Development of polyindole/tungsten carbide nanocomposite-modified electrodes for electrochemical quantification of chlorpyrifos

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Abstract

The present investigation deals with the development of a novel polymer nanocomposite (PNCs) electrodes for simple, selective and sensitive detection of chlorpyrifos (CHL). PNCs were developed using surfactant facilitated polymerization of indole using different concentrations (wt%) of WC ranging 5–30. Formation of PNCs was ascertained through diversified analytical methods. Electrodes were derived from PNCs over stainless steel substrate for electrochemical quantification of CHL. With concentration of WC, the DC conductivity ($10^{-2} \times \text{S/cm}$) of electrodes was increased ranging 3.54–0.75 at 313 K. Electrochemical impedance spectroscopy reveals well stability of electrodes in phosphate buffer (PBS, 0.1 M) at pH 7.4. The performance of electrodes towards detection and quantification of CHL was investigated through square wave voltammetry. Study reveals that detection and quantification of CHL were dependent on concentration of WC in nanocomposites. Square wave voltammetry reveals that the electrode derived from PNCs with 5 wt% of WC has rendered highest limits of detection and quantification of CHL (10^{-8} mol/L) up to 5.94 and 18. This work describes a viable method of preparation of synergistic blend of WC in PIN matrix having high electrical conductivity, rapid electron shift, huge surface area and enhanced stability for fast and précised electrochemical detection of CHL.

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Graphic abstract

Keywords Nanocomposite · Chlorpyrifos · Electrochemical sensing · Cyclic voltammetry · Square wave voltammetry · Quantification

Introduction

Organophosphates (OPs) are the esters, amide and thiol derivatives of phosphorous-based acid [1–3]. Low water solubility and high absorption coefficient impart long residual effect of OPs in soil. This allows the entry of OPs into food chain causing neurotoxicity to animals due to irreversible inhibition of acetyl cholinesterase (AChE) [4–6]. For such reasons, development of novel methods of detection of OPs has been the subject of investigation over decades. In this context, various chromatographic, mass spectrometric, electrophoretic, [7–10] and electrochemical [11–14] methods were developed for detection of OPs.

Chlorpyrifos (CHL, *o,o*-diethyl-*o*-(3,5,6-trichloro-2-pyridinyl)phosphorothioate) belongs to the family of OPs, used for crop protection as insecticide and nematicide. Realizing health hazards imposed over ecosystem, there has been growing concern on advancement of selective, precise, rapid and reliable approach for CHL detection. In this context, the quantification of CHL through chromatographic [15, 16] and electrochemical [17, 18] methods has been well established.

Among such methods, based on chromatography involves expensive instrumentation, multiple steps of preparation, immobilization and regeneration of samples, large consumption of chemicals, time along with low sensitivity of detection [19, 20]. However, electrochemical methods, specially based on square wave voltammetry (SWV), have received immense acceptance because of reasonable simplicity, high sensitivity and potential towards selective quantification of detection of CHL down to ng level [21–23]. SWV has also been used for detection of a wide range of OPs over nanocomposite-modified GCE. Nanocomposites employed for electrochemical detection of OPs were parathion [24–28], malathion [29, 30] and paraoxon [31, 32]. The nanocomposites employed for modification of GCE for OPs detection were zeolite [24], ZrO_2 [25], Au/Graphene [26, 27], ZrO_2 [28], SWNT/GO [29], MWCNT [30], Au/Pt [31] and ZrO_2 /MWCNT [32]. The nanomaterials used for detection of CHL were graphene [17], MWCNT [33–35], with nano- TiO_2 [36], carbon nitride [37], ferrocene [38], CuO [39]. Conducting polymers have been used as such or in the form of their nanocomposites for detection of CHL through SWV [24, 30]. Literature revealed

that a wide range of nano-composites has been employed for the detection of various OPs [24–32], including CHL [33–39]. To the best of our knowledge, no records are available on electrochemical detection of CHL over PNCs derived through immobilization of WC into PIN matrix.

