

Benzoylferrocene-modified carbon nanotubes paste electrode as a voltammetric sensor for determination of hydrochlorothiazide in pharmaceutical and biological samples

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Abstract The electrooxidation of hydrochlorothiazide (HCT) at the surface of a benzoylferrocene modified multi-walled carbon nanotube paste electrode was studied using electrochemical approaches. Under the optimized conditions (pH 7.0), the square wave voltammetric peak current of HCT increased linearly with HCT concentration in the ranges of 6.0×10^{-7} to 3.0×10^{-4} M. The detection limit was 9.0×10^{-8} M HCT. The diffusion coefficient ($D=1.75 \times 10^{-5}$ cm²/s) and electron transfer coefficient ($\alpha=0.45$) for HCT oxidation were also determined. The proposed sensor was successfully applied for the determination of HCT in human urine and tablet samples.

Keywords Hydrochlorothiazide · Carbon nanotubes · Carbon paste electrode · Voltammetry

Introduction

Drug analysis is an important branch of analytical chemistry and plays an important role in drug quality control and has a wide impact on public health. Therefore, developing sensitive, simple, rapid, and reliable method for the determination of active ingredient is valuable and necessary [1–3].

Electrochemical techniques have shown to be excellent procedures for the sensitive determination of organic molecules, including drugs and related molecules in pharmaceutical

sample and biological fluids. The advancements in electrochemical techniques in drug analysis are attributed to their simplicity, low cost, and relatively short time of analysis, compared with the other techniques [4, 5].

Carbon paste electrode (CPE) is a special kind of heterogeneous carbon electrodes consisting of mixture prepared from carbon powder and a suitable water-immiscible or nonconducting binder [6]. The use of carbon paste as an electrode was initially reported in 1958 by Adams [7]. In afterward researches, a wide variety of modifiers has been used with these versatile electrodes [8–10]. CPEs are widely applicable in both electrochemical studies and electroanalysis, thanks to their advantages such as very low background current (compared to solid graphite or noble metal electrodes), facility to prepare, low cost, large potential window, simple surface renewal process, and easiness of miniaturization [11]. Besides the advantageous properties and characteristics listed before, the feasibility of incorporating different substances during the paste preparation (which results in the so-called modified carbon paste electrode) allows the fabrication of electrodes with desired composition and, hence, with predetermined properties [12, 13].

Carbon nanotubes (CNTs) are molecular-scale wires that have attracted considerable attention due to their extraordinary structural, mechanical, electrical, and electrochemical properties as well as their promise in the field of material science [14]. It has been shown that application of CNTs results in extraordinary advantages over conventional electrodes, including enhanced mass transport (via thin layer diffusion besides the semi-infinite planar diffusion), catalysis, highly effective surface areas, high porosity, more adsorption, and reactive sites. Furthermore, control over the electrode macroenvironment can provide an important and feasible platform for electroanalysis, particularly in the design of the modified electrodes for electrochemical sensing [15].

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Hydrochlorothiazide (6-chloro-3,4-dihydro-2*H*-1,2,4-benzothiadiazine-7-sulfonamide-1,1-dioxide) (HCT) has gained attention because it is a benzothiazide diuretic that acts directly on the kidney by increasing the excretion of sodium chloride and water and, to a lesser extent, that of potassium ions. HCT is an antihypertensive substance and improves the action of other hypotensive substances, allowing a decrease in the dose of those below the level where these substances present secondary effects. Novello and Sprague observed the diuretic effect of thiazides with chlorothiazide in 1957 [16]. HCT is well absorbed, is shortly bound to plasma proteins, and mainly excreted unchanged in the urine [17]. Owing to the wide variety of analogous products developed in the following years, the clinical, forensic, and antidoping analysts require informative and unambiguous data about administered pharmaceuticals.

