



A non-conventional way to perform voltammetry



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ABSTRACT

In a conventional voltammetric experiment, the electroactive species is dissolved in solution, and then diffuses from the solution phase to the electrode phase. In our proposed non-conventional voltammetric experiment, the electroactive species is trapped in the electrode phase instead of being dissolved in solution. A non-aqueous solvent was first used to trap the organic species in a porous surface layer and the modified electrode then transferred to an aqueous buffer to conduct voltammetry measurements.

We tested the non-conventional voltammetric mode using a modified multi-walled carbon nanotube electrode containing mono-, di- and tri-nitroaromatic compounds trapped in the porous three-dimensional network of the CNTs. From these experiments, we conclude that the non-conventional mode produces higher peak currents and displacement of the peak potentials, yielding lower overpotentials. Furthermore, it is possible to obtain more selective voltammograms in the non-conventional mode, showing peaks that could not be resolved in the conventional mode.

These results are due to a change in the mass transport regime, with thin layer diffusion being the main transport method in the non-conventional mode, compared to semi-infinite diffusion in the conventional mode.

The proposed approach is an excellent alternative for performing voltammetric studies on insoluble or slightly soluble organic compounds.

1. Introduction

Carbonaceous materials have always been the materials of choice for electrodes in voltammetry, but the discovery of carbon nanotubes (CNTs) started a revolution in electrode materials. The discovery of CNTs is a rather controversial subject. The most cited paper is that of Ijima et al. in 1991 [1], although CNTs were actually discovered in 1952 by Radushkevich and Lukyanovich [2], but this discovery went unnoticed by Western scientists because their work was published in the Russian language.

One of the most important features of CNTs is the possibility of modifying them with organic or inorganic chemical compounds, dramatically changing the properties of the electrode phase. The modification can be achieved either by covalent attachment [3–5] or physisorption (non-covalent) [6,7] of the modifier on the three-dimensional array of CNTs. The covalent modification involves the formation of covalent bonds in the wall of the CNTs, changing the hybridization of the sp^2 carbon atoms to sp^3 . This change affects the conductivity of the CNTs due to the loss of π electrons from the nanotube structure [8]. The loss of conductivity causes a decrease in electrochemical activity, which is a disadvantage for an electrode material. In contrast, non-covalent functionalization relies on physical adsorption

based on weak interactions (e.g. hydrogen bonding, π - π stacking, electrostatic forces, Van der Waals forces and hydrophobic interactions). This is particularly attractive because it offers the possibility of attaching chemical functionality while preserving the sp^2 structure of the nanotubes and consequently leaves the electronic structure unchanged.

Recently we have reported a new method of modifying CNTs with aromatic nitrocompounds [9–12] which does not involve any covalent attachments. This new strategy is based on the encapsulation of the nitrocompound by trapping it within pores on the surface of a three-dimensional multiwalled carbon nanotube (MWCNT) array. Previous related studies by Compton et al. [13–16], which focused on voltammetry on electrode surfaces covered with porous layers of CNTs, concluded that the mass transport of the electroactive species to the electrode surface (assumed to be both the electrode substrate and the conductive modifying layer) arises from two components: first, semi-infinite diffusion from the solution bulk to the surface of the porous layer and, second, a component due to diffusion transport within the porous layer that can be approximated as thin layer diffusion. In their experiments, Compton et al. used electroactive species dissolved in a solution, while in this paper, we propose a simple modification to the normal voltammetric experiment. In a conventional voltammetric

