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Voltammetric Studies of Ciprofloxacin Hydrochloride at Poly(L-Tyrosine)/SnO_2 Nanoparticles Modified Carbon Paste Electrode

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Abstract- The tin oxide (SnO_2) nanoparticles were synthesized by the gel combustion method. The synthesized SnO_2 nanoparticles & L-tyrosine were used for the modification of carbon paste electrode. The voltammetric behavior of ciprofloxacin hydrochloride (CIP) on the poly(L-tyrosine)/SnO_2 nanoparticles modified carbon paste electrode was investigated by using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The proposed sensor was successfully applied for the determination of CIP in real samples such as CIP in ciprodac tablets. The practical application of the modified electrode in the determination of CIP has good selectivity and high sensitivity.

Keywords- Ciprofloxacin hydrochloride, Modified carbon paste electrode, Cyclic voltammetry

1. INTRODUCTION

The ciprofloxacin hydrochloride (CIP) chemically described as 1-cyclopropyl -6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid, monohydrochloride. CIP is used to treat or prevent certain infections caused by bacteria. CIP is also used to treat or prevent anthrax in people who may have been exposed to anthrax germs in the air [1]. CIP

belongs to the family of fluoroquinolone antibacterial agents that also includes norfloxacin, ofloxacin and some other molecules. These fluoroquinolone antibacterial agents are synthetic derivatives of 6-fluoro-4-oxo-quinoline-3-carboxylic acid. They are fluorinated at position 6 and mostly bear a piperazinyl moiety at position 7. Ciprofloxacin is one of the most potent quinolone derivatives in clinical use with a very broad spectrum of antibacterial activity and is often used as an antibacterial agent of last resort [2]. L-Tyrosine is well known as a kind of essential amino acids in human and herbivores bodies. It is a vital constituent of proteins, which are indispensable in human nutrition for establishing and maintaining a positive nitrogen balance [3]. It is sometimes added to dietary and food products and to pharmaceutical formulations because it is scarcely present in vegetables. TS has been determined to be a precursor of dopa, dopamine, thyroxin, and epinephrine-hormone or neurotransmitters [4-5].

Electro polymerization is a good approach to immobilize polymers to prepare polymer modified electrodes (PMEs) as adjusting the electrochemical parameters can control film thickness, permeation and charge transport characteristics. Polymer-modified electrodes have many advantages in the detection of analytes because of its selectivity, sensitivity and homogeneity in electrochemical deposition, strong adherence to electrode surface and chemical stability of the film [6]. Selectivity of PMEs as a sensor can be attained by different mechanisms such as size exclusion [7], ion exchange [8], hydrophobicity interaction [9] and electrostatic interaction [10-11].

Voltammetric methods have been used to determine organic drugs in pharmaceutical dosage forms and related metabolites in biological fluids. The advance in experimental voltammetric techniques in the field of analysis of drugs is due to their simplicity, high sensitivity, low cost and relatively short analysis time as compared with other ones.

Nanotechnology is concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical, and biological properties, phenomena, and processes due to their nanoscale size [12-14]. Nano-SnO_2 possesses excellent photo electronic properties, high gas sensitivities and a short response time as well as relatively higher conductivity than TiO_2 and SiO_2 [15-17]. The nanoporous structures of these inorganic oxide films greatly enhance the active surface area available for bioactive molecules. These films facilitate direct electron transfer process between biomolecules and electrodes. SnO_2 has been synthesized by different methods such as the sol–gel method, chemical vapor deposition (CVD), magnetron sputtering and hydrothermal treatment [18].

SnO_2 nano particles were synthesized by the gel combustion method. We used the SnO_2 nanoparticles to modify a CPE and this SnO_2 nanoparticles CPE again polymerized by L-tyrosine and then investigated the electrochemical behavior of CIP at the poly(L-tyrosine)/ SnO_2 nanoparticles modified CPE. There are no reports for quantitative determination of

ciprofloxacin hydrochloride (CIP) by using poly(L-tyrosine)/SnO_2 nanoparticles modified carbon paste electrode.

In the present work, the modification was carried out by preparing poly (L-tyrosine)/SnO_2 nanoparticles on carbon paste electrode for the electrochemical investigation of ciprofloxacin hydrochloride (CIP) by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

2. EXPERIMENTAL PART

2.1. Reagents and stock solution

Tin(II) chloride dehydrate ($SnCl_2.H_2O$, 99.99%, Merck), Nitric acid (HNO_3, 70%, Merck) Citric acid ($C_6H_8O_7$, 99.5%, Merck), Ciprofloxacin hydrochloride (CIP) and L-tyrosine, potassium chloride (KCl) were purchased from Merck and all other chemicals were of analytical grade. The electropolymerisation of L-tyrosine was performed in 0.2 M phosphate buffer. The phosphate buffer solution was prepared from KH_2PO_4 and K_2HPO_4 and the pH was adjusted with 0.1 N NaOH solution. The stock solution of the ciprofloxacin hydrochloride (10 mM) was prepared by dissolving it in water. 1 M potassium chloride (KCl) was used as supporting electrolyte for all analytes. Other chemicals used were of analytical grade except for spectroscopically pure graphite powder. All solutions were prepared with doubly distilled water. Freshly prepared CIP is used prior to measurements.

2.2. Apparatus

Electrochemical measurements were carried out with a model-201 electrochemical analyzer (EA-201 chemlink systems) in a conventional three-electrode system. The working electrode was carbon paste electrode, having cavity of 3 mm diameter. The counter electrode was platinum electrode with a saturated calomel electrode (SCE) as a standard reference electrode completing the circuit.

2.3. Preparation of SnO_2 nanoparticles

SnO_2 nanoparticles was synthesized by gel combustion method. The raw materials used as tin(II) chloride dehydrate, 6.2 mole of nitric acid which is used as an oxidizer and mixed in an appropriate ratio to form a tin nitrate solution, then 1.5 mole of citric acid which acts as fuel was added to solution, and solution was heated at 90 °C in a Pyrex vessel with constant stirring. When the temperature was raised to about 300 °C, the polymeric precursor underwent a strong, self-sustaining combustion reaction occurs with evolution of large volume of gases and swelled into voluminous and foamy ashes. The entire combustion process occurs in a few seconds. The produced ashes were then calcinated at 800 °C (for 1 h).

