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Synthesis of Carbon Nanofibers on Copper Nanopowders by Low-Temperature CVD

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Abstract

The article presents the results of experiments on the synthesis of carbon nanofibers by thermal chemical vapor deposition using copper nanopowders obtained by electric explosion of wire as catalysts. Stable growth of carbon nanofibers was carried out at temperatures significantly lower than normally used. The process parameters that are optimal for low-temperature growth of carbon nanofibers have been identified during the performed experiments. The synthesized samples have different diameters and morphology (from spiral to direct). Copper clusters are both at the ends and inside the fibers. The results of IR spectroscopy indicate that the structure of the obtained carbon nanofibers is polymeric. X-ray analysis revealed the presence of a halo on the diffraction patterns at small values of the angle 2θ, which proves that the grown structures have an amorphous nature. There are no groups that are responsible for long-range order in all Raman spectra. Studies by transmission electron microscopy showed that nanostructures do not have an internal channel and nanofibers are solid.

1. Introduction

Since their discovery, carbon nanotubes (CNTs) have been targets of numerous experimental and theoretical studies. The purposes of these experiments were study on the conditions of obtaining and analysis of their unique mechanical, chemical and electrical properties. Officially, it is assumed that the CNTs were first discovered in 1991 in the soot, which is formed on the electrodes under the arc discharge [1]. However, the existence of carbon nanotubes was reported earlier by Soviet scientists L.V. Radushkevich and V.M. Lukyanovich in 1952 [2]. These works have not attracted wide attention of the scientific community related to their publication only in Russian. Over the past two decades such methods as various types of chemical vapor deposition CVD (in RF and microwave discharge, DC plasma, as well as the method of hot filament), the synthesis in flames of hydrocarbons and arc discharge have been developed for producing carbon nanotubes [1, 3–5]. Despite the fact that these methods achieved a high level of quality, they are still far from complete control of important structural features, such as the length of the nanotubes, their diameter and chirality [6].

At present, several methods of preparation of metal nanoclusters are used for the synthesis of CNTs. One of the promising methods of obtaining nanopowders (NPs) is electric explosion of wire (EEW) – a nonequilibrium process in which a conductor is dispersed under pulsed electric current and products of the explosion are mixed with the environment. Electroexplosive NPs have several advantages compared with NPs obtained by other ways: they are resistant to oxidation and sintering at room temperature, characterized by high chemical and diffusional activity during heating [7].

A widely used method of obtaining CNTs is based on the process of decomposition of gaseous hydrocarbons in the presence of catalysts. The particles of metals (Co, Ni, and Fe) with the size of several tens of nanometers are most frequently used as catalysts [1]. Typically, the synthesis is carried out at high temperatures – 600–1200 °C and pressures belowatmospheric when using these metals.

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The experiments are usually conducted at high temperatures (600–900 °C)when copper catalyst is used in the thermal CVD method. In this case, various precursors of hydrocarbons (methane, acetylene, benzene, etc.) often in combination with inert gases as well as hydrogen, nitrogen, etc. are used [8, 9].

In recent years, more and more attention of researchers attracted to the low-temperature modes of obtaining carbon nanostructures (CNs) by CVD. The interest caused by several reasons. Firstly, the carbon containing source gases applied in the CVD growth processes (e.g., CH_4, C_2H_2, C_2H_4) are normally explosive. A process at lower temperatures is much safer. The low-temperature CVD process also simplifies remarkably the equipment and reduces consequently the cost. Secondly, the CVD processes are often accompanied by the coking. The process at lower temperatures mitigates the harmful deposition from the wall of a reaction chamber as well as gas channels. Finally and the most importantly, the growth at low temperatures is of great benefit to a lot of applications when the substrate material cannot withstand a high-temperature process. For example, to apply carbon nanofibers (CNFs) in semiconductor industry, the CVD process has to be compatible with the CMOS technology. It means the CVD temperatures must remain below 400–450 °C to avoid mechanical deterioration [10, 11].

Synthesis of CNs at low temperature CVD modes is carried out at different temperatures from 195 to 450 °C. The low-temperature CVD allows to synthesize various types of CNs, including carbon nanotubes, amorphous nanofibers, nanocoils, nanohelixs, nanosheets and branched CNs. A detailed overview of works on low-temperature synthesis of CNs is given in [10].

The aims of the study were determination of the lower temperature limit of the growth of carbon nanostructures on copper NPs and search for optimal conditions of low temperature (energetically favorable) synthesis using the most accessible hydrocarbons without expensive additives of inert and other gases.

2. Experimental

NPs were purchased from Tomsk Polytechnic University (Russia) to be used as catalysts in the synthesis of carbon nanostructures. The procedure of obtaining NPs, experimental details and the results of studies on their morphology and structure are described in detail in works [12–14].

The joint studies on the structure and morphology of EEW NPs, their catalytic activity and the possibility of synthesis of CNs on them by thermal CVD were carried out at the Department of surface and technology of new materials at the Institute of Materials Science of the University of Siegen (Germany) [14, 15].

Figure 1 presents the histogram of the size distribution, energy dispersive spectrum and SEM images of Cu NPs.

