Material Science and Engineering

Nano materials:

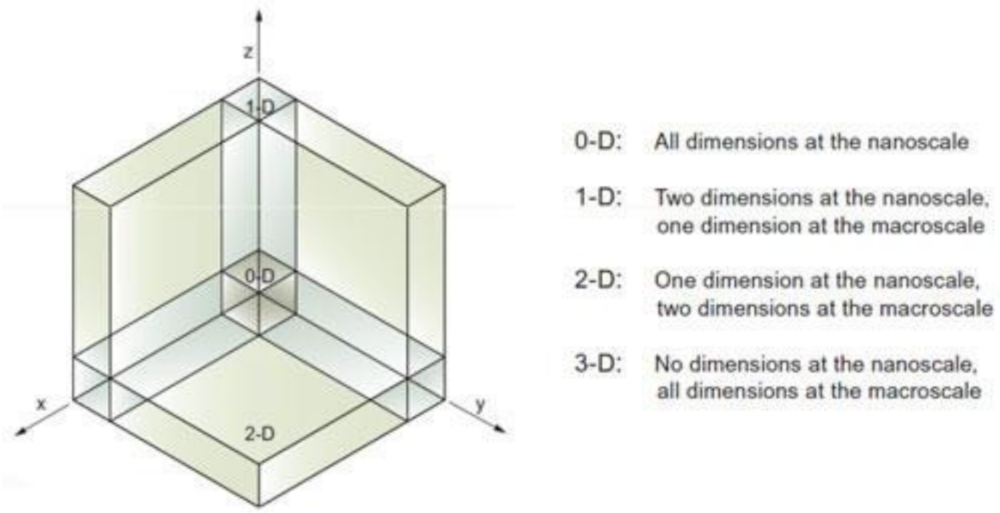
Nano materials can be metals, ceramics, polymeric materials or composite materials. Nano particles are particles within the size ranging from 1-50nm and nano materials having the components less than 100nm at least in one dimension. Typical nanomaterials include

1. Zero dimension nano structures, such as metallic, semi conducting and ceramic nano particles

2. One – dimension nano structures, such as nano wires, nanotubes and nano rods.

3. Two-dimension nano structures, such as graphene, nanofilms, nanolayers, and nano coatings

4. Three – dimension nano materials such as bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers, diamond, graphite.



Classification of Nanomaterials:

Nanoparticle : Nanoparticle or **ultrafine particle** is usually defined as a particle of matter that is between 1 and 100 (nm) in diameter. Nanoparticles exist in the natural world and are also created as a result of human activities. Because of their sub microscopic size, they have unique material characteristics, and manufactured nanoparticles may find practical applications in a variety of areas, including medicine, engineering, catalysis, and environmental remediation.

Nanoclusters: Metal Nanoclusters consist of a small number of atoms, at most in the tens. These Nanoclusters can be composed either of a single or of multiple elements, and typically measure less than 2 nm. Such Nanoclusters exhibit attractive electronic, optical, and chemical properties compared to their bulk materials.

Carbon nanotubes: CNTs are tubes made of carbon with diameters typically measured in nanometers. Carbon nanotubes often refer to **single-wall** carbon nanotubes **(SWCNTs)** with diameters in the range of a nanometer. Single-wall carbon nanotubes are one of the allotropes of carbon, intermediate between fullerene cages and flat graphene.Carbon nanotubes also often refer to **multi-wall** carbon nanotubes **(MWCNTs)** consisting of nested single-wall carbon nanotubes weakly bound together by vanderwaals interactions in a tree ring-like structure.

Nanowires: Nanowires can be made from a variety of conducting and semiconducting materials like copper, silver, gold, iron, silicon, zinc oxide and germanium. Nanowires can also be made from carbon nanotubes. Nanowires are less than 100 nanometers in diameter and can be as small as 3 nanometers. Typically, nanowires are more than 1000 times longer than their diameter. This leads to unique properties that are not seen in the bulk materials, like unique electrical properties.

Preparation of Nano materials:

Nano materials can be synthesized in a number of ways various methods employed for the synthesis is as follows:

i. **Sol-gel process:** It involves hydrolysis followed by condensation. A metal or metalloid is dispersed in acid or water to form a Sol (Finely divided solid particles dispersed in liquid). Gel is obtained from this sol by the removal of water (Gel is dispersion of a liquid throughout solid matrix).

