Sensors and Actuators B 210 (2015) 475–482

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Sensitive determination of chlorpyrifos using Ag/Cu alloy nanoparticles and graphene composite paste electrode

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ARTICLE INFO

Article history:
Received 1 September 2014
Received in revised form
27 December 2014
Accepted 5 January 2015
Available online 12 January 2015

Keywords:
Graphene
Ag/Cu alloy nanoparticles
Carbon paste electrode
Chloropyrifos
Differential pulse adsorptive stripping voltammetry
Well waters and soil samples

ABSTRACT

A novel Ag/Cu alloy nanoparticles and graphene nanocomposite paste electrode was fabricated and its electrochemical activity was investigated using cyclic voltammetry and electrochemical impedance studies. Electrochemical reduction of chlorpyrifos using the nanocomposite produced peak signal based on $2e^-$ reductive cleavage of C—Cl bond in trichloropyridine moiety. Increase in peak currents and decrease in overpotential for chlorpyrifos was observed for Ag/Cu–graphene nanocomposite compared to Ag–graphene, Cu–graphene, graphene paste and carbon paste electrodes. This could be attributed to the synergistic combination of graphene and Ag/Cu alloy nanoparticles with good adsorption, large surface area, increased active sites leading to fast electron transfer rates and high electrical conductivity of nanocomposite. A differential pulse adsorptive stripping voltammetric method was developed by using the above electrode for highly sensitive determination of chlorpyrifos under optimum instrumental and working conditions. A calibration plot of chlorpyrifos was studied over concentration range, 0.01–100 nM and detection limits of 4×10^{-12} M were achieved. The method was successfully applied to well waters and soil samples and recovery values were in good agreement with HPLC–UV method.

1. Introduction

Chlorpyrifos is an active member of OP pesticides widely used for pest control in agriculture and urban areas. Its toxic mechanism is based on the inhibition of acetyl choline esterase and on accidental entry into fish, birds and mammals causes similar neurotoxic effect. Hence, effective control of its residues in environment calls for highly sensitive analytical methods. The most commonly used ones are based on gas chromatography, high performance liquid chromatography coupled to ultraviolet–visible (UV–Vis) and mass spectrometry (MS) detectors [1–4]. These techniques are costly, sophisticated, time-taking and are mostly laboratory-oriented involving multiple sample extraction and clean-up steps. Different analytical approaches based on immunoassay, chemiluminescence, Fourier transform infrared spectroscopy (FTIR) were also reported [5–7]. Spectrophotometry was used with first ratio spectra derivative and boosting partial least squares for simultaneous determination of chlorpyrifos and atrazine, chlorpyrifos and carbaryl, respectively [8,9]. By using artificial neural networks and phosphotriesterase based sensors, selective detection of chlorpyrifos and chlorfenvinfos were achieved [10,11]. These methods possess low sensitivity and often involve multiple laboratory steps. Owing to their simple operation and cheap instrumentation, polarography and voltammetry studies are carried out for the determination of chloropyrifos using mercury electrodes, polyethylene dioxythiophene modified glassy carbon electrode, sepiolite modified carbon paste electrode [12–16].

A variety of electrochemical biosensors are developed based on acetylcholine esterase (AChE), tyrosinase and DNA immobilized on metal nanoparticles, carbon nanotubes and conducting polymers [17–22]. Alternative methods for chlorpyrifos such as optical fibre biosensor, surface plasma resonance immunosensor, amperometric immunosensor, photoelectrochemical sensor and impedance sensor are also reported [23–27]. Lately, ZnO nanoparticles-carboxylic graphene based ACHE sensor for chlorpyrifos and carbofuran was reported with wide linear range and low detection limits [28]. Most of above methods possessed narrow linear working range and others have high detection limits. In case of enzyme sensors though high sensitivity is achieved, various steps like immobilization, incubation and regeneration are involved. Hence, there exists a serious lack of simple, non-enzymatic highly sensitive voltammetric sensors for direct determination of chlorpyrifos.

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http://dx.doi.org/10.1016/j.snb.2015.01.016
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Development of electrochemical sensors is largely spurred by advances made in the field of carbon-based nanomaterials. The latest nanomaterial that caught the imagination of scientists worldwide is graphene and its composites. Graphene is a one-atom thick, two-dimensional sheet, sp^2 carbon based material with unique electrical, mechanical, thermal and optical properties [29,30]. Metal nanoparticles with their special properties play 5-fold role in the built-up of (bio)sensors as biocompatible supports for enzyme immobilization, as electrocatalysts, as promoters of electron transfer rate, as biomolecular labels and even as reactants in ion selective field effect transistor (ISFET) devices [31]. Integrated devices of graphene and metal nanoparticles provide potential sensing platforms for highly sensitive detection of analytes. Graphene is usually combined with noble and base metal nanoparticles (Pt, Au, Ag and Cu) resulting in improved sensitivity for analytes such as OP pesticides, nitroaromatic compounds and glucose [32–35].

Bimetallic nanoparticles on combination with graphene provide new advantages to composites such as good stability, enhanced catalytic activity, high surface areas, increased active sites and biocompatibility [36,37]. Carbon paste electrodes are most promising in sensor field as they are cheap, easily prepared, possess wide potential window with low background currents. To improve sensitivity, modified carbon paste electrodes are fabricated using metal nanoparticles, carbon nanotubes and nanoclays [38–40]. Recently much focus is on graphene paste electrodes due to its high sensitivity and good catalytic activity [41–47]. Hence, the present work proposes a novel Ag/Cu–graphene composite paste electrode prepared by easy, reproducible method and it is employed for non-enzymatic sensitive determination of chloropyrifos using differential pulse adsorptive stripping voltammetry. The proposed method is successfully applied to well water and soil samples and validated with HPLC–UV method.

