

# Preparation of an Electrochemical Sensor Based on a Nitrogen-Doped Graphene Modified Electrode and its Application for the Detection of Methyl Parathion

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We report a simple and sensitive electrochemical sensor that was successfully fabricated by using a nitrogen-doped graphene (NG)-modified glassy carbon electrode (GCE) for the electrocatalytic oxidation of methyl parathion (MP). The electrochemical behaviours of MP with the modified electrodes were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Due to its unique structure and properties, which originated from the nitrogen doping, NG showed high electrocatalytic activity towards MP in phosphate-buffered saline (PBS). The electrochemical sensor had a broad dynamic linear range and detection limit of 0.017  $\mu\text{M}$ . Under optimized conditions, the proposed sensor showed good stability and satisfactory selectivity. When applied for the detection of MP in river samples, the NG/GCE sensor demonstrated good recovery rates. This work might find promising applications in developing a new type of enzyme-free sensor.

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**Keywords:** Nitrogen-doped graphene, Electrochemical sensor, Methyl parathion, Modified electrode

## 1. INTRODUCTION

In modern agriculture, organophosphate pesticides (OPs) occupies an important position in pest control and crop yield increase [1]. Methyl parathion (MP), one kind of OPs, is widely used in agricultural production. The misuse of MP may result in food safety and environmental pollution problems [2,3]. Therefore, in view of human health and the environment, it is very necessary for human beings to find a simple assay way to identify and quantify MP in agricultural products, soil and water.

Many conventional methods have been used to analyse pesticides in the environment, such as chromatography [4,5], photometry [6,7], and mass spectrometry [8,9]. These analysis methods have the

characteristics of high sensitivity, high accuracy and high throughput. However, these analysis methods suffer from some drawbacks, including a complicated sample pretreatment process, expensive instruments, long analysis time and so on. Therefore, these methods are often unsuitable for routine analysis. An electrochemical method is an alternative and effective method due to its particular advantages, for instance, it is time saving, has high sensitivity, is inexpensive, and has a quick response and easy operation in real samples [10-13]. The detection of MP with a conventional electrode using the electrochemical method is difficult because of poor sensitivity. Recently, to achieve sensitive and selective determination of MP, many electrochemical methods have rapidly developed based on nanomaterial-modified electrodes [14-16].

As an emerging "superstar" material, graphene has attracted extensive attention in the field of electrochemical assays due to its high chemical stability and specific surface area, unique planar structure, and mechanical and electrical properties. [17-19]. The electrical properties of graphene have been improved by many strategies [20,21], such as a graphene compound with polymer [22], a graphene functionalized with metal nanoparticles [23] and a graphene modified with metal oxide deposits [24]. Recently, chemical doping techniques have emerged for the intrinsic modification of graphene to improve the electrochemical performance. Nitrogen plays a key role in chemical doping because nitrogen is approximately the same size as carbon atoms and has five available valence electrons to form strong valence bonds with carbon atoms, which leads to significant changes in the electrical properties of graphene. nitrogen-doped graphene (NG) has a strong electrocatalytic performance, a high conductivity, a large specific surface area and a large number of edge positions; therefore, it is a promising electrical material [25,26]. Recently, NG has been used for electrochemical sensors, such as assays for bisphenol A [27] and nimodipine [28]. In addition, NG can enhance the electrochemical reduction of hydrogen peroxide and accelerate the electron transfer for glucose oxidase in electrochemical sensors [29,30]. All of these results show that NG has great potential in preparing electrochemical sensing interfaces. However, we have not observed any literature on the detection of MP based on NG.

In this paper, NGs are prepared by a simple thermal treatment and are employed to modify glassy carbon electrodes to enhance the electrochemical signal of MP. Compared with a bare glassy carbon electrode and graphene oxide (GO)-modified electrode, the NG-modified electrode can greatly enhance the reduction peak of MP. In addition, the reduction peak of MP is sensitive to MP concentration, and the sensor presents a broad dynamic linear range. When it is employed to detect MP in water samples, the NG-modified electrode shows a good percentage of recoveries. According to these results, we think the NG-modified electrode is a promising strategy for an assay of MP in agricultural products, soil and water. This work will increase the range of applications of NG graphene in electrochemical sensors.

