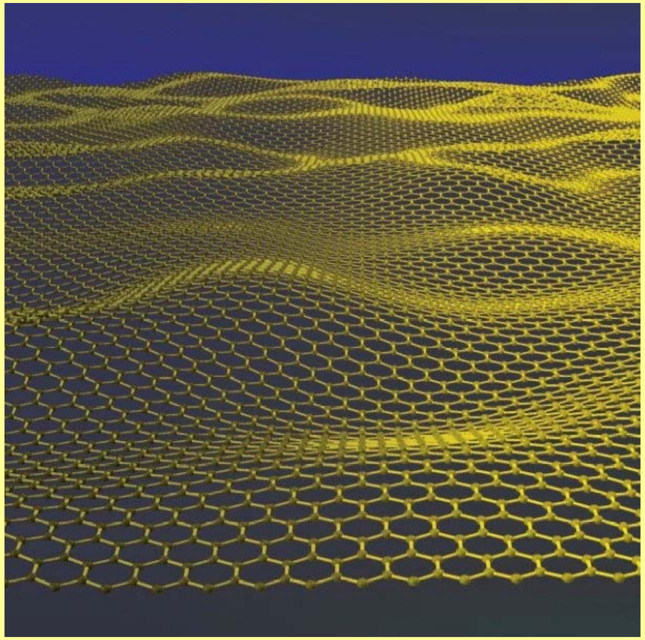
Layered Compounds



Two-dimensional layers

Graphite and Graphene

Clay Minerals

Layered Double Hydroxides (LDHs)

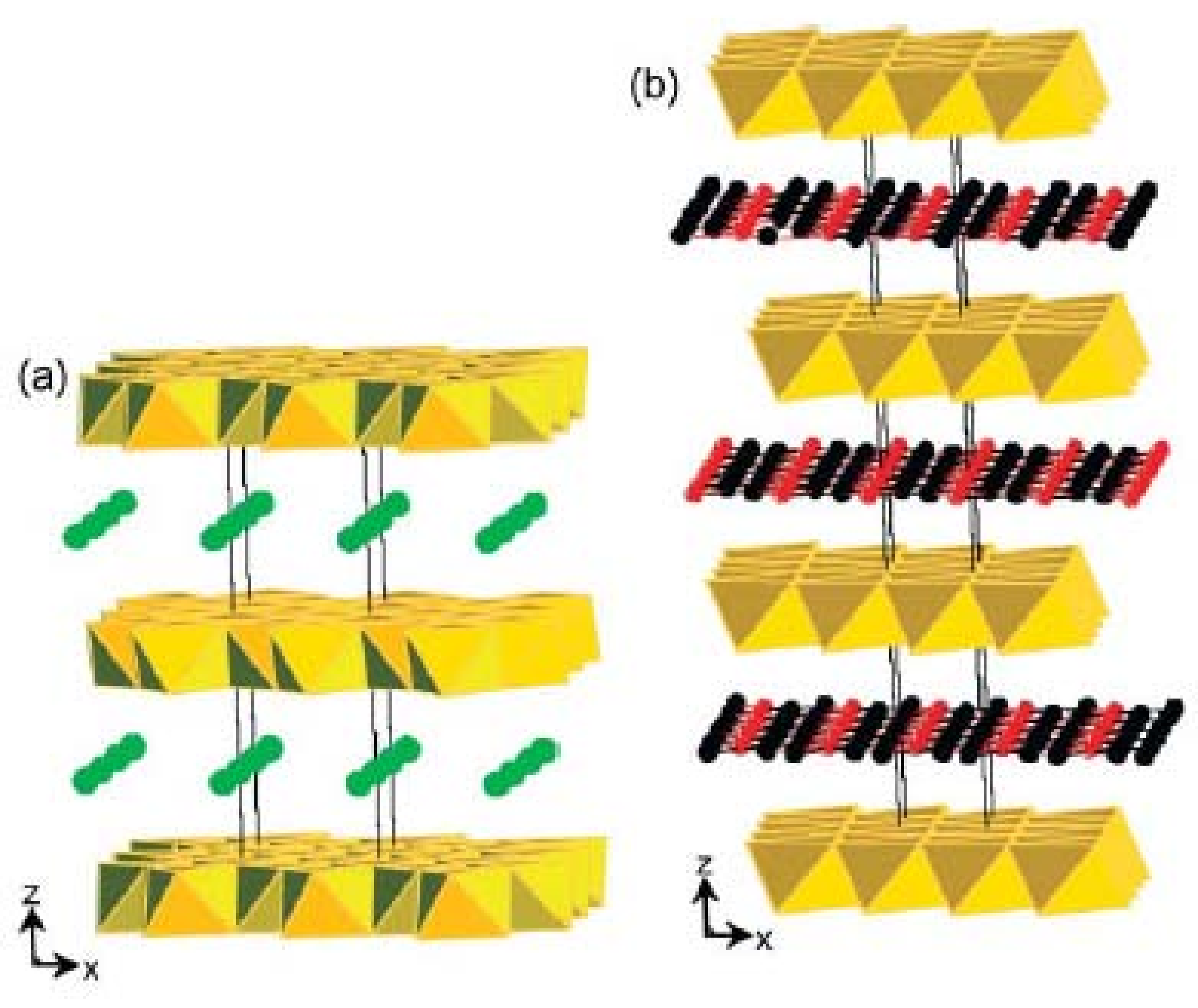
Layered Zirconium Phosphates and Phosphonates

Layered Metal Oxides

Layered Metal Chalcogenides - TiS_2, MPS_3 (M = V, Mn, Fe, Co, Ni, Zn)

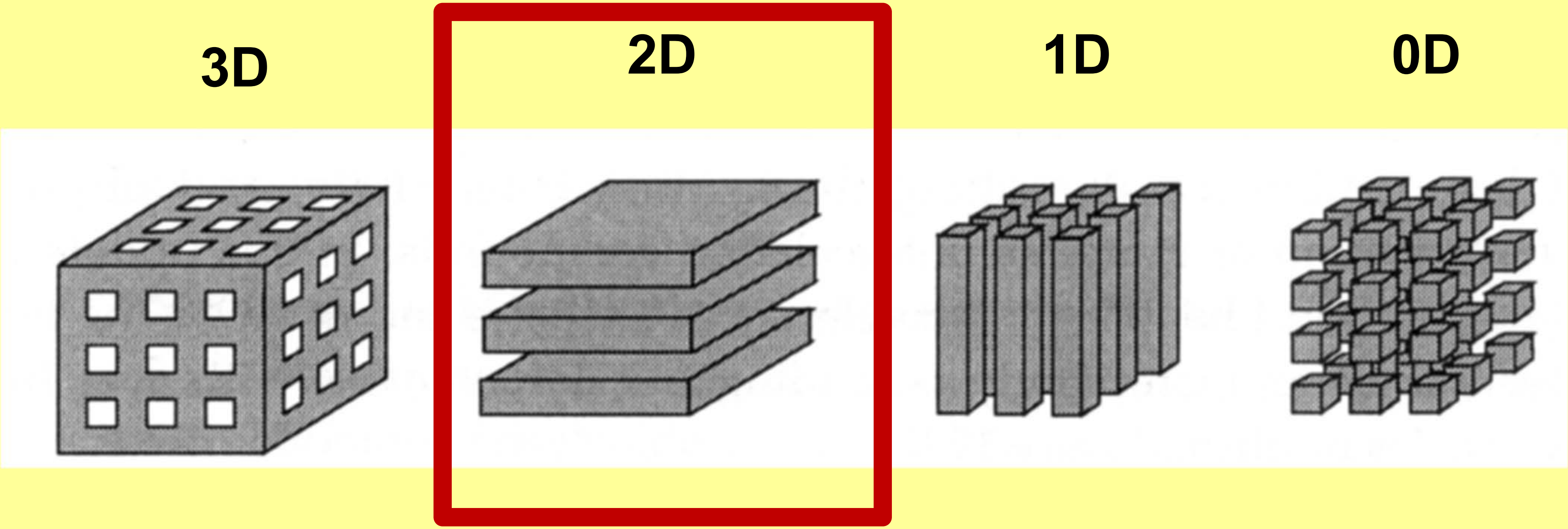
Alkali Silicates and Crystalline Silicic Acids

