

Electrochemistry and XPS of 2,7-dinitro-9-fluorenone immobilized on multi-walled carbon nanotubes

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Abstract We report that glassy carbon electrodes (GCE) modified with multi-walled carbon nanotubes (MWCNTs) can be derivatized with 2,7-dinitro-9-fluorenone (2,7-NFN). The derivatization procedure involves simple immersion of the MWCNT-modified electrode in a solution containing 2,7-NFN. SEM images indicate that the MWCNTs form a twisted, three-dimensional array that remains attached to the GCE surface. Both electrochemical and spectroscopic measurements (XPS) indicate that 2,7-NFN is immobilized on the electrode, most probably by being trapped within the pockets of the mentioned three-dimensional array. The electrode with the immobilized 2,7-NFN is sufficiently stable to resist washing but allows both its manipulation and reduction to form the hydroxylamine derivative. This derivative can be oxidized to form a nitroso compound. Both the nitroso and hydroxylamine derivatives are also trapped within the MWCNT surface pockets. Furthermore, depending on the selected working potential, the nature of the encapsulated compound, i.e., nitro, nitroso, or hydroxylamine derivative and mixtures thereof, can be selected. All these redox pathways were verified by cyclic voltammetry and XPS.

Keywords 2,7-Dinitro-9-fluorenone · MWCNT · Modified electrode

Introduction

In the last decade, the incorporation of carbon materials, such as carbon nanotubes (CNTs), has modified the concept for the electrode phase, changing the approach to electrochemistry. Specifically, the remarkable electronic and structural characteristics [1–7] of CNTs have attracted the attention of many electrochemical researchers, making them a material of choice as electrodes. One of the most interesting characteristics of the CNTs is their feasibility to be modified and the possibility of tailoring electrodes according to the needs of a particular application.

In general, the strategies for modifying CNTs [7] can be summarized into three main areas: (a) chemisorption, which implies the covalent bonding of the modifier to the CNTs either through chemical or electrochemical activation, (b) physisorption, which involves the physical adsorption of the modifier to the CNT, and (c) miscellaneous methods.

Different authors have performed the modification of CNTs with nitro groups or nitrocompounds. Wang et al. [8] efficiently introduced nitro groups on the surface of MWCNTs by conventional nitration procedures such that they can be subsequently reduced readily to amino groups. The obtained amino-modified MWCNTs are useful in a variety of applications, such as nanotube-reinforced polymers, anchoring active objects in catalysis, biological systems and sensors.

Compton et al. [9] reported the derivatization of multi-walled 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

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surface of a basal plane pyrolytic graphite (BPPG) electrode and were characterized by cyclic voltammetry. Another study [10] showed the derivatization of graphite powder or MWCN Ts by 4-nitrobenzylamine (4-NBA) 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, which was attributed to the two-electron, two-proton oxidation/reduction of the aryl-hydroxylamine/aryl-nitroso moieties.

Furthermore, we recently reported [11–13] that GCEs modified with MWCNTs can be derivatized by some nitroaromatic compounds by dipping the electrode in a solution containing the nitroaromatic for a few minutes 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 electrode potential, the derivatized electrode can be modified to nitroso or hydroxylamine derivatives.

Modification of electrodes with nitro groups has also been described on conventional electrodes, including glassy carbon electrodes (GCEs). Mano et al. [14] 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 reduced nicotinamide coenzyme (NADH).

In this paper, we reveal a new, modified electrode in which the nitrofluorenone derivative is immobilized in the electrode by trapping it within the pockets of a three-dimensional array of MWCNTs previously attached to the GCE surface. According to our hypothesis, this new electrode will present improved characteristics compared with those previously described for the naked GCE.

