U.P.B. Sci. Bull., Series B, Vol. 75, Iss. 2, 2013 ISSN 1454-2331

SINGLE-WALL CARBON NANOTUBES PURIFICATION AND OXIDATION

Constantin-Claudiu CIOBOTARU[1], Celina Maria DAMIAN[2], Horia IOVU[3]

A study to optimize the purification and oxidation reactions of single-wall carbon nanotubes (SWCNT) was realized. The main purpose of this study was the removal of amorphous carbon and metal particles resulted from carbon nanotubes synthesis and the oxidation of these purified nanotubes for grafting carboxyl functional groups on their surface. Purified and oxidized nanotubes were extensively characterized by analysis of Fourier transform infrared spectroscopy in order to demonstrate the purification and oxidation, Raman spectroscopy to quantify the defects introduced in the electronic structure, X-ray photoelectrons spectroscopy for surface elemental composition, thermogravimetric analysis, scanning electron microscopy and transmission electron microscopy.

Keywords: single-wall carbon nanotube, thermogravimetric analysis, purification, oxidation

1. Introduction

Since they were discovered by Iijima in 1991 [1], single wall carbon nanotubes (SWCNTs) have been studied by many researchers. SWCNTs have a wide range of properties such as mechanical, electronic, thermal, optical, pharmaceutical properties and very large surface area [2-6]. Even if SWCNTs have a lot of good properties, samples from commercial sources usually contain several impurities, especially amorphous carbon and metal particles, like Co or Mo, derived from the catalysts used for their synthesis [7]. The purification process can be achieved by several different methods. These are classified as oxidative methods which can be made in liquid phase or gas phase, chemical functionalization protocols, filtration and chromatography techniques, and microwave heating methods [8].

T. Suzuki et al. [9] described a method for SWCNTs purification which involves the use of high-pressure micro reactor. In this purification process the SWCNTs are mixed with distillated water and after that the liquid reacts with H_2O_2 in a quart container at different temperatures.

---

[1] PhD Student, Advanced Polymer Materials Group, University POLITEHNICA of Bucharest, Romania, e-mail: claudiuciobo@yahoo.com

[2] PhD, Advanced Polymer Materials Group, University POLITEHNICA of Bucharest, Romania

[3] Prof., Advanced Polymer Materials Group, University POLITEHNICA of Bucharest, Romania

Guo W. et al. have reported a procedure for SWCNTs purification in four-step [10]. First they made an oxidation process involving the use of HNO_3/HCl mixture. The second step was the freeze-drying, and the third step was the steam treatment, as the frozen mixture was heated and then the dissolution in HCl 6M was done.

Rosario-Castro B. [7] et al. described an oxidation process which requires the use of an acid mixture made by concentrated H_2SO_4 and HNO_3 (3:1 molar ratio). Thus the purified SWCNTs were suspended in this mixture and then sonicated and finally diluted in water. The diluted suspension was centrifuged several times, washed with distillated water, filtered and dried overnight under vacuum.

The aim of this study was to elaborate a cleaning procedure for SWCNTs that provides additional removal of amorphous carbon and metal catalyst particles used for the growth of SWCNTs from commercial source and the oxidation of these purified SWCNTs. The purification process is similar to that suggested by Karatepe et al. [11] with the difference that this method is carried out at different temperatures without using of H_2O_2. The method was optimized by monitoring the Mo content at different times of purification.

2. Materials and methods

2.1. Materials

Single-wall carbon nanotubes (SWCNTs) were purchased from Sigma Aldrich having chirality 6.5, more than 90% carbon basis, more than 77% carbon as SWCNTs, and diameter range between 0.7 and 0.9, produced by CoMoCAT$^{®}$ Catalytic Chemical Vapor Deposition (CVD) Method. Purification was made using a solution of hydrochloric acid 3M (Sigma-Aldrich: Fluka-25%). In order to remove the hydrochloric acid, samples were washed with ultra-pure water from Millipore Milli-DI Purification Pack device and filtered on 0.22 μm pore PTFE membrane.

Oxidation was made using a mixture of H_2SO_4 purchased form Sigma Aldrich having concentration 95-98% and HNO_3 received from Fisher Chemicals with concentration 70% and density 1.42 g/cm^3.

