Preparation, electrochemical behavior and electrocatalytic activity of chlorogenic acid multi-wall carbon nanotubes as a hydroxylamine sensor

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ABSTRACT

Electrochemical characteristics of an electrodeposited chlorogenic acid film on multi-wall carbon nanotubes glassy carbon electrode (CGA–MWCNT–GCE) and its role as a sensor for electrocatalytic oxidation of hydroxylamine are described. Cyclic voltammograms of the CGA–MWCNT–GCE indicate a pair of well-defined and nearly reversible redox couple with the surface confined characteristics at a wide pH range of 2.0–12.0. The charge transfer coefficient, α, and the charge transfer rate constant, k_s, of CGA adsorbed on MWCNT were calculated 0.48 and $44 \pm 2 \, s^{-1}$ respectively. The CGA–MWCNT–GCE shows a dramatic increase in the peak current and/or a decrease in the overvoltage of hydroxylamine electrooxidation in comparison with that seen at a CGA modified GCE, MWCNT modified GCE and activated GCE. The kinetic parameters of electron transfer coefficient, α, the heterogeneous electron transfer rate constant, k′, and exchange current, i_0, for oxidation of hydroxylamine at the modified electrode surface were determined using cyclic voltammetry. Four linear calibration ranges and high repeatability with relative standard deviation of 4.6%, for a series of four successive measurements in 17.7 μM hydroxylamine, are obtained at the CGA–MWCNT–GCE using an amperometric method. Finally, the modified electrode was successfully used for determination of spiked hydroxylamine in two water samples.

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1. Introduction

Hydroxylamine and its salts are commonly used as antioxidants [1]. They can also act as reducing agents in a myriad of organic and inorganic reactions [2]. Hydroxylamine is an intermediate in biological nitrification [2]. This has also been used in the past by biologists to introduce random mutations by switching base pairs from A to G, or from C to T [2]. This is to probe functional areas of genes to elucidate what happens if their functions are broken. Hydroxylamine can also be used to highly selectively cleave asparaginyl–glycine peptide bonds in peptides and proteins. It also bonds to and permanently disables (poisons) heme-containing enzymes. It is used as an irreversible inhibitor of the oxygen-evolving complex of photosynthesis on account of its similar structure to water. Some non-chemical uses include removal of hair from animal hides and photography developing solutions [3]. In the semiconductor industry, hydroxylamine is often a component in the "resist stripper" which removes photoresist after lithography. Hydroxylamine may explode on heating. It is an irritant to the respiratory tract, skin, eyes, and other mucous membranes. It may be absorbed through the skin, is harmful if swallowed, and is a possible mutagen [4]. The nitrate salt, hydroxylammonium nitrate, is being researched as a rocket propellant, both in water solution as a monopropellant and in its solid form as a

solid propellant. Therefore, from the industrial, environmental and health viewpoints, development of a sensitive analytical method for the determination of low levels of hydroxylamine is of significant importance. The determination of hydroxylamine is usually executed by spectrophotometry [5,6], chromatography [7,8], potentiometry [9], polarography [10] and other voltammetric methods [11–20]. However, the processes involved in many of these methods are extremely complex, and the linear ranges are relatively narrow and have low precision. Unfortunately, hydroxylamine cannot be electro-oxidized at bare carbon electrodes. In operation, electrode surface modification has been tried as a means to reduce the overvoltage and overcome the slow kinetics of many electrode processes. Several works in the literature have reported the hydroxylamine determination at the various chemically modified electrodes (CMEs) [11–20], which can significantly lower the overpotentials and increase the oxidation current response. We have previously reported that a coumestan derivative [12], rutin [13], an indenedione derivative [14] and ruthenium oxide [15] modified electrodes could be successfully used to determine hydroxylamine. All these reports have their advantages and limitations. Thus, it is necessary to have further efforts for the development of simple, rapid and sensitive chemically modified electrode that can improve the hydroxylamine determination.

