MINISTRY OF HIGHER EDUCATION, SCIENCE AND INNOVATION OF THE REPUBLIC OF UZBEKISTAN

NAMANGAN STATE UNIVERSITY
Department of Organic Chemistry

EDUCATIONAL AND METHODOLOGICAL COMPLEX

by subject

NANOCHEMISTRY AND NANOTECHNOLOGY

For 3 th year daytime education

Area of Knowledge:	500000-Gumanitar subjects
Area of Education:	5530000-Natural subjects
Bachelor Direction:	6053100 -Chemistry (daytime)

NAMANGAN-2023

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Lecture 1
Introduction to Nanochemistry and Nanotechnology

In the history of human development, several important historical stages associated with the development of new materials and technologies have been known.

Today, science has the opportunity to directly affect individual atoms and molecules, which has taken the development of nanotechnology to a completely new level. Creating and studying structures and objects with controlled parameters and defined properties at the nano-level is one of the most important technological challenges of today. These are the unique properties of materials in the nanostructured state, the possibility of creating "smart" materials with predetermined programmable properties, the processing of materials and changing their surface, the miniaturization of products, the creation of fundamentally new objects, devices, and even new industries and developing new technologies.

Nanotechnologies include a wide range of scientific, technological and industrial fields combined into a single technological culture based on working with substances at the level of individual atoms and molecules.

This includes processes that change not only new technologies, but also all branches of industry and areas of human activity, including health, economy and social spheres.

In the "Golden Ages" humanity reached such heights that it is very difficult for us to repeat it even with the modern development of technology and science. Our ancestors left us many secrets. These are the mysteries of durable Damascus steel (Figure 1), the composition of paints that allows them to retain their richness and not fade. Many of them are answered by nanotechnology.

Arabs created the technology of damascus steel 1000 years ago. It has now been found that this material holds carbon nanotubes. (Reinbold M., et al. Nature, 444 (2006) 286).

Figure 1. Damascus steel.

Democritus, an ancient Greek philosopher who lived around 400 BC, can be considered the "father" of nanotechnology, because he first used the word "atom" to describe the smallest particle of matter.

In the Middle Ages, artisan potters from the province of Umbria used nanotechnology: they covered ceramic objects with iridescent or metallic glaze (Figure 2). The samples shimmered in the sun, sparkled with a golden sheen, changed their color at different angles. As a result, Italian scientists found that the reason for such paint properties is the presence of tiny metal particles from 5 10^{-9} to 10^{-7} meters in diameter.

Figure 2. Lycurgus Cup

The "Lycurgus Cup" was created by the Romans before 640 BC. It changes color when illuminated from inside the cup. Gold and silver nanoparticles make this effect invisible. Introduction of nanotechnologies requires creation of new approaches to engineering education, adaptation to new ideas.

The prehistoric history of modern nanotechnologies is connected with the centuries-old research of scientists from many countries of the world and has its own long historical trace.

1661 Irish physicist and chemist R. Boyle, one of the founders of the Royal Society of London, expressed the properties of the smallest particles ("corpuscles") in his work "The Skeptical Chemist".

Criticizing Aristotle's view of matter as consisting of four basic principles (earth, fire, water, and air), he argued that all material bodies are composed of very small particles, which are quite stable and form different substances and bodies in different combinations.

Later, the ideas of Democritus and Boyle were accepted by the scientific community.

1857 English physicist M. Faraday, the founder of electromagnetic field theory, first obtained stable colloidal solutions of gold (systems in which the smallest particles of the dispersed phase can move freely and independently of each other). Later, colloidal solutions were widely used to create nanosystems.

1861 English chemist T. Graham divided substances into colloid (amorphous) and crystalloid (crystal).

The first application of nanotechnology can be attributed to the American inventor D. Eastman, the founder of the famous Kodak company, in 1883. A silver halogen emulsion film (for example, cellulose acetate) placed on a transparent elastic base was disintegrated under the influence of light to form pure silver nanoparticles. He prepared the photo film for the first time.

In 1900, the German physicist M. Planck introduced the concept of Planck's constant - considered the starting point for quantum theory, and its rules are important in explaining the properties of nanosystems.

In 1905, the famous physicist A. Einstein, the first scientist who used measurements in nanometers, theoretically proved that the size of a sugar molecule (Figure 3.) is one nanometer (10^{-9} m).

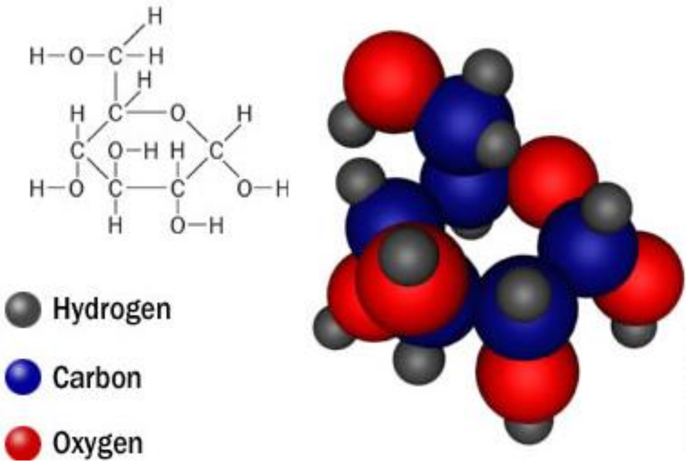


Figure 3. Sugar molecule

In 1924, French physicist Louis de Broglie proposed the idea of wave properties of matter, thereby laying the foundation for quantum mechanics, which studies the behavior of microscopic particles. The laws of quantum mechanics are especially important when creating nanoscale structures.

In 1931, German physicists M. Knoll and E. Ruska created an electron microscope, which became the prototype of a new generation of devices that allowed us to see the world of nano-objects.

1939 Siemens produced the first industrial electron microscope with a resolution of 10 nm. In general, the idea that in the future humanity will be able to create objects by assembling them "atom by atom" goes back to the famous lecture "There's plenty of room at the bottom" by one of the greatest physicists of the 20th century, professor at the California Institute of Technology Richard Feynman published in February 1960, the lecture materials were perceived by most of hiscontemporaries as fiction or a joke. Feynman himself said that in the future, having learned to manipulate individual atoms, humanity will be able to synthesize anything, i.e. use atoms as ordinary building material.

Many promising ideas (carving lines a few atoms wide using electron beams, manipulating individual atoms to create new small structures, creating electrical circuits on a nanometer scale, using nanometer structures) have been implemented today.

In 1974 the term "Nanotechnology" was first used by the Japanese physicist N. Taniguchi (Figure 4) in his lecture "On the Basic Concept of Nanotechnology" at an international conference. This term was used to describe the ultra-fine machining of materials at the nanometer level. The term "nanotechnology" has been proposed to refer to mechanisms smaller than one micrometer in size.

Figure 4. Feynman-Taniguchi-Drexler

In 1981 IBM (International Business Machines Corporation) employees German physicists G. Binning and G. Rorer created a scanning tunneling microscope (1986 Nobel Prize) - the first device that allows not only to obtain a three-dimensional image of a structure, but also to manipulate atoms, it became possible to collect any substance directly from them.

In 1985, a group of scientists consisting of G. Croteau (England), R. Curl, R. Smalley (USA) discovered a new allotropic form of carbon - fullerene and studied its properties (1996 Nobel Prize). The possibility of the presence of carbon molecules with high symmetry in a spherical form was predicted in 1970 by Japanese scientists E. Osawa and Z. Yoshilda.

In 1973, Russian scientists DA Bochvar and EG Halpern proved the stability of such molecules through theoretical quantum chemical calculations.

In 1986, the scanning atomic force microscope was created (authors - G. Binning, K. Kuatt, K. Gerber, IBM employees, 1992 Nobel Prize), which, unlike the scanning tunneling microscope, not only conducts electricity, but also any materials, including the structure of organic molecules, biological objects, etc., made it possible to study. E. Drexler, American futurologist, employee of the artificial intelligence laboratory of the Massachusetts Institute of Technology "Engines of creation: the coming era of nanotechnology"("Engines of Creation: The Coming Era of Nanotechnology")predicted the active development and practical application of nanotechnologies in his book (Figure 5). This prediction was gradually fulfilled.

Figure 5. Eric Drexler - the author of the concept of universal molecular robots.

In 1987 The first single-electron transistor was created by American physicists T. Futon and G. Dolan (Bell Labs).

French physicist J.M. Lehn introduced the concepts of "self-organization" and "self-assembly" that have become fundamental in the design of nano-objects.

In 1988-1989, two independent groups of scientists led by A. Fehr and P. Grunberg discovered the phenomenon of giant magnetoresistance (GMR). Allows data to be recorded on hard disks with atomic information density (Nobel Prize 2007).

In 1989 the first practical achievement of nanotechnology was demonstrated: using a scanning tunneling microscope manufactured by IBM, American researchers D. Eigler, E. Schweitzer placed three letters of the company's logo ("IBM") consisting of 35 xenon atoms on the surface of a nickel single crystal.

In 1990 a team of scientists led by W. Kretschmer (Germany) and D. Huffman (USA) created an effective technology for the synthesis of fullerenes, which helped to intensively study their properties and identify promising areas of their use.

In 1991 japanese physicist S. Iijima discovered a new form of carbon called local clusters - carbon nanotubes, which exhibited unique properties and led to revolutionary changes in materials science and electronics.

In Japan, the creation of techniques for manipulating atoms and molecules is considered a state program, and the project "Atomic Technology" has begun to be implemented.

In 1993, the first nanotechnology laboratory was established in the USA.

In 1994 the first demonstration of a laser based on self-assembled quantum dots (D. Bimberg, Germany) was performed.

In 1998 dutch physicist S. Dekker creates the first nanotransistor based on nanotubes.

Japan launches Astroboy program to develop space-capable nanoelectronics.

In 1999 american scientists M. Reed and D. Tour develop the principles of manipulation of single molecules and their chains. The elementary base of microelectronics overcomes the 100 nm barrier.

In 2000 a major nanotechnology research program called the National Nanotechnology Initiative (National Nanotechnology Initiative) is launched.

The German physicist R. Magerle proposes the technology of nanotomography - a three-dimensional picture of the internal structure of matter with a size of 100 nm is created. This project is financed by Volkswagen.

In 2002 Packard (USA) F. Cukes and S. Williams of the Hewlett Research Center receive a patent for the technology of creating chips based on molecular nanowires.

S. Dekker combines a carbon nanotube with DNA to create a single nanomechanism.

In 2004, the University of Manchester (Great Britain) developed graphene, a promising substitute for silicon in integrated microcircuits with a structure one atom thick (scientists A. Game and K. Novoselov were awarded the Nobel Prize in 2010 for the creation of graphene).

In 2005 Altair Nanotechnologies (USA) announces the creation of a nanobattery.

In 2005, Intel created a prototype processor with a size of about 65 nm. For now, it uses complementary metal-oxide semiconductors, but later it is planned to switch to quantum dots, polymer films and nanotubes.

Eric Winfrey in 2006(Eric Winfree)and Paul WK Rotemund(Paul WK Rothemund)From DNA structures, they created complex two-dimensional figures called DNA origami (Fig. 6).

Figure 6. Eric Winfrey and Paul Rothmund and DNA Origami

In 2006 Northwestern University researchers in the United States developed the first nanostructure "printing machine", a device that can simultaneously produce more than 50,000 nanostructures with atomic precision and the same molecular pattern on the surface, which will be the basis for mass production of nanosystems in the future.

Scientists of the California Institute of Technology (USA) create the first portable biosensor-blood analyzer (lab-on-a-chip portable laboratory).

In 2006, James Tur and colleagues at Rice University created a nanoscale machine made of oligo-(phenyleneethynylene) with alkynyl axes and four spherical C60 fullerene wheels (buckyballs) (Fig.7). Under the influence of temperature increase, the nanomachine moved on the gold surface. As a result, the buckyballs moved like the wheels of a regular car.

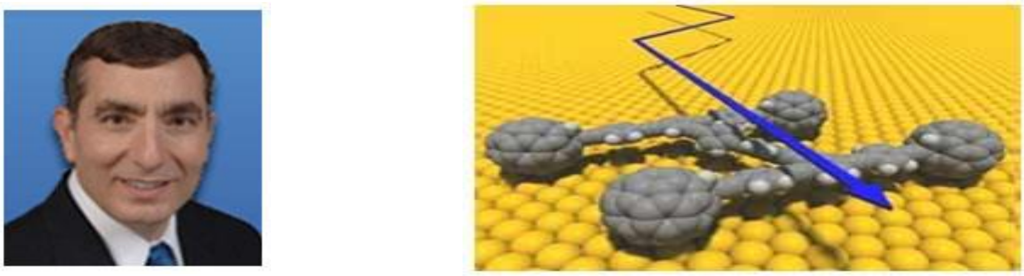


Figure 7. James Tour and the nanoscale machine

Institute of Technology (Georgia, USA) employees develop 12 nm scanning lithography technology.

in 2007. J. Fraser Stoddart synthesized ring molecules that could change their properties under the influence of electric current. In the future, this will allow the creation of molecular muscles.

In 2008, Nobel laureates in chemistry Osamu Shimomura, Martin Chalfie and Roger Y. Tsien isolated fluorescent cells from jellyfish and produced green fluorescent protein from them.(green fluorescent protein – GFP)separated. Green fluorescent protein is the substance that makes jellyfish glow in the dark (Fig. 8).

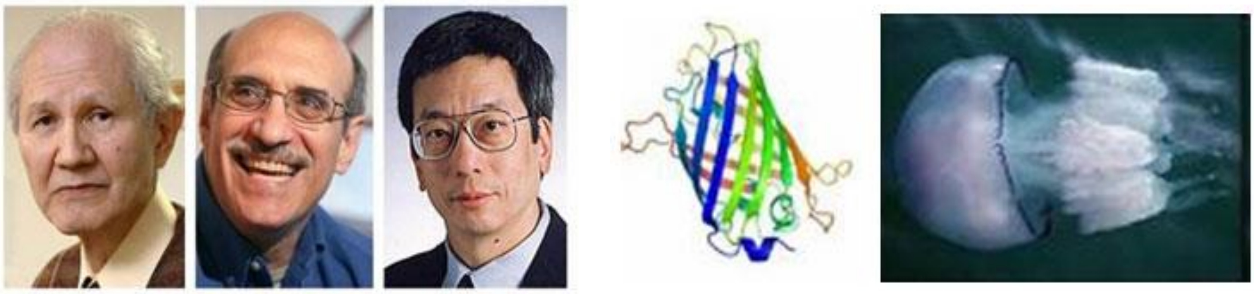


Figure 8. Osamu Shimomura, Martin Chalfie, and Roger Syanya and luminescent cells

In 2009, Japanese scientists Yoshiaki Sugimoto, Masayuki Abe, and Oscar Custans studied the selection and manipulation of individual atoms of silicon, tin, and lead using an AKM probe to build complex molecular structures at room temperature (Fig. 9).

Figure 9. Abbreviation "Si" written on tin with individual silicon atoms by Esiaki Sugimoto, Masayuki Abe, and Oskar Kustanse using an AKM probe

In 2011, German physicist Leonhard Grill used scanning tunneling microscopy (STM) to image the electronic and mechanical properties of individual molecules and polymer chains (Fig. 10).

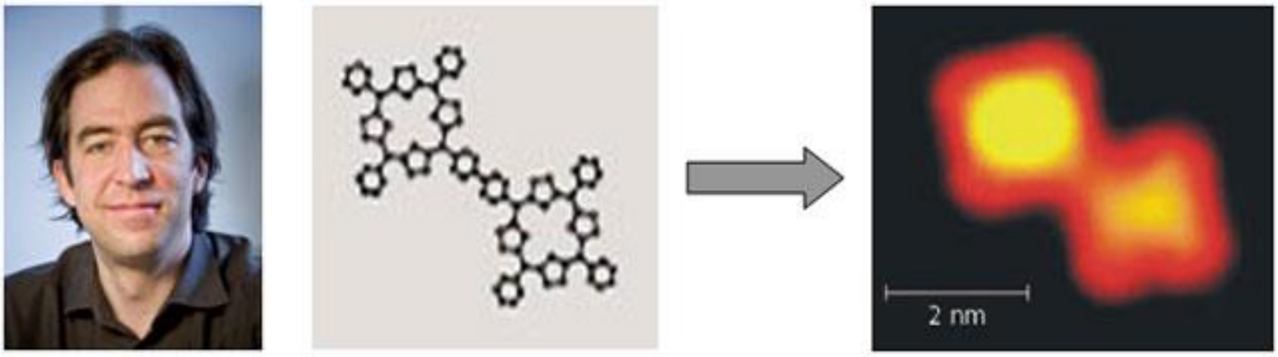


Figure 10. Polymer chain in Leonard Grill and STM

In 2012, German physicists Gerhard Meyer, Leo Gross, and Jascha Repp from IBM Research Zurich obtained images of the distribution of electronic charges in a molecule using a scanning probe microscope. This made it possible to determine the structure of individual molecules in sufficient detail, as well as to close and open individual chemical bonds (Fig. 11).

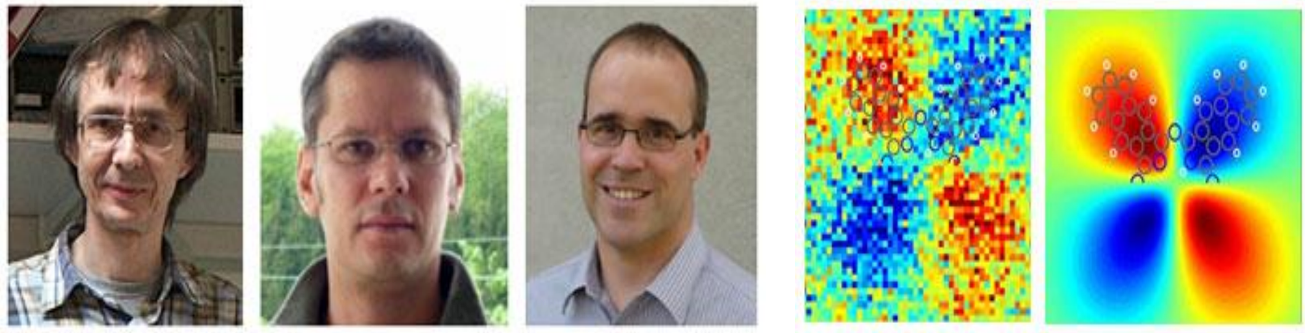


Figure 11. Gerhard Meyer, Leo Gross and Yasha Repp and the electron charge distribution in the naphthalocyanide molecule

The above and other researches, discoveries, inventions give a strong impetus to the use of nanotechnological methods in industry. Rapid development of practical nanotechnology begins. The first commercial nanomaterials appear - nanopowders, nanocoatings, bulk nanomaterials, nanochemical and nanobiological preparations; the first electronic devices, sensors for various purposes based on nanotechnology are created; many methods of obtaining nanomaterials are developed.

Scientists are conducting research in many countries of the world. In the world's leading universities and institutes (USA, Germany, Japan, Russia, England, France, Italy, Switzerland, China, Israel, etc.), nanostructure laboratories and departments have been established under the leadership of famous scientists.

Nanotechnologies are already being used in the most important areas of human activity - radio electronics, information industry, energy, transport, biotechnology, medicine and defense industry.

Today, more than 50 countries of the world are engaged in nano-research.

Lecture 2. General descriptions of methods of obtaining nanosystems

There are two main approaches to the synthesis of nanoparticles: "bottom-up" - from individual atoms and molecules, mainly using chemical reactions; "top down" - mechanical or other crushing of larger particles.

Let's take a closer look at the first approach. All bottom-up methods can be divided into two broad classes: 1) deposition of nanoparticles from the gas phase and 2) formation of nanoparticles in a colloidal solution. If the deposition from the gas phase occurs with a change in the composition of the substance, it is called chemical (CVD - chemical vapor deposition), if there is no chemical reaction during deposition, it is called physical (PVD - physical vapor deposition) (Fig. 16).

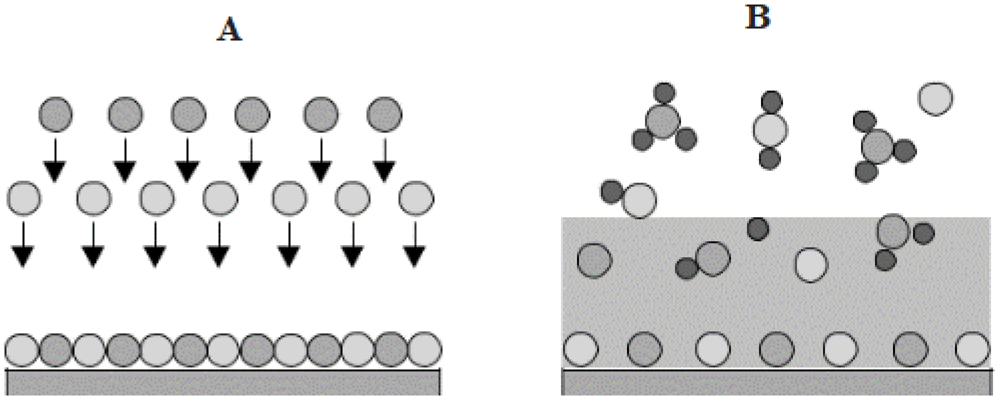


Figure 16. Comparison of physical (a) and chemical (b) deposition

Physical deposition from the gas phase is usually used to obtain nanoparticles of simple substances - mainly metals and some non-metals. For this, the substance is vaporized, the resulting vapor is transferred to the sink and cooled.

The deposition device includes four main elements: a vacuum chamber with a pump; the evaporating surface is the source of the substance; environment - vacuum or plasma containing ions of inert gas; the receiving surface (substrate) is collected on the surface of the nanoparticles.

The deposition process begins with the creation of a high vacuum (10^{-4}-10^{-6} Pa) in the chamber, after which the chamber is filled with an inert gas, often argon. During chemical precipitation, gases reacting with vaporized substance - oxygen, nitrogen, acetylene - are added to the chamber. Then the evaporation process begins. Various methods are used to vaporize the substance - heating with high-intensity pulsed laser radiation (laser ablation1), bombardment of electron beams in a high vacuum, exposure to gas discharge plasma, heating in an electric arc.

After cooling, atoms or molecules of the gas phase are deposited in the form of nanoparticles on a special surface - a substrate (substrate), which can be crystal faces, thin films, etc. The size and shape of the resulting nanoparticles are significantly related. deposition conditions (temperature, pressure, gas flow rate) and substrate properties. This is how metal nanoclusters are obtained - silver, gold, platinum metals, iron, cobalt, as well as metal oxides such as ZnO, TiO2, etc. By changing the deposition conditions, one-dimensional metal threads or more complex nanoassemblies can be obtained.

During chemical deposition, atoms and molecules of substances are adsorbed on the surface of the substrate, they are formed as a result of chemical reactions, which continue at a high temperature - from 600 to 1000 ° C. The reagents used for chemical deposition are called precursors, which are translated from Latin as "pre-emergence" from the synthesized nanoparticles. In a typical experiment, the precursor is vaporized when heated and sent to the reaction zone under the pressure of an inert gas, where it turns into a nanoproduct (Fig.17). Many chemical precipitation reactions require a catalyst that is used as a seed for crystallization.

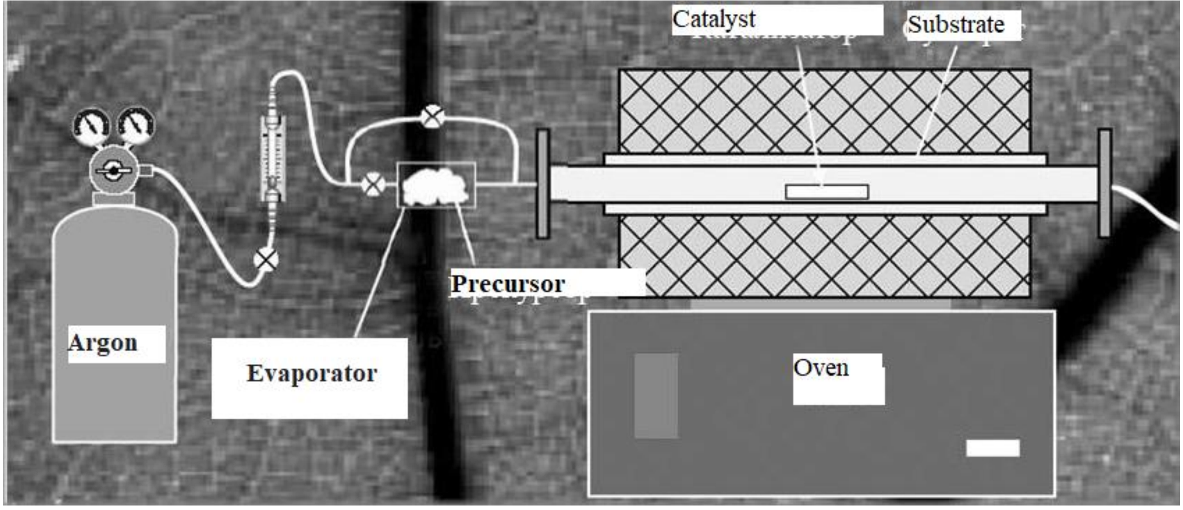
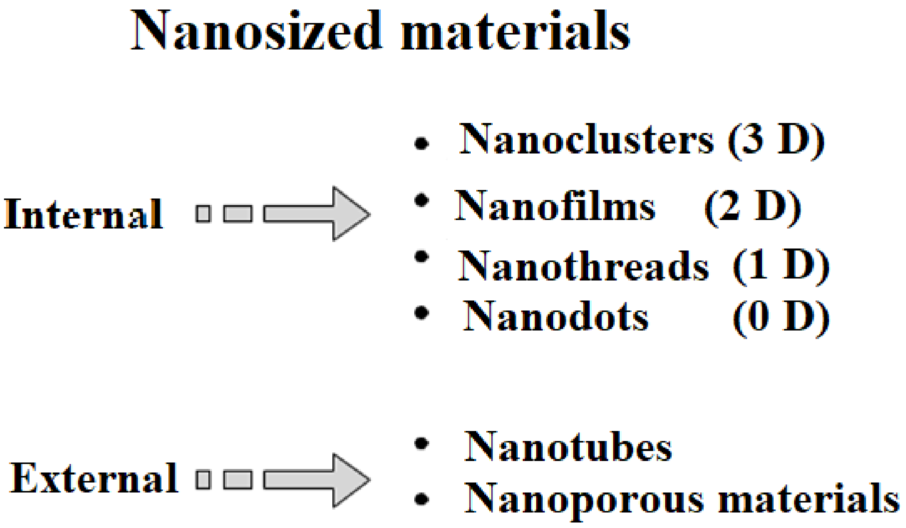


Figure 17. Schematic of the device for chemical deposition of nanoparticles from the gas phase

Lecture 3.Main types of nanosystems

There are different ways to classify nano-objects. According to their simplest, all nano-objects are divided into two large classes - solid ("external") and porous ("internal") (Scheme 1).

Scheme 1. Classification of nanoobjects (from the lecture of Prof. BV Romanovsky)



Solids are classified according to their size: 1) volumetric three-dimensional (3D) structures, which are called nanoclusters (cluster - cluster, cluster); 2) flat two-dimensional (2D) objects -

nanofilms; 3) linear one-dimensional (1D) structures - nanowires or nanowires (nanowires); 4) zero-dimensional (0D) objects - nanodots or quantum dots. Porous structures include nanoporous materials such as nanotubes and amorphous silicates.

This classification does not cover a very important class of nanoparticles - molecular aggregates obtained by supramolecular chemistry methods.

Nanoclusters

One of the most actively studied structures is nanoclusters- consists of metal atoms or relatively simple molecules. Since the characteristics of clusters are highly dependent on their size (size effect), their own classification has been developed for them - according to size (Table 3).

Table 3. Size classification of metal nanoclusters

(from the lecture of Prof. BV Romanovsky)

Number of atoms in a nanocluster	Diameter, nm	% of atoms on the surface	The number of inner layers	Cluster type
1	0.24-0.34	100	0	-
2	0.45-0.60	100	0	-
3–12	0.55-0.80	100	0	Small
13 – 100	0.8-2.0	92-63	1-3	Medium
102-104	2.0-10	63-15	4-18	Large
104-105	10-30	15-2	> 18	Huge
> 106	> 30	< 2	much	Colloidal particle

It turns out that the shape of nanoclusters depends significantly on their size, especially for a small number of atoms. The results of experimental studies combined with theoretical calculations showed that gold nanoclusters with 13 and 14 atoms have a planar structure, with 16 atoms - with a three-dimensional structure, and with 20 - form a face-centered cube. a cell reminiscent of the structure of ordinary gold.

It seems that this structure should be preserved as the number of atoms increases. However, it is not. In the gas phase, a particle consisting of 24 gold atoms has an unusual elongated shape (Fig. 33). Using chemical methods, other molecules can be attached to clusters from the surface, which are able to form more complex structures. It was found that when gold nanoparticles combine with fragments of polystyrene $[-CH_2-CH(C_6H_5)-]n$ or polyethylene oxide $(-CH_2CH_2O-)n$ molecules, when they enter water, they combine polystyrene fragments into cylindrical aggregates similar to colloidal particles. , and some of them reach 1000 nm in length.

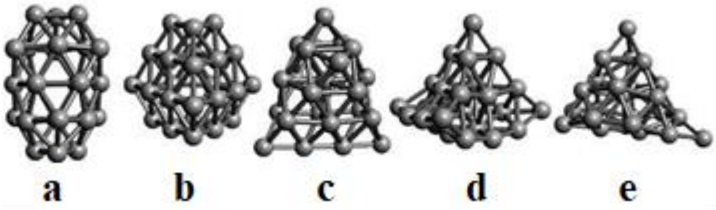


Figure 33. Possible structures of Au_{24} nanoclusters. The most stable of them is a structure.

Scientists suggest that such objects can be used as anti-cancer drugs and catalysts.

Natural polymers such as gelatin or agar-agar are also used as carriers of gold nanoparticles. By treating them with chloroauric acid or its salt, and then with a reducing agent, water-soluble nanopowders with the formation of bright red solutions containing colloidal gold particles are obtained.

Interestingly, nanoclusters are also present in ordinary water. They are agglomerates of individual water molecules connected to each other by hydrogen bonds. Saturated water vapor at room temperature and atmospheric pressure has been calculated to contain 10,000 dimers (H_2O) 2 , 10 cyclic trimers (H_2O) 3 , and one tetramer (H_2O) 4 per 10 million single water molecules.

In liquid water, particles of a much larger molecular weight, formed from several dozen or even hundreds of water molecules, have also been found. Some of them exist in several isomeric modifications, differing in the form and order of connection of individual molecules. In particular, many clusters are found in water at low temperatures, near the melting point. Such water is distinguished by its own characteristics - it has a higher density compared to ice and is better absorbed by plants. This is another example of how the properties of a substance are determined not only by its qualitative or quantitative composition, i.e. chemical formula, but also its structure, including at the nano level.

Among other nanoobjects, nanotubes have been studied the most. This is the name given to long-term cylindrical structures with dimensions of several nanometers. Carbon nanotubes were first discovered in 1951 by Soviet physicists L.V. Radushkevich and V.M. Lukyanovich, but their publication appeared a year later. Interest in them reappeared in the 1990s after the work of foreign researchers.

Recently, scientists have been able to synthesize boron nitride nanotubes, as well as some metals such as gold.

In terms of strength, they are significantly lower than carbon, but due to their much larger diameter, they can contain even relatively large molecules. To obtain gold nanotubes, heating is not necessary - all operations are carried out at room temperature. A colloidal solution of gold with a particle size of 14 nm is passed through a column filled with porous aluminum oxide. In this case, the gold clusters stick to the available holes in the aluminum oxide structure, and combine with each other into nano-tubes.

Examples of one-dimensional nano-objects are nanowires or nanowires - so-called extended nanostructures with a cross section of less than 10 nm. With this order of magnitude, the object begins to exhibit special, quantum properties. Let's compare a copper nanowire 10 cm long and 3.6 nm in diameter with the same wire but 0.5 mm in diameter. The dimensions of an ordinary wire are many times greater than the distance between atoms, so electrons move freely in all directions.

In a nanowire, electrons can only move freely
in one direction - along the wire, but not across, because its diameter is only a few times greater than the distance between atoms. Physicists say that in a nanowire, electrons are localized in the transverse direction and is delocalized in the longitudinal direction.

Carbon nanotubes are hundreds of times stronger than steel, and many of them are good conductors of heat and electricity. Speaking of Damascus knives, we have already mentioned them.

Nanowires

Nanowires of metals (nickel, gold, copper) and semiconductors (silicon), dielectrics (silicon oxide) are known. Under special conditions, the slow interaction of silicon vapor with oxygen can produce silicon oxide nanowires, in which cherry-like spherical silicon derivatives hang like branches. The size of such a "fruit" is only 20 microns (μm).

Molecular nanowires are slightly different from each other, an example of which is the DNA molecule - the storehouse of genetic information. Small amounts of inorganic molecular nanowires are molybdenum sulfides or selenides. A portion of the structure of one of these compounds is shown in Figure 34. Due to the presence of d-electrons in molybdenum atoms and the overlapping of partially filled d-orbitals, this substance conducts electricity.

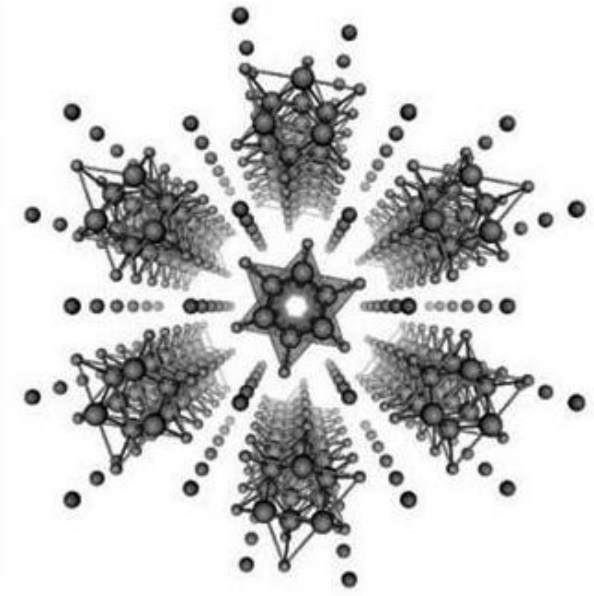


Figure 34. Structure of a molybdenum selenide nanowire composed of seven weakly interacting molecular chains.

Research on nanowires is currently conducted at the laboratory level. However, it is already clear that they will be in demand when creating new generation computers.

Semiconductor nanowires, like normal semiconductors, can be p- or n-type doped. Even now, p-n passing place of unusually small size have been created on the basis of nanowires. Thus, the foundations for the development of nanoelectronics are gradually being created.

The high strength of nanofibers makes it possible to reinforce them with various materials, including polymers, to increase their stiffness. And replacing the traditional carbon anode in lithium-ion batteries with a steel anode covered with silicon nanowires made it possible to increase the power of this current source by an order of magnitude.

Examples of two-dimensional nanoobjects are nanofilms. Due to their very small thickness (only one or two molecules), they transmit light and are invisible. Polymer nanocoatings made of polystyrene and other polymers reliably protect many things used in everyday life - computer screens, cell phone windows, eyeglass lenses.

Lecture 4. Carbon nanomaterials. General properties of carbon nanoforms

Allotropic forms of Carbon are devided to "Nano" and "Non-Nano". Among the wide range of nanomaterials available, we first of all, let's talk about simple substances formed from carbon. Carbon is a unique element: it is the only element that can form long (up to hundreds of thousands of atoms) chains of interconnected atoms - carbon skeletons of organic molecules. This is explained, first of all, by properties of the carbon-carbon bond (Table 4).

Table 4. Homonuclear bond energies (kJ/mol)

Chemical bonds	**C-C**	**N-N**	**O-O**	**Si-Si**	**P-P**	**S-S**
Bond energy	348	163	146	226	201	264

as shown above, carbon atoms form the strongest mutual bonds compared to other elements. Therefore, carbon chains are more stable than chains made of atoms of other elements. Due to the special strength of C-C bonds, the carbon skeleton of molecules remains unchanged in most chemical reactions.

In addition, carbon atoms can form different types of bonds with each other: single, double and triple, each of which corresponds to the hybrid state of the carbon atom. The bond energy between atoms increases significantly with increasing (Table 5).

Table 5.Carbon-carbon bond energy (kJ/mol)

Chemical bond	C-C	C=C	C≡C
Bond energy	348	612	838
Hybrid state of the carbon atom	sp^3	sp^2	sp

It is the variety of carbon skeletons and the types of chemical bonds between carbon atoms that explain the many allotropic forms of carbon known to date. Two of them - diamond and graphite - have been known to mankind since ancient times, and their molecular form (fullerenes) and "nanoforms" (nanodiamonds and nanotubes) were discovered several decades ago.

There are only two stable allotropic forms of carbon - graphite and diamond. This is confirmed by the state diagram of carbon, which shows the regions of existence of thermodynamically stable states of the substance in "pT" coordinates (Fig. 35.).

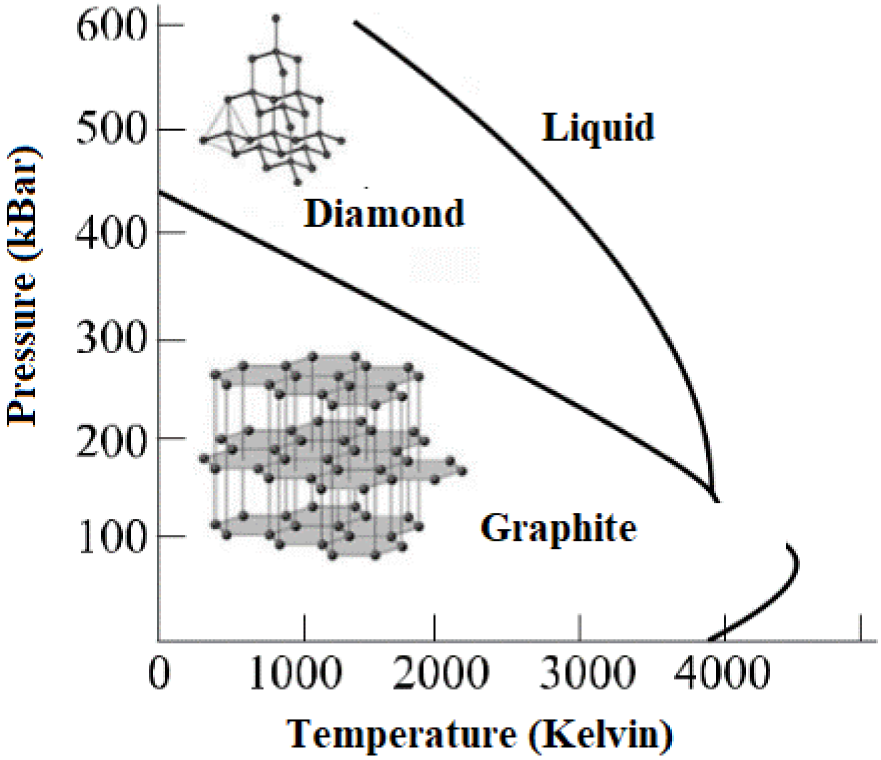


Figure 35. The state diagram of carbon

The diagram shows that graphite is the most stable form of carbon under normal conditions. It is he, according to the basic postulate of thermodynamics, that sooner or later all other forms, including the diamond, must rotate. However, the speed of such changes is so low that, in practice, it does not happen within a reasonable time. In order to obtain a diamond, it is necessary to create extreme conditions, first of all, high pressure - several hundred thousand atmospheres.

We also see that there are no fullerenes or nanotubes in the phase diagram. All of these are non-equilibrium or thermodynamically disproportional.

In no case can they be more stable than graphite or diamond.

Nanodiamonds

Of all the "nanoforms" of carbon, nanodiamonds are the closest to the natural state of carbon. Recall that ordinary diamond forms a very strong atomic crystal lattice, in which each carbon atom is in an sp3-hybrid state and is connected by single bonds to four neighbors located at the ends of the tetrahedron. All valence electrons of carbon atoms participate in the formation of bonds in diamond, so it does not conduct electricity and is a dielectric. The typical size of artificial diamond crystals obtained from graphite under high pressure and temperature is one to hundreds of micrometers (microns). Nanodiamonds have the same crystal structure as ordinary diamonds, but their crystals are much smaller in size: from 2 to 8 nm. Therefore, most of the carbon atoms are on the surface, and the properties of the atoms differ in size. . Indeed, the surface atoms have free valence and can stick together to form 5- and 6-membered rings.

Quantum chemical calculations of a 275-atom diamond particle (Figure 36 a) showed that these rings are interconnected as in the C60 fullerene structure, which we will discuss later. Thus, at room temperature, a diamond nanoparticle has a "diamond" core and a "fullerene" surface (Figure 36 b).

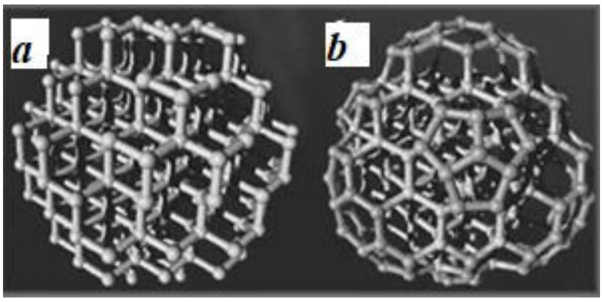


Figure 36. Bulk structure of diamond (a); diamond with nanoparticle fullerene-like surface (b).

A large number of bonds on the surface of nanodiamonds makes it very active, and therefore the reactivity of diamond nanocrystals is much higher than that of crystals of normal size. Ordinary diamond turns into graphite when heated to 1800 ° C in an inert atmosphere, and nanodiamond - only up to 1000 ° C. Normal diamond oxidizes in air only at temperatures above 900 ° C, while nanodiamond oxidizes at 450 ° C.

Particle size affects not only chemical, but also thermodynamic properties of diamond. Therefore, ordinary diamond is an endothermic substance at room temperature, because. the reaction heat of its formation from graphite is negative (Table 6).

In contrast, diamond with a particle diameter of 5 nm is an exothermic substance.

Table 6. Heats of formation of diamond and nanodiamond

The type of diamond	**Q_{form}(298 K), kDj/mol**	**ΔH (298 K), kDj/mol**
An ordinary diamond	-1.8	+1.8
nanodiamond (5 nm)	+4.0	-4.0

Carbon atoms located on the surface, unlike the main atoms, have a free valency and can attach atoms of other elements. The presence of active groups of atoms facilitates the chemical modification of the surface and makes it possible to control the properties of nanodiamonds. In all other aspects, nanodiamonds have the properties of ordinary diamonds, in particular, very high hardness and chemical inertness.

Nanodiamonds are mainly obtained by detonation synthesis - a method invented in the Soviet Union even before the advent of nanotechnology.

In the explosion of trotilwa hexane mixture, if there is no oxygen at the epicenter of the explosion, a temperature of more than 3000 ° C and a pressure of more than 200 thousand atmospheres are created. Under these conditions, the more stable form of carbon is not graphite, but diamond, so the carbon formed during the decomposition of organic matter turns into a very fine powder consisting of a mixture of approximately equal amounts of diamond and graphite.

The reaction time is only 100-500 nanoseconds - large diamond crystals do not have time to form in such a short time, so most crystals are nanoparticles. To remove graphite, the resulting mixture is heated to 250 ° C with a mixture of concentrated nitric and sulfuric acids. Oxidizing acids dissolve graphite but do not affect diamond. The purity of the obtained nanodiamonds reaches 99.5% (Fig.37).

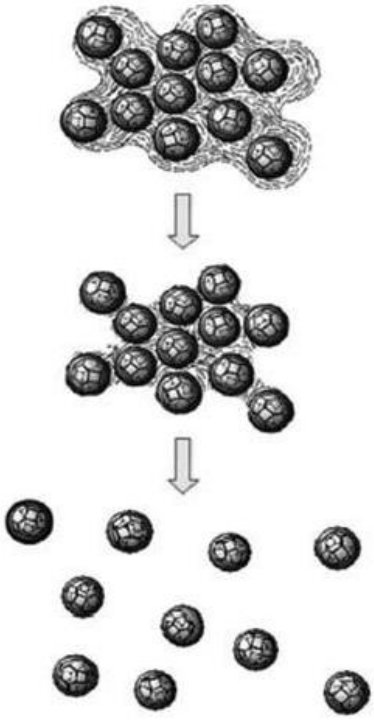


Figure 37. Isolation of diamond nanocrystals from the mixture formed during the explosion

Detonation nanodiamond - black-gray very fine powder with a grain size of 20-50 nm. Each grain consists of several dozen crystals with an almost perfect spherical shape. Interestingly, the diameter of the crystals is almost independent of the detonation conditions and is always between 2 and 8 nm.

Another method of obtaining nanodiamonds is chemical vapor deposition (CVD).

Diamond is deposited on a solid surface (substrate) as a result of chemical reactions with gaseous substances. Usually, hydrocarbons - methane and acetylene - or more complex organic compounds, for example, the decomposition of $C_{10}H_{16}O$ camphor when heated to 600-800 ° C, are used. During chemical deposition on the surface of the substrate, thin diamond films of different thicknesses are obtained. Silicone is usually used as a pad. Let's turn to practical applications of nanodiamonds. The most obvious of them is related to the mechanical properties of this material. Paste-shaped nanodiamonds are used as abrasives for ultra-fine polishing of surfaces, which can be used to obtain a mirror surface of solids of any geometric shape without defects. Because of their small size, nanodiamonds are easy to use as additives to other materials. The creation of composite materials from nanodiamonds with metals makes it possible to significantly increase the hardness of metal coatings and their resistance to corrosion.Incorporating nanodiamonds into polymers, rubber, and plastics also increases their strength, operating temperature range, and service life. The almost spherical shape of nanodiamond crystals allows them to be used in lubricating oils.

Another application of nanodiamonds is based on their surface activity. Nanodiamonds have a high specific surface, their chemical nature can be changed by introducing different functional groups. In addition, diamond nanoparticles have been proven to have biocompatibility and low toxicity.

All this allows them to be used in biology and medicine. Thus, in biology, nanodiamonds are already used as sorbents for the separation and purification of proteins by chromatography. In medicine, they can be used as adsorbents to remove unwanted and toxic compounds from the body (metabolic products, heavy metals, radionuclides), as well as carriers of drugs used for medicinal purposes (drugs, enzymes, isotopes, etc.). Currently, intensive research is being conducted on animals.

Lecture 5. Carbon nanotubes.

Another allotropic modification of carbon is close in structure to fullerenes -nanotubes. To visualize their structure, let's turn to the most stable form of carbon - graphite. Its crystal lattice consists of individual planar layers made up of regular hexagonal corners. Each carbon atom in the layer is in an sp2-hybrid state, bonded to three neighboring atoms; the angle between the bonds is 120 °. 3 of the 4 valence electrons of each atom participate in the formation of bonds within the layer. The electron clouds of the remaining electrons slightly overlap each other and connect the individual layers to each other. Bonds between layers are much weaker than bonds within layers.

