**Lecture 2**. Nanomaterials. Nanoparticles. Classification of nanoparticles.

**Nanomaterials** are [materials](https://en.wikipedia.org/wiki/Material) of which a single unit small sized (in at least one dimension) between 1 and 100 nm (the usual definition of [nanoscale](https://en.wikipedia.org/wiki/Nanoscopic_scale%22%20%5Co%20%22Nanoscopic%20scale)).

Nanomaterials research takes a [materials science](https://en.wikipedia.org/wiki/Materials_science%22%20%5Co%20%22Materials%20science)-based approach to [nanotechnology](https://en.wikipedia.org/wiki/Nanotechnology%22%20%5Co%20%22Nanotechnology), leveraging advances in materials [metrology](https://en.wikipedia.org/wiki/Metrology%22%20%5Co%20%22Metrology) and synthesis which have been developed in support of [microfabrication](https://en.wikipedia.org/wiki/Microfabrication%22%20%5Co%20%22Microfabrication) research. Materials with structure at the nanoscale often have unique optical, electronic, thermo-physical or mechanical properties

Nanomaterials are materials created **using nanoparticles** and / or by means of **nanotechnology** that have any unique properties due to the presence of these particles in the material.

**Nanoparticles** are the most fundamental components in the fabrication of a nanomaterials and nanostructures. The size of nanoparticles spans the range between 1 and 100 nm. They are far smaller than the world of everyday objects that are described by Newton’s laws of motion and Coulomb’s law of electrostatic interaction, but bigger than an atom or a simple molecule that are governed by quantum mechanics.

They have new properties and they are new object of science. Nanoparticle research is currently an area of intense scientific interest due to a wide variety of potential applications in different fields (electronics, biomedicine, optics and others).

Disperse phase nanoparticles can be distinguished by dimensions on one-dimensional, two-dimensional and three-dimensional nanoparticles (Fig. 6).



Figure 1. Scheme of three-dimensional, two-dimensional and one-dimensional nanoparticles

For three-dimensional particle all three dimensions are relate to the nanoscale less than 100 nm. These nanoparticles have very small curvature radius. Quantum dots (tiny particles of semiconductor material), nanoshells, nanorings, microcapsules, precipitates, colloid solutions (sols) and aerosols, microemulsions, nucleus particles of first type (crystals, droplets, gas bubbles), spherical micelles of surfactants can be regarded as three-dimensional particles.

Two-dimensional nanoparticles have two dimensions in nanoscale (other one dimension is extended). They are thin fibers, nanowires, capillaries and porous, cylindric micelles of surfactants and nanotubes.

One-dimensional nanoparticles have one dimension in nanoscale (other two dimensions are not confined to the nanoscale). Thin films, coatings, surfactant mono- and polylayers at the interfaces, including Langmuir-Blodgett films, lamellar micelles of surfactants are related to one-dimensional nanoparticles.

Nanoparticles can be not continuous. They consist of crystal grains, filaments or include hollows. The assemblage of nanoparticles (clusters, quantum dots) of certain size with the presence of functional connections form the nanostructures or nanostructured systems. They can be considered as bulk nanomaterials.

Bulk nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrary dimensions above 100 nm. With respect to the presence of features at the nanoscale, bulk nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers.

It should be noted that there is another classification of nanoparticles in scientific papers by numbers of dimensions not confined to the nanoscale 3-D (bulk), 2-D (quantum well), 1-D (quantum wire), and 0-D (quantum dot) systems.

The classification of the dispersed particles by their dimensions determines the colloidal chemical properties of nanoparticles. Dimensions significantly affect the dependence linking the physical parameters:

* coefficient of degree at distance in Newton's law of gravitation and the Coulomb electrostatic interaction in the case of three-dimensional space is equal to two, in the case of one-dimensional – to one.
* the dependence of heat capacity of solids at constant volume Cv on temperature T at sufficiently low temperatures for one-dimensional structures has the form C ~ f(T2), and for the three-dimensional (crystals of selenium, HF, MgSiO4) has a linear relationship C ~ f(T).

Thus, there is a specific, often nonlinear dependence of nanoparticle properties on dimension.

Nanoparticles can be amorphous or crystalline, metallic, ceramic or polymeric, integrated in a surrounding matrix material, deposited on a substrate.

