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A high sensitive voltammetric sensor for qualitative and quantitative determination of phenobarbital as an antiepileptic drug in presence of acetaminophen

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ABSTRACT

For the first time, the catalytic activity of phenobarbital (PB) in presence of acetaminophen (AC) was studied at the surface of modified electrode which prepared by incorporation of multi-walled carbon nanotube (MWCNT) and Pt-nanoparticles into a paste matrix. Preparation of this electrode was very simple and modified electrode showed an excellent character for electrocatalytic oxidization of acetaminophen and phenobarbital. Using differential pulse voltammetry (DPV), a highly selective and simultaneous determination of AC and PB has been explored at the modified electrode. Differential pulse voltammetry peak currents of AC and PB increased linearly with their concentrations at the ranges of 0.5–100 μM and 0.4–60 μM, respectively. Also, the detection limits for AC and PB were 0.17 μM and 0.1 μM, respectively. The method has been found selective and successfully implemented for the determination of AC and PB in human urine and pharmaceutical samples using standard addition method. The electrode exhibited an efficient catalytic response with good reproducibility and stability.

1. Introduction

Phenobarbital (phenobarbitone; PB, Fig. 1a) is the oldest used anticonvulsant [1] and one of minimum medical needs for a basic health care system [2]. It is effective in partial clonic–tonic crisis, and has some sedative action. It causes tolerance effects in long time use [3]. Despite the development of successive generations of antiepileptic drugs (AEDs) [4], PB has retained a unique position in the therapeutic facilities and is still the most widely prescribed treatment for epilepsy, as the most common serious brain disorders, worldwide [5]. Some methods have been reported for the determination of PB in pharmaceutical formulations or biological samples including capillary electrophoresis [6], potentiometric method [7] and liquid chromatography [8]. Although liquid chromatography has been widely recommended for determination of PB, because of its high sensitivity and selectivity [1], but it is time consuming, solvent usage intensive and requires expensive devices and maintenance.

Acetaminophen (N-acetyl-p-aminophenol or paracetamol; AC, Fig. 1b) has been used comprehensively all over the world as the reducer of fever and as a pain killer for the relief of moderate pain associated with backache, headache, arthritis and postoperative pain [9]. Overdoses of acetaminophen produce the accumulation of toxic metabolites, which may cause severe and sometimes fatal hepatoxicity [10,11] and nephrotoxicity [12]. Several analytical methods such as spectrophotometry [13], chromatography [14], titrimetry [15], capillary electrophoresis [16] and chemiluminescence [17] have been developed for the determination of acetaminophen. Whereas, acetaminophen and phenobarbital are widely used as analgesic and antipyretic agents for treating the symptoms of different painful processes, thus a simple, rapid and reliable method that could be easily and widely used for the simultaneous quantitative estimation of these compounds is necessary.

Among of different analytical methods [18–20], electrochemical determination has proved to be sensitive and reliable for the determination of numerous electroactive components [21,9,22]. On the other hand, the poor ability of bare electrodes in direct electrochemical activity of different electroactive materials has led to interest in the use of mediators and modified electrodes to catalyze the electrochemical oxidation and/or reduction of them [23].

The discovery of carbon nanotube (CNT) in 1991 opened up a new era in material science and nanotechnology [24]. The interesting electronic and photonic properties of CNT, such as large specific surface area, wide electrochemical window, flexible surface chemistry and unique property to accelerate electronic transfer, made CNT attractive for many applications [25,26]. Different techniques have been reported for preparation of modified electrodes with CNTs. Nandibewoor et al. [27] have reported modification a glassy carbon electrode by casting 15 μl of the black suspension of MWCNTs onto the electrode for determination of trazadone.

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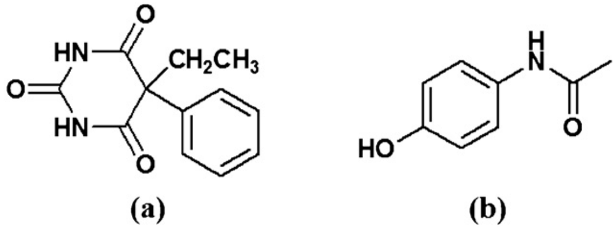


Fig. 1. Chemical structure of phenobarbital (a) and acetaminophen (b).

Also, CNT-modified carbon paste electrodes (CPEs) showed considerable improvements in electrochemical behavior of materials. Zhuang et al. reported the fabrication of CPE modified with MWCNTs for the determination of bergenin using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) [28]. They found that the oxidation peak current of bergenin increased significantly upon increase of the contents of MWCNT. Zhao et al. [29] have reported that superior electrocatalytic oxidation of hydrazine was possible at a MWCNT paste electrode. Composite matrix of CNTs-paste with other materials such as conducting polymers [30], metalloporphyrins [31], nanoparticles [32] are very attractive combination of materials for the development of electrochemical sensors. Our previous work had reported a kind of sensor based on combination of ferrocene carboxylic acid and TiO_2 nanoparticles into carbon paste matrix [33] for simultaneous determination of glutathione and tryptophan.

As all we know, platinum nanoparticles are of particular interest in the field of electrochemistry as a matrix of sensors [34–36]. Also, they have been effectively used in fuel cell technology [37] and the electrocatalytic oxidation of organic pollutants [38]. Through a suitable combination of CNTs and Pt-nanoparticles, very simple composite materials could be generated with higher surface areas, low cost and improved electrocatalytic activities compared with the individual component [39], which makes it to be an excellent platform for electrochemical sensing applications [40].

