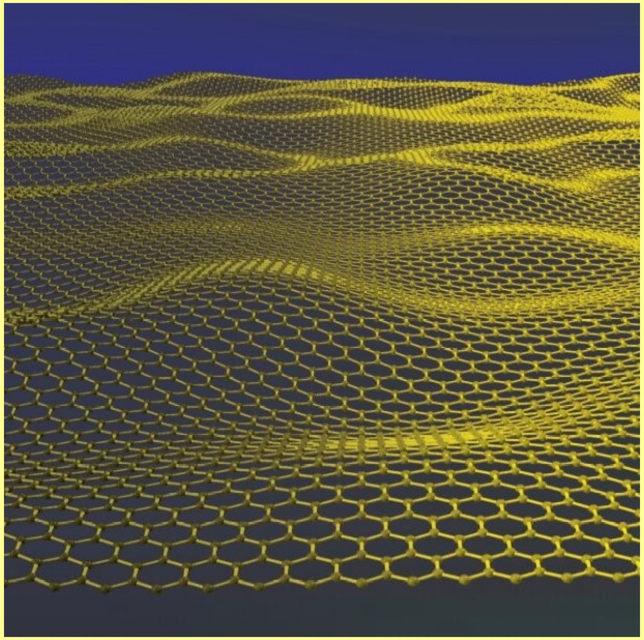
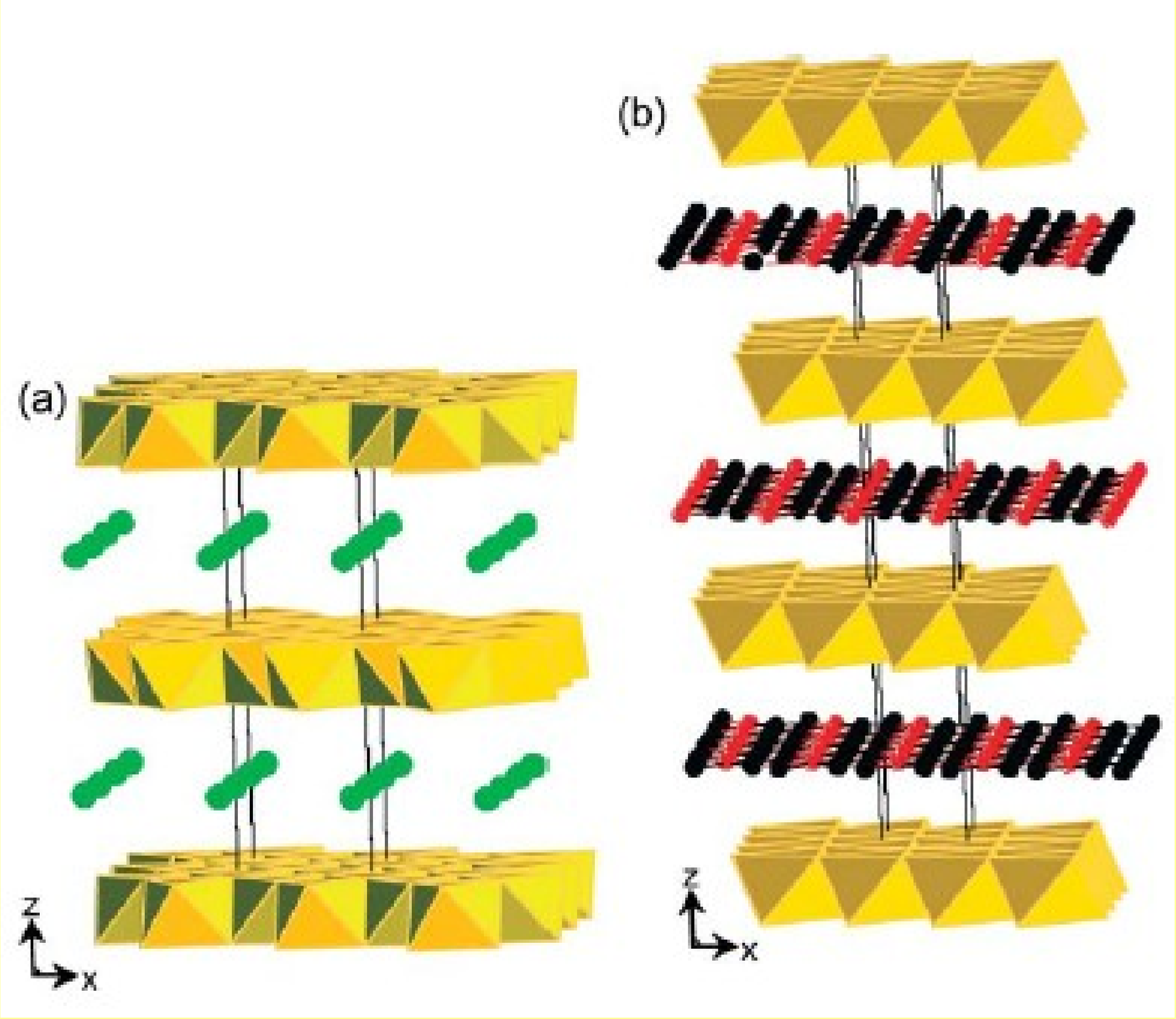
Layered Compounds

Two-dimensional layers



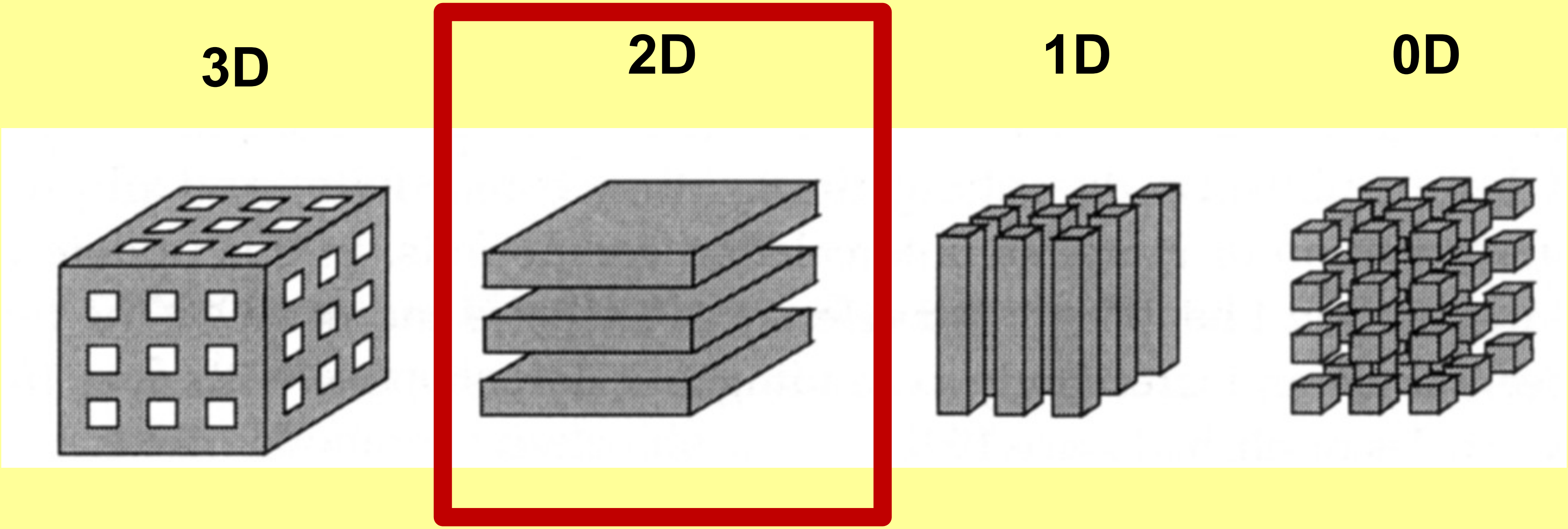
- Graphite and Graphene
- Clay Minerals
- Layered Double Hydroxides (LDHs)
- Layered Zirconium Phosphates and Phosphonates
- Layered Metal Oxides
- Layered Metal Chalcogenides - TiS_2, MPS_3 (M = V, Mn, Fe, Co, Ni, Zn)
- Alkali Silicates and Crystalline Silicic Acids

Layered Compounds



Host-Guest Structures

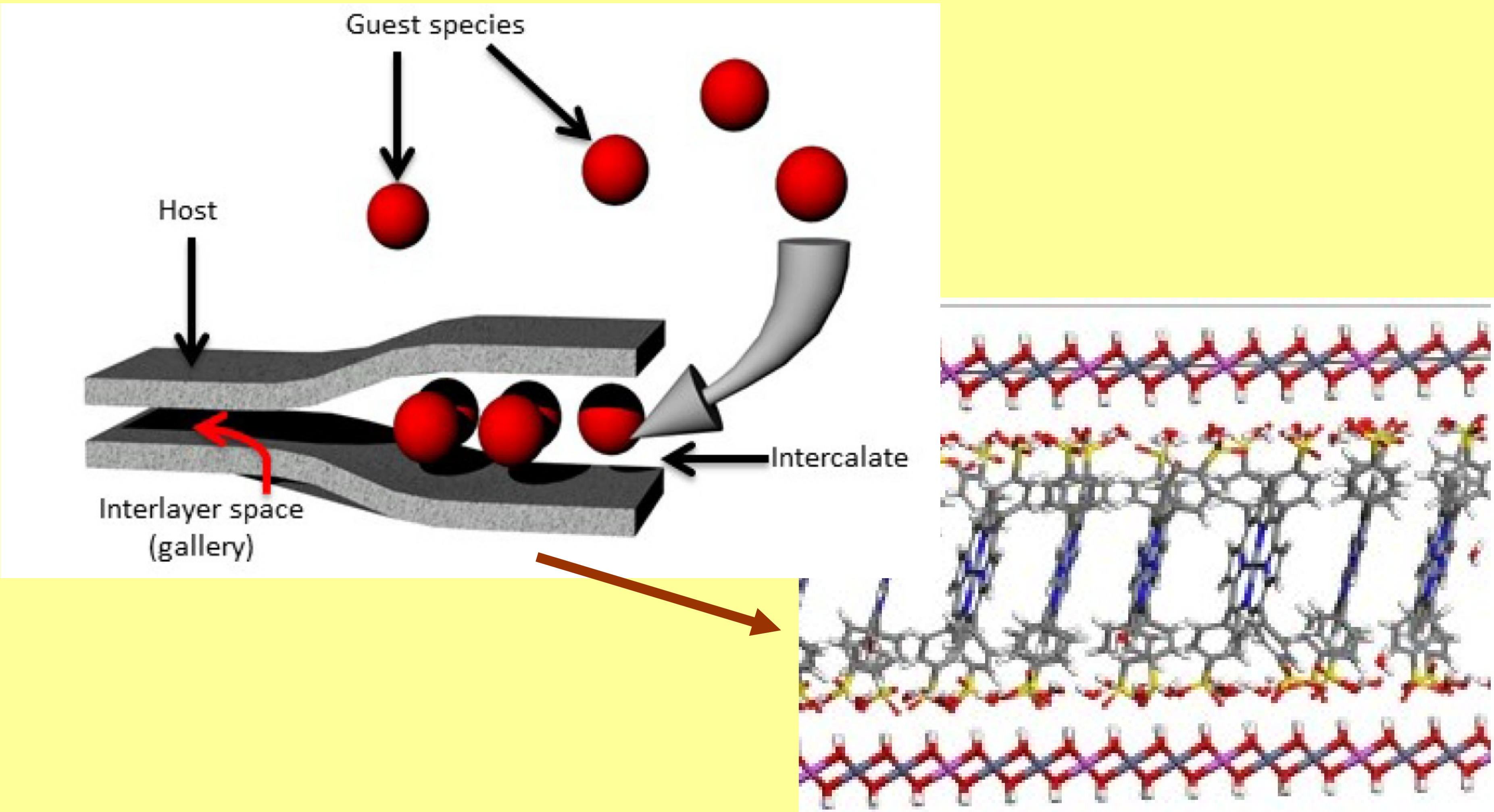
Host dimensionality



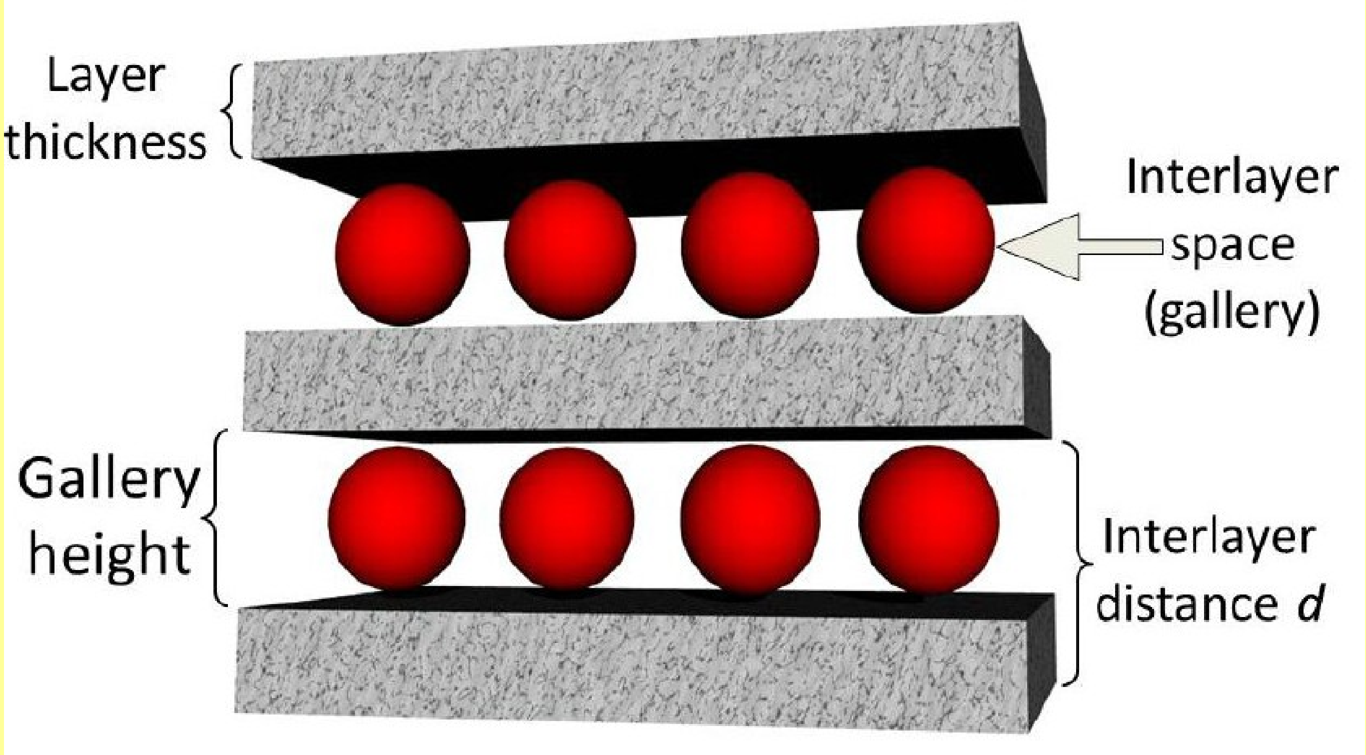
TOPOTACTIC SOLID-STATE REACTIONS = modifying existing solid state structures while maintaining the integrity of the overall structure

Intercalation

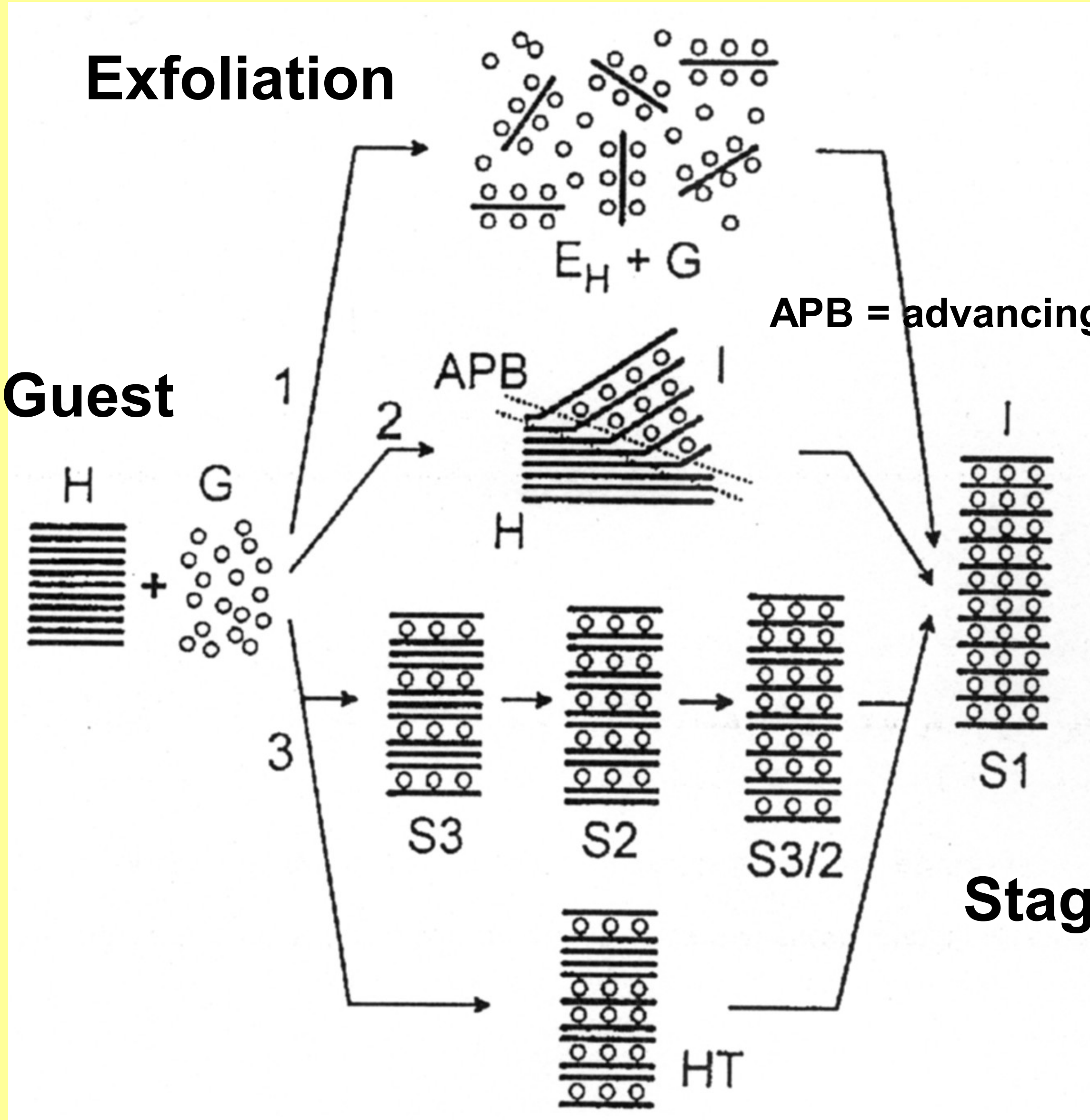
Intercalation Insertion of molecules between layers



