Analytica Chimica Acta 710 (2012) 58–64

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Dispersion of multi-wall carbon nanotubes in polyhistidine: Characterization and analytical applications

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ARTICLE INFO

Article history:
Received 2 September 2011
Received in revised form 22 October 2011
Accepted 25 October 2011
Available online 16 November 2011

Keywords:
Carbon nanotubes dispersion
Polyhistidine
Glassy carbon electrode
Ascorbic acid
Dopamine
Uric acid

ABSTRACT

We report for the first time the use of polyhistidine (Polyhis) to efficiently disperse multiwall carbon nanotubes (MWCNTs). The optimum dispersion MWCNT–Polyhis was obtained by sonicating for 30 min 1.0 mg mL^{-1} MWCNTs in 0.25 mg mL^{-1} Polyhis solution prepared in 75:25 (v/v) ethanol/0.200 M acetate buffer solution pH 5.00. The dispersion was characterized by scanning electron microscopy, and by cyclic voltammetry and amperometry using ascorbic acid as redox marker. The modification of glassy carbon electrodes with MWCNT–Polyhis produces a drastic decrease in the overvoltage for the oxidation of ascorbic acid (580 mV) at variance with the response observed at glassy carbon electrodes modified just with Polyhis, where the charge transfer is more difficult due to the blocking effect of the polymer. The reproducibility for the sensitivities obtained after 10 successive calibration plots using the same surface was 6.3%. The MWCNT-modified glassy carbon electrode demonstrated to be highly stable since after 45 days storage at room temperature the response was 94.0% of the original. The glassy carbon electrode modified with MWCNT–Polyhis dispersion was successfully used to quantify dopamine or uric acid at nanomolar levels, even in the presence of large excess of ascorbic acid. Determinations of uric acid in human blood serum samples demonstrated a very good correlation with the value reported by Wienner laboratory.

1. Introduction

Carbon nanotubes (CNTs) have attracted enormous attention for the development of new sensing technologies because of their unique physical, electronic, and chemical properties [1,2]. Due to their outstanding beneficial characteristics and their ability to promote electron transfer reactions, CNTs have opened the doors for designing a variety of electrochemical sensors and biosensors, as it has been extensively reviewed in the literature [3–6].

However, the insolubility of CNTs in water and organic solvents is a limitation for their use as modifiers in electrodes [3]. Therefore, it is necessary to functionalize them by covalent attachment or by dispersion in a given compound. Several routes have been attempted for dispersing CNTs, including the use of surfactants [7,8], polymers [9–21], ionic-liquids [22], hyaluronic acid [23], and mineral oil [24–30].

The performance of the electrodes modified with CNTs will depend on the efficiency of their functionalization or dispersion, thus, to find the conditions for an optimum functionalization of CNTs is a critical step.

The goals of this work are the design of a new avenue for dispersing multi-wall carbon nanotubes (MWCNTs) using polyhistidine (Polyhis) and the development of electrochemical sensors based on the modification of glassy carbon electrodes with this dispersion for the selective determination of dopamine and/or uric acid.

Dopamine (Do) is an ubiquitous neurotransmitter present in mammalian brain tissues and plays a vital role in the functioning of central nervous system. Many diseases are related to the changes of their concentration such as schizophrenia, Parkinson and Huntington's disease as well as drug addiction and HIV infection [31–34]. Uric acid (UA) is the principal final product of purine metabolism in the human body. Its abnormal concentration level is usually regarded as a sign of gout, hyperuricaemia, Lesch–Nyhan syndrome [35] and cardiovascular disorders [36]. Therefore, the development of methodologies that allow the sensitive and selective quantification of these biomarkers is highly required. As it is widely known, the major problem in the electrochemical detection of these biomolecules in body fluids is the coexistence of interfering compounds, mainly ascorbic acid (AA), since it oxidizes at potentials close to Do and UA oxidation, making very difficult their selective quantification. In the following sections we discuss the

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doi:10.1016/j.aca.2011.10.050

influence of the sonication time and Polyhis/MWCNT ratio on the efficiency of the dispersions as well as on the analytical application of glassy carbon electrodes (GCEs) modified with the resulting dispersion (GCE/MWCNT–Polyhis) for the sensitive and selective quantification of UA or Do in the presence of AA.

2. Experimental

2.1. Reagents

Polyhistidine (Polyhis) catalog number P9386, and dopamine (Do) were obtained from Sigma. Ascorbic acid (AA) and uric acid (UA) were purchased from Baker and Merck, respectively. Human blood serum samples (Standatrol S-E) were from Wiener Lab. Multiwalled carbon nanotubes (MWCNTs) of 15–45 nm diameter and 1–5 μm length were obtained from NanoLab, USA. Other chemicals were analytical reagent grade and used without further purification. Ultrapure water (ρ = 18 MΩ cm) from a Millipore-MilliQ system was used to prepare all the solutions. Polyhis solutions were prepared in 75:25 (v/v) ethanol/0.200 M acetate buffer solution pH 5.00. The stock solutions of AA, UA and Do were prepared in 0.050 M phosphate buffer pH 7.40 before starting each set of experiments, stored in ice bath, and covered with alumina foil until using.

