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Perspectives of Single-Wall Carbon Nanotube Production in the Arc Discharge Process

A.V. Krestinin[1]*, N.A. Kiselev[2], A.V. Raevskii[1], A.G. Ryabenko[1],
D.N. Zakharov[2] and G.I. Zvereva[1]

[1]Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow Region, 142432, Russia,
[2]Institute of Crystallography RAS, Leninskii Prospekt 59, Moscow, 117333, Russia

Abstract

Single-wall carbon nanotubes (SWNTs) promise wide applications in many technical fields. As a result purified SWNT material is sold now on the West market at more than $1000 per 1 gram. Thus developing an effective technology for SWNTs production rises to a very important scientific problem. The perspectives of three existing methods providing raw material in the technology of SWNT production have been analyzed. They are i) pulsed laser evaporation of graphite/metal composites, ii) evaporation of graphite electrodes with metal content in the arc discharge process, and iii) catalytic decomposition of the mixture of CO and metal carbonyl catalyst precursor. The observed dynamics of SWNT market points to replacing the laser method of SWNTs production by the arc process. The conclusion has been made that the technology based on the arc process will be the major one for the fabrication of purified SWNTs at least for the next five years. A reliable estimation of a low price limit of SWNTs was derived from a comparison of two technologies based on the arc discharge process: the first one is the production of SWNTs and the second one is the production of a fullerene mixture $C_{60} + C_{70}$. The main conclusion was made that the price of purified SWNTs should always be more by 2-3 times the price of fullerene mixture. The parameters of a lab-scale technology for the production of purified SWNTs are listed. A large-scale application of the developed technology is expected to reduce the price of purified SWNTs by approximately ten times. The methods now employed for the characterization of products containing SWNTs are briefly observed. It is concluded that electron microscopy, thermogravimetric analysis, absorption and Raman spectroscopy, measurement of the specific surface aria, optical microscopy – each in separation is not enough for extensive characterization of a sample containing SWNTs, and all these methods should be used together.

Introduction

Single-wall carbon nanotube (SWNT) can be thought of as a single graphene sheet wrapped into a cylinder. They are nicknamed by R.Smalley as buckytubes as well. The great expectation for a wide use of SWNTs in high-technological fields is based just not only on the elegant structure of a buckytube. The special nature of carbon combines with the molecular perfection of buckytubes to endow them with exceptionally high material properties (Table 1).

Buckytubes are the stiffest, strongest, and toughest fiber known presently [1]. Experimentally measured breaking strength of a buckytube is about 30 GPa and the Youngth's modulus is more than 1.0 TPa [1]. Thermal conductivity of buckytubes along the tube axis is as high as 6600 W/m·K [2], that is higher than of diamond. This result was obtained by molecular dynamics simulations with a carbon potential, which proved its accuracy by the calculations of thermal conductivity values for graphite and diamond in good agreement with experimental data. The room-temperature conductivity of bulk samples of SWNTs is greater than 200 W/m·K [3]. It is comparable to a good metal and within an order of magnitude of that of highly crystalline graphite and diamond. They are the first polymeric molecules with truly metallic conductivity [4,5]. In addition, they can carry the highest current density of any known material, measured as high as 10^6 - 10^9 A/cm^2 [6,7]. Bulk material of purified SWNTs has microporous structure with high

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*corresponding author. E-mail: kresti@icp.ac.ru

Table 1
Physical properties of separate buckytubes and bulk material of purified SWNTs.

Separate buckytubes	
Young's modulus	1.0-1.4 TPa (cf.: 200 GPa for high-strength steel) [1]
Tensile strength	30-100 GPa (cf.:1-2 GPa for high-strength steel) [1]
Thermal conductivity along a nanotube	≈ 6600 W/m×K(at list twice that of diamond) [2]
Electrical resistivity:of metallic-type nanotubes	0.03 μOhm×cm at 300 K [4]
Electrical resistivity:of nanotube ropes	10^{-4} Ohm×cm at 300 K (the most conductive fibers known) [5]
The highest current density measured	10^{6}-10^{9} A/cm^{2} [6,7]
Bulk material of purified SWNTs	
Microporous structure	porous diameters in the range of nearly 0.9 - 2.0 nm (distribution of SWNTs on their diameters) and porous diameter of ≈0.31 nm (width of channels between nanotubes in their ropes)
Specific surface area	1300 m^{2}/g (closed nanotubes), above 2000 m^{2}/g (open nanotubes) [8]

specific surface area being more than 1300 m^2/g [8]. The actual observed material properties - strength, electrical conductivity, etc. are degraded in most materials very substantially by the occurrence of defects in their structure. Buckytubes, however, achieve values very close to their theoretical limits because of their perfection of structure.

The properties of buckytubes listed in Table 1 clarify why SWNTs promise wide applications in many technical fields. Among the applications where research work is now in full-swing one could highlight the following.

Field Emission Displays

Buckytubes are the best-known field emitters of any material. This is understandable due to their high electrical conductivity and the sharpness of their tip. The latter means that they emit at especially low voltages, an important fact for building electrical devices that utilize this feature [4].

New heat and electrically conductive plastics

Buckytubes are ideal to provide plastics with thermal and electrical conductivity, since they have the highest aspect ratio of any carbon fiber. Composites with buckytubes have been shown to dramatically increase the bulk thermal and electrical conductivity at small loadings [3].

Structural Composites

Stiffness, toughness, and strength of buckytubes lead to a wealth of applications exploiting them, including advanced composites requiring high values in one or more of these properties.