In this paper, we tried to combine the electrocatalytic activity of Pt-nanoparticles and multi-walled carbon nanotube (MWCNT) together in a simple way to produce a composite matrix with high performance of heterogeneous catalytic activity. Whereas, Pt-nanoparticles cannot be easily attached to CNT and physically adsorbed particles can be easily removed, we incorporated them in a MWCNT paste matrix for fabrication of electrochemical sensor. To the best of our knowledge, no study has been reported so far, by combing the advantages of MWCNTs and Pt-nanoparticles, on the electrochemical determination of PB in presence of AC without any additional modification such as addition of electron transfer mediator or specific reagents. As prepared nano-Pt modified MWCNT composite is expected to possess the properties of the individual components with a synergistic or complementary effect. The main objectives of this nano-Pt modified MWCNT paste electrode (nPt-MWCNTPE) for determination of PB and AC are: very low detection limits, short time of the procedure and no use of electron transfer mediator.

2. Experimental

2.1. Apparatus and chemicals

Electrochemical measurements were carried out on an Autolab potentiostate/galvanostate (Eco Chemie BV, Netherlands) with data acquisition software, made available by the manufacturer (GPES and FRA 4.9 version). A digital pH-meter (Ion Analyzer 250, Corning) was used to read the pH of the buffered solutions. Carbon paste electrode (CPE), multi-walled carbon nanotube paste electrode (MWCNTPE) and nPt-MWCNTPE were used as a working electrode. An Ag|AgCl|KCl (3 M) electrode and a platinum wire were used as reference and counter electrodes, respectively. All electrochemical studies were performed at perimeter temperature. A Philips model XL30 scanning electron microscope (SEM) was used to determine the morphology of the synthesized Pt-nanoparticles sample. Transmission electron microscope (TEM) observations were carried out using a LEO 912AB transmission electron microscope operated at 120 kV.

All of solutions were prepared freshly with twice distilled water prior to use. AC and PB were obtained from Fluka. MWCNTs (>90%, O.D.: 10–15 nm, I.D.: 2–6 nm, length: 0.1–10 μm) were purchased from Sigma–Aldrich. High viscosity paraffin (density = $0.88\ g\,cm^{-3}$) from Fluka was used as the pasting liquid. Phosphate buffered solutions (PBS) 0.1 M for different pH values were prepared by mixing stock solutions of 0.1 M H_3PO_4, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4. Potassium chloride from Fluka was used

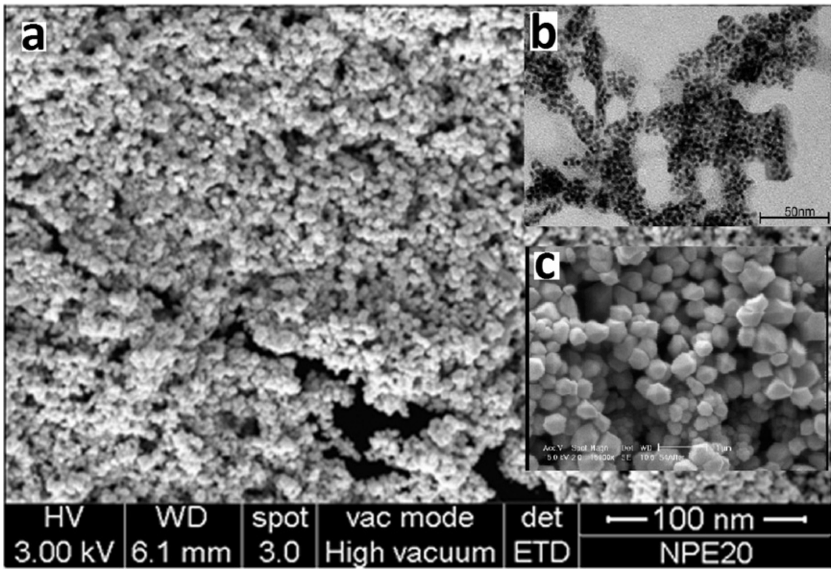


Fig. 2. The SEM (a) and TEM (b) images of Pt-nanoparticles. The magnified part of the SEM image is shown in (c).

