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Characterization of high quality carbon nanotubes synthesized via Aerosol -CVD

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Abstract

A new Aerosol assisted CVD method of synthesizinglarge amount ofhigh quality carbon nanotubes (CNTs) with good structural parameters has been developed. We report the optimization of the process by experimental variables of thesynthesis condition. The effect of temperature in the hot zone of the reactor was investigated, and 840-950 ^{0}C was chosen as an optimum synthesis temperature.

CNTs, obtained with different solvents as a carbon source have been analyzed, and ferrocene volume in cyclohexane solvent was varied, as the result of which has been grown MWCNTs with diameters of 10-85 nm and a small percent of SWCNTs with diameters of 0.85 and 1.14 nm.

The position of Fe nanoparticles in the CNTs was defined by TEM observations, which show 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).

Keywords

Aerosol-CVD; MWCNTs; SWCNTs; ferrocene; Raman spectroscopy; SEM; TEM

Highlights

- High purity CNTs were synthesized by Aerosol CVD method.
- The growth mechanism was studied and it was found that the optimal growth conditionsare different depending on carbon source
- The Raman spectroscopy analysis lets us assume that among MWCNTs small percentage of SWCNTs are present in the synthesized nanomaterial

1. Introduction

Carbon nanotubes (CNTs) – carbon made tubular structures of nanometer scale - have unique mechanical, thermal, electrical and optical properties, and it is of great interest to academic researchers and industry. Moreover, the CNTs with ferromagnetic nanoparticles inside are very interesting for many applications, such as sensors for magnetic force microscopy (MFM) [1-3], magnetic storage devices [4-6] and medicine (drug delivery) [7-9], due to their high specific ferromagnetic properties in addition to their mechanical stability, protection against oxidation and wear resistance. For successful application in nanoelectronic devices it is important to have CNTs with very high quality, without any impurities. The growth technology in this aspect plays an important role.

CNTs can be obtained by different methods; each having its own specificity, advantages and consequences. The synthesis methods can be classified as physical or high temperature: the method of arc-discharge[10-13] and the method of laser ablation [14-16]; and chemical or medium temperature: a method of chemical vapor deposition (CVD) [17-22]. Physical methods allow the production of single- or multi-walled CNTs; presenting very few defects, but the selectivity (the presence of amorphous carbon and other substances) and productivity is often low.

Methods of CNT synthesis in terms of providing the necessary physical (mechanical and electrical) parameters, quality, purity, quantity and reproducibility, as well as reasonable cost, are a key to their future use in practice. Among the different ways of elaboration, the method of chemical vapor deposition seems the most promising. CVD method attracts more attention because of its high performance and low cost of synthesized CNTs.

Aerosol-assisted CVD method is one of the last generation methods of synthesizing pure MWCNTs from different impurities and has some advantages such as no preliminary preparation of catalyst material, not require after-grow purification process by different acids, which lead to breakage of CNTs, and require additional cost [23].

In this article, we report newly developed Aerosol-assisted CVD (A-CVD) method to have more production yield of high purity CNTs and their characterization. The effect of various conditions of synthesis process (different temperatures and various carbon sources-solvents with ferrocene) on structure and physical properties of the synthesized Single and multi-wall CNTs have been analyzed.

Experimental details

For synthesis of CNTs the conventional aerosol-assisted chemical vapor deposition (A-CVD) technique from SCIDRE, Germany was used as illustrated in Fig.1.

