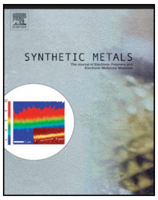
Synthetic Metals 190 (2014) 13–19

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Electrochemical sensor based on polyaniline nanofibers/single wall carbon nanotubes composite for detection of malathion

Shaker Ebrahim[a,*], Radwa El-Raey[b], Ahmed Hefnawy[a], Hesham Ibrahim[b], Moataz Soliman[a], Tarek M. Abdel-Fattah[c]

[a] *Department of Material Science, Institute of Graduate Studies and Research, Alexandria University, PO Box 832, Alexandria, Egypt*
[b] *Department of Environmental Studies, Institute of Graduate Studies and Research, Alexandria University, PO Box 832, Alexandria, Egypt*
[c] *Applied Research Center, Jefferson National Lab and Department of Molecular Biology and Chemistry, Christopher Newport University, Newport News, VA 23606, USA*

ARTICLE INFO

Article history:
Received 28 May 2013
Received in revised form 5 January 2014
Accepted 21 January 2014
Available online 13 February 2014

Keywords:
Polyaniline
Biosensor
Malathion
Differential pulse voltammetry
Carbon nanotubes

ABSTRACT

Detection of malathion (organophosphorous pesticide) based on composite of polyaniline nanofiber and single walled carbon nanotube deposited onto graphite electrode was investigated. >Fourier transforms infrared and UV–vis absorption spectra, X-ray diffraction, scanning electron microscope and cyclic voltammetry were used to characterize the prepared polyaniline. Malathion concentration was detected using differential pulse voltammetry technique at polyaniline–single wall carbon nanotubes modified graphite electrode. The fabricated polyaniline–single wall carbon nanotubes modified graphite electrodes have exhibited higher accuracy toward the reduction of malathion. Malathion was found to exhibit one well-defined reduction peak at pH 7. A linear response to malathion in the concentration range from 2.0×10^{-7} M to 14.0×10^{-7} M was observed. The minimum detection limit in the linear range for the modified electrodes was 2.0×10^{-7} M malathion. It was found that the single wall carbon nanotubes improved the sensitivity of the polyaniline salt graphite electrode from 5.4 mA/μM for polyaniline salt to 7.22 mA/μM.

1. Introduction

Environmental pollution is a serious concern in recent times due to the damage of the ecosystem around the world. Among the pollutants, pesticides are considered as hazardous chemicals used in agriculture [1]. Organophosphorous pesticides (OPs) are a group of organic pesticides that have high toxicity. The residue of the OPs in the natural environment generates a lot of pollution problems because of their lack of specificity as they affect non-target species. Malathion (*S*-1,2-bis(ethoxycarbonyl)ethyl *O*,*O*-dimethyl phosphorodithioate) is one of the most commonly used OPs, especially in Egypt. Malathion is also a broad spectrum agricultural insecticide used to control insects in fruits, vines, ornamentals, vegetables, field crops, glasshouse crops and in forestry. Humans can be exposed to malathion through ingestion, inhalation and absorption through the skin. Malathion is rapidly and effectively absorbed by all routes including via the gastrointestinal tract, skin, mucous membranes and lungs. Acute symptoms of malathion poisoning at high doses include nausea, headache, tightness in the chest, unconsciousness, convulsions and a “prolonged worsening illness”. Malathion can also act to suppress the immune system at relatively high doses [2]. The traditional techniques for detection of organophosphorous pesticides are chromatography including gas chromatography and high performance liquid chromatography. However, these methods have several disadvantages including high cost, long analysis time, necessity of highly trained personnel and inability to be used for continuous monitoring [3]. Biological techniques such as immunoassay and biosensors are also used for the determination of organophosphorous pesticides. Except for the same limitations encountered in chromatography techniques, another problem is the loss of activity of the acetylcholinesterase irreversibly inhibited by organophosphorous pesticides [4].

Electrochemical sensors using differential pulse voltammetry (DPV) have been developed for the determination of organophosphorous pesticides. DPV is often used to make electrochemical measurements of extremely small amounts of chemicals because in these measurements, the effect of the charging currents can be minimized, and thus high sensitivity can be achieved. Organophosphorous pesticides electrochemical determination was performed using nano-TiO_2 polymer film electrode [5], gold nanofibers-coated multiwall carbon nanotube-modified electrode [6], and multiwalled carbon nanotubes–poly(acrylamide)

---

* Corresponding author. Tel.: +20 124879137/+20 1224879137; fax: +20 34285792.
E-mail addresses: shebrahim@alex-igsr.edu.eg, shakerma2006@yahoo.com (S. Ebrahim).

0379-6779/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.synthmet.2014.01.021

nanocomposite film modified electrode [7], anionic liquid single-walled carbon nanotube paste coated glassy carbon electrode [8], gold nanofibers and Nafion film modified glassy carbon electrode [9], gold nanofibers–carbon nanotubes modified glassy carbon electrode [10], and stearic acid modified glassy carbon electrode [11].

Conducting polymers have a great deal of potential for applications due to their light weight, conductivity, mechanical flexibility and chemical stability; these application include light emitting devices, photovoltaic applications, electromagnetic shielding and chemical sensors [12]. Among the various conducting polymers, polyaniline (PANI) is an extensively studied polymer because of its high electrical conductivity, oxidative properties, environmental stability, ease of preparation and low fabrication cost [13]. Depending on the method of preparation PANI has three different fundamental forms: leucomeraldine (fully reduced), emeraldine base (EB: half oxidized) and pernigraniline (fully oxidized). The only electrically conducting one is the emeraldine salt form (ES: half oxidized), which is the protonated form of PANI-EB [14,15]. Conducting polymers have been used widely in the development of chemical sensors as the selective layer. The great deal of conducting polymer based sensor over the conventional techniques is that the conducting polymers have the potential to exhibit improved response properties and are sensitive to small perturbations. Conducting polymer based electrochemical sensors play an important role in the improvement of public health and the environment because rapid detection, high sensitivity, small size and specificity are achievable for environmental monitoring [16]. Electrochemical sensors based on polyaniline for detection of dopamine, aqueous ammonia and calcium ion Ca^{2+} were reported [17–19].

