

Carbon nanostructures containing boron impurity atoms: synthesis, physicochemical properties and potential applications

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Abstract

Introduction of substitution atoms into carbon nanotubes is an efficient tool of controlling their physicochemical properties which allows one to expand their practical applications. Boron is one of the most promising materials used for the modification of carbon nanotubes. However until now there has been no systematization of research data on the effect of boron impurity atoms on the properties of carbon nanotubes, and this limits potential industrial applications of this nanomaterial. In this work the most efficient currently existing methods of synthesizing carbon nanotubes containing boron impurity atoms have been discussed and the physicochemical properties of the obtained nanomaterials have been analyzed. Furthermore predictions as to their potential application domains have been made on the basis of available theoretical and experimental results. Comparison of the developed technologies has shown that the most efficient synthesis method is the catalytic vapor phase deposition. The mechanical, electronic and chemical properties of boron-carbon nanotubes have also been reviewed. For a more comprehensive analysis of the dependence of the physicochemical properties of carbon nanotubes on the concentration of boron impurity a model experiment has been carried out involving quantum mechanics instruments which has shown a direct correlation between the band gap of the material and the number of boron impurity atoms. The main practical application trends of boron-containing carbon nanotubes have been outlined.

Keywords

carbon nanotubes, boron-containing nanotubes, structural modification, conductive properties, adsorption, nanotube synthesis.

1. Introduction

Carbon-based nanostructures have been among the most important nanotechnology materials for several decades. Due to their unique properties they have found application in various branches of industry, science and engineering. However the synthesis of stable nanostructures with preset properties remains one of the key problems. One of the simplest tools for controlling the properties of

these materials is the functionalization of carbon nanotubes (CNT), i.e., modification of the sp^2 -hybridized nanotubes by reactions of substitution for similar heteroatoms or functional groups [1–3]. This method allows one to control the chemical properties of the nanotubes and to effectively modify their functionality and parameters thus expanding their potential applications [1–3]. Li, B, N, S, P, K and other elements have been discussed as doping impurities in literature. C. Kröckel [4] studied

in detail the possibility of CNT doping with potassium and the electron energy structure of the obtained nanomaterial. The possibility of nanotube doping with sulfur and phosphorus was discussed in numerous works [5–7]. H. Tavakol [8] showed that sulfur doping of CNTs avoids their oxidation. The data were confirmed in a model experiment based on the density functional theory by Monte Carlo et al. [9]. K. Saadat [9] studied the interaction of pure and sulfidized carbon nanotubes with methanol, methanethiol, water and dihydrosulfide.

Despite the large scope of research data on the interaction of CNT with various materials, boron (B) and nitrogen (N) remain the most suitable elements for the substitution reactions. Their use has a number of prerequisites, e.g. the oxidation/reduction properties of heteroatoms providing for their straightforward incorporation into the nanotube lattice [10]. In the choice of a doping material one should also pay attention to the safety and stability of the final material, while maintaining the main spatial parameters of the nanoobjects. The properties of nitrogen doped CNT were studied earlier from the standpoint of their application details [1]. These experiments suggested successful nanotube applications in various fields, e.g. as hydrogen adsorbents [11]. Below we will discuss the most efficient currently existing synthesis methods of CNTs containing boron impurity atoms, analyze the physicochemical properties of the obtained nanomaterials and predict their potential application fields on the basis of theoretical and experimental results.

2. Scientific prerequisites for boron modification of pure carbon nanotubes

From the viewpoint of electronic structure the boron and nitrogen atoms have a number of similarities. The reaction of pure CNT saturation with boron atoms allows one to modify the properties of semiconductor nanotubes towards metallic properties by lowering the Fermi level to the valence band [10]. The introduction of boron atoms in the structure of CNT walls reduces the charge inhomogeneity of the surface and hence improves the sorption properties of CNTs [12]. This opens wide opportunities for the application of boron doped CNT as catalysts [13], gas atom adsorbents [14], basis for the synthesis of composite materials [15] etc. The first mentioning of the experimental synthesis of boron doped CNT was by D. Carroll [16] who described the synthesis of boron-carbon nanotubes by the electric arc method, the anode being a boron nitride saturated material. Later works dealt with the synthesis of boron-saturated CNT by arc discharge, laser ablation, substitution reactions [17] and chemical vapor deposition (CVD) [14]. It was reported [18, 19] that CVD is the most universal and economically efficient method.

Figure 1 illustrates the development history of boron-carbon nanotubes since their discovery in 1991 until now. It can be seen from the time diagram that boron-carbon nanotubes have found applications in a wide variety of science and engineering branches. The first discussion of this problem was put forward by S. Peng [20] who studied sensor devices on the basis of modified CNT in order to determine their response and sensitivity to carbon monoxide and water molecules within model experiments. The presence of the response was confirmed by a decrease of the band gap of boron doped CNT upon exposure to water and carbon monoxide. Thus the model experiment showed that boron-containing nanotubes can react with molecules whose capability of bonding with pure CNT was never confirmed before. The sensitivity of the model device can be controlled by changing the concentration of the heteroatoms in the nanotubes. That experiment has entailed a number of works [4, 21–26] which dealt with various properties of CNTs containing boron impurity atoms in different concentrations. M. Ramadoss et al. [27] reported recently Ni/Ni₃Fe incorporation into boron-carbon nanotubes for accelerating oxygen evolution reactions. The production of a Ni/Ni₃Fe skeleton and boron-carbon nanotubes facilitates the transfer of ions/electrons and the release of oxygen bubbles thus improving the activity of the reaction in question. P. Ai et al. [13] reported an increase in the selectivity of dimethylxalate hydrogenation to ethanol with a boron-carbon nanotube based Cu catalyst. This effect originates from the high dispersion of copper and hence improved copper particle interaction with the CNT carrier having a suitable surface acidity. H. Muramatsu et al. reported recently [28] a nanoelectronic application of multi-walled nanotubes containing boron impurity atoms due to their thermoelectric properties. The study included selective saturation of outer tubes which proved to increase the electrical and thermal conductivity of multi-walled boron-carbon nanotubes. P. Wei et al. [21] discussed the efficiency of boron- and nitrogen-containing CNTs in accelerating oxygen reduction reactions and their battery fabrication applications. All the above cited works show that boron-carbon nanotubes show good promise due to their specific physicochemical properties that unleash their potential as one of the most efficient nanotechnology materials. Despite the great research interest to this category of materials there has been no detailed review of these materials in literature and no attempt has been made to systematize various works dealing with the study of their properties. Therefore we present below generalized data on the synthesis methods of boron-carbon nanotubes, study of their properties and prediction of their potential applications on the basis of the studies. To carry out this review we analyzed the most important recent works dealing with boron-carbon nanotubes. Along with a review of international research effort on the matter we analyzed domestic studies dealing with the subject.

