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Square Wave Voltammetric Analysis of Carbidopa Based on Carbon Paste Electrode Modified with ZnO/CNTs Nanocomposite and n-hexyl-3-methylimidazolium Hexafluoro Phosphate Ionic Liquid

Vinod Kumar Gupta[1, 2,**], *Saeed Rostami*[3], *Hassan Karimi-Male* [3,*], *Fatemeh Karimi*[4], *Mohsen Keyvanfard*[4], *Tawfik A. Saleh*[2]

[1] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India
[2] King Fahd University of Petroleum and Minerals Dhahran, Saudi Arabia
[3]Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran
[4] Department of Chemistry, Majlesi Branch, Islamic Azad University, Isfahan, Iran
[**]E-mail: vinodfcy@gmail.com;vinodfcy@iitr.ac.in (V.K. Gupta);* h.karimi.maleh@gmail.com

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In this study the electrochemistry of carbidopa (CD) was studied by electrochemical methods at a carbon paste electrode modified by ZnO/CNTs nanocomposite and room-temperature ionic liquid, n-hexyl-3-methylimidazolium hexafluoro phosphate (ZnO/CNTs/ILs/CPE). The oxidation peak potential of the CD at a surface of ZnO/CNTs/ILs/CPE appeared at 570 mV that was about 90 mV lower than the oxidation peak potential at the surface of the unmodified carbon paste electrode (CPE) under similar condition. Under the optimized conditions, the oxidation peak current of CD showed two linear dynamic ranges (in 0.09–450 μmol L^{-1}) with a detection limit of 0.05 μmol L^{-1}, using square wave voltammetry (SWV). The proposed sensor was successfully applied for the determination of CD in real samples such as pharmaceutical serum, water and urine.

Keywords: Carbidopa, ZnO/CNTs nanocomposite, n-hexyl-3-methylimidazolium hexafluoro phosphate, Square wave voltammetry

1. INTRODUCTION

Catecholamines are produced mainly by the chromaffin cells of the adrenal medulla and the postganglionic fibers of the sympathetic nervous system. Catecholamines have a half-life of a few minutes when circulating in the blood. They can be degraded either by methylation by catechol-O-methyltransferases (COMT) or by deamination by monoamine oxidases (MAO) [1]. Carbidopa is a

drug given to people with Parkinson's disease (PD) in order to inhibit peripheral metabolism of levodopa. CD is used in the treatment, among other diseases, of PD, a condition where patients are suffering from lack of the sufficient brain dopamine [2]. CD is known as an enzyme blocker and works by preventing the breakdown of levodopa in the bloodstream. This allows more levodopa to enter the brain, where it can decrease Parkinson's symptoms. By helping more levodopa gets into the brain so that less stays in the bloodstream, carbidopa can reduce some of levodopa's side effects such as nausea [3]. According to the above points, it is necessary for suggestion of a fast, sensitive and selective method for determination of CD in pharmaceutical and biological compounds.

The science of nanomaterials has created great excitement and expectation in the last decade at the nano-scale fundamental properties changes [4-10]. Metal oxide nanomaterials were used as suitable mediator in the preparation of electrochemical sensor in environmental, pharmaceutical and biological compounds analysis [11–15] and starting materials for preparing advanced structural ceramics. Also, nanocomposite based materials with variety of shapes, sizes and compositions are changing nowadays the analytical measurement [16-20].

Electrochemical sensors modified with ionic liquids (ILs) have received much attention due to their specific characteristics such as negligible vapour pressure, good chemical stability, high ionic conductivity and wide electrochemical windows in the last decade [21-25]. Based on the above mentioned points, combination of metal oxide nanomaterials and ILs could show some novel properties in the preparation of new sensors in pharmaceutical and biological compounds analysis [26-28].

In this work, we describe the synthesis and application of ZnO/CNTs as a suitable mediator and n-hexyl-3-methylimidazolium hexafluoro phosphate as a suitable binder in a carbon paste matrix for the voltammetric determination of CD. We also evaluate the analytical performance of the modified electrode for the voltammetric determination of CD in real samples such as water, urine and serum.

2. EXPERIMENTAL

2.1. Chemicals

All chemicals used were analytic reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. CD was from Sigma. Other reagents were used without further purification.

A 1.0×10^{-2} mol L^{-1} CD solution was prepared daily by dissolving 0.23 g CD (from Sigma) in water and the solution was diluted to 100 mL with water in a 100-mL volumetric flask. The solution was kept in a refrigerator at 4 °C in dark. More dilute solutions were prepared by serial dilution with buffer solution.

