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Synthesis, properties, and examples of the use of carbon nanomaterials

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The results of a series of works on the synthesis and investigation of various carbon nanostructures and elaboration of functional materials of their basis are generalized and reviewed. Fullerenes and single-, double-, and multi-walled carbon nanotubes were prepared by the electric arc evaporation of graphite and metal—graphite rods. Diverse types of carbon nanofibers and nanotubes were grown by the catalytic pyrolysis of ethylene and methane. Graphene structures were synthesized by the chemical reduction of graphite oxide. Methods for isolation, purification, and functionalization of carbon nanostructures were elaborated. Chemical transformations in the fullerene—metal phase—hydrogen system were studied. Methods for metal cluster application on carbon nanostuctures and formation of metal hydride—carbon composites were developed. The possibilities were elucidated of using carbon nanostructures for the development of hydrogen accumulating and hydrogen generating composites, for forming carbon—polymer and carbon—ceramic composites, for preparing hardening additives to polymers and glue compositions, and for producing high-performance catalysts for hydrogenation and redox processes in fuel cells.

Key words: fullerenes, carbon nanotubes, carbon nanofibers, graphene structures, electric arc synthesis, catalytic pyrolysis, chemical modification, composites.

Carbon nanostructures (fullerenes, carbon nanotubes and nanofibers, and graphene structures) are very attractive objects for both fundamental scientific researchers and applied workings out. They can widely be used in diverse areas of science and technology: in nanoelectronics, catalysis, and small-scale power engineering, for the development of constructional materials with high functional characteristics, *etc.*

The electric arc method, *viz.*, evaporation of graphite and metal—graphite electrodes in a dc arc, is most convenient for the synthesis of fullerenes and low-defect carbon nanotubes. Catalytic pyrolysis of carbon-containing compounds is used for the production of carbon nanofibers (CNF) of various types. The method of chemical and thermal reduction of graphite oxide seems promising for the formation of graphene structures in substantial amounts.

In the studies in the area of carbon nanostructures, we solved the problems on the development of optimum procedures for synthesis, purification, attestation, chemical modification, and formation of functional composite materials.

1. Electric arc synthesis of carbon nanostructures

Electric arc synthesis of carbon nanomaterials was carried out in a setup, whose reactor is schematically shown in Fig. 1. The setup makes it possible to vary the values of dc and voltage, rate of cathode movement, gap between the electrodes, pressure, composition of the medi-

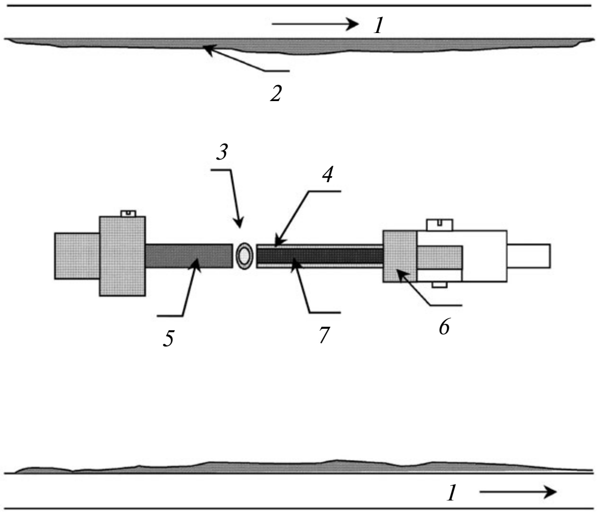

Fig. 1. Scheme of the reactor and the distribution of products of the electric arc evaporation of the graphite electrodes: *1*, cooling water; *2*, fullerene-containing carbon black; *3*, gap between the electrodes; *4*, deposit shell; *5*, anode; *6*, cathode; and *7*, MWNT-containing core of the deposit.

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um, *etc.*[1—3] Graphite rods of spectral purity were used as an anode (vaporized electrode) in the synthesis of multiwalled carbon nanotubes (MWNT) and fullerenes. For the synthesis of single- (SWNT) and double-walled carbon nanotubes (DWNT), a channel was drilled in the anode and filled with a mixture of metal and graphite powders. The buffer gas pressure was maintained constant during the synthesis. The gap between the anode and cathode remained unchanged within one experiment.

1.1. Synthesis of fullerenes and fullerene black. For the synthesis of fullerenes, we used graphite electrodes 6 mm in diameter and 200 mm long.[1,3] The syntheses were carried out in helium under 100 Torr at a current strength of 65—75 A and a voltage drop on the arc of ~18 V. The following procedure was carried out to determine the yield of fullerenes: the fullerene-containing carbon black was sifted through a sieve, weighed, and extracted with toluene in a Sohxlett apparatus. Extracts of fullerenes were evaporated on a rotary evaporator, washed with ether, dried to a constant weight, and weighed. The carbon black weight was 45—50% based on evaporated graphite, and the content of fullerenes in the carbon black was 17, 16.5, and 14.5 wt.% at a current strength of 65, 70, and 75 A, respectively.

The electric arc carbon black remained after the exhaustive extraction of fullerenes with toluene is commonly named fullerene black. Along with amorphous carbon black and graphite particles, the fullerene black contains a nanostructure with a particle size of 40—50 nm and a distorted surface with unconjugated simple and double carbon—carbon bonds. Fullerene black adsorbs considerable amounts of various gases, can enter nucleophilic addition reactions, catalyzes the dehydrocyclization of *n*-alkanes, and is a promising highly efficient support of metallic catalysts.[4—6] It was shown[3] by spectrophotometry of toluene extracts that the mole ratio of fullerenes C_{60} and C_{70} in the mixture is always constant and equal to 5.

1.2. Synthesis of multi-walled nanotubes. When graphite is evaporated in the dc arc discharge, a portion of evaporated carbon is condensed on a thick cathode as a gradually growing cylinder ("deposit") reaching several centimeters in length. The deposit consists of a rigid silvery shell and a soft black internal part containing columnar beams of MWNT. The yield of MWNT is higher for the use of anodes with a diameter of 9.8 mm than that for anodes 7.8 mm in diameter. The optimum conditions for the MWNT growth are a helium pressure of 500 Torr and a voltage of ~23 V at which the yield reaches 20—24 wt.%. The material derived from the deposit core contains polyhedral multilayer nanoparticles 20—100 nm in diameter and particles of amorphous carbon along with MWNT with an external diameter of 15—30 nm and the length >1 μm (Fig. 2). The oxidation of the product in air at 650—700 °C is enough for the removal of the amorphous component, fullerene-like hemispheres at the ends of MWNT and some nanoparticles. Nanotubes and graphite fragments (weight ~60%) remain in the solid phase after this treatment.[1,2,7]

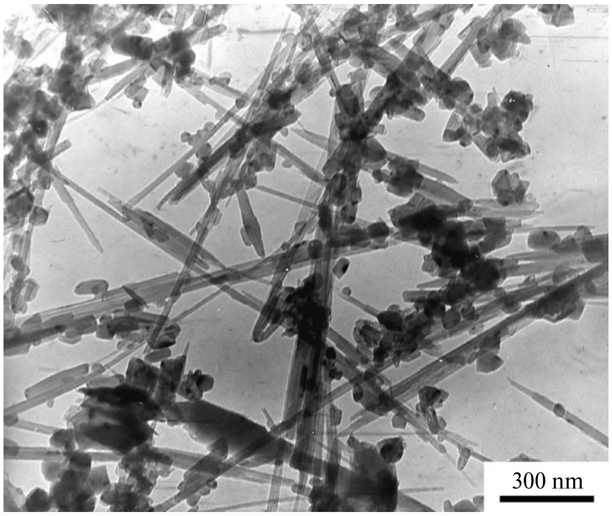


Fig. 2. Image of the products taken from the deposit.

1.3. Synthesis and isolation of single-walled nanotubes. It is known that metals of the iron group are catalysts of the electric arc of SWNT.[1,8—11] In this case, the yield of SWNT increases in the series Fe < Co < Ni. This dependence is related to the activity of metals in the reaction

$$C + M \longrightarrow M_3C \longrightarrow C(SWNT) + M. \qquad (1)$$

The use of bimetallic systems of a 3d-metal with Y, Ca, or rare-earth metals (REM) is more efficient for the synthesis of SWNT. The high yield of SWNT in the case of the 2Ni—REM system can be due to the thermal stability of carbides $(REM)C_2$ (1600—2300 °C), and the synergetic effect of the two-component system is expressed in the fact that one metal catalyzes the nucleation of SWNT and another metal promotes the tube growth. The catalytic system 3Co—Ni is also effective, although carbides of both metals, Co_3C and Ni_3C, are similar in thermal stability (300—500 °C). This fact contradicts an opinion that the mechanism of SWNT growth is directly related to the presence of REM and even to its boiling point.

