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Carbon nanotubes manufacturing using the CVD equipment against the background of other methods

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ABSTRACT

Purpose: The primary purpose of the article is to present the most popular techniques of manufacturing carbon nanotubes (CNTs). The Chemical Vapour Deposition (CVD) method is described in detail with special focus laid on the universality of such technique and on economic considerations. The outcomes of investigations presenting carbon nanotubes fabricated with the EasyTube® 2000 system are also demonstrated.

Design/methodology/approach: Electron microscopy was used for illustrating the structure and morphology of newly manufactured multiwalled carbon nanotubes.

Findings: The microscopic examinations conducted with high-resolution transmission electron microscopy have confirmed the homogeneity, high quality and purity of the manufactured carbon nanotubes.

Practical implications: Carbon nanotubes are currently valued because of their diverse applications. Depending on the structure, carbon nanotubes may act as conductors or semiconductors and such properties can be utilised in electronics. Other fields of application include optics, medicine, transportation (lightweight and robust constructions). CNTs are also utilised as elements of chemical and biochemical sensors, especially when coated with particles of precious metals (e.g. Pt, Au, Pd). Carbon nanotubes are also used as a reinforcing component in composites.

Originality/value: The characterisation of carbon nanotubes fabrication methods with special consideration to the chemical vapour deposition method by means of an EasyTube® 2000 device by FirstNano.

Keywords: Nanomaterials; Carbon nanotubes; Chemical Vapour Deposition CVD

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MATERIALS

1. Introduction

Nanotechnology is a rapidly developing domain of science. A number publications have appeared concerning the manufacturing methods of modern nanomaterials and innovative solutions. Iijam's publication of 1991 concerning carbon nanotubes (CNTs) aroused immense interest in the world of science. Carbon nanostructures are an attractive material and there are numerous ideas concerning the future applications of carbon nanotubes. Single-walled Carbon Nanotubes (SWCNs) are defined as nanostructures consisting of a single cylindrical rolled layer of graphene closed from both sides with semispheres of fullerenes. There are also Multi-walled Carbon Nanotubes (MWCNTs) having multiple cylindrical graphene layers. The distance between individual walls is theoretically 0.34 nm. There is also another classification of carbon nanotubes according to their chirality, i.e. a method of rolling the graphene making up a nanotube. Nanotubes with armchair, zigzag and chiral structures are therefore distinguished between. Carbon nanotubes are classified as one-dimensional structures (1D) due to their proportion of dimensions - the aspect ratio of even 10^9 in some cases. Such attractive carbon nanostructures possess numerous interesting physical and chemical properties, are lightweight, elastic and also resistant to bending, stretching and torsion. Their electrical conductivity is changing in an interaction with molecules of different chemical substances. This characteristic is strengthened after deposition of precious metals nanoparticles onto their surface, and such aspects had been described in earlier publications (e.g.: Au, Ag, Pt, Pd) [1-7].

A carbon material obtained in fabrication, apart from nanotubes, contains certain impurities. The following side products can be distinguished depending on the manufacturing technique: catalyst particles (e.g. Fe, Co, Ni particles), support materials and carbon impurities (amorphous carbon, fullerenes, carbon particles). Moreover, studies with high-resolution transmission electron microscopy reveal that carbon nanotubes have structural defects, e.g. the presence of five- and seven-membered rings in a hexagonal spatial lattice or the occurrence of voids. Single-walled carbon nanotubes have a more perfect structure, though. Physiochemical properties, including electrical and magnetic properties, depend in particular on their structural defects, chirality of nanotubes and their purity [8,9].

The purpose of the paper is to present the key carbon nanotubes fabrication methods with special focus on the CVD process. The products obtained with the EasyTube 2000 system are also presented and characterised.

2. Carbon nanotubes fabrication methods

There are several fabrication methods of carbon nanotubes, and the most popular ones include: electric arc discharge, pulsed layer deposition and chemical vapour deposition (CVD). Certain factors exist combining the carbon nanotubes fabrication methods: the presence of a source of carbon, presence of catalyst nanoparticles and supply of energy to the system [10]. CNT manufacturing with an electric arc is a method originally used for producing fullerenes. An electric arc is generated between two graphite electrodes as shown in Fig. 1. A carbon material is deposited onto a cathode by evaporating carbon atoms coming from the anode. This process is carried out in the atmosphere of argon or helium. A catalyst, e.g. Fe:Co, introduced into a cathode is necessary for producing single-walled nanotubes [8].