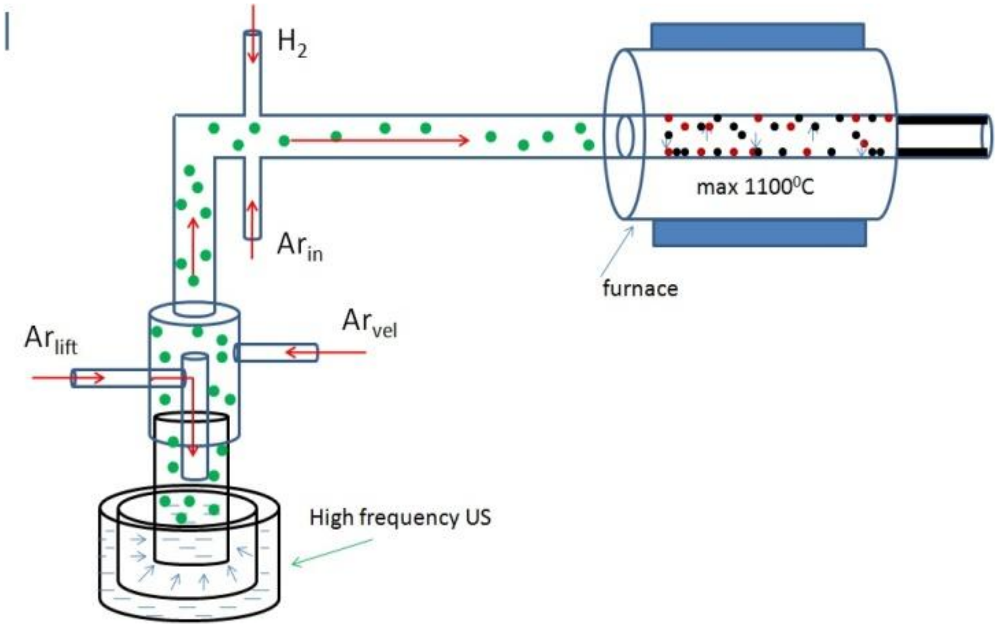


Fig. 1.Principal scheme of A-CVD equipment installed at the laboratory of RDCHT

The A-CVD system consists of horizontal quartz reactor (2m long and 45mm indiameter quartz tube) covered by movable electric furnace 35 cm long. 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). As a solution for the aerosol the carbohydrate liquids are suitable. The starting material is varying between 40-60 ml maximum. Depending from experimental condition and quantity of starting material, the production yield was 2.0-2.5 gr/h.

Development of the system in our laboratory resulted that with the addition of a carbon source continuously during the experiment (50-150 ml) we had the production yield of 20-30 gr/h. The quantity and quality of grown CNTs depends on many factors that will be analyzed later.

The following organic solvents were used: cyclohexane, alcohol, acetone and benzene mixed with ferrocene ($Fe(C_5H_5)_2$) catalyst in different concentrations. Ar/H_2 mixture was used as a transport gas.

The system was evacuated from air and filled with Ar. To obtain an aerosol the high frequency (800kHz) ultrasonic device (transducer) has been used. When the necessary furnace temperature was reached the formed aerosol was introduced to the system under total gas flow at 850 standard cubic centimeters per minute. H_2 gas was flowed to the system during the synthesis process. After deposition and cooling process the synthesized CNTs were scraped from the tubes without any wet–chemical assistance like in other CVD methods [23].

Each sample, synthesized under different conditions, was analyzed. Analytical scanning electron microscopy (ASEM) 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.

The structure of the CNTs was investigated using X-Ray diffraction. The characterization has been performed with a □ □ □ □ □ diffractometer. Three incident beams were monochromatized by a Goebel mirror. This means that CuK□ 1 and CuK□ 2 lines are present. CuK□ line has anintensity 10^{-3} times lower than CuK□ □ line.

The amorphous and crystalline phases of the CNT samples were analyzed by Raman spectroscopy using Tokio Instruments Nanofinder 30 Confocal Laser Spectroscope setup. Green laser line 532 nm was used to excite the sample. The beamwas sent through a 50x objective. All the measurements were performed at room temperature. The Raman signal was collected by a back-thinned CCD.

To obtain all-bands spectra the same variable parameters have been used for all samples:

1) Laser Power: 10mW;
2) Pinhole: 50µ;
3) Grating: 300 G/mm;
4) Exposure time: 10s; Accumulation: 2 times; Total time: 20s

To obtain RBM band spectra the following variable parameters have been used:

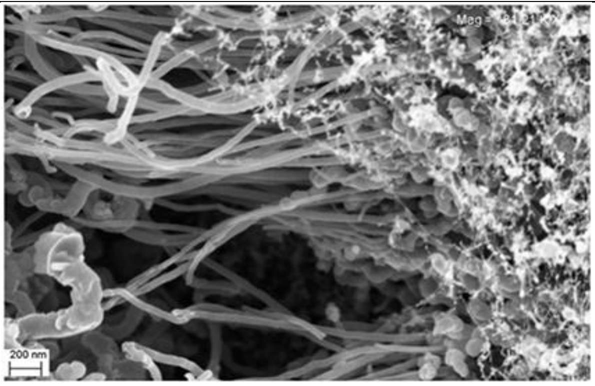
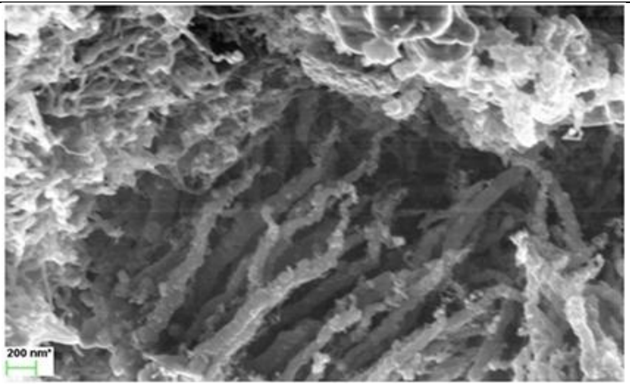
1) Laser Power: 5mW;
2) Pinhole: 100µ and 500µ;
3) Grating: 1800 G/mm;
4) Exposure time: 60s.

