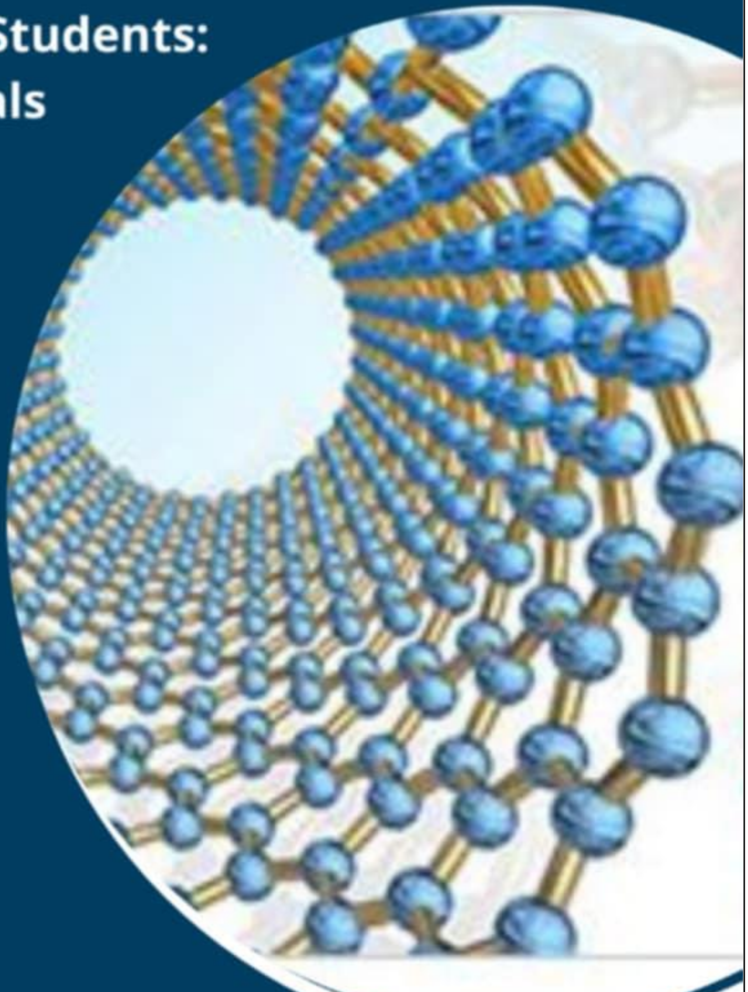
PEOPLE'S DEMOCRATIC REPUBLIC OF ALGERIA
MINISTRY OF HIGHER EDUCATION AND SCIENTIFIC RESEARCH
IBN KHALDUN UNIVERSITY - TIARET
FACULTY OF MATTER SCIENCES
DEPARTMENT OF PHYSICS

LECTURES

Nanomaterials

Level: 1st Year Master's Students:
Physics of Materials



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Preface

Nanoparticles and nanomaterials are extensively utilized in contemporary applications, stimulating significant technological interest that drives their development, enhancement of properties, and the discovery of novel characteristics. The advanced manipulation of nano-objects and the modification of their properties are progressively guiding us towards the atomic scale and the exploitation of quantum material properties.

These scientific and technological advancements pose questions regarding the challenges associated with the use of nanomaterials and the potential risks they present, particularly when they come into contact with the public.

This course handout is designed for first-year master's students specializing in materials physics and comprises four chapters.

In the first chapter, we introduce the foundational concepts necessary for understanding nanomaterials and their mechanical, thermodynamic, electrical, optical, magnetic, and chemical properties.

The second chapter addresses the manufacturing processes of nanomaterials, encompassing both top-down and bottom-up approaches, as well as physical and chemical treatment methods and their operating principles.

The third chapter concentrates on carbon nanotubes (CNTs), exploring their mechanical, electrical, and electrostatic properties, along with their applications.

The final chapter discusses the synthesis of nanomaterials, nanotechnologies, the diverse applications of these materials, as well as the toxicity and regulatory considerations of nanoparticles.

- ✓ **Teaching unit:** UED2.
- ✓ **Subject title**: Nanomaterials
- ✓ **Teacher responsible for the UE:** Mr. BOUADI Mohamed.
- ✓ **Teacher responsible for the subject**: Mr. KHARROUBI Abdelmalek.
- ✓ **Teaching objectives**
- ✓ At the end of this course, the student will have a clear idea of the opportunity to adopt nanomaterials technology and its impact on the environment, the economy and industry.
- ✓ **Recommended prior knowledge**
- ✓ The student must have taken a course on solid state physics and semiconductor devices.
- ✓ **Subject content:**
- ✓ Introduction: definitions and interests of nanotechnology.
- ✓ Basics of nanotechnology: properties and synthesis of nanomaterials (nanoparticles, nanotubes), overview of microfabrication technologies, nanofabrication technology, microsystems and nanosystems, instrumentation and nanoscience.
- ✓ Applications in different fields: nanomechanics and nanotribology, nanoelectronics, nanophotonics, nanobiotechnology and nanobiophotonics.
- ✓ Assessment method: Final exam (100%)
- ✓ References (Books and handouts, websites, etc.).

Contents

Contents

Figure List

Table List

General Introduction

General Introduction

Nanomaterials are central to the fields of nanoscience and nanotechnology. Nanostructure science and technology represent a broad and interdisciplinary domain of research and development that has experienced exponential growth worldwide in recent years. This field holds the potential to revolutionize material and product creation, expanding the range and nature of available functionalities. It has already made a significant commercial impact, which is expected to increase in the future.

Nanotechnology broadly refers to the design and manufacture of structures at the nanoscale, typically defined as 100 nanometers (nm) or smaller. This includes devices or systems created by manipulating individual atoms or molecules, as well as materials that contain very small structures. Nanomaterials are generally defined as materials with at least one external dimension measuring 100 nm or less, or with internal structures measuring 100 nm or less. These materials can exist in various forms, such as particles, tubes, or fibers.

Nanomaterials, even with the same composition as their bulk counterparts, may exhibit different physicochemical properties and behave differently if they enter the body, thus posing various potential risks. The study of nanomaterials and manufactured nano-objects is a rapidly expanding area of scientific research and industrial application. These materials have garnered significant attention due to their unique thermal, electrical, magnetic, and optical properties, which differ from those of the corresponding bulk materials.

Theoretical and experimental research into nanoparticles has been a subject of significant interest for many years, driven by their distinctive properties and the potential for groundbreaking applications across various fields.

Chapter I : Properties of Nanomaterials

I. History

The aspiration to manipulate atoms has long intrigued scientists.

- ✓ In 1959, physicist Richard Feynman asserted, "The principles of physics, as far as we can tell, do not oppose the possibility of manipulating things atom by atom."
- ✓ In 1970, J-M Lehn's research focused on using multiple chemical species to understand and construct nanoscale structures.
- ✓ In 1974, the term "nanotechnology" was first introduced by Japanese scientist N. Taniguchi, referring to the manufacture and utilization of nanometer-scale structures.
- ✓ In 1981, Gerd Binnig and Heinrich Rohrer invented the scanning tunneling microscope (STM), which enabled the determination of atomic shapes and the observation of atoms on conductive or semiconductive surfaces.
- ✓ In 1989, Donald Eigler achieved the first manipulation of matter at the atomic scale using the STM, arranging 35 xenon atoms to spell "IBM" on a nickel surface.
- ✓ In 1998, IBM's Zurich research laboratory observed a single molecule rotating, marking the discovery of a molecular rotor and paving the way for designing artificial molecular motors with nanometer-scale dimensions.
- ✓ In 1999, a nanomotor less than 100 nm in size was constructed.
- ✓ In 2004, the first British government report on nanosciences and nanotechnologies aimed to initiate public discourse on the opportunities and uncertainties of nanoscale technologies.
- ✓ In 2006, the Minatec campus, the largest European hub dedicated to micro and nanotechnology applications, was inaugurated.

I.2 Definitions

a- Nanoscience

Nanoscience is defined as the study of phenomena and the manipulation of materials at atomic, molecular, or macromolecular scales, where the properties significantly differ from those observed on a larger scale (Figure I.1).

b- Nanotechnology

Nanotechnologies are based on understanding and mastering the infinitely small. They represent a field of research and development involving the creation of new devices using tools or techniques that enable structuring matter at the atomic, molecular, or supramolecular level.

The characteristic scales of nanotechnologies range from 1 to 100 nanometers (nm).

c-What is a nanomaterial ?

A "nanomaterial" is composed of objects - nanoparticles, nanofibers, nanotubes, thin layers - with at least one dimension less than 100 nanometers; hence below the average size of a virus.

d- Nanoworld

The unit of reference in the nanoworld is the nanometer (abbreviated as nm). The prefix "Nano" comes from the Greek "**Nanos,**" meaning dwarf.

One nanometer is equivalent to one billionth of a meter(**1 nm = 10^{-9} m = 0.000000001 m**), which is approximately **1/50,000** of the thickness of a human hair.

The field under study is that of the infinitely small. The characteristic scale varies approximately from 1 to 100 nanometers (nm).

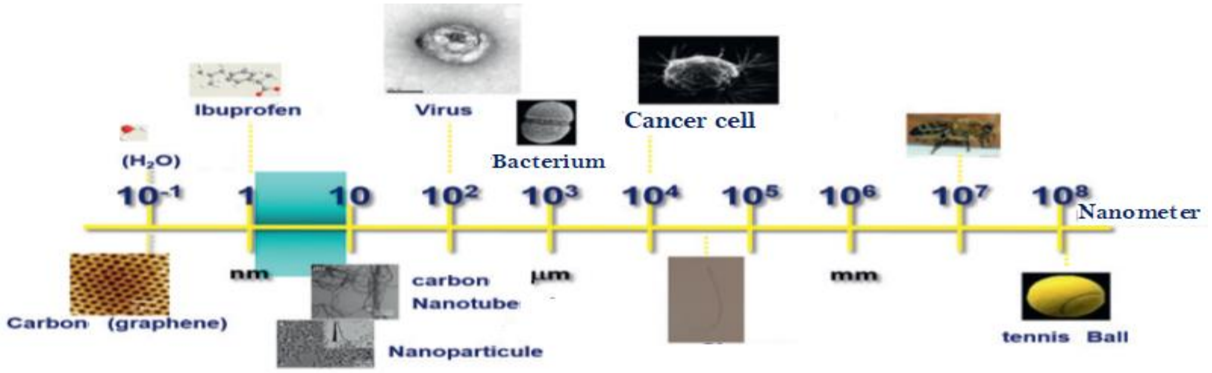


Figure I.1-Nanoscale size comparison chart showing nanostructures alongside more common objects.

I.3 Classification of Nanomaterials

There are two main families of nanomaterials (Figure I.2 and I.3):

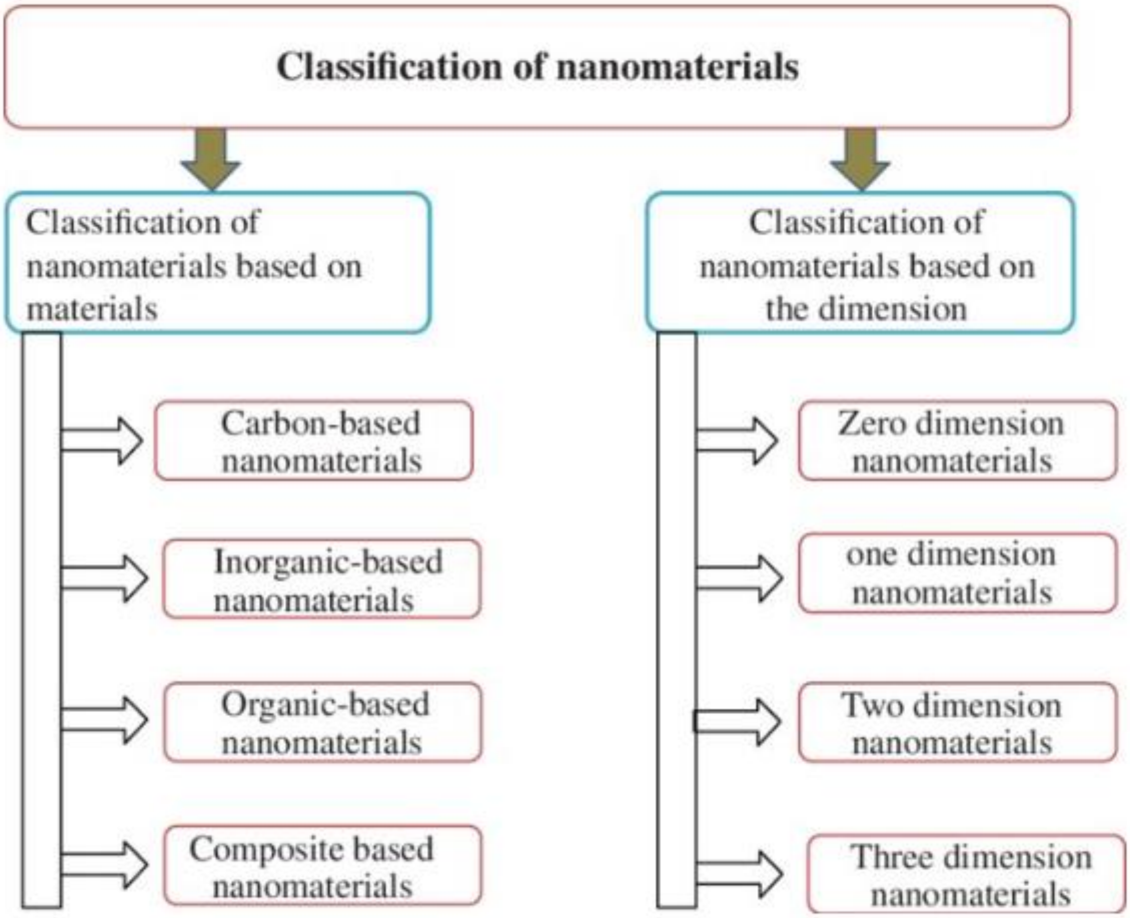


Figure I.2 - Schematic diagram showed the basic classification of nanomaterials

a) **Nano-objects :** are materials whose one, two, or three external dimensions are at the nanoscale, approximately between 1 and 100 nm. Among nano-objects, three categories can be distinguished:

-Nanomaterials zero dimension 0D:

These materials have diameters <100 nm and are referred to as nanoparticles, or nanocrystals. The term nanoparticle is generally used to encompass all constituent elements of nanoscale size 0D (irrespective of size and morphology), or those that are amorphous and have a relatively irregular shape.

When manufacturing nanoparticles, small size is not the only requirement. For any practical application, processing conditions must be controlled in such a way that the resulting nanoparticles have the following characteristics:

- Identical size of all particles (also known as nondimensional or with uniform size distribution).
- Identical Shape or morphology.
- Identical chemical composition and crystalline structure.
- Individually dispersed or monodispersed, meaning without agglomeration. In case of agglomeration, nanoparticles should be easily redispersible.
- Materials where all dimensions are measured on the nanoscale.

- One-dimensional nanostructures 1D:

Nanotube, Nanofiber, Nanowire, and Nanorod, the common feature of all these structures is that their diameters should be in the range of **1 to 100 nm**; generally, their lengths are in the micron range (or broader).

One dimension is outside the nanoscale and the other two dimensions are on the nanoscale. This leads to needle-shaped nanomaterials.

- 1D nanomaterials can be amorphous or crystalline.
- Monocrystalline or polycrystalline.
- Chemically pure or impure.
- Metallic, ceramic, or polymer.

- Two-dimensional nanostructured materials (2D):

One dimension is in the nanometer range, while the other two dimensions are not confined to the nanometer scale.

2D nanomaterials have plate-like shapes and include nanofilms, nanolayers, and nanocoatings.

b) Nanostructured materials:

Materials with dimensions larger than 100 nanometers in the third dimension (3D) that have an internal structure at the nanometer scale, composed of or containing other zero-, one-, or two-dimensional materials, such as aggregates and agglomerates of nano-objects.

Nano-objects can exist either as individual particles (primary particles) or as aggregates or agglomerates with sizes significantly larger than 100 nm.

Three-dimensional materials are not confined to the nanometer scale in any dimension and may have a nanocrystalline structure or involve nanoscale features.

Example: nanobeads (dendritic structures), nanocoils, nanocones, nanopillars, and nanoflowers.

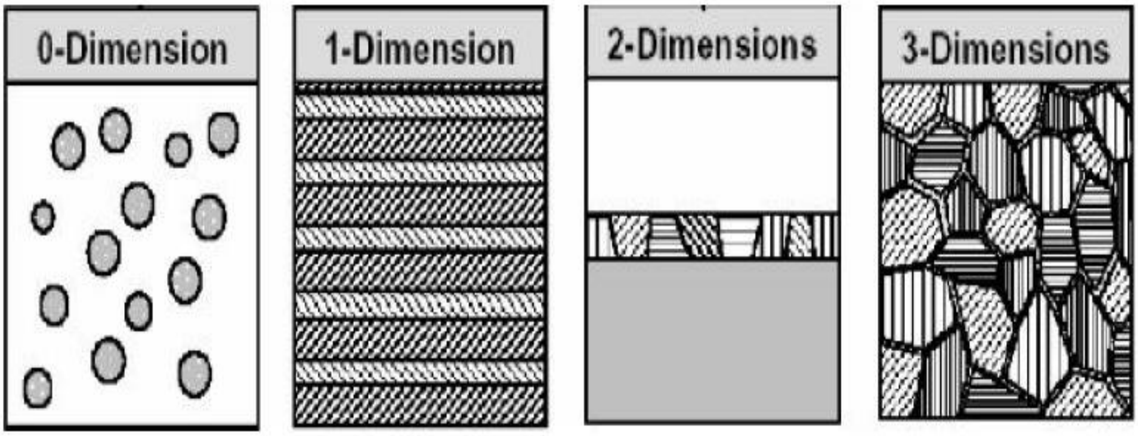


Figure I.3- The various classes of nanomaterials based on their dimensionality according to Siegel (1991); (a) nanoparticles or clusters of atoms. (b) multilayers consisting of nanoscale-thick layers. (c) nanostructured single layers. (d) nanocrystalline or 3D nanostructured materials.

I.4 Composition of Nanomaterials

In a polycrystalline material, a "grain" corresponds to a group of atoms belonging to the same crystalline lattice with the same orientation.

The diagram in Figure I.4 illustrates the atomic structure of a nanostructured material obtained through molecular dynamics with a Morse potential. In this diagram, atoms at grain boundaries are depicted in black, while atoms within the grains are shown in light grey.

The grain boundary is a region of atoms that are more or less disordered, allowing for the adjustment of disorientation between two grains.

Typically, in a polycrystalline material, the thickness of the grain boundary is small compared to the grain size. The fraction of grain boundaries becomes significant in relation to the volume occupied by the grains.

Various studies have attempted to define the structure of the grain boundary in nanomaterials.

Some, particularly the studies by R. W. Siegel, suggest that the structure of the grain boundary in fine-grained materials is the same as in materials with larger grain sizes, while other studies propose the opposite.

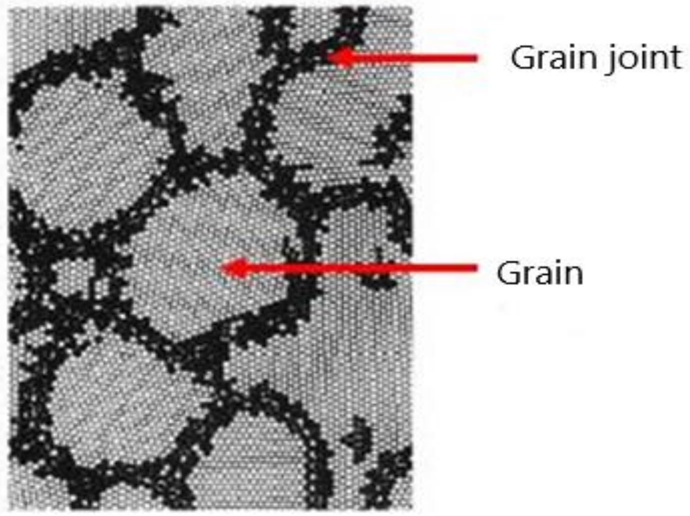


Figure I.4: Schematic representation of a 3D nanostructure, where the crystallized grains (in black) are connected by grain boundaries (in white) with different topological and/or chemical order.

I.5 Economic Issues

There are three main reasons for the growing interest of industrialists in nanoparticles and nanomaterials:

-Intrinsic Property Alteration: The reduction in size significantly alters the intrinsic properties of particles and materials, paving the way for more efficient or innovative compounds.

-Surface Area Enhancement: The smaller the particle, the larger its surface area relative to its volume, intensifying interactions between the particle and its environment. This characteristic makes catalysts based on nanopowders exceptionally effective.

-Uniformity and Size Dispersion: Transitioning from micro to nano-powders results in grains that are more uniform, often spherical, and exhibit low size dispersion.

Nanotechnologies encompass a wide range of technological fields, unified by the nanoscale size of structures. Notably, electronics and information and communication technologies increasingly rely on nanoscale structures.

The European Commission estimated that the global nanotechnology market slightly exceeded 40 billion euros in 2001.

According to the National Science Foundation (NSF, USA), the economic stakes associated with the rise of nanotechnologies worldwide from 2010 to 2015 were estimated to reach 1000 billion dollars annually across all sectors, directly impacting the employment of nearly 2 million people.

The economic impact of nanomaterials alone is estimated to represent a third of this sector, amounting to 340 billion dollars. This economic impact evolves in parallel with scientific production (Figure I.5).

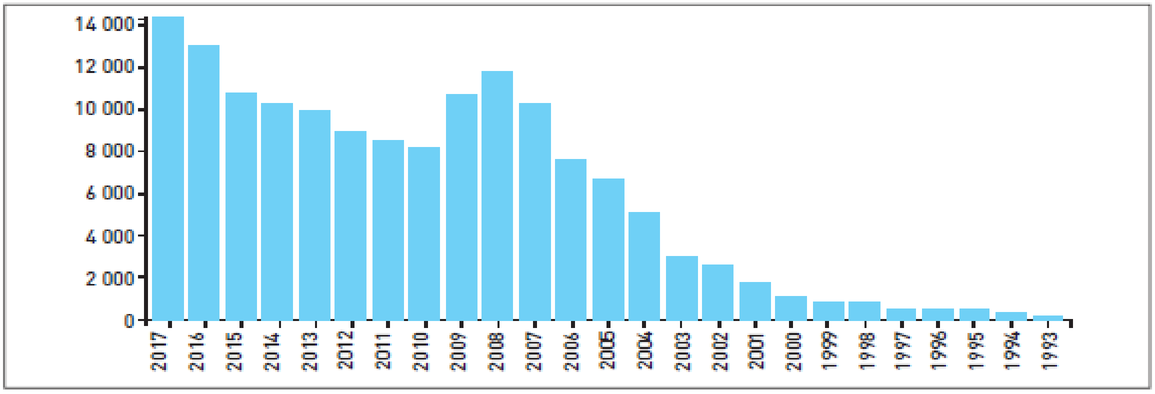


Figure I.5- The evolution of the annual number of scientific publications including the word "Nanotechnology" from 1993 to the 2017 illustrates the rapid growth of the field. Source: Web of Science.

I.6 Properties of Nanomaterials

I.6.1Mechanical Properties

The mechanical and plastic properties of materials such as metals and alloys are significantly influenced by the mobility of dislocations, which are linear defects within the crystal lattice. These dislocations can move at much lower yielding stresses compared to the theoretical yield stress of a perfect crystal. The presence and movement of dislocations affect the material's yield strength and overall mechanical behavior.

In nanostructured materials, the increased number of interfaces enhances the anchoring of dislocations, thereby improving mechanical strength, creep resistance, and hardness. Additionally, these interfaces can act as preferential sites for the recombination of point defects, which are often created under conditions such as irradiation.

This recombination process can further enhance the material's durability and resistance to damage.

Yield Strength

The Hall-Petch law is an important concept in materials science, particularly for understanding the mechanical behavior of polycrystalline materials.

This law states that the stress for deformation increases as the grain size decreases, meaning that a fine-grained polycrystalline material is harder than a coarse-grained one. For many materials, the yield strength ($\boldsymbol{\sigma}$) varies with grain size according to the Hall-Petch equation.

$$\boldsymbol{\sigma = \sigma_0 + \frac{k}{\sqrt{d}}} \qquad (\mathbf{I.1})$$

k: is the Hall-Petch constant, a coefficient.

d: is the average grain diameter.

$\boldsymbol{\sigma_0}$: is the original yield strength (for coarse-grained one) .

<u>Please note</u>: This equation is not valid for both very coarse-grained polycrystalline materials and extremely fine-grained materials.

Champion et al. (2002) conducted tests on two samples of copper with conventional grain size and nanocrystalline, noted as (µCu) and (nCu) respectively.

The experiment was carried out under identical conditions, and both samples were subjected to the same load.

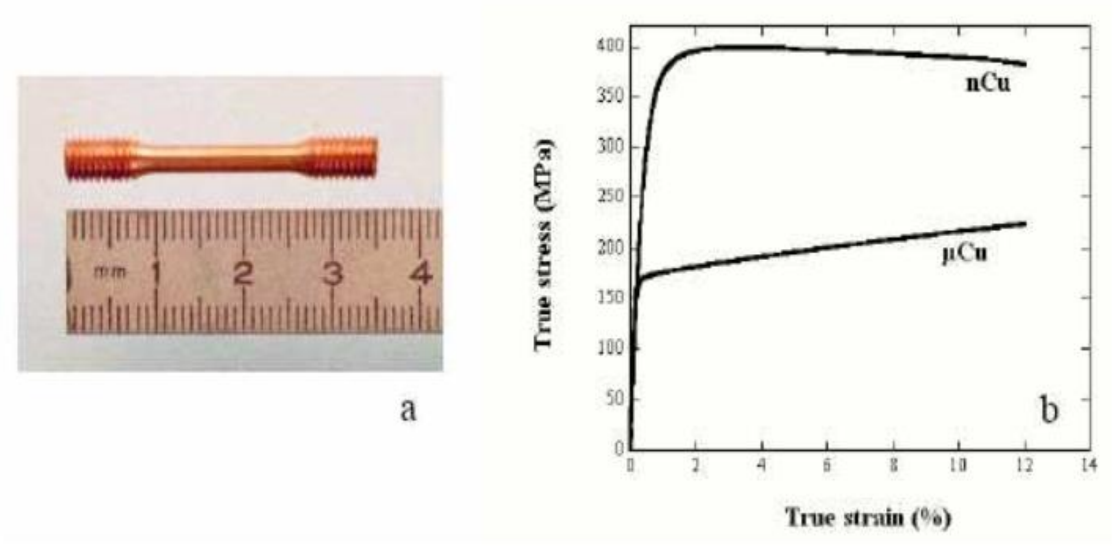


Figure I.6: (a) - monocrystalline copper sample, (b) - Stress-strain curve of (µCu) and (nCu) (Champion et al., 2002).

Figure I.6 shows the stress-strain curve obtained. It is observed that the yield stress of nCu, approximately 385 MPa, is much higher than that of µCu, approximately 165 MPa, representing an increase in yield stress of 43%, thus verifying the Hall-Petch law.

The increase in yield strength as grain size decreases is accompanied by a shift towards higher temperatures of the brittle-ductile transition.

This phenomenon, described by A.H. Cottrell, results from the interaction of dislocations with grain boundaries which act as obstacles to their propagation; dislocation pile-ups form until the leading dislocation in the pile reaches a threshold stress allowing it to transmit to the neighboring grain.

A similar phenomenon occurs in metals subjected to severe deformation, leading to the formation of a small-scale mosaic structure where the walls act in a similar manner.

The question is whether the behavior at $\mathbf{d}^{-1/2}$, well established across the range from millimeters to micrometers, continues for nanoscale crystals.

