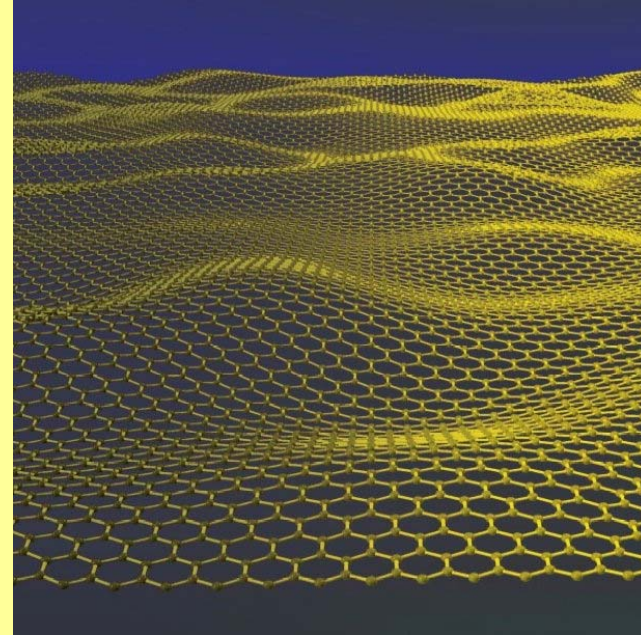


# Layered Compounds

## 2D = Two-dimensional layers

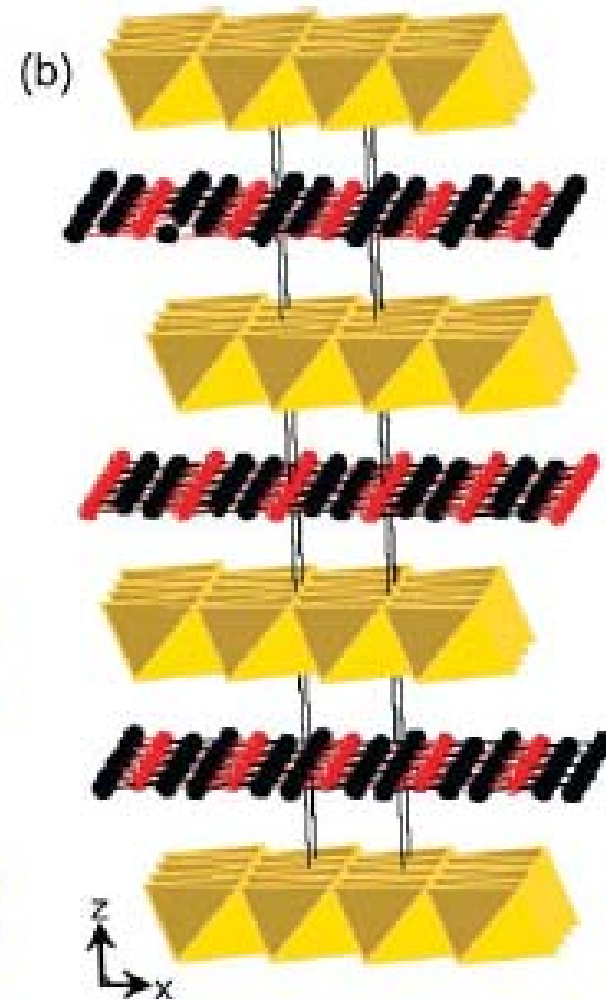
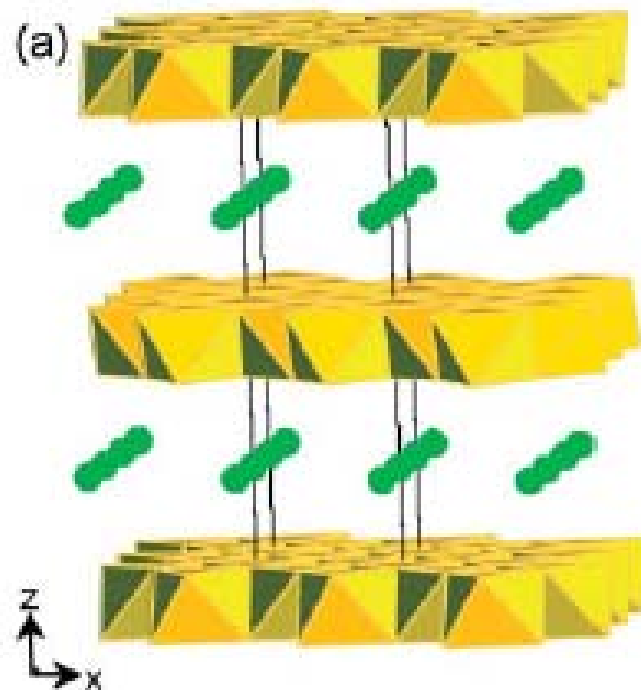
- Graphite and Graphene and the likes
- Clay Minerals, Mica
- Layered Double Hydroxides (LDHs)
- Layered Zirconium Phosphates and Phosphonates
- Layered Metal Oxides
- Layered Metal Chalcogenides -  $\text{TiS}_2$ ,  $\text{MoS}_2$ ,  $\text{WS}_2$ ,  $\text{MPS}_3$  (M = Ti, V, Mo, W, Mn, Fe, Co, Ni, Zn)
- Alkali Silicates and Crystalline Silicic Acids



# Layered Compounds

**Intra**layer bonding - strong  
(covalent, ionic)

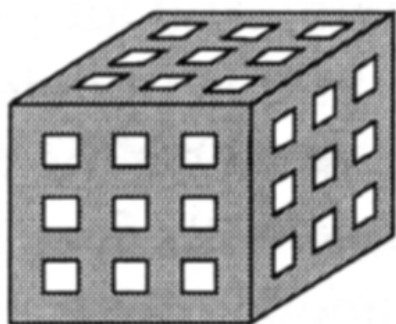
**Inter**layer bonding - weak  
(H-bonding, van der Waals)



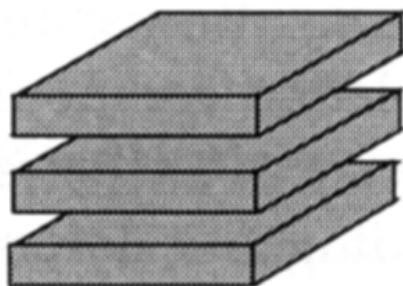
# Host-Guest Structures

## Host dimensionality

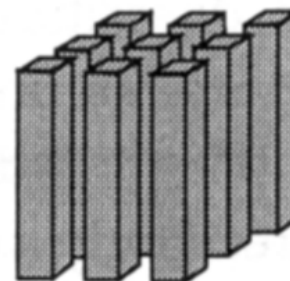
3D



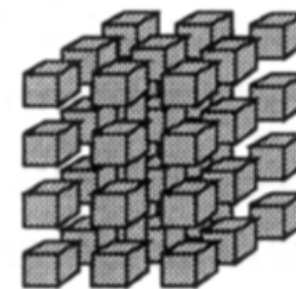
2D



1D



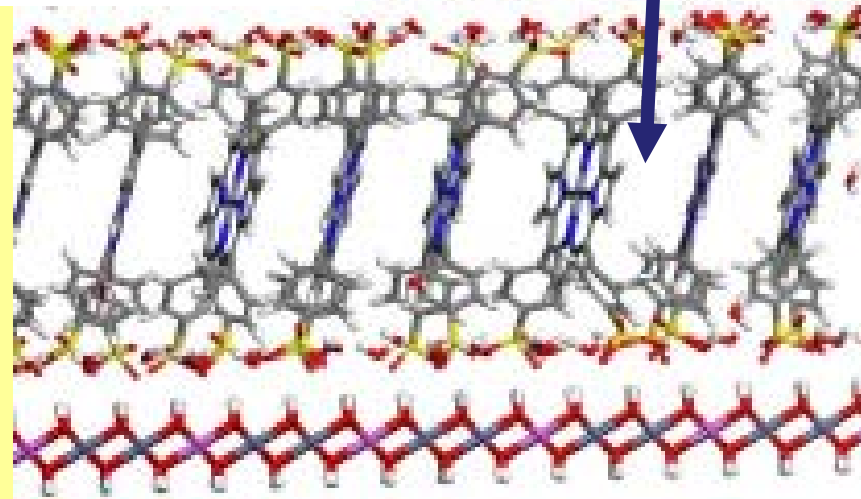
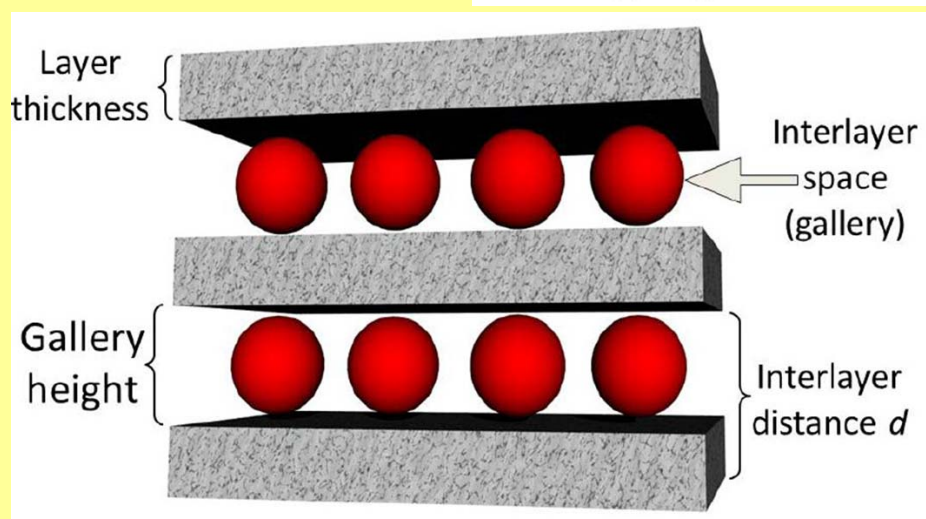
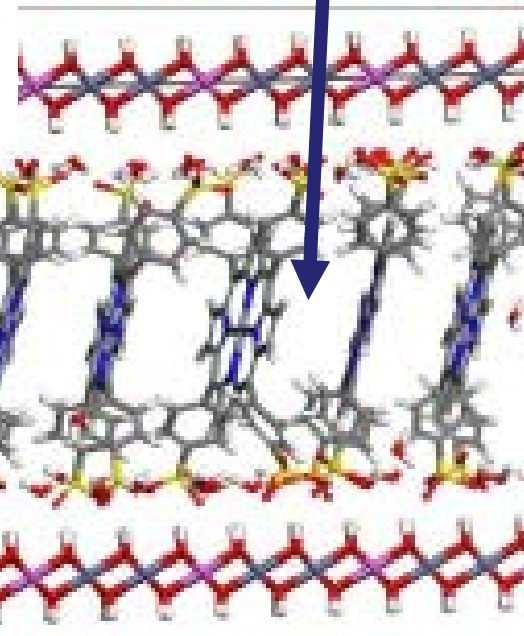
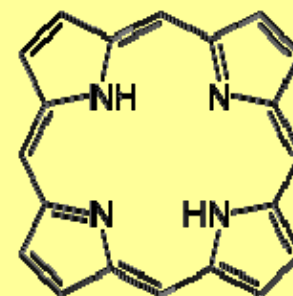
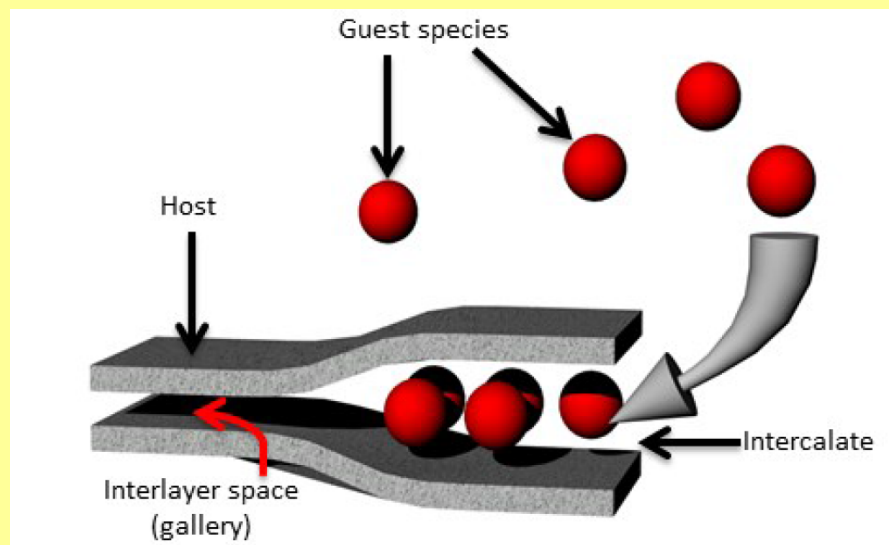
0D



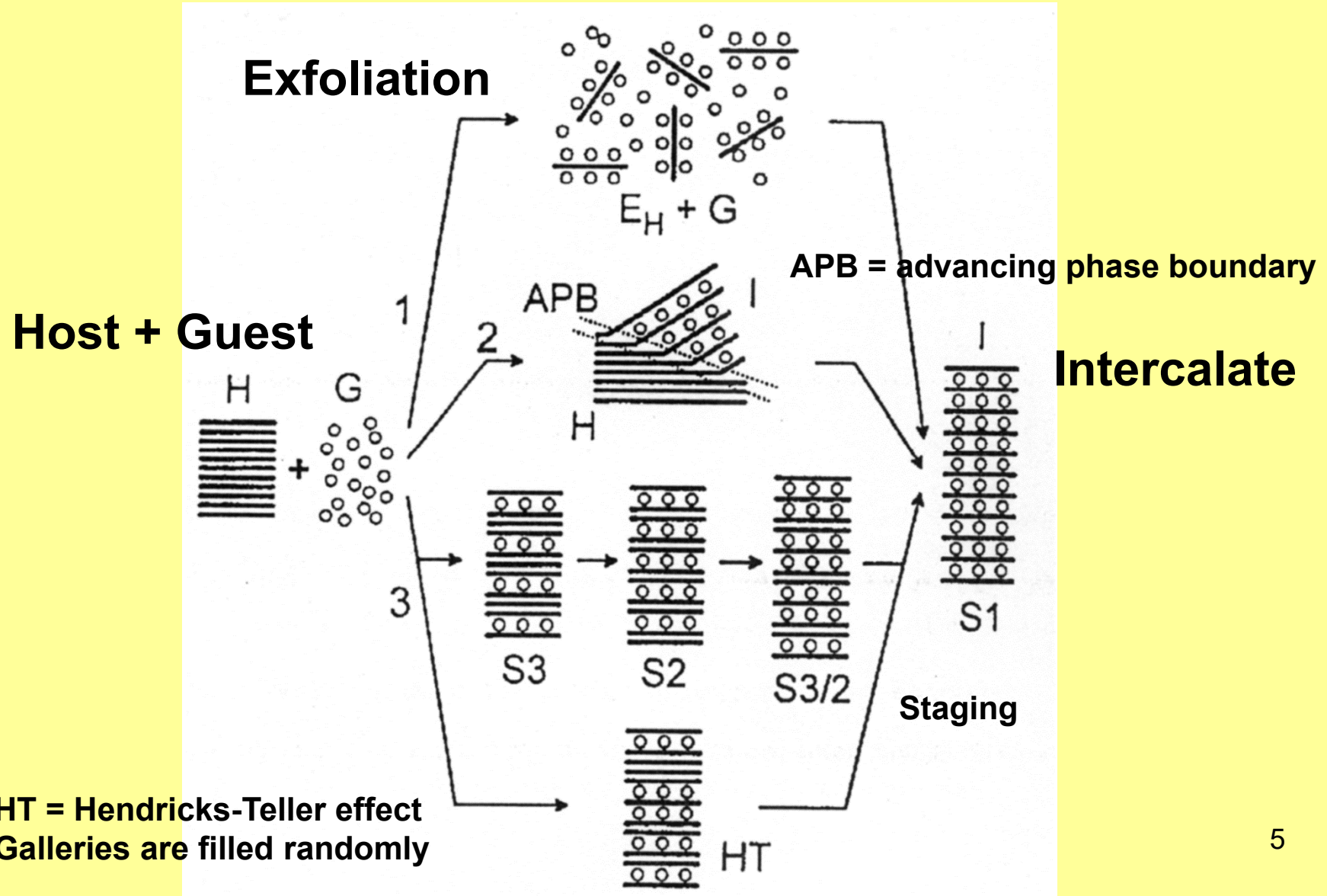
**Topotactic reactions** = modifying existing solid state structures while maintaining the integrity of the overall structure

# Intercalation

Intercalation = Insertion of guest molecules between layers



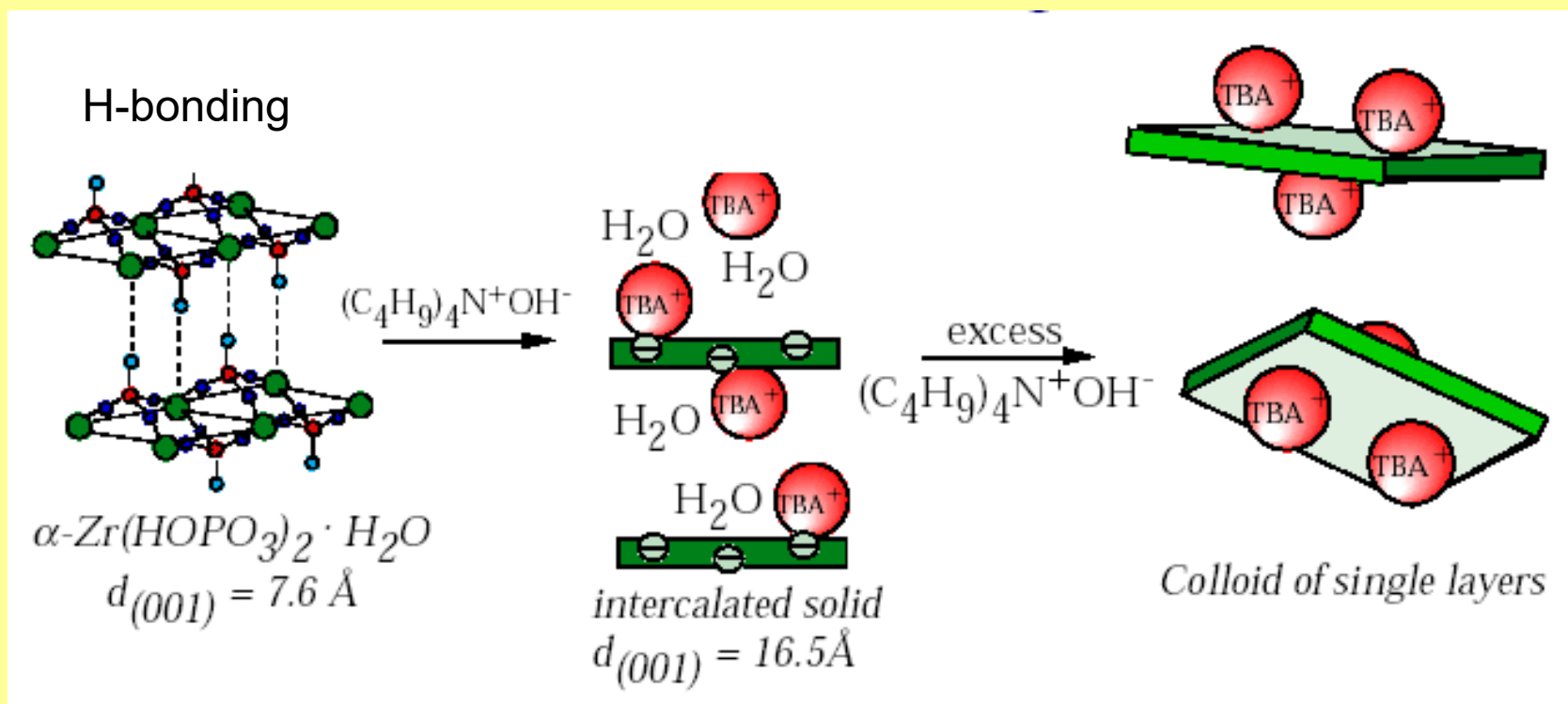
# Intercalation Mechanisms



HT = Hendricks-Teller effect  
Galleries are filled randomly

# Exfoliation

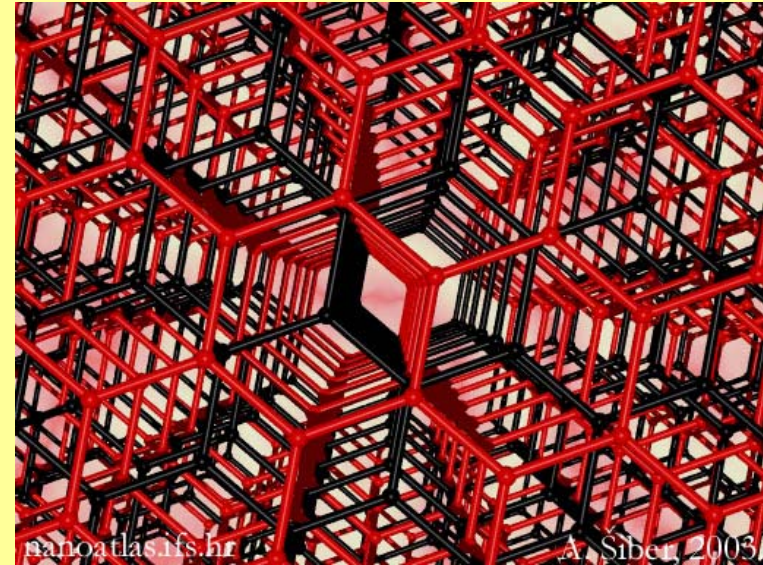
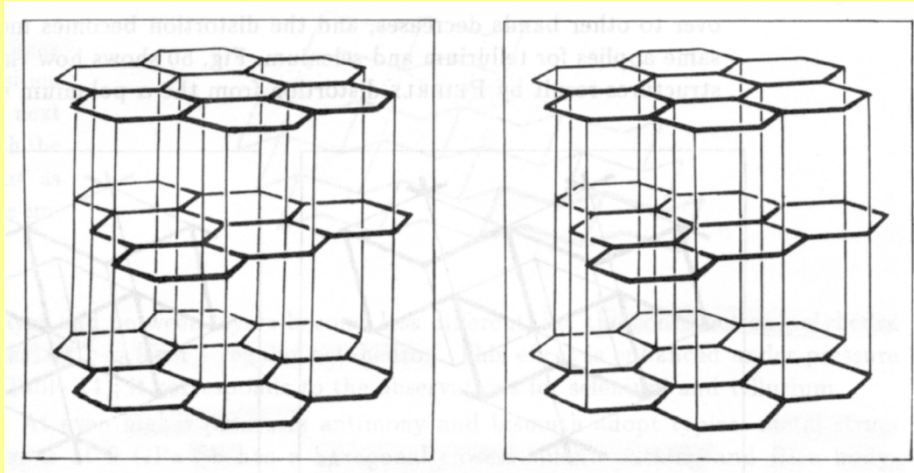
Decrease attractive forces between layers  
Separate layers