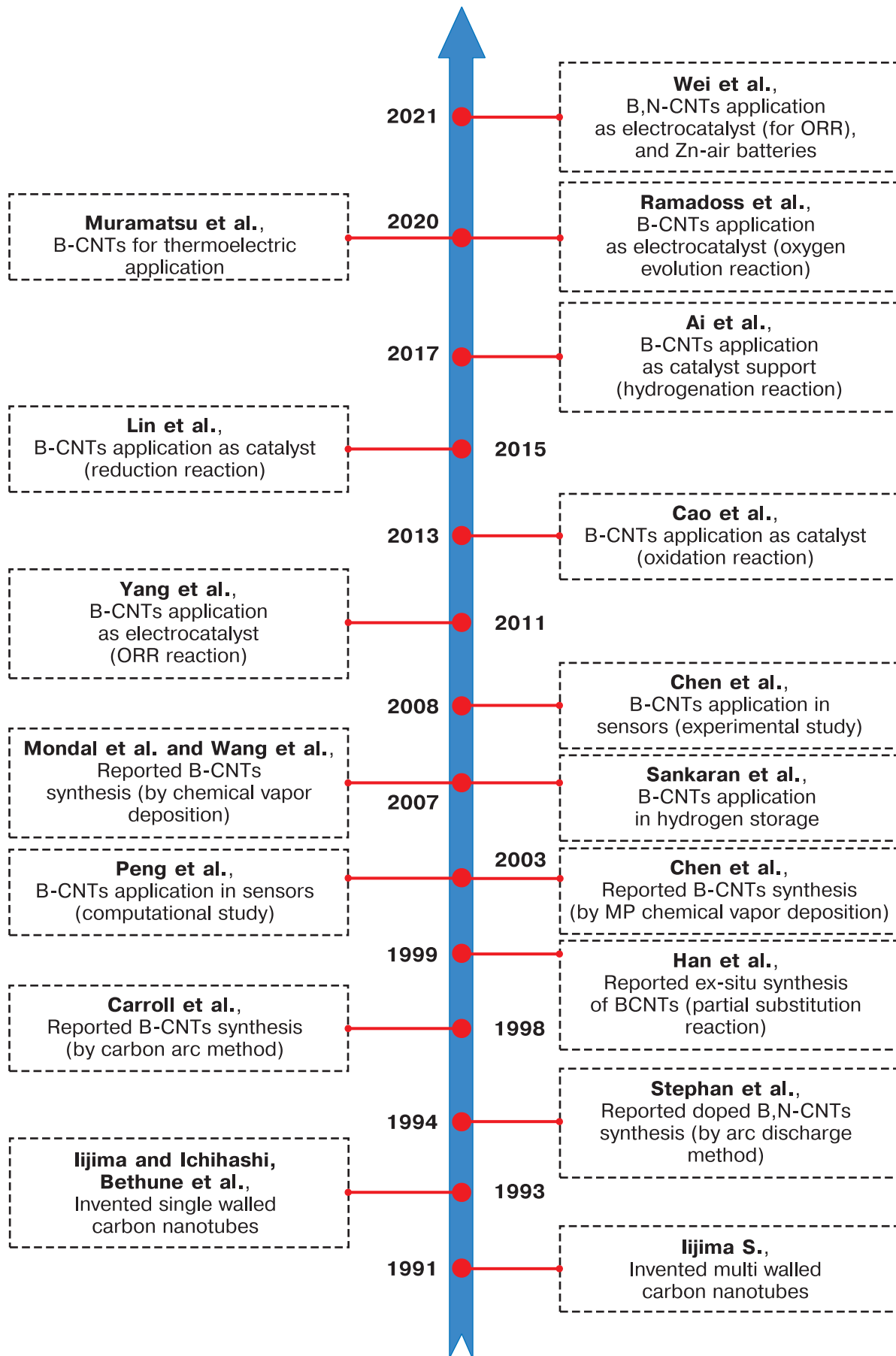


Figure 1. Works dealing with boron-carbon nanotubes [10].

3. Boron-carbon nanotube synthesis methods

3.1. Electric arc method

Both pure CNTs [29] and nanotubes containing boron impurity atoms [16] were first obtained using this method. This method is based on the formation of a glow discharge between a cathode and an anode for a preset duration in an inert gas atmosphere. O. Stephan et al. [30] suggested synthesizing the first boron-saturated CNT using a modified electric arc method. The anode for nanotube synthesis was in the form of a cell containing a mixture of boron and graphite powders. Current was passed through the modified anode and the cathode in a nitrogen gas atmosphere at 25 B and 100 A. The discharge produced boron doped graphene particles, boron-carbon nanotubes and nanowires containing <2 at.% boron.

D. Carroll et al. [16] synthesized boron-carbon nanotubes by carbon arc method with a boron content of 1–5 at.% and a nitrogen content of <1 at.%. The anode was BC_4N and the cathode was a graphite electrode. Current was passed through the arc chamber in a helium gas atmosphere (pressure 500 to 650 torr). The above cited brief descriptions of boron-carbon nanotube synthesis experiment setups suggest that the most important stage is the addition of boron to the anode material for introducing the boron impurity into the nanostructures. Then an arc discharge was produced between the anode and the cathode in an inert gas atmosphere (typically helium or argon). B. Wang et al. [31] described the synthesis of single-walled boron and nitrogen doped CNTs using amorphous CoNiB alloy as an anode in inert gas atmospheres.

3.2. Laser ablation

Based on high-energy laser exposure of a graphite rod for graphite evaporation from its surface due to high carbon particle temperatures achieved and further formation of CNT [32]. P. Gai et al. [33] suggested synthesizing CNTs containing boron impurity atoms using laser ablation of a target consisting of carbon with Co/Ni/B impurities. The final boron impurity concentrations were from 1.5 to 10 at.%, the microstructures being different for various impurity concentrations. J. Blackburn et al. [34] studied the evaporation of a graphite rod containing B and NiB impurities in inert gas atmospheres. Spectroscopic studies showed the concentration of the boron impurity atoms to be 1.8 at.%.

3.3. Substitution reaction

Based on the interaction of pure CNT with various precursors (e.g. B_2O_3 or H_3BO_3) in an inert gas atmosphere (typically helium or argon). This reaction is usually achieved at high temperatures (1000–2000 °C) for a pre-

set time (from 30 min to 4 h). A number of works described the application of these reactions for the synthesis of boron-containing nanotubes [17, 35–38]. For example, K. Fujisawa et al. [36] studied the effect of the substitution reaction on the conducting properties of CNT. Y. Lin et al. [35] obtained CNTs containing boron substitution atoms by annealing in the presence of boric acid as a precursor for studying the potential application of catalysts on the basis of boron-containing CNT with the goal of reducing the concentration of nitroarenes.

W. Chiang [37] suggested a modified method of substitution process that included a two-stage mechanism: growth of nanotubes and substitution reaction. Figure 2 shows the main stages of this process a detailed description of which is available elsewhere [37]. The nanotubes containing boron impurity atoms obtained in that experiment differed from those synthesized in any other experiments by the possibility of controlling the distribution of boron atoms in the nanotube by adjusting the reaction temperature and duration. Similar successful experiments were also described elsewhere (Y. Leu et al. [38]) and M. Yeh et al. [17]).

3.4. Chemical vapor deposition (CVD)

This method is one of the most widely used methods for the large-scale synthesis of CNT with a sufficiently low cost [18, 19]. The method implies the introduction of precursors into the reaction chamber at a preset temperature. This method is based on the decomposition of the raw materials into discrete molecules or components. Therefore the main requirement to this method for synthesizing high-quality CNTs is the size of the main reacting particles [19]. For boron-containing nanotubes boron atoms can be introduced by selecting a catalyst or precursors.

The synthesis of boron-containing nanotubes using this method was described in a number of works [12, 14, 39, 41–44]. P. Ayala [39] used the chemical vapor deposition method at high temperatures in vacuum for synthesizing boron-containing nanotubes. The $C_9H_{21}BO_3$ precursor with molecular oxygen was supplied through a horizontal reactor for synthesizing carbon-containing nanotubes. The furnace contained magnesium oxide coated steel particles and the reaction temperature was 790–890 °C. The diameter of the obtained nanotubes was 0.9 to 1.5 nm.

One of the key tasks to be solved for obtaining CNTs containing boron impurity atoms using this method is the selection of a suitable catalyst. Another key item is to achieve homogeneous catalyst deposition onto the substrate for the formation of an array of uniform boron-carbon nanotubes. Furthermore avoiding the effect of catalyst on the final reaction product is also an important problem the solution of which affects the final result [18]. On the contrary floating catalyst chemical vapor deposition (**FCCVD**) implies simultaneous introduction of carbon and catalyst particles thus excluding the possibility of their deactivation. Metallic compounds are typically used for FCCVD synthesis of nanotubes. After thermal

