

Section one: Essential Basics

Bonds

Covalent bond: Covalent bond is a form of chemical bonding that is characterized by the *sharing* of pairs of electrons between atoms, or between atoms and other covalent bonds. In short, attraction-to-repulsion stability that forms between atoms when they share electrons is known as covalent bonding. Covalent bonding includes many kinds of interactions, including δ -bonding, Π -bonding, metal-metal bonding.

Ionic bond (or electrovalent bond): Ionic bond is a type of chemical bond based on electrostatic forces between two oppositely-charged ions. In ionic bond formation, a metal donates an electron, due to a low electronegativity, to form a positive ion or cation. In ordinary table salt (NaCl), the bonds between the sodium and chloride ions are ionic bonds. Often ionic bonds form between metals and non-metals. The non-metal atom has an electron configuration just short of a noble gas structure. They have high electronegativity, and so readily gain electrons to form negative ions or anions. The two or more ions are then attracted to each other by electrostatic forces.

Metallic bond: Metal atoms typically contain fewer electrons in their valence shell relative to their period or energy level. These electrons can be easily lost by the atoms and therefore become delocalized and form a sea of electrons surrounding a giant lattice of positive ions. Metallic bonds are best characterized by the phrase "a sea of electrons".

Van der Waals forces (weak forces): Three types: London forces (dispersive force), dipole-dipole forces, and hydrogen bonding.

London forces are: weakest, but most numerous and influential; 2). Are quantum mechanical (instantaneous electron couplings)

Hydrogen bond is always involved with hydrogen atom, which is weaker than covalent, ionic and metallic bonds, but stronger than London forces and dipole-dipole forces.

Energy of bonds:

<i>Bond</i>	<i>Energy (Joules/bond)</i>
Ionic/covalent bonds	4.2×10^{-19}
Hydrogen bonds	3.3×10^{-20}
London and dipole bonds	3.3×10^{-21}

Quantum Numbers

There are *four* numbers that come into the theory of electron clouds as waves called quantum numbers:

- The first quantum number, *n*, is the principle energy level. This is the 1 in $1s^2$. It can have the values: 1, 2, 3, ...
- The second quantum number, *l*, is the sublevel. The *n*th principle energy level has *n* sublevels. It refers to these sublevels by letters: s, p, d, f, g, h, i, j, k, ... Sometimes numbers are used too: 0, 1, 2, 3, ...(*n*-1)
- The third quantum number, *ml*, is the orbital. Every sublevel has one or more orbitals. The s sublevel has 1 orbital, the p sublevel has 3 orbitals, the d sublevel has 5 orbitals, etc. These orbitals can be indicated by the number $ml = l, l-1, \dots, 0, -1, \dots, -l$
- The fourth quantum number, *ms*, is the spin of the electron. Electrons can be either spin up or spin down. *ms* can be either $+\frac{1}{2}$ or $-\frac{1}{2}$

$$E=h\nu$$

E is the energy of the photon, ν is the frequency of the photon, h is Planck's constant = $6.626068 \times 10^{-34} \text{ m}^2\text{kg/s}$.

Quantum mechanical effects

- _ Energy is discrete, not continuous in a quantum system.
- _ The electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes dominant when the nanometer size range is reached.
- _ Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications.

- a. opaque substances become transparent (copper);
- b. inert materials become catalysts (platinum);
- c. stable materials turn combustible (aluminum);
- d. solids turn into liquids at room temperature (gold);
- e. insulators become conductors (silicon).

8. Size concern

The volume of an object decreases as the third power of its linear dimensions, but the surface area only decreases as its second power. Because of that, a lot of mini-mechanical devices do not work at the nano scale.

9. Compounds for nanomaterials

Inorganic compounds: Carbon, Silicon, metal oxides (such as cerium oxide (CeO₂), zinc oxide (ZnO)) etc. Organic compounds: DNA, RNA, carborhydrate, etc.

Section two:

Nano definitions and nomenclatures

Nano as a word

Nano is a Greek word means dwarf or small man. In standard international units SIU, nano is used as a prefix that denotes to a fraction of billion (10^{-9}) for a given unit, for example: nanometer, nanogram, nanolitter ,.....etc., see the table:

<i>Prefix, abbreviation</i>	<i>Means</i>	<i>Power of 10</i>
Giga, G	1 billion	10^9
Mega, M	1 million	10^6
kilo, k	1 thousand	10^3
centi, c	1/100	10^{-2}
milli, m	1/1,000	10^{-3}
micro, μ	1/1,000,000	10^{-6}
nano, n	1/1,000,000,000	10^{-9}

Nanoscience

Is the basic study of systems and materials at a scale of nano i.e. 10^{-9} . Nanoscience can be defined as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales where properties significantly differ from those at larger scale. In fact, nanoscience is the study of nanoparticles NP_s .

Nanochemistry

Limitation of chemical reactions on nanometer length scale to produce chemical products with nanometer dimensions.

Nanostructured Materials

These are artificial materials rationally designed and manufactured with features possess at least one nanoscale dimension. Here, the nanoscale dimension is ranged between 1 nm to 500 nm; so it is unlike the common scale for nanomaterials which scales from 1 nm to 100 nm.

Nanotechnology

Nanotechnology is the application of nanoscience to a broad set of technologies that control and manipulate materials at the level of atoms and molecules to produce materials and devices with unique properties. In fact, nanotechnology may refer to the combination of multiple disciplines and technologies to enable creating, assembling, measuring or manipulating things at a nanoscale level. From another point of view, nanotechnology may refer to:

- ❖ The research and technology development in atomic, molecular or macromolecular level at a length scale of (1 - 100) nm or sometimes (1-500) nm.
- ❖ The creation of structures and devices with novel properties which function because of their small and/or intermediate size.
- ❖ The capability to control and manipulate systems scale in atomic level.

How small the nano is?

To understand how small the nano is, let us go through the examples shown in [Figure 1](#):

- ❖ Water molecule is almost 0.3 nm across.
- ❖ The average diameter of a red blood cell is ~ 7000 nm.
- ❖ The average diameter of human hair is ~ 80000 nm.

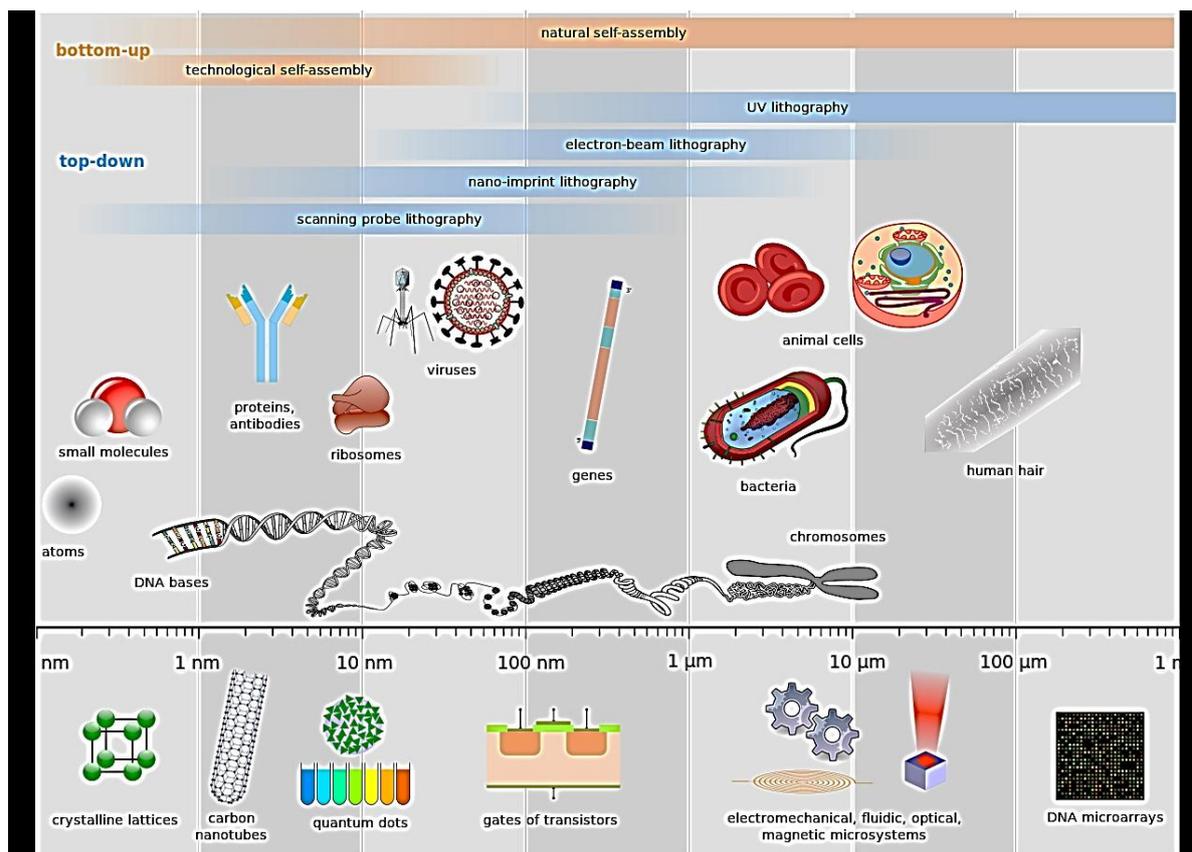


Figure 1 : Length scale for common examples averaged in nanoscale

Section three

Unique properties

Why nanomaterials are different?

In addition to the fact that nanoparticles possess high freedom of motion in nanomaterials and the fact that the effect of the electromagnetic waves on nanoparticles are more than the effect of the gravity forces, two essential factors cause the properties of the nanomaterials to differ from the properties of the other materials. These factors are: the quantum confinement (limitation) effect and the surface area increment effect. Such as factors may enhance reactivity, strength and electrical characteristics for the nanomaterials in a way that make it different from the other materials. These two factors are discussed as follows:

1. The quantum confinement effect: Quantum theory shows that when two atoms are brought close enough together to interact, each of the allowed electron energy levels within the atoms splits into two distinct but closely spaced energy levels as the atoms combine to form the two-atom system, see [Figure 2](#). In this Figure, note that in a two- atom system, three-atom system, four-atom system...etc. each allowed electron energy level is split into a set of two, three, four ...etc. separate but closely spaced energy levels. Clearly then, as we pack more and more atoms closely together each set of split energy levels contains more and more levels spread over the same energy range allowed at that particular radius from the nuclei, see [Figure 2](#) and [Figure 3](#). So, in a crystalline solid, such as a metal or a diamond, where billions upon billions (6.023×10^{23} atoms /mole of substance) of atoms are packed closely together, the energy levels within each set become so closely spaced in energy that they form a practically, *discrete energy band*, [Figure 4](#), or *continuous energy band*, [Figure 5](#).

In principle, the electrons of a single and isolated atom occupy *atomic orbitals*. Each orbital is found to be at a discrete energy level, [Figure 4](#). However, when multiple atoms join together to form into a molecule, their atomic orbitals combine to form *molecular orbitals*, each of which forms at a discrete energy level, [Figure 2](#). As more

atoms are brought together, the molecular orbitals extend larger and larger, and the energy levels of the molecule will become increasingly dense, [Figure 4](#). Eventually, the collection of atoms forms a giant molecule, or in other words, a solid. For this giant molecule, the energy levels are so close that they can be considered to form a continuum i.e. **continuous energy band** (mentioned above), see [Figure 5](#). In continuous energy band, the highest energy band that is occupied by electrons is called the **valence band** and the higher energy band that lies above the valence band is called the **conduction band**, [Figure 5](#).

At absolute zero the valence band is completely full with electrons and the material acts as an insulator. As the temperature increases some electrons gain sufficient thermal energy to escape from the valence band and cross the forbidden gap (known as *the energy gap* or E_g for short) into the conduction band. Once sufficient electrons have crossed the gap; the conduction of electric current becomes possible and hence conductivity increases, see [Figure 5](#). In this Figure, you may note how energy band theory can be used to describe the difference between *conductors*, *insulators* and *semiconductors*. If an electric field is applied to a solid, electrons in the valence and conduction bands can be accelerated by the field and gain energy. However, this can only happen if the electrons can move from their own energy level within the band to an unoccupied level of higher energy. **Semiconductors have electrical resistances between those of conductors and insulators [Bob Emery, 42 Douglas Adams, cited on 5th July 2016].** In [Figure 6](#) we show energy levels comparison in atoms, nanomaterials and bulk materials.

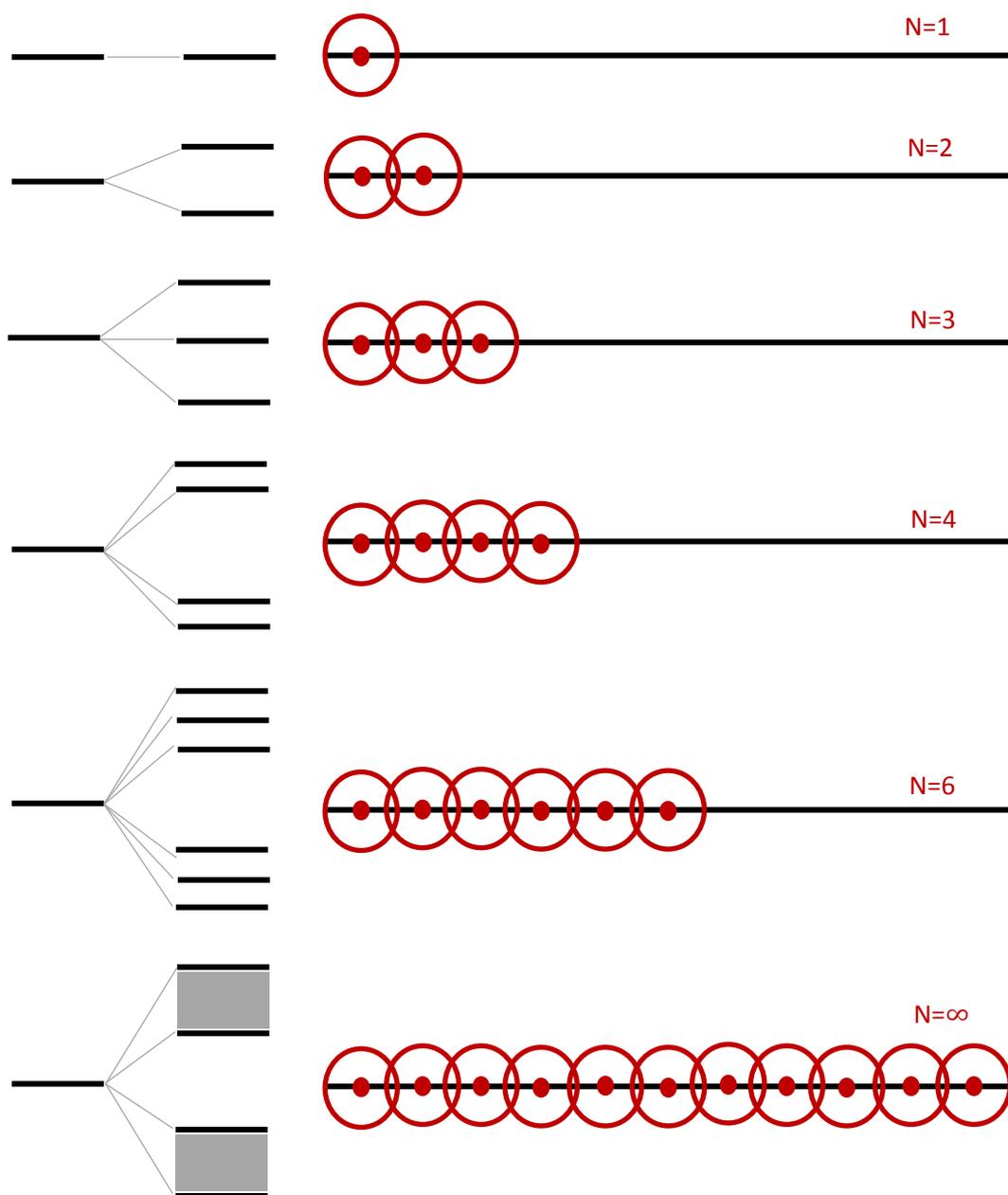
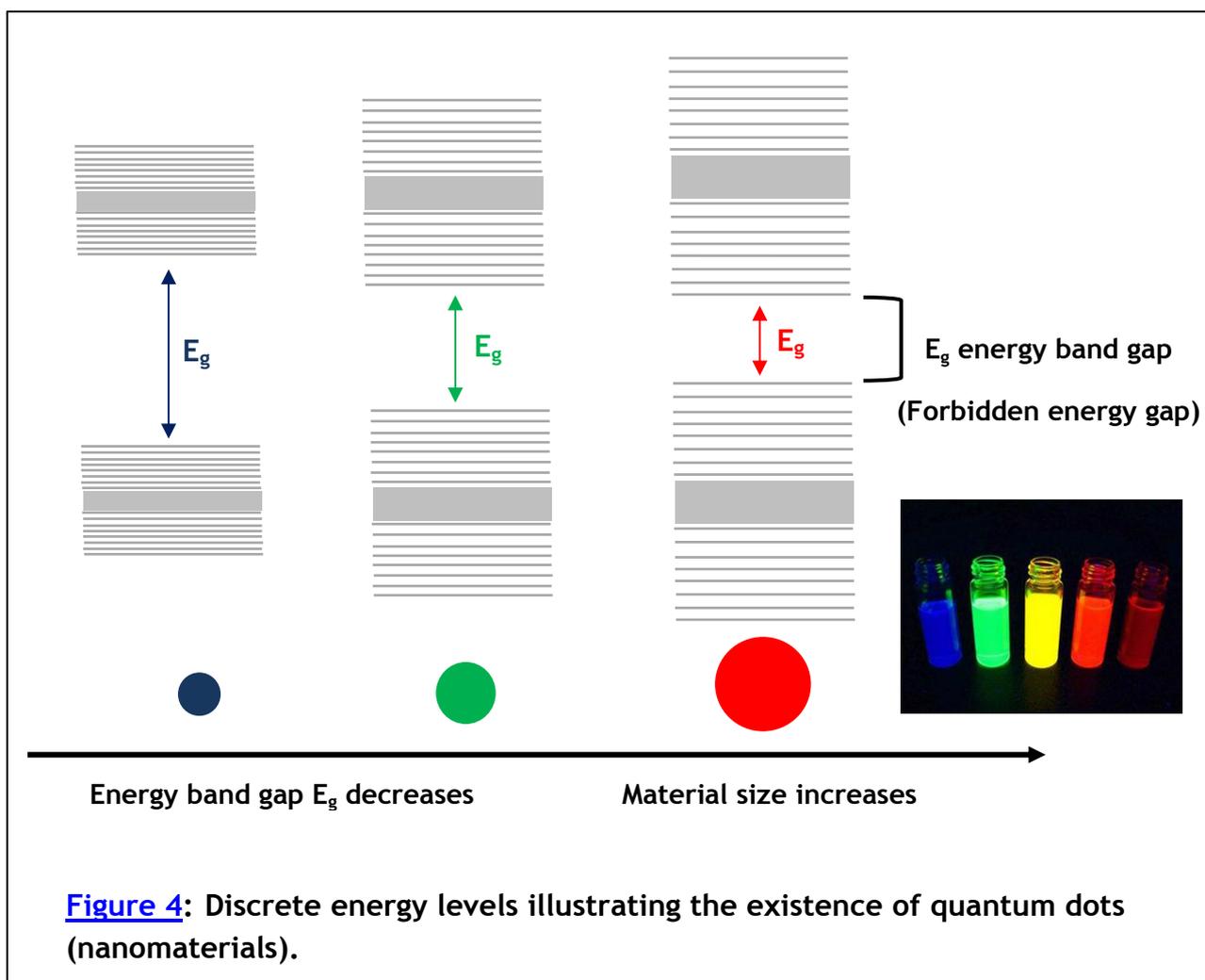
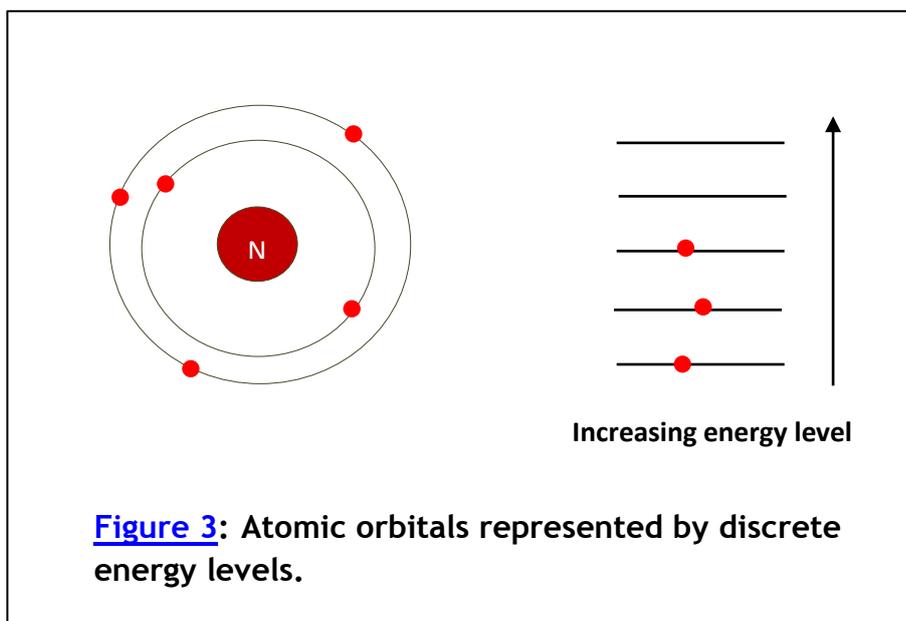


Figure 2: Molecular orbital formation as a result of atomic orbital combinations.