# Graphite

**ABABAB**

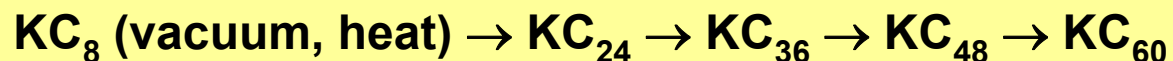


**Hexagonal graphite = two-layer ABAB stacking sequence**

**Graphite C-C  $sp^2$  sigma-bonding in-plane and out-of-plane p-orbital pi-bonding**

**The pi-type orbitals create the valence and conduction bands of graphite, very small band gap, metallic conductivity properties in-plane,  $10^4$  times that of out-of-plane electric conductivity**

# Graphite Intercalation



**KC<sub>8</sub> potassium graphite ordered structure**  
**Ordered K guests between the sheets of G**

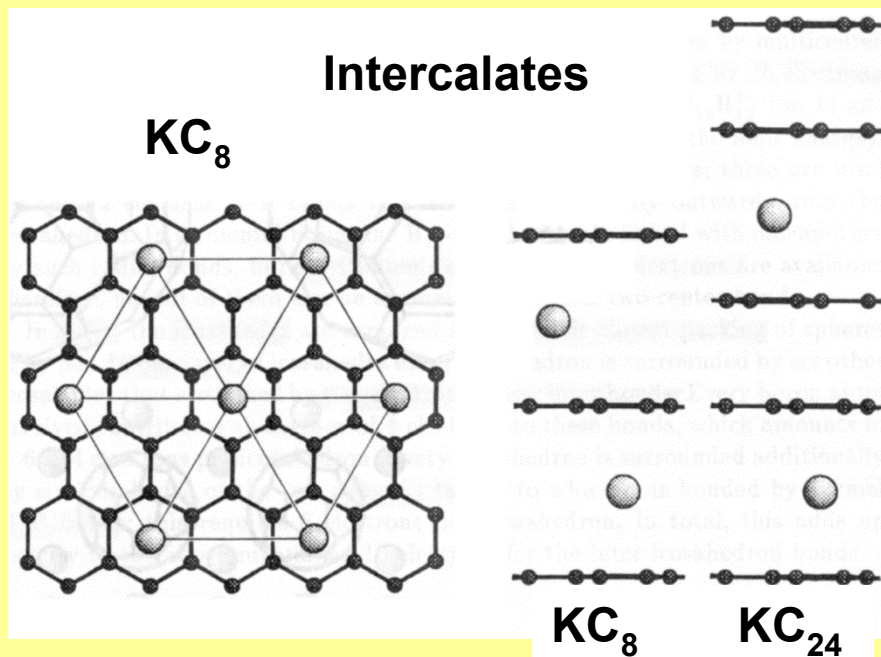
**AAAA stacking sequence**

**K nesting between parallel eclipsed hexagonal planar carbon six-rings**

**K to G charge transfer**

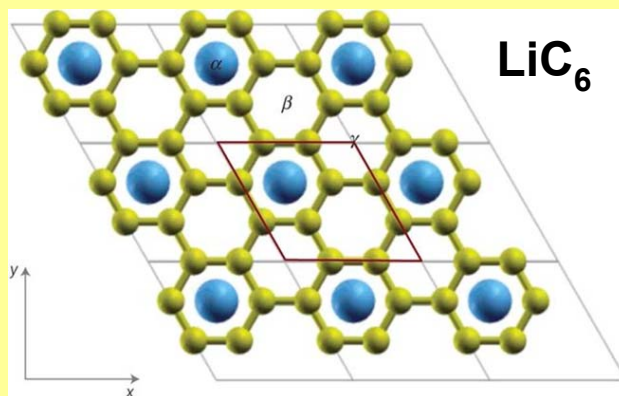
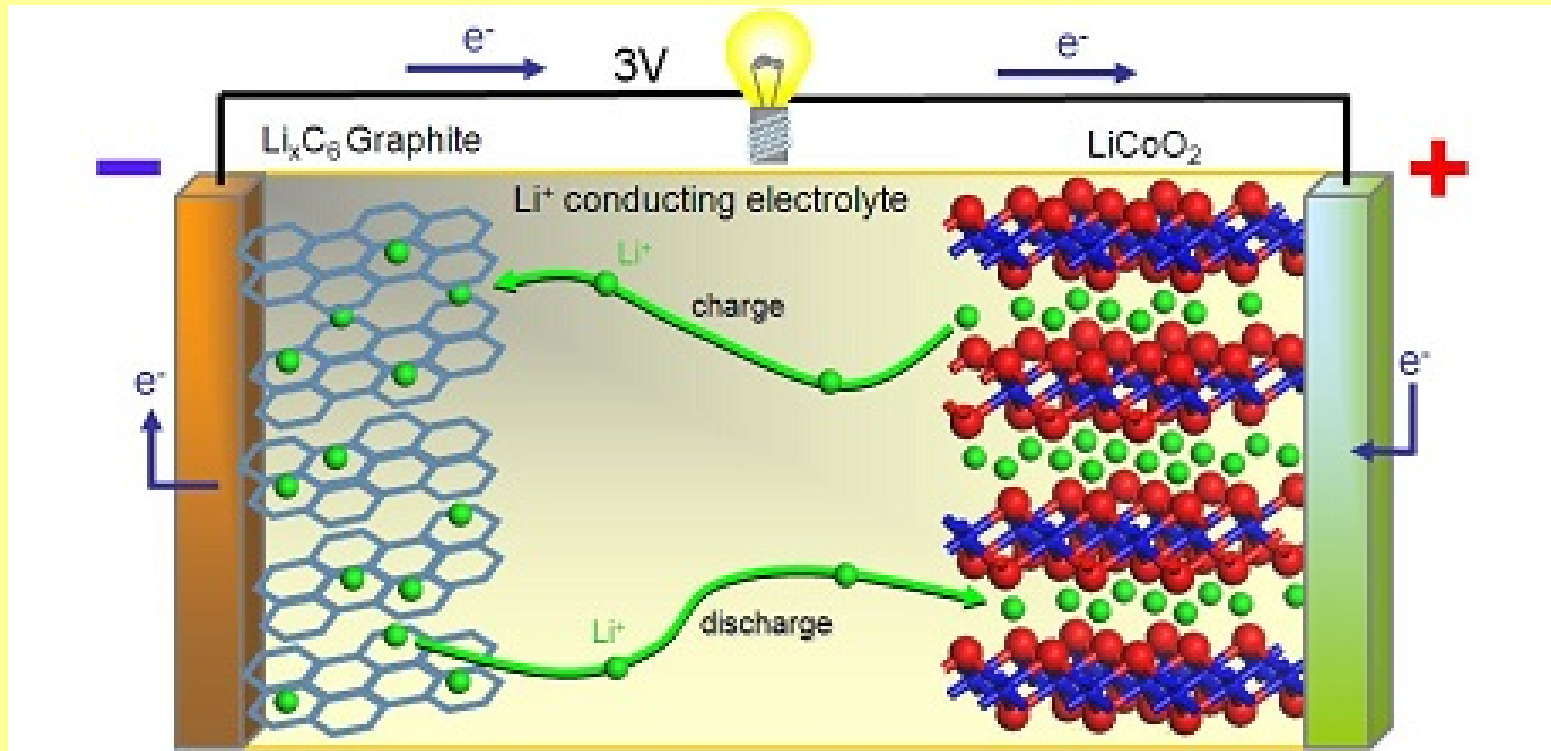
**Reduction of graphite sheets**  
**Electrons enter the conduction band**

**Ionic bonding K<sup>+</sup> C<sub>8</sub><sup>-</sup>**

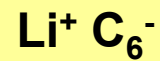




# Intercalation in Li-ion Cells



Li to G charge transfer



# Graphene

- 1962 H.-P. Boehm monolayer flakes of reduced graphene oxide
- 2004 Andre Geim and Konstantin Novoselov - Graphene produced and identified
- Exotic properties:
  - Firm structure
  - Inert material
  - Hydrofobic character
  - Electric and thermal conductivity
  - High mobility of electrons
  - Specific surface area (theor.):  $2630 \text{ m}^2\text{g}^{-1}$
- Application: diodes, sensors, solar cells, energy storage, composites, ...

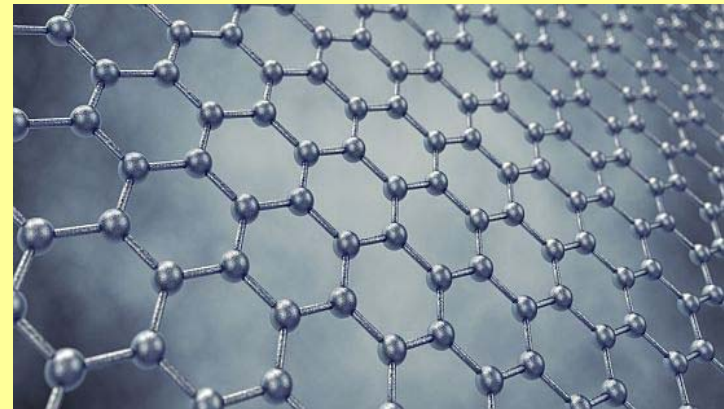


**K. Novoselov**

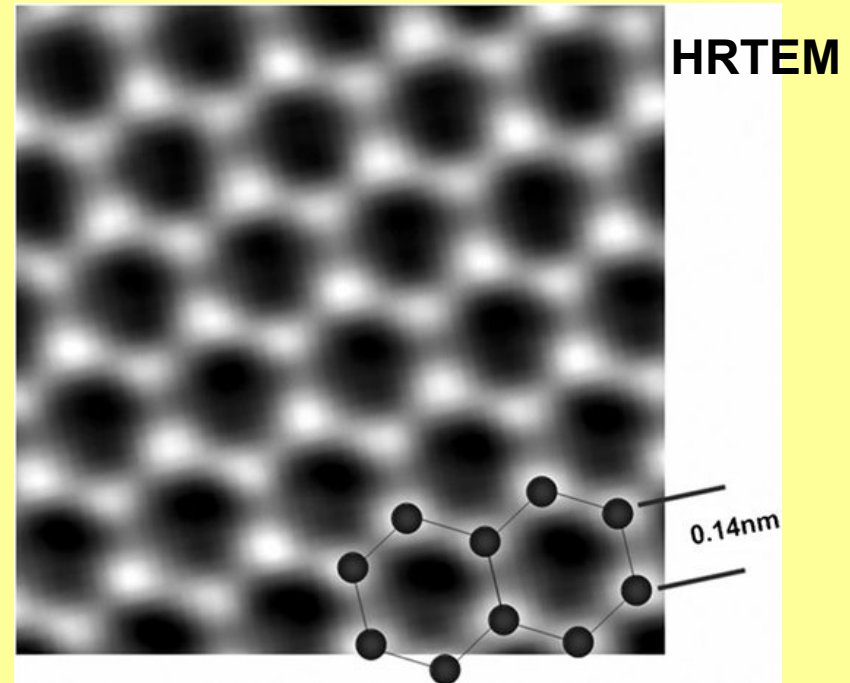
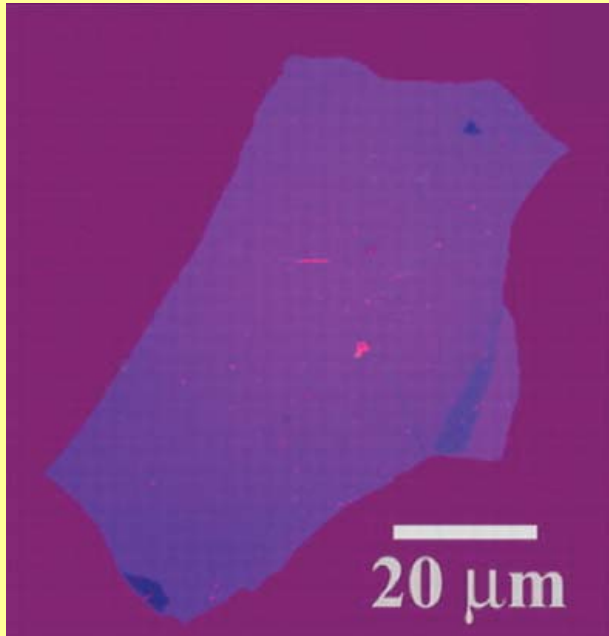


**A. Geim**

**2010 Nobel Prize in Physics**



# Graphene Properties



**High electric conductivity (metallic)**

**Optically transparent – 1 layer absorbs 2.3% of photons**

**High mechanical strength**

# Preparation of Graphene

## Top-Down

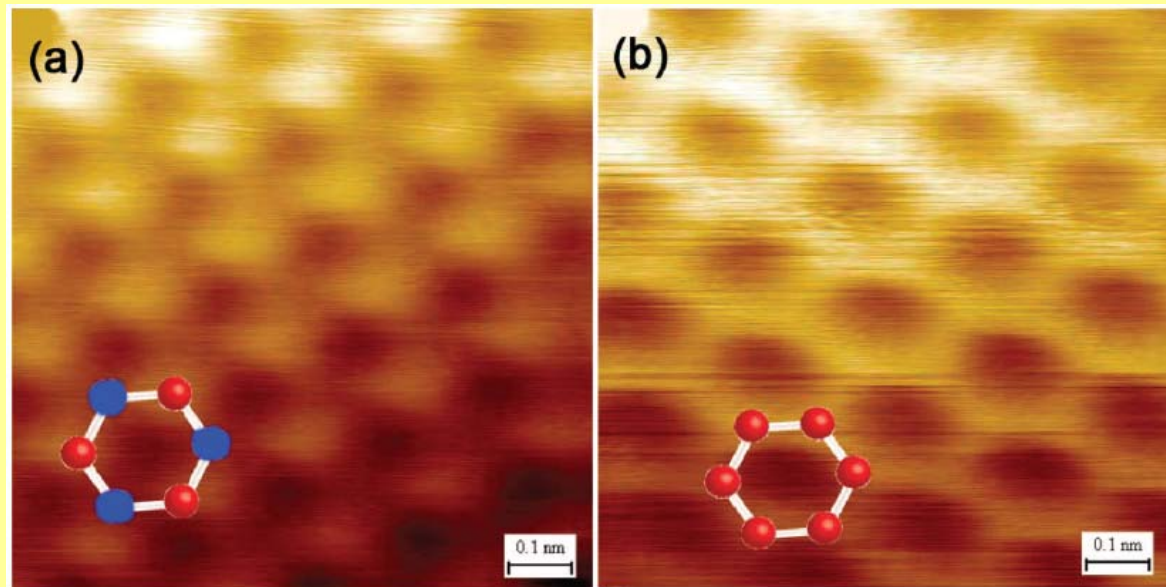
Mechanical exfoliation of graphite - Scotch tape – layer peeling, flaking

Chemical exfoliation of graphite (chemical, sonochemical)

## Bottom-Up

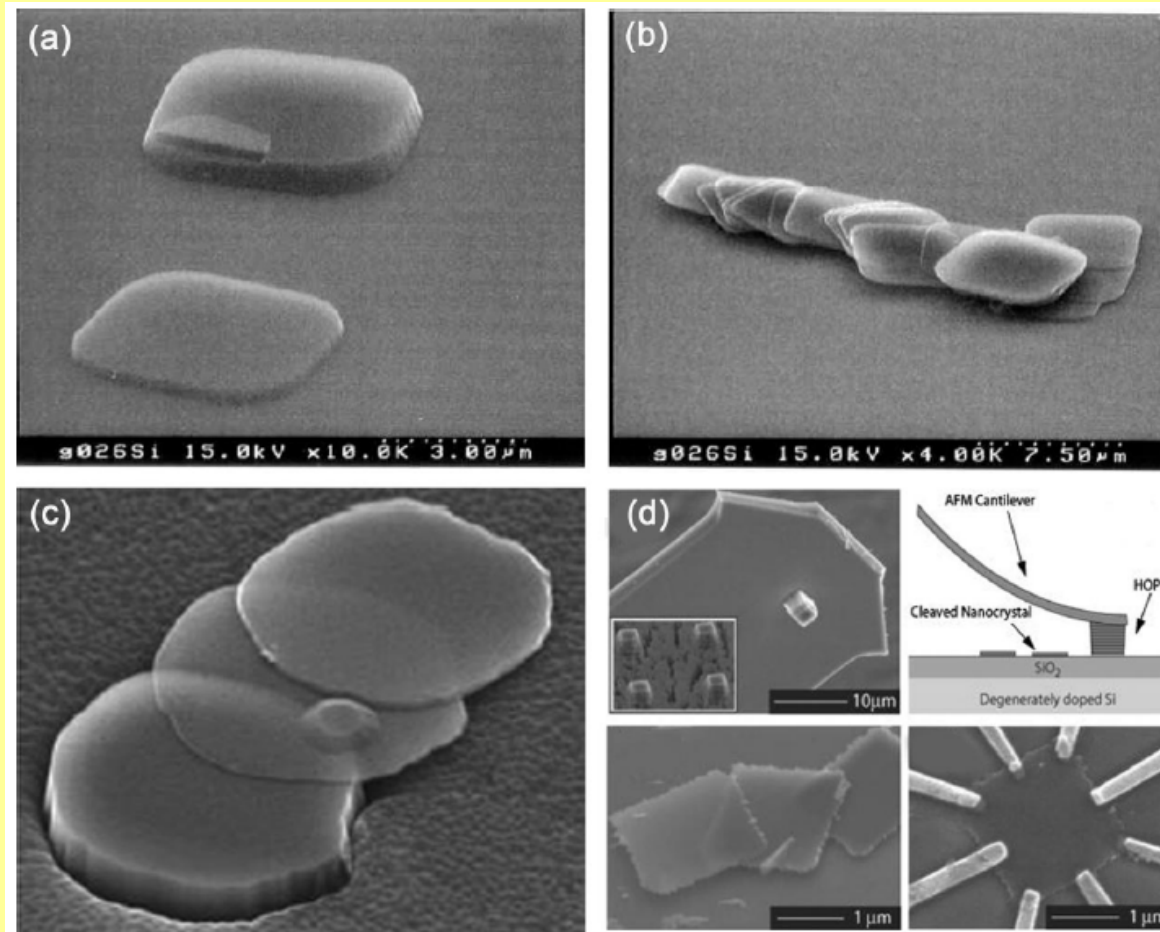
SiC pyrolysis – epitaxial graphene layer on a SiC crystal

CVD from  $\text{CH}_4$ ,  $\text{CH}_2\text{CH}_2$ , or  $\text{CH}_3\text{CH}_3$  on Ni (111), Cu, Pt surfaces



