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## NANOTECHNOLOGIES AND CARBON NANOPARTICLES

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### ABSTRACT

The article presents the prospects for the production and application of carbon-containing nanomaterials used in nanotechnology. These materials include graphene, carbon nanoparticles, and fullerenes. They can be, used, as dielectric, semiconducting, conductive, including superconducting materials. The article also expressed an opinion on the method of obtaining fullerene.

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**Introduction.** Nanotechnology is a science that deals with the creation of new, more complex materials, devices and systems using particles that are several nanometers in size (nm is part of a billion meters). The results of this science cover all spheres of the life of society. As one of the main technologies of the 21st Century, it is used in the production of nanotechnological materials and instruments, medicine, electronics, military industry, sensor technology, and so on, with the ability to create wide opportunities. Nanotechnological products are already used in various industries: in the production of cars and airplanes, computers, clothing items and even sports accessories [1-5].

It is believed that the beginning of nanotechnology was laid by Richard Feynman in 1959 with the lecture "There's Plenty of Room at the Bottom". In his lecture, he showed for the first time that, from the point of view of the fundamental laws of physics, he sees no obstacles to work at the molecular and atomic levels, manipulating separately molecules and atoms.

People used nanoobjects and nanotechnologies of the modern era in the old days in their lives. These include the example of colored glasses. For example, a cup of Lycurgus, made in the 4th century, kept in the British Museum, turns green when illuminated from outside, and turns red when illuminated from within. Electron microscopy studies have shown that this unusual effect is due to the presence of nanosized gold and silver in the glass. Thus, we can say with confidence that the Lycurgus cup (fig.1) is made of nanocomposite material.

In the Middle Ages, adding metal dust to glass produced glasses of different colors depending on the type and amount of metal. It has now been established that these glasses also have bactericidal properties, that is, they can disinfect the environment.



Fig 1. Lycurgus Cup, 4th century

At the beginning of the 20th Century, nanoscale particles could not be “seen” by the microscopes available at that time. After the discovery of the electron microscope in 1931, it became possible to “see” objects of submicron and nanometer size. After the creation of a scanning tunneling microscope in 1981, it became possible not only to obtain images of individual atoms, but also to manipulate these atoms. Thus, the technology that Feynman talked about in the lecture was created. But the emergence of technology does not at all mean understanding the essence of the process. For example, although the melting of steel has been known for a long time, the perception of its physical and chemical foundations was too far. Recall that the secret of the Damascus sword (steel) has not yet been fully disclosed. As you can see, the interaction of science and technology is not so simple.

For the first time the term nanomaterial (nanocrystal, nanostructure, nanophase, nanocomposite) was introduced and used in 1981-1986 by the American scientist G. Glater. An important role in the history of nanotechnology and the development of the ideology of nanoparticles was played by the discovery in the mid 80 - early 90s of the 20th century of carbon nanostructures - fullerenes and carbon nanoparticles, as well as the method of obtaining graphene in the 21st century.

Carbon has conflicting and unique properties that set it apart from other elements. Depending on the structure, it can be both dielectric and conductive, semiconducting, and semi-metallic material, be very hard and very soft, possess heat-insulating and heat-conducting characteristics. To do this, it is enough to compare diamond and graphite. Despite the fact that carbon is the eleventh most abundant element in nature, its atoms are able to form long molecules, connecting with each other, and the ability to be replaced by other elements led to the formation of an excessively large number of compounds.

The properties of carbon that we show vary at the macro level. When passing through the nanoscale, the unique properties of carbon are revealed. At this level of measurement, carbon atoms create nanostructural clusters that differ from each other in structure and size without the participation of other elements. These include fullerenes, graphenes, nanocarbons, etc.

Graphene is a layer of carbon atoms that resembles the hexagonal lattice of bees. The distance between carbon atoms in graphene is 0.142 nm [6,7].

The neck of an ordinary pencil consists of graphite layers of graphene. Since the distance between the layers is very large (0.334 nm), the connection between them (Van der Waals bond) is weak and they can slide over each other. Therefore, when graphite touches paper, “particles” consisting of graphene layers remain on the paper (fig. 2).

