

Development of ultrasensitive surfactants doped poly(3,4-ethylenedioxythiophene)/multiwalled carbon nanotube sensor for the detection of pyrethroids and an organochlorine pesticide

PL. Abirama Sundari · P. Manisankar

Received: 8 January 2010 / Accepted: 5 September 2010 / Published online: 19 September 2010
© Springer Science+Business Media B.V. 2010

Abstract Fabrication of nano size poly(3,4-ethylenedioxythiophene)/multiwalled carbonnanotubes film on a glassy carbon electrode (PEDOT/MWCNT/GCE) in the presence of anionic and cationic surfactants is reported. The modified composite electrodes were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies. SEM studies confirmed the formation of nano size film on the working electrode. Electroanalytical studies were carried out using the above prepared electrode by cyclic voltammetry (CV) and differential pulse stripping voltammetry (DPSV). This electrode exhibited higher sensitivity towards the reduction of cypermethrin (CYP), deltamethrin (DEL), fenvalerate (FEN) falling under pyrethroids family and an organochlorine pesticide dicofol (DCF). In CV, all the selected pesticides were found to exhibit one well-defined irreversible reduction peak at pH 13. Optimum conditions for DPSV were experimentally determined by varying several parameters. The practical application of the newly developed sensor was affirmed by quantification of the selected pesticides in spiked water samples.

Keywords Anionic surfactant · Cationic surfactant · Poly(3,4-ethylenedioxythiophene) · Pyrethroids · Organochlorine pesticide

1 Introduction

In this era of utilizing nanomaterials for various applications, electrochemical-sensing devices with nanostructured surfaces have attracted much attention [1]. In particular, multiwalled carbon nanotubes (MWCNTs) have been extensively employed for the fabrication of electrochemical sensors and biosensors with excellent electrocatalytic activity and enhanced sensitivity [2, 3]. CNTs have superior electrical properties, high specific surface area, and chemical stability, for this reason they are largely used in sensing applications [2–5]. Conducting polymers have also been used widely in the development of sensors because of their interesting electrical, optical and electrocatalytic properties [6, 7]. Thus in the recent years, interest has been shown on the synthesis of conducting polymer/MWCNTs composites that exhibit special properties of both individual components in a synergistic manner [8]. Addition of MWCNTs to polymer also results in a significant increase in the mechanical properties of polymer and enhances the electrical properties by facilitating the charge-transfer processes between these two components [9]. Composites of MWCNTs with poly(aniline) [10, 11], poly(pyrrole) [11, 12], poly(3,4-ethylenedioxythiophene) [11, 13], poly(diphenylamine) [14, 15] and poly(3-methyl thiophene) [16] were prepared for different applications. Among the polythiophene derivatives, PEDOT [17], electrosynthesized either in organic or in aqueous media, has the advantage of providing very stable and highly conductive films [18, 19].

Environmental pollution is a serious concern in recent times due to the damage of eco-system in the globe. Among the pollutants, pesticides are considered as hazardous chemicals used in agriculture. In particular, pyrethroids and organochlorine pesticides (OCPs) are widely used, as they control pests and diseases effectively in plant

PL. Abirama Sundari · P. Manisankar (✉)
Department of Industrial Chemistry, School of Chemistry,
Alagappa University, Karaikudi 630003, Tamil Nadu, India
e-mail: pms11@rediffmail.com

species. Because of their low biodegradability and high persistence, they are extensively found in environmental samples such as air, water, soil, sediments, food and biological tissues [20–23]. Moreover, these chemicals induce cancer and act as endocrine disrupters in several organisms due to their high degree of toxicity. Although the use of most pyrethroids and OCPs has been prohibited or limited in developed countries, they are still used in many developing and under developed countries for controlling of pests and insecticides [24–27]. In this purview, we have prepared a composite comprising of MWCNTs and PEDOT doped with surfactants in the intension of utilizing to good effect the twin advantages of high sensing potential of this particular conducting polymer PEDOT [28] and antifouling activity of the surfactants [29]. PEDOT nano particles with enhanced conductivity and processability were produced by polymerization in surfactant micellar solution [30]. Also, this work describes the sensing ability of newly fabricated electrodes and its sensing capability towards the voltammetric determination of CYP, DEL, FEN and DCF.

2 Experimental

2.1 Reagents

Multiwalled carbon nanotubes (MWCNTs) (I.D. \times length 2–15 nm \times 1–10 μ m) produced by arc method was purchased from Sigma-Aldrich (Bangalore, Karnataka). CTAB (AR-Rankem) (Chennai, Tamil Nadu), SDS (AR-Merck) (Bangalore, Karnataka), 3,4-ethylenedioxy thiophene (Sigma-

Aldrich) and Lithium perchlorate (Sigma-Aldrich) were purchased and used without further purification. 0.1 M stock solution was made up in ethanol for all the pesticides. For studies in aqueous media, 0.1 M H_2SO_4 (for pH 1.0), Britton Robinson Buffers (for pH 4.0, 7.0, 9.2) and 0.1 M NaOH (for pH 13.0) in 50% aqueous alcohol were used. Bench top pH meter model-Cyperscan 500 Eutech Instrument was used for pH measurements. Structures of all the selected pesticides were furnished in Table 1.

