Influence of oxidative treatment of carbon nanotubes on the electrochemical response of phenolic antioxidants

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Abstract

Non-functionalized carbon nanotubes presented higher current signals in determining phenolic antioxidants.

Introduction

A research field that encompasses several areas is nanotechnology, which enables new properties to materials with extremely reduced structures. Carbon nanotubes (CNT) are in this context. After the discovery of fullerene in the year 1991, new CNT structures were presented as graphene sheets rolled up in the form of a closed cylinder[1]. The use of nanostructured materials in electroanalysis offers unique properties such as increased mass transport, high surface area and higher signal to noise ratio (decrease in residual current)[2]. Functionalization of CNT enhances the electrical properties of these materials, which can improve the electrochemical signal[3]. The objective of this work was to evaluate the effect of oxidative treatment in CNTs on electrochemical oxidation of the antioxidants gallic acid (GA), pyrogallol (PY) and propyl gallate (PG).

Results and Discussion

Commercial (Sigma-Aldrich) multi-walled carbon nanotubes (MWCNT) of smaller diameter (SD, diameter of 6-9 nm and length of 5μm) were used in this work. The oxidative treatment of SD-MWCNTs was made by adding SD-MWCNT to a sulfonitric ($3H_2SO_4$: $1HNO_3$; v/v) solution. This mixture was sonicated for 4 h. After cooling to room temperature, cold deionized water was added and the resulting suspension was then filtered at reduced pressure. Filtered SD-MWCNTs were washed with deionized water until pH 7 and dried in an oven. The characterization by infrared spectroscopy showed characteristic υO-H and υC=O of the carboxylic acid, confirming the functionalization of the SD-MWCNT. X-ray diffraction revealed no metal on the walls of SD-MWCNT (or below the detection limit of the equipment), which discards the possibility of a possible electrocatalytic effect caused by metals contained in the cylindrical structure of the tubes. The images obtained by scanning electron microscopy showed that both non- (NT) and functionalized SD-MWCNTs (T) are homogeneous and have no particles on its surface. The effect of treatment on the SD-MWCNTs was evaluated in determining AG, PY and PG. A working glassy-carbon electrode (GCE) was modified by drop-casting with a 10-μL aliquot of a suspension of 1 mg mL^{-1} of SD-MWCNT (NT and T), followed by 30 min at 60 °C for drying. Britton-Robinson buffer solutions of pH 2, 4, 6, 8, 10 and a perchloric acid solution were tested as electrolyte. The selected electrolyte was 0.1 mol L^{-1} $HClO_4$ /ethanol 60:40, which presented the best peak resolution and greater signal strength. Cyclic voltammograms of AG, PY and PG presented two oxidation and reduction peaks in the potential range of 0.0 and +1.5 V in all tested electrodes. The SD-MWCNT-NT-modified GCE showed a current signal much larger than that obtained at SD-MWCNT-T-modified and unmodified GCE. Hydrodynamic voltammograms were obtained using stirred solutions in the amperometric detection mode and the highest current was observed at +1.1 V. Analytical curves with a linear range between 9.9 and 74.0 μmol L^{-1} were obtained under these conditions. The increased sensitivity with SD-MWCNT-NT-modified GCE can be seen in Table 1.

Table 1. Comparison of slopes of the analytical curves obtained using unmodified and modified GCE.

	Slope (μA/μmol L^{-1})		
Electrodes / Analytes	AG	PY	PG
GCE	0.11	0.14	0.07
SD-MWCNT-T	0.11	0.11	0.12
SD-MWCNT-NT	0.70	0.55	0.64

Conclusion

Non-functionalized SD-MWCNT-modified GCE presented substantial increase in sensitivity values for the three antioxidants compared to the other electrodes. These results indicate that the oxidative treatment step of MWCNTs is not necessary for this application, avoiding unnecessary expenditure of time and reagents without a gain of effective sensitivity.

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