Chapter 4

Nanomaterials: doing more with less

Nanomaterials are interesting in many respects. Some have been used (or developed) over a considerable time and have been manufactured by chance without any understanding of the microscopic structure of matter. This is for example the case of the "Lycurgus cup", a glass cup with a mythological scene made probably in Rome around the 4th century AD. It is a vessel known as a cage-cup which was made by blowing or casting a thick glass blank. The glass was then cut and ground away leaving a decorative cage at the surface. The cup is made with a dichroic glass probably synthesized by accident. A change of color of the cup is observed when it is illuminated from inside: the opaque green cup becomes glowing translucent red. This phenomenon is caused by gold and silver nanoparticles which were formed during the fabrication of glass. The technique was further developed during the medieval age to make stained glass windows. The so-called "Ruby glass" it is still used today in order to make cadmium free intensely red glass.

Nanomaterials and nature

Nanomaterials can be found everywhere in nature and have been part of the environment since our planet was created about 4.5 billion years ago. Fullerenes or graphene, which are of nanosize, have even been found in space while they have been synthesized by man only recently. Wood is one of the most common natural nanomaterials. It has a hierarchical scale structure. At the largest scale, wood contains soft fibers with a diameter of about 20-30 μm and a length typically between 2 and 5 mm. At an intermediate hierarchical scale, nanofibers are present with a diameter less than 100 nm and a length greater than 1 μm. The smallest scale contains crystallites with a width less than 5 nm and a length less than 300 nm. It turns out that mechanical properties improve as the size of the structure decreases. For example, the elasticity is multiplied by almost 12 and the strength by 100 as one goes from softwood structure to wood nanocrystals.

Nanocellulosic materials are also found in nature. These can be collagen fibrils originating from animal sources; nanofibers originating from wood, plants, crops or bacteria; crystals or whiskers deriving from wood, plants and crops. Cellulose nanocrystals or whiskers can be isolated by mechanical and chemical processes for subsequent use in polymer nanocomposite materials.

Nature has developed several ways to build macroscopic systems from nanobricks, like seashell or bones, for example. The synthesis is carried out using nanocrystals at moderate temperature and pressure. The biomineralization process involves calcium carbonate or phosphate. Biomimetic strategies are now frequently used.

4.1   Top-down and bottom-up approaches

The synthesis of nanomaterials is key to the future success of this new technology and in principle, the approaches to the synthesis of nanomaterials can be divided into two main classes: Top-down approaches and bottom-up approaches.

4.1.1   Top-down approaches

In top-down approaches, a bulk material is restructured (*i.e.* partially dismantled, machined, processed or deposited) to form nanomaterials (figure 4.1). The aggressive scaling of electronic integrated circuits in recent years can be considered the greatest success of this paradigm. For top-down methods, the challenges increase as devices size is reduced and as the desired component designs become larger and more complex. Also, the top-down assembly of nanocomponents over large areas is difficult and expensive.

4.1.2   Bottom-up approach

In bottom-up approaches nanomaterials are assembled from basic building blocks, such as molecules or nanoclusters (figure 4.2). The basic building blocks, in general, are nanoscale objects with suitable properties that can be grown from elemental precursors. The concept of the bottom-up paradigm is that the complexity of nanoscale components should reside
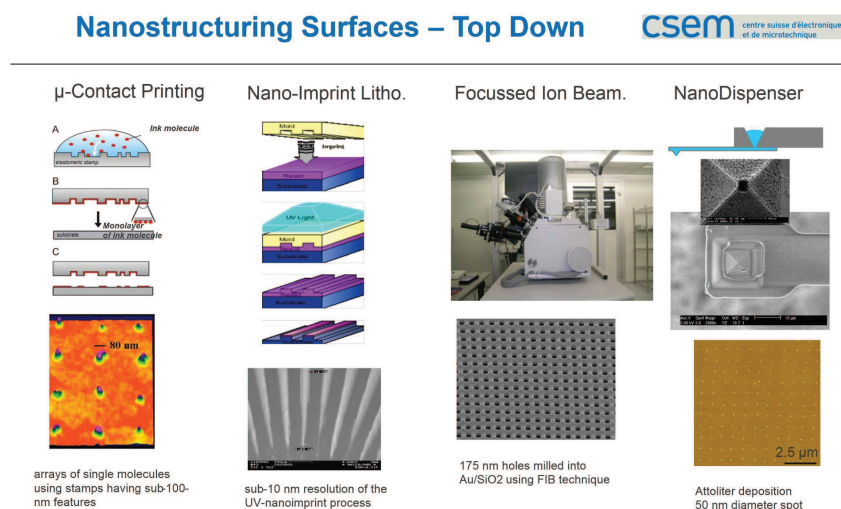
Figure 4.1: *Top-down nanosynthesis methods. Image courtesy of CSEM - International Conference on Mechatronics and Automation (ICMA), Beijing, China, August 2011.*

in their self-assembled internal structure, requiring as little intervention as possible in their fabrication from the macroscopic world.

A typical example of bottom-up processing is given in figure 4.3 for nanocomposite magnets from individual high-magnetization and high-coercivity nanoparticles. The assembling critically depends on availability of anisotropic (single crystal) hard magnetic nanoparticles. Anisotropic nanoparticles produced via surfactant-assisted high energy ball milling satisfy the major requirements for this application.