Due to the frequency in which HCT is prescribed and its abuse for the reduction of body weight by some athletes (who are categorized in several body weight classes) [18], its analysis is of great importance. Urinary recovery is the preferred way for analyzing and estimating bioavailability of HCT in humans [19] because it is not metabolized and excreted unchanged in urine [19]. Several methods have been proposed for the determination of HCT including chromatography, capillary electrophoresis, spectrophotometry, chemiluminescence, and electrochemical methods [20–22]. Owing to the high sensitivity and simplicity of the voltammetric techniques, this work was directed to study the voltammetric behavior of HCT and to find out simple, rapid, sensitive, and selective voltammetric procedure for HCT determination in human urine and in pharmaceutical tablets.

Experimental

Apparatus and chemicals

The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT 12, Eco Chemie, the Netherlands). The experimental conditions were controlled with General Purpose Electrochemical System software. A conventional three-electrode cell was used at 25 ± 1 °C. An Ag/AgCl/KCl (3.0 M) electrode, a platinum wire, and the benzoylferrocene-modified multi-walled carbon nanotube paste electrode (BFCNPE) were used as the reference, auxiliary, and working electrodes, respectively. A Metrohm 710 pH meter was used for pH measurements.

All solutions were freshly prepared with double distilled water. HCT and all other reagents were of analytical grade from Merck (Darmstadt, Germany). Tablets of HCT as pharmaceutical sample were purchased from Darou Pakhsh Company of Iran. The buffer solutions were prepared from orthophosphoric acid and its salts in the pH range of 2.0–11.0.

Multi-walled carbon nanotubes (purity more than 95 %) with o.d. between 10 and 20 nm, inner diameter (i.d.) between 5 and 10 nm, and tube length from 0.5 to 200 μm were prepared from Nanostructured and Amorphous Materials, Inc.

Synthesis of benzoylferrocene

A mixture of aluminum chloride (10.8 g, 80.66 mmol) and benzoyl chloride (11.3 g, 80.66 mmol) in 100 mL of dry methylene chloride was added to a solution of ferrocene (15.0 g, 80.66 mmol) in 100 mL of dry methylene chloride over a period of 15 min. The mixture was stirred at room temperature for 1 h and then hydrolyzed with dilute hydrochloric acid (60 mL, 3 M). The organic phase was washed with NaOH solution (50 mL, 1 M), saturated NaCl solution (50 mL), and H₂O (50 mL) and dried over anhydrous sodium sulfate. The solid which remained after evaporation of the solvent was recrystallized from toluene and *n*-hexane to give the pure product in 78 % yield, in the following method: red solid, mp 106–108 °C; ¹H NMR (400 MHz CDCl₃), δ (ppm)=4.17 (*s*, 5H), 4.58 (*t*, *J*=2.5 Hz, 2H), 4.90 (*d*, *J*=8.4 Hz, 2H), 7.44–7.56 (*m*, 3H), and 7.90 (*t*, *J*=2.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm)=70.22, 71.53, 72.51, 78.25, 128.07, 128.21, 131.45, 139.87, and 199.02.

Preparation of the sensor

The BFCNPEs were prepared by hand mixing 0.01 g of BF with 0.89 g graphite powder and 0.1 g CNTs with a mortar and pestle. Then, ~0.7 mL of paraffin oil was added to the above mixture and mixed for 20 min until a uniformly wetted paste was obtained. The paste was then packed into the end of a glass tube (ca. 3.4 mm i.d. and 15 cm long). A copper wire inserted into the carbon paste provided the electrical contact. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a clean paper.

For comparison, BF-modified CP electrode without CNTs, CNTs paste electrode (CNPE) without BF, and unmodified CPE in the absence of both BF and CNTs were also prepared in the same way.

