



Semester: II

CHEMISTRY OF FUNCTIONAL MATERIALS

(Category: Professional Core Course) Stream: CS (Theory and Practice)

Course Code	:	22CHY22C	CIE	:	100 Marks
Credits: L:T:P	:	3:0:1	SEE	:	100 Marks
Total Hours	:	42L+ 30P	SEE Duration	:	3 Hours

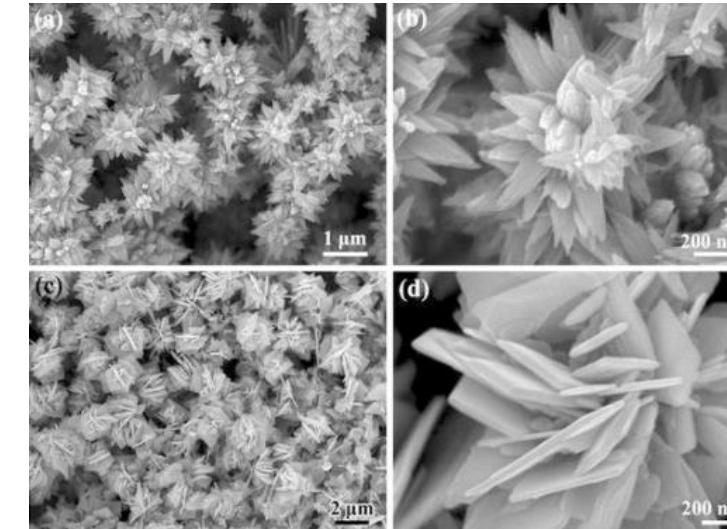
Unit-II- Nanomaterials and thin film fabrication techniques

C MANJUNATHA, Ph.D, MRSC

Assistant Professor, Department of Chemistry, RV College of Engineering
Bengaluru-560059, INDIA, Phone: +91 9036651277

E-mail: manjunathac@rvce.edu.in; manju.chem20@gmail.com

Introduction to Nanomaterials/Science/Technology



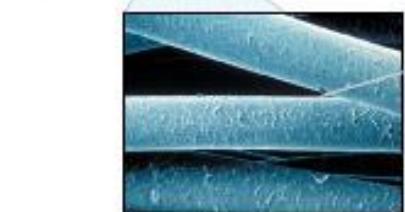
- ❖ **Nanomaterials** are commonly defined as materials with an average grain size less than 100 nanometers.
- ❖ The word "**nano**" originates from the Greek word "nanos" which means "dwarf". However, in scientific language it is a prefix which has a value equal to "one billionth, i.e. 10^{-9} ".
- ❖ Therefore, one nanometer is **one billionth of a meter ($1 \text{ nm} = 10^{-9} \text{ m}$)**.

Nano-dimension comparison

- 1.Diameter of a hydrogen atom is about 0.1 nm. If ten hydrogen atoms are aligned in a line, then the resulting length would be approximately 1 nm. Similarly, 1 nm is approximately 5 silicon atoms aligned in a line.

- 2.A single strand of human hair is around 20,000 nm in diameter. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair.

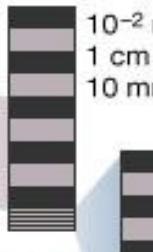
- 3.Size of a DNA molecule is about 2.5 nm.



human hair
10–50 μm wide



DNA
2–12 nm diameter



10^{-2} metre =
1 cm =
10 mm



10^{-3} metre =
1 mm =
1,000 microns (μm)



10^{-4} metre =
0.1 mm =
100 μm



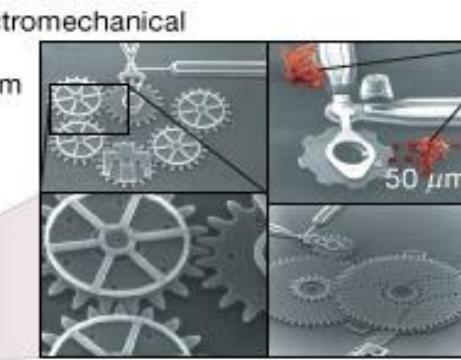
10^{-5} metre =
0.01 mm =
10 μm



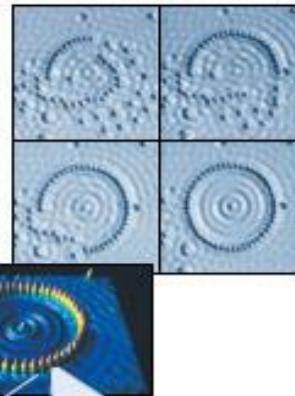
10^{-6} metre =
1 μm =
1,000 nanometres (nm)



10^{-7} metre =
0.1 μm =
100 nm =
1,000 angstroms (\AA)



red blood
cells



quantum corral of
48 iron atoms on
copper surface
positioned one at
a time with a scanning
tunneling microscope tip
14 nm corral diameter



carbon nanotube
2 nm diameter

Nanoscience and Nanotechnology

Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

*“**Nanoscience** is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale”*

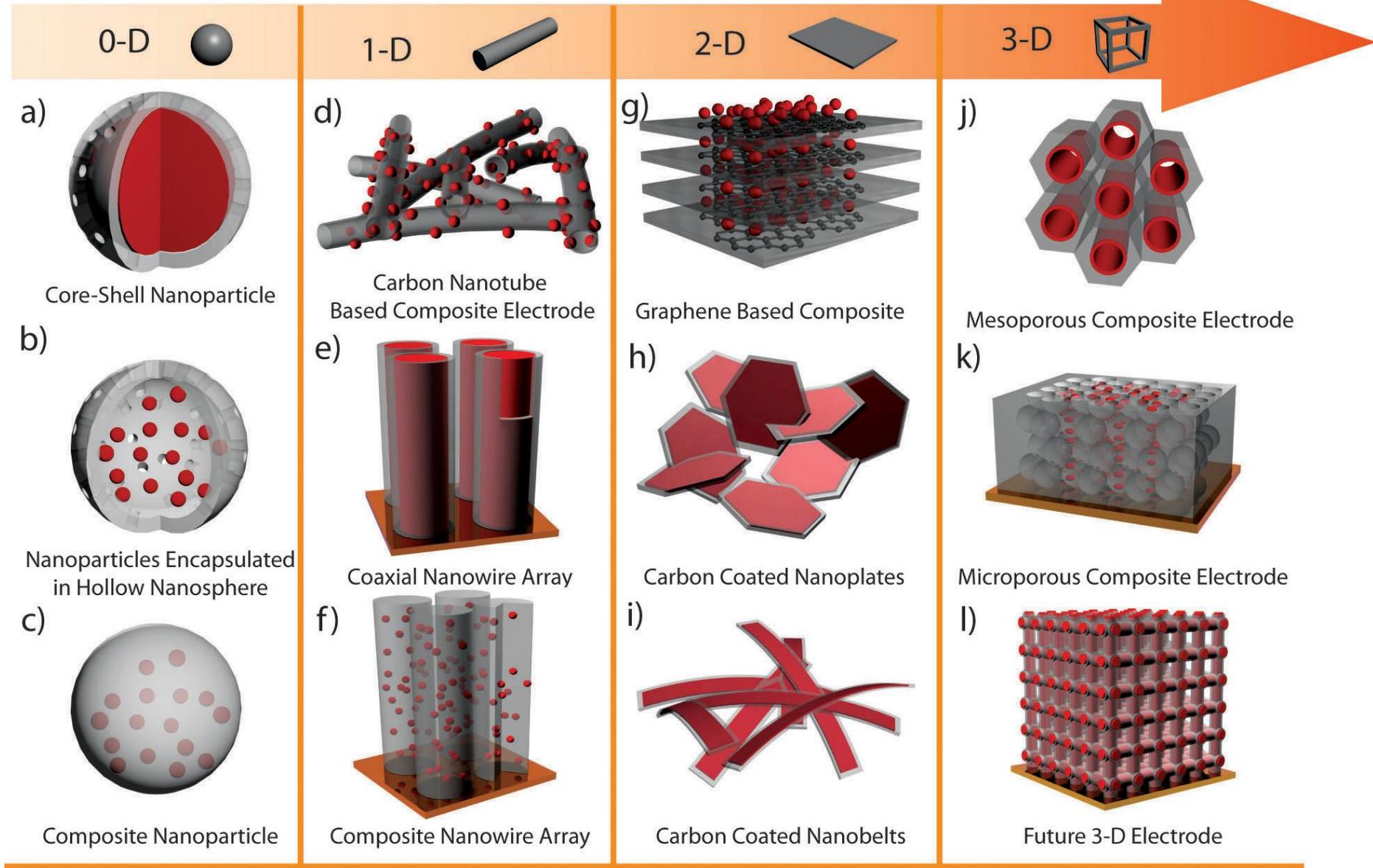
***Nanotechnologies** are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometre scale.*

Classification of Nanomaterials

Nanostructured materials are classified as

- a) ***Zero dimensional***: Nanomaterials are less than 100nm in all three dimensions.
- b) ***One dimensional***: Nanomaterials are less than 100nm in any two dimensions.
- c) ***Two dimensional***: Nanomaterials are less than 100nm in any one dimensions, and
- d) ***Three dimensional nanostructures***: Nanomaterials are aggregations of any of the above (0, 1, 2D) dimensional nanomaterial with greater than 100nm in all the three dimensions.

Heterogeneous Nanostructured Materials with Different Morphologies



Properties of Nanomaterials in comparison to bulk: Surface area, Optical, Catalytic properties

Properties of Nanomaterials

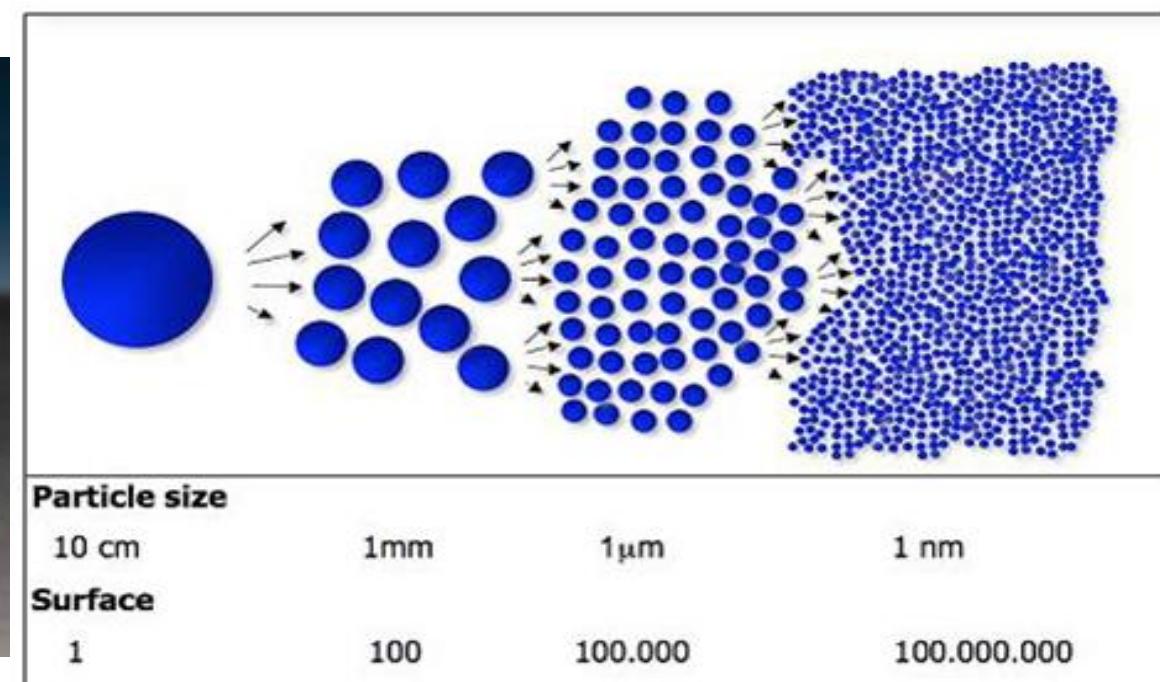
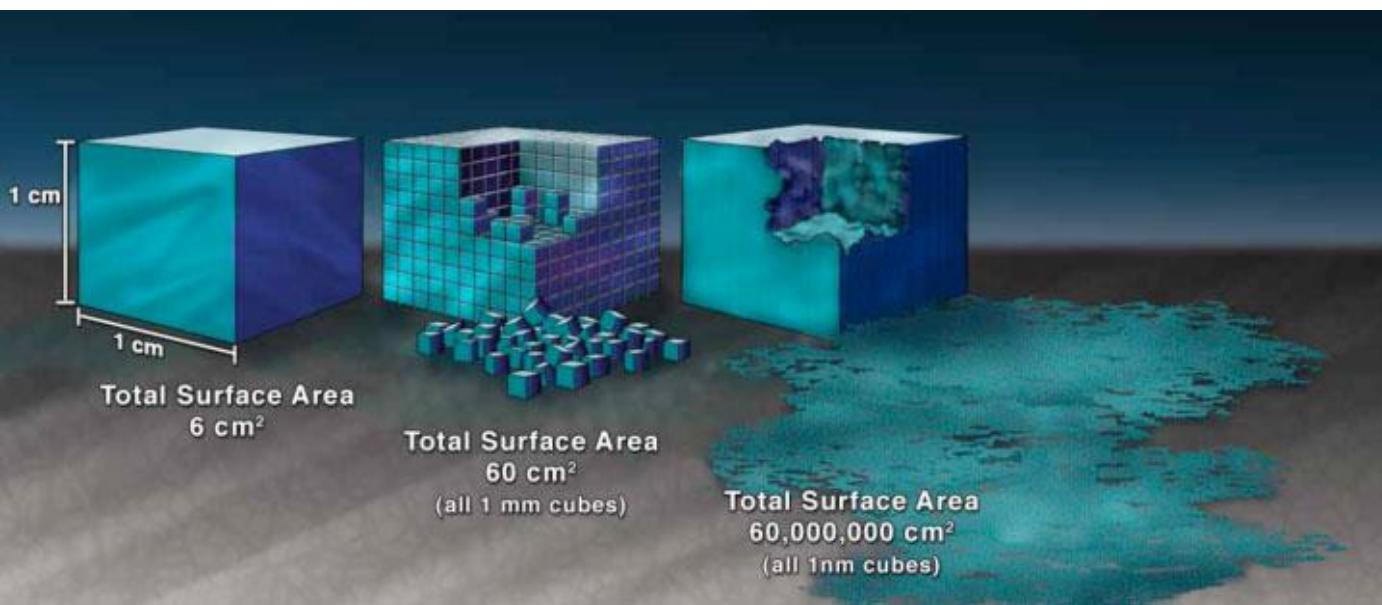
Nanomaterials have the structural features in between of those ***of atoms and the bulk materials.*** The properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them:

- (i) large fraction of surface atoms;***
- (ii) high surface energy;***
- (iii) spatial confinement,***
- (iv) reduced imperfections,***

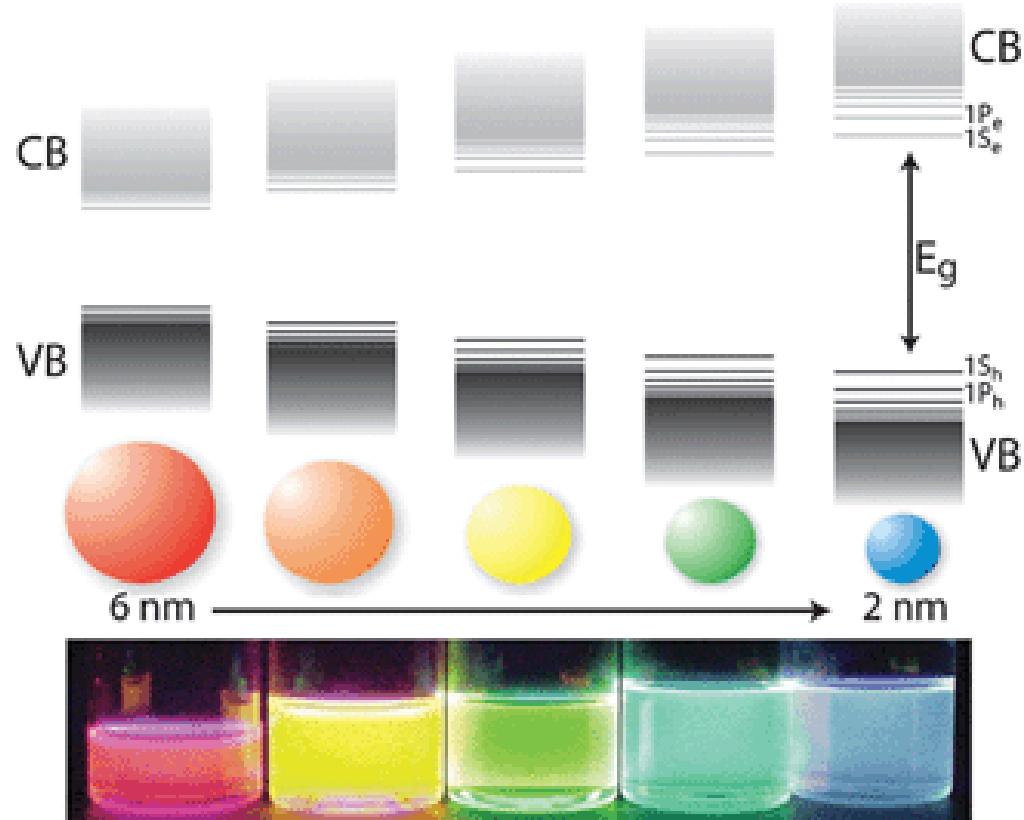
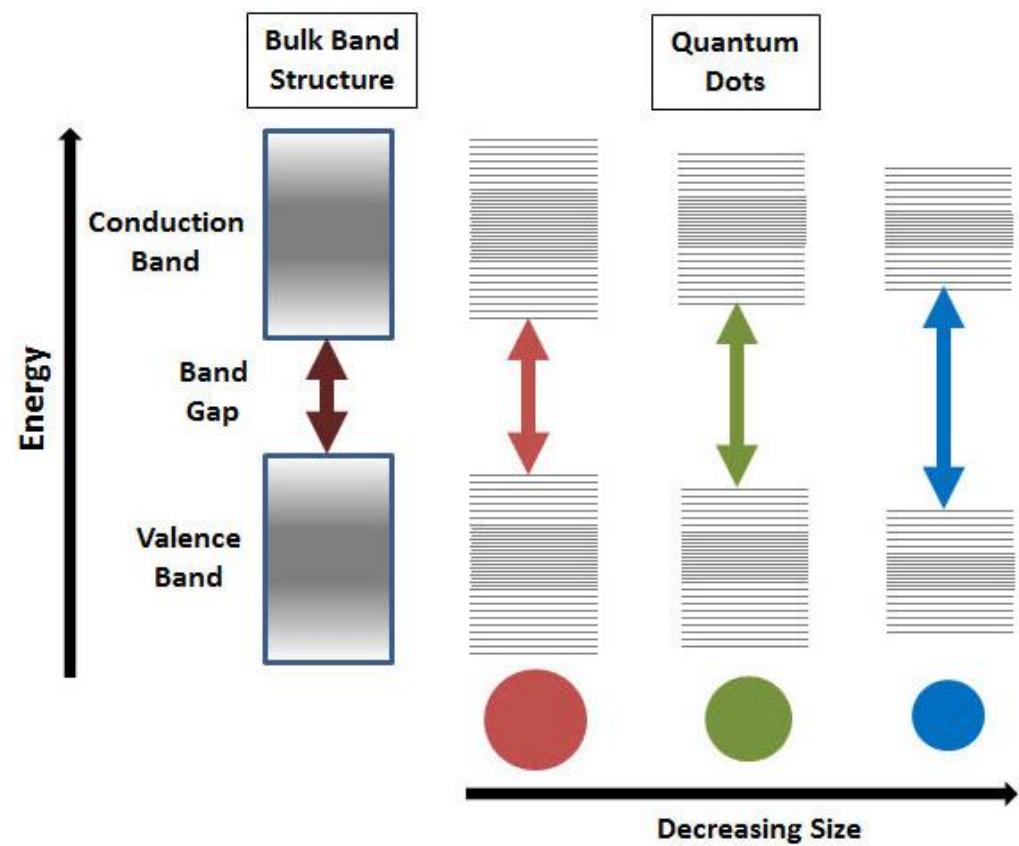
which do not exist in the corresponding bulk materials.

Surface area of Nanomaterials and bulk materials

- ❑ When particles are created with dimensions of about 1–100 nanometers (where the particles can be “seen” only with powerful specialized microscopes), the materials’ properties change significantly from those at larger scales.
- ❑ Properties such as **Optical, electrical, magnetic, and chemical reactivity** change as a function of the size of the particle.
- ❑ Nanoscale materials have far **larger surface areas** than similar masses of larger-scale materials. As surface area per mass of a material increases, a ***greater amount of the material can come into contact with surrounding materials, thus affecting reactivity.***



Band gap of nanomaterial increases with decrease in the size



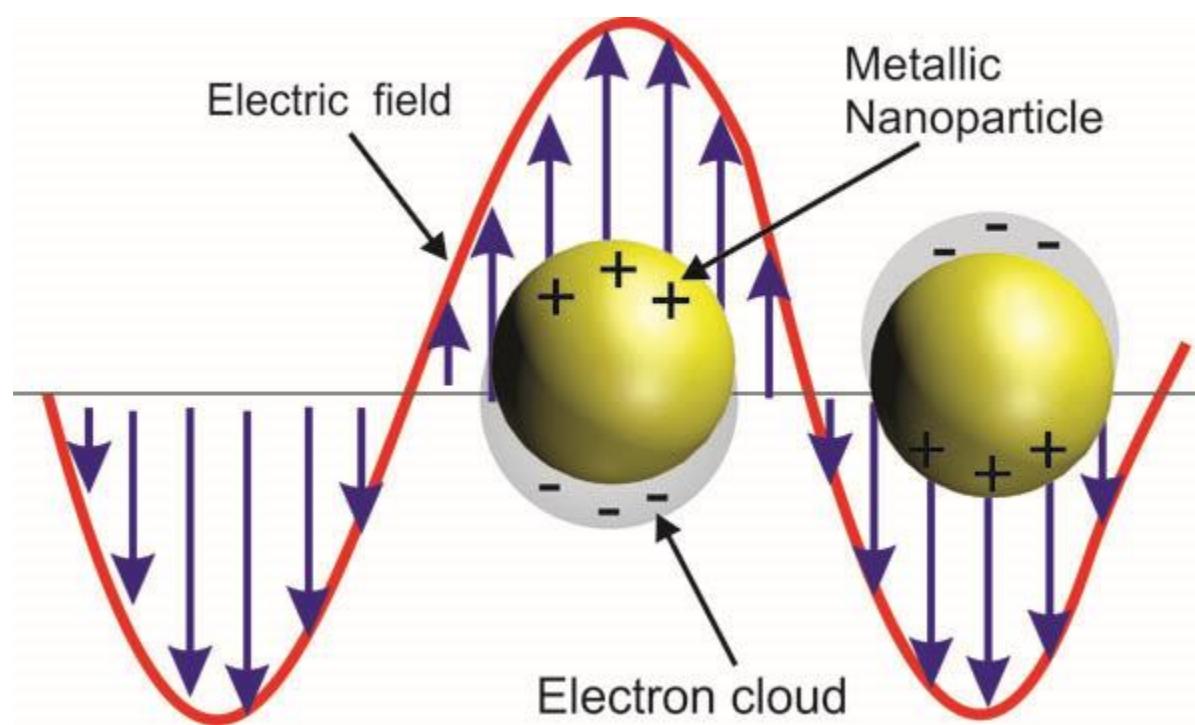
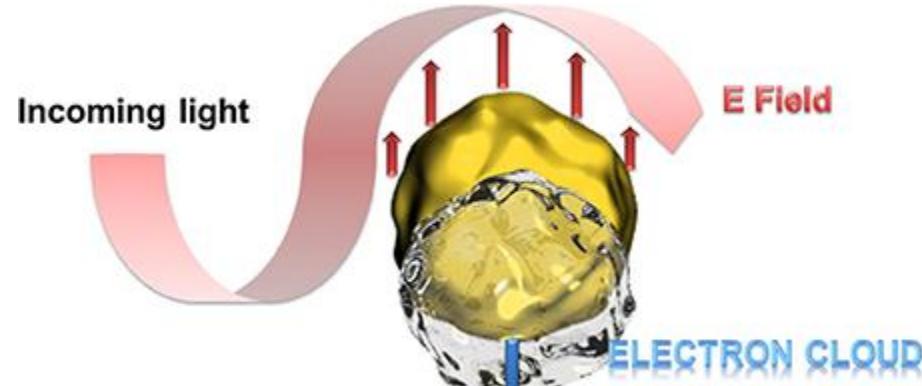
Optical Properties of Nanomaterials

One of the most fascinating and useful aspects of nanomaterial is their **optical properties**.

The change in optical properties is mainly due to the surface plasmon resonance and the increased energy level spacing.

Surface Plasmon Resonance (SPR): *The coherent excitation of entire free electrons in the conduction band may produce an in-phase oscillation with incident visible light, called surface Plasmon resonance. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface plasmon resonance is generated. Thus, plasmon resonance depends on the particle size.*

In solid state physics, the plasmon represents the collective oscillation of a free charge in a metal, and may be considered as a kind of plasma wave. The positive electrical charge in the metal is fixed and the free electron is free to move around it. An applied external electric field, as from a light source, causes the free electrons at the surface of the metal to vibrate collectively, giving rise to surface plasmons.



- “Since electrons are also **particles with an electric charge**, when they vibrate they also **generate an electric field**, and when the electric field from the vibration of free electrons and the applied external electric field (e.g., electromagnetic waves) resonate the resulting phenomenon is referred to as a **surface plasmon resonance**” that takes place at the surface of the metal.
- However, if light irradiates a solution that contains dispersed metal nanoparticles smaller than the wavelength of light, then depending on the electric field of light, the deviation produces a free electron at the surface of the metal. As a result, the weak or thick portions of the electric field appear on the nanoparticle surface and can be considered as a kind of polarization.

- Nanoparticles absorb visible light and produce surface plasmons.
- Small nanoparticles absorb blue-green wavelength of light, but they reflect red light.
- When size of the nanoparticles increases, wavelength of plasmon resonance absorption moves to longer wavelength (red wavelength) side. Now red light is absorbed and blue light is reflected, resulting in pale blue or purple colour for the particles.
- When particle size increase towards critical limit, SPR wavelength shifts to the IR spectrum of the radiation and visible lights are reflected. ***These properties find potential applications in biosensors.***

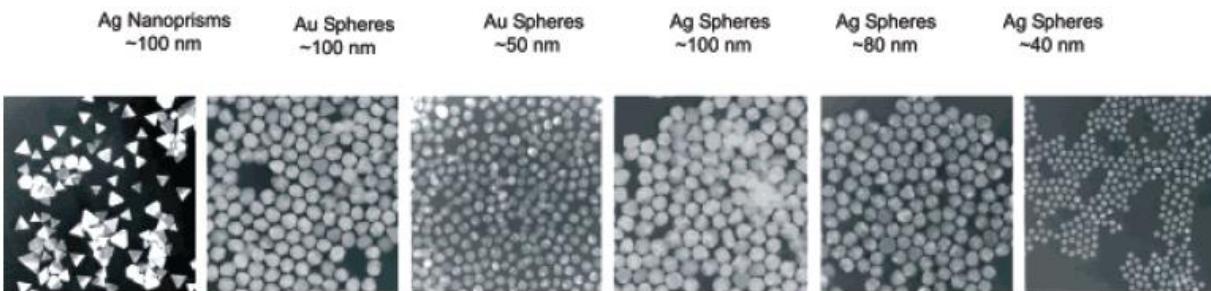
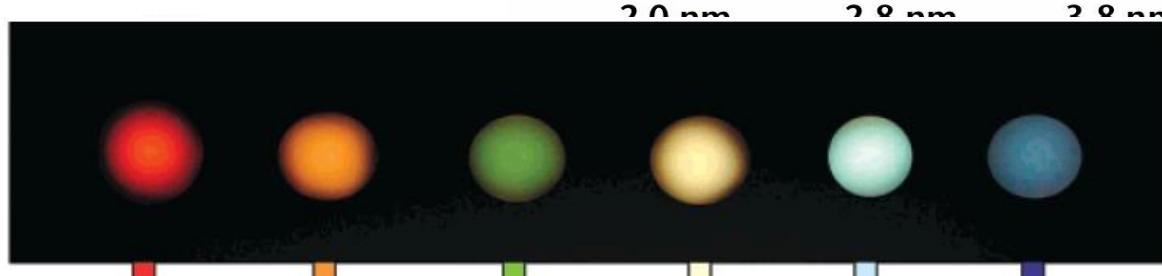
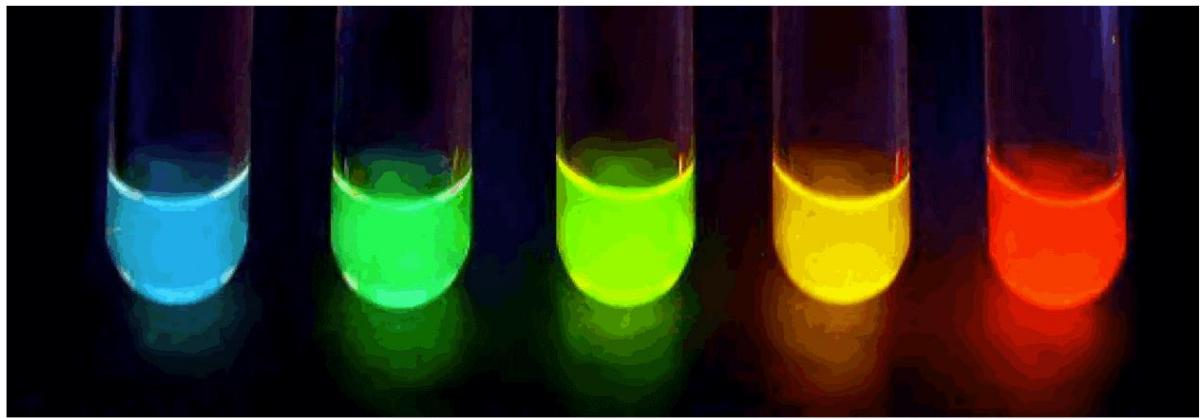
It should be noted that, metal nanorods exhibit two SPR modes, one due to **transverse** and the other due to **longitudinal** excitations. The wavelength of transverse mode is usually set at nearly **520 nm for gold and 410 nm for silver**. However, their longitudinal modes can be tuned to span from **visible region to near IR region** by controlling their aspect ratios.

