Full Paper

An Electrochemical Sensor Based on Ionic Liquid-Multiwall Carbon Nanotubes/Graphite Paste Electrode for Simultaneous Determination of Epinephrine and Xanthine in Pharmaceutical and Biological Samples

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Abstract- A graphite paste electrode (GPE) modified with 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) and multi-walled carbon nanotube (MWCNT), was prepared for simultaneous voltammetric determination of epinephrine (EN) and xanthine (XN). The prepared electrode ($BMIMPF_6$–MWCNT/GPE) showed an excellent catalytic activity in the electrochemical oxidation of EN and XN, leading to remarkable enhancements in the corresponding peak currents and lowering the peak potentials. The peaks current of linear sweep voltammograms (LSV) of EN and XN increased linearly with their concentration in the ranges of 0.30–60 µmol L^{-1} EN and 0.20–45 µmol L^{-1} XN in 0.1 M phosphate buffer solution (pH 7.0). The effects of both scan rate and pH on the anodic peak height of the EP oxidation and XN were discussed. The lowest detection limits (S/N= 3) were 0.209 µmol L^{-1} and 0.143 µmol L^{-1} for EP and XN, respectively. Therefore, the applicability of the voltammetric biosensor was demonstrated by simultaneous determination of EP and XN in human urine, human blood serum and ampoule. This modified electrode showed a good stability and repeatability during experiments.

1. INTRODUCTION

Epinephrine (EN), often called adrenaline, appertain to catecholamine family and an important hormone for the message transfer in mammalian central nervous system [1–3]. Variations of the EN concentration in organisms are caused a large number of diseases. In the role a chemical mediator serves as a neurotransmitter in different organs. Also, in medical is consumed as a emergency medicine [4,5]. Thus, it is important to determine of epinephrine concentration in plasma and urine, also, for studying its physiological function in clinical medicine [6,7].

Xanthine (XN) is generated after adenosine triphosphate decomposition in purine metabolism as an intermediate [8,9]. Xanthine is the first indicator of an abnormal purine profile, and can serve as a marker of acute hypoxia stress, cerebral ischemia and pre-eclampsia [10–12]. Since determination of xanthine in serum/urine is very important in the diagnosis and medical management of hyperuricemia, gout, xanthinuria and renal failure [13]. The amount of xanthine in the blood and the tissue samples should be easily analyzed for the diagnosis and the treatment of various diseases [13]. Carbon nanotubes (CNTs) are kinds of porous nanostructure materials which are currently in the forefront of materials research. CNTs have the ability to mediate electron transfer reactions with electroactive species in solution when used as an electrode surface modifier for designing new electrochemical sensors [14–16].

Another important class of novel materials for various electrochemical applications are ionic liquids (IL), due to their unique chemical and physical properties. IL is a liquid electrolyte which consists of a small anion and a bulky organic cation such as imidazolium and pyridinium [17]. Ionic liquid as 1-Butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) is compound composed of ions and exist in the liquid state below 298 K. Because of its high stability, high electrical conductivity and very low vapor pressure, ionic liquid hold great promise for green chemistry applications in general and for electrochemical applications in particular. In 2003, Fukushima et al. were the first to report that a thermally stable, highly conductive physical gel was formed with imidazolium ions and carbon nanotubes [18].

According to the above points, combination of CNTs and ILs could show some novel properties in the preparation of new sensors in pharmaceutical and biological compounds analysis [19–21]. In the present work, our aim was to develop a simple voltammetric sensor with fast preparation for selective, sensitive and simultaneous determination epinephrine and xanthine. The electrochemical behavior of EP and XN has been thoroughly investigated at the $BMIMPF_6$–MWCNT/GPE. The analytical feasibility of the approach was examined by measuring EP and XN content in different real samples with satisfactory results.

2. EXPERIMENTAL

2.1. Chemical reagent & preparation of solution

Epinephrine, Xanthine and 1-butyl-3-methylimidazolium hexafluorophosphate were reagent-grade from Sigma Aldrich. Graphite powder and paraffin oil (DC 350, density=0.88 g.cm^{-3}) purchased from Merck (Darmstadt, Germany) as the binding agent were used for preparing the pastes. The multi-wall carbon nanotubes (outer diameter: 20–30 nm; wall thickness: 1–2 nm; length: 0.5–2 μm and 95% pure) were purchased from Aldrich. These chemicals were used without further purification. Aqueous solutions were prepared with doubly distilled water (DDW). The stock solution of EP (0.01 M) was freshly prepared by dissolving epinephrine in DDW. Also, the stock solution of XN solution (0.01 M) was prepared by dissolving the solid in a small volume of 0.1 mol L^{-1} NaOH solution and diluted to reach desired concentration. A series of buffer solutions including H_3PO_4 (PBS) were prepared and pHs were adjusted using NaOH solution (0.1 M) in the range from 5.0 to 9.0. All voltammetric experiments were performed under nitrogen atmosphere and room temperature.