 Medium surrounding the nanoparticles can be gaseous, air and liquid. Gaseous dispersion medium can be divided on protective gases, reagent gases and gas carriers. Protective gaseous medium (nitrogen, argon) defenses the nanoparticles from air action at technological processes, basically from oxygen. Gas-reagents are used at semiconducting devices for imparting of necessary electrophysical properties. Changes of semiconductor properties are achieved due to diffusion. Gases-carriers are applied for protective coatings (oxygen and others) for processing of surface layer (chloric hydrogen).

Water and organic solvents, as well as liquids, such as freon relate to the liquid protective medium.

Nanodisperse systems have huge interface and additional excess of surface energy.

The area of interfaces mainly determines the properties of disperse systems. For nanoparticle the interface (Sint) reaches a considerable size, and consist of the specific surface area (Ssp), and additional area (Sad) charactering the structure of the particles, that is:

$S\_{int} = S\_{sp} + S\_{ad}$ (1)

Specific surface area is a total area of all the particles, often per 1 kg of the dispersed phase, equal to:

$S\_{sp}=^{6}/\_{ρd}$ (2)

where *d* – a diameter of particles, ρ – a density of particle material.

Considering the dispersion is D=1/*a*, specific surface, expressed in terms of dispersion, is:

$S\_{sp}=^{6D}/\_{ρ}$ (3)

Thus, Ssp is determined in accordance with the formula (2) by diameter of the nanoparticles.

One can estimate the surface of the nanoparticles as a dispersed phase of a disperse system according to equation (2). For nanoparticles composed of homogeneous mass (without pore) with diameter 10 nm (10-8 m) and a density of 3000 kg/m3, surface area Ssp calculated through the formula (2) is 2·105 m2/kg. The specific surface area of nanoparticles of low-melting compound nanoparticles without pores is presented in Table 1.

Table 1. Specific area of nanoparticles

|  |  |  |
| --- | --- | --- |
| Nanoparticles | Density ρ,103 kg/m3 | Specific area, Ssp, m2/kg |
| for nanoparticle of100 nm | for nanoparticle of 10 nm |
| Carbide (B4C),Boron nitride (BN) | 2.3-2.5 | (1.8-1.9)·104 | (1.8-1.9)·105 |
| Titanium nitride (TiN),Vanadium oxide (V2O3) | 5.0-5.4 | (1.1-12)·104 | (1.1-1.2)·105 |
| Wolfram carbide (WC) | 15.8 | 4·103 | 4·104 |

From Table 3 it is seen that the nanoparticle specific surface area can be equal to105 m2/kg. For comparison, the specific area of sugar particles is 5 m2/kg, powdered sugar about 500 m2/kg, and for flour – the sizes vary between 300 – 700 m2/kg. The increase of density from 2.3 to 15.8·103 kg/m2 and the growth of particle sizes (from 10 to 100 nm) results in a decrease of the specific area of the nanoparticles.

Nanoparticle specific area is determined by many factors: the dispersion, shape, structure and phase state of nanoparticle surface, degree of their aggregation. It should be noted that crystalline nanoparticles consist of grains which increase the specific surface area. Specific surface of iron hydroxide (Fe(OH)3) nanoparticles of the spherical form equals to 7.8·104 m2/kg, and needle shape – 1.2·105 m2/kg. The specific area of the oxide film with a two-dimensional structure equals to 7·104 m2/kg.

Nanoparticles of framing carbon structure – fullerenes and nanotubes have an additional specific area (Sad). Let us explain the meaning of Sad on example of carbon framing structure, in particular, fullerenes and nanotubes. Fullerenes was named in honour of the architect Fuller, who invented such structures for use in architecture. Fullerenes have a skeleton structure, very similar to soccer ball and consist of a "patch" – pentagons and hexagons. When peaks of these polygons consist of carbon atoms, then the fullerene C60 has the most stable form.

Fullerene C60 is the best-known form of carbon nanoparticle consisting of symmetric twenty hexagons. In addition to hexagons, there are pentagons that border only with hexagons. Thus, each hexagon has three common sides with adjacent hexagons and three of them with pentagons (Fig. 7). Fullerenes are allotropic molecular forms of carbon. In solid state the fullerene C60 is a crystal with densely packed cubic structure, forming the nanoparticles. The density of crystalline C60 under normal conditions is 1.69·103 kg/m3,i.e. significantly less than for nanoparticles represented in Table 1.