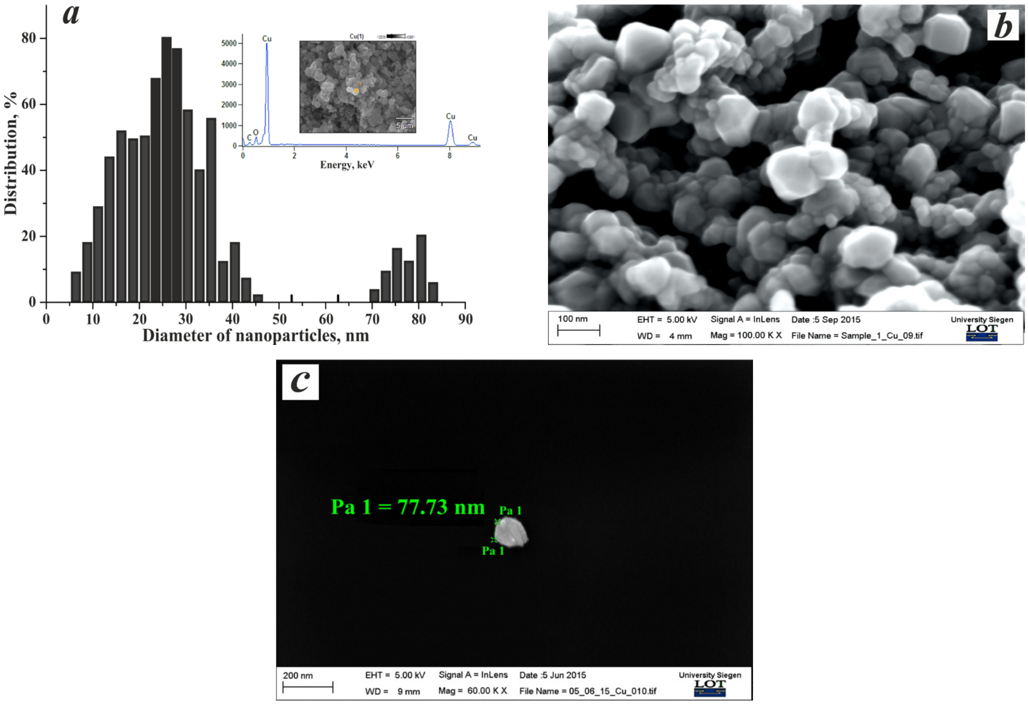

Fig. 1. The histogram of the size distribution and energy dispersive spectrum (a), SEM images of Cu NPs (b) and individual nanoclusters after separation in hexane (c).

The results of TEM studies on copper NPs are consistent with the results obtained by SEM. Copper NPs have a bimodal distribution. The average particle diameter of the first and the second fraction is 23.6 and 81 nm, respectively. SEM images of Cu powders show that agglomeration of metal particles with a smaller size (from 10 to 50 nm) around the clusters with size from 100 to 200 nm is present. Hexane allows to separate the individual Cu nanoclusters (Fig. 1c). The diameter of the clusters ranges from 20 to 100 nm. SEM images of Cu powder show that the copper nanoclusters have a distinct crystallographic faces and edges.

2.1. Synthesis of CNs

The growth of CNs was conducted in the volume of quartz reactor with an internal diameter of 90 mm placed inside 1150 mm long horizontal three-zone tube furnace (Carbolite Limited). The catalyst was loaded into a ceramic boat and mechanical pumping is carried out by backing pump for 30 min (up to pressure 10 mbar) after mounting of the sample to the volume of reactor. The reactor was heated to the desired temperature at a controlled rate (rate of heating varied between 5 and 10 °C/min). The working gas – acetylene was fed in the reactor to the required value of pressure after reaching the desired temperature. Pumping of residual gases and cooling the reactor to room temperature were carried out at a predetermined speed at the end of the synthesis (the time of experiments varied from 1 to 3 h). The scheme of technological equipment and the procedure of conduction of CNs synthesis were described in detail in works [14, 16, 17].

2.2. Methods and apparatus for the study of the morphology and structure of CNs

The field emission scanning electron microscope with ultra-high resolution of model Gemini Ultra 55 of the company Zeiss, with a device for X-ray microanalysis of the company «Thermo Scientific» was used to study the morphology of the samples. Two basic modes of shooting InLens and SE2 were selected for the study. InLens method provides the best resolution of SEM images of the surface morphology or cross section of the scanned sample. Shooting mode SE2 is the most preferred for obtaining accurate characteristics of the surface topography of the scanned sample. Investigations were carried out at the Institute of Materials Science of the University of Siegen (Germany).

Research by infrared (IR) spectroscopy was performed in the laboratory of physical and chemical research of chemical faculty of Al-Farabi Kazakh National University (Almaty, Kazakhstan) with a spectrometer Spectrum 65 FT-IR Spectrometer (in transmission mode).

The study on the structure of CNs is carried out by the method of X-ray analysis using diffractometers Philips X'Pert PRO MRD (Institute of Materials Science of the University of Siegen, Germany) and Rigaku D/max/2400 XRD (Shenyang National Laboratory of Materials Science, Chinese Academy of Sciences). Radiographs of samples were obtained using copper radiation (λ = 1.5406 Å) in digital form. Processing of X-ray spectra to determine the angular position and intensity of the reflection was performed in program OriginPro 8.1. PCPDFWIN program with the base of diffractometric data PDF-2 was used for the phase analysis.

The samples were investigated by Raman spectroscopy using spectrometer NT-MDT NTegra Spectra (laser wavelength λ = 473 nm) at the National Nanotechnology Laboratory of open type (Almaty, Kazakhstan).

The analysis of samples by transmission electron microscopy (TEM) was performed at the Institute of Nuclear Physics (Almaty, Kazakhstan) with a transmission electron microscope JEOL JEM-2100F.

3. Results and discussion

3.1. Determination of temperature limits of CNs synthesis on CuNPs

The experiments were performed at different temperatures (200–700 °C) and pressures (100–400 mbar) to determine the optimal conditions for low temperature synthesis of CNs.

The experiments have shown that the lower temperature limit of CNs synthesis is 250 °C over the entire range of pressure100–400 mbar (in 100 mbar increments). It is evident that catalytic decomposition of acetylene does not occur at lower temperatures.

Figure 2 shows SEM images of surfaces of Cu NPs after synthesis for 1 h at a pressure of 300 mbar, at temperatures close to the lower and upper limits of synthesis (determined experimentally).