Energy Storage

Buckytubes have the intrinsic characteristics desired for materials used as electrodes in batteries and capacitors, two technologies of rapidly growing importance. Research has shown that buckytubes have the highest reversible capacity of any carbon material for use in lithium-ion batteries [9]. In addition, buckytubes are outstanding materials for supercapacitor electrodes [4,10].

Fuel Cell Components

Buckytubes have a number of properties including high surface area and thermal conductivity that make them useful as electrode catalyst supports in proton exchange membrane fuel cells [10].

Molecular Electronics

Their geometry, electrical conductivity, and ability to be precisely derivatized, make buckytubes the ideal candidates for the interconnects in molecular electronics. In addition, they have been demonstrated themselves as switches [11].

There is a wealth of other potential applications for buckytubes, such as solar collection, nanoporous filters, catalyst supports and coatings of all sorts [4,10]. There are almost certainly many unanticipated applications for this remarkable material that will come to light in the years ahead, and which may prove to be the most important and valuable of all. In the last five years, the demand on SWNTs has been growing more rapidly than their production. As a result, purified SWNTs with a content of the principal product of more than 95 weight % is now on the Western market at a price of $1400 per 1 gram [12] more than one hundred times higher than the price of gold. Thus, the development of an effective technology of SWNT production at a price much less than the existing one rose to a very important scientific problem.

To reliably evaluate the potentials of SWNT applications in different technical fields the following questions should be answered: “What is the most efficient way for the SWNT production nowadays and which prices of SWNTs can be expected in the nearest future?” Here, an attempt has been made to answer these questions. For this purpose the SWNT synthesis methods and their potentials for the large-scale production of nanotubes are characterized. Further, the efficiency of the arc discharge method for a SWNT production technology is evaluated, and the features of such a technology are described which was developed in the Institute of Problem of Chemical Physics RAS in cooperation with the Institute of Crystallography RAS. Finally, methods for the certification of SWNT samples are briefly described.

Methods of SWNT synthesis and their potentials in large-scale production of buckytubes

The technology of SWNT production is devided into two major steps: the first one – synthesis of raw material containing the buckytubes, and the second one – the purification of the as-prepared SWNTs from by-products. There are three methods, which produce a raw material containing SWNTs and each one of them may be used in a technology of high quality purified SWNT production. These methods are listed in Table 2 together with their advantages and disadvantages. They are i) the pulsed laser evaporation of graphite/metal composites, ii) the evaporation of graphite electrodes with a metal content in the arc discharge process, and iii) the catalytic decomposition of a mixture of CO and a metal carbonyl catalyst precursor (mostly $Fe(CO)_5$). The third process was recently developed by R. Smalley and co-workers and was nicknamed the HiPco process [4,13]. Condensed products produced by the different methods contain the main common fractions: buckytubes, catalytic particles, soot particles and carbon coating. The latter appears as a cover of nanoparticles including ropes or bundles of nanotubes and varies in its structure from disordered carbon layers (amorphous carbon) to graphitic shells. For illustration, a typical structure of raw material as synthesized in the arc discharge process is shown in Fig.1.

As supported by the experimental data, the formation mechanism of nanotubes is the same in the first two high-temperature processes and differs from the third low-temperature process of the CO disproportionation. As to the technological performance and the price of the final product just the HiPco process would suit best for production of raw material. In this case the process of purification would be particularly cheep and efficient. However it is not clarified so far whether buckytubes fabricated by the HiPco process would be structurally perfect at the same degree as nanotubes synthesized in one of the high-temperature processes. Some experimental data point to poorer mechanical properties of the bucky-

Table 2

Advantages and disadvantages of the processes for synthesis of raw material

Method of production	Advantages	Disadvantages
i) Pulsed laser ablation (high temperature process)	High content of SWNTs Structure of by-products is favorable for purification Structurally perfect nanotubes in the final product	Low efficient Periodical Expensive Does not suit for large-scale production
ii) Arc discharge (high temperature process)	Moderate efficient Not expensive Structurally perfect nanotubes in the final product Suits for large-scale production	Periodical Low content of SWNTs
iii) HiPco process (low temperature process)	Continuous High content of SWNTs Suits for large-scale production	Quality of final product is unclear The SWNT properties differ from those of high temperature processes

