

# Two step electrochemical deposition of palladium and polyaniline on graphene dispersed glassy carbon electrode for electrochemical analysis of pesticide

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## Abstract

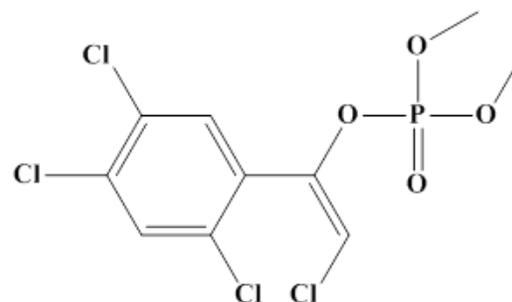
Herein we reported graphene (Gr) was firstly fabricated on glassy carbon electrode (GCE) by drop casting method, subsequently polyaniline (PAN) and Palladium (Pd) nanocomposite were fabricated by two step electrochemical depositing process on graphene dispersed glassy carbon electrode (Gr/GCE) and used as an electrochemical sensor for determination of Tetrachlorvinphos (TCP) pesticide in vegetables. Here most of the work has been focused on the preparation and characterization of modified electrode with cyclic voltammetry (CV) and scanning electron microscopy (SEM). The modified composite electrode unveiled significantly good voltammetric response on TCP. Square wave voltammetry (SWV) was used for determination of TCP at optimized conditions such as square wave frequency, step potential, pH of buffer, applied sample volume, accumulation potential and accumulation time. The well-defined reduction (C=C) peaks were acquired over the potential maximum around at -1.3V in acidic medium in Britton-Robinson (B-R) buffer solution at low current values. The low current peaks were obtained over the concentration of TCP at  $1.5 \times 10^{-6} \text{M}$  with lower detection limit and limit of quantifications are  $5.62 \times 10^{-10} \text{M}$  and  $2.65 \times 10^{-8}$  respectively. The composite modified electrode showed good stability and reproducibility. The proposed method was successfully applied for the present investigation with a great assure as an economical and simple sensor with furthermore a shorter analysis time and further the sensor also used for heavy metal detection in real samples. Copyright © 2016 VBRI Press.

**Keywords:** Graphene, polyaniline, palladium, cyclic voltammetry, tetrachlorvinphos.

## Introduction

Organophosphorous pesticides (OPs) are have been extensively used for pest control in agriculture due to their high insecticidal activity, acute toxicity and relatively short environmental persistence [1-5]. The usage of pesticides also founds a risk for water quality in agricultural areas owing to the fact that these components may pass through the soil and subsoil and pollute surface and ground water. Thousands of such cases, including several fatalities, are attributed to the normal agricultural use of pesticides. However, the extensive use of pesticides has badly impacted on the environment and human health. Tetrachlorvinphos [(Z)-2-Chloro-1-(2,4,5-trichlorophenyl)vinyl] dimethoxy phosphate (**Fig. 1**) was initially registered for use in the United States in 1966 by the U.S. Department of Agriculture. Tetrachlorvinphos was initially used on various food crops, livestock; agricultural uses include dermal application to livestock, as a larvicide in cattle, hog, goat, and horse feed, and in cattle feedlots and poultry houses. It is used for structural pest control and

for common outside usage to control flies. It has also been used on a different variation of crops, as well as fruits, grains, cotton and vegetables [6-9].



**Fig. 1.** Structures of Tetrachlorvinphos.

Graphene (Gr), a 2D monoatomic thick building block of a carbon allotrope, has arisen as a kind of new generation material of the twenty first century and it has drawn fabulous attention from both experimental and theoretical aspects [10]. It has been used in several areas

of fields of abundant research in recent years for the reason that of the unique electronic, thermal, and mechanical properties arising from its strict 2D structure and its potential technical applications [11-18].

Furthermore, numerous metal nanoparticles modified electrodes containing Pd, Au, and Pt as electro catalysts for electrochemical application [19-22]. Recently, in a comparative study on them the Pd nanoparticles were notorious as exceptional catalytic material for electrochemical application [23]. Pd nanoparticles were acquired either through electrodeposition or via chemical reduction of Pd salts [24-26]. Palladium nanostructures are of excessive focus due to their priceless, outstanding catalytic performance with the properties of lower cost, high efficiency and selectivity [27-29].