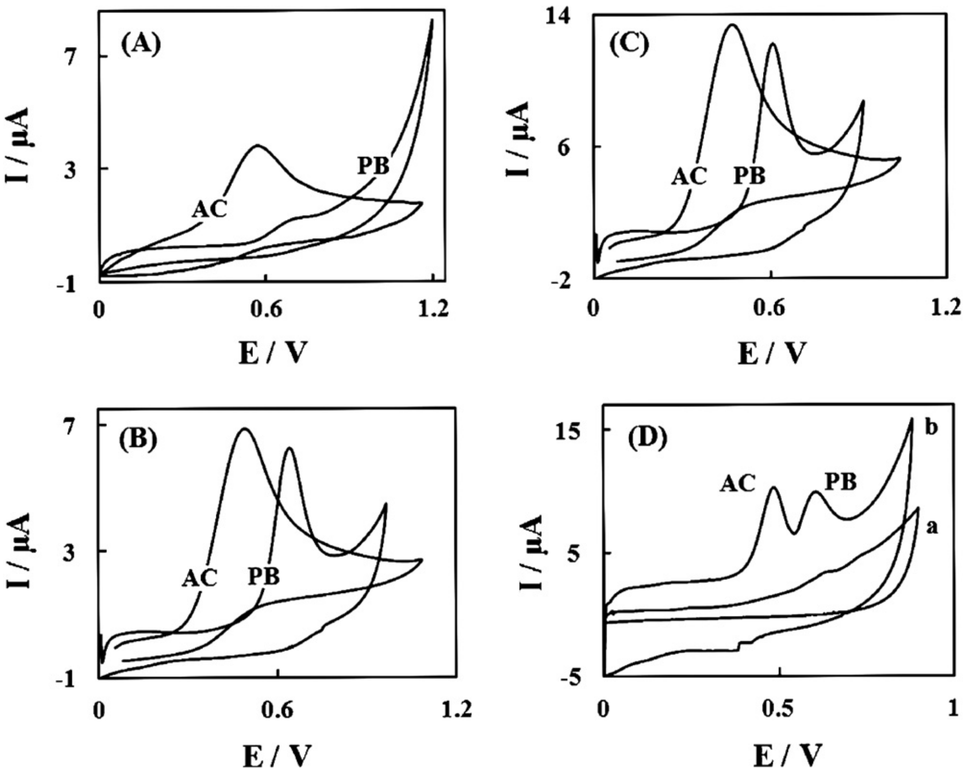


Fig. 3. Cyclic voltammograms of AC (50.0 μM) and PB (40.0 μM) at (A) bare CPE, (B) MWCNTPE and (C) nPt-MWCNTPE in 0.1 M PBS (pH 7.0). (D) Cyclic voltammograms of 15.0 μM AC + 25.0 μM PB at a CPE (a) and at nPt-MWCNTPE (b) in 0.1 M PBS (pH 7.0). In the all cases scan rate is 20 mV s^{-1}.

as the supporting electrolyte. The biological samples used in this work were obtained from Dr. Safiri Medical Diagnostic Laboratory, Babolsar, Iran. All other used reagents were of analytical grade.

2.2. Preparation of Pt-nanoparticles

The Pt-nanoparticles were obtained by reducing hexacholoroplatinate to metallic Pt with sodium borohydride in aqueous solution, as reported in other literatures [41,42]. For this purpose, H_2PtCl_6 (3.38 mM) was dissolved in 50 mL of doubly distilled water and an excess amount of $NaBH_4$ was then added to the H_2PtCl_6 solution under stirring. After 2 h, the Pt-nanoparticles were separated from the reaction mixture and washed with doubly distilled water three times. Finally, the purified Pt-nanoparticles were dried without any heat treatment. The resulting Pt-nanoparticles were grind and kept at 4 °C before using in the surface modification of electrodes. The morphology and nanostructure distribution of the Pt-nanoparticles were recorded by SEM and TEM (Fig. 2).

2.3. Preparation of the electrode

The nPt-MWCNTPE was prepared by mixing of Pt-nanoparticles, MWCNT with ratio 5.0% (w/w) and paraffin oil in a mortar to form a uniform paste. The paste was then packed into one end of a glass tube (ca. 3.4 mm i.d. and 10 cm long) and pressed tightly. A copper wire was inserted through the opposite end to establish an electrical contact. Prior to experiment, the surface of the prepared electrode was polished with fine paper. The unmodified electrodes were prepared in the same way without adding Pt-nanoparticles to the MWCNT paste (MWCNTPE) and using only graphite powder (CPE).

3. Results and discussion

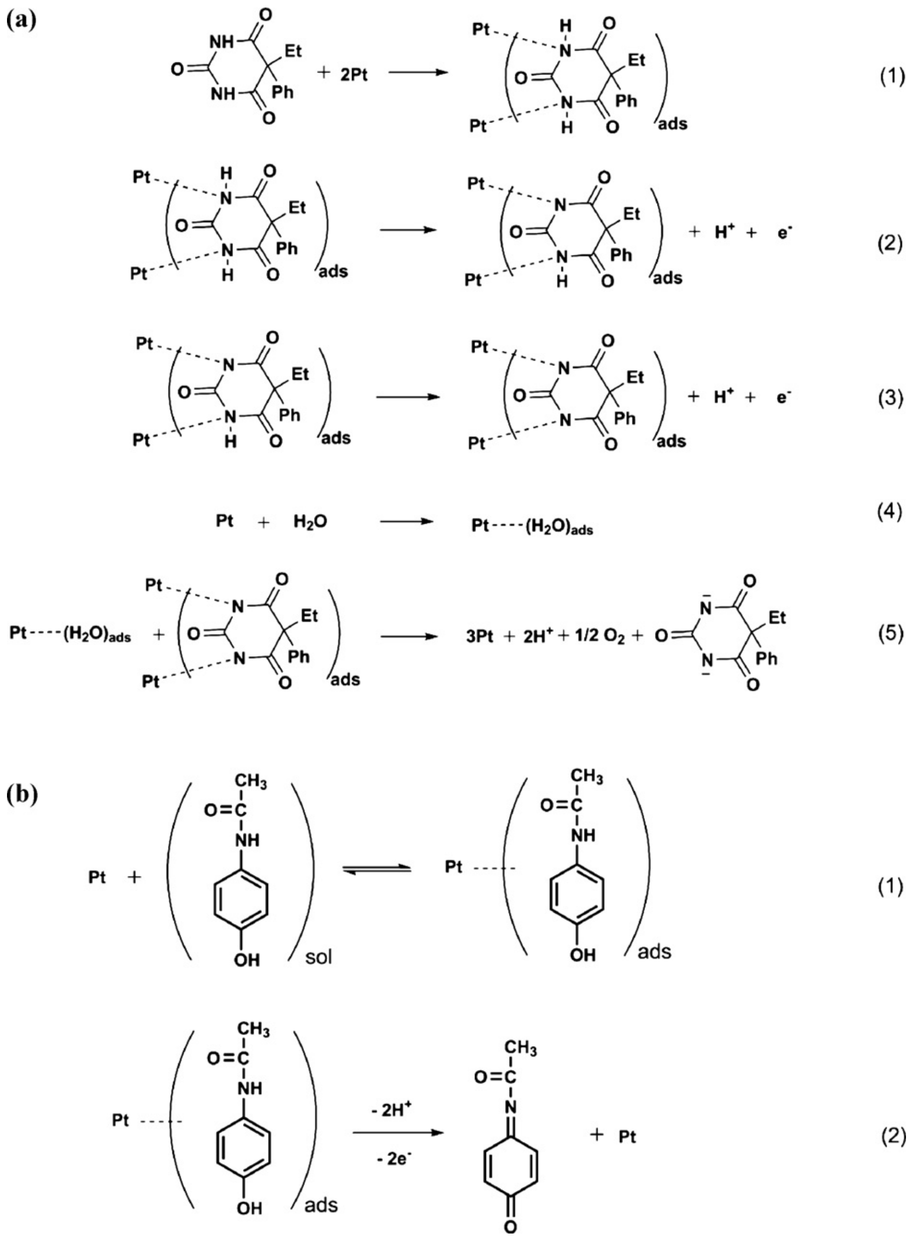
3.1. Cyclic voltammetric study of AC and PB