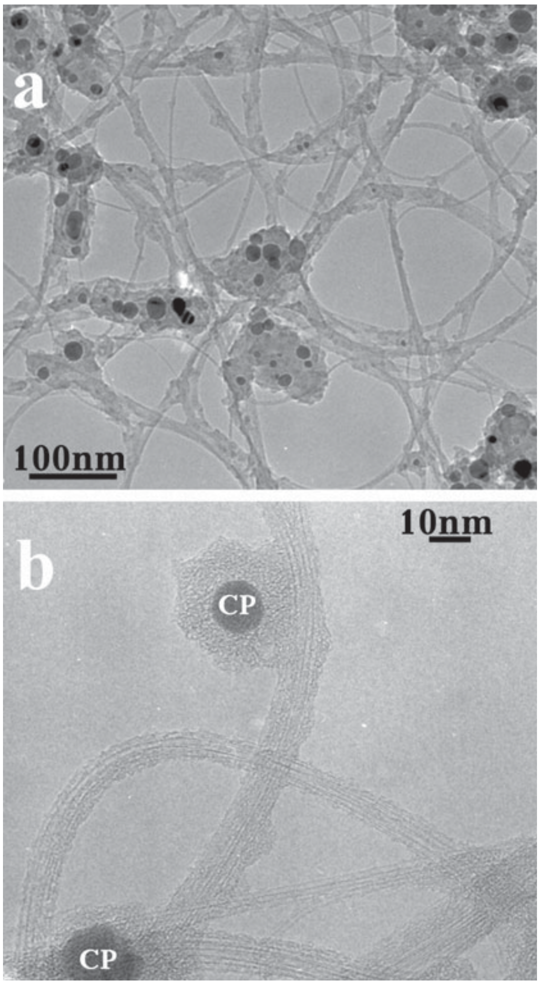

Fig. 1. HRTEM of raw material provided by the arc discharge process. a) Low magnification. Bundles of SWNTs, catalytic particles and carbon coating are shown. b) High resolution image of catalytic particles (CP) and nanotube bundles.

tubes fabricated by the low temperature process [10]. As concerned to high-temperature processes the laser ablation yields condensed products with a higher content of nanotubes (up to 40-60 weight % as producers claimed). In addition, the structure of by-products in this case is favorable for purification. Therefore, the purification of laser products is straightforward and provides a high level of recovery of SWNTs. It was the reason why purified SWNTs were prepared for the first time a few years ago by processing a condensed product of the pulsed laser evaporation process. The main shortages of the laser ablation process are its expensiveness and low efficiency. However the aforementioned advantages of this process made it to be the only way of production of purified SWNTs for the last few years. Now many improvements in technology of nanotube purification diminish the structural advantage of the laser ablation product as compared to the arc discharge product. The much highere efficiency of the arc discharge method has become of primary importance. To illustrate this conclusion the main producers of SWNTs known in the world market in 2001st year are listed in Table 3.

The dynamics of the SWNT market points to a replacement of the laser SWNT production method by the arc process. Almost the total volume of semiproducts in the world market being a material with a SWNT content in the range of 20-50 weight %, is made by the arc discharge nowadays. It is expected that the technology based on the arc process will be the major one for the fabrication of purified SWNTs at least for the nearest five years. It should be stressed that the production capacities of SWNT producers grow rapidly. For example, Nanoledge, a French firm, runs a reactor with the performance up to 150 g of raw material daily by the end of 2001. Since the arc process is becoming a main competitor for the production of raw material in the technology of large-scale production of SWNTs, the question of the low price limit for purified SWNTs fabricated by such a method arises.

Prices for SWNTs produced by the arc discharge method

As mentioned above, technology of SWNT production consists of two major steps: the first one – the synthesis of raw material containing buckytubes and the second one – the removal of metal and non-nanotube carbon from the sample. The following factors determine the cost of SWNT production: i) expenses of raw material fabrication; ii) expenses of raw material processing in the purification procedure; iii) percentage of SWNT recovery from raw material in the course of purification; iv) weight content of SWNTs in the final product. A reliable estimation of the low price limit of SWNTs could be obtained from the comparison of two technologies based on the same arc discharge process: the fist one is the production of SWNTs and the second one is the production of the fullerene mixture $C_{60} + C_{70}$. For this estimation, technological parameters are needed which characterize the arc process in both cases of SWNTs and fullerene synthesis. As for SWNT production the adopted values have been attained in our laboratory. In the case of fullerene production those values have been estimated based on the data pub-

Table 3

Production of SWNTs in the world in 2001 (based on the Internet data[a])

Producer	Supply of materials with SWNT content no more than 50 weight %, kg/year	Supply of materials with SWNT content more than 50 weight %, kg/year
Rice group (Smalley), USA (laser ablation process[b])	no data available	~ 1
Carbon Nanotechnologies Incorporated (HiPco process)	no data available	no data available
Carbolex, USA (arc discharge process)	< 1	does not offer
MER Corp., USA (arc discharge process)	6	~ 0.06
MER + Mistubishi, Japan (arc discharge process)	≈ 10	does not offer
Nanoledge, France (arc discharge process)	≈ 1	no data available
ILJIN Nanotech, Korea (arc discharge process)	< 1	no data available

[a] http://www.personal.rdg.ac.uk/~scsharip/tubes.html;
http://www.pa.msu.edu/cmp/csc/nanotube.html
http://www.scf.fundp.ac.be/~vmeunier/carbon.nanotube.html
http://www.mercorp.com

[b] The producer evaluates the SWNT content in the product at the level of 80 weight %, however the low specific surface area of the material (200-300 m^2/g) suggests that this value is much over-estimated.

lished by MER Corp., USA [4,12].

Price of raw material and its low limit

One of the main producers of fullerene mixture in the world market, MER Corp., sells the mixture of C_{60}+C_{70} at the price of $12.5 per 1 g (for orders more than 500 g, [12]). Neglecting the costs for fullerene extraction (they are small) and taken into account that the content of fullerenes in fullerene soot is about 7 weight % it follows that raw material for fullerene mixture production should cost $1 per g. (MER Corp. sells fullerene soot at the price of $2 per 1 g since the product contains beside fullerenes C_{60} and C_{70} higher fullerenes as well which may be extracted.) Thus, the price of raw material for SWNT production in the arc process might be taken as $1 per g. However, to have a more realistic estimation this value should be multiplied 2-3 times. There are two reasons why the price of raw material in the case of SWNT production should be always higher (in our estimation 2-3 times) than the price of fullerene soot. They are: a) additional costs for the purchase of catalysts and the preparation of graphite rods and b) lower efficiency of the arc process at optimized conditions in the case of SWNT production compared to fullerene production.