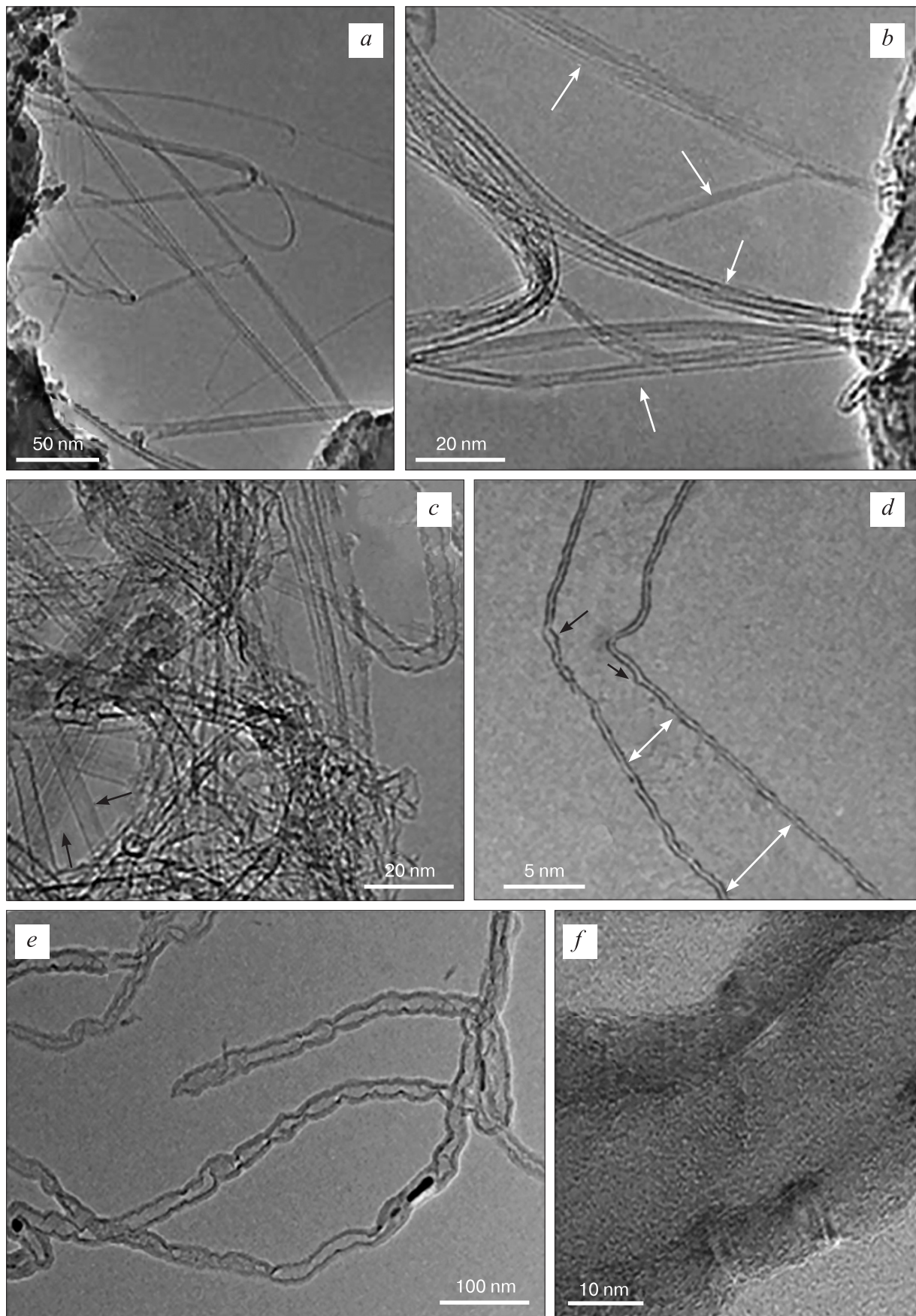


Figure 2. TEM images of (a and b) single-, (c and d) two- and (e and f) multi-walled boron-containing nanotubes synthesized using different methods: (a–d) triisopropyl borate decomposition; (e and f) with ethanol and triethyl borate. The technology of the nanotubes shown in Figs. (a and b) is described in [39]; (c and d) in [40]; (e and f) in [14]

decomposition of the metallic compounds their supersaturated vapors condensate to form metallic particles in the vapor phase [18]. Furthermore this technology does not require a substrate thus reducing the synthesis and further processing costs. One can therefore assume that FCCVD is the most preferable method for large-scale synthesis of nanoparticles [18, 19]. G. Keru et al. studied the possibility of synthesizing CNTs containing boron impurity atoms using the FCCVD method with toluene as a source of C, ferrocene as a component of catalyst and triphenylborane as a source of C and B [12]. N. Tsierkezos et al. [41] reported the synthesis of boron-containing nanotubes on a Si/SiO₂ substrate with chemical decomposition of ethyl alcohol and boric acid in the presence of ferrocene as a catalyst using the sputtering pyrolysis method. The authors used films consisting of nanotubes as electrodes for analysis of dopamine, uric acid and ascorbic acid. C. Preston et al. [42] described the synthesis of multi-walled boron doped CNT using CVD with solution sprinkling. The C source was alcohol and the B precursor was gaseous diborane, with Co : Mo : MgO being the catalyst.

K. Tomita et al. [43] suggested various CNT synthesis methods by catalytic vapor deposition using nickel boride (NiB) as a catalyst. The catalyst designed in that work consisted of a 10 nm thick tin layer and a 6 nm Ni layer on a SiO₂/Si substrate. Ethanol and Ar were supplied to the reactor at 700, 800 or 900 °C for the synthesis of CNT with boron impurity atoms. A. Sharma et al. [44] suggested a kinetic model of CNT synthesis in a fixed bed at different reaction temperatures, partial pressures, reactant flowrates, catalyst concentrations etc.. The authors used acetylene, boric acid and ferrocene/MgO as carbon, boron and catalyst sources, respectively. In 2019 S. Sawant et al. [14] studied the adsorption isotherm and adsorption kinetics of hydrogen. The boron-containing

nanotubes used in their experiment were synthesized by CVD with ethanol, ferrocene and triethyl borate as carbon, catalyst and boron sources, respectively.

4. Comparison between methods of synthesizing carbon nanotubes with boron impurity atoms

In this section various methods of synthesizing boron-carbon nanotubes will be analyzed. Table 1 summarizes parameters of different methods and provides evaluation of each method in terms of this criterion.

5. Properties of carbon nanotubes containing boron impurity atoms

When impurity atoms are introduced into carbon nanotubes a heterostructure forms on the nanotube surface [45]. Thus the impurities introduced determine the range of the key new properties achieved in the test nanomaterials. One should therefore select substitution atoms so to provide for their required effect due to their oxidation/reduction properties without distorting the system geometry because of their sizes [10]. Comparison between the main parameters of boron and carbon atoms is shown in Table 2.

As follows from Table 2 boron is the closest neighbor of carbon in the Periodic Table of Elements. Based on the number of valence electrons and the electrical negativity one can conclude that the bond length between B and C atoms will differ but slightly from the C—C bond length in carbon nanotubes.

Table 1. Comparison between methods of synthesizing boron-containing nanotubes

Parameter	Electric arc method	Laser ablation	Substitution reaction	FCCVD
Number of nanotubes synthesized	Small	Small	Large	Large
Quality of nanotubes obtained	High	High	High	High
Continuous fabrication potential	One batch per cycle	One batch per cycle	One batch per cycle	One batch per cycle / continuous fabrication possible
Method cost	High	High	Medium	Low
Special equipment requirements	Existing technologies to be modified	Special target selection	Reaction conditions selection	Reactor for large-scale nanotube synthesis can be developed without additional changes

Table 2. Physicochemical properties of boron and carbon atoms

Element	Number in Mendeleev Table	Electronic structure	Number of valence electrons	Atomic radius (nm)	Electrical negativity
B	5	1s ² 2s ² 2p ¹	3	180	2.04
C	6	1s ² 2s ² 2p ²	4	170	2.55

6. Physical properties

6.1. Electronic properties of boron-containing nanotubes

The introduction of boron impurity atoms changes the physical, chemical, mechanical and electrical properties of the nanotubes. As discussed in the previous section, boron introduction produced an inhomogeneous distribution of electron density in carbon nanotubes leading to an increase in the reactivity [39, 12]. Pure nanotubes may exhibit semiconductor or metallic properties depending on their radius and chirality. Boron addition to the structure of nanotubes may entail a wide range of changes in their electrical properties upon a change in the content of impurity atoms. The key work for understanding the properties of boron-carbon nanotubes published by A. Rubio [46] dealt with a detailed study of their band structure. Doping elements were used at impurity levels in bulk semiconductors for producing an acceptor state in the band gap at a low energy above the valence band. Thus it is safe to say that the higher the doping level the greater the Fermi level shift. When a certain boron concentration is exceeded the impurity levels hybridize with the carbon levels and form strongly dispersive “acceptor-like bands” [46]. Furthermore the structures of the valence bands are severely distorted because the levels of carbon atoms that are substituted by boron move upwards in energy [46]. The band structure distorted upon doping lowers the symmetry of the CNT and hence may avoid crossings between states, unlike for pure nanotubes. It was therefore concluded [47] that the introduction of boron impurity atoms is an efficient metallization method of carbon nanotubes. However the density of states at the Fermi level strongly depends on the geometry of the structures and varies non-monotonously with the B content [46].

6.2. Mechanical and thermal properties

H. Rezaia et al. [48] reported the low-temperature heat conductivity of nanotubes to decrease with an increase in the concentration of boron impurity atoms in zig-zag-shaped CNT. On the contrary, with an increase in temperature, an increase in the boron concentration improved the heat conductivity of the nanotubes. The effect of boron doping on the thermal and mechanical properties of graphene and diamond was also studied [59]. The presence of boron in graphene structures changed their properties from plastic to brittle. Also the addition of boron impurity atoms was found to efficiently reduce the heat conductivity of graphene. Along with boron doped nanotubes and graphene, diamond containing boron impurity atoms also exhibited a similar trend in the heat conductivity [49].

6.3. Chemical properties

The introduction of boron impurity atoms produces *p*-type states that add to the conducting properties of carbon nanotubes. For boron-containing nanotubes the vacant $2p_z$ orbital of B interacts with the π orbital of carbon for electron transfer. These electrons become quite active due to the low electrical negativity. As a result the O_2 molecules reduce in positively charged regions of B that support the oxygen reduction reaction [50]. For graphene, B doping favors the redistribution of the electron density and these electron-deficiency sites improve the bonding capacity of the N_2 molecules in the N_2 reduction reaction [51]. Furthermore these active centers hinder the binding of Lewis' acid H^+ in these centers under acidic conditions [51]. B. Viswanathan et al. [52] studied hydrogen adsorption on pure nanotubes and B atom doped nanotubes and found that the heteroatoms behave as active centers and exhibit a catalytic behavior. These sites are more susceptible to hybridization than carbon and facilitate the migration of solute hydrogen toward the equipotential surface of carbon. An important role in these processes belongs to the oxidation/reduction properties and the standard free energy of hydride formation [52].