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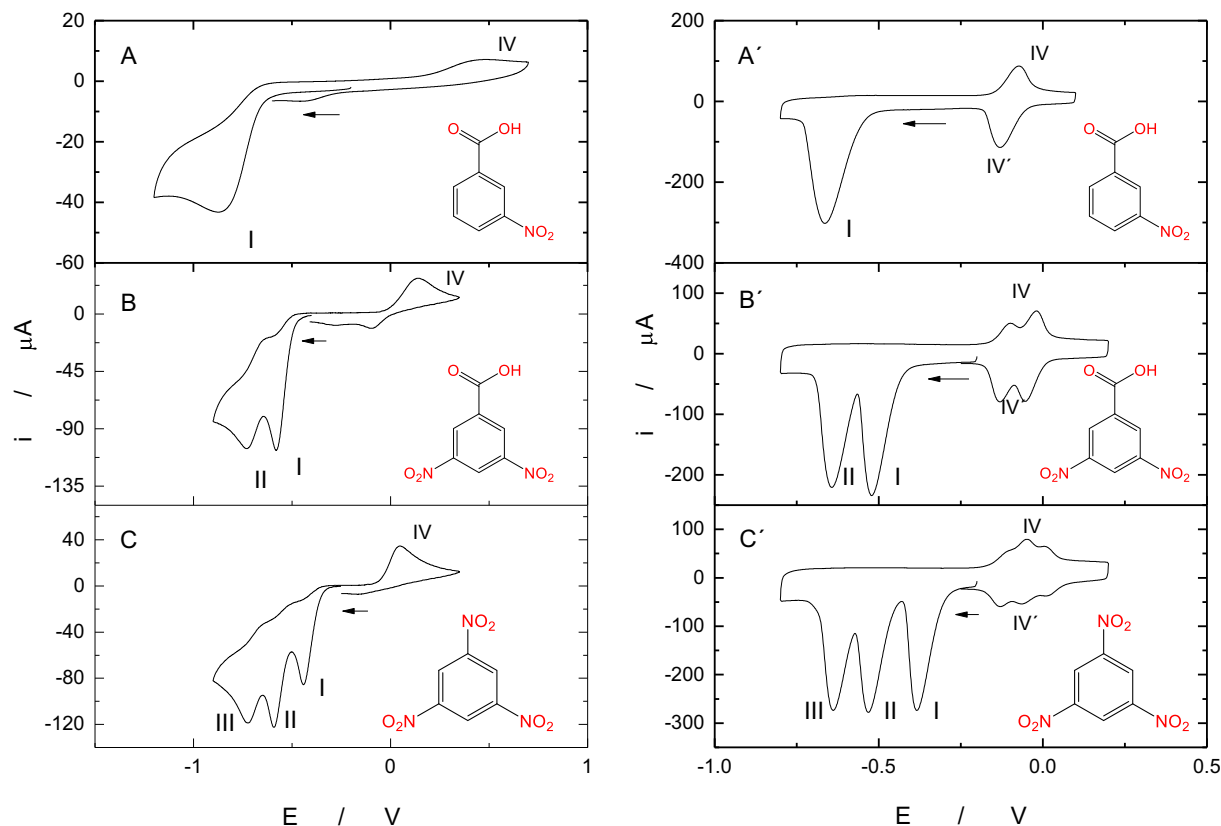


Fig. 1. Cyclic voltammograms of 3-nitrobenzoic acid (3-NB), 3,5-dinitrobenzoic acid (3,5-DNB) and 1,3,5-trinitrobenzene (1,3,5-TNB) using both: conventional voltammetry on a plain GCE and an electrolyte containing 0.2 mM of the nitrocompound in an 0.1 M phosphate buffer solution (PBS), pH = 7 (A,B,C); and non-conventional voltammetry on a GCE coated with MWCNTs incorporating the nitro compound, while the electrolyte was a plain 0.1 M phosphate buffer solution (PBS), pH = 7 (A',B',C'). Sweep rate = 100 mV/s.

experiment, the electroactive species is normally dissolved in the solution phase, but in this work we aim to conduct the voltammetric experiments with the electroactive species trapped or adsorbed in the electrode phase instead of being dissolved in solution. To achieve this we use an organic solvent to dissolve the electroactive species in the entrapment step and then transfer to an aqueous buffer for the detection step.

2. Experimental

2.1. Apparatus and reagents

Electrochemical measurements were performed in a conventional three-electrode cell. Voltammetric curves were recorded with a CHI 900 (CH Instruments Inc., USA) instrument. We used a glassy carbon electrode (GCE) measuring 3 mm in 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, respectively. All potentials are relative to the Ag/AgCl reference electrode.

MWCNTs (1.5 μm in length and 10 nm in diameter) were obtained from Dropsens S.L., Spain. All voltammetric experiments were performed after bubbling N_2 into the test cell for 10 min before each run. The temperature was held constant at 25 ± 0.1 °C.

