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Electrochemical Determination of Resveratrol Using a MWCNTs-COOH/Cu Modified Glassy Carbon Electrode

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ABSTRACT

In this study, we aimed to fabricate an electrochemical sensor based on copper nanoparticles and carboxylated multi-walled carbon nanotubes (MWCNTs-COOH/Cu/GCE) for the detection of resveratrol in grape seeds. Electrochemical methods including electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were employed to investigate the electrochemical behavior and performance of the sensor in a potassium ferricyanide-potassium ferrocyanide system. Differential pulse voltammetry (DPV) was used to study the electrochemical behavior of resveratrol on the sensor surface and optimize various key parameters affecting the sensor performance. The content of resveratrol was quantified using differential pulse voltammetry (DPV). Results: The highest sensitivity for resveratrol detection was achieved under the optimized conditions: a copper deposition potential of −0.4 V, a deposition time of 250 s, a buffer solution pH of 7.0, and a MWCNTs-COOH dosage of 6 µL. A good linear relationship was obtained for resveratrol in the concentration range from 1×10^{-8} *to* 1×10^{-7} *mol/L. The proposed sensor features simple preparation, excellent electrical conductivity, and high stability, providing a new method for the determination of resveratrol content.*

KEYWORDS
resveratrol, MWCNT-modified electrode, electrochemical sensor

INTRODUCTION

Resveratrol (3,4′,5-trihydroxy-stilbene) is a naturally occurring non-flavonoid polyphenolic compound that is widely distributed in plants such as grapes, peanuts, blueberries, mulberries, and Polygonum cuspidatum. Owing to its molecular structure(as shown in figure 1). containing three phenolic hydroxyl groups, resveratrol exhibits strong antioxidant activity and can be readily oxidized in electrochemical processes. In addition to its antioxidant properties, resveratrol has attracted considerable attention because of its anti-inflammatory, anti-tumor, anti-diabetic, and neuroprotective effects, showing broad potential in the fields of food science, medicine, and healthcare[1]. However, resveratrol is sensitive to light and easily undergoes isomerization and oxidation during storage and analysis, which may affect its stability and lead to inaccurate analytical results. Therefore, the development of a rapid, simple, and reliable method for the determination of resveratrol is of considerable significance。

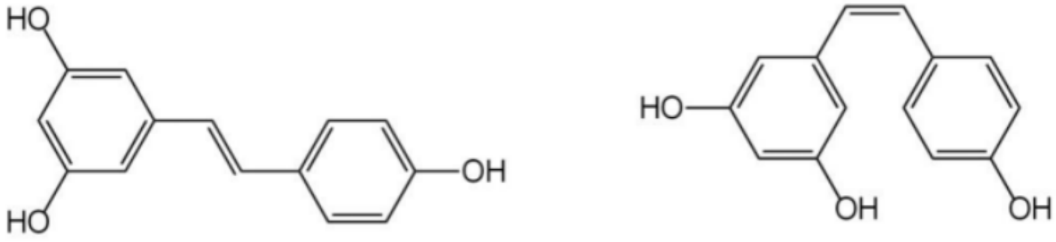

Figure 1. Chemical structure of trans- and cis-resveratrol

At present, a variety of analytical methods have been developed for the determination of resveratrol, including high-performance liquid chromatography (HPLC), thin-layer chromatography (TLC), gas chromatography-mass spectrometry (GC-MS), capillary electrophoresis (CE), fluorescence analysis, and liquid chromatography-mass spectrometry (LC-MS). Although these methods generally provide satisfactory sensitivity and accuracy, they often require expensive instrumentation, complicated sample pretreatment, and relatively long analysis times. In comparison, electrochemical analysis has become increasingly attractive because of its high sensitivity, rapid response, low cost, and simple operation. As a key component of electrochemical sensing systems, chemically modified electrodes can significantly enhance analytical performance through surface functionalization. In recent years, carbon nanomaterials and metal nanomaterials have been extensively employed as electrode modifiers due to their excellent conductivity, large specific surface area, and catalytic activity[2-3]. Among various nanomaterials, carboxylated multi-walled carbon nanotubes (MWCNTs-COOH) possess excellent electrical conductivity, structural stability, and abundant active sites, while copper nanoparticles can effectively improve electron transfer and electrocatalytic activity[4]. The combination of carbon nanotubes with metal nanoparticles is expected to generate a pronounced excellent electrical conductivity and high specific surface area effect, thereby reducing interfacial impedance and enhancing the electrochemical response of the target analyte. However, reports on the electrochemical determination of resveratrol based on MWCNTs-COOH/copper nanoparticle composite electrodes are still limited. In this study, a glassy carbon electrode modified with MWCNTs-COOH and copper nanoparticles was constructed for the electrochemical determination of resveratrol. The fabrication procedure, electrochemical behavior, optimization conditions, and practical application in grape seed extracts were systematically investigated(in figure 2).

