OPTIMIZATION OF SYNTHESIS CONDITION FOR HIGH QUALITY CARBON NANOTUBES

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High quality Multi Wall Carbon nanotubes (MWCNTs) have been synthesized in Aerosol –CVD reactor by the optimization of the synthesis process.

Scanning and Transmission electron microscopes have been used for characterization of CNTs, grown under different synthesis conditions (different values of reaction temperature and ferrocene/cyclohexane relation).

It was established that the reaction temperature between 840-950^{0}C and 15-18 mg/ml ferrocene/cyclohexane relation are optimal conditions for the synthesis of long (up to 650 μm) MWCNTs, which diameters range between 10 and 85 nm.

Keywords: CNTs, Aerosol-CVD, SEM, TEM, ferrocene.
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1. INTRODUCTION

The outstanding properties of carbon nanotubes (CNTs) as a functional material for electronic devices, computation, power generation, catalysis, medicine and drug delivery causes a great interest to understand what factors control the nanotube sizes, number of walls, the helicity and the defectiveness of the tubular structure during synthesis process; this is due to the fact that different structure of the tubes may result in great changes in their mechanical and electrical properties [1-4]. In general, CNTs are synthesized by arc discharge, laser ablation, chemical vapor deposition (CVD) and spray pyrolysis [5-8]. Although first two methods from above mentioned can produce high quality SWNTs, the available quantity from both arc discharge and laser ablation is limited. The other problem is to develop cost effective, eco- friendly method synthesis of high quality CNTs with good parameters and large scale.

In this paper we report about the characterization of CNTs, synthesized by Aerosol assisted Chemical Vapor Deposition (A-CVD) method, using various temperatures and catalyst concentration. Have been analyzed the influence of different technological conditions to structural and physical properties of the synthesized CNTs.

2. EXPERIMENT

To synthesize CNTs have been used horizontal quartz reactor (2 m length quarts tube) covered by movable electric furnace with 35 cm long and 22 cm in diameter. This technology is based on the injection of the solution in the reactor as an aerosol and its decomposition under high temperature (830-1000^{0}C). Cyclohexane (C_6H_{12}) and ferrocene ($Fe(C_5H_5)_2$) were used as chemical raw material and catalyst, respectively. The solution with different ferrocene/cyclohexane relation was transformed into an aerosol by the ultrasonic transducer (frequency - 800 kHz). The aerosol was injected to the quarts reactor, which equipped with high temperature movable furnace by using transport gas (Ar/H2 mixture). Each sample of the CNTs with different synthesis condition has been analyzed. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to observe morphology, and characterize geometric parameters (diameter, length, number of shells) of the obtained CNTs and Fe position in the CNT.

3. RESULTS AND DISCUSSION

To find optimal technological condition was changed some of parameters of the reaction: decomposition temperature, Fe content in the solution, gas flows, et.al. The temperature dependence was determined in the range of 830-1000^{0}C. Lower synthesis temperatures result to low carbon nanotube yield and SEM observations show that the increasing temperature led to formation of other carbon structure or pyrolytic carbon, which relative weight to CNTs is increasing in high temperatures (higher than 950^{0}C). At 1000^{0}C on quarts tube was deposited other carbon structures or pyrolytic carbon. Fig. 1 shows SEM pictures of carbon structures, grown at 840 and 1000^{0}C for comparison. It is observed that, increasing of reaction temperature near limit led to formation of more straight, smooth and longer CNTs, compared with low synthesis temperature (at 830^{0}C ~90 μm, 950^{0}C ~630 μm (see fig. 2).

Most of the CVD techniques require presence of metallic catalyst during the growth of CNTs, because it may affect not only successful growth, and also morphology, number of walls of the grown nanotubes.
Several metals used as catalyst, but shown that among of them Fe is more suitable for crystallization of the nanotubes and same time it is interesting for application point of view [9-11].

Has been varied the different volume of Fe catalyst in cyclohexane solvent in order to understand how influence the catalyst quantity to the end product. If ferrocene is absent in the cyclohexane solvent is not

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observed any deposition on quarts surface (was not grown CNTs). The volume of deposited product is increased by increasing ferrocene quantity in the solution. This process is limited, because more than 20 mq/ml in ferrosene/cyclohexane relation lead to saturation of solvent.

