



## Analytical Methods

# Non-enzymatic electrochemical platform for parathion pesticide sensing based on nanometer-sized nickel oxide modified screen-printed electrodes



Mohamed Khairy<sup>a,\*</sup>, Haytham A. Ayoub<sup>a,b</sup>, Craig E. Banks<sup>c</sup>

<sup>a</sup> Chemistry Department, Faculty of Science, Sohag University, 82524, Egypt

<sup>b</sup> Plant Protection Research Institute, A. R. C., Dokki, Giza, Egypt

<sup>c</sup> Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK

## ARTICLE INFO

## Keywords:

Parathion  
Organophosphate pesticides  
Nickel oxide  
Mesoporous nanoplatelets  
Screen-printed electrode  
Nanozyme.

## ABSTRACT

Nanozyme-based electrochemical sensors have attracted much attention because of their low cost, sensitivity and remarkable stability under extensive environmental and industrial conditions. Interestingly, the physical characteristics of the nanomaterials in terms of size, shape, composition, surface area and porosity dominate the electrochemical processes at electrode surfaces. Herein, we explore nickel oxide nanoplatelets (NPs) modified screen-printed electrode-based nanozyme sensors that displays high electrochemical activity including stability, sensitivity, selectivity and applicability for organophosphate pesticide (Parathion) determination. Differential pulse voltammogram of NiO-SPE in presence of parathion showed a characteristic peak current at  $-1.0$  V (vs. Ag/AgCl). The NiO-SPE platform allows determination of parathion over the concentration range of  $0.1$ – $30$   $\mu$ M with a limit of detection (LOD) of  $0.024$   $\mu$ M. The sensing platform is found to detect parathion of interferences without compromising the sensitivity of the sensor. Such interesting features offer a sensitive determination of parathion in water, urine and vegetable samples.

## 1. Introduction

Organophosphate (OP) pesticides have gained much popularity in increasing agricultural productivity (Mulchandani, Mulchandani, Chen, Wang, & Chen, 1999). They are widely used in pre- and post-harvest treatments to control multiple diseases of various fruits and vegetables (Albero, Brunete, & Tadeo, 2003; Ciucu, Negulescu, & Baldwin, 2003; Hsu et al., 1988). Their extensive use has caused serious risks to environment and human health. Despite being classed as persistent pesticides which have toxic environmental impacts, they are still widely used in many countries which have led to serious contamination of ground water and food samples. OP pesticides are potent acetyl cholinesterase (AChE) inhibitors capable of causing severe cholinergic toxicity following cutaneous exposure, inhalation, or ingestion (Diagne, Oturan, & Oturan, 2007). According to the European Union (EU), the maximum admissible concentrations of individual pesticide and their related compounds are  $0.1$   $\mu$ g L<sup>-1</sup> and  $0.05$  mg kg<sup>-1</sup> in drinking water and food of plant origin, respectively (EEC, 1980). About 3,000,000 people in worldwide are exposed to organophosphate each year, with up to 300,000 fatalities. Parathion is one of the highly toxic organophosphate pesticides, with orally median lethal dose (LD<sub>50</sub>) of  $3.0$  mg kg<sup>-1</sup> or by inhalation LC<sub>50</sub> of  $0.03$  mg L<sup>-1</sup> (Greenwood et al.,

1997; Qu, Min, Wei, Xiao, & Shi, 2008). Recently, parathion was banned or restricted in 23 countries including Europe and United states, but still used and imported illegally in more than 50 developing countries (IPCS, 1992). It has been estimated that only 0.1% of applied pesticides reach the target pests, leaving the bulk of the pesticides (99.9%) to impact the environment in water supplier and soil (Horrihan et al., 2002). Therefore, low-cost and sensitive determination of parathion in environment and water resources is urgently needed.

Numerous analytical techniques have been used for determination of parathion such as gas chromatography (GC) or high-performance liquid chromatography (HPLC) coupled with mass spectrometry, thermospray mass spectrometry, and flame photometry (Pugliese et al., 2004; Sadik, Land, & Wang, 2003; Sinha, Pal, Dewan, Mansuri, & Saiyed, 2006). Despite of their high sensitivity and accuracy, these methods are expensive, require pre-treatment and qualified technicians to obtain accurate results. Thus, development of a simple, rapid, selective and sensitive analytical technique for in-field OPs screening is of particular significance and necessity (Anandhakumar et al., 2014; Tang et al., 2011; Thotaa, & Ganesha, 2017; Wang et al., 2015). As a result, electrochemical-based techniques have gained much attention over the last decades. Several enzyme-based electrochemical biosensors have been developed (Lei, Mulchandani, Wang, Chen, & Mulchandani, 2005;

\* Corresponding author.

