
RAMAN SCATTERING STUDIES OF THE INFLUENCE OF THERMAL TREATMENT OF MULTI-WALLED CARBON NANOTUBES ON THEIR STRUCTURAL CHARACTERISTICS

I.B. YANCHUK, E.O. KOVAL'S'KA¹, A.V. BRICHKA¹, S.YA. BRICHKA¹

UDC 541.16
© 2009

O.O. Chuiko Institute of Surface Chemistry, Nat. Acad. of Sci. of Ukraine
(17, Gen. Naumov Str., Kyiv 03164, Ukraine; e-mail: evgeniya1209@ukr.net),

¹V.E. Lashkarev Institute of Semiconductor Physics, Nat. Acad. of Sci. of Ukraine
(45, Nauky Ave., Kyiv 03028, Ukraine)

The results of our researches concerning the Raman spectra of modified multi-walled carbon nanotubes (MWCNTs) are reported. The nanotubes were modified by sequentially treating them in nitric acid and burning them in an inert atmosphere of argon at a temperature of 500 or 1200 °C. Raman spectroscopy was used to determine the structural perfection of nanotubes and the degree of their graphitization. The method of temperature-controlled desorption together with mass-spectrometry was used to find the influence of oxygen-containing groups (defects) in MWCNTs on the Raman spectral characteristics of the latter. The results of our researches testify that the increase of the thermal treatment temperature gives rise to an enhancement of the graphitization degree of a nanotube structure.

1. Introduction

Nowadays, carbon nanotubes, both multi- and single-walled, continue to be of interest for a lot of researchers due to their extremely promising functional properties. These are their high mechanical strength and chemical stability, the submolecular dimensions of channels which are narrower than 0.5 nm, the electroconductivity which changes in a wide range, depending on the nanotube structure, high emission characteristics, the ability to form various functional groups on a surface, and the unique sorption properties which result from an extremely large value of the specific surface (up to 2600 m²/g).

Multi-walled nanotubes, in contrast to single-walled ones, are characterized by a wider variety of shapes and configurations. As the number of walls in multi-walled nanotubes increases, distortions of the perfect cylindrical shape become more and more pronounced. It is known [1] that the methods of molecular and atomic layering, as well as chemical deposition from a gas (vapor) phase, are effective for the fabrication of ordered graphite layers and materials on their basis with a wide range of properties. The method of chemical

deposition from vapors gives rise to less ordered and, hence, more chemically responsive MWCNTs [2]. The presence of defects and inhomogeneities in nanomaterials at a micron-size level governs the strength of products on their basis. Therefore, the development of a universal method for the identification of carbon materials and finding their structural features is extremely challenging. It is of special importance that the method used for the analysis were not destructive and would demand no special preparation of the specimen. We consider the Raman light scattering spectroscopy to be the most adequate method for this purpose. A capability to measure the Raman spectrum of every nanotube allowed such properties of carbon systems to be studied, which were not accessible before; in particular, these are the electron and phonon dispersions [3, 4].

In this paper, we report the results of our researches of MWCNTs produced by the method of chemical deposition from a gas phase making use of a catalyst, as well as their modified forms. Modification was carried out by increasing the burning temperature of specimens. The work aims at thoroughly studying both the parameters of spectral lines in the Raman spectra of modified carbon nanotubes and the nanotube structure, i.e. the specimen ordering degree. Simultaneously, we discuss the experimental data of IR spectroscopy and temperature-controlled desorption (TCD) with the monitoring of nanotubes by mass-spectrometry.

2. Experimental Part

Carbon nanotubes were synthesized using the method of catalytic pyrolysis of acetylene with Fe/MCM-41 as a catalyst [5, 6]. Iron acetylacetonate was deposited onto an MCM-41 surface during 30 min at a temperature of 150 °C. Then, acetylene was passed at a temperature of 700 °C for 40 min through a quartz reactor, the catalyst