The slight growth of CNs with a predominance of carbonization of copper clusters was observed at temperatures below 250 °C and above 300 °C (Fig. 2). However, further experiments have shown interesting results at the synthesis temperature of 375 °C and a pressure of 500 mbar, which will be given below.

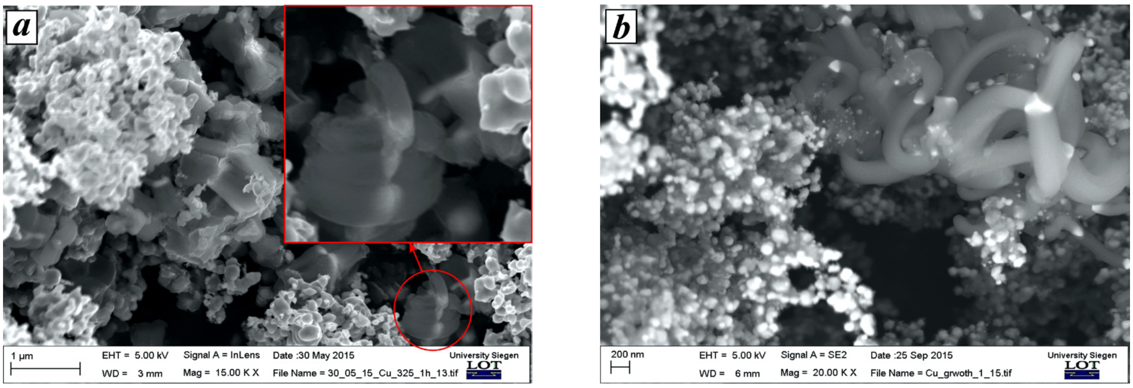

Fig. 2. SEM images of surfaces of Cu NPs after synthesis: (a) – 225 °C; (b) – 325 °C.

As a result of preliminary experiments the possibility of using NPs obtained by EEW as a catalyst for obtaining CNs was demonstrated. The lower and upper temperature limits of synthesis are also found throughout the range of pressure in which steady growth of CNs occurs.

3.2. SEM studies of CNs morphology

Further, more detailed studies were carried out on the separated copper clusters to study the process of nucleation and growth of individual CNs. NPs samples were suspended in hexane solution for separation. Further sonication of solution was performed (volume of suspension is 30 ml, frequency of ultrasound is 27 kHz, power of generator is 120 W, exposure was conducted for 30 min) and then drops of suspension of metal particles were deposited on a silicon substrate. Synthesis of CNs was carried out in a previously determined optimum range of experimental parameters (temperature – 250-300 °C, pressure – 100-400 mbar). Figures 3–6 show SEM images (shot in different shooting modes – InLens and SE2) with magnified most interesting fragments of synthesized CNs on the separated Cu clusters.

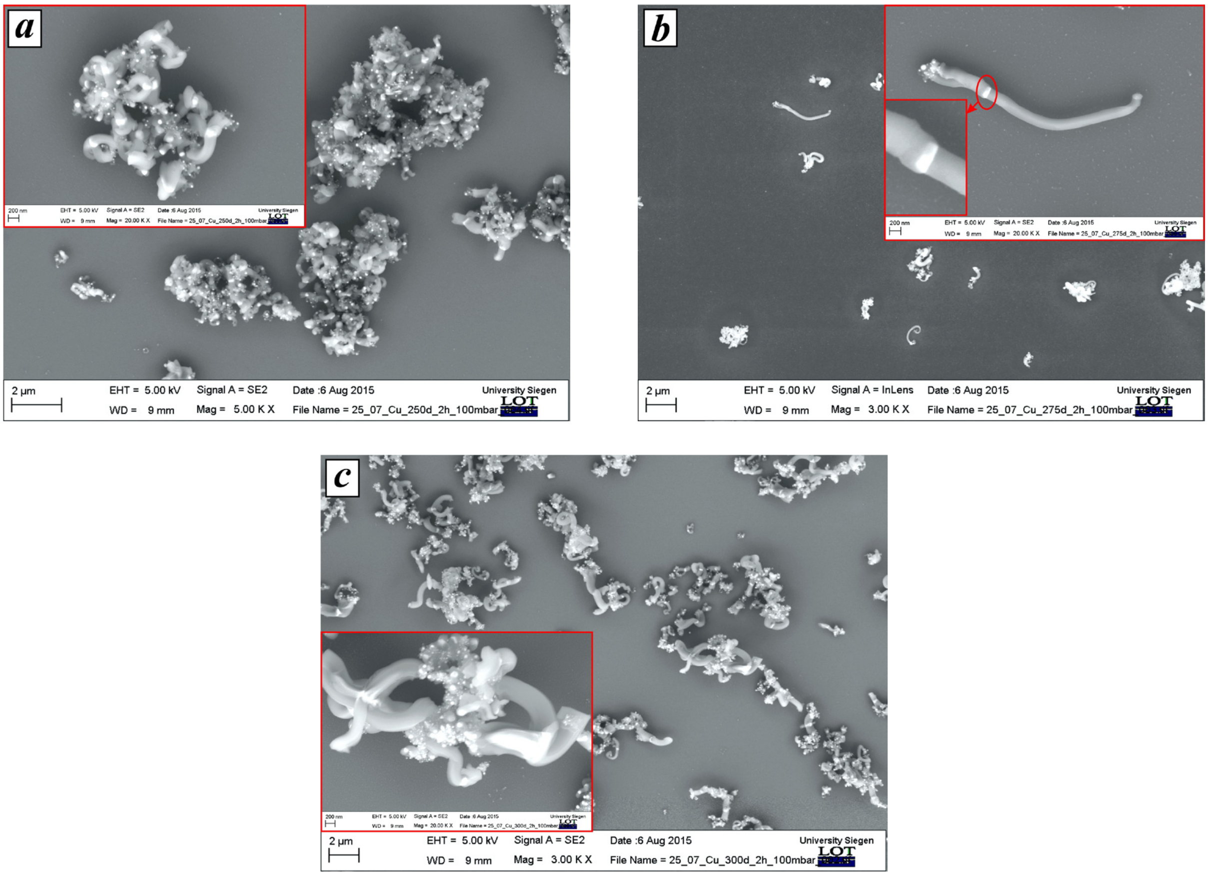

Fig. 3. SEM images of CNs on NPs and Cu clusters synthesize data pressure of 100 mbar: (a) – 250 °C; (b) – 275 °C; (c) – 300 °C.

