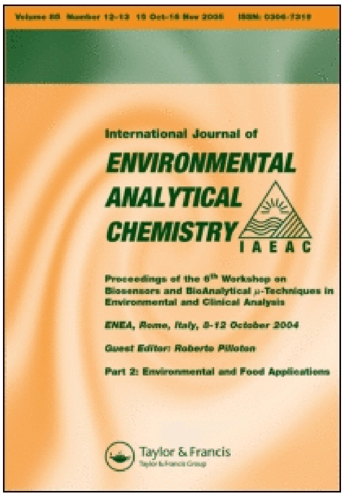

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Gold nanowires were produced by electrodeposition in polycarbonate membrane, with an average diameter of 200 nm and a height of about 2 μm. The nanowire array prepared by the proposed method can be considered as nanoelectrode ensembles (NEEs). An amperometric pesticides sensor based on gold NEEs has been developed and used for determination of phoxim and dimethoate in vegetable samples. The electrochemical performance of the gold NEEs has also been studied by the amperometric method. The electrode provided a linear response over a concentration range of 5.9×10^{-5} to 1.2×10^{-2} M for phoxim with a detection limit of 4.8×10^{-6} M and 6.3×10^{-5} to 1.1×10^{-2} M for dimethoate. This sensor displayed high sensitivity and selectivity, long-term stability and wide linear range. In addition, the ellipsis of enzyme and the reactivation of enzyme make the operation simple. This sensor has been used to determine pesticides in a real vegetable sample.

Keywords: pesticides; sensor; gold nanowire; polycarbonate membrane; nanoelectrode ensembles

1. Introduction

Organophosphorous pesticides (OPs), such as phoxim and dimethoate are widely used in agriculture due to their high efficiency and limited persistence in the environment [1]. Also they are well known as highly toxic compounds which can cause neurological diseases. These neurotoxic compounds inhibit acetylcholinesterase irreversibly, resulting in the buildup of the neurotransmitter, acetylcholine, which interferes with the muscular responses in vital organs and produces serious symptoms [2]. These are suspected for carcinogenic, and endocrine disruptor effects [3]. They are also used for chemical warfare and are potential hazard for human health and environmental food chains [4]. Evaluating and monitoring of these compounds from different environmental pollutants are imperative for human health protection and environmental control. There is a considerable interest in developing highly sensitive, selective, rapid and reliable analytical methods in their detection. Although current analytical techniques, such as gas

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chromatography [5] or liquid chromatography [6], high-performance liquid chromatography [7], mass spectrometry [8] are very sensitive and are capable of determining a large number of compounds, they are very time-consuming, costly, and are only performed by highly trained technicians.

Biosensors represent an alternative method to quickly detect neurotoxins and have been an actively researched area for several years. These biosensors have been developed based on the inhibition of enzymes (acetylcholinesterase, butyrylcholinesterase) [9,10] or the hydrolyzation of organophosphorus hydrolase [11] integrated with electrochemical, optical transducers [12] and piezoelectric transducers [13]. These methods are highly sensitive but have a slow response in multi-step indirect determination and the enzymes are inhibited irreversibly by many compounds. Furthermore, it needs to recover the activity of enzyme after the determination of pesticide [14], which makes the procedure of determination complex and reduces the lifetime of biosensor.

To circumvent these drawbacks, an electrochemical sensor based on a chemically modified electrode has been developed and proved to be a sensitive and selective method for the determination of organophosphorous pesticides [15]. Zen [16] reported a Nafion-modified glassy carbon electrode for the detection of parathion. Liu *et al.* developed a voltammetric sensor for the determination of parathion based on the use of a poly (carmine) film electrode [17]. Zhang *et al.* reported a simple amperometric sensor for the direct determination of OPs neurotoxic agents by using the ceria nanoparticles-nafion film modified electrode [18]. However, simply dropping the modified nanostructures onto electrode surface will result in a disarrayed and layered film, which will hinder the electron transfer. For an ideal sensor fabrication method, it would be a significant advancement if perpendicularly aligned nanotube or nanowire arrays can be formed as sensing devices [19].