2.2 Fabrication of PEDOT/MWCNT on glassy carbon electrode

1 mg MWCNT was dispersed into 1 mL of 0.1 M sodium dodecyl sulphate (SDS) by 30-min ultrasonic agitation to get a homogeneous MWCNT suspension. Then 5 μ L of the MWCNT-SDS suspension was coated on pretreated GCE surface and allowed to evaporate in an oven at 50 $^\circ\text{C}$. PEDOT was deposited by the electrooxidation of 0.01 M EDOT in acetonitrile medium containing 0.1 M lithium perchlorate as a supporting electrolyte and cycling the potential between -0.2 and 1.2 V.

2.3 Fabrication of CTAB and SDS doped PEDOT/MWCNT

PEDOT was electrodeposited on MWCNT/GCE from 0.01 M EDOT in the presence of 0.01 M CTAB or 0.01 M SDS and 0.1 M lithium perchlorate as a supporting electrolyte and cycling the potential between -0.2 and 1.2 V.

Table 1 Structure and physical properties of the selected insecticides

Compounds	Structure
Cypermethrin [(RS)- α -cyano-3-phenoxybenzyl (1RS)-cis, trans-3-(2,2-dichloro-vinyl)-2,2-dimethylcyclopropanecarboxylate]	
Deltamethrin [[cyano-(3-phenoxyphenyl)-methyl] 3-(2,2-dibromoethenyl)-2,2-dimethyl-cyclopropane-1-Carboxylate]	
Fenvalerate [α -cyano-3-phenoxybenzyl 2-(4-chlorophenyl)-3-methylbutyrate]	
Dicofol [2,2,2-trichloro-1,1-bis(4-chlorophenyl ethanol)]	

2.4 Electroanalytical studies

CV and DPSV experiments were used to study the electrochemical activity of newly fabricated electrodes towards the reduction of pyrethroids and organochlorine pesticide. These experiments were carried out using CHI 760C electrochemical workstation (CH Instruments, USA) coupled with a conventional three-electrode cell. Modified GCE's were used as the working electrode (area of plain GCE is 3 mm). Counter electrode was platinum wire. The potentials reported in this work are against Ag/AgCl reference electrode.

2.5 Real sample analysis

In order to assess the possible applications of the proposed method in the determination of pesticides, these samples are spiked with water and then analyzed using the following procedure. The water sample to be analyzed was prepared by adding known amount of CYP stock solution and pesticide-free water and then allowing them to stand 24 h. A glass column was filled with amberlite XAD-4 resin up to a height of 20 cm. The column was washed with ethanol, diethyl ether and distilled water. Then the spiked water was filtered through the column at an average rate of 10 mL min^{-1} . After completion of this process, the tap was closed and dichloromethane filled with column and then allowing them to stand for 20 min and then the

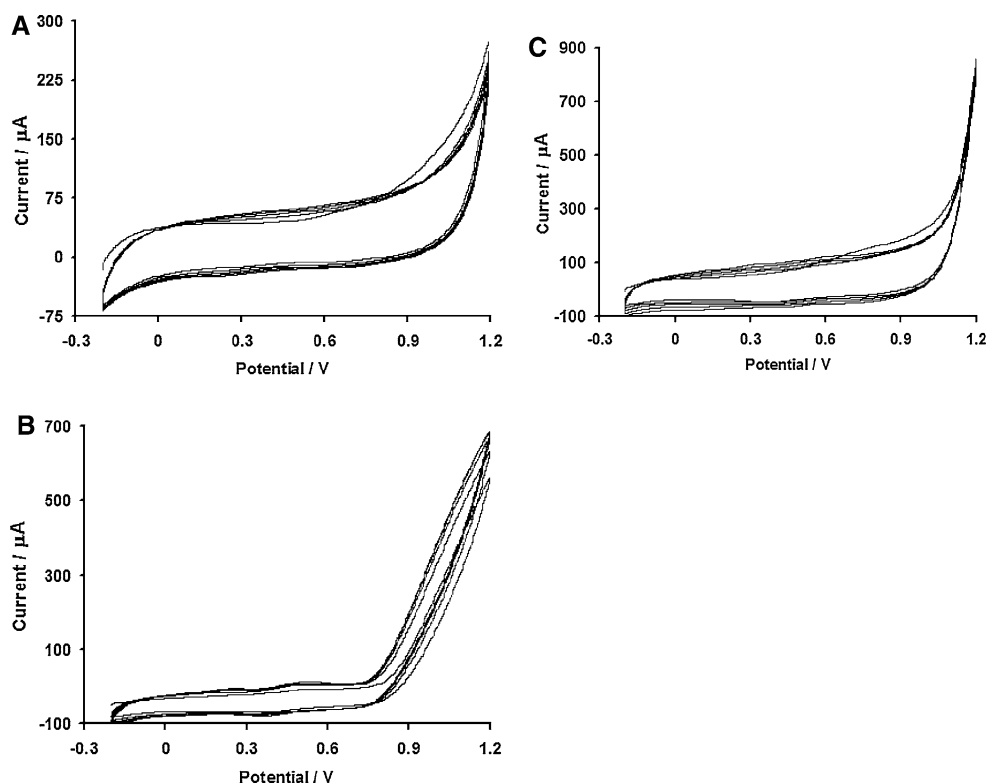
column was drained into a beaker. The extract was evaporated to dryness by gentle heating on a water bath. The residue was transferred into a 250 mL calibrated flask, dissolved in ethanol and made up to the mark. CYP was determined by differential pulse stripping voltammetric method. Percentage of recovery and relative standard deviations for CYP were determined for six different concentrations. Similar experiments were carried out for other pesticides and the results are discussed in Sect. 3.4.1.