A planar two-dimensional layer of regular hexagonal carbon atoms is called graphene. In 2004, a group of scientists from England and Russia managed to separate such a layer from a single crystal of graphite and place it in the form of a film on the surface of a silicon substrate. The layer turned out to be uneven - it had a wavy structure (Fig. 45), which confirmed the assumptions of scientists about the instability of two-dimensional crystals. If several layers of graphene are placed on top of each other, then the surface will be flat.

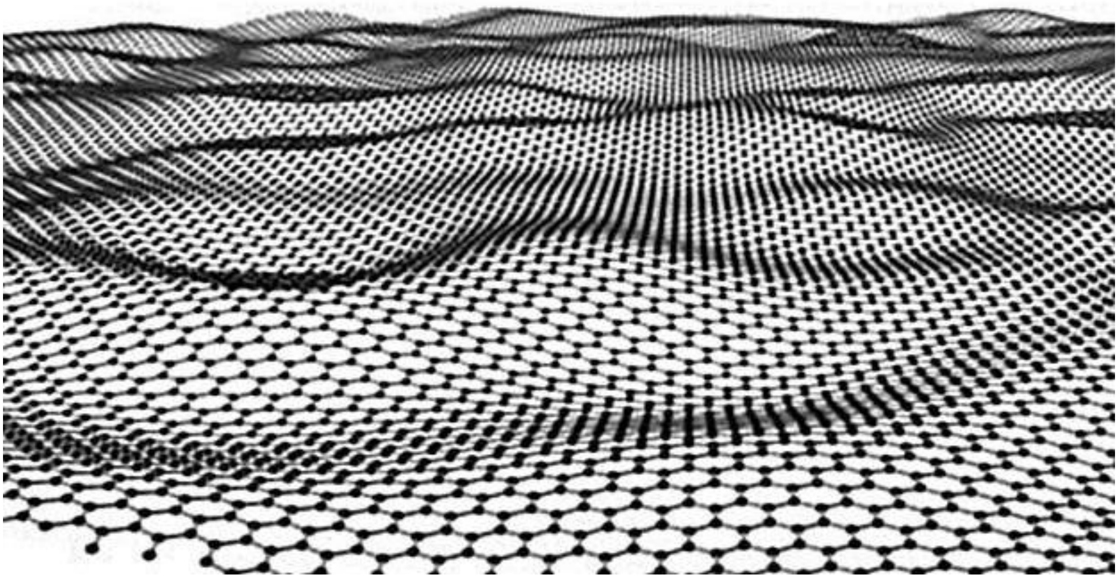


Figure 45. Graphene monolayer structure

If a rectangle is cut from a graphene layer and its opposite edges are connected, a hollow cylinder is obtained (Fig.46). Objects of this shape are called single-walled or single-walled carbon nanotubes.

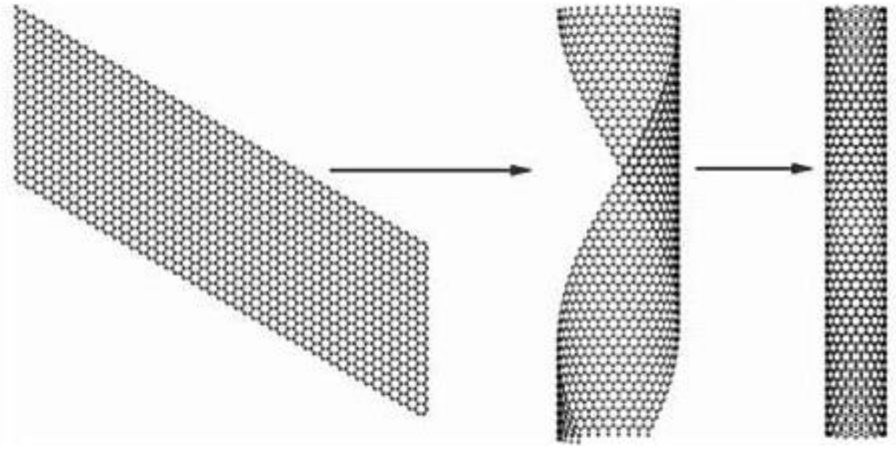


Figure 46. Formation of a single-walled tube when wrapping a graphene layer

Typical tubes have a diameter of several nanometers and a length of one to several micrometers, which allows them to be considered one-dimensional structures. Tubes can be nested inside each other like dolls called multi-walled or multi-layered (Fig. 47).

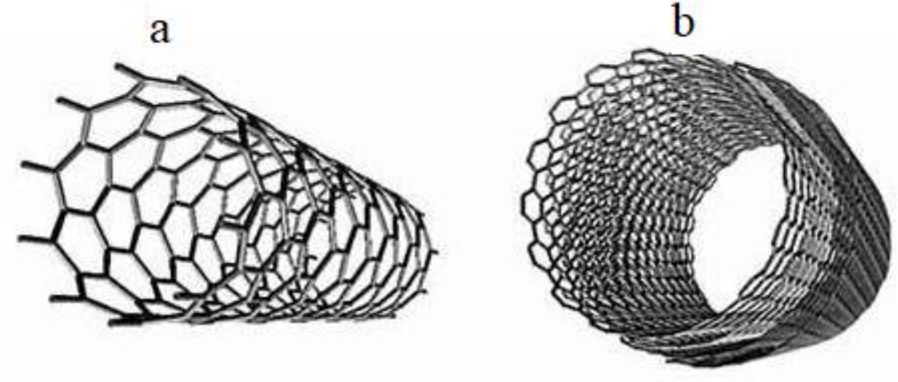


Figure 47. Single-walled (a) and multi-walled (b) carbon nanotubes

Nanotubes were discovered by accident, not as a result of targeted scientific research. In 1991, Japanese scientist Sijima vaporized graphite in an electric arc and obtained a deposit consisting of microscopic filaments and fibers on the cathode. Examination of the deposit using an electron microscope showed that the diameter of the filaments reaches several nanometers, and the length reaches micrometers. These were the first nanotubes. They contained different numbers of graphene layers and were multi-walled. And two years later, Ijima proposed a method of obtaining single-walled nanotubes.

Note that the first method of obtaining nanotubes is very similar to the method of fullerene synthesis. It can be assumed that if G. Kroto predicted to see the soot formed on the walls of the chamber with an electron microscope in 1985, he would have discovered nanotubes almost 6 years before the Japanese scientist.

Currently, three main methods of obtaining nanotubes are used.

1. Catalyst additives - the electric arc method with graphite electrodes containing iron or nickel allows:

mo fullerenes, to obtain a mixture of single- and multi-walled nanotubes with low yields.

2. In chemical vapor deposition, methane or ethanol vapor passes through a substrate heated to 600-800 °C, which decomposes into simple substances. One of the products of the reaction is deposited on the surface of the carbon substrate, forming nanotubes. This method makes it

possible to obtain multi-wall pipes with a high yield, but at the same time with a high concentration of defects.

3. The most modern method is based on laser vaporization of graphite catalysts. With its help, the most valuable single-walled nanotubes are obtained, and their characteristics - length and diameter - can be controlled by changing the type of catalyst, changing the temperature or adjusting the parameters of laser radiation.

True, the laser method is also the most expensive. Single-walled nanotubes are distinguished not only by their length and diameter, but also by another property called chirality. This feature is related to how the opening of the nanotube looks like in the plane of graphene (Figure 48.).

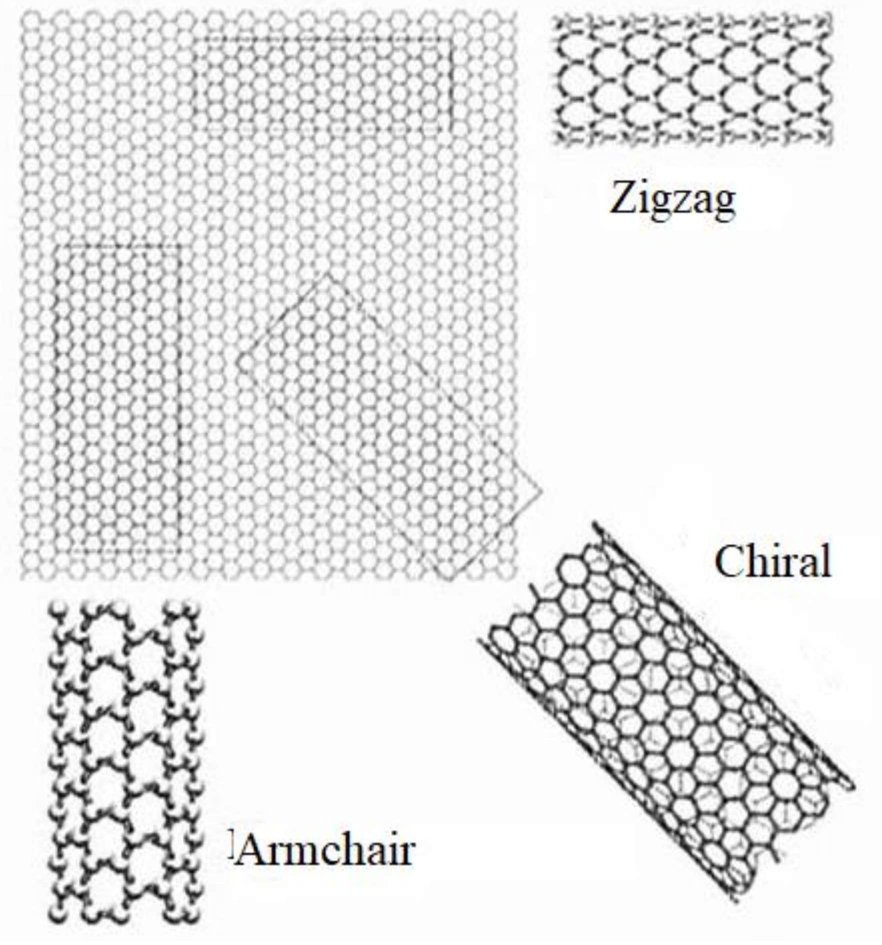


Figure 48. Propagation of nanotubes in the plane of graphene

To quantitatively classify the single-walled tubes in the hexagonal graphene lattice, vectors a1 and a2 are introduced into the hexagonal graphene lattice, as shown in Figure 49. Then AOBBR considers the rectangular distribution of tubes and presents the vector Ch as a linear combination connecting the opposite edges of the rectangle:

$$C_h = n\, a_1 + m\, a_2$$

The vector C_h is called chiral, it defines the diameter of the tubes, and the vector T perpendicular to it is translational, it defines the length of the tube. The set of numbers (n, m) is a characteristic of a nanotube.

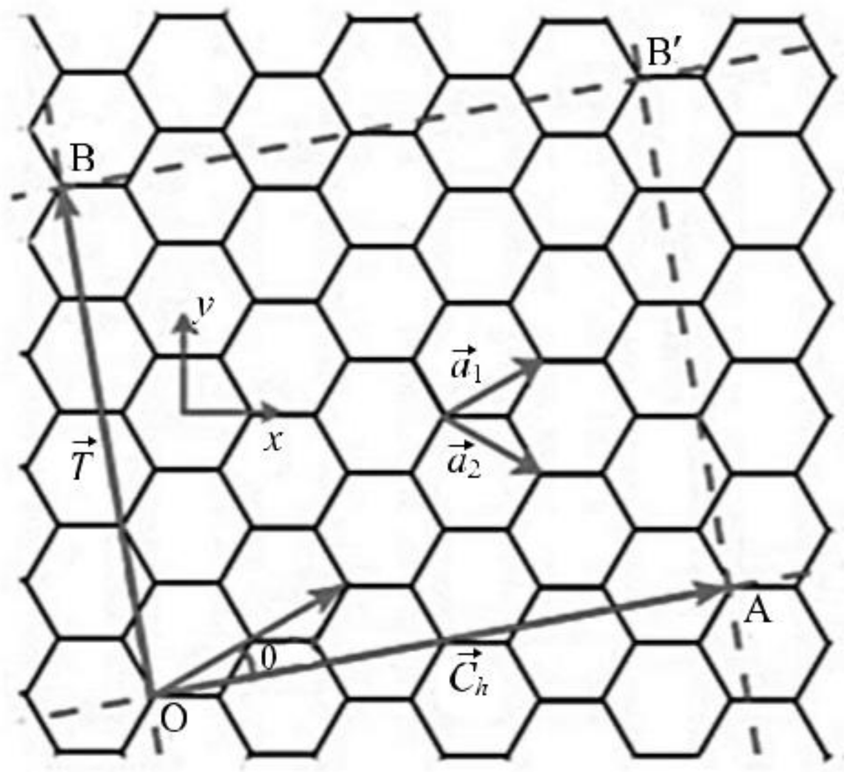


Figure 49. Quantitatively classify the single-walled tubes in the hexagonal graphene lattice

Ideal single-walled nanotubes have only regular hexagonal carbon atoms on their surface. Such nanotubes are cylinders with both ends open. They can be closed on one or both sides with a new type of fullerene or other surface hemispheres, but such tubes will no longer exist. Ideal - in addition to regular hexagons, they have pentagons or triangles on their surface (Fig. 50).

Figure 50. Closed nanotubes

Contains five-membered cycles. What properties make nanotubes a promising target for future nanotechnologies? Firstly, they have very high mechanical strength - single-walled pipes are several times stronger than most steel. Needless to say, nanotubes are not the first graphite-based carbon material. Common carbon fibers formed from long and thin sheets of graphite. Combining low density and high strength, they are widely used in the production of modern tennis rackets, bicycles, racing cars, etc.

However, nanotubes are the strongest carbon fibers. Unlike carbon fiber, nanotubes are not brittle. Therefore, they are used as fillers for polymer composites. The inclusion of carbon nanotubes in the composition of the composite increases the thermal and electrical conductivity of the material, significantly improves its mechanical properties, gives the composition certain functional properties (removal of static charges, scattering and absorption of radio emission, scattering and absorption of laser radiation, enhancement of electroluminescence).

The electrical properties of nanotubes are very interesting. Recall that graphite conducts electricity, its properties are between semiconductors and metals. On the other hand, nanotubes can exhibit both metallic and semiconducting properties depending on their structure, particularly the ratio of n and m indices.

Single-walled tubes have metallic conductivity if (n - m) is divisible by 3, otherwise the tube has a band gap of 0.1 to 0.3 eV is a semiconductor. The current is carried by the majority of nanotubes, that is: all the tubes of the "armchair" type and every third tube (n, m) of any family defined in m.

Like nanodiamonds, nanotubes have a high specific surface area (from 100 to 1000 m^2/g) and are good adsorbents. The presence of holes in the tubes allows them to be used to store gaseous substances or as capsules for active molecules.

Like fullerene, the surface of the nanotubes can be chemically modified to make them soluble. Nanotubes can form supramolecular complexes with biologically active molecules - proteins, polysaccharides, nucleic acids.

These substances can be adsorbed on the surface of the tubes or combined with them through covalent bonds, which allows the use of nanotubes in drug, gene and antigen delivery systems.

Due to their high specific surface area, nanotubes can be used as supports for heterogeneous catalysts. A new-generation miniature hydrogen-oxygen current source for portable devices has been created, in which nanotubes in the form of aggregates about 100 nm in size are part of the electrodes, which act as a substrate for the catalyst.

Nanotubes have at least two advantages over conventional electrodes: first, the reactant gases are hydrogen.

and oxygen - easily penetrate the electrode, and secondly, the catalyst - finely dispersed platinum - is applied to the surface of the tubes. Polyelectrolyte is used as a conductive medium. The energy capacity of the new source is 10 times higher than that of lithium batteries. This allows, for example, to ensure the continuous operation of a laptop for several days. New current sources are miniature, they provide great power, they charge much faster in batteries.

They also have disadvantages: due to the high reactivity of nanoparticles, they can irreversibly react with electrolytes and destroy their structure.

The unique electronic properties of nanotubes are used in diodes, transistors, electronic weapons, and probe microscopes. Because of the mechanical strength of nanotubes, they are used in composite materials, which can be used to produce ultra-light and super-strong fabrics for firefighter and astronaut clothing. Nanotubes are one of the important components of electromechanical nanodevices. It is not easy to list all the possible applications of nanotubes - many of them already exist. Now the main task of researchers is to create technologies that allow to obtain single nanotubes of a given size and shape.

Lecture 6. Types of nanocomposites

It is impossible to determine the properties of CM only by their characteristics, without taking into account the interaction of components.

CM is of two types: 1) hardened; 2) sometimes has special physical properties that are not found in natural materials.

Depending on the type of reinforcement component, composites can be divided into 3 main groups: dispersion-hardened (DHM), fiber-hardened (FHM) and eutectic (ECM), which differ in structure, high strength formation mechanism, anisotropy, etc.

Matrix materials can be metals and their alloys, organic and inorganic substances, polymers, ceramics and other substances (carbon, wax). Sometimes the matrix consists of not one, but two dissimilar materials, and is called a polymatrix CM. Reinforcing or reinforcing components are often fine powder particles or fibrous materials of various breeds.

The directional nature of CM properties naturally suggests that along with high mechanical properties in some directions, they have low properties in others.

The most important advantage of composites is the ability to create structural elements from them with predetermined properties that are fully compatible with nature and working conditions. The variety of fibers and matrix materials used in the creation of composites, as well as reinforcement schemes, allows for targeted control of strength, stiffness, working temperature and other properties by changing the composition, ratio and microstructure of the components. composites.

Fiber reinforcement (Fig.57) makes it possible to apply new principles of product design and production, based on the fact that the material and the product are created simultaneously within the same technological process.

As a result of combining the reinforcing elements and the matrix, a set of composite properties is formed, which not only reflects the initial properties of its components, but also includes properties that the isolated components do not have. In particular, the emergence of a number of new properties in composites is related to the heterogeneous structure, which determines the existence of a large boundary separation between the fibers and the matrix. Thus, the presence of a phase boundary significantly affects the fracture toughness of the material

increases.

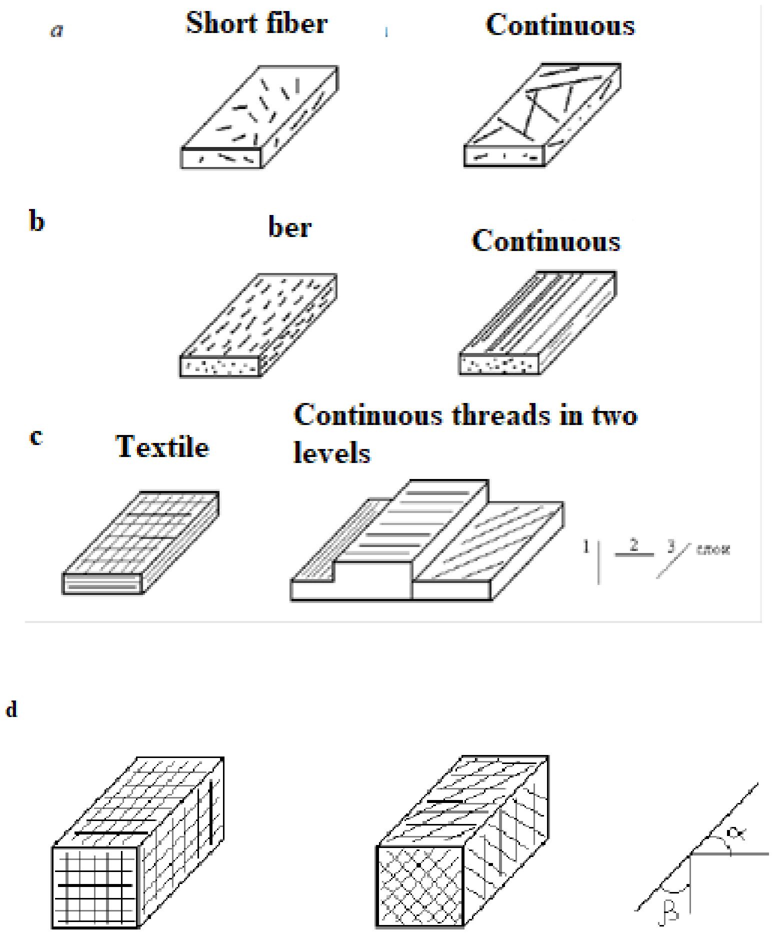


Figure 57. Classification of composites on a structural basis:

a - chaotic strengthening; b - one-dimensional reinforcement; c - two-dimensional reinforcement; d - spatially reinforced structures (SRS)

The resistance of any solid body to crack propagation is determined by the energy absorption mechanism at the tip of the growing crack.

In composites, transverse tensile stresses at the tip of a growing crack can cause fibers to separate from the matrix, and shear stresses at the boundary can cause delamination to propagate along the fibers. During peeling, energy is expended because the fibers must move relative to the matrix. Also, under additional loading, fibers may break in the matrix away from the crack plane. Therefore, reinforced materials are characterized by such mechanisms to increase the fracture toughness that homogeneous materials do not have.

Matrix materials. In composites, the matrix is an important element, which: 1)ensures the monolithicity of the composite; 2) determines the form of the product; 3)**the relative position of the reinforcing fibers** records; 4) distributes the applied stress over the volume of the material, provides a uniform pressure to the fibers and redistributes it if part of the fibers is destroyed; 5)**the method of manufacturing composite products** determines; 6)**the possibility of carrying out the design of the given dimensions** defines; 7) determines parameters of technological processes, etc.

Thus, matrix requirements can be divided into operational and technological requirements.

Operational requirements. These include requirements related to the mechanical and physicochemical properties of the matrix material. They ensure the performance of the composition under the influence of various operational factors.

1. The mechanical properties of the matrix must ensure the joint operation of the reinforcing fibers or particles under various types of loads.
2. The strength characteristics of the matrix material are crucial in shear loads, in loading the composite in directions different from the direction of the fibers, as well as in cyclic loading.
3. The nature of the matrix determines the level of working temperatures of the composite, the nature of changes in properties under the influence of the atmosphere and other factors. As the temperature increases, the strength and other properties of the matrix materials, as well as their bonding strength with many types of fibers, decrease. The matrix material also characterizes the resistance of the composite to the external environment, chemical resistance, partly thermal, electrical and other properties.

Technological requirements. Usually, the composition and the product from it happen at the same timeIt is determined by the processes that take place, that is, the processes of combining the reinforcing fibers with the matrix and the final formation of the product. The purpose of technological operations:

1) ensuring uniform distribution of fibers in the matrix of a certain volume (without touching each other);
2) maximum preservation of fiber strength properties;
3) to create a strong enough interaction at the fiber-matrix boundary separation.

Thus, the following requirements are imposed on the matrix material:

1) good wetting of fiber;
2) the possibility of preliminary preparation of semi-finished products (for example, prepregs) with subsequent production of products from them;
3) high-quality connection of multi-layer composites during molding;

4) low values of forming parameters (for example, temperature, pressure, etc.).

The following matrix materials are used for casting: Al, Cu, Fe, Mg, Ni, etc., as well as industrial alloys based on themis also used.

A composite material is a material consisting of two or more components that differ in nature or chemical composition.

Components in CM are combined into a monolithic single structure with separation at the boundary between structural components (components), their optimal combination allows obtaining a set of physico-chemical and mechanical properties that differ from the set of properties of the components.

The component that is continuous throughout the entire volume of the composite material is called the matrix.

A continuous, matrix-separated component or components is called a reinforcing or reinforcing component, or sometimes a filler. The concept of "improvement" means "introduced to the material to change its properties", but does not include the specific concept of "reinforcement".

Composite materials are classified according to several main characteristics:

- matrix material and reinforcing components;
- structure: geometry (morphology) and arrangement of components (structural components);
- method of obtaining;
- Areas of use

Composite materials are classified according to the geometry of the filler, its location in the matrix, and the nature of the constituents.

According to the geometry of the filler, composite materials are divided into three groups:

- with zero-dimensional fillers of the same order of magnitude in three dimensions;
- with a one-dimensional filler, one of their dimensions is significantly larger than the other two;
- with a two-dimensional complement, two dimensions of which are significantly larger than the third.

According to the location of fillers, three groups of composite materials are distinguished:

- with a uniaxial (linear) arrangement of the filler in the form of fibers, threads, threads in a matrix parallel to each other;
- reinforcing filler in the matrix in parallel planes, thread mats, with biaxial (plane) location of the film;
- with the triaxial (volumetric) location of the reinforcing filler and the absence of a preferential direction in its placement.

According to the nature of the components, composite materials are divided into four groups:

- composite materials containing a component of metals or alloys;
- composite materials containing a component of inorganic compounds of oxides, carbides, nitrides, etc.;
- composite materials containing non-metallic elements, carbon, boron, etc.;
- composite materials containing the component of organic compounds of epoxy, polyester, phenol, etc.

The properties of composite materials depend not only on the physical and chemical properties of the components, but also on the strength of the bond between them. Maximum strength is achieved if solid solutions or chemical bonds form between the matrix and the reinforcement.

A metal matrix is most commonly used in composite materials with zero filler. Metal-based compositions are reinforced with uniformly distributed dispersed particles of different fineness. Such materials are characterized by isotropic properties.

In such materials, the matrix perceives the entire load, and the dispersed particles of the filler prevent the development of plastic deformation. Effective hardening is achieved with a content of 5-10% filler particles.

In composite materials with one-dimensional fillers, reinforcements are one-dimensional elements in the form of thread crystals, fibers, wires connected to a single monolith by a matrix. It is important that the resistant fibers are evenly distributed in the plastic matrix. Continuous discrete fibers with cross-sectional dimensions from lobes to hundreds of micrometers are used to strengthen composite materials.

Thread-reinforced materials were developed in the early 1970s for aerospace structures. The main way to grow threads is to grow them from supersaturated steam (BK process). To produce especially high-strength threads of oxides and other compounds, the growth is carried out according to the BSK (vapor-liquid-crystal) mechanism: the oriented growth of crystals occurs from the vapor state through the intermediate liquid phase.

Threaded crystals are formed by pulling liquid through spinners. The strength of the crystals depends on the smoothness of the cross-section and surface.

Composite materials of this type are promising as materials resistant to high temperatures. To increase the efficiency of heat engines, gas turbine blades are made of nickel alloys reinforced with sapphire threads (Al2O3), which allows to significantly increase the temperature at the turbine inlet (tensile strength of sapphire crystals at a temperature of 1680 °). C above 700 MPa).

Reinforced filaments of aluminum oxide (Al2O3) are obtained by pressing and sintering aluminum powder (SAP (sintered aluminum powder)). The advantages of SAP appear at temperatures above 300 ° C, when aluminum alloys are softened. Dispersion hardened alloys retain the hardening effect up to 0.8 Liquid temperature.

SAP alloys are satisfactorily deformed, easily processed by cutting, welded by argon-rope and contact welding. Semi-finished products are produced from SAP in the form of sheets, profiles, pipes, foils. Compressors, fans and turbine blades, piston rods are made from them.

Dispersed particles of refractory phases such as Al2O3, SiO2, BN, SiC have low density and high modulus of elasticity. CM is usually produced by powder metallurgy, an important advantage of which is the isotropy of properties in different directions.

SAP grades used in Russia contain 6-23% Al2O3. As the volume concentration of aluminum oxide increases, the strength of composite materials increases.

Rocket nozzles were reinforced with sapphire crystals from tungsten and molybdenum powders, both in the form of caps and individual fibers, as a result of which it was possible to double the strength of the material at a temperature of 1650^{o}C. Reinforcement of fiberglass absorbent polymer with filament fibers increases their strength. Reinforcement of cast metal reduces its brittleness in structures. It is promising to strengthen the window with non-directional threads.

To strengthen composite materials, metal wire of various metals is used: steel, tungsten, niobium, titanium, magnesium of various compositions - depending on the working conditions. Steel wire is processed into woven meshes used to produce composite materials with reinforcement in two directions.

Boron fibers and silicon carbide are used to strengthen light metals. Carbon fibers have particularly valuable properties, they are used to strengthen metal, ceramic and polymer composite materials.

Eutectic composite materials are alloys with a eutectic or near-eutectic composition in which the oriented crystals formed during the oriented crystallization process act as a strengthening phase. Unlike traditional composite materials, eutectic materials are obtained in a single operation. Directional structure can already be obtained in ready-made products. The shape of the obtained crystals can be in the form of fibers or plates. Directional crystallization methods produce composite materials based on aluminum, magnesium, copper, cobalt, titanium, niobium and other elements, so they are used in a wide temperature range.

Classification of CM by matrix and reinforcing component materials. The characteristics of CMs in terms of matrix material and reinforcing components indicate their physical and chemical nature. According to the material of the matrix, there are:

1) Metal CM or composite materials based on metals and alloys. The most commonly used aluminum, magnesium, titanium, copper and alloys based on them.

2) CM based on intermetallic compounds, when chemical compounds of metals with metals are used as a matrix. This is a relatively new class of CM, in which heat-resistant intermetallic compounds Ti_3Al, TiAl, NiAl, Ni_3Al, etc. are used as the matrix material.

3) Ceramic CM. As the matrix of these materials, inorganic compounds of oxides, carbides, nitrides, etc. are used. This is a new class of CM, which has a perspective as a class of superheat-resistant materials.

4) CM based on non-metallic components. First of all, these are carbon-based CMs, which are considered one of the most promising structural materials, especially in combination with carbon fibers.

5) CM with polymer matrix. Epoxy, polyester and some other thermosetting resins, as well as polymer thermoplastics, are the most common group of structural composites.

Solid fillers are usually used as reinforcing components (fillers) of polymer composite materials (PCM): continuous and discrete fibers of various nature, fabrics and non-woven materials based on these fibers. The most common are plastics reinforced with glass, carbon, organic, boron and some other types of fibers.

Reinforcing components or fillers mainly determine the properties of CM. Currently, the strengthening components are:

- metals and alloys (steel, beryllium, titanium tungsten, etc.);
- non-metals such as carbon and boron;
- ceramics $A1_2O_3$, SiC, TiB_2, TiC, AlN, etc.;
- glasses, for example, glass E and glass S;
- organic substances, for example, lavsan, kevlar, polyethylene, etc.

Classification of composite materials by structure: geometry and arrangement of structural components. The classification of CM according to the geometry of the components remains somewhat controversial, since it is closely related to the classification based on the structure and location of the components and often does not distinguish between them.

According to this classification, CMs belong to one of the following classes:

- dispersion-reinforced composites and particle-reinforced composites;
- fibrous compositions;
- layered composite materials.

Taking into account the size and distribution of secondary stages or reinforcing components in each of the CM classes, subclasses can be distinguished:

- submicrostructured composites: particle size, fiber thickness from 1 µm (d≤1 µm) is much less;
- microstructured composites: particle size, fiber or layer thickness is (correctly) equal to one micrometer (d = 1 µm);
- macrostructured composites: the macroscopic dimensions of the components are equal to one millimeter (d≥0.1 mm).

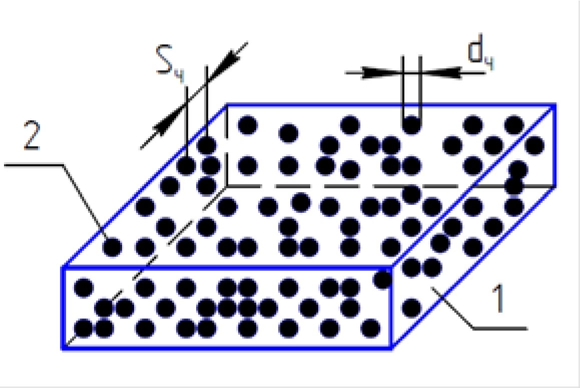


Figure 58. Schematic view of the microstructure of dispersion-hardened KM and particle-reinforced composites: 1 - matrix; 2 - reinforcing particles with a diameter d_4; S_4 is the distance between particles.

CM properties are considered according to the morphology of the phases or the geometry of the reinforcing components.

In the first case, CM refers to dispersion-reinforced compositions, and in the second – to particle-reinforced compositions.

Dispersion-hardened and particle-reinforced composite materials (Figure 52.). Geometrically, these composites belong to the same class because the reinforcing component is a zero-dimensional component with all three dimensions of the same order. Particles of the second component (phase) are randomly distributed in the matrix and, depending on their number, can strengthen the matrix, prevent the development of dislocation slip under load, or "lower" the matrix. applied load.

Particle size in dispersion-reinforced composites $d_4 \leq 1$ µm (submicrostructured composites) and their number is 1-15%. The efficiency of matrix hardening depends on the size of the particles and the distance between them. The greatest strengthening effect is observed when the particle size is less than 0.1 µm, the distance between them is $S_4 = 0.01\text{-}0.3$ µm, and the amount is about 15%.

The role of reinforcing particles is reduced to redistribute the applied load between the matrix and the filler rather than to strengthen the matrix. In addition, an important purpose of the matrix is to transfer the load to the reinforcing particles. If their content exceeds 25%, reinforcing particles play their role.

Fiber composite materials. These are mainly microstructured CM, characterized by the use of one-dimensional reinforcing components as fillers, one of whose dimensions is significantly greater than the other two. In fiber CMs, the plastic matrix is reinforced with high-strength fibers with a thickness of several micrometers to hundreds of micrometers (Fig. 59).

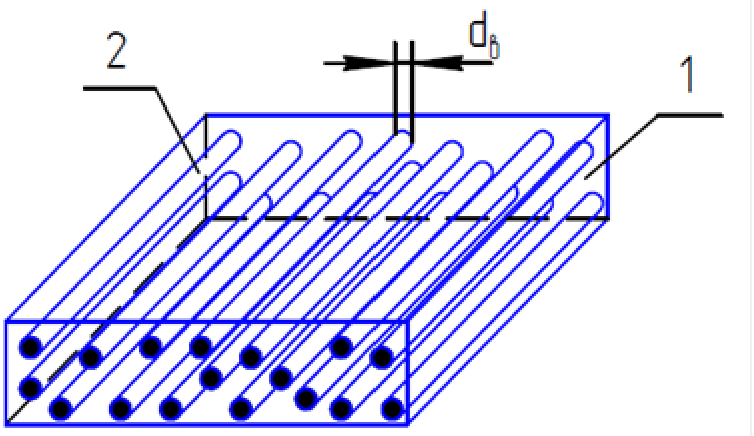


Figure 59. Schematic view of the fiber CM microstructure: 1 - matrix; 2 - reinforcing fibers with a diameter d_b

The composition of the fibers in the matrix can vary widely. Theoretically, the maximum fiber content can be up to 91%. However, in real conditions, already 80% volume fraction of fibers leads to the deterioration of the properties of the fiber composite.

the choice of the nature of the fiber is determined by the purpose of the composite and matrix material, primarily by the physicochemical nature of the interaction at the matrix-fiber interface. However, other things being equal, the set of properties of the fiber composite is determined by the geometric scheme of the reinforcement. One-dimensional reinforcement schemes with short fibers 1 (Fig. 60 b), short fibers 2 (Fig. 60 a) and long fibers 1(Fig. 60 a) can be used for any matrix, and the rest - mostly only polymer matrix for.

It should also be noted that two-dimensional (Fig. 60) and spatial reinforcement (Fig.60) schemes are most easily implemented in the production of parts and assemblies from polymer materials.

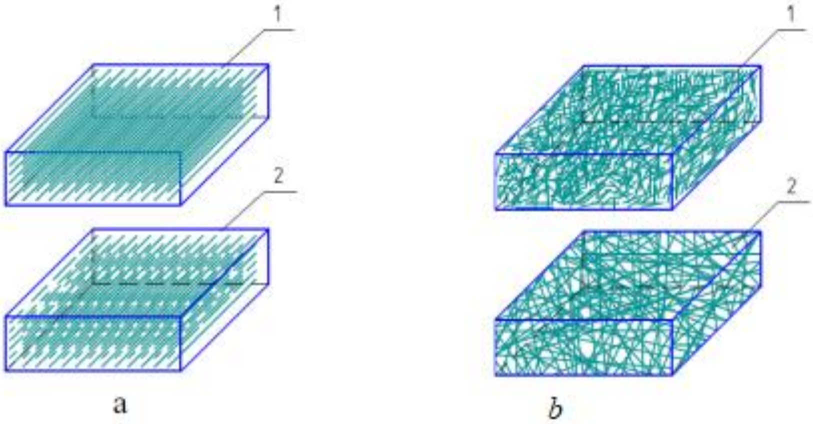


Figure 60. Schematic view of the microstructure of fibrous KM: a - one-dimensional reinforced: 1 - unidirectional continuous; 2 - unilateral short; b - randomly reinforced: 1 - short fibers; 2 - continuous fibers.

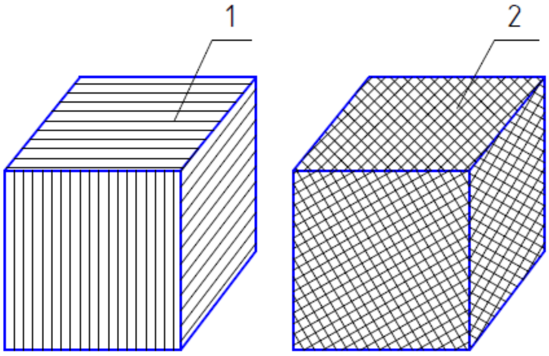


Figure 61. Schematic representation of the microstructure of spatially reinforced fiber CM:1 - three families of threads; 2 - N-families of threads.

3-layer ("sandwich") composite materials. This class of composites is characterized by the arrangement of phases or components in layers (Fig. 62).

They consist of two size components that are significantly larger than the third. Naturally, in layered composite materials, it does not make sense to divide the components into matrix and reinforcement. SubmicrostructuralAt the level, layered composites can be made by vapor deposition, and at the level of microstructure, layered eutectic structures formed as a result of oriented crystallization (for example, systems such as Al - $CuAl_2$, Cd-Sn, Al-Zn, Co-CoBe) and others).

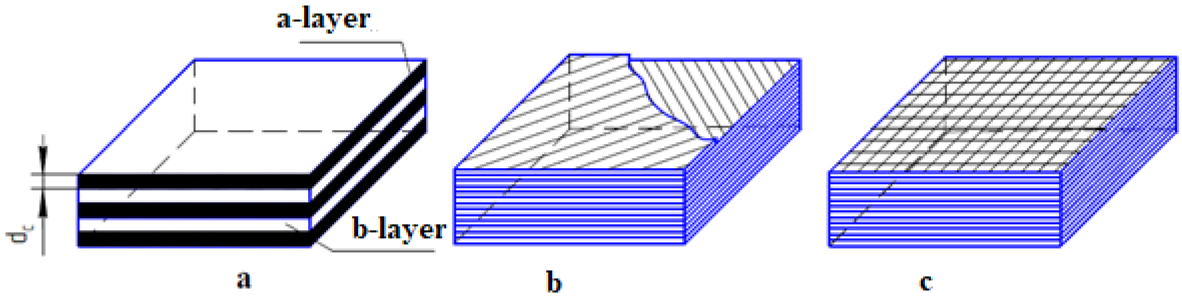


Figure 62. Schematic representation of the microstructure of layered CM: a - layer thickness with d_c ; b - layer reinforced with continuous threads; c - layered, reinforced with fabrics.

At the macroscopic level, layered composites can be made in metal-metal, polymer-polymer, metal-polymer pairs. They are layers of different materials with a thickness of 100 to 1000 µm and a different nature of separation at the boundary. At the same time, regardless of the nature of the interaction of the components at the boundary, the contact between the layers must be sufficient to prevent the irreversible movement of one layer against another under the influence of mechanical load and temperature.

Layered also includes a special form of CM known as structural honeycomb structures.

The structure of such CM consists of the following elements (Fig. 63): 1 – cover, two thin cover plates, 3- thick light aggregate core which separates the load-bearing plates and distributes the load between them, and 3- adhesive layers which connects the plates to the aggregate and transfers the load from the aggregate to the cover plates.

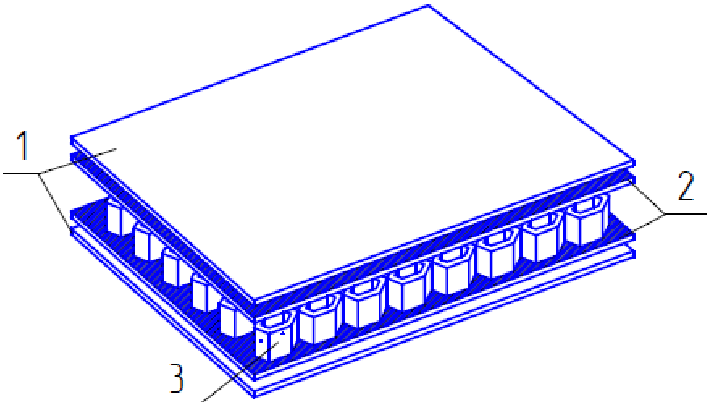


Figure 63. "Sandwich" CM structure: 1- coating, 2- adhesive layer, and 3-agregate.

One of whose horizontal plates "works" in compression, and the other in tension. The core of many honeycombs connecting the plates is similar to the vertical flange which "works" in shear and increases the bending stiffness.

Classification of composite materials by methods of producing. The classification of CM by production methods is to some extent conditional and temporary and reflects the current level of technological development.

A number of literature sources have proposed a classification for metallic CMs. In this case, the following processes of obtaining and processing composites are distinguished:

- chemical related to chemical, electrochemical and thermochemical deposition;
- gas and vapor phase due to condensation from gas and vapor phase;
- the liquid phase associated with directional crystallization and (or) impregnation of prepared filler frames;
- solid phase, primarily associated with powder technology, diffusion bonding and other thermomechanical technologies; - combined based on a combination of the above processes.

Classification of composite materials according to the purpose of use.CM can be conditionally divided into structural and functional.The latter represents a large group of materials with special properties. In addition to the need to perceive mechanical loads, CM must perform additional functions. Therefore, structural CM is functional to a certain extent, depending on the purpose, in addition to a set of mechanical properties, they must also have special properties, such as heat resistance and heat resistance, corrosion resistance, wear resistance, etc. Accordingly, structural CM should be divided into subclasses for different purposes or, optimally, the same composition should provide the required set of mechanical and special properties.

Composite materials are artificially created materials that consist of two or more components that differ in composition and are separated by a clear boundary and have new properties developed in advance.

Or fiber (dispersed particles) and binder (matrix) that make up a certain composition are called composite materials.

The component that is continuous throughout the entire volume of the composite material is called the matrix.

A continuous component separated in the volume of a composite material is called reinforcement.

Composite materials are metallic and non-metallic matrices (bases) with a given distribution of hardening substances (fibers, dispersed particles, etc.); effectively using the individual properties of the components of the composition.

CMs make it possible to have a given combination of heterogeneous properties: high specific strength and hardness, heat resistance, wear resistance, heat protection properties, etc. The spectrum of CM properties cannot be obtained using traditional materials. Their use makes it possible to create completely new designs that were previously unattainable.

Due ti CM, it became possible to make a new qualitative leap in increasing engine power, reducing the mass of machines and structures, increasing the weight efficiency of vehicles and aerospace vehicles.

The matrix gives the product the desired shape, affects the creation of the properties of the composite material, protects the reinforcement from mechanical damage and other environmental influences.

Metals and their alloys, organic and inorganic polymers, ceramics, carbon and other materials can be used as matrices in composite materials. The characteristics of the matrix determine the technological parameters of the process of obtaining the composition and its operational characteristics: density, specific strength, working temperature, resistance to fatigue failure and exposure to aggressive environments.

The reinforcing or reinforcing components are evenly distributed in the matrix. As a rule, they have high strength, stiffness and modulus of elasticity, and in these parameters they are significantly superior to the matrix. The term filler may be used instead of the term reinforcing component.

Advantages of composite materials:

- high specific power;
- high hardness (modulus of elasticity 130-140 GPa);
- high wear resistance;
- high fatigue resistance;
- It is possible to make dimensionally stable structures from CM.

In addition, different classes of compositions may have one or more advantages. Some benefits may not be available at the same time.

Disadvantages of composite materials:

Most classes of composites (but not all) have disadvantages:

- high price;
- anisotropy of properties;
- increasing the scientific capacity of production, the need for special expensive equipment and raw materials, as a result of the developed industrial production and scientific base of the country.

A different mechanism works in composite materials. A crack traveling in the matrix encounters an obstacle at the matrix-fiber interface. fibers prevent the development of cracks, and their presence in the plastic matrix leads to an increase in fracture toughness.

Thus, the composite system combines two opposite properties required for structural materials - high strength due to high-strength fibers and sufficient fracture resistance due to the plastic matrix and fracture energy dissipation mechanism.

CMs consist of a relatively plastic matrix material base and harder and stronger parts with fillers.

The properties of CM depend on the strength of the base, fillers and the bond between them.

The matrix binds the composition to the monolith, gives it shape and serves to transfer external loads from fillers to reinforcement. Depending on the base material, CMs are distinguished by metal matrix or metal composite materials (MCM), polymer-polymer composite materials (PPCM) and ceramic-ceramic composite materials (CCCM).

Composite materials consist of a metal matrix (often Al, Mg, Ni and their alloys) reinforced with high-strength fibers (fibrous materials) or finely dispersed refractory particles that are insoluble in the base metal (dispersion-reinforced materials). The metal matrix binds the fibers (dispersed particles) into a whole.

Non-metallic matrix composite materials. Non-metallic matrix composite materials have found wide application. Polymer, carbon and ceramic materials are used as non-metallic matrices. Of the polymer matrices, epoxy, phenol-formaldehyde and polyamide are most commonly used.

Pyrocarbon obtained from coked carbon matrices or pyrolyzed synthetic polymers. The matrix binds the composition and gives it shape

Hardener content in directed materials is 60-80 vol. %, undirected (with discrete fibers and threads) - 20-30 vol. %. the higher the strength and modulus of elasticity of the fibers, the higher the strength and stiffness of the composite material. The properties of the matrix determine the strength of the composite in shear and compression and resistance to fatigue failure.

Based on the type of reinforcement, composite materials are classified as glass fibers, carbon fibers with carbon fibers, boron fibers, and organic fibers.

In laminated materials, fibers, threads, tapes impregnated with a binder are laid parallel to each other in the laying plane. Flat layers are assembled into plates. Properties are anisotropic. For the performance of the material in the product, it is important to consider the direction of the acting loads. You can create materials with isotropic and anisotropic properties.

By changing the properties of composite materials, you can lay the fibers at different angles. Bending and torsional stiffness of the material depends on the order of laying the layers along the thickness of the package.

Laying of reinforcing elements of three, four or more threads is used.

The structure of three mutually perpendicular threads has the greatest application. Stiffeners can be located in axial, radial and circumferential directions. Three-dimensional materials can be of any thickness in the form of blocks, cylinders. Bulky fabrics have increased tear strength and cut resistance compared to layered fabrics. By extending the reinforcement along the diagonals of the cube, a system of four strands is constructed. The structure of the four threads is balanced, increasing the shear rigidity in the main planes. However, creating four-way materials is more difficult than creating three-way materials.

Lecture 7. Polymer nanocomposites

The feature is that the matrix is formed by various polymers that serve as a binder for reinforcement, which can be in the form of fibers, fabrics, films, glass fibers.

Forming of polymer composite materials is carried out by pressing, injection molding, extrusion, spraying.

Mixed polymer composite materials are widely used, they include metal and polymer components that complement each other's properties. For example, dry friction bearings are made of a combination of PTFE and bronze, which ensures self-lubrication and lack of creep.

Materials are created on the basis of polyethylene, polystyrene with fillers in the form of asbestos and other fibers with high strength and rigidity.

According to the structure of the filler, composite materials are divided into the following.

- fibrous (reinforced with fibers and threads),
- layered (films, plates, reinforced with layered fillers),
- dispersion-reinforced or dispersion-reinforced (with filler in the form of fine particles). (Fig. 64).

