INSTRUMENTS AND METHODS OF INVESTIGATION

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Equipment and techniques for carbon nanotube research

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Contents

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<u>Abstract.</u> Many nanotube applications, in particular those in nanoelectronic systems, require nanotubes with strictly defined electrophysical parameters. This paper reviews equipment and techniques for studying and measuring the most important of these parameters. Theoretical and experimental parameter values obtained from different techniques are compared. Ways of preparing nanotube-containing samples for investigation and measurement purposes are examined.

1. Introduction

Some scientists believe that our future can only be assured if we attain breakthrough progress in nanomaterials and nanotechnologies. Large-scale implementation of novel technologies, including nanotechnologies, in industrial production requires a high level of standardization that is impossible to achieve without priority development of research methods and measuring techniques for new materials [1, 2].

The development of methods for the study of nanomaterials, as well as techniques and facilities allowing precise determination of their structural and elecrophysical characteristics, is underway in many laboratories all over the world. Specifically, work on the fabrication and application of nanotubes is paralleled as before by experiments designed to obtain their detailed characteristics. Carbon nanotube (CNT) research and the creation of new CNT-containing materials constitute an important field of scientific activities, also covering issues of hardware support for measurements and the management and presentation of information. CNT

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Received 19 May 2009, revised 26 June 2009 Uspekhi Fizicheskikh Nauk **180** (3) 265–288 (2010) DOI: 10.3367/UFNr.0180.201003d.0265 Translated by Yu V Morozov; edited by A Radzig experiments, in turn, greatly contribute to the development of measuring instruments for the control of nanoscale objects [3].

However, the parameters of CNTs observed in experiment prove far less impressive than those predicted theoretically, due not only to the imperfection of their real structure but also to existing experimental difficulties. Indeed, it is not very easy to manufacture test specimens retaining intact nanotubes. Another problem is posed by the lack of adequate resolution in presenting the experimental results.

As is known, the unique properties of nanotubes are attributable to the fact that they have a very small diameter (less than 10 nm) and their structure is subject to quantum effects. Formally, the sphere of nanotube research encompasses objects of nanometer-scale dimensions (diameter, d; length, L; height, H), at least along one coordinate axis. In fact, however, the spectrum of objects of interest is much wider than that: from single-walled CNTs (d = 0.39; 0.7; 0.47; 1.36 nm and other values depending on the diameter of the tube-closing fullerene [4]) to multiwalled CNTs (d = 7.9 - 30 nm and even more) with one dimension (L) much greater than 10 µm [5]. Importantly, such objects contain a finite number of atoms, which accounts for the discrete atomic and molecular structure of their constituent matter and/or quantum character of their behavior.

Such systems are distinctive for one more fundamental property. Due to a variety of causes (both purely geometric and physical), the characteristic time of running various processes in these systems decreases with their size; in other words, their potential operation speed grows [6]. When considering any transfer process (current flow, heat conductivity, plastic deformation, etc.), one ascribes a certain effective mean free path $L_{\rm f}$ to the carriers and assumes that their scattering (or capture and death) for $L \ge L_{\rm f}$ occurs in the bulk and only weakly depends on the object's geometry. The situation changes dramatically for $L < L_{\rm f}$, when all transfer characteristics show strong dependence on the object's size.

Hence, the great applied and theoretical interest in CNT research arises first and foremost from the unusual structure

Thus, the main problem related to experimental CNT studies lies in the fact that the characteristic sizes of new materials are comparable with the atomic sizes, which implies the necessity to employ methods ensuring spatial superresolution, such as high-resolution transmission electron microscopy (TEM), scanning tunneling microscopy (STM), and atomic-force microscopy (AFM) with atomic resolution. Unfortunately, each of these methods is informative only in a limited range of nanotube diameters and fails to provide comprehensive information about the CNT material as a whole.

Therefore, nanotube-based electronic devices will be available only after the solution of technical problems, including reproducible fabrication of nanotubes with preset structural characteristics on a sufficient scale. It is clear that the first step toward this goal must be the development of reliable methods for control, identification, and characterization of nanotubes with the specified structural and electrophysical parameters.

2. Techniques for the study of CNT structure

To begin with, let us specify what is meant here by CNT structure. Each material has several interconnected structural levels that influence its properties. The first level relates to a crystalline one showing the mutual position of ions, atoms, or molecules in the crystal lattice. This level of substance organization is termed long-range order and characterizes ordering repeated over infinitely large distances. The short-range order characterizes ordering at distances commensurate with interatomic ones [7]. The notions of long- and short-range order are applicable to a condensed state of matter (liquid and solid aggregate states). The existence of long- and short-range orders ensues from interaction between particles. Particle disposition ordering is a coordination order. The next structural level is farther from the atomic state and relates to the presence of various linear and bulk defects in a solid [8].

New allotropic forms of carbon (carbon nanotubes and fullerenes) are collectively referred to as carbon carcass structures [9]. They are large (sometimes giant) molecules composed of carbon atoms alone. Their most characteristic feature is an unusual shape: they look like closed hollow shells. Formally, nanotubes can be described as giant linear fullerenes. The length-to-diameter ratio (aspect ratio) in CNTs ranges from 10 to 1000; therefore, they can be regarded as quasione-dimensional carbon carcass structures.

An ideal (defectless) single-walled CNT comprises a carbon strip shaped into a cylinder with the carbon atoms packed as in graphite. Such a one-atom-thick graphite layer is called graphene. Graphene is a layer of carbon atoms bound with sp²-bonds into a two-dimensional hexagonal crystal lattice [10].

However, many properties of nanotubes have nothing in common with those of graphite or fullerenes. Therefore, they can be viewed and studied as a self-contained material exhibiting unique physical and chemical properties [11, 12].

In fact, a nanotube has two separate surfaces with different physical and chemical characteristics. One (lateral or cylindrical) surface is the CNT proper, the other is its closed end shaped as half of a fullerene molecule.

A graphene sheet can be rolled up in different directions, either along a hexagon facet into an armchair tube ($\theta = 30^\circ$) or perpendicular to a facet into a zigzag tube ($\theta = 0^{\circ}$), and in all intermediate directions ($0^{\circ} < \theta < 30^{\circ}$). The tubes thus formed have different angles between the facet and the direction of the rolling, i.e., different chirality. The properties of CNTs depend on chirality, for example, armchair nanotubes conduct electric current like metals and are most stable. CNTs of other types are semiconductors with the width of the band gap dependent on chirality and diameter [13].

The diameter *d* of a nanotube is given by the size of the half-fullerene cap closing it. The first CNTs had a diameter around 1.36 nm that matched the size of the highly stable fullerene molecule C_{240} . CNTs 0.7, 0.47, and 0.39 nm in diameter are closed with stable symmetric fullerene molecules C_{60} , C_{36} , and C_{20} , respectively. Single-walled nanotubes (SWNTs) have a minimum and maximum diameter of 0.33 and 5 nm, respectively [14].

The length of a CNT is expressed in terms of the chiral vector $\mathbf{C}_{\rm h} = n\mathbf{a}_1 + m\mathbf{a}_2$ connecting two crystallographically equivalent sites on a two-dimensional graphene sheet (Fig. 1) [15, 16]. The uniqueness of the structure depicted in Fig. 1 is determined by a pair of integers (n, m) defining the chiral vector that, in turn, characterizes the two-dimensional structure of the CNT surface. Figure 1 shows the chiral angle between the chiral vector $\mathbf{C}_{\rm h}$ (labelled by OA in Fig. 1a) and the 'zigzag' direction ($\theta = 0^{\circ}$), as well as the angle between unit vectors \mathbf{a}_1 and \mathbf{a}_2 of the hexagonal lattice of the graphene sheet.

Figure 1 also displays the lattice vector **T** (labelled by OB in Fig. 1a) of a nanotube elementary cell, rotation angle Ψ , and translation τ , which characterize the main symmetry operation $R = (\Psi | \tau)$ for the CNT, i.e., helical turn through angle Ψ and translation vector shift τ along the tube axis. The diagram is constructed for (n,m) = (4,2). The number of different 'caps' that can be continuously attached to a nanotube is indicated under each pair of integers (n,m)(Fig. 1b). Large and small dots denote metallic and semiconducting nanotubes, respectively.

Multiwalled carbon nanotubes (MWNTs) demonstrate the greatest variety of structures, morphological parameters, and properties [17, 18]. An ideal MWNT has a Russian nesting doll structure and 'roll' type structure (Figs 2a and 2b, respectively). 'Papier-mache' type structures have also been found in real specimens (Fig. 2c) [19]. MWNTs usually have 10 or fewer layers, although some of them may have as many as tens of walls. Regardless of the structure, the layers in MWNTs are spaced approximately 0.34 nm apart, as in graphite, but in defective MWNTs the interlayer distance may reach 0.4-0.5 nm. A rise in the number of layers leads to the loss of ideal cylindrical shape. Sometimes, the outer shell assumes a polyhedral shape.

Thus, the diameter of a tube (tubes in MWNTs) and chirality (chiral index and/or chiral angle) may be considered the principal structural parameters of the two-dimensional cylindrical surface of CNTs. The perfection of the crystalline structure of graphene layers composed of carbon atoms that are located in nodal connections of hexagons is the main determinant of the quality (properties) of real CNTs, which, in turn, depends on many factors, of which the method of synthesis plays the central role [20, 21]. Consideration of other structural parameters characterizing CNTs is beyond the scope of the present review; the interested reader is referred to Refs [15, 16, 22].



Figure 1. Schematic of the formation of a CNT lateral surface as a result of rolling up a graphene layer into a tube in the direction given by the vector C_h and sewing the layer into a cylinder along lines OB and AB' (a). Lines OB and AB' are perpendicular to vector C_h at each end of C_h . Indices (n, 0) or (0, m) in notations (n, m) for $C_h = n\mathbf{a}_1 + m\mathbf{a}_2$ denote zigzag CNTs, and indices (n, n) relate to armchair CNTs. All other indices (n, m) refer to chiral CNTs (b). (Taken from Refs [15, 16].)



Figure 2. Models of multiwalled CNTs: (a) nesting doll; (b) roll, and (c) papier-mache.

2.1 Electron microscopy

The morphology and structure of such materials as CNTs can be visualized by a variety of methods. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are employed to study materials with atomic resolution. These methods provide qualitatively different information about the object being studied and are frequently used in combination. Reflection and emission electron microscopies, Auger and Lorentz electron microscopies, and other varieties are also realized as a rule with the help of adapters for conventional transmission and scanning electron microscopes [23–25]. Electron microscopy includes the preparation of the objects being studied, analysis and interpretation of results, besides observations proper.

