



A novel amperometric sensor for ascorbic acid based on poly(Nile blue A) and functionalised multi-walled carbon nanotube modified electrodes

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ARTICLE INFO

Article history:

Received 8 October 2012

Received in revised form

14 February 2013

Accepted 17 February 2013

Available online 24 February 2013

Keywords:

Poly(Nile blue A)

Multi-walled carbon nanotubes

Electropolymerisation

Ascorbic acid determination

Electrochemical impedance spectroscopy

ABSTRACT

A new type of modified electrode sensor for ascorbic acid has been prepared by deposition of multi-walled carbon nanotubes (MWCNT) and poly(Nile blue A) on the surface of glassy carbon electrodes. Nile blue A was electropolymerised either beneath (directly on glassy carbon) or onto the MWCNT layer by potential cycling in phosphate buffer solution at pH 6.0. Characterisation of the modified electrodes was carried out by cyclic voltammetry and electrochemical impedance spectroscopy. Quantitative determination of ascorbate was achieved by cyclic voltammetry and fixed potential amperometry in phosphate buffer solution at pH 5.3. The modified electrodes exhibited good sensitivity, wide linear range, a detection limit of 1.6 μM and good stability, showing that they can be used as sensors for ascorbic acid. There is no interference from compounds commonly found in clinical and pharmaceutical samples and the determination of ascorbic acid in commercial tablet samples was successfully performed.

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1. Introduction

Carbon nanotubes (CNT) have been used for a wide range of applications last decade due to their high electrical conductivity, high surface area, and electronic properties [1–4]. CNTs, single-wall (SWCNT) and multi-walled carbon nanotubes (MWCNT) showed a good chemical stability and affinity to biomolecules, since they have a unique structure. Thus, they have often been used in electrochemical sensors and biosensors [4,5–7] as enzyme [8–9] and protein (myoglobin and haemoglobin) [10–11] biosensors, immunosensors [12], and DNA sensors [13–14]. The insolubility of CNTs in all solvents is their principal drawback. Functionalisation of CNTs improves the solubility and processability; thus, new types of nanotube-based materials can be produced [15]. Various electrochemical biosensors based on CNTs can be prepared modifying them chemically or physically with redox mediators to improve the electrical and mechanical properties of the sensors [3,16–20].

Nile blue A (NB) is one of the electroactive phenoxazine dyes [21] recently used also as a redox mediator, and it can be easily adsorbed or electropolymerised from aqueous solution on the surface of solid electrodes [22,23]. Electrodes modified with Nile blue have been recently used as sensors and biosensors, especially

for the electrocatalytic oxidation of the nicotinamide-based coenzymes, NADH and NADPH [24].

Ascorbic acid (or ascorbate at higher pH) (AA), vitamin C, is a well-known water-soluble pharmaceutical compound. It is an effective reducing agent and biological antioxidant which is commonly used in foods and drugs. It is also important for industrial applications, since it prevents the colour and aroma changes of the products, thus extending their storage life. Electrochemical techniques have been widely used for the determination of AA in drugs and foods [25–28]. Various sensitive films on electrode substrates have been used for electrochemical AA determination such as Prussian Blue [29], copper hexacyanoferrate [30], tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) organic salt [31], a PVC/TTF-TCNQ composite [32], and an organoclay film [33]. Most recently carbon nanotubes modified electrodes were also employed: single-walled with ionic liquid, IL-SWCNT [34] or multi-walled together with ruthenium oxide hexacyanoferrate, MWCNT/RuOHCF [35] or polyaniline/polyacrylic acid, PANI/PAA/MWCNT [36].

Electrochemical impedance spectroscopy (EIS), a method which has been recently applied in the characterisation of electrochemical sensors and biosensors [37–40], has been used to gain valuable information about the electrochemical characteristics of the polyphenazine films, which is not possible by voltammetric techniques.

In this work, modification of glassy carbon electrodes (GCE) with functionalised-MWCNT and poly(Nile blue) (PNB) is

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reported. These modified electrodes were varied by changing the MWCNT loadings, the thickness of the PNB film, and the PNB film being formed either beneath or on the top of the MWCNT coatings. Their characterisation was achieved by cyclic voltammetry (CV) and EIS. The prepared electrodes were also used for determination of ascorbic acid by CV and fixed-potential amperometry. The results were optimised to obtain the best modification of GCEs with MWCNT coatings and PNB films in order to achieve a good sensor performance for AA. Different compounds were tested as possible interferents and finally, ascorbic acid was determined in two different pharmaceutical drugs.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes were from NanoLab, U.S.A., with ~95% purity, 30 ± 10 nm diameter and 1–5 μm length.

Nile blue A and N,N-dimethylformamide (DMF) were purchased from Fluka (Switzerland) and used without further purification. L-Ascorbic acid was obtained from Sigma (Germany) and used as received.

Phosphate buffer solutions (PB), 0.1 M pH 5.3 and 6.0, were prepared from sodium di-hydrogenphosphate and di-sodium hydrogenphosphate (Riedel-de-Haën, Germany), adjusting the pH if necessary with 5 M NaOH (Riedel-de Haën, Germany) solution. All chemicals were of analytical grade.

Millipore Milli-Q nanopure water (resistivity ≥ 18 M Ω cm), and analytical grade reagents were used for preparation of all solutions. Experiments were performed at room temperature, 25 ± 1 °C.