When the metal—graphite electrodes were used with the catalytic mixture 3Co—Ni (1.9 + 0.64 at.%), the highest yield of SWNT was 15—20% in the carbon black around the electrodes (so-called "collar" soot). In the Raman spectra of the "collar" soot in the "breathing" mode region, the absorption band maxima lie at 169, 179, and 187 cm^{-1}, which corresponds to SWNT diameters of 1.47, 1.38, and 1.32 nm. The highest yield of SWNT in the "collar" soot was 30—50% when the powder of the YNi_2 (0.95 + 1.9 at.%) alloy was used as a catalyst. The decomposition of the absorption bands in the Raman spectrum makes it possible to determine the positions of maxima corresponding to the SWNT with diameters of 1.87, 1.66, 1.49, 1.41, 1.32, and 1.15 nm. Thus, the diameters of the nanotubes obtained using the YNi_2 catalyst are substantially longer than the diameters of the SWNT formed when the 3Co—Ni catalyst is used.[1,8—10]

Experiments with the use of proposed by us powders of hydrogenated alloys Ni_2YH_2, Ni_3YH_2, and $Ni_7Y_2H_2$ show stable and uniform burning of the electric arc. In this case, the yield of SWNT is substantially higher than that using mixtures of Ni powders with Y and increases with an increase in the amount of nickel in the alloy.[1,8]

In the presence of a mixture of powders of 3d-metals 4Ni—X (4 + 1 at.%, X = Co, Fe, Mn, Cr, and V) as catalysts, the yield of SWNT in the "collars" formed and their weight decrease gradually in the series Mn > Cr > > Co > Fe ≈ V.[1,11] An increase in the stability of the arc discharge with the simultaneous increase in the gap between the electrodes and the soot weight on the reactor walls (so-called "near-wall" soot) are needed to increase the yield of SWNT. For this purpose, in the systems 4Ni—Mn and 4Ni—Cr a portion of nickel was replaced by cobalt: the content of metals was 3, 1, and 1 at.%, respectively. The use of these mixtures resulted in the more uniform "burning" of the arc and better controllability of parameters of the process. The content SWNT in the "collar" was estimated by spectroscopy in the near-IR, visible, and UV regions as follows: 25% (3Ni—Co—Mn), 14% (4Ni—Mn), 10% (3Ni—Co—Cr), and 9% (4Ni—Cr). For the highest yield of SWNT, the average particle size of Ni determined from the diffraction patterns was 14 nm, which is likely optimum for the synthesis of SWNT.[1]

The isolation of SWNT from condensed products of electric arc synthesis was carried out according to the scheme presented in Fig. 3. The procedure includes alternated stages of acidic treatment and thermal oxidation in air with the gradual temperature increase, as well as degassing *in vacuo* at high temperatures. The temperature of oxidation of amorphous carbon and carbon layers on the surface of metallic particles necessary for annealing was selected on the basis of the data of thermogravimetric oxidation in air. The stage-by-stage oxidation with air and treatments with acid are necessary, because metallic nanoparticles are usually covered with carbon layers and are not removed by the primary treatment with acids. Mainly "open" nanotubes are formed after the thermal treatment. This procedure can yield a material containing >70 wt.% of SWNT from the starting carbon black with ~10% of SWNT (Fig. 4).[1,8,9]

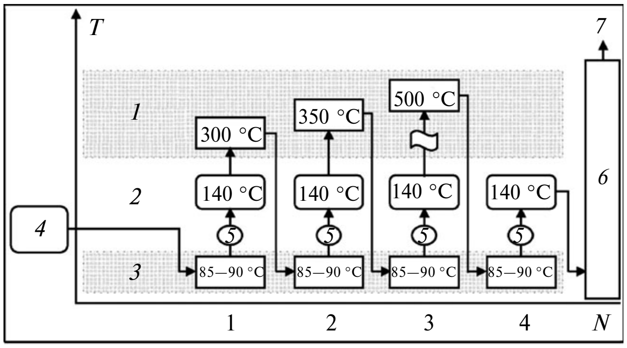


Fig. 3. Scheme of purification of single-walled nanotubes: *1*, heating in air for 0.5 h; *2*, drying; *3*, heating in HCl for 3 h; *4*, crude carbon black with SWNT; *5*, washing with water; *6*, heating *in vacuo* to 500 °C; and *7*, enriched SWNT; *N* is number of stage.

1.4. Synthesis of DWNT. The electric arc evaporation of the graphite electrode containing Ni, Co, Fe, and S (2.6, 0.7, 1.45, and 0.75 at.%, respectively) in a mixture of Ar with H_2 (175 + 175 Torr) produced DWNT with an external diameter of 1.9—5 nm and a diameter of the internal tube of 1.1—4.2 nm. High-resolution electron microscopy showed that the most part of the tubes had a specific structure and consisted of two concentric cylindrical graphene layers; *i.e.*, these tubes are DWNT (Fig. 5).[1,12]

1.5. Chemical modification of carbon nanotubes. Carbon nanotubes (CNT) can be modified *via* three directions: covalent addition to the ends of CNT or to the conjugated skeleton of the CNT; non-covalent adsorption or envelopment; and endohedral filling of the internal cavity (Scheme 1). The carboxyl groups of the CNT are trans-

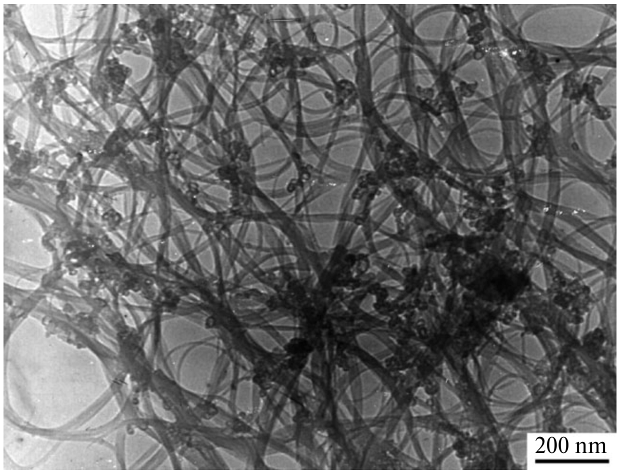


Fig. 4. Image of the products enriched in single-walled nanotubes.

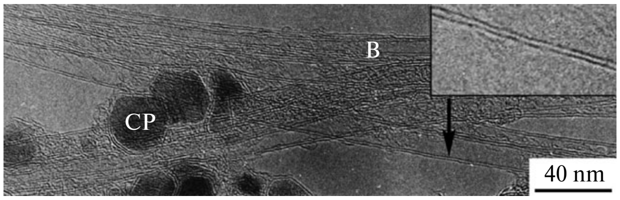
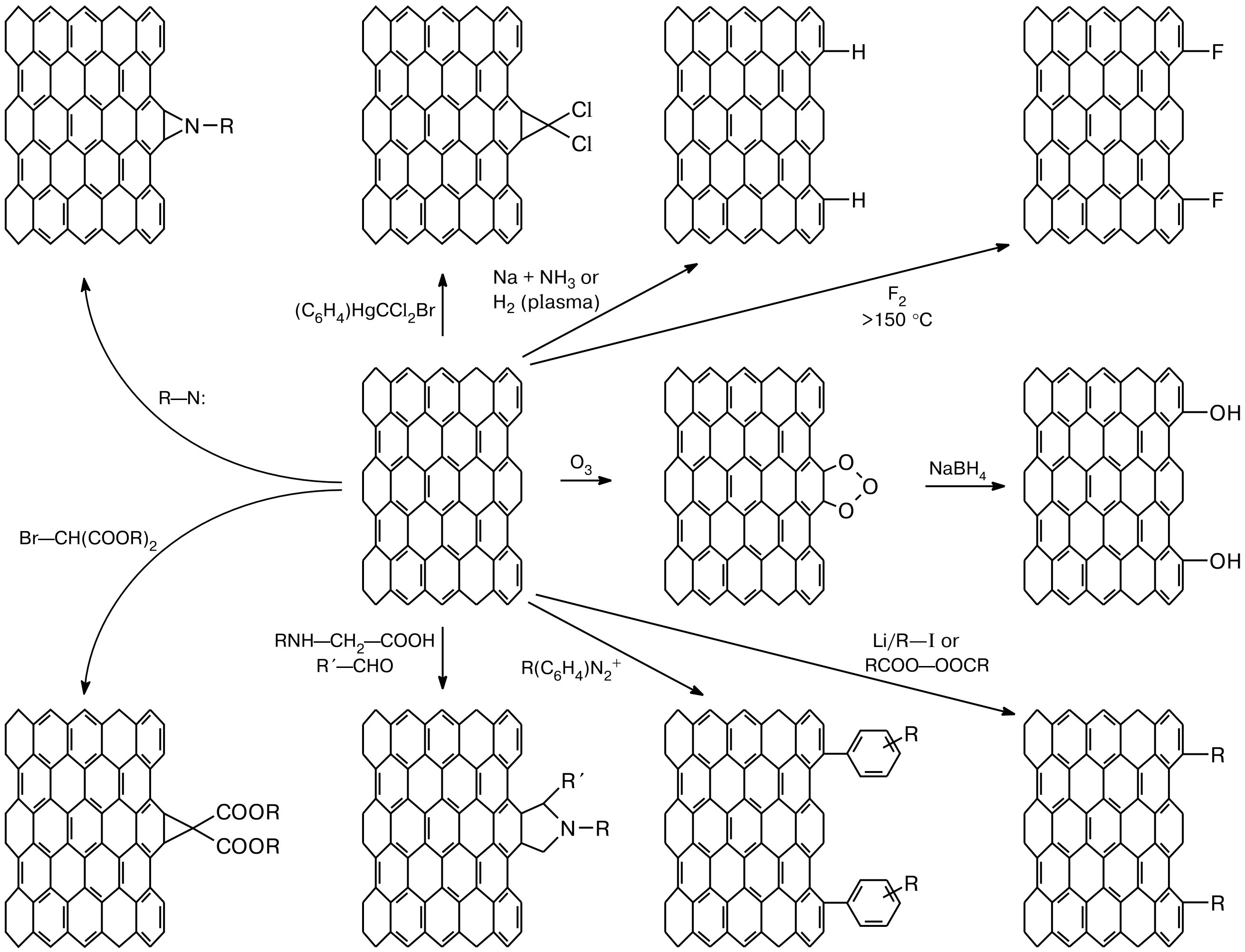


Fig. 5. Image of beams of double-walled nanotubes (B) and catalytic particles (CP).