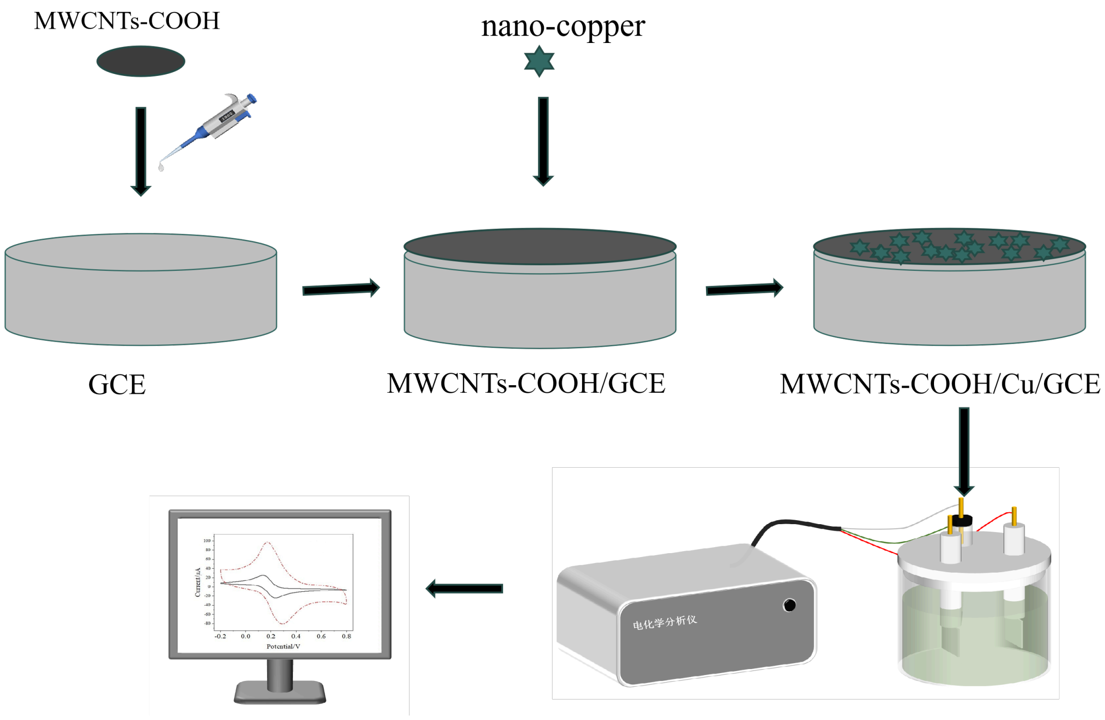

Figure 2. Technical route for the preparation of the electrochemical sensor and detection of resveratrol

MATERIALS AND METHODS

Chemicals and Reagents

All reagents used in this study were of analytical grade and used without further purification. Potassium ferricyanide ($K_3[Fe(CN)_6]$), potassium ferrocyanide ($K_4[Fe(CN)_6]$), potassium chloride (KCl), and copper sulfate ($CuSO_4$) were purchased from Sinopharm Chemical Reagent Co., Ltd.

Carboxylated multi-walled carbon nanotubes (MWCNTs-COOH, 30–50 nm) and Nafion solution (5 wt%) were obtained from Shanghai Adamas Reagent Co., Ltd.

Resveratrol standard (HPLC purity ≥ 98%) was purchased from Dr. Ehrenstorfer GmbH (Germany).

Al_2O_3 polishing powders (0.05 μm and 0.1 μm) and phosphate buffer solution (PBS, 0.02 mol/L) were used throughout the experiments. Ultrapure water (18.2 MΩ·cm) was used in all preparations.

Apparatus

Electrochemical measurements were performed using a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China).A conventional three-electrode system was employed, consisting of a glassy carbon electrode (GCE, Φ = 3 mm) as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.An ultrasonic cleaner (KQ-500B) was used for sample dispersion and cleaning procedures.

Pretreatment of the Glassy Carbon Electrode

Prior to modification, the GCE was polished sequentially with 0.1 µm and 0.05µm Al_2O_3 slurry on a polishing cloth in a figure-eight motion for approximately 3 min.After polishing, the electrode was thoroughly rinsed with ultrapure water and then ultrasonically cleaned in 0.01 mol/L nitric acid, ethanol (1:1), and ultrapure water for 10 s each to remove surface impurities[5].

Subsequently, the electrode was electrochemically activated in 0.5 mmol/L H_2SO_4 solution. Cyclic voltammetry was performed in 1.0 mmol/L $K_3[Fe(CN)_6]$ solution until a stable and reversible redox peak was obtained (peak potential separation < 80 mV, peak current ratio ≈ 1:1), indicating successful activation[6].

Preparation of the MWCNTs-COOH/Cu/GCE

A 0.5 wt% Nafion solution was prepared by diluting 2.5 mL of 5 wt% Nafion solution to 25 mL with 45% ethanol.Then, 2.0 mg of MWCNTs-COOH was dispersed in 1.0 mL of the prepared Nafion solution and ultrasonicated for 2 h to obtain a homogeneous suspension (2 mg/mL).

A volume of 5 µL of the suspension was drop-cast onto the pretreated GCE surface and dried naturally at room temperature to form the MWCNTs-COOH/GCE.

Subsequently, copper nanoparticles were electrodeposited onto the modified electrode in 0.05 mol/L $CuSO_4$ solution at a constant potential of −0.4 V for 250 s. After deposition, the electrode was rinsed with ultrapure water to remove residual solution, yielding the MWCNTs-COOH/Cu/GCE, a Cu/GCE was prepared under the same electrodeposition conditions on a bare GCE[7-8].

Preparation of Real Samples

Fresh grapes were purchased from a local supermarket. The seeds were separated, washed, and dried at room temperature.

The dried grape seeds were ground into powder using a mortar. Then, 2.0 g of the powder was mixed with 50 mL of 40% ethanol (solid–liquid ratio of 1:25) and subjected to ultrasonic extraction for 30 min.After centrifugation, the supernatant was collected and stored in the dark at 4 ℃.Prior to electrochemical analysis, 5 mL of the extract was transferred into a 25 mL volumetric flask and diluted to volume with PBS (pH = 7.0).

Electrochemical Measurements

Electrochemical experiments were carried out at room temperature using the CHI660E workstation.

Cyclic Voltammetry (CV)

CV measurements were performed in 1.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 mol/L KCl as the supporting electrolyte.The potential was scanned from −0.2 V to 0.6 V at a scan rate of 50 mV/s.

Electrochemical Impedance Spectroscopy (EIS)

EIS measurements were conducted in the same solution over a frequency range from 0.1 Hz to 100 kHz with an AC amplitude of 5 mV.

Differential Pulse Voltammetry (DPV)

DPV measurements were carried out in PBS (pH = 7.0) for the determination of resveratrol.The instrumental parameters were set as follows: pulse amplitude of 50 mV, pulse width of 50 ms, pulse period of 200 ms, and potential scan range from 0 V to 0.6 V[9-10].