On the other hand, another phenomenon comes into play and acts in the opposite direction: diffusion at the grain boundaries (or Coble creep), which causes deformation with a velocity expressed by the following relationship:

$$\acute{\boldsymbol{\varepsilon}} = (\boldsymbol{B\sigma VeD_J})/(\boldsymbol{d^3\ k_B\ T}) \qquad (\mathbf{I.2})$$

($\acute{\varepsilon}$):Strain rate

(σ): applied stress

(V) :atomic volume

(e): grain boundary thickness

Dj: diffusion coefficient at grain boundaries

k_B = 1.38 x 10-23 J.K^{-1}, Boltzmann constant

T: temperature

d: grain diameter

This is a type of Newtonian creep ($\acute{\varepsilon}$ is proportional to σ).

b) Fracture

The fracture strength of a material in a linear elastic regime is given by the following relationship:

$$\sigma_r = K_{Ic}/Ec^{1/2} \qquad (I.3)$$

Young's modulus, critical stress intensity factor (toughness), and critical defect size are key factors. The variation in grain size (d) tends to have an influence.

Therefore, as d decreases, σ_r increases. These principles, related to toughness and fracture stress, are particularly relevant in the field of ceramic nanocomposites.

The findings on Si3N4-SiC composites are particularly enlightening in this regard.

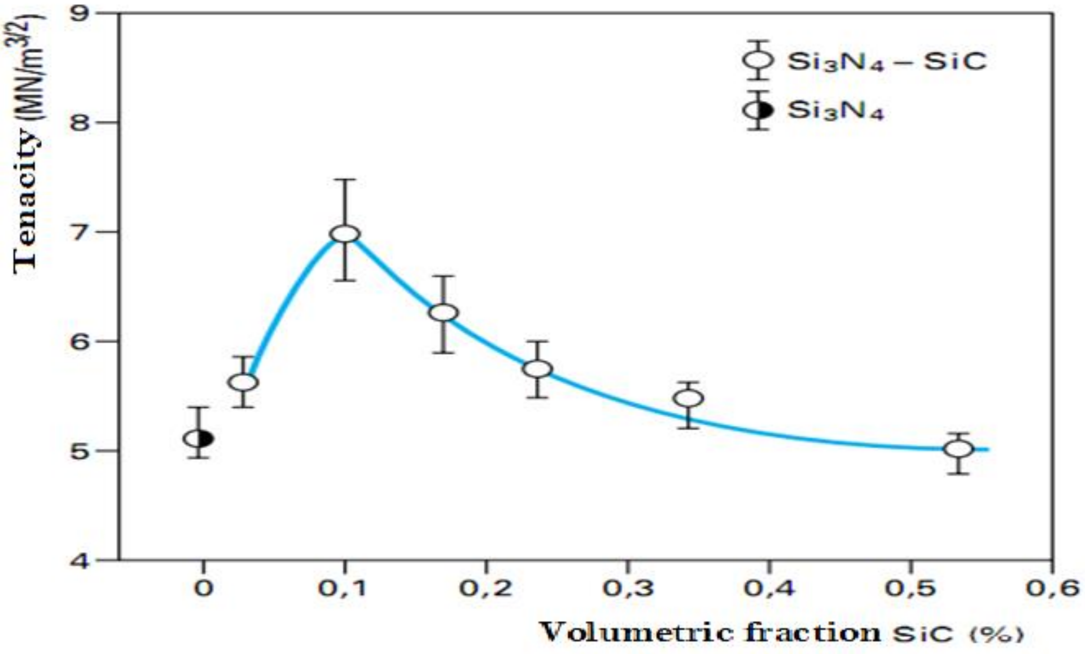


Figure I.7: Variation of the toughness of Si3N4-SiC components as a function of the SiC content.

In this case, Si3N4 is the predominant phase with a grain size of about 1 µm, and SiC is present both in the form of crystallites of approximately 0.3 µm at the grain boundaries, and as coherent nanoparticles within the grains.

As a result, the toughness and the rupture stress are approximately 1.5 times higher for Si3N4-SiC composites than for Si3N4 materials with a similar grain size (Figure I.7).

Depending on the situation, the particles act either as crack deflectors (in the case of intragranular particles), increasing K_{Ic} (i.e. toughness), or as grain size reducers, and thus critical defect (c) reducers (in the case of intergranular nanoparticles).

d-Superplasticity

Diminishing the size of a material to the nanoscale can trigger superplastic behavior, characterized by deformation without rupture reaching up to 100% or even 1000%.

This phenomenon arises when grain boundary sliding outweighs plastic deformation within the grains, facilitated by a higher 'surface/volume' ratio of the grains.

Several deformation models have been suggested, such as the Ashby and Verrall model (Figure I.8), referred to as 'grain switching', which describes this behavior but predicts a maximum deformation of only 55%.

A more recent model proposed by V. Paidar and S. Takeuchi, known as grain rolling, does not have this restriction.

$$(\boldsymbol{\varepsilon})' = (\boldsymbol{A\sigma^{n} d^{-p}})\ \mathbf{exp}\left(-\frac{\boldsymbol{\Delta G_a}}{\boldsymbol{k_B\, T}}\right) \qquad \textbf{(I.4)}$$

A: coefficient,

$\boldsymbol{\Delta G_a}$: activation free enthalpy of deformation,

p: grain size sensitivity coefficient, n: stress exponent,

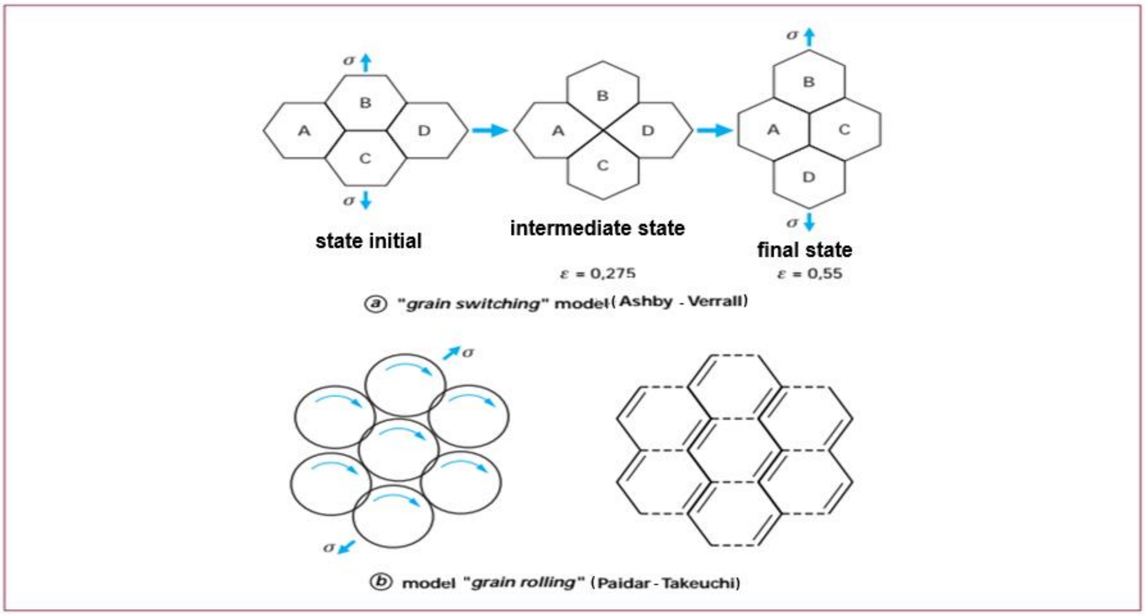


Figure I.8: Hot deformation mechanisms without changing grain morphology

Various deformation models can be expressed in this way, with specific values of n and p for each model. For example :

✓ Coble's deformation corresponds to n = 1, p = 3;

- ✓ It is generally accepted that a necessary condition to observe superplastic behavior is that n is less than or equal to 3;
- ✓ The Paidar and Takeuchi model gives values of around 2 for n and p, in line with most experiments;
- ✓ On the other hand, the Ashby and Verrall model, with a more complex mathematical formulation, gives n ≈ 1 to 2 and p = 1.
- ✓ Superplasticity in the case of metallic alloys often occurs for conventional grain sizes and accessible temperatures (for example, for aluminum alloys with d ≈ 10 mm and T ≈ 500°C, 1000 % elongation, $\acute{\varepsilon}$ = 10-4 µm.s^{-1}; for titanium, industrial implementation is carried out on conventional alloys at temperatures around 1000°C).
- ✓ The use of phases on the nanoscale would only be necessary for deformations at very high speeds $\acute{\varepsilon} = 10^{-4}$ µm.s^{-1}.
- ✓ For ceramics, diffusion coefficients are much lower, and it would be necessary to reduce to much smaller, likely nanoscale sizes to observe the phenomenon.

Few data are well established; for instance, compression measurements on nanocrystalline TiO_2 yield n = 3.5 and p = 1.5, but the experimental procedure was not aimed at verifying the accessibility of the very large deformations characteristic of superplasticity.

The only two cases so far where superplastic behavior has been confirmed are yttria-stabilized tetragonal zirconia with grains around 300 nm, and the cited Si3N4-SiC nanocomposites, where the authors attribute the presence of an intergranular liquid phase.

I.6.2Thermodynamic Properties

The proportion of atoms on the surface of a material plays a crucial role in its thermodynamic stability, especially when it is nanostructured (Figure I.9).

The thermodynamic energy of a material consists of a volume term and a surface term. The surface term arises from the additional energy required to create a surface.

Therefore, altering the proportion of surface atoms can influence the thermodynamic stability domain of the material.

$$dW = \gamma \, dA \qquad (\mathrm{I.5})$$

The equation, where **W** represents the work required to increase the surface area by a quantity of dA and γ represents the surface tension, is a fundamental concept in physics.

This equation expresses the relationship between work and the increase in surface area, considering the surface tension.

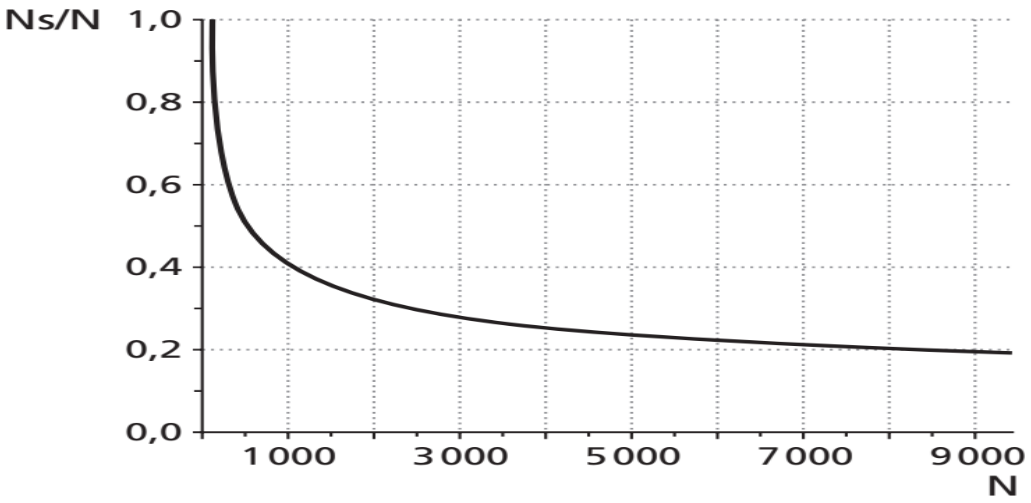


Figure 1.9: Surface atom proportion (Ns) for a spherical particle as a function of its atom number N. 2 nm corresponds to approximately 500 atoms and 5 nm to 8,000 atoms (according to Henri, 2006).

When studying nanomaterials, it is crucial to consider the relationship between the surface area and volume of particles. The surface area of a volume filled with particles increases inversely proportional to the radius of these particles. Consequently, the free energy of a nanomaterial is higher compared to that of a classical material.

This phenomenon has been long recognized in examples such as the transition of zirconia (ZrO_2) from a monoclinic to a tetragonal structure as grain size decreases, or the variation in the melting temperature of pure metals with particle size (Figure 1.10, Labastie, 2006). As particle size decreases, their surface energy increases, leading to compression stress within the particle.

This stress is inversely proportional to particle size and can cause a significant contraction of the lattice parameter. For instance, in copper, a contraction of a few percent can be observed for particles at the nanometer scale (Henri, 2006).

These observations underscore the importance of considering size effects in the study of materials at the nanoscale, as they significantly influence the properties and behavior of nanomaterials (Figure I.10).

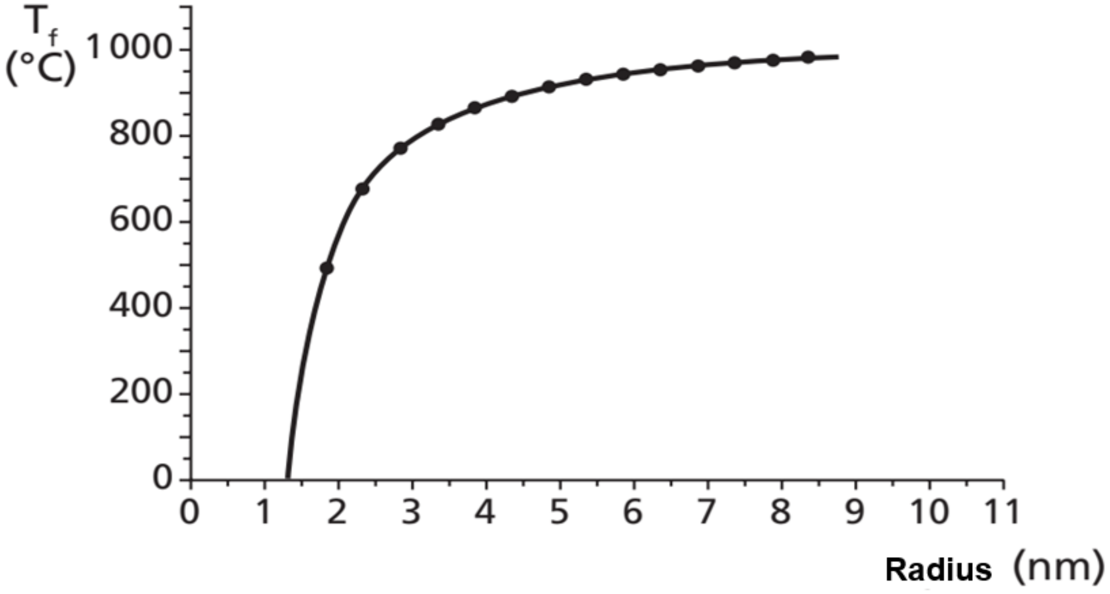


Figure 1.10: Effect of Particle Size on the Melting Temperature of Gold (adapted from Labastie, 2006)

I.6.3 Electrical Properties

Nanomaterials exhibit unique electrical properties due to their small size and high specific surface area. These properties can vary depending on the chemical composition, crystalline structure, and morphology of the nanomaterials.

Certain nanomaterials, such as carbon nanotubes and metallic nanoparticles, can have very high electrical conductivity due to their specific atomic structure.

Other nanomaterials, like nanowires and nanosheets, may exhibit semiconductor or insulating properties depending on their size and composition.

The electrical properties of nanomaterials are extensively studied for their potential use in applications such as electronics, sensors, and energy storage devices.

Specific configurations, such as nanoscale metal grains in an insulating matrix, are often discussed to illustrate key properties.

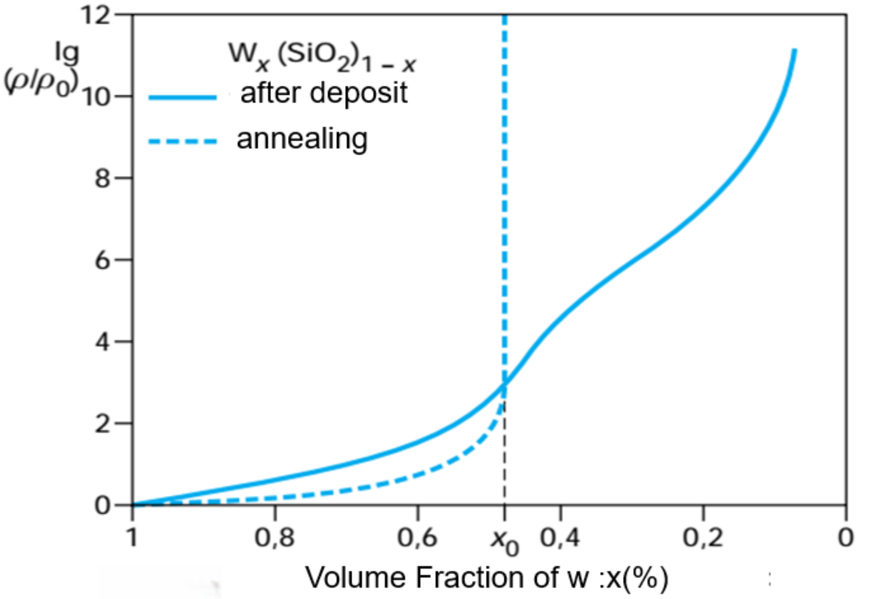


Figure I.11: Variation in resistivity at room temperature of thin layers of X as a function of the Y content.

When a material has an x rate greater than x_0 , it is possible to observe paths of electrical conduction within its structure ($W_x(SiO_2)_{1-x}$) (Figure I.10). Under these conditions, the material behaves like a metal, with a relatively low resistivity, on the order of 10^{-6} Ω.m. In this scenario, the resistivity coefficient, defined as dρ /dT, is positive (ρ=resistivity).

When the rate of metallic grains dispersed in the insulating matrix is less than x_0 ($x < x_0$), the paths of electrical conduction disappear and conduction between the metallic grains occurs through tunneling effects across the insulating matrix.

In this case ($x < x_0$), the resistivity increases by several orders of magnitude, but as the temperature (T) rises, this resistivity decreases according to the following law:

$$\rho(T) = \rho_0 \exp(T_0/T)^{1/2} \qquad (I.6)$$

At room temperature, the resistivity is ρ. This law is valid across the entire range of practical temperatures (where the material does not lose its nature).

b-Semiconductors called 'superlattices'

Superlattices are complex structures composed of alternating layers of different semiconductors, each with a nanometric thickness.

As these layers have different bandgap widths (Figure I.12), quasi-infinite potential wells form on those with the narrowest bandgap in both directions within the layer plane and nanometrically $\boldsymbol{L}$ in the perpendicular direction.

Due to the varied bandgap widths of these semiconductors, quasi-infinite potential wells form on the layers with the narrowest bandgap, in both directions in the layer plane (non-nanometric dimensions) and in the perpendicular direction (nanometric dimension).

For electron waves propagating in the nanometric dimension, the kinetic energy (E_k) is quantized and takes a specific form, with kinetic energies quantized according to the values:

$$\boldsymbol{E - E_c = n^2 h^2 / 8\, m^* L^2} \qquad \textbf{(I.7)}$$

Where: **n** : is an integer,

h: is the Planck constant,

$\boldsymbol{m^*}$ is the effective mass of electrons,

$\boldsymbol{E_c}$: is the energy at the bottom of the conduction band for the considered layer.

The mentioned kinetic energy values are obtained using an approximation based on the assumption of a potential well of infinite depth for the layer of the semiconductor with the largest bandgap.

This layer confines all electrons with energy lower than that at the bottom of the conduction band of this layer.

This condition also applies to the electrons in the layer with the smallest bandgap, even if their energy is higher than that of the bottom.

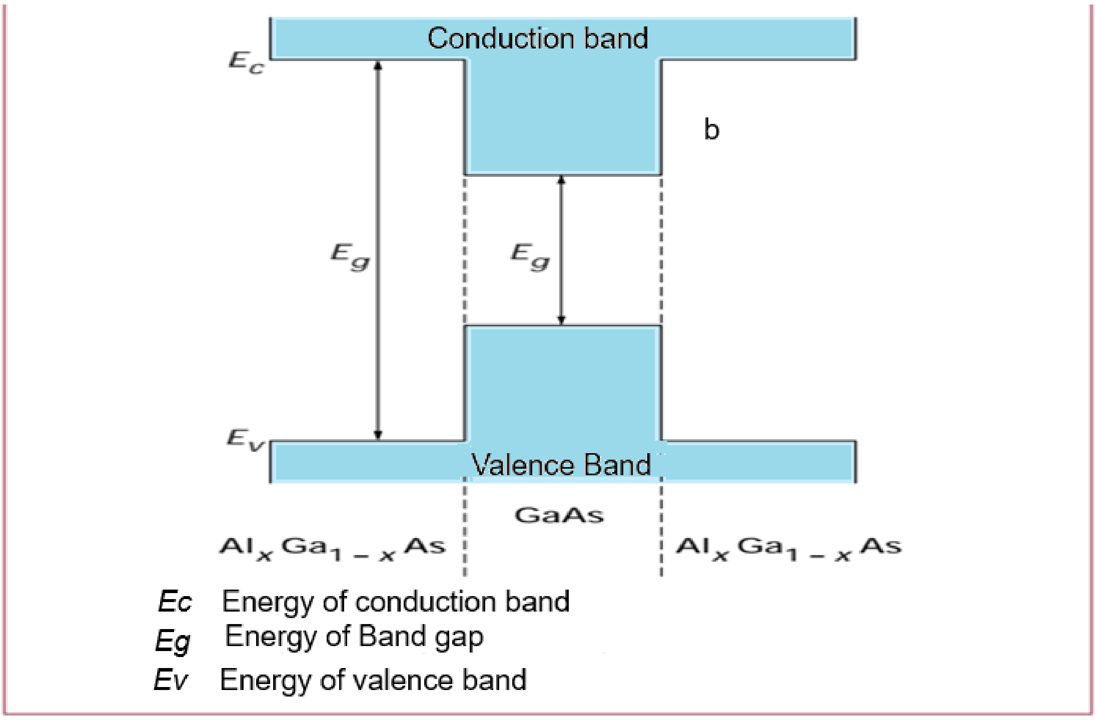


Figure I.12: Quantum well composed of a GaAs layer between two layers of $Al_xGa_{1-x}As$

c- Special property of superlattices: magnetoresistance

Magnetoresistance is a property of a 'superlattice' material. It involves the variation in electrical resistance (R) of the material when subjected to an external magnetic field.

Nanostructures have been the subject of extensive studies due to the significant effects they exhibit, especially in the alternating stacking structures of ferromagnetic and magnetically neutral materials.

In the absence of a magnetic field, the coupling between the ferromagnetic layers shows oscillating variations depending on the thickness of the neutral layers, leading alternately to the alignment and anti-alignment of the magnetic moments of the different layers.

This characteristic oscillation corresponds to the well-known phenomenon in magnetism physics, called oscillating polarization, which is related to the distance between the spin moments of conduction electrons (Ruderman-Kittel - Kaseya-Yoshida or RKKY interaction).

This phenomenon is responsible, for example, for the indirect long-range coupling of the magnetic moments of the 4f layers of rare earth metals.

When the moments are anti-aligned at zero field, the introduction of an increasing magnetic field leads to the progressive alignment of these moments and induces a significant decrease in the resistance (R) measured orthogonally to the layers:

$$\boldsymbol{R = R_0\left(1 - \alpha\frac{M^2}{M_S^2}\right)} \qquad \textbf{(I.8)}$$

Where **M**: magnetization, $\boldsymbol{M_S}$ saturation magnetization, **α**: magnetoresistance coefficient and $\mathbf{R_0}$: resistance at zero field.

The magnetoresistance coefficient α, measuring the variation in electrical resistance in the presence of a magnetic field, can reach remarkable values in certain structures.

Indeed, in configurations such as alternating nanolayers Fe-Cr, Co-Cu, Fe-Cu, this coefficient can rise to around 40% at room temperature, and even higher at low temperatures.

I.6.4 Optical Properties

I.6.4.1 Semiconductor Case

a) Photoluminescence of Confined Systems

Photoluminescence occurs when an electron-hole pair annihilates. The materials used are direct bandgap semiconductors, with $p = \hbar k$ conserving the momentum p (wave vector k with reduced Planck's constant). III-V and II-VI semiconductors fall into this category, unlike silicon, which has an indirect transition.

Consequently, light emission related to electron-hole recombination (or exciton annihilation in quantum terms) has a very low efficiency, around 10^{-6}.

Photoluminescence is emission in the visible spectrum, shifted towards higher frequencies (blue shift) for nanomaterials.

This phenomenon occurs as soon as at least one of the crystalline dimensions is nanometric. When a confinement space dimension becomes smaller than the Bohr radius of the excitons in the bulk material (quantum well), a quantification of similar levels appears as schematically illustrated in Figure I.13.

A relatively simple quantum mechanics calculation demonstrates that in the case of a quantum dot (system with nanometric dimensions).

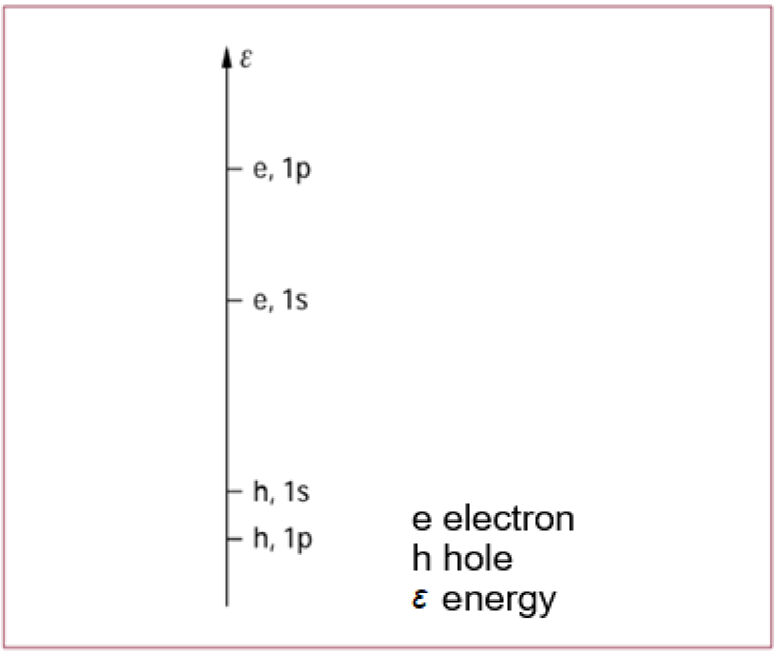


Figure I.13: Diagram of the energy levels of electronic states for the bulk material and for a quantum dot.

Energy of the electron-hole pair is as follows:

$$\boldsymbol{\varepsilon} = \boldsymbol{E_g} + \hbar^2/2\boldsymbol{m_e}(\boldsymbol{a_{n_e l_e/R}})^2 + \hbar^2/2\boldsymbol{m_h}(\boldsymbol{a_{n_h l_h/R}})^2 \qquad \textbf{(I.9)}$$

with $\boldsymbol{n}$ and $\boldsymbol{l}$: quantum numbers identical to those known for atomic structure,

$\boldsymbol{a_i}$: constants independent of the quantities related to the problem being addressed,

$\boldsymbol{m_e}$ and $\boldsymbol{m_h}$: effective masses,

e and **h** : indices referring to electrons and holes respectively,

R: box dimension.

Eg: width, in energy, of the band gap,

This energy (Ɛ) is higher than the band gap width (Eg) for the bulk material, by an amount that varies as $\mathbf{1/R^2}$.

For a constant potential inside a sphere, the quantification rule specific to the central Coulomb potential is not observed.

The materials preferentially used are compounds S-C II/VI (CdS, CdSe, CdTe) whose form is obtained from particles precipitated in glasses (see figure I.14), or from bulk materials obtained by nanolithography.

Figure I.14: Compared absorption spectra of micrometric CdS and CdS in the form of nanocrystals, formed in sodalite cages of zeolite Y, for two values of the CdS rate.

