

Complex study of single-wall nanotubes synthesized from C:BN mixtures

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Nanotubes with controllable characteristics are desirable for the majority of applications. Single-wall BN nanotubes demonstrate a wide bandgap irrespective of its diameter and chirality. The bandgap of single-wall carbon nanotubes varies from zero to 1.5 eV. One of the very attractive advantages of mixed C:BN nanotubes is a possibility to vary the bandgap by changing the ratio of C and h-BN fractions in the nanotube walls.

In this work single-wall nanotubes (SWNTs) have been synthesized from mixtures of C and hexagonal boron nitride (h-BN). Few series of samples with different C:BN ratios have been grown. A number of techniques has been used for their diagnostics: high-resolution transmission electron microscopy (HRTEM), Raman scattering, UV-VIS-NIR optical absorption, thermogravimetry (TGA). According to Raman spectra SWNTs were presented in all samples. HRTEM has shown a presence of various structures (single- and multi-wall tubes, shells, onions, cones, ribbons) in the samples synthesized initial mixtures with different content. On the base of TGA traces the presence of all 3 elements: B, N and C have been confirmed. The Raman and UV-VIS-NIR optical absorption spectra have been compared. The downshift of the "breathing" Raman modes were ascribed to the tube diameter enlargement in case of a big content of h-BN in the initial mixture. The same conclusion has been made from the average position shift of E₁₁ and E₂₂ bands in the optical absorption spectra. The observed spectra modifications have been considered as a confirmation of a presence of some amount of h-BN in the nanotube walls.

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Carbon nanotube chemical ethanol vapour growth methods for application in electronics and nanomechanics

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Carbon nanotube (CNT) possess unique properties for electronics, mechanics and sensors applications [1].

We have developed the carbon nanotube growth plant for carbon nanotube and nanofilament growth on different catalytic surfaces and wafers with dimensions up to 3 inches.

The plant (named CVDomna) consists of reactor furnace, electronic controller, forepump and the carbon-bearing steam-to-gas mixture (CSM) supply system. The temperature, pressure and gas flow rate are precisely controlled in CVDomna. The internal growth camera is made of silicon dioxide ceramics with low thermal conductivity. We have realised two deferent methods of CSM supply: by carbon-bearing liquid barbotage with CO₂ gas or with making use of evaporation chamber with temperature control.

In experiments we used the ethanol as carbon-bearing liquid. The carbon nanotubes and nanofilaments were grown on deferent catalytic surfaces: on the piece of stainless steel treated in $\hat{E}I$ nO₄; on the 5 nm thick nickel film, and on prepatterned draw in V-Ni-V film deposited on silicon wafer; nickel particles prepared with sol-gel methods.

The growth results were investigated in atomic-force microscope (AFM) and transmission electron microscope (TEM). It was shown than nanotubes have multiwall structures with 5-50 nm in diameter and up to 20 mkm long. The nanotube form and defect density are defined by the catalytic particle geometry and substrate material.

For demonstration of nanomechanics application we used silicon tips covered by sol-gel electrophoresis. The perpendicular nanotube growth on tip surface are preferred. For electronics applications it was shown that nanotubes grow on the energy-wise strained film sites like sharp cones and notches. It can be evaluated for aligned nanotube growth in predefined wafer sites.

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- [1] I.I. Bobrinetskii; Yu.A. Chaplygin, V.K. Nevolin, A.A. Stroganov, *Russian Microelectronics* **33**(5), 292-298 (2004).

Arc-synthesis of single-walled carbon nanotubes in nitrogen atmosphere

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Single-walled carbon nanotubes (SWNTs) are arguably the most known and studied representatives of ever-growing nanotube family. At the moment several techniques of their synthesis are known. Among them the arc-discharge is one of the simplest methods for production of gram-quantities of the material. Usually the synthesis is performed in inert gas (He, Ar). Another gases were also checked as a buffer medium, but not always with success. Surprisingly few articles are dedicated to arc-synthesis of carbon SWNTs in *nitrogen* atmosphere [1]. Nevertheless such approach could provide *N*-doped carbon nanotubes or serve as an intermediate step for production of heterophase C:BN nanotubes.

In this work arc-synthesis of SWNTs in N_2 atmosphere has been realized. A catalytic mixture C:Ni:Y₂O₃ (2:1:1) has been used.

