



Sensitive electrochemical detection of fenitrothion pesticide based on self-assembled peptide-nanotubes modified disposable pencil graphite electrode

Gulcin Bolat^a, Serdar Abaci^{a,*}, Tayfun Vural^b, Betül Bozdoğan^c, Emir B. Denkbas^b

^a Department of Chemistry, Faculty of Science, Hacettepe University, 06800, Ankara, Turkey

^b Department of Chemistry, Biochemistry Division, Hacettepe University, 06800, Ankara, Turkey

^c Nanotechnology and Nanomedicine Division, Institute of Science, Hacettepe University, 06800 Ankara, Turkey

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ABSTRACT

A novel, simple and sensitive fenitrothion (FT) sensor was developed based on as-synthesized peptide nanotubes (PNTs) on modified pencil graphite electrode (PGE). This modified electrode (PNT/PGE) was characterized by SEM, electrochemical impedance spectroscopy and cyclic voltammetry techniques. The electrochemical response of the PNT/PGE was linearly proportional to the concentration of FT over the range of 0.114 μM to 1.712 μM with a lower detection limit of 0.0196 μM (S/N = 3). The sensor was also applied for the detection of fenitrothion in tap water. The recoveries for the spiked water samples were between 94.9 and 103.6%. The results mentioned above show that the novel electrochemical sensor is an ideal device for FT determination.

1. Introduction

Organophosphorus (OP) pesticides are important classes of agricultural chemicals which are extensively used throughout the world due to their high toxicity to pests [1]. Their use in agriculture provides numerous benefits in terms of production and quality increase. However, due to intense usage, there is a possibility of leakage of these toxic compounds into environment through water or soil. The residue of the OPs can exist in the natural environment for long time and generates pollution problems as well as producing a potential hazard to human beings and animals and to the nature [2,3]. Moreover, OP pesticides are neurotoxic compounds which can irreversibly inhibit acetylcholinesterase enzyme and may cause negative effect on the nervous system as a result of excessive cholinergic neurotransmission [4–6].

Fenitrothion (FT), *O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate, is a contact insecticide and selective acaricide from the organophosphate family. It is a broad spectrum agricultural insecticide used to control the sucking, feeding or plant disease transmitting insects on cereals, cotton, rice and vegetables [7,8]. Fenitrothion is far less toxic than other OP species having insecticidal activity that is identical. Although it is more expensive, great extent of use of FT is recognized in countries where parathion has been banned. However, promiscuous application brings about presence of residues of such pesticides in natural waters and in foodstuffs. So, in the environmental monitoring, rapid, reliable and cheap sensing of these pesticides becomes important for public health protection [9].

Numerous analytical techniques for the analysis of organophosphorous compounds mostly based on gas chromatography [10,11], liquid chromatography [12,13] and mass spectrometry [14–16] have been developed in the last few years for the determination of pesticides in the environment. However, these methods have several disadvantages including high cost, being not environmentally friendly because of utilisation of the excess amounts of organic solvents for the extraction, preconcentration and clean-up steps, requirement of long analysis time, highly qualified personnel, and inability for in-field analysis [17,18]. Also, immunoassay methods have been used in measuring pesticide residues due to their specificity, sensitivity, rapidness, large parallel processing capacity and comparative cost effectiveness [19–22]. Despite that, they require a labeling process and multiple washing/sample preparation steps, which restrict their applications [21,22]. Also, cross-reactivity processes and the effect of sample matrix should be considered in some immunoassays [21,22].

On the other hand, the electrochemical techniques have been accepted as promising methods to detect OPs due to their advantages over above methods including excellent sensitivity, relative simplicity, low cost, short analysis time, minimal sample preparation and portability [2–4]. Enzyme-based electrochemical biosensors have been widely used for determination of OPs [23–26]. However, they are mostly limited by the denaturation of enzyme acetylcholinesterase and loss of enzyme activity. Mercury based electroanalytical techniques using (hanging mercury drop electrode) HMDE have been reported for the determination of fenitrothion with low detection limits [27,28]. But toxic

* Corresponding author.

E-mail address: sabaci@hacettepe.edu.tr (S. Abaci).

nature of the working electrode is considered incompatible from the environmental point of view. Non-enzymatic electrochemical sensors based on chemically modified electrodes have proved to be an alternative method for the sensitive determination of organophosphorous compounds. Electrochemically pretreated glassy carbon electrode (GCE) [2], graphene oxide modified GCE [29] and a molecularly imprinted polymer on a screen-printed carbon electrode for selective fenitrothion determination have been demonstrated [30]. Metal and metal oxide nanoparticles or polymer-nanoparticle composites were also used as the electrode modifiers in OPs sensing developments. A nano-TiO₂ polymer film [7], a nano TiO₂/nafion composite modified GCE [4] and metal phthalocyanines modified electrodes [31] were used for the determination of fenitrothion.