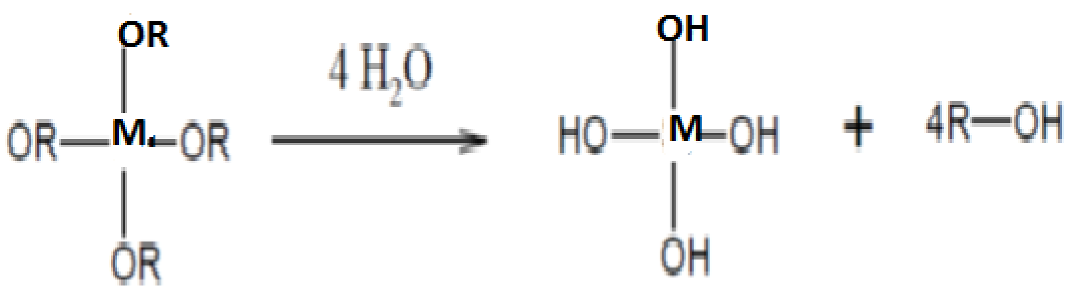
$$MOR + H_2O \rightarrow MOH + ROH \text{ (hydrolysis)}$$

Metal alkoxide

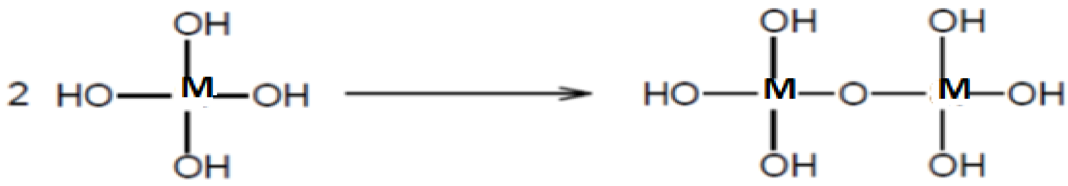
This process consists of 4 main steps:

1. Hydrolysis
2. Condensation followed by poly condensation
3. Gelation
4. Super critical drying

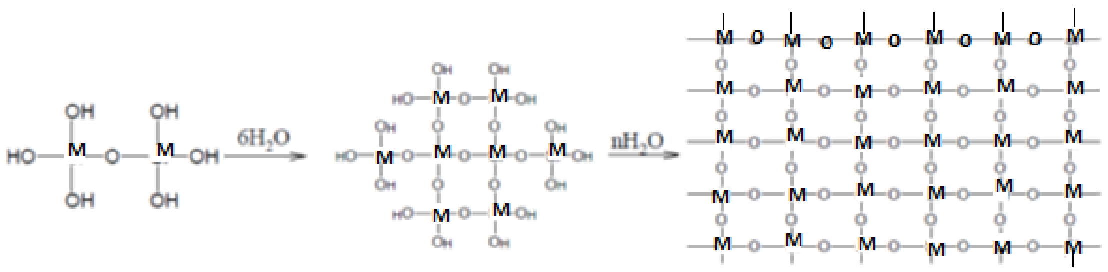
   1. Hydrolysis: It occurs by the addition of water to the material to form particles.



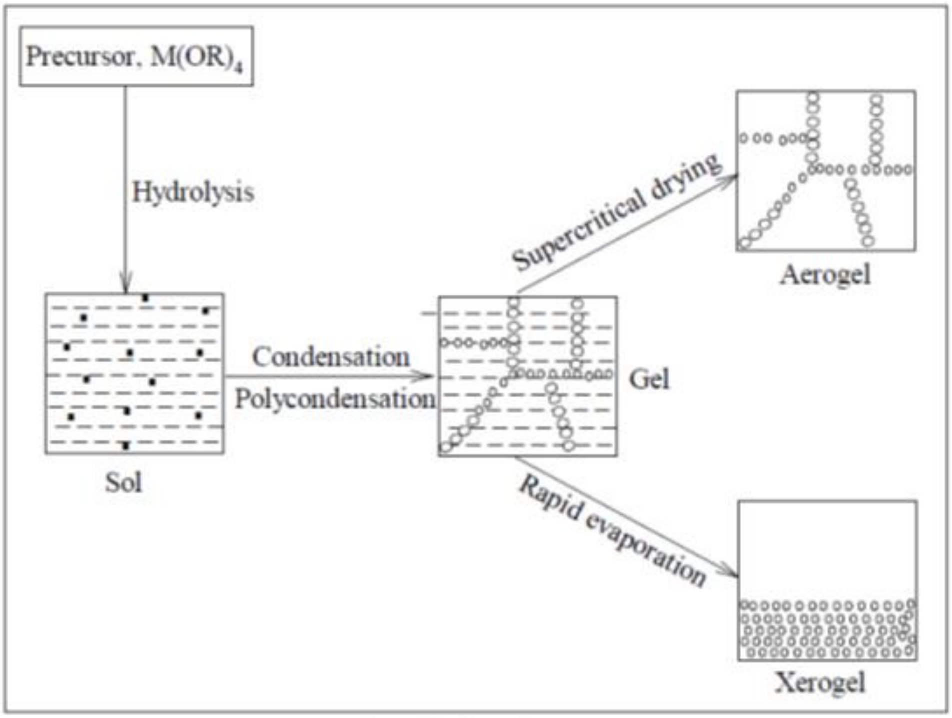
2. Condensation: Self-condensation of metal hydroxide produces linkages filled with byproducts of water and alcohol



3. Poly condensation : The condensation process continues to form polycondensed gel with M-O-M linkages



4. Drying: The gels are subjected to super critical drying in an autoclave. When subjected to critical temperature and critical pressure respectively in order to remove liquid from Gel to form the network structure.