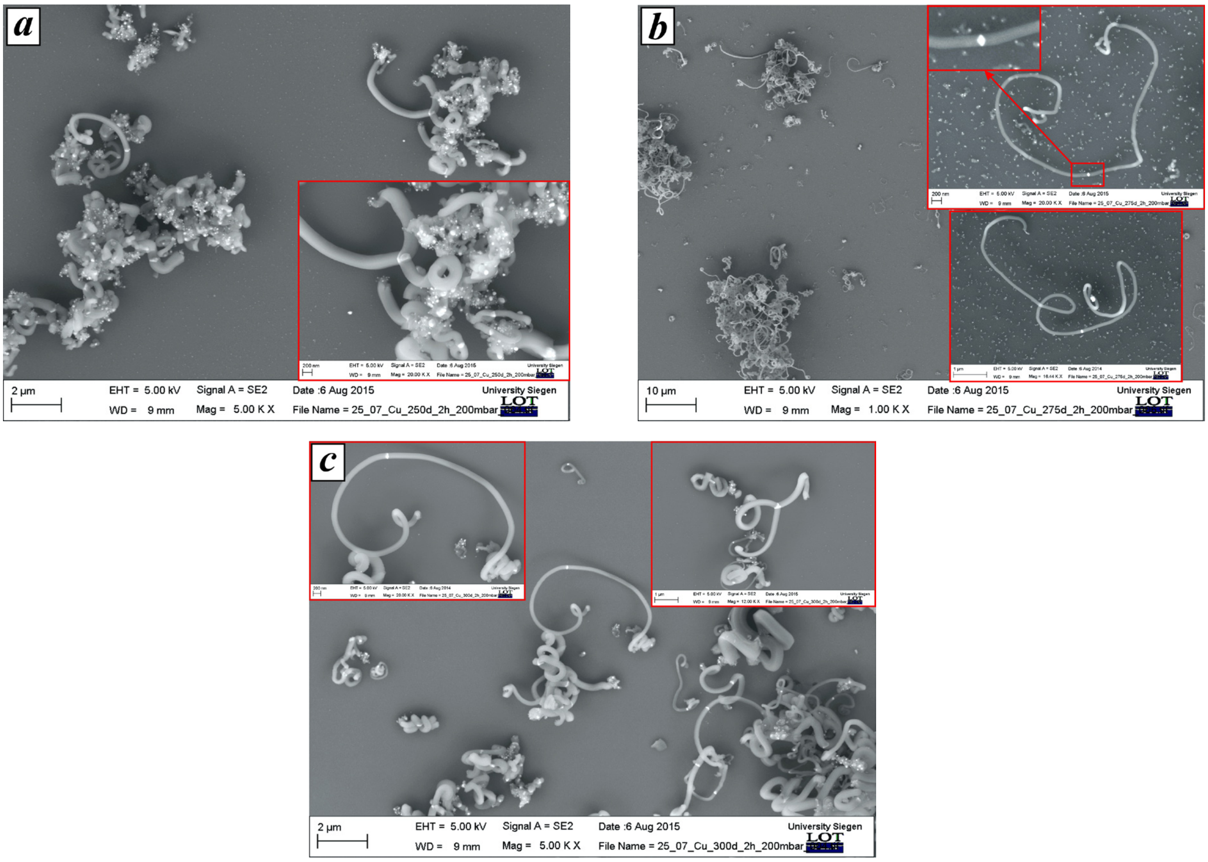

Fig. 4. SEM images of CNs on NPs and Cu clusters synthesized at a pressure of 200 mbar: (a) – 250 °C; (b) – 275 °C; (c) – 300 °C.