Results and discussion

Electrochemical properties of BFCNPE

BFCNPE was constructed, and its electrochemical properties were studied in a 0.1 M phosphate buffer solution (PBS) (pH 7.0) using cyclic voltammetry (CV) (Fig. 1). The experimental results show well-defined and reproducible anodic and cathodic peaks related to benzoylferrocene/benzoylferricenium redox system, which show a quasireversible behavior in an aqueous medium [23]. The electrode capability for the

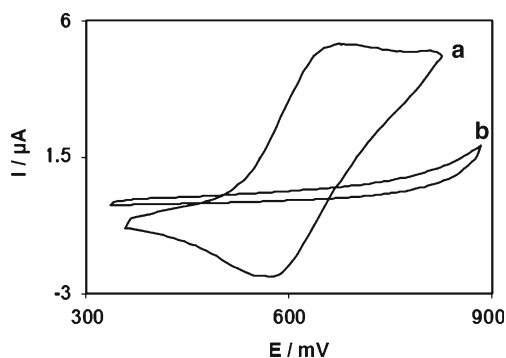


Fig. 1 CV of BFCNPE in 0.1 M PBS (pH 7.0) *a* and *b* as *a* at the surface of bare carbon paste electrode at scan rate 100 mV s⁻¹

generation of a reproducible surface was examined by cyclic voltammetric data obtained in optimum solution pH 7.0 from five separately prepared BFCNPEs (Table 1).

In addition, the long-term stability of the BFCNPE was tested over a 3-weeks period. When CVs were recorded after the modified electrode was stored in atmosphere at room temperature, the peak potential for HCT oxidation was unchanged, and the current signals showed less than 2.2 % decrease relative to the initial response. The antifouling properties of the modified electrode toward HCT oxidation and its oxidation products were investigated by recording the cyclic voltammograms of the modified electrode before and after use in the presence of HCT. Cyclic voltammograms were recorded in the presence of HCT after having cycled the potential 12 times at a scan rate of 10 mV s⁻¹. The peak potentials were unchanged, and the currents decreased by less than 2.1 %. Therefore, at the surface of BFCNPE, not only the sensitivity but the fouling effect of the analyte increase, and its oxidation product also decreases.

Electrocatalytic oxidation of HCT at a BFCNPE

The electrochemical behavior of HCT is dependent on the pH value of the aqueous solution, whereas the electrochemical properties of Fc/Fc⁺ redox couple are independent on pH. Therefore, pH optimization of the solution seems to be necessary in order to obtain the electrocatalytic oxidation of HCT. Thus, the electrochemical behavior of HCT was studied in 0.1 M PBS in different pH values (2.0 < pH < 11.0) at the surface of BFCNPE by cyclic voltammetry. It was found that the electrocatalytic oxidation of HCT at the

Table 1 Cyclic voltammetric data obtained for constructed BFCNPE in 0.1 M PBS (pH 7.0) at 100 mV s⁻¹

E_{pa} (V) ^a	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (V)	I_{pa} (μA)	I_{pc} (μA)
0.645±1.3	0.540±1.4	0.592±1.3	0.105±1.4	5.2±1.7	-2.4±1.6

All the values are RSD, in percent ($n=5$)

^a Versus Ag/AgCl/KCl (3.0 M) as reference electrode

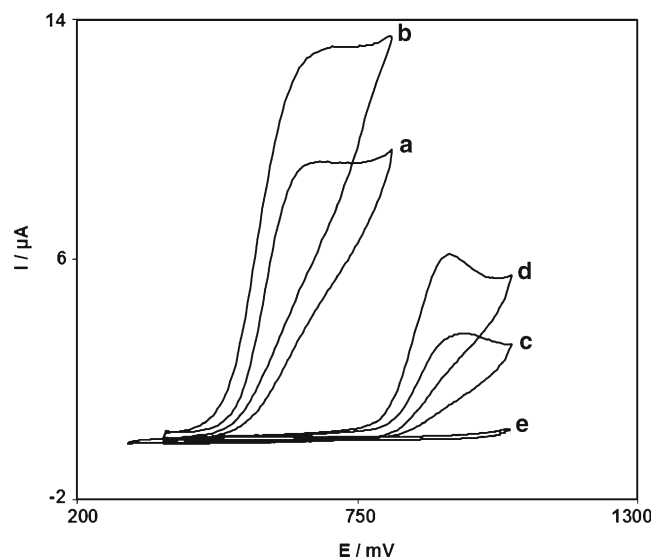


Fig. 2 CVs of BFCPE (*a*) and BFCNPE (*b*) in 0.1 M PBS (pH 7.0) containing 600.0 μM HCT. *c, d* CVs of CPE and CNPE in 0.1 M PBS (pH 7.0) containing 600.0 μM HCT; *e* CVs of CNPE in 0.1 M PBS (pH 7.0). In all cases, scan rate is 10 mV s⁻¹

surface of BFCNPE was more favored under neutral conditions than in acidic or basic medium.