Recently, conducting polymer-based nanostructures containing carbonaceous and inorganic nanomaterials have been used in electrochemical studies for various applications [40–44]. Amongst the family of conducting polymers, polyindole (PIN) has an edge over other, due to its sustained polymerization, high electrical conductivity, low manufacturing cost and less toxicity [45–49]. Sensing behavior of PIN is modified through doping transition metal-based dopants that channelize the electron transfer mechanism through polaron formation [50]. In this context, common dopants employed for PIN are gold [51], oxides of zinc and nickel [52], tin [53], iron [54], vanadium [55] and copper [56]. Nanocomposite of titanium carbide and poly(3,4-ethylenedioxythiophene) were prepared as an alternative electrocatalyst for dye-sensitized solar cell applications [57–60]. The present work proposed a novel and economical sensor for the trace level electrochemical detection of CHL, by utilizing WC-doped PIN nanocomposite.

Materials and methods

Materials

CHL with purity ($\geq 99.9\%$), chlorosulfonic acid ($> 99\%$), indole ($> 99\%$) and cetyltrimethylammonium bromide (CTAB) ($> 99\%$) were purchased from Sigma-Aldrich. Rest of the chemicals and solvents (purity $> 98\%$) were indigenously procured and used without further purification. Phosphate buffer (pH 7.4, 0.1 M) and stock solution of CHL (1.0×10^{-4} M) were prepared through traditional methods. In the present results, bare electrode, 5 wt% and 30 wt% PNCs-coated electrode are represented by [I], [II] and [III], respectively.

Preparation of nanocomposites

PIN along with various wt% fractions of WC ranging 5–30 [I–III] was synthesized by cationic surfactant method placed in two-necked glass reaction vessel implemented with mechanical stirrer and dropping funnel. To this, CTAB (2.7×10^{-3} mol) was added and the content was stirred @500 rpm over 6 h. To initiate the polymerization process, a solution of freshly prepared FeCl_3 (3.5 M) was added to content @1 mL/min keeping stirring to be continued over 24 h. A dark brown precipitate was produced, that was subsequently filtered and successively washed with deionized water till the filtrate became free from chloride ions. Isolated PNCs was left for 6 h at room temperature and then dried at 40°C at

400 mmHg for additional 8 h. PIN was also prepared under similar reaction conditions in the absence of WC [61, 62].

Preparation of electrodes

Working electrodes (WE) were prepared through depositing PNCs over stainless steel plates of 1 cm^2 area. Prior to deposition of PNCs, the plates were thoroughly finished with emery paper followed by ultrasonicated cleaning with acetone. A suspension of PNCs was prepared through ultrasonicated the composition of SPS (7.5×10^{-3} g) with graphite (5.0×10^{-3} g) and ammonium per sulfate ($80\text{ }\mu\text{M}$) in the presence of PNCs in NMP (1.5 mL) over 2 h. The suspension ($125\text{ }\mu\text{L}$) was applied over electrode and left at room temperature for 8 h, thereafter dried at $40^\circ\text{C}/400\text{ mm Hg}$ for additional 48 h (Scheme 1). The electrodes with mass thickness ranging $1.80\text{--}46.15 (\times 10^{-3}\text{ g})$ were obtained and employed for characterization [63].

Instrumentations

SEM images were recorded on JEOL, JSM 6610 LV at 0.2 KX ($7\text{ }\mu\text{m}$) and 15 kV. For this purpose, the electrodes were prepared via mentioned procedure. The SEM images were scanned under identical conditions for comparable results. The conductivity data were recorded over Keithley four-point probe conductivity nanovoltmeter with current (6221 A) and voltage source (2182 V) in the range of 313–373 K.

The activation energy (E_a) was deduced through Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_a/kT), \quad (1)$$

where σ is electrical electrodes conductivity, σ_0 is pre-exponential factor k is Boltzmann constant and T is absolute temperature [64].