Sol-gel process

Advantages:

1. It provides thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.

2. It produces thick coating to provide corrosion protection performance.

3. It provides a simple, economic and effective method to produce high quality coatings.

Applications:

1. It can be used in ceramics manufacturing processes as a means of producing very thin films of metal oxides for various purposes.
2. It has diverse applications in optics, electronics, energy, medicine (eg controlled drug release) and separation technology (eg chromatograph).

Characterization of Nano materials:

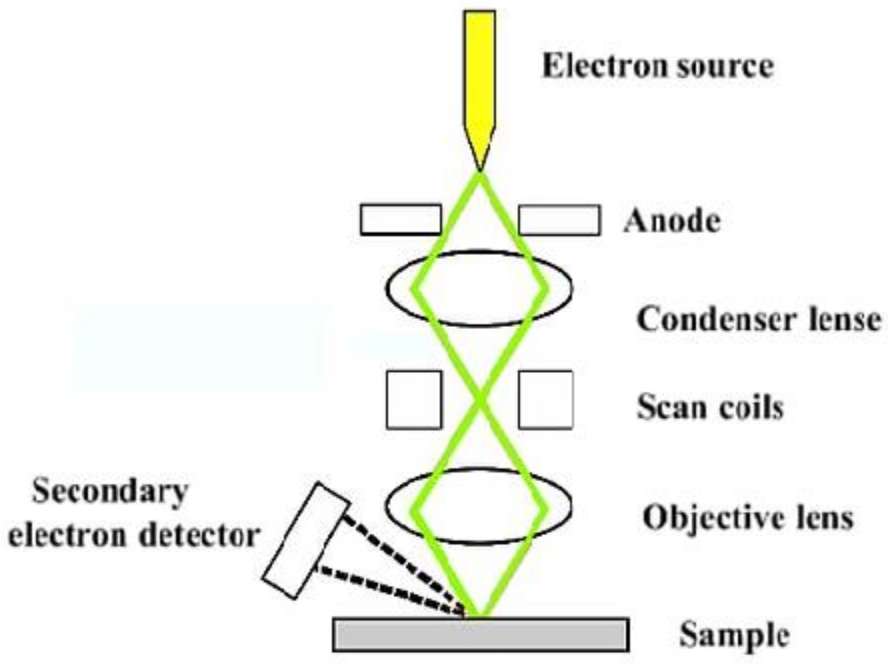
SEM method (Scanning electron microscopy):

SEM was developed in 1938 by Manfred Von Ardenne. It utilizes electron that have bounced off the surface of the specimen.

Basic principle: A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons. When the beam of electrons strikes the surface of the specimen and interacts with the atoms of the sample, signals in the form of secondary electrons, back scattered electrons and characteristic X-rays are generated that contain information about the sample.

Working:

The electron gun produces an electron beam when tungsten wire is heated by current. This beam is accelerated by the anode. The beam travels through electromagnetic fields and lenses, which focus the beam down towards the sample. Mechanisms of deflection coils guide the beam so that it scans the surface of the sample, in a rectangular frame. When the beam touches the surface of the sample, it produces secondary electrons, back scattered electrons, X-rays. The emitted secondary electron is collected by secondary electrons detector and converts into signal that is sent to a screen which produces final image. Additional detectors collect these X-rays, back scattered electrons and produce corresponding images.



Scanning Electron Microscope

SEM images gives information about

i) Topography: Texture / Surface of a sample.

ii) Morphology: Size, Shape, order of particles.

iii) Composition: Elemental composition of sample.

iv) Crystalline structure: Arrangement present within the sample.

APPLICATIONS OF SEM

SEM can be used in a variety of industrial, commercial, and research applications.

1. Elemental Analysis: SEM is especially useful to analyze elemental distribution (i.e. elemental mapping) in the sample. Keep in mind that typically the elemental information is collected from about 1 micron deep layer.

2. Materials Science: SEMs are used in materials science for research, quality control and failure analysis. In modern material science, investigations into nanotubes and nanofibres, high temperature superconductors and alloy strength, all rely heavily on the use of SEMs for research and investigation.

3. Semiconductor inspection: Reliable performance of semiconductors requires accurate topographical information. The high resolution three dimensional images produced by SEMs offers a speedy, accurate measurement of the composition of the semiconductor.