In the scanning electron microscope, the electron beam compressed by magnetic lenses into a thin (1-10 nm) probe scans the object's surface forming a raster pattern of thousands of parallel lines [25]. Secondary radiation (secondary electron emission, Auger electron emission, etc.) generated by electron bombardment of the surface is recorded in detectors and converted into video signals which modulate the electron beam in the cathode-ray tube (CRT). Due to synchronous beam sweep in the SEM column and CRT, the image on the CRT screen displays intensity distribution of one of the secondary emissions over the object's surface being scanned.

The choice of secondary radiation to be recorded depends on the aim of the study. The main operating regime of the scanning electron microscope, i.e., detection of secondary electrons, ensures maximum resolution. It is exemplified by Fig. 3 showing an SEM image of a solid mass (array) of carbon nanotubes obtained by chemical vapor deposition (CVD) of hydrocarbons on porous anodic aluminium oxide [26].

Development of methods for computer-aided processing of SEM images allows determination of the morphological parameters of the sample surface with the help of software and apparatus complexes. One such a complex described in Ref. [27] consists of a Hitachi S-800 scanning electron microscope connected through an interface block to an





Figure 3. (a) SEM image of a cleavage in CNT-containing porous anodic aluminium oxide, and (b) magnified (\times 18891) image of the area enclosed by the oval.

IBM-compatible PC and STIMAN applied program package. This technique makes it possible to analyze the microstructure from a series of multiscale images covering the entire spectrum of changes in the size of structural elements present in the sample of interest. The analysis yields data on the size and shape of such structural elements, their orientation in space, and specific surface area; in addition, integral characteristics of the microstructure can be calculated. The special subprogram for statistical treatment permits constructing histograms showing the distribution of structural elements over different parameters, such as equivalent diameter, surface area and total surface area, perimeter, shape coefficient and some others. Three-dimensional reconstruction of the sample's surface microrelief is performed using the STEREKON software package developed for the purpose [28]. The three-step algorithm of 3D reconstruction includes (1) preliminary treatment, (2) searching for and matching identical points on both stereoimages, and (3) computation of volume coordinates for the points at the surface under study from parallaxes between the pair elements identified on the stereoimages.

Transmission electron microscopy is based on electron microscopes in which a thin-film object is subjected to a beam of accelerated electrons with an energy of 50-200 keV [24]. Both the resolution and the informative value of TEM images are largely determined by the characteristics of the object under study and the mode of its preparation. In most cases, very thin (0.01 μ m or thinner) slices of the specimen are used, and the contrast of their images is enhanced by chemically treating the slice with heavy metal compounds (chemical contrast).

An ultramicrotome equipped with a glass or diamond knife is used to cut extremely thin slices (10-100 nm) of samples from epoxide-embedded CNT solid masses put through a special treatment beforehand.

For the purpose of TEM studies, CNT specimens are usually positioned in the focal plane of the electron beam and are normal to its axis. Such experiments provide information on the longitudinal, but not transverse, structure of tubes.

Results of structural studies of MWNTs are especially difficult to interpret due to the difficulty of obtaining electron microscope images of their end slices and the variability of interpreting the images of lateral sections. As mentioned in a preceding paragraph, MWNTs are represented by two structural variants. One is a multilayered nanotube consisting of several single-walled nanotubes nested into one another as in a Russian nesting doll, and the other implies that each MWNT is a rolled graphene sheet.

The validity of the former (nesting doll) model with cylindrically shaped layers is confirmed by electron microscope images (micrographs) showing MWNT ends capped by half-fullerenes; moreover, most images of MWNT lateral sections exhibit an equal number of graphene layers on either side of the nanotube axis (Fig. 4).

On the other hand, the possibility of MWNT intercalation observed in experiment provides evidence in favor of the rolled structure of nanotubes [29].

It was proposed to orient the nanotubes parallel to the direction of electron beam propagation [30]. This goal can be achieved by a special method of sample preparation in which a CNT bundle seen in a usual light microscope with moderate magnification is introduced using pincers into an epoxide material; this procedure over, the ends of the tubes are cut off with a diamond knife.



Figure 4. Multiwalled CNT: (a) model, and (b) electron microscope image.

Detailed analysis of TEM images of CNT cross sections thus obtained by performing a Fourier transform shows that only a very small number of CNTs are consistent with the traditional model of a nanotube as a seamless rolled graphite sheet. More typical is a structure formed by a few isolated graphite layers making up a papier-mache-like multilayer concentric structure. High-resolution TEM images show cylindrical structures with five (Fig. 5a), two (Fig. 5b), and seven (Fig. 5c) concentric walls [31].

High-resolution TEM makes it possible to estimate the diameters of individual SWNTs or their bundles and to determine whether they are empty or filled, or single or nested inside one another. It turned out that the experimentally examined structure of single-walled CNTs is in many respects different from the idealized picture (Fig. 6) [32]. Their cylindrical shape and tips are the first to be affected, which



Figure 5. First electron microscope images of multiwalled coaxial CNTs with different inner and outer diameters, obtained in Ref. [31].



Figure 6. TEM images of MWNTs synthesized by the CVD technique: (a) low-quality tube obtained at $450 \,^{\circ}$ C; (b) high-quality tube obtained at a temperature above $850 \,^{\circ}$ C, and (c) a tube with the tip encapsulated by a catalyst particle [32].

makes the tubes very much unlike ideal geometric figures [33, 34].

Moreover, a group of researchers including S Iijima, a pioneer in nanotube science, managed to observe and elucidate the nature of surface defects in single-walled CNTs [35]. The authors developed a special method based on the optical Fourier transformation of TEM images that enabled them to determine not only the diameters but also the chiral indices of CNTs and reveal changes in these parameters associated with the appearance of surface defects. It was shown that a surface defect in single-walled CNTs, caused by the action of an electron beam, changes the chiral indices from (17, 0), as in a semiconducting nanotube, to (18, 0) corresponding to metallic conductance. A composite CNT thus obtained exhibits properties of a nanodiode and may be used as a basic element for making superminiature integrated circuits.

As mentioned above, the structural features of MWNTs are much more difficult to study because they contain internal elements inaccessible to direct observation. TEM using an electron beam with a nanometer-sized cross section appears to be the best technique for this purpose. Researchers at the University of North Carolina, USA used an 80-keV beam ensuring a resolution as high as 0.34 nm and obtained diffraction images of a four-layered CNT with an inner diameter of 2.6 nm and an outer diameter of 5.0 nm (Fig. 7). Analysis of these TEM images gave chiral indices of all four nanotubes as (32, 1), (26, 24), (39, 25), and (64, 2). In contrast to the generally accepted concept that postulates an invariably constant interlayer distance in MWNTs (close to 0.34 nm), these authors observed its variation from 0.36 nm to 0.5 nm for the inner and outer layers, respectively, and offered an explanation for these changes [36].

The first transmission electron microscope with a computerized analyzer of elemental composition based on energy loss spectrometer was created in the 1980s. Electron energy loss spectrometry (EELS) is a well-known technique used for microanalysis in the scanning transmission mode [37]. The spectrometric system of two magnetic prisms and an electrostatic mirror placed between two intermediate lenses (rather than under the screen and the photographic camera, as usual) made it possible to flexibly control TEM image contrast, obtain aberration-free images of thick (up to 1 μ m) slices, and, as the main thing, selectively visualize elements in the range from B to U with a resolution on the order of 0.5 nm



Figure 7. (a) TEM image of a four-walled CNT with an inner diameter of 2.6 nm and an outer diameter of 5.0 nm; (b) electron-diffraction image of the same nanotube; (c) magnified image of the area enclosed by the quadrangle in Fig. 7b; (d) cross section of a four-walled CNT with different intertube distances, and (e) horizontal projection of the atomic structure of a four-walled CNT with chiral indices (32, 1), (26, 24), (39, 25), and (64, 02). All the walls exhibit semiconducting conductance. (Taken from Ref. [36].)

and a sensitivity of up to 10^{-20} g of the element. Taken together, these characteristics account for the advantage of electron microscopy over traditional X-ray spectral analysis used to study films and slices.

Diagnostics of CNT structure is possible with the aid of TEM in the electron diffraction mode that produces diffraction patterns (electronograms) giving an idea of the crystalline structure of the objects studied and permitting accurately measuring parameters of the crystal lattice [38].

The electron diffraction method was applied in Ref. [39] to study the structure of CNT bundles synthesized by CVD with the use of catalyst and based on the thermal decomposition of carbon-containing gases at the surface of a metallic catalyst at 500–1000 °C. Results of these experiments were considered in the framework of the kinematic theory of diffraction. Surprisingly, it was found that certain CNT bundles consisted of two-walled nanotubes, in contrast to an earlier work [40] where single-walled CNTs were described and bundles assumed to be twisted into a spiral comprising only two turns. The concept of two-walled CNT bundles better agrees with experimental findings. The authors made a detailed analysis of electron diffraction from small-sized CNT bundles in the form of a double spiral and showed that electrons are most likely scattered by bundles of two-walled CNTs.

High-resolution electron microscopy was developing rather slowly. Instruments dating to the 1950s had a resolving power of $\sim 2 \text{ nm}$ that was increased only to ~ 0.3 nm by the 1970s. The advent of 300-400-kV microscopes opened up an opportunity for further improvement of their resolving power which reached < 0.2 nm by the 1980s, and ≤ 0.15 nm in the 1990s. In the 1970s, microscopes became available in which electrons could be focused on a small area of the sample surface. They were used for a variety of purposes, viz. taking micrographs, diffraction experiments, radiographic analysis by energy dispersion spectrometry, and EELS with energy dispersion spectrometers. Scanning transmission electron microscopes created at that time for specialized investigations have been substantially improved in the last two decades. Enhanced image sharpness has been achieved by utilizing probes 0.1 nm in diameter and electron guns also used in high-resolution TEM. Trapping a signal in the high-angle ring aperture makes it possible to obtain images of crystalline structures by the Z-contrast (atomic number contrast) method; in many cases, it opens up possibilities for direct interpretation of the images. Monochromators for minimization of energy dispersion in the incident electron beam produce EELS spectra with an energy resolution of 0.15 eV [41].

2.2 Scanning probe microscopy (SPM)

The scanning tunneling microscope (STM) invented by G Binnig and H Rohrer in 1982 became another powerful tool in nanotechnology. Tens of modifications of SPMs are currently in use [43].