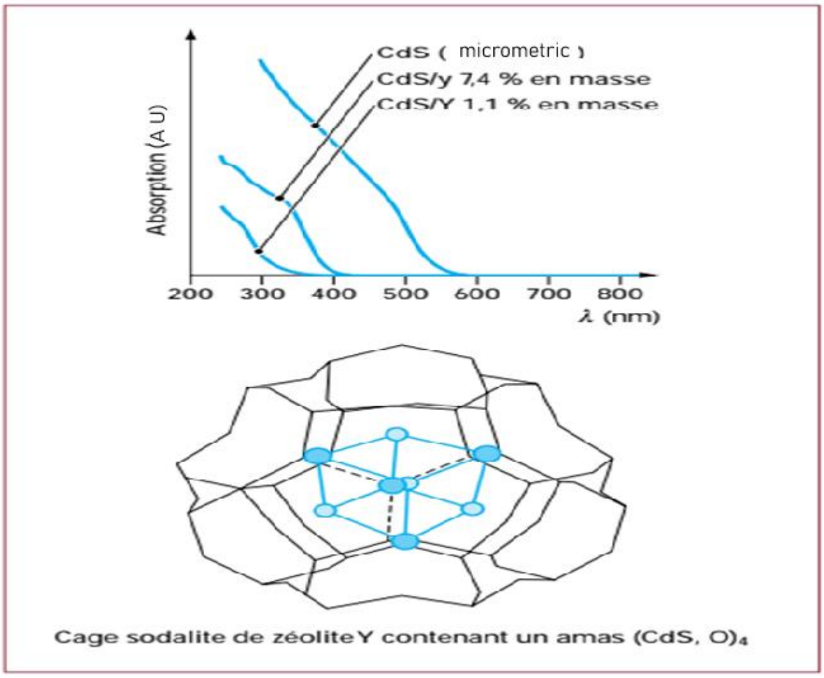


Figure I.14 Comparison of the absorption spectra of micrometric CdS and CdS in the form of nanocrystals, formed within sodalite cages of zeolite Y, for two different CdS concentration levels.

The photoluminescence depends on the energy of the occupied level, which can lead to non-linear effects. High luminosities can be obtained by optically pumping to excited levels.

This phenomenon is widely used in the development of optoelectronic devices, especially to replace electrical connections with optical connections or to manufacture light-emitting diodes (LEDs).

b) Photoluminescence of porous silicon

The photoluminescence of porous silicon reveals a significantly higher fluorescence yield than that of bulk silicon.

This phenomenon is attributed to the reduction in the size of the silicon particles, as in the case of porous silicon obtained by electrochemical etching of bulk silicon with hydrofluoric acid.

This change is accompanied by a shift in the frequency of the emitted light towards the blue, changing from $1{,}1\ eV$ for the bulk sample to $1{,}9\ eV$ for the nanoscale sample.

These observations are interpreted as a disturbance of the local crystalline structure, particularly a chemical modification of surface states or the emergence of quantum confinement in crystalline silicon nanoparticles surrounded by amorphous silicon or silica (SiO_2).

I.6.4.2 Isolators Case

Unlike semiconductors, where the width of the band gap generally corresponds to absorption in the visible range, the width of this band for insulators, which is wider, corresponds to absorption in the ultraviolet range.

However, similar to semiconductors, the absorption peaks of insulators shift towards higher frequencies when the particle size is reduced.

For instance, the insulator TiO_2 (titanium oxide), with a grain size of around 20 nm, reduces the wavelength (increases the frequency) of the beginning of the absorption band to less than 310 nm (Figure I.15).

Consequently, UVB radiation is attenuated more than UVA radiation (which is less energetic).

As the grain size increases, the absorption (or attenuation) starts closer to the visible range. This effect is utilized in the production of sunscreen filters to protect against UVB rays, which are closer to the visible spectrum.

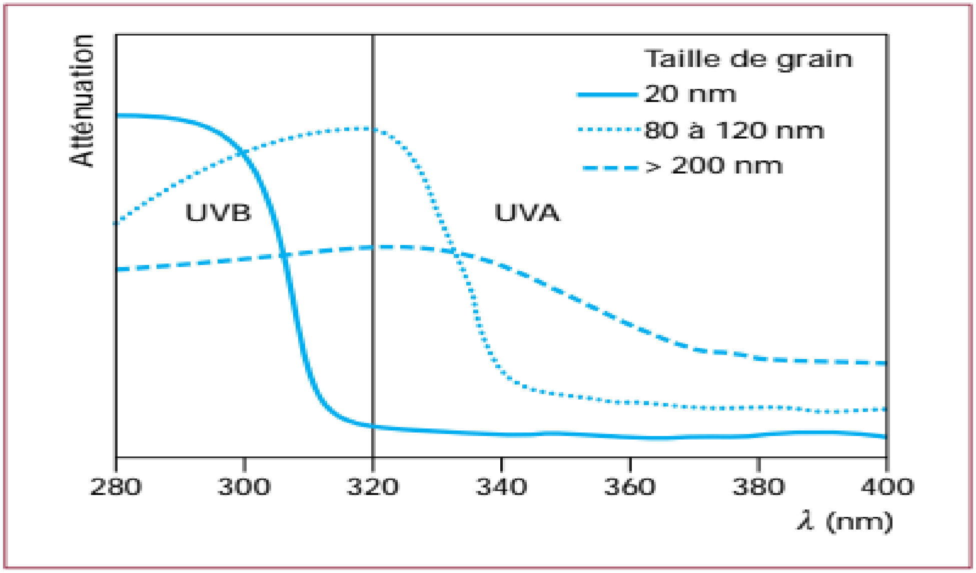


Figure I.15: UV Absorption Limit for TiO2 Depending on Grain Size

The optical properties of metal particles dispersed in an insulating medium exhibit generally classical effects that depend on the relationship between the particle size and the wavelength λ of the radiation.

When this relationship is established, a quasi-static domain is entered where the electromagnetic wave interacts bipolarly with the medium, polarizing the electron cloud and inducing excitations in this cloud (Plasmons).

In the specific case of nanoparticles, excitations of a particular type occur (surface plasmons) whose characteristics depend on the dielectric constants.

I.6.4.3 Optical Properties of Metal Particles Dispersed in an Insulating Medium

The observed effects are typically conventional and rely on the relationship between particle size and the wavelength λ of the radiation.

Once this relationship is established, it enters a quasi-static domain where the electromagnetic wave interacts dipolarly with the medium, polarizing the electron cloud and inducing excitations in this cloud (plasmons).

In the specific case of nanoparticles, excitations of a type occur (surface plasmons) whose characteristics depend on the dielectric constants of the matrix, particles, and their shape.

At the characteristic frequencies of surface plasmons - which can be multiple if the particles are not spherical - absorption bands in the visible and infrared spectrum correspond (Figure I.16).

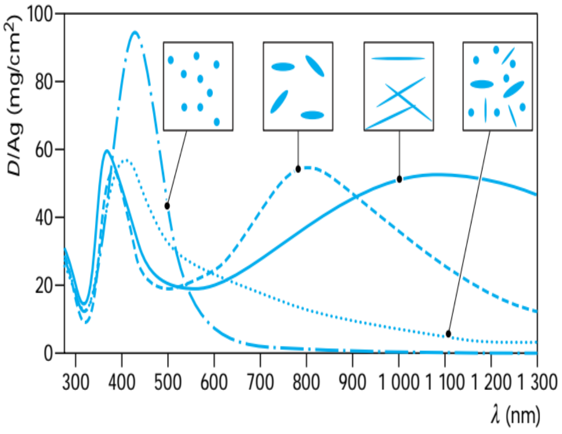


Figure I.16: Absorption Spectrum of a Silver Particle Distribution Depending on Particle Shape. The silver content, expressed in mg/cm^2.

Reducing the particle size leads to a significant increase in the absorption rate. When r ≈ λ and beyond, scattering comes into play and combines with absorption (Figure I.17).

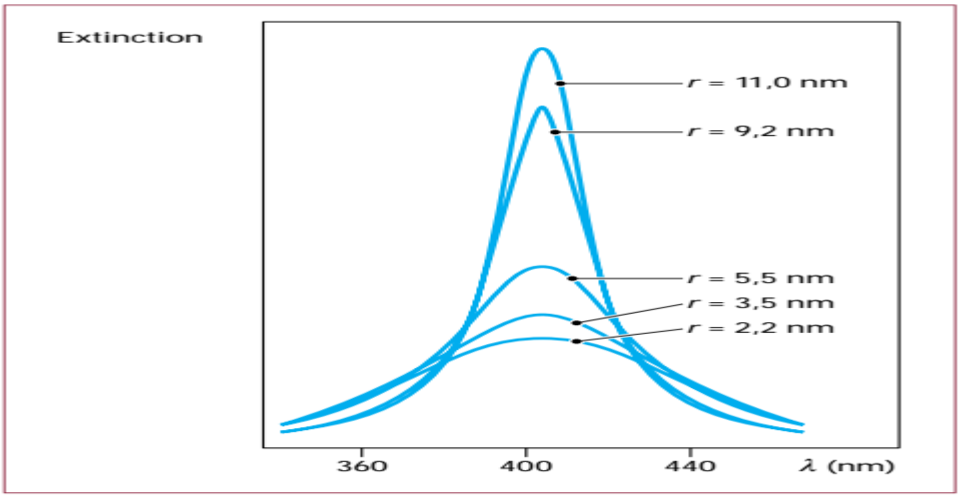


Figure I.17 Transmission coefficient of a granular silver layer as a function of particle size

I.6.5 Magnetic properties

The micro- or nanocrystalline structure of ferro or ferrimagnetic crystalline solids significantly affects the magnetic properties of these materials, depending on the existence of nanostructures derived from either perfectly structured large solids or solids with irregularities or defects.

a) Large perfect solids

In the category of magnetic properties of solids, we find saturation magnetization (Ms) and Curie temperature (Tc): the temperature at which a ferromagnetic or ferrimagnetic material loses its permanent magnetization to become paramagnetic.

These two characteristics only vary when the proportion of atoms near the crystalline surface becomes significant compared to those inside the grains.

Nanostructured iron is an example, such as powders obtained by evaporation under inert gas and passivated with a mixture of argon and air.

For powder grains smaller than 10 nm, saturation magnetization gradually decreases. At a size of 5 nm, Ms is divided by three compared to bulk iron.

This observed decrease in Ms cannot solely be attributed to the formation of iron oxides (Fe_2O_3 or Fe_3O_4), which form a shell around the nanometric iron crystallites.

It is the atoms near the 'iron-shell (oxide)' interface that see their Ms significantly altered.

b) Solids containing irregularities or defects

Solids containing irregularities or defects exhibit various magnetic properties such as magnetic permeability, coercively, remanence, etc.

The size of the crystallites can induce significant modifications to these properties when the dimensions become smaller than the size of the Bloch domains (Figure I.18).

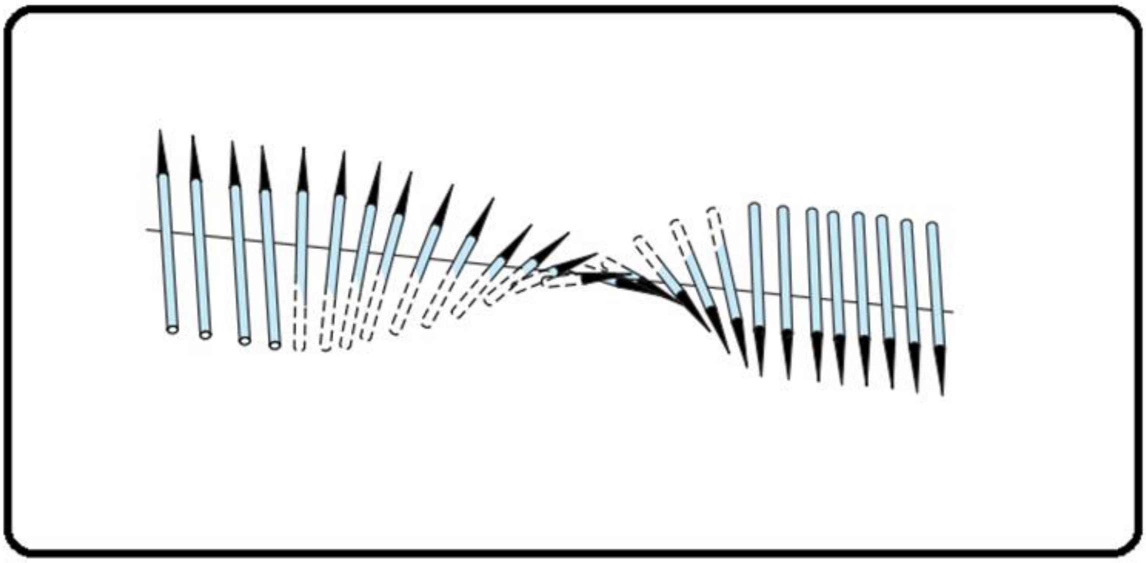


Figure I.18 Progressive flipping of magnetization (atomic magnetic moments) from one domain to the neighboring domain through a Bloch wall.

In the case of independent ferromagnetic crystals, another characteristic phenomenon known as "superparamagnetic" behavior emerges when their temperatures (T) are well below the Curie temperature T_c $(T << T_c)$, but significantly above the characteristic temperature T' for effects of magneto-crystalline anisotropy: with $(T >> T')$

$$T' = CV/k_B \qquad \textbf{(I.10)}$$

C : representing the anisotropy energy and **V** the volume.

At these temperatures, the observed laws resemble those of Curie paramagnetic, but the involved moments are no longer atomic moments but the total saturation moment (M_s) of a magnetic nanoparticle. In this scenario, the magnetic susceptibility (χ) is:

$$\chi = xVM_s/k_BT \qquad \textbf{(I.11)}$$

With x : the percentage of the total volume occupied by superparamagnetic particles.

The interactions between the moments are not negligible and can be considered by considering χ, to determine rather the Curie-Weiss law: $\boldsymbol{\chi(T)\ \alpha\ M_s/(\mathrm{T}-T_{sp})}$

where $\boldsymbol{T_{sp}}$ is a characteristic temperature of the coupling effects between moments.

At temperatures (T) lower than a certain temperature called blocking temperature (T_B) (T < T_B) and defined as:

$$\boldsymbol{T_B = T'\ln(\tau_m/\tau_0)} \qquad \textbf{(I.12)}$$

$\boldsymbol{\tau_m}$: is a characteristic time

$\boldsymbol{\tau_0}$: of the measurement a constant of the order of $\boldsymbol{10^{-11} s}$,

The behavior of the nanograins becomes complex and depends on the material's history. For example, the measured susceptibility of the material differs depending on whether it has been cooled under field application or off-field.

I .6.5 Chemical Properties

Given the dimensions of atoms and molecules, it is evident that chemistry is influenced by processes triggering chemical reactions and compound formation, occurring at the nanoscale or below.

However, changes in chemical properties are limited to phenomena maintaining the nanoscale characteristic of chemical structures, i.e. compounds where the nanoscale dimension of the final structure is preserved.

Materials at the nanoscale exhibit chemical properties distinct from those of large-scale materials. These differences mainly involve:

- Differences in chemical potentials and solubility,
- Increased chemical reactivity,
- Modification, particularly of electronegativity and ionization potential.

This modification leads to a change in redox potential, which increases as the size of nanoscale structures decreases.

These recent variations also exhibit the following characteristics:

- ✓ They are not monotonic for the smallest particles, meaning that these changes do not evolve.
- ✓ They are not correlated with the specific stability of certain chemical entities formed by clusters of atoms with specific numbers such as 8, 20, 40, 52 atoms, etc.

Furthermore, these changes in chemical properties, as well as electronic properties, can also be influenced by quantum confinement effects.

These aspects will be highlighted through a crucial example from the field of heterogeneous catalysis, particularly concerning catalysts such as transition metals and noble metals like Ni, Pd, and Pt.

I .6.5.1 Heterogeneous catalysis on transition metals

The concept of catalysis was introduced in 1835 by Jöns Jakob Berzelius. In chemistry and biology, it refers to the acceleration (increase in speed) of a chemical reaction by means of a substance called a catalyst that is not consumed by the overall reaction. Heterogeneous catalysts exist in different phases from the reactants.

For example, it could be a solid catalyst in a liquid reaction mixture. However, heterogeneous catalysts have the advantage of being easily separated from the reactants and products at the end of the reaction.

Transition metals, as catalysts, provide an easy way to achieve challenging transformations (Figure I.19), such as carbon-carbon bond formation reactions.

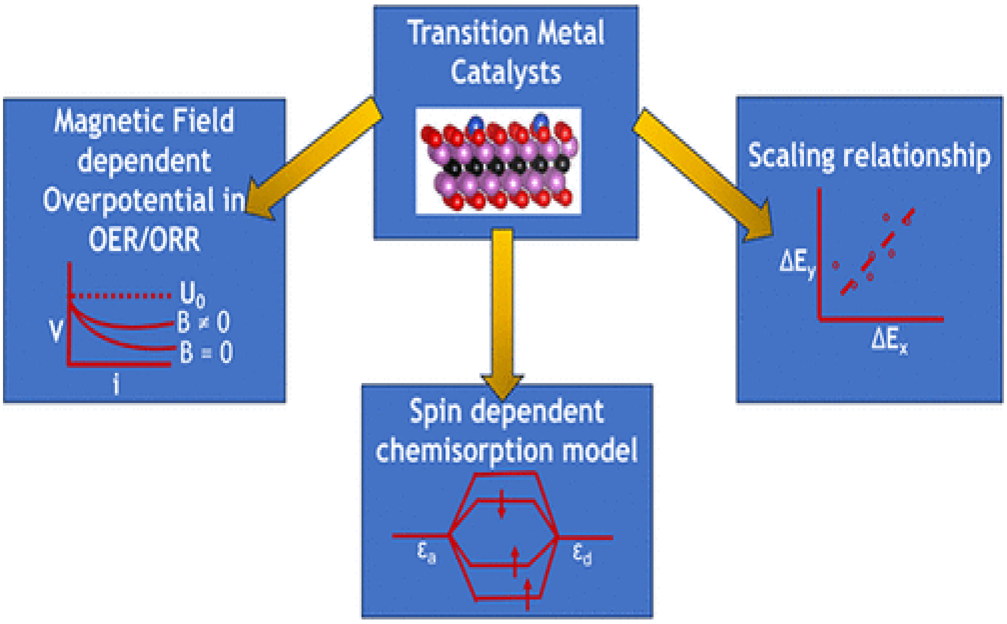


Figure I.19. Overview of heterogeneous catalysis on surfaces with 3D transition metals

Consequently, catalysis by transition metals plays a central role in a wide range of applications, including the synthesis of natural products and bioactive compounds, as well as the development of pharmaceuticals.

By utilizing their d orbitals, these catalysts can activate substrates and accelerate reactions through coordination, ligand substitution, insertion, elimination, etc., leading to the cleavage or formation of H–H, C–H, and C–C bonds.

1.7 Surface-volume /ratio

Many sources refer to the model that considers surface properties and highlights the ratio between surface and volume, known as the surface-volume ratio.

The surface of an element serves multiple functions: it can retain or release other elements, facilitate energy transmission, and initiate or conclude a chemical reaction.

As the size decreases, this model explains the effects observed due to a significantly higher proportion of surface atoms interacting with external elements.

Table I.1: Surface -Volume Ratio of a Cube

Cube length (cm)	Surface (cm^2)	Volume (cm^3)	Ratio S/V
2	2x2x6=24	2x2x2=8	24/8=3:1
8	8x8x6=384	8x8x8=512	384/512=0.75:1

When a material is divided into several nanomaterials, the total volume remains constant. However, by bringing together all the fragments, the total surface area increases, providing more significant and efficient functionalities.

Table I.2: Surface –length of a cube

Cube length (m)	Number of cubes	Total surface area (m^2)
1	1	6
0.1	1000	60
0.01	10^6	600
0.001	10^9	6000
10^{-9}	10^{27}	6000000000

It is evident from this table that when we reach the nanometer size $(10^{-9}m)$, we end up with a 10^{27} cubes, of total surface area $6000000000\ (m^2) = 6000\ km^2 \approx\ 1/7$ with a total surface area equivalent to that of Switzerland $(= 41.285\ (km^2))$.

When an "object" is reduced in size, according to the model, the proportion of atoms on the surface increases compared to those at normal size, which enhances the importance of surface effects and can lead to the emergence of new phenomena.

With more exposed surfaces and therefore more contact with the environment, energy transfer becomes very efficient, resulting in a significant increase in reaction speed.

In chemistry, a catalyst is a substance that enhances chemical reactions without being consumed or chemically altered (as is the case with enzymes).

The key characteristic of a catalyst lies in its active surface where reactions occur. It is observed that this active surface increases when the size of the catalysts decreases: the smaller they are, the higher the surface-to-volume ratio, which increases the importance of the active surface (Figure I.20) and promotes reaction speed.

The surface has a major influence on the material's reactions and, consequently, on its properties. In the case of the same material, the melting point will be lower on a small scale.

The properties of a material can be explained by models that take the surface into account.

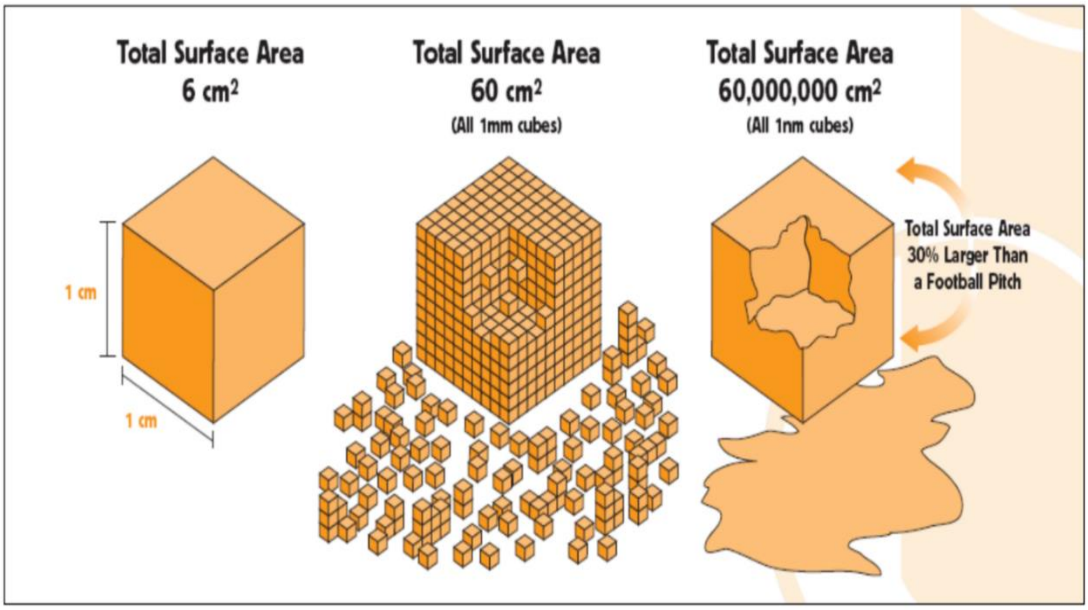


Figure I.20: Illustration of the Small Mass Paradigm: Large Surface Relevance for Food Security of Nanotechnology Applications in the Food and Beverage Industries - Ireland - September 2008 E. Gaffet, 2012

I.8 Particularities of Certain Categories of Materials

I.8.1 Ceramics

Ceramics form a vast family of materials in which the constituent atoms form ionocovalent bonds between them, for example, by combining metallic elements with non-metallic elements in oxides such as alumina (Al2O3), titanium dioxide (TiO2), and zirconia (ZrO2), or in borides, carbides, nitrides, etc.

Alumina, an oxide that can crystallize in various forms, including corundum, holds significant practical importance due to its high hardness, thermal stability, high melting point (2050°C), chemical inertness, as well as its thermal and electrical insulation properties.

Fragility and ductility are not intrinsic properties of materials but refer to a type of behavior under specific combinations of temperature and loading rates.

The observation that plastic can "make joints as well as jewellery" through brief transformation also applies to ceramics due to their superplastic behavior at certain temperature and loading rate ranges.

However, many common ceramics are fragile at room temperature due to imperfections like pores, cracks, especially those of micrometric dimensions, and defects such as grain boundaries, dislocations, voids, interstitials, and impurity atoms.

Table I.3: High-energy ball milling reaction of a mixture of Aluminum powder and an oxide

Initial Blend	**Reactive Mechanical**	**Alloy Final Ground Blend**
$(3/y)M_xO_y + 2Al$	→	$Al_2O3 + 3(x/y)M$
Micrometric particles →		Micrometric particles
Initial phases separated	→	Final phases (≠ initial phases)
with micrometric grain sizes mixed		with nanometric grain sizes

These characteristics make up the microstructure, a term also applicable to nanostructured materials, defined by the number, nature, structure, and geometry (size and shape) of the phases and their arrangement with the interfaces, interphases they form between each other, and their network defects.

Mechanical properties can be enhanced not only by better controlling synthesis, sometimes at the expense of process engineering methods but also by controlling crack propagation through microstructure optimization.

Thus, the mechanical performance of brittle ceramics can be improved by incorporating various reinforcements, such as ductile metals like iron, nickel, copper, or various alloys capable of attracting and stopping cracks.

- Characteristics of barium titanate in the nanograin state: Impact of grain size

As early as the 1950s, Kanzig et al. observed that the tetragonality of the BaTiO3 crystal lattice was reduced when the powder grains were small enough.

A more recent investigation with powders covering a wide range of grain size distributions has provided a more detailed picture of this reduction in tetragonality, showing that if the powder grains are smaller than 100 nm, barium titanate is cubic and paraelectric regardless of temperature.

Furthermore, it has been demonstrated that the phase transition temperature from the ferroelectric state to the paraelectric state, at standard atmospheric pressure, decreases steadily as the grain size is reduced.

The transition disappears when the grain size is less than 100 nm. However, this phenomenon is much less pronounced in ceramics, i.e., when the solid-gas interface presented by powder grains is replaced by the solid-solid interface presented by ceramic grains. This phenomenon illustrates the influence of size.

This phenomenon illustrates the influence of grain size on a physical property through a surface effect. Regarding the dielectric constant of BaTiO3, its dependence on grain size in this ceramic material has been known for a long time. As the grain size decreases, the characteristic curve = f(T) for BaTiO3 tends to flatten out.

The dielectric constant increases around room temperature, while it decreases during the ferroelectric-to-paraelectric phase transition near 120°C.

However, this trend is not monotonic, as shown in Figure I. 21: a maximum is obtained for the dielectric constant at room temperature when the grain size is around 700-800 nm, and the value of y is about five times higher than its value for mainly micrometric grains.

This grain size is currently sought after in $BaTiO_3$ dielectric ceramics.

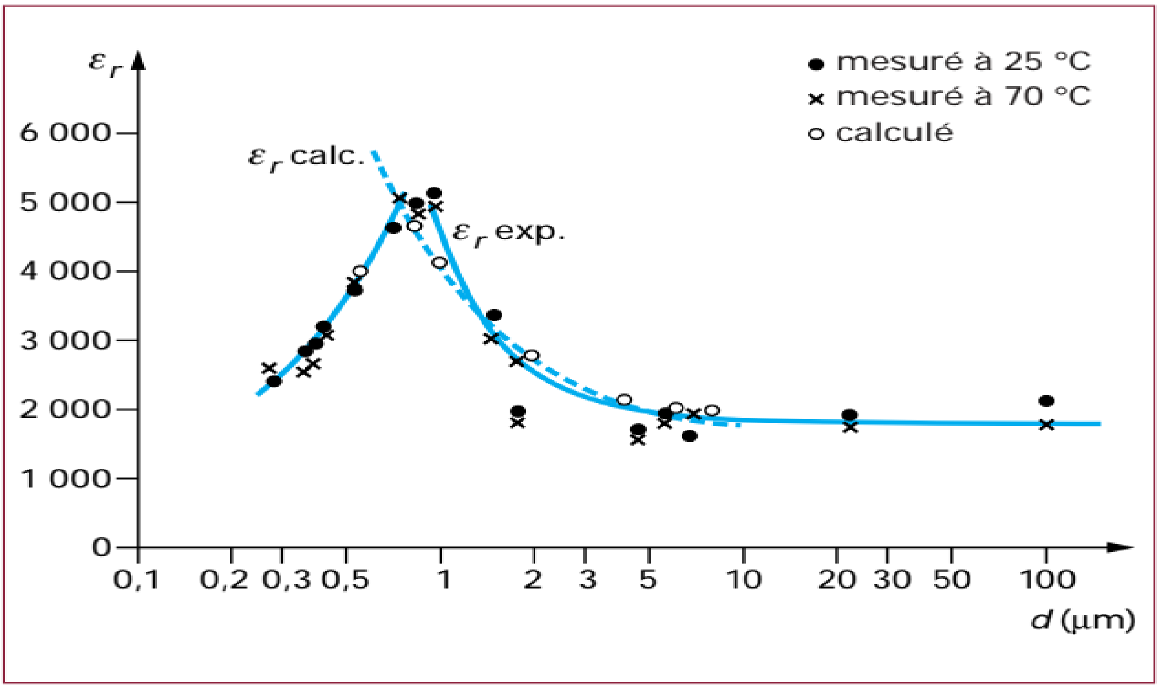


Figure I. 21: Relative dielectric constant at 25°C for $BaTiO_3$ in polycrystalline ceramics as a function of the average grain diameter in the ceramic.

