Int. J. Electrochem. Sci., 15 **(2020)** 559 – 566, doi: 10.20964/2020.01.49

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical Determination of Ferulic Acid in Pinellia Ternata Based on GOs/MWCNTs Nanocomposite Modified Electrode

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Received: 9 September 2019 / *Accepted:* 1 November 2019 / *Published:* 30 November 2019

The rapid electrochemical determination of ferulic acid (FA) was assiduously scrutinized by cyclic voltammetry (CV) using graphene oxide sheets (GOs) and multi-walled carbon nanotubes (MWCNTs) nanocomposites modified glassy carbon electrode. The synergistic out-come of GOs and MWCNTs resulted in superior electrocatalysis performance. Under optimal conditions, the peak current was proportional to FA concentration in the range of 0.24 μM to 32 μM, and 88 μM to 1.23 mM, with a relative low detection limit of 0.08 μM. Besides, it was successfully applied to detect FA in *Pinellia ternate* with recovery values in the range of 102.8%-113.2%, which made it a potential alternative tool for the quantitative detection of FA in pharmaceutical analysis and quality evaluation of traditional Chinese medicine.

Keywords: Ferulic acid; Pinellia ternate; Graphene oxide; Muti-walled carbon nanotubes; Electrochemical determination

1. INTRODUCTION

Ferulic acid (FA, 3-methoxy-4-hydroxy cinnamic acid) is an important efficacious ingredient of *Pinellia ternata, Angelica sinensis, Ligusticum chuanxiong, propolis, Semen Ziziphi Spinosae* and other traditional Chinese medicines [1-3]. Over the past few years, increasingly in-depth studies on the pharmacological activities of ferulic acid have shown that ferulic acid and its derivatives have many biological activities, such as antioxidant, antithrombotic, antineoplastic, hypolipidemic, anti-inflammatory, antimicrobial and immunomodulatory functions [4-8]. FA has been widely applied in the fields of medicine, cosmetics and health care [9-11]. Therefore, the establishment of a simple, fast, reliable and low-cost method for the determination of FA is of great practical significance.

At present, quantitative methods for FA mainly include high performance liquid chromatography, gas chromatography, thin layer chromatography, ultraviolet-visible spectroscopy, chemiluminescence, micellar electro-kinetic chromatography, etc. [12-17]. However, the pretreatment processes of these traditional detection methods are cumbersome and expensive. In recent years, electrochemical analysis has been shown to have wide application prospects in the field of drug analysis due to its high sensitivity, low detection limit and simple operation. The electrochemical behavior and quantitative determination of FA have been investigated using several working electrodes, such as glassy carbon electrode (GCE) [18], poly (diallyldimethylammonium chloride) (PDDA) functionalized graphene modified gold electrode [3], poly-aspartic acid modified electrode [19], and carbon paste electrode [20,21]. The performance of the modified electrodes depends on the properties of the modifier, which affects the selectivity and sensitivity of these electrodes to FA.

Graphene, which consists of a single layer of carbon atoms in a two-dimensional, closely packed honeycomb lattice, is a new carbon nanomaterial with excellent conductivity and high specific surface area, which make it widely used in the construction of electrochemical sensors [22-24]. However, pure graphene easily stacks due to the π- π bonding between layers, which greatly reduces its properties and hinders its applications. Multi-carbon nanotube is a one-dimensional carbon nanomaterial with unique chemical and physical properties, which makes it more attractive than other nanomaterials for various applications over other nanomaterials [25-27].

In this work, Graphene oxide (GO) has good dispersion in water due to the hydrophilic groups on its surface. Using this property, we prepared GOs/MWCNTs nanohybrid by using it to disperse MWCNTs. One-dimensional (1D) MWCNTs and 2D GOs were ultrasonically dispersed in water to form a stable suspended matter (GOs/ MWCNTs), which was used to be construct a FA electrochemical sensor. The morphology and structure of the nanohybrid were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrochemical behaviors of the sensor were evaluated by cyclic voltammetry (CV).

2. EXPERIMENTAL SECTION

2.1. Reagents and Apparatus

Graphene and MWCNTs were purchased from Pioneer Nanotechnology Co. (Nanjing, China). H_2SO_4 and FA were bought from Aladdin Chemical Reagents Co. Ltd. (Shanghai, China). All the reagents involved are analytical grade. All the experimental water is doubly distilled water.