RESULTS AND ANALYSIS

Electrocatalytic Activity Characterization of Different Modified Electrodes

The electrochemical activities of different modified electrodes were characterized using CV in a $[Fe(CN)_6]^{3-/4-}$ solution. The CV diagram showed an upper oxidation peak and a lower reduction peak; a peak currents value indicates easier reduction of Fe^{3+} in potassium ferricyanide. As shown in the experimental results, the peak currents followed the order of bare GCE < Cu/GCE < MWCNTs-COOH/GCE < MWCNTs-COOH/Cu/GCE. Both MWCNTs-COOH and nano-copper significantly increased the peak current compared to the bare electrode.

In figure 3, The MWCNTs-COOH/Cu/GCE exhibited the highest current response, indicating that a strong excellent electrical conductivity and high specific surface area effect occurred between the carbon nanotubes and the nano-copper particles。

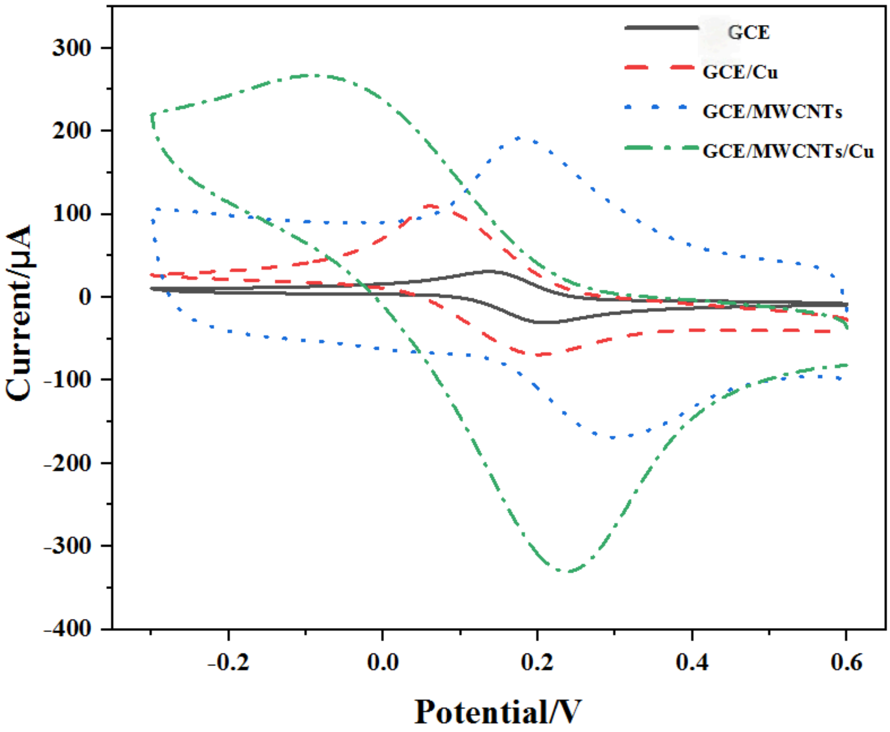

Figure 3. Cyclic voltammograms of potassium ferricyanide on different modified electrodes

Impedance Characterization of Different Modified Electrodes

In figure 4, Electrochemical impedance spectroscopy (EIS) was utilized to characterize the interfacial properties and electron transfer efficiency of the electrodes. A smaller spectral radius indicates lower impedance and better conductivity. The bare GCE exhibited the largest semicircle diameter, demonstrating the highest impedance. The resistance of the MWCNTs-COOH/GCE was significantly reduced, being only 1/25 of the bare electrode, owing to the large specific surface area provided by the carbon nanotubes. The Cu/GCE also showed improved conductivity. Notably, the impedance plot of the MWCNTs-COOH/Cu/GCE was almost a straight line, representing the lowest resistance and the fastest electron transmission rate, further confirming the successful compounding and excellent electrical conductivity and high specific surface area effect of the two materials.