The process was carried out, until the complete decomposition of the carbonaceous residues. Then the white powder SnO_2 nanoparticles was obtained [19].

2.4. Preparation of bare carbon paste electrode

The bare carbon paste electrode was prepared by hand mixing of graphite powder 70% and silicon oil 30% in an agate mortar for about 30 min to get homogenous carbon paste. The paste was then packed into the cavity of a Teflon tube electrode (3 mm diameter). Before measurement, the modified electrode was smoothened on a piece of transparent paper to get a uniform, smooth and fresh surface.

2.5. Preparation of the L-tyrosine polymer on SnO_2 nanoparticles modified carbon paste electrode

The poly (L-tyrosine) / SnO_2 nanoparticles modified carbon paste electrode was prepared by hand mixing of 70% graphite powder and 10 mg SnO_2 nanoparticle with 30% silicon oil in an agate mortar to produce a homogenous carbon paste. The paste was packed into the homemade cavity (3 mm in diameter) and then smoothed on a weighing paper. The electrical contact was provided by a copper wire connected to the paste in the end of the tube. Electrochemical polymerization of 1 mM L-Tyrosine is carried out in 0.2 M phosphate buffer solution (pH 4.0) by using cyclic voltammetry in the potential range from 500 to 1200 mV at sweep rate 50 mVs^{-1}. After 10 cycles, the surface of the electrode was washed with doubly distilled water to remove the physically adsorbed material. This modified electrode was immersed in PBS (pH 6.5) and electrochemical determination of CIP was carried out in a voltammetric cell in the potential range from 500 mV to 1200 mV. The same procedure was applied for all the sample analysis and all electrochemical measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. Characterization of prepared nanoparticles by XRD and SEM

Crystalline structure and crystallite size of SnO_2 nanoparticles were analyzed by Cu-K_α X-ray radiation (λ=1.5418A˚) in 2θ range from 20º to 80°, operating at 30 kV and 15 mA. The scan rate was 5°/min. The surface morphology and shape of the nanoparticles of powdered samples were investigated by scanning electron microscope (Hitachi Model S-3200N) XRD patterns of SnO_2 annealed at 800 °C for 1h are shown in Fig. 1, the average grain size was calculated using the Scherrer relation,

$$d = 0.89\frac{\lambda}{\beta\cos\theta} \quad (1)$$

Where d is the crystallite size, λ the wavelength of X-rays, β the full width of half maximum and θ the diffraction peak angle [20]. The crystallite sizes of samples are found to be 12 nm for sample SnO_2 nanoparticles by using Scherrer formula. Fig. 2 shows the typical SEM image of the SnO_2 nanoparticles. The particles are homogeneous with the average diameter of 12 nm. Fig. 1 shows the X-ray diffraction patterns of the nanoparticles prepared. We could see that the 2θ peaks are in agreement with the diffraction patterns from (110), (101), (200), (111), (210), (211) and (112), (220), (002), (310), (112), (301) planes. Particle size obtained from SEM analysis is comparable with crystallite size calculated from XRD spectra.