Scheme 1



formed into the chloroanhydride groups followed by the treatment with compounds containing amino and (more rarely) OH groups. The carbodiimide method is a milder method of grafting of amino compounds, for instance, biological preparations.

Fluorination is one of efficient methods for modification of carbon materials.[13—18] Depending on the fluorinating agent, structure, and properties of the starting materials, and fluorination conditions, such as the temperature and duration of the reaction and the presence of catalysts, the fluorination products can differ by both the fluorine content and the strength of the C—F bonds. The material with MWNT was fluorinated at 420 °C using electrolysis fluorine, which was diluted with nitrogen and contained 3 vol.% of gaseous HF. Depending on the duration and temperature of flurination, the samples containing from 10 to 55 wt.% of fluorine were obtained. The SWNT synthesized by the method of CO disproportionation are fluorinated at 150 °C, whereas the "arc" MWNT are fluorinated at ~400 °C. The atomic ratio C : F can reach 2. Annealing or treatment with hydrazine favors the regeneration of the starting CNT. Fluorine atoms can be replaced by functional groups using the treatment with organometallic compounds, amines, or alcohols, most frequently with ultrasonic treatment and vigorous stirring.

Alkyl and aryl radicals capable of adding to the lateral wall of CNT are generated by the thermal treatment of organic peroxides. An alternative variant is associated with the synthesis of CNT "salts" by the treatment with organolithium compounds followed by the reaction with, *e.g.*, alkyl halides. The thermal or photochemical decomposition of organic compounds bearing the azide group favors nitrene formation. The Prato reaction makes it possible to functionalize lateral walls of the nanotubes thus enhancing the probability of addition of biological preparations and fluorescent markers.

The covalent addition of polymer chains to the nanotube surface is possible for the enhancement of the adhesion interaction of the CNT and polymer matrix. One variant assumes the use of modified polymers, for example, polystyrene with the terminal azide group or polystyrenelithium, *etc*. Another variant is the addition to CNT of particles that initiate polymerization and subsequent supplement of the monomer. The non-covalent modification of CNT is most frequently used for the separation of "beams" into individual nanotubes and increasing their "solubility" in diverse media. For this purpose, surfactants, compounds with fused aromatic rings (for example, pyrene compounds), conjugated polymers (for instance, phenylene—vinylene derivatives), and biological preparations (DNA, RNA, and others) are used.

One of the most interesting properties of MWNT is the ability to emit electrons. The electric field strength necessary for achieving a current of 50 μA was 4.45 V μm^{-1} for the MWNT synthesized by the electric arc method. For the improvement of the emission characteristics of autocathodes of MWNT, the procedure of their doping with barium was developed. Barium has an electron work function of 2.49 eV, which is substantially lower than that for carbon (4.7 eV). The modified procedure of one-step filling of "closed" nanotubes by reflux in HNO_3 with the addition of barium nitrate followed by heating was used for doping. It turned out that the doping with barium decreases the working voltage of the cathode by ~30%.[1,19]

2. Synthesis of carbon nanostructures by catalytic decomposition of hydrocarbons

Catalytic pyrolysis of ethylene and methane was carried out in a horizontal quartz flow-type reactor at atmospheric pressure in the temperature range 400—1000 °C using mixtures of C_2H_4 or CH_4 with H_2 and Ar in various ratios (Fig. 6).[20—26] The composition of the gas phase was varied by changing the volume velocity of gas flows (5—100 cm^3 min^{-1}).

2.1. Pyrolytic synthesis of carbon nanofibers on the Ni-containing catalysts. Highly dispersed nickel powder is known to be one of the most high-performance catalysts for synthesis of carbon nanostructures by pyrolysis of hydrocarbons. We were first to propose powders of intermetallic compounds and nickel alloys with REM or magnesium obtained by hydride dispergation to be used as procatalysts decomposing upon the interaction with hydrocarbon to form metallic nickel and REM carbide or $MgNi_3C$. The influence of the pyrolysis temperature and the composition of the initial gas mixture on the formation and growth of carbon nanostructures were studied in detail and procedures for target synthesis of carbon nanotubes and nanofibers of diverse types were elaborated.[21—25] Coaxial conical carbon fibers of the "fir" type and planar parallel fibers of the "stack" type were obtained by ethylene pyrolysis at 500 °C. Diameters of these fibers are 100—200 nm on the average (Fig. 7). Fibers of the "fish spine" type with diameters of 20—40 nm were obtained at 700 °C. Multi-walled nanotubes with diameters of 10—20 nm were synthesized by methane pyrolysis at 900 °C.

2.2. Synthesis of carbon nanostructures on metallic catalysts supported on oxide powders. For the synthesis of thin carbon nanostructures (CNS), it is necessary to prevent sintering of catalytic particles during pyrolysis. For this purpose, various powdered catalyst supports can be used: oxides, carbides, or nitrides of magnesium, aluminum, titanium, zirconium, silicon, *etc*. Using powders Fe/MgO, Co/MgO, Ni/MgO, and Pt/MgO, as well as Co/SiO_2 and Co/Al_2O_3, as catalysts, we synthesized CNF 10 nm in diameter and nanotubes 3—5 nm in diameter. The yield, structure, and properties of carbon nanomaterials depend not only on the amount but also on the method of preparation of the catalyst. For example, the combined precipitation of aqueous solutions of $Mg(NO_3)_2$ and H_2PtCl_6 followed calcination gave the Pt/MgO catalysts

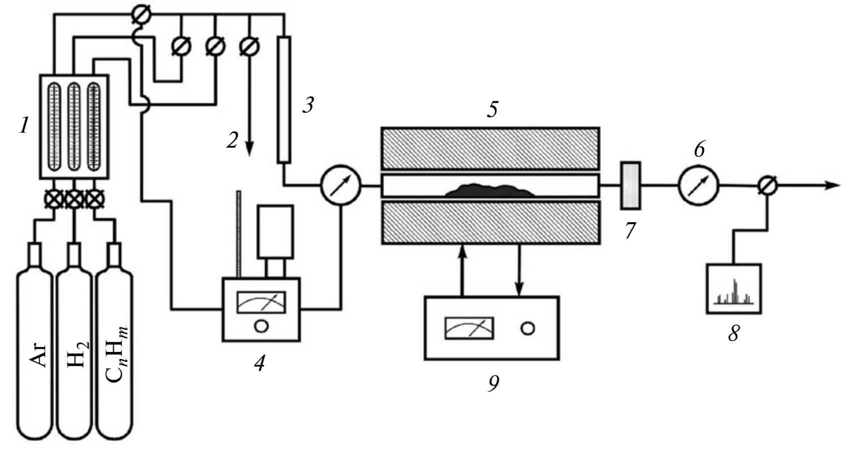


Fig. 6. Setup of the catalytic synthesis of carbon nanostructures: *1*, rotamers; *2*, vacuum; *3*, mixer; *4*, thermostat; *5*, furnace; *6*, flow meter; *7*, filter; *8*, mass spectrometer; and *9*, temperature regulator.

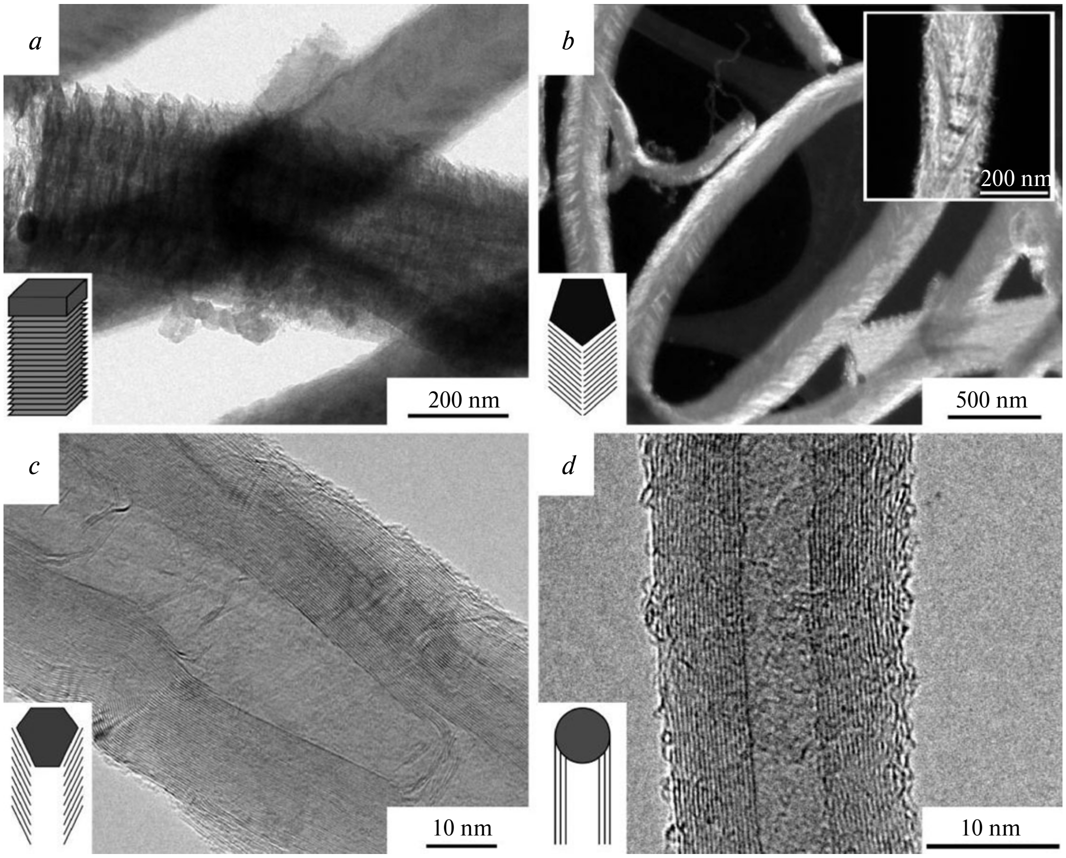


Fig. 7. Synthesized types of carbon nanostructures: *a*, fibers of the "stack" type; *b*, fibers of the "fir" type; *c*, fibers of the "fish spine" type; and *d*, multi-walled nanotubes.

