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Non-carbon nanotubes: synthesis and simulation

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Abstract. The discovery of a new allotropic form of carbon, extended nanometre-sized quasi-unidimensional tubular structures (carbon nanotubes), as well as broad prospects for the use of nanomaterials based on them initiated numerous studies in the search for, and design of, nanotubular structures based in other compounds. Some properties and the main methods for the synthesis of non-carbon nanotubes are considered. Studies on the simulation of the electronic structures of these unique objects are analysed. Results of experimental and theoretical studies along these lines are discussed. The bibliography includes 328 references.

I. Introduction

Intense studies on the nanotubular form of matter [tubulenes or nanotubes (NT)] have started following the discovery in 1991 of hollow cylindrical carbon-based structures, the lengths of which were several orders greater than their diameters, in cathodic condensates formed upon electrical arc discharge between graphite electrodes.[1] The new quasi-unidimensional carbon cluster was called 'fullerene tubulene' and its electronic spectrum (ES) was calculated.[2] It was found that the electronic spectrum of the carbon tube studied was characteristic of metals.

From the very beginning, considerable attention by experimenters and theoreticians was given to nanotubes as representatives of a new quasi-unidimensional allotropic modification of carbon in the series of previously known modifications, *viz*., $3D$ (diamond) $\rightarrow$ $2D$ (graphite) $\rightarrow$ $1D$ (carbyne) $\rightarrow$ $0D$ (fullerene). With time, nanotubes, which were exotic objects of unique experiments and theoretical calculations, became the subject of numerous physicochemical studies; their unusual properties became the basis for many daring technological solutions. At present, NT find broad practical application; now they are commercial products and are subject to marketing studies.

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Data on the structures and properties of carbon nanotubes, on the methods of their synthesis and on their uses can be found in many publications; they have been generalised in a number of monographs (see, *e.g*., Refs 3 – 7) and in many reviews (see, *e.g*., Refs 8 – 32).

In a number of reviews recently published in Russian scientific journals,[15, 16, 21, 24 – 27] the methods of synthesis and study of carbon NT were discussed.[15, 16] The main principles of the theoretical simulation of the geometrical and electronic structures of NT were described in a monograph [7] and in papers.[21, 26] The methods for the synthesis of such NT were described in detail by Rakov.[24] He also reported the most recent data on the chemistry and application of carbon NT considered as promising materials for modern technologies. Tarasov *et al*. [25] discussed the possibility of use of NT as 'tanks' for the storage of hydrogen. Basic information about carbon NT can be found elsewhere. [33, 34]

Shortly after the paper by Iijima [1] was published, scientists were challenged by a number of questions that are of major importance to the development of the physics and chemistry of NT and for the prospects of their practical application.

1. What is the nature of NT and what is the mechanism according to which they are formed? Are there any physical or chemical restrictions limiting the scope of compounds which can be obtained in a nanotubular form?

2. What physicochemical properties should a compound possess to be a potential initial substance for the synthesis of NT?

3. What are the specific features of methods that can be used to obtain non-carbon NT? What is their value in materials science and technology?

From the very start, the concept of non-carbon NT was developed due to combined efforts of experimenters (syntheses of NT and studies of their functional characteristics) and theoreticians (simulations of new nanotube forms, prediction of their structures and properties).

In 1992, the first non-carbon NT based on lamellar molybdenum and tungsten disulfides were synthesised.[35] In 1994, the possibility of existence of tubulenes based on hexagonal boron nitride (BN-nanotubulenes) was predicted.[36 – 38] Their dielectric properties were presumed to remain stable upon changes in their geometrical characteristics. This prediction was very important for the development of nanoelectronics; it initiated numerous studies on the synthesis of such NT.

A large number of non-carbon NT have been synthesised to date or their existence has been predicted. In addition to the NT mentioned above, others based on germanium silicide and tran-

sition metal dichalcogenides, sulfides and chlorides have been synthesised. The molecular and electronic structures of various hypothetical NT containing boron, phosphorus, silicon, germanium and transition metal diborides were simulated; the mechanisms of their growth were discussed and the properties of certain nanotubular structures were studied.

Boron–nitrogen and dichalcogen-containing NT were the subject of special analysis.[12,29] Some data on the synthesis and properties of non-carbon NT can be found in monographs [5,7,8] and reviews [11,14,19,21,24] devoted to carbon tubulenes.

The present review discusses the general state of studies on the synthesis and simulation of the molecular and electronic structures of non-carbon NT which were developed most intensely in the last years.

Along with the 'purely non-carbon' NT listed above, we also consider the class of 'transitional' nanotubular structures containing both carbon and other *p*-elements (boron, nitrogen and silicon). These NT possessing diverse properties can either be obtained together with carbon NT within the same synthetic procedure or synthesised using methods specifically developed for this purpose. Of these, chemical substitution is the most promising method in which carbon NT are used as the starting material.

The overwhelming majority of non-carbon NT have been obtained (or their synthesis is anticipated) on the basis of compounds that, like carbon, have lamellar (quasi-two-dimensional) crystal structures. Therefore, classifications and descriptions of atomic structures of non-carbon NT are performed, and their geometrical models are built,[7,12,21,29] on the basis of the concepts and methods developed for carbon NT.[3–10,15–32] Let us summarise briefly those to be employed below.

Ideal carbon NT have the form of cylinders whose walls are formed by hexagons, with carbon atoms in the vertices. The process of formation of a nanotubulene can be visualised as the rolling of a 'band' of carbon atoms cut out of a graphite monolayer (graphene network). A graphite layer can be 'cut' in different ways: along lines which are perpendicular to the C–C bonds or pass through these bonds, or else at a definite angle, namely the so-called chiral angle θ (Fig. 1 *a*). As the resulting 'bands' roll and their edges are linked together, two main NT types appear, *viz*., non-chiral and chiral. The so-called zigzag and dented non-chiral NT are distinguishable. The structures of the main NT types are shown in Fig. 1 *b*.

Using the base vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ of the graphene network, the following vector can be defined:

$$\mathbf{c}_h = n\mathbf{a}_1 + m\mathbf{a}_2 .$$

The main geometrical parameters of a tubulene, *i.e*., the diameter (D) and the chiral angle (θ), are related unambiguously to the base vectors of the graphene network through the following relationships involving the indices n and m:

$$D = \frac{|\, c_h \,|}{\pi} = a\sqrt{\frac{3(n^2 + m^2 + mn)}{\pi}},$$

$$\theta = \arctan\left(-\frac{\sqrt{3}m}{2n + m}\right),$$

where a indicates the interatomic distances in the planar network.

In terms of these indices, the corresponding NT are denoted as (n,m)-NT. All (n,m)-NT with $0 < \theta < 30^\circ$ are regarded as chiral (spiral). Non-chiral NT have $\theta = 0$ and 30°. At $\theta = 0$, a family of zigzag-shaped (n,0)-NT is formed; these were named according to the type of tube 'cross-section' (see Fig. 1). The chiral angle for the dented (n,n)-NT equals 30°.

The NT ends may be open or closed by 'caps' formed by fullerene hemispheres. Other (*e.g*., conical) 'cap' types are also possible. Single-layer and multilayer NT are known. The latter can consist of a system of concentric tubulenes or have a scroll-type structure. Nanotubes can be single or form diverse aggregates

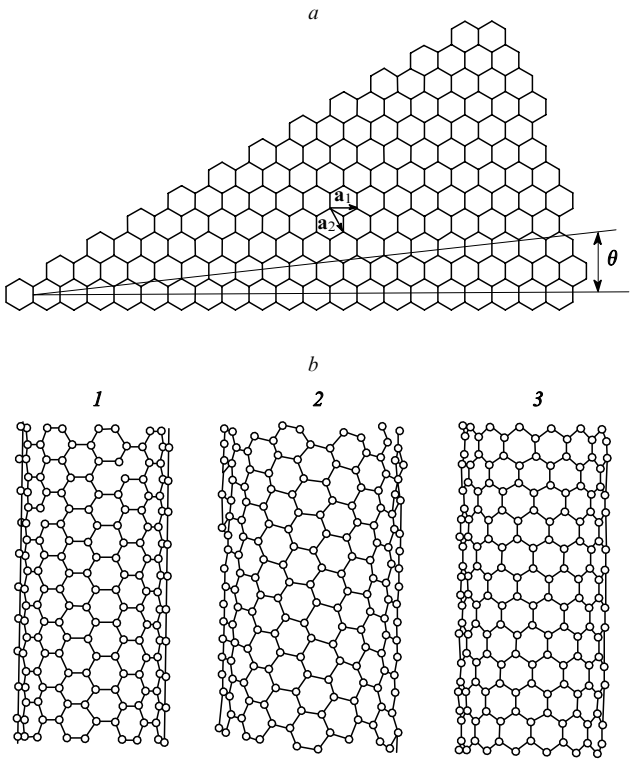


Figure 1. Model for the NT formation upon graphene layer rolling into a cylinder (*a*) and nanotube types (*b*).
NT: (*1*) non-chiral dented (n,n); (*2*) chiral (n,m); (*3*) nonchiral zigzag-like (n,0).

(braids, splices, *etc*.) that may involve other nanospecies (fullerenes). Many possible aggregates formed by carbon NT are described in a review by Rakov.[24] The majority of NT contain various defects (topological defects, rehybridisation defects, 'broken' bonds). Directed introduction of defects into NT makes it possible to adjust flexibly their functional properties. More detailed information about NT types, their geometry, and their properties mentioned above can be found in a number of papers.[3–32]

The material of this review is organised according to the following scheme. First, modern methods for the synthesis of non-carbon NT are considered. Further, we describe methods for the preparation of nanotubulenes from *p*-element compounds (BN, BC_x, CN_x, $B_xC_yN_z$), which are most structurally similar to carbon NT, and other classes of chemical compounds (transition metal dichalcogenides and oxides). Finally, we characterise methods (template synthesis and film 'folding') which are rather versatile and can be suitable for the synthesis of NT based on various melts and inorganic compounds.

After that, we discuss the results of theoretical simulation of the molecular and electronic structures of non-carbon NT by the methods of quantum chemistry and molecular dynamics. Data on the structural features and possible methods for the synthesis of hypothetical NT based on boron, silicon, phosphorus, CN_x, GaN, transition metal dichalcogenides and diborides and 'hybrid' nanotubular structures are considered. Special attention is paid to predictions of NT stability and properties. Data on the electronic properties of a number of NT formed in the B–C–N system are briefly discussed.[7,21]

Data about the physicochemical properties of non-carbon NT are far from being exhaustive yet, and their analysis is beyond the scope of this review. Some of the most interesting parameters of certain groups of non-carbon NT are briefly mentioned in the corresponding sections.

II. Methods for the synthesis of non-carbon nanotubes

1. Synthesis of nanotubes in the B–C–N system

The structures of nanotubes formed in the B–C–N system are similar to those of carbon tubulenes. The review of the methods for the synthesis of such non-carbon NT is given using the sequence in which the methods for the synthesis of carbon NT were considered by Rakov.[24] This will allow us to compare the potential of 'traditional' (for carbon NT) synthetic methods to that of new methods suggested for the synthesis of non-carbon NT.

a. Electric arc synthesis

Electric arc synthesis is the simplest method widely used for the synthesis of carbon NT (see Refs 9, 11, 15, 16, 24, 32). Numerous attempts to use this method for the synthesis of nanotubulenes in the B–C–N system have been reported. Of course, the standard method [11, 15, 24] should be modified so as to ensure the introduction of not only carbon but also boron and nitrogen into the reaction zone. As a rule, this is done using an appropriate composition of air (*e.g.*, the synthesis is performed in a flow of nitrogen) and/or of the electrode.

Since boron nitrides are insulators,[7, 36–38] in pure form they are unsuitable for the preparation of electrodes. BN-Nanotubulenes were first obtained in an electric arc discharge (in a helium atmosphere) between a copper cathode and an anode made of boron nitride enclosed in a tungsten shell.[39] The cathodic deposit was found to contain a wide variety of boron–nitrogen nanostructures with diverse morphology, including BN-nanotubulenes. The tubes consisted of a number of layers (the inner and outer diameters varied from 1 to 3 and from 6 to 8 nm, respectively, and the distance between the walls was ~0.33 nm); their lengths exceeded 200 nm. The ends of NT were 'capped' with tungsten-containing nanoparticles (which presumably consisted of tungsten borides or nitrides). The growth mechanism of BN-nanotubulenes was assumed [39] to involve catalysis by metal atoms.

A number of boron-containing phases, *e.g.*, ZrB_2 and HfB_2, have been studied as electrodes for the electric arc synthesis of NT in a flow of nitrogen.[40–43] In the latter case, the plasma contained metal atoms, which could serve as growth catalysts for BN-nanotubulenes.

Cumings [44] reported a high-performance method for the synthesis of NT based on BN; the electrodes consisted of elementary boron (99 at.%) and admixtures of cobalt or nickel (up to 1 at.%), which served as catalysts. The pressure of nitrogen in the chamber was kept at 380 Torr; the current was 60 A. The residue on the cathode arranged on the bottom of the chamber was grey; a thin layer of the product was also found on the chamber walls. Analysis of the structure of the product obtained showed that it contained only double-layer NT (with diameters of the outer and inner BN-cylinders equal to 2.9 and 2.2 nm, respectively, and with a distance of ~0.37 nm between their walls). These tubes formed bunches (bundles). No metal admixtures were found in the NT; the stoichiometric composition of the tubes matched the ratio B : N = 1 : 1. It should be noted that double-layer NT were also obtained from BN using HfB_2 cathodes.[40] The growth mechanism and kinetics of such double-layer NT have not been ascertained.