Intercalation



Intercalation



Exfoliation

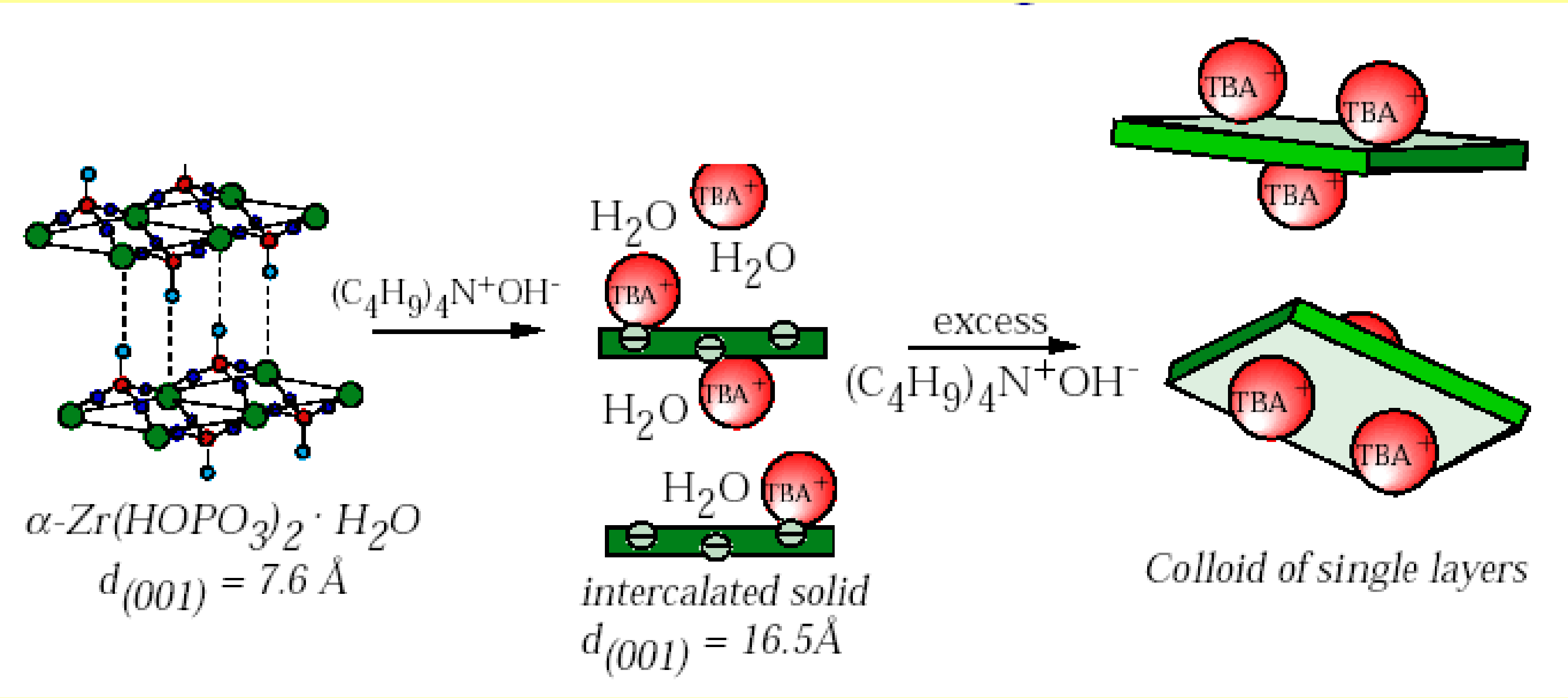
APB = advancing phase boundary

Host + Guest

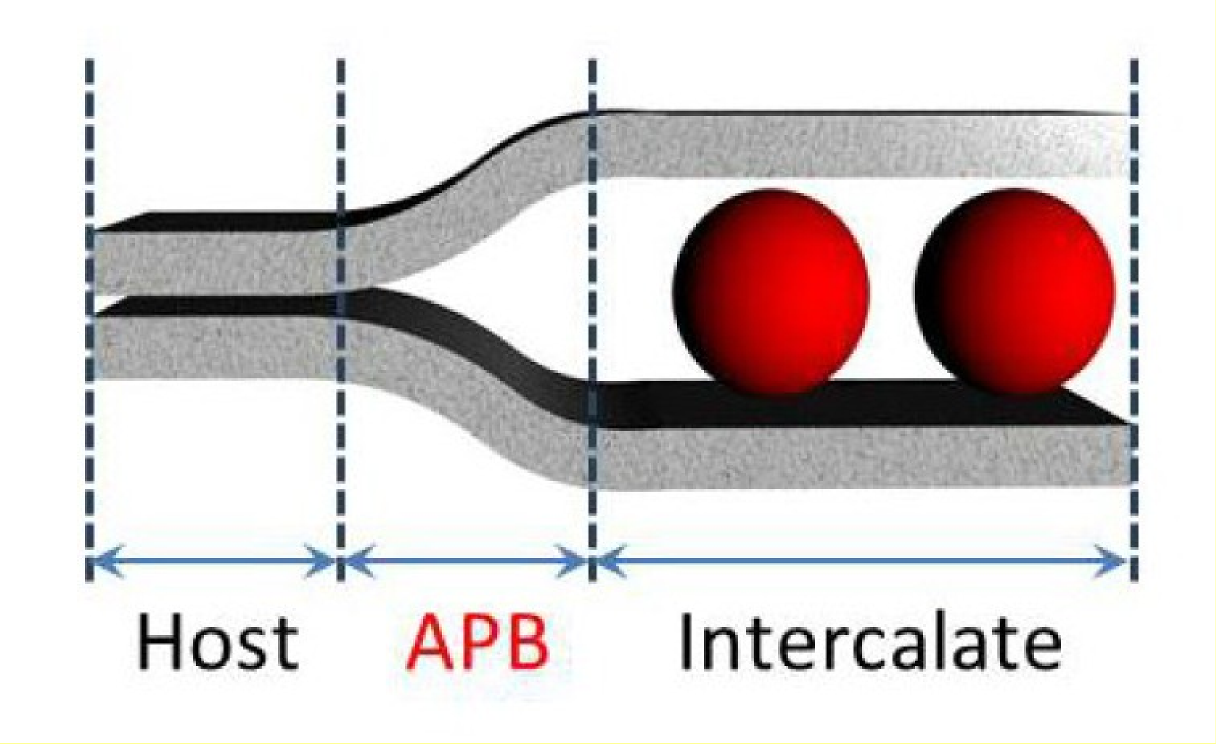
Intercalate

Staging

Exfoliation

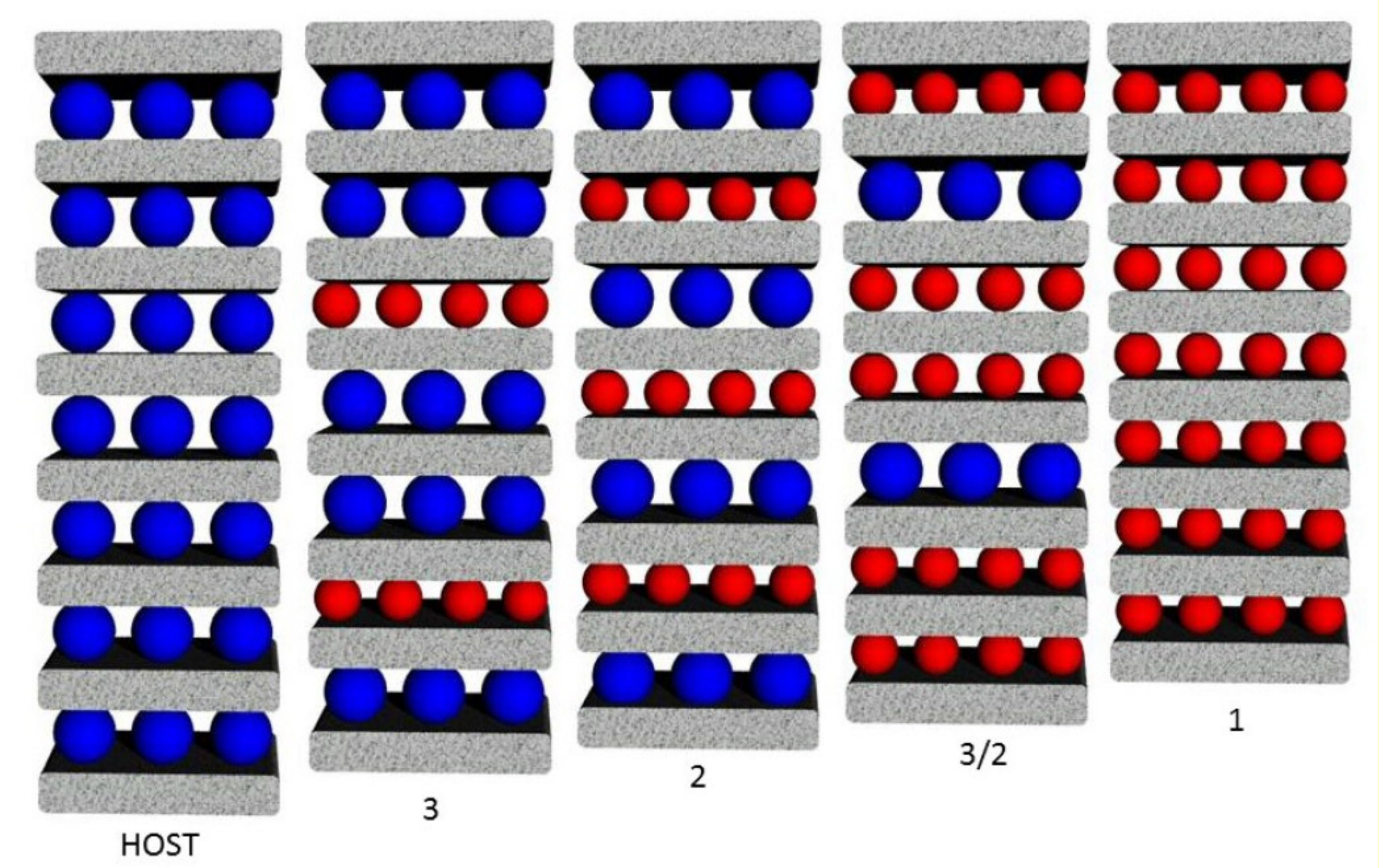


APB = advancing phase boundary

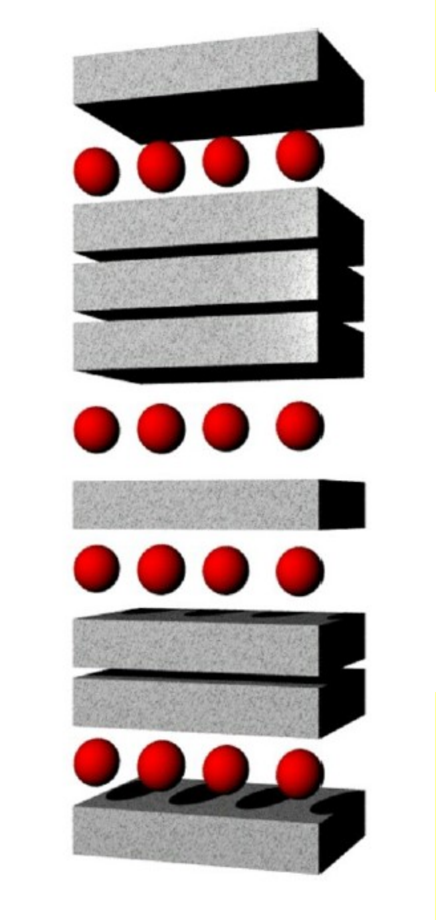


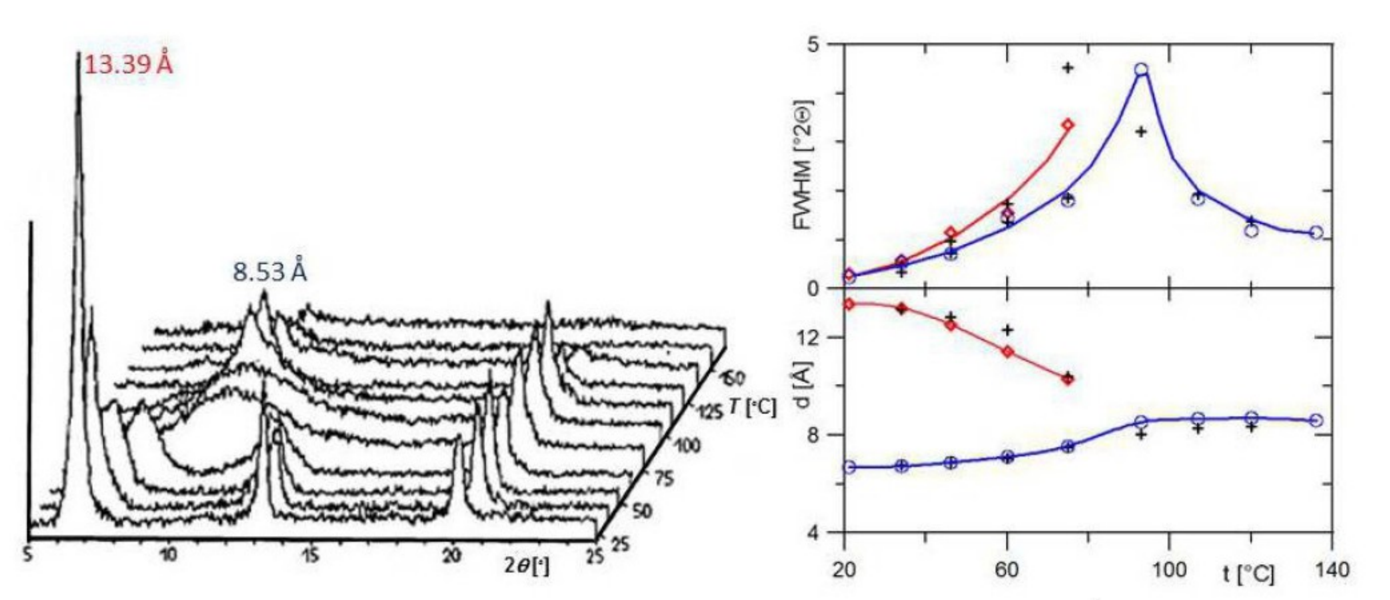
APB = advancing phase boundary

Staging



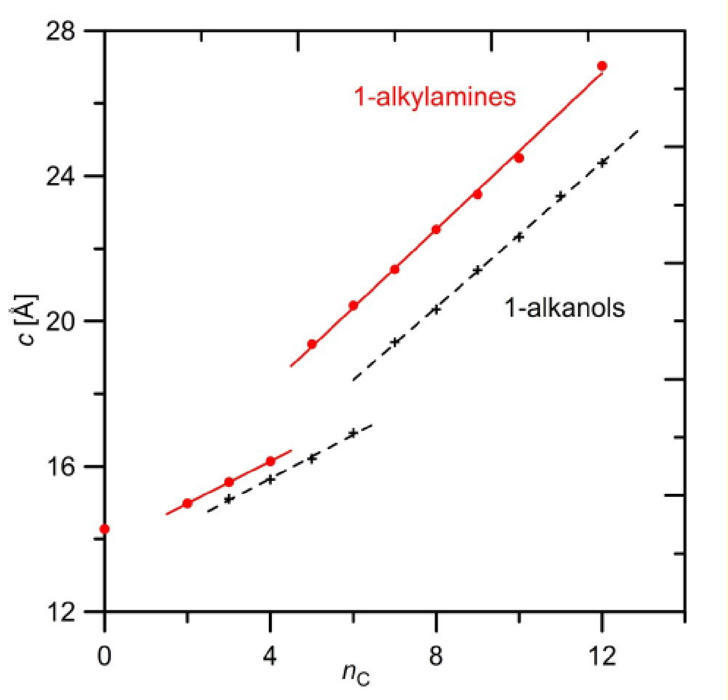
Hendricks-Teller effect

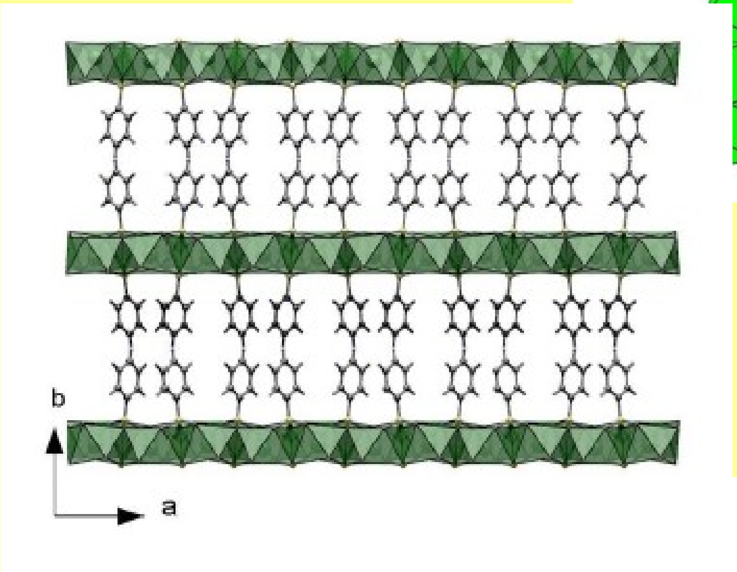


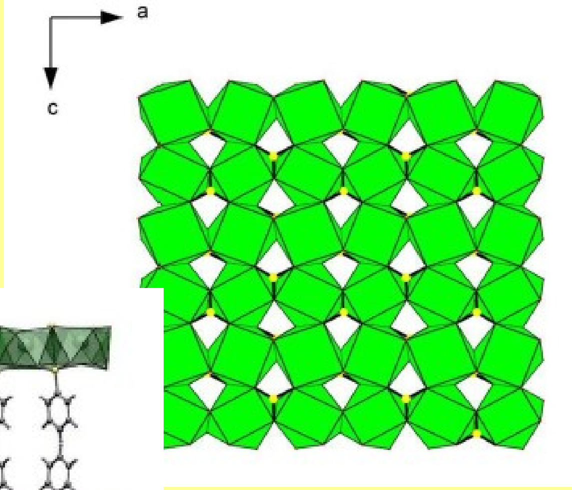


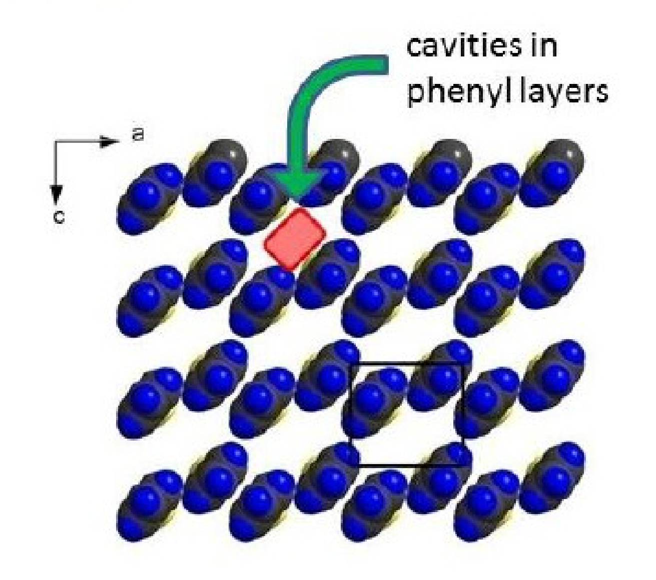
HT = galleries are filled randomly

Intercalation





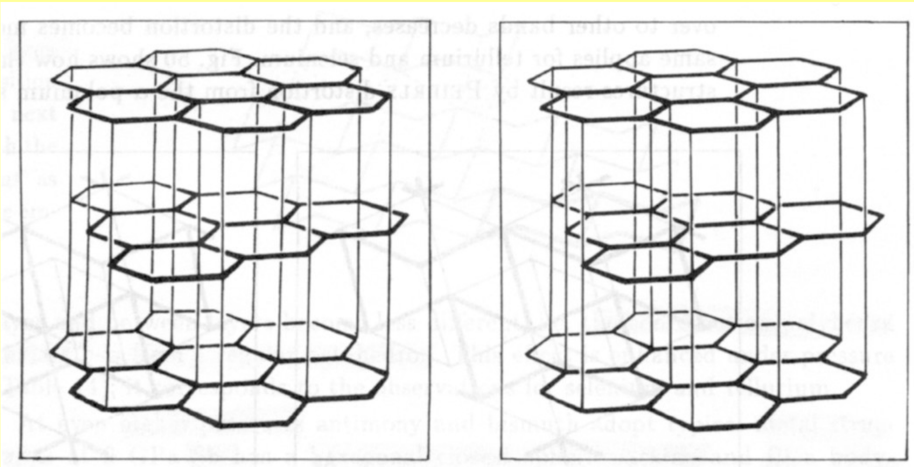


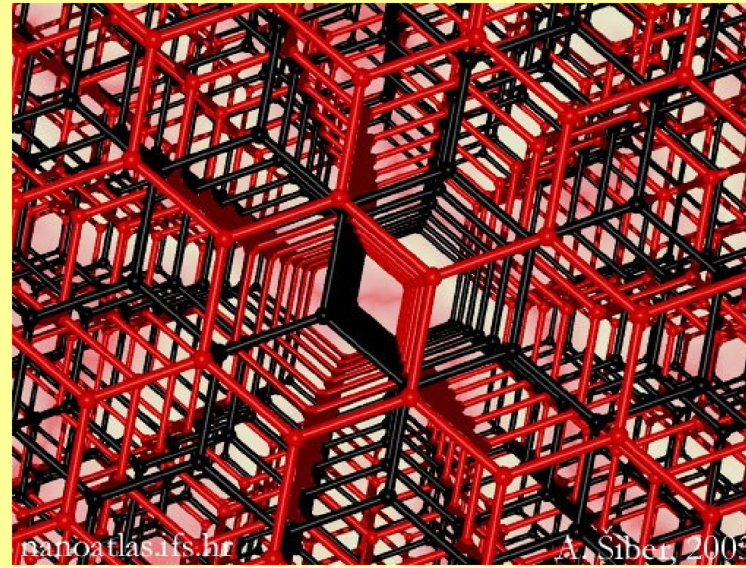


Dependence of the basal spacing of the intercalates of the alkylamines (circles) and alkanols (crosses) on the number of carbon atoms n_C in $SrC_6H_5PO_3 \cdot 2H_2O$

Graphite

ABABAB





Graphite sp^2 sigma-bonding in-plane p-p-bonding out of plane
Hexagonal graphite = two-layer ABAB stacking sequence

SALCAOs of the p-p-type 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 conductivity

Graphite

GRAPHITE INTERCALATION

G (s) + K (melt or vapour) → C_8K (bronze)

C_8K (vacuum, heat) → $C_{24}K$ → $C_{36}K$ → $C_{48}K$ → $C_{60}K$

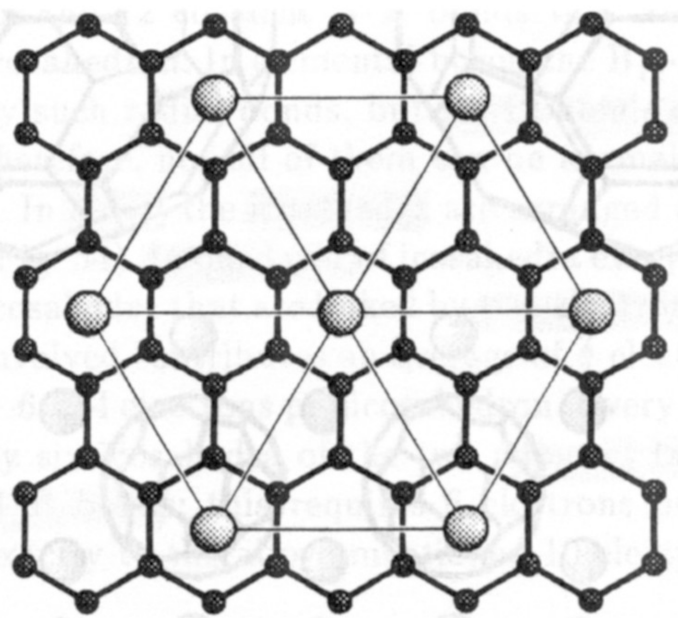
C_8K potassium graphite ordered structure