Layered Compounds



Host-Guest Structures

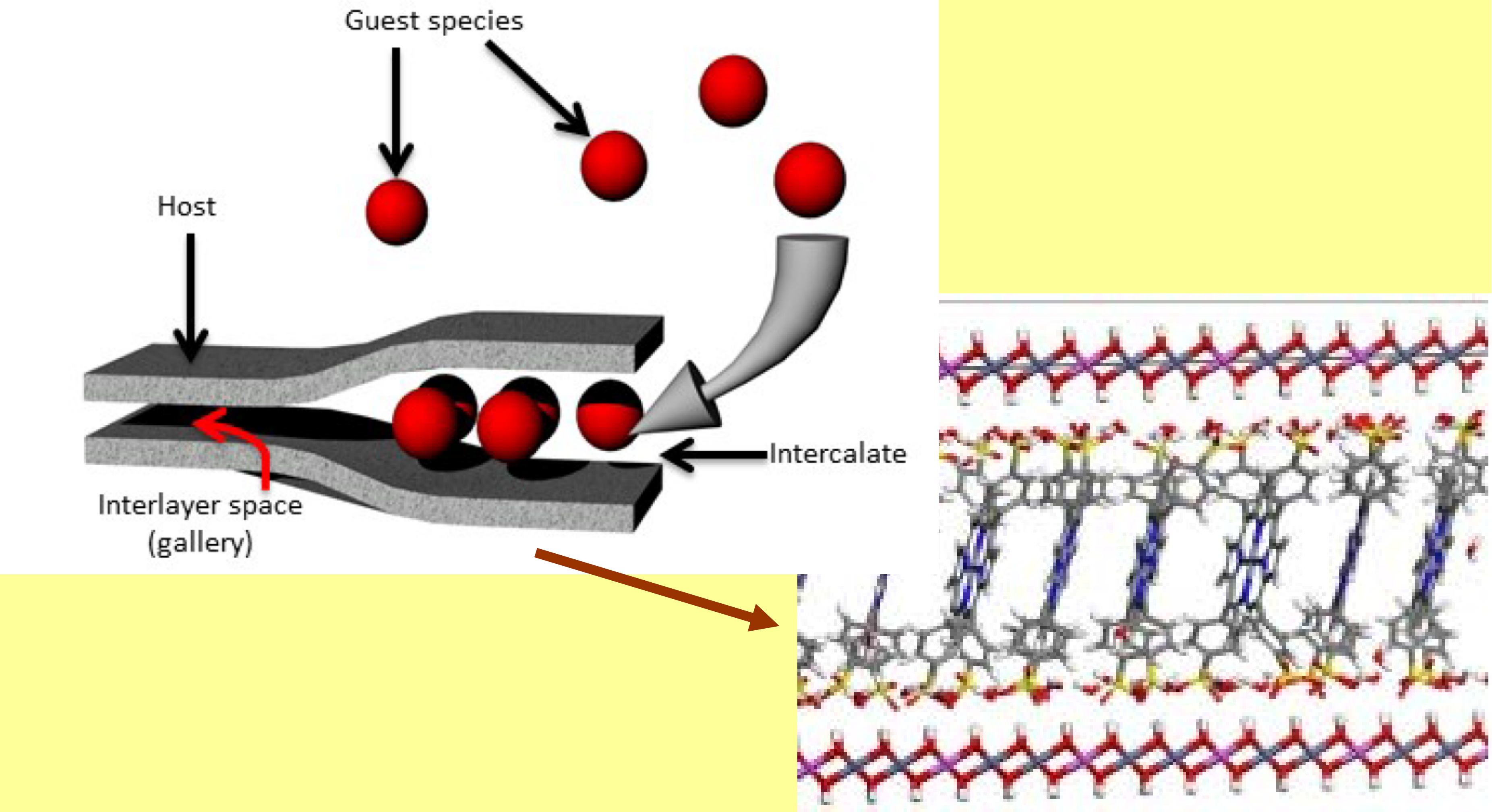
Host dimensionality



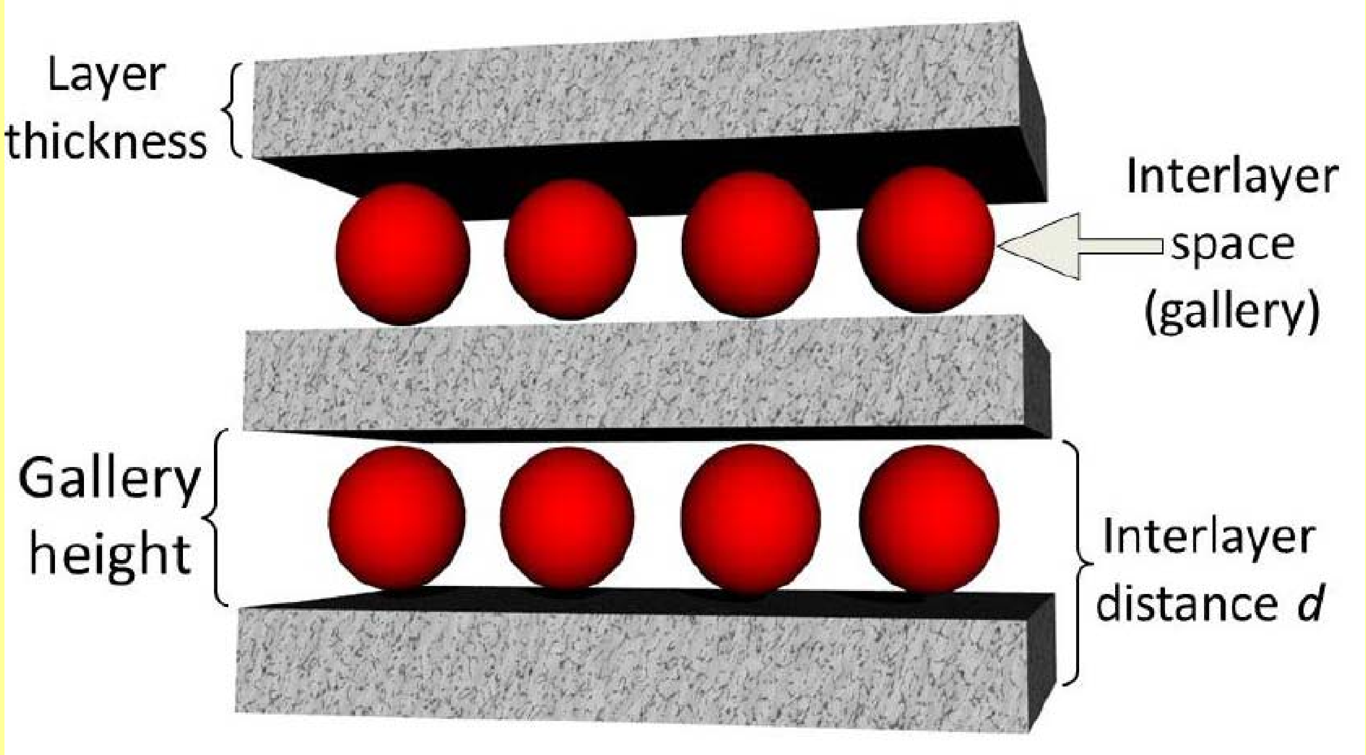
TOPOTACTIC SOLID-STATE REACTIONS = modifying existing solid state structures while maintaining the integrity of the overall structure

Intercalation

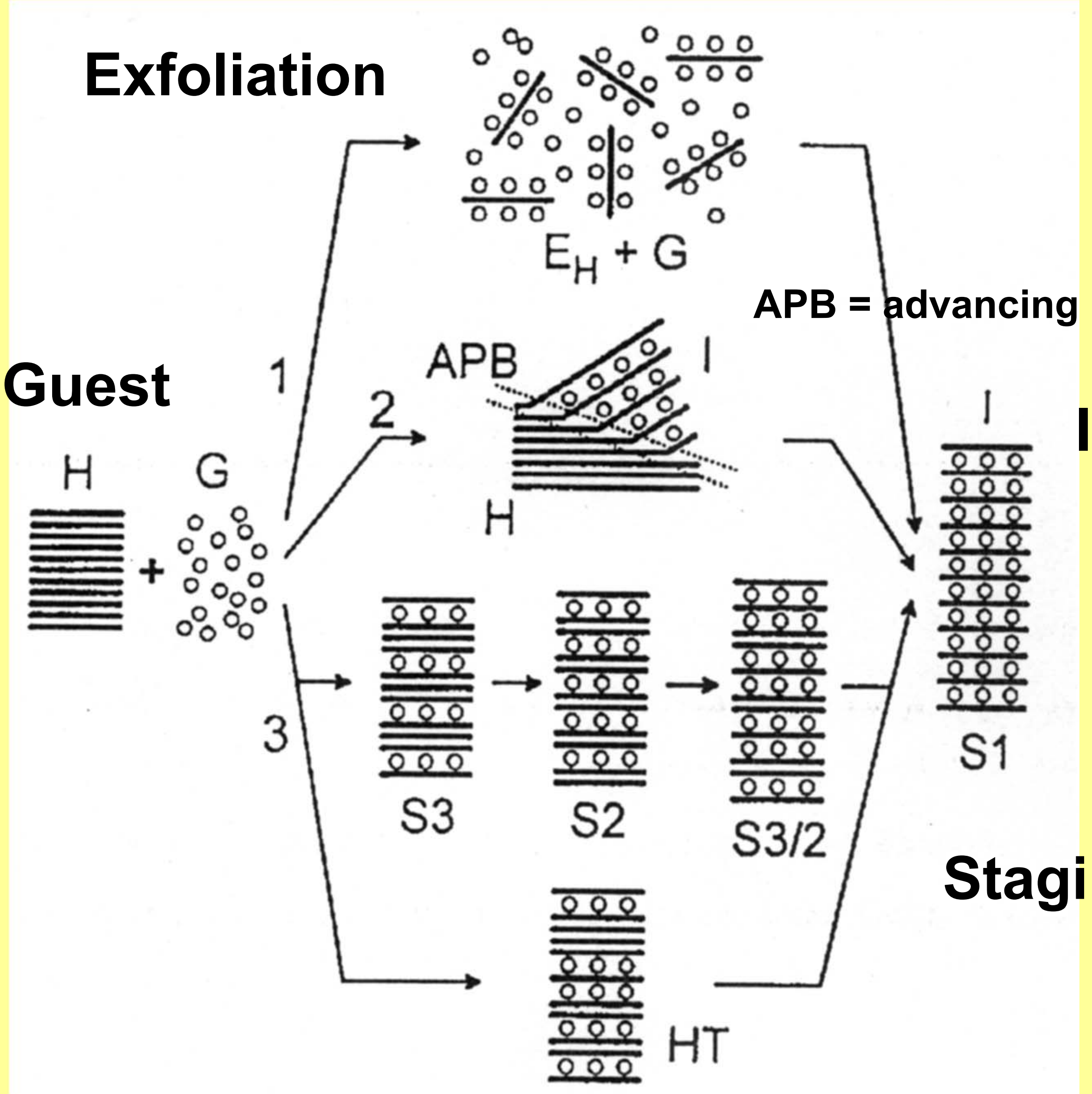
Intercalation Insertion of molecules between layers