Another CNT fabrication method is pulsed laser deposition used mainly for manufacturing single-walled nanotubes, in which a graphite disc is evaporated with a laser in the presence of shielding gas (argon or helium). A high pressure and temperature of approx. 1200 °C are used in the process. A carbon deposit is deposited onto a collector cooled with water. It is adequate to use a graphite disc containing a catalyst in case of SWCNTs, e.g. Ni or Co. The process diagram is shown in Fig. 2 [8,10].

The CVD is at present the most popular technique of manufacturing carbon nanotubes, mainly because lower process temperatures can be applied and owing to the diversity of forms of carbon nanotubes obtained (e.g. as a thin film, entangled packets or structures laid perpendicular to the substrate). Carbon nanotubes are formed due to the decomposition of a compound containing carbon nanotubes on a substrate with a uniformly deposited catalyst, usually Ni, Co or Fe. Ethylene, acetylene, methane or benzene is a carbon precursor usually. The CVD has many variants, including plasma-enhanced CVD - PECVD or plasma-assisted - PACVD, successfully used for carbon nanotubes fabrication [8,9,11,12].

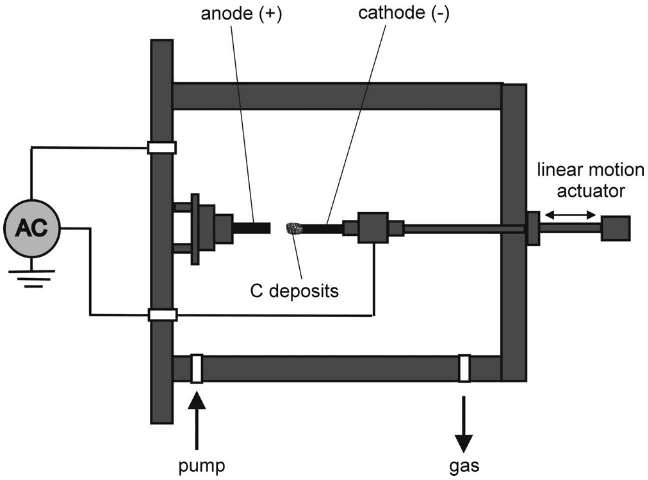

Fig. 1. CNTs' fabrication method with carbon arc discharge [13]

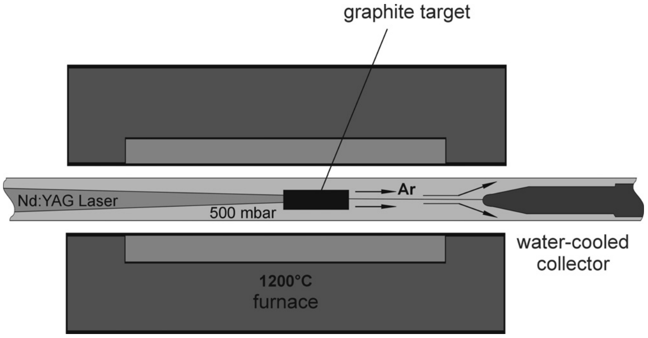

Fig. 2. CNTs' fabrication diagram with pulsed laser deposition [10]

The forms of this interesting nanostructures depend on manufacturing methods. On the table there are presented main difrencess between type of carbon nanotubes fabrication methods. Carbon nanotubes fabricated by ARC and LA are highly crystaline and posses low defekt concentrations. CVD's products exhibit more structural defects and are less crystalline than CNT's made using arc discharge method. In the other hand the CVD is more economic and effective metod. CNT's producing by CVD may be achieved in the various forms: as powder, thin or thick films, aligned verticaly to the substrate or entangled in bundles [8-11]. In the Table 1 comparing of carbon nanotubes fabricated using different methods is presented.