on which the thinnest nanofibers with a narrow diameter distribution are formed upon the decomposition of ethylene. Thin carbon nanotubes with diameters of 2—5 nm and a yield based on carbon of 17 g (g of Fe—Mo)$^{-1}$ were obtained by the pyrolysis of methane at 900 °C on the bimetallic catalyst Fe—Mo/MgO.[21,27]

2.3. Synthesis of CNS on the metallic catalysts supported on diverse plates. Synthesis of CNS on diverse plates has wide prospects for using in molecular electronics for the creation of nanotransistors, planar kinescopes, and cathode-ray illuminating lamps with low voltage and feeding powder and a high degree of spatial and time stability of emission characteristics. Plates of Si, SiO_2, and Si_3N_4, as well as TiN_x, were used as supports. On the Fe—Mo catalyst supported on SiO_2 by the precipitation method, carbon nanotubes of the bamboo-like structure were grown by ethylene pyrolysis. Thin nanotubes 2—5 nm in diameter, which are apart from each other at long distances (Fig. 8), were grown by methane pyrolysis on the same Fe—Mo catalyst supported on SiO_2/Si_3N_4 by high-frequency diode sputtering. Thus synthesized nanotubes can also overlap the gap 100 nm wide situated between the plate, which allows their electric conductivity to be experimentally measured.[21,28]

2.4. Catalytic synthesis of CNS in the presence of gas-phase additives. The introduction of elements with the valence different from that of carbon into the reaction zone can substantially affect the formation, growth, structure, and properties of CNS. We studied the influence of diverse gas-phase additives to ethylene on the yield and structure of formed carbon fibers. The catalytic pyrolysis of ethylene was carried out at 700 °C in the presence of vapors of H_2O, EtOH, NH_4OH, PCl_3, $(MeO)_3P$, Me_2SO_4, $(MeO)_3B$, and HCl. An additive of chlorine-containing compounds was found to favor an increase in the yield of the carbon products, while an additive of sulfur compounds

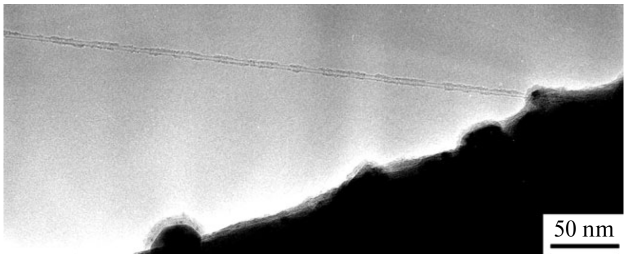


Fig. 8. Image of the carbon nanotube obtained on the catalyst $Fe—Mo/SiO_2/Si_3N_4$ by methane pyrolysis at 900 °C.

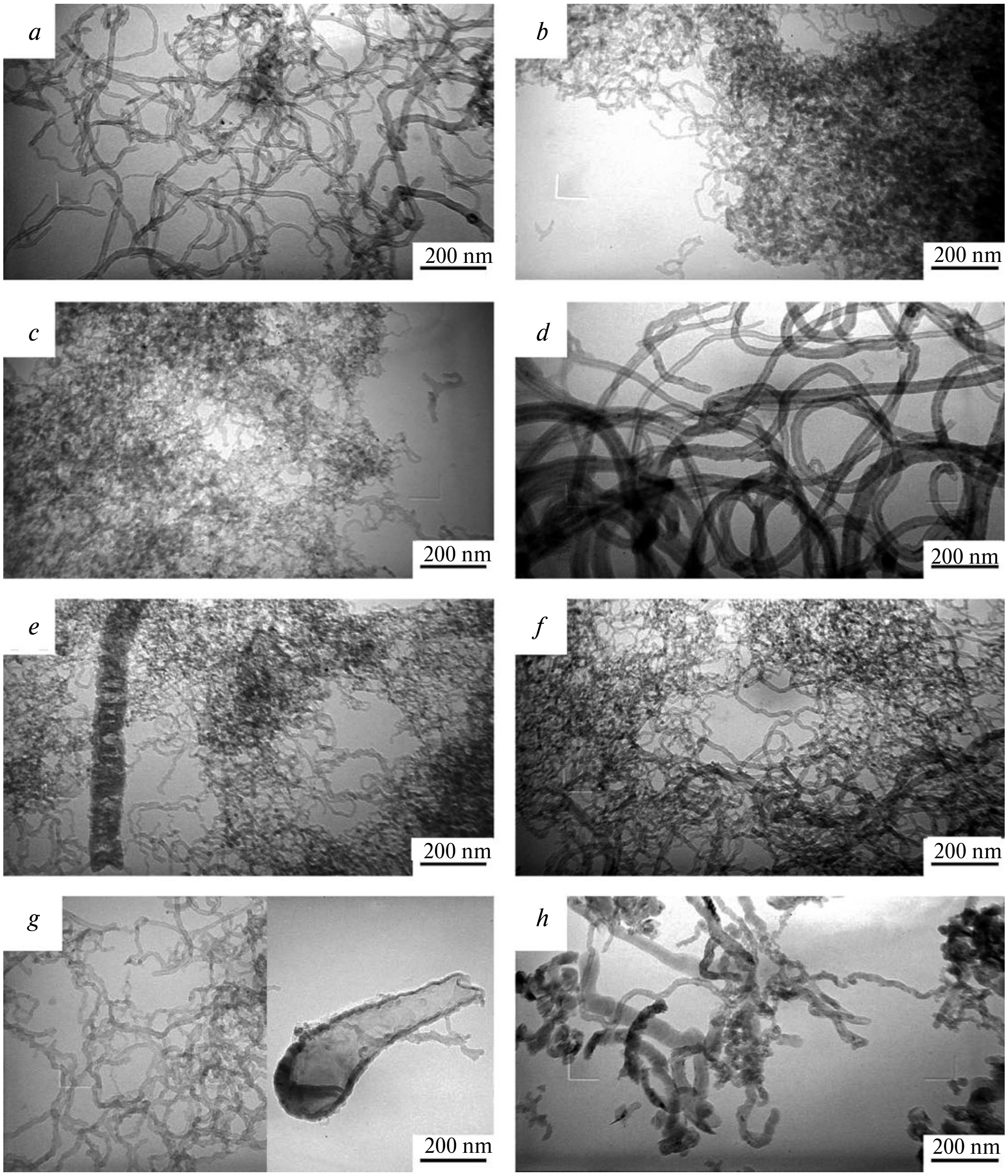


Fig. 9. Images of the pyrolysis products of C_2H_4 at 700 °C (*a*) and with addition of vapors of H_2O (*b*), EtOH (*c*), NH_4OH (*d*), PCl_3 (*e*), Me_2SO_4 (*f*), $(MeO)_3B$ (*g*), and HCl (*h*).

decreases the yield. The introduction of sulfur- and phosphorus-containing additives assists the growth of thinner fibers. Fibers of the "bamboo-like" structure are formed in the presence of ammonia, and the addition of water or ethanol vapor results in defects on the surface of the carbon fibers (Fig. 9).[29,30]

3. Synthesis of graphene structures

Low-layer graphene structures (LGS) were prepared by the reduction of oxidized graphite with hydrazine hydrate. The oxidized graphite was synthesized by the treatment of graphite with $KMnO_4$ in concentrated H_2SO_4.[31,32] The reduced powder was annealed for 1 h in an argon flow at 900 °C. The LGS obtained were characterized by X-ray diffraction as four-layer with sizes of nanoplates in the direction of axis *a* of 40—50 nm (Fig. 10).[33] The reduction of oxidized graphite under the conditions of ionic hydrogenation was studied, and the activity of the nickel-containing catalyst based on this graphite in the reductive dechlorination of polychlorine-containing aromatic hydrocarbons was shown.[34,35]

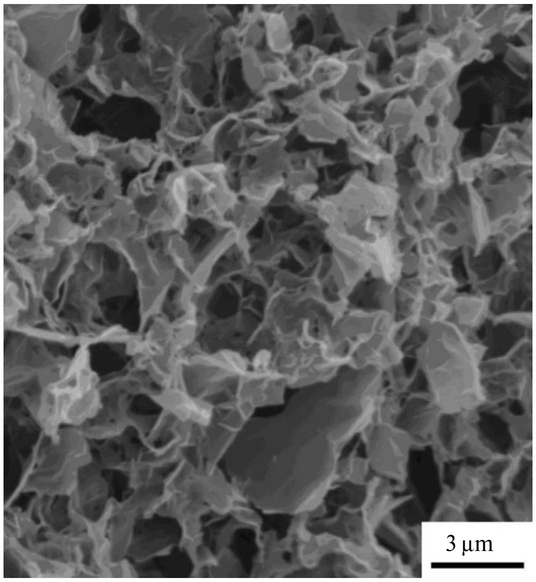


Fig. 10. Image of the low-layer graphene structures.

