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Article

Multiwall carbon nanotube paste electrode with 3,4-dihydroxy-cinnamic acid as mediator for the determination of glutathione in pharmaceutical and urine samples

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ABSTRACT

A sensitive and selective electrochemical sensor for the determination of glutathione (GSH) was developed using a modified multiwall carbon nanotube paste electrode with 3,4-dihydroxy-cinnamic acid as a mediator. This modified electrode showed very high electrocatalytic activity for the anodic oxidation of GSH. Under the optimized conditions, the electrocatalytic peak current showed a linear relationship with GSH concentration in the range of 0.5–400.0 $\mu\text{mol/L}$ with a detection limit of 0.1 $\mu\text{mol/L}$ GSH. The relative standard deviations for seven successive assays of 5.0 and 25.0 $\mu\text{mol/L}$ GSH were 2.2% and 2.7%, respectively. The modified electrode was used for the determination of GSH compounds in real urine samples.

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1. Introduction

Glutathione (GSH) is a biological thiol compound that is the main intracellular tripeptide in mammals. Its role in human metabolism includes protection against oxidative stress and detoxification of xenobiotics [1]. Changes in its concentration in biological fluids or tissues are a useful marker of certain disorders such as leukemia [2], diabetes [3], DNA base damages [4] and in the investigation of some kinds of cancer [5]. A number of methods have been proposed for the determination of GSH including titrimetry [6], spectrophotometry [7,8], spectrofluorimetry [9], high performance liquid chromatography [10–12], capillary zone electrophoresis [13,14], proton nuclear magnetic resonance (^1H NMR) [15,16], and enzymatic [17] and electrochemical methods [18–22]. Electrochemical methods have shown significant advantages in the analysis of different compounds in biological and pharmaceutical samples. These ad-

vantages are mainly attributable to the simplicity, low cost and relatively short analysis times of these compounds as compared to chromatography and other methods [23]. In recent years, chemically modified electrodes have attracted much notice due to their potential applications in various analyses [24,25].

Carbon nanotubes (CNTs) have a novel type of nanostructure with unique structural electronic and mechanical properties and have been studied extensively since their discovery [26–28]. Research over the past decade has revealed that the CNTs constituted a new form of carbon materials that are finding striking applications in many fields, such as energy conversion and storage [29], chemical actuators [30,31], and chemical sensing [32–36]. In the present work, we described the preparation of a multiwall carbon nanotube paste electrode (MWCNTPE) with 3,4-dihydroxy-cinnamic acid (3,4-DHCA) as a suitable sensor for the electrocatalysis and determination of

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GSH in aqueous buffer solution. The proposed method is selective, sensitive, and fast for the determination of GSH in real samples such as GSH tablets, urine, and hemolyzed erythrocyte.

2. Experimental

2.1. Apparatus and reagents

All the voltammetric measurements were performed using an Autolab PGSTAT 302N, potentiostat/galvanostat (Utrecht, The Netherlands) connected to a three-electrode cell, Metrohm (Herisau, Switzerland) Model 663 VA stand. This was operated by a computer (Pentium IV, 1200 MHz) with the Autolab software. A platinum wire was used as the auxiliary electrode. MWCNTPE and Ag/AgCl/KCl_{sat} were used as the working and reference electrodes, respectively. The electrode prepared with CNTs was characterized by scanning electron microscopy (SEM, Seron Tech. AIS 2100). A digital pH/mV meter (Metrohm model 710) was applied for pH measurements. Spectrally pure graphite powder (particle size < 50 μm) from Merck and multiwall carbon nanotubes (> 90% MWCNTs basis, $d \times l = (90\text{--}70\text{ nm}) \times (5\text{--}9\text{ }\mu\text{m})$) from Fluka were used for the preparation of the carbon paste electrode.

Phosphate buffer ($\text{NaH}_2\text{PO}_4\text{--Na}_2\text{HPO}_4\text{--NaOH}$ 0.1 mol/L) solutions (PBS) with different pH values were used. All chemicals used were analytic reagent grade purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. GSH was from Fluka.