The electrochemical behaviors of AC and PB at nPt-MWCNTPE have been investigated and their determination in presence of each other has been performed using cyclic voltammetry. The cyclic voltammograms of AC and PB at bare CPE, MWCNTPE and nPt-MWCNTPE are shown in Fig. 3. Table 1 compares the voltammetric data of AC and PB at the surface of different working electrodes. The MWCNTPE exhibited a well-defined irreversible oxidation peak at 0.491 V and 0.643 V for oxidation AC and PB, respectively (Fig. 3B), whereas the CPE electrode provided an ill-defined irreversible oxidation peak (Fig. 3A). The peak potential due to the oxidation of AC at the surface of nPt-MWCNTPE occurs at 0.470 mV, which is about 0.092 V and 0.021 V more negative than CPE and MWCNTPE, respectively. Also, the peak potential due to the oxidation of PB occurs at 0.609 V, which is about 0.106 V and 0.034 V more negative than CPE and MWCNTPE, respectively (Fig. 3C). Although, these negative shifts are approximately the same at the surface of MWCNTPE and nPt-MWCNTPE, but the higher enhanced peak current indicate an enhanced electron transfer rate for AC and PB at nPt-MWCNTPE. No cathodic peak was observed on the reverse scan of potential within the investigated potential range, because AC and

Table 1
Cyclic voltammetric parameters of AC and PB at the surface of different electrodes.

Parameter	CPE		MWCNTPE		nPt-MWCNTPE	
	AC	PB	AC	PB	AC	PB
$E_{p,a}$ (V)	0.562	0.715	0.491	0.643	0.470	0.609
$I_{p,a}$ (μA)	3.82	1.29	6.89	6.28	13.41	12.18

Concentration of AC and PB are 200 and 300 μM, respectively.



Scheme 1. Possible reaction pathways for electrooxidation of phenobarbital (a) and acetaminophen (b) at the surface of nPt-MWCNTPE.

PB oxidation are an electrochemically irreversible process at the surface of these electrodes.

With attention to useful information about electrochemical mechanism can be acquired from the relationship between peak current and scan rate of potential, the effect of scan rate on the electro-oxidation of PB at the nPt-MWCNTPE was investigated by cyclic voltammetry (Fig. 4A). A plot of peak height (I_p) versus the scan rate (ν) in the range of 10–200 mV s^{-1} was constructed (Fig. 4B). This plot was found to be linear, corresponding to the following equation: $I_p = 0.115,\ \nu + 7.4255$; $R^2 = 0.9947$, suggesting that electrode process was controlled by adsorption [43]. In order to obtain information on the rate determining step, the Tafel plot was drawn by using the rising part of the current–voltage curves of PB monitored at scan rate of 10 mV s^{-1} (Fig. 4C). This part of voltammogram, known as Tafel region, is affected by electron transfer kinetics between substrate (PB) and nPt-MWCNTPE [44]. The slope of this plot was 0.1088 (V/decade)$^{-1}$. This slope indicates a transfer coefficient of $\alpha_a = 0.45$ for a one electron transfer process.

For an irreversible anodic reaction, the relationship between E_p and ν describes by Laviron's theory [45] as follows:

$$E_P = E^{0'} - \left(\frac{RT}{\alpha_a nF}\right) \ln\left(\frac{RTk_s}{\alpha_a nF}\right) + \left(\frac{RT}{\alpha_a nF}\right) \ln \nu \qquad (1)$$

where $E^{0'}$ is formal standard potential, α_a, the charge transfer coefficient, n, the number of the electrons transferred involved in the oxidation process, F, the Faraday constant (96485 C/mol) and k_s, the standard heterogeneous reaction rate constant. R and T have their usual meaning. According to the slope of the straight line of E_p against ln ν (Fig. 4D), the value of $\alpha_a n$ was calculated to be 0.46. Also, the value of k_s can be determined from the intercept of the straight line of E_p vs. ln ν if the value of $E^{0'}$ is known. The value of $E^{0'}$ in Eq. (1) can be obtained from the intercept of E_p versus ν curve by extrapolating to the vertical axis at $\nu = 0$ [46]. From slope (0.0552), intercept (0.4483 V), $E^{0'}$ (0.6047) and $\alpha_a n$ (0.46) values, the value of k_s was calculated equal to 271 s^{-1}.