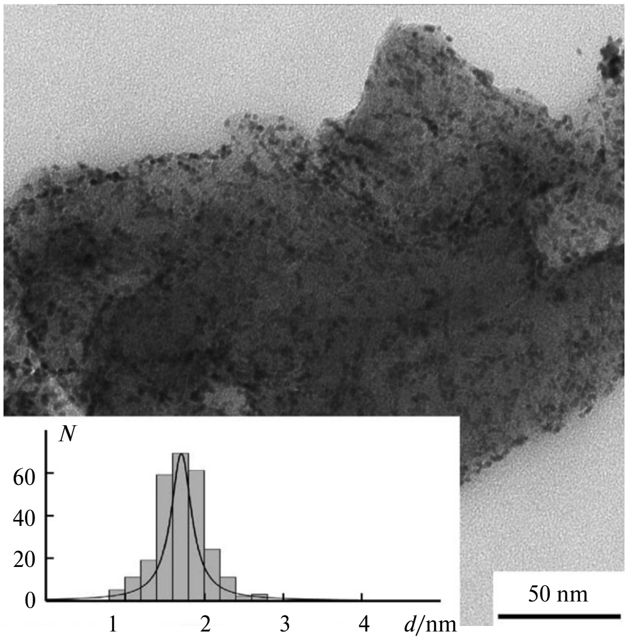


Fig. 11. Image and histogram (in inset) of the catalyst Pt/CNF obtained by the reduction of H_2PtCl_6 with ethylene glycol on the fibers 100—200 nm in diameter.

4. Examples of using CNS

The synthesized CNS are used for the preparation of various functional materials (hydrogen accumulating, hydrogen generating, carbon—polymer, and carbon—ceramic composites), for the production of hardening additives to polymers and to glue compositions, and for preparation of catalysts hydrogenation and redox processes in fuel cells.

4.1. Carbon nanomaterials as supports for catalysts. For the strong immobilization of platinum, the nanotube surface was functionalized by oxygen-containing groups: carboxyl, hydroxyl, and quinoid. For this purpose, the CNS were oxidized with concentrated nitric acid or a mixture of nitric and sulfuric acids. For preparation of hydrogenation catalyst, it is most convenient to add a solution of H_2PtCl_6 to an aqueous suspension of the oxidized CNS with pyridine under the conditions of ultrasonic treatment with continuous stirring and heating. For the reduction of Pt^{4+}, formic acid and a solution of sodium carbonate were added to the reaction mixture. Thus obtained catalyst turned out to be high-performance in the hydrogenation of decene and nitrobenzene.[36,37]

For the production of Pt—carbon catalysts for hydrogen—air fuel cells, we used also other procedures of platinum cluster supporting on carbon nanomaterials, for example, by the reduction of H_2PtCl_6 with sodium borohydride, ethylene glycol, or hydrogen. Platinum clusters with rather narrow size distribution and uniform distribution on the CNF surface were formed by the reduction in ethylene glycol under microwave irradiation (Fig. 11).[38—41]

The combination of catalytic and gas-diffusion layers in the low-temperature hydrogen—air fuel cell was attained by growing CNF on the Ni catalyst on the porous Spectracorp paper followed by the application of platinum clusters. The voltammetric characteristics of these systems somewhat exceed those known from the literature (Fig. 12).[38]

4.2. Carbon nanomaterials as hardening additives to polymers. Fullerenes and carbon nanotubes can successfully be used for the enhancement of the adhesion strength of epoxyamine composites applied in diverse glues and coatings. For example, it was found in the presence of up to 1.5% of fullerene C_{60} and a mixture of fullerenes C_{60}/C_{70} as a modifying additive to epoxide compositions that the gluing joints glass—binding—glass using polyethylene-polyamine as a solidifying agent exhibit a multiple increase in the adhesion strength (Fig. 13). The adhesion strength of the epoxyamine composition also increased over the glass and metallic surfaces upon the addition of small amounts (~0.2 wt.%) of carbon nanotubes and nanofibers.[42,43]

4.3. Use of carbon nanomaterials for the production of ceramic composites. Due to high electric conductivity, heat conductivity, chemical and thermal stability, and mechanical strength, carbon nanotubes and nanofibers can be used for the reinforcement of ceramic materials to increase their hardness, crack resistance, wear resistance, and electric conductivity. The technological schemes were developed for the preparation of composite materials carbon nanotubes—ceramic matrix. The schemes were accomplished when growing nanotubes in the volume of alumina nanopowder or preparing a mixture of nanotubes with nanopowders of tungsten, niobium, and tantalum carbides by

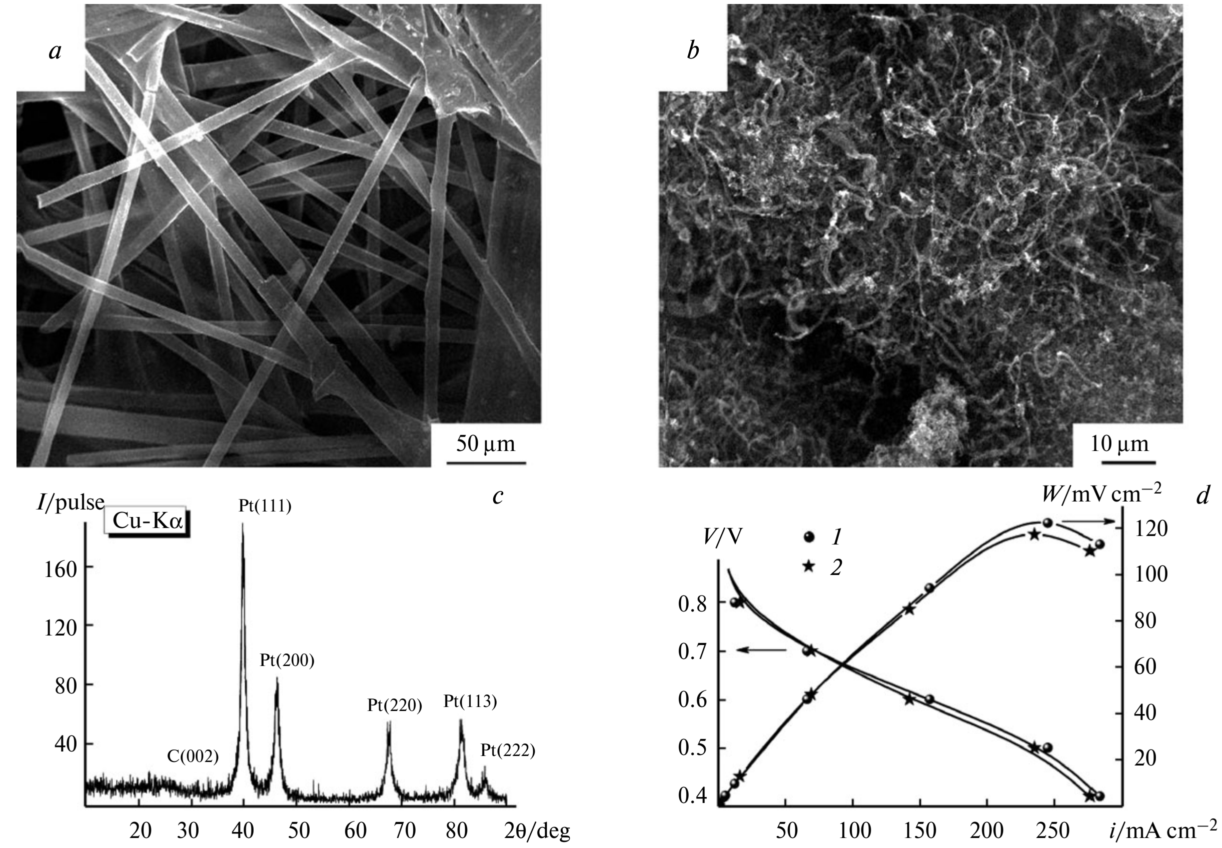


Fig. 12. Images of the Spectracorp carbon paper (*a*) and carbon nanofibers (*b*), the diffraction pattern of Pt clusters on the CNF surface (*c*), and the voltammetric characteristics of the membrane—electrode unit with the studied electrodes (*d*): *1*, electrode with Pt on carbon black E-TEK supported on the Spectracorp paper and *2*, electrode with Pt on CNF supported on the Spectracorp paper.

stirring followed by pressing in a vacuum chamber at 1400—1700 °C. The microstructure of the samples was studied. It was found that in samples with nanotubes grown in the powder volume the nanotubes were distributed more uniformly than in the samples obtained by mixing of the nanotubes and powders (Fig. 14). Additives of CNS affect the mechanical characteristics, heat conductivity, and electric conductivity of ceramic composites, that can be used for practical applications.[44]

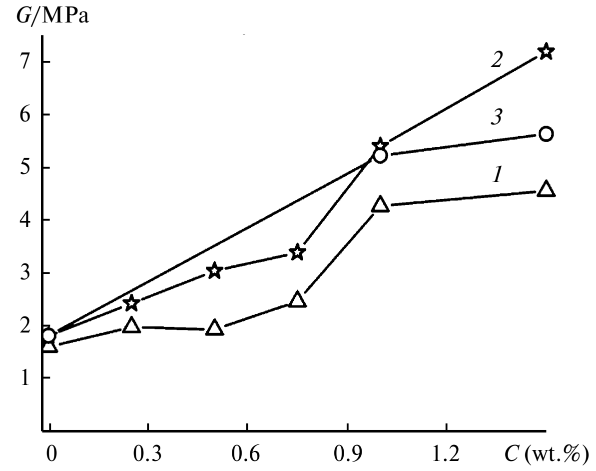


Fig. 13. Adhesion strength of the composition *vs* fullerene concentration: *1*, modifier C_{60}/C_{70}, solidification at 20 °C; *2*, modifier C_{60}/C_{70}, solidification at 80 °C; and *3*, modifier C_{60}, solidification at 80 °C; *C* is the fullerene concentration.