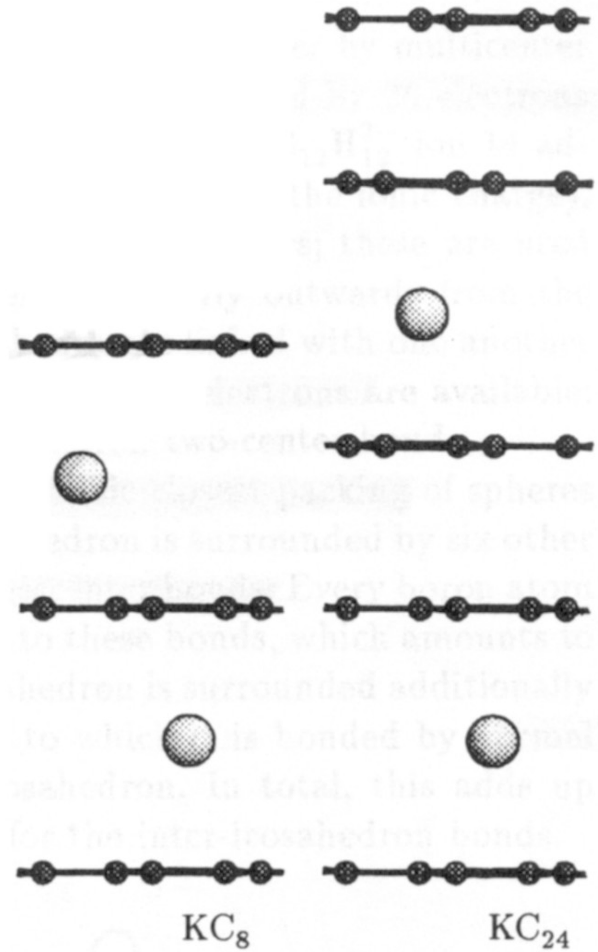
Ordered K guests between the sheets, K to G charge transfer

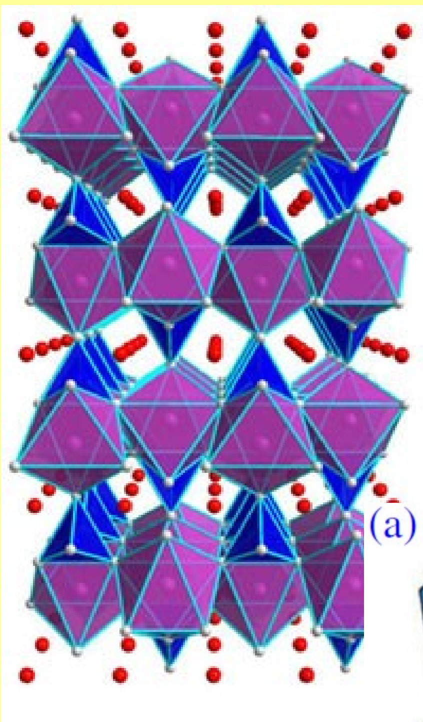
AAAA stacking sequence
reduction of graphite sheets, electrons enter CB
K nesting between parallel eclipsed hexagonal planar carbon six-rings

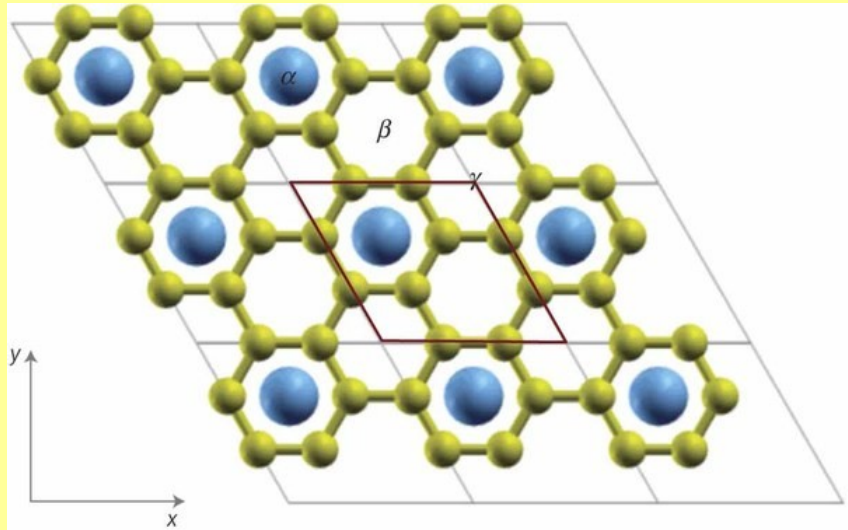
Graphite

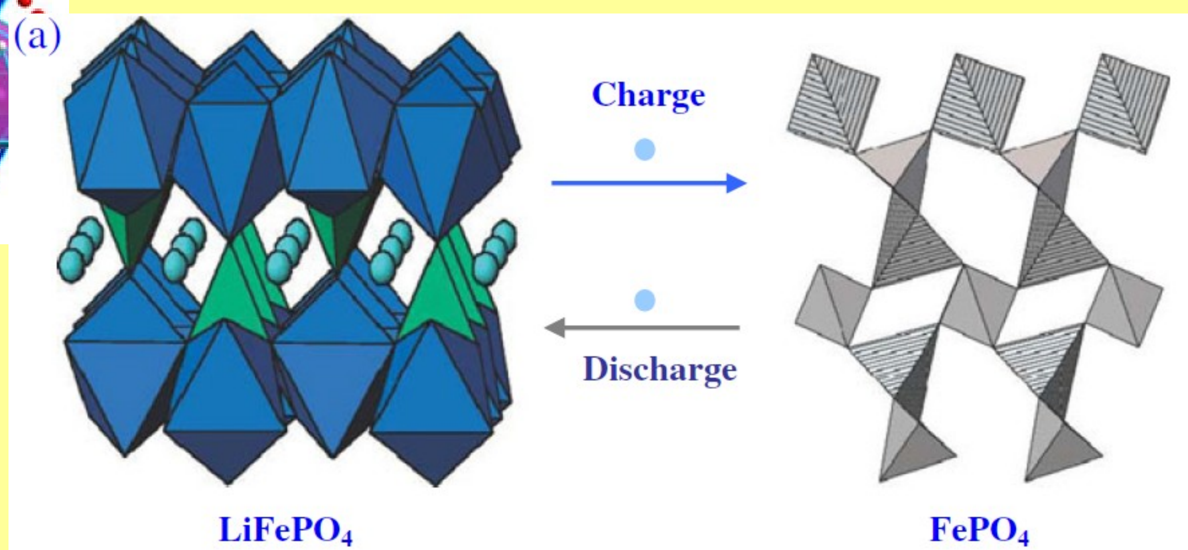
Intercalates



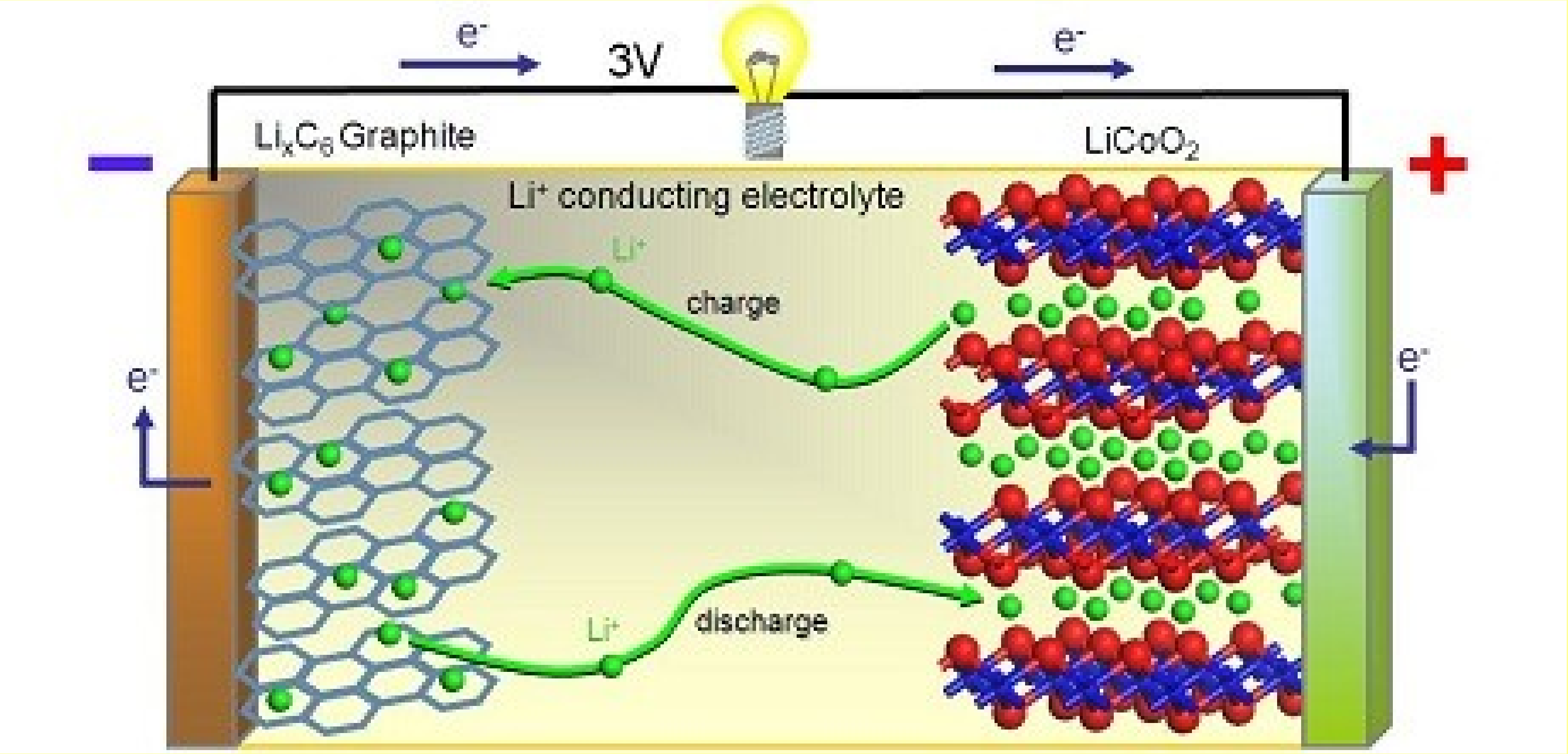





α
β
γ
y
x


(a)
Charge
Discharge
$LiFePO_4$
$FePO_4$

Li-ion Cells



e-
3V
e-
LixC6 Graphite
LiCoO2
Li+ conducting electrolyte
Li+
charge
e-
e-
Li+
discharge

Graphene

- **Discovery – 2004**
- **Exotic properties:**
  - **Firm structure**
  - **Inert material**
  - **Hydrofobic character**
  - **Electric and thermal conductivity**
  - **High mobility of electrons**
  - **Specific surface area (theoretically): 2630 m^2g^{-1}**

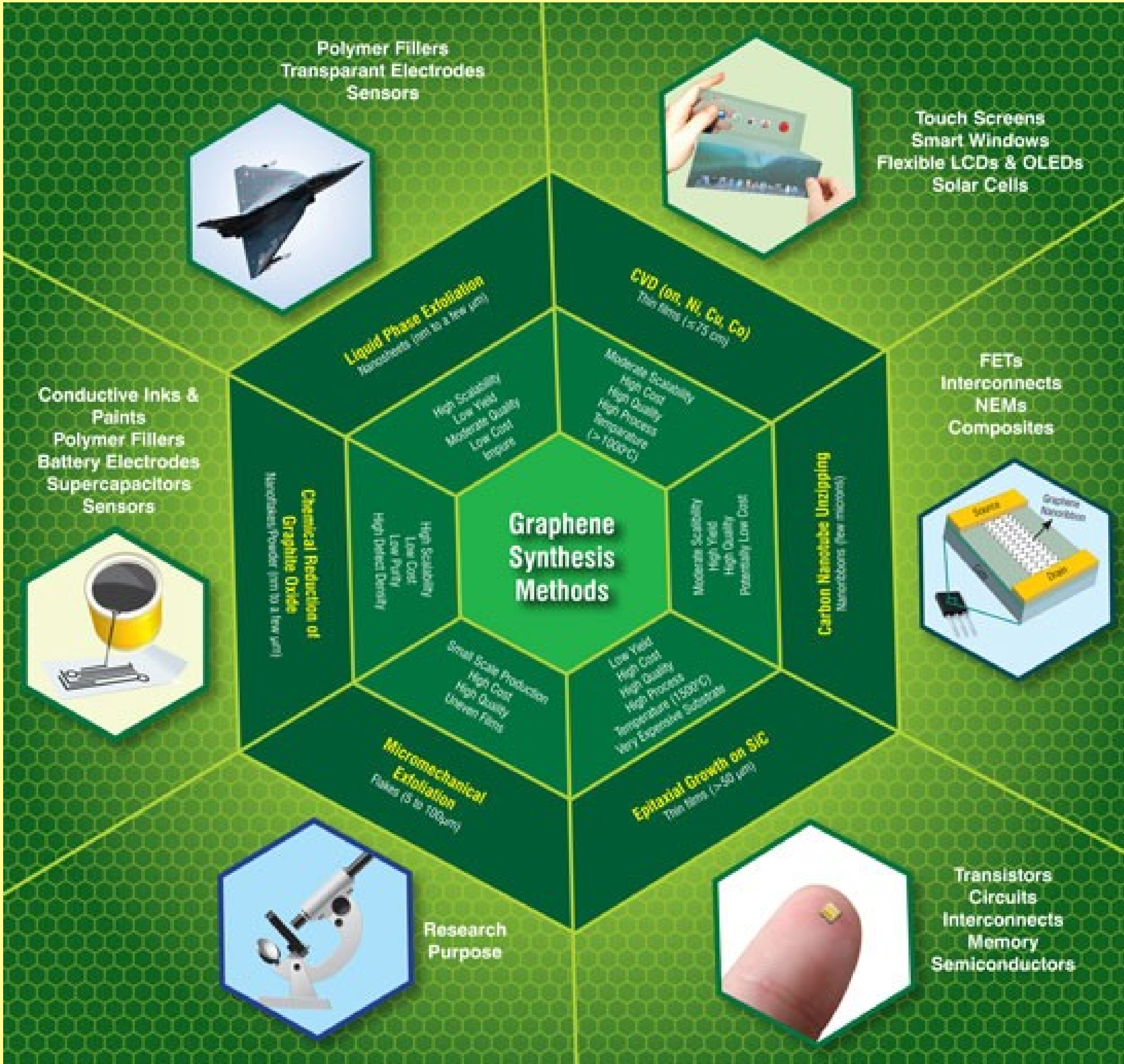
K. Novoselov

A. Geim

http://www.synchrotron.org.au/

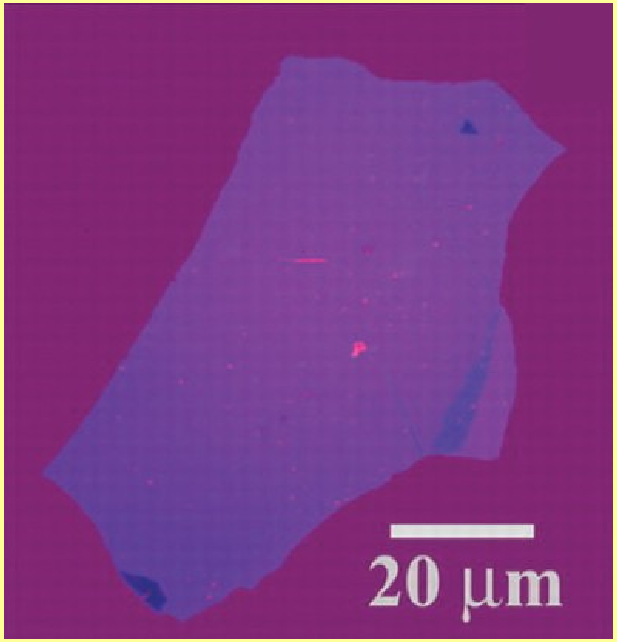
Sythesis of graphene

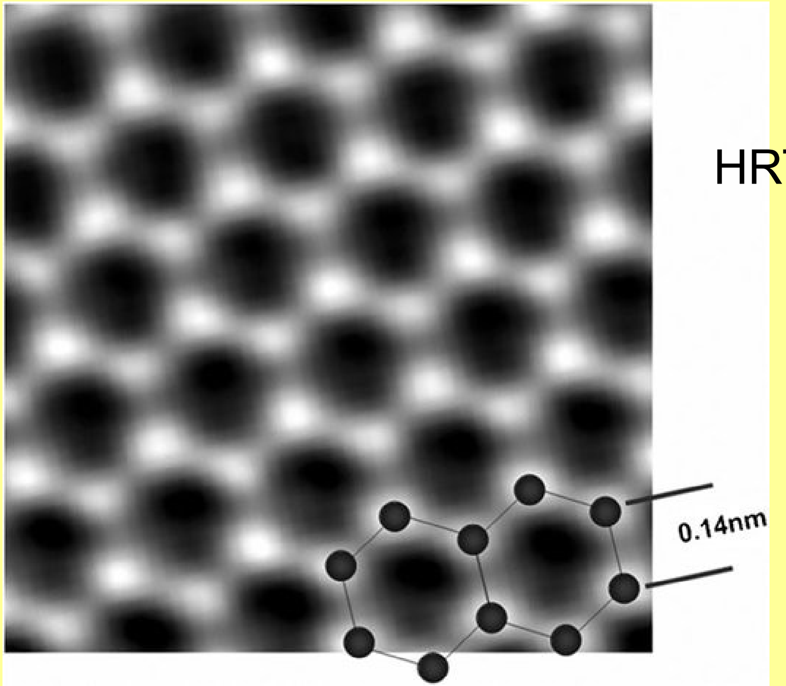
- Top down
  - Mechanical exfoliation
  - Chemical exfoliation
- Bottom up
  - CVD, epitaxial growth, …
- Defects
- Application: diodes, sensors, solar cell, energy storage, composites, …



http://www.nanowerk.com/what_is_graphene.php

Graphene





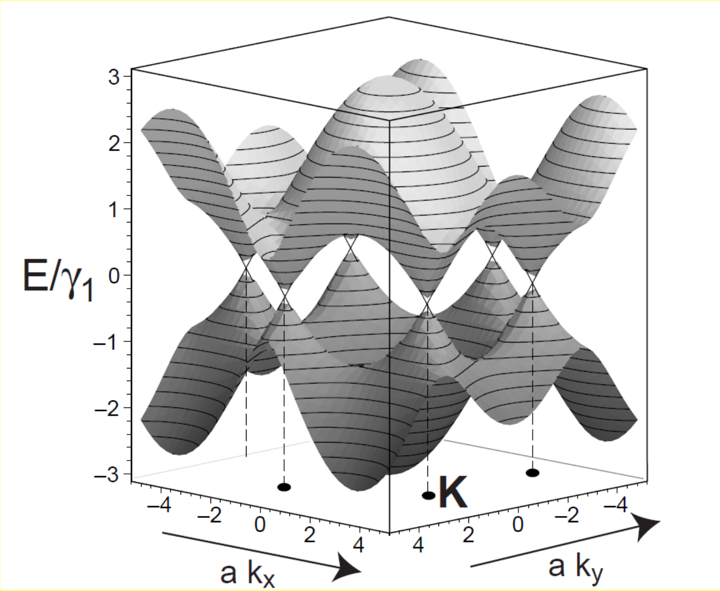
HRTEM

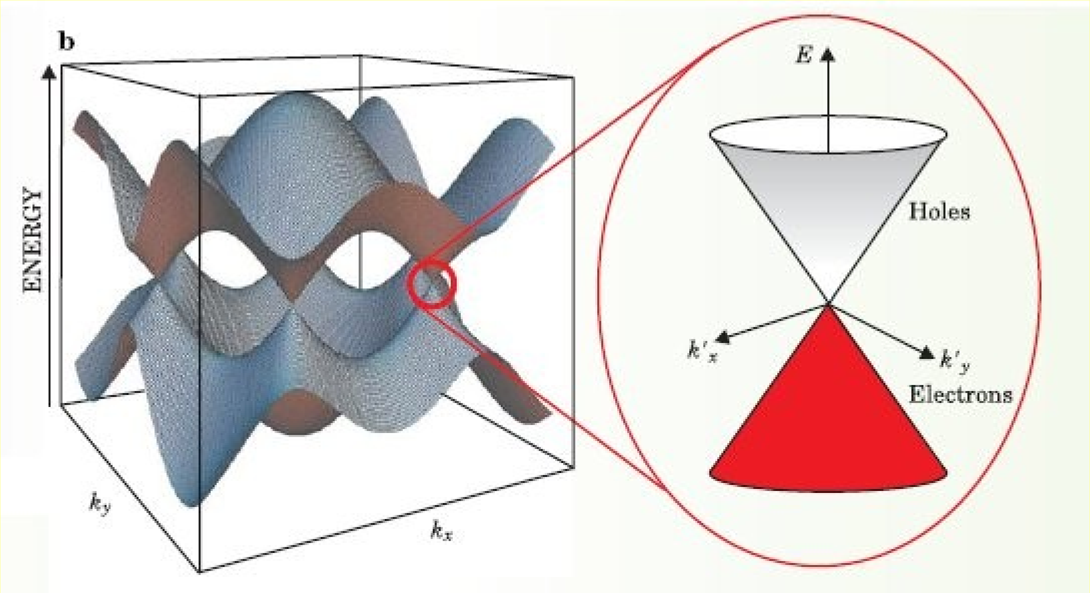
High electric conductivity (metallic)