The possible reaction pathways for electrooxidation of AC and PB on nPt-MWCNTPE in 0.1 M phosphate buffered solution (pH 7.0)

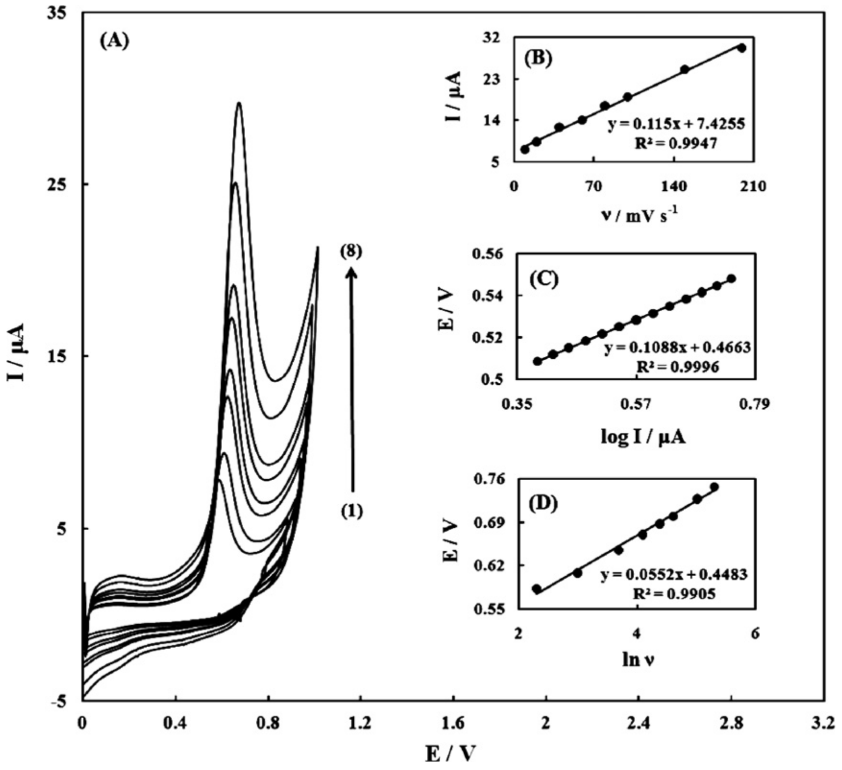


Fig. 4. (A) Cyclic voltammograms of 30.0 µM PB in 0.1 M phosphate buffer solution (pH 7.0) at various scan rates: (1) 10, (2) 20, (3) 40, (4) 60, (5) 80, (6) 100, (7) 150 and (8) 200 mV s^{-1} at nPt-MWCNTPE. Insets (B) plot of I_p versus ν. (C) Tafel plot derived from the rising part of voltammogram recorded at scan rate 10 mV s^{-1}. (D) Dependence of peak potential, E_p, on the ln ν obtained from cyclic voltammograms of (A).

can be proposed as shown in Scheme 1. Totally, in a possible oxidation reaction of PB, two hydrogens will remove by oxidation to create a more stable product of PB ring at the applied potential (Scheme 1a). The same conclusion holds for AC. In neutral media, AC oxidizes to N-acetyl-p-quinoneimine in a mechanism involving two protons and two electrons [11,47]. The possible mechanism for electro-oxidation of AC is shown in Scheme 1b.

3.2. Chronoamperometric measurements

Chronoamperometric measurements of PB at nPt-MWCNTPE were done by setting the working electrode potential at 610 mV and used for the measurement of the diffusion coefficient, *D*, of PB (Fig. 5A). According to Cottrell equation [43], for an electroactive material (PB in this case) with a diffusion coefficient of *D*, the

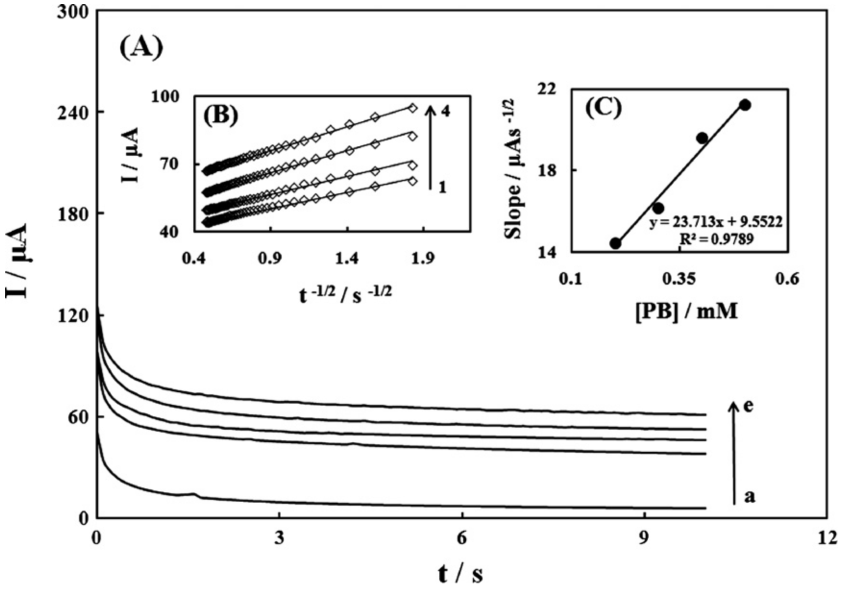


Fig. 5. (A) Chronoamperograms obtained in 0.1 M phosphate buffer solution (pH 7.0) in the absence (a) and presence of (b) 0.2, (c) 0.3, (d) 0.4 and (e) 0.5 mM of PB at nPt-MWCNTPE. (B) Plots of *I* vs. $t^{-1/2}$ obtained from chronoamperograms (b)–(e) in (A). (C) Plot of the slope of the straight lines against PB concentrations.