4.4. Carbon nanostructures as sorbents of hydrogen. The interaction of fullerenes with hydrogen and adsorption of hydrogen by carbon nanotubes and nanofibers were studied in detail. The direct interaction of fullerite with hydrogen afforded crystalline hydrofullerenes, and their structure and properties were studied. The method for the expansion of fullerite lattices by their hydrogenation followed by dehydration was developed. It was established that upon the hydrogenation of fullerite the cubic lattice remained unchanged and the unit cell parameter increased monotonically with an increase in the hydrogen content (Fig. 15). The procedures for the hydrogenation of fullerene-metallic compositions were developed, the optimum conditions for reversible interaction were determined, the reaction mechanism was proposed, and the chemical transformations in the system fullerene—metallic phase—hydrogen were studied in pressure and temperature ranges of 0.01—25 atm and 0—1000 °C, respectively.[45—52] The reactions in the systems fullerite—metal—hydrogen are

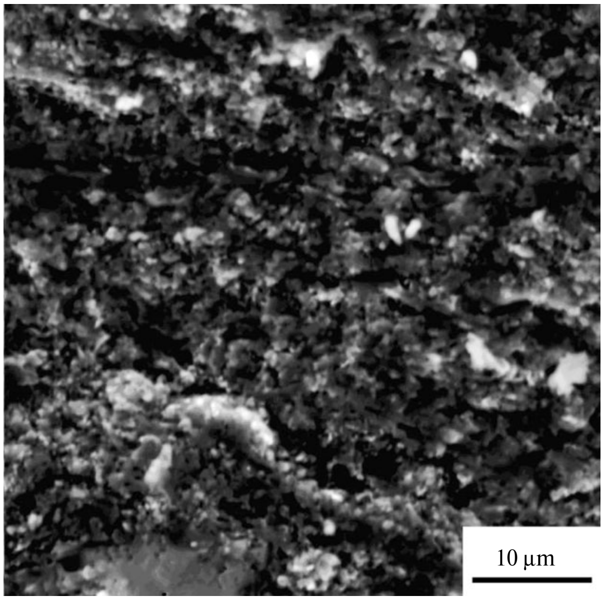


Fig. 14. Microstructure of the surface of the sample CNT/Al_2O_3 (1 wt.%) prepared by the hot pressing method at 1500 °C and 39 MPa.

described by the following schemes (pressure/MPa is indicated above the arrow in parenthesis):

$$\{C_{60} + M\} + H_2 \xrightarrow{570-670\ K\ (1-5)} \{C_{60}H_x + MH_y\}, \quad (2)$$

$$\{C_{60}H_x + MH_y\} \xrightarrow{600\ K} \{C_{60}H_x + M\} + 0.5y\,H_2 \xrightarrow{\sim 800\ K} \{C_{60} + M\} + 0.5(x + y)\,H_2, \quad (3)$$

$$C_{60}Pt + H_2 \xrightarrow{400-550\ K\ (1-3)} C_{60}PtH_x \xrightarrow{\sim 800\ K} C_{60}Pt + H_2, \quad (4)$$

$$C_{60}Pt + H_2 \xrightarrow{600-700\ K\ (1-3)} C_{60}H_x + Pt \xrightarrow{\sim 800\ K} C_{60} + Pt + H_2, \quad (5)$$

$$C_{60}Pd_{4.9} + H_2 \xrightarrow{400-550\ K\ (1-3)} C_{60}Pd_{4.9}H_x \xrightarrow{\sim 800\ K} C_{60}Pd_{4.9} + H_2, \quad (6)$$

$$C_{60}Pd_{4.9} + H_2 \xrightarrow{600-700\ K\ (1-3)} C_{60}H_x + PdH_y \xrightarrow{\sim 800\ K} C_{60} + 4.9\ Pd + H_2. \quad (7)$$

The amount of hydrogen adsorbed by the carbon nanotubes and nanofibers at 100 atm and 25 °C does not exceed 1 wt.%, whereas at 350 °C it is not higher than 3.5 wt.%. The amount of hydrogen adsorbed by the nanotubes was found to depend on the nanotube diameter (Fig. 16).[9,53–55]

4.5. Hydrogen accumulating and hydrogen generating metal—carbon composites. The procedures were developed for the formation of metal hydride—carbon composites by the mechanochemical treatment of mixtures of hydrides MgH_2 or AlH_3 and carbon materials (graphite, fullerene, and carbon nanofibers and nanotubes) in inert and hydrogen media.[56–60] It turned out that no new compounds were formed in the system MgH_2—carbon under the conditions of treatment in high-energy ball mills and under the quasi-hydrostatic conditions of high pressures and temperatures, but the γ-modification of magnesium hydride appeared. The mechanical activation of mixtures of MgH_2 with carbon materials (graphite, nanotubes, nanofibers, fullerenes) decreases the dehydrogenation temperature and increases the rate of repeated hydrogenation (Figs 17 and 18). Thus, the systems MgH_2—C can be used for the production of hydrogen accumulators of repeated action.

The desorption of hydrogen in the AlH_3—C system is limited by processes at the interface. The preliminary mechanical treatment of the AlH_3—C system can be used for controlling the temperature and rate of hydrogen evolu-

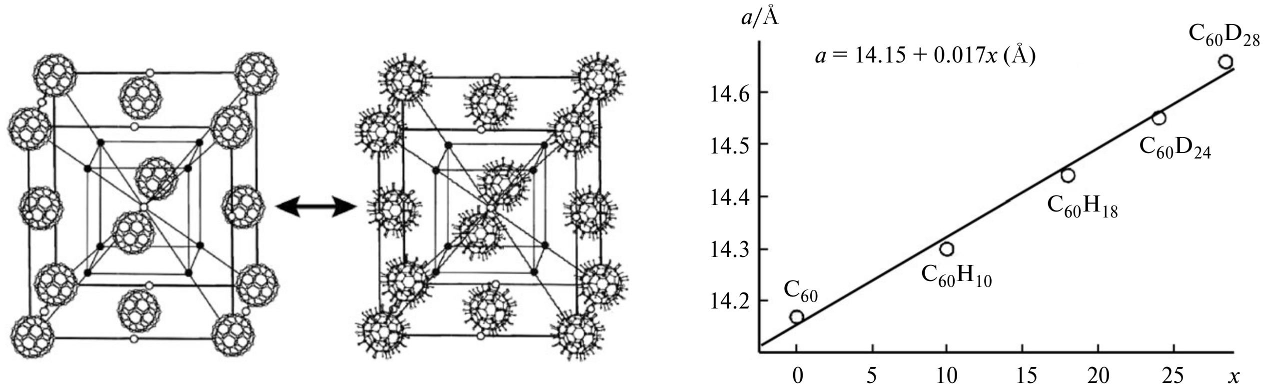


Fig. 15. Structures of fullerite C_{60} and hydrofullerite $C_{60}H_x$ and the dependence of the fcc lattice period (*a*) on the hydrogen content in hydrofullerite (*x*).