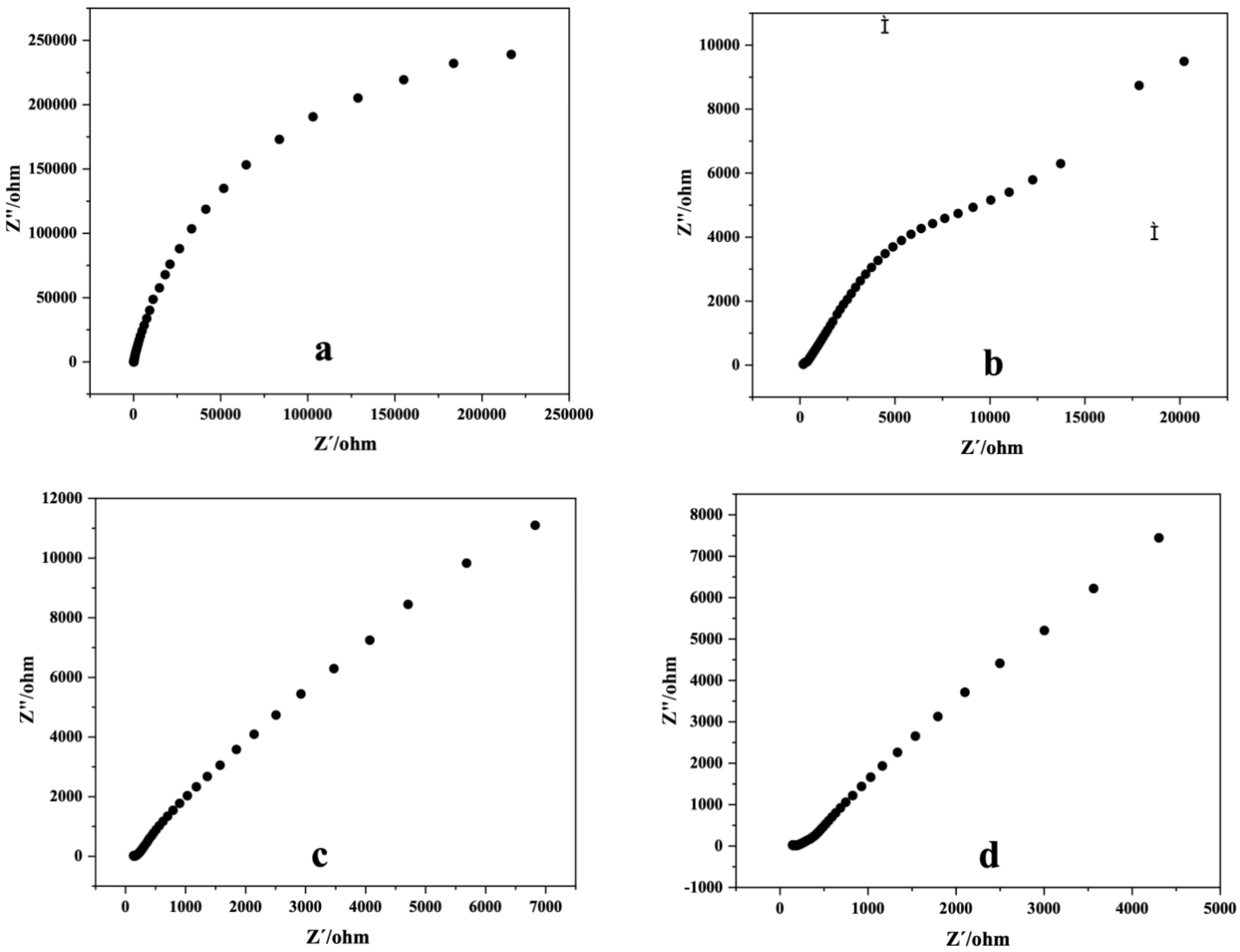

Figure 4. Electrochemical impedance spectra of different modified electrodes (a. bare GCE, b. MWCNTs-COOH/GCE, c. Cu/GCE, d. MWCNTs-COOH/Cu/GCE)

Electrochemical Response of Resveratrol on Different Electrodes

The DPV responses of 1.0× 10^{-5} mol/L resveratrol in pH 7 PBS buffer solution were investigated. The peak current of resveratrol on the bare electrode was the smallest. Upon modification with MWCNTs-COOH and nano-copper, the peak current increased, indicating good catalytic effects. When the electrode was simultaneously modified with both materials (MWCNTs-COOH/Cu/GCE), the peak current significantly surpassed the catalytic effect of any single material. This indicates that the composite structure increased the binding sites for resveratrol, accelerated the electron transfer rate, and achieved an obvious catalytic enhancement,as shown in figure 5, figure 6 and figure 7

Optimization of Experimental Conditions

To maximize the sensor’s analytical performance, the experimental parameters were systematically optimized:

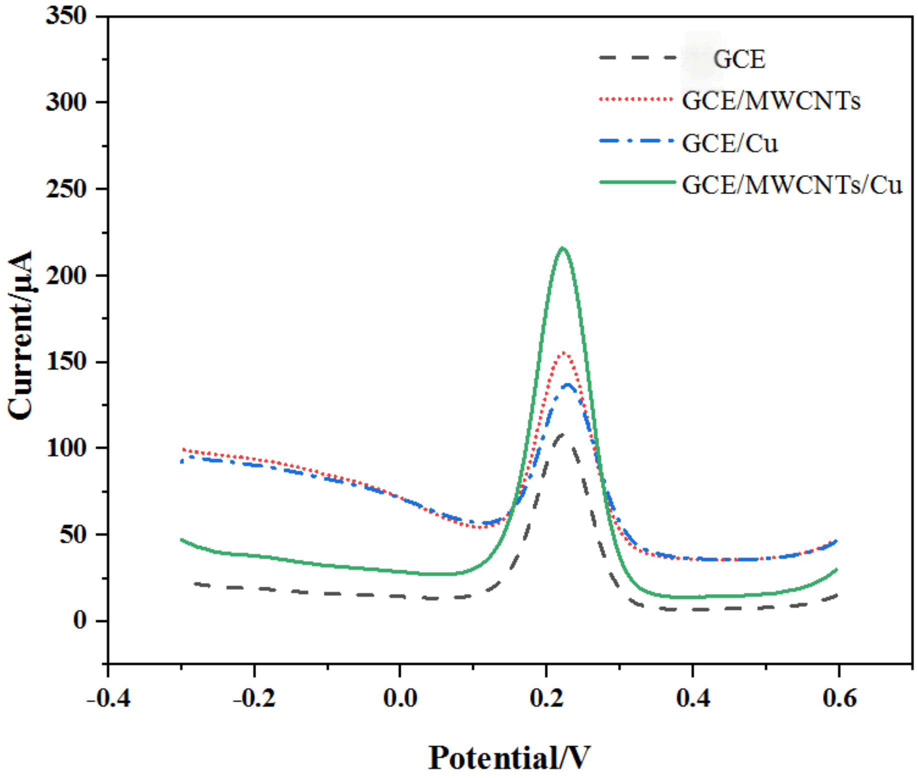

Figure 5. Differential pulse voltammograms of resveratrol on different modified electrodes

Optimization of Buffer Solution pH: Linear sweep voltammetry (LSV) was employed to evaluate pH values of 5.0, 6.0, 7.0, 8.0, and 9.0. With the change of pH, on the MWCNTs-COOH/Cu/GCE electrode, the reduction peak current increased rapidly when pH increased within the range of 5.0 to 9.0. The reduction peak current reached the maximum value at pH 7.0, which was significantly higher than that at other pH values. After pH > 7.0, the reduction peak current decreased sharply. Therefore, pH 7.0 was selected as the optimal condition for the determination of resveratrol in this experiment. The figure further shows that the peak potential shifted gradually with the increase of pH, indicating that H^+ was involved in the electrode reaction process, which might be an equivalent proton reaction process.