Experimental

Chemicals

2,7-Dinitro-9-fluorenone (2,7-NFN, 99 %) (Fig. 1) and dioxolane (1,3-dioxolane, 99.8 %) were supplied by Sigma-Aldrich[®]. Ethanol (95 %) and acetone were supplied by Lab-Tec (Chile). *Ortho*-phosphoric, glacial acetic and boric acid (H₃PO₄, CH₃COOH and H₃BO₃, 85, 95 and 99.5 %, respectively), potassium dihydrogen phosphate (KH₂PO₄, 99.5 %)

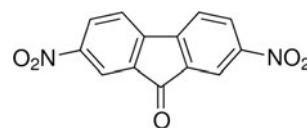


Fig. 1 Molecular structure of 2,7-NFN

and *di*-potassium hydrogen phosphate (K₂HPO₄, 99 %) were supplied by Merck[®]. Stock solutions of 1×10^{-3} M 2,7-NFN were prepared in dioxolane. Two support electrolytes were used: Britton-Robinson buffer 0.1 M (6.18 g of B(OH)₃, 5.7 mL of CH₃COOH and 6.74 mL of H₃PO₄ in 1 L of MilliQ water) whose pH was adjusted to different values using concentrated HCl and NaOH solutions and phosphate buffer solution (PBS, 0.1 M) (22.83 g of K₂HPO₄ and 13.81 g of KH₂PO₄ in 1 L of MilliQ water) whose pH was adjusted to 7.0 using concentrated HCl.

Equipment

Electrochemical measurements were performed using a BASi 100 voltammetric analyser. Measurements were performed with a conventional 3-electrode system: Glassy carbon (GC) 3 mm diameter (CH Instruments[®]) or MWCNT modified-GC was used as the working electrode, and a Pt wire and a Ag/AgCl (1 M KCl) electrode with a Teflon tip were used as the auxiliary and reference electrodes, respectively. A small electrochemical cell containing 8 mL of electrolyte solution was used. pH adjustment was monitored using a PMX 3000 WTW pH/Ion meter Microprocessor (basic pH) and a pH Meter 537 WTW Microprocessor (acidic pH).

Nitro-functionalized MWCNT-GC electrodes

The GC electrodes were polished with 0.3 and 0.05 μm particle size alumina and were washed with water. The modification with the MWCNTs was performed by drop coating following previously described procedures [13]. Briefly, 5 μL of MWCNT dispersion (3 mg/1 mL of dioxolane) was deposited on the surface of the GC electrode. The dispersant was left to dry at ambient temperature. The MWCNTs (1.5 μm length and 10 nm diameter) were obtained from Dropsens S.L., Spain.

The MWCNT-GC surface was functionalized by a dip coating process, which consisted of immersing the electrode surface in a 2,7-NFN solution in 1,3-dioxolane for 2–4 s. This specific accumulation time (t_{acc}) was optimized under no stirring conditions and open circuit potential. The electrode was then washed with water to remove the remaining solvent and excess non-trapped nitrocompounds in the MWCNTs array.

Finally, the modified electrode was submitted to a cyclic potential sweep in an appropriate potential range to generate the corresponding redox couple. First, the –NO₂ groups are

reduced (Eq. 1), and then, -NHOH or -NO species are generated (Eq. 2).



XPS characterization

X-ray photoelectron spectroscopy (XPS) data were recorded with a Phoibos 150 analyser equipped with nine channeltrons and non-monochromatic Mg $\text{K}\alpha$ radiation under a base pressure in the spectrometer better than 5×10^{-10} torr. The spectra were acquired using a constant pass energy of 20 eV, and the binding energies are accurate within ± 0.2 eV.

SEM images

For SEM measurements, glassy carbon discs (TED Pella brand, INC (N 16524)) measuring 12.7 mm in diameter were used. The discs were previously polished with suspensions of alumina particles measuring 0.05 and 0.1 μm in diameter. The morphology of the modified electrode was investigated by SEM using an Inspect Scanning Electron Microscope F-50 operated at 20 kV.

Results and discussion

Voltammetric characterization

In a previous paper, Mano et al. [14] described the electrochemistry and the stability of adsorbed layers of different nitrofluorenone derivatives on a GCE. The behaviour can be summarized according to the cyclic voltammogram displayed in Fig. 2a. After adsorption of the 2,7-NFN, the nitro groups are irreversibly reduced to the corresponding hydroxylamine derivatives in the first cathodic potential scan (initiated at -0.2 V, solid line) at potentials of -0.41 and -0.53 V (peaks 1 and 2 in Fig. 2a). In the reverse scan, the oxidation of the hydroxylamine derivatives to nitroso derivatives produces anodic peaks 3 and 4 at potentials of -0.09 and -0.01 V, respectively. In the second cathodic scan (dashed line in Fig. 2a), two cathodic peaks (3' and 4') corresponding to the reduction of nitroso to hydroxylamine derivatives appear at -0.10 and -0.02 V, respectively. Furthermore, in the cathodic second scan, the nitro reduction peaks disappear almost entirely. In the subsequent cycles, the redox couple reaction of the nitroso/hydroxylamine derivatives is detected.