To back up these claims typical parameters of the arc process for the production of SWNTs and fullerenes are listed in Table 4. As one can see the yield of raw material per single run in case of fullerene synthesis is 50 times as high as in case of SWNT production. The foreseen considerations entail the following conclusion: the low price limit of as-produced SWNTs at the level of $2-3 per 1 g seems to be a good estimation for the nearest 3-5 years.

The low price limit of high quality SWNTs

The average content of SWNTs in the condensed product of the arc process reached nowadays does not exceed 20 weight%. This value corresponds to approximately 70-80 volume % of SWNTs what is usually notified by producers. It should be stressed that the convectional flow in an arc reactor separates in part the condensed product, thus at some sites of the reactor one could collect a few condensed product with a SWNT content being much higher than the average one, on the contrary, at the other sites it would be much less than this average value. In laser ablation products the content of SWNTs may be significantly higher. While precise data have not been published, it would be reasonable to estimate the upper limit of SWNTs in condensed product of laser ablation as 40 weight %. To reach this value nearly one half of evaporated material should be converted

Table 4

Efficiency of the arc discharge process (under optimized conditions) in fabrication of raw material for fullerene and SWNT production.

	Fullerene synthesis	SWNT synthesis
Anode diameter	80 mm	8 mm
Anode mass	> 1000 g	10 g
Yield of raw material per one run	100 g (after recounting to 20% of $C_{60} + C_{70}$ in raw material)	2 g
Content of net product in raw material (wt.%)	20%	20%
Yield of net product per one run	20 g	0.4 g
Recovered mass of net product per one run	≈ 20 g	0.12-0.14 g

into SWNTs! Such a high quality of raw material is unlikely to be synthesized in the arc discharge process in the nearest future. Thus, a yield of SWNTs in 20-25 weight % in the condensed product seems to be a good estimate for the arc process.

The technology of purification, which is developed in our laboratory, allows to increase the content of SWNTs after processing raw material up to 50-60 weight % simultaneously preserving not less than 40% of present SWNTs. Further improvements of the purification technology might increase the percentage of preserved net product at this first stage of purification procedure up to 50%. It would be a prominent result for the nearest future. It should be stressed that the loss of a large portion of SWNTs in the course of purification is inevitable, since there are no physical or chemical processes, which could purify raw material from amorphous carbon keeping SWNTs intact. Neglecting the cost of purification one could estimate the price of such a semi-product with 50-60 wt.% content of SWNTs at \$10-\$15 per 1 g. For the estimation it is reasonable to assume that the purification costs doubles the price increasing it up to \$20-\$30 per 1 g (Table 5). Further purification of SWNTs entails additional loss of nanotubes. Nevertheless our experience showed that the product with a content of SWNTs in 90-95 wt.% is obtained from semi-product of the first stage with a loss of less than 50% SWNTs. The final product corresponds to the best material offered in the market nowadays and has an estimated price at the level of \$60-\$90 per 1 g.

To summarize the considerations made above one could come to the following conclusion: the price of purified SWNTs with a content of principal product of no less than 90-95 wt.% should always be more than the price of the fullerene mixture of C_{60}+C_{70} multiplied 2-3 times. The following main reasons

Table 5

Prices in the market of SWNTs

Producer	Raw material, \$/g	Semi-product of purification containing 50-70 wt.% of SWNTs, \$/g	High purity product containing more than 90-95 wt.% of SWNTs, \$/g
Rice group (Smalley), USA (laser ablation)	no data available	no data available	> 1000
Carbolex, USA (arc discharge process)	50-100		does not offer
MER Corp., USA (arc discharge process)	40	700	1400
Carbon Nanotechnology Incorporated (HiPco process)	500	750	no data available
Estimation of the prices for the technology elaborated in IPCP RAS	4-5	40-50	120-150
The low limit of the prices (arc discharge process)	2-3	20-30	60-90

cause this fact:

a) an increased material expenses in the production of raw material compared to fullerene soot;
b) large-scale process of raw material production has not been optimized so far, which has been done for synthesis of fullerene soot;
c) it is not possible to achieve a selectivity of the SWNT synthesis in the arc discharge process essentially higher than the selectivity of fullerene synthesis in the same process;
d) it is impossible to exclude significant losses of SWNTs in the process of their purification from by-products, which has been done in the process of fullerene extraction.

Nowadays level of SWNT production technology based on the arc discharge process

The authors do not know any published data on the efficiency of existing processes of purified SWNT production. That knowledge seems to be regarded as knowhow. It is a reason why we list here only generalized data on the lab-scale technology, which is used in our laboratory for production of purified SWNTs. The technology is developed by the authors as a result of long-term studies of the mechanisms of fullerene and carbon nanotube formation [14-18]. The main features of the technology are the following:

- The yield of raw material in the arc process consists of more than 20% of graphite/metal composite evaporated; the raw material contains not less than 15-20 wt.% of SWNTs.
- The first stage of purification increases the content of SWNTs up to 50-60 weight % simultaneously preserving not less than 40-50% of SWNTs present in the raw material. The main impurities of this semi-product are soot particles and metal catalyst (less than 1 wt.%).
- The second stage of purification yields a final product with a SWNTs content more than 90-95 wt.% and with a recovering of SWNTs present in the raw material on the level of 30-40%.
- The purification procedure can operate without surfactant and includes easily scaled-up technological processes such as oxidation in gas flow under appropriate temperature and composition conditions, reflux in inorganic acids and so forth. In additional, before purification procedure raw material undergoes a special process of separation, which improves the effectiveness of purification.