Using scanning electron microscopy (SEM), it was found that NT bundles are often joined to form 'knots' that have their own structures. These junctions consist of boron nanocrystals coated by multilayer shells, *i.e.*, the specific cocoons. Nano-cocoon layers are formed by graphite-like boron nitride. Cumings [44] suggested a method for removal of boron nanocrystallites from nanococoons; as a result, the latter become empty and resemble the well-known carbon 'onion-bulb' structures, the so-called onions.[3–6] It was suggested that hollow BN-nanococoons should be considered as a new nanomaterial for chemical and electrochemical industries. It is possible to vary the properties of such material deliberately by filling the cocoons with definite atoms or molecules.

Vaporisation of porous BC_4N was accompanied by simultaneous formation of carbon, BN- and mixed BNC-nanotubulenes;[45] however, homogeneous boron carbonitride NT could not be obtained, probably, because of differences between the vapour pressures of gaseous boron nitrides and carbon.

b. Laser synthesis

In addition to such methods to obtain carbon NT as vaporisation of the target (graphite) under electron and ion beams, sunlight, Joule heat (resistance vaporisation), yet another method became popular,[24] *viz.*, ablation of targets under laser irradiation. Attempts to use laser irradiation for the synthesis of nanotubulenes containing B, C and N have been reported.[46, 47] Hexagonal BN served as the target and high pressure of nitrogen was maintained in the chamber. The products contained BN-nanotubulenes and particles of cubical boron nitrides. A CO_2 laser was used to synthesise single-layer BN-nanotubulenes on a multigram scale.[48] It was found that the zigzag-shaped tubes form bunches; furthermore, small amounts of double-layer BN-nanotubulenes and fullerene-like clusters of boron nitride were detected.

Nanotubes (and nanoparticles) containing B, C and N atoms were also obtained by other methods of target irradiation. For example, electron microscopy allowed Golberg *et al.*[49] to observe *in situ* the formation of single- and multi-shell fullerene-type nanoparticles of boron carbide upon exposure of lamellar BC_3 to an electron beam; it cannot be ruled out that a densely packed structure, *viz.*, diamond doped with boron, was formed inside these particles. Proton–ion bombardment of boron pyronitride resulted in a microcomposite material which incorporated blocks of BN-nanotubulenes and possessed enhanced plasticity.[50]

c. Pyrolytic synthesis

Catalytic pyrolysis of hydrocarbons in the presence of metal catalysts is becoming one of the most widespread and promising methods for the synthesis of carbon NT.[24]

Pyrolysis of a $CH_3CN–BCl_3$ system in the presence of a cobalt powder at ~1270 K was first used [51] to obtain nanotubulenes and nanofibres with diverse morphologies and compositions. More detailed studies [52] of the reaction

$$CH_3CN–BCl_3 \xrightarrow{\Delta} BC_2N + 3\,HCl$$

showed that its products contained NT whose composition was close to BC_2N. However, the composition homogeneity was violated considerably in the NT walls and spontaneous separation occurred (presumably, during the NT growth) to give C/BN 'islets'. The most stable NT contained BN layers separated by graphite-like carbon layers.[52]

Sen *et al.* [53] found systems suitable for the synthesis of BCN- and CN-nanotubes using the pyrolytic method. These were obtained using the 1 : 1 $(CH_3)_3N–BH_3$ adduct and pyridine, respectively. The reactions were carried out at ~1270 K with cobalt as a catalyst. The products contained nanotubes with diverse chemical compositions and morphologies.

Pyrolysis of a mixture of acetylene with diborane (in an atmosphere of helium and hydrogen) [54] gave boron-containing carbon NT whose compositions varied from $C_{35}B$ to $C_{50}B$. The boron content in such tubes was close to the nitrogen content in CN-nanotubulenes.[53] Nitrogen-containing carbon NT were also found in products of catalytic pyrolysis of triazine.[55] Ma *et al.* [56, 57] used $B_4N_3O_2H$ as the precursor for the synthesis of BN-nanotubulenes.

d. Substitution reactions

Han *et al.* [58–60] described a new chemical method for the synthesis of NT based on replacement of carbon atoms by nitrogen and/or boron atoms in carbon NT. Carbon tubes obtained by one of the known technologies were used as the starting materials. This

method was employed to obtain a wide variety of boron–carbon (B_xC_{1-x}), boron–carbon–nitrogen ($B_xC_{1-x-y}N_y$) and boron–nitrogen (BN) multi- and single-layer NT, as well as their bundles.[58–66]

For example, Han *et al.*[60] synthesised ($B_xC_{1-x-y}N_y$)-nanotubes using a mixture of B_2O_3 with a product of arc synthesis which contained up to 70% carbon NT, together with fullerene-like nanoclusters and amorphous carbon with an admixture of particles of the metal catalysts (Fe/Ni). The reactions were carried out in a flow of nitrogen in the temperature range 1523–1803 K. The products were analysed using transmission electron microscopy and electron energy loss spectroscopy (EELS) (Fig. 2).

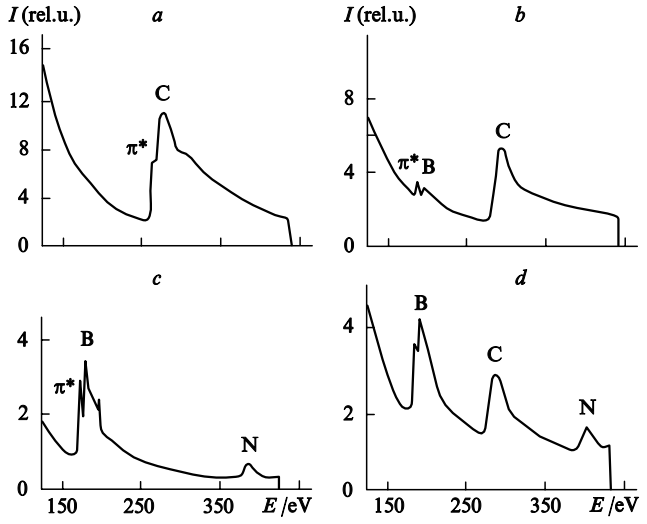


Figure 2. Electron energy loss spectra for the original carbon NT (*a*), NT with the composition B_xC_{1-x} ($x \approx 0.1$) (*b*), 'stoichiometric' BN-nanotubulenes (*c*), nanotubes $B_xC_{1-x-y}N_y$ ($x = y \sim 0.1$) (*d*) obtained by chemical substitution.[60]
The characteristic peaks in the spectra correspond to the presence of the respective elements, *viz.*, B, C and N.

Heating at 1523 K for 30 min resulted exclusively in boron–carbon NT (with the ratio B : C $\approx$ 0.1) joined as bundles. A mixture of single-layer (B_xC_{1-x})-, ($B_xC_{1-x-y}N_y$)- and BN-nanotubulenes was obtained at higher temperatures ($\sim$1623 K). On subsequent increase in temperature (to 1803 K), the original carbon NT was destroyed completely; the resulting major fraction was a mixture of hexagonal, rhombohedral and turbostatic boron nitride with insignificant admixtures of nano-sized BN-structures: nanocones, polyhedral nanoclusters and nanofibres. No formation of BN-nanotubulenes was detected. The morphology of the BCN-nanotubulenes obtained resembled that of the original carbon NT in many respects. ($B_xC_{1-x-y}N_y$)-Nanotubulenes were also obtained[67] as reaction products of carbon nanotubulenes and CN_x-nanotubulenes with B_2O_3 and ammonia. The reactions leading to BC- and BN-nanotubulenes can be described[58,59] by the following equations:

$$x\,B_2O_3 + (2+3x)\,C\ (\text{nanotubes}) \longrightarrow$$
$$\longrightarrow 2\,B_xC\ (\text{nanotubes}) + 3x\,CO,$$
$$B_2O_3 + 3C\ (\text{nanotubes}) + N_2 \longrightarrow$$
$$\longrightarrow 2\,BN\ (\text{nanotubes}) + 3\,CO.$$

The maximum boron content in (B_xC_{1-x})-nanotubulenes did not exceed $\sim$10 at.%. The bundles in ($B_xC_{1-x-y}N_y$)-nanotubulenes differed in the C : (B + N) ratios (Fig. 3). In certain cases, the 'stoichiometry' of N : B $\approx$ 1.0 was reached. This is due to the selective character of substitution:[60] the probability that 'pure' BN-nanotubulenes (or, at least, boron–nitrogen clusters in the

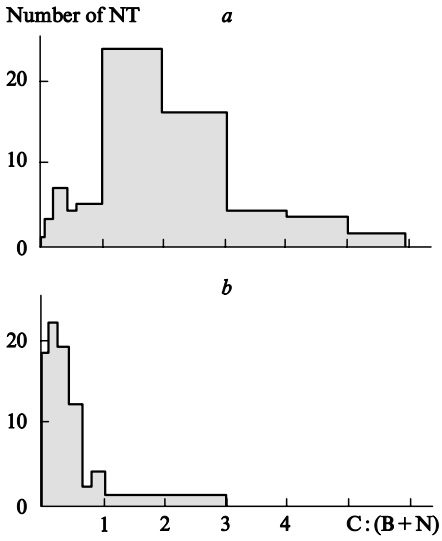


Figure 3. Composition histogram of multilayer BCN-nanotubulenes synthesised by chemical substitution from carbon NT (at 1773 K in a flow of nitrogen);[63]
(*a*) without oxides, (*b*) in the presence of MoO_2.

walls of the original carbon NT) are formed is much higher than the probability of NT formation if the replacement of carbon atoms by boron and nitrogen is purely statistical.

An interesting result was obtained by Han *et al.*[60] Inside single-layer BN-nanotubulenes, endohedral polyhedral BN-nanoclusters, described as four-shell octahedral BN-fullerenes with the composition $B_{12}N_{12}@B_{76}N_{76}@B_{208}N_{208}@B_{412}N_{412}$ (resembling carbon onion structures), were detected.[68] Similar hybrid nanotubular structures consisting of fullerenes located inside carbon NT ($C_n@C$) and carbon NT incorporating endofullerene chains ($M@C_n@C$) were also reported.[69,70]

Attractive features of the method suggested by Han *et al.*[58–61] are its ease and efficiency. The potential of the method is only limited by the amount of the original material available, *viz.*, carbon NT. Yet another important factor is the fixed size of the NT obtained in the system B–C–N, which is determined by the parameters of the matrices, *i.e.*, the carbon NT. The obvious drawback of the method is that it is difficult to synthesise NT with homogeneous chemical compositions.

This method was further developed[63,65,66] and used for the synthesis of bundles of multilayer BN-nanotubulenes. A mixture of carbon NT and boric anhydride was complemented with MoO_3 (see Ref. 63) or a mixture of MoO_3 with PbO (see Ref. 65) or MoO_3 with V_2O_5;[66] the process was conducted in a flow of nitrogen at 1503–1773 K. Analysis of the reaction product involving molybdenum trioxide by transmission electron microscopy (TEM) showed that it contained bundles of multilayer BN-nanotubulenes, the major fraction of which (up to $\sim$82%) had non-chiral zigzag geometry.[66] The ends of such NT were open in contrast to the NT obtained[58–60] in the absence of metal oxides.

The following scenario of the growth of BN-nanotubulenes was suggested,[66] taking into consideration that transition metal oxides are efficient oxidants for carbon. In the first stage, the terminal structures ('caps'), which close the carbon NT, are removed.

$$3\,C + B_2O_3 \longrightarrow 2\,B + 3\,CO,$$
$$3\,C + MoO_3 \longrightarrow Mo + 3\,CO,$$
$$5\,C + V_2O_5 \longrightarrow 2\,V + 5\,CO.$$

As a result, the gas phase can access the intra- and interlayer space of multilayer carbon NT. Further, carbon is simultaneously replaced outside and inside the carbon NT (Fig. 4). These

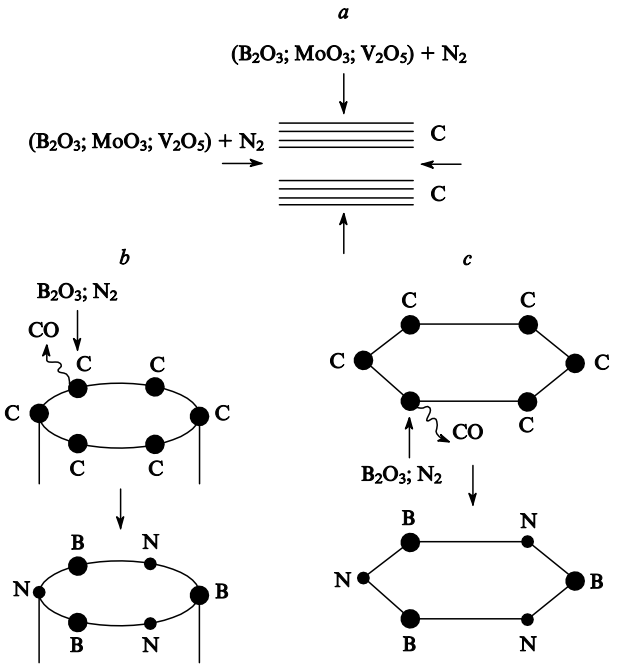


Figure 4. Scheme of the reaction of oxides and N_2 with multilayer carbon NT (*a*) in the reaction with its 'open' end (*b*) and its side surface (*c*) during chemical substitution in the synthesis of BN-nanotubulenes.[66]

processes mostly involve the diffusion mechanism;[71] as a result, growth of BN-nanotubulenes occurs.

High-resolution TEM was used to study the structure of BN-nanotubulene bundles obtained in the presence of PbO as the activator.[72] All NT had zigzag geometry, their diameters ranged from 20 to 30 nm and their axes were arranged strictly parallel. It was suggested to consider this product as a new nanomaterial. It is characterised by invariable dielectric parameters and low chemical reactivity (in comparison with carbon NT).