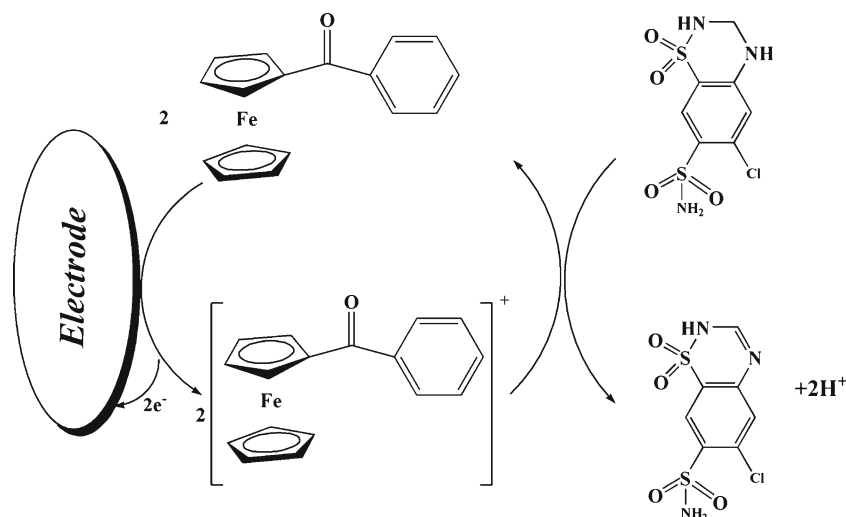
The variation of I_{pa} vs. the variation of pH was studied. Results showed that the anodic peak current value for electrooxidation of HCT were higher at a biological pH. Thus, the pH 7.0 was chosen as the optimum pH for electrocatalysis of HCT oxidation at the surface of BFCNPE.

Figure 2 depicts the CV responses for the electrochemical oxidation of 600.0 μM HCT at unmodified CPE (curve *c*), CNPE (curve *d*), BFCPE (curve *a*), and BFCNPE (curve *b*). As it is seen, while the anodic peak potential for HCT oxidation at the CNPE and unmodified CPE is 925 and 970 mV, respectively, the corresponding potential at BFCNPE and BFCPE is ~645 mV. These results indicate that the peak potential for HCT oxidation at the BFCNPE and BFCPE electrodes shift by ~280 and 325 mV toward negative values compared to CNPE and unmodified CPE, respectively. However, BFCNPE shows much higher anodic peak current for the oxidation of HCT compared to BFCPE, indicating that the combination of CNTs and the mediator (BF) has significantly improved the performance of the electrode toward HCT oxidation (Table 2). The BFCNPE, in 0.1 M

Table 2 Comparison of electrocatalytic oxidation of 600.0 μM HCT on various electrode surfaces at pH 7.0

Electrode	Anodic peak potential/mV	Anodic peak current/μA
BFCNPE	645	13.1
BFCPE	645	9.3
CNPE	925	6.2
CPE	970	3.5

Scheme 1 Electrocatalytic mechanism for the oxidation of HCT at the surface of BFCNPE



PBS (pH 7.0) and without HCT in solution, exhibited a well-behaved redox reaction (as shown in Fig. 1, curve a) and, with addition of 600.0 μM HCT, increased the anodic peak current (Fig. 2, curve b), indicating a strong electrocatalytic effect (see Scheme 1).

