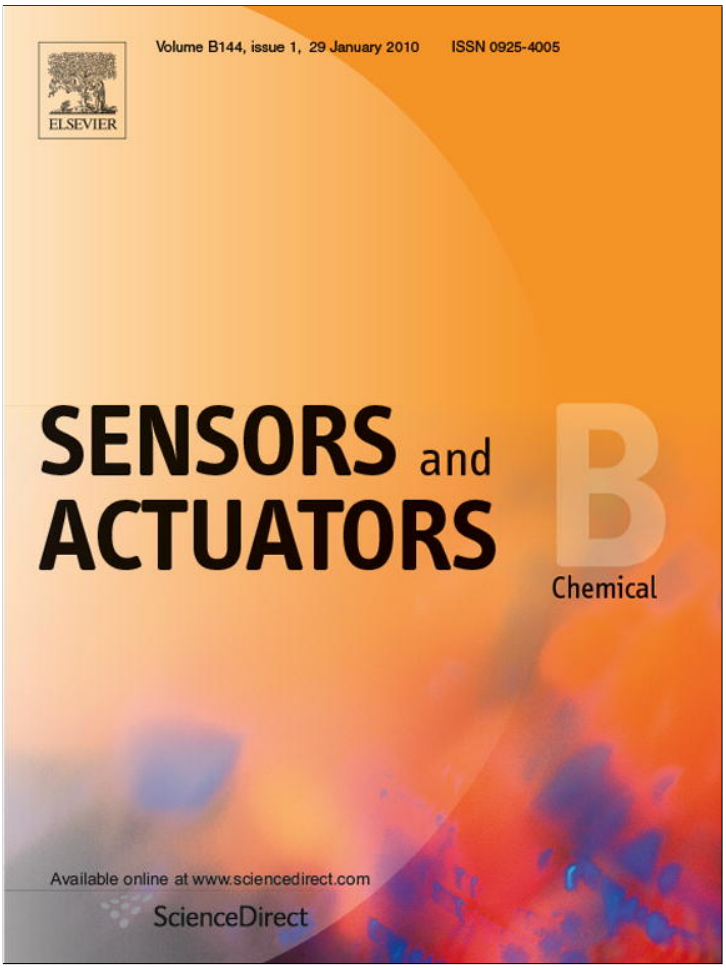

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Carbon nanotubes paste electrodes modified with a melanic polymer: Analytical applications for the sensitive and selective quantification of dopamine

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ABSTRACT

This work describes the advantages of carbon nanotubes paste electrodes (CNTPE) modified with a melanic polymer for the highly sensitive and selective quantification of dopamine. The polymer is electrogenerated from a 3.0×10^{-3} M L-dopa solution (in a 0.050 M phosphate buffer pH 7.40) by applying 0.80 V for 120 min. Two strategies for dopamine quantification are described, the amperometric detection at 0.200 V using 1.0×10^{-3} M ascorbic acid in the measurement solution to improve the sensitivity of the assay; and the adsorptive stripping detection with medium exchange using differential pulse voltammetry (DPV) as transduction mode. Detection limits of 2.0 nM and 20 nM were obtained with amperometry and adsorptive stripping, respectively. The interference of 5.0×10^{-4} M ascorbic acid and 5.0×10^{-5} M dopac was really negligible in both cases, demonstrating the advantages of the melanic polymer as permselective layer.

1. Introduction

Dopamine (Do) plays an important role in renal, hormonal and cardiovascular systems and is an ubiquitous neurotransmitter in mammalian brain tissues [1,2]. Changes in its concentration produce several diseases, like Parkinson, and schizophrenia caused by a decrease in Do levels [1]. Therefore, an extremely selective and sensitive quantification of Do is highly required.

After the pioneering work of Adams and coworkers [3], electrochemical methods have received enormous attention mainly due to the easy oxidation of Do at different electrodes [4]. However, the electrochemical quantification of Do suffers from the inconvenience that ascorbic acid (AA) and dopac, two metabolically related compounds present at high levels in nervous centers, are oxidized at similar potentials to Do [5].

