Chapter 1: Introduction to Nanotechnology and Nanomaterials

1-Nanotechnology

Nanotechnologies are based on knowledge and mastery of the infinitely small. They constitute a field of multidisciplinary research and development involving the manufacture of new materials and new devices using tools or techniques that make it possible to structure matter at the atomic, molecular or supramolecular level. The characteristic scales of nanotechnology range from 1 to 100 nanometers. The reference unit in the world of nanotechnology is therefore the nanometer (nm). The prefix nano comes from the Greek nannos which means dwarf or, Nain(e). A nanometer is a unit of measurement that is equivalent to one billionth of a meter (1 nm = 10^{-9} m = 0.000 000 001 m). A nanometer corresponds approximately to the size of 4 silicon atoms placed side by side, to 1/100 of the width of a DNA molecule, to 1/50,000 of the thickness of a human hair or to 1 /500,000 of the line thickness of a ballpoint pen.

At such dimensions, the material acquires unexpected and often totally different properties from those of the same materials at the micro or macroscopic scale, particularly in terms of mechanical resistance, chemical reactivity, electrical conductivity or fluorescence. Nanotechnologies therefore lead to the development of materials whose fundamental properties (chemical, physical, thermal, optical,2 biological, mechanical, magnetic, etc.) can be modified: they should be considered as new chemical substances. For example, gold is totally inactive at the micrometric scale whereas it becomes an excellent catalyst when it takes on nanometric dimensions. All major families of materials are concerned: metals, ceramics, dielectrics, magnetic oxides, polymers, carbons, etc.

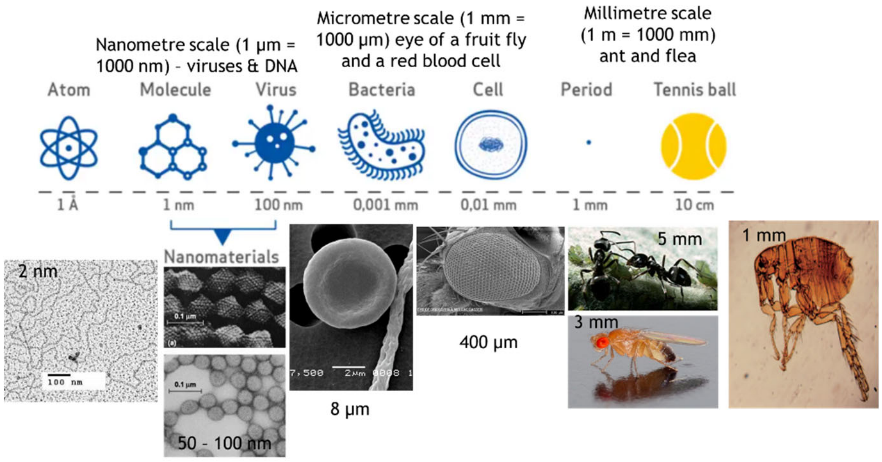


Fig 1: The characteristic scales of nanotechnology.

2-Nano-objects

Nanomaterials are materials composed or constituted wholly or partly of nano-objects which give them improved or specific properties of the nanometric dimension. Among nano-objects, it is possible to distinguish three main families: **Nanoparticles** or ultra-fine particles (UFP) in which none of the dimensions is greater than 100 nm. The term "nanoparticles" is rather reserved for particles manufactured and intended for industrial use, whether they are nanoparticles known and produced already for several years and whose tonnages are high, such as titanium dioxide or silica (they represent 95% of the nanoparticle market) or new nanoparticles such as fullerenes. Nanoparticles can be in the form of powder, suspension, solution or gel. The term "ultra-fine particles" refers more to particles that have always been present in the environment, such as volcano fumes, and old in the world of work, such as secondary emissions linked to certain industrial processes (by-products of mechanical, thermal processes: welding fumes, diesel emissions, etc.). **Nano fibers, nanotubes, nano filaments and nano**

rods, one of whose dimensions is greater than 100 nm. These terms are generally used to designate slender nano-objects whose dimensions range from 1 to a few tens of nanometers for the section and from 500 to 10,000 nanometers for the length. **Nano films**, nano layers and nano coatings, two of whose dimensions are greater than 100 nm.

3-Nanomaterials

Nano-objects can be used either as such or to develop new materials called nanomaterials and usually grouped into three categories:

- **Nano-filled or nano-reinforced materials:**
  These materials are developed by incorporating nano-objects into an organic or mineral matrix in order to provide a new functionality or to modify mechanical, optical, magnetic or mechanical and thermal properties. An example of this is nanocomposites. Various nano-objects are already used in many industrial applications such as: Silica fumes in concrete, to improve its fluidity and mechanical properties, alumina intended for polishing hard disks in microelectronics, black carbon used in printer inks and tires, organic and mineral-colored pigments incorporated in paints and varnishes, titanium dioxide used as protection against ultraviolet radiation in sun creams.
- **Surface nanostructured materials:**
  These materials are covered either with one or more nanolayers, or with nanoparticles which form a well-defined coating, making it possible to endow the surface with properties (resistance to erosion, resistance to abrasion, hydrophilicity, etc.) or new functionalities (grip, hardness, appearance, etc.). Such coatings already exist, for example to color glass packaging, provide a self-cleaning function or reinforce the surface of polymers.
- **Volume nanostructured materials:**
  These materials have an intrinsic nanometric structure (microstructure, porosity, nanocrystalline, etc.) which gives them particular physical properties. The nano-objects are, in this case, the constituent elements of the bulk material.

