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FUNCTIONALIZATION OF CARBON NANOTUBES

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ABSTRACT. The functionalization of single-walled carbon nanotubes (SWCNTs) is a timely topic in contemporary nanostructures literature. It is believed that modifications of SWCNTs properties could open the way towards real nanotechnology applications. In the present paper chemical functionalization of SWCNTs was performed to obtain first the carboxyl-functionalized species and then various synthetic approaches were investigated to obtain the target product (triethylene-glycol-functionalized SWCNTs), which can be used as a linker with medical purposes. The intermediate and final reaction products have been characterized by FT-IR spectroscopy, TEM analysis and micro-RAMAN spectroscopy.

Keywords: *nanotechnology, carbon nanotubes, functionalization*

INTRODUCTION

The concept of nanotechnology embraces applied science and technology. This field of study keeps developing day by day offering us information about the behavior of nanoparticles and their unique electrical, optical and magnetic properties [1]. Its practical use has many facets. This paper deals with the functionalization of SWCNT in order to increase their capacity of transporting therapeutic agents through cell membranes.

Carbon nanotubes can be classified in tree classes: single walled (SWCNT), double walled (DWCNT) and multiwalled (MWCNT) carbon nanotubes. They only consist of sp^2 hybridized carbon atoms (like the graphite), witch confer them a unique strength and toughness [2].

Depending on conditions, SWCNTs can form aggregates or they can exist as isolated tubes. Their ends can be opened or closed (the closing cap includes pentagons, also).

All SWCNTs can be represented by a pair of numbers, the so called chirality index (n, m) [3]. If n=m the tube is of armchair type, if one of the numbers is zero, then it is a zig-zag nanotube, and if $n \neq m \neq 0$ the tube is chiral (Figure 1).

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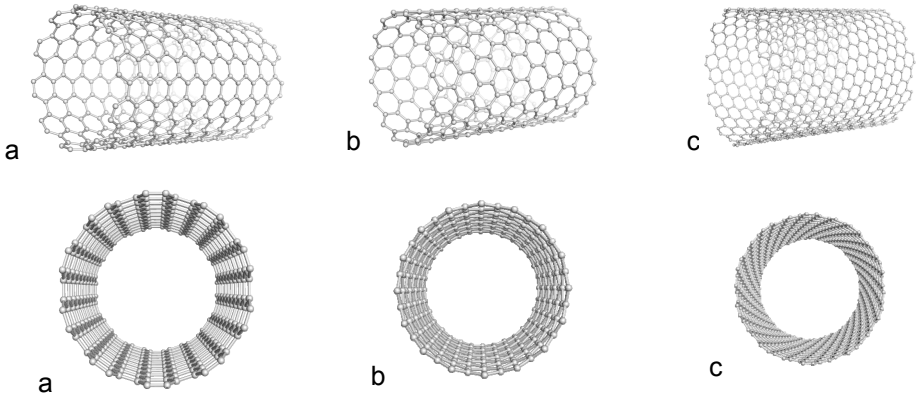


Figure 1. The tree types of SWCNTs (a – armchair; b – zig-zag; c - chiral)

Carbon nanotubes have incredible properties, such as hardness, thermal and electrical conductivity (all armchair nanotubes, 2/3 of the zig-zag type and 1/3 of the chiral ones are metallic, and the remaining ones are semi-conductors). Their tensile strength is 75 times higher than that of the steel, while their density is 6 times lower. Carbon nanotubes (CNT) are very light materials, bearing a density as low as 1.33-1.4 g/cm^3. Another excellent physical property of CNT is their elasticity which helps them regain their original form after bending[4]. CNT are not miscible with any kind of solution; they only make suspensions. They can be synthesized in various ways, such as: chemical vapor deposition, arc discharge, laser ablation etc. [4-7].

RESULTS AND DISCUSSION

In the proposed synthesis the intermediates and the product were characterized by IR and microRaman spectroscopy, respectively and TEM microscopy as well. By using the IR spectroscopy allowed one to follow the reaction steps and verify the intermediates the reaction product, respectively.

The first intermediate, SWCNT-COOH, was characterization by IR analysis as shown in Figure 2. This spectrum proves the presence of the carbonyl group (-C=O) at 1655 cm^{-1}, the carboxyl group (–COOH) group can be observed at 1395 cm^{-1} and 3137 cm^{-1} and the carbon-oxygen bond (-C-O) shows a peak at 1066 cm^{-1}.

