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CVD synthesis of MWCNTs using Fe catalyst

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ABSTRACT

Purpose: The primary aim of the article is to present the method of chemical vapour deposition (CVD) employed for fabrication of multi-walled carbon nanotubes in the presence of a catalyst. The basic growth mechanisms of carbon nanotubes are described and the nanostructural carbon materials are presented and characterised, obtained using the CVD method and an Fe catalyst deposited on a silicon substrate.

Design/methodology/approach: Scanning and transmission electron microscopy was applied for illustrating the structure and morphology of the synthesised multi-walled carbon nanotubes.

Findings: The microscopic examinations conducted with scanning electron microscopy and high-resolution transmission electron microscopy have confirmed the achievement of an ordered layer of multi-walled carbon nanotubes on a silicon substrate containing an Fe catalyst.

Practical implications: Carbon nanotubes, due to their unique properties, can be applied in various fields of technology, especially in medicine, optics, photovoltaics and electronic engineering. CNTs are also utilised as an active layer of chemical and biochemical sensors, especially when their outer surface is decorated with nanoparticles of precious metals. Carbon nanotubes are also used as a reinforcing phase in nanocomposite materials.

Originality/value: The characterisation of the chemical vapour deposition method used for synthesis of multi-walled nanotubes with a metallic catalyst with application of the EasyTube® 2000 device by FirstNano.

Keywords: Nanomaterials; Multi Walled Carbon Nanotubes MWCNTs; Chemical Vapour Deposition CVD; Catalyst

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MATERIALS

1. Introduction

Vapour deposition is a popular technology enhancing the durability of surface and properties of, in particular, tools and constructional parts. In industrial practice, Chemical Vapour Deposition (CVD) allows to achieve layers of, e.g. carbides or metal nitrides as a result of chemical reactions occurring in a reactor between gas atmosphere components and substrate components. This process occurs usually at the pressure of $1 \cdot 10^5$-$1{,}35 \cdot 10^3$ Pa, temperature of 900-1100°C. Apart from the classical CVD, plasma-assisted or activated vapour deposition is also distinguished, assisted with microwaves, radio waves, activated with a beam of UV rays, carried out under atmospheric or reduced pressure and others [1]. The CVD method has also proven to be an effective technology of producing Single-Walled Carbon Nanotubes and Multi-Walled Carbon Nanotubes (MWCNTs). Researchers have been interested in carbon nanomaterials for long. Carbon nanotubes, since the first publications concerning this topic, have been subject to intensive investigations, mainly due to their extensive applications, notably: in electronics, optoelectronics, medicine, textile and sports industry, they are also often added as a reinforcement in composites intended for constructional parts. Such cylindrical rolled layers of graphene, ended with halves of fullerenes, may be modified differently to enhance their application options [2-5]. The issue of producing nanotubes has not been thoroughly explained to date and remains to be discussive despite efforts made by many scientists. Some common properties of different models of nanotubes fabrication have been known, including the influence of the presence of a catalyst on the type of nanotubes fabricated [2]. A catalyst is a substance changing the speed of a chemical reaction, and, in the case of the CVD method, it facilitates decomposition of hydrocarbon gas.

The purpose of the paper is to present the method of chemical vapour deposition (CVD) employed for fabrication of multi-walled carbon nanotubes. Furthermore, the basic growth mechanisms of carbon nanotubes have been described and products obtained using the CVD method and Fe catalyst deposited on a silicon substrate are presented and characterised.

2. CVD method

The CVD has become the most widespread technique of manufacturing carbon nanotubes. Carbon microfibers were described in the literature in the mid-20th century, produced when performing experiments connected with thermal decomposition of hydrocarbons in the presence of metallic catalysts. Further reports, in particular from 1952, indicate that tubular carbon fibres with the diameter of 50-100 nm were formed due to thermal decomposition of carbon oxide at a temperature of 600°C. Iron was applied then as a catalyst. Carbon nanostructures have been attracting an increasing interest of scientists, however, a breakthrough in materials engineering and nanotechnology was seen not sooner than in 1991 with Iijim's publication, who inquisitively analysed and described carbon nanotubes fabricated with the electric arc discharge method [2-4].