Intercalation



Intercalation



Exfoliation

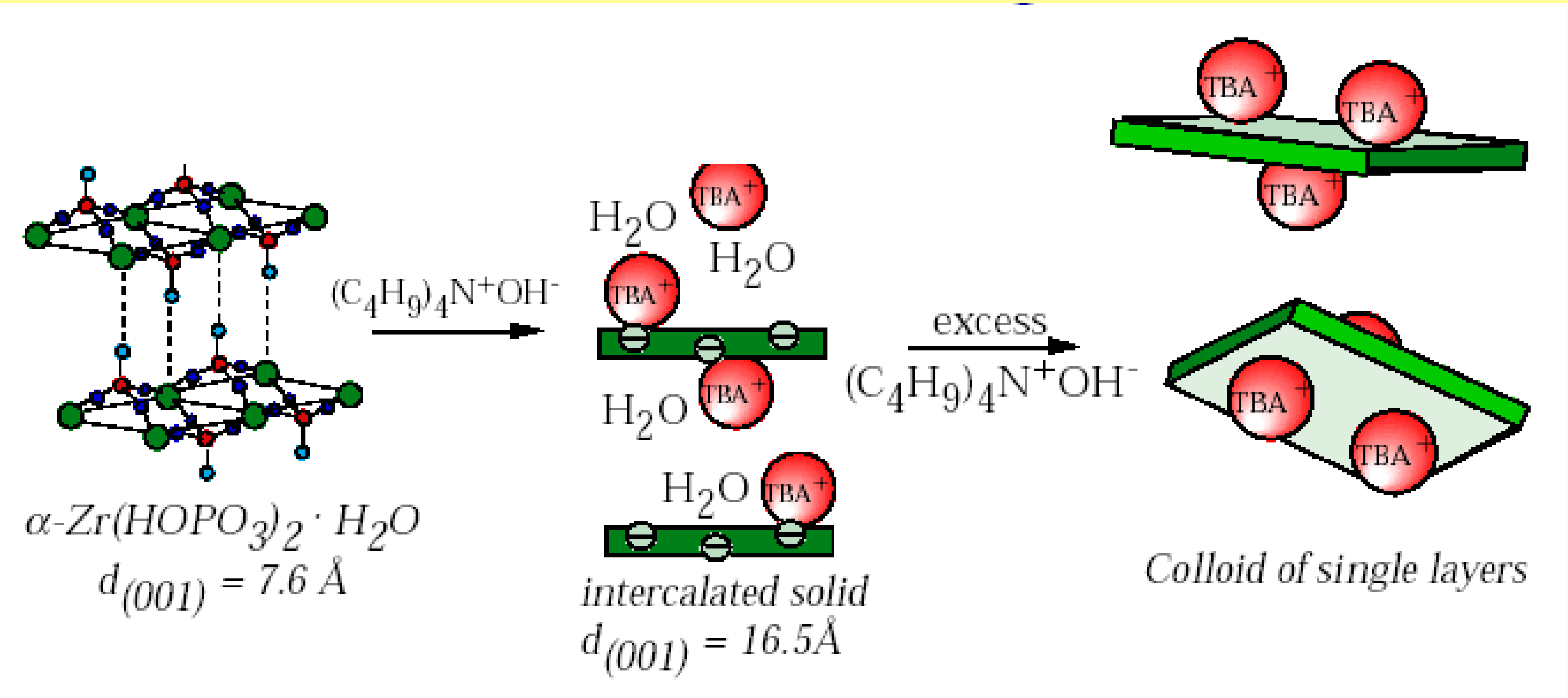
APB = advancing phase boundary

Host + Guest

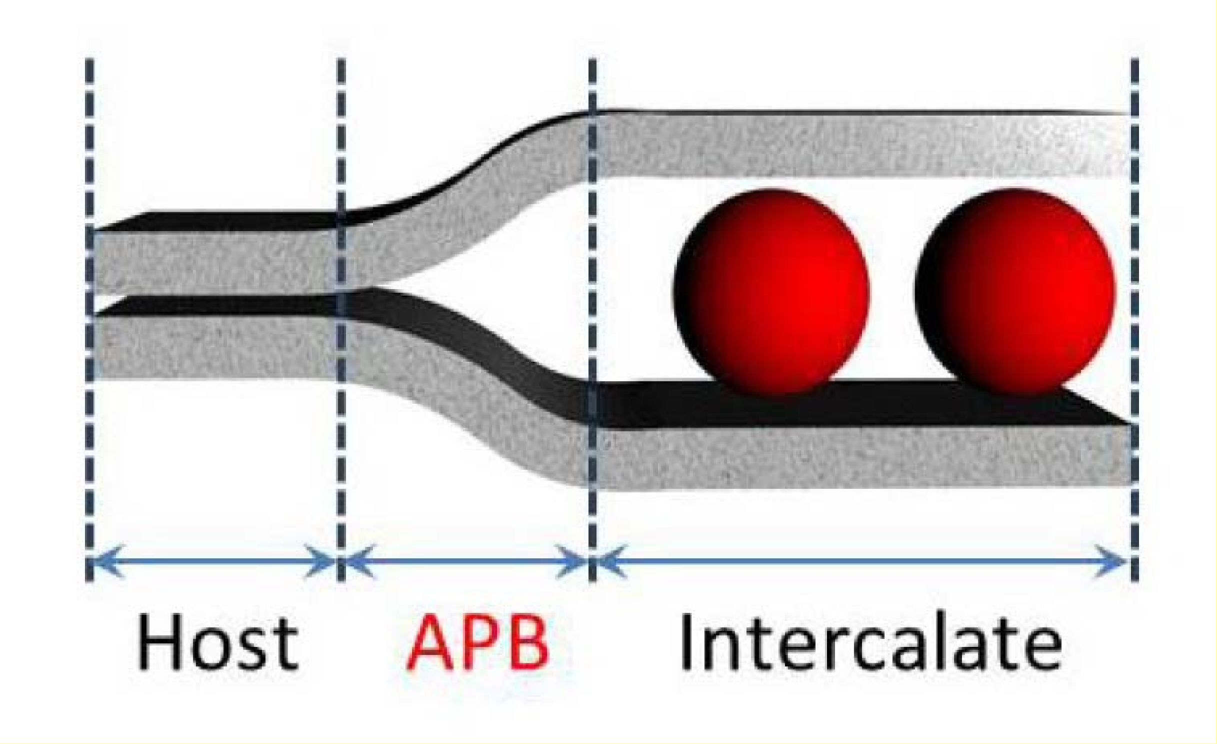
Intercalate

Staging

Exfoliation

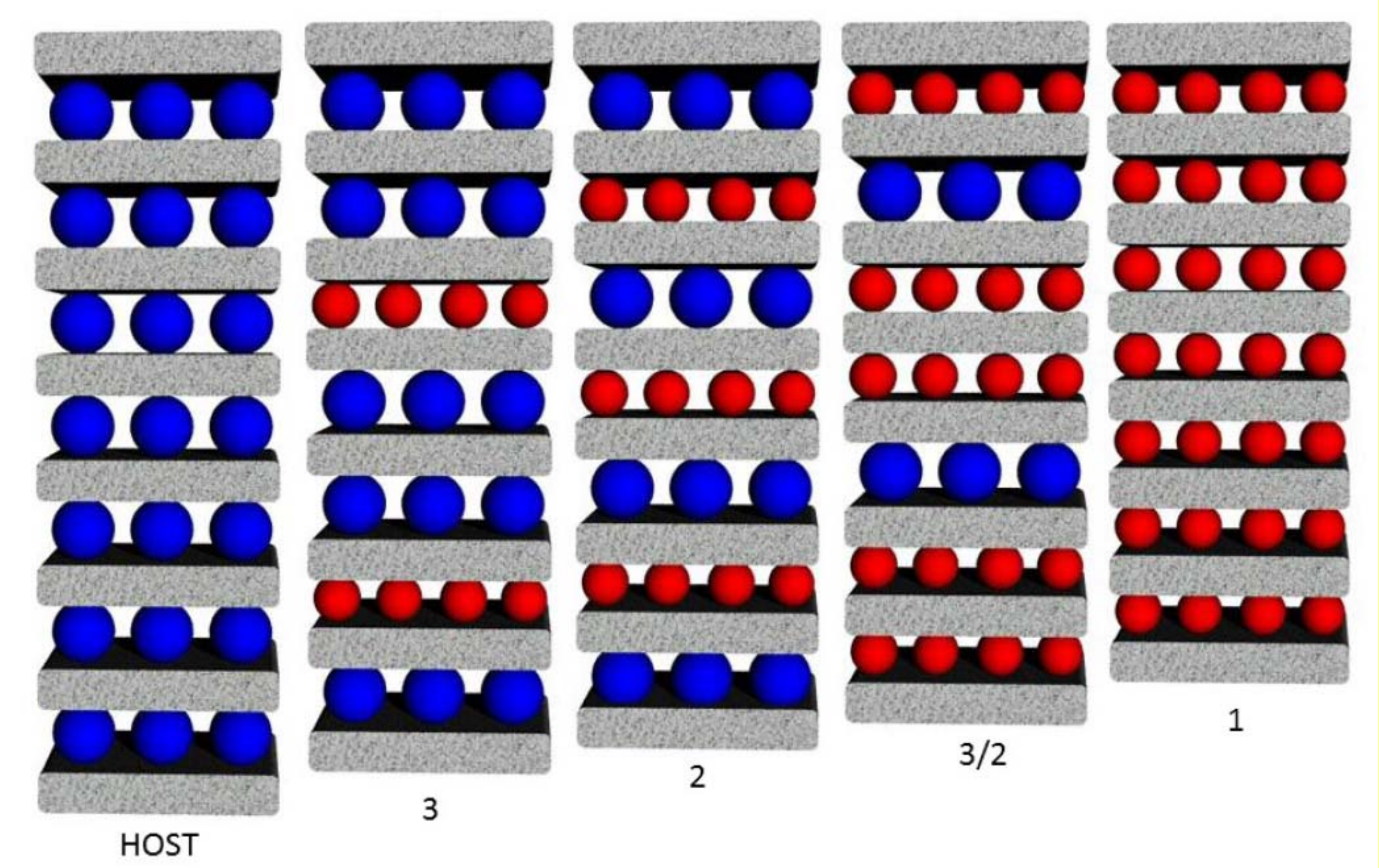


APB = advancing phase boundary

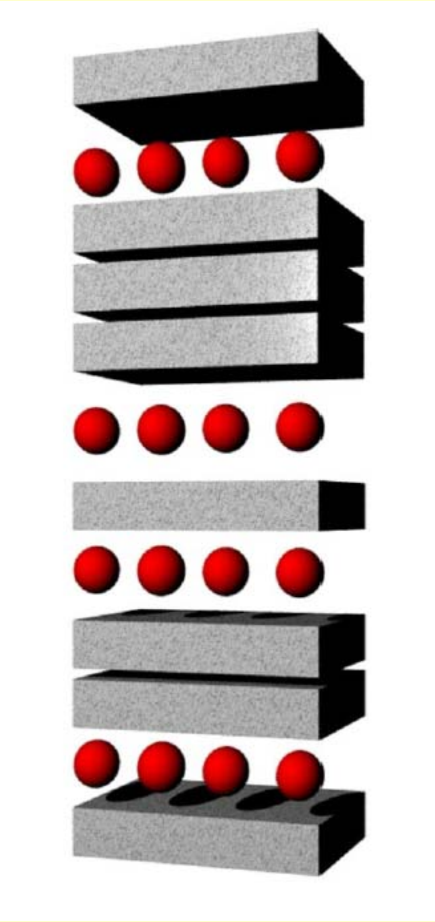


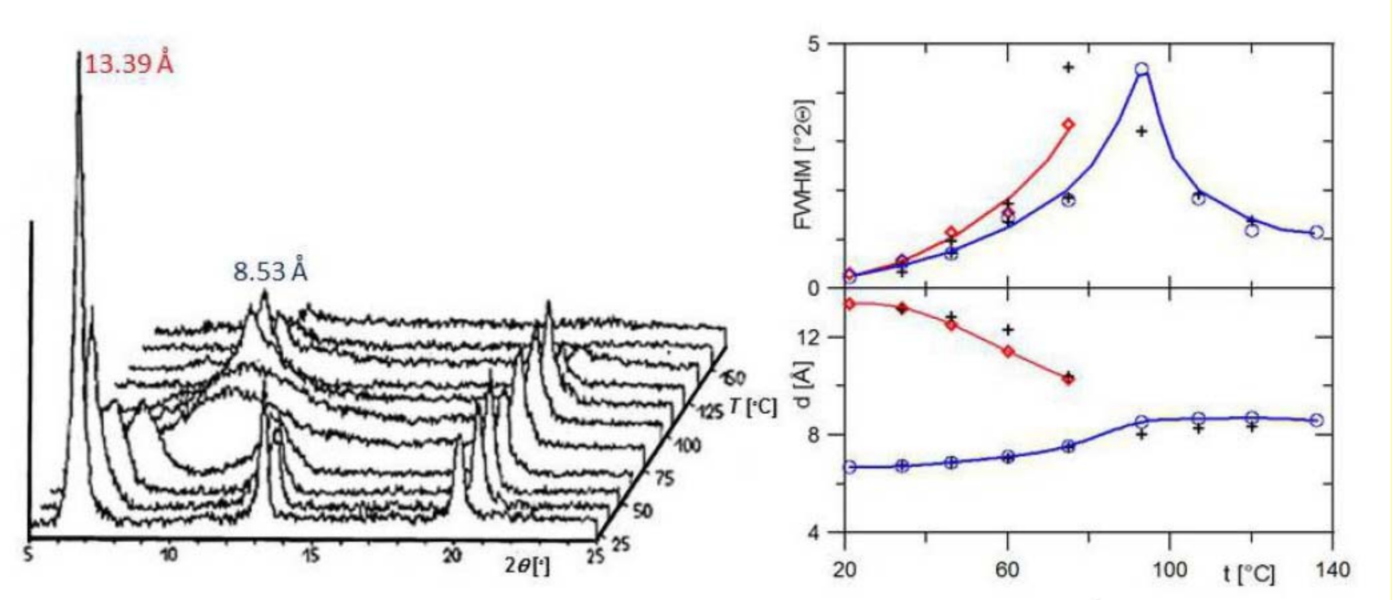
APB = advancing phase boundary

Staging



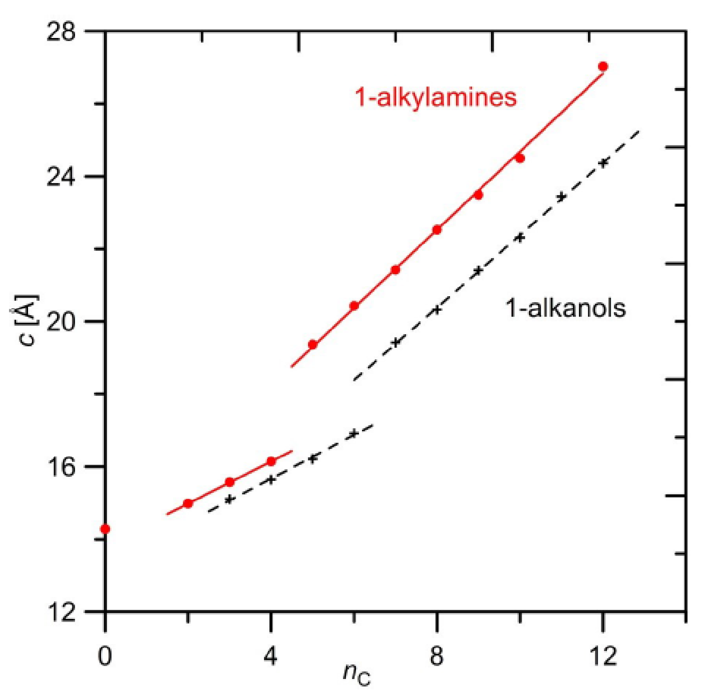