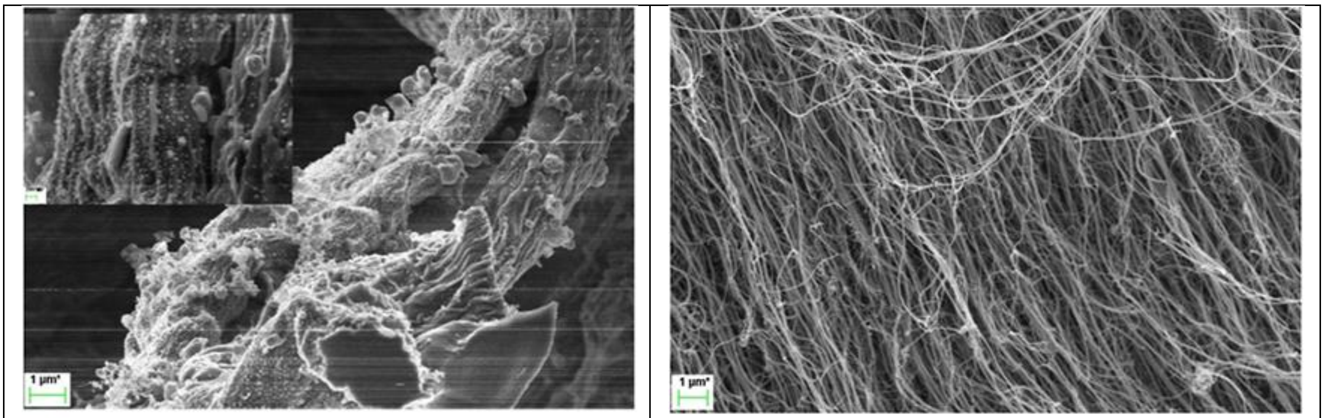
2. Results

The synthesis processes in A-CVD system were performed with different ferrocene concentration in different solvents. The temperature in the hot zone of the reactor is varied and it's influence oncharacteristics of obtained CNTs was analyzed.

3.1. Carbon sources

Different solvents have been used as a carbon sources in synthesis process of CNTs. The solvents were thoroughly mixed with ferrocene in same relative quantity (20 mg/ml). Experimental condition was the same for all used carbon sources for comparison (840^{0}C, gas flow at 850 standard cubic centimeters per minute).

	
a)	b)



c) d)

Fig.2. SEM pictures of Carbon yields obtained from different solvents: a)ethanol, b)acetone, c)benzene, d) cyclohexane

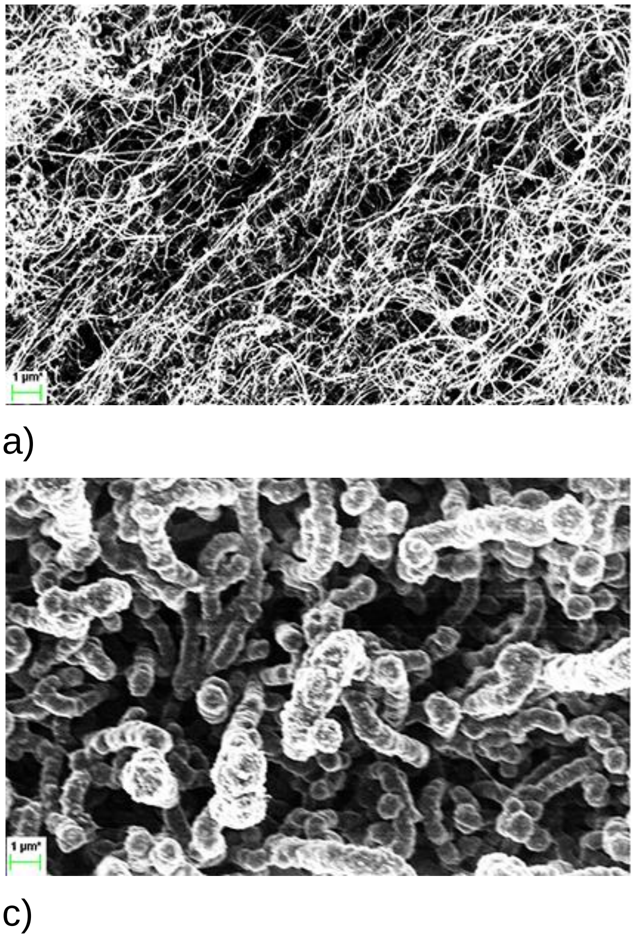
1. Ethanol or ethyl alcohol - molecular formula is C_2H_5OH. The ferrocene has dissolved well in ethanol compared with other used solvents. SEM picture shows that along with CNTs non-homogenic and different phases of carbon structures were obtained (fig. 2a). It will be discussed in the next works.
2. Acetone is the organic compound with formula $(CH_3)_2CO$. By using acetone as a solvent in the same concentration with other solvents the different phases of carbon structures have been obtained (Fig.2b.)
3. Benzene,C_6H_6, is the simplest aromatic hydrocarbon. When using benzene as a solvent in the same content with other solvents the different carbon structures were deposited, but CNTs were not observed (fig.2c).
4. Cyclohexane solvent – with molecular formula C_6H_{12} - is rather unreactive; being a non-polar, hydrocarbon has been used as carbon source. SEM and TEM analysis of the CNTs showed that by using cyclohexane as a solvent the tubular structures with different number of walls has been obtained. (Fig.2 d)

During the experiments it was observed that depending on the used solvents the aerosol formation and its introduction to the reactor was different, that has astrong influence on the reaction time and deposited product. In the case of using of ethanol as a solvent of the catalyst, thedifficulty generating aerosol was observed, which led to significant increasing of reaction time (40 ml solution evaporated during 2 hours). In the case of acetone unlike ethanol the aerosol was formed well and entire solution was evaporated in a short period (40 ml solution evaporated during 31 minutes).