Phosphate buffer solutions (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol L^{-1}), PBS, with different pH were used.

Spectrally pure graphite powder (particle size <50 μm), and high viscous paraffin oil (density = 0.88 kg L^{-1}) from Merck were used as the substrate for the preparation of the working electrodes.

2.2. Apparatus

Voltammetric study were performed in an analytical system, Autolab PGSTAT 302N, potentiostat/galvanostat connected to a three electrode cell, Metrohm Model 663 VA stand, linked with a computer (Pentium IV, 1200 MHz) and run with GPES and FRA 4.9 software. Frequency range of 100 kHz to 1.0 Hz was employed for impedance measurements. The AC voltage amplitude used was 5 mV, and the equilibrium time was 20 min. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an ($Ag/AgCl/KCl_{sat}$) electrode as a reference electrode were used. The working electrode was either an unmodified or modified carbon paste electrode.

2.3. Preparation of the modified electrode

ZnO/CNTs/ILs/CPE was prepared by mixing of 0.15 g of ionic liquid, 0.85 g of the liquid paraffin, 0.2 g of ZnO/CNTs, and 0.70 g of graphite powder. Then the mixture was mixed well for 50 min until a uniformly wetted paste was obtained. A portion of the paste was filled firmly into one glass tube as described above to prepare ZnO/CNTs/ILs/CPE. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper.

2.4. Preparation of real samples

Urine samples were stored in a refrigerator at 4^{o}C immediately after collection. Ten milliliters of each sample was centrifuged for 30 min at 2000 rpm. The supernatant was filtered using a 0.45 μm filter and then diluted five times with PBS (pH 6.0). The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. Standard addition method was used for the determination of morphine in real samples.

Serum samples were obtained from the Kerman Health Centre and were stored in a refrigerator immediately after collection. The serum sample was used without any pretreatment for real sample analysis.

2.5. Synthesis of ZnO/CNTs nanocomposite

The commercial MWCNT/COOH with tube diameters of about 10–20 nm was used. Certain amounts of purified CNTs (6 g) were dispersed into distilled water solution of NaOH (0.5 M; 100 mL) by ultrasonication for 25 min. In the next step is the supporting of zinc oxide on carbon nanotubes by a direct deposition process. 7.4 g $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 100 mL distilled water. Under constant magnetic stirring, the solution of $Zn(NO_3)_2 \cdot 6H_2O$ was added drop wise to the solution of CNTs at 50 °C through a dropping funnel. The rate of addition of the salt solution was kept approximately at 20 mL/h. After completion of the precipitation procedure, the mixture was stirred at

room temperature for 12 h, washed and filtered continually in distilled water (pH 7.0), and dried at 120 °C. The solid samples were then calcined at 300 °C for 2 h.

