



# Differential pulse voltammetric determination of methyl parathion based on multiwalled carbon nanotubes–poly(acrylamide) nanocomposite film modified electrode

Yanbo Zeng<sup>a,b</sup>, Dajun Yu<sup>a</sup>, Yanyan Yu<sup>a</sup>, Tianshu Zhou<sup>c</sup>, Guoyue Shi<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry and Shanghai Key Laboratory of Green Chemistry and Chemical Process, East China Normal University, 3663 Zhongshan Road(N), Shanghai, 200062, PR China

<sup>b</sup> College of Biological, Chemical Sciences and Engineering, Jiaying University, Jiaying 314001, PR China

<sup>c</sup> Department of Environmental Science, East China Normal University, 3663 Zhongshan Road(N), Shanghai, 200062, PR China

## ARTICLE INFO

### Article history:

Received 21 December 2011

Received in revised form 16 February 2012

Accepted 10 March 2012

Available online 20 March 2012

### Keywords:

Multiwalled carbon nanotubes–poly(acrylamide) nanocomposite  
Organophosphorus pesticides  
Methyl parathion  
Differential pulse voltammetry  
Electrochemical sensor  
Environmental water samples

## ABSTRACT

A sensitive electrochemical differential pulse voltammetry method was developed for detecting methyl parathion based on multiwalled carbon nanotubes–poly(acrylamide) (MWCNTs–PAAM) nanocomposite film modified glassy carbon electrode. The novel MWCNTs–PAAM nanocomposite, containing high content of amide groups, was synthesized by PAAM polymerizing at the vinyl group functionalized MWCNTs surface using free radical polymerization. The MWCNTs–PAAM nanocomposite was characterized by Fourier transform infrared spectroscopy, thermal gravimetric analysis and scanning electron microscopy. Electrochemical behavior and interference studies of MWCNTs–PAAM/GCE for methyl parathion were investigated. The experimental results demonstrated that the MWCNTs–PAAM/GCE exhibited a high adsorption and strong affinity toward methyl parathion compared with some metal ions and nitroaromatic compounds, which exist in environmental samples. The adsorbed amount of methyl parathion on the MWCNTs–PAAM/GCE approached the equilibrium value upon 5 min adsorption time. A linear calibration curve for methyl parathion was obtained in the concentration range from  $5.0 \times 10^{-9}$  to  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>, with a detection limit of  $2.0 \times 10^{-9}$  mol L<sup>-1</sup>. The MWCNTs–PAAM/GCE was proved to be a suitable sensing tool for the fast, sensitive and selective determination of methyl parathion in environmental water samples.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Organophosphorus (OP) pesticides have been widely used to protect agricultural crop against damaging caused by insect pests. During and after their application in agriculture, OP pesticides are transported by wind or water to environment as only a part of the applied amounts is bioactive [1,2]. This transport results in hazardous concentrations of pesticides and their metabolites in the surface water and soils, owing to their low solubility and bioaccumulation properties [3]. Thus, extensive usage of OP compounds with high toxicity has raised serious public concern regarding a great harm to humans and the environment [4]. Their toxicity depends on inhibiting the activity of enzymes controlling the functions of the nervous system, mainly acetylcholinesterase, which results in accumulation of acetylcholine at nerve endings. Excess acetylcholine at synaptic junctions in neurons causes fasciculation

and disrupts normal neural transmission, which leads to a state of hyperarousal, and paralysis of the muscles and the main respiratory center [5]. Therefore, for the sake of human health and environmental pollution control, it is vital to develop a fast, simple, and sensitive method for analysis of OP pesticides in environmental samples.

Many analytical techniques, including capillary electrophoresis [6], gas or liquid chromatography [7–9] and electrochemical method [10,11], have been applied to develop sensitive, convenient and effective methods for OP pesticides residue analysis. Chromatography techniques operate with high sensitivity, accuracy and high throughput, instrumental analysis, but they suffer from complicated pretreatment steps using toxic organic solvent and also long analysis time, and most of them require expensive equipment [12]. Electrochemical method possesses high sensitivity, good selectivity and low-cost instrumentation. Electroanalysis can be used to give appropriate results within a short time under field conditions or on-line monitoring, which is very fit to analyze OP pesticides concentration in environmental samples.