7. Experimental studies of atomic hydrogen adsorption on the surface of boron-carbon nanotubes

The search for an environment friendly fuel for stopping carbon and carbon monoxide atmospheric pollution has been one of the key topics for many researchers over the last 40 years [53]. Therefore one of the main tasks is the improvement of green technologies. Among them the transition to hydrogen fuel seems to be the most energy advantageous [53]. However the storage and transportation of hydrogen are problems that are still to be solved. Various methods have been tested: physical, chemical, electrochemical as well as storage of crystalline hydrogen [54].

A promising way to solve these tasks is to explore the possibility of using nanomaterials as potential hydrogen storage. A wide variety of materials from carbon nanostructures to borophen have been studied [55–61]. Researchers have developed two methods of synthesizing boron-containing nanotubes [62]: boron saturation of nanotubes in the course of substitution reactions with various physical and/or chemical catalysts (*ex-situ*) and synthesis of boron-carbon nanotubes from source precursors (*in-situ*). These types of boron-containing nanotubes may be a good storage of atomic hydrogen, and it would be interesting to compare between the results of hydrogen adsorption on these nanotubes and on carbon nanotubes that are already quite widely used and well-studied.

Experiments for hydrogen saturation of the obtained boron-containing nanotubes showed that the reaction

yields better results than for pure carbon nanotubes. For MWCNT this percentage was 0.02%, for SWCNT it was 0.022% and for boron-containing nanotubes, 0.157% (pressure 10 barr, temperature 303 K). Analyzing the adsorption-supporting mechanisms one should pay special attention to the charge distribution on the adsorbate surface. B. Viswanathan et al. [52] assumed that the presence of heteroatoms additionally initiates hydrogen adsorption. A detailed model experiment will unveil the main regularities of these processes and predict the most efficient concentration of boron impurity atoms that will help one to control the sorption processes.

8. Experimental studies of oxygen interaction with boron-containing nanotubes

One of the most important tasks of the chemical industry nowadays is the search for materials that can be used for the oxygen reduction reaction [63]. Platinum is currently used for this purpose but its high price encourages the search for new materials, including nanomaterials, that can efficiently adsorb and reduce oxygen. The experiment described by Y. Cheng et al. showed that boron doped carbon nanotubes participate efficiently in this reaction, although the mechanism of the reaction is still incompletely clear.

For the experiment [63] carbon nanotubes were annealed in the presence of boric acid for boron saturation and then oxygen-saturated for 4 hours. Then all the unwanted reaction products were removed by blowing the specimens with a nitrogen jet and cleaning in a water jet. The main physicochemical parameters of the specimens were studied using X-ray diffraction and transmission electron microscopy. The nanostructure topology and morphology images showed that the crystalline structure of the boron-containing nanotubes did not differ from that of the pure carbon nanotubes which were studied as references. The references were exposed to the same heat treatment and oxidation but without boric acid.

The X-ray diffraction studies showed that the boron-containing nanotubes with different concentrations of boron impurity atoms adsorb oxygen better than pure carbon nanotubes (Fig. 3).

Thus the experiments [63] showed that the nanotubes containing boron impurity atoms exhibit improved oxygen sorption properties and are therefore more efficient as a material for oxygen reduction reactions. This can be caused by the fact that the redistribution of the electron density related to the heterostructure of BC_n nanotubes leads to a more efficient chemisorption of atomic and molecular oxygen than for pure carbon nanotubes. However better understanding of the mechanism of this reaction requires a detailed model experiment for oxygen adsorption on the surface of boron-containing nanotubes.

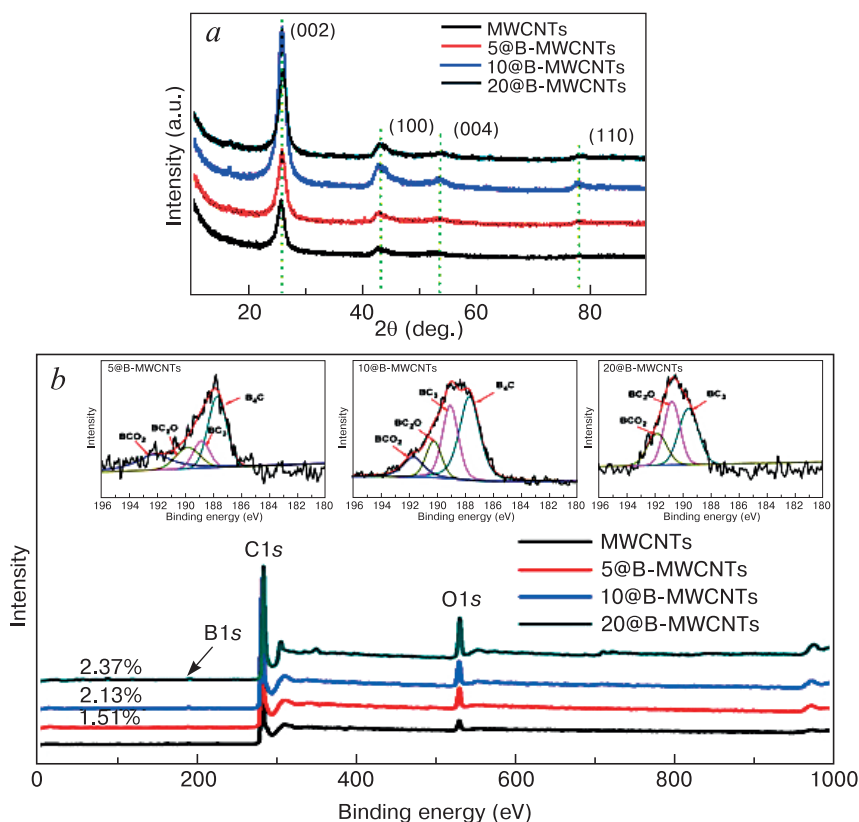


Figure 3. X-ray diffraction data for nanotubes: (a) pure nanotubes before oxygen exposure; (b) X-ray diffraction patterns for nanotubes exposed to oxygen [63].

9. Experimental studies of carbon-containing nanotubes with boron impurity atoms

Various measurements (e.g. electron paramagnetic resonance, magnetic susceptibility, specific resistivity, Hall effect and magnetoresistivity) showed that the carrier mobility and diamagnetic susceptibility of these materials strongly depend on the boron concentration. Earlier methods of boron addition to carbon were discussed [64]. They are usually of two types: (a) boron addition to carbon (i) before and (ii) after graphitization and (b) boron introduction into an organic precursor before carbonization. A recent discovery made during MWCNT generation by electric arc method is that the length of carbon nanotubes can be greatly increased if the graphite anode contains elemental boron [65–67], and that the BC_3 cells, among others, are incorporated into the hexagonal carbon network [65–67]. As a rule the length of carbon nanotubes ranges from 4 to 8 nm for C/arc synthesized materials and approx. from 10 to 200 nm for BC/arc synthesized ones, the nanotube diameters for these two types of nanostructures as measured based on TEM and SEM examination being close, i.e., 5–40 nm [65–68]. It is assumed that pentagons form in the presence of boron atoms and it is therefore believed that boron plays a key role at the open tip of the growing nanotube, e.g. in controlling the tube wall structure.

Electron spectroscopy confirmed the presence of boron in the CNT (see inset in Fig. 4: the 188 eV peak

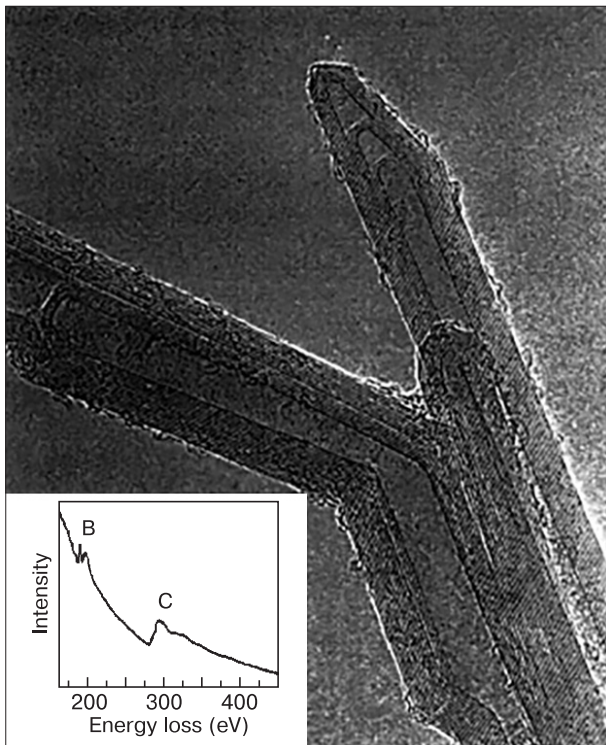


Figure 4. Image of boron-carbon nanotube tip. *Inset:* Electron spectrum with 188 eV peak [71].

corresponds to the sp^3 -hybridization case). Boron atoms were found both at the nanotube tips and in their walls. Since boron particles were delivered to the nanotube from boron nitride powder, one should specially note the absence of nitrogen atoms in the nanotube structure. This result is in agreement with another work [68] describing the mechanism of boron-carbon nanotube formation but in that experiment [68] the boron atoms were mostly located at nanotube tips.