4.1.3 Two approaches with the same goal

The practical applications of the two nanosynthesis approaches are demonstrated in figure 4.4.

4.1.4 The nanobulk stage (10-15 years)

Where are we heading in terms of nanomaterial synthesis? Two stages will be followed as nanotechnology develops: the *"nanobulk"* stage and the *"nanoworld"* stage. They are conceptually different and reflect the two major paradigms of nanofabrication.

In the nanobulk stage, which has already begun and that is expected to further develop for 10-15 years, the benefits of nanomaterials will be exploited at the macroscale. In this stage, a nanomaterial is classified by its action at the human scale with novel properties determined by its nanoscopic internal structure.

To clarify this, let us review a few realistic examples of bulk nanomaterials:

1. Cosmetics containing nanoparticles are be found on the market today;

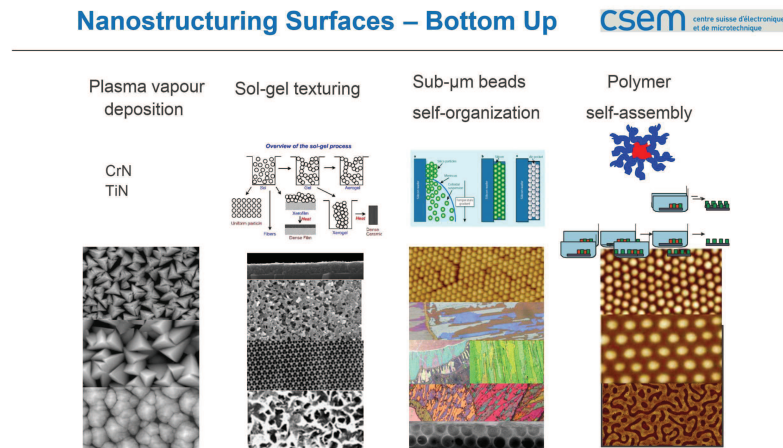**Nanotechnology in a nutshell,** *Christian Ngô & Marcel Van de Voorde*

Figure 4.2: *Bottom-up methods for nanosynthesis. Image courtesy of CSEM - International Conference on Mechatronics and Automation (ICMA), Beijing (China), August 2011.*
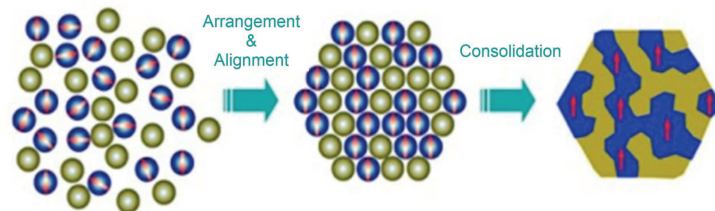

Figure 4.3: *Bottom-up fabrication of nanocomposite magnets. Image courtesy of P. Perlo Torino e-district, IFEVS - GENNESYS Barcelona conference 2010.*
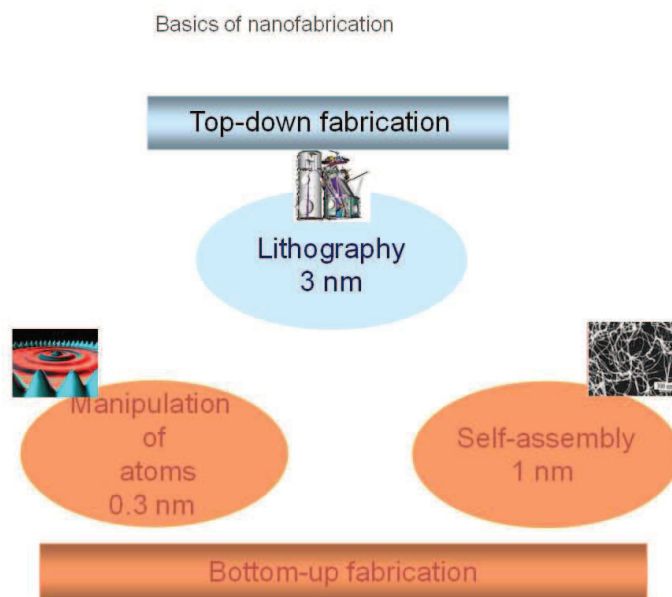
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Figure 4.4: *Schematic position of top-down and bottom-up fabrication mechanisms for nano-electronics Image courtesy of IMEC Louvain.*

2. In healthcare, nanoparticle suspensions or solutions can be injected into living tissues to help diagnostics or drug delivery;

3. Energy: large-scale nanostructured materials can enhance every type of surface- or interface-based chemical reaction, such as are important in energy generation, conversion and storage;

4. Automotive/infrastructure: composite materials containing nano-objects with extraordinary mechanical properties can result in outstanding performance enabling for instance the application of novel coatings with unprecedented resistances.

From the implementation point of view, it is clear that the most important figure of merit for the above-mentioned applications is yield. If nanomaterials are to be implemented in macroscale applications, cost-effective mass-production is essential. Important parameters will come into play such as uniformity, purity, toxicology and stability. Today, applied research will try to target these requirements, with the aim of using relatively cheap and environmentally-friendly synthesis facilities.