2.2. Apparatus

Electrochemical measurements were performed with EPSILON (BAS) and TEQ_02 potentiostats. The electrodes were inserted into the cell (BAS, Model MF-1084) through holes in its Teflon cover. A platinum wire and Ag/AgCl, 3 M NaCl (BAS, Model RE-5B) were used as counter and reference electrodes, respectively. All potentials are referred to the latter. A magnetic stirrer provided the convective transport during the amperometric measurements. Scanning electron microscopy (SEM) images were obtained with a Field Emission Gun Scanning Electron Microscope (FE-SEM, Zeiss, ΣIGMA model). MWCNTs dispersions were prepared using a TestLab ultrasonic bath (160 W, 40 kHz).

2.3. Preparation of glassy carbon modified electrodes

2.3.1. Preparation of the dispersions

(a) *MWCNT–Polyhis*: it was obtained by mixing 1.0 mg of MWCNTs with 1.0 mL of 0.25 mg mL^{-1} Polyhis solution followed by sonication for 30 min.
(b) *MWCNT–Ethanol/acetate buffer* (*MWCNT–Et*): the dispersion was prepared by mixing 1.0 mg mL^{-1} MWCNT in 1.00 mL of 75:25 (v/v) ethanol/0.200 M acetate buffer solution pH 5.00 followed by sonication for 30 min.

2.3.2. Modification of glassy carbon electrodes (GCE) with MWCNT–Polyhis (GCE/MWCNT–Polyhis), MWCNT–ethanol/acetate buffer (GCE/MWCNT–Et) and polyhistidine (GCE/Polyhis)

Before modification, the GCEs were polished with sand paper (BAS) and alumina slurries of 1.0, 0.30, and 0.05 μm for 1.0 min each. After polishing, the electrodes were rinsed with water and cycled 10 times in 0.050 M phosphate buffer solution between −0.200 V and 0.800 V at 0.100 V s^{-1}. Finally, an aliquot of 10 μL of MWCNT–Polyhis, MWCNT–Et or Polyhis (1.0 mg mL^{-1} prepared in 75:25 (v/v) ethanol/0.200 M acetate buffer solution pH 5.00) was dropped on the top of the polished GCEs, allowing the solvent to evaporate for 60 min at room temperature.

2.4. Procedure

The electrochemical experiments were carried out in a 0.050 M phosphate buffer solution pH 7.40. Amperometric experiments were performed by applying the desired potential (0.000 V) and allowing the transient current to reach a steady-state value prior to the addition of the analyte and the subsequent current monitoring. Differential pulse voltammetry (DPV) was performed with a pulse height of 0.004 V, a pulse amplitude of 0.050 V and a period of 200 ms. All the experiments were conducted at room temperature.

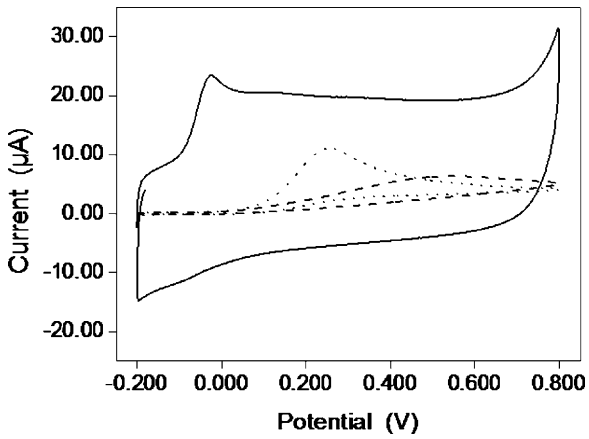

Fig. 1. Cyclic voltammograms for 5.0 × 10^{-4} M AA obtained at bare GCE (dotted line), GCE electrodes modified with 0.25 mg mL^{-1} Polyhis solution (dashed line), and GCE covered with (1.00:0.25) mg mL^{-1} MWCNT–Polyhis dispersion (solid line). Sonication time of the dispersion: 15 min. Supporting electrolyte: 0.050 M phosphate buffer solution pH 7.40. Scan rate: 0.100 V s^{-1}.

3. Results and discussion

3.1. Optimization and characterization of MWCNT–Polyhis dispersions

One of the critical steps when developing electrochemical sensors based on the use of dispersed CNTs is to obtain an efficient and stable dispersion to enable its homogeneous and robust deposition on the surface of the electrode. The influence of MWCNT/Polyhis ratio and the sonication time on the efficiency of the dispersion was evaluated electrochemically by cyclic voltammetry and amperometry using AA as redox marker.

