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FUNCTIONAL CARBON NANO FIBERS FROM FR-OXYGRAFEN

Yerevan 2017

CONTENT

Introduction

Analysis of the state and trends of nanoindustry objects development allows us to conclude that one of the most promising areas of nanotechnology is the synthesis of carbon nanomaterials (CNM) - fullerene-like structures, which are a new allotropic form of carbon in the form of closed, frame, macromolecular systems. Among these materials, a special place is occupied by carbon nanotubes (CNTs) and nanofibers (CNFs).

Carbon nanotubes (CNTs) and nanofibres (CNF) are of great interest due to their unusual mechanical, electrophysical and magnetic properties. The number of fundamental and applied studies of carbon nanostructures (ONS) is constantly growing. The development of effective technologies for the production of ONS opens up wide prospects for their use in hydrogen energy - for the creation of hydrogen-accumulating materials and electrodes of fuel cells, in catalysis - as catalyst carriers, in nanoelectronics - for creating one-dimensional conductors, nanosized transistors, cold electron emitters and supercapacitors, In technology - as additives to polymer and inorganic composites to improve mechanical strength, electrical conductivity and heat resistance.

New materials - ONT (single-layer carbon nanotubes), MNT (multilayered carbon nanotubes) and HB (carbon nano fibers) - have unique properties and wide potential applications. CNTs have a number of unique properties due to the ordered structure of their nanofragments: good electrical conductivity and adsorption properties, ability to cold emission of electrons and accumulation of gases, diamagnetic characteristics, chemical and thermal stability, high strength in combination with high elastic strain.

The most valuable of them (ONT) are produced by more than 10 firms in the US, Japan, South Korea and some European countries in quantities not exceeding tens of grams per day. In large quantities (kilograms and tens of kilograms per day) and a large number of firms produced MNT. The two companies are engaged in large-scale (up to hundreds of kilograms per day) production of HB.

In Russia, Belarus and Ukraine, HT and HB are synthesized on a laboratory scale, although the production and use of these materials are critical technologies.

The use of HB, MNT, and especially ONT, is constrained by their high cost and at a price that reaches, in the case of the purest ONTs, 500-750 US dollars per gram.

Formulation of the problem

For the organization of industrial production, a method is needed that, when scaled, would allow a sharp reduction in the current prime cost of the produced HT and HB. Only under this condition HT and HB will find wide application. The purpose of this work is to analyze the existing methods of obtaining and their hardware design, the choice of the most promising ways from the technical point of view to reduce the cost of materials.

Product Description

Carbon nano fibers (they are also carbon nanofibers) are carbon cylindrical nanostructures that are stacked layers of graphene in the form of cones, "cups" or plates.

Carbon can exist in the form of tubular microstructures called filaments or fibers. In recent decades, the unique properties of carbon fibers have expanded the scientific base and technology of composite materials.

. Carbon nano fibers (CNF) are a class of materials in which curved graphene layers or nanocones are composed in the form of a quasi-one-dimensional filament whose internal structure can be characterized by an angle α between the layers of graphene and the fiber axis. One common difference is noted between the two main types Fibers: "Herringbone", with densely laid conical graphene layers and large α, and "Bamboo", with cylindrical cups similar to graphene layers and small α, which are more similar to multilayer carbon Nano tubes. However, in the case of real CNTs, α is zero.

CNF attracted great attention of scientists with their potential thermal, electrical, shielding and mechanical properties. Due to their exceptional properties and low cost, they are now increasingly used in various materials, such as composites.

Receiving

Catalytic chemical gas-phase deposition (CCVD) or simply chemical gas-phase deposition (CVD) in various ways, such as thermal deposition and deposition in plasma, is the main commercial technology for producing CNF. In this case, the gas phase molecules decompose at high temperatures and carbon precipitates in the presence of transition metal catalysts on a substrate on which further growth of the fiber around the catalyst particles occurs. In general, this process involves separate steps, such as gas decomposition, carbon deposition, fiber growth, fiber thickening, graphitization and cleaning. The diameter of nanofibers depends on the size of the catalyst.

The CVD process for producing CNF is usually divided into two categories: a fixed catalyst process (serial) and a process with a "floating" catalyst (continuous). In a series production developed by Tibbets, a mixture of hydrocarbons with hydrogen and helium was passed over mullite (crystalline aluminosilicate) with a fine-dispersed iron catalyst held at 1000 ° C. Methane was used as the hydrocarbon in a concentration of 15% by volume.

In the furnace, fiber growth is initiated on the surface of the catalyst particles and continues until the catalyst is poisoned by impurities. The growth mechanism of the fiber is described by Baker and his colleagues, only a portion of the catalyst particles contacting the gas mixture grow fibers and the growth ceases as soon as the exposed part of the catalyst is impregnated, i.e., the catalyst becomes poisoned. The catalyst particles are coated with fibers with a final concentration of about several millionths of a fraction. At this stage, there is a thickening of the fibers.

. The most frequently used catalyst is iron, often enriched in sulfur, hydrogen sulphide, etc., in order to lower the melting point, and promote the penetration of carbon into the pores of the catalyst and, therefore, create more growth points. Fe / Ni, Ni, Co, Mn, Cu, V, Cr, Mo and Pd are also used as catalysts. Acetylene, ethylene, methane, natural gas, and benzene are most often used as carbon sources for producing CNF. Often, carbon monoxide (CO) is introduced into the gas stream to increase the yield of carbon by reducing the amount of iron oxides in the system.

2. Methods for obtaining HT and HB

There are three main groups of methods for obtaining HT and HB:

- Sublimation and desublimation of graphite (in an electric arc, with laser ablation, using concentrators of sunlight or Joule heat);

- decomposition or chlorination of carbides;

- decomposition or pyrolysis of carbon-containing gases.

Separate publications are devoted to the decomposition and chlorination of carbides.

Although these processes can be used to produce specific materials, the prospects for their use for the economical synthesis of NTs and HBs appear to be small.

The largest array of studies of the properties of NTs was performed on samples obtained by high-temperature methods of sublimation and desublimation of graphite.

These methods are used by some firms and even scaling and improvement of the plants (for example, for arc synthesis) is being carried out. However, the specifics of the processes are such that energy costs can not be significantly reduced here, and automation and scaling of installations, complete cleaning of the product requires considerable effort. The development of the laser ablation method has been discontinued.

At the same time, pyrolytic methods are most diverse in methods of organizing and activating processes. They are much better researched, implemented in simpler and easier scalable reactors. The products obtained in this way contain significantly less impurities than in arc synthesis, and do not require multistage and expensive cleaning.