The wavelength corresponding to the SPR depends on the kind of metal, the shape of the metal nanoparticle, and the extent of aggregation of the metallic nanoparticles.

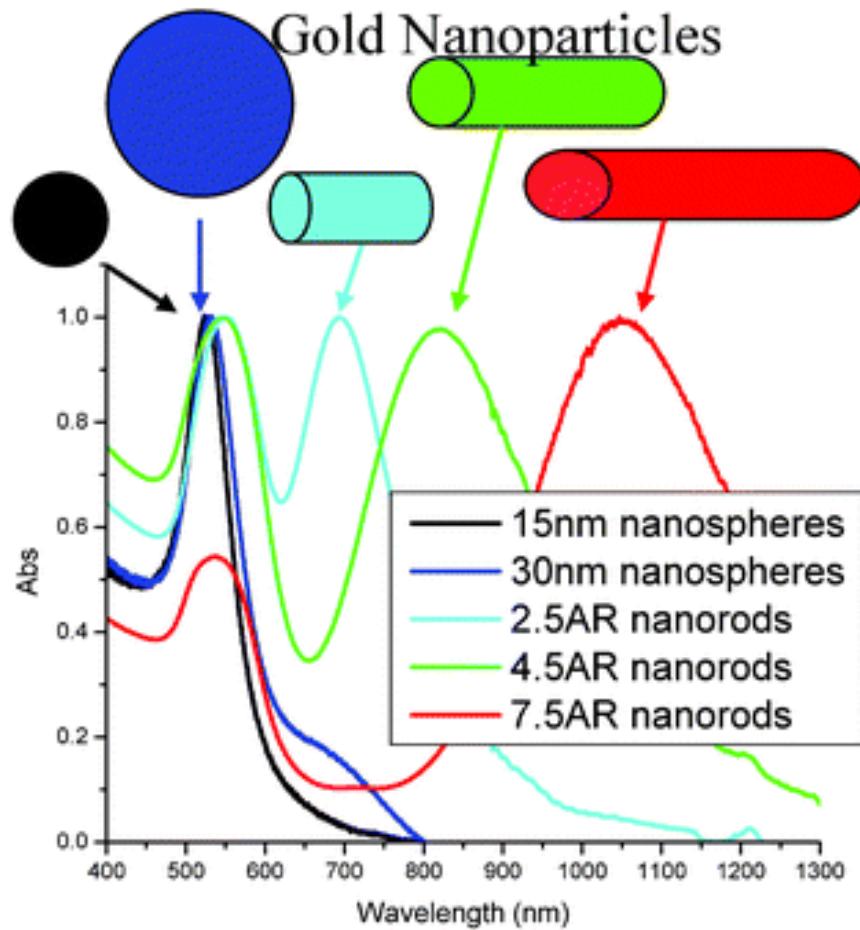
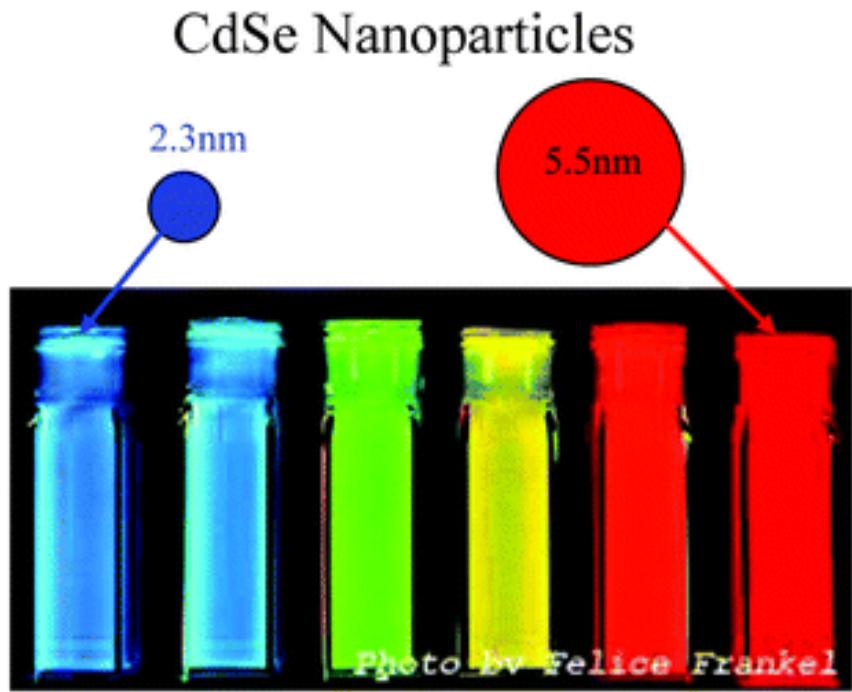
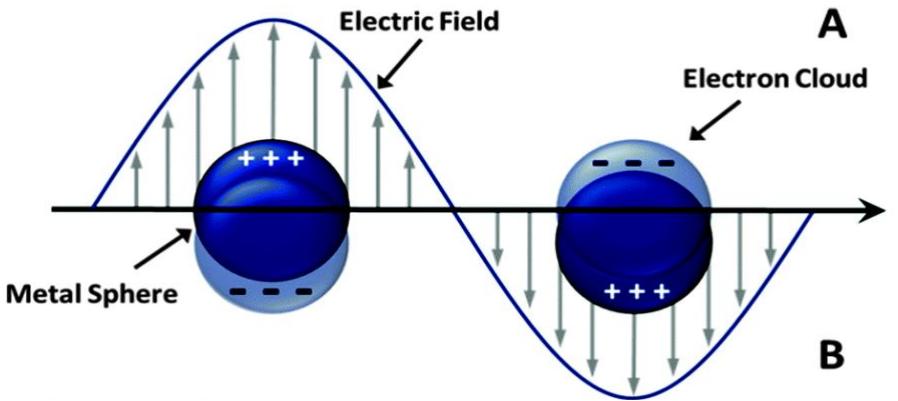
- ❖ For example, the wavelength of the SPR band maximum of a spherical **Au nanoparticle** is **520–550 nm**. If a colloidal Au nanoparticle solution is now irradiated with visible light at these wavelengths (520–550 nm), the visible light corresponding to the **green color** is absorbed and the particles now display a **red purple** color, which is the **complementary color to green**.
- ❖ In a colloidal **Ag nanoparticle** solution which has a SPR band maximum near **400 nm**, the **blue color** of the visible light is absorbed and the Ag nanoparticles now take on a **yellow color**, the complementary color to blue.



MACRO

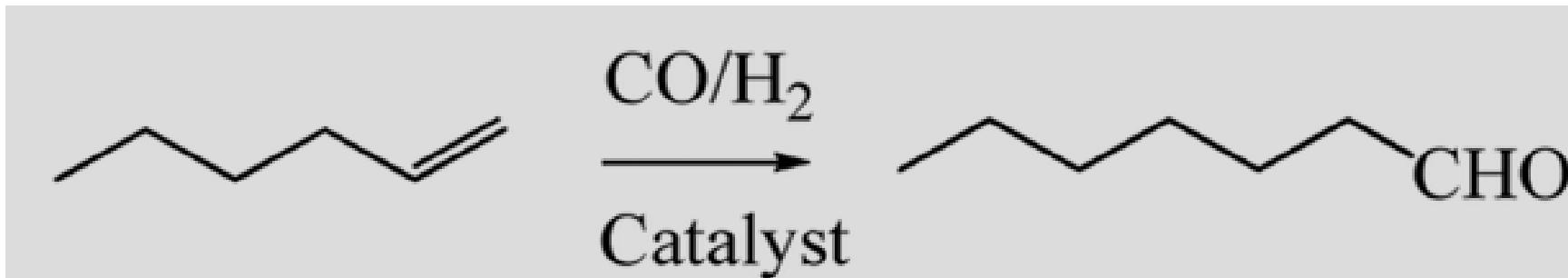


— 200nm (same for all the images)



- The rate of any chemical reaction depends on the number of active reaction sites on the catalyst.
- The surface area of nanoscaled catalyst is larger than that of bulk material.
- As compared to bulk catalyst, the nanoscale catalyst of same material with same quantity has more number of active sites.
- Because of unsaturated valencies of surface atoms of Nanoparticle catalyst, they catalyze the reactions at much faster rates due to higher surface energies as compared to their respective bulk partners.
- Therefore, the nanoscaled material is found to exhibit very high catalytic efficiency than the corresponding bulk material.

Hydroformylation of 1-Hexene over Rh/Nano -oxide



- The highest activity with 100% total conversion and 96% yield of aldehydes was obtained with the **Rh/nano-ZnO catalyst**.
- The **Rh/nano-ZnO catalyst** was found to be more stable and active than the corresponding rhodium catalyst supported on **bulk ZnO (76% yield)**.

Article

OPEN ACCESS

Hydroformylation of 1-Hexene over Rh/Nano-Oxide Catalysts

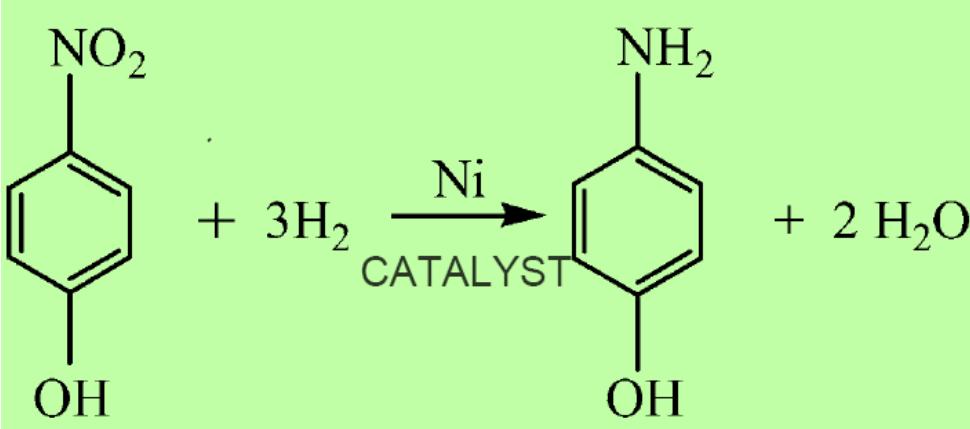
Maija-Liisa Kontkanen ¹, Matti Tuikka ^{1,2}, Niko M. Kinnunen ¹, Sari Suvanto ¹ and Matti Haukka ^{1,2,*}

catalysts

ISSN 2073-4344
www.mdpi.com/journal/catalysts

Catalysts 2013, 3, 324-337; doi:10.3390/catal3010324

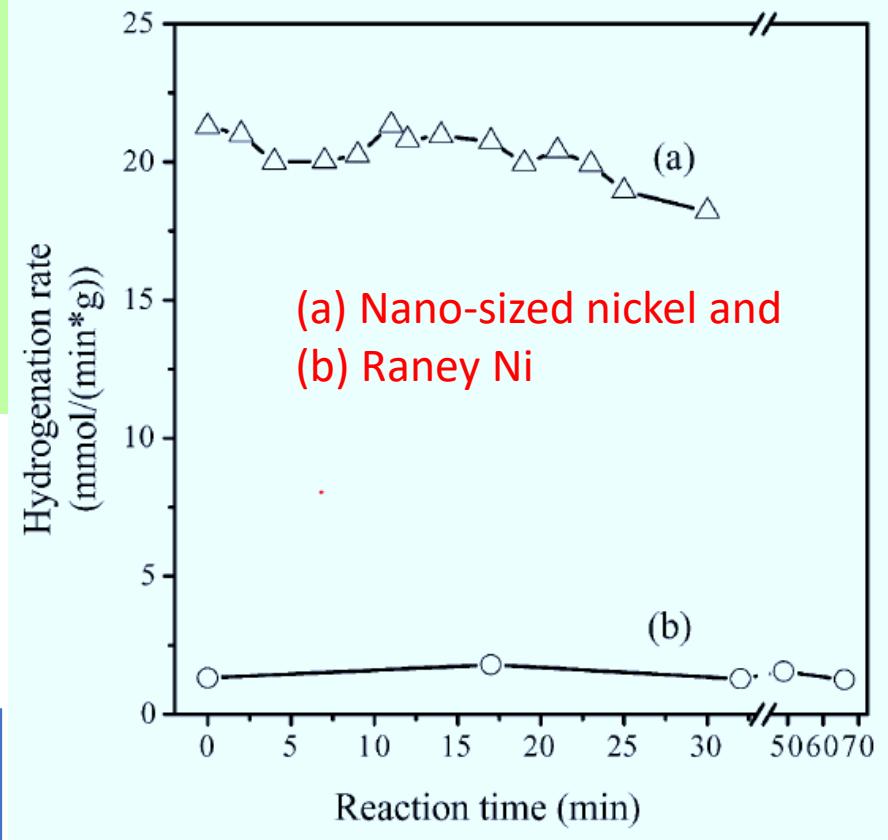
Catalytic hydrogenation of p-nitrophenol to p-aminophenol using nano-sized nickel



The hydrogenation rate of nano-sized nickel is about 15 times higher than that of Raney Ni at similar reaction conditions

The **nano-sized nickel** system suffers 54% deactivation, while the **Raney nickel** system suffers 80.4% deactivation only throughout six continuous hydrogenation cycles.

These results indicate that the catalytic stability of **nano-sized nickel** system is superior to that of the **Raney nickel system**



Synthesis of *p*-aminophenol from *p*-nitrophenol over nano-sized nickel catalysts

Yan Du, Hongling Chen*, Rizhi Chen, Nanping Xu

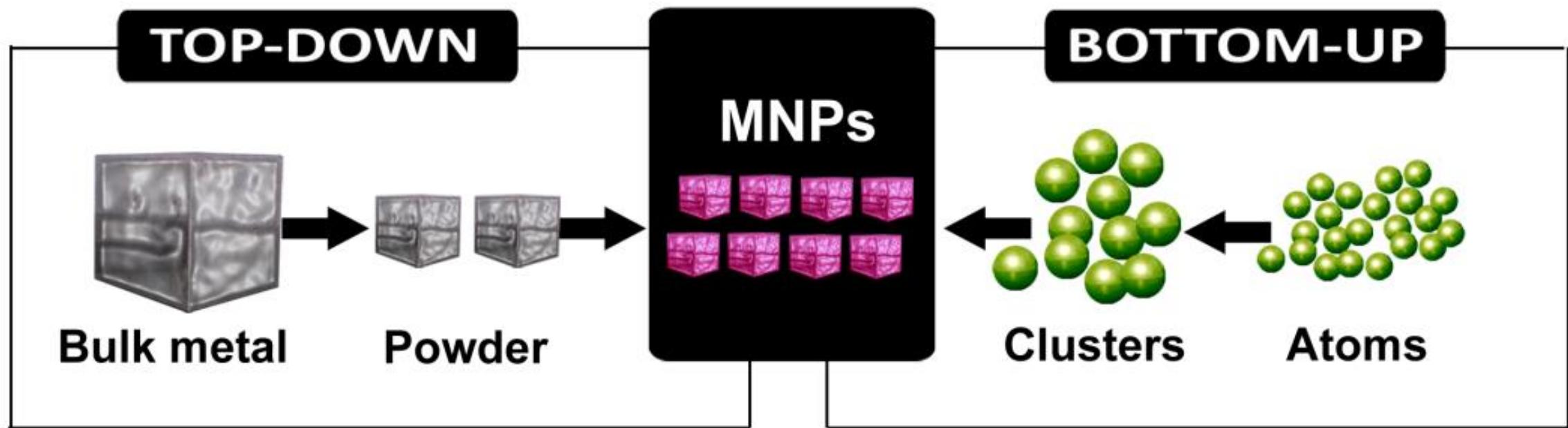
Applied Catalysis A: General 277 (2004) 259–264

Synthesis of Nanomaterials: SCS for metal oxide, Sol-Gel- for TiO_2 nanoparticles Carbon Nano materials

Researchers are active worldwide developing new preparation methods for functionally and technologically useful nanoparticles and nanostructures. Nature efficiently builds nanostructures by relying on chemical approaches. There are many methods developed to prepare nanomaterials, they are listed as chemical methods (bottom up) and physical methods (top down) as shown in Table.1

Table. 1 General methods of synthesis of nanomaterials

CHEMICAL METHODS (Bottom Up)	PHYSICAL METHODS (Top down)
Combustion Synthesis	Inert gas condensation
Hydrothermal	Sputtering
Sol-gel method	Molecular beam epitaxy
Micelles micro emulsion	Lithography
Single crystal growth	Ion beam technique
Colloidal methods	Chemical vapor deposition



1) Low temperature solution combustion (SCS) method

This method was discovered by **Prof. K. C. Patil** when the mixture of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and urea solution, rapidly heated around 500°C in a muffle furnace. The author observed that the solution mixture undergoes vaporization followed by vigorous ignition with an incandescent flame yielding voluminous white product which was identified as $\alpha\text{-Al}_2\text{O}_3$.

Combustion method: is a low temperature, time saving, energy efficient, self propagating method, involving **spontaneous exothermic redox reaction** between **metal nitrate and organic fuel**, used to prepare nanomaterials.

Principle: The method is based on the utilization of heat energy produced during the exothermic spontaneous redox reaction between an oxidizer (metal nitrate) and a reducing agent (organic fuel). The oxidizer can be of any metal nitrates and reducing agents may be organic fuels, such as glycine, oxalic acid, urea, hexamine, sugar, EDTA, Dextrose etc.

Metal nitrate + Fuel



nano Metal oxide + Gases

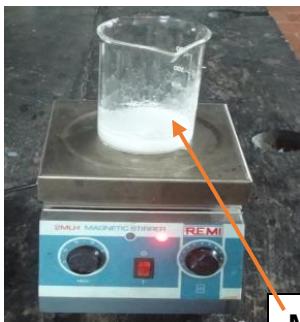
The amount of fuel can be calculated in such way that the total oxidizing valency of fuel should match with the total reducing valency of metal nitrate. The following formula can be used to calculate the amount of fuel:

$$\frac{\text{Wt. of fuel}}{\text{Mol. Wt. of fuel}} \times \text{Valency of fuel} = \frac{\text{Wt. of metal nitrate}}{\text{Mol. Wt. of metal nitrate}} \times \text{Valency of metal nitrate}$$

For the calculation of valency of fuel and metal nitrate, the valency to be considered for the elements such as of N, O, H, C, and M^{n+} are 0, -2, +1, +4 and +n respectively.

Procedure:

Step1: Weighing and mixing of the reactants



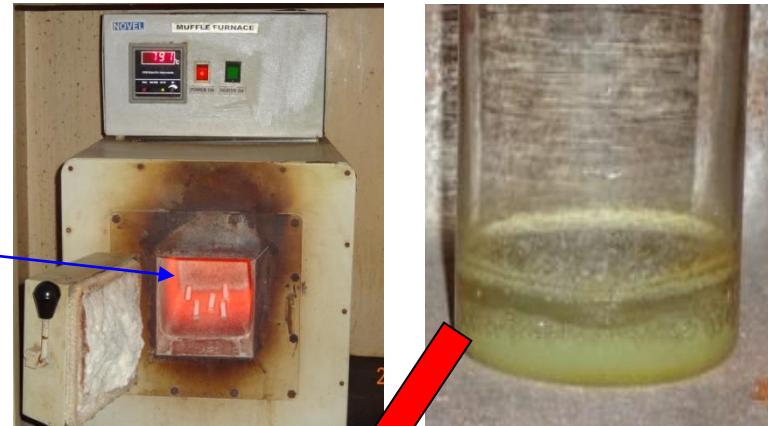
Weighing of all the reactants (metal nitrate and a fuel) according to stoichiometry, by using the above formula and dissolved in minimum quantity of distilled water in a beaker of suitable size.

The mixture is stirred on a magnetic stirrer till to get uniform solution as shown in figure (left side).

Magnetic stirrer on which uniform redox solution is obtained by stirring

Step 2: Evaporation and combustion

The uniformly mixed solution is kept in a furnace maintained at 500 °C



Evaporation
(boiling) of
water

Spontaneous/vigorous combustion occurs and propagates throughout the redox mixture



Final nano powder of corresponding metal oxide

- ❖ The clear solution is kept in a furnace (shown below) maintained at 500 °C.
- ❖ Firstly the solution undergoes evaporation that results in more concentrated, uniformly mixed viscous-gel type substance.
- ❖ After some time, the viscous-gel catches fire and propagates spontaneously in the redox mixture in the form of either a flame type or smouldering type.
- ❖ The combustion lasts for about 1-2 min.
- ❖ During the flame propagation large quantity of gasses and high temperature produced helps in the formation of respective nano metal oxide.
- ❖ The SCS has emerged as a viable technique for the preparation of advanced nano-metal oxide.

The most important advantages of SCS process are:

- ✓ It is an easy and fast process that uses relatively simple equipment.
- ✓ High-purity products can be easily prepared by using this method.
- ✓ Composition, structure, homogeneity, size and stoichiometry of the products can be controlled.
- ✓ High exothermicity of the metal nitrate–fuel reaction permits incorporation of desired quantity of dopants in the various hosts of industrially useful phosphors.
- ✓ This is the cheap method as compared to conventional solid state method

Stoichiometry calculation

$$\frac{\text{Wt. of fuel}}{\text{Mol. Wt. of fuel}} \times \text{Valency of fuel} = \frac{\text{Wt. of metal nitrate}}{\text{Mol. Wt. of metal nitrate}} \times \text{Valency of metal nitrate}$$

Valency calculation					
Zn(NO ₃) ₂ •6H ₂ O (Zinc Nitrate) 297 g/mol	Zn2+	2N	6O	6H ₂ O	Total Valency
	+2	2x0=0	6x(-2)=-12	6x0=0	-10
Al(NO ₃) ₃ •9H ₂ O (Aluminium nitrate) 375.14 g/mol	A3+	3N	9O	9H ₂ O	
	+3	3x0=0	9x(-2)=-18	9x0=0	-15
C ₆ H ₁₂ O ₆ (Glucose,) 180.156 g/mol	6C	12H	6O		
	6x(+4)=+24	12x(+1)=+12	6(-2)=-12		+24
NH ₂ -CH ₂ -COOH (Glycine) 75.07 g/mol	N	2O	5H	2C	
	1x0=0	2x(-2)=-4	5x(+1)=+5	2x(+4)=+8	+9

**Calculate the amount of glycine fuel required to
prepare nano ZnO using
3g of hydrated Zinc nitrate (Mol. Mass =297g/mo**

$$[(\text{Wt} \times \text{Valency})/\text{Mol Mass}] \text{ of Glycine} = [(\text{Wt} \times \text{Valency})/\text{Mol Mass}] \text{ of Zinc nitrate}$$
$$[(\text{Wt} \times 9)/75.07] \text{ of glycine} = [(8 \times 10)/297]$$

Wt of glycine = g

2. Sol-gel method

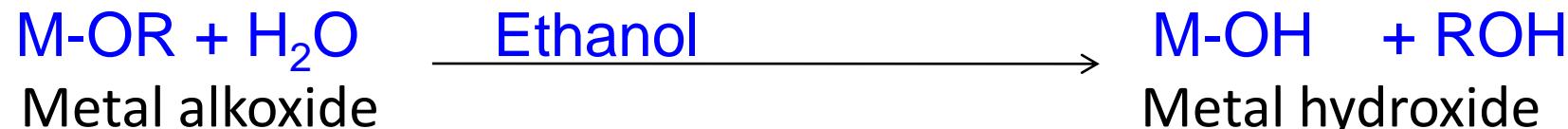
It is a wet chemical technique widely used for the fabrication of nano-structured ceramic materials and thin films.

Sol-gel process involves the conversion of precursor solution (usually metal salts or metal alkoxide) into a nano-structured inorganic solid through inorganic polymerization reactions catalyzed by water.

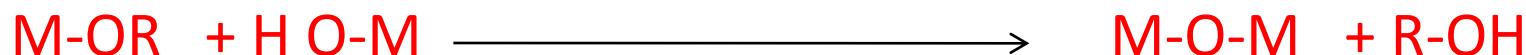
In general, metal alkoxides ($M-OR$) are widely used as precursors, because they readily react with water.

The reactions involved in the sol-gel process are

1) Hydrolysis



2) Condensation



Condensation..... Condensation CondensationofM-O-M results in to a polymer network in all the possible directions.

Process:

Step 1: Preparation of homogeneous solution either by dissolution of metal salt in water or metal alkoxide in an organic solvent (usually alcohol) that is miscible in water.

Step 2: ‘Sol’ formation by hydrolysis: It involves the conversion of homogeneous solution into a “sol”. (A stable dispersion of colloidal particles of precursors in a solvent is known as sol) due to hydrolysis reaction. During hydrolysis, the alkoxide groups (-OR) are replaced via the nucleophilic attack of the oxygen atom of a water molecules, results in release of alcohol and formation of metal hydroxide (sol).

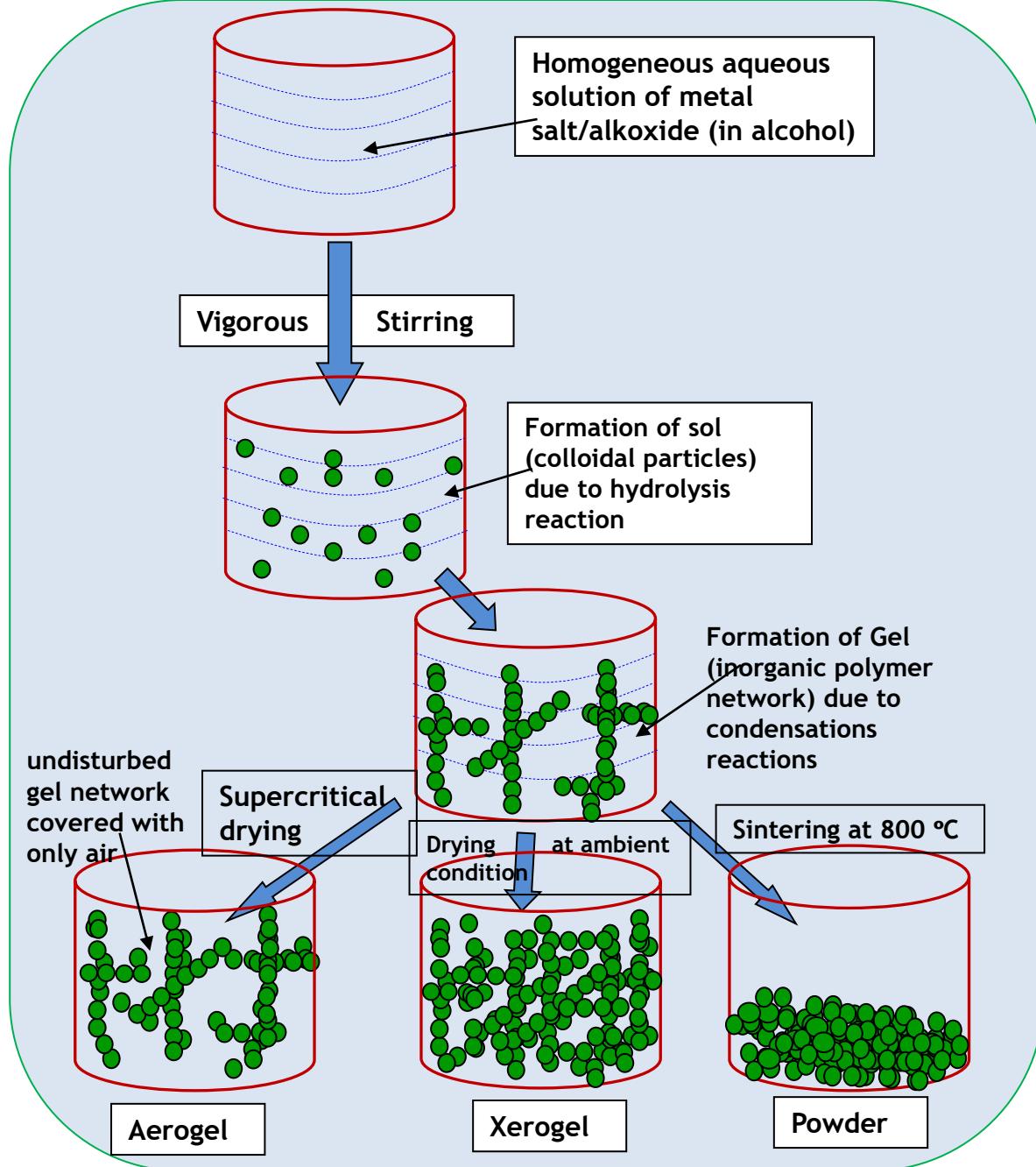
Step 3: ‘Gel’ formation by condensation

The colloidal solution is kept for aging. During aging condensation reaction between two metal hydroxyl/alkoxy species leads to M-O-M bonds with the release of $H_2O/R-OH$. This condensation process continues and finally results in a “gel”, an interconnected, a rigid and porous inorganic network covered completely with liquid phase. This transformation is called **Sol-Gel transition**.

