IIETA International Information and Engineering Technology Association
Advancing the World of Information and Engineering

Journal of New Materials for Electrochemical Systems
Vol. 25, No.3, July 2022, pp.214-218
http://new-mat.org
http://iieta.org/journals/jnmes

Synthesized Cobalt Tetroxide-Graphene Composite Film by Electrospinning and Modified Glassy Carbon Electrode for Ofloxacin Determination

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ABSTRACT

The purpose of this study was to determinate ofloxacin, the approach of electrospinning and electrochemical was adopted, metal oxide cobalt tetroxide (Co_3O_4)/graphene (*GR*) nanomaterials were electrodeposited on the surface of glassy carbon electrode, then prepared a new type of nanocomposite electrode (Co_3O_4/*GR*/*GCE*), it was successfully used to measure *ofloxacin*. The experiments show that the surface morphology of the modified electrode was characterized by scanning electron microscopy, and the Co_3O_4 nanoparticles and *GR* could be well modified on the surface of the glassy carbon electrode. The determination conditions of *ofloxacin* were optimized by the differential pulse voltametry (*DPV*). Under the optimal conditions, the linear relationship ranged from 0.45 to 170 μ M, and the minimum detection limit was 0.16 μ M (S/N = 3). Moreover, the recovery rate in the actual drug was good, and the relative standard deviations were all less than 5%. The impacts of the obtained results indicate that the modified electrode has good electrocatalytic performance for *ofloxacin*, and has good repeatability and practicability, and can significantly improve the detection sensitivity.

Keywords: *electrospinning, Co_3O_4/GR, carbon paste modified electrode, ofloxacin determination*

Received: 2022-05-06 Accepted: 2022-07-12 https://doi.org/10.14447/jnmes.v25i3.a09

1. INTRODUCTION

Given the high specific capacitance and excellent electrochemical reversibility, transition metal oxides are the primary materials for preparing electrochemical biosensor electrodes [1-2]. However, they have the disadvantages of poor electrical conductivity and cycling stability, which limits the electrochemical performance of electrode materials prepared. The researcher [3] found that incorporating graphene could make up for their deficiencies, because graphene has outstanding electrical conductivity and stability. Its high specific surface area can improve the electrode sensitivity, just like Co_3O_4 nanoparticles. Therefore, the experimenter [4] combined graphene and cobalt tetroxide to prepare composite materials, which meet the electrochemical requirements for capacitors. Due to Co_3O_4/*GR,* the composite material is one of the most popular and inexpensive electrode materials, solves the phenomenon of metal oxide accumulation [5-7] simultaneously, and especially dramatically improves the conductivity of electrode materials. At present, people mostly use hydrothermal and electrochemical deposition methods for electrode materials, to obtain excellent electrochemical performance.

Along with the development and application of nanomaterials, the researcher [8-10] has prepared Co_3O_4/*GR* composites with different morphologies and properties using various methods. Among them, Electrospinning technology has become a worldwide research hotspot, as shown in Figure 1, and various metal oxide fibers have been prepared [11-14]. The electrode material synthesized from Co_3O_4/*GR* nanofiber can improve the electrochemical properties of electrode materials, and have essential research significance. In particular, the low production cost and high specific electrical energy of Co_3O_4 are combined with the high electrical conductivity of graphene, which meets the performance requirements of electrode materials, and is helpful for the R&D of electrochemical analysis instruments.

As a modern instrumental analysis method, electrochemical analysis has the advantages of high sensitivity, good selectivity, short response time, and simple manner. Accurately detecting the content of active ingredients in drug molecules is very important for drug quality and patient safety. *Ofloxacin* is a quinolone antibacterial drug, which has a strong antibacterial effect.