However, solving specific issues and unveiling performance-limiting factors will call for a deep understanding of the chemical and physical processes involved in the fabrication. This is where basic research and characterisation techniques come in. Even if the ultimate aim is producing trillions of nominally-equivalent nanocomponents, the focus is put on the study of the synthesis of an *individual* nanocomponent, to understand how it is formed and how we can better control the process. What can occur during synthesis must be understood, including why two components may be nominally equivalent but not fully equivalent.
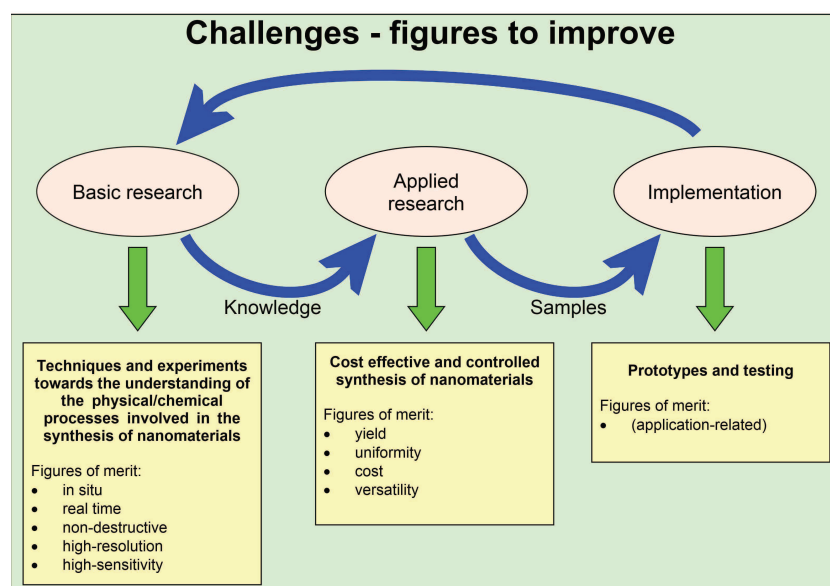
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Figure 4.5: *Roadmap for improvements of nanotechnology.*

4.1.5   The nanoworld stage (15-40 years)

This paradigm no longer considers nanocomponents as all nominally-equivalent, but aims to take advantage of the natural or induced diversity between nanoblocks. Different nano-units fabricated by the same technique may diversify to have different functions. Treating nanocomponents no longer as a mass but as individuals is obviously more challenging. It implies that the synthesis should have a very precise and independent degree of control over the structure of every single nano-object and/or the location where it is assembled or grown.

Technologically, the nanoworld stage is similar to the nanobulk one. However, basic and applied research now merge. The fabrication will no longer target mass production nor cheap strategies. The goal is to fabricate an "intelligent" nanoworld, without necessarily the driver of low cost. Precision will be more important than yield. Therefore, the facilities that only played a characterisation and fundamental role for the nanobulk could become the only possible way towards applied synthesis with nanoscale deterministic control. A good example is 3D lithography that uses high-brilliance synchrotron light to guide the process during manufacturing.

The development framework for the nanobulk stage can be summarised by diagram 4.5 which represents the traditional mode of innovation.

Top-down strategies already exist today and will continue to play an important role despite their intrinsic limitations. Bottom-up methods will drive the nanobulk stage and ultimately take over certain aspects of top-down processing via intelligent self-assembly. The history of nanosynthesis methods for electronic materials is shown in figure 4.6 as a function of a time showing a crossing point around 2010.

4.2   Nanostructuration

Nanomaterials are important because they can be used in many domains giving strategic assets to those who use and develop them. This point is, for example, pointed out by Eiji
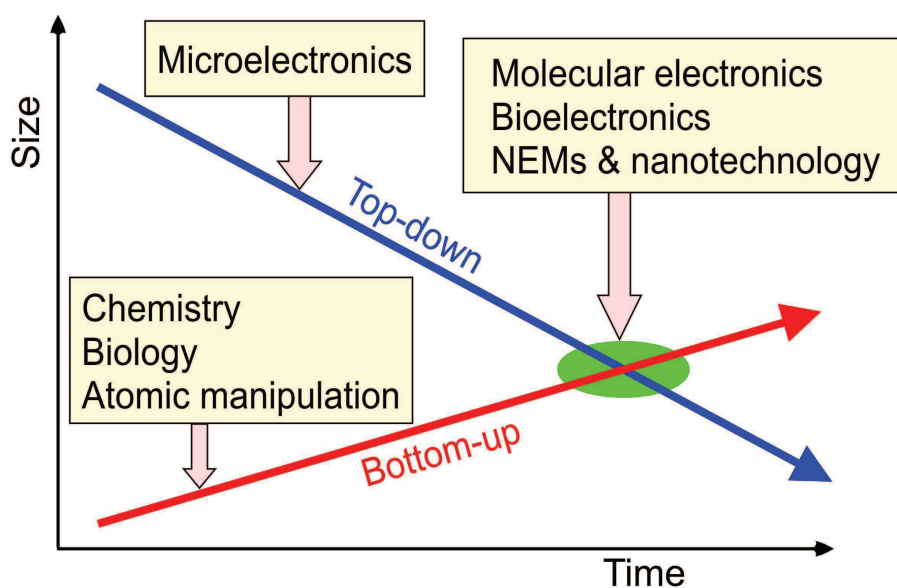
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Figure 4.6: *Convergence from Top-down and Bottom-up approaches in the case of nanoelectronics.*
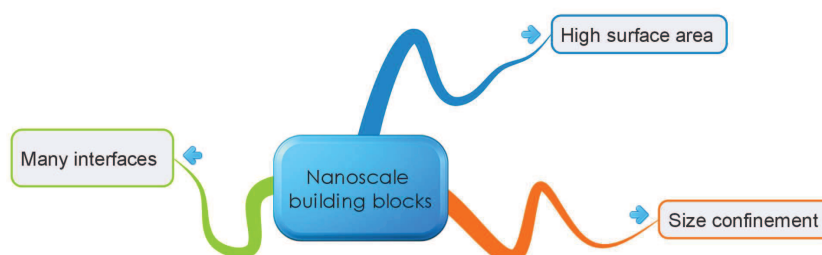