Step 4: Drying of gel:

It involves removal of liquid phase from gel network. There are different ways of drying gel:

- If the gel medium is dried, by removing the liquid solvent (under hyper critical conditions) without destroying the gel network, “**aerogel**” is produced.
- If the solvent is dehydrated by under ambient conditions (removal of R-OH groups), “**xerogel**” are produced.
- If the gel network is sintered at high temperature ($800^{\circ}C$), densification, decomposition of gel results in complete collapse of gel net into powder.



Example: Preparation of TiO_2 by Sol-gel method:

Chemicals required: Titanium isopropoxide [$Ti(O(CH(CH_3)_2)_4$], absolute alcohol, distilled water, HNO_3

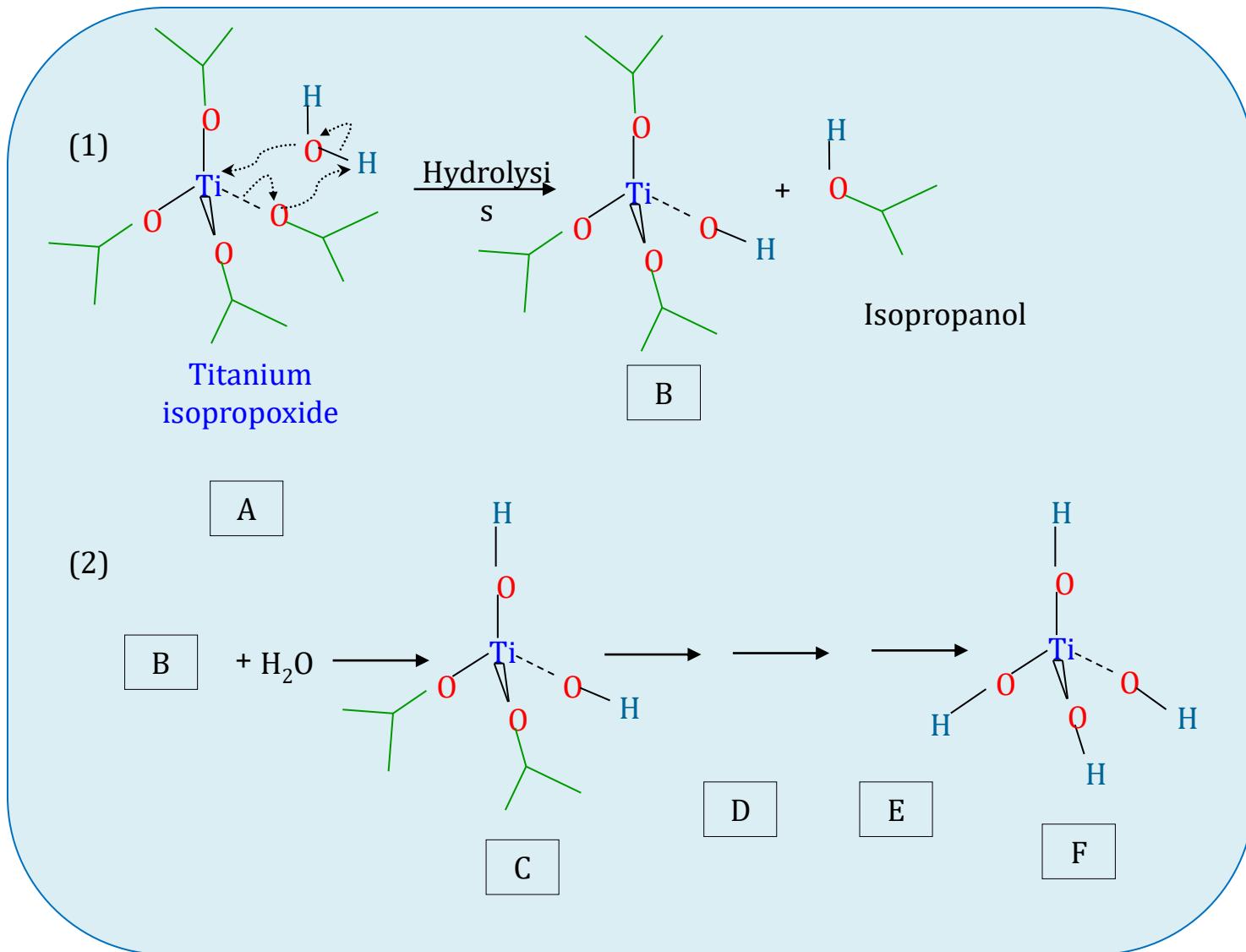
Equipments/glassware:

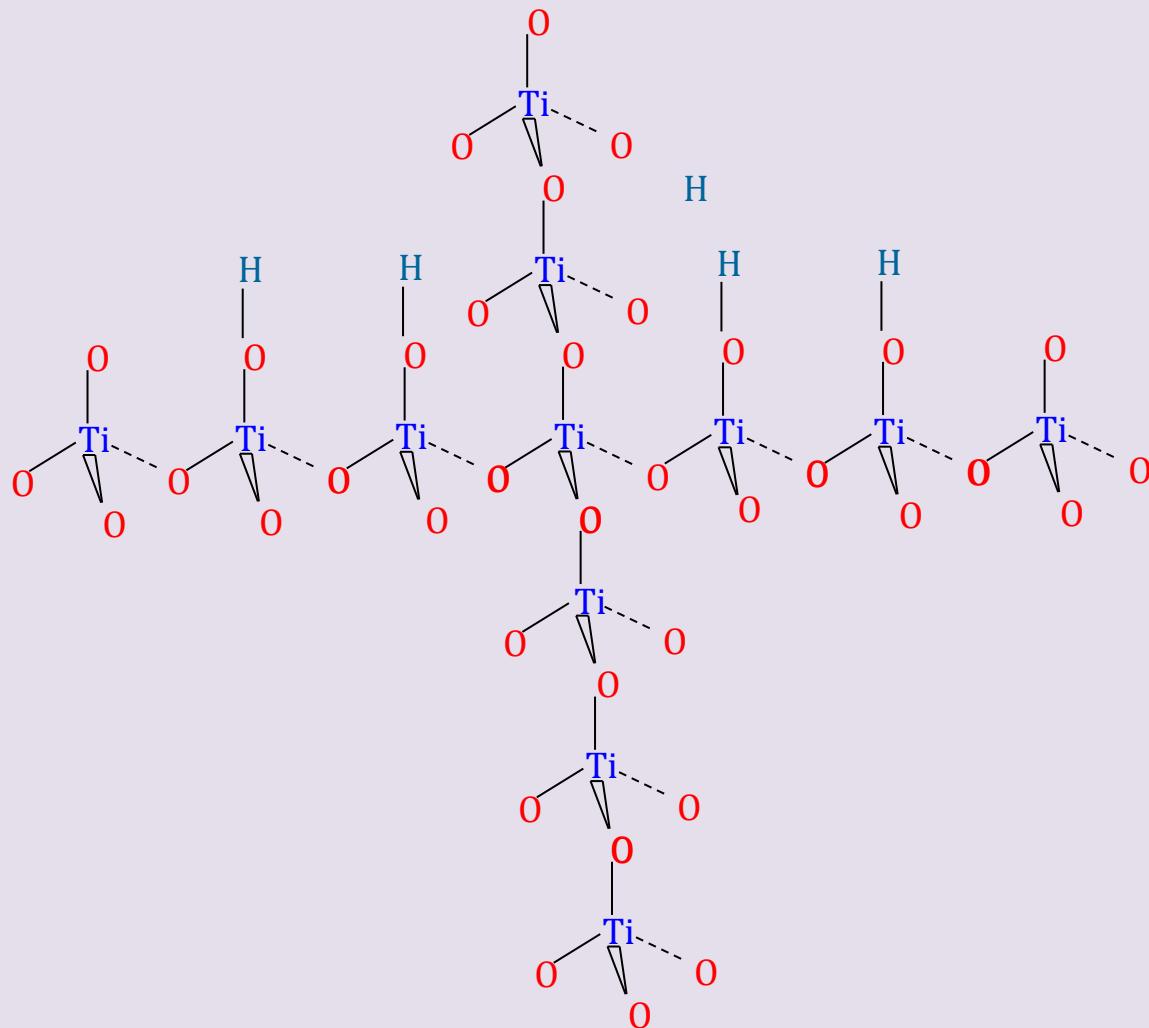
- 250 ml glass beaker, magnetic stirrer, Furnace, oven.

Procedure: Stoichiometric quantity of titanium (IV) isopropoxide is dissolved in absolute ethanol and distilled water in the ratio of $Ti:H_2O=1:4$. HNO_3 is added to adjust pH and restrain the hydrolysis process of the solution.

- The solution is vigorously stirred for 30 min in order to form sol (a suspension of colloidal particle).
- The sol is kept for aging for about 24 h. During aging sol is transformed into gel. (It is due to polycondensation and formation of inorganic network).
- In order to obtain TiO_2 nanoparticles, the gels are dried at 120 °C for 2 h to evaporate water and organic solvent. Then the dry gel is sintered at 450 °C for 2 h to obtain TiO_2 nanoparticles.

Reaction mechanism: Nucleophilic (H_2O) attack on alkoxy group.



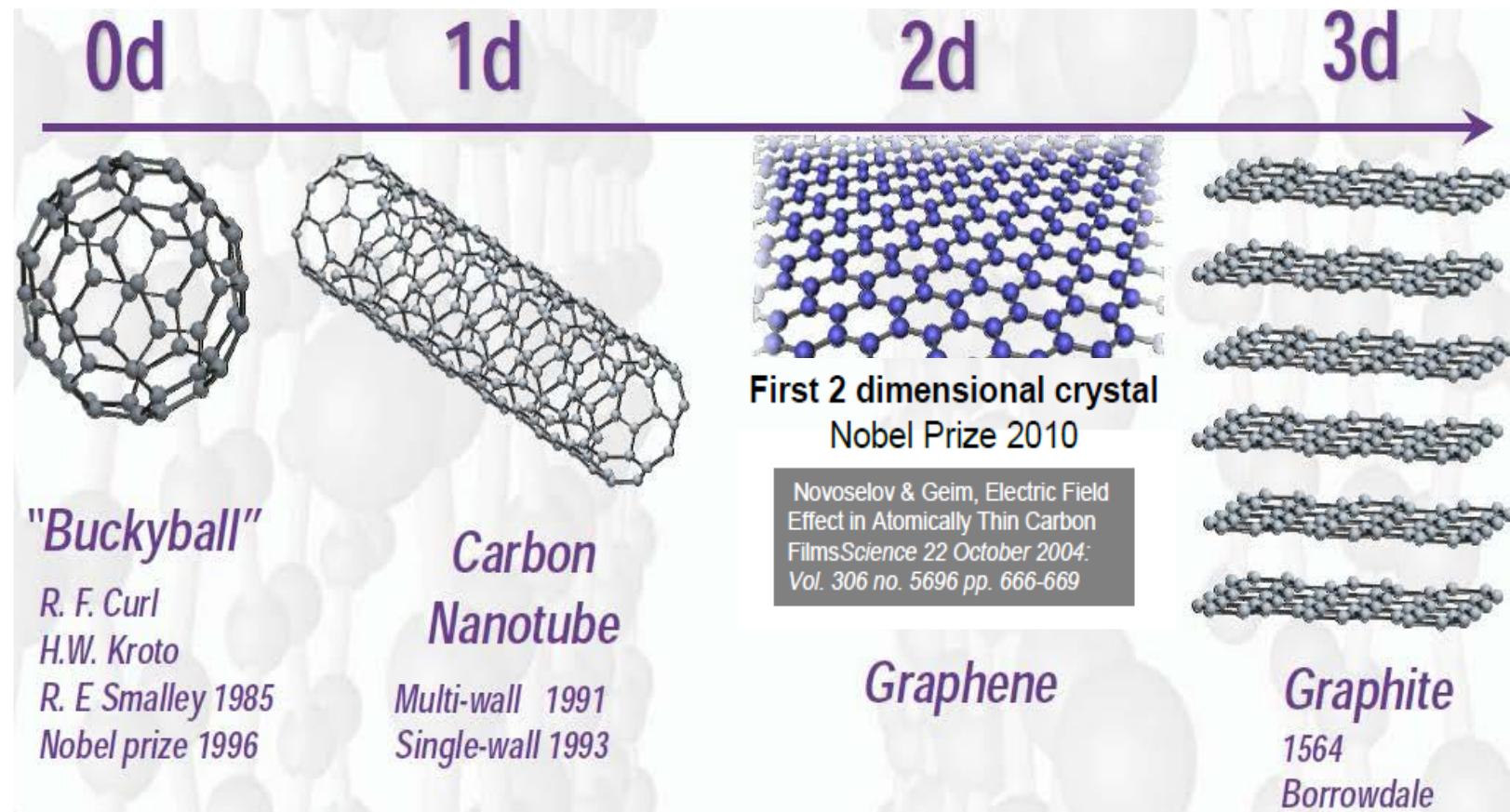


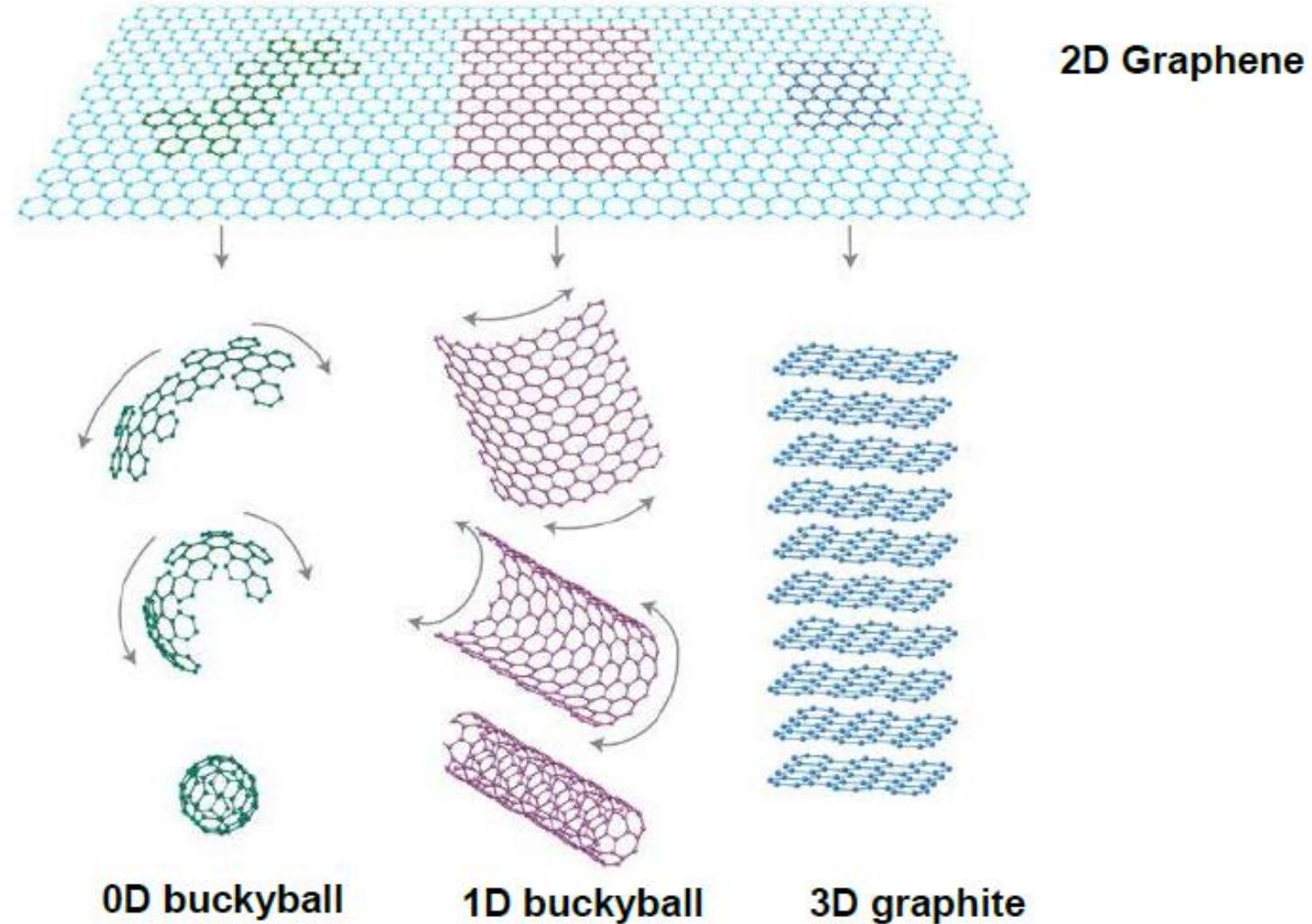
The advantages of this technique are evident.

- ❖ It is a simple and economic technique, as the fabrication does not need expansive machinery or apparatuses.
- ❖ It offers a high flexibility as one can produce materials with a wide range of stoichiometry and additional dopants.
- ❖ It allows the fabrication of high quality coatings.
- ❖ The starting materials are easily to obtain, not expensive and available in a high purity.
- ❖ Nanomaterials of variety of shapes can be prepared.

Carbon nanotubes

Carbon is an incredibly versatile element. Depending on how atoms are arranged, it can produce hard diamonds or soft graphite. Carbon materials can exist in various dimensions. The fig below clearly shows the various forms of carbon materials.





A. K. Geim & K. S. Novoselov
Nature Materials 6, 183 - 191 (2007)

Carbon nanotubes

In 1970, **Morinobu Endo**, First carbon filaments of nanometer dimensions was prepared, as part of his PhD studies at the University of Orleans in France. He grew carbon fibers about 7 nm in diameter using **a vapor-growth technique**. Filaments were not recognized as nanotubes and were not studied.

*In 1991, while experimenting on fullerene and looking into soot residues **Sumio LIJIMA** invented two types of nanotubes namely single walled carbon nanotubes (SWNTs) and multi walled carbon nanotubes (MWNTs). SWNT consists only of a single graphene sheet with one atomic layer in thickness, while MWNT is formed from 2 to several tens of graphene sheets arranged concentrically into tube structures.*

Definition:

Carbon nanotubes are a new form of a hexagonal network of carbon atoms rolled up in the form of cylindrical shape.

 Japanese | English Access to Lab. / Papers / Contact us / Links and Data

Main

Top
What's new
Topics

Research

Carbon nanotube
Li-ion battery
Super Capacitor
Analysis and

Teacher

Prof. Morinobu Endo
Morinobu Endo
INTERNET
INTERVIEW
26.10.2012.com
Interview Pros.
Asktojaiyoshi
Associate Pros.

Member

Carbon Science &
Faculty Staffs
Doctorate
Student & Bachelor
Graduates
... B.S

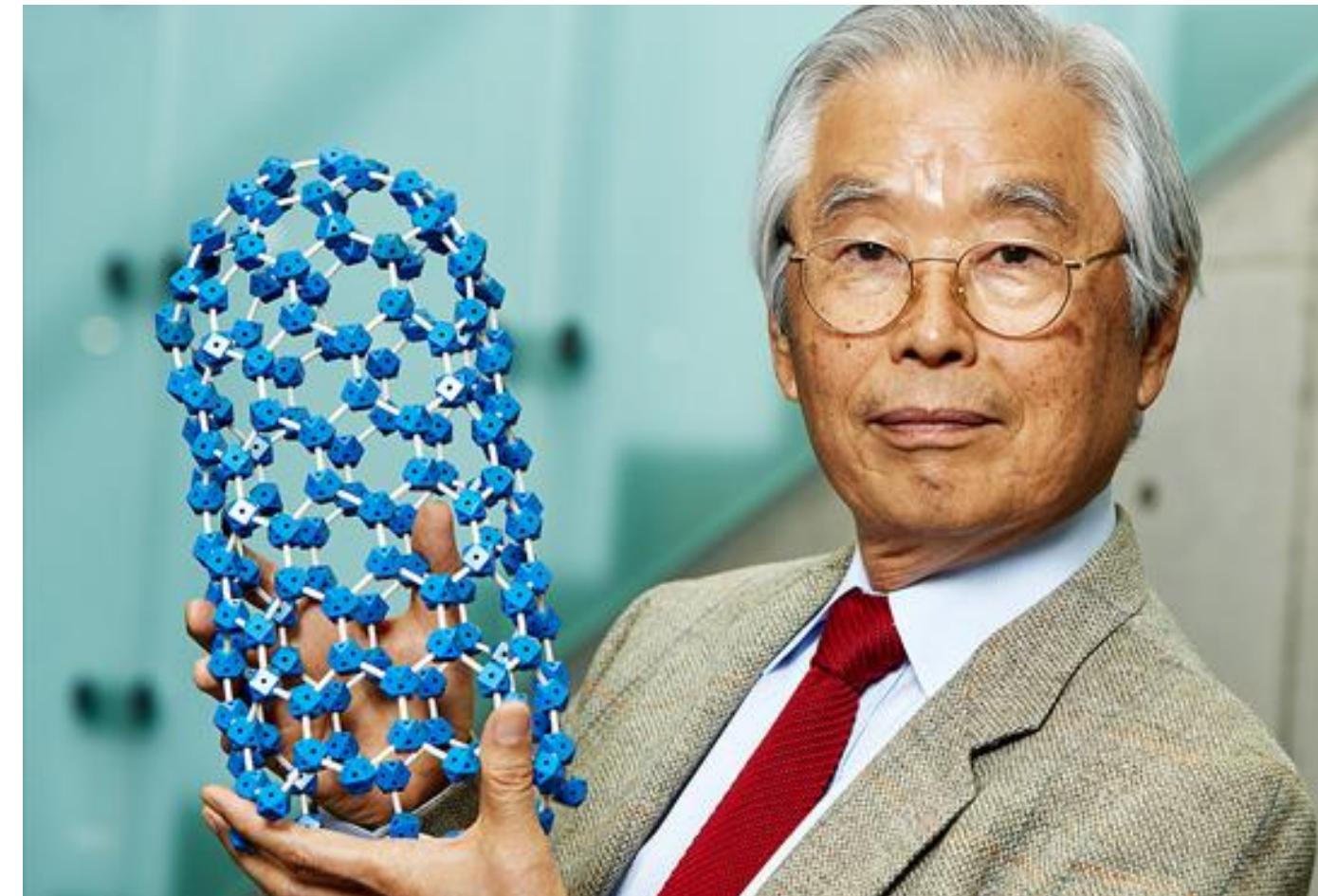
Position Professor Electrical & Electronic Engineering, Faculty of Engineering, Shinshu University

Date of birth September 28, 1946

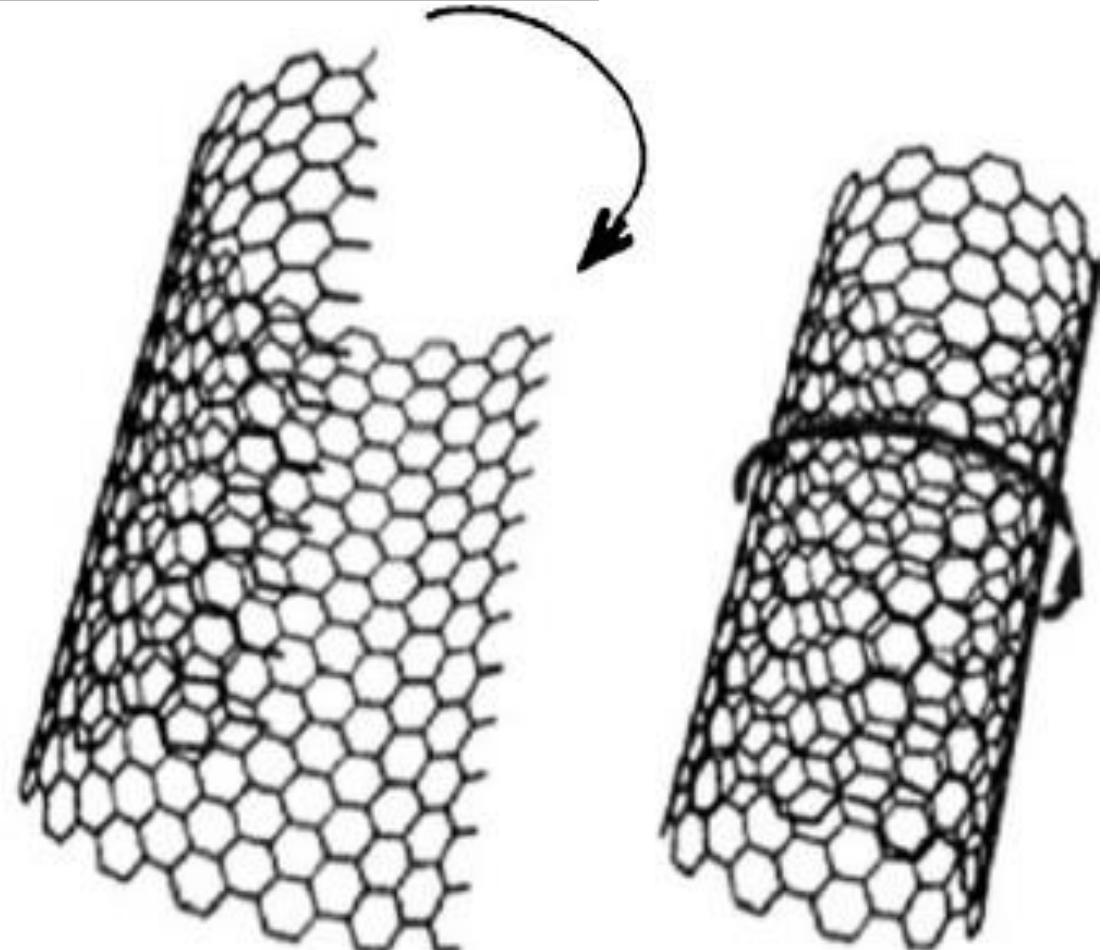
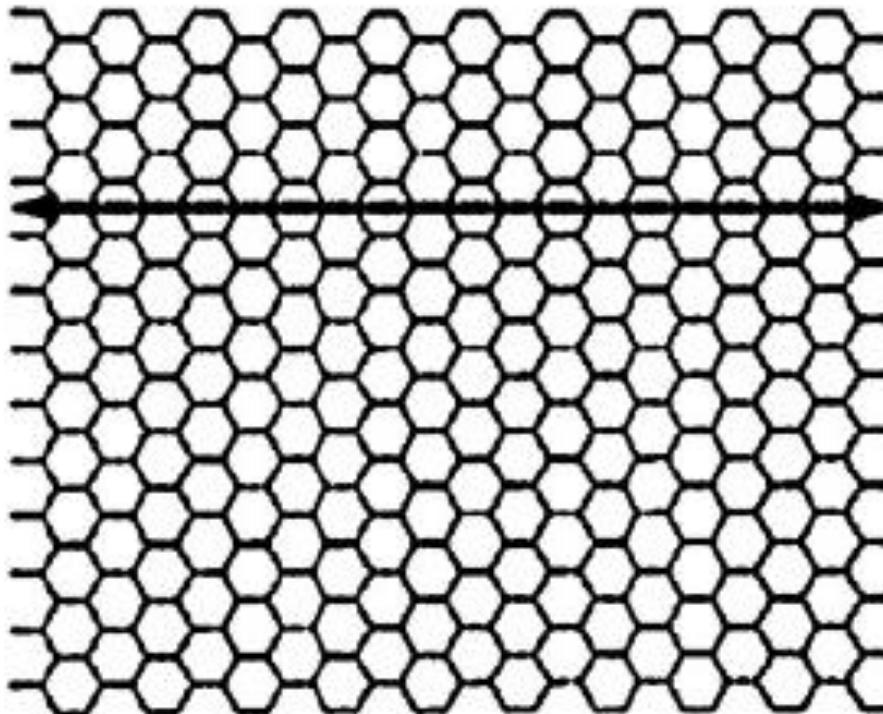
Contactable Address Faculty of Engineering Shinshu University, 4-17-1 Wakasato, Nagano-shi 380-8553, Japan

