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Probing the surface of oxidized carbon nanotubes by selective interaction with target molecules

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ABSTRACT

Screen printed carbon electrodes (SPCE) were modified with pristine and oxidized carbon nanotubes (CNT_{prist} and CNT_{ox}, respectively). The extent of CNT oxidation evaluated by TGA increased with the time of reflux in nitric acid. The CNT_{ox} surface coverage by quinoid/phenolic functional groups was quantified by their voltammetric response at low redox potentials. Cyclic voltammetry was performed with SPCE-CNT_{ox} on solutions of hydroquinone, dopamine and ferricyanide used as model compounds. The sensitivity of reduced/oxidized forms of these molecules to the oxygen-containing functional groups of the CNT_{ox} was evaluated by the current intensity. Compounds with phenol/amine groups show a large increase of the current intensity with increasing CNT oxidation, while for carbonyl containing compounds only a negligible effect was perceived. Molecules that can hydrogen bond to the CNT functional groups interact better with the electrode surface, and this is supported by theoretical calculations. This showcases the use of CNT_{ox} modified SPCE for selective sensing.

1. Introduction

The modification of electrodes with carbon nanotubes (CNT) is currently employed in numerous applications as a way to improve their performance. The presence of metallic ions, nanographitic and amorphous carbon impurities in pristine CNT is recognized to be in the origin of CNT electrocatalytic properties. Compton's group has shown that trace amounts of metal impurities play a critical role in the electrocatalytic properties of CNT [1]. Likewise, Pumera's group demonstrated that the electrocatalytic oxidation of amino acids by CNT was actually induced by the presence of metal-based impurities [2]. The nanographitic and amorphous carbon impurities on CNT were also found to facilitate the heterogeneous electron transfer (HET) to biological compounds [3, 4]. Since the nature and amount of impurities may vary markedly, comparison of results using CNT from different sources can be extremely challenging and their purification is generally performed before use.

There are different purification methods for CNT [5], based on the use of surfactants, organic solvents or oxidation by acids. The CNT treatment with concentrated solutions of mineral acids [6] can be carried out by reflux, sonication or microwave treatment. These procedures can last from a few minutes to several hours [7]. The acidic treatments can be effective in removing metal ions trapped between the CNT walls [5]. Oxidation also opens holes in CNT walls and cuts the tubes [5]. The creation of edge-plane defect sites in the CNT sp^2 structure and introduction of oxygen-containing moieties [6] are identified as key factors that may favor [5,8,9] or be detrimental [10] to specific electrochemical reactions.

Although it is recognized that the performance of CNT-modified electrodes is affected by their oxidation, the selective properties of electrodes modified by oxidized CNT are not yet clear. The effect of oxidation extent on the nature of oxygen functional groups is not thoroughly understood and all contributions to clarify this matter are relevant.

The work reported herein explores the effect of the oxidation extent of multiwall CNT by reflux with concentrated nitric acid during different times. The functionalization degree of oxidized CNT (CNT_{ox}) is characterized by thermogravimetric analysis (TGA). The voltammetric performance of screen-printed carbon electrodes modified with oxidized CNT (SPCEs-CNT_{ox}) is evaluated using relevant analytes, such as dopamine and hydroquinone and is correlated with the surface coverage by oxygen groups. The nature of oxygen containing moieties developed by the oxidative treatment is discussed considering the voltammetric results.

2. Experimental section

2.1. CNT oxidation

Pristine multiwall CNT (CNT_{prist}, Nanocyl NC 7000) were mixed with 100 mL of 65% HNO_3 and refluxed for 1–8 h at 110 °C. Samples were cooled down and the dispersion was centrifuged for 20 min at 6000 rpm. The sedimented CNT_{ox} were filtered through a polycarbonate

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filter (Whatman pore size 0.45 μm). Subsequently, CNT_{ox} were rinsed with water until the filtrate reached a neutral pH. CNT_{ox} were dried in vacuum overnight at 80 °C (Büchi glass oven B-580).

2.2. Electrodes

SPCEs (DropSens DRP-110) with a carbon disk working electrode ($r = 2$ mm), a carbon auxiliary electrode and a silver pseudo-reference electrode were used.

2.3. SPCEs modification

SPCEs were modified by depositing 4.7 μg of CNT by drop casting of CNT_{ox} suspensions (1.12 ± 0.06 mg/mL, ethanol: water (1:1)) or CNT_{prist} suspensions (0.60 ± 0.01 mg/mL, methanol: water (1:1)) on the working electrode. The drop was then left to dry in air.

2.4. Voltammetry

Cyclic voltammetry was carried out by placing 50 μL of solution to cover the three electrodes. Measurements were performed with an Autolab PGSTAT30 potentiostat/galvanostat (Ecochemie), controlled by GPES software. Solutions of dopamine (DA; Sigma) and hydroquinone (HQ, May & Baker, Ltd.) were prepared in 0.15 M, pH 3.2 or 7.4, phosphate buffers (PB), whereas potassium ferricyanide (FC, José Gomes Santos) solutions were prepared in 0.10 M KCl.

2.5. TGA

A Modulated Thermogravimetric Analyser Q500 (TA Instruments) was used in gradient mode for analysis of the weight yield of CNT oxidation. Samples were heated from room temperature to 800 °C at 10 °C min^{-1} under a constant nitrogen flow of 60 mL min^{-1}.

3. Results and discussion

Concentrated oxidizing acids are often used to eliminate impurities present in CNT, but are also known to induce CNT oxidation [1,11,12]. The final oxidation level greatly depends on the oxidizing acid used, as well as on the reaction conditions (concentration, temperature and time). Therefore it is difficult to predict the extent to which CNT acid treatment can actually change the performance of CNT modified electrodes [13]. In order to understand this issue, we oxidized CNT by refluxing with concentrated nitric acid for different times (1, 2, 3, 6 and 8 h). The CNT_{ox} were characterized by TGA and the response of modified electrodes was analyzed by cyclic voltammetry.