Thus, the parameters characterized the efficiency of the developed technology are not far away from those which are characteristic for the process with upper limit of efficiency. Large-scale application of developed technology is expected to decrease the price for purified SWNTs down by approximately ten times (Table 4). High-resolution transmission electron microscopy (HRTEM) image of the purified final product with a content of SWNTs more than 90 wt.% is shown in Fig. 2. The specific surface area of the sample is about 1300 m^2/g.

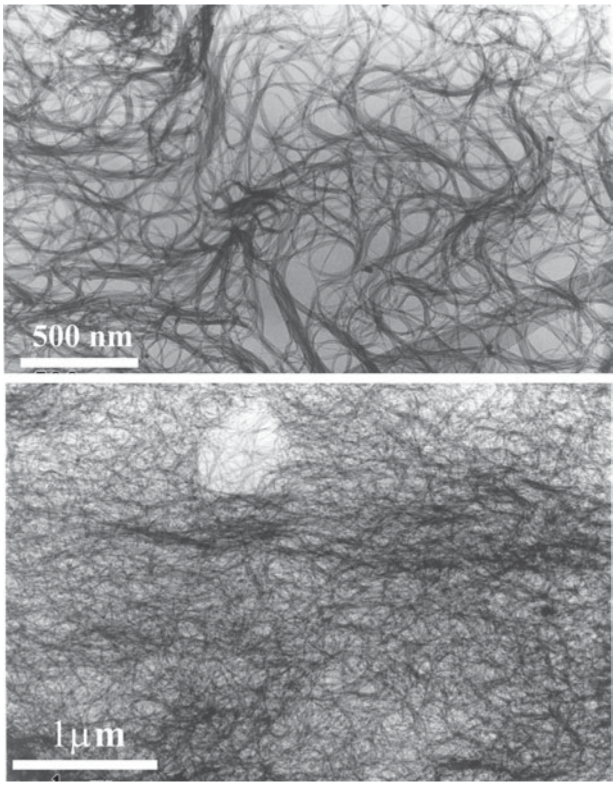

Fig. 2. TEM of a sample with more than 90 weight % of SWNTs.

Methods of SWNT product certification

Various features of a SWNT sample are of primary importance in different applications. Among those are the following: a) the percentage of SWNTs in the sample, type and structure of impurities; b) the ratio of nanotubes with open and closed ends; c) the diameter distribution of nanotubes; d) the size distribution in nanotube length; e) whether is the surface of nanotubes clean or has functional groups, surfactants; f) to what extend nanotubes do aggregate in ropes and bundles? Now existing method of SWNT characterization are not able to answer all these questions. Below the features of different methods for certification of SWNT samples are shortly describe.

Electron microscopy

Transmission electron microscopy is the only method, which provides detailed study of nanoparticle structure in dispersed materials. Together with analytical electron microscopy this method provides a unique information on the structure with atomic resolution and chemical composition of a nanoparticle at the same time. Under low magnification electron microscopy allows to estimate fractional composition of the material on the semi-quantitative basis. In spite of time-consuming and high price HRTEM remains irreplaceable in studying the mechanism of nanoparticles' formation and of their destruction in chemical processes. The method does not suit for quantitative characterization of bulk dispersed material.

Thermal gravimetric analysis

The first attempt to find out a quantitative and cheap method for measuring content of SWNTs in dispersed products was made by applying thermal gravimetric analysis. It was revealed by this technique, that the oxidation rate of a sample of high purity SWNTs achieved its maximum at the temperature about 735°C, and more than 98 wt.% was consumed in the temperature range of 550-850°C [19]. Since this results were obtained under processing raw material synthesized by a laser ablation method we undertook special studies to know whether thermal gravimetric analysis could be applied to certification of SWNT samples produced during processing raw material synthesized in the arc discharge process [17]. The data of thermal gravimetric analysis of a purified sample is shown in the Fig. 3. Curves 1 and 1' nearly exactly coincide with the corresponding data for SWNTs produced by the laser ablation method. More than 95% of sample's weight was consumed in the temperature range of 550-850°C. Thus one may suppose that impurities in the sample constitute less than 5 wt.%. Nevertheless electron microscopy revealed that the sample contains much more impurities. A part of non-nanotube material was separated by centrifugation. Thermal gravimetric analysis revealed that the oxidation of these carbon particles proceeds in the same way as purified SWNTs (cf. curves 1 and 1', 2 and 2' in Fig. 3). Thus in quantitative certification of SWNT samples by thermal gravimetric analysis one can easily obtain confusing results.

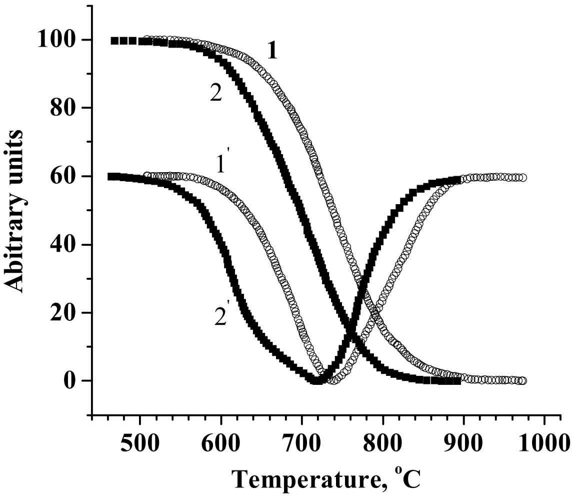

Fig. 3. Thermal gravimetric analysis of two SWNT samples. 1 and 2 are weight loss and 1', 2' are their derivatives. Minimum on the curve 1' is recorded at 740°C and the same one on the curve 2' is recorded at 725°C.