2.2. Apparatus

All electrochemical experiments were performed using an SAMA 500 Electroanalyser (SAMA Research Center, Iran) controlled by a personal computer. A conventional three-electrodes cell assembly consisting of a platinum wire as an auxiliary electrode, a saturated calomel electrode (SCE) as a reference electrode and modified carbon paste electrode (BMIMPF$_6$–MWCNT/GPE) as working electrode were used. A Metrohm 744 pH/ion meter was used for pH measurements. TEM images were taken using a Philips CM120 transmission electron microscopy with 2.5 A˚ resolutions.

2.3. Preparation of the working electrode

BMIMPF$_6$–MWCNT/GPE was prepared by hand mixing 0.20 g of BMIMPF$_6$ with 0.75 g graphite powder and 0.05 g MWCNTs with a mortar and pestle. Then, 0.9 mL of paraffin oil was added to the above mixture and mixed for 30 min until a uniformly wetted paste was obtained. A portion of the resulting homogeneous paste was packed into of the glass tube. A copper wire inserted into the graphite paste provided an electrical contact. To obtain the best conditions in preparation of the modified electrode, we optimized the ratio of multi-wall carbon nanotubes and the ionic liquid in BMIMPF$_6$–MWCNT/GPE. 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. For comparison, MWCNT modified graphite paste electrode (MWCNT/GPE) without BMIMPF$_6$ and unmodified graphite paste electrode in the absence of MWCNT and BMIMPF$_6$ were also prepared in the same way.

2.4. Preparation of real sample

Fresh urine and blood serum samples were obtained from the Omid Clinical Laboratory (Zahedan, Iran) without any pretreatments. Samples of urine and blood serum were stored in a refrigerator immediately after collection. 10 mL of each sample was centrifuged for 20 min at 2000 rpm. The supernatant was filtered using a 0.45-μm filter and then diluted ten times with PBS (pH 7.0). The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. For the determination of recovery of Ep and XN in samples of urine and blood serum was used spiking method. 1 mL of the EP injection solution (specified content of EP is 1 mg per mL, Darou Pakhsh Company; Iran) was diluted to 10 mL with phosphate buffer, then a 100 μL portion of the solution was diluted in a voltammetric cell to 10 mL of 0.1 M phosphate buffer (pH 7.0).

3. RESULTS AND DISCUSSION

3.1. TEM characterization of modified electrodes

The TEM image of the BMIMPF$_6$–MWCNT/GPE sample is shown in Fig. 1. It can be seen that with added multiwall carbon nanotubes and 1-butyl-3-methylimidazolium hexafluorophosphate as ionic liquid to graphite paste increase surface area at a surface of modified electrode and it can cause for increasing currents in voltammetric investigations in EP and XN analyses.
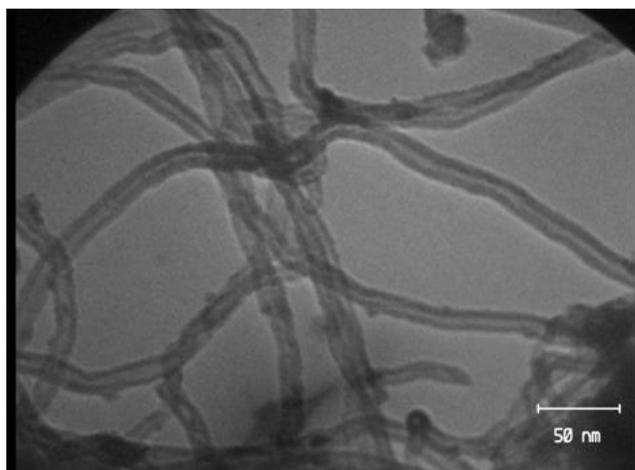