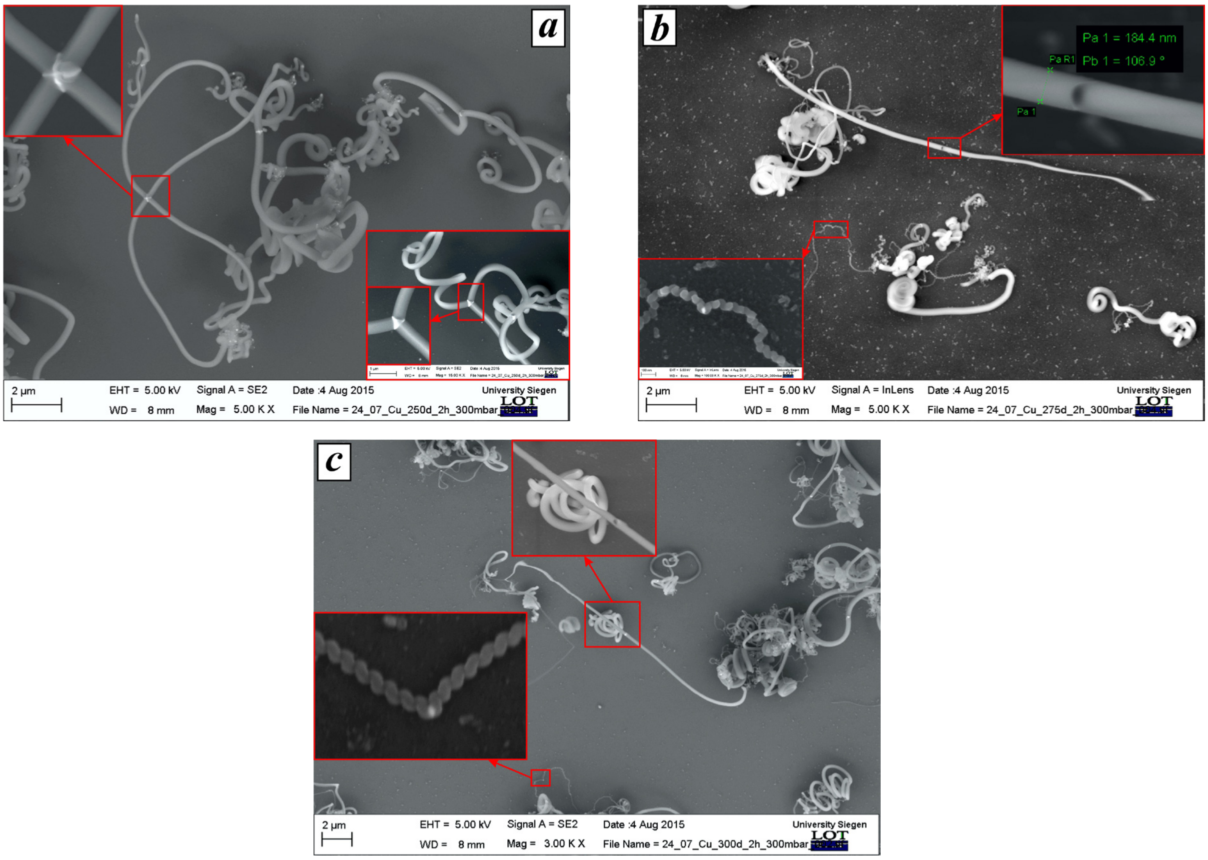

Fig. 5. SEM images of CNs on NPs and Cu clusters synthesized at a pressure of 300 mbar: (a) – 250 °C; (b) – 275 °C; (c) – 300 °C.

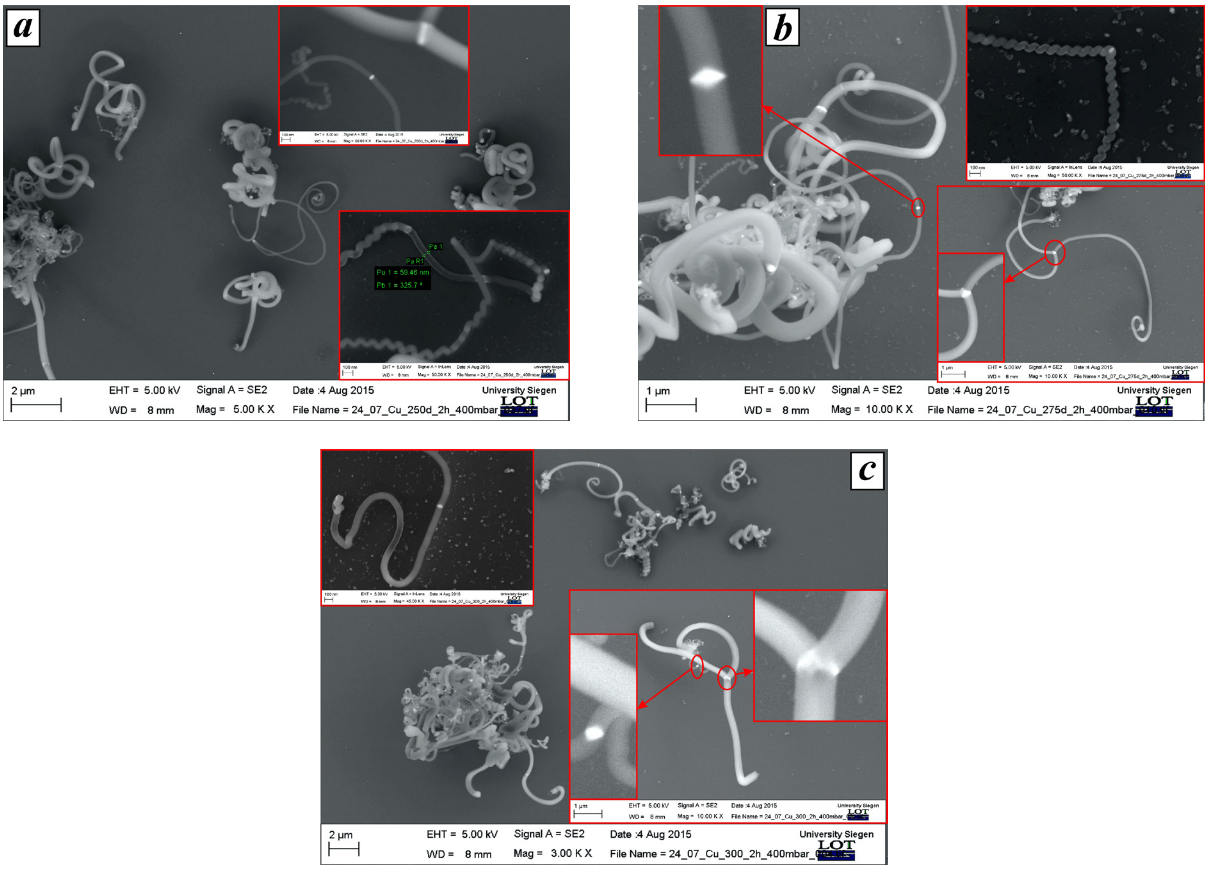

Fig. 6. SEM images of CNs on NPs and Cu clusters synthesize data pressure of 400 mbar: (a) – 250 °C; (b) – 275 °C; (c) – 300 °C.