Hendricks-Teller effect

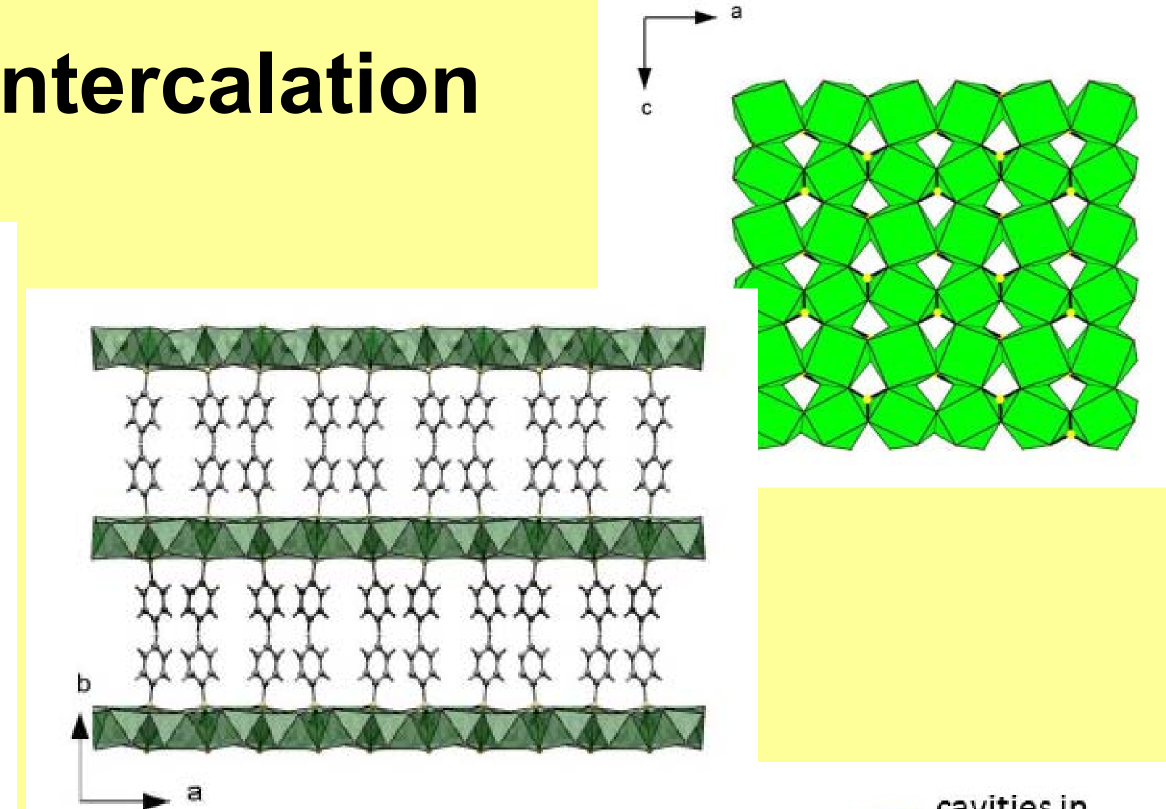


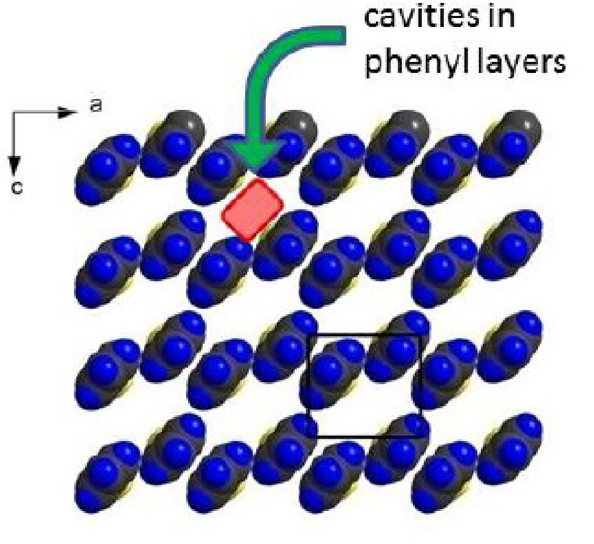


HT = galleries are filled randomly

Intercalation



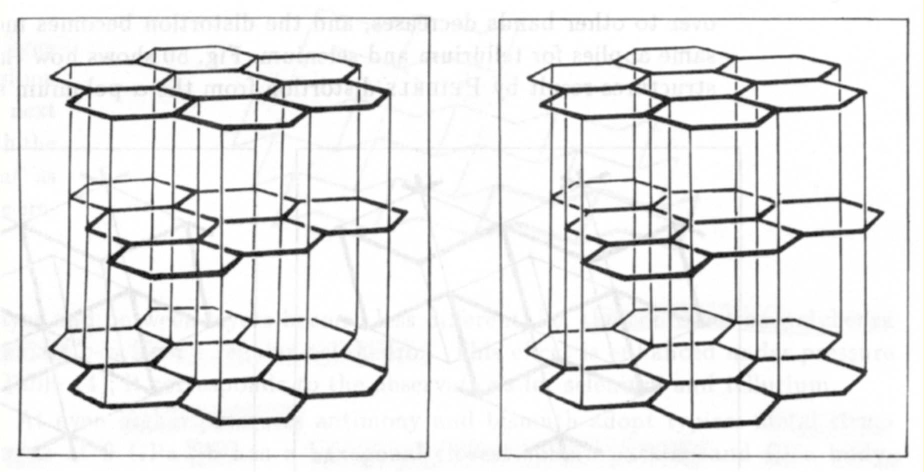


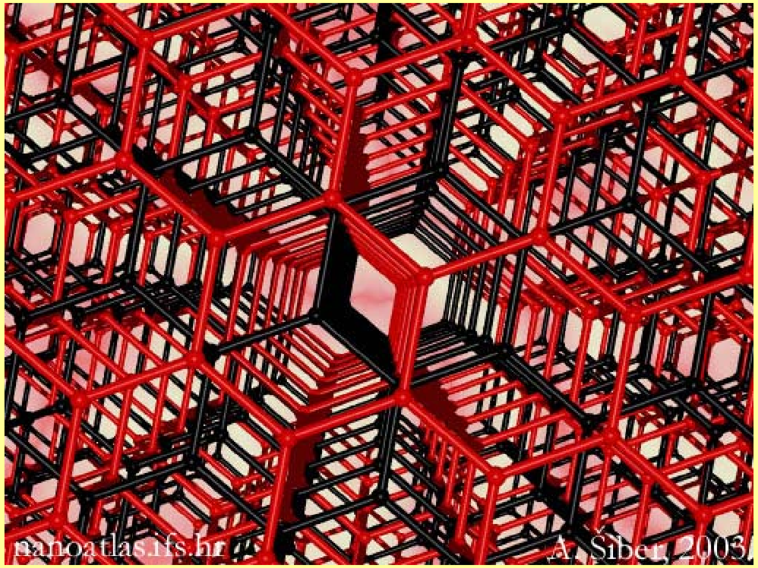


Dependence of the basal spacing of the intercalates of the alkylamines (circles) and alkanols (crosses) on the number of carbon atoms n_C in $SrC_6H_5PO_3 \cdot 2H_2O$

