UNIT-IV

SMART MATERIALS FOR SENSORS

UNIT-IV **Smart sensors and devices** **09 Hrs**	
RFID and IONT materials: Synthesis, properties and applications in logistic information, intelligent packaging systems (Graphene oxide, carbon nanotubes (CNTs) and polyaniline). **Sensors**: Introduction, types of sensors (Piezoelectric and electrochemical), nanomaterials for sensing applications (Strain sensors, gas sensor, biomolecules and volatile organic compounds).	

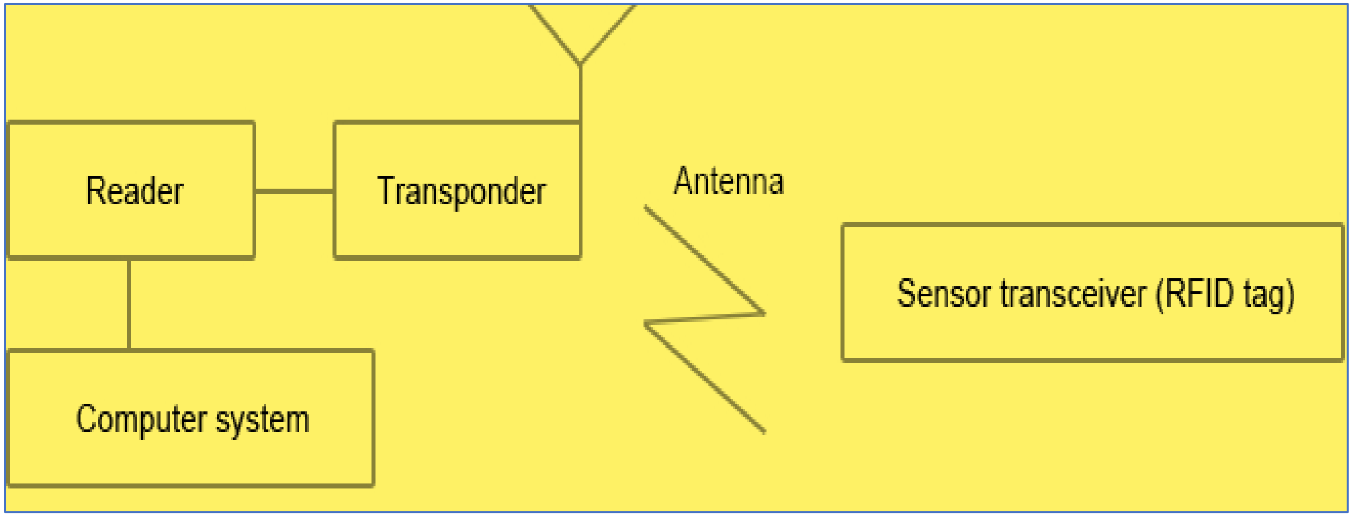
Internet of Things (IoT) technology

IoT technology is an integration of internet and sensor network, via (Radio Frequency Identification) RFIDs devices.

If this technology involve the smart devices made-up of nanomaterials, it is called Internet of nano things (**IONTs**).

RFID: It is a wireless, an electronic device/tag, which uses electromagnetic field to identify, track and connect with the objects attached with tags. The required data/information of the object is collected and recorded by means of radio frequency signal.

Working principle of RFID system



- The RFID system consists of RFID TAG, ANTENNA, TRANSPONDER, READER, COMPUTER
- RF signals with a specific frequency are transmitted by READER through ANTENNA.
- When 'RFID TAG' enters the 'READER' area, the ANTENNA will transmit induced current, which activates the 'RFID TAG' to transmits the information to the 'READER'. (Passive system)
- In case of active system, when the RFID TAG enters the READER area, the embedded battery powers the RFID TAG in order to complete the communications with each other.
- After 'READER' reads the self-coded information, it will send the same to 'COMPUTER' for exchanging and managing the data.

Classification of RFID tags
Based on the power requirements

Passive RFID Tag: It is a RFID tag with no inbuilt power source (Battery) designed to use in small range (up to 10 m) tracking systems, operates on low, high or ultra-high frequency. However, it receives power from the reading antenna, whose electromagnetic wave induces a current in the RFID tag's antenna. It is very thin and has a long service life.

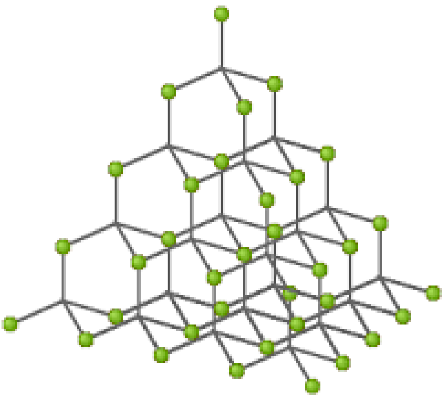
Active RFID Tag: It has its own power source, such as battery, inbuilt. It is used for long scanning and reading range (up to 100 m), operates only at high frequency. The price is relatively high, volume is larger than the Passive tag because of the built-in battery.

RFID is classification based on the working frequency range

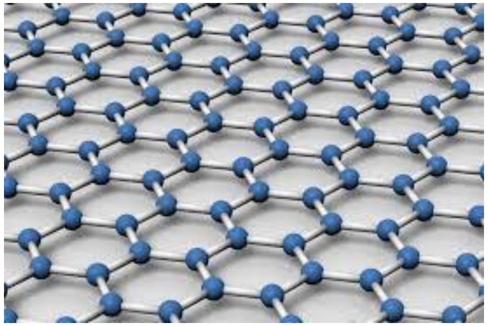
Types	Low-Frequency	High-Frequency	Ultra High-Frequency
Frequency Range	100~500 KHz	10~15 MHz	850~950 MHz~2.45 GHz
inductive distance	shorter	longer	longest
reading speed	slower	relatively high	fastest
penetration ability	good	Avearge	bad

Carbon Nano-tubes:

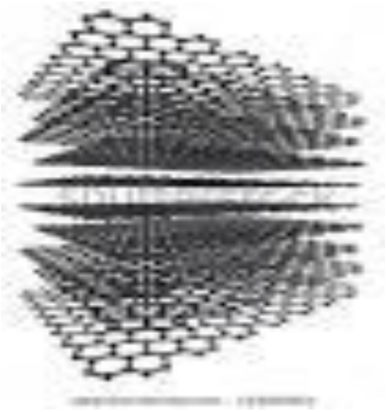
- **Allotropes of carbon**



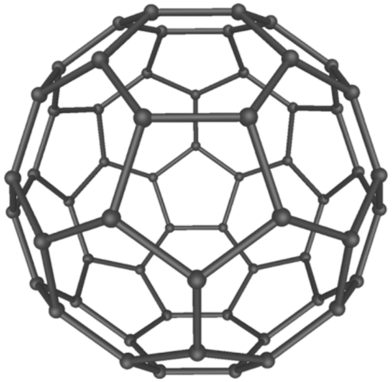
Diamond



Graphene



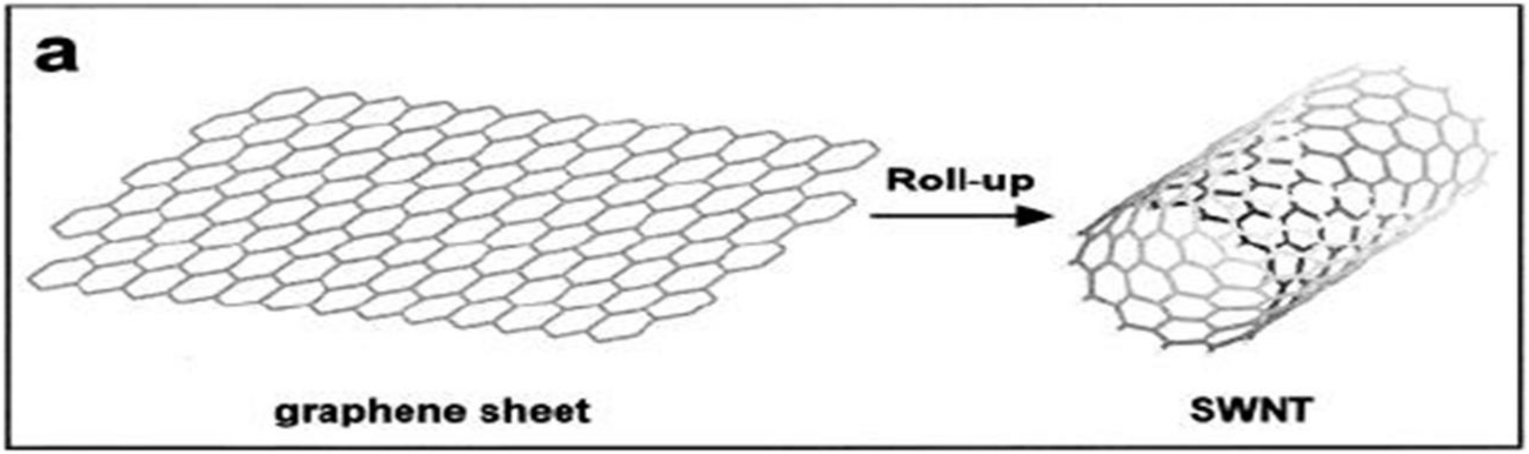
Graphite

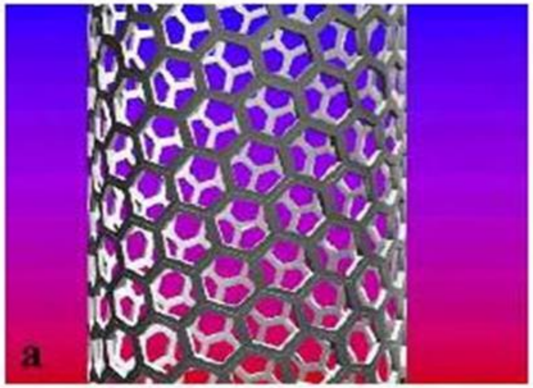


Fullerene

Carbon Nano-tubes:

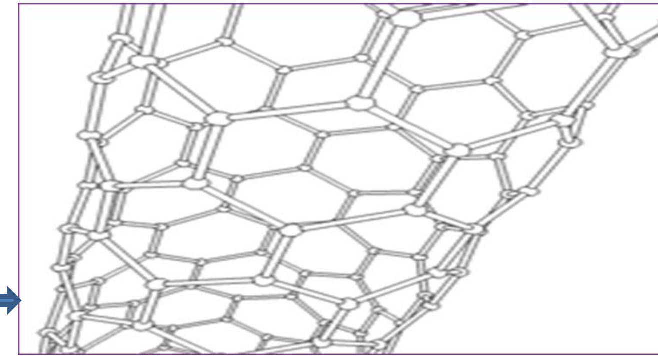
- CNT: Rolling-up a graphene sheet to form a tube





Carbon Nano-tubes:

- Unique properties of CNT's



Carbon nanotubes, composed of interlocking carbon atoms, are 1000x thinner than an average human hair – but can be 200x stronger than steel.