All electrochemical experiments were carried out on a CHI 660D electrochemical workstation (Chenhua Instruments Co., Shanghai, China), which contained a three-electrode system, working electrode (bare or modified electrode), reference electrode (saturated calomel electrode) and auxiliary electrode (a platinum wire or sheet). The surface morphologies of composites were examined using a scanning electron microscope (SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, Philips Fei Co., Hillsboro, OR).

2.2. Preparation of rGOs/MWCNTs nanocomposite

The preparation method of the GOs/MWCNTs nanocomposite is as follows: 5 mg GOs and 5 mg MWCNTs were dispersed in 50 mL water, then ultrasonic treated for 30 min to obtain assembled black GOs/MWCNTs nanocomposite.

2.3 Electrodes modification

Prior to modification, the glassy carbon electrode (GCE) with 4 mm diameter was firstly polished with 0.3 and 0.05μm alumina slurry to obtain mirror like surface, respectively. Then sonicated in ethanol and deionized water for 5 min and dried at room temperature. Using a micro-injector to draw 5 μL of above mentioned as-prepared GOs/MWCNTs nanocomposite suspension onto the electrode surface, after drying at room temperature, the GOs/MWCNTs/GCE was constructed.

3. RESULTS AND DISCUSSION

3.1 Characterization of GOs/MWCNTs

The morphologies and microstructures of GOs/MWCNTs were investigated by SEM (Fig 1A) and TEM (Fig 1B). The long and curly MWCNTs were adsorbed onto the GOs sheet planes. Compared with pure GOs, the addition of MWCNTs increased the porosity of the electrode.

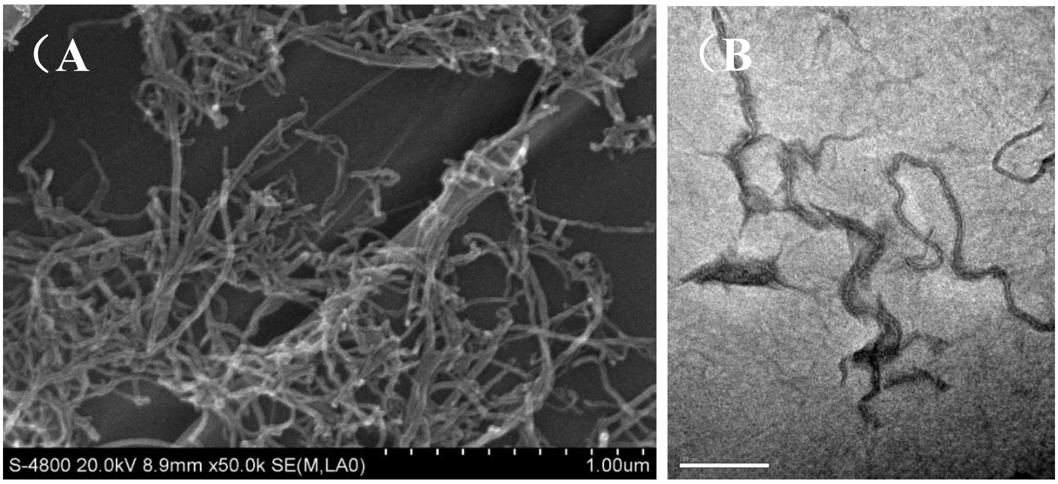


Figure 1. SEM (A) and TEM (B) image of GOs/MWCNTs.

3.2 Cyclic voltammetric behaviors of the modified electrode

Fig 2 shows the cyclic voltammograms (CVs) of the bare GCE (curve a), MWCNTs/GCE (curve b) and GOs/MWCNTs/GCE (curve c) in 5 mL 0.05 M H_2SO_4.