Metallic nanowires are of great interest from a fundamental point of view as well as for future applications. The nanoelectrode ensembles (NEEs) show improved signal to noise ratios, high faradaic current density, fast electron-transfer rate, enhanced sensitivities, better detection limit and the large surface area of NEEs with increasing the number of electroactive sites. Highly ordered metallic NEEs are particularly important in obtaining scaled-up functional devices used as microelectrodes, probes, and data storage devices [20,21]. Gold is one of the mostly researched noble metals as its potential applications have been demonstrated in the fields of sensors or nanoelectrode ensembles. Gold NEEs are confirmed to have high surface area with efficient mass transport characteristics and show to be excellent in performance, such as enhancing the ratios of signal to noise and the improving of detection limit [22,23].

In this paper, considering the advantages of NEEs and the properties of gold, gold nanowire ensembles, were synthesised in polycarbonate (PC) membranes by means of the one-step electrochemical deposition method. The diameter of each nanowire is about 200 nm with a height of about 2 μm. The electrode can be considered as NEEs with each nanowire acting as a single nanoelectrode. Based on the catalysis of gold nanowires to the electrochemical oxidation of phoxim and dimethoate, the direct response of gold NEEs toward these two kinds of pesticide has been studied. The as-prepared sensor displayed high sensitivity, quick response to phoxim and dimethoate, good stability, wide linear range and better detection limits. Besides, this sensor omits enzyme and the reactivation of enzyme, which makes the operation simpler and the lifetime of the sensor longer.

2. Experimental

2.1 *Apparatus and reagents*

Cyclic voltammetric and amperometric measurements were carried out on XJP-821(C) polarograph (Jiangsu, China). Scanning electron microscopy (SEM) analysis was performed by using XL30ESEM-TMP microscope (Philips, Ltd. Holland). The three-electrode cell (10 mL) was constituted of the gold NEES modified glassy carbon (GC) electrode as the working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum foil electrode as counter electrode. All potentials were measured and reported versus the SCE.

Track-etched porous polycarbonate (PC, 0.2 µm) membrane was provided by Whatman (Anodisc 47, 0.2 µm). Phoxim and dimethoate were produced by Jiangsu Baoling Chemical Co., Ltd. (Jiangsu, China). Chlorothalonil was produced by institute of pesticide, Yunnan Normal University (Yunnan, China). The other chemicals, such as chloroauric acid tetrahydrate ($HAuCl_4.4H_2O$), perchloric acid ($HClO_4$) were of analytical-reagent grade and used as received without further purification, and doubly distilled water was used throughout. For the determination of phoxim, the supporting electrolyte was 0.067 M phosphate buffer solution (PB) with ethanol (v/v: 1:1).The supporting electrolyte for the determination of dimethoate was 0.067 M phosphate buffer solution (PB), which was prepared with KH_2PO_4 and Na_2HPO_4.

2.2 *Synthesis of gold nanowire*

For the electrodeposition of gold nanowires, a thin film of Au (~30 nm) was first sputtered onto one face of the PC membrane to make the membrane conductive. A copper wire (5 cm) was connected to the PC membrane sputtered with thin gold film by using graphite conductive adhesive. The preparation of PC membrane was finished after the conductive adhesive dried at room temperature. Electrodepositions were performed in 1% (w/w) $HAuCl_4$ solution containing 0.1 M perchloric acid at a constant potential of 0.18 V. The PC membrane was placed in the $HAuCl_4$ solution for 10 min before electrodeposition. After depositing for 40 min, the synthesis of gold nanowires was completed.

2.3 *Preparation of gold NEEs*

Glass carbon electrode (3 mm diameter) was first polished with emery paper and alumina slurry, successively rinsed thoroughly with absolute alcohol and distilled water in ultrasonic bath, and dried in air.

Firstly, a piece of the deposited PC membrane was placed gold-side down onto the surface of electrode. Then, chloroform was dropped onto PC membrane for several times to release Au nanowire. After the volatilizing of the chloroform, the residual polycarbonate will paste the film with Au nanowires onto the surface of the GCE with good stability and good conductivity. The electrode was washed successively using ethanol and water. A bare GC electrode (3 mm diameter) was used as a comparison.

2.4 *Pretreatment of the samples*

For pesticide-recovery tests in vegetables, spinach samples were pretreated according to the following procedure [24]: a weighed amount of sample, crushed and ground into powder with absolute sodium sulfate, was extracted with 60 mL acetone for 30 min. The solution was then filtered. The dregs were washed with 20 mL acetone and incorporated into the filtrate. The resulting filtrate solution was concentrated to 14 mL with a water bath at 40°C. 1 mL condensate was concentrated to almost dry with the water bath at 40°C, 10 ml PB solution was added to dissolve the sample. The resulting solution was used in the recovery test and real-sample analysis with the gold NEEs.

