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Highly Sensitive Determination of Niclosamide Based on The Graphitized and Carboxylated Multi-Walled Carbon Nanotubes Modified Glassy Carbon Electrode

Meimei Guo^{*}, Tingting Wu, Gan Zhu, Yunhang Liu, Mengyuan Zhao, Yansheng Shen, Yu Zhou, Lumei Chen, Xiangxing Guo, Qian Wang, Runqiang Liu^{*}, Hongyuan Zhao^{*}

Henan Institute of Science and Technology, Xinxiang, 453003, China *E-mail: <u>guommhist@163.com</u>, <u>liurunqiang1983@126.com</u>, <u>hongyuanzhao@126.com</u>

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A simple and rapid electrochemical sensor was prepared by using the graphitized and carboxylated multi-walled carbon nanotubes decorated glassy carbon electrode (GR-MWCNTs-COOH/GCE) for the sensitive detection of niclosamide (NA). The carboxylation contributes to the uniform dispersion of MWCNTs because of the good wettability of carboxyl groups. Moreover, the graphitization of MWCNTs could enhance the electrical conductivity of multi-walled carbon nanotubes, which helps provide higher electrochemical response. The obtained GR-MWCNTs-COOH/GCE sensor presented a gratifying limit of detection of 3.1 nM with fitting equation of y=-10.456x+0.566 (R²=0.999). Furthermore, the prepared electrochemical sensor has good practical performance with acceptable repeatability and reproducibility for the simple and rapid determination of NA.

Keywords: Electrochemical sensor; Niclosamide; Graphitized and carboxylated MWCNTs; Electrochemical behavior

1. INTRODUCTION

Organochlorine pesticides are mainly used to prevent and control the insect diseases. As one of organochlorine pesticides, niclosamide (2,5-dicloro-4-nitrosalicylanilide, NA) can not only quickly kill the crop pests but also resist the infectious diseases of aquatic organisms [1-3]. Despite its wide use as anthelmintic drug, NA has toxic effects on some land plants and aquatic fishes. It is quite important to properly deal with the negative effects of the use of NA [4-6].

At present, several analysis techniques such as gas-liquid chromatography and high-performance liquid chromatography have been developed for analyzing NA [7, 8]. However, some defects such as high cost and time-consuming affect the detection efficiency. As a result, the simple and portable analytical methodology is valuable for the low-cost and efficient determination of NA [9]. It has been

reported that electrochemical analysis techniques are gaining popularity because of their advantages of simple operation, low cost, and high analysis efficiency [10-12]. Modification materials (carbon nanotubes, graphene, noble metal, nanoclay, etc.) are very important for the design of high-performance electrochemical sensors [13-17]. Among these materials, carbon materials have important value and significance to optimize the electrochemical sensing electrode. Especially, carbon nanotubes (CNTs) with one-dimensional nanotube morphology have been widely applied for the fabrication of high-performance electrochemical sensors because of high electrical conductivity and large specific surface area [18-20].

Herein, a simple and rapid electrochemical sensor was prepared by using the graphitized and carboxylated multi-walled carbon nanotubes decorated glassy carbon electrode (GR-MWCNTs-COOH/GCE) for the sensitive NA detection of niclosamide (**Scheme 1**). The carboxylation contributes to the uniform dispersion of MWCNTs because of the good wettability of carboxyl groups. Moreover, the graphitization of MWCNTs could enhance the electrical conductivity of multi-walled carbon nanotubes, which helps provide higher electrochemical response. The obtained GR-MWCNTs-COOH/GCE sensor displayed superior NA detection property.



Scheme 1. Schematic diagram of GR-MWCNT-COOH/GCE sensor for NA detection.

2. EXPERIMENTAL

2.1 Fabrication of GR-MWCNTs-COOH/GCE sensor

To fabricate the NA sensor, the bare GCE was decorated by using the double-functionalized GR-MWCNTs-COOH. Compared with the conventional MWCNTs, GR-MWCNTs-COOH was optimized

with graphitization and carboxylation. GR-MWCNTs-COOH (10 mg) was dispersed in N,Ndimethylformamide solution by means of ultrasonication for 30 mins. Then, the bare GCE was polished for the fabrication of NA sensor. The alumina powders were used as polishing materials. After ultrasonic cleaning and drying treatment, the polished GCE surface was deposited by dropping the GR-MWCNTs-COOH suspension (5 μ L, 2 mg mL⁻¹) followed with the further drying treatment by using the infrared lamp to prepare the GR-MWCNTs-COOH/GCE sensor.