Chemical vapour condensation is a very popular method of producing carbon nanotubes, mainly due to economic considerations and possible application of diverse substrates and producing different forms of carbon material. Carbon nanotubes can condense perpendicular to the substrate (forming a so-called forest) as entangled packets, or create a thin or thick film on the substrate. The form of the deposit produced depends on the CVD method variation, substrate type and process parameters. The advantage of the CVD technique is also better control over process parameters as compared to other CNT fabrication methods [2,3].

In the context of carbon nanotubes fabrication, the fabrication method is referred to as thermal - thermal CVD or catalytic - catalytic CVD deposition. The process is carried out at the temperature of 600-1200°C in the presence of shielding gas (e.g. Ar, He, H_2) and a metallic catalyst. Chemical vapour deposition, the scheme of which is shown in fig.1, consists in decomposition of vapours of chemical compounds containing carbon atoms and dosed to the working chamber, of which nanotubes are formed in the next stage.

Gaseous hydrocarbons (e.g. methane, ethylene, acetylene) or carbon oxide, liquid hydrocarbons (e.g. benzene, alcohol) are usually a carbon precursor, which are heated in a flask outside the working chamber, and then their vapours are transported to the reaction chamber in the stream of another gas (e.g. Ar). Substances in the solid state, such as camphor or naphthalene, used as a source of carbon are also placed in a reaction chamber. It can be concluded according to literature that single-walled carbon nanotubes are synthesised at higher temperatures, e.g. 750-1250°C, while the diameter of catalyst nanoparticles used for producing them is usually 1 nm. An adequate temperature for the process of manufacturing multi-walled carbon nanotubes does not exceed 900°C, and metallic

catalyst nanoparticles intended for their growth are larger than for SWCNT and amount to 50 nm [2-4,6-8].