On the other hand the features and application of conducting polymers, such as polypyrrole polythiophene and polyaniline (PAN) have fascinated major interest in recent years [30-32]. Amongst these polymers polyaniline (PAN) was considered as one of the most favourable electrode materials due to its high capacitive characteristics and lower cost than many other conducting polymers [33]. Mainly, electroactive polymers and nanomaterial combined electrodes fetched distinctive attention for the detection numerous important chemical compounds. In noble metal nanoparticles, palladium keens an extraordinary importance because of its biocompatibility for the detection of various types of biological compounds [34]. Electrodeposition and electrochemical behaviour of palladium particles at electrochemical active polymers have more applications in various fields [35-38].

Nonetheless few reports have been reported on palladium and polymer combination of sensors such as Gordana *et. al* reported recent advances in polyaniline composites with metals, metalloids and nonmetals [39]. Anjali *et.al* reported nanocomposite of Pd–polyaniline as a selective methanol sensor [40]. Mamas *et.al* reported preorganized composite material of polyaniline and palladium nanoparticles with high electrocatalytic activity to methanol and ethanol oxidation [41]. Fen Guo *et. al* reported palladium dispersed in three-dimensional polyaniline networks as the catalyst for hydrogen peroxide electro reduction in acidic medium [42]. We are also reported in our previous work on palladium and graphene composites for pesticide analysis, another one polyaniline, graphene composite for drug metabolite analysis [43,44]. In recent Zhixiang *et. al* reported facile method to prepare Pd/graphene–polyaniline nanocomposite and used as new electrode material for electrochemical sensing [45] but it was on hydroquinone and catechol. Many chapters and books also reported on graphene modified electrodes for electrochemical sensors [46,47].

In the present study we prepared initially graphene was fabricated by drop casting on GCE then palladium and polyaniline were deposited using cyclic sweep according to our previous reports. Nevertheless to the best of my knowledge no any report on Pd/PAN/Gr composite in the literature for determination of Tetrachlorvinphos. The proposed method was successfully applied for the present investigation.

## Experimental

### *Apparatus and materials*

Electrochemical studies were carried out by Autolab PG STAT101 supplied by Metrohm Autolab B.V. Netherlands. A three electrode system comprising of a glassy carbon electrode modified with Palladium (Pd), polyaniline (PAN) and graphene (Gr) composites (Pd/PAN/Gr/GCE) as a working electrode. Graphene (Gr) obtained from dropsence Spain, hi purity PdCl<sub>2</sub> and polyaniline (PAN) obtained from Sigma Aldrich (India). Saturated Ag/AgCl/KCl as a reference electrode and Pt wire as a counter electrode obtained from local scientific labs. Electrode surface morphology study was carried out by SEM instrument model OXFORD INCA PENTA FETX3 CARL ZEISS from Japan. An Elico LI-120 pH meter supplied by Elico LTD, Hyderabad, India, was used to determine the pH of the buffer solution.

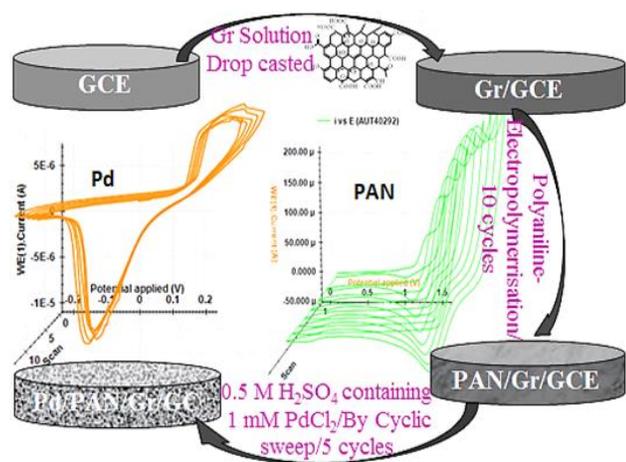
### *Chemicals and reagents*

All reagents were of analytical grade and ultrapure water was used during all the detection process. Pesticide standards TCP were obtained from local pesticide shop at Tirupati, India. Standard solutions 1.5×10<sup>-6</sup>M of TCP were prepared freshly obtained by dilution from stock solution (1×10<sup>-3</sup>M). Britten-Robinson buffer was prepared from 0.04 mol L<sup>-1</sup> solutions each of O-phosphoric acid, acetic acid, boric acid and the pH was adjusted using 0.2 mol L<sup>-1</sup> NaOH solution. All the chemicals and solvents used were of analytical grade obtained from Merck (Mumbai, India).dissolving these reagents in ultrapure water and adjusting to the desired pH with sodium hydroxide and hydrochloric acid solutions. All solutions were filtered through a 0.45 mm membrane filter and then degassed by sonication and evacuation. All other chemicals were of analytical grade and used without further purification.