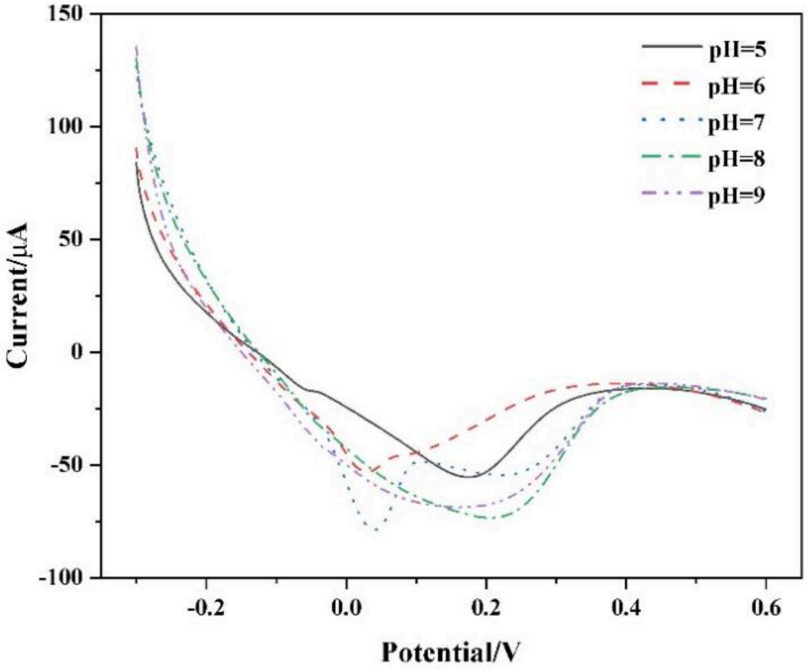

Figure 6. Linear sweep voltammograms of resveratrol at different pH values

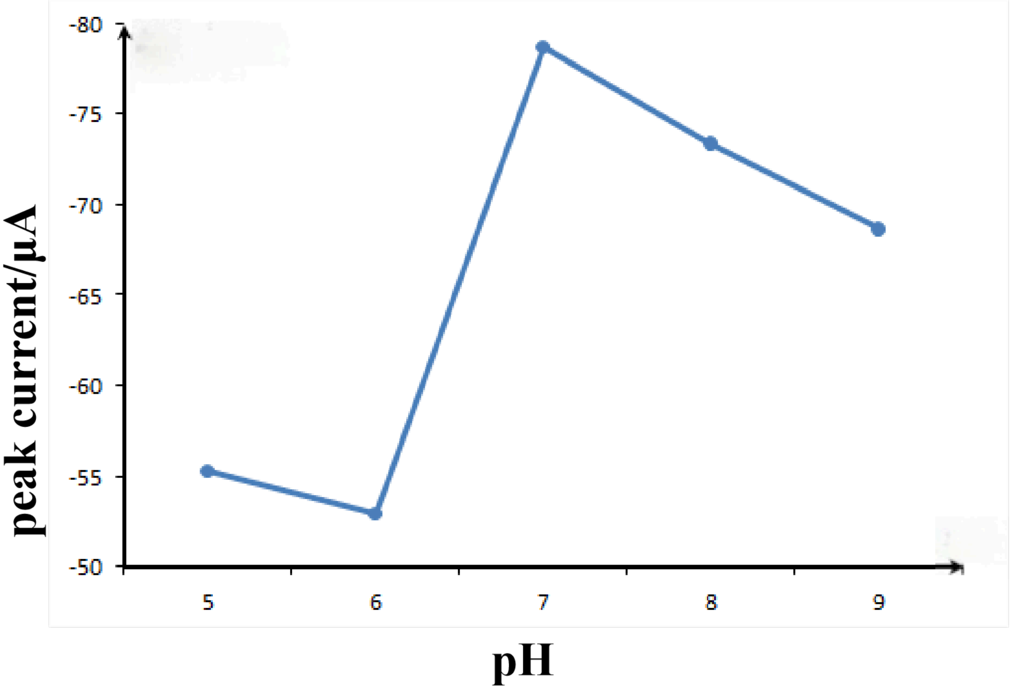

Figure 7. Effect of pH on the LSV peak current of resveratrol

Optimization of Scan Rate: The effect of scan rates (30, 50, 70, 100 mV/s) was examined using CV. At around 0.1 V, a reduction peak appeared. When the scan rate was 50 mV/s, the reduction peak current reached a maximum of 113 μA. As the scan rate increased to 100 mV/s, the peak current dropped to 89.79 μA, while at 30 mV/s, it was only half the size of that at 50 mV/s.This indicates that the reversibility of the redox reaction of resveratrol on the electrode surface gradually deteriorates, which is unfavorable for the determination. However, the oxidation peak current and reduction peak current gradually increase. Therefore, considering comprehensively, 50 mV·s^{-1} was adopted for the subsequent determination in the experiment. The current reduction is attributed to unstable electrode interface and complex kinetic limitations at high scan rates。(figure 8,figure 9).