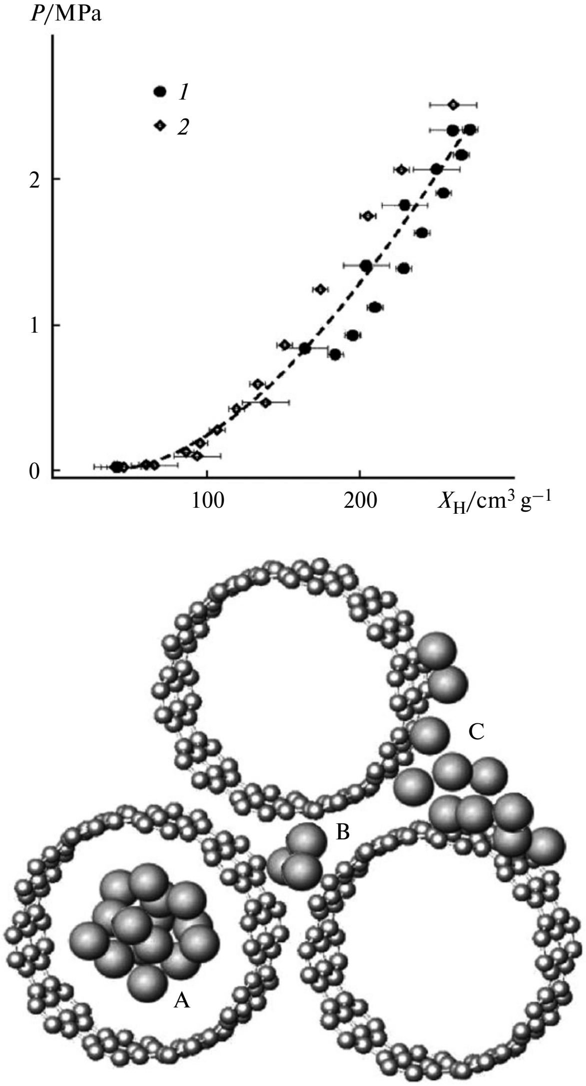


Fig. 16. Isotherms of adsorption (*1*) and desorption of H_2 (*2*) by carbon nanotubes at –196 °C and the sites of hydrogen adsorption (A, B, C) in the SWNT beam.

tion from AlH_3-based generators. It turned out that the introduction of carbon at the mechanical treatment of MgH_2 impedes the agglomeration of the MgH_2 particles, favors an additional increase in the surface, and prevents the formation of a continuous layer of $Mg(OH)_2$ during hydrolysis. An increase in the dose of mechanochemical influence from 4 to 20 kJ g^{-1} increases the reactivity of the composite and the further dose increase somewhat deteriorates activity because of particle agglomeration (Fig. 19). The composites prepared can be used for the creation of chemical hydrogen generators. The regularities of the influence of mechanical activation on the kinetic parameters of thermal decomposition of AlH_3 were determined.

Thus, the optimum procedures for the synthesis of various CNS (fullerenes, nanotubes, nanofibers, graphene structures) were developed at the Laboratory of Hydrogen

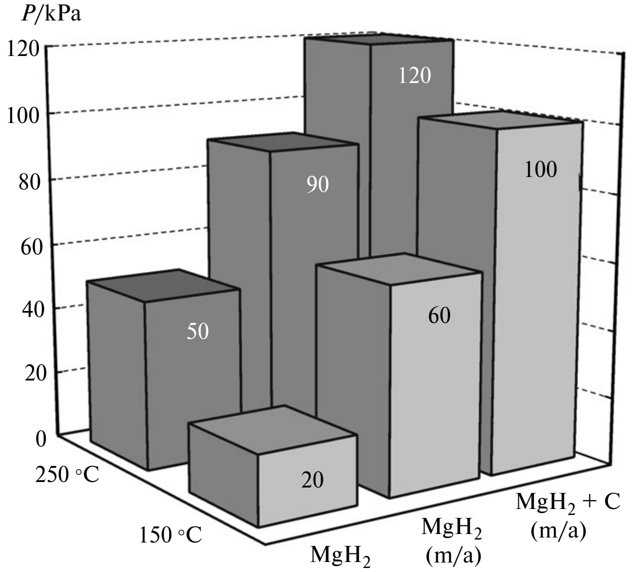


Fig. 17. Pressure of hydrogen evolved from the composites MgH_2—carbon at 150 and 250 °C; m/a designates mechanical activation.

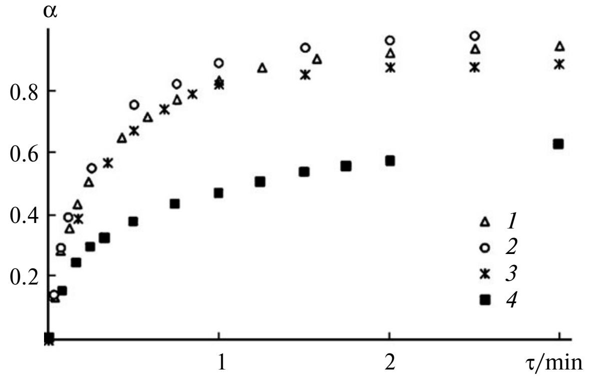


Fig. 18. Degree of repeated hydrogenation of magnesium (α) at 330 °C after the thermal decomposition of the composite MgH_x/C with the carbon content 10 (*1*), 25 (*2*), and 50 wt.% (*3*), as well as MgH_x (*4*).

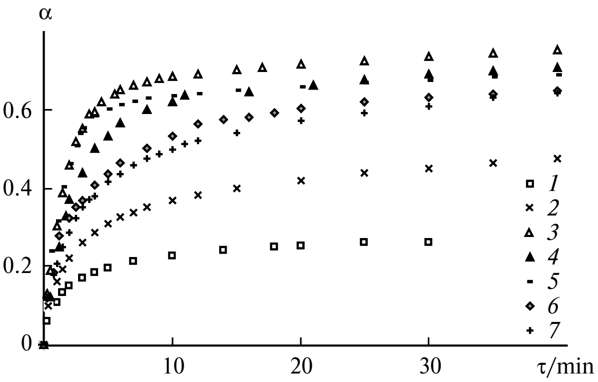


Fig. 19. Conversion (α) *vs* duration of hydrolysis of the samples MgH_2—C (10 wt.%) treated in a ball mill at various doses of influence: 4 (*1*), 13 (*2*), 20 (*3*), 25 (*4*), 40 (*5*), 50 (*6*), and 80 kJ g^{-1} (*7*).

Accumulating Materials of the Institute of Problems of Chemical Physics (Russian Academy of Sciences). The methods for their isolation, purification, and functionalization were elaborated. The possibilities of their use for the production of diverse functional materials (metal—carbon, carbon—polymer, and carbon—ceramic composites, hardening additives to polymers and glue compositions, and catalysts of hydrogenation and redox processes in fuel cells) were revealed.

References

1. V. E. Muradyan, Ph. D. (Chem.) Thesis, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 2004, 160 pp. (in Russian).
2. B. P. Tarasov, V. E. Muradyan, Yu. M. Shul´ga, N. S. Kuyunko, V. M. Martynenko, Z. A. Rumynskaya, O. N. Efimov, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2002, No. 6, 4 (in Russian).
3. P. V. Fursikov, Ph. D. (Chem.) Thesis, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 2002, 150 pp. (in Russian).
4. S. D. Kushch, V. E. Muradyan, A. P. Moravskii, P. V. Fursikov, *Neftekhimiya*, 1997, **37**, 112 [*Petroleum Chemistry* (*Engl. Transl.*), 1997, **37**].
5. P. V. Fursikov, S. D. Kushch, V. E. Muradyan, G. I. Davydova, Eu. I. Knerel´man, A. P. Moravsky, *Mol. Cryst. Liq. Cryst.*, 2000, **C13**, 319.
6. N. S. Kuyunko, S. D. Kushch, V. E. Muradyan, A. A. Volodin, V. I. Torbov, B. P. Tarasov, in *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Ed. T. N. Veziroglu, Springer, Dordrecht, 2007, 213.
7. Yu. M. Shul´ga, I. A. Domashnev, B. P. Tarasov, A. M. Kolesnikova, E. P. Krinichnaya, V. E. Muradyan, N. Yu. Shul´ga, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2002, No. 1, 70 (in Russian).
8. B. P. Tarasov, V. E. Muradyan, Yu. M. Shul´ga, E. P. Krinichnaya, N. S. Kuyunko, O. N. Efimov, E. D. Obraztsova, D. V. Schur, J. P. Maehlen, V. A. Yartys, H. J. Lai, *Carbon*, 2003, **41**, 1357.
9. B. P. Tarasov, J. P. Maehlen, M. V. Lototsky, V. E. Muradyan, V. A. Yartys, *J. Alloys Comp.*, 2003, **356—357**, 510.
10. V. E. Muradyan, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2008, No. 2, 45 (in Russian).
11. J. Gavillet, A. Loiseau, C. Journet, F. Willaime, F. Ducastelle, J.-C. Charlier, *Phys. Rev. Lett.*, 2001, **87**, 275504.
12. J. L. Hutchison, N. A. Kiselev, E. P. Krinichnaya, A. V. Krestinin, R. O. Loutfy, A. P. Morawsky, V. E. Muradyan, E. D. Obraztsova, J. Sloan, S. V. Terekhov, D. N. Zakharov, *Carbon*, 2001, **39**, 761.
13. Yu. M. Shul´ga, V. E. Muradyan, V. M. Martynenko, B. P. Tarasov, N. V. Polyakova, *Mass-spektrometriya* [*Mass Spectrometry*], 2005, **2**, 41 (in Russian).
14. Yu. M. Shul´ga, V. E. Muradyan, V. M. Martynenko, B. P. Tarasov, N. V. Polyakova, *Fullerenes, Nanotubes, and Carbon Nanostructures*, 2006, **14**, 243.
15. Y. M. Shulga, T.-C. Tien, C.-C. Huang, S.-C. Lo, V. E. Muradyan, N. V. Polyakova, Y.-C. Ling, R. O. Loutfy, A. P. Moravsky, *J. Electron Spectroscopy and Related Phenomena*, 2007, **160**, 22.
16. M. M. Brzhezinskaya, N. A. Vinogradov, A. Zimina, V. E. Muradyan, Y. M. Shul´ga, A. S. Vinogradov, *Appl. Phys. A*, 2009, **94**, 445.
17. M. M. Brzhezinskaya, V. E. Muradyan, N. A. Vinogradov, A. B. Preobrajenski, W. Gudat, A. S. Vinogradov, *Phys. Rev. B*, 2009, **79**, 155439.
18. M. M. Brzhezinskaya, N. A. Vinogradov, V. E. Muradyan, Yu. M. Shul´ga, R. Puttner, A. S. Vinogradov, W. Gudat, *Fiz. Tverd. Tela*, 2009, **51**, 1846 [*Sov. Phys. Sol. State* (*Engl. Transl.*), 2009, **51**].
19. K. N. Nikolski, A. S. Baturin, V. S. Bormashov, A. S. Ershov, L. D. Kvacheva, D. A. Kurnosov, V. E. Muradyan, A. A. Rogozinskiy, D. V. Schur, E. P. Sheshin, A. P. Simanovskiy, Yu. M. Shulga, R. G. Tchesov, S. Yu. Zaginaichenko, in *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Ed. T. N. Veziroglu, Springer, Dordrecht, 2004, 123.
20. P. V. Fursikov, B. P. Tarasov, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2004, No. 10, 24 (in Russian).
21. A. A. Volodin, Ph. D. (Chem.) Thesis, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 2006, 135 pp. (in Russian).
22. A. A. Volodin, P. V. Fursikov, Yu. A. Kasumov, I. I. Khodos, B. P. Tarasov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2005, 2210 [*Russ. Chem. Bull.*, *Int. Ed.*, 2005, **54**, 2281].
23. A. A. Volodin, P. V. Fursikov, B. P. Tarasov, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2002, No. 6, 34 (in Russian).
24. A. A. Volodin, P. V. Fursikov, B. P. Tarasov, in *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Ed. T. N. Veziroglu, Springer, Dordrecht, 2007, 53.
25. A. A. Volodin, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2008, No. 2, 53 (in Russian).
26. A. A. Volodin, P. V. Fursikov, Yu. A. Kasumov, B. P. Tarasov, in *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Ed. B. Baranowski, Springer, Dordrecht, 2008, 297.
27. A. A. Volodin, E. V. Gerasimova, L. A. Frolova, Yu. A. Dobrovol´skii, B. P. Tarasov, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2007, No. 9, 49 (in Russian).
28. A. A. Volodin, P. V. Fursikov, Yu. A. Kasumov, I. I. Khodos, B. P. Tarasov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2006, 1372 [*Russ. Chem. Bull.*, *Int. Ed.*, 2006, **55**, 1425].
29. A. A. Volodin, B. P. Tarasov, in *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Ed. B. Baranowski, Springer, Dordrecht, 2010, 195.
30. A. A. Volodin, B. P. Tarasov, *Abstrs Int. Conf. "Hydrogen Materials Science and Chemistry of Carbon Nanomaterials" (Ukraine, Crimea, Yalta, August 25—31, 2009)*, Kiev, 2009, 442.
31. S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. B. T. Nguyen, R. S. Ruoff, *J. Mater. Chem.*, 2006, **16**, 155.
32. V. E. Muradyan, V. S. Romanova, A. P. Moravskii, Z. N. Parnes, Yu. N. Novikov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2000, 1023 [*Russ. Chem. Bull.*, *Int. Ed.*, 2000, **49**, 1325].
33. V. E. Muradyan, E. A. Sokolov, N. P. Piven´, S. D. Babenko, S. R. Allayarov, *Pis´ma Zh. Tekhn. Fiz.* [*Journal of