## 2. MATERIALS AND METHODS

### 2.1. Materials and Reagents

Graphite was ordered from the Qingdao Tianhe Graphite Co., Ltd., MP was purchased from the Aladdin Reagent Co., Ltd, and glycine was ordered from Sigma. Phosphate-buffered saline (PBS, 0.1

M) solutions were prepared by mixing NaOH, Na<sub>2</sub>HPO<sub>4</sub>, and NaH<sub>2</sub>PO<sub>4</sub>. PBS with various pH values was prepared by titrating 0.1 M H<sub>3</sub>PO<sub>4</sub> or 0.1 M NaOH. All other reagents were of analytical reagent grade and used without further purification. Water used throughout all experiments was purified with the Millipore system (18.2 MΩ cm).

## 2.2. Apparatus

The surface features of NG were characterized by scanning electron microscopy (SEM, PHILIPSEXL-30ESEM) at an accelerating voltage of 15 kV. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out on a CHI660C electrochemical workstation (Chenhua Instruments, Shanghai, China). A bare or modified glassy carbon electrode (GCE, 3-mm diameter) was the working electrode, a platinum wire was the auxiliary electrode, and a saturated calomel electrode was the reference electrode employed in the electrochemical system.

A gas chromatograph (Shimadzu 7AG, Japan) was used for quantitative determination of the methyl parathion. An ultrasonic cleaner (KQ 100E, 100 W, Kunshan, China) was employed to exfoliate the GO. All the pH values of PBS were measured with a PHS-3C precision pH metre (Leici Devices Factory of Shanghai, China).

## 2.3. Preparation of the NG

GO was synthesized from graphite by an improved Hummers method. GO was mixed with glycine at a mass ratio of 1:8 (GO:glycine) in water. Before being poured into an alumina crucible, the mixture was sonicated for two hours. Under an argon atmosphere, the temperature of the mixture gradually increased from room temperature to 500 °C and was kept for 2 h. Last, the final product was directly collected from the alumina crucible.

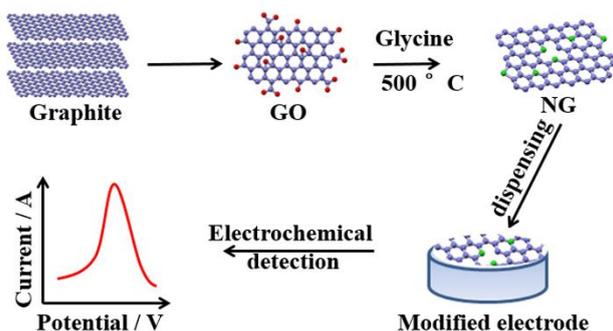
## 2.4. Preparation of NG modified electrode

Prior to the experiments, bare glass carbon electrodes (GCE, 3-mm diameter) were carefully polished on a mirror-shine surface with a polishing cloth with 1.0-, 0.3- and 0.05-μm alumina powder. Next, the electrodes were successively sonicated in distilled water, absolute ethanol and doubly deionized water for 5 min in each solution and then dried gently by N<sub>2</sub> streaming. After that, the prepared bare electrode was coated with 6 μL NG and dried in the air at room temperature to obtain a NG/GCE. For comparison, a GO/GCE was prepared by coating with 6 μL GO and drying in air at room temperature. Then, the NG/GCE was used for the electrochemical analysis of MP (scheme 1). All experiments were performed at room temperature.

## 2.5. Electrochemical measurements

CV and DPV were performed at room temperature. A certain amount of MP and 3 mL electrolytic buffer were added into a glass cell. The solution was aerated with nitrogen for 8 min. Then, a three-

electrode system was used to assay MP. CV was used to investigate the electrochemical behaviour of the NG/GCE towards MP. DPV experiments (with a step increment of 4 mV, pulse amplitude of 50 mV, and pulse period of 0.2 s) were employed to reach the quantitative assay.