In all above mentioned cases using the 40ml of different starting material gave asmall quantity of the end product, compared to the ferrocene/cyclohexane solution. According to these results, to obtain the CNTs with good structure the cyclohexane was chosen as an optimum solvent among them. Therefore all the subsequent experiments and analysis were carried out on the samples grown using ferrocene/cyclohexane solution.

3.2. Growth temperature

The growth temperature is one of the main parameters and has a dominant effect during CNTs growth process. The growth temperature was determined in the range of 830-1000^{0}C (see Fig 3). Lower synthesis temperatures results in low carbon nanotube yield while SEM observations show that the increasing temperature led to formation of other carbon structures or pyrolytic carbon, which relative weight to CNTs is increasing at high temperatures (higher than 900^{0}C). It is observed that at 1000^{0}C other carbon structure or pyrolytic carbon was formalized on quarts tube (fig.3c). Besides that, increasing of reaction temperature near to limit led to formation of more straight, smooth and longer CNTs. (at 840^{0}C ~90 μm, 950^{0}C ~630 μm (see Fig.4)).



a)

b)

c)

Fig3. SEM picture of the CNTs deposited at different temperatures : a) 830; b) 900; c) 1000^oC

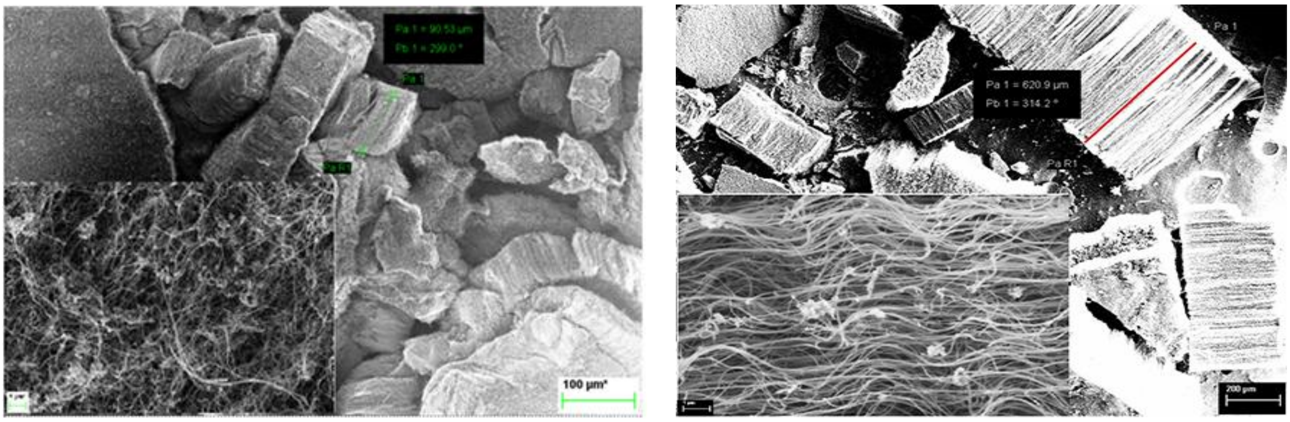


Fig.4. CNTs, grown at 830^{0}C (left) and 950^{0}C (right)