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) → $C_{24}K \rightarrow C_{36}K \rightarrow C_{48}K \rightarrow C_{60}K$

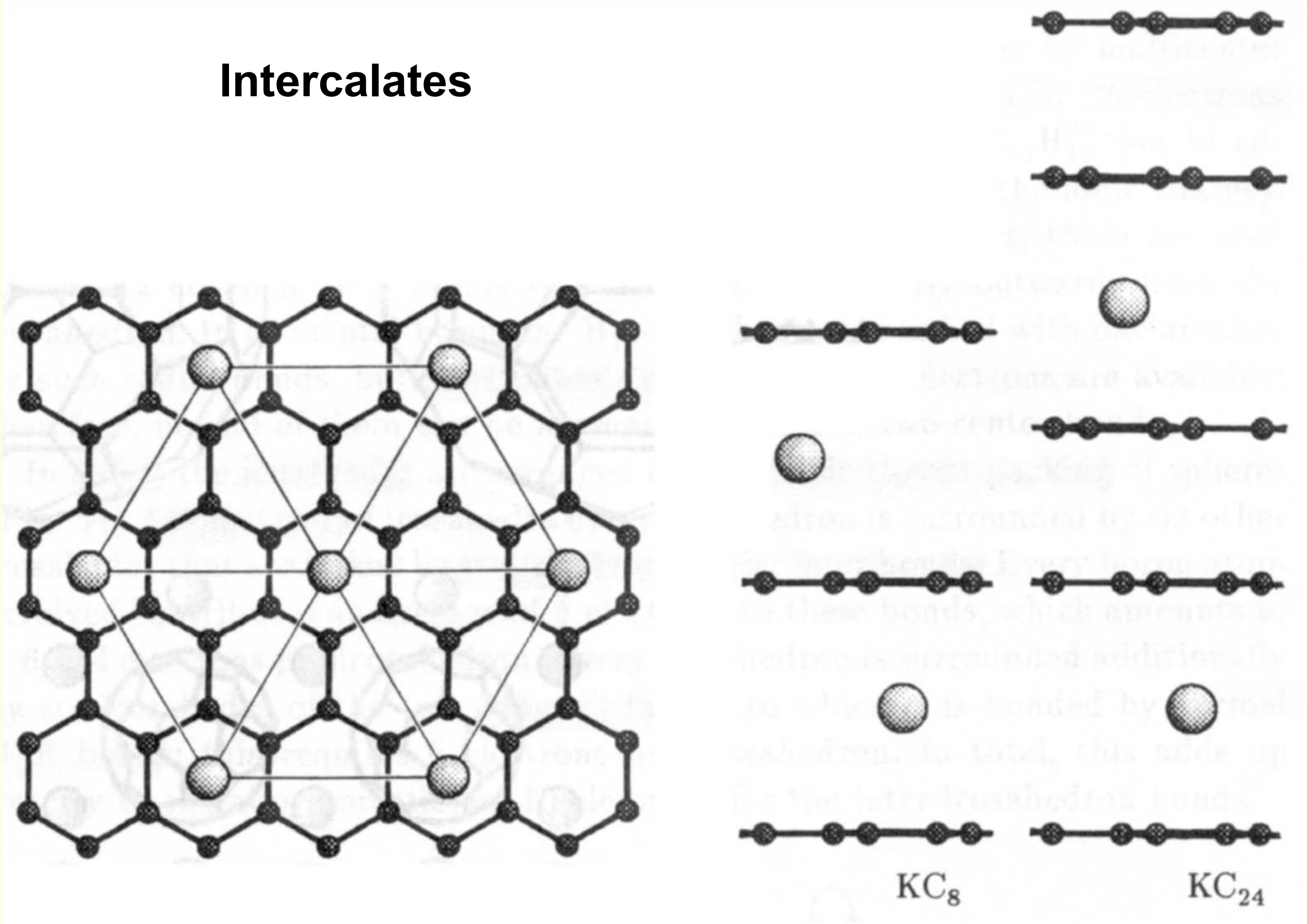
C_8K potassium graphite ordered structure

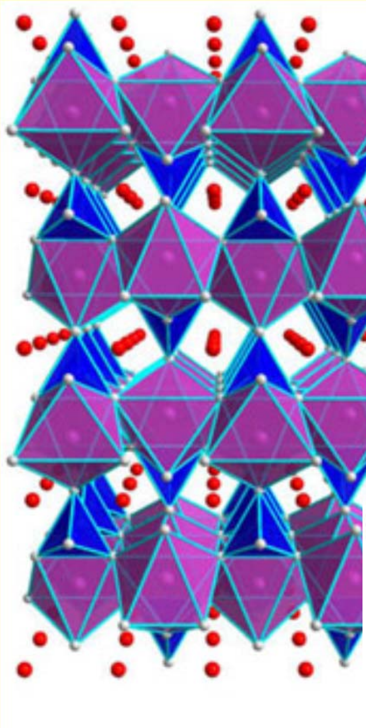
Ordered K guests between the sheets, K to G charge transfer

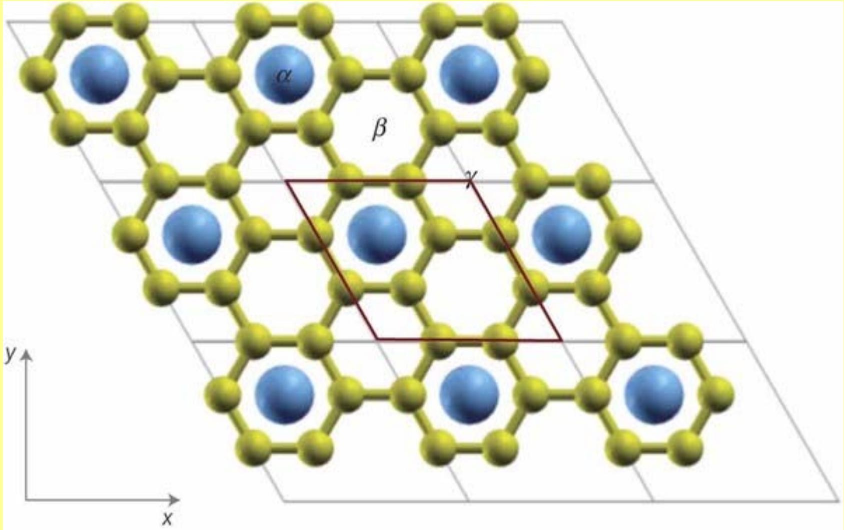
AAAA stacking sequence
reduction of graphite sheets, electrons enter CB
K nesting between parallel eclipsed hexagonal planar carbon six-rings