Figure 4.7: *Properties of nanoscale building blocks which will have tremendous consequences for nanostructured materials.*

Kobayashi, from Panasonic, who says: "*Those who control materials control technology*". Scientists are now able to create a wide variety of building blocks that they assemble to make nanostructured materials. Using nanoscale building blocks allows us to have high surface areas, many interfaces and, in the case of nanostructures, size confinement (figure 4.7).

The nanostructuration of materials may lead to several changes of the properties of materials:

- A global change of the properties can be obtained. This is, for example, observed by including nanoparticles in a polymer material. Because there is a huge interface area between the nanoparticles and the polymer, an interaction between the two components takes place which modifies the properties of the bulk material. This happens for tires where carbon black is used to improve their properties, particularly their durability. This is also the case in cements. Concrete is a building material extensively used around the world. It is a low cost and easy to manufacture material with good structural properties. However, it has a low resistance to tensile forces and is porous. A considerable improvement of its properties is obtained by adding silica
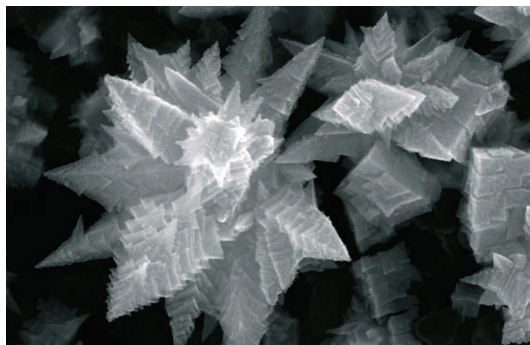
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Figure 4.8: *Nanostructuration of platinum in the form of nanoparticles. Clef CEA n°59. Courtesy of CEA. The results have been obtained by the CEA in the framework of a Challenge innovation program.*

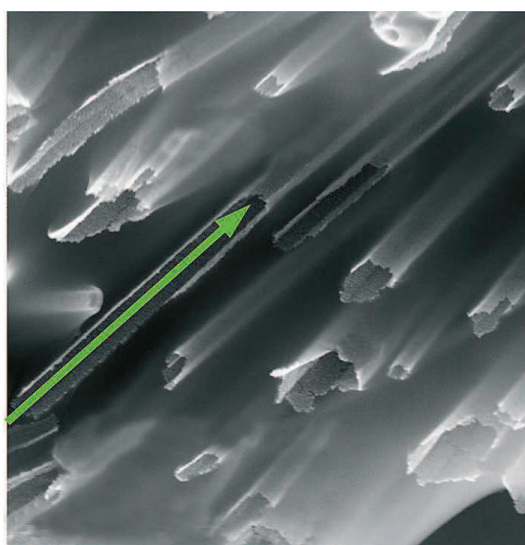

Figure 4.9: *Nanostructuration of platinum in the form of porous nanotubes. Clef CEA n°59. Courtesy of CEA.*

smoke containing silica nanoparticles. Concrete with silica smoke is significantly less porous and less permeable to water, which is for example valuable when this material is in contact with sea water.

- Nanoparticles can also be used to introduce specific optical, magnetic, and catalytic properties. In many cases, it is the characteristics of the nanoparticles which are important and not the interaction with the inert matrix housing them, but interfaces between nanoparticles and host matrix or support can play an essential role, especially when charge transfer is involved: role of triple lines (or points) in nanocatalysts, role of surface states in luminescence.

Figures 4.8 and 4.9 show examples of the nanostructuration of platinum. In figure 4.8, the nanostructuration is done in the form of nanoparticles. The length of the horizontal figure is about 800 nm.

In figure 4.9, the nanostructuration of platinum is produced in the form of porous nanotubes which could be used in catalysis. The green arrow indicates the oriented

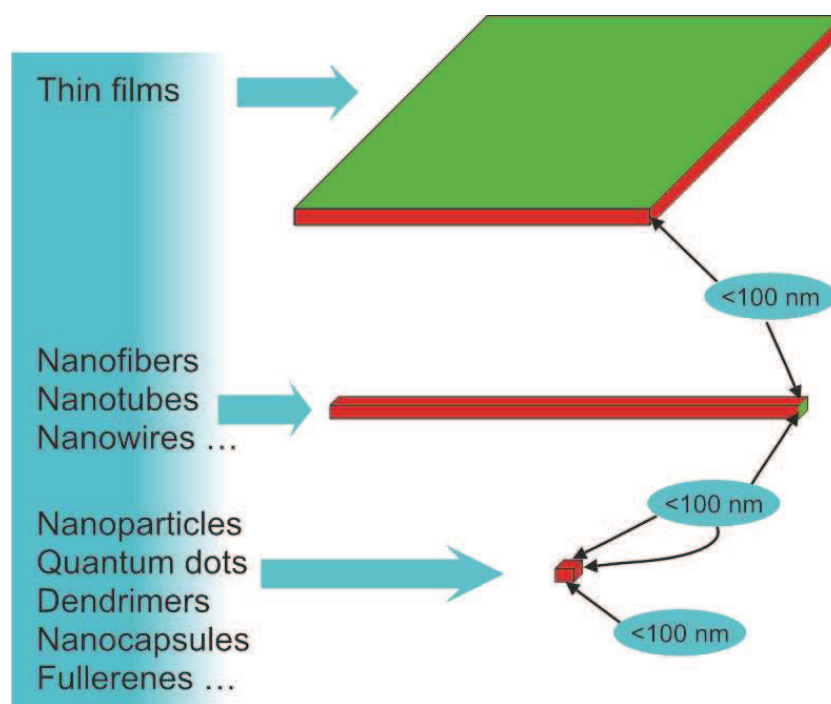**Nanotechnology in a nutshell,** *Christian Ngô & Marcel Van de Voorde*