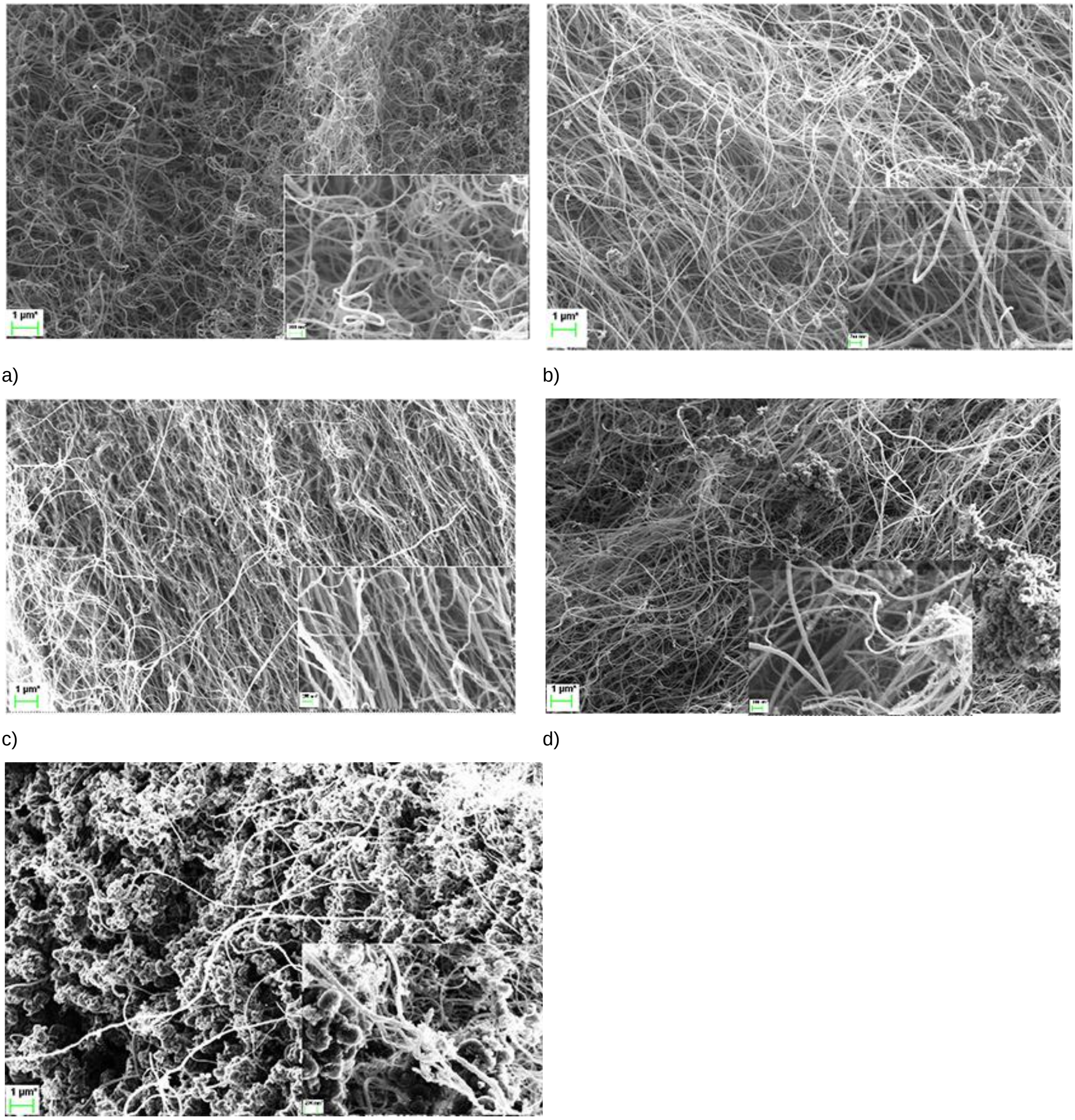
3.3. Different amount of ferrocene in cyclohexane solvent

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 and compounds were used as catalyst [24-28], but it has been shown that among them Fe is cheaper and more effective in crystallization of the nanotubes and at the same time it is interesting froman applicationalpoint of view[30,31].

There are some methods ofusing Fe based catalyst, such as thin films of Fe composites or pure Fe deposited on Si or SiO_2 substrates, $FeCl_2$ coated film [32], solid catalyst material, prepared by combustion reaction from nitrides of metals[23,33,34].

As was mentioned earlier, cyclohexane was defined as an optimum solvent among all tested solvents. In our experiments the different amount of catalyst in this solvent has been varied in order to find an optimal concentration of Fe catalyst to get Carbon Nanotubes with good parameters and to get maximum quantity of the end product. In the case of absence of ferrocene in the cyclohexane solvent the deposition on quarts surface was not observed. The quantity of deposited product was increased by increasing ferrocene quantity in the solution (fig.5). It was observed that if relation of ferrocene/cyclohexane goes higher than 20 mg/ml the solution is saturated and not all of ferrocene was dissolved in the cyclohexane. Fig.5 shows a series of SEM-images of different concentration of Ferrocene dissolved in the cyclohexane. 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 for new catalytic centers instead of continuing the growth of CNTs which has already begun. This process is chaotic.



a) b)

c) d)

e)

Fig.5. SEM pictures of the samples of MWCNTs with different Ferrocene concentration in cyclohexane:

a) 5mg/ml; b)10 mg/ml; c)15 mg/ml;d) 17.5 mg/ml; e)20 mg/ml

4. Discussion

In practice since 1989 the different CVD techniques to synthesize single- and multi-wall CNTs have been used, pure or filled by different nanoparticles of metals and compounds [35-45]. Aerosol-assisted CVD method used by our group, which allows to use only liquid carbon sources has some advantages to other CVD techniques, because post growth cleaning by acids is not needed [23, 46,47]. In this paper we are focused on determination of optimal synthesis conditions to growing high quality CNTs using Fe as the catalyst. These optimal synthesis conditions are defining by temperature, carbon source, H_2 and Ar gas flows, and formation of aerosol. It was determined that the structure parameters, diameter, growth rate of CNTs are strongly dependent on reaction temperature, and gas flow rate of the aerosol. These parameters were adjusted to get the experimental conditions optimized. Several experiments have showed that the optimum synthesis temperature in our system is about 840-950^{0}C, because lower temperatures (<840^{0}C) in the reactor led to decrease in quantity of the end product and higher (>950^{0}C) temperature - formation of other carbon structures or pyrolytic carbon as mentioned in section B. The elemental analysis of the CNT samples shows only C and Fe presence in the products. (Fig.6).