Optically transparent – 1 layer absorbs 2.3% of photons

High mechanical strength

Graphene



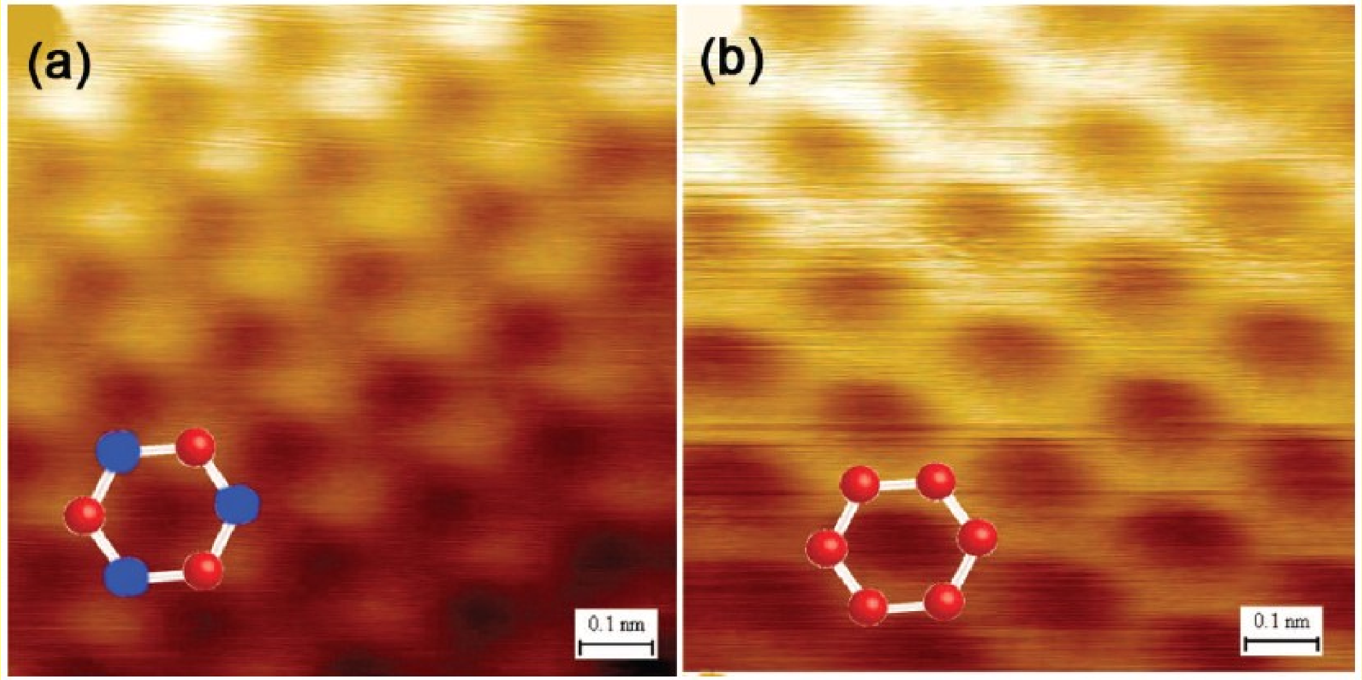


LCAO-band structure of graphene

Graphene

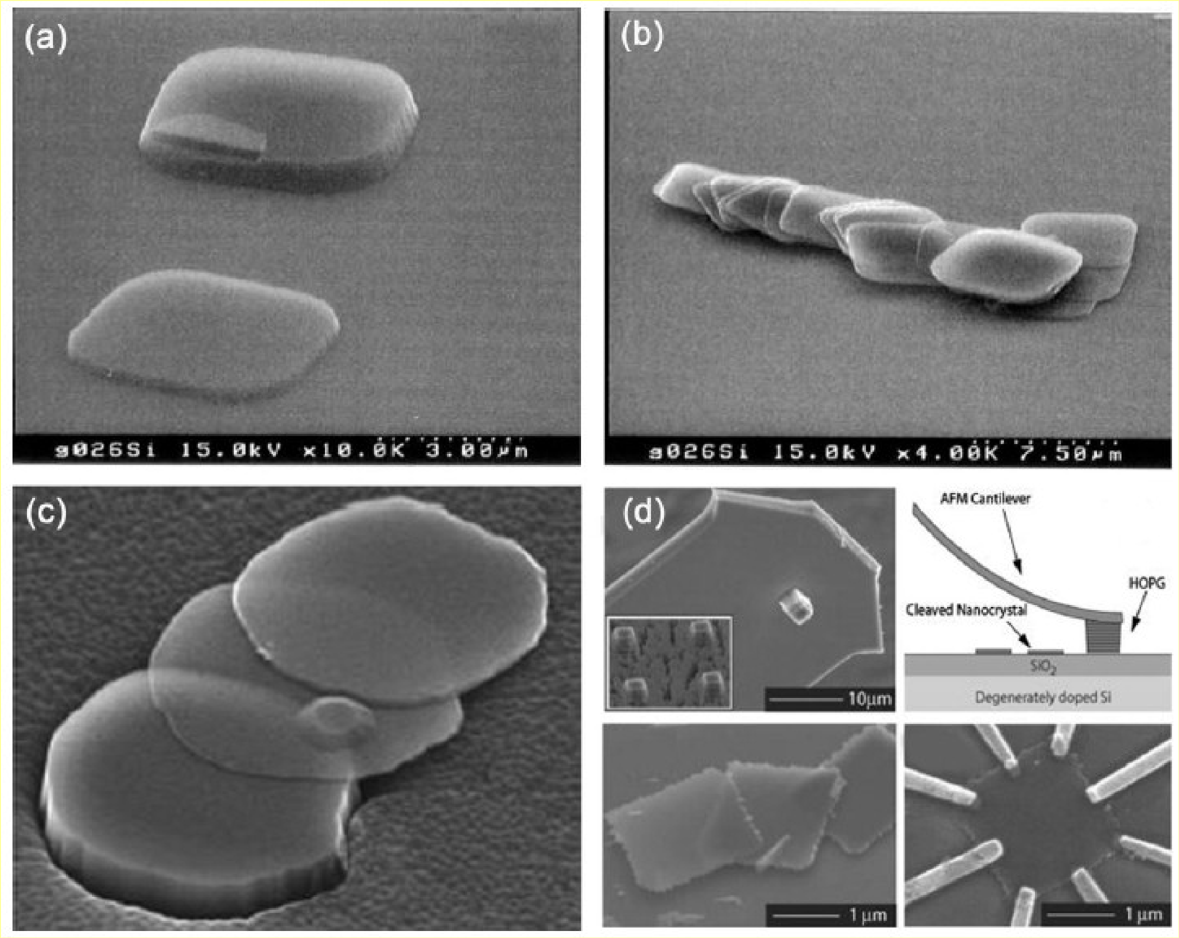
Preparation:

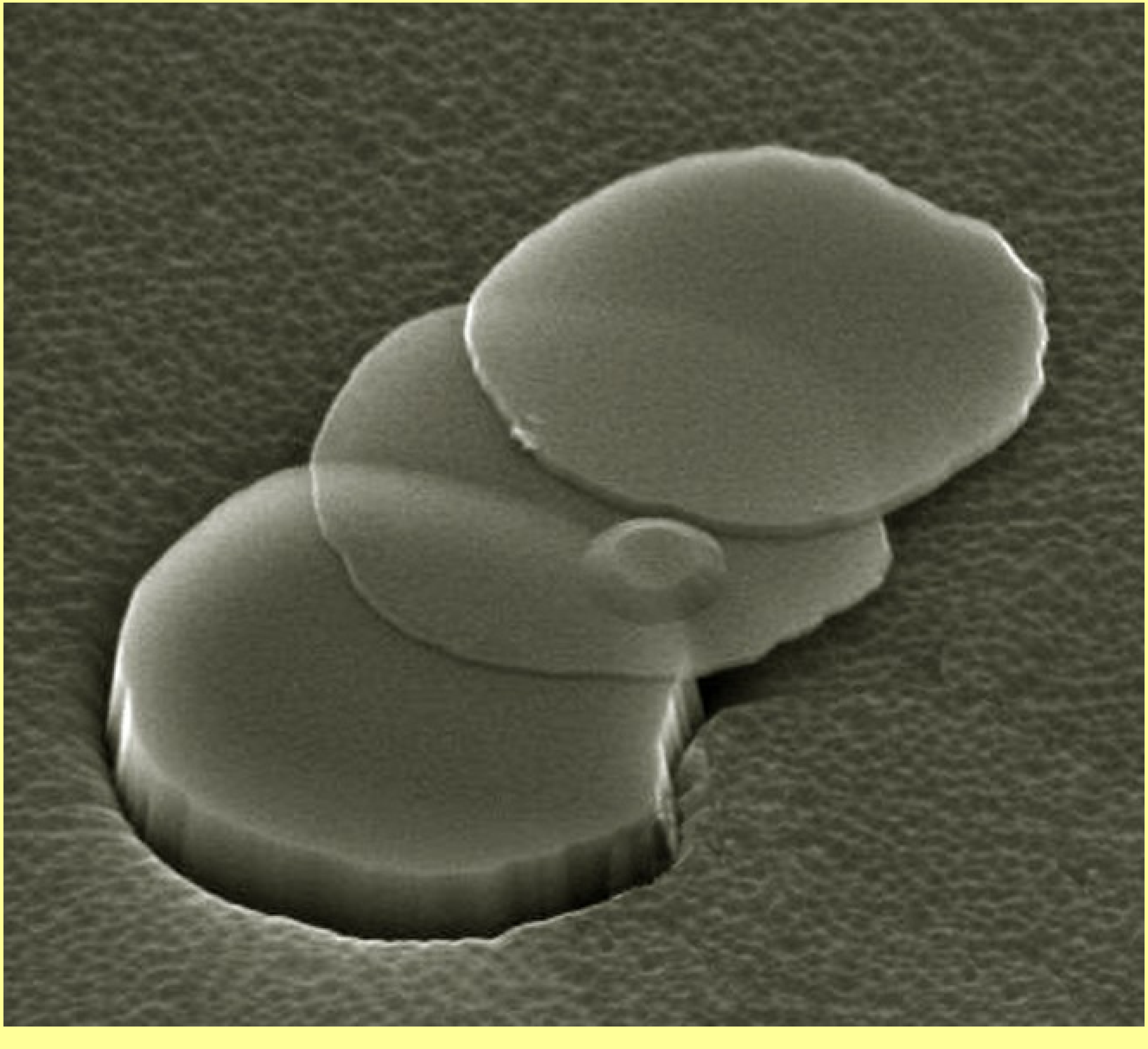
- **Scotch tape – layer peeling, flaking**
- **SiC pyrolysis – epitaxial graphene layer on a SiC crystal**
- **Exfoliation of graphite (chemical, sonochemical)**
- **CVD from CH_4, CH_2CH_2, or CH_3CH_3 on Ni (111), Cu, Pt surfaces**



Scotch tape – Layer peeling

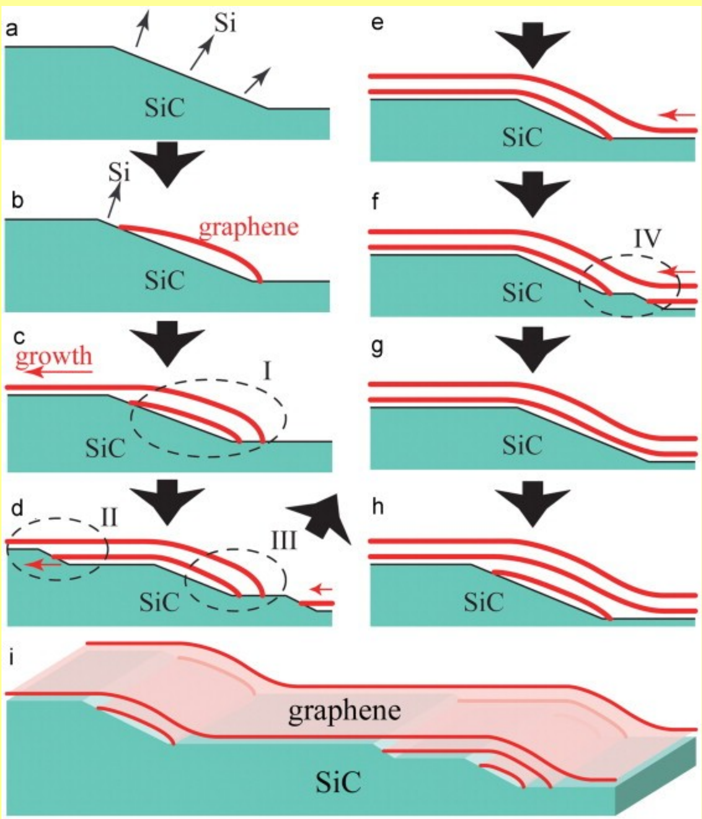
Mechanical exfoliation

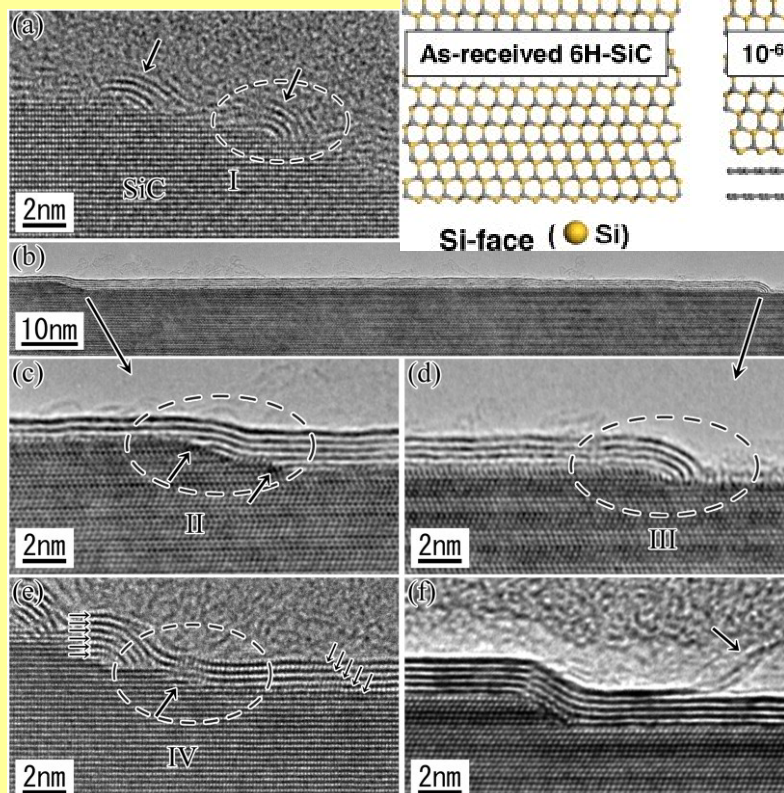


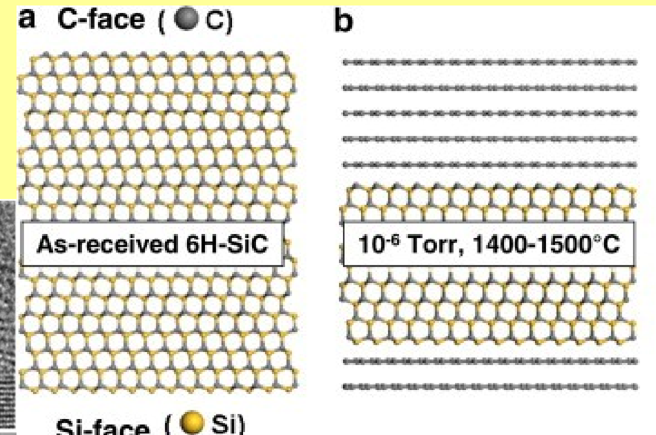


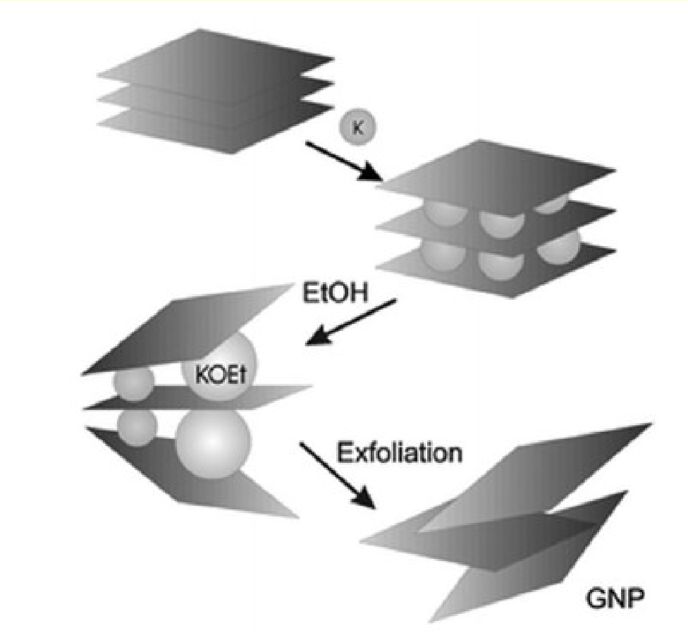
SiC pyrolysis

- **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**





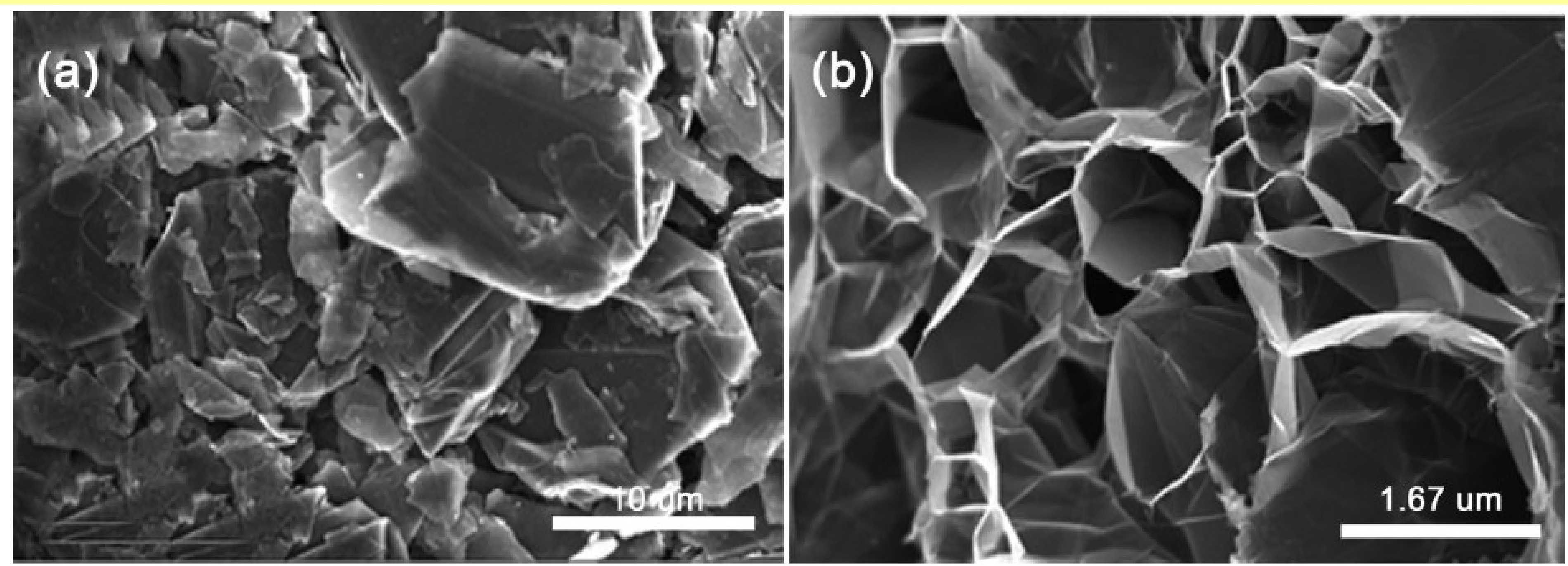




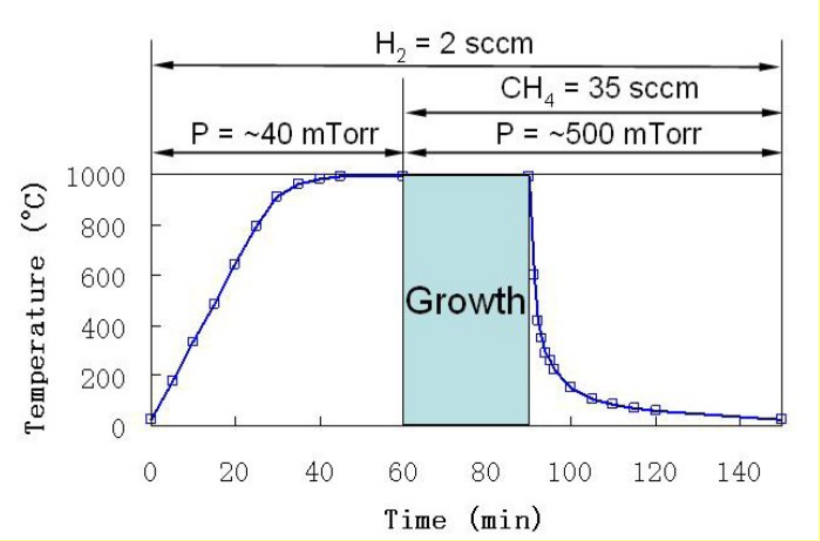
Exfoliation

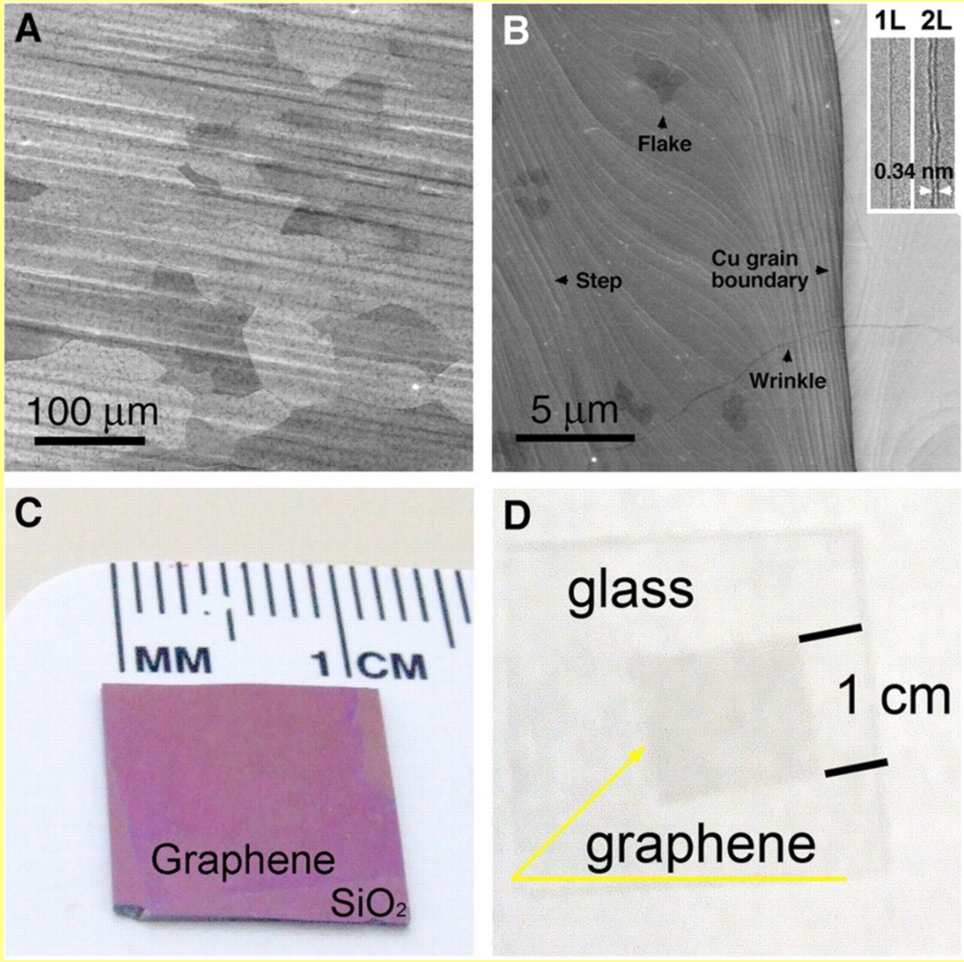
Chemical exfoliation (surfactant)

Sonochemical exfoliation



CVD from CH_4 / H_2 on Metal Surfaces





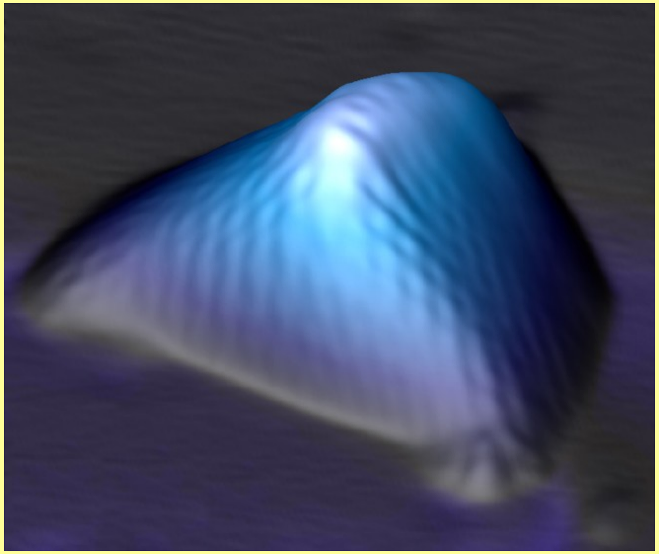
(A) SEM - graphene on a copper foil
(B) High-resolution SEM - Cu grain boundary and steps, two- and three-layer graphene flakes, and graphene wrinkles. Inset (B) TEM images of folded graphene edges. 1L, one layer; 2L, two layers.

