), C is the concentration of the ferricyanide and υ is the scan rate. The electrochemical surface areas of the GCE and Pt@r-GO@MWCNTs/GCE were calculated to be 0.0710 and 0.2295 cm^2, respectively.

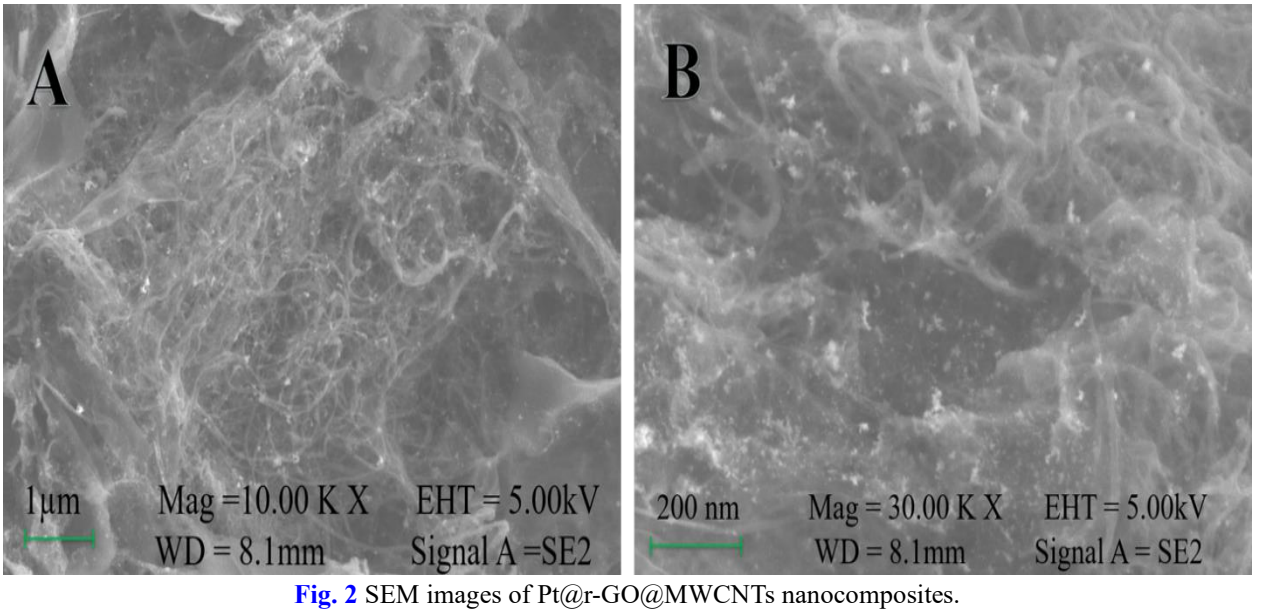

Fig. 2 SEM images of Pt@r-GO@MWCNTs nanocomposites.