The voltammogram is different when the GCE is replaced with MWCNT-GC electrodes prepared and functionalized with 2,7-NFN according to the procedure described in the

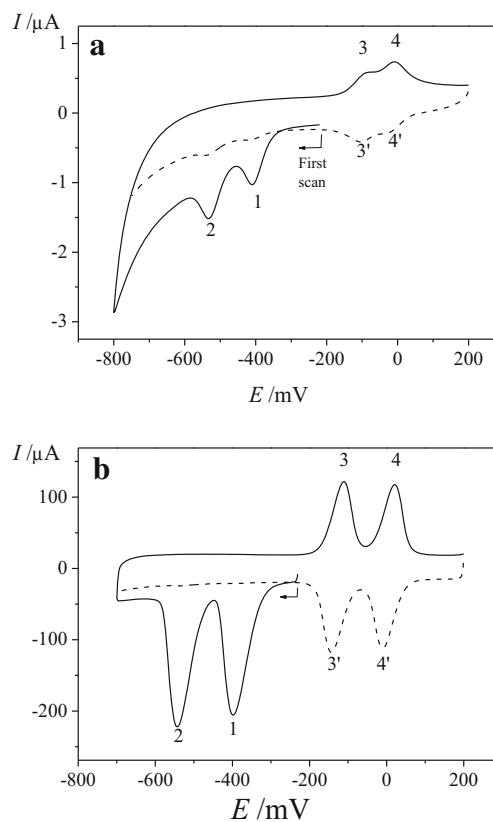


Fig. 2 GCE (a) and MWCNT-GCE (b) electrodes modified with 2,7-NFN 1×10^{-4} M in dioxolane. Cyclic voltammetry in PBS at pH 7.0. Scan rate 0.1 V s^{-1}

experimental section. The cyclic voltammograms of the first and reverse scans (solid line) and the second cathodic scan (dashed line) are shown in Fig. 2b. In the first scan, two sharp peaks (peaks 1 and 2 in Fig. 2b) with potentials peaks of -0.40 and -0.54 V can be observed corresponding to the reduction of each nitro group present in the compound. The nitro groups are reduced to the hydroxylamine derivatives, which are subsequently oxidized to nitroso derivatives in the reverse anodic scan, producing peaks 3 and 4 at potentials of -0.11 and 0.02 V, respectively. In the second cathodic scan (dashed line in Fig. 2b), two cathodic peaks (3' and 4') corresponding to the reduction of nitroso to hydroxylamine derivatives appear at -0.14 and -0.01 V, respectively. In the second cathodic scan, the nitro reduction peaks disappear entirely, showing that the trapped nitro compounds were reduced in the first scan. In the subsequent cycles, only the redox couple reaction of the nitroso/hydroxylamine derivatives is detected. The nitroso/hydroxylamine derivative couple was maintained over several scans when the electrode was cycled between -0.3 and 0.2 V at pH 2, indicating that the redox couple is immobilized in the electrode network.

As observed (Fig. 2), well-resolved peaks of 2,7-NFN are obtained with MWCNTs compared to the bare GC electrode, but the main difference is the extraordinary increase in the

peak current for all the peaks (two orders of magnitude higher compared with the bare electrode). Consequently, the use of our new proposed electrode based on trapped 2,7-NFN in the MWCNT array allows a considerable increase in sensitivity and selectivity of the voltammetric response.

Summarizing the above results, peaks 1 and 2 correspond to the process described in Eq. (1), whereas peaks 3, 4, 3' and 4' obey the process described in Eq. (2). To corroborate the pH dependence claimed in Eqs. (1) and (2), we verified our MWCNT-modified electrode with 2,7-NFN trapped within the MWCNT array at different pHs of the solution.