Fig. 1 shows the voltammetric response for 5.0 × 10^{-4} M AA solution at different electrodes: bare glassy carbon (dotted line), glassy carbon covered by 0.25 mg mL^{-1} Polyhis (dashed line), and GCE covered by MWCNT–Polyhis dispersion (1.00 mg mL^{-1} MWCNT/0.25 mg mL^{-1} Polyhis) (solid line). AA is irreversibly oxidized at bare GCE (E_p = 0.260 V, i_p = 10.7 μA). When the electrode is covered by Polyhis, the oxidation peak is shifted to more positive potentials (E_p = 0.560 V) and the current significantly decreases (i_p = 5.7 μA). This behavior is attributed to the blocking effect of the polymer that makes more difficult the AA charge transfer. Likewise, cyclic voltammetric experiments performed at GCE/Polyhis with other analytes such us UA and Do presented similar behavior, confirming the blocking effect of Polyhis (not shown). In the presence of MWCNT at the electrode surface (GCE/MWCNT–Polyhis) the overvoltage for the oxidation of AA drastically decreases (E_p = −0.021 V) demonstrating that AA can be oxidized at this electrode despite the blocking effect of Polyhis due to the catalytic activity of CNTs. A significant increase in the capacitive currents is also observed at GCE/MWCNT–Polyhis, due to the increment in the electroactive area. It is important to point out that at HOPG with high density of edge-plane defects, the peak potential for AA oxidation is similar to that at GCE/MWCNT–Polyhis, indicating that the decrease in the overvoltage for AA oxidation is really due to the catalytic activity of edge-plane like defects present in MWCNT (not shown). Therefore, these results clearly demonstrate that the catalytic activity of CNTs

Table 1
Sensitivity obtained from amperometric measurements performed at 0.000 V using different GCE modified with MWCNT–Polyhis prepared with different concentrations of Polyhis. Other conditions as in Fig. 2.

Polyhisconcentration (mg mL^{-1})	Sensitivity (μA M^{-1})	r
0.12	$(101.7 \pm 0.7) \times 10^3$	0.9998
0.25	$(115.3 \pm 0.9) \times 10^3$	0.9998
0.50	$(86.6 \pm 0.6) \times 10^3$	0.9999
1.00	$(31.1 \pm 0.1) \times 10^3$	0.9999
3.00	$(8.8 \pm 0.1) \times 10^3$	0.9996

towards the oxidation of AA makes possible the oxidation of AA at potentials lower than at bare GCE even in the presence of Polyhis.

Fig. 2 shows the amperometric response for successive additions of 2.0×10^{-6} M AA at 0.000 V using GCE/MWCNT–Polyhis prepared with different polymer concentrations: 0.12 (a), 0.25 (b), 0.50 (c), 1.00 (d), and 3.00 (e) mg mL^{-1}. The response is fast and clearly defined after each addition of AA when the dispersion is prepared with 0.12, 0.25, and 0.50 mg mL^{-1} Polyhis, becoming slower and less defined for electrodes obtained with dispersions prepared with higher Polyhis concentration. The corresponding average sensitivities, obtained from three calibration plots with different electrodes, are summarized in Table 1. From these results, it is clear that Polyhis is an excellent dispersing agent for MWCNT. In fact, Polyhis efficiently disperse MWCNTs through the wrapping of the tubes facilitated by the interaction of imidazole moieties with their walls, and the repulsion generated by the positively charged amine groups of the polymer that makes more favorable the interaction of the mixture with the solvent. However, as the concentration of Polyhis increases, the blocking effect of the polymer becomes predominant over the CNTs catalytic activity, and the sensitivity decreases. In all cases there is a linear response up to 2.0×10^{-5} M AA. Amperometric experiments performed with Polyhis in the absence of MWCNTs gave a very poor response (sensitivity $(3.01 \pm 0.02) \times 10^2$ μA M^{-1}) (not shown), in agreement with the significant decrease in the AA oxidation signal shown in Fig. 1. Experiments performed with GCE/MWCNT–Et gave a sensitive response (sensitivity $(91 \pm 1) \times 10^3$ μA M^{-1}), although the dispersion was not stable, being rapidly separated in two clearly distinguishable phases. Therefore, 0.25 mg mL^{-1} was the optimum amount of Polyhis to efficiently disperse 1.0 mg mL^{-1} MWCNT in 75:25 (v/v) ethanol/acetate buffer solution (0.200 M, pH 5.0) after 15 min sonication time. It is important to mention that the selected

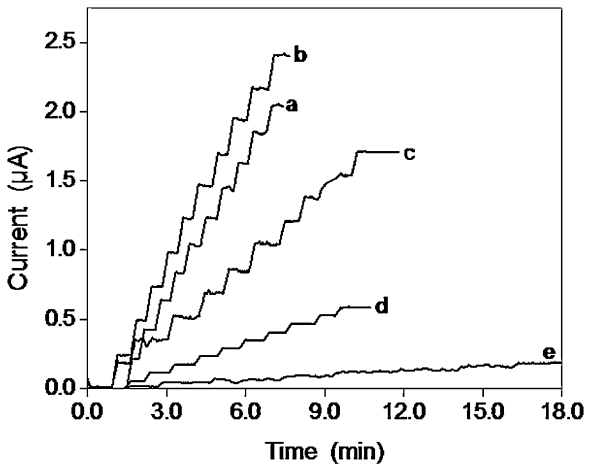

Fig. 2. Amperometric recordings for successive additions of 2.0×10^{-6} M AA obtained at GCE modified with MWCNT–Polyhis dispersions prepared with 1.00 mg mL^{-1} MWCNTs and different Polyhis concentrations: 0.12 (a), 0.25 (b), 0.50 (c), 1.00 (d), and 3.00 (e) mg mL^{-1}. Working potential: 0.000 V. Supporting electrolyte: 0.050 M phosphate buffer solution pH 7.40.