Also, there are a few papers regarding the electrochemical and electrocatalytic activity of chlorogenic acid, (1S,3R,4R,5R)-3-[(E)-3-(3,4-dihydroxyphenyl)prop-2-enoyl]oxy-1,4,5-trihydroxycyclohexane-1-carboxylic acid [21–23]. Chlorogenic acid (see Scheme 1 for

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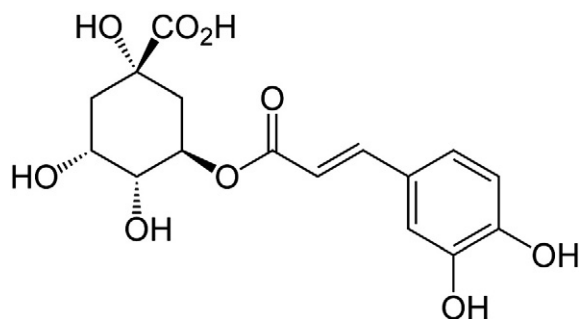
Scheme 1. Structure of chlorogenic acid (CGA).

structure) is a family of naturally occurring organic compounds. It is an important biosynthetic intermediate [24]. It also is one of the phenols found in coffee, bamboo *Phyllostachys edulis* [25], as well as many other plants [26]. This compound, long known as an antioxidant and an inhibitor of the tumor promoting activity of phorbol esters, also slows the release of glucose into the bloodstream after a meal [27].

Carbon nanotubes (CNTs) have witnessed tremendous interest in nanoscience and nanotechnology due to their large surface area, unique architecture, and remarkable mechanical and electrical properties [28–30]. Moreover, owing to their excellent characteristics of chemical stability, low mass density and low resistivity, CNTs became ideal electrode materials and have been widely used in electrochemistry and electroanalytical chemistry [31–35].

As a follow-up of our studies to fabricate various chemically modified electrodes, investigation of their electrocatalytic behavior and application for the determination of various analytes [12–15,33–35], in this study we employed a chlorogenic acid multi-wall carbon nanotubes modified glassy carbon electrode (CGA–MWCNT–GCE) for electrocatalytic oxidation of hydroxylamine. The results show that the reversibility of CGA is significantly improved at the MWCNT modified GCE in comparison with GCE alone. Also, the electrocatalytic oxidation of hydroxylamine at the CGA modified GCE, MWCNT modified GCE and activated GCE was investigated and the results were compared with those obtained at the CGA–MWCNT–GCE. The results indicate that a combination of MWCNT and CGA remarkably improves the sensitivity of hydroxylamine determination. Our findings indicate that this modified electrode offers several distinct advantages including good stability, high surface charge transfer rate constant, good repeatability, wide linear concentration ranges, and technical simplicity for determination of hydroxylamine. Finally, to evaluate the utility of the modified electrode for analytical applications, it was used for voltammetric determination of hydroxylamine in two water samples.

2. Experimental section

Electrochemical experiments were carried out with AUTOLAB modular electrochemical system (ECO Chemie, Utrecht, Netherlands) equipped with a PGSTA 30 module and are driven by GPES 4.9 software, in conjunction with a three-electrode cell. A saturated calomel electrode (SCE), a platinum wire and a chlorogenic acid multi-wall carbon nanotube modified glassy carbon electrode were used as reference, counter and working electrodes, respectively. The surface morphology of the electrode surface was characterized by an AIS-2100, Seron Technology scanning electron microscopy (SEM) apparatus at a voltage of 20 keV. The pH measurements were done with a Metrohm model 691 pH/mV meter. All experiments were carried out at ambient temperature.

Hydroxylamine, chlorogenic acid (CGA), dimethyl formamide (DMF), and the chemical used for preparation of buffer solutions were reagent grade from Merck Company and used as received. The multi-wall carbon nanotubes (>95% purity, 10–20 nm diameter, and 5–20 μm length) were obtained from Nanolab Inc. (Brighton, MA). The

immobilizing solution of MWCNT was prepared by introducing 5 mg of MWCNT into 5 ml of DMF. Phosphate buffer solutions (0.1 M) were prepared from 0.1 M H_3PO_4–NaH_2PO_4, and the pH was adjusted with 0.1 M H_3PO_4 or 2.0 M NaOH.

