

# Synthesis of Nanomaterials

Nanotechnology: Principles and Practices

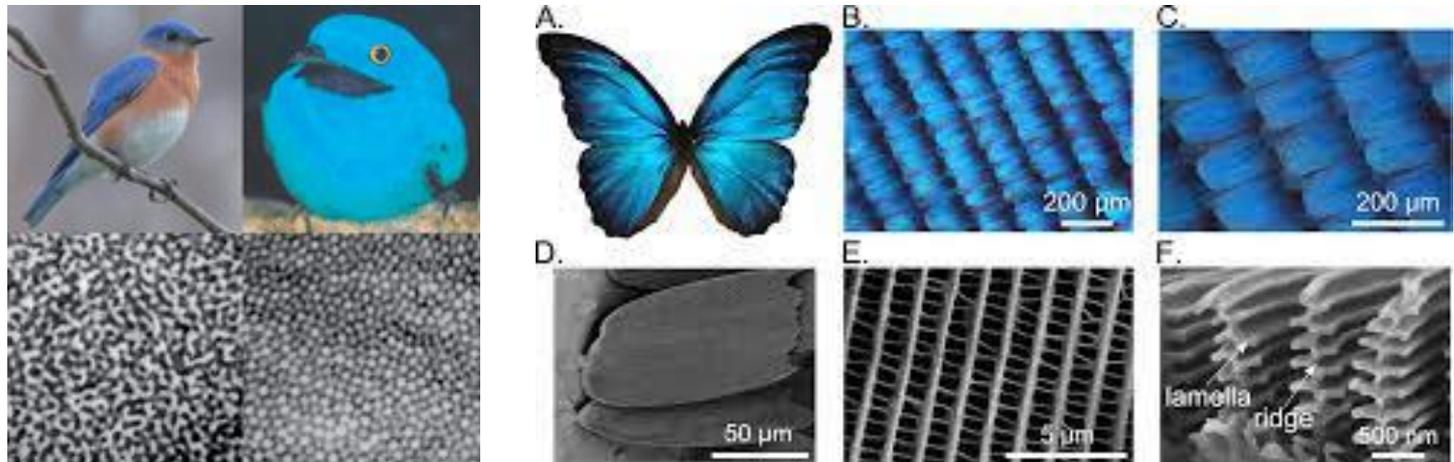
2022-2

# **5. Self Assembly & 6. Some special nanomaterials**

# 5. Self Assembly

## 5.1 Self Assembly

- Self assembly applies for spontaneously formed, reversible, locally ordered, thermodynamically stable assemblies
- Self assemblies are very sensitive and can transform back to the state of disorder.
- Self assembly initially, during the twentieth century, was considered to be limited to biological world where origin of beautiful colours of peacock feathers, butterfly wings and many birds or insects were understood as a result of ordered structures.



# 5. Self Assembly

## 5.1 Self Assembly

- Microscopy analysis reveals that often there are micro plus nano or just nanostructures involved.
- Phenomenon of self assembly occurs at many length scales and is not only limited to tiny objects but even gigantic astronomical objects like stars, planets, galaxies and entire universe which have been considered as a kind of self assembly
- Observations of self assembly in naturally occurring living and non-living world have led scientists to understand what leads to the ordered or random assemblies of some smaller entities, blocks, motifs or units.
- Self assemblies are formed spontaneously by weak interactions like  $\pi$ - $\pi$  , van der Waals, colloidal, electrical, optical, shear or capillary forces

# 5. Self Assembly

## 5.1 Self Assembly

- Recognition of importance of self assembly and its origin has led scientists to make deliberate attempts to fabricate self assembled organic, inorganic or materials useful to obtain novel, electrical, mechanical, magnetic or optical materials with unprecedented properties.
- Langmuir-Blodgett films, micelles, liquid crystals, layers obtained by dip-pen lithography, deposition of materials in the voids of the self assembled spheres, and anodization of alumina templates with ordered pores are some of the methods to realize self assembled structures with desired materials
- Such structures are useful to create photonic band gap materials, novel sensors, lasers, Bragg mirrors, electroluminescent devices, photovoltaic solar cells to name a few

# 5. Self Assembly

## 5.2 Mechanism of Self Assembly

- The self assembly involves weak to strong forces and nanoscopic to gigantic structures in one, two or three dimensions.
- The self assembly can be a result of very weak forces like van der Waals interaction, hydrogen bonds, static charges, magnetic interactions and so on.
- The driving force behind the self assembly has been recognized as due to attempt of any system to go to the lowest energy state
- Ability of a system to go to a well ordered low energy state depends upon the availability of units of same size and shape.
  - ➔ Molecules with definite shape, number of atoms and therefore size, already in the state of low energy are good candidates for the self assembly.