Fig. 1. TEM images of BMIMPF$_6$–MWCNT/GPE

3.2. Electrochemical characterization of EP and XN on the surface of various electrodes

Cyclic voltammograms (CVs) recorded for the oxidation of 4 μM epinephrine and 3μM xanthine in 0.1 M phosphate buffer of pH 7.0 at the surface of unmodified (GPE), modified

graphite paste electrode with multi-wall carbon nanotube (MWCNT/GPE) and with multi-wall carbon nanotube and 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF$_6$–MWCNT/GPE) are shown in Fig. 2 As can be seen at the GPE (curve a in Fig. 2), a broad and small oxidation peak for XN around 0.72 V and wide anodic wave with an anodic peak potential for EP were observed about 0.23 V. Fig. 2b demonstrates that MWCNTs can effectively catalyze the electro-oxidation of XN and EP and greatly improve the peak shapes.
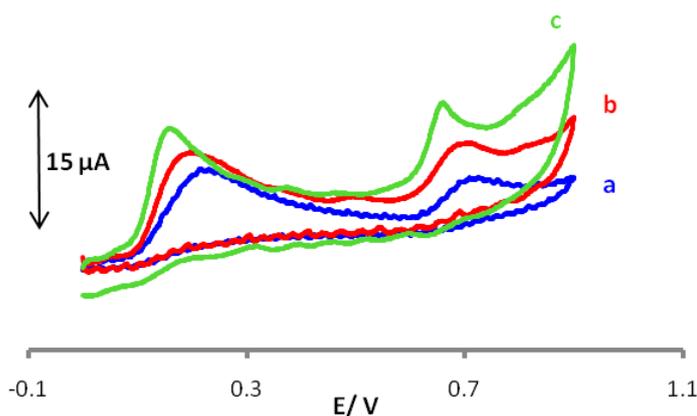
Fig. 2. CVs of 4 µM EP and 3 µM XN in 0.1 M PBS (pH 7.0) with scan rate 50 mVs^{-1} at GPE (a), BMIMPF$_6$/GPE (b) and BMIMPF$_6$–MWCNT/GPE (c)

The enhancement in peak currents and the lowering of overpotentials are clear evidences of catalytic effects of BMIMPF$_6$ toward the EP and XN redox reactions (Fig. 2c). Such a noticeable enhancement of anodic current revealed that by lowering the anodic overpotential of the electrode process, the kinetics of electron transfer for EP and XN improves remarkably at the BMIMPF$_6$–MWCNT/GPE. Therefore, resulting in a remarkably increased response toward the redox reactions of EP and XN was in contrast to the behavior from other electrode modifications.

3.3. Influence of solution pH on the oxidation of EP and XN

The effect of solution pH on the electrochemical response of the BMIMPF$_6$–MWCNT/GPE towards EP and XN in the simultaneous determination of 20 µmol L^{-1} EP and 25 µmol L^{-1} XN was investigated using CV method. Cyclic voltammograms EP and XN respect to pH of the electrolyte in the pH range from 5 to 9 are shown in Fig. 3a. It was observed (Fig. 3b & 3c) that oxidation potentials of EP and XN shift to less positive potential with increasing solution pH which is a consequence of the deprotonation involved in the oxidation process that is facilitated at higher pH values. Variation of the corresponding oxidation peak potentials and pH obeyed the following equations:

$$E_{pa} (EP) = 0.663 - 0.069pH \ (R^2 = 0.996) \tag{1}$$

$$E_{pa} (XN) = 1.171 - 0.067pH \quad (R^2 = 0.997) \tag{2}$$
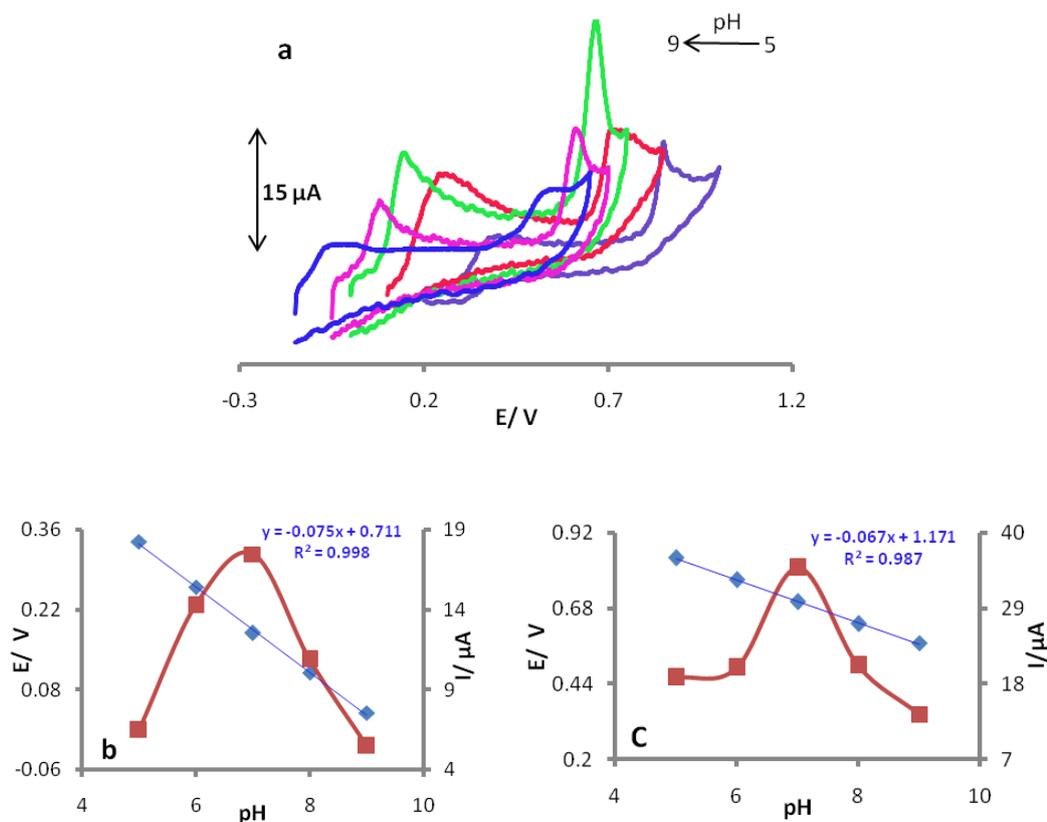
Fig. 3. PH effect on peak current responses and peak potential responses of EP and XN at BMIMPF$_6$–MWCNT/GPE (a); Insertions show the dependence of anodic peak currents and anodic peak potentials with pH for EP (b) and XN (c). Cyclic voltammograms were measured scan rate 20 mV s^{-1} with 10 μM EP and 25 μM XN

In a Nernstian systems, the slope of the variation of Ep as a function of solution pH is 0.059 (m/n) V/pH, where m and n are the number of protons and electrons involved in the electrode process, respectively [22]. It can be seen that the anodic peak currents of EP and XN increase with raising the solution pH until it reaches 7 (Fig. 3b & 3c). However at higher pH the EP and XN oxidation peak current starts to diminish. Therefore, the pH value of 7, which is close to biological pH value, was chosen as an optimum solution pH for further experiments.

3.4. Effect of scan rate on the oxidation of EP and XN

The cyclic voltammogram of BMIMPF$_6$–MWCNT/GPE at various scan rate (10–300 mV s^{-1}) in the presence 0.40 mM of EP and 1.0 mM of XN were studied (Fig. 4a). As is seen from Fig. 4b, there is a linear correlation between the anodic currents and v$^{1/2}$, suggesting that the kinetics of the overall process are controlled by mass transport of epinephrine and

xanthine from the bulk solution to the electrode surface. Tafel plots that were drawn from the data of the rising part of the current–voltage curve were recorded at a scan rate of 20 mV s^{-1} (not shown). These part of the voltammogram, known as Tafel region, were affected by the electron-transfer kinetics between EP and XN with surface of BMIMPF$_6$–MWCNT/GPE, assuming the deprotonation of the substrate as a sufficiently fast step. In this condition, the number of electrons involved in the rate determining step can be estimated from the slope of the Tafel plot [23]. Slopes of 0.151 and 0.200 V decade^{-1} are obtained for the Tafel plot for EP and XN, respectively. According to Tafel slope equation and attained slopes (0.151 and 0.200 V decade^{-1}), the transfer coefficients were calculated 0.61 for EP and 0.7 for XN. Using the slopes of the Fig. 4b and according to Eq. (3) [24], the approximate values for the total number of electrons involved in the anodic oxidation of EP and XN emerge to be n=2.15≃2 and n=1.91≃2, respectively.