In the following, only the methods of the third group are considered. According to the chemical composition of carbon-containing raw materials, these methods are divided into:

- disproportionation of CO,

- Pyrolysis of hydrocarbons (CH4, C2H2, C6H6, etc.)

- Pyrolysis of compounds CHhOy (for example, alcohols),

- pyrolysis of heteroatomic compounds CHxAyBz (A, B = N, O, S, Cl ..., for example amines).

The most valuable materials, ONT, are obtained mainly from CO (at temperatures 700-1200 oC) and CH4 (700-900 oC). Thus, two US companies bet on the processes of obtaining ONT by disproportionating the CO-process HiPco (developed at the Rice University) and the CoMoCAT process (the University of Oklahoma, the method is described only in brief advertisements). Both these processes require not only high temperatures, but also high pressures (10 atm or more). In the case of HiPco, general disadvantages of processes with a volatile catalyst are added to this.

Therefore, scaling up the processes of CO decomposition is much more complicated and expensive than processes based on catalytic pyrolysis of CH4 and other hydrocarbons.

. Variants of catalytic pyrolysis

By the methods of organization, the processes are divided into those using a supported catalyst or a volatile catalyst (vaporous or as a sprayed organic solution). Activation of processes with a supported catalyst can be carried out:

- Thermally (external heating, hot filament, partial combustion of hydrocarbon),

- in plasma (different types of discharge),

- using a laser (selective excitation of vibrational modes),

- with detonation.

The variant with a hot thread is used only in laboratory practice.

Partial combustion of hydrocarbons and detonation synthesis are associated with low yield of target materials. Quite intensive studies of methods for the synthesis of NT in the flame of hydrocarbons have been discontinued. Laser chemical processes have not yet reached the industrial stage. Plasma reactors operate at low gas pressures and are therefore already limitedly applicable for large-scale production, although they have clear prospects for use to produce specific products and products. Therefore, the main way to activate processes with a catalyst on a support is thermal at external heating.

Activation of processes with a volatile catalyst is also usually carried out using external heating. The processes are carried out in injection reactors. One of the drawbacks of processes with a volatile catalyst is the low values of the CCP and the difficulty in controlling the magnitude of the CCP. The specificity of all the variants of catalytic pyrolysis is such that the catalyst of the process is "one-time", and for the isolation of HT or HB it is removed by dissolution. Therefore, the amount of CPC, as well as the costs of cleaning from catalyst residues when cheap hydrocarbons are used, strongly affects the cost of the materials produced.

4. Features of the kinetics of processes

One of the main problems in the catalytic synthesis of ONS is the production of the desired structure with a high selectivity of a carbon material and with the necessary physicochemical characteristics. The analysis of literature data shows that the chemical nature and size of particles of the active component of the catalyst, the methods of its fixing on various supports (substrates), the chemical nature and porosity of the carrier, the pressure, the pyrolysis temperature, the composition of the initial gas mixture, and Also the duration of the process. The use of binary mixtures of metals, metallic composites or intermetallic compounds as catalysts, as well as the introduction of various additives (promoters) in the catalyst composition in a number of cases increase the efficiency of the formation and growth of ONS.

Therefore, the study of the influence of various parameters of the catalytic synthesis of ONS on their structure and properties serves as the basis for solving the problem of directed synthesis of carbon nanostructures with a given structure and functional properties.

The kinetics of catalytic pyrolysis has been studied only for processes with the formation of HB. The processes of obtaining MNT and ONT from the kinetic side are almost not investigated. Therefore, we can talk only about some common features and draw the most preliminary conclusions.

The increase in the mass of HB on the catalyst in time can usually be represented by an S-shaped curve having an initial induction period, an increase in the process speed section, a process speed deceleration section; The saturation region on the curve determines the value of the CCP (the specific capacity of the catalyst (the amount of HB formed by the catalyst mass cushion before its termination), with the temperature increasing the reaction rate at the initial section W and the maximum value W at the inflection point of the S- The value of the CCP is reduced.

To calculate and simulate the formation of HB, the results of kinetic studies can be used.

When obtaining HB in processes with a catalyst on a carrier, the ratios of the values of G and CCP are controlled by the temperature and properties (activity) of the catalysts. Optimum can be considered a catalyst that provides both relatively high values of W (and hence the value of G) and relatively high values of CCP, for example 50-100 g / g.

. If HB in catalytic pyrolysis processes is obtained at relatively low temperatures (550-700 oC) and long contact time (20-60 min and more), the formation of MNT requires higher temperatures (600-900 oC) and a shorter contact time (10- 30 min). The conditions for the synthesis of ONT differ even more: the temperature rises to 800-1000 oC, the contacting time is reduced to 1-5 minutes. Another condition is the excess of hydrogen.

The mechanism of MNT and HB formation, on the one hand, and ONT, on the other, is different. In the first case, the catalyst particle is localized on the growing tip (vertex growth), in the second - remains on the carrier (root growth). The processes of growth of ONT proceed without an induction period. For the synthesis of ONT, different catalysts are required than for the preparation of HB, while the chemical composition of the active component and the carrier can be the same. The change in reaction conditions for the preparation of ONT, as a rule, has a strong effect not only on the purity of the product, but also on its morphology.

The value of the CCP in the transition from HB to ONT decreases noticeably and rarely exceeds 1-2 (in the CoMoCAT process, using a catalyst on a carrier, it is equal to 0.25 and is reached in 2 hours).

All that has been said above complicates the choice of apparatus for the production of ONT by catalytic pyrolysis.

5. Hardware processing of processes

The supported catalyst may be in a stationary, agitated, suspended (incident, fluidized or vibrating) or filtering bed.

The overwhelming majority of the literature on the synthesis of NTs and HBs is devoted to periodic processes and only isolated ones are semicontinuous.

The American firm Hyperion Catalysis International, Inc. patented a semi-continuous vertical fallout reactor (diameter 0.3 m, total height 20 m, height of the reaction zone 10 m).

This is the largest unit for the synthesis of HB and MNT, which is described in the literature.