We used a 0.1 M phosphate buffer solution (PBS), with a pH of 7, as the aqueous medium. The 3-nitrobenzoic acid (3-NB), 3,5-dinitrobenzoic acid (3,5-DNB) and 1,3,5-trinitrobenzene (1,3,5-TNB) were obtained from Sigma-Aldrich.

All other reagents were of analytical grade.

Stock solutions of 3-NB, 3,5-DNB and 1,3,5-TNB were prepared at a concentration of 2×10^{-2} M in ethanol.

2.2. Preparation of MWCNT suspensions and modified GCEs

Before each modification, the GCE was cleaned by polishing with 0.3 μm and 0.05 μm alumina and then washed thoroughly with water. The MWCNTs were dispersed in 1,3-dioxolane by sonicating for 5 min. The sonication procedure was repeated three times. The MWCNTs were immobilized by drop casting 5 μL of the MWCNT dispersion on the GCE. The modified electrodes were obtained by drying the dispersion at room temperature.

2.3. Encapsulation and voltammetry of nitrocompounds

The voltammetric determination was performing using a GCE modified with MWCNTs (MWCNT-GCE) with a nitrocompound encapsulated within the MWCNT structure. The encapsulation process involved dipping the MWCNT-GCE into an ethanol solution containing 2 mM of the nitrocompound. The optimum dipping time was 4 s, and no potential was applied during the dipping step. As a result of the dipping step, the nitrocompound was encapsulated in the modified electrode. The electrode was then washed with Milli-Q water, yielding the modified electrodes 3-NB-MWCNT-GCE, 3,5-DNB-MWCNT-GCE and 1,3,5-TNB-MWCNT-GCE. The modified electrode was then immersed in an electrochemical cell containing only an aqueous medium (PBS at pH 7), and the potential was scanned between 0.75 V and -1.20 V vs. Ag/AgCl to record the voltammetric curve.

3. Results and discussion

In a conventional voltammetric experiment, the electroactive species is dissolved in solution, and then diffuses from the solution phase to the electrode phase. In this work, we explored a different way of

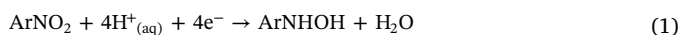
Table 1

Peak potential values for the reduction of the nitro groups of 3-nitrobenzoic acid (3-NB), 3,5-dinitrobenzoic acid (3,5-DNB) and 1,3,5-trinitrobenzene (1,3,5-TNB) obtained from conventional or non-conventional cyclic voltammetry (see Fig. 1).

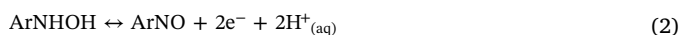
	Conventional			Non-conventional		
	Ep ^I /V	Ep ^{II} /V	Ep ^{III} /V	Ep ^I /V	Ep ^{II} /V	Ep ^{III} /V
3-NB	−0.87			−0.65		
3,5-DNB	−0.60	−0.73		−0.50	−0.63	
1,3,5-TNB	−0.46	−0.60	−0.73	−0.36	−0.52	−0.62

performing this type of experiment. The main difference is that the electroactive species is trapped in the electrode phase rather than being dissolved in solution. The procedure involves: firstly, dipping a MWCNT-modified electrode into a non-aqueous solution of the electroactive compound and, secondly, removing the electrode from the non-aqueous solution and washing with water and then, thirdly, introducing the modified electrode containing the electroactive species into a solution containing only the aqueous buffer and subjecting it to a potential sweep. To summarize, we used one solution to incorporate the electroactive species into the three-dimensional MWCNTs electrode array and a different solution to obtain the voltammogram. To incorporate the electroactive species into the porous layer of the MWCNTs, we used a solution containing the electroactive species dissolved in an organic solvent, while the voltammogram was run in an aqueous buffer solution. To demonstrate this approach, we have selected three different nitroaromatic compounds, each with a different number of nitro groups: 3-nitrobenzoic acid (3-NB), 3,5-dinitrobenzoic acid (3,5-DNB) and 1,3,5-trinitrobenzene (1,3,5-TNB).