3 Results and discussion

3.1 Fabrication and characterization of electrodes

PEDOT/MWCNT/GCE was prepared by placing MWCNTs on GCE and subsequent polymerization of EDOT by potential cycling method as detailed in experimental section. Figure 1A displays the growth behaviour of 0.01 M EDOT on MWCNT/GCE. Increase in peak current seen in the consecutive cycles suggested polymer growth on the electrode surface. Figure 1B revealed the polymerization of 0.01 M EDOT in the presence of 0.01 M SDS (anionic surfactant). Increase in peak current was observed with increase in the number of cycles indicative of polymer formation. In the case of CTAB (cationic surfactant) (Fig. 1C) doped PEDOT/MWCNT, only marginal increase in peak current between successive cycles was observed.

Fig. 1 Cyclic voltammetric growth behavior of **A** PEDOT/MWCNT/GCE and **B** CTAB; **C** SDS doped PEDOT/MWCNT/GCE in acetonitrile medium, 0.1 M LiClO_4 as a supporting electrolyte and sweep rate of 0.1 V s^{-1}



However an increase in the overall peak current showed that the polymer growth was good on the electrode surface. Surfactants doped PEDOT/MWCNT film exhibited higher conductivity than undoped one. This observation can be attributed to the facilitation of exchange of electron between the monomer and the electrode. Out of the two surfactants employed, growth behaviour of SDS doped PEDOT/MWCNT was better than CTAB as evidenced from good conductivity between successive cycles and overall peak current as per earlier report [31].

Scanning electron micrograms of above fabricated electrodes were presented in Fig. 2. As can be seen from SEM microgram of PEDOT/MWCNT/GCE (Fig. 2A), polymerization of EDOT has taken place in the network of MWCNTs. Also MWCNTs provide nano backbone for the polymerization of same. The average tube size of the material was approximated to be 50 nm. As in the case of surfactants doped PEDOT/MWCNT/GCE, all tubes are seriously tangled to form compact nanostructures, which possess higher stability and uniformity than undoped one. Here too, the tube size was 50 nm (Fig. 2B, C). In the presence of surfactants, one can find different PEDOT deposition on MWCNT matrix and fine tubular morphology than the undoped film. Figure 3A–C depicts the X-ray diffraction patterns of modified electrode surfaces, which show substantial amorphous nature, the characteristic behaviour of the polymer.

3.2 Electrochemical response of pesticides at the fabricated electrode systems

CV was utilized for examining and comparing the electrochemical signal of newly fabricated electrode systems to the selected pesticides. In order to study the effect of pH, five pH values viz., 1.0, 4.0, 7.0, 9.2 and 13.0 were chosen. The study was made using 1.0 mM L⁻¹ CYP, DEL, FEN and 0.99 mM L⁻¹ DCF at a sweep rate (ν) of 0.1 V s⁻¹. All the selected pesticides gave better response at pH 13.0. The effect of sweep rate (ν) was studied by varying it from 0.025 to 0.500 V s⁻¹. Figure 4A–C provide details regarding the electrochemical behaviour of pyrethroids CYP, DEL and FEN at pH 13.0 and a sweep rate of 0.1 V s⁻¹. All compounds exhibited one cathodic peak at -1.39 V (132.7 μ A), -1.38 V (145.9 μ A) and -1.37 V, (161.1 μ A) for CYP, -1.49 V (84.58 μ A), -1.49 V (105.7 μ A) and -1.48 V (130.6 μ A) for DEL, -1.43 V (98.92 μ A), -1.42 V (126.3 μ A), and -1.41 V (143.0 μ A) for FEN at PEDOT/MWCNT/GCE, PEDOT(CTAB)/MWCNT/GCE, PEDOT(SDS)/MWCNT/GCE respectively. Figure 4D indicates the details of representative CVs obtained at PEDOT/MWCNT/GCE, PEDOT(CTAB)/MWCNT/GCE, PEDOT(SDS)/MWCNT/GCE in pH 13.0 medium containing 0.99 mM L⁻¹ DCF, at a sweep rate of 0.1 V s⁻¹. It showed one well-defined cathodic peak at