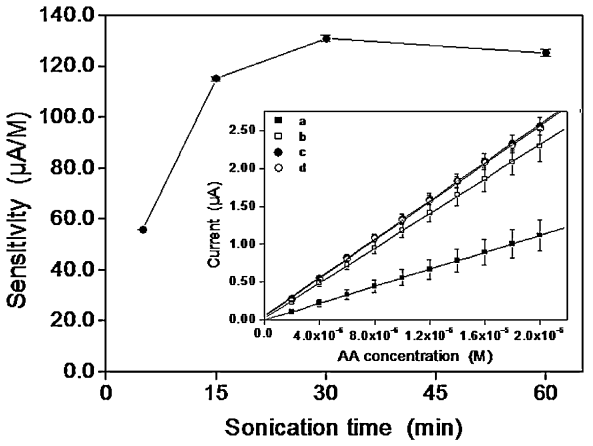

Fig. 3. Sensitivities obtained from amperometric recordings at GCE/MWCNT–Polyhis (1.00:0.25) mg mL^{-1} for successive additions of AA as a function of the sonication time between 5 and 60 min. The inset shows the corresponding calibration plots. The sensitivities are the average of five measurements obtained with fresh surface. Other conditions as in Fig. 2.

solvent was ethanol/water mixture 75:25 (v/v) since it allowed the better compromise between an efficient CNT–Polyhis dispersion and a relatively fast solvent evaporation rate that makes possible to obtain a uniform deposit on the GC electrodes.

The morphology of GCE modified with MWCNT–Polyhis was also evaluated by SEM. Fig. 3A–C displays images of glassy carbon disks modified with MWCNT–Polyhis prepared with different MWCNT/Polyhis ratios obtained after sonicating the mixture for 15 min. The image of GCE modified with (1.00:0.25) MWCNT–Polyhis dispersion (A) reveals a uniform layer of polymer embedding the MWCNT, although the GC surface was not completely covered. As the polymer concentration increases (B and C), the deposit segregates leaving areas with thick aggregates and regions with a thin film. For glassy carbon disks modified with the dispersion prepared with 0.50 mg mL^{-1} Polyhis, a uniform thin layer of mainly polymeric material with only few embedded MWCNTs is observed in areas where the deposited film is thin and no aggregates are seen at first sight. When the polymer concentration is higher than 1.00 mg mL^{-1} (not shown), the uncovered areas reveal just polymer/buffer salt deposits but no MWCNTs. In the thick aggregates areas, a more "crumbled" look of MWCNT groups appears as the polymer concentration increases. These aggregates go from "crumbles" covered with a thick layer of MWCNT-polymer film for 0.50 mg mL^{-1} concentration, to almost individuals "crumbles" for higher concentrations. In the latter cases, MWCNT aggregates are slightly connected one to each other by very few points where the thin MWCNT-polymer film still stents like a spider web. At higher magnification, outermost CNT are clearly evident, although inner ones are packed into a dense polymeric matrix (not shown).

The sonication time is another important variable when evaluating the dispersion of MWCNT in a polymeric matrix. Fig. 3D shows an image obtained for a glassy carbon disk covered with a (1.00:0.25) MWCNT–Polyhis dispersion prepared by sonication for 30 min. The image reveals a distribution of MWCNT more homogeneous than the one observed in the images for the (1.00/0.25) MWCNT/Polyhis dispersion prepared with 15 min sonication (Fig. 3A). Fig. 4 shows the effect of the sonication time (between 5 and 60 min) on the sensitivity obtained from amperometric experiments performed at 0.000 V on GCE/MWCNT–Polyhis using AA as redox marker. The results correspond to the average of five measurements obtained with fresh surfaces each time. The inset displays the corresponding calibration plots. The sensitivity increases in a factor of 2 when the sonication time increases

