



# A biocompatible nano TiO<sub>2</sub>/nafion composite modified glassy carbon electrode for the detection of fenitrothion

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## ABSTRACT

A biocompatible nano TiO<sub>2</sub>/nafion composite modified glassy carbon electrode was developed for the detection of fenitrothion. This composite electrode was characterized by SEM, XRD, UV-visible, FTIR, TGA and cyclic voltammetry. Electrochemical techniques such as cyclic voltammetry, differential pulse voltammetry and amperometry were used for the detection of fenitrothion. Such modified electrode produced high sensing current which is one of the promising characteristics of the electroanalytical sensor. The linear relationship between sensing current and concentration is obtained in differential pulse voltammetry technique for the fenitrothion concentration ranging from 0.2 to 4 μM with LOD and LOQ of 0.0866 and 0.2889 μM respectively. The peak currents were reproducible with the relative standard deviation of 5.1% ( $n = 6$ ). The peak current obtained from the cyclic voltammetry is stable even after 50 cycles. The recovery rate for the spiked water sample was calculated and compared with the data obtained by HPLC analysis.

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## 1. Introduction

Pesticide is a substance or mixture of substances used to kill any pest. Pesticides can increase the agricultural production by preventing the crop losses from insects and other pests. Organophosphorus (OP) pesticides are important classes of pesticides which are extensively used throughout the world. As a result of excessive usage of these pesticides, there is a possibility to run-off these toxic compounds into natural water bodies. In addition, pesticides and their residues can exist in the soil for long time and produce adverse effect to human beings and animals [1,2]. Moreover, all OP pesticides inhibit the nervous system enzyme acetylcholinesterase (AChE) and hence they are termed as anticholinesterase insecticides [3]. So in the environmental monitoring, rapid sensing of these pesticides becomes necessarily important for our homeland security and health protection [4–7]. Various analytical techniques such as gas or liquid chromatography [8–10], mass spectrometry [11] have been developed for the sensing of OP pesticides in the environment. Due to the high cost, laborious, requirement of highly qualified personnel, utilisation of the large amount of organic solvents and maintenance prohibit the wide usage of these instruments in the analysis of pesticides. Thus, there is a need for compact, inexpensive sensing devices for pesticides detection. Electroanalytical sensors are more suitable to full-

fill the above requirements because of its easy fabrication, low cost, compact nature, low detection limits and also can perform the analysis in the field condition [12–14].

Fenitrothion is one of the OP pesticides which shows good redox behavior at the electrode surface. Polarographic determination of fenitrothion has been reported [15]. The toxicity of the mercury cannot be ignored in the polarographic determination method. Moreover, the reduction current obtained only in nano-ampere and the appearance of two peaks complicates the analysis. Liquid chromatography with electrochemical detection using carbon electrodes has been used to determine fenitrothion in river water samples. The reported detection limit is in the ppb level [16]. The liquid chromatography is costlier analytical technique. Moreover, it produces more organic solvent wastes which are not suitable for the environment. Differential pulse stripping voltammetry with chemometrics [17] and adsorptive stripping square wave voltammetry [18] using HMDE have been reported for the determination of fenitrothion in the mixture of other OP pesticides and in river water samples with the detection limits of 0.0162 μM and 0.0057 μM respectively. Square wave voltammetric determination of fenitrothion in commercial samples on HMDE has also been reported with the detection limit in ppb level [19]. Eventhough lower detection limits were obtained for the above mercury based electroanalytical techniques, these methods are not advocated from the environmental point of view. Nano TiO<sub>2</sub> polymer film electrode has been reported for the voltammetric determination of fenitrothion with the detection limit of 0.001 μM [20]. The preparation of this nano TiO<sub>2</sub> polymer film

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electrode is not simple and involves many steps. In a recent publication carbon ceramic electrode has also been employed for the determination of fenitrothion in river water samples and the reported detection limit is 0.0016  $\mu\text{M}$  [21]. This carbon paste electrode has to be prepared afresh for each measurements.