The IR spectrum of the second intermediate (SWCNT-COCl) (Figure 3) proves the presence of the group C=O of the chloride acid at 1705 cm^{-1} while the peak corresponding to the hydroxyl group from COOH (1395 cm^{-1} and 3137 cm^{-1}) disappeared.

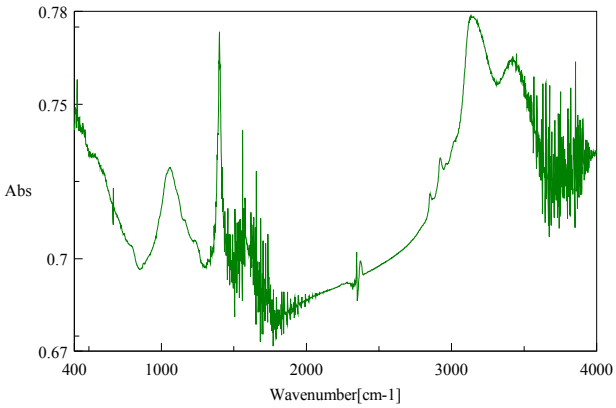


Figure 2. IR spectrum of SWCNT-COOH

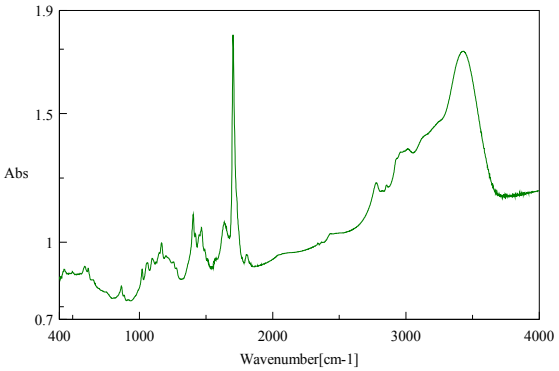


Figure 3. IR spectra of SWCNT-COCl

The IR spectrum of the final product is presented in Figure 4.

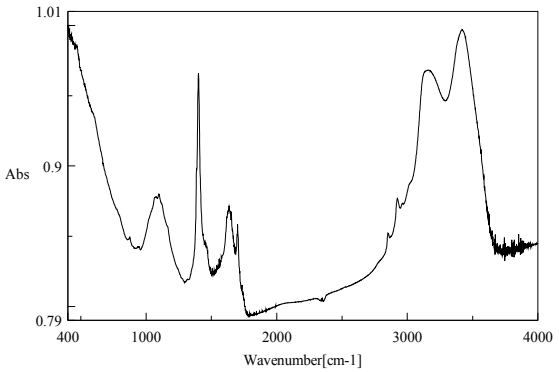
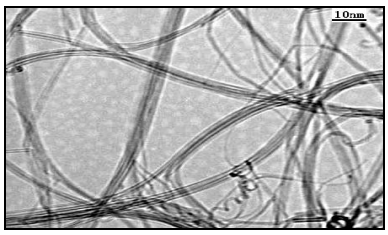


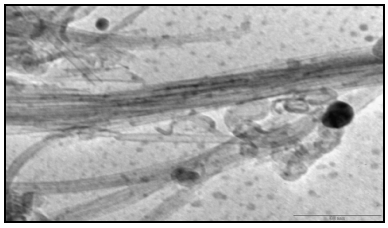
Figure 4. IR spectrum of SWNT-CO-O-$(CH_2)_2$-O-$(CH_2)_2$-O-$(CH_2)_2$-OH

The IR spectrum of the target product shows a peak at 1107 cm^{-1} which proves the presence of an ether bond (C-O-C), another peak at 1400 cm^{-1} of the $–CH_2$ group from the tryethylene-glycol. The peak at 1705 cm^{-1}, corresponding to the C=O bond from the chloride acid, (Figure 3) was missing but a peak at 3137 cm^{-1}, for the –OH group from the products chain end appeared.