3. Results and discussion

3.1 *Morphological characterisation of the prepared gold nanowire*

During the electrolysis process, the colour of the PC membrane changed from white to reddish indicated that the gold was electrodeposited in the pores of the membrane. After depositing for 40 mins, the gold nanowires were obtained by etching away the membrane. The morphology of the nanowire array was characterised by SEM in Figure 1. The nanowires are vertically oriented with an average diameter of about 200 nm, which corresponds to the size of the nanopore in the membrane. The length of the nanowire after depositing for 40 mins is about 2 μm. It can also be seen from the image that each nanowire is aligned vertically, making each nanowire work as an individual nanoelectrode [25].

3.2 *Estimation of the electroactive surface area of the gold NEE*

Figure 2 represents cyclic voltammograms (CVs) of the gold NEEs (a) and the bare GC electrode (b) in 5 mM K3Fe(CN)6 containing 0.1 M KCl at 100 mVs-1. The well-defined oxidation and reduction peaks due to the Fe3+/Fe2+ redox couple were observed at -0.250 and -0.165V, respectively. According to the Randles-Sevcik equation [26]:

$$I_p = 2.69 \times 10^5 A D^{1/2} n^{3/2} \gamma^{1/2} C$$

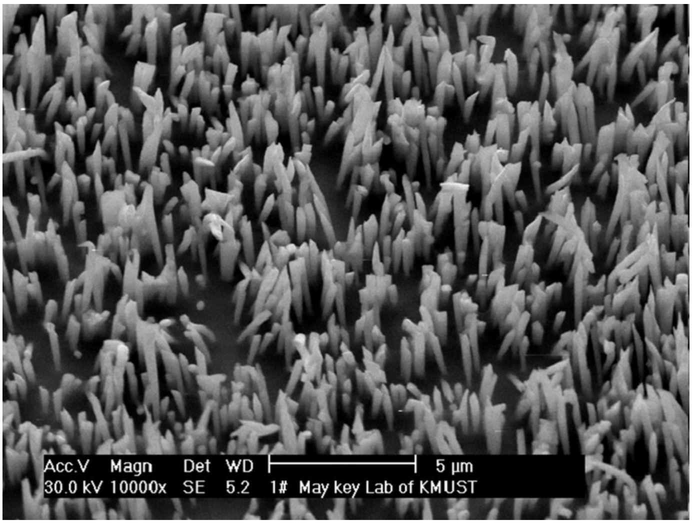
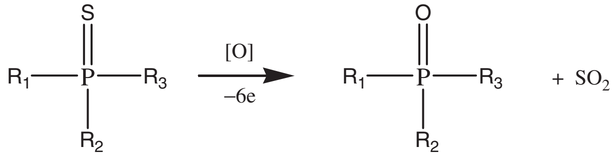


Figure 1. SEM image of the gold nanowire.

From this equation one can conclude that the electroactive surface area (A) is a linear function of the peak current of the redox couple when D, n, γ, and C are constant values. The electroactive surface area for gold NEEs was about 20 times larger than the bare GC electrode.

3.3 *The mechanism of the amperometric detection of pesticides*

The typical electrochemistry oxidation of oganophosphorous pesticides can be expressed as follows [27]:



$$R_1-\overset{\overset{\displaystyle S}{\|}}{\underset{\underset{\displaystyle R_2}{|}}{P}}-R_3 \xrightarrow[-6e]{[O]} R_1-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R_2}{|}}{P}}-R_3 + SO_2$$

Organophosphorous pesticides can be oxidised on the electrode surface, and an oxidation current, which is proportional to the concentration of pesticide, can be observed.

