

Highly sensitive detection of hesperidin using AuNPs/rGO modified glassy carbon electrode

Yang Gao, Xiufeng Wu, Hui Wang,* Wenbo Lu,* and Mandong Guo*

E-mail: wanghui@sxnu.edu.cn, luwb@sxnu.edu.cn, guomd@sxnu.edu.cn

Table S1. Comparison of the hesperidin assay performance of the designed sensor with other reported methods.

Method	Linear range (mol L ⁻¹)	LOD (mol L ⁻¹)	Sensibility (A mol L ⁻¹ cm ⁻²)	Reference
Mesoporous SiO ₂ /CPE	5.0×10 ⁻⁷ – 2.5×10 ⁻⁵	2.5×10 ⁻⁷	/	1
Capillary electrophoresis with electrochemical	5.0×10 ⁻⁶ – 1.0×10 ⁻³	6.5×10 ⁻⁷	/	2
rGO/SWCNTs/GCE	5.0×10 ⁻⁸ – 3.0×10 ⁻⁶	2.0×10 ⁻⁸	/	3
Adsorptive stripping voltammetry at bare HMDE	5.0×10 ⁻⁷ – 8.0×10 ⁻⁶	3.0×10 ⁻⁷	/	4
Bare glassy carbon electrode	1.0×10 ⁻⁷ – 1.0×10 ⁻⁴	3.0×10 ⁻⁸	/	5
The proposed method	8.0×10 ⁻⁶ – 5.0×10 ⁻⁸	8.2×10 ⁻⁹	18.04	This work

Materials and methods

Materials and apparatus

Hesperidin was obtained from aladdin (Shanghai, China). Graphite powder (30 μm) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Chloroauric acid tetrahydrate was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Pericarpium Citri Reticulatae was purchased from Tongrentang (Linfen, China). All the chemical reagents were of analytical reagent grade, and used without any further purification. All aqueous solutions were prepared by ultrapure water.

Cyclic voltammetric (CV) were performed on a LK2005A electrochemical workstation (Tianjin LANLIKE Instruments Co., China) under ambient temperature. A common three-electrode system was put into use containing a bare or modified GCE (2 mm in diameter) as the working

electrode, a platinum wire as the auxiliary electrode and an Ag/AgCl (sat. KCl) as the reference electrode. During the electrochemical measurement, all solutions were purged with nitrogen to eliminate oxygen reduction waves. The pH measurements were carried out on PHS-3C exact digital pH meter (Leici Instrumental Factory, Shanghai, China). Scanning electron microscope (SEM) images were performed on a JSM-7500F (JEOL, Japan), equipped with energy dispersive X-ray spectrometry (EDX), which was employed to determine the composition of AuNPs nanoparticles deposited on the rGO thin film. FT-IR was recorded on an ALPHA infrared spectrometer (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) data of the samples was collected on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Preparation of the GO

GO was prepared from graphite powder by a modified Hummers' method.^{6,7} 1.5 g graphite powder was mixed with 4.5 g (0.053 mol) NaNO₃, then the mixture was added in 125 mL (2.3 mol) of 98% H₂SO₄ and stirred evenly. 4.5 g KMnO₄ (0.028 mol) was gradually added meanwhile keeping the temperature less than 20 °C and magnetic stirring for 4 hour. The mixture was then stirred at 35 °C for 30 min and then heated at 105 °C for 1 hour. The reaction was terminated by addition of ultrapure water (400 mL), 10 mL (0.1 mol) of H₂O₂ solution (w=30%) and HCl (w=35%, 0.12 mol). The resulting mixture was washed through repeated centrifugation and filtration with ultrapure water. Finally, the GO product was obtained after dried in a vacuum at 60 °C. GO aqueous suspension (1 mg mL⁻¹) was dispersed into the ultrapure water, and bath sonicated for 1 h.