The effect of scan rate on the electrocatalytic oxidation of HCT at the BFCNPE was investigated by cyclic voltammetry (Fig. 3). As can be observed in Fig. 3, the oxidation peak potential shifted to more positive potentials with increasing scan rate, confirming the kinetic limitation in the electrochemical reaction. Also, a plot of peak height (I_p) vs. the square root of scan rate ($\nu^{1/2}$) was found to be linear in the range of 2–50 mV s^{-1} , suggesting that at sufficient overpotential, the process is diffusion rather than surface controlled [23] [Fig. 3(A)].

A plot of the scan rate-normalized current ($I_p/\nu^{1/2}$) vs. scan rate [Fig. 3(B)] exhibits the characteristic shape typical of an EC process [23].

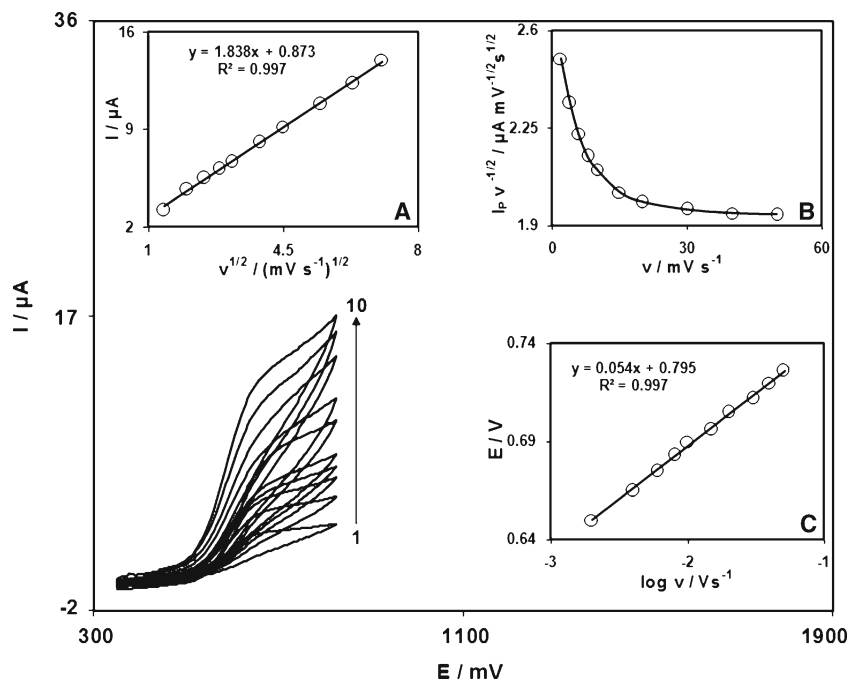
The Tafel slope (b) can be obtained from the slope of E_p vs. $\log \nu$ using Eq. (1) [24] as follows:

$$E_p = b/2 \log \nu + \text{constant} \quad (1)$$

The Tafel slope was found to be 0.108 V (Fig. 3, inset C), which indicates that a one-electron transfer process is the rate-limiting step assuming a transfer coefficient (α) is about 0.45.

Figure 4 shows the Tafel plot for the sharp rising part of the voltammogram at the scan rate of 4 mV s^{-1} . If deprotonation of HCT is a sufficiently fast step, the Tafel plot can

Fig. 3 CVs of BFCNPE in 0.1 M PBS (pH 7.0) containing 300.0 μM HCT at various scan rates; numbers 1–10 correspond to 2, 4, 6, 8, 10, 15, 20, 30, 40, and 50 mV s^{-1} , respectively. Insets, variation of A anodic peak current vs. $\nu^{1/2}$; B normalized current ($I_p/\nu^{1/2}$) vs. ν ; C anodic peak potential vs. $\log \nu$



