A simple derivatization of multiwalled carbon nanotubes with nitroaromatics in aqueous media: Modification with nitroso/hydroxylamine groups

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ABSTRACT

We report that GCE modified with MWCNTs can be derivatized by the nitroaromatic drug nitrendipine (NTD) ((RS)-ethyl methyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate) simply by dipping the electrode in a solution of 0.1 M Britton–Robinson buffer containing 0.1 mM NTD (pH 2) for 4 min at open circuit. The derivatized electrode is thus reduced, producing the corresponding hydroxylamine derivative-modified electrode, which can be further oxidized to the nitroso derivative. A stable nitroso/hydroxylamine derivative couple appears if the modified electrode is conveniently cycled. With proper selection of the adequate potential, the derivatized electrode can be modified as nitroso or hydroxylamine derivatives.

1. Introduction

The electrochemistry of nitroaromatic compounds has been widely studied on conventional electrodes, however only a few papers are devoted to applications of nitro compounds on carbon nanotubes (CNTs) [1–8].

Modification of electrodes with nitro groups has been described on conventional electrodes, including Au and glassy carbon electrodes (GCEs)[9–11]. Ortiz et al. [9] described the electrochemistry of 4-nitrophenyl modified GCEs in aqueous media using aromatic diazonium salts; in addition, Gui et al. [10] recently published a comparative study of the electrochemical reduction of 4-nitrophenyl covalently grafted on gold and GCE surfaces by electrochemical reductive adsorption of the corresponding diazonium salt. Mano et al. [11] used nitrofluorenone derivatives to modify the surface of GCEs. Subsequent reduction of one or more nitro groups of the nitrofluorenone derivative led to reversible NO/NHOH redox couples on the surface. This reaction has been used for the electrocatalytic oxidation of NADH.

Compton et al. [12] reported the derivatization of multiwalled carbon nanotubes (MWCNTs) by chemical reduction of 4-nitrobenzenediazonium tetrafluoroborate with hypophosphorous acid. The formed 4-nitrophenyl-MWCNTs (NB-MWCNTs) were abrasively immobilized onto the surface of a basal plane pyrolytic graphite (BPPG) electrode and characterized by cyclic voltammetry. Another study [13] showed that graphite powder and MWCNTs can be derivatized by 4-nitrobenzylamine (4-NBA) simply by stirring the graphite powder or MWCNTs in a solution of acetonitrile containing 10 mM 4-NBA. The resulting 4-NBA-MWCNT powder was abrasively immobilized onto the surface of a clean BPPG electrode. The results of the cyclic voltammetric characterization for both 4-NBA-MWCNT- and NB-MWCNT-modified electrodes were qualitatively identical, producing a quasi-reversible couple after the first sweep, attributed to the two-electron, two-proton oxidation/reduction of the aryl-hydroxylamine/aryl-nitroso moieties.

Nitrendipine (NTD), (RS)-ethyl methyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate, is a nitroaromatic compound with pharmacological activity as a calcium channel-blocking drug. The electrochemical reduction of NTD on Hg, GC and carbon paste (CP) electrodes in hydroalcoholic solutions has been the subject of voltammetric investigations [14–16], but its voltammetric behavior on MWCNTs remains unexplored. The voltammetric reduction of NTD in aqueous medium generally follows the pattern of all nitroaromatics, producing a single irreversible 4-electron 4-proton reduction peak according to the following, well-known Eq. (1):

$$Ar-NO_2 + 4e^- + 4H^+ \rightarrow Ar-NHOH + H_2O \qquad (1)$$

and a quasi-reversible wave attributed to two-electron, two-proton oxidation/reduction of the aryl-hydroxylamine/aryl-nitroso moieties, according to the following Eq. (2):

$$Ar-NHOH \rightleftharpoons Ar-NO + 2e^- + 2H^+ \qquad (2)$$

Based on our interest in drug interactions, we aimed to immobilize drugs, such as NTD, on electrodes. In the present study, we developed a simple in situ procedure to modify the MWCNTGC electrode with NTD or either aryl-hydroxylamine or aryl-nitroso derivatives of NTD.