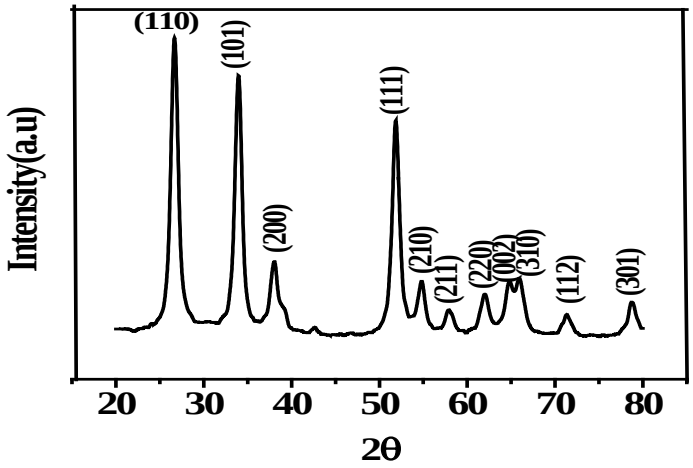


Fig. 1. XRD pattern of the synthesized SnO_2 nanoparticles

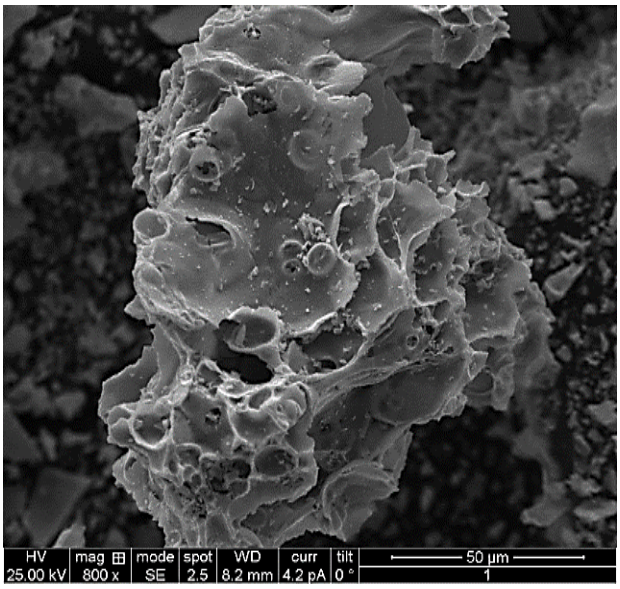


Fig. 2. SEM images of synthesized SnO_2 nano particles

3.2. Electropolymerisation of L-tyrosine on SnO_2 nanoparticles modified carbon paste Electrode

SnO_2 nanoparticles modified carbon paste electrode (SNMCPE) was prepared as discussed in above 2.5 which was electropolymerized by L-tyrosine. A solution of monomer L-tyrosine was oxidized to an activated form that polymerizes to form a polymer film directly on the electrode surface. This procedure results in few pinholes since polymerization would be accentuated at exposed (pinholes) sites at the electrode surface. Electro catalysis at a SnO_2 nanoparticles modified carbon paste electrode is usually an electron transfer reaction between the SnO_2 nanoparticles modified carbon paste electrode and solution substrate which, when mediated by a immobilized redox couple (i.e., the mediator), proceeds at a lower over potential than would otherwise occur at the bare electrode and enhances the peak current. Electropolymerisation of 1 mM L-tyrosine was fabricated in 0.2 M phosphate buffer solution on SnO_2 nanoparticles modified CPE. The film was grown on SnO_2 nanoparticles modified CPE by cyclic voltammetric scans between 500 to 1200 mV. The optimized scan number under the experimental conditions was determined as 10 for reaching the steady response. As shown in Fig. 3, in the first cycle, with the potential scanning from 500 to 1200 mV the anodic peak was observed at 946 mv corresponding to the oxidation of L-tyrosine. The peak descended gradually with the increase in cyclic time; such decrease indicates the formation of poly (L-tyrosine) membrane. On the surface of the SnO_2 nanoparticles modified CPE by eletropolymerization. L-tyrosine was oxidized to free radical at the surface of SnO_2 nanoparticles modified CPE rapidly resulting in the possible structure of electropolymerised poly (L-tyrosine). After polymerization the poly (L-tyrosine) / SnO_2 nanoparticles modified CPE was carefully rinsed with distilled water to remove the physically adsorbed material. Then the film electrode was transferred to an electrochemical cell and cyclic voltammetric sweeps were carried out to obtain electrochemical steady state.

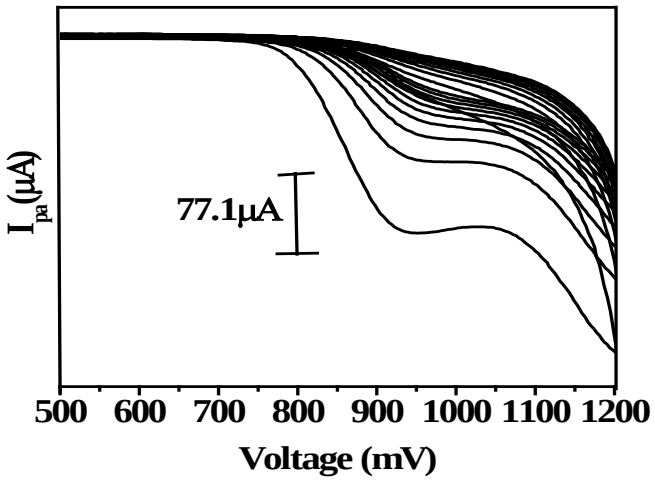
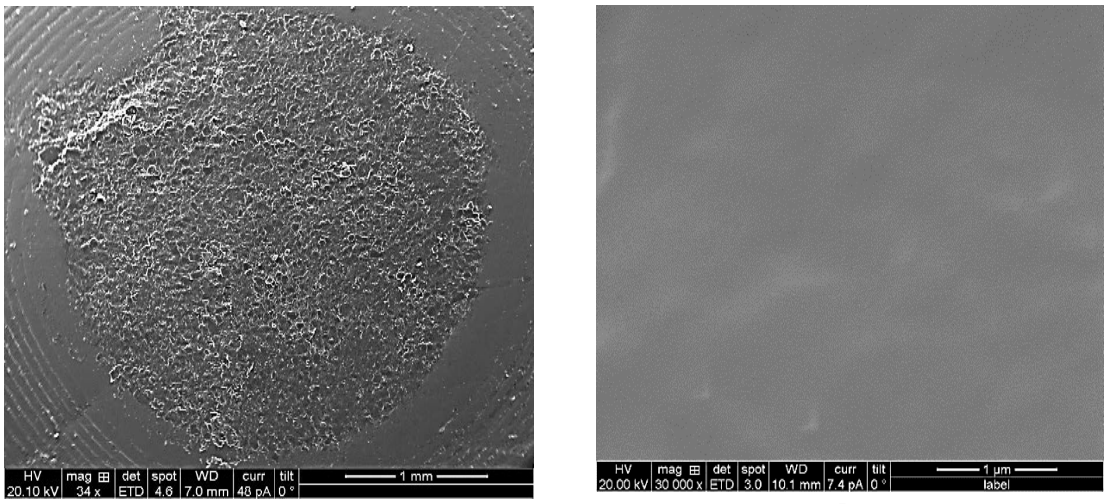


Fig. 3. Electropolymerisation of L-tyrosine on SnO_2 nanoparticles modified CPE

3.3. SEM Characterization of poly(L-tyrosine)/SnO_2 modified carbon paste electrode

Fig. 4a and Fig. 4b explain the surface morphology of bare CPE and poly (L-tyrosine)/SnO_2 nanoparticles modified CPE respectively using scanning electron microscopy. The surface of bare CPE was formed by irregularly shaped micrometer-sized flakes of graphite. The modified electrode had a typical uniform arrangement of L-tyrosine molecules on the surface of SnO_2 nanoparticles modified CPE (SNMCPE) [21].