3.4 *Cyclic voltammetry characterisation*

Cyclic voltammograms of pesticides at bare GC electrode and gold NEEs are shown in Figure 3. It can be seen that 0.0048 M phoxim and 0.0048 M dimethoate has no obvious redox signals at the bare GC electrode (curve a and b). The response of the gold NEEs in 0.067 M PB (pH 7.5) displays a background current in curve (c). However, under the same condition, phoxim (curve d) and dimethoate (curve e) yields a very obvious

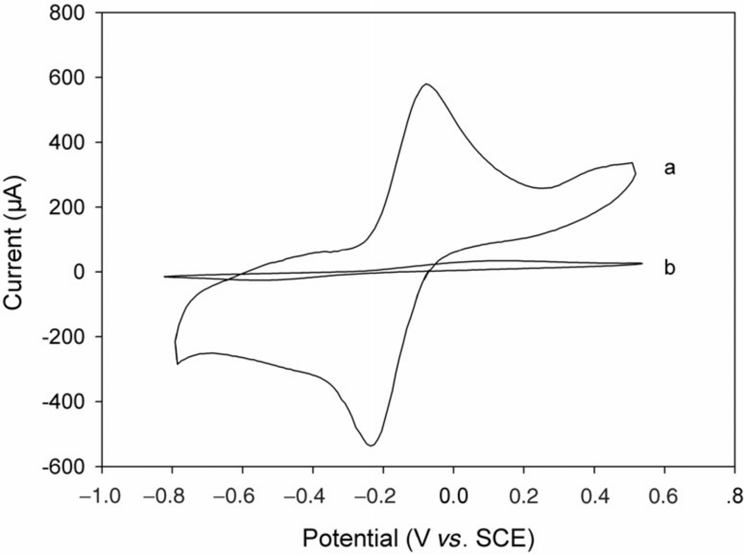


Figure 2. Cyclic voltammograms of gold NEEs (a) and bare GC electrode (b) in 5 mM $K_3Fe(CN)_6$ containing 0.1 M KCl. Scan rate, 100 mVs^{-1}.

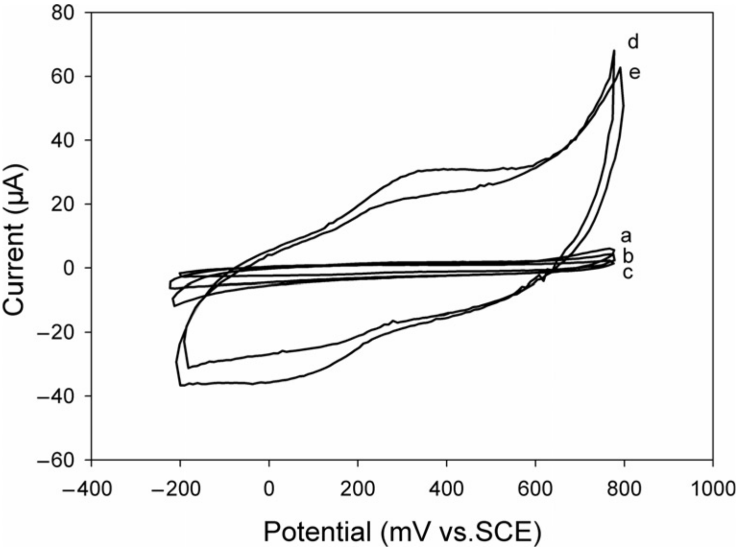


Figure 3. Cyclic voltammograms of various electrodes at different soluion. (a): bare GC electrode in 0.067 M PB with 0.0048 M phoxim added; (b): bare GC electrode in 0.067 M PB (pH 7.5) with 0.0048 M dimethoate added; (c): gold NEEs in 0.067 M PB (pH 7.5) without pesticides; (d): gold NEEs in 0.0067 M PB (pH 7.5) containing 0.0048 M phoxim; (e): gold NEEs in 0.0067 M PB (pH 7.5) containing 0.0048 M dimethoate, scan rate: 100 mVs^{-1}.

oxidation peak, the anodic current attributed to the redox process of pesticides at the gold NEEs. The increased current response indicated the response of the catalysis activity of gold NEEs to phoxim and dimethoate.

Typical cyclic voltammograms of the gold NEEs in 0.067 M PB (pH 7.5) containing 0.0048 M pesticides at different scan rates from 20 to 100 mVs^{-1} are shown in Figure 4. The peak currents are proportional to the square root of the scan rate, showing typical diffusion-controlled electrochemical behaviour.

3.5 *Effect of the gold nanowires on the response of electrode*

The electrochemistry oxidation of organophosphorous pesticides can occur in gold NEEs and bare GC electrode. To discern the role of gold nanowires, the responses of the electrode with and without gold nanowires were studied. From Figure 5, it can be seen that the direct response of the electrodes toward phoxim and dimethoate and the sensitivity and correlation coefficient of the calibration curve of gold NEEs were better than bare GC electrode, indicating the better catalysis of gold nanowires to organophosphorous pesticides.