The evolution of the voltammograms at different pHs between pH 2 and 11 is shown in Fig. 3. The voltammograms are well-resolved, and the corresponding peak potentials, E_p , shifted with pH according to the pH dependency in Eqs. (1) and (2). The dependence of the E_p vs pH for all the peaks is shown in Fig. 4, and the corresponding slope values are shown in Table 1. From the similarity of the slope values from peaks 1 and 2, it is obvious that both peaks obey the same mechanism (Eq. 1). Analogously, the similarities of the slope from

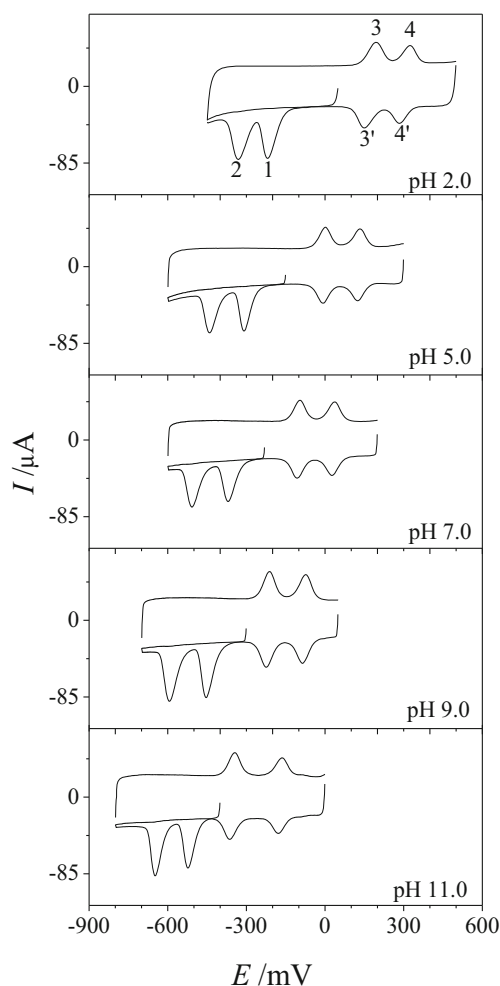


Fig. 3 Effect of pH on the MWCNT-2,7-NFN electrodes. Britton-Robinson 0.1 M buffer solution

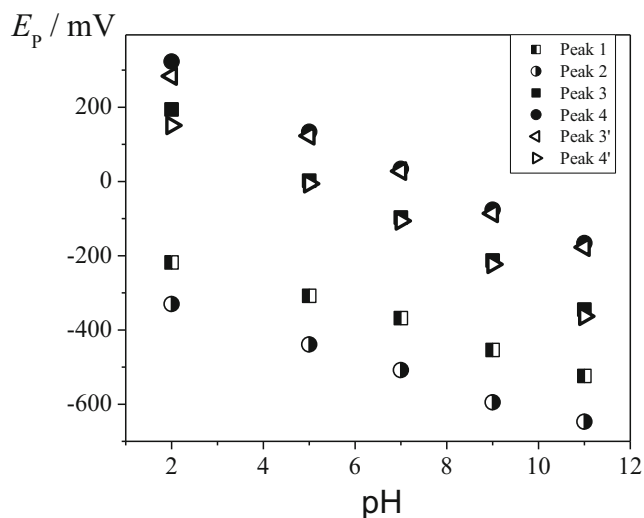


Fig. 4 Peak potential dependence with pH for all the peaks of 2,7-NFN

peaks 3, 4, 3' and 4' also are indicative that such peaks obey the same mechanism (Eq. 2). Furthermore, the irreversibility of the peaks 1 and 2 leads to that the value of the slope differs considerably from the 0.059 V/pH for the reversible case. In the case of peaks 3, 4, 3' and 4' that obey reversible couples, they are much closer to the theoretical value of 0.059 V/pH for transfers with the same number of electrons and protons.

From the voltammetric point of view, 2,7-NFN was trapped within the MWCNT array and was reduced to the hydroxylamine derivative. The oxidation of the hydroxylamine derivative causes the formation of the nitroso derivative. The results are consistent with both nitroso and hydroxylamine derivatives being trapped within the MWCNT array. Furthermore, depending on the selected working potential, the nature of the encapsulated compound, i.e., nitro, nitroso or hydroxylamine derivative and mixtures thereof, can be selected.