Some examples of nano-objects and nanomaterials

- **Fluorescent nano crystals**

Cadmium selenide (CdSe) is a fluorescent material. When prepared in the form of nanoscale grains (nanocrystals), quantum effects appear due to the small dimensions of the grains. Illuminated in ultraviolet, the nanocrystals emit a light whose color changes according to their size (this color is, for example, respectively blue and red for grain sizes of 2 nm and 5 nm).

These materials can be used for molecular labeling, ie to act as a fluorescent probe and to trace chemical reactions or biological processes in living cells.

Other fluorescent nanocrystals have been developed. Semiconductor nanocrystals (also called quantum dots) of cadmium selenide type

Fig 2: CdSe Quantum Dots.

- **Carbon nanotubes**

Discovered about fifteen years ago, carbon nanotubes constitute, with other molecules called fullerenes, the third crystalline form of carbon (the first two being graphite and diamond). The structure of a carbon nanotube can be represented by one or more sheets of graphite (carbon atoms arranged in a flat hexagonal network like a honeycomb) rolled up on themselves, or around each other. others, and which can be closed at their extremities by a half-sphere. The internal diameter of a carbon nanotube is of the order of a few nanometers and its length can reach several micrometers (they can be considered as fibers). Carbon nanotubes are divided into 2 categories: single-wall nanotubes (SWNT: Single Wall Carbon Nanotubes) and multi-wall nanotubes (MWNT: Multi Wall Carbon Nanotubes). Due to their very simple and very stable structure, carbon nanotubes have remarkable physical, mechanical and electrical properties (excellent thermal and electrical conductivity, high mechanical strength: a carbon nanotube is 100 times stronger and 6 times lighter than steel) which lead to numerous and promising applications. Carbon nanotubes can thus be used to develop high-performance composite materials, conductive polymers or even technical textiles. They are already used in the fields of sports equipment (bicycles, tennis rackets, etc.), aeronautics, automotive, defence, medicine, etc. The bulk nanotube powder also has multiple potential applications such as hydrogen storage and the manufacture of batteries for electric cars.

Fig 3 : graphite block.

- **Nano Modified Coatings**

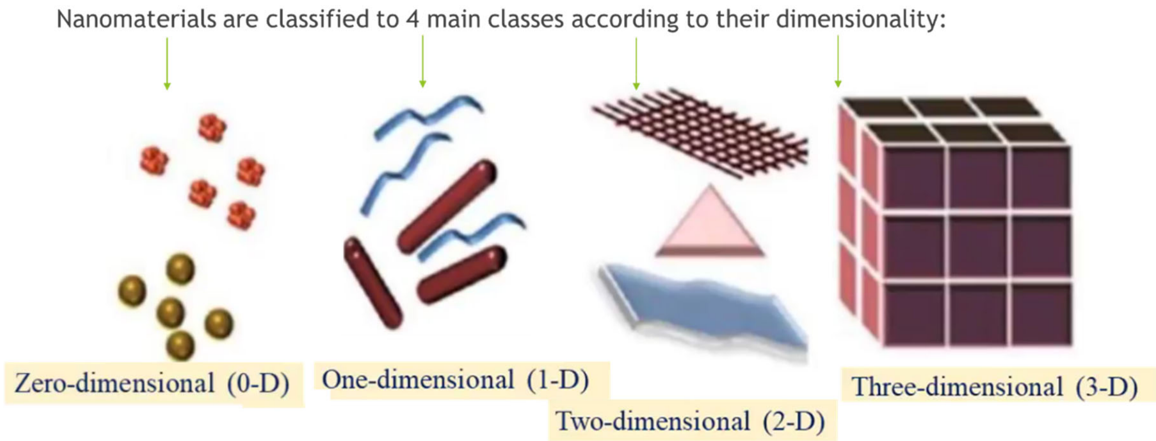
Inspired by the plant world, nano-modified coatings are currently under development. The surface of the lotus leaf is coated with nano wax crystals that form a network of tiny pillars similar to a studded plank. The water drops cannot wet the surface and remain spherical without spreading because they are supported by these pillars. Likewise, the grains of dust do not adhere and are washed away with the first rain. Manufacturing such artificial surfaces by biomimicry using nanomaterials is a considerable industrial challenge as the applications are numerous: anti-dirt windows, easy-to-wash paints, antibacterial coatings, etc. Millimetric drop of water on a hydrophobic textured substrate: the drop keeps the shape of a pearl. The texture is a network of regularly organized dots, which gives the material its colors.