These methods (as evident from the name) have much in common in that they utilize a probe (usually a sharp needle with a tip radius of ~ 10 nm) and a scanning mechanism moving the probe over the sample, surface in three dimensions. Motor-driven three-coordinate stages serve for rough positioning of the sample, while precision scanning is performed by three-coordinate piezoactuators that move the needle or the sample tens of micrometers in directions *x* and *y* and several micrometers along the *z*-axis to within fractions of an angström [44].

All known methods of SPM can be arbitrary categorized as follows. $^{\rm l}$

Scanning tunneling microscopy: low voltage ($\sim 0.01 - 10$ V) is applied across the conducting tip and the sample and tunneling current depending on the properties and position of atoms on the object's surface is measured in the gap. STM can be used not only to measure the diameter and length of an element but also to obtain data on the helicity (angle of twist) of each nanotube, its deformation, and the mutual position of the tubes in a bundle. The maximum spatial resolving power of STM devices is one hundredth of a nanometer along the perpendicular to the sample surface. Microscope operation depends on electron tunneling through the vacuum barrier. A change by a factor of 1000 in the tunneling current with a change in the barrier width commensurate with the atomic size ensures high resolving power of the method.

Atomic force microscopy: it makes use of changes in the force with which the needle is attracted to the sample surface at its different points. The needle is attached to the end of a cantilever having a given stiffness and capable of bending under the action of weak van der Waals forces arising between the sample surface and the tip of the needle. Deformation of the cantilever is measured from the deflection of the laser beam incident on its rear surface or from the piezoresistive effect occurred in the cantilever itself upon its bending.

Near-field optical microscopy: here, the probe is a light waveguide (optical fiber) narrowing toward the end facing the object to a diameter smaller that the light wavelength. Due to this, the light wave does not emerge from the waveguide too far but only slightly protrudes from its end. A laser and a detector of radiation reflected from the free end of the waveguide are mounted on its opposite end. Both the phase and the amplitude of the reflected light change when the distance between the sample surface and the tip of the probe is small; this change gives rise to a signal used to construct a three-dimensional image of the surface.

Atomic resolution is achieved in the most advanced modifications of tunneling and atomic force microscopes. The size and the cost of scanning probe microscopes are much less than the same characteristics of conventional electron microscopes, while the former have greater potentialities. They can be operated at room, elevated, or cryogenic temperatures, in the air, in a vacuum or in liquids, in strong magnetic and electric fields, under microwave and optical radiation, etc. Probe techniques are suitable for investigating a variety of materials (conducting, dielectric, biological, etc.) without their preliminary time-consuming preparation. They can be used for local determining atomic configurations and the magnetic, electric, thermal, chemical and some other properties of various surfaces [46].

Besides its value as a research technique, scanning tunneling microscopy may also be helpful in such procedures as atom capturing and relocating, assembling of one-atomwide conductors, running of local chemical reactions, and the manipulation of isolated molecules [47].

The resolving power of conventional electron microscopes is too low to directly discriminate between nanotubes with different chiralities. Therefore, measurement of CNT diameter is the main method for the determination of the chirality. A high-resolution atomic image of the nanotube is indispensable for reliable measurement of the chiral angle. Remarkable progress in measuring nanotube chiral indices was achieved by virtue of tunneling electron microscopy. It measures the angle between the nanotube axis and the most densely packed atomic rows. Graphite scanning in the tunneling regime has some peculiarities that should be taken into account; namely, the surface structure is represented only by half of the atoms with overlapping orbitals in the second sublayer [48]. This sublayer effect is unavoidable in MWNTs. Also, an error can be introduced by the cylindrical shape of nanotubes because the result of the scanning with the needle in the constant current regime represents a convolution of the probe and tube surfaces.

In Ref. [49], the chirality of MWNTs was determined with a modified Solver-P47H scanning probe microscope (Zelenograd, Russia) operated in the air at room temperature. Its changeable STM head with a hard scanner (maximum scanning range of 12 µm) was mounted on a vibroprotective block equipped with a suspension system. The needle for STM was mechanically cut from a platinum-iridium wire. The acoustic protection system was additionally improved to reduce vibrations of the probe and the substrate during scanning. Components were divided into smaller fractions by sonication-driven dispersion in a dimethyl alcohol solution. After that, the mixture was washed in nitric acid and annealed at 800 °C for a few minutes to decrease the concentration of unstable nanostructured admixtures, such as C-C complexes, graphite planes, and amorphous carbon. Nevertheless, the resulting mixture retained large fractions that had to be removed during sample preparation for the study. The nanotube-enriched mixture was spread over a fresh crack (the fact essential for nanotube adhesion) in a pyrolytic graphite substrate. Large fragments were removed from the substrate using an air gun.

STM measurements were made at a constant current with minimal feedback amplification to simulate the flying needle regime. The voltage applied between the needle and the substrate varied from 20 to100 mV, and the current for different measurements was in the range of 40-200 pA.

Figure 8 presents the results of examinations of several CNT surfaces for which the chiral angle and the number of atoms visible in the cross section normal to the nanotube axis were calculated; also, tube width and height were measured. These data are included in Table 1.

As shown in Fig. 8a, b, the chirality of small-diameter nanotubes is close to zero within the possible accuracy of measurements. It should be emphasized that the hexagonal structure composed of 6 atoms is well apparent in Fig. 8a, whereas CNTs in Fig. 8b have a triangular structure contain-

¹ See Golovin Yu I *Nanotekhnologii: Nanotekhnologicheskaya Revolyutsiya Startovala* (Nanotechnologies: The Nanotechnological Revolution Has Started): www.abitura.com/modern_physics/nano/nano2.html.



Figure 8. (a) STM images of CNTs with atomic resolution. The chiral angle between hexagon rows and the tube axis is shown for each CNT; (b) two nanotubes with a small chiral angle; (c) CNT with a large chiral angle. (Taken from Ref. [49].)

 Table 1. Results of measurements of CNT parameters using scanning probe microscopy [49].

Type of CNT	θ , degrees	Number of visible atoms	Width, nm	Height, nm	Diameter of a free CNT *	Diameter of a free CNT**	
a b c	1.5 2.0 32.1	8 4 13	2.5 1.8 7.0	0.43 0.22 1.30	1.04 0.62 3.0	1.36 0.63 3.17	
* Elliptical cross section of a tube on the substrate. ** Atom counting.							

ing only half of the real surface-forming atoms. An effect related to the emergence and disappearance of the second atomic sublayer in the surface topography is also apparent during the scanning of the flat surface of pyrolytic graphite upon variation of the scanning parameters, such as voltage and current. These parameters determine the distance between the substrate surface and the tip of the probe; in the end, they determine the cross section distribution of current density of tunneling electrons in the gap and the form of the resulting image. Naturally, the electric properties of CNTs, namely metallic or semiconducting conductance, enhance this effect. Nanotubes of greater diameter (Fig. 8c) may have several layers in their structure, and the large chiral angle (32.1°) does not introduce an appreciable perturbation in the image of the hexagonal structure of their surfaces.

Table 1 shows values obtained by direct measurement of the width and height of the visible part of a CNT, taking account of the correction for image broadening resulting from the cylindrical shape of the nanotube. This shape is responsible for the changes in the direction of the tunneling current density vector, leading to an increase in the image diameter. Moreover, a nanotube acted upon by van der Waals forces from the substrate cannot retain its cylindrical shape and acquires an oval cross section [50].

Measurements of the tube height confirm this inference. Forces acting from the probe can flatten nanotubes. Tube flexure may come into play especially in experiments performed under atmospheric conditions (the so-called selfcompressed tunneling regime).

It is believed that the distortion is insignificant and deviates by fractions of percent from the graphite lattice constant, implying the possibility of calculating the CNT diameter from the number of atoms arranged on the circumference for a nonchiral nanotube and those aligned along the quasicircular trajectory in the case of a chiral CNT. In the latter case, the result obtained needs to be projected on the normal to the tube axis. The acceptable error amounts to 1-2 atoms located at lateral surfaces. It is equally possible to estimate the CNT diameter on the assumption that the nanotube cross section at the surface is close to elliptical. Diameters of free CNTs calculated by the two methods are presented in Table 1. It can be seen that experimental widthto-height ratios vary from 8.2 for the narrowest tube to 5.4 for the widest one. The ratio of the theoretical diameter of a free CNT to its experimentally found height on a substrate varies from 3.2 to 2.3.

Thus, the authors of Ref. [49] first achieved atomic-scale resolution of the CNT surface in the air and analyzed the factors responsible for image distortion. They used the experimental data to calculate the chiral angle and the diameter of free CNTs.

Reference [51] reports the results of determining chirality of individual SWNTs at T = 4 K using an STM. The authors prepared CNTs by pulsed laser-beam irradiation of the graphite surface in the presence of a metallic catalyst that produced soot containing SWNT bundles around 1.4 nm in diameter. The soot dispersed in dichloroethane was treated by ultrasound to untwist the bundles and separate free CNTs. Nanotubes thus obtained were applied to an Au(111) film and studied by STM at T = 4 K. The study exemplified detailed parameters of two individual CNTs, one of which was a semiconductor with a 0.80-eV wide band gap, a diameter of 1.0 ± 0.1 nm, a chiral angle of $26^{\circ} \pm 1^{\circ}$, and a chiral index of either (12, 1) or (13, 1). The other CNT exhibited metallic conductance and had a diameter of 1.27 ± 0.09 nm, a chiral angle of $21.1^{\circ} \pm 1^{\circ}$, and a chiral index of (15, 3).

2.3 X-ray structural analysis

The methods described in Sections 2.1 and 2.2 are suitable for studying either the surface of a sample (SEM) or a thin bulk sample (TEM).

However, a central task of nanodiagnostics reduces to elucidating the atomic structure of nanoobjects with an accuracy much higher than their characteristic dimensions. The properties of nanoobjects are known to alter significantly even upon such a small change in the interatomic distance as 5×10^{-3} nm. The resolving power of the available microscopes is insufficient to reveal such changes.

The nondestructive investigation of bulk nanoscale materials, yielding quantitative information about their elemental and chemical composition, is possible using preferably X-rays that penetrate deep into substance and interact with its electrons in a specific manner. Widely applied in current research are microscopic methods based on X-ray photoelectron spectroscopy [52], X-ray fluorescence [53], and scanning and transmission X-ray microscopes [54].

Roentgenoscopy provides an insight not only into the surface properties of a sample but also into its volume (threedimensional) structure, regardless of thickness and other geometric parameters. However, the spatial resolving power of these methods is limited by the characteristics of focusing optics and as yet does not exceed 5 nm [55]. Therefore, lensless devices based on the use of X-ray diffraction are deemed promising for the purpose [56]. Researchers in the USA and Australia were the first to apply resonant X-ray diffraction microscopy to visualize the nanostructure of bulk materials [57].