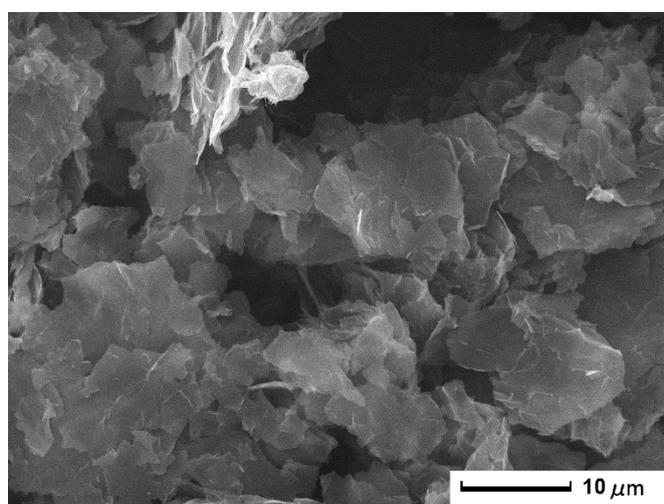


**Scheme 1.** Schematic drawing for preparing the NG/GCE and detecting MP.

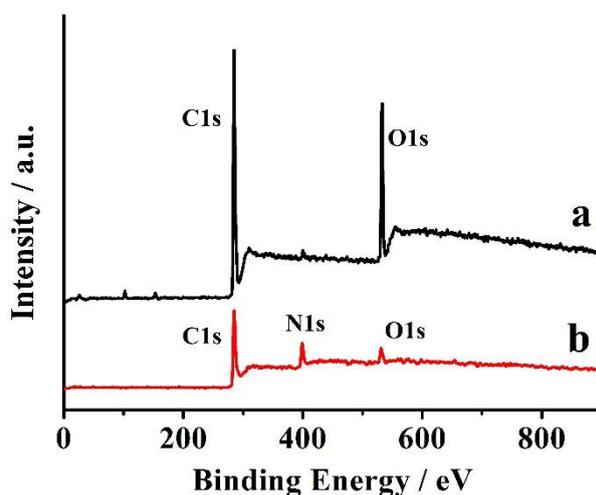
### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of NG

The morphology of NG was investigated by scanning electron microscopy, as shown in Figure 1. The synthesized NG sheets showed a characteristically crumpled and overlapped multilayer surface structure. This morphology is consistent with the results of the literature on graphene [31]. The crumpled structure section benefits from the  $\pi$ - $\pi$  interactions within the sheets of graphene. This crumpled nature enhances the surface area on the electrode and enhances the performance of electron transfer.



**Figure 1.** Scanning electron microscopy images of NG



**Figure 2.** X-ray photoelectron spectra of GO (a) and NG (b).

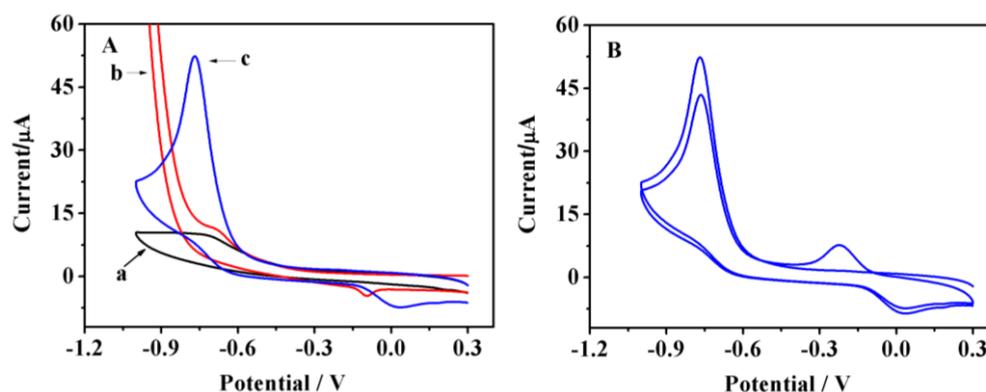
As a surface-sensitive quantitative spectroscopic technique, X-ray photoelectron spectroscopy (XPS) is usually employed to characterize the elemental composition of a 5-10-nm thick surface layer. The chemical composition of NG and GO was investigated by XPS, as shown in Figure 2a. There were two obvious peaks in the curve of GO, which were located at 287 and 535 eV and corresponded to C1s and O1s, respectively. However, there were three obvious peaks in the curve of NG (Figure 2b), which were located at 286, 403, and 533 eV and corresponded to C1s, N1s, and O1s, respectively. The presence of the N peak confirmed that the nitrogen was doped into the graphene. Moreover, the ratio of the peak of C1s and O1s in GO was higher than that of NG. This result is because oxygen functional groups in the NG were removed from the GO.