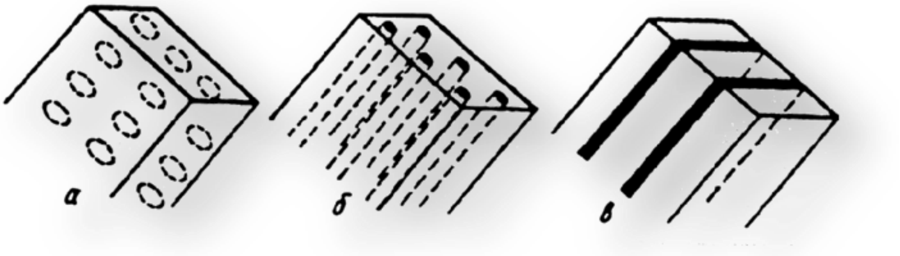


Figure 64. Schemes of the structure of composite materials:

a) solidified by dispersion; b) fibrous; c) layered

1. Reinforcement in fiber CM can be fibers of various forms: threads, tapes, various woven nets. Reinforcement of fiber CM can be carried out according to one-axis, two-axis and three-axis scheme (Fig. 64, a).

The strength and stiffness of such materials are determined by the properties of the reinforcing fibers that take the main load. Reinforcement gives a greater increase in strength, but it is technologically easier to harden the dispersion.

2. Layered composite materials (Fig. 64, b) are assembled from alternating layers of filler and matrix material (sandwich type). Filler layers in such CMs can have different orientations. Filler layers of different materials with different mechanical properties can be used alternately. Non-metallic materials are usually used for layered compositions.

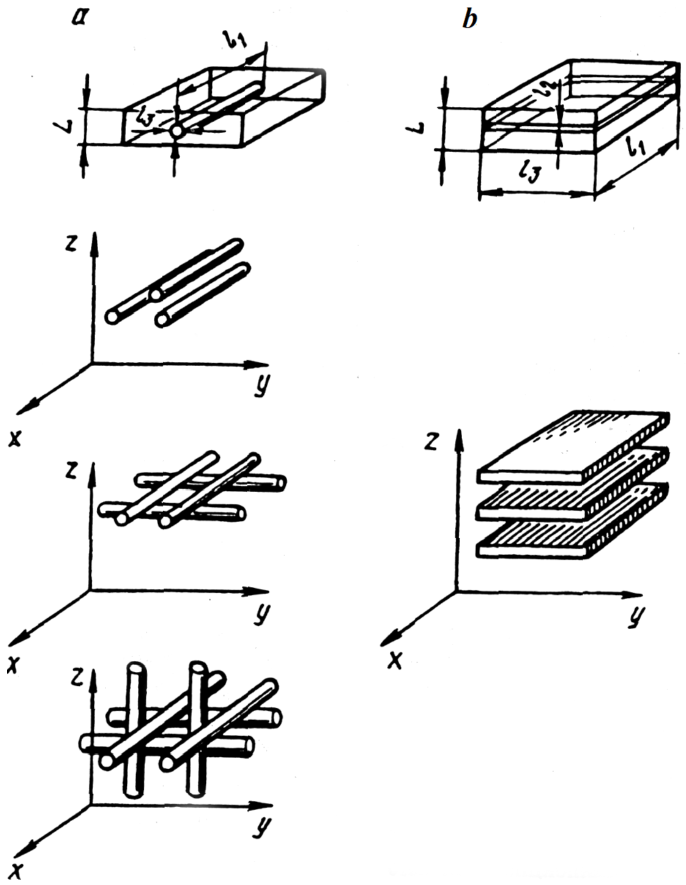


Figure 64. Schemes of reinforcement of fiber (a) and layered (b) composite materials.

3. Small, uniformly distributed refractory particles of carbides, oxides, nitrides, etc., which do not interact with the matrix and do not dissolve in it up to the melting temperature of the phases, are introduced into the CM artificially solidified by dispersion. The smaller the filler particles and the smaller the distance between them, the stronger the CM. unlike fibers, in dispersion-reinforced CMs, the main bearing element is the matrix. The ensemble of dispersed filler particles strengthens the material by resisting the movement of dislocations under load, which prevents plastic deformation. Effective resistance to dislocation motion is created up to the melting temperature of the matrix,

Composite fiber materials. Composite materials differ from traditional alloys in higher stress and endurance limit (50-10%), modulus of elasticity, stiffness coefficient and cracking sensitivity. The use of composite materials increases the rigidity of the structure, while reducing its metal consumption.

The strength of composite (fibrous) materials is determined by the properties of fibers; the matrix should mainly redistribute the stresses between the reinforcing elements. Therefore, the strength and modulus of elasticity of the fibers must be significantly greater than the strength and modulus of elasticity of the matrix.

Hard reinforcing fibers sense the stresses that appear in the composition under load, giving it strength and stiffness in the direction of the fibers.

To strengthen aluminum, magnesium and their alloys, boron fibers, as well as fibers from refractory compounds (carbides, nitrides, borides and oxides) with high strength and elastic modulus are used. High-strength steel wire is often used as fibers.

Molybdenum wire, sapphire fibers, silicon carbide and titanium boride are used to strengthen titanium and its alloys.

Increasing the heat resistance of nickel alloys is achieved by strengthening them with tungsten or molybdenum wire. Metal fibers are also used in cases where high heat and electrical conductivity are required. Promising hardeners for high-strength and high-modulus fiber composite materials are threads made of aluminum oxide and nitride, silicon carbide and nitride, boron carbide, etc.

Metal-based composite materials have high strength and heat resistance, while they have low plasticity. At the same time, fibers in composite materials reduce the rate of propagation of cracks initiated in the matrix, and sudden brittle fracture almost completely disappears. A characteristic feature of fiber uniaxial composite materials is the anisotropy of mechanical properties along and across the fibers and low sensitivity to stress concentrators.

The anisotropy of the properties of fiber composite materials is taken into account in the design of parts to optimize the properties by matching the resistance field with the stress fields.

The main disadvantages of composite materials with one- and two-dimensional reinforcement are low resistance to interlaminar shear and transverse shear. Volumetric reinforcing materials are deprived of this.

Dispersion reinforced composite materials. In contrast to fiber composite materials in dispersion-reinforced composite materials, the matrix is the main element that carries the load, and the dispersed particles inhibit the movement of dislocations in it. High strength **10-500 nm** is achieved by the particle size, the average distance between them is 100-500 nm and is uniformly distributed in the matrix.

Depending on the volume composition of solidification phases, strength and heat resistance do not obey the law of additivity. (**Additivity** (lat. additivus - added) is a property of a quantity in which the value of the quantity corresponding to the whole object is equal to the sum of the values of the quantities corresponding to its parts. in a certain class of objects that can be divided into parts. For example, the additivity of volume means that the volume of the whole body is equal to the sum of the volumes of its component parts.

The optimal composition of the second phase for different metals is not the same, but usually does not exceed 5-10% by volume.

The use of stable refractory compounds insoluble in the metal matrix (thorium, hafnium, yttrium oxides, complex compounds of oxides and rare earth metals) as reinforcement phases allows to maintain high strength of the material. In this regard, such materials are often used as heat-resistant. Dispersion-reinforced composite materials can be obtained on the basis of many metals and alloys used in engineering.

The most commonly used alloys based on aluminum are SAP (sintered aluminum powder).

The density of these materials is equal to the density of aluminum, they are not inferior to it in terms of corrosion resistance and can even replace titanium and corrosion-resistant steels when working in the temperature range of 250-500°C. In terms of long-term durability, they are superior to wrought aluminum alloys. For SAP-1 and SAP-2 alloys, the long-term strength at a temperature of 500°C is 45-55 MPa.

Great prospects for nickel dispersion reinforced materials. Nickel-based alloys 2-3 vol. % thorium dioxide or hafnium dioxide. The matrix of these alloys is usually a solid solution of Ni + 20% Cr, Ni + 15% Mo, Ni + 20% Cr and Mo. Alloys hardened nickel with thorium dioxide, hardened nickel with hafnium dioxide and hardened with thorium oxide Ni + 20% Cr matrix) are widely used. These alloys have high heat resistance. Dispersion-reinforced composite materials, as well as fibrous ones, are resistant to softening with increasing temperature and holding time at a certain temperature.

Fiber glass. Fiberglass is a composite consisting of a synthetic resin as a binder and a fiberglass filler. Continuous or short glass fibers are used as a filler. The strength of fiberglass increases sharply with a decrease in its diameter (due to the effects of inhomogeneities and cracks that appear in thick pieces). The properties of Shishatola also depend on its alkaline content; the best performance of non-alkaline glasses in aluminoborosilicate. Unoriented fiberglass contains a short fiber as a filler. This allows you to press parts of complex shapes with metal fittings. The material has isotopic strength properties that are much higher than press powders and even fibrous materials. Representatives of such material are glass fibers, as well as DGF (dimensional glass fibers), which are used for the production of power electrical parts, mechanical engineering parts (spools, pump seals, etc.).

Oriented fiberglass has a filler in the form of long fibers arranged in oriented individual strands and carefully bonded with a binder. This provides high strength fiberglass. Fiberglass can operate at temperatures from - 60 to 200 °C, as well as in tropical conditions, withstanding large inertial overloads.

They are used for the production of high-strength parts with fittings and threads.

Carbon fibers. Carbon fibers (carbon plastics) are compositions consisting of polymer binder (matrix) and hardeners in the form of carbon fibers (carbon fibers).

The high C-C bond energy of carbon fibers allows them to maintain strength at very high temperatures (up to 2200°C in neutral and reducing environments) as well as at low temperatures. Fibers are protected from oxidation by protective coatings (pyrolytic). Unlike glass fibers, carbon fibers are poorly wetted by binder (low surface energy), so they are etched. This increases the level of activation of carbon fibers due to the content of the carboxyl group on their surface. The interlayer shear strength of carbon fiber increases by 1.6-2.5 times. Binders are synthetic polymers (polymeric carbon fibers); pyrolysis synthetic polymers (coked carbon fibers); pyrolytic carbon (pyrocarbon carbon fibers).

Carbon fibers are characterized by high static and dynamic fatigue resistance, which preserves this property at normal and very low temperatures (the high thermal conductivity of the fiber prevents the self-heating of the material due to internal friction). They are resistant to water and chemicals. The thermal conductivity of carbon fiber is 1.5-2 times higher than that of glass fiber.Carboglass fibers contain glass fibers that reduce the cost of the material as well as carbon glass fibers.

Lecture 8. Nanomaterials for energy

The main thing necessary for life is energy. Only the energy obtained from the environment allows living systems to resist the growth of entropy and the desire of nature to bring everything to a state of equilibrium, the onset of which is predicted by the second law of thermodynamics. The Earth's main external energy source is solar radiation. Every year, the Earth receives $6x10^{24}$ J from the Sun, i.e. About 1000 J per second per 1 m^2 of surface. A little more than half of this energy is absorbed, the rest is reflected by the atmosphere and the surface.

Humanity as a whole produces about $5x10^{20}$ J of energy per year (2006 data). Modern energy has a clear fuel nature and more than 90% is based on the oxidation of coal, oil and gas, as well as their processing products. As a result of oxidation reactions, the energy of chemical bonds of fuel molecules is converted into heat and work. Quantitative measurements of heat and work are described by the thermodynamics of chemical reactions.

According to the first law of thermodynamics, there are two forms of energy transfer: orderly, related to changes in external parameters - work, and irregular, causing only changes in temperature - heat. The heat released or absorbed in a chemical reaction at constant pressure (Q) is equal to the change in the enthalpy of the reaction in absolute value:

$$Q = -\Delta H.$$

Here, heat is considered positive if it is released to the environment. Using Hess's law, the heat of reaction can be expressed in terms of the energies of the formed and broken bonds:

$$-\Delta H = \Sigma E_{form} - \Sigma E_{destr}.$$

When organic compounds are burned, CO2 and H2O are formed, which are characterized by high bond energies: E(C=O) == 743 kJ / mol, E(O–H) = 463 kJ / mol, so organic substances very caloric - the specific heat of combustion of hydrocarbons is about 50 kJ / g.

Part of the heat of chemical reactions can be converted into work (W). The limit value of this part establishes the second law of thermodynamics, from which it follows that the maximum work that can be obtained as a result of a chemical reaction * is equal to the loss of Gibbs energy of the reaction:

$$W_{max} = -\Delta G,$$

where G = H – TS, T – absolute temperature, S – entropy. It follows from this relation that work can only be done by spontaneous reactions with $\Delta G < 0$.

During the processing of natural fuels, part of the combustion energy is used directly in the form of heat, for example, to heat residential buildings, and the rest is used to produce work in the form of mechanical energy (cars), electricity (Figure 78.)

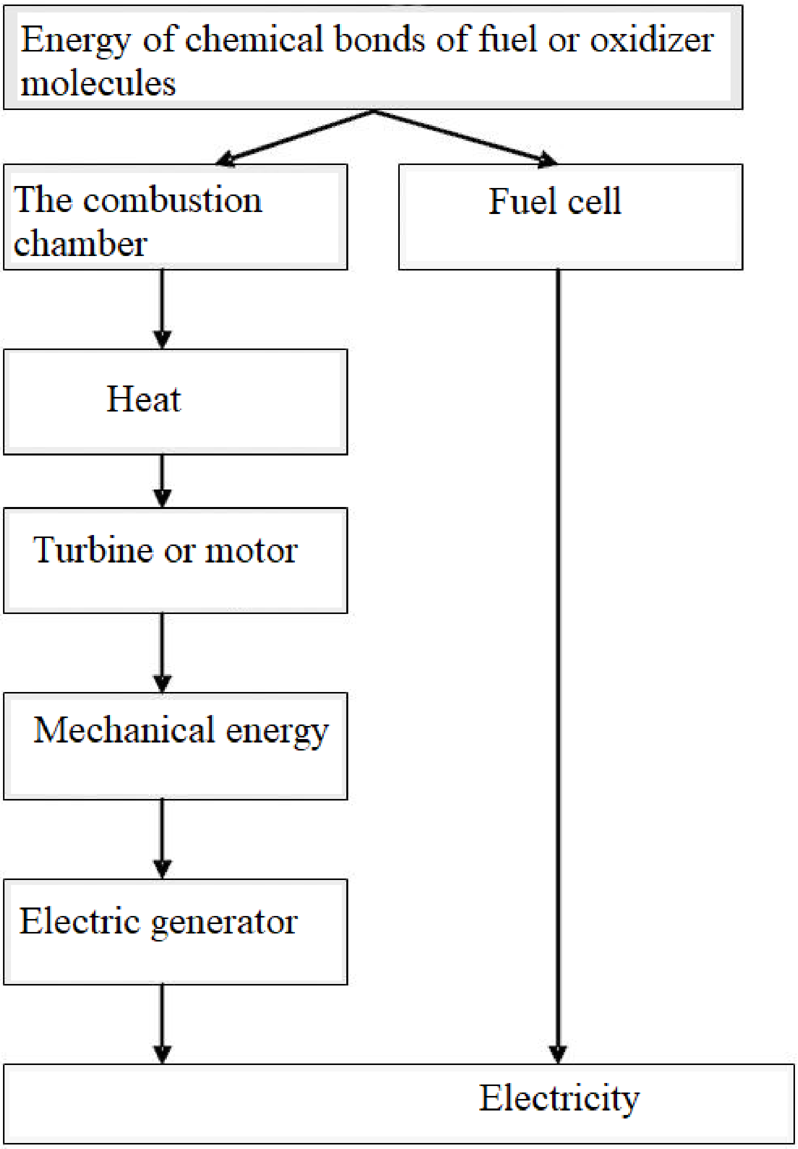


Figure 78. Production of electricity through the energy of chemical reactions

For example, in the reaction of complete combustion of methane

$$CH_4 \text{ (g.)} + 2O_2 \text{ (g.)} = CO_2 \text{ (g.)} + 2H_2O \text{ (g.)}$$

Since the enthalpy change is $\Delta H = -802$ kJ/mol and the Gibbs energy is $\Delta G = -801$ kJ/mol, almost all of the heat of this reaction can be changed. to work. Pre-authorized devices.

Humanity's demand for energy is increasing, so at the beginning of the new millennium, at the highest political level, a proposal was put forward to develop an energy support program for the sustainable development of humanity and the improvement of the ecological condition of the Earth. One of the most promising ways to implement this program is hydrogen energy.

The production of energy from hydrogen is based on the reaction of its oxidation with oxygen to water: to convert the energy of a chemical reaction into work are called fuel cells, we will talk about them in more detail in the next section.

Conventional energy sources are not renewable, their reserves gradually dry up: some are enough for hundreds, others for several decades.

$$\mathbf{H_2 \text{ (g.)} + 1/2O_2 \text{ (g.)} = H_2O \text{ (liq)}}$$

Enthalpy change in this reaction $\Delta H = -286$ kJ/mol,and Gibbs energy change $\Delta G = -237$ kJ/mol. This means that during the combustion of 1 mole or 2 g of hydrogen, 286 kJ of heat is released, of which 237 kJ (that is, 83% or five sixths) can be converted into useful work, namely electricity. The remaining 49 kJ / mol (or more, since the efficiency of any device does not reach 100%) is dissipated in the form of heat.

As an energy source, hydrogen has many advantages over hydrocarbon feedstocks.

First, this element is abundant on Earth. Fifteen out of every 100 atoms in the Earth's crust are hydrogen. There are about 100 thousand billion (10^{14}) tons of hydrogen in the World Ocean alone. But oil, natural gas, and biomass still exist. Second, hydrogen is the most energy-intensive fuel. Its specific heat of combustion is 143 kJ/g, which is 3 times lower for hydrocarbons. In addition, hydrogen can be considered an environmentally friendly fuel, because. the product of its processing is pure water. Even by mixing hydrogen and gasoline in car engines, emissions of nitrogen and carbon oxides, as well as unburned hydrocarbons, are reduced several times.

However, along with the advantages, hydrogen also has many disadvantages.

First, hydrogen is needed in the free state to obtain energy. There is a lot of hydrogen on Earth, but it is almost absent in the form of a simple substance. It depends on its physical and chemical properties. Hydrogen is the lightest of all gases, hence its attractive force

To Earth - the smallest, and the speed of movement - the highest, and during the existence of the Earth, all hydrogen evaporated into space. In addition, air contains only gases that do not react with oxygen, and when hydrogen is ignited, it easily interacts with it.

Thus, hydrogen must be obtained, and this requires a large amount of energy. Currently, the main method of obtaining hydrogen (85% of world production) is based on the conversion of methane, which is the main part of natural gas, into steam.

$$CH_4 + H_2O = CO + 3H_2$$

$$CO + H_2O = CO_2 + H_2$$

The main disadvantage of this method is the formation of a by-product - carbon dioxide.

Other methods of isolating H_2 are coal steam reforming, electrolysis of water and aqueous solutions, pyrolysis of biomass).

Another disadvantage of hydrogen is its explosive nature. A mixture of hydrogen with air is explosive in wide concentrations. However, the high diffusion rate of H_2 prevents it from building up to high concentrations, so under realistic conditions, hydrogen is not as explosive as natural gas. Finally, it is difficult to turn hydrogen into a liquid state, because its boiling point is very low, and at high pressures it "flows" through the walls of a cylinder or gas pipe. Therefore, the existing natural gas transportation infrastructure for hydrogen can only be used after appropriate upgrades, which are estimated to cost trillions of dollars.

Thus, it is necessary to develop effective, economical and safe methods for the creation of hydrogen technologies: a) hydrogen production; b) its transportation and storage; c) oxidation of hydrogen for energy.

The direct reaction between hydrogen and oxygen to produce energy is used only in astronautics, where liquid hydrogen serves as a fuel for rocket engines and liquid oxygen is an oxidizer.

For automobile internal combustion engines, this method does not justify itself, because. During the burning of hydrogen, a very high temperature occurs, in which the components of the air intensively react with each other with the formation of toxic nitrogen oxides.

Nanomaterials for hydrogen storage

Another important challenge to which nanochemistry can make an important contribution is the compact and safe collection and storage of hydrogen for use in fuel cells. The ideal would be a hydrogen storage device contains a large amount of hydrogen in a small volume and readily supplies it when needed. Several radically different approaches to hydrogen storage have been proposed, one of which is based on the use of carbon materials, particularly nanotubes.

All methods of hydrogen storage can be divided into three large classes: physical, physicochemical (adsorption) and chemical. Each of them has its advantages, disadvantages and scope. The most traditional are physical methods. Gaseous hydrogen is stored in cylinders with a capacity of several liters to several cubic meters at a pressure of 35 atm, and liquid hydrogen is stored in special cryogenic tanks at low temperatures. The main advantage of balloon storage is its simplicity

and lack of energy consumption for gas production; disadvantages - low bulk density and the possibility of leakage.

Among the materials capable of adsorbing hydrogen, carbon materials attract special attention. It has long been known that low-density activated carbon can absorb up to 7-8% (wt.) of hydrogen at a pressure of 4 MPa and a temperature of 65-75 K. In the last decade, scientists have focused on carbon nanomaterials - nanotubes and fullerenes, transition metals connected with atoms. These materials are relatively cheaper and are more easily renewed than others, besides, they have a low density. The main advantage of carbon nanotubes is the ability to store hydrogen at low pressure. The adsorption capacity of carbon materials can be increased by adding metals that catalyze hydrogen dissociation, among which palladium is one of the best.

One of the mechanisms of hydrogen absorption by nanotubes is chemisorption, i.e. adsorption of hydrogen H_2 on the tube surface, followed by dissociation and formation of CH chemical bonds. Full saturation of all carbon atoms with hydrogen allows to reach a mass fraction of 7.7% of bonded hydrogen. True, chemisorption is not very convenient for storing hydrogen, because it is difficult to isolate the bonded hydrogen: CH bonds are completely broken only at 600 ° C. A more acceptable binding mechanism is reversible physical adsorption of molecular hydrogen due to Van der Waals interactions.

Moreover, even hydrogen that is not physically or chemically bonded can fill the voids inside a nanotube or between the walls of multiwalled tubes. Calculations show that if the diameter of the tube is 3 nm, the mass fraction of hydrogen inside the tube can reach 15%. However, the work with carbon nanomaterials has not yet gone beyond the laboratories and they have not found industrial application in hydrogen storage.

Among materials that chemically bind hydrogen, light and active metals such as magnesium or calcium are the most promising. Magnesium forms an ionic hydride with hydrogen, which contains 7.6% (wt.) of hydrogen. True, the reaction between ordinary metallic magnesium and gaseous hydrogen proceeds very slowly. To speed it up, magnesium is used in the form of micro and nanoparticles or alloys such as Mg2Ni or Mg2Cu are used.

A more promising approach is based on the creation of composite materials that combine the advantages of their components and are deprived of their disadvantages. Thus, we mentioned above a new composite material based on carbon black containing fullerene and magnesium hydride capable of reabsorbing 65 g of hydrogen per 1 liter of sorbent and rates and temperatures of absorption reactions, hydrogen release by composite materials can be controlled using catalytic additives and the formation of nanostructured materials. Therefore, light metal hydrides remain one of the most promising objects for creating hydrogen storage technologies.

Research on various aspects of hydrogen energy is being carried out rapidly in many scientific laboratories, and it is difficult to predict which of them will reach the level of technology. One thing is certain - these technologies will not work without nanochemistry. At the same time, one should not expect fundamental breakthroughs and solutions in the field of energy from nanochemistry, which is only one of the fields of chemistry. Its skilled application can significantly improve the quantitative properties of traditional materials and create new materials with the necessary properties.

Lecture 9. Polymer blends

Polymer blends are compositions consisting of two (rarely three or more) polymers, the preparation of which has the following main goals: gain in properties due to a synergistic effect; facilitating the processing of the main polymer by adding another polymer; economical effect due to the addition of a cheaper (more accessible) component; expansion of the raw material base; disposal of waste plastics, both by adding polymers that improve properties, and by using a naturally occurring mixture of secondary polymers; increasing the biodegradability of synthetic polymers during natural aging or to facilitate waste disposal and improve the environment, by adding biopolymers (starch, polylactides, etc.) to synthetic polymers.

Most polymer blends contains a few percent of an additive - a compatibilizer that improves the mutual dispersion of polymers during mixing and increases the strength of the polymer-polymer bond. Such highly dispersed polymer blends are referred to as polymer alloys.

The spontaneous process of mutual dissolution of polymers, which occurs with a decrease in the thermodynamic potential, is a rare phenomenon, since the change in entropy is small, and exothermic mixing is typical for polymers that differ in polarity. Therefore, polymer blends are basically dispersions (emulsions) of one polymer in a matrix of another. Due to the presence of a two-phase structure, an extended interfacial layer arises in the mixture layer. At the polymer-polymer interface, rather fast diffusion of the kinetic segments of the polymer macromolecule takes place in the absence of diffusion of macromolecules. A new phenomenon arises - segmental solubility in the interfacial layer.

The greater the difference in the polarity of the polymers, the smaller the layer thickness and the lower the adhesive strength of the contacting polymers. Graft and block copolymers with blocks of the same nature as the contacting polymers are often used as compatibilizers. The length of the blocks should be sufficient for the formation of a network of entanglements in each phase after the blocks have diffused into the related phase. Increasingly, compatibilizers are being used that are not block copolymers but have an affinity for one or both polymers. In the absence of a theory, the search for a compatibilizer for a given pair of polymers is carried out by trial and error. In rubber blends, an increase in bond strength is achieved by covulcanization. Due to the partial mutual solubility of polymers, some interdiffusion of macromolecules occurs, so the thickness of the interfacial layer increases to micron sizes.

Mixing of polymers in the melt is carried out in batch mixers (Banbury mixer, in the laboratory - Brabender mixer) or continuous (single- and twin-screw extruders) action. Other methods of mixing (in solution, emulsion, polymerization of the monomer in the mass of another polymer) are used mainly for research purposes. Mixing in the melt is most effective at equal or close values of viscosity. The particle size in the mixture is 1–10 µm under optimal mixing conditions. A large difference in viscosity leads to particle sizes up to 50 µm, at equal viscosities and in the presence of interfacial additives, the particle size approaches 0.1 µm. An increase in the content of the introduced polymer increases the probability of coalescence of particles, and in the range of 30–70% by volume, both the added and the matrix polymer form continuous phases.

When studying the phase structure of a mixture of polymers, the presence or absence of particles, their size and shape are investigated. The absence of particles visible in an electron microscope is characteristic of mutually soluble polymers. The presence of particles of the dispersed phase (phase composition) is determined by the methods of measuring transparency (appearance of turbidity), the method of dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC). The appearance of a second maximum of mechanical losses on the temperature dependence indicates a two-phase structure of the S. p. (two glass transition temperatures). The DSC method is similar, which makes it possible to fix the glass transition or melting temperatures of polymers in a mixture, i.e., the presence or absence of a two-phase structure.

The presence of particles of the dispersed phase suggests the possibility of migration of non-polymeric ingredients from one phase to another. This is typical for plasticizers, antioxidants, dyes, and other low molecular weight ingredients. Migration occurs during storage, operation and especially during mixing. In the latter case, the filler particles can "migrate" according to their affinity for the polymers of the mixture. This is especially true for rubber compounds.

The primary and most basic assessment of the mixing efficiency is the “property-composition” curve (the dependence of the properties of S. p. on the ratio of components). The properties of the polymers in the mixture make it possible to calculate the additive dependence "property - composition". Comparison of the experimental curve "property - composition" with an additive dependence makes it possible to evaluate the effect of mixing: positive, if the "property" index for the mixture is better than the additive value, and negative if the opposite effect. Improvement of properties allows us to consider polymers "compatible", deterioration - "incompatible". These two concepts are not directly related to the mutual solubility of polymers, but more often to the correct choice of mixing conditions.

Blending polymers solves two important problems: increasing the impact resistance of plastics and improving their processability. The introduction of rubber into plastic makes it resistant to impact (impact strength increases); with a high content of rubber, an effect occurs plasticization of polymers. To increase the impact strength, it is necessary to create such a disperse structure that would make it possible to preserve the modulus of the matrix polymer as a structural material. The addition of a few percent of rubber to PS or its copolymer with acrylonitrile made it possible to create large-tonnage materials - impact-resistant PS and ABS plastic; the introduction of a few percent of elastomers, PE or its modifications. copolymers into polycarbonates, polyamides, polyesters, etc. led to the emergence of an extensive class of impact-resistant plastics. The introduction of the 2nd polymer facilitates the processing of many. high-temperature plastics such as polysulfones, polyphenylene oxides, aromatic polyamides, etc.

Mixing of polymeric materials is a technological process used to introduce ingredients of polymeric materials (vulcanizing agents, fillers, plasticizers, stabilizers, etc.) into the polymer, as well as to combine various polymers in order to obtain homogeneous mixtures.

Polymer systems, which include several polymers, have been used for a long time to obtain materials that combine the properties of both immiscible polymers. So, at the beginning of the 20th century, they tried to reduce the fragility of polystyrene by adding rubber. This eventually led to the creation of a wide range of high-impact plastics, the brittleness of which was drastically reduced by the presence of an elastomer microphase.

An effective way to obtain new materials with the necessary properties is the mixing of two or more thermoplastics - a complex physical and chemical process that occurs under the influence of mechanical and temperature fields.

The field of polymer blends (or alloys) has experienced tremendous growth over the past two decades in the scope and complexity of its scientific base, as well as technological and commercial development. This explains the relevance of this topic.

At various stages of the development of the science of polymers, the focus of attention of researchers turned out to be one or another area, important both from a scientific and practical point of view. Currently, attention is focused on polymer blends, since their practical significance is obvious.

The study of the physical and mechanical properties of polymer blends has led to a revision of the existing fundamental ideas and opened up new areas of research and solution of practical problems. From this point of view, the mixing of polymers is in many ways similar to copolymerization as a way to achieve desired properties by combining different chemical structures. The only difference is that mixing allows this goal to be achieved physically, and not chemically (as in the case of copolymerization) by.

Lecture 10. Nanocatalysis

One of the most promising applications of nanoparticles is related to catalysis. Recall that catalysis is the change in the rate of a reaction in the presence of a catalyst. Catalysis is considered positive if the reaction rate increases and negative if the rate decreases. Negative catalysis is otherwise called inhibition.

Catalyst A substance is called a substance that directs a chemical reaction along a different path and thereby changes its speed.

The catalyst participates in the reaction, but is not consumed in it, i.e. after its completion remains unchanged in form and quantity.

Catalysts play a huge role in our lives. Some chemical reaction in living organisms is not complete without biological catalysts - enzymes. Modern civilization cannot be imagined without catalysts, because almost all common materials - products of the chemical and petrochemical industries - are obtained as a result of catalytic processes. The production of electricity by chemical reactions also requires the participation of catalysts.

Good catalysts should combine three main qualities - activity, selectivity and stability. The activity of a catalyst measures how many times the rate of a reaction changes in its presence. Often, along with the main reaction, side reactions are also accelerated, which lead to the formation of unnecessary or harmful products. To avoid this, the catalyst must be selective; ideally, change the rate of only the desired reaction and not affect competing processes. During operation, the catalyst gradually loses its qualities. This happens because its surface gets dirty over time, pores become clogged, or the shape of active centers changes. The stability of a catalyst is characterized by its service life. The creation of highly active stable catalysts with good selectivity is one of the priority areas of modern chemical science.

Finding the right catalyst for a chemical reaction is a real art. Everything is taken into account here: the size of the molecules, their energy, orientation in space, availability, possible economic effect and many other factors. It is no coincidence that the composition of most catalysts used in the chemical industry is patented, and many are even classified.

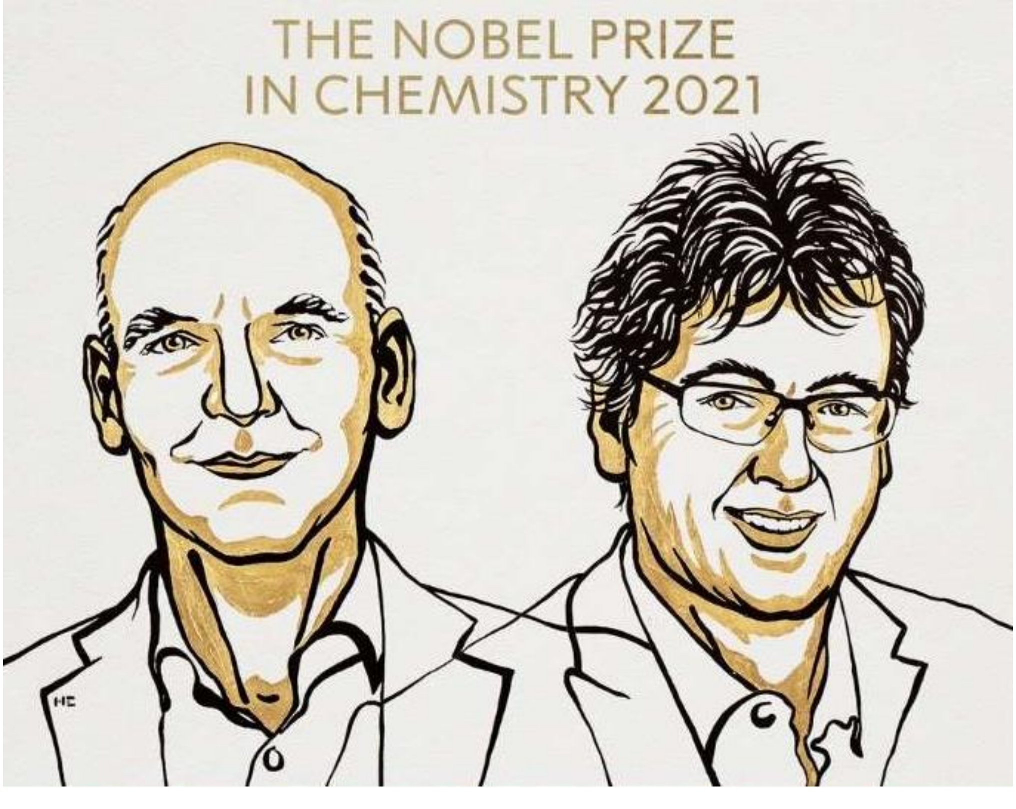


Figure 79. Nabel laureates German chemist Benjamin List and English organic chemist David

The creation of a new efficient catalyst is a serious scientific discovery that often wins prestigious awards. Six Nobel Prizes in Chemistry have been awarded for discoveries in the field of catalysis. The American chemist R. Zeir considers catalysis to be the concept "which most fully characterizes the essence of chemistry", since it not only demonstrates the ability of substances to transform, but also emphasizes the role of man in this process, demonstrates our ability to control the world around us.

German chemist Benjamin List and English organic chemist David (Fig.79.) discovered a new type of catalyst - a catalyst based on organic molecules.Until then, two types of catalysts were known - metals and enzymes.

Catalysts are extremely diverse in type, composition and methods of preparation, but they all have a number of common properties. The mechanism of action of all catalysts is, in principle, the same: catalysts act as an intermediary between the reactants and reaction products. They react with the starting materials and form intermediate compounds, which are further converted into products, and the catalyst is regenerated, i.e. returns to its original state.

For example, the compound reaction

$$A+B=P$$

the presence of a catalyst (K) can proceed in two stages

First, the catalyst reacts with substance A:

$$A+K=AK$$

(this stage can be either reversible or irreversible), and the intermediate product AK then reacts with substance B, forming product P, while the catalyst is regenerated:

$$AK+B=P+K.$$

the state of the reactants and products and are completely independent of the reaction path. Recall the important thermodynamic relationships between them: if the reaction proceeds at a constant temperature, then

$$\Delta G=\Delta H-\mathrm{T}\Delta S,$$

(the equilibrium constant is expressed in terms of thermodynamic functions in the standard state).

The independence of the equilibrium constant from the presence of a catalyst means that the catalyst cannot shift the position of chemical equilibrium and affect the yield of products. All he can do is speed up or slow down the achievement of a state of equilibrium. Inability to change thermodynamic functions chemical reaction is a fundamental property of catalysts. It actually follows from the definition. According to him, the catalyst does not change the state of the reactants and products. If he could do this, then he would not be a catalyst, but an ordinary participant in the reaction - a reactant or a product.Without changing the thermodynamics, the catalyst dramatically affects process kinetics. It directs the reaction along a different path and changes its mechanism. The new pathway is characterized by a different activation energy – lower in the case of positive catalysis and higher in the case of negative catalysis. In many manuals, the path of a catalytic reaction is depicted by an energy curve with one maximum. This is an overly simplistic view that focuses on only one catalytic effect - the change in activation energy. At the same time, the mechanism of catalysis itself, associated with the formation of intermediate compounds, remains behind the scenes.In fact, even the simplest mechanism of catalysis involves at least two stages and the formation of one stable intermediate - a complex of the reagent with the AK catalyst. Therefore, the energy curve should contain two maxima, corresponding to the transition states of both stages, and one minimum, corresponding to the formation of AK.

If the change in activation energy is $\Delta E = E_{noncat} - E_{cat}$, then, using the Arrhenius equation for the rate constant, we can evaluate the effect of the catalyst on the reaction rate, i.e. catalyst activity. For example, the decomposition of hydrogen peroxide in an aqueous solution is haracterized by an activation energy of 76 kJ, and in the presence of a catalyst (I-) the activation energy decreases to 57 kJ·mole-1. The reaction rate due to the catalyst at room temperature increases 2000 times.

Classification of catalytic reactions

All chemical reactions involving catalysts can be divided into two large classes - homogeneous, i.e. In a flowing homogeneous system - gas phase or solution, and heterogeneous - those that appeared at the interface between substances. Biological catalysts - enzymatic reactions that occur under the influence of enzymes can be divided into a separate class.

An example of homogeneous catalysis is the decomposition of ozone in the gas phase in the presence of nitrogen (II) oxide, which proceeds according to a two-step scheme:

$$\mathbf{O_3+NO=O_2+NO_2}$$

$$\mathbf{O_3 + NO_2 = 2O_2 + NO}$$

Nitrogen oxide (II) is present in the exhaust gases of jet engines, so the flights of jet planes cause the depletion of the Earth's ozone layer.

The intermediate product of this catalytic reaction is nitric oxide (IV). If we add the equations of each of the stages and reduce the same formulas in the left and right parts, we get the general stoichiometric reaction equation:

$$\mathbf{2O_3 = 3O_2}$$

Of greatest practical interest are heterogeneous catalytic reactions. These include many industrial reactions in which gaseous substances react with each other in the presence of solid catalysts, such as the synthesis of SO_3 or NH_3. Oxidation of exhaust gases in car converters also takes place in the presence of solid catalysts. It is interesting that organic molecules are formed due to heterogeneous processes in space - this happens on the surface of cosmic dust particles.

Catalyst surface plays an active role in heterogeneous reactions in which reactants and catalyst are in different aggregate states.

$$\mathbf{2CO + 2NO = 2CO_2 + N_2}$$

For example, the oxidation reaction of carbon monoxide (II) with nitrogen oxide (II) is significantly accelerated in the presence of the transition metal rhodium. To understand why this happens, let's look at the process step by step. First, oxide molecules from the gas phase approach the catalyst surface and combine with it - they are adsorbed (Fig. 80a). On the surface, the bond between the oxygen and nitrogen atoms in the NO molecule is broken (Fig.80b), after which the O atom joins the CO molecule, and the released nitrogen atoms combine to form an N2 molecule connected to the catalyst surface (Fig. 80c).

Finally, the reaction products - CO2 and N2 - are separated (desorbed) from the surface and the reaction is completed. Thus, the reaction is accelerated due to the decomposition of NO molecules on the metal surface into atoms that are more active than molecules.

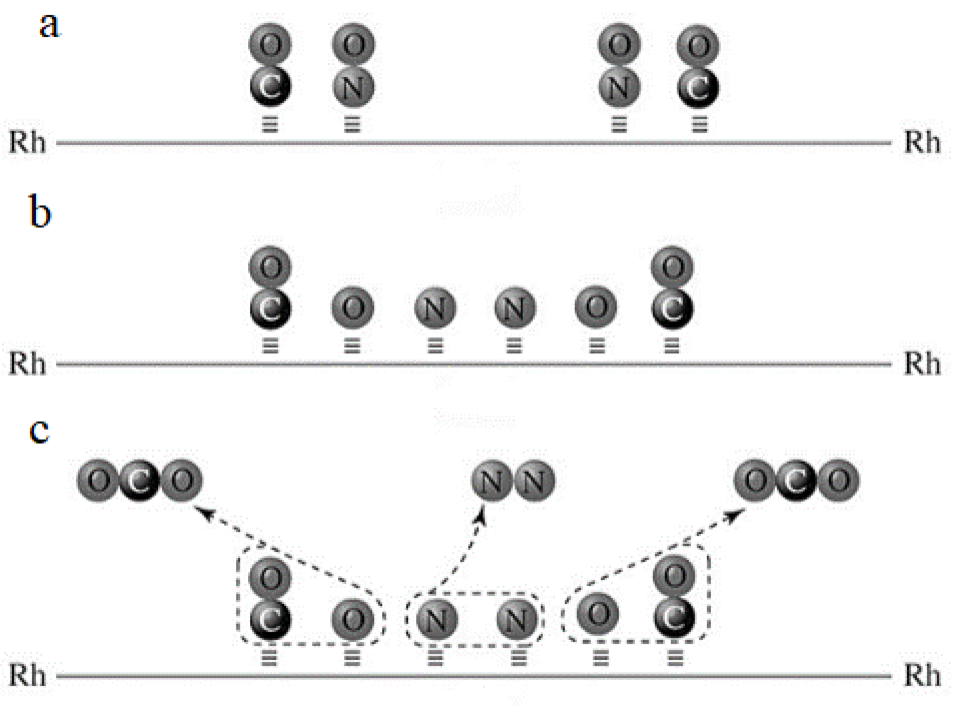


Figure 80. Mechanism of catalytic oxidation of carbon monoxide

The simplest scheme of heterogeneous catalysis is as follows. Let the initial reaction be described by the equation A + B = P. Let us denote the free areas on the catalyst surface (catalytic centers) by the letter Ω. At the first stage, a molecule of one of the substances occupies an area on the surface:

1) A (g.) +Ω= A (surf.).

Then there are two possibilities. Either the adsorbed molecule A reacts with the molecule B, which is in the gas phase, forming a molecule of the product P on the surface:

2) A (reverse) + B (r) = P (surf.)

or first the B molecule is adsorbed on the surface

catalyst:

2a) B (d.) +Ω= B (surf.),

already there, on the surface, the product is formed: 2b) A (surface) + B (surface) = P (surf.) +Ω.

At the final stage, the product molecule detaches from the surface and passes into the gas phase, while the area on the surface is freed:

3) P (surf.)= P (g.) +Ω.

By a similar mechanism, one of the most important industrial reactions occurs - the synthesis of ammonia from simple substances. For the discovery of this mechanism, the German chemist G. Ertl received the Nobel Prize in Chemistry in 2007. He proved that on the surface of the catalyst - metallic iron -both participants in the reaction - and hydrogen, nitrogen - are adsorbed and decomposed into atoms. The complete mechanism for the synthesis of ammonia from simple substances is:

$$H_2(g.) + \Omega = 2H\ (surf.),$$

$$N_2(g.) + \Omega = 2N\ (surf.),$$

$$N\ (surf.) + H\ (surf.) = NH\ (surf.),$$

$$NH\ (surf.) + H\ (surf.) = NH_2(surf.),$$

$$NH_2(surf.) + H\ (surf.) = NH_3(surf.),$$

$$NH_3(surf.) = NH_3(g.).$$

The limiting stage of the process is the second: it proceeds the lowest speed. This mechanism, along with several others, was proposed even before the work of Ertl, but the latter managed not only to experimentally prove its truth, but also to determine the energies of individual stages, i.e. construct an energy diagram of the entire process (Fig. 81). The adsorption of substances on the catalyst surface is usually leads to a significant weakening of chemical bonds and facilitates their breaking, so the activation energy of heterogeneous reactions $E_{heterog}$, as a rule, significantly, by hundreds of kJ/mol, lower than for the same reactions occurring in the gas phase without catalyst E_{gom}(Table 9).

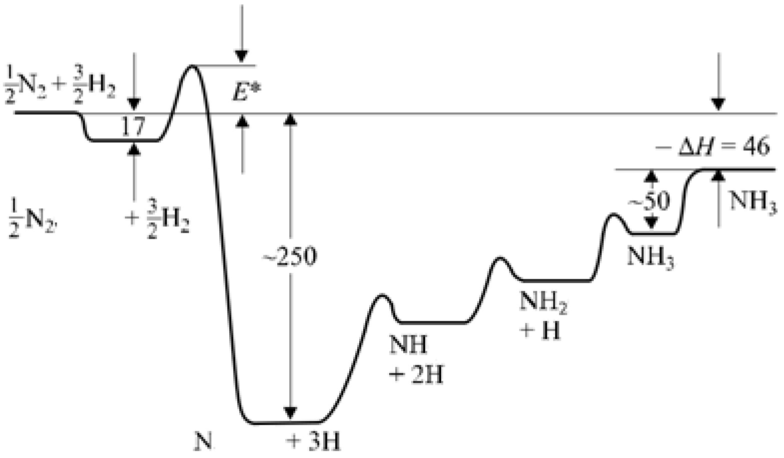


Figure 81. Energy diagram of ammonia synthesis from simple substances on the catalyst surface. Energies are given in kJ/mol

Table 9. Activation energies of some reactions occurring in the gas phase

Reaction	**Catalyst**	**E_{gom}, kJ/mol**	**E_{geter}, kJ/mol**
$2HI = H_2 + I_2$	Pt	180	60
$2NH_3 = N_2 + 3H_2$	W	330	160
			175
	Fe		200
	Os		
$CH_4 = C + 2H_2$	Pt	330	230
$2SO_2 + O_2 = 2SO_3$	Pt	250	63

Lecture 11. Physical and chemical properties of nanoparticles.

Nanoparticles are generally referred to as objects that are composed of atoms, ions, or molecules and are less than 100 nm in size. An example of this is metal particles. We have already talked about gold nanoparticles. In black and white photography, silver bromide breaks down when light hits the film. This leads to the appearance of metallic silver particles consisting of several tens or hundreds of atoms. It has been known since ancient times that water in contact with silver can kill pathogenic bacteria. The healing power of such water is explained by the composition of the smallest particles of silver in it, these are nanoparticles! Due to their small size, these particles can be separated from individual atoms,

It is known that many physical properties of matter, such as color, thermal and electrical conductivity, melting point, depend on particle size. For example, the melting temperature of gold nanoparticles with a size of 5 nm is 250° lower than that of ordinary gold (Fig.15). As the size of gold nanoparticles increases, the melting temperature increases and reaches a value of 1337 K, which is typical for a conventional material (this is also called the bulk phase or macrophase).

