ELECTROCHEMICAL MODIFICATION OF NANOSTRUCTURED CARBON MATERIALS WITH N AND P FUNCTIONALITIES

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Introduction

Nanostructured carbon-based materials, as graphene and carbon nanotubes (CNTs), have demonstrated outstanding mechanical, optical, chemical and electronic properties, as a result of their structure and surface chemistry. Surface chemistry modification procedures in carbon materials have received important attention since the change in the surface chemistry permits to tailor the properties of the material, allowing a remarkable increase in their potential applications. Covalent functionalization methods have been strongly developed and are very much used to add certain heterotaoms or surface molecules, being versatile and scalable methods. However, functionalization conditions may generate important structural changes, which can deteriorate or inhibit some of the properties of the carbon material. Therefore, mild non-destructive surface-modification procedures have been the center of the attention, as a route to surface nano-engineering, for designing new functional materials that maintain most of the interesting properties of the pristine material.

In many cases of carbon materials functionalization, formation of radicals and active species with high reactivity towards carbon atoms has been the fundamental principle to functionalize carbon-based materials. Electrochemical methods arise as a promising alternative to generate with a high selectivity active species at the carbon-electrolyte interphase, allowing a precise control on the degree of modification and nature of the incorporate species, with a minimum damage in the bulk properties of the carbon materials.

Materials and Methods

Glassy-carbon electrodes were modified by drop-casting with 10 µL of nanostructured carbon materials dispersion (1 $mg{\cdot}mL^{-1}$). Electrochemical modification was performed employing cyclic voltammetry in a standard three-electrode cell configuration, using 4-Aminophenyl phosphonic Acid (4-APPA) in aqueous solution. Different upper potential limit of functionalization was chosen to observe the effect of this parameter in the functionalization

Electrochemical characterization in different electrolytes without modifier agent was employed to evaluate the electrochemical behavior of the functionalities. XPS, Raman Spectroscopy and TEM have been also used.

Results and Discussion

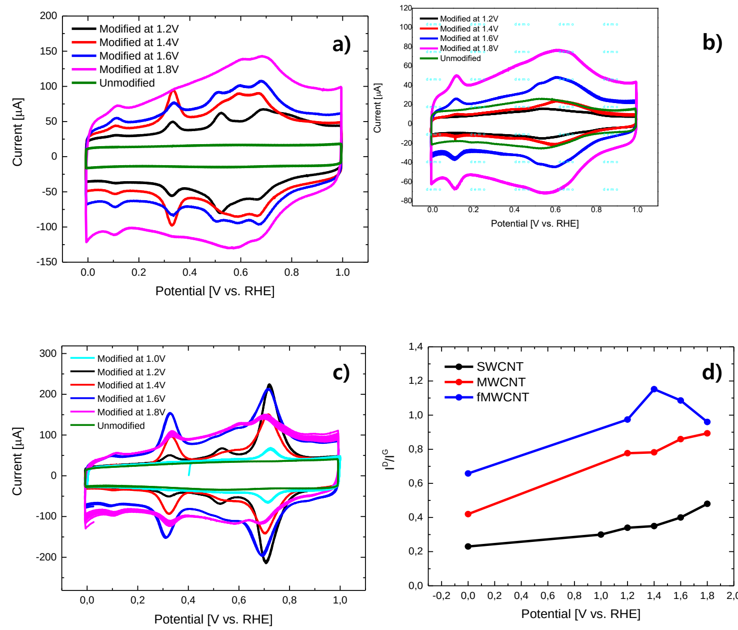

Figure 1. Electrochemical and physico-chemical characterization of carbon nanotubes modified with 4-APPA at different potentials at 50 mV·s^{-1} in acid conditions: a) MWCNT, b) fMWCNT, c) SWCNT and d) Plot Raman I^D/I^G vs. Potential of modification for the different carbon materials employed.

Electrochemical modification of nanostructured carbon materials has been done with 4-APPA by oxidative conditions. The cyclic voltammograms of 4-APPA modified carbon nanotubes (Figure 1) show an increase in the double-layer capacitance and the appearance of different surface redox process associated with the anchored phosphonic-containing species and oligomers on the carbon material surface. Additionally, electrochemical behaviour of modified electrodes shows an important dependence with the pH conditions. The amount of N and O functionalities incorporated in nanostructured carbon materials presents a direct relationship with the applied potential. The formation of defects in the graphene structure is also observed (Fig. 1-d).

Conclusions

Electrochemical modification of nanostructured carbon materials has been successfully obtained using aqueous media. The amount of incorporated N and P functionalities depends on the applied potential.

Acknowledgment

The authors would like to thank MINECO and FEDER (MAT2016-76595-R) for the financial support. A.F.Q.J. gratefully acknowledges Generalitat Valenciana for the Santiago Grisolia grant (GRISOLIA/2016/084).