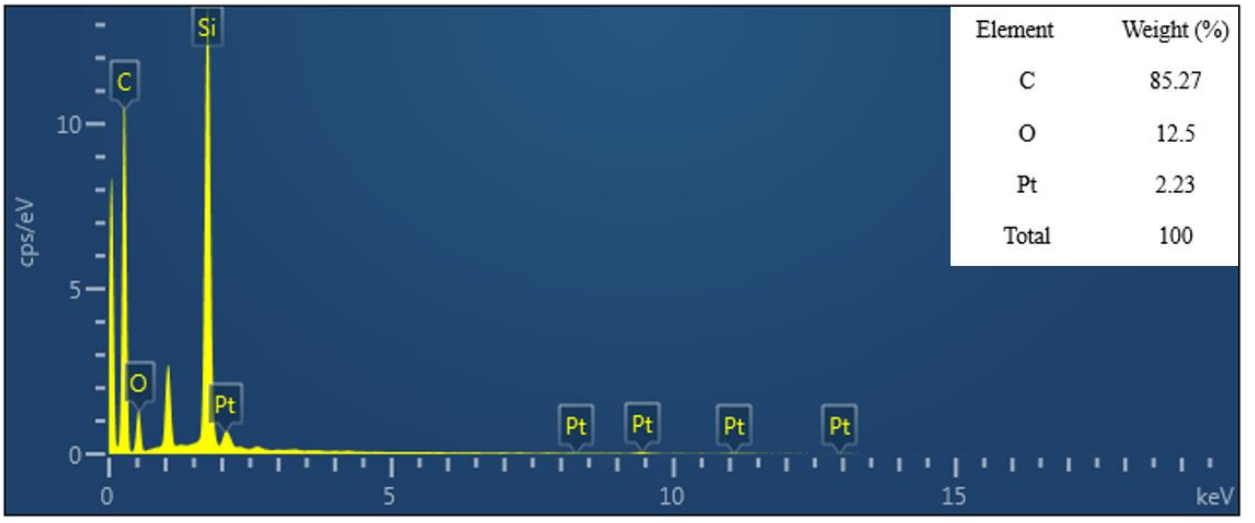

Fig. 3 EDS for Pt@r-GO@MWCNTs nanocompasites.

3.3 Electrochemical behaviors of chlorogenic acid at different electrodes

Cyclic voltammetry and differential pulse voltammetry were used to study and compare the electrochemical behavior of chlorogenic acid on different modified electrodes. Fig. 4A shows the CV plots of 20μmol dm^{-3} chlorogenic acid on bare GCE and Pt@r-GO@MWCNTs/GCE-containing in 0.1 M PBS buffer solution at pH 6.0. As can be seen, when bare GCE was the working electrode, a pair of redox peaks appeared around 0.21 V, which indicated that GCE had some catalytic effect on the oxidation and reduction of chlorogenic acid. When the Pt@r-GO@MWCNTs nanocomposites were modified onto GCE, we observed a large back current and the electrochemical signal of chlorogenic acid was obviously enhanced.

As can be seen in Fig. 4B, compared with bare GCE, chlorogenic acid showed a very obvious oxidation peak on Pt@r-GO@MWCNTs/GCE, and the current signal of the oxidation peak was amplified by nearly 60 times. This is attributed to the relatively large specific surface area, good electrical conductivity and catalytic properties of the Pt@r-GO@MWCNTs nanocomposites. Therefore, Pt@r-GO@MWCNTs/GCE can be used for the detection of chlorogenic acid.

3.4 Effect of scanning rate

The effect of different scanning rates on the electrochemical behaviour of chlorogenic acid was investigated using cyclic voltammetry, as shown in Fig. 5A, with the increase of the scanning rate, the redox peak current of chlorogenic acid increased, and the redox potential was almost unchanged. As shown in Fig. 5B, there was a good linear relationship between the redox peak current of chlorogenic acid and the scanning rate, and the linear equations were I_{pc} (μA) = - 0.5181 ν(mV/s) - 5.0116 (R^2 = 0.9939); I_{pa} (μA) = 0.3599 ν(mV/s) - 3.3498 (R^2 = 0.9963). The experimental results indicate that the redox reaction of chlorogenic acid on Pt@r-GO@MWCNTs/GCE is a reversible adsorption-controlled process.