The phase structure and surface morphologies of the double-functionalized GR-MWCNTs-COOH were characterized by XRD and SEM analysis techniques. XRD pattern was applied to study the on the phase structure, and SEM image was used to confirm the surface morphology. The electrochemical performance of the GR-MWCNTs-COOH/GCE sensor were obtained by CHI660E workstation.

3. RESULTS AND DISCUSSION

3.1 Structure and surface morphology



Figure 1. SEM images of (a) conventional MWCNTs and (b) double-functionalized GR-MWCNTs-COOH.

In order to analyze the surface morphology, both conventional MWCNTs and doublefunctionalized GR-MWCNTs-COOH were studied by SEM analytical technique. Fig. 1(a) provides the SEM analysis result of conventional MWCNTs on the electrode surface. MWCNTs display an uneven distribution with certain level aggregate phenomenon. Fig. 1(b) provides the SEM analysis result of double-functionalized GR-MWCNTs-COOH on the electrode surface. By contrast, MWCNTs display uniform particle size distribution. No aggregate phenomenon can be observed in the SEM image, which mainly benefits from the hydroxyl and carboxyl groups [21, 22].



Figure 2. XRD patterns of (a) conventional MWCNTs and (b) double-functionalized GR-MWCNTs-COOH; (c) FTIR spectrum of double-functionalized GR-MWCNTs-COOH; (d) picture of (A) conventional MWCNTs and (B) double-functionalized GR-MWCNTs-COOH suspension.

Fig. 2(a-b) show the XRD analysis results of conventional MWCNTs and double-functionalized GR-MWCNTs-COOH. As shown in Fig. 2(a), MWCNTs present significant characteristic diffraction peaks of carbon materials [23, 24]. There are no impurity diffraction peaks, suggesting the high purity of MWCNTs. The XRD pattern of double-functionalized GR-MWCNTs-COOH present more sharp and strong diffraction peak, which may be related to the graphitization of carbon nanotubes [25, 26]. Fig. 2(c) provides the FTIR spectrum of double-functionalized GR-MWCNTs-COOH, which agrees with the characteristic spectrum of carbon nanotubes. Fig. 2(d) provides the picture of conventional MWCNTs and double-functionalized GR-MWCNTs-COOH suspension. It can be found that the conventional MWCNTs suspension presents stratification phenomenon because of the hydrophobic property of carbon materials. By contrast, the double-functionalized GR-MWCNTs-COOH suspension present better uniformity than that of conventional MWCNTs, which has much to do with the carboxylation of MWCNTs. The carboxylation contributes to the uniform dispersion of MWCNTs because of the good wettability, which suggests the existence of a certain amount of carboxyl groups [21, 22].

3.2 Electrochemical characterization

Fig. 3 shows the Cyclic voltammetry (CV) measurement result of the bare GCE, MWCNTs/GCE, and GR-MWCNTs-COOH/GCE sensors. Both conventional MWCNTs and double-functionalized GR-MWCNTs-COOH decorated GCE sensors have more obvious reversible redox peaks than that of the bare GCE sensor. Among these three sensors, the bare GCE sensor showed the lowest peak values (I_{pa} =43.6 μ A, I_{pc} =-47.93 μ A). The MWCNTs/GCE sensor displayed gratifying redox peaks (I_{pa} =103.1 μ A, I_{pc} =-124.2 μ A) because of the high conductivity property of MWCNTs [25, 26]. Compared with these two sensors, the GR-MWCNTs-COOH/GCE sensor displayed the highest redox peaks (I_{pa} =142.1 μ A, I_{pc} =-154.5 μ A). The above results show that the undecorated GCE sensor has no obvious electrochemical response, which agrees with the reported work [27]. After modifying GCE with double-functionalized GR-MWCNTs-COOH, the high conductivity property and large specific surface area enhanced the electrochemical response of the fabricated sensor [28-30]. The carboxylation contributes to the uniform dispersion of MWCNTs because of the good wettability of carboxyl groups [21, 22]. Moreover, the graphitization of MWCNTs could enhance the electrical conductivity of multi-walled carbon nanotubes, which helps provide higher electrochemical response [31, 32].



Figure 3. CV curves of the bare GCE, MWCNTs/GCE and GR-MWCNTs-COOH/GCE sensors.