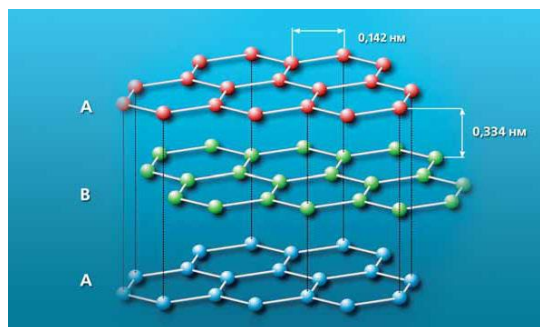


Fig.2. Crystal structure of graphite

The production of two-dimensional stable, free (without a substrate) graphene from a three-dimensional graphite structure caused a revolution in this field since two-dimensional structures made

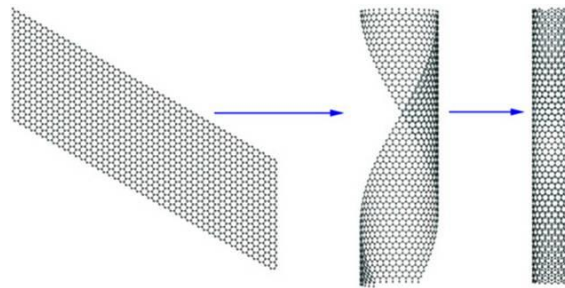
it possible to have very high electronic properties. Therefore, the electronic properties of graphene are currently being investigated in hundreds of laboratories around the world [6].

It has been established by theoretical modeling that transistors can be made from graphene, and its speed is hundreds of times higher than that of modern silicon transistors. Silicon processors currently allow multiple operations per second without overheating. Since electrons pass through graphene without resistance, heating is negligible. In addition, graphene itself is capable of quickly dissipating heat since it conducts heat well. For these and other reasons, graphene-based electronics can operate at higher speeds and frequencies [7].

The advantage of graphene is not only in its speed. Silicon retains its electronic properties up to 10 nm. Graphene not only retains and even enhances its electronic properties, but also retains its basic physical properties, even if its dimensions are less than 1 nm.

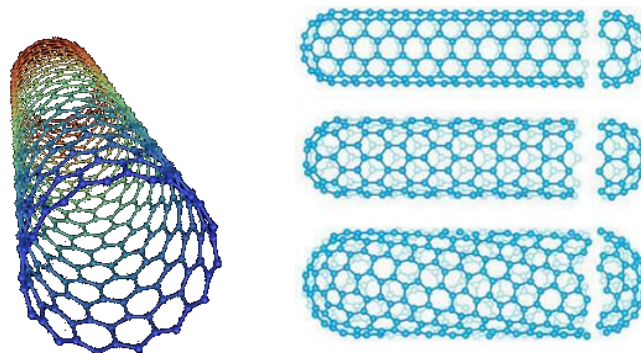
For the method of obtaining graphene, Russian-English physicists A.K. Geim and C.S. Novoselov were awarded the 2010 Nobel Prize.

Promising directions for the development of nanotechnology are closely related to carbon nanotubes. Carbon nano-sleeves are skeletal structures made of only carbon atoms. What a carbon nanotube can be understood by imagining the process of converting graphene into a tube by twisting a graphene layer (fig. 3).



*Fig. 3. Manufacturing a nanotube from graphene*

The properties of nanotubes depend on the tilt angle of graphene. Of course, nanoparticles are not made from graphene layers; they themselves are formed under certain conditions, for example, on the surface of electrodes during an arc discharge between carbon electrodes. During the discharge, carbon atoms come out to the surface and join together, forming nanoparticles of different types: single-layer, multi-layer, and with different tilt angles (fig. 4).



*Fig.4. On the left - a schematic description of a combined carbon nanotube, on the right - double: from top to bottom, flat and spiral nanotubes*

The diameter of single-walled nanotubes is usually 1 nm, and the length is more than a thousand times, about 40 microns. They develop perpendicular to the cathode surface and appear to be spontaneous accumulations of carbon atoms. Depending on the angle of twisting, the nanotubes have either high conductivity like metals or semiconducting properties.

The bond of carbon atoms in nanotubes with each other has a record strength. In them, Young's modulus (resistance to tension and compression pressure) exceeds 1TPa, which is 1 million atmospheres more than that of diamond. The thermal conductivity of nanotubes is 8 times higher than that of copper. The current density in tubes can be a thousand times higher than in copper.