This method is based on sharp changes in X-ray scattering atomic coefficients near absorption edges; in other words, it is suitable for studying the elemental and chemical compositions of substances. Diffraction patterns of coherent X-ray radiation obtained on both sides of the absorption edge are used to retrieve the spatial distribution of elements.

Methods of X-ray structural analysis are inapplicable to nanoobjects that cannot be crystallized and are devoid of long-range order; hence, the importance of developing techniques for the study of the three-dimensional structure of such objects. Reference [58] presents a method for such investigations with an accuracy of 2×10^{-3} nm based on the fitting of XANES (X-ray absorption near-edge structure spectroscopy) data using multidimensional interpolation of spectra as a function of structural parameters.

The above methods may be useful for estimating the diameter and the length of individual nanotubes or their bundles, the angle of twisting (chirality) of each tube, the mutual position of nanotubes in a bundle, and the elemental and chemical compositions of the specimen. However, they require thorough and time-consuming (up to several days) sample preparation.

2.4 Raman scattering spectroscopy

Raman scattering spectroscopy (RSS) is widely applied to identify various forms of carbon [59]. This method proved equally informative for nanostructured carbon materials, including CNTs [60]. The efficiency of RSS is due to the relationship between the diameter of single-walled CNTs and the radial breathing mode frequency. Raman spectra of carbon are characterized by two modes: G (line shift $\Delta v = 1580$ cm), and D ($\Delta v = 1350$ cm⁻¹). Their width and relative intensity reflect carbon structural properties [61].

The limiting spatial resolution of RSS is only 1 μ m and does not permit seeing atoms.² However, changes in light interaction with a nanoscale object recorded in Raman spectra are determined by the object's size [62]. Due to this, RSS analysis makes it possible to rather quickly and reliably detect SWNTs in the deposits and determine their diameters even in the course of an experiment.

Reference [63] describes an experimental study of SWNT synthesis by laser ablation of a graphite target in the presence of a catalyst using a combination of RSS and electron microscopy.

Figure 9 demonstrates a typical Raman spectrum of the deposit obtained in this experiment. The Raman spectrum of an SWNT consists in fact of two modes: tangential and radial. The absence of D mode ($\Delta v = 1350 \text{ cm}^{-1}$) suggests the absence of amorphous carbon in the deposit. The tangential

 $\sup_{\substack{I = 1 \\ 1200 \\ 1300 \\ 1400 \\ 1500 \\ \Delta v, cm^{-1}}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1}} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1} \\ \Delta v, cm^{-1} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1} \\ \Delta v, cm^{-1} \\ \Delta v, cm^{-1} \\ \Delta v, cm^{-1} \sum_{\substack{I = 1 \\ I = 1 \\ \Delta v, cm^{-1} \\ \Delta v,$

Figure 9. Typical Raman spectra of a deposit containing SWNTs: I—tangential mode, and 2—radial mode.

mode ($\Delta v = 1580 \text{ cm}^{-1}$) exhibits a splitting characteristic of SWNTs. In principle, the temperature shift of the maximum of this mode can be used to estimate the concentration of SWNTs in ablation products. Such analysis for two experiments carried out at a laser power of 600 and 800 W points to a strong power dependence of SWNT content in the deposit at normal helium pressure, all other conditions being identical. A rise in the laser radiation power by 200 W resulted in a fourfold increase of SWNT content, which reached 20% (by volume) at 800 W. The radial or breathing mode located in the range of $\Delta v = 150-200 \text{ cm}^{-1}$ contains important information about the distribution of SWNTs in the deposit over diameter. SWNT diameter *d* can be estimated from the frequency shift of the radial mode using the relation [64]

$$d = \frac{223.75}{\Delta v}$$

Here, Δv is the Raman frequency shift in reciprocal centimeters, and *d* is the SWNT diameter in nanometers. As shown in Fig. 9, the radial mode spectrum relates to a set of bundles and this allows deducing the diameter distribution of nanotubes. It was shown that SWNTs 1.1-1.5 nm in diameter were synthesized at a laser radiation power of 5×10^4 W cm⁻² on the target surface. The spectral maximum was associated with the diameter 1.2 nm, thus suggesting the predominance of nanotubes with a chiral index (9, 9) in the deposit. The position of the main peak of the tangential mode in the high-frequency part of the Raman spectrum corresponded to 1587 cm⁻¹, giving one more piece of evidence of the presence of SWNTs with a relatively small diameter in the deposit [65].

However, the resolving power of RSS is insufficient to study individual nanotubes. A sample containing a large number of CNTs is needed to achieve the desired spectral resolution.

Possibility of a change in exciting radiation wavelength upon replacement of the laser or use of a tunable laser led to the development of the method of resonant Raman scattering that normally occurs when the exciting light frequency falls within the absorption frequency range of the substance. This

² See http://www.chemport.ru/chemical_encyclopedia_article_1730html/.

method permits determining low concentrations of substances [62].

Modern spectrometers record Raman spectra of colorless and stained samples containing up to 10^{-4} g (or ml) of the material. High-speed spectrometers based on pulsed lasers record Raman spectra for 10^{-9} s; some systems combining a laser and a microscope permit obtaining the Raman spectra of objects as small as 1 µm.

Reference [66] describes studies of the structure of individual SWNTs by resonant RSS. SWNTs were obtained by chemical deposition onto an Si/SiO₂ substrate coated with a catalyst (iron nanoparticles). Observations with an atomicforce microscope showed that the surface was covered by individual CNTs 1-3 nm in diameter to a density of 63 μ m⁻². Resonant Raman spectra of isolated CNTs were analyzed in a frequency range from 100 to 1900 cm⁻¹ using laser radiation with a wavelength of 785 nm (energy of 1.58 eV) and a power of 25 mW focused onto a spot 1 µm in diameter. Resonant Raman scattering occurred when the energy difference between van Hove singularities coincided with the laser radiation energy to an accuracy of about 0.1 eV. The sensitivity of resonant RSS was high enough to detect signals from individual SWNTs. The authors of Ref. [66] determined chiral indices and diameters for a large number of individual CNTs. The best agreement between experimental data was achieved on the assumption that the nanotube diameter d(nm) is expressed through the shift of radial breathing mode Δv (cm⁻¹) by the relation $d = 248/\Delta v$. The coefficient in this relation is essentially different from that accepted in an earlier study (223.75 cm⁻¹ nm) [64].

The resonant scattering scenario can also be utilized to estimate nanotube distribution over diameter in the material of interest and obtain information about its electronic properties.

However, this method is less suitable for determining chiral indices for tubes of great diameters. In this case, the number of CNTs of a different structure being resonant with the laser radiation frequency increases; it precludes unambiguous identification of the nanotube structure.

Researchers at the Natural Sciences Center, A M Prokhorov General Physics Institute, Moscow, and K G Boreskov Institute of Catalysis, Novosibirsk (www.chem.msu.su/rus/ journals/chemlife/2000/nanatr.html) maintain that RSS constitutes the fastest and most convenient method for the study of SWNTs with a diameter less than 2 nm. It is much less sensitive if applied to nanotubes 2-5 nm in diameter that need the different approaches to be utilized (transmission or tunneling microscopy).

2.5 Electron spectroscopy

Certain authors studied CNT chemical composition and electronic properties by electron spectroscopy methods, namely Auger spectroscopy and X-ray photoelectron spectroscopy.

Auger electron spectroscopy (AES) is employed to investigate energy spectra of Auger electrons produced during electron beam irradiation of the material of interest. AES is widely applied to determine the elemental composition of solid surfaces and the electronic structure and chemical state of atoms in a sample.

The spectra of Auger electrons are recorded by Auger spectrometers consisting of a source of ionizing radiation, a sample chamber, an energy analyzer, and an electron detector. Ionizing radiation comes as electron beams with an energy of 3-10 keV or higher (in instruments with a spatial resolving power below 0.1 µm). Auger spectrometers permit studying energy spectra in the form of dependences N(E) - E and [dN(E)/dE] - E, where N(E) is the Auger electron yield (or current intensity), i.e., the number of Auger electrons emitted by the object under study per unit time.

Auger electron spectra provide a basis for the qualitative and quantitative elemental analysis of the samples. The spectra in coordinates [dN(E)/dE]-E are used for this purpose since they ensure enhanced sensitivity and accuracy of the analysis. The element present in a sample is identified from kinetic energy *E* of Auger electrons, which is dependent only on electron binding energy at electron levels and, consequently, is determined by the nature of the atoms. Moreover, the shape of Auger peaks in the spectra is sensitive to the chemical state of the atoms, as is well apparent in transitions involving valence electrons.

The accuracy of the analysis by this method ranges 10-15%, while sensitivity varies from 0.01 to 10 at. %, depending on the element being detected.

The thickness of a layer accessible to analysis on a solid surface is given by the depth from which Auger electrons are liberated, which is, in turn, a function of their energy and varies from 0.5 to 2.0 nm for different metals. This depth being small, contamination of the surface with adsorbed atoms is an important source of errors introduced to the results of the analysis; therefore, spectrometric measurements are made in a strong vacuum $(10^{-6}-10^{-8} \text{ Pa})$ to avoid them. Moreover, Auger electron spectrometers are supplied with the ion guns (sources of rare gas ions), which are employed for cleaning the surface studied and carrying out layer-by-layer analysis.

Photoelectron spectroscopy (PES) constitutes a method for the investigation of the electronic structure of matter using the photoeffect caused by ultraviolet (UV) radiation. A photon-absorbing atom emits an electron (photoelectron), while photon energy hv (v is the radiation frequency, and h is the Planck constant) minus electron binding energy E_b is transferred to the photoelectron and can be measured as its kinetic energy E_{kin} :

 $E_{\rm b} = hv - E_{\rm kin}$.

Photoelectron spectroscopy and X-ray photoelectron spectroscopy (XPES) sometimes come under the common name of electron spectroscopy. The distinction between the two methods is arbitrary. The term PES refers to energies $hv \le 60$ eV, while XPES refers to higher values of hv.

Photoelectron spectroscopy permits studying electronic and vibrational levels of molecules, surface effects, and other characteristics. PES helps to detect Fermi level position and electron density distribution in solids. Measurement of adsorption may reveal the character of molecule adherence to the surface (physical adsorption or chemisorption), the nature of molecule–surface interactions, and the role of different molecular orbitals in these interactions. See Refs [67–69] for more information about PES techniques.