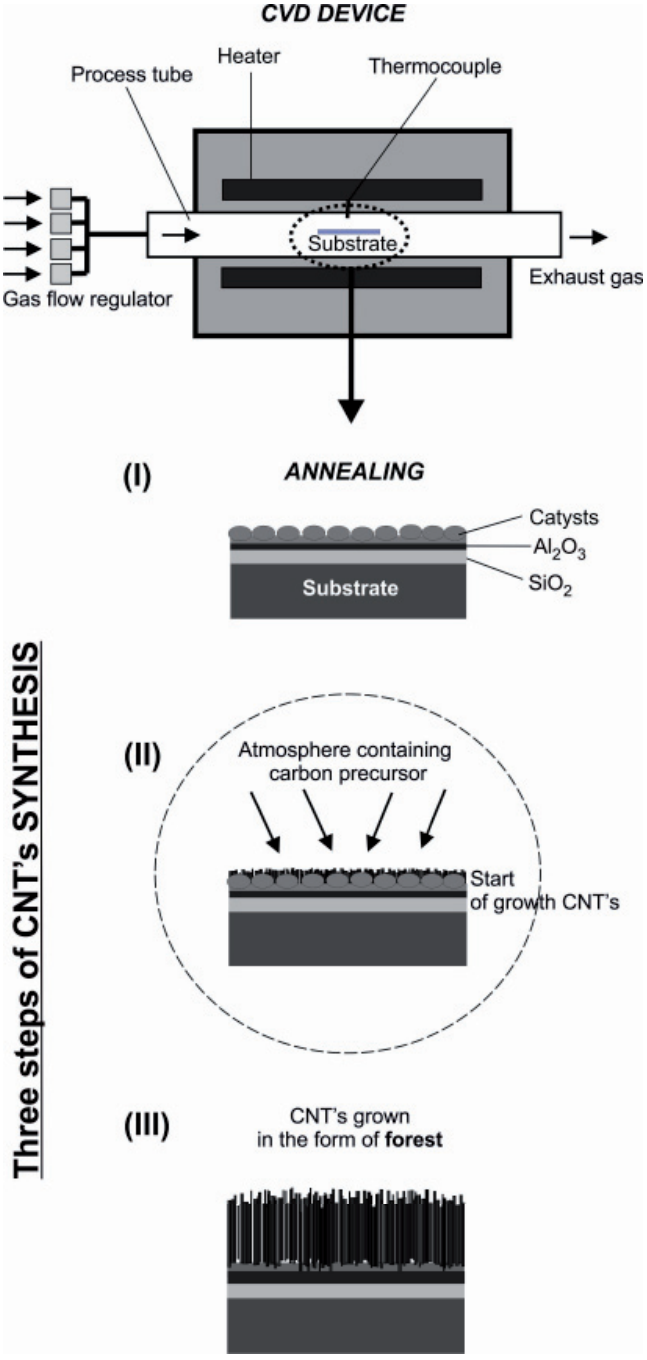

Fig. 1. Fabrication of carbon nanotubes with the CVD method

Two key variants of the CVD technique are differentiated in the context of carbon nanotubes fabrication, and they relate to the way a catalyst is supplied. A reaction takes place between a catalyst and a carbon precursor during pyrolysis, and the final product of the process are condensed carbon nanotubes deposited on the working chamber walls or on a pre-prepared substrate. A catalyst is placed directly on a substrate in the other variant. The substrates used most often include, notably: Ni, Si, SiO_2, Cu, Cu/Ti/Si, stainless steel, glass, and a substrate with $CaCO_3$ more rarely. A substrate prepared with a catalyst deposited is inserted into the working chamber and is the place where carbon nanotubes are growing [3,7-8]. A so-called carbon nanotubes forest, i.e. densely arranged carbon nanomaterials growing perpendicular to the substrate can only be achieved now with the CVD method, and such a forest is interesting for nanoelectronics.

The type of the catalyst is an important factor used at the stage of nanotubes fabrication decisive for their size, structure and purity. The following elements can be a catalyst: Fe, Ni, Co, Pt, Pd, Rh, Gd, Y, La, In, Sn and their compounds [9,10]. Catalysts in the form of nanometric layers or nanoparticles are usually used for CNT synthesis. Fe, Co, Ni metals are most widespread due to high carbon solubility in such metals at high temperatures and a fast carbon diffusion rate. Catalystic activity, substrate deposition method and catalyst morphology are the key variables of the carbon nanotubes fabrication process and are also crucial for achieving high process efficiencies [3].

3. Growth of CNTs with the use of catalyst

There is no one theory until today explaining the mechanism of nanotubes growth. The references [11] contain a description explaining the growth of carbon nanotubes in the following steps:

- **Step 1.** Decomposition of hydrocarbon to hydrogen and carbon, chemisorption of the formed carbon over active centres of a catalyst being mainly in the liquid state. High chemical activity of carbon atoms enables their dissolution in a catalyst.
- **Step 2.** Discussion of carbon atoms within the catalyst particle and its supersaturation with the forming amorphous carbon. Creation of the carbide phase or precipitation of crystalline carbon in the form of graphite as a result of lowering temperature. Creation of

nuclei on the catalyst surface and then growth of carbon nanotube owing to constant inflow of carbon atoms.

- **Step 3.** Surface diffusion of carbon occurring owing to distribution of carbon on the catalyst surface. Different rates of coal transport to the catalyst surface and its diffusion inside the grain may cause local collection of carbon atoms within the catalyst particle, which has influence on decrease in the active area of the catalyst.
- **Step 4.** The end of carbon nanotubes growth due to lower carbon solubility in the catalyst (so-called deactivation) caused by a lowering process temperature.

Two types of carbon nanotubes growth mechanisms can be differentiated based on the discussed model of carbon materials growth [12-13]. Tip-growth of carbon nanotubes is seen when a catalyst nanoparticle is detached from the substrate and remains on the surface of the nanotube being formed. Base-growth is experienced when a catalyst remains on the nanotube growth substrate. The tip and base growth models of carbon nanotubes manufactured with presence of a catalyst are shown in Fig. 2.