E-mail address: [mohamed.khairy@science.sohag.edu.eg](mailto:mohamed.khairy@science.sohag.edu.eg) (M. Khairy).

Mulchandani, Chen, Mulchandani, Wang, & Chen, 2001; Mulchandani et al., 1999; Raghu et al., 2012). These biosensors can be used for determination of carbamate and organophosphorous pesticides due to inhibition mechanism of cholinesterase enzymes (AChE). For example; immobilization of enzyme onto silica-gel films with gold nanoparticles and enzyme entrapped silica gel on carbon paste electrodes have been reported for determination of methyl parathion. However, the denaturation of AChE enzymes results in the instability and short lifetime of the biosensor, which mostly limits the operational applications. Moreover, the enzyme can be affected by different kind of contaminations such as heavy metals in environmental samples, which makes the direct determination of organophosphorous pesticides lack of selectivity and even leads to false positive results. Therefore, enzyme-less and/or nanozyme electrodes for electrochemical sensing are highly recommended (Lin, Lu, & Wang, 2004; Pedrosa, Miwa, Machado, & Avaca 2006; Xu, Wu, Hu, & Cui, 2002)

Nanomaterials have been widely utilized to develop various electrochemical-based nanozyme sensors (Khairy et al., 2017; Mahmoud, Khairy, Rashwan, & Banks, 2017; Mahmoud, Khairy, Rashwan, & Banks, 2016). ZrO<sub>2</sub> nanoparticles (NPs) (Parham, & Rahbar, 2010), multiwalled carbon nanotubes–poly(acrylamide) nanocomposite (Zeng, Yu, Yu, Zhou, & Shi, 2012), titania NPs (Li, Li, Yang, Xu, & Hu, 2011), Pd/MWCNTs nanocomposite (Huang, Zhang, Chen, & Yu, 2010), *para*-Sulfonatocalix[6]arene modified silver NPs and ZrO<sub>2</sub>/Au nano-composite (Bian, Li, & Li, 2010; Wang & Li, 2008) have been recently used for determination of organophosphorous pesticides. These electrode reactions involved reduction of nitro-group in the pesticide molecule. Although, nickel and copper were commonly used in heterogeneous catalytic reduction of nitro-aromatic compounds to corresponding amines in a very high yield and a very high chemoselectivity, there is no report elucidating the electrochemical behaviour of parathion on Cu- and Ni-derived electrodes (Aditya, Pal, & Pal, 2015; Cyr, Huot, Belot, & Lessard, 1990; Huang & Lessard, 2016). Huang and Lessard observed that, the formation of oxide layer on Cu and Ni surfaces altered the reversibility and enhanced the peak current of nitro-compounds. Hence, in the present manuscript, we have synthesized nickel oxide nanostructures with hexagonal platelet-like morphology (NPs) *via* template-less hydrothermal method. It was found that, NiO NPs sample is a well crystalline material with large surface area and wormlike mesoporous network. The NiO NPs suspension was casted of graphite screen-printed electrode and explored for developing a nanozyme parathion biosensor. It was found that, the nano-sized architectures and porosity of NiO NPs play key roles in the sensing performance in real samples.

## 2. Experimental

### 2.1. Materials and reagents

All chemicals were of the highest analytical grade available and were used as received without further purification, parathion (HPLC; 99.7%), chlorpyrifos (HPLC; 99.7%) and imidacloprid (HPLC; 99.7%), *p*-nitrophenol, nickel chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O), ammonium hydroxide (NH<sub>4</sub>OH; 28%), ethanol, ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O), calcium chloride (CaCl<sub>2</sub>), potassium iodide (KI), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O). All solutions were prepared using doubly distilled water with resistance more than 18.2 MΩ cm. Britton Robinson (B. R.) buffer solutions were prepared by mixing boric acid, citric acid, phosphoric acid (0.05 mol L<sup>-1</sup>) and the pH was adjusted by addition of sodium hydroxide solution (1.0 mol L<sup>-1</sup>). A stock solution of 0.5 mM parathion was prepared in ethanol.