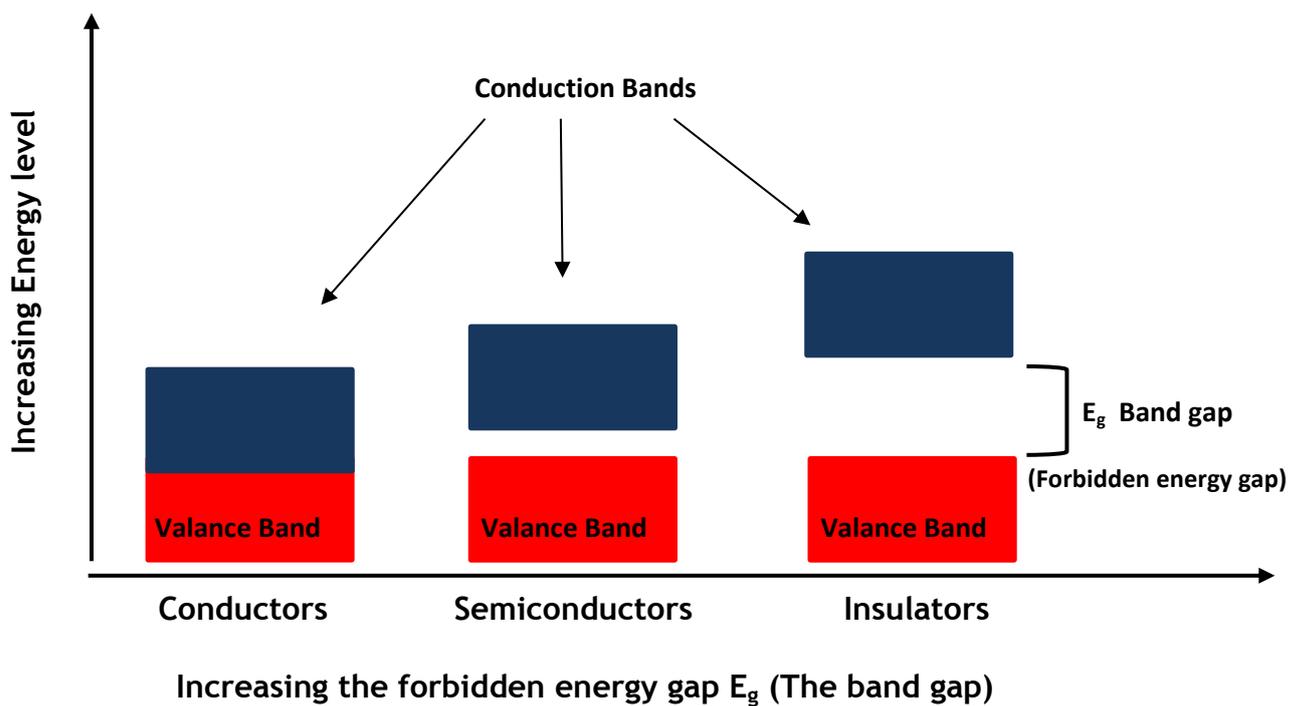


Figure 5 : Continuous energy bands in bulk materials.

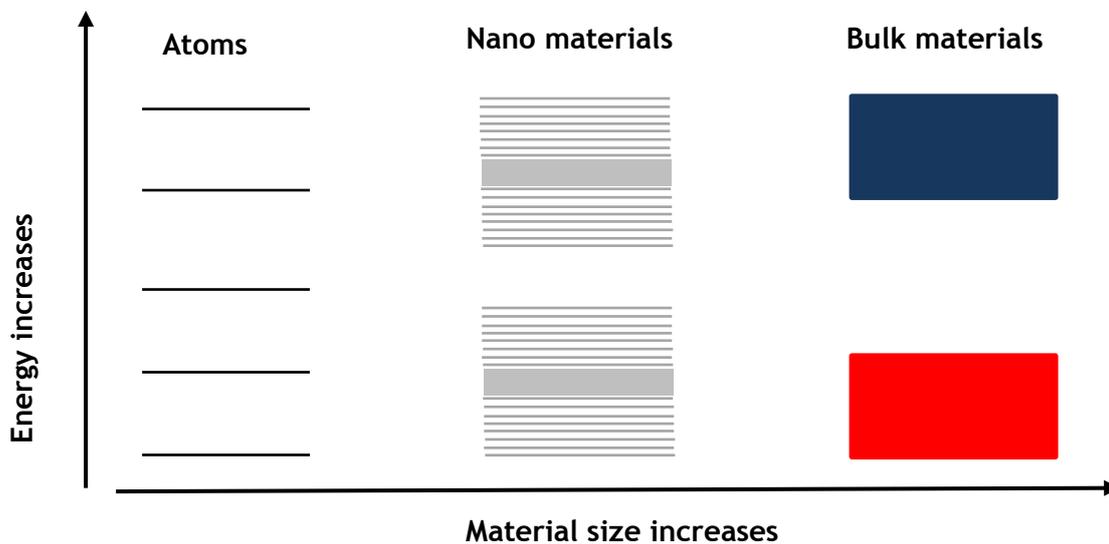


Figure 6: Energy levels comparison in atoms, nanomaterials and bulk materials.

2. The surface area increment effect: An important aspect for the nanomaterials is that their properties are highly affected by their sizes. Studies have found that nanomaterials have a relatively larger surface area in comparison with the same volume or mass for the bulk materials. This is because the ratio of the surface area to the volume is huge. To understand this aspect, let us go through few examples:

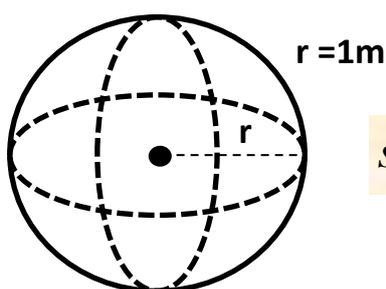
Example 1: consider a sphere with a radius of r:

Its surface area = $4\pi r^2$.

Its volume = $\frac{4}{3}\pi r^3$

Its surface area to volume ratio = $3/r$.

Hence, if the radius of the sphere decreases then its surface to volume ratio increases.



$$\text{surface area} = 4\pi r^2 = 4 \times 3.14 \times 1m^2 \Rightarrow 12.56m^2$$

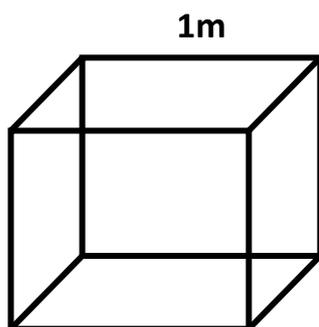
Example 2: consider a cube with a width of w:

Its surface area = $6w^2$.

Its volume = w^3

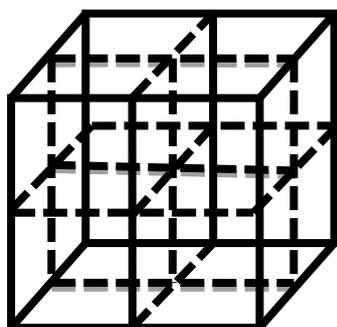
Its surface area to volume ratio = $6/w$.

Hence, if the width of the cube decreases then its surface area to volume ratio increases.



$$\text{surface area} = 6 \times 1m^2 \Rightarrow 6m^2$$

Having a cube with a volume of 1m^3 and a surface area of 6m^2 divided into eight pieces simply means its surface area becomes 12m^2 . Similarly, when the same volume is divided into 27 pieces then its surface area becomes 18m^2 . This clearly means when a given volume is divided into smaller pieces then the surface area increases. Applying this concept on material particles would come up with a conclusion that if a particle size decreases then its surface area increases and hence a greater proportion of atoms are found at the surface compared to those inside the particle. This is why materials made out of nano particles have a much greater surface area per a given volume in comparison with materials made out of bulk particles. Thus, materials made out of nanoparticles are chemically more reactive than materials made out of bulk particles.



$$\frac{1}{2} m \quad \text{surface area} = 6 \times \left(\frac{1}{2} m\right)^2 \times 8 = 12m^2$$

Repeat 24 times

8 Cubes Side L
 Each has Surface area $6L^2$
 Total Surface Area $48L^2$

1 Cube
 Length of sides $2L$
 Surface area $24L^2$

For example, 5 cubic centimeters - about 1.7 cm per side - of material divided 24 times will produce 1 nanometer cubes and spread in a single layer could cover a football field

How to estimate the surface area to volume ratio (S/V) and the specific surface (S/W(g)):

Example; Calculate the S/V and the S/W of 1 cm³ of spherical nano ZnO crystals with radius of 6nm, let the density 1.5g/cm³?

Number of particles (NOP) = total volume(v) / (v₀)volume of single particle
 ($\frac{4}{3} * \pi * R^3$)

$$\text{NOP} = \frac{1 \text{ cm}^3 * 10^{21} \text{ (nm/cm)}^3}{\left(\frac{4}{3} * 3.14 * (6)^3\right) \text{ nm}^3}$$

$$= 11 * 10^{17}$$

$$\text{Total surface area(S)} = \text{NOP} * \text{surface area of single particle}(4 * \pi * R^2)$$

$$= 11 * 10^{17} * 4 * 3.14 * (6)^2$$

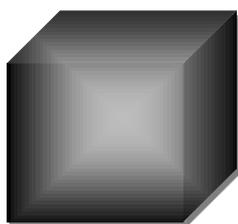
$$= 5 * 10^{20} \text{ nm}^2$$

$$= 500 \text{ m}^2$$

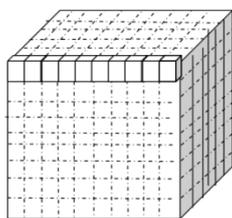
$$S/V = 500 \text{ m}^2 / \text{cm}^3$$

$$S/W = S / (w = v/d) = 500 / 1.5 / 1 = 333.34 \text{ m}^2/\text{g}$$

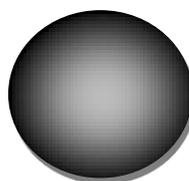
Exercise: Calculate the S/V and the S/W of 1 cm³ of cubical nano ZnO crystals with side length of 6nm, let the density 1.5g/cm³?



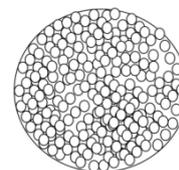
1cm³ of cubical particle



1cm³ of cubical particles of 6 nm in side length



1cm³ of a spherical particle



1cm³ of spherical particles of 6 nm in radius

In addition to the vast increase in the surface area per unit mass, nanoscale sizes result in unique chemical, mechanical, electronic, photonic and magnetic properties. Also, new chemicals of common chemical elements may be formed in nanoscale sizes e.g. fullerenes, carbon nanotubes, titanium oxide, zinc oxide and other layered compounds. Between the dimensions of atomic scales and the dimensions of bulk scales, the condensed matter exhibits some remarkable specific properties that significantly differ from the properties of bulk materials. Some peculiar properties are known, however a lot more yet to be discovered. The following are just a few examples:

1-Melting point and phase transition temperatures for nanomaterials may have a significantly lower melting point or phase transition temperature and appreciably reduced lattice constants in comparison with bulk materials. This is due to a huge fraction of surface atoms in the total amount of atoms.

2-Colour and optical properties of nanomaterials may significantly differ from those for bulk crystals. For example, colors of metallic nanoparticles change with sizes due to surface plasmon resonance. Optical absorption peaks of semiconductor nanoparticles shift to a short wavelength due to band gap increment.

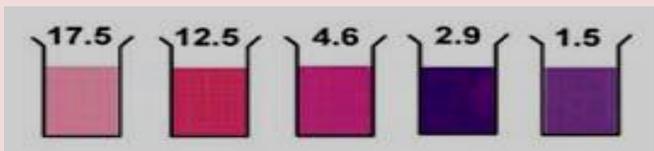
3-Electrical conductivity of nanomaterials may significantly enhanced due to a better ordering in the entire microstructure e.g. in polymeric fibrils. In bulk materials, electrical conductivity decreases with reduced dimensions due to surface scattering.

4- Chemical properties of nanomaterials such as ionization and electron affinity may differ from those for the bulk materials.

5-Magnetic properties of nanomaterials also differ from those for the bulk materials e.g. gold and platinum become magnetic materials.

6- Mechanical properties of nanomaterials may reach the theoretical strength, that's one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is due to defects reduction e.g. CNT'S are 100 times stronger than steel.

A very common example which illustrates some of the differences above is gold, See table 1:

<u>Table 1</u>	
Nano gold	Bulk gold
1. Its melting point depends on its particle sizes; it decreases with size decreasing and hence varied between 400 C° to 1150 C°	1. It has a definite melting point of 1150C°
2. Can be magnetized	2. Cannot be magnetized
3. Chemically active so it could be used as a catalyst	3. Chemically inert
4. May takes as many colors as yellow, blue, red, pink, violet; highly depends on its particle sizes.  <p style="text-align: center;"><i>Pink red maroon blue violet</i></p>	4. A fixed color of yellow
5. Less electrically conductive	5. More electrically conductive

More examples are:

Copper: is an opaque substance becomes transparent.

Platinum: is an inert substance becomes catalyst.

Aluminum: is a stable substance turns to combustible.

Silicon: is an insulators becomes conductors.

A general comparison between nanomaterials and bulk materials (named here as nanostructures and microstructures, respectively) are shown in table 2:

<u>Table 2</u>		
Sector	Nanostructure	Microstructure
Physics	Quantum mechanical	Semi-classical
Electron nature	Wave-like	Particle -like
E or k-space	Discrete	Continuous
Current	Quantized	Continuous
Decision	Probabilistic	Deterministic
Fabrication	Nano-fabrication	Micro-fabrication
Surface area volume	Very large	Small
Packing	Very high	Low

Section four

Nanomaterials classification

There are different ways to classify nanomaterials:

1. Based on dimensions:

In principle, crystal particles are known to have three dimensions in space; namely as: x, y and z. Based on the dimensions method, nanomaterials are used to have orders start from 0 to 3; and these orders depend on how many *non-nanoscale* dimensions of x, y and z may exist in the particle. For example:

1. 0D or zero dimensions nanomaterials: these are materials with all three dimensions are at the nanoscale level i.e. there is no micro-dimension in x, y and z directions. Examples of 0D materials are: gold nanoparticles, quantum dots of ZnO and quantum dots of PbS. In terms of quantum confinements, 0D nanocrystals exhibit three quantum confinements because the effect of the quantum confinements appears only with the nanoscale dimensions; and hence 0D nanocrystals would have to have three quantum confinements in three directions, see Figure 4.1.

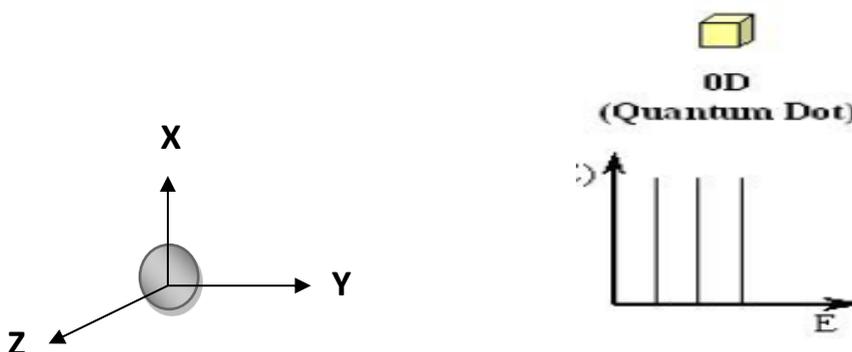


Figure 4.1: 0D nanomaterials

2. 1D or one dimension nanomaterials: These are materials with only one dimension at the microscale level and hence the other two dimensions are at the nanoscale level.

Examples of 1D materials are: carbon nanotubes, Ni wires and Fe nanorods. In terms of quantum confinements; and for the same reason in 1, 1D nanocrystals exhibit quantum confinements into two directions, see Figure 4.2.

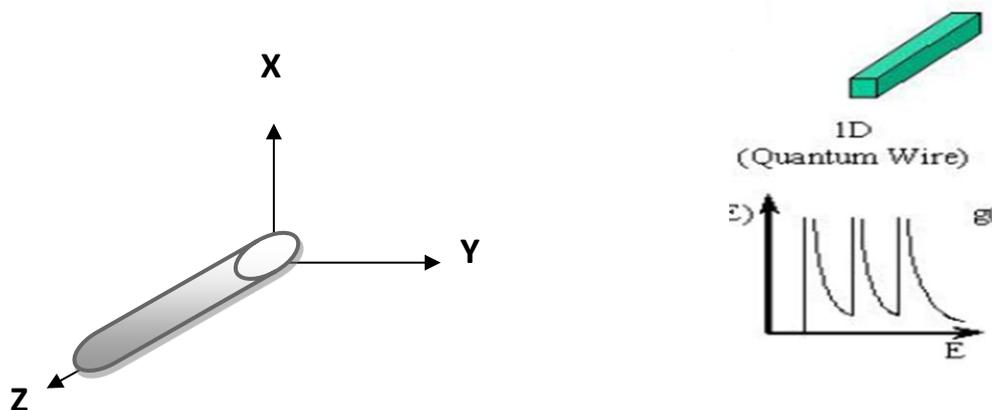


Figure 4.2: 1D nanomaterials

3. 2D or two dimension nanomaterials: These are materials with two dimensions at the microscale level and hence only one dimension is at the nanoscale level. Examples of 2D materials are: Gold nano films and Silver nano films. In terms of quantum confinements; and for the same reason in 1, 2D nanocrystals exhibit quantum confinements in one direction only, see Figure 4.3

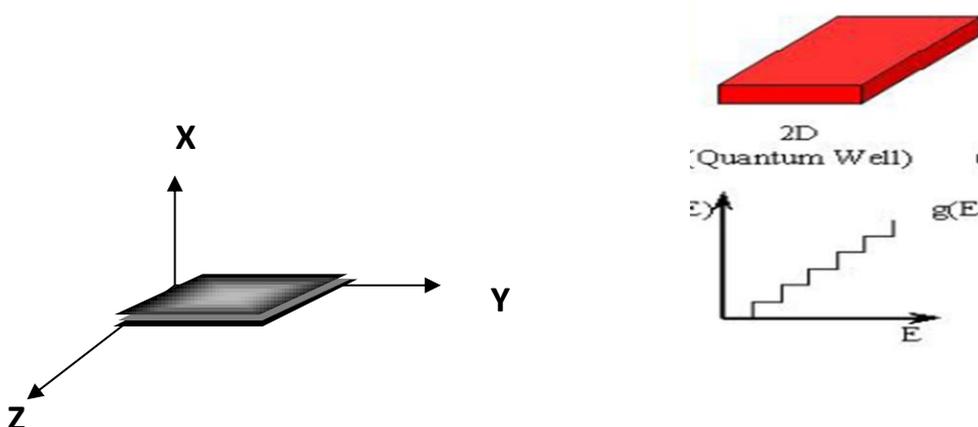


Figure 4.3: 2D nanomaterials

4. 3D or three dimension nanomaterials: These are materials with three dimensions at the microscale level and hence no dimensions are at the nanoscale level (the question is why it is called nanomaterials then?). Examples of 3D materials are: composites and

clusters (these are polymers with nanoparticles) polystyrene with nano MgO. In terms of quantum confinements, 3D nanocrystals exhibit no quantum confinements in any direction, see Figure 4.4.