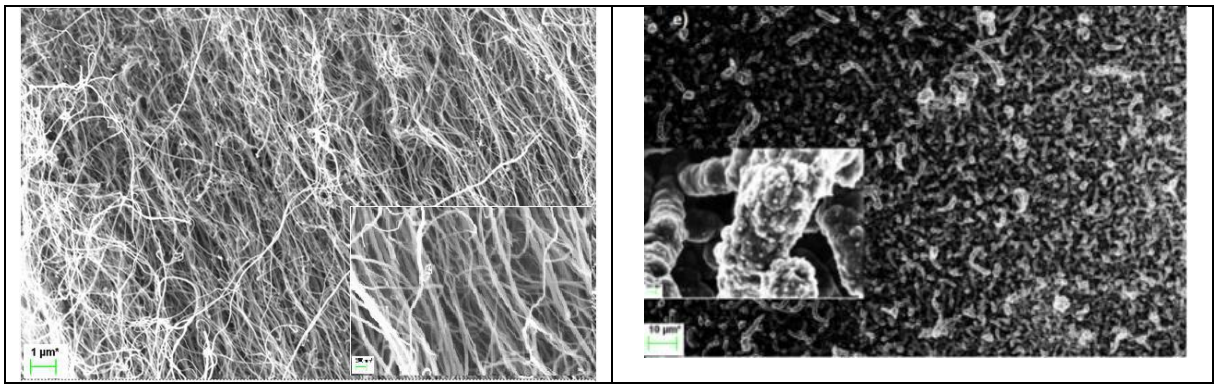

Fig.1. SEM pictures of CNTs grown by Aerosol CVD method: left – growth temperature -840^{0}C; right- growth temperature -1000^{0}C

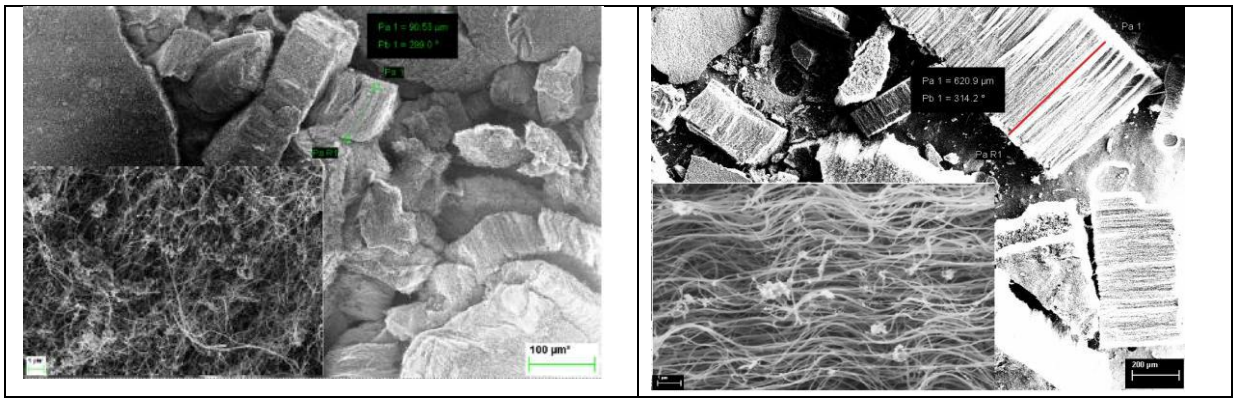

Fig.2. CNTs, grown at 830^{0}C (left) and 950^{0}C (right)

It was observed that relative concentration of other carbon structures or pyrolytic carbon to CNTs is increasing with increasing Fe concentration in the solution. It can be assumed that due to increasing the numbers of the catalyst centers, which were involved in growth of carbon nanotubes, after decomposition by temperature the carbon atoms were seeking after new catalytic centers instead of continuing the growth of CNTs, which has already begun. This process is chaotic. TEM observations of CNTs have provided with more detailed information about diameter, number of walls, structure and position of the catalyst in the CNTs. The number of the walls increases with increasing CNT diameter. The C layers are nicely visible for all CNTs (fig. 3).

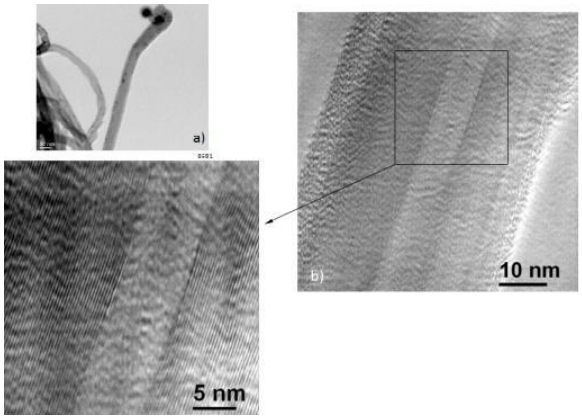

Fig.3. a) CTEM image of a CNT with diameter D ≅ 45 nm. b) HR-TEM image taken along the CNT. c) High magnification of the squared area of b).

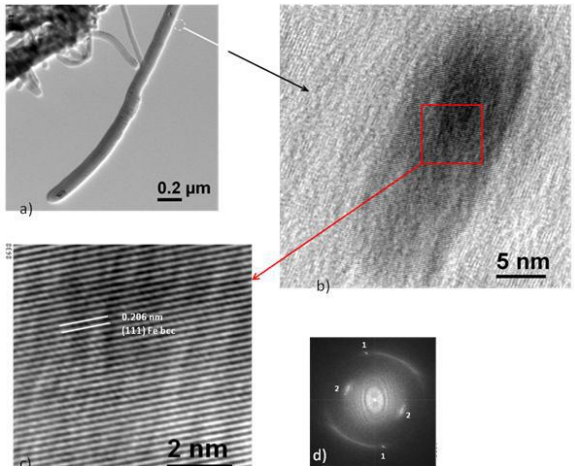

Fig.4. HR-TEM results of CNTs. b) is the HR-TEM image of the dash-circled area of a) with its magnification in c).