Fig. 1a shows the weight loss of CNT due to thermal degradation, evaluated by TGA. CNT_{prist} display a negligible weight loss at 800 °C (≈1%), in contrast, CNT_{ox} show increasing weight losses (from 8 to 23%) with oxidation time, Fig. 1a, inset. The weight loss provides an estimate of the functionalization degree as it results from the loss of chemical groups/molecules bonded to the CNT walls. Different functional groups can be introduced by oxidation such as: hydroxyl-phenolic, carbonyl-quinone, carboxyl and lactone [6,14–16]. The fact that the different weight vs. temperature curves of CNT_{ox} display similar shapes hints that the nature of the functionalization introduced by oxidation is similar despite the treatment duration.

Electrochemical characterization of the functional groups bonded to the CNT walls is shown in Fig. 1b. Cyclic voltamograms (CVs) were obtained from SPCEs modified with CNT_{prist} (SPCE-CNT_{prist}) or with CNT_{ox} (SPCE-CNT_{ox}) by drop casting. While CVs from SPCE-CNT_{prist} exhibit a current that is mainly constant, those from SPCE-CNT_{ox} display two broad bands corresponding to the oxidation and reduction of the CNT_{ox} functional groups. The small increase in capacitive currents observed for higher oxidation times may be due to an increase of the double-layer charge separation associated to a decrease of pi–pi interactions between CNT_{ox} and the electrode surface. In contrast, the faradaic current, which depends on the concentration of electroactive groups, increased with the CNT_{ox} oxidation time, as depicted in Fig. 1b.

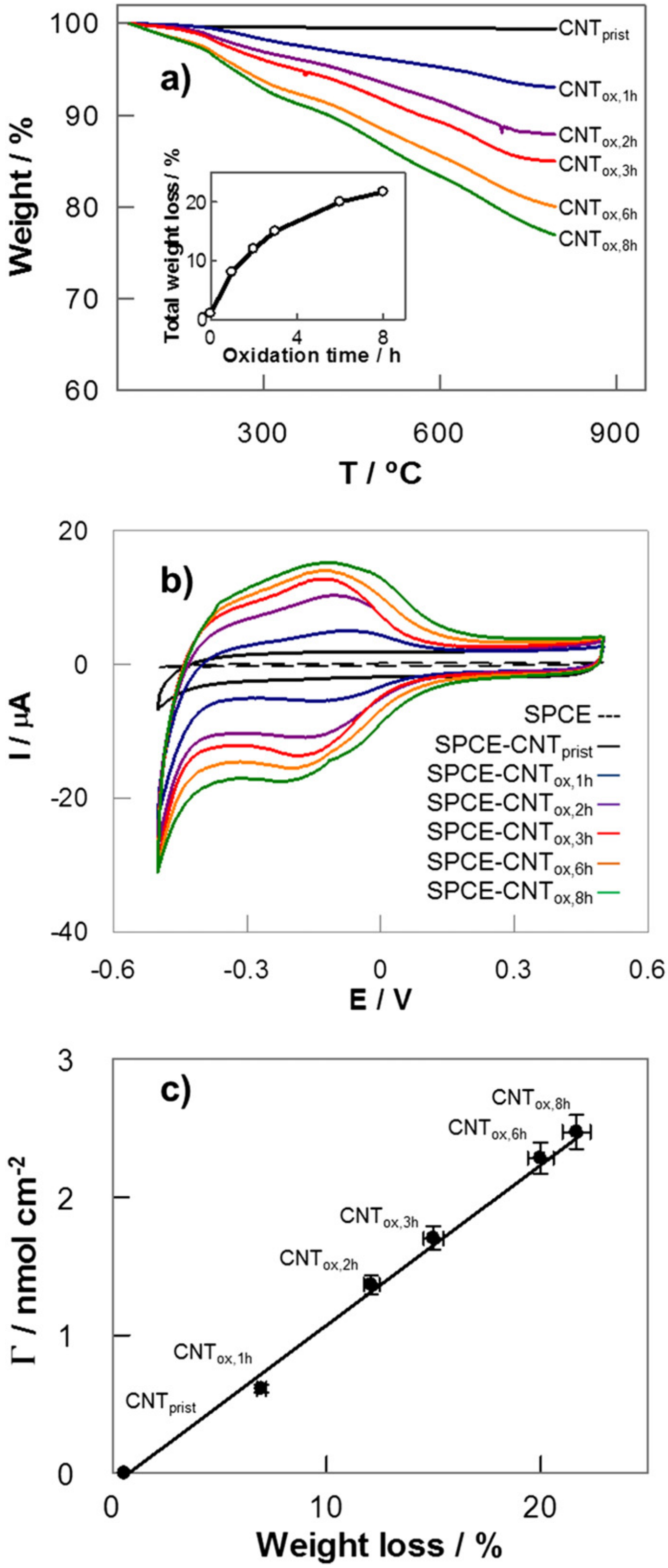

Fig. 1. (a) TGA heating curves of CNT_{prist} (black) and CNT_{ox} at increasing oxidation times (1 to 8 h). Inset: total weight loss at 800 °C. (b) CVs (100 mV s^{-1}) of SPCE-CNT_{prist} and of SPCE-CNT_{ox} at increasing oxidation times (1 to 8 h) in 0.15 M PB solutions, pH 3.2. (c) Relation between surface coverage (Γ) and the weight loss at 800 °C ($y = 0.12x - 0.16$; $R^2 = 0.997$).