Electrochemistry Communications 38 (2014) 15–18

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Short communication

Non-enzymatic organophosphorus pesticide detection using gold atomic cluster modified electrode

Sukeri Anandhakumar, Krishnamoorthy Dhanalakshmi, Jayaraman Mathiyarasu *

Electrodics and Electrocatalysis Division, CSIR-Central Electrochemical Research Institute, Karaikudi - 630 006, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 6 October 2013
Received in revised form 16 October 2013
Accepted 16 October 2013
Available online 24 October 2013

Keywords:
Non-enzymatic sensor
Gold atomic clusters
Organophosphorus pesticides
Square wave voltammetry

ABSTRACT

In this work, we report the detection of organophosphorous pesticides, particularly methyl parathion using gold atomic clusters (AuACs) non-enzymatically employing square wave voltammetry (SWV). Synthesis of surfactant stabilized gold atomic clusters on a polycrystalline gold electrode was executed by a simple potentiodynamic cyclic voltammetry technique. The clusters are characterized using UV–visible spectroscopy and transmission electron microscopy techniques. The electroanalytical results exhibited linear behavior in the micro (10–80 μM) as well as nanomolar (1–10 nM) concentration ranges and the detection limit is found to be 0.65 nM (S/N = 3). The proposed sensor matrix is evaluated with real samples and the results are in good agreement with high performance liquid chromatographic (HPLC) analysis.

1. Introduction

Organophosphorus (OPs) compounds are intrinsically used as pesticides and chemical warfare agents due to its low cost and effective activity for pest control [1]. They exert toxic effect when inhaled or absorbed through skin because, such compounds are highly neurotoxins [2]. Continuous exposure of OPs causes severe effects, such as headache, dizziness, blurred vision, nausea & vomiting, reduced heart beat, loss of coordination, fever, coma and death [3]. Therefore, rapid detection of OPs is a serious concern for human health and environmental safety [4]. A number of techniques are available for OP detection including spectroscopy [5], gas or liquid chromatography [6,7] and mass spectrometry [8]. They are more complicated, requiring centralized laboratories, analytical resources and often result in a lengthy turnaround time [9].

Recently, enzyme/antibody based immuno assays are reported for the sensitive and accurate detection of organophosphorus pesticides. However, the poor chemical/physical stability of the enzyme and antibody limits their applications [10]. The enzyme activity is lost due to the contamination of heavy metals and pesticides which causes lack of selectivity [11]. On the other hand, solid-phase extraction was introduced to enrich and detect OPs to avoid the biological reagents [12]. Carbon nanotubes (CNTs) have been reported as excellent sorbent material for nitroaromatic OP molecule adsorption due to its π-conjugated interaction upon the benzene ring [13]. Zirconia (ZrO_2) was used as a selective sorbent for OP compounds, which possess strong affinity to phosphoric groups [3]. However, ZrO_2 readily loses their surface area when used as high surface area catalyst [2]. Therefore, it is highly desirable to develop a simple, fast, sensitive, field deployable and user-friendly analytical platform for the analysis of OPs in the environmental samples.

Nanostructure materials have enormous significance due to their remarkable applications in various areas such as optical, electrical and magnetic devices, catalysis and sensors [14,15]. It is reported that gold clusters are more catalytic than their bulk or nano counterparts [16,17]. This is because of the high surface to volume ratio of the gold atomic clusters having large number of binding site accessible for catalysis and sensing. It is expected here that organophosphorus pesticides may occupy/utilise these binding sites and this may enhance a catalytic reduction of methyl parathion. Surprisingly, little attention has been given to the atomic cluster for the voltammetric sensing applications. Recently, Nambiar et al., reported electrocatalytic sensing of cysteine using hybrid gold atomic cluster-cobalt oxide scaffolds and also ultrasensitive voltammetric determination of catachol at gold atomic cluster/poly (3,4-ethylenedioxythiophene) nanocomposite electrodes [15,18]. However, to the best of our knowledge, no attempt has been made for the development of voltammetric determination of OPs using gold atomic cluster. In addition, nitroaromatic OP pesticides, such as methyl parathion, paraoxon, and fenitrothion exhibit good redox behaviour at the electrode surface [19]. Therefore, it is anticipated that the high surface to volume ratio and electronic structure of gold atomic cluster may facilitate the electron transfer processes and enhance the sensitivity towards the OP detection.

In this work, a "*non-enzymatic*" electrochemical sensor based on gold atomic clusters and its enhanced sensitivity towards OP pesticide particularly methyl parathion is reported for the first time. Compared to the bulk gold and gold nanoparticles modified electrodes, the AuACs show enhanced sensitivity with the required selectivity towards the reduction of methyl parathion.

* Corresponding author. Tel.: +91 4565 241340; fax: +91 4565 227779.
E-mail address: almathi@cecri.res.in (J. Mathiyarasu).

1388-2481/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.elecom.2013.10.017

2. Experimental

2.1. Reagents

All chemicals, methyl parathion (Aldrich), acetonitrile, cetyltrimethylammonium bromide (CTAB), 4-nitrophenol, nitrobenzene, nitroaniline, and potassium chloride (Merck) were used as-received and Milli-Q water was used in all experiments.