Semicontinuous operation of injection reactors is organized. One of the Chinese firms on a laboratory scale implemented periodic removal of sediment from the walls of the reactor (presumably using special ejectors). The method with the localization of deposition not on the walls of the reactor, but in its volume was adopted by the Japanese company Nikkiso (Nikkiso Co., Ltd.) and, possibly, some other companies. In advertising messages it is indicated that it is continuous

Fluidized bed reactors

Processes in semi-continuous reactors with a fluidized or vibrating layer of catalyst have been or are being developed in Russia (GKBoreskov Institute of Catalysis of the SB RAS), England, France, Holland and the USA. The productivity of the reactors was ahead of all of the Chinese engineers (Qinhua University and Shaanxi Nanfeng Company): at the end of 2001 they received 15 kg / h HB in the batch process.

. The need for prior activation (reduction) of the catalyst in a stream of H2 or its mixtures with other gases, a strong increase in the initial particle size and the volume of the layer during the deposition of HB make it difficult to continuously maintain the process. It is difficult to organize a countercurrent phase contact. However, these shortcomings can be overcome. To stabilize the hydrodynamic regime, particles of inert materials can be introduced into the bed or specially prepared catalysts can be used.

When receiving ONT, some restrictions are dropped. In August 2003, it was planned to implement the CoMoCAT process in a pilot plant with G = 40 g / h (~ 1 kg / day), and by mid-2004, create a ten times more productive installation.

7. Reactor with a stirred bed

A laboratory continuous horizontal tubular reactor for conducting pyrolysis of methane in a stirred catalyst bed with a countercurrent of gas and solid phases was developed at the Kurchatov Institute of Chemical Technology. In the reactor, whose length is 1 m, and the diameter is 0.06 m, the value of G is adjusted to 15 g / h for purified HB and can be increased. The change in the rate of catalyst movement along the length of the reactor makes it possible to control the contact time within a wide range, thereby allowing for an optimal ratio of G (-reactor productivity, g / h, W-rate of formation of HB and HT, g / h) and CCP, Countercurrent phase contact - exclude the activation stage of the catalyst.

Conclusions

The analysis allows to conclude that the most promising for the creation of large-scale cost-effective production of NT and HB are the processes of catalytic pyrolysis of cheap natural flammable gases, the use of supported catalysts, and the conduct of processes in fluidized or stirred bed reactors. It is also likely that reactors of one and the other type will find application for the production of carbon nanomaterials, differing in morphology and fields of application.

Application of carbon nanofibers

Potential applications of carbon nanofibers are:

(1) additives to polymers;

(2) catalysts;

(3) electron-field emitters for electron-beam illumination elements;

(4) a flat panel display;

(5) gas discharge tubes in telecommunication networks;

(6) absorption of electromagnetic waves and shielding;

(7) energy conversion;

(8) Lithium-battery anodes;

(9) for storing hydrogen;

(10) nanotubes (by filling or coating);

(11) nanoprobes for STM, AFM, and EFM tips;

(12) nanolithography;

(13) nanoelectrodes;

(14) the delivery of the medicament;

(15) sensors;

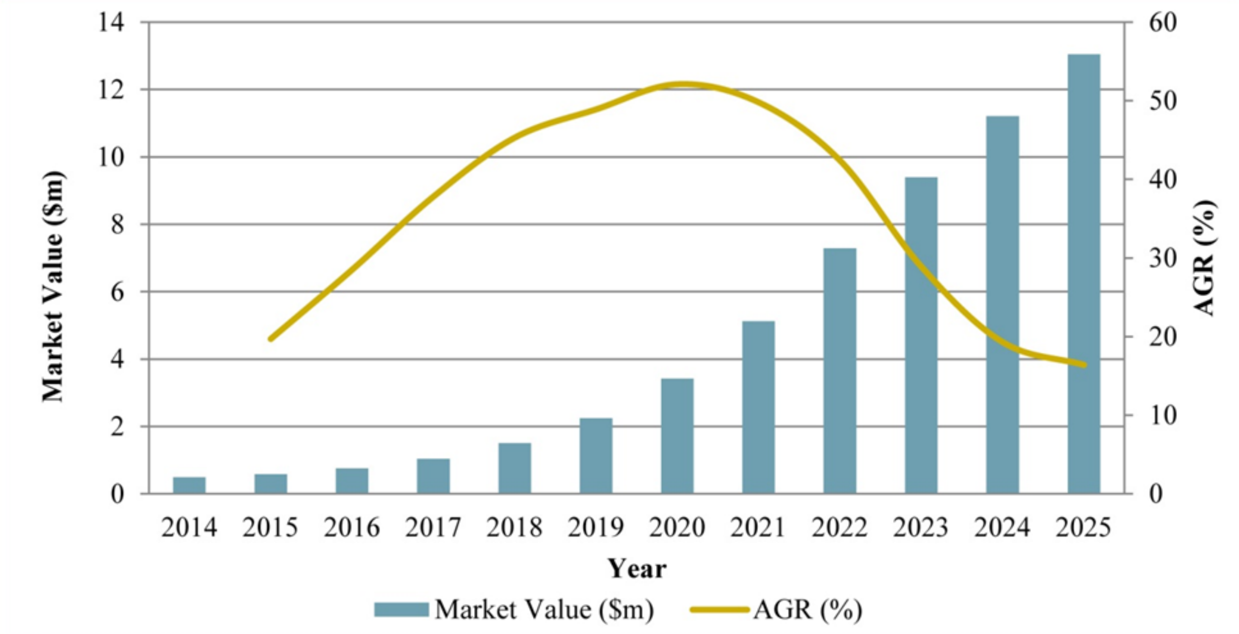
(16) reinforcements in composite materials;

(17) supercapacitor.

Carbon nanotubes (carbon nanotubes, CNTs) are molecular compounds belonging to the class of allotropic modifications of carbon. They are extended cylindrical structures with a diameter from one to several tens of nanometers and a length of one to several microns.

Carbon nanotubes today act as the most promising nano material. This is evidenced by the growth rates inherent in the market: in 2013, the increase in relation to the previous year exceeded 40%. The growth in demand for nanotubes on a global scale is due to their unique physico-chemical properties and the ability to optimize the characteristics of products related to various industries.