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2. Experimental

2.1. Apparatus and reagents

Electrochemical measurements were carried out in a conventional three-electrode cell. Voltammetric curves were recorded on a CHI 900 (CH Instruments Inc., USA) instrument. We used a GCE with a 3-mm diameter (Model CHI104, CH Instruments) as the working electrode. A platinum wire (BASiMW-1032) and an Ag/AgCl/NaCl electrode (0.3 M) (BASi MF-2052) were used as the auxiliary and reference electrodes. All potentials are referred to relative to the Ag/AgCl reference electrode.

The MWCNTs (1.5 μm length and 10 nm diameter) were obtained from Dropsens S.L., Spain. All work was with MWCNTs, but will abbreviate to CNT for simplicity.

All voltammetric experiments were obtained after bubbling with N_2 for 10 min in the cell before each run. The temperature was held constant at 25 ± 0.1 °C.

We used a 0.1 M Britton–Robinson buffer, pH 2 (6.74 ml boric acid, 6.183 g phosphoric acid and 5.72 ml of 0.1 M acetic acid and filled to 1 L with H_2O), as the aqueous medium. All aqueous solutions were prepared with deionized water purified with a Milli-Q Ultrapure water system.

NTD was obtained from Laboratorio Chile S.A. All of the other reagents were of analytical grade.

Stock solutions of NTD were prepared at a constant concentration of 2×10^{-2} M in ethanol. The working solutions were prepared by diluting the stock solution with 0.1 M Britton–Robinson buffer, pH 2 to obtain solutions with final concentrations of 0.1 mM NTD.

2.2. Preparation of CNT suspensions and modified GCEs

Before each modification, the GCE was cleaned by polishing with 0.3 μm and 0.05 μm alumina, and then was washed thoroughly with water. The CNTs were dispersed at 4 mg/mL with water by sonication for 5 min. The sonication procedure was repeated three times. Immobilization of CNTs was performed by casting the GCE with 5 μL of the CNT dispersion. The optimum conditions were obtained by drying the dispersion dropped onto the GCE for 20 min at 50 °C in an oven.

2.3. Procedures to modify CNTGCE

NTD accumulation: The modified CNTGCE was immersed in a stirred (250 rpm) solution of 0.1 M Britton–Robinson buffer containing 0.1 mM NTD, pH 2. The optimum accumulation time was 4 min and no potential was applied during this step, yielding the modified electrode NTD-CNTGCE.

Voltammetric transduction: After the accumulation process, the NTD-CNTGCE was submitted to cyclic voltammetry (CV) at sweep rates between 20 mV/s and 250 mV/s, according to different procedures: (A) the first procedure involved a conventional CV experiment of the NTD-CNTGCE in a solution of 0.1 M Britton–Robinson buffer containing 0.1 mM NTD, pH 2, using the following potential parameters: initial potential $(E_i) = 0$ V; low potential $(E_l) = -0.7$ V and high potential $(E_h) = +0.6$ V vs. Ag/AgCl and starting with a negative sweep potential; (B) the second procedure involved removal and washing of the modified electrode after the accumulation process and then inserting it in a second cell containing only a buffer solution; next, the CV experiment was run using the following potential parameters: $E_i = 0$ V; $E_l = -0.7$ V and $E_h = +0.6$ V and starting with a negative sweep potential; (C) the third procedure involved a CV experiment including a first electrolysis at -0.7 V for 30 s. Next, the Britton–Robinson buffer + NTD solution was removed and the electrodes were washed completely with the buffer. After washing, the electrodes were inserted in a second cell containing only Britton–

Robinson buffer, and the CV experiment was carried out using the following potential parameters; $E_i = 0$ V, $E_h = +0.6$ V and $E_l = 0$ V, starting with the positive sweep potential; (D) the fourth procedure involved a CV experiment including a first electrolysis at -0.7 V for 30 s; then, the Britton–Robinson buffer + NTD solution was removed, and the electrodes were washed completely with the buffer. After washing, the electrodes were inserted in a second cell containing only Britton–Robinson buffer. A second electrolysis was carried out at 0.6 V for 30 s, and then the CV experiment was performed using the following potential parameters: $E_i = +0.6$ V, $E_h = +0.6$ V and $E_l = 0$ V, starting with the negative sweep potential.