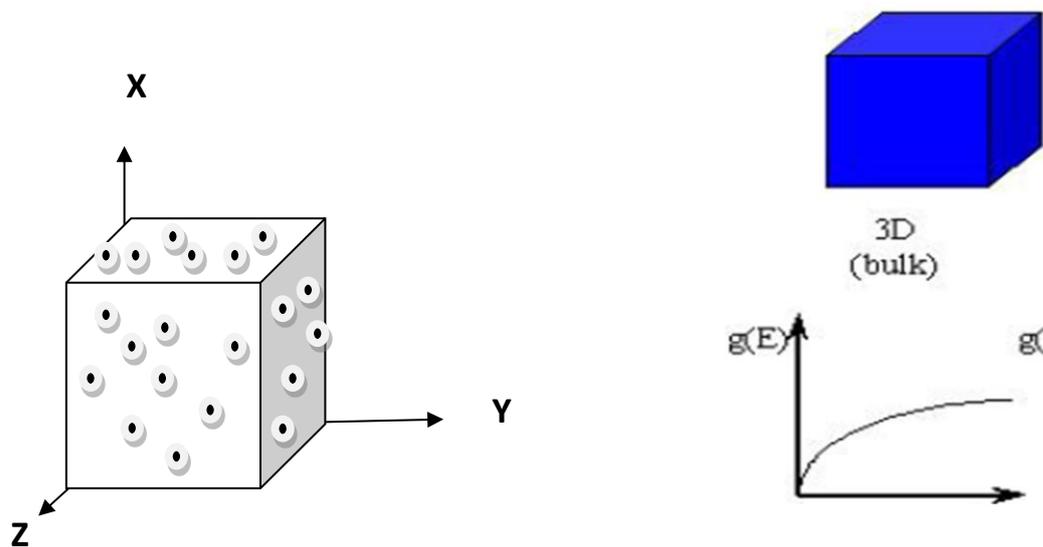
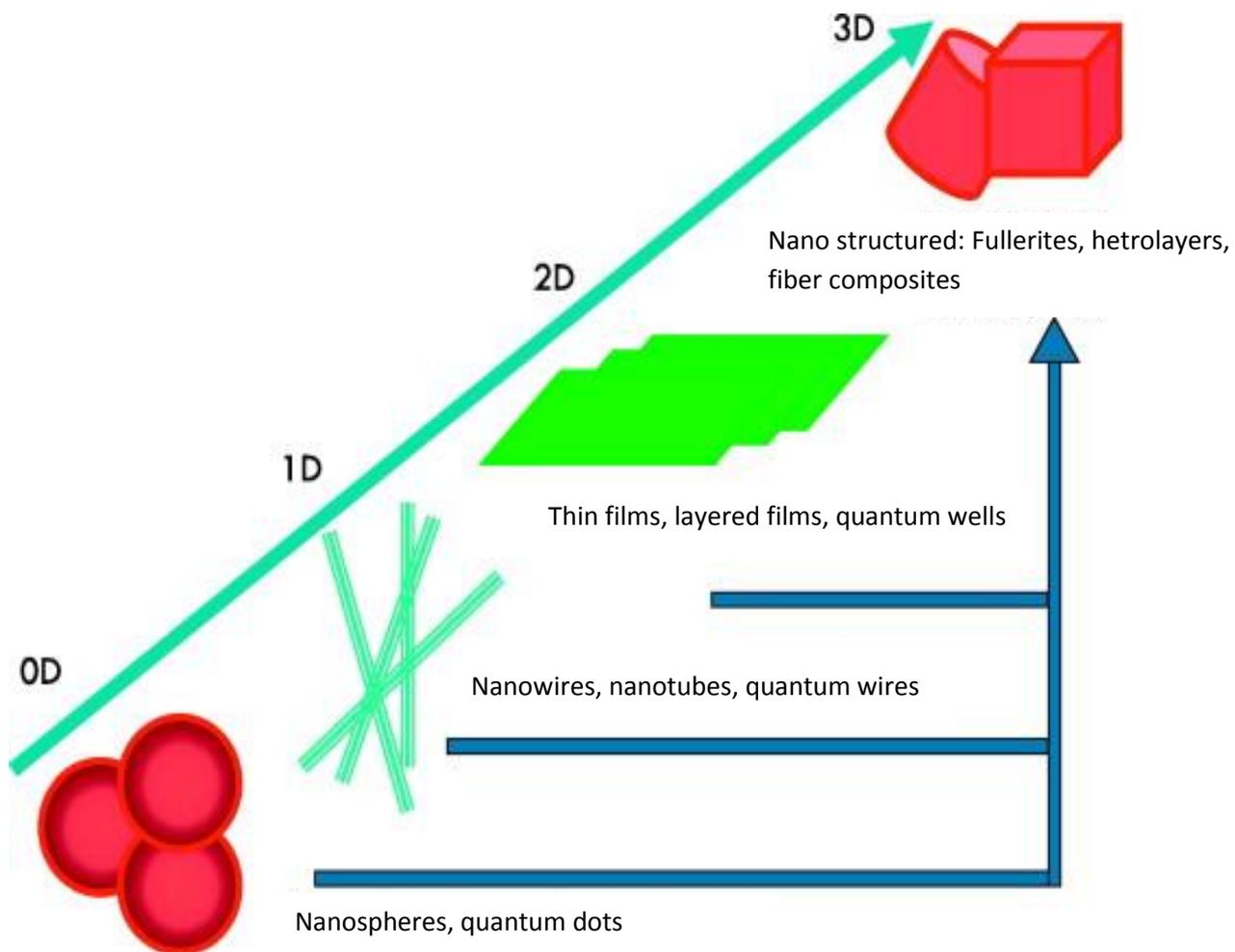


Figure 4.4: 3D nanomaterials

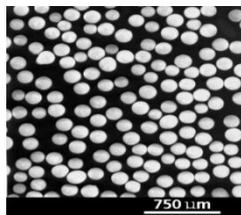
Summery plot for classification above:



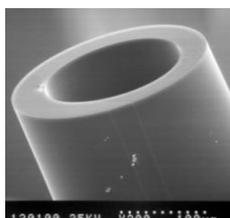
2. Based on shapes:

Nonmaterials usually take different shapes such as: spherical, cubical, tubes, wires, rods and films; therefore they could to be named by shapes as following:

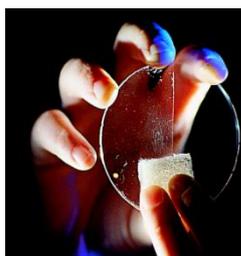
1. Nanoparticles or nanospheres: such as quantum dots of ZnO, PbS and nanogold



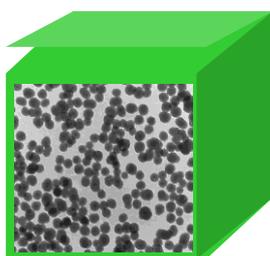
2. Nanotubes or nanowires or nanorods: such as carbon nanotubes of W and Ni wires



3. Nanoscale thin films or ultra-thin films such as: nano films of Ag and Au



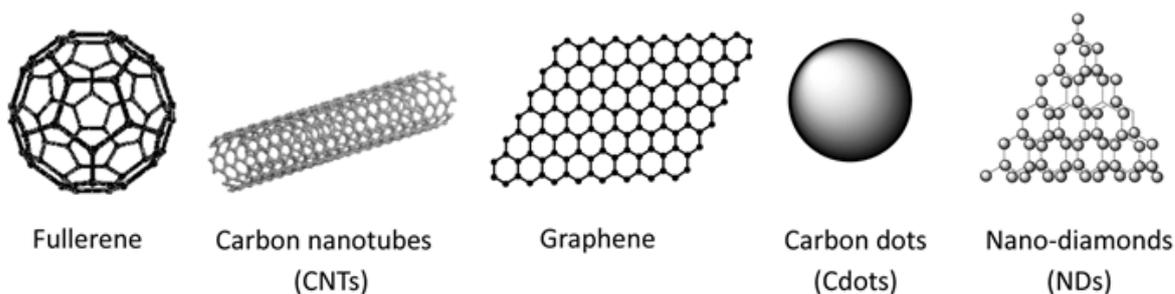
4. Nanocomposites: a material comprised of many nanoscale inclusions such as nanoparticles.



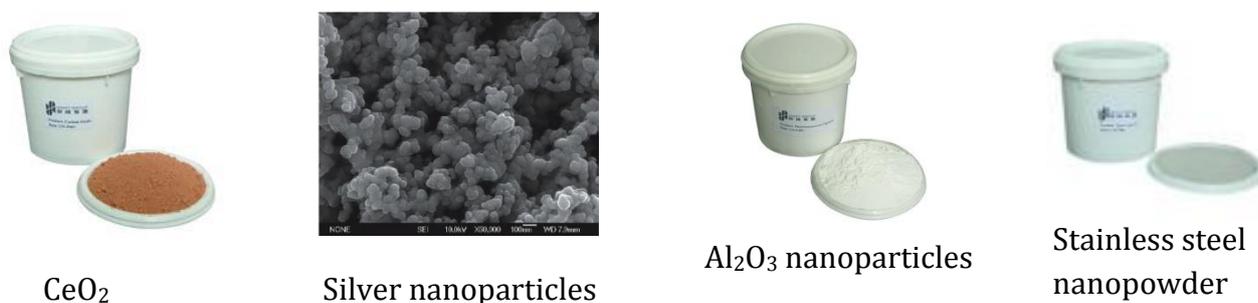
3. Based on compositions:

Nanomaterials could be classified according to their elemental composition, for example:

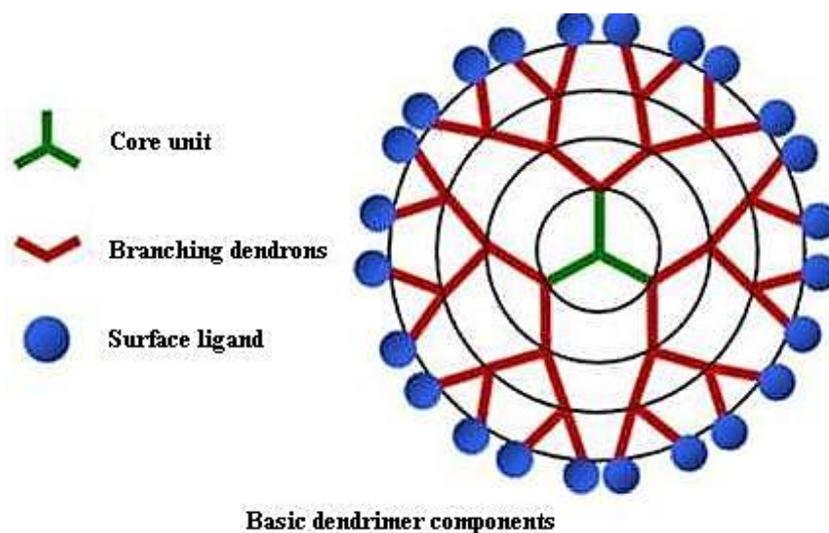
1. Carbon Based Materials, such as: hollow spheres and ellipsoids like Fullerene, spherical and ellipsoidal like carbon dots, sheets like Graphene, in addition to tubes like carbon nanotubes.



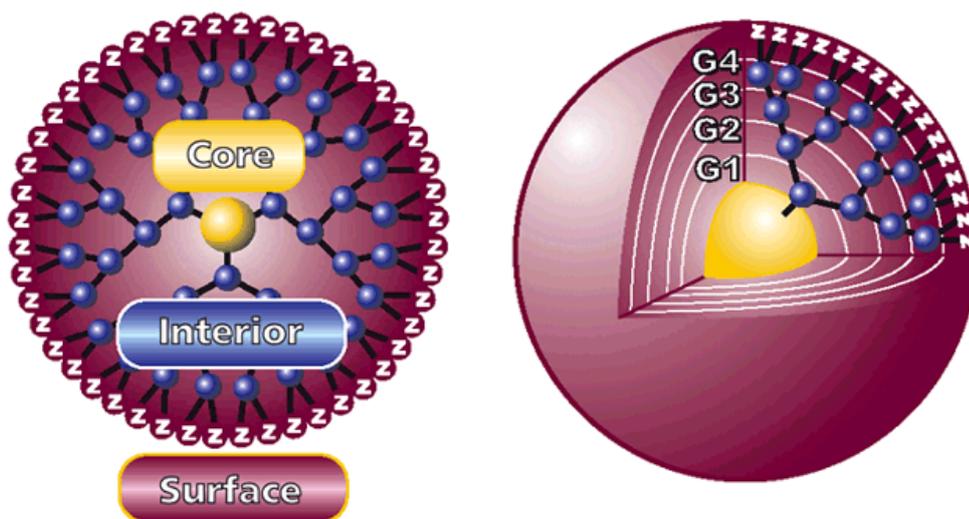
2. Metal Based Materials, such as: quantum dots, gold nanoparticles, silver nanoparticles and metal oxides like titanium dioxide.



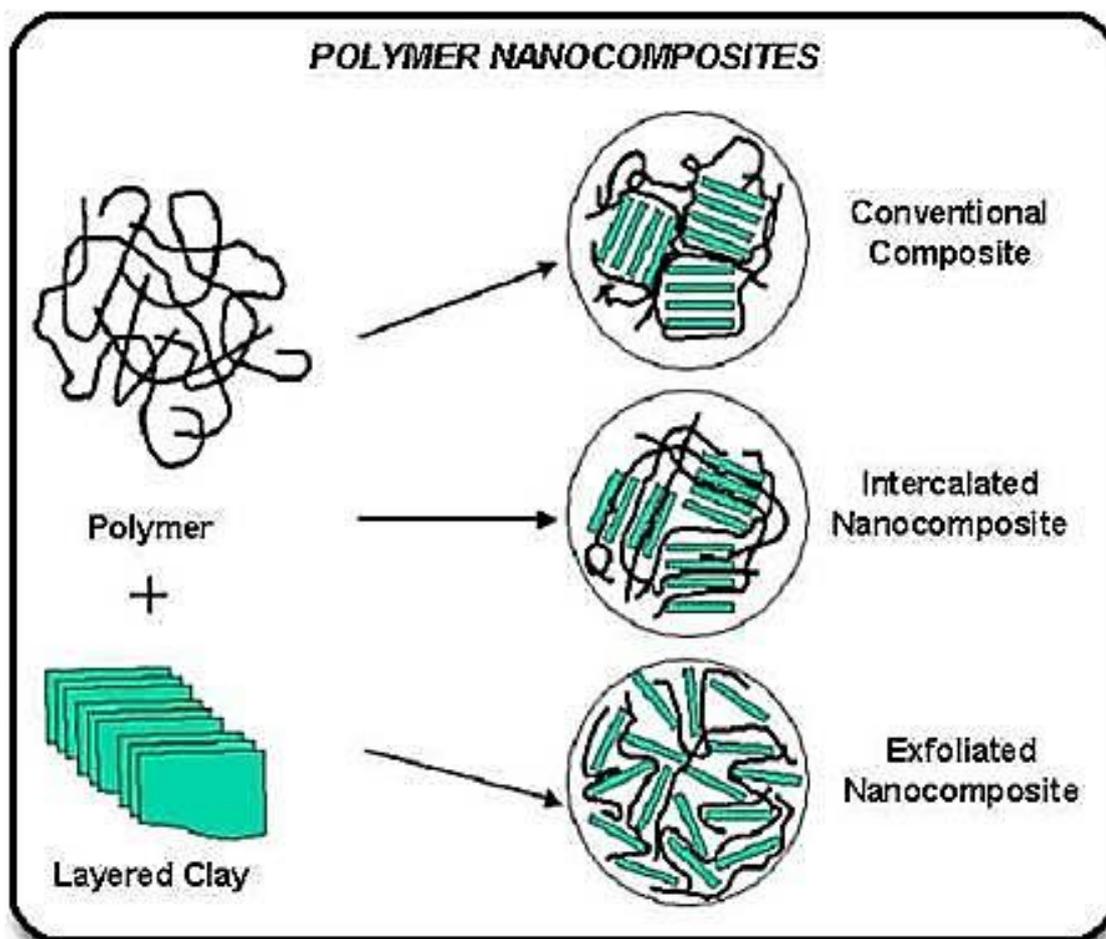
3. Dendrimers: these are polymers sized in nano scale and built up from branched units e.g. Polyamidoamine (PAMAM) dendrimers.



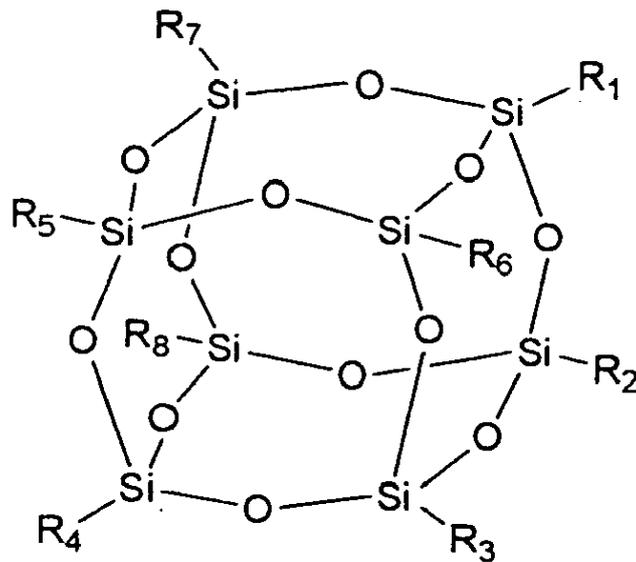
Dendrimers



4. Nanocomposites: these are materials with nanoscale structures that improve the macroscopic properties of products. Composites means is to combine nanoparticles with other nanoparticles or with larger bulk-type materials e.g. polystyrene with nano MgO. Examples of nanocomposites are: clay, polymer, carbon, or a combination of these materials with nanoparticle building blocks.