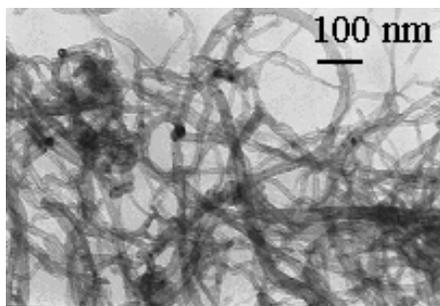
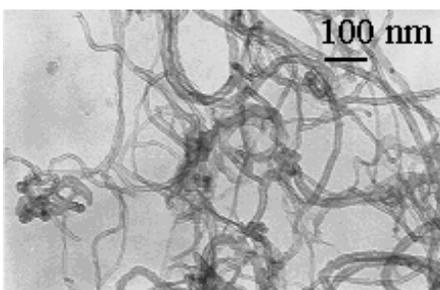
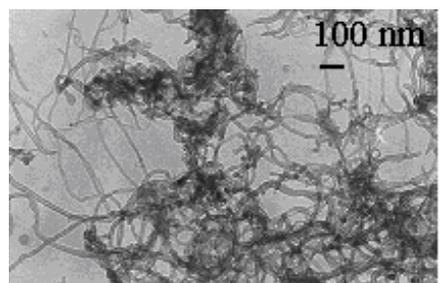
*a**b**c*

Fig. 1. Transmission electron micrographs of MWCNTs: initial (*a*) and burned in an inert atmosphere of argon for 1 h at 500 (*b*) and 1200 °C (*c*)

having been placed inside before. The synthesized carbon composite was treated with a 44% HF solution at room temperature to remove the silicious phase. To refine MWCNTs from other carbon phases, as well as from the catalyst, the specimens were treated in concentrated HNO₃ at 80 °C and burned at 580 °C for 0.5 h. Additionally, the nanotube specimens were subjected to ultrasound for 12 h in concentrated nitric acid. The fabricated nanotubes (MWCNT_{init}) were burned in an inert argon atmosphere at a temperature of

500 (MWCNT₅₀₀) or 1200 °C (MWCNT₁₂₀₀) for 1 h to study the influence of thermal treatment on the structural characteristics of nanotubes.

MWCNTs were identified by transmission electron microscopy (TEM) on a JEMOOCX-II microscope. The specific surface of specimens was measured by applying the chromatographic method to check the low-temperature desorption of argon [helium was used as a carrier gas (93.5%), and argon as an adsorbate gas (6.5%)]. Raman spectra were registered by means of a double monochromator with a photoelectronic multiplier operating in the photon counting mode. Specimens were excited by subjecting them to the radiation from an Ar⁺-laser with a wavelength of 488 nm. Reflection IR-spectra in the range 4000 – 400 cm⁻¹ were registered on a Nexus FTIR spectrometer equipped with a “Smart Collector” diffuse reflectance attachment. Before the spectrum registration, MWCNT specimens were mixed with calcined KBr in the 1:4 ratio. TCD with mass-spectrometry was used to study gaseous products that were emanated during the heating of synthesized specimens. The mass spectra were recorded with the help of the inlet system of a MX 7304A mass-spectrometer (the production association “Selmi”, Sumy, Ukraine) in the range 2 – 250 Dalton. The rate of temperature scanning was 0.17 °C/s.

3. Experimental Results and Discussion

In Fig. 1, the transmission electron micrographs of MWCNTs—as-synthesized (MWCNT_{init}, panel *a*) and burned at 500 (MWCNT₅₀₀, panel *b*) and 1200 °C (MWCNT₁₂₀₀, panel *c*)—are exhibited. Some nanotubes, as well as their groups and bunches, turned out twisted and bent. The growth of the treatment temperature did not affect the morphological features of nanotubes; therefore, there were probably no substantial variations in their structure at a macroscopic level.

Bent and not rectilinear shapes of nanotubes can be explained by their elasticity and the presence of defects. A good many of defect types are known [7], which appear in MWCNTs in the course of their synthesis or as a result of their following treatment. For instance, topological defects are stimulated by the elbow bends of graphene walls, because a certain number of pentagons and heptagons become incorporated into them, so that their cylindrical shape is distorted. Point defects can also emerge in nanotubes and affect their shape. Defects in the form of surface oxygen-containing functional groups, which are generated in the course of MWCNT refining

or when carbon and air oxygen get in contact, are considered as those forming a special group.