FT-IR spectra were recorded on Thermo Nicolet ranging $4000\text{--}500\text{ cm}^{-1}$ in KBr. XRD spectra were recorded over Rigaku-Geigerflex, X-Ray diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154\text{ nm}$) with 2θ ranging $10^\circ\text{--}90^\circ$ at 30 kV and 15 mA. Simultaneous TG-DTA-DTG was conducted over EXSTAR TG/DTA 6300 at sample weight (mg) ranging $10.50\text{--}10.55$ at $10^\circ\text{C}/\text{min}$ in air.

The electrochemical studies of prepared electrodes were performed in PBS (0.1 M) over IVIUM Potentiostat–Galvanostat using a triple-electrode cell assembly. WE were fabricated through depositing PNCs over SS plates. Pt foil (1 cm^2) and Ag/AgCl were used as auxiliary and reference electrodes. All peak currents (μA) and peak potentials (V) were expressed in due units. Calibration curves were obtained from SWV by plotting maximum peak current and respective increasing concentration of CHL.

Limit of detection (LOD) and limit of quantification (LOQ) were calculated from calibration curve using formula:

Scheme 1 Preparation of electroactive material and modification of electrode using PNCs for CHL sensing

Fig. 1 FT-IR Spectra of **a** WC, **b** PIN and **c** [II]

LOQ = 10 s/m and LOD = 3.3 s/m, where *s* is intercept and *m* is slope of the calibration curve. Stability of electrodes was investigated through electrochemical impedance spectra (EIS) and circuit simulation was conducted using Randles diagrams.

Results and discussion

Spectral analysis

PIN shows characteristic wave numbers (cm^{-1}) corresponding to $\nu\text{N-H}$ (3138.00), $\nu\text{C-H}$ (2925.39), $\nu\delta\text{O-H}$ (1617.78) $\nu\text{C-C}$ (1454.64) and $\delta\text{Ar-H}$ (745.48). The wave numbers at 2925.39 and 2852.80 attribute to interaction of CTAB with

Fig. 2 XRD spectra of **a** PIN, **b** WC and **c** [II]

PIN. The wave number at 1110.96, 1334.07 and 1568.39 cm^{-1} correspond to $\nu\text{C-N}$, $\nu\text{C=N}$ and $\delta\text{N-H}$ deformation [65].

WC has shown by the low-frequency fingerprint region at 665.82 cm^{-1} [66].

[III] shows all the characteristic absorption bands of PIN. EM shows absorptions corresponding to $\nu\text{N-H}$ (3137.12), $\nu\text{C-H}$ (3017.8) and symmetric stretches of WC near the low-frequency fingerprint region (655.84) and out-of-plane

Fig. 3 SEM–EDX of electrodes coated with WC (**a₁**, **b₁**), PIN (**a₂**, **b₂**) and PIN/WC (**a₃**, **b₃**)

deformation for C–H (746.58) (Fig. 1). Interaction of WC has shifted the wave number of PIN to lower values.

XRD

The XRD spectra of the PIN, WC and [III] are shown in Fig. 2. Broad peak at 20.35° attributes to amorphous nature of PIN. Debye–Scherrer calculations provided the corresponding crystallite size of nanoparticles ranging

10–22 nm [67]. Diffraction peaks at 31.68° (2.82), 35.71° (2.51), 48.38° (1.88), 64.05° (1.45), 65.76° (1.42), 73.37° (1.29), 75.63° (1.25), 77.26° (1.23), 84.26° (1.15) correspond to [001], [100], [101], [110], [002], [111], [200], [102], [201] planes of WC. The planes of hexagonal were well matched with JCPDS 73-0471 [68]. Diffraction peaks at 31.03° (2.95), 35.31° (2.54), 47.88° (1.89), 63.65° (1.46), 72.96° (1.29), 75.15° (1.26), 76.87° (1.23), 83.81° (1.15) corresponding to [001], [100], [101], [110], [111], [200], [102], [201] planes reveal the presence of WC in PIN matrix.

Surface morphology of electrodes

Morphology of fabricated electrodes along with quantitative elemental composition was analyzed through SEM–EDX study. To compare the morphology, all electrodes were imaged under identical conditions at 1 KX, 10 μ m and camera width of 10 ± 1 nm. EDX spectrum shows the presence of W and high C content in the EM as well as quantity of other elements. EDX represents qualitative detection of elements present in EM. To simulate the emission of X-rays, high-energy beam of charged particles was focused on to the EM. The difference between energies of higher and lower energy shell is released in the form of X-rays which is measured by spectrometer.