Technical Physics Letters], 2010, **36**, 106 (in Russian); N. P. Piven´, V. E. Muradyan, S. D. Babenko, S. R. Allayarov, E. A. Sokolov, *Khim. Vys. Energ.*, 2010, **44**, 380 [*High Energy Chem.* (*Engl. Transl.*), 2010, **44**].
34. V. E. Muradyan, M. G. Ezernitskaya, V. I. Smirnova, N. M. Kabaeva, Yu. N. Novikov, Z. N. Parnes, M. E. Vol´pin, *Zh. Obshch. Khim.*, 1991, **61**, 2626 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1991, **61**].
35. Y. M. Shulga, V. M. Martynenko, V. E. Muradyan, V. A. Smirnov, G. L. Gutsev, *Chem. Phys. Lett.*, 2010, **498**, 287; V. A. Smirnov, A. A. Arbuzov, Yu. M. Shul´ga, S. A. Baskakov, V. M. Martynenko, V. E. Muradyan, E. I. Kresova, *Khim. Vys. Energ.*, 2011, **45**, 60 [*High Energy Chem.* (*Engl. Transl.*), 2011, **45**].
36. S. D. Kushch, N. S. Kuyunko, B. P. Tarasov, *Kinet. Katal.*, 2009, **50**, 895 [*Kinet. Catal.* (*Engl. Transl.*), 2009, **50**].
37. S. D. Kushch, N. S. Kuyunko, B. P. Tarasov, *Zh. Obshch. Khim.*, 2009, **79**, 542 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2009, **79**].
38. E. V. Gerasimova, Ph. D. (Chem.) Thesis, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 2011, 150 pp. (in Russian).
39. E. V. Gerasimova, A. A. Volodin, I. V. Arkhangel´skii, Yu. A. Dobrovol´skii, B. P. Tarasov, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2007, No. 7, 92 (in Russian).
40. A. A. Volodin, E. V. Gerasimova, B. P. Tarasov, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2009, No. 1, 140 (in Russian).
41. E. V. Gerasimova, B. P. Tarasov, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2009, No. 8, 25 (in Russian).
42. V. E. Muradyan, A. A. Arbuzov, Yu. N. Smirnov, *Zh. Obshch. Khim.*, 2009, **79**, 634 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2009, **79**].
43. A. A. Arbuzov, Ph. D. (Chem.) Thesis, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 2011, 140 pp. (in Russian).
44. Yu. V. Blagoveshchenskii, K. V. Van, A. A. Volodin, V. M. Kiiko, A. A. Kolchin, N. I. Novokhatskaya, B. P. Tarasov, A. N. Tolstun, *Kompozity i nanostruktury* [*Composites and Nanostructures*], 2010, 30 (in Russian).
45. B. P. Tarasov, N. F. Gol´dshleger, A. P. Moravskii, *Usp. Khim.*, 2001, **70**, 149 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2001, **70**, 149].
46. V. I. Trefilov, D. V. Shchur, B. P. Tarasov, Yu. M. Shul´ga, A. V. Chernogorenko, V. K. Pishuk, S. Yu. Zaginaichenko, *Fullereny — osnova materialov budushchego* [*Fullerenes As a Basis for Materials of the Future*], ADEF-Ukraina, Kiev, 2001, 148 pp. (in Russian).
47. B. P. Tarasov, V. N. Fokin, A. P. Moravsky, Yu. M. Shul´ga, V. A. Yartys´, *J. Alloys Comp.*, 1997, **253—254**, 25.
48. B. P. Tarasov, V. N. Fokin, A. P. Moravskii, Yu. M. Shul´ga, *Zh. Neorg. Khim.*, 1997, **42**, 920 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1997, **42**].
49. B. P. Tarasov, *Zh. Obshch. Khim.*, 1998, **68**, 1245 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 1998, **68**].
50. B. P. Tarasov, V. N. Fokin, A. P. Moravskii, Yu. M. Shul´ga, *Izv. Akad. Nauk*, *Ser. Khim.*, 1998, 2093 [*Russ. Chem. Bull.* (*Engl. Transl.*), 1998, **47**, 2145].
51. Yu. M. Shul´ga, B. P. Tarasov, *Pis´ma v Zh. Eksp. Teor. Fiz.*, 1998, **68**, 239 [*JETP Lett.* (*Engl. Transl.*), 1998, **68**].
52. B. P. Tarasov, Yu. M. Shul´ga, V. N. Fokin, V. N. Vasilets, N. Yu. Shul´ga, D. V. Schur, V. A. Yartys, *J. Alloys Comps*, 2001, **314**, 296.
53. D. V. Schur, B. P. Tarasov, S. Yu. Zaginaichenko, V. K. Pishuk, T. N. Veziroglu, Yu. M. Shul´ga, A. G. Dubovoi, N. S. Anikina, A. P. Pomytkin, A. D. Zolotarenko, *Int. J. Hydrogen Energy*, 2002, **27**, 1063.
54. B. P. Tarasov, N. F. Gol´dshleger, *Al´ternativnaya energetika i ekologiya* [*Alternative Power Engineering and Ecology*], 2002, No. 3, 20 (in Russian).
55. D. V. Schur, B. P. Tarasov, Y. M. Shul´ga, S. Y. Zaginaichenko, Z. A. Matysina, A. P. Pomytkin, *Carbon*, 2003, **41**, 1331.
56. R. V. Lukashev, Ph. D. (Chem.) Thesis, Mos. Gos. Univ., Moscow, 2008, 112 pp. (in Russian).
57. R. V. Lukashev, S. N. Klyamkin, B. P. Tarasov, *Neorg. Mater.*, 2006, **42**, 803 [*Inorg. Mater.* (*Engl. Transl.*), 2006, **42**].
58. R. V. Lukashev, N. A. Yakovleva, S. N. Klyamkin, B. P. Tarasov, *Zh. Neorg. Khim.*, 2008, **53**, 389 [*Russ. J. Inorg. Chem.* (*Engl. Transl.*), 2008, **53**].
59. R. V. Lukashev, B. P. Tarasov, S. N. Klyamkin, in *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Ed. T. N. Veziroglu, Springer, Dordrecht, 2007, 193.
60. D. N. Borisov, P. V. Fursikov, B. P. Tarasov, *Int. J. Hydrogen Energy*, 2011, **36**, 1326.

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