-1.35 V (151.9 μ A), -1.36 (157.4 μ A) and -1.35 V (162.8 μ A). Absence of anodic peak in all cases indicated irreversible electron transfer process, which in turn was confirmed by fractional value of transfer coefficient (α) (0.4–0.63). All pesticides underwent diffusion controlled adsorption process at all modified systems when linear increase in peak current with lower sweep rates (ν) and linearity with square root of sweep rate ($\nu^{1/2}$) at higher sweep rates were observed. The slope value (0.55–0.69) obtained from the plot between log ν vs. log i_p showed diffusion controlled adsorption nature of all the selected pesticides. Herein, for all the four pesticides, peak current was higher at surfactants doped PEDOT/MWCNT. This may be due to spontaneous adsorption of surfactants on the surface of MWCNTs by hydrophobic interactions and the resultant formation of a monolayer of surfactants on the electrode surface [32, 33]. The improved response is due to enhanced adsorption of pesticides in surfactants adsorbed layer. The weak hydrophobic adsorption of surfactants on hydrophobic and smooth surface of MWCNTs is the key for improving the sensitivity and antifouling capacity of carbon nanotube-based electrochemical sensors by surfactants [32, 33]. Among the two surfactants employed, PEDOT(SDS)/MWCNT/GCE showed higher current response. This is because, cationic radicals of PEDOT formed during the electropolymerisation [34] in the micellar environment of SDS, spontaneously reacts with the anionic end of SDS, resulting in the formation of compactly arranged tubular structures. The increase in surface area of PEDOT–SDS matrix offers a favourable platform for sensitive detection of selected pesticides.

3.3 Electroanalytical determination of pesticides

All the selected pesticides are electroactive and responded well in CV. Hence, adsorptive stripping voltammetric studies were performed for the determination of above-said pesticides in PEDOT(SDS)/MWCNT/GCE. Differential pulse stripping was chosen for the present study.

Herein, accumulation potential varied and higher peak current response was obtained at 0.1, 0, 0.2 and 0 V for CYP, DEL, FEN and DCF respectively. Absence of anodic and cathodic deposits shows adsorption of neutral substrate on the electrode. Accumulation time varied between 5 and 60 s for all the pesticides and maximum peak current was observed at an accumulation time of 15 s for CYP and DCF, 20 s for DEL and 10 s for FEN. Accumulation of these pesticides on the best performing electrode surface was examined from changes in the modified electrode surface before and after accumulation process. Surface morphology of pesticides accumulated surfaces was determined through SEM. Irregular adsorption CYP was found from Fig. 2D. Figure 2E suggesting small ball like particles dispersed