A large number of strategies have been proposed to overcome this problem. The modification of electrode surfaces with different polymers has allowed the highly selective Do quantification in the presence of excess of AA [6]. Pandey et al. [7] have reported the micromolar detection of Do at glassy carbon electrode (GCE) modified by electropolymerization of poly(indole-6-carboxylic acid). Yu and coworkers [8] have described the simultaneous determination of Do, AA and uric acid (UA) at ordered mesoporous carbon/Nafion composite films deposited on GCE, with detection limits of 0.5 μM. An electrochemical sensor for Do and serotonin obtained by covalent modification of 5-hydroxy tryptophan on GCE has been proposed by Li et al. [9]. Luong and coworkers [10] have reported the selective nanomolar (50 nM) detection of Do in the presence of 3,4-dihydroxyphenylalanine (L-dopa), AA, UA and other Do metabolites by using a boron-doped diamond modified by successive polymerization of tyramine and pyrrole-1-propionic acid. Hu and coworkers [11] have described the simultaneous determination of Do, AA and UA at a GCE modified by polymerization of acid chrome blue. Our group has reported the nanomolar detection of Do even in the presence of large excess of AA and dopac at different carbon electrodes (graphite and glassy carbon composite electrodes, carbon fiber, glassy carbon and graphite) modified with an electrogenerated melanic polymer [12–14].

In the last years, the use of carbon nanotubes (CNT) to develop electrochemical transducers has received great attention due to their known advantages [15,16]. CNTs present unique structural, mechanical, geometric and chemical properties [15,17] that make them a very attractive material for the development of electrochemical sensors. In fact, sensors based on CNTs have largely improved the electrochemical response of several compounds of

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clinical, biological and environmental interest [18,19]. Chen and Yogeswaran [20] have proposed the successful discrimination of AA and Do signals by using GCE, gold and ITO modified with a dispersion of MWCNT and an electrogenerated film of poly(methylene blue). Hu et al. [21] have reported the use of a GCE modified by casting with a suspension of carbon nanotubes in dihexadecyl hydrogen phosphate and distilled water followed by the solvent evaporation at room temperature for the quantification of Do and 5-hydroxytryptamine, with detection limits of 1.1×10^{-8} M and 5×10^{-9} M for dopamine and 5-hydroxytryptamine, respectively.

This article reports the successful use of carbon nanotubes paste electrodes (CNTPE) modified with melanic polymers electrogenerated from L-dopa (CNTPE-Mel) as detectors for the quantification of Do in the presence of high excess of AA and dopac. The CNTPE has been proposed by our group in 2003 [22] and it has been used for the detection of several analytes of clinical and environmental interest [23–26]. To the best of our knowledge, this is the first report about the electrogeneration of melanic polymers at CNT-based electrodes and their analytical applications. The influence of the polymeric layer preparation conditions on the analytical performance of the resulting sensor is critically evaluated in the following sections. The CNTPE-Mel was used for the quantification of Do following two strategies, the amperometric detection and the adsorptive stripping with medium exchange associated with the differential pulse voltammetric quantification.

2. Experimental

2.1. Reagents

L-β-3,4-Dihydroxy-phenylalanine (L-dopa), 3,4-dihydroxyphenyl acetic acid (dopac), 3-hydroxytyramine (dopamine, Do), and L-(+)-ascorbic acid (AA) were purchased from SIGMA. Multiwalled carbon nanotubes (MWCNT) powder was obtained from NanoLab (U.S.A.), 95% purity, 20–50 nm diameter and 1–5 μm length. All stock solutions were prepared before starting each set of experiments and stored under refrigeration in dark. Diluted solutions were prepared just before use from the stock solutions. Other chemicals were of analytical-reagent grade. All solutions were prepared with water from a Milli-Ro Milli-Q system (18 MΩ cm).

2.2. Apparatus

Electrochemical experiments were performed with EPSILON (BAS) and μAutolab (EcoChemie) 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 and accumulation step experiments.