SEM and EDX of WC, PIN and PNCs are sequentially shown in Fig. 3a1–a3 and b1–b3, respectively. The dark and bright phases in SEM images represent the morphology of PIN and WC, respectively. Electrodes derived from PIN show a co-continuous morphology without any distinct phase separation. SEM of PIN-coated electrode showed granular structure with rough morphology, which concludes that the nature of particles formed was irregular. Blending of PIN with WC, has afforded with rough morphology. It is observed from SEM images that intercalation of WC into PIN matrix also increases, which leads to roughness in electrode surface. The synergy between the constituents may be weak or strong, which is regulated by the technique used for synthesis of the composite [69]. The reason of surface roughness may be due to the non-homogenized distribution of WC into polymer phase during the procedure of electrode preparation. The morphological structure of PNCs is found to be different from PIN and reveals homogeneous dispersion of WC nanoparticles into PIN matrix.

Thermal stability

Information regarding thermal stability of PIN as well as [III] is provided by thermal studies (Fig. 4). The weight loss caused by evaporation of physically adsorbed moisture and residual solvents is observed in the curves at a temperature lower than 200°C . The weight residue (Wr) corresponding

Fig. 4 a TG–DTA–DTG of WC, b TG–DTA–DTG of PIN, c TG–DTA–DTG of III

to TG is expressed as %w/w. DTA signals and rate of degradation of samples in DTG are expressed as mV and mg/Cel, respectively. The heat of fusion data revealed through DTA has been expressed in mJ/mg. TG onset shows thermal stability of WC up to 384°C . WC shows weight gain of 104.90% due to oxidation at 528°C [22]. Decomposition of WC was progressed at the rate of -21.97×10^{-3} mg/ $^\circ\text{C}$ at 552°C with DTA signal (0.22 mV) at 548°C . Decomposition of WC was concluded at 597°C leaving char residue of 114.70 wt% (Fig. 4a).

PIN was decomposed with TG onset at 337°C leaving 79.4% Wr. Decomposition of PIN was progressed at the rate of 197.6×10^{-3} mg/ $^\circ\text{C}$ at 559°C with DTA signal (0.65 mV) at 543°C . Decomposition of PIN was concluded at 573°C

Fig. 5 **a** σ DC of electrodes, **b** effect of voltage on σ DC of electrodes, **c** effect of temperature on the conductivity of electrodes. **d** Arrhenius plots of electrodes

Fig. 6 Comparison of CV curves of [I] and [II] electrode

leaving char residue of 1.90 wt%. DTA reveals fusion of PIN with ΔH_f of -10.6×10^3 mJ/mg (Fig. 4b). [III] shows single-step decomposition with TG onset at 328 °C leaving 85% Wr. The collective weight loss of 15.0% wt indicates that due to filling of WC, the thermal stability of PIN was compromised. Decomposition of [III] was progressed at the rate of 0.858 mg/°C at 519 °C with DTA signal (0.61 mV) at 520 °C. TG endset of [III] was appeared at 538 °C leaving 36.2% char residue. DTA reveals fusion of [III] with

ΔH_f of -7.44×10^3 mJ/mg (Fig. 4c). Thermal data reveal that due to addition of WC, the thermal stability of [III] was compromised.