2.2. Preparation of the electrode

To eliminate any metal oxide catalyst in the nanotubes, the MWCNTs were refluxed in 2.0 mol/L HNO_3 for 12 h, and then washed with twice distilled water and dried at room temperature. Graphite powder (0.900 g) was dissolved in diethyl ether and hand mixed with 0.100 g CNTs in a mortar and pestle. The solvent was evaporated by stirring. A syringe was used to add paraffin to the mixture, which was 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.

2.3. Preparation of real samples

Human whole blood was obtained from the Majlesi Health Center and erythrocytes were separated from the whole blood by removing the plasma. The human whole blood (2.0 mL) was first centrifuged for 10 min at 3000 r/min. The supernatant (plasma) was discarded and the remainder was mixed with 5 mL of 0.9% NaCl solution. The solution was centrifuged for another 5 min at 3000 r/min and the supernatant (diluted plasma) was again discarded. The washing procedure with NaCl solution was repeated three times to remove the plasma almost completely.

The erythrocyte pellets were hemolyzed with water (1:1, v/v). For protein precipitation, the hemolysate was mixed with 5-sulfosalicylic acid (10%, m/v) in the ratio of 2:1 (v/v). This mixture was centrifuged under the same conditions described above. Then, the supernatant was divided to two parts: one for spectrophotometric determination and another for the proposed electrochemical method. For spectrophotometric measurements with a reference method [37], the Ellman method was used, which is based on the reaction of GSH and DTNB (Ellman's reagent) to generate 2-nitro-5-mercapto-benzoic acid. The absorbance was monitored spectrophotometrically at 412 nm.

The urine samples were stored in a refrigerator immediately after collection. The sample (10 mL) was centrifuged for 20 min at 2000 r/min. The supernatant was filtered using a 0.45 μm filter and then diluted 5 fold with PBS (pH 7.0). The solution was transferred into the voltammetric cell for analysis without any further pretreatment. The standard addition method was used for the determination of GSH in real samples.

The tablet solution was prepared by completely grinding and homogenizing seven tablets of GSH, labeled to have 100 mg per tablet (Chongqing Yaoyou Pharmaceutical Co., Ltd., China). Then, 10 mg of each tablet powder was accurately weighed and dissolved in 100 mL water by ultrasonication. After mixing completely, the mixture was filtered on an ordinary filter paper, 10 mL of which was subsequently transferred into a 100 mL volumetric flask and diluted to the mark with water. Then, 1.0 mL of the solution plus 4.5 mL of the buffer (pH 7.0) was used for analysis using the standard addition method.

2.4. Optimization of 3,4-DHCA concentration

The influence of 3,4-DHCA concentration on the electrocatalytic oxidation peak current was studied at two different concentrations of GSH at pH 5.0, and in the range of 100.0 to 700 $\mu\text{mol/L}$ 3,4-DHCA. The results showed that by increasing the concentration of 3,4-DHCA up to 500 $\mu\text{mol/L}$ the peak current increased, while higher concentrations of 3,4-DHCA caused a slight decrease in the magnitude of the peak current, which may be due to the formation of 3,4-DHCA aggregates. Therefore, 500 $\mu\text{mol/L}$ 3,4-DHCA concentration was selected for further studies.

3. Results and discussion

3.1. SEM characterization

Figure 1 shows SEM images of the MWCNTPE and carbon paste electrodes (CPE). As can be seen at the surface of CPE, layers of irregular flakes of graphite powder were present that were isolated from each other. After MWCNTs were added to carbon paste, it can be seen that MWCNTs were distributed on the surface of electrode with a special three dimensional structure, indicating that the MWCNTs were successfully assimilated on the MWCNTPE.

3.2. Electrochemistry of 3,4-DHCA

Fig. 1. SEM images of CPE (a) and MWCNTPE (b).