2.2. Instrumentation

A three-electrode electrochemical cell was used for CV, chronoamperometry, and EIS measurements. It contained a MWCNT- and PNB- modified glassy carbon working electrode of diameter 5.5 and 1.5 mm, a platinum foil as counter electrode, and a saturated calomel electrode (SCE) served as reference. All CV and chronoamperometry measurements were performed using a computer-controlled μ -Autolab Type II potentiostat/galvanostat with GPES 4.9 software (Metrohm-Autolab, The Netherlands).

EIS measurements were carried out with a PC-controlled Solartron 1250 Frequency Response Analyser coupled to Solartron 1286 Electrochemical Interface using ZPlot 3.1 software (Scribner Associates, USA). A sinusoidal voltage perturbation of root-mean-square amplitude 10 mV was applied in the frequency range between 65 kHz and 0.1 Hz with 10 frequency steps per decade, integration time 60 s. Fitting to equivalent circuits was performed with ZView 3.1 software (Scribner Associates, USA).

The pH measurements were carried out with a CRISON 2001 micro-pH-meter (Crison Instruments, Spain) at room temperature.

2.3. Electrode preparation

MWCNT (120 mg) were stirred in 10 mL of a 3 M nitric acid solution for 24 h at room temperature. The solid product was filtered and washed several times with nanopure water until the filtrate became close to neutral (pH \approx 7). The functionalised MWCNTs were then dried in an oven at 80 °C for 24 h [2].

The dried MWCNTs were dispersed in DMF, 0.2 and 1.0%, and sonicated for 4 h to ensure a homogeneous mixture. Before the coating, GC electrode (with a diameter of 5.5 mm) was cleaned by polishing with diamond spray (Kemet International Ltd., U.K.), then sonicated in Milli-Q nanopure water and finally rinsed with

Table 1
Modification of GC electrodes by MWCNT and PNB.

Modified electrode	MWCNT-DMF dispersion	Γ (MWCNT)/ mg cm ⁻²	NB electro-polymerisation cycles
PNB/MWCNT-1	20 μL , 0.2%	0.17	5
MWCNT/PNB-1	20 μL , 0.2%	0.17	17
PNB/MWCNT-2	10 μL , 1.0%	0.42	5
MWCNT/PNB-2	10 μL , 1.0%	0.42	17
PNB/MWCNT-3	20 μL , 1.0%	0.84	5
MWCNT/PNB-3	20 μL , 1.0%	0.84	17

nanopure water. Coating of GC electrode was performed using three different loadings of MWCNT in DMF: 20 μL /0.2% (MWCNT-1), 10 μL /1.0% (MWCNT-2), and 20 μL /1.0% (MWCNT-3). Then, 10 or 20 μL of the MWCNT-DMF dispersion was dropped by using a micropipette on the surface of the GC electrode and allowed to dry at room temperature [41].

Electropolymerisation of NB was performed either prior to MWCNT coating (denoted as MWCNT/PNB) or on the top of MWCNT (denoted as PNB/MWCNT). It was carried out by cycling the potential in the region from -0.6 to $+1.2$ V vs SCE at a scan rate of 50 mV s⁻¹ for 5 or 17 cycles in 0.1 M PB at pH 6.0 containing 0.5 mM NB monomer. Then, it was left to dry overnight in air at room temperature. The modification conditions of the GCE with MWCNT and PNB are listed in Table 1. The surface concentration of MWCNT cast on the electrode was calculated from its dispersion in DMF dividing it by electrode geometric area.

2.4. Sample preparation

Pharmaceutical samples of aspirin and paracetamol with vitamin C, containing 240 mg and 250 mg ascorbic acid, respectively, were purchased from local pharmacy. Before testing, the samples were prepared by simply dissolving in water. The determination of ascorbic acid was performed by amperometry at fixed potential using standard addition method.

3. Results and discussion

3.1. Preparation and characterisation of MWCNT- and PNB-modified GC electrodes

Various MWCNT- and PNB-modified GC electrodes were prepared by changing (i) the loadings of MWCNT, (ii) the number of cycles for electropolymerisation of NB, and (iii) the position of the PNB film, either beneath or on the top of MWCNT coatings, Table 1. Electropolymerisation of NB was carried out by potential cycling in 0.1 M PB at pH 6.0 containing 0.5 mM of NB monomer. These polymerisation conditions were chosen in agreement with the detailed study between pH 5 and 8 in previous work [42], which showed that these settings lead to the formation of polymer films with the most well-defined voltammetric peaks and the most stable PNB film.

Cyclic voltammograms of NB electropolymerisation on the surface of GCE and on the top of MWCNT of 20 μL of 1.0% MWCNT-DMF loading are presented in Fig. 1. The irreversible oxidation peak at ~ 0.9 V, formation of the monomer radical, decreased with the number of cycles. The CVs of NB show two redox couples. The first redox couple at around -0.4 V is due to oxidation/reduction of the NB monomer. The other redox couple at around -0.1 V corresponds to oxidation/reduction of PNB and the peaks increase linearly in height with the number of cycles as PNB forms a film. Comparing the CVs of PNB on bare GCE and on the MWCNT coatings, the polymer redox couple peaks obtained

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