Two sets of experiments have been made. In the first set the arc current was fixed at 65A while the gas pressure varied from 50 Torr to 750 Torr (atmospheric pressure). The obtained soot has been analyzed by Raman spectroscopy. A “gas pressure window” for a successful synthesis of SWNTs has been established as 100-450 Torr. For the pressure values out of this range the Raman spectra were typical for disordered graphite.

In the second set the *nitrogen* pressure was fixed at 350 Torr (as the optimum pressure derived from the first set). The arc-current current varied from 45A to 115A. The SWNT Raman signal has been detected in the range 55A -75A. Out of this range the signal of disordered (or amorphous) graphite was detected. Synthesis under the same conditions has been performed also in *He* atmosphere. Since the thermal conductivity of *nitrogen* is significantly lower compared to *helium*, the conditions of SWNTs optimal growth were realized at lower currents and/or pressures.

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[1] Y. Makita et al., *Eur. Phys. J. D* **34**, 287 (2005).

Fe-filled carbon nanotubes produced by microwaves

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Since their discovery, carbon nanotubes, both single-walled and multiwalled, have been a focus in materials research. Fundamental research and application development hinge on high-quality nanotube materials and controlled routes to their organization and assembly. The development of a highly efficient one-step technique was carried out to obtain long and aligned carbon nanotubes with or without Fe filling. The aligned carbon nanotubes (CNTs) were synthesized by microwave (MW) irradiation heating from a ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$. In this research, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM) study the growth of aligned carbon nanotubes by microwave heating. As a contribution of this method, the aligned multi-layer carbon nanotubes were obtained. CNTs have a metal particle at the tip of each tube. This carbon nanostructure promises to become important in fuel cells and in nanoscale engineering of other systems.

Synthesis of Bismuth nanotubes by microwave irradiation

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The electronic properties in bismuth bulk promise unusual properties in bismuth nanotubes. So we have used software about the first-principles molecular dynamics to study the stabilities and electronic properties of bismuth nanotubes. In this paper we report synthesis of Bi nanotubes by microwave irradiation (IMW) heating; being this method easier and cheaper than the common synthesis methods. The samples were warmed up in vacuum during 5, 10 and 15 minutes in a conventional microwave oven of 2.45 GHz and 800 W. The resulting Bi nanotubes were characterized using Transmission Electron Microscopy (TEM) for its structure and Atomic Force Microscopy (AFM) for its size.

New electroexplosion methods for synthesis of nanocarbon

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New technologies were developed for manufacturing of novel carbon nanomaterials (CNM) - fullerene-like clusters of the C₆₀-C₇₀ types and higher, nanotubes, nanodiamonds, carbyne,- based on the idea of a high-energy plasmochemistry synthesis with use of the methods of electrical wire explosion, spark erosion of graphite and metallic materials, and electric breakdown of organic liquids.

The suggested methods are characterized by an impact of high temperatures and pressures (which amount to 10⁵K and 300-500 MPa, respectively), electrical and magnetic field (field density amounts to 10⁶ V/1) on the material. It causes an evaporation of carbon in the form of clusters, plasmochemical reactions of synthesis with following ultraspeed quenching of the reaction products, what results in appearing new allotropic forms of carbon. It has been ascertain the effective possibility to control the spectral composition of the produced CNM through variation of the time-energy parameters of the synthesis process, type of material (graphite, iron, nickel, copper and others) and surrounding mediums (toluene, benzene, ethanol, hexane and others), and catalyst use. The fact of production of the fullerene-like clusters without the use of graphite as a material for the synthesis has been established. It can be explained as a result of destruction of surrounding organic medium in strong electric field at high temperature and pressure with following directional self-organization of destruction products.

The advantage of electro-explosive methods of synthesis of fullerenes and other CNM is that the facility works at the atmospheric pressure and an amount of technological operations is decreased in comparison with traditionally used technologies, what substantially decreases their prime cost.

Catalytic growth of nanotubes over carbon felt

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Catalytic decomposition of methane has great potential for hydrogen and carbon production. This process allows producing clean hydrogen and nanostructured carbon from natural gas. Ni- and Fe-based systems are known as ordinary catalysts for methane decomposition. These catalysts may include alumina, silica, zeolites, etc. For this reason the carbon nanotubes should be admixture free, because their electrical, chemical, thermal and mechanical prosperities strongly depend on their purity. Therefore the carbon felt are very promising support for catalytic methane decomposition. This solution is to decrease admixture content in the final product.