CARBON NANO-TUBES

Extra ordinary strength

Thermal Properties

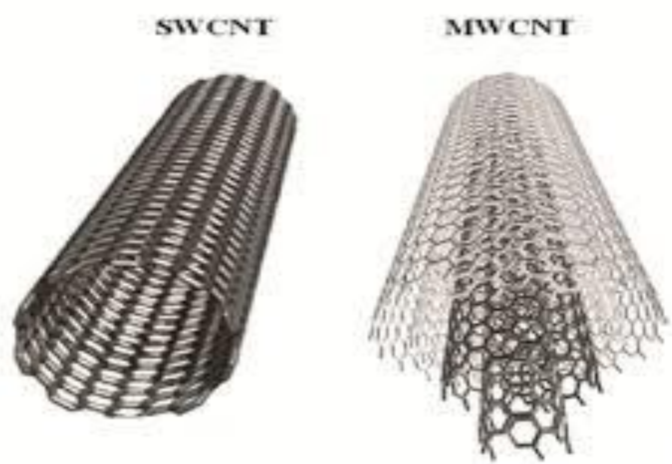
Good Electrical Properties

Carbon Nano-tubes:

CARBON NANOTUBES

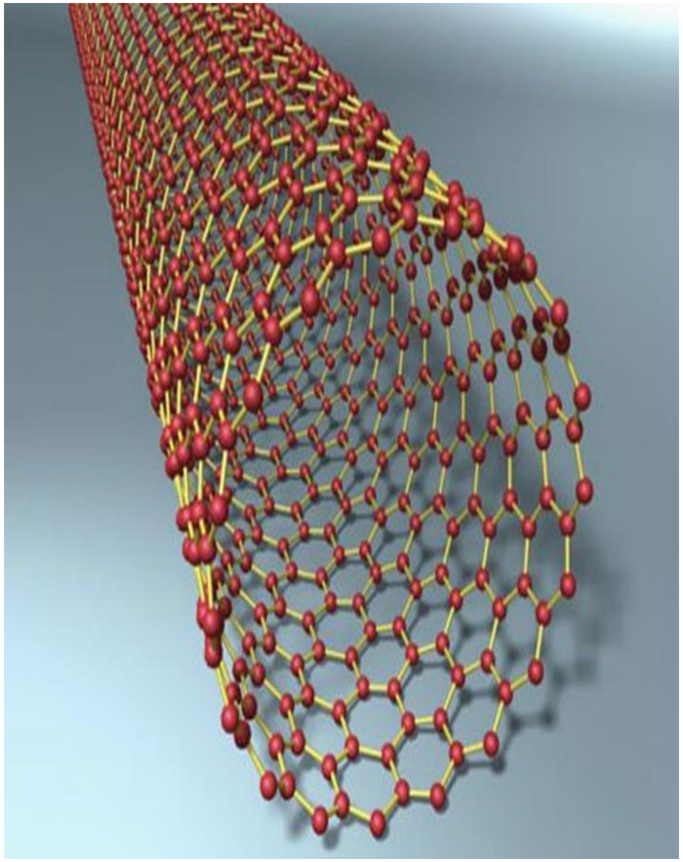
SINGLE-WALLED(SWNT)

MULTI-WALLED(MWNT)

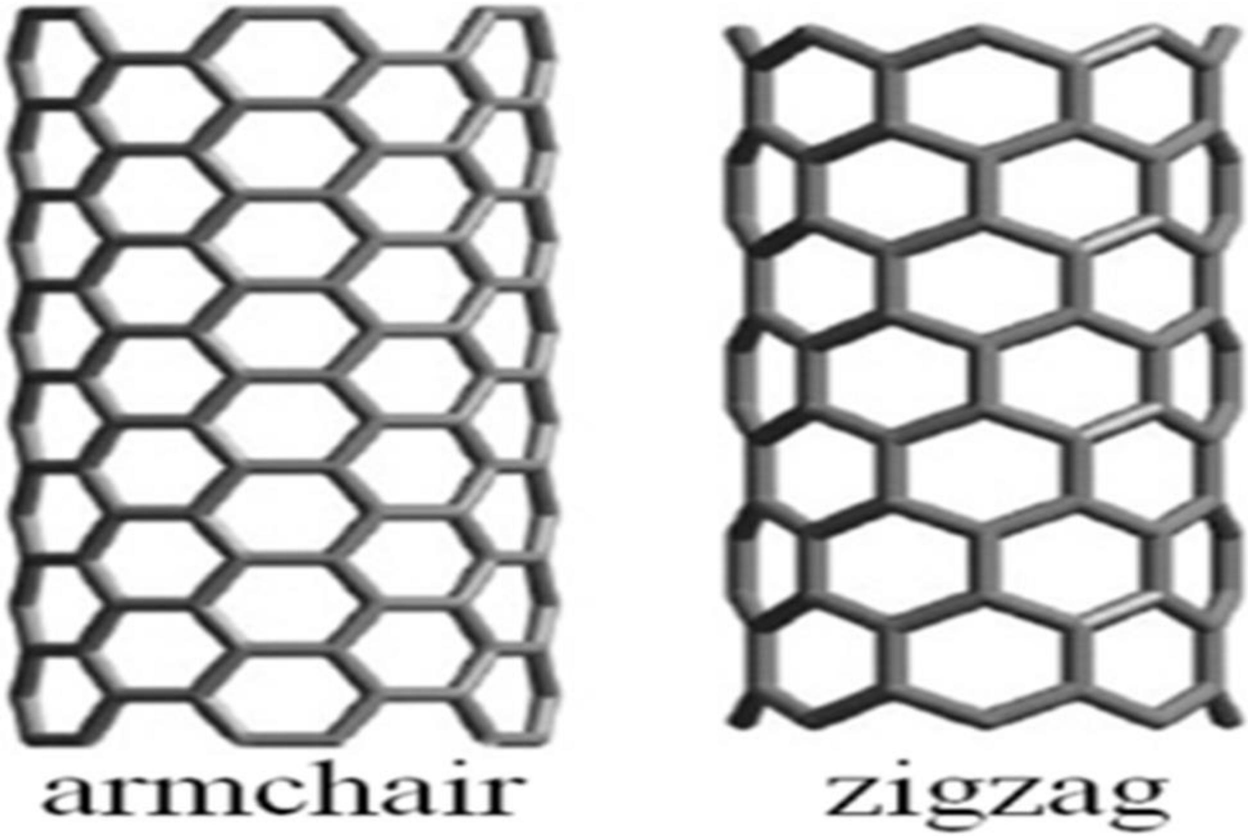


Single walled Carbon Nano-tubes: (SWCNT)

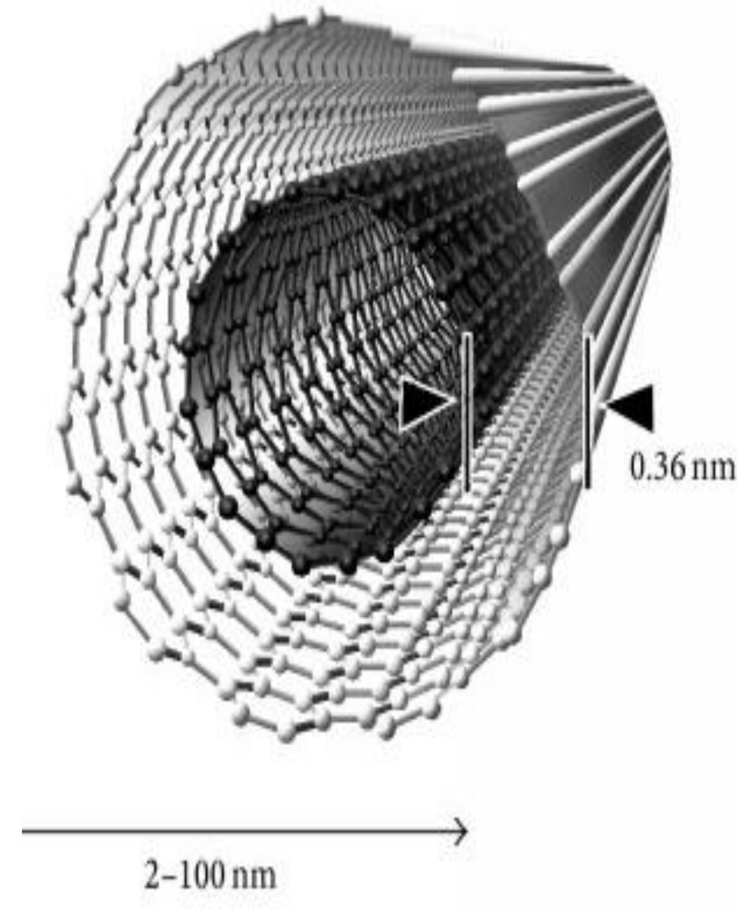
- Diameter of close to 1 nanometer
- Tube length that can be many millions of time longer



Types of Single walled Carbon Nano-tubes: (SWCNT)

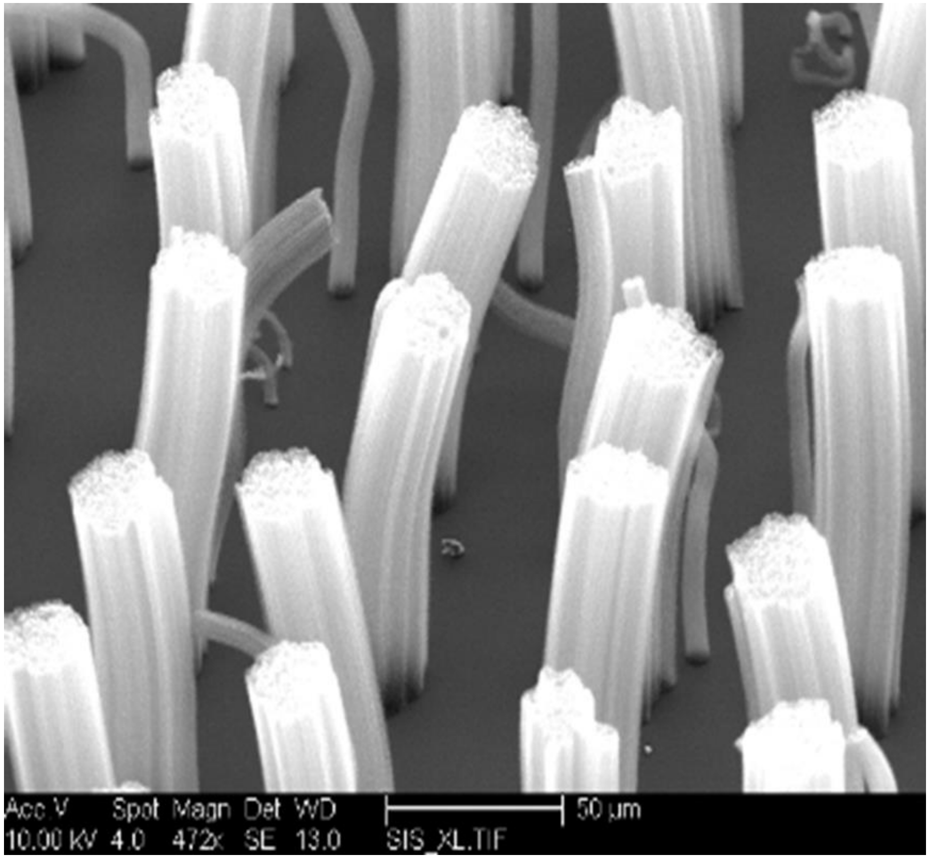


Types of Multi walled Carbon Nano-tubes: (MWCNT)



