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ORIGINAL PAPER

A new strategy for simultaneous determination of cysteamine in the presence of high concentration of tryptophan using vinylferrocene-modified multiwall carbon nanotubes paste electrode

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Abstract The electro-oxidation of cysteamine (CA) and tryptophan (TP) were studied by vinylferrocene-modified carbon nanotubes paste electrode using cyclic voltammetry, chronoamperometry, electrochemical impedance spectroscopy, and square wave voltammetry. This modified electrode exhibits persistent electron-mediating behavior followed by well-separated oxidation peaks towards CA and TP with decreasing their overpotentials. For the mixture containing CA and TP, the peaks potential well separated from each other. Using the modified electrode, the kinetics of CA electrooxidation was considerably enhanced by lowering the anodic overpotential through a catalytic fashion. Using square wave voltammetry, simultaneous determination of AC and TP has been explored at the modified electrode. Their square wave voltammetrics peaks current increased linearly with their concentration at the ranges of 0.09–500 and 5.0–1,000 μM, respectively with the detection limits of 0.05 and 1.0 μM, respectively. The modified electrode was successfully used for the determination of the analytes in real samples with satisfactory results.

Keywords Cysteamine and tryptophan determination · Vinylferrocene · Multiwall carbon nanotubes paste electrode · Voltammetry

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Introduction

The closed topology and tubular structure of carbon nanotubes [1–3] make them unique among different carbon forms and provide pathways for chemical studies. A number of investigations [4–8] have been carried out to find the applications of nanotubes in catalysis, hydrogen storage, intercalation, etc.

Nephropathic cystinosis is a rare autosomal recessive disease characterized by an excessive intra lysosomal cystine accumulation due to a defect of its transport system in the lysosomal membrane [9]. This metabolic trouble leads to a multisystemic disease affecting all organ systems. Thus, within the first years of life, newborn children develop a renal Fanconi syndrome with polyuria, glucosuria, phosphaturia, and aminoaciduria. During their first decade of life, children are affected by growth impairment and progressive decline in renal function leading to hemodialysis or renal transplantation. In affected children, cystine accumulation is also responsible for delayed complications such as hypothyroidism, retinopathy, myopathy, pancreatic dysfunction, and dementia [10]. First is the in vitro experiment of the cystine-depleting effects of cystamine on cystinotic fibroblasts [11]. These results were confirmed on leukocytes in vivo [11]. The underlying mechanism of action was shown to be a disulphide exchange reaction between cysteamine and cystine. The product of the reaction, a mixed disulphide of cysteamine and cystine, is carried out of the lysosome by a lysine porter which is not defective in cystinosis patients [9, 10]. Based on this biochemical evidence, cysteamine appears to be a promising treatment for cystinosis. Several

long-term clinical trials have shown that cysteamine administration (as cysteamine hydrochloride) stabilizes renal function, delays glomerular deterioration, and improves linear growth [9]. Therefore, determination of this compound is very important. Several methods have been reported for the determination of cysteamine (CA) in different samples including chromatography [12–14], electrophoresis [15], gas chromatography with flame photometric detection [16], ion exchange chromatography [17], and electrochemical methods [18, 19] using modified electrodes.

Tryptophan (TP) is an essential amino acid, meaning that humans must consume it in their diet to survive. This compound is a precursor for the important biological molecules serotonin, melatonin, and niacin. It has also been implicated as a possible cause of schizophrenia in people who cannot metabolize it properly. When improperly metabolized, it creates a byproduct in the brain that is toxic, causing hallucination and delusions [20]. Due to its low abundance in vegetables, this compound is sometimes added to staple food products and pharmaceutical formulas [21]. Different methods such as spectrophotometry [22], chemiluminescence [23] high-performance liquid chromatography [23], and electrochemical methods [24–26] have so far been available for the determination of TP. Comparing with other technologies, electrochemical method is more desirable because of its convenience and low cost.

Cysteamine is the chemical compound with the formula $HSCH_2CH_2NH_2$. It is the simplest stable aminothiol and a degradation product of the amino acid, cysteine. On the other hand, tryptophane is an essential amino acid that has the same overpotential and the same overall structure to cysteamine. Therefore, it is necessary to develop a sensitive and selective method to measure each of those compounds separately, and/or simultaneously.