3.3 Electrochemical behavior of NA

The NA detection performance of the bare GCE, MWCNTs/GCE and GR-MWCNTs-COOH/GCE sensors was analyzed by CV measurement technique. Fig. 4 provides the CV measurement result of 30 μ M NA at these sensors. It can be found that the peak current response of the bare sensor is quite weak, which hardly reflect the NA detection performance. By contrast, the MWCNTs/GCE sensor displayed gratifying peak current response because of the high conductivity property and large specific surface area of MWCNTs [23, 24].



Figure 4. CV curves of 30 μ M NA at the bare GCE, MWCNTs/GCE and GR-MWCNTs-COOH/GCE sensors.



Figure 5. Impact of pH value on the NA detection performance of GR-MWCNTs-COOH/GCE sensor: (a) DPV curves, (b) relationship of pH with peak current, (c) relationship of pH with peak potential; (d) relationship of pH with adsorption time.

Moreover, the peak current response of GR-MWCNTs-COOH/GCE was highest than that of the

bare GCE and MWCNTs/GCE sensors, which has much to do with the carboxylation and graphitization of MWCNTs [33, 34]. The carboxylation contributes to the uniform dispersion of MWCNTs because of the good wettability of carboxyl groups [21, 22]. Moreover, the graphitization of MWCNTs could enhance the electrical conductivity of multi-walled carbon nanotubes, which helps provide higher electrochemical response [31, 32]. The above results affirm that the construction of GR-MWCNTs-COOH/GCE electrochemical sensor is an effective method for the detection of NA.

3.4 Experiment optimization

3.4.1 Influence of pH value

Fig. 5(a) provides the impact of pH value on the DPV measurement result of 30 μ M NA at the GR-MWCNTs-COOH/GCE sensor. The peak current response increases firstly and then decreases with the increasing of pH value. Fig. 5(b) provides the change relationship of pH with peak current. When the pH value is 8.0, the GR-MWCNTs-COOH/GCE sensor can obtain a quite satisfactory maximum value, but the further increase of pH presents an adverse impact on the NA detection property. Such phenomenon is intimately connected to the influence of acid and alkaline on the electrochemical reaction of NA at the GR-MWCNTs-COOH/GCE sensor. The strong acid environment has lots of H+ ions, which limits the reaction from –NHOH to –NO, while the strong alkaline environment only involves a trace mount of H+ ions, which produce an adverse impact on the the subsequent redox reaction of NA [17, 35, 36]. Fig. 5(c) provides the change relationship of pH with peak potential. As shown here, the peak potential (Ep) presents a linear relationship with pH value, and the corresponding fitting equation is E_{pa} =-0.0564pH+0.2492 (R²=0.9974). The gratifying slope value of 56.4 mV pH⁻¹ suggests the two-electron and two-proton process of NA detection at the GR-MWCNTs-COOH/GCE sensor [17, 37, 38].

3.4.2 Influence of accumulation time

Fig. 5(d) provides the impact of accumulation time on the NA detection property. It can be found that the NA detection property is intimately connected to the accumulation time. With the increasing of accumulation time, the peak current response presents a gradually increasing trend. The GR-MWCNTs-COOH/GCE sensor could show the peak current maximum value of 213.4 μ A when the accumulation time is 360s. As the accumulation time further increases, the peak current response of NA detection remained stable due to the adsorption saturation state of NA at the GR-MWCNTs-COOH/GCE sensor.

3.4.3 Influence of scanning rate

Fig. 6(a) provides the impact of scanning rate on the CV curve of 30 μ M NA. The corresponding scan rates is from 20 mVs⁻¹ to 200 mVs⁻¹ with frequency interval of 20 mVs⁻¹. It can be found that the peak current response of CV curves has a satisfactory linear relationship with the scanning rate. both cathodic peak current and anodic peak current increases gradually with the increasing of the scan rate.

Fig. 6(b) provides the corresponding regression equation. The regression equations were y=0.5024x-6.5859 (R²=0.9989) and y=-0.5157x+6.4483 (R²=0.9994), indicating the controlled adsorption process of NA detection reaction at GR-MWCNTs-COOH/GCE sensor [15-17].



Figure 6. Impact of scanning rate on the NA detection property of the GR-MWCNTs-COOH/GCE sensor: (a) CV curves of 30 μM NA and (b) relationship of peak current with scanning rate.

3.5 NA Analytical performance of GR-MWCNTs-COOH/GCE sensor



Figure 7. Impact of NA concentration on the DPV measurement at the GR-MWCNTs-COOH/GCE sensor: (a) DPV curves and (b) relationship of peak current with NA concentration. NA Concentration: 0.01, 0.05, 0.1, 0.5, 1.0, 3.0, 5.0, 7.0, 10 μ M; the inset figure in (b) is the calibration curve of peak current with NA concentration.