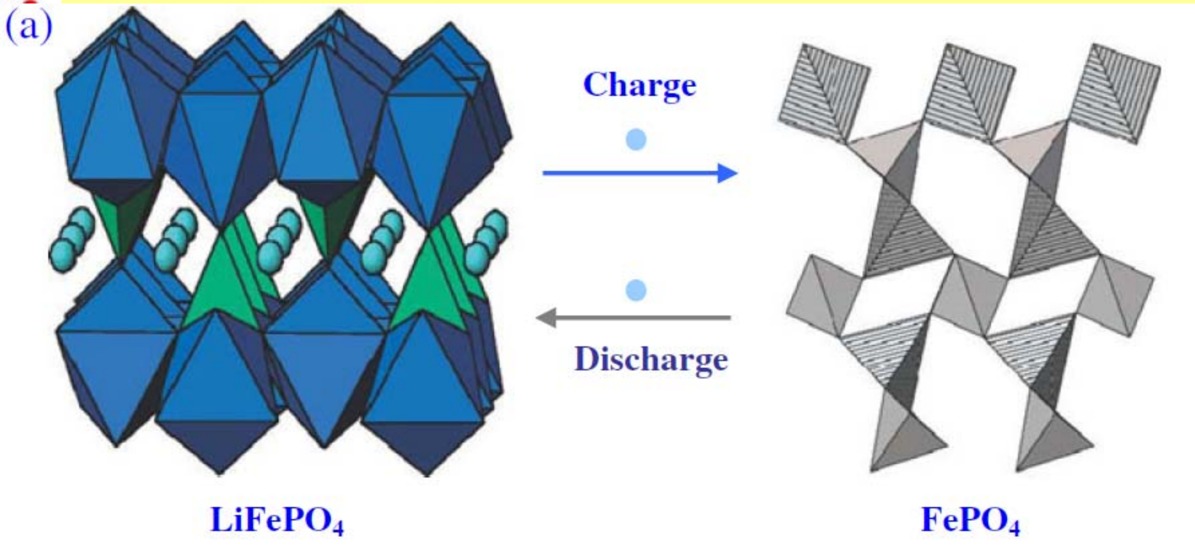
Graphite

Intercalates

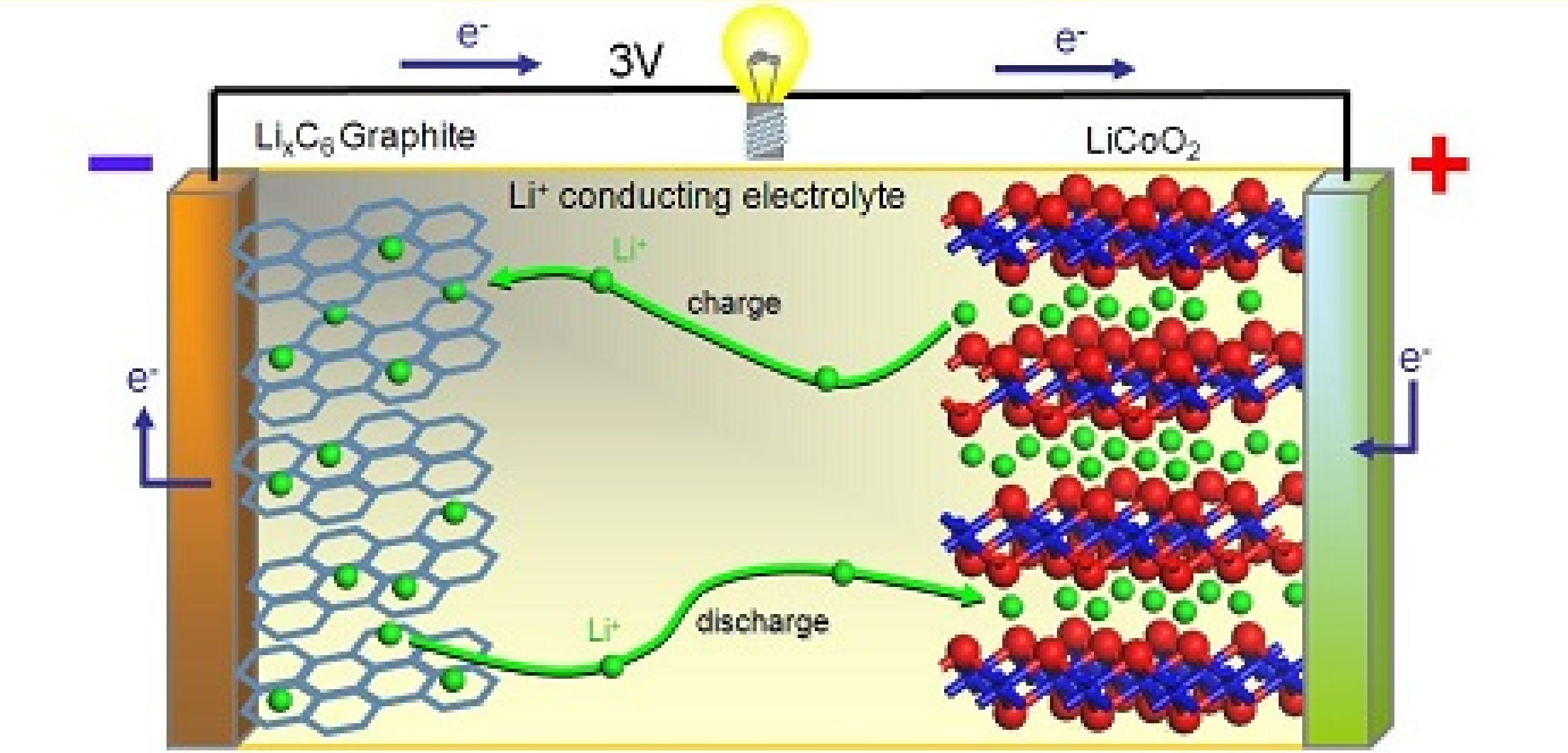





α
β
γ
y
x


(a)
Charge
Discharge
$LiFePO_4$
$FePO_4$

Li-ion Cells


e⁻
3V
e⁻
Li$_x$C$_6$ Graphite
LiCoO$_2$
−
+
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}**

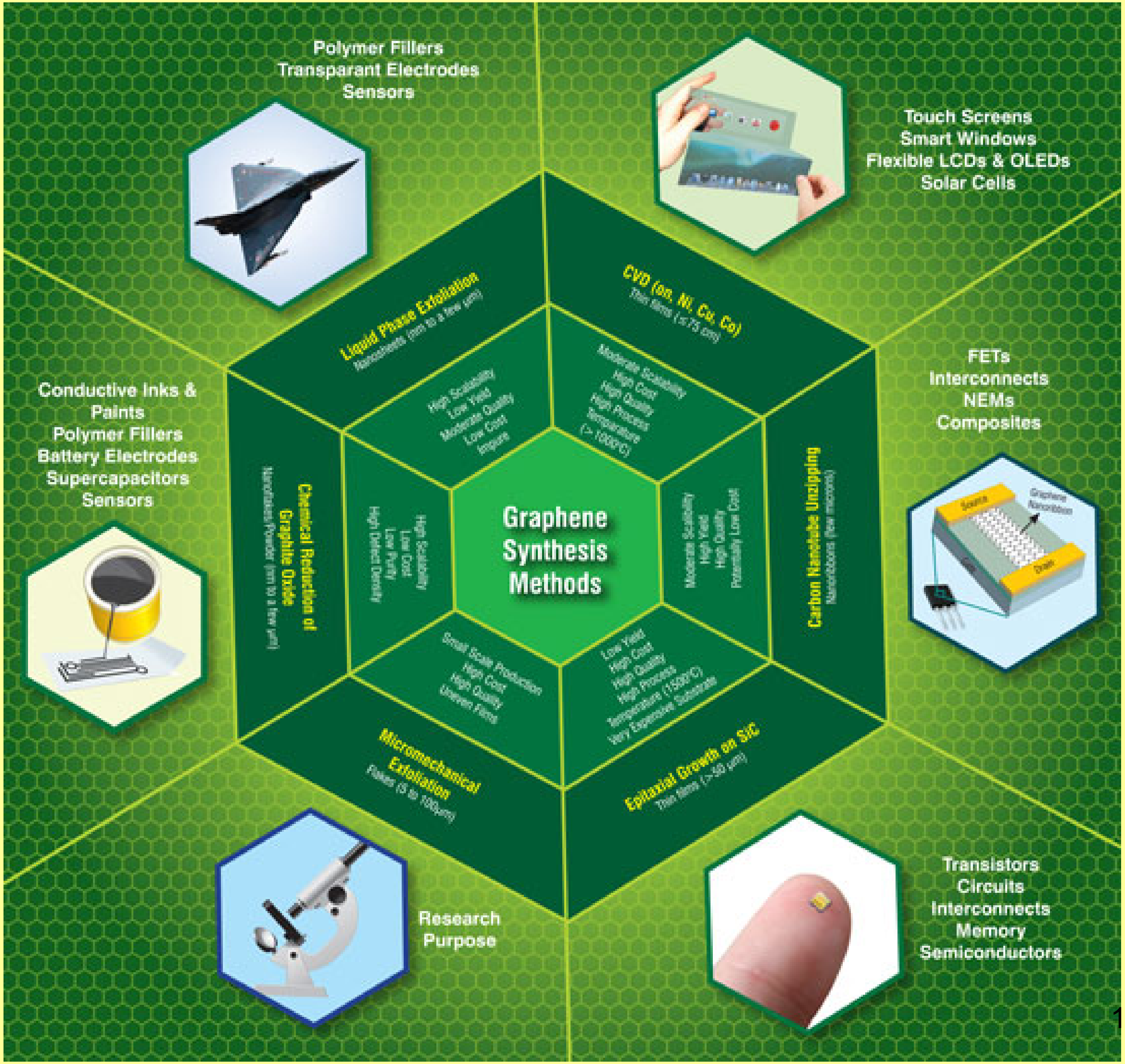
K. Novoselov

A. Geim

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

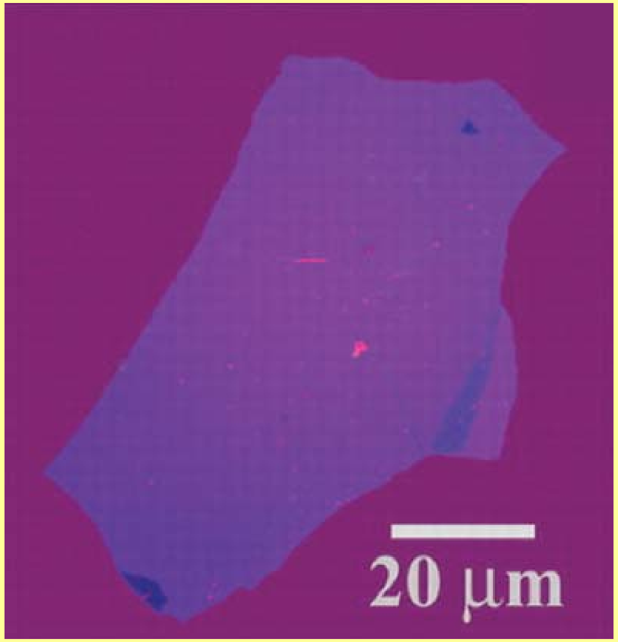
Sythesis of graphene

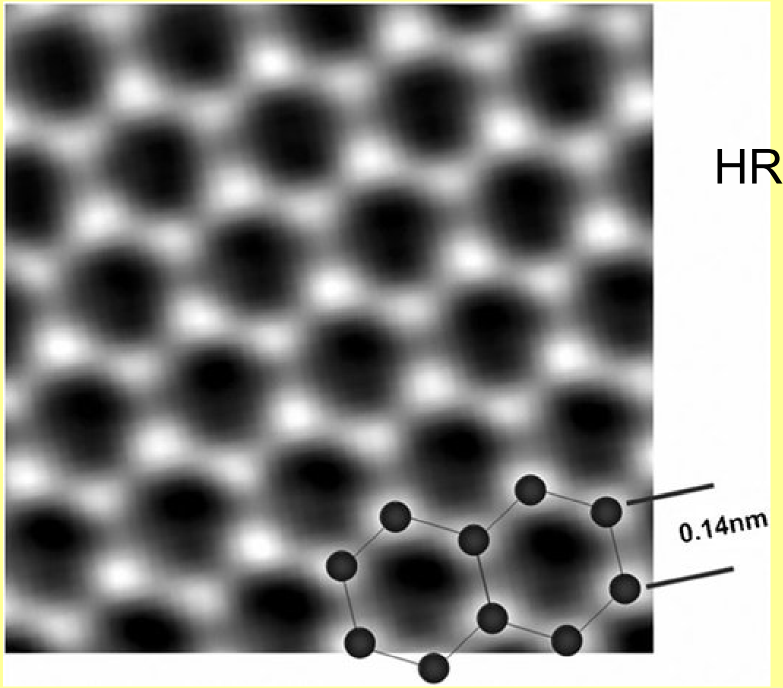
- Top down
  - Mechanical exfoliation
  - Chemical exfoliation
- Bottom up
  - CVD, epitaxial growth, …
- Defects
- Application: diodes, sensors, solar cell, energy storage, composites, …