To the best of our knowledge, most previously published electrochemical studies have dealt with individual determination of CA or TP utilizing carbon paste electrodes or other kinds of modified electrodes. We reported a simultanious determinaton of CA and TP at the surface of a modified-multiwall carbon nanotubes paste electrode [27] and there is not any report on the simultaneous determination of CA and TP, using modified electrodes. In this study, we have used voltammetric and electrochemical impedance spectroscopic techniques to study the electrochemical behavior of CA and TP at a multiwall carbon nanotube paste electrode modified with vinylferrocene. The detection limit, linear dynamic range, and the sensitivity to CA with vinylferrocene-modified carbon nanotubes paste electrode (VFMWCNTPE) are comparable to, and even better than, those recently developed which use voltammetric methods. Comparisons of the results obtained from the proposed method and those from recently reported electrochemical methods are given in Table 1.

Experimental

Chemicals

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Double-distilled water was used throughout. Vinylferrocene from Fluka and CA from Aldrich were used as received.

High viscose paraffin (d=0.88 kg L^{-1}) from Merck was used as the pasting liquid for the preparation of the paste electrodes. Spectrally, pure graphite powder (particle size, <50 μm) from Merck and multiwall carbon nanotubes (>90% MWCNTs basis), $d \times l$=(110–150 nm)×(5–9 μm) from Fluka were used as the substrate for the preparation of the electrodes.

A 1.0×10^{-3} M CA solution was prepared daily by dissolving 0.0077 g cysteamine in water and the solution

Table 1 Comparison of the efficiency of some electrochemical methods in the determination of cysteamine

Electrode	Method	LOD (μM)	LDR (μM)	Sensitivity μA $(\mu M)^{-1}$	Ref.
SWNT–Nq/GCE[a]	DPV	3.0	5.0–270	0.05807	[30]
PDMA/FMCPE[b]	CV	79.7	80–1,140	–	[17]
Nq/Au[c]	DPV	5.2	8.0–550	0.015	[18]
p-APMCNTPE[d]	DPV	0.15	0.5–300	0.2436	[27]
VFMWCNTPE	SWV	0.05	0.09–500	0.3393	This work

LOD limit of determination, *LDR* linear dynamic range, *CV* cyclic voltammetry, *SWV* square wave voltammetry

[a] Single-wall carbon nanotube-1,2-naphthoquinone-4-sulfonic acid modified glassy carbon electrode

[b] Poly-*N*,*N*-dimethylaniline/ferrocyanide film-modified carbon paste electrode

[c] 1,2-Naphthoquinone-4-sulfonic acid sodium (Nq)-modified gold electrode

[d] *p*-Aminophenol modified carbon nanotubes paste electrode

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. Further dilution was made with buffer solution.

A 1.0×10^{-3} M tryptophan solution was prepared daily by dissolving 0.0240 g tryptophan in a buffer solution, pH 7.0 under ultrasonication for several minutes, and then it was diluted with water to 100 mL in a 100-mL volumetric flask. Further dilution was made with buffer solution. Phosphate buffer (sodium dihydrogen phosphate and disodum monohydrogen phosphate) solutions with different pH values were used.

Apparatus

Electrochemical impedance spectroscopy, cyclic voltammetry, and square wave voltammetry were performed in an analytical system, Autolab with PGSTAT-302 N (Eco Chemie B. V., Utrecht, The Netherlands). The system was run on a PC using GPES and FRA 4.9 software. For impedance measurements, a frequency range of 100 kHz to 0.10 Hz was employed. The AC voltage amplitude was at 5 mV and the equilibrium time was 10 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 was used. The working electrode was either an unmodified carbon nanotubes paste electrode or VFMWCNTPE.

Scanning electron microscopy (SEM, XLC Philips) was used for the characterization of the surfaces of the electrode prepared with carbon nanotubes. A pH meter (Corning, Model 140) with a double junction glass electrode was used to check the pH levels of the solutions.

Preparation of the electrode

Ten milligram of vinylferrocene was hand-mixed with 890 mg of graphite powder and 100 mg of carbon nanotubes in a mortar and pestle. Using a syringe, 0.88 g of paraffin was added to the mixture and mixed well for 40 min until a uniformly wetted paste was obtained. The paste was then packed into a glass tube. 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. The unmodified carbon paste electrode (CPE) was prepared in the same way without adding vinylferrocene and carbon nanotubes to the mixture to be used for comparison purposes.