A HR-TEM study of a Fe-rich area of the CNTs is presented in fig. 4. The fringes of the lattice planes have a spacing of 0.206 nm which pretty agrees with the spacing of the (111) planes of Fe bcc. The FFT (fast Fourier transform), i.e. electron diffraction pattern, from the Fe-rich area and surrounding matrix (fig. 4d) confirms that conclusion. In fig.4d the spots 1 are due to the (111) planes of Fe bcc, whilst spots 2 give d_{hkl} = 0.340 nm that pretty agrees with the spacing of the (002) planes of graphite (d_{002}= 0.3395 nm, according to the WebEMAPS)

For the smaller thicknesses, only some discontinuous segments of C layers are visible (fig. 5 right). This anyway may be sufficient to confirm that also the small NTs have a MW (6-8 layers) structure although quite irregular and discontinuous.

The inner channel also increases from ~2.2 to ~15 nm for D increasing from 11 to 60 nm but then drops to ~6 nm for D=85 nm (fig. 6).

TEM results show that MWCNTs, which is observed, are partially filled by pure Fe and it was also found at different positions along the CNT, not only at the CNT tip (fig.7). This has been concluded by applying several operation modes of the TEM: X-EDS, EF-TEM, HAADF, HR-TEM.

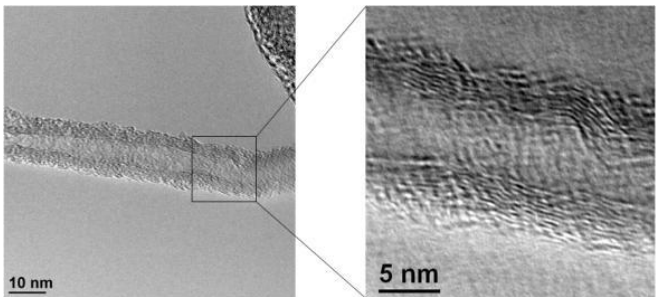

Fig.5. Left: HR-TEM image of a CNT with diameter D~13 nm. Right: high magnification of the squared area.

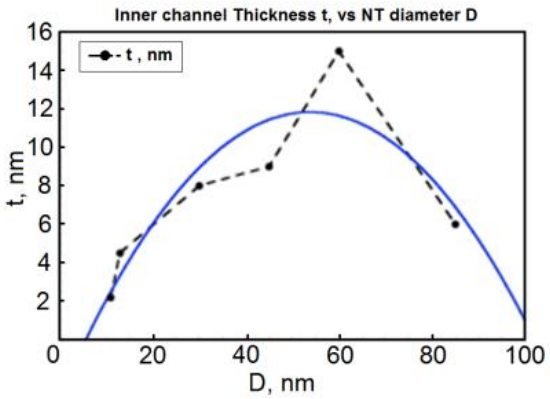

Fig.6. Thickness (t) of the inner channel as a function of the NT diameter (D). The black dots are the experimental data while the blue parabolic curve is a tentative fitting.

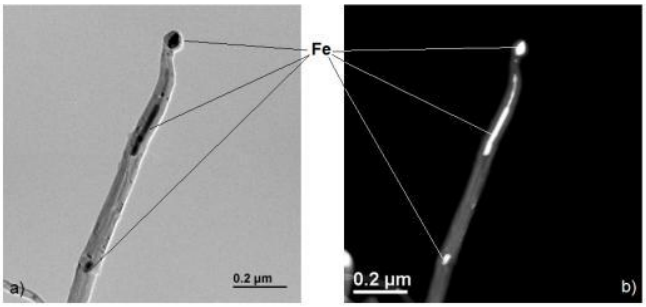

Fig.7. a) CTEM image of CNT; b) Corresponding HAADF image.

4. CONCLUSION

It was grown long (up to 650 µm) multiwall carbon nanotubes, which diameters between 10 and 85 nm by optimization of synthesis process in the Aerosol-CVD system.

It was established that the reaction temperature between 840-950^{0}C and 15-18 mg/ml ferrocene/cyclohexane relation are optimal condition for synthesizing of high quality CNTs.

TEM observations of grown CNTs have provided with more detailed information about diameter, number of walls, structure and position of the catalyst in the CNTs. The number of the walls increases with increasing CNT diameter up to 85 nm. The distance between the CNT walls is calculated 0.340 nm, corresponding to graphite (002). For the smaller thicknesses (~10-15 nm) only some discontinuous segments of CNT walls are visible. This anyway may be sufficient to confirm that also the small CNTs have a MW (6-8 layers) structure although quite irregular and discontinuous.

Has been defined that Fe nanoparticles were situated not only in the tip of the tubes, and also along the length of the nanotube (in the inner channel of the CNTs) and no other impurities or composites are present in the tubes or around of them.

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