AES studies of surface layers in nanotubes showed [70] that the electron energy spectrum and the density of states in the samples are similar to the same parameters of C_{60} fullerenes, while electronograms of film surfaces suggest third- and sixth-order symmetry in the position of atoms in these layers. Based on these findings, the authors proposed a scenario of formation (growth mechanism) of nanotube structures from C_{60+18n} clusters.

The results of an examination of nanotube surfaces using AES and EELS reported in Ref. [71] were obtained by measurements in an ultrahigh vacuum (5 \times 10⁻¹⁰ Torr) with a high-resolution electron spectrometer ($\Delta E/E = 0.2\%$). The exciting current density did not exceed 10^{-7} A cm⁻² to avoid structural damage to the sample surface by electron bombardment. The resulting Auger spectra were analyzed by an original method specially developed for the purpose. The study gave evidence of a C₆₀-like arrangement of atoms on the surface of a structure comprising prolate molecules 1 nm in diameter close to the diameter of a C_{60} molecule. These data were confirmed by PES, which demonstrated the presence of large amounts of oxygen on the film surface after exposure to the air; C_{60} molecules were prone to adsorb this oxygen. In other words, the surface of this nanofibrous carbon structure exhibited chemical activity comparable with that of a C_{60} fullerite.

The electronic structure of SWNTs was investigated by XPES, EELS, and AES in paper [72]. Specifically, the satellite structure near the core C 1s-lines in XPES spectra on the side of high binding energies in the range 284-330 eV was studied; it was shown to be related to the excitation of π and $\pi + \Sigma$ plasmons. Another aspect of this work was the influence of the bombardment by argon ions with an energy of 1 keV on the shape of the spectra. The form of satellite C 1s-spectra proved sensitive to bombardment by Ar^+ in the range of energy losses from 10 to 40 eV, corresponding to excitation of $\pi + \Sigma$ plasmons. AES demonstrated the presence of argon on the ion-irradiated surface. Its concentration increased with increasing ion irradiation dose to ~ 4 at. %. Based on comparative analysis of these findings and the literature data, the authors arrived at the qualitative conclusion that valence angles between carbon atoms forming SWNT walls undergo deformation at sites irradiated by Ar⁺ ions.

3. Main electrophysical properties of CNTs

3.1 Transport properties of CNTs

It is not only the structural parameters of matter but also electrophysical ones (mechanical properties, melting temperature, electrical and thermal characteristics) (see Ref. [73] and also http://www.crnano.org/whatis.html) that change in the nanoscale world. For example, the resistance R_0 of nanoresistors does not at all depend on their size and material; it is only determined by two fundamental physical constants [74]:

$$R_0=\frac{h}{2e^2}=12.9\,\,\mathrm{k}\Omega\,,$$

where *e* is the electron charge $(1.6 \times 10^{-19} \text{ C})$, and *h* is the Planck constant $(6.6 \times 10^{-34} \text{ J s})$. Quantity R_0 is called the quantum of electrical resistance, bearing in mind that all nanoresistors have equal resistance. It turned out that the passage of electric current through nanoresistors, including carbon nanotubes, is not accompanied by the release of Joule heat. Such unusual conductance independent of the resistor length or cross section area and unaccompanied by heat release is referred to as *ballistic* conductance [75, 76]. The conductance of nanoscale structures, the size of which is commensurate with the electron phase coherence length in a given material, is determined by quantum interference effects. Such a situation takes place in purely ballistic and quasibal-

listic regimes of charge carrier transfer. The latter regime allows weak scattering of charge carriers, typical of most real nanostructures regarded as slightly disordered systems [77]. The electron's phase coherence length is the distance between the two nearest points at which the electron undergoes inelastic scattering leading to a change in the electron wave phase. Transport phenomena in low-dimensional structures and, specifically, in CNTs are considered at greater length in Refs [77] and [78], respectively.

Because nanotubes are not heated in the transfer processes, they can carry currents of extremely high density, e.g. over 10^7 A cm⁻². Were such CNTs to possess ordinary (not ballistic) conductance, their temperature would rise, theoretically, to 20,000 K, or much higher than their burning temperature (700 K) in the air. However, the relative importance of ballistic transport significantly decreases with a rise in the temperature and length of a real tube; instead, diffusion mechanisms begin to prevail. A detailed analysis of different carrier transport mechanisms in CNTs can be found in the review by Eletskii [78].

It is these unique physical and technical properties of CNTs that attract the interest of researchers.

The dependence of the electrical properties of nanotubes on their geometric parameters was predicted based on the quantum-chemical computation of their band structure. It was shown that the metallic band structure is characteristic of CNTs for which the difference (n-m) between chiral indices is divisible by three, i.e., one third of nanotubes. The width of the band gap is also unambiguously related to nanotube diameter and the chiral indices [79].

Reference [80] describes a computing method for the electronic structure and electrical conductance of armchair SWNTs having different diameters. It also reports calculated data indicating that one qualitative characteristic (constant conductance despite increasing tube diameter) is consistent with experimental evidences, e.g., such as given in paper [81]. It is, however, difficult to analyze the numerical correspondence between theoretical conductances of CNTs predicted in Ref. [80] and experimental values because the model takes into account only ballistic transport, for which conductance of the sample is unrelated to its length. At the same time, conductance of real nanotubes (G) is a function of their length due to electron scattering on impurities and phonons at low and elevated temperatures, respectively [81]. Therefore, G values obtained should be interpreted as the conductance of ideal armchair SWNTs at temperatures tending toward absolute zero.

Theoretically, the electronic structure of CNTs is equivalent to that of an infinitely long graphene layer as wide as the circumference length of the corresponding nanotube [82]. The electronic structure of the graphene layer (calculated for the first time in 1947) is given by the fact that its elementary cell contains two atoms having 8 electrons that take part in bond formation. Hence, there are 4 valence bands totally filled with electrons at absolute zero. Orbitals of electrons in carbon atoms incorporated into graphene layers overlap, which accounts for their high mobility. As a result, resistivity of the layer is low (0.4 $\mu\Omega$ m under normal conditions). The mobility of electrons in the direction perpendicular to the layers is much lower, while resistance is higher. The density of free charge carriers in graphene layers is on the order of one electron per 1,000 atoms-there are holes and electrons regardless of temperature. Due to this, the graphene layer functions as a conductor.

It follows from the above that the symmetry type, diameter, and electronic structure of SWNTs are almost fully characterized by integer-valued chiral indices (n, m)that are, in turn, unambiguously related to the parameters of an elementary cell of the graphene layer. In other words, SWNTs are one-dimensional quantum structures as far as their electrical properties are concerned [13]. The electronic properties of MWNTs can be formally explained in terms of the band model of quasitwo-dimensional graphite (Q2DG) [83-85], which was developed earlier for the interpretation of the electronic properties of many carbon materials having a well-apparent two-dimensional graphite structure of the planar type [86, 87]. Because typical MWNTs with a diameter of 10-30 nm are regarded as quasione-dimensional objects, the applicability of the Q2DG model to these objects had to be substantiated, as in the studies by Kotosonov et al. [83-85, 88]. Numerical calculation of the density of states for MWNTs with different numbers of layers was made in Ref. [88] taking into account interactions between them. The results were compared with available experimental data, bearing in mind that samples in real experiments consist of a large number of tubes and that calculated values need to be averaged over nanotubes of different diameters and chiralities

Moreover, MWNTs differ from SWNTs by exhibiting a wider variety of shapes and configurations. For the majority of structures obtained by different authors, the average interlayer distance equals 0.34 nm, as in graphite. However, there is increasingly greater deviation from the ideal cylindrical shape with a rise in the number of layers, and the distance between them may change. In certain cases, the outer shell assumes a polyhedral shape, while in others the surface layer constitutes a structure with irregularly arranged carbon atoms. Finally, the ideal hexagonal mesh of the outer layer of a nanotube may have defects in the form of pentagons and septagons, resulting in the distortion of the cylindrical shape [89].

All these features need to be taken into consideration in a theoretical analysis of transport processes and interpretation of experimental data.

It required extraordinary experimental skills to practically verify the above theoretical findings. The small size of CNTs did not allow directly measuring the electrical resistivity (ρ) of SWNTs by the four-contact (probe) method until 1996 [90]. Figure 10 presents a schematic of the measurement of CNT electrical resistivity by the four-probe method (a) and an AFM image of (b) four- and (c) two-contact connections to an individual CNT. It was shown that tube resistivity varied in a broad range, from 5×10^{-6} to $0.8\;\Omega$ cm, and the minimum value of ρ proved an order of magnitude lower than in graphite. Such a spread was due to the fact that the nanotubes, both SWNTs and MWNTs, may have either metallic or semiconducting conductance. The tungsten contacts used in the experiment were deposited by electron beam sputtering and had a cross section 100 times that of the nanotubes.

Because designers of CNT synthesis concentrate their efforts on the method of chemical deposition from the vapor (gas) phase, which is based on thermal decomposition of carbon-containing gases on the surface of a metallic catalyst at 500-1000 °C [91-93], electrode systems for CNT-containing test specimens must be thermally stable and possess high mechanical strength. Traditional heat-resistant electrode materials are tungsten, molybdenum, and their compounds



Figure 10. Schematic of the measurement of CNT electrical resistivity by the four-probe method: 1—insulating substrate, 2—gold bonding pads, 3—tungsten lead-in paths, 4—carbon nanotube (a); an AFM image of (b) four- and (c) two-contact connections with an individual CNT.

obtained by sputtering composite targets. Therefore, the resistance of individual nanotubes may prove significantly less than that of lead-in paths or direct contact junctions.

Ballistic transport of carriers in MWNTs possessing quantized conductance occurs at the resistance of 12.9 k Ω ($G_0 = 2e^2/h$) [94]. Advances in experimental techniques by 2001 made possible measurements on MWNTs 8.6 nm in diameter that demonstrated the ability of nanotubes with minimal resistivity $\rho = 5 \times 10^{-6} \Omega$ cm to carry a huge current density amounting approximately to 1.8×10^{10} A cm⁻². At T = 250 °C, such current persists for two weeks (334 h) without tube degradation due to electromigration [95, 96]. The power liberated in a nanotube due to its finite quantum resistance at a current density on the order of 10⁷ A cm⁻² is ~ 0.003 W, which corresponds (bearing in mind the size of the tube) to a very high temperature. It suggests ballistic transport of electrons in MWNTs within a certain temperature range because they travel from one end to the other without hindrance. Such charge transfer occurs without heat release, which means that CNTs have a negative temperature coefficient of resistance [97].