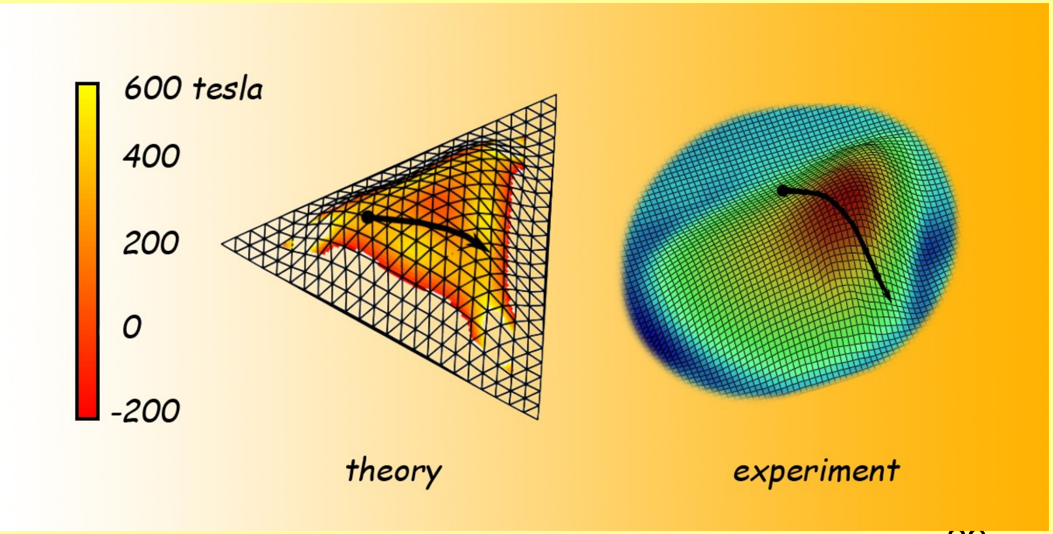
Graphene transferred onto
(C) a SiO_2/Si substrate
(D) a glass plate

Graphene on SiO_2

Pseudo-magnetism

Graphene on platinum grown from ethylene at high temperatures.
Cooled to low temperature to measure STM to a few degrees above absolute zero.
Both the graphene and the platinum contracted – but Pt shrank more, excess graphene pushed up into bubbles, size 4-10 nm x 2-3 nm
The stress causes electrons to behave as if they were subject to huge magnetic fields around 300 T
(record high in a lab, max 85 T for a few ms)





Graphene family

Graphene

hBN

BCN

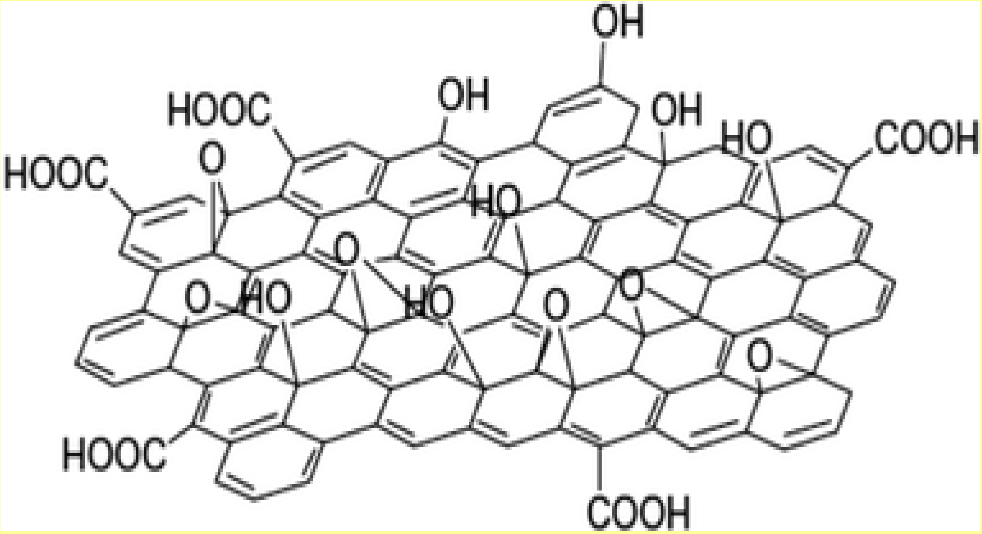
Fluorographene

graphene oxide

C3N4

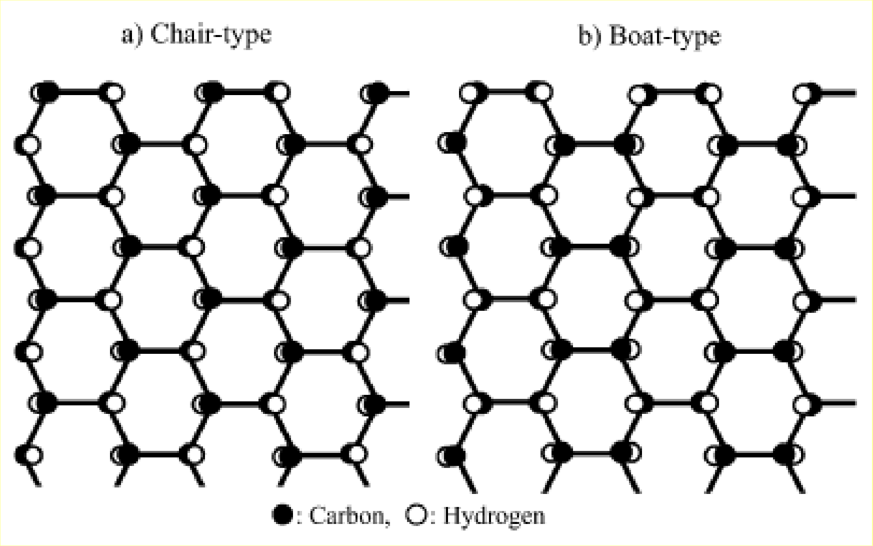
Graphene oxide

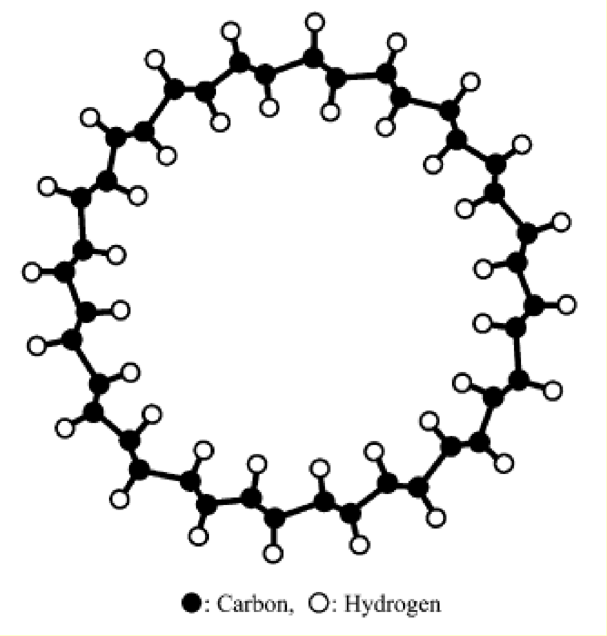
- More reactive than graphene
- Presence of oxygen groups: -OH, -COOH, =O, -O- hydrophilic character
- Electric insulator
- Specific SA (theoretically): 1700-1800 m^2g^{-1}
- Hummers method



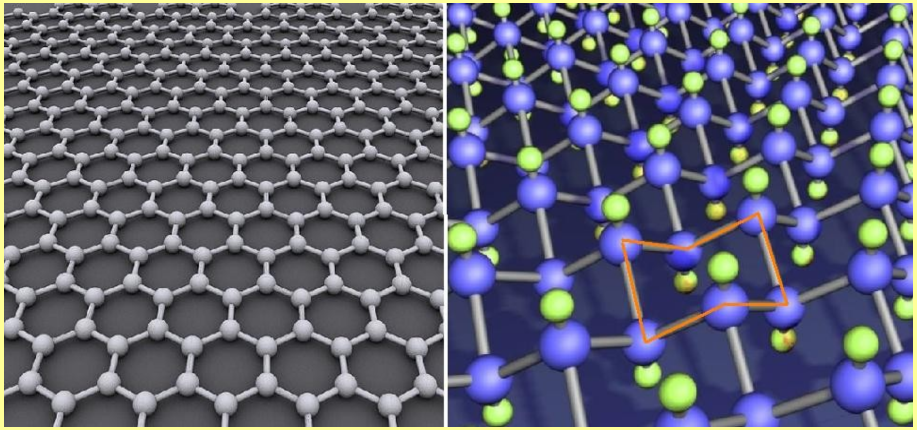
Graphane – hydrogenated graphene

- 2009 (graphene + cold hydrogen plasma)
- Two conformations: chair x boat
- Calculated binding energy = most stable compound with stoichiometric formula CH
- Chair type graphane insulating nanotubes



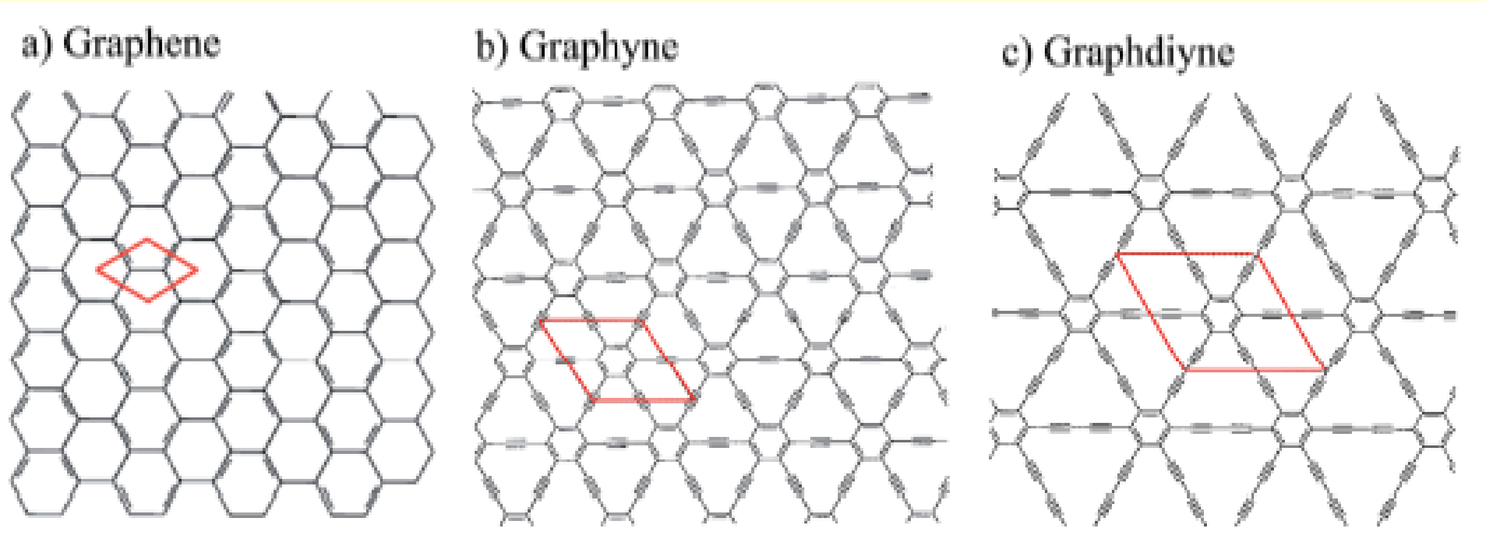


Fluorographene



- Monolayer of graphite fluoride
- Chair type x boat type-strong repulsion
- Sythesis:
  - Graphene + XeF_2/CF_4 (room temperature)
  - Mechanical or chemical exfoliation of graphite fluoride
  - By heating graphene in XeF_2 gas at 250 °C
- Graphene + XeF_2 at 70 °C – high-quality insulator, stable up to 400 °C (resemblence with teflon)

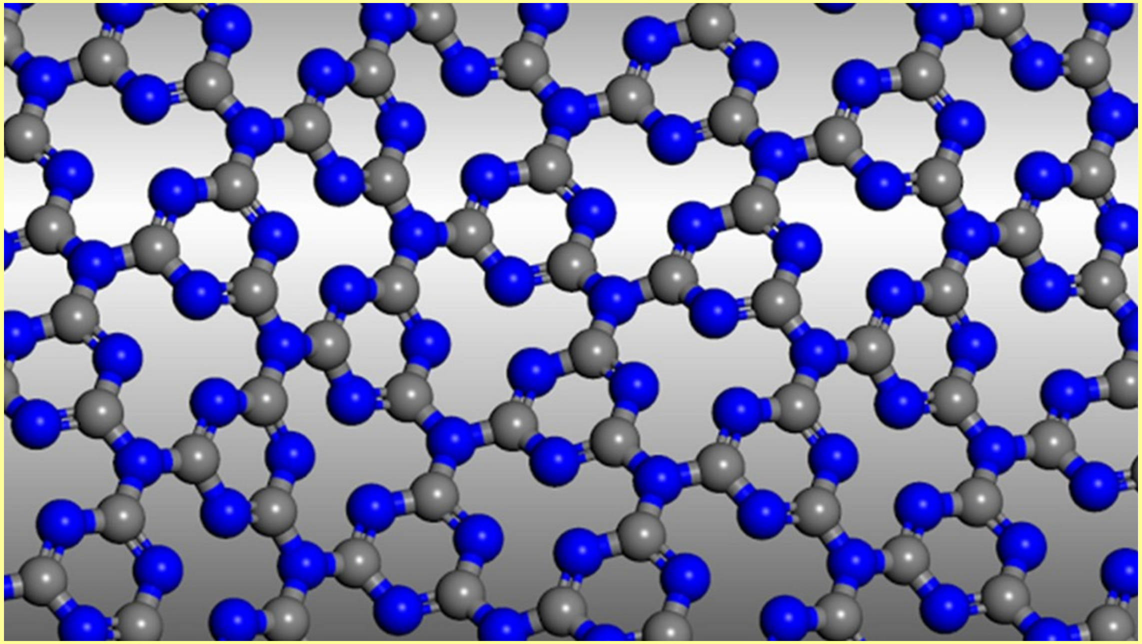
Graphyn, graphydiyn



- **Predicted**
- **“Non-derivatives“ of graphene**
- **Semiconductors**
- **Movement of electrons as in graphene but only in one direction**

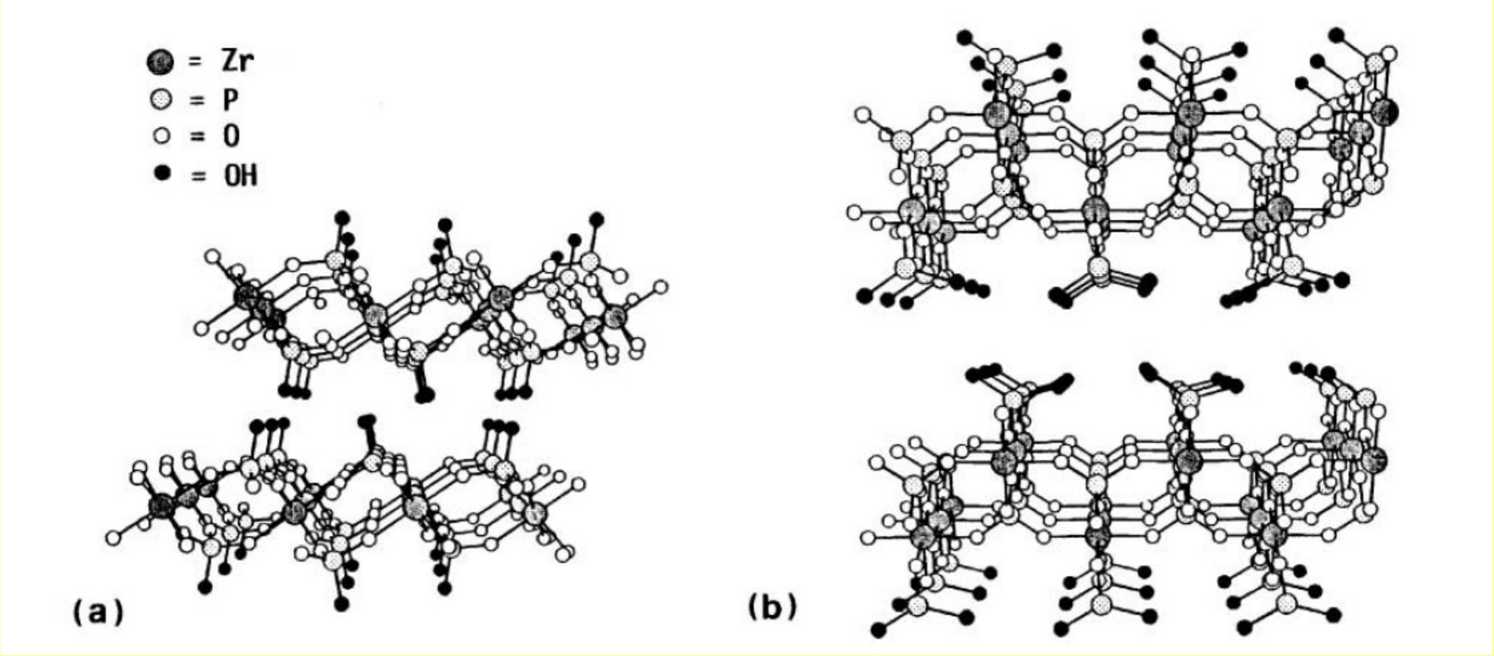
Triazine-based graphitic carbon nitride (TGCN)

“graphitic carbon nitride” (“g-C_3N_4”)



band gap 1.6 - 2.0 eV
small band gap semiconductors
Si (1.11 eV), GaAs (1.43 eV), and GaP (2.26 eV)

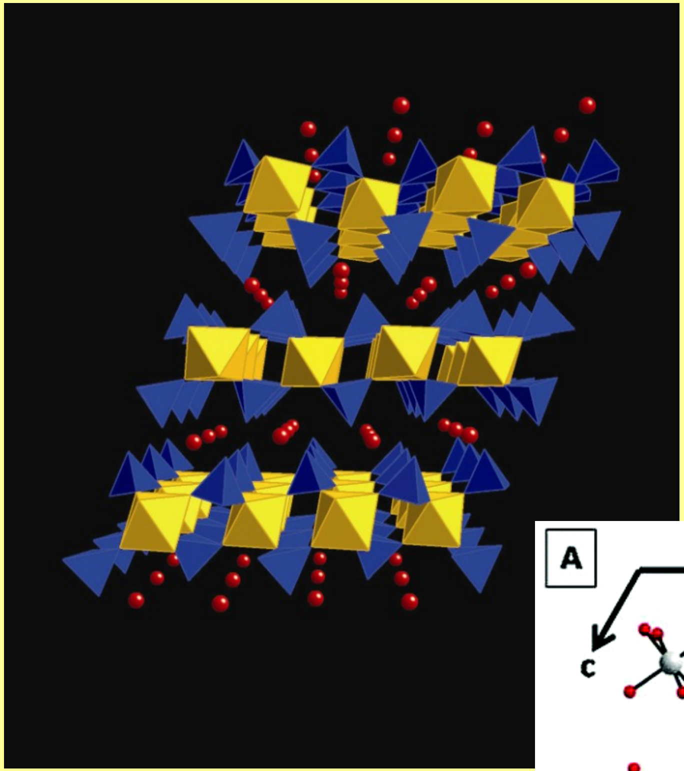
Layered Compounds - Zirconium Phosphates