Education B.S., Dept of Electrical Engineering, Shinshu University, Nagano-city, Japan (March 1969)
M.S., Dept of Electrical Engineering, Shinshu University, Nagano-city, Japan (March 1971)

Dr. in Engineering, Nagoya University, Nagoya, Japan



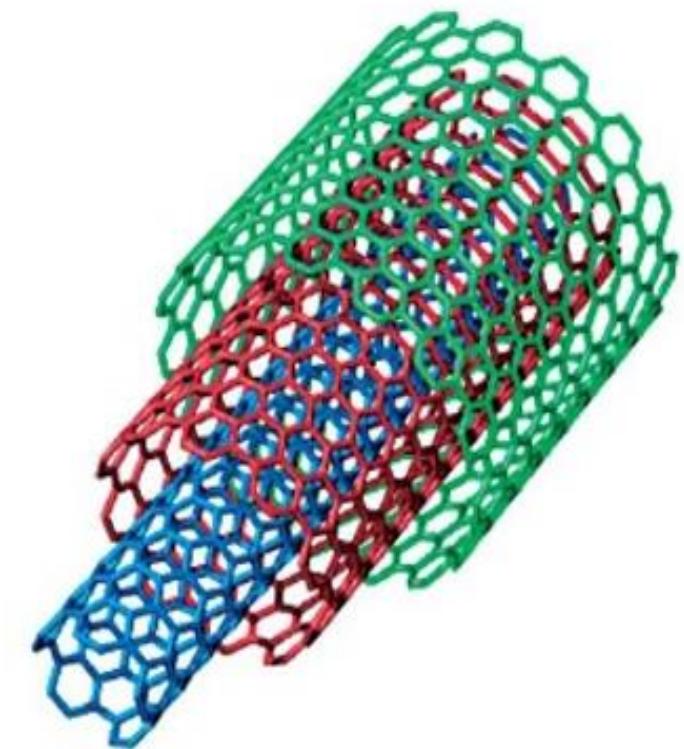
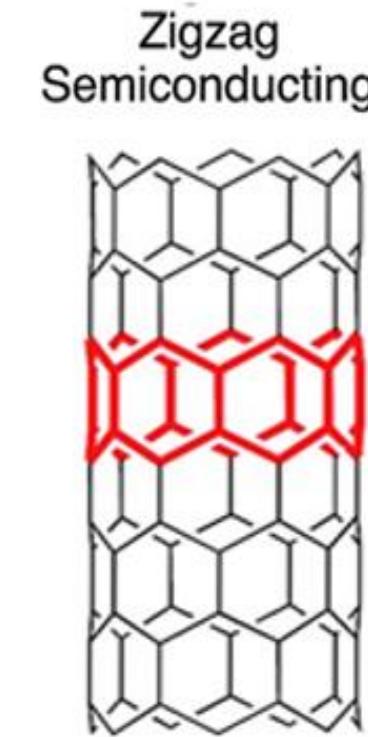
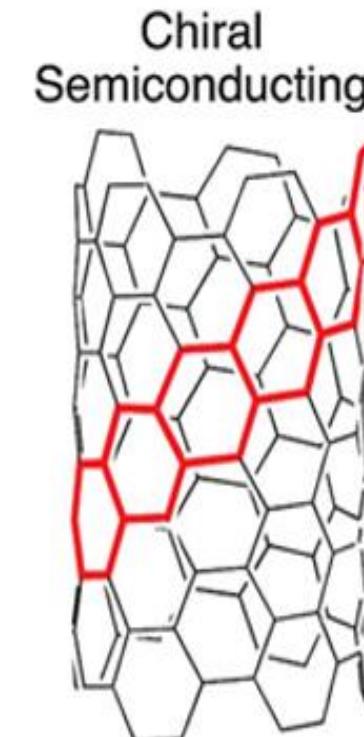
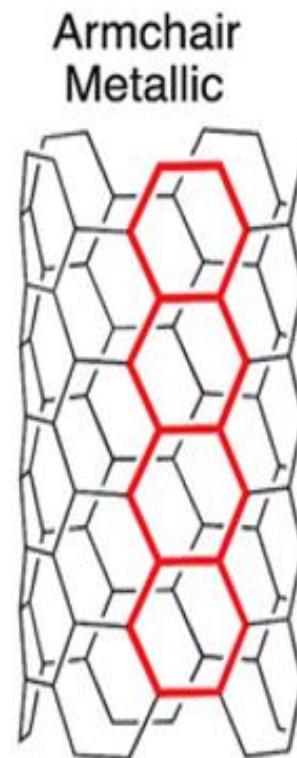
Graphene and Carbon nanotubes



Different forms : (Types of CNTs)

1) Single-Wall Nanotube (SWNT) (a. Arm Chair, b. Chiral c. Zig-Zag)

2) Multi-Walled Nanotubes (MWNT) Multiple rolled layers of graphene sheets, More resistant to chemical changes than SWNTs



SWCNT

MWCNT



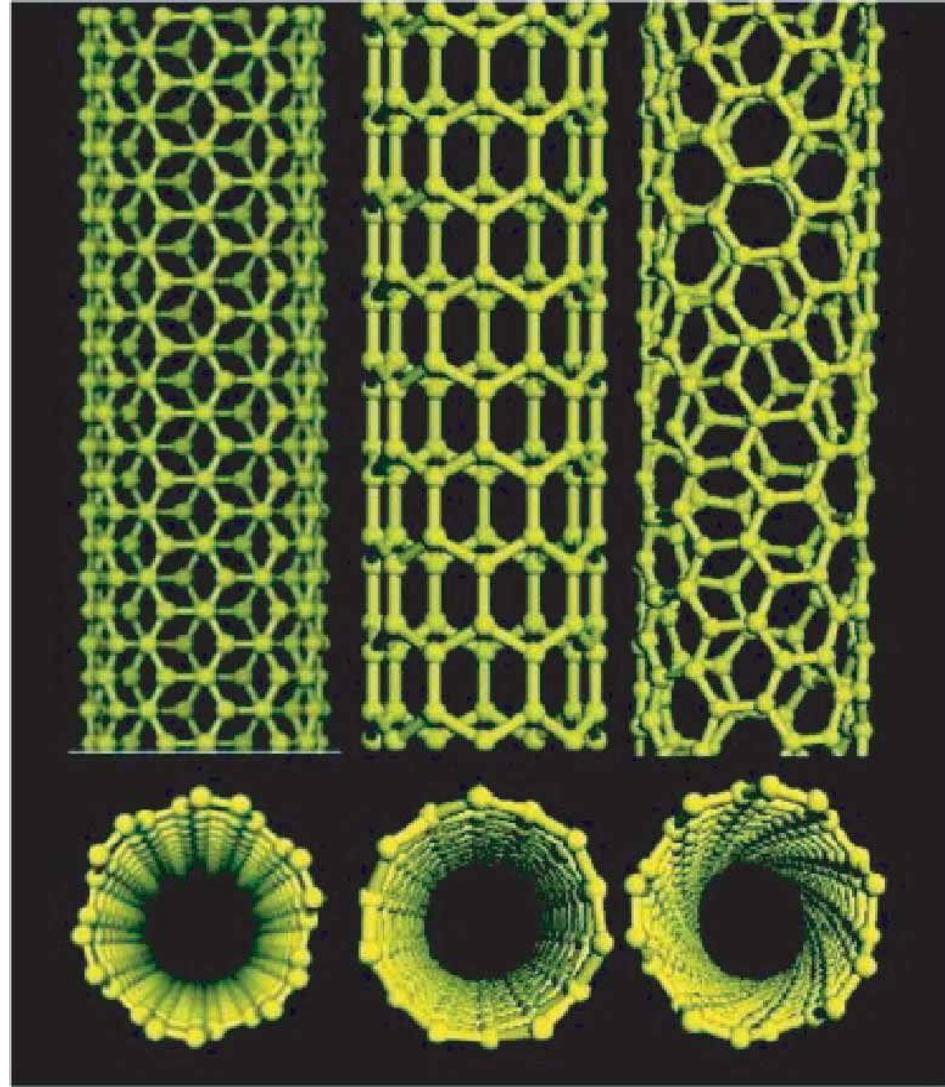
armchair



zigzag



chiral

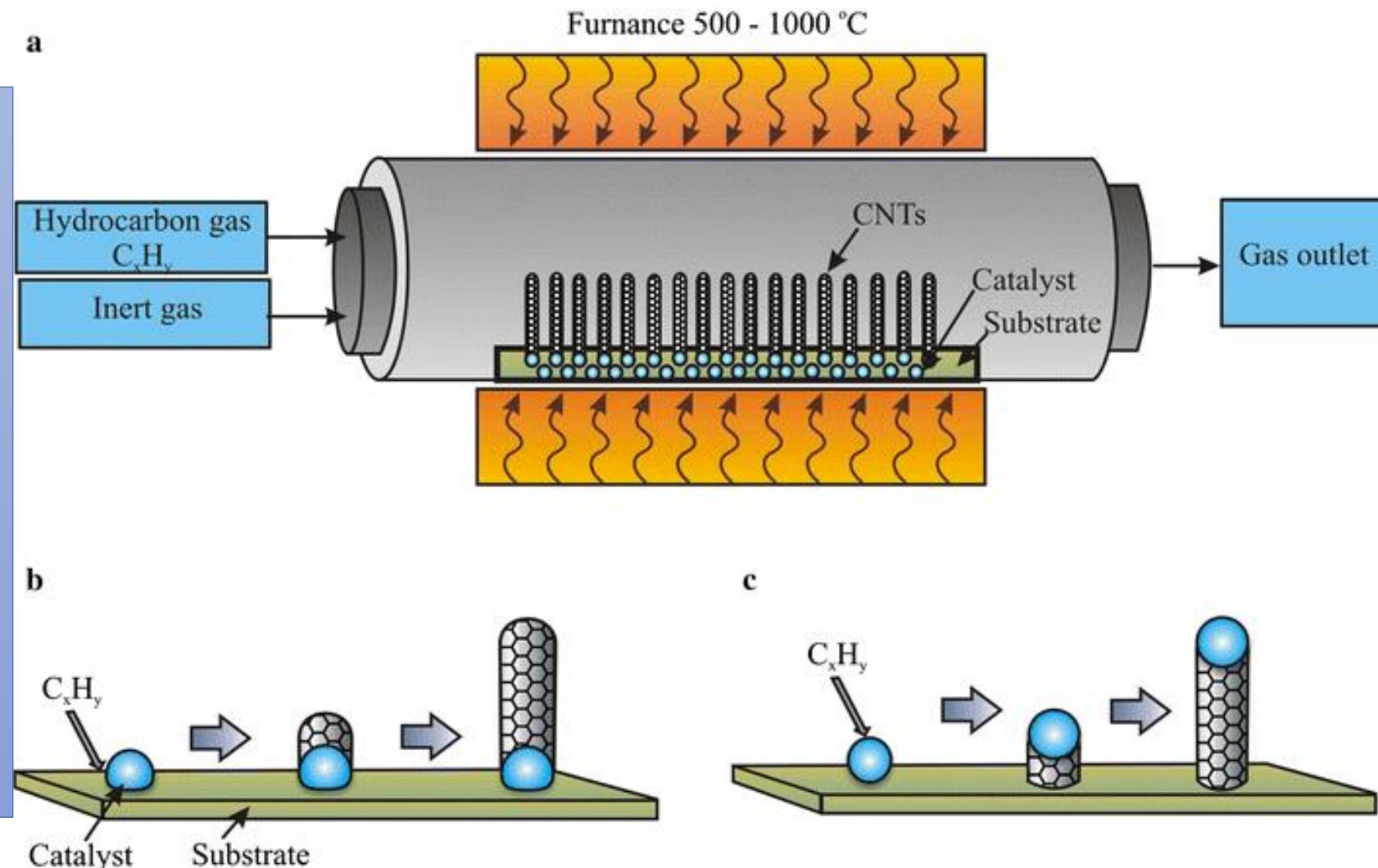


Synthesis of CNTs by modified CVD

method:

Chemical Vapor Deposition: Requirements:

- High Temperature Tubular furnace (500 to 1500 °C)
- Source of Carbon: Methane, ethylene, hydrocarbon gas, xylene, natural gas
- Substrate: carbon, quartz, silicon
- Inert gas: Argon, Hydrogen, Nitrogen
- Catalyst: Ferrocene, Nickallocene, Cobaltocene



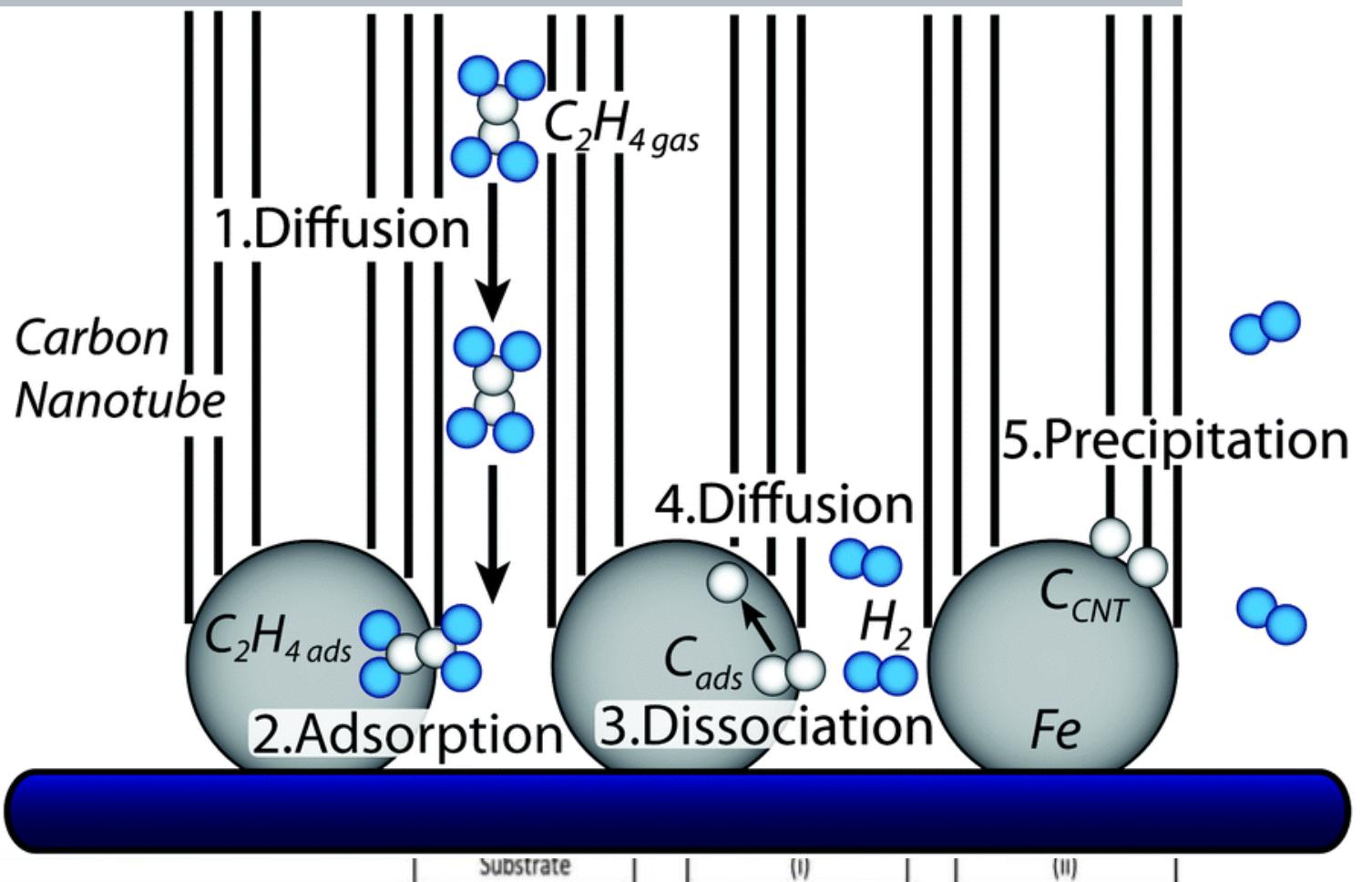
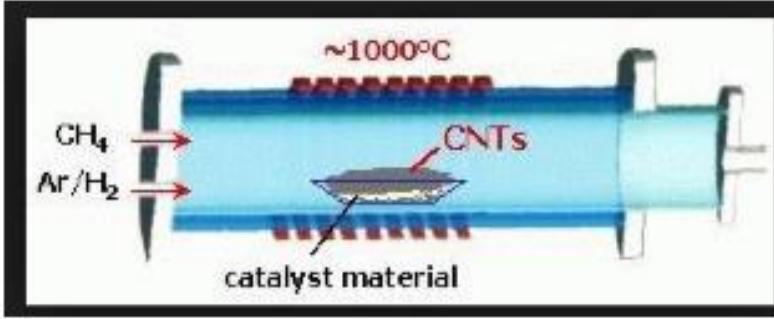
Zaytseva, O., Neumann, G. Carbon nanomaterials: production, impact on plant development, agricultural and environmental applications. *Chem. Biol. Technol. Agric.* **3**, 17 (2016). <https://doi.org/10.1186/s40538-016-0070-8>

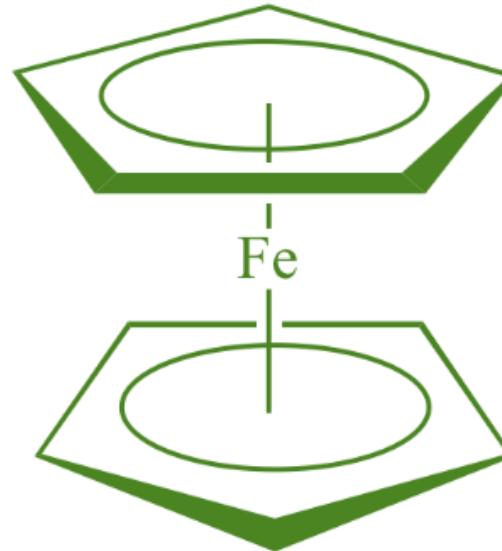
Steps: Procedure involves as follows

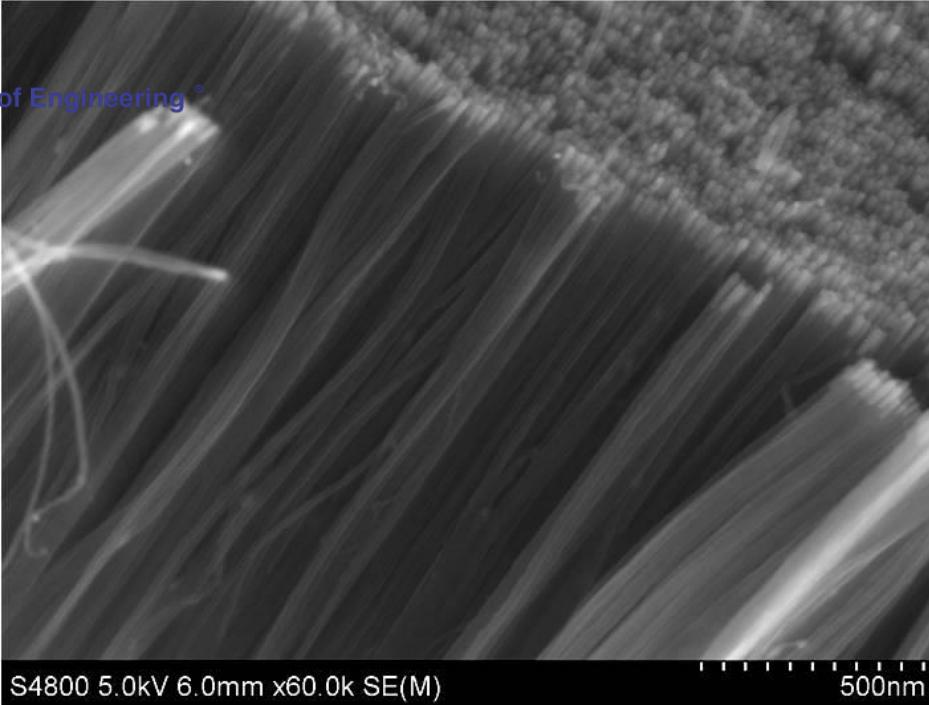
- ❖ The cleaned quartz/carbon/silica substrate is placed in the middle of the tubular furnace.
- ❖ In order to maintain the inert atmosphere inside the furnace, initially the air/oxygen present inside the tubular furnace has to be removed by passing the argon or nitrogen gas for about 30 min.
- ❖ After maintaining the inert gas atmosphere, the required temperature is set with slow heating rate.
- ❖ The hydrocarbon precursors in gaseous forms along with ferrocene and Benzene/toluene vapors are pumped into the reaction chamber.
- ❖ The furnace is heated up to 850–1000 °C and 550–700 °C for SWCNT and MWCNT production respectively.
- ❖ Initially, at high temperature, due to the thermal decomposition of hydrocarbon, carbon atoms are formed and dissolved in the metal nanoparticle catalyst.
- ❖ Once the threshold concentration of carbon in the catalyst is reached, a semi fullerene cap type of structure is formed due to precipitation of carbon atoms. This acts as a seed for further crystal growth, which further continues to grow in tubular form resulting in CNT.
- ❖ After the formation of CNT on catalyst is completed as shown in the above figure, the supply of the reactant/catalyst vapors are stopped.
- ❖ Then the furnace temperature is reduced slowly to room temperature and supply of the inert gas also stopped.
- ❖ The CNT formed on catalyst is taken out along with the substrate, subjected to purification.

Zaytseva, O., Neumann, G. Carbon nanomaterials: production, impact on plant development, agricultural and environmental applications. *Chem. Biol. Technol. Agric.* **3**, 17 (2016). <https://doi.org/10.1186/s40538-016-0070-8>

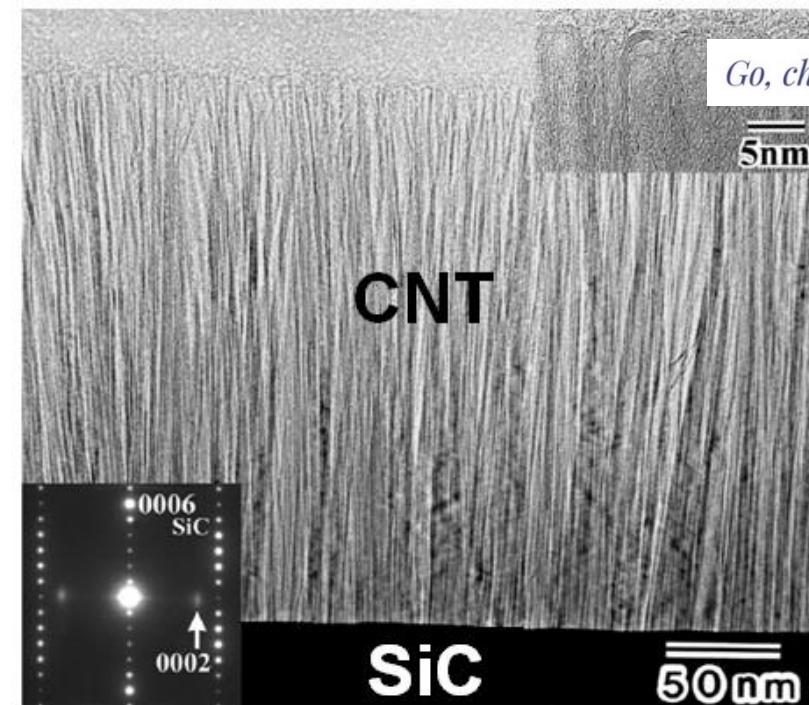
CNT growth mechanism in CVD

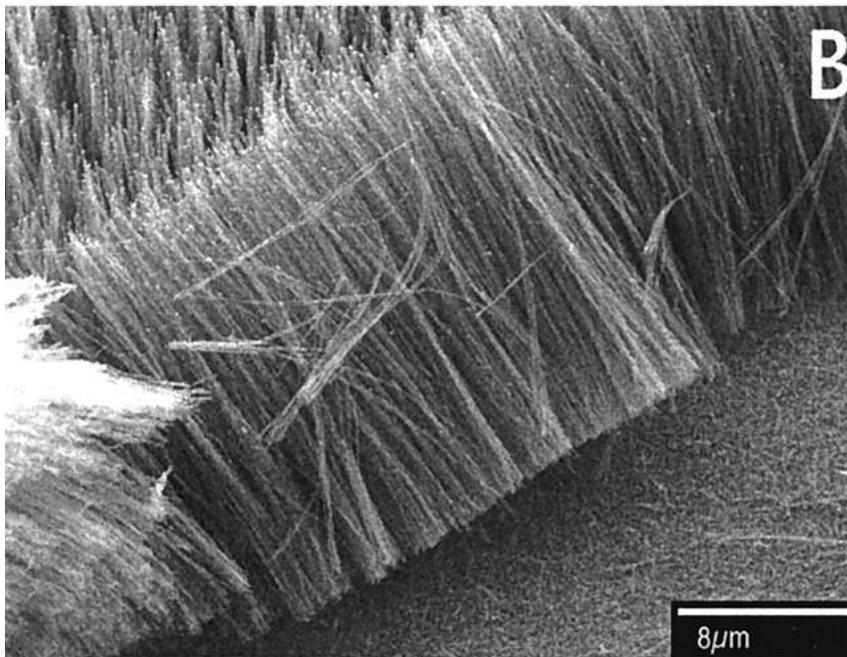
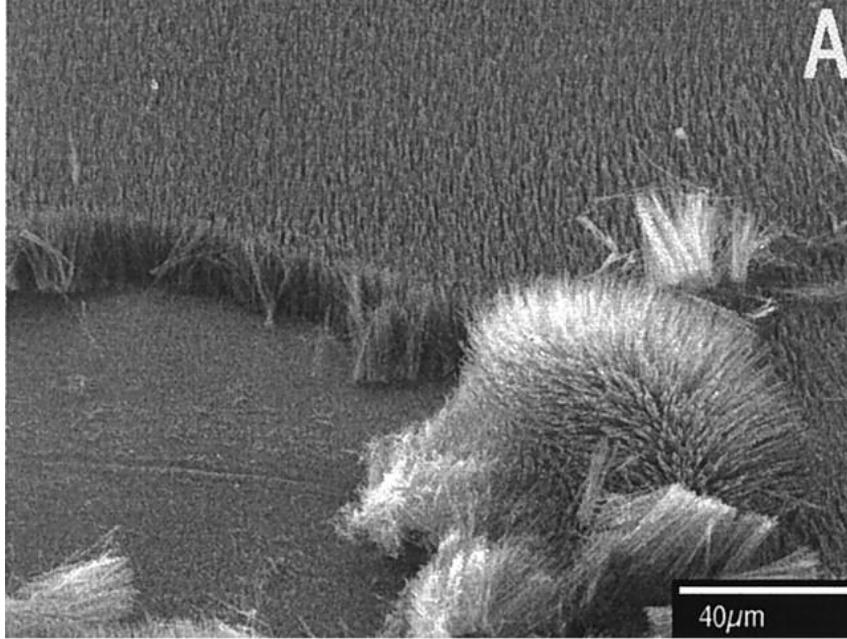






S4800 5.0kV 6.0mm x60.0k SE(M)





Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass, Z. F. RenZ. P. HuangJ. W. XuJ. H. WangP. BushM. P. Siegaland P. N. Provencio , Science
6 Nov 1998, Vol 282, Issue 5391
pp. 1105-1107
DOI: [10.1126/science.282.5391.1105](https://doi.org/10.1126/science.282.5391.1105)

Importance of CVD:

- The three main parameters for CNT growth in CVD are the atmosphere, carbon source, catalyst, and growth temperature.
- Low-temperature (600–900°C) yields MWNTs, whereas a higher temperature (900–1,200°C) reaction favors SWNTs growth.
- The most commonly used catalysts for CNT growth are the transition metals (Fe, Co, Ni) from carbon sources like organometallocenes (ferrocene, cobaltocene, nickelocene), nitrates and others.
- A correlation was found between the size of catalyst particles and the nanotube diameter. Hence, metal nanoparticles of controlled size can be used to grow CNTs of controlled diameter.
- The CVD method allows CNT growth in a variety of forms, *such as powder, thin or thick films, aligned or entangled, straight or coiled, or even a desired architecture of nanotubes at predefined sites on a patterned substrate.*
- It also offers better control over growth parameters in comparison to other synthesis methods.