Thus, conducting CNTs with high conductance and heat conductivity (thermal stability) used as conductors in nanoelectronic devices and integrated microcircuits are capable of carrying currents of extremely high density without being heated and ensure significantly enhanced reliability at nanometer-sized (up to 22 nm) design specifications [98].

The contribution of imperfect metal-nanotube contacts lying in the interconnection layer plane should be taken into account when measuring CNT resistance [99]. It would be preferable that all MWNT layers be contacted and the conjugation (contact) region be over 10 nm. It may be essential for the point contact of an AFM-based analyzer,





Figure 11. (a) Experimental setup with a scanning four-probe head to measure the resistance of individual nanostructures; (b) TEM image of an experimental MWNT, and (c) position of the four-probe head on an MWNT that was initially aligned with the contacts, viz. centered, using one of the microcantilevers. (Taken from Ref. [100].)

which, along with the probe – CNT contact, contributes to the resistance being measured.

The authors of Ref. [100] proposed straightforward measuring MWNT resistivity with a four-probe head manufactured by conventional silicon microprocessing technology (Fig. 11). This device permits determining the resistivity of individual nanostructures, taking into account contact resistance, and studying volt–ampere characteristics at different distances between the measuring probes. It was shown that this method has a relatively small measurement error, from ± 1.5 to $12 \text{ k}\Omega$, which grows due to the spread of results of ten successive measurements (from ± 0.1 to $1 \text{ k}\Omega$). In this case, contact resistance may range $15-50 \text{ k}\Omega$; in other words, the two-contact method gives a large error.

In Ref. [101], the electrical conduction of nanotubes was measured with electrodes fabricated by electron-beam lithography on the surface of a silicon substrate in the form of micron-sized strips from a Ti/Ag alloy, spaced 0.8 μ m apart. A single nanotube was placed between the metallic electrodes using a nanomanipulator, and its volt-ampere characteristics were studied in air at different temperatures and under exposure to optical radiation. The dark conductivity measured along the 1 μ m length of the tube was significantly lower than the theoretical one. The authors attributed this discrepancy to the influence of oxygen adsorbed on the surface of the CNT; oxygen created impurity centers that served as traps for the carriers. This conjecture is confirmed by measurements of conductivity in similar objects under vacuum conditions.

Representative results of resistance measurements are reported in Refs [96, 100, 102]. Table 2 [96] compares resistance data measured for two CNTs obtained by twoand four-contact methods. Evidently, the results may differ by a factor of two (100%) depending on the measuring technique.

The resistance of isolated CNTs and their bundles was measured with superconducting and metal electrodes in Ref. [103]. Tunneling contacts of CNTs to aluminium electrodes were obtained and volt–ampere characteristics of transitions were studied in the range from room temperature to 300 mK. It was shown that the resistance of individual nanotubes is mostly determined by their defects and is too high for many practical applications. The resistance of bundles is much lower if there is a small number of conducting tubes having good enough tunneling contacts with the electrodes. Structures containing CNT bundles can

Table 2. Comparative resistance of two CNTs measured by two- and fourcontact methods [96].

Nanotube number	Ι	II
Diameter, nm	8.6	15.3
Length, nm	2.6	2.5
Measuring method	Constant voltage,	Constant current,
-	two-contact	four-contact
Voltage, V	25*	17 **
Current, mA	10.4 **	10.0*
Resistance, kΩ	2.4	1.7
Current density, A cm ⁻²	1.8×10^{10}	5.4×10^{9}
Scattering power, mW	260	170
Scattering power density,		
$mW \mu m^{-1}$	100	68
	•	•

* Given value maintained by power supply.

** Mean measured value.

be described in the framework of a model with the Schottky barrier.

Reference [104] describes one more peculiarity of CNT electronic properties, namely long-term persistence of circulating currents induced by an external magnetic flux, even at above-room temperatures. The role of magnetic processrelated currents circulating in the tube circumference attracted the attention of researchers soon after the discovery of nanotubes. It was theoretically predicted that diamagnetic susceptibility may reach $\sim 10^{-2}$ CGSM units mol⁻¹, i.e., two orders of magnitude higher than in graphite, if the magnetic field is oriented along the axis of the CNT with a mean radius of r = 8 nm. Quite remarkable magnetic properties are inherent in CNT aggregates in the form of columns whose surfaces look like the sparse woven cobweb of multiwalled CNTs (Fig. 12). Such structures are synthesized in electric discharge plasma. If nanotube columns are placed in a magnetic field perpendicular to their longitudinal axis, they capture the magnetic flux because the magnetic field induces currents that persist at helium temperatures and only slightly decay at room temperature. This phenomenon resembles the one known to occur in multiply connected superconducting structures. A special experiment was undertaken in which a sample in the form of CNT columns was kept in contact with the captured magnetic flux at 100 °C for 2 hours. As a result, the magnetic moment decreased only two-fold, which suggested a very slow decay of the current circulating in the multiply connected structure. In other words, conductance along nanotube channels was significantly different from that observed in conventional metallic conductors.

The authors of Ref. [105] measured the electrical resistance of a single MWNT at different temperatures and magnetic



Figure 12. Model of a columnar structure of cathode deposits synthesized in electric discharge plasma. MWNTs appear in the form of a dense disordered network on the column side surfaces and in the form of a sparse nanotube cobweb in the space between them. (Taken from Ref. [104].)

field strengths. The nanotubes for the study were obtained by the standard arc discharge method using graphite electrodes. Electrical contacts were formed by electron-beam lithography. The 800-nm-long tubes had a diameter of ~ 20 nm. As temperature varied between 0.05 and 100 K, the current flowing through the CNT was 1–10 A and the sample conductance ranged $(1-3) \times 10^{-5} \Omega^{-1}$. Application of a magnetic field of up to 14 T caused a rise in conductance proportional to the field induction, but its temperature dependence (a gradual increase at low temperatures and exponential growth at temperatures above 1–3 K) remained unaltered. Analysis of experimental data indicates that MWNTs behave like disordered conductors of reduced dimensions.

In Ref. [106], the electrical properties of SWNTs were studied by the method simulating electron transport in defectless free-lying nanotubes 1 µm in length having no chemically or mechanically induced distortions. Individual CNTs as-grown without wet chemical treatment were positioned with their ends on two platinum contacts with a tungsten sublayer (Pt-on-W), as demonstrated in Fig. 13. The contacts were spaced by a gate electrode placed under the tube. The assembly exhibited well-marked quantum properties in a wider energy range than in experiments with CNTs fabricated directly on the substrate. Different regimes of lowtemperature electron transport were apparent in metallic and semiconducting (narrow- and wide-bandgap) CNTs. The high quality of CNTs made it possible to study electron band structure, including nonlinear dispersion. The authors emphasized that high-quality suspended carbon nanotubes are almost ideal quantum conductors for basic research.

Up to now, researchers have been able to assemble CNTs into single transistors with predictable characteristics. However, the high susceptibility of nanotubes to the influence of the environment poses the problem of reproducibility of results. For example, the properties of CNTs may change under the effect of impurities that interfere in current flow and alter the characteristics of CNT-based devices. Such interactions, usually manifested at the local level, change electron density in different components of an integrated circuit and even within a single CNT. A deeper insight into the mechanisms of the action of local environment on the electrical charge in CNTs is needed to increase the reliability of transistors manufactured with the use of nanotubes; hence, the great importance of measuring local changes in nanotube electron density. A group of researchers affiliated with the Thomas J Watson Research Center reported solving this problem in an on-line issue of Nature Nanotechnology dated October 14, 2007 [107]. They continuously monitored the



Figure 13. (a) Schematic of the investigation of SWNT electrical properties by a method simulating electron transport in free-lying nanotubes; (b) 1-µm-long defectless SWNTs were utilized. (Taken from Ref. [106].)



Figure 14. Illustration of the method making use of the relationship between atom and electron motions to represent variations in electron density in the form of changes in atomic vibration frequency in a nanotube.

frequency of light emitted by a nanotube (Raman scattering) and recorded its minor variations that paralleled changes in electron density in the tube. The method took advantage of the relationship between the motions of atoms and electrons to represent changes in electron density as changes in the atomic vibration frequency in CNTs (Fig. 14).

Analysis of electron–phonon interactions in CNTs provided a basis for the development of an efficacious method for assessing the feasibility of using them as conducting and semiconducting components in micron-sized computer circuits of the future.

The possibility of identifying CNTs and analyzing their conducting properties from phonon spectra was demonstrated in an earlier study by Russian researchers [108] who calculated such spectra for carbon nanotubes of various diameters and chiralities.

Even in a very primitive model, CNT conductance must correspond to the conductance along a graphite plane (the measured values are spread over a wide range and exceed theoretical ones by an order of magnitude [109, 110]), and depends not only on chirality but also on the perfection of structural (the presence of defects) and sorption (the presence of added radicals OH, CO, etc.) properties [111], as well as on ambient conditions [112] and resistance of contacts with CNTs. The influence of contact resistance on the parameters being measured is described at length in review [99].

The first experimental and theoretical studies on defective CNTs reported in Refs [113, 114] were focused on the evaluation of a drop in the work function of impurity-doped CNTs. The authors of Ref. [113] compared experimental and calculated data on the ionization potential and work function of nanotubes doped with Si, Sn, Ti, Pb, and Ge atoms. A given doping element introduced into the growth chamber diffused into the newly synthesized CNTs. The working function was deduced from autoemission volt–ampere characteristics.

An interesting approach to MWNT research was proposed in paper [115]. Multiwalled catalytic CNTs were prepared by thermochemical decomposition of acetylene on the surface of a catalyst: 5% composition (2Fe:1Co)/CaCO₃) (CVD method). The catalyst was obtained by codeposition of active components from nitrate solutions. The innovative aspect of this method was the presence of an oxidizing gas (CO_2) in the gaseous medium surrounding the sample to inhibit the formation of a carbon amorphous phase during the nanotube synthesis. Electron microscopy disclosed that CNTs contained less than 5 at.% of an amorphous carbon admixture.