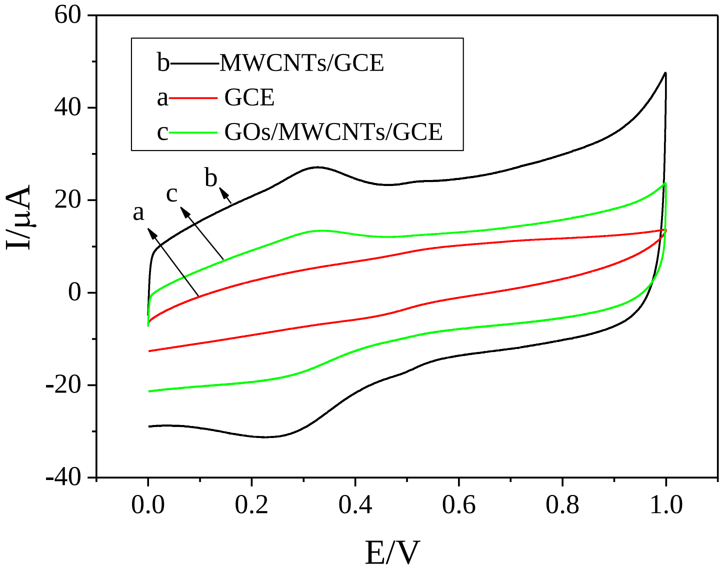


Figure 2. CVs of the bare GCE (curve a), MWCNTs/GCE (curve b) and GOs/MWCNTs/GCE (curve c) in 5 mL 0.05 M H_2SO_4.

From the figure, there is no obvious redox peak at the bare GCE (curve a). When MWCNTs were added, an obvious redox peak appeared at approximately 0.3 V. However, after adding GOs, the peak current of the electrode significantly decreased possibly due to the poor electrical conductivity of GOs. This also reveals that the modified electrode is successfully prepared.

3.3 Electrocatalytic behaviors of FA on modified electrode

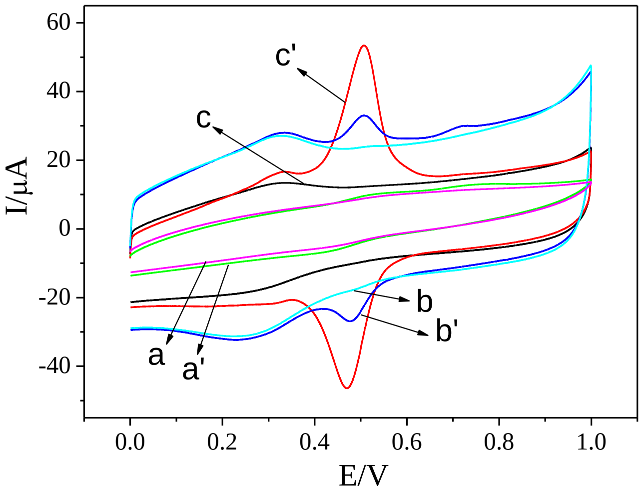


Figure 3. CVs of the bare GCE (curve a and a'), MWCNTs/GCE (curve b and b') and GOs/MWCNTs/GCE (curve c and c') in the absence and presence of the same concentration of FA.

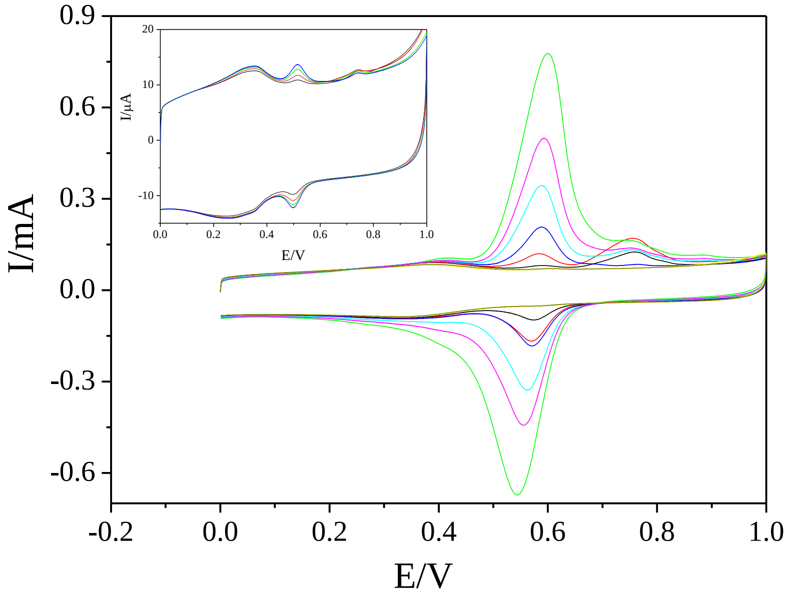


Figure 4. The CVs of the GOs/MWCNTs/GCE toward different concentrations of FA in 0.05 M H_2SO_4.