3. RESULTS AND DISCUSSION

3.1. Synthesis nanocomposite characterization

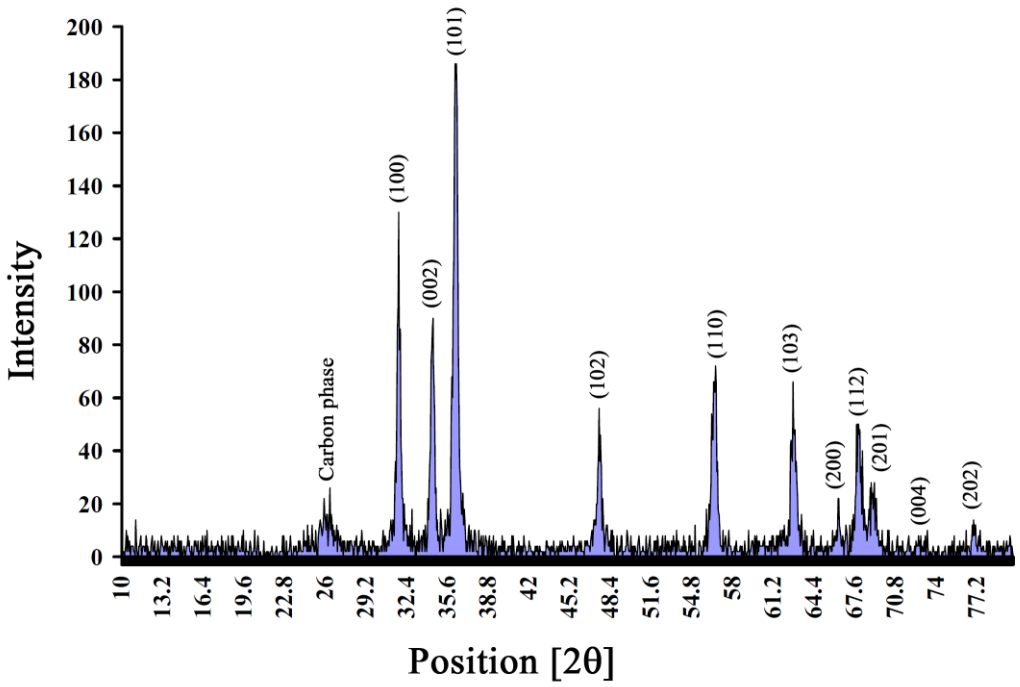

Figure 1. XRD patterns of as-synthesized ZnO/CNT nanocomposite

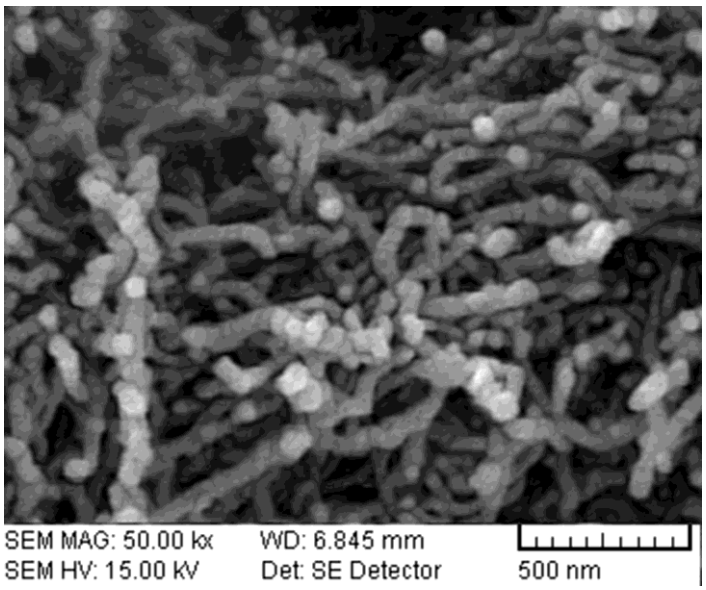

Figure 2. SEM image of ZnO/CNTs synthesis in this work.

ZnO/CNT nanopowders were analyzed by XRD analyses (Fig. 1). The XRD pattern of ZnO/CNT nanopowders, in the 2θ range of 10–80°, is shown in Fig. 1. It clearly proves the presence of ZnO nanoparticle, with a diffraction peak at about 26° from CNTs. An average diameter of as-synthesized ZnO nanoparticle was calculated from the broadness peak of 2θ=35.6 by using Scherrer equation ($D = K\lambda/\beta \cos\theta$), and it is about 70.0 nm. The morphology of the as-grown nanostructures was characterized by SEM. Typical SEM micrograph of the ZnO/CNTs is shown in Fig. 2. The results show the presence of ZnO nanostructure grown on carbon nanotubes.

3.2. Electrochemical investigation

According to previous reports, the oxidation peak current of CD is closely related to the pH value of electrolyte solution [2]. Therefore, the effect of pH was investigated using cyclic voltammetry technique. In order to ascertain this, the voltammetric response of CD at a surface of ZnO/CNTs/ILs/CPE was obtained in solutions with varying pH. It was found that the oxidation peak current increased gradually from pH 4.0 to 6.0, and then the current conversely decreased when the pH value increased from 6.0 to 7.0. Therefore pH 7.0 was chosen as the optimal experimental condition in this work. The relationship between the oxidation peak potential and pH was also constructed. A linear shift of E_{pa} towards negative potential with an increasing pH can be obtained and obeyed the regression equation of E_{pa} (V) = -0.053 pH + 0.889 (R^2 = 0.998), which indicates that protons are directly involved in the oxidation of CD (Figure 3).