$$I_p = 3.01 \times 10^5 n[(1-\alpha)n_\alpha]^{1/2} A C_b D^{1/2} v^{1/2} \tag{3}$$
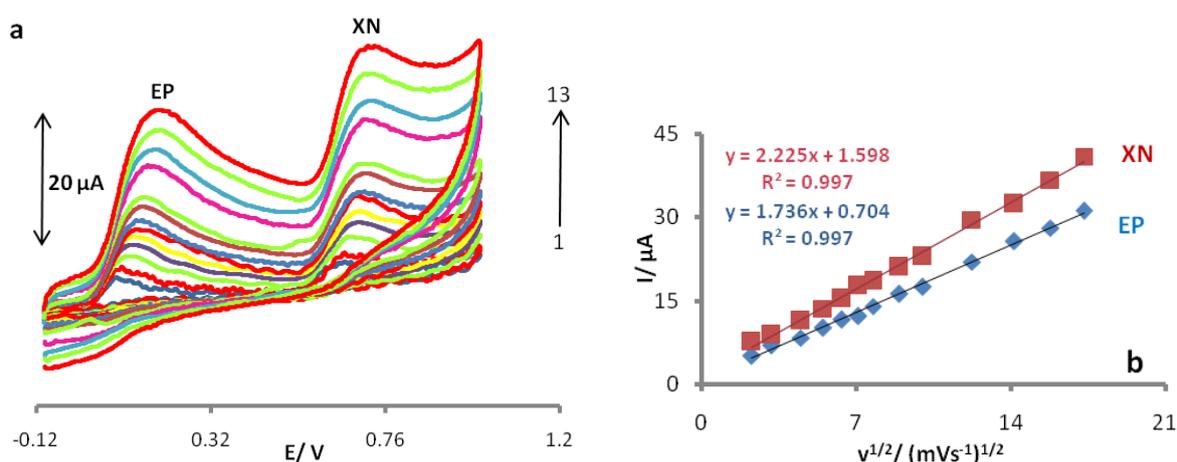
Fig. 4. CVs of 0.40 mM of EP and 1.0 mM of XN with different scan rates (from 1-13) 10, 20, 30, 40, 50, 60, 80, 100, 150, 200, 250, and 300 mV s^{-1} at BMIMPF$_6$–MWCNT/GPE (a); Plot of peak currents *vs.* square root of scan rate for EP and XN (b)

3.5. Chronoamperometric study

The chronoamperometry was employed for analytes of EP and XN at chemically modified electrodes, separately. Chronoamperometric measurements of EP at BMIMPF$_6$–MWCNT/GPE were carried out by setting the working electrode potential at 300 mV for various concentrations of EP (Fig. 5a).
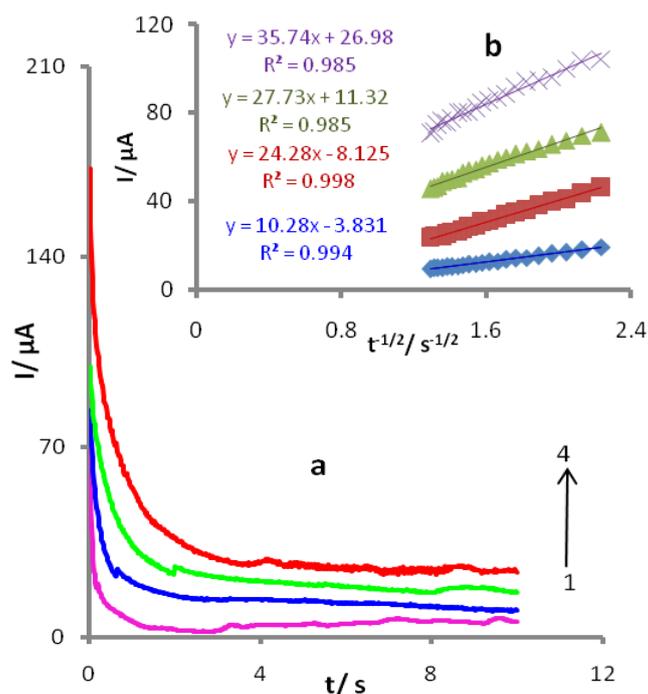
Fig. 5. Chronoamperometric response of the modified BMIMPF$_6$–MWCNT/GPE in 0.1 M phosphate buffer solution (pH 7.0) at potential step of 0.3 V for different concentrations of EP. The letters 1–4 correspond to 0.4, 0.6, 0.8, and 1.0 mM EP (a); plots of I versus t$^{-1/2}$ obtained from the Chronocoulograms (b)
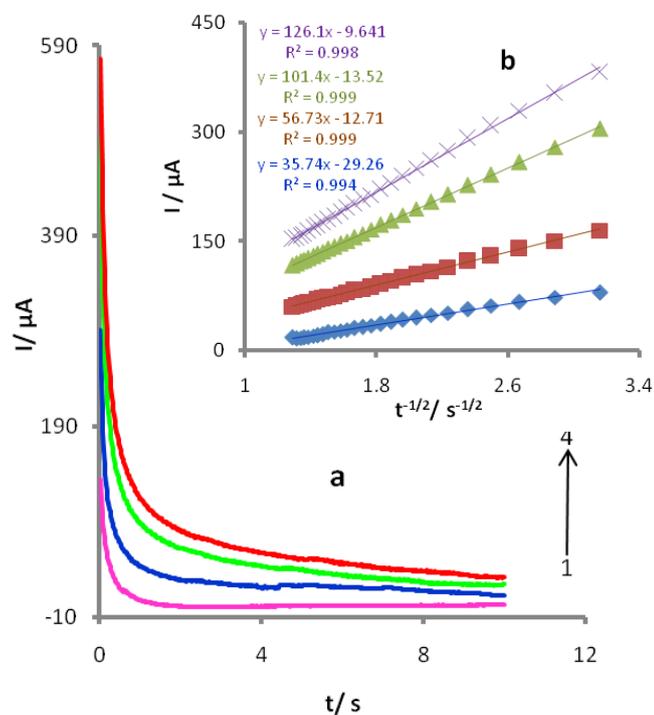