3. Results and discussion

We prepared a modified CNTGC electrode by casting a dispersion of CNTs on a GCE according to the above-described procedure. Next, the CNTGCE was dipped in a voltammetric cell containing a solution of 0.1 M Britton–Robinson buffer, 0.1 mM NTD, at pH 2 for 4 min at open circuit. Next, we carried out a cyclic voltammetric experiment, according to the above-described procedure A. Fig. 1(a) shows cyclic voltammograms for the first (solid line) and second (dotted line) scans. In the first scan, a large sharp peak, which is due to the irreversible 4-electron 4-proton reduction (Eq. (1)) of the nitro
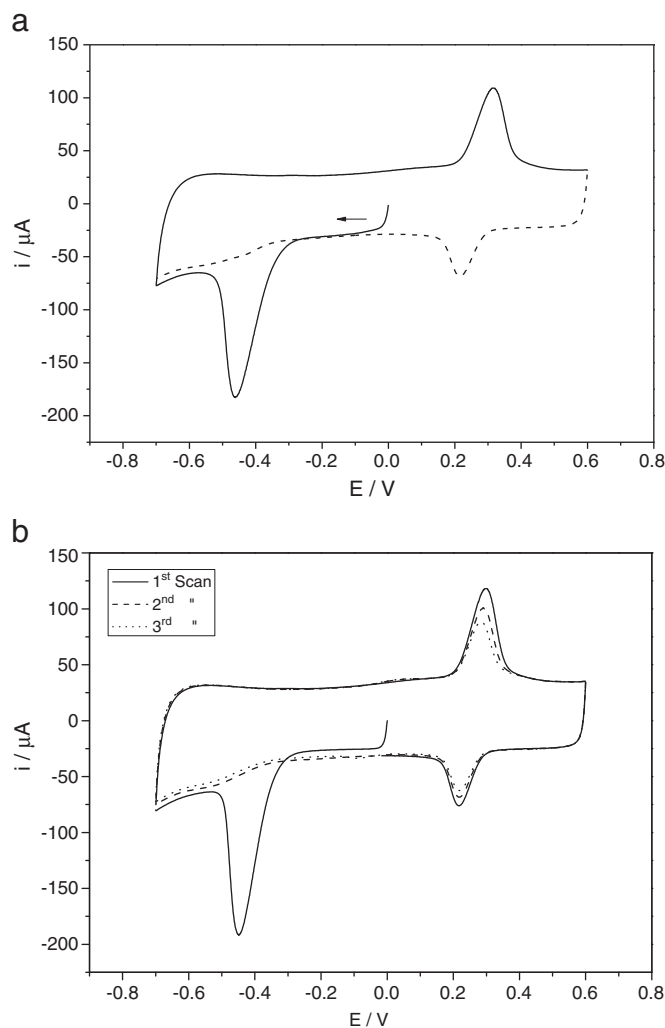
a

b

Fig. 1. (a) Cyclic voltammograms from a solution of 0.1 M Britton–Robinson buffer, 0.1 mM NTD, at pH 2 after accumulation for 4 min at open circuit on a CNTGCE according to procedure A. First scan (solid line) and second scan (dashed line). (b) Cyclic voltammograms of 0.1 M Britton–Robinson buffer at pH 2 on NTD-CNTGCE, according to procedure B. 0.1 V/s.