Among the electrochemical methods, enzyme-based electrochemical biosensors have developed in the past few years to

\* Corresponding author. Tel.: +86 21 62237105; fax: +86 21 62237105.  
E-mail address: [gyshi@chem.ecnu.edu.cn](mailto:gyshi@chem.ecnu.edu.cn) (G. Shi).

monitor OP pesticides [13–17]. However, the denaturation of enzymes results in the instability and short lifetime of use for the sensor, which mostly limits the operational applications. In addition, the enzyme can be inhibited by many kinds of contamination such as heavy metals in environmental samples, which makes the direct determination of OP pesticides lack of selectivity and even leads to false positive result [18]. Therefore, in order to eliminate the influence of enzyme on the analysis of OP pesticides in environmental samples, some more effective methods were proposed to directly detect OP pesticides without using enzymes. Recently, electrochemical sensors based materials with no enzymes have been used in the fabrication of OP pesticides electrochemical sensors [10,11,19–29], such as  $ZrO_2$  nanoparticles [10], nanometer-sized titania [11], Pd/MWCNTs nanocomposite [19], and pSC6 modified silver [23].  $ZrO_2$ -nanoparticles modified electrode was fabricated for the detection of OP pesticides based on a strong affinity between nano- $ZrO_2$  and OP pesticides molecules [10,21,22,24]. Hu and co-workers developed a novel and simple sensor for dichlofenthion based on nanometer-sized titania photocatalysis coupled with a screen-printed carbon electrode [11]. Pd/MWCNTs nanocomposite modified electrode was developed for the determination of methyl parathion [19]. Li and co-workers presented pSC6 modified silver nanoparticles electrochemically deposited on glassy carbon electrode for electrochemical detection of methyl parathion [23].

Multiwalled carbon nanotubes (MWCNTs) as nanomaterial have attracted great attention for their unique structural, mechanical, and electrical properties since their discovery [30]. In order to introduce functional groups on MWCNTs and broaden the application fields of MWCNTs, composite materials based on the desirable merging of MWCNTs and polymers have gained growing interest [31,32]. Recent electrochemical studies reveal that the nanocomposite of MWCNTs and polymers are very promising in the design of electrochemical sensors and biosensors [31–36]. For example, MWCNTs and poly(methacrylic acid) (PMAA) nanocomposites prepared by free radical polymerization has been used for the detection of uric acid [32]. MWCNTs and polyaniline nanocomposites achieved by electrochemical grafting have been used for the determination of pesticides [33] and glucose [36]. In this work, a sensitive electrochemical differential pulse voltammetry method was developed for detecting methyl parathion (MP) based on MWCNTs–PAAM nanocomposite film modified glassy carbon electrode. The novel MWCNTs–PAAM nanocomposite, containing high content of amide groups, was synthesized by PAAM polymerizing at the vinyl group functionalized MWCNTs surface using free radical polymerization. The amino functionalized material exhibited good adsorption for OP pesticides molecules [37]. Similarly, the MWCNTs–PAAM/GCE showed a high adsorption and strong affinity toward MP compared with some metal ions and nitroaromatic compounds, which exist in environmental samples. The detection of MP for MWCNTs–PAAM/GCE was performed rapidly with wide linear range ( $5.0 \times 10^{-9}$ – $1.0 \times 10^{-5}$  mol L<sup>-1</sup>) and low detection limit of  $2 \times 10^{-9}$  mol L<sup>-1</sup> (S/N=3), which was better than some traditional materials modified electrode [1,10,19,20,23,25–29]. These merits made it suitable for MP determination in environmental water samples.