According to the curve, we need to understand what contributes to the dielectric constant and explain its dependence on grain size.

Two characteristics of barium titanate that both contribute to the dielectric constant are strongly influenced by grain size:

- The crystalline structure, as mentioned above,
- The ferroelectric domain microstructure.

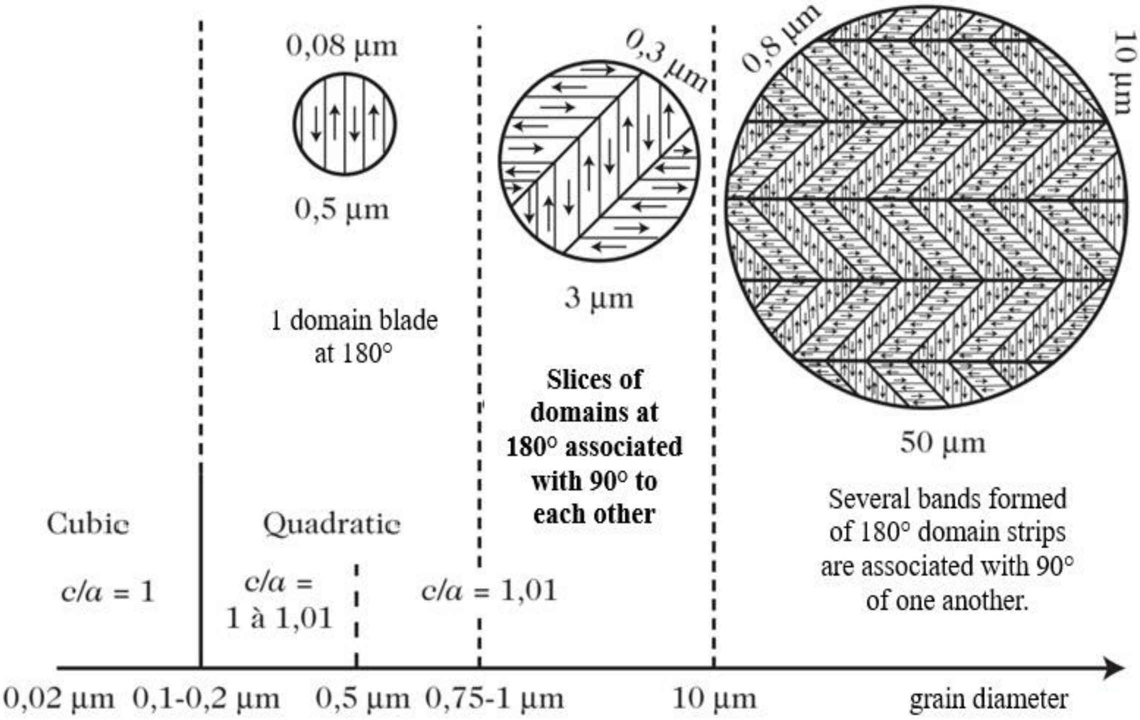


Figure I.22: Ferroelectric domain microstructure of BaTiO3 in the polycrystalline ceramic state as a function of the average grain diameter in the ceramic.

Indeed, it has been demonstrated that the ferroelectric domain microstructure in $BaTiO_3$ ceramics is closely related to the grain size (refer to Figure I.22).

Comparing the information obtained from Figures I.21 and I.22, we observe that the maximum value of the dielectric constant coincides with the transition from a microstructure associating domains at 180° and domains at 90°, for grain sizes larger than 0.8 µm, to a microstructure comprising only domains at 180°, for grain sizes below this value.

In this case, the phenomenon illustrates, for the same material, the influence of grain size on the physical property through a confinement effect.

A microstructure with nanometric grains that does not have 90° domains also presents another advantage: it almost eliminates all dielectric losses of ferroelectric origin.

I.8.2: Materials obtained by dispersions in polymers

a) Charged elastomers

These polymers typically contain solid nanoparticles ranging in size from 10 to 100 nm. These charged elastomers provide very high resistance to abrasion, in addition to other mechanical properties for common use.

b) Polymer-mineral particle nanocomposites

The main objective is to enhance the mechanical properties of polymers by using sematic minerals as reinforcement.

These sematic minerals, such as clay (montmorillonite), can be dispersed in a polymer matrix by gradually separating their layers through the intercalation of a liquid.

This intercalation is facilitated in adjustable pH aqueous solutions, but more complex in organic liquids.

However, by replacing metal ions with organic cations between the clay layers, successful intercalation in organic liquids can be achieved.

When this substitution is successfully done, the intercalation of organic cations allows for the dispersion of clay particles into individual layers, thus providing effective reinforcement to the polymeric material (Figure I.23).

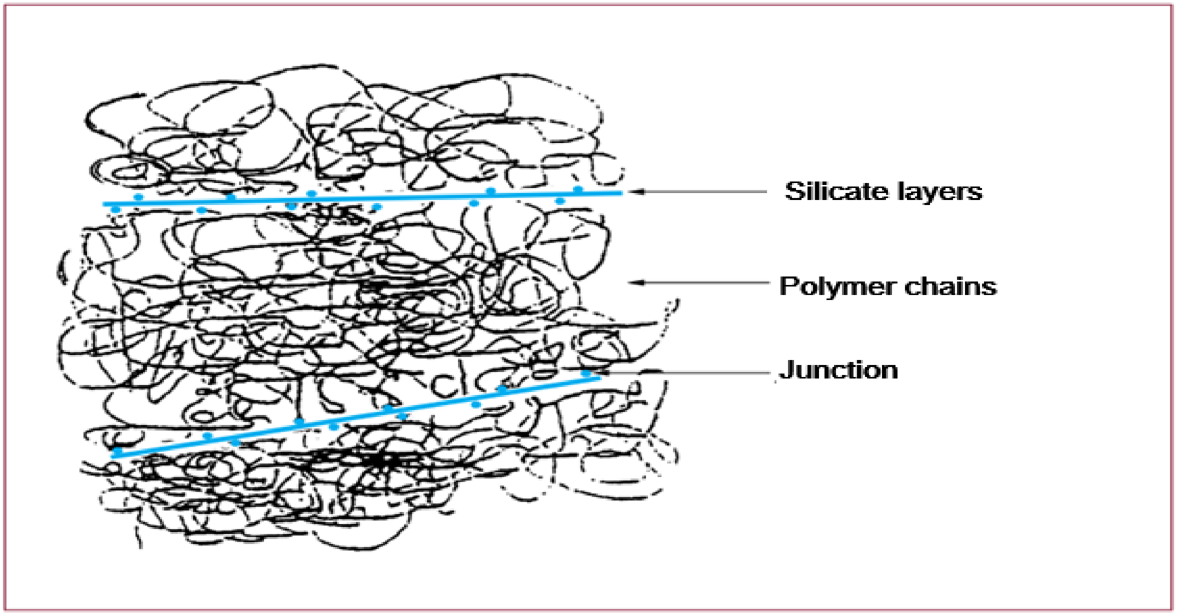


Figure I.23: Distribution, after exfoliation (extraction of metal ions), of single layers of smectite clay in a polymer matrix.

Chapter II : Manufacturing Processes of Nanomaterials

II- Nanomaterial Manufacturing Processes

Scientists conduct research to develop new materials with improved properties, more functionalities, and at a lower cost than existing ones.

Various physical and chemical methods have been developed to enhance the performance of nanomaterials with improved properties to achieve better control over particle size, from distribution methods to nanomaterial synthesis.

In general, the top-down and bottom-up approaches are the two main methods for synthesizing nanomaterials (Figure II.1).

The two approaches for developing nano-objects and manufactured nanomaterials are:

A. Top-down approach: the starting material is in a solid state.

B. Bottom-up approach: synthesis of materials from the atomic level. In these techniques, the starting material is either in a gaseous or liquid state.

II.1 Top-down approach:

This process is based on the typical treatment of materials in a solid state.

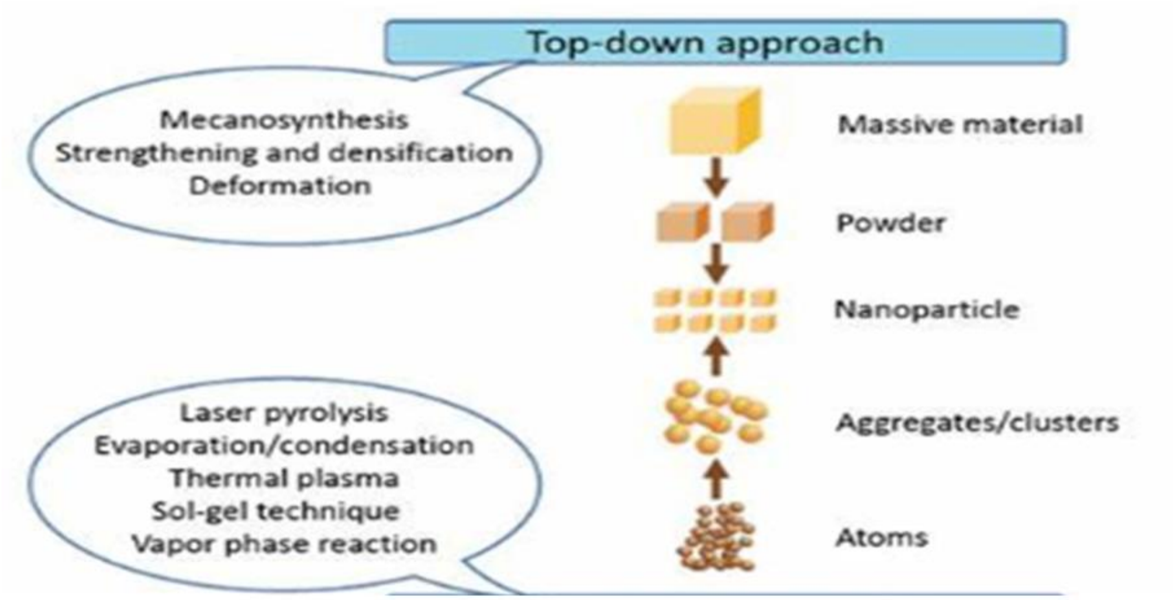


Figure II.1 : The two approaches for developing nano-objects and manufactured nanomaterials(www.nanosmile.org)

Its route is based on the bulk material and makes it smaller by breaking down larger particles using physical processes such as crushing, milling, or grinding.

This route is generally not suitable for preparing materials of uniform shape, and it is very challenging to achieve very small particles even with high energy consumption.

The major issue with the top-down approach is the imperfection of the surface structure. Such imperfections would have a significant impact on the physical and surface chemistry properties of nanostructures and nanomaterials.

It is well known that the conventional top-down technique can lead to crystallographic damage to the processed product.

This approach is used to produce:

a- Mechanical methods

- Engraving cutting, grinding
- Grinding

b- Lithography techniques

- ✓ Electron beam lithography.
- ✓ Focused lithography.

- Advantages

- ✓ Large-scale production: deposition on a large substrate is possible.
- ✓ Chemical purification is not required.

- Disadvantages:

- ✓ Wide size distribution (10-1000 nm).
- ✓ Various particle shapes or geometries.
- ✓ Control of deposition parameters is difficult to achieve.
- ✓ Impurities: constraints, defects, and imperfections are introduced.
- ✓ Expensive technique.

II.2 Bottom-up:

This involves the accumulation of a material from the bottom up: atom by atom, molecule by molecule, or group by group.

This method is more commonly used to prepare most materials on the nanoscale with the ability to generate uniform size, shape, and distribution.

It effectively covers chemical synthesis and precisely controls the reaction to inhibit further particle growth.

Although the bottom-up approach is not new, it plays an important role in the manufacturing and processing of nanostructures and nanomaterials.

The bottom-up process is used to produce at the supramolecular level.

All bottom-up techniques use either a gaseous state or a liquid state of matter as the starting material.

Physical and chemical processing methods are:

a- Physical techniques:

Physical vapor deposition (PVD): involves the condensation of species in the vapour phase.

- ✓ Evaporation (thermal, electron beam).
- ✓ Cathodic sputtering.
- ✓ Plasma arc.
- ✓ Laser ablation.

b- Chemical techniques CVD:

Chemical vapor deposition of reactive species

- ✓ PECVD (RF-PECVD, MPECVD).
- ✓ Electrodeposition, sol-gel method, pyrolysis.

- Advantages:

- ✓ Ultra-fine nanoparticles, nanocapsules, nanotubes can be prepared.
- ✓ Deposit parameters can be controlled.
- ✓ Narrow size distribution is possible (1-20 nm).
- ✓ Less expensive technique.

- Disadvantages:

- ✓ Large-scale production is challenging.
- ✓ Chemical purification of nanoparticles is necessary.

II.3 General Techniques for Nanomaterial Fabrication

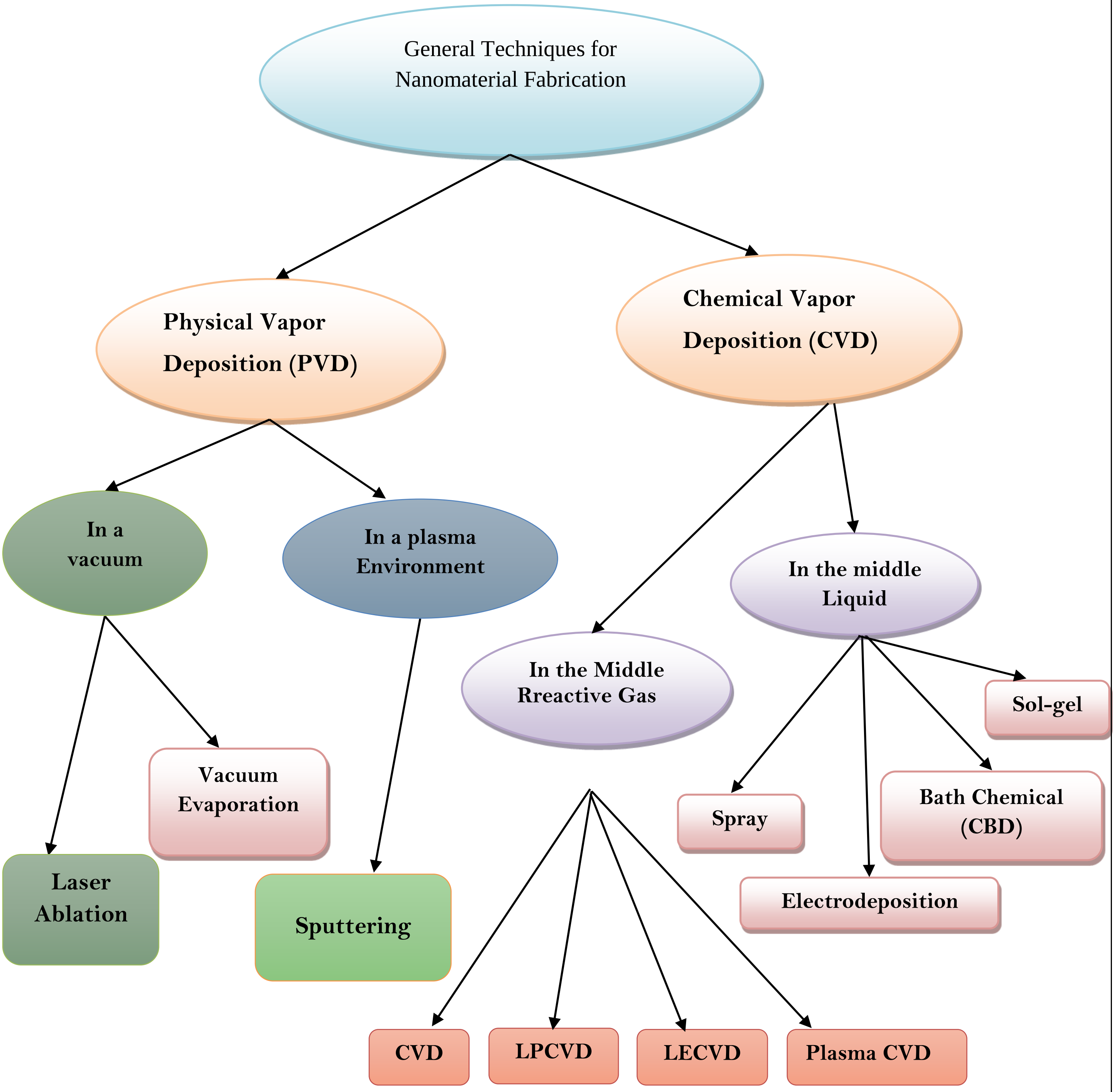


Figure II.2: General Methods for Nanomaterial Deposition

II.4 Fabrication by Physical Means

II.4.1 Evaporation-Condensation

This method involves evaporating a metal through heating and then condensing the metal vapor to obtain nanopowders consisting of dispersed nanoscale particles.

Figure II.3 shows the "historic" process developed by Gleiter. It involves evaporating a material in a partial atmosphere and collecting nano-aggregates on a cold finger.

The type of heating depends on the metal's vapor pressure, i.e. its ability to evaporate, which is influenced by the strength of the chemical bond and the surface state (oxidation).

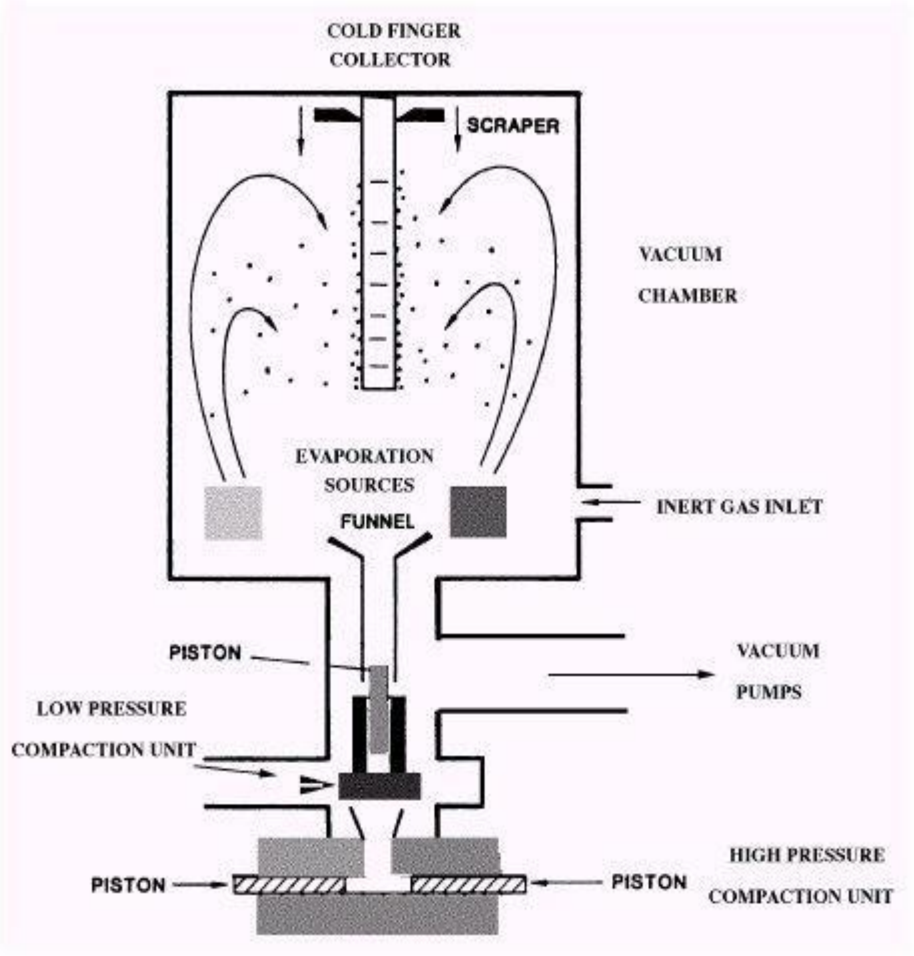


Figure II.3: Evaporation/condensation process developed by Gleiter

Metals such as Fe, Ni, Co, Cu, Pd, Pt produce sufficient vapour through radiative (1200°C) and inductive heating (2000°C). In laboratory settings, 50 to 100 g/h of material is produced.

Oxygen-reactive (Al, Cr, Ti, Zr) and refractory metals (with very low vapor pressure, Mo, Hf, Ta, W) require more powerful heating methods: electron beam heating (3000°C), inductive plasma heating, and/or coupled with electric arc (3000°C to 14000°C).

When metallic particles are placed in a reactive atmosphere, typically oxygen, the resulting nanoparticles are the oxide of the initial metal after oxidation reaction. The challenge of this technique lies in controlling the nanoscale size.

Nanopowders are obtained by rapid cooling of the metallic vapor, ensuring the formation of a large population of particles, and then limiting their growth and coalescent coagulation.

This preparation method is used in the industrial production of metallic and ceramic nanopowders (mentioned above) after the reaction. Production reaches several tens of tons per year.

The formed nanopowders are powdery systems with high pollution potential (aerosol formation) if production and handling chains are exposed to the atmosphere. These nanopowders are also highly pyrophoric in air (prone to explosion and fire).

II.4.2 Laser pyrolysis

Laser pyrolysis is classified among the physical techniques for synthesizing nanoparticles from the gas phase. It originated in the United States in 1981 and was introduced in France, at CEA, two years later.

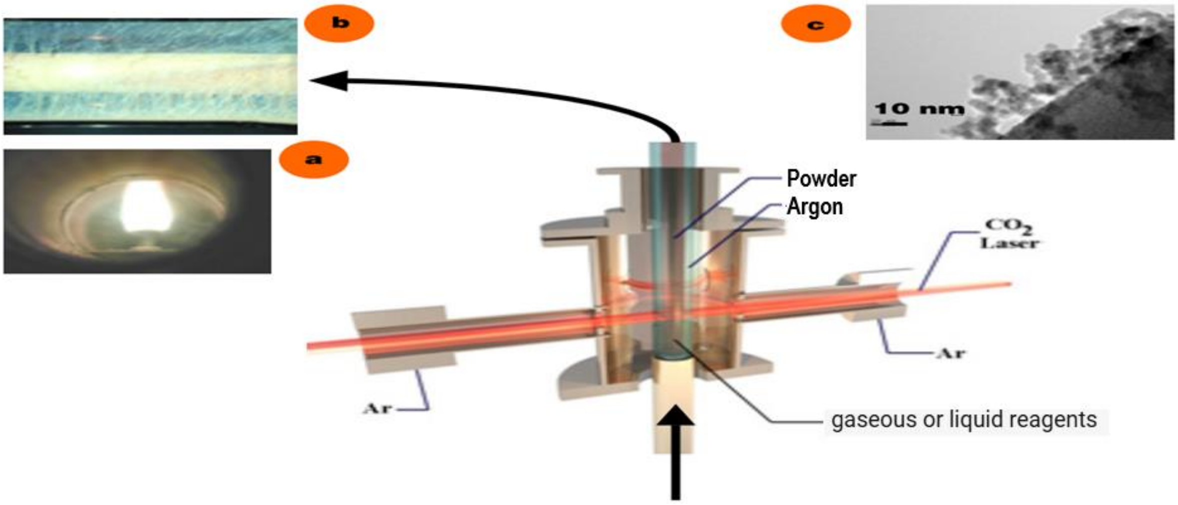


Figure II.4 : Illustrates the principle of a laser pyrolysis reactor: (a) reaction flame; (b) nanoparticles accumulating on a filter; (c) transmission microscopy images of nanoparticles.

It is based on the interaction between a gaseous or liquid precursor and the emission of a CO_2 laser, requiring resonance between the laser emission spectrum and the absorption spectrum of at least one of the reactants.

Energy transfer occurs through the excitation of the vibrational levels of molecules absorbing the laser energy. Typically, the medium operates at a pressure close to atmospheric pressure, allowing rapid energy transfer from laser-excited molecules to the reactive medium, leading to quick thermalization.

A typical reactor (Figure II.4) dissociates precursors, forming an incandescent flame (a) where nanoparticles are generated and then quenched upon flame exit. The particles are subsequently collected on filtering barriers (b). Figure (c) illustrates an example of silicon nanoparticles.

II.4.3 Physical Vapor Deposition (PVD)

PVD is a method for depositing films through physical vapor deposition in a vacuum environment. In this method, a high-energy electron beam from a source (typically a filament) is focused on a target.

Atoms evaporate from the target's surface upon electron beam impact, transferring energy to the surface. In a vacuum environment, these vapors travel and deposit onto a substrate above the target. The vacuum conditions enhance efficient material deposition by increasing the mean free path of the vapors.

The deposition is carried out under vacuum at a pressure of about 10^{-3}-10^{-4} Pa to reduce collisions between evaporated atoms and those of the residual gas, thus limiting contamination of the deposited layers and increasing the deposition rate.

The main evaporation techniques vary depending on the mode of evaporation used: heating (Joule effect, induction), electron beam bombardment, laser beam, electric arc.

Resistance and induction heating allow for coatings to be obtained at a high deposition rate but require considerable power to vaporise the most resistant compounds.

However, particles removed from the source have relatively low energy, affecting adhesion. Moreover, evaporation and deposition of alloys can be disrupted if the compounds have significantly different melting temperatures or saturated vapor pressures.

Electron beam bombardment is currently the most commonly used evaporation method due to its high bombardment energy allowing for the vaporisation of refractory materials and its high deposition rate of up to 50 µm/s.

Despite its ease of implementation, this process has issues related to the generation of electrostatic emissions that can cause sparks and substrate sputtering when evaporating dielectric materials.

Laser ablation evaporation is a technique using a pulsed laser beam to evaporate the target in an ultravacuum environment. The laser pulses induce the evaporation of materials in the form of plasma, ensuring the purity of the deposits based on the purity of the target (Figure II.5).

This process allows for the deposition of various high-purity materials at room temperature, facilitating coating on various substrates.