4. Biological Sciences: In biological sciences, SEMs can be used on anything from insects and animal tissue to bacteria and viruses. Uses include:

a. measuring the effect of climate change of species.

b. identifying new bacteria and virulent strains

c. vaccination testing

5. Medical Science: Broadly speaking, SEMs are used in medical science to compare blood and tissue samples in determining the cause of illness and measuring the effects of treatments on patients (while contributing to the design of new treatments). Common uses include:

a. identifying diseases and viruses

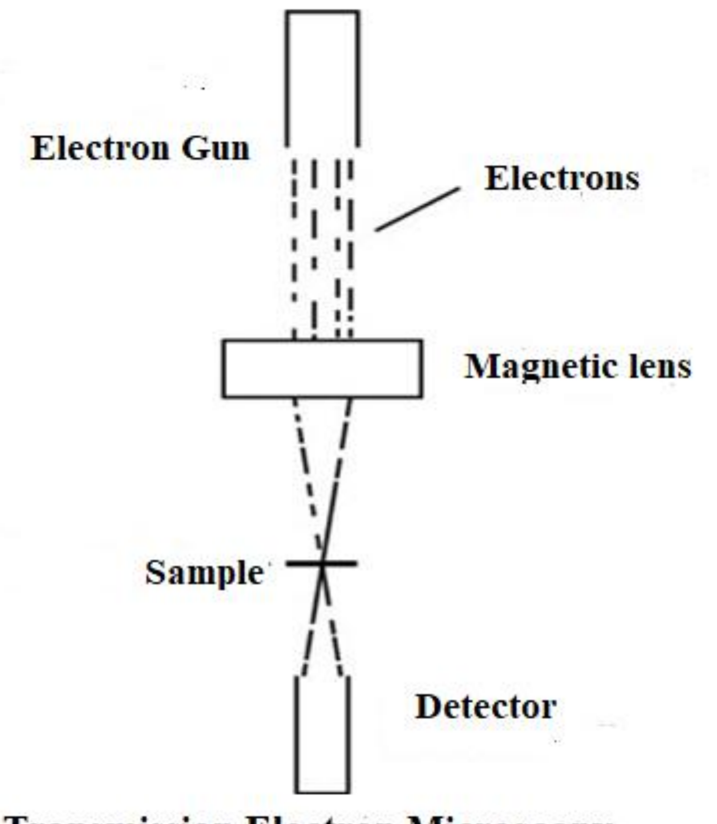
b. testing new vaccinations and medicines

c. comparing tissue samples between patients in a control and test group

TEM method (Transmission electron microscopy):

Principle: TEM operates on the same basic principle as light microscope but uses electrons instead of light. When an electron beam passes through a thin-section specimen of a material, electrons are scattered. A sophisticated system of electromagnetic lenses focuses the scattered electrons into an image or a diffraction pattern, or a nano analytical spectrum depending on the mode of operation.

Working: The beam of electrons from the electron gun is focused into a small, thin coherent beam by the use of the condenser lens. This beam is restricted by the condenser aperture, which exclude high angle electrons. The beam then strikes the specimen and part of it is transmitted depending upon the thickness and electron transparency of the specimen. This transmitted portion, is focused by the objective lens into an image on phosphor screen or charge coupled device (CCD) camera. The image then passed down the column through the intermediate and projector lenses, is enlarged all the way.



Transmission Electron Microscopy

TEM Applications

1. A Transmission Electron Microscope is ideal for a number of different fields such as life sciences, nanotechnology, medical, biological and material research, forensic analysis, gemology and metallurgy as well as industry and education.
2. TEMs provide topographical, morphological, compositional and crystalline information.
3. The images allow researchers to view samples on a molecular level, making it possible to analyze structure and texture. This information is useful in the study of crystals and metals, but also has industrial applications.
4. TEMs can be used in semiconductor analysis and production and the manufacturing of computers.

Carbon nanotubes:

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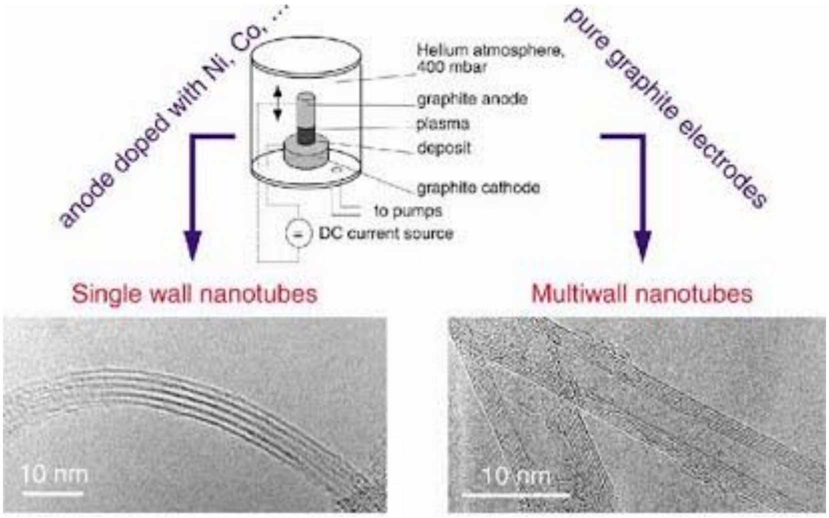
Each carbon in a carbon nano tube is SP^2 hybridized and each atom is joined to three neighbouring atoms. CNT's can be single walled or multiwalled.

i) Single-walled carbon nano tubes (SWCNT's): These are long wrapped graphene sheets with length to diameter ratio of 1000. It can be obtained by wrapping one atomic layer of graphene.