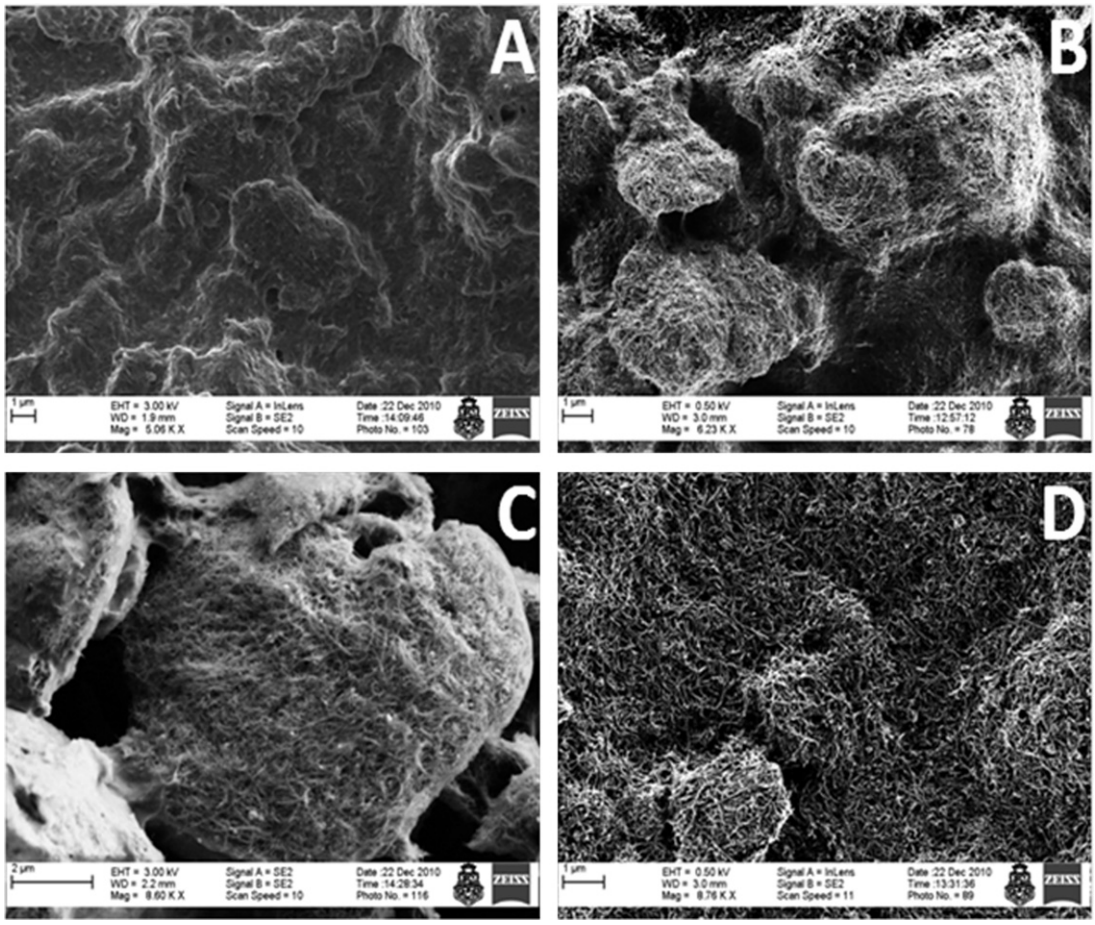

Fig. 4. SEM images of glassy carbon disks modified with dispersions of 1.00 mg mL^{-1} MWCNTs in solutions of Polyhis of different concentration: 0.25 (A), 0.50 (B), and 1.00 (C) mg mL^{-1}, after 15 min sonication (A, B, and C, respectively), and 0.25 mg mL^{-1} Polyhis after 30 min sonication (D).

from 5 to 15 min, to level off thereafter, indicating that the sonication step is necessary to obtain an efficient dispersion of MWCNTs. The highest sensitivity was obtained after 30 min sonication $(131 \pm 1) \times 10^3$ μA M^{-1}, $r = 0.9998$. Under these conditions the detection limit for the redox marker, AA, was 0.30 μM (taken as $3.3\sigma/S$, where σ is the standard deviation of the blank signal and S, the sensitivity) and the response time (for reaching the 90% of the stationary response) was 12 s.

Therefore, the deposit morphology, the homogeneity and coverage of the surface, as well as the dispersability of MWCNT in the polymeric matrix, strongly correlate and explain the higher signals and better reproducibility obtained by amperometry for the electrode modified with (1.00:0.25) MWCNT–Polyhis dispersion prepared by sonication for 30 min. Thus, 30 min was selected as the optimum sonication time for subsequent work.

The stability of the GCE modified with MWCNT/Polyhis is a very important aspect to be considered for further applications in biosensors developments. Fig. 5 shows the sensitivity towards AA obtained at 0.000 V at different GCE/MWCNT–Polyhis prepared with the same MWCNT–Polyhis dispersion as a function of the storage time at room temperature. No significant changes are observed even after 45 days, period at which the sensitivity remains in a 94.0% of the original one. The GCE/MWCNT–Polyhis also presents an excellent short-term stability, since the R.S.D. for 10 successive amperometric experiments for AA performed at 0.000 V using the same electrode surface was 6.3%.

In summary, the results indicate that Polyhis is an excellent dispersing agent for MWCNT and that the best conditions to efficiently disperse MWCNT in Polyhis is to mix 1.0 mg mL^{-1} of MWCNT with 0.25 mg mL^{-1} Polyhis (prepared in 75/25 (v/v) ethanol/acetate buffer solution (0.200 M pH 5.00)) and sonicate for 30 min.