2.2. Methods

2.2.1. SWCNTs purification

The main reason for purification was the removal of amorphous carbon and the metals catalyst particles used to the growth of SWCNTs. Thus 100 mg of SWCNTs were milled in order to decrease agglomerated dimensions and then 100 ml solution 3M of hydrochloric acid was added. The mixture was heated at 70 °C in silicone oil bath and kept under a stirring rate of 500 rpm for 24 h. Then other samples were subjected to the same purification method, but for 48 h, for 72 h, respectively. After that the mixture was filtered on 0.22 μm pore PTFE membrane and washed with ultra-pure water until the pH reached neutral value. Purified carbon nanotubes were dried under vacuum for 48 h at room temperature (see Fig 1).

2.2.2. SWCNTs oxidation

Because of their very small size, SWCNTs can be used as carriers. For that reason the carbon nanotubes should be first functionalized. Thus 100 mg of SWCNTs purified as described above were milled in order to decrease agglomerated particles and then 80 ml of mixture of sulfuric acid and nitric acid (3:1 molar ratio) were added. The mixture was heated at 70 °C in silicone oil bath and kept under stirring rate of ~400 rpm for 4 hours. Then the mixture was cooled and ultra-pure water was added. Next the mixture was filtered to remove the acid residues. After filtration ultra-pure water was added and the mixture was sonicated in a sonication bath for 90 min. Then the mixture was filtered, washed with ultra-pure water, in order to reach a neutral pH, and dried in a vacuum oven for 48h at room temperature (see Fig. 1).

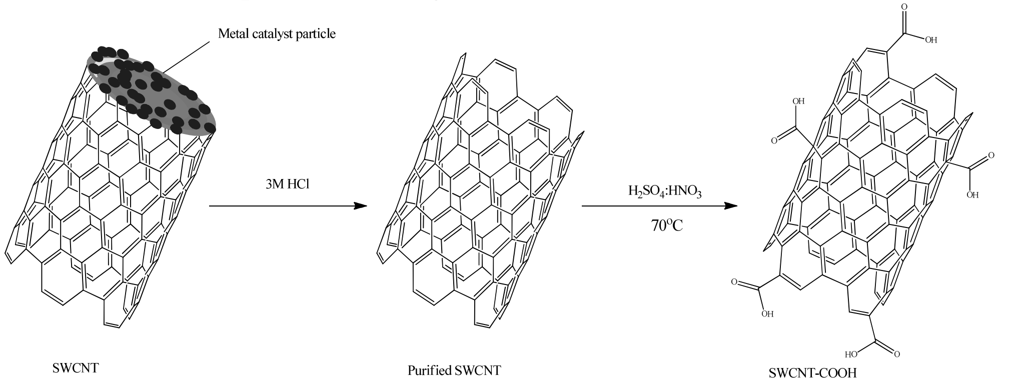


Fig. 1. SWCNTs purification and oxidation reactions

2.3. Advanced characterization

Fourier transform infrared spectroscopy (FTIR) spectra of SWNCTs, purified SWCNTs and oxidized SWCNTs were registered on an Bruker Vertex 70 equipment in 400 ÷ 4000 cm^{-1} range with 4 cm^{-1} resolution and 32 scans. The samples were analyzed in KBr pellets.

Raman spectra of SWNCTs, purified SWCNTs and oxidized SWCNTs were recorded on a DXR Raman Microscope (Thermo Scientific) by 532 nm laser line. The 10x objective was used to focus the Raman microscope.

Thermogravimetry analysis (TGA) of the samples was done on Q500 TA equipment, using nitrogen atmosphere from 20 °C to 900 °C with 10 °C/min heating rate.

The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Scientific K-Alpha equipment, fully integrated, with an aluminum anode monochromatic source. Survey scans (0-1200 eV) were performed to identify constitutive elements.

Study by the transmitted electron microscopy was performed using transmission electron microscopy of high resolution (HRTEM) G2 F30 Tecnai type with linear resolution of 1 Å and a punctual resolution of 1.4 Å. Small amounts of powder were immersed in water or tetrahydrofuran (THF), the suspension was homogenized by ultrasonication. Using a copper grid covered with a layer (with holes) very thin carbon fine particles were collected from homogenized suspension. The samples obtained were examined by transmission electron microscopy in bright field (TEMBF) and transmission electron microscopy of high resolution (HRTEM).