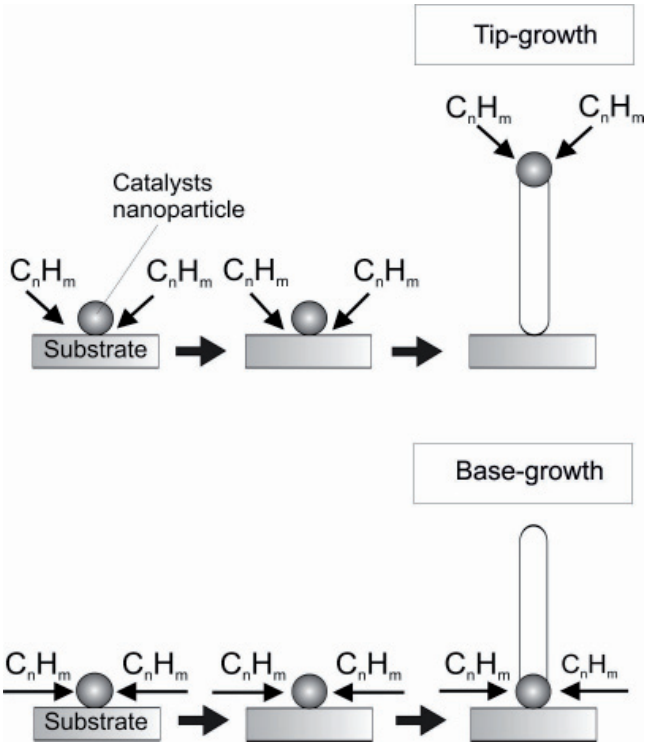

Fig. 2. Carbon nanotubes growth models with presence of catalyst

Physiochemical characteristics of the catalyst are an important factor in the nanotube structure formation process. One of the factors crucial for the nanotube growth process is the size of catalyst particles. In the case of a catalyst with the diameter of ~1 nm, one active centre exists on its surface at most, contributing to growth of a single single-walled carbon nanotube. The growth of subsequent graphene layers is prevented, therefore, no transformation into a multi-walled nanotube takes place [14]. Moreover, the presence of a catalyst with its sizes exceeding the diameter of nanotubes, and at the same time having more than one active centre is conditioning the growth of at least several single-walled nanotubes. Rapid growth of single-walled nanotubes assuming the form of sea urchins is observed in the presence of a catalyst of metals of rare earths such as Y, La, Gd [15,16]. The size of the catalyst particle is therefore significant for the type of nanomaterials produced in a catalytic pyrolysis of hydrocarbons, as confirmed by results of research [17].

4. Experimental

4.1. Materials

Multi-walled carbon nanotubes were fabricated with the chemical vapour deposition (CVD) method using an EasyTube® 2000. The carbon nanotubes were synthesised on a silicon substrate containing a catalyst in the form of a thin film and two buffer layers (2 nm of Fe, 15 nm of Al_2O_3 and SiO_2). Ethylene (C_2H_4) was the source of carbon. The growth of nanotubes took place in an oven at the temperature of 700-800 °C. A silicon substrate containing a catalyst was placed on a feeder, and then a specimen was introduced in the presence of H_2 and Ar into the heated oven and the substrate was heated for 15 minutes. Following the heating, hydrocarbon gas was introduced into the chamber, supplied for 15-45 minutes. Following the end of the growth process, hydrocarbon supply was stopped, the feeder was removed together with a specimen from the oven, the specimen was removed, the system was purged with the presence of Ar flowing for 5 minutes, the oven was gradually cooled to 200 °C, the system was purged again and the process was finished. The specimens were placed directly on a feeder or in a quartz holder.

4.2. Research methodology

The nanostructures obtained were observed using electron microscopes: a scanning and transmission

microscope. SEM images were made using a scanning electron microscope SEM Supra 35 by Carl Zeiss equipped with the X radiation spectrometers: an energy dispersion EDS and wavelength WDS spectrometer and a system for analysing diffraction of back scattered electrons EBSD by EDAX. The high resolution and the precision imaging of the preparations viewed was achieved by applying a high-performance In-lens SE detector working with low beam voltage and with a very small distance of the preparation examined to the electron gun (working distance).

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. 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.

