SURFACE FUNCTIONALIZATION OF MWCNTS TOWARDS BIOMATERIALS APPLICATIONS

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Introduction

Since raw carbon nanotubes (CNTs) are entirely hydrophobic, their applications as biomaterials require surface functionalization. Such modifications are one of the main strategies to improve the dispersibility in the polar solvent of choice. Additionally, the presence of functional groups enables the anchoring of molecules to carbon surfaces, including attachment of bioactive compounds. Recently, the topic is intensively explored. Functionalization can either be covalent or noncovalent and the strategy applied depends mostly on the target application.

The chemical nature of introduced functional groups, their surface concentration and location have a significant impact on the properties of carbon nanotubes. For such materials, oxygen-containing functional groups are most often introduced. These include the carboxyl, hydroxyl and epoxy groups. Polar oxygen groups (due to the electronegativity difference between carbon and oxygen atoms affect mostly the wettability of the carbon surface and its electron-donor properties, which are often taken into account when designing carbon materials for specific applications, especially in the context of biomaterials [1].

One of the problems with applications of carbonaceous materials is the difficulty in obtaining good quality suspensions in water and other polar solvents. Oxygen-containing functional groups improve the wettability and transform hydrophobic surfaces into hydrophilic what is considered a key modification since improving the biocompatibility of carbon-based implantable materials. The introduction of functional groups substantially changes the electronic properties of carbon materials. Indeed, as reported elsewhere the work function was indicated as a suitable parameter to assess the quality of biomaterials' surface.

The work aimed to investigate the effect of functionalization of multi-wall carbon nanotubes using the wet chemistry method and oxygen plasma treatment on the properties of the carbon materials. The effect of functionalization was evaluated in terms of the quality of the obtained suspensions in polar solvents monitoring the sedimentation of carbon materials in times.

Materials and Methods

MWCNTs used in the study were purchase from NanoAmor (>98%, inner diameter 20-30 nm). The materials were functionalized either using wet chemical methods or plasma treatment (see details in TABLE 1) [2]. The investigated materials were characterized with the use of Raman Spectroscopy (structural changes) and work function measurements (surface changes).

Results and Discussion

Raman spectroscopy revealed significant differences in the intensity ratio of the maxima (ID/IG). The comparison between unmodified and modified MWCNTs (wet methods and oxygen plasma) revealed an increase in the ID/IG ratio after modifications. Thus, the obtained spectroscopic profiles indicated defects introduction, which can be associated with breaking of the C-C bonds upon formation of oxygen functional groups.

TABLE 1. The list of investigated samples together with the applied modification parameters.

samples	**wet chemical methods**
H16	16 h H_2O_2 + H_2SO_4
K8	8 h H_2SO_4 + HNO_3 (3:1)
K16 ½	16 h H_2SO_4 + HNO_3 (1.5:1)
K16	16 h H_2SO_4 + HNO_3 (3:1)
samples	**plasma functionalization**
MWCNTs 0.1 min	0,1 min., 0,2 mbar, 60 W
MWCNTs 5 min	5 min., 0,2 mbar, 60 W
MWCNTs 20 min	20 min., 0,2 mbar, 60 W
MWCNTs 60 min	60 min., 0,2 mbar, 60 W

Electrodonor properties of MWCNTs modified with the wet methods and by oxygen plasma treatment were measured with the use of Kelvin Probe. The results show that oxygen functional groups have a great influence on the electronic properties of MWCNTs. The unmodified material work function value was 4.58 eV. Both modifications significantly increase the work function values, for wet methods the ΔΦ was in the range of 0.1-0.3 eV (FIG. 1), while for oxygen plasma-treated samples the increase was substantially larger 0.7-1.1 eV.

In order to compare the stability of the modifications performed with the use of wet methods and plasma, suspensions of carbon materials in water, ethanol and acetone were prepared and their sedimentations were followed for 36 days. It was found that modifications with wet chemical methods were stable for 30 – 60 days while plasma modifications diminish within 24h.

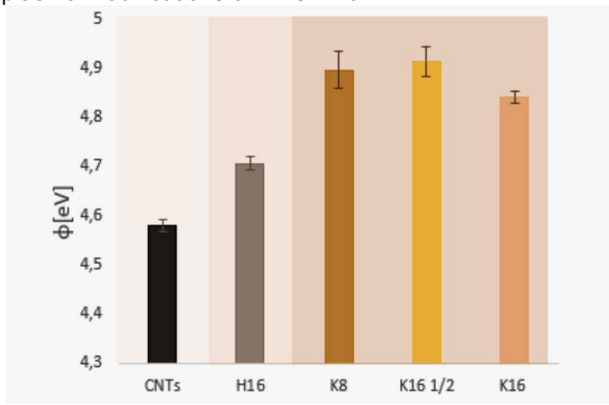

FIG. 1. The changes in work function values of the investigated carbon nanotubes modified with wet chemical methods (CNTs: unmodified reference sample, for other labels see TABLE 1).

Conclusions

The obtained results clearly show the necessity of careful selection of the functionalization method for specific applications. Moreover, the modification process parameters precisely adjusted for both of the applied methods (for wet methods: modification time and type of oxidant, for plasma method: modification time, partial pressure gas, generator power) are of key importance.

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References

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