Scanning electron microscopy

To investigate whether the surface morphology of the nanostructure of the MWCNT network could be affected by either the functionalization performed by dipping and/or the electrochemical procedure, we collected SEM images of the modified electrodes from different samples: (a) MWCNT-GC electrode without treatment, (b) MWCNT-GC electrode functionalized

Table 1 Slope of the peak potential dependence with pH for all the peaks of 2,7-NFN

Slope dE_p/dpH (V/pH)					
Peak 1	Peak 2	Peak 3	Peak 4	Peak 3'	Peak 4'
-0.034	-0.036	-0.059	-0.054	-0.051	-0.056

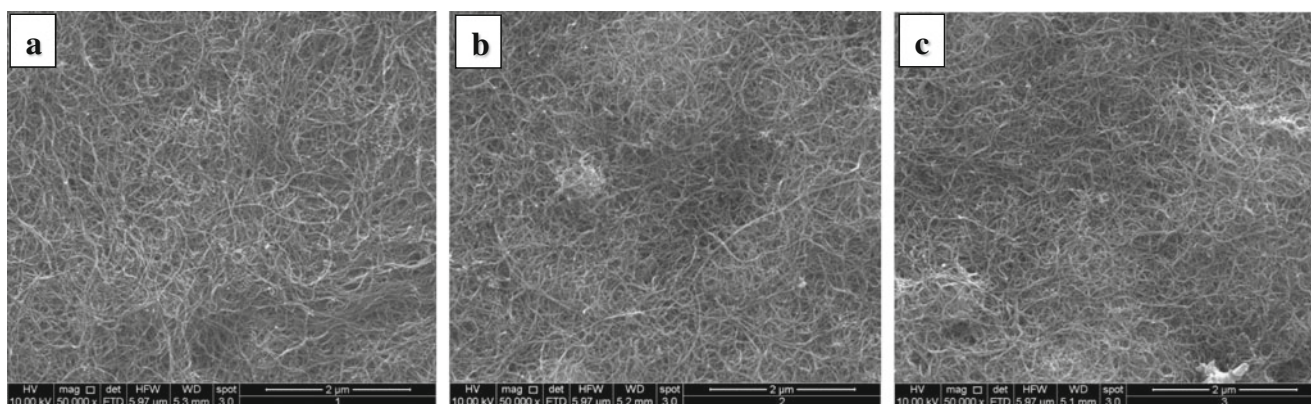


Fig. 5 SEM images of MWCNT-GC (a), 2,7-NFN-MWCNT-GC disc without an electrochemical treatment (b), 2,7-NFN-MWCNT-GC disc with both $-\text{NO}_2$ groups reduced to $-\text{NHOH}$ groups (c). Magnification $\times 50,000$

with 2,7-NFN and (c) MWCNT-GC electrode functionalized with 2,7-NFN after the electrochemical procedure.

The SEM images (Fig. 5) show the net-like distribution of the MWCNTs on the GC electrode surfaces. The result indicates that the modification of the GCE surface with the MWCNTs was successfully achieved (Fig 5a). The MWCNTs on GC follow a uniform pattern. However, no changes in morphology or in the orientation of the MWCNTs have been observed after dipping the modified GCE in the nitrocompound solution in dioxolane (Fig 5b) or after potential scans (Fig 5c). Therefore, the modified electrode remains stable because no significant changes are observed in the MWCNT array.

X-ray photoelectron spectroscopy

With the purpose of confirming the presence of 2,7-NFN in the MWCNT-GCE and its subsequent electroreduction to form hydroxylamine and nitroso compounds, we used XPS to characterize the various functional groups present in the samples and follow their evolution after the electrochemical reactions. The spectra were recorded on three different samples: (i) MWCNT-GCE without treatment, (ii) MWCNT-GCE functionalized with 2,7-NFN and (iii) MWCNT-GCE functionalized with 2,7-NFN after three potential scans (as detailed in the voltammetric characterization).