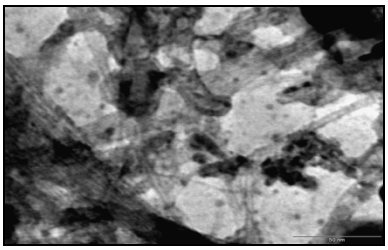
The TEM microscopy images are shown in Figure 5: in comparison to the non-functionalized SWCNTs (5.a), the –COOH groups attached to the nanotubes are clearly seen in 6.b and 6.c (the final product).



a – zoom of 120000x



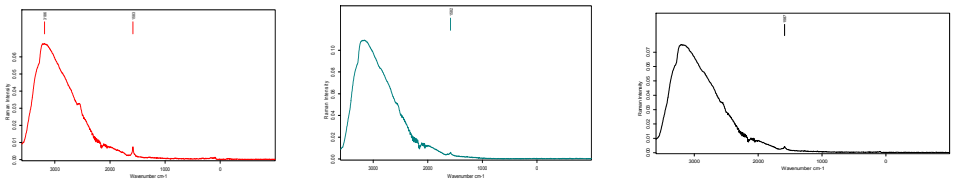
b – zoom of 100000x



c – zoom of 100000x

Figure 5. a – SWCNT; b – SWCNT-COOH; c - SWNT-CO-$[O-(CH_2)_2]_3$-OH

The microRaman spectroscopy is a very sensitive tool, which allows one to observe fine structural modifications. From the spectrum represented in Figure 6 (a, b and c) we can see two important peaks: at 1585 cm^{-1} the so called G-band (a lower intensity band) and at 3186 cm^{-1} a higher intensity band. The G band for non-functionalized SWCNT was recorded at 1583 cm^{-1}, for SWCNT-COOH at 1582 cm^{-1} while in the case of final product at 1587 cm^{-1}.



a. b. c.

Figure 6. a – SWCNT; b – SWCNT-COOH; c - SWNT-CO-$[O-(CH_2)_2]_3$-OH

Because in all three no any significant deviations were seen, especially at the G band, we can conclude that, during the functionalization processes, the carbon nanotubes did nof suffer any structural modifications.

CONCLUSIONS

Based on the IR, TEM and microRaman analysis, we proved the synthesis of the intermediates and the final product, that will be used in further biological studies, with the purpose of transporting therapeutic agents through cell membranes into the desired cells.

EXPERIMENTAL SECTION

The experimental part of this study was elaborated relying on the literature data available so far, the reaction parameters and reactive quantities being optimized according to available materials and resources. The experiment has multiple steps, represented in Figure 7.

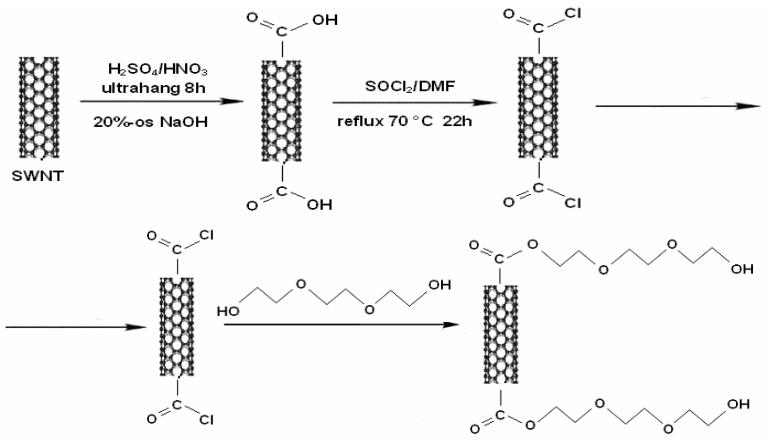


Figure 7. Experiment steps

The first step consists in the functionalization of SWCNTs by energic oxidation, with a mixture of H_2SO_4/HNO_3. The obtained carbonyl functionalized SWCNTs were then reacted with $SOCl_2$ resulting the acid chloride functionalized species. As a last reaction step, the above obtained functionalized SWCNTs were reacted with triethylene-glycol in order to obtain the desired product: triethylene-glycol-functionalized SWCNTs.

The importance of this study relies on the fact that these kind of functionalized SWCNTs have medical use, also.

