GREEN CHEMISTRY

Introduction: The term green chemistry is defined as: "The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances". (Or) "Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products." (Or) "Green chemistry consists of chemicals and chemical processes designed to reduce or eliminate negative environmental impacts. The use and production of these chemicals may involve reduced waste products, non-toxic components, and improved efficiency." Basic twelve principles of green chemistry:

TWELVE PRINCIPLES OF GREEN CHEMISTRY

1. **Prevention:** It is better to prevent waste than to treat clean up waste after it is formed. This based on the concept of "stop the pollutant at the source".
2. **Atom economy:** Synthetic methods should be designed to maximize the incorporation of all raw materials used in the process in to the final product, instead of generating unwanted sided or waste products.
3. **Less hazardous chemical use:** Synthetic methods should be designed to use and generate substances that possess little or no toxicity human health and environment.
4. **Design for safer chemicals:** Chemical products should be designed so that they not only perform their designed function but are also less toxic to the human and environment.
5. **Safer solvents and auxiliaries:** Solvents and separating agents should not be used whenever possible. If their use cannot be avoided, they should be used as mildly or innocuously.
6. **Design for energy efficiency:** Energy requirement of chemical processes should be recognized for their environmental and economical impact and should be minimized. Synthetic methods should be conducted at mild temperature and pressure.
7. **Use of renewable feedstock:** A raw material or feedstock should be renewable rather than depleting, wherever technically and economically practicable.
8. **Reduction of derivatives:** Use of blocking groups, protection / deprotection, temporary modification of physical / chemical processes should be avoided whenever possible.
9. **Catalysis:** A catalytic reagent (as selective as possible) is superior to stoichiometric reagents.

10. **Design for degradation:** Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation product.
11. **Real time analysis for pollution prevention:** Analytical methodologies need to be improved 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 form of substances used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires. Plants should be designed as to eliminate the possibility of accidents during operations.

GREEN CHEMICAL APPROACHES

MICROWAVE SYNTHESIS: A microwave is a form of electromagnetic energy, which falls at the lower end of the electromagnetic spectrum between infrared and radio frequencies. While fire is now rarely used in synthetic chemistry, the Bunsen burner was also replaced by the mantle, oil bath or hot plate as a source of applying uniform heat to a chemical reaction. Heating chemicals for their reactions by microwave energy is generally referred to as micro wave-assisted organic synthesis. It is based on the principle of dipolar polarization and ionic conduction mechanism.

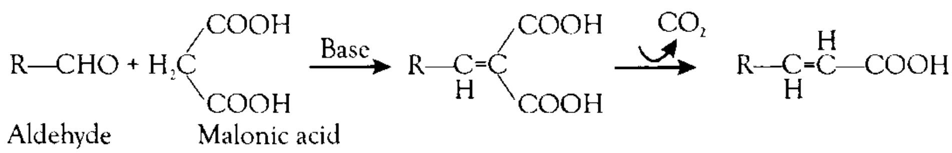
Advantages

- The difference between microwave energy and other forms of radiation is that microwave energy is non- ionizing and therefore does not alter the molecular structure of the compounds being heated – it provides only thermal activation.
- Uniform heating
- Enhanced reaction rates
- Reduce reaction times
- Higher yields
- Purity in final product
- Greater selectivity
- Low operating cost: economic for the synthesis of a large number of organic molecules, Reduction in unwanted side reaction

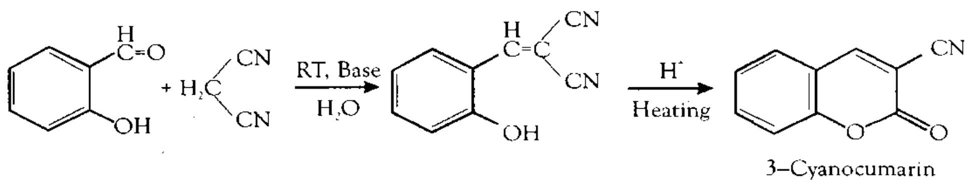
AQUEOUS PHASE EXTRACTION: In view of the environmental concerns caused by pollution of organic solvents, chemists all over the world have been trying to carry out organic reactions in aqueous phase. The advantages of using water as a solvent are its low cost, non-inflammable, devoid of any carcinogenic effects, and high specific heat resistance.

Ex: Knoevenagel reactions: The condensation of carbonyl compounds (mostly aromatic aldehydes) with active methylene compounds in presence of weak base like ammonia/amine/ pyridine is known as Knoevenagel reaction.