Figure 6a (i) shows the C 1s spectrum recorded from the MWCNT-GC sample. The spectrum is similar to that previously

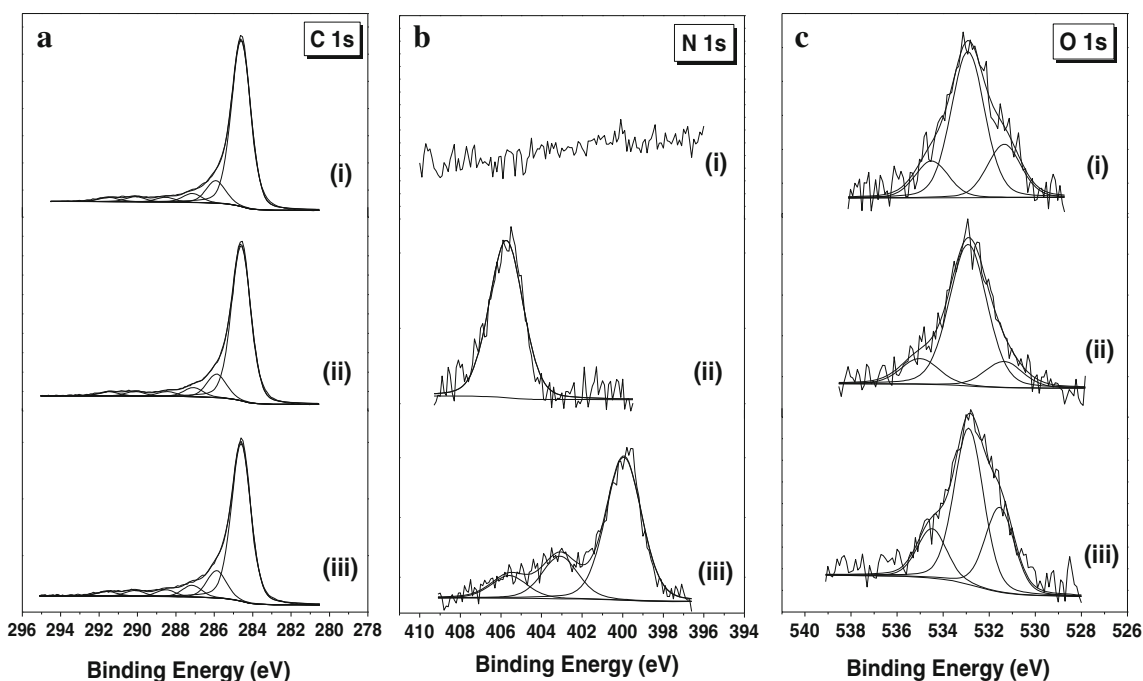


Fig. 6 (a) C 1s, (b) N 1s and (c) O 1s XPS core-level spectra recorded from GC discs modified with (i) MWCNT-GC electrode without treatment, (ii) MWCNT-GC electrode functionalized with 2,7-NFN and

(iii) MWCNT-GC electrode functionalized with 2,7-NFN after three potential scans (as detailed in the voltammetric characterization)

reported for this type of material [15]. It is composed of an intense peak at 284.6 eV, characteristic of carbon in a graphite structure (sp^2 hybridization), and several other minor peaks at higher binding energies. The corresponding binding energies and their assignment to different functional groups are collected in Table 2. The spectra recorded from the other two samples, Fig. 6a (ii) and (iii), are virtually identical, and only minor variations in the intensity of the different components are observed.

The N 1s spectra recorded from the different samples are shown in Fig. 6b. As expected, the MWCNT sample did not produce a nitrogen signal (Fig. 6b (i)). This was not the case, however, for the MWCNT-GC functionalized with 2,7-NFN, which gave a single peak centred at 406.3 eV (Fig. 6b (ii)). This binding energy is characteristic of $-NO_2$ groups [16–19]. The result indicates that the functionalization of the carbon nanotubes with the nitro-containing compound was successfully achieved. The spectrum recorded from the MWCNT-GC with 2,7-NFN after the electrochemical procedure (Fig. 6b (iii)) was considerably more complex and contained at least three main contributions. The most intense contribution, located at 400.3 eV, is associated with $-NHOH$ groups [20]. The second one, centred at 403.9 eV, can be ascribed to $-NO$ groups [21], and the less intense contribution at 406.2 eV corresponds, as stated above, to $-NO_2$ groups. Taken together, the results indicate that the electrochemical treatment causes the reduction of a significant amount of NO_2 groups. The process proceeds mainly through the formation of compounds containing $-NHOH$ (68 %) and $-NO$ groups (21 %). The XPS data show that 11 % of the initial nitro-containing compounds remain unaltered under the electrochemical conditions used. This result is slightly different than that found during the voltammetry characterization, where no nitro reduction current was observed in the second cathodic scan, indicating that all the nitro compounds had been reduced (Fig. 2b). This difference is due to the different sensitivity to detect the different functional groups of both techniques.