Scanning electron microscopy (SEM) was done on a Quanta Inspect F, a FEI instrument, with a field emission electron gun, 1.2 nm resolution and X-ray energy dispersive spectrometer having an accelerating voltage of 30kV.

3. Results and discussion.

3.1. XPS Analysis

From the synthesis of CNTs by CVD process a small amount of catalyst is remaining in the final commercially available product. Thus, XPS analysis is useful to monitor the removal of these types of impurities by purification reaction. XPS spectra presented in Fig. 2 and XPS date from Table 1 show the decrease of Mo quantity from samples of SWCNTs after purification. It can be shown that the best result was obtained for purification process at 48 h. An interesting observation was that, after 72 h purification time, the content of the Mo catalyst was not lowered, this being explained by the use of different samples, and not the cumulation of times for the same sample.

Table 1

XPS data for SWCNTs as-received, SWCNTS purified and SWCNTS oxidized

Samples / At %	SWCNTs	SWCNTs p24h	SWCNTs p48h	SWCNTs p72h	SWCNTs-COOH p48h
C1s	96.43	95.50	96.09	96.45	79.91
O1s	3.25	3.50	3.78	3.37	18.97
Mo3d	0.32	0.14	0.13	0.18	0
F1s	0	0.86	0	0	1.12

The best efficiency of purification time was noticed for the 48 h method, this being considered as optimal purification process in our study.

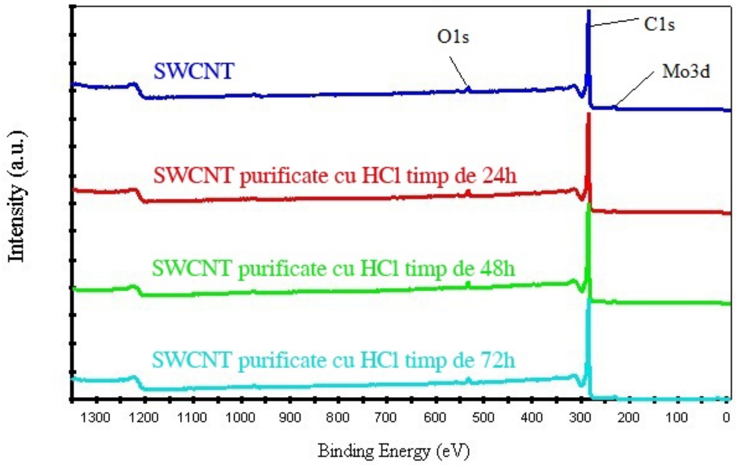


Fig. 2. XPS spectra for SWCNTs and SWCNTs purified at 24, 48, and 72 h.

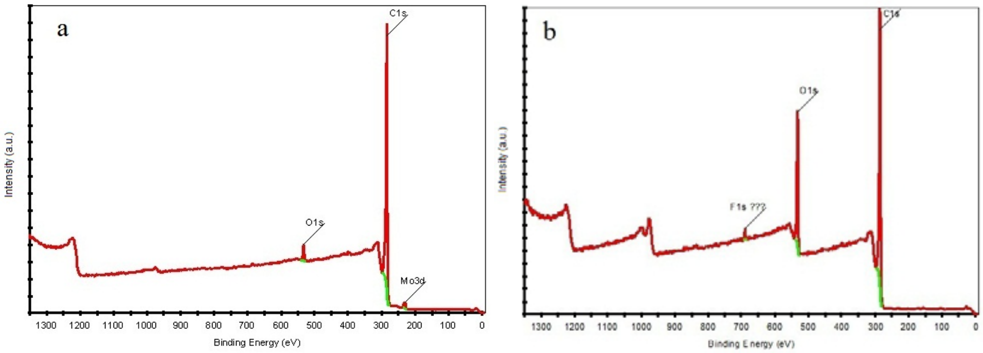


Fig 3. XPS spectra for: a. SWCNTs; b. SWCNTs purified at 48h and oxidized

The XPS spectra presented in Fig. 3 show the increase of oxygen concentration from 3.78 % to 18.97 % after oxidation process. This demonstrates that SWCNTs was successfully oxidized. The presence of F1s in XPS spectra of SWCNTs is explained by the use of PTFE membranes for filtration process. Also after oxidation process the amount of Mo3d was reduced to 0 %.