Preparation of real samples

The Pericarpium Citri Reticulatae as real samples were dried at 60 °C for 2 h and then pulverized. The extraction of Pericarpium Citri Reticulatae was performed as following: 0.1 g powder sample was soaked in 60.0 mL ultrapure water for 24 h, and ultrasonicated for 30 min at the room temperature. Then, the sample was filtered, and the filtrate was collected. Additionally, the ultrapure water was added into the residue and sonicated for 20 min. At last, merging all the filtrate and the solution was adjusted to 100.0 mL for measurement.

Fabrication of modified electrodes

Before using, the GCE was burnished with 0.3, 1.0 μm alumina powder, respectively, and then was rinsed with the ultrapure water followed by sonicated in ethanol, HNO_3 (v/v=1:1) and ultrapure water successively. The cleaned electrode was allowed to dry at room temperature.

Firstly, the rGO/GCE was prepared by CV for 15 cycles in a phosphate buffer solution (PBS, pH 7.8) containing 1.0 mg mL^{-1} GO at a scan rate of 50 mV s^{-1} between -1.5 V and $+1.0 \text{ V}$.⁸⁻¹⁰ Then the rGO/GCE was immersed into 0.04 % HAuCl_4 ($9.7 \times 10^{-6} \text{ mol}$) solution with a PBS (pH 7.02), and electrochemical deposition was conducted by CV at a potential range from -0.6 to 1.5 V at a scan rate of 100 mV s^{-1} for 15 cycles to give AuNPs/rGO/GCE.^{11,12} After that, the modified electrode was dried at room temperature. In order to better contrast, rGO/GCE was prepared by CV for 15 cycles in PBS (pH 7.8) containing 1.0 mg mL^{-1} GO at a scan rate of 50 mV s^{-1} between -1.5 V and $+1.0 \text{ V}$ on the surface of GCE. Additionally, AuNPs/GCE was obtained by CV for 15 cycles in 0.04 % HAuCl_4 solution with a PBS (pH 7.02) at a scan rate of 100 mV s^{-1} between -0.6 V and $+1.5 \text{ V}$.

In addition, in order to confirm that Au was electrodeposited on the surface of rGO/GCE, CV for the electrochemical deposition of rGO/GCE in 0.04 % HAuCl_4 solution with a PBS (pH 7.02) at a scan rate of 100 mV s^{-1} is shown in Fig. S1. All the electrochemical measurements are performed at N_2 atmosphere. The result shows that the reduction peak currents of Au at 0.38 V significantly increased with increasing the deposition cycles, moreover, the oxidation peak currents at 0.94 V are slightly increased. This indicates that AuNPs has been modified on the surface of rGO/GCE.

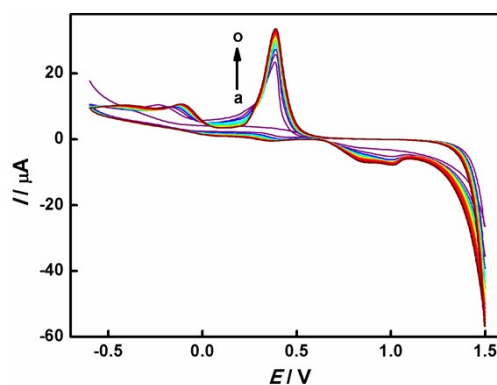


Fig. S1 CV for the electrochemical deposition of rGO/GCE in 0.04 % HAuCl_4 solution with a PBS (pH 7.02) at a scan rate of 100 mV s^{-1} (a–o: from 1 to 15 cycles).

Electrochemical measurements

0.1 mol L⁻¹ HAc–NaAc (pH 3.6) was used as the electrolyte solution for the determination of hesperidin in all experiments. Cyclic voltammograms (CV) of hesperidin were recorded in the potential range from 0.2 V to 1.6 V at a scan rate of 50 mV s⁻¹. The Amperometric i – t Curve of hesperidin were recorded in the electrode potential of 1.21 V. The modified electrode was immersed into 0.1 mol L⁻¹ HAc–NaAc (pH 3.6) after electrochemical measurement and performed by scanning the potential from 0.0 to +1.0 V at 100 mV s⁻¹ for 10 cycles.

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