# 5. Self Assembly

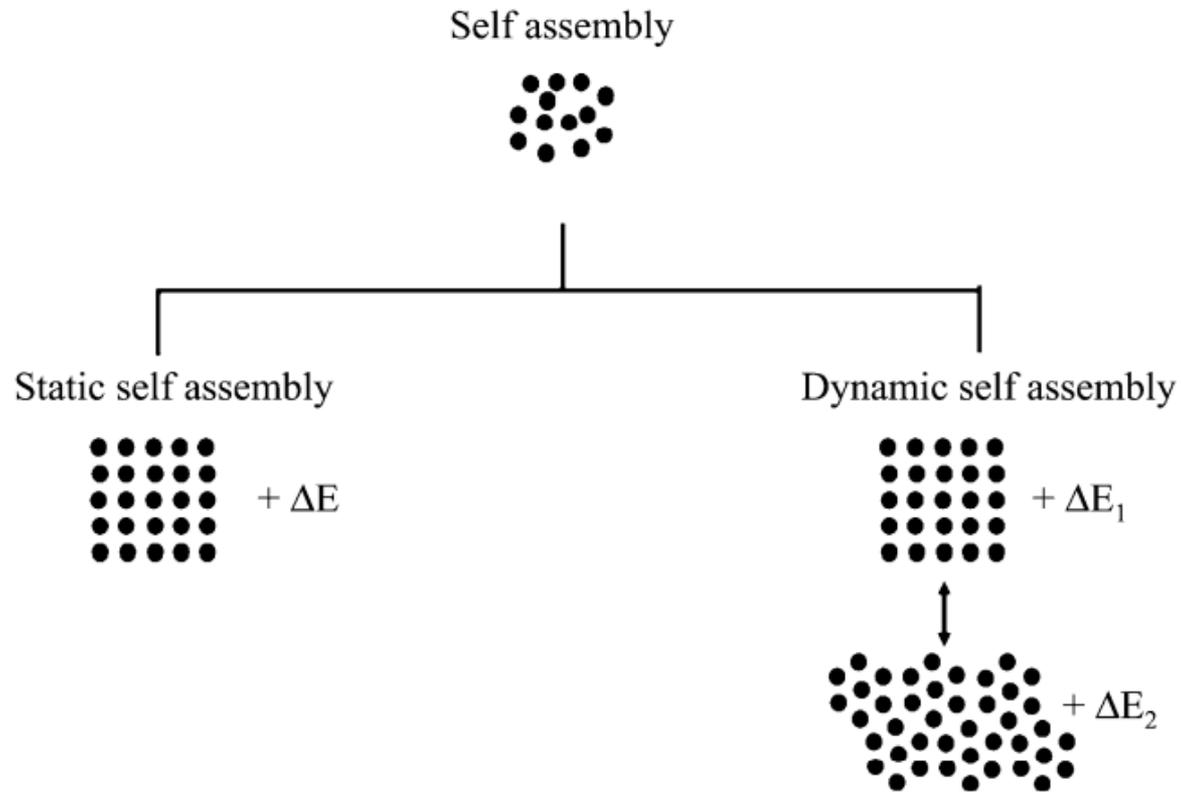
## 5.2 Mechanism of Self Assembly

- When the building blocks (one, two or more types of building blocks also can form self assemblies) are available for self assembly, state of minimum energy may be attained spontaneously in the absence of any external force
- Self assembly may occur in the presence of an external driving force like **temperature, pressure, magnetic field** and so on.
- These two types viz. assembly in the absence and presence of an external driving force are known as *static* and *dynamic* assemblies
  - ➔ **Static assembly** is realized when system achieves minimum energy state and can stay there unless it is subjected to strong external forces. Formation of ordered crystalline structure from a melt can be considered as an example of static self assembly
  - ➔ **Dynamic self assembly** involves constant influence of external force from the ambient. If the energy intake from the ambient stops, the self assembly can leave the state of organized structure and de-assemble

# 5. Self Assembly

## 5.2 Mechanism of Self Assembly

- *static* and *dynamic* assemblies

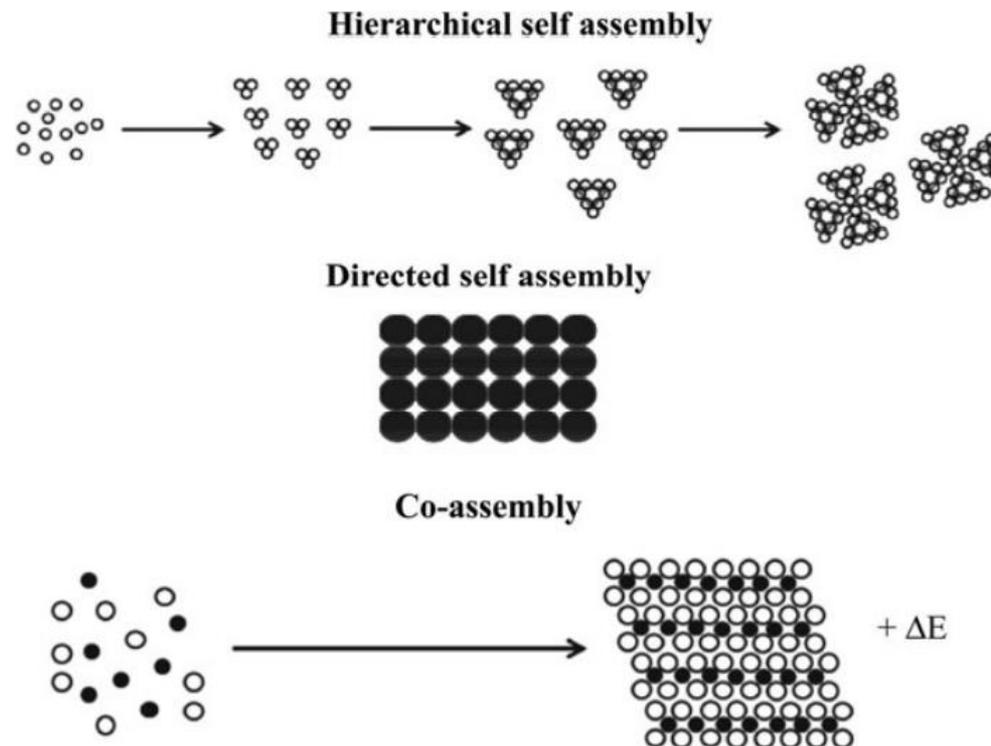


**Fig. 5.1** Two types of self assemblies

# 5. Self Assembly

## 5.2 Mechanism of Self Assembly

- The static and dynamic assemblies can be further divided into ‘**hierarchical self assembly**’, ‘**directed self assembly**’ and ‘**co-assembly**’



**Fig. 5.2** Hierarchical, Direct and co-assembly

# 5. Self Assembly

## 5.2 Mechanism of Self Assembly

- Hierarchical self assembly is characterized by small range, medium range and long range interactions of one type of a building block.
- Directed self assembly occurs when the building blocks occupy the pre-designed places like some portions of a lithographically patterned substrate, pores in membranes or spaces between ordered particles.
- Co-assembly, as the name suggests, can be formed with two or more types of blocks which can fit into each other

# 5. Self Assembly

## 5.3 Some Examples of Self Assembly

### 5.3.1 Self Assembly of Nanoparticles Using Organic Molecules

- Preformed inorganic nanoparticles can be assembled on solid substrates through some organic molecules adsorbed on their surfaces.