Organic medium reaction:



Water medium:



NANOMATERIALS

Introduction: Nano means one billionth i.e. $\frac{1}{1000000000}$ or 10^{-9} and therefore a nano meter is just one billionth of a meter. **Nano materials** are those which possess at least one dimension in the nano scale i.e. 1 to 100 nm. Nanotechnology is a field of applied science focused on the design, synthesis and application of materials and devices on the nanoscale.

When a bulk material is changed into Nano sized particle, the properties also change. The properties that are changed at nano scale are:

PROPERTIES OF NANO MATERIALS

1. **The physical properties** like melting point, adsorption and catalytic activity are dependent on the surface area or more precisely the surface to volume ratio. As the size of the particle decreases, the surface to volume ratio increases tremendously. More atoms are on the surface rather than in the bulk (inside of a particle). Therefore, the melting point decreases, the catalytic activity, adsorption increases as the particle size decreases.
2. **The optical properties and electric properties** depend on the band structure or density of states. As the particle size decreases, the band gap increases in semiconducting materials and therefore shows different colours with different sizes. (Ex. CdTe particles in solution show colours from blue, green, yellow red as the size increases from 1 to 50 nm.
3. **The magnetic properties** of magnetic (Ferro, anti-Ferro, Para and dia) materials change with size of the particles i.e. as the size approaches individual domain size, they can be magnetized to a great extent and multi domain structure disappears and we get single domain structure. Ex. Fe particles of size below 16 nm can be magnetized to more than the bulk iron.
4. **The mechanical properties** of ceramics which are usually brittle can be enhanced to a large extent if the crystallite sizes are small in the nano-range rather than highly crystalline nature. Because of the small crystallites embedded in amorphous matrix, they get more malleability (less brittle) and still have high tensile strength. Carbon nanotubes have high mechanical strength because of rigid structure of hexagonal carbon atoms.
5. **Chemical Properties** Based on the surface area to volume effect, nanoscale materials have

a) Increased total surface area.

b) Increased number of atoms accessible on the surface.

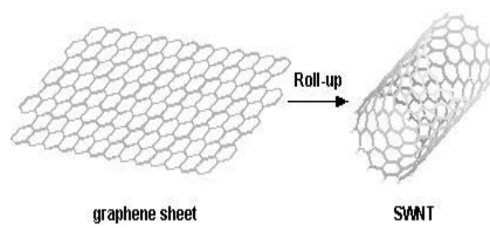
c) Increased catalytic activity of those large number surface atoms.

d) Different/tunable surface catalytic properties by the change in shape, size and composition. Hence, nanoscale catalysts can increase the rate, selectivity and efficiency of various chemical reactions.

CLASSIFICATION OF NANO MATERIALS

CARBON NANO TUBES (CNTs)

- Carbon Nano Tubes (CNTs) were discovered by S. Iijima in the year 1991.
- They are long, thin tube like cylinders made of hexagonal rings of carbon atoms, Bonded covalently by sp^2 hybridization



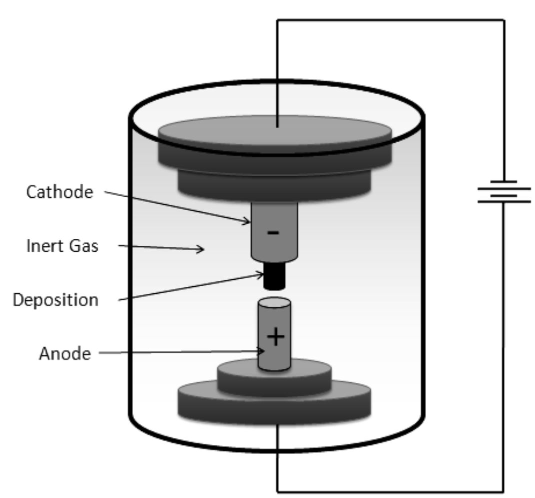
- A sheet of graphite is rolled into a cylinder or twisted to make a tube of few nm in diameter and upto hundreds of micrometres long (length to diameter ratio 28,000,000 :1)
- These nano tubes have a hemispherical "cap" at each end of the cylinder (closed CNTs) And they can be open also (open CNTs)
- CNT diameter = ~1.2 nm
- CNTs are two types depending upon the way in which they are arranged.