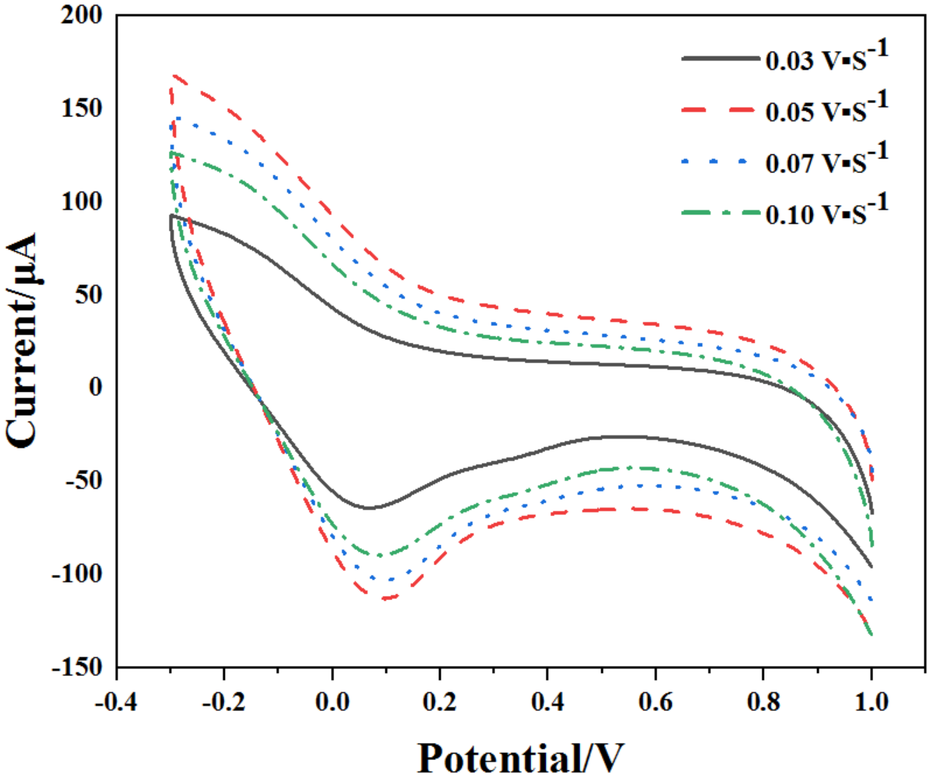

Figure 8. Cyclic voltammograms of resveratrol at different scan rates

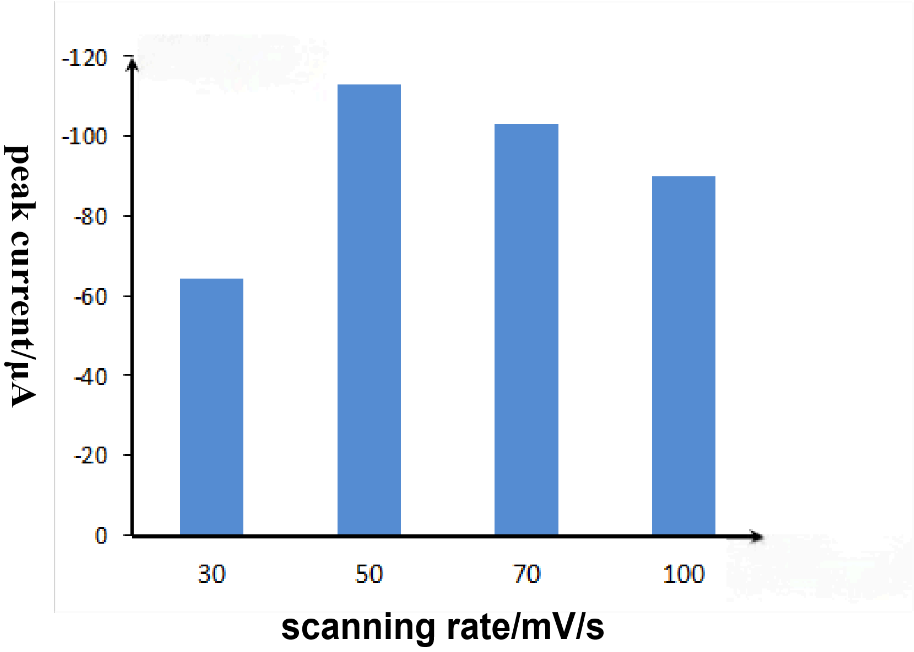

Figure 9. Effect of scan rate on the CV peak current

Optimization of MWCNTs-COOH Modification Amount: Drop-casting volumes of 3.0, 4.0, 5.0, 6.0, and 7.0 µL were tested. The oxidation and reduction peak currents followed the order of 6 µL > 7 µL > 5 µL > 4 µL > 3 µL. At 6 µL, the oxidation peak current was 205.2 µA, and the reduction peak current was 235.4 µA, showing obvious reversible behavior. At 7 µL, the currents decreased to 191.8 µA and 202.4 µA, respectively. Volumes that were too low provided insufficient sensitization, while excessive amounts caused the Nafion to form a thick film that hindered electron transfer and exceeded the effective diameter of the GCE. Hence, 6 µL was the optimal volume(figure 10,figure11).

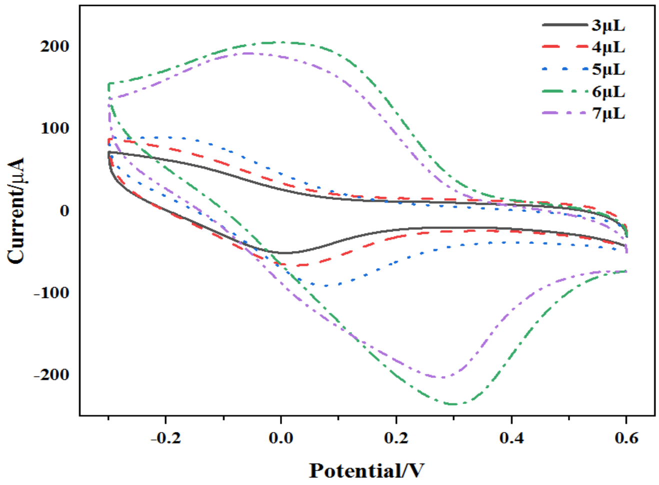

Figure 10. Cyclic voltammograms of resveratrol with different modification volumes of MWCNTs-COOH

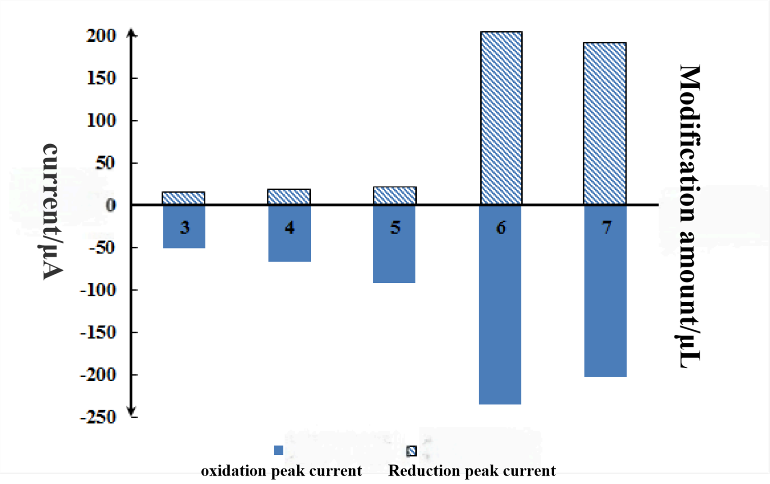

Figure 11. Effect of modification volume on the CV peak currents

Optimization of Cu Deposition Potential: Deposition potentials from −0.3 V to −0.7 V were investigated. The highest oxidation-reduction peak current was observed at −0.4 V. The choice of deposition potential affects the morphology and size of the Cu nanoparticles. At −0.4 V, the resveratrol response curve showed a reversible morphological state with the maximum current, making it the optimal potential.Optimization of Cu Deposition Time: Deposition times of 150, 200, 250, 300, and 350 seconds were evaluated using LSV. Times of 150 s and 350 s yielded the lowest peak currents. A time that is too short deposits insufficient nano-copper particles, while a time that is too long creates an overly thick layer that increases resistance. The highest peak current was achieved at 250 seconds, representing the optimal thickness for electron transfer. As shown in figure 12 and figure 13.

