



# Innovative approach for the electrochemical detection of non-electroactive organophosphorus pesticides using oxime as electroactive probe



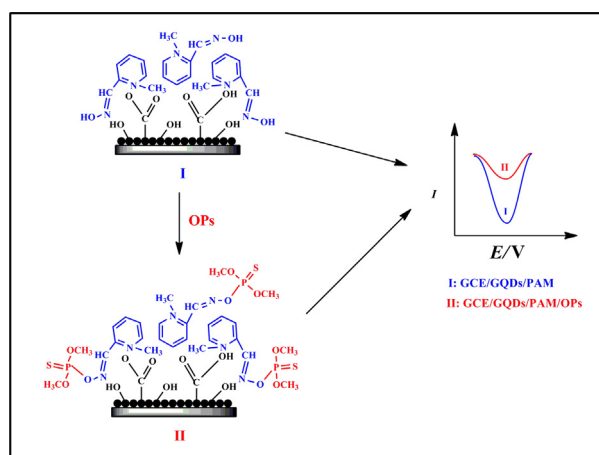
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## HIGHLIGHTS

- Novel approach for electrochemical detection of non-electroactive OPs was proposed.
- PAM was used as electroactive probe for the first time.
- The detection system displayed high sensitivity and promptness.
- The developed sensor was used in real samples with satisfactory results.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 19 September 2014

Received in revised form 13 May 2015

Accepted 14 May 2015

Available online 3 June 2015

### Keywords:

Electrochemical detection

Pralidoxime

Organophosphorus pesticides

Electroactive probe

## ABSTRACT

An innovative approach for sensitive and simple electrochemical detection of non-electroactive organophosphorus pesticides (OPs) was described in this report. The novel strategy emphasized the fabrication of an oxime-based sensor via attaching pralidoxime (PAM) on graphene quantum dots (GQDs) modified glassy carbon electrode. The introduction of GQDs significantly increased the effective electrode area, and then enlarged the immobilization quantity of PAM. Thus, the oxidation current of PAM was obviously increased. Relying on the nucleophilic substitution reaction between oxime and OPs, fenthion was detected using PAM as the electroactive probe. Under optimum conditions, the difference of oxidation current of PAM was proportional to fenthion concentration over the range from  $1.0 \times 10^{-11}$  M to  $5.0 \times 10^{-7}$  M with a detection limit of  $6.8 \times 10^{-12}$  M ( $S/N=3$ ). Moreover, the favorable detection performance in water and soil samples heralded the promising applications in on-site OPs detection.

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## 1. Introduction

Organophosphate pesticides (OPs) are the most widely used pesticides in agriculture due to their high effectiveness for insect eradication and relatively low persistence under natural

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**Table 1**  
Recovery studies of fenthion in spiked river water and soil samples ( $n=3$ ).

Sample	Taken (nM)	Found (nM)	Recovery (%)	RSD (%)
River water	0.10	0.0946	94.6	4.7
	1.00	1.034	103.4	3.9
	10.00	10.53	105.3	4.2
Soil samples	0.10	0.102	102.0	5.6
	1.00	0.954	95.4	3.3
	10.00	10.48	104.8	4.5

conditions [1]. However, because of the ability of irreversible inhibition of acetylcholinesterase (AChE) and bioaccumulation effects in human body, OPs exhibit acute toxicity to human health through their residues in agricultural products and contaminated water [2]. Therefore, accurate and sensitive detection methods are in urgent demand for the screening of OPs residues. Conventional analytical methods for OPs detection such as gas chromatography, mass spectrometry, liquid chromatography coupled with mass spectrometry (LC/MS) or gas chromatography (GC/MS) [3–5] are still considered to be the most reliable techniques owing to their high selectivity and adequate sensitivity. However, these laboratory-based chromatographic analytical techniques are under-determined by their disadvantages of time-consuming, complicated sample pretreatment, requirements for sophisticated instrument and skilled professional, which limits their applications for on-site detection in most settings, especially in emergency cases. As a result, portable sensors that can be applied for on-site rapid detection are of great practical interest.

In the past few decades, electrochemical methods were emerged as the most promising alternative technique for on-site detection of OPs due to their inherent virtues such as low cost, miniaturization and automation, simple preparation and high sensitivity [6]. Enzyme/antibody-based electrochemical biosensors have been found extensive used in OPs detection. Although high sensitivity and specificity can be achieved, the poor chemical/physical stability of the enzymes and antibodies prevents their use in harsh environments of acids, bases or organic solvents, and high temperature [7]. To meet the requirements of rapid warning and field deployment, much attention has been given to direct electrochemical sensing of OPs in recent years. In general, these analyses utilize the electrochemical redox of analyte as detection signals, which is only suitable for sensing of OPs with inherent redox activity such as methyl parathion, paraoxon and fenitrothion [8,9]. How can other OPs without electrochemical redox activity be detected using similar methods? It is still a great challenge for numerous researchers.