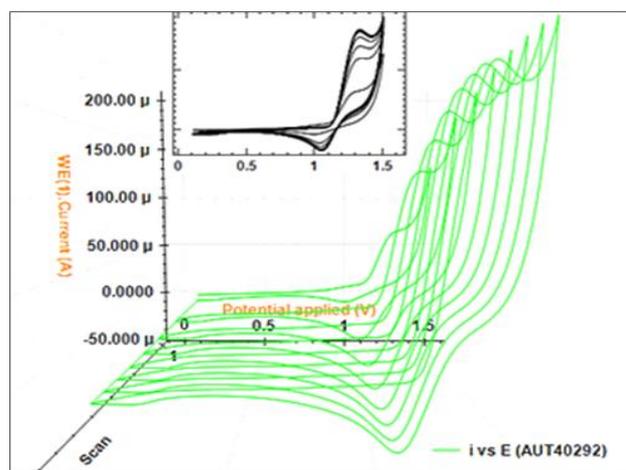
### *Preparation of Pd/PAN/Gr/GCE*

According to our previous work [43,44] the working electrode was prepared, briefly before fabrication of composites, a bare glassy carbon electrode (GCE) with 3 mm in diameter was polished with abrasive paper and soaked with ethanol and redistilled water to remove the trace remainder. Then, the working electrode was cycled in 1 mM K<sub>3</sub>Fe(CN)<sub>6</sub> solution vs Ag/AgCl/KCl at a scan rate of 50mV s<sup>-1</sup> until a pair reversible CV peaks were achieved, indicating that the surface of glassy carbon electrode was cleaned. The electrode was another time rinsed with redistilled water and cleaned in an ultrasonic bath. A 5 μL graphene solution was dropped onto the cleaned glassy carbon electrode and dried under air, to obtain a graphene modified glassy carbon electrode, represented as Gr/GCE. The polyaniline (PAN) film was in situ polymerized on the Gr/GCE by cyclic voltammetry between 0.0V to 1.50V at scan rate 100 mVs<sup>-1</sup> for ten cycles in the solution of 0.1 mol/L aniline containing 0.25 mol/L H<sub>2</sub>SO<sub>4</sub>. The modified electrode was acquired and it was signified as PAN/Gr/GCE. Then the PAN/Gr modified GCE was shifted to an electrochemical cell with 10 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 1.0 mM PdCl<sub>2</sub> and

apply cyclic voltammetric sweep recorded consecutive cyclic voltammograms in the potential range between  $\pm 0.3\text{V}$  vs Ag/AgCl/KCl reference electrode at the scan rate of  $50\text{ mV/s}$ , to obtain stable voltammograms. The prepared electrode is signified as Pd/PAN/Gr, the nanocomposite film modified GCE was then rinsed with double distilled water and used for further electrochemical studies. The electrode modification process schematic diagram was shown in **Fig. 2A** and consecutive cyclic voltammograms (10 cycles) of PAN deposited on Gr/GCE was shown in **Fig. 2B**. It is clearly explains the polymerization of PAN on Gr/GCE. **Fig. 2C** depicts the typical cyclic voltammograms for five cycles by electrodeposition of Pd particles on PAN/Gr/GCE. Finally the obtained composite electrode was denoted as Pd/PAN/GR/GCE and it is used for further application.



**Fig. 2A.** Schematic graphical representation of fabrication of palladium, polyaniline and graphene nanocomposite on the surface of the glassy carbon electrode.