(a) **(b)**

Fig. 4. (a) SEM image of bare CPE; **(b)** SEM image of poly (L-tyrosine)/ SnO_2 nanoparticles modified CPE (PLTSNMCPE)

3.4. Electrochemical response of potassium ferrocyanide at poly(L-tyrosine)/SnO_2 nanoparticles modified carbon paste electrode (PLTSNMCPE)

Potassium ferrocyanide was used as the electrochemical redox probe to investigate the electrochemical properties of poly(L-tyrosine)/SnO_2 nanoparticles modified CPE (PLTSNMCPE). The cyclic voltammogram of potassium ferrocyanide at (curve (a)) in Fig. 5 showed that the redox peak current increased than that of bare CPE (curve (b)) in Fig. 5. At the bare CPE the cyclic voltammogram of $K_4[Fe(CN)_6]$ showed a pair of redox peaks, with the anodic peak potential at 241 mV and the cathodic peak potential at 119 mV in 0.1 M KCl. However for PLTSNMCPE a pair of redox waves of $K_4[Fe(CN)_6]$ were observed with greatly increase of the peak current. The anodic peak potential was located at 237 mV and the cathodic peak potential at 123 mV respectively. The results of the enhancement of peak current showed excellent catalytic ability of PLTSNMCPE. The effective area of the modified electrode was found to be 0.0450 cm^2.

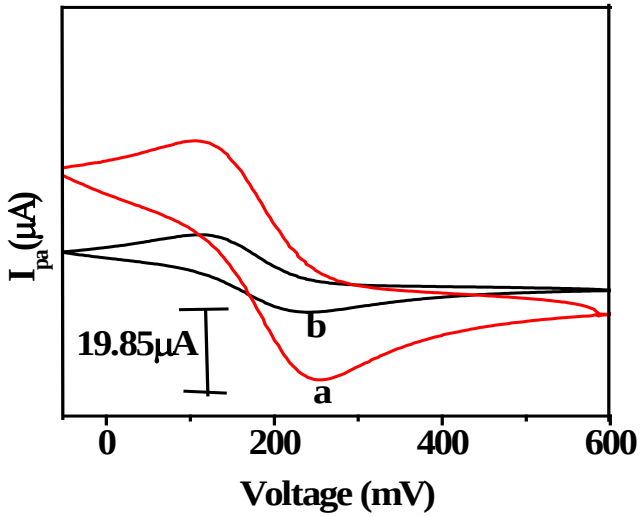


Fig. 5. Comparison of 0.1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution at PLTSNMCPE (a) and bare CPE (b)

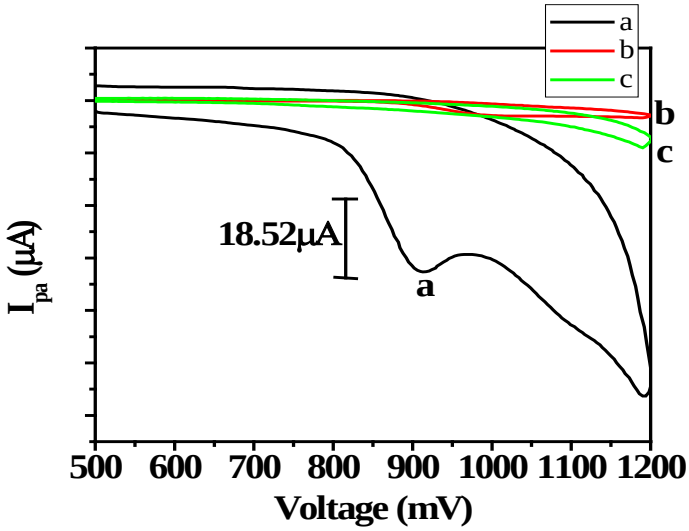


Fig. 6. Comparision of 0.1 mM CIP at PLTSNMCPE (a) Bare CPE (b) and Blank solution at PLTSNMCPE (c) pH 6.5, scan rate 50 mVs^{-1}

3.5. Electrochemical behavior of ciprofloxacin hydrochloride at PLTSNMCPE

The electrochemical behavior of ciprofloxacin hydrochloride (CIP) was investigated in 0.2 M phosphate buffer solution of pH 6.5 at PLTSNMCPE using cyclic voltammetric technique**.** Fig. 6 shows cyclic voltammogram of 0.1 mM ciprofloxacin hydrochloride (CIP) at bare CPE (curve b) and at PLTSNMCPE (curve a) and at blank solution of PLTSNMCPE) (curve c). Above studies showed that only one oxidation peak at 1046 mV and a anodic peak current of 3.8 µA at bare CPE, whereas an oxidation peak at 913 mV and a anodic peak

current of 18.52 µA at PLTSNMCPE, in the potential range 500 to 1200 mV. No reduction peak was observed in the reverse scan, suggesting that the electrochemical reaction is a totally irreversible process and the oxidation peak at the bare CPE is broad due to slow electron transfer, while the response was considerably improved at PLTSNMCPE and the peak potentials shifted to negative direction, the shape of the peak turns sharper and the peak current increased significantly.

3.6. Effect of pH

The electro oxidation of CIP was studied at 1 mM stock solution over pH range from 2.5 to 9.5 using 0.2 M PBS at a scan rate of 50 mV/s on PLTSNMCPE using cyclic voltammetry. The oxidation peak current increases with increase of pH from 2.5 to 6.5 and becomes maximum and peak potential shifted negatively. While pH beyond 6.5, a great decrease of the oxidation peak current could be observed, then it decreased gradually with the further increasing the pH of solution. Shown in Fig. 7.