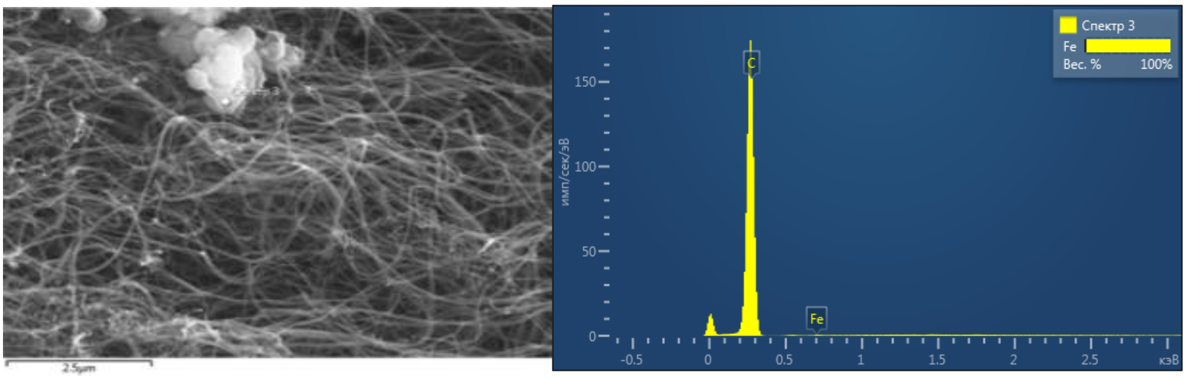


Fig.6.EDS analysis of CNTs grown by using ferrocene/cyclohexanesolution

Different nanotubes were analyzed by TEM and the following pictures areshowing the partial locationof Fe inside the tubes, but this location is random(not ordered)and no other impurities or composites are present in the tubes or around them. This fact is confirmed by TEM observation of the samples. The top part of the CNT was analysed by EF-TEM (Fig.7). a) is the CTEM image while b) gives the X-EDS map of Fe. The EF-TEM maps of C and Fe are reported in c) and d), respectively, while the coloured overlap of c) and d) is reported in fig. e). Excellent agreement between morphology (a) and EF-TEM maps is obtained.

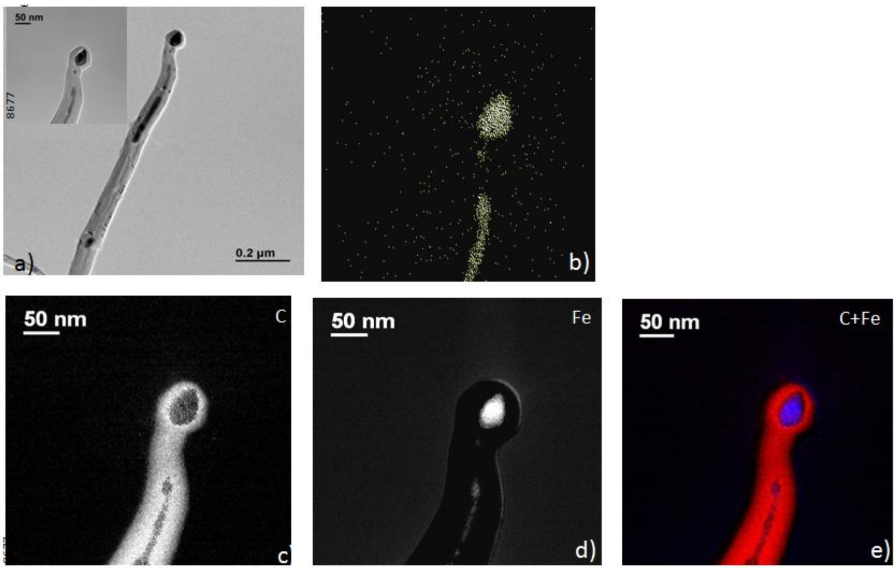


Fig.7. a) CTEM images of one CNT, b) corresponding X-EDS map of Fec) and d) EF-TEM maps of C and Fe, respectively(bright means high concentration), e) coloured overlap of c) and d).

A HR-TEM study of a Fe-rich area of the CNTs is presented in fig. 8.The fringes of the lattice planes have a spacing of 0.206 nm which pretty muchagrees 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. 8d) confirms that conclusion. In fig.8d the spots 1 are due to the (111) planes of Fe bcc, whilst spots 2 give d_{hkl} = 0.340 nm that pretty muchagrees with the spacing of the (002) planes of graphite (d_{002} = 0.3395 nm, according to the WebEMAPS)