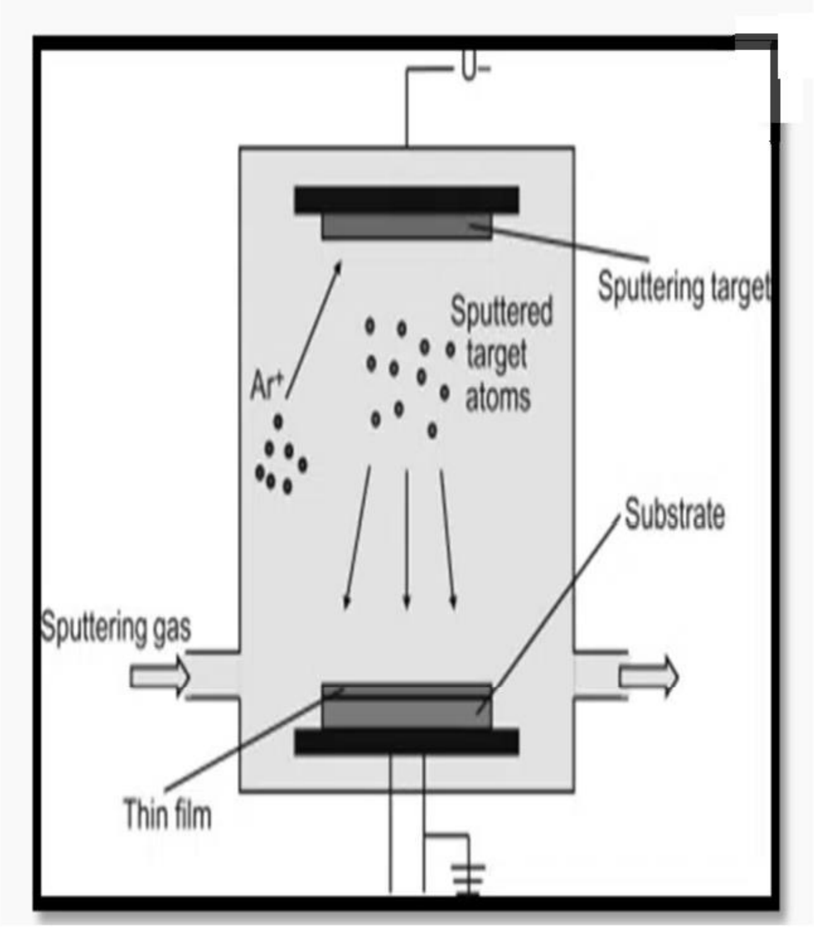


Figure II.5: Operation principle of the PVD technique

Additionally, target evaporation can also be achieved by the erosion of an electrode through high-intensity electric arcs in a reactive or inert atmosphere. The ejected atoms are mainly ionised and then directed towards the substrate by an electric field.

This method, long used for depositing thin films of carbon and metals, generates a high density of electrons, promoting the ionisation of ejected solid particles. Consequently, a uniform coating is obtained, even on samples with complex shapes.

Overall, arc evaporation is an energy-efficient process that enables significant deposition speeds (around 2µm/min), including the production of alternating multilayers using multiple target electrodes.

II.4.4 : Cathodic sputtering

Cathodic sputtering is a process where atoms are released from a solid target material due to bombardment by energetic particles such as ions and atoms. The atoms released from the target can then be deposited as thin films on substrates and are commonly referred to as PVD by sputtering (Figure II.6).

The process involves the transfer of momentum from incident ions/atoms to the target materials through collisions. The average number of atoms ejected from the target per incident particle is known as the sputtering yield.

This yield depends on the angle of incidence of ions, the energy of ions, the masses of ions and target atoms, the surface binding energy of atoms in the target, and the crystal orientation of the target when crystals are used as targets.

There are various approaches to generate sputtering, including the use of DC (direct), AC (alternative), and RF (radio-frequency) plasmas or external ion beams.

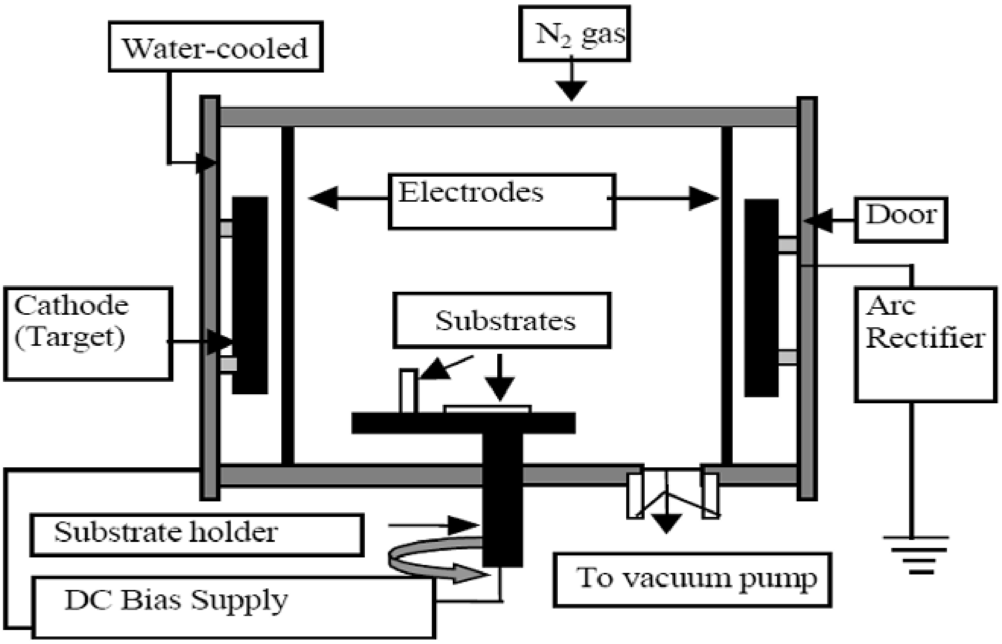


Figure II.6: Schematic of the physical vapor deposition process by cathodic arc

Cathodic sputtering offers several advantages compared to other PVD techniques, including:

(1) deposition over a large area compared to pulsed laser deposition;

(2) convenience for depositing thin films of alloys/composites and materials with high melting points;

(3) prevention of device damage from X-rays generated by electron beam evaporation.

However, cathodic sputtering also has the following disadvantages:

(a) a more complex setup than pulsed laser deposition;

(b) an increased risk of contamination due to plasma use and a relatively lower vacuum level;

(c) the film morphology can be rougher or damaged due to bombardment by energetic growth species and aggregation of growth species under relatively high deposition pressures.

II.5 Chemical processing

II.5.1 Chemical Vapor Deposition (CVD) process

In Chemical Vapor Deposition (CVD), a thin layer of material is deposited on a substrate by providing a mixture of reactive gases (volatile compounds such as SiH_4, $SiCl_4$, WF_6, etc.) and carrier gases (H_2, Ar, etc.).

For example, a thin film of Si_3N_4 can be deposited using SiH_4, NH_3 and Ar according to the reaction:

$$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2 \quad \textbf{(II.1)}$$

The chemical vapor deposition process involves the following steps (Figure II.7):

- Transport of reactive gaseous species to the surface.
- Adsorption of species on the surface.
- Catalyzed heterogeneous reactions on the surface.
- Surface diffusion of species to growth sites.
- Nucleation and film growth.
- Desorption of gaseous reaction products and transport of reaction products away from the surface.

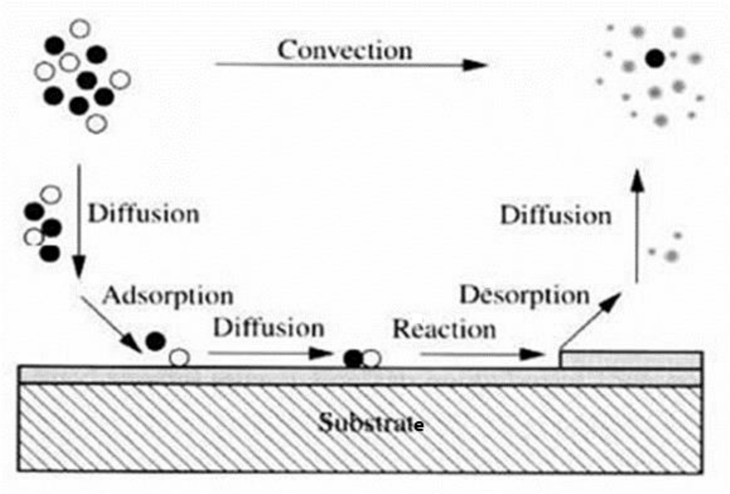


Figure II.7: Illustration of the various stages of the CVD process

In chemical vapor deposition, vapor generated from a precursor is thermally decomposed or reacts with another precursor vapor or gas inside the evaporation apparatus. Nucleation, condensation, and coagulation of precursor particles generate solid-state particles.

Particle sizes obtained by CVD can range from molecular size to hundreds of micrometers. Some advantages of gas-to-particle conversion method include small particle size (from a few nm to mm), narrow size distribution, high particle purity, etc.

However, the formation of hard aggregates due to gas-phase agglomeration poses challenges in synthesizing high-quality bulk materials.

The advantage of this technique is the quick implementation for obtaining thin layers, even at relatively low temperatures.

However, the drawback is the heaviness of the equipment, making the synthesis of thin layers quite expensive. Moreover, only small surfaces of the order of square centimeters can be processed.

Driven by numerous applications, various variants of this technique have been developed.

- ✓ Low-pressure Chemical Vapor Deposition (LPCVD) operates between 1 atm and 10^{-8} Torr and is widely used for quality control of layers.

- ✓ Atomic Layer Chemical Vapor Deposition (ALCVD) involves the sequential deposition of layers of different materials that must react to form a monolayer before starting a new one.
- ✓ Metalorganic Chemical Vapor Deposition (MOCVD) is a CVD process based on deposition and reaction (decomposition) using more reactive precursors such as organometallics (MOCVD) reacting at low temperatures (300-800 °C).

I.5.2 Enhanced Chemical Vapor Deposition by Plasma (PECVD)

Enhanced Chemical Vapor Deposition by Plasma offers a clear advantage with a lower deposition temperature than thermal CVD.

In this process, plasma generated from various sources including direct current (DC), radiofrequency alternating current (RF) (Figure II.8), and microwaves is used to enhance the reaction between precursors.

In DC plasma, reactive gases are decomposed and ionized using a direct current electrical discharge to create plasma, while in RF plasma, reactive gases are decomposed and ionised, generating a time-varying plasma that is initiated and extinguished repeatedly.

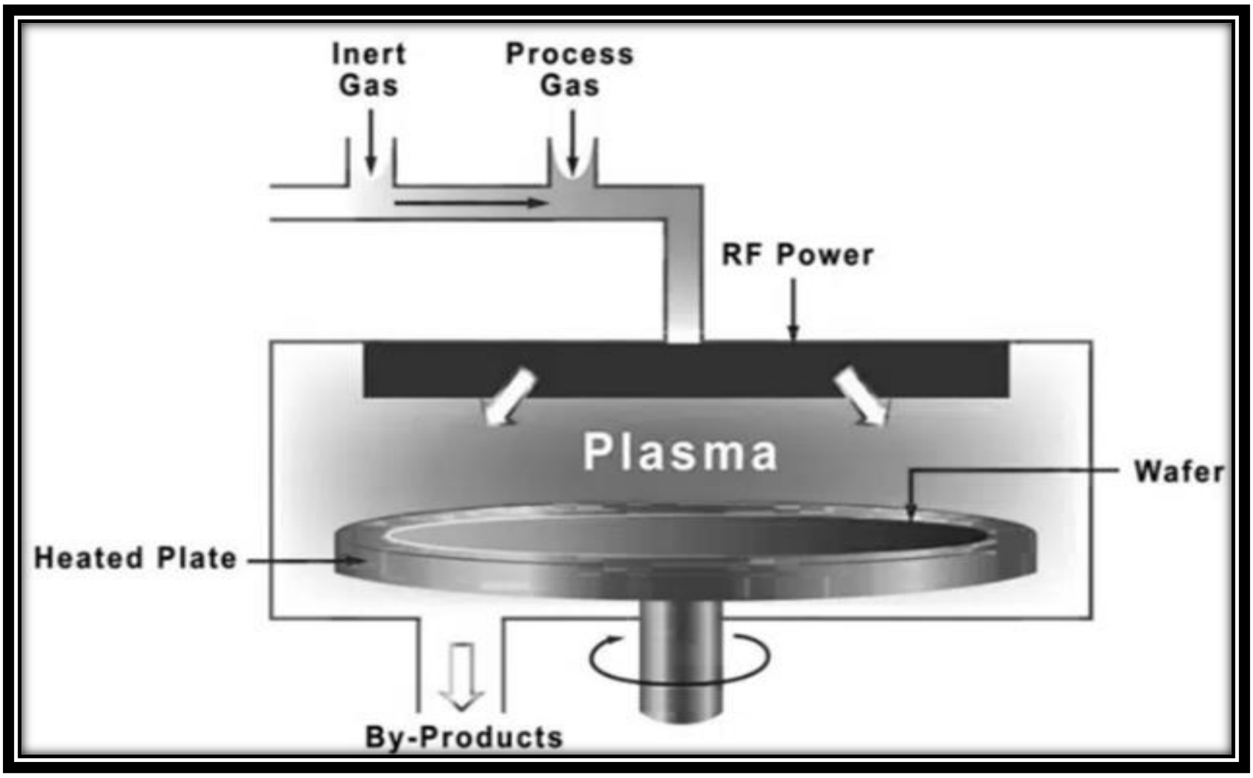


Figure II.8 : Improved CVD Process with Plasma (PECVD)

Nowadays, RF plasma-enhanced CVD is commonly used to deposit SiC films on a silicon substrate using a mixture of $SiCl_4$, CH_4, H_2, and Ar.

Microwaves are utilised to generate plasma in Microwave-assisted CVD (MW-CVD).

Their primary effect is to oscillate electrons, which upon colliding with gas atoms and molecules, produce significant ionization percentages. This technique also enables specific substrate-selective growth. Vertically aligned carbon nanotube arrays are typically grown using MW-CVD.

II.6 Sol-Gel Synthesis

The first material synthesized using the sol-gel method was silica, initially described by J.J. Ebelmen. However, it took nearly a hundred years for this idea to be industrially adopted, with the first sol-gel patent filed in 1939 in Germany by Schott Glaswerke for manufacturing rear-view mirrors, which were only commercialized in 1959.

The sol-gel process is widely employed industrially today, especially for producing thin films and powders (TiO_2, SiO_2, ZnO...) on various substrates.

This method is particularly well-suited for creating homogeneous materials in the form of powders and films with high optical, optoelectronic, and photocatalytic performance.

During synthesis via the sol-gel route, the molecular precursors in the initial solution, the sol, polymerize through various mechanisms to form an oxide network, the gel.

Drying followed by thermal treatments eliminate organic compounds to form inorganic oxide materials.

II.6.1 The Precursors

The precursors constituting "the solution" can be of two types. They are either colloidal particles dispersed in a liquid or organometallic precursor dissolved in a solvent. Regardless of their nature, the precursor is dissolved before being hydrolyzed.

The polymerization of these precursors leads to a three-dimensional interconnected solid network that is stable due to the formation of M-O-M bonds. The system is then in a gel state.

Different types of material shaping obtained through the sol-gel process are shown in Figure II.9.

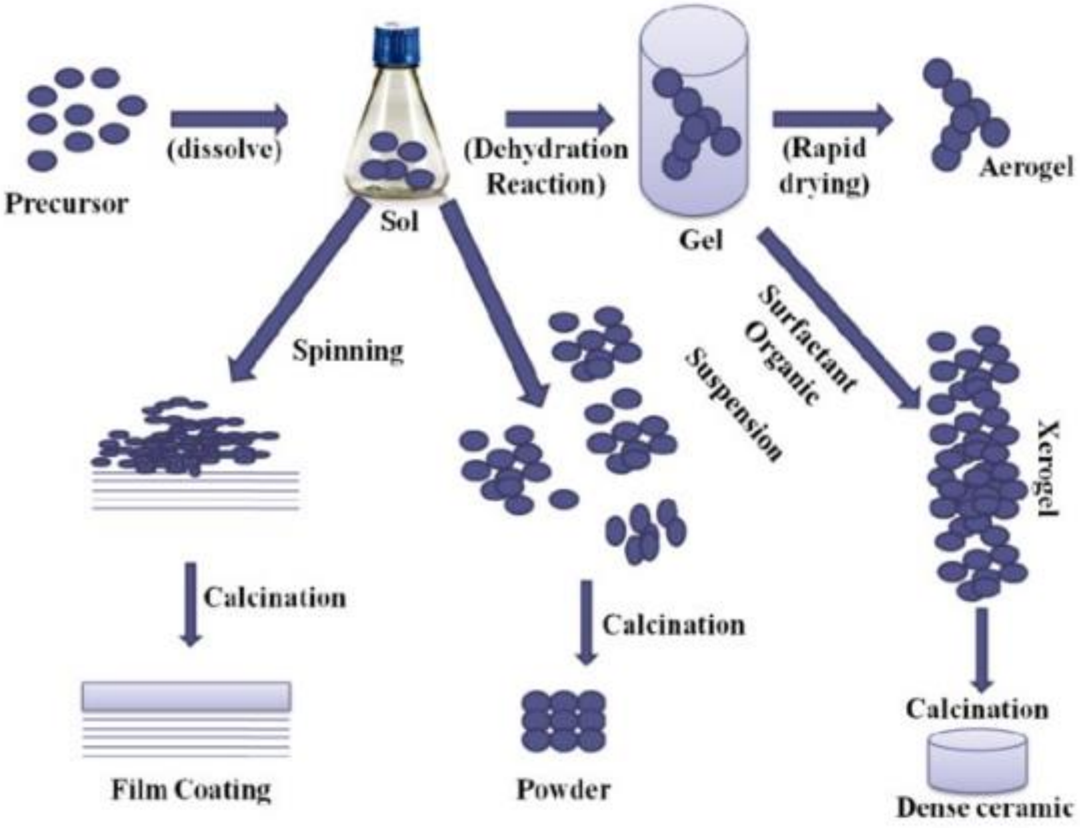


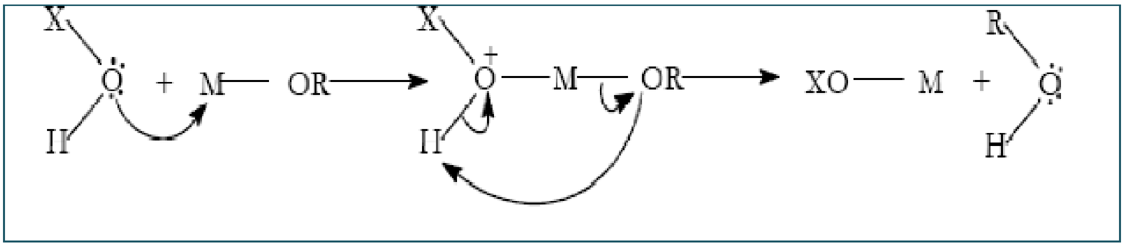
Figure II.9: *Different types of material formatting obtained through sol-gel processing.*

✓ Inorganic precursors: (metal cation type salts): in this case, hydrolysis is carried out by adjusting the pH of the aqueous solution.

✓ Metal-organic precursors: the most commonly used are metal alkoxides dispersed in an organic solvent (usually the parent alcohol of the alkoxide).

✓ Hydrolysis involves replacing alkoxide ligands (-OR) with hydroxyl ligands (-OH).

✓ Condensation reactions of hydroxyl ligands produce oligomers or polymers composed of M-O-M bonds (Figure II.10).



Condensation reactions of hydroxyl ligands producing oligomers or polymers composed of M-O-M bonds.

Oxidation state:	Z	Z-1	Z
Metal coordination:	N	N+1	N

The chemical reactivity of the metal alkoxide in these nucleophilic substitution reactions mainly depends on:

- The strength of the nucleophile (X-OH).

- The electrophilic nature of the metal atom.

The metal's ability to increase its coordination (the number of groups that can associate with the metal atom) and thus form oligomers.

The degree of unsaturation of the metal's coordination can be expressed by the difference N-Z where N is the maximum coordination of the transition metal in the oxide and Z is the oxidation number of the neutral metal.

Metal alkoxides are highly reactive species due to the presence of very electronegative alkoxy groups (-OR) that stabilise the metal in its highest oxidation state and make it highly reactive to nucleophilic groups.

Therefore alkoxides are extremely sensitive to hydrolysis and require either handling in a controlled atmosphere, the use of stabilising agents, or both.

a- Hydrolysis Step

To obtain oxides from alkoxides, they need to condense at room temperature. Therefore, the hydrolysis of the -OR groups is a necessary activation step to generate hydroxyl groups -OH. This is the initiation step or partial hydrolysis.

$$M-(OR)_n + H_2O \rightarrow HO-M-(OR)_{n-1} + R-OH$$

This step involves water consumption and alcohol release for the formation of reactive monomers. During this stage, the precursor's functionality is created.

Regarding polycondensation: After hydrolysis, the metal's coordination sphere is altered, but its coordination remains unchanged.

b- Condensation step:

The -OH groups generated during hydrolysis are good nucleophiles and, during the condensation step, lead to the formation of oxygen bridges between two metal nuclei (oxo-metal bridges M-O-M).

Like hydrolysis, condensation alters the metal's coordination sphere but does not increase its coordination.

$$(OR)_{n-1}-M-OH+RO-M-(OR)_{n-1}\rightarrow(OR)_{n-1}-M-O-M-(OR)_{n-1}+R-OH$$

During condensation, if the metal centers are closely positioned, nucleophilic addition reactions of terminal -OR and -OH groups can occur on other neighboring metal centers.

$$(OR)_{n-1}-M-OH+RO-M-(OR)_{n-1}\rightarrow(OR)_{n-1}-M-O-M-(OR)_{n-1}+R-OH$$

This is known as polymerization in this case.

$$(OR)_{n-1}-M-OH+HO-M-(OR)_{n-1}\rightarrow(OR)_{n-1}-M-O-M-(OR)_{n-1}+H_2O$$

These reactions occur when the metal's coordination is unsaturated and sterically hindered. They result in an increase in the metal's coordination.

$$(OR)_{n-1}-M-OH+HO-M-(OR)_{n-1}\rightarrow(OR)_{n-1}-M-O-M-(OR)_{n-1}+H_2O$$

II.6 Aerosol Gel

This process involves generating a mist of solution and bringing it to the substrate where it deposits (see Figure II.10).

This technique offers very interesting possibilities, especially when the substrate has complex surfaces. However, it is challenging to use for large areas.

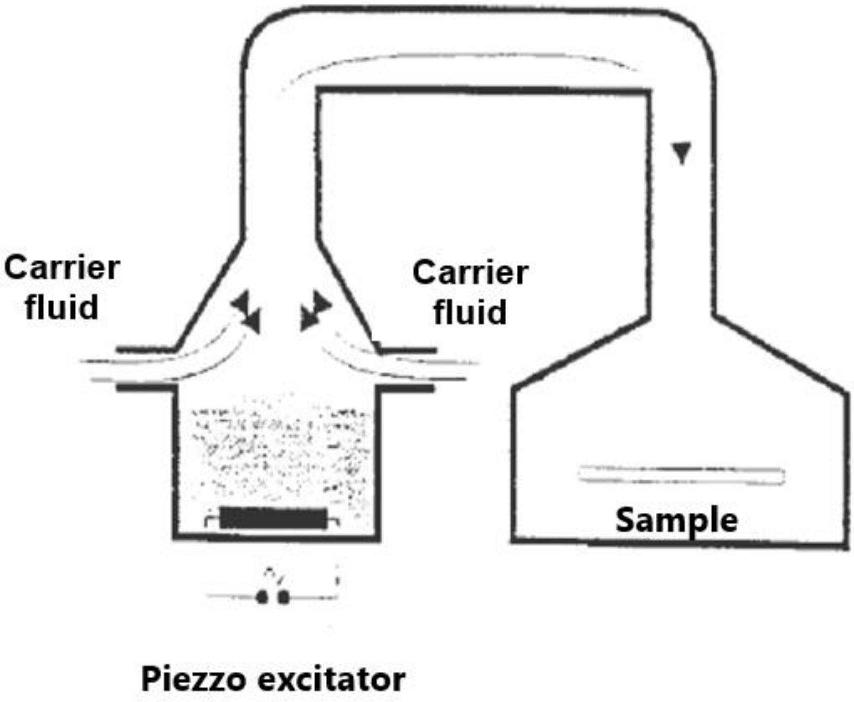


Figure II.10: Thin Film Deposition by Centrifugal Coating

II.7 Spin-Coating Centrifugation

The "spin-coating" technique involves creating a thin layer through centrifugation from an excess solution deposited on a substrate. The preparation of a layer involves four essential phases:

- ✓ Depositing the solution on the substrate.
- ✓ Acceleration: marking the start of rotation, causing the liquid to flow towards the outer edges of the substrate.
- ✓ Uniform rotation: facilitating the ejection of excess solution in droplet form and uniformly reducing the layer thickness.
- ✓ Evaporation: during this stage, the substrate continues to rotate at a constant speed, with the most volatile solvents evaporating, leading to a decrease in the deposited layer's thickness.

These steps of depositing a thin layer are outlined in Figure II.11.

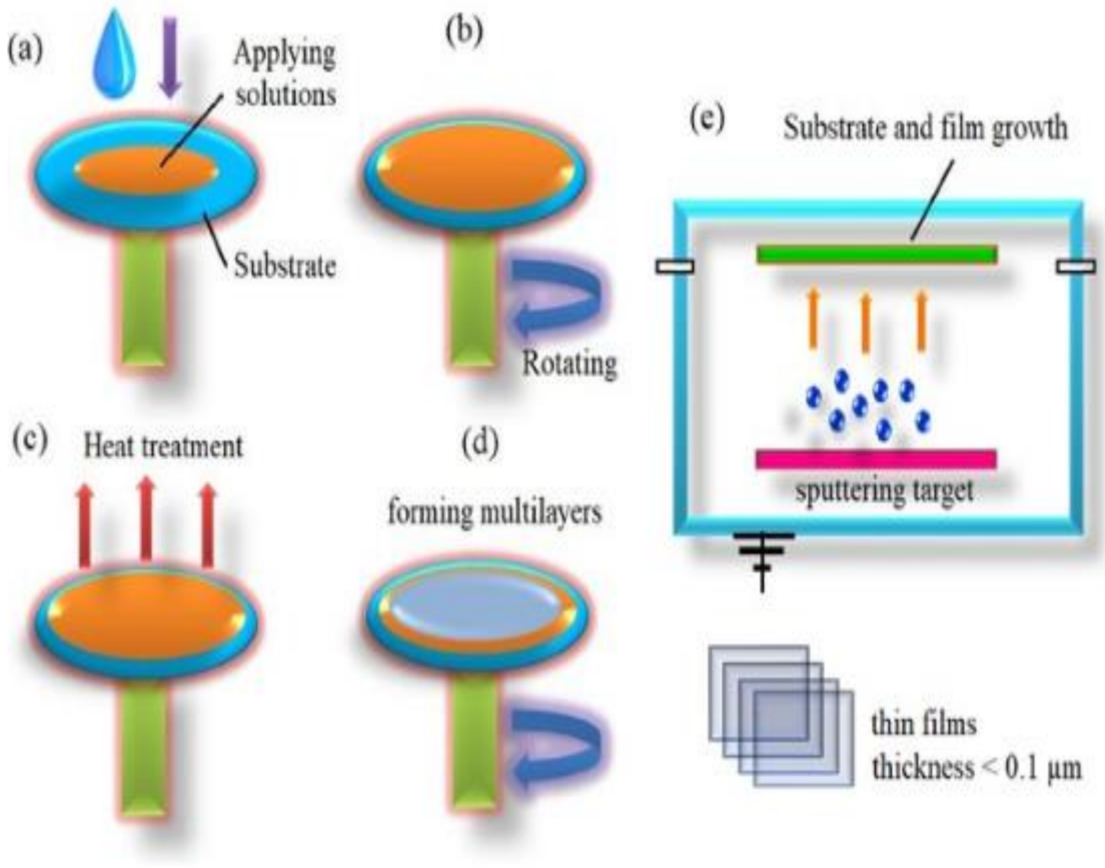


Figure II.11: Schematic representation of Spin-Coating Centrifugation principle

This technique is advantageous for its ease of implementation and enables the production of high-quality layers on flat substrates of a few cm² in size.

The deposited thickness (d) depends on various parameters, as demonstrated by empirical relationships.

$$\boldsymbol{d = A.\left(\frac{3\eta e}{2\rho\omega^2}\right)^{1/3}} \qquad \textbf{(II.2)}$$

(η), density (ρ), rotation speed (ω), and initial thickness (e).

This relationship indicates that, for a given viscosity, adjusting the layer thickness is achievable by setting the rotation speed.