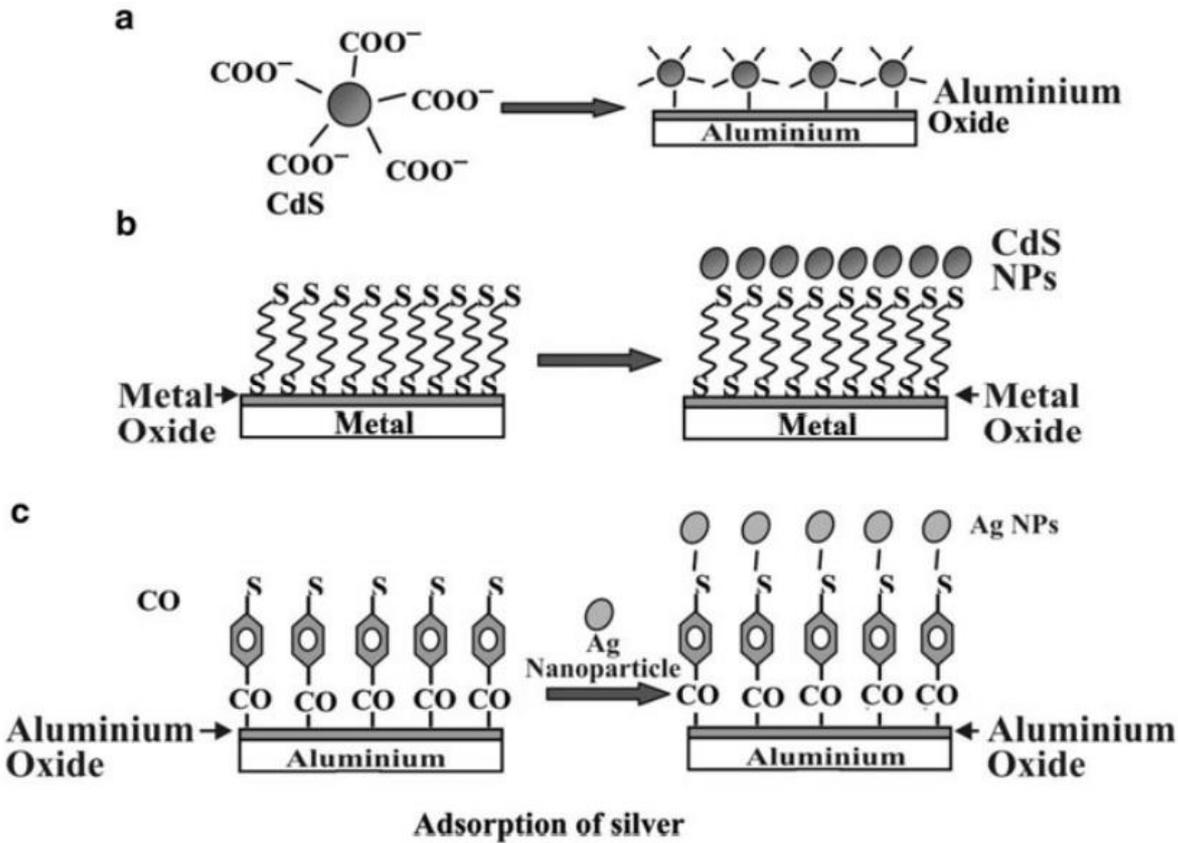


Fig. 5.3 Self assembly of nanoparticles

# 5. Self Assembly

## 5.3 Some Examples of Self Assembly

### 5.3.1 Self Assembly of Nanoparticles Using Organic Molecules

- CdS nanoparticles functionalized with carboxylic ( $-\text{COO}^-$ ) group can be transferred to aluminium thin films
  - Dithiols adsorbed on metal surfaces also could adsorb CdS nanoparticles
  - Silver particles have been adsorbed on oxidized aluminum layers using bi-functional molecule such as 4-aluminium layers carboxyl thiophenol. Molecules bind to aluminum oxide layer through carboxylic group and thiol attaches to silver particles
  - Using a two-phase reaction alkanethiol or alkylamine capped gold, silver, palladium etc. nanoparticles have been self assembled
- ➔ Here chemical reaction takes place in an aqueous medium. The particles are then transferred into an organic solvent and drop casted on an appropriate solid substrate. Solvent is allowed to evaporate which leaves self assembled layer.

# 5. Self Assembly

## 5.3 Some Examples of Self Assembly

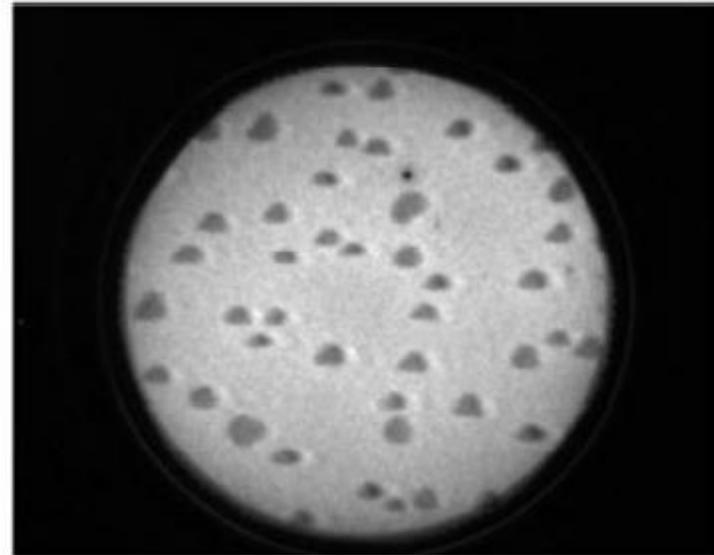
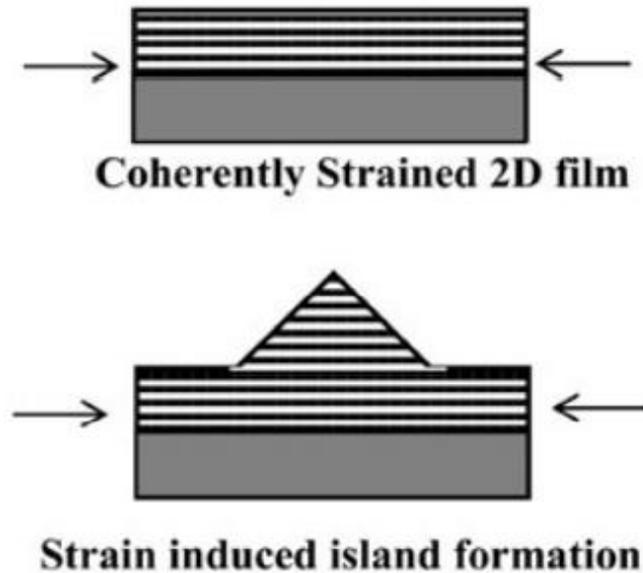
### 5.3.2 Self Assembly in Inorganic Materials