Figure 5.28 Italy Graphene Market Forecast 2015-2025 ($m, AGR%)



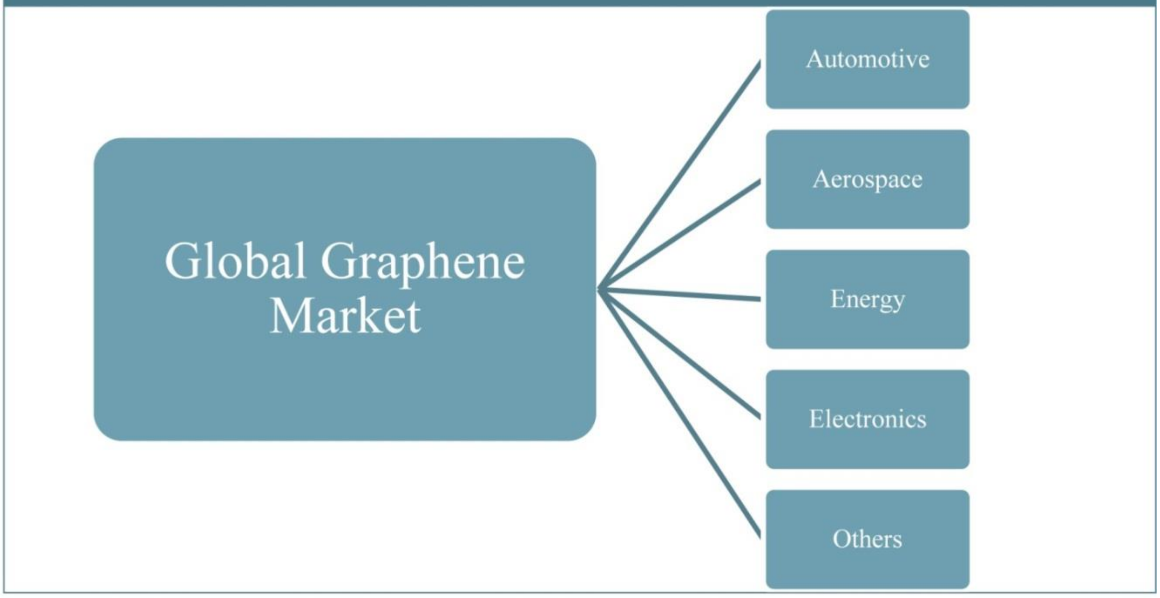
Source: *visiongain 2015*

Table 4.4 Energy Graphene Market Forecast 2015-2025 ($m, AGR %, CAGR %, Cumulative)

	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2015-2025
Market Value ($m)	2.25	2.61	3.27	4.24	5.68	7.45	10.42	14.09	17.58	21.04	24.51	28.95	139.85
AGR (%)		16.2	25.1	29.7	34.0	31.1	39.8	35.2	24.8	19.7	16.5	18.1	
CAGR (%) 2015-20			31.9			2020-25				22.7			
CAGR (%) 2015-25							27.2						

Source: *visiongain 2015*

Figure 1.2 Global Graphene Market Segmentation



Source: *visiongain 2015*

The world market of CNTs, as well as coatings based on them, according to Future Markets, over the past three years could grow by about 40%. According to the optimistic estimates of the consultant, the sales of pipes in 2016 amounted to 4.1 million tons, on pessimistic ones - 3.7 million tons. International experts predict this niche a great future. By 2020, the consumption of CNTs can increase to 10.5 - 12 million tons. The growth drivers should be metallurgists, electronics engineers, power engineers, machine builders and representatives of the medical and military-industrial complex.

Scope of application; In the automotive, aerospace, power, electronics and composites.

Scope of application

Electrochemical sources of current

• Polymers and composites

• Elastomers and rubber

Competitive advantages

•100 times stronger than steel

• High temperature stability (up to 600 ° C in air)

• Huge surface area (more than 500 m2 / g)

• One of the world's best electrical conductors

Creation of composites based on industrial polymeric materials (conductive composites, composites for protection against electromagnetic radiation, impact-resistant composites); Substitutes for graphite in current collectors, brushes of electric motors and other products; Electrodes of lithium-ion chemical sources of current; Electrodes of super capacitors; Fuel cell electrodes; In the form of nano paper - filters for aggressive media; In the form of colloidal solutions - limiters of laser radiation.

Carbon fiber market conditions

The world market of carbon fibers and materials based on them has been steadily growing in recent decades, and only in the last eight years it has grown fivefold in physical terms. Most of the carbon fiber is produced in a complex and multistage process from specially prepared polymeric raw materials, mainly polyacrylonitrile (PAN) or viscose. Developers of this technology (mainly Japanese companies) have made great strides in reducing the production cost and increasing the strength of ordinary fiber over the past twenty years, which has led to an increase in sales primarily in civil aircraft construction.

The global market of coalcomposites will reach $ 35.75 billion by 2020. The global market for carbon composites (carbon fiber reinforced composites) will grow from the current $ 20.92 billion to an impressive level of $ 35.75 billion by 2020. This forecast is provided by Marketsand Markets, an information and analytical company. In terms of value, the global carbon fiber market will reach $ 3.51 billion by 2020. The average annual growth rate in this period will be about 9.1 points. This growth will be due to increased demand from such aircraft manufacturing companies as Airbus and Boeing. In addition, growth in demand for coal composites will also be affected by such segments of consumption of composite materials as automotive (in the light of stricter environmental standards and efficiency standards), civil engineering, wind power and the production of sporting goods. Composite materials (including carbon composites) are actively used in the above-mentioned industries due to the physical, mechanical and consumer properties that products obtained on their (composites) have. Thus, carbon composites are increasingly used in aircraft construction because the weight-to-strength ratio of such materials largely exceeds that of any of the metal alloys. In practice, these properties have a positive effect on the strength and efficiency of airliners, which are able to carry more weight and save fuel, which ultimately positively affects the profitability of air travel and airline profitability. The growth in demand for composite materials in the aircraft industry is driven by the growth in production (from the named category of materials) of the aircraft components and components: ailerons, vertical stabilizers, wings, gondolas and others. We do not need to follow the examples, among the latest innovations in aviation technology, whose creation would have been impossible without the active use of composite materials, can be safely called: Airbus A380 and A350; Boeing B-787. At the moment, the fuselage of the 787th Boeing is made of carbon fiber, which reduced its weight by 20%. This year, it is planned to increase the production of B-787 airliners from 10 to 12 units per month, which clearly demonstrates the expected growth in demand for carbon composites. Serious consumption volumes will also be observed from Airbus, which received orders from Qatar Airways and Delta for 80 and 25 A350 vessels, respectively.

The demand segment on the part of aviators will also support the production of US Black Hawk combat helicopters. Given the data given, it is not surprising that North America will be the largest market (according to experts' forecasts) in the field of coalcomposites. The growth in demand will be ensured by an increase in the consumption of composite materials by the aircraft. Reliable fasteners for Composites Fasteners bighead glued or molded saves time.