This study is devoted to catalytic non-oxidative methane conversion to hydrogen and carbon nanotubes over carbon felt based catalysts. The catalysts were prepared by impregnation with Ni-containing aqueous or ethanol solutions. The support activation was realized by either treating with KOH (CF-B) or heating at 800°C (CF-T). The loading amounts of Ni were 5, 10 and 20 wt.%. The activity tests for the catalysts in the decomposition of methane were carried out at atmospheric pressure in a conventional gas-flow system. Prior to the reaction, the catalysts were reduced with hydrogen at 450°C. Decomposition of methane was carried out in the range from 450 to 700°C. During the reaction, the gases were sampled and analyzed by GC.

The thermal gravimetric analysis showed the destruction of base-treated carbon felt at 450°C in air. In the contrast, the other samples were more stable. The temperature of destruction of these supports was about 600°C. The catalyst 20%Ni/CF-B was the most efficient catalyst for methane decomposition. The conversion of methane was 12% at 550°C for this sample. The high resolution SEM images of this sample showed that the resulting carbon nanotubes were cone-shaped with Ni particles encapsulated into the tubes.

Formation of carbon nanotubes systems by using an monolytic foam porous aluminum oxide as template

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Nanostructured carbon materials are potentially of great technological interest for the development of electronic, catalytic and hydrogen-storage systems. Due to a number of advantageous characteristics, such as uniformity in pore size, high surface areas and large pore volumes, porous carbon prepared through template-based approaches are currently the object of research attention. Nanoporous carbon materials were synthesized by using the ordered mesoporous silicals as template. Unfortunately mesoporous silica matrixs are high dispersed materials and obtained replicated carbon is powder too.

Here we describe the method of preparing of the monolithic carbon material. Carbon nanotubes are obtained in porous structure of template via especially prepared monolithic foam aluminum oxide. The plate of aluminum was oxidized by steam to prepare the monolithic sample of aluminum oxide with BET surface area 400 m²/g. Porous foam monolithic aluminum oxide was impregnated by sucrose as carbon precursor. After carbonization the resulting Al₂O₃/C materials were then chemically treated to dissolve selectively the Al₂O₃ matrix. The structure of the synthesized carbon is the replica of template.

The carbon replicas were studied by nitrogen and water adsorption measurements, scanning and transmissions electron microscopies. It was shown that the BET surface area is 415 m²/g, including the surface area of mesopores – 40 m²/g. The parameters of porous structure of carbon materials were calculated from nitrogen adsorption using comparative plot method and Dubinin – Radushkevich equation. Carbon materials have small micropores (radii 0.3 nm) with high adsorption energy $E_0 = 29.2$ kJ/mol. Methods of molecular spectroscopy (FTIR–spectroscopy and FT-Raman spectroscopy) show that system is build from aligned single-wall carbon nanotubes with very small mean diameter (1–2 nm).

SWCNT synthesis in rarefied gas and plasma flows

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Our growth reactor exploits a combination of low-pressure gas phase CVD growth with an electrophoretic cell. It consists of a gas feedthrough system, an evacuated bell jar with heated stainless steel tube and a cylindrical electrode. A gas mixture containing the carbon feedstock gas (C_2H_2) and buffer gases (Ar, H_2) is blown through the hot vertical stainless steel tube. Iron catalyst particles are synthesized by thermal decomposition of iron pentacarbonyl directly in the reactor. The hot tube is placed inside the vacuum chamber and connected to a vacuum pump through a filter, where carbon soot is collected. Pressure is varied by control of the gas flow rate and the pumping speed by inlet and outlet valves. Electric field may be induced inside the reactor by applying a voltage between the hot tube wall and a retractable coaxial central electrode.

Three regimes were explored - "thermal CVD" without field, "PECVD" with field higher than breakdown value, and "electro trapped CVD" with intermediate field. Experiments were made in flow of $C_2H_2/Ar/H_2$ mixture with a small impurity of $Fe(CO)_5$ injected for catalytic iron clusters creation. We have analyzed nanostructured carbon deposit on both electrodes and outlet filter with TEM, SEM and micro-Raman microscopy.

The obtained results showed that electrophoresis of CNTs at relatively low electric fields caused the motion of CNTs to the electrodes, predominantly to the anode. Analysis of the times required for such a CNT separation, taking into consideration the viscous forces and growth time in a thermal CVD reactor, does not allow to combine them in one set up. CNT charging in plasma creates a much more powerful way of controlling CNT transport and separation.