Some approaches for OPs assay based on oxime compounds have aroused much interest recently. Oximes, such as pralidoxime (PAM), have been utilized as effective antidotes for OP compounds. As a kind of super nucleophile, oxime can reversibly bind to OP-inactivated AChE then attach to the free OPs, efficiently reversing and preventing other irreversible binding of OPs to AChE [6]. Taking advantage of the good reactivity between oximes and OPs, several oxime-based sensors have been developed by means of colorimetric [10], fluorescent [11], and chemiluminescent [12] methods. Surprisingly, little attention has been given to oxime-based electrochemical assays, despite of the simplicity, promptness and compact nature of electrochemical instrument. Herein, we proposed a novel strategy for non-electroactive OPs sensing relying on the nucleophilic substitution reaction between oxime and OPs. The strategy involved constructing a graphene quantum dots (GQDs) modified glassy carbon electrode (GCE) and

attaching PAM, a common used antidotes for OPs, on GQDs via electrostatic attraction and  $\pi$ - $\pi$  stacking interaction. Using the electrochemical oxidation of PAM as detection signal, fenthion, a chosen model of non-electroactive organophosphorus, was quantified through measuring the change in oxidation current of PAM before and after reaction with target analyte. It is anticipated that this novel method will open new opportunities for fast, simple, and sensitive analysis of OPs in environmental and biological samples.

## 2. Experimental

### 2.1. Reagents and apparatus

Fenthion (*O,O*-dimethyl-*O*-(4-methylthio-*m*-tolyl)phosphorothioate) was purchased from Sigma-Aldrich (USA), and its stock solution was prepared in anhydrous ethanol. Graphite powder, chitosan and pralidoxime iodide (pyridine-2-aldoxime methoiodide, PAM) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Phosphate buffer solution (PBS) was prepared by mixing stock solutions of 0.1 M  $\text{NaH}_2\text{PO}_4$  and 0.1 M  $\text{Na}_2\text{HPO}_4$  and adjusting the pH with 0.1 M NaOH or 0.1 M HCl. All chemicals were of analytical reagent grade and all the aqueous solutions were prepared with redistilled water.

Electrochemical experiments were performed with a CHI660C electrochemical workstation (Shanghai Chenhua Co., China). A conventional three-electrode system was used, comprising a bare or modified GCE as working electrode, a platinum wire as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. All electrochemical measurements were performed at room temperature ( $25 \pm 2^\circ\text{C}$ ). The transmission electron microscopy (TEM) observations were obtained using the JEOL-1200EX TEM (Japan). X-rays photoelectron spectroscopy (XPS) was performed with a VG ESCALAB 250 spectrometer using a non-monochromatized Al K $\alpha$  X-ray source.

### 2.2. Preparation of graphene quantum dots

Graphene quantum dots (GQDs) were synthesized according to the following steps [13]. Firstly, graphene oxide (GO) was synthesized from natural graphite powder by a modified Hummer's method [14] (detailed in Supplementary data). The synthesized GO was dispersed in water to obtain a yellow-brown aqueous solution with the aid of ultrasonication. Subsequently, GO solution (30 mL, 0.5 mg/mL) was mixed carefully with concentrated  $\text{HNO}_3$  (8 mL) and  $\text{H}_2\text{SO}_4$  (2 mL). Then the mixture was heated and refluxed under microwave irradiation for 2 h in a microwave oven operating at a power of 240 W. After cooling to room temperature, the mixture was kept under mild ultrasonication for a few minutes, and the pH was tuned to 8 with NaOH in an ice-bath. The suspension was filtered through a 0.22  $\mu\text{m}$  microporous membrane to remove the large tracts of GO and a deep yellow solution was separated. At last, the mixture solution was dialyzed in a dialysis bag (retained molecular weight: 8000–10,000 Da) and dried for further use.

### 2.3. Preparation of the modified electrode

A schematic graph of the fabrication process is shown in Scheme 1. Prior to modification, the bare GCE was polished to a mirror-like surface with 0.3 and 0.05  $\mu\text{m}$  alumina slurry on micro-cloth pads and then thoroughly cleaned before use. Graphene quantum dots (GQDs) were synthesized according to Li's method with some modification [13]. Subsequently, 5  $\mu\text{L}$  of GQDs suspension (2.0 mg/mL in 0.05% (w/v) chitosan solution) was

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