Electrical conductivity in nanotubes does not obey Ohm's law, in which electrical resistance is expressed by the well-known expression:

$$R = \frac{\rho L}{S} ; \tag{1}$$

where  $\rho$  is the resistivity of the conducting material;  $L$  is its length;  $S$  is cross-sectional area.

In this case, the resistance of a nanoparticle is determined by two fundamental physical constants, regardless of its size and material [8]:

$$R_0 = h/(2e^2) = 12,9 \text{ k}\Omega, \tag{2}$$

where  $e$  is the electron charge ( $1.6 \times 10^{-19}$  Kl);  $h$  - Planck's constant ( $6.6 \times 10^{-34}$  Joule /sec);  $R_0$  - electrical resistance is called quantum, because the resistance of all conductors in the nanosystem is the same.

Resistivity quantization is not the only conductivity feature in a nanosystem. Sometimes, when the current passes through the nanowire, no "Joule heat" is released. Unusual conductivity, which does not depend on the length, width of the conductor in the nanosystem and where heat release is not observed, is called ballistic conductivity ("ballo" - in Greek to throw, "ballistics" - the science of the movement of artillery projectiles, bullet, etc.). This is explained by the fact that electrons, like well-ejected projectiles, pass through nanowires without colliding atoms in the nodes of the crystal lattice.

Quantum (discrete) conductivity in carbon nanotubes was discovered when determining the dependence of resistance on length. In experiments, the nanotube diameter was 1.4–50 nm, and the length was 1–5  $\mu\text{m}$ . Despite the fact that the sizes varied in such a wide range, the resistance value for all nanotubes was the same 12.9 k $\Omega$ .

Electrons conduct current in conductors and create an "electron cloud". The rms momentum  $p$  of one of the electrons can be found in the expression for the mean square energy  $E$  of an ideal gas particle:

$$E = p^2/(2m_e) = 3kT/2, \tag{3}$$

where  $k$  is the Boltzman constant ( $1.38 \times 10^{-23}$  Joule /K);  $m_e$  is the electron mass ( $9,1 \times 10^{-31}$  kg). At  $T=300\text{K}$   $p=10.6 \times 10^{-28}$  kg·m/sec.

It is known that each particle can be represented as a wave with a length  $\lambda = h/p$ . For metal with electronic conductivity  $\lambda = 6.2$  nm. This means that for carbon nanotubes, the diameter of which is several nanometers or less, the electronic conductivity will have a mainly wave character. Electrons through such nanotubes will pass through the way light waves pass through light transmitters. Thus, in the nanosystem, the concept of electricity turns into optics, while the Joule loss of distribution is eliminated at the boundary of the nanosystem, for example, in places where the sizes of nanotubes are commensurate with conductors of ordinary size.

As we have already noted, nanotubes have ballistic conductivity, and no losses arise in it. Then we can assume that its length is less than the mean free path of an electron.

Let us assume that a voltage  $U$  is given between sections  $A$  and  $B$  of the nanotube. A current  $I$  flows through it (fig. 5).

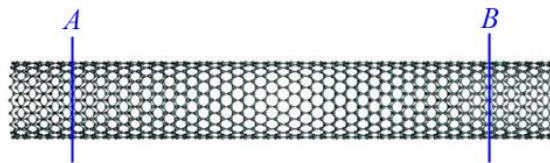


Fig.5. Schematic representation of a carbon nanotube

Taking into account that the energy does not propagate, then the change in the electron energy between the sections  $A$  and  $B$  will be  $\Delta E = eU$ . The change in energy occurs in the time interval  $\Delta t$  when the electron passes between the cross-section  $A$  and  $B$ .

According to the Heisenberg uncertainty principle  $\Delta E \cdot \Delta t \approx h$ , from here:

$$U \approx h/(e \cdot \Delta t). \tag{4}$$

Let us estimate the current intensity in the nanotubes. A nanotube is a homogeneous quantum structure. Inside it, like in a helium atom, there can be only two electrons with different spin values. This means that the current between sections  $A$  and  $B$  of the nanotube will be:

$$I = 2e/\Delta t \tag{5}$$

Their expressions (4) and (5), one can find the resistance between segments *A* and *B* in the cross-section of the nanotube  $R_o$ :

$$R_o = U/I = h/(2e^2). \quad (6)$$

This expression, as expected, repeats expression (2).