Raman scattering

It was discovered that the shift of Raman scattering in the range of ~100 ~250 cm^{-1} (so called radial breathing mode (RBM) of SWNTs) is determined by buckytube diameter. Spectra of three SWNT samples with different purity are shown as example in Fig. 4. The tube diameter can be estimated by using a simple relation $\omega_r = 224/d$, where ω_r is RBM Raman frequency (cm^{-1}) and d is the tube diameter (nm) [20]. This relation allowed on the basis of measurement of Raman scattering intensities to calculate the diameter distribution of SWNTs in the sample [21]. It is unclear so far what the accuracy of the method is. However this approach seems to be very promising for development of a simple procedure for characterization of SWNTs in their diameter distribution.

On the basis of Raman spectroscopy a new method of carbon nanotube purity estimation has been developed by E. Obraztsova and co-workers [22]. In this method the spectra of carbon soot containing different amounts of nanotubes are registered under heating from a probing laser beam with step-by-step increased power density. The rate of the material temperature rise versus the laser power density determines the slope of a corresponding graph and corre-

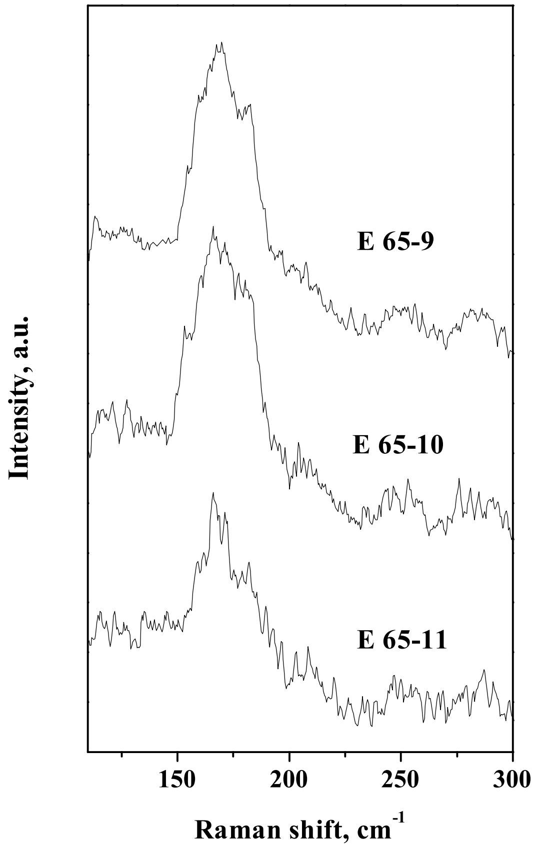

Fig. 4. Raman scattering measurements for SWNT samples of different purity.

lates strongly with the nanotube content in the soot. After calibration done by comparison of the Raman and the other data for the nanotube percentage in the same samples the method is able to provide a quantitative estimation of the sample's purity. It seems to be accurate in the intermediate range of nanotube contents between 10-20 wt.% and 80-90 wt.%.

Absorption spectroscopy

Theoretical works indicated that SWNTs have characteristic electronic structure due to a low dimensionality. Well-spaced and symmetric structures, called van Hove singularities, appear in the local density of states of nanotubes due to the one-dimensional nature of the conduction electron states in nanotubes [23]. UV-via-near-IR spectra of purified SWNTs are shown in Fig. 5 and provide evidence of this phenomenon. The peak centered at 1700 – 1800 nm is due to the first van Hove singularity in semiconducting nanotubes while the second van Hove singularity is seen centered at 900 – 1000 nm. A third set of peaks centered near 650 - 750 nm is assigned to the first van Hove transition of metallic SWNTs. The van Hove peaks are superimposed on a background that decreases smoothly from the ultraviolet to the near infrared.