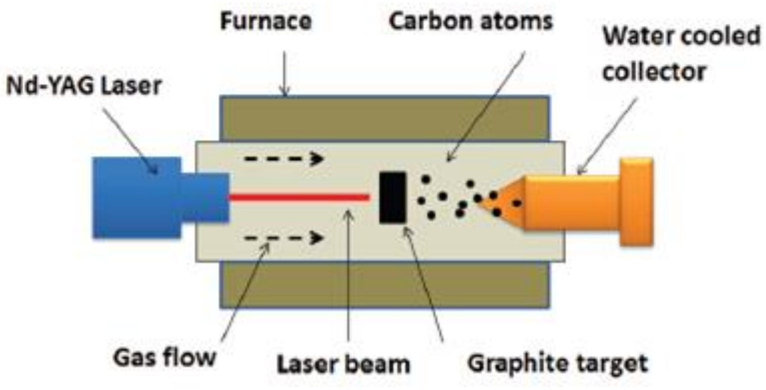
ii) Multi-walled carbon nano tubes (MWCNT's): They consist of concentric SWCNT's with different diameters with an inter layer spacing of 3.4A0. MWCNT's have more than one surface with in it.

Synthesis of Carbon nanotubes: Carbon nanotubes are produced by three main techniques as follows:

1. **Arc discharge:** This method is used for producing C_{60} fullerenes. Nanotubes are created through arc vapourisation of two carbon rods placed end to end to end separated approximately by 1mm. In a enclosure fitted with inert gas (He, Ar) of 50 to 100 A, driven by approximately 20V creates a high temperature discharge. vapourises one of the carbon rod and forms a small rod shaped deposits on other rod.



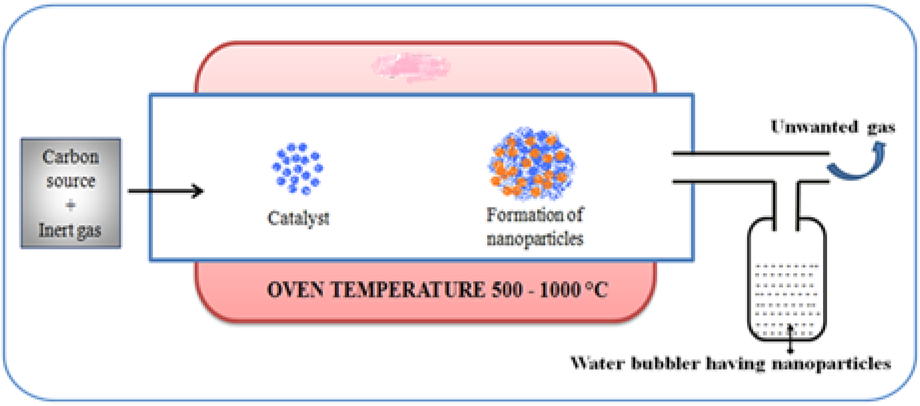
2. **Laser ablation method:** A pulsed or continous laser is used to vapourise a graphite target in an oven 1200^0C. Then oven is fitted with helium or argon gas in order to keep pressure at 500 Torr. A very hot plume forms, then expands and cools rapidly. As the vapourised species cool, small carbon molecules and atoms quickly, condense to form a large clusters.



Laser Ablation method

3. **Chemical vapour deposition [CVD]:**

CVD synthesis is achieved by putting a carbon source in the gas phase and using a energy source, such as plasma or a resistive heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include Methane, Carbon monoxide and Acetylene. The energy source is used to “crack” the molecule into reactive atomic carbon. Thus, the carbon diffuses towards the substrate which is heated and cooled with a catalyst (usually a first-row transition metal such as Ni, Fe or Co) where it will bind. Excellent alignment, as well as positional control on nanometer scale, can be achieved by using CVD. Control over the diameter as well as growth rate of the nanotubes can also be maintained.



Chemical vapour deposition [CVD]

Properties of carbon nanotubes (CNT):

a) CNT's are one of the strongest and stiffest materials known, in terms of tensile strength and elastic modulus respectively.

b) Young's modulus is in the range 1-5 TPa(Tera Pascal) for single walled CNT's and the tensile strength is about 150GPa for multi walled CNT's.

c) CNT's can be either metallic or semi conducting depending upon the chirality.

d) CNT's are known to exhibit super conductivity below 200C.

e) CNT's will be able to achieve conductivities 20 times more than that of copper. The temperature stability of CNT's is estimated to be up to 28000C in vacuum and about 7500C in air.