Preparation of real samples

Five cystagone 150 mg capsules (produced by Mylan Drug Company) were completely ground and homogenized. Then, 10 mg of the powder was accurately weighed and dissolved with ultrasonication in 100 mL of ethanol–water (1:2) solution. Different amounts of the solution plus 10 mL of 0.10 M buffer (pH 7.0) were used for the analysis.

Urine samples were stored in a refrigerator immediately after collection. Ten milliliters of the sample was centrifuged for 10 min at 2,000 rpm. The supernatant was filtered using a 0.45 μm filter and then diluted five times with the buffer (pH 7.0). The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. Standard addition method used for the determination of CA and tryptophan in real samples.

Recommended procedure

The modified multiwall carbon nanotube paste electrode was polished with a white and clean filter paper. To prepare a blank solution, 10.0 mL of the buffer solution (pH 7.0) was transferred into an electrochemical cell. The initial and final potentials were adjusted to 0.0 and +1.00 V vs. Ag/AgCl, respectively. The SW voltammogram was recorded with an amplitude potential of 50 mV and frequency of 10 Hz to give the blank signal and labeled as I_b. Then, different amounts of CA and/or TP were added to the cell using a micropipette. The SW voltammogram was recorded again (similar to the above procedure) to get the analytical signal (I_s). Calibration curves were constructed by plotting the net catalytic peak current vs. the CA and/or TP concentration.

Results and discussion

SEM characterization of the electrodes

The microscopic structure of VFMWCNTPE was examined using SEM. Figure 1a shows the presence of vinylferrocene in the carbon nanotubes paste matrixes. As shown in Fig. 1a, vinylferrocene on the surface of MWCNTs is distributed and it did not change the morphology of MWCNTs. In addition, it can be clearly seen that MWCNTs dispersed homogeneously and improved reproducibility. Note that no mediator particle is shown at the unmodified carbon nanotubes paste electrode (Fig. 1b).

Electrochemistry of the mediator

Vinylferrocene was used as a suitable mediator for the determination of CA. The electrochemical properties of VFMWCNTPE were studied by cyclic voltammetry in a buffer solution (pH 7.0). The inset in Fig. 2 shows the cyclic voltammograms of VFMWCNTPE at various scan rates (υ=10–450 mV s^{-1}). The experimental results show

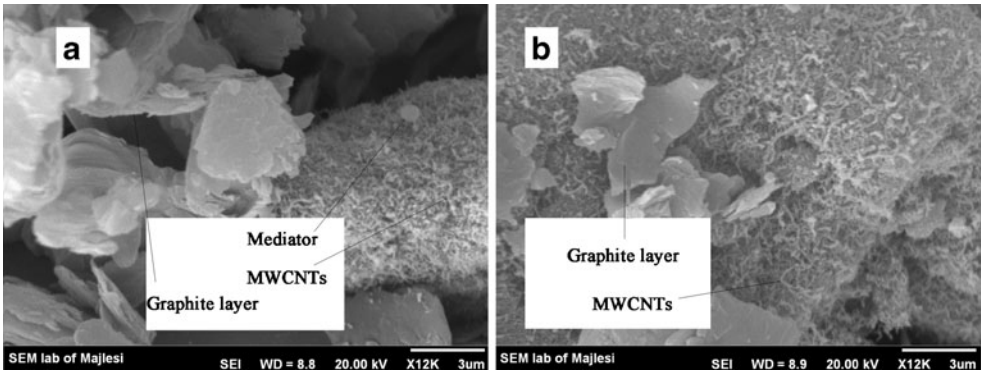

Fig. 1 SEM image of **a** VFMWCNTPE and **b** CNTPE

well-defined and reproducible anodic and cathodic peaks related to Fc/Fc^+ redox couple with quasireversible behavior with a peak separation potential of ΔE_p= 100 mV ($E_{pa} - E_{pc}$).