3.2. FT-IR Analysis

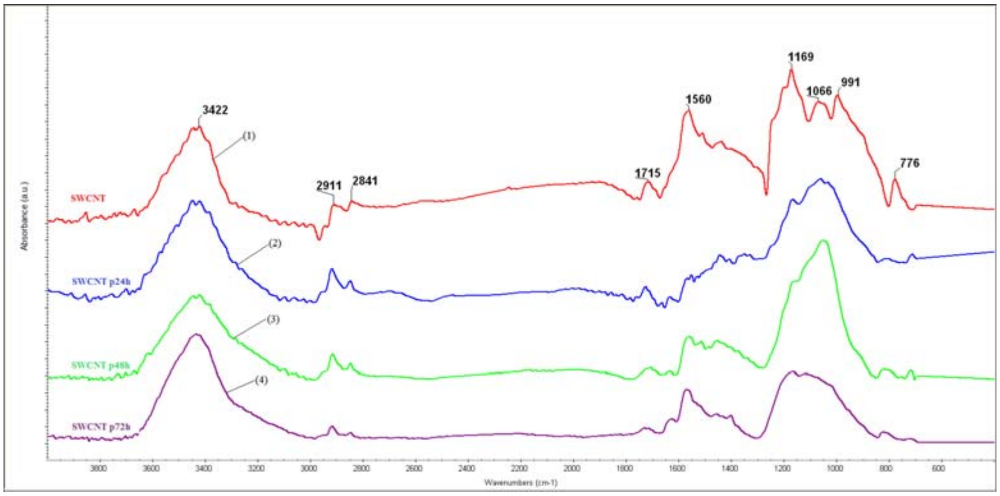


Fig. 4. FT-IR spectra of SWCNTs (1) and SWCNTs purified at 24 (2), 48 (3), and 72h (4)

FT-IR spectra shown in Fig. 4 correspond to SWCNTs as-received and SWCNTs purified at different times: 24, 48 and 72 h. The absorption at 3422 cm^{-1} is assigned to the –OH stretching vibration from water absorbed during pellet preparation. Carbon nanotube synthesis determined the bands at 2911 cm^{-1} and 2841 cm^{-1} corresponding to C-H stretching vibration, and the bands at 1715 cm^{-1} and 1560 cm^{-1} assigned to C=O stretching vibration [12].

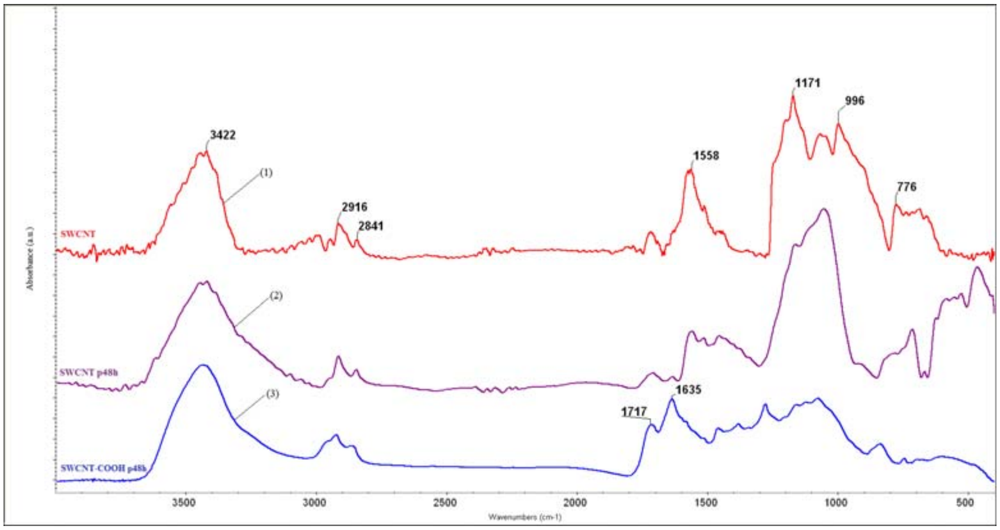


Fig. 5. FT-IR spectra of SWCNTs (1), SWCNTs purified at 48h (2) and SWCNTs-COOH (3).

From the purified and oxidized SWCNTs spectra it can be noticed the appearance of two new peaks at 1717 and 1635 cm^{-1} corresponding to C=O stretching vibration, fact which is another proof that SWCNTs were successfully oxidized [13-14].

