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Article

Application of 3,4-dihydroxycinnamic acid as a suitable mediator and multiwall carbon nanotubes as a sensor for the electrocatalytic determination of L-cysteine

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ABSTRACT

A highly sensitive electrochemical sensor was prepared for the determination of L-cysteine using a modified multiwall carbon nanotubes paste electrode in the presence of 3,4-dihydroxycinnamic acid (3,4-DHCA) as a mediator, based on an electrocatalytic process. The results indicate that the electrode is electrocatalytically efficient for the oxidation of L-cysteine in the presence of 3,4-DHCA. The interaction between the mediator and L-cysteine can be used for its sensitive and selective determination. Using chronoamperometry, the catalytic reaction rate constant was calculated to be 2.37×10^2 mol^{-1} L s^{-1}. The catalytic peak current was linearly dependent on the L-cysteine concentration in the range of 0.4–115 μmol/L. The detection limit obtained by linear sweep voltammetry was 0.25 μmol/L. Finally, the modified electrode was examined as a selective, simple, and precise new electrochemical sensor for the determination of L-cysteine in real samples.

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1. Introduction

Amino acids are a class of biologically significant organic compounds because of their incorporation in the molecular structure of proteins. Amino acids can be metabolized to produce energy. This is especially important during fasting when the breakdown of muscle protein is a major energy source. Cysteine is an important sulfur containing amino acid. It is a semi-essential amino acid, which means that it can be biosynthesized in humans [1]. L-Cysteine is a highly significant bioactive compound and is known to be an active site in the catalytic function of certain enzymes known as cysteine proteases, and in many other peptides and proteins [2]. Different methods have been reported for the determination of L-cysteine in biological samples. These include chromatography [3–5], electrophoresis [6], spectrophotometry [7–10], and chemiluminescence [11]. Electroanalytical methods have attracted much attention in recent years for the determination of L-cysteine and other thiol compounds because of their high sensitivity, accuracy, low cost, and simplicity [12–15]. It is well known that the direct electrochemical oxidation of L-cysteine at the surface of a bare carbon electrode is irreversible; therefore, a high overpotential is required for their oxidation [15]. Thus, modified electrodes are necessary for the determination of this compound.

Carbon nanotubes (CNTs) are significant nanostructural materials that are used as building blocks in nanotechnology. CNTs have generated much interest for future applications because of their field emission and electron transport properties, their high mechanical strength and high conductivity [16].

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The modification of electrode substrates with CNTs for use in analytical sensing has been reported to result in low detection limits, high sensitivities, the reduction of overpotentials, and resistance to surface fouling [17–22].

In a continuation of our recent studies concerning the preparation of chemically modified electrodes [23–30], we describe the application of a multiwall CNT paste electrode (MWCNTPE) as a voltammetric sensor for the determination of L-cysteine in the presence of 3,4-dihydroxycinnamic acid (3,4-DHCA) as a suitable mediator. Additionally, we used the modified electrode as a new and sensitive sensor for the determination of L-cysteine in real samples such as urine, water, and serum.

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, and a Metrohm (Herisau, Switzerland) Model 663 VA stand linked to a computer (Pentium IV, 1,200 MHz). Autolab software was also used. A platinum wire was used as the auxiliary electrode. The 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 used for pH measurements. Spectrally pure graphite powder (particle size < 50 μm) from Merck and MWCNTs (> 90% MWCNTs basis, $d \times l$ = (90–70 nm) × (5–9 μm) from Fluka were used as the substrate for the preparation of the carbon paste electrode.

Phosphate buffer (NaH_2PO_4-Na_2HPO_4-NaOH, 0.1 mol/L) solutions (PBS) with different pH values were used.

All chemicals used were of analytical reagent grade and purchased from Merck (Darmstadt, Germany) unless otherwise stated. Doubly distilled water was used throughout. L-cysteine and 3,4-DHCA were purchased from Merck.

2.2. Preparation of the electrode

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 50 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 excess paste out of the tube and polishing it with weighing paper.

2.3. Preparation of real samples

Urine samples were stored in a refrigerator immediately after collection. Each sample (10 mL) was centrifuged for 10 min at 2000 r/min. The supernatant was filtered using a filter (0.45 μm) and then diluted 100 times with universal buffer solution (pH = 7.0). The solution was transferred to a voltammetric cell for analysis without any further pretreatment. The standard addition method was used for the determination of L-cysteine in the real samples.

2.4. Optimization of the 3,4-DHCA concentration

The influence of 3,4-DHCA concentration on the electrocatalytic oxidation peak current was studied at pH = 7.0, and in the range of 300 to 800 μmol/L 3,4-DHCA. As shown in Fig. 1, by increasing the concentration of 3,4-DHCA up to 500 μmol/L the net electrocatalytic peak current increased, whereas higher concentrations of 3,4-DHCA caused a decrease of the magnitude of the peak current, which may be due to the formation of 3,4-DHCA aggregates. Therefore, a 3,4-DHCA concentration of 500 μmol/L was selected for further study.

3. Results and discussion

3.1. Characteristics of the MWCNTPE

Figure 2 shows SEM images of CPE and MWCNTPE. On the surface of the CPE, a layer of irregular flakes of graphite powder was present and they were isolated from each other. After MWCNTs were added to the carbon paste, the MWCNTs were distributed on the surface of the electrode in a special three-dimensional structure, indicating that the MWCNTs successfully modified the electrode.

The active surface areas of the modified electrodes were estimated from the slope of a I_p vs $v^{1/2}$ plot for a known concentration of $K_2Fe(CN)_6$, based on the Randles-Sevcik equation:

$$I_{pa} = 2.69 \times 105 n^{3/2} A D_R^{1/2} v^{1/2} C_0 \quad (1)$$

where I_{pa} refers to the anodic peak current, n is the electron transfer number, A is the surface area of the electrode, D_R is the diffusion coefficient, C_0 the concentration of $K_2Fe(CN)_6$, and v is the scan rate. For C_0 = 1.0 mmol/L in a KCl electrolyte (0.10 mol/L) with n = 1 and $D_R = 7.6 \times 10^{-6}$ cm/s and from the slope of the I_p-$v^{1/2}$ relationship, the microscopic areas were calculated. The active surface areas were 0.055 and 0.10 cm^2 for the CPE and the MWCNTPE, respectively. The results show that the

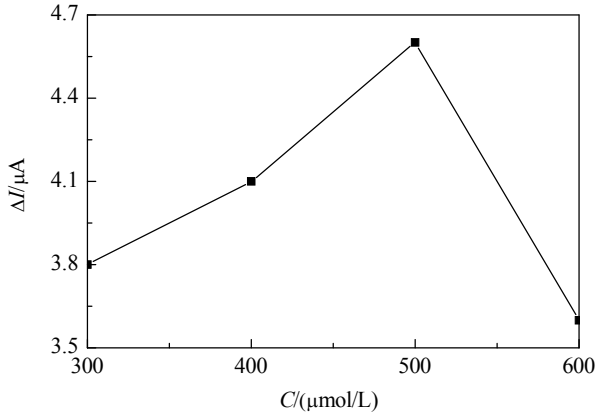

Fig. 1. Effect of 3,4-DHCA concentration on the net anodic peak current of L-cysteine (700 μmol/L). Scan rate 20 mV/s, pH = 7.0.

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