Carbon nanotubes paste electrodes (CNTPE) were prepared by mixing in an agate mortar MWCNTs (60.0%, w/w) and mineral oil (Aldrich) (40.0%, w/w). A portion of the resulting paste was packed firmly into the cavity (3.0 mm diameter) of a Teflon tube. The electric contact was established via a stainless steel screw. A new surface was obtained by smoothing the electrode onto a weighing paper.

Melanin-modified electrode (*CNTPE-Mel*) *preparation*: The melanic polymer was obtained at CNTPE from a stirred air saturated 0.050 M phosphate buffer solution pH 7.40 containing 3.0×10^{-3} M L-dopa by applying a constant potential of 0.80 V for 120 min. Once the polymer was grown, the electrode was washed with water and cycled in supporting electrolyte between −0.20 V and 0.80 V at 0.100 V/s (5 cycles) before using.

2.3. Procedure

2.3.1. Direct amperometric determination of Do

The experiments were performed at 0.200 V by successive additions of Do to a 0.050 M phosphate buffer solution pH 7.40 in the presence of 1.0×10^{-3} M ascorbic acid. Some comparative experiments were performed without the addition of AA.

2.3.2. Determination of Do by DPV-adsorptive stripping with medium exchange

This scheme consisted of two steps: (I) *Dopamine preconcentration*: performed by immersion of CNTPE-Mel in a phosphate buffer solution containing Do (alone or in the presence of AA and dopac) for a given time at open circuit potential under stirring conditions; (II) *DPV-stripping:* performed in a 0.050 M phosphate buffer solution pH 7.40 by differential pulse voltammetry (DPV) between −0.200 V and 0.600 V with a pulse height of 4 mV, a pulse amplitude of 50 mV and a period of 200 ms, without stirring. Between steps I and II the electrode was rinsed with the phosphate buffer solution for 10 s. Between experiments the electrode was regenerated by cycling three times under the same conditions as those used for the step II, to ensure good reproducibility.

All the experiments were conducted at room temperature.

3. Results and discussion

3.1. Direct amperometric determination of Do

Fig. 1 displays cyclic voltammograms obtained at 0.100 V/s for 1.0×10^{-3} M Do (A), AA (B), and dopac (C) at CNTPE (dotted line) and CNTPE-Mel (solid line). In the case of Do, the oxidation current increases from 32.5 μA to 73.9 μA, the peak potential separation changes from 99 mV to 194 mV and the peak currents ratio increases from 2.8 to 3.7. Thus, although the voltammetric response of Do at CNTPE-Mel is more sensitive, it is less reversible, suggesting that, even when the interaction of Do with the polymeric matrix is favoured, the difussional effect of the polymer exerts an important negative influence on its voltammetric response. Regarding AA and dopac, there is an interesting effect on the electrochemical behaviour at CNTPE covered with the melanic polymer. The oxidation current of AA at the peak potential value decreases 99.5% (22.90 μA vs. 0.12 μA) while the one for dopac diminishes 98.9% (16.6 μA vs. 0.19 μA), demonstrating the excellent permselective properties of the polymeric layer, in agreement with previous results [12].

Fig. 2 compares hydrodynamic voltammograms for 1.0×10^{-6} M Do at CNTPE (a) and at CNTPE-Mel in the absence (b) and in the presence (c) of 1.0×10^{-3} M AA. Do oxidation current increases when the polymer is present at the electrode surface due to the favourable interaction of Do with the polymer, in agreement with Fig. 1 (Fig. 2b vs. a). Taking into account that the electrogenerated polymer represents an important barrier for negatively charged compounds, and that AA easily reduces the product of Do oxidation (dopaminequinone) [12,13], we performed a hydrodynamic voltammogram for Do in a 0.050 M phosphate buffer solution pH 7.40 containing 1.0×10^{-3} M AA (Fig. 2c). Since under these conditions there is a local increase of Do at the interface due to the chemical reaction between dopaminequinone and AA, the sensitivity largely improves. Another interesting advantage offered by CNTPE-Mel is the possibility to obtain an important oxidation current at potentials at which there is no response at the bare CNTPE (as it was shown in Fig. 1). Previous studies have demonstrated that the sensitivity for Do does not change for AA concentrations in the buffer solution higher than 1.0×10^{-3} M [12].