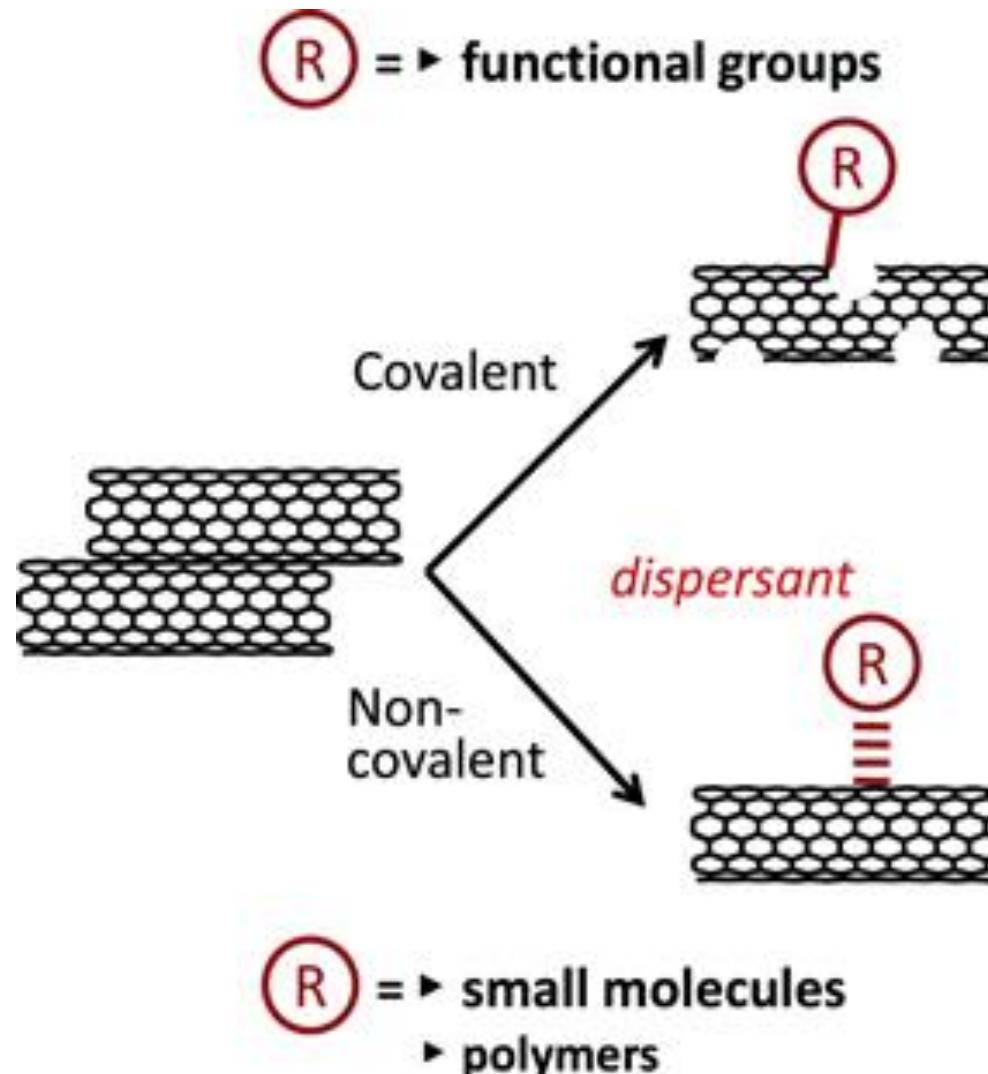


Functionalization of Carbon Nanotubes

Despite CNTs's exceptional properties, there are two main limitations that hinder its use. The surface energy of CNTs is significantly different from that of matrices such as common organic solvents or polymers and **CNTs may not have chemical affinity to the organic matrices** and thus, the dispersion of CNTs into matrices is the biggest obstacle in practice.

The modification/ functionalization of CNTs with other materials, makes it the most attractive and ultimate candidate for a many applications which includes nanodevices, to organic electronics. The modification/ functionalization of CNTs can be simply divided into
a) Chemical (covalent) and b) Physical (noncovalent) functionalization

Chemical functionalization is based on the covalent bond of functional groups onto carbon form of CNTs. It can be performed at the end caps of nanotubes or at their sidewalls which have many defects. Direct covalent sidewall functionalization is associated with a change of hybridization from *sp²* to *sp³* and a simultaneous *loss of p-conjugation system*.

advantage

- high dispersion stability

disadvantage

- loss of inherent properties
- structural damage,
- shortening

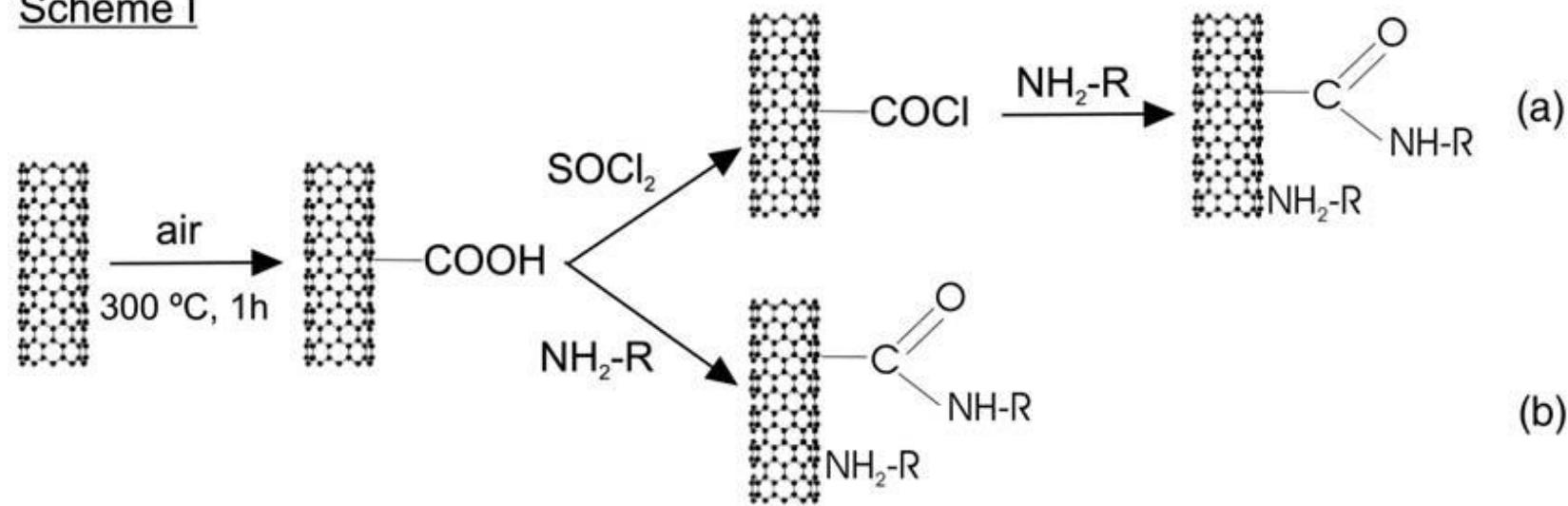
advantage

- easy procedure
- minimum damage

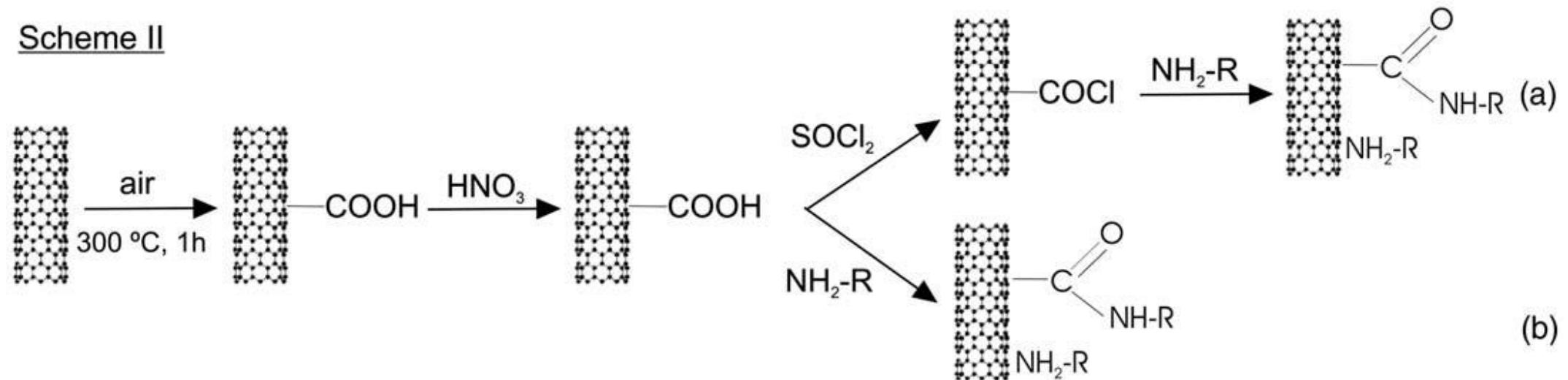
disadvantage

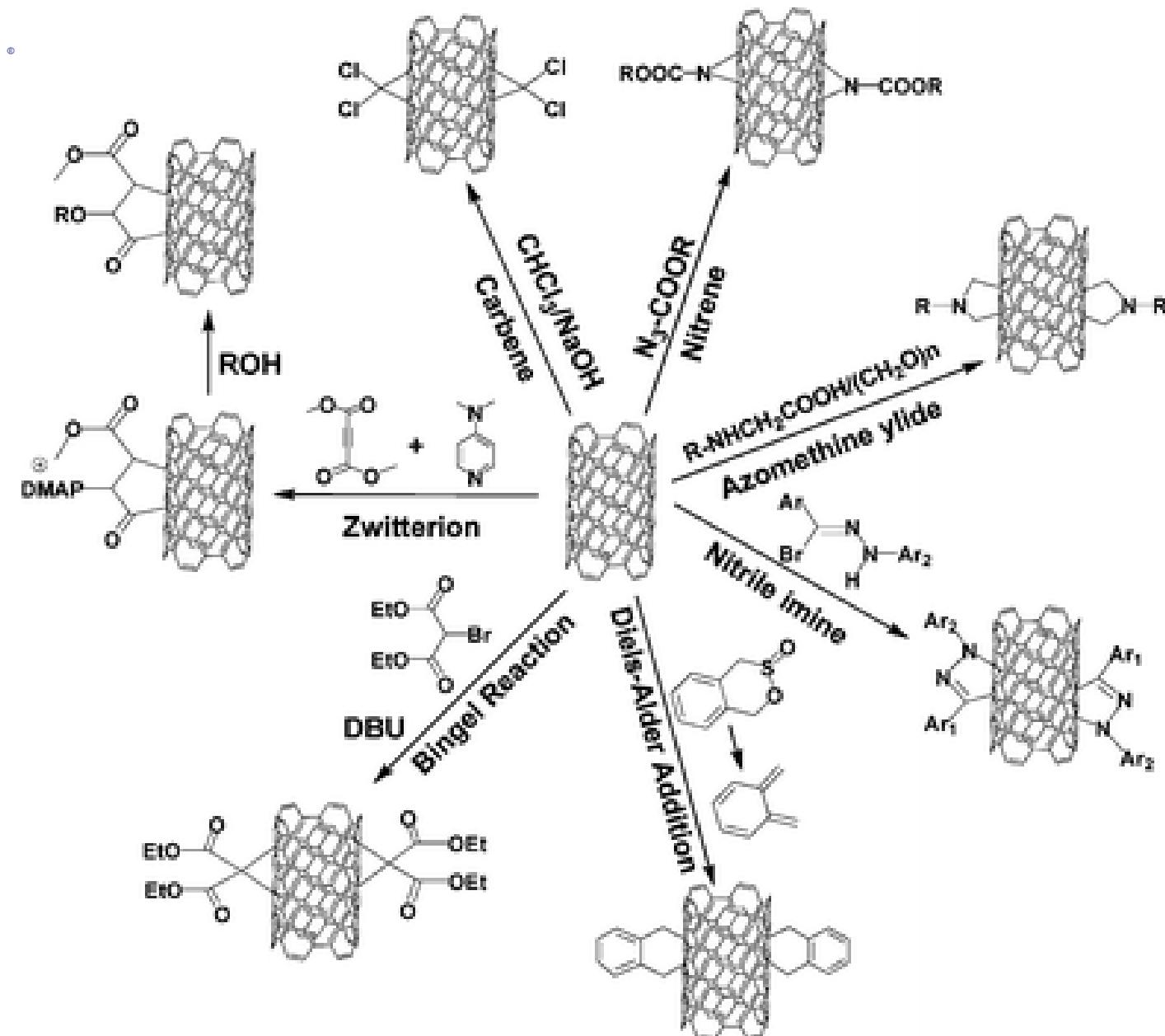
- weak coating stability

Scheme I

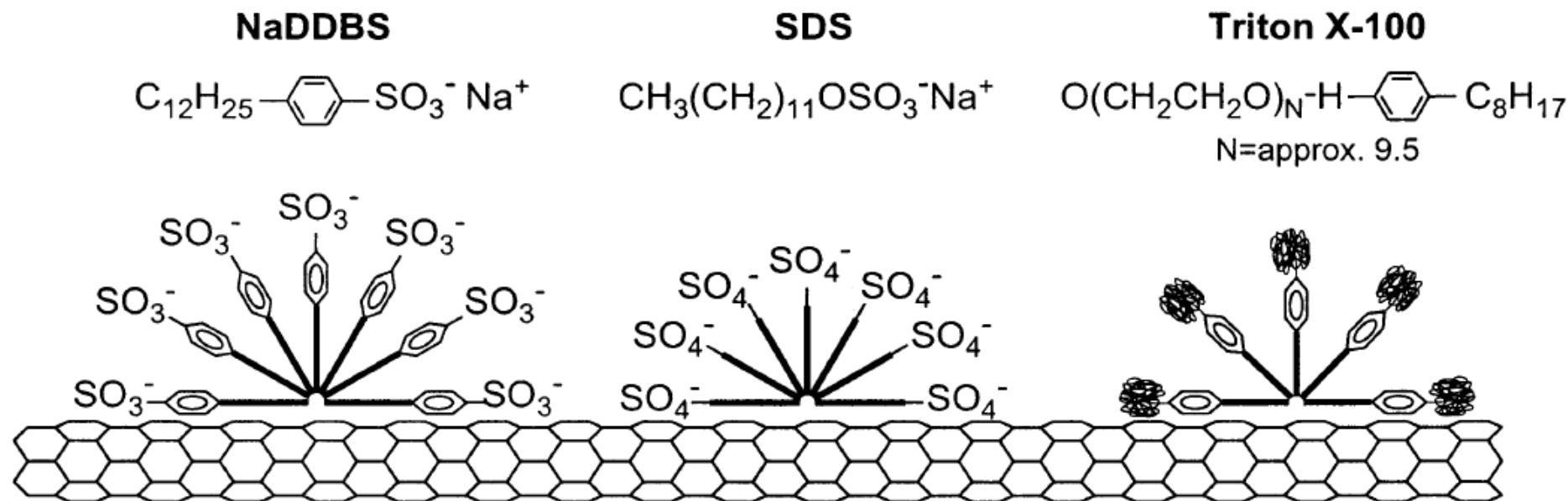


Scheme II





b) Non-covalent functionalization: It **does not destroy the conjugated system** of the CNTs sidewalls, and therefore it does not affect the final structural properties of the material. The CNTs are functionalized **non-covalently by aromatic compounds, surfactants, and polymers**, employing **π - π stacking or hydrophobic interactions** for the most part. In this approaches, the non-covalent modifications of CNTs can do much to preserve their desired properties, while improving their solubilities quite remarkably. (Ex: aromatic small molecule absorption, polymer wrapping, surfactants, biopolymers)



Properties of CNTs:

- ❑ 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
- ❑ Nanotubes can be either **electrically conductive or semi conductive**, depending on their **helicity**.
- ❑ These one-dimensional fibers exhibit **electrical conductivity as high as copper, thermal conductivity as high as diamond.**
- ❑ Strength 100 times greater than steel at one sixth the weight, and high strain to failure.
- ❑ Can act as both thermal conductors and thermal insulators.

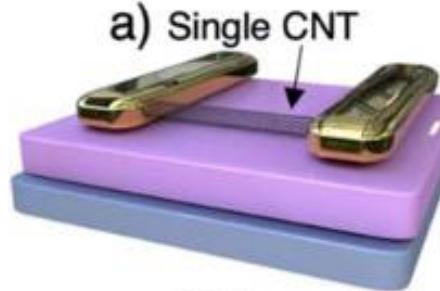
Selected electrical and mechanical properties of carbon nanotubes

Properties	CNTs	Other materials
Thermal conductivity (W/mK)	>3000	Copper= 400 Carbon fiber (pitch)=1000 Carbon fiber (PAN)=8-105
Electrical conductivity (S/m)	10^6 - 10^7	Copper= 6×10^6 Carbon fiber (pitch)= $2-8.5 \times 10^6$ Carbon fiber (PAN)= $6.5-14 \times 10^6$
Young's modulus (Tpa)	1-5	Steel=0.18-0.2 Kevlar=0.06-0.18 Diamond= 0.1-0.12
Tensile strength (Gpa)	15-150	Steel=0.38-1.55 Kevlar=3.6-3.8

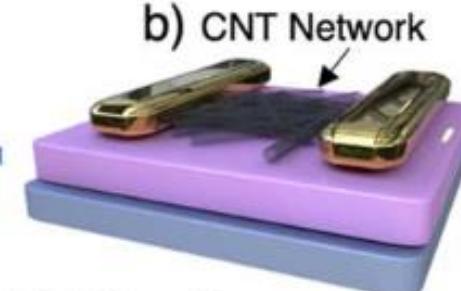
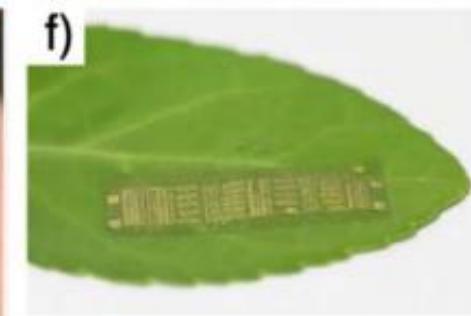
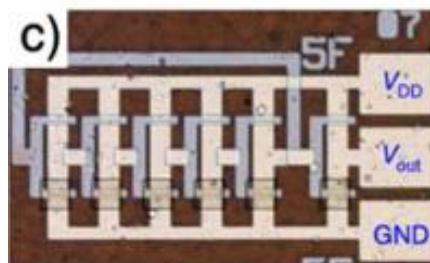
Property	Carbon Fibers		Carbon Nanotubes
	T300 PAN based	P120 Pitch Based	
Diameter (μm)	7	10	0.05
Density (g/cc)	1.76	2.17	~2.0
Elastic Modulus (GPa)	231	827	1000-1400
Ultimate Tensile Strength (GPa)	3.75	2.41	7-10
Thermal Conductivity (W/mK)	8	640	>2000
Coefficient of Thermal Expansion, CTE (ppm/K)	-0.6	-1.45	-1 (isotropic)
Electrical Resistivity (micro-ohm-m)	18	2.2	<0.1

Applications of CNTs:

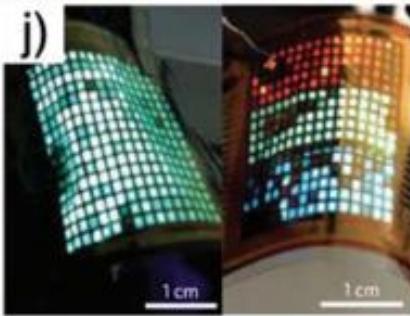
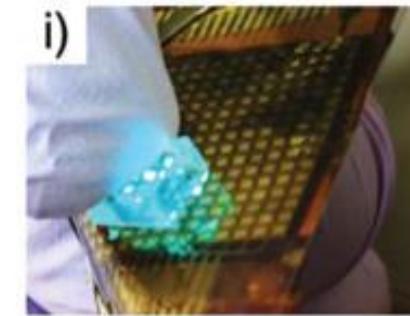
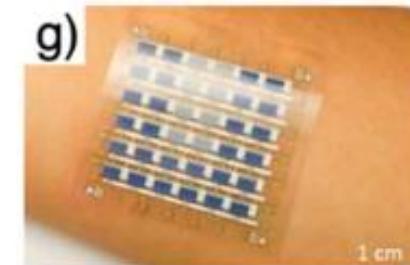
- Sensor, RFIDs,
- Optoelectronic devices (Field Emission Display (FED))
- As *electrodes* in batteries, *capacitors* and *super capacitor electrodes*.
- As *electrode catalyst supports* in *Polymer Electrolyte Membrane (PEM) fuel cells*
- *Hydrogen* Storage material in hydrogen fuel car.
- As electrically *powered artificial* muscles.
- Electrocatalyst for water splitting, H₂ production.
- Adsorbent and photocatalyst for organic pollutants degradation.
- Sensor for heavy metal ion, gases, volatile organic compounds and biomolecules.
- Drug carriers



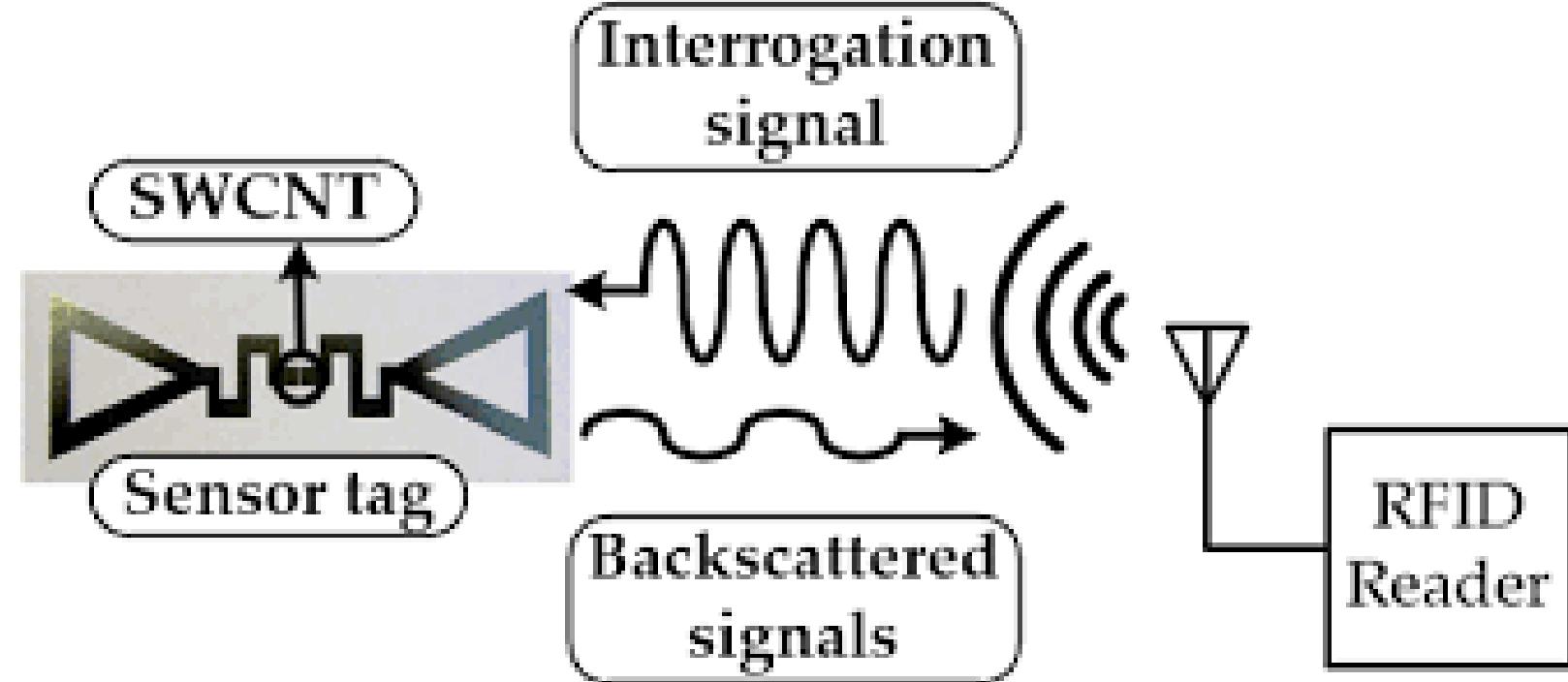
Flexible Circuits



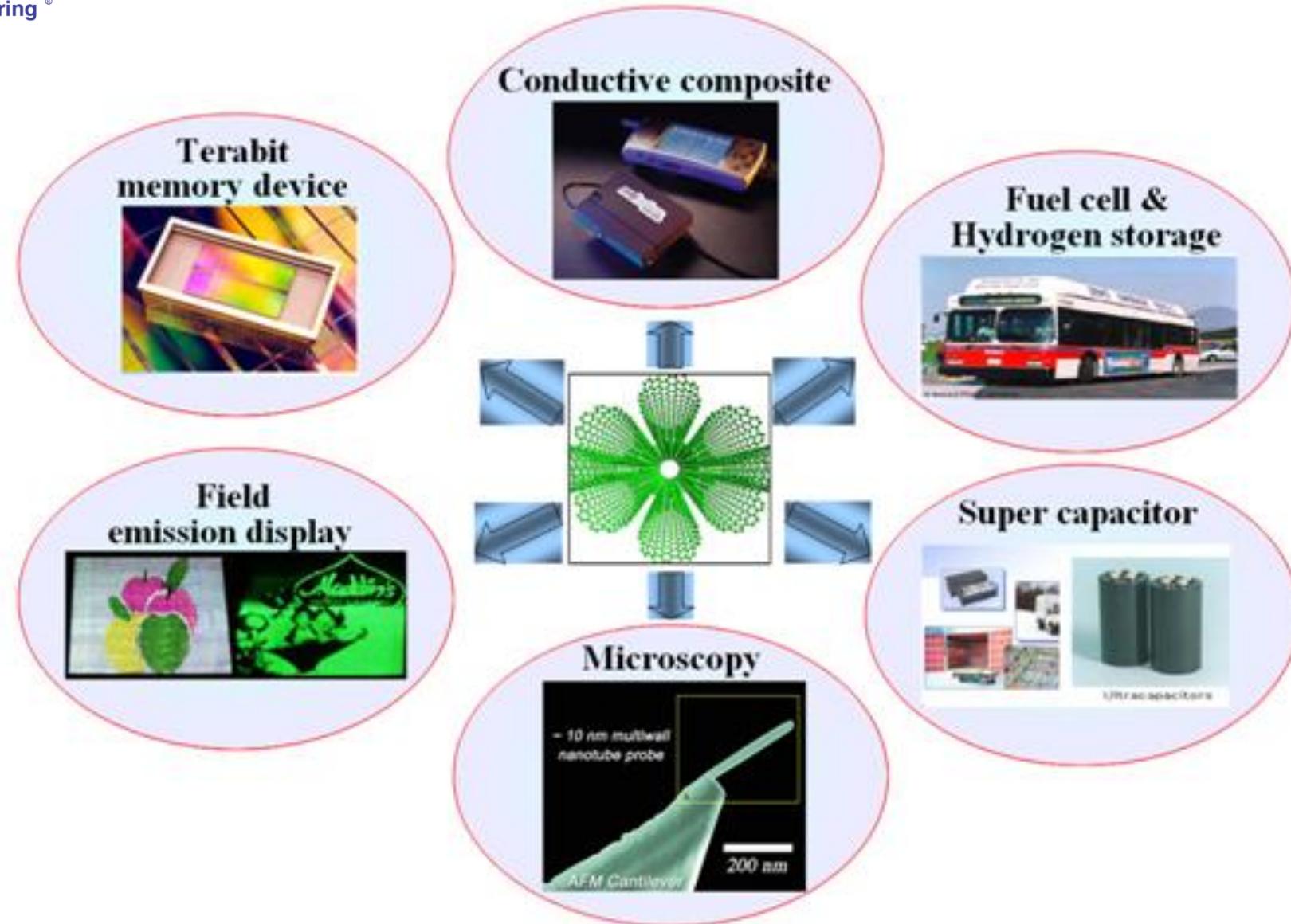
Low-Cost Displays



<https://doi.org/10.1088/2399-1984/ab5f20>



<https://doi.org/10.3390/s18061958>



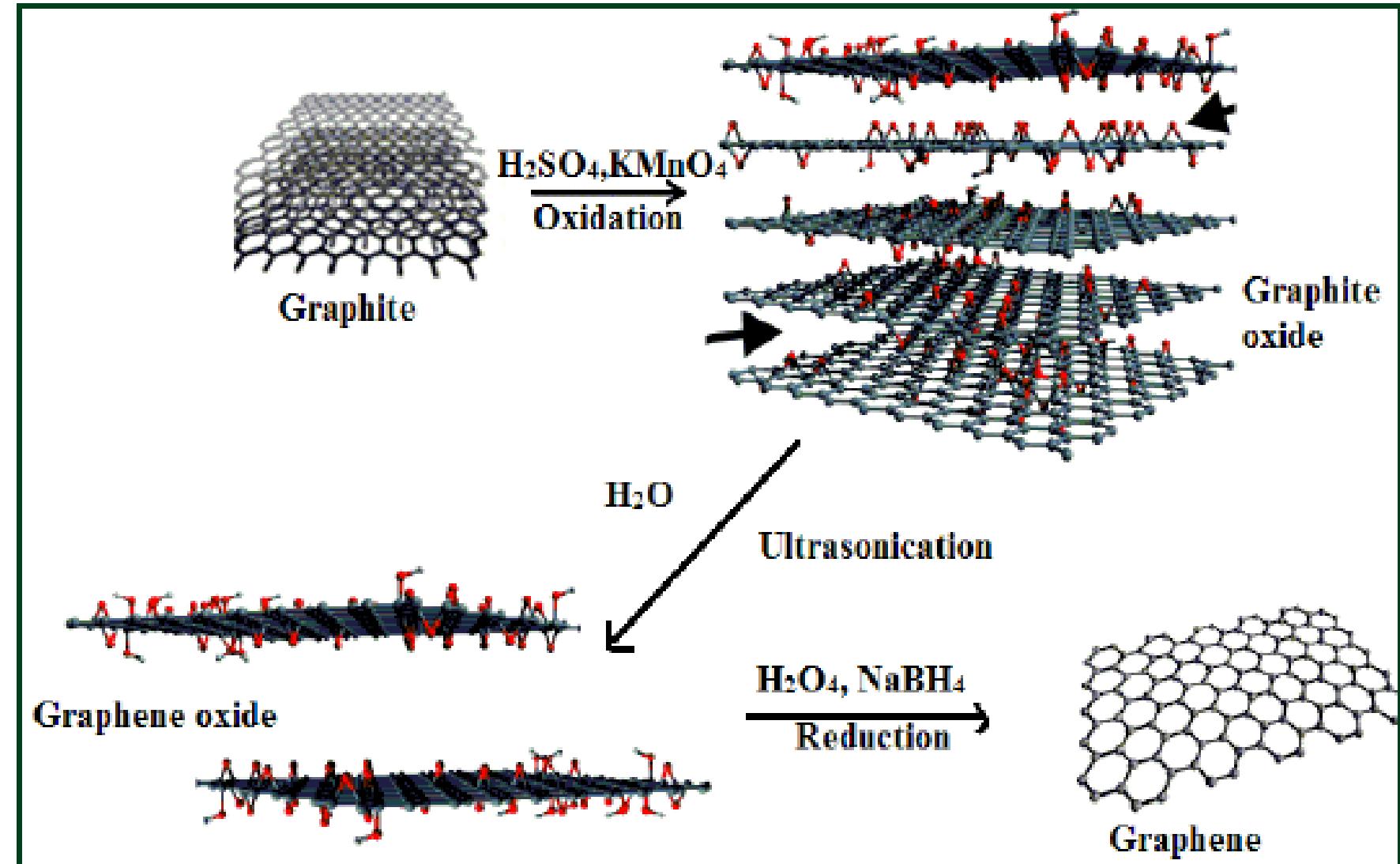
Graphene: *The perfect atomic lattice in single sheet.* *The carbon nanomaterial having only surface.*

- Graphene, an excellent electronic material, discovered in 2004 by **A. K. Geim** and **K. S. Novoselov**, and received Nobel prize in chemistry for this discovery in 2010.
- It has enormous potential in the electronic device community, for example, field-effect transistor, transparent electrode, etc.