3.3. Raman spectroscopy

Raman spectroscopy is a very useful tool for SWCNTs characterization. Raman spectra presented in Fig. 6 showed that the purification process led to an increase of defects on SWCNTs surface. This can also be explained by the removal of metals derived from catalyst used to the nanotube synthesis. This was demonstrated by the increase of band from 1300 cm^{-1}.

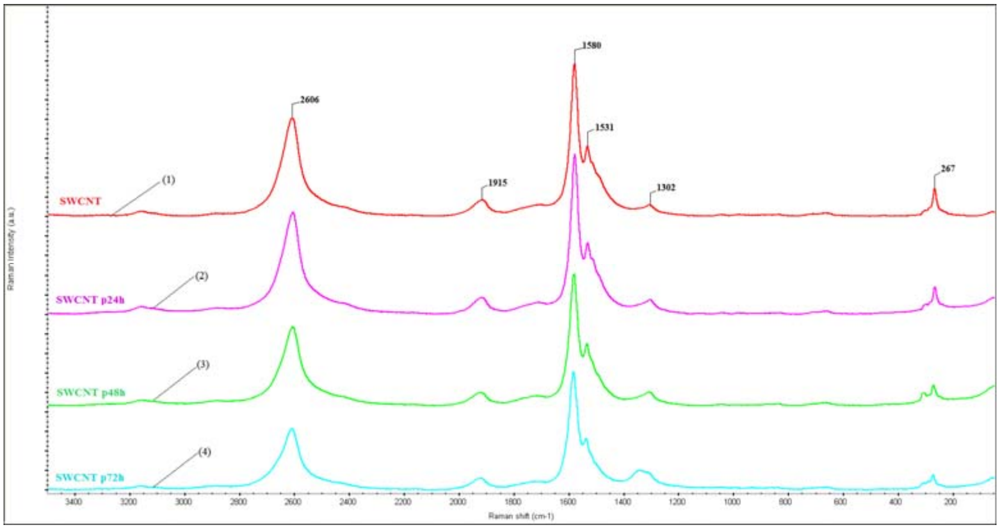


Fig. 6. Raman specta of SWCNTs (1) and SWCNTs purified at 24 (2), 48 (3), and 72 h (4).

Fig. 7 shows that the oxidation process of purified SWCNTs induced the defect formation on SWCNTs side-walls, because the D band increased. Moreover, the band from 2600 cm^{-1} (known as G’ band) disappeared, due to the extreme oxidation conditions. The band from 265 cm^{-1} also disappeared, as a result of the presence of acid anions inside the tubes which were inserted during oxidation process [15-16].

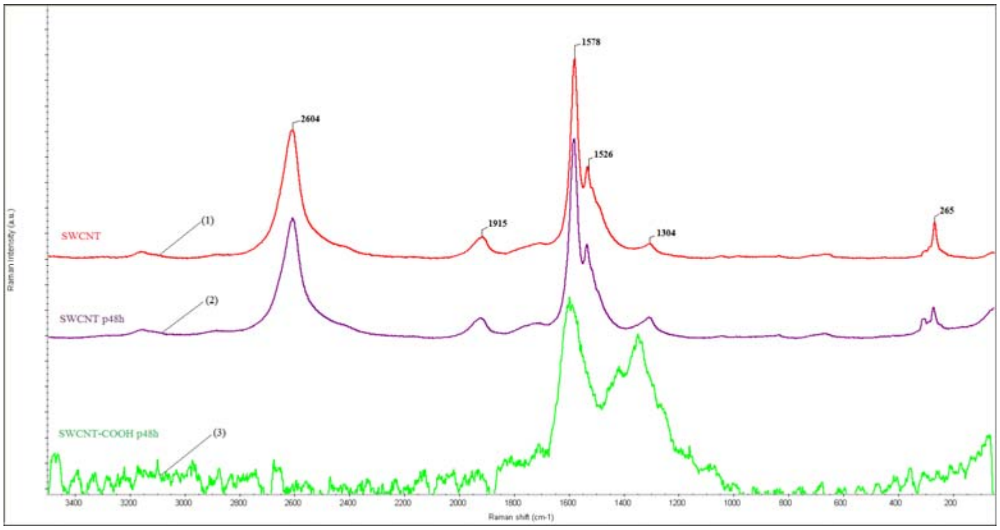


Fig. 7. Raman spectra of SWCNTs (1), SWCNTs purified at 48h (2) and SWCNTs-COOH (3).