(a) A single walled nanotubes (SWNT)

(b) A multi walled nanotubes (MWNT)

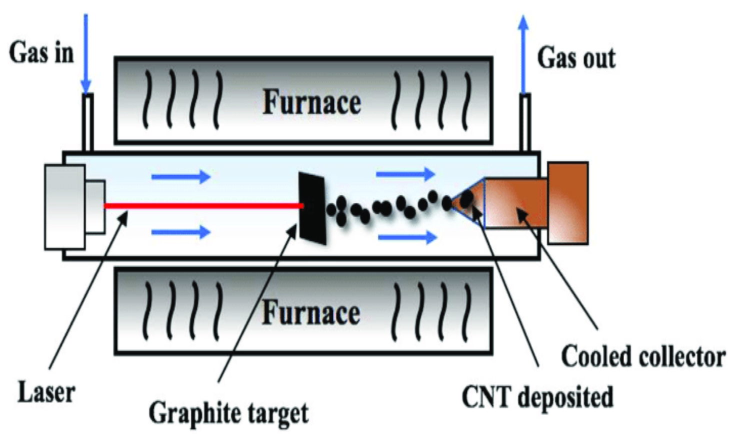
PREPARATION OF CARBON NANO TUBES

ARC DISCHARGE METHOD (Krotschmer and Huffman method, 1990)



- Electrical discharge between graphite electrodes (mixed with metal catalyst like (Fe, Co, Ni etc.) in an atmosphere of Helium, argon at low pressure 50 -700 mbar produces carbon nano tubes along with other carbon mass.
- A direct current of 50-100 A and voltage of 20V creates high temperature arc between the electrodes.
- The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod.
- The resulting soot (on the graphite cathode, inner walls of evaporation chamber) is scraped and dissolved in polar organic solvents. The metal catalysts are separated by treating with mild acid/base and then dissolved in aromatic organic solvent (coloured solution).
- The coloured solution is separated from the black insoluble soot (settling at the bottom).
- Pressure of Helium & Argon, their ratio, the current & voltage, the catalyst type, size and content, the distance between electrodes etc. determine the type of CNTs their quality, quantity and diameter

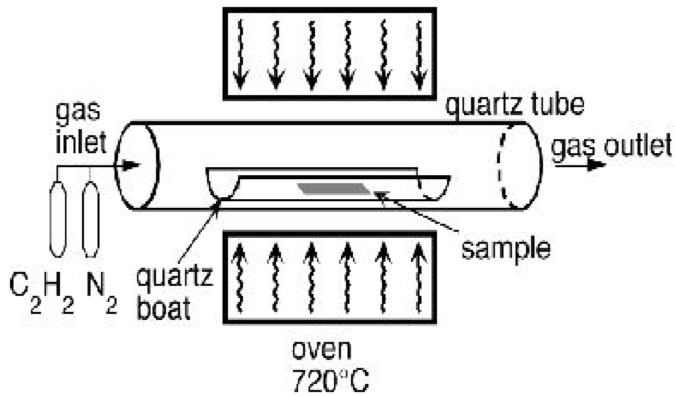
LASER ABLATION METHOD



- In this method, a high energy pulsed laser vaporizes a graphite target in a high temperature reactor, while an inert gas like He or Ar is fed into the chamber (500 Torr)
- A pulsed or continues laser is used to vaporize a graphite target in an oven at 1200^{o}C
- The main difference between continues and pulsed laser, is that the pulsed laser demands much higher intensity.
- A very hot vapour forms, then expands and cools rapidly.

- The nano tubes develop on the cooler surface (water cooled copper collector) of the reactor as the vaporized carbon condenses
- This method has an yield of 70 % and mainly produces SWNTs with controllable diameter depending on reaction temperature
- However, it is more expensive than arc discharge or CVD

CHEMICAL VAPOUR DEPOSITION



- A substrate is prepared with metal catalyst particles (Ni, Co, Fe or a combination). The diameter of CNTs will depend on size of metal particles. This can be achieved by patterned or masked deposition of metal, annealing or etching of a metal layer
- The substrate is heated to approximately 700^0 C
- To initiate growth of CNTs, two gases are fed into the reactor
- Process gas: ammonia, nitrogen and hydrogen
- Carbon containing gas: CO, acetylene, Methane, ethanol etc.
- Using thermal annealing or chemical etching results in cluster formation on the substrate.
- The temperatures for the synthesis of nanotubes by CVD are generally within the 650-900^{o}C range.
- The typical yield for this CVD method approximately 20-100%