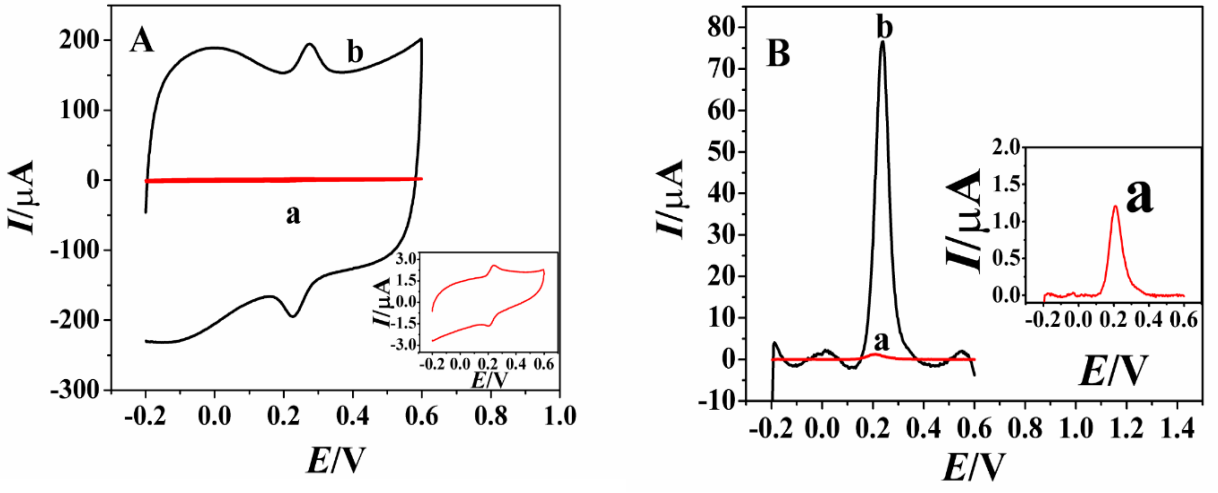

Fig. 4 (A) Cyclic voltammograms of 20 μmol dm^{-3} chlorogenic acid in 0.1 M PBS (pH = 6.0) buffer on bare GCE and Pt@r-GO@MWCNTs/GCE; (B) Cyclic voltammograms of 20 μmol dm^{-3} chlorogenic acid in 0.1 M PBS (pH = 6.0) buffer on bare GCE and Pt@rGO@MWCNTs/GCE Differential pulse voltammograms.

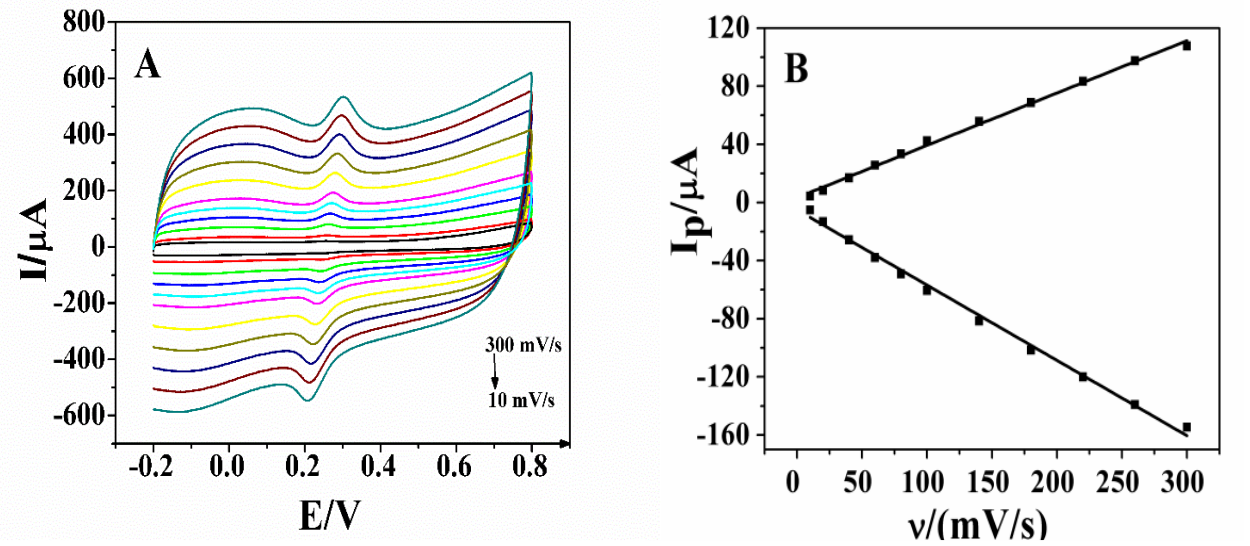

Fig. 5 (A) CV plots of 20 μM chlorogenic acid on Pt@r-GO@MWCNTs/GCE at different scanning rates (10, 20, 40, 60, 80, 100, 140, 180, 220, 260, and 300 mV s-1); (B) Linear plots of the redox peak currents of chlorogenic acid versus the scanning rates.