• Hexcel поглотила Formax 2016 space industry and military industry, wind power and the automotive industry. Such a scenario is well known to industry companies that continue to actively increase their production capacities and core assets. Only for the last two months there was a whole series of branch mergers and acquisitions. The most notable of which were:

• Meggitt redeemed Cobham plc

• Solvay absorbed Cytec

• Hexcel absorbed Formax

Another characteristic feature of this market is the active penetration of composite materials into the production of cars. As in the case of aviation equipment, composites can achieve significant weight loss and improve the efficiency of movement. The key incentives here are constantly stricter environmental standards and requirements. The most recent example of the effective use of composite materials is the new BMW iseries, which (due to carbon fiber) "lost weight" by 300 kg. Another example of the active use of composite materials in the automotive industry is the Cadillac CT6. It should be noted that the active penetration of composite materials into the auto industry will be ensured, including by counter motion - many car manufacturers actively enter into joint industry projects and create their development and production centers in the field of composite materials, which (in our opinion) is the key A signal for industry companies and investors for the future prospects of this industry

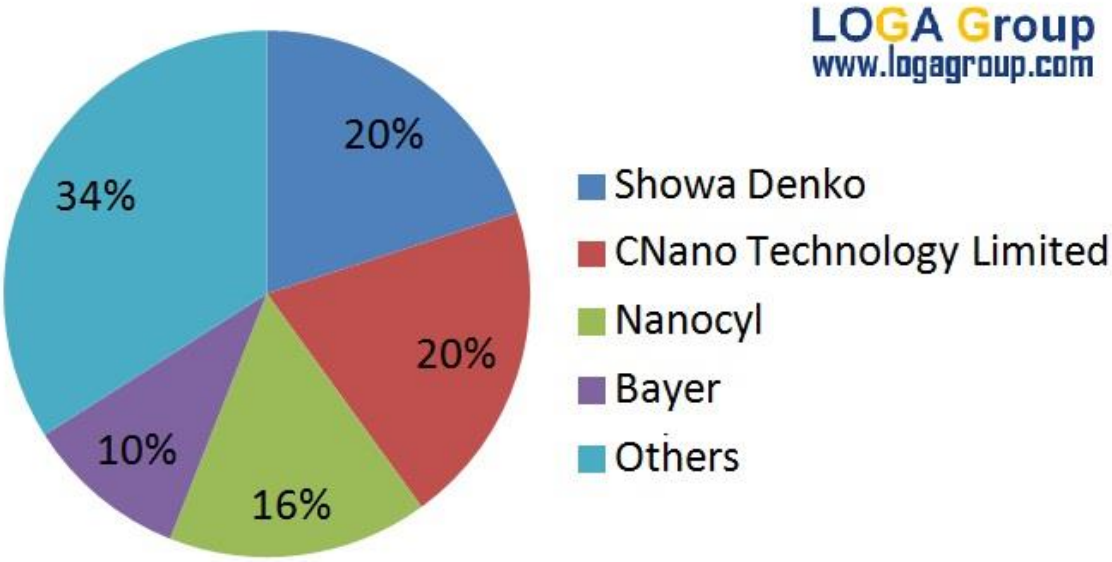
Nano tubes for the joy of green Direct effect is obtained when using them in the so-called. "Green energy". In order to reduce greenhouse gas emissions worldwide, electric vehicles and hybrid vehicles are being introduced. Batteries and super capacitors are used as power sources in such machines. Batteries Batteries have a significant drawback - low charging speed and number of charge-discharge cycles. The best lithium-ion batteries have a resource limited to a thousand cycles. Moreover, as the resource is developed, the capacity of the battery decreases. All owners of smartphones and tablets are familiar with this phenomenon. The use of nanotubes in the manufacture of a negative electrode for lithium-ion batteries allows to increase the capacity of batteries, and the service life. But with the speed of charging nothing can be done - it is limited by the physics of the process itself. Super capacitors Super capacitors are another promising source of power for road transport. Its main advantage is a high charging speed, which is not inferior to the rate of filling of gasoline into the tank. Only here the capacity of these devices is forty times less than that of batteries. Nevertheless, in different countries super capacitors are tested on public transport. Their charge is enough for a smooth start from the bus. They are also used in electric transport as backup power supplies: when a line breaks, a tram can travel several kilometers on super capacitors to the next stop or to a working section of the power network. If you look in the school textbook of physics, then you can find the formula for the dependence of the capacitance of the capacitor on the geometric parameters of the electrodes. From this formula it follows that the larger the surface area of the electrodes, the greater the capacitance of the capacitor. Nano tubes have a huge specific area. It would be tempting ideas to use them for the manufacture of super capacitor electrodes.

Competitors

Carbon nanotubes and nano fibers abroad are produced in quantities of more than 1000 tons per year and are widely used as fillers in composites, filter components, catalyst carriers, gas sensor sensing elements, super capacitor electrodes, lithium-ion batteries, for creating electrically conductive coatings and Other

According to the forecast of analysts of Lux Research (Boston), in 2018 the world market will require for its needs about 1520 tons of graphene plates and about 2016 tons of nanotubes.

The main producers of CNTs in. Were Showa Denko (20%), CNano (20%), Nanocyl (16%) and Bayer (10%).



США. According to Markets and Markets (USA), in 20015 the world market of carbon nanotubes and materials based on them, which grows annually and develops at a significant pace, can reach $ 252 million.

Among the manufacturers there are already their leaders, this is:

• Nanocyl S.A. - Belgium

• Nanoledge, CNRI, Arkema - France

• Thomas Swan, Dynamics Lab. - United Kingdom

• Bayer, Germany

• Carbon Nanotechnologies, Hyperion Catalysis, Ebay, NanoLab, CarboLex, MER, Tailored Materials Corp., SweNT - USA

• Shenzen Nanotech Port Co. - China

• Mitsui, Showa Denko - Japan

• Raymor Industries Inc. - Canada

Business models of manufacturers

To date, there are three main areas of application of CNTs:

• production of materials based on CNT;

• production of products based on CNT;

• production of products based on CNT with additives.

The largest segment of the market is the production of materials from CNT. The share of this segment is about 70%. Approximately 20% of the market falls on the segment of production of products from CNT. Examples of final products can be nanofilms and nano composites. About 10% of the market falls on the segment of production of products based on CNT with additives, but this segment is fast-developing and promising and has a high growth potential. Many major manufacturers carry out various research projects to develop a technology for the use of CNTs with different additives, but to date only one company has this technology. This technology allows you to receive a product with certain technical characteristics, depending on the requirements of a specific customer, which makes it possible to make the final product more quality and resource-saving.