The structure of fullerene is characterizing by a cavity inside the peculiar carbon “ball”. The surface of fullerenes forms a three-dimensional system. Furthermore, additional surface Sad (1) happens due to the two-dimensional internal cavity of fullerenes. Thus, fullerenes combine three-dimensional and two-dimensional surfaces (Fig. 6) due to the faces of hexa- and pentagons i.e. form a three-dimensional-two-dimensional dispersed phase. Consequently, interfacial surface reaches a huge quantity – more than 106 m2/kg, i.e. million square meters (or square kilometre) per one kilogram of product.



Figure 2 – Fullerens: C60, C70, C90

Various modifications of fullerenes whose number of atoms varied from 36 to 540 have been studied (Fig. 2). If some substance is introduced into the fullerene, then its properties will dramatically change and even an insulator turn into a superconductor. In 1991 the Japanese professor Sumio Injima discovered long carbon cylinders known as nanotubes. Nanotubes (Fig. 3) are composed of more than one million carbon atoms and presented as cylinders with a diameter of 0.5 nm and a length of several tens of microns, i.e. not nanosized quantities. Nanotubes can be related to the two-dimensional disperse systems (Fig. 4). The huge interfacial surface area is achieved due to not nanosized length dimension of tubes, about hundreds of thousands m2/kg. On the walls of a nanotube the carbon atoms are located at the peaks of regular hexagons.



Figure 3 – Structure of carbon nanotube.

In addition, the nanotubes have internal porosity, pore size reaches a few nm. They form an additional surface. Specific area can reach km2 per kg of substance mass as that of fullerenes. The volume of the inner cavity may include other substances, adding the unique properties of the nanotubes. Another [allotrope](https://en.wikipedia.org/wiki/Allotrope) form of carbon nanoparticles called as a graphene. Graphene consists of a single layer of carbon atoms arranged in an [hexagonal lattice](https://en.wikipedia.org/wiki/Hexagonal_lattice). Graphene is a two-dimensional structure in the form of a sheet (not a spiral).



Figure 4 – Structure of graphene

Thus, fullerenes and nanotubes can form nanostructures with a huge area of the interface. Fullerenes and carbon nanotubes consist of the same crystal structures but differ in a shape. Depending on the packaging of the elementary units and structure sizes fullerenes and carbon nanotubes form the interface and can be considered as disperse systems.

Nanoscale particles constitute a special form of so called fractal structure (fractals are plurality with irregularly branched structure). Their elementary cell are *clusters* (with a diameter not more than 20 nm) woven (Fig. 4) in threads with length which can reach to tens of micrometers, i.e. not nanosized values.



Figure 4 – Structure of fractal cluster: model consisting of 106 of the primary particles (clusters)

For this reason, clusters can be referred to two-dimensional disperse systems.

Clusters are systems of interconnected atoms or molecules. If these bonds are realized by the Van der Waals forces, the clusters are not capable to form an interface. Increase of the number of molecules in clusters containing ions, their interaction can exceed the Van der Waals forces, that leads to the formation of nanoparticles as disperse systems. Clusters efficiently are formed in a supersaturated vapour when the gas escapes from the nozzle; they can form crystallization centres as an intermediate stage of a microdroplets formation.

Fractal cluster is defined as a system with a minimum particle size ro as a structure element and the maximum rf as the size of the cluster. The number of particles N(r) in a bulk with linear dimensions r (ro ≤ r ≤ rf ) equals to:

N(r) ~ (r/ro)n, (4)

where n – parameter called as a fractal dimension.

Fractal dimension is an indicator of imperfection of the system. It should satisfy inequality n <a, where a – the size of the space which a fractal cluster forms (a = 2 for surface, a = 3 for a bulk). At the expense of the special structure the cluster has a huge interface, and it can be up to 1 km2 per kilogram, as well as nanotubes.

So, one of the main essential feature of nanoparticles is their considerable interfacial area due to both nanoparticle sizes and their structures.

**Revision questions:**

1. What are nanomaterials?
2. What are nanoparticles?
3. Classify the nanoparticles by dimensions.
4. What are peculiarities of nanoparticles?
5. Give the examples of one-dimensional, two-dimensional and three-dimensional nanoparticles.
6. How dimension can influence on a nanoparticle property?
7. To what kind of nanoparticles do nanotubes relate by their dimension?
8. How one can characterize the gaseous media surrounding the nanoparticles?
9. How you can characterize the interfacial area of nanoparticles?
10. How you can describe the specific area of nanoparticles? Give examples.
11. What is the feature of fullerene C60?
12. How do you understand the fractal structure of nanoparticles? Give example.
13. How you can explain the influence of structure on specific area?