From table 2 it can be seen that I_D/I_G ratio is getting higher as the purification time increases. A possible explanation of these findings can be the increase of defects number (considered as sp^3 hybridized C atoms) resulted in the end cap area of the nanotubes after purification. Compared to literature [11] the difference between the I_D/I_G ratio of raw SWCNTs and purified SWCNTs is lower, meaning that the sidewalls of the nanotubes are not affected and the amount of the amorphous carbon is lower. Besides, the I_D/I_G ratio for oxidized SWCNTs is much higher than for as-received SWNCTs and SWCNT purified at different times [15].

Table 2

Raman data for SWNCTs as-received, purified SWCNTs and oxidized SWCNTs

Samples	I_D	X_D, cm^{-1}	I_G	X_G, cm^{-1}	I_D/I_G
SWCNTS	115.0	1308.3	1556.4	1581.2	0.07
SWCNTS p24h	128.4	1303.5	1501.5	1578.3	0.09
SWCNTS p48h	174.2	1311.0	1679.1	1582.9	0.10
SWCNTS p72h	20.1	1344.8	122.9	1584.7	0.16
SWCNTS-COOH	226.9	1349.6	284.7	1598.4	0.78

3.4. Thermogravimetric analysis (TGA)

The as-received SWCNTs start to decompose near to 180 °C and continue with decomposition of amorphous carbon close to 315 °C (Fig. 8) [17]. It can be seen that the increase of purification time leads to an increase of weight loss. This demonstrates that the SWCNTs were purified from the amorphous carbon and metal particles, like Co or Mo, derived from the catalyst which would not decomposed in the temperature domain of the analysis.

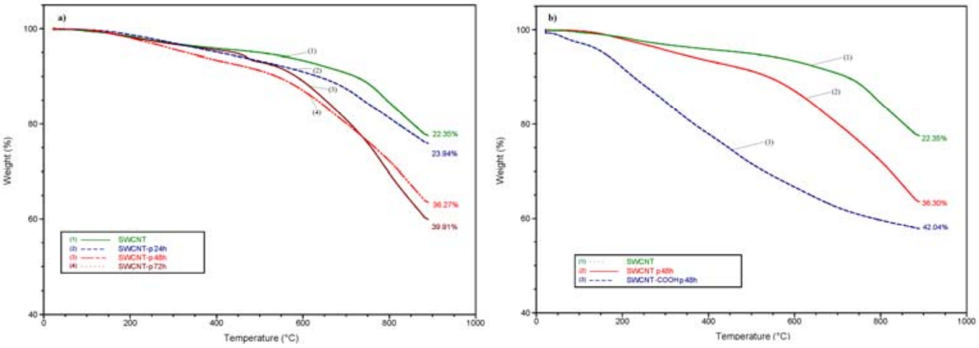


Fig. 8. TGA curves of: a) as-received SWCNTs (1) and SWCNTs purified at 24 (2), 48 (3), 72 h (4); b) as-received SWCNTs (1), SWCNTs purified at 48h (2) and SWCNTs-COOH (3).

Fig. 8 b) shows that TGA curve for SWCNTs-COOH p48h exhibits a different shape. This is explained by the presence of COOH groups. Therefore, the decarboxylation and dehydrogenation of –COOH groups introduced by oxidation process occur between 25-200 °C [16]. Moreover, the weight loss increases, being explained by the presence of defects on sidewall of SWCNTs induced by oxidation process.

3.5. Morphological characterization

The surface morphology of as-received SWCNTs and purified SWCNT at 48h was studied by scanning electron microscopy (Fig. 9) and transmission electron microscopy (Fig. 10).