Table 1.
Characteristic of carbon nanotubes fabricated with the CVD method, with electric arc and pulsed layer deposition [own study based on 8,9]

Methods	CVD	ARC	L-A
Forms	powder, thin or thick films, verticaly aligned (like a forest), entangled bundles	cigar like deposit (MWCNT's) fluffly web-like materials (SWCNT's)	condense as ropes or bund les (SWCNT's)
Characteristic of CNT's	highly pure	highly crystalline exhibit few defects	highly crystalline low defect concentrations
Main byproducts	CVD materials contain more metal catalysts particles	polyhedral particles, amorphous carbon, encapsulated metal catalysts particles (during SWCNT's production)	amorphous carbon, encapsulated metal catalyst particles

3. Synthesis of carbon nanotubes with the chemical vapour deposition method (CVD) using EasyTube® 2000 device

An EasyTube® 2000 device by FirstNano shown in Fig. 3 is used at the Scientific and Didactic Laboratory of Nanotechnology and Materials Technologies, Institute of Engineering Materials and Biomaterials of the Silesian University of Technology for manufacturing carbon nanotubes and graphene with chemical vapour deposition (CVD).

Fig. 3. EasyTube® device by FirstNano used for carbon nanotubes synthesis

The EasyTube® 2000 system allows for a repetitive synthesis of high-quality carbon nanotubes. The device incorporates a control and process unit. The process is controlled with a computer with appropriate CVDWinPrC software installed for, mainly, adjusting process temperature, flow of process gases, data recording and for presenting such data graphically. Fig. 4 shows a control panel enabling to view the stages of the manufacturing process carried out, to introduce modifications into the programmed manufacturing process and also to observe progress of the task handled.

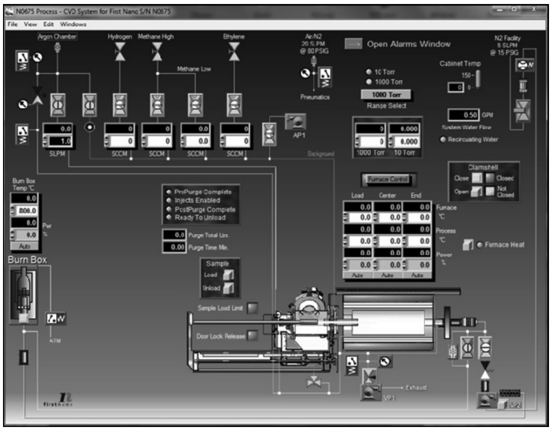

Fig. 4. EasyTube® 2000 control panel

Fig. 5. Oven situated in the central unit allowing to reach process temperature of 1100°C

Fig. 6. Quartz process pipe situated in the oven

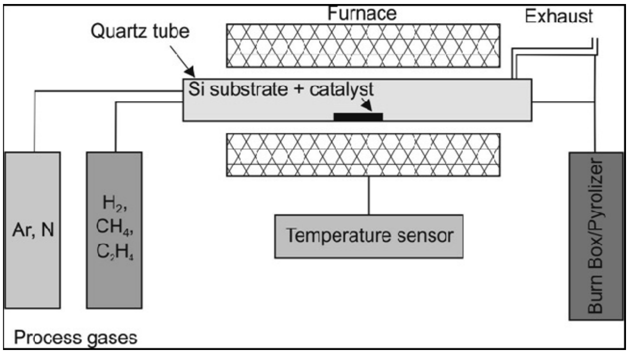

Fig. 7. Schematic of a carbon nanotubes synthesis unit with CVD [prepared based on [11]

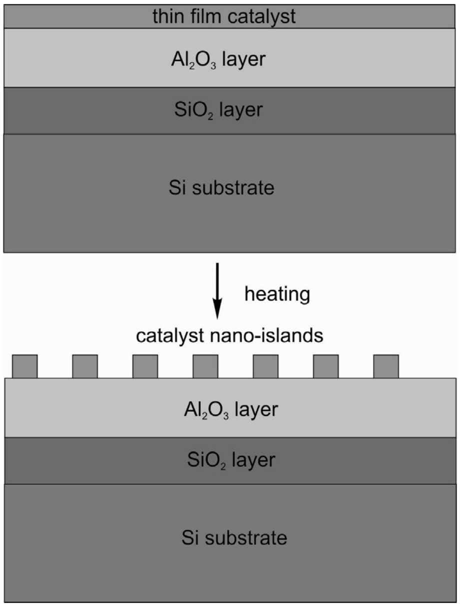

Fig. 8. Schematic of structure of silicon substrate with SiO_2, Al_2O_3 layers deposited and metallic catalyst layer [14]