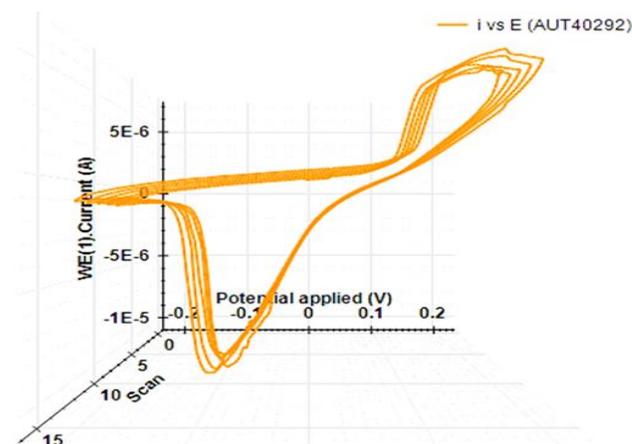


**Fig. 2B.** The 3D Cyclic voltammograms (inset 2D S2) of electro polymerization of PAN on Gr/GCE from 0.25 mol/L H<sub>2</sub>SO<sub>4</sub> and 0.1 mol/L aniline potential between 1.0V to 1.5V for ten consecutive cyclic voltammograms at the scan rate of  $100\text{ mV/s}$ .

#### Analytical procedure

A working standard solution of TCP ( $1.5 \times 10^{-6}\text{M}$ ) was prepared from the stock solution ( $1.0 \times 10^{-3}\text{M}$ ) 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 4.0) was taken into electrolytic cell. The solution was purged with nitrogen gas for 15 min prior to measurement. After that we carried out the procedure for determination of TCP by square wave voltammetry.



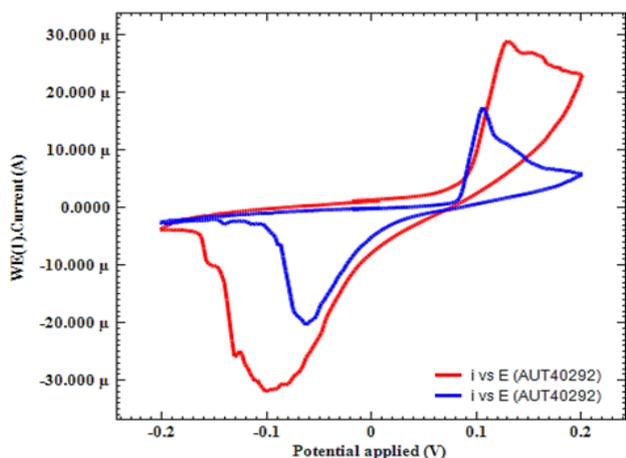
**Fig. 2C.** Cyclic voltammograms 3D, (S2) of electrodeposition of Pd nanoparticles on PAN/Gr/GCE from 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 1.0mM PdCl<sub>2</sub> potential scan between  $\pm 0.3\text{V}$  about five consecutive cyclic voltammograms at the scan rate of  $50\text{ mV/s}$ .