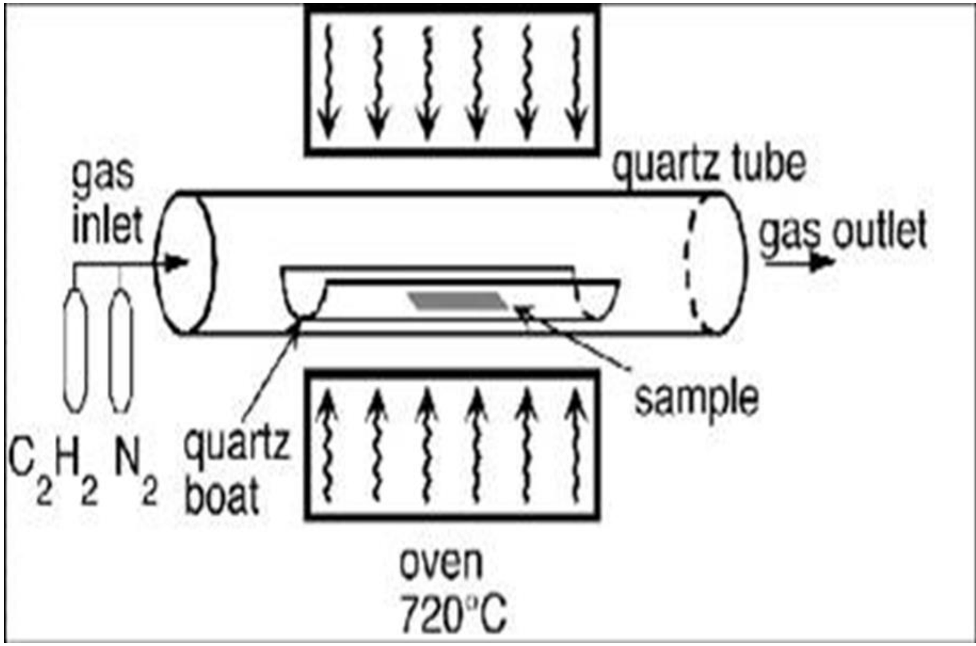
Methods of preparation of CNT's

- Chemical Vapor Deposition (CVD)
- Arc Discharge
- Laser Ablation
- Ball Milling



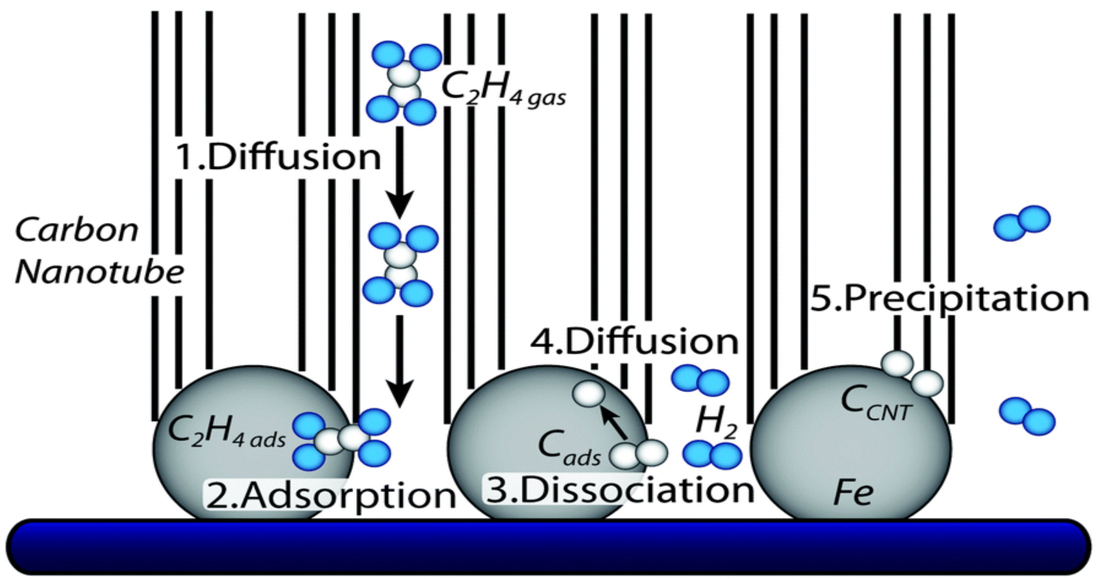
Chemical Vapor Deposition Method (CVD):

- One of the most common methods of carbon nanotube synthesis.
- Temperature between 650 – 1200ºC.
- Yield is usually about 30%.
- Source of carbon: Methane Carbon monoxide, Acetylene gasses.
- Usually, a silicon plate coated with iron particles is the substrate.
- After energy transfer, the carbon molecule binds to the substrate.



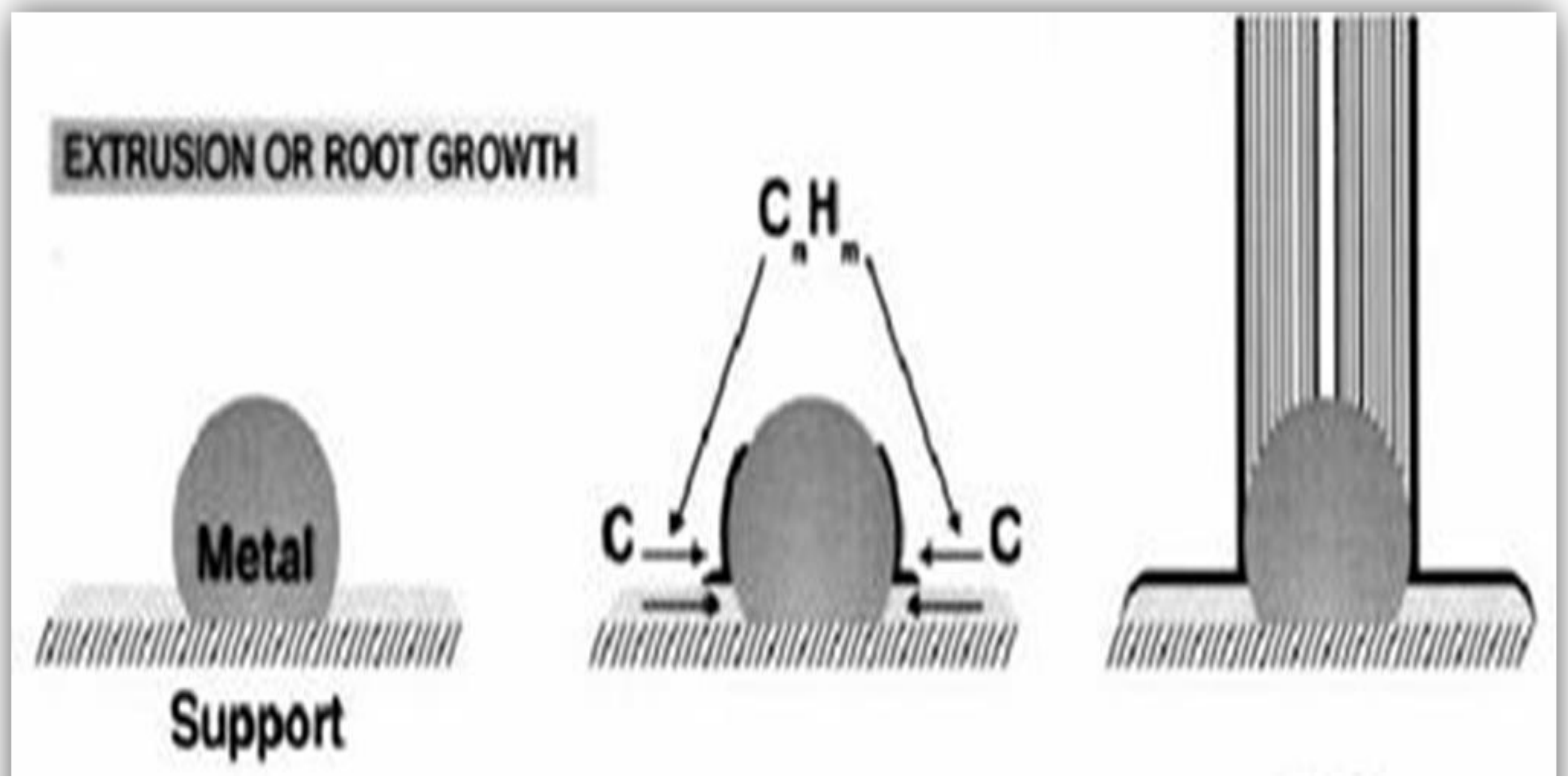
Mechanism of CNTs growth:

1. **Diffusion** of Hydrocarbon gas
2. **Adsorption** of Hydrocarbon gas on the surface-active site of catalyst particles.
3. **Dissociation** (Homolytic fission) of Hydrocarbon into highly reactive free radicals of ‘C’ and ‘H’.
4. **Repetition** of steps 1, 2 and 3 leading to increase in concentration (saturation) of free radicals.
5. **Precipitation** (aggregation) of carbon free radicals results into crystal growth in the form tube on the surface. ‘H’ free radicals escape as H_2 gas.