Specimens involved nanotubes with the external diameter ranging from 5 to 62 nm and the wall thickness ranging from 1 to 12 nm, which testified that the latter are multi-walled (Fig. 1). The thickness of nanotube walls corresponded to 3 to 34 graphene layers. In work [8], it was pointed out that MWCNTs synthesized following the catalytic pyrolysis method and making use of a Fe/MSM-41 catalyst had the external diameters of 10 to 30 nm. The MWCNTs synthesized by us were similar by their diameters to those obtained in work [8]. As the temperature of MWCNT treatment grew, a reduction of the specific surface of specimens from 592 to 273 m²/g was observed. This fact is associated with physical and chemical processes that run at elevated temperatures and brought about a reduction of the surface that was accessible for argon owing to the sintering and aggregation of specimen particles.

When modifying MWCNTs by nitric acid, we applied ultrasound irradiation, which improved the access of the reagent to the carbon surface and, hence, enhanced the amount of chemisorbed oxygen. Ultrasonic treatment allowed us to obtain crushed and shortened MWCNTs. The thermal treatment of MWCNTs also resulted in structural variations in nanotubes.

Raman spectroscopy allows all the forms of carbon to be studied: fullerenes, carbon nanotubes, amorphous carbon, polycrystalline carbon, etc. The positions, halfwidths, and relative intensities of spectral bands are governed by the nature of the chemical bonds of carbon.

In Fig. 2, the Raman spectra of MWCNT_{init}, MWCNT₅₀₀, and MWCNT₁₂₀₀ specimens are depicted. The appearance of the characteristic *G*-band evidences for the presence of valence vibrations of *sp*²-hybridized bonds, similarly to what occurs in graphite. The emergence of *D*-band testifies to the two-dimensional disordering in graphene layers of nanotubes and is an indicator of the bending of *sp*²-hybridized bonds of carbons. As a rule, the Raman spectra of MWCNTs reveal these two bands: one at about 1590 cm⁻¹ (*G*-band induced by the tangential *E*_{2g} mode of valence vibrations of *sp*²-hybridized bonds of carbons) and the other at about 1340 cm⁻¹ (*D*-band induced by a completely symmetric *A*_{1g} vibration of aromatic *sp*²-hybridized carbon rings). The Raman spectra of carbon nanotubes synthesized following the matrix method have two intense bands with the maxima at 1590 and 1302 cm⁻¹, which evidences for a larger number of defects and distortions in the graphene layers of MWCNTs. The known Raman spectral lines for disordered graphites are

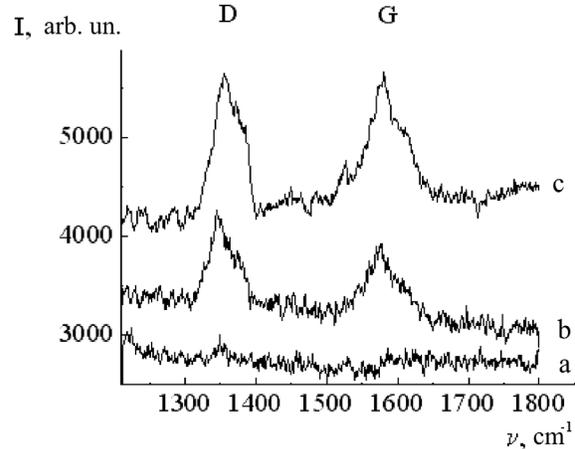


Fig. 2. Raman spectra of MWCNTs: initial (a) and burned in an inert atmosphere of argon for 1 h at 500 (b) and 1200 °C (c)

located in the ranges 1570 – 1585 and 1350 – 1300 cm⁻¹ [9].

No *G*-peak and a low-intensity *D*-peak were observed in the spectra of the initial carbon specimen (Fig. 2). This fact may be associated with a strong broadening of lines. The origin of such a behavior of MWCNT_{init} spectra can evidently be traced back to the conditions of specimen synthesis. The treatment of MWCNTs by ultrasound for a long time in the concentrated nitric acid environment induces considerable disorders of their structure. The MWCNT walls consist of graphene layers, similar to graphite, which form a closed surface. A large broadening of *G*- and *D*-bands, which are observed in MWCNT_{init} spectra, is associated with the dramatic disordering of graphene layers in MWCNTs, so that their Raman spectral manifestations are hardly appreciable.