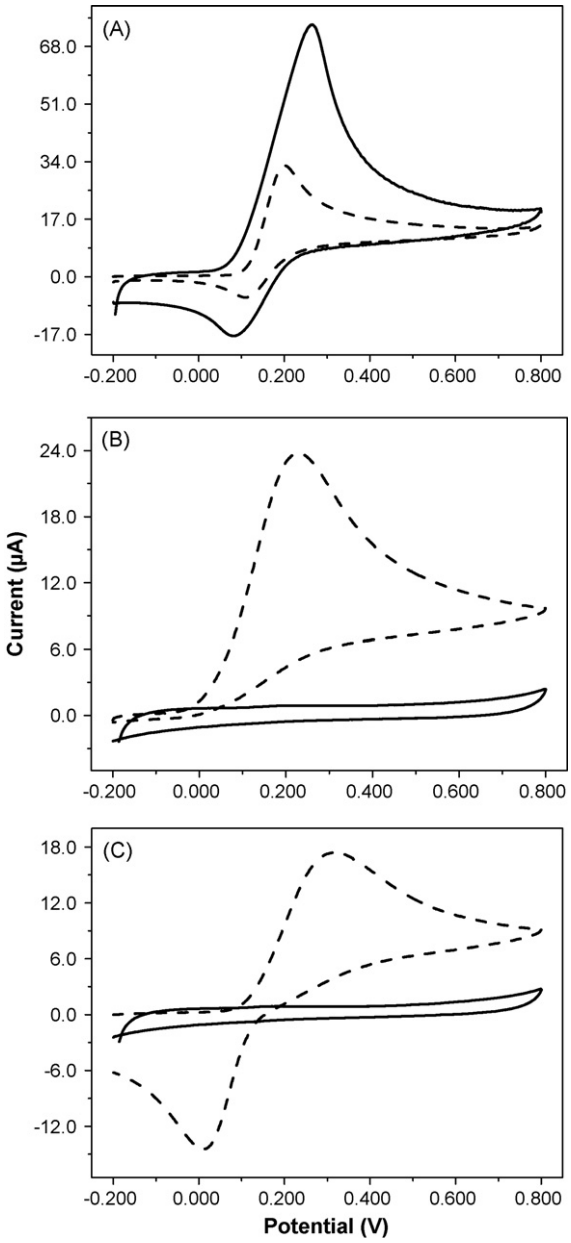

Fig. 1. Cyclic voltammograms obtained for 1.0×10^{-3} M Do (A), AA (B), and dopac (C) at CNTPE (- - -) and at CNTPE-Mel (—). Scan rate: 0.100 V/s.

The selectivity of the electrochemical quantification of Do is a crucial aspect. We evaluate the interference of AA and dopac on the response to Do from amperometric experiments at 0.200 V under the selected conditions. Fig. 3 shows the amperometric response at 0.200 V for five successive additions of 1.0×10^{-4} M AA and one addition of 5.0×10^{-5} M dopac followed by the addition of 1.0×10^{-6} M Do. Almost no interference was observed for AA (2.6%) and dopac (0.9%) even at such high levels that correspond to the maximum physiological concentrations. Similar experiments were performed by successive additions of uric acid (UA, up to 5.0×10^{-4} M) and acetaminophen (up to 1.0×10^{-3} M). For the maximum level of UA, the interference was 3.6%, while for acetaminophen, it was 2.5% (not shown). It is important to remark that the permselective properties of the electrogenerated melanic polymer are dependent on the preparation conditions. Amperometric recordings obtained during the polymer formation from a 3.0×10^{-3} M L-dopa solution at three different potentials: 0.80 V, 0.90 V and 1.00 V demonstrated that, as the polymerization