## Results and discussion

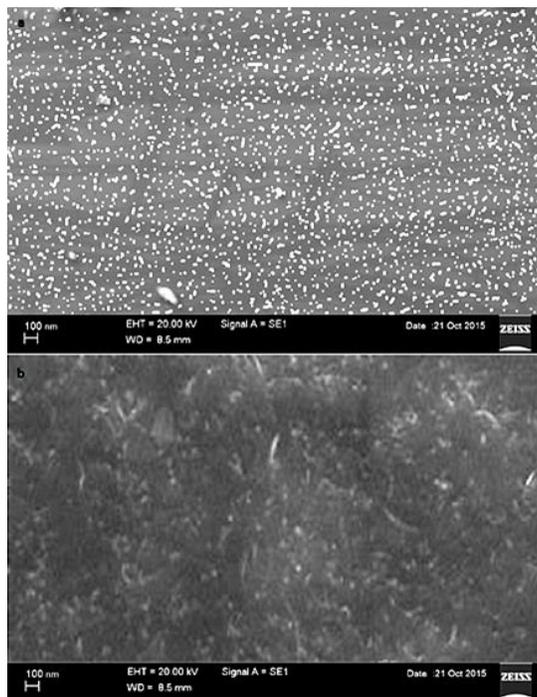
#### Characterization of Pd/PAN/Gr/GCE

Cyclic voltammograms (CV) of PAN deposition process on Gr/GCE surface, which arises at the positive potential of 0.0 V and ends at the potential of 1.5V, it shows the redox peaks but at low reduction potential and current are observed, so, the peaks clearly explain that the PAN deposited on the surface of electrode (Gr/GCE) continuously its shown in **Fig 2B**. These result specified that PAN/Gr nanocomposite film reveals worthy electric conductivity and electrically active. Now, the oxidation peak of Pd particles arise at the potential of 0.20V and the reduction process takes place at the -0.10V. The fabricated Pd particles are oxidized and to form a Pd oxide layer at 0.15V on the electrode surface. After that the remaining Pd oxides are reduced on the negative scans, for the reason that of hydrogen adsorption process. During this repetitive cycling process, the reduction and oxidation peaks of the Pd particles were obviously growing on the PAN/Gr/GCE surface, its depicts in **Fig. 2C**. It is evident to the modification of Pd nanoparticles on the surface of PAN/Gr/GCE. Pd/PAN/Gr was made with different amounts of weights of PdCl<sub>2</sub> from 0.25 mM to 0.1.0mM and the voltammetric reaction towards the stability, at each volume was tested by use of CV in 0.5M H<sub>2</sub>SO<sub>4</sub> solution at potential between  $\pm 0.3\text{V}$ . The outcome shown that the amount of PdCl<sub>2</sub> increased from 0.25 mM to 1.0mM, the redox peak current enriched linearly and the formed Pd nanoparticles attached strongly on the surface of PAN/Gr/GCE, once raise the amount of PdCl<sub>2</sub> after 1.0mM the current response is slowly but surely reduced, so the surface of electrode turns into unstable caused by Pd nanoparticles are over loaded on PAN/Gr/GCE, red line at 1.0mM and blue line at 0.25mM. Therefore 0.25mM is lower and 1.0mM is

higher (optimum) it's clearly shown in **Fig. 3**, so 1.0mM amount of PdCl<sub>2</sub> is preferred as the finest amount for fabricate Pd nanoparticles on the surface of Gr/GCE for electroanalytical application.



**Fig. 3.** Cyclic voltammetric response of Pd nanoparticles on PAN/Gr/GCE, different PdCl<sub>2</sub> concentrations blue line 0.25mM (low), red line at 1.0mM (optimum) in 0.5M H<sub>2</sub>SO<sub>4</sub> solution at scan rate 50 mV/s.



**Fig. 4.** SEM images of (a) Pd nanoparticles on GCE surface and (b), Pd/PAN/Gr/GCE.

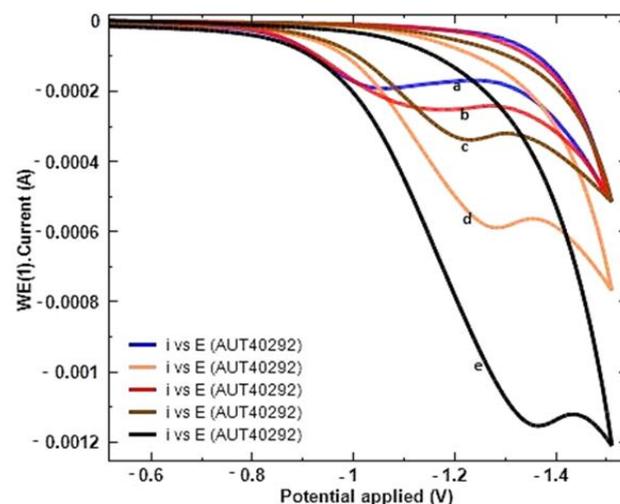
#### Morphological study

The modified working electrode Pd/Gr/GCE was examined by SEM analysis in terms of morphology and size of the Pd nanoparticles particularly and we reported previously about PAN/Gr, Pd/Gr [40,41]. **Fig. 4** depicts the SEM images of construction of Pd nanoparticles on the Gr/GCE surface and PAN/Gr/GCE respectively. Here, it shows clearly that the formed Pd nanoparticles were equally dispersed on the surface of the Gr/GCE and PAN/Gr/GCE. The SEM images of Pd/Gr/GCE which it obviously reveals that the Pd nanoparticles are

homogenously binding up throughout the PAN/Gr/GCE and the scattering of the nanoparticles are almost stable throughout the electrode surface. The immobilized Pd/PAN/Gr nanocomposite on the surface of the GCE remains stable and there is no distortion in shape. In conclusion from these results, it is obvious that the size and morphology for the formation of Pd nanoparticles were uniformly attached on the PAN/Gr/GCE surface and good stability.