High-resolution TEM analysis of the structures of multilayer BN-nanotubulenes showed that 'packs' of adjacent layers with hexagonal and rhombohedral types coexist, the wall structure changes from dented to zigzag-shaped and noticeable polygonisation of NT cross-sections takes place.[73]

The substitution method was also used to obtain 'nanocables', *i.e.*, BN-nanotubulenes filled with an alloy of Ni (40%) and Fe (60%).[74] In the first stage, carbon NT with nanoparticles of the alloy at the ends were obtained. These NT were then placed in a mixture of gaseous B_2O_3 and N_2 and kept for 30 min at the melting point of the alloy (1723 K). Two processes occurred simultaneously, *viz.*, filling of the cavities with the iron–nickel alloy (due to the capillary effect), and change in the composition of the tube ('shell') due to chemical substitution.

It should be noted that the first SiC-nanotubulenes were obtained using the substitution reaction.[75] Large-diameter carbon NT and gaseous SiO were used as the starting materials.

e. Miscellaneous methods

A number of methods for the synthesis of BCN-nanotubulenes based on thermal reactions have been suggested.

Carbothermal reduction of amorphous boron oxide with simultaneous nitridation (at 1373–1723 K)[76] gave a product containing cylindrical BN-nanotubulenes with various configurations (including bent or kinked ones, T-shaped, 'bamboo-shaped') and nanostructures in the form of concentric truncated cones. The overall reaction can be described by the following equation:

$$B_2O_3(\text{amorph.}) + 3\,B_4C + 7\,N_2 = 14\,BN + 3\,CO.$$

Cylindrical (closed) multilayer NT formed bundles; their junctions contained multi-shell onion-type BN-particles which served as growth centres. The tube diameters ranged from 10 to 500 nm; the length-to-diameter ratios ranged from 3 to 30. Nanotubes grew both in the gas and in the solid phase. The growth of bamboo-shaped NT involved alternation of cylindrical and onion-type fragments:

NT – onion – NT – onion.

It was assumed that certain structures incorporated B_3N_4 heptagons, which ensured contacts at the junctions of cylindrical fragments. The obvious drawback of this synthetic method is that the forms of the nanotubulenes obtained are too diverse and that no method to control the formation of NT with required parameters is available.

Nanotubes and nanocones based on BN were also obtained by thermal treatment of rhombohedral β-boron at 1470 K in the presence of graphite-like boron nitride and lithium vapour.[77] Growth of zigzag-shaped NT was observed at the edges of graphite-like BN particles. BN-Nanofibres were found to appear upon annealing (~2000–2370 K) of BN powder in the presence of iron.[78]

2. Dichalcogenide nanotubulenes

Transition metals dichalcogenides MX_2 (X = S, Se, Te) were the first inorganic compounds to attract the attention of researchers as compounds that are potentially suitable for the synthesis of tubular nanostructures. These compounds have a distinct quasi-two-dimensional structure. For example, molybdenum and tungsten disulfides have lamellar structures (of the MoS_2 type, space group $P6_3/mmc$) consisting of packs of S–(Mo,W)–S layers; the metal atoms are in a trigonal-prismatic environment[79] and the layers are packed due to van der Waals forces.

Numerous NT based on tungsten, molybdenum and niobium dichalcogenides have been synthesised to date, mostly by chemical methods.

The formation of fullerene-like species and fragments of cylindrical nanostructures consisting of WS_2 and MoS_2 was first observed upon thermal treatment of tungsten or molybdenum films on quartz substrates in a flow of H_2S/H_2.[35,80] Remskar *et al.*[81,82] used chemical transport reactions to obtain MoS_2 and WS_2 cylindrical nanocrystals and tubular structures (MoS_2 microtubes several millimetres long with wall thickness smaller than 0.1 μm). Galvan *et al.*[83–85] proposed a low-temperature (< 100 °C) activation method to obtain WS_2-nanotubulenes involving treatment of condensed tungsten disulfide with concentrated nitric acid. A new material consisting of WS_2-based NT was obtained using WO_x nanoparticles.[85]

In the synthesis of fullerene-like molybdenum disulfide particles, a gas phase reaction of MoO_{3-x} with H_2S at 1073–1223 K gave MoS_2-nanotubulenes as side products.[86,87] The tubes consisted of 5–10 MoS_2 layers on average, were several micrometres long and were mixed with MoS_2 (2H-polytype).

The methods for the preparation of dichalcogenide nanotubes (and nanofibres) and for the synthesis of fullerene-like polyhedral particles of these compounds are being developed in parallel.[88] Both NT and polyhedral hollow or filled nanoparticles of *d*-metal dichalcogenides are often obtained in a single experiment.

Molybdenum disulfide particles with 3–5 nm diameters were synthesised[89] by laser ablation of MoS_2 targets. Laser-induced vaporisation of tungsten and molybdenum disulfides in argon at 720–1320 K gave[90] various hollow and metal-filled multilayer nanoparticles. For example, the major fraction obtained upon vaporisation of WS_2 at 1320 K consisted of nanoparticles with 10–15 nm diameters containing 4–8 concentric layers of WS_2. The bulk of filled nanoparticles was found to contain a stabilised β-W phase, which is unstable under ordinary conditions, as the filler metal. In addition, the products contained tubular nanostructures.

Certain properties of dichalcogenide NT were summarised in a review by Zhu *et al.*[88] Hollow WS_2-onions are promising as solid lubricants;[89,91] their tribological properties can be optimised by filling the cavities with tungsten carbide. The synthesis of such 'composite' particles is based on the pyrolysis of WC nanoparticles in hydrogen sulfide.[92]

The properties of MS_2-nanotubulenes have not been studied in sufficient detail. It was found that disulfide nanotubes are semiconductors; they possess low chemical reactivities.[93] Normally, multilayer NT contain numerous defects in the outer layers, whereas the inner walls generally have nearly ideal structures, which is reflected in the conducting properties of NT.[94–96] The coalescence and the growth mechanism of WS_2-nanotubulenes to give 'braids' have been studied;[97] a method for changing the conducting properties of these NT under the effect of the substrate was suggested.[98] The application of WS_2-nanotubulenes in scanning microscopy was discussed;[99] several versions of the growth mechanism of these NT were suggested [100] and the adsorption of methane on their surfaces was studied.[101]

In addition to the syntheses of nanotubulenes based on transition metal disulfides, attempts were undertaken to obtain nanostructures of other dichalcogenides as well. For example, bombardment of niobium diselenide with electrons resulted in $NbSe_2$-nanotubulenes, a few nanometres long, closed on one end.[101,102] By varying the accelerating voltage and the current density, $NbSe_2$-onions were obtained as well. A similar technique was used successfully to synthesise $MoTe_2$- (Refs 103–106) and WSe_2-nanotubulenes.[102] Nath and Rao [107] considered a method to obtain NT by reduction of tungsten and niobium triselenides or by decomposition of ammonium selenometallates in an atmosphere of hydrogen. Recently, methods for the preparation of $CuInS_2$-nanotubulenes [108] and Bi_3Se_4-nanorods [109] were proposed.

3. Oxide nanotubes

Transition metal oxides are widely used to construct diverse nanostructured functional materials in the form of films, nanorods, and mesoporous materials.[110–122] Some of these nano-objects are obtained with the use of carbon NT. For example, filling the internal cavities of carbon NT with V_2O_5, MoO_3, PbO, or Bi_2O_3 particles followed by chemical removal of the carbon shell gave oxide nanofibres and nanotubular ceramics.[123–125]

Nanotubulenes of transition metal (vanadium and titanium) oxides have not been synthesised until recently.[126–133] The sol–gel method was found to be efficient for this synthesis [126–129] (for more detail about colloid methods to obtain nanostructures, see Refs 134 and 135).

Krumeich e*t al.*[126] used the sol–gel method to obtain multilayer vanadium oxide NT (VO_x-nanotubulenes). Ethanolic solutions of vanadium(V) triisopropoxide and an amine $C_nH_{2n+1}NH_2$ ($4 \leqslant n \leqslant 22$) or α,ω-diamine $H_2N[CH_2]_nNH_2$ ($14 \leqslant n \leqslant 20$) in the molar ratio 2 : 1 were stirred for 1 h in an inert atmosphere and hydrolysed. Ageing of the system for 12–96 h resulted in an orange composite, which gave a black product upon hydrothermal treatment for 2–7 days (at 450 K) in an autoclave. The composition, structure and certain properties of the product obtained were examined by X-ray diffraction, XPS and TEM and by magnetic susceptibility measurements.

It was found that the major components of the composites were nanostructures with tubular morphologies, whose outer and inner diameters were 5–50 and 15–150 nm, respectively, and whose lengths were up to 15 μm. Special experiments to study the cross-sections of the resulting VO_x-nanotubulenes showed them to be multilayered.[127,128] Both spiral (scroll-shaped) NT and those in the form of a set of concentric cylinders with organic molecules intercalated between the cylinders were detected. Spiral NT are formed most commonly. Mixed structures were also observed. Figure 5 shows the cross-section types of multilayer NT. The figure shows the defects of NT packs. Certain NT contain regions with parallel arrangement of VO_x-layers, both inside the tubes and in the vicinity of junctions between the adjacent tubes. The number of NT layers varies from 2 to 30; they are built of tetrahedra (VO_4) and of square pyramids (VO_5).[126] These polyhedra also serve as structural elements of the crystalline phases α-$V_{1.08}P_{0.92}O_5$, $(NH_4)_2V_3O_8$, $K_2V_3O_8$ and $BaV_7O_{16} \cdot n\,H_2O$. The distance between the adjacent NT layers (1.6–3.8 nm, Table 1) changes proportionally to the length of the alkylamine molecule serving as the intercalant. The overall molecular formula of NT can be written as $VO_xO_{y/2}[C_nH_{2n+4}N]_y$. Attempts to obtain 'pure' VO_x-nanotubulenes by removal of organic molecules upon thermal treatment are probably hopeless, as the tubes undergo complete degradation at temperatures > 520 K. It is more likely that amines can be replaced by cations of alkali or alkaline-earth metals (*e.g.*, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}). This method may become efficient for modifying the properties of VO_x-nanotubulenes. Replacement of monoamines by diamines in NT results in a noticeable decrease in the interlayer distances (from 1.6–3.8 to 0.9–1.0 Å). Specimens of the composite manifest semiconducting properties.

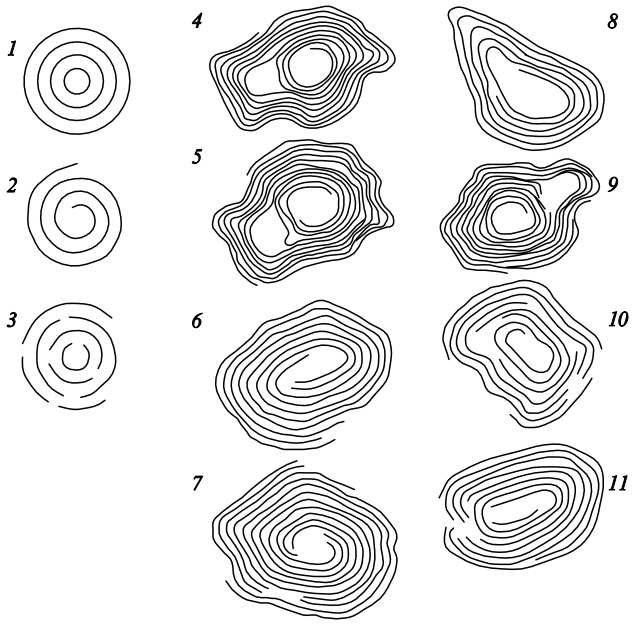


Figure 5. Models (*1–3*) and different cross-section structures (*4–11*) of multilayer NT;[127]
(*1*) concentric cylinders ('Russian matreshka'), (*2*) scroll, (*3*) 'papier-mache'; (*4–11*) typical cross-sections of vanadium-oxide NT.

Table 1. Chemical composition, distances between the VO_x-layers, magnetic moments of vanadium atoms (MM) and relative concentrations of V^{4+} ions in $VO_xO_{y/2}[C_nH_{2n+4}N]_y$-nanotubulenes.[126]

Composition	Interlayer distance /nm		MM /μ_B	$[V^{4+}]$ (%)
	XRD [a]	ED [a]		
$VO_{2.40}[C_4H_{12}N]_{0.25}$	1.66	1.58	1.16	45
$VO_{2.30}[C_6H_{16}N]_{0.27}$	1.96	1.62	1.41	66
$VO_{2.47}[C_{10}H_{24}N]_{0.27}$	2.50	2.17	0.99	33
$VO_{2.40}[C_{11}H_{26}N]_{0.27}$	2.59	2.16	1.20	48
$VO_{2.40}[C_{12}H_{28}N]_{0.26}$	2.77	2.21	1.17	45
$VO_{2.42}[C_{14}H_{32}N]_{0.27}$	3.02	2.43	1.13	42
$VO_{2.45}[C_{16}H_{36}N]_{0.26}$	3.20	2.63	1.03	35
$VO_{2.37}[C_{18}H_{40}N]_{0.26}$	3.48	2.86	1.25	52
$VO_{2.43}[C_{22}H_{47}N]_{0.30}$	3.80	3.16	1.18	46

[a] Data obtained by X-ray (XRD) and electron (ED) diffraction.