- It is possible to spontaneously create the quantum dots for example of germanium (Ge) on silicon (Si) or indium arsenide (InAs) on gallium arsenide (GaAs).
  - ➡ The origin of self assembly is strain induced
- Germanium and silicon have only 4 % lattice mismatch. Therefore Ge can be deposited epitaxially on Si single crystal upto 3–4 monolayers. Although grown (hetero)epitaxially, the layers of deposited Ge are highly strained (coherently i.e. without any defects or dislocations). When further deposition takes place, the lattice strain caused by depositing Ge on Si with different lattice constants cannot be accommodated.
- This results in spontaneous formation of nanosized islands or quantum dot

# 5. Self Assembly

## 5.3 Some Examples of Self Assembly

### 5.3.2 Self Assembly in Inorganic Materials



**Fig. 5.6** Growth mechanism of Ge on Si and photograph showing island formation (Field of view 10  $\mu\text{m}$ )

# 5. Self Assembly

## 5.3 Some Examples of Self Assembly

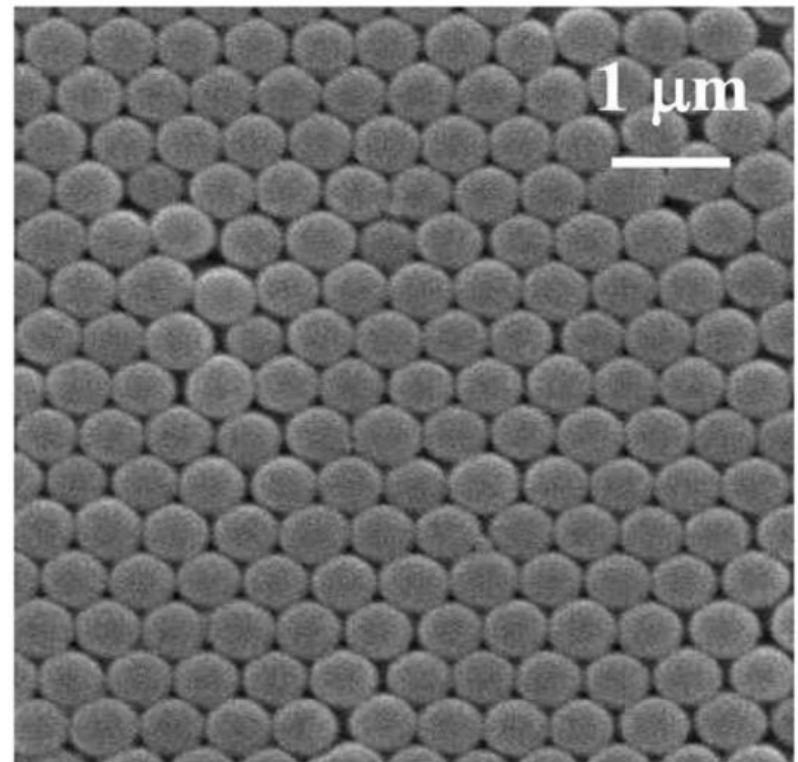
### 5.3.2 Self Assembly in Inorganic Materials

- Preformed inorganic particles of materials like silica ( $\text{SiO}_2$ ), titania ( $\text{TiO}_2$ ), polymer beads or latexes are able to organize themselves just by sedimentation also.

➡ They need to have very uniform size

- The particles synthesized in aqueous medium are simply allowed to evaporate from the solution drop placed on a glass substrate. After some time the particles self assemble due to **weak van der Waals interaction amongst the particles.**