(a) α-zirconium phosphate = $Zr(HPO_4)_2.H_2O$
interlayer spacing 7.6 Å

(b) γ-zirconium phosphate = $Zr(PO_4)(H_2PO_4)2H_2O$
interlayer spacing 12.2 Å

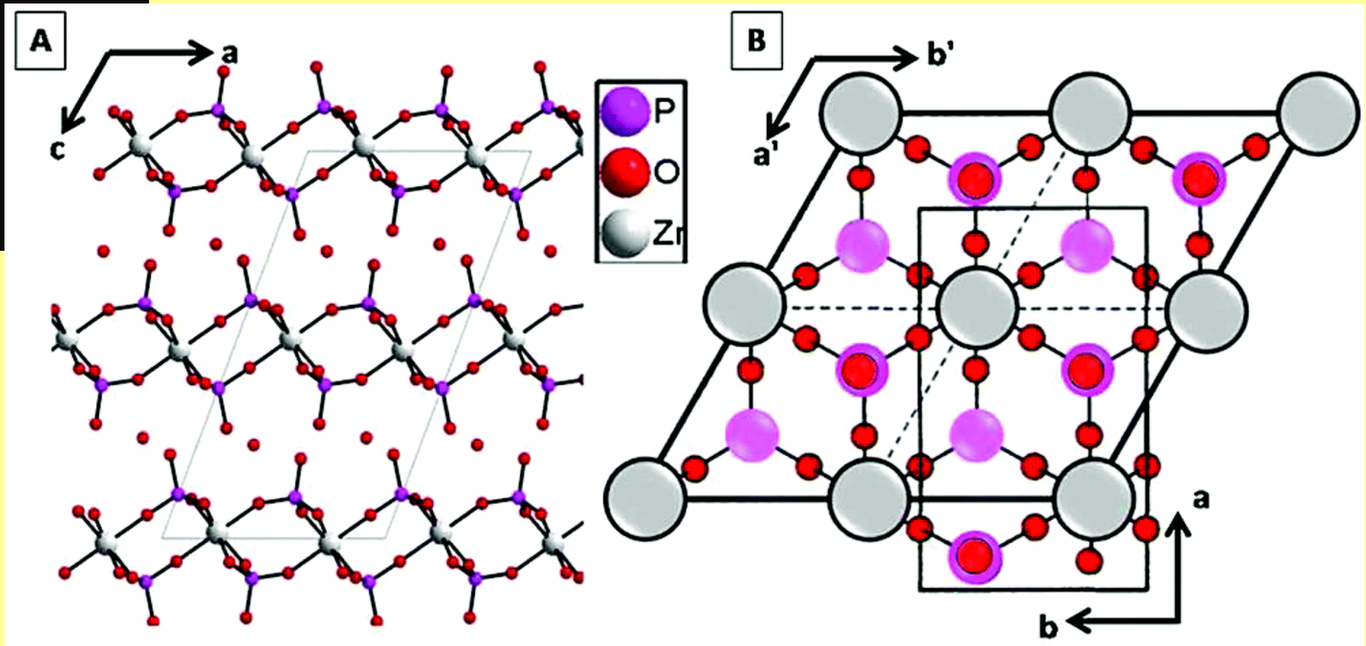
Layered Compounds - Zirconium Phosphates



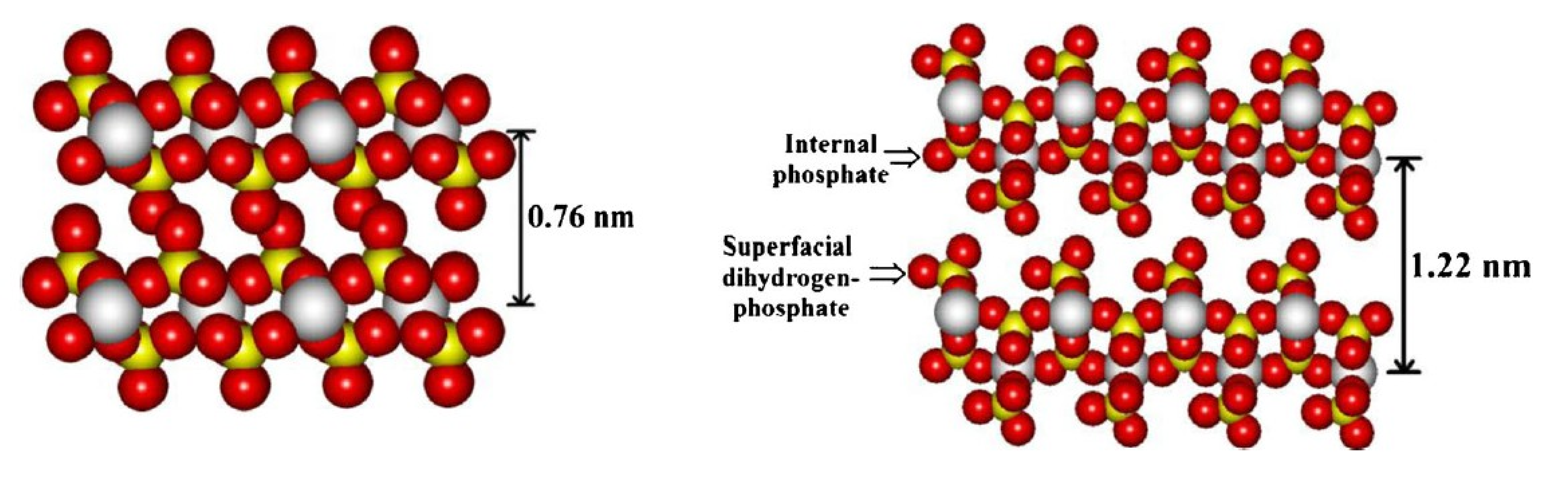
α-zirconium phosphate

$Zr(HPO_4)_2.H_2O$

interlayer spacing 7.6 Å



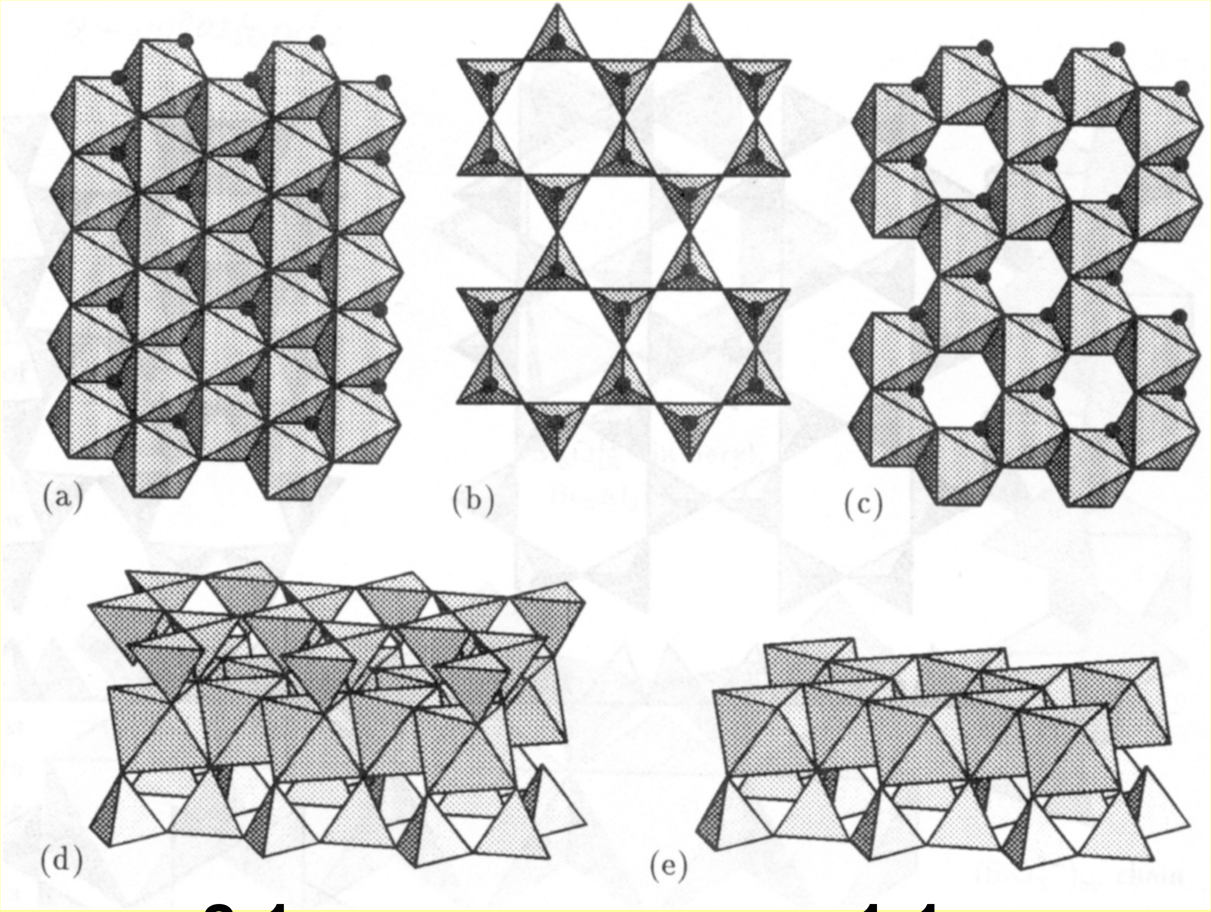
Layered Compounds - Zirconium Phosphates



(a) α-zirconium phosphate = $Zr(HPO_4)_2.H_2O$
interlayer spacing 7.6 Å

(b) γ-zirconium phosphate = $Zr(PO_4)(H_2PO_4)2H_2O$
interlayer spacing 12.2 Å

Clay Minerals



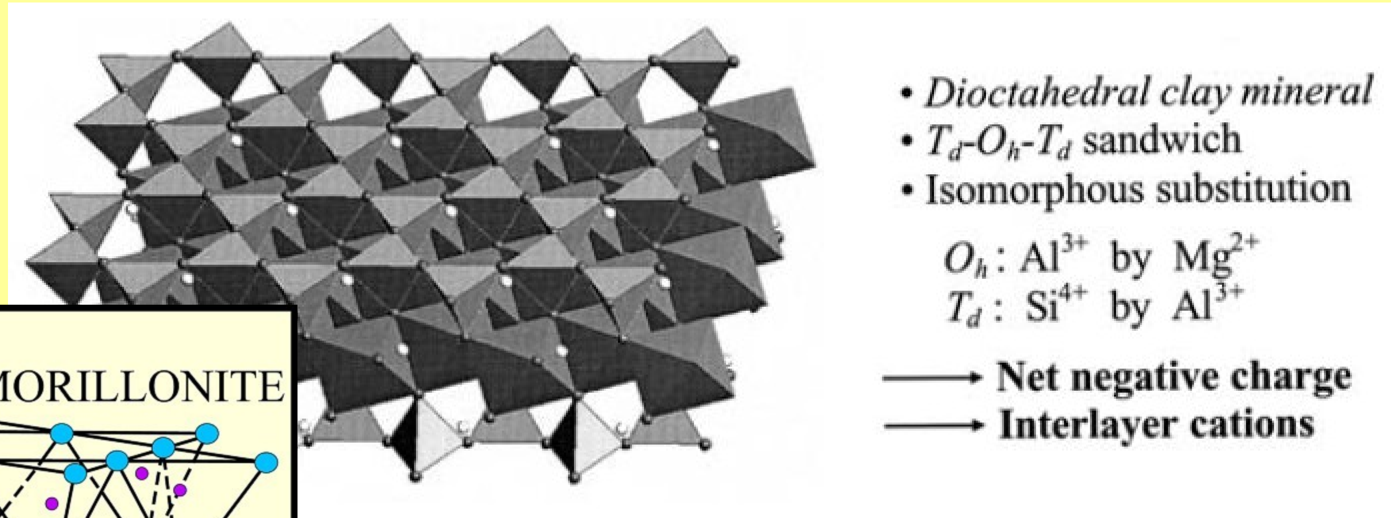
2:1

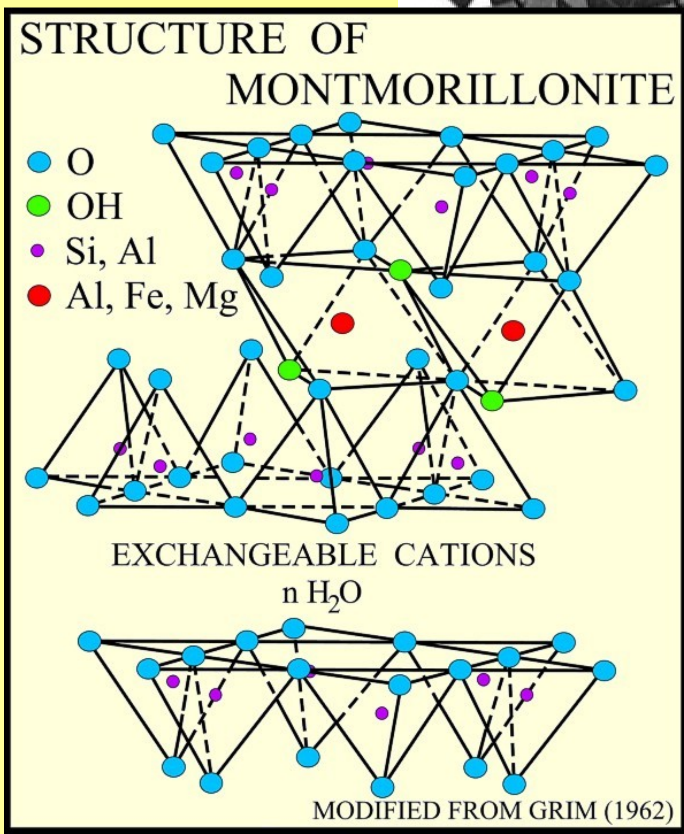
montmorillonite

1:1

kaolinite

Montmorillonite





$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot 10H_2O$

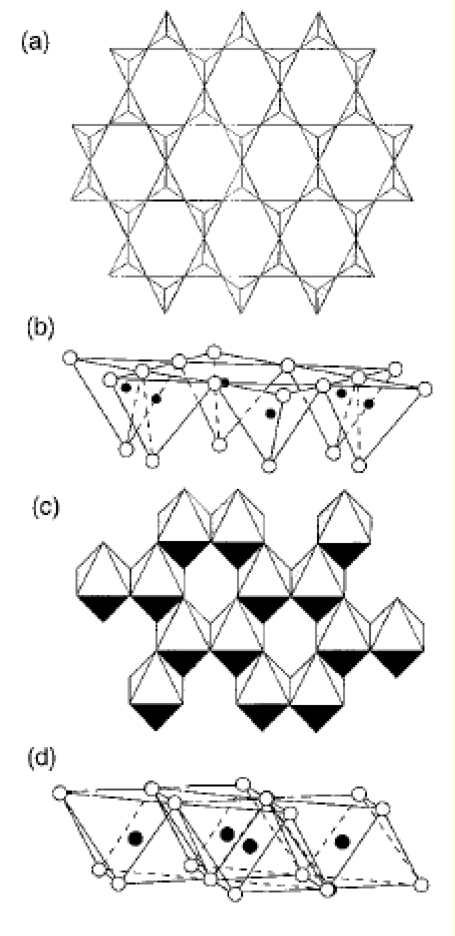
Clay Minerals

A clay $[Si_4O_{10}]^{4-}$ tetrahedral (T) sheet in
(a) top view and (b) side view

A clay octahedral (O) sheet
(c) top view and (d) side view

The $[Al_4O_{12}]^{12-}$ dioctahedral
top view is shown in (c)

$[Mg_6O_{12}]^{12-}$ trioctahedral
top view would show
a continuous sheet of octahedral units



Clay Minerals

N_2 sorption isotherms

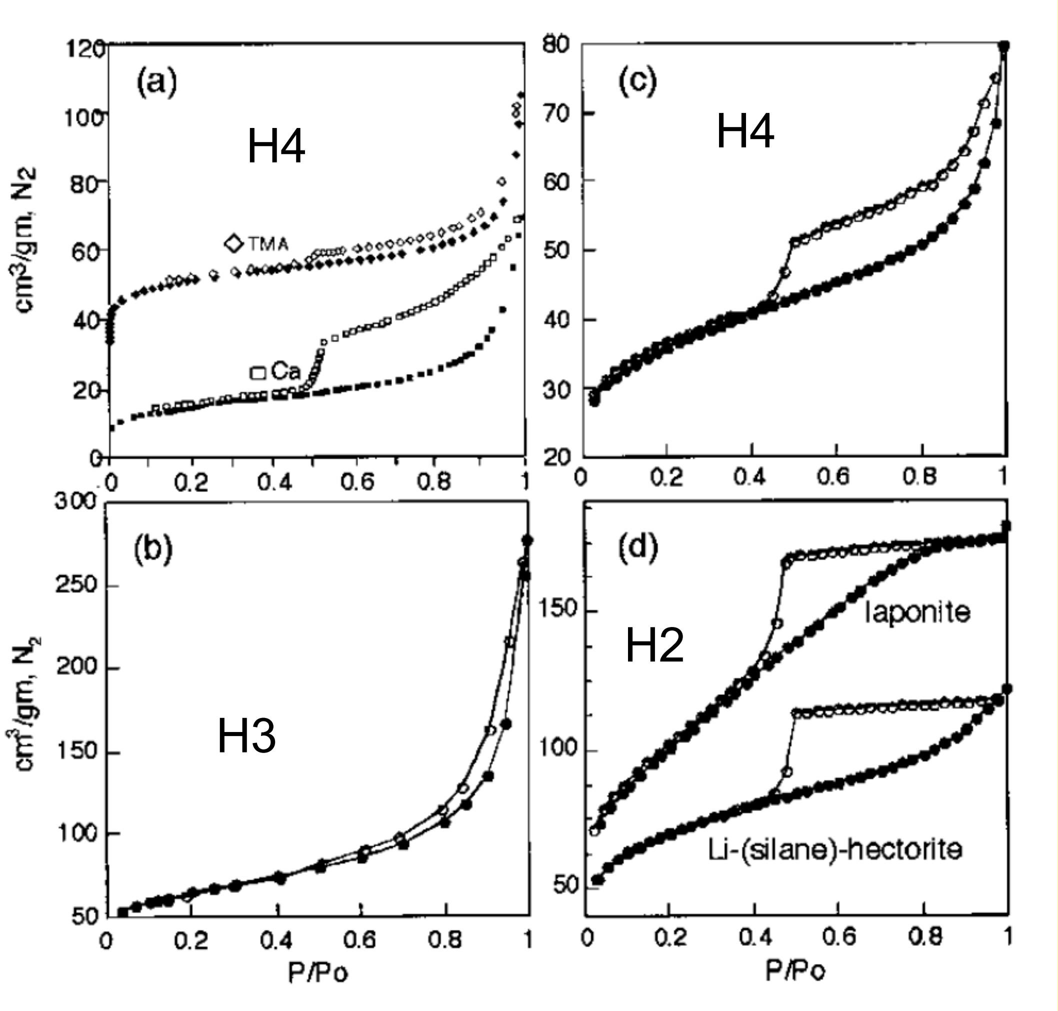
(a) TMA- and Ca-montmorillonite

(b) An Italian sepiolite

(c) Natural SHCa-1 Na-hectorite

(d) synthetic laponite and Li-(silane)-hectorites

Closed symbols = adsorption
Open symbols = desorption



Surface Area

the most important parameters of clays with respect to catalytic applications

TABLE 3 N_2 BET Surface Areas of Various Clay Minerals

Clay	Outgassing conditions	S. A., m^2/g
Kaolinite[a,b]	200 °C, overnight, $<10^{-2}$ torr	8.75
Na,Ca-montmorillonite[a,c]	same	31.0
Ca-montmorillonite[a,d]	same	80.2
Ca-montmorillonite[a,e]	same	93.9
Na-hectorite[a,f]	same	64.3
Laponite[g]	105 °C, overnight, 10^{-3} torr	360
Sepiolite[h]	96 °C, 3 h	378
Palygorskite[h]	95 °C, <70 h	192

nonpolar guest molecules N_2 do not penetrate the interlayer regions

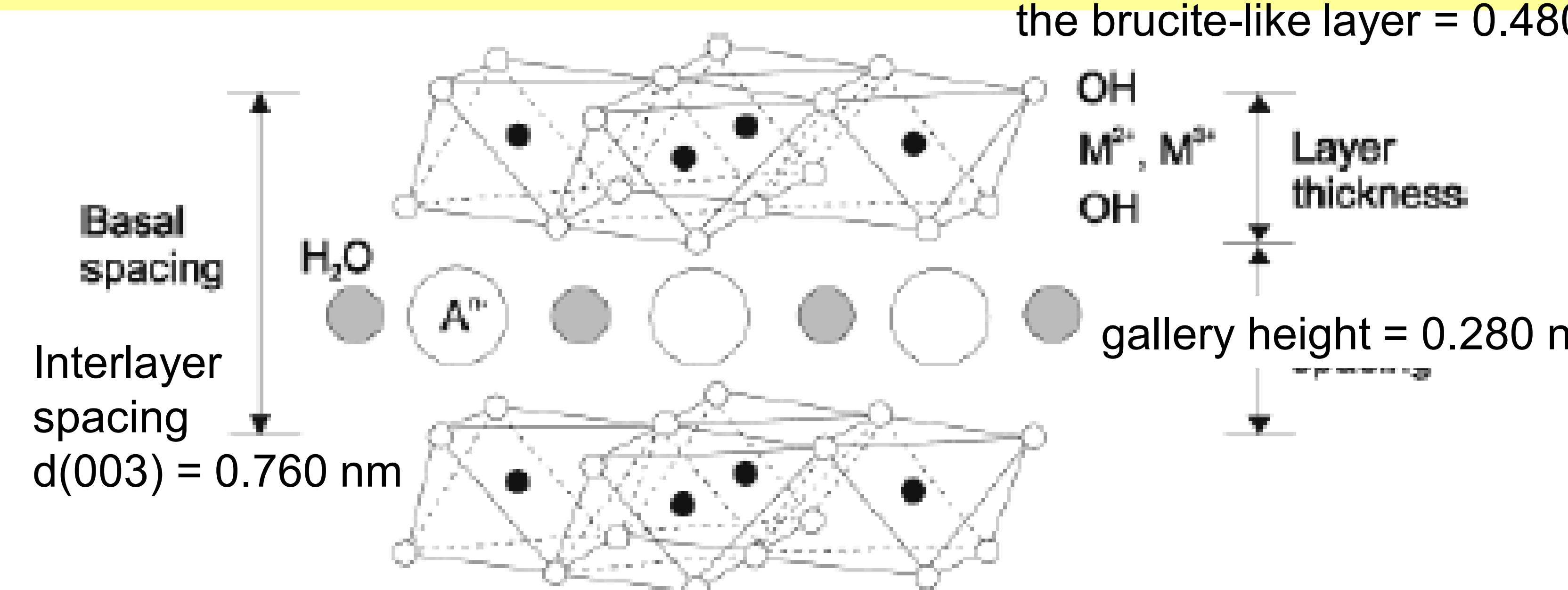
Na^+ forms of smectites and vermiculites – no penetration
larger ions (Cs^+ and NH_4^+ keep the basal planes far enough) - limited penetration