### 3.2. Voltammetric behavior of MP

The electrocatalytic behaviour of the NG towards the MP is examined in this section. The CV was performed with different electrodes in the potential range of -1.0 to 0.3 V. When  $8.0 \times 10^{-4}$  mol/L MP was added into PBS (pH 7), weak reduction peaks were observed at -0.72 V on a bare GCE (curve a in Figure 3A) and at -0.71 V on a GO-modified GCE (curve b in Figure 3A). The CV of MP on a NG-modified electrode showed a remarkable reduction peak at -0.73 V (curve c in Figure 3A). Compared with the bare GCE or GO/GCE, the peak current obtained on the NG-modified GCE was much larger, which demonstrated the excellent electrocatalytic activity of NG towards MP.

We used cyclic voltammetry to scan MP for 2 cycles (Figure 3B). The initial potential was 0.3 V, and the termination potential was 1.0 V. In the reduction process of the first cycle, there was a remarkable reduction peak at -0.73 V, which was attributed to  $\text{NO}_2\text{-MP}$  being reduced to  $\text{NHOH-MP}$ . In the oxidation process of the first cycle, an oxidation peak was observed at -0.03 V, which was attributed to  $\text{NHOH-MP}$  being oxidized to  $\text{NO-MP}$ . During the second cycle, there was a reduction

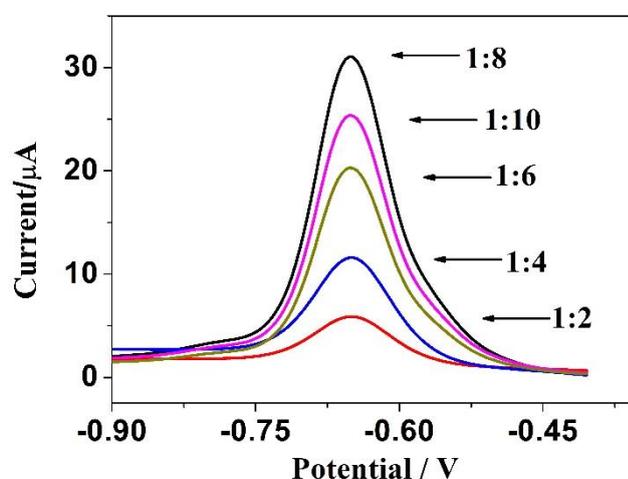
peak at -0.21 V, which was attributed to NO-MP being reduced to NHOH-MP. The electrocatalytic behaviour of MP on a NG-modified GCE is in agreement with previous reports [32-34].



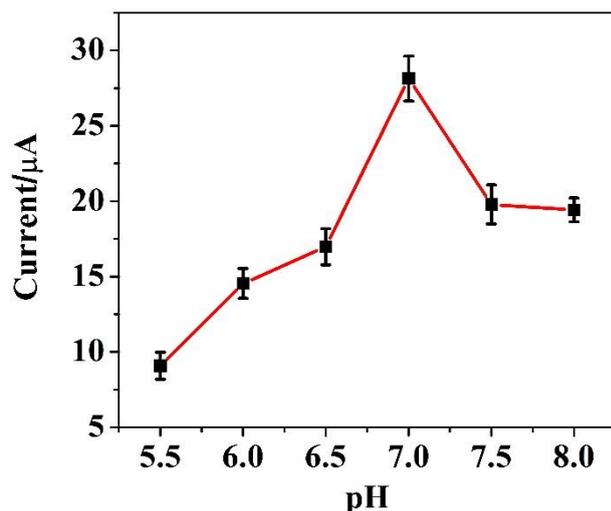
**Figure 3.** (A) Cyclic voltammety responses of the bare GCE, GO/GCE, and NG/GCE in 0.2 M PBS (pH 7.0) containing  $8.0 \times 10^{-4}$  mol/L MP. (B) Cyclic voltammety responses of NG/GCE in 0.2 M PBS (pH 7.0) containing  $8.0 \times 10^{-4}$  mol/L MP for 2 cycles.