group of the NTD molecule to the corresponding hydroxylamine derivative, was observed at -0.47 V. When the scan direction was reversed, we observed only one oxidation peak at 0.32 V, with its corresponding reduction peak at 0.2 V. This redox couple is due to the quasi-reversible 2-electron, 2-proton oxidation/reduction couple (Eq. (2)) of the hydroxylamine/nitroso derivatives. In the second scan, the peak due to the reduction of the nitro group to the hydroxylamine derivative completely disappeared in spite of the homogeneous medium containing the nitro compound. This behavior was maintained in successive scans. These results confirm that all of the adsorbed NTD was reduced in the first scan and the active sites on the electrode were occupied by other adsorbed species (i.e. the adsorbed hydroxylamine derivative), hindering the reduction of NTD from the homogeneous medium. The same behavior (Fig. 1 (b)) was observed if the experiment was carried out in two different steps according to procedure B. Therefore, we hypothesized that NTD is adsorbed on the modified CNTGCE by dipping the electrode in the NTD solution at open circuit for 4 min, producing a nitrendipine modified electrode (NTD-CNTGCE). As shown in Fig. 1, the cyclic voltammetric behavior is qualitatively similar to those previously reported for MWCNTs modified with nitrobenzene or 4-nitrobenzy-lamine [12,13]. These results are surprising because our procedure to obtain nitroaromatic modified MWCNT was substantially different, involving only a dipping procedure at open circuit. By contrast, the other MWCNTs were prepared by chemical modification of the nanotubes and then abrasively immobilized onto the surface of a clean BPPG electrode.

We also carried out experiments in which the accumulation step and a first-reduction step at −0.7 V were performed in a solution containing NTD + buffer. After this step, the electrode was removed from the solution; after a complete washing with buffer, we inserted the electrode in a new fresh solution containing only the buffer and then submitted it to the CV process according to the above-described procedures C or D. From the results displayed in Fig. 2(a), we deduced that NTD was adsorbed on the CNTs and then reduced to the hydroxylamine derivative at −0.7 V, producing a modified electrode with a hydroxylamine derivative (NTDOH-CNTGCE) able to be manipulated (removed from the initial solution containing NTD + buffer, washed and inserted in the new solution without NTD) and submitted to CV experiments. As shown in Fig. 2(b), we also demonstrated the formation of a nitroso derivative modified electrode (NTDNO-CNTGCE). By manipulating the potential selection over the NTD-CNTGCE, we could produce NTDNO-CNTGCE or NTDOH-CNTGCE. Potentials more positives than 0.4 V or more negatives than 0.1 V produce nitroso or hydroxylamine derivative modified CNTGC electrodes, respectively. Although Fig. 2(a) and (b) shows only five scans, the oxidation/reduction wave of the nitroso/hydroxylamine derivative couple was maintained over several scans when the electrode was cycled between 0 and 0.6 V. Fig. 2(c) shows the result of 100 successive cycles between 0 and 0.6 V, consistent with both nitroso and hydroxylamine derivatives remaining adsorbed on the electrode surface but with an approximately 75% loss of signal after 100 cycles, most likely due to desorption.

We also used nitrobenzene and found a qualitatively similar behavior to NTD; however, we observed diminished adsorption of the nitro compound, indicating that the nitroaromatic moiety of NTD is responsible for the voltammetric response. The dihydropyridine moiety produces an increased adsorption on the CNT. Further work is being conducted to extend the revealed procedure to other aromatic nitrocompounds.