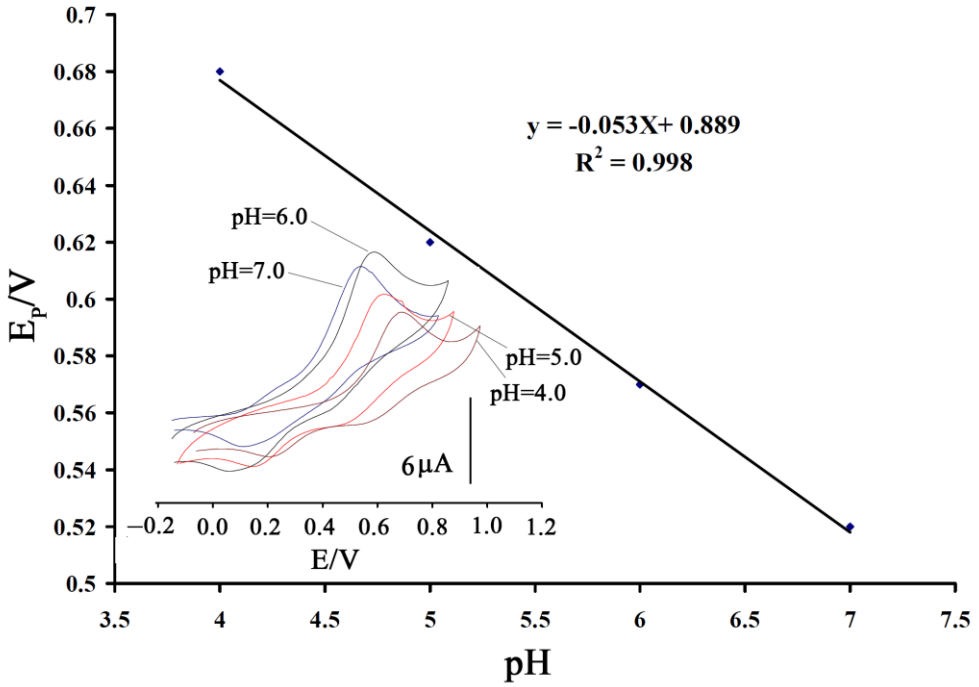

Figure 3. Current–pH curve for electrooxidation of 100.0 μmol L^{-1} CD at ZnO/CNTs/ILs/CPE with a scan rate of 100 mV s^{-1}. Inset: influence of pH on cyclic voltammograms of CD at a surface of the modified electrode, (pH 4, 5, 6 and 7, respectively).

A slope of 53 mV/pH suggests that the number of electron transfer is equal to the proton number involved in the electrode reaction. Because the two electrons involved in the oxidation of CD (catechol oxidation peak in this case) at ZnO/CNTs/ILs/CPE, the transfer proton number was 2.

The effect of pH on the anodic peak current was investigated (Fig. 4). The results showed that when the pH exceeded pH 6.0, the peak currents began to decrease and even disappearedwith further increasing the buffer pH. Therefore, pH 6.0, PBS, was selected for all the experiments.