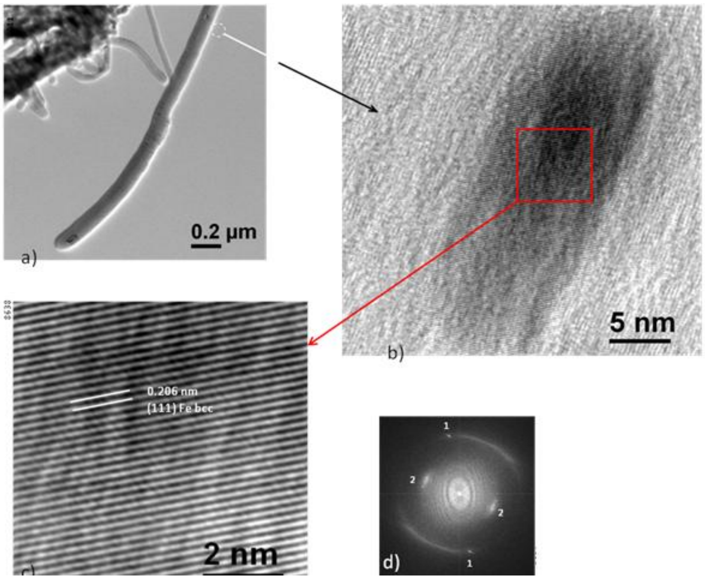


Fig.8. HR-TEM results of CNTs. b) is the HR-TEM image of the dash-circled area of a) with its magnification in c).

The nature of synthesized CNTs is also confirmedby XRD studies[48, 49]. XRD patterns of the sample grown at 840^{0}C CNT are shown in Figure 9.Peaks indexed to (002) (2θ=25.77°), (100), (101) (2θ=43.62°) reflects hexagonal structure. The presence of 002 peaks in the XRD data, suggests multi-walled nature of carbon nanotubes. According to Bragg law q vectorhas been calculated, which reaches a maximum value at 18.2 nm^{-1}.A spacing value of d=2π/qmax=0.345 nmfor the distance between the graphitic layers has been defined. Thisvalue is in agreement with those found from TEM analysis.

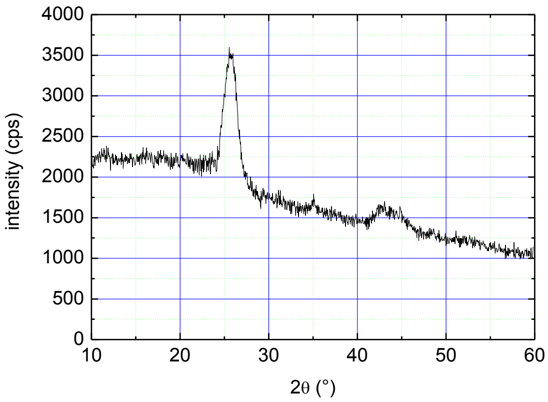
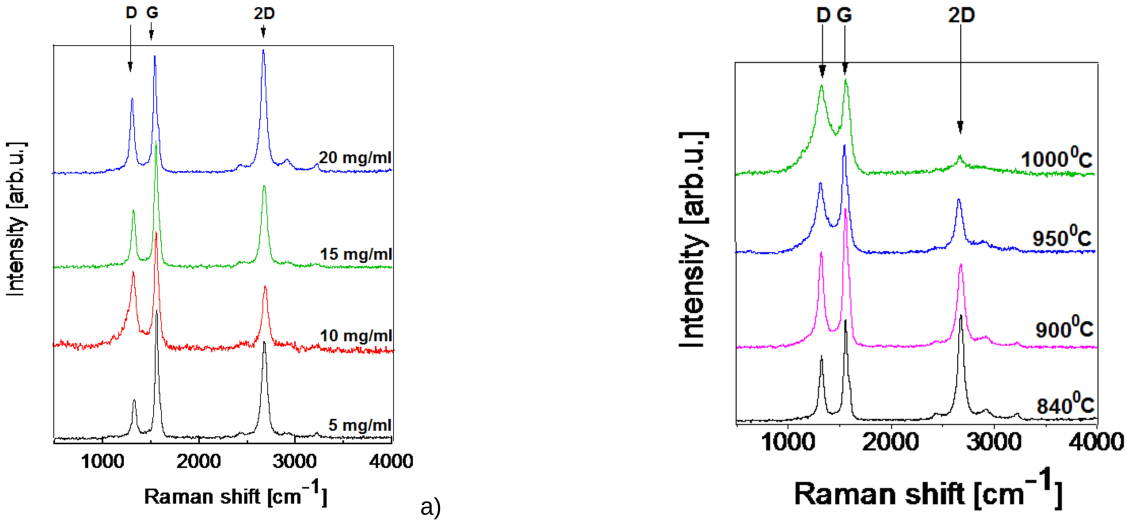


Fig.9. X-Ray patterns of MWCNTs grown at 840^{0}C

In Fig.10 the Raman scattering spectra (RSS) are shown for CNTs, grown at temperatures 840-1000^{0}C by using ferrocene/cyclohexane solution with concentration of 5-20 mg/ml. 3 intensive bands are observed: 1349-1355 cm^{-1} (defect induced D band),1583-1592 cm^{-1} (tangential oscillation G band), and 2698-2707 cm^{-1} (second order of D band -2D (or G') band). In the whole spectra the D line intensity, which is associated with presence of carbon containing impurities, other symmetry-breaking defects or disorders in MWCNTs,is lower than intensity of G band.The ratio between D band and G band - I_D/I_G value of synthesized MWCNTs is about 0.31, this is a confirmation that disorder within carbonaceous materials and nanotubes, i.e. defects within the nanotubes, obtained by our method is not high, in comparison with results of other synthesis methods [49,50].