To our best knowledge, there are no voltammetric methods that have been published for the determination of OPs using polyaniline–carbon nanotube modified graphite electrode. In this work, nanofibers of dodecylbenzene sulfonic acid (DBSA) doped PANI were prepared and characterized using infrared spectra, ultraviolet–visible spectra, scanning electron microscope, X-ray diffraction, and cyclic voltammetry. The use of DPV technique to determine the concentrations of the malathion using PANI–carbon nanotube modified graphite electrode is reported for the first time.

2. Experimental

2.1. Materials

Aniline monomer was obtained from (Sigma Company). The dodecyl benzene sulphonic acid was obtained from (Oil Extracts Company Egypt). Sodium dihydrogen orthophosphate, disodium hydrogen orthophosphate, orthophosphoric acid and sodium hydroxide were purchased from (El-Gomhoria Chemical Company Egypt). Acetone, chloroform, hydrogen peroxide and hydrochloric acid were purchased from (El-Gomhoria Chemical Company Egypt). All solutions were prepared in double distilled water.

2.2. Preparation of polyaniline

Polyaniline hydrochloride was prepared by chemical oxidative polymerization with hydrogen peroxide as the oxidant. Typically, 8 g of aniline was dissolved in 900 ml hydrochloric acid 1 M, and then 0.02 g of ferrous chloride ($FeCl_2$) was dissolved in 225 ml water. The two solutions were then mixed in a beaker and stirred with a magnetic stirring bar. During stirring, 100 ml of hydrogen peroxide (H_2O_2) (6%) was drop wise added to the solution to initiate the polymerization of polyaniline. The stirring was continued for 48 h to ensure the completion of polymerization. The green powder of polyaniline hydrochloride was collected on a filter paper using a vacuum filtration system and washed with double distilled water until the filtrate became colorless, then dried at 50 °C for 24 h. The PANI hydrochloride was undoped with ammonia solution (5%) and stirred for 3 h. The blue powder of polyaniline base (PANI-EB) was collected on a filter paper using vacuum filtration and washed with water until filtrate became neutral, then dried at 50 °C for 24 h. For doping the EB form, 0.1 g of PANI-EB powder was pasted with 0.25 g of dodecylbenzene sulphonic acid (DBSA) and dissolved in 25 ml of chloroform. The green solution of polyaniline in the emiraldine salt (PANI-ES) was obtained.

2.3. Preparation of modified working electrode

Before modification, the graphite electrode (1 cm in diameter) was washed with double distilled water. EB was dissolved in dimethylformamide. The graphite electrode was immersed in 2 ml of the solution of PANI-ES or PANI-EB for 48 h and dried for 30 min at 50 °C. The graphite electrode was also modified using solution of PANI-ES–carbon nanotube where 0.0016 g of single walled carbon nanotube (SWCNT) was added to 2 ml of PANI-ES and stirred in ultrasonic for 15 min.

Metallic SWCNTs were synthesized by chemical vapor deposition (CVD) of methane at 1193 K on iron-based catalysts as described in detail in reference [20]. For a methane CVD experiment, 10 mg of the catalysts was placed in a quartz tube mounted in a tube furnace. An argon flow was passed through the quartz tube as the furnace was heated to reach 1193 K. The Ar flow was then replaced by methane (99% purity) at a flow rate of 1500 cm^3/min under 1.25 atm. head pressure. The methane flow lasted for 10 min and subsequently was replaced by argon, and the furnace was cooled to room temperature. The diameter of an individual single wall nanotube was found to be equal to 1.05 nm.

2.4. Characterization techniques

Fourier transform of infrared (FTIR) spectra of PANI-ES and PANI-EB were obtained using Perkin Elmer spectrophotometer. Ultraviolet–visible (UV/VIS) absorption spectra of PANI-ES and PANI-EB solutions were obtained using UV–Visible spectrophotometer (Evolution 600 double beam scanning UV–visible spectrophotometer, Thermo scientific, USA). X-ray diffraction scans were obtained using (X-ray 7000 Shimadzu-Japan) at room temperature in the Bragge angle range from 10 to 80 degree. Scanning electron microscope (SEM) of PANI-ES, PANI-EB and PANI-ES SWCNT composite were obtained using SEM “JEOL JSM 6360LA”, Japan. The prepared modified working electrodes were characterized using cyclic voltammetry (CV) using a poteniostat Gamry G750 potentiostat/galvanostat with pilot integration controlled by PHE200 software. Cyclic voltammetry was performed in the range of −0.5 V to 1 V with scan rate of 25 mV/s.

2.5. Detection of malathion using PANI working electrodes

Malathion was purchased from (Agro chemicals). A stock solution (0.00625 M) was prepared in Acetone. The stock solution of malathion was diluted with an appropriate amount of phosphate buffer (0.1 M) of pH 7 to obtain malathion solutions in a concentration range of 10^{-7} M. The detection of malathion was carried out in a three electrode voltammetric cell using platinum wire as a counter electrode, Ag/AgCl as a reference electrode and the PANI electrodes as working electrodes, with 50 ml of supporting electrolyte solution. DPV was performed in the range of −0.5 V to 0.7 V, step size of 20 mV, sample period of 5 s, pulse time of 0.1 s and pulse size of 20 mV. DPV was performed to different concentrations