PROPERTIES OF CNTs

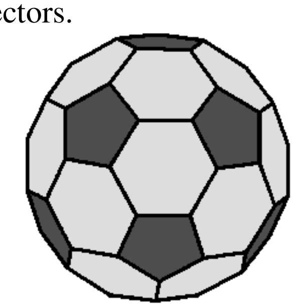
- It is the strongest, stiffest in terms of tensile strength and elasticity property. This strength results from the covalent sp2 bonds formed between the individual carbon atoms.
- High Electrical Conductivity
- Very High Tensile Strength

- Highly Flexible- can be bent considerably without damage
- Very Elastic ~18% elongation to failure
- High Thermal Conductivity
- Low Thermal Expansion Coefficient
- Good Field Emission of Electrons
- Highly Absorbent
- High Aspect Ratio (length = ~1000 x diameter)

APPLICATIONS OF CARBON NANOTUBES

- They find application in conductive and high strength composites, energy storage and energy conversion devices, sensors and nano meter sized semiconductor devices.
- They are used as Nano probes in meteorology and biological and chemical investigations.
- CNT can be functionalized with bio active peptides, proteins, nucleic acids and drugs.
- Functionalized CNT display low toxicity and are used in the field of nanobiotechnology and nano medicine.
- Hydrogen can be stored in the carbon nanotubes, which is in turn used for the fuel cells. The SWNTs are effective as a hydrogen-storage material for fuel cell electrical vehicle.
- CNTs can replace platinum as the catalyst in fuel cells, which could reduce fuel cells overall cost.
- A catalyst having CNTs makes a reaction safer and selective.
- CNTs are used for the electrochemical reaction of oxygen
- Carbon nano tubes are being highly used in the fields of efficient drug delivery and bio sensing methods for disease treatment and health monitoring.
- Carbon nanotubes can be used as multifunctional biological transporters and near-infrared agents for selective cancer cell destruction.
- Due to high electrochemically accessible surface area, high electrical conductivity and useful structural properties, SWNT and MWNTs in highly sensitive glucose detectors.

FULLERENES

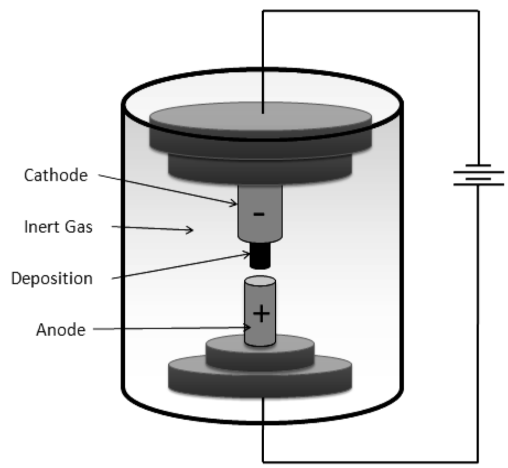


Fullerenes are CNTs are allotropic forms of carbon. The diamond and graphite structures of carbon are well known and main allotropes of carbon with tetrahedral and planar arrangement of carbon atoms respectively.

- Fullerenes (C_{60} and others) were discovered by R. F. Curl., H. W. Kroto, R. E. Smalley in 1985 and they were awarded Nobel Prize in Chemistry 1996.
- They are closed structures of only carbon atoms, each bonded covalently by sp^2 hybridization (one double bond, two single bonds)
- The double bonds are usually given for hexagons only
- C_{60} is a polygon (truncated icosahedron) with 12 pentagons and 20 hexagons (like a soccer ball). Diameter = 1 - 2 nm (Icasohedron)

PREPARATION OF FULLERENES

ARC DISCHARGE METHOD (Krotschmer and Huffman method, 1990)



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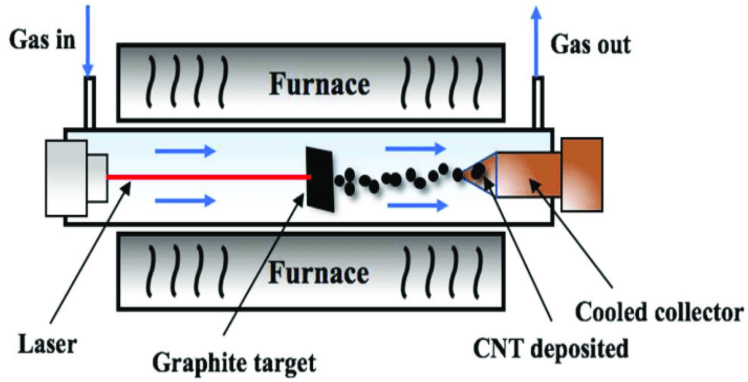