Boron-containing CNT have the same 3D ordering as ordinary graphite structures exhibiting the 101 X-ray reflection (Fig. 5). This ordering in multi-walled nanotubes which are usually synthesized in practice is distinguished by clear and straight boundaries between single-walled nanotubes [69]. As a rule MWCNT do not exhibit a clear 3D structure due to the presence of regions with screw and cylindrical symmetries within a single nanotube [70, 71]. It was predicted [68] that the introduction of boron impurity atoms should cause the formation of zigzag-type nanotubes. This assumption was checked with an electron diffraction study of single boron-containing nanotubes and their agglomerations. Multiple experiments showed that the zigzag shape of nanotubes is actually the most frequent occurrence among boron-containing nanotubes. One can assume that multi-walled nanotubes can also be expected to be predominantly zigzag-type, resulting in clear and straight boundaries seen at nanotube cross-sections. For CNT these results can be achieved by two ways: clear separation of nanotube layers or synthesis of inter-layer separating structures. A detailed TEM study of boron-containing nanotubes was reported [67].

X-ray diffraction showed that the number of layers in multi-walled boron-containing nanotubes is approx. 42 which is in agreement with the structure of MWCNT [68]. Figure 5 shows splitting of the 004 peak for boron-containing nanotubes which corresponds to a fluctuation of the inter-wall distance in nanotubes with an increase in

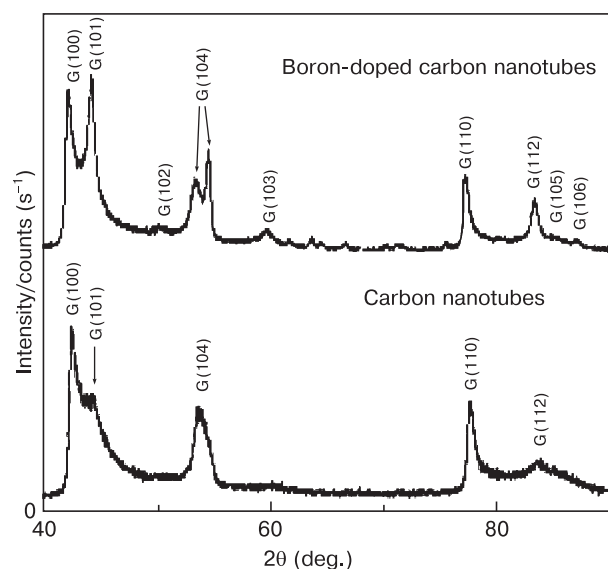


Figure 5. X-ray diffraction patterns of (top) boron-doped and (bottom) multi-walled carbon nanotubes [67].

the number of layers in the cross-section. By and large these results agree with the TEM data.

The introduction of boron atoms into carbon hexagons causes a distortion of the symmetry and produces oscillations that are detected in the IR range. Data for nitrogen doped graphite [72] showed that the distortion of the hexagonal symmetry makes the nanomaterial suitable for IR spectroscopic study. However for boron-containing nanotubes this could cause certain problems because it is believed that the formation of the BC_3 structures is predominantly an edge process whereas IR spectroscopy is the most efficient for studying the central part of an array [73].

Spectroscopic patterns of multi-walled and boron-containing CNTs are shown in Fig. 6. The spectra were taken at 514.5 and 632.8 nm. It can be seen that the peaks at below 1700 cm^{-1} are by approx. 20% broader for boron-containing nanotubes than for MWCNT. However the difference between the test nanostructures is the strongest between the intensities in the D and G ranges. For multi-walled carbon nanotubes this ratio is 0.06 whereas for the boron-containing nanotubes it is 0.90 for 514.5 nm. For 632.8 nm the ratio increases from 0.10 for the MWCNT to 1.40 for the boron-containing nanotubes. This difference

can be accounted for by the introduction of boron atoms which distort the ordering of the carbon nanostructures. Now it is worth dwelling upon the electronic structure of the test nanostructures.

To study the conducting properties of the boron-containing nanotubes we used microwave conductivity measurements. The data are shown in Fig. 6. The boron-containing nanotubes proved to be metallic unlike the MWCNT which were temperature-induced semiconductors. The study showed that the conduction band of the BC_3 nanostructures is above the Fermi level by about 2/3 of the distance between the L and X Brillouin zones [74]. The introduction of boron in the electronic structure increases the concentration of carriers (holes) thus increasing the conductivity. Nevertheless the BC_3 nanostructure is an impurity one which causes a decrease in the carrier mobility. Taking into account the spectroscopic data one can assume an increased concentration of boron atoms at nanotube tips entailing but moderate change in the conducting properties of entire surface of the boron-containing nanotubes.

The BC_3 nanostructures occur typically in the outer layers rather than in the inner ones. D. Carroll et al. [16]

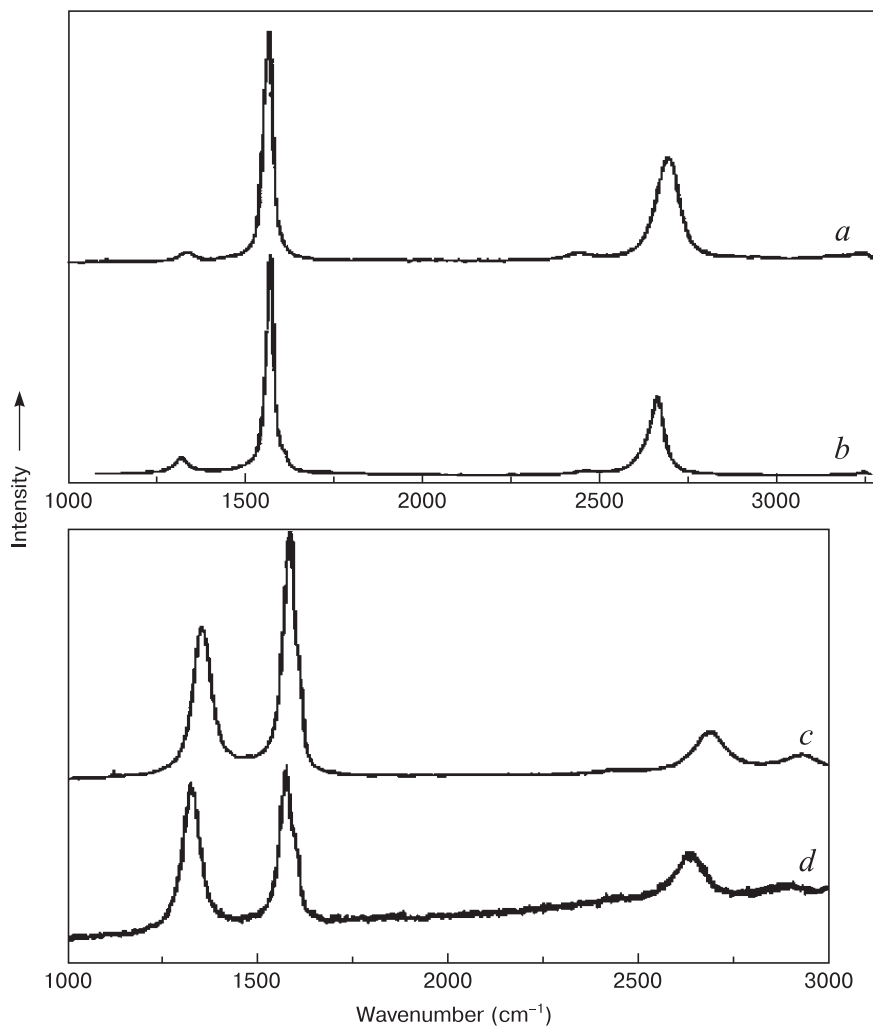


Figure 6. Top: (a) 514.5 nm and (b) 632.8 nm Raman emission spectra for MWCNT. Bottom: (c) 514.5 nm and (d) 632.8 nm Raman emission spectra for boron-containing nanotubes [73].

studied the density of states in boron-containing nanotubes using scanning tunneling microscopy and found no energy gap in the BC₃ nanostructures.

The tendency of boron atoms to occupy the outer layers of multi-walled nanotubes is accounted for by the fact that substitution reactions require a lot of energy even in the outer layers, whereas in the inner layers the energy consumption of substitution reactions would be even higher due to a greater stress, the process therefore becoming energetically unfavorable [75].