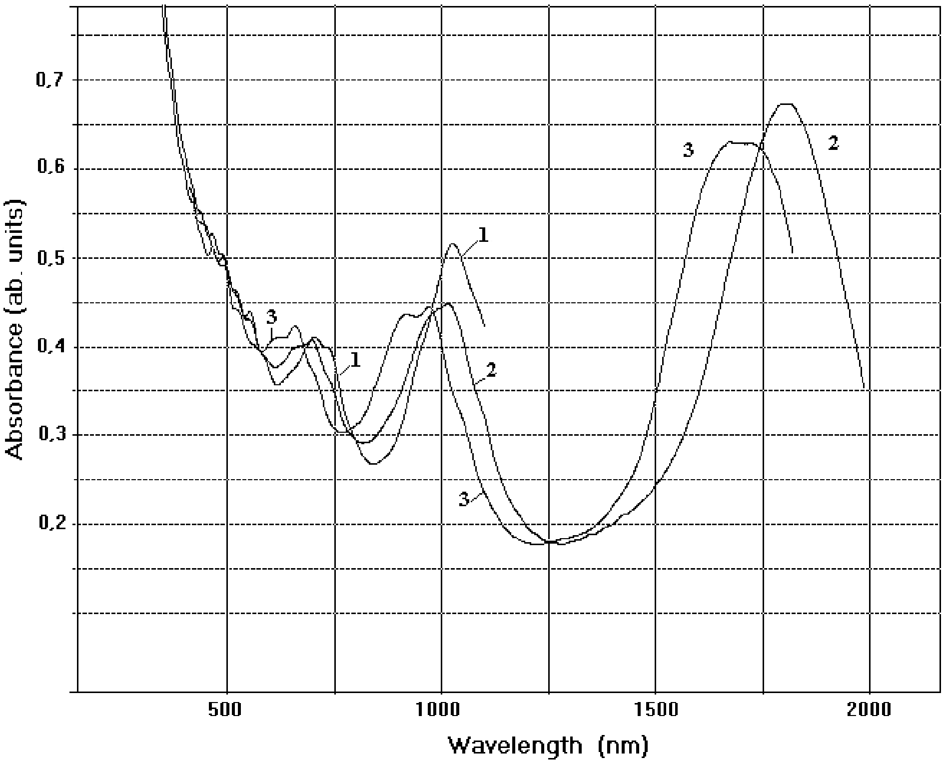

Fig. 5. UV-vis-near-IR spectra. 1- high quality purified SWNTs of IPCP-group, 2- a purified SWNT sample of MER Corp., 3 - as a reference a SWNT sample of Smalley-group. SWNTs in the samples differ in their diameter distribution.

The location of the van Hove peaks is a sensitive function of the SWNT diameter. Smaller diameter tubes exhibit van Hove transitions at shorter wavelengths. The observed peaks are due to overlapping van Hove transitions from all nanotube sizes that are present. The dependence of the band gap of semiconducting SWNTs on diameter has been measured and published in the literature [24]. Smalley and coworkers [25] believe that UV-vis-near-IR spectra could be a more reliable measure of SWNT diameter distribution in comparison to Raman scattering since the transition moments of van Hove singularities for different diameters are likely to be similar and only weakly dependent on tube diameters. If it took place the size of the peaks should well correlate with the percentage of SWNTs in a sample, therefore measurement of optical absorption could be an express-method for certification of SWNT samples. There are some obstacles on the way. First it was discovered that the intensities of van Hove transitions increased strongly after annealing of nanotubes in vacuum or inert atmosphere at 800-900°C. It means that absorbance values of nanotubes depend on some characteristics of their surface which are unknown so far. For instance, other studies have shown that the van Hove features are completely absent for partially alkylated SWNTs with retention of the continuum background [26]. Nevertheless absorption spectroscopy now is the most promising method for measurement of SWNT content in a sample on the quantitative basis. For illustration absorption spectra of three SWNT samples are shown in the Fig. 5. It is evident that nanotubes in the samples have different diameter distributions.

Specific surface area of SWNT samples

Specific surface area of a SWNT sample depends strongly on nanotube purity and for purified SWNTs amounts to ~ 1300 m^2/g. It was discovered, that specific surface area strongly depends on whether nanotubes are open or closed and for partially open nanotubes, even poor purified, it may be raised to the value of about 2000 m^2/g. Specific surface area depends as well on how clean the surface of nanotubes. For instance, application of surfactants in purification procedure decreases specific surface area of purified SWNTs down to ~600 m^2/g. These results will be published soon elsewhere [8].

Optical microscopy of SWNT samples

The presence of carbon nanotubes in dispersed products controls reological and optical properties of the sample and is easily revealed in the optical microscope. In Fig. 6 a mat of purified SWNTs in optical microscope is shown. Optical microscopy methods allow to determine the distribution of nanotubes in the sample and their quality (short or long), to locate sites with soot particles, to control effectiveness of purification procedure and on the qualitative basis to determine the degree of purity of final products. All these features make optical microscopy a cheep and rapid method for analysis of dispersed products with SWNTs in research laboratories and by customers. Application of optical microscopy to nanotube investigation is discussed in details elsewhere [27].

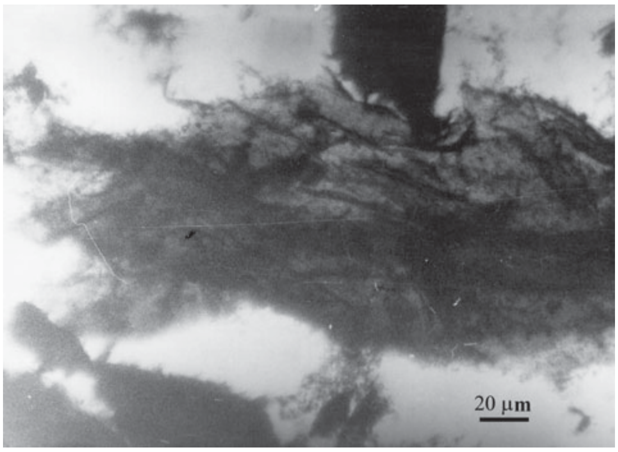

Fig. 6. A mat of purified SWNTs in the optical microscope.

Just recently a technique for measurement of the length distribution of SWNTs was developed and described as following [28]. First, a suspension of SWNTs containing mostly individuals and a few small bundles is produced by aggressive sonication of purified SWNT samples in surfactants such as Triton-X. Then the tubes from such a suspension are deposited on a silicon wafer coated with a self-assembled monolayer that has an amine termination [29]. And, finally, a direct measurement of the length distribution function of the suspended SWNTs one can easily performed by an atomic force microscope.

Conclusions

Technology of SWNTs' production on the basis of the arc discharge process is cheaper and productive in comparison with the laser ablation method. This technology seems to be the principal one for production of high quality purified SWNTs in the nearest future.