Key consumers

Энергетика (производители батареек, солнечных модулей, топливных элементов). Данные компании используют нано трубки в различных формах при производстве конечных продуктов. Текущими потребителями являются: NEC, Samsung, LG, Ballard Power Systems и другие. The world wound of CNT can be divided into three main groups of consumers:

• Manufacturers of plastics and composites. These companies use CNT as additives to enhance the properties of the final product. These plastics and composites are used in various fields - the defense industry, sports goods, aerospace, automotive, etc. Current consumers are: Solvay, DuPont, Sabic, Zyvex, Creanova, Hyperion, RTP and others;

• Manufacturers of electronics. These companies buy nano tubes and use them in the production of final products when thin films and layers are applied. Current consumers are: Intel, NEC, Samsung, IBM, Fujitsu, LG, Toshiba and others;

Energy (manufacturers of batteries, solar modules, fuel cells). These companies use nanotubes in various forms in the production of end products. Current consumers are: NEC, Samsung, LG, Ballard Power Systems and others.

Крупнейшим потребителем углеродных нано трубок и материалам на их основе в мире, по данным отчета The global markets for carbon nanotubes to 2020 консалтинговой компании Future Markets, являются страны Азиатско- Тихоокеанского региона (47%), второе место занимает Северная Америка (28%), третье — Европа (24%).

All works using this material were limited to a high price - $ 123,70 US per one gram of nanotubes, and the world demand for them is tens of thousands of tons.

The two main reasons are high cost and lack of scalable production technology. $ 100,000 per 1 kilogram of one walled carbon nanotubes - outside of economic applicability (aluminum ~ $ 2 / kg), this is really very expensive. And the world production volume of 1 ton is too little.

Carbon nano material (CNM) is one of the new, but rapidly progressing materials with a very wide range of applications. Moreover, the most popular demand in the foreseeable future will be multi-layered carbon nanotubes (MWNTs), to improve many properties of composite materials, and, first of all, strength.

World production of MWNTs is growing, but consumption is constrained due to the lack of mass production, and, as a consequence, their high cost.

It is known that the most promising way of obtaining MWCNT is the thermocatalytic decomposition of carbon-containing gas with the subsequent synthesis of MWCNTs, due to more favorable, "soft" process conditions (temperature and energy consumption), and also relatively low capital costs.

The method is being intensively investigated, but an acceptable hardware solution for industrial many tonnage production has not yet been found.

An extremely large number of variants of the implementation of the method, which showed good results in laboratory and semi-industrial scale, when organizing large-scale production were difficult to implement, but the creation of such a production is urgently needed.

With the goal of solving the problem of the introduction of nano-carbon pipes into production, a new concept is proposed to be the use of new nano-carbon materials with functioning properties in replacement of one and many-walled nano-carbon tubes, a production technology that is complex and the cost of the product is very high.

It is proposed to apply FR - Oxigrains instead of one and multilayer carbon nanotubes.

The purpose of this applied scientific research and experimental development, Development and development of a unique product based on carbon nanomaterials for the production of a new functioning nanocarbon material FR - Oxigrafen is an analog of graphite oxide and a precursor for the production of graphene.

The way of obtaining FR-Oxigrafen is an innovative high-tech, highly economical energy-saving and environmentally friendly technology.

An innovative method for obtaining high-quality nanocarbon FR-Oxigrafen, a unique method of pyrolysis of nanocrystalline cellulose, is developed in which graphitization (graphenization) is performed while maintaining the structure and morphology of the nanocrystal cell of the carbon matrix of the starting material-nanocrystalline cellulose.

Experimental samples of nano-crystalline carbon materials (carbon nanotubes, graphene) are made.

A new functional material based on nanoscale modifications of carbon FR - Oxigrafen has been developed. The technology of obtaining carbon nanomaterials FR - Oxigrafen with the given set of unique adsorption, energy storage, mechanical, electronic and optical properties is developed and mastered.

The uniqueness of FR - Oxigrafenes lies in the content in the carbon matrix of the nanomaterial, free radicals, which gives it unique properties and can be used both in the traditional and in the new field of science and technology - carbon nanotechnology, microelectronics and optoelectronics.

Depending on the synthesis conditions, FR - Oxigrafen may have the properties of both a semiconductor and a dielectric. This makes it possible to widely use graphite oxide in electroluminescent devices, supercapacitors, electronics and other fields.

The reliability of the developed materials was confirmed by an analysis of the composition and morphology of the product synthesized, as well as by the study of some of its physico-chemical properties (chemical stability, thermal stability, specific all, electrical conductivity, etc.).

Description FR - Oxigrafen

FR - Oxygen-free nano-carbon multilayer tubular tubes

FR -Oxigrains are carbon, (quasi-one-dimensional), nanoscale filamentous formations of poly crystalline graphite of cylindrical form with an internal channel.

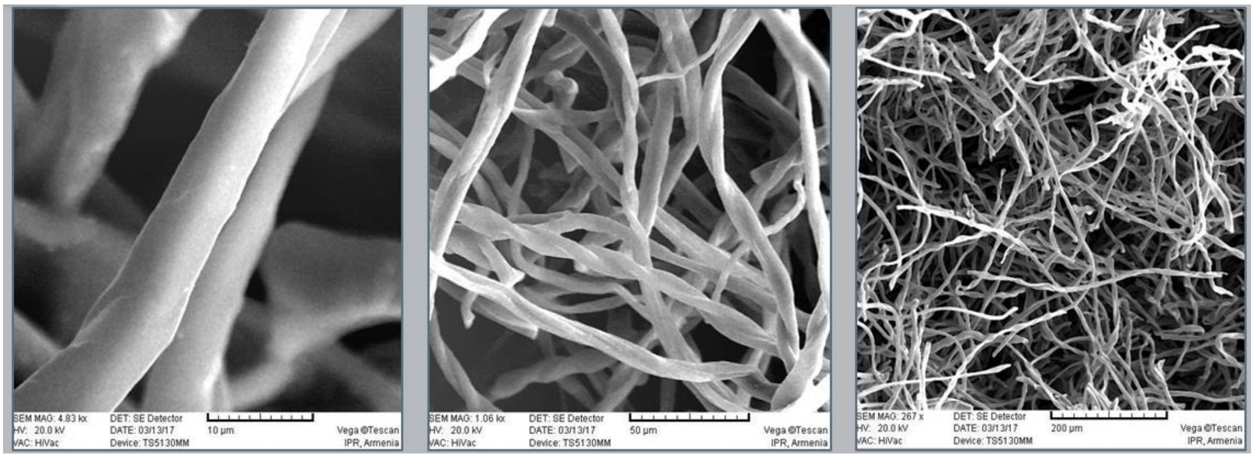
Microtubes FR - Oxigrains consist of nano sized crystallites

Thickness of micro-filaments FR-oxygrafens (diameter of tubes) 2-10 µm. The length of the filaments is up to 100 µm.