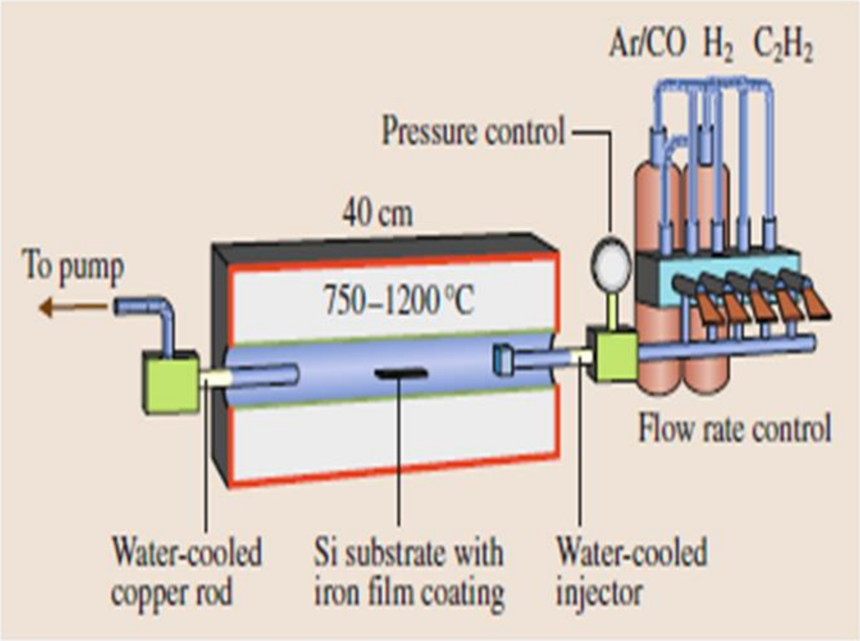
Chemical Vapor Deposition Method (CVD):

➢ Growing of nano tube on the surface of a substrate:

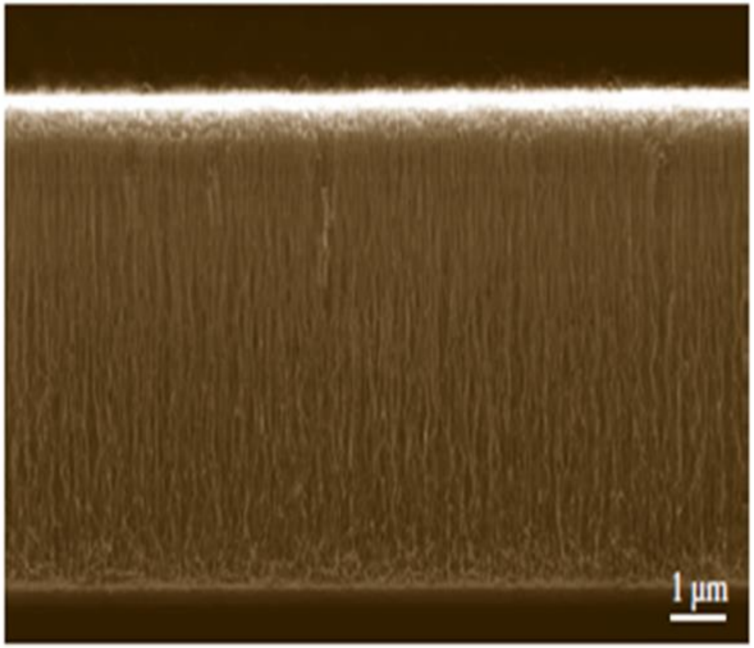


Chemical Vapor Deposition Method (CVD):

➢ Schematic view of the CVD Process:



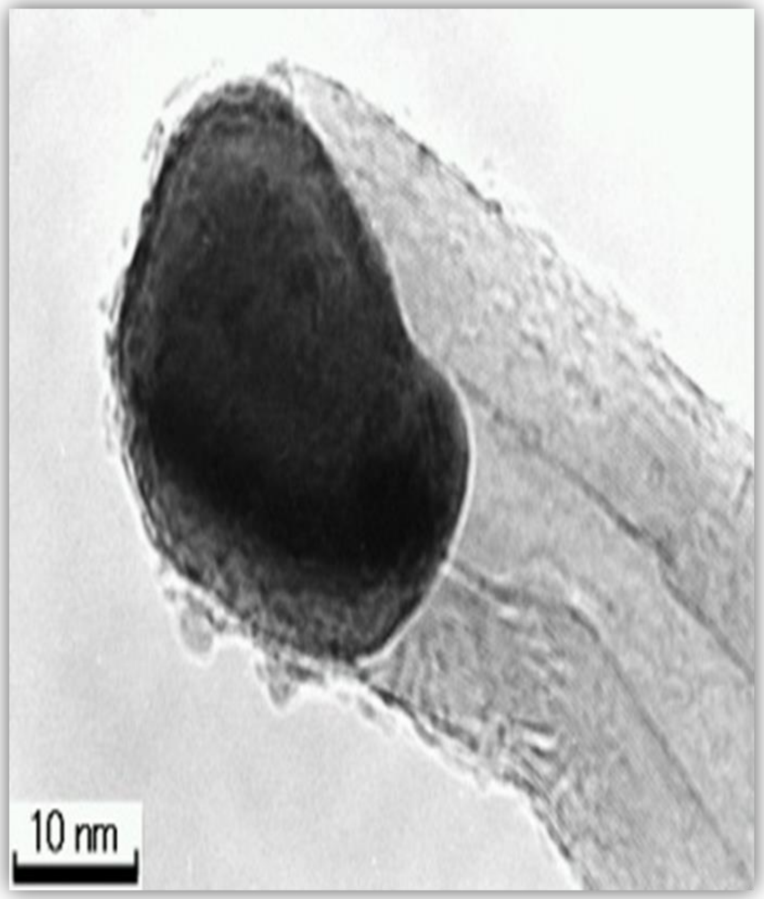
Schematic of thermal CVD system setup generally utilized in aligned CNT growth (courtesy Atomic Physics, Göteborg University)



SEM image of a vertically aligned carbon nanotube array (after [4.65])

Chemical Vapor Deposition Method (CVD):

- Advantages
  - Easy to increase scale to industrial production
  - Large length
  - Simple to perform
  - Pure products



- Disadvantage
  - Defects are common

Comparison between SWNT and MWNT

S. No	SWNTs	MWNTs
1	Single layer of graphene.	Multiple layer of graphene.
2	Catalyst is required for synthesis.	Can be produced without catalyst.
3	Bulk synthesis is difficult as it requires proper control over growth and atmospheric condition.	Bulk synthesis is easy.
4	Purity is poor.	Purity is high.
5	A chance of defect is more during fictionalization	A chance of defect is less but once occurred it's difficult to improve.
6	Less accumulation in body.	More accumulation in body.
7	Characterization and evaluation is easy	It has very complex structure.
8	It can be easily twisted.	It cannot be easily twisted.

Properties of CNT's

- Carbon-carbon bonds are one of the strongest bond in nature, **Composed entirely of sp^2 bonds.**
- 132,000,000:1 Length-To-Diameter Ratio.
- Diameter of 3 to 9 nm.
- Lengths in the millimeter range.
- Extremely high Young's modulus.

Material	Young's modulus (GPa)
Steel	190-210
SWNT	1,000+
Diamond	1,050-1,200

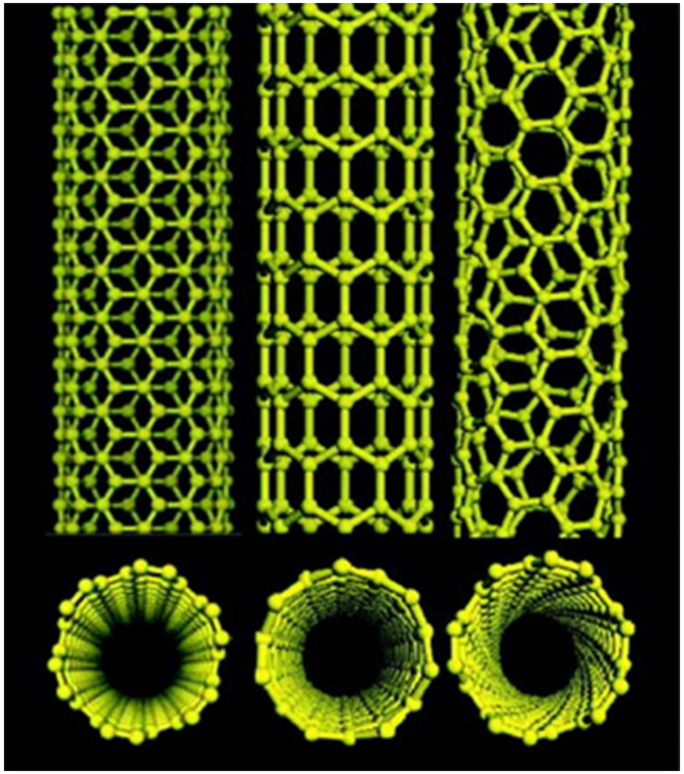
Properties of CNT’s

Electrical Properties

- If the nanotube structure is armchair then the electrical properties are metallic.

- If the nanotube structure is chiral then the electrical properties can be either semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor.

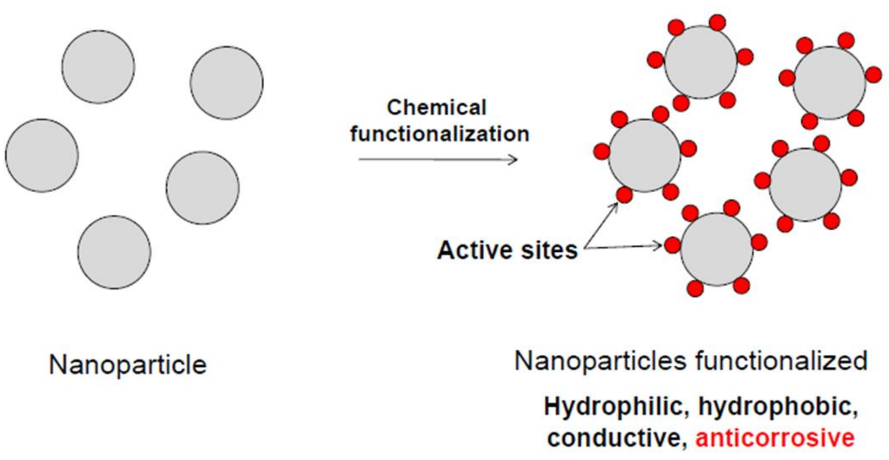
- In theory, metallic nanotubes can carry an electrical current density of 4×10^9 A/cm^2 which is more than 1,000 times greater than metals such as copper.

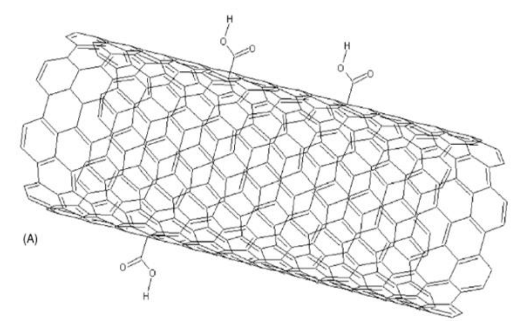


Functionalization of CNT’s

- Chemical modification of carbon nano tubes by inserting different functional group.

- Most of the applications require the functionalization of carbon nanotubes, such as changing the surface properties to make nanotubes soluble in different media, or attaching functional groups or polymer chains for specific utilizations of modified nanotubes.