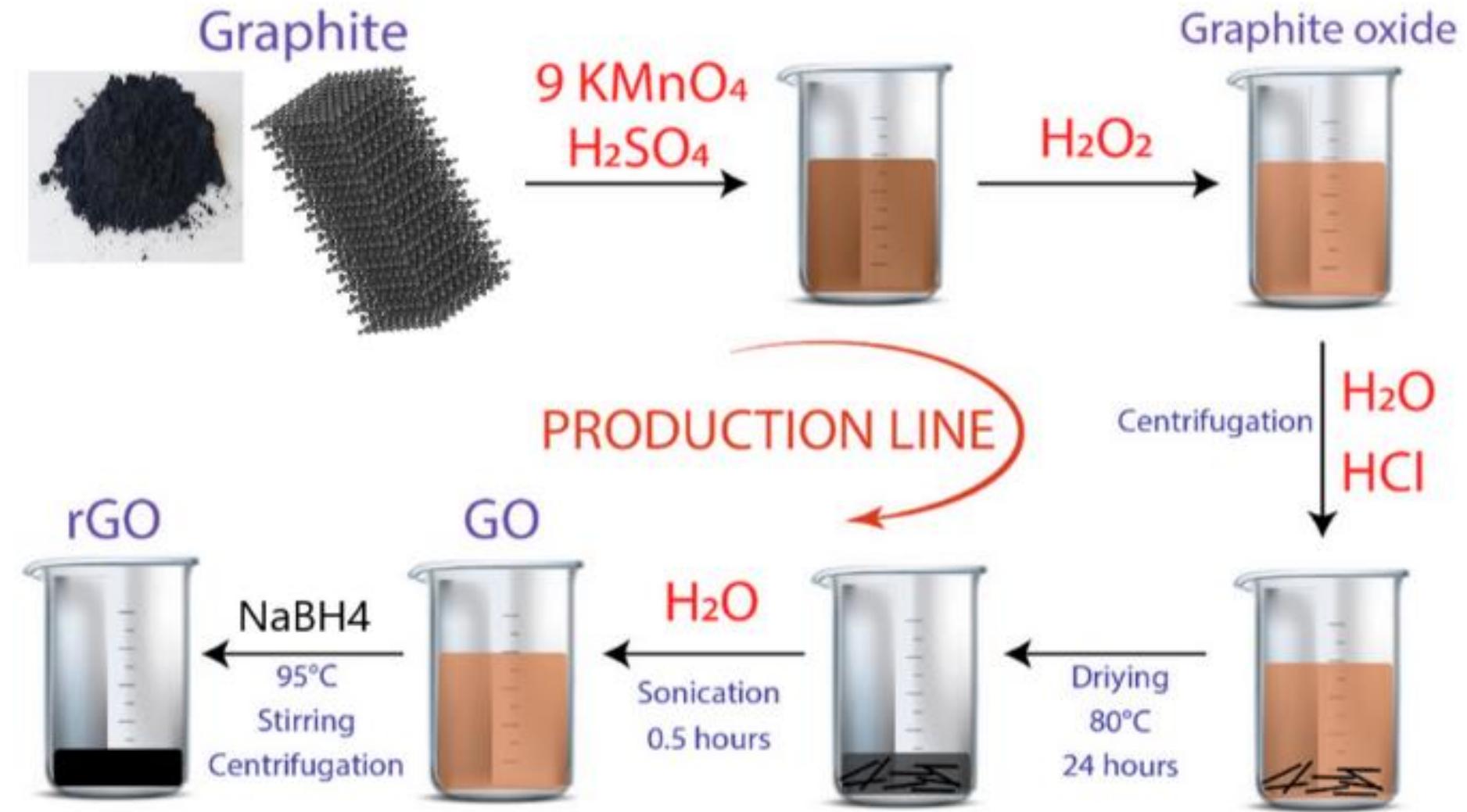
Graphene is an allotrope of carbon made of a single layer of carbon atoms that are bonded together in a repeating pattern of hexagons.

- ❑ It is one million times thinner than paper;
- ❑ It is also the basic structural element of other allotropes, including charcoal, carbon nanotubes and fullerenes.
- ❑ Spherical carbon nanomaterials are referred to as *fullerenes*, while cylindrical ones are called *carbon nanotubes*.
- ❑ SWCNT contains one graphene sheet that rolls up to form a cylinder. MWCNT consist of several graphene sheets rolled up together to form concentric cylinders with large annular space at centre.

Synthesis of Graphene Oxide and Reduced Graphene Oxide (rGO) Modified Hummer's Method



Synthesis of Graphene Oxide and Reduced Graphene Oxide (rGO) Modified Hummer's Method



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

Graphite powder (2 g) + 1 g sodium nitrate + 46 ml H₂SO₄ (dissolved with stirring in ice bath)

Slow addition of KMnO₄ (6 g) during stirring of 30 minutes (temperature remains below 20°C)

Stir for 30 minutes at 40°C and add 80 ml of water

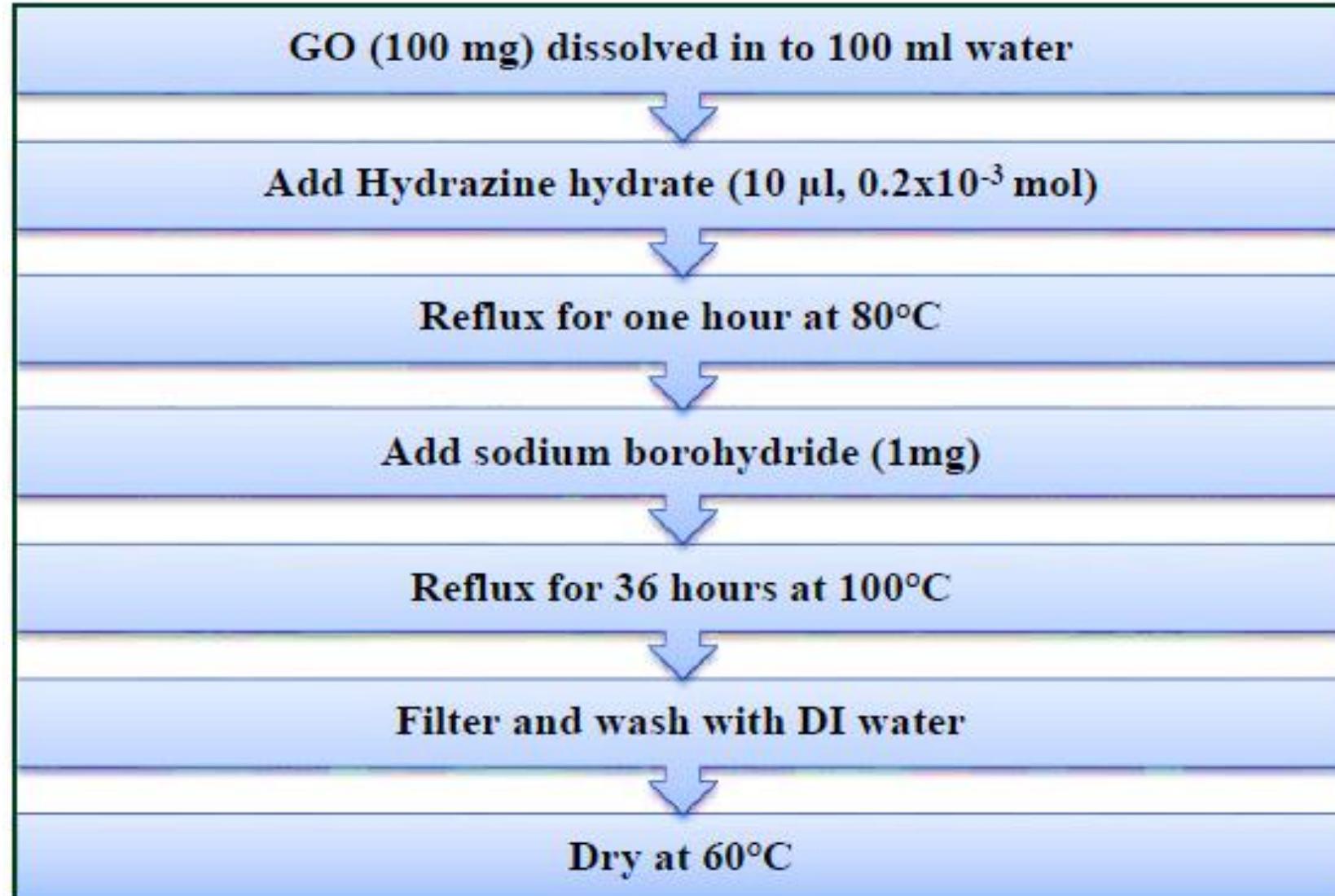
Stir for another 90 minutes at 90°C and add 200 ml water and 6 ml H₂O₂

Filter and wash the solution with DI water and HCl

Dissolve filtered paste in 100 ml water and ultrasonicate for 1 hour

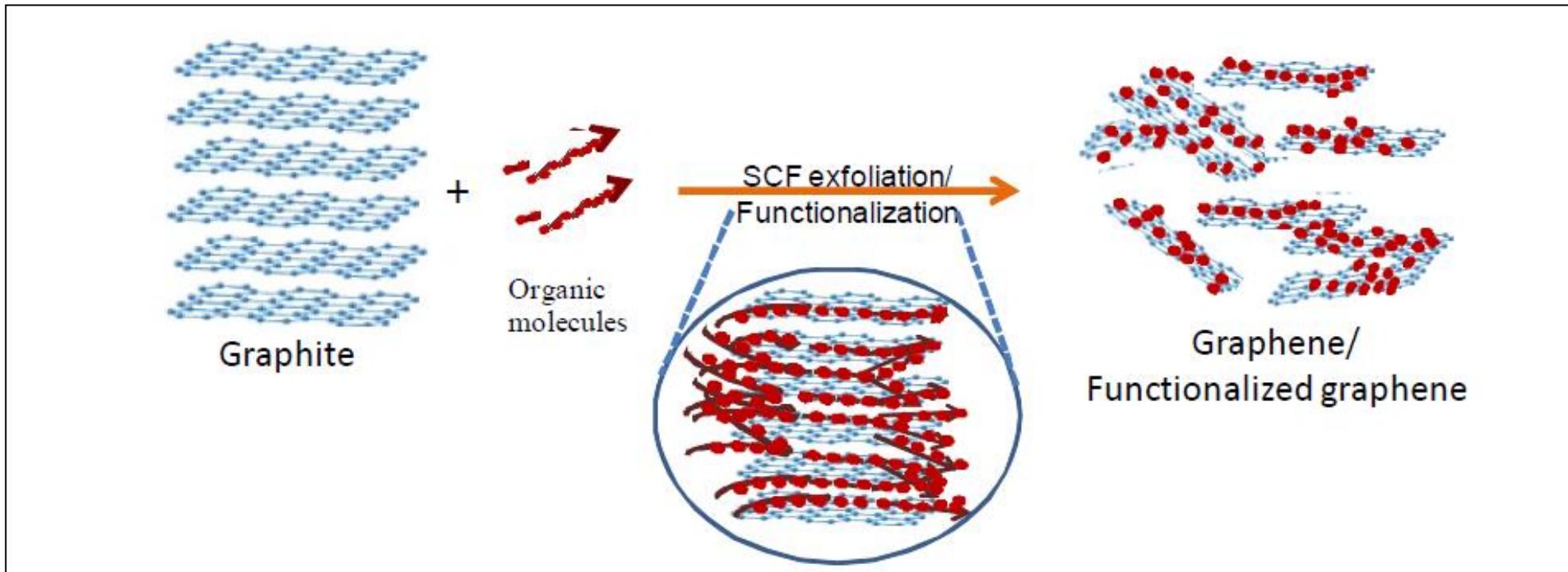
Centrifuge the solution and dry the obtained GO powder at room temperature

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



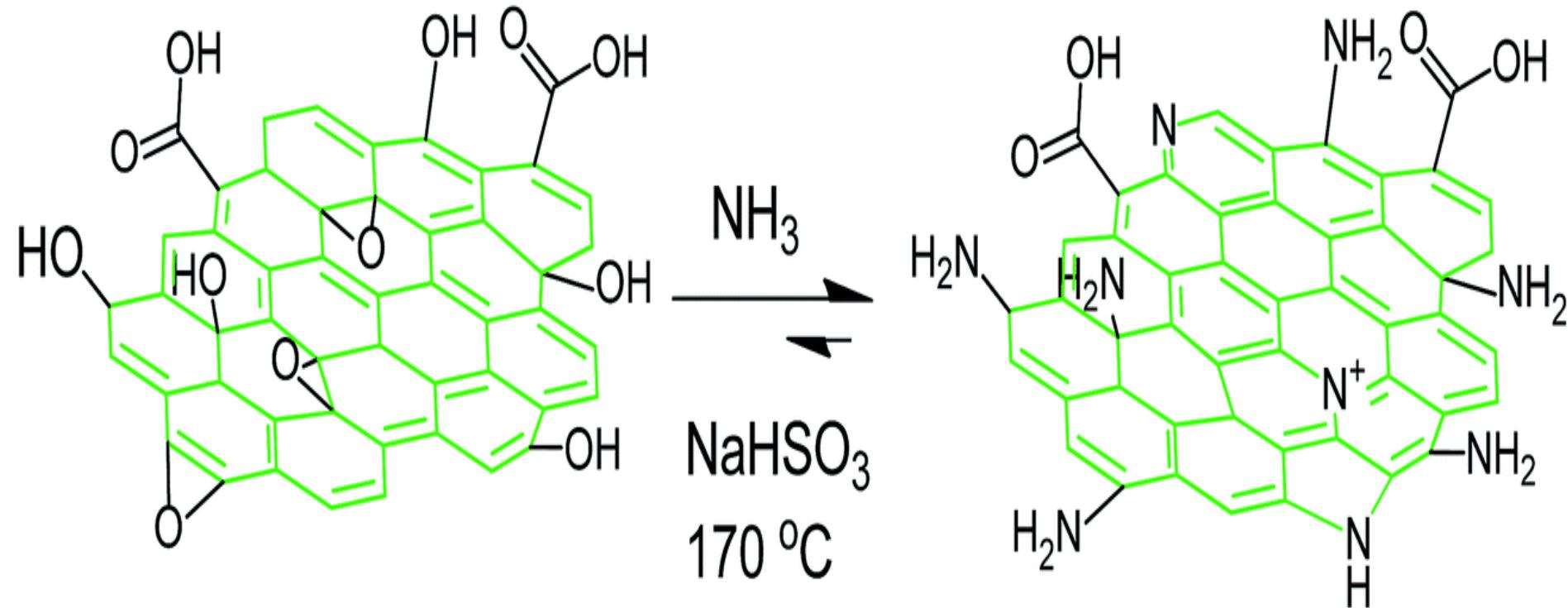
Functionalisation of Graphene:

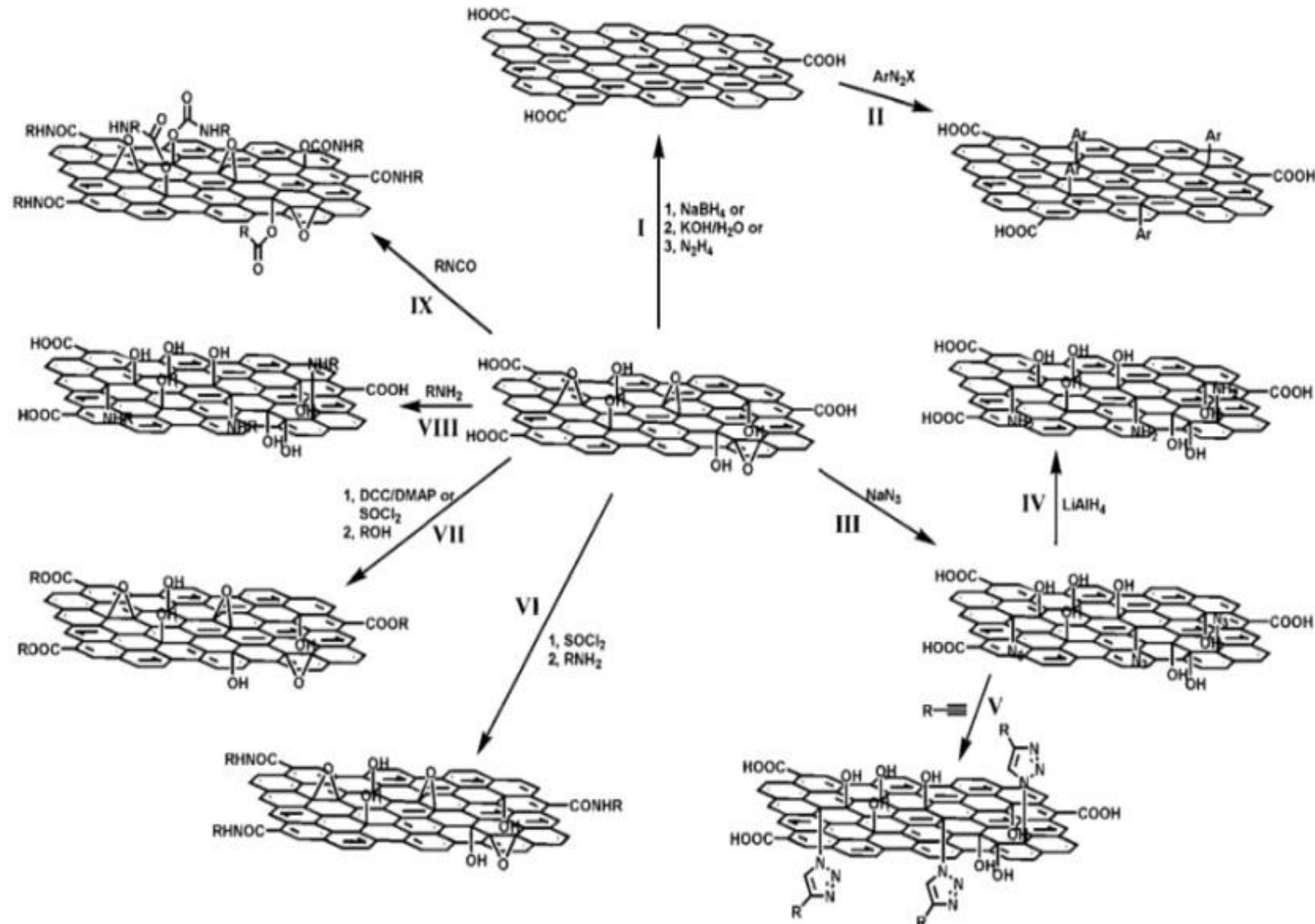
Graphene has been functionalized by both covalent and noncovalent means to disperse or solubilize them in different solvents

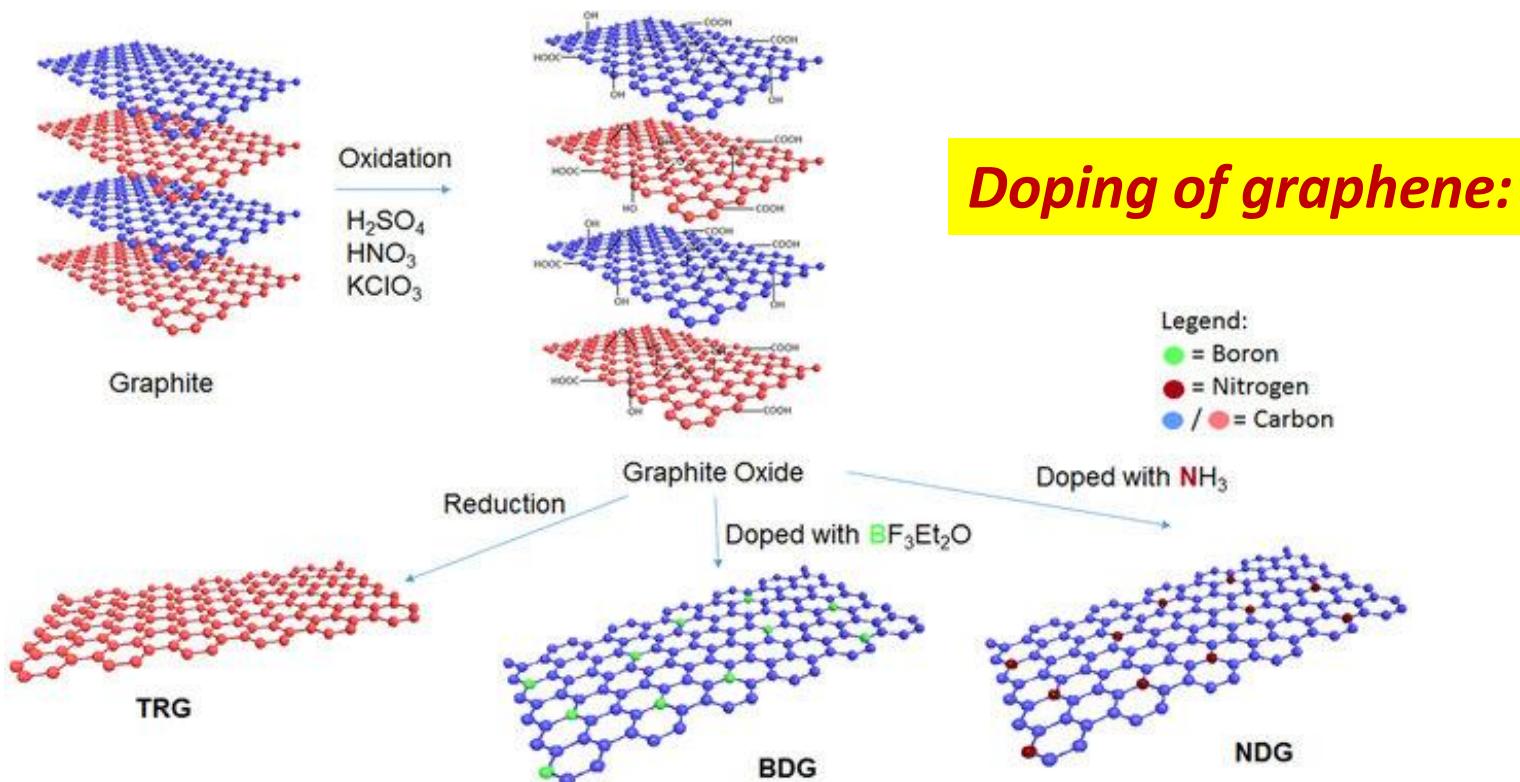
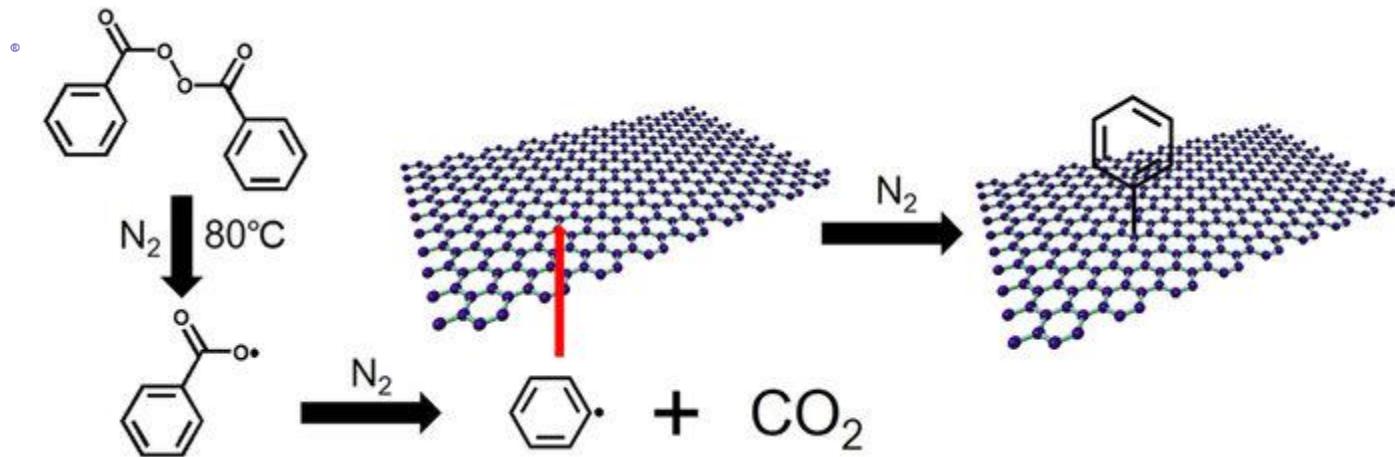


Functionalisation of Graphene:

Graphene has been functionalized by both covalent and noncovalent means to disperse or solubilize them in different solvents

