Usage of AFM, SEM and TEM for the research of carbon nanotubes

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This report is focused on a studying of single-walled carbon nanotubes (SWCNTs) by different microscopic methods. It is important for the number of researches to know basic parameters of SWCNTs, especially a diameter and length of one nanotube or a bundle of nanotubes and a number of nanotubes in the bundle. For determination of these parameters Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were used.

Keywords carbon nanotubes, Trasmission Electron Microscopy, Scanning Electron Microscopy, Atomic Force Microscopy

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are nanometric cylinders consisting of a single graphene sheet wrapped up to form a tube. They were discovered in 1993 [1,2] and their first electrical measurements were performed in 1997-1998 [3,4].

The discovery of SWCNTs opened a new field of interest. Using of this material is very important in several fields of science and technology, due to their excelent mechanical and electrical properties [5,6]. SWCNTs occur mainly in thick bundles, where they are combined by van der Waals attractions.

There are the different kinds of methods to produce SWCNTs, such as thermal chemical vapor deposition (CVD), laser ablation, catalytic chemical vapor deposition (CCVD), plasma enhanced chemical vapor deposition (PECVD) or arc discharge. SWCNTs used in this work were prepared by arc discharge.

The reason for the usage of AFM, TEM and SEM for nanotubes analysis is very simple. AFM is a powerful tool in manipulating and characterizing the properties of nanostructures. TEM has been traditionally applied to characterizing the interior structures of nanomaterials. Due to this method atomic planes of nanoparticles can be observed.

2. Materials and methods

2.1. Arc Discharge

SWCNTs used in this work were prepared by arc discharge [7]. It was the first available method for the their production. It is the most common and one of the easiest methods of carbon nanotubes production. Fig. 1 shows a scheme of apparatus for producing carbon nanotubes. This apparatus is connected to a vacuum line with a diffusion pump, and to a helium supply.

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As the cathode and anode two graphite electrodes, usually of high purity, are used in this method. Usually, the anode is a long rod of approximate diameter 6 mm and the cathode is much shorter of diameter 9 mm.

A direct current of 50A to 100 A, driven by potencial difference of approximately 20-40 V creates a high temperature discharge between the two electrodes. The discharge vaporizes the surface of one of the carbon electrodes, and forms a small rod-shaped deposit on the other electrode. High yielding production of CNTs depends on the uniformity of the plasma arc and on the temperature of the deposit forming on the carbon electrode.

To produce the SWCNTs the graphite rod must contain metal catalyst powder (Co, Ni, Fe). The pressure in the evaporation chamber and the current are the most important parameters of producing high quallity SWCNTs.
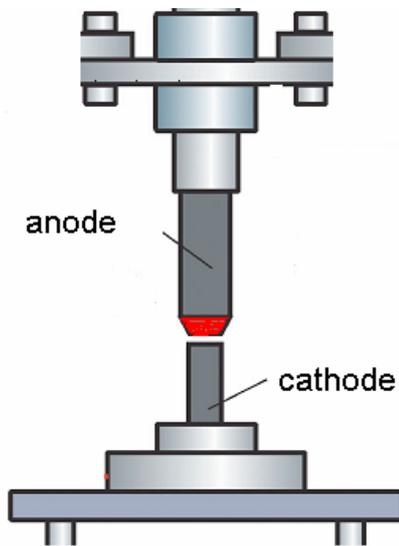

Fig.1 Scheme of apparatus producing carbon nanotubes ([8])

2.2. Sample preparation

The suspension of single-walled carbon nanotubes for AFM, TEM and SEM methods was prepared by the same principle. Nanopowder of SWNTs was added in ethanol and exposed to ultrasonic waves. For TEM method, one drop of the suspension was placed on 300 mesh copper grip, which was coated with holey carbon film. Then the sample was dehydrated at 40˚C. In case of SEM, the obtained solution was dropped on a sillicon slide. This sample was dehydrated at 40˚C. For AFM, the obtained solution was dropped on a mica. Then was the sample dehydrated at 50˚C.