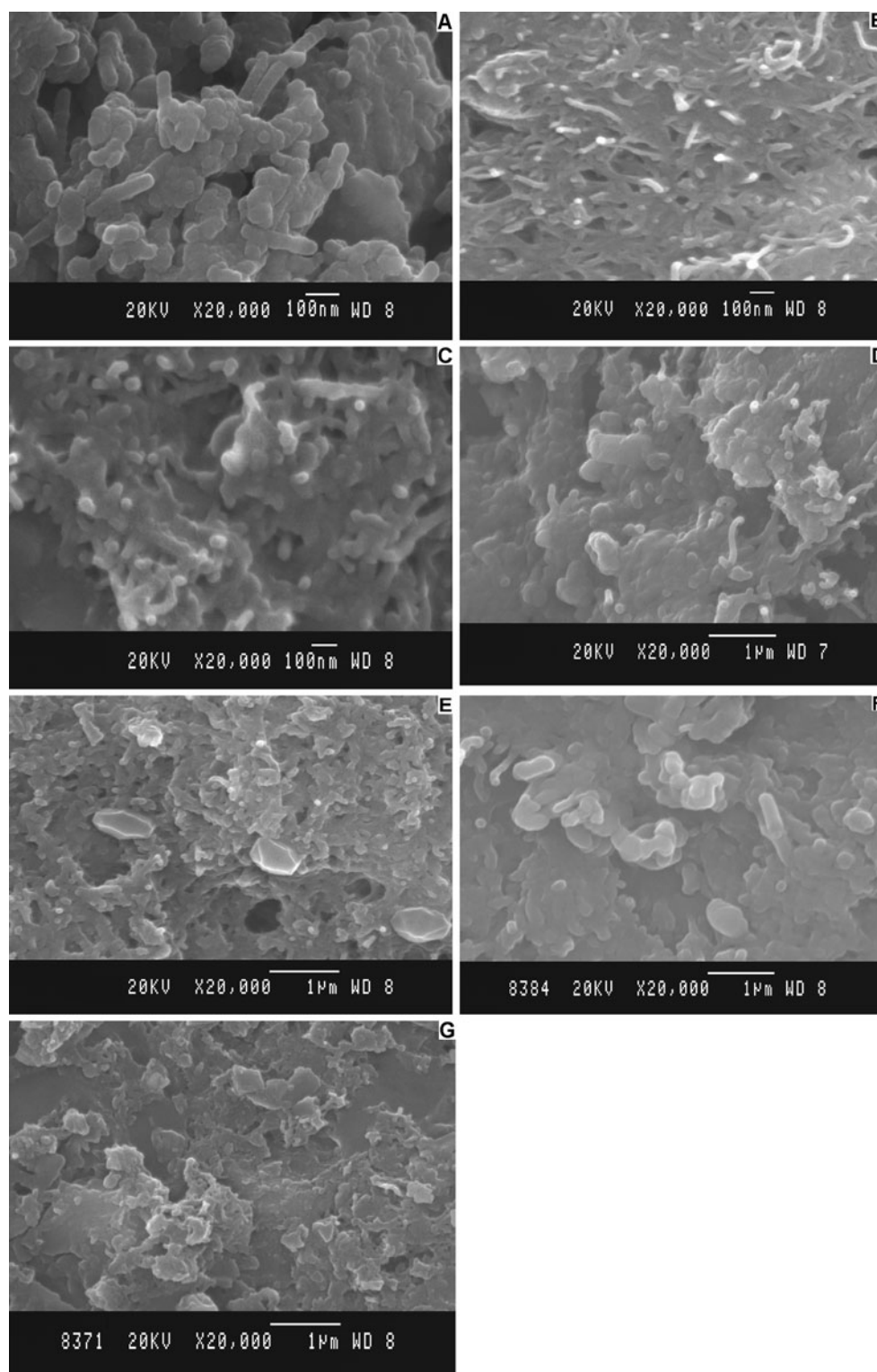
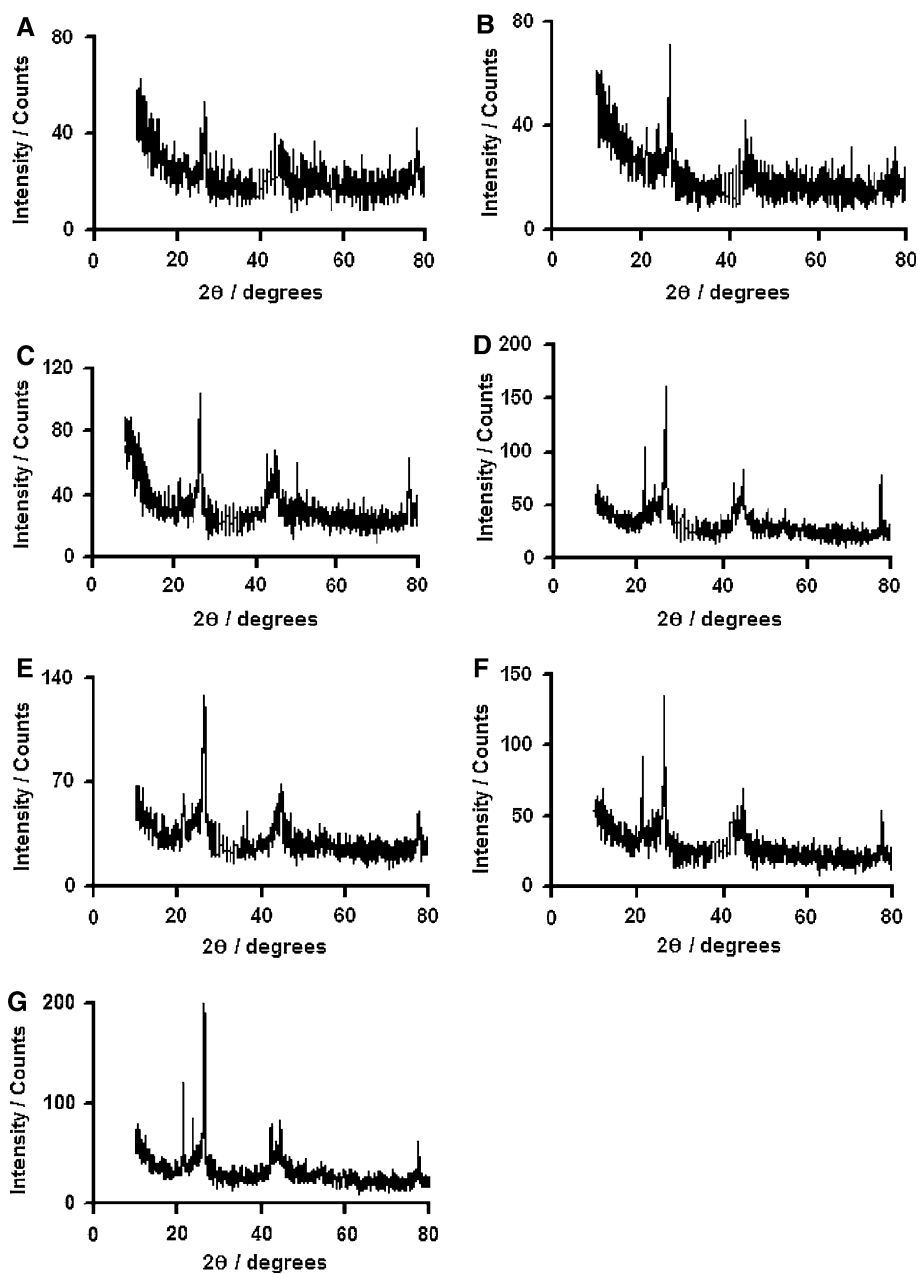


Fig. 2 SEM micrographs of **A** PEDOT/MWCNT/GCE; **B** PEDOT(CTAB)/MWCNT/GCE; **C** PEDOT(SDS)/MWCNT/GCE and **D** CYP; **E** DEL; **F** FEN; **G** DCF adsorbed on PEDOT(SDS)/MWCNT/GCE modified system

randomly on the modified surface. Mixed needle and stick-like structure are observed from FEN adsorption (Fig. 2F). Figure 2G indicates a small broken leaf-like structure,

suggesting the adsorption of DCF. All these factors confirm adsorption process. XRD patterns of pesticides adsorbed surfaces are slightly different from that of pesticides

Fig. 3 XRD patterns of **A** PEDOT/MWCNT/GCE; **B** PEDOT(CTAB)/MWCNT/GCE; **C** PEDOT(SDS)/MWCNT/GCE and **D** CYP; **E** DEL; **F** FEN; **G** DCF adsorbed on PEDOT(SDS)/MWCNT/GCE modified system



adsorbed surfaces (Fig. 3D–G) that showed additional sharp peaks due to little increase in crystalline nature of adsorbed pesticide molecules.