# Scotch Tape – Layer Peeling

## Mechanical exfoliation

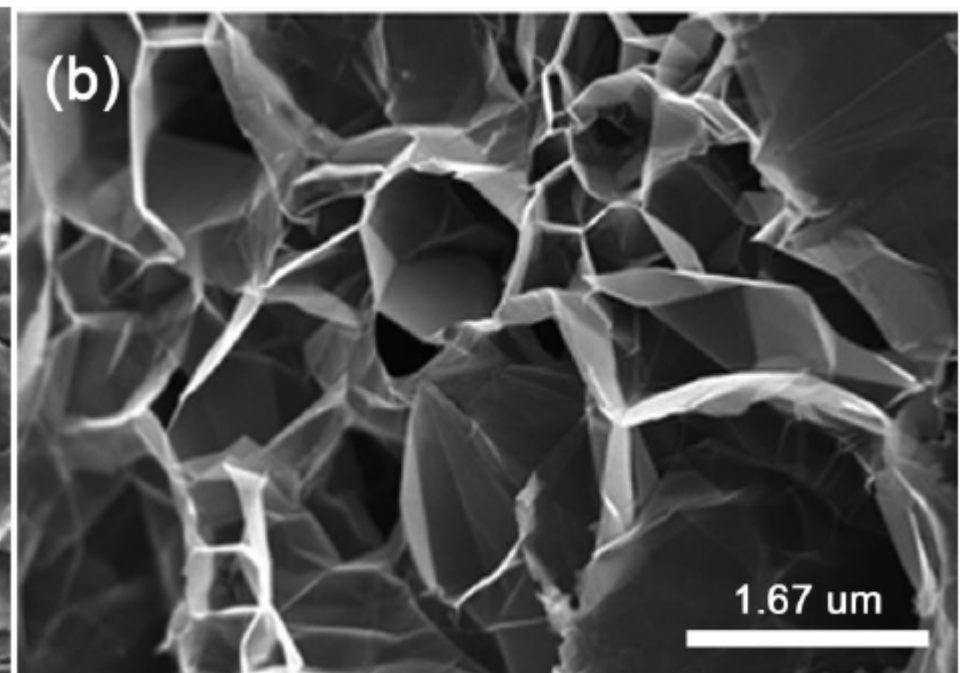
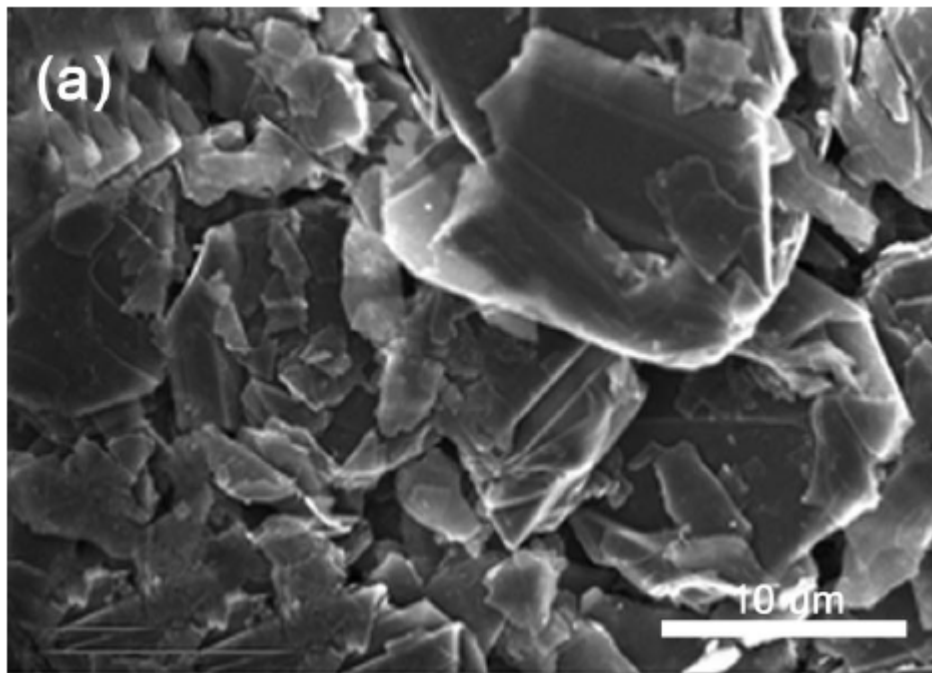
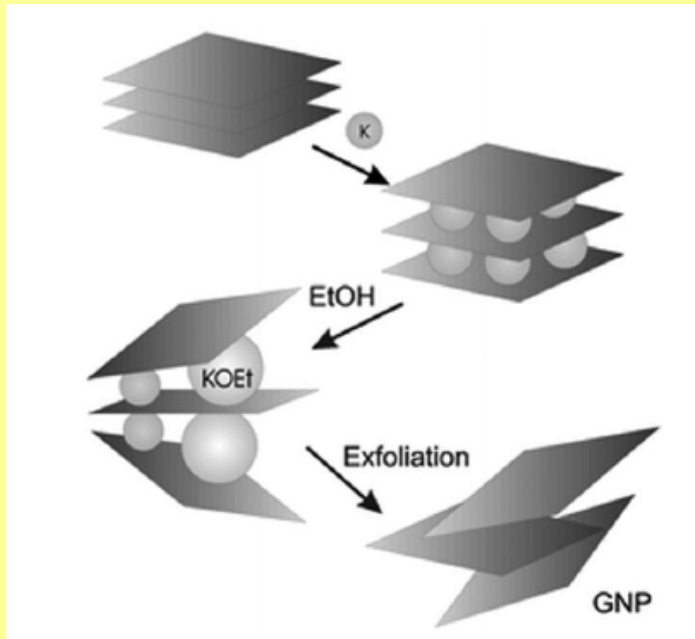




# Exfoliation

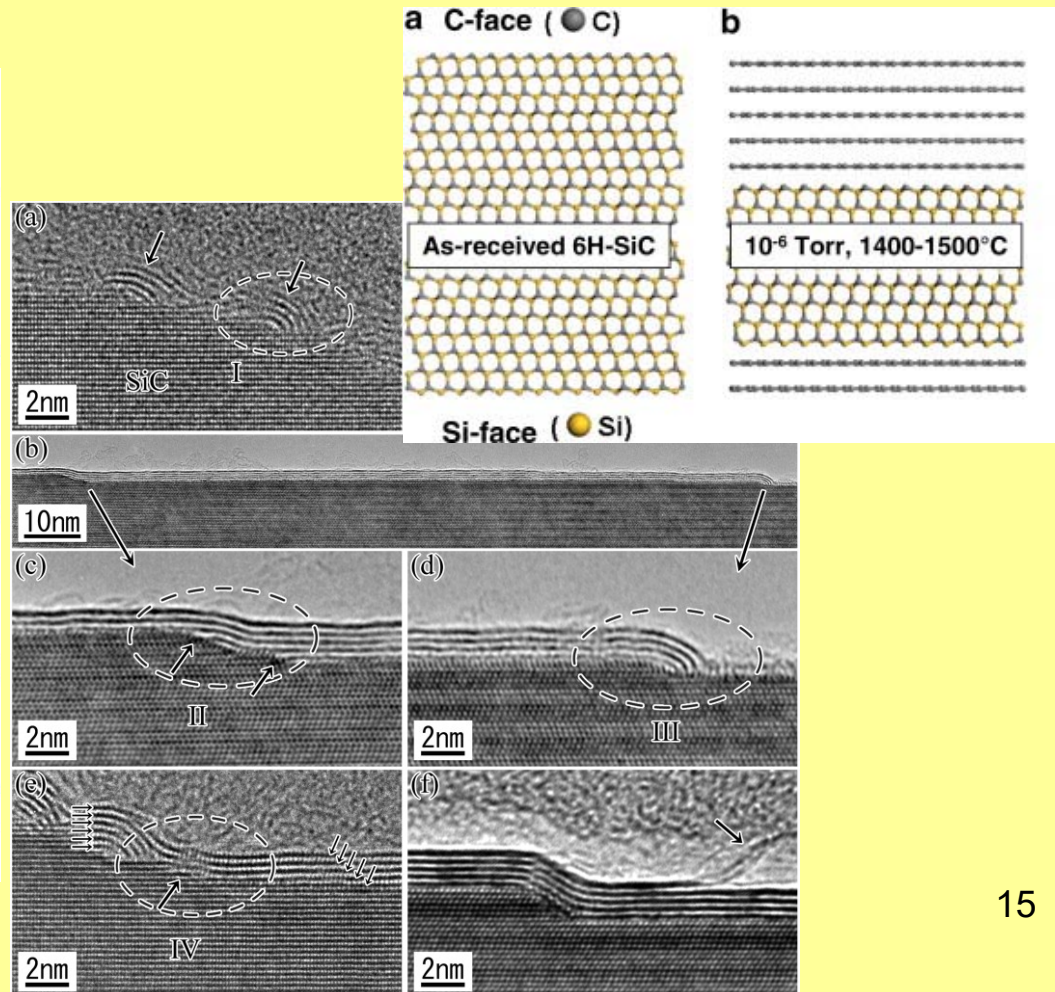
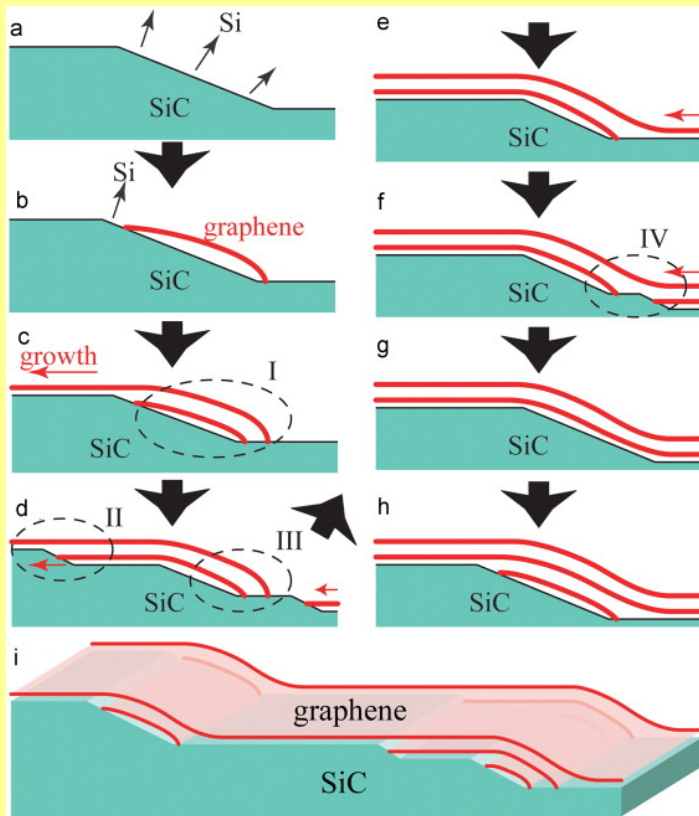
Chemical exfoliation (surfactant)

Sonochemical exfoliation

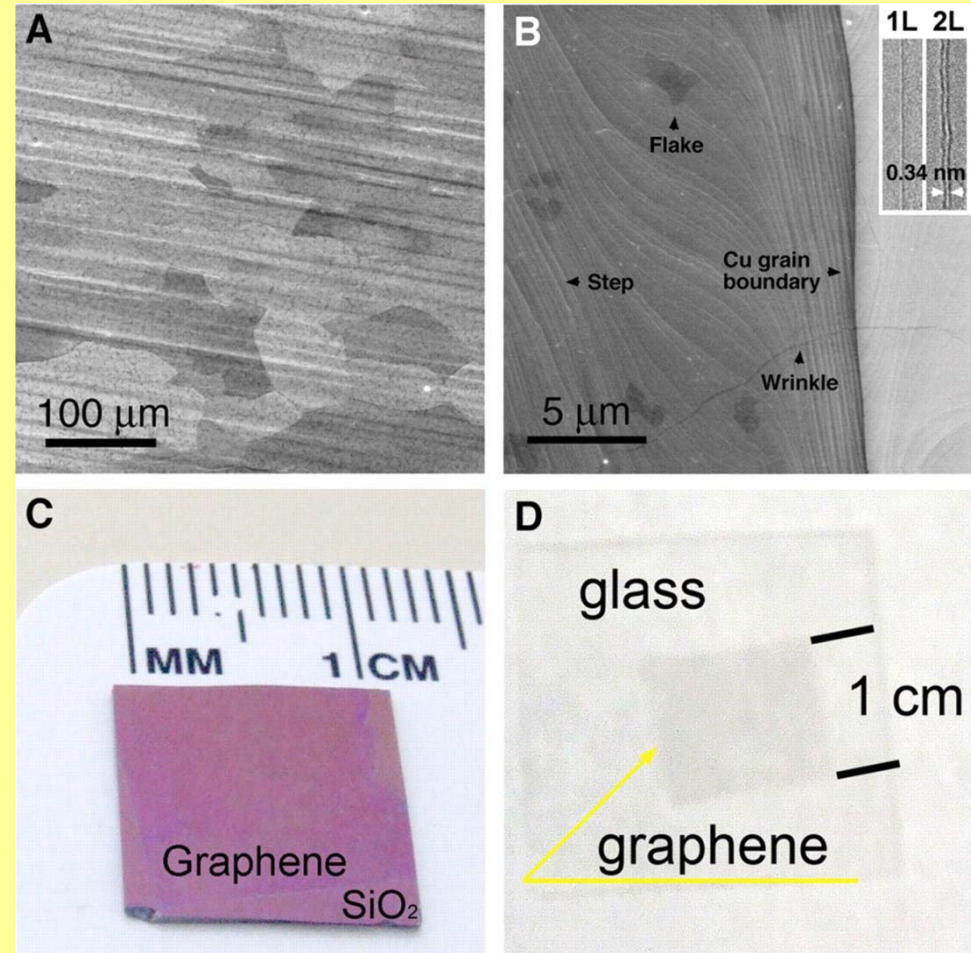
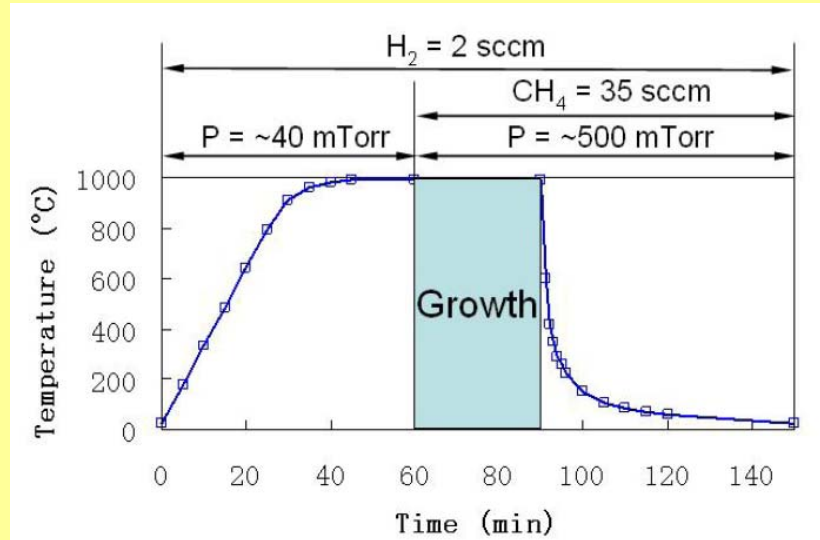


# SiC Pyrolysis

- Annealing of the SiC crystal in a vacuum furnace (UHV  $10^{-10}$  Torr)
- Sublimation of Si from the surface at 1250 - 1450 °C
- The formation of graphene layers by the remaining carbon atoms



# CVD from CH<sub>4</sub> / H<sub>2</sub> on Metal Surfaces



(A) SEM - graphene on a Cu foil  
 (B) High-resolution SEM - Cu grain boundary and steps, two- and three-layer graphene flakes, and graphene wrinkles. Inset (B) TEM images of folded graphene edges  
 1L = one layer; 2L = two layers

Graphene transferred onto  
 (C) a SiO<sub>2</sub>/Si substrate  
 (D) a glass plate

# Graphene Family

Graphene

Graphene oxide

Fluorographene

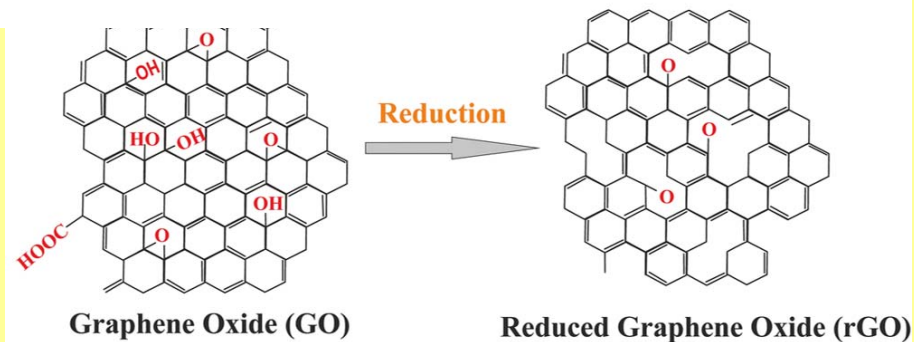
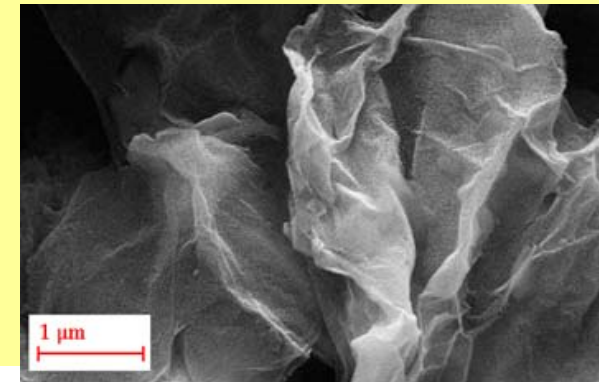
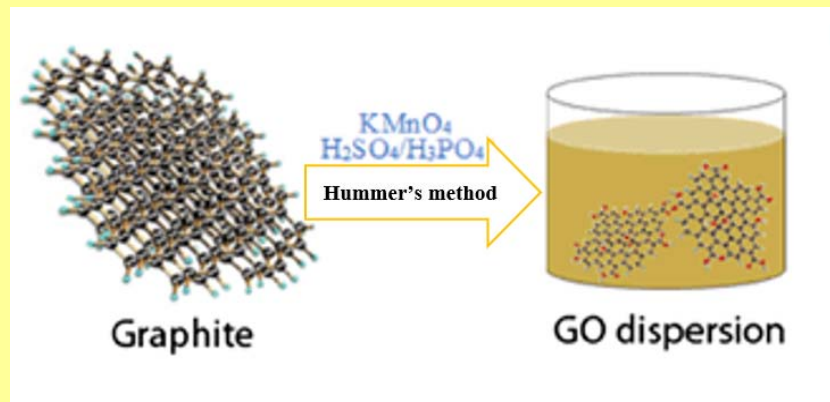
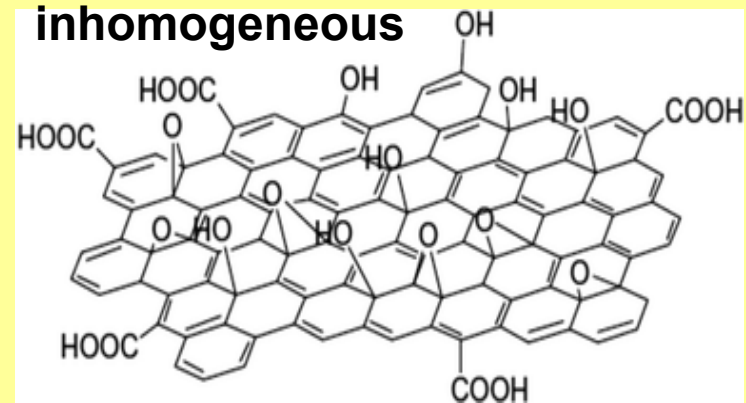
Graphitic Carbon Nitride  $C_3N_4$

Phosphorene



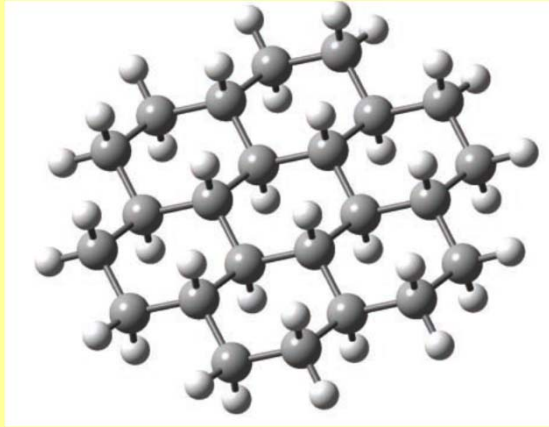
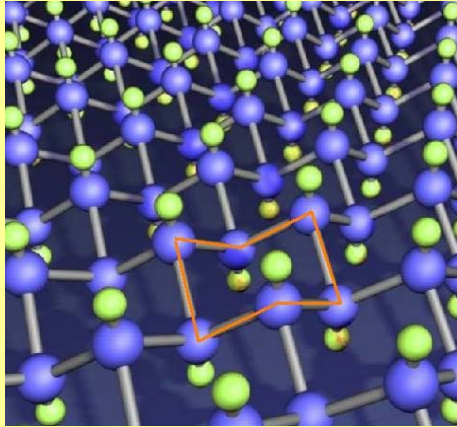
# Graphene Oxide

- More reactive than graphene
- Presence of oxygen groups: -OH, -COOH, =O, -O- hydrophilic character
- Electric insulator
- Specific SA (theoretically): 1700-1800 m<sup>2</sup>g<sup>-1</sup>
- Hummers method