II.8 Spray Pyrolysis

Thin layers can also be obtained using the Spray Pyrolysis Deposition (SPD) technique. Spray is a deposition technique used to prepare thin and thick films, ceramic coatings, and powders.

Unlike other film deposition techniques, spray pyrolysis is a very simple and relatively cost-effective method (especially in terms of equipment costs). Spray pyrolysis does not require high-quality substrates or chemicals.

The method has been used for depositing dense films, porous films, and for powder production. Even multilayer deposits can be easily prepared using this technique.

Spray pyrolysis has been employed for several decades in the glass industry and in solar cell production.

Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller. Figure II.12 illustrates the schematic diagram of this technique.

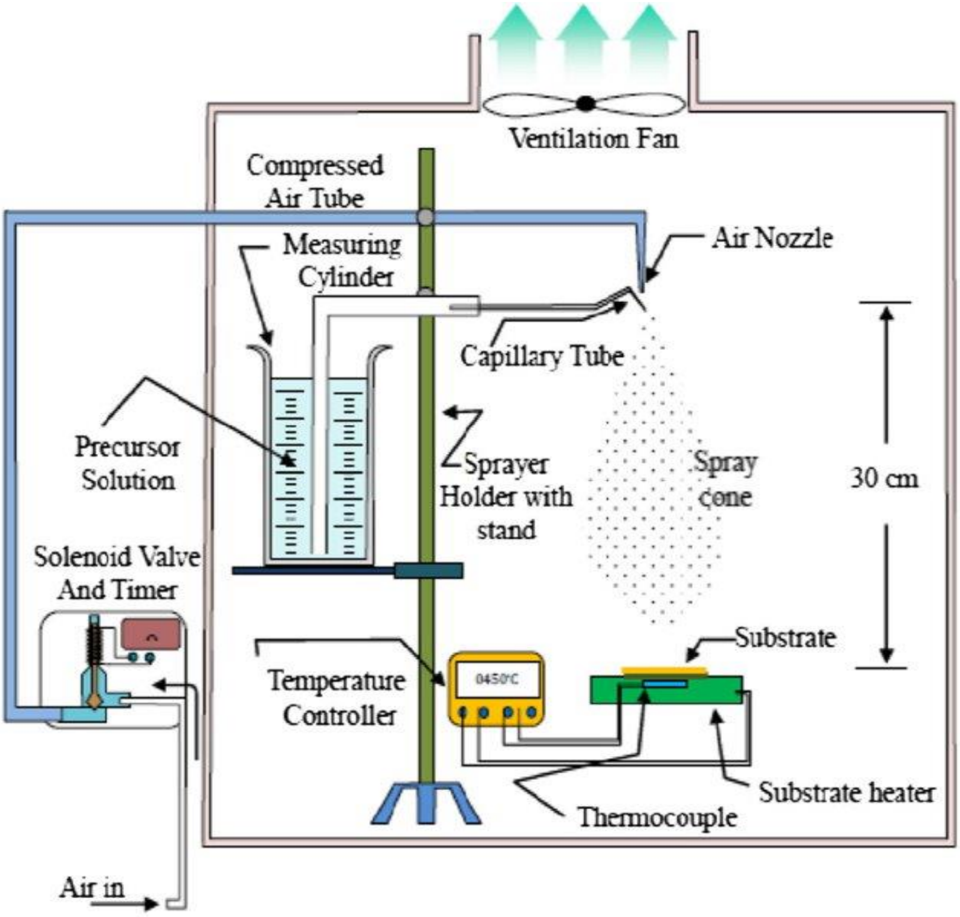


Figure II.12. Spray pyrolysis device schematic

II.9. The deposition process known as "dip-coating"

This method involves immersing the substrate in the solution and withdrawing it under very controlled and stable conditions to obtain a film of reproducible thickness. As the substrate is withdrawn, the liquid will flow over it.

At the end of the flow, the substrate is covered with a uniform film. Figure (II.13) illustrates the different stages of "dip-coating".

This first step (dipping) has little influence on the process. The second step (extraction) is done at a constant speed.

During this step, the solution is drained, and the solvent evaporates from the exposed part. These two phenomena continue as the sample is withdrawn from the solution.

We will discuss in more detail the physical phenomena involved in the substrate withdrawal.

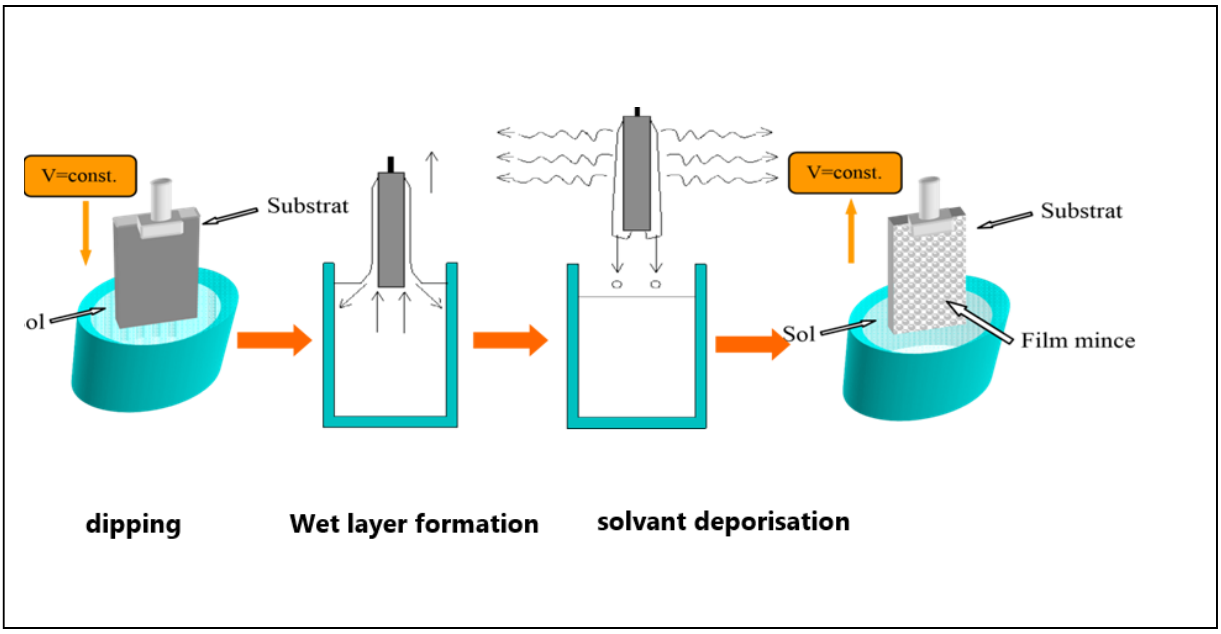


Figure II.13 Detail of the dip-coating process: Substrate immersion in the solution, layer formation during substrate withdrawal, and film gelation through solvent evaporation.

. Once the flow ceases, the substrate is coated with a uniform and highly porous film. Structural changes in the dip-coated film are depicted in Figure II.14.

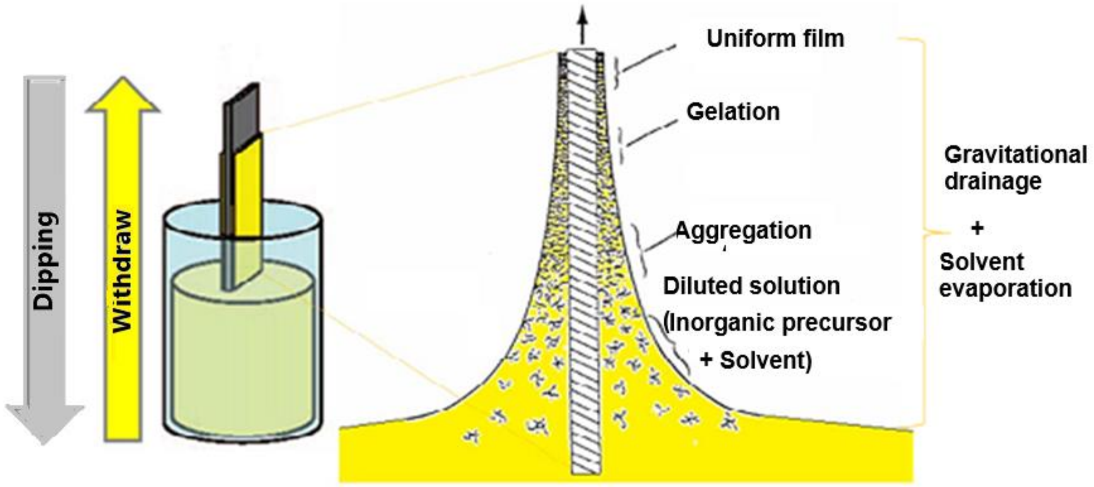


Figure II.12: Schéma de la formation de la couche par la méthode du trempage-tirage.

These changes result from solution drainage, solvent evaporation, condensation, and capillary forces, all occurring simultaneously.

Adjusting certain parameters can achieve the desired thickness of the deposited layer. When liquid viscosity (η) and substrate withdrawal speed are enough to minimize meniscus curvature, the deposited film thickness (h) is determined by the equation:

$$\boldsymbol{h = c\left\{\frac{\eta\nu_0}{\rho g}\right\}^{\frac{1}{2}}}$$

Where (νo) is the withdrawal speed, (ρ) is density, (g) is the gravitational constant, and is a constant value of 0.8 for liquids considered Newtonian.

In cases where substrate withdrawal speed and viscosity are low (common in the Sol-gel process), the previous equation is modified to incorporate surface tension (γ), resulting in:

$$\boldsymbol{h = 0.94\left(\frac{(\eta\nu_0)^{\frac{2}{3}}}{\gamma^{\frac{1}{6}}\rho g^{\frac{1}{2}}}\right)} \qquad \textbf{(II.3)}$$

In this case, the second relationship seems to be better suited. From these relationships, we can conclude that it is sufficient, for example, to modify the substrate withdrawal speed to vary the thickness of the deposited film.

This speed adjustment can be coupled with a dilution of the solution to decrease the concentration and thus reduce the amount of material carried by the liquid.

For withdrawal speeds on the order of a decimeter per minute, it is possible to produce thin layers with thicknesses of a few tens of nanometers.

Chapter III: Carbon Nanotubes (CNT)

III.1 Definition:

Carbon nanotubes (CNT) and fullerenes are carbon allotropes characterized by a hollow structure and extraordinary thermal, electrical, and mechanical properties.

Spherical fullerenes are also called buckyballs, while cylindrical ones are known as nanotubes. The walls of these structures are made up of a single layer of carbon atoms called graphene.

Although carbon is ubiquitous in nature, CNTs are an artificial form of carbon. Among them, CNTs have superior structural properties and fascinating characteristics that have led to their use and opened a wide range of possible studies and functional applications.

The development and characterization of inorganic hybrids composed of metal oxides (MO) and CNTs are of increasing interest in terms of superior electronic, optical, and mechanical properties.

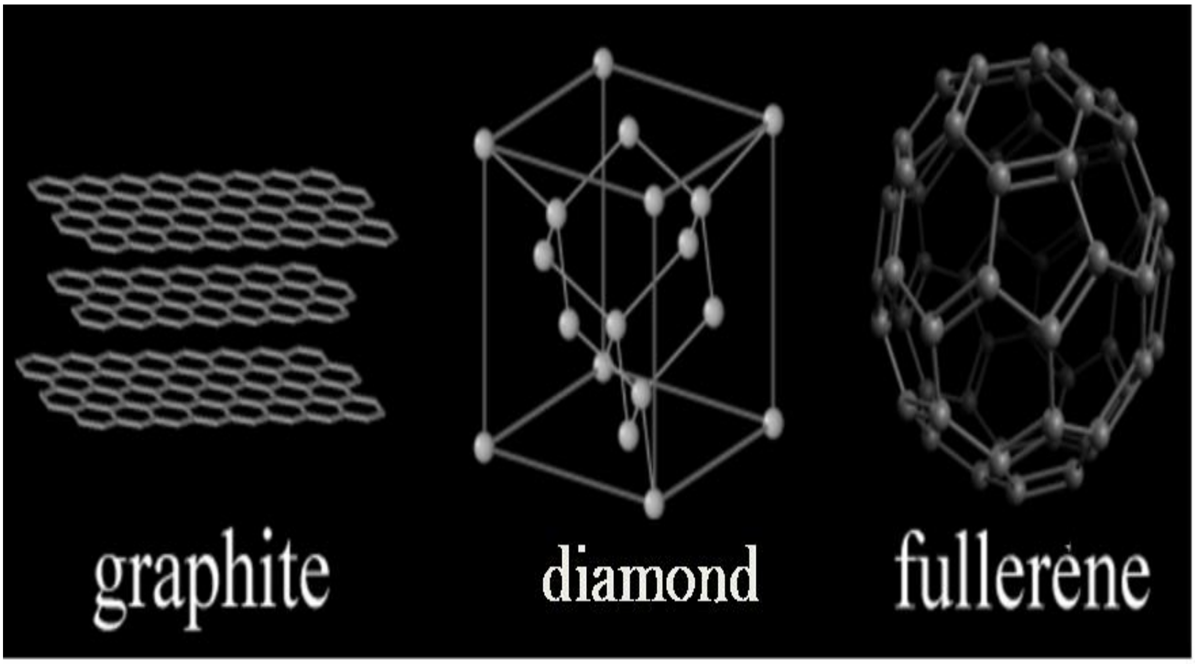


Figure III.1 Different forms of ~~a~~ Carbon

In the 1980s, two pure forms of carbon were known:

- ✓ Graphite, where atoms are arranged in parallel planes, forming what is called graphene. Graphite is brittle due to the weak bonding between the planes. It is used in pencil manufacturing.

- ✓ Diamond, more compact and harder than graphite. Its structure, also found in other materials like silicon crystal, is known for its strength.
- ✓ The discovery of spherical fullerenes in 1985, having a structure like a football, marked a turning point (Figure III.1).
- ✓ These nanoscale assemblies were named fullerenes or Buckminster fullerenes, in tribute to the architect Buckminster Fuller and his work on geodesic domes. Fullerenes, representing a third state of carbon, coexist with other more marginal forms such as andalusite.
- ✓ By 1990, industrial production of fullerenes became feasible. This technique involves creating an electric arc between two graphite electrodes. Spherical fullerenes have various applications in materials, cosmetics, electronics, etc. Fullerenes encompass not only spherical structures but also carbon nanotubes, formed by graphene folded into a tube.
- ✓ Discovered in 1991 by the Japanese physicist Sumio Iijima by adapting the arc discharge process, the initially obtained nanotubes were multi-walled, with several concentric nested tubes.

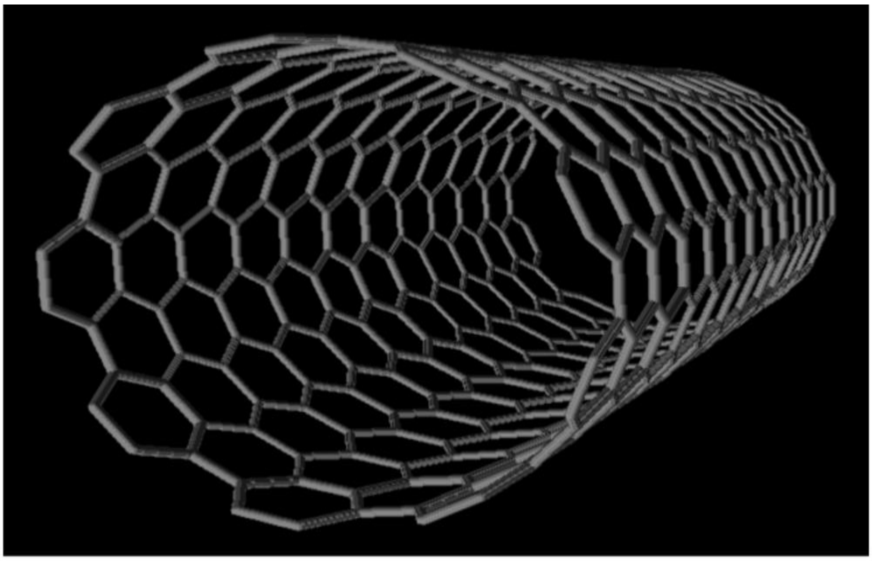


Figure III.2 Carbon Nanotube (double bonds are not shown)

- ✓ In 1993, Sumio Iijima and Donald S. Bethune successfully produced single-walled carbon notubes (Figure III.2) using two distinct methods. The average diameter of a single-walled carbon nanotube is around one nanometer.

  To synthesize a carbon nanotube, the electric arc method can be utilized.

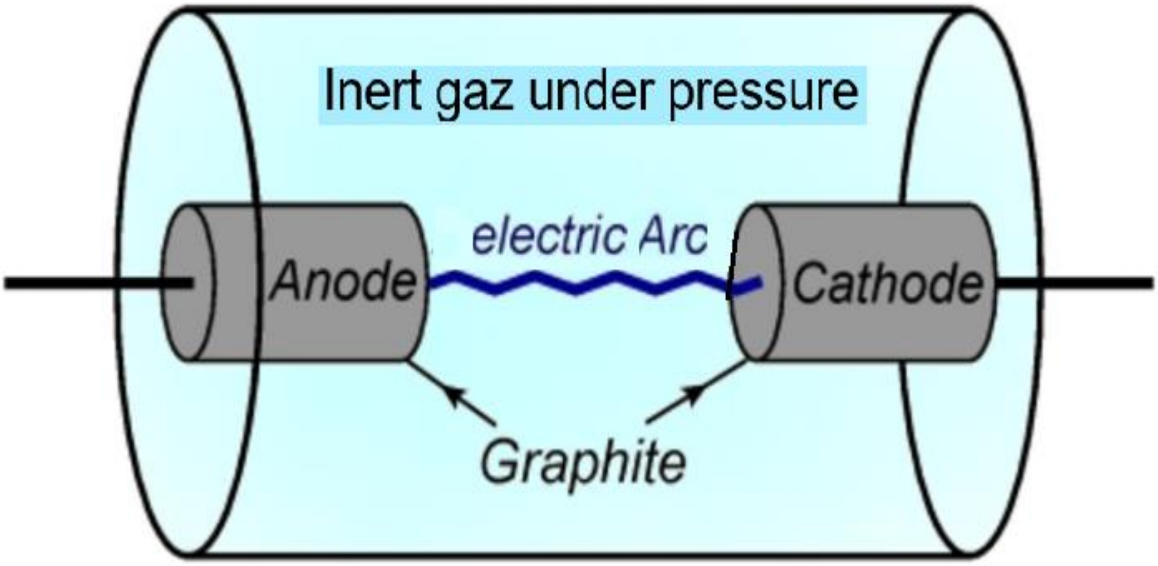


Figure III.3 Carbon Nanotube Synthesis Technique

This method, similar to the one used for the previously mentioned production, was employed by Sumio Iijima (Figure III.3).

The electric arc generates local temperatures of approximately 6000 °C, vaporizing part of the graphite anode. The carbon atoms then condense on the cathode to form nanotubes.

There are variations: carbon atom vaporization can be done using a laser or a solar furnace.

The chemical vapor deposition method, also known as CVD (Chemical Vapor Deposition), is currently the most efficient way to produce carbon nanotubes.

It involves introducing a carbon source (such as toluene, benzene, or cyclohexane) and a metallic precursor (ferrocene or nickelocene) into a vacuum chamber.

This mixture, in aerosol form, is carried by a chemically inert gas such as argon and heated to around 200 °C.

The chamber, also known as the reactor, is maintained at a temperature between 600 °C and 900 °C. Under the influence of heat, the components of the aerosol fragment, leading to the deposition of metallic particles on the chamber walls at the nanoscale.

The carbon atoms then attach to these metallic nanoparticles to form a "cage" that gradually stretches with the continuous influx of new carbon atoms, thus giving rise to carbon nanotubes.

The technique in Figure III.4 synthesizes carbon nanotubes by growing them perpendicularly to the surface of the walls if the aerosol is injected.

When the injection stops, a layer of carbon nanotubes forms. By projecting the aerosol in multiple jets, overlapping layers of nanotubes are obtained.

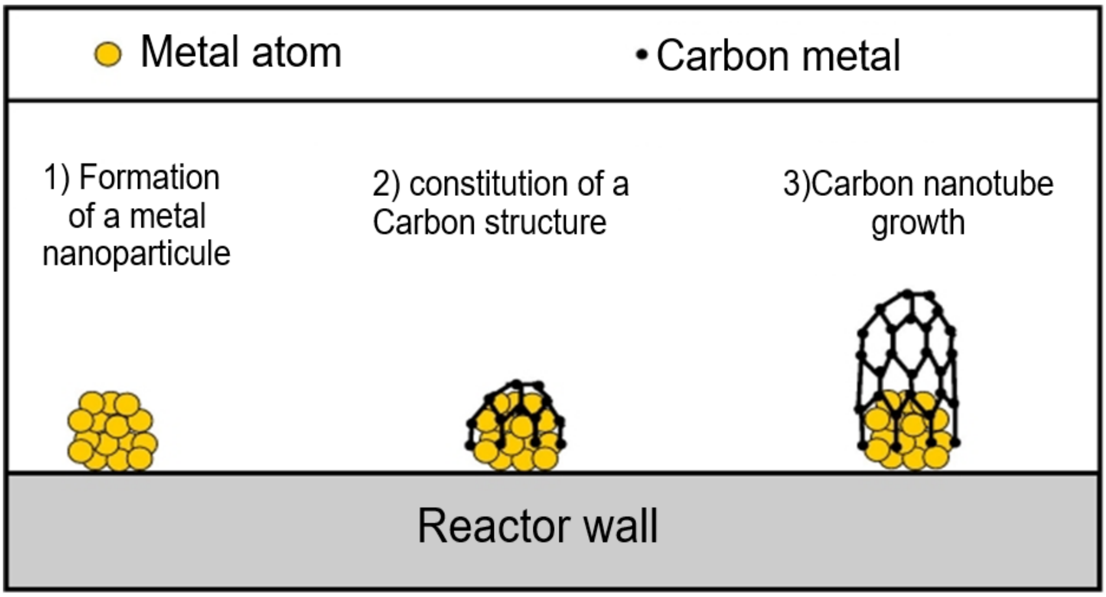


Figure III.4 :The method for producing nanotubes

One advantage of this method is the production of very similar nanotubes. Their length is determined by the duration of the aerosol jet, usually on the order of a millimeter, but it is possible to produce nanotubes reaching several centimeter's.

III.1.1Properties of carbon nanotubes:

There are three types of nanotubes classified based on how the atomic structure is rolled (helicity) (Figure III.5):

- The armchair structure, also known as the sawtooth structure, is characterized by the visible pattern at one open end of the nanotube.
- The zigzag structure, named for its distinctive pattern at the end of the nanotube.
- The chiral structure, distinguished by hexagons connected to form a helix along the tube, unlike the other structures where adjacent rings are observed.

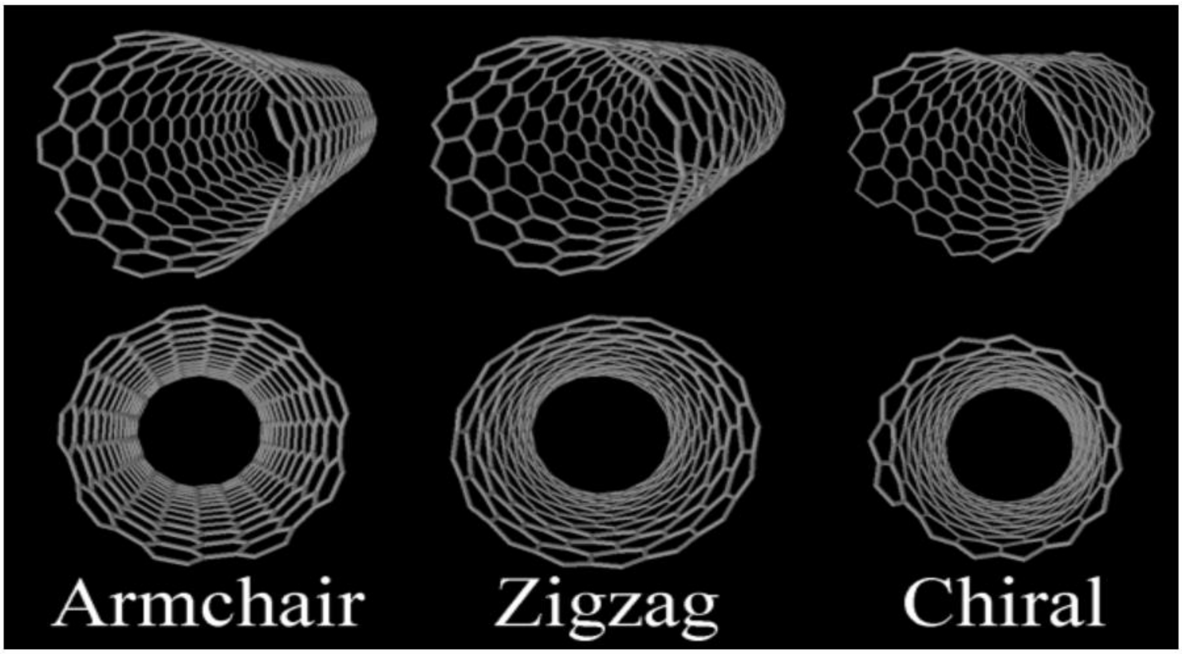


Figure III.5 Nanotube Structures

These three structures are generated simultaneously during the production of nanotubes, with no current possibility of producing only one type at a time. It is worth noting that nanotubes are often capped at their ends by a carbon half-sphere, like a "spherical fullerene split in two".

In terms of their mechanical properties, carbon nanotubes are extremely strong due to the regular arrangement of their atoms.

They can be compared to a metal tube that is more resistant to bending than a bar of the same mass made of the same material.

With a density six times lower than steel, carbon nanotubes are 100 times stronger. Their density is around 1.3 grams per cubic centimeter. Like carbon fibers, nanotubes exhibit some flexibility.

III.1.1.1 Electrical Properties

Semiconductors have specific energy bands for electrons, such as the valence band and the conduction band. Chiral and zigzag carbon nanotubes are semiconductors with a small energy gap between these two bands, while armchair nanotubes, with band overlap, are conductors, offering potentially higher conductivity than copper.

At low temperatures, carbon nanotubes can even become superconductors.

III.1.1.2 Electrostatic Properties

A lightning rod, consisting of a metal tip connected to the ground at the top of a building, is used to divert lightning to protect the structure by channeling electricity.

Due to their pointed geometry, nanotubes can also exploit the tip effect to manipulate electrons precisely, allowing controlled electrical discharges with a potential difference of 1V.

III.1.1.3 Thermal Properties

Carbon nanotubes can withstand high temperatures up to 2000 °C in a vacuum and 750 °C in the air, and they are excellent heat conductors.

III.2 Some Applications of Nanotubes

"Carbon nanotubes are so beautiful that they must be useful for something" - R. E. Smalley, Nobel Prize in Chemistry 1996 (co-discoverer of fullerenes).

✓ New materials incorporating carbon nanotubes, which would be stronger and lighter than those we currently know.

✓ New textile fibres. At the same mass, a carbon nanotube thread is more efficient than a spider silk thread. Nanotubes could enable the production of bulletproof vests.

✓ Nanoelectronics. Due to their size and semiconductor nature, nanotubes pave the way for nanoelectronics. Carbon nanotubes could then replace silicon, which is currently the main material in electronics.

✓ Flat screens, using cutting-edge nanotube technology to inject electrons onto luminescent dots (sub-pixels).

✓ Nanotips, for nano-manipulation or nano-observations.

✓ Medical applications: nanorings (described in the following section).

✓ Synthetic membranes: a layer of nanotubes could form a membrane that only allows certain molecules to pass (through the nanotubes).