Figure 4.10: *Classification where 1D, 2D and 3D objects have one, two or three dimensions in the nanometer range.*

porous catalytic nanostructure. The length of the horizontal figure corresponds to about 7 μm.

4.3 Classifying nanostructured materials

There are several ways to classify nanomaterials. This depends very much on the applications and philosophy which are adopted. We shall just present here two extreme classifications which can be found in the literature.

In the first one, the focus is done on the macroscopic dimensions of the material. Nanomaterials are then defined as materials containing structures having at least one dimension less than about 100 nm. According to this definition, a thin film (with a thickness less than 100 nm) is considered as a nanomaterial (figure 4.10) since one of the dimensions is nanometric. Thin films have been used for a long time, before there was any interest in "nanotechnology". If two dimensions are "nano", we have nanofibers, nanowires *etc.*, and if all three dimensions are "nano" we have quantum dots.

In this classification this no reference to the structure of the material.

Another classification, which might be more relevant as far as the nanostructure of a material is concerned, is to consider the dimensionality of the nanoscale component with which the material is made. A nanostructure is said to have one dimension, for example, if it has a length larger than 100 nm in one direction only. According to this definition, a nanoparticle is considered to have zero dimension (it has no dimension with a length larger than 100 nm). A wire or a fiber is a 1-dimensional object and a thin film a 2-dimension nanostructure. To summarize, 0D nanomaterials contain spheres or clusters which are considered as point-like particles. 1D nanomaterials contain nanofibers, wires,

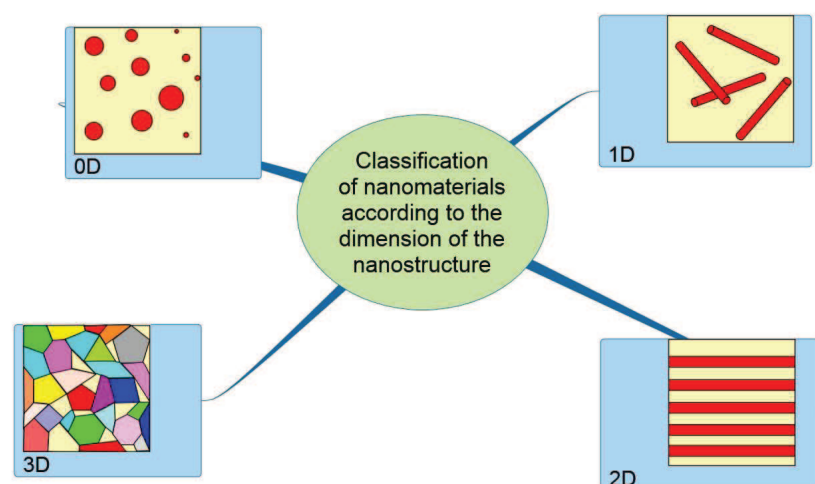**Nanotechnology in a nutshell,** *Christian Ngô & Marcel Van de Voorde*

Figure 4.11: *Classification of materials according to the dimensionality of the nanostructures. 0D, 1D, 2D and 3D nanostructured materials are sketched in this figure. In the 2D illustration, we have 2D layers embedded in the bulk and in the 3D crystallites or grains.*
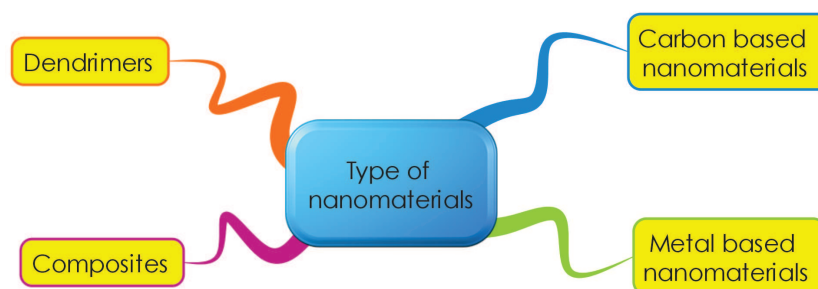

Figure 4.12: *Different types of nanomaterials according to their composition (see text).*

rods, *etc.*, 2D use films, plates, multilayers, or networks. 3D nanomaterials are nanophase materials consisting of equiaxed nanometer-sized grains. This is shown schematically in figure 4.11.