4.3. Results and discussion

The photographs of the carbon nanotubes produced with the EasyTube® 2000 system, being the result of own observations made with the scanning and transmission electron microscope, are presented in figures 3-4 (SEM) and 5-9 (TEM). A layer of vertically laid carbon nanotubes growing on a silicon substrate covered with a Fe catalyst was achieved. The diameter of the fabricated carbon nanotubes produced is approx. 10-15 nm. In the case where a specimen is positioned directly on a feeder in a synthesis process, the height of a carbon nanotubes layer is about 180 μm (Fig.3). The height of a carbon nanotubes layer grew twofold to the level of about 360 μm (Fig. 4) after placing the specimen in a quartz holder located on the feeder. It can be concluded that a full range of carbon nanotubes surface imaging was achieved under the observations made, starting with clusters of nanotubes (Figs 5-6) to clearly discernible graphene planes creating the nanotubes' structure (Figs 8-9). The material analysed is relatively pure, deprived of large quantities of metallic impurities and amorphous carbon deposits. Single catalyst particles shown as light precipitations were observed during investigations in the STEM mode with the HAADF detector (Fig.6). This type of studies is adequate for materials the components of which are strongly differing in their ordinal number (so-called Z contrast), producing strong contrast. The occurrence of metallic residues in the form of elongated catalyst particles closed in a structure of multi-walled carbon nanotubes, as is true for Fig.7, may be caused by stress induced by carbon material surrounding the catalyst particle (Fig.8). A catalyst in the spherical form is shown on photo 9.

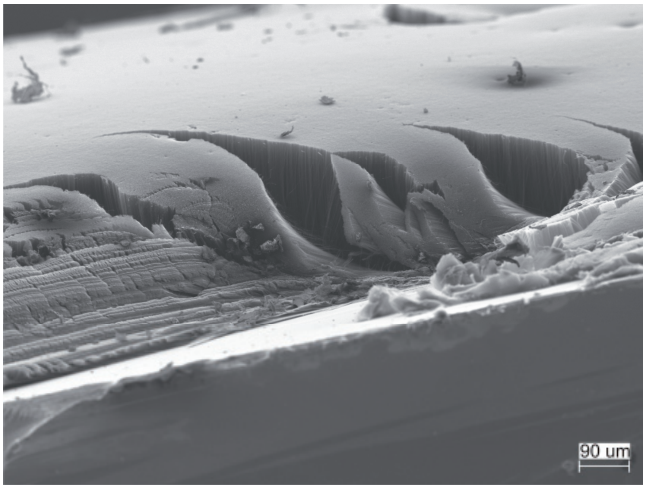

Fig. 3. SEM image of carbon nanotubes manufactured with the CVD method on the silicon substrate with an Fe catalyst (the synthesis time of 45 min., a specimen placed directly on a feeder). The specimen presented was turned by 90°

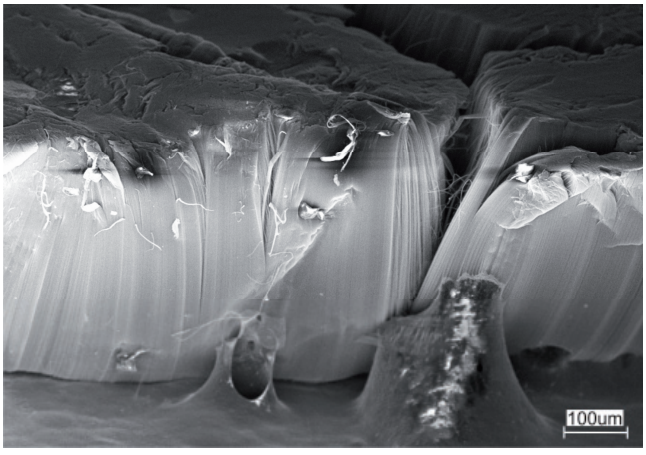

Fig. 4. SEM image of carbon nanotubes manufactured with the CVD method on the silicon substrate with an Fe catalyst (the synthesis time of 45 min., a specimen placed in a quartz holder). The specimen presented was turned by 90°