Electrical conductivity

The linear variation in I–V (Fig. 5a) at room temperature implies the ohmic conduction behaviour of WC in PIN [70]. The increased conductivity attributes to high conductivity of WC as well as interaction between PIN and WC which favored charge transfer process [71]. Effect of WC on σ DC of electrodes was studied under various voltages ranging 1–100 V at room temperature (Fig. 5b). It was found that the conductivity of the [III] increased with concentration of WC and maximum for 100 V which is 3.54×10^{-2} S cm $^{-1}$. The σ DC measurements were also performed at temperature range 313–373 K (Fig. 5c). It was observed that increasing value of σ DC with temperature defines the semiconducting behaviour of PNCs and maximum σ DC was observed for [III]. Increase in σ DC with temperature attributes to enhanced charge mobility across PNCs. Using theoretical Arrhenius model, the calculated activation energies for

Fig. 7 Mechanism of electro-chemical reaction of the binary composite indicating electron transfer

Fig. 8 **a** CV of [I] vs. Ag/Ag^+ electrode recorded in 0.1 M PBS (pH 7.4) at scan rates 0.04, 0.06, 0.08, 1.0, 1.5 and 2.0 mV/s. **b** CV of [II] composite fabricated SSPE recorded in 0.01 M PBS (pH 7.4) at scan

rates 0.04, 0.06, 0.08, 1.0, 1.5 and 2.0 mV/s. **c** [III] composite fabricated electrode

Fig. 9 Linear regression curve between anodic peak current and root of scan rate

PIN, WC and [III] were found as 0.035, 0.028 and 0.019 eV (Fig. 5d).

EC behavior of modified electrode

Cyclic voltammetry

CV is the most popular continuous wave technique employed to investigate the redox behavior and electron transfer kinetics of molecules over electrochemically active surface. CV presents the set of anodic (E_{pa}) and cathodic peak (E_{pc}) potentials along with respective anodic (i_{pa}) and cathodic (i_{pc}) peak currents. Potential applied across WE moves back and forth past the formal potential. This leads to current flow across the electrode that renders the redox behavior of analyte [72, 73].

Redox behavior was investigated through scanning the CV of CHL in PBS (0.1 M, pH 7.4) @ 40 mV s⁻¹ over WE derived from PNCs [I] and [II] (Fig. 6). Voltammograms were recorded till fivefold degeneracy in potential window of −0.11 to +0.55. [I] has rendered a well-defined redox behavior with peaks peak potentials (−V) ranging 0.089–0.418 V. Under identical conditions, [II] has shown the peak potentials (−V) of 0.093 V and 0.43. Increase in peak current attributes to the formation of electron-conducting tunnel during redox reaction of CHL over [II]. The electron transfer mechanism during redox behavior of CHL over [II] has been presented in Fig. 7. Based on peak potential deduced from CV of [II], the redox behavior of CHL over electrodes was found to lead according to one electron transfer mechanism between electrode surface and CHL generating synergy on EC properties [74].

Fig. 10 SWV curves and calibration plot of **a** [I], **b** [II] and **c** [III] against increasing CHL amount in pH 7.4 of PBS

Effect of scan rate on CV

Frequent elevation in scan rate has raised the i_{pa} (μA) of [I] from 0.084 to 0.279 (Fig. 8a). The coinciding anodic peak potential was observed ranging from −0.089 to −0.013 V. At the same time, there was reduction in i_{pc} (−μA)

Fig. 11 Electrochemical impedance spectra of [I], [II] and [III] electrodes

ranging 0.079–0.235 with corresponding E_{pc} (– V) ranging 0.418–0.454. For [II] with increase in scan rate (Vs^{-1}) from 0.04 to 0.2, there was subsequent increase in I_{pa} , E_{pa} , I_{pc} and E_{pc} ranging 0.111–0.329, – 0.093 to – 0.065 V, – 0.099 to – 0.325 and – 0.43 to – 0.52, respectively (Fig. 8b). However, no redox behavior was shown by [III] irrespective of scan rate (Fig. 8c). Figure 9 shows linear regression curve for [II] between I_{pa} and square root of scan rate. A comparative account reveals higher electrochemical behavior of [II] over [I].