**Fig. 5.7** SEM image of self assembled silica ( $\text{SiO}_2$  particles) on glass slid



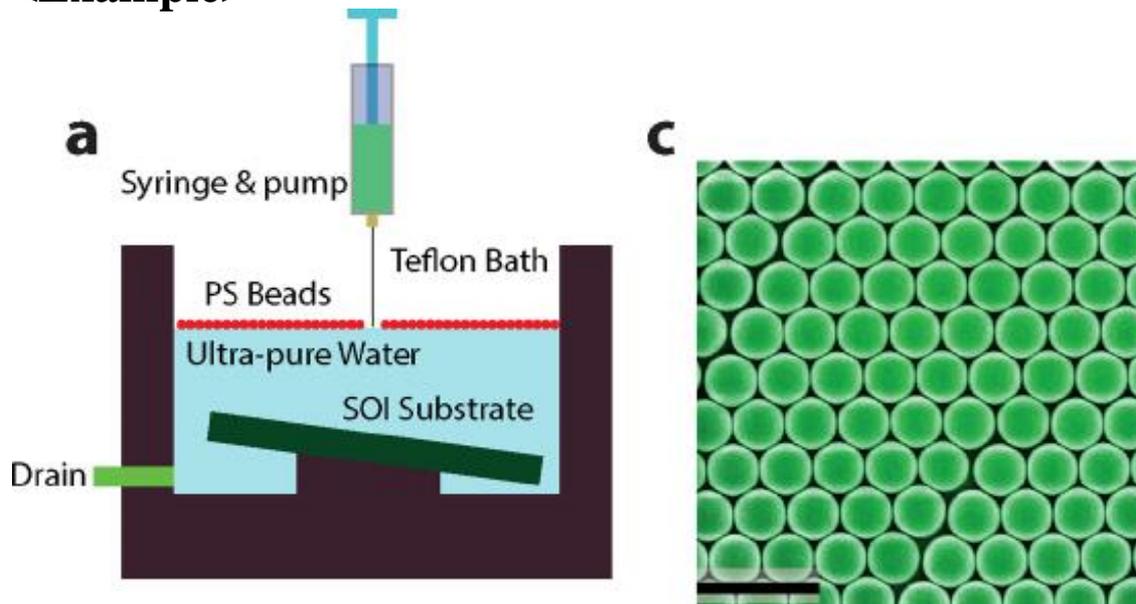
# 5. Self Assembly

## 5.3 Some Examples of Self Assembly

### 5.3.2 Self Assembly in Inorganic Materials

- The driving force is the capillary force. Minimization of surface energy takes place by forming a hexagonal network. The uniform size of the particles is helpful to make an ordered two dimensional network of particles.

<Example>



(a) Schematic of the self-assembly based nanosphere lithography technique. PS particles are first assembled in a monolayer at an air – water interface. The monolayer is then transferred to the SOI substrate by slowly draining the water from the bottom of the Teflon bath.

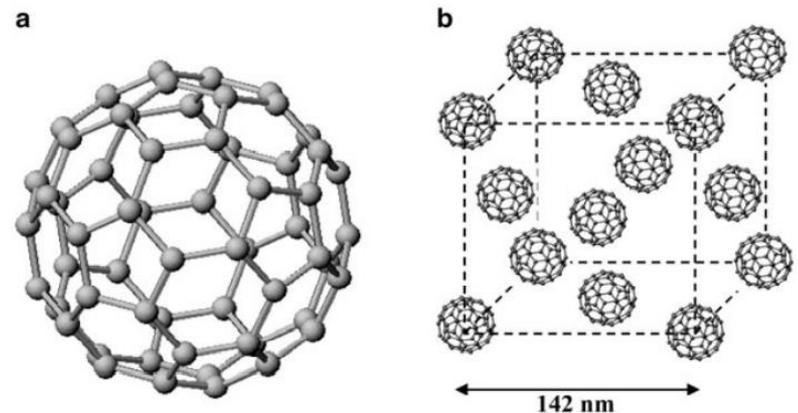
(c) hexagonal close-packed polystyrene spheres (green, false color) of diameter 820 nm

# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.1 Fullerenes

- Crystalline carbon can exist in diamond, graphite, fullerene, carbon nanotubes and graphene forms.
- Fullerene was discovered around 1985. Fullerene crystal is a molecular crystal having Face Centered Cubic (FCC) structure.
- All the carbon atoms are located on the surface of a nearly spherical figure. Fullerenes can have 60, 70, 78 or more (specific or magic) number of carbon atoms on the surface, out of which 60-atom molecule (or cluster) is the most stable and spherical in shape.



**Fig. 6.1** (a) Fullerene C<sub>60</sub> and (b) Crystalline form of C<sub>60</sub>

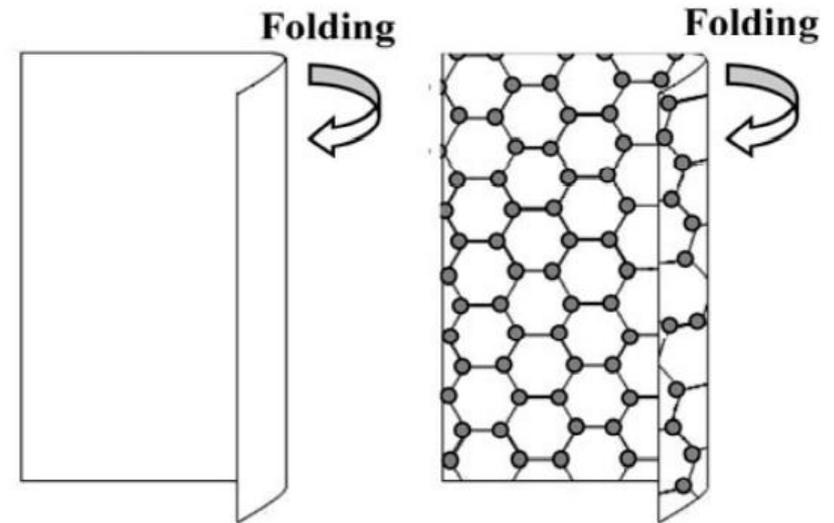
# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.2 Carbon Nanotubes (CNTs)

- Carbon nanotubes can be considered as cylinders made of graphite sheets, mostly closed at the ends, with carbon atoms on the apexes of the hexagons, just like on a graphite sheet.

- One can consider carbon nanotube as folding of a graphite sheet (it is only an imaginary sheet, actual growth can be different), just like one rolls a piece of paper into a cylindrical form



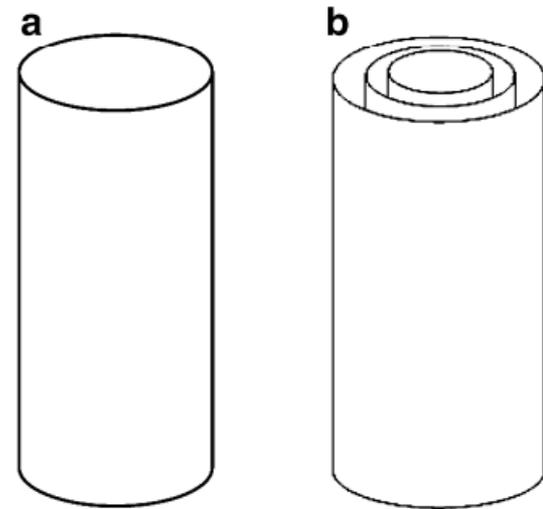
**Fig. 6.2** Rolling the carbon sheet to obtain carbon nanotube

# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.2 Carbon Nanotubes (CNTs)