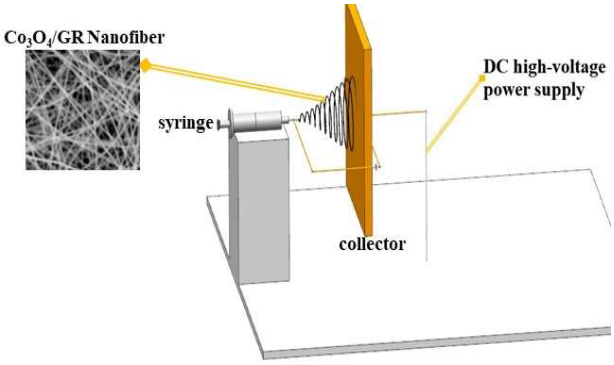

Figure 1. Electrospinning process

However, *Ofloxacin* has adverse reactions, which may lead to renal dysfunction, rising liver enzyme, blood cell decrease, platelet reduction, gastrointestinal dysfunction, allergic

reactions, or main symptoms may also occur [15]. At present, the methods for the determination of *Ofloxacin* mainly include the spectrophotometry [16, 17], the fluorescent spectrum method [18], the chemiluminescence method [19], the chromatography method [20, 21], the capillary electrophoretic method [22, 23], and modified electrode electrochemical method [24-27]. In the above-mentioned method, the modified electrode electrochemical method has good accuracy and sensitivity due to its simple operation, low cost, and good accuracy. However, the electrochemical detection of *Ofloxacin* on the nude electrode is unsatisfactory, this is due to the deceleration of electrons.

Therefore, the study is devoted to synthesizing a new electrode material by electrospinning, and then to electrodepositing GR and Co_3O_4 onto GCE surfaces using cyclic voltammetry (*CV*), thereby making Co_3O_4/*GR*/*GCE* modified electrode, often used to test *Ofloxacin* detection with differential pulse voltammetry (*DPV*). The work has obtained superior electrochemical performance, and it is expected to be significantly improved in terms of sensitivity, fast response, and sample recovery rate. The research innovatively used electrospinning to prepare Co_3O_4/*GR* nanofibers and make Co_3O_4/*GR*/*GCE* modified electrodes, which is beneficial for creating a simple, feasible, sensitive, rapid, and effective electrochemical analysis method for the determination of *Ofloxacin* in drugs.

2. EXPERIMENTAL

2.1. Instruments and reagents

Equipment and instruments for preparing nanofibers mainly include electrospinning equipment (NS-1, Tsingtao Junada Technology Co., Ltd.), ultrasonic cleaner (KQ3200DE, Kunshan Ultrasonic Instrument Co., Ltd.), and muffle furnace (SX2-8-10G, Shanghai Kuncheng Scientific Instrument Co., Ltd.). Afterwards, synthesis of Co_3O_4/*GR*/*GCE* modified electrodes was applied three-electrode system (control electrode/carbon paste electrode GCE, platinum electrode, and saturated calomel electrode), particularly electrochemical performance tests were carried out on an electrochemical work-station (CHI660E, Beijing Hua Ke Tian Technology Co., Ltd.), and Solartron 1255B impedance/crystal phase analyzer system (Scribner Associates, Inc.). Additionally, Morphological characterization of the electrode materials was performed at a field emission electron microscope (EM-30, Shanghai Yiting Electromechanical Technology Co., Ltd.), and phase analysis of the synthesized nanomaterials was utilized by X-ray diffractometer (D8 Advance diffractometer, Bruker, Germany).

Experimental drug reagents mainly contain, graphene (Shanghai Juna Technology Co., Ltd.), cobalt nitrate hexahydrate (Xilong Science Co., Ltd.), polyvinylpyrrolidone (PVP, Tianjin Kemeiou Chemical Reagent Co., Ltd.), *Ofloxacin* (Shandong Lukang Pharmaceutical Group Saite Co., Ltd.), and other reagents were purchased from Sinopharm Group Chemical Reagent Co., Ltd. Apart from that, all the reagents were of analytical grade, the experimental water was double distilled water (*DDW*), and the supporting electrolyte was 0.1 M phosphate buffer solution (*PBS*). The experiments were carried out at room temperature.