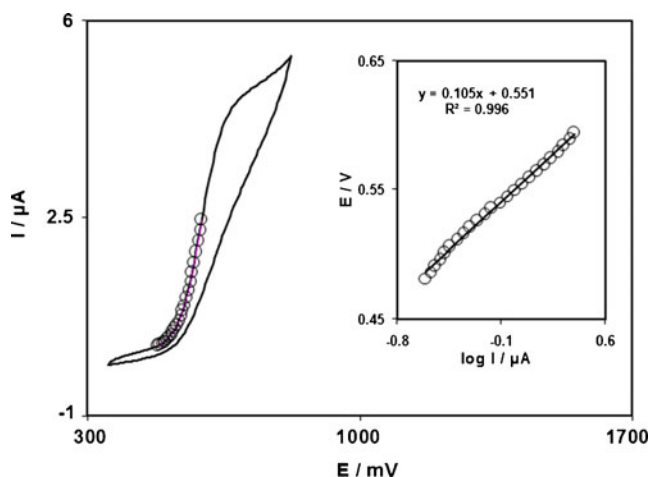


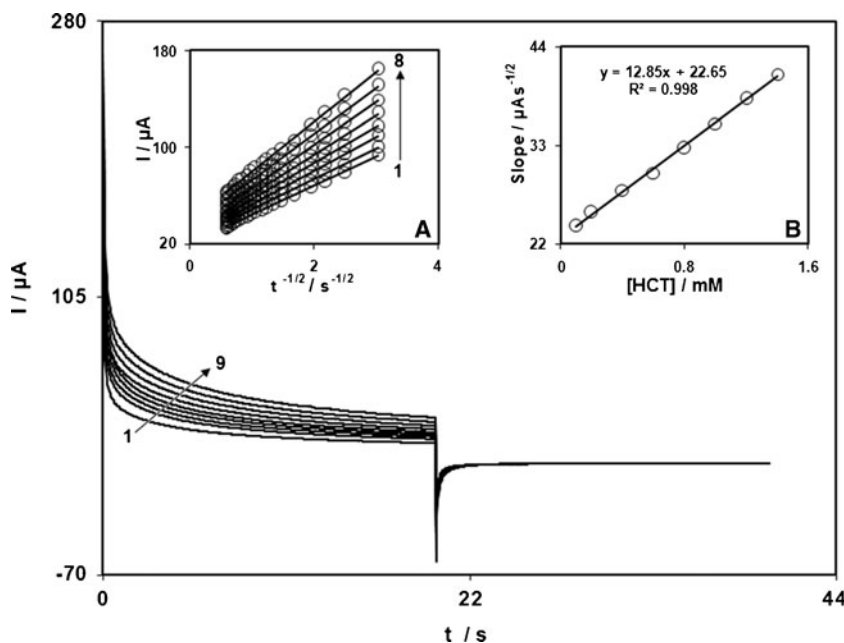
Fig. 4 Cyclic voltammogram (at 4 mV s^{-1}) of a BFCNPE in 0.1 M PBS (pH 7.0) containing $300.0 \mu\text{M}$ HCT. The points are the data used in the Tafel plot. The inset shows the Tafel plot derived from the cyclic voltammogram

be used to estimate the number of electrons involved in the rate-determining step. A Tafel slope of 0.105 V was obtained which agrees well with the involvement of one electron in the rate-determining step of the electrode process [23], assuming a charge transfer coefficient, α of 0.44.

Chronoamperometric measurements

Chronoamperometric measurements of HCT at BFCNPE were carried out by setting the working electrode potential at 0.7 V (at the first potential step) and at 0.5 V (at second potential step) vs. Ag/AgCl/KCl (3.0 M) for the various concentrations of HCT in PBS (pH 7.0) (Fig. 5). For an

Fig. 5 A Chronoamperograms obtained at BFCNPE in 0.1 M PBS (pH 7.0) for different concentrations of HCT. The numbers 1–9 correspond to 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4 mM of HCT. Insets, A plots of I vs. $t^{-1/2}$ obtained from chronoamperograms 2–9 and B plot of the slope of the straight lines against HCT concentration



electroactive material (HCT in this case) with a diffusion coefficient of D , the current observed for the electrochemical reaction at the mass transport-limited condition is described by the Cottrell equation [23]. Experimental plots of I vs. $t^{-1/2}$ were employed, with the best fits for different concentrations of HCT [Fig. 5(A)]. The slopes of the resulting straight lines were then plotted vs. HCT concentration [Fig. 5(B)], from the resulting slope and Cottrell equation as follows:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2} \tag{2}$$

where D and C_b are the diffusion coefficient (in square centimeter per second) and the bulk concentration (in mole per cubic centimeter), respectively; the mean value of the D was found to be $1.75 \times 10^{-5} \text{ cm}^2/\text{s}$.