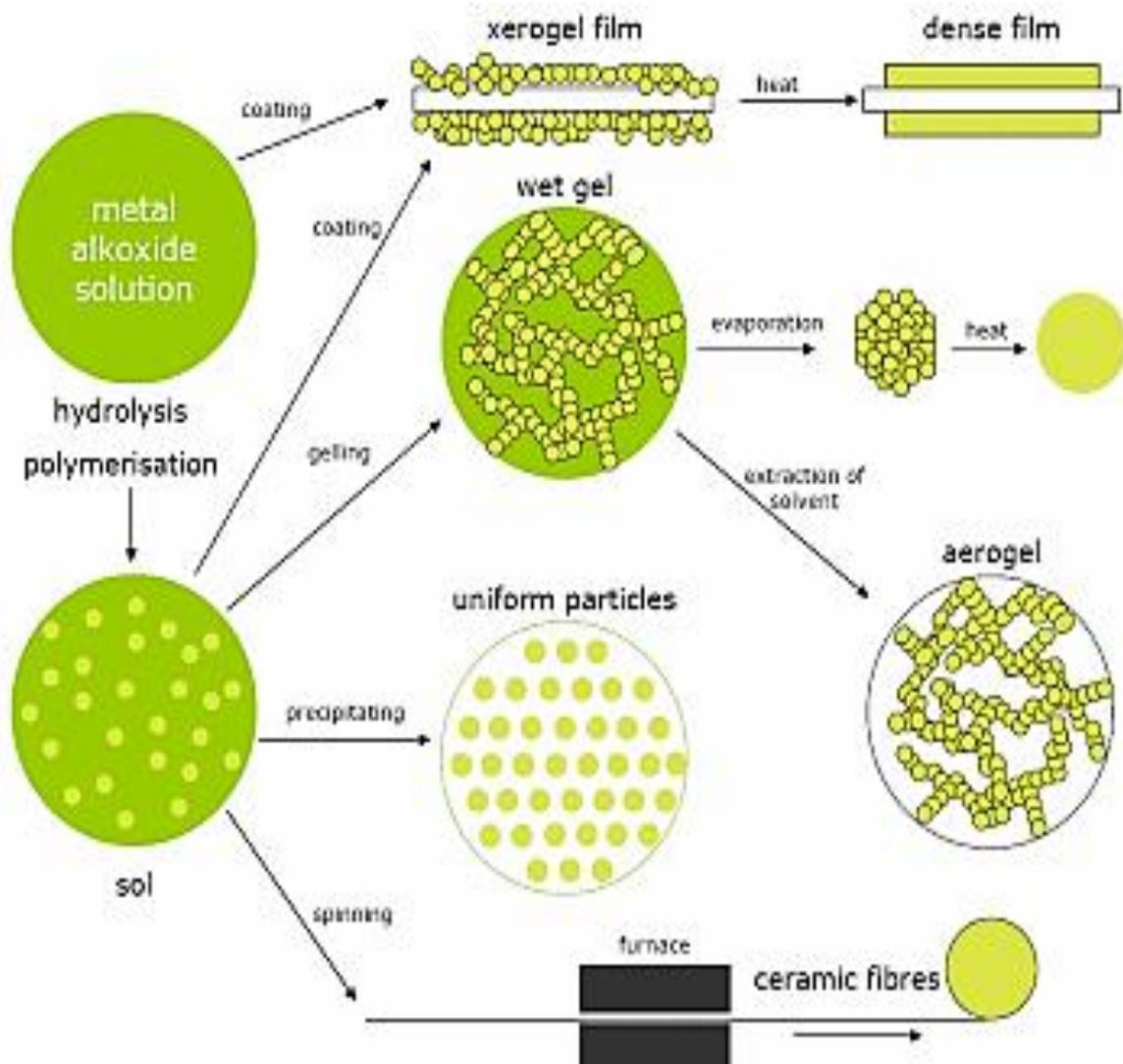


5. Inorganic-Organic Hybrid Nanoparticles: These are inorganic materials, such as silsesquioxane cage structure- like hybrid molecules of silicon and oxygen, mixed with organic materials, such as polymers, to bond to the organic molecule and to one another forming large weave through the polymer. The result is a nanostructured organic-inorganic hybrid polymer. Example: Polyhedral oligomeric silsesquioxanes (POSS) are nanostructures with the empirical formula of $[\text{RSiO}_{1.5}]_n$, where R may be a hydrogen atom or an organic functional group, e.g., alkyl, alkylene, acrylate, hydroxyl or epoxide unit. POSS may be referred to as a silica nanoparticle consisting of a silica cage core, as well as other organic functional groups attached to the corners of the cage. POSS consists of both organic and inorganic matter with an inner core of inorganic silicon and oxygen and an outer layer of organic constituents, which could be either polar or nonpolar. The POSS chains act like nanoscale reinforcing fibers, producing extraordinary gains in heat resistance.



Polyhedral oligomeric silsesquioxanes (POSS)

6. Nano-Intermediates: these are metal alkoxides (titanium isopropoxide), metal organic compounds, as their uses in producing nanomaterials by sol-gel process.



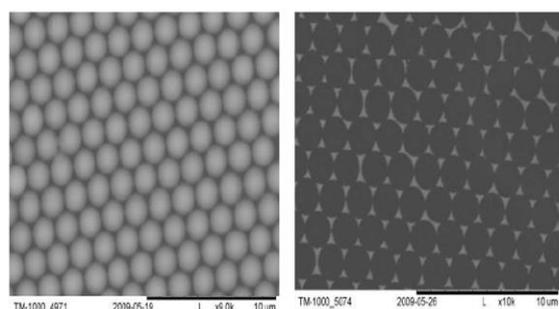
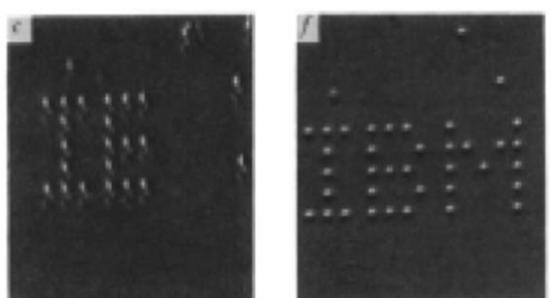
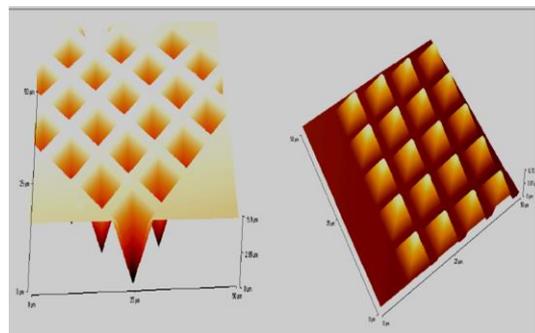
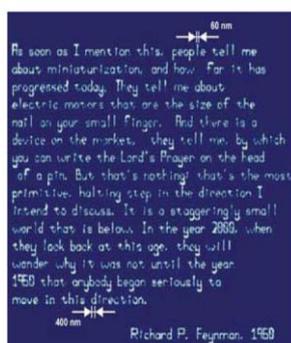
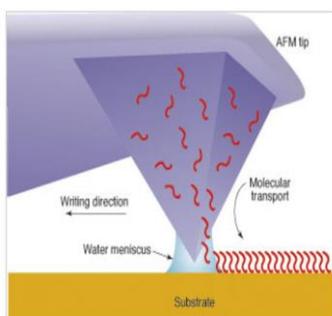
Section five

Preparation methodologies

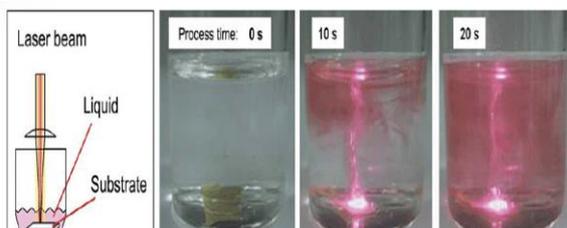
There are two main different approaches to fabrication (preparation, synthesis) ;

The first is; Top - Down approaches: Start with the bulk material and “cut away material” to make what you want

- 1-Grinding/Milling
- 2-Nanolithography
 - Conventional Mask
 - Scanning E-Beam,I-Beam
 - Soft Nanoprinting
 - spherical



3-Laser ablation



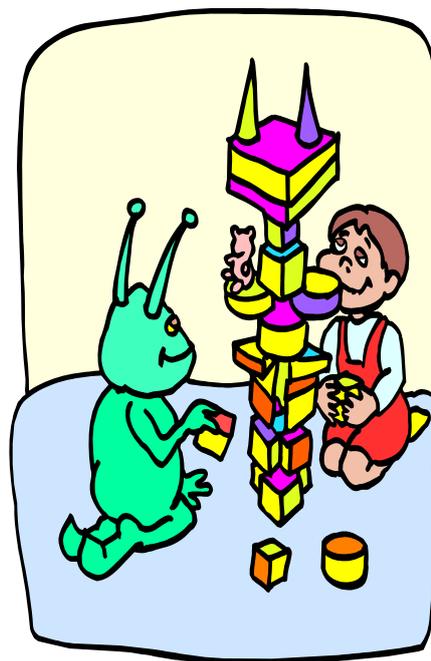
The second is; Bottom – Up approaches: Building what you want by assembling it from building blocks (such as atoms and molecules). Atom-by-atom, molecule-by-molecule, or cluster-by-cluster

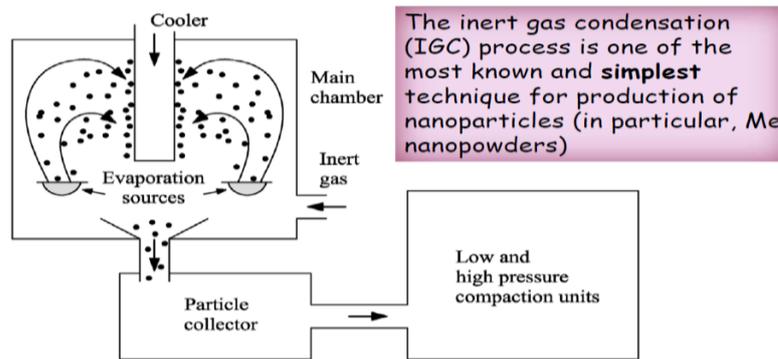
1-Gaseous phase methods

- CVD chemical vapor deposition and MOCVD
- IGC inert gas condensation
- MBE molecular beam epitaxy and MOVPE metal oxide vapor phase epitaxy
- ALD atomic layer deposition
- Flame pyrolysis (Combustion)
- Thermolysis
- Ion Implantation

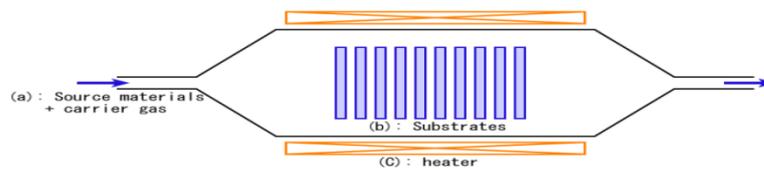
2-liquid phase methods

- MSA molecular self-assembly
- Superamolecular chemistry
- CBD chemical bath deposition
- Sol-gel process
- Single crystal growth
- Electrodeposition/electroplating
- Anodizing
- Molten salt electrolysis
- Hydrothermal
- Polyol
- Colloidal
- Water - oil microemulsions

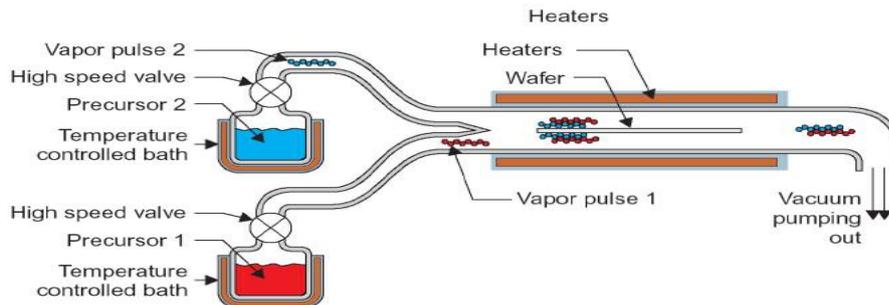




IGC inert gas condensation

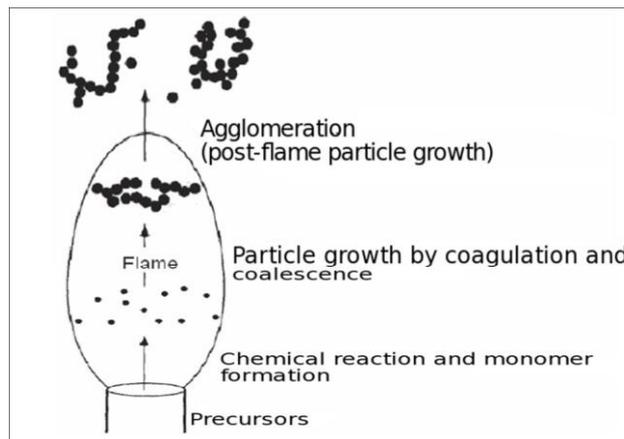


CVD chemical vapor deposition

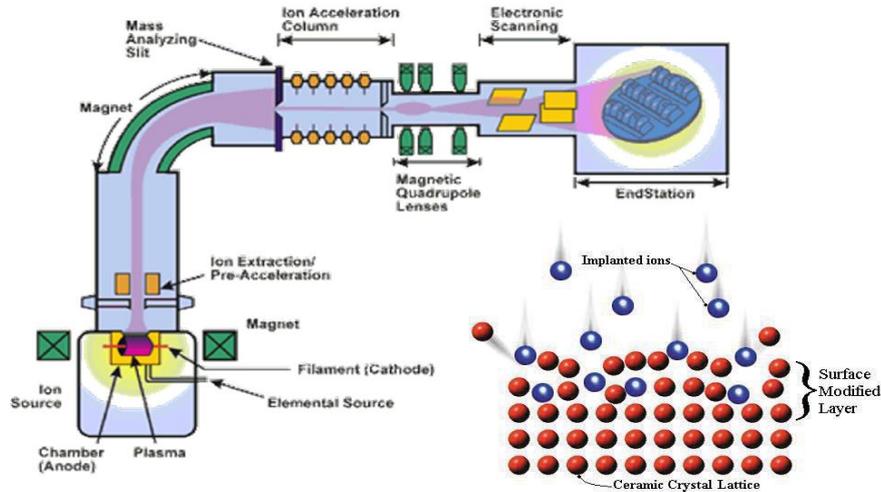


ALD atomic layer deposition

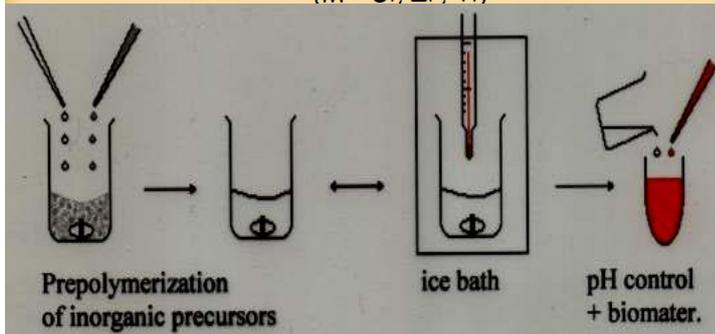
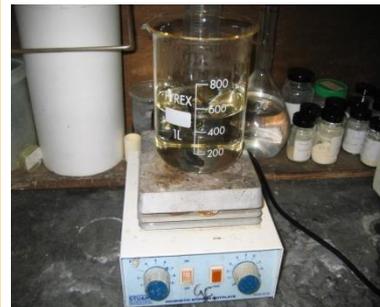
Flame pyrolysis
(Combustion)



ION IMPLANTATION

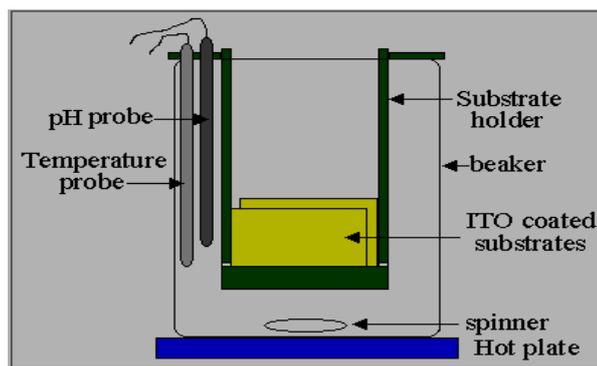


Ion Implantation



Sol-gel

Sol-Gel-Processing formation of Me-O-Me bonds in solution .e. Si-O-Si



CBD chemical bath deposition

Colloidal synthesis

The synthesis of colloidal nanomaterials is based on a three-component system composed of:

precursors, organic surfactants, and solvents

3-solid phase methods

4-biological methods

Section six Chemical Vapor Deposition Techniques (CVD)

Deposition can also take place due to a chemical reaction between some reactants on the substrate. In this case reactant gases (precursors) are pumped in to a reaction chamber (reactor). Under the right conditions (T, P), they undergo a reaction at the substrate. One of the products of the reaction gets deposited on the substrate. The by-products are pumped out.

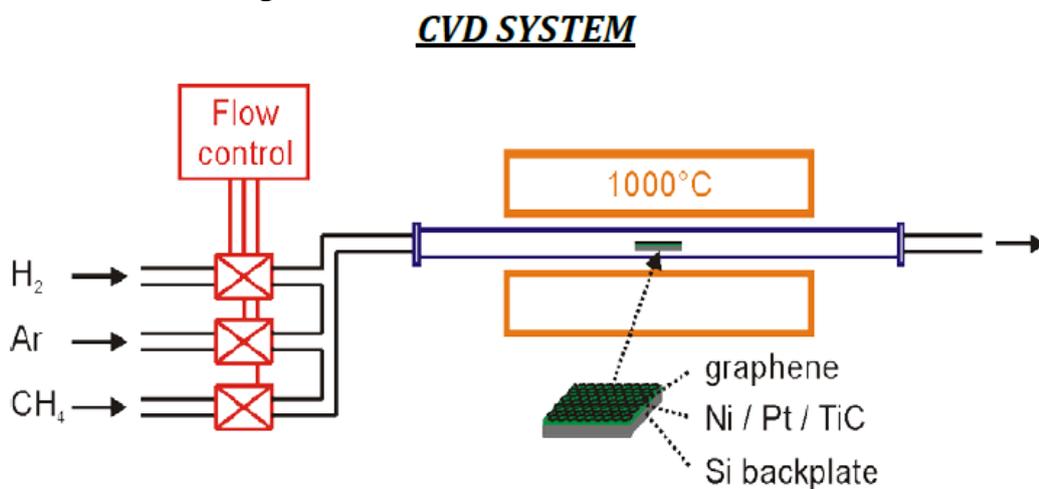
The key parameters are chemical (reaction rates, gas transport, diffusion).

Advantages:

- 1- high growth rates possible
- 2- can deposit materials which are hard to evaporate
- 3- Good reproducibility
- 4- can grow epitaxial films

Disadvantages

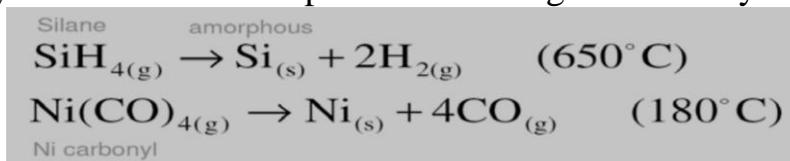
- 1- high temperatures
- 2- complex processes
- 3- Toxic and corrosive gasses



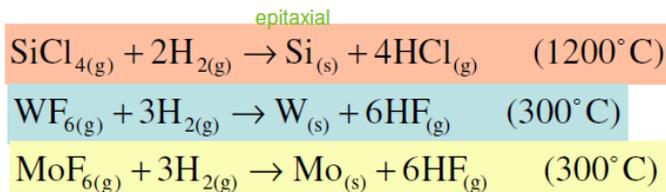
- | | |
|-----------------|---------------------------------|
| 1- GAS SOURCE | 4- SUBSTRATE GASES |
| 2- FLOW CONTROL | 5- FLUE GAS BYPRODUCT TREATMENT |
| 3- FURNACE | 6- VACUUM |

CVD Reaction Types

1- Pyrolysis chemical decomposition or change induced by heat

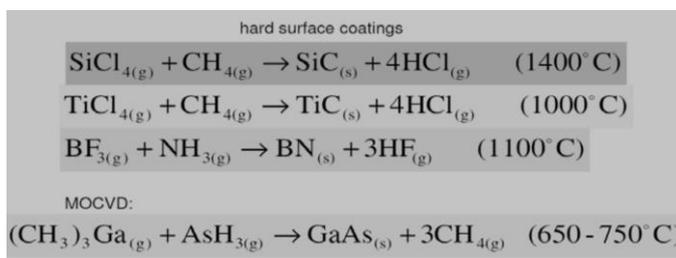
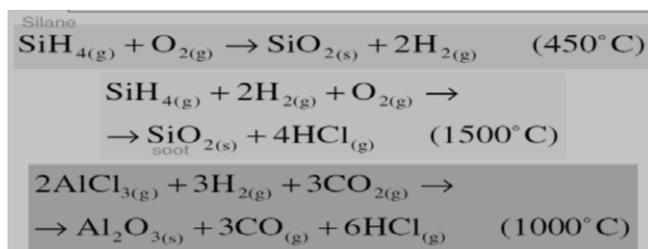


2- Reduction Any process in which electrons are added to an atom or ion (as by removing oxygen or adding hydrogen); always occurs accompanied by oxidation of the reducing agent

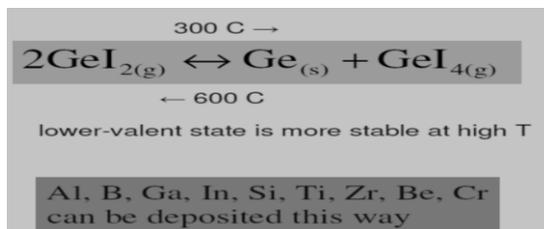


3- Oxidation; Is any electrochemical process which involves the formal oxidation state of an atom or atoms (within a molecule) being increased by the removal of electrons. E.g. iron(II) can be oxidized to iron(III):

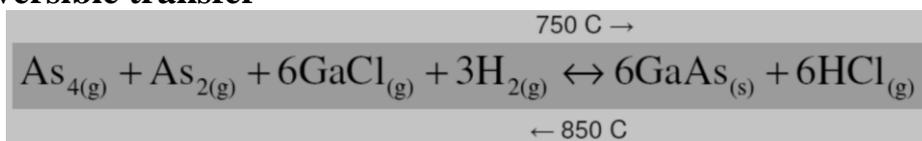
4- Compound formation



4- Disproportionation chemical reaction in which a single substance acts as both oxidizing and reducing agent, resulting in the production of dissimilar substances



6- Reversible transfer



CVD Reactor Types

A- According to the Chamber pressure:

1 - atmospheric-pressure (APCVD);

mass-transport limited region,
fast deposition,
poor step coverage

2- low-pressure (LPCVD)

surface reaction rate limited
excellent purity, uniformity and step coverage
low deposition rates
requires vacuum system

B-according to the Reactor heating type:

1- Hot-wall

Particle contamination (Peel off)
requires periodic cleanup

2 - Cold-wall

no reaction on the wall
difficult to control the real T

C-Plasma-Enhanced CVD

D-FIB-Enhanced CVD

Section seven

Sol-gel technique

Sol-gel can be defined as the formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid; The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. A method was needed where dust was reduced (compared to the ceramic method) and which needed a lower sintering temperature. In addition, it should be possible to do the synthesis by remote control. The main benefits of sol-gel processing are the high purity and uniform nanostructure achievable at low temperatures. And many other advantages can be achieved such as;

- to “dissolve” the compound in a liquid in order to bring it back as a solid in a controlled manner.
- Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds.
- The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, be a gelation reaction.
- Enables mixing at an atomic level.
- Results in small particles, which are easily sinterable.
- enable production of low temperature phases.