Two new methods for the preparation of VO_x-nanotubulenes from vanadium oxotrichloride and pentoxide as the starting compounds have recently been proposed.[130] Both processes are carried out in two stages. In the first stage, a solution of $VOCl_3$ (or V_2O_5) with the amine $C_nH_{2n+1}NH_2$ ($11 \leqslant n \leqslant 20$) is hydrolysed to give a gel; in the second stage, hydrothermal treatment is conducted to yield NT. If V_2O_5 is used, amines are directly intercalated between the pentoxide layers. The resulting NT can be described by the general formula $VO_{2.42\pm0.03}\cdot(C_nH_{2n+4}N)_{0.27\pm0.01}$ ($11 \leqslant n \leqslant 20$). If $VOCl_3$ is used, the general formula of the NT is $VO_{2.45\pm0.05}(C_nH_{2n+4}N)_{0.27\pm0.01}$ ($11 \leqslant n \leqslant 16$). The NT morphology is similar to that described above. The low cost of the product obtained is worth a special note.[130]

Pillai *et al.*[131] succeeded in synthesising a unique type of multilayer vanadium oxide NT with periodically alternating distances between the VO_x-layers by changing pH of the medium. Ammonia was added to the reaction mixture obtained upon hydrolysis of an ethanolic solution of vanadium(V) triisopropoxide to pH 10. The final product was obtained in accordance with the procedure described above (see Ref. 126). It was found that the outer diameters of the resulting NT (>250 nm) were much larger than those of the NT obtained without ammonia (at pH 4–8); however, the lengths of the former (2–5 μm) were much smaller than those of the latter. The walls of the NT obtained in the presence of NH_3 are composed of regularly alternating VO_x layers; between these, amine molecules and NH_4^+ are intercalated alternately (the VO_x-VO_x interlayer distances are 2.0 and 0.9 nm, respectively). The NT structures contain various defects, for example, violation of periodic alternations of the interlayer distances; in certain cases, breakdown of layers (both inner and outer ones) occurred. The fact that NT contain defects was interpreted[131] as an indication of their high stability. The overall chemical formula of the new NT could be expressed as $[(NH_4)_yVO_x]\,[(C_nNH_3)_zVO_x]$; the defects are present in the $[(C_nNH_3)_zVO_x]$ layers. It is possible to control the structure of vanadium-oxide NT by changing the pH of the gel. It is assumed[131] that 'pure' $[(NH_4)_yVO_x]$-nanotubulenes with small interlayer distances can be synthesised at pH ~12. On the other hand, it is known[127] that it is ammonium vanadate $[(NH_4)_2V_3O_8]$ that is formed under these conditions.

In addition to particles with well-shaped tubular morphologies, products with ribbon-like structures and intermediate forms could be revealed by SEM in these composites.

Syntheses of TiO_2-nanotubulenes from solution[132] and with the use of mesoporous Al_2O_3 (see Ref. 133) were reported.

4. $NiCl_2$-Nanotubulenes

Hacohen *et al.*[136] were the first to synthesise halogen-containing nanotubular structures, namely, $NiCl_2$-nanotubulenes. Nickel dichloride has lamellar structure (of the $CdCl_2$ type, space group $R3m$); its specific feature is that it has ferro- and antiferromagnetic types of spin ordering inside the layers and between them, respectively. Multilayer NT were obtained; their cross-sections were up to ~7 nm, while the lengths were several micrometres. The tubular structures remained stable for a few days. It is assumed[136] that the most interesting applications of such structures may be related to their unusual magnetic characteristics.

5. Miscellaneous methods for the synthesis of non-carbon nanotubes

a. Template synthesis

The template method of synthesis is used to obtain nanotubular composites, *i.e.*, multilayer NT containing layers with different chemical compositions. Stable NT (normally, carbon nanotubes) are used as the support, which is then coated with layers of various metals or compounds.[124, 137–141]

The interest in nanotubular composites is due both to the possibility of preparation of tubular forms of those materials which are as yet unknown as isolated NT, and to specific properties of the composites themselves (*e.g.*, they behave as 'interfaces' between the adjacent cylinders of different chemical nature).

It should be noted that the method for the application of coatings on carbon NT is similar to that for the chemical modification of their surfaces, in which the composition of the outer layers of multilayer carbon NT is carried out by doping (substitution).[142–146]

Seeger *et al.*[142] proposed a method for the application of SiO_x-coatings on multilayer carbon NT at room temperature (in addition to the high-temperature method[138]). The low-temperature (colloid) method is based on the formation of positively charged centres on the surface of multilayer carbon NT followed by deposition of negatively charged colloidal SiO_x particles onto this surface. The high-temperature method[138] is based on the thermal decomposition ($T > 503$ K) of tetraethoxysilane

$$Si(OC_2H_5)_4 \longrightarrow SiO_2 + 2\,C_2H_5OH + 2\,C_2H_4\,,$$

adsorbed on multilayer carbon NT.

The low-temperature SiO_x coatings had the form of continuous amorphous layers 3–10 nm thick with included nanocrystallites; the high-temperature process resulted in a non-uniform SiO_x layer, ~10 nm thick (complete covering of the support surface could not be reached). In both cases, no chemical interaction occurred between the contacting SiO_x layers and the multilayer carbon NT; the oxide film coated the NT directly without formation of any intermediate (*e.g.*, carbide) layers.

The method used to obtain ZnS-nanotubulenes[147] may be regarded as a combination of the template and substitution approaches. Highly structured semiconducting zinc oxide films which incorporated single-crystal ZnO columns obtained by non-equilibrium electrodeposition on a conducting substrate (glassy SnO_2) were used as the support.[148–150] The columns (several micrometres high, with diameters of 100–300 nm) were oriented orthogonally to the substrate.

The process of formation of ZnS-nanotubulenes is based on the ion-exchange reaction

$$ZnO + H_2S \xrightarrow{Ar,\,673\,K} ZnS + H_2O.$$

After exposure for 15 min, the thickness of the ZnS layer on the ZnO columns was ~15 nm; complete transformation of ZnO-columns into ZnS-nanotubulenes did not occur. The untransformed column matrix (ZnO) was removed by treatment with dilute H_2SO_4. The resulting hollow ZnS tubes (open or closed) with wall thickness of ~10 nm maintained the surface morphology of the original crystallites; their cross-sections had polygonal shapes.

It is expected that other types of substitution may result in a wide range of NT with diverse chemical compositions, *e.g.*, tubular forms of semiconducting CuO, CuS, CdS, CdTe, ZnTe, *etc*.

b. Film 'rolling'

As noted above, it is compounds which form phases with quasi-2*D* structures under equilibrium conditions that are usually considered as potential candidates for the synthesis of NT.

A fundamentally new approach to the problem of obtaining the nanotubular form of matter has been developed.[151, 152] It was proposed to form NT from thin films. The principle of this method (which is subdivided[151] into the 'general' and 'special' methods) is demonstrated in Fig. 6.

'General' method. A thin film is applied on a double-layer support the top layer of which can be removed by selective etching. Following the etching, an edge of the film is detached from the support, bent and placed atop the film. The tubular structure is formed in the bent region (see Fig. 6). For instance, this method was used to obtain silicon–germanium NT up to 12 μm long and with a diameter of ~230 nm. The thickness of one layer was 16 nm and was determined by the conditions of the film deposi-

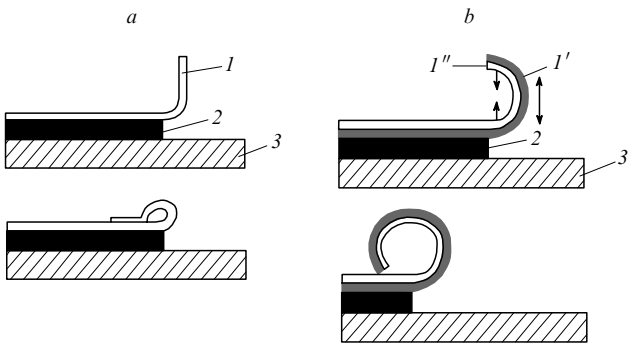


Figure 6. General (*a*) and special (*b*) film 'rolling' methods for obtaining NT;[151]
(*1*) single-layer (double-layer) film that forms nanotubes; (*2*) a top support layer removed upon selective etching; (*3*) a bottom support layer. Arrows show the force directions when a double-layer film is rolled.

tion. Yet another procedure of the synthesis of SiGe films [151] gave NT with up to 50 nm diameter and a wall thickness of ~6 nm.

'Special' method. Double-layer films made of different materials are used; the interatomic distances in the material of the outer film layer (*1′*) should be larger than those in the inner film layer (*1″*) (see Fig. 6). After etching and detaching a film edge from the substrate, each material tends to restore its original structure; owing to the resulting mechanical stress, the free film edge bends upwards, makes a full turn and forms a tube. In the case of prolonged etching, the film edge can make several turns to give specific rolls that resemble the familiar 'scroll'-type carbon tubes. This method made it possible to obtain tubes up to 20 μm long and with a diameter of 530 nm from double-layer InAs/GaAs,[152] InGaAs/GaAs [153] and SiGe/Si films [154] and from epitaxial SiGe films.[155]

It is important that the thickness of NT 'walls' obtained by this method, *i.e.*, the number of layers in the multilayer NT, depends exclusively on the film technology used and can vary over a wide range, down to a monoatomic layer. The approach suggested [151, 152] does not impose fundamental restrictions on the chemical compositions of individual NT layers, which allows tubular hetero-structures to be formed from multilayer films. Yet another important advantage is that it is possible to set exactly the location of the NT on the support: it is defined by the position of the film edge and by the etching time. Thus, the main factors in the manufacturing of NT within this approach are the choice of the film deposition method (which defines the size and chemical composition of the resulting NT), the time of chemical etching and the elastic properties of the material of the NT-forming film. It is expected [151] that this approach will provide single-crystal NT of many semiconductors.

III. Simulation of the structures and prediction of the properties of nanotubulenes based on boron, silicon, germanium and phosphorus

The search for new methods for the synthesis of non-carbon NT is performed in parallel with active studies on theoretical simulation of their configuration and electronic structure. Generally, the majority of studies employ zone or cluster models, as well as modern methods of density functional theory (DFT). Furthermore, structural features and kinetics of NT formation are studied by molecular dynamics methods. Details on specific approaches and computational schemes can be found in the original studies discussed below.

In addition to the conventional energy and electronic characteristics of NT, such as energy bands, electronic state densities (SD), interatomic interaction parameters and charge states, the so-called strain energy is often calculated (E_{str}). This parameter is defined as the difference between the energy of the flat atomic layer and the corresponding NT. It is considered as an estimate of the energy required to transform a compound in crystalline (lamellar) modification to the tubular form. By comparing the E_{str} for the known (carbon) NT and hypothetical non-carbon NT, it is possible to make conclusions on the probability of accessing the latter.

Compounds that have stable or metastable lamellar phases become the most common subjects of a theoretical search for non-carbon NT. In general, the methods used to build geometrical models of such NT resemble those for the carbon NT.[7, 21, 26, 30] Their classification is also carried out by analogy with carbon NT (using *n*, *m* indices).

1. Boron-based nanotubulenes

A number of studies [156–165] deal with prediction of the tubular structures of boron, which are electron-deficient in comparison with carbon NT. A number of techniques were used to simulate the boron NT formation process.

The formation of B-nanotubulenes was simulated by the 'cluster assembling' method. In the first calculation stage, the Hartree–Fock and DFT methods were used to determine the sizes and configurations of small (several atoms) isolated boron clusters; after that, their association was considered. For example, starting from a B_7 hexagonal pyramid, a large number of topologically different B_n clusters were constructed: quasiplanar (quasi-2*D*), convex and three-dimensional. Planar structures were found to be most stable (see also Refs 166 and 167). Convex structures are less stable. The stability of these structures increases [156, 159] if they incorporate a combination of two base clusters, *viz*., hexagonal and pentagonal pyramids.

Boustani *et al.* [164] and Gindulyte *et al.* [165] simulated boron-based NT. They evaluated the stability of the isomers of the tubular form of the B_{32} cluster, the structures of which are shown in Fig. 7. It was found that the stability of these isomers decreases with a decrease in the diameter. In contrast, as the diameter increases (the curvature of the cylinder walls decreases), their energies approach that of the most stable planar form of boron.

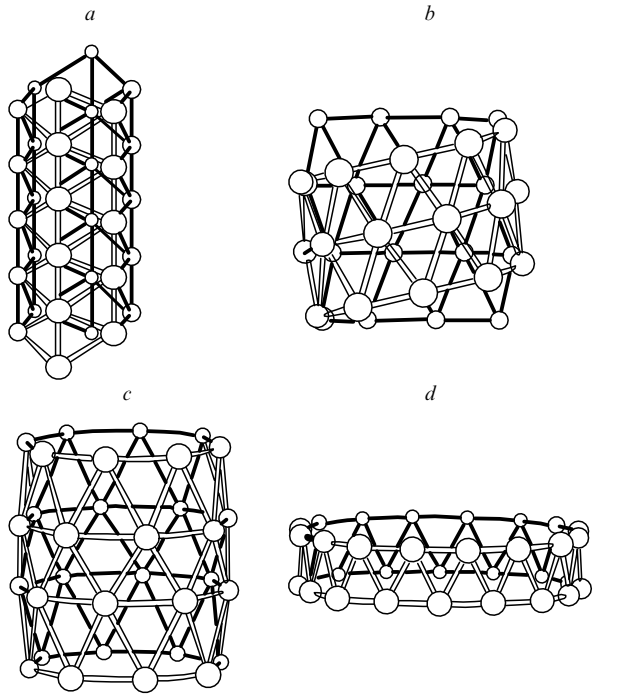


Figure 7. Model structures with C_{2h} (*a*), C_2 (*b*), D_4 (*c*, *d*) symmetry types for cylindrical B_{32} clusters with different diameters.[164]

A competition between the following factors affecting the stability of the isomers was noted:[164] first, the high deformation energy of the planar layer, which increases abruptly with an increase in the curvature and prevents the formation of tubes with small diameters; second, the energy gain due to the coupling of broken (side) bonds in planar layers when they are rolling into a cylinder. Thus, it is quite possible to synthesise boron NT, but their diameters should be relatively large. Examples of such extended boron NT built like carbon NT were considered by Gindulyte *et al.*[165]

The formation of NT in the bulk of α-boron quasi-crystals may be expected.[158] Calculations of local structural deformations for a 'compressed' boron quasi-crystal with rhombohedral lattice showed that closed hollow structures considered as precursors of the growth of extended NT are possible in this system.[168] The formation of boron NT may be critically affected by admixtures of various elements, *e.g.*, carbon or nitrogen.