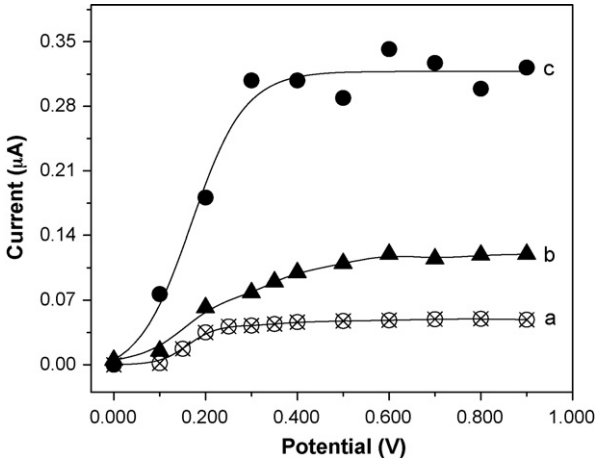

Fig. 2. Hydrodynamic voltammograms for 1.0×10^{-6} M Do at CNTPE (a) and at CNTPE-Mel in the absence (b) and in the presence (c) of 1.0×10^{-3} M AA. Supporting electrolyte: 0.050 M phosphate buffer solution pH 7.40.

potential becomes higher, the conversion of L-dopa into melanic polymer is faster, the polymerization is less efficient, and the current obtained after 120 min potentiostatization is higher, with the consequent increase in the of AA and dopac interference (not shown).

Fig. 4 displays amperometric recordings at 0.200 V for successive additions of 1.0×10^{-6} M Do (A) performed in the presence of 1.0×10^{-3} M AA in the buffer solution. A well-defined response is obtained after each addition of Do. Even for additions of 1.0×10^{-8} M Do a clear response is also obtained (not shown) demonstrating the advantages of the polymeric layer that makes possible a high increase in sensitivity. Fig. 4B displays the calibration plots obtained for additions of 5.0×10^{-8} M Do at CNTPE-Mel (with 1.0×10^{-3} M AA in the buffer solution). While there is almost no response at bare CNTPE for such small Do concentrations (not shown), the sensitivity obtained at CNTPE-Mel is $(3.04 \pm 0.09) \times 10^5$ μA M^{-1}. The detection limit at CNTPE-Mel was 2.0 nM Do (taken as 3.3 times the standard deviation of the blank signal/sensitivity ratio). For comparison, it is interesting to mention that the current for 1.0×10^{-7} M Do is 41 times higher at CNTPE-Mel than at bare CNTPE. The reproducibility for the sensitivities obtained from eight calibration plots using four polymer modified electrodes was 12%.

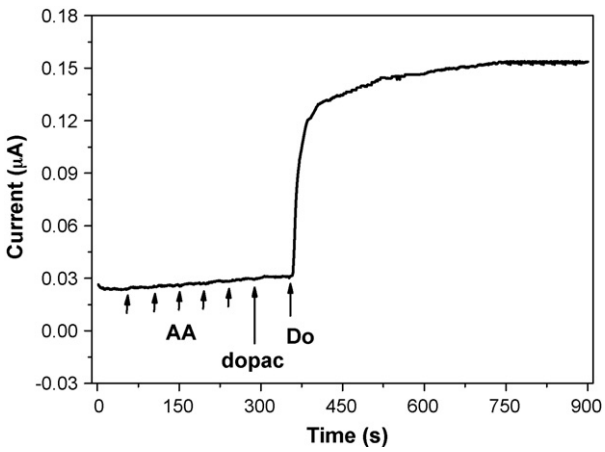

Fig. 3. Amperometric recording obtained at CNTPE-Mel at 0.200 V for five successive additions of 1.0×10^{-3} M AA, one addition of 5.0×10^{-5} M dopac and one addition of 1.0×10^{-6} M Do. Supporting electrolyte: 0.050 M phosphate buffer solution pH 7.40.