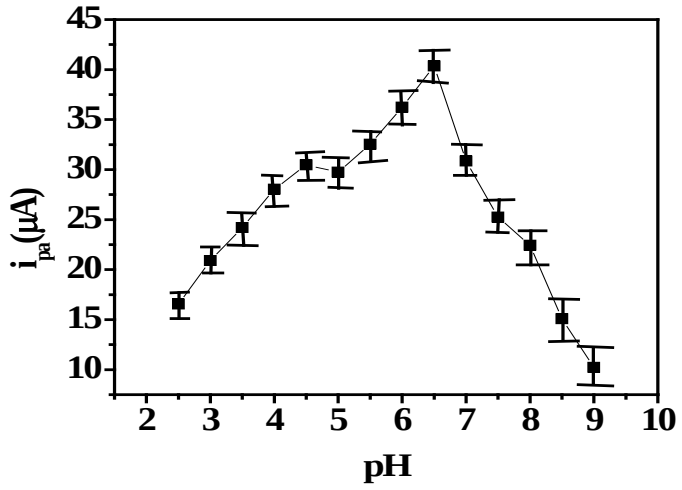


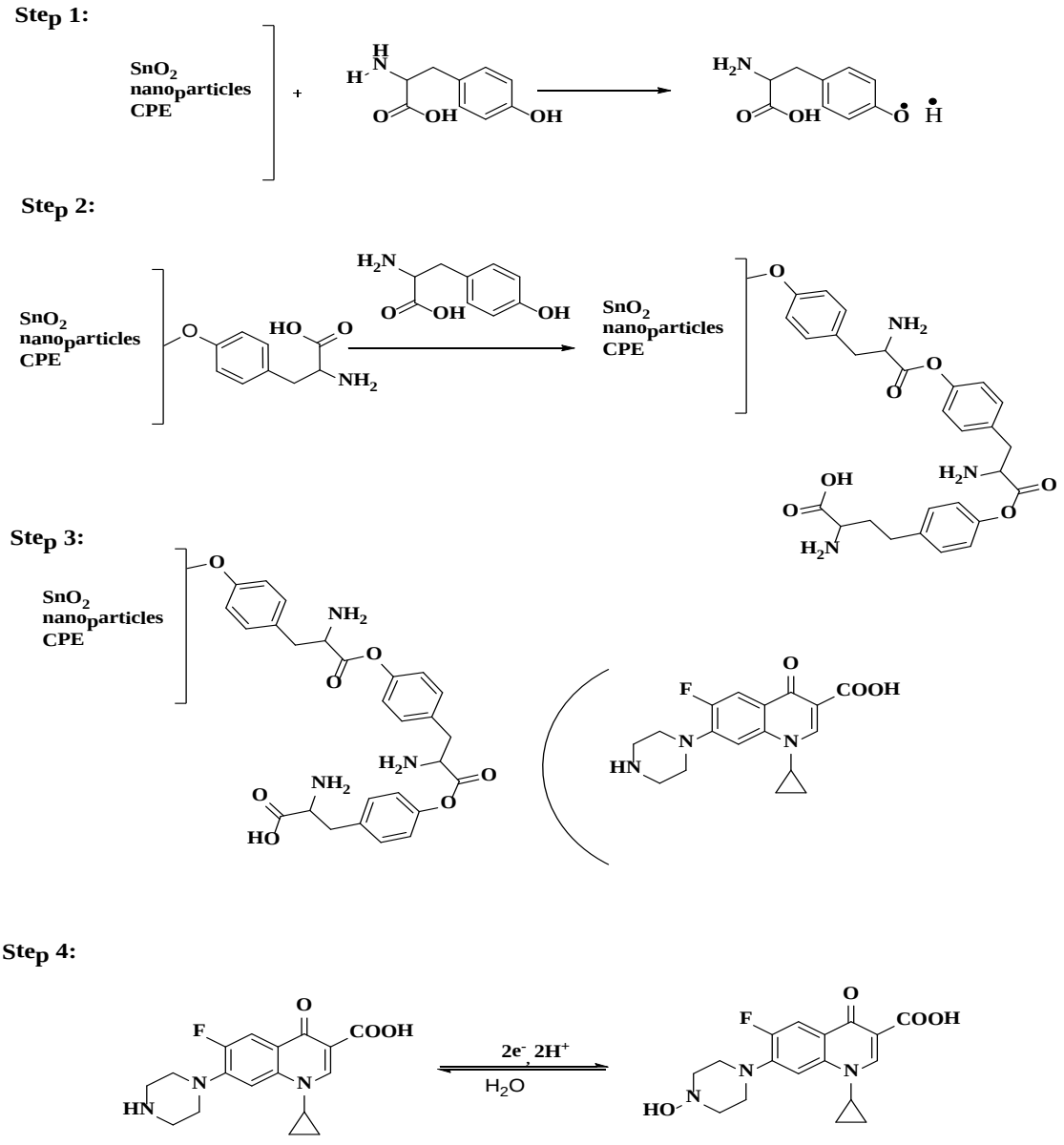
Fig. 7. Plot of current *vs*. pH (2.5–9.0) of 0.1 mM CIP at PLTSNMCPE

3.7. Effect of scan rate

Useful information involving electrochemical mechanism usually can be acquired from the relationship between peak current and scan rate. The effect of scan rates on the electrochemical response of 0.1 mM ciprofloxacin hydrochloride (CIP) at PLTSNMCPE was studied at different scan rates 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mVs^{-1} and the cyclic voltammogram was shown in Fig. 8a. A linear relationship with a correlation coefficient of R=0.99488 was obtained between the oxidation peak current and square root of scan rate in the range of 10-100 mVs^{-1} shown in Fig. 8b. Which revealed that a diffusion controlled

process occurring at PLTSNMCPE. According to Laviron's theory [22] the slope is equal to $RT/\alpha n_{\alpha}F$.

As for a totally irreversible electrode reaction On the basis of the above discussion, the n_{α} was calculated as 1.8032, which indicated that two electron was involved in the oxidation process of CIP at PLTSNMCPE. The electrochemical reaction process for CIP at PLTSNMCPE is given in Scheme 1. From the deduced mechanism of ciprofloxacin hydrochloride (CIP), an intermediate of a free radical was formed. It may be just the free radical polymerizes and deposit on the electrode surface, which agrees with the phenomena of voltammograms recorded from multi-cycle [23].