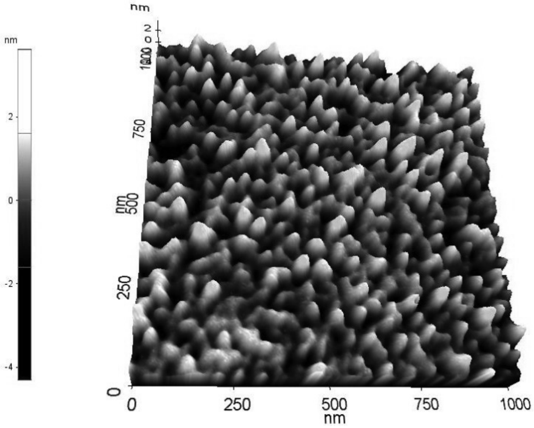

Fig. 9. AFM photograph of silicon substrate topography used for the growing of multi-walled nanotubes.

Nanomaterials can be produced with the EasyTube® 2000 device by using the key base of recipes in the system (single-walled or multi-walled nanotubes), and also by modifying them, checking the correctness of the prepared technological process and programming the author methods of carbon nanotubes' synthesis using N0675 recipeEditor2 software. The device's basic process unit consists of an oven shown in Fig. 5 and a process quartz pipe shown in Fig. 6.

The growth process of carbon nanotubes is carried out on a silicon substrate where buffer layers of SiO_2, Al_2O_3 are deposited to prevent the formation of metal silicide which could complicate a synthesis process [12-13] and a layer of a metallic catalyst which, after heating in the right temperature, is broken and single isolated catalyst nanoparticles are formed. An example of a construction/structure of a silicon substrate for growing multi-walled carbon nanotubes is shown in Fig. 8, while Fig. 9 shows a photo of a silicon substrate topography using an atomic force microscope AFM.

4. Experimental

4.1. Experimental

Multi-walled carbon nanotubes were synthesised with the chemical vapour deposition (CVD) method using an EasyTube® 2000 device on a silicon substrate containing a catalyst in the form of a thin film and two buffer layers (0.5 nm of Fe, 15 nm of Al_2O_3 and SiO_2). Nanotubes are grown in an oven at a temperature of 750°C for 45 minutes using ethylene (C_2H_4) as a source of carbon.

4.2. Research methodology

Do The Transmission Electron Microscopy (TEM) technique was used for viewing the nanocarbon materials obtained. The TEM images were made using a transmission electron microscope STEM TITAN 80-300 by FEI fitted with an electron gun with

FEG field emission, a condenser spherical aberration corrector, STEM scanning system, light and dark field detectors, HAADF (High Angle Annular Dark Field), and EFTEM energy image filter and an EDS spectrometer. Carbon with the ordinal number (Z=6) belongs to the group of light elements poorly dispersing high-energy electrons, which is associated with weak contrast and, as a consequence, difficulties in imaging. Another problem arises from a destructive character of a high-energy beam of electrons in relation to carbon materials. The exact imaging of the structure and morphology of the studied nanotubes was possible by applying an accelerating voltage of (80 and 300 kV) in the studies. The preparations for transmission electron microscopy investigations were prepared by dispergating the carbon nanotubes obtained in ethanol using an ultrasound washer, and then by depositing them using a pipette with droplets onto a copper mesh covered with a carbon film. The material deposited as a droplet was dried with free air at room temperature.

The degree of defects of the obtained carbon nanotubes' structure was examined using a Raman in Via Reflex Raman Spectrometer by Renishaw fitted with a confocal Research Grade microscope by Leica where specimens can be observed in the reflected and transiting light. Excitations were carried out with a line with the wavelength of λ= 514 nm of an ion-argon laser with the capacity of 50 mW, with a plasma filter for 514 nm. The laser capacity adjustment range is between 0.00005% to 100% inclusive. The measurements were recorded using Long Working Distance (LWD) lens with magnification of x 20. The materials for investigations using a Raman spectroscope were prepared by depositing a nanotube material onto a glass substrate. The so prepared preparations were examined over the entire range of spectrum registration of 50-4100 cm^{-1}.

4.3. Results and discussion

The photographs of carbon nanotubes produced with the EasyTube 2000 system being the result of own observations made with the transmission electron microscope are presented in Figures 10-15.