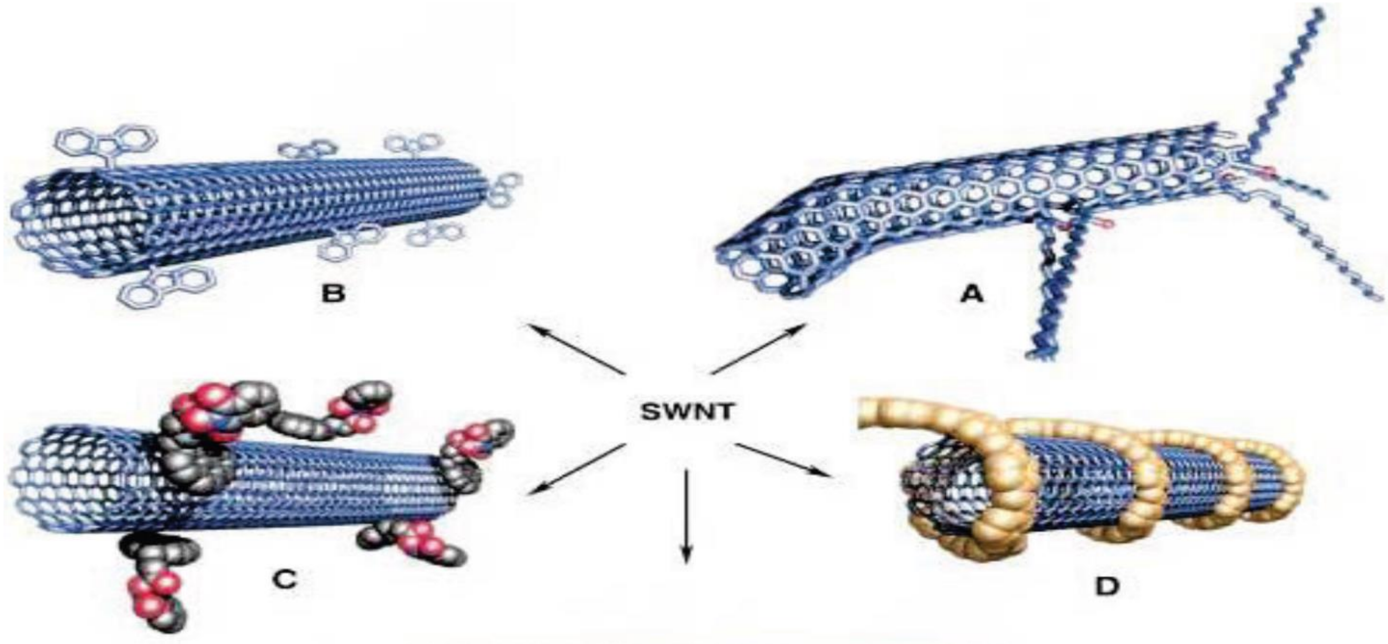
Types of Functionalization of CNT's

- <u>Endohedral functionalization</u>; CNTs are treated by filling their inner empty cavity with different molecules or nano particles

- **Eg: SWNT filled with C60 fullerenes**

Types of Functionalization of CNT’s

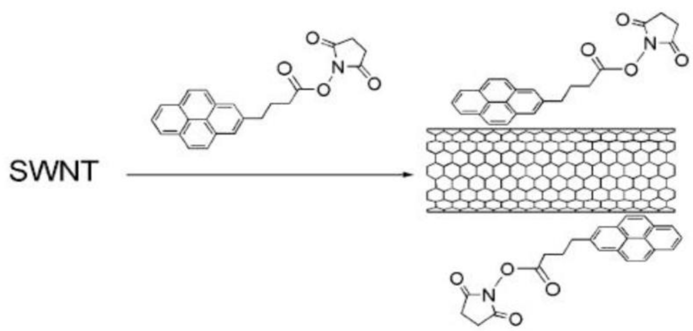
- Exohedral functionalization; CNTs are attached with other functional groups on their outer surfaces.



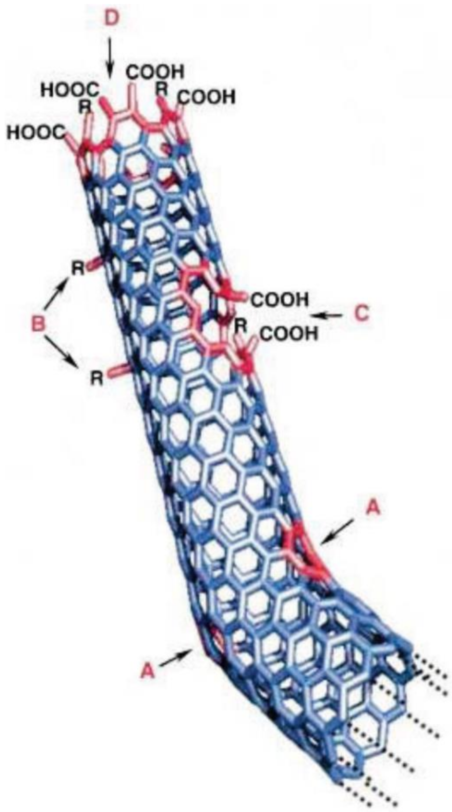
- **Defect functionalization (A)**
- **Covalent sidewall functionalization (B)**
- **Noncovalent functionalization with surfactants (C)**
- **Polymer wrapping (D)**

Types of Functionalization of CNT's

➢ Examples of functionalization:



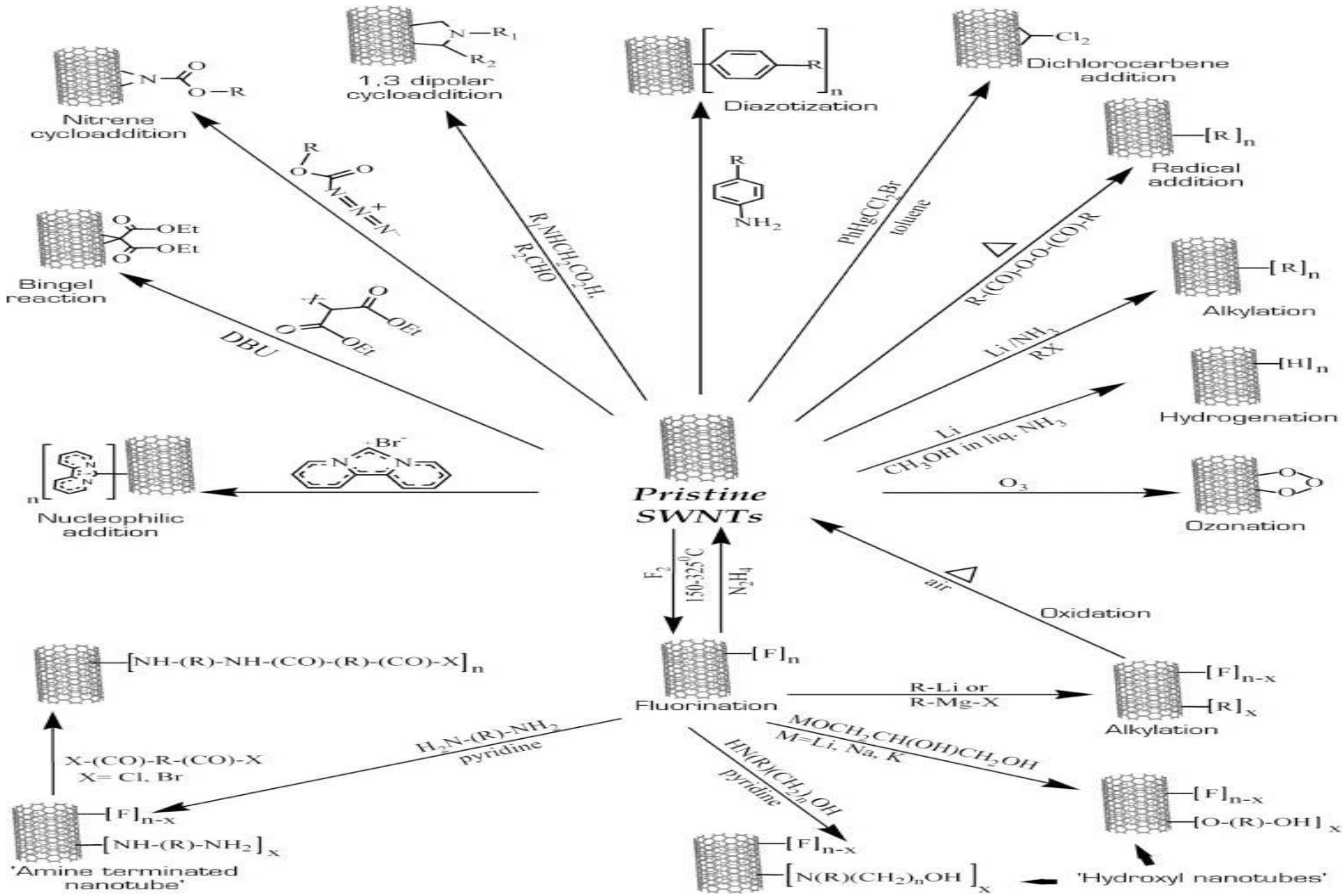
Interaction of nanotubes with pyrene derivatives



- The figure shows open end of the SWNT terminated with –COOH groups.
- This method was used to graft amine moieties onto carbon nanotubes

Types of Functionalization of CNT's

- **Examples of functionalization:**



Applications of CNT's

➢ Coating and Films:

- ➢ CNT-based transparent conducting films.
- ➢ Alternative to expensive indium tin oxide (ITO).
- ➢ Flexible, and not brittle.
- ➢ Application in.
  Displays
  Touch screen devices
  photovolatics

Applications of CNT's

➢ Nanotubes In Efficient Solar Cells

- Scientists have developed the 'blackest black' colour using carbon nanotubes

- Use of carbon nanotubes in solar cells could vastly improve their efficiency.

Applications of CNT's

➢ Nanotubes In Sporting Equipment

- Badminton racquet manufacturer Yonex incorporates carbon nanotubes into their cup stack carbon nanotubes racquets.

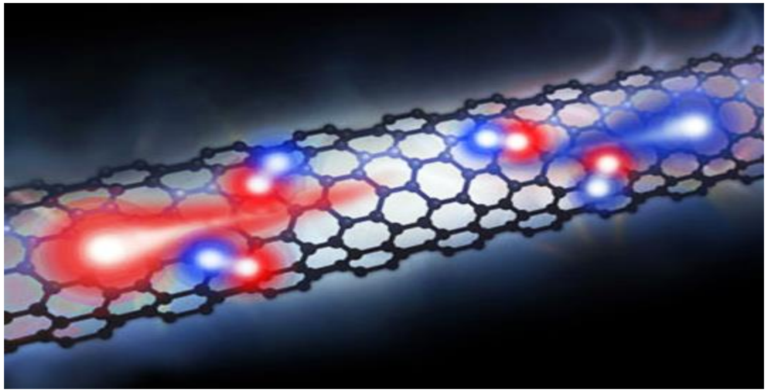
- American baseball bat manufacturer Easton Sports has formed an alliance with a nanotechnology company Zyvex to develop baseball bats incorporating carbon nanotubes.

- Tennis racquets also incorporate carbon nanotubes.

Applications of CNT’s

➢ In cancer treatment

- CNTs are tubular materials with nanometer-sized diameters and axial symmetry, giving them unique properties that can be exploited in the diagnosis and treatment of cancer.