Scheme 1. Reaction mechanism

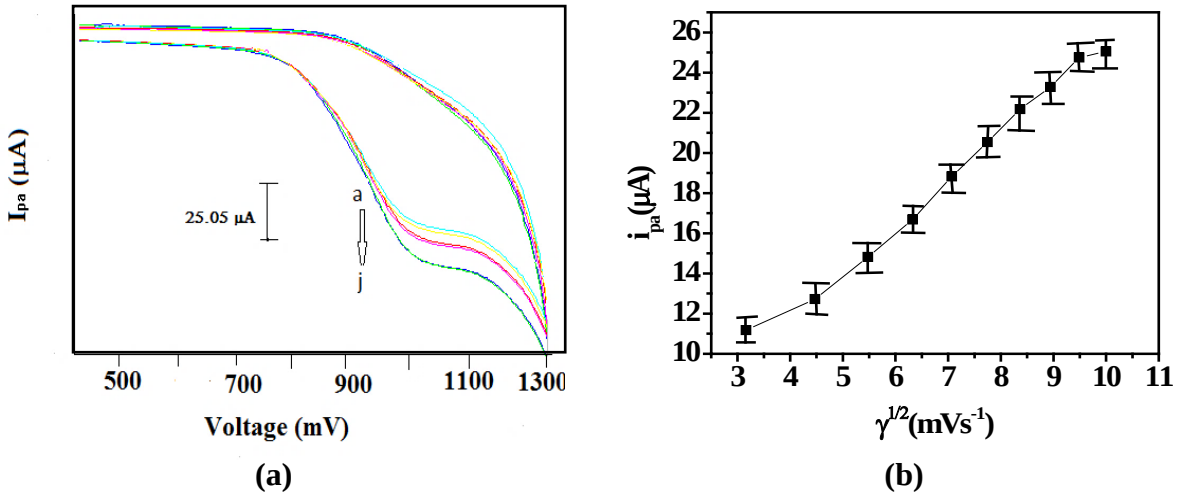


Fig. 8. (a) Cyclic voltammograms of 0.1 mM CIP at the PLTSNMCPE with different scan rates were (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 70, (h) 80 (i) 90, (j) 100 mVs^{-1}; **(b)** The plot of current *vs*. square root of scan rates of CIP at PLTSNMCPE

3.8. Calibration of ciprofloxacin hydrochloride (CIP) concentration

A series of ciprofloxacin hydrochloride solution from 1×10^{-5} to 1×10^{-4} M were prepared to investigate the relationship between the oxidation peak current (I_{pa}) and concentration of ciprofloxacin hydrochloride at PLTSNMCPE at a scan rate of 50 mV/s. Fig. 9a Shows as the concentration of CIP increases, the current also increases and at higher concentration the potential shifts towards negative direction. The plot of current (i_{pa}) *vs*. concentration shows linear Fig. 9b and is explained by a linear regression equation: I_{pa} (μA)=139.767 (10^{-5} M)+4.7837 (R=0.9923).

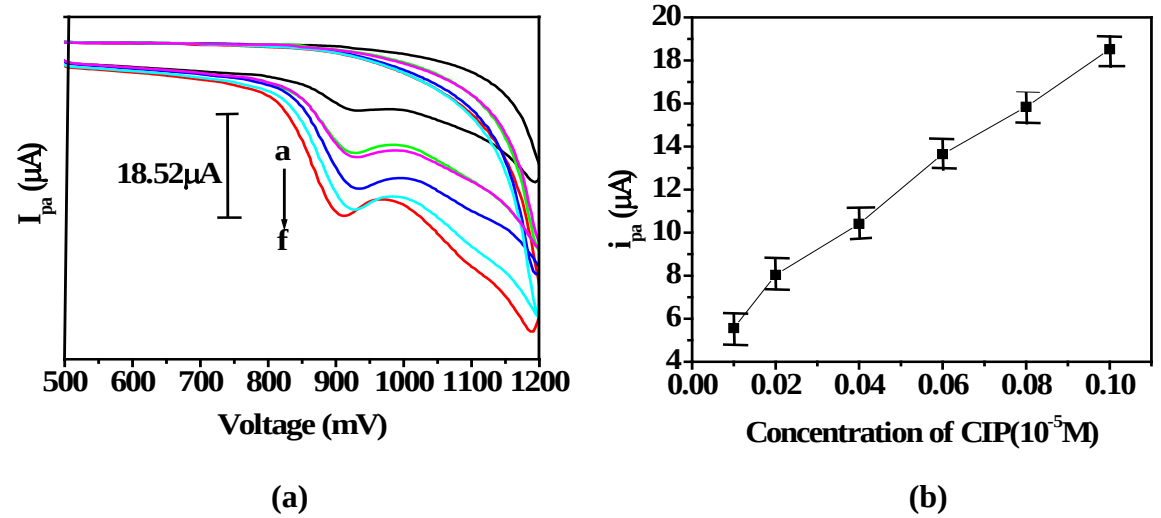


Fig. 9. (a) Effect of variation of concentration of CIP (a) 1×10^{-5} M, (b) 2×10^{-5} M, (c) 4×10^{-5} M, (d) 6×10^{-5} M, (e) 8×10^{-5} M, (f) 1×10^{-4} M on current at PLTSNMCPE; scan rate 50 mVs^{-1}; **(b)** The plot of current *vs*. CIP concentration at PLTSNMCPE

The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.10×10^{-7} M and 0.33×10^{-7} M, respectively.

The LOD and LOQ were calculated from the peak current using the following equation:

LOD = 3S/M, LOD = 10S/M

Where S is standard deviation and M is the slope of calibration plot.

3.9. Ciprofloxacin hydrochloride (CIP) studies by differential pulse voltammetry (DPV)

Differential pulse voltammetry (DPV) was used to investigate the possibility of PLTSNMCPE for determination of CIP (Fig. 10). The current responses of this CIP changed by changing the concentrations of CIP. As illustrated in DPV responses of the modified electrode for CIP increased linearly with increase of their concentrations. This can be described by linear regression equation for CIP in the range of 1×10^{-5} to 1×10^{-4} M is given by, i_{pa} (μA)=0.953+18.1C (r=0.9928). The limit of detection (LOD) and limit of quantification (LOQ) were found to be 0.646×10^{-7} M and 2.15×10^{-6} M, respectively.