The peak maxima in the Raman spectra of MWCNT₅₀₀ specimen (Fig. 2) were observed at 1573 cm⁻¹ for *G*-band and 1351 cm⁻¹ for *D*-band. *G*-band was asymmetric and had a shoulder at 1609 cm⁻¹ (it was *D'*-band, which we associated with the collective modes of MWCNTs, where the bonds C–C, C=C, C–O, and C=O are engaged). The maxima of MWCNT₁₂₀₀ peaks (Fig. 2,c) were located at 1573 cm⁻¹ for *G*-band and at 1360 cm⁻¹ for *D*-band (*D'*-band was at 1606 cm⁻¹). One can see that the positions of *G*-band maxima are identical in MWCNT₅₀₀ and MWCNT₁₂₀₀ spectra, whereas the positions of the *D*-band maxima differ considerably. A displacement of the *D*-maximum in the spectrum of MWCNT₁₂₀₀ specimen by 9 cm⁻¹ toward the high-frequency range evidences for a reconstruction of carbon bonds that are responsible for *A*_{1g} vibrations.

The integral ratio between the band intensities I_D/I_G allows the degree of ordering or graphitization of the carbon structure to be characterized [10]. In the spectra of highly crystalline graphite, D -band is absent, which indicates the 100%-degree of specimen graphitization. The ratio $I_D/I_G=1.12$ and 0.5 for the $\text{MWCNT}_{\text{init}}$ and MWCNT_{1200} spectra, respectively. Hence, the ratio of intensities for the MWCNT_{500} spectrum is 2.24 times that for the MWCNT_{1200} one, which testifies to a higher graphitization degree in the MWCNT_{1200} specimen in comparison with that in the MWCNT_{500} one. Hence, the number of defects in graphene layers decreases in the series $\text{MWCNT}_{\text{init}} > \text{MWCNT}_{500} > \text{MWCNT}_{1200}$. The band intensity ratio for MWCNTs synthesized following the matrix method ($I_D/I_G > 1$) is known to be close to similar spectral characteristics of amorphous carbon, whereas the intensity ratio for disordered graphites $I_D/I_G < 1$ [11]. Thus, the MWCNTs synthesized by us are quite similar by their optical properties to disordered types of carbon in sp^2 -hybridizations and, therefore, have similar structural elements.

According to theoretical calculations, the intensity ratio I_D/I_G is directly connected with the position of G -peak and with the ratio between sp^3 and sp^2 carbon atoms. Ferrari and Robertson proposed a model of "three-stage amorphization trajectory", which allows the Raman spectra of amorphous carbon films to be interpreted quantitatively [12]. Since MWCNTs have a graphite-like two-dimensional structure, as amorphous carbon does, their spectral characteristics can be interpreted in the framework of this model. For the MWCNT_{500} specimen, the ratio $I_D/I_G = 1.12$ testifies to the presence of sp^2 - and sp^3 -hybridized atoms of carbon. For the MWCNT_{1200} specimen, the ratio $I_D/I_G = 0.5$ evidences for the domination of sp^2 -hybridized carbon atoms. The described I_D/I_G ratios are related to the presence of sp^3 -carbon, which gives rise to the bending of sp^2 -carbon. They testify to the presence of surface functional groups, point-like and other defects [13]. Our experimental data did not confirm that the position of the G -peak maximum changed at different I_D/I_G -values (in particular, MWCNT_{500} and MWCNT_{1200} spectra had maxima at 1573 cm^{-1}).

The G -band halfwidth is also associated with a bending of carbon angular bonds [12]. This characteristic confirms the conclusion made above that the MWCNT_{1200} specimen with a G -band halfwidth of 40 cm^{-1} has the most ordered structure. The G -band halfwidth of the MWCNT_{500} specimen is 16 cm^{-1} larger than that of the MWCNT_{1200} specimen and testifies

to a higher disordering in the specimen structure. A substantial broadening of G -band (or its total absence) in $\text{MWCNT}_{\text{init}}$ specimens confirms the absence of a near-range order in graphene layers of nanotubes. Whence, it follows that the growth of the specimen burning temperature gives rise to a reconstruction of the carbon structure, the latter tending to a thermodynamically stable structure of ordered graphite.

By analyzing the positions of the characteristic band maxima and the values of integral intensity ratios I_D/I_G and taking the band halfwidths into account, a conclusion can be drawn that the MWCNT_{1200} specimen structure is mainly composed of sp^2 -hybridized and ordered carbon atoms. The MWCNT_{500} specimen structure is more disordered in comparison with that of the MWCNT_{1200} specimen. The structure of $\text{MWCNT}_{\text{init}}$ specimens is characterized by the largest amount of defects, which is the key factor for the wall structure of carbon nanotubes.