Many nonmercury based solid electrodes and chemically modified electrodes have been reported as above for the determination of pesticides. However, the electrochemical response is strongly influenced by the surface of the working electrode. During electrochemical measurements for the pesticide molecules on the solid electrode the sensing current decreases with time. This may be due to the fouling of the working electrode by the adsorption of the reduction products of the pesticide molecules. This is one of the major problem in producing reproducible electrochemical responses at solid electrodes [1]. Various chemical modifications have been reported to improve the performance of the electrode in pesticides sensing [1,22–26]. The conducting polymers have been used as the modifier because of its various advantages like increasing the permeability of the electroactive species to the electrode surface, simple modification procedure, stability of the film for longer time and produce reproducible results over the bare electrodes [27–29]. Even though various conducting polymers are used as electrode modifier, nafion is perhaps the most interesting because of its dual function. It attracts the cationic species towards the electrode surface and repels the anionic species away from the electrode surface. Moreover, it also possesses thermal stability, chemical inertness, mechanical strength and antifouling properties [30–35]. Metal and metal oxide nanoparticles are also used as the electrode modifier because they possess extreme small particle size, high surface area, high surface-to-volume ratio and better catalytic activity [36–39]. Zirconia ( $\text{ZrO}_2$ ) nanoparticles were used as the electrode modifier for the electrochemical sensing of organophosphorus pesticides since it has strong affinity towards the phosphoric group [40]. Titania ( $\text{TiO}_2$ ) an inorganic metal oxide have been used in various sensor developments due to its high surface area, strong adsorptive ability, chemical inertness, thermal stability, nontoxicity and good biocompatibility [41–45]. Phosphate and carboxylic groups have the ability to bind on the  $\text{TiO}_2$  nanoparticles and enhance the electron transfer processes [46]. In recent years, the conducting polymers with metal oxide nanoparticles composites have attracted more attention for researchers [47–52]. The composite electrode consists of conducting polymer–metal nanoparticles enhance the facile flow of electronic charge when compared with the conducting polymer or the metal nanoparticles individually [53].  $\text{TiO}_2/\text{CNT}$  nanocomposite modified electrode was used for the electrochemical biosensing of cancer cells [54]. Nano  $\text{TiO}_2$  polymer film electrode has also been reported for the voltammetric determination of fenitrothion with higher sensing current compared to bare glassy carbon electrode [19]. The nano  $\text{TiO}_2/\text{nafion}$  has been used as the sensing anode for nitric oxide detection [55]. In our earlier report, the nanosilver/nafion composite modified glassy carbon electrode was successfully employed for the electrochemical sensing of methyl parathion and parathion [56]. In continuation of our efforts for the development of nanomaterials based sensor for pesticides a nano  $\text{TiO}_2/\text{nafion}$  composite modified glassy carbon electrode (GCE) for the electrochemical sensing of fenitrothion is reported in this paper. To the best of our knowledge, this is the first report for the sensing of fenitrothion at this composite modified electrode. The nano  $\text{TiO}_2/\text{nafion}$  composite electrode reported in this paper has the following advantages namely, it is biocompatible, non mercury based electrode, easy preparation and higher stability with higher sensing current. Cyclic voltammetry, differential pulse voltammetry and amperometry were used for electrochemical sensing of fenitrothion. The results were well consistent with the results obtained by high performance liquid chromatography. SEM and XRD were used

for the surface characterization of the composite film modified electrode. TGA was used to find out the thermal stability of the composite film. UV visible spectroscopy and IR spectroscopy were used to find out the interactions between the nafion and the  $\text{TiO}_2$  nanoparticles. Electrochemical characterization using cyclic voltammetry was also carried out.

## 2. Experimental

### 2.1. Apparatus

Cyclic voltammetry, differential pulse voltammetry and amperometry were performed with the computer controlled Autolab PGSTAT 30 (Eco Chemie, Netherlands) electrochemical system. A three-electrode configuration consisting of nano  $\text{TiO}_2/\text{nafion}$  coated GCE (Alfa Aesar 3 mm diameter) as the working electrode, platinum foil as the counter electrode and saturated calomel electrode (SCE) as the reference electrode was used. X-ray diffraction (XRD) patterns were recorded in a PANalytical diffractometer Model PW3040/60 X'pert PRO operating with  $\text{Cu K}\alpha$  radiation ( $k = 0.15406 \text{ nm}$ ) generated at 40 kV and 20 mA. Scans were done at  $3^\circ \text{ min}^{-1}$  for  $2\theta$  values between  $20^\circ$  and  $90^\circ$ . SEM was done with a Hitachi Model S-3000H with 10 kV (acceleration voltage). HPLC analysis carried out with an LC-10AT pump and SPD-10A detector (Shimadzu, Japan) at 254 nm with a Shimpack CLC ODS-18 column. FTIR spectrum of the composite was recorded by using Perkin Elmer (UK Paragon-500) spectrometer. UV visible spectra were recorded by using Cary 500 NIR–UV visible spectrometer. Thermogravimetric analysis was carried out by using SDT Q 600 (TA Instruments) thermal analyzer. Electrochemical experiments were carried out in a 10 mL voltammetric glass cell at room temperature ( $30 \pm 1^\circ\text{C}$ ). Prior to electrochemical measurements, the solutions were deoxygenated by purging with pure nitrogen for 15 min.

### 2.2. Reagents

Fenitrothion was purchased from Accu Standard, USA. Stock solution of fenitrothion (3607  $\mu\text{M}$ ) was prepared from methanol. Working solution was prepared daily by dilution with Britton–Robinson buffer (B–R) of pH 5.5. The B–R buffer solution of required pH was prepared by adding 0.2 M sodium hydroxide solution into the mixed acid, containing 0.04 M of each boric, ortho-phosphoric and acetic acids. Nafion (5 wt.% in aliphatic alcohols and water mixture) were purchased from Sigma–Aldrich (St. Louis, MO, USA). The nano  $\text{TiO}_2$  powder prepared by the procedure explained in Ref. [57] was used in this work. Other reagents used were of analytical reagent grade and double distilled water was used to prepare aqueous solutions throughout the experiments.

### 2.3. Preparation of nano $\text{TiO}_2/\text{nafion}$ composite film modified GCE

The GCE was hand polished with the fine emery paper (1/0, 2/0, 3/0, 4/0), rinsed thoroughly with doubly distilled water, cleaned successively in 10% NaOH solution, 1:1  $\text{HNO}_3\text{--H}_2\text{O}$  (v/v) and methanol each for 2 min and dried in air. Then 4 mg of nano  $\text{TiO}_2$  powder was dissolved in 4 mL of 0.5 wt.% nafion solution. The electrode was coated with 6.9  $\mu\text{L}$  of the nano  $\text{TiO}_2/\text{nafion}$  composite solution to cover the surface of the GCE by drop-dry method. The solvent was left to evaporate for 3 h in air whereupon uniform film was formed over the entire electrode surface. This nano  $\text{TiO}_2/\text{nafion}$  modified GCE was used for electrochemical experiments.

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