Bulk nanomaterials are larger objects made from structures having well-identified domains with an average size less than 100 nm, for instance the grain size in ceramics. For comparison, the diameter of a human hair is about 100,000 nm and the size of a single particle of smoke is around 1,000 nm.

In this case a nanoparticle is considered to have zero dimension, a wire, 1 dimension There are several ways to classify nanostructured nanomaterials, but this depends, to some extent, on the applications under consideration. As sketched in figure 11, a nanomaterial can be classified according to the dimension of the nanostructure used to make it: zero dimensional (0D), one dimensional (1D), two dimensional (2D) and three dimensional (3D).

It is also possible to classify nanomaterials in families reflecting their composition. This gives, as a possibility, the classification shown in figure 4.12. It is possible to distinguish the four types of nanomaterials as indicated in figure 4.12.

Carbon-based nanomaterials are composed mostly of carbon. They play such an important role in applications as well as in the historical development of the nanotechnology

domain that the next chapter will be completely devoted to them. This classification includes fullerenes, carbon nanotubes, graphene and the like.

Metal-based nanomaterials are materials made of metallic nanoparticles like gold, silver, metal oxides, *etc.* For example, titanium dioxide (TiO_2) nanoparticles are extensively used in applications such as paint, sunscreen, and toothpaste.

Dendrimers are nanosized polymers built from branched units. They can be functionalized at the surface and can hide molecules in their cavities. A direct application of dendrimers is for drug delivery.

Composite nanomaterials contain a mixture of simple nanoparticles or compounds such as nanosized clays within a bulk material. The nanoparticles give better physical, mechanical, and/or chemical properties to the initial bulk material.

4.4 Nanostructured materials

Nanostructured materials are materials with structures in the nanoscale range (1-100 nm). The properties of the nanostructured materials depend on the size and nature of their microstructure. If the characteristic length scale of the microstructure is comparable to the lengths associated with fundamental physical phenomena, large changes in the properties of the material compared to a non-nanostructured material can be observed. The whole structure – like for many materials - can be in or out of thermodynamic equilibrium. Using crystallites of nanometer size of elements like gold or sodium chloride, for instance, can produce a great variety of nanostructuration depending on the crystallographic orientation, the chemical composition of the mixture and the possibility to have non-equilibrium structures which provides certain property advantages.

Nanoparticles are of course often used as building blocks to make nanostructured materials. They can be of various natures: fullerenes, nanotubes, nanocrystallites, nanofibers, *etc.* If the simplest building blocks of nanostructured nanomaterials are nanoparticles, more complicated elementary structures can be used as well, as in nanocomposites, for example.

Nano-intermediates are the building blocks of nanostructured materials. Nanoparticles are the simplest objects we may think of from which to build nanomaterials. However, it is not always easy to align nanoparticles according to a given template by self-assembly. There are only few examples (mainly sulphides or selenides) combining with success soft templates, self-alignment of nanoparticles by dipolar interactions and oriented attachment resulting in 1D structures or hierarchical structures. Hard nanotemplates can be designed using different techniques such as electron lithography, for example, or anodization as for alumina membranes. Soft nanotemplates (such as mesophases and micellar systems) may also be used in the synthesis of nanoparticles with controlled size and shape, or mesoporous materials.

Films with a thickness less than 100 nm, supramolecular assemblies, dispersions of nanoparticles, *etc.* are nano-intermediates currently used to improve different technologies such as solar cells, batteries, catalysts, and drug delivery systems.
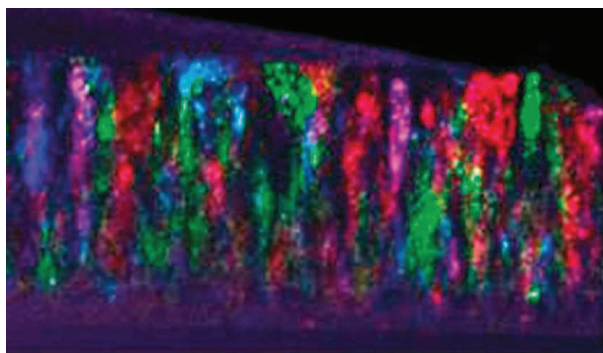
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Figure 4.13: *Transverse view of a thin film of FeHf(N,O) nanostructured material. The ferro-magnetic grains have a size between 5 nm and 10 nm, finely dispersed across a high-resistivity amorphous matrix. This gives the material a high permeability and a high resistivity. From clef CEA n°59. Courtesy of CEA.*
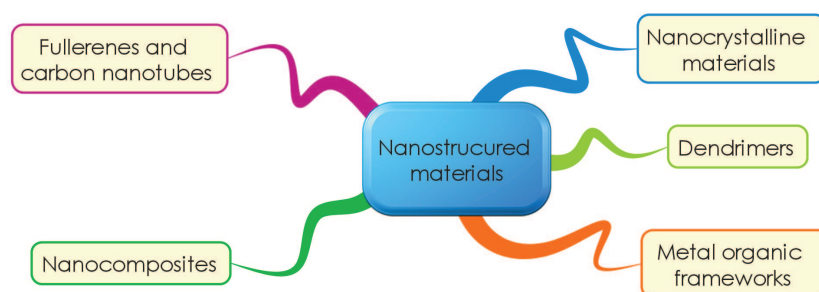

Figure 4.14: *Families of nanostructured materials.*

Example of a nanostructured film

An illustration is shown in figure 4.13. The picture shows a transverse section observed with a transmission electron microscope of a nanostructured FeHf(NO) film. The horizontal length of figure 4.13 is about 750 nm. Ferromagnetic grains of a size between 5 and 10 nm are dispersed inside a high resistivity amorphous matrix. The resulting nanostructured film has both high resistivity and high saturation magnetization value. These properties, obtained at the CEA, are interesting because they allow integrating this material in circuits close to inductive components, while minimizing parasitic capacities at high frequency operation (up to more than 2GHz).