2. Experimental

2.1. Materials and methods

Graphene was obtained from Dropsens, Spain and Ag/Cu alloy nanoparticles (purity, Ag: 96–98%, size: ≤100 nm), Ag nanoparticles (purity, Ag: 99%, size: <100 nm) and Cu nanoparticles (purity, Cu: 99%, size: <100 nm), graphite, mineral oil and chloropyrifos standard were procured from Sigma-Aldrich, USA. All other chemicals were obtained from Merck, India and were of AR-grade. Britton–Robinson (BR) buffers of pH 2–10 were prepared from 0.04 M solution each of *O*-phosphoric acid, acetic acid, boric acid and the pH was adjusted using 0.2 M NaOH solution. A stock solution of chlorpyrifos (1 mM) was prepared in ethanol (AR-grade).

2.2. Instrumentation

All electrochemical studies were carried out using CHI 660D electrochemical workstation (CH Instruments, USA). A three electrode system consisting of Ag/Cu–graphene paste electrode (Ag/Cu–GRPE), Ag–graphene paste electrode (Ag–GRPE), Cu–graphene paste electrode (Cu–GRPE), graphene paste electrode (GRPE) and carbon paste electrode (CPE) were employed as working electrodes, a Ag/AgCl (3 M KCl) electrode as a reference electrode and Pt wire as counter electrode were used. Measurement of pH for buffer and test solutions were carried out using an Elico LI-120 pH metre. All experimental recordings were carried out at a room temperature of 25 °C. HPLC–UV studies were carried out using Agilent 1100 series HPLC system equipped with UV detector (Agilent, USA) and a XDB-C_{18} with dimensions: 250 mm × 4.6 mm (i.d.) and particle size: 5 μm column was used for separation. Mobile phase was a mixture of acetonitrile and Milli-Q water (75:25 (v/v)) with an injection volume of 20 μL and a flow rate of 1 mL/min at a temperature of 25 °C.

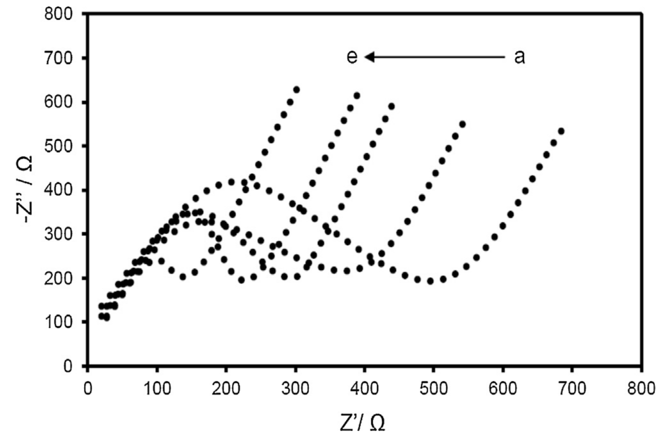

Fig. 1. Nyquist plots of (a) CPE, (b) GRPE, (c) Cu–GRPE, (d) Ag–GRPE, (e) Ag/Cu–GRPE using 5 mM $[Fe(CN)_6]^{3-}$ in 0.1 M KCl.

2.3. Fabrication of Ag/Cu–graphene paste electrode (Ag/Cu–GRPE)

The present working electrode, Ag/Cu–GRPE is prepared from a black, homogeneous paste of Ag/Cu alloy nanoparticles, graphene (GR), and mineral oil mixed well in optimum amounts of 65/5/30 (w/w) % using mortar and pestle. The paste is inserted into the core of teflon tube with the help of spatula and electrical connection was given by means of a copper wire from the other end of the tube. The surface of the paste electrode is pressed against a smooth surface of tissue paper and dried prior to its use for voltammetric studies. Further Ag–GRPE and Cu–GRPE (graphene/Ag or Cu nanoparticles/mineral oil, 65/5/30 (w/w) %), GRPE (graphene/mineral oil, 70/30 (w/w) %) and CPE (graphite/mineral oil, 70/30 (w/w) %) were fabricated and were employed in present electrochemical studies.

2.4. Electron transfer resistance of Ag/Cu–GRPE

Electrochemical impedance spectroscopy (EIS) readily provides information on modified electrode interfaces with respect to changes in the electron transfer resistance towards redox molecule. Hence, impedance studies were carried out with 5 mM $[Fe(CN)_6]^{3-}$ in 0.1 M KCl using frequency range 0.1 to 10^6 Hz (Fig. 1) with AC signal of 5 mV. Nyquist plots were obtained consisting of semicircular part at low frequencies and linear part at high frequencies. Electron transfer resistance, R_{ct} can be recorded from the semi circular diameter of the plot. R_{ct} values for different electrodes were found to increase in the following order, Ag/Cu–GRPE (140 Ω) < Ag–GRPE (230 Ω) < Cu–GRPE (290 Ω) < GRPE (380 Ω) < CPE (500 Ω). Compared to all electrodes including CPE, low electron transfer resistance is obtained for Ag/Cu–GRPE because of its large surface area, high electrical conductivity, more electrical conduction pathways resulting in fast electron transfer rate.

2.5. Differential pulse voltammetric procedure for chlorpyrifos

A working standard of chlorpyrifos (100 nM) was prepared from the stock solution using double distilled water. 10 mL of the test solution containing 1.0 mL of the working standard and 9.0 mL of the BR buffer (pH 2.0) was taken into electrolytic cell. The solution was purged with nitrogen gas for 15 min prior to measurement. The electrode is kept at −0.2 V for a period of 90 s during preconcentration step at a stirring rate of 2500 rpm. Stirring is stopped