2.3. TEM observation

Transmission Electron Microscope JEOL 2010F- type-high contrast (HC) was used to observe the internal structure of sample. The microscope had accelerating voltage from 80 to 200 kV and standard magnification from 1000 to 800000 times. Illuminating system consisted of cool beam electron gun with pre-centered LaB_6 filaments. There were three-stage condenser lens (1st, 2nd, 3rd) and five apertures. A beam total angle was 2˚ in all directions.

Evacuation system was created by oil rotary pump and oil diffusion pump for rough evacuation and by sputter ion pump for fine evacuation. Ultimate pressure was 10^{-5} Pa order (sample chamber).

Images were acquired using peltier-cooled CCD camera KeenView. CCD chip in this camera provides maximum resolution of 1376x1032 pixels with a 12bit dynamic range (4096 gray values). The KeenView supports frame rates of more than 20 images per second at 2x binning and of 10 images per second at full resolution. This high frame rate is ideal for locating suitable sample segments directly on screen. Platform iTEM was used for images analysis. Accelerating voltage 200 kV and magnification 100000-400000 times were used in this work.

2.4. SEM observation

Scanning Electron Microscope with high resolution is powerful instrument for imaging of fine structures of materials and nanoparticles fabricated by the nanotechnology. For SWCNTs observation and their morphological analysis the Field Emission Scanning Electron Microscope JEOL JSM- 6700F was used. The resolution of secondary electron image (SEI) of the microscope is 1.0 nm (at accelerating voltage 15 kV) or 2.2 nm (at accelerating voltage 1 kV). Accelerating voltage is changing from 0.5 to 2.9 kV in 10 V steps and from 2.9 to 30 kV in 100 V steps. Magnification is from 25 to 19 000 times for low magnification mode and from 100 to 650 000 times for high-resolution mode. The cold field emission gun (FEG) W <310> as a source of electrons is used. It works at the vacuum order 10^{-8} Pa and generates electrons with small energy spread, which is suitable for obtaining high resolution at low accelerating voltages.

This microscope works in three basic imaging modes: SEI - secondary electron image with the in lens (Everhart-Thornley) detector (signal SE I+SEII), LEI - low secondary electron image with the low (Everhart-Thornley) detector (signal SE I+SE II+SE III +BSE) and AUX1 - backscattered electron image with the scintillation BSE detector based on the YAG single crystal under sample (signal BSE) which enable to observe the compositional contrast. The resolution of backscattered electron image with the mentioned BSE detector is units of nanometers. The basic configuration of the FE SEM is supplemented by the energy dispersive analyzer X-ray analyzer INCA (Oxford Instruments) with range of analyzed elements from the boron (atomic number Z=5) to uranium (Z=92). Maximal sample size is 150 mm x 10 mm.

For imaging of micromorphology of SWCNTs sample the accelerating voltage 5.0 kV and SEI secondary electron mode was used.

2.5. AFM observation

Atomic Force Microscope Explorer ThermoMicroscopes was used as an indirect method for morphological analysis of the sample. Maximum scanning size of the microscope probe was 2x2 μm. Resolution of AFM was 300x300 pixels. Our sample was measured in non-contact mode. Nominal diameter of tip was 10 nm.