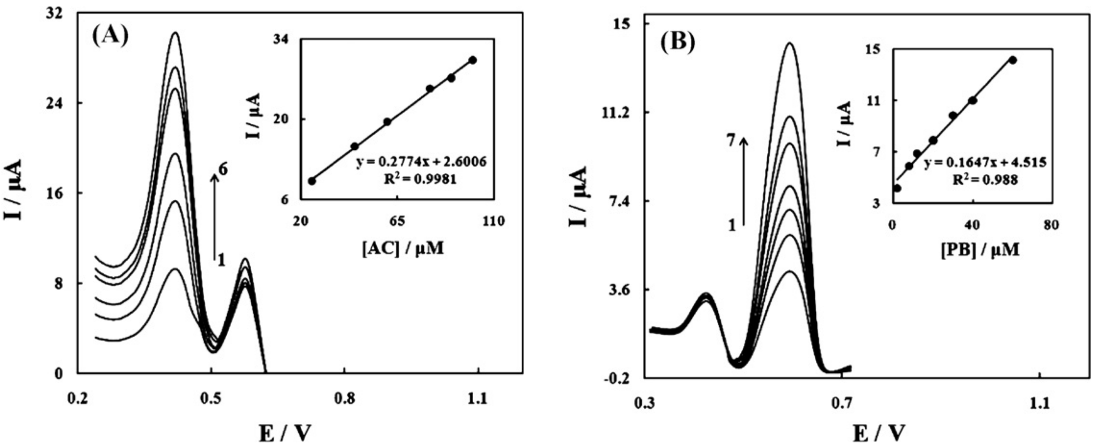


Fig. 6. (A) Differential pulse voltammograms of nPt-MWCNTPE in 0.1 M PBS (pH 7.0) containing 20.0 μM PB and different concentrations of AC: (1) 25.0, (2) 45.0, (3) 60.0, (4) 80.0, (5) 90.0 and (6) 100.0 μM. Inset: plot of the electrocatalytic peak current as a function of AC concentrations. (B) Differential pulse voltammograms of nPt-MWCNTPE in 0.1 M PBS (pH 7.0) containing 10.0 μM AC and different concentrations of PB: (1) 2.0, (2) 8.0, (3) 12.0, (4) 20.0, (5) 30.0, (6) 40.0 and (7) 60.0 μM. Inset: plot of the electrocatalytic peak current as a function of PB concentrations.

current for the electrochemical reaction (at a mass transport limited rate) is described by the following equation:

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

where D and C_b are the diffusion coefficient (cm^2 s^{-1}) and the bulk concentration (mol cm^{-3}), respectively. Under diffusion control (mass transport), a plot of I vs. $t^{-1/2}$ is linear, and the value of D can be obtained from its slope. Fig. 5B shows the fitted experimental plots for different concentrations of PB. The slopes of the resulting straight lines were plotted vs. the PB concentration (Fig. 5C), and the mean value of D was found to be 4.92×10^{-6} cm^2 s^{-1}.

Table 3
Effect of different interferences on the voltammetric signal of AC and PB at nPt-MWCNTPE.

Interfering agent	Concentration (μM)	Signal change (%)	
		AC	PB
Dopamine	10	+0.2	+0.001
Ascorbic acid	60	+1.4	~0.0
L-Dopa	10	+0.3	~0.0
Epinephrine	10	+1.0	~0.0
Tryptophan	20	~0.0	+2.3
L-Cysteine	20	+0.01	+1.2
Uric acid	100	+1.8	+1.25

Table 4
Determination of AC and PB in pharmaceutical samples ($n = 5$) at nPt-MWCNTPE.

Sample	AC[a]		PB[b]	
Added (μM)	50.0	60.0	40.0	30.0
Found (μM)	49.4	60.08	39.23	29.60
Recovery (%)	98.8	100.1	98.07	98.66
R.S.D. (%)	±1.1	±0.04	±0.05	±0.08
Labelled claim (mg)	325	500	100	25
Mean Amount found (mg)	320	497	97.46	24

[a] Hakim Pharmaceutical Co., Tehran, Iran.
[b] Darou Pakhsh Pharmaceutical Manuf. Co., Tehran, Iran.

3.3. Calibration plots and limits of detection

Since, differential pulse voltammetry (DPV) has the advantage of an increase in sensitivity and better characteristics for analytical applications, therefore, differential pulse voltammetry experiments were performed using nPt-MWCNTPE in phosphate buffer solution containing various individual concentrations of AC and PB. The results show the electrocatalytic peak currents of AC oxidation at the surface of nPt-MWCNTPE were linearly dependent on the AC concentrations, over the range of 0.5–100 μM with a slope and correlation coefficient of 0.2774 μA/μM and 0.9981, respectively. In addition, the electrode responses were linear with PB concentrations ranging from 0.4 to 60 μM with a regression equation of $I_p = 0.1647C_{PB} + 4.515$ ($R^2 = 0.988$), where C_{PB} concentration is in μM. The detection limits defined as $3S_b/m$ (where S_b is the standard deviation of the blank signal ($n = 8$) and m is the slope of the calibration curve) were found to be 0.17 and 0.1 μM for AC and PB, respectively. As expected, a very low LOD (0.17 and 0.1 μM) at the nPt-MWCNTPE was obtained, which can be attributed to the presence of Pt-nanoparticles in structure of modified electrode. The obtained detection limit for AC is comparable with values reported by other research groups for electrocatalytic oxidation of AC at the surface of chemically modified electrodes by other mediators (Table 2). The relative standard deviation of 10 successive scans was 3.6% for 10 μM PB, indicating excellent reproducibility of modified electrode. Furthermore, the stability of the modified electrode has been investigated. The peak current does not change after storage in air for 7 days. The modified electrode retained 90% of its initial response up to 1 month.

