Graphene@activated carbon modified electrode for electrochemical behavior analysis of quercetin

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Abstract. In this paper, graphene (Gr) and coconut shell activated carbon (AC) modified electrode was developed for electrochemical behavior analysis of quercetin. Porous AC was prepared from coconut shell. The Gr was obtained by electrodeposition of graphite oxide on AC surface. The electrochemical behavior of quercetin was analyzed by Gr@AC electrode, and results show that the detection range of quercetin is 6 μmol/L to 100 μmol/L (R²=0.9977). The detection limit (LOD) is 0.5 nmol/L (3σ/slope), and the recommended method has a good recovery for the detection of quercetin in real urine.

1. Introduction
Quercetin is a flavonoid drug molecule with anti-inflammatory, anti-allergic, antioxidant and anti-tumor properties [1]. Quercetin widely exists in many natural plants and can be used in clinical medicine. Therefore, it is necessary to establish an analytical method for quercetin. There are many analytical methods for quercetin, including electrochemical detection [2], high performance liquid chromatography [3], spectrophotometry [4] and capillary electrophoresis [5]. Although these methods can be used for the analysis and determination of quercetin, the electrochemical method is the most suitable at present [6, 7]. Because it has the advantages of simple operation and cheap equipment [8, 9].

Multi pore activated carbon (AC) has the characteristics of large surface area, less environmental damage and stable chemical properties [10], so it can be used as a good electrode material for electrochemistry [11]. In addition, graphene (Gr) has excellent conductivity, electrochemical stability and large specific surface area [12-14]. It has been widely used in the field of electrochemistry [15].

In this paper, Gr was coated on the surface of porous AC by potentiostatic deposition. Due to the synergistic effect of porous AC and Gr, the response signal of quercetin was enhanced. The method was also applied to the electrochemical performance analysis of quercetin in real urine.

2. Experimental
2.1. Instruments and Reagents
First, the experiments of cyclic voltammetry were performed on an electrochemical workstation (Model: CHI660E, Shanghai Chenhua Instrument Co., Ltd, China). Ag-AgCl as reference electrode and platinum wire as auxiliary electrode, the three-electrode detection system was constructed using modified electrode as working electrode.
Quercetin was provided by Shanghai Macklin Biochemical Co., Ltd. And Shanghai Aladdln Biochemical Technology Co, Ltd provided us with graphene oxide (1mg/mL). Nafion perfluorinated resin solution (5wt%, lower aliphatic alcohols and water containing 15-20% water) was purchased from lianshiyun commercial network technology (Hainan) co. ltd, which was diluted to 0.5wt% by deionized water. Phosphate buffer solution (1×PBS, 8 mM Na₂HPO₄, 136 mM NaCl, 2 mM KCl) was purchased from Beijing Labgic technology co., ltd.

2.2. Activation of glassy carbon electrode
Glassy carbon electrodes were first polished with Al₂O₃ powder and then washed with deionized water. The dry glassy carbon electrode was placed in a H₂SO₄ solution of 0.5 mol/L and activated by cyclic voltammetry in a voltage range of -0.3 V to 1.5 V. The glassy carbon electrode was then washed with deionized water and put into a vacuum chamber for drying.

2.3. Preparation of GR@AC electrode
The prepared GC electrode was immersed in 1.0 mg/ml graphene oxide solution, and the deposition point was set at -1.3V Graphene 400s was reduced on the surface of Gr electrode by potentiostatic deposition method. Finally, GR-AC electrode was obtained.

3. Results and discussion

3.1. Electrochemical behavior of different electrodes
In 0.1 mol/L PBS buffer solution with pH 3, the electrochemical behavior of quercetin at 10⁻⁴ mol/L at different modified electrodes was studied. The results were shown in the Figure 1. For the unmodified glassy carbon electrode, the voltage was 0.252V with the peak current of 2.500 μA. Compared with the unmodified electrode, the current of AC electrode increased significantly, but there was no redox peak. The possible reason was that the three-dimensional pore structure had a strong adsorption effect on quercetin. The peak current of Gr@AC curve was 201.6 μA at 0.3V, which was obviously larger than that of the unmodified electrode and AC electrode. The reason was that Gr had excellent guidance performance. The above results confirm that we have successfully prepared Gr@AC electrode.