10. Potential applications of boron-carbon nanotubes

10.1. Hydrogen storage

From the viewpoint of nanotubes application as hydrogen storage, the key requirement is the presence of heteroatoms capable of efficiently intensifying hydrogen adsorption without modifying the structure and geometry of the nanotube [76]. Potential applications of boron-carbon nanotubes as atomic hydrogen storage have been extensively studied [14, 77–81]. M. Sankaran et al. [77, 78] studied the atomic hydrogen sorption activity of CNTs containing boron impurity atoms. For single-substituted B the hydrogen dissociation energy is 5.85 eV whereas for double-substituted B in adjacent sites this energy reduces to 3.88 eV. Furthermore for two B atoms substituted in alternative sites the dissociation energy is even lower, 0.28 eV. These data confirmed the importance of boron impurity atom positions for hydrogen storage. Furthermore S. Sawant et al. [14] synthesized CNT containing boron impurity atoms using FCCVD and reported hydrogen accumulation of 0.137 and 2.7 wt.% at 303 and 77 K, respectively, for a 10 bar pressure. These accumulation figures are far greater than for many pure and doped carbon nanotubes [14, 80]. Viswanathan et al. [52] hypothesized that the heteroatoms act as alternative active centers of hydrogen activation. In this case B introduction into CNT produces an electron-deficient structure of the CNT and generates defects at the CNT surface. Alongside with providing the possibility of controlling the electron properties, B substitution causes a distortion of the CNT surface. Therefore there is more surface area available for hydrogen adsorption. It was also found that the hydrogen accumulation is 18 times greater at 77 K as compared with the 303 K figure due to the stronger Van der Waals forces at a lower temperature. Sawant et al. [14] obtained data on the equilibrium hydrogen adsorption which showed the best agreement with the Langmuir monolayer physical adsorption isotherm model. The authors also studied the hydrogen adsorption kinetics on the surface of carbon nanotubes containing boron impurity atoms. About 95% of the equilibrium hydrogen accumulation figure was achieved in the first 30 sec, suggesting a high adsorption

rate. It was furthermore found that the experimental data agree well with the pseudo-second order kinetic model having a 0.99 regression coefficient.

Along with B-containing CNT, hydrogen adsorption was studied for B- and N-containing CNT [80]. The hydrogen concentration in boron-containing nanotubes (B = 2.02 at.%) was higher than in the boron- and nitrogen-containing ones (B = 1.5 at.%, N = 1.34 at.%). M. Ni et al. [82] studied hydrogen adsorption in boron-carbon nanotubes with well-dispersed Ni atoms using the density functional theory. The authors reported a possible hydrogen adsorption of 3.8 wt.% if Ni atoms do not form clusters. It was found that boron-carbon nanotubes additionally doped with nickel act as a catalyst for hydrogen adsorption. P. Liu et al. [81] reported a study of hydrogen storage in CNT and ruthenium doped boron-carbon nanotubes using the density functional theory. They found that the Ru binding energy for boron-carbon nanotubes is higher than for pure nanotubes. The stronger covalent bond between the Ru and B atoms supported the higher Ru atom adsorption capacity than for the Ru-C atomic bond. This also reduced the clustering and agglomeration between the Ru atoms. Furthermore the closest H neighbors of the B atoms exhibit the tendency to form strong covalent bonds which force the Ru atoms toward more intense electron transfer to other H atoms. This favors hydrogen adsorption.

Summarizing the multiple opinions, hydrogen adsorption isotherm interpretations and reaction kinetics descriptions it is safe to say that hydrogen interaction with boron-carbon nanotubes has been well studied experimentally. The higher hydrogen adsorption of boron-carbon nanotubes is accounted for by the presence of B impurity atoms in contrast to pure CNTs. Interestingly, boron-carbon nanotubes can also be used as filler for the improvement of the electrical, mechanical and structural properties of composite materials [22]. The use of boron-carbon nanotubes as filler for fast self-heating molded polyurethane nanocomposite was studied [22]. Furthermore multi-walled nanotubes were used as filler for increasing the hydrogen adsorption efficiency of NaAlH₄ [83–86], Ti–NaAlH₄ [87], Pd nanoparticles [87], MgH₂–NaAlH₄ [88] etc. However the applicability of boron-containing nanotubes as atomic hydrogen storage or their potential incorporation in composite nanomaterials used for this purpose has not been studied completely yet.

10.2. Catalyst applications

CNTs can be used as a catalyst or a catalyst carrier due to their unique properties such as regular cylindrical shape that produces a nanochannel, a graphene-like structure of the side nanotube surface and the *sp*² hybridized state of the carbon atoms [89]. The addition of impurity heteroatoms to the combination of the abovementioned properties should substantially increase the efficiency of carbon nanotubes in these applications. As discussed in the previous sections, a B heteroatom is an adjacent element of

carbon having one less electron than carbon. B substitution reactions in nanotubes can modify the properties of their surface and generate additional regions having inhomogeneous physicochemical properties in the CNT structure. These regions can act as localization pinning centers both for the reactants and for the metallic nanoparticles on the carrier [90].

Using boron-containing nanotubes as catalyst, Y. Lin et al. [35] studied the reduction reactions for about 19 nitroarenes and observed a good conversion (~99%) of all the substrates and a selectivity of >88% for the desired reaction products. Boron-containing nanotubes were re-used as a catalyst for more than 10 times with but slight difference in conversion and product selectivity (and there were no changes in the Raman spectra of the B-CNT). It was shown [35] that N_2H_4 (a reactant producing strong electrons) is possibly adsorbed on nanotube regions containing boron atoms (with electron deficiency) to form a weak B–H bond that stabilizes the intermediate products of hydrogen. This can be caused by the stronger hydrogen adsorption on the surface of boron-containing nanotubes in comparison with other CNTs [14, 77, 80]. Moreover the nitroarene substrate forms a π – π bond with the benzene ring of the catalyst, while the O atoms of the nitrogroup adsorb activated H atoms and eventually support the high selectivity of the target product and the efficient use of N_2H_4 . P. Ai et al. [91] reported the hydration of dimethylxalate to ethanol with a Cu catalyst based on CNT containing boron impurity atoms. The synergetic effect of the metallic and acid centers (the boron lattice) accounts for the higher conversion and selectivity of ethanol. This can be related to the possibility of the acid centers to catalyze dehydration and the metallic centers to act as the active phase for hydrogenation. The presence of the B particles in the CNT structures increases the dispersion of the Cu particles but the size of the Cu particles decreases gradually with an increase in the B concentration. CNTs containing boron impurity atoms were also used as a catalyst for the aerobic oxidation of cyclohexane [92]. It was shown that oxidation reactions do not occur at low boron impurity atom concentrations. Unlike earlier described reactions CNTs containing substituted boron atoms limit oxidation reactions, possibly due to its electron deficient nature. The efficiency of boron doped CNT as an auxiliary material for catalysts requires further study, and this is a new application field.

10.3. Electric catalysis

The oxygen reduction reaction is the slowest in fuel cells any of aggregation state. This can be caused by the higher binding energy of the O_2 molecule (498 kJ/mole) [93, 94]. These reactions are typically implemented using sets of noble metals. These metals (mainly platinum) act both as the cathode and the anode due to their exclusive ability to adsorb and dissociate gases. These materials however have obvious application restrictions due to their high price and low abundance, poor tolerance to methanol and

intense carbon monoxide contamination [95]. For solving these problems CNTs containing boron impurity atoms were studied as an electrode material for electric catalysis reactions.

The main synthesis methods of boron doped CNT are shown above in Table 1. L. Yang et al. [96] used the CVD method for the synthesis of nanotubes for oxygen reduction reaction. The major prerequisite for the use of this material was the possibility of bonding between the regions of boron atom localization and oxygen due to their electrochemical properties. This assumption was confirmed by the improvement of energy consumption and the initial and peak potential levels. Similar reactions were implemented by Y. Cheng et al. [97], T. Li et al. [98] and M. Yeh et al. [17] who described the application of boron-carbon nanotubes for oxygen reduction reaction, dopamine oxidation and triiodide oxidation, respectively. S. Wang et al. [99] studied the electrochemical oxidation of methanol with the use of boron-containing nanotubes reinforced with platinum nanoparticles. Their results showed that the introduction of boron impurity atoms produces a clear platinum superlattice over the nanotube surface and reduces platinum contamination by carbon monoxide molecules. This increased the resistance of the material to carbon monoxide and hence provided for a higher electrochemical activity in methanol oxidation reactions. S. Park et al. [100] and Y. Cheng et al. [101] reported the synthesis of platinum-reinforced boron-carbon nanotubes for electric oxidation of methanol and silver-reinforced boron-carbon nanotubes for oxygen reduction reaction. The use of Ni/Ni₃Fe/boron-carbon nanotubes catalyst for oxygen conversion reactions was reported [27]. The unique porous hexagonal structure and the location of regions that are inhomogeneous from the electron energy viewpoint entailed the formation of unique electric states similar to *p*–*n* junctions between the nanotubes and Ni/Ni₃Fe and hence the formation of a large number of oxygen modifications that are required for the reaction. Y. Zhao et al. [50] described the use of boron and nitrogen doped CNT for oxygen reduction reactions. The formation of heterostructures induced by the impurity atoms increased the sorption properties of the nanotubes due to the formation of π bonds. This increased the efficiency of boron and nitrogen doped nanotubes in oxygen reduction reactions. Z. Kou et al. [102] studied the possibility of using boron and chlorine doped nanotubes for the efficient implementation of these reactions.