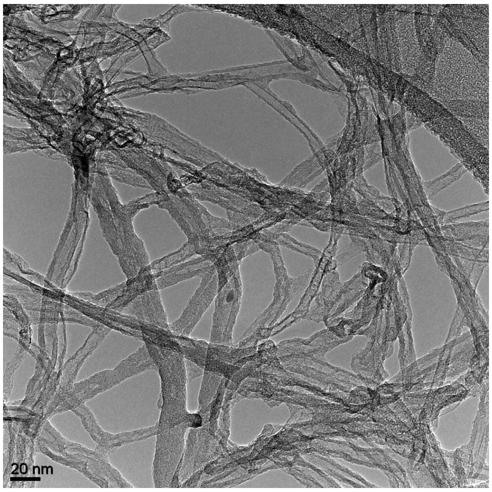

Fig. 10. TEM image of multi-walled carbon nanotubes

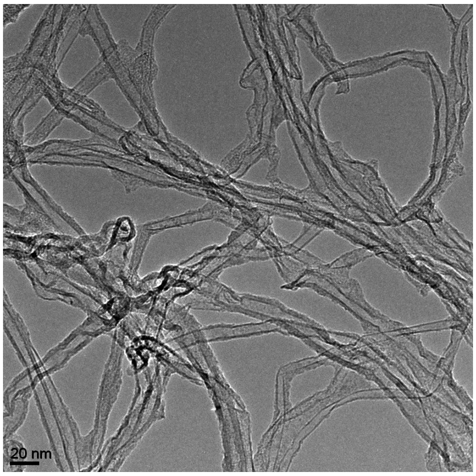

Fig. 11. TEM image of multi-walled carbon nanotubes

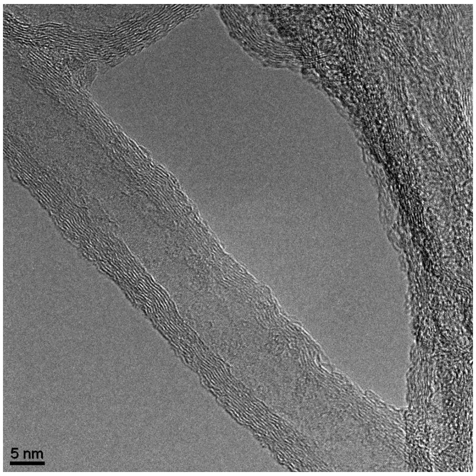

Fig. 12. HRTEM image of single multi-walled carbon nanotube

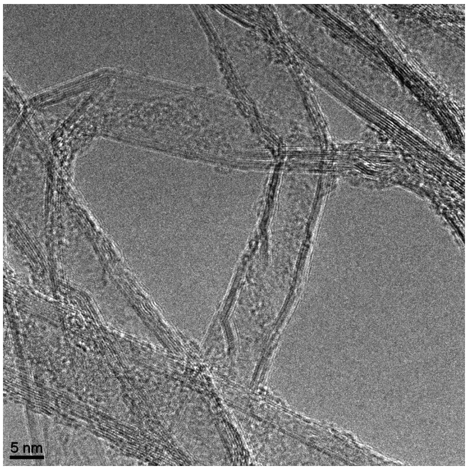

Fig. 13. HRTEM image of multi-walled carbon nanotubes

It can be observed that a full range of carbon nanotubes surface imaging was achieved under the investigations made, starting with clusters of nanotubes to clearly discernible graphene planes creating the nanotubes' structure (Fig. 12). The number of planes creating the structure of multi-walled carbon nanotubes can be estimated at approx. 8-10. The nanotubes observed are homogenous, and their diameter is approx. 10-20 nm, which is well visible in HRTEM images (Figs. 12, 13). The outcomes also confirm that the material analysed is pure, i.e. deprived of metallic impurities and amorphous carbon deposits. Single cases of metallic residues in the form of catalyst particles were also observed (Fig. 14). An elongated catalyst particle shape signifies its active part in the carbon nanotube growth process (Fig. 15).