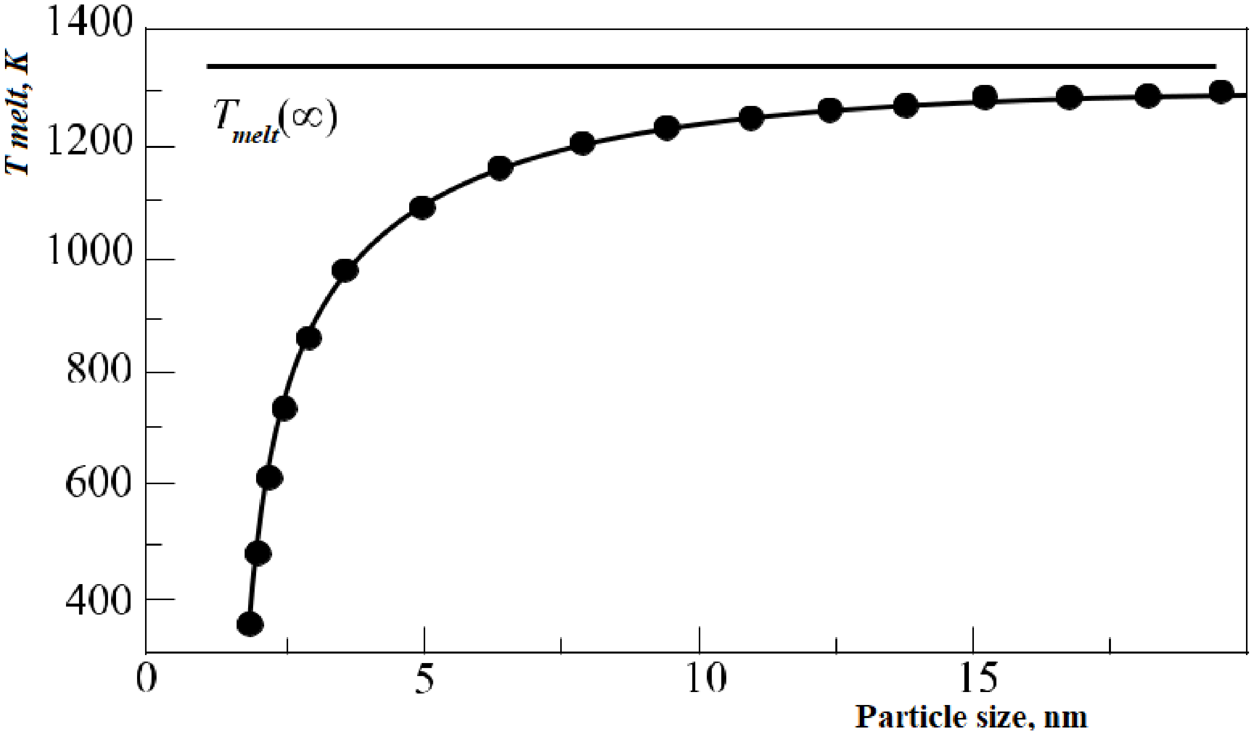


Figure 15. Dependence of the melting temperature of gold on the particle size. The dots indicate the experimental data, the solid curve is calculated using the Gibbs–Thomson equation.

Glass is colored when it contains particles comparable in size to the wavelength of visible light, meaning they are nano-sized. This explains the bright color of medieval stained glass, which contains metal nanoparticles of various sizes or their oxides. And the electrical conductivity of the material is determined by the mean free path - the distance traveled between two collisions with electron atoms. It is also measured in nanometers. If the size of a metal nanoparticle turns out to be smaller than this distance, then one should expect the appearance of special electrical properties in the material that are not characteristic of a normal metal. Thus, nano-objects are not only small in size, but they are also distinguished by the special properties they exhibit that act as an integral part of the material. For example, the color of "golden ruby" glass or a colloidal solution of gold is not from one gold nanoparticle, but from their ensemble, i.e. a large number of particles located at a certain distance from each other.

Individual nanoparticles containing no more than 1000 atoms are called nanoclusters. The properties of such particles are significantly different from the properties of a crystal containing many atoms. This is due to the special role of the surface. In fact, reactions involving solids occur on the surface rather than in the volume. An example of this is the interaction of zinc with hydrochloric acid. If you look closely, you can see that hydrogen bubbles appear on the surface of the zinc, and the atoms located in the depths do not participate in the reaction. Atoms lying on the surface have more energy because. they have fewer neighbors in the crystal lattice. A gradual decrease in particle size leads to an increase in total surface area, leads to an increase in the share of atoms on the surface and an increase in the role of surface energy. Especially high in nanoclusters where most of the atoms are located on the surface. Therefore, it is not surprising that, for example, nanogold is many times more chemically active than ordinary gold. For example, gold nanoparticles of 55 atoms (diameter 1.4 nm) deposited on the surface of TiO_2 serve as a good catalyst for the selective oxidation of styrene to benzaldehyde by atmospheric oxygen:

$$\mathbf{C6H_5–CH=CH_2 + O_2 \rightarrow C_6H_5–CH=O + H_2O}$$

while gold particles with a diameter of more than 2 nm and more do not show catalytic activity at all.

Aluminum is stable in air, and aluminum nanoparticles are instantly oxidized by atmospheric oxygen, turning into Al2O3 oxide. Studies have shown that in air, aluminum nanoparticles with a diameter of 80 nm are grown with an oxide layer 3 to 5 nm thick. Another example: it is known that ordinary silver does not dissolve in dilute acids (except nitric acid). However, very small silver nanoparticles (no more than 5 atoms) dissolve even in weak acids such as vinegar with the release of hydrogen. It is enough to make the acidity of the solution pH = 5.

The dependence of the physicochemical properties of nanoparticles on their size is called the size effect. This is one of the most important effects in nanochemistry. He already found a theoretical explanation in terms of classical science, that is, chemical thermodynamics. Thus, the size dependence of the melting point is explained by the fact that the atoms inside the nanoparticles experience additional surface pressure that changes the Gibbs energy.

Physical reasons for the unique properties of nanomaterials

The strongest changes in the properties of nanomaterials and nanoparticles occur around 10-100 nm crystallite sizes. For nanoparticles, the proportion of atoms located in a thin surface layer (thickness is usually taken to be about 1 nm) is significantly increased compared to meso- and microparticles. Indeed, the fraction of atoms close to the surface S is proportional to the ratio of the surface area to the volume V of the particle. If we define the characteristic particle size (crystallite) as D, then:$S/V \sim D^2/D^3 \sim 1/D$. Surface atoms, unlike atoms in the bulk of a solid, do not contain all bonds with neighboring atoms. The unsaturation of the bonds is even higher for atoms located on the protrusions and edges of the surface.

Surface atoms, unlike atoms in the bulk of a solid, do not contain all bonds with neighboring atoms. The unsaturation of the bonds is even higher for atoms located on the protrusions and edges of the surface. As a result, strong distortions of the crystal lattice occur in the near-surface layer, and even a change in lattice type is possible. Another point is that the free surface has an infinite capacity for point and line crystal defects (primarily vacancies and dislocations).

At small particle sizes, this effect increases significantly, which can lead to the appearance of many structural defects on the surface and the purification of the nanoparticle material from structural defects and chemical impurities. Currently, it has been found that the processes of deformation and fracture proceed in the thin surface layer before the internal volumes of the metal material, which is mainly the occurrence of a number of physical effects, including. physical yield strength and physical fatigue limit.

For nanoparticles, the entire material acts as a near-surface layer, the thickness of which is estimated to be in the range of 0.5-20 microns. It is also possible to demonstrate subtle physical effects that manifest themselves in the specific nature of the interaction of electrons with a free surface.

Another reason for the unique properties of nanomaterials is the increase in the volume fraction of interfaces with a decrease in the size of grains or crystallites in nanomaterials. In this case, the volume fraction of the following components can be distinguished: interfaces, grain boundaries, and end junctions.

It seems that grain when the size decreases from 1 μm to 2 nm, the volume fraction of the intergranular component (interfaces) increases from 0.3 to 87.5%. At a grain size of about 5 nm, the volume fractions of intergranular and intragranular components reach the same value (50% each). After the grain size is below 10 nm, the fraction of ternary compounds begins to increase strongly. This is due to the anomalous decrease of hardness in this range of grain sizes. Extensive experimental studies have shown that grain boundaries with a high density have a non-equilibrium character due to the presence of grain boundary defects.

This disequilibrium is characterized by the excess energy of grain boundaries and the presence of long-range elastic stresses; grain boundaries have a crystallographically ordered structure, and grain boundary dislocations and their complexes serve as sources of elastic fields. The disproportion of grain boundaries leads to the appearance of high stresses and distortions of the crystal lattice, changes in interatomic distances, and the appearance of significant displacement of atoms up to the loss of long-range order. As a result, the microhardness increases significantly.

Another important factor operating in nanomaterials is the tendency to form clusters. Facilitation of the migration of atoms (groups of atoms) along the surface and across the interfaces, and the presence of attractive forces between them, which are greater for nanomaterials than for conventional materials, is often self-evident. leads to organizing processes. island, columnar and other cluster structures in the substrate. This effect is already being used to create ordered nanostructures for optics and electronics

Another reason for the uniqueness of the properties of nanomaterials is that in transfer processes (diffusion, plastic deformations, etc.), this transfer is associated with the existence of a certain effective mean free path of L_e carriers. In the characteristic dimensions of the area where the transfer processes take place, Le is much larger. carrier scattering is negligible, but at sizes smaller than Le, the transfer begins to be significantly size- and shape-dependent. In the case of nanomaterials as Le. for example, it can be the diffusion length and the mean free path of dislocations.

A number of scientists point to the possibility of manifestation of the quantum size effect for materials with crystallite sizes of D<10 nm in the low nanoscale.

Lecture 12. Modern research methods of nanosystems and nanostructures.

Studying the qualitative and quantitative composition of objects at the molecular level, spectral analysis is mainly used.Spectral analysis is based on the ability of molecules to interact with various types of radiation: electromagnetic and acoustic waves, mass and energy distributions of elementary particles, etc. In the emission and absorption methods of analysis, the composition is determined from the emission or absorption spectra, and the mass spectrometric analysis is carried out from the mass spectra of atomic or molecular ions.

To study nano-objects, the same "classical" methods are used as in chemistry, biology and physics. However, in order to "see" nanoparticles with one's own eyes, it was necessary to create fundamentally new instruments and equipment. Scanning probe microscopes were the first devices that made it possible to observe and move nano-objects.

Nanotools in biology and medicine, these are molecules or supramolecular structures, the size of which does not exceed 150–200 nm, which make it possible to visualize, detect, and correct in situ changes and disturbances in biological structures and their fragments.

Nanodevices have a more complex structure, the size of which does not exceed 3-4 microns. Nanodevices are characterized by the relative autonomy of their functioning and have a much greater selectivity. They are designed to materially change a certain substrate, can provide a multi-stage process and work as external agents.

Nanoneedle designed to study intracellular processes, as well as the delivery of dosed portions of various molecules (fluorescent quantum dots, DNA, RNA). An atomic force microscope probe with an attached multilayer carbon nanotube allows penetration into cells without significant damage to the membrane

One such device (Fig.27)was recently developed and demonstrated by a group of researchers from Drexel Univ., Philadelphia (USA).The authors used multiwalled carbon nanotubes with a diameter of about 200 nm and a length of up to 60 μm.The inner cavity of the nanotube was filled with a ferromagnetic fluid containing iron oxide particles ~10 nm in diameter.

The suspension containing carbon nanotubes was injected into a conventional glass pipette using a syringe. Under the action of an external magnetic field, the nanotubes are oriented along the axis of the pipette, causing them to move in the direction of the hole. A thin glass layer placed between the magnetic wire and the pipette was wetted by the liquid inside the pipette, which contributed to the release of carbon nanotubes from the pipette hole, while the nanotube formed a thin pipette tip.

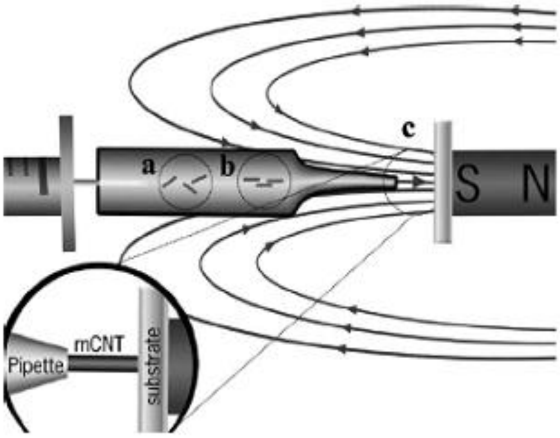


Figure 27. **Device for intracellular manipulations based on carbon nanotubes**

Laser (or optical) tweezers is a device that uses a focused laser beam to move microscopic objects. Near the focal point of a laser beam, light pulls everything around it into focus (Fig.28).

Researchers at Harvard University back in 1999 constructed the first general purpose nanotweezers using a pair of electrically controlled carbon nanotubes. The nanotweezers are designed to capture and move cells without damaging them.

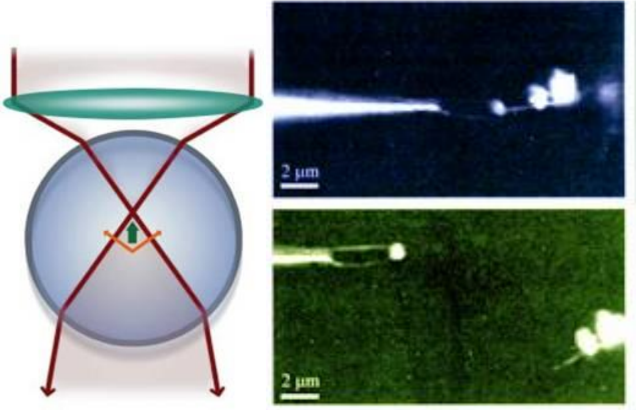


Figure 28. Nanotweezer

The technique for early diagnosis of joint diseases using a scanning atomic force microscope was developed in Swiss clinics. For diagnostics, a nanometer probe of an atomic force microscope (sensor with a needle) is inserted into the knee and the characteristics of the cartilage tissue are studied and the degree of wear of the articular cartilage is determined.

Tiny mouse articular cartilage was used as a model for testing this diagnostic method, which underwent changes as the rodent grew older. Thanks to this, doctors have learned to track changes in a person's joints, even before the onset of symptoms of osteoarthritis.

Japanese scientists led by professor Toshio Fukuda from the University of Nagoya used an organic nanotube 10 μm long, with inner and outer diameters of 50 and 400 nm, respectively, to create a nanopipette.

The tube was fixed in a conventional glass micropipette with an inner diameter of 1.8 μm, and the remaining space between the tubes was filled with a resin that hardens under the action of light.

It is planned to dose the volume of the liquid supplied through the pipette with the help of an electric voltage applied to the nanotube - according to the calculations of scientists, they will be able to achieve an accuracy of the order of a femtoliter, i.e., 10−15 liters.

Such nanopipettes have a great potential for use in medicine, since their working volumes make it possible to carry out operations literally with individual cells (the volume of 1 cell is approximately 1000 femtoliters), introducing or extracting tiny amounts of a substance without damaging the cell itself.

Scientists from the University of California and the Berkeley National Laboratory have managed to create a nanotool with precise spatial positioning capable of delivering dosed portions of various molecules and DNA fragments into the cell (Fig.29). They presented a "needle" based on a carbon nanotube, capable of piercing the cell membrane without damaging it, even with repeated "injection" after half an hour.

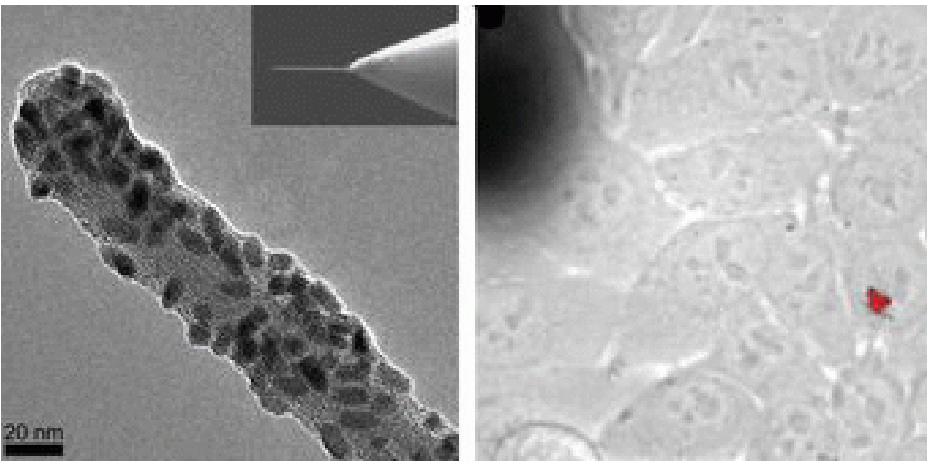


Figure 29. Streptavidin-coated nanoneedle with applied quantum dots. Fluorescence of quantum dots inside the cell.

The original mechanism of the nanosyringe was proposed by scientists at the Department of Bioengineering, Faculty of Biology, Moscow State University Shaitan K.V.,TurlayE.V., Kirpichnikov M.P. This technique is based on the ability of polypeptide molecules to spontaneously pack into a nanotube in a conformation close to the calfa-helix due to thermal fluctuations. Under external influence, these molecules can disintegrate or sharply increase in volume, pushing out the contents of the nanotube, i.e. the system works like a nanogun or nanosyringe.

Lecture 13. Scanning tunneling and atomic strain microscopes.

There are several types of scanning probe microscopes - this is an atomic force microscope (AMS) and a scanning tunneling microscope (STM) operating on a similar principle. There are other types of scanning microscopes: electric force (ESM), magnetic force (MSM), near-field optical (NOM), etc. Scanning probe microscopy (SPM) is one of the most powerful modern methods for studying the morphology and local properties of a solid surface.

The scanning tunneling microscope (STM), the first of a family of probe microscopes, was invented in 1981 by Gerd Binnig and Heinrich Rohrer, who proposed a fairly simple and very effective way to study a surface with the highest resolution up to atomic. For these studies, these Swiss scientists were awarded the Nobel Prize in 1986. The creation of an atomic force microscope capable of feeling the forces of attraction and repulsion that arise between individual atoms made it possible, finally, to see and manipulate nano-objects. Modern electron and atomic force microscopes provide a magnification of 5,000,000 times.

In recent years, the rapid development of nanoscience has become possible due to the availability of methods for determining the structure and structure of nanoobjects. Among them, the most important role belongs to electron microscopy and scanning probe microscopy (it would be more correct to say "nanoscopy").

An ordinary optical microscope, even of the best quality, does not allow to see not only individual atoms, but also nanoparticles. This is because it uses visible light with a wavelength of 400-700 nm to capture the image. It is known from wave optics that radiation with a wavelength l cannot distinguish two objects if the distance between them is much smaller than l. Therefore, in an optical microscope, you can see living cells, the size of which is microns (that is, thousands of nanometers), but smaller things are not visible. This requires radiation with a very short wavelength. In the early 1930s, German engineers E. Ruska and M. Knoll instead of light, as it is known, A way out was found when they proposed the use of a stream of electrons with wave properties and corresponding to a moving electron of a certain wavelength, which depends on its energy. In 1931, Ruska and Knoll created the first electron microscope, which could magnify images only 400 times, but it already incorporated all the principles used in modern instruments.

Currently, electron microscopes can achieve a magnification of 90 million times and a spatial resolution of 0.06 nm, which is smaller than the size of most atoms.

The devices of optical and electron microscopes have many things in common. They consist of a source of radiation, a system for focusing radiation on the object being studied, and a recording device - a detector. In an electron microscope, an electron gun is used as an electron source, an electromagnetic lens is used to focus the electron beam, and a fluorescent screen is used as a detector.

According to the measurement method, transmission and scanning (scanning) electron microscopes are distinguished. They provide different information about the object and are often used together.

In transmission electron microscope, an electron beam passes through a very thin (<100 nm) layer of a substance and provides information about its internal microstructure. A microscope is a device consisting of a long wide tube - an electron gun, a condenser (electron lens) and a fluorescent screen connected to a camera or computer, on which an image appears. An electron gun contains a tungsten filament that is heated by electricity. At this temperature, tungsten atoms begin to emit electrons. Electrons pass into the object in a high vacuum because electrons ionize any gas. In even more powerful microscopes, electrons are created by a silicon crystal in a strong electric field. The object is placed under the microscope not as a fragment, but in the form of a film or thin section. When the microscope is working, the object is illuminated by a beam of electrons. Some of the electrons interacting with the atoms of the substance are bent and fall into the magnetic lens systems, forming an image of the internal structure of the object on a fluorescent screen. Scattered electrons are stopped by diaphragms, which allows you to adjust the contrast of the image.

All microphotographs are mainly black and white, they are not capable of transmitting color, although researchers often give them one color or another. As the electrons are absorbed by the molecules that make up the air, a vacuum is created in the space through which the electron beam passes in the microscope. An electron microscope is a very expensive piece of equipment and is only available in large research laboratories.

In comparison with transmission microscopes the scanning electron microscopes (SEM) (Fig. 22) create an image of the external surface of a sample by scanning it with an electron beam compressed by a magnetic lens at a resolution of about 5 nm. After the light interacts with the surface, the electrons scatter and enter the detector, which registers the signal and converts it into an image of the surface. Signal intensity depends on surface relief, the size of the particles and their chemical composition. All of these can be detected using a scanning electron microscope.

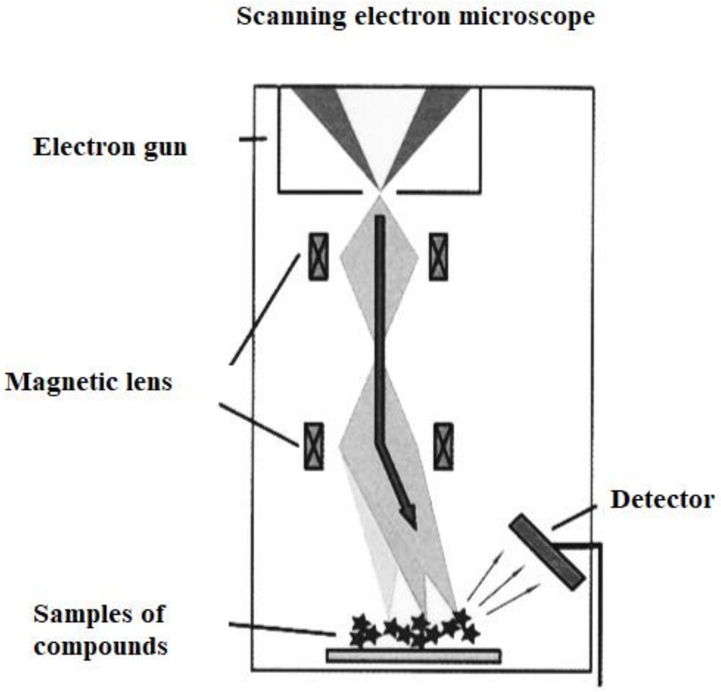


Figure 22. Scanning electron microscope device

There are other types of scanning devices. The first scanning tunneling microscope (STM) was created in 1981. The microscope contains a miniature probe - the thinnest needle made of gold, which slides over the surface of the sample being studied. The tip of this needle is so thin that it consists of only one atom! This allows it to approach the sample to a distance of about one nanometer. A small positive charge appears on the surface of the needle, so electrons flow from the surface of the sample to the probe. In this case, the probe is not in contact with the surface, although it is very close to it! This phenomenon of particles passing through a potential barrier unhindered is called the tunneling effect. The probe moves over the sample and scans the surface using special miniature motors that can set the step to 0.01 nm! Usually, the probe moves along the surface at a constant height and the change in the value of the tunnel current is recorded. The electron current through the probe is converted into an image of the surface. In another method, the probe tip is moved along the sample surface in such a way that the tunneling current is kept constant, while the change in the distance from the probe to the surface is recorded. The trajectory of the probe tip also reflects the surface of the sample.

3.2. Atomic force microscope

In an atomic force microscope (AFM), designed similarly to the STM, the van der Waals repulsion of the probe from the sample surface is measured instead of the tunneling current. The probe has nanometer dimensions and is attached to a micro spring - a cantilever (Fig. 23).

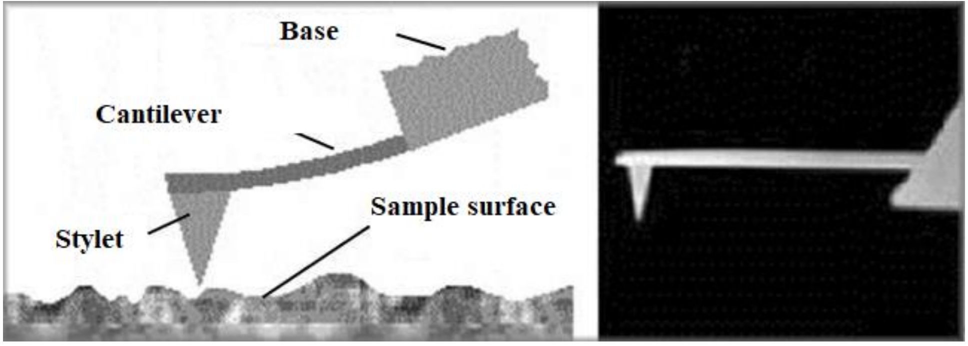


Figure 23. Schematic image and electron micrograph of a typical cantilever with a probe

Forceful interaction of the probe tip with the studied nanoobject leads to the bending of the cantilever, which is usually determined, the value of the bending is studied using an optical system prepared according to the scheme of the optical trap (Fig. 24.). In this scheme, the tilting of the cantilever moves the position of the laser beam, which is reflected in the four-section photodiode. This action changes the ratio of photocurrents from different sections, which are measured using electronic circuits.

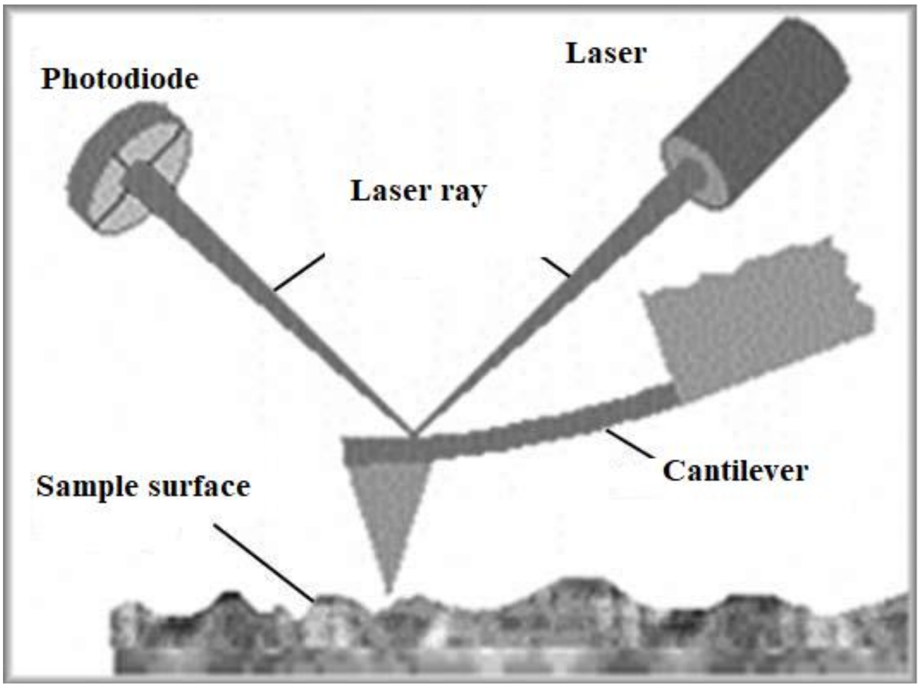


Figure 24. The scheme of the system for measuring the bending value of the cantilever through an optical system

The simplest procedure of AFM work is to measure the bottom relief of the surface. In this case, the sample moves under the probe along a predetermined trajectory, and the cantilever tilt (and the force of interaction between the probe tip and the surface nanostructure) is measured using an optical detection system. The spatial dimensions of the AFM depend on the size of the cantilever and the curvature of its tip, and in principle can exceed the capabilities of the SEM (Fig. 24). Unlike the latter, AFM does not require a very high vacuum and can work in ordinary air or even in a liquid environment, which allows the study of biological objects. The disadvantages of AFM include that it is significantly lower than SEM in terms of scanning speed.

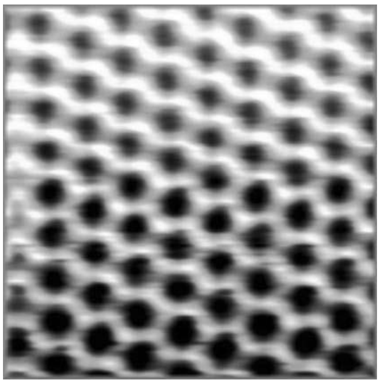


Figure 25. AFM image of graphite surface (www.physik.uni-augsburg.de/exp6). Image size (2×*2) nm*^{2}

Using AFM, it is possible not only to study the arrangement of atoms on the surface of the sample, but also to change the structure of the surface. To do this, use the physical interaction of the probe with the surface, apply its electrochemical oxidation using the probe, or use the interaction of the surface atoms with the probe to mechanically move them from one place to another, thereby performing lithography possible process at the nano level. In 2005, Japanese scientists (Sugimoto Y.E.A. Nature Materials, 2005, V. 4, pp. 156-159) created an image of the chemical signature of tin with 120 atoms of this element using ultrahigh vacuum AFM. germanium on the surface (Fig. 26). Image taken at room temperature.

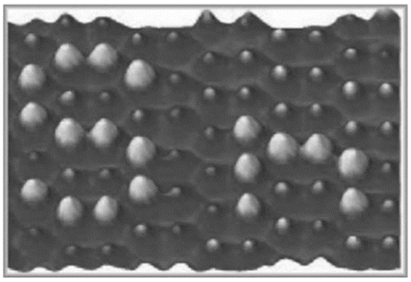


Figure 26. An example of AFM-Nanolithography.Image size (7.7×4.8) nm2

In addition to various types of microscopes, many other physical methods are used to study nano-objects, such as X-ray scattering, spectroscopy, and mass spectrometry. Different methods complement each other well, and it can be noted that it is now possible to describe in detail the actual structure of nanoparticles with high spatial resolution. However, the experimental equipment and research for this is so expensive that it is often difficult to obtain even in large research centers.

Lecture 14. Application of nanosystems in science and technology

Nanotechnology as a scientific and technical direction provides the ability to create and change objects in a controlled way, including the ability to create and change components with dimensions less than 100 nm, which have fundamentally new qualities. and a set of techniques and methods that allow them to be integrated into fully functioning macroscale systems. .

Fundamental studies of phenomena occurring in structures with sizes less than 100 nm have stimulated the development of a new field of knowledge that will bring about revolutionary changes in the technologies of the 21st century in the near future. Such structures correspond to such a state of matter, if radically new phenomena appear and dominate their behavior, including quantum effects, statistical temporal changes of properties and their scaling with the size of the structures, the dominant surface secret, absence. defects in the size of single crystals, significant energy saturation that determines high activity in chemical reactions, sorption processes, sintering (c) 1997, combustion, etc.

The difference between the properties of small particles and the properties of a massive material has been known to scientists for a long time and is used in various fields of technology.

Examples of nanoscale structures include commonly used aerosols, color pigments, and colored glasses colored with colloidal metal particles. Impressive examples are related to biology, where wildlife shows us nanostructures at the level of the cell nucleus. In this sense, nanotechnology itself as a scientific field is not new. The qualitative feature of nanotechnology is a new level of knowledge about the physical and chemical properties of matter.

At the same time, the exclusivity of nanotechnology - new technological technologies of knowledge, conceptual changes in the directions of development of medicine, economic production, changes in ecological, social and military words. properties of nano-sized materials. An important distinguishing feature of the nanometer scale is the ability of molecules to self-organize into structures with different functional purposes, as well as to create structures similar to themselves (self-replication effect). New, unique molecular compounds are made by methods called mechanosynthesis. Experiments have been conducted in which thousands and tens of thousands of molecules not found in natural materials,

The use of the above properties for practical purposes is the essence of nanotechnology. On its basis, examples of nanostructured ultra-hard, ultra-light, corrosion- and wear-resistant materials and coatings, catalysts with a highly developed surface, nanoporous membranes for fine liquid purification systems, and ultra-high-speed nanoelectronic devices have already been introduced.

The special structure and properties of small atomic aggregates are of great scientific interest, because they are intermediate between the structure and properties of isolated atoms and massive (fine) solids. The main question in the study of the state of nanocrystals is whether there is a clear, precise boundary between the state of the bulk substance and the state of the nanocrystal, how quickly it increases, and at what stage of the association of atoms does this or that state appear? if the properties of a bulk crystal are complete, is there a critical size of a grain or particle below which the properties of a nanocrystal appear, and above - for a bulk (bulk) substance? There is no complete answer to this question yet. This is not surprising - after all, this is a general philosophical question about the transition from quantity to quality.

The physical properties of ultradisperse media (UDM) open great prospects for the use of these media in mechanical engineering, the chemical industry, and other areas of science, technology, and industry. It is especially promising to use such tools in the creation of composite materials. A unique combination of mechanical, electrical, thermal, magnetic, optical and other properties was found in dispersed phases. UDM applications are based on the specific characteristics of their properties, which are significantly different from the properties of the same materials in single or polycrystalline, as well as amorphous states.

The variety of properties of UDM is related to the specific nature of the state of atoms and electrons in small particles ($1\text{-}10^2$ nm), which are the main morphological element of UDM. Recently, materials consisting of particles of several nanometers (10^{-9} m) are called nanophase or nanomaterials.

Significant changes in UDM properties occur when individual particle sizes decrease to $\leq 10^2$ nm. In this range, there is a conditional transition region of dimensions, above which the properties of a macroscopic solid dominate, and below, the properties of macromolecules.

As the particle size decreases, the role of the surface increases dramatically, which is comparable to the role of volume effects. When the dimensions less than 10^3 nm are reached, there is a radical change in the arrangement of atoms on the surface of the particles and a change in the nature of interatomic bonds, and then it is often impossible to distinguish bulk and surface properties.

An important parameter of UDM is the particle size distribution.

When changing the function type, the quality of the environment properties may change. Each method is characterized by its own distribution function. Often, the distribution is characterized by a normal or log-normal distribution. Each of them corresponds to a certain mechanism of particle formation. The main mechanisms are: non-diffusion (growth of particles at the phase boundary), diffusion (transport of particles over large distances) and coagulation (particles stick together in collisions). The first mechanism is characterized by a normal distribution, and the third is characterized by a log-normal distribution. The diffusion mechanism results in a mixed distribution with a tail toward larger particles.

A feature of small particles is the imbalance of shape and structure associated with the technological features of production. Manufacturing technology leaves its mark on features that manifest themselves in almost all applications. It can be said that when the technological conditions of synthesis and physico-chemical processing change, a new material is created that remembers the history of its origin right up to its application. The importance of production conditions indicates the need to consider methods of producing small particles.

Science begins with definitions. Everyone is familiar with concepts such as microquantity (mass of substances measured in micrograms), microanalysis (analysis of microsizes), microelectronics (simplified: electronic devices with the smallest dimensions of individual parts in micrometers or fractions of micrometers). The prefix "micro" in numbers means parts per million.

A similar prefix "nano-" (billionth) is often used in numbers. However, if we remember that the size of individual simple molecules is determined by nanometers, we can understand what objects are interesting for nanotechnology. Nanotechnology intersects with various scientific and engineering disciplines, it is difficult to give a single definition. Here are some definitions:

- miniaturization of technology: design and production of intelligent miniature machines programmed to perform specific tasks;
- the art of manipulating materials on an atomic and molecular scale, especially creating microscopic devices (robots);

- the ability to produce objects and structures atom by atom similar to the processes in the cells of living organisms.

Classification of nanotechnologies. There are three directions in nanotechnology: "wet", "dry" and computer.

Nanotechnology refers to the study of biological systems that exist in the aquatic environment and include genetic material, membranes, enzymes (biocatalysts) and other cellular components. Such nanometer-sized structures are known to have emerged and developed as a result of the evolution of organisms.

"Dry" nanotechnology comes from physical chemistry and the science of surface phenomena aimed at obtaining structures from carbon (e.g., nanotubes), silicon, various metals, and inorganic materials in general. His ultimate goal is to create functional devices that can self-assemble like "wet" structures, but without relying on evolution.

Computer nanotechnology makes it possible to model complex molecules and systems, calculate their relative stability and predict their behavior. It takes a long time to create analogues of what nature has created over hundreds of millions of years. Modeling and calculations make it possible to shorten this period dramatically (up to several decades).

Many experts understand nanotechnology as the production and use of materials whose particles or layers are measured in a few nanometers or tens of nanometers. Terms such as nanomaterials, nanocrystals, and nanocomposites are widely used.

Nanotechnology can also be conditionally divided into two areas - nanomaterials technology and molecular nanotechnology.

The chemical and physical properties of pure solids do not depend on their mass and particle size. For example, the solubility of bismuth in copper at room temperature is one. The melting point of pure iron has a single value, the phase transition temperature of pure zirconium dioxide from tetragonal to cubic modification has a single value, as well as the band gap of pure silicon. The same applies to many other properties of substances. However, when moving to nanoparticles, the properties change.

The Gibbs-Thomson equation has been known for a long time and relates the melting temperature of crystals to their size. According to this equation, 50 nm platinum particles should melt not at 2045 K, but at a lower temperature of 300 K. The melting temperature of individual particles of TiC-TiB_2 eutectic of 10 nm is reduced by 450 K compared to the temperature in the conventional system. The transition to nanocrystals leads to an increase in the heat capacity of palladium by more than one and a half times, and four thousand times the solubility of bismuth in copper. increases the self-diffusion coefficient of copper at room temperature by 21 degrees (!). Brittle substances such as TiO_2 and CaF_2 are transformed into plastic in the form of nanoparticles.

It is also important to change the electronic properties of substances and their magnetic properties as the size decreases to nanometers.

The physical nature of most transfer processes will be different. Thus, the transition to the quantum effect in metals is observed at a particle size of 1-2 nm, and in semiconductors at 50-100 nm. This means that nature has set a limit to the miniaturization of modern microelectronic devices, in a few years silicon electronics will reach its limit, and if we set the goal of further miniaturization of electronic devices, we should look now. new principles of their creation.

What is the reason for such drastic changes in the fundamental properties of substances? The answer is obvious: first of all, with a change in the ratio of surface and mass atoms of individual particles. The surface of the most ideal crystal can be thought of as a large two-dimensional or even bulk defect, with the surface atoms usually spaced closer together than the atoms in the crystal lattice volume and having an increased energy reserve. Up to a certain particle size, the proportion of these atoms is small, and their contribution to the general properties of the substance can be neglected. In nanoparticles, the properties of surface atoms become crucial. From this point of view, formations with no more than 1000 atoms and no more than 10 nm in size are considered nanoparticles.

Engineers have long focused on materials with small particle sizes. It is known that they are sintered at lower temperatures than coarse dispersions and in some cases allow to obtain unique products, for example, transparent ceramics. However, the specific properties of these substances make them difficult to obtain. Excessive surface energy causes the nanoparticles to stick together and coalesce. In addition, there is no inert environment for nanoparticles, they are chemically active and often lose their unique properties when they interact with other substances. Obtaining and storing nanomaterials requires great skill from technologists.

A vivid example is the creation of a polymer-based composite that fills silver nanoparticles. At a concentration of only a few ten thousandths of a percent of silver, the composition has an unusually strong bactericidal effect.

Nanoparticles are often obtained in two main ways: from the gas phase (condensation or chemical precipitation, flame processes, plasma, etc.) and colloid-chemical, in particular, sol-gel (transferring the solution to a colloidal state and later). treatment). Nanomaterials include not only equiaxed (same length, width, and height) small-sized particles. These include wires and threads with a diameter of several or tens of nanometers, multilayered forms with the same thickness of individual layers; compositions containing fillers from nanoparticles, nanowires, nanoplates.

The processes of self-assembly of micelle-like structures studied in colloidal chemistry, where the molecules are "different", may play an important role.

Common nanomaterials include fullerenes and carbon nanotubes. In the near future, we can watch TVs hanging on the wall: flat-screen devices where carbon nanotubes will be the emitters (source) of electrons.

Molecular nanotechnology. The basic idea of molecular nanotechnology is to synthesize any stable chemical substance, imagine a molecule, draw its structure, theoretically calculate its stability, and then look for ways to synthesize it, no matter how fantastic they may seem. The famous physicist R. Feynman expressed this idea in 1959: "As I understand it, the principles of physics do not speak of the impossibility of creating things atom by atom."

Lecture 15. Nanostructures based on natural polymers.

Electron microscopic studies of various cellulose materials have been carried out for many years, beginning in 1940. During this time, a very extensive experimental material has been accumulated and very interesting data of a theoretical and applied nature have been obtained. Systematic studies of scientists around the world have shown that one of the main factors determining the properties of polysaccharides, in particular cellulose and chitin, is the so-called supramolecular structure.

For cellulose and chitin, the main elements of the supramolecular structure are microfibrils containing several hundred macromolecules, and microfibrils, in turn, form larger associates, up to 10–20 nm.

Chitin fibrils are highly oriented aggregates of macromolecules 25–50 nm in diameter, which in turn consist of microfibrils 2.5–2.8 nm in diameter.

Researchers in the field of polysaccharides propose to distinguish between some structural elements, and the terminology adopted by them differs from that used by other scientists: macromolecule, crystallite, microfibril, fibril.

Among scientific publications, works on the preparation and electron microscopic studies of cellulose and chitin nanocrystals are widely represented.

A significant contribution to the solution of the problem of the crystallite structure of polysaccharides was made by the works of Renby and employees.

The length of crystallites, according to electron microscopy, ranges from 20–85 nm (for various types

artificial cellulose fibers) up to 65–220 nm (for natural cellulose). At the same time, the shape of crystallites also differs markedly: crystallites of natural cellulose have a pronounced anisodiametric shape (the ratio of length to diameter l/d).

Based on studies of the products of heterogeneous hydrolysis of cellulose, estimates of the sizes of crystallites, Renby concluded that they correspond to the sizes of micelles included in fibrillar elements.

He interpreted these data in terms of the existence of crystalline and amorphous regions along cellulose microfibrils without strict periodicity. Preston as a result of electron microscopy and X-ray studies suggested that the plane of the crystal lattice in crystallites native cellulose are oriented parallel to the surface of the structure elements. The sizes of cellulose crystallites in the transverse direction were determined on the basis of electron microscopic and X-ray data on the expansion of reflections, and a value of 50–62 Å was obtained.

for cotton cellulose. Krassig and Kitchen, studying hydrolyzed cellulose preparations of various origins by electron microscopy, evaluated the strength of fibers after partial hydrolysis and came to the conclusion that the length of cotton “morphological units” (crystallites) is 1200–2000 Å, and that of artificial fiber is 600–1000 Å.

From the above data, it can be seen that there is no agreement in the experimental results on determining the size, nature, and shape of fibrils and microfibrils. Perhaps this is due to the dependence of the structure of cellulose on its source.

In the work of Simonsen, nanocrystals are obtained from wood cellulose in the process of hydrolysis and under

under the influence of shear forces, the particles are then rubbed. It has been microscopically established that cellulose nanocrystals from wood have dimensions from 3 to 5 nm in width and 20–200 nm in length; from cotton - 3–7 nm wide, 100–300 nm long.

Cellulose nanocrystals represent a new alternative for the production of biocompatible and optically transparent nanocomposites with high strength. In the work of Benvides and Kitchenz, water

suspensions of rod-shaped nanocrystals, the length of which, according to electron microscopic data, is in the range from 20 to 400 nm and diameters less than 10 nm, were obtained by acid hydrolysis

cellulose powder. Formation of isotropic and chiral nematic liquid crystal phases was observed as a function of the concentration of cellulose nanocrystals. An aqueous nanocrystalline suspension is a biphasic state between the isotropic and liquid crystalline phases. The relative volume, concentration and size of the particles of each phase were investigated, particle size fractionation achieved

sequential separation of two phases. Transmission electron microscopy shows the dimensional dependence of nanocrystals on phase behavior and degree of fractionation. In this work, the structure and physicochemical properties of polysaccharides were studied and it was concluded that polysaccharides (crab and mushroom chitin, as well as crab chitosan) have a complex supramolecular structure. They belong to fibrillar polymers, and microfibrils consist of amorphous and highly ordered microregions; A consequence of this structure is, firstly, the presence of two glass transition temperatures in polysaccharides. Second, they exhibit several secondary small-scale relaxation transitions of an endothermic nature, which can be attributed to g- and β-transitions. Thus, if we rely on the theory of the amorphous-crystalline structure of polysaccharides, then their supramolecular structure can be characterized by crystallographic parameters, degree crystallinity, crystallite size and defectiveness, structural characteristics of amorphous areas, sizes of fibrillar formations and other parameters. Creation of composite materials containing fillers of nanoscale dispersion level, is a new and promising direction in the development of materials science. One of the promising variants of this direction - the use of natural polysaccharides with a pronounced fibrillar structure, to improve the physical and mechanical properties of various polymers, accelerate their biodegradability at the end of the service life, obtaining polymeric materials with special properties (for example, separating membranes), etc. The limiting factors in the creation of such composites are the dispersion of polysaccharide fibrils to a nanoscale level and, at the same time, the preservation their rod-shaped configuration with a high ratio of length to diameter. An original method for obtaining nanocomposites based on chitin and polyacrylic acid has been developed. polyacrylamide and polylactide, consisting of nanofibrils of the filler - chitin, included in the polymer matrix, with a wide range of degrees of filling - 0.05–25%. Basic dispersant the effect on polysaccharide fibrils was through their preliminary swelling in water or in various aqueous solutions and subsequent polymerization (or polycondensation) of monomers. As conducting polymerization of a water-soluble unsaturated monomer in the interfibrillar space chitin nanofibrils are dispersed in the polymer matrix, giving it exceptional mechanical properties.

properties.

A number of glycerol-plasticized starch (PC) biocomposites have been successfully prepared in using 0-40% by weight of cellulose Rami nanocrystals (RN) as a filler. Nanocrystals Ramies were prepared from ramie fibers by acid hydrolysis and had a length of 538.5±125.3 nm and a diameter 85.4±25.3 nm on average. The morphology, thermal behavior and mechanical properties of the compounds were examined by scanning electron microscope, differential thermal analysis, measurements mechanical properties. The results indicate that the synergistic interaction between fillers and between filler and PC matrix plays a key role in the strengthening of composites. It is shown that at 50% relative humidity in PC/CNC composites, an increase in strength occurs. in tension and Young's modulus from 2.8 to 6.9 MPa and from 56 to 480 MPa, respectively, with an increase in the CNC content from 0 to 40% by weight. Polysaccharides and other cationic polymers are used in pharmaceuticals for their ability to control the release of antibiotics. Chitosan (CHS) provides a long release of the combined medicines. The preparation of CS and CS/DNA NPs of certain sizes and shapes using a new and simple osmotic method has been reported. It has been microscopically established that the average diameter of the CZ NPs is 45 ± 9 nm, and CP/DNA NPs, 38 ± 4 nm. Patented methodology can be easily modulated by variation solvent-non-solvent pair, temperature, type of polymer giving nanoparticles with different sizes. The assembly of natural polysaccharides with inorganic layered solids can also lead to the formation of bionanocomposites in which the biopolymer becomes intercalated between layers of the inorganic host. Intercalation is a complex process that can simultaneously engage in several mechanisms. Thus, in addition to hydrogen bonding, certain biopolymers interact with inorganic layers through ionic bonds, in the case of polysaccharides, proteins and nucleic acids, which can intercalate as polyelectrolytes, through an ion exchange reaction.