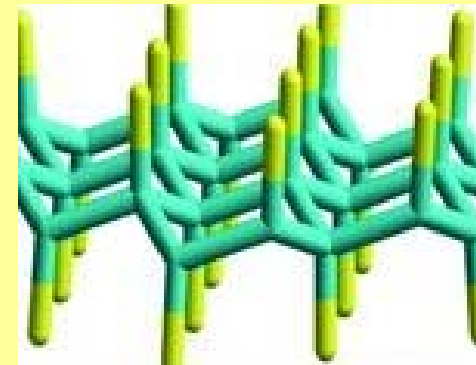




# Fluorographene / Graphene Fluoride



A puckered cyclohexane-ring  
Chair conformation  
Each carbon bears a fluorine  
alternately above and below  
the ring



- Monolayer of graphite fluoride (CF)
- Synthesis:
  - Graphene + XeF<sub>2</sub> (70 °C)
  - Mechanical exfoliation of carbon monofluoride (CF)<sub>n</sub>
  - Liquid-phase exfoliation of graphite fluoride with sulfolane
- High-quality insulator, resistivity > 10<sup>12</sup> Ω, an optical gap = 3 eV
- Mechanical strength - a Young's modulus = 100 N m<sup>-1</sup>
- Inert and stable up to 400 °C in air, similar to Teflon

# Graphitic Carbon Nitride

1834 Berzelius, Liebig

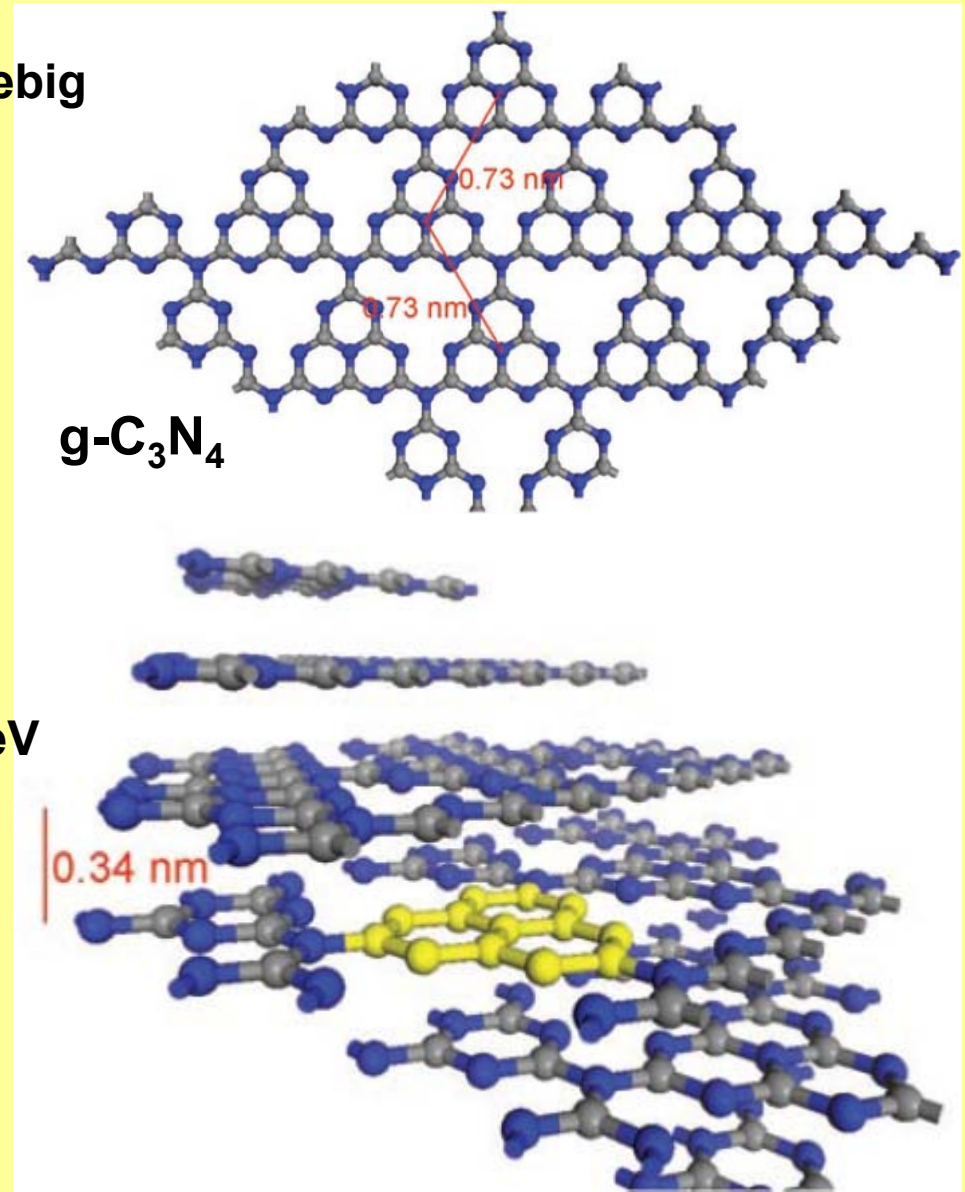
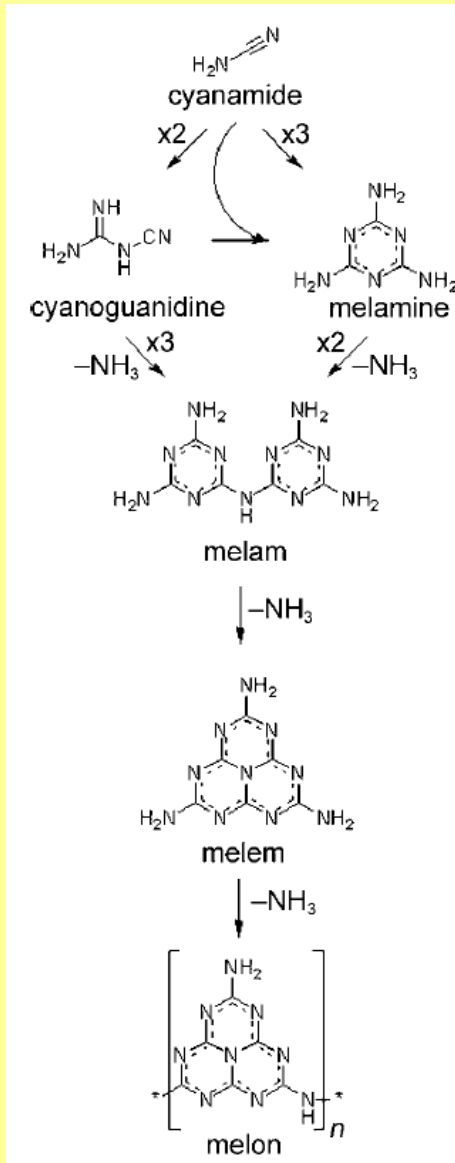
Temperature-induced  
condensation

Dicyandiamide  
 $\text{NH}_2\text{C}(=\text{NH})\text{NHCN}$

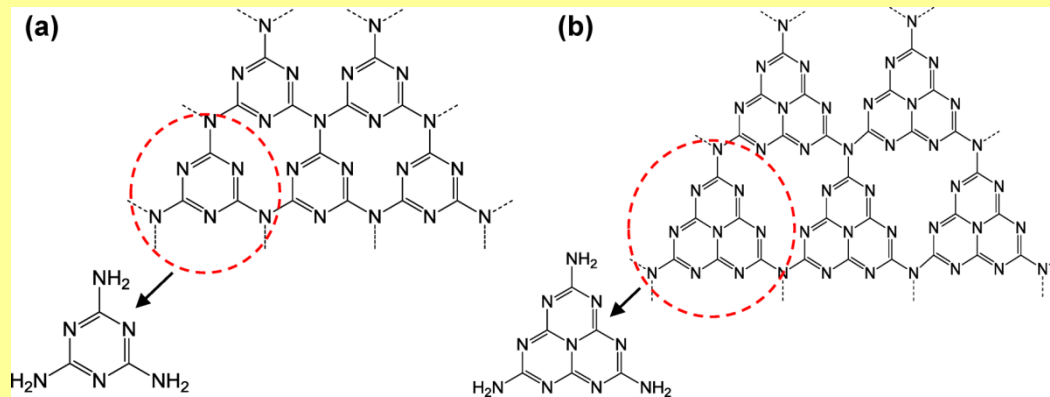
In a LiCl/KCl melt

Band gap 1.6 - 2.0 eV

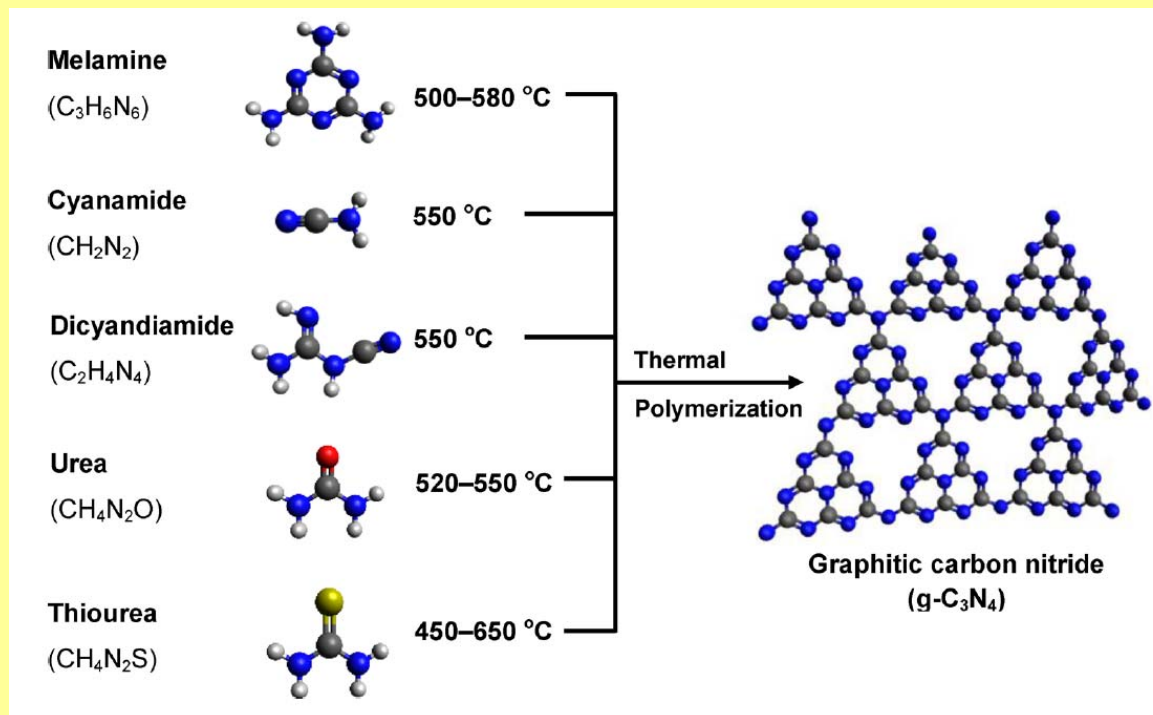
Small band gap  
semiconductors  
Si (1.11 eV), GaAs  
(1.43 eV), and GaP  
(2.26 eV)



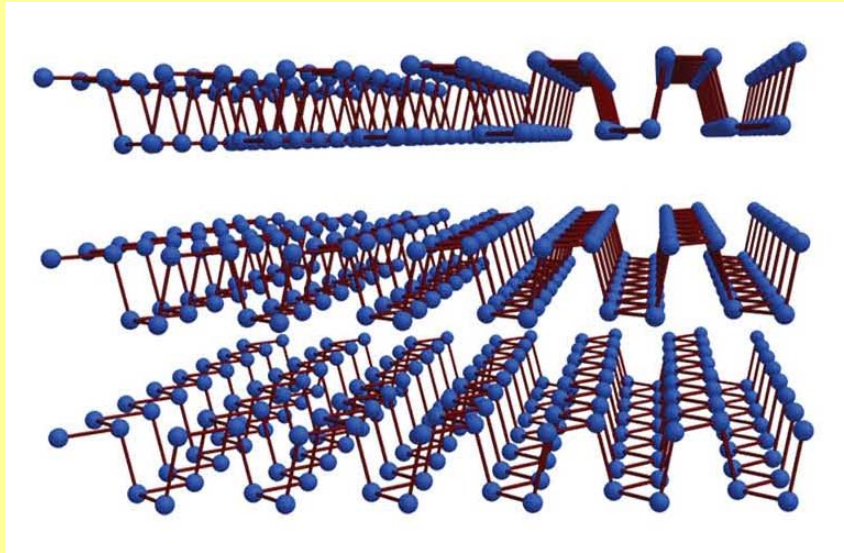
# Graphitic Carbon Nitride



(a) triazine and (b) tri-s-triazine (heptazine)



# Phosphorene



## Black phosphorus

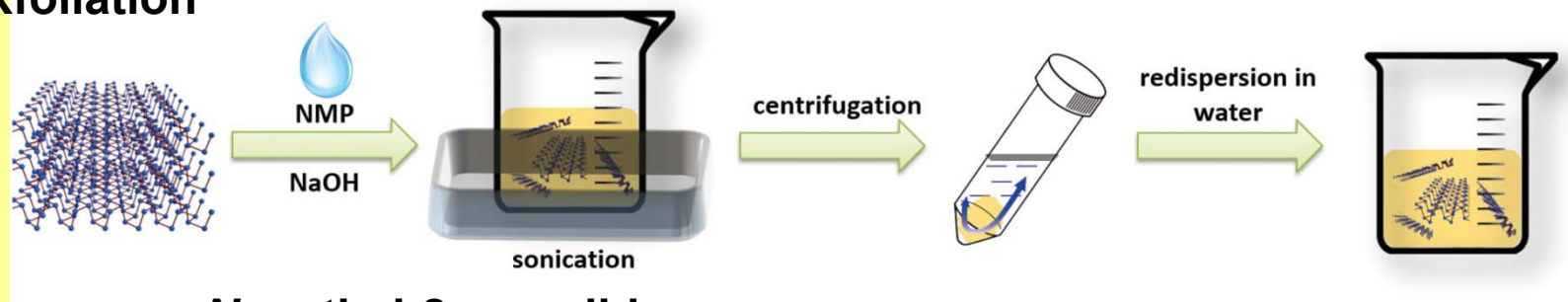
Orthorhombic

$a = 3.31 \text{ \AA}$ ,  $b = 4.38 \text{ \AA}$ ,  $c = 10.50 \text{ \AA}$

$\alpha = \beta = \gamma = 90^\circ$

Space group  $Bmab$

## Exfoliation



***N*-methyl-2-pyrrolidone**

**Semiconductor - direct band gap**

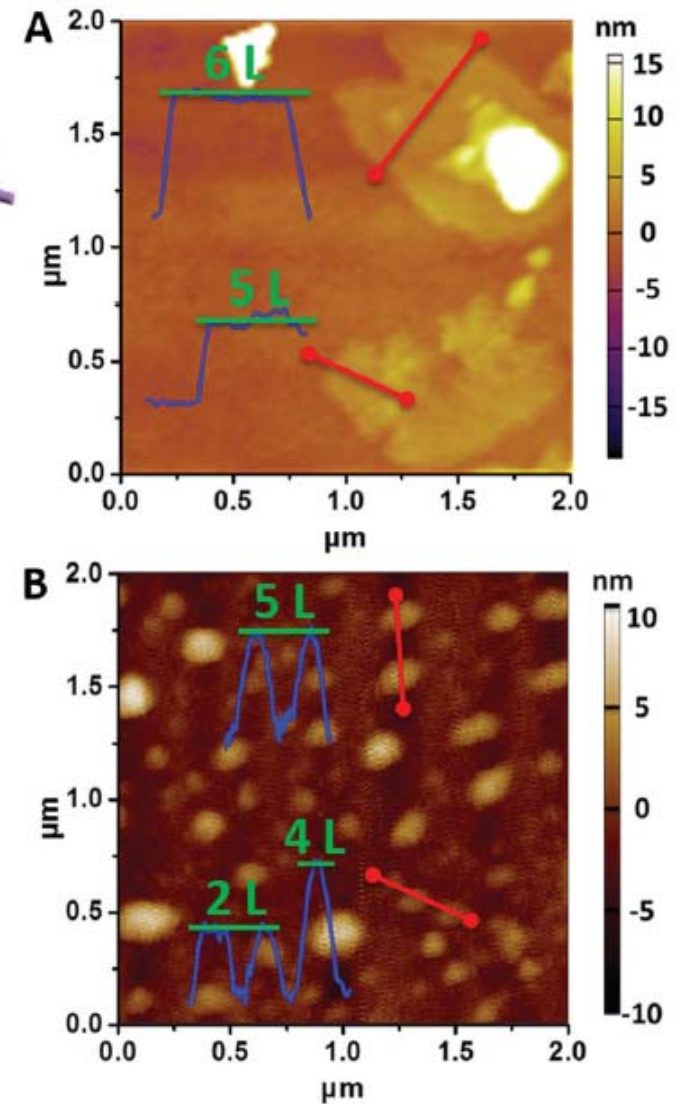
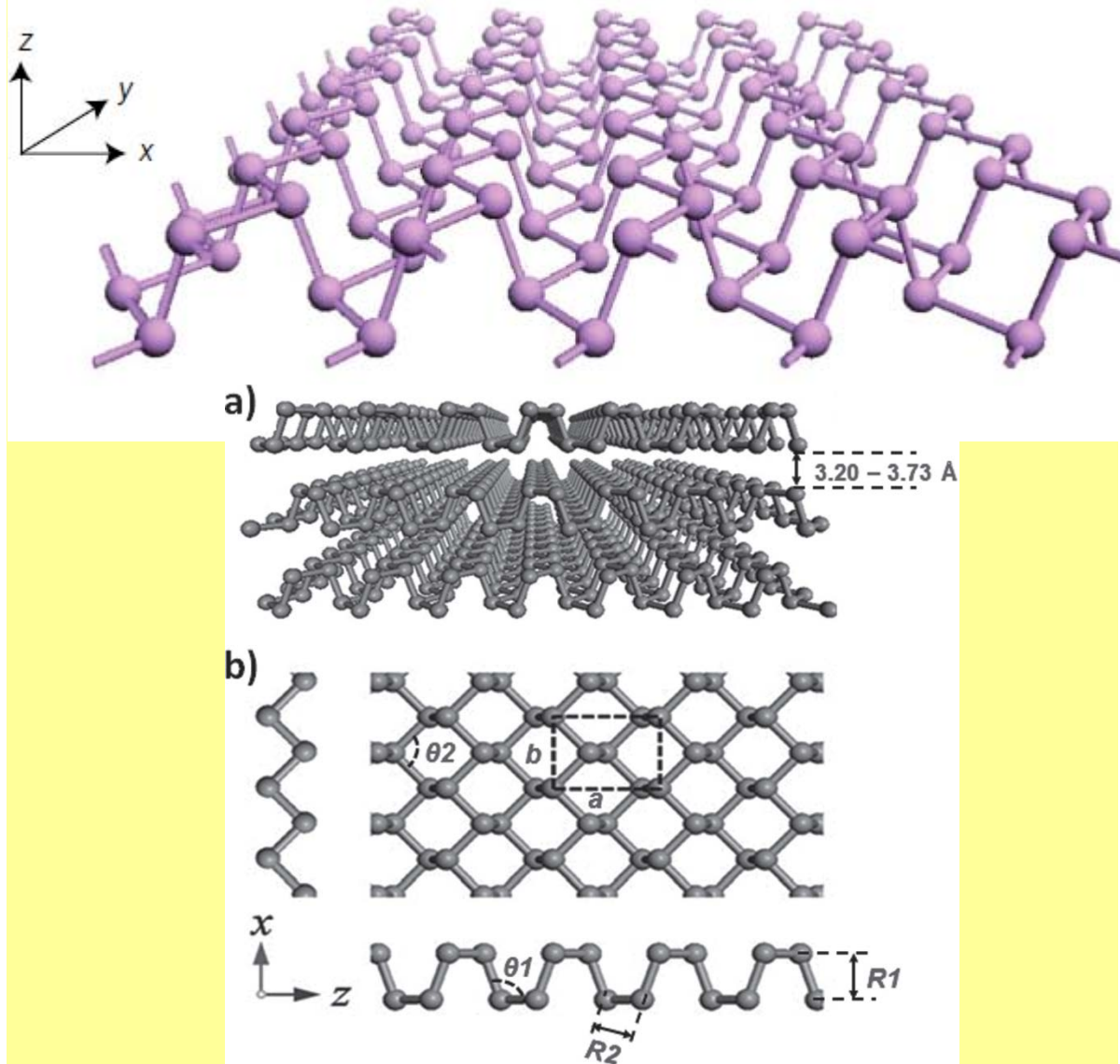
**bulk black P 0.3 eV**