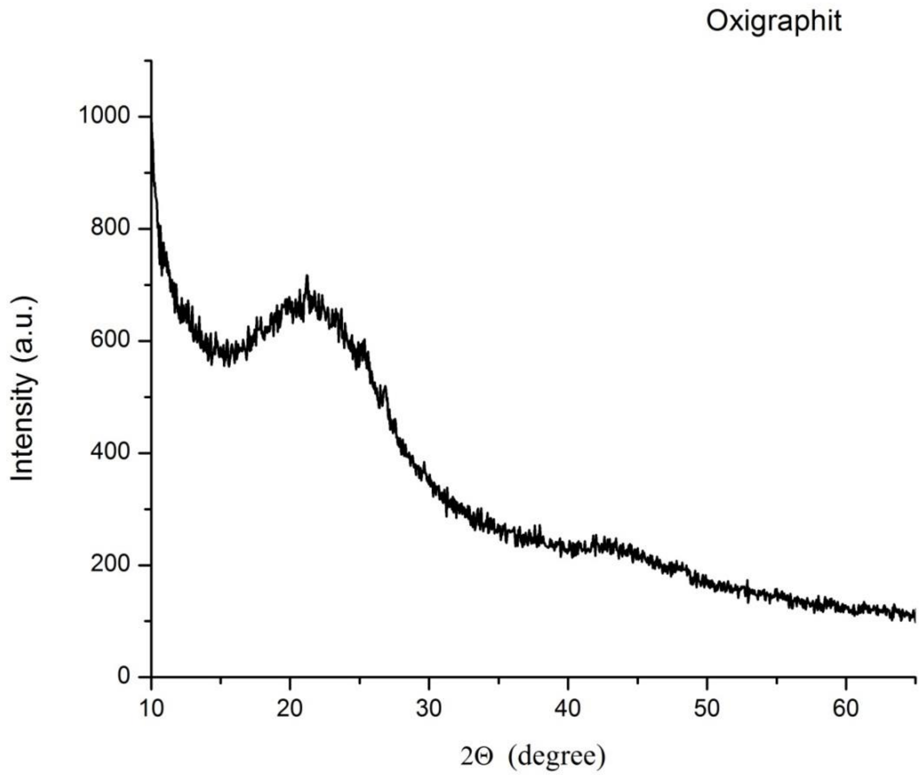
Microfibrils contain several hundred macromolecules; The dimensions in the transverse direction are from 4 to 10-20 nm, the average length of the crystallites is 7-10 nm.

FR - The oxigraphenes, after ultrasonic treatment in a liquid medium, transform into a low-layered graphene with a particle thickness of 0.34 to 4 nm.

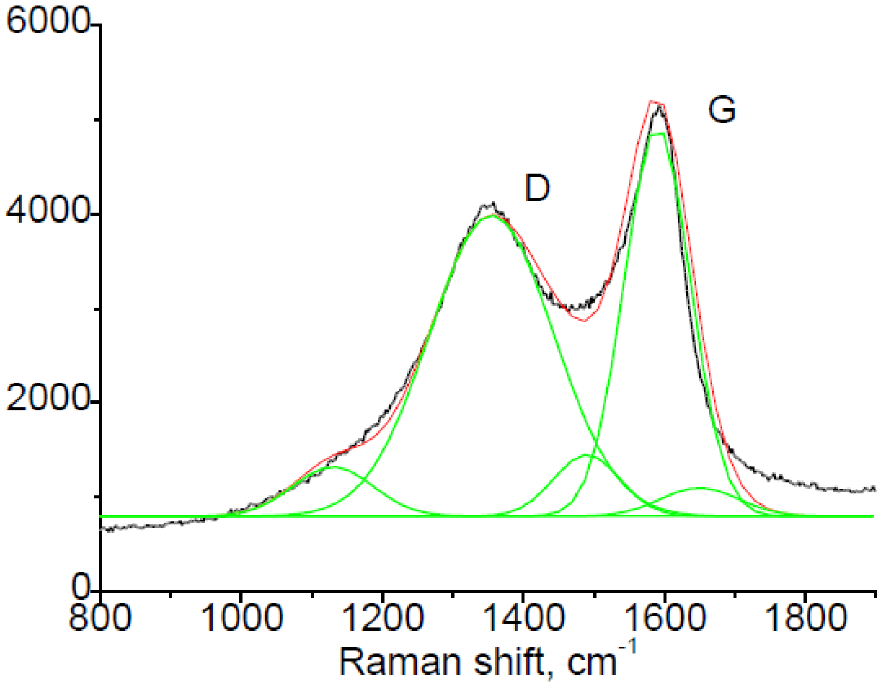
Appearance FR-Graphene oxide, Black fluffy material



FR -Oksigrafen according to AFM



Radiographs FR -Oksigrafena



Raman spectrum of carbon synthesized by carbonization of NFC.

FR-graphene oxide is a nano-crystalline carbon, with an analogous structure of graphene and fullerene and glassy carbon.

The structure and dimensions of the FR tubes were studied by scanning electron microscopy, the two-dimensional graphene structure of the tube walls was confirmed by X-ray diffraction.

The morphology of the synthesized material is similar to the structure of the initial precursor of the nano crystalline cellulose material, but differs from it by the carbon content, which can reach up to 100% in FR-oxigraphenes.

Properties of FR - Oxy graphenes

Total impurities,%: ≤1

Bulk density, g / cm-3 0.03-0.05

Specific surface, m2 / g-1 ≥300-320

Thermal stability in air, OC ≤600

In a neutral gas or in a vacuum, it does not break down and does not melt when heated to 3000 ° C

It is chemically neutral and resistant to corrosion when exposed to acids, alkalis, and solvents.

FR - Oxigraphenes is a super sorbent with the greatest absorption capacity among known materials. FR - The oxygene sorbent has a gigantic internal surface - more than 1000 sq.m. For 1 gram.

FR - Oxigrains are, nano fibrils, in the form of single-layer, meow-layered carbon structures of tubular structure.