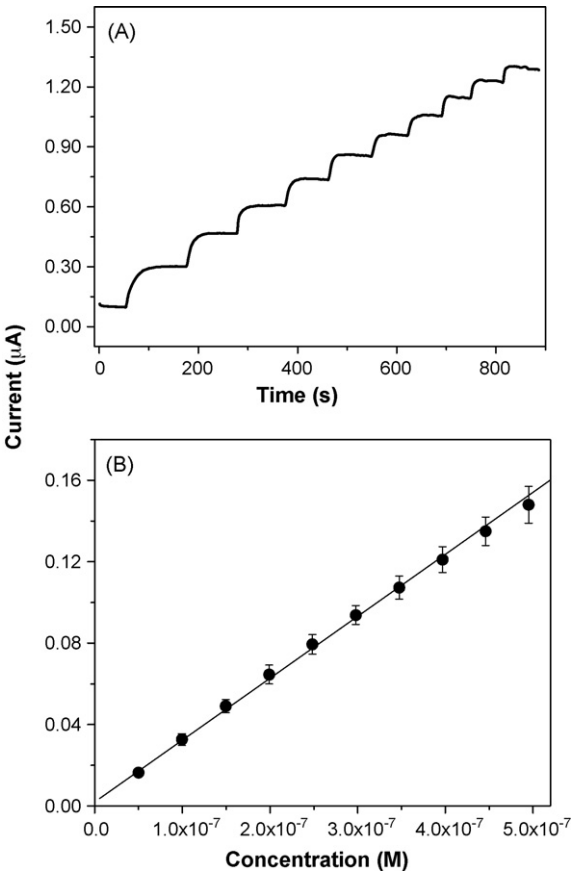

Fig. 4. Amperometric recordings obtained at 0.200 V for successive additions of 1.0×10^{-6} M Do (A) in the presence of 1.0×10^{-3} M AA. (B) Calibration plots obtained for additions of 5.0×10^{-8} M Do at CNTPE-Mel with 1.0×10^{-3} M AA in the buffer solution. Supporting electrolyte: 0.050 M phosphate buffer solution pH 7.40.

3.2. Detection of Do by differential pulse voltammetry-adsorptive stripping with medium exchange

Even when the amperometric determination of Do at CNTPE-Mel has demonstrated to be highly sensitive, we also develop another analytical methodology to quantify Do based on the adsorptive stripping with medium exchange. Under these conditions, since the determination is done in a sample-free buffer solution, it is possible to largely decrease the matrix effects.

Fig. 5 shows DPVs obtained in a 0.050 M phosphate buffer solution after 5.0 min accumulation at open circuit potential in 5.0×10^{-7} M Do (A), 1.0×10^{-3} M AA (B), and 5.0×10^{-5} M dopac (C) at bare CNTPE (dotted line) and at melanin-modified CNTPE (CNTPE-Mel, solid line). The results demonstrate that at bare CNTPE is not possible to quantify Do in the presence of AA and dopac due to the immediacy of their oxidation potentials and the adsorption of dopac and AA. On the contrary, at Mel-CNTPE, there is a significant enhancement of the Do oxidation signal (0.0645 μA at bare CNTPE vs. 0.574 μA at CNTPE-Mel) while there is no response neither for AA or dopac due to the expected repulsion of these compounds by the melanic polymer. Therefore, in addition to the improvement in Do oxidation signal, the presence of the melanin layer at the CNTPE surface, allows a selective quantification of Do.

Fig. 6 displays the DPV response obtained in a fresh 0.050 M phosphate buffer solution after 5.0 min accumulation at open circuit potential in a 5.0×10^{-7} M Do solution alone (dotted line) and 5.0×10^{-7} M Do + 1.0×10^{-3} M AA + 5.0×10^{-5} M dopac (solid line). The oxidation current for Do alone was 0.574 μA, while in the presence of AA and dopac, it was 0.610 μA, that is just 6.3% higher than