3.2. Analytical applications of GCE/MWCNT–Polyhis

The analytical application of GCE/MWCNT–Polyhis was evaluated in connection with the quantification of Do or UA in the presence of AA. It is widely known that the simultaneous

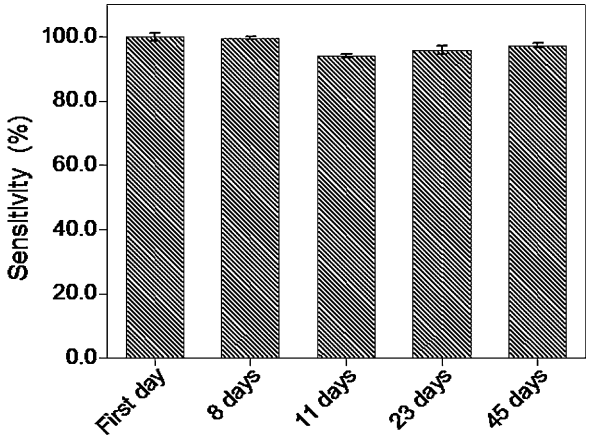

Fig. 5. Sensitivities towards AA obtained from amperometric experiments performed at 0.000 V at GCE modified with MWCNT–Polyhis (1.0 mg mL^{-1} MWCNT in 0.25 mg mL^{-1} Polyhis sonicated for 30 min) as a function of the storage time at room temperature. Other conditions as in Fig. 2.

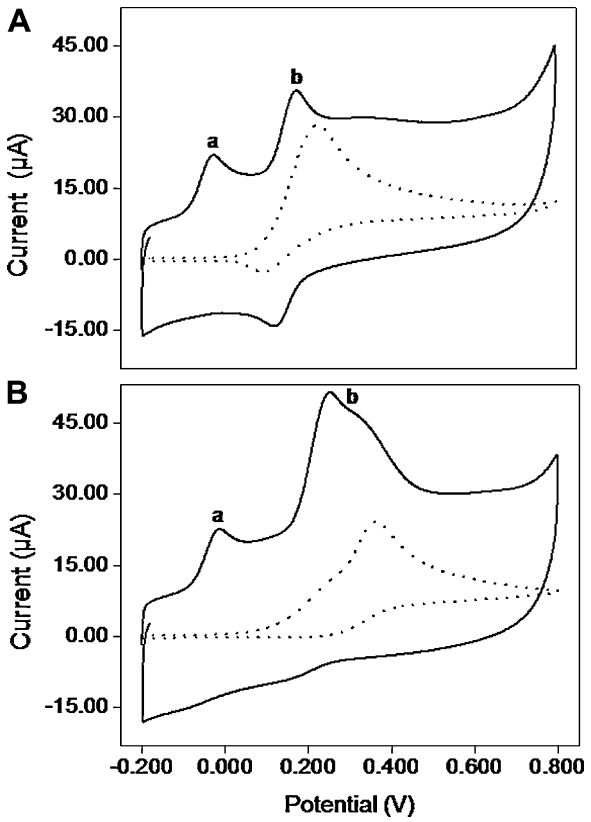

Fig. 6. Cyclic voltammograms obtained at bare GCE (dotted line) and GCE/MWCNT–Polyhis (solid line) for a mixture of 5.0×10^{-4} M AA and 5.0×10^{-4} M Do (A) or 5.0×10^{-4} M AA and 5.0×10^{-4} M UA (B). Supporting electrolyte: 0.050 M phosphate buffer solution pH 7.40. Scan rate: 0.100 V s^{-1}.

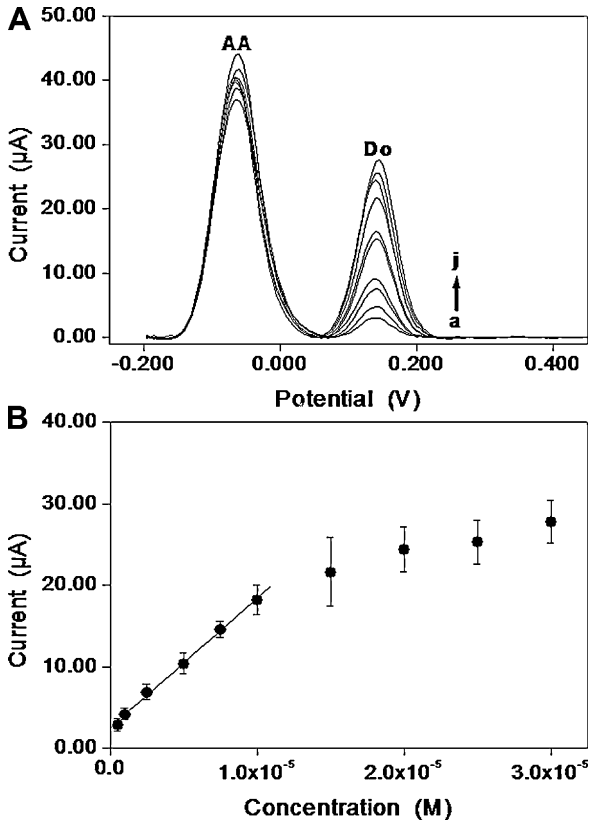

Fig. 7. (A) Differential pulse voltammetry response at GCE/MWCNT–Polyhis for mixtures containing 1.0×10^{-3} M AA and increasing concentrations of Do between 5.0×10^{-7} and 3.0×10^{-5} M. (B) Calibration plot obtained from the DPV recordings shown in (A). Supporting electrolyte: 0.050 M phosphate buffer solution pH 7.40. Pulse height: 0.004 V; pulse amplitude: 0.050 V; period: 200 ms.