Square wave voltammetry

The SWV experiments have been performed in the potential window (V) from – 2.0 to 2.0 at pulse amplitude 2 mV, scan increment 20 mV and frequency 25 Hz. A comparative SWV voltammograms of electrodes in 0.1 M PBS (pH 7.4) at varying concentrations of CHL are sketched in Fig. 10a–c. The presence of WC in the PIN matrix has raised the peak current that attributes to increase in the sensitivity towards PNCs. With concentration of CHL, the peak was increased over [I] from 6.204 to 7.808 (Fig. 10a). Under identical conditions, the peak currents of [II] and [III] were raised in the

range of 7.699–8.99 and 9.892–11.90 (Fig. 10b, c). Linear range of proposed CHL sensor was found to be 25×10^{-7} to $225 \times 10^{-7} \text{ mol L}^{-1}$ and calibration curves obtained between maximum peak current and concentration of CHL added in SWV were used to calculate LOD and limit of quantification LOQ.

The proposed sensor demonstrates acceptable quantification of CHL with significantly low LOD values. The calibration plots for quantification of CHL at [I], [II] and [III] was obtained by studying the effect of increase in CHL concentration on peak current. The LOD obtained for [I], [II] and [III] are $4.8 \times 10^{-8} \text{ mol L}^{-1}$, $5.94 \times 10^{-8} \text{ mol L}^{-1}$ and $4.49 \times 10^{-8} \text{ mol L}^{-1}$. LOQ for [I], [II] and [III] are $14.5 \times 10^{-8} \text{ mol L}^{-1}$, $18 \times 10^{-8} \text{ mol L}^{-1}$ and $13.6 \times 10^{-8} \text{ mol L}^{-1}$, respectively. The correlations between the concentration and peak current were in linear relation with correlation coefficient (r) for [I], [II] and [III] was 0.979, 0.982, 0.971, respectively, indicating good correlation.

Electrochemical impedance spectroscopy

The impedance data have been expressed in Hz and spectrum was examined by equivalent electrical circuit model (Fig. 11). The elements of the circuit are general electrical components, which include polarization resistance or charge transfer, solution resistance and a double-layer capacitor. EIS measurements were managed by FRA. Nyquist plots at higher and lower frequency range appeared as semicircle attributing to electron transfer resistance (R_{et}). High impedance in the form of semicircular loop was observed at the surface of electrodes covered with coating of PNCs; whereas, loops were opened within 24 h representing the destruction of coating.

For [I], R_p was 8.506×10^2 and $|Z|$ appeared at 1.200×10^3 . For [II], R_p was 4.973×10^2 and $|Z|$ appeared at 6.396×10^2 . [III] has shown R_p of 2.669×10^2 and $|Z|$ appeared at 2.998×10^2 . With the fabrication of electrode with PNCs, the diameter of semicircle decreased, which shows that PNCs possess high electrical conductivity with low charge transfer resistance. It is observed from

Fig. 12 SEM images of II electrode **a** At 1.0 KX, **b** At 2.7 KX

Fig. 11 that the diameter of the semicircles was successively decreased in the order from [I] to [III], that indicates successive increase in electron transfer at the surface of PNCs-coated electrode. Best semicircular loop in [III] represents highest charge storage and capacitive behavior of [III]. In case of EIS studies [II], opening of semicircular loop indicates the diffusion of electrolyte and that is also responsible for cracking of electrode surface as shown in SEM images (Fig. 12a, b).

Conclusion

A series of electrochemical polymer nanocomposite (PNC)-based electrode was developed by an easy and effective chemical oxidative polymerization method using various concentrations of WC ranging 0–30 wt%. Electrodes from PNCs were developed over SS plates and used for electrochemical quantification of chlorpyrifos (CHL) in phosphate buffer (PBS, 0.1 M) at 7.4. Electroanalytical methods based on square wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS) reveal immense feasibility of electrodes towards quantification of CHL with stability in PBS. The electrical and electrochemical behavior of electrodes was found synergistic with concentration of WC in PIN. DC conductivity of electrodes was found in increasing order with concentration of WC. Electrodes with 5 wt% of WC have shown enhanced redox behavior of CHL with limits of detection and quantification (10^{-8} mol L⁻¹) up to 5.94 and 18. Study reveals that incorporation of WC in PIN provides a novel nanohybrid electrode coating material for efficient detection of CHL.

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Compliance with ethical standards

Conflict of interest No potential conflict of interest was reported by the author.

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