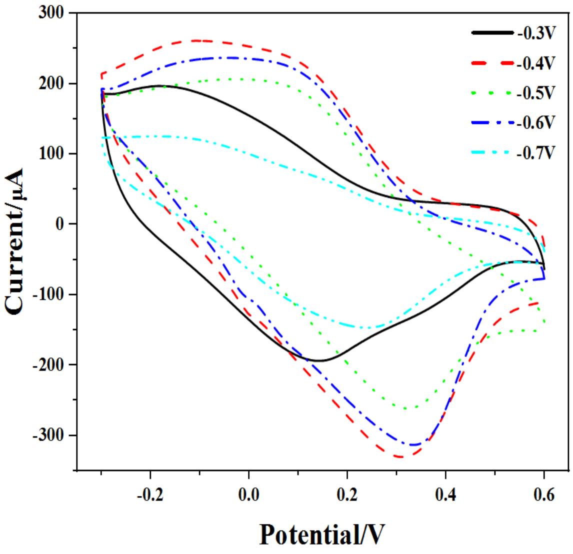

Figure 12. Cyclic voltammograms of resveratrol at different deposition potentials

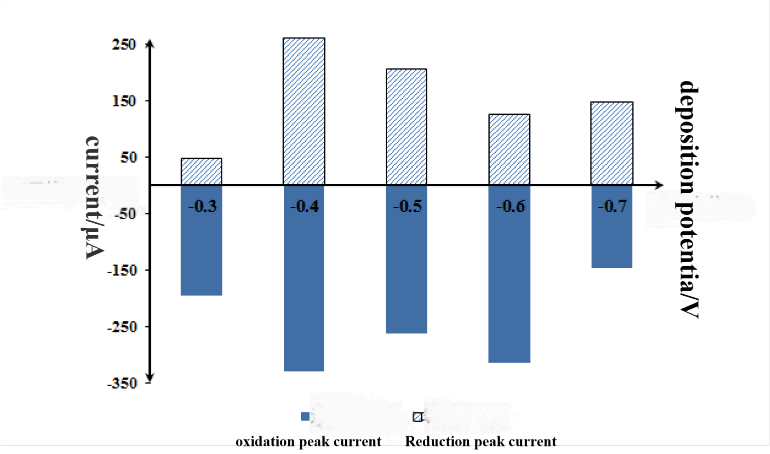

Figure 13. Effect of deposition potential on the CV peak currents

Plotting of the Standard Curve

Under the optimal experimental conditions, DPV experiments were conducted on standard resveratrol solutions ranging from 1× 10^{-7} to 1× 10^{-8} mol/L. The results demonstrated that the peak current increased proportionally with the concentration. The linear regression equation was established as I = 1987.3c + 14.895, with an excellent correlation coefficient (R^{2}) of 0.988, indicating a wide linear response range for the sensor. This superior performance is a direct result of the excellent electrical conductivity and high specific surface area between the MWCNTs-COOH and nano-copper composite, as shown in figure 14 and figure 15.

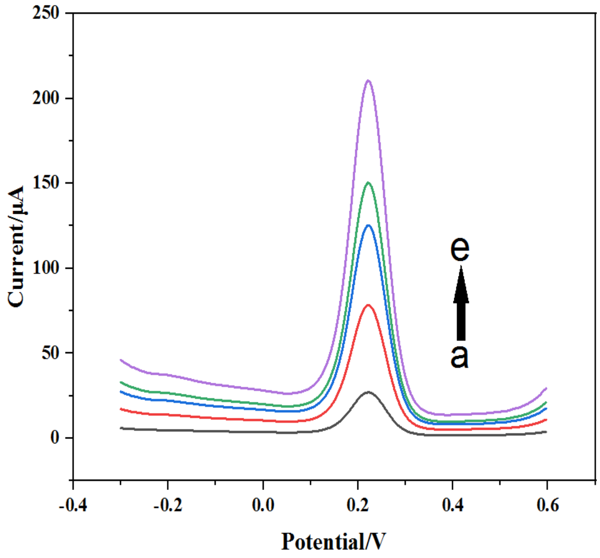

Figure 14. Differential pulse voltammograms of resveratrol at different concentrations (a to e: 1×10-8 to 1×10-7 mol/L)