### 3.3. Optimization of experimental conditions

The composition content of NG had an important influence on sensitivity enhancement. Here, serials of NG with different volume ratios of GO to glycine (1:2, 1:4, 1:6, 1:8 and 1:10) were prepared to modify a GCE and to detect MP. As shown in Figure 4, the DPV peak current increased with an increasing GO to glycine ratio from 1:2 to 1:8, which indicated that an increased amount of nitrogen can enhance the catalytic ability. When the GO to glycine ratio was higher than 1:8, the peak of the MP decreased due to excessive nitrogen doping affecting the catalytic performance of the NG-modified electrode. Therefore, a GO to glycine ratio of 1:8 was chosen as the optimum ratio.

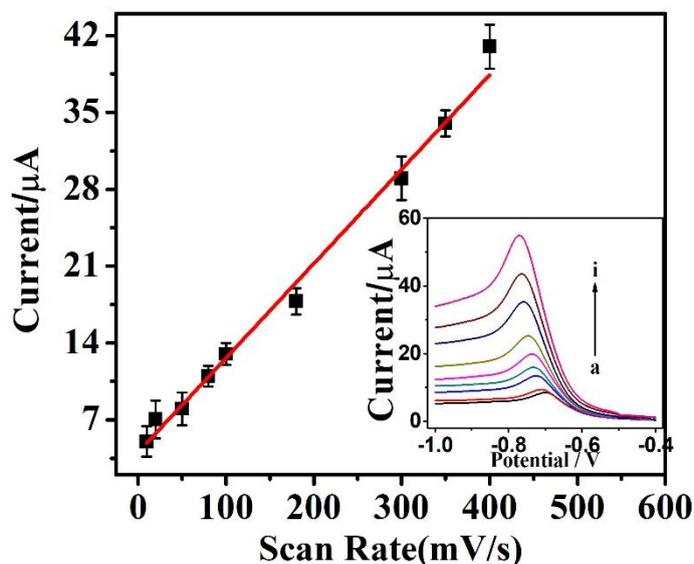


**Figure 4.** Comparison of the DPV peak current for MP ( $2.0 \times 10^{-4}$  mol/L) with NG/GCE based on different ratios of GO to glycine (1:2, 1:4, 1:6, 1:8 and 1:10).



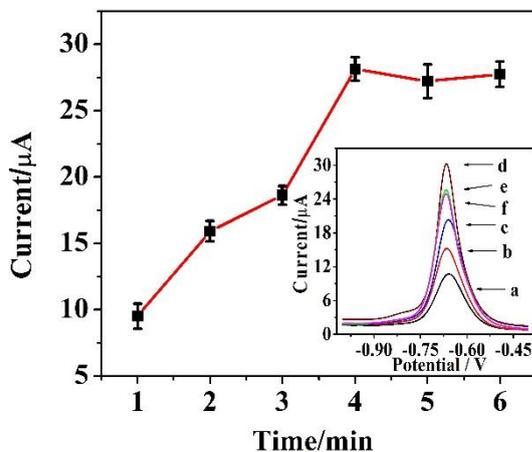
**Figure 5.** Effects of pH values on DPV responses of a NG/GCE with the presence of  $2.0 \times 10^{-4}$  mol/L MP in 0.2 M PBS

The pH value of the detected solution plays an important role in the electrochemical method. To optimize the electrocatalytic response of a NG/GCE towards MP, the effect of pH values on the NG/GCE was investigated by using a DPV technique from 5.5 to 8.0. Figure 5 shows that the peak current increases with an increasing solution pH from 5.5 to 7.0, and then the peak decreases. This result is because MP is unstable in an alkaline solution. Therefore, 0.2 M PBS with pH 7.0 was chosen as the buffer in all experiments.