A **sol** is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. An aerosol is particles in a gas phase, while a sol is particles in a liquid,

A **gel** consists of a three dimensional continuous network, which encloses a liquid phase, In a colloidal gel, the network is built from agglomeration of colloidal particles

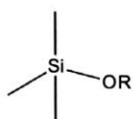
The Colloidal (particulate) gels = agglomeration of dense colloidal particles

Any sol-gel procedure may include the following steps:

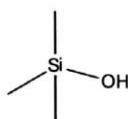
1- Hydrolysis of molecules. Formation of a sol.

2- Condensation or sol-gel transformation

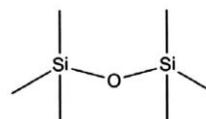
For example ; The starting point for formation of a silica gel may be alkoxides or silanols. These are reacted to siloxane group.



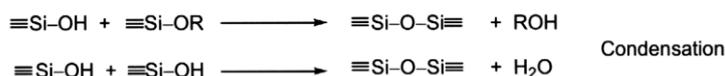
Alkoxide



Silanol



Siloxane



The condensation process is dynamic, and may be steered in the desired direction by adjusting the proper parameters.

Parameters which influences the condensation process:

a- Type of precursor

The stability and reactivity of the silicon alkoxides are influenced by a steric factor. Bulky ligands slow down the hydrolysis:



b- The ratio between alkoxide and water (R_w); **The water ratio, R_w . (OR/H₂O)**



The reaction states that a water ratio of $R_w = 2$ (OR/H₂O) is needed to convert everything to SiO₂. A water ratio of $R_w=1$ leads to complete hydrolysis but no condensation.

Increasing the water content (i.e. lower R_w) will reduce condensation

Reducing the water content increases the condensation

c- Type of catalyst used

The electron density on Si will influence the reaction rate.



Acid catalyzed reaction demands high electron density

Base catalyzed reaction demands low electron density

This results in:

Acid catalyzed: **more straight chains**

Base catalyzed: **more branched network**

d- Type of solvent and ratio; the polarity, dipolar moment, viscosity, protolytic/non protolytic properties are important for the reactions taking place.

Polar solvents stabilize polar gels by hydrogen bonding.

Non-polar solvents are better for systems which are not completely hydrolyzed.

e- Temperature

f- pH

g- Relative and absolute concentrations of the reactants.

3- Gelation

During reaction, objects will grow. However, a gel may not form As the sol aggregates the viscosity will increase until a gel is formed. The sol-gel transition (gel-point) is reached when a continuous network is formed.

The gel-time is determined as the time when it is possible to turn the container upside-down. All fluid is kept in the gel, and the volume is maintained.

4- Ageing; structure modifications with time depending on temperature, solvent and pH conditions. When the gel is formed, a large number of sol particles and clusters will still not have reacted. Ageing of the gel is therefore a very important stage in the process. The gel point is not a thermodynamic event. As the viscosity rapidly increases, the solvent is “trapped” inside the gel. The structure may change considerably with time, depending on pH, temperature and solvent. The gel is still “alive”. The liquid phase still contains sol particles and agglomerates, which will continue to react, and will condense as the gel dries. The gel is originally flexible. Groups on neighbouring branches will condense, making the gel even more viscous. This will squeeze out the liquid from the interior of the gel, and shrinkage occurs. This process will continue as long as there is flexibility in the gel.

5- Drying

Removing of the solvent phase. Method influenced by the intended use of the dried material : When the liquid is removed from the gel several things may happen. When the liquid in the gel is replaced by air, major changes to the network structure may occur.

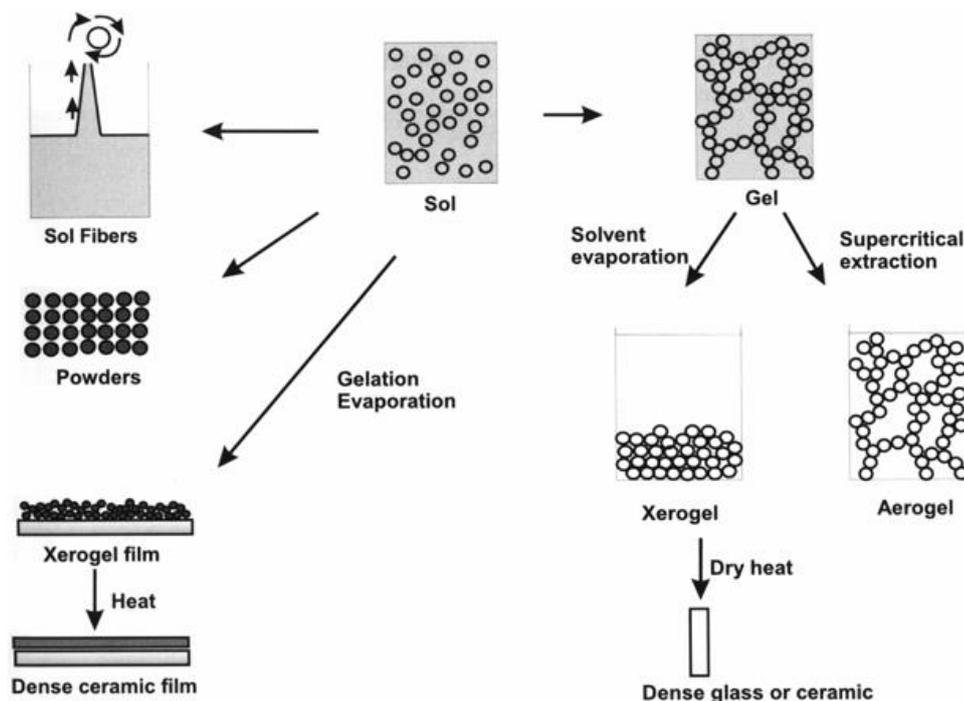
If the structure is maintained, an **aerogel** is formed. If the structure collapses, a **xerogel** is formed. Normal drying of the gel leads to structural collapse due to capillary forces drawing the walls of the pores together, and reducing the pore size. Cracking may occur when the tension in the gel is so large that it cannot shrink anymore. Gas will enter the pores with a thin film of liquid on the walls. This will evaporate and only isolated spaces with liquid are left.

6- Densification

heating to convert the dried gel to a dense ceramic. For silica gels, the following reactions occur :

- desorption of physically adsorbed solvent and water from the walls of micropores (100-200°C)
- decomposition of residual organic groups into CO₂ (300- 500°C)
- collapse of small pores (400-500°C)
- collapse of larger pores (700-900°C)
- continued polycondensation (100-700°C)

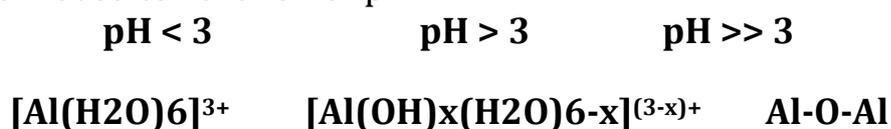
Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films.



If the gel is dried by evaporation, then the capillary forces will result in shrinkage, the gel network will collapse, and a **xerogel** is formed.

If drying is performed under supercritical conditions, the network structure may be retained and a gel with large pores may be formed. This is called an **aerogel**, and the density will be very low ($< 0.005 \text{ g/cm}^3$).

Metals may be used for formation of gels, almost as silicon. However, many metals will form oxides when increasing pH. The water molecules of the hydrated metal ions are more acidic than for Si, and hydrolyses will occur. The reactions are moved toward lower pH.

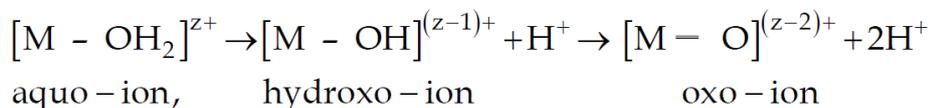


Types of precursors;

1- Metal (Si, Ti, Zr, Al, B...) alkoxides precursors: the metal-organic route with metal alkoxides in organic solvent are largely used. The reactions are all similar to the ones above reported for silicon alkoxides. The mechanism are also similar to the ones described, in the following, for the silicon alkoxides, based on nucleophilic attack to the central atom.

2- Inorganic salts; also, very often used the inorganic route with metal salts in aqueous solution (chloride, oxychloride, nitrate..) : much cheaper and easier to handle than metal alkoxides, but their reactions are more difficult to control, salts in water give, in fact, solvated cations. The charge transfer from

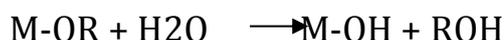
the bonding orbitals of water molecules to empty d orbitals of transition metal makes the water molecule more acidic.



General mechanisms in the metal-organic route

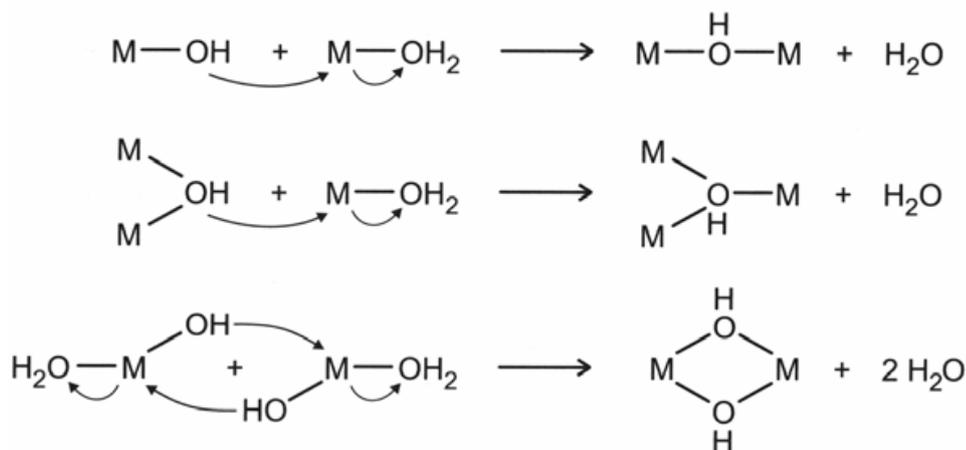
Based on the growth of **metal oxo polymers** in a solvent " inorganic step polymerization reactions through hydrolysis and condensation of metal alkoxides M(OR)_Z, where M = Si, Ti, Zr, Al, Sn, Ce., OR is an alkoxy group and Z is the valence or the oxidation state of the metal

first step : hydroxylation upon the **hydrolysis** of alkoxy groups :



second step : polycondensation process leading to the formation of branched oligomers and polymers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy groups ; 2 competitive mechanisms :

1-Olation: Hydroxy bridges are formed by nucleophilic substitution, where an OH group attacks and water leaves. It is important that water is not coordinated too hard to the metal in order for this reaction to occur. The smaller the charge and the larger the metal ion, the larger the olation rate.



Oxolation is a condensation reaction where an oxo-bridge is formed. If the metal is under-coordinated, the oxolation happens by fast nucleophilic addition reactions: A network may be formed via two routes:



Applications and limitations of sol-gel techniques

Advantages

- 1- Sol-gel processes allow the synthesis of ceramics of **high purity**, because organometallic alkoxy precursors can be purified by distillation or recrystallisation
- 2- **high degree of homogeneity**, because reagents are mixed at the molecular level
- 3- **low or high porosity**, by using appropriate heat treatment and firing times
- 4- **the ability to prepare glasses** of materials which cannot be obtained as amorphous solids by cooling from the liquid state
- 5- **the capability of obtaining fully-dense amorphous solids** at temperatures lower by hundreds of centigrade degrees than those required for conventional compaction/densification or for melting
- 6- **the ability to obtain materials with novel distributions** of phases contained therein...

Disadvantages (drawbacks):

- 1- **high cost** for the majority of alkoxide precursors
- 2- **long processing times**
- 3- **volatiles production**
- 4- **shrinkage**
- 5- development of stresses leading to **fragmentation**

Applications:

A-novel glasses produced from gel precursors, The physical properties of gel-derived glasses are usually closely similar to those of glasses obtained from the melt. The most attractive feature is the development of novel glass compositions : CaO-SiO₂ or Na₂O-ZrO₂-SiO₂ with high ZrO₂ content, which simply cannot be obtained from the melt because the cooling rate must be very high to avoid detectable crystallization.

B-fibers : using appropriate hydrolysis conditions, continuous fibers may be drawn from solutions of metal alkoxides and converted to glass fibers by heating

(ex : ZrO₂-SiO₂ or Na₂O-ZrO₂-SiO₂). Fibers can also be prepared by extruding gelled solutions (colloidal as well as polymeric gels) through dies of appropriate diameter (ex : polycrystalline alumina, microcrystalline Al₂O₃-Cr₂O₃-SiO₂, mullite 3Al₂O₃& 2SiO₂, aluminum borosilicate 3Al₂O₃&B₂O₃&3SiO₂)

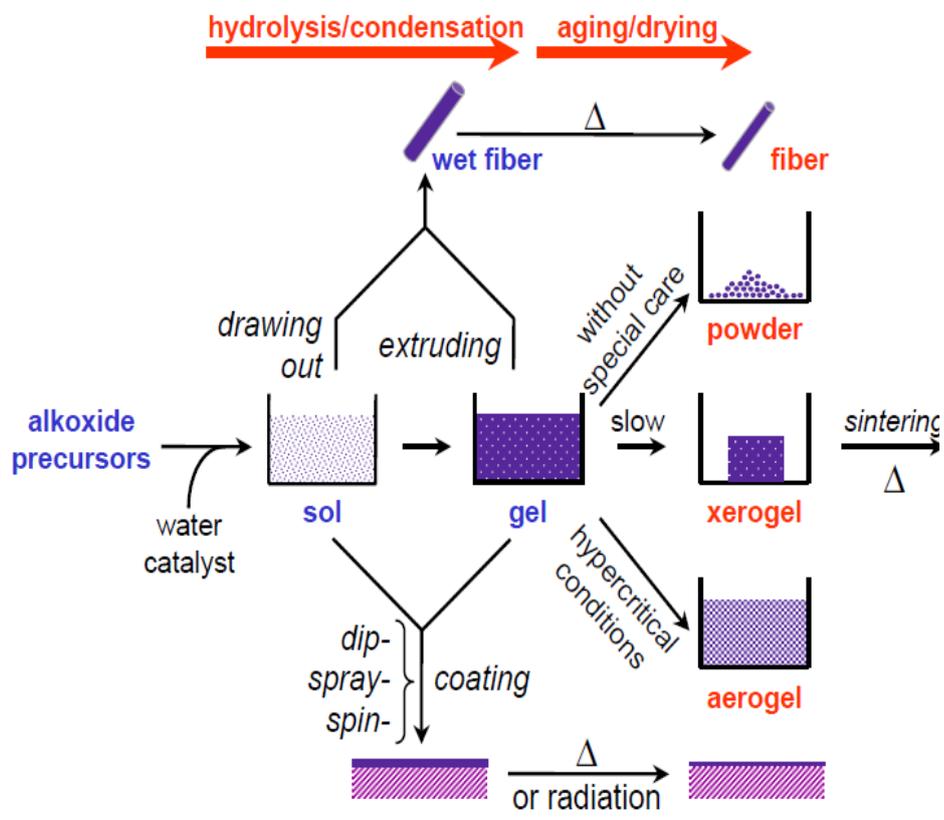
C-abrasives : after gelation and drying, the material is crushed (a simple process with frangible dried gel) and sized. The sized powders are then fired. In this way, Al₂O₃ abrasive 1 – 18 particles with uniformly dispersed ZrO₂ particles and a very fine grain size (< 300 nm) can be obtained. Such abrasive particles have superior grinding performance compared with fused or sintered Al₂O₃-based abrasives in a number of applications

D-thin films and coating : the permissible drying rates, consistent with the avoidance of fracture, were evaluated and found to vary inversely with the thickness of the body being dried. This limitation leads naturally to the main use of gels in **coating applications**, where the thickness are small and the drying rates can be correspondingly high. Some of the coating-type applications which seem well suited

for sol-gel techniques include :

- 1- **antireflection coatings** (single layer or multilayer films)
- 2- **absorbing coatings**
- 3- **filters** for lighting and optical purposes
- 4- **semiconducting coatings**
- 5- **protective layers** (both chemical and thermal)
- 6- **independent films**, prepared by; - " pouring alkoxide solutions onto liquids which do not mix with the solution and allowing the film to hydrolyze , - pouring the solution onto non-wetting surfaces such as Teflon - forming films using wire rings with solutions of appropriate viscosity

summary of sol-gel process, techniques and products



Section eight

Nanostructure Identification

(nano identification Techniques)

As the nanomaterials are not new as for centuries, the preparing & using nanoparticles during that period were lacking of the powerful instrument which measure size of particles & correlation of properties. Recently new techniques are evolved for characterization and analysis of nanomaterials which gives a revolution to development of nanochemistry and Nanotechnology. some of these techniques used for analysis & characterization of nanomaterials include;

- 1- Diffraction Techniques (XRD); Diffraction techniques are often used in average particle size analysis as well as structural determination. Some of the diffraction techniques are;
 - X-ray Diffraction (XRD),
 - electron diffraction
 - small angle X-ray Scattering (SAXS),and
 - small angle Neutron scattering (SANS).