Since there is no heating in nanotubes (theoretically), they can have a high density (more than  $107 \text{ A/sm}^2$ ) for the passage of current. If carbon nanotubes had ordinary (not ballistic) conductivity, then the temperature in them at such a density of such a current would rise to 20,000 K, which would be much higher than their combustion temperature (700K). The presence of ballistic conductivity allows many times to reduce the size of electronic circuits.

The demand for nanotubes is very high. And this is estimated in billions of dollars. The shape of nanotubes allows them to be placed in two types: chaotic and ordered, which affects the quality of materials. It is possible to modify nanotubes, that is, to combine various chemical groups and nanoparticles in them. It also changes the quality of both nanotubes and materials made from them [9,10].

Rubber made of long and entangled nanotubes is resistant to destruction under cyclic loading at temperatures from  $-140$  to  $+900^\circ\text{C}$ . Its performance is significantly superior to silicone rubber, which is considered the best elastic material. The thickness of a simple macromaterial - nanopaper made of nanotubes - is 3–10 nm. Filters are prepared from nanoparticles, which help to purify water from salts, destroy viruses, protect against electromagnetic waves, they are used to make heating parts, sensors, etc.

If an electric potential is applied to the ribbons made of parallel-located nanotubes at temperatures of  $80 \div 1900\text{K}$ , they can be strongly stretched (artificial muscle). Such converters of electrical energy into mechanical energy are more efficient than piezoelectrics [11].

The use of nanotubes in nanocomposites, mainly polymer nanocomposites, is becoming more and more widespread. When a small number of nanotubes is added, the properties of polymers change greatly, electrical conductivity is formed in them, thermal conductivity increases, mechanical properties improve, and chemical and heat resistance increases. When nanotubes are added to ceramic composites, their electrical and thermal conductivity increases, their resistance to electromagnetic rays increases and, most importantly, their resistance to cracks. Metal composites are also widely used. The mechanical strength of copper composites is two to three times that of copper. Hybrid composites usually consist of three components: polymer or inorganic fibers (fabrics), nanotubes, and connectors. This class includes prepreps. Nanotubes increase the mechanical strength of prepreps by 30-50%. Prepreps are widely used in the automotive, aviation and shipbuilding industries. They are also used for making body armor and sports equipment. When used in the blades of 49 m wind power plants, their weight is reduced from 7.3 tons to 5.8 tons.

Carbon atoms evaporate from the heated graphite surface and merge with each other, forming molecules not only in the form of nanotubes, but even in the form of spherical or ellipsoidal convex closed polygons. In these molecules, carbon atoms are located at the vertices of regular hexagons and pentagons that form the surface of a sphere or ellipsoid. Such molecular compounds of carbon atoms are called fullerenes, after the American engineer, designer, and architect R.B. Fuller [12-14].

The most symmetrical and best studied fullerene consists of 60 carbon atoms ( $\text{C}_{60}$ ). It consists of 20 hexagons and 12 pentagons in the shape of a cut icosahedron (fig. 6) and resembles a soccer ball, about 1 nm in diameter (fig.7).

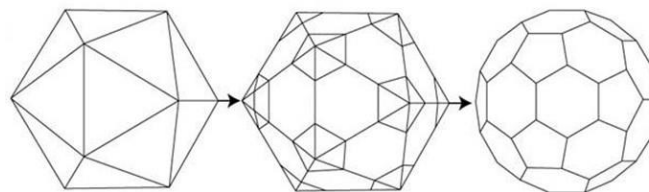


Fig.6. a) icosahedron (20 triangular sides); b) the formation of pentagonal and hexagonal sides with a cut of the icosahedron; c) section of the icosahedron (12 pentagonal, 20 hexagonal)

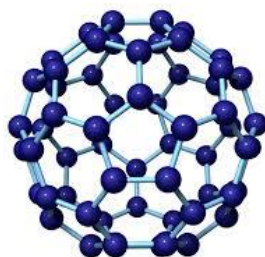


Fig.7. Fullerene  $C_{60}$

For the discoveries of fullerenes, the American physicist R. Smola, British physicists H. Kroto and R. Kerley were awarded the Nobel Prize in 1996. Fullerenes  $C_{60}$  are considered a symbol of nanotechnology [15].