Preparation of graphene oxide funktsionizirovannogo FR - Oksigrafena

The preparation of FR-Oxigrafen from nano crystalline cellulose is carried out by carbonization of NFC, a unique pyrolysis process carried out at low temperatures, at which a carbon hexagonal matrix of nano-crystalline carbon is formed.

Thanks to the use of a specially prepared precursor of NFC, a special catalyst, medium and pyrolysis regimes, carbon micro filaments are formed, which consist of crystalline nano-carbon fragments, graphene-like napkins.

In the proposed pyrolysis process, the turbostratic crystalline structure of the pyrocarbon formed is substantially ordered and is closer to the graphene carbon structure, compared to the micro-filament structure obtained from the NFC by known pyrolysis processes.

The proposed method of carbonization is highly productive, forgive, cheap and effective. Synthesis is carried out by low-temperature SHS reaction (Self-propagating high-temperature synthesis method) is energy-saving and does not require special complex equipment.

Comparative analysis of carbonation methods of NFC

Compared with the known method of producing carbon microtubes by electric arc method, gas-phase catalytic hydrocarbon deposition and laser ablation, the proposed method has the advantage, both in terms of productivity, economic, technological expediency, and the ability to synthesize nano-carbon materials with specified parameters and properties.

Advantages of the developed technology for obtaining nano carbon FR - Oxigrafen compared to the known ones: availability, cheapness, expressiveness, reproduced, manufacturability and scalability, the technique does not require the use of toxic and explosive reagents, severe synthesis conditions and expensive equipment.

Development of environmentally safe mass production of oxygrafene.

A new method for obtaining nano carbon FR - Oxigrafens is a cheap and high-tech way of obtaining a functioning oxide of graphene and graphene in tangible amounts by a method of affordable raw materials.

Business concept

The main areas of application of CNT FR - Oxigrafen are: heating elements, protection against electromagnetic radiation, composite materials, batteries and fuel cells. The products are used in the automotive, aerospace, construction, wind power and energy sectors.

The raw material for the production of CNTs are nano cellulose obtained from cotton wool.

The uniqueness of the product is a technology that allows you to obtain intermediate products with certain technical characteristics, depending on the requirements of a particular consumer, which makes it possible to make the final product more efficient resource-saving.

Effects from the implementation of the project results:

Reducing the cost of production of single-layer and multilayer carbon nanotubes FR - Oxigrafen and graphene, increasing physical and mechanical properties of carbon composites.

Expected output - 250 tons of nanotubes in FR - Oxigrafena year.

Preparation of FR - Oxigrafen by catalytic pyrolysis of nano cellulose by original technology on a continuously operating reactor.

Estimated prime cost for large-scale production will be 2 - 5 US dollars per 1 kg.

Forms and volumes of commercialization of project results:

The project will be implemented in 3 stages:

1. Laboratory research and development of synthesis technology and properties of FR-Oxigrafen;

2. Pilot small-scale production of FR - Oxigrafen;

3. Commercialization of development results, organization of large-scale production of FR - Oxigrafen.

Terms of the project (years of implementation)

2017-2018. Laboratory research and development of technology of synthesis and properties of FR - Oxigrafen, synthesis of 10-20 kg per month;

2019-2020. Pilot small-scale production of FR - Oxigrafen with a capacity of 18 tons per year;

2020-2022. Planning and organization of production of FR - Oxigrafen with a capacity of 250 tons per year;

Financial feasibility of the project

The implementation of the project will require investment:

1. Laboratory research and development of technology of synthesis and properties of FR - Oxigrafen, synthesis of 10-20 kg per month; - 400 000 $ USA

2. Pilot production of FR - Oxigrafen with a capacity of 18 tons per year; - 2 million $ USA

3. Production of FR - Oxigrafen with a capacity of 250 tons per year; - $ 12 million

Total need for financial costs: - $ 14.4 million US

Payback period and expected income from production

Annual productivity of FR-Oxigrafen 250T.

Cost of 1 kg FR-Oxigrafen, 5 $ USA

Sales price 1KG FR -Oxigraphene 50 $ USA *

Revenue from the sale of 1KG FR-Oxygenen 45 $ USA

Expected annual income from production of FR-Oxigrafen 11 000 000 $ USA

The planned payback period of capital expenditures is ~ 2 years

(2 years after the commissioning of production).

Pilot production of FR - Oxigrafen with a capacity of 18 tons per year, after commissioning will be self financing enterprise with a profitability of 1 000 000 $ USA per year.

The planned payback period of capital expenditures of pilot production is ~ 2 years

(2 years after commissioning of pilot production).

* Selling valuable FR-Oxigrafen, 10 times lower compared to the market price of graphene oxide and 100 times lower compared to the market price of graphene, which ensure a highly competitive product in the market.

Legal protection:

There are patents on the method of obtaining carbon materials, on the method of obtaining catalysts and on a reactor for synthesis, a number of developments are carried out at the level of know-how.

Forms of cooperation:

Direct investments;

- participation in the project on a compensation basis in the form of deliveries of finished products, etc.
- contracts for new developments;
- contracts for the supply of nanotubes and nano fibers, functionalized nanotubes and nano fibers, dispersions of nanotubes and nano fibers, catalysts.
- contracts for the sale of technology.

Protecting the results of intellectual activity

The application for the invention "Development of a highly economical, environmentally friendly method for obtaining nanocarbon material FR - Oxigrafen" was filed. As the development and research of new nanocarbon composites based on FR-Oxigrafen are completed, a new 7 patents will be issued.

Project implementation status:

1. Research of the latest achievements in the field of nano-carbon materials. A comparative analysis has been made between the known and novel production method, oxygrafen and graphene.

2. The technological process of synthesis of nano carbon tubes from FR-Oxigrafen by a special method of pyrolysis of nano crystalline cellulose was developed. The regimes and catalysts for the synthesis of FR-oxigraphene, the method of low-temperature pyrolysis, and SHS synthesis have been determined.

3. The laboratory synthesis of FR-oxigrafen samples was carried out.

4. The composition and structure and some properties of the synthesized substance FR-Oxigrafen, scanning electron microscopy and X-ray diffraction were studied.

5. The composition of the structure and the expected property and technologies for obtaining nano composites based on FR-Oxigrafen are modeled, in priority directions.

6. The process of functionalization (grafting of functional groups) of nanotubes and nanofibers has been worked out, which allows obtaining their stable dispersions in water, ethanol, dimethylformamide and dimethyl sulfoxide with a concentration of up to 10 g / l and introducing them into polymer matrices.

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