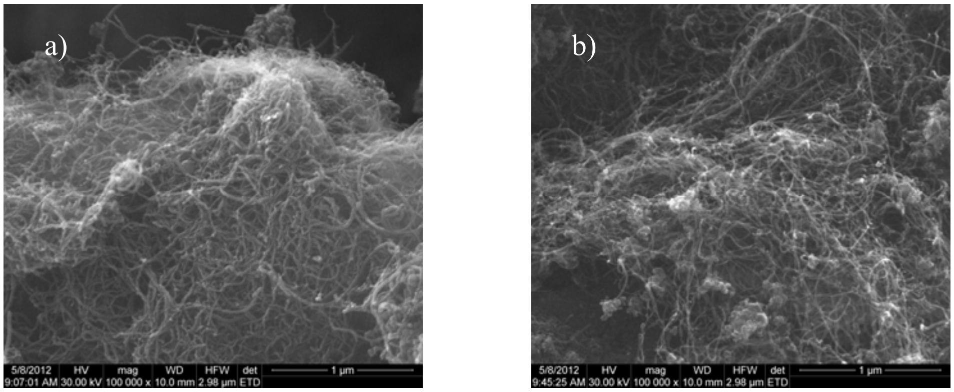
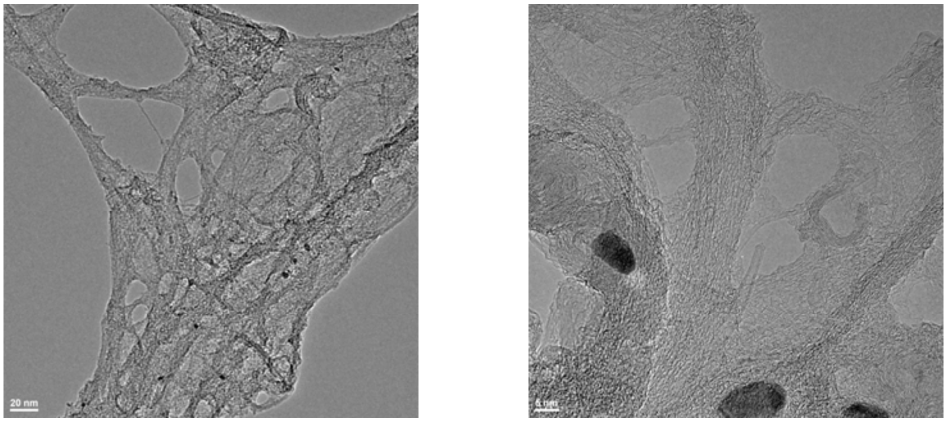


Fig. 9. SEM images of: a) as-received SWCNTs; b) SWCNTs purified at 48h



a) b)

Fig 10. TEM images of: a) as-received SWCNTs; b) SWCNTs purified at 48h

The comparison of SEM and TEM images from as-received SWCNT and purified SWNCT could clearly define the differences between before and after the purification process. It can be observed that the as-received SWCNTs are agglomerated and include particles of metals used during the synthesis [7].

In the case of purified SWCNT at 48h it can be observed that the nanotubes are not so crowded and the small black particles representing the metals used to the SWCNTs synthesis were removed [18].

4. Conclusions

A study was accomplished in order to optimize the purification reaction of singlewall carbon nanotubes by treatment with 3M HCl at different times: 24, 48 and 72 h. By using Thermogravimetry analysis, Raman spectroscopy and X-ray photoelectrons spectroscopy, it was demonstrated that SWCNTs were purified and the optimal purificatio time is 48 h.

Compared to literature data, the method described showed lower amorphous carbon content after purification, and lower sidewall defects, given by I_D/I_G ratio calculated from Raman spectra

The oxidation of SWCNTs was proved by FTIR spectra which show distinctive bands assigned to C=O bond. The TGA analysis showed the decarboxylation of carboxyl groups in the temperature range of 25-200 °C. The oxidation of SWCNTs was also proved by the increase of O_{1s} content through

XPS and by the increase of the defects number of C sp^3 type through RAMAN spectroscopy.

Acknowledgement

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/107/1.5/S/76903.

REFERENCES

[1] *S. Ijima*, Helical microtubules of graphite carbon, Nature, **vol.** 354, November 1991, pp.56–88.

[2] *J. N. Coleman, U. Khan, W. J. Blau, Y. K. Gun'ko*, Small but strong: A review of the mechanical properties of carbon nanotube–polymer composites, Carbon **vol.** 44, issue 9, August 2006, pp. 1624–1652.

[3] *P.L. Lai, S.C. Chen, M.F. Lin*, Electronic properties of single-walled carbon nanotubes under electric and magnetic fields, Physica E: Low-dimensional Systems and Nanostructures, **vol. 40**, issue 6, April 2008, pp. 2056–2058.