Synthesized CNTs were next purified from the catalyst to open their ends. Purification was performed by boiling them in 10% hydrochloric acid for 6-12 h, followed by washing in distilled water, filtration, and air drying. Under certain conditions, the resulting CNTs were rather similar in terms of diameter (~ 20 nm), a fact of importance in MWNT research. The samples used in the study were a powder pressed into an ampule to a state in which its resistive properties no longer depended on the degree of compression. The conductance was measured by the four-contact scheme in a temperature range of 4-300 K. The temperature was measured by an iron-rhodium resistance thermometer. Contact with the material was through a silver wire 0.1 mm in diameter. Uncontrollable effects of the environment on the properties of the samples during storage were excluded by keeping them in a vacuum (10^{-2} Torr) at 500 K for 12 h prior to measurements. The samples were then placed in the measuring chamber that was pumped down with a forepump to a pressure of 10^{-2} Torr for 2 h and filled with gaseous helium or its mixture with other gases (air, oxygen, methane, hydrogen). The measuring error reached ~ 0.1 %. The results obtained were reproducible for each of the gas mixture composition. They suggested that adsorption/desorption processes might be accompanied by capillary condensation of the gases at CNT junctions, leading to enhanced resistivity at their respective melting temperatures: 64 K for nitrogen, 54 K for oxygen, 90 K for methane, and 14 K for hydrogen. Resistivity did not fall back to the starting value after completion of the cooling/heating cycle in experiments with the presence of oxygen, either as a result of the disintegration of intertube contacts or due to residual oxygen adsorption on the nanotube surfaces.

3.2 Other properties of CNTs

The transport properties of CNTs (first and foremost conductance) are directly or indirectly related to other parameters of nanotubes (heat conductivity, mechanical and emission characteristics). It is natural to expect that these parameters should depend on many factors, including measuring techniques.

By way of example, quantum-mechanical calculations predict that the tensile strength of defect-free SWNTs exceeds 100 GPa, thus corresponding to the feasibility for a cord with a 1 mm² cross section to hold a load of over 10 metric tons. However, the measured tensile strength of CNTs is much smaller (28 GPa), although the discrepancy arises not so much from the real value of this parameter as from the method used to test the mechanical properties. It is practically impossible to prepare test samples without injuring the tubes during their preparation (with the result that the mechanical parameters change). It is equally difficult to obtain images of the test samples with a resolution high enough to elucidate the nature of the crack. A group of American researchers headed by H Espinosa (Department of Mechanical Engineering, Northwestern University, Illinois, USA) reported experiments, the results of which are in excellent agreement with theoretical predictions. Experimentalists managed to overcome existing technical problems,

having prepared almost ideal nanotubes, and obtained accurate and reliable data on changes in their geometry at breakdown. These results are available on-line [116]. The value of this work lies in the fact that it is the first to yield experimental information on the MWNT ultimate strength consistent with that provided by quantum-mechanical computations. The authors determined experimentally Young's modulus, stress-at-break, and breaking strain for an individual CNT as 1 TPa, 100 GPa, and 11%, respectively. These findings are at variance with the previous hypothesis that irradiation must promote degradation of the atomic structure. Moreover, a rise in the allowable load is shown to depend on increasing the electron-beam irradiation dose.

A detailed description of CNT mechanical properties and methods for their investigation can be found in Refs [117, 118]. Emission properties of CNTs and relevant methods are considered in the review by Eletskii [20].

Based on above consideration, it can be concluded that high-resolution TEM, STM, and RSS are the most informative methods and those of choice for CNT research.

4. Methods for preparing samples for CNT research

Methods of sample preparation are of paramount importance for the study of the structural and electrophysical properties of CNTs.

As a rule, various modes of chemical treatment are used for the purpose. It is therefore appropriate to briefly consider here the chemical nature of CNTs. It has long been known that systems having a size intermediate between single molecules and crystals, such as carbon nanotubes, possess specific chemical properties studied by colloidal chemistry, which started to rapidly develop only in the 1990s when the nanoparticle concept was formulated based on the discovery of a family of fullerenes (carbon molecular clusters) in 1985. Fullerenes should be regarded in the context of molecular paradigm: they are individual molecules, even if unusual ones, that can be studied by classical methods of molecular chemistry. In contrast, carbon nanotubes and carbon nanobulbs (multilayered fullerenes), chemically speaking, are polymeric carbon structures (nonmolecular polymeric forms of carbon) resembling known for a long time allotropic modifications of this element, such as graphite, diamond, and carbin (a filamentous polymer).

The main difficulty encountered in nanotube chemistry is the intrinsic insolubility of these structures. In this respect, they are closer to graphite than to fullerenes, which are soluble in organic solvents. For this reason, CNTs of different sizes cannot be separated by liquid chromatography; this difficulty is obviated by passing their suspension through a porous material. CNT solubilization techniques have recently been developed. It proved possible to solubilize derivatized SWNTs in such solvents as dipolar dimethylsulfoxide [119]. Moreover, CNT surfaces can be functionalized in a variety of reactions used in organic and elemento-organic chemistry.

It is especially difficult to isolate CNTs from so-called carbon (nanotube) deposits. Usually, pure CNTs are extracted from carbon condensates by one of two methods. The first is selective oxidation in an oxygen-containing atmosphere. The chemical stability of CNTs having no free bonds is significantly higher than that of graphite or metal particles. Due to this, carbon soot, fullerenes, and other admixtures are the first to be oxidized in carbon deposits, which retains only CNTs after the reaction is over. A disadvantage of this technique is that the weight of the end product constitutes only 4% of the starting material. In the second method, CNTs are isolated after intercalation of copper compounds contained in them. Further thermoactivated decomposition of these compounds leaves copper on all structural forms of carbon except nanotubes. Copper acts as a catalyst in the subsequent oxidation in which all carbon structures other than CNTs become oxidized [21, 120].

Solid unpurified SWNTs constitute a mixture of soot particles and nanotube bundles comprised of long filaments (CNT bundles) and agglomerates (soot particles). To produce pure CNTs, soot is usually removed by treatment with concentrated nitric acid and annealing in the air at a high enough temperature (over 700 °C). The tubes are separated by prolonged ultrasonic treatment of the suspension (US dispersion) in surfactant (SAS) solutions [118, 121]. CNT solutions are used when doing in vivo studies. To this effect, nanotubes assembled in bundles or filaments are subjected to dispersion, either mechanically or by the methods (physical or chemical) changing the surface energy. Mechanical methods (e.g., US treatment) separate CNTs from one another but can damage them. Chemical treatment leads to covalent functionalization of the nanotube surface, which enhances their wettability and adhesiveness but may introduce defects, as in the treatment with acids at high temperatures. Recently, noncovalent functionalization of CNTs by SAS or polymers has been extensively used to prepare aqueous and organic solutions [121]. Ultrasound is widely applied in combination with SAS to split the ends of nanotube bundles and thereby facilitate penetration of the SAS.

The products of synthesis are also separated by filtration, centrifugation, and chemical and thermochemical methods.

The choice of the deposit purification technique strongly depends on the mode of CNT synthesis. For example, a cathode deposit of MWNTs, obtained by thermal sputtering of graphite electrodes in arc discharge plasma, is placed in methanol and treated by ultrasound. This procedure yields a suspension that is subjected to centrifugation after the addition of water. Large soot particles adhere to the centrifuge walls, while the nanotubes continue to float in the suspension. Then nanotubes are collected and washed with nitric acid and dried in an oxygen/hydrogen (1:4) flow at 750 °C for 5 min. The end product is a sufficiently light porous material composed of MWNTs around 10 μ m in length having a mean diameter of 20 nm. CNT content in the carbon deposit may amount to 69% [122].

Material synthesized by conventional methods using catalysts contains admixtures that are difficult to remove, such as, primarily, catalyst particles enclosed in a multilayered graphite shell. Researchers from Beijing University, China [123] undertook multistep purification of cotton-woollike soot synthesized by the arc discharge method. This material, containing $\sim 36\%$ of SWNTs approximately 1.36 nm in diameter, was deposited on the walls of the discharge chamber. Thermal decomposition of a 10-cm anode rod produced 500-700 mg of soot. Its CNT content was measured at each successive stage of the purification procedure by SEM, TEM, RSS, and thermogravimetric analysis (TGA). The soot was first subjected to oxidation in a weak (100 cm³ min⁻¹) air flow at 320° for 1 hour, which selectively eliminated a large number of amorphous carbon particles. Thereafter, the sample was submerged in an aqueous HNO₃ solution (2.6 M) and treated by ultrasound for 5 min. The resulting suspension was heated in a microwave oven for 1 h and centrifugated. The black deposit was thoroughly washed with deionized water for 30 min and annealed in the air at 450°. In this way, practically all amorphous carbon particles and other multilayered graphite structures were removed from the sample, which contained only traces of metallic catalyst. Degree of purification of the sample was estimated to be 97 wt.%. Comparison of cottonwool-like samples and standard fabric-like ones synthesized by the traditional method showed that one and the same purification procedure ensured much better purification of the former than the latter. It is emphasized that the cottonwool-like soot could be synthesized only in a rather narrow range of discharge currents (between 70 and 80 A).

The authors of Ref. [124] used a microscopic membrane and oxidation in the air to purify SWNTs obtained by the arc discharge method. This purification procedure allowed carbon and metal nanoparticles, as well as other impurities, to be removed and enabled the SWNTs to be characterized at their different stages of purification by TGA, high-resolution TEM, and RSS methods. The validity was confirmed in experiment. SWNTs were purified to greater than 90%.

Many applications (e.g., in nanoelectronic systems) require nanotubes with strictly specified electrophysical characteristics. However, standard methods employed to synthesize CNTs (thermal sputtering of graphite in an arc discharge or under laser radiation, thermal decomposition of gaseous hydrocarbons in the presence of a catalyst) produce nanotubes with highly variable parameters depending on their diameter and chirality. Such CNTs exhibit properties of both metals and semiconductors with different widths of the band gap or concentrations of carriers. For example, synthesis of CNTs by the arc discharge method using a graphite electrode yields for the most part MWNTs with a diameter from one to several dozen nanometers. They differ in chirality, which accounts for the differences in their electronic structures and electrical characteristics. The distribution of these CNTs by size and chiral angle critically depends on the arcing conditions and fails to be reproduced from one experiment to another. This fact, taken together with the large variety of tube sizes and shapes contained in a cathode deposit, does not allow such CNTs to be considered as a material with well-definite properties. This problem was partly resolved by utilizing strong oxidizers. Application of these latter compounds to the purification and treatment of CNTs is possible due to the fact that reactivity of an extended graphite layer (CNT surface) containing six-member graphite rings is much lower than that of a spheroidal surface also containing a certain number of five-member rings [125]. Another approach to obviating these difficulties reduces to sorting CNTs by geometric and electronic parameters. For electronic applications, this procedure must ensure that tens of millions of nanotubes are sorted out within a realistic time frame. A few ways to address this issue have been proposed.