electrochemical quantification of UA or Do in the presence of AA is very difficult since these compounds are oxidized at similar potentials [37,38]. Fig. 6A depicts cyclic voltammograms obtained at 0.100 V s^{-1} at bare GCE (dotted line) and at GCE/MWCNT–Polyhis (solid line) for a mixture of 5.0×10^{-4} M AA and 5.0×10^{-4} M Do. As expected, at GCE the mixture of AA and Do gives just a broad peak that involves the oxidation of both analytes. On the contrary, at GCE/MWCNT–Polyhis (solid line) it is possible to distinguish both contributions due to the significant decrease in the overvoltage for the oxidation of AA, and obtain an increase in the oxidation currents due to the increment of the electroactive area compared to the individual contributions at bare GCE (not shown). Fig. 6B displays cyclic voltammograms obtained at 0.100 V s^{-1} at bare GCE (dotted line) and at GCE/MWCNT–Polyhis (solid line) for a mixture of 5.0×10^{-4} M AA and 5.0×10^{-4} M UA. Similar to the mixture of AA and Do, the decrease in the overvoltage for the oxidation of AA makes possible the resolution of the AA and UA oxidation (Fig. 6B).

Here, we propose the use of GCE/MWCNT–Polyhis and differential pulse voltammetry (DPV) for the determination of Do or UA in the presence of AA. Fig. 7A displays the DPV response for increasing concentrations of Do from 5.0×10^{-7} to 1.0×10^{-4} M at GCE/MWCNT–Polyhis in the presence of 1.0×10^{-3} M AA. Two well-defined peaks are observed at −0.060 V and 0.140 V for the oxidation of AA and Do, respectively. The corresponding calibration plot is depicted in Fig. 7B. The sensitivity is $(1.59 \pm 0.04) \times 10^6$ μA M^{-1}, ($r = 0.998$), the linear range goes from 5.0×10^{-7} to 1.0×10^{-5} M, the detection limit is 15 nM (taken as it was previously indicated), and the quantification limit is 45 nM (taken as $10\sigma/S$). These results confirm that it is possible to detect Do at nM levels even in the presence of a large excess of AA.

Fig. 8A depicts the DPV response for increasing concentrations of UA from 5.0×10^{-7} M to 6.0×10^{-5} M at GCE/MWCNT–Polyhis in the presence of 1.0×10^{-3} M AA. The oxidation of AA and UA are clearly separated since the peak potential for AA oxidation is −0.060 V, while the one for UA oxidation is 0.215 V. The corresponding calibration plot is displayed in Fig. 8B. There is a linear relationship between current and UA concentration between 5.0×10^{-7} and 1.0×10^{-5} M UA. The average sensitivity is $(1.08 \pm 0.05) \times 10^6$ μA M^{-1} ($r = 0.995$), the detection limit is 32 nM, and the quantification limit, 97 nM (limits of detection and quantification were obtained as it was previously indicated).

Table 2 compares the linear range and detection limit for Do and UA obtained using GCE/MWCNT–Polyhis and different glassy carbon electrodes modified with CNTs proposed by other authors. The results demonstrate that our sensor is highly competitive and allows to obtain detection limits for Do quantification that, with the exception of MWCNT-Nafion [39], SWCNT-Nafion on poly(3-ethylthiophene) [40], boron doped MWCNT [50] and gold nanorods on MWCNT [55] modified GCE are comparable or even better than those previously reported [41–49,51–54]. In the case of UA, our detection limits are comparable to the one obtained with MWCNT–iron doped natrolite zeolite–chitosan modified GCE [53] and better than others included in Table 2 [38,41,43,44,54].

To verify the effectiveness of the proposed electrochemical sensor, the MWCNT–Polyhis modified GCE was used to determine the concentration of UA in human blood serum samples (Standatrol S-E, Wiener Lab.). The UA concentration obtained after 9 determinations was $(2.6 \pm 0.5) \times 10^{-4}$ M, which is in good agreement with the value reported by the laboratory (3.0×10^{-4} M), suggesting that

Table 2
Comparison of the linear ranges and detection limits for Do and UA obtained with GCE/MWCNT–Polyhis and different CNTs-modified GCE.