**monolayer phosphorene 1.5 eV**



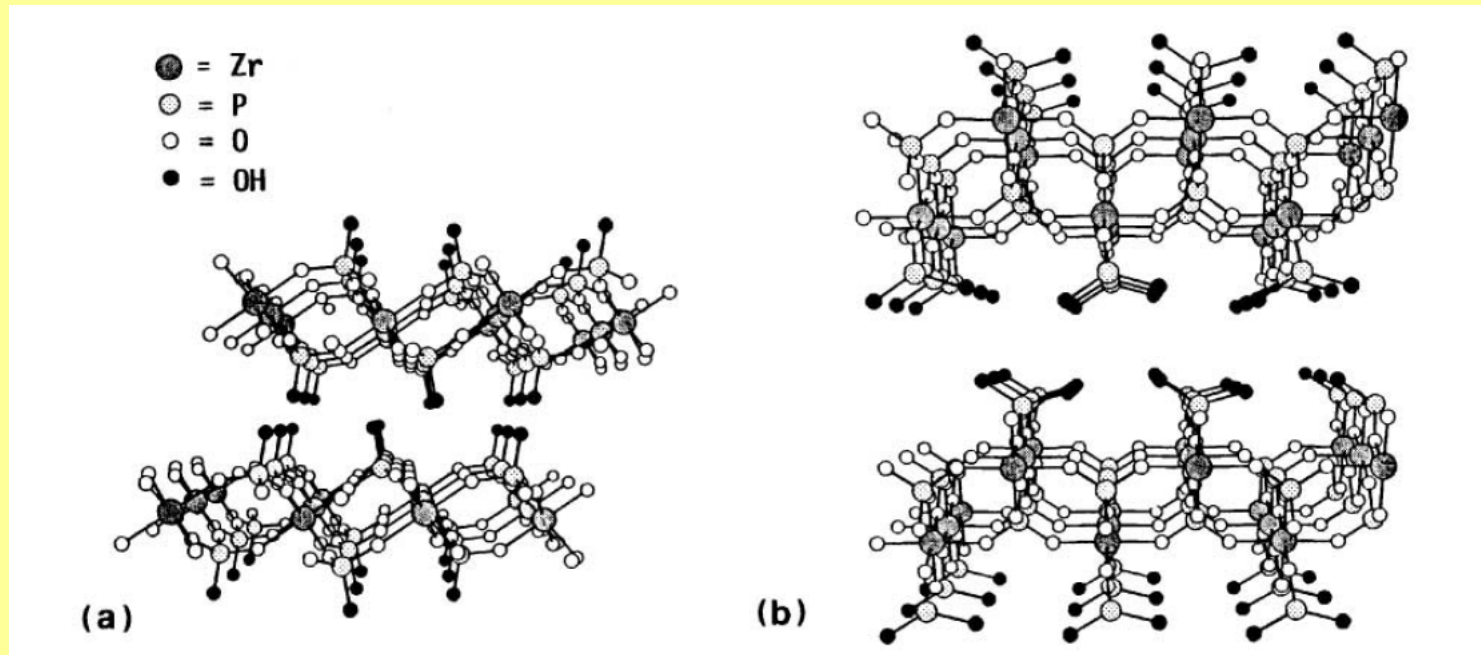
# Phosphorene

Height-mode AFM images  
single-layer phosphorene  
ca. 0.9 nm





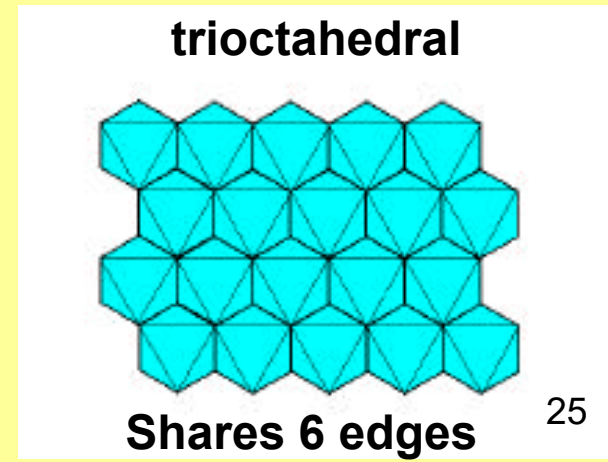
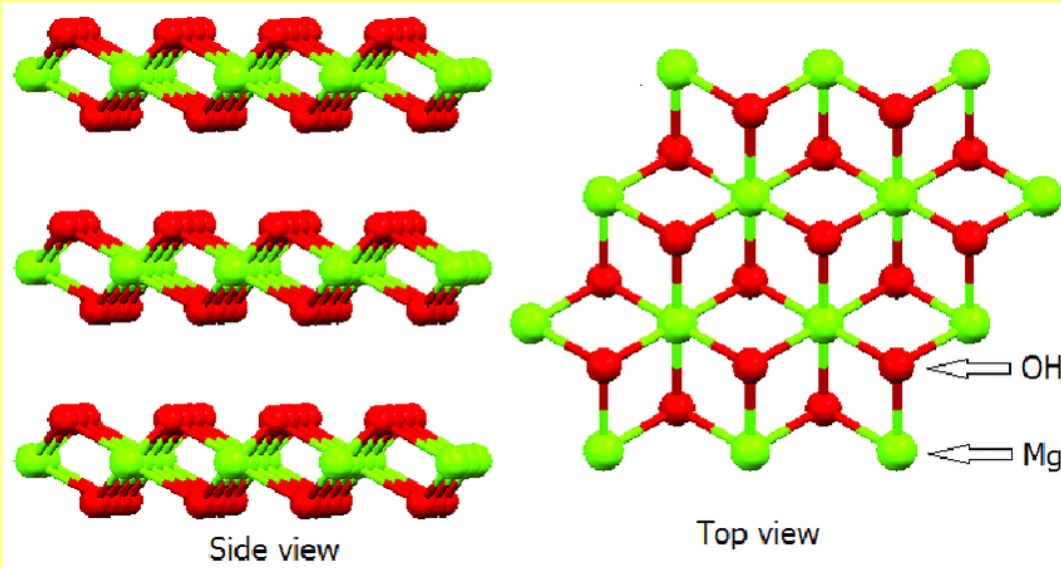
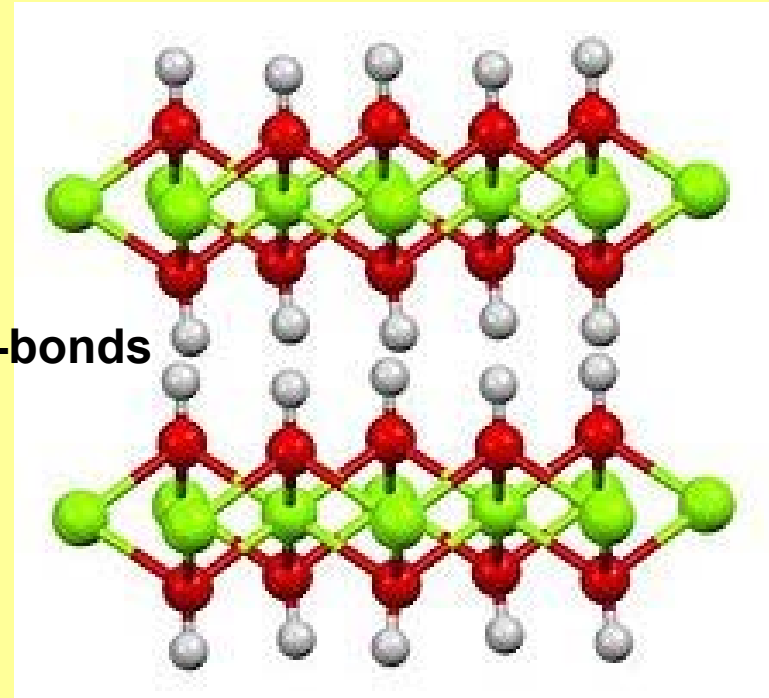
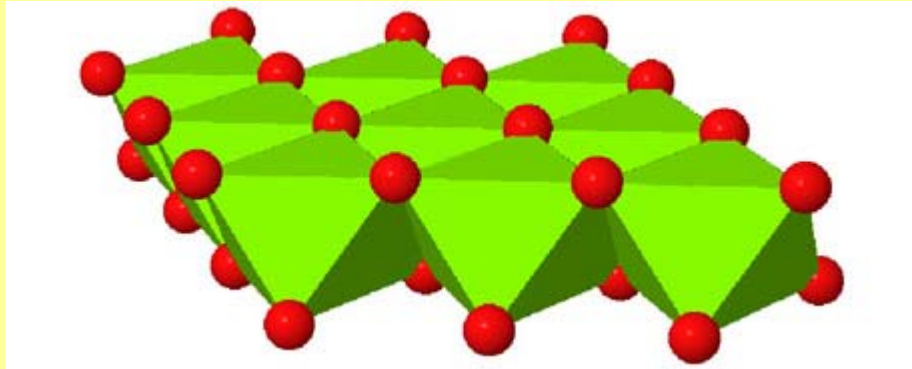
# Zirconium Phosphates



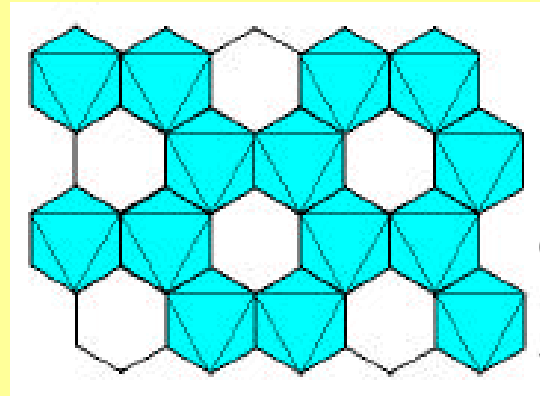
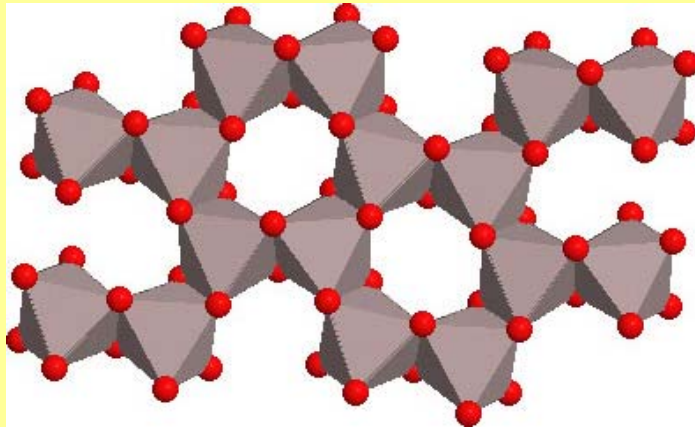
(a)  $\alpha$ -zirconium phosphate =  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$   
interlayer spacing 7.6 Å

(b)  $\gamma$ -zirconium phosphate =  $\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$   
interlayer spacing 12.2 Å

# Brucite - $Mg(OH)_2$



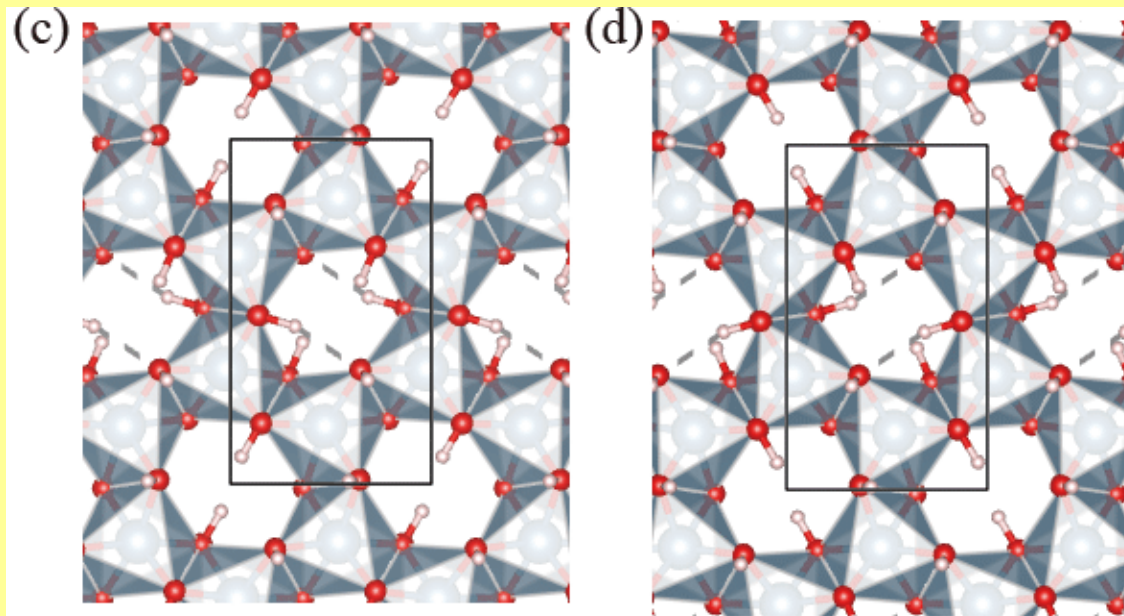
# Bayerite and Gibbsite - $\text{Al}(\text{OH})_3$



dioctahedral

Shares 3 edges

Opposite faces of a single layer  $\text{Al}(\text{OH})_3$  (A and B sides, respectively)

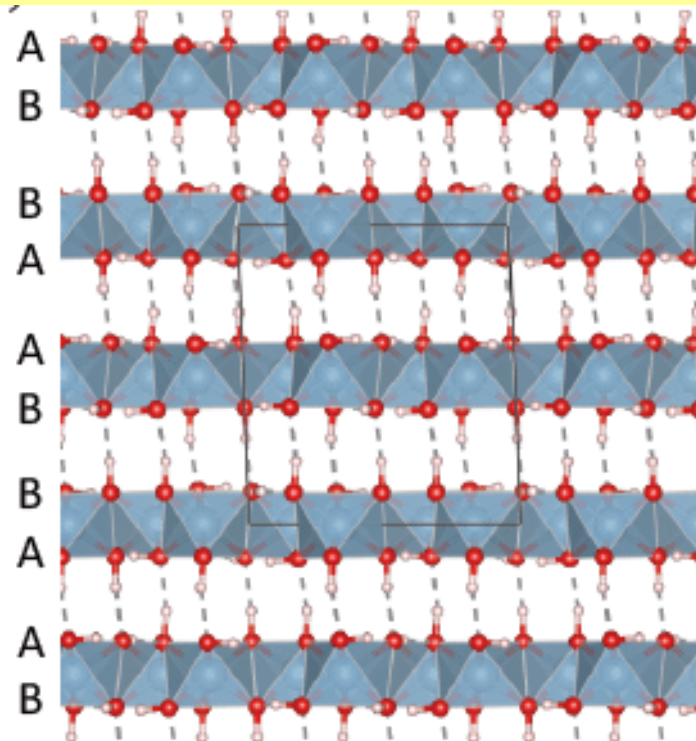
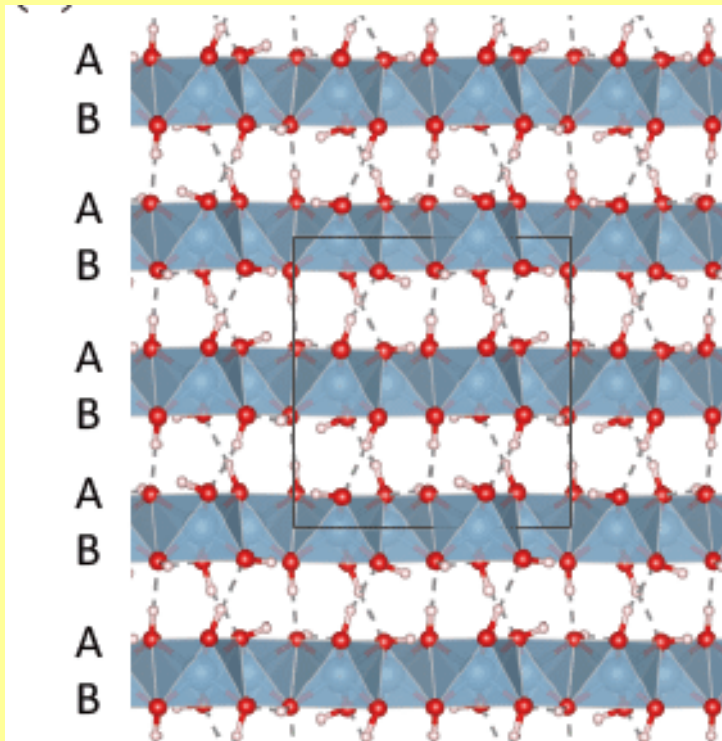


# Bayerite and Gibbsite - $\text{Al}(\text{OH})_3$

Bayerite and Gibbsite phases have **an identical single layer** as the building block

Bayerite is stacked  
by AB-AB sequence  
HCP of oxides

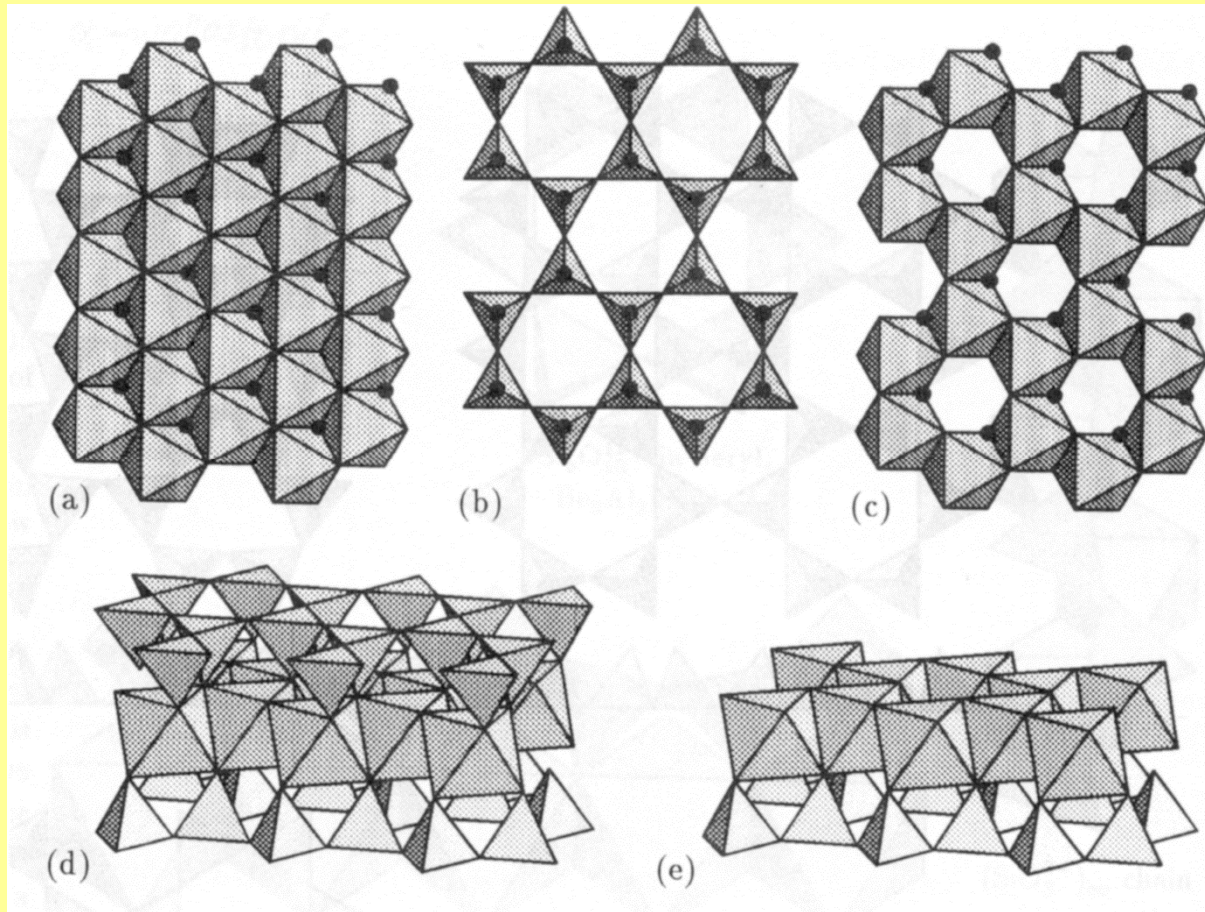
Gibbsite is stacked  
by AB-BA sequence  
CCP of oxides





# Clay Minerals

$[\text{Si}_4\text{O}_{10}]^{4-}$  tetrahedral sheet



$[\text{Mg}_6\text{O}_{12}]^{12-}$   
trioctahedral  
sheet of  
octahedral  
units

$[\text{Al}_4\text{O}_{12}]^{12-}$   
dioctahedral  
sheet of  
octahedral  
units