## 2. Experimental

### 2.1. Reagents

MWCNTs–COOH were obtained from Shenzhen Nanotech. Co., Ltd. (Shenzhen, China). Acrylamide (AAM), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), 1,3-dinitrobenzene (DNB) and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma–Aldrich Chemical Co. (USA). Methyl parathion (MP)

was obtained from Dr. Ehrenstorfer GmbH Co. (Germany). 3-Aminopropyltriethoxysilane (APTES) and vinyltriethoxysilane (VTEOS) were purchased from TCI Co., Ltd. (Japan). Azodiisobutyronitrile (AIBN) was purchased from Sinopharm Group Chemical Regent Co., Ltd. (Shanghai, China). Other chemicals used were of analytical grade, and purchased from Sinopharm Group Chemical Regent Co., Ltd. (Shanghai, China). All compounds were used without further purification. The stock solution ( $0.001$  mol L<sup>-1</sup> MP) was prepared in ethanol and stored at 4 °C. Phosphate buffer solution (PBS, 0.2 M, pH 7.0) was prepared with  $NaH_2PO_4$  and  $Na_2HPO_4$ . Double distilled water was used throughout.

### 2.2. Apparatus

Electrochemical measurements were performed on a CHI 660c electrochemical workstation (CH Instruments Co., Shanghai, China) with a conventional three electrode system comprising platinum wire as auxiliary electrode, saturated calomel electrode (SCE) as reference electrode and the modified or unmodified glass carbon electrode (3 mm diameter, GCE) as working electrode, containing a 10 mL of glass cell.

Fourier transform infrared spectroscopic measurements were performed on NEXUS 670 Fourier transform infrared spectrometer (Nicolet, USA). Thermal gravimetric analysis (TGA) was conducted on a TGA/SDTA851e instrument from room temperature to 600 °C with a heating rate of 10 °C min<sup>-1</sup> in the nitrogen flow (Mettler Toledo Co., Switzerland). Surface morphological images were taken by a HITACHI S-4800 scanning electronic microscopy (Hitachi Co. Ltd., Tokyo, Japan).

### 2.3. Preparation of MWCNTs–PAAM nanocomposite

#### 2.3.1. Synthesis of MWCNTs–COCl

A suspension of 0.3 g of MWCNTs–COOH in 30 mL of  $SOCl_2$  was placed in a 100 mL round bottom flask and refluxed at 80 °C for 24 h under a dry air atmosphere [38]. The solid was washed by anhydrous tetrahydrofuran for several times to remove the excess  $SOCl_2$  and dried in a vacuum oven to give MWCNTs–COCl.

#### 2.3.2. Synthesis of MWCNTs–APTES

0.3 g MWCNTs–COCl obtained as outlined above was reacted with 25 mL of APTES in 25 mL of N,N'-dimethyl formamide (DMF) under a dry air atmosphere at 120 °C for 48 h. 0.2 mL of triethylamine was added as phase transfer catalyst. After reaction, the product was filtered, washed with ethanol, and dried in a vacuum oven overnight, giving MWCNTs–CONH(CH<sub>2</sub>)<sub>3</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (MWCNTs–APTES).

#### 2.3.3. Synthesis of MWCNTs–Si–C=C

The C=C modified MWCNTs was synthesized based on the reaction between MWCNTs–APTES and VTEOS with the method of aqueous ammonia as catalyst [39]. 1.0 mL of VTEOS was added to a suspension of 0.1 g MWCNTs–APTES in 20 mL of toluene. The above solution was stirred for 10 min, and then 0.5 mL of aqueous ammonia as catalyst was added. The mixture was stirred at room temperature over night. The product was collected by centrifugation and washed with ethanol. The solid was dried over night in a vacuum oven to obtain vinyl group functionalized MWCNTs (MWCNTs–Si–C=C).

#### 2.3.4. Preparation of PAAM polymerizing on the surface of MWCNTs

40 mg of MWCNTs–Si–C=C was suspended in 20 mL of chloroform in a 100 mL round bottom flask. AAM (0.5 mmol) and EGDMA (2.5 mmol) were added into the above solution and stirred for 1 h. Then, 10 mg of AIBN as the initiator was added and the mixture

Download English Version:

<https://daneshyari.com/en/article/578204>

Download Persian Version:

<https://daneshyari.com/article/578204>

[Daneshyari.com](https://daneshyari.com)