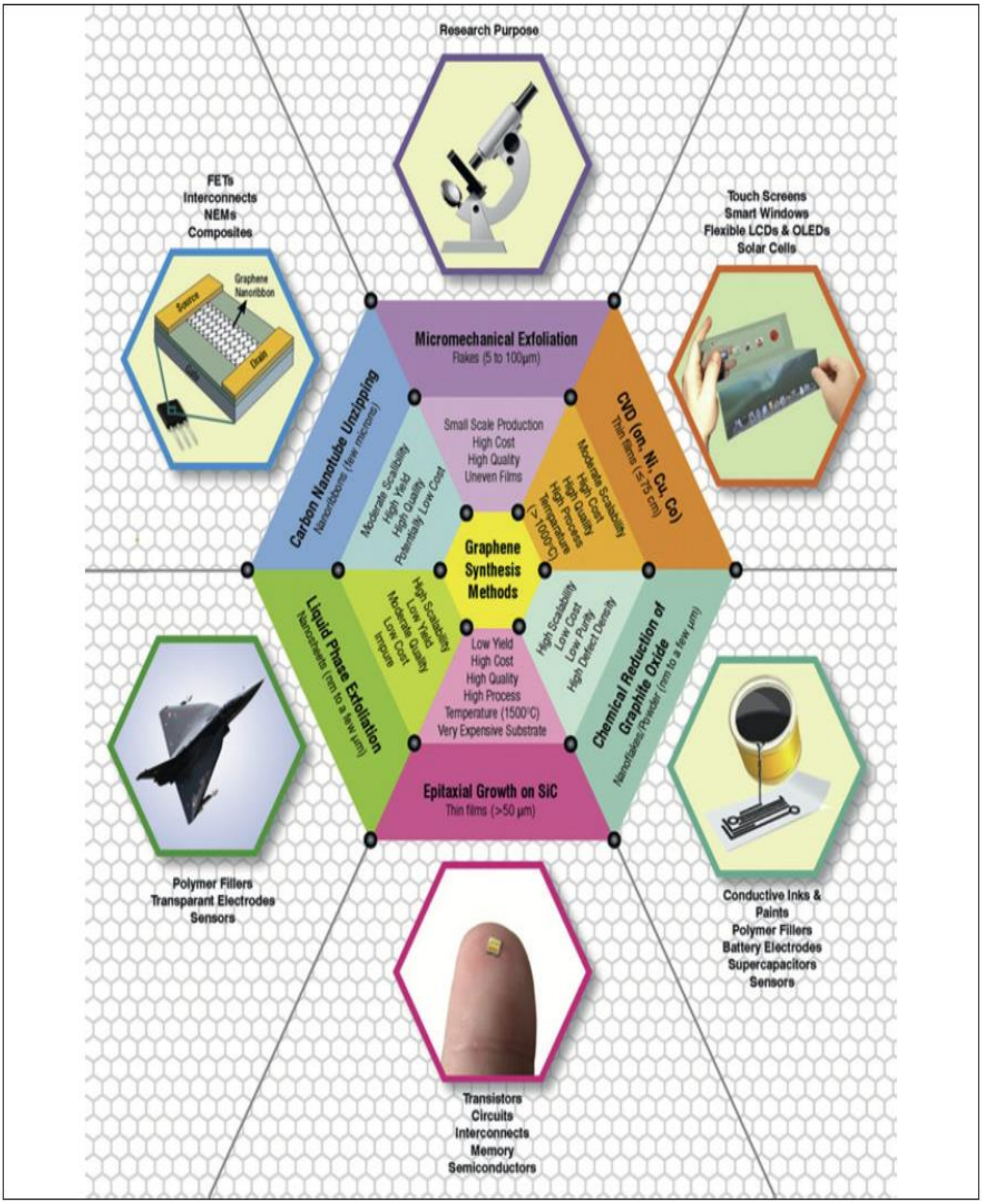


Figure III.6: The applications of graphene are numerous, with the main ones being electronics and composite polymers.

Source: reproduced from Mittal G. et al. (2015). A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. Journal of Industrial and Engineering Chemistry, 21: 11-25 .

Carbon nanotubes are a rapidly developing technology (Figure III.6). However, a current limitation is the still very high cost for manufacturing nanotubes, up to 1000€ per gram for single-walled nanotubes.

Furthermore, concerns exist about their potential biological effects on humans and the environment.

In the field of electronics, generations of machines depositing and etching thin metal layers have succeeded each other for decades.

The mechanical industry has not only been able to use products from these new technologies (for example in watchmaking) but has also been able to manufacture its own miniaturized products with the same tools.

Several devices used by the public, illustrating this convergence of microelectronics and micromechanics.

The use of nanostructures in solar cells improves the efficiency of converting solar energy into electricity.

Interpenetrating networks are particularly useful for spatially separating photon absorption and charge carrier collection. This is crucial for dye-sensitized solar cells and organic polymer solar cells.

III.3 Nanomaterials for photovoltaic conversion

In the case of dye-sensitized solar cells and organic polymer solar cells, photons generate electron-hole pairs (excitons) in an organic molecule. This dissociation of electron-hole pairs is facilitated by the cell structure and controlled nanostructures.

The resulting charge carriers can then be collected and used in an external circuit to generate electricity. In dye-sensitized solar cells, photons excite electrons in a dye absorbed on a semiconductor, transitioning from HOMO to LUMO molecular states.

Subsequently, they are transferred to the semiconductor's conduction band. This design resolves the conflict between the thickness of dye that photons must traverse for efficient absorption and the much lower thickness of dye absorbed on the semiconductor.

A porous nanostructure infused with electrolyte reconciles these constraints by allowing photons to pass through enough thickness of dye, ensuring optimal efficiency.

Organic cells face a similar challenge since the material's photon absorption thickness (10 to 20 µm) is significantly greater than the distance over which excitons (associated electron-hole pairs) can diffuse before recombination.

Interconnected networks of donor and acceptor polymers help overcome this contradiction.

The key challenge lies in the optimal control of nanostructure topology. Various quantum effects are also leveraged to enhance efficiency. Optimizing the photon absorption range can be achieved by adjusting the bandgap width through nanoparticle size, an approach particularly explored in silicon technologies.

Another method involves converting photons with energy that is too low (up-conversion) or too high (down-conversion) into the effective absorption range; the use of quantum wells, for example, enhances the down-conversion efficiency of ultraviolet photons by phosphors.

A promising, albeit still emerging idea, is to recover energy carriers higher than the bandgap width before their thermalization.

This can be achieved through energy-selective contacts established with nanoparticles of appropriate size. Progress in nanostructure control has paved the way for new photovoltaic technologies, offering alternatives to conventional single- or polycrystalline silicon solar cells.

These advancements help optimize the efficiency and performance of solar cells, thus contributing to the development of solar energy as a renewable energy source.

III.4 Materials for thermoelectricity

Thermoelectric materials have advanced significantly in recent years, largely due to the shift towards nanostructures.

Thermoelectricity enables the direct conversion of heat flux into electrical energy or, conversely, the transfer of heat between a cold source and a hot source, following the principles of refrigeration or heat pumps.

This process occurs without moving parts or compression cycles.

Conduction electrons have a higher average energy on the hot side due to thermal excitation. The temperature gradient causes these electrons to diffuse towards the cold side, generating electricity from the heat.

However, the resulting electron accumulation creates an electric field that opposes further diffusion. This electric field can be controlled by an external source to facilitate cooling or heating.

Historically, applications of thermoelectric materials have been limited by low efficiency. Effective performance requires a high thermoelectric coefficient (Seebeck coefficient), high electrical conductivity, and low thermal conductivity.

The traditional approach aimed to reduce phonon diffusion through a complex architecture of bulk materials, favoring phonon optical modes and the insertion of heavy atoms that vibrate independently of the lattice.

Recent advancements have significantly improved the efficiency of many materials in laboratory settings. This has been achieved through nanostructuring, which enhances the thermoelectric properties by further reducing thermal conductivity while maintaining or increasing electrical conductivity. The expected future expansion in the field of thermoelectric system applications holds promise for more efficient and practical uses of these materials.

III.5 Energy Storage

Fuel cells, supercapacitors, and batteries will play a key role in upcoming energy infrastructure developments by facilitating energy storage, and nanomaterials hold the promise of significant progress in these various systems. Proton exchange membrane fuel cells (PEMFC) (Figure III.7) operate at low temperatures.

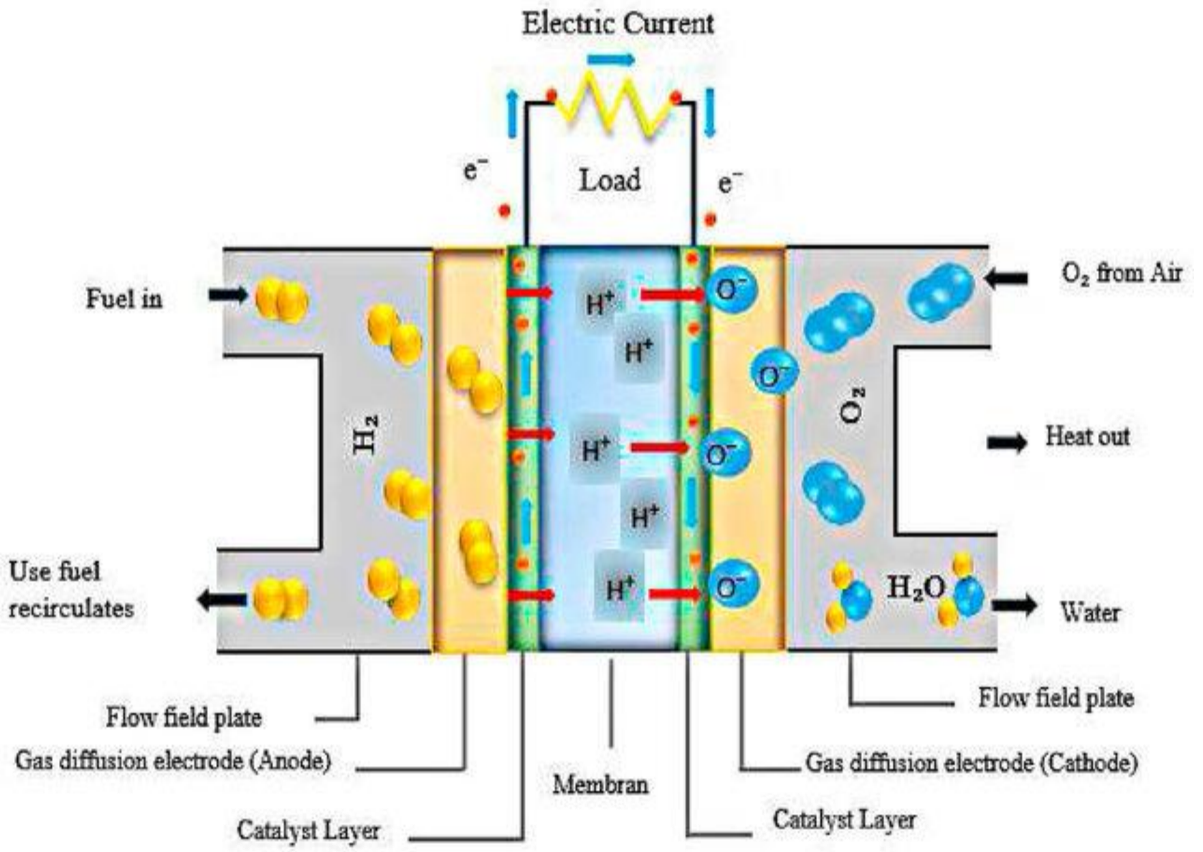


Figure III.7: Schematic diagram of a proton exchange membrane fuel cell.

The diagram illustrates their basic principle. Challenges related to their use (temperature stability, reaction kinetics) can be overcome through nanotechnologies. Although these cells are typically limited to 80°C, surpassing 100°C is preferable to enhance reactivity and thermal dissipation.

The mechanical resistance to heat and the swelling sensitivity of the polymer membrane, which ensures the electrolytic conduction between the anodic and cathodic compartments, are critical points. Integrating silica nanoparticles can enhance these aspects.

Using platinum as a catalyst poses a challenge due to its high cost and the potential inhibition of the reaction by carbon monoxide from hydrocarbons.

Adopting core-shell nanostructures helps reduce the amount of required platinum. Furthermore, integrating carbon nanotubes can also enhance overall efficiency.

High-temperature fuel cells typically operate between 500 and 1000°C. It is preferable to maintain a lower temperature to extend lifespan and reduce costs, but the operating temperature is determined by the properties of the solid electrolyte membrane.

Through Nano-engineering and the synthesis of anion-conducting membranes using sol-gel processes, it is possible to achieve membranes operating at lower temperatures by enhancing various aspects such as specific surface area, number of reactive sites, mechanical strength, and electrical conductivity.

Furthermore, Nano structuring of electrode materials can improve their efficiency, although their stability still needs to be reinforced.

III.5.1 Rechargeable batteries

The reversible energy storage in batteries involves redox reactions within the material. For high-energy density lithium-ion batteries, nanostructuring has enhanced speed, reversibility, capacity, and durability during cycles.

Nanostructuring of electrode materials increases capacity through new reactions, for example, extending the thermodynamic stability range of active phases or enabling better intercalation or conversion ratios.

It also enhances reversibility and kinetics through various processes.

This nanostructuring, applied to current collectors using interpenetrating geometries (such as nanowires and foams) that amplify surface area and reduce the collection distance compared to the active material thickness, significantly improves kinetics under high currents.

Chapter IV : Nanomaterials and Theirs Applications

IV. Applications in various fields

IV.1 Nanoparticle Applications: Gold

IV.1.1 Nanotechnology and New Medicines

Gold nanoparticles are relatively easy to produce compared to other types of nanoparticles due to their high chemical stability. The uses of gold nanoparticles are mainly catalytic and include DNA detection and carbon monoxide oxidation.

Gold has superior conductivity, allowing gold nanoparticles to be used in various probes, sensors, and optical applications.

- ✓ Photoacoustic imaging
- ✓ Cancer therapy (safe and biocompatible target for thermal ablation by photon)
- ✓ Explosive initiation (reducing energy requirements and improving safety and portability expanding its use as a catalyst in combustion efficiency).
- ✓ Storage and release of hydrogen at room temperature.

A major challenge today is targeting therapeutic molecules to the organ, tissue, or diseased cell. Back in the early 20th century, German bacteriologist Paul Ehrlich already dreamt of a "magic bullet" capable of specifically delivering a drug to the relevant site of action.

This dream is now much closer to reality, thanks to the advancements in nanotechnology and the ability to target medicines.

Many active compounds have physical and chemical characteristics (hydrophilicity, molecular weight, etc.) that do not facilitate their passage through biological barriers separating the administration site from the site of action.

Other active molecules like DNA and proteins also face enzymatic barriers that rapidly degrade and metabolize them. The barriers to overcome are typically highly complex systems involving various elements (epithelium, endothelium, cell membrane) and components (mechanical and physicochemical barriers, enzymatic barriers).

To achieve therapeutic concentrations at the site of action, a considerable loss of the drug in other tissues or cells must be accepted, leading to significant, sometimes prohibitive levels of toxicity.

For these reasons, drug carriers have significantly evolved in recent years. Through new physico-chemical concepts, pharmaceutical research has developed submicron-scale delivery systems capable of protecting the active molecule from degradation and controlling the release of the active molecule both in time and space.

IV.1.1. 1 Artificial carrier: liposomes and nanoparticles

Drug carriers, designed for intravascular injection, are a product of nanotechnology. Nanoparticles are typically obtained either by size reduction from a larger object or by assembling smaller elementary objects, such as atoms or molecules.

Drug carriers can be manufactured using either of these approaches, leveraging the fundamental concepts of physical chemistry to construct supramolecular entities (ordered or disordered).

In practical terms, the size of carriers intended for injection into the bloodstream must be considerably smaller than a micrometer to avoid thromboembolism (blood vessel obstruction).

We will describe three types of carriers: conventional liposomes and two new types of nanoparticles resulting from recent developments. The first topic thus concerns a new method for synthesising multilamellar liposomes, while the rest focuses on polymer nanoparticles with two compartments.

IV.1.1.2 Description of the tribological system. Surfaces and Lubricants.

A tribological system involves two surfaces in relative motion. These two elements are commonly referred to as the first bodies. They can be similar, like bones covered with cartilage in joints, or different, like a pen rubbing against paper, or even an eyelid sliding over a contact lens.

The two surfaces in contact are separated by an interface typically known as the third body. This is the sliding region between the contacting objects that may undergo physico-chemical changes compared to the bulk objects.

It can be a liquid lubricant (such as tears or synovial fluid in joints) or solid lubricant (graphite, Teflon, or molybdenum disulphide) added to facilitate sliding.

The interface can also consist of wear particles or a transfer film deposited on the surfaces. The third body can reduce friction and wear, extending the contact's lifespan.

To study a tribological system, several factors must be considered. The most important ones are the mechanics of contact and the adhesion between surfaces.

The goal of contact mechanics is to describe bodies in physical interaction: how stresses are distributed and how bodies deform.

The roughness and morphology of the contacting surfaces usually govern the contact of macroscopic bodies due to their multi-contact nature. In contrast, in nanotribology, a single contact is dealt with, a single asperity, with well-defined geometry.

In the case of a single-asperity contact, a complete description of contact mechanics must consider the mechanical properties of the objects in contact and their adhesion energy (the energy required to separate two surfaces after they come into contact).

Various mechanisms underlie this interaction, which need to be added to the applied external force (load) to describe the deformation of the objects in contact.

Adhesion depends on the chemical nature of the objects in contact and physicochemical parameters such as temperature and humidity. Nanoparticles are widely used in various industrial sectors and are found in many everyday products.

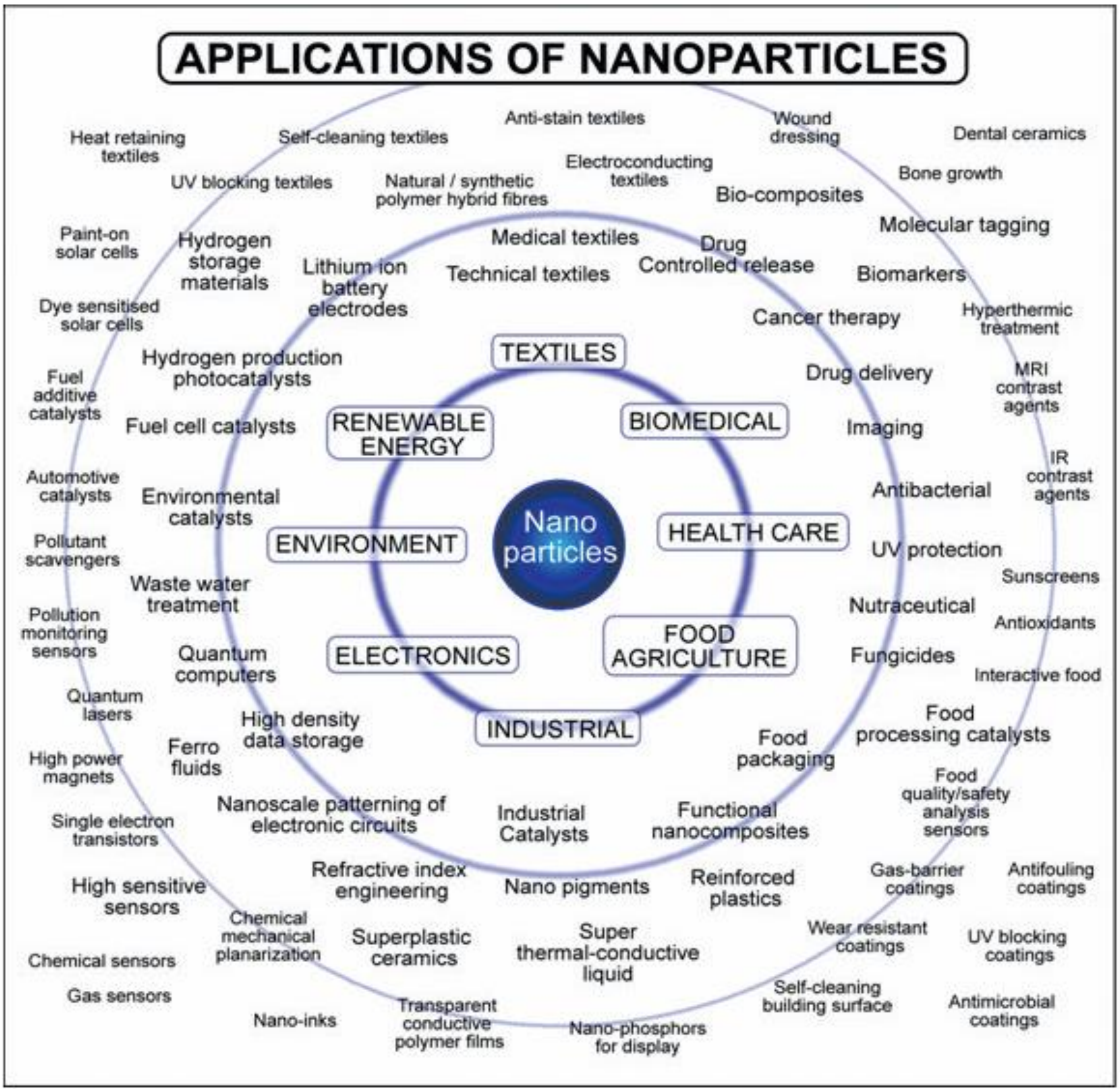


Figure IV.1: Application of nanoparticles in industrial sectors and everyday products.

IV.2 Experimental Techniques in Nanotribology

To make significant advances in the characterization of interfacial phenomena, it is necessary to have experimental tools that allow working on a single contact (a single asperity), with well-controlled geometry and chemistry. Such devices now exist.

The most commonly used one is the Atomic Force Microscope (AFM). This technique enables achieving a nanoscale contact between a very fine tip and a substrate. Another, less commonly used device is the Surface Forces Apparatus (SFA).

This apparatus also ensures a single contact, this time on a microscopic scale, between two smooth surfaces at the atomic level. Due to the size of their contact area, these two techniques are complementary.

In a single contact, size effects on friction can indeed occur, especially between molecular and supramolecular scales. A third device used for nanotribology studies is the Quartz Crystal Microbalance (QCM).

IV.2 .1 Quartz Crystal Microbalance (QCM)

The quartz crystal microbalance has long been used to precisely measure very low masses (from a few nanograms to a few micrograms) before being cleverly used for friction measurements in the late 1980s by Krim and Widom .

The QCM consists of a thin quartz monocrystal on which two metal electrodes are deposited. Applying an alternating potential difference between the two electrodes causes the quartz crystal to vibrate due to its piezoelectric properties.

When the potential difference is stopped, the crystal continues to oscillate with a damping oscillation amplitude over time.

In a nanotribology experiment, a film is deposited on one of the electrodes. The presence of this film causes a slight decrease in the oscillation frequency due to the increase in mass and an increase in damping due to the friction between the film and the electrode, if the film is weakly bound to the electrode and can slide on its surface.

This allows the friction between the film and the electrode to be characterized. Krim and Widom studied the friction of a monoatomic film of krypton on a gold electrode using QCM. They found that observed frictional forces provide valuable information about the properties of the studied material and contribute to enriching our understanding of tribological phenomena at the nanoscale.

IV.3. Elementary processes of friction

Friction is not a fundamental force; rather, it results from several complex phenomena. Understanding the fundamental mechanisms of friction is challenging because they depend on the properties of materials both in volume and on the surface, the environmental conditions of the system, and the spatial and temporal scales involved in shear. Several factors contribute to the complexity of friction:

- ✓ Dry vs. Lubricated Friction: Dry friction differs significantly from lubricated friction.
- ✓ Vibrational and Electronic Friction: Friction due to the propagation of vibrations (phonons) in materials and electronic friction, especially in metallic surfaces, can be significant.

✓ Surface Roughness and Chemical Inhomogeneity: The roughness of surfaces and their chemical inhomogeneity often play a major role in the friction of macroscopic objects.

✓ Adhesion and Elastic Properties: Adhesion between surfaces and the elastic properties of the materials can be crucial.

✓ Plastic Deformation: Irreversible plastic deformation of the contacting surfaces is often involved in friction, indicating that it is not solely a surface phenomenon but also involves the local layers near the sheared interface.

✓ Capillary Condensation: This can resist the sliding of hydrophilic surfaces in humid environments.

✓ Wear and Energy Dissipation: In the presence of wear, energy dissipation mechanisms related to morphological and chemical modifications of the superficial layers of materials subjected to friction must be considered.

✓ Tribochemistry: Chemical reactions induced by friction (tribochemistry) can occur on surfaces and/or in a lubricating film, adding additional energy dissipation mechanisms.

The list of mechanisms causing friction forces is extensive, and their understanding is not always well-established. Here, we will focus on certain fundamental dissipation mechanisms occurring in a single contact with controlled geometry. The examples chosen to illustrate the approach and the importance of this discipline have all been obtained using an SFA-nanotribometer.

IV.4 Micro-nanotechnologies that are revolutionizing optics and optoelectronics.

IV.4 .1 Quantum structures and self-organization.

During the 1980s and 1990s, the development of III-V semiconductor growth techniques on GaAs or InP substrates such as molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD) enabled deposition accuracies close to the thickness of a molecular layer (≈ 0.2 nm).

This led to the realization of semiconductor heterostructures where charge carriers (electrons and holes) were confined within the layers, forming narrow potential wells with the creation of electronic energy sub-bands within the conduction and valence bands.

This quantum well structures truly revolutionized the world of optoelectronic components, especially laser diodes, reducing threshold current densities to values below 40 $A.cm^{-2}$.

Mastering the growth of ultra-thin layers also, almost simultaneously, eliminated the need for matching crystal lattice conditions. In fact, the nanometer-scale thicknesses of quantum wells often fall below critical dislocation thicknesses when lattice mismatch with the substrate is around one to two percent.

In other words, the layers forming the heterostructures, wells, and/or barriers may be under strain without being dislocated.

IV.5 Nanophotonics Influences the Field of Nanotechnologies

Nanophotonics has become a reality thanks to the latest developments in nanotechnologies. In turn, the new concepts brought by nanophotonics will enable advancements in the field of nanotechnologies. Potential benefits include improvements in optical lithography processes, enhanced optical data storage, and the integration of optical interconnections into integrated circuits.

The penetration of nanotechnologies into the field of biology is also closely linked to solutions within nanophotonics. Below, we illustrate some of the expected progress in nanophotonics and will specifically focus on optical interconnections

IV.5.1 Optical Interconnections: Nanophotonics Serving Electronics

The advanced miniaturisation of transistors has led to a dramatic increase in the integration density of electronic circuits, which now contain several hundred million transistors per cm^2.

However, the densification of metal interconnections in these circuits presents major issues by affecting the propagation of electrical signals, slowing them down, distorting them, and causing them to become out of sync. Typically, more than ten levels of interconnections are distinguished.

The initial levels correspond to local connections between transistors, intermediate levels provide medium-distance connections within the "functional blocks" of the electronic circuit, and the final levels are for global connections enabling the propagation of "global" signals on the chip, especially the clock signal.

The propagation of the clock signal alone dissipates nearly 30% of the power supplied to the circuit, including the lines used to distribute this signal and the repeaters necessary for its amplification and reshaping during propagation.

Various "all-electronic" solutions are suggested to address these challenges, aiming to reduce energy consumption and resulting heating.

However, it is uncertain whether all issues can be resolved through this approach, and solutions involving a more profound technological breakthrough, such as on-chip optical interconnections, are currently being explored.

Optics could potentially aid electronics, with the hope that optical interconnections are less dissipative than metal interconnections and also enable faster signal distribution.

The concept of introducing wavelength division multiplexing, as seen in optical telecommunications, is being considered.

IV.6 Nanotechnology: The 11 Most Impressive Advances

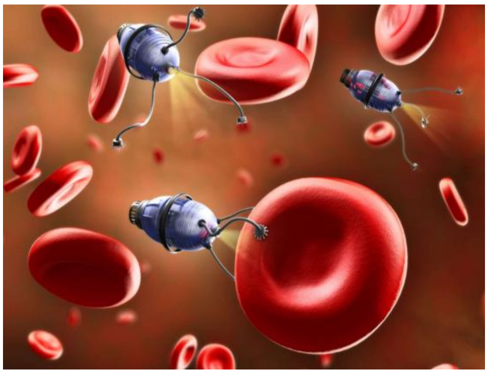
As technological and computer advances are currently globalizing, discoveries in nanotechnology are gradually finding their place in various fields.