- 2- Electron Microscopy
 - A- Scanning Electron Microscope(SEM)
 - B- Transmission Electron Microscope(TEM)

- 3- Scanning Probe Microscope(SPM)
 - A- Atomic Force Microscope(AFM)
 - B- Scanning Tunneling Microscope(STM)

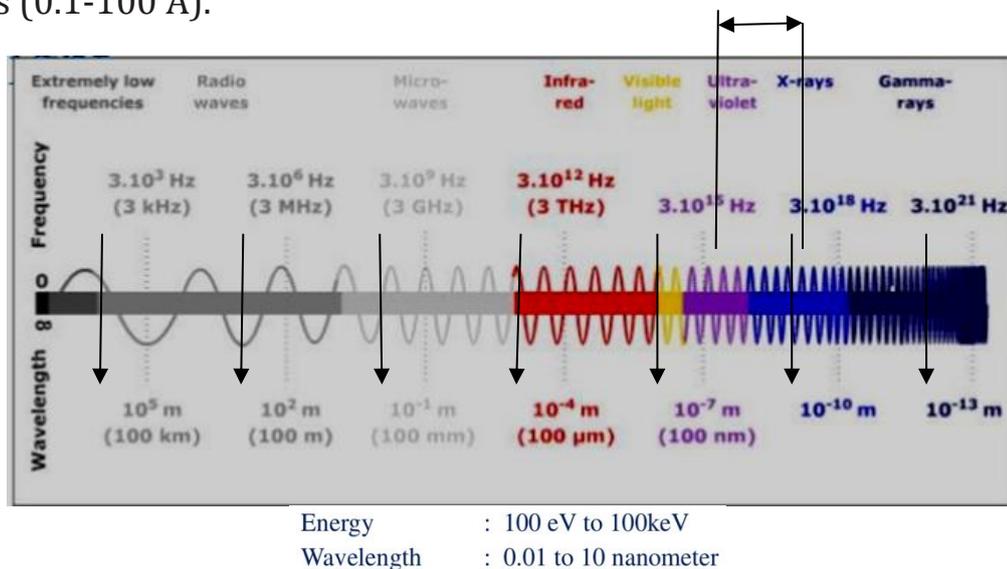
Characteristic Information

- **Crystallographic Information(XRD,SEM,AFM)**
How the atoms are arranged in the object.
- **Topography (SEM,AFM)**
The surface features of an object or "how it looks", its texture.
- **Morphology(SEM,TEM,AFM)**
The shape and size of the particles making up the object.
- **Composition(XRD,XRF,AAS)**

The elements and compounds that the object is composed of and the relative amounts of them;

1- X-ray Diffraction (XRD)

X-rays are electromagnetic waves with a wavelength in the range of interatomic distances (0.1-100 Å).



This match of length scales makes them suitable for the study of crystalline materials. For single-phase materials the crystal structure can be obtained directly using X-Ray diffraction (XRD). With the help of a database of known structures XRD can be used for phase identification. Also crystal size, strain and preferred orientation of polycrystalline materials can be measured. The related technique of X-ray reflection enables accurate determination of film thickness.

the uses and applications are:

- 1- phase identification
- 2- texture or preferential orientation
- 3- crystallite size and residual stress
- 4- in-situ temperature and pressure studies
- 5- high resolution diffraction
- 6- layer thickness measurements

Principles

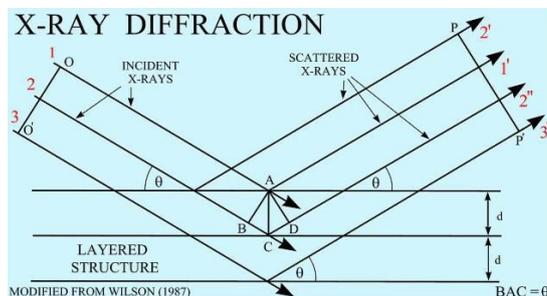
When X-ray radiation is directed on a sample, the X-rays are scattered (“diffracted”) by electrons present in the material. If the atoms in the material are arranged in a regular structure, i.e. if the material is crystalline, this scattering results in maxima and minima in the diffracted intensity. The signal maxima follow Bragg’s law

$$n\lambda = 2d \sin\theta$$

example; $\lambda = 1.54 \text{ \AA}, 2\theta = 38$

$$d = 1.54 \text{ \AA} / (2 * \sin (38 / 2)) = 2.35 \text{ \AA}$$

Here n is an integer, λ is the X-ray wavelength, d is the distance between crystal lattice planes and θ is the diffraction angle.



When the intensity of detected X-rays is plotted as a function of angle θ an X-ray diffraction pattern is obtained, which is characteristic for the sample material thin layers of only a few nanometers can be investigated. Phase identification can be done by matching the XRD pattern with reference patterns of pure substances. The width of a diffraction peak is influenced by the crystallite size: a large crystallite size causes sharp reflections, whereas a small size leads to broad reflections. The effect crystal size can have on an XRD pattern is shown in the figure below.

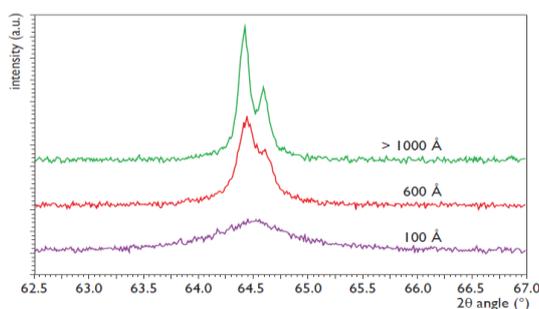
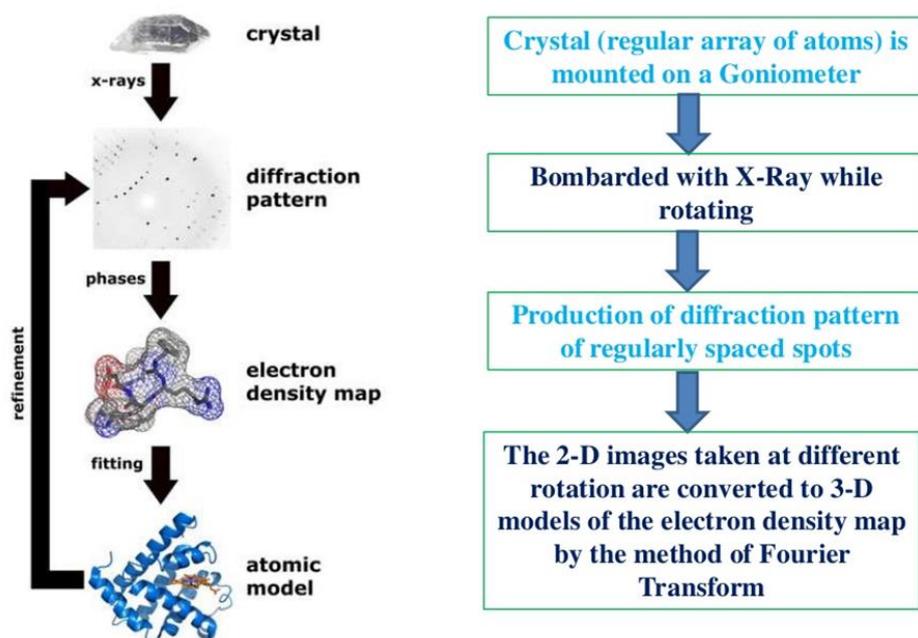


Fig. 4: XRD peak profiles of polycrystalline silver with different crystallite sizes.

The working steps of XRD are shown in the following diagram;



Calculation of crystalline size (thickness) by Scherrer equation;

$$t = \frac{K * \lambda}{B * \cos \theta_B}$$

t = thickness of crystallite

K = constant dependent on crystallite shape (0.89)

λ = x-ray wavelength

B = FWHM (full width at half max) or integral breadth

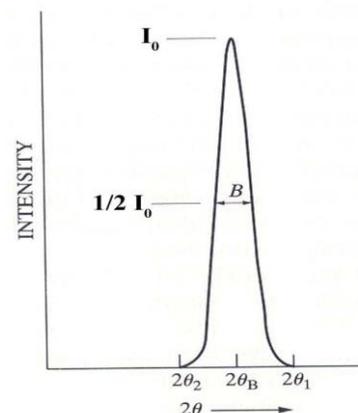
θ_B = Bragg angle

Note; 20%-30% accuracy at best.

Example; $\lambda = 1.54 \text{ \AA}$, $2\theta = 98.25$, $B = 0.1^\circ$

$$B = (0.1^\circ) * \pi / 180 = 0.00174$$

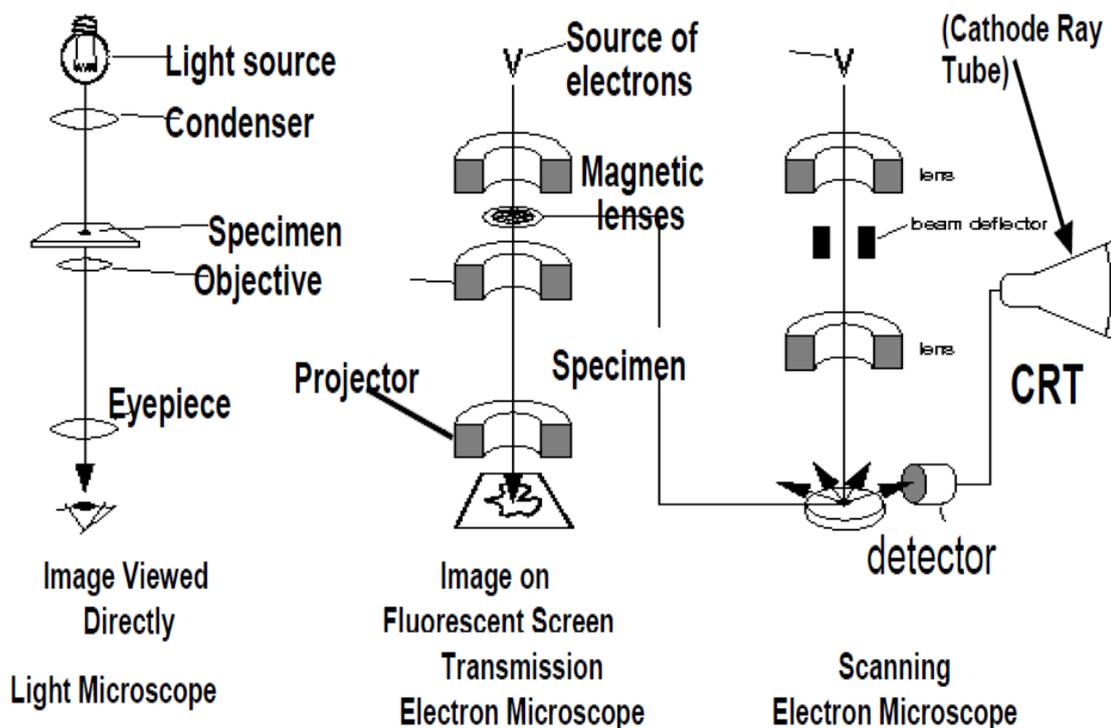
$$t = 0.89 * \lambda / (B \cos \theta_B) = 0.89 * 1.54 \text{ \AA} / (0.00174 * \cos (98.25 / 2)) = 1200 \text{ \AA}$$



2- Electron Microscope (SEM & TEM)

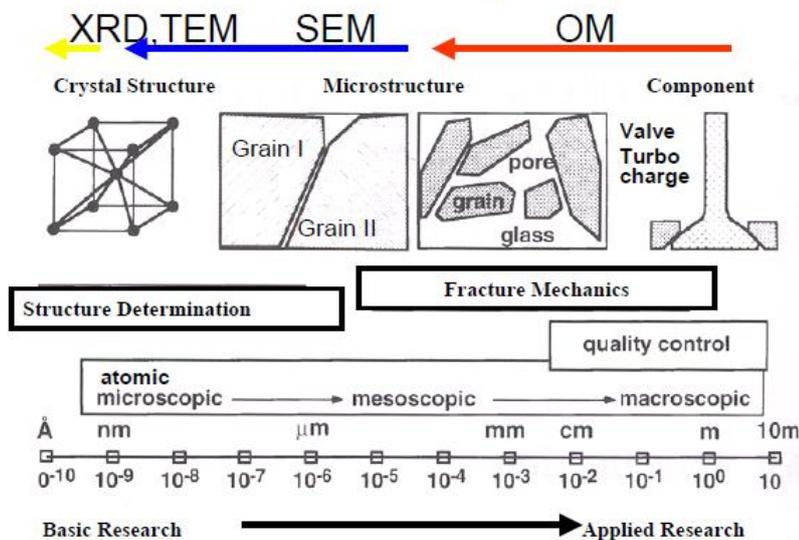
- Electron microscopes are scientific instruments that use a beam of energetic electrons to examine objects on a very fine scale.
- Electron microscopes were developed due to the limitations of Light Microscopes which are limited by the physics of light.
- In the early 1930's this theoretical limit had been reached and there was a scientific desire to see the fine details of the interior structures of organic cells (nucleus, mitochondria...etc.).
- This required 10,000x plus magnification which was not possible using current optical microscopes.

Comparison of OM,TEM and SEM



The transmission electron microscope (TEM) was the first type of Electron Microscope to be developed and is patterned exactly on the light transmission microscope except that a focused beam of electrons is used instead of light to "see through" the specimen

Scale and Microscopy Techniques



Advantages of Using SEM over OM

	Mag	Depth of Field	Resolution
OM:	4x – 1400x	0.5mm	~ 0.2mm
SEM:	10x – 500Kx	30mm	1.5nm

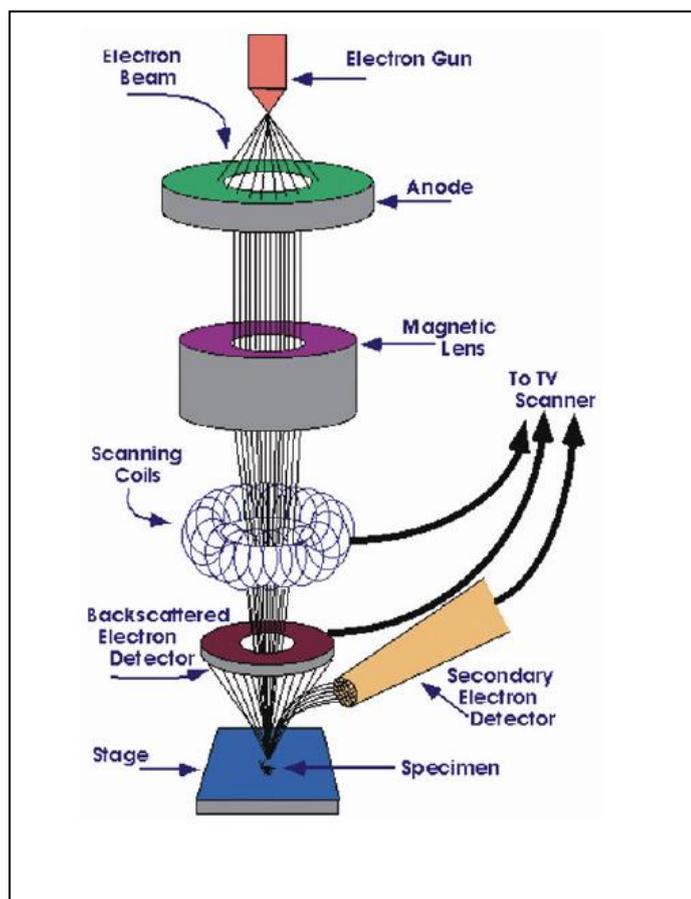
The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time and produces an image that is a good representation of the three-dimensional sample.

The combination of higher magnification, larger depth of field, greater resolution, compositional and crystallographic information makes the SEM one of the most heavily used instruments in academic/national lab research areas and industry.

Electron Microscope Components:

1. Electron optical column consists of:
 - electron source to produce electrons
 - magnetic lenses to de-magnify the beam
 - magnetic coils to control and modify the beam
 - apertures to define the beam, prevent electron spray, etc.
2. Vacuum systems consists of:
 - sample chamber which "holds" vacuum, pumps to produce vacuum
 - valves to control vacuum, gauges to monitor vacuum
3. Signal Detection & Display consists of:
 - detectors which collect the signal
 - electronics which produce an image from the signal

- 4- Infrastructure Requirements: Power Supply, Cooling system, Vibration-free floor, Room free of ambient magnetic and electric fields



3- Scanning Probe Microscopy (SPM)

Scanning probe microscopy covers several related technologies for imaging and measuring surfaces on a fine scale, down to the level of molecules and groups of atoms. At the other end of the scale, a scan may cover a distance of several micrometers in the x and y directions few micrometers in the z direction. SPM technologies share the concept of ;

- 1- scanning an extremely sharp tip (3-50 nm radius of curvature) across the object surface.
- 2- The tip is mounted on a flexible cantilever, allowing the tip to follow the surface profile .
- 3- When the tip moves in proximity to the investigated object, forces of interaction between the tip and the surface influence the movement of the cantilever.
- 4- These movements are detected by selective sensors. Various interactions can be studied depending on the mechanics of the probe.

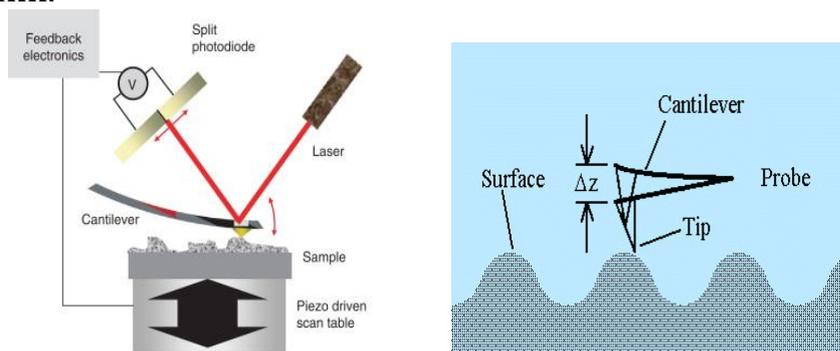
The two most common scanning probe techniques are:

First; Atomic Force Microscopy (AFM) measures the interaction force between the tip and surface. The tip may be dragged across the surface, or may vibrate as it moves. The interaction force will depend on the nature of the sample, the probe tip and the distance between them.

Second; Scanning Tunneling Microscopy (STM) measures a **weak electrical current** flowing between tip and sample as they are held a very distance apart

Atomic Force Microscopy

The Atomic Force Microscope was developed to overcome a basic drawback with STM - that it can only image conducting or semiconducting surfaces. The AFM, however, has the advantage of imaging almost any type of surface, including polymers, ceramics, composites, glass, and biological samples. Most AFMs use a laser beam deflection system, where a laser is reflected from the back of the reflective AFM lever and onto a position-sensitive detector. AFM tips and cantilevers are microfabricated from Si or Si₃N₄. Typical tip radius is from a few to 10s of nm.

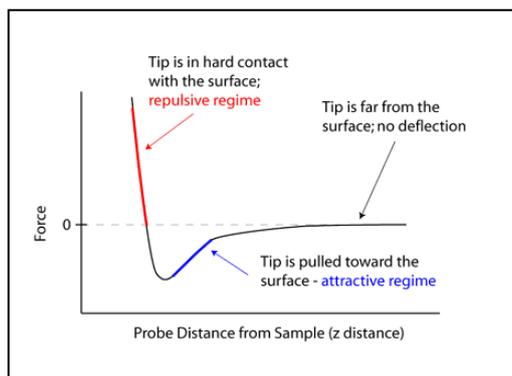


Beam deflection system, using a laser and photodetector to measure the beam position.

Because the atomic force microscope relies on the forces between the tip and sample, knowing these forces is important for proper imaging. The force is not measured directly, but calculated by measuring the deflection of the lever, and knowing the stiffness of the cantilever. Hook's law gives

$$F = -kz,$$

where F is the force, k is the stiffness of the lever, and z is the distance the lever is bent.



Operation Modes of AFM

1-Contact Mode: contact mode is widely used for small, high-speed atomic resolution scans and is known as variable-deflection mode. As the tip is raster-scanned across the surface, it is deflected as it moves over the surface corrugation. In constant force mode, the tip is constantly adjusted to maintain a constant deflection, and therefore constant height above the surface because the tip is in hard contact with the surface, the stiffness of the lever needs to be less than the effective spring constant holding atoms together, which is on the order of 1 - 10 nN/nm. Most contact mode levers have a spring constant of $< 1\text{N/m}$.

2-Noncontact mode“tapping mode”**;** Noncontact use of an oscillating cantilever. A stiff cantilever is oscillated in the attractive regime, meaning that the tip is quite close to the sample, but not touching it (hence, “noncontact”). The forces between the tip and sample are quite low, on the order of pN (10^{-12} N). The detection scheme is based on measuring changes to the resonant frequency or amplitude of the cantilever.

Part of the oscillation extends into the repulsive regime, so the tip intermittently touches or “taps” the surface. Very stiff cantilevers are typically used, as tips can get “stuck” in the water contamination layer. The advantage of tapping the surface is improved lateral resolution on soft samples. Lateral forces such as drag, common in contact mode, are virtually eliminated. For poorly adsorbed specimens on a substrate surface the advantage is clearly seen.