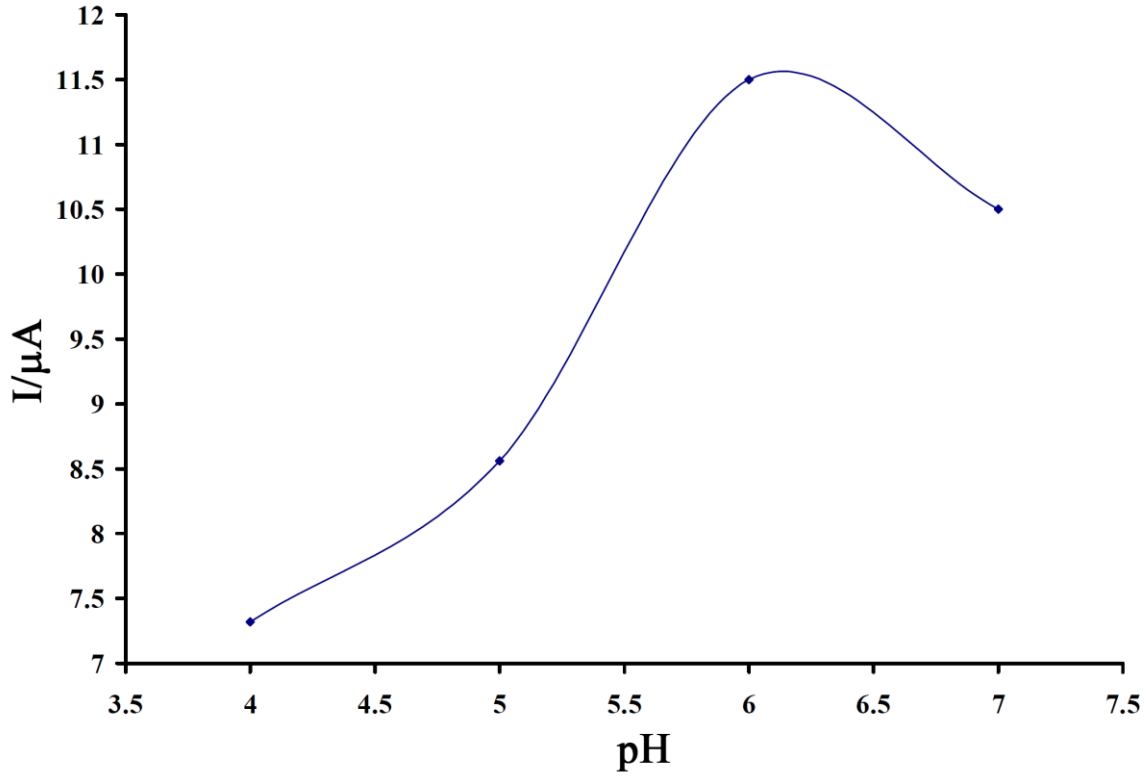

Figure 4. Current–pH curve for electrooxidation of 100.0 μM CD at ZnO/CNTs/ILs/CPE with a scan rate of 100 mV s^{-1}.

Figure 5 shows cyclic voltammograms of 200 μmol L^{-1} CD at pH 6.0 at the surface of different electrodes with a scan rate of 100 mV s^{-1}. ZnO/CNTs/ILs/CPE exhibited significant oxidation peak current around 570 mV with the peak current of 27.9 μA (Fig. 5, curve a). In contrast, low redox activity peak was observed at ZnO/CNTs/CPE (Fig. 5, curve c) and at unmodified CPE (Fig. 5 curve d) over the same condition. The CD oxidation peak potential at ZnO/CNTs/CPE and at CPE observed around 641 and 660 mV vs. the reference electrode with the oxidation peak current of 11.5 and 8.22 μA, respectively. In addition, at the surface of bare ILs/CPE, the oxidation peak appeared at 593 mV with the peak current was 20.4 μA (Fig. 5, curve b), which indicated the presence of ILs in CPE could enhance the peak currents and decrease the oxidation potential.

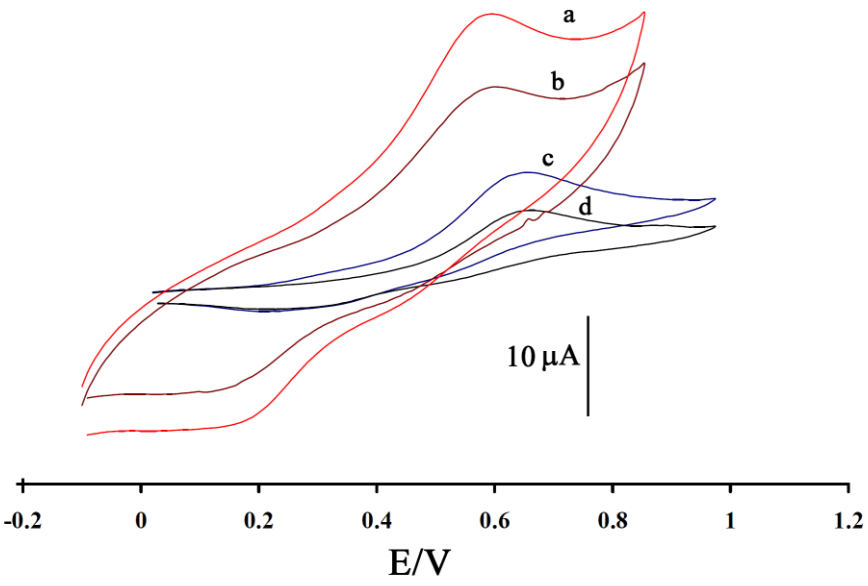

Figure 5. Cyclic voltammograms of (a) ZnO/CNTs/ILs/CPE, (b) ILs/CPE, (c) ZnO/CNTs/CPE and (d) CPE in the presence of 200 μmol L^{-1} CD at pH 6.0, respectively.