Even in the case of successful development of HiPco process for SWNT fabrication the arc technology retains a noticeable segment in the market as a productive method of high quality SWNTs.

Costs of SWNT technology on the basis of the arc method remains always higher by 2-3 times than the costs of fullerene mixture production in the arc process. Decreasing the costs of fullerene synthesis is surely to entail the progress and decrease of the costs of SWNT production.

Advance to large-scale level the developed technology of SWNT production should decrease prices of high quality SWNTs at least by 10 times and boost applications of SWNTs to the large extent.

No one alone of the existing certification methods of SWNT samples is able to provide exhaustive description of the sample's properties. All of the methods - HTEM, SEM, Raman scattering, UV-vis-near-IR spectroscopy, thermal gravimetric analysis, absorption measurements, optical microscopy should be applied together.

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References

1. Yu M.-F., Bradley S.F., Arepalli S., Ruoff R.S., Phys. Rev. Lett. 84 : 5552 (2000).
2. Berber S., Kwon Y.-K., Tomanek D., Phys. Rev. Lett. 84 : 4613 (2000).
3. Hone J, Llaguno M.C., Biercuk M.J., Johnson A.T., Batlogg B., Benes Z., Fischer J.E., Appl. Phys. A 74 : 339 (2002).
4. E.Osawa (ed.), Perspectives of fullerene nanotechnology, Kluwer Academic Publishers, Dordrecht, Boston, London, 2001.
5. Thess A., Lee R., Nikolaev P., Dai H., Petit P., Robert J., Xu C., Lee Y.H., Kim S.G., Rinzler A.G., Colbert D.T., Scuseria G.E., Tomanek D., Fischer J.E., Smalley R.E., Science 273 : 483 (1996).
6. Ebbesen T.W., Lezec H.J., Hiura H., Bennett J.W., Ghaemi H.F., Thio T., Nature, 382 : 54 (1996).
7. Wei B.Q., Vajtai R., and Ajayan P.M., Appl. Phys. Lett. 79 : 1172 (2001).
8. Our measurements using BET method and krypton adsorption. In preparation for publication.
9. Gao B., Bower C., Lorentzen J.D., Fleming L., Kleinhammes A., Tang X.P., McNeil L.E., Wu Y., Zhou O., Chem. Phys. Lett., 327 : 69 (2000).
10. Rakov E.G., Uspekhi Chimii, 70 : 44479 (2001).
11. Tans S.J., Verschueren A.R.M., and Dekker C., Nature (London) 393 : 49 (1998).
12. http://www.mercorp.com
13. Chiang I.W., Brinson B.E., Huang A.Y., Willis P.A., Bronikowski M.J., Margrave J.L., Smalley R.E., Hauge R.H., J. Phys. Chem. B 105 : 8297 (2001).
14. Krestinin A.V., Moravsky A.P., Chem. Phys. Lett. 286 : 479 (1998).
15. Krestinin A.V., Moravskii A.P., and Tesner P.A., Chem. Phys. Reports 17 : 1687 (1998).
16. Krestinin A.V., Moravskii A.P., Chem. Phys. Reports 18 : 515 (1999).
17. Zvereva G.I., Krestinin A.V., Muradyan V.E., Tarasov B.P., Fursikov P.V., Zakharov D.N., Fullerenes and fullerene-like structures, Belarussian University, Minsk, 2000, p.78.
18. Hutchison J.L., Kiselev N.A., Krinichnaya E.P., Krestinin A.V., Loutfy R.O., Morawsky A.P., Muradyan V.E., Obraztsova E.D., Sloan J., Terekhov S.V., Zakharov D.N., Carbon 39 : 761 (2001).
19. Dillon A. C., Gennett T., Jones K. M., Alleman J. L., Parilla P. A. and Heben M. J., Adv. Mater. 11 : 1354 (1999).
20. Bandow S., Asaka S., Saito Y., Rao A.M., Grigorian L., Richter E., Eklund P.C., Phys. Rev. Lett. 80 : 3779 (1998).
21. Takizawa M., Bandow S., Yudasaka M., Ando Y., Shimoyama H., Iijima S., Chem. Phys. Lett. 326 : 351 (2000).
22. Terekhov S.V., Obraztsova E.D., Lobach A.S., Konov V.I., Appl. Phys. A. 74 : 393 (2002).
23. Kim P., Odom T.W., Huang J., Lieber C.M., Phys. Rev. Lett. 82 : 1225 (1999).
24. Wildoeer J.W.G., Venema L.C., Rinzler A.G., Smalley R.E., Dekker C., Nature 391 : 59 (1998).
25. Chiang I.W., Brinson B.E., Smalley R.E., Margrave J.L., Hauge R.H., J. Phys. Chem. B 105 : 1157 (2001).
26. Boul P.J., Liu J., Mickelson E.T., Huffman C.B.,

Smalley R.E., Chem. Phys. Lett. 310 : 367 (1999).
27. In preparation for publication.
28. Walters D.A., Casavant M.J., Qin X.C., Huffman C.B., Boul P.J., Ericson L.M., Haroz E.H., O'Connell M.J., Smith K., Colbert D.T., Smalley R.E., Chem. Phys. Lett. 338 : 14 (2001).
29. Liu J., Casavant M.J., Cox M., Walters D.A., Boul P., Lu W., Rimberg A.J., Smith K.A., Colbert D.T., Smalley R.E., Chem Phys. Lett. 303 : 125 (1999).

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