**Figure 6.** Effects of the scan rate on the current responses of a NG/GCE with the presence of  $8.0 \times 10^{-5}$  mol/L MP in 0.2 M PBS (pH 7). Inset: corresponding LSV curves (a: 10 mV/s, b: 20 mV/s, c: 50 mV/s, d: 80 mV/s, e: 100 mV/s, f: 180 mV/s, g: 300 mV/s, h: 350 mV/s, and i: 400 mV/s).

The effect of the different scan rates on the peak current of MP with linear sweep voltammetry has been studied from 10 to 400  $\text{mV s}^{-1}$ . In Figure 6, the peak currents of MP shift positively while increasing the scan rate. Plots of currents against the scan rate show a linear relationship over the range above with a regression equation:  $I (\mu\text{A}) = 4.035 + 0.087 v$  ( $v$ , millivolts per second,  $R^2=0.99081$ ). We believe that the reduction reaction of MP is surface-controlled.

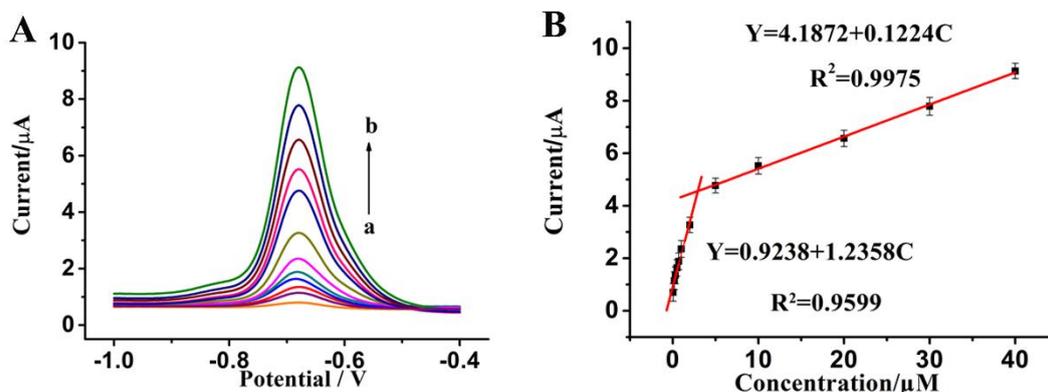


**Figure 7.** Effects of the accumulation time on the current responses of a NG/GCE with the presence of  $2.0 \times 10^{-4}$  mol/L MP in 0.2 M PBS (pH 7). Inset: corresponding DPV curves (a: 60 s, b: 120 s, c: 180 s, d: 240 s, e: 300 s and f: 360 s).

Accumulation time is an important factor that may affect the adsorption of MP on the electrode surface. The effect of accumulation time (in the range of 60–360 s) on the peak current responses of MP was studied with a NG/GCE. In Figure 7, the peak current obviously increases while extending the accumulation time up to 240 s. As the accumulation time increases, the peak current increases little and tends to be stable after 240 s. This outcome may be attributed to the saturation adsorption of MP on the NG/GCE. Consequently, the optimal accumulation time of 240 s was employed in further experiments.

### 3.4. Analytical performance to MP

Differential pulse voltammograms at different concentrations of MP were recorded using their maximum signal conditions. Calibration plots for MP are shown in Figure 8. The amperometric NG/GCE sensor had a broad dynamic linear range. At low concentration conditions, the linear relationship between the peak current and the concentration of MP was obtained over a concentration range from 0.05–2.0  $\mu\text{M}$ . The linear regression equation was  $I (\mu\text{A}) = 0.9238 + 1.2358C$ , ( $R^2 = 0.9599$ ). At high concentration conditions, the linear relationship between the peak current and the concentration of MP was obtained over a concentration range from 5.0–40  $\mu\text{M}$ . The linear regression equation was  $I (\mu\text{A}) = 4.1872 + 0.1224C$ , ( $R^2 = 0.9599$ ).