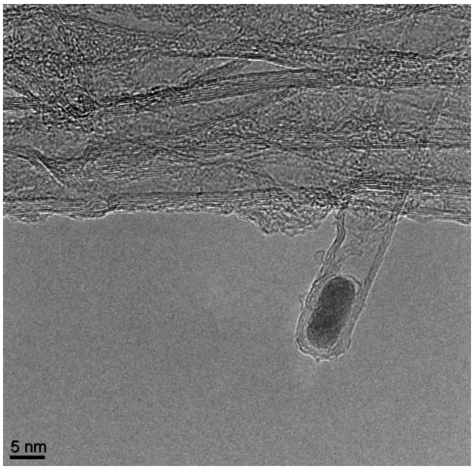

Fig. 14. HRTEM image of single catalyst particle in the multiwalled carbon nanotube structure

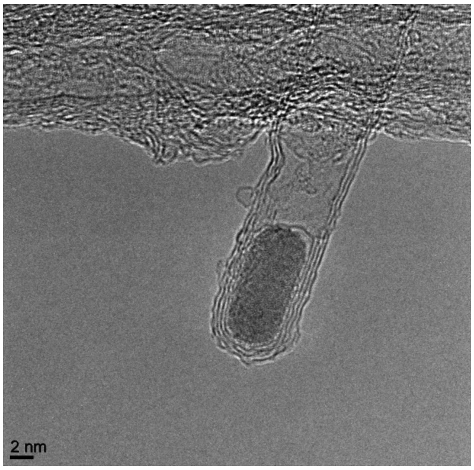

Fig. 15. HRTEM image showing an elongated catalyst particle shape

Fig. 16 presents a Raman spectrum of the multi-walled carbon nanotubes fabricated. A spectrum of multi-walled carbon nanotubes is characterised by the occurrence of the following bands: 1345 cm^{-1} (D band corresponding to the degree of nanotubes structure disorder), 1576 cm^{-1} (G band corresponding to the degree of nanotubes graphitisation) and 2685 cm^{-1} (2D band corresponding to stresses). One can be certain when analysing the shape of D and G modes and the ratio of their I_D/I_G intensity that we deal with multi-walled carbon nanotubes. Besides, no presence of RBM (Radial Breathing Mode) bands was observed in the investigations performed which also confirms the use of multi-walled carbon nanotubes.

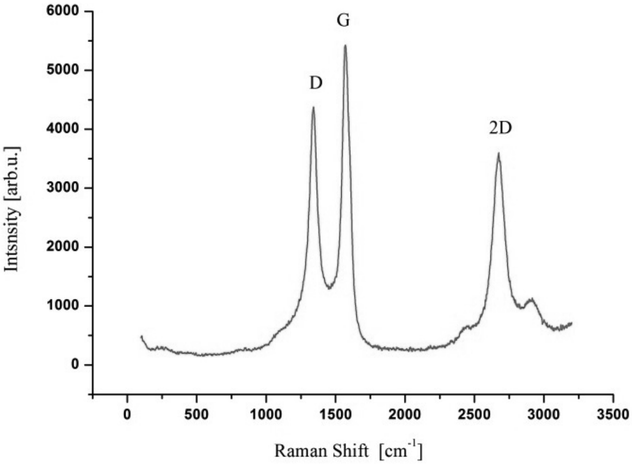

Fig. 16. Raman spectrum of multi-walled carbon nanotubes

5. Conclusions

Very fast advancements have been seen in the research efforts concerning nano-objects. Pure and functionalised carbon nanotubes have enjoyed the strong interest due to their diverse applications, mainly as a component of nanocomposites. It is therefore reasonable to develop and optimise manufacturing methods so that the quality of nanotubes is as good as possible and the manufacturing process is simple and efficient.

The EasyTube® 2000 system being the equipment of the Institute of Engineering Materials and Biomaterials allows for a controlled synthesis of high-quality carbon nanotubes for such set parameters as: the type and concentration of hydrocarbon gas, inert gas, hydrogen, process temperature and time, type of catalyst. Microscopic observations using the transmission electron microscope have confirmed the homogeneity and high quality of the carbon nanotubes fabricated. The diameter of the nanotubes within the whole area of the analysed material was approx. 10 nm. The outcomes also confirm that the material analysed is pure, i.e. deprived of metallic impurities and amorphous carbon deposits. Single cases of metallic residues in the form of catalyst particles were also observed. The Raman spectrum of the multi-walled carbon nanotubes produced is characterised by the presence of D, G and 2D bands. One can be certain when analysing their shape and the ratio of their ID/IG intensity that we deal with multi-walled carbon nanotubes. Besides, no presence of RBM (Radial Breathing Mode) bands in spectra was observed in the investigations performed, which also confirms the fact that multi-walled carbon nanotubes were fabricated.

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