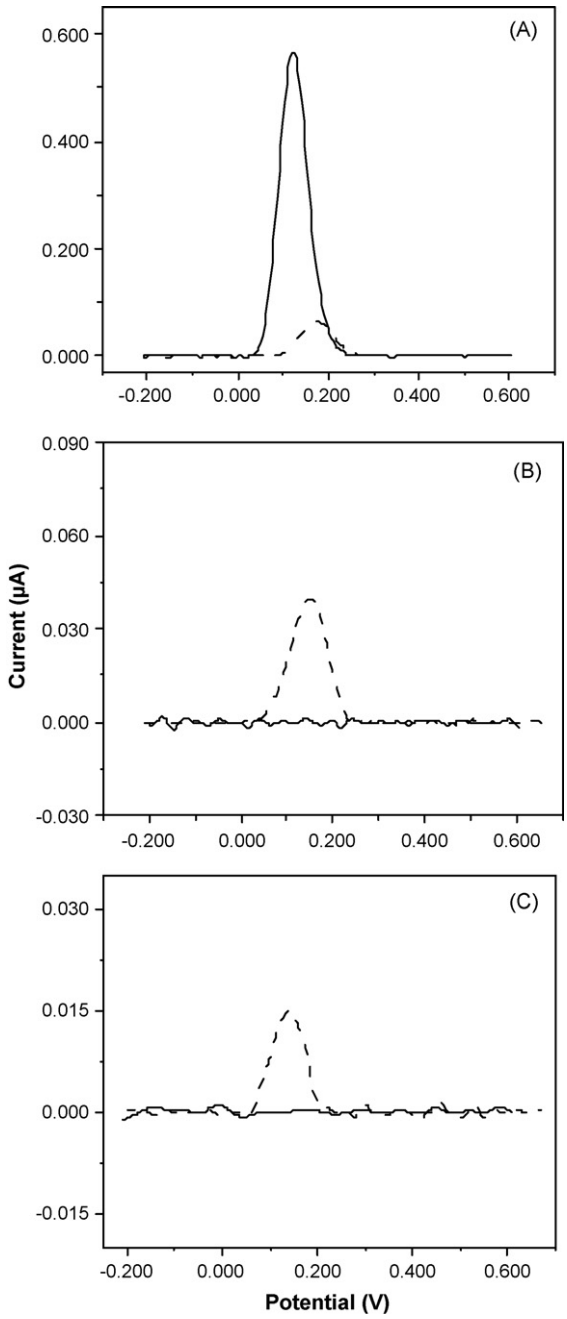

Fig. 5. Differential pulse voltammograms obtained in a 0.050 M phosphate buffer solution pH 7.40 after 5.0 min accumulation at open circuit potential in 5.0×10^{-7} M Do (A), 1.0×10^{-3} M AA (B); and 5.0×10^{-5} M dopac (C) at bare CNTPE (dotted line) and at CNTPE-Mel (solid line). Pulse height: 4 mV; pulse amplitude: 50 mV; period: 200 ms.

the signal obtained for Do alone. This small difference indicates that even for such a high excess of AA (2000-fold) and dopac (100-fold) there is no interference in the DPV-adsorptive stripping of Do.

The influence of the adsorption time during the accumulation step on the analytical performance of the sensor was also evaluated for 1.0×10^{-7} M Do. The voltammetric signal increases almost linearly at the beginning, to level off at around 5.0 min (not shown). Longer times produce almost no changes in the voltammetric signal. Therefore, a time of 5.0 min was selected for further experiments.

Fig. 7A shows DPVs for different concentrations of Do from 5.0×10^{-8} M to 5.0×10^{-7} M and Fig. 7B displays the corresponding calibration plot. The sensitivity is $(1.21 \pm 0.03) \times 10^{6}$ μA M^{-1}