3.5 The effect of pH

The electrochemical behaviour of chlorogenic acid in PBS buffer solutions of different pH was investigated using differential pulse voltammetry. Fig. 6A shows the DPV plots of 20μM chlorogenic acid on Pt@r-GO@MWCNTs/GCE in PBS buffer solutions of different pH. From Fig. 6B, it can be observed that the oxidation peak current of chlorogenic acid increases with the increase of pH, when the pH is less than 6.0, and it reaches the maximum when the pH is 6.0, and then decreases with the increase of pH. Therefore, we chose 6.0 as the optimal pH. Fig. 6C exhibits the effect of pH of PBS buffer solution on the oxidation peak potential of chlorogenic acid. From the Fig. 6C, we can be observed that the oxidation peak potential of chlorogenic acid shifted negatively with the increase of pH, and the magnitude of the oxidation peak potential showed a good linear relationship with pH, and the linear equation was E_{pa} (V) = - 0.0624 pH + 0.6144 (R^2 = 0.9992), and the slope of the equation was 62.4 mV/pH, According to Equiton 1 the ratio of the number of protons to electrons transferred during the oxidation reaction of chlorogenic acid was found to be 1.05. This indicates that the oxidation process of chlorogenic acid is an isoproton and isoelectron transfer process. It is consistent with the literature report.[59]

3.6 Effect of accumulation time and accumulation potentials

The accumulation time and accumulation potential have a great influence on the sensitivity of electrochemical sensors. To further optimise the detection conditions, we investigated the effects of different accumulation times and accumulation potentials on the electrochemical behavior of 20 μM chlorogenic acid using differential pulse voltammetry. As shown in Fig. 7A, at an accumulation potential of -0.1 V, the oxidation peak current of chlorogenic acid gradually increased with the accumulation time and reached a maximum at 150 s. After 150 s, the oxidation peak current started to decrease. This is due to the fact that the accumulation of chlorogenic acid on Pt@r-GO@MWCNTs/GCE has reached a saturation equilibrium at 150 s. The accumulation of chlorogenic acid on Pt@r-GO@MWCNTs/GCE has reached a saturation equilibrium at 150 s. Therefore, we chose 150 s as the optimal accumulation time. Then, we investigated the effect of the enrichment potential on the oxidation peak current of chlorogenic acid, as shown in Fig. 7B, at an accumulation time of 150 s, the oxidation peak current of chlorogenic acid increased with the increase of the accumulation potential, and the oxidation peak current of chlorogenic acid reached the maximum at an accumulation potential of -0.1 V. After that, the peak current gradually decreased with the increase of the accumulation potential. Therefore, we chose -0.1 V as the optimal enrichment potential for the subsequent determination.

3.7 Quantitative detection of chlorogenic acid

In order to obtain the linear regression equation for the detection of chlorogenic acid by Pt@r-GO@MWCNTs/GCE. Under the optimal conditions, we used differential pulse voltammetry to quantify different concentrations of chlorogenic acid. Fig. 8A shows the DPV plots of different concentrations of chlorogenic acid on Pt@r-GO@MWCNTs/GCE in 0.1 M PBS buffer at pH 6.0. As can be seen in Fig. 8B, the oxidation peak current of chlorogenic acid increased with the increase of chlorogenic acid concentration and showed a good two-stage linear relationship between the oxidation peak current of chlorogenic acid and the concentration in the range of 0.005-20 μM, with the following linear equations: low concentration (0.005-2 μM): I_p (μA) = 9.6018C (μM) +4.2084 (R^2 = 0.9974); High concentration (2-20 μM): Ip (μA) = 2.9258C (μM) +192493 (R^2 = 0.9974). The limit of detection (C_m) was calculated according to the formula C_m=3b/m (2) and was 0.001 μM (S/N=3). Compared with the modified electrodes that have been reported for the