2.2 Precursor configuration

Above all, preparation of liquid A. The experiment weighed 0.877 g polyvinylpyrrolidone (k90 PVP), next to add it into 10 ml absolute ethanol. After stirring for 30 minutes with a magnetic stirrer, and then use an ultrasonic machine for 40 minutes to remove the dissolved gas in the solution. Secondly, prepare solution B. Weigh 0.4158 g cobalt nitrate hexahydrate and 0.0462 g graphene, and the molar ratio of both is 9:1. After that, it was dissolved in 5 ml absolute ethanol, and stirred for 30 minutes to dissolve the solute fully. Thirdly, add solution B into A, and continue stirring for 16 hours, which should maintain adequate magnetic stirring time to obtain a homogeneous liquid. The purpose is to have the appropriate solution viscosity, and to get the desired morphology of the spun fibers.

2.3 Preparation of modified electrodes

The test mixed 2g carbon powder and 0.315g liquid paraffin, and stirred evenly to form fine particles. Next to put the mixture into the electrode tube. Then, take a 4 mg sample fired and dispersed it in an admixture containing 30 μL Nafion solution, 0.75 ml deionized, and 0.25 ml absolute ethanol, and use an ultrasonic machine for 40 minutes to keep the healthy solution mixed. Finally, the work loaded 5μL suspension on a glassy carbon electrode using a pipette, then prepared a Co_3O_4/*GR*/*GCE* modified electrode. After waiting to dry completely, the surface of the electrode should be polished smooth to ensure sufficient sensitivity.

The fibers prepared by electrospinning were placed in a muffle furnace for heat treatment. The calcination was started at room temperature, ramped up to 600°C at a rate of 5°C/min, and held at a constant temperature for two hours. When the furnace was air-cooled to the original temperature, the experiment obtained black Co_3O_4/*GR* fiber material powder. Then, put the tin foil into the drying box and keep it warm at 70°C, as shown in Figure 2.

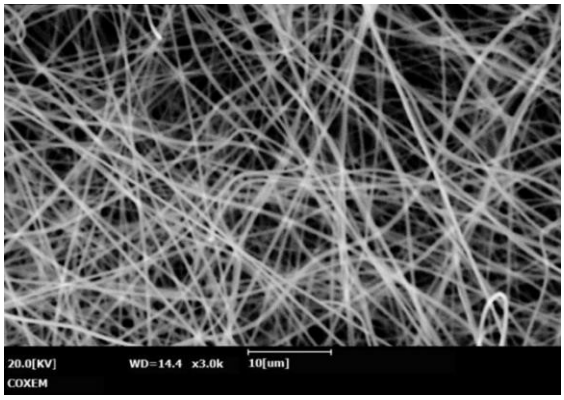

Figure 2. Morphology of Co_3O_4/*GR* fibers

3. RESULTS AND DISCUSSION

3.1 Characterization of electrode materials

While electrospinning, the controlled variable method used to change different parameters to prepare cobalt tetroxide fibers with different diameters. Under a certain solute ratio, the work applied 10-11V voltage intensity, adjusted spray distance to 15cm, 0.05mm/min spray rate, and 40-45% humidity environment, eventually, obtaining the fiber structure with uniform diameter and thickness. The morphology of the calcined Co_3O_4/*GR* composite powder is shown in Figure 3, it can be observed that Co_3O_4 is dispersed

on the graphene, but there is still a partial agglomeration phenomenon, which aggregates to form a block. Comparing the electron microscope images of pure Co_3O_4 nanosheets, it can be found that it has better uniform distribution with graphene-doped Co_3O_4 composites.