#### Cyclic voltammetric studies on Pd/PAN/Gr/GCE

Electrochemical behaviour of TCP was studied using different electrodes GCE, PAN/GCE, Gr/GCE, Pd/Gr/GCE and Pd/PAN/Gr/GCE by cyclic voltammetry. The well-defined reduction peaks were obtained at around potential between -1.25V to -1.35V for TCP ( $1.5 \times 10^{-6}$ M) in different electrodes (Fig.5) at pH.4.0. It might be attributed to electro-chemical reduction of alkenyl group ( $>C=C<$ ) of TCP in acidic medium involving two electron reduction and no anodic peak was observed in the reverse scan path its signifying that irreversibility of the reduction. Here in **Fig. 5** the cyclic voltammograms clearly explains Pd/PAN/Gr/GCE exhibits well defined reduction peaks at potential -1.35V. The remaining electrodes also exhibits good reduction peaks but compare to remaining electrodes Pd/PAN/Gr/GCE shows well defined reduction peaks at very low current values. It can be describes that the synergistic influence of fast electron transfer rate, high electrical conductivity, , large surface area and increased active sites leading to high catalytic activity of Pd/PAN/Gr/GCE. Additionally, the adsorption of TCP was more feasible for Pd/PAN/Gr/GCE; the nanocomposite might enhance the peak current.

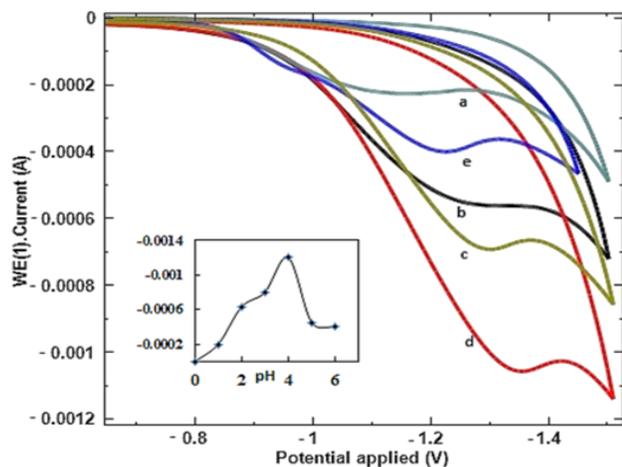


**Fig. 5.** Cyclic voltammograms of TCP at different electrodes (a) GCE, (b) PAN/GCE, (c) Pd/GCE, (d) Pd/Gr/GCE and (e) Pd/PAN/Gr/GCE at pH 4.0, scan rate 100 mV/s in B-R buffer solution.

#### Effect of pH

Solution pH affects the performance of peak current and reduction mechanism, so we studied the effect of pH on the electrochemical behaviour of the modified electrodes. The relationship between chemical reduction efficiency and pH of the solution was obtained by cyclic

voltammetric study; the results are shown in **Fig. 6**. The reduction peak current was enhanced when increasing the pH from pH 1.0 to 4.0, the peak current reaching a maximum current at pH 4.0. Furthermore, whereas from pH 4.1 the buffer solution caused the reduction peak current gradually decreased slowly, specifying that a low electron transfer rate. Progressive fall in peak current with increasing pH indicates the role of proton in the reduction under study hence pH 4.0 was selected optimum based on maximum and well defined peak currents. Here low current peaks indicating that reduction of TCP at  $>C=C<$  and involves equal electrons and protons like dichlorvos [40].

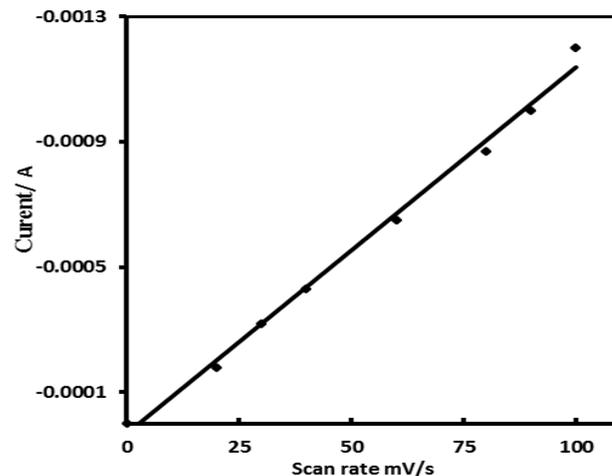


**Fig. 6.** Cyclic voltammograms of TCP at different pH values from pH 1.0 to pH-5.0 (a) pH 1.0, (b) pH 2.0, (c) pH 3.0, (d) pH 4.0 and (e) pH 5.0, also insert pH vs current curve at different pH values in B-R buffer solution at concentration  $1.5 \times 10^{-6} M$ .