By controlling the equilibrium concentration of chitosan in dilute acetic acid, it is possible to control the access of the biopolymer to the space of the montmorillonite intermediate layer, leading to a bionanocomposite with one, two or even more layers of intercalated polymer. The intercalation of chitosan into Namontmorillonite under certain conditions for obtaining a biopolymer can lead to exfoliation of the layered silicate, which is confirmed by the results of transmission electron microscopy. Yongzhe and Simonsen studied CNC and MCC as fillers in CMC nanocomposites.

The composite material was composed of CMC, MCC or ZNK with glycerol as a plasticizer. The concentration of CNA and MCC varied from 5 to 30%, while the concentration of glycerol remained at 10%. For composites filled with CNC, the strength and stiffness are higher compared to the composite with MCC. Some heat treatments impart water resistance to nanocomposites.

CNC is used as a reinforcing material in polymer composites to improve mechanical and physical properties. USDA Forest Products labs have observed an improvement in polypropylene strength at as little as 2% CNA. In this work, the researchers optimized the methods

preparation and obtaining a specific morphology of the composite to further improve the mechanical and physical properties of thermoplastics reinforced with CNC.

The papers consider the use of cellulose NPs, as well as some synthetic and natural polymers in the food industry and agriculture. The problem of overcoming biological incompatibility barriers with the help of specially synthesized NPs based on chitin derivatives is discussed in a review by Prego, Alonsi-Sinde, Vila and others, devoted to topical issues of nanomedicine.

The reviews provide electron micrographs of a large number of different cellulose NPs obtained by acid hydrolysis, which show a wide variety of sizes and shapes. polymer NPs.

A very large number of works that have appeared over the past 5–6 years are devoted to problems associated with NPs in natural polymers, primarily such as cellulose and chitin. Significant Interest

presents an article by Prof. Simonsson of the University of Oregon, which examines the use of various cellulose-containing raw materials and waste from the point of view of opportunities obtaining cellulose NPs from them and their application. The experimental data of the author and other researchers indicate that the introduction of cellulose NPs into various synthetic polymers, primarily

polyethylenes and polypropylenes, as well as polyvinyl chlorides, polyurethanes and others, leads to a sharp

improving a number of their performance characteristics, such as shear modulus, breaking stress, heat resistance, hydrophilicity, gas and air permeability, and many others, and for this it is enough to introduce less than 10% of cellulose NPs. It is very important that such materials are biodegradable. Of particular interest for polymers such as polypropylene is a significant improvement in its dye-up with the addition of 5–7% cellulose NPs, which is very important in the manufacture of fabrics and other products.

The problem of compatibilization in systems of cellulose NPs and a synthetic polymer is especially considered. In this regard, many different approaches are proposed, including physical and chemical modification of the NP surface, chemical modification of the matrix polymer, the use of amphiphilic reagents, hydrophobic and hydrophilic functional groups, etc. Of great interest is the possibility of physical modification of the surface of cellulose NPs by their etching in various gas discharges and treatment with alkalis.

The work of Wang, Kiu and others discusses the possibility of mechanochemical activation of components for obtaining compositions of cellulose - polyethylene, as well as the physicochemical properties of such systems are considered.

The papers present data on the filling of synthetic polymers with cellulose fillers, at the same time, there is a noticeable improvement in the strength characteristics and an increase in the modulus of such compositions, especially at elevated temperatures. Eichorn and Young evaluated the Young's modulus of microcrystalline cellulose in terms of the possibilities of using cellulose fillers.

The problem of compatibilization in systems based on polyolefins and cellulose NPs is considered in a series of papers by Belgasem et al. They propose modification of cellulose NPs with silanes and siloxanes, maleic and phthalic anhydride, epoxidation with dicarboxylic acids, grafting some synthetic polymers to their surface, regulating their chain length, as well as sulfonation and phosphorylation.

Miyazaki and co-workers present data on the improvement in the strength properties and build-up of polypropylene materials when they are formed with the addition of small amounts of cellulose NPs.

A number of works are devoted to the preparation of compositions based on synthetic and natural rubbers reinforced with the so-called Whiskers of chitin (particles several hundred nanometers long, such as elementary fibrils), which form a reinforcing mesh in the matrix. Films from similar compositions on

based on chitosan were obtained by Blackwell et al.
Iolovich and Leikin propose a method for obtaining cellulose NPs in the form of a suspension, paste, and dry
product with a particle size of ~200 nm, which are aggregates of nanocrystals up to 75 nm and 10–15 nm wide. It is planned to use this nanocellulose as an additive to adhesives, paints, paper and to obtain reinforced biodegradable plastics based on PVC.
Detailed reviews on nanocomposites containing cellulose NPs as a filler, problems of their preparation, properties, modifications, and applications are contained in the works.
Nanocomposite films were successfully prepared from cellulose and tourmaline nanocrystals with a diameter of 70 nm. The structure and properties of the composite films were characterized by X-ray diffraction, SEM and TEM studies, differential scanning calorimetry, and tensile testing. The results show that tourmaline nanocrystals were distributed in cellulose matrix, while maintaining the original structure of nanocrystallites in composite films. The loss of peaks in the DTA spectra and the decomposition temperature in the curves of the differential scanning calorimetry of the films of the compositions are significantly shifted towards low temperatures, which indicates that the nanocrystals partially break the intermolecular H-bonds of cellulose and this leads to
decrease in thermal stability. Composite films had good tensile strength (92–107 MPa) and showed a clear antibacterial effect against Staphylococcus aureaus at tourmaline content 4–8% by weight. Thermally sensitive hydroxypropyl cellulose nanoparticles have been synthesized and particle sizes have been studied by light scattering as a function of concentration.
polymers and reaction temperatures.
Nanotube materials were obtained by Japanese scientists using natural cellulose substances (filter paper) as a substrate, and their morphology was determined by scanning and transmission electron microscopy.
Porous and non-porous nanostructures were assembled using cellulose fibers as a substrate with metallic Ag.
New inorganic-organic hybrid materials composed of semiconducting cadmium sulfide (CdS) nanocrystals and regenerated cellulose were obtained using the method
in situ synthesis. Cellulose was dissolved in 6% by weight NaOH/4% by weight aqueous urea/thiourea solution at low temperature followed by the addition of cadmium chloride (CdCl2).

Nanocrystals

CdS were successfully grown in situ in cellulose solution. Nanocomposite films containing homogeneous CdS nanoparticles were obtained by casting them from a solution.

In the work of Lang Sue et al., polymer-nanocrystalline films were obtained using the layer-by-layer deposition method. Monolayers of chitin and cellulose nanocrystals (CNCs) were alternatively absorbed onto Si substrates to obtain a thin film. The elastic modulus of the films was measured by Brillouin light scattering (for 250 nm films). Comparison of the behavior of surface and volume acoustic

regimes made it possible to explain the effect of the thickness of individual layers relative to the total film

thickness. Short CNCs with a length of ~200 nm were obtained by hydrolysis of filter paper powder in sulfuric

acid; crystals with a length of up to several microns - bleaching and hydrolysis using sulfuric acids. It has been shown that the modulus of chitosan/CNA films is higher than that of PDDA/CNA films.

Chitin and cellulose NPs were isolated from shrimp shells and wood pulp, respectively. [40]. The specific surface area of these particles, measured with Congo red dye, ranges from 250 to 350 m2/g, depending on the starting material. woofers have been superficially modified various chemical groups ranging from aliphatic esters to ε-caprolactone oligomers.

The goal was to change the surface of the particles in such a way that their interaction and distribution in the thermoplastic polymer matrix would lead to the creation of improved nanocomposite materials. The growth of interaction and dispersion of particles leads to an improvement in the thermal and mechanical performance of the material.

An analysis of the literature on polysaccharide nanoparticles provides a solution to the general problems of the structure and properties of nanoparticles; it has been established that nanosized particles isolated from polysaccharides have many

properties.

In such compositions, it was possible to observe a fundamental improvement in a number of characteristics, primarily physical and mechanical, especially at elevated temperatures, dyeability, hydrophilicity, biodegradability, etc. Of no less interest are data on the use of polysaccharide NPs as matrices for the immobilization of enzymes and various biologically active substances, in the finishing of textile materials, as components of food and cosmetic products, etc.

Practical work

Topic 1. Essence of nanochemistry

Why has the nanoscale attracted the attention of scientists? Let's think. Imagine that a gold cube with a side of 1 m weighs 19.3 tons and contains a lot of atoms. Let's divide this cube into eight equal parts. Each of them is a cube with an edge equal to half of the original. The total surface has doubled. However, in this case, the properties of the metal itself do not change (Figure 12). We will continue this process further. As the length of the edge of the cube approaches the size of large molecules, the properties of the substance become completely different. We have reached the nano level, ie. obtained cubic nanoparticles of gold, which have a large total surface area, this leads to many unusual properties that distinguish them from ordinary gold. For example, gold nanoparticles are uniformly distributed in water and form a colloidal solution - sol.

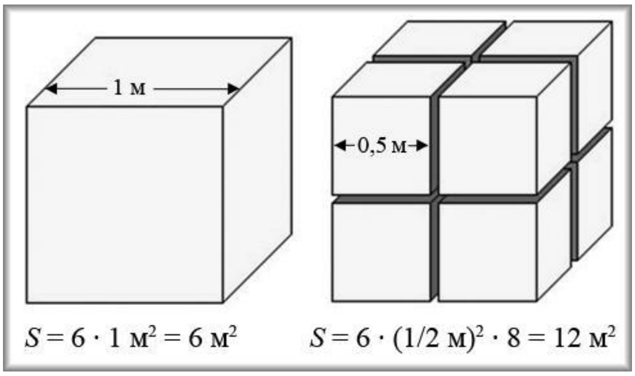


Figure 12. The division of the cube led to an increase in its surface area

Depending on the size of the particles, gold sol can be orange, purple, red and even green in color (Figure 13).

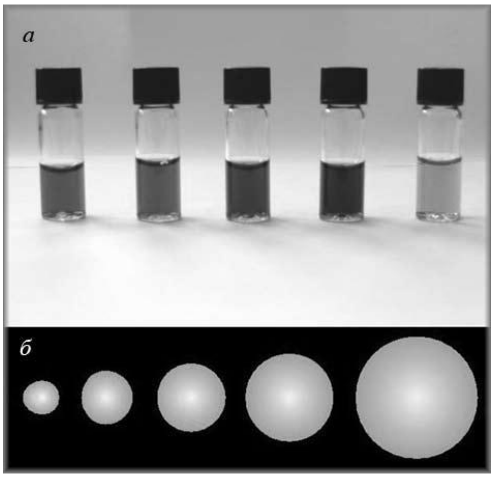


Figure 13. The color of gold sols (a) depending on the size of the particles

The history of obtaining gold salts by reduction of their chemical compounds goes back to the distant past. Perhaps they were called the "elixir of life" made of gold, mentioned by the ancients. The famous physician Paracelsus, who lived in the 16th century, mentions the preparation of "melting gold" and its use in medicine. Scientific research on colloidal gold began only in the 19th century. Interestingly, some of the solutions prepared at that time are still preserved. In 1857, the English physicist M. Faraday proved that the bright color of the solution is due to the small size of the gold particles and their dispersion in suspension. Currently colloidal gold from chloroauric acid (chlorohydrochloric acid). It is prepared by increasing the stability of the sol as a result of reducing it with sodium borohydride in toluene and adding a surfactant to it.

Note that this approach to extracting nanoparticles from individual atoms is bottom-up. This type of nanoparticle synthesis is typical for chemical methods. Above we described the extraction of nanoparticles by splitting the gold cube, now we used the opposite approach - that is, top-down, such methods are based on breaking up the particles using physical methods (Fig.14).

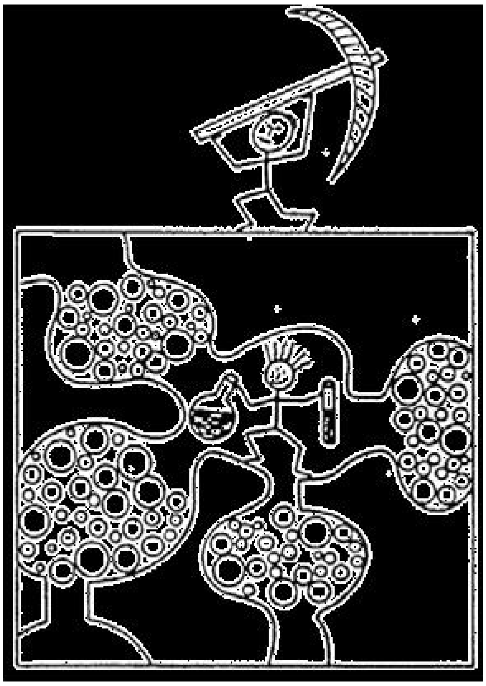


Figure 14. Two approaches to obtaining nanoparticles: above - descending (physical), below - ascending (chemical). (From the book of G.B. Sergeev "Nanochemistry").

Nanoscience develops at the junction of chemistry, physics, material science and computer technology. It has many applications. The use of nanomaterials in electronics is expected to increase the capacity of memory devices by a thousand times and, as a result, reduce their size. It has been proven that the introduction of gold nanoparticles into the body together with X-rays inhibits the growth of cancer cells. Interestingly, gold nanoparticles themselves do not have a healing effect. Their role is to absorb X-rays and direct them to the tumor.

Doctors are also waiting for the completion of clinical trials of biosensors for the diagnosis of oncological diseases. Nanoparticles are already being used to deliver drugs to body tissues and improve the absorption efficiency of poorly soluble drugs. The use of silver nano-particles in packaging films allows to extend the shelf life of products. Nano-particles are used in new types of solar cells and fuel cells - devices that convert fuel combustion energy into electricity. Their use in the future will make it possible to abandon the burning of hydrocarbon fuels in thermal power plants and internal combustion engines of vehicles - and in fact, they are the biggest contributors to the deterioration of the environmental situation on our planet. Thus, nanoparticles serve to create environmentally friendly materials and methods of energy production.

The tasks of nanoscience are aimed at studying the mechanical, electrical, magnetic, optical and chemical properties of nano-objects - substances and materials. Nanochemistry, as one of the components of nanoscience, deals with the development of synthesis methods and the study of the chemical properties of nano-objects. It is closely related to materials science because nano-objects are part of many materials. Medical applications of nanochemistry are important, including the synthesis of substances close to natural proteins or the creation of nanocapsules that serve to transport drugs.

Achievements in the field of nanoscience serve as the basis for the development of nanotechnologies - technological processes of production and use of nano-objects. Nanotechnology is very different from the examples of the chemical industry that are considered in a school chemistry course. This is not surprising - after all, nanotechnologists manipulate objects with a size of 1–100 nm, that is, with particles that have the size of individual large molecules.

There is a strict definition of nanotechnology1: it is the study, design, production of structures, devices and systems to obtain objects of nanoscale elements (1-100 nm) with new chemical, physical, biological properties. The key in this definition is the last part, which emphasizes that the main task of nanotechnology is to obtain objects with new properties.

Nanochemistry as an independent science has emerged in the last 10 years. The study of nanostructures is common to many scientific disciplines, and nanochemistry occupies one of the leading positions among them, as it creates opportunities for the creation, production and research of new nanomaterials superior in quality to natural materials.

Nanochemistry is a science that studies the properties of various nanostructures, as well as develops new methods of obtaining, studying and modifying them. The main task of nanochemistry is to establish the relationship between the size of nanoparticles and their properties.

The equivalent size of nanochemistry research objects is in the nanorange (0.1 - 100 nm).

Nanochemistry is a science that studies the production and properties of various nanosystems. Nanosystems are a collection of bodies surrounded by a gas or liquid medium. Such bodies can be in the form of multi-atomic clusters and molecules, nanocrystals. These are intermediate forms between atoms and macroscopic bodies. Nanochemical objects can be classifyed by phase state (Table 1).

Table 1. Classification of nanochemical objects by phase state

Phase condition	Atomic unit (single atom)	Clusters	Nanoparticles	Compact substances
Diameter, nm	0.1-0.3	0.3-10	10-100	

Number of roofs	1-10	$10\text{-}10^6$	$10^6\text{-}10^9$	More than 10^9

The word "nano" (from the Greek nanos - tiny) means one billionth of something (we are talking about size, so we say nanometer - one billionth of a meter).

An atom (Greek atomos means "indivisible") is the smallest particle of a chemical element. It is known that an atom is not indivisible, because it consists of a nucleus and electrons. For convenience, scientists are considered the atom to have the form of the ball. Several atoms combine to form a molecule. All substances in nature, including humans, consist of atoms and molecules.

All atoms, as well as some small molecules, are known to have a size of 1 nm (nanometer).

Nanotechnology involves the production of products with atomic and molecular structure by manipulating atoms and molecules.

Preliminary studies of nanomaterials have shown that compared to traditional materials, they have fundamental properties such as heat capacity, modulus of elasticity, diffusion coefficient, magnetic properties, mechanical properties, etc. Therefore, nanostructured materials can be considered solid bodies, which are fundamentally different from their usual crystalline or amorphous state.

In the formation of modern professional training and personal professional qualities (basic competencies) of future specialists: development of logical, analytical, critical thinking skills; self development; formation of personal responsibility in decision-making; development of general abilities; accuracy and productivity in solving problems cannot be realized without knowledge in the field of nanotechnology.

The range of objects of nanochemistry is constantly expanding. Chemists have always tried to understand the properties of nanometer-sized objects. This leads to the rapid development of colloidal and macromolecular chemistry.

In the 80s and 90s of the 20th century, electron, atomic force and tunnel microscopy methods made it possible to observe the movements of nanocrystals of metals and inorganic salts, protein molecules, fullerenes and nanotubes (Table 2).

Table 2. Objects of nanochemical research

Nanoparticles	**Nanosystems**

Fullerenes	Crystals, solutions
Tubulins	Aggregates, solutions
Protein molecules	Solutions, crystals
Polymer molecules	taxes,gels
Nanocrystals of inorganic substances	Aerosols, colloidal solutions, precipitates
Micelles	Colloidal solutions
Nanoblocks	Solids
Langmoor–Blodgettfilms	Bodies with a surface film
Clusters in gases	Aerosols
Nanoparticles in layers of different substances	Nanostructured films

Thus, the following main features of nanochemistry can be distinguished:

1. The geometric dimensions of objects correspond to the nanometer scale;
2. Objects and their complex show new properties;
3. It is possible to control and manipulate objects;
4. Other objects and devices assembled on the basis of objects exhibit new consumer characteristics.

Nanoparticles consisting of atoms of inert gases are the simplest nanoobjects. Atoms of inert gases with completely filled electron shells interact weakly with each other through van der Waals forces. The solid sphere model can be used to describe such particles.

Both covalent and metallic bonds can be formed in metal clusters of several atoms. Metal nanoparticles have high reactivity and are often used as catalysts. Metal nanoparticles usually have a regular shape - octahedron, icosahedron, tetradecahedron.

Fractal clusters - objects with a branched structure include: colloids, various aerosols and aerogels. Molecular clusters are clusters composed of molecules. Many clusters are molecular, and their number and diversity are very large. In particular, many biological macromolecules are included in molecular clusters.

Fullerenes are hollow particles formed by polygons of carbon atoms united by covalent bonds. A special place among fullerenes is the C_{60} particle with 60 carbon atoms, similar to a microscopic soccer ball.

Nanotubes are hollow molecules that consist of about 1,000,000 carbon atoms and are single-walled tubes about one nanometer in diameter and several tens of microns in length. On the surface of the nanotube, carbon atoms are arranged at the ends of regular hexagons.

Topic 2. Chemical methods of synthesis

2.2. Chemical methods of synthesis

Precursors for carbon nanotubes are methane or benzene. During the decomposition of methane under the influence of temperature in the presence of a catalyst (transition metal nanoparticles), carbon atoms are formed:

$$CH4 = C + 2H2,$$

catalyst particles alternately form a carbon tube that acts as a nucleus. Carbon atoms accumulate on the surface of the substrate,

the metal passes through the nanoparticle and attaches to the nanotube growing from the bottom up (Fig.18).

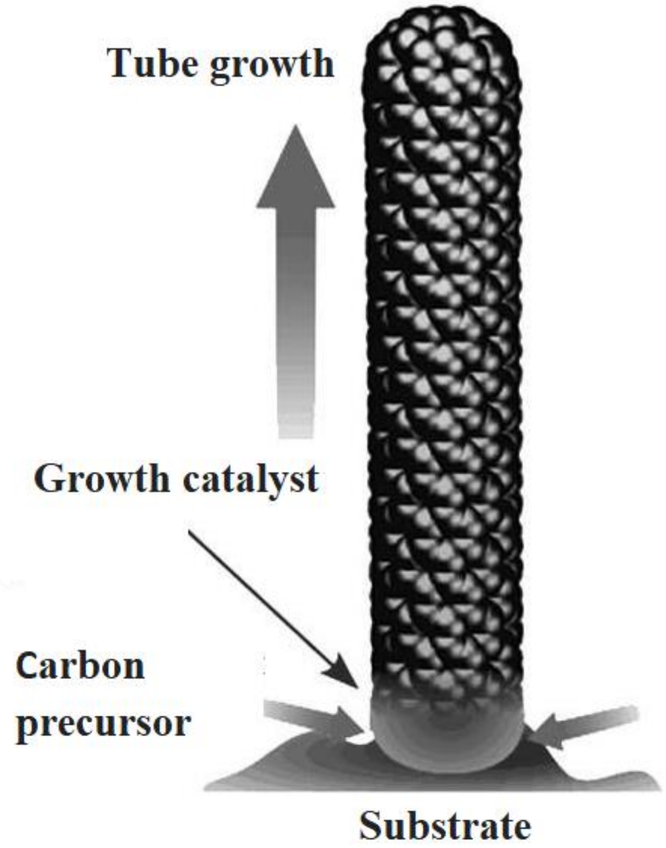


Figure 18. Carbon nanotube formation during methane decomposition

The diameter of the resulting tube is determined by the diameter of the catalyst particle. Instead of methane, other existing hydrocarbons can be used for chemical carbon deposition: ethylene, acetylene, ethane.

During the decomposition of benzene, the tube is no longer formed from atoms, but from carbon six-membered rings (hexagons), which are connected to each other by separating hydrogen molecules. Catalysts such as aromatization (dehydrocyclization) of alkanes are used for this reaction.

Volatile compounds that can dissociate into metal atoms and gas molecules are usually used to obtain metal nanoclusters. For example, nickel carbonyl $Ni(CO)4$, a colorless liquid, readily converts to metallic nickel when heated:

$$\mathbf{Ni(CO)4 = Ni + 4CO}$$

an example is the decomposition of $LiN3$ lithium azide:

$$\mathbf{2LiN3 = 2Li + 3N2}$$

allows obtaining metal clusters with a diameter of less than 5 nm. Individual metal nanoclusters readily react and therefore unstable. To stabilize them, organic molecules - ligands - are attached to atoms located on the surface.

Oxide nanoparticles are more resistant to external influences. They are usually obtained by burning substances in a fire, rather than by decomposition. Nanoparticles of the oxides of these elements are obtained by spraying fine powders of silicon, aluminum and other metals in a fire:

$$\mathbf{Si + O2 = SiO2}$$

$$\mathbf{4Al + 3O2 = 2Al2O3}$$

As a result of oxidation of titanium chloride (IV) vapors with oxygen, nanoparticles of titanium oxide are formed:

$$\mathbf{TiCl4 + O2 = TiO2 + 2Cl2}$$

In all of these reactions, individual oxide nuclei are first formed and then larger nanoparticles are formed. It is important that the oxide particles remain in the reaction zone for a short time - at the level of a thousandth of a second, otherwise they will be so large that they will far exceed the "nanolevel".

Nanoparticles can also be obtained under much milder conditions, for example in the liquid phase. We earlier talked about colloidal solutions of gold, which were obtained by M. Faraday more than 150 years ago. Typically, metal nanoparticles are obtained by reducing various gold(III) compounds, such as salts(Fig.17.).

One of the standard methods for obtaining colloidal solutions of tin, first described in 1951, is the reduction of $NaAuCl_4$ with sodium citrate (medium sodium salt of citric acid) in the presence of 12-aminododecylthiol $H_2N(CH_2)_{12}SH$. In this case, the citric acid salt loses one carboxyl group (decarboxylation occurs), and the secondary alcohol group CH-OH is oxidized to the ketone C=O.

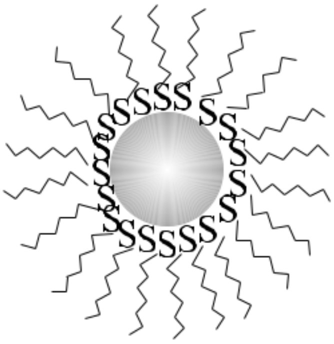


Figure 19. Gold nanoparticle covered with a layer of aminoalkanethiol molecules

In addition, the amino acids on the surface of the nanoparticles make them "soluble" in water - of course, this is not a true solution, but a colloid. The Au-S covalent bond is very strong, so the nanoparticles are stable in solution. The size of the nanoparticles depends on the concentration of 12-aminododocylthiol, which stabilizes them.

A more modern method called the Brust-Shifrin method is used to obtain gold nanoparticles in an organic solvent. It is as follows. An aqueous solution of chloroauric acid $HAuCl_4$ is mixed with an excess of a solution of tetraoctylammonium bromide $[N(C_8H_{17})_4]$ +Br- in toluene. The latter substance in an organic solvent forms a "na-no-reactor", a colloidal particle whose interior is hydrophilic and whose exterior is hydrophobic. In the inner volume of such particles, $HAuCl_4$ chloroauric acid dissolves and thus passes from the aqueous phase to the organic state.

Sodium borohydride $NaBH_4$ is added to the resulting mixture, which serves as a reducing agent. Inside the micelle, $HAuCl_4$ turns into gold, its atoms combine into nanoparticles covered with a $[N(C_8H_{17})_4]^+Br^-$ layer. The size of the formed nanoparticles is from 2 to 6 nm, depending on the concentration of the initial solutions. If desired, nanoparticles can be obtained in solid form - for this, it is enough to evaporate the organic solvent with slight heating. Gold atoms are not strongly bound to the quaternary ammonium salt, so to increase the stability of the nanoparticles, an organic substance containing sulfur, for example, dodecylthiol $C_{12}H_{25}SH$, is added to the solution.

Gold clusters can also be embedded inside titanium oxide nanotubes. A suspension of nanotubes is prepared in water under the influence of ultrasound, and then the required amount of chloroauric acid $HAuCl_4$ is added to the solution. Organic substances that stabilize clusters, for example, thiourea $(NH_2)_2CS$, are also added to the solution. They also act as repellants. The resulting gold nanoparticles enter the nanotubes and stick in them. It remains only to heat the nanotubes to separate them from the solution and remove the organic matter.

Hydrolysis at high temperature is often used to obtain oxide nanoparticles in solutions. Thus, by heating a solution of iron (III) chloride at 95 ° C, a nano powder of iron (III) oxide is obtained:

2FeCl3 + 3H2O = Fe2O3 + 6HCl

In this case, hydrolysis proceeds irreversibly, because the hydrogen chloride formed is poorly soluble in very hot water and comes out in a gaseous state.

As a result, the hydrolysis equilibrium shifts to the right. The iron (III) hydroxide initially formed during hydrolysis decomposes and forms an oxide.

Often, during hydrolysis, individual nanoparticles combine into larger aggregates or form a colloidal solution - a sol, which then turns into an insoluble gel. For example, the hydrolysis of orthosilicic acid esters (tetraalkoxysilanes) results in silicic acid gel:

$$\mathbf{Si(OR)_4 + 3H_2O = SiO_2|H_2O\downarrow + 4ROH}$$

If the researcher is faced with the task of obtaining individual nanoparticles of silicon oxide, then it is necessary to introduce a substance into the solution that prevents the association of individual particles. As a result of polymerization of ethers of unsaturated acids, they form a spatial network (matrix) containing silicon oxide nanoparticles.

Nanoparticles of semiconductor materials are deposited from solutions using exchange reactions. For example, zinc selenide nanoparticles are obtained by passing a stream of hydrogen selenide through a weak solution of zinc acetate:

$$\mathbf{Zn(CH_3COO)_2 + H_2Se = ZnSe\downarrow + 2CH_3COOH.}$$

Surfactants such as oleic acid are added to the salt solution to prevent particles from sticking together and forming a coarse-grained precipitate. Quantum dots are obtained in this way - semiconductor nanocrystals confined in all three spatial dimensions.

It should be noted that all the above synthesis methods lead to the formation of nanoparticles characterized by a certain size distribution. The higher this distribution, the higher the quality of the synthetic method. For example, when reducing palladium (II) compounds with hydrogen, clusters with a diameter of 1.3-2.6 nm, with an average diameter of 2.0 nm, are formed. At the same time, many nanotechnologies require particles of exactly the same size - monodisperse.

To obtain monodisperse systems, the mixture of nanoparticles obtained by traditional methods is separated by size using various physical methods - precipitation, electrophoresis or selective adsorption through molecular sieves. In the second case, porous materials based on silicon oxide with fixed pore sizes are used as adsorbents (Fig.20).

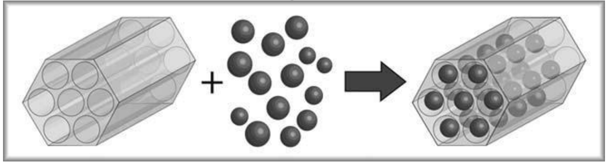


Figure 20. Size-selective adsorption of nanoparticles using molecular sieves (Kolesnik I.V. et al. v Mendeleev Communications, 2009)

The kinetic law of the formation of nano-sized particles is that the formation of the crystal phase occurs at a high speed, but the growth rate is very slow. These characteristics of nanoparticle synthesis determine the technological methods of production.

All methods of obtaining nanoparticles can be divided into two large groups. The first combines methods that allow obtaining and studying nanoparticles, but it is difficult to create new materials based on these methods. These include very low temperature condensation, chemical, photochemical and radiation options, and laser vaporization.

The second group includes methods based on obtaining nanomaterials based on nanoparticles. This includes mechanochemical grinding, gas phase condensation separation, plasma-chemical methods and various other options.

Obtaining particles by enlarging and aggregating individual atoms, or "bottom-up" and "top-down" approaches. The first approach mainly refers to chemical methods of obtaining nano-sized particles, and the second to physical methods.

Extraction of nanoparticles in the gas phase. Obtaining nanoparticles by the "evaporation-condensation" process. The following processes are often carried out in the gas phase: evaporation - condensation (evaporation in an electric arc and plasma), precipitation, topochemical reactions (reduction, oxidation, decomposition of solid phase particles).In the "evaporation-condensation" process, liquid or solid substances are vaporized in a low-pressure inert gas atmosphere at a temperature, and then the vapor is cooled and condensed. This method makes it possible to obtain particles with sizes up to several hundred nanometers. Nanoparticles smaller than 20 nm are usually spherical, while larger ones can be angular. Usually, the vaporizing substance is placed in a heating device and a heating chamber with a diaphragm, through which the vaporized particles of the substance enter the vacuum space (with a pressure of about 0.10-0.01 Pa). a molecular beam is produced. Particles moving in an almost straight line condense on the cooled substrate. Gas is released from the device through a valve.

Topic 3. The main types of nanomaterials structures

The properties of nanomaterials are mainly determined by the distribution nature, shape and chemical composition of the crystallites (nano-sized elements) of which they are composed. In this regard, it is appropriate to classify the structures of nanomaterials according to these characteristics. According to the form of crystallites, nanomaterials are divided into layered

(layered), fibrous (columnar) and equiaxed. Of course, the layer thickness, fiber diameter and grain size take values of 100 nm or less.

According to the chemical composition of crystallites and the characteristics of their boundaries, four groups of nanomaterials are usually distinguished. The first category includes materials with the same chemical composition of crystallites and interfaces. They are also called single-phase. Examples of such materials are pure metals with a nanocrystalline equiaxial structure and layered polycrystalline polymers. The second group includes materials with a different composition of crystallites, but the boundaries of which are the same in chemical composition. The third group includes nanomaterials, in which both crystallites and boundaries have different chemical compositions.

The fourth group is represented by nanomaterials, in which nanoscale deposits (particles, fibers, layers) are distributed in a matrix with a different chemical composition. This group includes, in particular, dispersion reinforced materials.

Single semiconductor nanocrystals (such as zinc sulfide ZnS or cadmium selenide CdSe) with a size of 10–50 nm are called quantum dots.

They are zero-dimensional nano-objects. Such nano-objects contain from one hundred to one hundred thousand atoms. When a quantum semiconductor is irradiated, an "electron-hole" pair (exciton) appears in the quantum dot, whose movement is restricted in all directions. Therefore, the excitation energy levels are discrete. When transitioning from an excited state to a ground state, a quantum dot emits light, and the wavelength depends on the size of the dot. This ability is being used in the development of next-generation lasers and displays.

Quantum dots can also be used as biological markers, linking them to specific proteins. Cadmium is very toxic, so when manufacturing quantum dots based on cadmium selenide, they are covered with a protective shell of zinc sulfide. And zinc is combined with small organic ligands to obtain water-soluble quantum dots needed for biological applications.

The world of nanostructures already created by scientists is very rich and diverse. Almost all macro objects of our ordinary world can be found in it. It has unique flora and fauna, unique lunar landscapes and labyrinths, chaos and order.

A large collection of various images of nanostructures can be found at www.nanometer.ru. Does all this find practical use? Of course not. Nanoscience is still very young - it is only 20 years old! And like any young organism, it develops very quickly and only begins to bring benefits. So far, nanotechnology has been brought to the level of nanotechnology, but the percentage of implementation is constantly growing, and in a few decades our generations will be confused - how could we live without nanotechnology!

The first category includes materials in the form of solid bodies, the size of which does not exceed 100 nm in one, two or three spatial coordinates. Such materials include nano-sized particles (nanoparticles), nanowires and nanofibers, ultra-thin films (thickness less than 100 nm), nanotubes, etc. Such materials can have a single structural element or crystallite (for dust particles) to several layers of them (for). Film). In this context, the first category can be classified as nanomaterials in the form of nanomaterials or nanoproducts with a small amount of structural elements.

The second category includes materials in the form of small-sized products with a characteristic size in the range of approximately 1 μm ... 1 mm. Usually these are wires, tapes, films. Such materials already contain a significant amount of structural elements, and they can be classified as nanomaterials in the form of a large number of structural elements (crystallites) or microproducts.

The third category is massive (or other bulky) nanomaterials with product dimensions in the macro range (more than a few mm). Such materials consist of a large number of nano-sized elements (crystallites) and in fact polycrystalline materials with a grain size of 1...100 nm.

In turn, the third category of nanomaterials can be divided into two classes.

The first class includes single-phase materials (according to the terminology of microstructured homogeneous materials, the structure and/or chemical composition of the material varies only at the atomic level. Their structure, as a rule, is far from equilibrium. Such materials include, for example, glasses, gels, supersaturated solid solutions. The second class includes microstructurally inhomogeneous materials, consisting of nano-sized elements (crystallites, blocks) with different structure and/or composition.

The second and third categories of nanomaterials correspond to narrower definitions of nanocrystalline or nanophase materials.

The fourth category includes composite materials containing components of nanomaterials. In this case, nanomaterials belong to the first category (nanoparticles and/or nanofiber composites, thin film products modified by surface layer or ion implantation) and the second category (for example, composites reinforced with fibers and/or particles). nanostructure, modified nanostructured surface layer or coating materials)

It is also possible to distinguish composite materials with complex use of nanocomponents.

Topic 4. Fullerenes

Fullerenes have become one of the most studied objects of chemistry in the last 20 years. This is the name of the allotropic modification of carbon and composition Cn (n> 20). The most stable of them is a molecule containing 60 carbon atoms, called C_{60} true fullerene. Fullerene has many unusual physical and chemical properties, which make it a very promising object for scientific research and creation of nanotechnology.

The properties of substances are determined by their structure. First consider the structure of the fullerene molecule. It is called "the roundest molecule found in nature": all carbon atoms are located on the surface of the sphere at the ends of pentagons (pentagons) and hexagons (hexagons) (Fig. 38 a). There are a total of 20 hexagons and 12 pentagons, and all pentagons are surrounded by hexagons only, i.e. separated from each other. The radius of the sphere is 0.357 nm. In terms of shape and arrangement of pentagons and hexagons, the molecule completely resembles a soccer ball (Fig. 38 b).

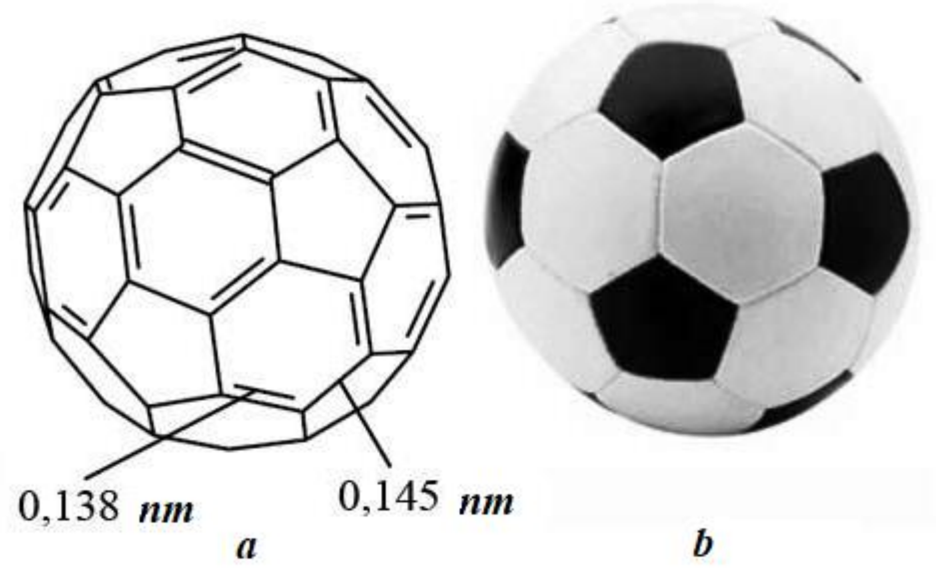


Figure 38. Fullerene C_{60} molecule (a) and soccer ball (b)

Molecules of other fullerenes are much less symmetrical (Figure 30) and thermodynamically less stable than C_{60}. This condition is important to get the second one.

All carbon atoms in C_{60} are in the sp^2 hybrid state. Each atom is connected to three neighbors by single s-bonds. It takes three of the four valence electrons. The fourth electron participates in the formation of the general p-electron system of the molecule. However, in contrast to benzene, the electrons are completely delocalized and the bond length is the same in fullerene, which can be separated by twofold and single bonds, the lengths of which are 0.138 and 0.145 nm, respectively. Therefore, also due to its non-planar structure, fullerene is not considered an aromatic molecule.

Rather, it is considered a globular polyalkene because it contains 30 double bonds that are weakly conjugated to each other. All of them are collected only in six-membered cycles.

The existence of a spherical form of carbon was theoretically proved in the 1970s. and C_{60} molecules were discovered in 1985 by the English scientist G. Kroto and his colleagues in the plasma formed during the laser vaporization of graphite (Fig. 39).

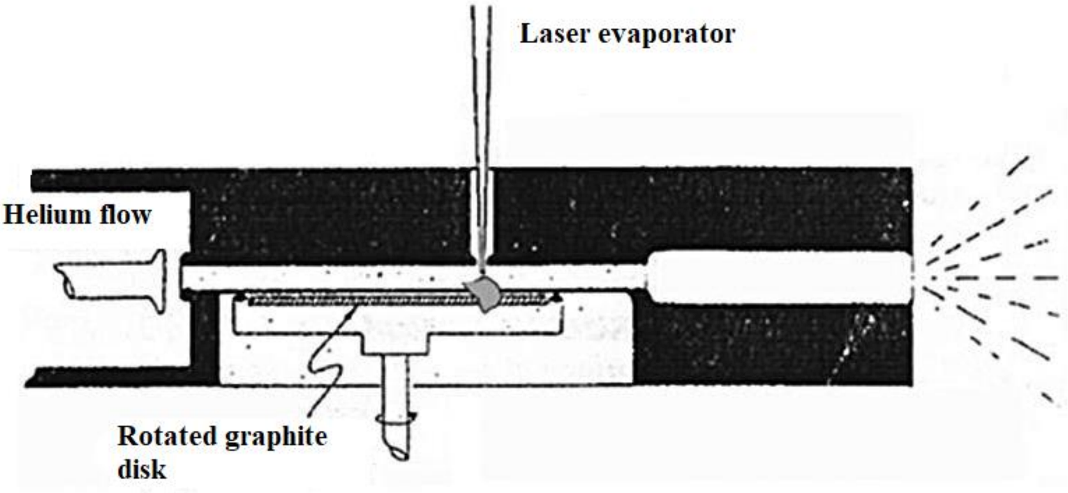


Figure 39. The scheme of device which provided discovered fullerenes

In their experiments, laser light was directed at a disk-shaped graphite target placed in a furnace at a temperature of 1200 ° C. The resulting carbon vapors were carried away by the helium stream and deposited on the walls of the chamber. Analysis of precipitation products using mass spectrometry showed the presence of substances with molecular weights of 720 and 840 in their composition. These were the first fullerenes - C_{60} and C_{70}.

In the first experiment, the yield of fullerene was very low. A few years later, a group of German scientists led by W. Kretchmer and D. Hoffmann synthesized fullerene in macroscales. The electric-arc fusion method they proposed turned out to be very simple. They used an electric arc that occurs between two carbon electrodes due to voltage in the application

In the arc, the temperature reaches several thousand degrees, which leads to the evaporation of graphite from the electrodes. In the cooler parts of the installation, outside the arc, gaseous carbon settles as soot, which contains up to 12% fullerenes, mainly C_{60} with C_{70} added.

Among other cyclic forms of carbon, these two types of fullerenes have the lowest energy, so they accumulate from the gas phase together with graphite. When toluene or other organic solvents are added to the mixture, the fullerenes go into solution. You can separate C_{60} from C_{70} in a chromatographic column.

The electric arc method in various modifications is still the main method of laboratory and industrial production of fullerenes, and it is impossible to achieve their yield higher than 12% on an industrial scale. The commercial price of pure (99.5%) fullerene C60 is about 60 thousand uzbek sums, and 36 thousand sums per gram of unrefined, mixed with C_{70}.

Fullerenes have not yet been found in nature. In the early 1990s, there were reports of their presence in the mineral shungite (named after the village of Shunga in Karelia).

This mineral is mined only in Karelia and is a natural amorphous carbon. In part, these properties were associated with fullerenes, but deeper research did not confirm the presence of fullerenes in shungite.

A solid fullerene has a molecular crystal lattice with C_{60} molecules at its nodes. They are nonpolar, so the van der Waals bonds between them occur due to dispersion interaction (attraction of induced dipole moments). Elementary cell has the shape of a cube: the molecules are located at the ends of the cube and in its middle – such cell is called cubical face-centered.

There are very large spaces between the molecules in the lattice, in which M_3C_{60} may contain alkali metal atoms forming with fullerene compounds, where M = K, Rb, Cs. These compounds are called fullerides. Unlike fullerene itself, fullerides have an ionic crystal lattice.

When heated in an inert atmosphere, fullerene sublimates without melting, when cooled to 260 K, the crystal structure changes: a solid phase with a primitive cubic lattice is formed.

The density of fullerene is 1.7 g/cm3, which is much lower than that of diamond and graphite. It's not surprising - after all fullerene C_{60} has many voids both within and between molecules. Because fullerene is non-polar, it is very poorly soluble in water, and is much more soluble (several grams per liter) in non-polar organic solvents. It is the only allotropic form of carbon that is at least slightly soluble!

Pure fullerene does not conduct electricity. This is because electrons cannot pass between molecules in the crystal lattice.

However, when irradiated with light, the electrical resistance of the crystals decreases, which means that fullerene has photoconductivity. Conductivity can be increased in another way - by adding alkali metal atoms to fullerene. Thus, the fullerides in M_3C_{60} become superconductors at low temperatures. The highest junction temperature is set to the superconducting state (38 K) for cesium fulleride, Cs_3C_{60}. The mechanism of superconductivity in such compounds has not yet been elucidated.

Strictly speaking, fullerene in macroscopic quantities, in the form of powder, is not a nanomaterial, although it is composed of particles and molecules of almost nanometer size. In such a substance, the nanolevel does not manifest itself - for this, it is necessary to create nano-clusters from fullerene molecules or transfer it to a colloidal solution, where the particles of the dispersed phase have tens and hundreds of nanometers.

Consider the chemical properties of fullerene. C_{60} fullerene, which has 30 double bonds in the molecule, has a much higher reactivity.

Since the discovery of fullerene, tens of thousands of compounds based on it have already been obtained, so we can assume that fullerene has become one of the basic building blocks of organic chemistry. Its role in modern chemistry is comparable to that of benzene as the progenitor of a large class of aromatic compounds.

All fullerene derivatives are divided into two classes: "endo" (internal) and "exo" (external). Endohedral - inclusion compounds in which atoms or small molecules are enclosed in a fullerene sphere (denoted by M@C60).

It is not yet possible to insert particles into the already formed fullerene sphere by breaking CC bonds and cross-linking, so endohedral derivatives are prepared at the "time of formation" of fullerenes. If the electrodes used in the electric arc synthesis of fullerene include metal impurities, a small part of them can enter the fullerene sphere formed in the gas phase. The first endohedral compound of lanthanum, $La@C_{60}$, was discovered. The metal in it cannot leave the carbon cage, but retains its magnetic properties and affects the electronic state and reactivity of the carbon cage.

Endohedral compounds are used in medicine, for example, the compound with the funny name "gadofullerene" $Gd@C_{82}$ is used as a label in magnetic resonance imaging.

"Exo" compounds are formed as a result of addition reactions to the double bond of fullerene. In fact, the C_{60} molecule can attach up to 60 monovalent atoms or groups of atoms, but complete attachment is not observed in practice, because in this case the carbon skeleton is very strongly disturbed and the added product becomes unstable.

Fullerene adds hydrogen and halogens under different conditions to ordinary substances. The most saturated compounds with hydrogen and fluorine are $C_{60}H_{36}$ and $C_{60}F_{48}$, respectively.

Addition reactions of compounds allow, first of all, to introduce various functional groups into the fullerene core and thereby change its chemical nature, for example, to obtain biologically active fullerene derivatives that are well soluble in water. Secondly, with the help of such reactions, fullerene can be incorporated into complex supramolecular complexes of various architectures (Fig.40).

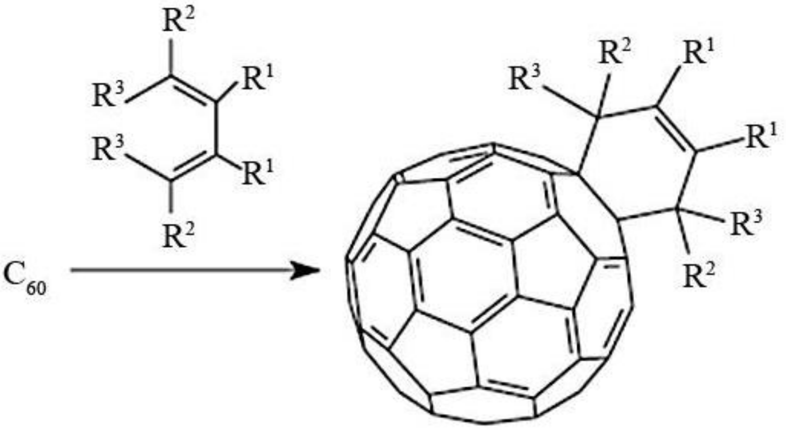


Figure 40. Reaction of incorporating fullerene into supramolecular complexe.