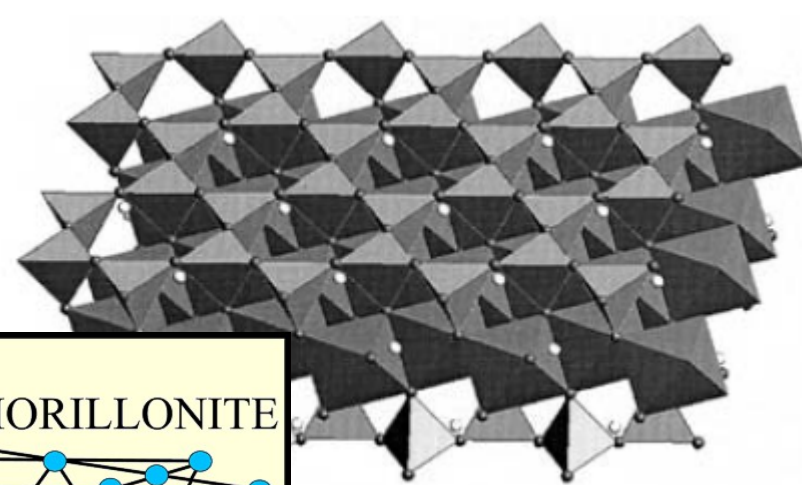
**2:1**

montmorillonite

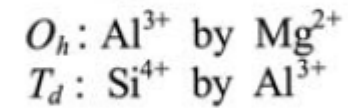
**1:1**

kaolinite

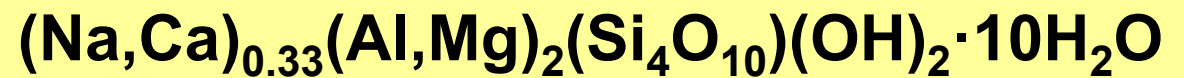
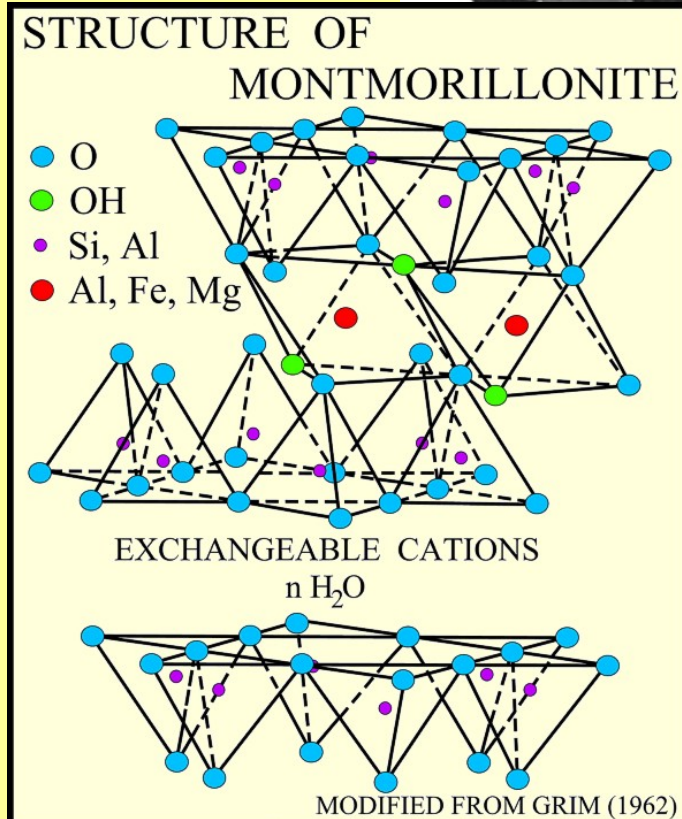
# Montmorillonite



- Dioctahedral clay mineral
- $T_d-O_h-T_d$  sandwich
- Isomorphous substitution



- Net negative charge
- Interlayer cations



# Phyllosilicate Minerals

Structure	Interlayer Charge	Trioctahedral (Y <sup>2+</sup> )	Diocahedral (Y <sup>3+</sup> )
O	~0	Brucite	Gibbsite
TO	~0	Serpentine	Kaolinite
TOT	~0	Talc	Pyrophyllite
TOT O TOT	~0	Chlorite	
TOT (X <sup>+</sup> , X <sup>2+</sup> , H <sub>2</sub> O) TOT expandable clay	~0.2-0.6	Saponite (smectite)	Montmorillonite (smectite)
	~0.6-0.9	Vermiculite	
TOT (X <sup>+</sup> , X <sup>2+</sup> ) TOT non-expandable clay	~0.5-0.75	-	Illite
TOT X <sup>+</sup> TOT true mica	1	Phlogopite, Biotite	Muscovite, Paragonite
TOT X <sup>2+</sup> TOT brittle mica	2	Clintonite	Margarite

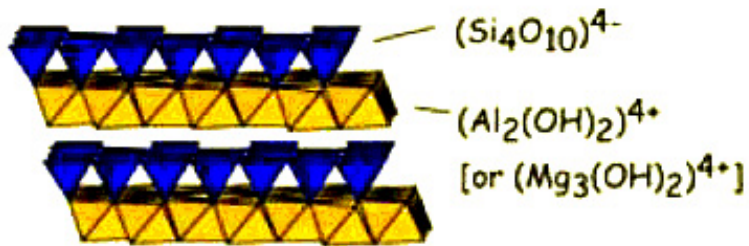
**T = tetrahedral sheet**  
**O = octahedral sheet**



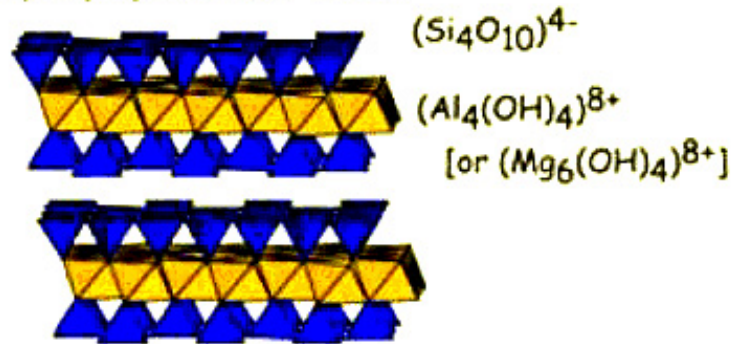


# Phyllosilicate Minerals

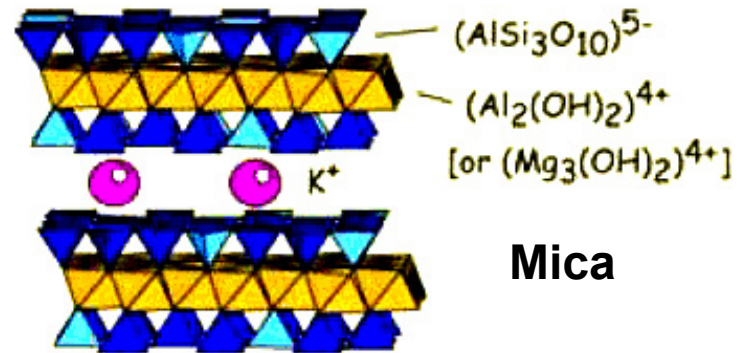
Kaolinite (or Antigorite)



Pyrophyllite (or Talc)

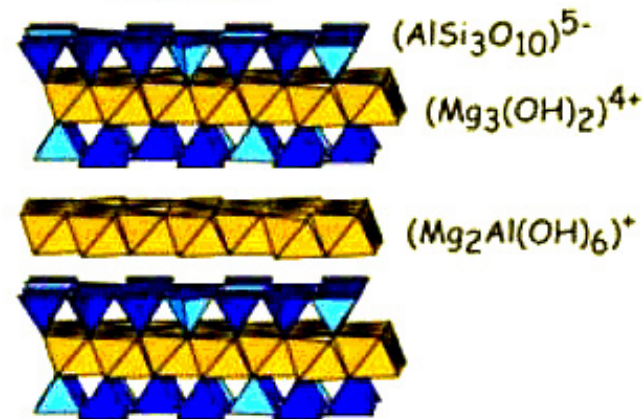


Muscovite (or Phlogopite)



**Mica**

Chlorite





# Layered Double Hydroxides

The layered structure of LDH is closely related to brucite  $\text{Mg}(\text{OH})_2$

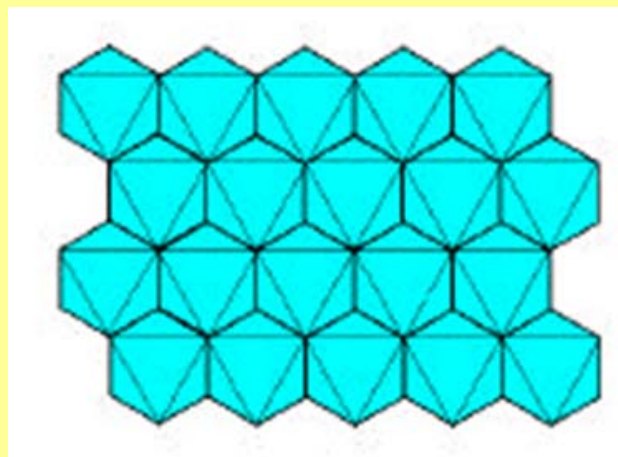
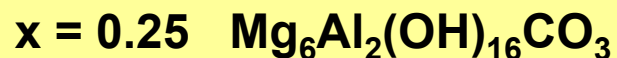
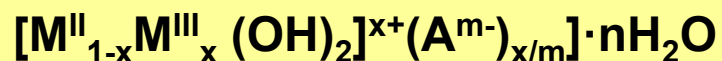
A brucite layer,  $\text{Mg}^{2+}$  ions octahedrally surrounded by six  $\text{OH}^-$  the octahedra share 6 edges and form an infinite two-dimensional layer the brucite-like layers stack on top of one another either rhombohedral (3R) or hexagonal (2H) sequence

Natural mineral

Hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$  - 3R stacking

Brucite layers,  $\text{Mg}^{2+}$  substituted partially by  $\text{Al}^{3+}$

Layers have positive charge



# Hydrotalcite

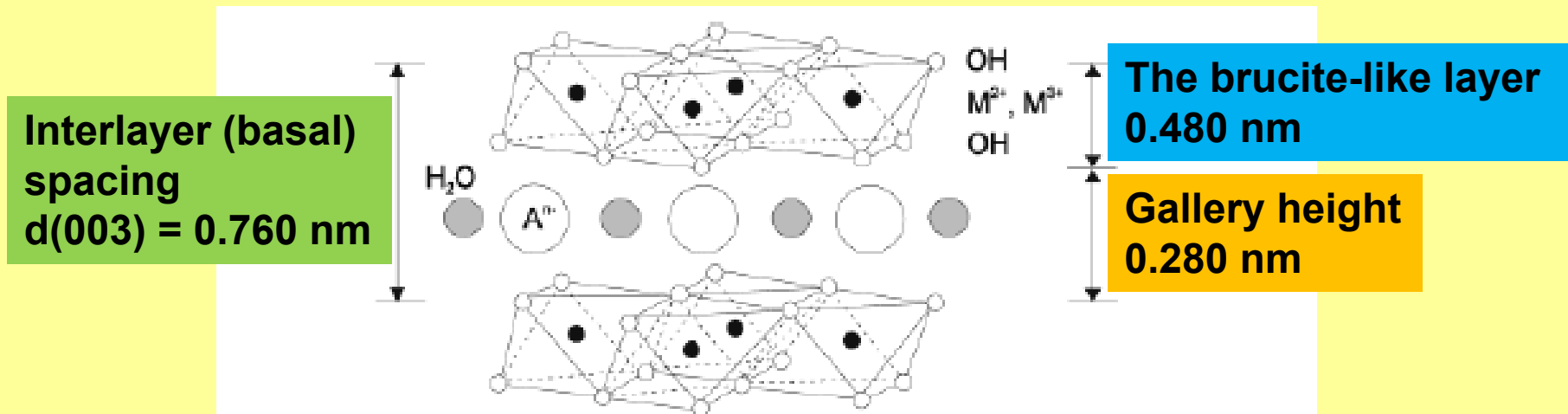
Hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$  - 3R stacking

Unit cell parameters:  $a = 0.305 \text{ nm}$       $c = 3 d(003) = 2.281 \text{ nm}$

The interlayer spacing:  $d(003) = 0.760 \text{ nm}$

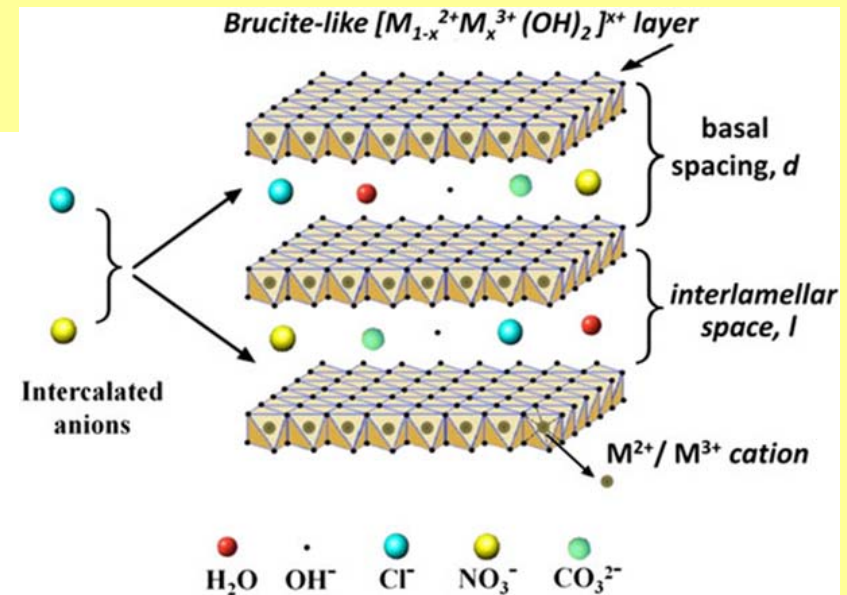
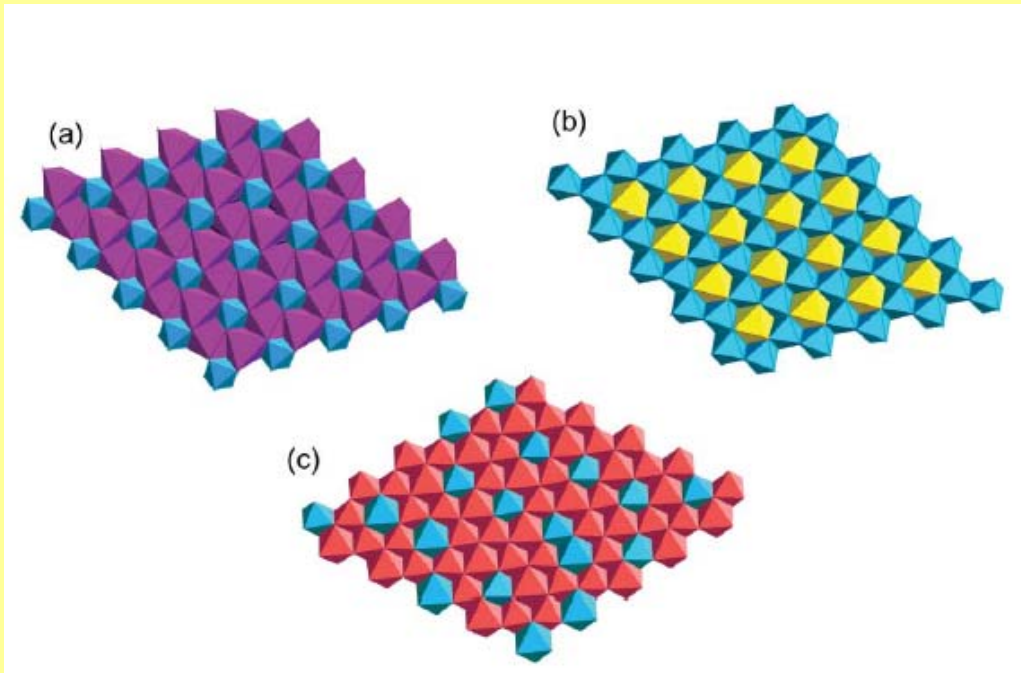
the spacing occupied by the anion (gallery height) =  $0.280 \text{ nm}$

a thickness of the brucite-like layer =  $0.480 \text{ nm}$



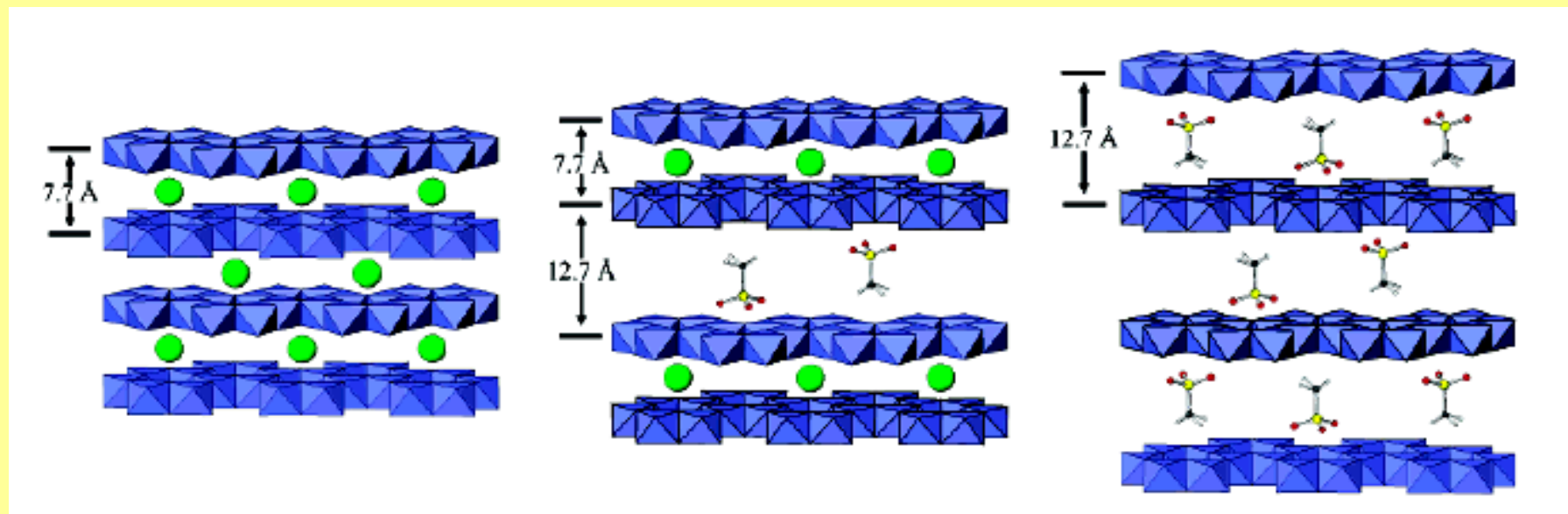
# Layered Double Hydroxides - Hydrotalcites

Brucite layers,  $M^{2+}$  substituted partially by  $M^{3+}$   
 Layers have positive charge



(a)  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (b)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}$  (c)  $[\text{Mg}_{2.25}\text{Al}_{0.75}(\text{OH})_6]\text{OH}$

## Intercalation to LDH



The intercalation of methylphosphonic acid (MPA) into Li/Al LDH

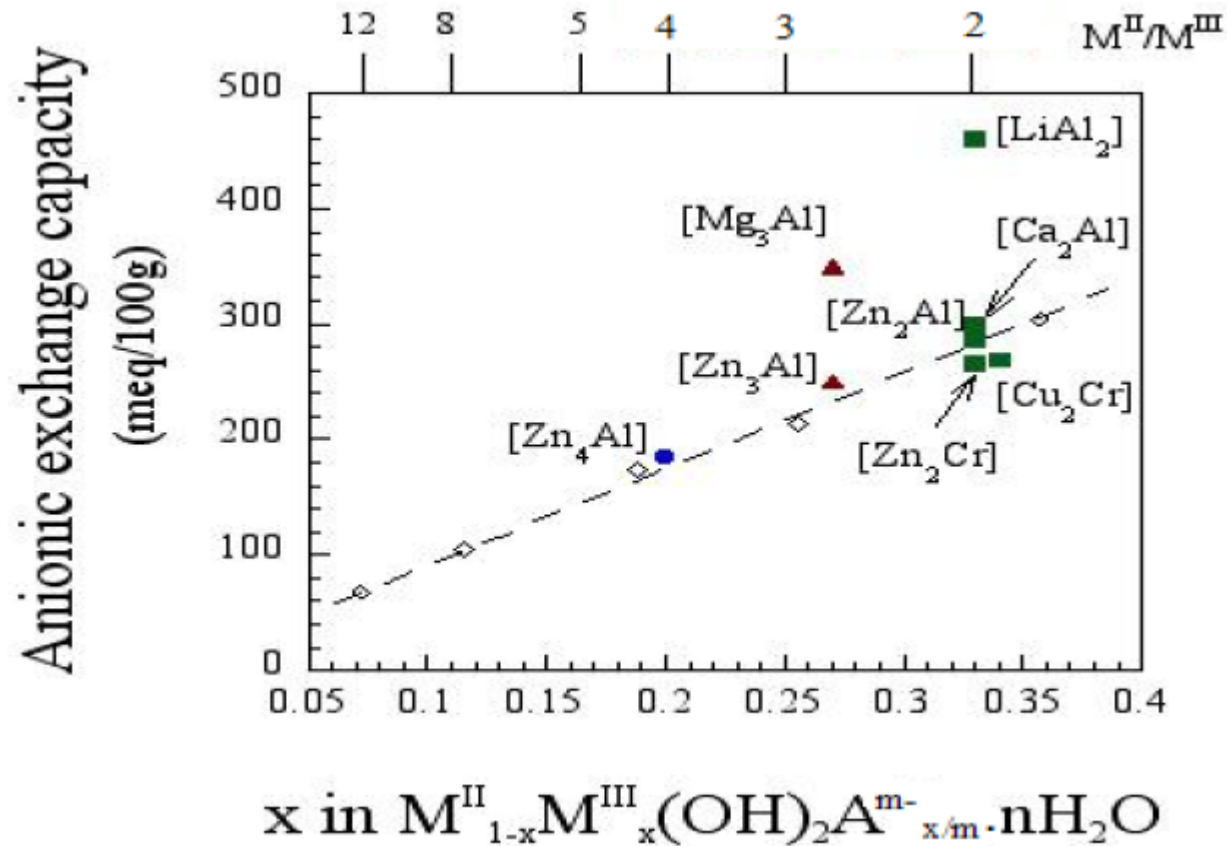
(a)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot\text{H}_2\text{O}$