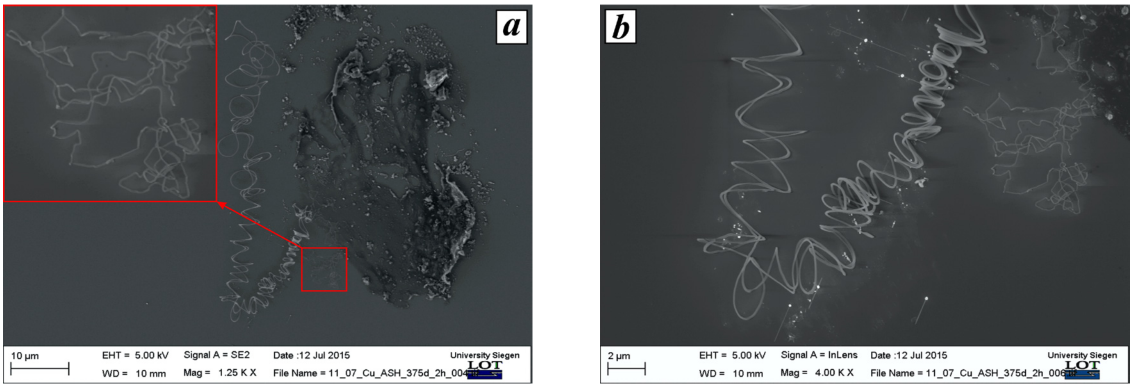

Fig. 7. SEM images of CNs on the separated Cu NPs.

As seen in SEM images, CNs have different diameters (50–200 nm) and morphology (from spiral to branched and straight). Clusters of copper are both at the ends and inside CNs. The branched CNs were also revealed. Figures 5–6 show the SEM images of 2, 3 and 4-branched CNs. Such symmetrical branched CNs were observed at the temperature range – 250–300 °C and a pressure of 300–400 mbar. Obviously, the diameter and shape of CNs are determined by the size and symmetry of copper nanoclusters.

The modes at which the growth of highly extended CNs occurs were detected in the course of experiments. Figure 7 shows SEM images of samples with different resolutions synthesized at 375 °C and a pressure of 500 mbar.

The growth of CNs was observed in all optimum experimental range for NPs as well as the separated samples.

3.3. IR spectroscopy of CNs

Investigation of samples by IR spectroscopy was carried out in the range from 500 to 4000 cm^{-1} to determine all functional groups on the surface of the carbon nanostructures. Figure 8 presents characteristic infrared spectrum of synthesized CNs.

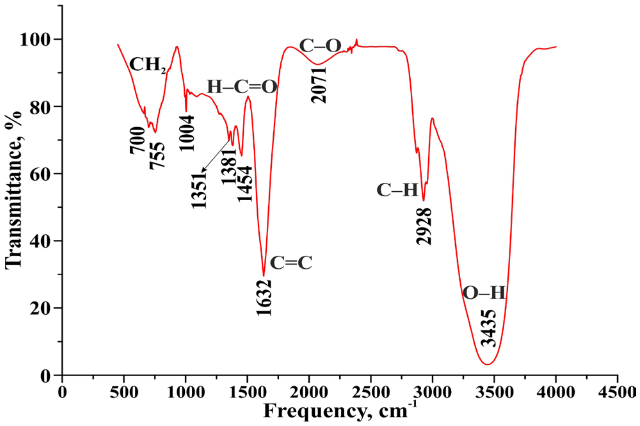

Fig. 8. IR spectrum of CNs synthesized at a pressure of 400 mbar and a temperature of 300 °C.

A broad peak at 3435 cm^{-1} corresponds to O–H stretching of the hydroxyl groups. Carboxyl groups may be present on the surface of CNs due to partial oxidation. The signal amplification within 1004 and 2071 cm^{-1} may be due to C–O stretching. Peak at 755 cm^{-1} arises from the presence of –CH$_2$ oscillations. Groups in the region of 1351, 1381 and 1454 cm^{-1} correspond to the H–C stretching modes of H–C=O in carboxyl groups, while the peak at 1632 cm^{-1} corresponds to C=C stretching of carbon nanotubes [18]. The results of IR spectroscopy reveal that the structure of grown CNs is polymeric.

3.4. X-Ray analysis of CNs

Figure 9 shows a typical X-ray spectrum of synthesized CNs on copper NPs.

X-ray analysis of CNs on EEW Cu NPs showed typical diffraction peaks of metallic copper. All spectra show no reflection characteristic of graphite. A halo which indicates the amorphous nature of the grown nanostructures is present for small values of angle 2θ confirming the results of IR spectroscopy.

3.5. Investigation of CNs by Raman spectroscopy

Figure 10 shows the Raman spectra of CNs on Cu NPs obtained at different temperatures (250–300 °C) and pressures (100–400 mbar).

All CNs preferably show peaks *D* and *G* at Raman spectra of samples obtained at a pressure of 100 mbar. It can be seen that the position of *G* peak shifted to higher frequencies in all samples, which could be an indication of graphitization [19]. Peak *D* is also shifted from about 1300 to 1392.5, 1357.1 and 1347.5 cm^{-1}, but the intensity of this peak is not so high, indicating a small amount of defects in nanostructures. All spectra present no groups that are responsible for long-range order at 2500–2600 cm^{-1}. It can be assumed that the samples have an amorphous structure based on these results.

The Raman spectra of samples synthesized at a pressure of 200 mbar show even a greater shift of *G* peak. The peak position varies from 1589.7 to 1602.3 cm^{-1}, indicating a significant graphitization of sample [20]. Also, this may be indicated by the absence of 2D peak. It may be noted the shift of *D* peak from 1357.1 to 1370 cm^{-1} with increase in temperature. Intensity of *D* peak in these samples is also low, it appears as a shoulder in the samples which means that CNs have few defects.

G peak is observed at the range of 1583.4–1592.8 cm^{-1} for CNs obtained at a pressure of 300 mbar. Peak *D* can be observed only in spectrum of the third sample at 1376.4 cm^{-1}. The intensity is smaller than that of the *G* peak, indicating a small amount of defects in the structure. The samples also show no crystallinity, as there is no peak of long-range order.