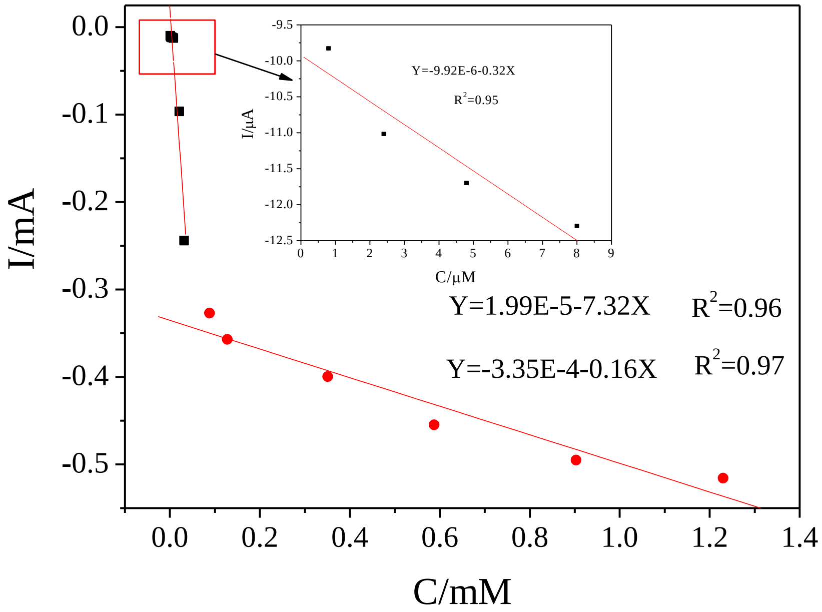


Figure 5. The linear relationship between reduction peak current and concentration.

The electrocatalytic behaviors recorded in the absence and presence of the same concentration of FA at the bare GCE (curves a and a'), MWCNTs/GCE (curves b and b') and GOs/MWCNTs/GCE (curves c and c') were shown in Fig 3. As can be seen from the figure, bare GCE has no obvious catalytic effect on FA. Although the background current of MWCNTs/GCE (curve b) is larger than that of

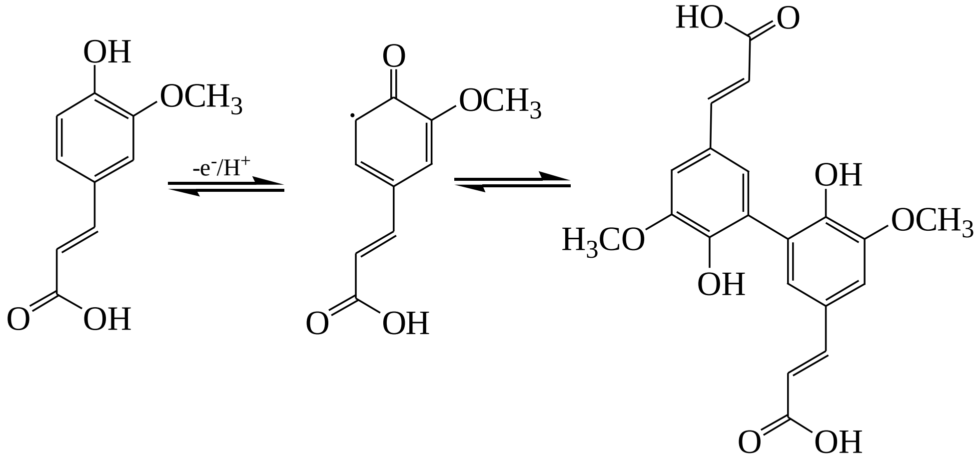
GOs/MWCNTs/GCE (curve c), its catalytic effect on FA (curve b') is not as strong as that of GOs/MWCNTs/GCE (curve c'). The catalytic peak current of the former increases by about 30 mA, while the latter by 50 mA. These results may be attributed to the synergistic out-come of combining GOs with MWCNTs.