The 2D (or G') band attributed to the overtone of the D band is observed in all spectra with highest I_{2D}/I_G ratio of 1.04 in sample grown at 840^{0}C and lowest of 0.24 at in sample grown at 1000^{0}C. It is seen that low catalyst concentration caused partly relative decrease of the intensity of D band in the Raman spectra.The increase of temperature has resulted in widening of bands and definite increasing of D band intensity and decrease of 2D band intensity.

The highest 2D peak intensity ratio is observed in the spectra of the samples with high ferrocene concentration. It is probably caused by presence of the double layer graphene clusters characterized by high 2D band with intensity comparable to G band [51-53]. The increasing of D band intensity and widening to the G band were observed in the samples grownabove 900^{0}C. The samples grown at 950^{0}C and 1000^{0}C are characterized as pyrolytic carbon film with microcrystalline graphite clusters. The observed double peak behavior in the Raman spectrum indicates a Disordered Carbon (DC) film with D (defect) band a little bit lower than G (graphite) band unlike Glassy Carbon (GC) films where D is higher than G. With fairly sharp G (1565 sm-1) and D (1330 sm-1) bands, this material contains highly crystalline regions, yet with very small dimensions [54-57].



a) b)

Fig.10. Raman spectra of the samples: a) samples grown at 840^{0}C by using different ferrocene/cyclohexane relation; b) samples grown in various temperatures by using ferrocene/cyclohexane relation 20 mg/ml

Radial oscillation or breathing mode - RBM band between 100 and 300 cm^{-1} is detected in the Raman spectra of the samplesgrown at 840^{0}C (Fig. 11), which indicates the presence of SWCNTs with diameters 0.85 and 1.14 nm[57].

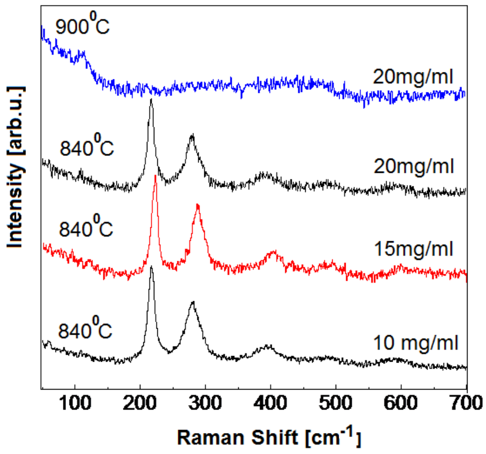


Fig.11. RBM bands of the samples grown at different synthesis conditions

Thiswas expected, because very big variations in diameter of the CNTs areobserved by SEM and TEM analysis, besides thatit is possible to analyzesome different parts of the sample at the same time by Raman spectroscopy method differing from TEM observations. Several experiments show that in the samples grown at temperature higher than 840^{0}C the RBM band was not observed, which confirmsthe absence of SWCNTs or their very small quantity.The small peaks in the range of 400-600 cm-1 are observed on the spectra. Their nature will be analyzed in the following works.

5. Conclusion

Aerosol-assisted CVD method for the synthesis of pure CNTs in relatively large amount (20-30 gr/h) was developed. The different carbon sources and experimental conditions were used in order to grow more pure, long and smooth CNTs with smaller diameter. Our experiments shows that by this method CNT can't grow in the case of ferrocene absence in the solution.

X-Ray diffraction and Raman spectroscopy analysis show that there are no other impurities and not much defects present in the grown CNTs.

RBM band was observed in the samples grown at 840°C and not observed in the samples grown at a higher temperature, since the outer tube restricts the breathing mode in the case of several tubes surrounding each other (concentric tubes). RBM band is an indication that among the MWCNTs with diameter 10-85 nm, a small percent of SWCNTs have been grown with the diameters of 0.85 and 1.14 nm.

The ratio between D band and G band - I_D/I_G value of synthesized MWCNTs is less than 1.0, which confirms that disorder within carbonaceous materials and nanotubes, i.e. defects within the nanotubes is increasing at synthesis temperature higher than 840^{0}C, but never have been observed glassy carbon (GC) like bands, when D band is higher than G band.

The position of Fe nanoparticles in the CNTs were defined by TEM observations, which show that Fe nanoparticles are situated not only in the tip of the tubes, and also along the length of the nanotube (in the inner channel of the CNTs). The results of SEM and TEM analysis give a reason to assume that in our synthesis process the tip-growth mechanism is dominating [58] EDS analysis show that besides CNTs, agglomerates with other Carbon structures have pure Fe nanoparticles inside them, and not any oxides, which lets us to make a conclusion that**,** at temperatures higher than 840^{0}C Fe covered with amorphous carbon or disordered CNTs is formed among the CNTs with different diameters and length.

Acknowledgements

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