The direct electrooxidation of CA requires a large overpotential at unmodified electrode surfaces (unmodified CPE; Fig. 3, curve e) and at unmodified carbon nanotubes paste electrode (CNTPE; Fig. 3, curve f). In order to test the electrocatalytic activity of VFMWCNTPE, cyclic voltammograms were obtained in the absence and presence of CA. Figure 3 curves a and c shows the cyclic voltammograms of the VFMWCNTPE in 0.1 M phosphate buffer (pH 7.0) in the absence and presence of 400 μM CA, respectively. The addition of CA to the solution resulted in a dramatic change in the voltammogram, with a large enhancement of the anodic current and virtually reduced current in the reverse sweep, which indicate a strong catalytic effect. In the same conditions, this phenomenon can occur at a surface of vinylferrocene-modified carbon paste electrode (VFMCPE) with lower anodic peak current (lower sensitivity) in comparison to VFMWCNTPE, which is relative to multi-wall carbon nanotubes with high conductivity in VFMWCNTPE matrix. The anodic peak potential for the oxidation of CA at VFMWCNTPE and VFMCPE are about 380 and 390 mV while at CPE and CNTPE, it was 770 and 750 mV, respectively. Thus, a decrease in overpotential and enhancement in the peak current is achieved with the modified electrode. The electrocatalytic oxidation of CA at low potentials is also very useful for practical applications, since there is less risk for interfering of electrochemical reactants to take place. The effect of scan rate on the electrocatalytic oxidation of 800 μM CA at VFMWCNTPE was investigated by cyclic voltammetry (Fig. 4, inset). The oxidation peak potential shifts towards a more positive potential with increasing scan rates, confirming the kinetic limitation of the electrochemical reaction. Also, a plot of peak height (I_p) against square root of scan rate ($\nu^{1/2}$), in the range of 12–26 mV s^{-1}, was constructed (Fig. 4) and found to be linear. It suggests that at sufficient overpotential, the process is diffusion rather than surface controlled.

It is well-known that the electrochemical behavior of CA is dependent on the pH of the aqueous solution, whereas the electrochemical property of Fc/Fc^+ redox couple is independent of the solution pH. The results showed that the

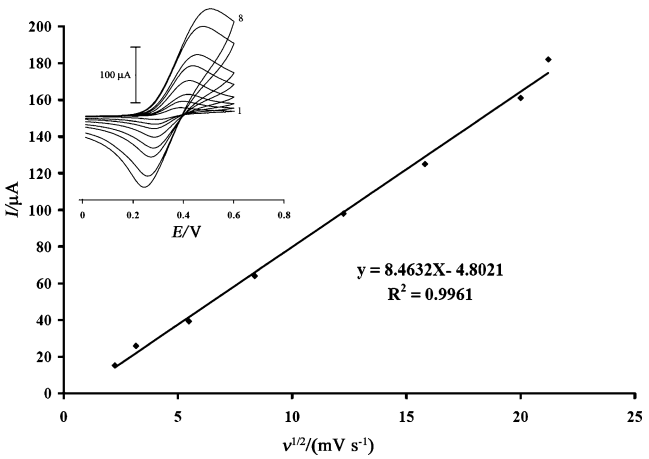

Fig. 2 Plot of I_{pa} versus $\nu^{1/2}$ for the oxidation of VFMWCNTPE. *Inset* cyclic voltammograms of at various scan rates of *1* 10.0, *2* 20.0, *3* 30.0, *4* 70.0, *5* 150.0, *6* 250.0, *7* 4,000, and *8* 450 mV s^{-1} in 0.1 M PBS (pH 7.0)

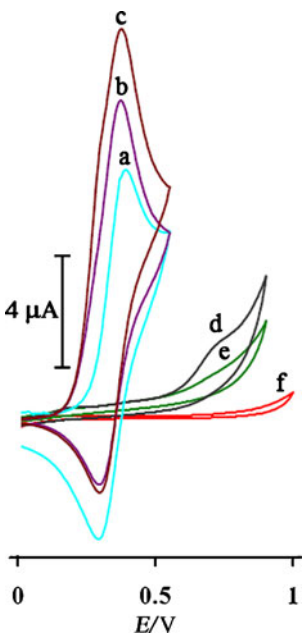

Fig. 3 Cyclic voltammograms of **a** 0.1 M PBS (pH 7.0) at VFMWCNTPE; **c** 0.1 M PBS (pH 7.0) in the presence of 400 μM CA at VFMWCNTPE with a scan rate of 20 mV s^{-1}; **b** is as **c** at VFMCPE; **d** is as **c** and **e** is as **b** at CNTPE and CPE, respectively. **f** Cyclic voltammogram CNTPE in 0.1 M PBS (pH 7.0)