3.2. pH optimization
The equations are an exception to the prescribed specifications of this template. You will need to determine whether or not your equation should be typed using either the Times New Roman or the
Symbol font (please no other font). To create multileveled equations, it may be necessary to treat the equation as a graphic and insert it into the text after your paper is styled.

![Figure 2](image1.png)

**Figure 2.** (A) DPV curve of quercetin at $10^{-4}\text{mol/L}$ at different PH (PH 2.0, 3.0, 4.0, 5.0, 6.0) on GR/GC; (B) the relationship between $E_0$ and the buffer PH

3.3. **Linearity and sensitivity**

Quercetin was prepared at different concentrations (6, 40, 60, 80 and 100 μmol/L) with pH 3. The quercetin solution was detected by differential pulse voltammetry with Gr@AC electrode as shown in Figure 3. As shown in Figure 3A, the linear equation was $I (A) = 0.0086C + 1.70142 \ (R^2=0.9977)$ with the detection limit (LOD) of 0.5 nmol/L (3σ/slope), and the detection range of quercetin is 6 μmol/L to 100 μmol/L, indicating that the recommended method has a very high LOD.

![Figure 3](image2.png)

**Fig 3.** (A) The DPV curves of quercetin at different concentrations (6, 40, 60, 80, and 100 μmol/L); (B) Relationship curve between different concentration values and oxidation peak current value.

3.4. **The selectivity of Gr@AC electrode**

The Gr@AC electrode was used as the working electrode to detect $1\times10^{-4}\text{mol/L}$ quercetin and its different similar molecules (dopamine, sodium dodecyl sulfate, glycine, lactobiose and glucose) by differential pulse voltammetry. The results were shown in Figure 4. Compared with other similar molecules, the peak current of quercetin increased significantly, indicating that the proposed detection system has a good selectivity for quercetin.
Fig 4. Selectivity of the GR/GC electrode.

3.5. Quercetin detection in true urine
The urine was put in a 2 μL centrifuge tube, and then was centrifuged at a rate of 12000r/min for 3 min. The supernatant was obtained, and was diluted to 500 times with PBS solution of PH 3. The different concentrations (60, 80, 100 μmol/L) of quercetin were prepared by diluted urine. The recoveries were shown in the Table 1. The recoveries were between 98% and 105%, showing that the sensitivity of the Gr@AC electrode perform well in the determination of quercetin in urine.

Table 1. Recovery of quercetin in actual urine.

| Samples | Added (μM) | Found (μM) | Recovery (%) | Standard Deviation(n=3) (μM) |
|---------|------------|------------|--------------|-----------------------------|
| 1       | 40         | 40.548     | 100.98       | 0.534                       |
|         |            | 39.799     |              |                             |
| 2       | 80         | 82.400     | 102.40       | 0.611                       |
|         |            | 82.133     |              |                             |
|         |            | 81.233     |              |                             |
| 3       | 100        | 99.89      | 100.47       | 1.612                       |
|         |            | 102.30     |              |                             |
|         |            | 99.24      |              |                             |

4. Conclusions
The activated carbon (AC) was fabricated by coconut shell powder, and then graphene (Gr) was obtained by electrodeposition of graphite oxide on AC surface. The AC has good electrical conductivity and large surface area. In addition, we have studied the electrochemical behavior of Gr@AC sensor. The detection limit (LOD) is 0.5 nmol/L (3σ/slope), and the recommended method has a good recovery for the detection of quercetin in real urine.