- CNTs have the potential to deliver drugs directly to targeted cells and tissues. Alongside the rapid advances in the development of nanotechnology-based materials, elucidating the toxicity of nanoparticles is also imperative

Carbon nano tubes (CNT's)

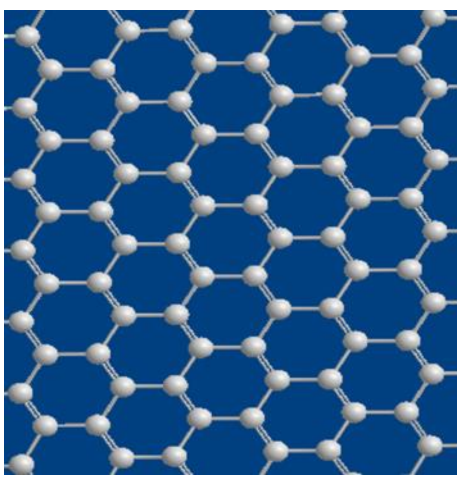
- **Hazards:**

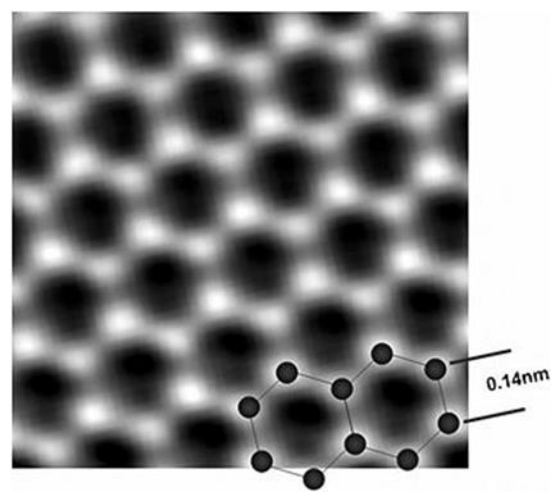
- **According to scientists at the National Institute of Standards and Technology, carbon nanotubes shorter than about 200 nanometers readily enter into human lung cells similar to the way asbestos does, and may pose an increased risk to health.**

- **Carbon nanotubes along with the majority of nanotechnology, are an unexplored matter, and many of the possible health hazards are still unknown.**

GRAPHENE

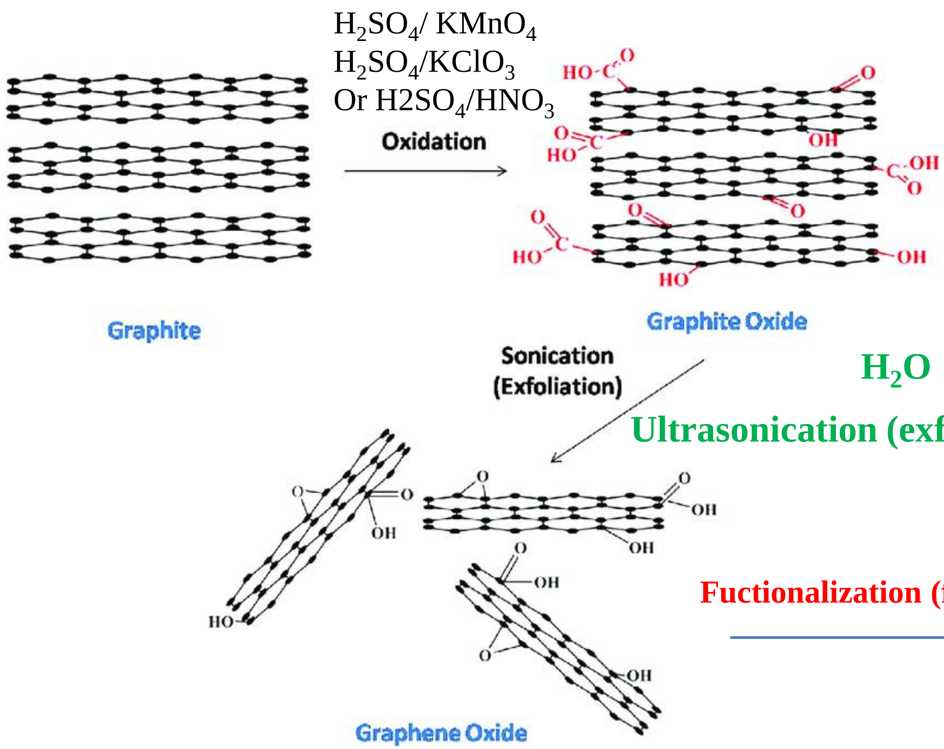
- A single sheet of graphite is called graphene.
- It is sp^2 hybridized $\rightarrow$ covalently bonded.
- The bonding between the graphene sheets in graphite is of van der Walls type.
- 2-dimensional, crystalline allotrope of carbon





Synthesis of Graphene by Graphite oxide method

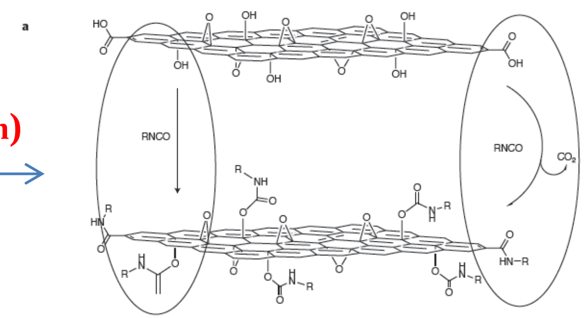
➢ Modified Hummer's method



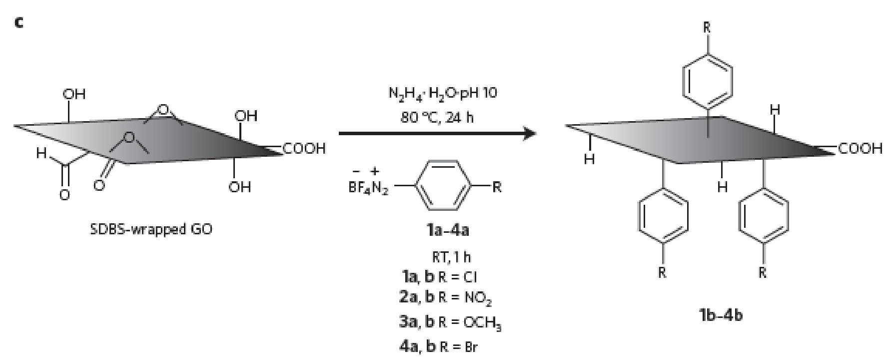
H_2O

Ultrasonication (exfoliation)

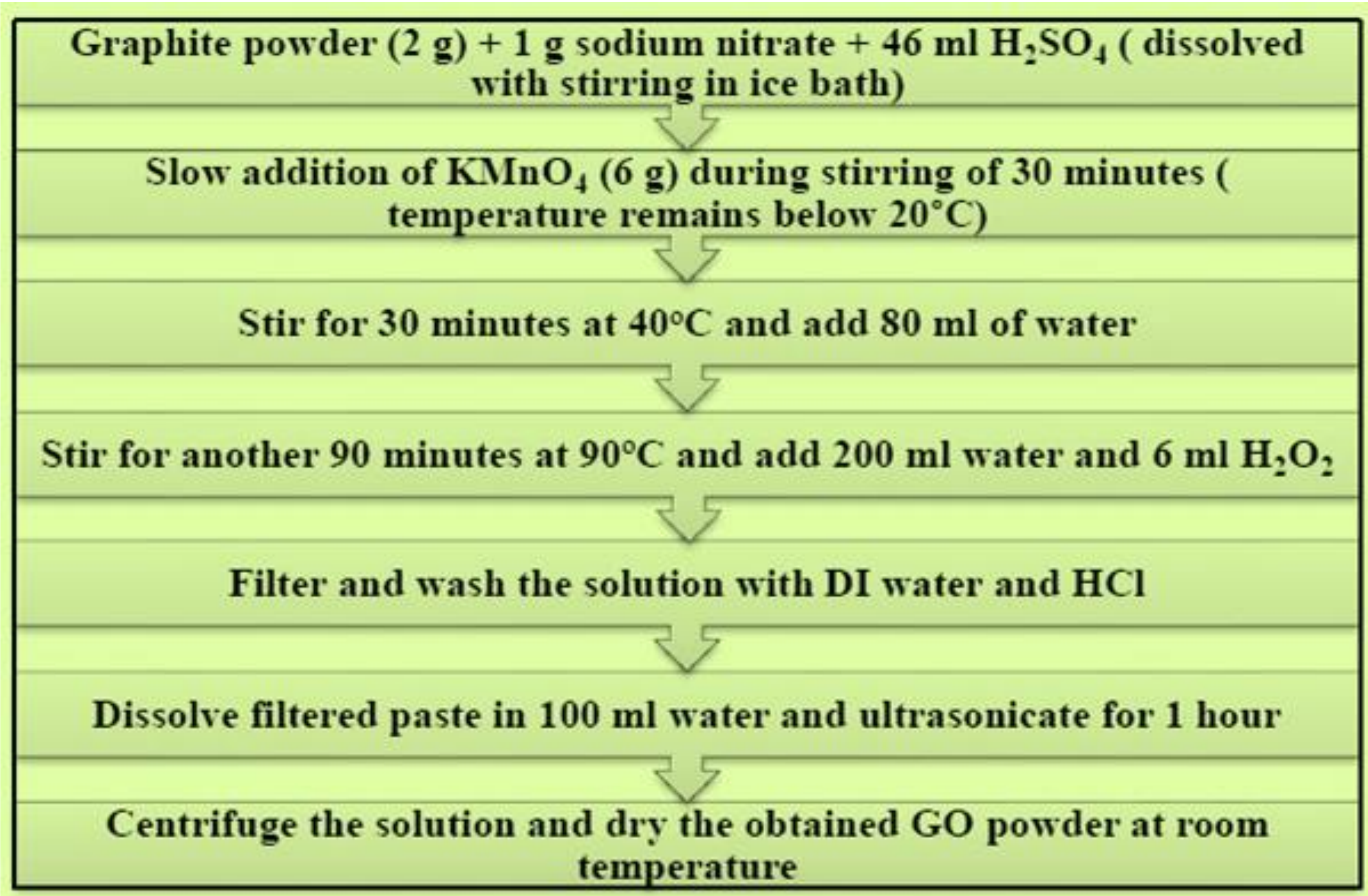
Fuctionalization (for better dispersion)



Graphene Oxide
monolayer or few layers



Stage I - Synthesis of GO (graphene oxide) from graphite powder



Stage-II: Synthesis of Graphene from GO (graphene oxide)

GO (100 mg) dissolved in to 100 ml water

↓

Add Hydrazine hydrate (10 µl, 0.2×10^{-3} mol)

↓

Reflux for one hour at 80°C

↓

Add sodium borohydride (1mg)