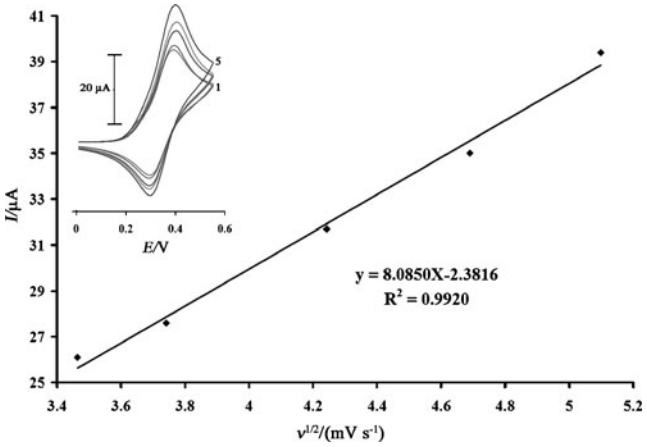

Fig. 4 Plot of I_{pa} versus $\nu^{1/2}$ for the oxidation of CA at VFMWCNTPE. *Inset* cyclic voltammograms of 800 μM CA at various scan rates; *1* 12.0, *2* 14.0, *3* 18.0, *4* 22.0, and *5* 26 mV s^{-1} in 0.1 M PBS (pH 7.0)

maximum electrocatalytic current was obtained at pH 7.0. Therefore, pH 7.0 was chosen as the optimum pH for the determination of CA at VFMWCNTPE.

Tafel plot was used to estimate the transfer coefficient (α). The Tafel plot was developed for the VFMWCNTPE using the data derived from the raising part of the current–voltage curve. The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$ which comes up to 9.1153 V $decade^{-1}$. We obtained n_α as 0.6. Assuming n=1, then α=0.45.

In chronoamperometric studies, we determined the diffusion coefficient (D) of CA. The experimental plots of I vs. $t^{-1/2}$ were employed with the best fits for different concentrations of CA. Chronoamperometric measurements for different concentrations of CA at VFMWCNTPE were accomplished by setting the working electrode potential at 0.2 and 0.55 as the first- and second-step potentials. The slopes of the resulting straight lines were then plotted vs. CA concentrations using the Cottrell equation to obtain the following equation:

$$I = n\mathrm{FAD}^{1/2}C_b\pi t^{1/2} \quad (1)$$

The diffusion coefficient for CA was calculated as (5.67± 0.01)×10^{-4} cm^2 s^{-1} [27]. In addition, chronoamperometric method can be used for the evaluation of rate constant for the chemical reaction between CA and the redox sites in VFMWCNTPE, k_h, according to the method of Galus [28]:

$$I_C/I_L = \pi^{1/2}\gamma^{1/2} = \pi^{1/2}(k_hC_bt)^{1/2} \quad (2)$$

where, I_C is the catalytic current of VFMWCNTPE in the presence of CA, I_L the limited current in the absence of CA, C_b bulk concentration of CA, M, k_h, and t are the catalytic rate constant (M^{-1} s^{-1}) and time elapsed (s), respectively. Based on the slope of the I_C/I_L vs. $t^{1/2}$ plot, k_h can be obtained for a given CA concentration. From the values of

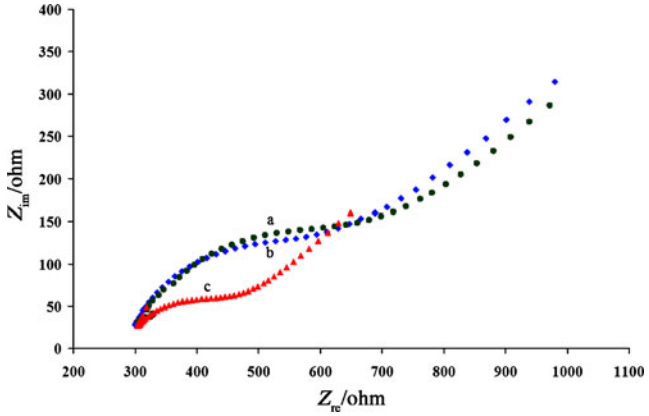

Fig. 5 Nyquist diagrams of VFMWCNTPE **a** in the absence, **b** in the presence of 500 μM TP, and **c** in the presence of 500 μM CA in 0.1 M PBS (pH 7.0)

the slopes, an average value of k_h was found to be (3.18± 0.02)×10^2 M^{-1} s^{-1}. The value of k_h also explains the sharp feature of the catalytic peak observed for the catalytic oxidation of CA at the surface of VFMWCNTPE.