Using the TCD method and IR spectroscopy, we tried to study the defects induced by oxygen-containing functional groups in nanotubes and, simultaneously, to estimate the influence of such defects on MWCNT optical properties. The IR spectra obtained for our specimens gave little information, because nanotubes absorb IR radiation very much. Moreover, they are classed as badly polarizable structures, and this fact interferes with the excitation of irradiation spectra. The TCD method together with the monitoring by mass-spectrometry allows one to estimate the amount of chemisorbed oxygen and the types of functional groups on the carbon surface by analyzing the CO and CO₂ desorption spectra [14].

In Fig. 3,I, the TCD spectra of modified MWCNTs are depicted. The profiles of CO₂ emanation from the $\text{MWCNT}_{\text{init}}$ (a) and MWCNT_{500} (b) specimens have three high-temperature maxima each. Those maxima are associated with carboxylic and lactonic functional groups and with the anhydride of carboxylic acid. In the desorption spectra of specimens burned at $1200 \text{ }^\circ\text{C}$ (Fig. 3, I-c), the CO₂-signal was not observed, which is related to the destruction of the above-mentioned functional groups.

In Fig. 3,II, the emanation spectra of CO from carbon nanotubes are shown. In the $\text{MWCNT}_{\text{init}}$ case (Fig. 3, II-a), the gas desorption was observed in the range $330\text{--}850 \text{ }^\circ\text{C}$, and this desorption is associated with the destruction of carboxylic acid anhydride, phenolic, etheric, and ketonic functional groups and quinone. The start of CO emanation from the surface of the specimen burned at $500 \text{ }^\circ\text{C}$ (Fig. 3, II-b) was observed at $390 \text{ }^\circ\text{C}$,

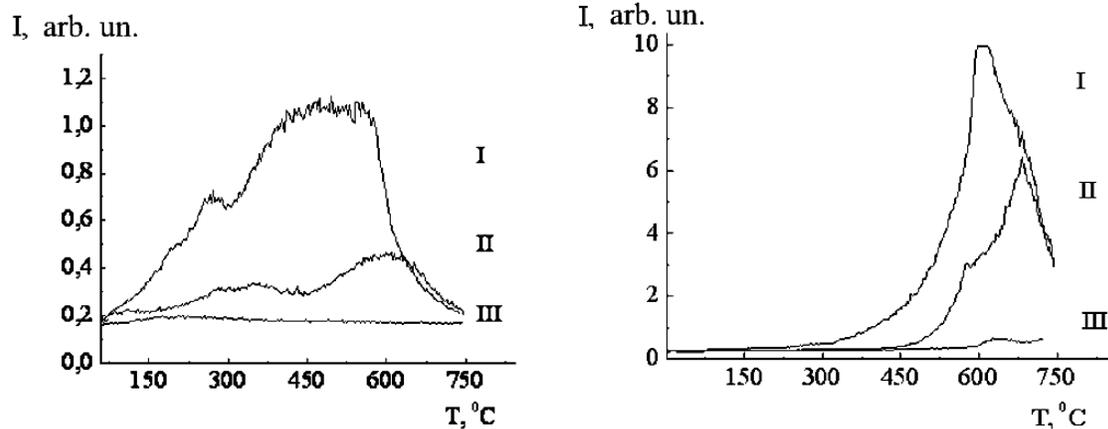


Fig. 3. TCD spectra of CO₂ (I) and CO (II) for various MWCNTs: initial (a) and burned in an inert atmosphere of argon for 1 h at 500 (b) and 1200 °C (c)

which is related to the partial destruction of functional groups of carboxylic acid anhydride. For the specimens burned at 1200 °C (Fig. 3, II-c), a low-intensity signal was observed, which testifies to the presence of a residual amount of chemisorbed oxygen on the carbon surface.

If the MWCNT treatment temperature grows, the relative intensity of *D*-band in the Raman spectrum with respect to that of *G*-band decreases, which correlates with the overall reduction of the amount of chemisorbed oxygen (defects) on the carbon surface. For the MWCNT₁₂₀₀ specimen, the intensity of *D*-band remains high even in the absence of oxygen on the surface. This fact testifies to a substantial number of structural defects in nanotubes which are not related to the presence of heteroatoms. It is probable that only some part of such defects becomes “healed” in the course of the specimen burning.