2. Nanotubulenes based on silicon and germanium

The possibility of preparing NT consisting of silicon, which is a carbon analogue, still remains debatable. This is explained by great differences in the energy states of the atoms of these elements. It is known[169] that the most stable electronic configuration for the carbon atom is sp^2, whereas for silicon it is sp^3. Therefore, graphite is the most energetically favourable crystalline form for carbon, whereas a diamond-like structure is the most favourable for silicon. In the nano-state, carbon exists as atomic chains, hollow fullerene-like clusters and NT, whereas silicon does not form any polyhedral nanoparticles.[170]

The first calculations of the energy and electronic states of hypothetical silicon-based NT formed by rolling of ribbon-shaped graphite-like structures of a layer composed of silicon atoms [nonchiral (6,6)- and (10,0)-NT and chiral (8,2)-NT] were carried out by the DFT method.[171] The dependence of the electronic properties of such NT on their types is similar (see the corresponding reviews [7, 21, 26, 30]) to that of similar carbon NT. This is evident from the state densities for silicon NT shown in Fig. 8: the zigzag (10,0)-NT is a semiconductor with narrow energy gap, whereas the dented (6,6)-NT has metallic conductivity. Of interest are comparative energy evaluations of various carbon and silicon structures. The total energies (E_{tot}) of a silicon atom within a graphite-like network and in an NT are 0.79 and 0.83 eV lower than in crystalline silicon. The energy of cohesion (E_{coh}) of silicon atom in NT is only 82% of E_{coh} in a diamond-like crystal, whereas the E_{coh} of carbon atom in NT and in crystal (graphite) differ by no more than 1%. According to estimates,[171] the energies required for rolling of networks consisting of carbon and silicon atoms into tubular structures are very similar (0.04 – 0.05 eV per atom). Presumably, the main problem in the synthesis of silicon NT is that it is difficult to obtain silicon in a lamellar (graphite-like) form.

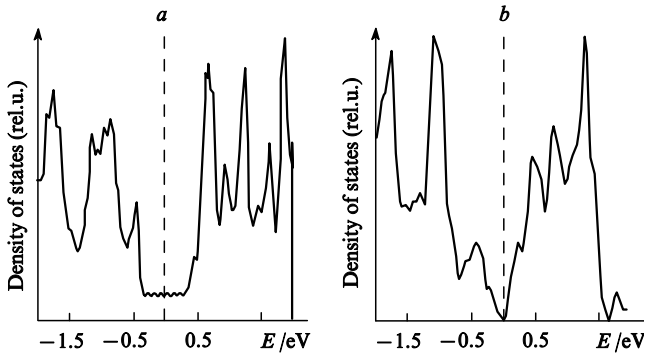


Figure 8. Full densities of states for silicon (6,6)- (*a*) and (10,0)- (*b*) nanotubulenes.[171]
Vertical lines show the Fermi energy.

Calculations on mixed carbon – silicon NT showed[172] that the Si → C replacement energy within carbon NT is ~3.1 eV per atom. If a silicon admixture is present, it generates resonance states ~0.7 eV above the Fermi level in the electronic spectrum of a metallic carbon (6,6)-NT. A silicon atom within a semiconducting carbon (10,0)-NT gives rise to a local electronic level arranged ~0.6 eV above the valence band.

Seifert *et al.*[173, 174] calculated the electronic states and analysed the stability of silicon-containing NT based on silanes and siloxanes with complex composition. In such NT, the silicon atoms forming the tube frame are surrounded by hydrogen atoms or by hydrogen atoms and OH groups.

Like silicon, crystalline germanium has a diamond-like structure with sp^3 bond type; its quasi-2*D* modifications (of the $CaSi_2$ type[175] or $CaGe_2$ type[176]) are also known. Recently, polymers containing networks of germanium atoms (GeH hexagonal layers) were synthesised.[177] According to calculations,[178] these compounds should be semiconductors (the width of the forbidden band is $E_g \approx 1.4$ eV). The DFT method was used[179] to simulate the electronic properties of hypothetical (*n*,0)- and (*n*,*n*)-NT ($n = 6-10, 20$) based on GeH. The cross-sections of (8,0)- and (8,8)-GeH-nanotubulenes, which are the most stable of those described above, are shown in Fig. 9. It was shown[7, 21, 26, 30] that the dependence of the energy deformation of NT on its diameter (*D*) has the form:

$$E_{str} \approx \frac{1}{D^2}. \quad (1)$$

All of these tubes are semiconductors; the forbidden band width varies considerably depending on the NT diameter [from 1.33 to 1.16 eV for (20,20)- and (7,0)-NT, respectively]. Possible methods for the synthesis of these NT include[179] topochemical reactions and synthesis from molecular GeH_4.

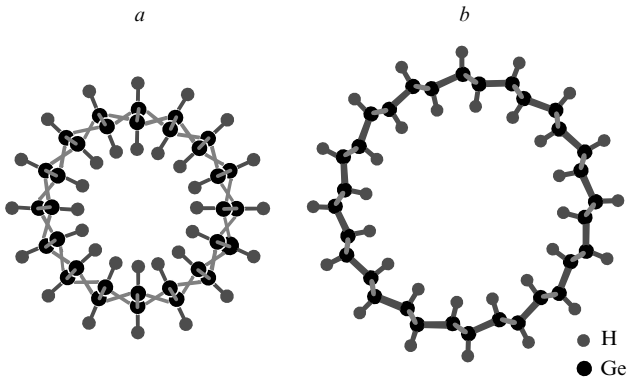


Figure 9. Structures of cross-sections (8,0)- (*a*) and (8,8)- (*b*) for GeH-nanotubulenes.[179]

3. Phosphorus nanotubulenes

Orthorhombic black phosphorus is the most stable allotropic form of elementary phosphorus. The crystals of black phosphorus consist of graphite-like networks, the distance between which (0.36 nm) is much longer than the length of the P – P bonds in the network (0.223 nm). Unlike the planar graphene layers, the networks of phosphorus atoms are 'bulged'; this is explained by the repulsion of unshared electron pairs in the neighbouring atoms.

Seifert and Hernandez[180] compared the electronic and energy characteristics of an isolated network of black phosphorus with those of a number of hypothetical single-layer NT. In the initial stage, the structures of P-nanotubulenes (of zigzag and dented types) were constructed from ribbons of planar graphite-like layer of phosphorus atoms rolled to make a cylinder. After that, their geometry was optimised with respect to the axial displacements of atoms. Generally, relaxed structures of P-nanotubulenes are

similar to the structures of carbon NT and only differ in the type of six-membered rings. In the case of P-nanotubulenes, these rings have the form of cyclohexane rings consisting of phosphorus atoms.

The strain energy (E_{str}) of phosphorus NT is considerably higher than the E_{str} of carbon NT with similar diameters. This difference increases as the tube diameter decreases, which is explained [180] by changes in the electronic configurations of the carbon and phosphorus atoms in the networks. As a graphene network consisting of sp^2 carbon atoms folds, the increase in the wall curvature increases the contribution of the sp^3 orbitals.[181] For a phosphorus network consisting of sp^3 phosphorus atoms, minimisation of the repulsion energy of unshared electron pairs of adjacent atoms occurs due to the maximum increase in the distances between adjacent phosphorus atoms upon their displacement from the network plane (the network 'bulging' mentioned above). As such a 'bulged' network is folded, the distances between the unshared electron pairs of certain phosphorus atoms decrease, resulting in rapid increase in E_{str}. However, the E_{str} of phosphorus NT at $D > 1.23$ nm is no higher than 0.1 eV per atom, which is comparable with the deformation energies of the corresponding carbon NT.

These energy estimates suggest that there are no obstacles to the existence of P-nanotubulenes. However, it should be expected that NT with rather large diameters will be formed. The following methods may be used to obtain P-nanotubulenes: the template method, a modification of the method for the synthesis of thin phosphorus films upon luminescent decomposition of PH_3 [182] and sublimation of phosphorus in the presence of catalysts.

It was noted [180] that phosphorus NT should have semiconducting characteristics invariable with respect to diameter changes (E_g changed in the range from 0.9 to 1.99 eV). Considering that the properties of phosphorus and arsenic are similar, the possibility that As-nanotubulenes may exist cannot be ruled out.

IV. Theoretical models of nanotubes based on *p*- and *d*-element compounds

1. Models of nanotubes consisting of B, C and N atoms

It was found in early studies [4–8] of carbon NT that their properties could be affected by doping.

The cyclic cluster model and the semiempirical quantum-chemical MNDO method were used to study the charge distribution in carbon (6,6)-NT doped (one atom per unit cell) with one of the atoms: B, N or Si, in neutral, anionic and cationic state.[183] It was found that the distortions introduced by the dopants propagated along the NT to longer distances than across the NT. Distortions from charged dopants have a longer range than those from neutral atoms.

The local structural deformations of carbon NT appearing upon doping with single boron or nitrogen atoms were estimated.[184] In the case of nitrogen, the effects of structure relaxation are weak. Doping with boron resulted in displacement of the nearest carbon atoms by $\sim$0.011 nm along the B–C bonds.

Scanning tunnelling spectroscopy and calculations within the DFT were used to study the effect of boron atoms on the properties and growth of carbon NT.[185, 186] Doping of multilayer carbon NT with boron confers on them metallic properties; the boron atoms are segregated to form separate islets in NT walls.[185] A boron admixture prevents the formation of 'caps' and favours the preferable growth of (*n*,0) type NT.[187] This mechanism does not apply to dented NT; this fact can be used for growing selectively NT of certain geometries. Electrophysical studies [188] showed that doping of carbon NT with boron increases the paramagnetic susceptibility of the latter. Furthermore, their thermal factors of electrical conductivity are positive.

a. Boron nitride

Boron nitride was the first compound suggested for the synthesis of non-carbon NT. Quantum-chemical methods [36–38] revealed a number of interesting features of BN-nanotubulenes. Unlike carbon NT, the conducting properties of which are determined by their diameters and chiralities,[4–8] BN-nanotubulenes are wide-gap semiconductors ($E_g \approx 5.5–6.0$ eV), which is important for the development of materials with predetermined properties. More detailed information about the electronic and energy characteristics of 'ideal' single- and multilayer BN-nanotubulenes can be found in a monograph [7] and in a number of reviews.[21, 29, 30]

In recent years, BN-nanotubulene structures were mostly simulated using the molecular dynamics method.[76, 189] The properties of the following tube types were compared:[76] chiral, zigzag-shaped, dented (built of graphite-like networks of B_3N_3 hexagons) and those built of four- (B_2N_2) and eight-membered (B_4N_4) rings. The latter type of BN-nanotubulenes were found to be the less stable.

The elastic properties of BN-nanotubulenes were estimated:[190] their Young modulus (Y) was 14 times higher than that for crystalline graphite-like BN, and comparable to the extremely high Y predicted [191, 192] for carbon NT (1–6 TPa). This agrees with the subsequent measurements [193] of the Young modulus for multilayer and single-layer carbon NT (0.4–4.0 TPa). The experimental studies [194] on the elastic properties of mutlilayer BN-nanotubulenes give values which are in good agreement with calculations [190] ($Y \approx 1.22 \pm 0.24$ TPa). Of the currently known elongated nanostructures with dielectric properties, BN-nanotubulenes are characterised by extreme values of the Young modulus comparable to those of glassy fibres.[195, 196]

The growth mechanisms of BN-nanotubulenes depend on their structures and differ considerably for (*n*,0)- and (*n*,*n*)-nanotubes.[197, 198] The determining role in the growth process belongs to the specifics of the formation of terminal structures by virtue of B–N binding, these bonds being much more favourable than the B–B and N–N bonds. Zigzag NT stop to grow once 'caps' have formed. Dented NT grow by addition of extra atoms near the NT ends. The role of BN-rings of different types (in particular, five-membered rings) in the formation of BN-nanotubulene 'caps' and polyhedral boron nitride clusters, which are heteroatomic fullerene analogues, was discussed.[199–207]

b. Boron carbides

Unlike BN-nanotubulenes, the type of electronic properties of BC_3-nanotubulenes changes from metallic to semiconductor-type with the increase in their diameters.[207] It is possible to increase the conductivity (hole concentration) of such NT by partial replacement of carbon atoms by 'superstoichiometric' boron atoms. Halogen atoms can serve as electron donors, as is observed for a number of intercalated graphites. The value of E_{str} for BC_3-nanotubulenes is lower than that for carbon NT, which is in agreement with experimental data on their syntheses (see above).

c. Carbon nitrides

The existence of condensed carbon nitride (CN_x) and the extreme (comparable to that of diamond) hardness of β-C_3N_4 (the β-Si_3N_4 structure type) were predicted.[208, 209] Subsequently, CN_x was synthesised successfully (in amorphous, film and nanocrystalline states [210–217]) and both various polymorphous modifications of crystalline CN_x and its tubular nanostructures were simulated theoretically.