#### Voltammetric parameters

In order to obtain the mechanism of electrochemical reactions can be determined from the relationship between peak current and scan rate. Consequently, we studied the effect of different scan rates on the electrochemical reduction of TCP. The amount should be attributed to the deposition and the surface area was obviously improved in the resulting nanocomposite, signifying that the effect of Pd/PAN/Gr composite delivers proficient outcomes for the electrochemical reaction of TCP with enhanced voltammetric response. **Fig. 7** shows the plot of the peak current vs scan rate for TCP at optimum conditions using cyclic voltammetry at different scan rates from 0 mV/s to 100 mV/s at Pd/PAN/Gr/GCE. The pesticide TCP reduction peak currents increased gradually with increasing scan rate, its clearly indicating that the conductivity of the surface of the electrode gradually increased with scan rate. The linear relationship between scan rate and peak current suggests that the reduction of TCP was typical adsorption controlled process, which can be used to quantitatively analyse the TCP present at the electrode surface. To reduce the effects of background current and still achieve high sensitivity, 100 mV/s was selected as the optimum scan rate for subsequent experiments. Accumulation time (tacc) and accumulation potential (Eacc) were also studied over the range 0 to 120s and -0.5 V to -1.5 V

using square wave voltammetry respectively. Well defined current peaks were obtained at potential -1.3V and time 120s respectively. Its shows that, no further accumulation of TCP was possible because of complete saturation of modified electrode surface with the pesticide.



**Fig. 7.** Plot of the peak current vs scan rate (from 0.1 mV/s to 100 mV/s) using Cyclic voltammetry at optimum conditions.

#### Determination of TCP in vegetable samples

Vegetables (Cabbage and Tomato) samples were collected from an agricultural field, where the pesticide TCP had been spiked. 20.0 gm of sample was before soaked with 20 mL solution of ethanol with distilled water, filtered and then filtrate was centrifuged at 2000 rpm for few minutes. The filtrate was quantitatively moved into a 100 mL calibrated flask and made up to the mark with 50% ethanol. Washings and moved in to a 50 mL calibrated flask and aliquots were analyzed as per to the recommended procedure. The obtained results for the determination of the TCP in vegetable samples are summarized in **Table.1**. The recoveries of TCP obtained are in the range from 94.20 % to 98.80%, which shows the accuracy and reproducibility of the recommended method.

**Table 1.** Recovery study of TCP in Vegetable samples.

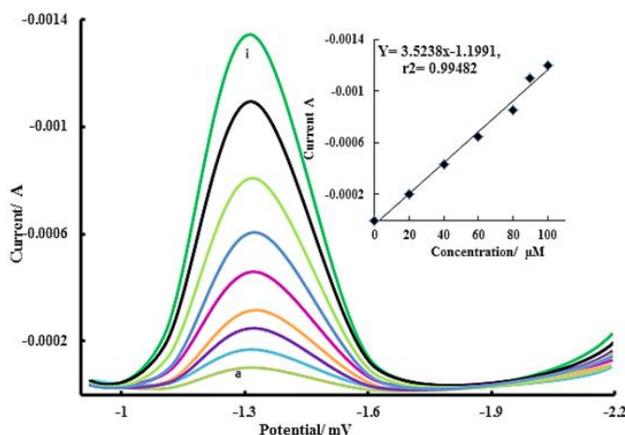
Samples	Added(M)	Found(M)	*Recovery (%)	RSD
Cabbage	$1.0 \times 10^{-3}$	$0.96 \times 10^{-3}$	96.00	2.52%
	$2.5 \times 10^{-4}$	$2.35 \times 10^{-4}$	94.20	3.36%
	$3.0 \times 10^{-5}$	$2.87 \times 10^{-5}$	95.66	3.43%
	$1.5 \times 10^{-6}$	$1.46 \times 10^{-6}$	97.33	2.96%
Tomato	$1.0 \times 10^{-3}$	$0.97 \times 10^{-3}$	97.00	3.02%
	$2.5 \times 10^{-4}$	$2.47 \times 10^{-4}$	98.80	3.86%
	$3.0 \times 10^{-5}$	$2.96 \times 10^{-5}$	98.66	2.68%
	$1.5 \times 10^{-6}$	$1.48 \times 10^{-6}$	98.66	2.72%