Fig 4 shows the electrocatalytic behaviors of the GOs/MWCNTs/GCE toward different concentrations of FA in 0.05 M H_2SO_4. Obviously, the redox peak current of gradually increases with the increase in FA concentration. The response of the electrode to low FA concentrations is shown in the inset of Fig 4. Fig 5 shows the linear relationship between the peak current and FA concentration and shows that the peak current reduction is proportional to the concentration of FA over the ranges 0.24 μM to 32 μM and 88 μm to 1.23 mM with a relative low detection limit of 0.08 μM. Finally, the performance of the modified electrode is compared with that other sensors for FA detection, and the results are shown in Table 1. It can be seen from the table that this work has obvious advantages in detection limit under the same technical conditions. The detection method used by electrochemical sensors to phenols with lower detection limits are DPV. In short, the detection limit with a wide linear range is higher than this work and the linear range with a lower detection limit is not as wide as this work. Compared with pure MWCNTs [28] and GOs [2], the results are more obvious. The excellent results may be mainly due to the synergistic out-come of combining GOs with MWCNTs. Finally, the electrocatalytic mechanism of FA is discussed, and the results are shown in Scheme 1.

Table 1. Comparison of analytical performance of present sensor with other sensors reported in the literature

Modified electrode	Linear range (μM)	Detection limit (μM)	Technique used	Reference
[a] GCE	50-1000	1.0	SV	[18]
[b] CPE/MWCNTs – Ag	0.04-1000	0.03	CA	[20]
[c] DDAB/nafion/CPE	2-12000	0.39	CV	[21]
[d] PDDA-G/GCE	0.09-52.5	0.02	DPV	[3]
[e] MWCNT/GCE	10-5000	0.1	CV	[28]
[f] ERGO/GCE	0.08-38.9	0.02	DPV	[2]
[g] PAA/GCE	0.91-3000	0.3	DPV	[19]
GOs/MWCNTs/GCE	0.24-1230	0.08	CV	This work

[a] glassy carbon electrode
[b] carbon paste electrodes modified by Multi-walled carbon nanotubes and Ag
[c] Didodecyldimethylammonium Bromide/Nafion Composite Film-modified Carbon Paste Electrode
[d] poly(diallyldimethylammoniumchloride) functionalized graphene- modified GCE
[e] Multi-walled carbon nanotubes modified GCE
[f] reduced graphene oxide modified GCE
[g] poly-aspartic acid modified GCE



Scheme 1. The electrochemical catalytic mechanism of FA on the electrode.

3.4 Application in the real samples and recovery test

Fifty grams of dry *Pinellia ternata* was ground to a powder, and 10-fold ethanol was added twice for extractions, once for 1.5 h and then filtered and merged twice. The extract was concentrated and then diluted with methanol after it was removed. Precision removal of 100 μL of sample above the diluent in 10 mL 0.05 M H_2SO_4, pull mixing, until the system was stable, and cyclic voltammetry was then used to determine the content of FA (using the standard addition method).

Table 2. Determination of FA in *Pinellia ternate* samples by standard addition method.

Samples	**Added /μmol·L^{-1}**	**Found [a] /μmol·L^{-1}**	**Recovery/%**
1	20.00	22.64±0.3	113.2
2	20.00	21.50±0.3	107.5
3	20.00	20.55±0.2	102.8

[a] Mean ± SD of three measurements.

The results presented in Table 2 show that the sensor can be used to determine the content of FA in traditional Chinese medicines accurately, sensitively and rapidly.

4. CONCLUSIONS

In summary, an electrochemical sensor for FA based on GOs/MWCNTs modified GCE was successfully constructed in this work. The performance of the sensor was excellent owing to the good electrical conductivity, strong absorption ability, large effective surface area and the synergistic outcome of combining GOs with MWCNTs. The sensor was used to detect FA in *Pinellia ternata* samples with satisfactory recoveries from 102.8%-113.2%. Therefore, this study provides a promising platform for broadening the application of GOs and MWCNTs in the field of pharmaceutical analysis.

ACKNOWLEDGMENTS

The Department Education Project of Guizhou Province (KY[2015]450, KY[2015]388, KY[2018]471), The Joint Foundation Project of Guizhou Province (LH[2015]7587, LH[2016]7058, LH[2016]7044), The Science and Technology Bureau Project of Bijie City ([2016]21), the National Natural Science Foundation of China (81860701), Chemical Engineering Experimental Teaching Demonstration Center of Guizhou Province, Key disciplines of Applied Chemistry and chemical engineering and Technology in Guizhou Province supported this work.

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