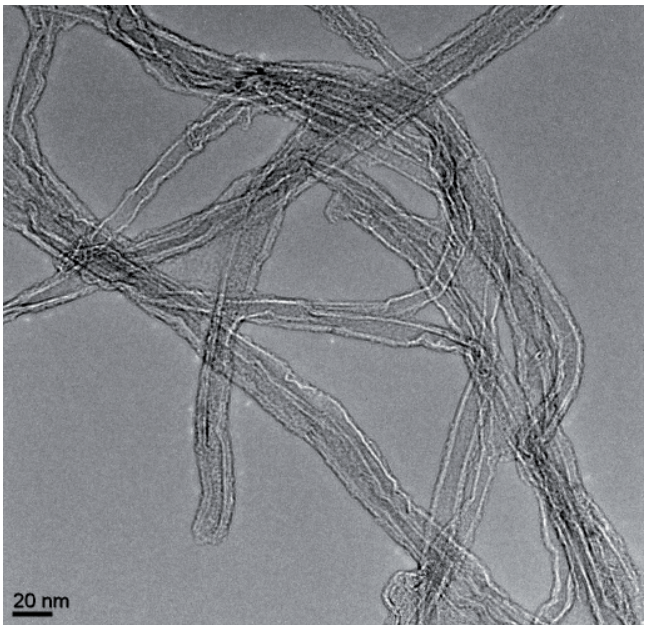

Fig. 5. TEM image of multi-walled carbon nanotubes

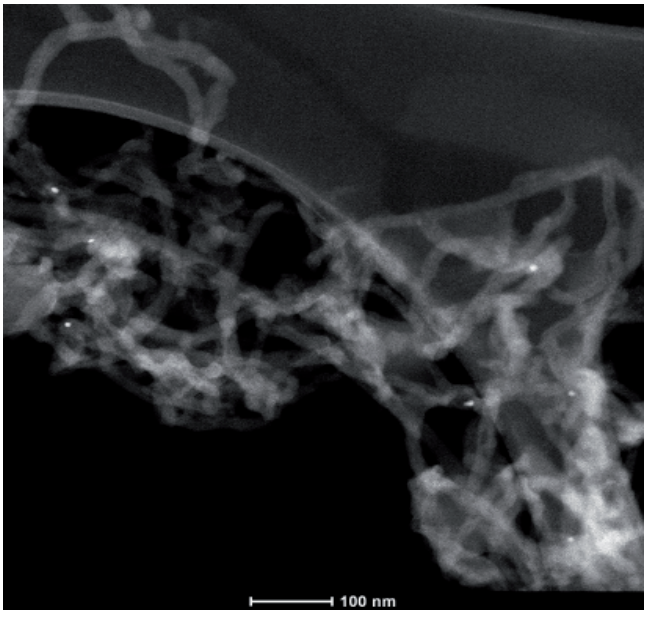

Fig. 6. HAADF image of multi-walled carbon nanotubes containing catalyst particles visible as light points

The observations allow to conclude that a catalyst particle is lifted. from the substrate upwards in the growth process, which is consistent with the tip growth mechanism of nanotubes described in the literature and signifies the active participation of a catalyst in the growth process of MWCNTs.

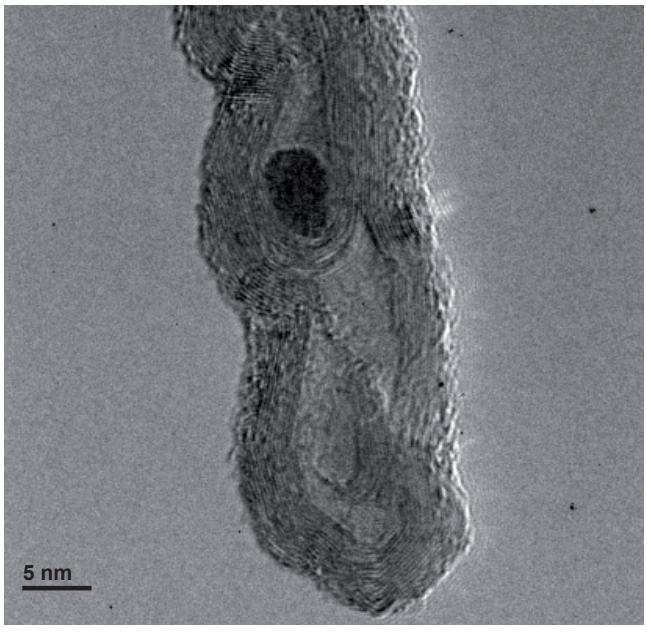

Fig. 7. HRTEM image of MWCNTs together with single catalyst particle in the multi-walled carbon nanotube structure