The proposed derivatization procedure involves the physisorption of NTD on CNTGCEs, producing the accumulation of the nitrocompound on the active sites of the electrode. This physisorption is likely due to a hydrophobic effect and π–π bonds between the nitrendipine molecules and the CNTs. Indeed, π–π interactions have been used to explain the adsorption of organic molecules with a C=C double
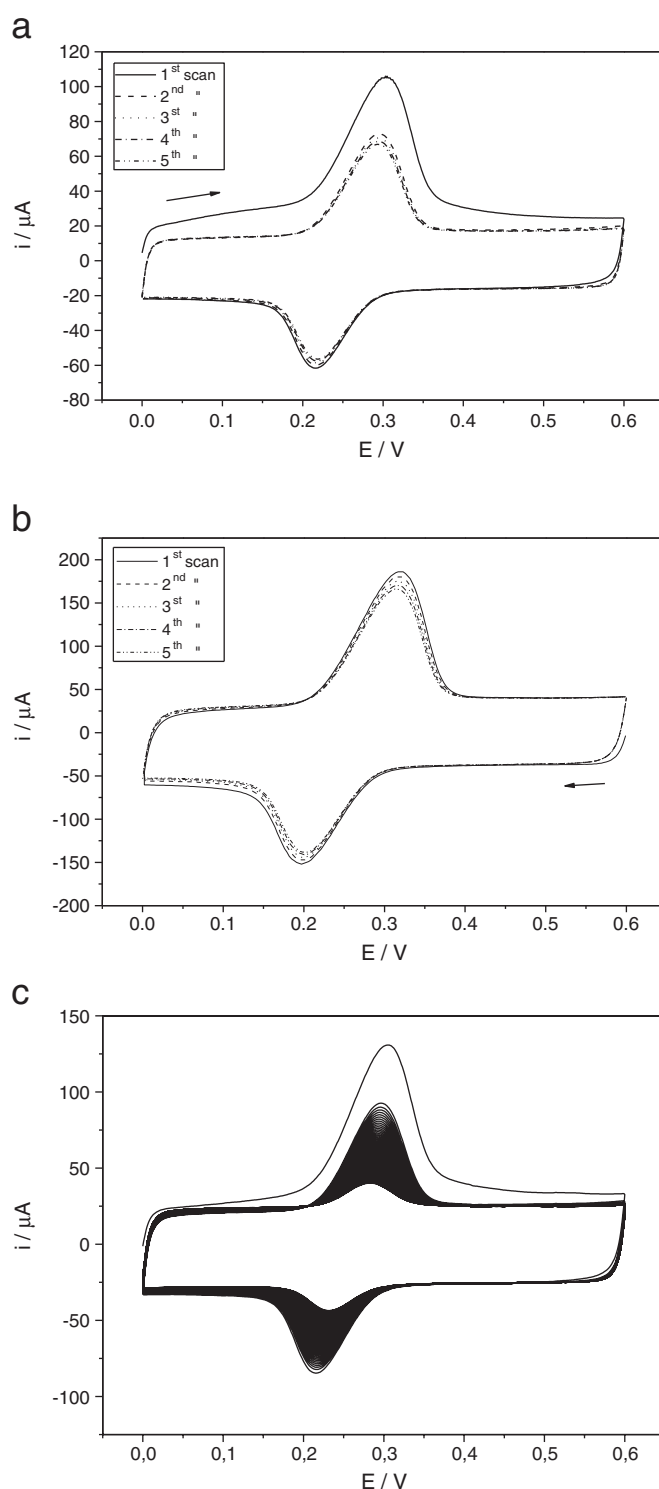

Fig. 2. Cyclic voltammograms from a solution containing only 0.1 M Britton–Robinson buffer at pH 2 on a CNTGCE modified according to: (a) procedure C, $E_i = 0$ V, $E_h = +0.6$ V and $E_l = 0$ V, starting with the positive sweep potential. 0.1 V/s; (b) procedure D, $E_i = +0.6$ V, $E_h = +0.6$ V and $E_l = 0$ V, starting with the negative sweep potential; (c) one hundred successive cyclic voltammograms according to procedure C, $E_i = 0$ V, $E_h = +0.6$ V and $E_l = 0$ V, starting with the positive sweep potential. 0.1 V/s.

bond or a benzene ring on the surface of CNTs; the π electrons of the organic compound interact with the π electrons of the benzene rings on the CNT surface through π–π electron coupling [17]. A recent study on the adsorption of nitro-substituted aromatics on SWCNT described that the mechanism is predominantly physisorption

through π–π stacking, with additional contributions from NO$_2$ groups [18].

The full width at half height (FWHH) of the NHOH/NO (and even the NO$_2$) peaks is quite narrow (~100 mV), which suggests a fairly uniform environment that the NTD molecules are in. Probably the CNT surface to have randomly aligned tubes, which would present pockets of surfaces in all sorts of environments. Perhaps the NTDs is trapped in these pockets that survive washing and it giving the voltammetric signal.

4. Conclusions

We derivatized a CNTGCE with an aromatic nitro compound, NTD, using an easy procedure involving a first accumulation step by dipping the CNTGCE in a solution of 0.1 M Britton–Robinson buffer containing 0.1 mM NTD at pH 2 for 4 min at open circuit. After the accumulation process, the nitro-derivatized electrode is sufficiently stable enough to be washed, manipulated and further reduced to form an hydroxylamine-derivatized electrode, which also can be oxidized to form a nitroso-derivatized electrode.

Further work is being conducted to extend the revealed procedure to other aromatic nitrocompounds.

Acknowledgements

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