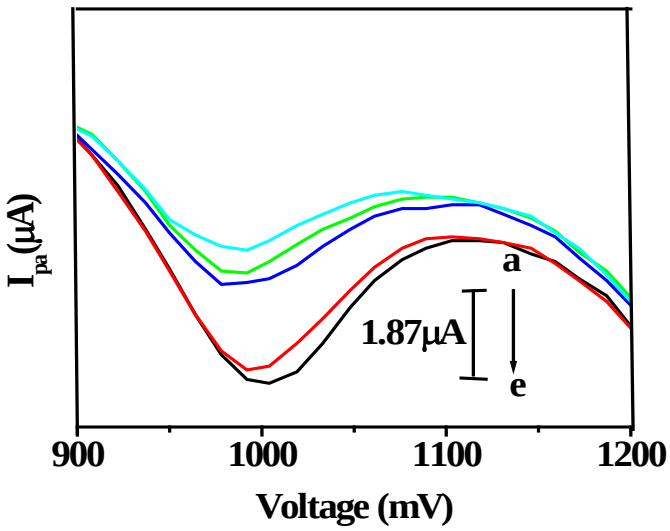


Fig. 10. DPV of CIP of (a) 1×10^{-5} M, (b) 2×10^{-5} M, (c) 3×10^{-5} M, (d) 4×10^{-5} M, (e) 5×10^{-5} M

3.10. Pharmaceutical determination of CIP in tablets

In order to validate the proposed method ciprofloxacin hydrochloride was determined in the commercially available as ciprodac tablets (declared content is 500 mg/tablet labeled on the sample). Ten tablets each containing 500 mg/tablet of ciprofloxacin hydrochloride were accurately weighed and the average value was determined. The tablets were then grind into a fine powder and an accurately weighed quantity of powder was dissolved in deionized water and transferred to a 100 ml volumetric flask. The resulting mixture was sonicated for 20–30

min to ensure that ciprofloxacin hydrochloride was completely dissolved. Then the mixture was filtered to remove the insoluble and the residue was washed several times and then diluting it to the required concentration in PBS (pH 6.5).

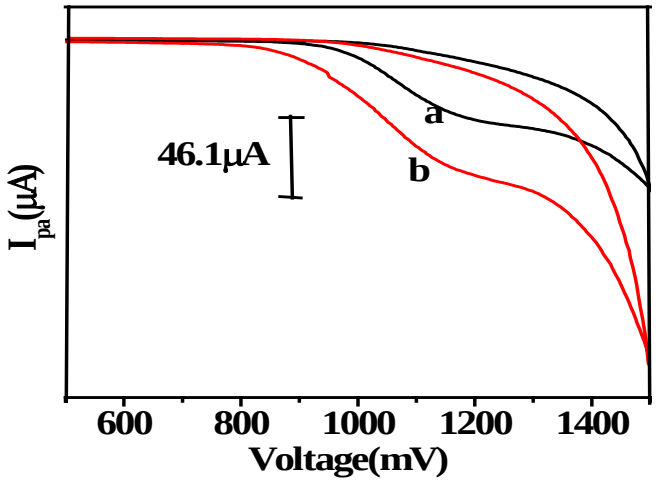


Fig. 11. Typical cyclic voltammograms for the determination of CIP in Ciprodac tablet sample at bare CPE (curve a) and at PLTSNMCPE (curve b) with a scan rate of 50 mVs^{-1}

The quantitative determination of ciprofloxacin hydrochloride was conducted according to the above mentioned experimental procedure under the optimum experimental conditions. The results of ciprofloxacin hydrochloride in commercial tablets obtained from cyclic voltammetric determination are presented in Table 1. Voltammogram for the determination of ciprofloxacin hydrochloride in the commercial tablet confirms the one peak. A typical cyclic voltammograms for the determination of ciprofloxacin hydrochloride in commercial ciprodac tablets at bare carbon paste electrode and poly (L-tyrosine) / SnO_2 nanoparticles modified carbon paste electrode were shown in Fig. 11. The detection limit obtained with several other modified electrodes using cyclic voltammetry shown in Table 2.

Table 1. Cyclic voltammetric response of CIP in ciprodac tablets at PLTSNMCPE

Sl.no	**Specified amount (mg)**	**Detected amount (mg)**	**Recovery%**	**RSD%(n=5)**
1	500	497.01	99.402	0.306
2	500	501.03	100.20	
3	500	499.43	99.88	
4	500	499.02	99.80	
5	500	500.34	100.68	

Tables 2. Comparison of detection limit of different modified electrodes

Electrode	**Detection limit (M)**	**Techniques**	**Reference**
DNA/GC	0.117×10^{-6}	Differential pulse anodic stripping voltammetry	[24]
Cd(II)/Graphene modified electrode	5.9×10^{-8}	Anodic stripping voltammetry	[25]
Hanging Mercury dropping electrode(HMDE)	7×10^{-9}	Square wave voltammetric method	[26]
Poly(L-Tyrosine) SnO_2 nanoparticles carbon paste electrode	10×10^{-9}	Cyclic voltammetry technique	Present work

3.10.1. Electrocatalytic response of CIP and ENRO at poly (L-tyrosine)/SnO_2 nanoparticles MCPE

It is well known that Enrofloxacin (ENRO) widely coexists with CIP in chemical compounds. Therefore avoiding ENRO interference is an important target for any CIP analytical methods. In Fig. 12, the voltammetric response of CIP and ENRO at PLTSNMCPE at pH 6.5 with scan rate 50 mVs^{-1}. PLTSNMCPE CIP exhibited enhanced peak currents in the presence of ENRO. The Three well oxidation peaks separated between CIP and ENRO.