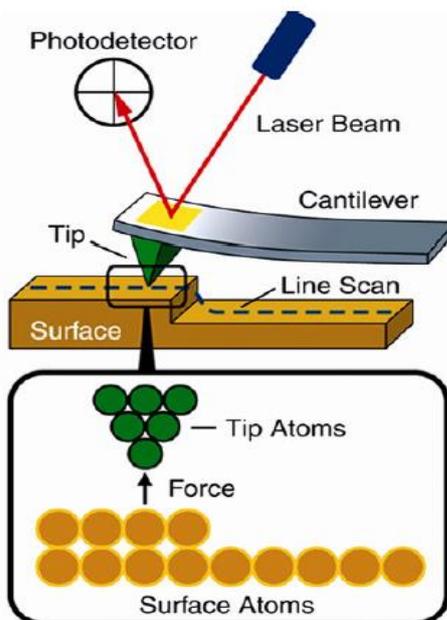


Fig. 7— Schematic diagram of AFM¹¹

Scanning-Tunneling Microscope

STM provides atomic-scale resolution of surfaces and is also being developed to move atoms on surfaces. STM relies on a purely quantum-mechanical phenomenon: tunneling. The main components are drawn in ;

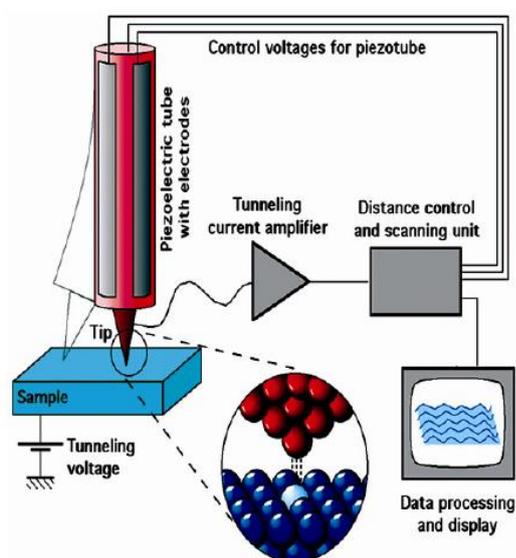


Fig. 10— Schematic view of an STM¹⁷

A limitation of the STM is the requirement for a conducting sample. The STM relies on the fact that electrons near surfaces have wave functions which decay into the vacuum outside the surface boundary the microscope consists on a conducting tip(W or Pt-Ir) connected to a current-measuring circuit. When the

tip is in close proximity to the surface (≈ 1 nm), the decaying wave function from the surface could overlap with the tip, i.e., the surface electron has a finite probability of being in the tip. Since the latter is conducting, the electron under a voltage V (1-10 V) can then move creating a current. This current is known as a tunneling current whose magnitude (as for all tunneling currents) is very sensitive to the surface-tip separation.

The STM has also been used to carry out chemical reactions on surfaces. This relies on a tip-sample interaction. The force can be either attractive or repulsive.

Section nine

Important Historical Events in Nanoscience

Early examples

Early examples of nanostructured materials were based on craftsmen's empirical understanding and manipulation of materials. Use of high heat was one common step in their processes to produce these materials with novel properties.

4th Century:

The **Lycurgus Cup** (Rome) is an example of **dichroic glass**; colloidal gold and silver in the glass allow it to look opaque green when lit from outside but translucent red when light shines through the inside.



9th-17th Centuries:

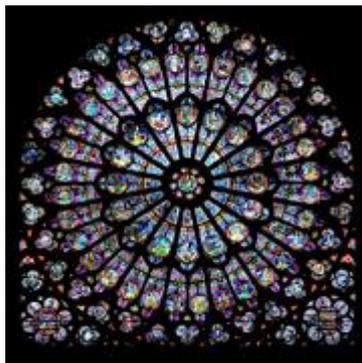
Glowing, glittering **“luster” ceramic glazes used in the Islamic world**, and later in Europe, contained silver or copper or other metallic nanoparticles.



*Polychrome
lustreware bowl,
9th C, Iraq,
British Museum*

6th-15th Centuries:

Vibrant **stained glass windows** in European cathedrals owed their rich colors to nanoparticles of gold chloride and other metal oxides and chlorides; gold nanoparticles also acted as **photocatalytic air purifiers**.



*The South
rose window
of Notre
Dame
Cathedral,
ca 1250*

13th-18th Centuries:

“**Damascus**” **saber blades** contained carbon nanotubes and cementite nanowires—an ultrahigh-carbon steel formulation that gave them strength, resilience, the ability to hold a keen edge, and a visible moiré pattern in the steel that give the blades their name.



(Left) A Damascus saber (photo by Tina Fineberg for The New York Times).
(Right) High-resolution transmission electron microscopy image of carbon nanotubes in a genuine Damascus sabre after dissolution in hydrochloric acid, showing remnants of cementite nanowires encapsulated by carbon nanotubes (scale bar, 5 nm)

1857

Michael Faraday discovers colloid gold

This suspension of gold nanoparticles in solution was totally transparent in some lighting, but in other lighting conditions could produce differently coloured solutions of ‘ruby, green, violet or blue.



1905

Albert Einstein explains the existence of colloids

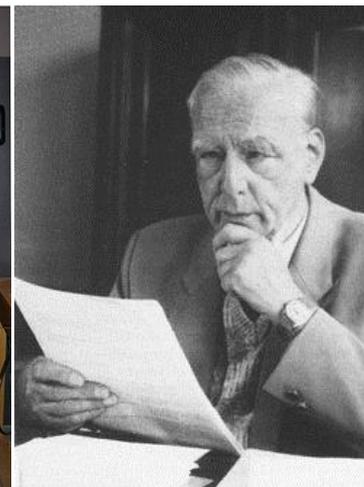
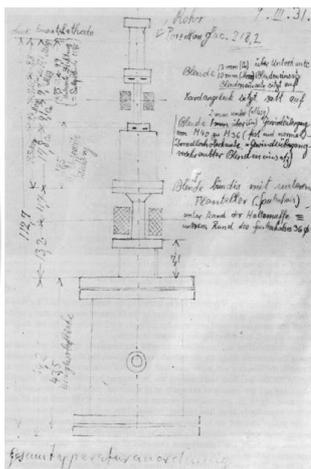
This theory was confirmed by the experiments of Jean-Baptiste Perrin, which contributed toward Perrin's 1926 Nobel prize.

1931

Max knoll & Ernst Ruska: invented Electron microscope



Ernst Ruska
(1906-1988)



1932

Langmuir discovers layers of atoms one molecule thick

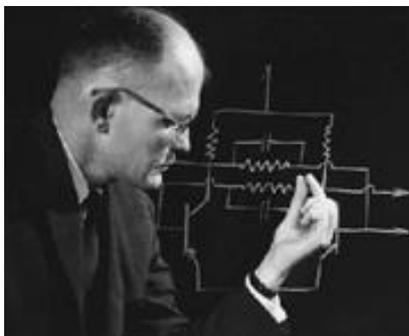
Langmuir established the existence of monolayers (layers of atoms or molecules one atom thick). These monolayers have peculiar two-dimensional qualities, and led to the development of a totally transparent glass produced by forming a thin film of fluorine compound on the surface. He was awarded the Nobel prize in 1932 for this work on thin films.

1956

Arthur von Hippel at MIT introduced many concepts of—and coined the term—“molecular engineering” as applied to dielectrics, ferroelectrics, and piezoelectrics

1958

Jack Kilby of Texas Instruments originated the concept of, designed, and built the first integrated circuit, for which he received the Nobel Prize in 2000.



1959

Feynman suggests that there is ‘plenty of room’ to work at the nanoscale

Richard P. Feynman gave a ground-breaking speech ‘There’s plenty of room at the bottom’ where he discussed the possibility of controlling materials at the level of atoms and molecules – this was the first vision of the possibilities of science and technology at the nanoscale. He became a Nobel laureate in 1965.



1965

Intel co-founder Gordon Moore described in *Electronics* magazine several trends he foresaw in the field of electronics. One trend now known as “**Moore’s Law**,” described the density of transistors on an integrated chip (IC) doubling every 12 months (later amended to every 2 years). Moore also saw chip sizes and costs shrinking with their growing functionality—with a transformational effect on the ways people live and work. That the basic trend Moore envisioned has continued for 50 years is to a large extent due to the semiconductor industry’s increasing reliance on nanotechnology as ICs and transistors have approached atomic dimensions.

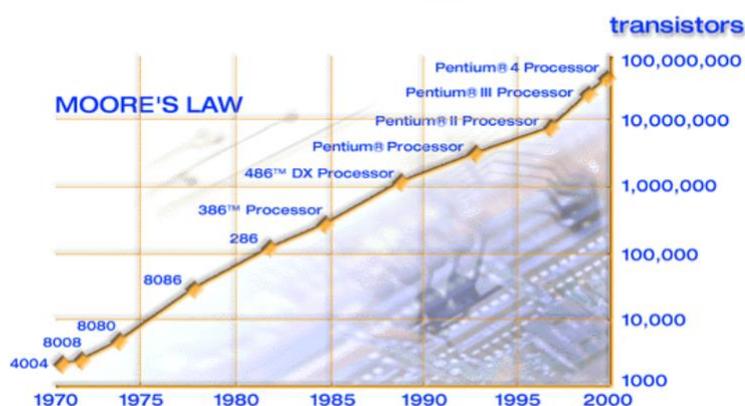
Moore's Laws:

Gordon Moore, one of the founders of the Intel corporation, came up with two empirical laws to describe the amazing advances in integrated circuit electronics.

Moore's first law says that the amount of space required to install a transistor on a chip shrinks by roughly half every 18 months.

Moore's second law, the cost of building a chip manufacturing plant doubles with every other chip generation, or roughly every 36 months.

Moore's Law Holding!



1974

Norio Taniguchi (University of Tokyo) The word 'nanotechnology' first used

The term 'nanotechnology' was coined in 1974. He used the word to refer to 'production technology to get the extra high accuracy and ultra fine dimensions, i.e. the preciseness and fineness on the order of 1 nm (nanometre).

1981

IBM invent a machine which can move single atoms around

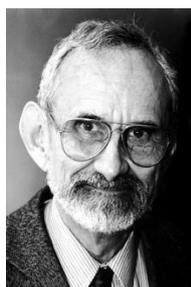
Gerd Binnig and Heinrich Rohrer invented the Scanning Tunneling Microscope (STM) at IBM. They were awarded the Nobel prize in 1986 for this work. **at the Zurich Research Lab in 1981**



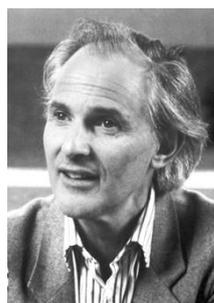
1985

A new form of carbon is discovered: C60

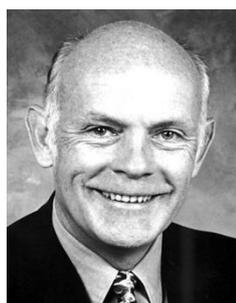
Richard Smalley, Robert Curl and Harold Kroto discovered C60 for which they were awarded the Nobel Prize in 1996. C60 is more commonly known as a buckyball as the 60 carbon atoms are arranged into a sphere made of 12 pentagons and 20 hexagons (exactly like a football).



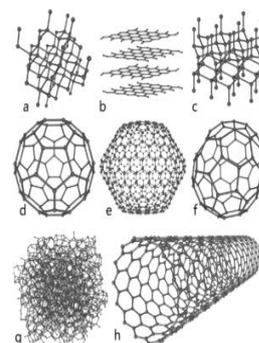
Robert F. Curl Jr



Sir Harold W. Kroto

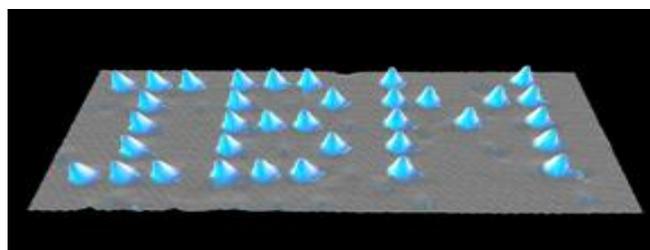


Richard E. Smalley



1986

K.Eric Drexler: writing with a STM tool.



1990

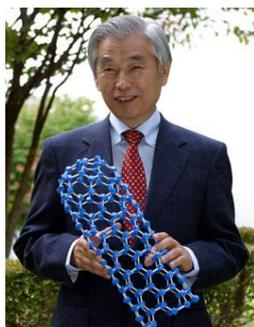
IBM demonstrate ability to control the position of atoms IBM logo in atoms

IBM research scientist Don Eigler showed that the position of atoms could be controlled precisely. Using the STM he maneuvered 35 xenon atoms on a nickel surface so that they spelled out 'IBM'. This was achieved at high vacuum and in the supercooled temperature of liquid helium.

1991

Carbon nanotubes discovered

Sumino Iijima discovered a process to make ‘graphitic carbon needles ranging from 4nm to 30nm in diameter and 1 micron in length.



1992

C.T. Kresge and colleagues at Mobil Oil discovered the **nanostuctured catalytic materials MCM-41 and MCM-48**, now used heavily in refining crude oil as well as for drug delivery, water treatment, and other varied applications.

1993

Professor Richard E. Smalley envisioned the *first nanotechnology center in the world.*

1993

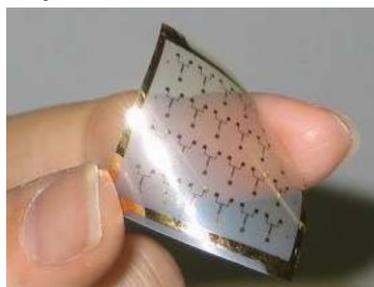
First high-quality quantum dots prepared

Murray, Norris and Bawendi synthesise the first high quality quantum dots of nearly monodisperse CdS CdSe and CdTe quantum dots are very small particles with interesting optical properties.

1997

Lucent Technologies fabricated the ‘nanotransistor’

It was only 60nm wide and 1.2nm thick



1999–early 2000’s:

Consumer products making use of nanotechnology began appearing in the marketplace, including lightweight nanotechnology-enabled automobile bumpers that resist denting and scratching, golf balls that fly straighter, tennis rackets that are stiffer (therefore, the ball rebounds faster), baseball bats with better flex and "kick," nano-silver antibacterial socks, clear sunscreens, wrinkle- and stain-resistant clothing, deep-penetrating therapeutic cosmetics, scratch-resistant glass coatings, faster-recharging batteries for cordless electric tools, and improved displays for televisions, cell phones, and digital cameras.

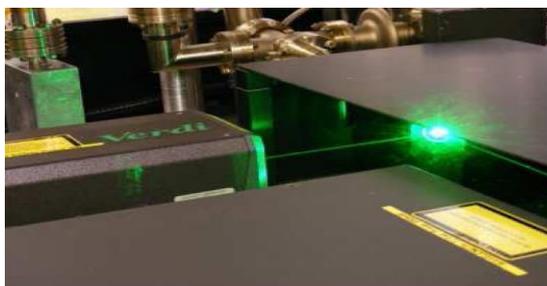


2000

Lucent Technologies with Oxford University created the first DNA motor

2000

Eigler et al: Construction of quantum mirrors



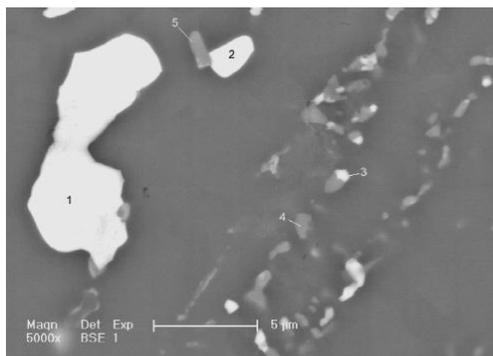
2001

Prototype fuel cell made using nanotubes

Nanohorns, irregularly shaped nanotubes, were developed as fuel cell for hydrogen-based fuel such as methanol. They group together creating a high surface area ideal for catalysts. NEC corporation announced that the latest generation weigh under 2 pounds, when fully fuelled, and power a laptop for 5 hours before needing refuelling.

2001

Florian Bambers: Soldering of nanotube with e-beam.



2002

Stain-repellent trousers reach the high street

Clothing embedded with nanoparticles that produce a stain-repellent coating has been developed. Nano-care™ khakis have the fabric fibres coated with nanowhiskers 10–100nm in length. This new stain-repellent fabric is available from a number of high street retailers and is available in trousers, shirts and ties.

2003

Prototype nano-solar cells produced

Prototype solar cells have been made by Nanosolar Inc. in California. They use conducting polymers and nano-based particles. These cells are also produced in flexible sheets, making them suitable for many applications.

2004

Intel launches the Pentium iv ‘PRESCOFT’ processor based on 90 nm technology.

2005

Erik Winfree and Paul Rothemund from the California Institute of Technology developed theories for **DNA-based computation** and “**algorithmic self-assembly**” in which computations are embedded in the process of nanocrystal growth.

2006:

James Tour and colleagues at Rice University built a **nanoscale car** made of oligo(phenylene ethynylene) with alkynyl axles and four spherical C60 fullerene (buckyball) wheels. In response to increases in temperature, the nanocar moved about

on a gold surface as a result of the buckyball wheels turning, as in a conventional car. At temperatures above 300°C it moved around too fast for the chemists to keep track of it.

2007:

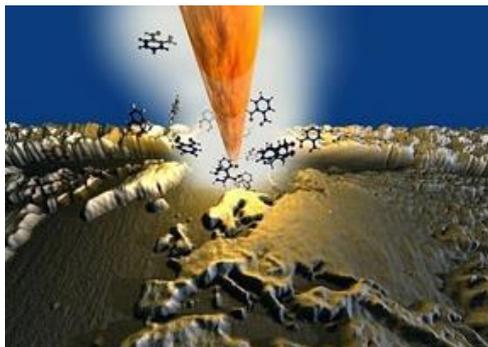
Angela Belcher and colleagues at MIT built a **lithium-ion battery with a common type of virus** that is nonharmful to humans, using a low-cost and environmentally benign process. The batteries have the same energy capacity and power performance as state-of-the-art rechargeable batteries being considered to power plug-in hybrid cars, and they could also be used to power personal electronic devices. (Image at right.)

2009–2010:

Nadrian Seeman and colleagues at New York University created several **DNA-like robotic nanoscale assembly devices**. One is a process for creating 3D DNA structures using synthetic sequences of DNA crystals that can be programmed to self-assemble using “sticky ends” and placement in a set order and orientation. Nanoelectronics could benefit: the flexibility and density that 3D nanoscale components allow could enable assembly of parts that are smaller, more complex, and more closely spaced. Another Seeman creation (with colleagues at China’s Nanjing University) is a “DNA assembly line.” For this work, Seeman shared the Kavli Prize in Nanoscience in 2010.

2010

IBM used a silicon tip measuring only a few nanometers at its apex (similar to the tips used in atomic force microscopes) to chisel away material from a substrate to create a complete nanoscale 3D relief map of the world one-one-thousandth the size of a grain of salt—in 2 minutes and 23 seconds. This activity demonstrated a powerful patterning methodology for generating **nanoscale patterns and structures as small as 15 nanometers** at greatly reduced cost and complexity, opening up new prospects for fields such as electronics, optoelectronics, and medicine. (Image below.)



2013

Stanford researchers develop the first carbon nanotube computer.