Table 2
Voltammetric response characteristics of different modified electrodes for AC determination.

Electrode	Method	LOD (μM)	E_p	pH	Reference
Boron-doped diamond electrode	SWV[a]	0.49	0.80	4.5	[48]
Nano TiO_2/polymer/GCE	DPV	2.0	0.397	7.0	[47]
Boron-doped diamond electrode	DPV	0.85	0.75	1.96	[49]
Carbon-coated nickel magnetic nanoparticles/GCE	DPV	2.3	0.52	3.0	[50]
Poly(taurine)/MWNT/GCE	DPV	0.5	0.38	7.38	[51]
nPt-MWCNTPE	DPV	0.17	0.47	7.0	This work

[a] Square wave voltammetry.

Table 5
Simultaneous determination of AC and PB in urine samples at the surface of nPt-MWCNTPE.

Sample	Spiked (μM)		Found (μM)		Recovery (%)		RSD (%)	
	AC	PB	AC	PB	AC	PB	AC	PB
Urine	0.0	0.0	–	–	–	–	–	–
	5.0	8.0	4.9	7.8	98	97.5	1.1	1.9
	10	16	10.1	15.7	101	98.1	2.8	1.7
	20	25	20.1	25.1	100.5	100.4	2.3	2.4
	30	40	29.9	40.3	99.7	100.7	2.6	1.6

3.4. Simultaneous determination of AC and PB at nPt-MWCNTPE

The main objective of this study was to measure AC and PB simultaneously. For this purpose, the effective application of the nPt-MWCNTPE for electro-oxidation processes of AC and PB in the mixture was investigated when the concentration of one species changed while the other species was kept constant. The results are shown in Fig. 6A and B. As it can be seen, the peak current of AC increased with an increase in AC concentration when the concentration of PB was kept constant (Fig. 6A). Similarly and obviously, as shown in Fig. 6B, keeping the concentration of AC constant, the oxidation peak current of PB was positively proportional to its concentration, while that of AC did not change. The obtained DPV response with two well-distinguished anodic peaks, corresponding to the oxidation of AC and PB, is indicating that the simultaneous determination of AC and PB is possible at the nPt-MWCNTPE.

3.5. Interference studies

Under the optimum experimental conditions, the possible interference was investigated for the determination of AC and PB at the surface of nPt-MWCNTPE. The experimental results (Table 3) show that modified electrode yield a small change response for the interfering agents within the same concentration level. It confirms that nPt-MWCNTPE can be considered as a good electrochemical sensor for recognition of AC and PB.

3.6. Sample analysis

The described method was successfully applied for determination of AC and PB in tablet and urine samples by standard addition method (*n* = 5). The obtained results demonstrate the capability of the modified electrode for the determination of AC and PB in real samples.

3.6.1. Determination of AC and PB in tablet

The acetaminophen tablet (2 tablets, labeled 500 and 325 mg) and phenobarbital tablet (2 tablets, labeled 100 and 25 mg) were finely grinded in a mortar with pestle and the obtained powders was dissolved separately in 100 mL distilled water by ultrasonication. Then, different adequate amount of prepared solutions was diluted to 10 mL with phosphate buffer (pH 7.0) and transferred to the voltammetric cell for the voltammetric determinations. The results are presented in Table 4.

3.6.2. Analysis of AC and PB in human urine serum

For preparing the urine sample, 10 mL of the sample (healthy volunteers, male, 20) was centrifuged for 15 min at 1500 rpm. The supernatant was filtered out and then 2 mL of the result solution was diluted to 10 mL with 0.1 M phosphate buffer solution (pH 7.0) in a voltammetric cell for the voltammetric determinations. The results are given in Table 5. Satisfactory recovery of the experimental results was found for AC and PB. The reproducibility of the method was demonstrated by the mean relative standard deviation (RSD).

4. Conclusions

This work demonstrates the construction of an nPt-MWCNTPE and its application in simultaneous determination of AC and PB for the first time. The results showed two well-defined redox peaks for oxidation of AC and PB at the surface of the nPt-MWCNTPE, which were large enough to determine AC and PB individually and in presence of each other. The oxidation peak currents obtained using DPV were linearly dependent on the AC and PB concentrations and the detection limits for AC and PB were 0.17 and 0.1 μM, respectively. The high current sensitivity, low detection limit and high selectivity of the nPt-MWCNTPE for the detection of PB in presence of AC prove its potential sensing applications. Finally, nPt-MWCNTPE was used for determination of AC and PB in some real samples.