3.6 *Optimisation of experimental variables*

The experimental variables, which can affect the amperometric determination of pesticides, including the pH of the supporting electrolyte and applied potential, were investigated.

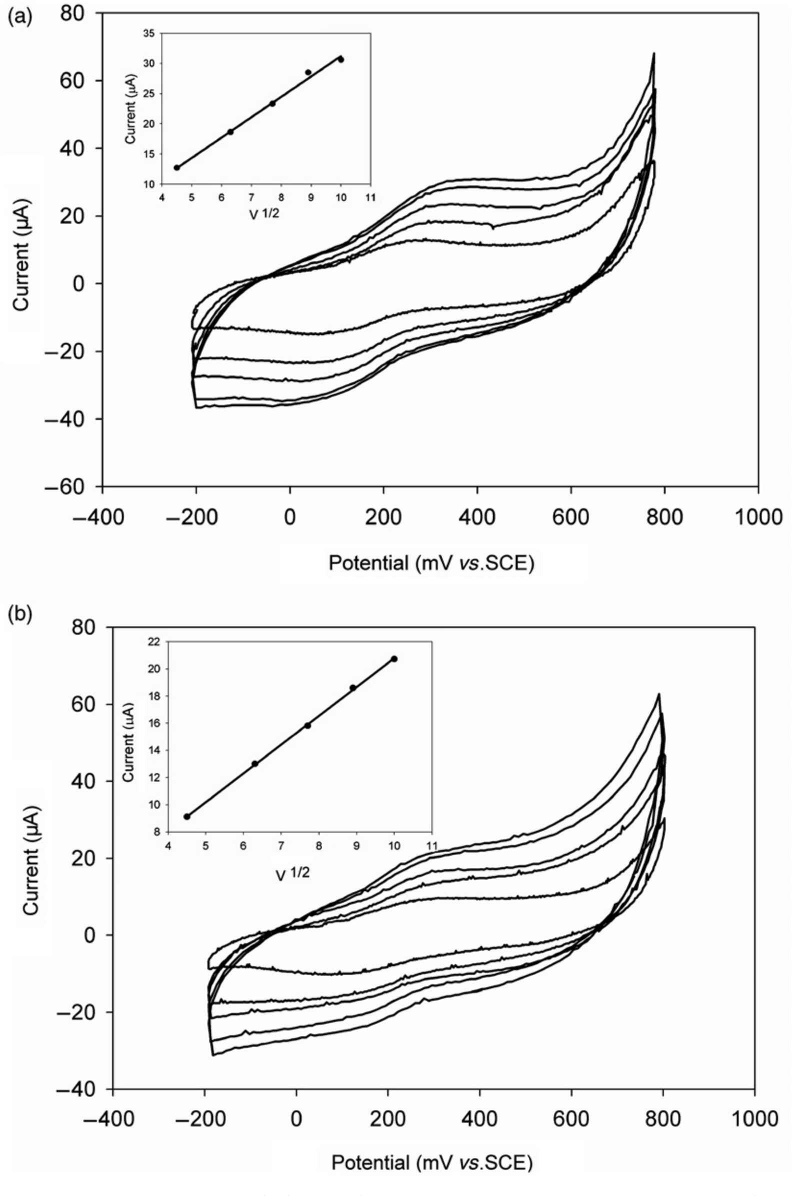


Figure 4. Cyclic voltammograms of the gold NEEs in 0.067 M PB (pH 7.5) in the presence of 0.0048 M phoxim (a) and 0.0048 M dimethoate (b) at various scan rates (from inner to outer curves: 20, 40, 60, 80, 100 $\mathrm{mVs^{-1}}$). Inset: plots of peak current *vs.* $v^{1/2}$.

3.6.1 *Effect of pH*

The influence of the pH of the assay solution over the range 5.0 to 8.6 on the amperometric response of the gold NEEs to phoxim at a fixed concentration of 1.0 mM in PB was investigated. Figure 6 shows that the optimum pH was 7.5. Therefore, pH 7.5 was fixed for the rest of the experiments.