4. Specificities of nanomaterials

If we want to distinguish nanomaterials from so-called classic materials, we consider a nanomaterial, an object for which one or other of its physico-chemical characteristics presents a sudden variation for a decreasing size of its crystallites. Typically, this critical crystallite size is in the range 10 – 100 nm. It is closely linked to the targeted characteristic but also for a property specific to the nature of the material itself (inorganic, organic, semiconductor, metallic). It is necessary to distinguish 4 main classes of nanomaterials according to the dimensionality:

- **Dimension 0:** this class of nanomaterials covers nanoparticles with a dimension of less than a hundred nanometers.
- **Dimension 1**: We find ultrafine fibers, nanotubes. The diameter of these objects is a few tens of nanometers for a length now reaching a few millimeters.
- **Dimension 2**: These are deposits in thin layers. This category includes multilayers for electronic applications but also, for the past ten years, “hyperhard” coatings for mechanical applications (resistance to friction and/or abrasion).
- **Dimension 3**: Massive nanomaterials constitute this class. In addition to nanostructured micron powders essentially produced by mechanical processes of the mechanosynthesis type. In this class all thick coatings (from a few tens of micrometers to a few millimeters). These coatings can be produced electrochemically or by plasma deposition.

The four main families of nanomaterials: ultrafine particles (0D), multilayers (1D), thick coatings (2D) and bulk nanomaterials (3D: nanostructured micron powders and dense or porous nanostructured bulk materials)



5. Properties of nanomaterials

The study and use of nanostructured materials are experiencing considerable growth due to their particular properties compared to bulk materials. All major families of materials are concerned: metals, ceramics, dielectrics, magnetic oxides, silicate frameworks, carbons, polymers, etc. Due to their size, nanomaterials have different characteristics on the macroscopic scale. The essential characteristic of nanoparticles is based on their very large specific surface. In other words, the particularly important ratio "number of atoms on the surface / total number of atoms of the aggregate".

Indeed, when the size of a particle decreases, the number of particles per gram increases considerably: this number is multiplied by 1,000,000 when the diameter of a particle changes from 100 nm to 1 nm. At the same time, for an equivalent quantity of material (ie one gram of material having a density of 10 g/cm3), the particle/environment surface area is multiplied by a factor of 100 (Table I). On the other hand, the reduction in the diameter of the particles leads to an increase in the proportion of atoms present on the surface (5% of the atoms of a 30 nm particle are on the surface, against 20% for a 10 nm particle and 50% for a 3 nm particle) (Table I). A given mass of nanomaterials in the form of nanoparticles will therefore be more reactive than the same mass made up of larger particles.

Nanometric structures then make it possible to obtain new materials with specific mechanical, electrical, magnetic, optical and catalytic properties or combinations of original properties, sometimes differing from the properties of the same material on a different scale. If it is a crystalline solid, the reduction in grain size leads to a larger interface at inside the material and thus can modify its mechanical and electrical properties.

Another important parameter is the chemical composition of nanomaterials, which can be metals, metal oxides, polymers, composite materials or biomolecules. It is also necessary to take into account the tendency to agglomeration and the formation of aggregates of nanoparticles, which can take different shapes and reach a micrometric size. Such agglomeration can significantly modify the properties of nanoparticles, which is why nanomaterials are often stabilized by the use of coatings.

5.1. Physical properties:

- The size, shape, specific surface and the ratio between width and height
- If they can fit together
- The distribution of the number by size
- The smooth or raised appearance of the surface
- The structure, including the crystal structure and defects of the crystal
- Their degree of solubility

5.2. Chemical properties:

- Molecular structure
- Composition, including purity and known impurities and additives
- If stored in a solid, liquid or gas
- Surface chemistry
- Attraction by water molecules or oils and fats

5.3. Mechanical properties

Regarding the mechanical properties, the effect of the nanostructure results in a phenomenon of superplasticity. The example below shows an extremely high elongation (more than 5,000%) for a nanocrystalline copper material obtained by cold rolling.

Nanostructured nanoceramics can also be shaped by superplastic deformation. Nanomaterials make it possible to improve the resistance of materials without compromising their ductility because the size of the nanoparticles limits the stress concentrations.

5.4. Electrical properties

The introduction of nanoparticles and/or nanotubes can drastically modify the electrical conductivity of materials deemed to be insulating. In the example below, the electrical conductivity reaches 3345 S/m for an addition of 15% vol of single-wall type carbon nanotubes in an alumina matrix, corresponding to a modification of 13 orders of magnitude of the initial value.

5.5. Optical properties

The nanoparticles have dimensions smaller than the wavelengths of visible light (380 – 780 nm), which improves the optical properties of the material.

5.6. Thermal (heat) transfer properties

The addition of nanoparticles can make it possible to improve certain properties with low volume fractions. Indeed, the addition of iron or copper nanoparticles can modify the thermal conductivity of heat transfer fluids. An addition of 0.2% by volume fraction of iron nanoparticles results in an increase of more than 10% in thermal conductivity.

5.7. Barrier Properties

In polymer matrix nanocomposites, the incorporation of clay increases the barrier properties with respect to water and gases due to the increase in the distance to be traveled by the molecules which diffuse. The silicate lamellae are impermeable to water and gases.