The cyclic voltammograms of 3,4-DHCA at the surface of MWCNTPE in 0.1 mol/L PBS (pH 5.0) are shown in Fig. 2(a). As can be seen, the cyclic voltammogram exhibited an anodic peak at the forward scan of the potential related to the oxidation of 3,4-DHCA_(red) to 3,4-DHCA_(ox). In the reverse scan of the potential, a cathodic peak appeared, which was related to the reduction of 3,4-DHCA_(ox) to 3,4-DHCA_(red). A pair of quasi-reversible peaks were observed at $E_{pa} = 0.30$ V and $E_{pc} = 0.17$ V versus Ag/AgCl. The half-wave potential ($E_{1/2}$) was 0.24 V versus Ag/AgCl and ΔE_p ($E_{pa} - E_{pc}$) was 0.13 V. The electrode process was quasi-reversible, with ΔE_p , greater than the expected value ($59/n$ mV) for a reversible system. The plot of the anodic peak current was linearly dependent on $v^{1/2}$ for all scan rates (Fig. 2(b)). This behavior indicated that the nature of the redox pro-

Fig. 2. (a) Cyclic voltammograms at various scan rates in 0.1 mol/L PBS (pH 5.0): (1) 5 mV/s; (2) 10 mV/s; (3) 15 mV/s; (4) 20 mV/s; (5) 60 mV/s; (6) 100 mV/s. (b) Plot of I_{pa} versus $v^{1/2}$ for the oxidation of 500 $\mu\text{mol/L}$ 3,4-DHCA at a surface of MWCNTPE.

cess is diffusion controlled.

The active surface areas of the modified electrodes were estimated from the slope of the I_p versus $v^{1/2}$ plot for a known concentration of $\text{K}_2\text{Fe}(\text{CN})_6$, based on the Randles-Sevcik equation [38]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_R^{1/2} v^{1/2} C_0 \quad (1)$$

where I_{pa} refers to the anodic peak current, n is the electron transfer number, A refers to the surface area of the electrode, D_R is the diffusion coefficient, C_0 refers to the concentration of $\text{K}_2\text{Fe}(\text{CN})_6$, and v is the scan rate. For 1.0 mmol/L $\text{K}_2\text{Fe}(\text{CN})_6$ in 0.10 mol/L KCl electrolyte with $n = 1$ and $D_R = 7.6 \times 10^{-6}$ cm²/s, from the slope of the $I_{pa} - v^{1/2}$ curve, the areas were calculated. The active surface areas were 0.08 and 0.13 cm² for CPE and MWCNTPE, respectively. The result showed that the presence of MWCNTPE gave an increase in the active surface of the electrode.

3.3. Electrocatalytic oxidation of GSH

Figure 3(1) shows the voltammetric behavior of 3,4-DHCA in the buffer solution (pH 5.0). The cyclic voltammetric responses for the electrochemical oxidation of 150 $\mu\text{mol/L}$ of

Fig. 3. Cyclic voltammograms of 500 $\mu\text{mol/L}$ 3,4-DHCA at the surface of MWCNTPE and CPE in 0.1 mol/L PBS (pH 5.0) at a scan rate of 20 mV/s. (1) In the absence of GSH at MWCNTPE; (2) In the presence of 150 $\mu\text{mol/L}$ GSH at CPE; (3) In the presence of 150 $\mu\text{mol/L}$ GSH AT CPE; (4) as (3) and (5) as (2) for the in the absence of 3,4-DHCA; (6) In the absence of GSH and 3,4-DHCA at MWCNTPE.