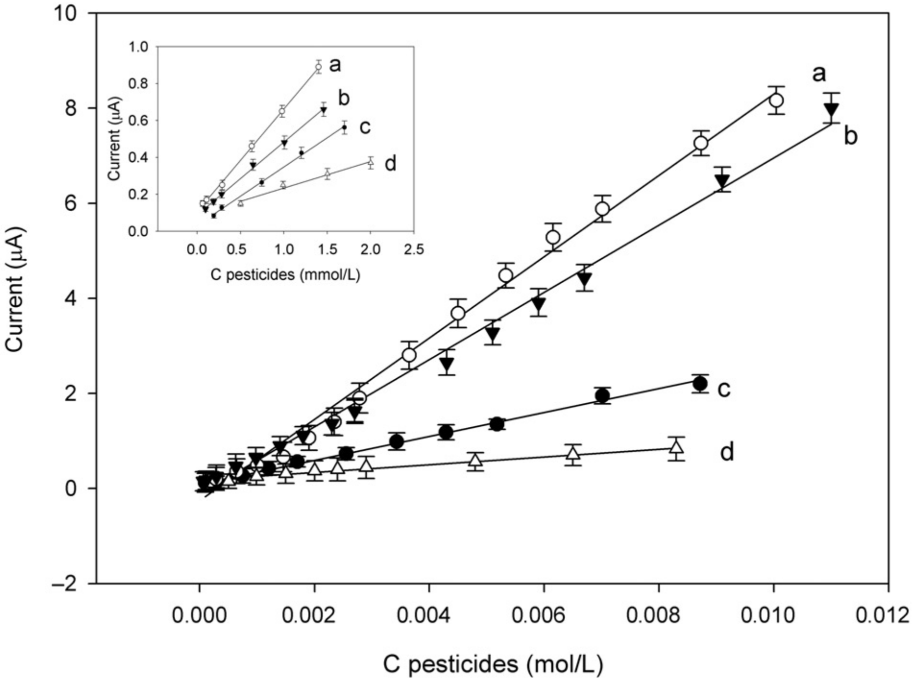


Figure 5. Calibration curve of the response of different electrodes toward pesticides. (a): gold NEEs toward phoxim; (b): gold NEEs toward dimethoate; (c): bare GC electrode toward phoxim; (d): bare GC electrode toward dimethoate. The inset shows the part of the enlarged linear curve in the range of low pesticide concentration.

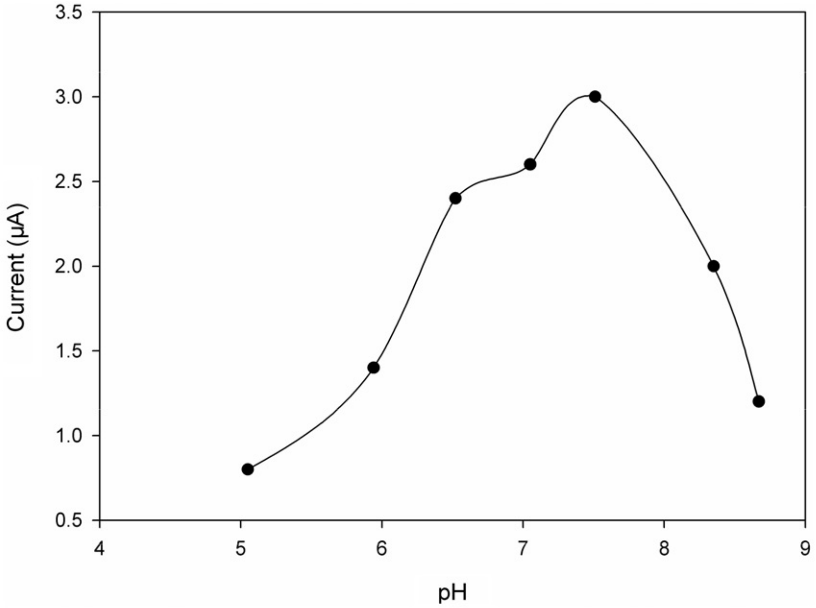


Figure 6. Effect of pH on the gold NEEs response in 0.067 M PB containing 1.0 mM phoxim.

