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Modification of MWNTs obtained by thermal-CVD

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Abstract

In the present work multi-wall carbon nanotubes (MWNTs), which were synthesized on uncoated silicon by an easily scaled-up catalytical chemical vapor deposition (CVD), were subjected to three different functionalization treatments. Both acid treatment, by means of a HNO_3–H_2SO_4 1:3 mixture or chlorosulfuric acid (HSO_3Cl) solution, and high temperature basic digestion with sodium hydroxide (NaOH) were involved. The efficiency of these methods were investigated by thermo-gravimetric analyses (TGA), Raman spectroscopy, Brunauer–Emmett–Teller (BET) analysis, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray (EDX) and electron microscopy (SEM, TEM) techniques, and the results were compared. Among the various treatments that have been tested, the 1:3 solution of nitric and sulphuric acid was the most effective in modifying the CNT surface, inducing the formation of functional groups that may be used in biological applications.

Keywords: Multi-wall carbon nanotubes; XPS; Functionalization

1. Introduction

Recently, carbon nanotubes, in particular multi-walled ones (MWNTs) have generated a great interest in bio-technological areas because of their interesting properties. Many applications for MWNTs have been proposed, and some have been demonstrated, which include biosensors, drug and vaccine delivery vehicles, protein transporters, artificial muscles and novel biomaterials [1–3]. However to expand and optimize the use of carbon nanotubes (CNTs) in this research field, it is necessary to chemically modify and functionalize their surfaces to support biomaterials. The chemical modification of CNTs is a compulsory step to link a wide variety of active molecules to the surface, to improve the solubility either in common organic solvents or in aqueous solution [4] and to aid in the purification process. This is very difficult to perform since CNTs are large molecules with thousands of carbon atoms in a very inert aromatic delocalized system, which is practically insoluble in all the solvents and consequently difficult to handle.

The purpose of this work is to compare the covalent modifications generated by a series of different acidic and basic treatments on multi-wall nanotubes, grown by the catalytic thermal-CVD described in other papers [5,6], in order to identify the most effective process that leads to the creation of functional groups (such as carboxylic or sulphonic groups) on the CNT surface. These groups can then be converted to the corresponding amides with long aliphatic chains that are essential for the formation of covalently bonded adducts with biological molecules [7].

2. Experimental

Multi-walled CNTs were grown by thermal-CVD at 850 °C in a horizontal quartz tube housed in a cylindrical furnace. An inert gas flow (N_2) carried the gas mixture of carbon precursor and metal catalyst towards the center of the furnace, where the gases pyrolysis led to the deposition of a CNT layer on the silicon substrate. The carbon precursor used was camphor, a natural and inexpensive hydrocarbon; iron was the metal catalyst provided by ferrocene precursor, added in solid mixture with camphor before its evaporation [5,8].

Three methods were performed under strong conditions, to attain the functionalization of the carbon nanotube external

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