3. Results

The first used method was AFM. On the Fig.2, bundles of single walled carbon nanotubes among carbon particles can be observed. This method gives us information only about the length of nanotubes and approximate valuation of the bundles diameter. It was impossible to determine accurate value of diameter, because some of nanotubes didn't lie directly on a mica and oscillated under the daze.
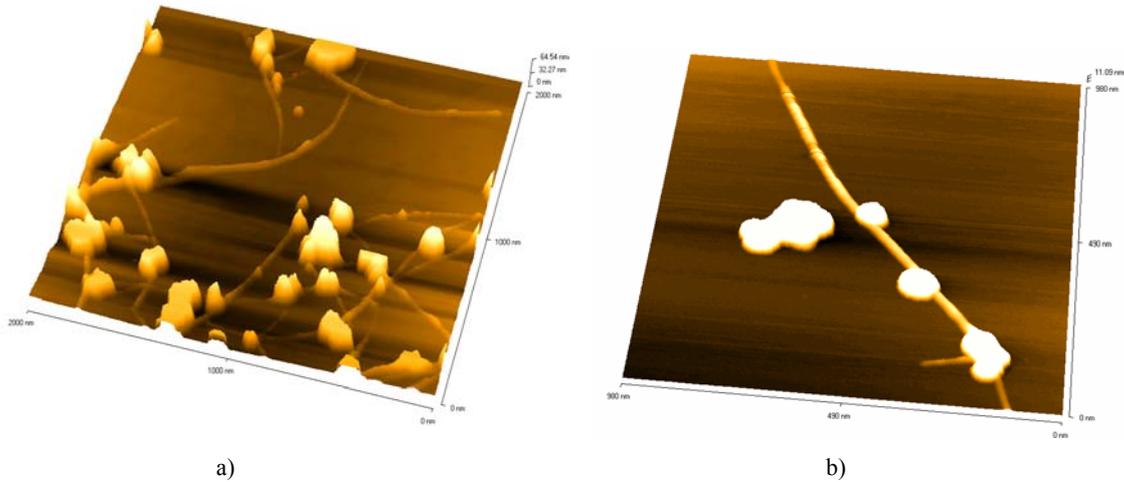
a)   b)

Fig. 2 a) ,b) AFM image of the single-walled carbon nanotubes

Due to requirement of accurate diameter of bundles SEM method was used. This method gives information mainly about surface morphology of the sample (Fig.3a, b) and about chemical composition of the sample (Fig.4a),b)). Metallic catalyst particles can be well-defined displayed using AUX1 mode (Fig.5). The only measurable parameters are a size of carbon particles and a diameter and length of bundles. Information about diameter of one nanotube is impossible to find.
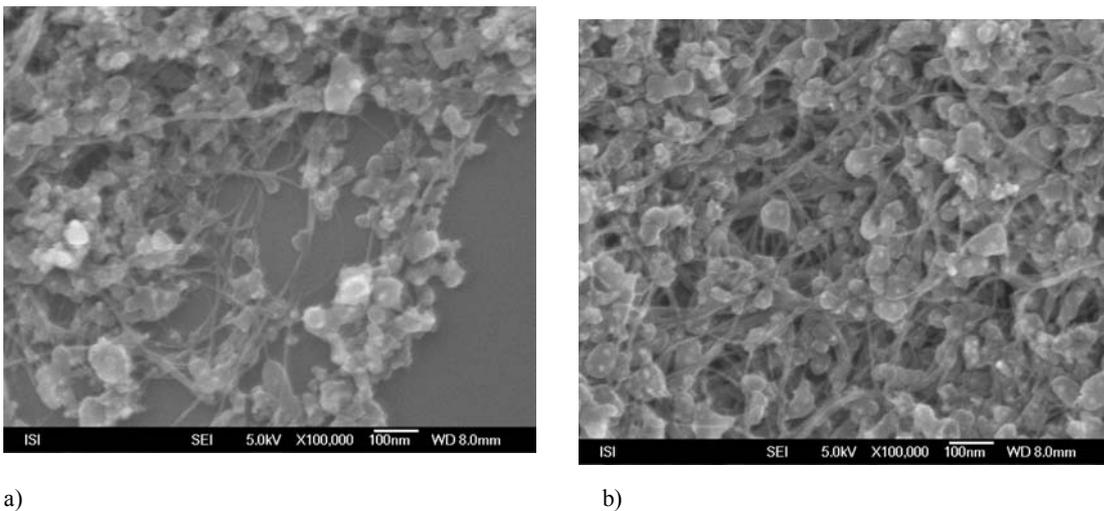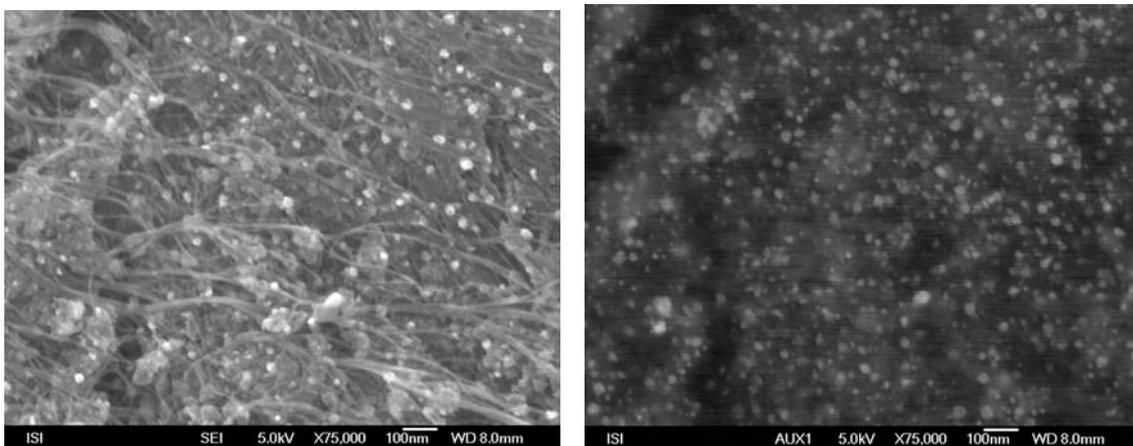