Fundamental electronic properties of CN_x with the structures of the α-Si_3N_4,[218–220] Zn_2SiO_4 and α-$CdIn_2Se_4$ [219, 220] types and of a series of its quasi-2*D* modifications [219–222] were considered. A lamellar structure containing graphite-like networks formed by a combination of triazine rings with nitrogen bridges was suggested for C_3N_4.[221] Each carbon atom in the network is bound to three nitrogen atoms; each of the latter has only two closest neighbours. Planar C_3N_4-networks can be packed according to *ABAB*... type (the Bernal structure) or *ABCABC*... type (the rhombohedral graphite structure).[222] The mean C–N bond length is $\sim$0.136 nm (which is close to the sum of the Sleyter radii for the carbon and nitrogen atoms), the C–N–C bond

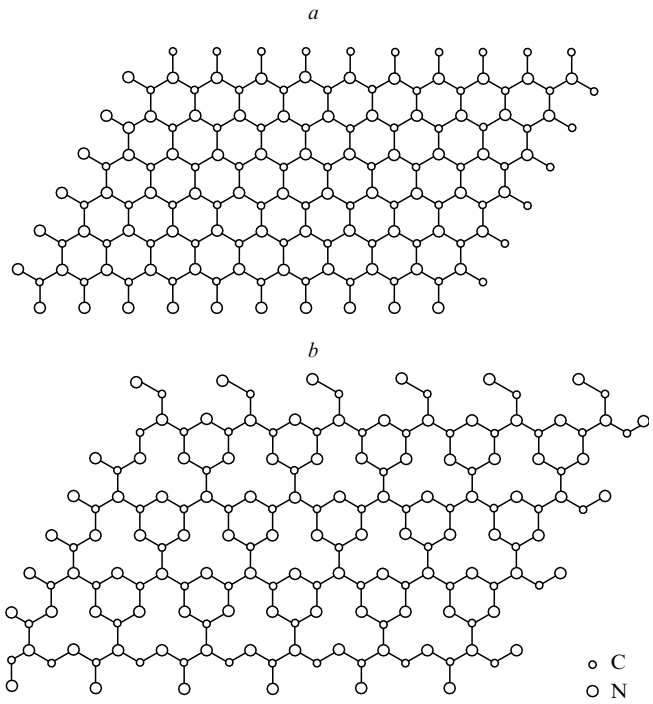


Figure 10. Planar networks used to simulate NT with compositions CN (*a*) and C_3N_4 (*b*).[225]

angle is 116° (see Ref. 221). It was found[223] that vacancies appearing in the N-sublattice of cubic C_3N_4 favour its transformation into a pseudoplanar form. A number of other densely packed and lamellar modifications of carbon nitride have also been suggested (see the review[224]).

The structures of non-chiral single-layer (*n*,*n*)- and (*n*,0)-CN-nanotubulenes with different stoichiometry are described by networks similar to those of the C_3N_4 layers mentioned above and a hypothetical graphite-like layer with the composition CN (Fig. 10).[225,226] All CN_x-nanotubulenes, irrespective of their structures and diameters, have metallic conductivity. Their deformation energy increases with a decrease in diameter, but it is smaller than that of carbon NT. In turn, E_{str} for CN-nanotubulenes is smaller than E_{str} for NT based on C_3N_4 (Fig. 11). It is assumed[225] that the interlayer distances in multilayer CN_x-nanotubulenes will be ~0.04 nm smaller than those in multilayer carbon NT. The sp^2-configuration of nitrogen atoms favours the stability of NT.

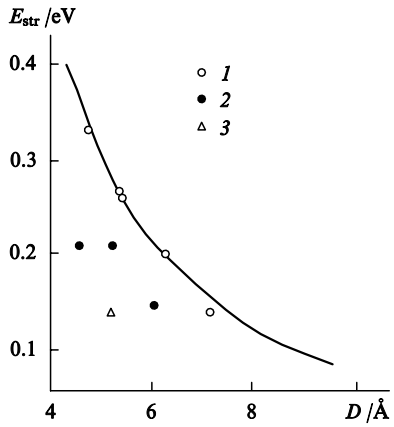


Figure 11. Deformation energy–diameter relationships for C- (*1*), C_3N_4- (*2*) and CN-nanotubulenes (*3*).[225]

The formation of fullerene-like molecules, NT and CN_x crystals was simulated by the molecular dynamics method.[227] The simulation started from a planar fragment of a graphite network forming a cluster of 96 carbon atoms; in this system, the structural deformation upon replacement C → N in the N:C range 0.07–1.00 was studied. The CN_x layer remained planar up to the nitrogen content of ~20%; then it became 'corrugated' due to deviation of atoms (up to ~0.07 nm) away from the plane. It is believed[228] that this results from occupying the antibonding π*-orbitals (which is visible in photoelectron spectra) and formation of new, rather stable N–N bonds. The CN_x crystals may have various types of the layered packing of such deformed nitrogen–carbon networks. In should be noted that when a critical nitrogen content (~20%) is reached, a different type of structural evolution of this system is possible to result in NT or a fullerene-like molecule.[227] It is important that stabilisation of the tubular and molecular states is attained at different system stoichiometry, *viz*., CN and C_3N_4, respectively.

It is of note that only CN_x-nanotubulenes and nanofibres with relatively small *x* values ($x \leqslant 0.04-0.05$) are known.[229–236] Their electronic properties are interpreted on the basis of calculations for carbon NT containing nitrogen admixtures.[236,237] In the general case, replacement of some carbon atoms in an NT by nitrogen atoms (electron dopants) increases the population of the energy bands and 'metallisation' of the NT. Admixtures of nitrogen create donor levels near the edge of the conduction band in carbon NT.[236,237] Introduction of nitrogen atoms results in the formation of local pyridine-like fragments within NT walls; this explains the subtle features of electronic state distribution near the Fermi level, which may be important when creating nano-sized devices with hetero-transitions based on these NT.[236]

d. Boron carbonitrides

Theoretical construction of nanotubular structures was carried out based on a lamellar form of boron carbonitride BC_2N the electronic spectrum of which has been studied previously.[238–240] It was assumed that the intralayer charge anisotropy, which causes the formation of 'channels' with increased and decreased electron density in BC_2N networks,[238–243] would be preserved when these networks are rolled into cylinders (according to the chiral type) and would result in spiral motifs. As a result, circular currents would appear in BC_2N-nanotubulenes, and such NT may be considered as nano-solenoids (Fig. 12).

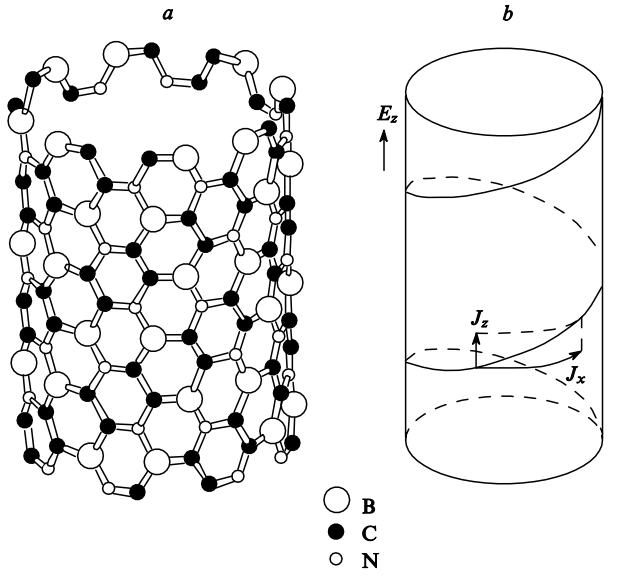


Figure 12. A variant of the atomic structure of a BCN-tube (*a*) and the scheme of circular currents therein (*b*).[241]
E_z is the direction of the external field.

Nanotubes with small diameters maintain the conductivity type characteristic of the original BC_2N monolayers. The metallic type of conductivity of (n,m)-NT can change to the semiconductor type at certain diameters and chirality. The most stable are those (n,n)-NT which contain the maximum number of strong C–C and B–N bonds. Miyamoto *et al.*[243] analysed the conditions required for the appearance of circular currents in such NT.

Attempts were made to describe the role of defects in the properties of BC_2N-nanotubulenes.[241,243] Partial replacement of carbon atoms by boron (or nitrogen) resulted in donor (or acceptor) admixture states for $B_{1+x}C_{2-x}N$ (or $BC_{2-x}N_{1+x}$) in the electronic spectra. Miyamoto *et al.*[243] considered the role of electron (or hole) carriers in the formation of chiral currents in BC_2N-nanotubulenes.[243]

Analysis of the general trends in the formation of the atomic structure of BC_2N-nanotubulenes performed on the basis of results of theoretical studies showed that such nanotubulenes are characterised by the formation of BN- and C-islets.[244,245] The BC_x-nanotubulenes should undergo similar spontaneous segregation into regions consisting of carbon atoms and BC_3 fragments. These phenomena can give rise to quantum dots and heterotransitions.

2. Nanotubes based on gallium nitride and selenide

The possibility of obtaining tubular structures for other compounds of Group III–V elements, which do not form lamellar structures under equilibrium conditions, was analysed for GaN (Ref. 246) and GaSe.[247]

In the first stage, the structures of a hypothetical crystalline graphite-like GaN were simulated by the DFT method and the equilibrium distances Ga–N in the layer were determined (0.178 nm).[246] The difference between the bond energies of sphalerite-like (s) and graphite-like (g) phases of gallium nitride was found to be small, namely, 0.36 eV per atom. This value is smaller than the energy difference between s-GaN and its metastable cubic (sodium chloride-like) modification (0.5 eV per atom), which is considered[246] to be evidence of the possibility of obtaining a lamellar allotrope of GaN.

The next simulation stage involved calculations of the electronic structure and E_{str} of gallium–nitrogen (n,n)- and $(n,0)$-NT as a function of their diameters. Sawada and Hamada[248] estimated the minimum possible NT sizes corresponding to zigzag-like (5,0)- and dented (2,2)-NT. It was found that E_{str} changes inversely to the square of the NT diameter; the geometry type of the walls of such tubes (unlike carbon ones[249]) only slightly affects E_{str}. On the contrary, this factor becomes important for the dielectric properties of GaN-nanotubulenes: although both tube types are wide-gap semiconductors [*e.g.*, the values of E_g for (5,5)- and (9,0)-GaN-nanotubulenes are 2.15 and 2.16 eV, respectively], dented (n,n)-NT, like the hypothetical g-GaN, have indirect type of inter-band transitions. Zigzag-like $(n,0)$-NT have direct type of the transitions. The E_g of $(n,0)$-tubes decreases most significantly with a decrease in diameter. The GaN-nanotubulenes (like BN-nanotubulenes[7]) were found to manifest a relaxation effect: the atoms of the cationic (Ga) and anionic (N) sublattices are displaced by ~0.005 nm from the surface of an ideal cylinder: the gallium atoms are displaced towards the tube axis, whereas the nitrogen atoms are displaced in the opposite direction. Similar properties are also typical of GaSe-nanotubulenes.[247]

It is assumed that GaN-nanotubulenes can be obtained by template synthesis using carbon NT as the substrate.[246] This will probably result in multilayer tubes with various chemical compositions (C/GaN nanotubular composites) with a metal–semiconductor interface. To date, tubular composites which are carbon NT partially filled with GaN, as well as separate GaN rods with 7–10 nm diameters and up to 40 μm long, have been synthesised.[250] These specimens were obtained in an electric arc in an atmosphere of nitrogen with a graphite cathode and an anode containing a mixture of gallium nitride, graphite and nickel powder.

'Pure' GaN-nanotubulenes [with E_g values ~0.45 eV higher than those of the cubic phase of GaN (see Refs 246, 251, 252)] can be used in nanosized optoelectronic devices that are necessary, *e.g.*, in colour displays.

3. Sulfide nanotubes

Nanotubes based on lamellar molybdenum and tungsten disulfides were constructed[253,254] from fragments of triple-layer packages S–(Mo,W)–S rolled into cylinders along certain chosen directions of the two-dimensional lattice. The tubes were classified (by analogy with the carbon NT) as non-chiral zigzag-like (n,n)- and dented $(n,0)$-NT. The theoretical electron diffraction patterns built for these structures[253] well describe the experimental data.[255] Seifert *et al.*[253,254] used the DFT method in the strong bond approximation to study the dependence of the electronic properties and stability of a series of disulfide NT on their diameters. For example, the diameters of $(n,0)$- and (n,n)-WS_2-nanotubulenes ($n = 6, \ldots, 22$) ranged[254] from ~1.1 [for (6,6)- and (10,0)-NT] to ~3.1 nm [for (18,18-NT)]. For MoS_2-nanotubulenes, the diameters ranged from 0.8 to 2.6 nm.[253] The maximum diameters of model NT used in these studies were close to the minimum diameters of the disulfide NT synthesised.

The energy and electronic characteristics of all disulfide NT have certain common features,[253,254] which are also characteristic of crystalline phases.[255,256] Three bands are observed in the valence band of WS_2-nanotubulenes, *viz.*, *A*, *B* and *C* (Fig. 13), which result from contributions of quasi-framework S3*s*- (band *A*), hybridised S3*p*–W5*d*- (band *B*) and W5*d*-states (band *C*). The W5*d*-states dominate in the vicinity of the lower edge of the conduction band. All (W,Mo)S_2-nanotubulenes are narrow-gap semiconductors. However, $(n,0)$-NT are semiconductors with direct transition in point Γ, whereas the family of (n,n)-NT is characterised by indirect transition type (Fig. 14). The forbidden band width increases with a decrease in the tube diameter, but it

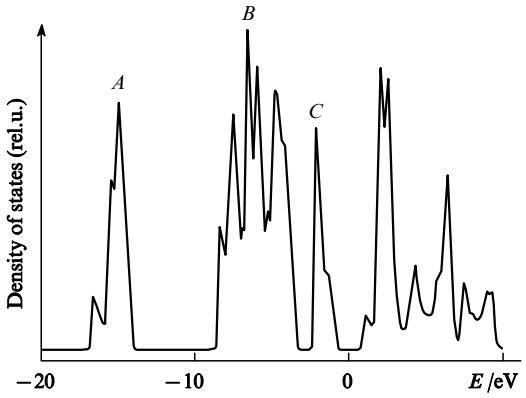


Figure 13. Full density of states for (18,18)-WS_2-nanotubulene. $E_F = 0$.[254]

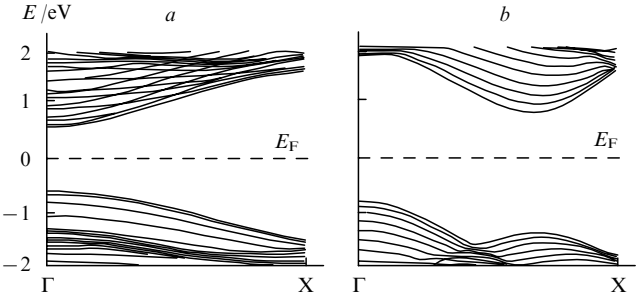


Figure 14. Energy zones for (22,0)- (*a*) and (18,18)- (*b*) WS_2-nanotubulenes.[254]
Horizontal lines show the Fermi energies.

remains smaller than the E_g for three planar S–(W,Mo)–S layers. This result agrees with optical experiments [256] which showed that E_g in the electronic spectrum of WS_2-nanotubulenes was smaller than that for crystalline tungsten disulfide.