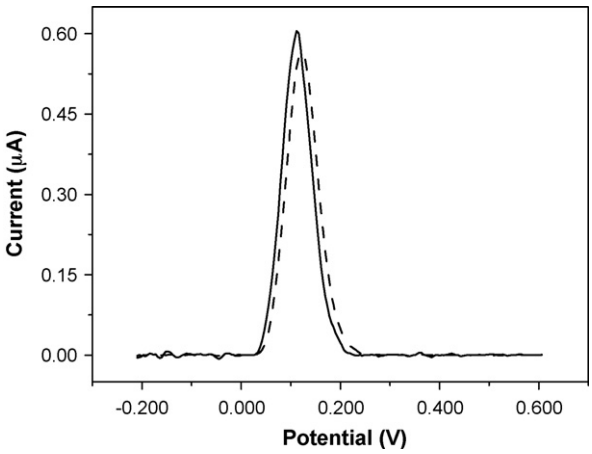

Fig. 6. Differential pulse voltammograms obtained in a 0.050 M phosphate buffer solution pH 7.40 after 5.0 min accumulation at open circuit potential in 5.0×10^{-7} M Do alone (dotted line) and 5.0×10^{-7} M Do + 1.0×10^{-3} M AA + 5.0×10^{-5} M dopac (solid line). Other conditions as in Fig. 5.

($r = 0.992$), the linear range is up to 1.0×10^{-6} M, and the detection limit is 2.0×10^{-8} M. The R.S.D. for four successive Do determinations using the same surface was 9.0%. The sensitivities for electrodes prepared with four different polymers and two electrodes for each polymer, gave an R.S.D. of 2.7%.

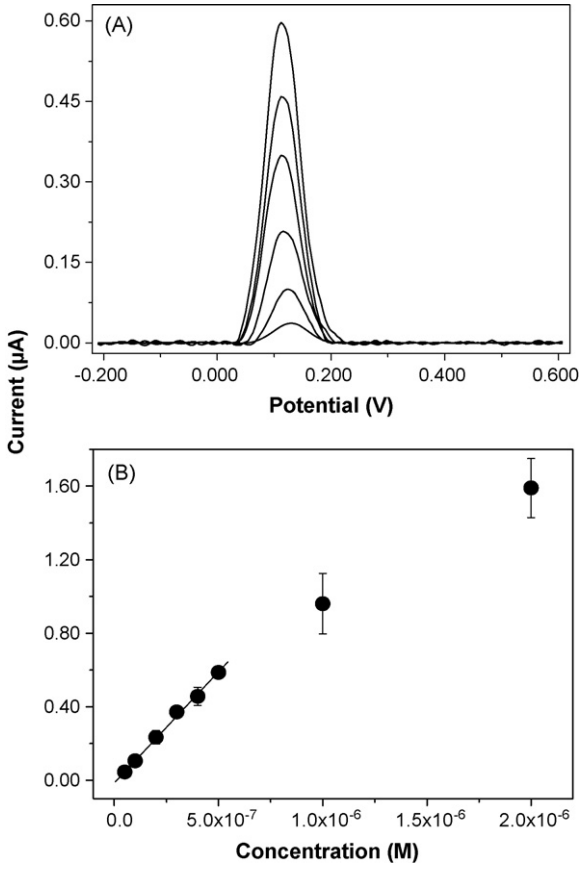

Fig. 7. (A) Differential pulse voltammograms obtained in a 0.050 M phosphate buffer solution pH 7.40 after 5.0 min accumulation at open circuit potential in Do solutions of different concentrations: 5.0×10^{-8} M; 1.0×10^{-7} M; 2.0×10^{-7} M; 3.0×10^{-7} M; 4.0×10^{-7} M; and 5.0×10^{-7} M. (B) Calibration plot obtained from (A). Other conditions as in Fig. 5.

4. Conclusions

The polymerization of L-dopa at CNTPE at potentials even lower than at other carbon surfaces [13] has demonstrated to be highly successful. The resulting melanin-modified CNTPE presents excellent advantages for the quantification of Do due to the permselective properties of the polymer and the presence of CNTs. In this way, it was possible to detect nM levels of Do in a highly selective way, either by amperometry or by adsorptive stripping after medium exchange, with no interference of large excess of AA and dopac, usual interferents in nervous centers. The detection limits were lower than previously reported methodologies [8,10] and similar to others [12–14,26], demonstrating the efficiency of the proposed sensor.

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