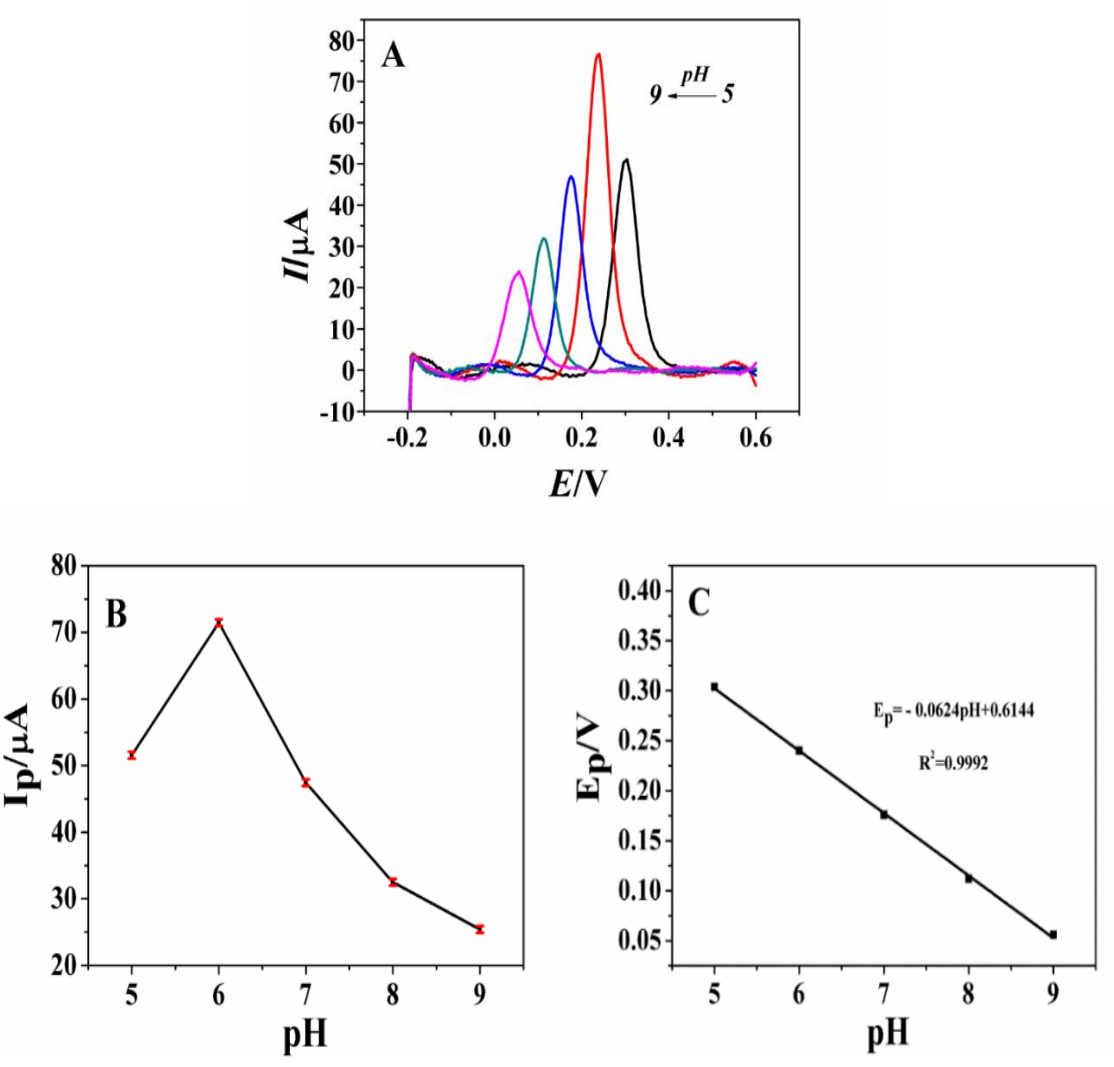

Fig. 6 (A) DPV plots of 20 μM chlorogenic acid on Pt @ r-GO @ MWCNTs/GCE in 0.1 M PBS buffer at different pH; (B) oxidation peak current of chlorogenic acid (C) oxidation peak potential versus pH.

detection of chlorogenic acid (Table 1),[59-63] Pt@r-GO@MWCNTs/GCE presented a broader linearity and lower detection limit for the detection of chlorogenic acid.

3.8 Selectivity, stability and reproducibility of Pt@r-GO@MWCNTs/GCE

In order to evaluate the selectivity of Pt@r-GO@MWCNTs/GCE for chlorogenic acid detection, we investigated the effect of interfering substances on chlorogenic acid detection using the DPV method. As shown in Table 2,