GSH at the surface of MWCNTPE (Fig. 3(3)), and at the surface of the CPE (Fig. 3(2)) in the presence of the mediator. On the other hand, Fig. 3(4) and (5) are in the absence of 3,4-DHCA. As can be seen, the anodic peak potentials for the oxidation of GSH at MWCNTPE (Fig. 3(3)) and CPE (Fig. 3(2)) in the presence of mediator are 300 mV. Note that GSH oxidation at the surface of MWCNTPE (without the mediator, Fig. 3(4)), and at the surface of CPE (without the mediator), did not take place at the surface of the CNTPE up to +1.00 V. As can be seen, the electroactivity of GSH on the MWCNTPE and CPE in the presence of the mediator was significant, with a strongly defined peak potential around 300 mV versus the Ag/AgCl/KCl_{sat} electrode. Thus, a decrease in the over-potential and enhancement of the peak current for GSH oxidation were achieved with the MWCNTPE and CPE in the presence of the mediator. Such behavior is indicative of an electrocatalytic mechanism (see Scheme 1) [39–42]. Similarly, when we compared the oxidation of GSH at the surface of MWCNTPE and CPE with mediator, it was observed that a dramatic enhancement of the anodic peak current occurred at MWCNTPE versus the value obtained with CPE. As can be seen, in the presence of the mediator, oxidation of GSH can occur at the potential of the mediator, and the MWCNTs increased the oxidation current of it. These results clearly showed that the combination of MWCNTPE and the mediator (3,4-DHCA) definitely improved the characteristics of the electrode for the oxidation of GSH.

The effect of scan rate on the electrocatalytic oxidation of 200 $\mu\text{mol/L}$ GSH at the modified electrode was investigated by linear sweep voltammetry (Fig. 4(a)). The oxidation peak potential shifted with increasing scan rates towards a more positive potential, confirming the kinetic limitation of the electrochemical reaction. Also, a plot of peak height (I_p) against the square root of scan rate ($v^{1/2}$) in the range 2–30 mV/s was constructed, which was found to be linear, suggesting that at a sufficient overpotential, the process is diffusion rather than surface reaction controlled (Fig. 4(b)).

To obtain further information on the rate determining step, a Tafel plot was developed for the GSH measurement at the

Scheme 1. Electrocatalytic mechanism for the determination of GSH at the surface of MWCNTPE in the presence of the mediator.

Fig. 4. (a) Cyclic voltammograms of 200 $\mu\text{mol/L}$ GSH in the presence of 500 $\mu\text{mol/L}$ 3,4-DHCA at various scan rates in 0.1 mol/L PBS (PH 5.0). (1) 2 mV/s; (2) 5 mV/s; (3) 10 mV/s; (4) 15 mV/s; (5) 20 mV/s; (6) 25 mV/s; (7) 30 mV/s. (b) Plot of I_{pa} versus $v^{1/2}$ for the oxidation of 200 $\mu\text{mol/L}$ GSH in the presence of 500 $\mu\text{mol/L}$ 3,4-DHCA at the surface of MWCNTPE.

MWCNTPE in the presence of the mediator using the data derived from the rising part of the current-voltage curve (Fig. 5(a)). The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3RT$, which comes to 0.0899 V decade⁻¹. We obtained n_α as 0.35. Assuming $n = 1$, then $\alpha = 0.35$.

Fig. 5. Tafel plot of 500 $\mu\text{mol/L}$ 3,4-DHCA at the surface of MWCNTPE in 0.1 mol/L PBS (pH 5.0) at a scan rate of 10 mV/s in the presence of 200 $\mu\text{mol/L}$ GSH.

Fig. 6. (a) Chronoamperograms obtained at the MWCNTPE in the absence (1) and in the presence of 200 (2), 300 (3), and 400 μmol/L (4) GSH in a buffer solution (pH 5.0). (b) Dependence of I_c/I_L on the $t^{1/2}$ derived from the chronoamperogram data.