A substantial negative shift of the currents starting from oxidation potential for CD and dramatic increase of current of CD indicated the catalytic ability of ZnO/CNTs/ILs/CPE to CD oxidation. The results indicated that the presence of ZnO/CNTs on ZnO/CNTs/ILs/CPE surface had great improvement with the electrochemical response, which was partly due to excellent characteristics of ZnO/CNTs such as good electrical conductivity, high chemical stability, and high surface area. The suitable electronic properties of ZnO/CNTs together with the ionic liquid gave the ability to promote charge transfer reactions, good anti-fouling properties, especially when mixed with a higher conductive compound such as ILs when used as an electrode.

The effects of scan rate (in the range of 10–140 mV s^{-1}) on the peak current at ZnO/CNTs/ILs/CPE in 0.1 mol L^{-1} PBS (pH 6.0) in the presence of 120 μmol L^{-1} CD was investigated using cyclic voltammetry (Fig. 6, inset). As shown, the peak currents increased linearly with the square root of the scan rate, which indicates a diffusion controlled oxidation process occurring at ZnO/CNTs/ILs/CPE [29-33]. On the other hand, the peak potential shifts in negative direction when the scan rate increases, meaning that the electrochemical reaction is irreversible. At higher scan rate, the dependence of the peak potential (E_{pa}) and ln(ν) showed a linear relationship with a regression equation of:

$E_{pa} = 0.0274 \ln(\nu) + 0.4435$ (r^2=0.9920, E_p in V, ν in V s^{-1}) (1)

According to the following equation:

$E_{pa} = E^{0/} + m\,[0.78 + \ln(D^{1/2}k_s^{-1}) - 0.5\ln m] + (m/2)\ln(\nu)$ (2)

With

$m = RT/[(1-\alpha)n_\alpha F]$ (3)

where E_{pa} is oxidation peak potential, $E^{0/}$ is the formal potential ,ν is the sweep rate, k_s is electron transfer rate constant. A plot of $E_{pa}=f(\ln(\nu/V\ s^{-1})$ yields a straight line with slopes equal to

$2(RT/[(1–\alpha)n_\alpha F)$. where R=8.314 J mol^{-1} $^0K^{-1}$, T=298 ^0K and F=96485 C mol^{-1}. The value of $n(1–\alpha)$ is calculated 0.76 from Eq. (3), which indicates that the activation free energy curve is not symmetrical in such an irreversible oxidation process.

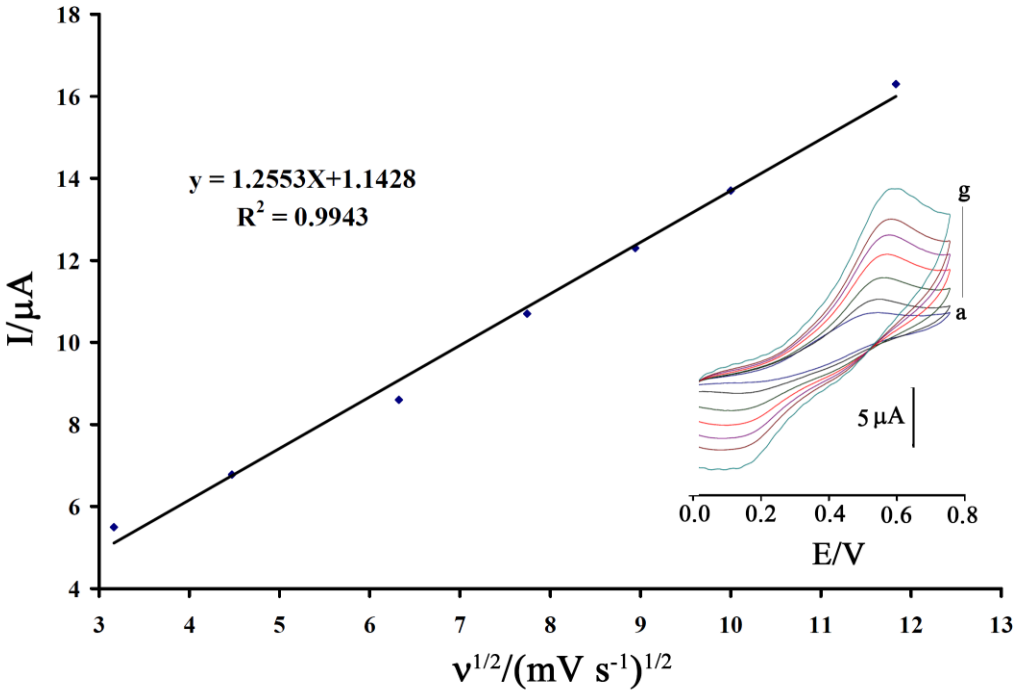

Figure 6. Plot of I_{pa} versus $\nu^{1/2}$ for the oxidation of CD at ZnO/CNTs/ILs/CPE. Inset shows cyclic voltammograms of CD at ZnO/CNTs/ILs/CPE at different scan rates (from a-g) of 10, 20, 40, 60, 80, 100 and 140 mV s^{-1} in 0.1 M phosphate buffer, pH 6.0.