Chronoamperometry can also be employed to evaluate the catalytic rate constant, k , for the reaction between HCT and the BFCNPE according to the following method of Galus [25]:

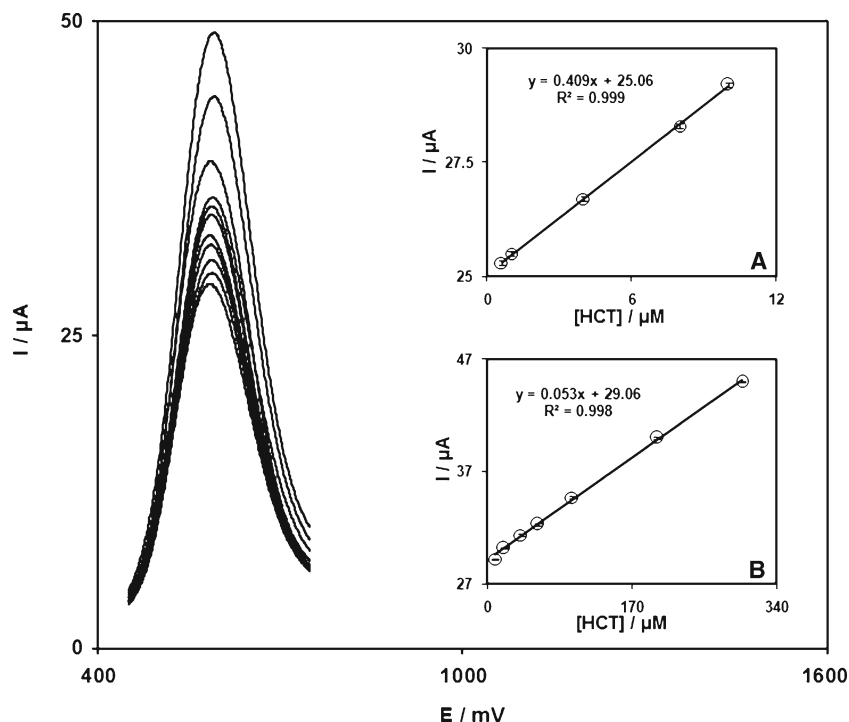
$$I_C/I_L = \gamma^{1/2} [\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \tag{3}$$

where I_C is the catalytic current of HCT at the BFCNPE, I_L is the limited current in the absence of HCT, and $\gamma = kC_b t$ is the argument of the error function (C_b is the bulk concentration of HCT). In cases where γ exceeds the value of 2, the error function is almost equal to 1, and therefore, the above equation can be reduced to the following equation:

$$I_C/I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (kC_b t)^{1/2} \tag{4}$$

where t is the time elapsed. The above equation can be used to calculate the rate constant, k , of the catalytic process from the slope of I_C/I_L vs. $t^{1/2}$ at a given HCT concentration. From

Fig. 6 SWVs of BFCNPE in 0.1 M PBS (pH 7.0) containing different concentrations of HCT. From *inner to outer* correspond to 0.6, 1.0, 4.0, 8.0, 10.0, 20.0, 40.0, 60.0, 100.0, 200.0, and 300.0 μM of HCT. *Inset*, plots of the electrocatalytic peak current as a function of HCT concentration in the range of 0.6 to 10.0 μM (A) and 10.0 to 300.0 μM (B)



the values of the slopes, the average value of k was found to be $6.38 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