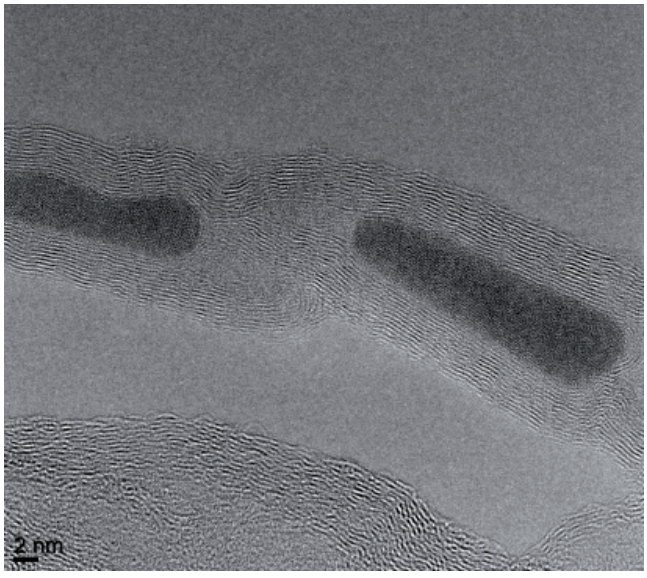

Fig. 8. HRTEM image of multi-walled carbon nanotubes together with elongated catalyst particles in the multi-walled carbon nanotube structure

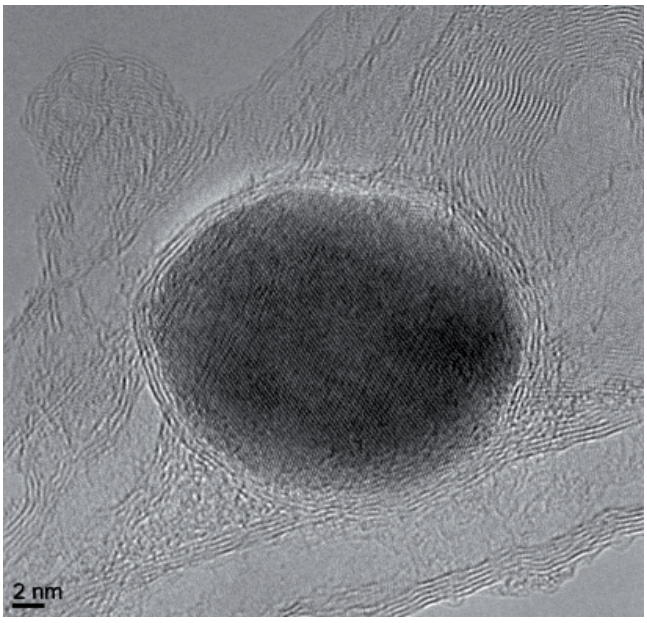

Fig.9. HRTEM image of multi-walled carbon nanotubes with spherical catalyst particle in the multi-walled carbon nanotube structure

Moreover, photos 7-9 also show that graphene planes are surrounding a catalyst particle, which may cause limitation of carbon precursor access to the catalyst, thus inhibiting the carbon nanotubes growth process and residual impurities in the metallic form.

5. Conclusions

The EasyTube® 2000 system enables to synthesise high-quality multi-walled carbon nanotubes condensing on a silicon substrate with an Fe catalyst deposited as a thin film (2 nm) with the CVD method for the set parameters such as: type and concentration of flow gases: hydrocarbon gas, shielding gas, hydrocarbon, and also process temperature and time. A catalyst has an effect on the type of the nanotubes being formed and constant supply of hydrocarbon gas to the catalyst particle surface leads to continuation of the MWCNTs growth process. Microscopic observations with the scanning transmission microscope and transmission electron microscope have confirmed that a layer of multi-walled carbon nanotubes was produced in The placement and form of such particles proves active participation of a catalyst in the growth process according to the proposed tip growth mechanism of nanotubes. If the supply of hydrocarbon is cut off to the catalyst surface, breakdown of a carbon precursor is hindered, causing an inhibited formation process of carbon nanotubes.

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