Other stripping parameters such as Initial scan potential (E_{is}), pulse amplitude (AP) and pulse width (PW) are also influencing the peak current response. For all pesticides, E_{is} varied from -0.200 to -1.200 V and optimum values were found to be -0.800 V for CYP, -1.000 V for DEL, FEN and -0.900 V for DCF. An increase in peak current was identified, when pulse amplitude was changed from 0.025 to 0.075 V. Hence AP of 0.075 was chosen for all pesticides. The decrease in peak current was noted, when pulse

width was changed from 0.025 to 0.1 s. Hence, for all pesticides pulse width of 0.025 s was preferred.

The representative differential pulse stripping voltammograms are given in Fig. 5. Under the best possible experimental conditions, effect of pesticide concentration on stripping signal was studied. Calibration plots were made which indicated linear dependence of peak current with concentration and it was found to be good from 0.015 to $5 \times 10^4 \mu\text{g L}^{-1}$, 0.063 to $5 \times 10^4 \mu\text{g L}^{-1}$, 0.061 to $5 \times 10^4 \mu\text{g L}^{-1}$ and 0.01 to $5 \times 10^4 \mu\text{g L}^{-1}$ for CYP, DEL, FEN and DCF on PEDOT(SDS)/MWCNT/GCE system respectively. Detection limit obtained here is

Fig. 4 Cyclic voltammograms of 1 mM L^{-1} of **A** CYP; **B** DEL; **C** FEN and **D** DCF (0.99 mM L^{-1}) on (a) PEDOT/MWCNT/GCE, (b) PEDOT/(CTAB)MWCNT/GCE, (c) MWCNT(SDS)/GCE at pH 13 and sweep rate of 0.1 V s^{-1}

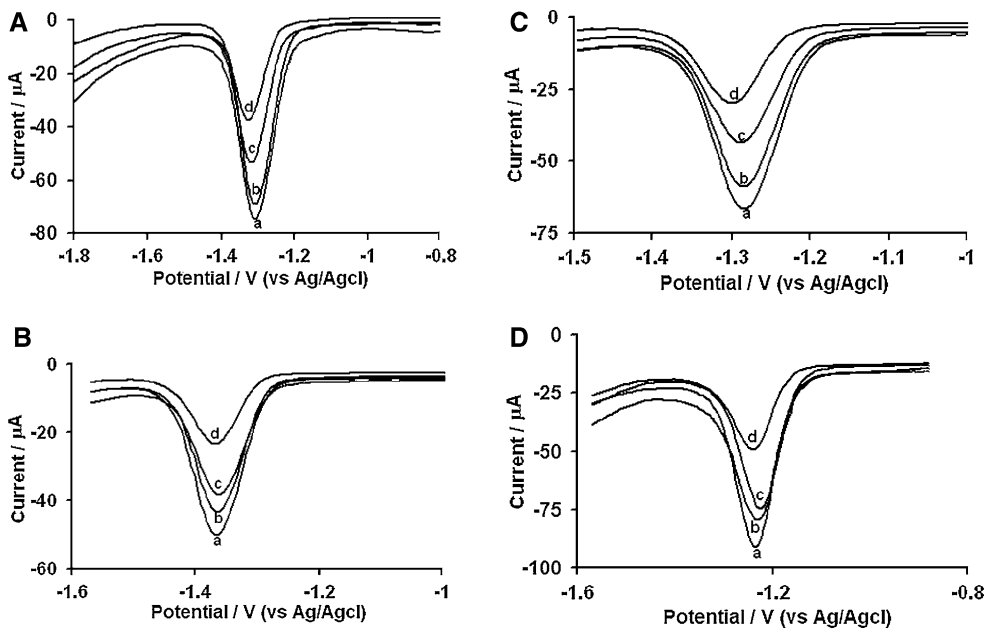
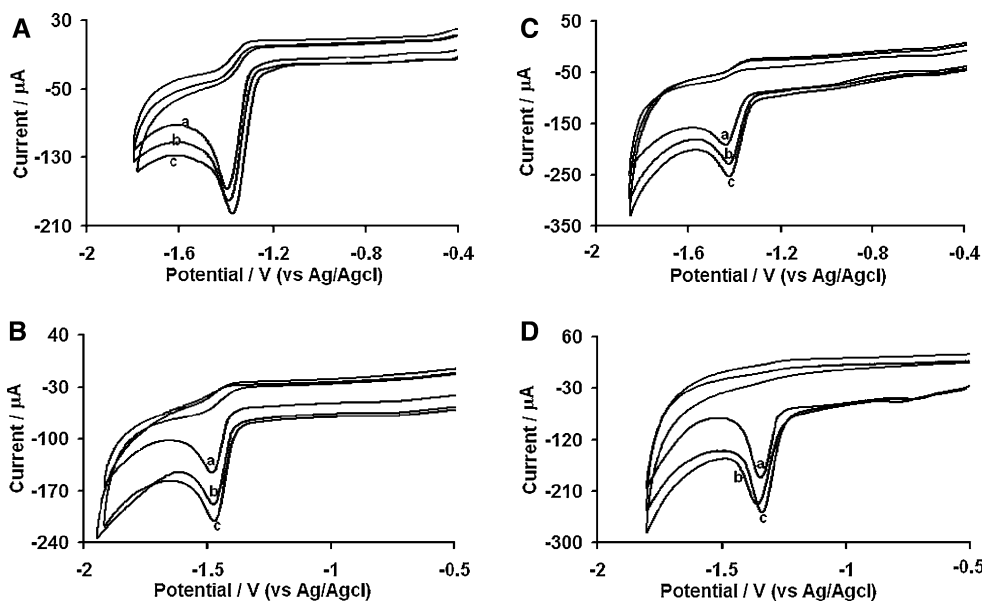