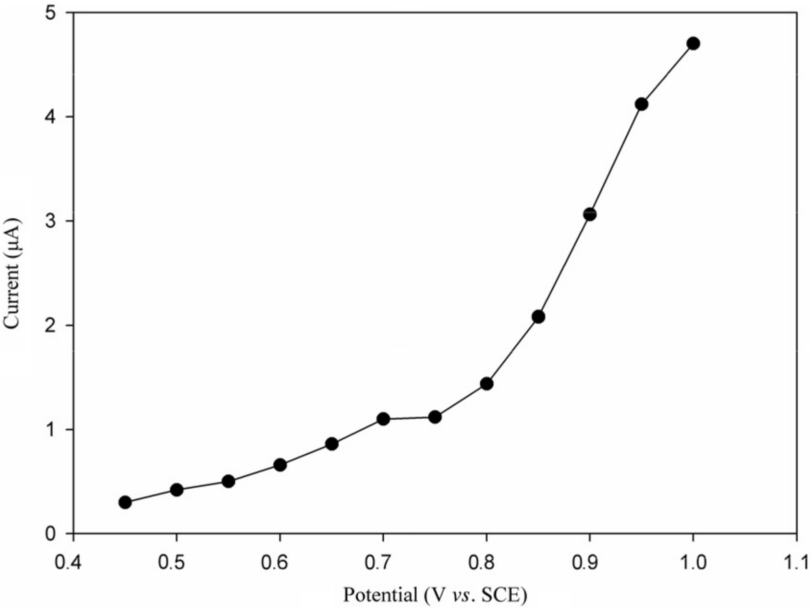


Figure 7. Effect of applied potential on the gold NEEs response when phoxim was 1.0 mM in 0.067 M PB (pH 7.5).

3.6.2 *Effect of applied potential*

The effect of applied potential on the gold NEEs response was investigated in the presence of 1.0 mM phoxim and is shown in Figure 7. As the potential increases from 0.45 to 1.0 V, the sensitivity of the electrode increased significantly. To avoid interference at high applied potentials, a potential of 0.7 V (vs. SCE) was selected as the applied potential for amperometric measurements.

3.7 *Response characteristics of gold NEEs*

Figure 8 displays the dynamic response of the gold NEEs for successive additions of a fixed amount of pesticides under optimised experimental conditions. Gold NEEs exhibited a rapid and sensitive response to the change of pesticides concentration. Table 1 shows that sensitivity and the correlation coefficient of calibration curve of gold NEEs were better than those of bare GC electrode. The results prove that the gold NEEs have good electrocatalytic behaviour.

The detection limit of phoxim was lower than the value 6.7 μM reported by Zhang *et al.* [18] using ceria nanoparticles-nafion film.

3.8 *Interference*

To assess the selectivity of the sensor, 12 possible interferents was investigated. Table 2 shows that few substances interfere with the determination of pesticides except ascorbic acid, indicating the oxidation of ascorbic acid at the applied potential (+0.7 V).

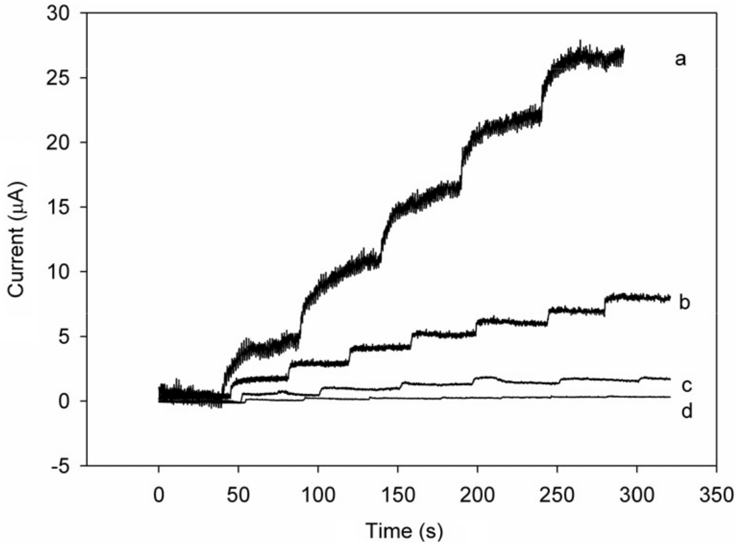


Figure 8. Dynamic response of different electrodes to successive addition of pesticides with 0.5 mM step in 0.067 M phosphate buffer (pH 7.5) at applied potential of 0.7 V *vs*. SCE. (a): gold NEEs with phoxim added; (b): gold NEEs with dimethoate added; (c): bare GC with phoxim added; (d): bare GC electrode with dimethoate added.

