

Preparation and Surface Functionalization of MWCNTs: study of the composite materials produced by interaction with a iron phthalocyanine complex

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The production and application of nanocomposite materials can find various fields of interest, such as electronic components, selective sensors, heterogeneous catalysts, energy storage, etc. Many of these composites are formed due to (or are created by) specific interactions that occur at the **nanomaterials surfaces**. In the present case we have studied the interactions of multiwall carbon nanotubes (MWCNTs) with a commercially available iron organometallic compound, Iron(III) phthalocyanine-4,4',4'',4'''-tetrasulfonic acid (FePc), which is a hydrated monosodium salt, compound that contains oxygen (see scheme 1). Considering the above mentioned importance of the solid surface interactions with molecular compounds, as reported for instance for the graphene oxide with phthalocyanine hybrids [1] where the pi-pi bonds seem to be the key factors, we have previously treated the MWCNTs in order to modify their surface functionalities. So lab produced MWCNTs, prepared as described in [2], were treated with nitric acid solutions, in order to incorporate oxygen (carboxylic acids, phenols, etc) functions and, subsequently, aliquots of these oxidized samples were contacted with ethylenediamine, in order to turn the surface active sites to basic properties. In short in the way of preparing hybrids materials MCNTs-FePc, we present here the main features associated with the preparation and characterization of these composites solids.

A part from the preparation and surface functionalization of MWCNTs, the production of MWCNTs-FePc hybrids involves the contact of the solids with FePc (Aldrich) aqueous solutions. These suspensions were stirred using a magnetic stirrer for 17 hours at room temperature. Once the excess of solvent was removed using a rotary evaporator the resulting solids materials were dried in an oven at 373 K for 18 hours to ensure it was completely solvent-free. The resulting materials were studied by a battery of techniques. For the MWCNTs surface area and pore size distribution were determined from nitrogen adsorption isotherms at 77 K (NAI), and the incorporated functional groups were evaluated by thermogravimetric analysis under inert gas (ATG) and temperature programmed desorption under vacuum (TPD). In addition their surfaces were analyzed by X-ray Photoelectron Spectroscopy (XPS). The MWCNTs-FePc samples were also studied by XPS and by Infrared Spectroscopy (FTIR). This second method would aid in the determination of modifications in the molecular structure of the FePC molecule, if any. Finally the amounts of FePc incorporated on the hybrid solids were determined by ATG.

Figure 1 presents some images by Transmission Electron Microscopy (TEM) of the as prepared MWCNTs, methods described in reference [2]. The TEM analysis of the surface functionalized materials does not reveal any significant structural modification. From the NAI surface area values (BET method) were determined. So for the as-synthesized MCNTs a value of 90 m²/g was obtained, while the oxidation treatment results in an increase of surface area, up to 120 m²/g, the reaction with ethylenediamine gave a surface area value of 82 m²/g. By FTIR it is not possible to establish features about the surface groups, due to the absorbent-reflecting character of MWCNTs. However TGA and TPD determinations and the complementary XPS analysis, clearly provide valuable information that we have tried to summarize in the Scheme 1, which is relevant from the point of view of the surface species existing in the modified materials.

For the composite or hybrid solids, FTIR does not provide significant insides, with the exception that FePc compound suffers a loss of hydrated water molecules (see scheme 1), which can be the responsible of the weight loss observed in the ATG experiments. Also comparing the ATG of the three composite samples (MWCNTs-FePc, Oxidized-MWCNTs-FePc and Aminated-MWCNTs-FePc) we are able to detect that the amount of incorporated FePc complex is close to 14 wt %. It appears that the lowest amount of FePc is incorporated on de aminated surfaces. On the other hand Binding Energies determined from the XPS spectra, for the Fe2p_{3/2} species are not modified when interacting with the functionalized surfaces. This is indicating that covalent or ionic bonds are produced, thus we have to conclude that the **surface dominant interactions** in these composites are pi-pi types, as has been repeatedly reported for graphitic surfaces and aromatic compounds [3]. From the XPS analysis we have also determined chemical composition (surface atomic percentage) of the hybrid materials. These results are presented in Table 1. It can be noticed that percentage of Fe detected just in the original

FePc complex is significant lower than theoretical chemical content. Also in the composite solids the Fe percentage is high due to the additional presence of residual iron, which was incorporated in the MWCNTs during the preparation procedure (from the $\text{Fe}(\text{CO})_5$ used as catalyst). All these differences observed and summarized in Table 1 underline the relevance of the surface modification treatments in the final compositions of the prepared hybrid materials.

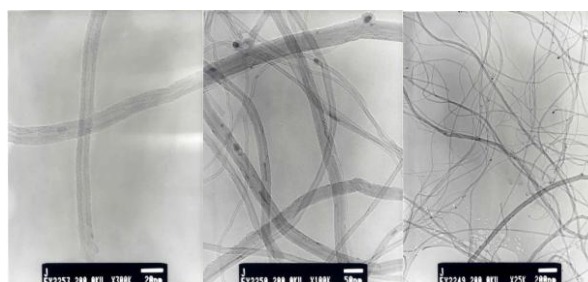
References

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 [2] Sampedro-Tejedor P, Maroto-Valiente, A, Nevskaja, DM, Muñoz V, Rodriguez-Ramos I, Guerrero-Ruiz A, Diamond & Related Mater., **16** (2007) 542-549.
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Table 1: Chemical composition of the composite materials as determined from XPS

Sample	Atomic percentage %				
	C1s	O1s	Fe2p 3/2	N1s	S2p
MWCNTs-FePc	86.64	10.28	0.27	1.63	1.20
Oxidized-MWCNTs-FePc	83.64	10.05	0.20	2.94	2.46
Amminated-MWCNTs-FePc	85.88	9.15	0.22	3.03	1.33
FePc	69.65	21.98	0.14	3.94	4.10
FePc (theoretical)	53.33	23.33	1.67	13.33	6.67

Figure 1: TEM images of the original MWCNTs sample.



Scheme 1: Representation of surface modified NWCNTs and the reagent FePc molecules.