Size catalyst particles distribution after TCVD growth was measured. Estimations of diameter particles based on collisions frequency of iron atoms and duration of stay in hot zone given result correspond to experimental data.

SWNT in synthesized materials were observed which is no ordinary for our carbon feedstock and growth temperature. That it is consequence of limited catalyst particles size. TEM image analysis showed that distribution of diameter particles have maximum at 2–2.2 nm (fig. 1) and could be fitted by log-normal distributions. SWNT diameters estimated from Raman measurements correspond to the particle diameters. Diameter of SWNT measured with RBM spectra of material correlate with distribution of catalyst particles.

Carbon nanofibers and MWNTs formation on stainless steel at atmospheric pressure

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Nanofibers (NF) with small fraction of multi walled nanotubes (MWNT) were grown in a gas phase CVD reactor under atmospheric pressure. Feedstock gas (C_2H_2) with a buffer gases (Ar, H_2) was blown through heated (900-1100K) stainless steel tube. Temperature, flow rates of all gases and catalyst concentration were controlled. In part of experiments iron catalyst was delivered to reactor hot zone by bubbling controllable portion of Ar flow through liquid iron pentacarbonyl at 0°C. In other part NFs and MWNTs were synthesized directly on stainless steel wall. Samples of carbon nanostructures were collected from stainless steel tube and outlet water-cooled rod and filter separately. TEM, SEM and TGA were used for analysis of nanostructured carbon.

Experiments were performed with different partial gas flow rates and temperatures. In all experiments carbon soot from stainless steel tube contained nanofibers with diameter 40–100 nm and different amount of amorphous carbon, depending on growth conditions. Material collected from water-cooled rod and filter is similar. It consists of encapsulated iron particles, amorphous carbon and small amount of MWCNT. We have detected carbon nanofibers with diameter of few hundred nanometers formed on the stainless still tube without iron catalyst particles. Chemical analysis of nanofiber soot showed content of 0.38% Fe and 0.04% Ni originated from steel composition. In most productive regimes almost 100% of gaseous carbon feedstocks were transformed to carbon nanostructures. We discuss the formation of carbon structures in terms of morphology of austenite stainless steel and artificial catalytic particles. Size distribution of nanofibers grown without iron catalyst addition is correlated with grain structure of austenite stainless steel.

Plasmas treatment as a tool of carbon nanotubes adsorption capacity increase

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The increasing of an active surface and accessible internal space of carbon nanotubes (CNT) comprises the important problem which is partially solved by application of various chemical methods and, also by using thermal vacuum treatment and/or ultrasonic technique. At the same time a possibility of sorption ability as well as CNT capacity activation with the use of plasma-chemical technique still has not been practically investigated in spite of their obvious perceptivity in realization of processes of this type.

One-wall CNT samples were exposed to plasma-chemical treatment in our experiences. Pressure in reactor, plasma composition, current density in a bunch as well as exposition time, were varied in order to optimize the parameters of the process. Control of the enhancement of accessible CNT pore space was realized by measurements of sorption of carbon tetrachloride and methyl alcohol saturated vapors at a room temperature.

Stable increase of sorption speed and CNT internal volume capacity as a result of treatment were found out in all experiments without exception. The molecules adsorbed play a role of chemical sensors. It is characteristic that non-polar CCl_4 use provides quite reliable and reproduced volumetric porosity test: herewith, close to equilibrium values of pore volume (V_p) can be measured after 6-8 hours of adsorption. Contrary, in the case of methanol, sorption is usually lasting for day, and after that the molar content always turns out to be 1.5-2 times less than that measured with CCl_4 . The limited CNT volume capacity as well as significant loss of adsorption rate in case of methanol use, probably are explained by its primary sorption on CNT outside surface followed by seriously activated diffusion into channels, whereas CCl_4 molecules are readily condensed in nanotubes pore space.

With the use of optimized plasmas process conditions, CNT pore space can be increased more than 4 times: V_p activation from 0.4 up to 1.7 cm^3/g serves as typical example. In this case the amount of adsorbed CCl_4 exceeds CNT mass at almost 3 times. Thus, there are reliable reasons to consider plasmas treatment as effective method of "opening" the internal space of carbon nanotubes and total increasing their sorption ability.