Peptide nanotubes (PNTs) are a class of organic nanotubes with a diameter of 1–100 nm and micrometer length formed by self-assembly of peptides. Diphenylalanine dipeptide (NH₂-Phe-Phe-COOH, FF) is a peptide fragment of the core amino acid sequence of β -amyloid A β (16–20), KLVFF. Gazit's group in 2003, reported that this diphenylalanine can self-assemble to form peptide nanotubes [32]. β -sheet alignment and aromatic moieties of diphenylalanine provide directionality and energetic support for formation of aromatic stacking via π - π interactions that play a key role in formation of these supramolecular structures. FF-PNTs are reported to possess porous, multi-walled nanostructures with a hexagonal crystal structure consisting of six diphenylalanine molecules which create channels filled with water [33,34]. The FF-based peptide nanoassemblies offer attractive properties for various nanotechnological and biomedical applications as they can be synthesized, easily and inexpensively, and show solubility in water. The high number of hydrogen bonds involved in their structure provides good mechanical, thermal and chemical stability [35]. PNTs are biocompatible [36] and show a remarkable similarity to carbon nanotubes (CNTs) in their morphology and aspect ratio [37]. Unlike CNTs, exposure to oxygen, N₂O, and NH₃ has little effect on their electric properties, they have good solubility properties and they can be easily formed under mild conditions without any expensive techniques like chemical vapor deposition (CVD). The nanocrystalline asymmetric structure of FF-PNT provides unique electric, piezoelectric, ferroelectric and optical properties and their physical properties can be easily manipulated with numerous biological and chemical modifications [38–40]. The charge transport and electrical conductance properties of the PNTs were demonstrated by Santhanamoorthi et al. [41]. Because of these characteristics, PNTs have lots of application areas like environmental and medical biosensors [42,43], molds for nanofabrication of inorganic nanomaterials [32], carrying systems [44], functional composite materials [45,46], energy and substance storages [47]. Because of their nanostructures, flexibility in functionality and their molecular-recognition properties, PNTs can be used as a supporting matrix to create useful bioelectrochemical interfaces [37,42,43]. By depositing the PNTs on the surface of electrodes, the PNTs-modified electrodes with desired properties such as improved signal-to-noise ratio and specificity, can be fabricated. Recently, Yemini et al. reported that FF-PNTs deposited onto graphite electrodes improved the electrochemical performance of the electrode [37] and the enzymatic production of hydrogen peroxide was enhanced on PNTs modified electrode for the sensitive detection of glucose [48]. Since then, PNTs modified electrodes have been used for different kinds of electrochemical sensing applications including environmental monitoring [49], dopamine [50], H₂O₂ [43] and a pathogenic bacteria, *Escherichia coli* O157:H7 [42] sensing. In our earlier report, disposable pencil graphite electrodes (PGEs) modified with PNTs were characterized and successfully employed for the electrochemical analysis of Vitamin B₁₂ [51]. To our

knowledge, a PNT electrode for electrochemical detection of fenitrothion has not been reported before. In this study, a novel diphenylalanine peptide nanotubes based electrochemical biosensing platform is described. The preparation of the PNTs and the sensor surfaces were simple, cheap and rapid. Voltammetric studies showed that the biocompatible, well-ordered, self-assembled peptide nanotubes on pencil graphite electrodes significantly improved the electrochemical parameters of pencil graphite electrodes in non-enzymatic FT sensing.

2. Materials and methods

2.1. Reagents

Fenitrothion (*O,O*-dimethyl-*O*-[3-methyl-4-nitrophenol]phosphorothiate) was purchased from Sigma (USA). Stock solution of fenitrothion was prepared from ethanol. The BR (Britton Robinson) buffer solution of required pH was prepared by adding 0.2 M sodium hydroxide solution into the mixed acids, containing 0.04 M of each boric, ortho-phosphoric and acetic acid. Zwitterionic diphenylalanine dipeptides (NH₂-L-Phe-L-Phe-COOH) were purchased from Bachem (Bubendorf, Switzerland). The peptide nanotubes (FF-PNTs) were easily prepared by the procedure previously published in Ref. [51]. In the process; lyophilized powder form of diphenylalanine was dissolved in water. The prepared 6 mg mL⁻¹ PNT solution was kept in 60 °C. Self-assembly process driven by weak intermolecular forces, such as hydrogen bonding, π - π interactions, and hydrophobic/hydrophilic interactions occurred in aqueous solution during cooling at room temperature. Finally, the hydrogen-bonded tubular ensembles were formed individually between the backbone of the peptide and water molecules. Other reagents used were of analytical reagent grade and double distilled water was used to prepare aqueous solutions throughout the experiments.

2.2. Instruments

All electrochemical measurements were performed using a potentiostat/galvanostat (CH Instruments, model 660C). A conventional three electrode system was employed for electrochemical sensing: a pencil graphite electrode (PGE) as the working electrode, an Ag/AgCl/3 M KCl as reference and a platinum wire as the auxiliary electrode. The peptide nanotube modified electrodes were then used as the working electrodes. The surface characterization of unmodified, modified electrodes was performed by scanning electron microscope (SEM) (FEI Quanta 200 FEG, USA).

2.3. Preparation of PNT modified pencil graphite electrode (PNT/PGE)

A green, facile and cost effective approach for the preparation of sensor was used. The peptide nanotubes modified pencil graphite electrodes were prepared via passive adsorption method. Pencil leads (one-cm) were immersed into the vials containing 6.0 mg mL⁻¹ peptide nanotube solution for different times (15, 30, 60, 90 min) in order to form peptide nanotube layer at the electrode surface. The highest peak currents for FT reduction was obtained for 30 min of adsorption time and the response of the electrode did not change appreciably after an immobilization time of 30 min so this value was selected as optimum adsorption time. Then PNT modified PGEs were allowed to dry for 10 min. The electrodes were then rinsed with ultrapure water for 10 s. Each experiment was performed with a freshly modified new surface.

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