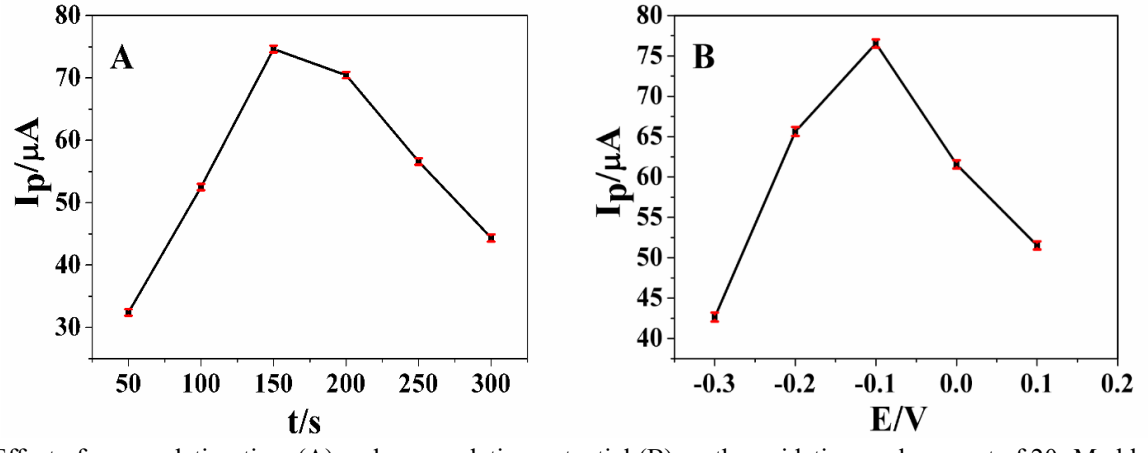

Fig. 7 (A) Effect of accumulation time (A) and accumulation potential (B) on the oxidation peak current of 20 μM chlorogenic acid on Pt@r-GO@MWCNTs/GCE.

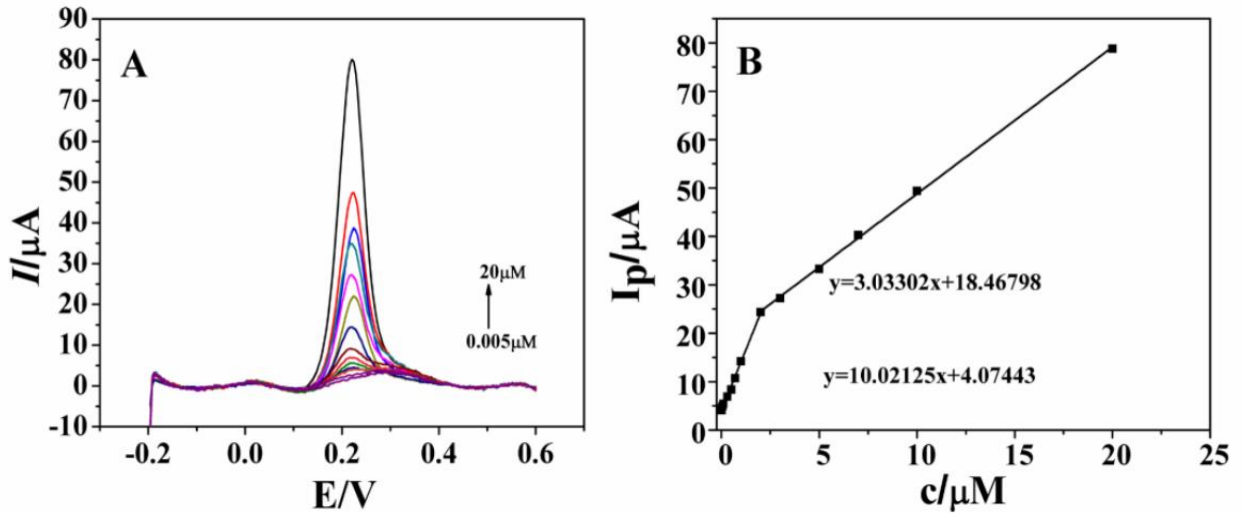

Fig. 8 (A) Differential pulse voltammograms of chlorogenic acid on Pt@r-GO @ MWCNTs/GCE at different concentrations (0.005-20 μM) in 0.1 M PBS (pH = 6.0) buffer solution; (B) Linear plot of oxidised peak currents of chlorogenic acid different concentration.

Table 1. Comparison of Pt-r-GO @ MWCNTs/GCE with previously reported literature for electrochemical detection of chlorogenic acid.