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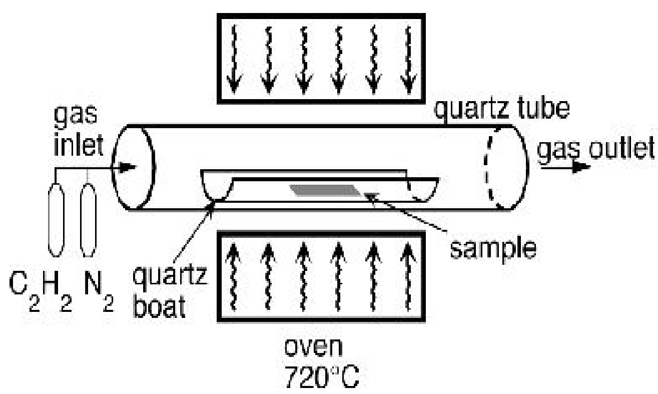

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PROPERTIES OF FULLERENES

- Physical properties: C_{60} is a mustard coloured solid. When the thickness of the film increases, it appears brown to black
- It is moderately soluble in the common organic solvents, especially aromatic hydrocarbons.
- Mechanical Properties: It has high tensile strength and also highest packing density of all known structures
- Thermal properties: Thermally stable upto 600 ^{o} C. it undergoes sublimation under
- Electrical Properties: It has high electrical conductivity, when doped with alkali metals; they show even superconductivity (Eg. KC_{60})
- They are difficult to oxidize
- They are good acceptors of electrons (used in polymer solar cells) and electronic energy

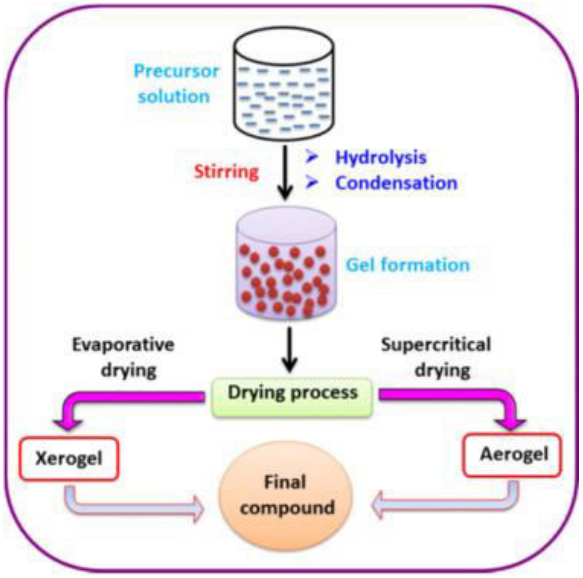
APPLICATIONS OF FULLERENES:

- Fullerenes can easily accept electrons; hence they may be used as charge carrier in batteries.
- Fullerenes can be used as organic photovoltaic.
- Alkali metal fullereids are super conductors.
- It can also be used as a soft ferromagnetic.
- Its spherical structure makes it suitable for the use as lubricant.

SOL-GEL PROCESS FOR THE PREPARATION OF NANOMATERIALS

The sol–gel process is a wet-chemical technique used for the fabrication of both glassy and ceramic materials. In this process, the sol (or solution) evolves gradually towards the formation of a gel-like network containing both a liquid phase and a solid phase. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form a colloid. The precursor used in sol-gel process for the synthesis of nanoporous materials are metal alkoxidesM(OR). They readily react with water to form gels.

Examples: Tetra methoxysilane [Si(O_3CH_4)], Tetra ethoxysilane [Si($O_2C_5H_4$)], Tetra butoxytitanate [Ti($O_4C_9H_4$)]

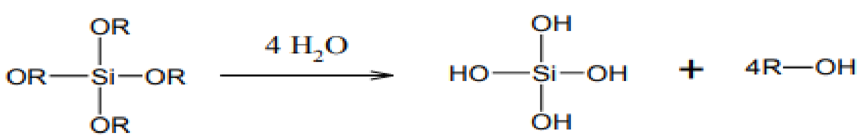


Process (Synthesis of silica aerogel)

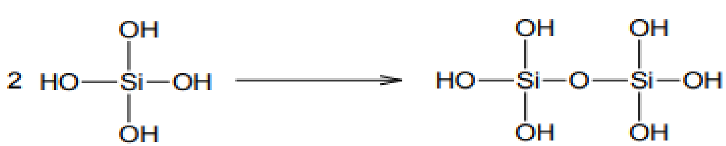
This process consists of four main steps.