The cyclic voltammetric behaviour of the above compounds in 0.1 M PBS at pH 7 was examined using both conventional cyclic voltammetry (Fig. 1A, B and C) and non-conventional cyclic voltammetry, as displayed in Fig. 1A', B' and C'. In the first cathodic scan, we can observe one, two or three irreversible reduction peaks (I, II and III), depending on the number of nitro groups in the molecule. Each peak corresponds to the reduction of a nitro group in the nitroaromatic molecule, according to equation [9]:



In the reverse scan, oxidation of the hydroxylamine derivative to the nitroso derivative produces an anodic peak IV (or peaks, depending on the number of nitro groups in the molecule). Furthermore, in the second cathodic scan, it is also possible to see a peak (or peaks) IV', corresponding to the reduction of the nitroso derivative to the hydroxylamine derivative. Consequently, the peaks IV and IV' form a quasi-reversible couple represented by the equation [9]:



It can be seen from Fig. 1 that significantly different voltammograms are obtained when the nitrocompounds are reduced while trapped in the MWCNTs (non-conventional mode, Fig. 1A', B' and 1C') compared with the case in which the nitrocompounds in solution are reduced at the bare GCE (conventional mode, Fig. 1A, B and C). The main difference is a large increase in the peak current for all of the peaks, demonstrating a considerable increase in the sensitivity of the voltammetric response when the electroactive species is trapped in the conducting porous layer of the MWCNT. Another difference is related to the shift of the peak potentials depending on the voltammetric mode, which considerably affects the selectivity. It is clear that the non-conventional mode produces peaks with better resolution. The most extreme case to visualize this difference can be seen in the peaks corresponding to the ArNO/ArNHOH quasi-reversible couple for 1,3,5-TNB (Fig. 1C, C'). In the case of non-conventional voltammetry, it was possible to resolve each of the three couples produced by each of the nitro groups. In contrast, it was not possible to resolve the

corresponding ArNO/ArNHOH couples using the conventional mode.

From the peak potential values shown in Table 1, other differences between the two voltammetric modes can be deduced. In the case of the mono-substituted nitro derivative (3-NB) the non-conventional voltammetry considerably facilitates reduction of the nitro group. In fact, the nitro group is more easily reduced by approximately 200 mV compared with the case of conventional voltammetry. In the case of compounds with two or three nitro groups (3,5-DNB and 1,3,5-TNB) the reduction of the first nitro group is influenced by the electron acceptor character of the accompanying nitro groups, which facilitate its reduction. Consequently, as shown in Table 1, we can see that $\text{Ep}^{\text{I}} > \text{Ep}^{\text{II}} > \text{Ep}^{\text{III}}$, for both conventional and non-conventional voltammetry, however, the reduction of the nitro group is always favoured in the non-conventional mode compared to the conventional one.

Summarizing the above experiments, we can conclude that higher peak currents and displacement of the peak potentials tend to yield lower overpotentials when using non-conventional voltammetry. In other words, higher peak currents and lower overpotentials are obtained when the electroactive species is adsorbed in the porous layer of the electrode phase compared to the case where the electroactive species is dissolved in the solution phase and diffuses to a flat electrode.

According to previous studies by Compton et al. [13–16], the mass transport of an electroactive species to the electrode surface arises from two components: first, semi-infinite diffusion from the solution bulk to the surface of the porous layer and, second, a component due to diffusion transport within the porous layer that can be approximated as thin layer diffusion. In the non-conventional voltammetric experiment there are no electroactive species in the solution phase, all the electroactive species being confined in the porous layer of MWCNTs, and therefore only thin layer diffusion occurs.

4. Conclusions

A new, non-conventional voltammetric experiment was developed, which involves firstly trapping a nitroaromatic electroactive species on the surface of a modified MWCNT electrode, then washing the electrode and finally applying a potential scan in a fresh buffer solution. Using the above approach, it is possible to trap the electroactive species in the porous network of the MWCNTs on the electrode, prioritizing thin-layer-type mass transport, and leading to larger peak currents and smaller concentration overpotentials.

In this work, we have demonstrated this non-conventional approach using nitroaromatic compounds, but the method could be extended to any other organic compounds that could be trapped within the three-dimensional network of the MWCNTs.

In addition, this method is an excellent alternative for performing voltammetric studies on insoluble or slightly soluble organic compounds.

Finally, the experimental results of this paper are a very good example of the work of Compton et al. [13–16] regarding the thin layer model used to explain the effect of diffusion within a porous layer.

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