Nanotechnological progress could bring about significant changes in our lives in the coming years. Technological progress has been advancing rapidly for about a decade and continues to impress many. This is also the case with nanotechnologies, which are developing in almost every field, from computer science to textiles. To fend out more, explore the following 11 nanotechnological advanced.

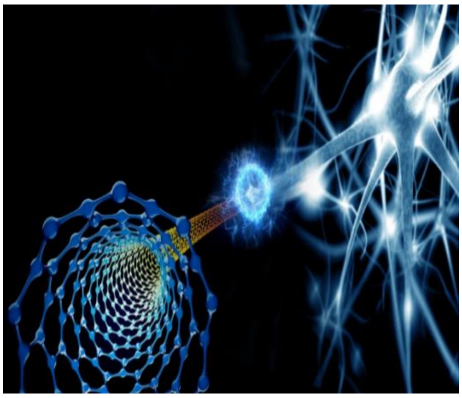
1- The latest nanotechnology contact lenses

In 2020, the company Innovega in Bellevue, WA, developed a display lens placed in the center of a contact lens.

As small as the eye's pupil, the optical elements it consists of do not obstruct vision.



2- A nanotechnology sensor to prevent heart attacks



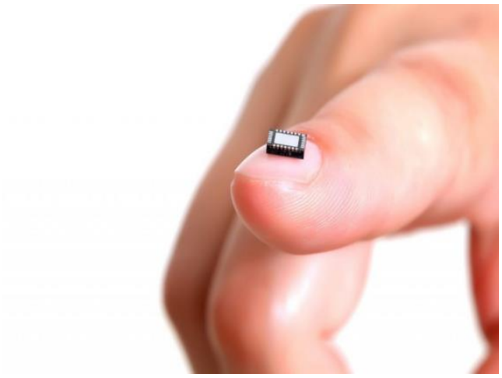
Eric Topol, MD, from Scripps Health collaborated with Axel Sherer, PhD, from Caltech to create nanosensors. These medical devices issue an alert well before heart attacks occur by detecting the precursor to a heart attack using tiny nanocirculation sensor chips. These chips then send a signal to the patient's smartphone in case of an alert.

3- Effective black silicon against bacteria

Australian and Spanish researchers have created a nanomaterial in black silicon with tiny spikes on its surface. The wings of an Australian dragonfly inspired scientists to develop this device.

They discovered that the insect's wings have tiny spikes that kill bacteria.

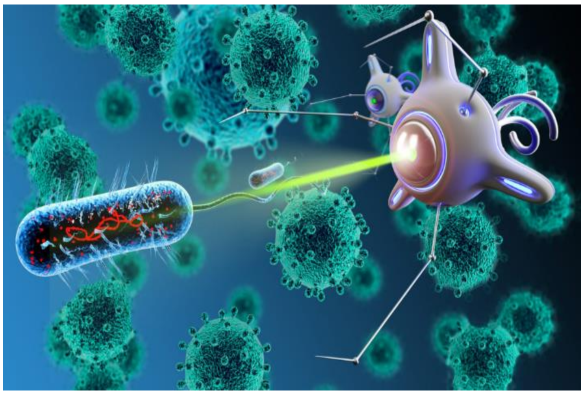
4- The small 3D-printed nanotechnology battery



Researchers at Harvard School of Engineering and Applied Sciences have devised a way to 3D print miniature batteries.

For this purpose, these batteries could power applications such as biomedical sensors and skin monitoring systems.

5- The Revolution in Ocular Surgery



Scientists from the Multi-Scale Robotics Lab at ETH Zurich have developed a magnetically guided microrobot. Implanted in the eye, it can perform precise surgery.

Powered by external magnetic fields, these magnetic microrobots called Octomag can deliver precise quantities of medication.

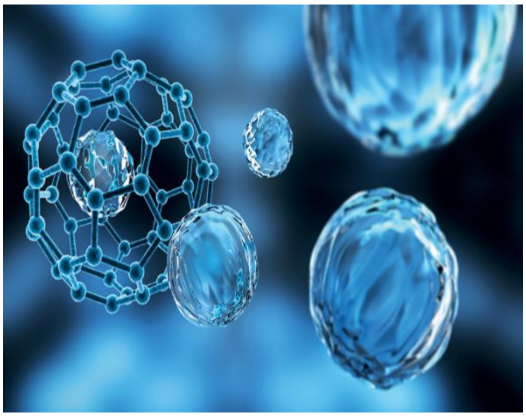
6- Ultra-flexible electronic chips

Swiss scientists have developed ultra-flexible electronic chips capable of wrapping around a hair strand. These researchers designed this device using thin stacked layers of polyvinyl with an electronic circuit.

Based on nanotechnology, these chips potentially adapt to mobile devices as well as a range of medical applications.

In fact, researchers have already attempted to integrate these tiny electronic devices into an artificial eye and a glaucoma monitor.

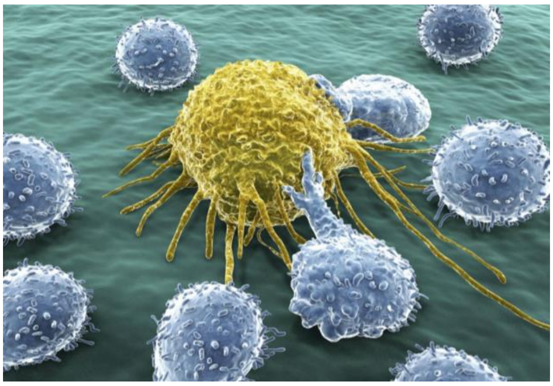
7- . The Development of Biodegradable Electrodes



Bettinger and Whitacre are pioneers in biotechnology and nanotechnology. These two professors in materials science and biomedical engineering discovered digestible battery substances in food.

These essentially enable powering medical instruments that patients could ingest.

8- The Applications of Nanotechnology in Oncology

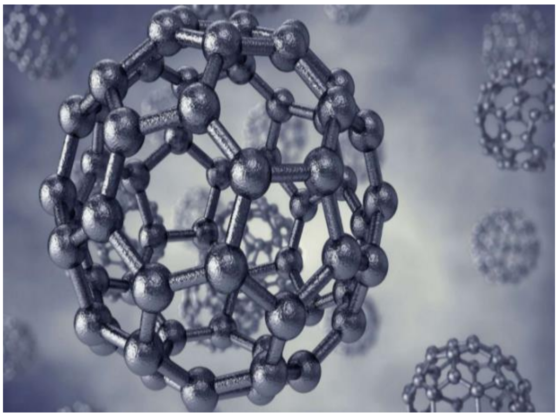


According to scientists at Cornell University, nanoparticles are highly effective in delivering anticancer therapies.

These researchers were able to introduce tiny gold alloy particles into the bloodstream and cancer cells.

The goal is to heat the infected cells to kill them.

9- Silver Germ Killers



In recent years, scientists have been increasingly utilizing silver nanoparticles due to their effectiveness in combating bacteria. Consequently, many industries are incorporating nanoparticles in the production of various items such as toothbrushes, self-disinfectants, clothing, and more.

However, the potential health risks associated with silver are still under scrutiny.

10-The development of a nanotechnological breathalyser for diabetics

At Western New England University is a notable advancement. This device can detect acetone levels in breath to determine blood sugar levels.

Overall, nanotechnology research is progressing rapidly across various fields for our benefit, emphasizing the importance of supporting researchers striving to enhance our lives.

IV.7 Characterization of Nanomaterials

. Various parameters such as size, concentration, shape, etc., must be determined according to regulations. These techniques are complementary and allow for a comprehensive characterization of nanoparticles.

IV.7.1 Analysis Techniques.

Many parameters are used to characterize nanoparticles such as concentration, shape, size, size distribution, structure, crystallinity, composition, surface area, surface functionality, surface charge, and aggregation state (Figure IV.2).

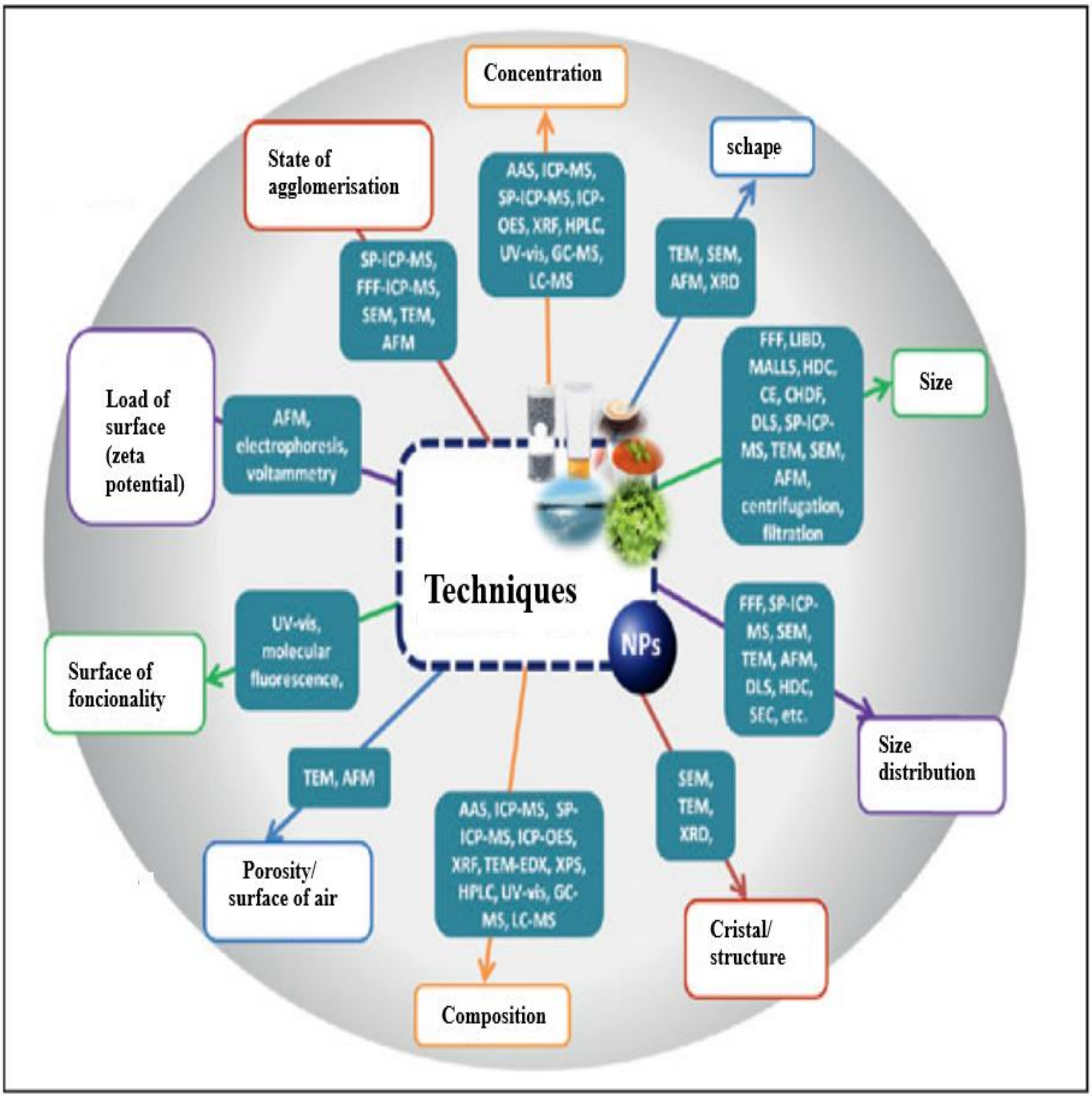


Figure IV.2: Available techniques for the analysis of nanomaterials.

According to European regulations, all these parameters should be determined. A comprehensive characterization like this is challenging for a single laboratory to achieve.

Additionally, the cost of these analyses is often high due to the use of sophisticated techniques.

Therefore, only the nature, size, size distribution, and concentration of nanoparticles are usually measured. Various techniques are available to obtain this information, and there is no universal technique but rather complementary techniques.

When summarizing the research conducted on nanoparticle analysis (Figure IV-2), over a third of the studies focus on techniques for specific nanoparticle characterization. Other studies typically rely on measuring the total element content.

For instance, in the characterization of titanium dioxide, the total titanium concentration is often measured.

These elemental analyses are predominantly spectrometric methods, with ICP-MS (Inductively Coupled Plasma Mass Spectrometry) being a common choice due to its sensitivity in elemental analysis. However, ICP-MS is a destructive technique that subjects the sample to a high-temperature argon plasma, which limits the information about particle size under normal ICP-MS conditions.

Microscopy is the most prevalent technique for nanoparticle characterization, representing 36% of applications (Figure IV-2).

Other notable techniques include separative methods such as Asymmetrical Flow Field-Flow Fractionation (AFF-FF) or chromatography, and ICP-MS in single-particle mode, which is gaining popularity.

IV.8 Toxicity and Regulation of Nanoparticles

IV.8.1. The main exposure pathways to nanoparticles

The presence of nanoparticles in products we consume daily leads to an increasingly significant exposure. Currently, the lack of epidemiological data hinders a comprehensive assessment of potential risks associated with manufactured nanomaterials in common consumer products.

However, there is a growing number of publications focusing on determining toxicological and ecotoxicological data. Three main exposure pathways have been identified: digestive, dermal, and respiratory pathways (Figure IV-3).

The risk through inhalation (Figure IV-3A 4A) primarily affects individuals professionally exposed to manufactured nanomaterials. The respiratory system is the first organ exposed.

Nevertheless, air contamination in non-professional settings by ultrafine particles and frequent use of sprays containing nanoparticles can also contribute to this exposure pathway.

Regarding nanoparticulate titanium dioxide, studies suggest a potential carcinogenic risk through inhalation, leading to its classification in Group 2B by the International Agency for Research on Cancer (IARC).

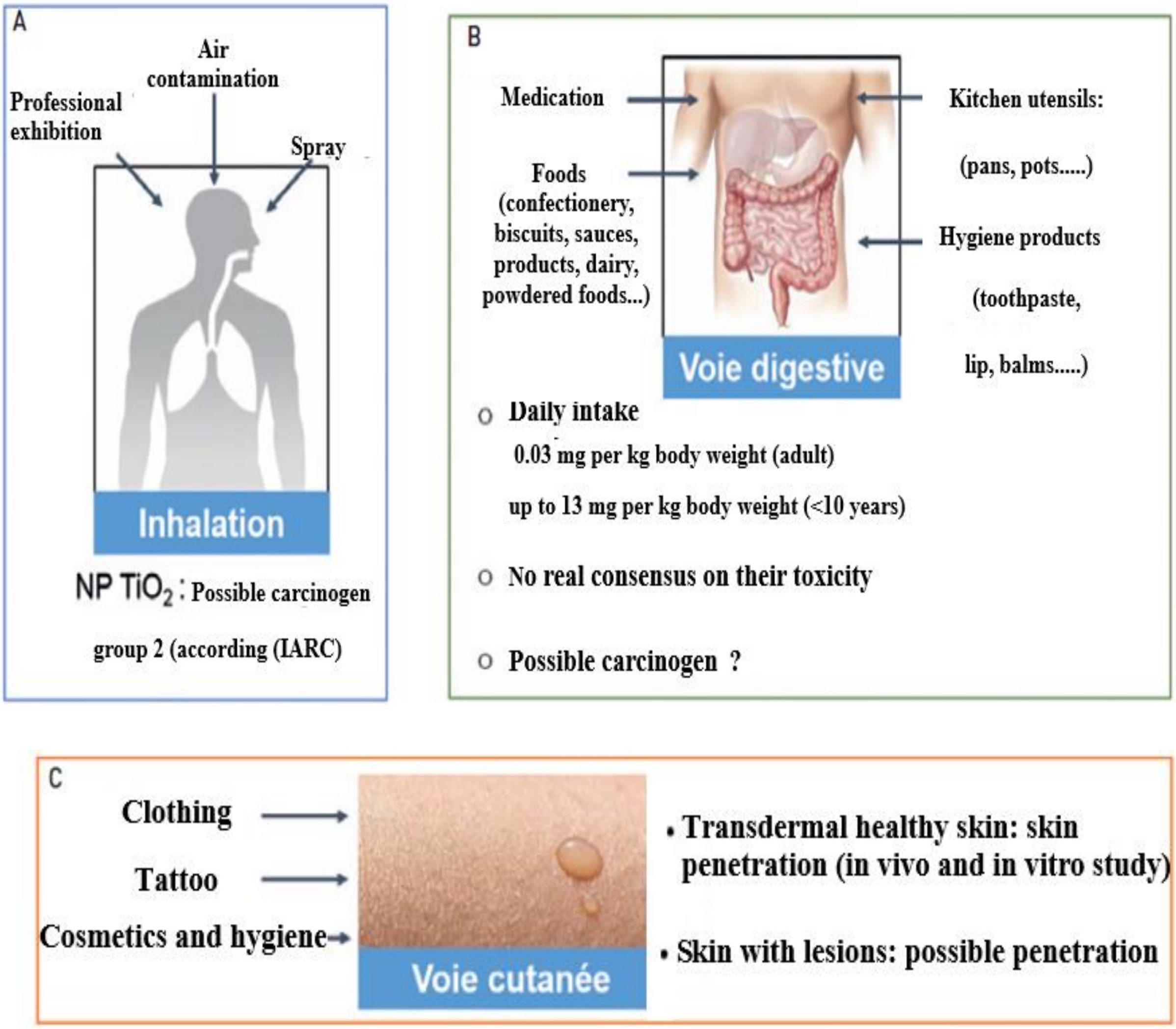


Figure IV.3: Exposure pathways to nanoparticles in humans

They are important considerations. The main exposure routes to nanoparticles in humans include:

A) occupational exposure and presence of nanoparticles in the air or in certain sprays;

B) exposure through medications, food products, kitchen utensils, and hygiene products via ingestion.

Daily intake through ingestion in children is estimated to be nearly forty times higher than in adults. However, there is no clear consensus on the toxicity of nanoparticles;

C) exposure to nanoparticles through clothing, tattoos, cosmetics, or hygiene products occurs through skin contact. Yet, there would be no penetration if the skin is intact.

Oral exposure mainly results from consuming food products containing TiO2 nanoparticle-based additives (Figure 4B). Other sources include the intake of medications with TiO2 added as an excipient for white coloring, and the potential ingestion of certain hygiene products (such as toothpaste, balms, or lipsticks).

Additionally, the release of nanoparticles from cooking utensil coatings during food preparation can also contribute to oral exposure. Studies have measured the daily intake of titanium dioxide nanoparticles (6,7) (Figure 4B).

While adults may ingest 0.03 mg per kg of body weight (6), children under 10 years old may invest up to 13 mg per kg of body weight (7), particularly through significant consumption of sweets. Limited research is available on assessing the risks associated with nanoparticle ingestion, but existing studies suggest potential health effects on digestive and reproductive organs (Figure 4B).

In 2016, the European Food Safety Authority (EFSA) authorized the use of additive E171 but recommended further studies to better understand its impact on the reproductive system. Nanoparticle exposure through the skin primarily occurs via cosmetics and hygiene products.

Less common sources include tattoos (ink may contain inorganic nanoparticles based on desired color) and the use of smart clothing directly on the skin (Figure 4C). Most in vitro or in vivo studies indicate that nanoparticles do not penetrate the dermis (8) and therefore cannot be distributed to organs through the bloodstream.

The presence of a skin lesion (erythema, burn, sunburn, etc.) would facilitate penetration without, however, reaching the very deep layers of the dermis (Figure 4C).

Conclusion

Nanoparticles and nanomaterials are ubiquitous and of significant technological interest, driving their development, enhancement of properties, and discovery of new characteristics. The manipulation of nano-objects is becoming increasingly refined, enabling the modification of their properties and an expanding focus on the atomic scale and the exploitation of quantum aspects of matter.

These scientific and technological advancements raise questions about the challenges related to their utilization and the potential risks associated with the use of these nanomaterials, particularly when they meet the general public.

Nanotechnologies have experienced significant growth over the past two decades, offering great potential for innovation and change. This growth is evident in the exponential increase in literature and patents in these fields. Nanotechnologies are primarily divided into three major areas:

1. **Information and Communication Technologies**: This includes optoelectronics, computing, and sensors.
2. **Health**: Applications include medical imaging, early diagnosis, targeted drugs, implants, prosthetics, and artificial tissues.
3. **Materials**: Nanomaterials have applications across most indust.

There are overlaps between these areas, such as in the development and application of sensors. The continued expansion of nanotechnologies promises further advancements and integration across various sectors, highlighting both the innovative potential and the need for careful consideration of associated risks.

Application Exorcises

Section A: Multiple Choices

1). Which one of the following materials cannot be seen by simple microscope?

○ Nanomaterials

○ Bulk materials

○ Both a and b

○ None of the above

2). Which one of the following is an example for nanomaterial?

○ Nano silica

○ Sand

○ Cement

○ All of the above

3). The creating of nanoscale materials by chemically or physically breaking down the larger materials is known as ………………… approach in nanotechnology?

○ Top-down

○ Bottom-up

○ Bottom-down

○ None of the above

5). Which of the following is an example for nanowires of insulators?

○ Silicon dioxide

○ Nickel

○ DNA

○ None of the above

6). The polymeric nanoparticles come under ………………… dimensional nanomaterials?

○ Zero

○ One

○ Two

○ Three

7). The bulk nanomaterials come under …………………dimensional nanomaterials?

○ Zero

○ One

○ Two

○ Thre

8). Which one of the following neurotoxic effects comes under liposomes nanomaterial?

○ Cognition defects

○ Necrosis

○ Astrogliosis

○ None of the above

9). What is the standard form of CNFs?

○ Carbon Nanofibers

○ Carbon Nanographene

○ Carbide Nanographene

○ None of the above

10). Which one of the following is an example for top-down approach?

○ Ball milling technique

○ Sol-gel process

○ Both a and b

○ None of the above

11). The measurement range of electron microscopy is around ……………… meters?

○ 1 m

○ 1 nm

○ 10 m

○ 12 mm

12). Which one of the following is an example for molecular nanowires?

○ Silicon dioxyde ○ Titanium dioxyde

○ DNA ○ None of the above

13). Which one of the following is an example for templates?

○ Nano channel glass

○ Gold

○ Silver

○ None of the above

14). The adsorption of molecules is high in ………………… materials?

○ Nanomaterials

○ Bulk materials

○ Both a and b

○ None of the above

15). Which one of the following neurotoxic effects comes under quantum dots?

○ Cell function damage

○ Increases oxidative stress

○ Both a and b

○ None of the above

16). The measurement range of dynamic light scattering is around ………………… meters?

○ 1 m ○ 10 m

○ 5-500 nm ○ 12 mm

17). The spirals and springs come under ………………… dimensional nanomaterial?

○ One

○ Two

○ Three

○ None of the above

18). The CVD reactors are categorized into ………………… types?

○ One

○ Two

○ Three

○ Four

19). Which one of the following is an example for nanowires of semiconductors?

○ Silicon dioxide

○ Titanium dioxide

○ Silicon

○ None of the above

20). Which one of the following is an example for bottom-up approach?

○ Ball milling technique

○ Both a and b

○ None of the above

○ Sol-gel process

21) The four types of Artificial nanomaterials are …………………

○ Carbon-based, non-metallic, composites and ceramics

○ Carbon-based, metallic, composites and ceramics

○ Carbon-based, non-metallic, composites and dendrimers

○ Carbon-based, metallic, composites and dendrimers

22) On both ends of the CNTs, which carbon nanostructure is placed?

○ Graphite

○ Diamond

○ C_{60}

○ Benzene

22) Quantum dots can be used in …………………

○ Crystallography

○ Optoelectronics

○ Mechanics

○ Quantum physics

23)What's the procedure in Top-down fabrication method?

○ Nano-particles -> Powder -> Bulk

○ Powder -> Bulk – > Nano-particles

○ Bulk -> Powder – > Nano-particles

○ Nano-particle – > Bulk -> Powder

24) Which of the following is an example of Bottom Up approach?

○ Attrition

○ Colloidal dispersion

○ Milling

○ Etching

25) CVD stands for …………………

○ Carbon vapor density

○ Chemical vapor density

○ Chemical vapor deposition

○ Carbon vapor deposition

26) Chemical solution deposition is also known as …………………

○ Sol-gel

○ CVD

○ Plasma spraying

○ Laser pyrolysis

27) Typical precursor used in sol-gel are …………………

○ Metal oxides

○ Metal dioxides

○ Metal alkoxides

○ Metal fluorides

28) The smaller the particles, the longer the mean free path.

○ True ○ False

29) The greater the surface tension of a liquid, the worse the wetting would be of a solid surface.

○ True ○ False

30) Photolithography is a type of patterning technique.

○ True ○ False

Section B: Concept Questions

1. What is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales called?
2. Which type of nanomaterials are classified based on their dimensions?
3. What is the main factor that decides the optical properties of a nanomaterial?
4. During the process of coagulation, a grain boundary is not formed. Why is that so?
5. Briefly investigate the reason why a significant influence of strain energy is expected only for very small particles.
6. The greater the surface tension of a liquid, the worse the wetting would be of a solid surface. How so?
7. The larger the particles, the shorter the mean free path. How so?
8. The higher the ionic charge in compounds, the higher the surface energy. How so?
9. What is special with nanoparticles of metal oxides to be used in gas detection applications?
10. The response of gas sensors utilizing nanoparticles is faster and the signal better compared to sensors in which conventional materials are used. Why?
11. The basic concept of nanomotors is based on a phenomenon of electro-migration of liquid metal droplets at the surface of a multiwall carbon nanotube, and the anisotropy of surface energy of a non cubic metal. What does the underlined text mean?
12. It is extremely difficult to produce gas-phase synthesized particles of high vapor pressure materials. Why is that?
13. What are nonporous materials? Give examples.
14. Write the classification of nonporous materials.
15. Write the basic principle of sol-gel process.
16. List any two advantages of sol-gel process.
17. What are the applications of sol-gel process?

18. What are the precursors used in the sol—gel process? Give examples.

19. Write the various steps involved in the sol-gel process.

20. List any two properties of nonporous materials.

21. Specify any two applications of nonporous materials.

22. What are advantages of CVD process?

23. What is the basic principle of CVD process?

24. What are the precursors used in CVD process?

25. Specify any two types of CVD process.

26. Mention the applications of CVD method.

27. What is PVD? Mention the various methods of PVD.

28. List any two advantages of PVD process.

29. Write any two applications of PVD process.

30. What is the role of nanomaterials in the field of nuclear power engineering?

31. Write a short note on the role of nanomaterials in material surface protection.

32. What are carbon nanotubes ?

33. Differences between SWCNT and MWCNT.

34. How are CNTs classified based on chirality or helicity or asymmetry?

35. Mention the application of CNTs.

36. Define top-down nanofabrication and bottom-up nanofabrication.

37. What are the unique properties of CNTs?

38. Describe the synthesis and application of nanowires.

39. What are nonporous materials? How are nonporous materials synthesized by sol gel method?

40. Explain briefly the advantages and applications of sol-gel process.

41. Discuss the main properties and applications of nonporous materials.

42. Describe briefly the synthesis of nanomaterials by chemical vapor deposition process.

43. List the advantages and applications of chemical vapor deposition process.
44. What is CVD? Explain the different types of CVD reactors, mechanism of CVD.
45. What is PVD? Explain the basic principles of any two PVD methods.
46. Describe the advantages and applications of chemical vapor deposition process.
47. Discuss broadly about the applications of nanomaterials.
48. Write an account of carbon nanotubes.
49. Explain the electrical properties of carbon nanotubes.
50. Write the mechanical properties of CNTs.

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