10.4. Sensors

S. Peng et al. [20] suggested the possibility of developing a new type of nanosized devices by introducing heteroatoms (B atoms) into carbon nanotubes for the efficient detection of carbon monoxide or water molecules. The authors found that during the reaction of substitution of some carbon atoms for boron the physical properties of the material undergo significant changes at impurity localization sites. One of these properties is the reaction

capacity of the nanotube (specifically the site where the B impurity atom is located). This change entails a change in the bond energy and a more efficient adsorption of gas molecules on the nanotube surface. The authors suggest the interaction between a boron-containing nanotube and a gas molecule to be detected as a change in the conducting properties of the CNT. The next stage of their study showed that the sensitivity of these nanosensors to the molecules studied is quite high and can be further increased by increasing the concentration of the impurity atoms. J. Talla et al. [103] and J. Adjizian et al. [104] studied the sensitivity of sensors on the basis of boron-containing nanotubes to carbon monoxide, NO, hydrogen, NO₂, water and C₂H₂ using the density functional theory. Also, theoretical calculations using the density functional theory were carried out by R. Wang et al. [105] and Y. Zhang et al. [106] for the sensitivity of boron-containing nanotubes to formaldehyde, hydrocyanic acid and chlorine cyanide. The boron-containing nanotubes exhibited a high sensitivity to formaldehyde in comparison with pure nanotubes due to the strong interaction between the negatively charged oxygen atoms and the positively charged boron atoms in the nanotube.

S. Yao [107–108] carry out intense experimental work for the application of boron-containing nanotubes as biosensors. X. Chen et al. [107] reported a sensor on the basis of glassy carbon with applied boron-containing nanotubes and its use for the study of glucose. C. Deng et al. [108] also studied this problem. While in the former of the abovementioned works the sensor was submerged into a thin film containing the test substance, the latter work described the interaction of the sensor with a fixed specimen. In the latter case the sensors exhibited a higher

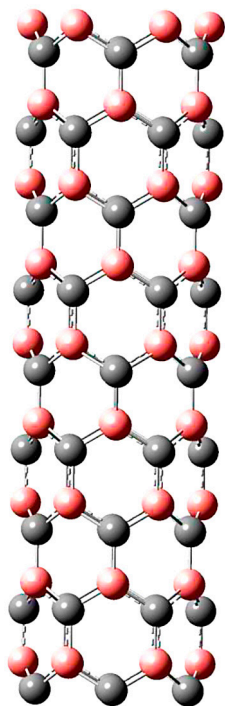


Figure 7. BC cluster of (6,0) nanotube.

stability and resistivity to interaction with other products contained in the test specimen, e.g. uric acid and ascorbic acid.

11. Simulation of carbon nanotubes with different contents of boron impurity atoms

Due to the growing interest demonstrated in various branches of industry to the control of properties of nanomaterials used, their detailed study is of crucial importance and quite timely. The results of experimental works described in the previous sections did not demonstrate a clear correlation between the concentration and orientation of boron impurity atoms and the physicochemical properties of the modified nanotubes. Model experiments for various types of boron-carbon nanotubes can be helpful in identifying these regularities [109, 110].

For this reason a stagewise theoretical study of the correlation between the semiconducting properties of boron-carbon nanotubes using the density functional theory and MNDO was carried out [111].

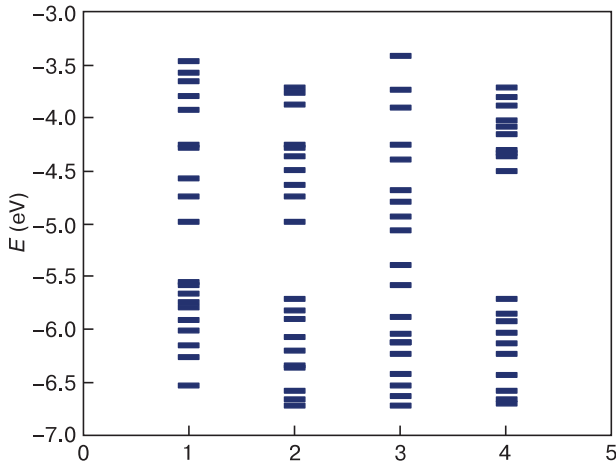
For the model experiment, boron-carbon nanotubes containing 50% boron impurity atoms were studied, i.e., the case where each second carbon atom is substituted for a B atom. The test materials were (*n*,0) nanotubes [111]. Figure 7 shows a BC cluster of a (6,0) nanotube for illustration of the mutual arrangement of the B and C atoms.

Nanotubes with different diameters were chosen for the study, i.e., zigzag type (*n*,0) nanotubes, where the index *n* = 4, 6, 8, 10, 12. The nanotube cluster length was at least 8 layers of hexagons along the main nanotube axis, and the number of hexagons at the perimeter of the nanotubes was *n* in accordance with the twisted object construction principle [112]. The main calculation method was the density functional theory. For all the nanotube clusters regardless of their diameter the bond length between the B and C atoms was chosen equal to 0.14 nm. The theoretical studies allowed determining the main parameter affecting the semiconducting properties of the nanotubes, i.e., the band gap. Band gap as a function of nanotube diameter is shown in Table 3.

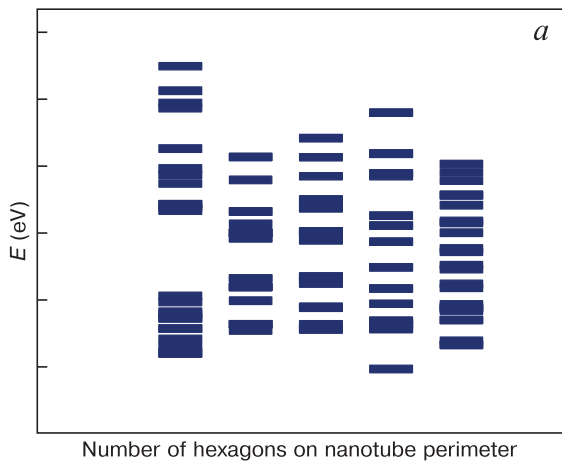
Furthermore the model experiment provided source data for the construction of single-electron spectra of the nanotubes (Fig. 8) which suggest that the levels of the atomic orbitals group into bands which are considered as the valence band and the conduction band in accordance with the commonly accepted classification. The energy gap values shown in Table 3 which were calculated as the difference between the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) allow classifying the CNTs containing 50% boron impurity atoms as narrow-band semiconductors regardless of the nanotube diameter. Studies of the structure of the atomic orbitals and the

Table 3. Energy gap of boron-containing nanotubes and pure carbon nanotubes as a function of nanotube diameter

Nanotube diameter (nm)	ΔE_g (eV) (C)	ΔE_g (eV) (BC ₃)	ΔE_g (eV) (BC ₃)		ΔE_g (eV) (BC)
			Type A	Type B	
0.3	0.81	0.13	0.81	0.54	0.02
0.47	0.81	0.69	0.54	0.54	0.09
0.63	0.27	0.26	0.26	0.54	0.02
0.77	0.27	0.19	0.19	0.54	0.02
0.95	0.27	0.69	0.07	0.54	0.02

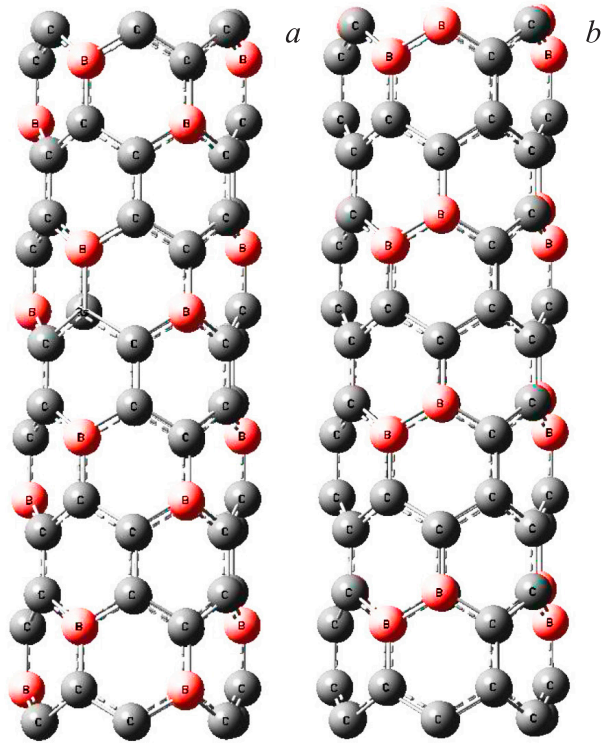
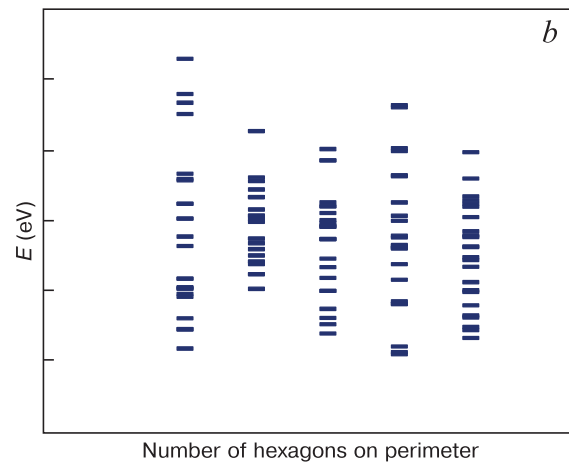
**Figure 8.** Single-substituted energy spectra of CNT (6,0) BC₃ structure.

electron density distribution between the orbitals showed that the s and p orbitals of the C atom and the s orbitals of the B atom form the valence band of the nanotube whereas the $2p$ orbitals of the B and C atoms form the conduction band. The introduction of impurity atoms into the structure of the nanotube produces an inhomogeneous charge distribution. That is, a redistribution of the electron density from the boron atoms to the carbon atoms occurs with the positive charge $Q = 0.8$ and the negative charge $Q = -0.7$ being generated on the boron and carbon atoms, respectively.