Chronoamperometric measurements of GSH at MWCNTPE in the presence of the mediator were carried out by setting the working electrode potential at 0.0 V (at the first potential step) and at 0.4 V (at second potential step) versus Ag/AgCl/KCl_{sat} for different concentrations of GSH in buffered aqueous solution (pH 5.0) (Fig. 6(a)). The rate constant for the chemical reaction between GSH and the mediator at the surface of MWCNTPE, k_h , was evaluated by chronoamperometry according to the method of Galus [41]:

$$I_c/I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (k_h C_b t)^{1/2} \quad (2)$$

where I_c is the catalytic current of GSH at MWCNTPE in the

presence of mediator, I_L is the limited current in the absence of GSH, and t (s) is the time elapsed. The above equation can be used to calculate the rate constant of the catalytic process, k_h . From the slope of the I_c/I_L versus $t^{1/2}$ plot, k_h was obtained for a given GSH concentration (Fig. 6(b)). Based on the values of the slopes, the average value of k_h was found to be $9.8 \times 10^2 \text{ mol}^{-1} \text{ L s}^{-1}$. The value of k_h explains the sharp feature of the catalytic peak observed for catalytic oxidation of GSH at the surface of MWCNTPE in the presence of mediator.

3.4. Dynamic range and limit of detection

Linear sweep voltammetry was used to determine the concentration of GSH. The results showed two linear segments with different slopes. For 0.5–2.0 μmol/L of GSH, the regression equation was $\Delta I_p(\mu\text{A}) = (3.346 \pm 0.041) C_{\text{GSH}} + (0.146 \pm 0.023)$ ($R^2 = 0.992$, $n = 5$). For 2.0–400.0 μmol/L GSH, the regression equation was $\Delta I_p(\mu\text{A}) = (0.039 \pm 0.002) C_{\text{GSH}} + (6.890 \pm 0.855)$ ($R^2 = 0.998$, $n = 6$). C_{GSH} (μmol/L) is concentration of GSH and ΔI is net electrocatalytic current. The detection limits, according to the definition of $Y_{\text{LOD}} = Y_B + 3\sigma$, was determined as 0.1 μmol/L for GSH.

This detection limit, linear dynamic range, and sensitivity for GSH with the modified electrode is comparable or even better than those obtained by using several other modified electrodes (Table 1).

3.5. Interference study

In order to evaluate the selectivity of the proposed method in the determination of GSH, the influence of various foreign species on the determination of 10.0 μmol/L GSH was investigated. The tolerance limit was taken as the maximum concentration of foreign substances, which caused no more than $\pm 5\%$ relative error in the determination. The results reported in Table 2 showed that no conventional cations, anions, or organic substances affected the peak current of GSH.

3.6. Stability and reproducibility

The repeatability and stability of the MWCNTPE in the presence of 3,4-DHCA were investigated by cyclic voltammetry

Table 1

Comparison of the efficiency of some electrochemical methods for the determination of GSH.

Electrode	Modifier	pH	LOD (μmol/L)	LDR (μmol/L)	Sensitivity (μA μmol ⁻¹ L)	Ref.
Carbon paste	2,7-BFEF	7.0	0.50	0.92–11	1.997	[43]
Carbon paste	FC	7.0	2.10	2.2–3000	0.017	[19]
MWCNTPE	Chlorpromazine	4.0	0.16	0.3–18.3	0.541	[44]
Glassy carbon	Well-aligned/carbon nanotubes	7.0	0.20	0.4–16.4	0.010	[45]
Glassy carbon	PQQ/PPy	8.4	13.2	—	—	[46]
Carbon paste	TTF-TCNQ	7.0	0.30	5–340	—	[47]
EPPGE	—	7.0	2.70	10–80	—	[48]
Carbodiimide matrix	Glutathione peroxidase	7.8	15	19–140	—	[49]
Glassy carbon	Horseradish peroxidase	7.0	0.03	0.04–90	0.024	[50]
MWCNTPE	3,4-DHCA	5.0	0.10	0.5–400	3.4346	this work

2,7-BFEF: 2,7-bis(ferrocenyl ethyl)fluoren-9-one; FC: ferrocene; PQQ/PPy: pyrroloquinoline quinone into polypyrrole; TTF-TCNQ: tetrathiafulvalene-tetracyanoquinodimethane; EPPGE: edge-plane pyrolytic-graphite electrode.