Applications of CNT’s:

1) In conducting polymers.

2) In electronics such as memory, semiconductor components and transparent conducting films for touch screens, displays and solar cells.

3) They can act as unique catalyst in various industrial chemical reactions.

4) CNT’s are effective for controlled drug delivery and distribution of drugs inside the body.

5) Hydrogen can be strored in the carbon nontubes which in turn used for fuel cells. CNT’s can replace platinum as catalyst in fuel cells.

6) CNT’s are used for the treatment of cancer.

Green Chemistry:

Green chemistry may be defined as: The design of chemical products and processes that minimize the use and generation of hazardous substances which have negative impact on human health and the environment.

Twelve principles of Green Chemistry:

Paul Anastas and John Warner of the U.S. Environmental protection agency formulated 12 principles of Green chemistry. They are as follows

1. **Prevention:**
It is better to prevent waste than to treat or clean up waste after it has been created.

2. **Atom Economy:**

Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.

3 **Less Hazardous Chemical Synthises:**

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Designing Safer Chemicals:**

Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5.Safer Solvents and Auxiliaries:

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.

6. **Design for Energy Efficiency:**

Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstocks:**

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. **Reduce Derivatives:**

Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis:**

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation:**

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. **Real-time analysis for Pollution Prevention:**

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. **Inherently Safer Chemistry for Accident Prevention:**

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Green solvents:

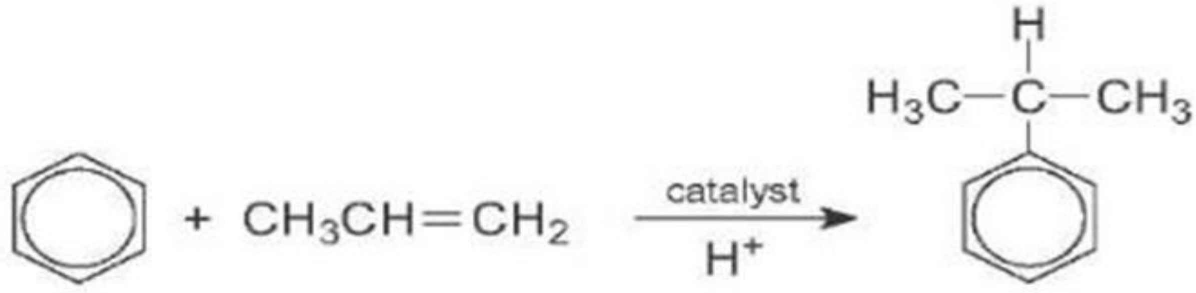
Green solvents were developed as a more environmentally friendly alternative to petrochemical solvents. Ethyl lactate, for example, is a green solvent derived from processing corn. Ethyl lactate is the ester of lactic acid. Ethyl lactate solvents are commonly used solvents in the paints and coating industry and have numerous attractive advantages including being 100% biodegradable, easy to recycle, non-corrosive, non-carcinogenic, and non-ozone-depleting.

Green catalyst:

Green catalysts are the catalysts which are eco-friendly, can be regenerated hence reused multiple times and thus minimise waste production during process. Greener catalysis means moving away from stoichiometric processes to homogenous and heterogeneous catalytic reactions using organic, organometallic, inorganic and biological catalysts.

Benzene and propene are converted into cumene in the manufacture of phenol. This reaction needs an acid catalyst, such as aluminium chloride.

A solid zeolite with acid groups, such as ZMS-5 is now the favoured catalyst:

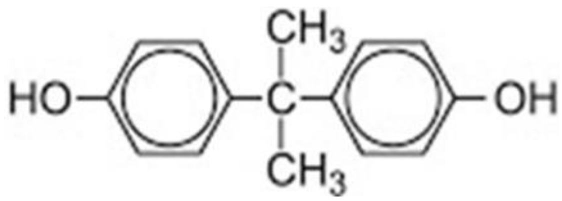


The zeolite is more eco-friendly as the effluent is much cleaner and can be used at lower temperatures and pressures.

Green reactant:

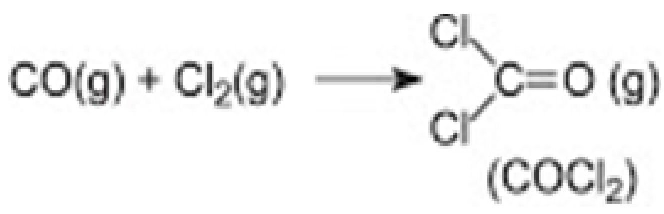
The family of polycarbonates contains very important polymers which are used where high optical properties combined with strength are needed.