**Figure 8.** (A) Differential pulse voltammetry responses of a GN/GCE in 0.2 M PBS with different concentrations of MP: 0.05, 0.2, 0.3, 0.5, 0.7, 1, 2, 5, 10, 20, 30 and 40  $\mu\text{M}$  (from a to b). (B) Linear relationship between the peak current ( $n=10$ ) and concentrations of MP.

**Table 1.** Comparison of the proposed method with other reported methods of MP determination

Type of electrodes	Technique	LOD ( $\text{mol L}^{-1}$ )	Linear range ( $\text{mol L}^{-1}$ )	References
lipase@ZIF-8/Chit/GCE	DPV	$2.8 \times 10^{-7}$	$1.0 \times 10^{-7}$ – $4.0 \times 10^{-5}$	[14]
OPH-bacteria/OMCs/GCE	DPV	$1.5 \times 10^{-8}$	$8.0 \times 10^{-8}$ – $3.0 \times 10^{-5}$	[15]
Lipase mobilized CPE	DPV	$2.6 \times 10^{-5}$	$1.0 \times 10^{-5}$ – $7.0 \times 10^{-5}$	[16]
CPME -AB	DPV	$3.9 \times 10^{-8}$	$1.0 \times 10^{-7}$ – $7 \times 10^{-5}$	[35]
NiO-SPE	DPV	$2.4 \times 10^{-8}$	$1.0 \times 10^{-7}$ – $3.0 \times 10^{-5}$	[36]
Silver/nafion coated GCE	DPV	$8.7 \times 10^{-8}$	$3.0 \times 10^{-7}$ – $1.4 \times 10^{-6}$	[37]
TiO <sub>2</sub> @DA@S/H/E nanoenzyme modified electrodes	SWV	$2.4 \times 10^{-7}$	$5.0 \times 10^{-7}$ – $1.0 \times 10^{-4}$	[38]
BCL@MOF nanofibers/chitosan/GCE	DPV	$6.7 \times 10^{-8}$	$1.0 \times 10^{-7}$ – $3.8 \times 10^{-5}$	[39]
HAuNPs/rGO/GCE	SWV	$1.2 \times 10^{-7}$	$3.0 \times 10^{-7}$ – $1.0 \times 10^{-5}$	[40]
CuNPs@GR-MIPs	DPV	$2.4 \times 10^{-8}$	$5.0 \times 10^{-7}$ – $5.0 \times 10^{-3}$	[41]
AchE/ERGO/Nf/GCE	SWV	$1.0 \times 10^{-9}$	$2.0 \times 10^{-9}$ – $7.0 \times 10^{-7}$	[42]
Au NS-AChE/GCE	CV	$1.2 \times 10^{-10}$	$5.0 \times 10^{-10}$ – $2.5 \times 10^{-8}$ $2.5 \times 10^{-8}$ – $3.0 \times 10^{-7}$	[43]
NG/GCE	DPV	$1.7 \times 10^{-8}$	$5.0 \times 10^{-8}$ – $4 \times 10^{-5}$	This work

Abbreviations:

CPME –AB: carbon paste modified electrode with activated biochar

NiO-SPE: NiO-SPE: nickel oxide nanoplatelets (NPs) modified screen-printed electrode

Silver/nafion coated GCE: anosilver/nafion composite electrode

TiO<sub>2</sub>@DA@S/H/E nanoenzyme modified electrodes: amino acids serine (S), histamine (H) and glutamic acid (E) conjugated titanium dioxide nanoparticle modified electrode

BCL@MOF nanofibers/chitosan/GCE: Burkholderia cepacia lipase@ metal organic framework nanofibers and chitosan modified electrode

SWV: square wave voltammetry

HAuNPs/rGO/GCE: hollow gold nanoparticles and reduced GO modified glassy carbon electrode

CuNPs@GR-MIPs: Molecular imprinted polymers on copper nanoparticle–decorated vinyl-functionalized graphene

AchE/ERGO/Nf/GCE: acetyl cholinesterase (AChE) immobilized on reduced GO (ERGO)-Nafion (Nf) modified glassy carbon electrode

Au NS-AChE/GCE: acetylcholinesterase immobilized gold nanosphere (Au NS) modified glassy carbon electrode

When the MP concentration was low, MP was reduced by the catalytic action of graphene, and the local concentration on the electrode surface was exhausted rapidly, which resulted in a high response sensitivity of the electrode. When the MP concentration was high, the reaction time between the nanomaterial and MP was long, and the reaction time window was large. In addition, reaction products may have contaminated the electrode surface, resulting in a lower slope. The surface was saturated at high concentrations. Therefore, the sensor showed different linear correlations in different concentration ranges [44,45].