References

[1] C.M. Monzón, M.R. Delfino, M.C. Sarno, M.R. Delfino, J. Argent. Chem. Soc. 96 (2008) 101.
[2] World Health Organization, Initiative of Support to People with Epilepsy, WHO, Geneva, 1990.
[3] P. Lorenzo, A. Moreno, J.C. Leza, I. Lizasoain, M.A. Moro, Farmacología Básica y Clínica, 17 ed., Médica Panamericana, España, 2005.
[4] M.J. Brodie, J.A. French, Lancet 356 (2000) 323.
[5] P. Kwan, M.J. Brodie, Epilepsia 45 (2004) 1141.
[6] A. Haque, X. Xu, J.T. Stewart, J. Pharm. Biomed. Anal. 21 (1999) 1063.
[7] J.L.F.C. Lima, M.C.B.S.M. Montenegro, A.M.R. Da Silva, J. Pharm. Biomed. Anal. 8 (1990) 701.
[8] L.J.C. Love, S. Zibas, J. Noroski, M. Arunyanart, J. Pharm. Biomed. Anal. 3 (1985) 511.
[9] T.L. Lu, Y.C. Tsai, Sens. Actuators B: Chem. 153 (2011) 439.
[10] M.T. Olaleye, B.T.J. Roch, Exp. Toxicol. Pathol. 59 (2008) 319.
[11] J.B. Raoof, R. Ojani, M. Baghayeri, M. Amiri-Aref, Anal. Methods (2012), doi:10.1039/c2ay05494a.
[12] M. Mazer, J. Perrone, J. Med. Toxicol. 4 (2008) 2.
[13] H. Filik, D. Aksu, R. Apak, I. Sener, E. Kılıc, Sens. Actuators B: Chem. 136 (2009) 105.
[14] C. Nebot, S.W. Gibb, K.G. Boyd, Anal. Chim. Acta 598 (2007) 87.
[15] M.K. Srivastava, S. Ahmad, D. Singh, I.C. Shukla, Analyst 110 (1985) 735.
[16] T. Perez-Ruiz, C. Martinez-Lozano, V. Tomas, R. Galera, J. Pharm. Biomed. Anal. 38 (2005) 87.
[17] W. Ruengsitagoon, S. Liawruangrath, A. Townshend, Talanta 69 (2006) 976.
[18] Q. Li, X. Liu, Y. He, J. Biomed. Nanotechnol. 5 (2009) 565.
[19] G. Signore, R. Nifosí, L. Albertazzi, R. Bizzarri, J. Biomed. Nanotechnol. 5 (2009) 722.
[20] Y. Zheng, P. Cloutier, D.J. Hunting, L. Sanche, J. Biomed. Nanotechnol. 4 (2008) 469.
[21] M. Mazloum-Ardakania, H. Beitollahi, M.A. Sheikh-Mohseni, H. Naeimi, N. Taghavinia, Appl. Catal., A 378 (2010) 195.
[22] R. Jain, J.A. Rather, Colloids Surf. B 83 (2011) 340.
[23] S. Mandal, D. Roy, R.V. Chaudhari, M. Sastry, Chem. Mater. 16 (2004) 3714.
[24] S. Iijima, Nature 354 (1991) 56.
[25] S.K. Smart, A.I. Cassady, G.Q. Lu, D.J. Martin, Carbon 44 (2006) 1034.
[26] G.G. Wildgoose, C.E. Banks, H.C. Leventis, R.G. Compton, Microchim. Acta 152 (2006) 187.
[27] R.N. Hegde, N.P. Shetti, S.T. Nandibewoor, Talanta 79 (2009) 361.
[28] Q. Zhuang, J. Chen, J. Chen, X. Lin, Sens. Actuators B: Chem. 128 (2008) 500.
[29] Y.D. Zhao, W.D. Zhang, H. Chen, Q.M. Luo, Talanta 58 (2002) 529.
[30] P.D. Hale, H.L. Lan, L.I. Boguslavsky, H.I. Karan, Y. Okamoto, T.A. Skotheim, Anal. Chim. Acta 251 (1991) 121.
[31] R. Joseph, K. Girish Kumar, Drug Test. Anal. 2 (2010) 278.
[32] M. Mazloum-Ardakani, H. Beitollahi, M.K. Amini, F. Mirkhalaf, M. Abdollahi-Alibeik, Sens. Actuators B: Chem. 151 (2010) 243.
[33] J.B. Raoof, R. Ojani, M. Baghayeri, Sens. Actuators B: Chem. 143 (2009) 261.
[34] L. Xu, Y. Zhu, L. Tang, X. Yang, C. Li, Electroanalysis 19 (2007) 717.
[35] L. Xu, Y. Zhu, L. Tang, X. Yang, C. Li, J. Appl. Polym. Sci. 109 (2008) 1802.
[36] M. Yang, Y. Yang, Y. Liu, G. Shen, R. Yu, Biosens. Bioelectron. 21 (2006) 1125.

[37] Z. Liu, X.Y. Ling, X. Su, J.Y. Lee, J. Phys. Chem. B 108 (2004) 8234.
[38] H. Tang, J. Chen, L. Nie, D. Liu, W. Deng, Y. Kuang, S. Yao, J. Colloid Interface Sci. 269 (2004) 26.
[39] C. Jiang, H. Chen, C. Yu, S. Zhang, B. Liu, J. Kong, Electrochim. Acta 54 (2009) 1134.
[40] S. Hrapovic, Y.L. Liu, K.B. Male, J.H.T. Luong, Anal. Chem. 76 (2004) 1083.
[41] J.H. Choi, K.W. Park, B. k. Kwon, Y.E. Sung, J. Electrochem. Soc. 150 (2003) 973.
[42] J.H. Yoon, G. Muthuraman, J. Yang, Y.B. Shim, M.S. Wona, Electroanalysis 19 (2007) 1160.
[43] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, 2001.
[44] M.H. Pournaghi-Azar, H. Razmi-Nerbin, J. Electroanal. Chem. 488 (2000) 17.
[45] E. Laviron, J. Electroanal. Chem. 101 (1979) 19.
[46] Y. Wu, X. Ji, S. Hu, Bioelectrochemistry 64 (2004) 91.
[47] S.A. Kumar, C.F. Tang, S.M. Chen, Talanta 76 (2008) 997.
[48] B.C. Lourenc, R.A. Medeiros, R.C. Rocha-Filho, L.H. Mazo, O. Fatibello-Filho, Talanta 78 (2009) 748.
[49] W.Y. Su, S.H. Cheng, Electroanalysis 22 (2010) 707.
[50] H. Razmi, M. Harasi, J. Iran Chem. Soc. 5 (2008) 296.
[51] S.F. Wang, F. Xie, R.F. Hu, Sens. Actuators B: Chem. 123 (2007) 495.