4. Conclusions

Our study of the parameters of Raman spectral lines of modified multi-walled carbon nanotubes shows that the growth of the treatment temperature increases the degree of graphitization of the nanotube structure, which is associated with the ordering of *sp*²-hybridized carbon atoms. Using the TCD method together with mass-spectrometry, we established that the oxygen-containing groups (defects) in MWCNTs affect their Raman spectral characteristics. The results obtained testify to a possibility to synthesize MWCNTs with various defect numbers, which directly influences the reaction ability of nanotubes.

1. I.P. Suzdalev, *Nanotechnology. Physics and Chemistry of Nanoclusters, Nanostructures, and Nanomaterials* (Komkniga, Moscow, 2005) (in Russian).
2. E.G. Rakov, *Russ. Khim. Zh.* **48**, 12 (2004).
3. M.S. Dresselhaus, F. Villalpando-Paez, Ge.G. Samsonidze, S.G. Chou, G. Dresselhaus, J. Jiang, R. Saito, A.G. Souza Filho, A. Jorio, M. Endo, and Y.-A. Kim, *Physica E* **37**, 81 (2007).
4. G.G. Samsonidze, R. Saito, N. Kobayashi, A. Gruneis, J. Jiang, A. Jorio, S.G. Chou, G. Dresselhaus, and M.S. Dresselhaus, *Appl. Phys. Lett.* **85**, 5703 (2004).
5. K.V. Katok, V.A. Tertykh, S.Ya. Brichka, and G.P. Prikhod'ko, *Mater. Chem. Phys.* **96**, 396 (2006).
6. K.V. Katok, V.A. Tertykh, S.Ya. Brichka, and G.P. Prikhod'ko, *J. Therm. Anal. Calorimetry* **86**, 109 (2006).
7. A.V. Eletsii, *Usp. Fiz. Nauk* **167**, 945 (1997).
8. O. Chen, R. Xu, and D. Yu, *Polymer* **47**, 7711 (2006).
9. A.V. Brichka, G.P. Prikhod'ko, S.Ya. Brichka, and A.A. Chui-ko, *Khim. Fiz. Tekhnol. Poverkhn.* **11**, 326 (2006).
10. Z.G. Huang, Z.P. Guo, A. Calka, D. Wexler, and H.K. Liu, *J. Alloys Compounds* **427**, 94 (2007).
11. S.S. Bukalov, L.A. Mikhailitsyn, Ya.V. Zubavichus, L.A. Leites, and Yu.N. Novikov, *Russ. Khim. Zh.* **50**, 83 (2006).
12. A.C. Ferrari and J. Robertson, *Phys. Rev. B* **61**, 14095 (2000).
13. W. Chen, T. Xiaoming, P. Xue, and X. Cheng, *Appl. Surf. Sci.* **252**, 1404 (2005).
14. S.Ya. Brichka, G.P. Prikhod'ko, A.V. Brichka, and Yu.A. Kislyi, *Neorg. Mater.* **40**, 1455 (2004).

Received 25.05.08.

Translated from Ukrainian by O.I. Voitenko

ДОСЛІДЖЕННЯ ВПЛИВУ ТЕРМІЧНОЇ ОБРОБКИ
БАГАТОШАРОВИХ ВУГЛЕЦЕВИХ НАНОТРУБОК
НА ЇХНІ СТРУКТУРНІ ХАРАКТЕРИСТИКИ
МЕТОДОМ КОМБІНАЦІЙНОГО
РОЗСІЯННЯ СВІТЛА

I.B. Янчук, Є.О. Ковальська, А.В. Бричка, С.Я. Бричка

Резюме

В роботі запропоновано результати досліджень модифікованих багатошарових вуглецевих нанотрубок методом комбіна-

ційного розсіяння світла. Нанотрубки модифікували обробкою азотною кислотою і подальшим прожарюванням в інертній атмосфері при температурах 500 і 1200 °С. Спектроскопією комбінаційного розсіяння світла встановлено структурну досконалість нанотрубок і ступінь графітизації зразків. Методом температурно-програмованої десорбції з мас-спектрометричним контролем встановлено вплив кисневмісних груп (дефектів) вуглецевих нанотрубок на їхні спектральні характеристики. Результати досліджень свідчать про збільшення ступеня графітизації структури нанотрубок із зростанням температури їх обробки.