### 2.2. Synthesis of nickel oxide NPs

The nickel oxide NPs material was synthesized as described previously by us *via* simple hydrothermal treatment of nickel precursor NiCl<sub>2</sub>·6H<sub>2</sub>O in basic medium (El-Safty, Khairy, Ismael, & Kawarada,

2012; Khairy & El Safty, 2013). A 20 mmol L<sup>-1</sup> NiCl<sub>2</sub> dissolved in 50 mL of doubly distilled water. The pH of nickel solution was adjusted to pH 10 using NH<sub>4</sub>OH. Subsequently, the solution was diluted to 70 mL and transferred into a Teflon-lined stainless-steel autoclave with a capacity of 100 mL and then heated at 160 °C for six hours. The autoclave allowed cooling to room temperature. The obtained green precipitate of Ni(OH)<sub>2</sub> was washed several times, dried at 60 °C and thermally treated in air at 300 °C for three hours.

### 2.3. Fabrication of Screen-printed electrodes (SPEs)

The SPEs were fabricated in-house with appropriate stencil using a DEK 248 screen-printing machine (DEK, Weymouth, U.K.). These electrodes have been used extensively in previous studies (Foster, Metters, Kampouris, & Bank, 2014; Khairy et al., 2017; Mahmoud et al., 2017; Mahmoud et al., 2016). For their fabrication, first, a carbon-graphite ink formulation (product code C2000802P2 Zensor; Gwent Electronic Materials Ltd., U.K.) was screen-printed onto a polyester (Autostat, 250 μm thickness) flexible film (denoted throughout as standard-SPE). This layer was cured in a fan oven at 60 °C for 30 min. Next, a silver/silver chloride reference electrode was included by screen-printing Ag/AgCl paste (product code C2040308D2; Gwent Electronic Materials Ltd., U.K.) onto the polyester substrates and a second curing step was undertaken where the electrodes were cured at 60 °C for 30 min. Finally, a dielectric paste (product code D2070423D5; Gwent Electronic Materials Ltd., U.K.) was then printed onto the polyester substrate to cover the connections. After a final curing at 60 °C for 30 min, these SPEs are ready to be used. These SPEs with a working electrode of 3 mm diameter have been shown to exhibit a heterogeneous electron transfer (HET) rate constant, *k*<sup>o</sup>, of ca. 10<sup>-3</sup> cm s<sup>-1</sup>, as measured using the [Ru(NH<sub>3</sub>)<sub>6</sub>]<sup>3+/2+</sup> redox probe (Foster et al., 2014; Khairy et al., 2017)

### 2.4. Nickel oxide nanoparticles modified SPE

The SPEs were modified with NiO NPs by utilizing a simple drop-casting method. A suspension solution of NiO NPs (1.0 g L<sup>-1</sup>) was prepared in distilled water; A 5 μL of NiO NPs suspension was dropped onto the SPE surface and left it to dry for 30 min. Then, NiO-SPE are ready to use for further experiments. In order to estimate the active surface areas of bare/unmodified SPE and NiO-SPE, CV experiments of the redox couple [Fe(CN)<sub>6</sub>]<sup>4-/3-</sup> solution in 0.1 M KCl at different scan rates was carried out and then Randles-Sevcik equation was applied as following:

$$I_p = 2.69 \times 10^5 n^3/2 A D_0 v^{1/2} C_0$$

where *I*<sub>p</sub> is the peak current (A), *n* is number of electrons (*n* = 1), *A* is the active area of electrode (cm<sup>2</sup>), *D*<sub>0</sub> is the diffusion coefficient (cm<sup>2</sup>/s; 7.2 × 10<sup>-6</sup> cm<sup>2</sup>s<sup>-1</sup>), *v* is the potential scan rate (Vs<sup>-1</sup>) and *C*<sub>0</sub> is the bulk concentration (0.5 mmol L<sup>-1</sup>). The peak currents were linearly proportional with square root of scan rates. Thus, the values of active surface areas were determined to be 5.12 × 10<sup>-2</sup> and 9.62 × 10<sup>-2</sup> cm<sup>2</sup> for unmodified SPE and NiO-SPE, respectively.

### 2.5. Determination of parathion in water sample

Tap water sample was collected and acidified to the appropriate pH by addition of small amount of hydrochloric acid solution (0.1 mol L<sup>-1</sup>). Consequently a recovery experiment was performed on the tap water sample. The sample was spiked with standard solution of parathion and then a standard addition protocol performed in triplicate *via* recording of DPV responses.

Download English Version:

<https://daneshyari.com/en/article/7585557>

Download Persian Version:

<https://daneshyari.com/article/7585557>

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