Fullerene easily undergoes nucleophilic, radical and cycloaddition reactions. The latter is especially important for the synthesis of practically important fullerene derivatives. Thus, in diene synthesis reactions ([2+4]-cycloaddition), fullerene acts as a dienophile and adds dienes to form six-membered rings.

[2+1]-cycloaddition reactions lead to the formation of three-membered rings in the fullerene framework. In the Bingel reaction between fullerene and 2-bromomalonic ether, a cyclopropane ring is formed from the double bond of fullerene(Fig. 41.):

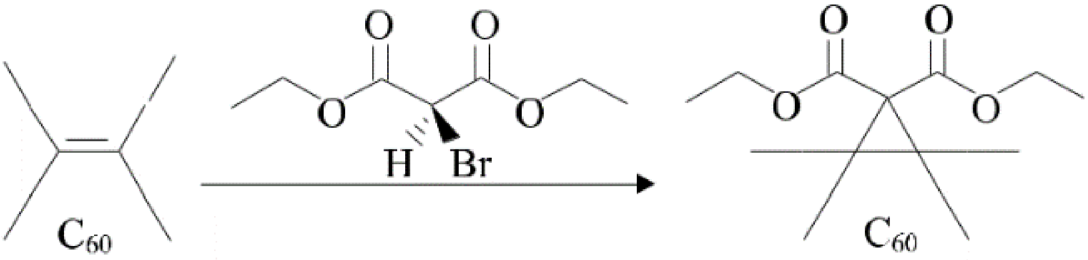


Figure 41. The Bingel reaction between fullerene and 2-bromomalonic ether

This reaction serves as the basis for the construction of various organic nanostructures based on the fullerene fragment.

Reactions of joining fullerene molecules to each other are of the [2+2]-cycloaddition type and occur under UV irradiation of fullerene or under high pressure. Depending on the conditions, a dimer (Fig. 42.), a trimer, a linear polymer, or a two-dimensional array of interconnected fullerene spheres set network can be formed.

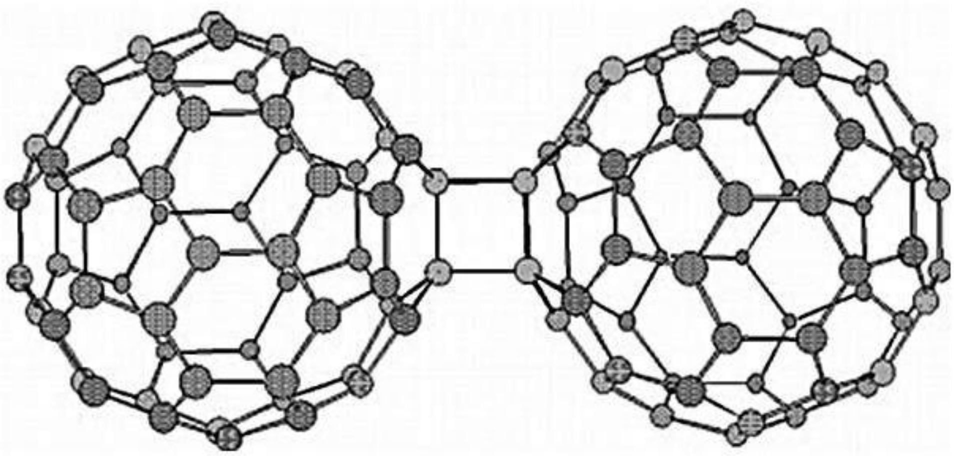


Figure 42. Fullerene dimer C_{120}

The electronic properties of fullerene are very important for applications. Fullerene is an electron-deficient compound and serves as a good electron acceptor. It can accept from one to six electrons. Active metals, complex compounds of transition metals or organic molecules can be donors. Many organic molecules exhibit donor properties when excited.

The electronic state that carbon nanomaterials enter when they absorb light. By combining such molecules in a complex with electron acceptors such as fullerene, devices for converting light energy into electrical energy are obtained. In October 2008, it was reported that the American company Konarka started the production of solar cells, in which an organic polymer served as an electron donor, and nanostructures based on fullerenes served as an acceptor.

Fields of application of fullerene are very diverse. The unique combination of electronic properties, symmetric bulk structure, and high reactivity make fullerene an ideal component for creating supramolecular nanomaterials and electronic devices. Based on it, electrochemical sensors for detecting ions, solid ion-selective electrodes, monolayers generating current in radiation, catalysts for oxidation reactions of organic substances were created. Supramolecular nanocomplexes of fullerene and porphyrins with reverse electron transfer from porphyrins to fullerenes are the basis of artificial photosynthesis devices in the future.

Fullerene derivatives easily penetrate biological membranes, so they are used as labels and indicators in biomedical research. Fullerene easily binds free radicals and can act as an antioxidant in the body. Endohedral compounds inside the radionuclide fullerene can be used to create anticancer drugs. To do this, fullerene is modified with functional groups that allow it to accumulate in tumor cells, after which radioactive radiation from the nuclide inside destroys these cells.

An alternative method of cancer treatment is photodynamic therapy. When irradiated with UV rays, fullerene goes into an excited electronic state and can transfer excess electronic energy to oxygen molecules, which then go into a singlet state. And singlet oxygen is able to destroy diseased cells (Fig.43).

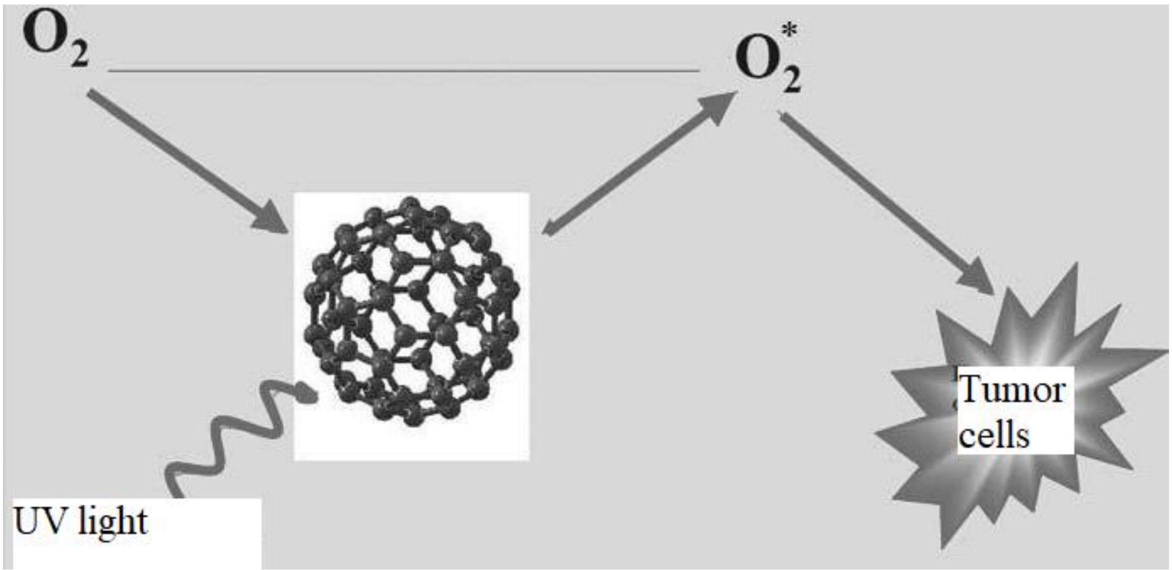


Figure 43. Scheme of photodynamic therapy with fullerene

The main obstacle to the use of fullerene in medicine - its poor solubility - is overcome by chemical modification of the surface of the sphere and the addition of hydrophilic groups to it. Thus, the solubility of hexabasic acid obtained from fullerene is up to 70 g/l. Another way to increase the solubility of fullerene in water is to use surfactants.(Fig. 44.).

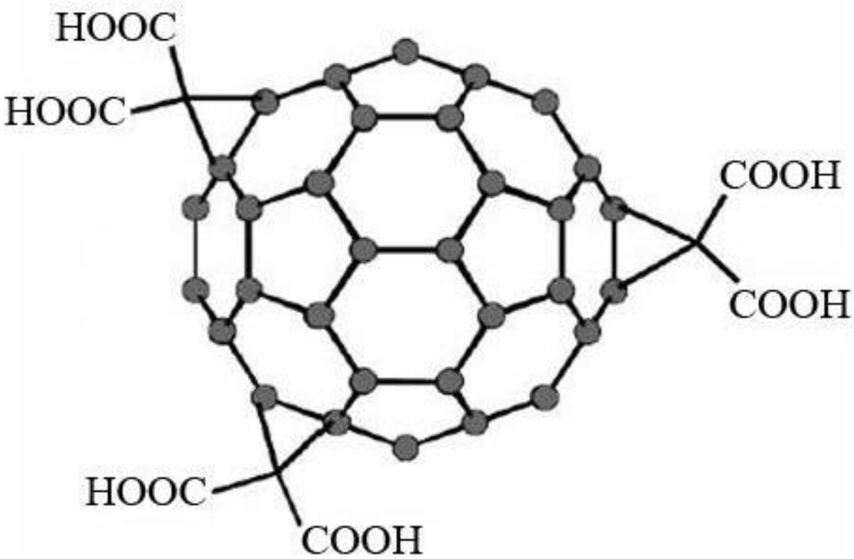


Figure 44. Water-soluble fullerene derivative

An interesting application has been found by fullerene in hydrogen energy. Russian scientists have created a new composite material based on fullerene-containing carbon black and magnesium hydride, which has the ability to recover a record amount of hydrogen and can serve to store this gas in power plants. By adding magnesium hydride powder to glycerine-treated carbon black powder, the scientists prepared a sorbent capable of absorbing up to 65 g/l of hydrogen.

Topic 5. Classification and properties of carbon nanotubes

Another allotropic modification of carbon is close in structure to fullerenes -nanotubes. To visualize their structure, let's turn to the most stable form of carbon - graphite. Its crystal lattice consists of individual planar layers made up of regular hexagonal corners. Each carbon atom in the layer is in an sp2-hybrid state, bonded to three neighboring atoms; the angle between the bonds is 120 °. 3 of the 4 valence electrons of each atom participate in the formation of bonds within the layer. The electron clouds of the remaining electrons slightly overlap each other and connect the individual layers to each other. Bonds between layers are much weaker than bonds within layers.

A planar two-dimensional layer of regular hexagonal carbon atoms is called graphene. In 2004, a group of scientists from England and Russia managed to separate such a layer from a single crystal of graphite and place it in the form of a film on the surface of a silicon substrate. The layer turned out to be uneven - it had a wavy structure (Fig. 45), which confirmed the assumptions of scientists about the instability of two-dimensional crystals. If several layers of graphene are placed on top of each other, then the surface will be flat.

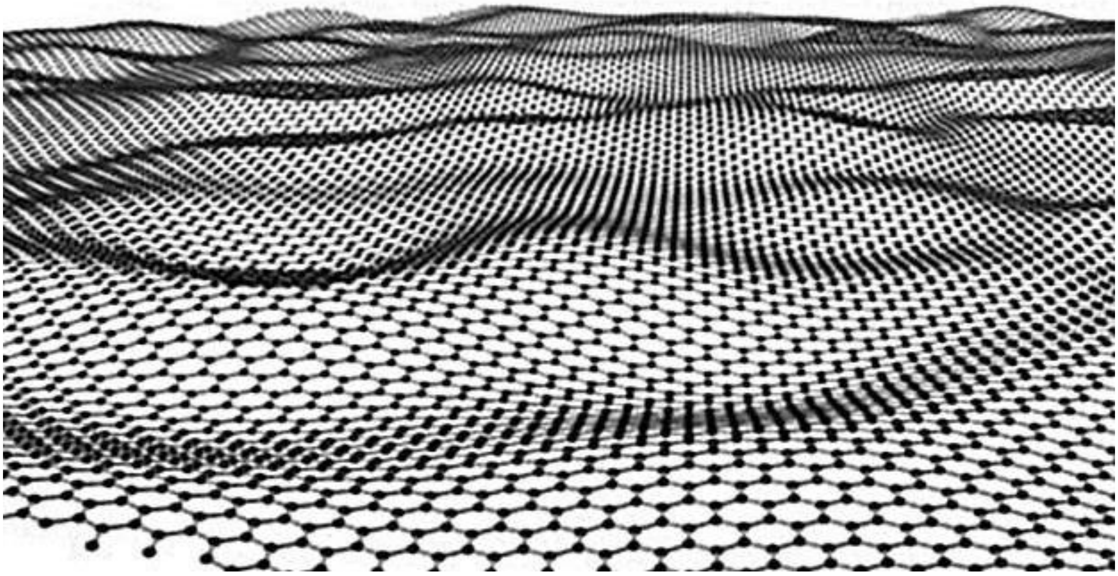


Figure 45. Graphene monolayer structure

If a rectangle is cut from a graphene layer and its opposite edges are connected, a hollow cylinder is obtained (Fig.46). Objects of this shape are called single-walled or single-walled carbon nanotubes.

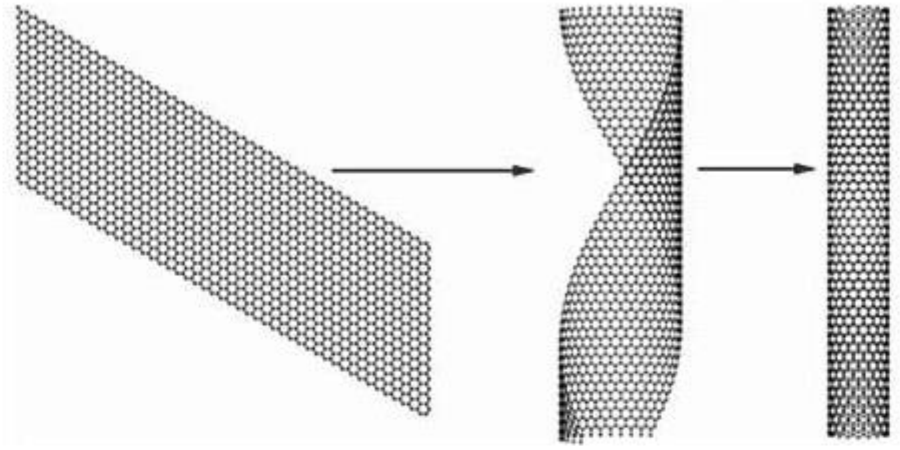


Figure 46. Formation of a single-walled tube when wrapping a graphene layer

Typical tubes have a diameter of several nanometers and a length of one to several micrometers, which allows them to be considered one-dimensional structures. Tubes can be nested inside each other like dolls called multi-walled or multi-layered (Fig. 47).

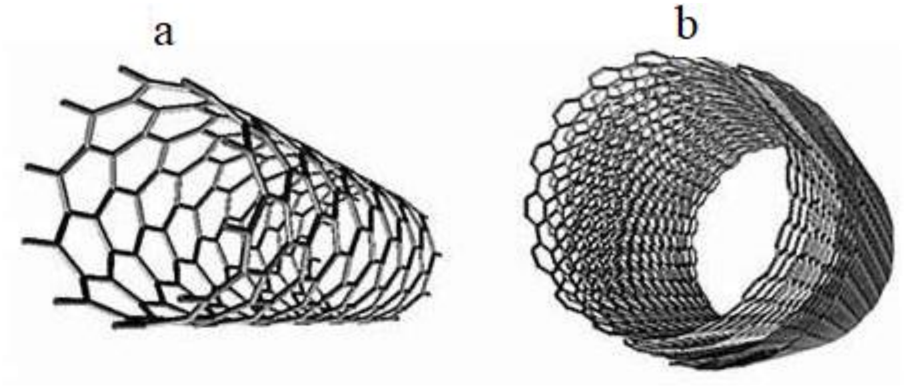


Figure 47. Single-walled (a) and multi-walled (b) carbon nanotubes

Nanotubes were discovered by accident, not as a result of targeted scientific research. In 1991, Japanese scientist Sijima vaporized graphite in an electric arc and obtained a deposit consisting of microscopic filaments and fibers on the cathode. Examination of the deposit using an electron microscope showed that the diameter of the filaments reaches several nanometers, and the length reaches micrometers. These were the first nanotubes. They contained different numbers of graphene layers and were multi-walled. And two years later, Ijima proposed a method of obtaining single-walled nanotubes.

Note that the first method of obtaining nanotubes is very similar to the method of fullerene synthesis. It can be assumed that if G. Kroto predicted to see the soot formed on the walls of the chamber with an electron microscope in 1985, he would have discovered nanotubes almost 6 years before the Japanese scientist.

Currently, three main methods of obtaining nanotubes are used.

1. Catalyst additives - the electric arc method with graphite electrodes containing iron or nickel allows:

mo fullerenes, to obtain a mixture of single- and multi-walled nanotubes with low yields.

2. In chemical vapor deposition, methane or ethanol vapor passes through a substrate heated to 600-800 °C, which decomposes into simple substances. One of the products of the reaction is deposited on the surface of the carbon substrate, forming nanotubes. This method makes it possible to obtain multi-wall pipes with a high yield, but at the same time with a high concentration of defects.

3. The most modern method is based on laser vaporization of graphite catalysts. With its help, the most valuable single-walled nanotubes are obtained, and their characteristics - length and diameter - can be controlled by changing the type of catalyst, changing the temperature or adjusting the parameters of laser radiation.

True, the laser method is also the most expensive. Single-walled nanotubes are distinguished not only by their length and diameter, but also by another property called chirality. This feature is related to how the opening of the nanotube looks like in the plane of graphene (Figure 48.).

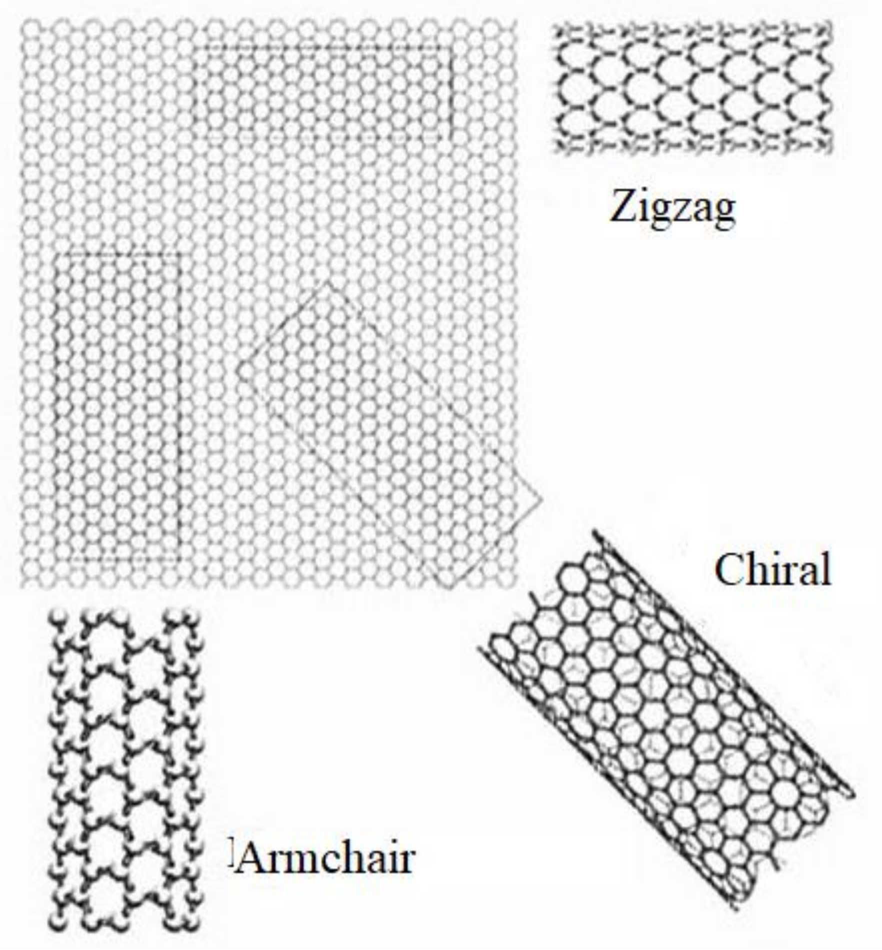


Figure 48. Propagation of nanotubes in the plane of graphene

To quantitatively classify the single-walled tubes in the hexagonal graphene lattice, vectors a1 and a2 are introduced into the hexagonal graphene lattice, as shown in Figure 49. Then AOBBR considers the rectangular distribution of tubes and presents the vector Ch as a linear combination connecting the opposite edges of the rectangle:

$$C_h = n\, a_1 + m\, a_2$$

The vector C_h is called chiral, it defines the diameter of the tubes, and the vector T perpendicular to it is translational, it defines the length of the tube. The set of numbers (n, m) is a characteristic of a nanotube.

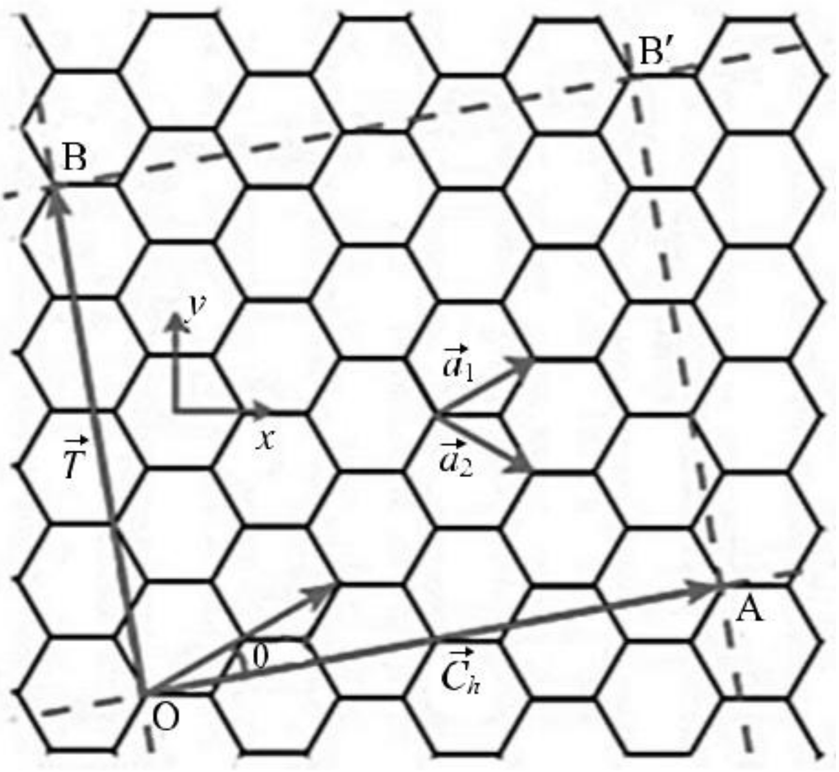


Figure 49. Quantitatively classify the single-walled tubes in the hexagonal graphene lattice

Ideal single-walled nanotubes have only regular hexagonal carbon atoms on their surface. Such nanotubes are cylinders with both ends open. They can be closed on one or both sides with a new type of fullerene or other surface hemispheres, but such tubes will no longer exist. Ideal - in addition to regular hexagons, they have pentagons or triangles on their surface (Fig. 50).

Figure 50. Closed nanotubes

Contains five-membered cycles. What properties make nanotubes a promising target for future nanotechnologies? Firstly, they have very high mechanical strength - single-walled pipes are several times stronger than most steel. Needless to say, nanotubes are not the first graphite-based carbon material. Common carbon fibers formed from long and thin sheets of graphite. Combining low density and high strength, they are widely used in the production of modern tennis rackets, bicycles, racing cars, etc.

However, nanotubes are the strongest carbon fibers. Unlike carbon fiber, nanotubes are not brittle. Therefore, they are used as fillers for polymer composites. The inclusion of carbon nanotubes in the composition of the composite increases the thermal and electrical conductivity of the material, significantly improves its mechanical properties, gives the composition certain functional properties (removal of static charges, scattering and absorption of radio emission, scattering and absorption of laser radiation, enhancement of electroluminescence).

The electrical properties of nanotubes are very interesting. Recall that graphite conducts electricity, its properties are between semiconductors and metals. On the other hand, nanotubes can exhibit both metallic and semiconducting properties depending on their structure, particularly the ratio of n and m indices.

Single-walled tubes have metallic conductivity if (n - m) is divisible by 3, otherwise the tube has a band gap of 0.1 to 0.3 eV is a semiconductor. The current is carried by the majority of nanotubes, that is: all the tubes of the "armchair" type and every third tube (n, m) of any family defined in m.

Like nanodiamonds, nanotubes have a high specific surface area (from 100 to 1000 m^2/g) and are good adsorbents. The presence of holes in the tubes allows them to be used to store gaseous substances or as capsules for active molecules.

Like fullerene, the surface of the nanotubes can be chemically modified to make them soluble. Nanotubes can form supramolecular complexes with biologically active molecules - proteins, polysaccharides, nucleic acids.

These substances can be adsorbed on the surface of the tubes or combined with them through covalent bonds, which allows the use of nanotubes in drug, gene and antigen delivery systems.

Due to their high specific surface area, nanotubes can be used as supports for heterogeneous catalysts. A new-generation miniature hydrogen-oxygen current source for portable devices has been created, in which nanotubes in the form of aggregates about 100 nm in size are part of the electrodes, which act as a substrate for the catalyst.

Nanotubes have at least two advantages over conventional electrodes: first, the reactant gases are hydrogen.

and oxygen - easily penetrate the electrode, and secondly, the catalyst - finely dispersed platinum - is applied to the surface of the tubes. Polyelectrolyte is used as a conductive medium. The energy capacity of the new source is 10 times higher than that of lithium batteries. This allows, for example, to ensure the continuous operation of a laptop for several days. New current sources are miniature, they provide great power, they charge much faster in batteries.

They also have disadvantages: due to the high reactivity of nanoparticles, they can irreversibly react with electrolytes and destroy their structure.

The unique electronic properties of nanotubes are used in diodes, transistors, electronic weapons, and probe microscopes. Because of the mechanical strength of nanotubes, they are used in composite materials, which can be used to produce ultra-light and super-strong fabrics for firefighter and astronaut clothing. Nanotubes are one of the important components of electromechanical nanodevices. It is not easy to list all the possible applications of nanotubes - many of them already exist. Now the main task of researchers is to create technologies that allow to obtain single nanotubes of a given size and shape.

Topic 6. Classification of composite materials by matrix and reinforcing component materials

The characteristics of CMs in terms of matrix material and reinforcing components indicate their physical and chemical nature. According to the material of the matrix, there are:

1) Metal CM or composite materials based on metals and alloys. The most commonly used aluminum, magnesium, titanium, copper and alloys based on them.

2) CM based on intermetallic compounds, when chemical compounds of metals with metals are used as a matrix. This is a relatively new class of CM, in which heat-resistant intermetallic compounds Ti_3Al, TiAl, NiAl, Ni_3Al, etc. are used as the matrix material.

3) Ceramic CM. As the matrix of these materials, inorganic compounds of oxides, carbides, nitrides, etc. are used. This is a new class of CM, which has a perspective as a class of superheat-resistant materials.

4) CM based on non-metallic components. First of all, these are carbon-based CMs, which are considered one of the most promising structural materials, especially in combination with carbon fibers.

5) CM with polymer matrix. Epoxy, polyester and some other thermosetting resins, as well as polymer thermoplastics, are the most common group of structural composites.

Solid fillers are usually used as reinforcing components (fillers) of polymer composite materials (PCM): continuous and discrete fibers of various nature, fabrics and non-woven materials based on these fibers. The most common are plastics reinforced with glass, carbon, organic, boron and some other types of fibers.

Reinforcing components or fillers mainly determine the properties of CM. Currently, the strengthening components are:

- metals and alloys (steel, beryllium, titanium tungsten, etc.);
- non-metals such as carbon and boron;
- ceramics $A1_2O_3$, SiC, TiB_2, TiC, AlN, etc.;
- glasses, for example, glass E and glass S;
- organic substances, for example, lavsan, kevlar, polyethylene, etc.

Topic 7. Polymer nanocomposites

The feature is that the matrix is formed by various polymers that serve as a binder for reinforcement, which can be in the form of fibers, fabrics, films, glass fibers.

Forming of polymer composite materials is carried out by pressing, injection molding, extrusion, spraying.

Mixed polymer composite materials are widely used, they include metal and polymer components that complement each other's properties. For example, dry friction bearings are made of a combination of PTFE and bronze, which ensures self-lubrication and lack of creep.

Materials are created on the basis of polyethylene, polystyrene with fillers in the form of asbestos and other fibers with high strength and rigidity.

According to the structure of the filler, composite materials are divided into the following.

- fibrous (reinforced with fibers and threads),
- layered (films, plates, reinforced with layered fillers),

- dispersion-reinforced or dispersion-reinforced (with filler in the form of fine particles). (Fig. 64).

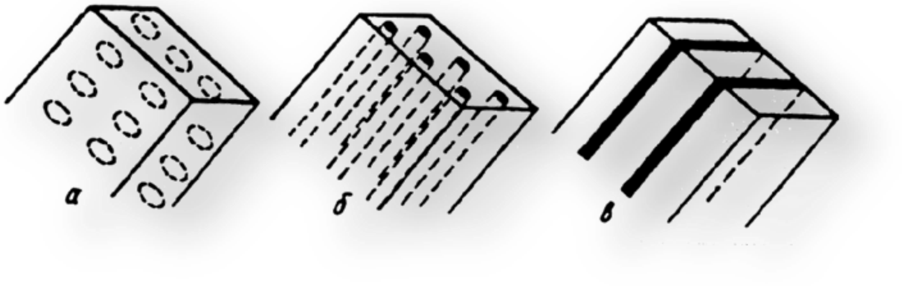


Figure 64. Schemes of the structure of composite materials:

a) solidified by dispersion; b) fibrous; c) layered

1. Reinforcement in fiber CM can be fibers of various forms: threads, tapes, various woven nets. Reinforcement of fiber CM can be carried out according to one-axis, two-axis and three-axis scheme (Fig. 64, a).

The strength and stiffness of such materials are determined by the properties of the reinforcing fibers that take the main load. Reinforcement gives a greater increase in strength, but it is technologically easier to harden the dispersion.

2. Layered composite materials (Fig. 64, b) are assembled from alternating layers of filler and matrix material (sandwich type). Filler layers in such CMs can have different orientations. Filler layers of different materials with different mechanical properties can be used alternately. Non-metallic materials are usually used for layered compositions.

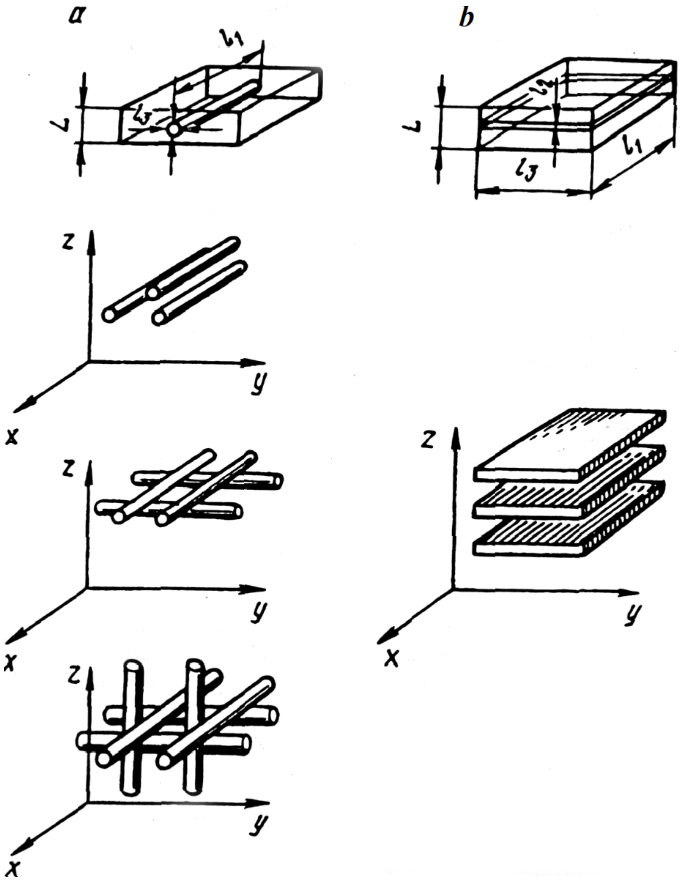


Figure 64. Schemes of reinforcement of fiber (a) and layered (b) composite materials.

3. Small, uniformly distributed refractory particles of carbides, oxides, nitrides, etc., which do not interact with the matrix and do not dissolve in it up to the melting temperature of the phases, are introduced into the CM artificially solidified by dispersion. The smaller the filler particles and the smaller the distance between them, the stronger the CM. unlike fibers, in dispersion-reinforced CMs, the main bearing element is the matrix. The ensemble of dispersed filler particles strengthens the material by resisting the movement of dislocations under load, which prevents plastic deformation. Effective resistance to dislocation motion is created up to the melting temperature of the matrix.

Topic 8. Nanoceramics

Physical methods of obtaining nano powders are of great practical importance, in which the formation of nanoparticles occurs under extreme conditions (high temperature and process speed), which leads to the formation of a disproportionate structure of the dispersed phase.

Therefore, first of all, technologies based on impulse processes with a high rate of change of thermodynamic parameters of the system attract attention.

One of the promising methods of obtaining nano powders of a wide range of inorganic materials is the technology based on the process of electric explosion of the conductor. Depending on the conductors and the type of gas surrounding the metal of the conductor, electric explosion allows obtaining nano powders of metals, alloys, chemical compounds or nano powders with a composite composition.

The main advantages of this technology compared to other physical methods of obtaining nano powders are:

- high efficiency of energy transfer reaches 90%;
- the possibility of flexible regulation of the parameters of the technological process and, accordingly, the characteristics of the obtained nano powders;
- relatively small distribution of size particles;
- low cost of the equipment, its simplicity, small weight and size parameters.

A number of organizations in Russia and abroad have created experimental equipment for the production of nanopowders by electric explosion, their operation shows the prospects of further development of the direction to the industrial level.

When synthesizing nano powders of chemical compounds, the process of electric explosion of the conductor is carried out in an active gas. A number of works have shown the fundamental possibilities of synthesizing iodides, sulfides, magnesium and aluminum carbides, aluminum nitrides, magnesium, titanium, zinc, zirconium, tantalum and rhodium, metal carbides and fluorides under electric explosion conditions.

Carbide release can be controlled by varying the amount of electrical energy supplied to the wire and the subsequent rate of decrease in the temperature of the gaseous medium. The discharge of nitride increases with the charging voltage of the capacitors and the gas pressure surrounding the conductor. As the concentration of oxygen in the argon atmosphere increases, the yield of aluminum oxide increases.

A special feature of nano powders is that they are sintered in the front of a self-propagating thermal wave, which allows us to talk about the presence of excess stored energy in the powders. This is due to the presence of an energy-saturated charge structure in the particles. In the temperature range of 200-270 ° C, the excess energy of silver nano powder was 370-740 kJ/kg.

It is promising to synthesize nanofibers of aluminum oxide phases and use them as highly effective sorbents of inorganic pollutants, to change the composition of lubricants, to use electro explosive nanopowders as catalysts for synthesizing aluminum nitride during combustion of nanowire mixtures. Dispersed aluminum powders and particles for the production of ultrafine molybdenum disulfide are their agglomeration.

Sintering of metal nanopowders leads to the formation of mass agglomerates of strongly connected particles in nanopowder - fractal clusters.

The study of the fractal dimension (D) of aluminum nano powders showed that its value is in the range of $2.57 \leq D \leq 2.93$ and increases with the increase of the average particle size.

It follows from the self-similarity of the fractal cluster that an increase in powder dispersion leads to an increase in the average size of the agglomerates in the powder.

A study of the properties of aluminum nitride particles, the dependence of the dispersion of nano powders of aluminum oxide and nitride and the composition of the chemical compound in the powder on the parameters of electric explosion, as well as a comparative analysis. heats of formation of chemical compounds and vaporization of metals indicate that formation of chemical compounds occurs immediately adjacent to the particle surface or in the vapor-gas region on the particle surface.

During the nitriding process, a solid reaction product is formed, the cluster coagulation process stops, and the particle growth stops. In the process of oxidation, the reaction product is in the liquid phase and the growth of the particles can continue, in particular, with an increase in the pressure of the gaseous environment.

During the nitriding reaction, the average size of the particles should not exceed 10 nm. However, the actual particle sizes of the composites are significantly higher (average size is about 50 nm). This confirms that cluster coagulation begins before the bulk of the explosion products mix with the gas surrounding the conductor.

Depending on the type of gas (Ar, N_2 or NH_3, Ar + O_2) and the metal of the conductor, metal particles or particles of oxides (according to the Al_2O_3 diagram) or nitrides (according to the AlN diagram) are formed. The dashed line shows the conditional limit of loss of continuity of explosion products.

Different methods of powder metallurgy - compaction of nano powders, solid plastic deformation and crystallization from an amorphous state - provide wide opportunities for obtaining nanomaterials. The compressibility of dispersed powders is significantly affected by parameters such as average particle size, amount of impurities, surface condition, particle shape and pressing method. Uniaxial pressing is widely used for pressing nano powders: static (in molds, stamping), dynamic (magnetic pulse, explosive) and vibration (ultrasound). To obtain homogeneous materials of high density, comprehensive (isostatic) pressing is used: hydrostatic, gas-static, quasi-hydrostatic (in special molds under high pressure). The intensive plastic deformation (PD) method is also used - twisting under high pressure.

A promising way to obtain nanomaterials is the sintering of nanopowders under pressure. Hot isostatic pressing and high temperature gas extrusion methods are used to obtain compacts of Ni, Fe and WC-Co nanopowders with solid properties.

The PD method, which consists of compression with large deformations at relatively low temperatures (below 0.3-0.4 Tmelt, where Tmelt is the melting point of the material) under conditions of high applied pressure, allows obtaining large amounts of non-porous nanocrystalline metals. and alloys. Traditional methods of deformation - rolling, drawing, pressing, etc. ultimately lead to a decrease in the section of the processed part and do not allow to achieve a large degree of grain refinement. Unconventional methods - twisting under hydrostatic pressure, equal channel angular pressing, variable bending - allow the workpiece to be deformed without changing the cross-section and shape, and the desired high level of deformation and grain refinement. As of today, nano- and sub-microcrystalline structures were obtained during PD in metals and their alloys. Such a structure leads to a change in physical and mechanical properties (a significant increase in strength while maintaining plasticity, an increase in wear resistance, and the manifestation of high-speed and low-temperature superplasticity).

Topic 9. Nanomaterials for fuel cells

At moderate temperatures, hydrogen is oxidized in fuel cells - this is the name of the device where the energy of oxidation-reduction reactions is converted.

converted into electricity. In a fuel cell, oxidation and reduction reactions take place at different electrodes - cathode and anode - and are separated in space. Between the electrodes is an electrolyte - usually an alkaline or acid solution. The efficiency of fuel cells is the highest among various devices that generate electricity; for the best samples it can reach 90%.

Many types of hydrogen fuel cells have been developed, differing in electrolyte type, operating temperature, power, and efficiency. The main types of fuel cells and their properties are listed in the table.

Let's look at the design of these devices on the example of one of the modern types, a fuel cell with a proton-permeable membrane. It uses porous electrodes coated with a catalyst (thin platinum metals), and a solid polymer membrane acts as an electrolyte, which conducts protons in an aqueous solution, but does not conduct electricity.

At the anode, the catalyst accelerates the conversion of molecular hydrogen into hydrogen ions (H^+) and electrons. H^+ ions pass through the membrane to the cathode, where they react with atmospheric oxygen in the presence of a catalyst and turn into water. Free electrons enter the outer circuit. General chemical reaction:

$$H_2 + 1/2O_2 = H_2O$$

Table 8. The main types of fuel cells (FC) and their properties

Alkaline FC	The electrolyte is a concentrated KOH solution (85% in high temperature cells and 35-50% at low temperatures (< 120 °C)). This FC was used in spaceships "Buran" and "Shuttle". Requires pure oxygen therefore electricity is expensive, under Earth conditions is rarely used. Normal efficiency - 60%
Proton-permeable membrane FC	The electrolyte is a permeable solid polymer membrane. It forms H^+ ions. High current density, small mass, volume and price. Low operating temperature - (below 100 °C). These fuel cells are ideal for transportation application of small stationary sources nix flow. Contribution - 5% of the total heat production capacity
Phosphoric acid FC	Electrolyte - 100% phosphoric acid, contains embedded in a silicon carbide matrix. These are fuel cells were the first to find a commercial application: energy sources in hospitals, airports. Efficiency: from 40 to 85%.

Carbonated FC	The electrolyte is a mixture of sodium and potassium carbonates, $LiAlO_2$ is present in the ceramic matrix. Operating temperature - from 600 to 700 ° C, catalyst - nickel. Efficiency - from 60 to 80%. USA and Japan demonstrated mini-installation, with using these fuel cells with a capacity of up to 1.8 MV.
Solid oxide FC	Electrolyte is a conductive ceramic material Containing O_2- ions, usually it is ZrO. Operating temperature - from 650 to 1000 ° C. Efficiency - 60%. Suitable for large-scale use noncommensurate current sources.

Compared to other current sources, these fuel cells (Table 8.) provide more power per unit mass, they are compact, light and operate at a low temperature of about 80 °C. Due to these qualities, they are the most promising energy sources that can replace automobile internal combustion engines.

Alkaline fuel cells are used in autonomous power systems in astronautics and the Navy. Their main disadvantage is the need to use pure oxygen, not air, as an oxidizer, since the presence of CO_2 in the reacting gases is unacceptable. In solid oxide fuel cells, the role of an electrical conductor is played by oxygen ions O^{2-}. Electrolyte is a thin layer of ceramic material that conducts O^{2-} ions.

Ceramic is a nanostructured composition based on metallic nickel and zirconium oxide added with yttrium oxide ($Ni - ZrO_2 (Y_2O_3)$).

In the composite, ZrO_2 (Y_2O_3) serves to transport O^{2-} ions, while metallic Ni is necessary to remove electrons and atomize molecular hydrogen to a certain extent. In addition, the reactant must be in a highly dispersed form to increase the surface area. The composite is a porous material that contains a package of open horizontal zirconium dioxide tubes with an inner diameter and a wall thickness of 3-5 nm, freely permeable to gaseous hydrogen, and filled with nanoclusters of metallic nickel.

During the operation of the element at the cathode, oxygen molecules attach electrons and are converted into ions, which pass through the composite and participate in the oxidation of molecular hydrogen to water:

$$1/2O_2 + 2e = O^{2-} \text{ –reduction (cathode);}$$

$$H_2 + O^{2-} - 2e = H_2O \text{ –oxidation (anode).}$$

The released electrons enter the external circuit, which creates an electric current.

Solid oxide cells operate at temperatures from 600 to 1000 ° C - the highest temperature of all chemical power sources. Their efficiency is also one of the highest - about 60%.

In addition, solid oxide elements do not require expensive catalysts, and the requirements for the purity of the reactant gases are very simple. All this makes solid oxide fuel cells prime candidates for the role of current sources in many industries.

How does nanochemistry contribute to the development of hydrogen energy? One application we have considered is the synthesis of nanostructured materials for ion-conducting membranes. Another, related, is related to the deposition of catalysts on the surface of the electrodes.

In alkaline and acidic fuel cells, expensive platinum is used as an oxidation and reduction catalyst. To create economically useful resources, the amount of platinum in them should be reduced at least 4 times compared to the existing one (while maintaining the overall catalytic activity). To do this, you can reduce the size of the catalyst particles to nanometers, which increases the specific surface of the catalyst. Another, more elegant method is to prepare the catalyst particles not only of a certain size, but also of the desired shape, which provides the most reaction centers per unit surface.

All these problems are solved by nanochemistry methods and can be brought to the level of technology. Finally, you can add cheaper metals like nickel to save the catalyst.

Nanostructured materials are also used to produce electrodes. Thus, carbon nanotubes can serve as electrodes in miniature current sources. By creating specially shaped tubes, it is possible to dramatically increase not only the gas permeability of the electrodes, but also the activity of the catalyst deposited on the tubes. Controlling the structure and properties of the "electrode-catalyst" system at the nanometer level is the basis of future hydrogen energy technologies.

Topic 10. Obtaining polymer blends

Polymer blends can be produced in a variety of ways, but the most common is melt blending of polymers. In this method, the main type of deformation is shear. The mixing of high-viscosity polymers with each other or with loose or liquid ingredients is carried out mainly under the action of mechanical forces (due to the high viscosity of the mixture, diffusion is extremely slow). The ingredients are introduced in the form of more or less large pieces (from a few mm to tens of cm), which are also crushed during the mixing process (i.e., are subjected to dispersion). The operational characteristics of products depend not only on the uniformity of the distribution of the mixed ingredients, but also on the completeness of the course of physical and chemical processes during mixing, for example, the swelling of the polymer in the plasticizer.

The mixing process includes several stages: grinding of solid components; introduction of components into the rubber; dispersion of agglomerates; mixing.

The mixing mechanism of components can be considered as a deformation of a multicomponent system, as a result of which the thickness of the layers of mixed materials decreases and the contact surface between them increases. Shear deformations in the system during mixing should occur until the thickness of the layers becomes sufficiently small.

The total shear strain will be equal to the product of the shear rate and the mixing time. An increase in shear stresses always contributes to the intensification of dispersion. Each system has its own critical shear stress, below which it does not occur. If the dispersion is insufficient, the properties of the vulcanizates may deteriorate.

In order to obtain vulcanizates with good properties from rubber compounds having low viscosity when shear stresses are low, it is necessary to increase the mixing time, i.e. shear deformation.

The process of mixing rubber with ingredients is accompanied by a number of physical, chemical and chemical phenomena that significantly affect the state of the mixture and the mixing itself.

When mixing, diffusion and dissolution of some components in the mixture occur, which leads, on the one hand, to their more uniform distribution, and on the other hand (especially with the introduction of plasticizers), to a significant decrease in viscosity and shear stress. In the case of the introduction of some powdered rubber-insoluble ingredients (carbon black), a significant increase in the viscosity of the mixture is possible due to the formation of a strong carbon black-rubber structure (carbon black gel).

When mixed, as a result of the action of emerging shear stresses, mechanochemical processes occur: the destruction of the polymer, accompanied by a decrease in its viscosity (plastication), and the activation of the interaction of the polymer with the filler, accompanied by an increase in viscosity.

The action of various factors that determine the mixing process often turns out to be mutually opposite, therefore, the mixing mode should be selected in accordance with the equipment used, taking into account the composition of the rubber compound, the requirements for the quality of the mixture, and the economic indicators of the mixing process.

In order to obtain a high quality rubber compound, it is necessary in the mixing process: to ensure deformation and shear stress sufficient for mixing and dispersion, but not leading to replasticization of the mixture; to determine the optimal temperature conditions of the process, on which shear stresses, energy consumption during mixing, thermal-oxidative degradation of rubber and scorching of the rubber mixture depend, and also to ensure a high intensity of the process, which determines labor productivity.

Mixing in solution. This is a mixture of two solutions of polymers in a common solvent. If the mixture of solutions is transparent, then it is single-phase, and the concentration of the mixture of polymers is less than the critical concentration of separation of these polymers in a common solvent. The “worse” the solvent is, the lower its thermodynamic affinity for the polymer, the lower the delamination concentration.