a)   b)

Fig.3 a), b) represent SEM images of SWCNTs with particles of amorphous carbon and metallic catalyst acquired in secondary electron mode

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a)   b)

Fig.4 a) represent SEM images of SWCNTs with metallic catalyst particles acquired in secondary electron mode, b) the same place displayed using backscattered electron mode
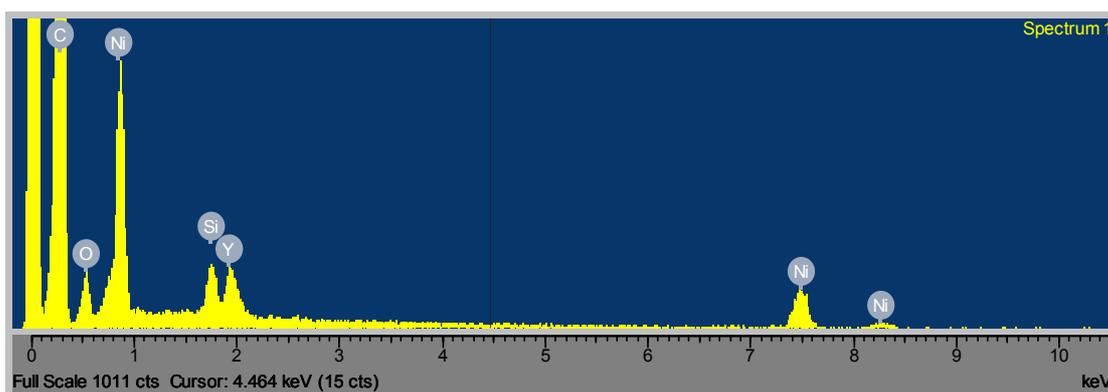

Fig.5 represent EDX spectrum of the sample, Ni and Y belong to metallic catalyst particles