(b) second-stage intermediate, alternate layers occupied by Cl and MPA anions

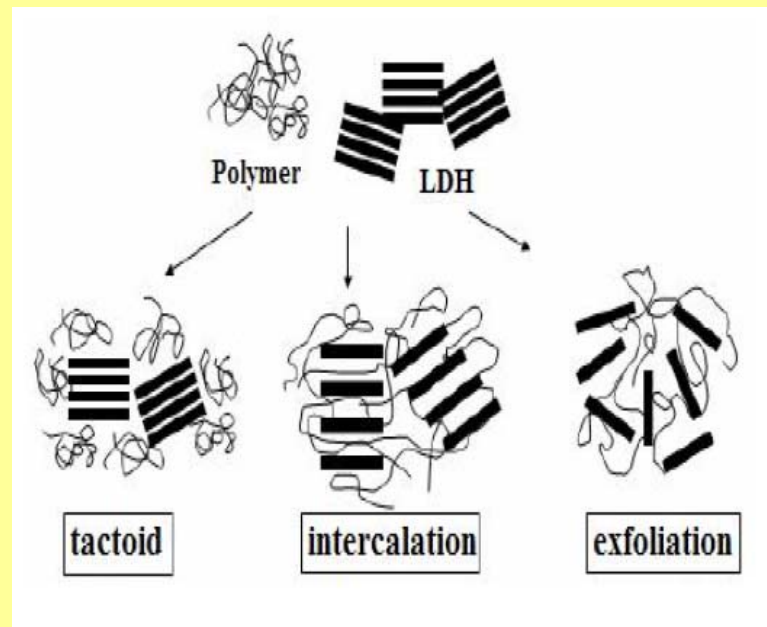
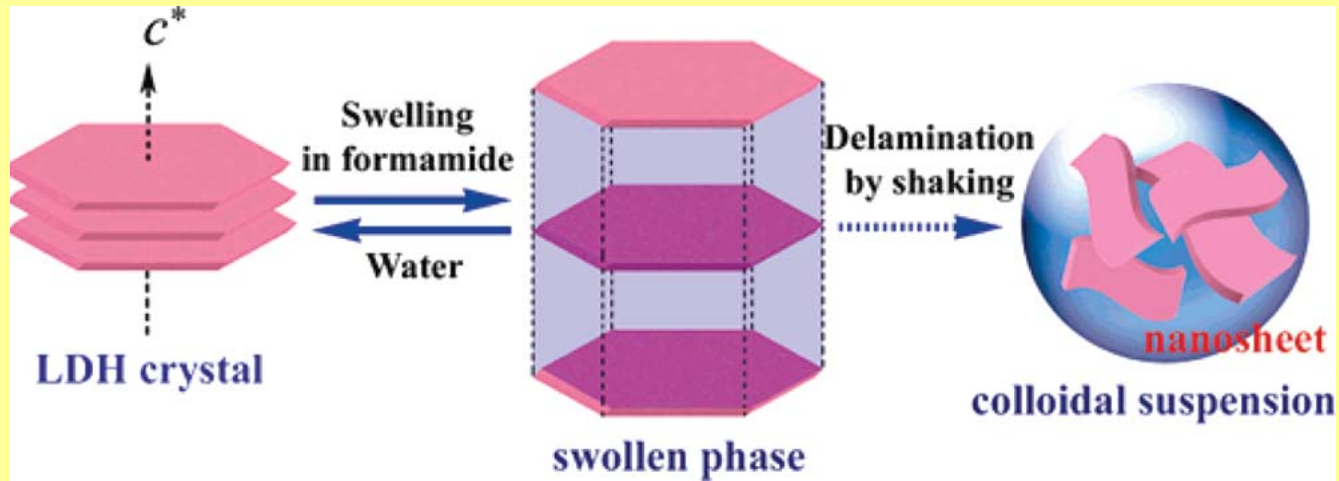
(c) first-stage product with all interlayer regions occupied by MPA



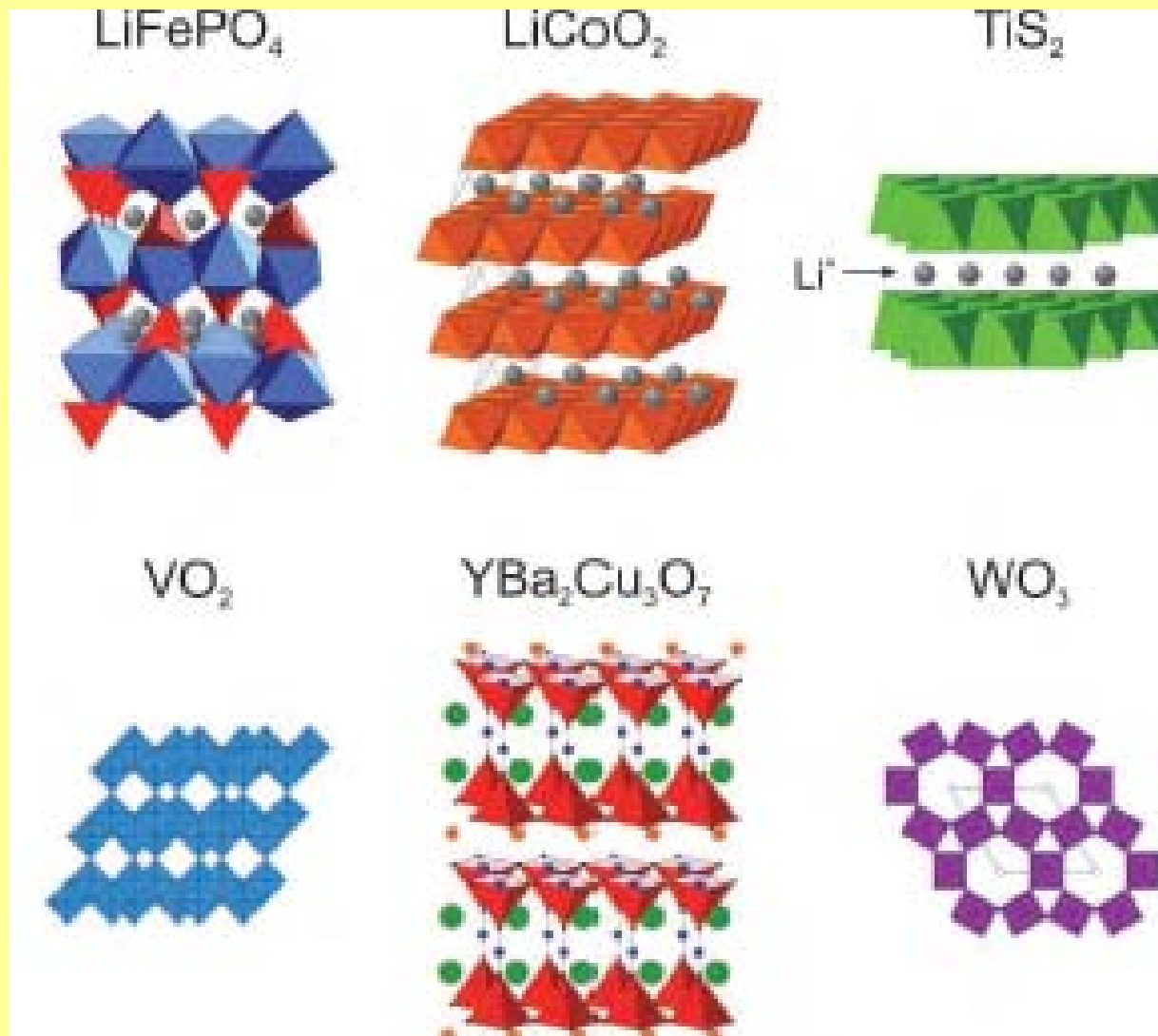
# The Anionic Exchange Capacity (AEC)



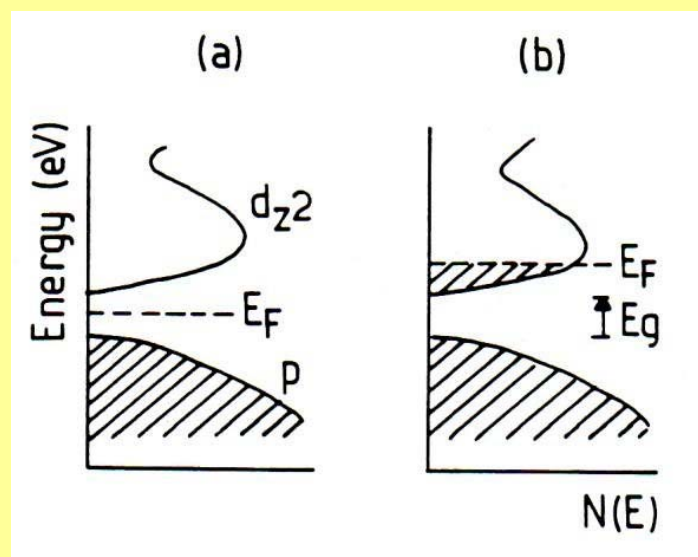
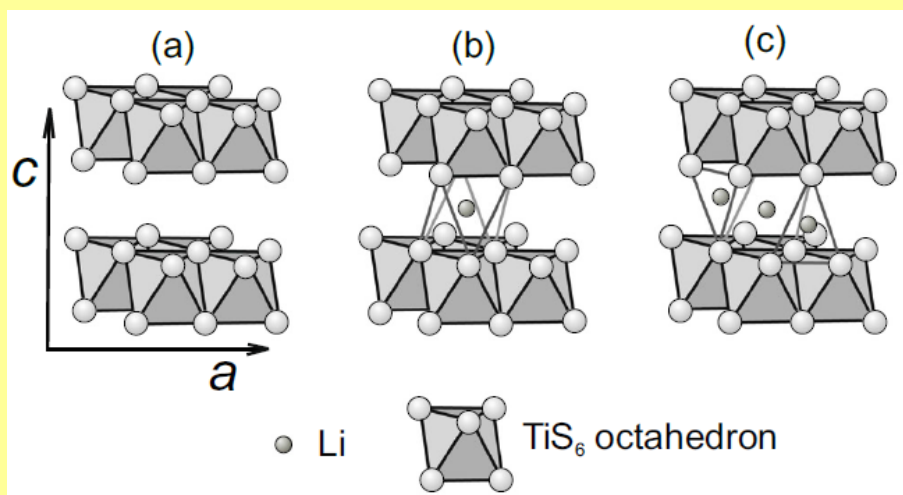
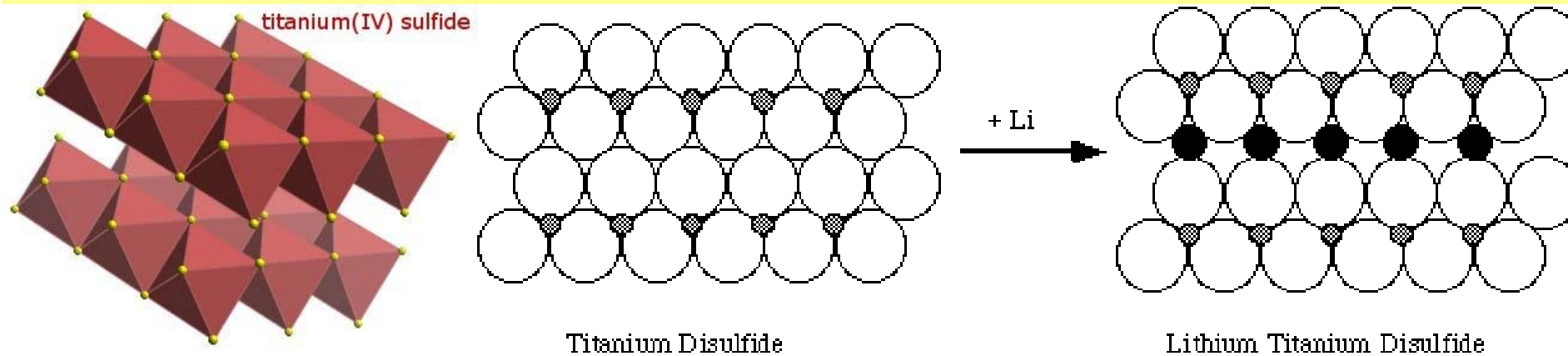
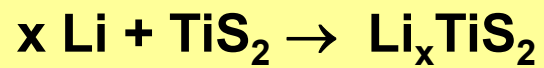
# LDH Composite Structures



# Li Intercalation Compounds

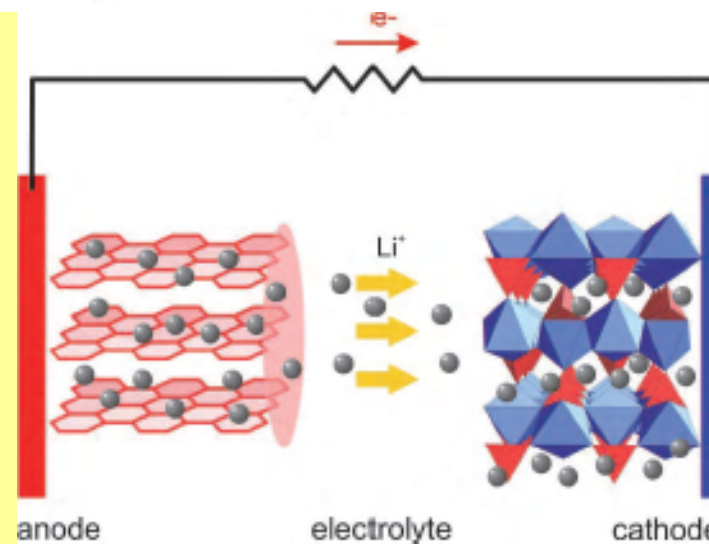
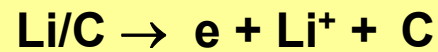
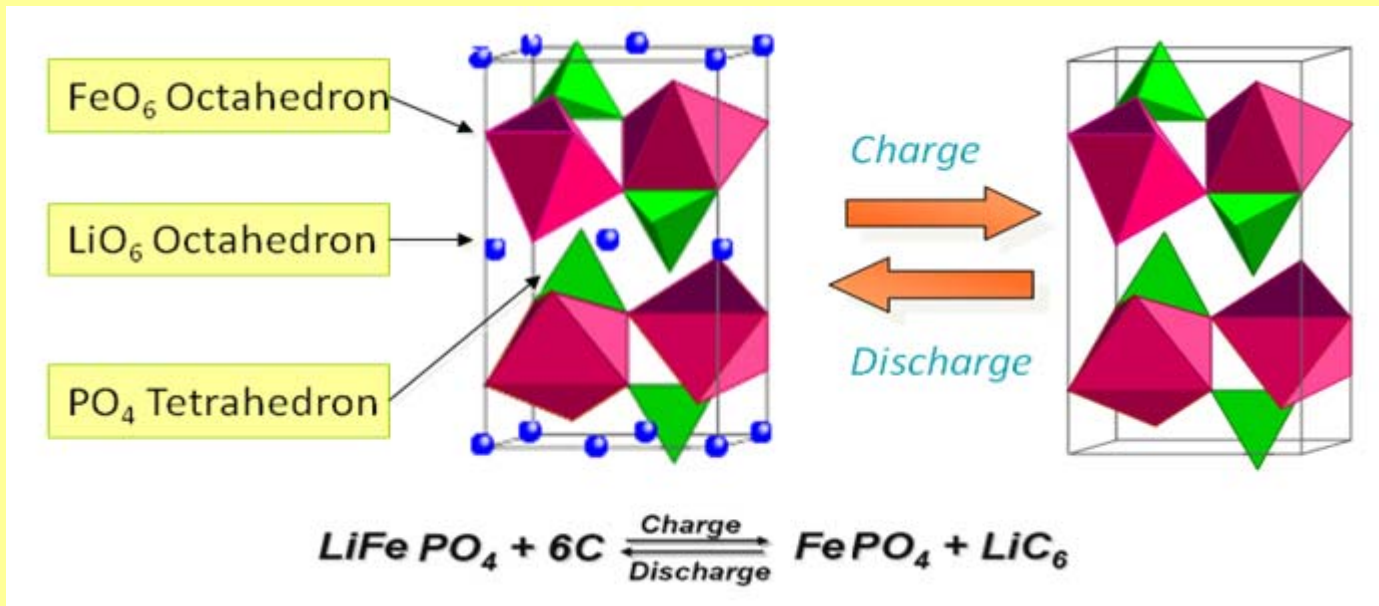