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References

[1] Chen, X.-L.; Chai, G.-R.; Liu, S.; Yang, H.-W., Quercetin protects against diabetic retinopathy in rats by inducing heme oxygenase-1 expression. Neural Regeneration Research 2021, 16, (7), 1344.

[2] Wang, C.; Yang, L.; Hu, Y.; Zhu, J.; Xia, R.; Yu, Y.; Chen, J.; Zhang, Z.; Wang, S.-L., Isoliquiritigenin as an antioxidant phytochemical ameliorates the developmental anomalies of zebrafish induced by 2,2′,4,4′-tetrabromodiphenyl ether. Science of The Total Environment 2019, 666, 390-398.

[3] Yang, X.; Guo, Q.; Yang, J.; Chen, S.; Hu, F.; Hu, Y.; Lin, H., Synergistic effects of layer-by-layer films for highly selective and sensitive electrochemical detection of trans-resveratrol. Food chemistry 2021, 338, 127851.

[4] Tyakht, A.; Kopeliovich, A.; Klimenko, N.; Efimova, D.; Dovidchenko, N.; Odintsova, V.; Kleimenov, M.; Toshchakov, S.; Popova, A.; Khomyakova, M.; Merkel, A., Characteristics of bacterial and yeast microbiomes in spontaneous and mixed-fermentation beer and cider. Food Microbiology 2021, 94, 103658.

[5] Jain, A.; Soni, S.; Verma, K. K., Combined liquid phase microextraction and fiber-optics-based cuvetteless micro-spectrophotometry for sensitive determination of ammonia in water and food samples by the indophenol reaction. Food chemistry 2021, 340, 128156.

[6] Galindo-Luján, R.; Pont, L.; Sanz-Nebot, V.; Benavente, F., Classification of quinoa varieties based on protein fingerprinting by capillary electrophoresis with ultraviolet absorption diode array detection and advanced chemometrics. Food chemistry 2021, 341, 128207.

[7] Liu, X.; Li, S., Control Method Experimental Research of Micro Chamber Air Pressure via a Novel Electromagnetic Microvalve. 2017, 921-925.

[8] Dou, H.; Zhang, C.; Li, L.; Hao, G.; Ding, B.; Gong, W.; Huang, P., Application of variable spray technology in agriculture. IOP Conference Series: Earth and Environmental Science 2018, 186, 012007.

[9] Lu, J.; Hou, J.; Ouyang, Y.; Luo, H.; Zhao, J.; Mao, C.; Han, M.; Wang, L.; Xiao, J.; Yang, Y.; Li, X., A direct PCR–based SNP marker–assisted selection system (D-MAS) for different crops. Molecular Breeding 2020, 40, (1).

[10] Pei, S.; Cheng, H.-M., The reduction of graphene oxide. Carbon 2012, 50, (9), 3210-3228.

[11] Yu, X.-Y., Imaging mass spectrometry tackles interfacial challenges in electrochemistry. Current Opinion in Electrochemistry 2017, 6, (1), 53-59.

[12] Ning, N.; Huang, W.; Liu, S.; Zhao, Q.; Zou, H.; Yu, B.; Tian, M.; Zhang, L., Highly stretchable liquid metal/polyurethane sponge conductors with excellent electrical conductivity stability and good mechanical properties. Composites Part B: Engineering 2019, 179, 107492.

[13] Zhang, Y.; Nsabimana, A.; Zhu, L.; Bo, X.; Han, C.; Li, M.; Guo, L., Metal organic frameworks/macroporous carbon composites with enhanced stability properties and good electrocatalytic ability for ascorbic acid and hemoglobin. Talanta 2014, 129, 55-62.

[14] Sakagami, H.; Hirai, S.; Ohno, T.; Matsuda, T., Effects of reduction conditions on the formation of porous MoOx from MoO3. Microporous and Mesoporous Materials 2021, 310, 110586.

[15] Mandler, D., Chiral self-assembled monolayers in electrochemistry. Current Opinion in Electrochemistry 2018, 7, 42-47.