The TEM was used due to its ability to measure nanotube diameter in the bundle. From the TEM image (Fig.6 a, b) it is possible to determine directly the diameter of one nanotube and bundle diameter. Due to this information number of nanotubes in the bundle can be found out.
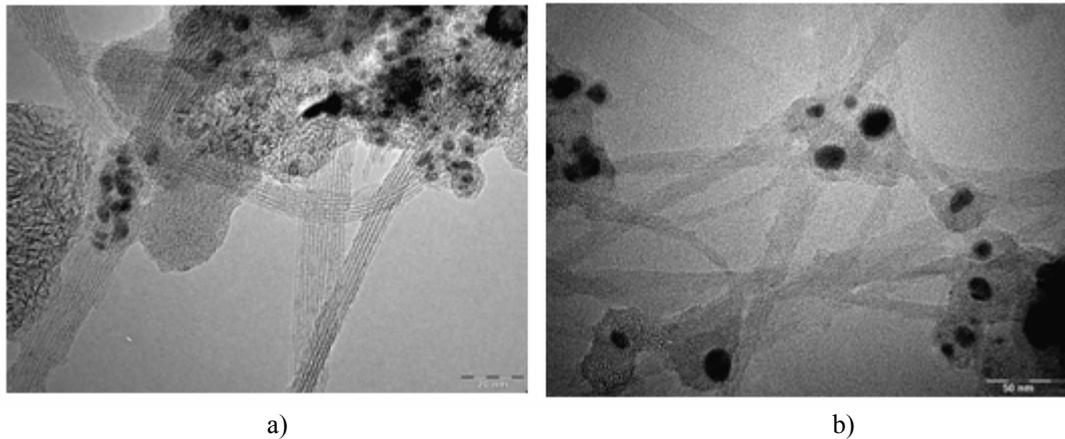
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<center>a)</center>

<center>b)</center>

Fig. 6 a), b) TEM image of the SWCNTs bundles with particles of metallic catalyst and amorphous carbon, fig. a) marker 20 nm, b) marker 50 nm

Sometimes some nanotubes in the sample are not in bundle, so they are alone (Fig.7 a), b)). In this case we can determine nanotube length and diameter directly.
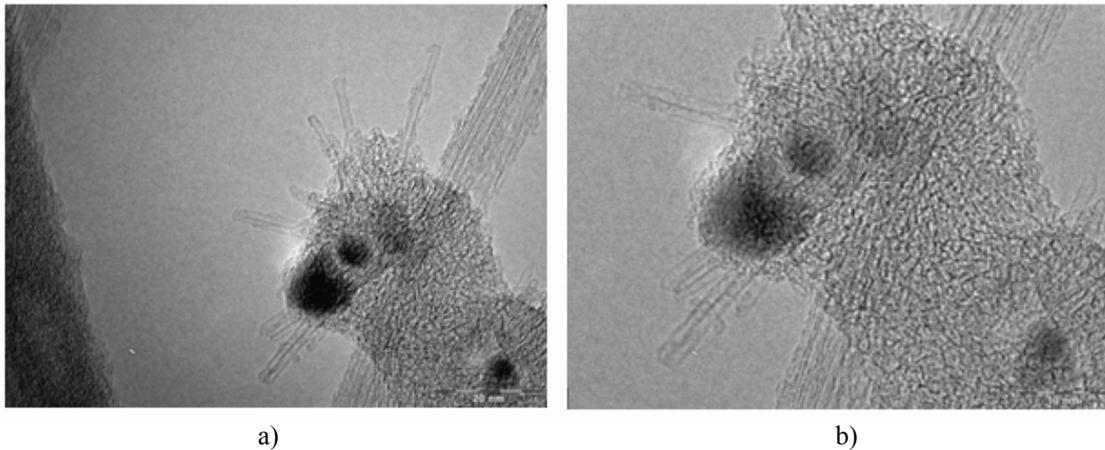

<center>a)</center>

<center>b)</center>

Fig. 7 a, b TEM image of the single-walled carbon nanotubes, fig. a) marker 20nm, fig b) marker 10 nm.

4. Conclusion

This study shows methods that are possible to use for measuring of carbon nanotubes basic parameters. It is evident, that the best method for detail analysis of carbon nanotubes is TEM. Due to high resolution of transmission electron microscope the sample can be observed even in atomic resolution. SEM and AFM give us information about surface morphology only.

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