1. Hydrolysis of precursors
2. Gelation followed by polycondensation
3. Supercritical drying

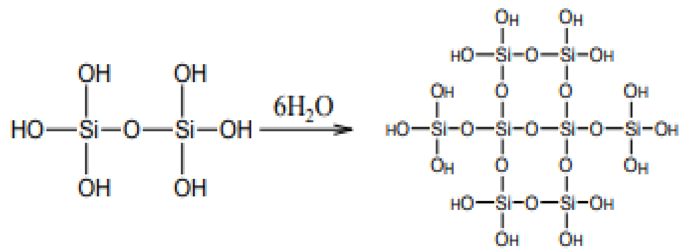
1. **Hydrolysis:** it occurs by the addition of water to9 any one of the precursor material to form Metal 1. Hydroxide particles.



2. **Condensation:** the self condensation of metal hydroxide groups produces M-O-M linkages filled with byproducts of water and alcohol.



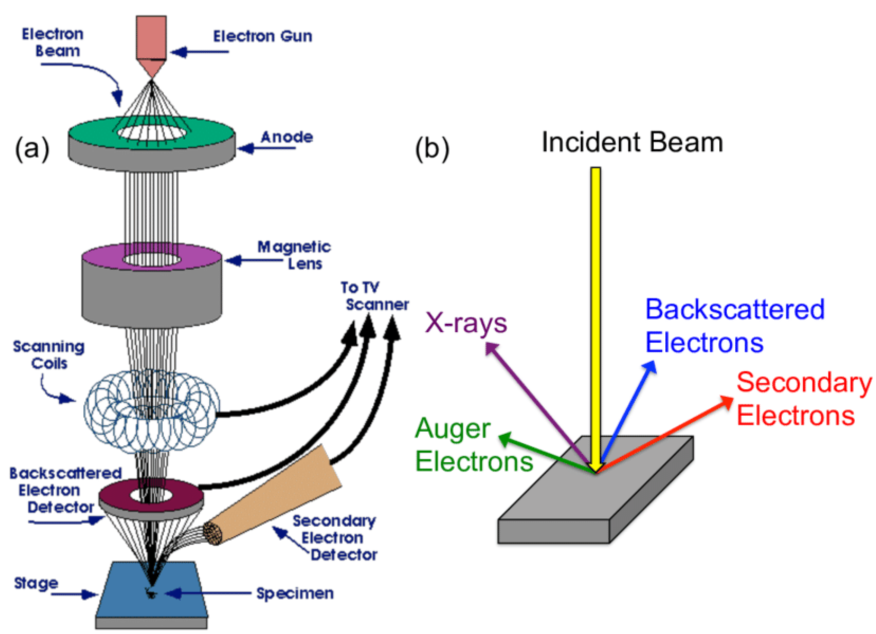
3. **Poly condensation:** The condensation process continue to form poly condensed M-O-M linkages



4. **Drying:** The gels are subjected to super critical drying in an autoclave. The critical pressure and critical temperature used are 78 bar and 294°C respectively in order to remove liquid from silica gel to form the network structure of silica aerogel.

SCANNING ELECTRON MICROSCOPE (SEM)

Scanning electron microscope is an improved model of an electron microscope. SEM is used to study the three dimensional image of the specimen.



Principle: When the accelerated primary electrons strike the sample, it produces secondary electrons. These secondary electrons are collected by a positive charged electron detector which in turn gives a 3- dimensional image of the sample.

Construction: It consists of an electron gun to produce high energy electron beam. A magnetic condensing lens is used to condense the electron beam and a scanning coil is arranged in-between magnetic condensing lens and the sample. The electron detector (Scintillator) is used to collect the secondary electrons and can be converted into electrical signal. These signals can be fed into CRO (Cathode Ray Oscilloscope) through video amplifier.

Working: Stream of electrons are produced by the electron gun and these primary electrons are accelerated by the grid and anode. These accelerated primary electrons are made to be incident on the sample through condensing lenses and scanning coil. These high speed primary electrons on falling over the sample produce low energy secondary electrons. The collection of secondary electrons is very difficult and hence a high voltage is applied to the collector. These collected electrons produce scintillations on to the photo multiplier tube are converted into electrical signals. These signals are amplified by the video amplifier and are fed to the CRO (Cathode Ray Oscilloscope). By similar procedure the electron beam scans from left to right and the whole picture of the sample is obtained in the CRO (Cathode Ray Oscilloscope) screen.