Section ten

Application of nanomaterials

A basic understanding of physics and chemistry, and some knowledge of materials science, is necessary to understand the properties and behavior of nanomaterials, the unique properties of nanomaterials encourage belief that they can be applied in a wide range of fields,

The main such properties include;

- 1- Large surface area to volume
Better catalytic efficiency through higher surface-to-volume ratio
- 2- Electrical conductivity
Increased electrical conductivity in ceramics and magnetic nanocomposites, increased electric resistance in metals
- 3- Chemical properties
Corrosion protection for machinery
- 4- Thermal properties
equipment, heat resistance for turbines and engines, thermal insulation equipment and building materials, etc.
- 5- Wetting properties
Antigraffiti, antifouling, Lotus-effect, self-cleaning surface for textiles and ceramics, etc.
- 6- Magnetic properties
Increased magnetic coercivity up to a critical grain size superparamagnetic behaviour
- 7- Mechanical properties
Improved hardness and toughness of metals and alloys ductility and superplasticity of ceramic
- 8- Optical properties
Spectral shift of optical absorption and fluorescence properties, increased quantum efficiency of semiconductor crystals
- 9- Biological properties
Increased permeability through biological barriers (membranes, blood-brain barrier, etc.), improved biocompatibility

Current and emerging applications of nanoparticles

Electronic, optoelectronic magnetic applications	Biomedical, pharmaceutical cosmetic applications	Energy, catalytic structural applications
<ul style="list-style-type: none"> • Chemical–mechanical polishing • Electroconductive coatings • Magnetic fluid seals and recording media • Multilayer capacitors • Optical fibers • Phosphors • Quantum optical devices 	<ul style="list-style-type: none"> • Antimicrobials • Biodetection and labeling • Biomagnetic separations • Drug delivery • MRI contrast agents • Orthopedics/implants • Sunscreens • Thermal spray coatings 	<ul style="list-style-type: none"> • Automotive catalyst • Membranes • Fuel cells • Photocatalysts • Propellants • Scratch-resistant coatings • Structural ceramics • Solar cells

<p>Automotive industry</p> <ul style="list-style-type: none"> • lightweight construction • painting (fillers, base coat, clear coat) • catalysts • tires (fillers) • sensors • Coatings for wind-screen and car bodies 	<p>Chemical industry</p> <ul style="list-style-type: none"> • fillers for paint systems • coating systems based on nanocomposites • impregnation of papers • switchable adhesives • magnetic fluids 	<p>Engineering</p> <ul style="list-style-type: none"> • wear protection for tools and machines (anti blocking coatings, scratch resistant coatings on plastic parts, etc.) • lubricant-free bearings
<p>Electronic industry</p> <ul style="list-style-type: none"> • data memory (MRAM, GMR-HD) • displays (OLED, FED) • laser diodes • glass fibres • optical switches • filters (IR-blocking) • conductive, antistatic coatings 	<p>Construction</p> <ul style="list-style-type: none"> • construction materials • thermal insulation • flame retardants • surface-functionalised building materials for wood, floors, stone, facades, tiles, roof tiles, etc. • facade coatings • groove mortar 	<p>Medicine</p> <ul style="list-style-type: none"> • drug delivery systems • active agents • contrast medium • medical rapid tests • prostheses and implants • antimicrobial agents and coatings • agents in cancer therapy

Textile/fabrics/non-wovens <ul style="list-style-type: none"> ● surface-processed textiles ● smart clothes 	Energy <ul style="list-style-type: none"> ● fuel cells ● solar cells ● batteries ● capacitors 	Cosmetics <ul style="list-style-type: none"> ● sun protection ● lipsticks ● skin creams ● tooth paste
Food and drinks <ul style="list-style-type: none"> ● package materials ● storage life sensors ● additives ● clarification of fruit juices 	Household <ul style="list-style-type: none"> ● ceramic coatings for irons ● odors catalyst ● cleaner for glass, ceramic, floor, windows 	Sports /outdoor <ul style="list-style-type: none"> ● ski wax ● antifogging of glasses/goggles ● antifouling coatings for ships/boats ● reinforced tennis rackets and balls

Examples of the established applications of nanomaterials; ,

- microelectronics,
- synthetic rubber,
- catalytic compounds,
- photographic supplies,
- inks and pigments,
- coatings and adhesives,
- ultrafine polishing compounds,
- UV absorbers for sun screens,
- synthetic bone,
- ferrofluids,
- optical fiber cladding, and cosmetics.
- fabrics and their treatments,
- sports equipment,
- flat panel displays,
- drug delivery systems, and
- pharmaceuticals.
- filtration,
- dental materials,
- surface disinfectants,
- diesel and fuel additives,
- hazardous chemical neutralizers,
- automotive components,
- electronics,
- scientific instruments

An materials with nano special properties may introduces in many application as example the Nanofluids are a relatively new class of fluids which consist of a base fluid with nano-sized particles (1–100 nm) suspended within

Applications of nanofluids

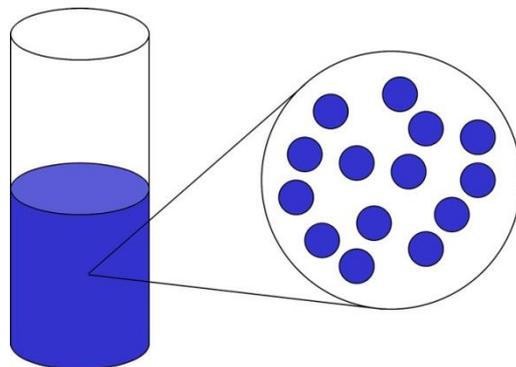
- 1-Transportation (Engine cooling/vehicle thermal management)
- 2-Electronics cooling
- 3-Defens & Space

4-Nuclear systems cooling

5-Heat exchanger

6-Biomedicine

7-Other applications (heat pipes, fuel cell, Solar water heating, chillers, domestic refrigerator, Diesel combustion, Drilling, Lubrications, Thermal storage,...)



In more details and according to the types of application the following points can be described;

1-Electronics

Microelectronics.

Many of the current microelectronics applications are already at a nanoscale. During the last four decades, the smallest feature of a transistor shrunk from 10 μm down to 30 nm. The ultimate objective of microelectronics fabrication is to make electronic circuit elements that are nanoscopic. For example, by achieving a significant reduction in the size of circuit elements, the microprocessors (or better said, nanoprocessors) that contain these components could run faster and incorporate more logic gates, thereby enabling computations at far higher speeds.

CNTs are exciting alternatives to conventional doped semiconductor crystals due to their varied electronic properties, ranging from metallic, to semiconducting, to superconducting.

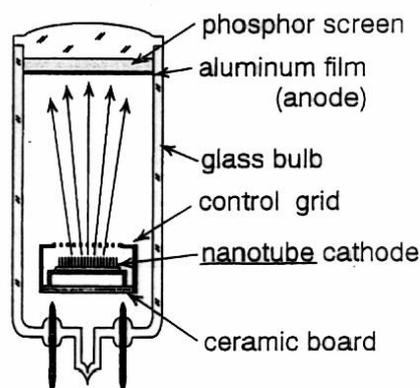
Displays.

The resolution of a television or a monitor improves with reduction of pixel size. The use of nanocrystalline materials can greatly enhance resolution and may significantly reduce cost.

Also, flat-panel displays constructed with nanomaterials may possess much higher brightness and contrast than conventional displays owing to the enhanced electrical and optical properties of the new materials. CNTs are being investigated for low voltage field-emission displays. Their combination of

mechanical and electrical properties makes them potentially very attractive for long life emitters.

Thin carbon NTs have ideal geometry for electron emission due to their smallest atomistic tip radius that result in turn to a high electric field strength, in order of magnitude greater than a work function of electrons. Moreover CNTs are known to exhibit; the **high strength, melting temperature, resistance to aggressive media** as graphite, and are able to work in technical vacuum. **Cold emitter on base of CNTs** was proposed to be a key element for the future flat panel TV set as being the **alternative for hot emitters** on base of electron-beam tube, that make **possible to avoid high dangerous asseverated 20-30 kV voltages**. At ambient temperature the CNT are able to emit electrons and current of the same density as the standard tungsten cathode operating at high temperatures and voltages. Set-up of light panel display on base of CNTs clamped at cathode and oriented in the anode direction



Data storage.

Devices, such as computer hard-disks function based on their ability to magnetize a small area of a spinning disk to record information, are established nano-applications. Discs and tapes containing engineered nanomaterials can store large amounts of information. Future avenues for magnetic recording that will drastically increase the capability of data storage include spintronics and nanowires.

High energy density batteries.

New nanomaterials show promising properties as anode and cathode materials in lithium-ion batteries, having higher capacity and better cycle life than their larger-particle equivalents . Among them are: aerogel intercalation electrode materials, nanocrystalline alloys, nanosized composite materials, carbon nanotubes, and nanosized transitionmetal oxides.

High-sensitivity sensors.

Due to their high surface area and increased reactivity, nanomaterials

could be employed as sensors for detecting various parameters, such as electrical resistivity, chemical activity, magnetic permeability, thermal conductivity, and capacitance.

2-Transportation and telecommunication

Car tires.

Nanoparticles of carbon black ranging between 10 nm - 500 nm act as a filler in the polymer matrix of tires, and are used for mechanical reinforcement.

Car bumpers.

Clay particle based composites containing plastics and nano-sized clay are used to make car exteriors that are lighter and twice as resistant to scratches than usual materials .

3-Imaging

Scanning microscope imaging.

SWCNTs have been used as probe tips for atomic-force microscopy imaging of antibodies, DNA, etc. Nanotubes are ideal probe tips for scanning microscopy due to their small diameter (which maximizes resolution), high aspect ratio, and stiffness.

Molecular-recognition AFM tips.

SWCNTs with attached biomolecules are attached to AFM tips, and used for “molecular-recognition” in order to study chemical forces between molecules

4-Biomedical applications

Nanoscaffolds.

Nanofiber scaffolds can be used to regenerate central nervous system cells and possible other organs. Experiments performed on a hamster with severed optic tract demonstrated the regeneration of axonal tissue initiated by a peptide nanofibers scaffold

Antimicrobial nanopowders and coatings.

Certain nanopowders, possess antimicrobial properties. When these powders contact cells of *E. coli*, or other bacteria species and viruses, over 90% are killed within a few minutes. Due to their antimicrobial effect, nanoparticle of silver and titanium dioxide (<100nm) are assessed as coatings for surgical masks .

Bioseparation.

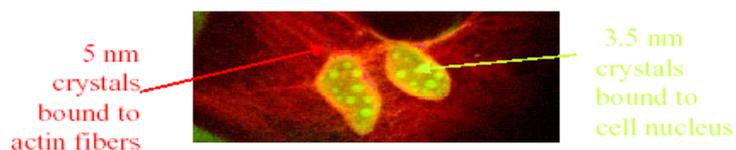
Nanotube membranes can act as channels for highly selective transport of molecules and ions between solutions that are present on both side of the membrane . For example, membranes containing nanotubes with inside

diameters of molecular dimensions (less than 1 nm) separate small molecules on the basis of molecular size, while nanotubes with larger inside diameters (20–60 nm) can be used to separate proteins .

Drug delivery.

The ability of nanoparticles to target and penetrate specific organs and cells contributes to their toxicity, however, this ability may be exploited in nanomedicine. Nanospheres composed of biodegradable polymers can incorporated drugs, allowing the timed release of the drug as the polymer degrades . When particles are set to degrade in an acid microenvironment, such as tumor cells or around inflammation sites, this allows site-specific or targeted drug delivery.

Nanocrystals as Fluorescent Biological Labels



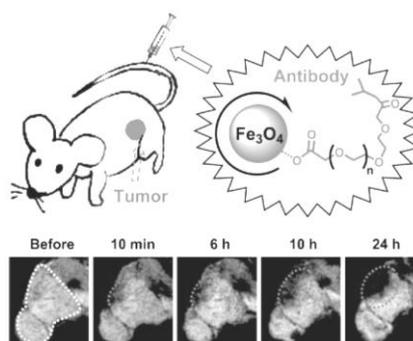
- ▶ Significant advantages over conventional dyes:
- ▶ Reduced photobleaching
- ▶ Multi-color labeling, parallel screening
- ▶ Infrared labels, blood diagnostics
- ▶ Molecular size nanocrystals are bio-compatible, with many other possible applications

Biofunctional devices based on magnetic nanoparticles

- Delivery and controlled release of therapeutics
- Bioswitches for organ function
- Imaging

Biocompatible magnetic nanocrystals with reactive moieties on the surface were generated by means of a “one-pot” reaction and used directly in cancer detection by being coupled with a specific cancer-targeting antibody and the magnetic nanocrystals have potential application in MRI.

Magnetic nanoparticles serving as biodetection agents



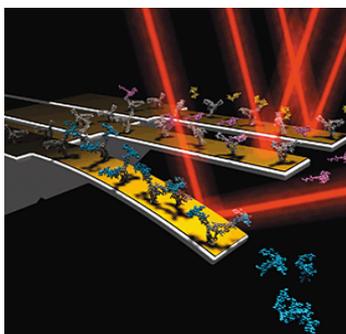
Tissue Engineering

Nano/micro particles, including living animal cells, bacteria, and colloidal gold (100 nm), can be optically guided and deposited in arbitrarily defined three-dimensional arrays, a process called “laser-guided direct-writing.”

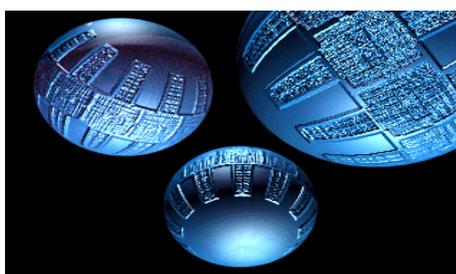
Detection of Chemical and Biological Warfare Agents

One technique uses atomic force microscopy with a sandwich immunoassay attaching magnetic beads to a microfabricated cantilever sensitive to small displacements.

BioCOM Chip



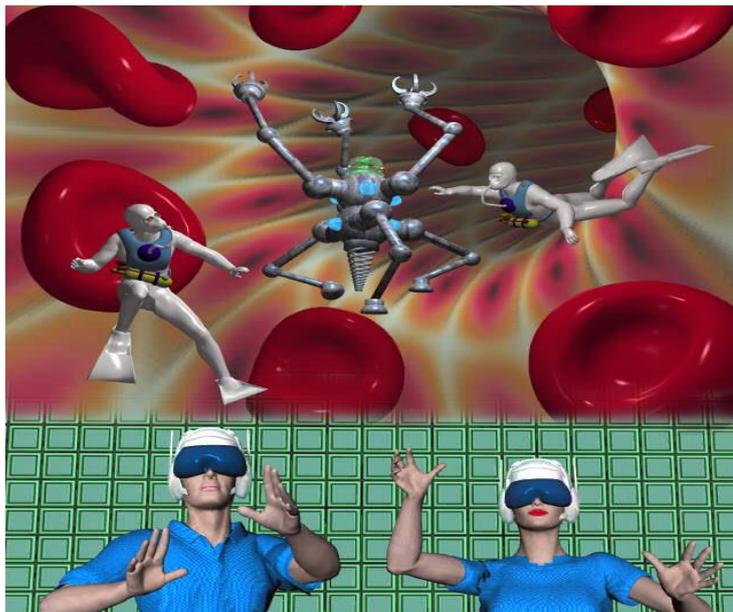
Respirocytes: A Mechanical Artificial Red Blood Cell



Fixing Damaged Blood Cells



In the Near Future: Humanoid Shaped Nanorobots



5- Cosmetics

Titanium dioxide and zinc oxide become transparent to visible light when formed at the nanoscale, however are able to absorb and reflect UV light, being currently used in sunscreens and in the cosmetic industry.

6-Coatings

Nanomaterials have been used for very thin coatings for decades, if not centuries. Today thin coatings are used in a vast range of applications, including architectural glass, microelectronics, anticounterfeit devices, optoelectronic devices, and catalytically active surfaces. Structured coatings with nanometer-scale features in more than one dimension promise to be an important foundational technology for the future.

Self-cleaning windows.

Self-cleaning windows have been demonstrated that are coated in highly hydrophobic titanium dioxide. The titanium dioxide nanoparticles speed up, in the presence of water and sunlight, the breakdown of dirt and bacteria that can then be washed off the glass more easily.

Scratch resistant materials.

Nanoscale intermediate layers between the hard outer layer and the substrate material significantly improve wear and scratch resistant coatings. The intermediate layers are designed to give a good bonding and graded matching of mechanical and thermal properties, leading to improved adhesion.

7- Textiles.

Nanoparticles have already been used in coating textiles such as nylon, to provide antimicrobial characteristics , Also the control of porosity at the nanoscale and surface roughness in a variety of polymers and inorganic materials led to ultrahydrophobic - waterproof

Another list of field of applications are shown below;

1-Power/Energy

- Dye-sensitized solar cells (e.g. using TiO₂)
- Hydrogen storage (e.g. using metal hydrides)
- Improved anode and cathode materials for solid oxide fuel cells
- Thermal control fluids (e.g. using Cu)
- Environmental catalysts (e.g. ceria as diesel additive to improve combustion efficiency)
- Automotive catalytic converters



- Miniaturised varistors (e.g. doped ZnO)
- Fuel cell catalysts (e.g. platinum in PEM cells)
- Conducting polymers for bipolar plates in fuel cells
- Improved electrodes in batteries and supercapacitors (increased capacity, more rapid charging)
- Increased efficiency of hydrogen generation from water (e.g. from solar)
- Catalysts for gas to liquid technologies, coal gasification technologies, biodiesel and other synthetic fuels, etc,

1- Healthcare/medical

- Targeted drug delivery
- Alternative drug and vaccine delivery mechanisms (e.g. inhalation, oralin place of injection).
- Bone growth promoters
- Cancer treatments
- Biocompatible coatings for implants
- Sunscreens (e.g. using ZnO and TiO₂) / cosmetics
- Biolabeling and detection (e.g. using Au)
- Carriers for drugs with low water solubility
- Fungicides (e.g. using ZnO)
- MRI contrast agents (e.g. using superparamagnetic iron oxide)
- New dental composites
- Biological binding agents (e.g. for high phosphate levels)
- Antiviral, antibacterial (e.g. Ag), anti-spore non-chemical creams and
- powders (using surface tension energy on the nanoscale to destroy biological particles)

2- Engineering

- Cutting tool bits (e.g. WC, TaC, TiC, Co)
- Spark plugs (e.g. using nanoscale metal and ceramic powders)
- Chemical sensors
- Molecular sieves
- Wear-resistant / abrasion-resistant coatings (e.g. using alumina, Y-Zr₂O₃)
- Nanoclay-reinforced polymer composites
- Lubricants and sealants / hydraulic additives (e.g. Cu MoS₂)
- Pigments
- Self-cleaning glass (e.g. using TiO₂)
- Propellants (e.g. using Al)
- Structural and physical enhancement of polymers and composites
- Enhanced thermal spray coating techniques (e.g. based on TiO₂, TiC-Co)
- Inks: conducting, magnetic, etc. (using metal powders)
- Flame retardant polymer formulations
- Rubber composites such as car tyres (e.g. carbon black)
- Anti-scattering layers in photographic film

3- Consumer goods



- Anti-counterfeit devices
- Barrier packaging using silicates
- Ski wax
- White goods (e.g. anti-scratch, easy-cleaning coatings, etc.)
- Glass coatings for anti-glare, anti-misting mirrors (e.g. using TiO₂)
- Sports goods: tennis balls, rackets (e.g. using nanoclays)
- Water- and stain-repellent textiles
- Pyrotechnics and explosives (e.g. using Al)
- Additives in paints (e.g. anti-bleaching effect, scratch resistance, etc.)
- Tiles coated (e.g. anti-scratch using alumina)

4- Environmental

- Water treatment (photo-catalyst treatments, e.g. using TiO₂)
- Self-cleaning glass (e.g. using TiO₂ based nanostructured coatings)
- Anti-reflection coatings
- Sanitary ware
- Soil remediation (e.g. using Fe)
- Controlled delivery of herbicides and pesticides
- Anti-fouling coatings (reduce chemical use)

5- Electronics

- Nanoscale magnetic particles for high-density data storage
- EMI shielding using conducting and magnetic materials
- Electronic circuits (e.g. using Cu, Al)
- Display technologies including field-emission devices (e.g. using conducting oxides)
- Ferro-fluids (e.g. using magnetic materials)
- Optoelectronics devices such as switches (e.g. using rare-earth-doped ceramics)
- Conductive coatings and fabrics (e.g. using rare-earth-doped ceramics)
- Chemical mechanical planarization - *CMP* (e.g. using alumina, silica, ceria)
- Coatings and joining materials for optical fibres (e.g. based in Si)
- solar cells - similar requirements to both coating and catalyst applications
- improved electrodes - similar to catalytic applications
- antibacterials, antivirals, antifungals - similar to catalytic applications

- sensors - similar to medical applications (strict size and morphology
- constraints but the value lies in the system/device as a whole)
- pigments / inks - similar to coatings
- propellants / explosives - similar to catalysts
- data storage media similar to coatings