The polycarbonate most used is manufactured from bisphenol-A, whose structure is:

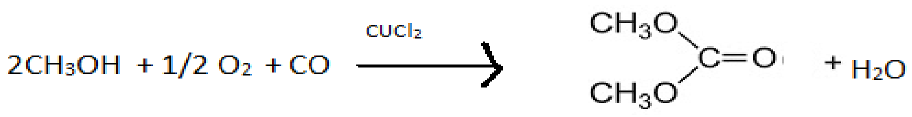


The polycarbonate is manufactured by a condensation reaction between bisphenol A and either carbonyl chloride or diphenyl carbonate.

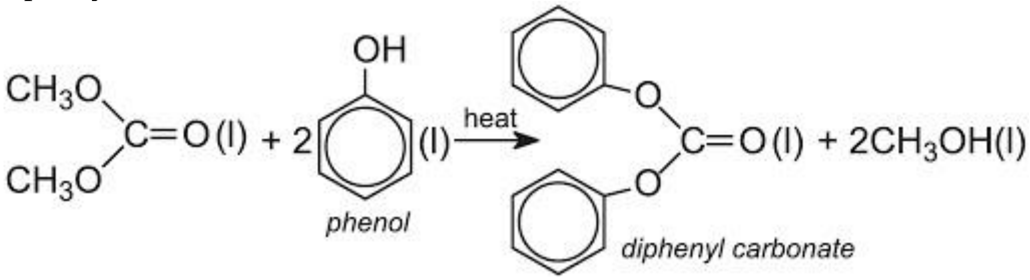
Carbonyl chloride is a very poisonous gas, manufactured from other hazardous gases, carbon monoxide and chlorine



On the other hand, diphenyl carbonate is produced from dimethyl carbonate, which is readily manufactured from methanol, carbon monoxide and oxygen in the liquid phase, in presence of copper (II) chloride.



Dimethyl carbonate, when heated with phenol in the liquid phase, forms the diphenyl carbonate:



Overall, the process for the production of polycarbonate that uses diphenyl carbonate is less hazardous than that using carbonyl chloride.

Band theory of solids:

Band theory of solids is the extension of molecular orbital theory to solids. The important aspects of band theory are

1) Solids exist in the form of crystals due to the close packing of spherical atoms.

2) When the atoms come close, the atomic orbitals of the valence shells combine to form molecular orbitals.

3) The partially and completely filled orbitals overlap to form an array of atoms in the crystal.

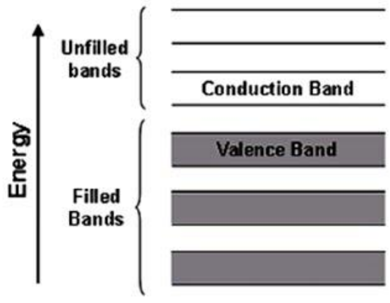
4) Upon interaction of energy levels of large number of identical atoms, each energy level splits up into a number of infinitesimal energy levels. So in major band we can find large

number of small bands. All these energy bands are continuous. So an electron in a solid crystal can thus occupy any of these large number energy level, within the band.

5) There are two types of bands.

a. Overlapping band: It is an higher band over lapping lower band.

b. Non-overlapping bands: There will not be any overlapping of some bands.



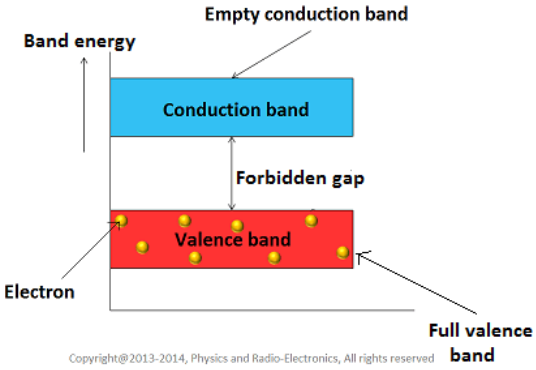
6) Valence electrons occupy various band energy levels such band is called valence band. It may contain

a. Partially or completely filled band or

b. Completely filled with electrons (like Be and Mg)

7) The conduction band will be above the valence band. The conduction band may be empty or partially filled with the electrons.

8) The gap between the valence band and conduction band is forbidden gap. The energy gap is the width of the forbidden gap.



9) A solid can exhibit conductivity only when either a partially filled valence band or completely filled valence band overlaps with the next higher empty band.