Nanostructured materials can be ordered into different families indicated in figure 4.14. Fullerenes and carbon nanotubes will be treated in the next chapter.

4.4.1   Nanocrystalline materials

Nanocrystalline materials include metals or metal oxides like ceramics nanoparticles as building blocks. The building blocks are nanometer-sized crystallites. Nanocrystalline materials are inhomogeneous structures at the nanoscale. They differ from microstructurally homogeneous structures like gels. The atomic structure, the crystallographic orientation

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and the chemical composition can be chosen to provide required macroscopic properties. Furthermore, a strategy can be used to assemble the building blocks, for example concerning the interface arrangement between the building blocks (such as the grain boundaries). The way the heterogeneous structure looks is an important issue regarding many of the properties of the nanostructured materials. Taking materials with the same chemical composition but of different structures, it turns out that nanostructured nanomaterials having a lot of grain boundaries at the nanoscale have their properties strongly modified compared to a single crystal structure or an amorphous structure like glass.

A high density of grain boundaries, obtained during processing or by careful engineering, changes some of the properties of the bulk material, making it more valuable for many applications. The changes depend upon the size of the nanostructures and could for example lead to increased ductility of the material or a lower melting point. Because of the small dimensions involved at the interfaces, quantum effects can appear. Metal nanocrystalline materials are often used in heterogeneous catalysis.

4.4.2 Dendrimers

A dendrimer is a macromolecule made up of monomers which assemble into a tree structure around a central core. It is a highly branched 3D structure offering a large surface functionality and versatility. Dendrimer comes from the Greek word "dendra" meaning a tree. Dendrimers are used in nanoparticle synthesis or they can encapsulate nanoparticles.

Dendrimers can be synthesized either by a divergent method or by a convergent method. In the divergent method, which is mostly used, the dendrimer grows outwards from a multifunctional core molecule. In the first step, the core molecule reacts with a monomer molecule containing one reactive group and two dormant groups leading to a first-generation dendrimer. After activating the dormant group of the first step dendrimer, the monomer reacts again and a second-generation dendrimer is obtained. The process is repeated until the desired size is obtained and, at each step, a new layer is added. The divergent method allows the preparation of large quantities of dendrimers.

Dendrimer chemistry was introduced in 1978 by F. Vögtle and collaborators. The first family of dendrimers was synthesized in 1985 by D.A.Tomalia. The macromolecule has a spherical structure. Modern synthesis methods allow a precise control over the molecular design of the dendrimer. It is possible to tailor the size, the shape, the surface and interior chemical functionalization, the flexibility and the topology of the dendrimer. Grafting new chemical functions onto the surface of the dendrimer is also possible.

In the simple divergent synthesis method schematically displayed in figure 4.15, there is only one type of terminal group located at the surface of the dendrimer. However more complex dendrimer structures can be synthesized. For example, different chemical bonding can be made at some generation steps in a divergent synthesis method, creating layer-block dendrimers (figure 4.15).

In the convergent method, the dendrimer is constructed by steps, starting from the end groups and progressing inwards. When the branches are large enough, they are attached to the multifunctional core molecule.

Dendrimers can be used as nanocarriers in medical applications such as drug delivery, diagnostics, and tumour therapy. Their structure and synthesis can be tailored to fulfill specific applications.

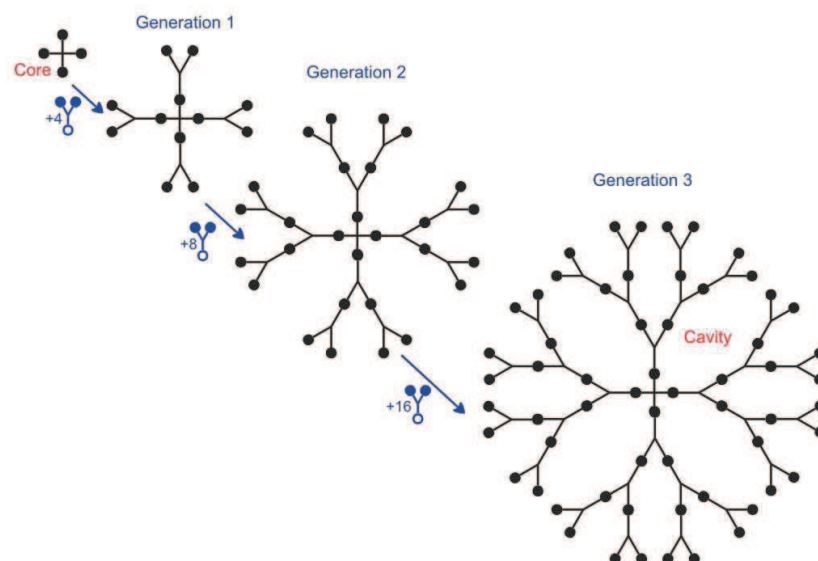Most synthesized dendrimers have a single function at their surface and they are