Fig. 7 shows the impact of NA concentration on the DPV measurement at the GR-MWCNTs-COOH/GCE sensor in PBS solution. The corresponding NA concentration is from 0.01μ M to 10μ M. The results showed that the DPV peak current have a positive correlation relationship with NA concentration. With the increasing of NA concentration, the DPV peak current presents a gradually increasing trend, which agrees with the reported works [17, 35]. Fig. 7(b) provides the relationship of peak current with NA concentration. It can be seen that the peak current displays a linear relationship with NA concentration. The corresponding regression equation is y=10.456x+0.5656 (R²=0.9992). According to the calculation results, the limit of detection of the GR-MWCNTs-COOH/GCE sensor is 3.1 nM, and the corresponding linear NA concentration is from 0.01 μ M to 10 μ M. It is important to note that the inset figure in Fig. 7(b) is the calibration curve of peak current and NA concentration, which can accurately reflect the change relationship of peak current with NA concentration. Table 1 lists the NA detection performance comparison of the developed sensor with previous reports [39-42]. As shown here, the developed GR-MWCNTs-COOH/GCE show good NA detection performance. The carboxylation of MWCNTs could promote the homogeneous dispersion of multi-walled carbon nanotubes due to the enhanced surface wettability of carboxyl groups, which helps provide larger electrochemical active surface area and more efficient electron transport channels [21, 22]. Moreover, the graphitization of MWCNTs could enhance the electrical conductivity of multi-walled carbon nanotubes, which helps provide higher electrochemical response [31, 32].

Electrode	Detection limit (nM)	Linear range (µM)	Reference
GCE	80	1-1000	[39]
GCE	20.5	0.05-1	[40]
SWCNTs/GCE	15	0.023-19	[41]
PEDOT/GCE	10.9	0.075-7.50	[42]
GR-MWCNTs-COOH/GCE	3.1	0.01-10	This work

 Table 1. Comparison of different NA electrochemical sensors.

3.6 Reproducibility and repeatability

Five GR-MWCNTs-COOH/GCE sensors were fabricated by the same technology for the NA detection. Fig. 8(a) shows the peak currents of NA in 0.1 M PBS containing 30 μ M NA detected by five different modified sensors. The relative standard deviation (RSD) value of peak current values on these five sensors was 2.01%. Fig. 8(b) shows the peak current response of NA measured on the same electrode for five consecutive measurements. It can be found that the RSD of five different measurements was 4.14%. These results showed that the fabricated GR-MWCNT-COOH/GCE sensor had good reproducibility and repeatability.



Figure 8. (a) reproducibility and (b) repeatability of the GR-MWCNT-COOH/GCE sensor.

3.7 Practical feasibility

To confirm the practicability of GR-MWCNT-COOH/GCE sensor, tap water and lake water were filtered by using a standard 0.22 μ m filter and then spiked with NA standard solutions. All samples were measured for three times. Table 2 lists the analytical result of NA. It can be found that the GR-MWCNT-COOH/GCE sensor presents satisfactory recoveries of 97.0%-102.2% and relative standard deviation (RSD) values of 2.52-4.38, which suggests the good practicability.

	-				
-	Sample	MP added	MP found	Recovery (%)	RSD
		(µM)	(µM)		(%)
Tap water Lake water	Tap water	5.00	5.04	100.8	3.11
		10.00	9.92	99.2	4.38
	I alza watan	5.00	5.11	102.2	2.52
	Lake water	10.00	9.70	97.0	3.16

Table 2. Analytical results of MP in real samples using GR-MWCNT-COOH/GCE sensor.

4. CONCLUSION

In this work, the graphitized and carboxylated MWCNTs were applied for the decoration of GCE surface to fabricate the GR-MWCNTs-COOH/GCE sensor for the NA detection. The double-functionalization could enhance the electrochemical sensing performance of the fabricated sensor towards NA. The carboxylation contributes to the uniform dispersion of MWCNTs because of the good wettability of carboxyl groups. Moreover, the graphitization of MWCNTs could enhance the electrical conductivity of multi-walled carbon nanotubes, which helps provide higher electrochemical response. Thanks to the synergistic effect of carboxylation and graphitization of MWCNTs, the GR-MWCNTs-COOH/GCE sensor showed superior NA detection property.

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