Fig. 6. (a) Chronoamperograms obtained at BMIMPF$_6$–MWCNT/GPE in 0.1 M PBS (pH 7.0) for different concentrations of XN. The numbers 1–4 correspond to 1.0, 3.0, 5.0, and 7.0 mM of XN. (b) plots of I *vs.* t$^{-1/2}$ obtained from chronoamperograms

Similarly, by setting the working electrode potential at 700 mV for XN were carried out (Fig. 6a). For an electroactive material with a diffusion coefficient of $D/cm^2 s^{-1}$, the current observed for the electrochemical reaction at a mass transport limited condition is described by the Cottrell equation [23].

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

We have employed a plate of I versus $t^{-1/2}$ that will be linear, the mean values of diffusion coefficients 2.03×10^{-5} and 9.92×10^{-6} cm²/s for EP and XN be obtained, respectively (Fig. 6b & 7b).
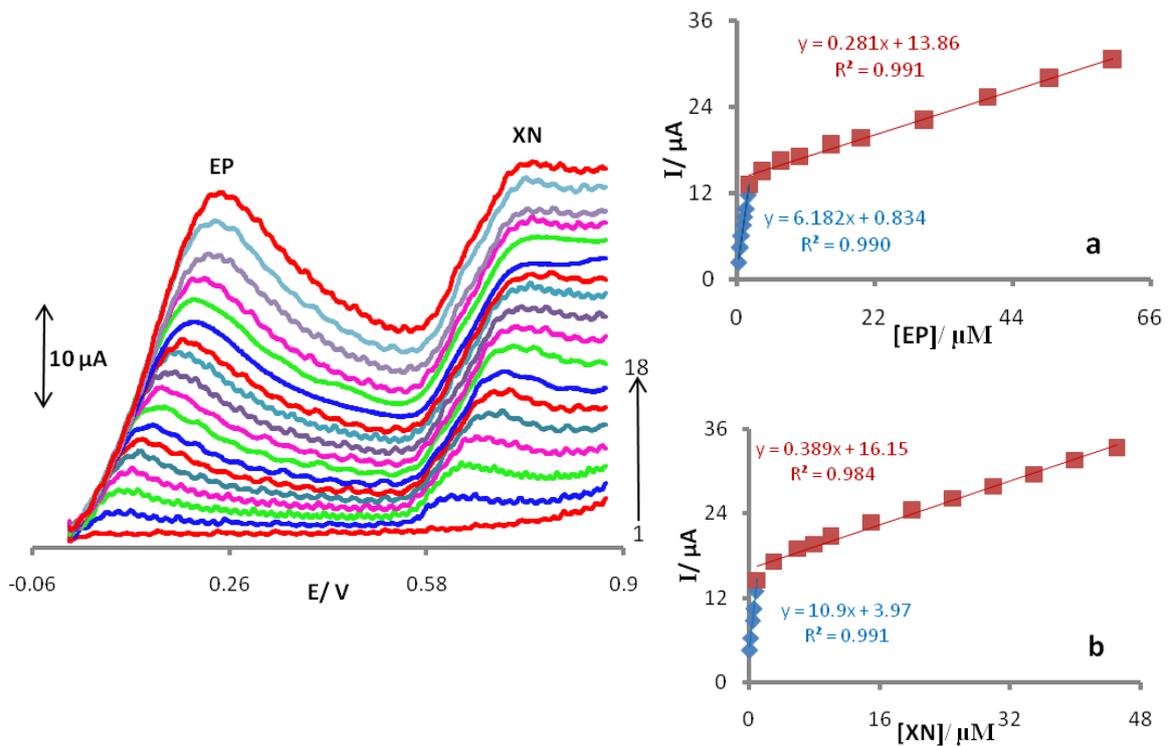