Electrode	Method	Linear range (μM)	Limit of detection (μM)	Ref.
(CS/MWCNTs)6/GCE	DPV	0.1 — 225 0.02 — 0.1	0.0117	[59]
Poly (aminosulfonic acid) /GCE	CV	0.4—12	0.08	[60]
Graphite powder -nujol-Cu(II)complex/carbon paste Ir-BMI.PF6-PPO.	SWV	8 — 145	0.8	[61]
Polyphenol oxidase/Carbon paste	SWV	3.48 — 49.5	0.915	[62]
Bean sprout homogenate-CS microspheres/Carbon paste bean sprout homogenate-silica/ Carbon paste	CV/SWV	4.89 — 320 4.89 — 48.5	0.802 0.852	[63]
Pt@r-GO@MWCNTs/GCE	DPV	0.005 — 2 2 — 20	0.001	This work

the oxidation peak current signals of chlorogenic acid did not change significantly in the presence of 1000-fold concentration of $NaNO_3$, NH_4F, $MnSO_4$, $CaCl_2$, Zn $(AC)_2$ and 100-fold concentration of citric acid, tartaric acid, cystine, glucose, ascorbic acid and oxalic acid. This indicates that the modified electrode has good selectivity. In addition, four modified electrodes were prepared under the same conditions and placed under refrigeration (4 °C) for 7, 14 and 21 days for the detection of chlorogenic acid. The decrease in the oxidation peak current of chlorogenic acid was less than 6.1 %. This result indicates that the Pt@r-GO@MWCNTs /GCE has good stability for the detection of chlorogenic acid. In the table, the samples responses are expressed as a confidence interval 95% probability (n = 3).

Table 2. Effect of interference components on the oxidation peak current signal of chlorogenic acid.

Interference	Concentration (mol L^{-1})	Signal change (%)
		Chlorogenic acid
$NaNO_3$	0.02	2.67 ± 0.11
NH_4F	0.02	-2.53 ± 0.96
$MgSO_4$	0.02	2.60 ± 0.39
$CaCl_2$	0.02	-3.33 ± 0.58
$Zn(AC)_2$	0.02	0.81 ± 0.13
Citric acid	0.002	6.44 ± 0.72
Tartaric acid	0.002	6.62 ± 0.11
Cystine	0.002	4.18 ± 0.45
Glucose	0.002	3.66 ± 0.68
Ascorbic acid	0.002	4.10 ± 0.94
Oxalic acid	0.002	-4.25 ± 0.95

3.9 Real sample detection

In order to evaluate the practical applicability of Pt@r-GO@MWCNTs/GCE, three parallel determinations of chlorogenic acid in serum samples were carried out using the standard addition method. The results are shown in Table 3. The recoveries of chlorogenic acid in the actual serum samples were between 98.7 and 104.3 %, and the RSD values were less than 6.5 %, which indicated that our prepared Pt@r-GO@MWCNTs/GCE could be applied to the detection of chlorogenic acid in the actual serum samples.

4. Conclusions

In this paper, Pt@r-GO@MWCNTs nanocomposites were prepared using a simple one-pot method to investigate the electrochemical behaviour of chlorogenic acid at different electrodes. Due to the large specific surface area, good

Table 3. Detection of chlorogenic acid in actual serum samples.

Sample	Added (μM)	Found (μM)	Recovery（%）	RSD（%）
1	8	8.07 ± 0.32	100.9	1.6
2	6	5.99 ± 0.24	99.8	1.7
3	0.4	0.42 ± 0.02	104.3	1.9
4	0.2	0.20 ± 0.03	98.7	6.5

electrical conductivity and catalytic properties of Pt@r-GO@MWCNTs, Pt@r-GO@MWCNTs/GCE showed strong electrochemical response to chlorogenic acid compared to bare GCE. Under the optimal conditions, the detection of chlorogenic acid by Pt@r-GO@MWCNTs/GCE presented a low detection limit of 0.001μM and a good linearity in two bands (0.005~2 μM and 2~20 μM) at an accumulation potential of - 0.1 V and an accumulation time of 150 s in a 0.1 M PBS buffer solution at pH 6.0. In addition, the sensor has good selectivity, stability and reproducibility and the recoveries of chlorogenic acid in the actual serum samples were between 98.7 and 104.3 %, and the RSD values were less than 6.5 %, which indicated that our prepared Pt@r-GO@MWCNTs/GCE could be applied to the detection of chlorogenic acid in the actual serum samples.

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Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable.

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