↓

Reflux for 36 hours at 100°C

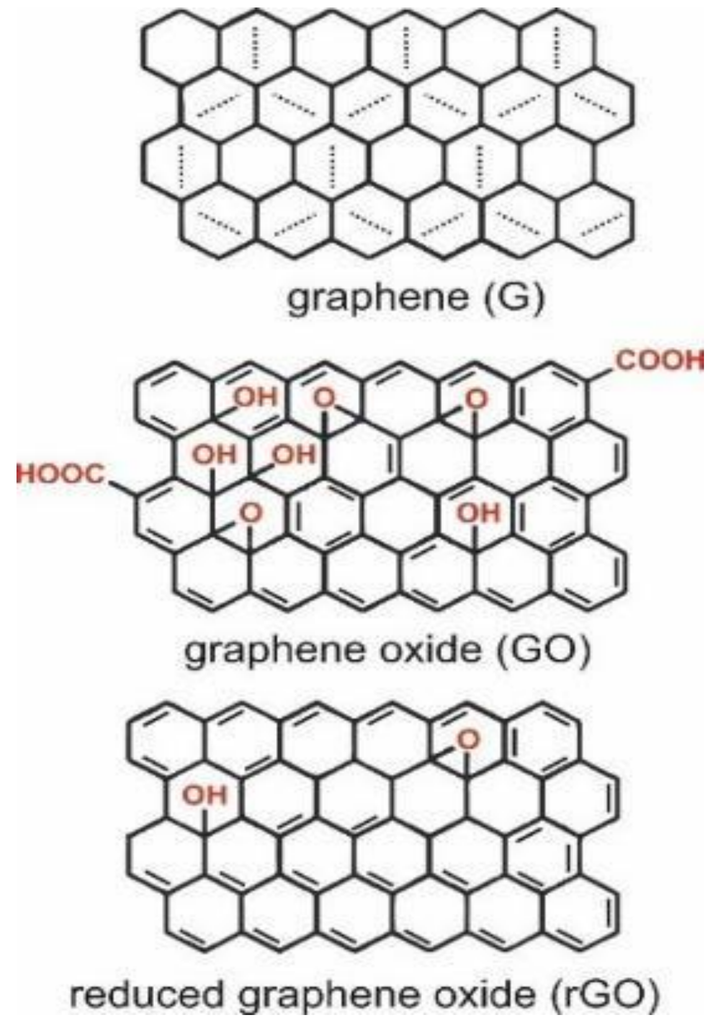
↓

Filter and wash with DI water

↓

Dry at 60°C

Graphite
9 KMnO4
H2SO4
H2O2
Graphite oxide
PRODUCTION LINE
Centrifugation
H2O
HCl
rGO
GO
NaBH4
95°C
Stirring
Centrifugation
H2O
Sonication
0.5 hours
Driying
80°C
24 hours



graphene (G)
COOH
OH
O
HOOC
graphene oxide (GO)
reduced graphene oxide (rGO)

Properties of GRAPHENE

- Conductive: Electrons are the particles that make up electricity. So when graphene allows electrons to move quickly, it is allowing electricity to move quickly. It is known to move electrons 200 times faster than silicon because they travel with such little interruption. It is also an excellent heat conductor. Graphene is conductive independent of temperature and works normally at room temperature.
- Strong: As mentioned earlier, it would take an elephant with excellent balance to break through a sheet of graphene. It is very strong due to its unbroken pattern and the strong bonds between the carbon atoms. Even when patches of graphene are stitched together, it remains the strongest material out there.
- Flexible: Those strong bonds between graphene's carbon atoms are also very flexible. They can be twisted, pulled and curved to a certain extent without breaking, which means graphene is bendable and stretchable.
- Transparent: Graphene absorbs 2.3 percent of the visible light that hits it, which means you can see through it without having to deal with any glare.

Applications of GRAPHENE

- **OLED Technologies**
- **Body Armour**
- **Lightweight Aircraft/vehicles**
- **Photovoltaics**
- **Superconductor/battery**
- **Filtration**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CONDUCTING POLYMERS

- Polymers whose conductivity is comparable to that of metals are called conducting polymers.

Requirements for conducting polymers

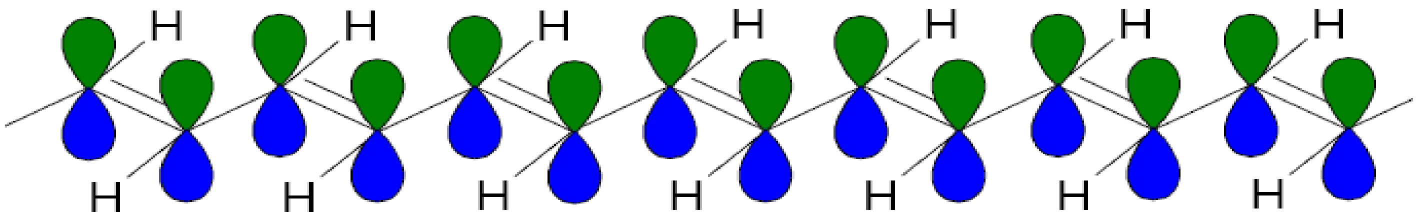
1. Linear structure with rigid chains
2. Extensive conjugation in polymeric backbone.

- These materials in pure form are not conducting but on doping their dconductivity increases enormously.

Examples:
1. Polyacetylene
2. Polypyrrole
3. Polyaniline

Conjugated polymers → Alternating single and double bonds

Conjugated polymers → Delocalized π-electrons



Nobel Prize in Chemistry 2000

"For the Discovery and Development of Conductive Polymers"

Polyacetylene

$\sigma \sim 10^{-5}$ Scm^{-1}

$\downarrow$ I_2doping

$\sim 10^{3}$ Scm^{-1}

Alan Heeger
University of California at Santa Barbara

Hideki Shirakawa
University of Tsukuba

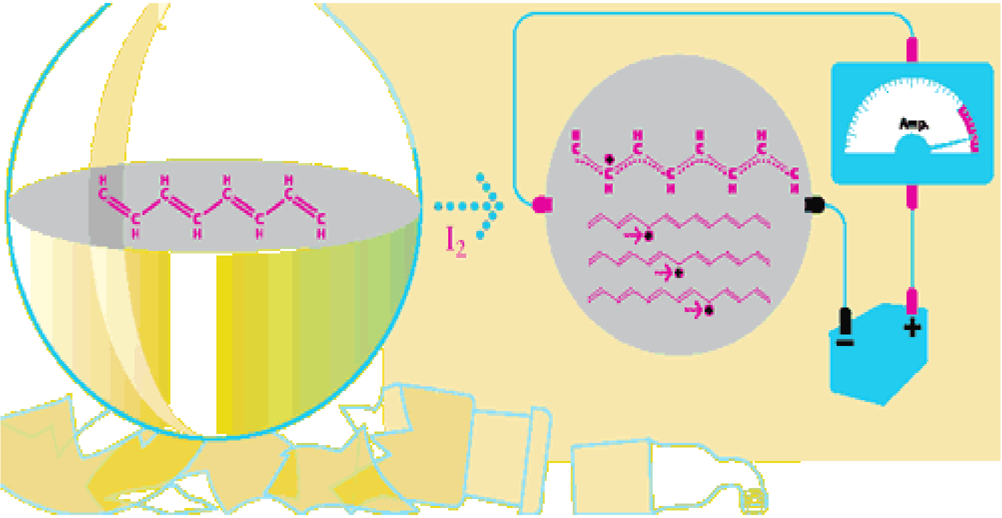
Alan MacDiarmid
University of Pennsylvania

Noble Prize in Chemistry 2000

Doping process

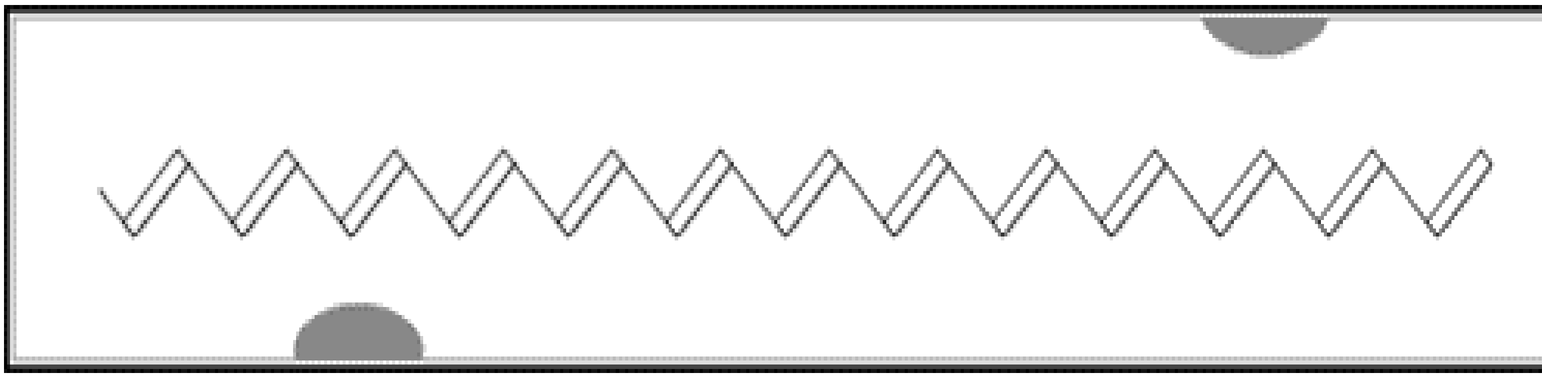
Oxidative Doping, or Halogen doping or p-type doping

- The halogen doping transforms polyacetylene to a good conductor.



Oxidation with iodine causes the electrons to be jerked out of the polymer, leaving "holes" in the form of positive charges that can move along the chain.

- The iodine molecule attracts an electron from the polyacetylene chain and becomes I_3^-. The polyacetylene molecule, now positively charged, is termed a radical cation, or ***polaron*.**



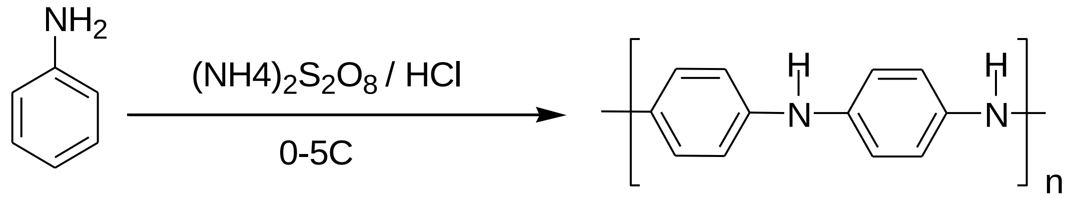
- The lonely electron of the double bond, from which an electron was removed, can move easily. As a consequence, the double bond successively moves along the molecule.
- The positive charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily.

POLYANILINE (PANI)

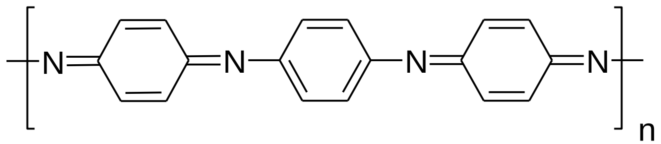
- Prepared by redox polymerization of aniline using APS (Ammonium Peroxydisulfate) $NH_4S_2O_8$ as oxidant.

- Distilled aniline(0.2M) is dissolved in 300cm^3 of 1M HCl.

- APS (0.5M) is dissolved in 200ml HCl (1M) and added to the aniline solution maintaining the temperature 0-5^{o}C.