When a film of the mixture is obtained by drying, with the slow removal of the solvent, the delamination occurs so deeply and completely that a transparent film can be obtained, consisting of completely separated layers of one and the other polymer. By rapidly removing the volatile solvent, good dispersion of the dispersed phase particles in the matrix polymer can be achieved after removal of the solvent. Even better dispersion in the mixture is achieved if a clear solution of the mixture is poured into a large amount of a precipitant (usually methyl alcohol or acetone).

Molecular dispersion of the polymer in the polymer can be achieved by sublimation of the solvent from a frozen solution of the mixture (eg in benzene). The solution concentration should be equal to or lower than the coil overlap concentration. Such a low concentration of the initial solution also affects the supramolecular structure of each polymer, so that, for example, natural rubber or gutta-percha sublimated from a 1% solution have several times lower strength while maintaining crystallinity.

Mixing in the polymer-monomer system. Elastomers swell well in monomers of a different chemical nature, just as thermoplastics can be soluble in a wide range of monomers. If the monomer contains a polymerization initiator, it may polymerize in the bulk of the polymer. A highly dispersed mixture of polymers is obtained. The peculiarity of the process is that with an increase in the molecular weight of the polymerizing monomer, delamination occurs in microvolumes of the swollen mass and particles of the dispersed phase are formed. In the 1980s–90s, intensive work was carried out to obtain interpenetrating polymer networks (IPNs). Ideally, these are two compatible cross-linked polymers one inside the other. The two networks are not chemically bound into each other, but they are also inseparable as a result of the presence of fixed entanglements of dissimilar macromolecules.

The mixture of ethyl acrylate and epoxy oligomer contains a polyamine hardener. Upon heating, the polycondensation of the oligomer occurs with the formation of a network polymer, and upon subsequent irradiation of the mixture with UV light, the polymerization of ethyl acrylate occurs.

Topic 11. Application of nanocatalysts

The great prospects of catalysis by nanoparticles are related to two situations. First, as the particle size decreases, an increasing fraction of atoms appears on the surface and a smaller and smaller fraction appears in the volume, so the catalyst consisting of nanoparticles has a large specific surface and can be very active in heterogeneous reactions.

Second, there is a size effect: many properties of nanoparticles depend on their size, so by changing the latter, not only the activity, but also the selectivity of the nanocatalyst can be controlled.

So, for example, in the work of Professor B.V. Romanovsky with colleagues, the size effect was proved for the oxidation of methanol on a mixed oxide of lanthanum and cobalt $LaCoO_3$ (Fig. 83).

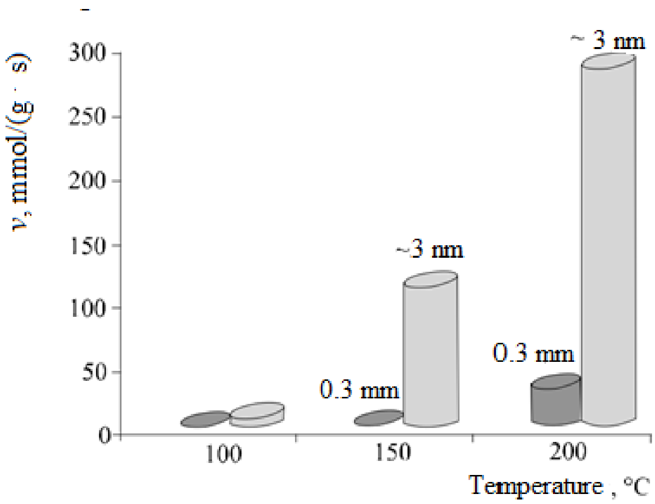


Figure 83. Dependence of the rate of methanol oxidation onLaCoO3 at different temperatures from the particle size of the catalyst.

When catalyst particles are reduced to nanometer sizes, the increase in the reaction rate was observed. The catalytic properties of nanoparticles were first discovered in mid. 1990s. It turned out that gold nanoclusters containing from8 to 20 atoms, catalyze the oxidation of carbon monoxide with oxygen:

$$2CO+O_2= 2CO_2$$

at low temperatures, down to -70 °C. Under these conditions, ordinary gold does not show any activity. When the particle size decreases to 5 nm and below, the crystal structure of the metal changes there is a catalytic effect. Similar picture observed for other noble metals - platinum, rhodium, palladium. The reaction yield depends on the number of atoms in the metal cluster and temperature (Fig. 84). For each cluster, there is an optimal temperature at which the catalyst is most efficient.

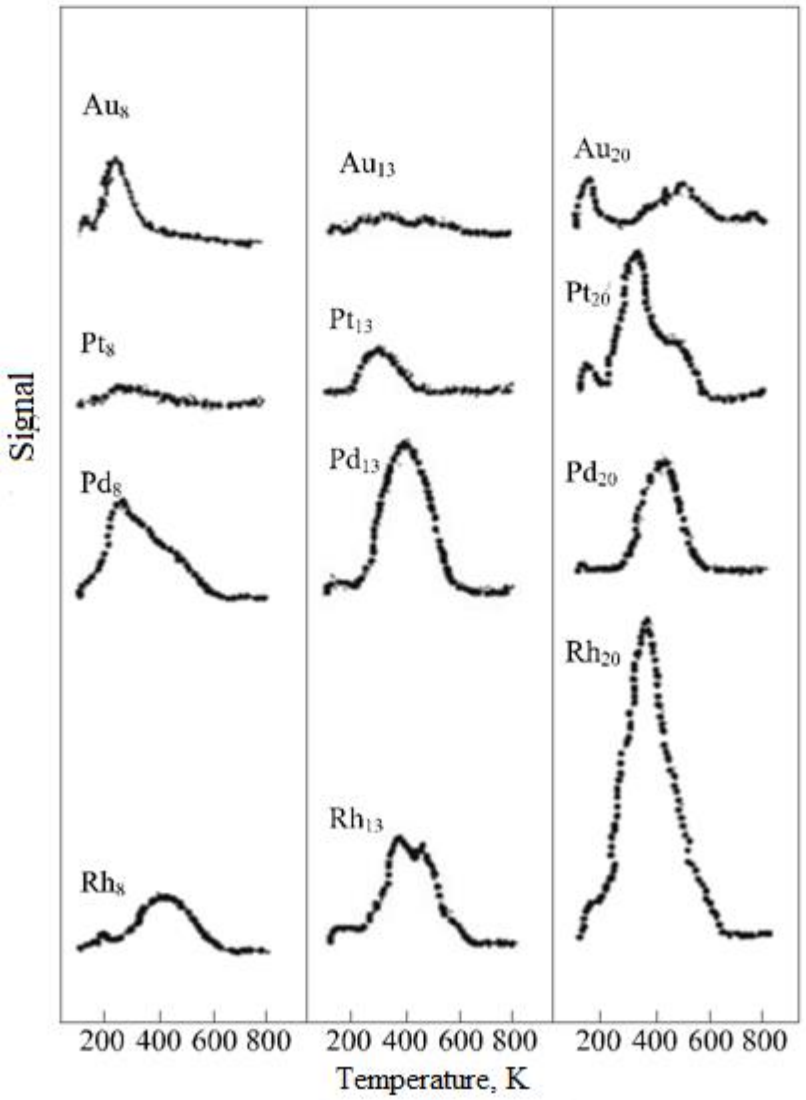


Figure 84. Dependence of CO2 yield during CO oxidationon temperature and number of atoms in a metal cluster (Heiz U., Sanchez A., Abbet S., Schneider W.D Chem. Phys., 2000, v. 262, p. 189–200.)

Nanoclusters themselves are not yet catalysts. For the production of catalysts, metal nanoparticles are prepared either in the form of colloidal solutions or applied to a solid support. In the latter case, metal clusters are obtained in the gas phase, separated by size (number of atoms), and then deposited on a substrate—a thin film of metal oxide (MgO, TiO_2, Fe_2O_3) (Fig. 85). The film thickness is several nanometers, or about a dozen molecular layers. The thickness of the film and its structure have a great influence on the properties of the catalyst: the most active are those clusters that are located near the point defects of the film.

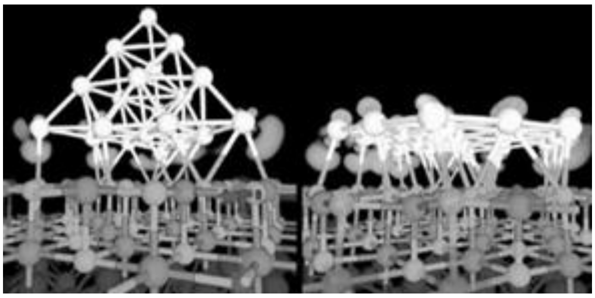


Figure 85. Gold nanoclusters on film MgO. Depending on the film thickness, the clusters have a bulk or planar structure

Interestingly, even a single metal atom deposited on a film can serve as a catalyst. So, for example, for the synthesis of benzene from acetylene according to the scheme requires high temperature (600 °C) and activated charcoal in as a conventional catalyst. In the presence of MgO films containing isolated palladium atoms, benzene is formed even at room temperature (although in a low yield).

$$\mathbf{3C_2H_2 \rightarrow C_6H_6}$$

But for a reaction proceeding at a higher temperature, 150 °C, requires a cluster containing at least 7 palladium atoms. Calculations show that in all cases the film plays a key role - inert atoms palladium are activated due to charge transfer from film defects. To explain the dependence of the nanocatalyst activity on particle size can be used principles of thermodynamics. An increase in internal pressure leads to an increase in the molar Gibbs energy of a substance in a nanoparticle compared to the bulk phase. Let us find out on a specific example how this can affect the properties of the catalyst.

Particles can use the principles of thermodynamics. Before we mentioned that a substance enclosed in a small spherical volume is under increased pressure due to the effect of surface tension. An increase in internal pressure leads to an increase in the molar Gibbs energy of the substance in the nanoparticle compared to the bulk phase. Let's see how this can affect the properties of the catalyst in a concrete example.

Metals of the iron subgroup are effective catalysts for the hydrogenation of CO (Fisher-Tropsch reaction):

Fe, Co

$$SO + 3H_2 \rightarrow SH_4 + H_2O$$

The catalyst (for example, cobalt) is often used in the form solid spherical nanoparticles (Fig. 86). Reducing the particle size of the catalyst significantly increases the catalytic activity.

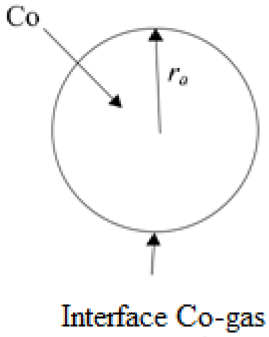


Figure 86. Spherical particle cobalt

However, with a decrease in the size of Co particles, a side reaction of catalyst oxidation begins to occur:

$$Co\ (solid) + H_2O\ (g.) \rightarrow CoO\ (solid.) + H_2(g.).$$

In this case, a bulk phase of cobalt oxide is formed in the reaction vessel. This leads to irreversible weight loss of the catalyst. Cobalt oxide can also form on the surface of solid cobalt particles. In this case, a spherical oxide layer forms around the catalyst particles (Fig. 87), and the catalytic activity decreases.

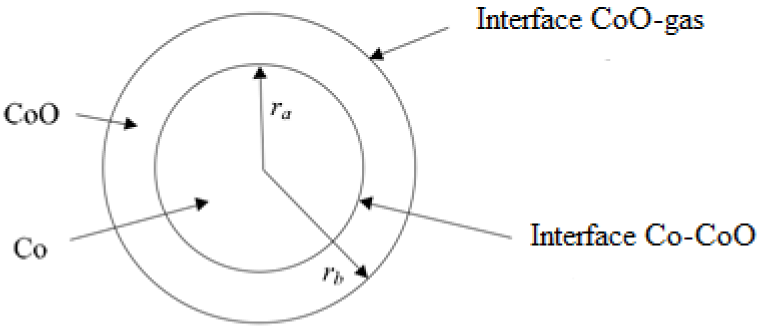


Figure 87. Spherical particle Co coated with a spherical layer of CoO

Thermodynamic calculations show that if oxidation results in the formation of a bulk CoO phase, then to protect cobalt nanoparticles from oxidation it is necessary to increase their size r_a. If cobalt oxide itself is a part of the nanoparticles (see Fig. 87.), then to prevent catalyst oxidation, it is necessary to reduce the nanoparticle radius r_a. Thus, we see that particle size reduction can promote both beneficial and undesirable reactions.

Another type of catalysts whose active centers have nanometer sizes are microporous crystalline aluminosilicates, or zeolites. According to their composition, they can be considered as mixed oxides of aluminium, silicon and alkali or alkaline earth metals. They may also include water of crystallization. For example, natural faujasite zeolite has the composition: $29MOx29Al_2O_3x134SiO_2x240H_2O$, where M = Na_2, Ca, Mg.

The properties of zeolites are determined by the presence in their structure many channels and cavities that can accommodate foreign ions or neutral molecules (Fig. 88). Aluminosilicate channels and cavities are strong enough, thereforezeolites can serve as a medium for chemical reactions to occur in them. Because of this, they have long been used in many industrial processes; however, only in the last two decades, technologies for the directed synthesis of zeolites with specified nanometer sizes of channels and cavities have been developed. This paved the way for the creation of entire classes highly selective catalysts for the petrochemical industry So, the synthetic zeolite ZSM-5 (from the English Zeo lite Socony Mobil) of $Na_n[Al_nSi_{96-n}O_{192}]and16H_2O$($n < 27$) is used to synthesize p-xylene (1,4-dimethylbenzene) from toluene and methanol

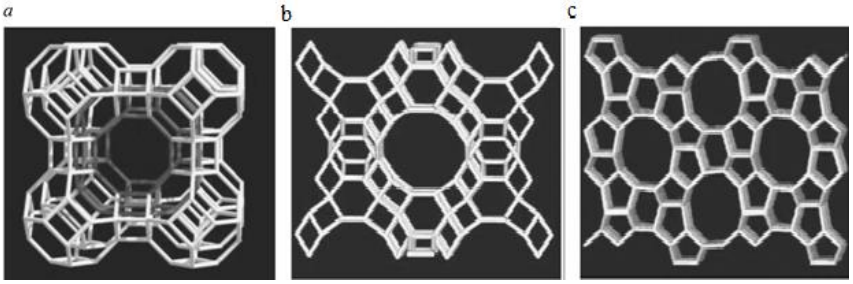


Figure 88. Some types of porous structure of zeolites: a – zeolite A; b – zeolite Y; c – zeolite ZSM-5

The reaction takes place inside the cavity of the zeolite. Product reaction has a linear structure and is able to quickly diffuse through the channels of the zeolite. Along with p-xylene, some amounts of ortho- and meta-isomers are also formed, however, due to their larger size, they are retained inside the channels and, therefore, are much less mobile (Fig. 89). Thus, the ZSM-5 catalyst exhibits high selectivity in this reaction. This is a consequence of the structural correspondence between the diameter of zeolite channels and the size of p-xylene molecules.

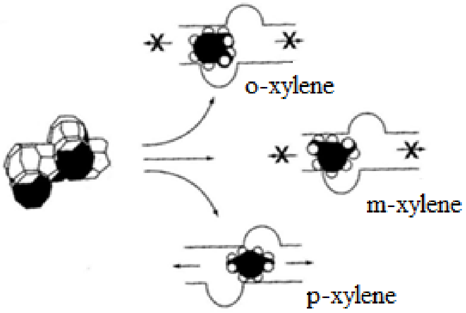


Figure 89. Diffusion of isomeric xylenes through zeolite channels

The selectivity of nanocatalysts can be associated not only with the structural, but also with the energy effect. Recently, in 2008 it was found that gold nanoclusters Au_{55}, deposited on the surface of silicon dioxide serve as catalysts for the selective oxidation of styrene $C_6H_5CH=CH_2$atmospheric oxygen to benzaldehyde, $C_6H_5CH=O$; the selectivity of the process exceeds 80%. This is due to the fact that nanoparticles adsorb molecular oxygen and contribute to its dissociation on the surface to atomic oxygen. The latter serves as an oxidizing agent, and the oxidation occurs only partially and stops at the aldehyde stage.

One of the interesting and promising applications of nanoparticles is related to photocatalytic reactions. Photocatalysis called the change in the rate of reaction caused by the combined action of light and a catalyst. There are several types of photocatalytic reactions: in some, light acts on the catalyst, turning it into an active state, after which a normal chemical reaction occurs; in others, the light is absorbed by the substrate, and the catalyst accelerates the photochemical transformation.

Let us consider the mechanism of action of photocatalysts using the example of one of the most common - titanium dioxide TiO_2 (Fig. 85.). This is a semiconductor with an energy gap between valence band and conduction band is 3.2 eV. When this substance absorbs a photon corresponding to a wavelength of 320–400 nm, an electron (e) passes from the valence band to the conduction band, and a positively charged electron vacancy remains in the valence band - a “hole” (h+). If on the surface TiO_2air oxygen is adsorbed, electrons are attached to its molecules, forming reactive oxidizing ions $O_2{}^{2-}$. The hole reacts either with water or with any adsorbed organic (in some cases inorganic) compound. The resulting OH radicals are also capable of oxidizing any organic compound.Harmful organic and inorganic pollutants, bacteria and viruses are adsorbed on the surface of the TiO2 photocatalyst, applied to a pushy carrier (photocatalytic filter). Under the influence of light from a UV lamp, they are oxidized to carbon dioxide and water.

Photocatalysts based on TiO_2 nanopowders can used to purify a wide variety of substances - water, air, oil. In the latter case, sulfur-containing impurities are primarily oxidized.Research in the field of nanocatalysis has already led to the creation of a number of new technologies. So, in Japan, a catalyst for the decomposition of methane has been created. It is a grid of thin carbon fibers coated with nickel compound nanoparticles. When passing methane through a grid heated to $500^{O}C$, it is decomposed into simple substances:

$$CH_4 = C + 2H_2.$$

This technology can be used in hydrogen fuel cells, because the resulting hydrogen is of high purity.

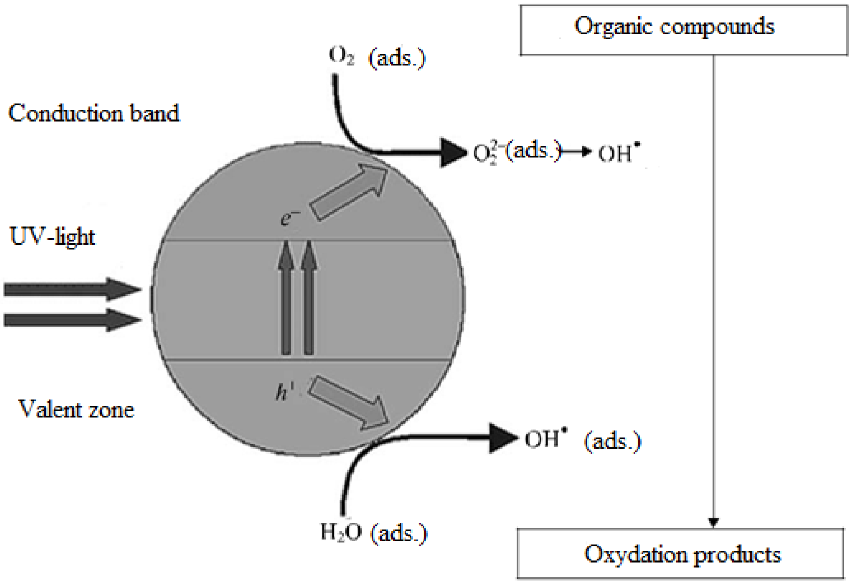


Figure 90. The principle of operation of a semiconductor photocatalyst

One of the most promising applications of nanocatalysis isproduction of hydrocarbon fuel from coal. When coal is heated in the presence of catalysts, impurities containing sulfur and nitrogen are removed. The resulting pure carbon is hydrogenated to form liquid hydrocarbons, which are used as diesel fuel. It is this technology that is planned to be implemented in China, which has large natural coal reserves.

Modern requirements for the quality of liquid fuels are very strict. In particular, quite stringent standards for the sulfur content of gasoline and diesel fuel have been adopted in many countries. For the cleaning crude oil from sulfur use a process called desulfurization, or desulfurization. Its catalyst is molybdenum disulfide MoS_2. MoS nanoclusters$_2$2–3 nm in size effectively bind sulfur atoms, which then easily react with hydrogen on the cluster surface:

$$S+H_2=H_2S$$

in the form of hydrogen sulfide are removed from the cleaned sample. The addition of small amounts of nickel and cobalt (Fig. 91) increases the activity of the catalyst by an order of magnitude.

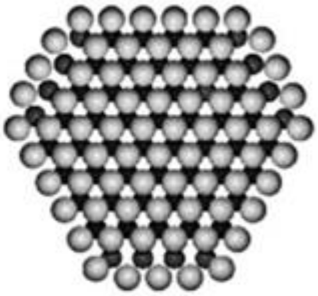


Figure 91. Structure of nanoparticlesMoS$_2$, modified with Co andNi. Light balls are S atoms, dark balls are metal atoms.

Nanocatalysts have found commercial applications not only in industry, but also in everyday life. Thus, gold nanoparticles on a substrate of iron oxide Fe_2O_3used in odor absorbers.

Works on the creation and application of nanocatalysts are at the stage of very active research, and some of them have already reached the level of technology. The most interesting, of course, is happening in the field of science: the main task of scientists is to understand the general principles that govern catalytic reactions at the level of nanoparticles. As for industrial applicationsHowever, the main thing here is to earn money: the commercial effect from the use of a catalyst must exceed the cost of the catalyst itself. Due to the fundamental difference between the two goals - "understand" and "earn" - not all scientific discoveries find industrial application. And this applies not only to nanocatalysis, but also to other areas of chemistry.

Topic 12. Nanoinstruments

Nanoscales. Modern laboratory ultramicrobalances are capable of weighing up to 0.1 nanogram (10-10 g), which is many times greater than the weight of nanoparticles. One of the main problems of weighing microparticles is the enormous influence of extraneous external factors (temperature, humidity, vibration, air flows, van der Waals forces, Brownian motion, etc.).

With an increase in the accuracy and sensitivity of the scales, the significance of extraneous factors only increases.To work with nanoparticles, employees of the Georgia Institute of Technology (USA) created special nanobalances.

These balances consist of a thin cantilever - a nanotube about 4 microns long. The figure shows the procedure for weighing the virus, the mass of which is 22 femtograms (1 fg = 10–15 g).

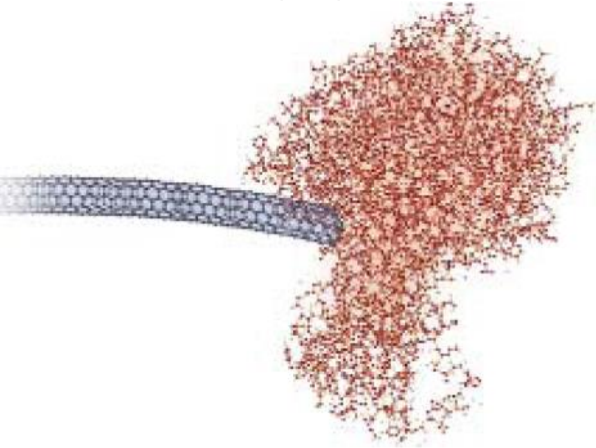


Figure 30. Nanoscale

In 2009, French and American scientists created a plate microbalance to measure the weight of nanoparticles. The design of these balances consists of an ultra-thin metal plate mounted on several electrodes.

The principle of operation of plate nanobalances is based on the fact that when a weighed molecule approaches, the plate begins to vibrate. The vibration intensity is sensed and measured by electrodes that are connected to a computer.

A feature of the equipment was the speed and accuracy of measurements. Practical tests were carried out on the measurement of the mass of immunoglobulins

Nanorobots. In the most general sense, the difference between the concepts of "machine" and "living organism" lies in the "artificial" and "natural", respectively, of their origin. Nanotechnologies have shown the possibility of creating artificial analogues of living systems, controlling natural processes and creating artificial devices based on living objects that can work in vivo.

Doctors plan to use nanorobots for emergency delivery of drugs directly into the infected tissue and into the cell through its cytoplasm.

Nanorobots will be able to penetrate into the tissues of the body, this will also help to deal with genetic disorders.Other medical nanorobots are being designed to accurately diagnose and monitor diseases and collect data about the human body.

For several decades, persistent attempts have been made to build micro- and nanorobots for medical applications.

In 2002, Ishiyama K and collaborators at Tohoku University developed miniature magnetically driven rotating screws designed to travel through veins and deliver drugs to infected tissues and tumors for thermal destruction.

In 2003, a group of researchers from Montreal created a microrobot containing ferromagnetic particles and working using the variable magnetic fields of MRI.

In 2005, researchers led by Brad Nelson at the Swiss Federal Institute of Technology in Zurich developed this technology and built a microrobot. (~200 microns) for injection into the body through a syringe. Nelson's microrobot successfully maneuvered in the aquatic environment using the external energy of magnetic fields.

Gordon's group at the University of Manitoba (Canada) also proposed magnetically controlled "cytobots" and "karyobots" for wireless intracellular and intranuclear manipulations.

The main function of the nanorobot is to move through the human circulatory system. For targeted movement, a nanorobot must have an appropriate navigation system, consisting of several types of different sensors for monitoring the environment, navigation, communication, and work with individual molecules. The nanorobot also needs a powerful transport system that delivers individual atoms and molecules from storage to nanomanipulators and back. To work with affected structures, the device must be equipped with a set of nanomanipulators. The material from which a nanorobot should be made must be biocompatible with the human body, and for successful operation, it is necessary to have transceiver devices that allow nanorobots to communicate with each other.

A typical medical nanodevice would be a micron (μm) sized robot assembled from nanoparts. These pieces will range from 1 to 100 nm (1 nm = 10-9 m), and should constitute a workable machine, measuring about 0.5-3 μm (1 μm = 10-6 m) in diameter. Three microns is the maximum size for blood flow medical nanorobots. is the minimum capillary size.

Surgical nanorobots can be introduced into the body through the vascular system or at the ends of catheters into various vessels and other cavities in the human body. The surgical nanorobot operates inside the human body and will be able to perform various functions, such as searching for pathology, as well as diagnosing and correcting various injuries.

Such a surgical nanorobot can be controlled by an on-board computer using ultrasonic signals.

To date, there have already been some practical achievements in the use of surgical nanorobots in cellular nanosurgery. For example, a micropipette less than 1 μm in diameter has been used to completely cut off dendrites from single neurons without damaging cell viability.

According to scientists, by 2020 we should expect the appearance of industrial nanorobots based on hard diamondoid materials. These nanorobots will have fully autonomous subsystems, including onboard sensors and molecular computers, motors, manipulators, and power sources.

The creation of complex nanorobot systems will require special technologies based on positional self-assembly. This technology will involve collecting and placing molecular parts, moving them along controlled trajectories similar to the movement of robots that produce cars on automobile assembly lines.

Mechanosynthesis using silicon atoms was first performed in 2003 (Oyabu N, Custance O, Yi I, Sugawara Y, Morita S.).

To power the nanorobot, it is proposed to use both the patient's own body and forces outside this body. A nanorobot with electrodes in place can form a battery based on electrolytes found in the blood. The nanorobot could carry a small supply of chemicals that would become a fuel source when combined with blood.

To actively move through the bloodstream, nanorobots need some kind of vehicle in the patient's body, and the propulsion system must be relatively powerful for its size.

Israeli scientists have created a microrobot that is only a few millimeters long and uses small appendages to grip and crawl through blood vessels. Scientists manipulate his limbs by creating a magnetic field outside the patient's body.

Specialists at the University of California at San Diego have already created miniature nanorobots (Fig.31). that operate under the control of an external magnetic field. These nanorobots are already capable of performing a number of fairly complex jobs, including drug delivery to the destination, microsurgical operations. These nanobots are made up of gold and nickel segments held together with silver straps. To control these robots, an external electromagnet is used, the field of which acts on segments made of nickel, the only magnetic material in the design of this nanorobot. An alternating magnetic field of a certain shape, generated by a magnet, causes the body of the robot to bend, making oscillatory movements, reminiscent of the movement of a fish body in water.

Figure 31. Nanorobot developed by Jinxing Li group (University of San Diego).

A promising area for the use of nanorobots is the Roboblood project. This development by Professor R. Fritas (California) is a complex of medical nanorobots capable of living and functioning in the human body, performing a wide variety of blood functions, including the circulation of respiratory gases, glucose, hormones, waste products, cellular components, and the process of cytoplasm division.

"Roboblood", which includes about 500 trillion microscopic nanorobots with a total weight of about 2 kg, consumes 30,200 watts of energy, depending on the type of human activity.

The system conforms to the shape of the blood vessels and can serve as a complete replacement for the natural circulatory system. In other words, nanorobots form the circulatory system and function in it.

It is understood that these nanorobots will be made of biocompatible material, and biological nutrition will be obtained from glucose and oxygen. The advantages that robotic blood provides are the fight against pathogenic microbes, and regular “cleansing” and strengthening of blood vessels, which prevents diseases such as atherosclerosis, varicose veins, etc., automatic treatment of damaged cells and even replacement of diseased genes with healthy ones.

One of the problems standing in the way of launching microrobots is the lack of a navigation system that could accurately guide them through the circulatory system to the target. So far, medical nanorobots cannot themselves determine the paths of movement in a living body. It is necessary to radically improve the methods of their orientation and direction to their destination.

Using magnetic resonance imaging (MRI), doctors could locate the nanorobot and track it by detecting its magnetic field (Fig. 32.). Scientists at Montreal Polytechnic showed a few years ago that they could detect, track, control, and even move a nanorobot using MRI. They tested their findings by maneuvering a small amount of small magnetic particles into a pig's arteries using special software on an MRI machine. Other methods for detecting nanorobots include the use of radioactive tags, X-rays, radio waves, microwaves, or heat.

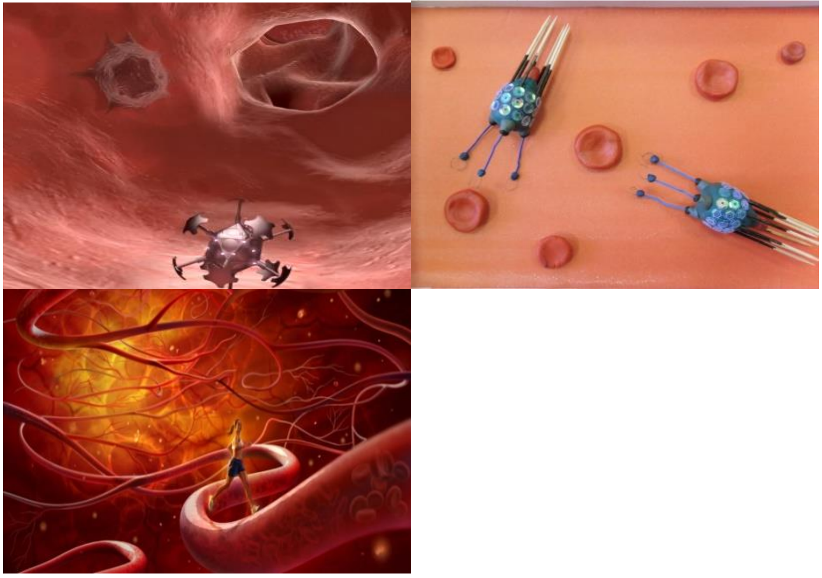


Figure 32. Navigation of nanorobots

A group of researchers representing Johns Hopkins University have succeeded in constructing the first nanorobot that can pass the initial laboratory experiments.

The uniqueness of this development lies in the possibility of using it for medicinal purposes in the human body. The size of the device in diameter is less than 0.1 mm.

The nanorobot manages to freely enter the human body, and then, guided by the emerging biochemical signals of cells as an indicator, resist the growth of malignant tumors.

The design of the nanorobot is very unusual - the development has a body and 3 pairs of peculiar limbs ending in claws. Thanks to them, the nanorobot manages to have an effect on the particles of the tissues of the human body.

The unique device does not need an additional power source, it is able to charge thanks to thermal, biochemical and magnetic waves. This nanorobot is capable of penetrating into living tissue and looking for certain cells in it, given by the program.

Modern nanorobotics is not yet developed enough to actually perform any medical operations in the human body, but it allows setting tasks for building more advanced nanodevices and nanobiorobots.

The first application of nanodevices in medicine will undoubtedly be patient monitoring. This will consist in compiling a structural model of the human body, which takes into account the location of each cell by (this is especially important for studying the processes taking place in the cerebral cortex), mapping the cardiovascular system, monitoring the functioning of the nervous system, controlling various implants and prostheses, which by that time will enter into everyday medical practice.

Topic 13. Concepts of nanotechnology

Nanotechnology as a scientific and technical direction provides the ability to create and change objects in a controlled way, including the ability to create and change components with dimensions less than 100 nm, which have fundamentally new qualities. and a set of techniques and methods that allow them to be integrated into fully functioning macroscale systems. .

Fundamental studies of phenomena occurring in structures with sizes less than 100 nm have stimulated the development of a new field of knowledge that will bring about revolutionary changes in the technologies of the 21st century in the near future. Such structures correspond to such a state of matter, if radically new phenomena appear and dominate their behavior, including quantum effects, statistical temporal changes of properties and their scaling with the size of the structures, the dominant surface secret, absence. defects in the size of single crystals, significant energy saturation that determines high activity in chemical reactions, sorption processes, sintering (c) 1997, combustion, etc.

The difference between the properties of small particles and the properties of a massive material has been known to scientists for a long time and is used in various fields of technology.

Examples of nanoscale structures include commonly used aerosols, color pigments, and colored glasses colored with colloidal metal particles. Impressive examples are related to biology, where wildlife shows us nanostructures at the level of the cell nucleus. In this sense, nanotechnology itself as a scientific field is not new. The qualitative feature of nanotechnology is a new level of knowledge about the physical and chemical properties of matter.

At the same time, the exclusivity of nanotechnology - new technological technologies of knowledge, conceptual changes in the directions of development of medicine, economic production, changes in ecological, social and military words. properties of nano-sized materials.

An important distinguishing feature of the nanometer scale is the ability of molecules to self-organize into structures with different functional purposes, as well as to create structures similar to themselves (self-replication effect). New, unique molecular compounds are made by methods called mechanosynthesis. Experiments have been conducted in which thousands and tens of thousands of molecules not found in natural materials,

The use of the above properties for practical purposes is the essence of nanotechnology. On its basis, examples of nanostructured ultra-hard, ultra-light, corrosion- and wear-resistant materials and coatings, catalysts with a highly developed surface, nanoporous membranes for fine liquid purification systems, and ultra-high-speed nanoelectronic devices have already been introduced.

The special structure and properties of small atomic aggregates are of great scientific interest, because they are intermediate between the structure and properties of isolated atoms and massive (fine) solids. The main question in the study of the state of nanocrystals is whether there is a clear, precise boundary between the state of the bulk substance and the state of the nanocrystal, how quickly it increases, and at what stage of the association of atoms does this or that state appear? if the properties of a bulk crystal are complete, is there a critical size of a grain or particle below which the properties of a nanocrystal appear, and above - for a bulk (bulk) substance? There is no complete answer to this question yet. This is not surprising - after all, this is a general philosophical question about the transition from quantity to quality.

The physical properties of ultradisperse media (UDM) open great prospects for the use of these media in mechanical engineering, the chemical industry, and other areas of science, technology, and industry. It is especially promising to use such tools in the creation of composite materials. A unique combination of mechanical, electrical, thermal, magnetic, optical and other properties was found in dispersed phases. UDM applications are based on the specific characteristics of their properties, which are significantly different from the properties of the same materials in single or polycrystalline, as well as amorphous states.

The variety of properties of UDM is related to the specific nature of the state of atoms and electrons in small particles (1-10^2 nm), which are the main morphological element of UDM. Recently, materials consisting of particles of several nanometers (10^{-9} m) are called nanophase or nanomaterials.

Significant changes in UDM properties occur when individual particle sizes decrease to $\leq 10^2$ nm. In this range, there is a conditional transition region of dimensions, above which the properties of a macroscopic solid dominate, and below, the properties of macromolecules.

As the particle size decreases, the role of the surface increases dramatically, which is comparable to the role of volume effects. When the dimensions less than 10^3 nm are reached, there is a radical change in the arrangement of atoms on the surface of the particles and a change in the nature of interatomic bonds, and then it is often impossible to distinguish bulk and surface properties.

An important parameter of UDM is the particle size distribution.

When changing the function type, the quality of the environment properties may change. Each method is characterized by its own distribution function. Often, the distribution is characterized by a normal or log-normal distribution. Each of them corresponds to a certain mechanism of particle formation. The main mechanisms are: non-diffusion (growth of particles at the phase boundary), diffusion (transport of particles over large distances) and coagulation (particles stick together in collisions). The first mechanism is characterized by a normal distribution, and the third is characterized by a log-normal distribution. The diffusion mechanism results in a mixed distribution with a tail toward larger particles.

A feature of small particles is the imbalance of shape and structure associated with the technological features of production. Manufacturing technology leaves its mark on features that manifest themselves in almost all applications. It can be said that when the technological conditions of synthesis and physico-chemical processing change, a new material is created that remembers the history of its origin right up to its application. The importance of production conditions indicates the need to consider methods of producing small particles.

Science begins with definitions. Everyone is familiar with concepts such as microquantity (mass of substances measured in micrograms), microanalysis (analysis of microsizes), microelectronics (simplified: electronic devices with the smallest dimensions of individual parts in micrometers or fractions of micrometers). The prefix "micro" in numbers means parts per million.

A similar prefix "nano-" (billionth) is often used in numbers. However, if we remember that the size of individual simple molecules is determined by nanometers, we can understand what objects are interesting for nanotechnology. Nanotechnology intersects with various scientific and engineering disciplines, it is difficult to give a single definition. Here are some definitions:

- miniaturization of technology: design and production of intelligent miniature machines programmed to perform specific tasks;
- the art of manipulating materials on an atomic and molecular scale, especially creating microscopic devices (robots);

- the ability to produce objects and structures atom by atom similar to the processes in the cells of living organisms.

Classification of nanotechnologies. There are three directions in nanotechnology: "wet", "dry" and computer.

Nanotechnology refers to the study of biological systems that exist in the aquatic environment and include genetic material, membranes, enzymes (biocatalysts) and other cellular components. Such nanometer-sized structures are known to have emerged and developed as a result of the evolution of organisms.

"Dry" nanotechnology comes from physical chemistry and the science of surface phenomena aimed at obtaining structures from carbon (e.g., nanotubes), silicon, various metals, and inorganic materials in general. His ultimate goal is to create functional devices that can self-assemble like "wet" structures, but without relying on evolution.

Computer nanotechnology makes it possible to model complex molecules and systems, calculate their relative stability and predict their behavior. It takes a long time to create analogues of what nature has created over hundreds of millions of years. Modeling and calculations make it possible to shorten this period dramatically (up to several decades).

Many experts understand nanotechnology as the production and use of materials whose particles or layers are measured in a few nanometers or tens of nanometers. Terms such as nanomaterials, nanocrystals, and nanocomposites are widely used.

Nanotechnology can also be conditionally divided into two areas - nanomaterials technology and molecular nanotechnology.

The chemical and physical properties of pure solids do not depend on their mass and particle size. For example, the solubility of bismuth in copper at room temperature is one. The melting point of pure iron has a single value, the phase transition temperature of pure zirconium dioxide from tetragonal to cubic modification has a single value, as well as the band gap of pure silicon. The same applies to many other properties of substances. However, when moving to nanoparticles, the properties change.

The Gibbs-Thomson equation has been known for a long time and relates the melting temperature of crystals to their size. According to this equation, 50 nm platinum particles should melt not at 2045 K, but at a lower temperature of 300 K. The melting temperature of individual particles of $TiC-TiB_2$ eutectic of 10 nm is reduced by 450 K compared to the temperature in the conventional system. The transition to nanocrystals leads to an increase in the heat capacity of palladium by more than one and a half times, and four thousand times the solubility of bismuth in copper. increases the self-diffusion coefficient of copper at room temperature by 21 degrees (!). Brittle substances such as TiO_2 and CaF_2 are transformed into plastic in the form of nanoparticles.

It is also important to change the electronic properties of substances and their magnetic properties as the size decreases to nanometers.

The physical nature of most transfer processes will be different. Thus, the transition to the quantum effect in metals is observed at a particle size of 1-2 nm, and in semiconductors at 50-100 nm. This means that nature has set a limit to the miniaturization of modern microelectronic devices, in a few years silicon electronics will reach its limit, and if we set the goal of further miniaturization of electronic devices, we should look now. new principles of their creation.

What is the reason for such drastic changes in the fundamental properties of substances? The answer is obvious: first of all, with a change in the ratio of surface and mass atoms of individual particles. The surface of the most ideal crystal can be thought of as a large two-dimensional or even bulk defect, with the surface atoms usually spaced closer together than the atoms in the crystal lattice volume and having an increased energy reserve. Up to a certain particle size, the proportion of these atoms is small, and their contribution to the general properties of the substance can be neglected. In nanoparticles, the properties of surface atoms become crucial. From this point of view, formations with no more than 1000 atoms and no more than 10 nm in size are considered nanoparticles.

Engineers have long focused on materials with small particle sizes. It is known that they are sintered at lower temperatures than coarse dispersions and in some cases allow to obtain unique products, for example, transparent ceramics. However, the specific properties of these substances make them difficult to obtain. Excessive surface energy causes the nanoparticles to stick together and coalesce. In addition, there is no inert environment for nanoparticles, they are chemically active and often lose their unique properties when they interact with other substances. Obtaining and storing nanomaterials requires great skill from technologists.

A vivid example is the creation of a polymer-based composite that fills silver nanoparticles. At a concentration of only a few ten thousandths of a percent of silver, the composition has an unusually strong bactericidal effect.

Nanoparticles are often obtained in two main ways: from the gas phase (condensation or chemical precipitation, flame processes, plasma, etc.) and colloid-chemical, in particular, sol-gel (transferring the solution to a colloidal state and later). treatment). Nanomaterials include not only equiaxed (same length, width, and height) small-sized particles. These include wires and threads with a diameter of several or tens of nanometers, multilayered forms with the same thickness of individual layers; compositions containing fillers from nanoparticles, nanowires, nanoplates.

The processes of self-assembly of micelle-like structures studied in colloidal chemistry, where the molecules are "different", may play an important role.

Common nanomaterials include fullerenes and carbon nanotubes. In the near future, we can watch TVs hanging on the wall: flat-screen devices where carbon nanotubes will be the emitters (source) of electrons.

Topic 14. Medical application of nanosystems

In fact, the science of nanomedicine does not yet exist, there are only nanoprojects whose application to medicine will eventually give results.

Perhaps the first cyborgs should be considered 15 blind patients at the University of Baltimore, who in the 90s were implanted with a device that allowed them to see without the help of their eyes. These electronic devices did not make it possible to distinguish newspaper text, but people began to see light and recognize colors. Every time a screen on a blind person's eye registers an ordinary object, a miniature computer in the viewing temple converts the image into pulses. In turn, the electrodes "translate" them into an imaginary sensation of light corresponding to a certain spatial image. Such artificial vision systems are not intended for individual patients,

Scientists have studied the behavior of sugar-coated nanoparticles, which have proven useful for cancer treatment, at high temperatures. Researchers conducted an experiment on mice - in three out of four experimental animals, heated nanoparticles destroyed cancer tumors without further recurrence (Fig. 67).

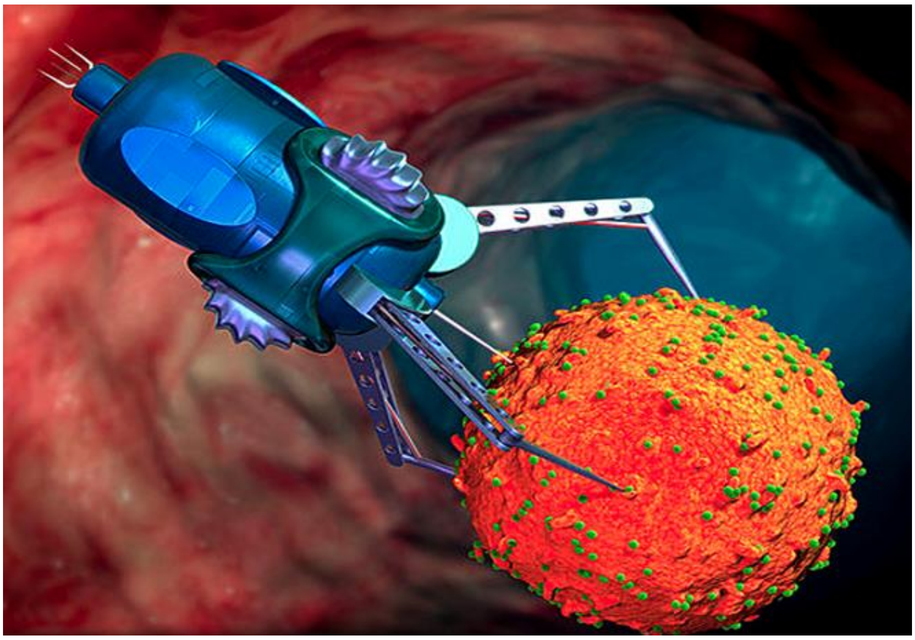


Figure 67. Nanorobot catching a virus

Imagine you have the flu (that is, you still don't know you have it). The artificially enhanced immune system reacts immediately, and tens of thousands of nanorobots begin to recognize the flu virus. Not a single virus will be left in your blood in a few minutes! Future nanorobots will be able to regenerate cells. They can restore even a very old person to a state of youth.

Figure 68. Point delivery of drugs to the human body

Humanity moves from operations on organs to operations on molecules and becomes almost immortal. People frozen by cryonics can be resurrected many years later with the help of millions of robots.

Nanorobots in medicine can literally do everything: diagnose the condition of any organs and processes, intervene in these processes, deliver drugs (Figure 68.), connect and destroy tissues, synthesize new ones. In fact, nanorobots can permanently rejuvenate a person by replicating all his tissues. At this stage, scientists developed a complex program that mimics the design and behavior of nanorobots in the body. Ultra-detailed aspects of maneuvering in the arterial environment, searching for proteins using sensors. Scientists have conducted virtual research to study nanorobots for the treatment of diabetes, abdominal cavity, brain aneurysms, cancer, biodefense against toxic substances.

Topic 15. Nanostructures based on natural polymers.

Chitin fibrils are highly oriented aggregates of macromolecules 25–50 nm in diameter, which in turn consist of microfibrils 2.5–2.8 nm in diameter.

Researchers in the field of polysaccharides propose to distinguish between some structural elements, and the terminology adopted by them differs from that used by other scientists: macromolecule, crystallite,

microfibril, fibril.

Among scientific publications, works on the preparation and electron microscopic studies of cellulose and chitin nanocrystals are widely represented.

A significant contribution to the solution of the problem of the crystallite structure of polysaccharides was made by the works of Renby and employees.

The length of crystallites, according to electron microscopy, ranges from 20–85 nm (for various types

artificial cellulose fibers) up to 65–220 nm (for natural cellulose). At the same time, the shape of crystallites also differs markedly: crystallites of natural cellulose have a pronounced anisodiametric shape (the ratio of length to diameter l/d).

Based on studies of the products of heterogeneous hydrolysis of cellulose, estimates of the sizes of crystallites, Renby concluded that they correspond to the sizes of micelles included in fibrillar elements.