Electrochemical impedance spectroscopy

To study the catalytic effect, we compared the charge transfer coefficient of the modified electrode in the absence and presence of 500 μM TP and CA as shown in Fig. 5 (curves a–c). In the presence of CA (curve c), the diameter of the semicircle decreases in comparison to its absence, confirming the ability of the mentioned electrocatalyst for the oxidation of CA. This is due to the instant chemical reaction of CA with the high valence of vinylferrocene species. The catalytic oxidation of CA occurred via the participation of high-valence of vinylferrocene species, virtually causing an increase in the surface concentration

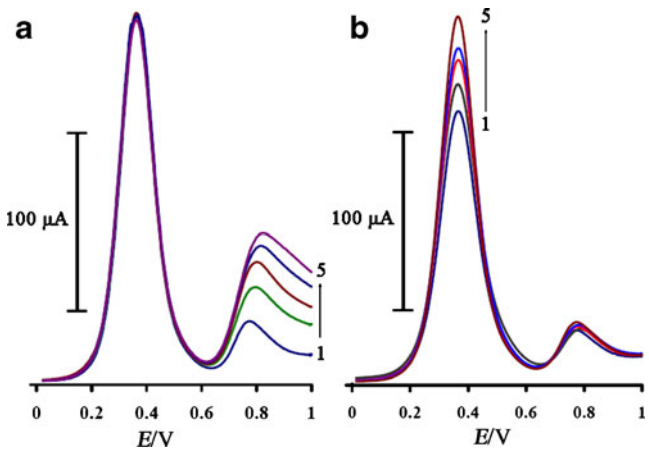

Fig. 6 Square wave voltammograms of CA and TP under the optimum conditions. Conditions **a** 420 μM CA with TP concentrations of *1* 115, *2* 233, *3* 313, *4* 360, and *5* 400 μM; **b** 125 μM TP with CA concentrations of *1* 114, *2* 300, *3* 340, *4* 360, and *5* 420 μM

Table 2 Interference study for the determination of 20.0 and 30.0 μM CA and TP, respectively, under the optimized conditions

Species	Tolerante limits ($W_{substance}/W_{analytes}$)
Glucose, fructose, lactose, sucrose	1,000
K^+, SCN, $C_2O_4^{2-}$, Br^-, NH_4^+, Ca^{2+}, Mg^{2+}, ClO_4^-, SO_4^{2-}, SCN^-, F^-, CO_3^{2-}	800
Thiourea, vitamin B_2, urea	700
Glycine, valine, methionine, lucine, alanine, phenylalanine, glutamic acid	600
Starch	Saturation
Ascorbic acid	1

of the low-valence species of the electrocatalyst. Thus, the charge transfer resistance declined, depending on the concentration of CA in the solution. In the same condition for TP, we could not see any change in diameter of the semicircle. This phenomenon shows that the oxidation of TP could not be catalyzed by vinylferrocene. So, simultaneous determination of these compounds are possible at a this modified electrode.

Figures of merit

Square wave voltammetry was used to determine CA and TP concentrations. The SW voltammograms clearly show that the plot of the peak current versus CA concentration is linear for 0.09–500 μM of CA with the regression equation of $\Delta I_p(\mu A)=(0.3406\pm0.0020)C_{CA}+(3.4915\pm0.0812$; $R^2=0.9994$, $n=14$). The regression equation for TP is $\Delta I_p(\mu A)=(0.1773\pm0.0010)C_{AC}+(5.8846\pm0.0851$; $R^2=0.9916$, $n=10$) in the range of 5.0–1,000 μM, where C is micromolar concentration of the compounds and ΔI_p is the net peaks current.

The detection limit was determined at 0.05 μM CA and 1.0 μM TP according to the definition of $Y_{LOD}=Y_B+3\sigma$ [29]. This value of detection limit, the linear dynamic range, and the sensitivity for CA observed for the VFMWCNTPE are comparable and even better than those obtained for several other modified electrodes (Table 1).