Fig. 7. Linear sweep voltammograms of BMIMPF₆–MWCNT/GPE 0.1 mol/L PBS (pH 7.0) containing different concentrations of EP and XN

The numbers 1–18 correspond to: 0, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5, 1.8, 2.0, 4.0, 7.0, 10, 15, 20, 30, 40, 50 and 60 µM of EP and 0, 0.4, 0.5, 0.7, 0.9, 1.5, 1.5, 3.0, 6.0, 9.0, 12, 15, 20, 26, 32, 38 and 44 µM of XN. Inset (a) represents the variations of anodic peak currents *vs.* epinephrine concentration. Inset (b) represents the variations of anodic peak currents *vs.* xanthine concentration.

3.6. Simultaneous determination of EP and XN at BMIMPF₆–MWCNT/GPE

Linear sweep voltammetry (LSV) was used for Simultaneous determination of EP and XN. Fig. 7 shows linear sweep voltammograms and their corresponding calibration curves

obtained at BMIMPF$_6$–MWCNT/GPE for various concentrations of EP and XN. For EP, two linear dynamic range from 0.3 μmol L^{-1} to 2.0 μmol L^{-1}, with a calibration equation of I$_p$(μA)=6.182C$_{EP}$ (μmol L^{-1})+0.834 (R^2=0.990), and 2.0 μmol L^{-1} to 60 μmol L^{-1}, with a calibration equation of I$_p$(μA)=0.281C$_{EP}$ (μmol L^{-1})+13.86 (R^2=0.991), also a limit of detection (LOD) from first segment of 0.209 μmol L^{-1} (S/N=3) was obtained (Fig. 7 Inset a).
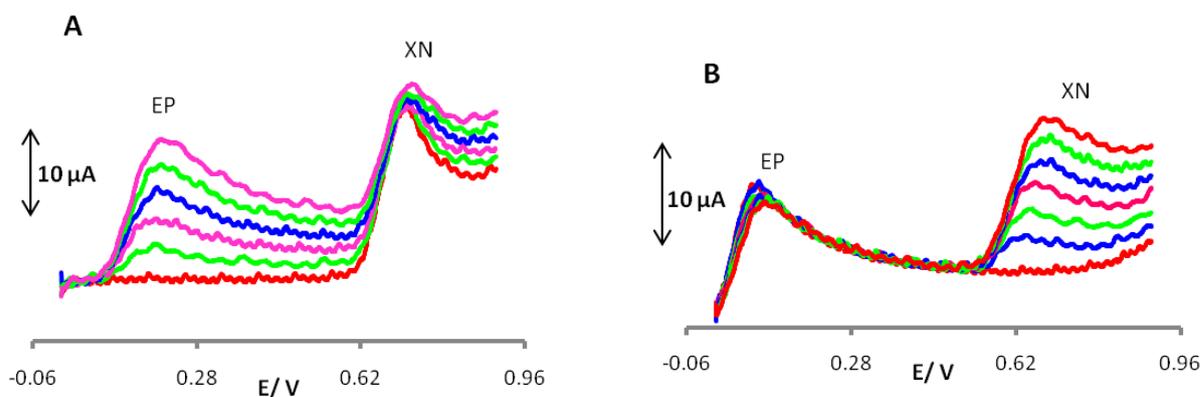
Fig. 8. (A) LSVs at the BMIMPF$_6$–MWCNT/GPE in 0.1 M, pH 7.0 (A) containing XN (1.0 μM) and different concentrations of EP (from down to up): 0, 0.7, 1.1, 1.5, 1.7 and 1.9 μM; (B) containing EP (2.0 μM) and different concentrations of XN (from down to up): 0, 0.7, 5.4, 7.9, 12.9, 15.4 and 18.9 μ