Fig. 5 Differential pulse stripping voltammograms of **A** CYP; **B** DEL; **C** FEN; **D** DCF on (a) PEDOT(SDS)/MWCNT/GCE, (b) PEDOT(CTAB)/MWCNT/GCE, (c) PEDOT/MWCNT/GCE at $50 \mu\text{g L}^{-1}$ (d) real sample

comparatively lower than earlier reports [35–38] and the results are provided in Table 2.

3.3.1 Repeatability and stability of the modified electrode

The electrode capability for reproducibility was examined by CV data obtained in optimum pH from six separately prepared modified electrodes under the same experimental conditions. Reproducibility is fairly good with a standard error of about 2.5%. In addition, long-term stability of the

fabricated electrodes was tested over a four-week period. When CV's were recorded after the electrode was stored in an atmosphere at room temperature, the peak potential was unchanged and the current signals showed only less than 2.4% decrease of the initial response. Also, reproducibility of stripping signal was understood from the relative standard deviation (1.8–3.0%) calculated for six identical measurements at a concentration level of $10 \mu\text{g L}^{-1}$ in DPSV. The low RSD values indicate good reproducibility of the present method, compared to other techniques [38, 39].

Table 2 Comparison of LOD's with available methods

S. no.	Techniques	Pesticides			
		CYP	DEL	FEN	DCF
1	Gas chromatography-Mass spectrometry ($\mu\text{g kg}^{-1}$) [35]	0.495	0.106	0.06	–
2	Gas chromatography—time of flight mass spectrometry (ng mL^{-1}) [36]	10	–	3	3
3	Microwave assisted headspace solid-phase microextraction (ng L^{-1}) [37]	1	2.6	1.3	–
4	Solid-phase extraction and liquid chromatography/electrospray ionization ion trap mass spectrometry (mg kg^{-1}) [38]	0.02	0.03	0.02	–
5	Voltammetric method (ng L^{-1}) [Present method]	0.015	0.063	0.061	0.01

Table 3 Tolerance limit of anions and other pesticides in the determination of $250 \mu\text{g L}^{-1}$ of CYP, DEL, FEN and DCF at the modified systems

Anions	Tolerance limit ($\mu\text{g L}^{-1}$)	Other pesticides	Tolerance limit ($\mu\text{g L}^{-1}$)
Cl^{-1}	450	Phenol	500
Br^{-1}	400	Malathion	525
I^{-1}	420	Methyl parathion	550
SO_4^{2-}	450	Endosulfan	450
NO_3^{-}	300	–	–

3.3.2 Interference study

The influence of various substances as potential interference compounds on the determination of these pesticides was studied. Tolerance limit is defined as the maximum concentration of interfering substance that caused an error less than 5% for the determination of above said pesticides. The results are presented in Table 3. Herein, wide range of interferents was studied compared to other methods [35–39].

3.4 Analytical applications

3.4.1 Recovery studies in real samples

We examined the applicability of modified electrode for the determination of pesticides in water samples. These recoveries indicate that, the proposed voltammetric method can be easily applied to real samples. Precision and accuracy of this method was determined after dosing known amount of analytes into environmental sample solution. The percentage of recoveries with standard error of all insecticides is presented in Table 4. Stripping voltammograms thus obtained are given in Figs. 5A(b)–D(b) on the same system. The percentage of recovery obtained by this method is comparatively higher than solid-phase extraction and liquid chromatography/electrospray ionization ion trap mass spectrometric method [38] and voltammetric method reported by Oudou et al. [39].

Table 4 Percentage recovery of selected pesticides from water samples

Pesticides	Spiked ($\mu\text{g L}^{-1}$)	Found	Recovery (%)	RSD ^a
CYP	25	23.54	94.16	2.8
	100	96.25	96.25	3.2
DEL	25	23.40	93.60	2.7
	100	95.98	95.98	3.1
FEN	25	24.10	96.40	2.6
	100	95.65	95.65	2.9
DCF	25	24.42	97.68	3.3
	100	97.01	97.01	3.5

^a n = 6

4 Conclusions

The role of electrochemistry in pesticides analysis has been well defined and is likely to get preference when newer sensors are reported with attractive limits of detection. Herein, easily prepared surfactants doped PEDOT/MWCNT film modified GCE was used to investigate the electrochemical behaviour of CYP, DEL, FEN and DCF. The prepared material showed characteristic properties of both constituents, i.e. good electron transfer ability and large surface area. This electrode improved the electrochemical response drastically, which clearly demonstrates the electrocatalytic activity of modified film in the reduction of above-said pesticides. In particular, SDS doped PEDOT/MWCNT electrode gave stable and reproducible response and shows the determination range of 0.01 to $5 \times 10^4 \mu\text{g L}^{-1}$. MWCNT modified film also provides a nanobackbone for the polymerization of EDOT, which is confirmed through SEM studies. Also, SEM micrographs and XRD pattern revealed the adsorption of pesticide molecules on modified film. Further, a sensitive DPSV method was developed for the determination of pesticides in real samples with good results. It can be envisioned that conducting polymer/carbon nanotubes composite film made by this simple approach would have great potentials in the development of pesticide sensors.