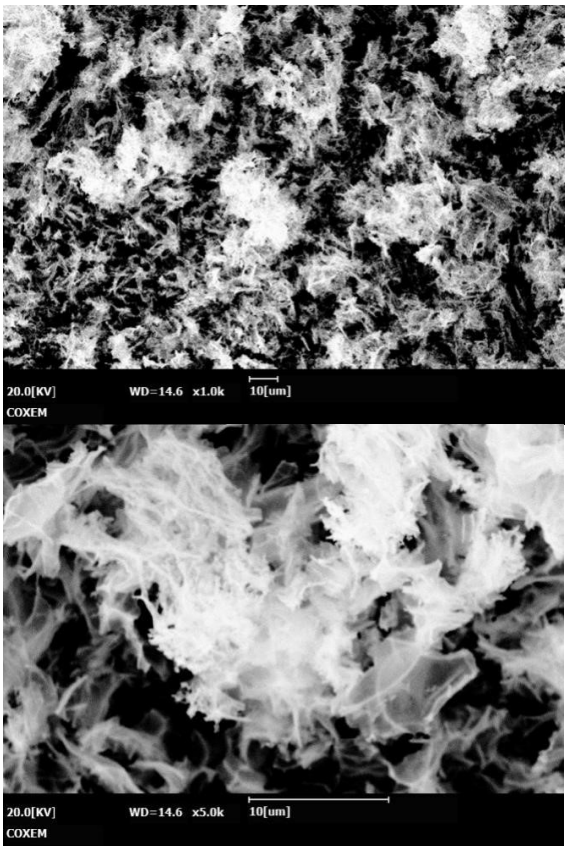

Figure 3. Electron microscope images of Co_3O_4 powder at different magnifications

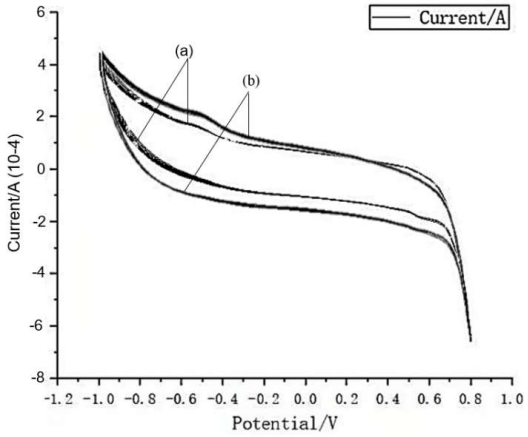

Figure 4. *CV* curves: (a) modified electrode (b) control electrode

3.2 Electrochemical performance

Co_3O_4/*GR*/*GCE* modified electrode has a big impact on electrochemical performance. To prevent the electrode from deteriorating. The point area measured is large enough, and there is no reaction between the electrode material and the chemical constituents in the electrolyte. In addition, Loss and electrolyte composition change. Therefore, in the cyclic voltammetry experiment, the potential window was selected between -1V and 0.8V, the initial scanning polarity was positive with 20 scanning segments, and the sensitivity was 1×10^{-4}, in Figure 4.

Figure 4(a) shows that a weak reduction reaction occurs on the modified electrode, due to the response of $Co^{3+}+e^{-}\rightarrow Co^{2+}$. However, Figure 4(b) shows that no oxidation reaction occurs. The reason is that cobalt undergoes electron transfer in Co_3O_4, and the decrease of Co^{3+} concentration leads to the increase of the cathode peak current. That is, the reduction peak is formed. The investigation found that the reaction speed of the Co_3O_4/*GR*/*GCE* electrode is slow, which is owing to the weaker reaction between ions and the electrode surface, as well as the lower reversible reaction rate.

4. OPTIMIZATION OF EXPERIMENTAL PARAMETERS

4.1 Correction of curves and disturbances

Under optimal conditions, the study performed linear Determination of *Ofloxacin* by *DPV* Method. As shown in Figure 5, the oxidation current of *Ofloxacin* increased with its concentration. And the linear relationship of *Ofloxacin* on Co_3O_4/*GR*/*GCE* is in the range of 0.35-175 μM, and it is worth mentioning that the minimum detection limit is 0.16 μM (S/N=3). The linear equation is: Ip/μA = 1.416 + 0.0808 C/μM (R = 0.9964).