The repeatability and stability of the VFMWCNTPE were investigated using cyclic voltammetry measurements of 1.0 and 50.0 μM CA and TP, respectively. The relative standard deviation (RSD%) for seven successive assays were 1.5% and 2.3%, respectively. When using four different electrodes, RSD% for four measurements was 2.8%. When the electrode was stored in our laboratory at room temperature, the modified electrode retained 98% of its initial response after a week and 94% after 35 days. These results indicate that VFMWCNTPE has both a good stability and a satisfactory reproducibility so that it can be used for CA determination.

The effective application of the VFMWCNTPE for simultaneous determination of CA and TP was demonstrated by concurrently changing CA and TP concentrations. The SW voltammetric results confirm the simultaneous determination of CA and TP with well-distinguished two-anodic peaks at potentials of 370 and 830 mV. In addition, analytical experiments were carried out either by varying CA concentration (114–420 μM) in the presence of fixed amounts of TP (125 μM) and/or varying TP concentration (115–400 μM) in the presence of fixed amounts of CA (420 μM) at pH 7.0 (Fig. 6a and b). The results show no considerable intermolecular interactions during the oxidation of the compounds at the surface of the modified electrode. It can also be noted from these results that the responses to CA and TP at VFMWCNTPE are relatively independent. The sensitivity of the modified electrode towards the oxidation of CA in the absence and presence of TP were found to be 0.3393±0.0041 and 0.3406±0.0020 μA μM, respectively, which indicates that the oxidation processes of CA and TP at VFMWCNTPE are independent and that the simultaneous

Table 3 Determination of CA and TP in drug and urine samples

Sample	Added (μM) CA	Expected (μM) CA	Found (μM) CA	Standard method (μM) [27]	Added (μM) TP	Expected (μM) TP	Found (μM) TP	Standard method (μM) [27]
Tablet[a]	–	0.50	0.48±0.02	0.54±0.07	–	–	–	–
	14.5	15.0	14.8±0.3	14.6±0.9	–	–	–	–
Urine	–	30.0	30.6±0.6	31.1±1.1	10.0	10.0	9.9±0.8	10.9±1.0
	20.0	50.0	50.4±0.4	51.0±1.2	40.0	50.0	50.4±0.5	50.6±0.6
Urine[b]	–	–	8.5±0.2	8.4±0.6	–	–	–	–
	10.0	18.51	18.4±0.3	18.6±0.5	20.0	20.0	20.3±0.3	20.4±0.5

±shows the standard deviation

[a] 150 mg capsules produced by Mylan Drug Company (Italy)

[b] Sampling was made after 3.0 h from a man who is safe and used cystamine

or independent measurements of the two analytes are, therefore, possible without any interference.

Interference study

In order to evaluate the selectivity of the proposed method for the determination of CA and TP, we investigated the influence of various foreign species frequently found with CA and TP in pharmaceutical formulations such as lactose, sucrose, fructose, starch, and sodium chloride using the modified electrode used for the determination of 1.0 μM CA and 10.0 μM and TP as shown in Table 2. The tolerance limit was taken as the maximum concentration of foreign substances causing approximately ±5% relative error in the determination. The results show the selectivity of the electrochemical method for simultaneous determination of CA and TP.

Determination of CA in real samples

In order to demonstrate the electrocatalytic oxidation of CA and TP in real samples, we examined the voltammetric determination of CA in pharmaceutical and urine samples. For the real samples, each sample was analyzed in triplicate by standard addition method. The result of CA and TP determination were also compared with the standard method [16, 26]. The results, reported in Table 3, demonstrated the ability of VFMWCNTPE for voltammetric determination of CA and TP with a high selectivity and a good reproducibility.

Conclusion

This work demonstrates the construction of a chemically modified carbon paste electrode by the incorporation of multiwall carbon nanotubes and vinylferrocene as modifying species. The electrochemical behavior of the vinylferrocene was studied by cyclic voltammetry. The results showed that the oxidation of CA is catalyzed at pH 7.0, with the peak potential of CA shifted by 370 mV to a less positive potential at the surface of the VFMWCNTPE. A low detection limit, together with the ease of preparation and regeneration of the electrode surface, as well as a long time of stability and reproducibility, makes the system discussed above useful in the construction of simple devices for the determination of CA. The VFMWCNTPE exhibits high electrocatalytic activity in the oxidations of CA and TP. The modified electrode displays higher selectivity in voltammetric measurements of CA and TP. The separation of the oxidation peak potentials for CA–TP was approximately 460 mV by square wave voltammetry.

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