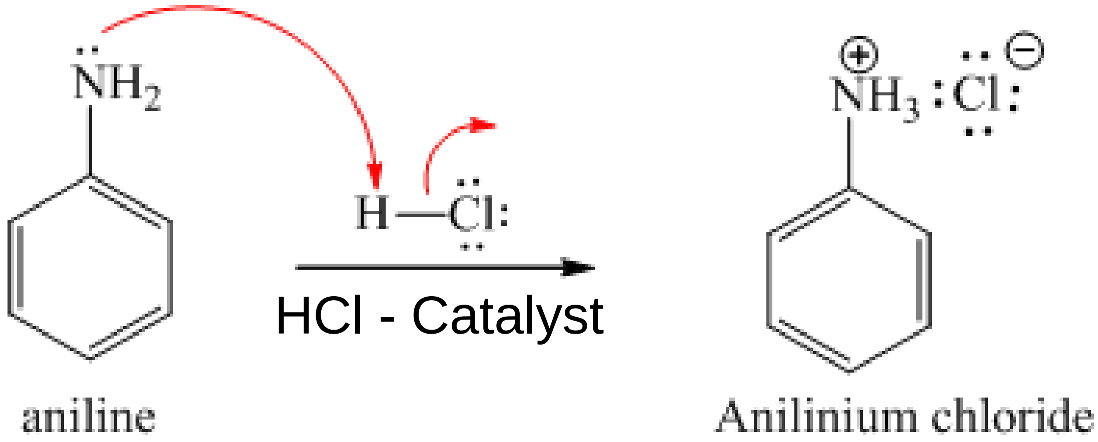


Leucoemaraldine
(non Conducting form)



Emaraldine form
conducting form

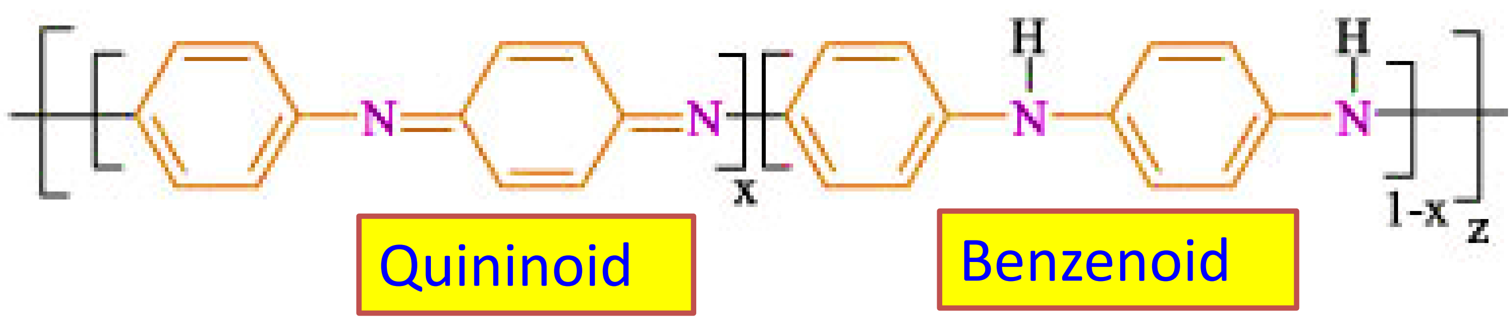
Polyaniline polymerization reaction

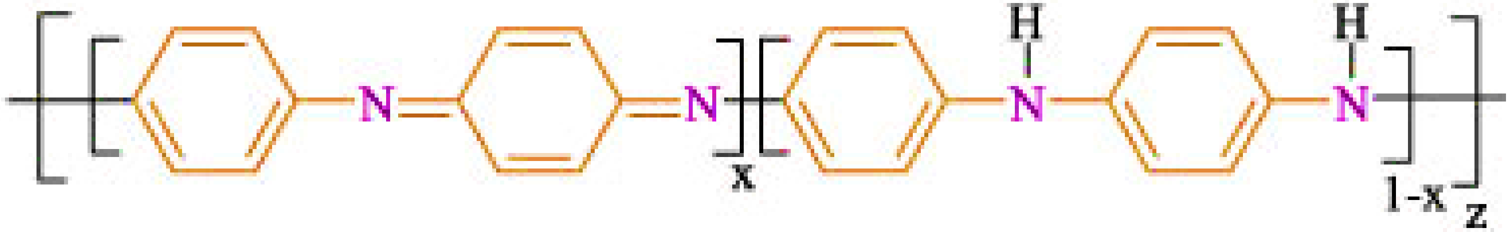


Polyaniline is synthesized by oxidative polymerization of aniline

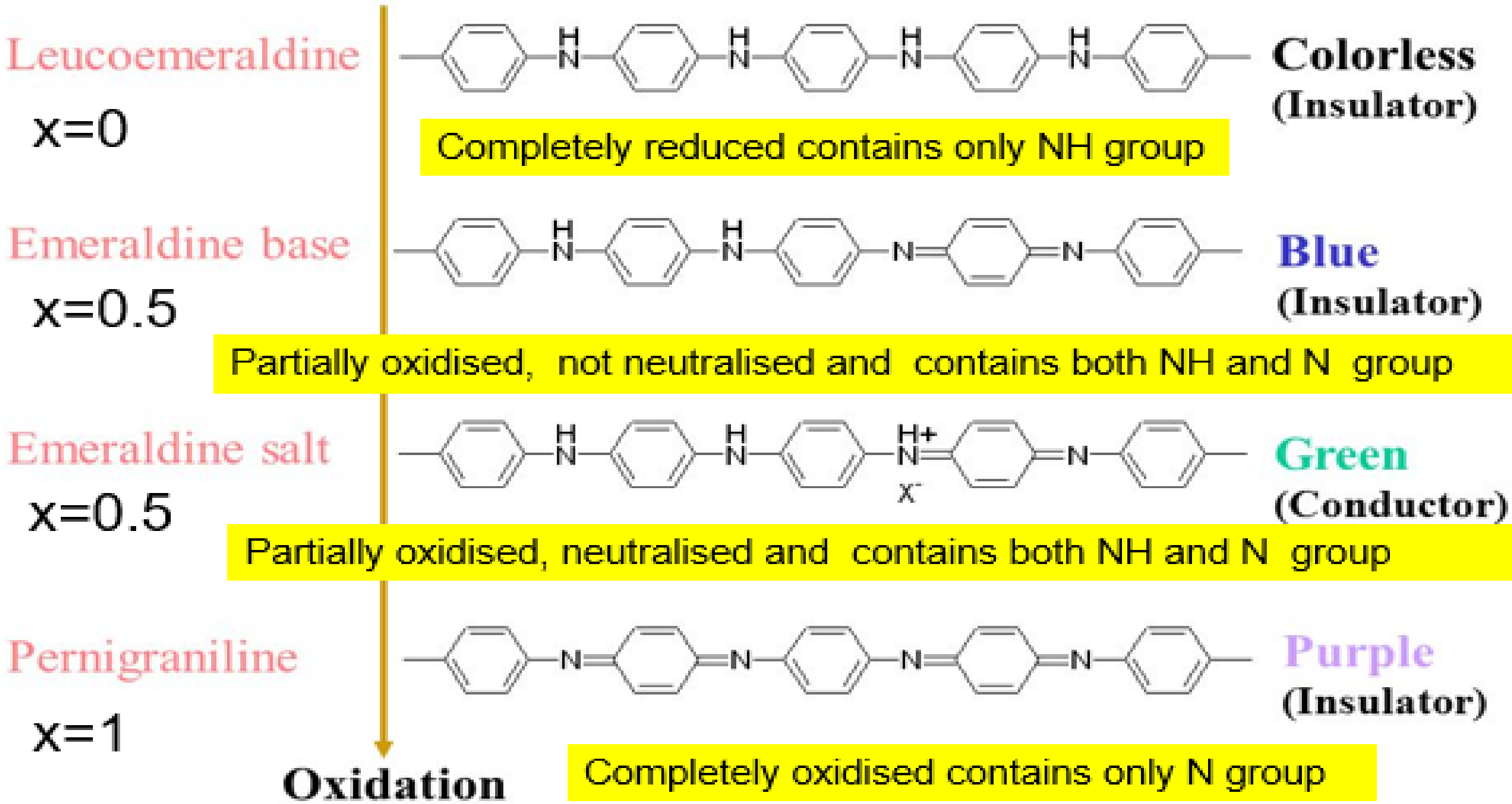
Stirring at ~(0-5)°C

$(NH_4)_2S_2O_8$ Oxidant



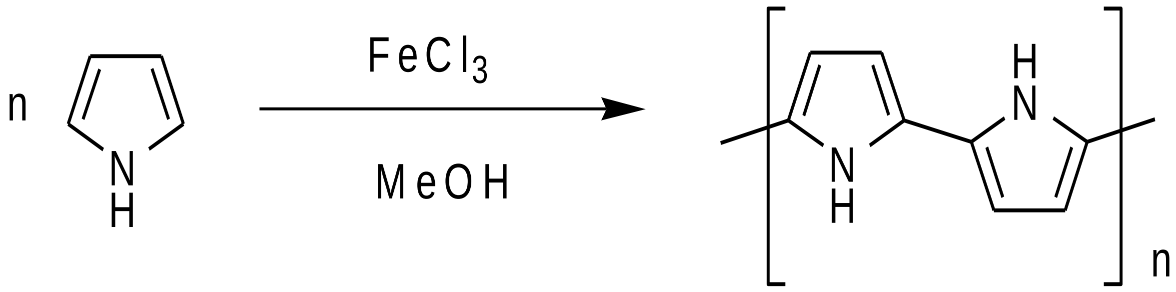


Different forms of POLYANILINE



POLYPYRROLE

- Prepared by the polymerisation of pyrrole in presence of $FeCl_3$ in methanol.



APPLICATIONS OF CONDUCTING POLYMERS

1. Energy Harvesting

- Cocnducting polymers can be used as catalyst support for fuel cells and to sensitize cathode electrocatalysts.

- Inexpensive microporous polyaniline (PANI) is used as a substitute for platinum to construct the counter electrode in dye-sensitized solar cells (DSSCs).

- Nano Polypyrrole incorporated graphene oxide can be used as an efficient counter electrode for platinum-free dye-sensitized solar cells.

APPLICATIONS OF CONDUCTING POLYMERS

2. Sensing applications

- Polypyrrole nanowire doped $FeCl_3$, assessed for chemical sensing application, specifically pH monitoring.

- Bovine serum albumin (BSA), a protein incorporated polypyrrole film can be used for detection of Urea.

- Single Polypyrrole nanowires-based sensors showed good limit of detection and sensitivity and excellent selectivity for gaseous ammonia.

- Polyaniline can be used in conductometric sensors.

- PANI/CuCl2 as a hydrogen sulphide sensor

- PANI nanofiber reinforced nanocomposite crystal microbalance sensor as HCl sensor

APPLICATIONS OF CONDUCTING POLYMERS

3. Defence applications:

- Conducting PANI and Polypyrrole can be used in Radar Absorbing materials (Materials that absorb incident electromagnetic energy and convert that energy to other forms—typically heat).

Photo conducting polymers:

- Photo conductive polymers conduct electricity only in the presence of light.

- They are insulators or partially conductive in darkness.

- This property of photoconductivity is due to the ability to create free charge carriers(electron holes) by absorption of radiation and subsequent transport of these carriers to the electrode.

- Eg: Polyvinyl Carbazole

THANK YOU