The groups *D* and *G* are located in the range of 1360.3–1389.3 cm^{-1} and 1586.5–1592.8 cm^{-1}, respectively, in the spectra of the samples synthesized at a pressure of 400 mbar. 2D group is not observed in these samples.

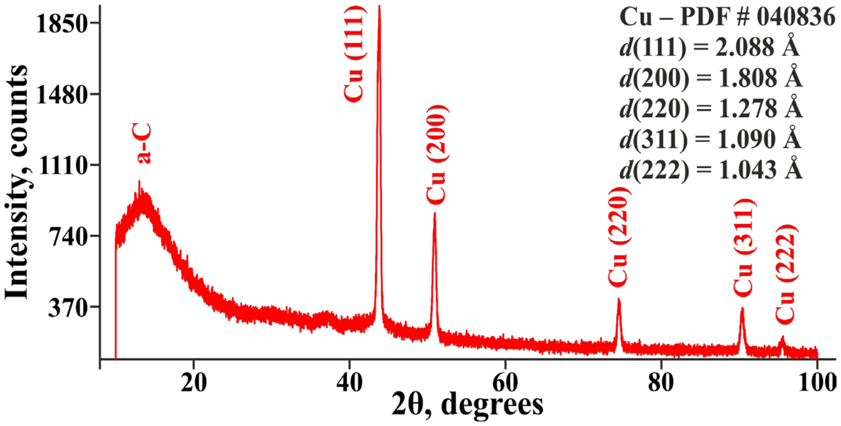

Fig. 9. X-ray spectrum of CNs obtained at a temperature of 275 °C and pressure of 300 mbar.

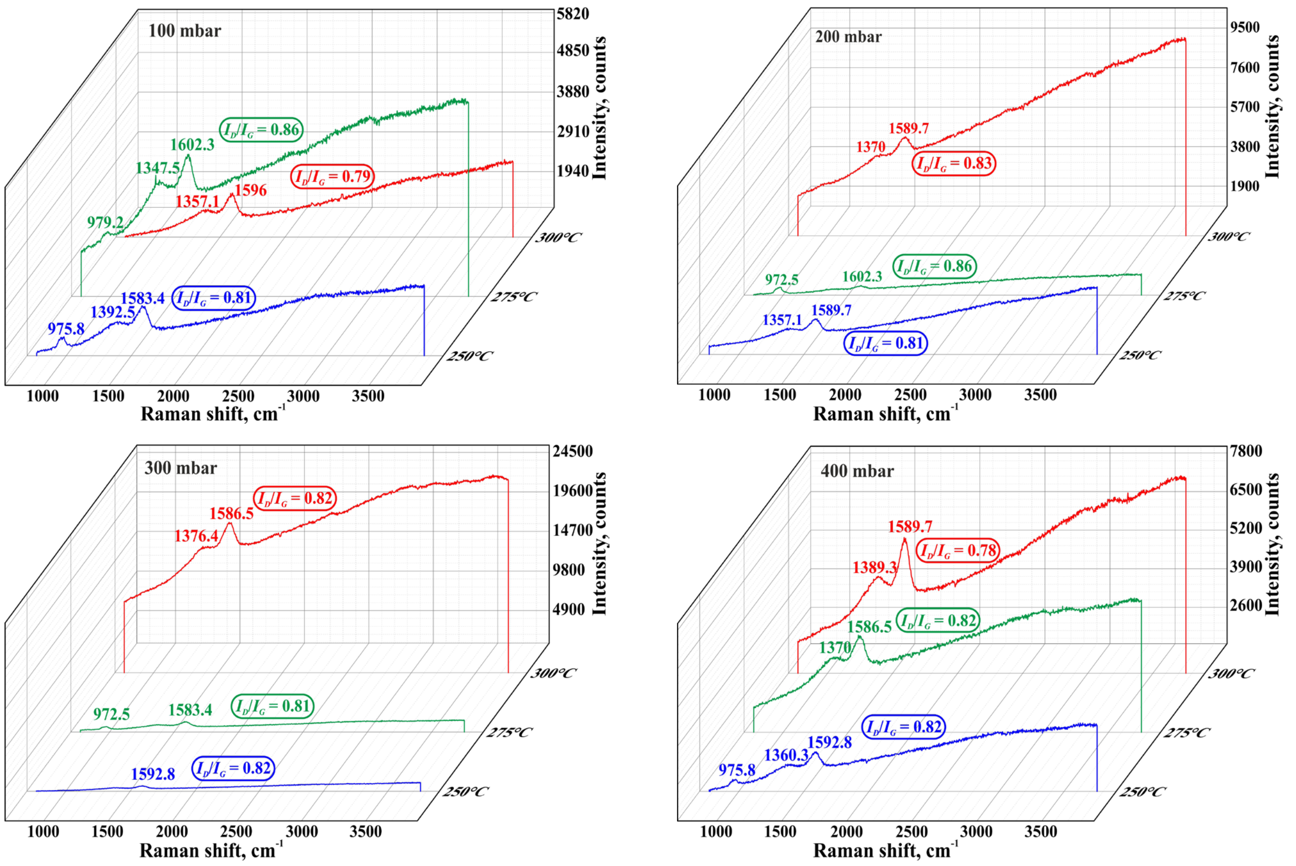

Fig. 10. RS spectra of CNs on Cu NPs.

In general, CNs are not very different from each other in structure, since the ratio of the intensities of *D* and *G* peaks are in the range of 0.81 to 0.86 for many samples. The obtained nanostructures are nanofibers (CNF) with an amorphous structure judging by the width and the shape of the peaks, which is consistent with the results of IR spectroscopy and X-ray analysis.