Layered Double Hydroxides

LDH = layered double hydroxides
HT = hydrotalcites
Natural mineral hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$

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

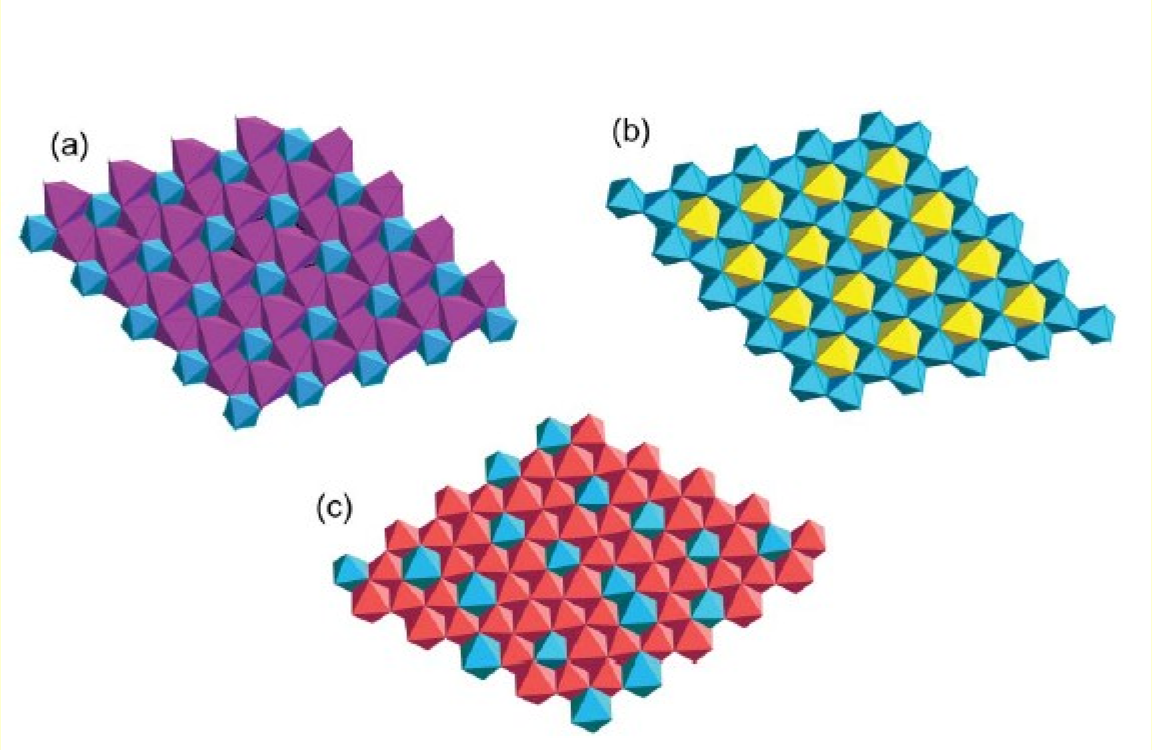
Layers have positive charge



Hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$

Hydrotalcites

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



(a) $[Ca_2Al(OH)_6]_2SO_4.6H_2O$ (b) $[LiAl_2(OH)_6]Cl$ (c) $[Mg_{2.25}Al_{0.75}(OH)_6]OH$

Hydrotalcite

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

a brucite layer, Mg^{2+} ions octahedrally surrounded by six OH^-
the octahedra share 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

Hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ - 3R stacking

$$[M^{II}_{1-x}M^{III}_x (OH)_2]^{x+}(A^{m-})_{x/m}]\cdot nH_2O$$

x = 0.25 $Mg_6Al_2(OH)_{16}CO_3$

x = 0 $Mg(OH)_2$

Hydrotalcite

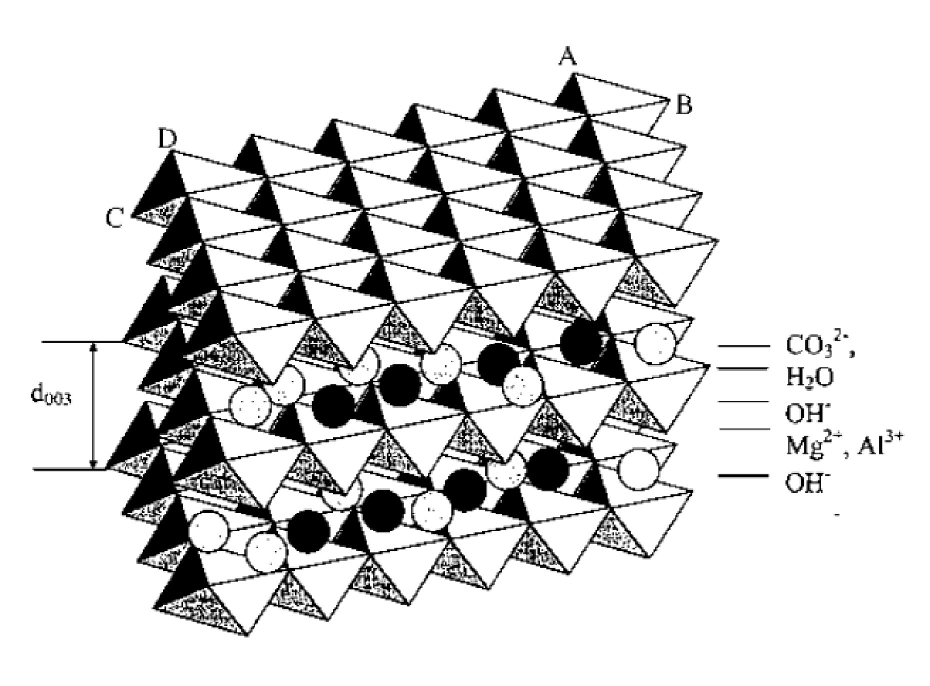
The interlayer spacing *c′* is equal to *d*003, 2*d*006, 3*d*009, etc.;

$c' = (d003 + 2d006 + \ldots + nd00(3n)) / n$

The cell parameter *c* is a multiple of the interlayer spacing *c′*

$c = 3c'$ for rhombohedral (3R)

$c = 2c'$ for hexagonal (2H) sequences



Hydrotalcite

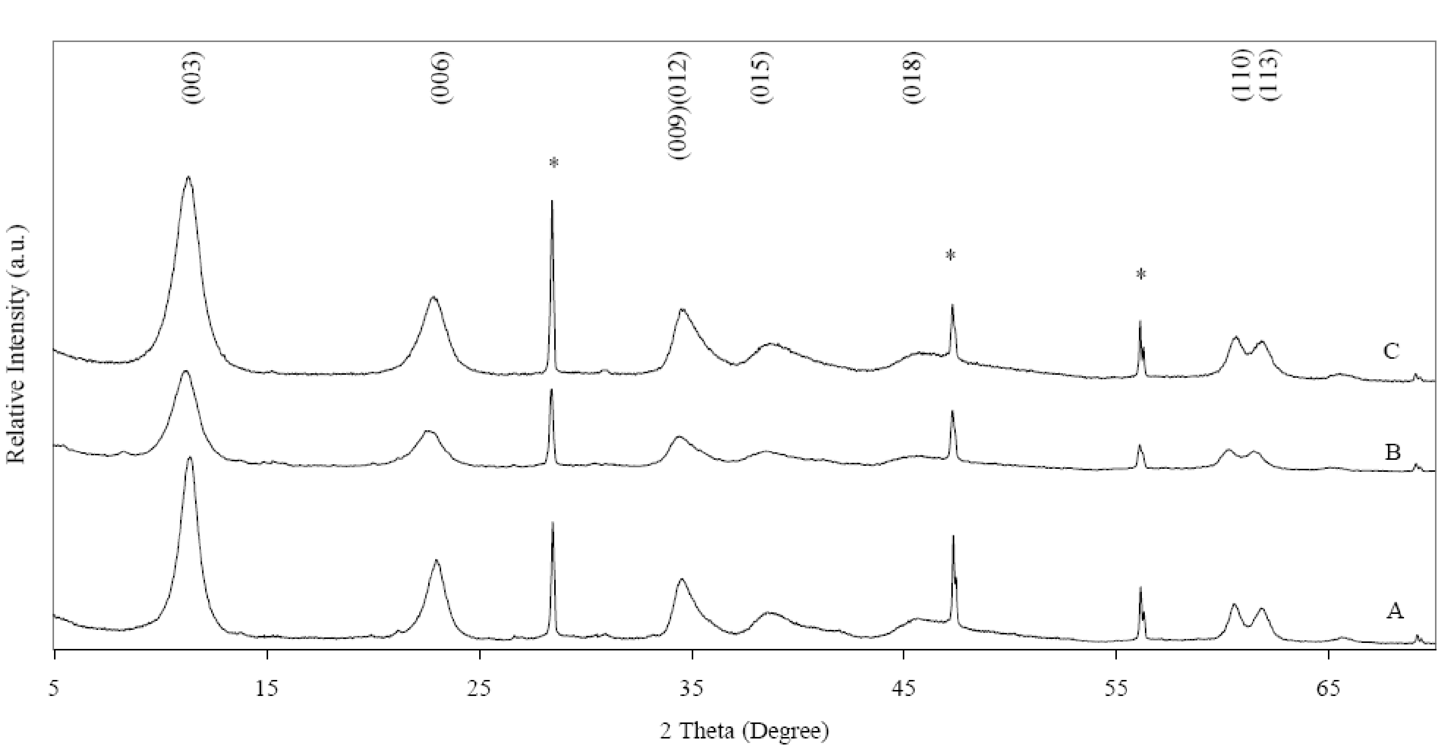
Hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ - 3R stacking

unit cell parameters

a = 0.305 nm   c = 3d(003) = 2.281 nm

the interlayer spacing: d(003) = 0.760 nm
the spacing occupied by the anion (gallery height) = 0.280 nm
a thickness of the brucite-like layer = 0.480 nm
the average M—O bond = 0.203 nm
the distance between two nearest OH^- ions in the two opposite side layers = 0.267 nm shorter than a (0.305 nm) and indicative of some contraction along the c-axis.

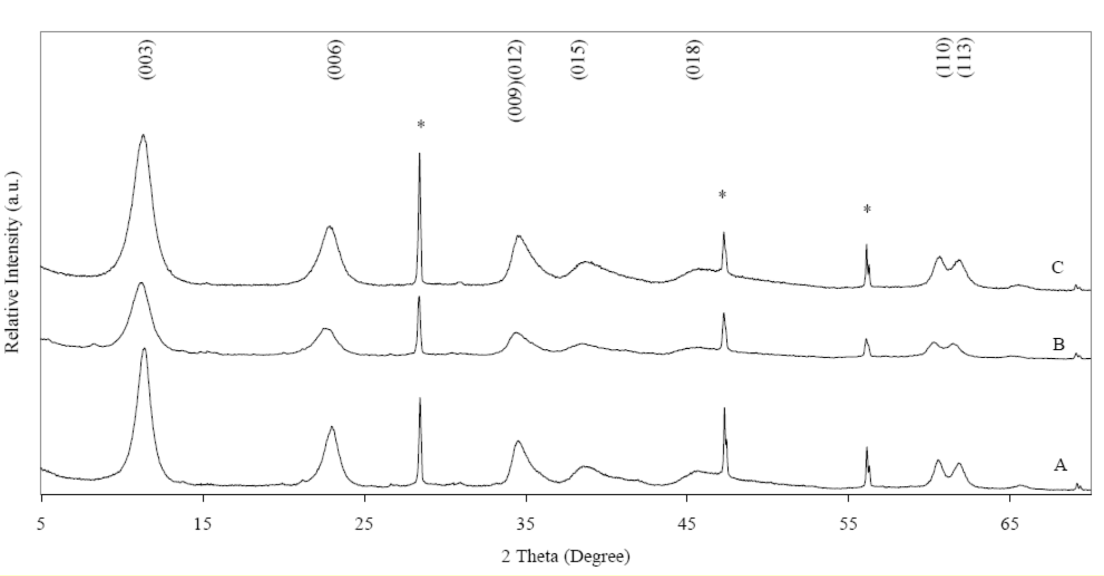
XRD Patterns of LDH



XRD patterns of layered double hydroxides synthesized by coprecipitation method with various cations composition:
A – Mg/Al; B- Mg/Co/Al; C- Mg/Ni/Al

*** = Reflections from Si crystal used as a reference**

XRD Patterns of LDH



rhombohedral structure
the cell parameters *c* and *a*

The lattice parameter $a = 2d(110)$ corresponds to an average cation–cation distance

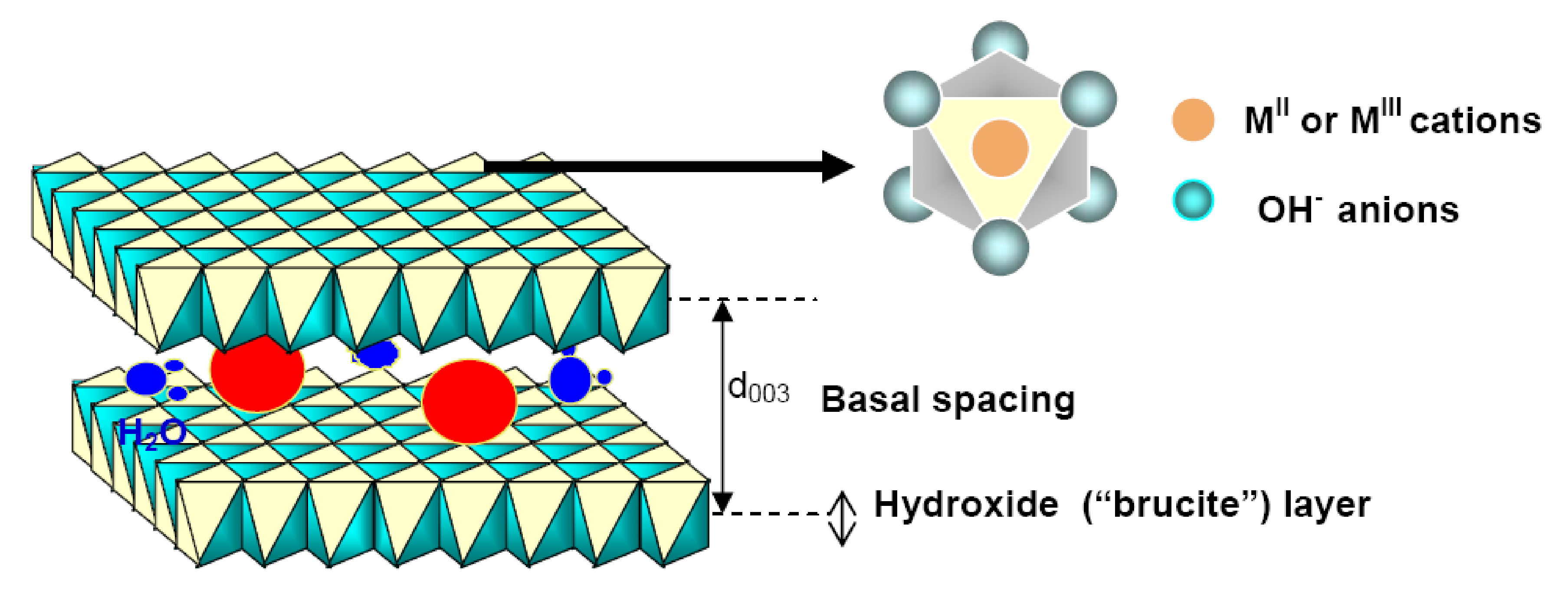
The *c* parameter corresponds to three times the thickness of $d003$

$c = 3/2\ [d003+2d006]$

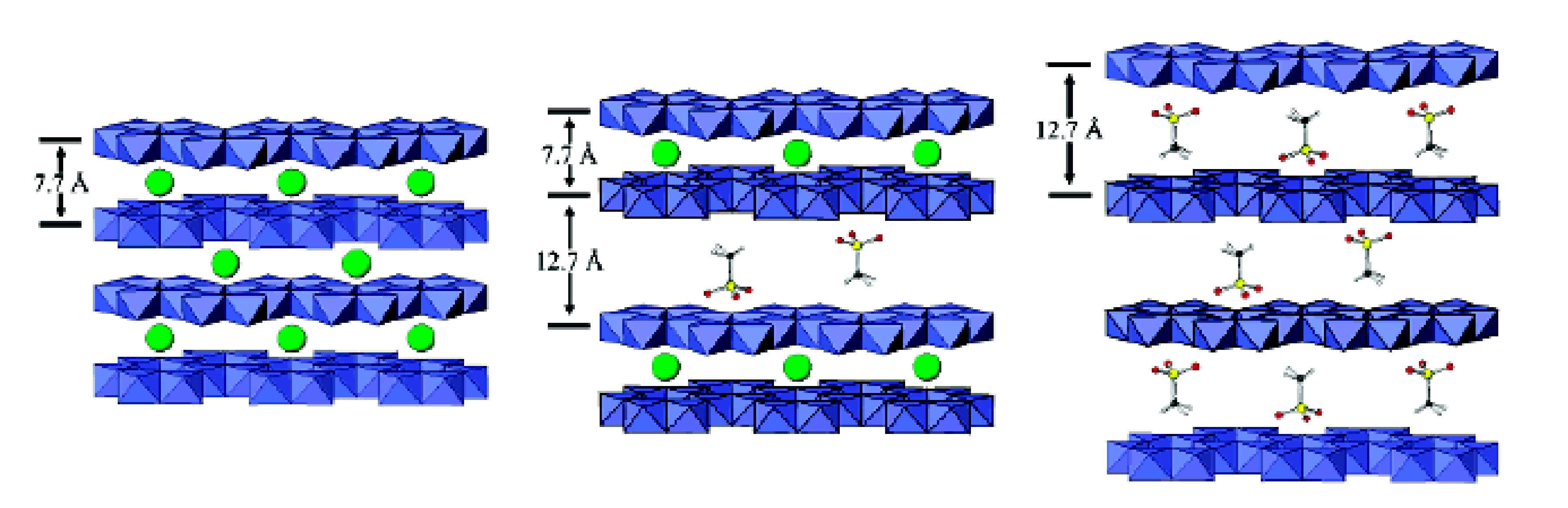
Layered Compounds

LDH = layered double hydroxides
hydrotalcites
mineral $Mg_6Al_2(OH)_{16}CO_3.4H_2O$

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



Intercalation to LDH



the intercalation of methylphosphonic acid into Li/Al LDH

(a) $[LiAl_2(OH)_6]Cl.H_2O$
(b) second-stage intermediate, alternate layers occupied by Cl and MPA anions
(c) first-stage product with all interlayer regions occupied by MPA.