2.2. Apparatus

All the electrochemical measurements were performed with a PalmSens portable electrochemical analyzer (BV, Netherland) using a conventional three-electrode system. The electrogenerated AuACs on a gold electrode surface, platinum foil and Ag/AgCl (3.0 M NaCl) were used as working, counter and reference electrodes respectively. All the potential is reported versus Ag/AgCl reference electrode at ambient temperature (25 ± 1 °C). Square wave voltammetry (SWV) measurements were carried out in 0.1 M KCl solutions after purging argon gas for 20 min in order to remove dissolved oxygen. For SWV measurements, the current versus potential profile was measured in the cathodic direction with the following parameters; step potential: 5 mV; frequency: 10 Hz; amplitude: 50 mV; and equilibrium time: 5 s.

UV–visible measurements were carried out using BioTek Synergy H1 hybrid multi-mode microplate reader (Gen5 software) and transmission electron microscopic (TEM) images were recorded using a Philips CM 200 transmission electron microscope working at 200 keV. For TEM analysis, samples were prepared drop-casting the AuAC solution onto the carbon-coated copper grids.

2.3. Electrogeneration of gold atomic clusters (AuACs) on polycrystalline gold surface

The AuACs were prepared according to a recent report [20] and briefly, pre-treated polycrystalline gold electrode was cycled in a CTAB aqueous solution (50 mM) in the potential region of 0 to 1.7 V for 20 cycles at a scan rate of 0.1 V s^{-1}. An orange–yellow colour was appeared on its surface indicated the formation of AuACs. CTAB played a dual role as supporting electrolyte as well as stabilizer for electrogenerated AuACs. Then, the electrode was washed with Millipore water and dried at room temperature. The electrode coated with gold atomic clusters was then employed for the reduction of methyl parathion. Citrate stabilized gold nanoparticles (AuNPs) were also prepared to study the relative performance.

3. Results and discussion

3.1. Optical and microscopic characterization of AuACs

Fig. 1A shows the UV–visible absorbance spectrum of electrochemically synthesised AuACs. The spectrum structured with bands at 390, 480, 540 and 740 nm and ascribed to the inter-band (d-sp) and intra-band (sp–sp) electronic transitions. The spectral response reveals a molecule like behaviour that is entirely different from the SPR band of the spherical gold nanoparticles [20]. Dispersion of AuACs cast over carbon-coated copper grid for TEM analysis as well. Fig. 1 (B to D) shows the TEM micrographs of the clusters at different magnifications. These images clearly reveal that the electrochemically prepared gold particles are of atomic cluster level

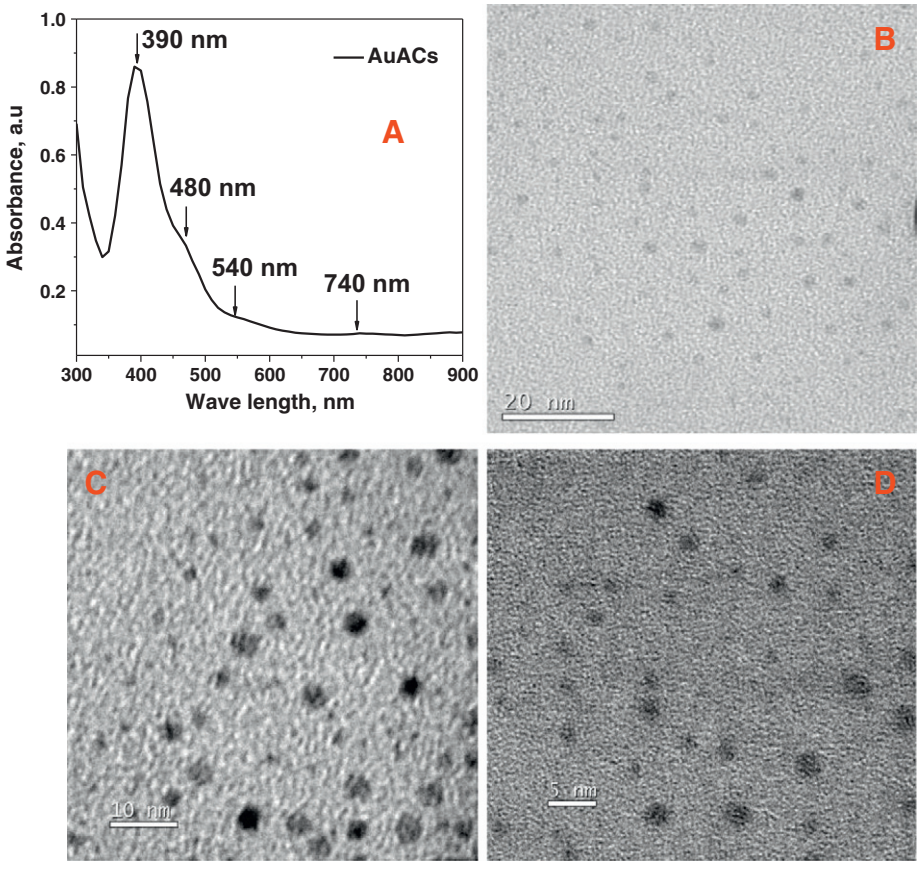

Fig. 1. Optical and microscopic characterisation of electrochemically prepared AuACs. (A) UV–visible spectrum; (B–D) TEM images at different magnifications.