SWNTs 0.7–1.1 nm in diameter synthesized by laser ablation method were ultrasonically dispersed in an aqueous solution in the presence of an SAS (sodium dodecylsulfate or sodium dodecylbenzolsulfonate) [126]. These compounds can be encapsulated inside a CNT and give rise to a water-soluble complex. The relationship between CNT density and structure was established from the characteristics of optical absorption spectra of the samples containing CNTs with different chirality indices. The measurement data are presented in Fig. 15a, which compares the absorption spectra of solutions enriched in CNTs exhibiting metallic (1) and semiconducting (2) properties. These data were used to deduce the dependences of the relative concentration of CNTs with chirality indices (6, 5), (7, 5), and (9, 5)/(8, 7) (curves 2, 3, and 1, respectively) on the density of complexes of different SASs, as displayed in Fig. 15b–d. The solutions were centrifugated in commercial centrifuges with a radius of 38 and 110 mm at 64,000 and 41,000 rpm, respectively, at



Figure 15. Optical absorption spectra of solutions rich in nanotubes with metallic (*I*) and semiconducting (*2*) properties (a), and the density dependence of a relative concentration of nanotubes with different chirality indices (6, 5), (7, 5), and (9, 5)/(8, 7) (curves 2, 3, and *I*, respectively) for different SASs (b–d). (Taken from Ref. [126].)

It was shown in Ref. [127] that the application of standard microelectronic technologies permits not only separating CNTs differing in a conductance type but also aligning them with respect to each other as a prerequisite for creating highperformance transistors. CNTs with different sorption characteristics were separated by a method commonly used in microelectronics to deposit thin coatings on silicon plates for photolithography or plasmochemical etching. To this effect, a functional coating solution is fed onto a rapidly rotating silicon plate and the plate is then dried in an oven. As a result, the plate becomes covered by a thin homogeneous layer of a given substance. American researchers [127] proposed covering a rapidly rotating plate with a CNT suspension in an organic solvent. Under the action of the centrifugal force, the nanotubes are flung along the surface to the periphery of the plate or beyond its edges, but some of them adsorb better than other and are halted on the plate longer, thus permitting their separation. The plate surface is preliminarily treated, so as to impart the necessary chemical properties to it. This process, called surface modification in chemical technologies, was realized utilizing a special class of compounds-silansthat adhere to the silicon surface by forming a strong chemical bond and carry a functional organic group determining in the long run the chemical properties of the plate surface. It turned out that surface modification by phenyl radicals facilitates adsorption of metallic CNTs, whereas the carbon skeleton having an amine functional group fairly well adsorbs semiconducting nanotubes.

Direction of cutting of the test sample

sample in epoxide resin (nanotubes remain entangled). (Taken from Ref. [128].)

Lines of expected MWNT orientation By adjusting centrifugation conditions, the researchers were able to completely separate different types of CNTs at the plate surface. Moreover, they revealed that their method permitted at a time aligning over 70% of the tubes along a certain direction, with only less than 10% of them undergoing deflection. Thus, a rather simple and long-developed industrial technique can be applied to fabricate CNTs sorted out and aligned on a substrate.

Researchers from Sydney University, Australia proposed a new method for separating and lining up CNTs in a polymer matrix [128]. It is well known that the introduction of CNTs into polymers yields composite materials with markedly improved properties. However, most composites contain randomly oriented and substantially entangled CNTs. Nanotubes are usually dispersed by US treatment in such solvents as acetone, but this method is inefficient: CNTs either remain entangled or break down into small fragments and become defective (after prolonged treatment). Besides, it is difficult to fabricate a reinforced composite from short CNTs. Furthermore, it is important to have composite materials containing unidirectional CNTs.

A variety of methods have been proposed to texturize nanotubes, including mechanical stretching [129], centrifugation [130] and alignment in a magnetic field [131]. However, the fact that the viscosity of the matrix has a profound effect on both separation and texturization was disregarded.

With this in mind, the authors of Ref. [128] developed an efficacious mechanical method for simultaneous separation and texturization of long entangled CNTs in epoxide resin (Fig. 16). They prepared composites of epoxide resin and MWNTs, placed them between two steel disks, and exerted a

60 nm

Figure 16. Illustration of a mechanical method for simultaneous separation and texturization of long entangled CNTs in epoxide resin: (a) schematic of CNT texturization in a matrix after exerting the shearing force; (b) CNTs are oriented in the direction of shear (from left to right); (c) cross section (A-A in Fig. 16a) through a solid mass of oriented MWNTs in the matrix (arrows indicate broken CNTs), and (d) randomly distributed CNTs of the control

а

Direction of disk rotation b

constant shearing force on them with a rate of 0.22 s^{-1} (Fig. 16a). The figure shows MWNTs aligned in the direction of the shear (Fig. 16b) or transversely (Fig. 16c), with fairly well visualized cross sections. For comparison, a similar composite undergoing no shear is presented in Fig. 16d, where CNTs remain entangled. The authors elucidated that efficacious texturization and separation are feasible if definite viscosity is imparted to the matrix by the addition of a curing agent. As expected, the characteristics (e.g., bending modulus) of the composite containing unidirectional CNTs proved better than in the control sample. Moreover, the addition of MWNTs decreased the formation rate of cross-linking bonds in the epoxide resin.

High-resolution TEM, SEM, and SPM are the principal methods for measuring the purity of CNT preparations. Results of TGA and differential thermal analysis (DTA) can also be used to evaluate the degrees of purification and functionalization of CNTs.

Thermogravimetry [132] represents an analytical technique that measures changes in the sample weight depending on the sample's temperature in the conditions of a programmed variation of ambient temperature. A TGA facility consists of a thermobalance (for continuous gravimetry), an oven wherein the sample is enclosed, temperature-measuring instruments (thermocouples with self-recording devices), and a programmed thermoregulator. Two scenarios of thermogravimetric experiments are feasible: isothermal (at a constant oven temperature), and a more popular dynamic one (at a varied oven temperature and a constant, as a rule, heating rate). Both scenarios yield time and temperature dependences of sample weight variation (thermogravimetric curve) or its rate (differential thermogravimetric curve).

Differential thermal analysis is applied to investigate physical and chemical transformations accompanied by heat release or consumption. The essence of the method consists in measuring the temperature difference between the sample of interest and the reference one, simultaneously subjected to identical heating or cooling. Reference samples are usually made of inert materials having thermal capacity and conductivity similar to the same characteristics of the study sample and undergoing neither structural nor phase changes in a given temperature range. For this reason, the temperature difference between the study and reference samples arising from their simultaneous heating or cooling is caused by endoor exothermal transformations or reactions in the material being tested. A detailed description of instruments for DTA is available at the site www.netzsch-thermal-analysis.com/ru/ products/differential-scanning-calorimeter, in textbook [133], and (as applied to nanotubes) at the Nanometer site (www.fnm.msu.ru/documents/1/nanometr1) and in textbook [134].

Optical absorption spectroscopy and TGA were employed in Ref. [135] to study the thermal stability of rough and purified SWNT samples obtained by gas-phase decomposition of CO on Fe particles under high pressure (HiPCO method). Analysis of optical absorption spectra showed that thermal oxidation of the starting material occurred relatively rapidly and uniformly due to the catalytic effect derived from the presence of Fe particles. The onset of CNT breakdown in the initial and purified samples occurred at ~ 250 and ~ 300 °C, respectively. Metallic SWNTs were oxidized faster than semiconducting ones.

Researchers at the National Institute of Standards and Technology (NIST, USA) developed a new sensitive expressmethod for the evaluation of the CNT quality [136]. CNT properties are known to vary considerably with size, homogeneity, and degree of purification. The effectiveness of the new method was assessed by electron microscopy. The micrographs thus obtained show the inhomogeneous structure of the material, including large amounts of other allotropic forms of carbon, and traces of metal particles (residues of catalysts used in the manufacturing process).

In the method being described, the CNT-containing material is deposited on a quartz crystal. The crystal is gradually heated to remove various carbon components of the study material (allotropic carbon modifications) having different evaporation temperatures. As a result, the mass of the material on the crystal changes. Measurement of the crystal's resonant frequency reveals vibrations proportional to the mass of the deposited material, allowing its stability to be evaluated at different temperatures. Sensitive elements based on quartz crystals, allowing detection of nanogramscale changes in the mass, were widely used in the past to identify various gaseous and liquid substances, including toxic ones.

Researchers at NIST verified the new method utilizing tens of samples of commercial CNTs, and compared the results with those obtained by the standard thermogravimetric technique. They used electron microscopy to gather additional information about the CNTs of interest.

The two methods yielded similar data, but the new simpler one allows nanogram samples to be analyzed, in contrast to the milligram quantities required in the standard TGA approach.

5. Conclusions

Comprehensive investigations into the nature of CNTs are underpinned by analysis of their structural order and stability, as well as the quantitative and qualitative determination of both well-known and quite new properties depending on the conditions of synthesis and functioning.

The advent of CNT-based nanoelements required the development of new methods and devices for studying their properties and brought to life a new field of research — nanodiagnostics. The author of Ref. [137] defines nanodiagnostics as the totality of specialized research techniques designed to study the structural, morphotopological, mechanical, electrophysical, optical, and biological properties of nanomaterials and nanosystems, to analyze nanoquantities of substances, and to measure the metric parameters with nanoscale accuracy. In other words, the functionally significant features of nanodiagnostics include accuracy and sensitivity at the nanolevel, as well as the possibility of studying nanoquantities of substances.

The most popular methods of CNT research presently in use are high-resolution transmission electron microscopy, scanning tunneling microscopy, atomic-force microscopy, Raman scattering spectroscopy, Auger electron spectroscopy, X-ray photoelectron spectroscopy, and a dozen others.

They need to be supplemented by express-methods to control CNT chemical composition and geometry, the properties of CNT-based nanoobjects, their electrical, magnetic, and acoustic fields, and the physical and chemical properties, with special reference to the ways the 'nanoworld' manifests itself compared with traditional microscopic objects [137], such as:

• unusual forms of symmetry and specific interfaces;

• the predominance of self-ordering and self-organization phenomena over artificial organization processes;

• high 'field' (electrical, magnetic) activity and 'catalytic' (chemical) selectivity of the surfaces of CNT-based ensembles, including integrated compositions of inorganic and organic origin;

• the peculiar character of energy and charge transfer processes characterized by low energy consumption and high rate.

Of great importance are procedures with which CNT samples are prepared, currently dominated by high-temperature synthesis techniques. It is far too premature to speak about standardization of these methods, but it will doubtless be needed when standard research equipment and computerized data analysis come into wide use.

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