Charge transfer in disulfide NT occurs in the direction W(Mo) → S.[253,254] For MoS_2-nanotubulenes, the effective charges are ~0.9 e (0.44 e per sulfur atom), which is much smaller than the formal ionic charges in the crystal (Mo^{4+}, S^{2-}). The deformation energies for disulfide NT are higher than those of carbon NT with the same diameters. In turn, the E_{str} of zigzag-like (Mo,W)S_2-nanotubulenes is somewhat higher than the E_{str} for dented ones.

Seifert *et al.*[253] studied the effect of topological defects (in the form of four- and eight-membered rings) on the structure of the 'caps' on closed NT and polyhedral nanoparticles (Mo,W)S_2 (see also Ref. 257). Milosevoc *et al.*[258] considered the general geometrical aspects of the structure of dichalcogenide NT, determined the symmetry groups of single-layer NT based on 2H- and 3R-polytypes of MoS_2 and WS_2 and discussed some of their properties that depend on the system symmetry (in particular, such as splitting of the energy bands, rules of selection and structures of the phonon spectra).

It is assumed [253] that the semiconductor conductivity type of (Mo,W)S_2-nanotubulenes can be changed to the metallic type if the constituent molybdenum or tungsten atoms are partially replaced by niobium atoms. Recently,[259] annealing of Nb_2O_5-coated $W_{18}O_{49}$ nanorods at 1100 °C in H_2S atmosphere gave the first 'mixed' NT with the composition $W_{1-x}Nb_xS_2$ ($x \leqslant 0.2$). Their properties have not been studied so far.

The DFT method was used to evaluate the stabilities and simulate the electronic properties of hypothetical (*n*,*n*)- and (*n*,0)-NbS_2-nanotubulenes [260] {n = 6, ..., 22, the NT diameters ranged from ~1.0 [for (6,6)- or (10,0)-NT] to ~2.4 nm [for (14,14)-NT]}. It was found that the strain energy E_{str} of NbS_2-nanotubulenes obeys Eqn (1), and that it is higher than that of carbon NT with the same diameters. This fact was explained by a higher energy consumption for rolling of a fragment of an S–Nb–S triple-layer sheet into a tube, in comparison with similar consumption required for rolling of a graphene monolayer. The energy bands of the tubes considered above differ only slightly from each other and from the energy bands of planar niobium disulfide layers.[261] The states of these bands near the Fermi level (predominantly of Nb4*d*-type) have high density, which determines their metallic properties; this, in turn, gives a reason to expect [260] that NbS_2- and $NbSe_2$-nanotubulenes may manifest superconductivity. It was noted [260] that the onset of superconductivity may be due to an increase in the electron–phonon interaction and an increase in the critical temperature (T_c) in tubular niobium disulfide structures in comparison with the T_c for its crystal [~5.6–6 K (see Ref. 262)].

It was suggested that NbS_2-tubes could be obtained by thermal treatment of NbO_x nanorods in an H_2S atmosphere or by using template synthesis on carbon NT as the templates. The latter method gave [263] long nanostructures, *viz.*, niobium disulfide tubes and rods.

4. Boride nanotubes

A broad class of lamellar materials comprises metal diborides (MB_2) and other MX_2-phases (X = Be, Si, Ga, Hg, Zn, Cd, Al, Cu, Ag, Au) with the AlB_2 type structure (space group D^1_{6h}–$P6/mmm$).[264,265] These materials aroused particular interest due to the discovery, in 2001, of a superconducting transition in MgB_2 ($T_c \approx 40$ K).[266] Since then, superconducting MgB_2 has been obtained as single crystals, dense and porous ceramics, films, long wires and bands, as well as in a nano-structured state; numerous studies of its properties have been carried out (see the reviews [267,268]).

Chernozatonskii [269] analysed whether MgB_2 can exist as an NT. Double-layer MgB_2-nanotubulenes were simulated by rolling (by the chiral and non-chiral types) ribbon-like fragments cut from two adjacent layers of a MgB_2 crystal. It was assumed that stabilisation of the electron-deficient boron layer occurred due to partial electron transfer (Mg → B); the bond between the coaxial, oppositely charged Mg- and B-cylinders is partially ionic, and the distance between them is similar to the interlayer distance in an MgB_2 crystal. According to molecular dynamics estimates, diboride (*n*,*n*)-NT, which have a minimum deformation energy if the diameter of the 'outer' B-tube is ~19 Å [for (11,11)-MgB_2-nanotubulenes], are more stable. The author's conclusions are based on estimates of the lattice instability of the MgB_2 and AlB_2 type structures [270] formed by alternating (in the sequence ...MXMX...) planar hexagonal metal networks (M) and graphite-like nonmetal layers (X).

Synthesis of magnesium-diboride NT is most likely to give tubes of a dented type. Considering the results of calculation of the electronic structures of crystalline MgB_2 (see Refs 267, 271–274), it is assumed [269] that such tubes should have metallic conductivity. It is also assumed that they may have superconducting properties (see Refs 7 and 272 on the superconductivity in carbon NT).

A number of NT structures based on ZrB_2 have been reported. It is assumed [269] that the 'caps' of closed MB_2-nanotubulenes can have the form of structures with defects in the M- and B-shells as five- and four-membered rings. Probably, diborides may also exist as multilayer structures, such as multilayer NT, or as onions. Such systems as (7,7)@(11,11)@(15,15)-NT and $(MgB_2)_{180}$@$(MgB_2)_{288}$, the so-called bifullerene, may serve as examples.

The DFT method was used to calculate several structures,[275] the prototypes of AlB_2-nanotubulenes. It was found that all diboride NT should have metallic conductivity.

V. Models of hybrid nanotubular structures

1. Intercalated BN-nanotubulenes

Particular interest is attracted to the control of the properties of NT and synthesis of new nanocomposite materials with nontrivial functional properties based on these. Chemical modification of NT is one of the most effective methods to solve these problems. The properties of NT can be changed in various ways, for example,

(1) by introducing compounds — intercalants (atoms or molecules) — into the internal cavity of single-layer or multilayer NT, into the space between layers (neighbouring walls) of multilayer NT or into cavities between the adjacent NT in NT braids or in nanotubular crystals;

(2) by adding foreign atoms or molecules to the broken bonds of atoms belonging to the terminal groups of open NT, to atoms of the 'caps' of closed NT or to atoms of the outer surface of NT walls (adsorption on NT surface);

(3) by replacing partially the NT atoms by atoms of some other kind (NT 'doping').

These modification methods became most popular for carbon NT (see the reviews [15–17,21–28]). For non-carbon NT, simulations of intercalated nanotubulenes and 'symbiotic' tubular structures are used most frequently. In the latter case, this idea was used for the possible formation of various 1*D*-heterostructures [the so-called symbiotic boron carbonitrides, *viz.*, (C + BN)-nanotubulenes] in addition to 'ideal' NT with a regular distribution of different kinds of atoms over the nodes in a B–C–N system.[276] It is expected that the conducting properties of such NT would vary widely. Certain experimental data on their synthesis were mentioned above.

Chernozatonskii *et al.*[277] considered hypothetical BCN-nanotubular structures consisting of alternating C- and BN-fragments as representatives of 'symbiotic' NT. Considering the similarity of the bond lengths C–C (0.142), C–N (0.150) and B–N (0.145 nm in graphite-like planes), such heterostructures can be formed,[276] *e.g.*, as a result of the growth of carbon NT on

substrates containing BN nanocrystallites, or as a result of the formation of BN-nanotubulenes on diamond crystallites, or due to both processes occurring simultaneously. Yet another way to obtain these kinds of structures is chemical doping; as the carbon atoms are replaced by B and N, the latter form BN-'islets' within the original carbon NT.

Simulation of symbiotic tubular structures in the B–C–N system made it possible to predict a number of interesting properties for them.[277, 278] It was suggested to consider C–BN-nanotubulenes containing rings of carbon atoms as a new class of quasi-one dimensional systems with quantum dots in which the local disturbance of the energy of electronic states exceed a certain characteristic value (usually $kT_{\text{room}} \approx 0.024$ eV). The crystal orbital method in one-orbital approximation was used to calculate the electronic spectrum of zigzag-like (n,0)-BN-nanotubulenes (n = 5, 6, 9, 27, 72) in which a number of (B,N)-atomic rings in the bulk or at the ends of open tubes were replaced by rings of carbon atoms. The states of the terminal carbon rings form a number of discrete levels around the dielectric gap of BN-nanotubulenes; as the number of carbon atoms increases, these levels are transformed into mini-bands. For example, the spectrum of carbon states (in the dielectric gap) for (27,0)-CBN-nanotubulenes consists of two groups of levels the widths of which are 0.7 and 1.7 eV. A similar effect (Fig. 15) was noted for the states of bridging carbon rings between the fragments of neighbouring NT. It is assumed that the existence of 'quantum dots' (or 'quantum rings',[278, 279] *i.e.*, conducting carbon rings at the ends or between dielectric BN-nanotubulenes) can result in unusual properties of these structures, *e.g.*, lead to resonance effects in external magnetic fields. Lammert *et al.*[280] discussed the results of doping of carbon NT with boron and nitrogen admixtures carried out in order to obtain structures containing chains of quantum dots. Such structures can be regarded as models of novel quantum nano-devices.

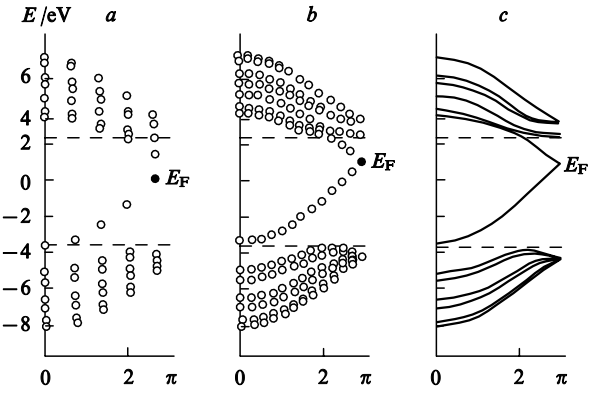


Figure 15. Energy zones for $(BN)_3C_2(BN)_3$ fragments of 'symbiotic' (n,0)-nanotubes;[277]
n = 9 (*a*), 24 (*b*), 72 (*c*).

The electronic characteristics of the hetero-transitions in NT consisting of the C/BN, BC_2N/BN segments (the superlattice model) were found[279] to be stable against changes in the radii, chirality type and the number of layers in these NT.

Intercalated boron-nitride NT present yet another type of 'tubular composites'. Rubio *et al.*[281] calculated the electronic spectra of (4,4)-BN-nanotubulenes which incorporated potassium or aluminium 'fibres' arranged along the cylinder axis. The evaluated intercalation energies (the differences between the full energies of the composite and its constituents, namely, the NT and the metal 'fibre') were much smaller than the intercalation energies for similar systems with carbon NT. In the system K@(4,4)-BN-nanotubulene, no new states appear in the electron energy spectrum. In the system Al@(4,4)-BN-nanotubulene, additional levels of Als,p-type appear in the energy gap, and the electronic spectrum of this system becomes similar to a superposition of the spectrum of a monoatomic chain of aluminium atoms and the spectrum of (4,4)-BN-nanotubulene. The density of electron carriers, which define the conductivity of intercalated BN-tubes, is concentrated inside the cylinder, hence such NT are preferable (as compared to carbon NT) when making nano-wires with predefined parameters. It is deemed possible to intercalate silver and gold atoms into BN-nanotubulenes.

Hernandes *et al.*[282] presented a new idea that a molecular diode can be created on the basis of carbon NT intercalated with boron and nitrogen. A nano-diode consists of a carbon (10,0)-NT (with metallic conductivity). A 'fibre' along the axis of this tube has two parts, *viz.*, one formed by boron atoms (p-dopants) and the other formed by nitrogen atoms (n-dopants). According to calculations, n–p-doping results in a potential barrier ($\sim$1 eV) between the adjacent sections of the tube containing the boron and nitrogen parts of the 'fibre', respectively. Jishi *et al.*[283] discussed the electronic states of (n,n)-BC_3-nanotubulenes (n = 2, 3, 4) intercalated with a chain of bromine atoms.

2. 'Symbiotic' nanostructures: metal–carbon cages (met-carbs) in nanotubes

The effect of intercalation on the properties of NT for more complex systems was considered by Ivanovskii *et al.*[284, 285] It was noted[284] that the formation processes, stabilities and properties of M@C type nanosystems obtained upon intercalation of NT with atoms of various metals depends on the nature of the intercalant and the atoms that form the NT. For example, lead, zinc, nickel and copper atoms readily penetrate the carbon NT (these metals are either inert to carbon under equilibrium conditions or form unstable carbide phases[286]). On the contrary, introduction of atoms of Group IV–VI d-metals, which readily form carbides, is hindered: their strong interactions with the carbon atoms in the NT walls would result in the deformation and destruction of the latter. Obviously, similar reasons should prevent the synthesis of M@NT type nanostructures (where M are atoms of the Group IV–VI d-elements) based on BN-, BC- and BCN-nanotubulenes.