Sensor layer	Analyte	Linear range (M)	Detection limit	Reference
MWCNT-Nafion	Do	1.0×10^{-8}–1.0×10^{-5}	2.5 nM	[39]
SWCNT-Nafion on poly(3-ethylthiophene)	Do	2.0×10^{-8}–1.0×10^{-6}	5.0 nM	[40]
[a]LBL deposition SWCNT and cetylpyridinium bromide	Do	4.0×10^{-6}–1.2×10^{-4}	0.6 μM	[41]
	UA	2.0×10^{-6}–9.0×10^{-2}	7.0 μM	
Nanohybrid of SWCNT–ferrocene	Do	5.0×10^{-6}–3.0×10^{-5}	50 nM	[42]
SWCNT-overoxidized polypyrrole	Do	1.0×10^{-6}–5.0×10^{-5}	0.38 μM	[43]
	UA	2.0×10^{-6}–1.0×10^{-4}	0.74 μM	
MWCNT-poly(acrylic acid)	Do	4.0×10^{-8}–3.0×10^{-6}	20 nM	[44]
	UA	3.0×10^{-7}–1.0×10^{-5}	110 nM	
Laccase on MWCNT-modified GCE	Do	1.0×10^{-6}–3.0×10^{-5}	0.4 μM	[45]
MWCNT-Nafion-tyrosinase	Do	5.0×10^{-6}–2.3×10^{-5}	0.52 μM	[46]
Boronic acid functionalized MWCNT	Do	5.0×10^{-8}–5.0×10^{-4}	<0.5 μM	[47]
MWCNT–polyethylenimine	Do	1.0×10^{-5}–1.0×10^{-4}	0.92 μM	[37]
MWCNT–polylysine	UA	1.0×10^{-5}–8.0×10^{-5}	2.2 μM	[38]
Cobalt phthalocyanine modified MWCNT	Do	3.11×10^{-6}–9.32×10^{-5}	0.26 μM	[48]
Poly(methyleneblue) electrogenerated on MWCNT–modified GCE	Do	5.0×10^{-5}–2.3×10^{-3}	8.53 μM	[49]
Boron-doped MWCNT	Do	3.0×10^{-6}–1.5×10^{-5}	1.4 nM	[50]
MWCNT–chitosan–vitamin K_3	Do	2.0×10^{-6}–1.0×10^{-4}	0.18 μM	[51]
Nitric acid functionalized MWCNT	Do	3.0×10^{-6}–2.0×10^{-4}	0.8 μM	[52]
MWCNT–iron ion doped natrolite	Do	7.35×10^{-6}–8.33×10^{-4}	1.05 μM	[53]
zeolite–chitosan	UA	2.3×10^{-7}–8.33×10^{-5}	33 nM	
Poly(pyrocatechol violet) electrogenerated on carboxylated MWCNT-modified GCE	UA	3.0×10^{-7}–8.0×10^{-5}	0.16 μM	[54]
Gold nanorods on MWCNT-modified GCE	Do	5.0×10^{-7}–1.8×10^{-5}	0.8 nM	[55]
MWCNT-polyhistidine	Do	5.0×10^{-7}–1.0×10^{-5}	15 nM	This work
	UA	5.0×10^{-7}–1.0×10^{-5}	32 nM	This work

[a] Layer-by-layer.

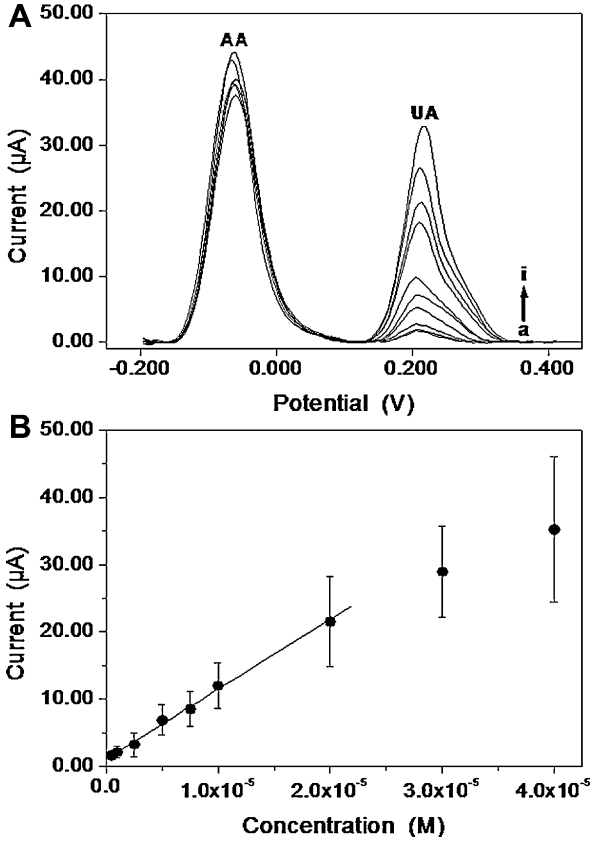

Fig. 8. (A) Differential pulse voltammetry response at GCE/MWCNT-Polyhis for mixtures containing 1.0×10^{-3} M AA and increasing concentrations of UA between 5.0×10^{-7} and 4.0×10^{-5} M. (B) Calibration plot obtained from the DPV recordings shown in (A). Other conditions as in Fig. 7.

the biosensor can be used for the determination of UA in such a complex sample as human blood serum.

4. Conclusions

We report for the first time the successful use of Polyhis to disperse MWCNTs. SEM and amperometric experiments demonstrated that the ratio MWCNT/Polyhis and the sonication time have an important influence on the efficiency of the MWCNT–Polyhis dispersion. Glassy carbon electrodes modified with this dispersion demonstrated to be very active platforms that largely improve the electrooxidation of AA and make possible the highly sensitive and selective quantification of Do or UA in the presence of a large excess of AA such as 1.0×10^{-3} M.

Acknowledgements

The authors thank CONICET, ANPCyT, SECyT-UNC, Ministerio de Ciencia y Tecnología de Córdoba for the financial support. P.R.D. thanks CONICET for the postdoctoral fellowship.

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