# Li Intercalation Compounds





# Li Intercalation Compounds

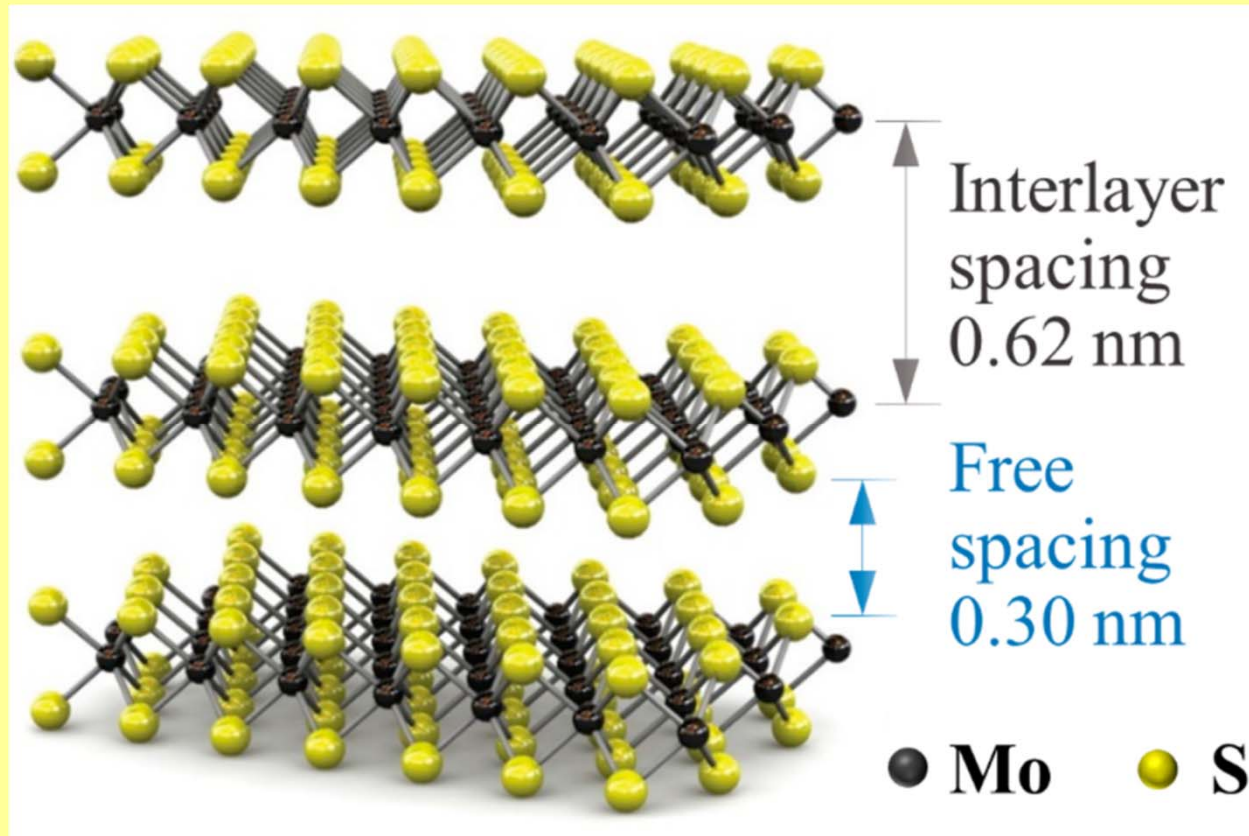


# Molybdenum Disulfide (MoS<sub>2</sub>)

Mineral molybdenite

Hydrodesulfurization catalyst  
at edges

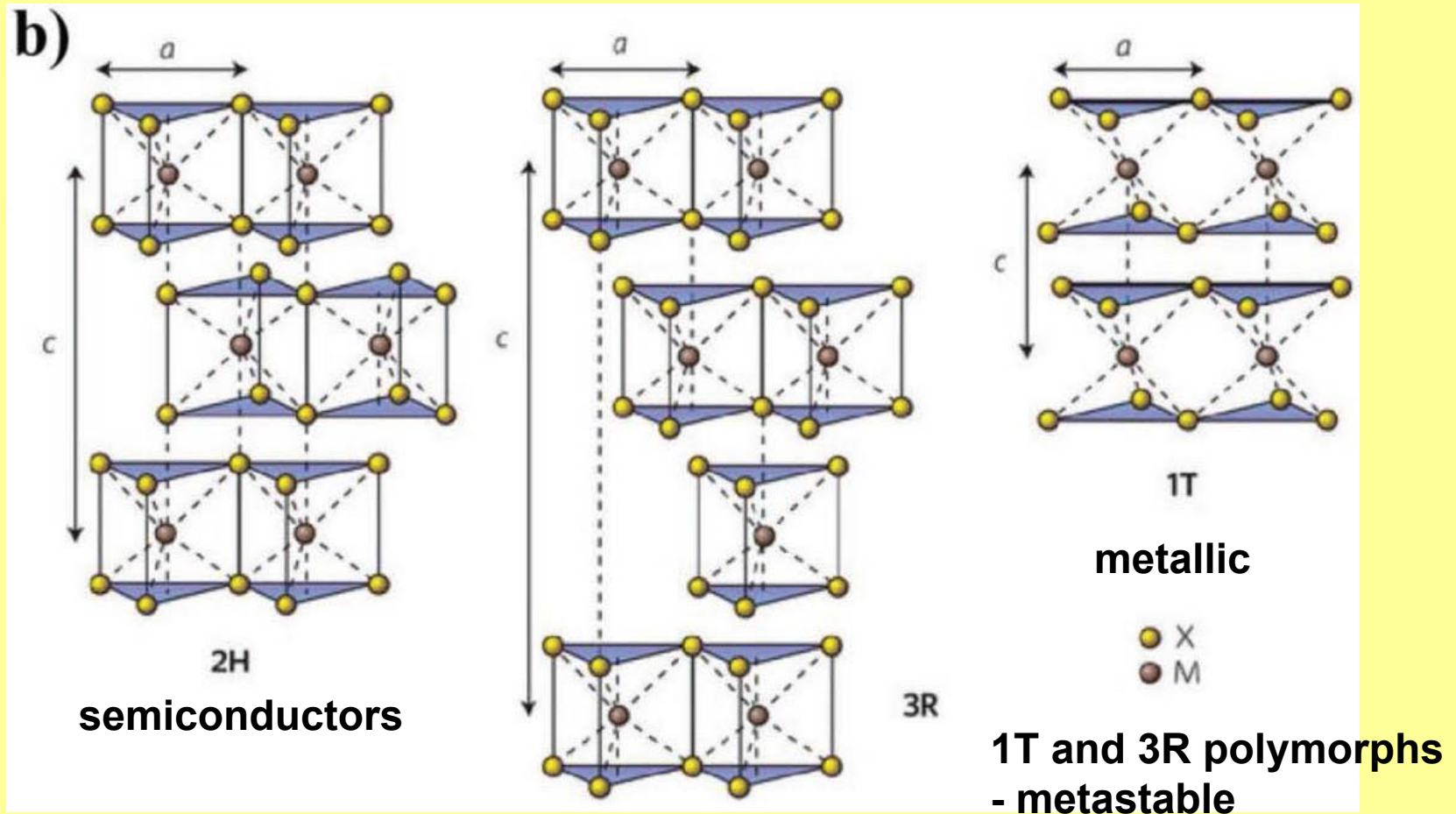
Lubricant



# Polymorphs of MoS<sub>2</sub>

MoS<sub>6</sub> trigonal prismatic

MoS<sub>6</sub> octahedral



2H phase - thermodynamically stable

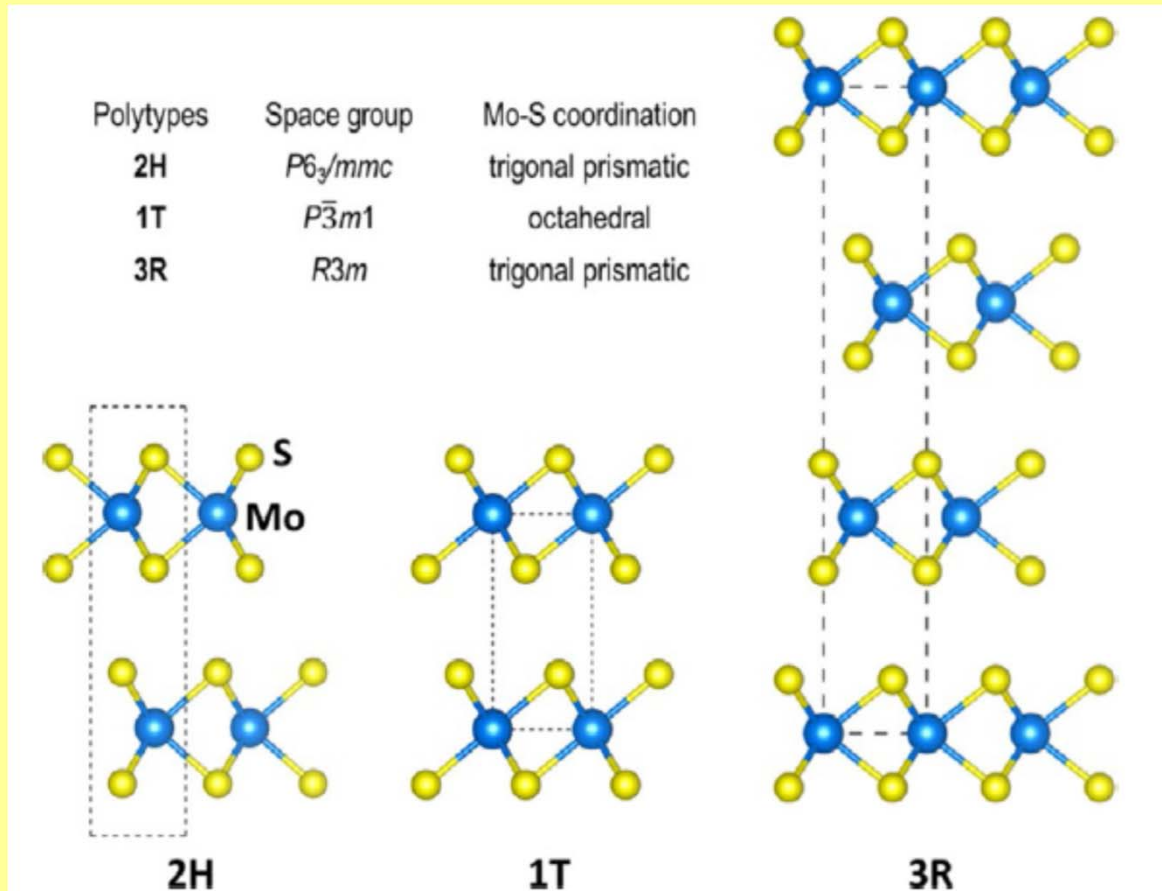
# Polymorphs of MoS<sub>2</sub>

2H, 3R - MoS<sub>6</sub> trigonal prismatic

1T - MoS<sub>6</sub> octahedral

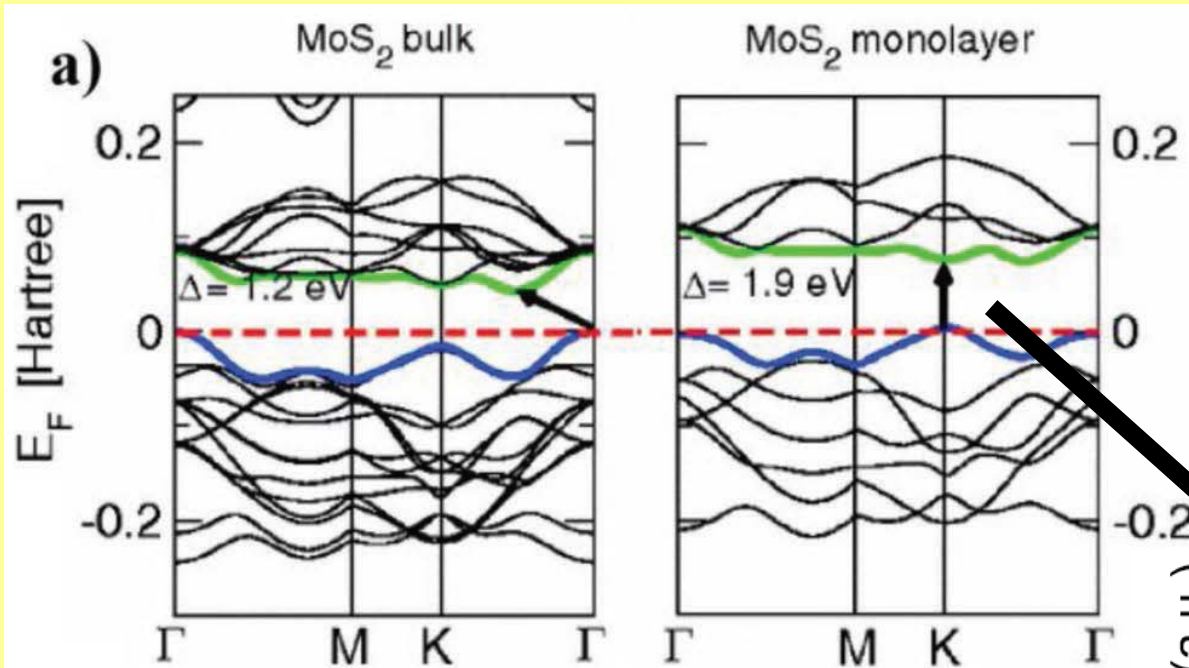
Digit = number of monolayers in the unit cell

Letters: T = trigonal, H = hexagonal, R = rhombohedral





# Monolayer of Molybdenum Disulfide



An indirect band gap  
1.29 eV

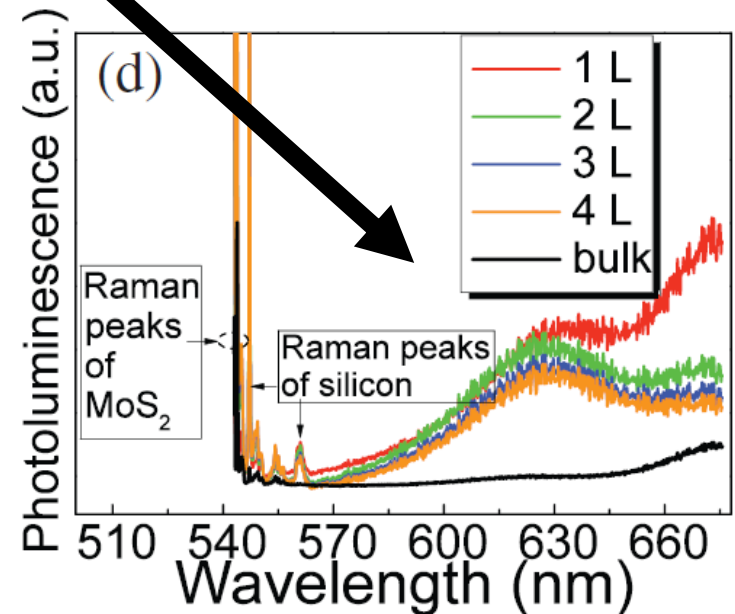
A direct band gap  
1.9 eV (2H)

Conduction band

Fermi level

Valence band

photoluminescence



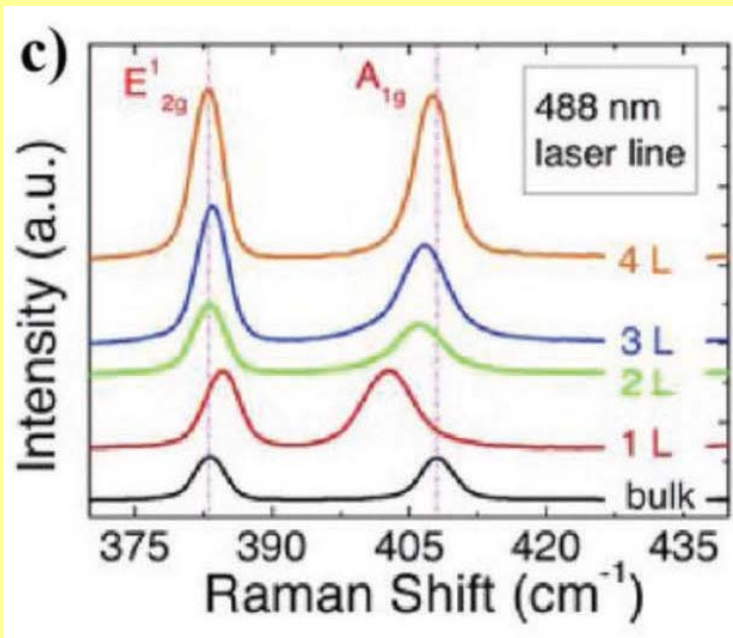
# Monolayer of Molybdenum Disulfide

MoS<sub>2</sub> nanosheets - all sulfur atoms exposed on surfaces

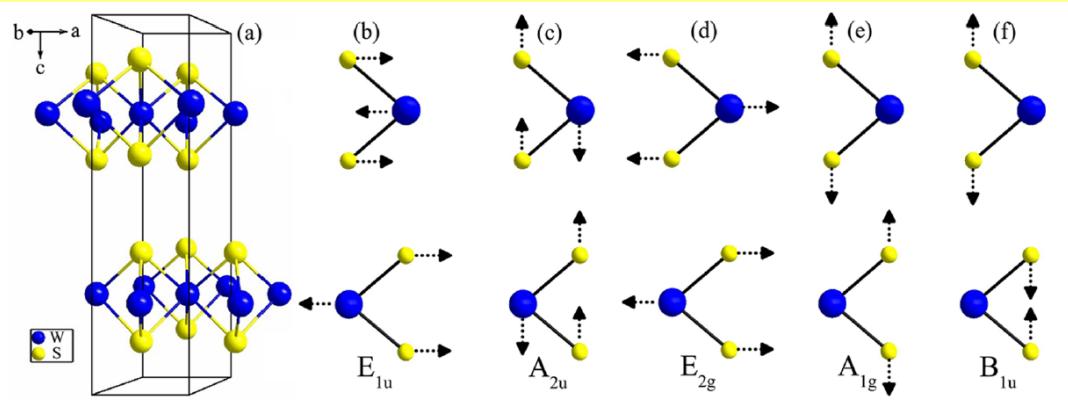
S = a soft Lewis base - a high affinity for heavy metal ions (e.g., Hg<sup>2+</sup> and Ag<sup>+</sup>) = soft Lewis acids

MoS<sub>2</sub> nanosheets

- high adsorption capacity - abundant sulfur adsorption sites
- fast kinetics - easy access to adsorption sites

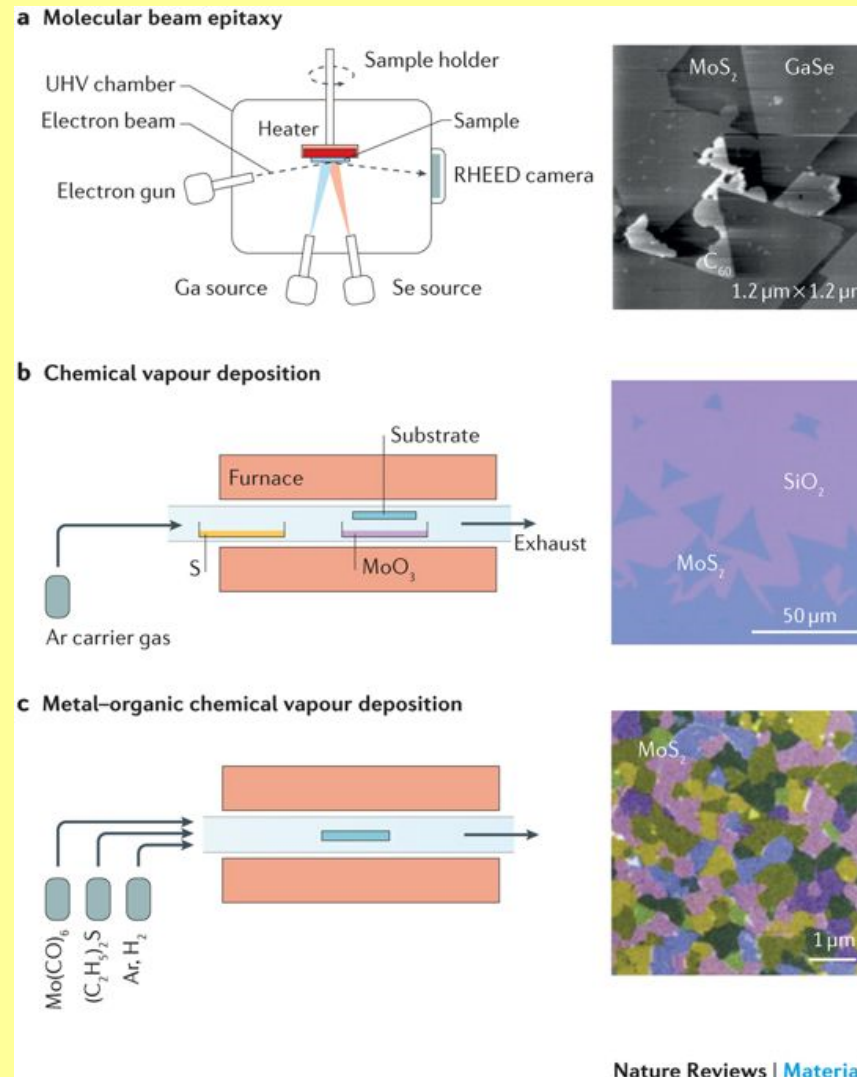


Frequency of A<sub>1g</sub> band is increasing while that of E<sub>2g</sub><sup>1</sup> is decreasing with increase in number of layers



(b,c) infrared and (d-f) Raman-active

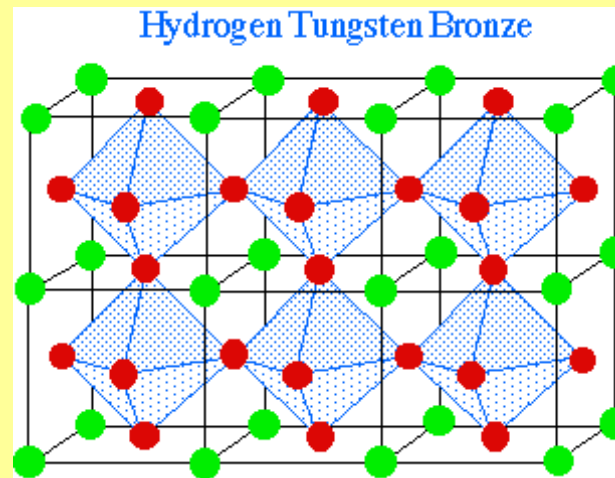
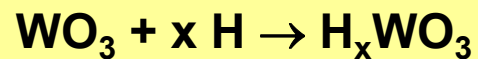
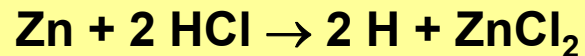
# Synthesis of Molybdenum Disulfide



# 3D Intercalation Compounds

## Tungsten trioxide $\text{WO}_3$

Structure =  $\text{WO}_6$  octahedra joined at their corners =  $\text{ReO}_3$   
= the perovskite structure of  $\text{CaTiO}_3$  with all the calcium sites vacant

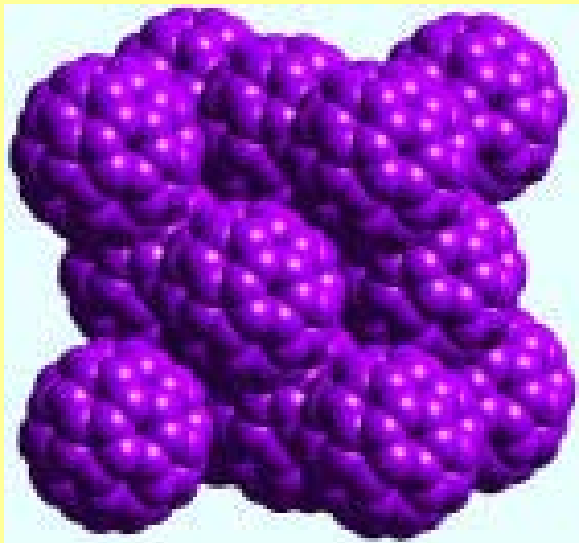
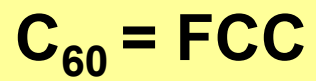


The color and conductivity changes are due to the intercalation of protons into the cavities in the  $\text{WO}_3$  structure, and the donation of their electrons to the conduction band of the  $\text{WO}_3$  matrix

The material behaves like a metal, with both its conductivity and color being derived from free electron behavior

The coloration reaction used in electrochromic displays for sun glasses, rear view mirrors in cars

# 0D Intercalation Compounds



Octahedral voids (N)  
Tetrahedral voids (2N)

K