It is assumed[284, 285] that new nanostructures incorporating Group IV–VI d-metals can be prepared if the latter are introduced into NT as their 'own' stable nanostructures. For example, these are represented by polyhedral clusters containing metal atoms along with carbon atoms, the so-called met-carbs, discovered not so long ago (in 1992).[287, 288] Metallocarbohedranes with the composition M_8C_{12} are the most stable of them. Metal–carbon nanoparticles with other compositions and structures have also been obtained (see, *e.g.*, the reviews[289–293]).

Ivanovskii *et al.*[284, 285] calculated the energy and electronic characteristics of hybrid quasi-one-dimensional nanosystems (M_8C_{12}@NT), *i.e.*, crystals formed by regular chains of met-carbs {$[M_8C_{12}]_\infty$, where M = Sc, Ti, V, Zr, Nb} arranged along the axis of single-layer C-, BN-, BC_x-, $B_xC_{1-x-y}N_y$, Si- and GaN-nanotubulenes.

Analysis of the electronic structures of a number of systems belonging to quasi-unidimensional M_8C_{12}@(12,0)-NT type (Fig. 16) was carried out with consideration of the chemical composition of the NT, mutual arrangement of met-carbs and NT (displacement of the met-carbs along the axis and rotation around the tubulene axis were simulated) and the electron concentration (EC) in the system defined by the nature of the transition metal.[284] 1D-Crystals incorporating the following met-carbs were considered: Sc_8C_{12}, Ti_8C_{12}, V_8C_{12}, Zr_8C_{12} and Nb_8C_{12}. It was found that the electronic spectrum of a quasi-1D Ti_8C_{12}@BN crystal consists of five occupied bands formed by the N2s-, C2s,2p-, (C2s,2p + N2p)-, (N2p-B2s,2p + Ti3d)-, C2p- and Ti3d-states. The first four bands contain the states responsible for the chemical bonds in Ti_8C_{12} nanostructures and in BN-nanotubulenes. The states of transition metals around the Fermi level are responsible for the bonds of the neighbouring met-carbs in the chain and for the chain–NT interactions.

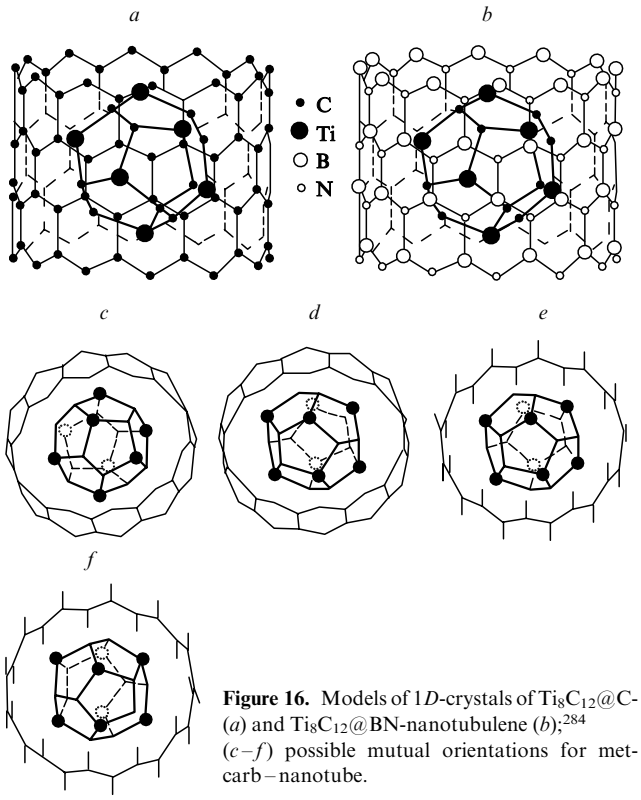


Figure 16. Models of 1*D*-crystals of Ti_8C_{12}@C-(*a*) and Ti_8C_{12}@BN-nanotubulene (*b*);[284] (*c*–*f*) possible mutual orientations for met-carb–nanotube.

It should be noted that stabilisation of a $[Ti_8C_{12}]_\infty$ polymeric chain occurs in a 1*D*-crystal of Ti_8C_{12}@BN-nanotubulene. However, the interatomic bonds in the NT and met-carbs change by no more than 1%–3%. In other words, the main types of the bonds which make these structures stable in the 'isolated' state are preserved in the crystal, which is evidence in favour of the stability of the simulated 'symbiotic' nanosystems. Ivanovskii *et al.*[284, 285] analysed the stability of this type of 1*D*-crystal depending on the position of the met-carbs and the NT and on the nature of the metal atom. Calculations for 1*D*-crystals incorporating Sc_8C_{12} and BN-nanotubulene in which the number of electrons per met-carb is less than 8 [as compared to the number of electrons per met-carb for Ti_8C_{12}@(12,0)-BN-nanotubulene] showed that there are no bonds between the met-carbs. In contrast, the increase in EC on going to the V_8C_{12}@(12,0)-BN-nanotubulene system favours a noticeable increase in the population of these bonds (by ~54%). Thus, it is possible to control both the bond strength and the stability of a system as a whole, as well as its dielectric properties, by changing the EC in the system (for example, by changing the chemical composition of the met-carbs by 'doping' them [293]).

It should be noted that a number of hybrid systems incorporating two types of stable nanostructures, *viz.*, fullerenes enclosed into an NT (C_n@C type)[69] and NT incorporating endofullerene chains (M@C_n@C type),[70] have recently been synthesised.

VI. Conclusion

Development of methods for the synthesis of non-carbon NT is now the leading direction in experimental studies on these unique subjects. Along with attempts to apply the methods known for the synthesis of carbon NT to the synthesis of other inorganic compounds in nanotubular form, elaboration of many 'special' synthetic methods is currently in progress.

In addition to physical methods, such as electric arc synthesis and laser ablation,[3–6, 15, 16, 24] which are particularly popular for producing carbon NT, chemical synthesis is becoming more and more important. In many cases, carbon NT serve as starting materials for the synthesis of non-carbon NT (chemical substitution, template synthesis).

It is difficult at the moment to compare the methods existing for the synthesis of non-carbon NT with respect to their productivity and effectiveness. It is possible that, even in the future, it will be hard to prefer some specific 'versatile' method, because the efficiency of each synthetic method depends on the chemical nature of the non-carbon NT.

The stage at which experimental studies are today is characterised by research into the synthesis of as wide a range of non-carbon NT as possible. The majority of studies describe the synthetic procedures and report the chemical compositions and morphology of the products. However, studies on physicochemical and functional properties are only occasional. These are only reported in selected studies and are far from being comprehensive.

Although it is possible to speak now of inorganic, physical, colloid, polymer and analytical chemistry of carbon NT,[27] it is too early to distinguish any particular areas of chemistry of non-carbon NT. The materials science of non-carbon NT is also in its infancy. Many suggestions to use them in practice are based on theoretical simulations and are far from technological solutions. The wide-scale production of non-carbon NT is also a problem yet to be solved.

Theoretical models have been developed for those non-carbon NT which have (or assumed to have) the closest similarity to carbon tubulenes. Ideal models of non-carbon NT in the shape of ideal cylinders rolled from a monoatomic sheet (or a polyatomic layer) remain the basis for describing these structures. Problems of describing various defects in non-carbon NT, processes of their growth and association into 'braids', films and crystals still need to be solved. There are no published data on the electronic and energy characteristics and properties of composite NT (*e.g.*, oxide NT that comprise oxide layers and an organic component). Problems of theoretical simulation also include NT reactivity and deviation of non-carbon NT from ideal morphology.

* * *

When this review was being prepared for publication, new interesting results appeared dealing with the synthesis and study of the properties of new non-carbon NT and materials based on them, as well as with their theoretical simulation. The most important studies are briefly considered below.

Tang *et al.*[294] proposed a simple method for the synthesis of boron–nitrogen NT by thermal treatment of a mixture of elementary boron and iron oxide (in the ratio 15 : 1) in a flow of gaseous NH_3. Chemical deposition from the gas phase onto a support containing Al_2O_3 particles with sizes of several micrometres gave multilayer (containing from two to five concentric layers) BN-nanotubulenes with unusually large inner diameters (8–10 nm).[295] Guo *et al.*[296] developed a two-stage process for chemical deposition from the gas phase, which allowed them to obtain Y-shaped splices of boron–carbon-nitride NT. Ma *et al.*[297] obtained a 'coaxial cable', *i.e.*, a carbon NT filled with iron 'core' and containing dielectric boron–nitrogen nanotubulenes as the housing. It was confirmed by EELS that the carbon and boron–nitrogen layers in such heterostructures are separated from each other.

Studies on dichalcogenide NT were continued. Thermal decomposition of $(NH_4)Mo_{1-x}W_xS_4$ in an inert atmosphere or in hydrogen gave single-layer and multilayer NT with 'mixed' composition $Mo_{1-x}W_xS_2$ ($x < 0.1$)[298] containing new defect types. A method for the synthesis of sulfide NT with the composition $Cu_{5.5}FeS_{6.5}$ was suggested.[299] Pyrolysis of a mixture of WO_{3-x} with carbon NT in an $N_2 + H_2S$ atmosphere gave new composite structures, *viz.*, single-layer carbon NT encapsulated in multilayer WS_2-nanotubulenes.[300] Problems of hydrogen accumulation in MoS_2-nanotubulenes were discussed.[301]

Synthesis of silicon NT, both open and closed on the ends, with inner diameters of ~60–80 nm was reported.[302] They were obtained by deposition of a mixture of $SiCl_4$ with hydrogen onto a Ni_xMg_yO support that served simultaneously as a catalyst.

Interesting results were reported by Bao *et al.*[303] who obtained nano-sized nickel tubes by electrochemical deposition of metallic nickel in pores of an alumina membrane. These nanostructures manifest magnetic properties. Li *et al.*[304] were the first to obtain gallium-nitride NT.

Progress was also achieved in methods for the synthesis of oxide nanotubulenes. New schemes for the preparation of vanadium-oxide NT were discussed.[305, 306] Dobley *et al.*[306] were the first to obtain mixed NT with the composition $Mn_{0.1}VO_{2.5+\delta}$ by ion-exchange reactions. A method for the synthesis of TiO_2, ZrO_2, Nb_2O_5 and Ta_2O_5 metal-oxide nanotubulenes using organic crystallites as templates was discussed.[307] Reactions of crystalline TiO_2 (anatase or rutile) with a NaOH solution gave a multilayer titanium-oxide NT with distances of $\sim$0.75 nm between the adjacent layers.[308] The chemical compositions of the tubes (*viz.*, the Ti : O ratio) vary widely. A compacted set of titanium oxide-based NT was found in a product of anodic oxidation of pure titanium.[309] The NT diameters range within 25–65 nm; their ends closed on the support side form a barrier layer resembling porous Al_2O_3.

GeO_2 nanorods of 50–150 nm diameters and a few hundred micrometres long were obtained.[310] Studies of the photoluminescent properties of these nanostructures showed that they are promising as materials for optoelectronic nanodevices. The sol–gel method was used to obtain semiconducting Ga_2O_3 and In_2O_3 nanotubulenes with $\sim$100 nm diameters.[311]

Maurin *et al.*[312] studied the electrochemical doping of carbon electrodes built of NT with lithium; a number of other issues of the electrochemistry of lithium-doped carbon NT were considered elsewhere.[313, 314] The positron annihilation method was used to study multilayer carbon NT doped with potassium, rubidium and cesium.[315] A review paper[316] discussed methods for the synthesis of composites containing metal atoms intercalated in carbon NT and the role of metal atoms as NT growth catalysts, as well as the results of studies of these composites by molecular dynamics and quantum-chemical methods.

A new composite material consisting of multilayer carbon NT in amorphous SiO_x has been obtained.[317] Furthermore, the SiO_x/NT structure was simulated by a strong-bond DFT method. The sol–gel method was used to obtain yet another new composite containing vanadium pentoxide and carbon NT, which may be promising as lithium battery electrodes.[318]

Studies on C_n@C-nanotubulene hybrid systems (fullerenes in nanotubes) were continued.[319–321] The local electronic states of the C_{60}@C-nanotubulene system were studied by scanning tunnelling microscopy[319] and EELS.[320] It was concluded[320] that fullerene–NT interactions occur due to weak van der Waals forces. The methodological aspects of the use of EELS spectroscopy for studies on the optical and electronic structures of C_n@C-nanotubulenes were analysed.[321]

Interesting results were obtained in theoretical simulation of the systems in question.[322] For example, calculations for a set of hypothetical SiC-nanotubulenes by DFT made it possible to suggest that they can be synthesised by injection of holes.[323] The type of the interband transition in these metastable tubular structures (*i.e.*, whether direct or indirect transitions occur) depend on their chirality. The E_{str} of these NT were found to be smaller than the E_{str} of the corresponding carbon NT.

Much attention is paid to the development of microscopic models of 'hybrid' nanostructures. Based on calculations of the potential energies for systems containing spherical and ellipsoid fullerenes inside carbon NT, the 'optimum' sizes for the fullerenes to be incorporated were discussed.[324] The molecular dynamics method was used to calculate the energy states and the elastic and tribological parameters of fullerenes in (*n,n*)-C-nanotubulenes (where $n = 5-10$).[325] A very interesting problem was considered by Liu *et al.*:[326] they optimised model 'hybrid' nanostructures in the form of carbon NT containing a monoatomic 'fibre' of carbon atoms inside (along the axis). It was shown that for the NT with diameters larger than $\sim$0.43 nm the fibre turns into a spiral along the NT axis.

Non-empirical DFT calculations of the energy states of C_{60} fullerene in boron–nitrogen NT were carried out.[327] It was estimated that incorporation of fullerenes into (9,9)- and (10,10)-NT is exothermic, which implies that such 'hybrid' structures can actually be synthesised. It was shown that they would be semiconductors.

The formation mechanism of yet another type of 'hybrid' structure, *viz.*, small-size ionic KI crystallites inside carbon NT, was studied by molecular dynamics methods.[328]

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