Then the behavior of the conducting properties of the CNT with a decrease in the content of the boron impurity atoms in the nanotube was studied [113, 114]. That is, the next test materials were boron-carbon nanotubes BC₃, i.e., those containing 25% boron. Due to the lower concentration of the B atoms there were different variants of their orientation on the nanotube surface denoted as nanotube types A and B (Fig. 9).

For nanotubes with the carbon and boron atomic ordering corresponding to the A type structure the band gap ΔE_g calculation results according to the above described principles revealed two important features of the electronic structure of the test nanotubes. First, these

**Figure 9.** Atomic ordering variants in BC₃ clusters of (6,0) nanotubes: (a) mutual arrangement of the B and C atoms in the A type nanotubes; (b) mutual arrangement of the B and C atoms in the B type nanotubes.**Figure 10.** Single-electron spectra of (6,0) CNT having a BC₃ structure: (a) A type atomic ordering; (b) B type atomic ordering.

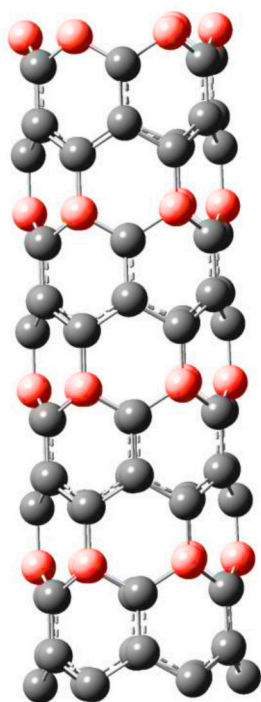


Figure 11. Atomic ordering variant of B and C atoms in a BC_5 cluster of a (6,0) type nanotube.

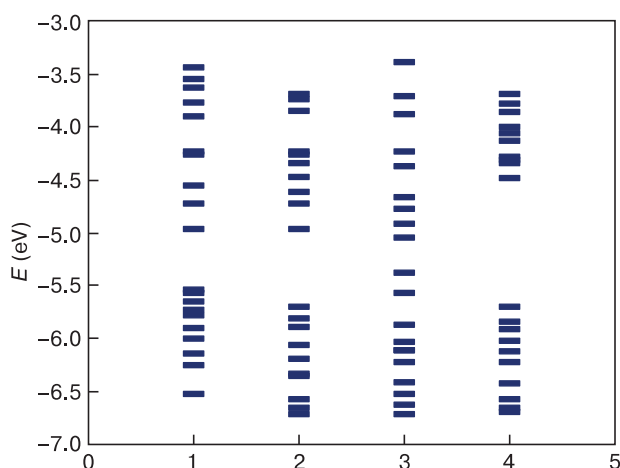


Figure 12. Single-electron spectra of (6,0) type CNT having a BC_5 structure.

nanotubes are semiconductors by conductivity type and second, by analogy with pure CNTs, they have a relationship between the nanotube diameter and the band gap, i.e., an increase in d leads to a decrease in ΔE_g . The energetic structure of the test B type nanotubes, e.g. the band gap, showed them to be narrow-gap semiconductors. Analysis of the electronic structure of the nanotubes showed that their valence band is formed by the s and p orbitals of the C atoms and the s orbitals of the B atoms. The band gap values of the nanotubes are summarized in Table 3. By analogy with the equilibrium concentration of the B and C atoms the introduction of impurity atoms into the nanotube structure produces an inhomogeneous charge distribution. This entails a redistribution of the electron density from the boron atoms acquiring the

positive charge $Q = 0.13$ to the carbon atoms acquiring the negative charge $Q = -0.07$ [115, 116].

Single-electron spectra of the test carbon nanotube types with boron impurity atoms are shown in Fig. 10.

The final stage of the study of the effect of boron impurity atoms on the electronic structure of the CNTs was a study of the case of the minimum B atoms concentration, i.e., the case of only one C atom substitution in the hexagon. This nanotube can be denoted as a BC_5 nanotube. The atomic ordering variant for a BC_5 nanotube is shown in Fig. 11 for a (6,0) nanotube.

The above listed band gap values suggest that BC_5 nanotubes are narrow-band semiconductors according to their conductivity type. The band gap of the nanotubes varies in a periodical manner with an increase in the nanotube diameter [114]. Figure 12 shows single-electron spectra of a (6,0) type CNT having a BC_5 structure.

Table 3 is drawn up for convenience of comparison between the values of the band gap with an increase in CNT diameter for CNT with different contents of boron impurity atoms.

Analysis of all the experimental concentrations of boron impurity atoms in CNT suggests the following conclusions. (n,n) type nanotubes are dielectrics [117, 118], whereas boron-containing ($n,0$) type nanotubes are narrow-band semiconductors. At boron impurity atom concentrations of below 25% the band gap of the nanotubes increases. This can be accounted for by the presence of charge distribution inhomogeneities on the surface of boron-containing nanotubes because boron atoms accumulate positive charge whereas the electron density is concentrated at carbon atoms. When the equilibrium concentration of boron and carbon atoms is achieved the energy gap collapses almost to zero. Thus the main conclusion from analysis of the change in the band gap of carbon nanotubes with a change in the concentration of boron impurity atoms is the theoretically proven possibility of controlling the conductivity of the nanotubes by introducing different quantities (percentage) of boron atoms.

The results of the model experiment suggesting semi-conducting properties of CNTs containing boron impurity atoms are in agreement with practice [119]. It was found that the presence of boron impurity atoms leads to the above-described changes in the band gap and the conclusion was made that one should expect the resistivity of nanotubes to decrease with an increase in temperature. Thus the theoretical calculations add the data of experimental studies support a better understanding of the processes occurring in nanotubes, and the agreement between the experimental data and the simulation results is yet more proof of the correctness of the quantum-chemical methods and models used.

12. Conclusions

Carbon nanotubes have for a long time been subject of multiple research works world over. Several thousands

of reports on the topic are published annually. However, nanotubes containing impurity atoms, e.g. boron have been studied to a far less extent. Most of the works on the topic have dealt with boron-containing nanotube synthesis methods. More detailed studies of the properties and potential applications are not abundant in literature.

Boron has a smaller atomic size than carbon. Therefore the nanostructures produced as a result of the respective substitution reactions are more stable than those produced by substitution for other chemical elements, and one can therefore expect successful practical application of boron doped nanotubes. The main disadvantages of boron doped nanotubes are the absence of a commercial nanomaterial technology and the lack of possibility to control the concentration of boron impurity atoms. A key to these problems is the CVD technology of CNTs containing boron impurity atoms. Industrial scalability of this process is only a matter of time provided there is a systematic approach to the development of this nanotube technology aimed at obtaining ample information on the process features and the desired final product. Thus, despite the emphasis of most researchers on various CNT technologies containing boron impurity atoms, the CVD technology remains quite important and timely.

Carbon nanotubes containing boron impurity atoms can find application in various fields of science and

engineering. In the exploration of the possibility of hydrogen adsorption these nanotubes have shown the best results compared with undoped nanotubes or nanotubes containing nitrogen impurity atoms and boron and nitrogen containing CNTs. Industrial applications of nanotubes require more detailed studies of nanotubes containing different boron impurity concentrations and exploration of the possibility to develop composite materials on their basis. Catalyst applications of CNTs containing boron impurity atoms have been studied in a greater detail. The presence of boron impurity atoms in nanotubes improves their reaction capacity due to charge redistribution in the heterostructure. However, studies of the chemical properties of boron-carbon nanotubes synthesized using substitution reactions will offer even greater application opportunities. Results of boron doped CNT applications in sensor technologies are also impressive. It is the introduction of impurity atoms that allows detecting a number of important chemical compounds, and varying dopant concentration in nanotubes allows one to control the sensitivity of nanosensors.

Summing up it is safe to say that boron is one of the most promising materials for substitution reactions in CNT. It only depends now on researchers to which extent the whole inherent potential of this nanomaterial will be explored.

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