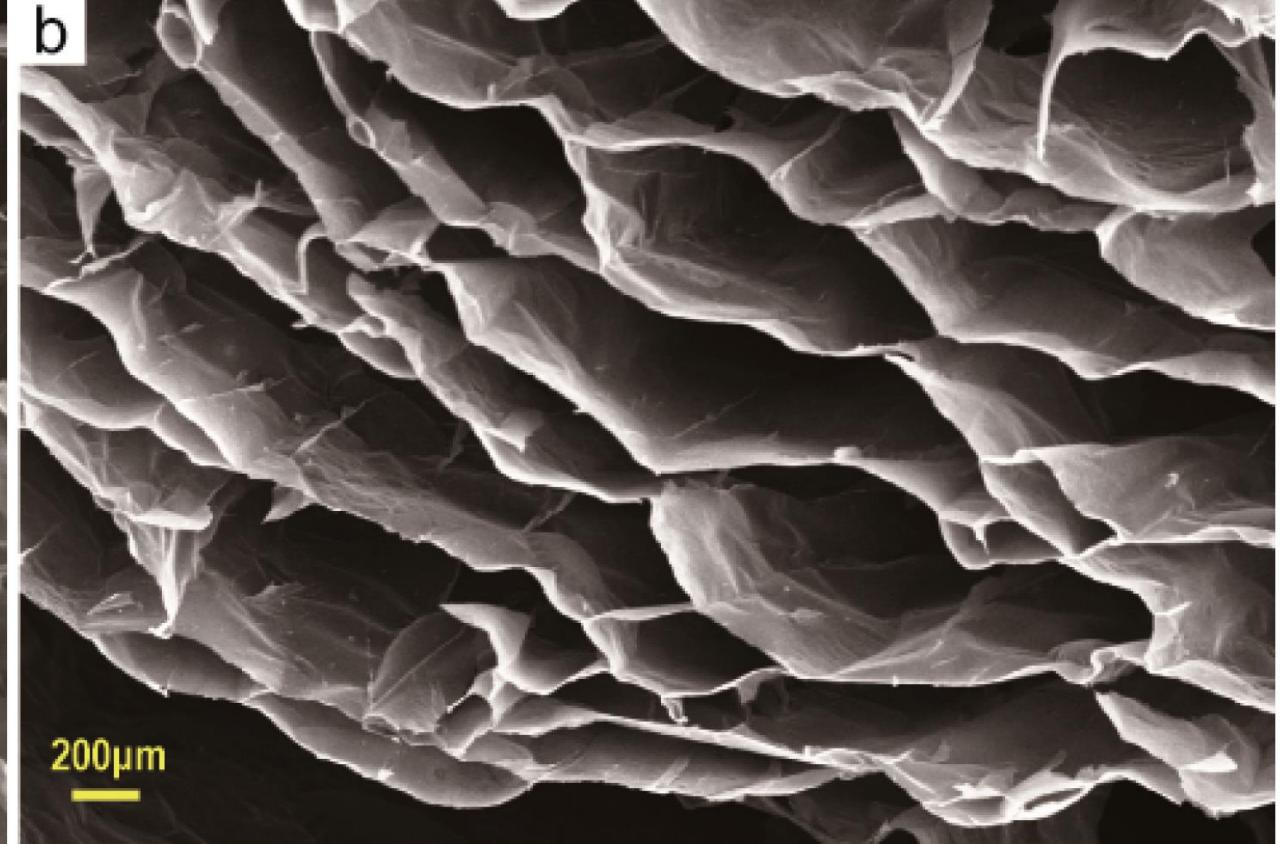
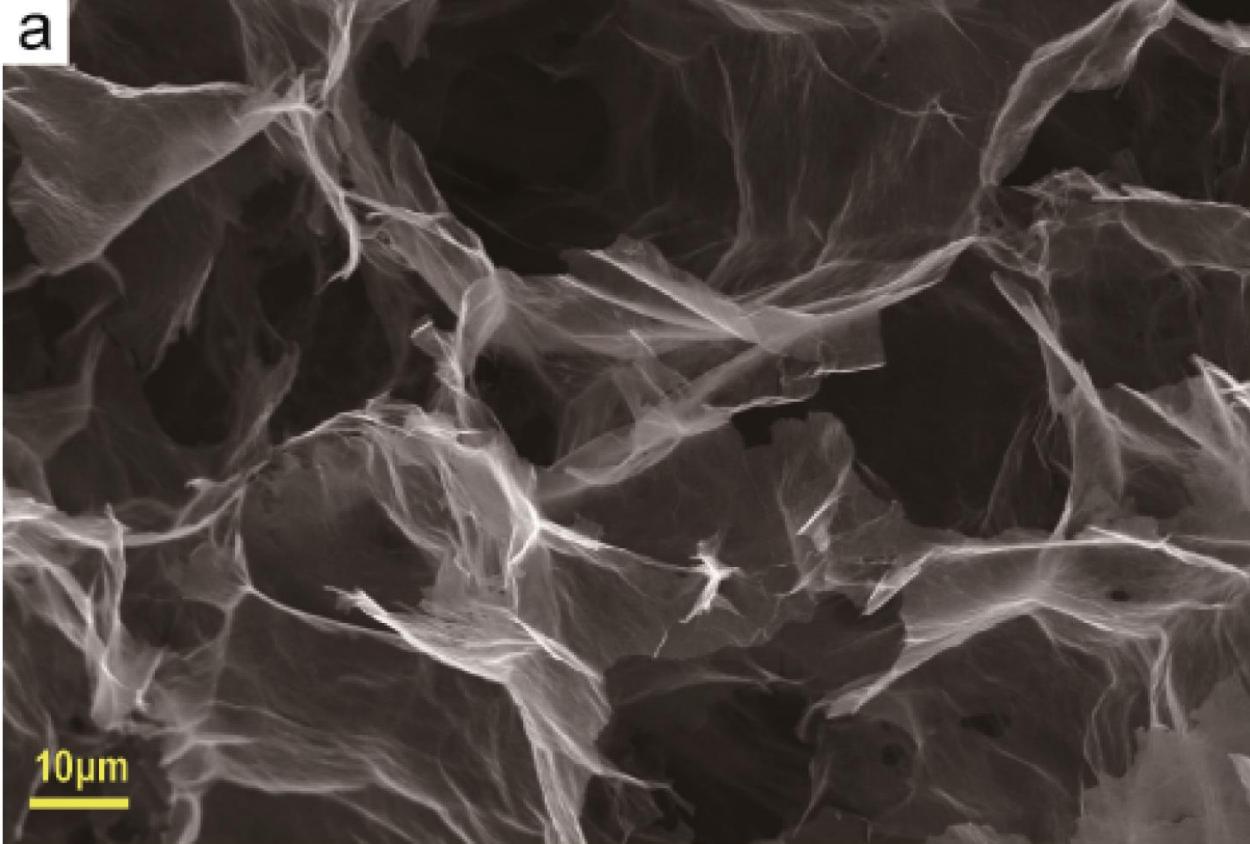






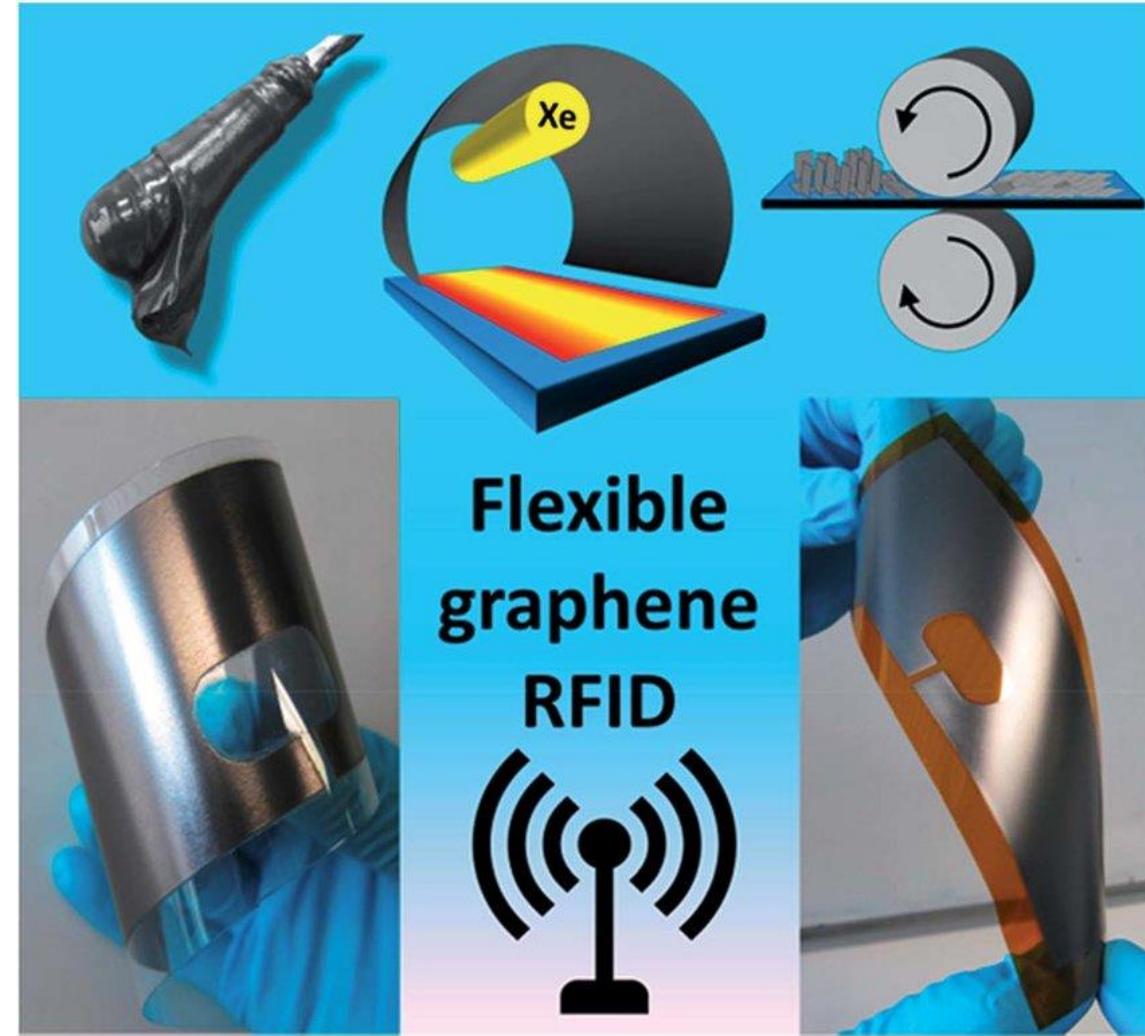
SEM images of Graphene

<https://doi.org/10.3390/ma13153271>



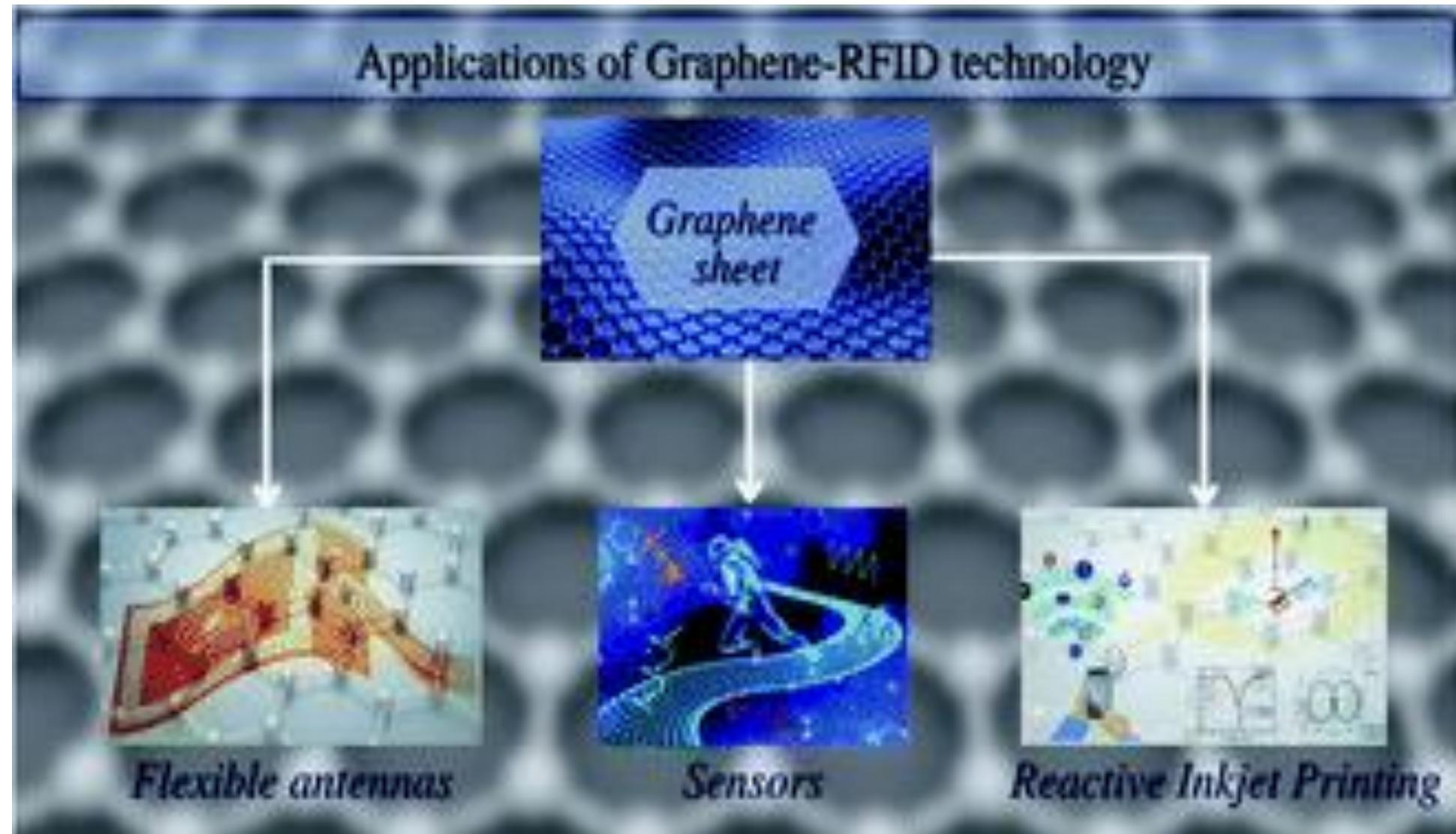
Applications of Graphene

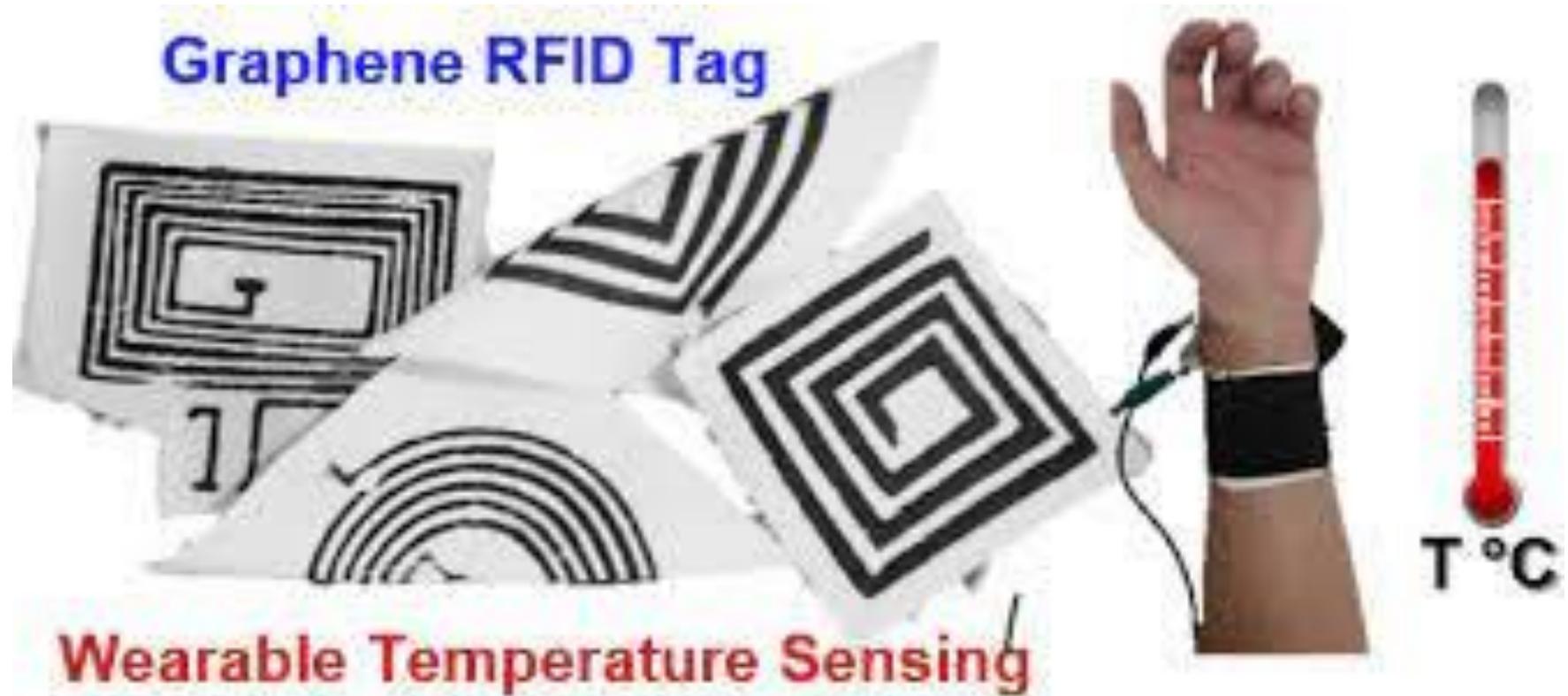
Go, change the world®



Applications of Graphene

Go, change the world®



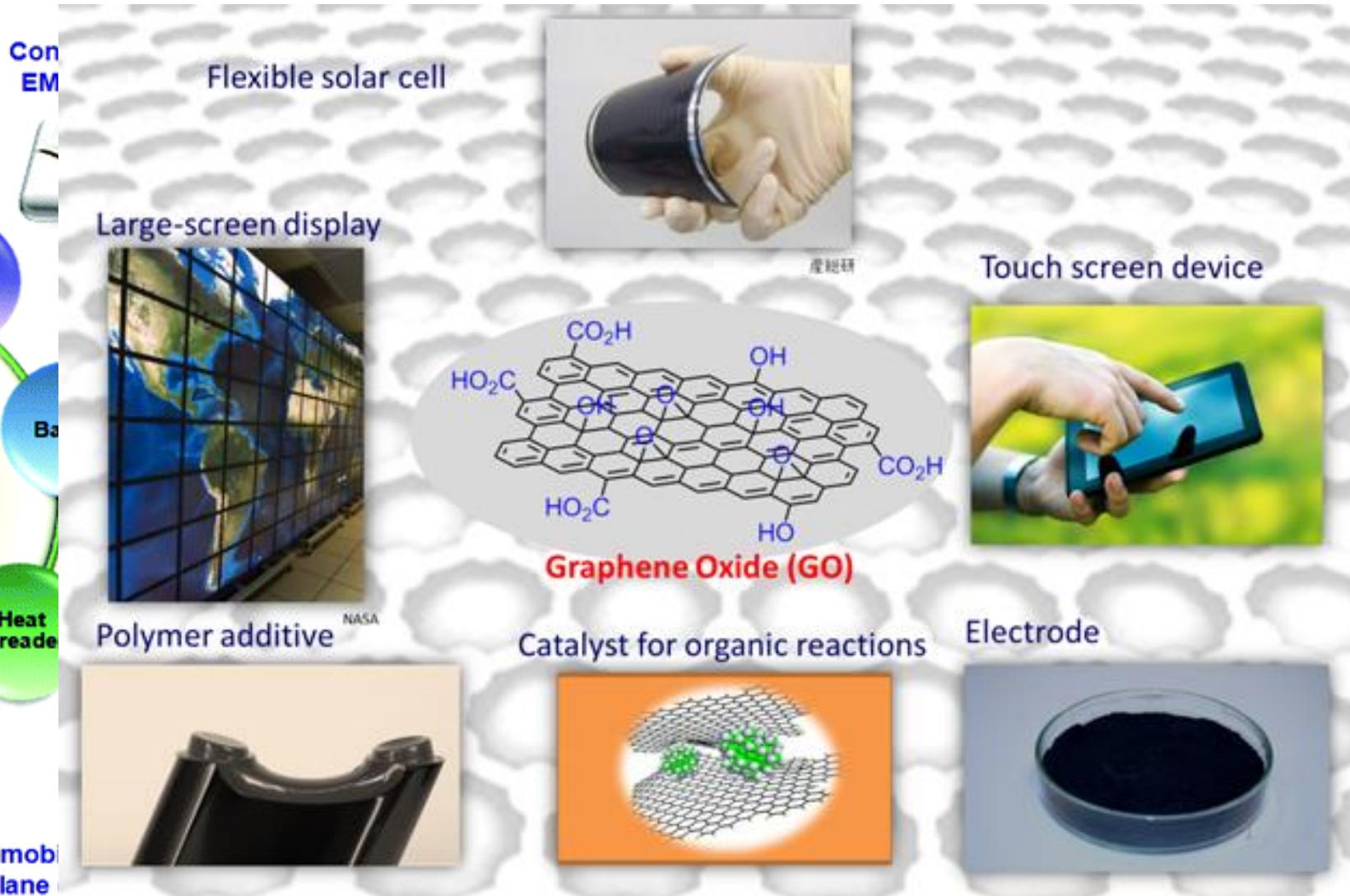
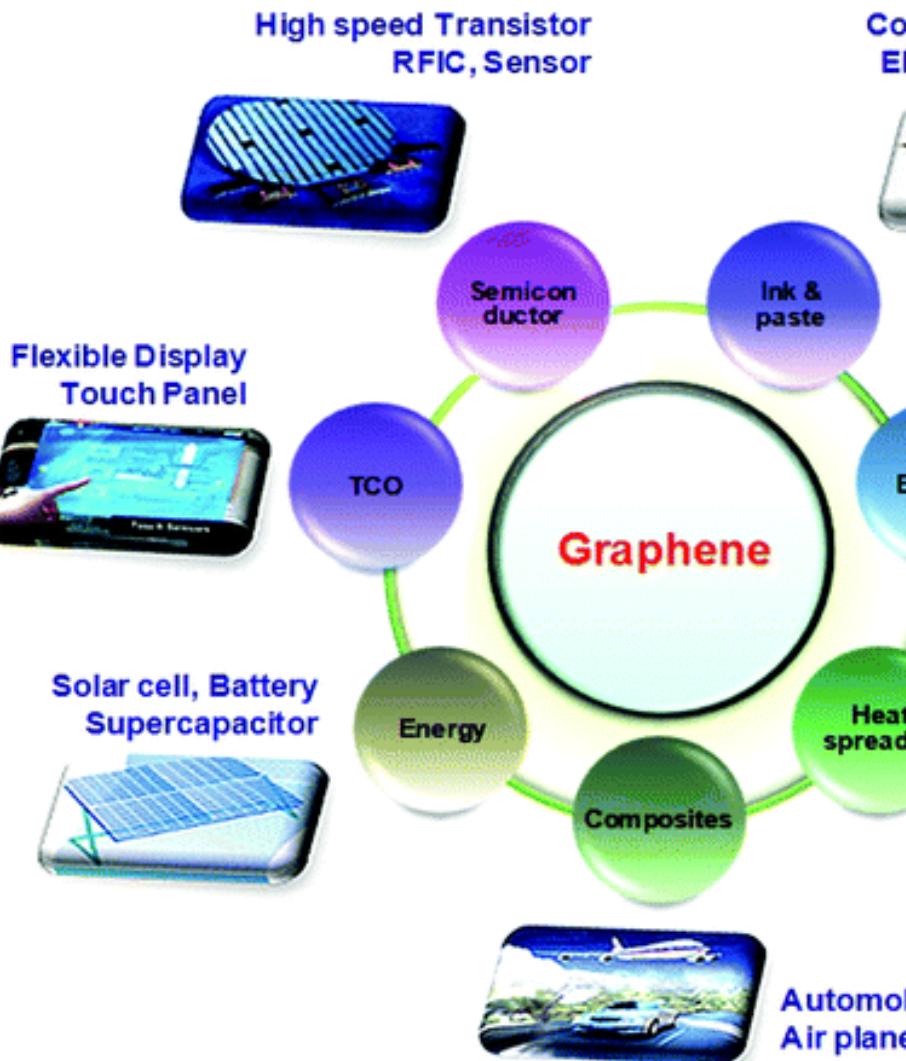


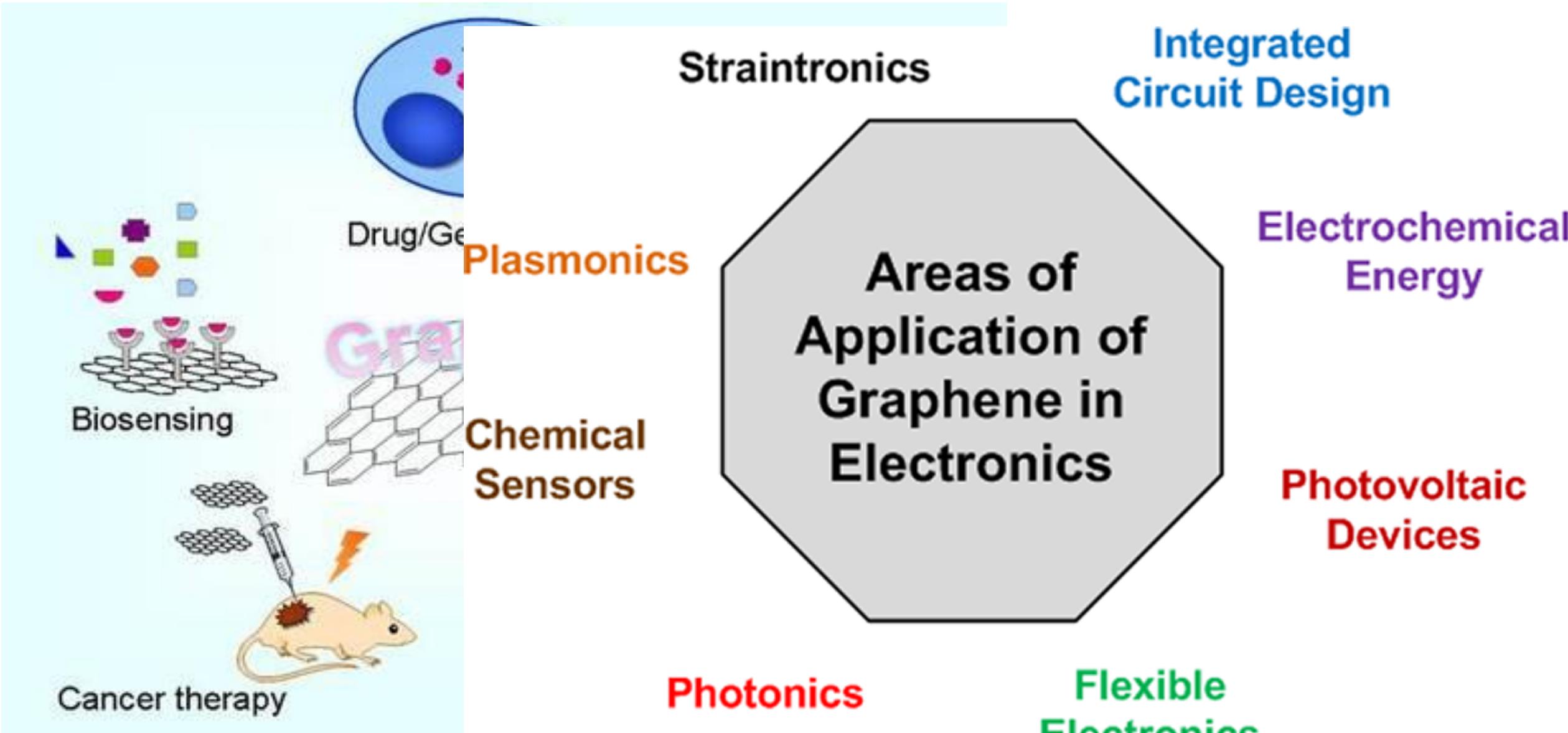
Applications of Graphene

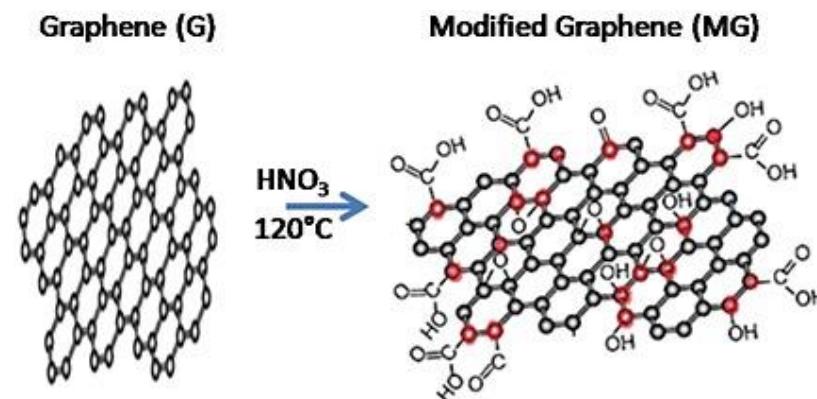
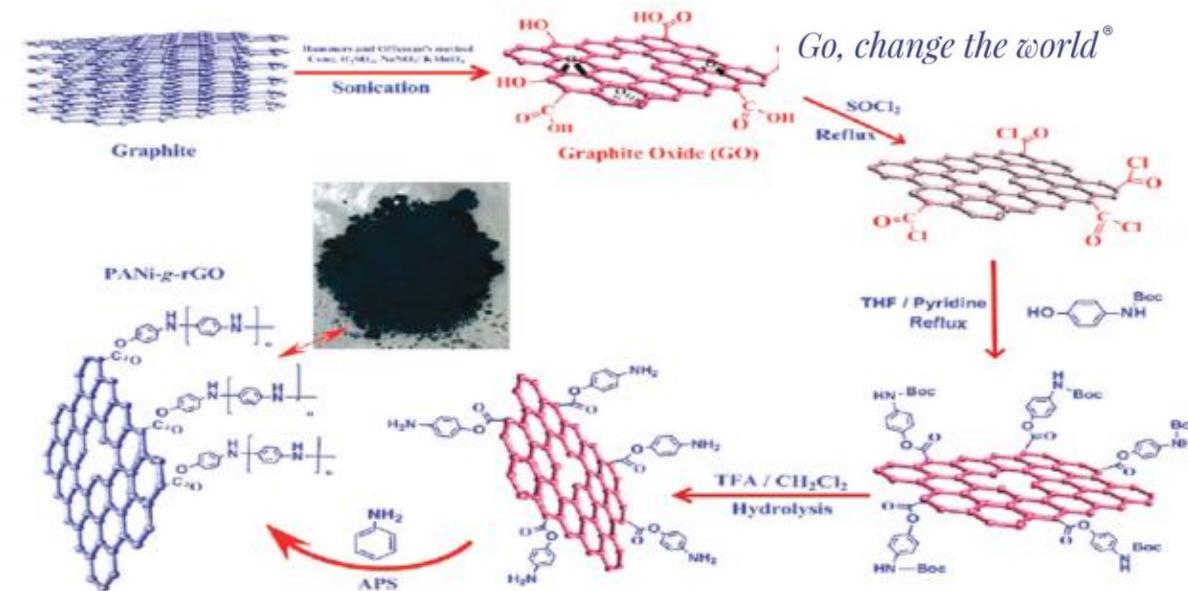
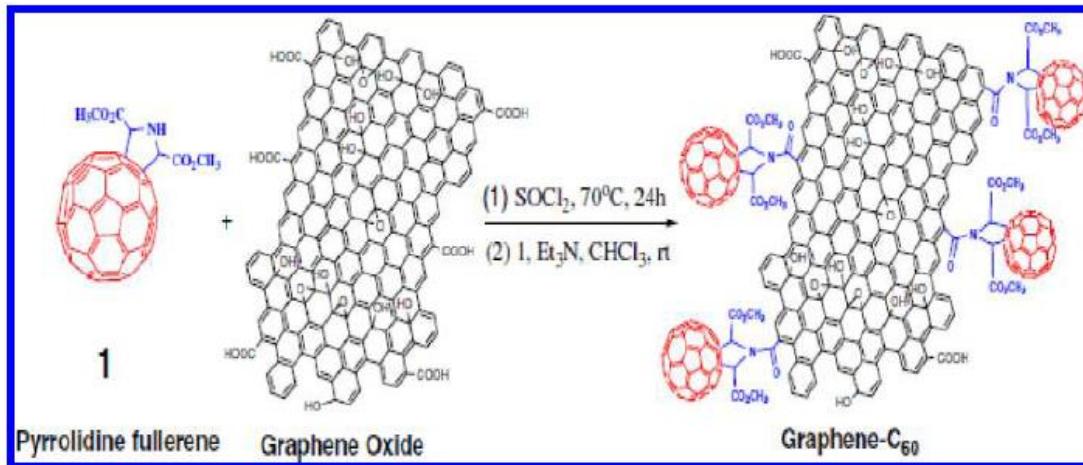