3.6. Investigation of CNs on EEW Cu NPs by TEM

Figure 11 shows the most interesting TEM images of synthesized CNs.

As seen in Fig. 11, the synthesized CNs do not have an internal channel and nanofibers are solid. Thus, TEM studies confirm the findings previously made on the basis of Raman spectroscopy, infrared spectroscopy and X-ray analysis.

4. Conclusion

The experiments demonstrated the possibility of using Cu NPs obtained by EEW as catalysts for synthesis of CNF. Stable growth of CNF was carried out at temperatures significantly lower than commonly used by thermal CVD on copper catalysts. The experiments have shown that the lower temperature limit for low-temperature synthesis of NPs and the separated copper powders is 250 °C and an optimum temperature range is 250–300 °C, the growth of CNF was observed over the entire pressure range of 100–400 mbar (in 100 mbar increments). CNF have different diameters (50–200 nm) and morphology (from spiral to straight). Copper clusters are located at the ends and inside of CNF. The results of X-ray analysis showed the presence of a halo at small values of the angle 2θ, which indicates the amorphous nature of the grown structures. Raman spectra of all studied samples are presented by two characteristic carbon (graphite) *D* and *G* peaks at 1347.5–1392.5 cm^{-1} and 1583.4–1602.3 cm^{-1}, respectively. All spectra show no groups that are responsible for long-range order. TEM studies have shown that CNF do not have an internal channel and nanofibers are solid.

The results obtained in the course of research have a high potential for the development of efficient, low-energy, low-cost technology for obtaining CNFs without the use of expensive gas and the ability to control the structure and properties of macroscopic parameters of CNFs. The synthesized CNFs do not have high crystallographic properties (degree of crystallinity, the geometric orientation, etc.) However, the use of such CNFs is

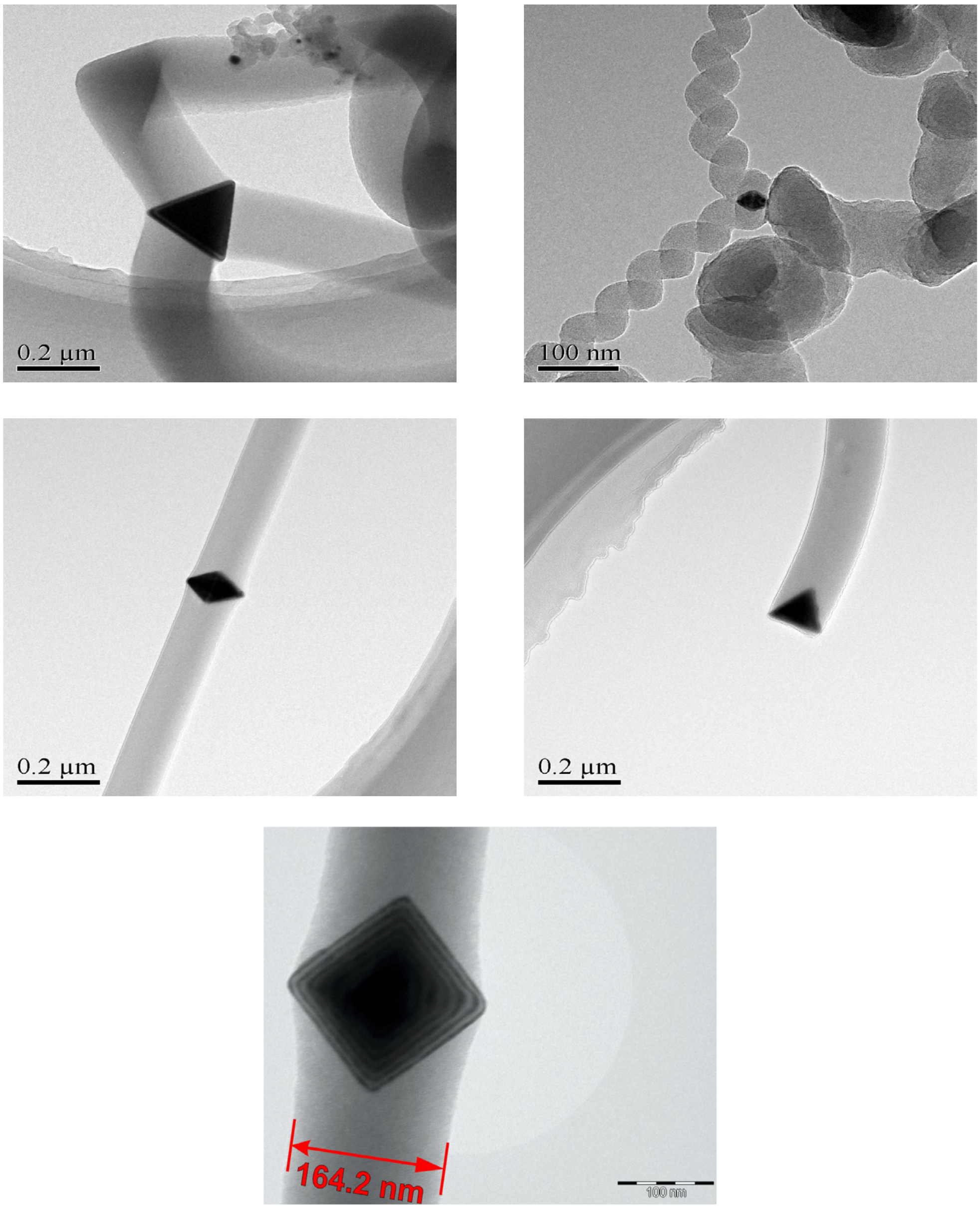

Fig. 11. TEM images of CNs synthesized on the separated Cu NPs.

promising in the fields of industry, which do not require structural perfection (such as reinforcing component in the concrete, polymers, plastics, ceramics and other materials; the basis for active sorbents; composite materials in the manufacture of medical prostheses).

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