A comparison of the performance of electrochemical sensors for detecting MP is shown in Table 1. Various kinds of sensors were used for detecting MP based on activated biochar, nickel oxide nanoplatelets, nanoenzymes, lipase, and mesoporous carbon. The detection limit of our sensor was lower than that of sensors based on activated biochar, nickel oxide nanoplatelets, nanoenzymes, lipase, mesoporous carbon, and lower than that of sensors based on graphene composited from other nanoparticles [40,41]. Compared with sensors based on enzymes [42,43], the detection limit of this sensor was higher. However, the preparation process of our modified nanomaterials is simpler, and this sensor does not use biological enzymes that are prone to inactivation. Therefore, the performance of this sensor is comparable to previous sensors.

The determination of MP in samples could be influenced by the coexisting interfering agents. Therefore, under optimal experimental conditions, we investigated several possible interferents, including  $\text{Zn}^{2+}$ ,  $\text{NO}_3^-$ , carbendazim and carbaryl. An obvious current response was observed with the addition of  $5.0 \times 10^{-7}$  mol/L MP, whereas the response current remained almost the same after the addition of  $5.0 \times 10^{-6}$  mol/L of various interfering agents. This result suggests that those interferents did not affect the reduction of MP at the NG/GCE. This interference-free behaviour indicates that a NG/GCE has high selectivity, which could be applied successfully to the determination of MP samples.

To investigate the reproducibility of the inter-electrode, eight sensors were prepared under identical conditions and then used to detect the peak current of MP. The relative standard deviation (RSD) of response for the eight sensors to detect  $5.0 \times 10^{-7}$  mol/L MP was 5.21%. In addition, eight measurements of  $5.0 \times 10^{-7}$  mol/L MP using the same NG/GCE yielded an RSD of 4.92%. These results reveal acceptable reproducibility. When the sensor was not in use, it was stored in air at ambient temperature and tested every day. No obvious current decrease in MP was observed after two weeks of storage. It kept 90% of its initial current after a month. This implied that the proposed sensor possessed good stability.

### 3.5. Sample analysis

To evaluate the application performance of this proposed sensor, a NG-modified glassy carbon electrode was utilized to detect the concentration of MP. Different concentrations of MP were added to the river samples and then detected 3 times in parallel under the optimal experimental conditions. The results are shown in Table 2. The RSD of these methods was less than 4.25%. The recovery range for this sensor was 97.56 –103.15%. As a comparison, gas chromatography (GC) was used to detect the river samples as well. We found that the results obtained by this sensor agreed with those of GC. Through

this experiment, we believe that the developed approach has excellent accuracy as well as GC in these river water sample analyses. The results demonstrate that the practical applicability of this sensor for the determination of MP is satisfactory.

**Table 2.** Results of MP in river samples by GC and this sensor

Sample	Added ( $\mu\text{g}$ )	GC method		This sensor	
		Found ( $\mu\text{g}$ )	Found ( $\mu\text{g}$ )	RSD (%)	Recovery (%)
1	25.00	24.98	24.39	4.25	97.56
2	40.00	40.90	41.26	3.76	103.15
3	50.00	49.86	49.32	3.92	98.64

#### 4. CONCLUSIONS

In this paper, NG-modified glassy carbon electrodes were successfully developed for sensitive electrochemical determination of MP by voltammetry. The sensor exhibited superior sensitivity, selectivity and stability. The unique advantage of sensitivity was provided by the catalytic performance of the NG. Moreover, recovery measurements of MP in river samples showed that the sensor had practical application value. Due to its simple structure, convenient operation and excellent sensing feature, the proposed sensor fabricated using nanomaterial-modified glassy carbon electrodes can pave a promising way for the facile and sensitive analysis of organophosphorus pesticides.

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