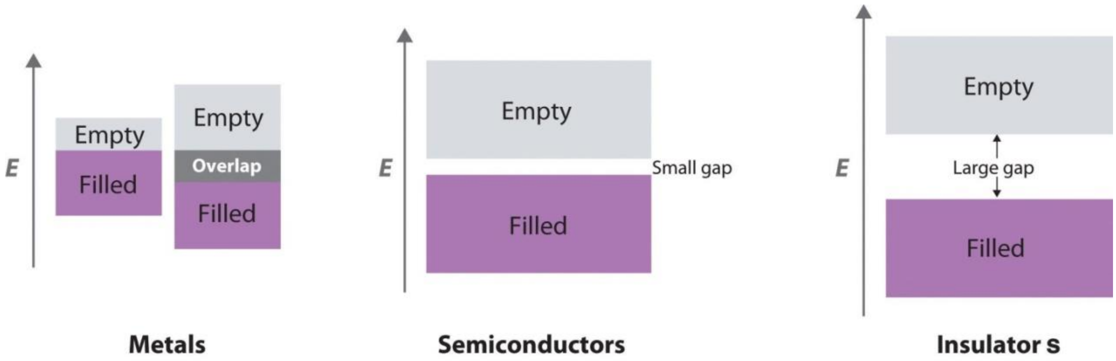
10) Insulator will have tightly bound valence band electrons. So to mobilize them large quantities of electric potential is required.

11) A solid can behave as a semiconductor if

i) It has filled valence band

ii) It has empty conduction band

iii) A narrow gap between these two bands

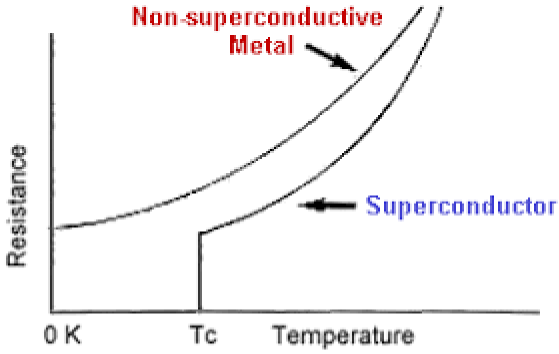


Super conductors:

Metals conduct electricity at a ordinary temperature and offers resistance to the flow of electric current. But at a particular temperature, below 0^0C, the metals conduct electricity in such a way that there will be no resistance to the flow of electric current. Then the metal is said to be super conducting and that particular temperature is called critical temperature (Tc). At this state the metals are diamagnetic and are repelled by magnets.

Kammerlingh onnes (in 1913) observed the phenomenon of super conductivity when mercury is cooled with liquid helium became super conducting at around 4K.

The resistivity variation of a normal metal and a super conducting metal with temperature is shown below



Preparation of superconductor:

The 1-2-3 superconductor may be synthesized by mixing 0.60 g of yttrium oxide with ***"stoichiometric quantities"*** (see below) of barium peroxide and copper (II) oxide according to the equation:

- $2Y_2O_3 + 8BaO_2 + 12CuO \rightarrow 4YBa_2Cu_3O_6 + 5O_2$

The $YBa_2Cu_3O_{7-x}$ is prepared by grinding the reactants together, strongly heating calcinating at 900–950 °C for 8-12 hours, pelletizing the powder mixture, heating or sintering the pellet at 950 °C for 12 or more hours, then maintaining the product at 500°C for 12-16 hours. On slow cooling in oxygen atmosphere, $YBa_2Cu_3O_6$ is converted to nonstoichiometric, superconducting $YBa_2Cu_3O_{7-x}$ forms by uptake and loss of oxygen **.**

Properties of super conductors:

1) They have higher resistance than other elements at ordinary temperatures.

2) Addition of impurity to a super conducting element decreases the critical temperature.

3) There will not be any change in either the thermal expansion or elastic properties of super conducting element during transition.

4) There will not be any electromagnetic effects at super conducting state.

5) A strong magnetic field destructs the super conducting property.

6) Meissner effect: Application of strong magnetic field to a super conductor followed by cooling below its transition temperature would result in the expulsion of all magnetic flux from interior of super conductor.

Applications of super conductivity:

There are number of important applications of super conductivity. Some of them are mentioned here

1) Super conducting magnets can generate high fields with low power consumptions. Such magnetic fields find their application in scientific and research equipments.

2) In the field of medicine: Magnetic Resonance Imaging (MRI) is very useful as a diagnostic tool. Based on the production many cross – sectional images, any abnormalities in body tissue and organs can be detected. Magnetic Resonance Spectroscopy (MRS) is useful the chemical analysis of tissues.

3) Other applications in which super conductivity is used are:

i) Electrical power transmission: By using super conducting materials electric power loss is minimized to a great extent and the equipment operates at low voltage.

ii) Magnets required for high energy particle accelerator can be prepared by using the phenomenon of super conductivity.

iii) Super conductivity helps in high-speed switching and signal transmission.

iv) The phenomenon of super conductivity can be useful in the high-speed magnetically levigated trains. The magnetic levigation results from magnetic repulsion.

v) Memory or storage elements on computers function on the principle of super conductivity.

vi) Amplification of very small direct current and voltage is possible with the help of super conductivity.