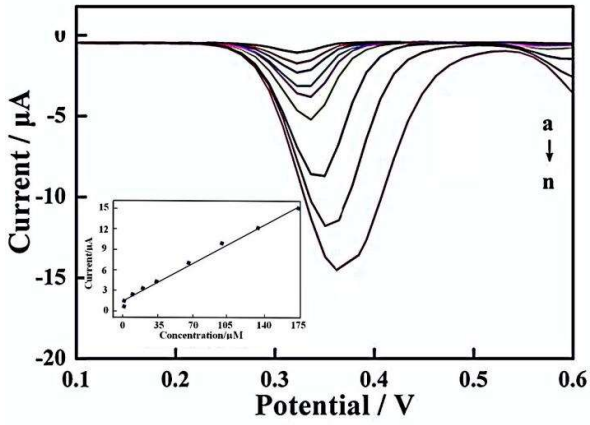

Figure 5. *DPV* curves when different concentrations of *Ofloxacin* are placed in Co_3O_4/*GR*/*GCE*, and the inset is the standard linear curve (a→n: 0.35-175μM)

Additionally, the work evaluated the selectivity and anti-interference ability of Co_3O_4/*GR*/*GCE* for *Ofloxacin* detection, and discussed the interference degree of some important living substances and common metal ions in the *Ofloxacin* detection. An interference test was performed in 0.1 M pH 3.5 phosphate buffer solution containing one μM of *Ofloxacin*, and a particular interfering substance was added to the test solution. Tolerance (±5%) defined should remark detection error caused by the response signal, due to the effect of an external substance on the test substance. Eventually, most common ions and living substances had not interfered determination, it shows that the method created by the experimental study has good selectivity for the determination of *Ofloxacin*.

4.2 Reproducibility and stability

The reproducibility was obtained by the *DPV* method for eight consecutive measurements, and adopted the same Co_3O_4/*GR*/*GCE* electrode, was simultaneously in the same 0.1 M *PBS* solution containing ten μM of *Ofloxacin*, and the relative standard deviation was calculated as 1.79%. It shows that the reproducible performance of the Co_3O_4/*GR*/*GCE* modified electrode is excellent. In addition, the modified *GCE* was placed for ten days before the test of *Ofloxacin*. The experiment acquired a 3.92% lower current, when compared with the same modified electrode prepared on-site, which indicates the modified electrode has good stability.

4.3 Analysis of actual samples

To confirm the practical application of the modified electrode, Co_3O_4/*GR*/*GCE* was used to detect the content of *Ofloxacin* pharmaceuticals. During the measurement, the test placed 20 μL sample solutions (1 mg/mL) into ten ml *PBS* solution (0.1 M, pH 3.5), and used it for measurement. Table 1 shows the determination results of *Ofloxacin* in medicines, and also confirms the reliability of the modified electrode in practical application.

Table 1. Determination results of *Ofloxacin* (n=4)

Samples	Spiked (μM)	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Tablet 1	15.21	10.00	25.05	98.94	2.50
Tablet 2	27.24	20.00	47.86	102.30	1.60
Human serum	0.03	10.00	10.0302	100.67	1.02
	0.06	20.00	20.0598	99.67	1.78

5. CONCLUSIONS

The study prepared Co_3O_4/*GR* by electrospinning, namely, the complex of Co_3O_4 and *GR* was successfully developed and applied. Hence, Co_3O_4/*GR*/*GCE* was composed, and the synthetic method is to coat Co_3O_4/*GR* nanomaterials on the surface of carbon electrodes electrochemically by CV electrochemical deposition. The work improved the electron transfer rate and oxidation signal of *Ofloxacin* on the modified electrode surface, and showed excellent electrocatalytic performance. In addition, the modified electrode shows good sensitivity and stability for the determination of *Ofloxacin*, and also has reliable determination results in actual drug detection.

ACKNOWLEDGEMENT

This work is supported financially by Henan Engineering Technology Research Center (Yuke 2016-221-Gaoxin No. 35), the third batch of Zhihui Zhengzhou 1125-Talents Gathering Program-Innovative Talents (Zheng Zheng[2018]-No.45-15), the critical scientific research project of Henan University in 2023, "Controllable Preparation of Polymetallic Honeycomb Electrode Materials and Development and Application of Electrochemical Biosensors" (Education Office Technology No. [2022]150). And thank for the special funding and equipment support of the visiting professor at North China University of Water Resources and Electric Power (Grant No.: 4001-40734).

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