Intercalation to LDH

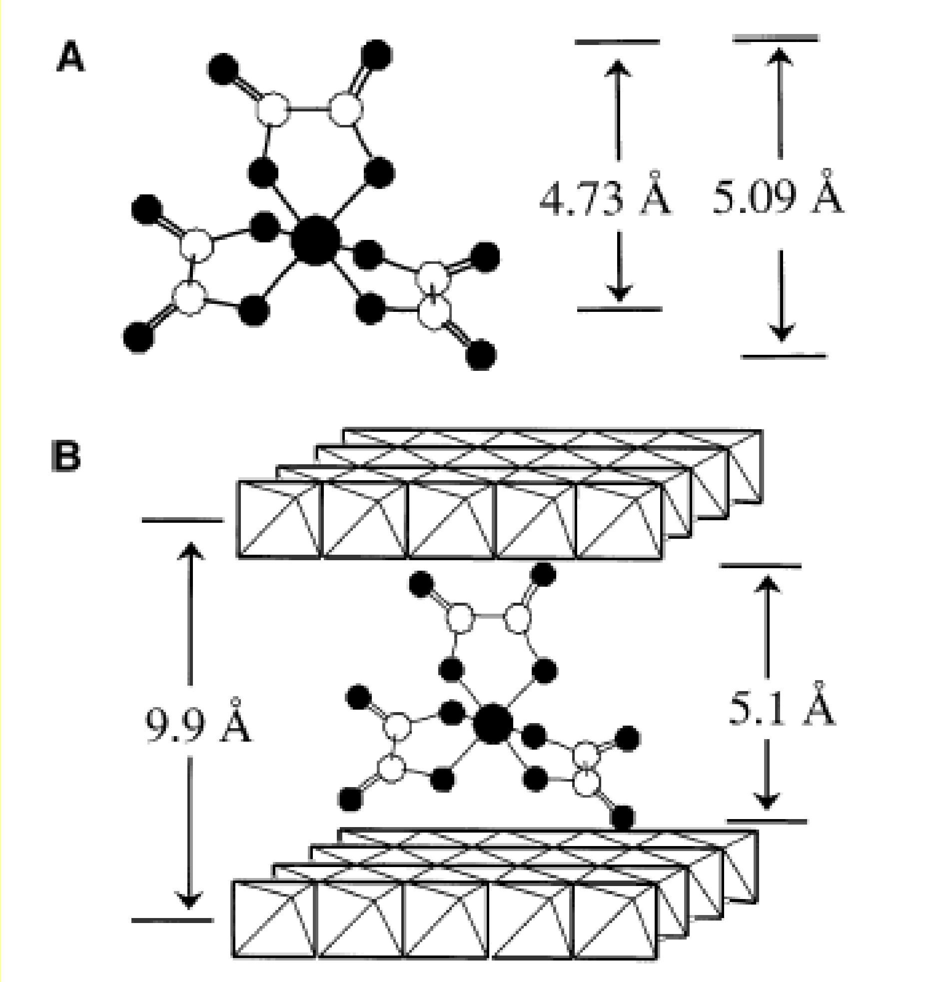
LDH = layered double hydroxides

hydrotalcites mineral $Mg_6Al_2(OH)_{16}CO_3.4H_2O$

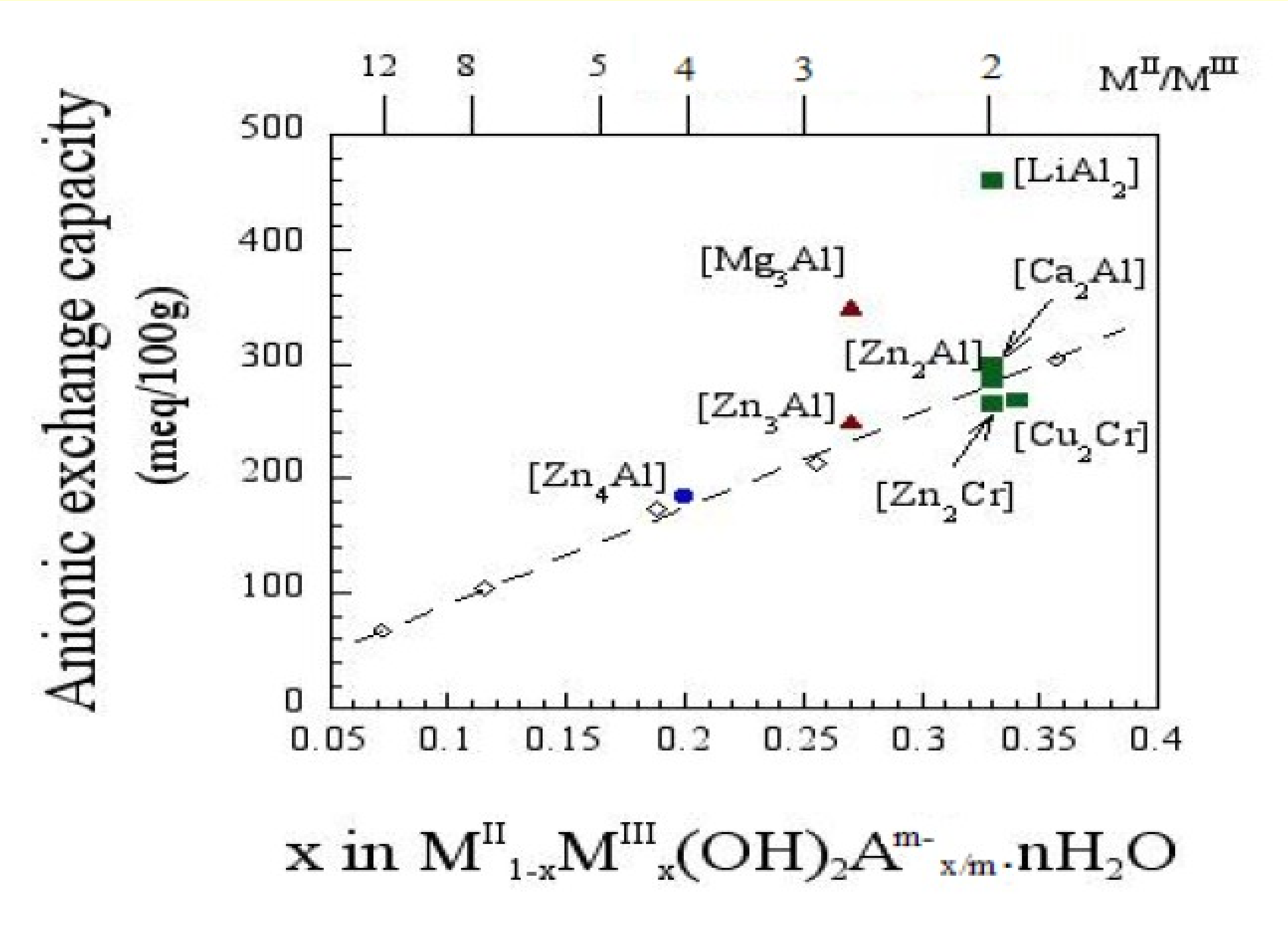
Brucite layers, Mg^{2+} substituted partially by Al^{3+}

Layers have positive charge

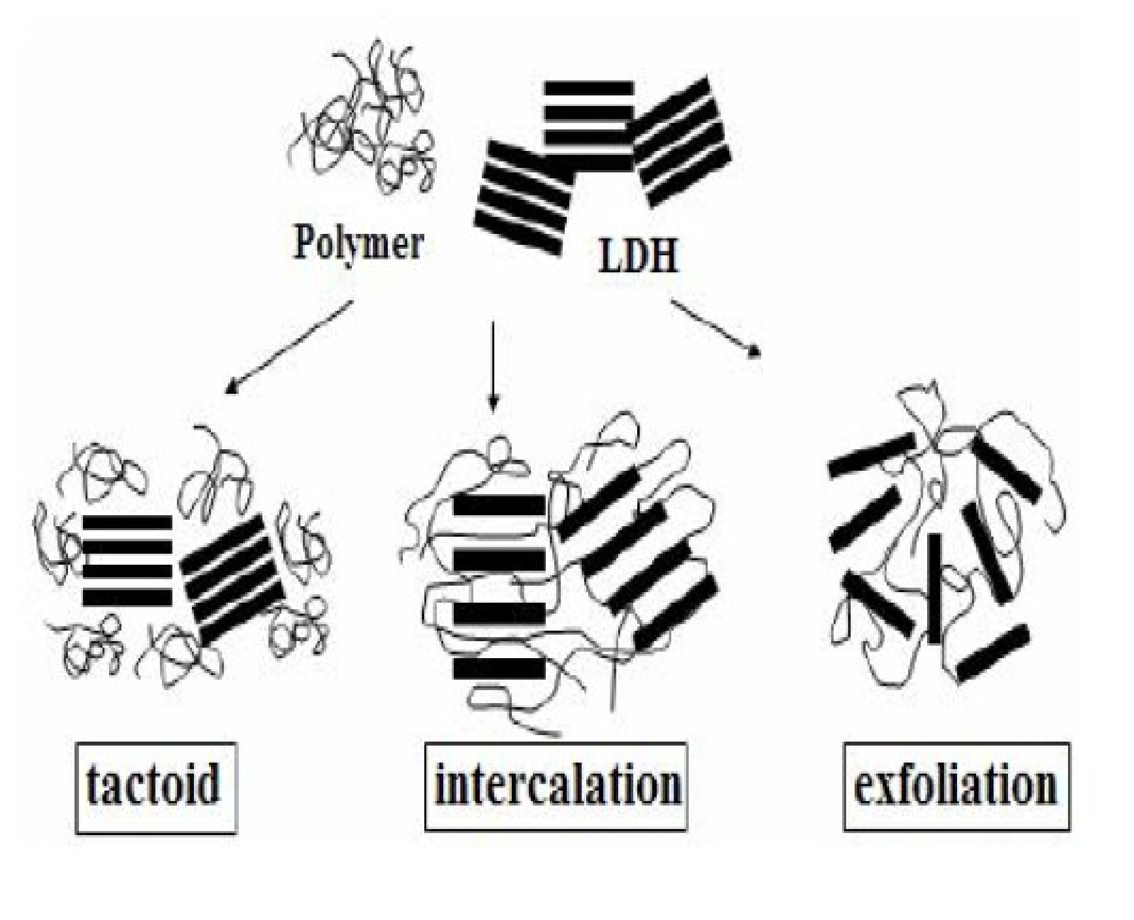
Intercalate anions $[Cr(C_2O_4)_3]^{3-}$



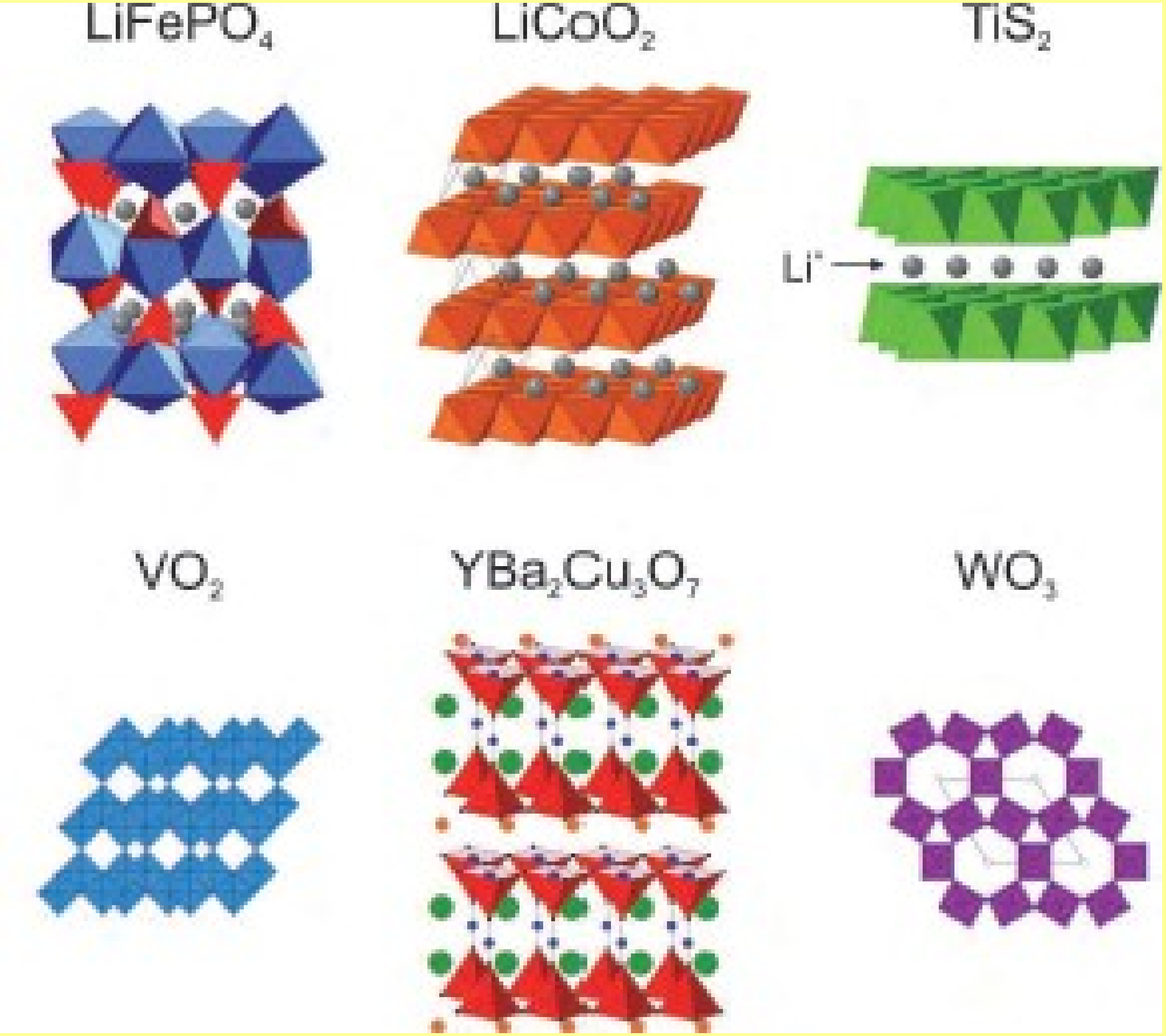
The anionic exchange capacity (AEC)



Types of the composite structures

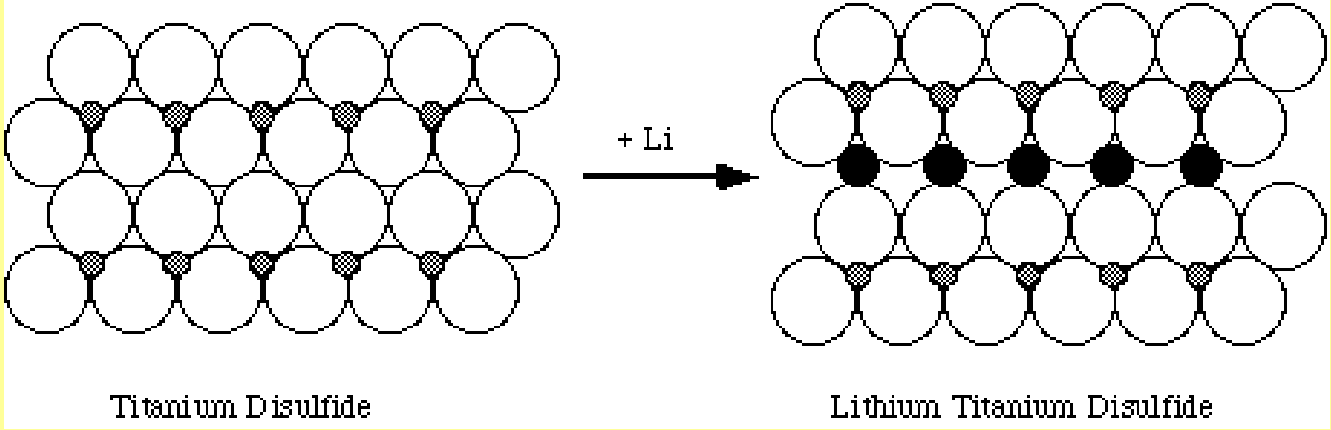


Li Intercalation Compounds

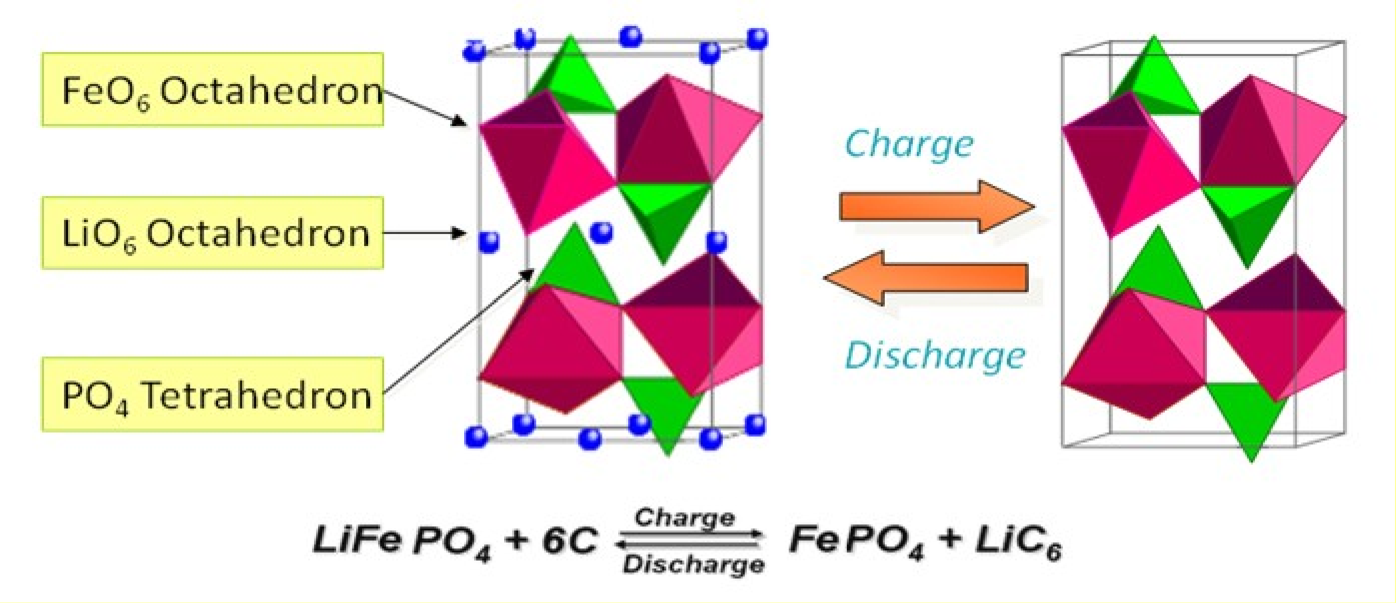


Li Intercalation

$x\ Li + TiS_2 \rightarrow Li_xTiS_2$

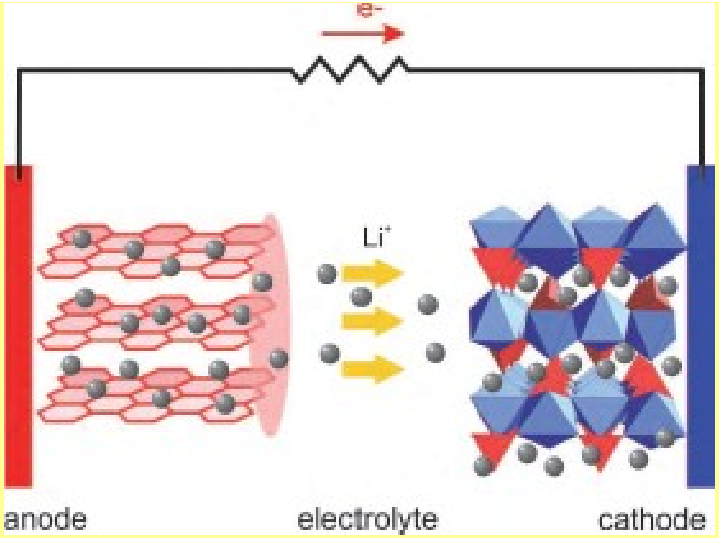


Li Intercalation



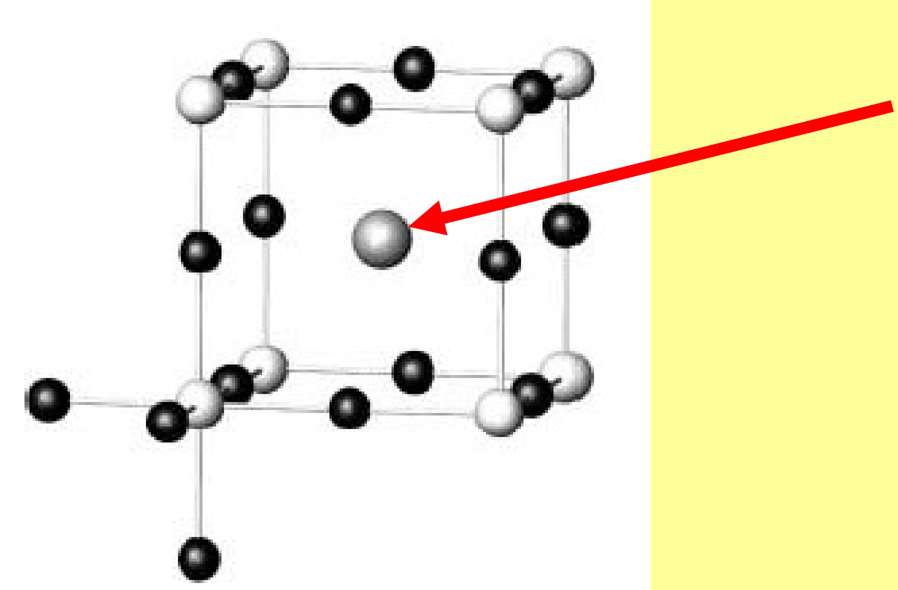
Li/C $\rightarrow$ e + Li$^+$ + C

Li$^+$ + e + $FePO_4 \rightarrow$ $LiFePO_4$



3D Intercalation Compounds

Cu_3N and Mn_3N crystallize in the (anti-) ReO_3-type structure



the large cuboctahedral void in the structure can be filled

By Pd to yield (anti-) perovskite-type $PdCu_3N$

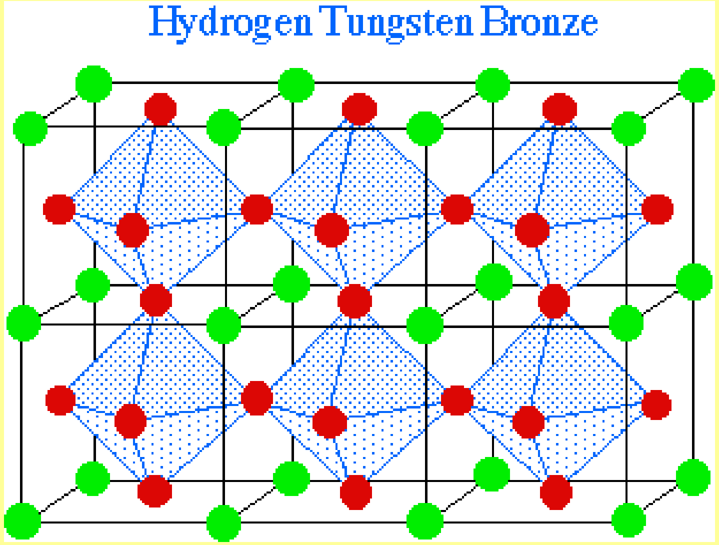
By M = Ga, Ag, Cu leading to MMn_3N

3D Intercalation Compounds

Tungsten trioxide structure
= WO_6 octahedra joined at their corners
= the perovskite structure of $CaTiO_3$ with all the calcium sites vacant

$Zn + 2\ HCl \rightarrow 2\ H + ZnCl_2$

$WO_3 + x\ H \rightarrow H_xWO_3$



The color and conductivity changes are due to the intercalation of protons into the cavities in the WO_3 structure, and the donation of their electrons to the conduction band of the 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

C_{60} = FCC

$K_3 C_{60}$