Calibration plot and limit of detection

Since square wave voltammetry (SWV) has a much higher current sensitivity and better resolution than cyclic voltammetry, it was used to estimate the limit of detection of HCT (Fig. 6). The plot of peak current vs. HCT concentration consisted of two linear segments with slopes of 0.409 and 0.053 $\mu\text{A } \mu\text{M}^{-1}$ in the concentration ranges of 0.6 to 10.0 μM and 10.0 to 300.0 μM , respectively. The decrease in the sensitivity (slope) of the second linear segment is likely due to kinetic limitation. The lower detection limit, C_m , was obtained by using the equation $C_m = 3s_b/m$, where s_b is the standard deviation of the blank response (in microampere), and m is the slope of the calibration plot ($0.409 \mu\text{A } \mu\text{M}^{-1}$). The data analysis presents the value of lower limit detection of HCT to be 0.09 μM . This value is comparable with values reported by other research groups for electrocatalytic oxidation of HCT (see Table 3).

Interference study

The influences of various foreign species on the determination of HCT were investigated. The tolerance limit was taken as the maximum concentration of the foreign substances which caused an approximately $\pm 5\%$ relative error in the determination. L-Lysine, glucose, NADH, acetaminophen, L-asparagine, glutamic acid, glycine, folic acid, uric acid, tryptophan, and phenylalanine did not show interference in the determination of HCT, but L-cysteine and D-penicillamine showed interferences.

Real sample analysis

Determination of HCT in HCT tablet sample

In order to evaluate the analytical applicability of the proposed method, it was applied to the determination of HCT in HCT tablet. Based on the repeated SWV responses ($n=5$) of the diluted analytes and the samples that were spiked with specified concentration of HCT, measurements were made

Table 3 Comparison of the efficiency of some modified electrodes used in the electrocatalysis of HCT

Electrode	Modifier	Technique	pH	Scan rate (mV/s)	LOD	LDR	Ref
Carbon paste	Ferrocenedicarboxylic acid	Square wave voltammetry	9.0	10	$3.7 \times 10^{-8} \text{ M}$	$8.0 \times 10^{-8} - 5.0 \times 10^{-4} \text{ M}$	[20]
Glassy carbon	–	Differential pulse voltammetry	3.3	100	5.0 ng ml^{-1}	$24 - 320 \text{ ng ml}^{-1}$	[21]
Carbon nanotube paste	BF	Square wave voltammetry	7.0	10	$9.0 \times 10^{-8} \text{ M}$	$6.0 \times 10^{-7} - 3.0 \times 10^{-4} \text{ M}$	This work

Table 4 The application of BFCNPE for determination of HCT in HCT tablets and urine samples ($n=5$)

Sample	Sample no.	Original content (μM)	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
HCT tablet						
	1	10.0	0	9.8	98.0	2.7
	2	10.0	30.0	41.5	103.7	3.4
	3	10.0	40.0	51.1	102.2	2.4
	4	10.0	50.0	59.5	99.2	1.7
Urine						
	1	–	0	–	–	–
	2	–	15.0	15.5	103.3	3.4
	3	–	30.0	29.6	98.7	1.9
	4	–	60.0	61.1	101.8	2.8

for determination of HCT concentrations in the HCT tablet. The results are listed in Table 4. The results in Table 4 show the relative standard derivations (RSD, in percent), and the recovery rates of the spiked samples are acceptable. Thus, the modified electrode can be efficiently used for determination of HCT in HCT tablet.

Determination of HCT in urine sample

In order to evaluate the analytical applicability of the proposed method, also, it was applied to the determination of HCT in urine samples. The results for determination of the HCT in real samples are given in Table 4. Satisfactory recovery of the experimental results was found for HCT. The reproducibility of the method was demonstrated by the mean relative standard deviation.

Conclusions

The BFCNPE was prepared and used for the investigation of the electrochemical behavior of HCT. Two pairs of well-defined redox peaks were obtained at the BFCNPE. The BFCNPE showed excellent electrocatalytic activity for the redox of HCT. Compared with the bare electrode, the

oxidation current of HCT increased greatly, and the oxidation peak potential shifted negatively by 325 mV. This sensor showed wide linear range (0.6 to 300.0 μM) with good detection limit (0.09 μM) for HCT. This sensor was successfully applied to determine the HCT in some real samples such as HCT tablets and urine samples.

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