Chronoamperometric measurements of different concentrations of CD at ZnO/CNTs/ILs/CPE were done by setting the working electrode potential at 650 mV (Fig. 7A). In chronoamperometric studies, we have determined the diffusion coefficient, D, of CD. From slopes of I versus $t^{-1/2}$ using the Cottrell equation (Fig. 7 B):

$$I = nFAD^{1/2} C_b \pi^{-1/2} t^{-1/2} \quad (4)$$

According to the above equation and data obtained from chronoamperometry we calculated a diffusion coefficient of 3.81×10^{-5} cm^2 s^{-1} for CD.

Dynamic range and detection limit are very important parameter in determination of electroactive materials [34-57]. So, in continuous square wave was used to determine the concentration of CD. Voltammograms clearly showed two linear dynamic range that the plot of the peak current versus CD concentration is linear for 0.09 – 3.5 μmol L^{-1} of CD, the regression equation was $I_p(\mu A) = (0.9856\pm0.0312)C_{CD} + (0.331\pm0.0214)$ (r^2 = 0.9945, n = 5) and for 3.5 – 450 μmol L^{-1} of CD, the regression equation was $I_p(\mu A) = (0.1091\pm0.0045)C_{CD} + (6.3399\pm0.8731)$ (r^2 = 0.9954, n = 8), where C is μmol L^{-1} concentration of CD and I_p is the peak current. The detection limit was determined at 0.05 μmol L^{-1} CD according to the definition of $Y_{LOD} = Y_B + 3\sigma$.

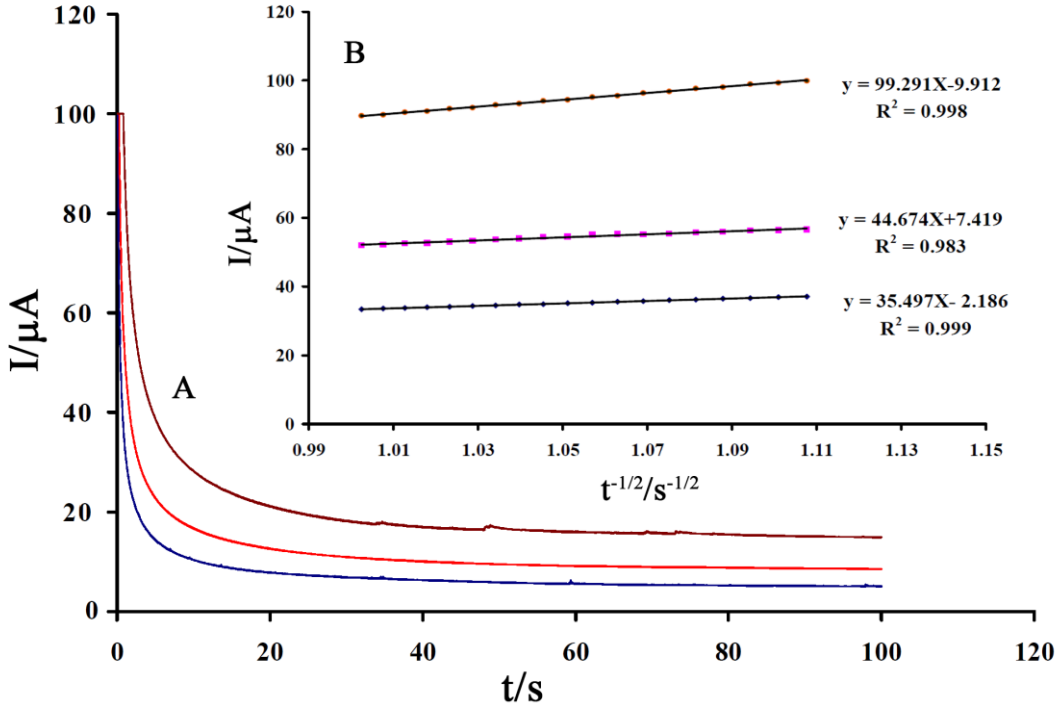

Figure 7. A) Chronoamperograms obtained at ZnO/CNTs/ILs/CPE in the presence of a) 250; b) 350 and c) 450 μmol L^{-1} CD in the buffer solution (pH 6.0). B) Cottrell's plot for the data from the chronoamperograms.