Fullerenes are currently obtained only by artificial synthesis. The conditions of their occurrence, structure, properties, and field of application have been intensively studied in recent years. It has been established that fullerenes are obtained in large quantities during an arc discharge in the content of soot accumulated on the graphite surface.

Fullerenes are found naturally in shungite (rock), fulgurite (sand, quartz struck by lightning), meteorites, minerals aged 65 million years at the bottom of the seas and oceans. Fullerenes on Earth are formed when natural gas is burned, and lightning is released. In 2011 study of air over the Mediterranean Sea showed fullerenes in each of 43 air samples from Barcelona to Istanbul. Fullerenes were found in large quantities in space in 2010 as a gas, and in 2012 in a solid form [16].

Since each fullerene carbon atom ( $C_{60}$ ) simultaneously refers to two hexagons and one pentagon, all  $C_{60}$  atoms are equivalent. But the C-C bonds do not have the same length. The length of the C=C bond of two hexagons is 1.39 Å, and the length of the C-C bond, which is both a side of a hexagon and a pentagon, is 1.44 Å. The study of the properties of fullerene  $C_{60}$  shows that it has 4 stable isomers, the atomic mass does not change and is equal to 720 units.

Another widespread fullerene is  $C_{70}$ , which differs from  $C_{60}$  in the presence of 10 carbon atoms in the equatorial part, so  $C_{70}$  is slightly longer, resembling a rugby ball in its shape. Compounds with high (heavy) fullerene containing a large number of carbon atoms (up to 400) are formed in small amounts and often have a complex isomeric structure. Of the higher fullerenes ( $C_n$ ), the most studied are  $n = 74, 76, 78, 80, 82$  and  $84$ .

The first fullerenes were obtained by acting on solid graphite with laser beams and separating it from vapor condensation. In 1990, fullerenes were produced in grams in a helium atmosphere at low pressure by burning graphite electrodes in an electric arc. As a result of anodic erosion, soot accumulates in the chamber walls; it contains a certain amount of fullerene. It is dissolved in benzene or toluene, and fullerenes  $C_{60}$  and  $C_{70}$  are obtained in pure form from the solution in a ratio of 3:1 and about 2% heavier fullerenes.

The mechanism of formation of fullerenes is unknown, since the processes occurring in the burning part of the arc are thermodynamically unstable, which complicates theoretical analysis.

The cost of one gram of  $C_{60}$  over the past 15-20 years has dropped from \$ 10 thousand to \$ 5, which allows their real use.

A molecular fullerene crystal is a semiconductor with a band gap of  $\sim 1.5$  eV, most of its properties are identical to other semiconductors, which allows them to be used in electronics as a diode, transistor, photocell, etc.

When fullerenes are used as an additive in the growth of diamond plates by the CVD (Chemical Vapor Deposition) method, the growth rate is increased 5 times. High thermal conductivity and chemical resistance make them a promising material for micro-electronics.

It has been found that doping of crystalline semiconducting molecular fullerene ( $C_{60}$ ) with an alkali metal produces a material with metallic conductivity - fullerite. At low temperatures, it turns into a superconducting state. Doping of the  $C_{60}$  crystal is carried out at several hundred °C when exposed to metal vapors. This gives a structure of the  $X_3C_{60}$  type (X is an alkali metal atom). In the potassium compound  $K_3C_{60}$ , the superconducting state is formed at 19 K. This is a record high for molecular superconductors. Then it was revealed that the superconducting state also exists in  $XY_2 C_{60}$

compounds (X, Y are alkali metal atoms). A record index of these superconductors ( $T_{cr} = 33K$ ) was found in the compound  $RbCs_2 C_{60}$  [17].

Carbon nanoparticles can be used as dielectric, semiconducting, conductive and structural materials, their field of application is gradually increasing.

In general, nanostructured materials science is one of the factors indicating the level of development of science and technology in the country.

**Conclusions.** Thus, our studies allow us to note the following results:

1. Carbon nanoparticles can be used both as a structural and electrical material: dielectric, semiconducting, conducting, including superconducting.

2. At steel works, during melting steel by an arc discharge, the formation and release of fullerenes on graphite electrodes has not been studied. Such research has promising possibilities.

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