[4] *Z. Han, A. Fina*, Thermal Conductivity of Carbon Nanotubes and their Polymer Nanocomposites: A Review, Progress in Polymer Science, **vol. 36**, issue 7, July 2011, pp. 914-944.

[5] *R.B. Chen, C.H. Lee, C.P. Chang, C.S. Lue, M.F. Lin*, Electronic and optical properties of finite carbon nanotubes in a static electric field, Physica E: Low-dimensional Systems and Nanostructures, **vol. 34**, issue 1-2, August 2006, pp. 670–673.

[6] *M. Foldvari, M. Bagonluri*, Carbon nanotubes as functional excipients for nanomedicines: I. pharmaceutical properties, Nanomedicine: Nanotechnology, Biology, and Medicine, **vol. 4**, issue 3, September 2008, pp. 173–182

[7] B. *I. Rosario-Castro, E. J. Contés, M. Lebrón-Colón, M. A. Meador, G. Sánchez-Pomales, C. R. Cabrera*, Combined electron microscopy and spectroscopy characterization of as-received, acid purified, and oxidized HiPCO single-wall carbon nanotubes, Materials characterization, **vol. 60**, issue 12, December 2009, pp. 1442 – 1453.

[8] *T. Park, S Banerjee, T. Hemraj-Benny, S. S. Wong*, Purification strategies and purity visualization techniques for single-walled carbon nanotubes, Journal of Materials Chemisty**, vol. 16**, issue 2, 2006, pp. 141–154.

[9] *T. Suzuki, S. Inoue, Y. Ando*, Purification of single-wall carbon nanotubes by using high-pressure micro reactor, Diamond & Related Materials, **vol. 17**, issue 7-10, July-October 2008, pp. 1596–1599.

[10] *W. Guo, Z. Dou, H. Li, Z. Shi, H. Sun, Y. Liu*, An efficient strategy for the purification of cloth-like single walled carbon nanotube soot produced by arc discharge, Carbon, **vol. 48**, issue 13, November 2010, pp. 3769 – 3777.

[11] *N. Karatepe, N. Yuca*, Hydrogen adsorption on carbon nanotubes purified by different methods, International journal of hydrogen energy, **vol 36**, issue 17, August 2011, pp. 11467 – 11473.

[12] *H. M. Park, K. H. Kim, S. H. Lee, D. H. Park, Y. K. Hong, J. Joo*, Electrochemical polymerization of polypyrrole (PPy) and poly(3-hexylthiophene) (P3HT) using

functionalized single-wall carbon nanotubes, Colloids and Surfaces A: Physicochem. Eng. Aspects, **vol. 313–314,** February 2008, pp. 72–76.

[13] *M. M. Stylianakis, J. A. Mikroyannidis, E. Kymakis*, A facile, covalent modification of single-wall carbon nanotubes by thiophene for use in organic photovoltaic cells, Solar Energy Materials & Solar Cells, **vol. 94**, issue 2, February 2010, pp. 267–274

[14] *E.B. Barros, A.G. Souza Filho, V. Lemos, J. Mendes Filho, S.B. Fagan, M.H. Herbst, J.M. Rosolen, C.A. Luengo, J.G Huber*, Charge transfer effects in acid treated single-wall carbon nanotubes, Carbon, **vol. 43,** issue 12, October 2005, pp. 2495–2500.

[15] *L. Lafi, D. Cossement, R. Chahine*, Raman spectroscopy and nitrogen vapour adsorption for the study of structural changes during purification of single-wall carbon nanotubes, Carbon, **vol. 43**, issue 7, June 2005, pp. 1347–1357

[16] *H. Kitamura, M. Sekido, H. Takeuchi, M. Ohno*, The method for surface functionalization of single-walled carbon nanotubes with fuming nitric acid, Carbon, **vol. 49**, issue 12, October 2011, pp. 3851 –3856

[17] *J. Li, Y. Zhang*, A simple purification for single-walled carbon nanotubes, Physica E: Low-dimensional Systems and Nanostructures, **vol. 28**, August 2005, pp. 309–312.

[18] *S. Han, S. Oh, L. Tan, J. Baek*, One-pot purification and functionalization of single-walled carbon nanotubes in less-corrosive poly(phosphoric acid), Carbon, **vol. 46,** *November* 2008, pp. 1841–1849.