3.3. Stability and reproducibility of the ZnO/CNTs/ILs/CPE

Stability and reproducibility are two important parameters in preparation of sensor [58-65]. After the ZnO/CNTs/ILs/CPE was stored for 2 weeks at 4 ˚C, only a small decrease of peak current sensitivity with a relative standard deviation (RSD) of 2.1% for 100 μmol L^{-1} CD was observed, which can be attributed to the excellent stability of the modified electrode. Furthermore, the reproducibility of the determination was performed with seven successive scans in the solution containing 100 μmol L^{-1} CD. The RSD value was found to be 2.9% for the CD, indicating excellent reproducibility of the modified electrode. The electrode can be immersed in an aqueous media pH 6.0 for 40 min with stable response. After that, the background current began to increase, which may be due to the partly leakage of ionic liquid from the electrode and the roughness of the electrode surface was increases gradually.

3.4. Interferences study

A systematic study was carried out to examine the influence of some foreign substances on the determination of 10 μmol L^{-1} CD at an optimum condition pH 6.0. The ZnO/CNTs/ILs/CPE could tolerate interferences from other organic compounds. For example, 900-fold of glucose, sucrose, lactose and fructose, valine, methionine, lucine, tryptophan, glycine, ascorbic acid (ascorbic acid minimized by using ascorbic oxidase enzyme) and histidine and 500-fold concentrations of urea and

thiourea and 400-fold concentrations of metal ions (e.g. Na^+, Al^{3+}, F^-, SO_4^{2-}, K^+, Cl^-, SCN^-, Br^-, Mg^{2+}, Ca^{2+}, CO^{2+} and Li^+), and 200-fold concentration of uric acid are influenced the current response of 10 μmol L^{-1} CD (signal change below±3%), revealing that the proposed method had excellent selectivity to CD detection.

3.5. Real sample analysis

To investigate the applicability of the proposed sensor for the voltammetric determination of CD in real samples, we selected urine, water and serum samples for the analysis of their CD contents. The proposed method was also compared with a published method [2], the results of which are given in Table 1. Those results clearly demonstrate and confirm the capability of the ZnO/CNTs/ILs/CPE in the voltammetric determination of CD with high selectivity, accuracy, and good reproducibility.

Table 1. Determination of CD in real samples.

Sample	Added (μmol L^{-1})	Found (μmol L^{-1})	Published method (μmol L^{-1}) [2]	F_{ex}	F_{tab}	t_{ex}	$t_{tab(98\%)}$
Urine	—	<LOD	<LOD	—	—	—	—
	5.0	4.8±0.4	5.6±0.7	8.5	19.0	1.9	3.8
	10.0	10.5±0.6	10.7±0.8	—	—	—	—
Water	—	<LOD	<LOD	—	—	—	—
	15.0	14.7±0.6	15.8±0.9	12.2	19.0	2.7	3.8
Pharmaceutical serum	—	<LOD	<LOD	—	—	—	—
	20.0	20.7±0.9	21.0±1.1	13.5	19.0	3.3	3.8

± Shows the standard deviation (n=3).

4. CONCLUSION

In this work an n-hexyl-3-methylimidazolium hexafluoro phosphate modified carbon paste electrode was fabricated and further modified with ZnO/CNTs to get a ZnO/CNTs/ILs/CPE. Due to the interaction of ILs with ZnO/CNTs, the fabricated ZnO/CNTs/ILs/CPE showed excellent electrochemical behaviours and the characteristics of ZnO/CNTs/ILs/CPE were investigated by XRD, SEM, cyclic volatmmetry, chronoamperomtry and square wave voltammetry, respectively. The electro-oxidation behaviours of CD on the modified sensor were further studied with electrochemical parameters calculated. Under the optimum conditions, the oxidation peak current was proportional to the CD concentration in the range of 0.09 to 450 μmol L^{-1} with the detection limit of 0.05 μmol L^{-1}. The proposed sensor was successfully applied to the CD detection in real samples such as water, serum and urine.

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