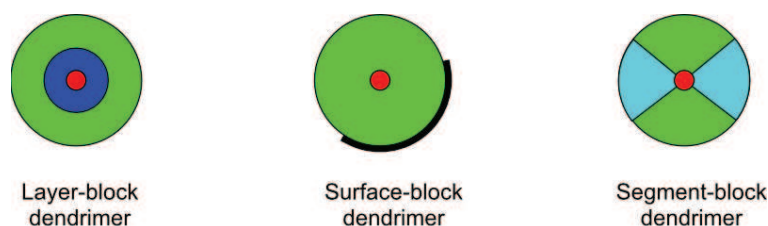Figure 4.15: *Schematic synthesis of a dendrimer by the divergent method.*

Figure 4.16: *There can be sophisticated architectures of dendrimers (se text). Blue and green colors correspond to two different generations in the building up of the dendrimer.*

generated with similar sequences. However there also exist other kinds of dendrimers, called layer-blocks, where the chemical sequences between two generations can be different. These are mainly synthesized by the divergent method (left segment of figure 4.16). Using the convergent method, two types of complex dendrimer structures can be obtained. If part of the surface of the dendrimer has a different chemical function than the other, the dendrimer is called surface-block (central segment of figure 4.16). If some volume parts, starting from the core, are different, these are called segment-block dendrimers (right part of figure 4.16).

4.4.3   Metal organic frameworks

Hybrid materials are interesting because they can have both the good physical properties of ceramics and the advantage of organic molecules in terms of reactivity and functionalization. There is great interest in hybrid materials containing silicon atoms in organic polymers such as polyhedral silsesquioxanes. The name of these structures comes from the fact that each silicon atom is bound to one and a half oxygen atoms. The global chemical formula reads $RSiO_{3/2}$, where R is either hydrogen or a hydrocarbon group. They can have a cage structure (from cubic or hexagonal to dodecagonal prisms) allowing

placement of small molecules to be put inside.

These hybrid materials turn out to be interesting in electronics (low dielectric constant films) or photonics (light emitting diodes).

They are also interesting as a support for catalysts for both homogeneous and heterogeneous systems. Chromium or vanadium metals can be used in catalysts. Silsesquioxanes can also be used in pH-sensors.

Silsesquioxanes can be functionalized to produce antimicrobial coatings. For example, quaternary ammonium salts can be used to make functionalized polyhedral oligomeric silsesquioxanes. Quaternary ammonium salts have the ability to kill bacteria and fungi while being harmless to humans and animals.

4.4.4 Nanocomposites

A nanocomposite is a material composed of several phases where at least one of the phases has one, two or three dimensions less than 100 nm. It can also be made of nanostructures occurring in repeating units. Nanoparticles are often combined with bulk materials because they improve their properties.

Thanks to the presence of nanostructures in the bulk, the material may become stronger, have a higher ductility, be lighter, *etc.* The final properties depend on the process of manufacturing, of the nature of the nanostructure and its arrangement within the bulk material. As mentioned earlier, carbon black nanoparticles are used in the rubber of tires. Besides the effect of making black-colored tires, this substance improves the strength and tensile properties, the tear and abrasion resistance and increases the hardness of the tire. The improvement from the reinforcement increases with the concentration of carbon black nanoparticles up to a certain point until it decreases. Many mechanisms are involved in this reinforcement but they are basically due to the interaction between the grains of black carbon and the rubber material. Another example is aluminum alloys were even parts-per-million (ppm) concentration of nano-impurities drastically changes the properties of the initial material by increasing their strength and corrosion resistance.

Nanocomposite materials can be multilayer structures. There are several ways to make multilayers: by gas phase deposition, or from self-assembly of monolayers. In some cases, spinodal decomposition can be used to obtain multilayered structures in the bulk of mixed oxides (TiO_2- SnO_2 for example). Magnetic multilayered materials used in storage media are an example of multilayer nanocomposites.

Polymer-clay nanocomposites also have successful applications today. They can improve significantly the properties of an initial polymer at low cost. For example they are less flammable while maintaining good mechanical properties. This is not the case when flame retardant additives to polymers are traditionally incorporated.

The size of the nanostructures incorporated into the nanocomposite may provide specific applications. For example, nanostructure sizes less than 5 nm are interesting for catalytic applications. Hard magnetic materials have nanostructures typically less than 20 nm. If the size of the nanostructures is less than 50 nm, nanocomposites show refractive index changes while if the size is less than 100 nm mechanical strengthening or superparamagnetism can be observed.

One can classify nanocomposites as organic, inorganic, or inorganic/organic. Inorganic/organic composites can be made by sol-gel techniques, by adding nanoparticles.

One can also classify nanocomposites as ceramic-matrix, metal-matrix or polymer-

matrix nanocomposites. Ceramic-matrix nanocomposites are materials where the ceramic (oxides, nitrides, silicides, *etc.*) is the main component. The second component can be a metal. These nanomaterials have improved optical, electrical, magnetic, and/or corrosion-resistance properties compared to traditional materials.

Metal-matrix nanocomposites are reinforced similarly to traditional metal-matrix composites using for example carbon nanotubes. Another application is the manufacture of superthermite (called also nanothermite) materials which are highly energetic materials containing an oxidizer and a reducing agent. The explosive reaction proceeds much faster than in the case of thermite materials manufactured with microparticles. This kind of material has military applications as explosives or propellants and in pyrotechnics.

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