- It is also possible that many concentric cylinders may be formed as a nanotube. Such concentric nanotubes are termed as Multi Wall Carbon Nanotubes (MWCNT). The distance between their walls is 0.334 nm.
- This is similar to what one gets between two graphite layers in a single crystal. MWCNT are most common and easily formed
- Under certain conditions, it is possible to obtain even Single Wall Carbon Nanotubes (SWCNT)



**Fig. 6.3** (a) SW and (b) MW tubes

# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.2 Carbon Nanotubes (CNTs)

- MWCNTs can be turned into SWCNTs using some etching methods. SWCNTs have diameters ranging from 1 to 2 nm. MWCNTs have outer diameters ranging from 2 to 25 nm. The concentrically formed MWCNTs are, however, rotationally disordered (turbotactic).
  - ➔ Both MWCNTs (conductor) and SWCNTs (semiconductor) have their own range of applications and studied rigorously.
- Three types of carbon nanotubes (we will consider here only the SWCNT for the sake of simplicity) are possible viz. **armchair**, **zigzag** and **helical**, under appropriate conditions of growth.

# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.2 Carbon Nanotubes (CNTs)

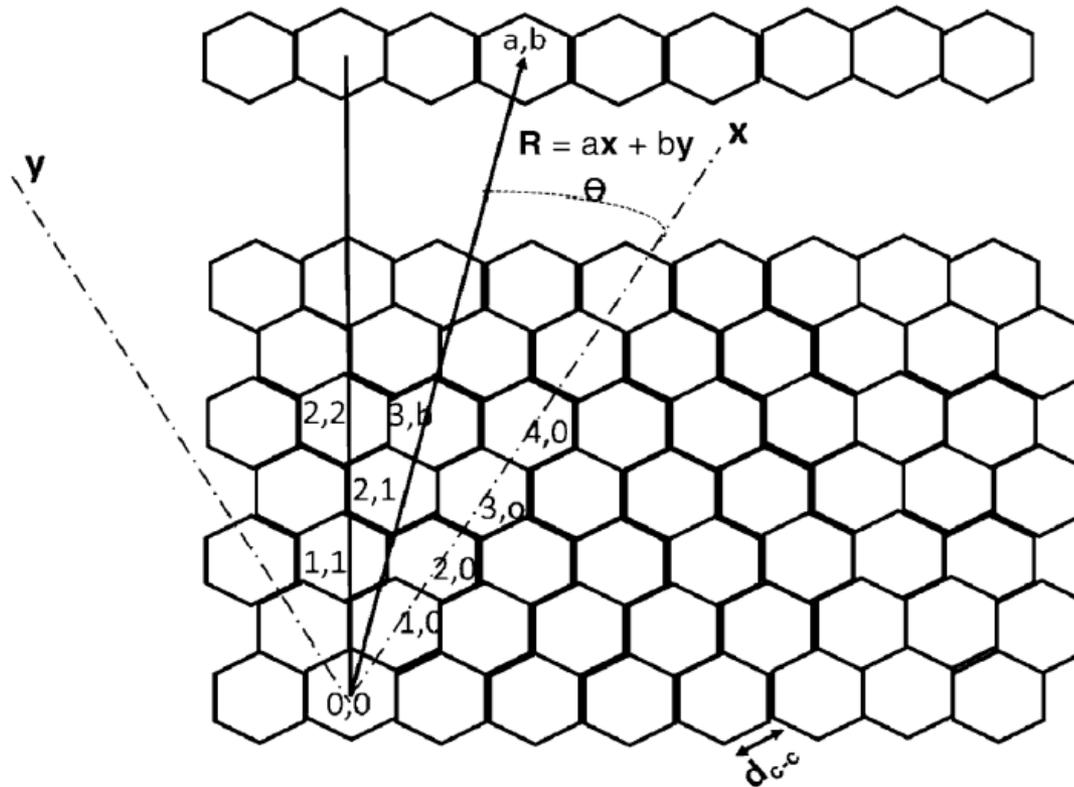


Fig. 6.4 (a) SW and (b) MW tubes

# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.2 Carbon Nanotubes (CNTs)

- **Zigzag CNT:** These are formed for  $\Theta = 0$  and chirality  $(a, 0)$ . i.e. by folding parallel to x-axis. The name zigzag has been given due to zig zag arrangement of carbon atoms