<https://doi.org/10.1021/acsnano.9b00319>

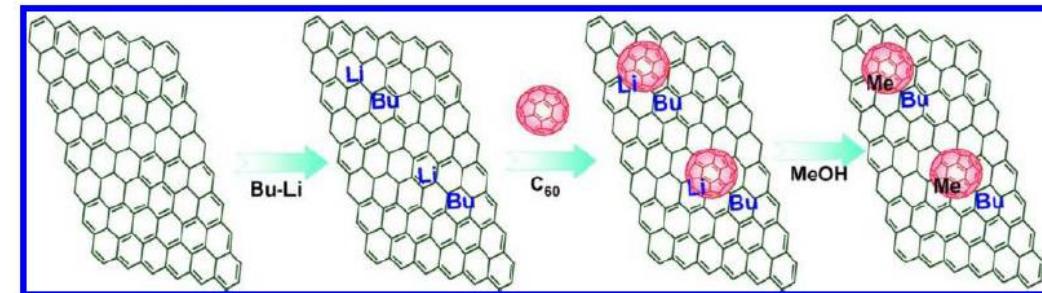
Applications of Graphene



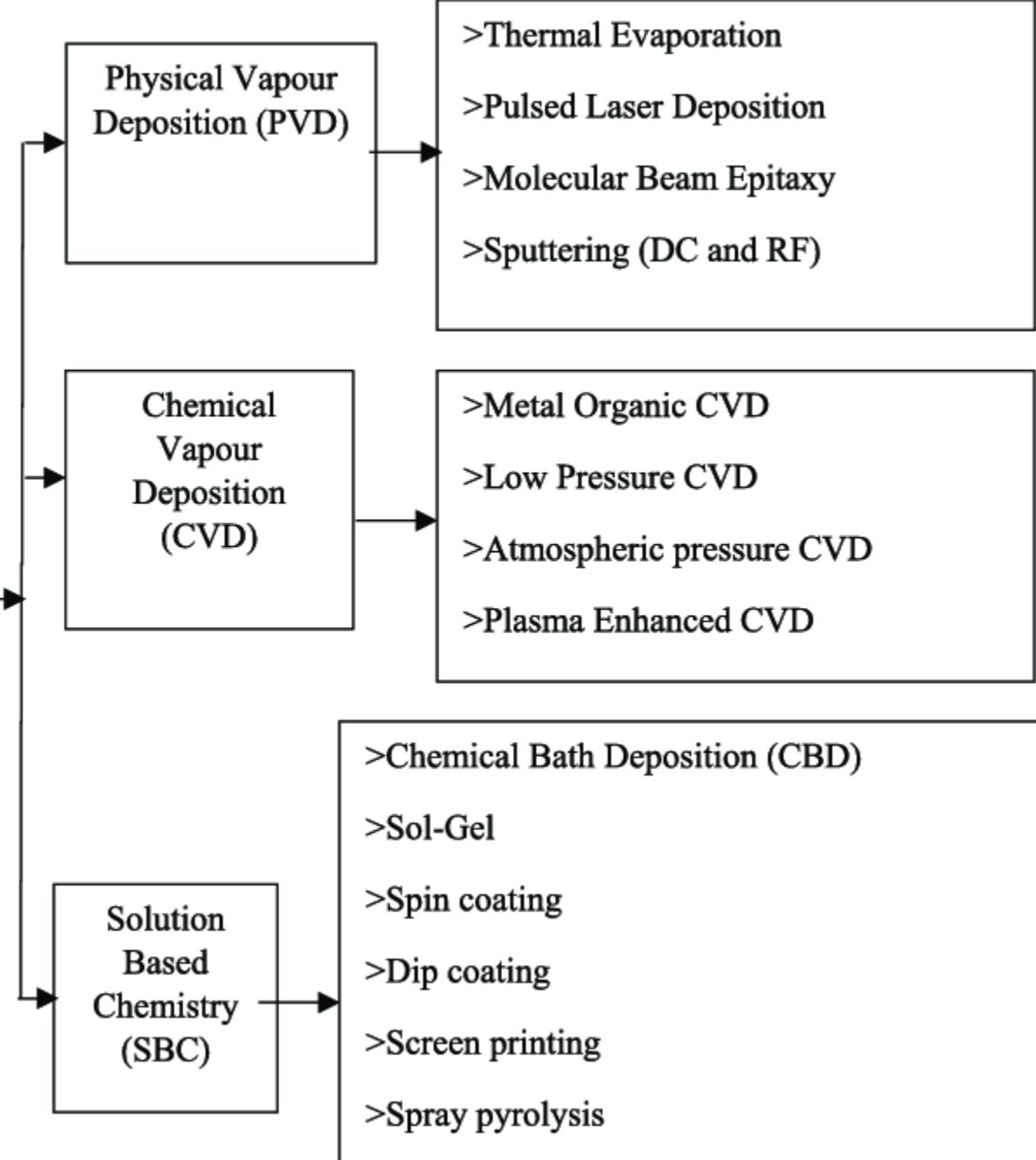




SCHEME 4. Synthetic Route for Grafting C₆₀ onto Graphene through Lithiation Reaction with n-Butyllithium. Adapted from reference 24 with permission. Copyright 2011, American Chemical Society.

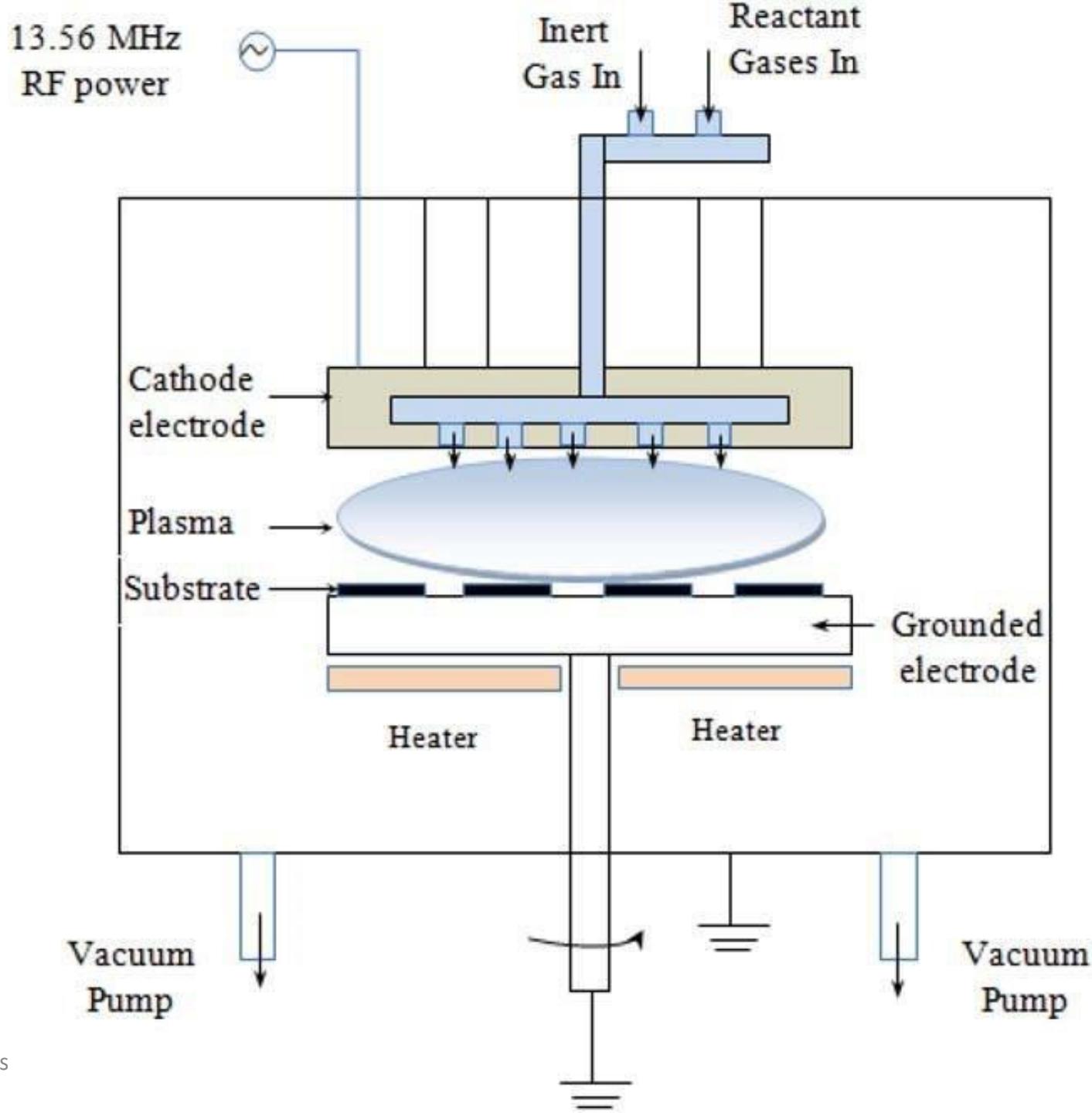


Thin film Deposition techniques



Plasma-enhanced chemical vapor deposition (PECVD)

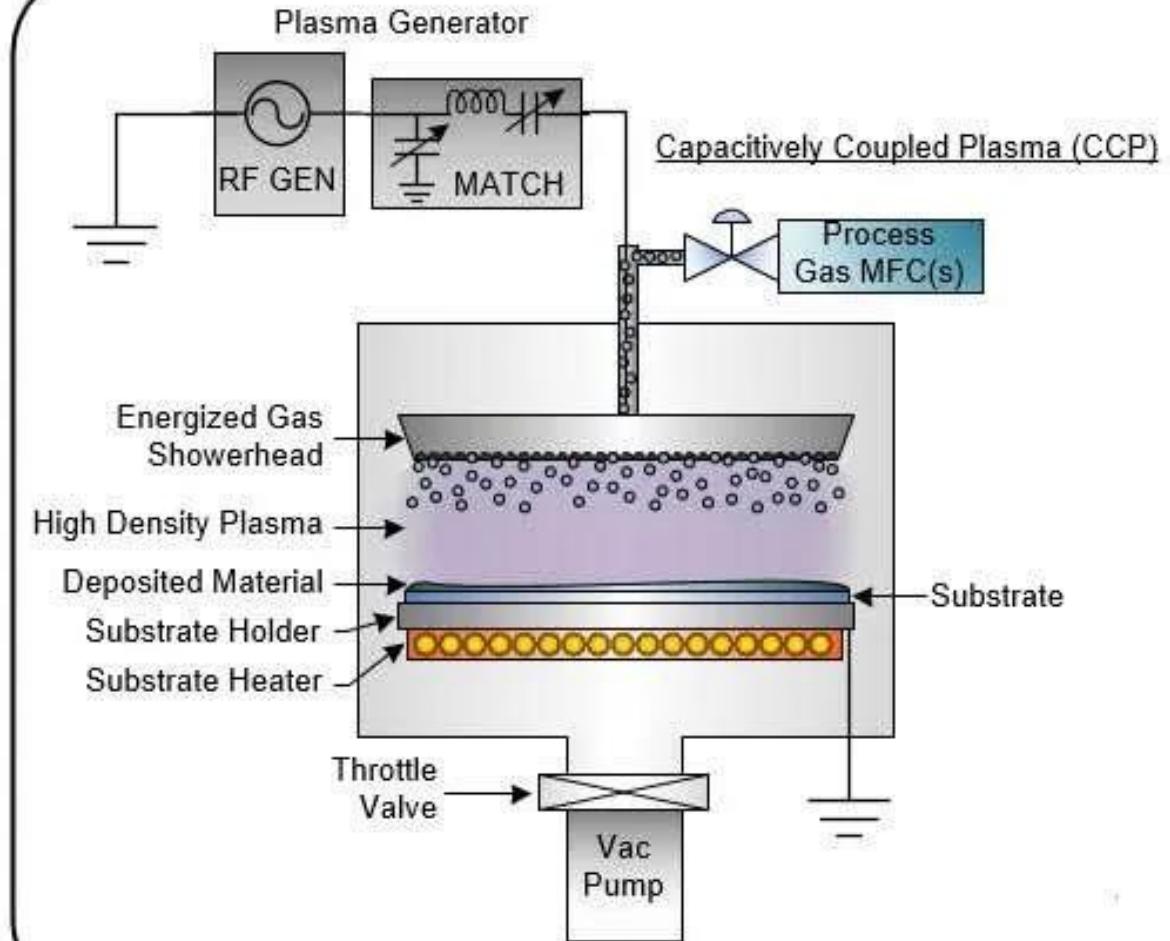
It is a chemical vapor deposition process used to deposit thin films from a gas state (vapor) to a solid state on a substrate. Chemical reactions are involved in the process, which occur after creation of a plasma of the reacting gases. It is a low temperature vacuum thin film deposition process used to apply coatings on surfaces that would not be able to withstand the temperatures of more conventional CVD processes.



How does Plasma Enhanced Chemical Vapor Deposition Work?

- For typical semiconductor applications, the substrate is placed in the deposition chamber between two parallel electrodes — a grounded electrode and usually an RF-energized electrode. The substrate is heated in the range of 250°- 350°C.
- Precursor gases such as silane (SiH_4) and ammonia (NH_3) (if Si_3N_4 thinfilms to be made) are typically mixed with inert gases such as argon (Ar) or nitrogen (N_2) to control processes. These gases are introduced into the chamber via a shower head fixture over the substrate that helps to spread the gas more evenly onto the substrate.
- The plasma is ignited by electrical discharge (100 – 300 eV) between the electrodes, creating a glowing sheath around the substrate that contributes to thermal energy driving the chemical reactions.
- These reactions first occur in the plasma as a result of precursor gas molecules colliding with highly energized electrons which then, via gas flow, travel to the substrate where they react and are absorbed on the substrate surface to grow films. The chemical bi-products are then desorbed and pumped away, completing the deposition process.
- Higher gas flow rates can yield higher deposition rates, which along with operating temperatures, control properties such as thickness, hardness or refractive index.

Diagram of Direct PECVD Process Reactor



What are the Advantages of PECVD?

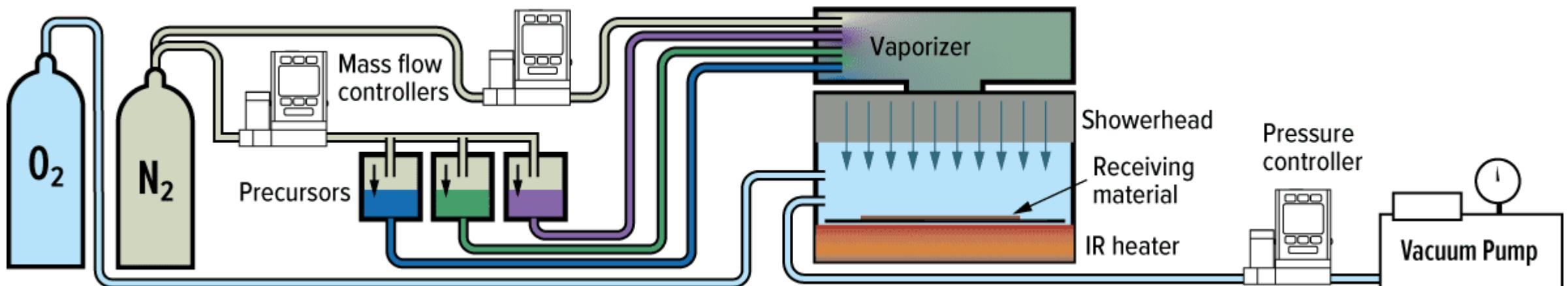
The primary advantages of PECVD over conventional CVD are

- lower deposition temperatures,
- good conformity and step coverage on uneven surfaces,
- tighter control of the thin film process and high deposition rates.

While standard CVD temperatures are usually conducted in 600°C to 800°C, PECVD temperatures range from room temperature to 350°C, which enables successful applications in situations where the higher CVD temperatures could potentially damage the device or substrate being coated. By operating at a lower temperature, it creates less stress between thin film layers that have different thermal expansion/contraction coefficients.

Metal organic chemical vapor deposition (MOCVD)

It is a process used for creating high purity crystalline compound semiconducting thin films and micro/nano structures. Precision fine tuning, abrupt interfaces, epitaxial deposition [growth of a thin crystal of any solid consisting of atoms or molecules that are arranged in a regular structure on top of another crystal], and a high level of dopant control can be readily achieved. It is widely adopted in R&D and industry for advanced optoelectronics, high power and high speed electronics applications.



Process: In general, to produce III-V semiconductor thin films, the respective chemicals are vaporized and transported into the reactor together with other gases. Therefore, the critical chemical reaction takes place that turns the chemicals into the desired crystal (the compound semiconductor) in the form thin films on the substrate.

- In MOCVD ultrapure precursor gases are injected into a reactor, usually with a non-reactive carrier gas (N_2). In III–V semiconductors, the metallic element is carried by an organic gas such as trimethylgallium ($Ga(CH_3)_3$) and trimethylindium ($In(CH_3)_3$) along with arsine (AsH_3) or phosphine (PH_3). The process temperature and pressures are typically in the range of 300 to 900°C and 10–100 torr, resulting in relatively fast growth rates.
- As the precursors approach the semiconductor wafer placed on heater, they undergo pyrolysis and the subspecies absorb onto the semiconductor wafer surface. Surface reaction of the precursor subspecies results in the incorporation of elements into a new epitaxial layer of the semiconductor crystal lattice.
- In this technique, reactant gases are combined at elevated temperatures in the reactor to cause a chemical interaction, resulting in the deposition of materials on the substrate.

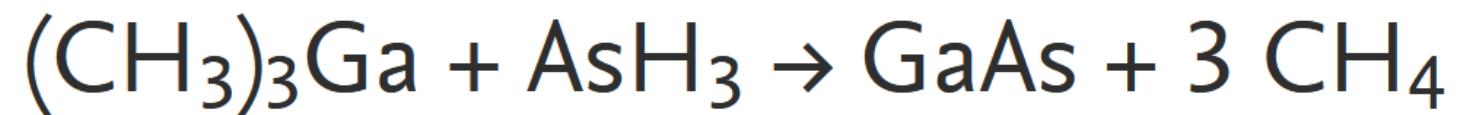
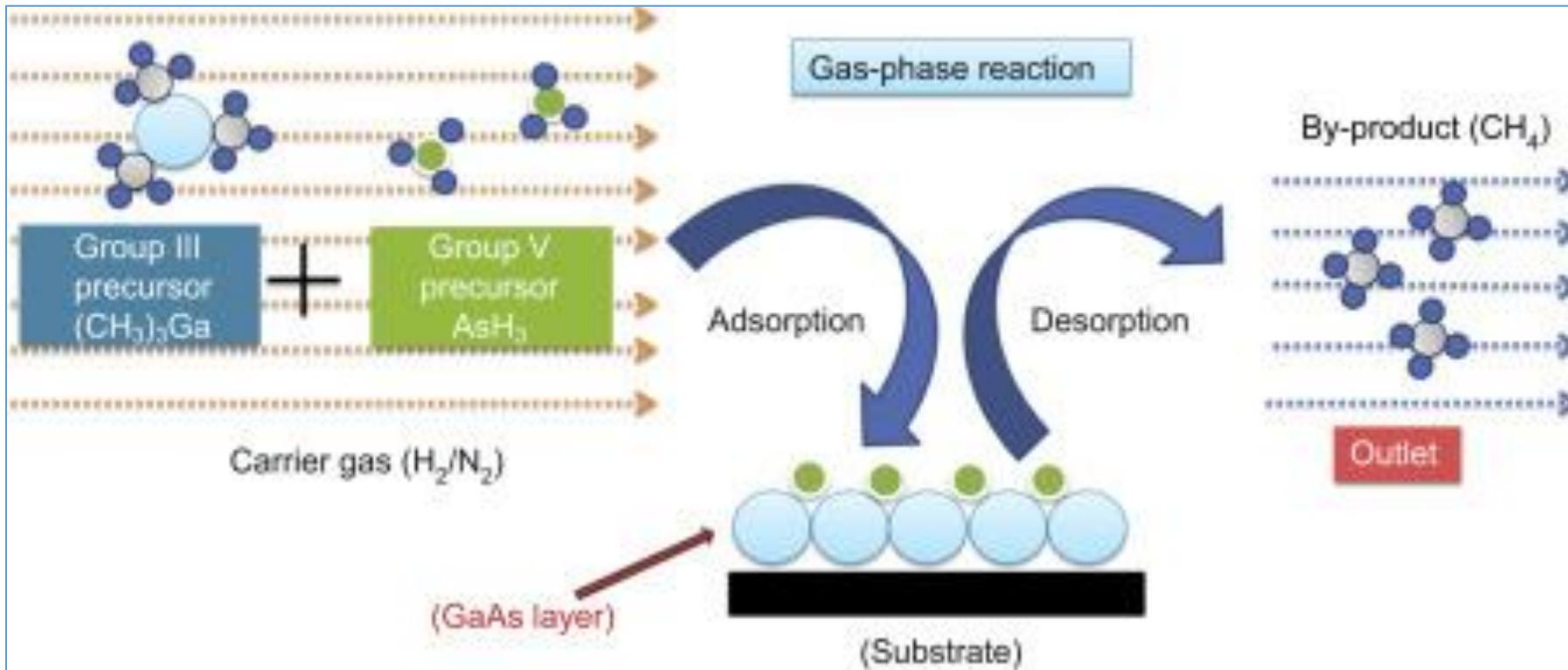
A reactor is a chamber made of a material that does not react with the chemicals being used. It must also withstand high temperatures. This chamber is composed by reactor walls, liner, a susceptor, gas injection units, and temperature control units. Usually, the reactor walls are made from stainless steel or quartz. Ceramic or special glasses, such as quartz, are often used as the liner in the reactor chamber between the reactor wall and the susceptor. To prevent overheating, cooling water must be flowing through the channels within the reactor walls.

A substrate sits on a susceptor which is at a controlled temperature. The susceptor is made from a material resistant to the metalorganic compounds used; graphite is sometimes used. For growing nitrides and related materials, a special coating, typically of silicon nitride, on the graphite susceptor is necessary to prevent corrosion by ammonia (NH_3) gas.

Conditions: High temperature results in higher growth rate and facilitates to eliminate the carbon residuals from the precursor. Controlled Pressure plays an important role on the domain size and morphology of the film. It is suggested that higher pressure facilitates the large single-crystal domain, while lower pressure drives coalescence few layer film.

One drawback of MOCVD is the toxic and explosive nature of the precursor gases, which makes them difficult to use in small research laboratories. Nevertheless, MOCVD is a scalable process amenable to volume manufacturing because many substrates can be simultaneously placed in the chamber. As a result, it is widely used in the manufacture of quantum well lasers, LEDs, and other components.

Formation reaction mechanism of GaAs thin fil by MOCVD



<https://www.sciencedirect.com/topics/materials-science/metal-organic-chemical-vapor-deposition>

Various Organometallic precursors used in MOCVD

Aluminium

Trimethylaluminium (TMA or TMAI), Liquid, Triethylaluminium (TEA or TEAI), Liquid

Gallium

Trimethylgallium (TMG or TMGa), Liquid, Triethylgallium (TEG or TEGa),Liquid

Indium

Trimethylindium (TMI or TMIn), Solid, Triethylindium (TEI or TEIn), Liquid

Di-isopropylmethylindium (DIPMeIn) , Liquid,Ethyldimethylindium (EDMIn) ,Liquid

Germanium

Isobutylgermane (IBGe) , Liquid, Dimethylamino germanium trichloride (DiMAGeC), Liquid

Tetramethylgermane (TMGe), Liquid, Tetraethylgermanium(TEGe), Liquid

Nitrogen

Phenyl hydrazine, Liquid
Dimethylhydrazine (DMHy), Liquid
Tertiarybutylamine (TBAm), Liquid
Ammonia NH₃, Gas

Phosphorus

Phosphine PH₃, Gas
Tertiarybutyl phosphine (TBP),
Liquid
Bisphosphinoethane (BPE), Liquid

Arsenic

Arsine AsH₃, Gas
Tertiarybutyl arsine (TBAs), Liquid
Monoethyl arsine (MEAs), Liquid
Trimethyl arsine (TMA₃), Liquid

Antimony

Trimethyl antimony (TMSb), Liquid
Triethyl antimony (TESb), Liquid
Tri-isopropyl antimony (TIPSb),

Cadmium

Dimethyl cadmium (DMCd), Liquid
Diethyl cadmium (DECd), Liquid
Methyl Allyl Cadmium (MACd), Liquid

Tellurium

Dimethyl telluride (DMTe), Liquid
Diethyl telluride (DETe), Liquid
Di-isopropyl telluride (DIPTe) , Liquid

Titanium

Alkoxides, such as Titanium
isopropoxide or Titanium ethoxide

Selenium

Dimethyl selenide (DMSe), Liquid
Diethyl selenide (DESe), Liquid
Di-isopropyl selenide (DIPSe), Liquid
Di-tert-butyl selenide (DTBSe), Liquid

Zinc

Dimethylzinc (DMZ), Liquid
Diethylzinc (DEZ), Liquid

Semiconductors grown by
MOCVD

III-V semiconductors

AlP, AlN, AlGaSb, AlGaAs,
AlGaN_xP, AlGaN, AlGaP

GaSb, GaAsP, GaAs, GaN, GaP

InAlAs, InAlP, InSb, InGaSb,
InGaN

GalnAlAs, GalnAlN, GalnAsN,
GalnAsP, GalnAs, GalnP

InN, InP, InAs, InAsSb

II-VI semiconductors

ZnSe, HgCdTe, ZnO, ZnS...