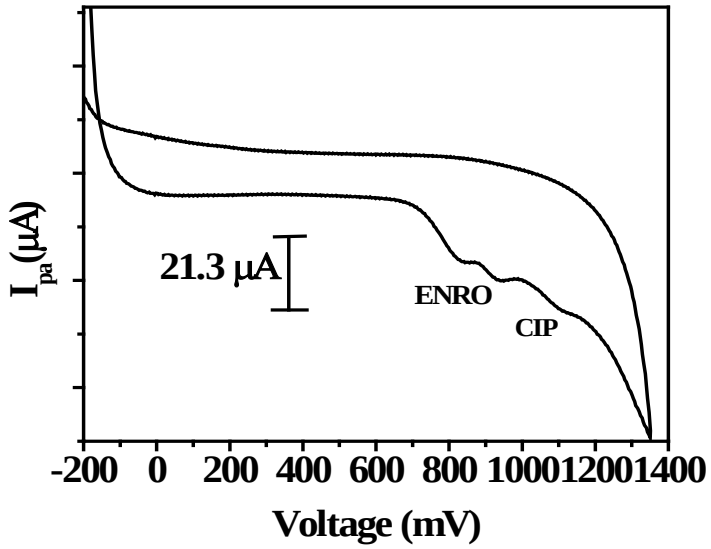


Fig. 12. Cyclic voltammogram obtained for oxidation of ENRO and CIP at PLTSNMCPE at scan rate of 50 mVs^{-1}, 0.2 M PBS (pH 6.5)

The electrocatalytic anodic of CIP was obtained at 1280 mV and ENRO was found to be at 850 and 936 mV. This result shows that PLTSNMCPE acts as good sensor for the detection of CIP in the presence of ENRO.

4. CONCLUSION

In the present study, a chemically modified poly(L-tyrosine)/SnO_2 nanoparticles modified carbon paste electrode based on the electropolymerisation has been prepared for the electrochemical determination of ciprofloxacin hydrochloride (CIP). Results showed that the oxidation peak current of ciprofloxacin hydrochloride (CIP) was improved at poly(L-tyrosine)/SnO_2 nanoparticles modified CPE. The electrochemical response is diffusion controlled and irreversible in nature. A linear concentration range was found to occur from 1×10^{-5} to 1×10^{-4} M. The probable reaction mechanisms involved in the oxidation of ciprofloxacin hydrochloride (CIP) were also proposed. The applicability of the proposed voltammetric method for the assay of ciprofloxacin hydrochloride (CIP) was examined by analyzing the commercially available ciprodac tablets (declared content is 500 mg of ciprofloxacin hydrochloride in one tablet) and successfully applied for the determination of ciprofloxacin hydrochloride in pharmaceutical dosages.

REFERENCES

[1] B. Uslu, B. Bozal, and M. E. Kuscu, Open Chem. Biomed. Met. J. 3 (2010) 108.
[2] Y. Cai ,Y. Zhang, S. Su, S. Li, and Y. Ni, Frontier. Biosci. 2 (2007) 1946.
[3] J. P. Jin, and X. Q. Lin, Electrochem. Commun. 6 (2004) 454.
[4] A. Carlsson, and M. Lindqvist, Naunyn-Schmiedeberg's Arch. Pharmacol. 303 (1978) 157.
[5] P. J. Currie, N. Chang, S. Luo, and G. H. Anderson, Life Sci. 57 (1995) 1911.
[6] P. R. Roy, T. Okajima, and T. Ohsaka, Bioelectrochemistry 59 (2003) 11.
[7] X. L. Wen, Y. Jia, L. Yang, and Z. L. Liu, Talanta 53 (2001) 1031.
[8] E. Ekinci, G. Erdogdu, and A. E. Karagozler, J. Appl. Polym. Sci. 79 (2001) 327.
[9] M. Pontie, C. Gobin, T. Pauporte, F. Bedioui, and Devynck, J. Anal. Chim. Acta 411 (2000) 175.
[10] H. Zhao, Y. Z. Zhang, and Z. B. Yuan, Electroanalysis 14 **(**2002) 445.
[11] H. Zhao, Y. Z. Zhang, and Z. B. Yuan, Anal. Chim. Acta 454 (2002) 75.
[12] Y. Sun, Adv. Funct. Mater. 20 (2010) 3646.
[13] M. S. El-Deab, and T. Ohsaka, Angew. Chem. Int. Ed. 45 (2006) 5963.
[14] H. B. Na, J. H. Lee, K. An, Y. I. Park, M Park, I. S. Lee, D. H. Nam, S. T. Kim, S. H. Kim, and S. W. Kim, Angew. Chem., Int. Ed. 46 (2007) 5397.

[15] M. Acciawi, C. Canevial, M. Mari, M. Mattoni, R. Ruffo, R. Scotti, F. Morazzoni, D. Barreca, L. Armelao, and E. Tondello, Chem. Mater. 15 (2003) 2646.
[16] K. N. Yu, Y. H. Xiong, Y. L. Liu, and C. S. Xiong, Phys. Rev. B 55 (1997) 2666.
[17] E. Topoglidis, Y. Astuti, F. Duriaux, M. Gratzal, and J. R. Durrant, Langmuir 19 (2003) 6894.
[18] J. H. Kang, Z. Jin Young Kim, and D. Young Jeon, J. Electrochem. Soc. 152 (2005) 33.
[19] M. P. Rajeeva, C. S. Naveen, A. R. Lamani, and H. S. Jayanna, AIP Conf. Proc. 183 (2013) 1536.
[20] L. Patterson, Phys. Rev. Online Arch. (Prola) 56 (1939) 978.
[21] A. Caro, F. Bedioui, and J. H. Zagal, Electrochim. Acta 47 (2002) 1489.
[22] E. J. Laviron, Electroanal. Chem. 52 (1974) 355.
[23] M. P. Deepak, G. P. Mamatha, and B. S. Sherigara, IJPC 4 (2014) 122.
[24] N. Diab, I. Abu-shqair, R. Salism, and M. Al-sabu, Int. J. Electrochem. Sci. 9 (2014) 1771.
[25] J. Shan, Y. Liu, R. Li, C. Wu, L. Zhu, and J. Zhang, J. Electroanal. Chem. 738 (2015) 123.
[26] A. F. Al-ghamdi, and A. d. Bani-yaseen, Russian J. Electrochem. 50 (2014) 355.