Table 2Interference study for the determination of 2.0 $\mu\text{mol/L}$ HCY under the optimized conditions.

Species	Tolerance limit (W/W)
Li^+ , Br^- , NO_3^- , SCN^- , SO_4^{2-} , Br^- , glucose, fructose, lactose, sucrose, Ca^{2+}	1000
Hystidine, alanine, phenyl alanine, methionine, glycine, methanol, ethanol, tryptophan, L-theronine, L-isoleucin, L-orinthime	800
Starch	Saturation
Ascorbic acid *, urea	500

*After addition of 1 mmol/L ascorbic oxidize.

Table 3

Concentration values obtained from the proposed and Elman methods for GSH analysis in hemolysed erythrocyte, urine, and tablets.

Sample	Proposed method	Elman method [37]	F_{ex}	$F_{\text{tab}, (0.05); 2, 2}$	t_{ex}	$t_{\text{tab}} (98\%)$
Hemolyzed erythrocyte	4.55 ± 0.10	4.87 ± 0.22	5.5	19	1.5	3.8
	6.32 ± 0.22	5.98 ± 0.62	9.5	19	1.8	3.8
	5.55 ± 0.35	5.85 ± 0.87	10.3	19	2.5	3.8
Urine	<LOD	<LOD	—	—	—	—
	20.55 ± 0.72	20.85 ± 0.87	12.5	19	2.9	3.8
	30.55 ± 0.55	30.77 ± 0.78	11.2	19	2.7	3.8
Tablet	9.87 ± 0.35	9.86 ± 0.63	6.2	19	1.7	3.8
	15.10 ± 0.22	14.32 ± 0.45	5.8	19	1.6	3.8

The concentration of Hemolyzed erythrocyte was in mmol/L and the concentrations of the urine and tablet samples were in $\mu\text{mol/L}$. F_{ex} : Calculated F -value; $F_{\text{tab}, (0.05); 2, 2}$: Reported F value from F -test table with 95% confidence level and 2/2 degree of freedom; t_{ex} : Calculated t ; $t_{\text{tab}} (98\%)$: Reported t value from t -student test table with 98% confidence level.

measurements of 5.0 and 25.0 $\mu\text{mol/L}$ GSH. The relative standard deviation (RSD%) for seven successive assays were 2.2% and 2.7%, respectively. When using three different electrodes, the RSD% for four measurements was 3.1%. When the electrode was stored in our laboratory at room temperature, the modified electrode retained 96% of its initial response after a week and 93% after 35 d. These results indicate that MWCNTPE has both good stability and satisfactory reproducibility.

3.7. Determination of GSH in real samples

In order to evaluate the applicability of the modified electrode for measuring GSH in real samples, GSH values in human erythrocyte, GSH tablets, and urine samples were determined. In addition, the results were compared with those obtained from the spectrophotometric method [37], which is usually used as the standard method for glutathione determination. The results are reported in Table 3. Clearly, the modified electrode was capable of the voltammetric determination of GSH with high selectivity and good reproducibility.

4. Conclusions

3,4-DHCA is a suitable mediator for the electrocatalytic oxidation of GSH in aqueous solution at pH 5.0. In cyclic voltammetry, the oxidation of GSH occurred at a potential of 300 mV at the surface of the multiwall carbon nanotube paste electrode in the present of 3,4-DHCA, while the oxidation GSH did not take place at the surface of a carbon nanotube paste electrode without 3,4-DHCA up to +1.0 V. The proposed method gives a selective, simple, and precise new sensor for the voltammetric determination of GSH in real samples such as hemolyzed erythrocyte, GSH tablets, and urine.

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Graphical Abstract

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Multiwall carbon nanotube paste electrode with 3, 4-dihydroxy-cinnamic acid as mediator for the determination of glutathione in pharmaceutical and urine samples

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A novel nanosensor for a sensitive and selective electrochemical sensor for the determination of glutathione in real samples such as tablet, urine, and hemolyzed erythrocyte.

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