\*Each at five determinations

#### Calibration curve and analytical application of the nanocomposite

Square wave voltammetric method was used for the determination of pesticide, the variation of peak current with the concentration of TCP was studied by recording peak signals under the optimum conditions, the square

wave voltammograms were shown in Fig. 8. It clearly shows that peak currents increased linearly with TCP concentration over the range 0  $\mu\text{M}$  to 100  $\mu\text{M}$ . Linear regression equation was expressed as  $Y = 3.5238x - 1.1991$  with correlation coefficient,  $R^2 = 0.9948$ . The detection limits for TCP was calculated as  $5.62 \times 10^{-10} \text{M}$  based on three times the standard deviation 'S' of 5 blank responses and 'm' is the slope of calibration line (3S/m). The electrode, Pd/PAN/GR/GCE was stored at 4°C in refrigerator and tested for its stability over a period of four weeks. The electrode performance was good about 96% of its primary response of TCP, its indicating that it has good storage stability. The Repeatability of the electrode was determined by ten replicate determinations of TCP using the same electrode that led to RSD value of 2.52%. Fabrication reproducibility was determined by using five new electrodes prepared by identical procedure for TCP measurement which gave RSD value of 3.86% indicating excellent reproducibility of the electrode. The modified Pd/PAN//Gr/GCE was also investigated by CV in terms of stability. The composite electrode shows good stability by consecutive 10 cycles of CV test (Fig not shown), a slight fall of peak current was perceived with increase of scanning cycle, but the reduction peak current retained 96 % of its initial current after it was tested by consecutive CV scan. This indicates that the Pd/PAN/Gr film did not peel off from the surface of GCE through 10 times of CV cycles.



**Fig. 8.** Square wave voltammograms of TCP at Pd/PAN/Gr/GCE in B-R buffer solution at pH 4.0, with different concentrations from (a) to (i) 0  $\mu\text{M}$  to 100  $\mu\text{M}$ , inset calibration curve for cons vs current, scan rate 100mV/s. (See Fig S3 for 0-20 $\mu\text{M}$ ).

### Interferences

The coexisting components were employed into account for this application. In the study,  $1.5 \times 10^{-6} \text{M}$  of TCP was selected as a specific concentration. The generous maximum concentration of the coexisting substance was determined, in which the substance caused Pd/Gr/GCE intensity change of approximately  $\pm 3$ . We also study the effect of the inorganic ions like  $\text{CO}_3^{2-}$ ,  $\text{Zn}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{SO}_4^{2-}$  found that they did not affect the results and some other organophosphorous pesticides, such as omethoate, trichlorfon, methyl parathion and dichlorvos, do not interfere. The interferences of some metal ions, such as  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  can be removed by the

alkaline hydrolysis procedure, according to our previous work [41]. In our study, other organophosphorous pesticides at optimized condition are hardly to be detected, so the present method was very insightful to determine pesticides.

### Conclusion

The combination of Pd, PAN and graphene composite made enrichment of over reduction potentials and peak currents for TCP using electroanalytical techniques and also it's a novel sensor. Cyclic voltammetry and square wave voltammetry studies have demonstrated the high catalytic activity of the nanocomposite which was ascribed to its increased active surface area, high electrical conductivity leading to fast electron transfer rate. Association of Pd, PAN and Gr improved the electrical conductivity with high stability of sensor response. Further, graphene contributes to good adsorption of TCP. The method was satisfactorily applied for vegetable samples with excellent recoveries. The present sensor mainly involves cheap ease of preparation, high sensitivity, good selectivity, wide linear range with low detection limits, repeatability and reproducibility. Therefore, it could be predicted that the present sensor serve as for highly sensitive detection of TCP in vegetable samples.

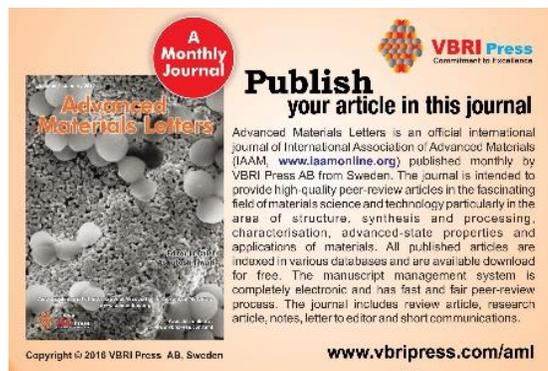
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