He interpreted these data in terms of the existence of crystalline and amorphous regions along cellulose microfibrils without strict periodicity. Preston as a result of electron microscopy and X-ray studies suggested that the plane of the crystal lattice in crystallites native cellulose are oriented parallel to the surface of the structure elements.

The sizes of cellulose crystallites in the transverse direction were determined on the basis of electron microscopic and X-ray data on the expansion of reflections, and a value of 50–62 Å was obtained.

for cotton cellulose. Krassig and Kitchen, studying hydrolyzed cellulose preparations of various origins by electron microscopy, evaluated the strength of fibers after partial hydrolysis and came to the conclusion that the length of cotton “morphological units” (crystallites) is 1200–2000 Å, and that of artificial fiber is 600–1000 Å.

From the above data, it can be seen that there is no agreement in the experimental results on determining the size, nature, and shape of fibrils and microfibrils. Perhaps this is due to the dependence of the structure of cellulose on its source.

In the work of Simonsen, nanocrystals are obtained from wood cellulose in the process of hydrolysis and under under the influence of shear forces, the particles are then rubbed. It has been microscopically established that cellulose nanocrystals from wood have dimensions from 3 to 5 nm in width and 20–200 nm in length; from cotton - 3–7 nm wide, 100–300 nm long.

Cellulose nanocrystals represent a new alternative for the production of biocompatible and optically transparent nanocomposites with high strength. In the work of Benvides and Kitchenz, water suspensions of rod-shaped nanocrystals, the length of which, according to electron microscopic data, is in the range from 20 to 400 nm and diameters less than 10 nm, were obtained by acid hydrolysis cellulose powder. Formation of isotropic and chiral nematic liquid crystal phases was observed as a function of the concentration of cellulose nanocrystals. An aqueous nanocrystalline suspension is a biphasic state between the isotropic and liquid crystalline phases. The relative volume, concentration and size of the particles of each phase were investigated, particle size fractionation achieved sequential separation of two phases. Transmission electron microscopy shows the dimensional dependence of nanocrystals on phase behavior and degree of fractionation. In this work, the structure and physicochemical properties of polysaccharides were studied and it was concluded that polysaccharides (crab and mushroom chitin, as well as crab chitosan) have a complex supramolecular structure. They belong to fibrillar polymers, and microfibrils consist of amorphous and highly ordered microregions;

A consequence of this structure is, firstly, the presence of two glass transition temperatures in polysaccharides. Second, they exhibit several secondary small-scale relaxation transitions of an endothermic nature, which can be attributed to g- and β-transitions. Thus, if we rely on the theory of the amorphous-crystalline structure of polysaccharides, then their

supramolecular structure can be characterized by crystallographic parameters, degree crystallinity, crystallite size and defectiveness, structural characteristics of amorphous areas, sizes of fibrillar formations and other parameters.

Creation of composite materials containing fillers of nanoscale dispersion level, is a new and promising direction in the development of materials science. One of the promising variants of this direction - the use of natural polysaccharides with a pronounced fibrillar structure, to improve the physical and mechanical properties of various polymers, accelerate their

biodegradability at the end of the service life, obtaining polymeric materials with special properties (for example, separating membranes), etc. The limiting factors in the creation of such composites are the dispersion of polysaccharide fibrils to a nanoscale level and, at the same time, the preservation their rod-shaped configuration with a high ratio of length to diameter. An original method for obtaining nanocomposites based on chitin and polyacrylic acid has been developed.

O‘ZBEKISTON RESPUBLIKASI
OLIY TA’LIM, FAN VA INNOVATSIYALAR VAZIRLIGI

NAMANGAN DAVLAT UNIVERSITETI

“TASDIQLAYMAN”
O‘quv ishlari bo‘yicha prorektori
_____________ D.Xolmatov
“ ” _____________ 2023-yil

NANOKIMYO VA NANOTEXNOLOGIYA
FANINING

O‘QUV DASTURI

3-kurs, kunduzgi ta’lim shakli uchun

Bilim sohasi: **500000 – Tabiiy fanlar, matematika va statistika**
Ta’lim sohasi: **5530000 – Fizika va tabiiy fanlar**
Ta’lim yo‘nalishi: **60530100 – Kimyo**

Namangan-2023

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I. FANNING MAZMUNI

Fanni o‘qitishdan maqsad - fanni o’qitishdan maqsad talabalarga zamonaviy nanotehnologiyani ilmiy asoslarini talabalrga yetkazish, nanozarrachalarni olish usullarini, nanotuzilmalarni tadqiqot usullarini, nanosistemalarni va nanotuzilishga ega materiallarni ishlatilish sovhalarini o’rgatishdan iboratdir.

Fanning vazifasi - Nanozarrachalar ishlab chiqarishning asosiy usullari haqida *ko’nikma berish, n*anozarrachalarni tashqi va ichki (g’ovaqli) sinflari uch o’lchovli 3D, nanoklasterlar, ikkio’lchovli 2D, chiziqli biro’lchovli 1D, nolo’lchovli 0D tuzilishga ega nanotuzilmalarni ajratish, uglerodli nanomateriallar haqida tushuncha berish, an'anaviy va muqobil energiya manbalari haqida tushuncha berish, nanozarrachalar va seolitlar, shu jumladan nanozarrachalarni tayyorlash usullari va qo'llanilish sohalaridagi kataliz jarayoni haqida talabalarga bilim berishdan iborat.

II. ASOSIY NAZARIY QISM (MA’RUZA MASHG‘ULOTLARI)

II.1. Fan tarkibiga quyidagi mavzular kiradi:

1-mavzu. Nanokimyo va nanotexnologiya faniga kirish

Nanokimyo va nanotexnologiya tushunchalari. Nanotexnologiyaning shakllanish tarixi. Nanokimyoning nanokimyodagi o'rni**.**

2-mavzu. Nanotizimlarni olish usullarini umumiy tafsiflari

Nanozarrachalar ishlab chiqarishning asosiy usullari. Gaz fazasidan ajratib olishning fizik va kimyoviy usullari. Kolloid eritmalarda olish.

3-mavzu. Nanotizimlarni asosiy turlari

Nanozarrachalarni tashqi va ichki (g’ovaqli) sinflari, Uch o’lchovli 3D, nanoklasterlar, ikkio’lchovli 2D, chiziqli biro’lchovli 1D, nolo’lchovli 0D.

4-mavzu. Uglerodning nanoshakllarini umumiy hossalari

Uglerodli nanomateriallar. Uglerodning allotropik shakllari. Nanoolmoslar. Fullerenlar va ularning hosilalari. Nanotubalar, ularning tasnifi va xossalari. Uglerod nanoformlarining umumiy xossalari.

5-mavzu. Uglerodli nanotubkalar

Nanokompozit materiallar uchun to'ldirgichlar. Qatlamli aluminosilikatlar

6-mavzu. Nanokompozitlar turlari

Polimer nanosistemalarda nanozarrachalarni yaratish. Polimer aralashmalaridagi nanotasvirdagi morfologik tuzilmalarning xilma-xilligi va olingan materiallarning elastik-mustahkamlik xususiyatlarining ko'rsatkichlari.

7-mavzu. Polimer nanokompozitlari

Nanokompozit polimer materiallar. Sintetik va tabiiy polimerlarga asoslangan polimer aralashmalaridagi nano tuzilmalar. Nanotuzilmalar hosil bo'lishida blokopolimerlarning kompyutibilizator sifatida ahamiyati.

8-mavzu. Energetika uchun nanomateriallar

Energiya uchun nanomateriallar. An'anaviy va muqobil energiya manbalari. Yoqilg'i elementlaridagi nanomateriallar. Vodorodni saqlash uchun nanomateriallar.

9-mavzu. Polimer aralashmalari

Nanopolimer mahsulotlarining assortimentini kengaytirish va bir polimerning ba'zi xususiyatlarining kamchiliklarini boshqasi hisobiga yo'q qilishning eng istiqbolli usullari.Tayyor mahsulotni olish uchun polimerlarni aralashtirishga an'anaviy yondashuvlar (ekstruzion aralashtirish), elastomer ishtirokida polimer aralashmalarini ishlab chiqarishning bir bosqichli texnologiyasi va reaktsion in'ektsion kalıplama (RIM-jarayon).

10-mavzu. Nanokataliz

Nanokataliz. Katalizatorlarning umumiy xususiyatlari. Katalitik reaktsiyalar tasnifi. Strukturaviy va energetik muvofiqlik tamoyillari. Nanozarrachalar va seolitlar, shu jumladan nanozarrachalarni tayyorlash usullari va qo'llanilish sohalaridagi kataliz.

11-mavzu. Nanozarrachalarni fizik va kimyoviy hossalari

Nanozarrachalar va nano tuzilmalarning termofizik, elektrofizik, optik, magnit, yarimo'tkazgichli, suyuq kristalli, supero'tkazuvchi va boshqa xususiyatlari noorganik, organik tabiatning qattiq, kolloid va suyuq tizimlarida. Nanoobyektlarning o'lchami

12-mavzu. Nanotizimlarni va nanotuzilmalarni zamonaviy tagqiqot usullari

Nanotuzilmalarni aniqlashda fizik-kimyoviy tadqiqotlar. Nanozarrachalarni o'rganish usullari. Elektron mikroskopining ishlash printsipi.

13-mavzu. Skanerlovchi tunnell va atom kuchlanish mikroskoplari

Elektron mikroskopga qaraganda atom kuchi mikroskopining afzalliklari va kamchiliklari.

14-mavzu. Nanotizimlarni ilm va texnikada qo’llanilishi

Nanotuzilmalarni sanoat tarmoqlarida ishlatilishi.Nanotexnika va nanotexnologiyaning yutuqlaridan foydalanib, energiyani konvertatsiya qilishning termoelektrikligi va nanoyurilish materiallari

Turli sanoat va qishloq xo'jaligi uchun nano tuzilmali materiallar va preparatlar yaratishning amaliy jihatlari. Nanostrukturali dorilar va tibbiy asboblarning yangi avlodi.

15-mavzu. Tabiiy polimerlar asosidagi nanotuzilmalar

Xitozan asosidagi nanotolalar va nanozarrachalar.

II.2. MA’RUZA MAVZULARINING TAQSIMLANISHI

№	Mavzular	Soati
1	Nanokimyo va nanotexnologiya faniga kirish	2
2	Nanotizimlarni olish usullarini umumiy tafsiflari	2
3	Nanotizimlarni asosiy turlari	2
4	Uglerodli nanomateriallar. Uglerodning nanoshakllarini umumiy hossalari	2
5	Uglerodli nanotubkalar.	2
6	Nanokompozitlar turlari	2
7	Polimer nanokompozitlari	2
8	Energetika uchun nanomateriallar	2
9	Polimer aralashmalari	2
10	Nanokataliz.	2
11	Nanozarrachalarni fizik va kimyoviy hossalari.	2
12	Nanotizimlarni va nanotuzilmalarni zamonaviy tagqiqot usullari.	2
13	Skanerlovchi tunnell va atom kuchlanish mikroskoplari.	2
14	Nanotizimlarni ilm va texnikada qo’llanilishi	2
15	Tabiiy polimerlar asosidagi nanotuzilmalar.	2
	Jami:	**20**

III.1. AMALIY MASHG‘ULOT MAVZULARINI

1-mavzu. Nanokimyo va nanotexnologiya faniga kirish

Nanokimyo va nanotexnologiya tushunchalari. Nanotexnologiyaning shakllanish tarixi. Nanokimyoning nanokimyodagi o'rni**.**

2-mavzu. Nanotizimlarni olish usullarini umumiy tafsiflari

Nanozarrachalar ishlab chiqarishning asosiy usullari. Gaz fazasidan ajratib olishning fizik va kimyoviy usullari. Kolloid eritmalarda olish.

3-mavzu. Nanotizimlarni asosiy turlari

Nanozarrachalarni tashqi va ichki (g’ovaqli) sinflari, Uch o’lchovli 3D, nanoklasterlar, ikkio’lchovli 2D, chiziqli biro’lchovli 1D, nolo’lchovli 0D.

4-mavzu. Uglerodning nanoshakllarini umumiy hossalari

Uglerodli nanomateriallar. Uglerodning allotropik shakllari. Nanoolmoslar. Fullerenlar va ularning hosilalari. Nanotubalar, ularning tasnifi va xossalari. Uglerod nanoformlarining umumiy xossalari.

5-mavzu. Uglerodli nanotubkalar

Nanokompozit materiallar uchun to'ldirgichlar. Qatlamli aluminosilikatlar

6-mavzu. Nanokompozitlar turlari

Polimer nanosistemalarda nanozarrachalarni yaratish. Polimer aralashmalaridagi nanotasvirdagi morfologik tuzilmalarning xilma-xilligi va olingan materiallarning elastik-mustahkamlik xususiyatlarining ko'rsatkichlari.

7-mavzu. Polimer nanokompozitlari

Nanokompozit polimer materiallar. Sintetik va tabiiy polimerlarga asoslangan polimer aralashmalaridagi nano tuzilmalar. Nanotuzilmalar hosil bo'lishida blokopolimerlarning kompyutibilizator sifatida ahamiyati.

8-mavzu. Energetika uchun nanomateriallar

Energiya uchun nanomateriallar. An'anaviy va muqobil energiya manbalari. Yoqilg'i elementlaridagi nanomateriallar. Vodorodni saqlash uchun nanomateriallar.

9-mavzu. Polimer aralashmalari

Nanopolimer mahsulotlarining assortimentini kengaytirish va bir polimerning ba'zi xususiyatlarining kamchiliklarini boshqasi hisobiga yo'q qilishning eng istiqbolli usullari.Tayyor mahsulotni olish uchun polimerlarni aralashtirishga an'anaviy yondashuvlar (ekstruzion aralashtirish), elastomer ishtirokida polimer aralashmalarini ishlab chiqarishning bir bosqichli texnologiyasi va reaktsion in'ektsion kalıplama (RIM-jarayon).

10-mavzu. Nanokataliz

Nanokataliz. Katalizatorlarning umumiy xususiyatlari. Katalitik reaktsiyalar tasnifi. Strukturaviy va energetik muvofiqlik tamoyillari. Nanozarrachalar va seolitlar, shu jumladan nanozarrachalarni tayyorlash usullari va qo'llanilish sohalaridagi kataliz.

11-mavzu. Nanozarrachalarni fizik va kimyoviy hossalari

Nanozarrachalar va nano tuzilmalarning termofizik, elektrofizik, optik, magnit, yarimo'tkazgichli, suyuq kristalli, supero'tkazuvchi va boshqa xususiyatlari noorganik, organik tabiatning qattiq, kolloid va suyuq tizimlarida. Nanoobyektlarning o'lchami

12-mavzu. Nanotizimlarni va nanotuzilmalarni zamonaviy tagqiqot usullari

Nanotuzilmalarni aniqlashda fizik-kimyoviy tadqiqotlar. Nanozarrachalarni o'rganish usullari. Elektron mikroskopining ishlash printsipi.

13-mavzu. Skanerlovchi tunnell va atom kuchlanish mikroskoplari

Elektron mikroskopga qaraganda atom kuchi mikroskopining afzalliklari va kamchiliklari.

14-mavzu. Nanotizimlarni ilm va texnikada qo’llanilishi

Nanotuzilmalarni sanoat tarmoqlarida ishlatilishi.Nanotexnika va nanotexnologiyaning yutuqlaridan foydalanib, energiyani konvertatsiya qilishning termoelektrikligi va nanoyurilish materiallari. Turli sanoat va qishloq xo'jaligi uchun nano tuzilmali materiallar va preparatlar yaratishning amaliy jihatlari. Nanostrukturali dorilar va tibbiy asboblarning yangi avlodi.

15-mavzu. Tabiiy polimerlar asosidagi nanotuzilmalar

Xitozan asosidagi nanotolalar va nanozarrachalar.

III.2. AMALIY MASHG‘ULOT MAVZULARINI TAQSIMLANISHI

№	Amaliy mashg‘ulot mavzulari	Soati
1	Nanokimyo va nanotexnologiya faniga kirish	2
2	Nanotizimlarni olish usullarini umumiy tafsiflari	2
3	Nanotizimlarni asosiy turlari	2
4	Uglerodli nanomateriallar. Uglerodning nanoshakllarini umumiy hossalari	2
5	Uglerodli nanotubkalar.	2
6	Nanokompozitlar turlari	2
7	Polimer nanokompozitlari	2

8	Energetika uchun nanomateriallar	2
9	Polimer aralashmalari	2
10	Nanokataliz.	2
11	Nanozarrachalarni fizik va kimyoviy hossalari.	2
12	Nanotizimlarni va nanotuzilmalarni zamonaviy tagqiqot usullari.	2
13	Skanerlovchi tunnell va atom kuchlanish mikroskoplari.	2
14	Nanotizimlarni ilm va texnikada qo’llanilishi	2
15	Tabiiy polimerlar asosidagi nanotuzilmalar.	2
	Jami	**30**

V.1. MUSTAQIL TA’LIM VA MUSTAQIL ISHLAR

1	Kimyoviy sensorlarda nanotrubkalarni qo’llanilishi
2	Katalizator nanozarrachalari
3	Nanozarrachalarni kriokimyosi
4	Polimer nanokompozitlari
5	Zamonaviy tibbiyotda nanozarrachalarni o’rni
6	Nanozarrachalar tuzilishini computer modellash
7	Nanokimyo va nanotehnologiyada “O’lcham ta’siri” tushunchasi
8	Metall oksidlarini nanozarrachalarini olinishi va hossalari
9	Kvant nuqtalarni olinishi va hossalari
10	Dendrimerlar nanozarracha va makromolekula ko’rinishida
11	Fullerenlar nanomateriallarning zamonaviy texnologiyasida
12	Uglerodsiz nanotrubkalar
13	Nanotuzilmalar sirtlarini tadqiqot qilish usullari
14	Nanokompozitlarni olish usullari
15	Nanotuzilga tolalar. Olinishi va hossalari

VI. FAN O‘QITILISHINING NATIJALARI (SHAKLLANADIGAN KOMPETENTSIYALAR)

Fanni o‘zlashtirishi natijasida talaba:

✓ Nanokimyo va nanotexnologiya fanlar tizimida tutgan o‘rni, obyekti va predmeti, shakllanishi, rivojlanishi, zamonaviy tuzilishi haqida ***tasavvur va bilimga ega bo‘lishi***;

✓ Nanozarrachalar ishlab chiqarishning asosiy usullari haqida, Nanozarrachalarni tashqi va ichki (g’ovaqli) sinflari uch o’lchovli 3D, nanoklasterlar, ikkio’lchovli 2D, chiziqli biro’lchovli 1D, nolo’lchovli 0D tuzilishga ega nanotuzilmalarni ajratish ***ko‘nikmalariga ega bo‘lishi***;

✓ Uglerodli nanomateriallar haqida tushunchaga, an'anaviy va muqobil energiya manbalari haqida ko’nikmalarga, nanozarrachalar va seolitlar, shu jumladan nanozarrachalarni tayyorlash usullari va qo'llanilish sohalaridagi kataliz jarayoni haqida, nanozarrachalar va nano tuzilmalarning termofizik, elektrofizik, optik, magnit, yarimo'tkazgichli, suyuq kristalli, supero'tkazuvchi va boshqa xususiyatlari haqida, muammolar bo‘yicha yechimlar qabul qilish malakasiga ***ega bo‘lishi kerak.***

VII. TA’LIM TEXNOLOGIYALARI VA METODLARI

✓ ma’ruzalar;
✓ interfaol keys-stadilar;
✓ seminarlar (mantiqiy fikrlash, tezkor savol-javoblar);
✓ guruhlarda ishlash;
✓ individual loyihalar
✓ jamoa bo‘lib ishlash va himoya qilish uchun loyihalar

VIII. KREDITLARNI OLISH UCHUN TALABLAR

Fanga ajratilgan kreditlar talabalarga har bir semestr bo'yicha nazorat turlaridan ijobiy natijalarga erishilgan taqdirda taqdim etiladi.

Fan bo'yicha talabalar bilimini baholashda oraliq (ON) va yakuniy (YaN) nazorat turlari qo'llaniladi. Nazorat turlari bo'yicha baholash: 5 – "a'lo", 4 – "yaxshi", 3 – "qoniqarli", 2 – "qoniqarsiz" baho mezonlarida amalga oshiriladi.

Oraliq nazorat har semestrda bir marta yozma ish shaklida o'tkaziladi.

Talabalar semestr davomida fanga ajratilgan amaliy mashg'ulotlarda muntazam, har bir mavzu bo'yicha baholanib boriladi va o'rtachalanadi. Bunda talabaning amaliy mashg'ulot hamda mustaqil ta'lim topshiriqlarini o'z vaqtida, to'laqonli bajarganligi, mashg'ulotlardagi faolligi inobatga olinadi.

Shuningdek, amaliy mashg'ulot va mustaqil ta'lim topshiriqlari bo'yicha olgan baholari oraliq nazorat turi bo'yicha baholashda inobatga olinadi. Bunda har bir oraliq nazorat turi davrida olingan baholar o'rtachasi oraliq nazorat turidan olingan baho bilan **qayta o'rtachalanadi**.

O'tkazilgan oraliq nazoratlardan olingan baho **oraliq nazorat natijasi** sifatida qaydnomaga rasmiylashtiriladi.

Yakuniy nazorat turi semestrlar yakunida tasdiqlangan grafik bo'yicha **yozma ish** shaklida o'tkaziladi.

Oraliq (ON) va yakuniy (YaN) nazorat turlarida:

Talaba mustaqil xulosa va qaror qabul qiladi, ijodiy fikrlay oladi, mustaqil mushohada yuritadi, olgan bilimini amalda qo'llay oladi, fanning (mavzuning) mohiyatini tushunadi, biladi, ifodalay oladi, aytib beradi hamda fan (mavzu) bo'yicha tasavvurga ega deb topilganda – **5 (a'lo) baho**;

Talaba mustaqil mushohada yuritadi, olgan bilimini amalda qo'llay oladi, fanning (mavzuning) mohiyatini tushunadi, biladi, ifodalay oladi, aytib beradi hamda fan (mavzu) bo'yicha tasavvurga ega deb topilganda – **4 (yaxshi) baho**;

Talaba olgan bilimini amalda qo'llay oladi, fanning (mavzuning) mohiyatini tushunadi, biladi, ifodalay oladi, aytib beradi hamda fan (mavzu) bo'yicha tasavvurga ega deb topilganda – **3 (qoniqarli) baho**;

Talaba fan dasturini o'zlashtirmagan, fanning (mavzuning) mohiyatini tushunmaydi hamda fan (mavzu) bo'yicha tasavvurga ega emas, deb topilganda – **2 (qoniqarsiz) baho** bilan baholanadi.

ASOSIY ADABIYOTLAR:

1. Нанотехнологии. Азбука для всех. Под ред. акад. Ю.Д.Третьякова. М.: Физматлит, 2008.
2. Суздалиев И.П. Нанотехнология: физико- химия нанокластеров, наноструктур и наноматериалов. М. «Ком Книга» 2006.
3. Сергеев Г.Б. Нанохимия. М.: Книжный дом Университет, 2006.

QO‘SHIMCHA ADABIYOTLAR:

1. Рашкович Л.Н. Атомно-силовая микроскопия процессов кристаллизации в растворе. Соросовский образовательный журнал. 2001, т. 7, № 10.
2. Сидоров Л.Н., Юровская М.А. и др. Фуллерены. М.: Экзамен, 2004;
3. Рыбалкина М. Нанотехнологии для всех. М., 2005.
4. Еремин В.В. Теоретическая и математическая химия. Гл. 4, § 4. М.:МЦНМ О, 2007.

AXBOROT MANBAALARI

1) www.natlib.uz.
2) www.Ziyo.net.
3) www.chemistry.ru.
4) www.ximik.ru.

Namangan davlat universiteti tomonidan ishlab chiqilgan va tasdiqlangan:

- “Organik kimyo” kafedrasining 2023-yil, “___”-iyundagi № _____-sonli majlisida muhokama qilingan va tasdiqqa tavsiya etilgan.

- Tabiiy fanlar fakulteti kengashining 2023-yil, “___”-iyuldagi № _____-sonli majlisida ma’qullangan va tasdiqqa tavsiya etilgan.

- NamDU o’quv-uslubiy kengashining 2023-yil, “___”-iyuldagi № _____- sonli majlisida muhokama qilingan va tasdiqlangan.

Fan /Modul uchun mas’ul:
D.M. Sattarova – NamDU, Organik kimyo kafedrasi dotsent v.b., kimyo fanlari falsafa doktori.

Taqrizchilar:
Sh.V.Abdullayev – NamDU, Organik kimyo kafedrasi professori, kimyo fanlari doktori.
A.M.Karimov – NamDU, Organik kimyo kafedrasi dotsenti, kimyo fanlari doktori.

NamDU o’uv-uslubiy boshqarma boshlig’i	**X. Mirzaaxmedov**
Tabiiy fanlar fakulteti dekani	**A. Baratov**
Organik kimyo kafedrasi mudiri	**A. Rasulov**
Tuzuvchi	**D. Sattarova**

MINISTRY OF HIGHER EDUCATION, SCIENCE AND INNOVATION OF REPUBLIC OF UZBEKISTAN

NAMANGAN STATE UNIVERSITY
ORGANIC CHEMISTRY DEPARTMENT

«APPROVED»
Vice Rector for Academic
Affairs ______ D. Holmatov
«__» __________ *2023 y*

WORKING TRAINING PROGRAM BY SUBJECT NANOCHEMISTRY AND NANOTECHNOLOGY

For 3 rd year daytime education

Area of Knowledge:	500000-natural subjects
Area of Education:	5530000-Physic and natural subjects
Bachelor Direction:	60530100-Chemistry (daytime)

NAMANGAN – 2023

Subject/Code module **NNt 2504**	**Study year** **2023-2024**	**Term** **5**	**ECST-Credits** **4** (2/2)	
Subject/Module type Elective	**Study Language** English		**Weekly Lesson Hours** 2	
1	**Subject name**	**Audience training (hours)**	**Independent study (hours)**	**Total load (hours)**
	Nanochemistry and nanotechnology	60	60	120

I. SUBJECT CONTENT

The content of science. The purpose of teaching science is to convey the scientific foundations of modern nanotechnology to students, to teach methods of obtaining nanoparticles, research methods of nanostructures, nanosystems and nanostructured materials.

The task of the subject is to teach about the main methods of nanoparticle production, to describe nanoparticle external and internal (porous) classes of three-dimensional 3D, nanoclusters, two-dimensional 2D, linear one-dimensional 1D, and nanostructures with non-dimensional 0D structure. separation, understanding of carbon nanomaterials, understanding of conventional and alternative energy sources, nanoparticles and zeolites, including nanoparticle preparation methods and catalysis process in applications.

II. MAIN THEORETICAL PART (LECTURES)

II.I. Content of Subject:

Topic 1. Introduction to Nanochemistry and Nanotechnology

Concepts of nanochemistry and nanotechnology. The history of the formation of nanotechnology. The role of nanochemistry in nanochemistry.

Topic 2. General descriptions of methods of obtaining nanosystems.

Basic methods of nanoparticle production. Physical and chemical methods of gas phase extraction. Obtaining in colloidal solutions.

Topic 3. Main types of nanosystems

External and internal (porous) classes of nanoparticles, three-dimensional 3D, nanoclusters, two-dimensional 2D, linear one-dimensional 1D, dimensionless 0D.

Topic 4. General properties of carbon nanoforms.

Carbon nanomaterials. Allotropic forms of carbon. Nanodiamonds. Fullerenes and their derivatives. Nanotubes, their classification and properties. General properties of carbon nanoforms.

Topic 5. Carbon nanotubes.

Fillers for nanocomposite materials. Layered aluminosilicates

Topic 6. Types of nanocomposites

Creation of nanoparticles in polymer nanosystems. Diversity of morphological structures in nanopatterns in polymer mixtures and indicators of elastic-strength properties of the obtained materials.

Topic 7. Polymer nanocomposites.

Nanocomposite polymer materials. Nanostructures in polymer mixtures based on synthetic and natural polymers. Importance of block polymers as computerizers in the formation of nanostructures.

Topic 8. Nanomaterials for energy

Nanomaterials for energy. Traditional and alternative energy sources. Nanomaterials in fuel cells. Nanomaterials for hydrogen storage.

Topic 9. Polymer blends.

The most promising methods of expanding the range of nanopolymer products and eliminating the shortcomings of some properties of one polymer at the expense of another. ection molding (RIM-process).

Topic 10. Nanocatalysis.

Nanocatalysis. General properties of catalysts. Classification of catalytic reactions. Principles of structural and energetic compatibility. Nanoparticles and zeolites, including nanoparticle preparation methods and catalysis in applications.

Topic 11. Physical and chemical properties of nanoparticles.

Thermophysical, electrophysical, optical, magnetic, semiconductor, liquid crystalline, superconducting and other properties of nanoparticles and nanostructures in solid, colloidal and liquid systems of inorganic, organic nature. The size of the nanoobjects

Topic 12. Modern research methods of nanosystems and nanostructures. Physicochemical studies in the determination of nanostructures. Methods of studying nanoparticles. The working principle of an electron microscope.

Topic 13. Scanning tunneling and atomic strain microscopes.

Advantages and disadvantages of atomic force microscopy compared to electron microscopy.

Topic 14. Application of nanosystems in science and technology

Use of nanostructures in industries. Thermoelectricity of energy conversion and nanomovement materials using the achievements of nanotechnology and nanotechnology.

Practical aspects of creating nanostructured materials and preparations for various industries and agriculture. A new generation of nanostructured drugs and medical devices.

Topic 15. Nanostructures based on natural polymers.

Chitosan-based nanofibers and nanoparticles.

II.2. Distribution of lecture topics

№	Topics	Hours
	Term V	
1	Introduction to Nanochemistry and Nanotechnology	2
2	General descriptions of methods of obtaining nanosystems	2
3	Main types of nanosystems	2
4	Carbon nanomaterials. General properties of carbon nanoforms	2
5	Carbon nanotubes	2
6	Types of nanocomposites	2
7	Polymer nanocomposites	2
8	Nanomaterials for energy	2
9	Polymer blends	2
10	Nanocatalysis.	2
11	Physical and chemical properties of nanoparticles	2
12	Modern research methods of nanosystems and nanostructures	2
13	Scanning tunneling and atomic strain microscopes	2
14	Application of nanosystems in science and technology	2
15	Nanostructures based on natural polymers	2
	By the term	**30**
	Total hours:	**30**

II.1. SUBJECTS OF PRACTICAL TRAINING

Topic 1. Essence of nanochemistry

Concepts of nanochemistry and nanotechnology. The history of the formation of nanotechnology. The role of nanochemistry in nanochemistry.

Topic 2. Chemical methods of synthesis.

Basic methods of nanoparticle production. Physical and chemical methods of gas phase extraction. Obtaining in colloidal solutions.

Topic 3. The main types of nanomaterials structures

External and internal (porous) classes of nanoparticles, three-dimensional 3D, nanoclusters, two-dimensional 2D, linear one-dimensional 1D, dimensionless 0D.

Topic 4. Fullerenes

Carbon nanomaterials. Allotropic forms of carbon. Nanodiamonds. Fullerenes and their derivatives. Nanotubes, their classification and properties. General properties of carbon nanoforms.

Topic 5. Classification and properties of carbon nanotubes.

Fillers for nanocomposite materials. Layered aluminosilicates

Topic 6. Classification of composite materials by matrix and reinforcing component materials

Creation of nanoparticles in polymer nanosystems. Diversity of morphological structures in nanopatterns in polymer mixtures and indicators of elastic-strength properties of the obtained materials.

Topic 7. Polymer nanocomposites.

Nanocomposite polymer materials. Nanostructures in polymer mixtures based on synthetic and natural polymers. Importance of block polymers as computerizers in the formation of nanostructures.

Topic 8. Nanoceramics

Topic 9. Nanomaterials for fuel cells

Nanomaterials for energy. Traditional and alternative energy sources. Nanomaterials in fuel cells. Nanomaterials for hydrogen storage.

Topic 10. Obtaining polymer blends

The most promising methods of expanding the range of nanopolymer products and eliminating the shortcomings of some properties of one polymer at the expense of another. ection molding (RIM-process).

Topic 11. Application of nanocatalysts

Nanocatalysis. General properties of catalysts. Classification of catalytic reactions. Principles of structural and energetic compatibility. Nanoparticles and zeolites, including nanoparticle preparation methods and catalysis in applications.

Topic 12. Nanoinstruments

Physicochemical studies in the determination of nanostructures. Methods of studying nanoparticles. The working principle of an electron microscope.

Topic 13. Concepts of nanotechnology.

Topic 14. Medical application of nanosystems

Use of nanostructures in industries. Thermoelectricity of energy conversion and nanomovement materials using the achievements of nanotechnology and nanotechnology.

Practical aspects of creating nanostructured materials and preparations for various industries and agriculture. A new generation of nanostructured drugs and medical devices.

Topic 15. Nanostructures based on natural polymers.

Chitosan-based nanofibers and nanoparticles.

III.2. DISTRIBUTION OF TOPICS OF PRACTICAL TRAINING

№	Topics	Soati
	V term	
1	Essence of nanochemistry	2
2	Chemical methods of synthesis	2
3	The main types of nanomaterials structures	2

4	Fullerenes	2
5	Classification and properties of carbon nanotubes	2
6	Classification of composite materials by matrix and reinforcing component materials	2
7	Polymer nanocomposites	2
8	Nanoceramics	2
9	Nanomaterials for fuel cells	2
10	Obtaining polymer blends	2
11	Application of nanocatalysts	2
12	Nanoinstruments	2
13	Concepts of nanotechnology	2
14	Nanostructures based on natural polymers.	2
15	Medical application of nanosystems	2
	By the term	**30**
	Total hours:	**30**

№	**Subject of independent education**
	V term
1	Use of nanotubes in chemical sensors
2	Catalyst nanoparticles
3	Cryochemistry of nanoparticles
4	Polymer nanocomposites
5	The role of nanoparticles in modern medicine
6	Computer modeling of nanoparticle structure
7	The concept of "Size effect" in nanochemistry and nanotechnology
8	Preparation and properties of metal oxide nanoparticles
9	Derivation and properties of quantum dots
10	Dendrimers are in the form of nanoparticles and macromolecules
11	Fullerenes in modern technology of nanomaterials
12	Carbonless nanotubes
13	Methods of researching surfaces of nanostructures

14	Methods of obtaining nanocomposites
15	Nanostructured fibers. Derivation and properties
	By the term
	Total hours:

V. RESULTS OF SCIENCE EDUCATION (COMPETENCIES TO BE FORMED)

As a result of mastering the subject, the student:

As part of the issues to be implemented in the process of mastering the science of "Nanochemistry and Nanotechnology", the bachelor:

- Must have skills and experience in the main methods of nanoparticle production;
- Separation of nanoparticles into external and internal (porous) classes of three-dimensional 3D, nanoclusters, two-dimensional 2D, linear one-dimensional 1D, non-dimensional 0D nanostructures;
- Gaining an understanding of carbon nanomaterials;
- It is necessary to acquire skills about traditional and alternative energy sources;
- Gain knowledge about nanoparticles and zeolites, including nanoparticle preparation methods and catalysis process in fields of application;
- Gaining knowledge about thermophysical, electrophysical, optical, magnetic, semiconductor, liquid crystal, superconducting and other properties of nanoparticles and nanostructures.

✓ VI. EDUCATIONAL TECHNOLOGIES AND METHODS

- ✓ lectures;
- ✓ interactive case studies;
- ✓ logical thinking, quick questions and answers;
- ✓ work in groups;
- ✓ preparation of presentations;
- ✓ individual projects;
- ✓ projects for teamwork and protection

VII. REQUIREMENTS FOR OBTAINING CREDITS

Credits allocated to science are provided to students in case of positive results from the types of control for each semester.

Intermediate (ON) and final (YaN) control types are used to assess students' knowledge of science.

Evaluation by control types: 5 - "excellent", 4 - "good", 3 - "satisfactory", 2 - "unsatisfactory" assessment criteria.

Midterm control is conducted once per semester in the form of oral or written work.

During the semesters, students are regularly evaluated and graded on each subject in practical (seminar) classes. In this case, the student's timely and complete completion of practical (laboratory) training and independent educational tasks, as well as his activity in training are taken into account. Also, the grades received on practical (laboratory) training and independent educational tasks are taken into account in the evaluation by the type of interim control. In this case, the average of the grades obtained during each intermediate control type is re-averaged with the grade obtained from the intermediate control type.

The grade obtained from the intermediate controls is recorded in the record as the result of the intermediate control.

The final control type is conducted at the end of semesters in the form of oral or written work according to the approved schedule.

In intermediate (ON) and final (YaN) control types:

A student makes independent conclusions and decisions, can think creatively, observes independently, can apply the acquired knowledge in practice, understands the essence of science (topic), knows, can express, tell, and is considered to have an idea about science (topic) – **5 (excellent) grades;**

When the student conducts independent observation, can apply the acquired knowledge in practice, understands the essence of the science (topic), knows, can express, tell and has an idea about the science (topic) - **4 (good) grade**;

When the student is able to apply the acquired knowledge in practice, understands the essence of the science (subject), knows, can express, tell and has an idea about the science (subject) - **3 (satisfactory) grade;**

When it is considered that the student has not mastered the science program, does not understand the essence of the science (topic) and does not have an idea about the science (topic) - he is evaluated with a grade of **2 (unsatisfactory**)

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MAIN LITERATURE:

1. Нанотехнологии. Азбука для всех. Под ред. акад. Ю.Д.Третьякова. М.: Физматлит, 2008.
2. Суздалиев И.П. Нанотехнология: физико- химия нанокластеров, наноструктур и наноматериалов. М. «Ком Книга» 2006.
3. Сергеев Г.Б. Нанохимия. М.: Книжный дом Университет, 2006.

ADDITIONAL LITERATURE:

1. Рашкович Л.Н. Атомно-силовая микроскопия процессов кристаллизации в растворе. Соросовский образовательный журнал. 2001, т. 7, № 10.
2. Сидоров Л.Н., Юровская М.А. и др. Фуллерены. М.: Экзамен, 2004;
3. Рыбалкина М. Нанотехнологии для всех. М., 2005.
4. Еремин В.В. Теоретическая и математическая химия. Гл. 4, § 4. М.:МЦНМ О, 2007.

INFORMATIONAL SOURCES

1) www.natlib.uz.
2) www.Ziyo.net.
3) www.chemistry.ru.

4) www.ximik.ru.

Curriculum developed and approved by Namangan State University

- The curriculum was discussed and recommended for approval at the general meeting of the Department of “Organic Chemistry” the meeting No__ “___ “ June 2023.
- The curriculum was discussed and recommend for approval in the meeting No____ of the Faculty of Natural Sciences “____” July 2023-year.
- The curriculum of the subject was discussed and approved by the educational and methodological council of NamSU meeting No.___ “___" July 2023-year.

Subject /Responsible for the credit:

D.M. Sattarova – NamSU, Associate Professor of the Department of Organic Chemistry, Doctor of Philosophy (PhD) in the field of chemical sciences.

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Taqrizchilar:

Sh.V.Abdullayev – NamSU, Professor of the Department of Organic Chemistry, Doctor of Chemical Sciences.

A.M.Karimov – NamSU, Associate Professor of the Department of Organic Chemistry, Doctor of Chemical Sciences.

Control questions

1. What is nanoscience? Nanotechnology?

2. Explain the phrase "Every substance has a nano level."

3. Describe the role of nanochemistry in nanoscience.

4. Using the information given in the lecture, calculate the number of gold atoms in 1 m3 and 1 nm3.

Answer. 5.9x1028; 59.

5. One of the founders of nanoscience, the American physicist R. Feynman, speaking about the theoretical possibilities of mechanical manipulation of individual atoms in 1959, said the famous phrase: "There's plenty of room at the bottom") How do you understand the scientist's speech?

6. What is the difference between physical and chemical methods of obtaining nanoparticles?

7. Explain the meaning of the terms "nanoparticle", "cluster", "nanotube", "nanowire", "nanofilm", "nanopowder", "quantum dot".

8. Explain the meaning of the concept of "size effect". In what features does it manifest itself?

9. Copper nano powder, unlike copper wire, dissolves quickly in hydroiodic acid. How to explain this?

10. Why is the color of colloidal gold solutions with nanoparticles different from the color of ordinary metal?

11. The radius of a spherical gold nanoparticle is 1.5 nm, and the radius of a gold atom is 0.15 nm. Calculate how many gold atoms it contains

in the nanoparticle.

Answer. 1000.

12. What types of clusters does the Au55 particle belong to?

13. In addition to benzaldehyde, what other products can be formed during the oxidation of styrene with atmospheric oxygen?

14. What are the similarities and differences of water obtained as a result of melting ice?

and water formed during the condensation of steam?

15. Give examples of 3-dimensional nanoobjects; 2; one; 0.

16. Why are there no carbon nanomaterials in the carbon phase diagram?
17. Why does diamond not spontaneously turn into graphite at room temperature? Why is high pressure necessary for this reaction?
18. Write the reactions of carbon with concentrated nitric and sulfuric acids. Why do you think graphite enters these reactions but diamond does not?
19. Give examples that confirm the difference between the properties of nanodiamond and normal diamond.
20. What properties of nanodiamonds ensure their wide practical application? 21. Why can't the C60 molecule be considered aromatic?
22. Why are higher fullerenes practically not formed in gaseous carbon deposition?
23. Fullerene is a highly endothermic substance: 2350 kJ/mol is absorbed when formed from graphite. At the same time, a large amount of heat is released during the synthesis of fullerene from individual carbon atoms in the gas phase. Explain these facts.24. How does fullerene become a water-soluble form? Suggest two ways.
25. What properties of fullerene can be used in practice
character?
26. Methane decomposition reaction

CH4 (g.) = S (tv.) + 2H2 (g.)
proceeds by absorbing heat. What factors help shift the equilibrium toward solid carbon?
27. State several ways to classify nanotubes.
28. Can fullerene be considered a carbon nanotube?
29. List the main methods of synthesis of carbon nanotubes
side.
30. What do all allotropic carbon nanoforms have in common?
31. How much of the sun's absorbed light energy does humanity use?
32. Why does the enthalpy and Gibbs energy change almost the same in the combustion reaction of methane?
33. What are the advantages and disadvantages of hydrogen as an energy source?

34. List the main tasks that need to be solved for the development of hydrogen energy.
35. Why is there no free molecular hydrogen on Earth? Explain this fact based on the physical and chemical properties of hydrogen.
36. List the most important ways of obtaining hydrogen. Try to evaluate the environmental impact of their use.
37. What part of hydrogen is separated from water and what part from methane in steam reforming of methane?
38. What types of hydrogen-oxygen fuel cells do you know? How are they different and what do they have in common?
39. Write the equations of the half-reactions of the electrode in the carbonate fuel cell.
40. Calculate the mass of hydrogen in a 100 l cylinder at room temperature.
41. Explain the difference between nanoscience and nanotechnology.
42. What stages does the innovation chain include?
43. What can serve as a source of energy for nanomotors?
44. Give an example of a natural nanomotor.
45. Describe the structure of a nanomotor that converts light energy into mechanical work.
46. What causes a nanocar to move on a surface?
47. From the substances listed below: a) diamagnets; b) paramagnets; c) ferromagnets.
Oxygen, iron, sodium, carbon oxide (IV), aluminum, iron oxide (II, III).
48. What is ferritin? What role does it play in the body?
49. Define nanomedicine.
50. In your opinion, what might be the advantage of nanomedicine over conventional medicine?
51. Do you believe in the future of nanotechnology?

General issues

1. Objects of nanotechnology

2. Properties of nano-sized objects

3. The main stages of nanotechnology development

4. Connection between nanochemistry and nanotechnology

5. Types of "bottom-up" methods of deposition of particles from the gas phase

6. How chemical and physical precipitation occurs

7. Stages of the grinding process in obtaining nanoparticles

8. In what ways is evaporation carried out during the deposition of particles from the gas phase

9. Laser ablation

10. How carbon nanotubes are formed

11. The method of obtaining metal nanoclusters

12. Formation of nanoparticles from colloidal solution

13. Obtaining nanoparticles of oxides in solution

14. Obtaining nanoparticles in a monodisperse state

15. Solid and porous types

16. Classification by size

17. Types of nanoclusters

18. Nanotubes, nanowires, nanofibers

19. Dendrimers

20. Supramolecular structure

21. Whiskers

22. quantum dots

23. Polymer nanocomposites

24. Fillers for nanocomposites

25. Production of polymer nanocomposites

26. Polymer nanocomposites based on organoloys

27. Fire-resistant nanocomposites

28. Allotropic forms of carbon.

29. Nanodiamonds.

30. Fullerenes and their derivatives.

31. Nanotubes, their classification and properties.

32. General properties of carbon nanoforms.

33. Carbon nanotubes and their production

34. General properties of catalysts.

35. Classification of catalytic reactions.

36. Principles of structural and energetic compatibility.

37. Nanoparticles and zeolite preparation methods and fields of application.

38. Application of nanocatalysis

39. Preparation of nanocatalysts

40. Photocatalysis

41. Catalyst ZSM-5

42. Properties of nanomaterials

43. Quantum size effects

44. Chemical properties of nanoparticles

45. Polymer mixtures and their types

46. Optical and electron microscope main parts

47. The principle of transparent, scanning electronic operation

48. Working principle of the tunnel microscope

46. Working principle of atomic stress microscopes

47. Application of nanosystems in industry

48. Application of nanosystems in medicine

49. Application of nanosystems in energy

50. Nanomaterials in fuel cells.

GLOSSARY

Nanoclusters- consists of metal atoms or relatively simple molecules.

"**Nanoforms"** of carbon, nanodiamonds are the closest to the natural state of carbon

Carbon fibers (carbon plastics) are compositions consisting of polymer binder (matrix) and hardeners in the form of carbon fibers (carbon fibers).

Fiberglass is a composite consisting of a synthetic resin as a binder and a fiberglass filler.

Polymer blends are compositions consisting of two (rarely three or more) polymers, the preparation of which has the following main goals: gain in properties due to a synergistic effect.

Nanoparticles are generally referred to as objects that are composed of atoms, ions, or molecules and are less than 100 nm in size.

Nanotools in biology and medicine, these are molecules or supramolecular structures, the size of which does not exceed 150–200 nm, which make it possible to visualize, detect, and correct in situ changes and disturbances in biological structures and their fragments.

Nanodevices have a more complex structure, the size of which does not exceed 3-4 microns.

Nanoneedle designed to study intracellular processes, as well as the delivery of dosed portions of various molecules (fluorescent quantum dots, DNA, RNA). An atomic force microscope probe with an attached multilayer carbon nanotube allows penetration into cells without significant damage to the membrane

Laser (or optical) tweezers is a device that uses a focused laser beam to move microscopic objects. Near the focal point of a laser beam, light pulls everything around it into focus.

Atomic force microscope (AFM), designed similarly to the STM, the van der Waals repulsion of the probe from the sample surface is measured instead of the tunneling current

Nanotechnology as a scientific and technical direction provides the ability to create and change objects in a controlled way, including the ability to create and change components with dimensions less than 100 nm, which have fundamentally new qualities. and a set of techniques and methods that allow them to be integrated into fully functioning macroscale systems.

The basic idea of **molecular nanotechnology** is to synthesize any stable chemical substance, imagine a molecule, draw its structure, theoretically calculate its stability, and then look for ways to synthesize it, no matter how fantastic they may seem.