Acknowledgment The authors would like to thank, Department of Science and Technology (DST), New Delhi, India for their financial support (Vide Project No. SR/S1/PC-16/2005 dt. 26.09.2007).

References

1. Katz E, Willner I, Wang J (2004) *Electroanalysis* 16:19
2. Wang J (2005) *Electroanalysis* 17:7
3. Merkoci A, Pumera M, Llopis X, Perez B, Valle MD, Alegret S (2005) *Trends Analyt Chem* 24:826
4. Vairavapandian D, Vichchulada P, Lay MD (2008) *Anal Chim Acta* 626:119
5. Manso J, Mena ML, Yanez-Sedeno P, Pingarron JM (2008) *Electrochim Acta* 53:4007
6. Gerard M, Chaubey A, Malhotra BD (2002) *Biosens Bioelectron* 17:345
7. Mullane APO, Dale SE, Day TM, Wilson NR, Macpherson JV, Unwin PR (2006) *J Solid State Electrochem* 10:792
8. Kymakis E, Amaratunga GAJ (2002) *Appl Phys Lett* 80:112
9. Cochet M, Maser WK, Benito AM, Callejas MA, Martinez MT, Benoit JM (2001) *Chem Commun* 1450:1
10. Manesh KM, Santhosh P, Komathi S, Kim NH, Parka JW, Gopalan AI, Lee K-P (2008) *Anal Chim Acta* 626:1
11. Peng C, Jin J, Chen GZ (2007) *Electrochim Acta* 53:525
12. Tsai YC, Li SC, Liao SW (2006) *Biosens Bioelectron* 22:495
13. Woo HS, Czerw R, Webster S, Carroll DL (2001) *Synth Met* 116:369
14. Santhosh P, Manesh KM, Gopalan A, Lee KP (2007) *Sens Actuators B* 125:92
15. Chen X, Yang Y, Ding M (2007) *Anal Chim Acta* 557:52
16. Augi L, Pena-farfal C, Yanez-Sedeno P, Pingarron JM (2007) *Electrochim Acta* 52:7946
17. Vasantha VS, Phani KLN (2002) *J Electroanal Chem* 520:79
18. Li G, Pickup PG (2000) *Phys Chem Chem Phys* 2:1255
19. Taskova V, Winkels S, Schultze JW (2001) *Electrochim Acta* 46:759
20. Tanabe S, Iwata H, Tatsukawa R (1994) *Sci Total Environ* 154:163
21. Wania F, Mackay D (1996) *Environ Sci Technol* 30:390A
22. Porazzi E, Martinez MP, Fanelli R, Benfenati E (2005) *Talanta* 68:146
23. Zhou Q, Xiao J, Wang W, Liu G, Shi Q, Wang J (2006) *Talanta* 68:1309
24. Leone AD, Ulrich EM, Bodnar CE, Falconer RL, Hites RA (2000) *Atmos Environ* 4:4131
25. Goncalves C, Alpendurada MF (2002) *J Chromatogr A* 968:177
26. Dong C, Zeng Z, Li X (2005) *Talanta* 66:721
27. Ye F, Xie Z, Wu X, Lin X (2006) *Talanta* 69:97
28. Manisankar P, Viswanathan S, Mercy Pusphalatha A, Rani C (2005) *Anal Chim Acta* 528:157
29. Hu C, Yang C, Hu S (2007) *Electrochem Commun* 9:128
30. Choi JW, Han MG, Kim SY, Oh SG, Im SS (2004) *Synth Met* 141:293
31. Manisankar P, Vedhi C, Selvanathan G, Gurumalles Prabu H (2007) *J Appl Polym Sci* 104:3285
32. Richard C, Balavoine F, Schultz P, Ebbesen TW, Mioskowski C (2003) *Science* 300:775
33. Yurekli K, Mitchell CA, Krishnamoorti R (2004) *J Am Chem Soc* 126:9902
34. Manisankar P, Vedhi C, Selvanathan G (2007) *J Polym Sci A* 45:2787
35. Huang Z, Li Y, Chen B, Yao S (2007) *J Chromatogr B* 853:154
36. Patil SH, Banerjee K, Dasgupta S, Oulkar DP, Patil SB, Jadhav MR, Savant RH, Adsule PG, Deshmukh MB (2009) *J Chromatogr A* 1216:2307
37. Li H-P, Lin C-H, Jen J-F (2009) *Talanta* 79:466
38. Chen T, Chen G (2007) *Rapid Commun Mass Spectrom* 21:1848
39. Oudou HC, Alonso RM, Jimenez RM (2001) *Electroanalysis* 13:72