The first step of the synthesis, as we mentioned above, was the synthesis of carboxyl functionalized SWCNTs and was performed according to C. Lynam et. al[6]. The procedure was the following: 20 mg of SWCNTs were suspended in a mixture of H_2SO_4/HNO_3 (ratio 3:1) in a well dried flask and left in an ultrasonic bath for 8 hours. After this reaction time the obtained mixture was diluted with bi-distilled water afterwards being neutralized with a 20% NaOH solution to pH 7. Later, the solution was filtered through PTFE membrane and the product dried.

The SWCNT-COOH intermediate, weighted 8 mg, was further suspended in a freshly distilled mixture of $SOCl_2$/DMF (ratio 20:1) in a well dried flask[7]. This time the ultrasonic bath lasted for 20 minutes. Afterwards the mixture was refluxed in a stiring oil bath for 22 hours at 70°C. After cooling down, the mixture was distilled (to half of its volume), this way the remaining undesired $SOCl_2$ being removed. To make sure that all of the $SOCl_2$ was removed, the mixture was washed through with dioxane. The next step was rotavaporizing the mixture and than drying it for 48 hours under vacuum dryer.

The last step was the obtaining of the final product: triethylene-glycol-functionalized SWCNT s (SWCNT-CO-O-$(CH_2)_2$-O-$(CH_2)_2$-O-$(CH_2)_2$-OH)). First we attached to the SWCNT-COCl a six ringed 1,6-diol in order to position the hydroxyl group from the end of the chain further away from the carbon nanotubes. 4 mg SWCNT-COCl was suspended in a mixture of 40 µL triethylene-glycol and 1,5 mL 1,4-dioxane in a previously well dried flask. This was followed by sonication for 10 minutes and then refluxed for 52 hours at 110°C, under stirring on an oil bath. After cooling down, the mixture was filtered under vacuum and washed with 3x5 mL of THF (tetrahydrofuran) in order to remove the remaining triethylene-glycol, then dried for 24 hours in a vacuum dryer.

Instruments Used

The ultrasonic bath used for the dispersion of SWCNTs: TRANSSONIC 460/H, ELMA AUSTRIA, 100W, 40 kHz. To remove the remaining unwanted solvents we used the ROTAVAPOR P BÜCHI. The IR spectra of the intermediates was performed with a Fourier IR spectroscope (spectral range 7500-370 cm^{-1}, rezolution > 0.5 cm^{-1}, Michelson type interferometer, DLATGS detector). The analyzed samples were mixed with KBr and pressed into the form of a transparent tablete by hydraulic pressing.

For the electronmicroscopic illustration of the intermediates and of the final product, a transmission electron microscopy TEM was used (Hitachi Automatic TEM H7650, accelerating voltage 40-120 kV, zoom 200x-600000x).

For microRaman spectra, a FRA 106/S module was attached to the Fourier IR spectroscope, and to the module a microscope (Nikon ECLIPSE E400 – spectral range 3600-70 cm^{-1} for Stokes lines and 2000-100 cm^{-1} for the anti-Stokes lines, resolution > 1 cm^{-1}, Nd:YAG laser, ultrasensitive D418-T Ge detector) was linked with an optical wire.

Chemicals Used

The starting material was SWCNT synthesized by Chengu Organic Chemicals Co. Ltd, with the following characteristics: diameter 1-2 nm, lenght ~ 30 μm, purity > 90 tf%, special surface size (SSA) > 380 m^2/g, electrical conductivity > 10^2s/cm, production method CVD (chemical vapor deposition).

Reagents: 98% sulfuric acid (H_2SO_4, Mw = 98.08 g/mol, ρ_f = 1.84g/cm^{-3}), 70% nitric acid (HNO_3, Mw = 39.997g/mol, ρ_{sz} = 2.1g/cm^3), sodium hydroxyd (NaOH), tionil chloride ($SOCl_2$, Mw = 118.97g/mol, ρ_f = 1.638g/cm^3), N,N-dimethyl-formamide (DMF, Mw = 73.09g/mol, ρ_f = 0.944g/cm^3), tryethylene-glycol ($C_6H_{14}O_4$, Mw =150.17g/mol, ρ_f =1,1g/cm^3), tetrahyrofuran (THF, C_4H_8O, Mw = 72.11g/mol , ρ_f = 0.8892g/cm^3).

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