Table 1. Response characteristics of electrode to pesticides.

	Gold NEEs		Bare GC electrode	
Parameters	Phoxim	Dimethoate	Phoxim	Dimethoate
Linear equation	$i = -0.26 + 855.8 \times C$	$i = -0.12 + 703.9 \times C$	$i = 0.08 + 251.7 \times C$	$i = 0.18 + 80.8 \times C$
Linear range	5.9×10^{-5} to 1.0×10^{-2} M	6.3×10^{-5} to 1.1×10^{-2} M	1.9×10^{-4} to 8.7×10^{-3} M	5.0×10^{-4} to 8.3×10^{-3} M
Detection limit	4.8×10^{-6} M	5.3×10^{-6} M	1.0×10^{-4} M	3.0×10^{-4} M
Correlation coefficient	0.993	0.993	0.991	0.979

However, heavy metal ions, which can inhibit AChE, have no significant interference to this sensor. This result proved that the gold NEEs sensor had better selectivity than the biosensor based on the inhibition of pesticide to AChE.

3.9 *Real sample analysis*

As a preliminary evaluation of the validity of the proposed electrochemical sensor, the recovery of pesticides in spinach samples was tested. Varying amounts of phoxim and dimethoate was added to the spinach samples (Table 3). The recoveries are satisfactory. This results shows that the gold NEEs could be used for the determination of phoxim and dimethoate.

Table 2. Possible interferences tested with the gold NEEs.

	Phoxim		Dimethoate	
	$C_{interferences}/C_{phoxim}$	$i_{interferences}/i_{phoxim}$	$C_{interferences}/C_{dimethoate}$	$i_{interferences}/i_{dimethoate}$
Chlorothalonil	5.1	0.10	6.0	0.03
Citric acid	4.4	0.04	4.0	0.11
Glucose	7.4	0.01	4.0	0.06
Alanine	3.4	0.04	5.1	0.04
Ascorbic acid	3.4	6.9	2.0	10.9
Tartaric acid	3.4	0.08	3.0	0.12
Oxalic acid	3.4	0.03	6.0	0.16
Glutamic acid	3.4	0.01	5.1	0.15
Pb^{2+}	3.4	0.08	6.0	0.05
Cd^{2+}	4.4	0.06	6.0	0.06
Hg^{2+}	4.4	0.14	6.0	0.15
Cu^{2+}	4.4	0.16	6.0	0.03

Table 3. Recovery tests for pesticides in spinach sample.

Phoxim			Dimethoate		
Adding concentration (M)	Recovery concentration (M)	Recovery (%)	Adding concentration (M)	Recovery concentration (M)	Recovery (%)
3.0×10^{-4}	3.2×10^{-4}	106.7	3.0×10^{-4}	3.1×10^{-4}	103.7
6.0×10^{-4}	5.7×10^{-4}	95.0	6.0×10^{-4}	6.4×10^{-4}	106.7
8.9×10^{-4}	8.7×10^{-4}	97.8	8.9×10^{-4}	8.6×10^{-4}	96.9

3.10 *Repeatability and stability of the gold NEEs*

The repeatability of the response current of the gold NEEs was studied at a phoxim concentration of 0.5 mM. The variation coefficient was 4.02% for five successive assays. The stability and lifetime of the electrode were tested by measuring the electrode response with 0.5 mM of phoxim over 150 days. The response current of the sensor decreased to 94.5% after 120 days which is better than that of the biosensor based on the inhibition of pesticide to AChE [4]. When not in use, the electrode was stored dry at room temperature.

4. Conclusion

In this paper, gold nanowire was synthesised by electrodeposition. Based on the electrochemistry oxidation of pesticides at 0.7 V, the direct detection of gold NEEs toward phoxim and dimethoate has been studied. The nanostructuring improves analytical performances of the corresponding sensors compared with conventional electrodes. The possible interferents such as chlorothalonil, citric acid and heavy metal ions have no significant interference. The determination of pesticides in a vegetable sample was satisfactory. Gold NEEs displayed higher selectivity and a better detection limit. Besides, due to the omission of enzyme and the reactivation of enzyme, the simpler operation procedure and the longer lifetime of the sensor makes it superior to other techniques.

Acknowledgements

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