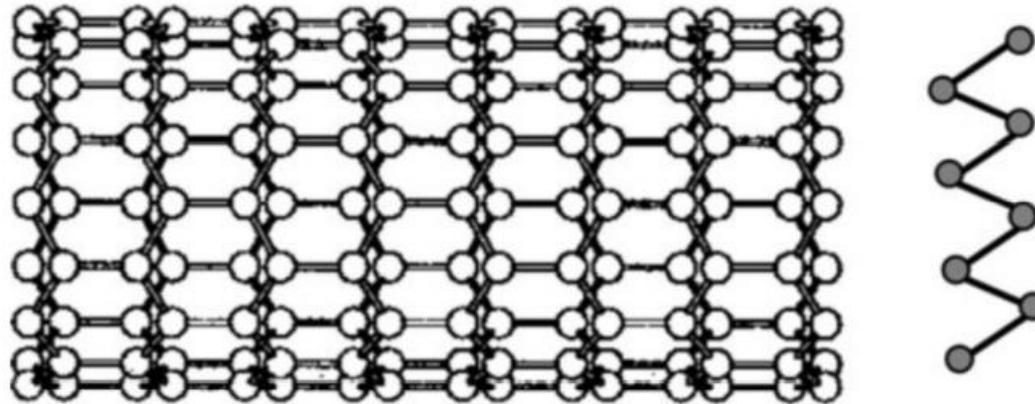


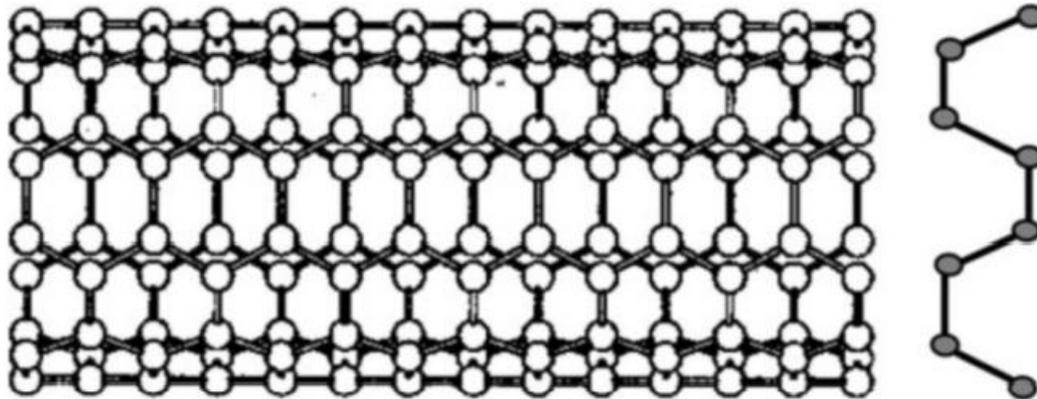
Fig. 6.5 Zigzag CNT

# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.2 Carbon Nanotubes (CNTs)

- **Armchair CNT:** These are formed for the angle  $\Theta = \pi / 6$  and chirality  $(a, a)$ . These also are 'achiral in nature'



**Fig. 6.5** Armchair CNT

# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.2 Carbon Nanotubes (CNTs)

- **Helical CNT:** These are obtained when angle  $\theta$  is anywhere between 0 and  $\pi/6$  and chirality is (a, b).

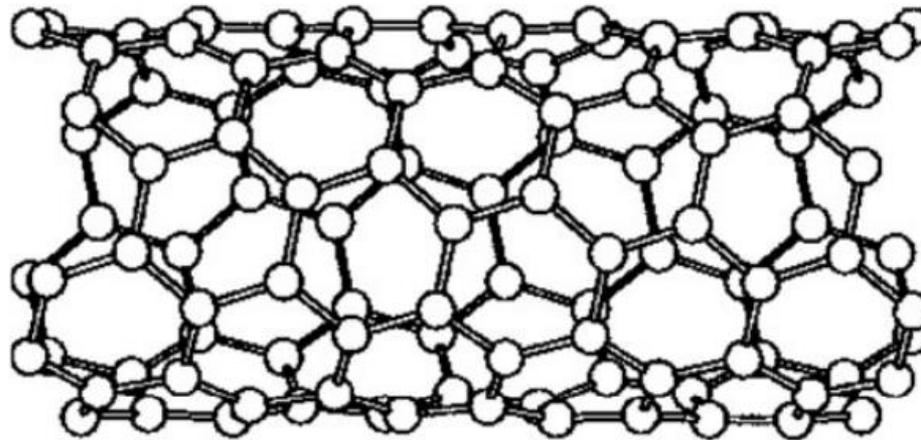


Fig. 6.6 Helical CNT

Table 11.1 Comparison between different types of CNTs

Type of CNT	R	$\theta^\circ$	Cross section
Zigzag (achiral)	a, 0	0	Trans
Armchair (achiral)	a, a	30	Cis
Helical (chiral)	a, b	$0 < \theta < 30$	Mixture of trans and cis

# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

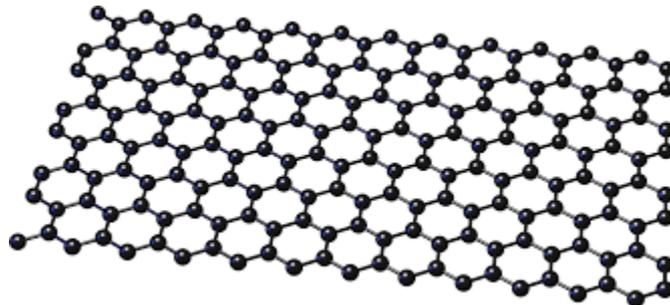
### 6.1.3 Graphene

- **Graphene** is just a single layer of graphite crystal.

simply peeling them off using a scotch tape

chemical vapour deposition

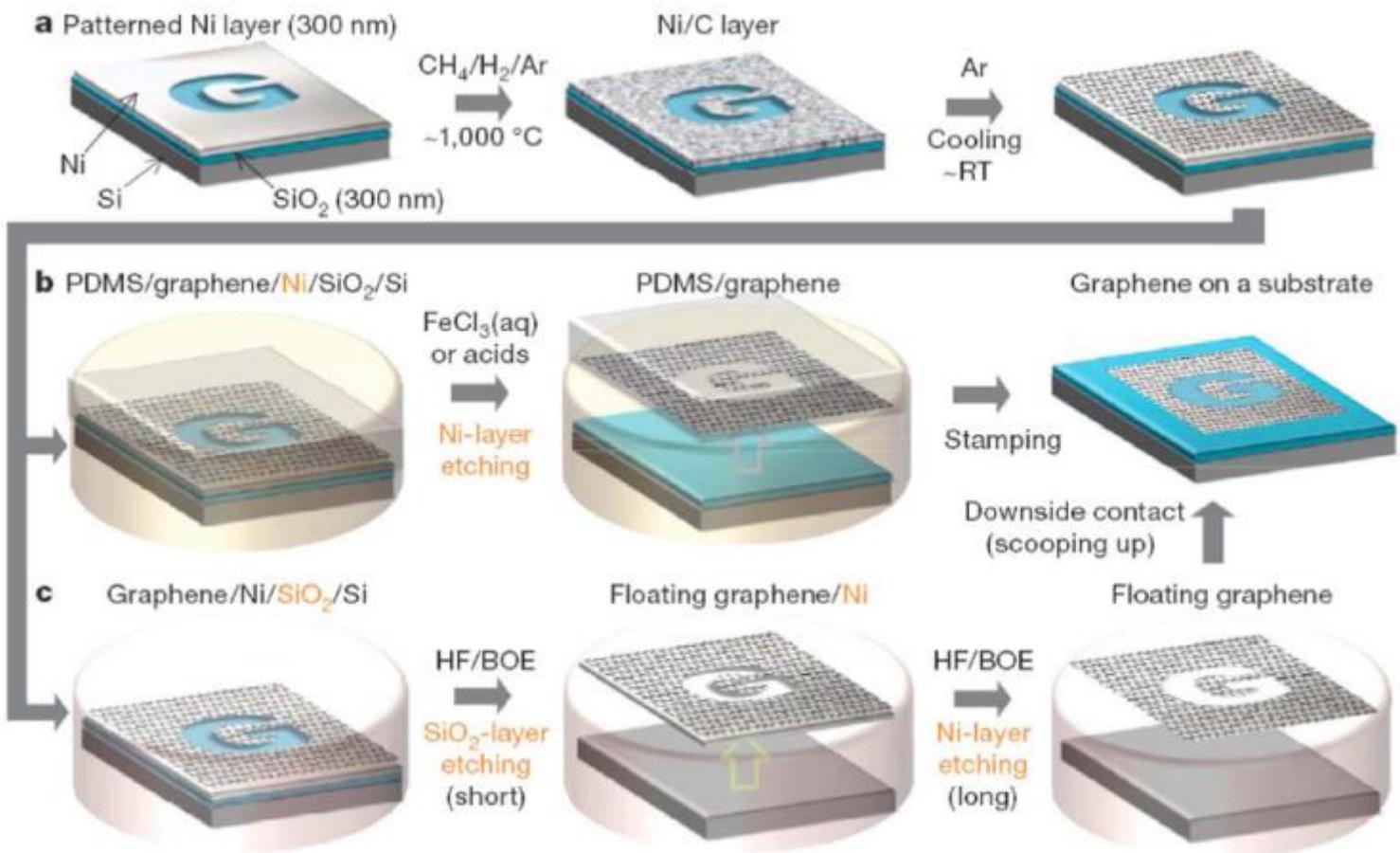
- The electron mobility of graphene at room temperature is very large and its resistivity is even smaller than silver. Mechanical properties of graphene are superior to steel. It is ~ 200 times stronger compared to steel.



# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

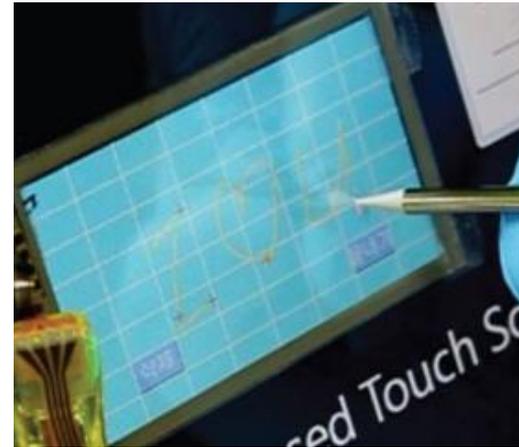
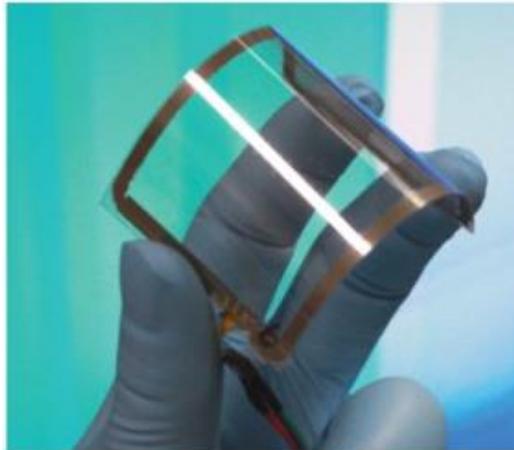
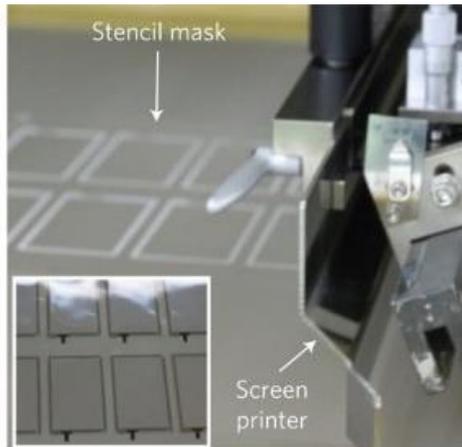
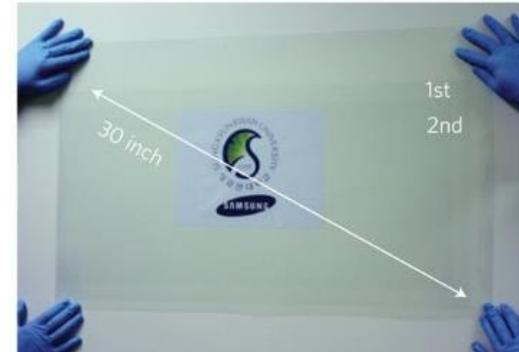
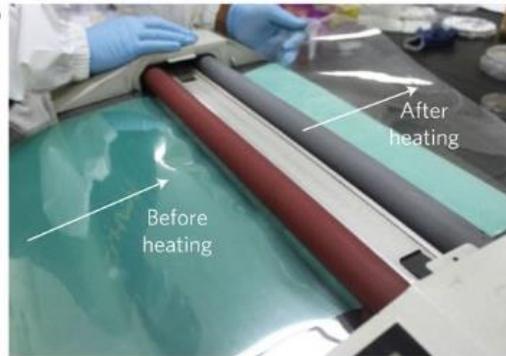
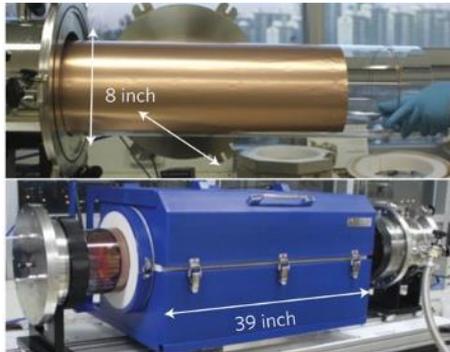
### 6.1.3 Graphene



# 6. Some Special Nanomaterials

## 6.1 Carbon Nanomaterials

### 6.1.3 Graphene



**Thank you**