Figure 6c collects the O 1s spectra obtained from the different samples. The spectrum corresponding to the MWCNT displays three different components (Fig. 6c (i)). The main one, appearing at 532.9 eV, can be assigned to $\underline{O}=C$ bonds or $O-C=\underline{O}$ bonds, and the component at 531.5 eV can be associated either to $\underline{O}-C$ bonds or physically adsorbed oxygen on the nanotube external wall [22]. The component at 534.5

can be ascribed either to $\underline{O}-C=O$ groups or adsorbed water [22, 23]. These organic species correspond to the terminal functional groups usually present on the nanotubes. The spectrum recorded from the sample containing the NO_2 -functionalized MWCNT-GC, Fig. 6c (ii), shows these three contributions with different relative intensities. In particular, the intensity of the component located at 532.9 eV increases significantly (73 % in the present sample compared with 62 % observed in the Fig. 6c (i)). This is related to the presence of $-NO_2$ groups in this sample because it is expected that the binding energy of the oxygen species pertaining to such a group is close to 533.0 eV [16]. The spectrum corresponding to the MWCNT-GC sample with both $-NO_2$ groups reduced to $-NHOH$ groups (Fig. 6c (iii)) also shows the three mentioned components, although their relative intensity changes with respect to the previous sample. The central component decreases its intensity (54 %), whereas the intensity of the contribution at 531.5 eV increases significantly (13 % in the last sample vs 29 % in the present sample). We associate this with the presence of oxygen species belonging to $NHOH$ groups. The relative intensity of the third component shows meaningless changes along the series (16, 13 and 17 %, respectively).

Conclusions

We have shown that by the appropriate modification of a GCE with MWNCTs and the subsequent trapping of 2,7-NFN within the three-dimensional array of the MWCNTs on the GCE, it is possible to obtain electrodes with better characteristics than the bare GCE. In particular, we have observed an increase in the peak current of approximately two orders of magnitude, which makes these electrodes especially suitable for applications, such as the quantitative determination of nitro aromatic compounds.

Additionally, a nitroso/hydroxylamine derivative couple was electrogenerated in situ from 2,7-NFN at the modified electrode by cycling the potential in the range between -0.3 and 0.2 V at pH 2, indicating that the redox couple is immobilized in the electrode network. This redox couple could be used as a mediator in the electrocatalysis of NADH, as has been previously shown in the bare electrode [14]. With

Table 2 Assignment of the binding energies of the various components observed in the C 1s spectra to different organic species [15]

Binding energy (eV)	Assignment
284.6	Graphitic structure (sp^2)
285.9	C-C single bonds corresponding to defects on the nanotube structure (sp^3)
287.2	C-O single bonds in alcohols, phenols and ethers
288.6	C=O double bonds in ketones and quinones
290.1	O-C=O double bonds in carboxylic acids, carboxylic anhydrides and esters
291.5	$\pi-\pi^*$ shake-up satellite from sp^2 hybridized carbon atoms

this purpose, work is currently being conducted in our laboratory.

By means of XPS, we confirmed that the nitro compounds have been successfully incorporated into the modified electrodes. The redox products R-NHOH and R-NO, generated from the initial 2,7-NFN, have also been detected. As it is well known, the electrochemical measurements are able to detect electron transfer; therefore, different chemical mechanisms can be postulated. However, the precise nature of the chemical species involved cannot be directly determined. The spectroscopic measurements allowed us to confirm the expected nature of these chemical species.

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