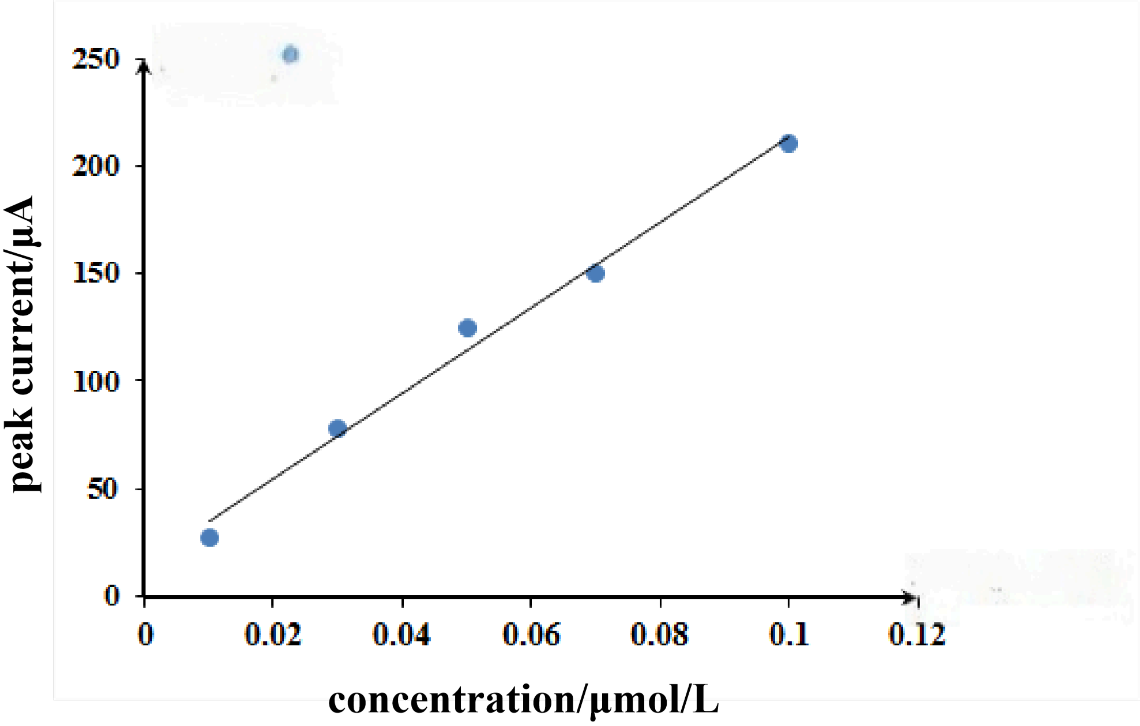

Figure 15. Calibration curve of the peak current versus resveratrol concentration

Stability and Reproducibility of the Electrode

The reproducibility and stability of the electrode have a significant impact on the determination results. The fabricated MWCNTs-COOH/Cu/GCE was used to detect 1.0× 10^{-5} mol/L resveratrol for six repetitive DPV measurements. The detection results were highly stable, yielding a relative standard deviation (RSD) of 0.59%, which strongly proves that the proposed sensor has exceptional repeatability and stability.

Actual Sample Determination

To evaluate its practical utility, the optimal MWCNTs-COOH/Cu/GCE was applied to test the prepared grape seed extract. The DPV graph revealed a distinct characteristic current peak between 0.1 V and 0.2 V, with a peak current value of 126.6 µA. By substituting this current value into the established standard calibration curve, the resveratrol content in the grape seed sample was calculated to be 0.056 µmol/L. This demonstrates that the fabricated sensor can be successfully deployed for the actual detection of resveratrol in real samples(in figure 16).

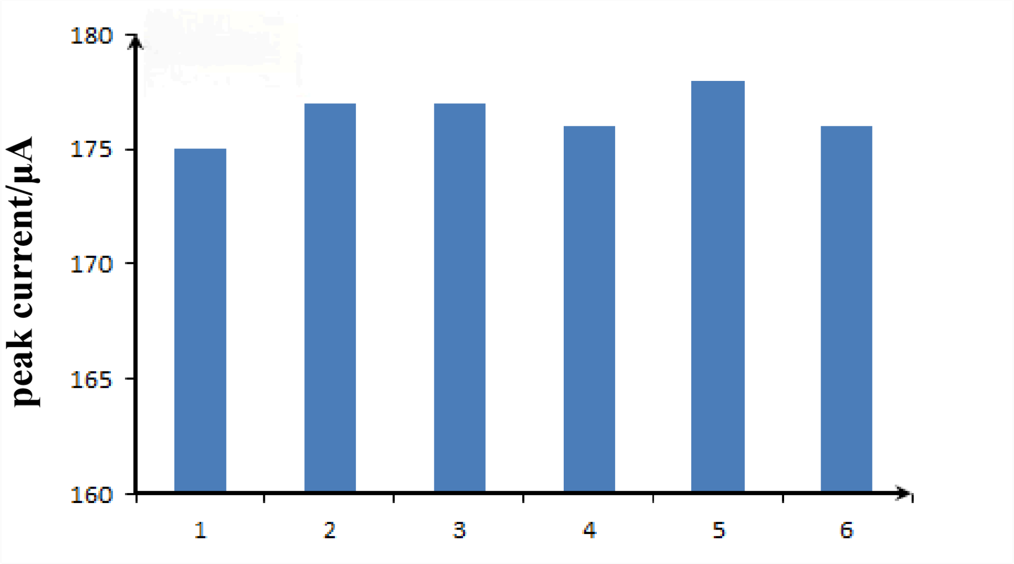

Figure 16. Peak currents of resveratrol for six repetitive measurements

CONCLUSION

In this comprehensive study, a novel, rapid, and accurate electrochemical method for the detection of resveratrol was successfully constructed. By combining the unique advantages of MWCNTs-COOH and nano-copper, a excellent electrical conductivity and high specific surface areaactive composite film was formed on the GCE surface. This synergy increased the electrode's active surface area, accelerated the electron transfer rate, and reduced the internal resistance, thereby significantly enhancing the electrochemical activity of resveratrol. Utilizing DPV, quantitative detection was achieved with a linear range of 1× 10^{-7} to 1× 10^{-8} mol/L, a linear equation of I = 1987.3c + 14.895, and an R^2 of 0.988. The sensor also exhibited outstanding repeatability and stability. When applied to actual grape seed extracts, a characteristic peak was successfully identified, allowing for accurate quantitative analysis. In the future, combining this nanomaterial platform with multidisciplinary approaches, such as molecular imprinting technology, could further improve the specific recognition mechanism and stability of the sensor, paving the way for its commercialization and broad application in food and pharmaceutical analysis.

Author Contributions

Conceptualization – Lijuan Zhao; methodology – Yiren Xu; formal analysis – Zaiqiong Liu; investigation – Yan Zheng; resources – Min Li; writing-original draft preparation – Jianqiang Zhang, Yiren Xu and Jiale Zhu; writing-review and editing – Zaiqiong Liu , Yan Zheng and Jianqiang Zhang; visualization – Min Li; supervision – Jiale Zhu. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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