The procedure of fabrication of the various modified electrodes is as follows. A glassy carbon electrode (GCE) was first carefully polished with alumina on a polishing cloth and the electrode was placed in doubly distilled water and was subject to ultrasonic bath to remove adsorbed particles. After being cleaned, for electrochemical activation of the electrode, it was immersed in 0.1 M sodium bicarbonate solution and was activated by a continuous potential cycling from −1.1 to 1.7 V at a sweep rate of 100 mV s^{-1}, until a stable voltammogram was obtained. For preparation of CGA modified GCE (CGA–GCE), the activated GCE (AGCE) was rinsed with doubly distilled water and was modified by cycling the potential between 0.0 mV and 900 mV (at 20 mV s^{-1}) for 12 min in a 1.0 mM solution of CGA in 0.1 M acetic acid. For fabrication of the MWCNT modified GCE (MWCNT–GCE), a 15 μL of DMF–MWCNT solution (1 mg/1 mL) was placed directly onto the AGCE surface and dried at room temperature to form a MWCNT film at the GCE surface and preparation of the MWCNT–GCE. The CGA–MWCNT modified GCE (CGA–MWCNT–GCE) was prepared by immersion of MWCNT–GCE in 0.1 M acetic acid solution containing 1.0 mM CGA and it was modified with the same procedure that was described for CGA–GCE. After the CGA film had formed on the multi-wall carbon nanotube surfaces, the modified electrode was rinsed thoroughly with water and dipped into the buffer solution to test its electrochemical behavior. Subsequently, the potential was scanned for 20 cycles at 100 mV s^{-1} over the range of 20 to 240 mV, in 0.1 M phosphate buffer solution (pH 7.0), so as to obtain a stable redox response for the surface-immobilized films. The results show that the initial decay observed in all cases for redox response, might be due to the release of CGA that is adsorbed weakly to the surface and can be displaced somewhat easily.

3. Results and discussion

3.1. Electrochemical characterization of the CGA–MWCNT–GCE

The electrochemical behavior of the modified electrodes was characterized by cyclic voltammetry. The representative cyclic voltammograms obtained for CGA–GCE and CGA–MWCNT–GCE, after 20 cycles between 20 mV and 240 mV, at 100 mV s^{-1}, in 0.1 M phosphate buffer solution (pH 7.0) containing no deliberately added electroactive materials, are shown in Fig. 1, curves a and b, respectively. As can be seen, for CGA–GCE a redox couple (Fig. 1, curve a) with low peak currents, relatively high peak separation (about 55 mV), low capacitance currents and for CGA–MWCNT–GCE a pair of well defined redox couple of CGA (Fig. 1, curve b) with high peak response, low peak potential separation (about 32 mV) and relatively high capacitance currents are observed. The increase of the peak currents and decrease of the peak potential separation for CGA–MWCNT–GCE, indicate that the reversibility of CGA is significantly improved at the MWCNT surface. For a reversible surface redox process in which no reactants from the solution take place, the peak separation should be zero [36,37]. The relatively small peak separations might arise due to non-ideal behavior cased by the effects of charge transfer and uncompensated ohmic drop [36,37]. Also, we concluded that MWCNT will increase the surface area of the modified electrode, so the background voltammetric response (capacitance current) and sensitivity of MWCNT-coated surface are higher than that for the bare surface.

Fig. 2A illustrates the cyclic voltammograms of CGA–MWCNT–GCE in 0.1 M phosphate buffer solution (pH 7.0) as the supporting electrolyte at various scan rates. When the potential was scanned between 20 and 240 mV, a surface-immobilized redox couple with conditional formal potential, $E^{0'}$, value 130 mV was observed. In addition, $E^{0'}$ is almost independent of potential scan rate for sweep rates ranging from 10 mV to 1000 mV s^{-1}, suggesting facile charge