Table 1. Comparison the proposed electrode with other electroanalytical electrodes for the determination EP

Electrode	pH	Linear range (μM)	Detection limit (μM)	Ref.
FePc-modified CPE	4.0	1 –300	0.500	[5]
IL/CNTPE	7.0	0.3– 450	0.090	[25]
MWCNT/CFE	7.0	2.0 – 50	3.400	[26]
CuFe$_2$O$_4$/ILs/CPE	7.4	0.1–400	0.070	[27]
DH-CN/CPE	7.0	5.0–20	1.000	[28]
CNT/SSE	-	2.0-100	2.000	[29]
BMIMPF$_6$– MWCNT/GPE	7.0	0.3 –60	0.209	This work

For XN, two linear dynamic range from 0.2 μmol L^{-1} to 1.0 μmol L^{-1}, with a calibration equation of I$_p$(μA)=10.9C$_{EP}$ (μmol L^{-1})+3.97 (R^2=0.991), and 1.0 μmol L^{-1} to 45 μmol L^{-1},

with a calibration equation of $I_p(\mu A)=0.389C_{EP}$ ($\mu mol\ L^{-1}$)+16.15 (R^2=0.984), also a limit of detection (LOD) from first segment of 0.143 $\mu mol\ L^{-1}$ (S/N=3) was obtained (Fig. 7 Inset b). Similar calibration graphs for determination of EP or XN in the presence of different concentrations of EP or XN were obtained, indicating that they do not interfere in the determination of each other (Fig. 8). The figures of merit, such as linear range and limit of detection for EP are compared with those from other published works on modified electrodes in Table 1.

3.7. Real Sample Analysis

The proposed biosensor was successfully applied to the simultaneous determination of EP and XN in human blood serum, human urine and EP ampul at optimum conditions by linear sweep voltammetry (Table 2). The samples were prepared (refer to section of 2.4) before analysis and spiked with appropriate amounts of EP and XN. Good recoveries were obtained for spiked samples providing further evidence that this is a reliable method for the direct simultaneous determination of EP and XN in biological sample.

Table 2. The application of BMIMPF6–MWCNT/GPE for simultaneous determination of EP and XN in real samples (n=5)

Sample	Spiked (µM)		Found (µM)		Recovery (µM)		RSD* (%)	
	EP	**XN**	**EP**	**XN**	**EP**	**XN**	**EP**	**XN**
Human Urine	0	0	ND**	ND	-	-	-	-
	0.60	0.50	0.59	0.52	98.83	104.00	2.60	1.76
	1.30	1.20	1.27	1.24	97.69	103.33	2.40	1.54
	1.80	2.50	1.78	2.46	98.89	98.40	1.80	2.30
	3.00	10.00	3.12	9.69	104.00	96.90	2.08	1.10
Human Blood Serum	0	0	ND	ND	-	-	-	-
	0.60	0.60	0.58	0.62	96.67	103.33	1.56	2.13
	1.20	2.50	1.17	2.58	97.50	103.20	1.68	1.34
	1.50	5.00	1.55	0.97	103.33	97.00	1.95	2.77
	4.00	9.00	4.12	8.83	103.00	98.11	2.54	1.29
Ampul	5.46	0	4.45	ND	-	-	-	-
	0.5	0.4	5.94	0.41	99.66	102.50	1.35	2.61
	1.5	1.2	7.09	1.24	101.87	103.33	1.86	1.74
	3.5	3.3	8.72	3.19	97.32	96.66	2.37	2.37
	5.0	4.5	10.83	4.41	103.54	98.00	2.12	2.71

*RSD relative standard deviation, **ND not detected

4. CONCLUSIONS

The findings of this study indicate that the BMIMPF$_6$–MWCNT/GPE exhibits electrocatalytic activity to EP and XN oxidation. The electrochemical behavior of the modified electrode depends heavily on the solution pH. Some of kinetic parameter such as transfer coefficient (α), number of electron in redox reaction (n) and diffusion coefficient (D) were found. The simple fabrication procedure, wide linear range, low detection limit and high stability suggest that this electrode will be a good and attractive candidate for practical applications. Furthermore, the time used for the electrode preparation in this method is lower than prior method.

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