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

Graphene





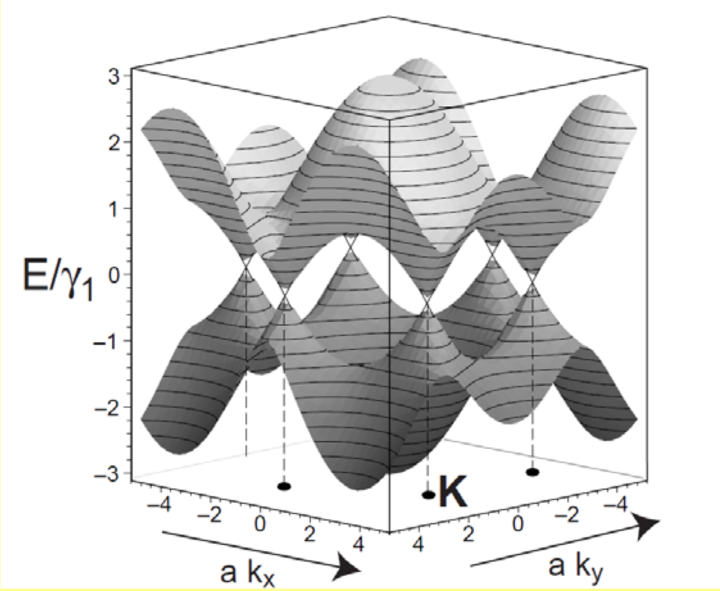
HRTEM

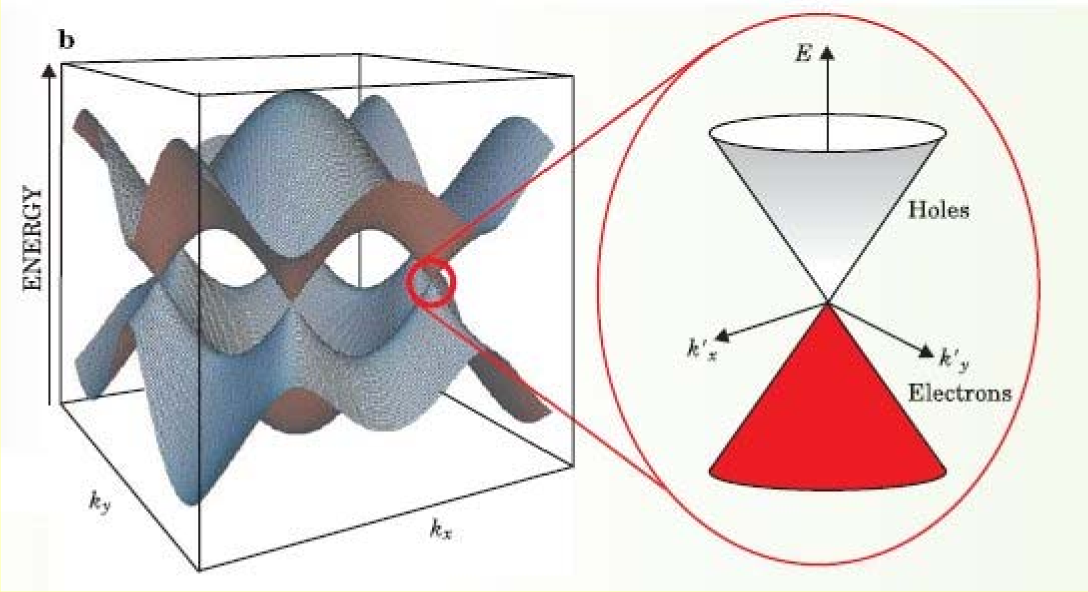
High electric conductivity (metallic)

Optically transparent – 1 layer absorbs 2.3% of photons

High mechanical strength

Graphene



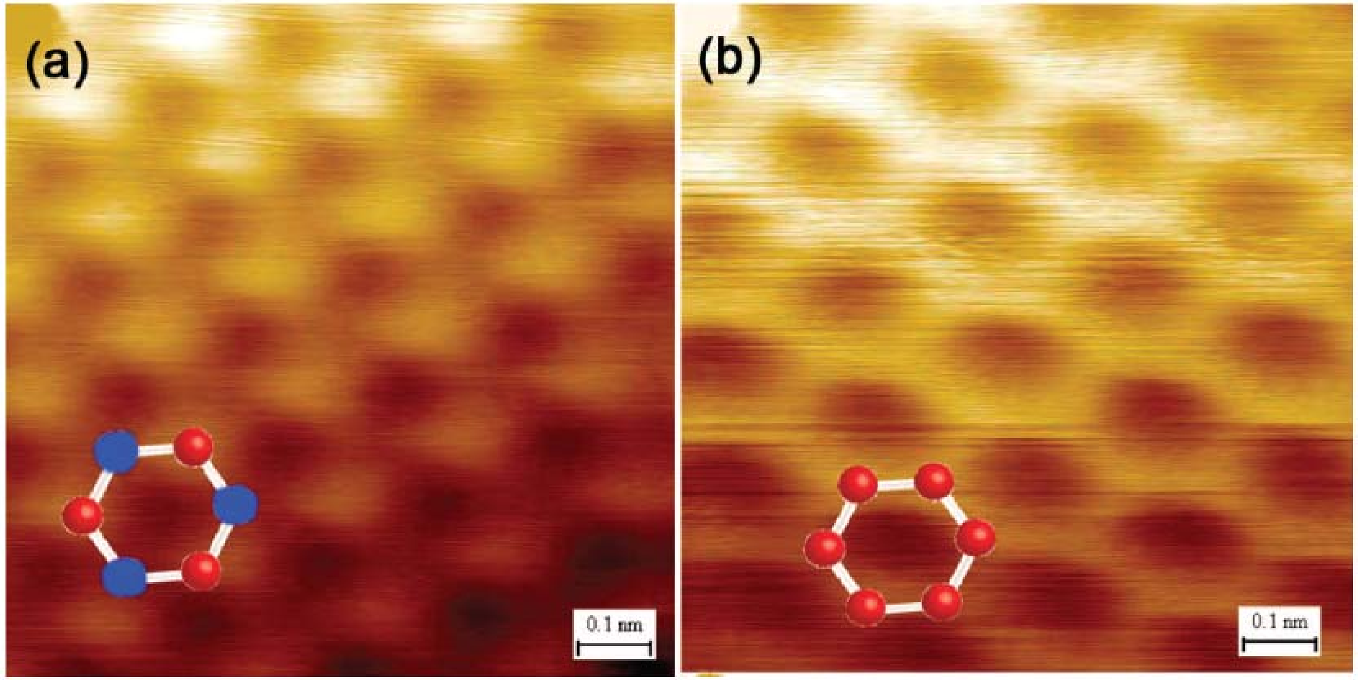


LCAO-band structure of graphene

Graphene

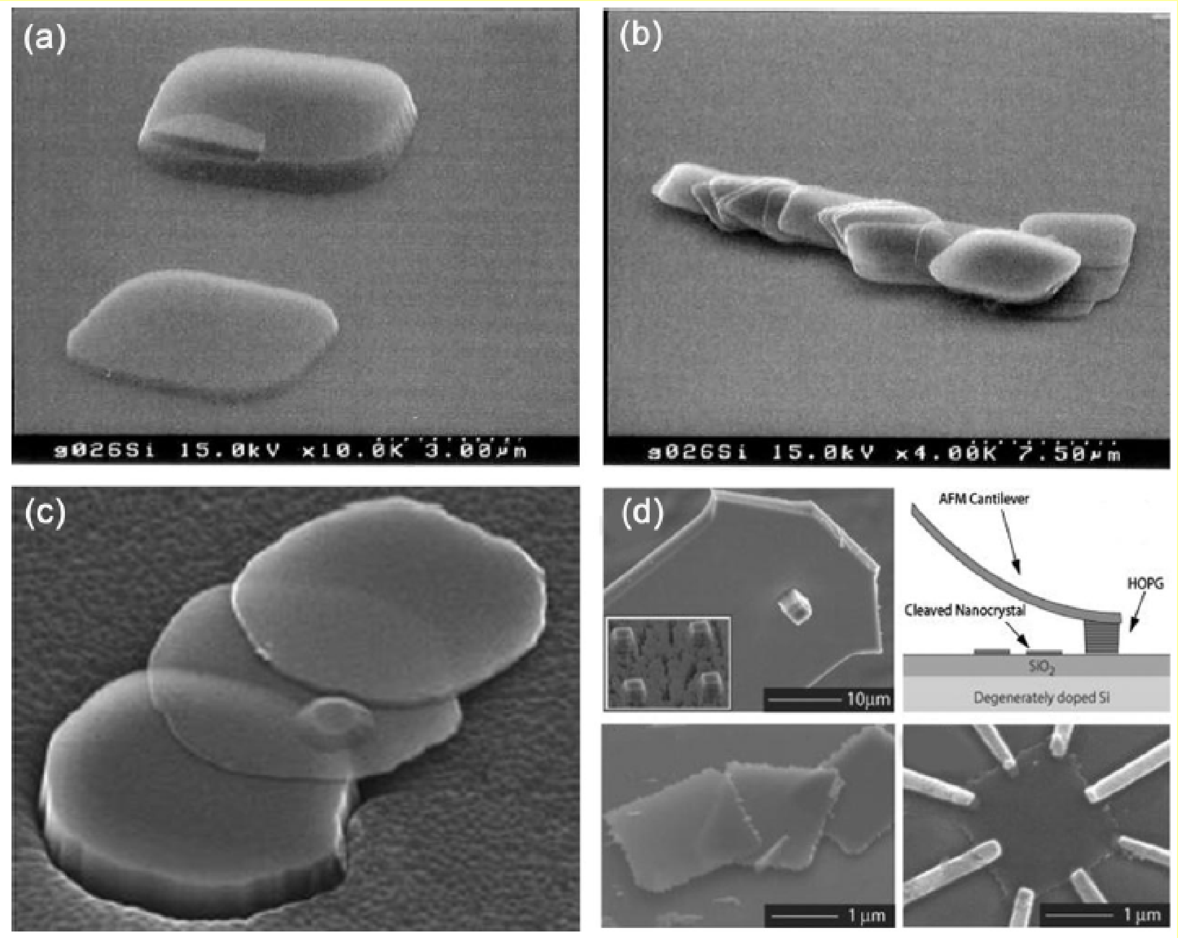
Preparation:

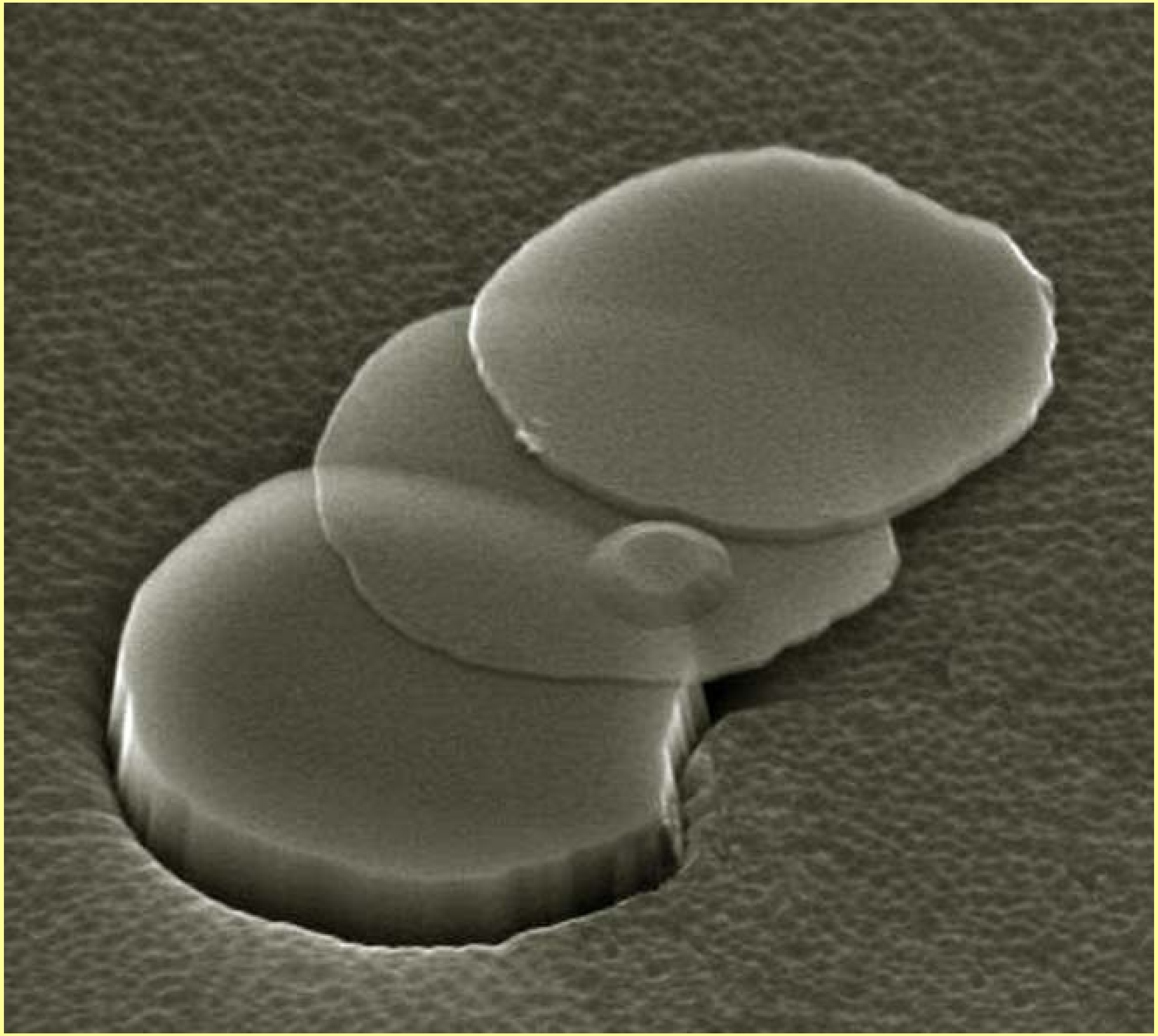
- **Scotch tape – layer peeling, flaking**
- **SiC pyrolysis – epitaxial graphene layer on a SiC crystal**
- **Exfoliation of graphite (chemical, sonochemical)**
- **CVD from CH_4, CH_2CH_2, or CH_3CH_3 on Ni (111), Cu, Pt surfaces**



Scotch tape – Layer peeling

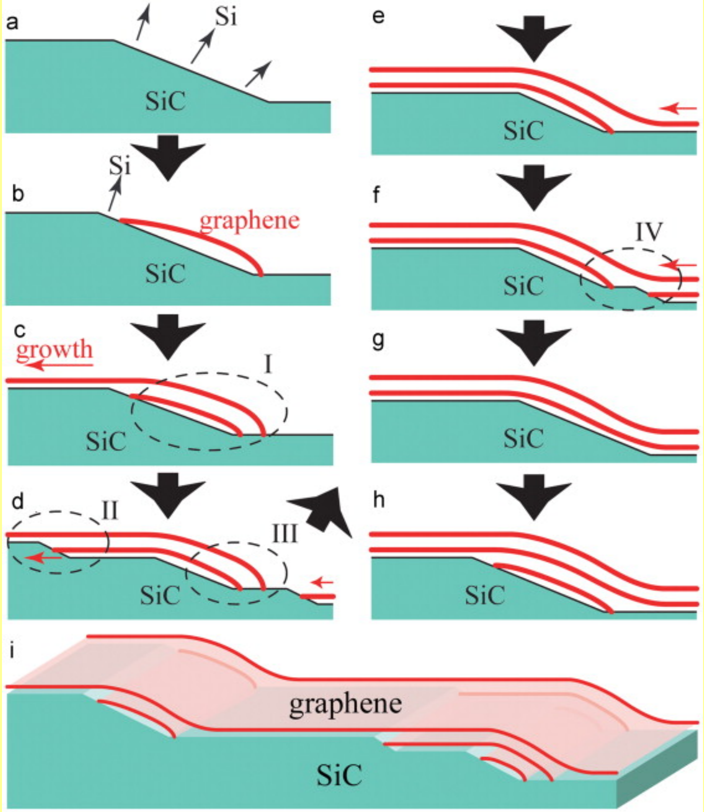
Mechanical exfoliation

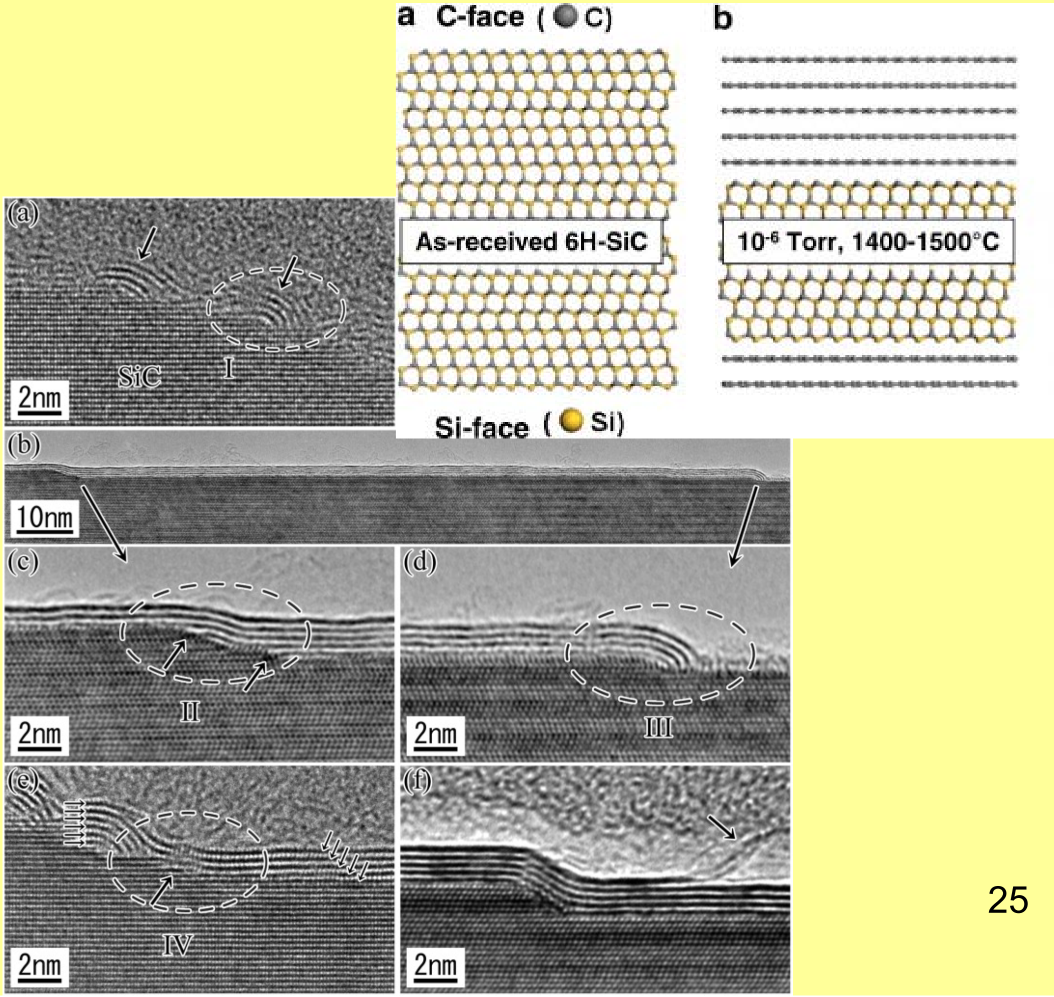


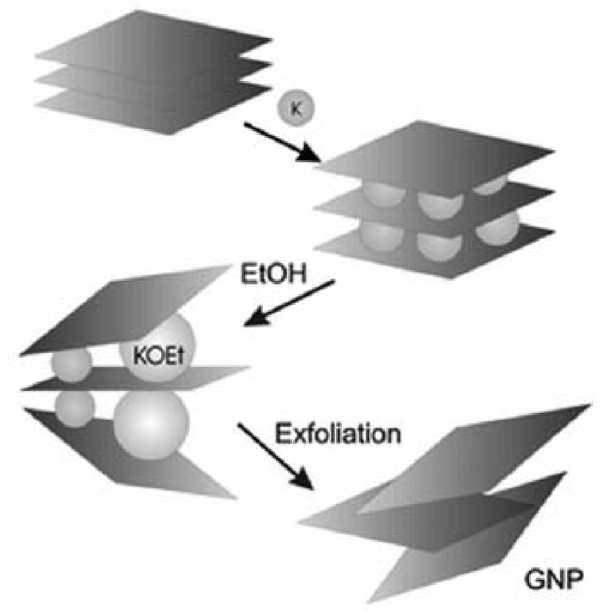


SiC pyrolysis

- 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



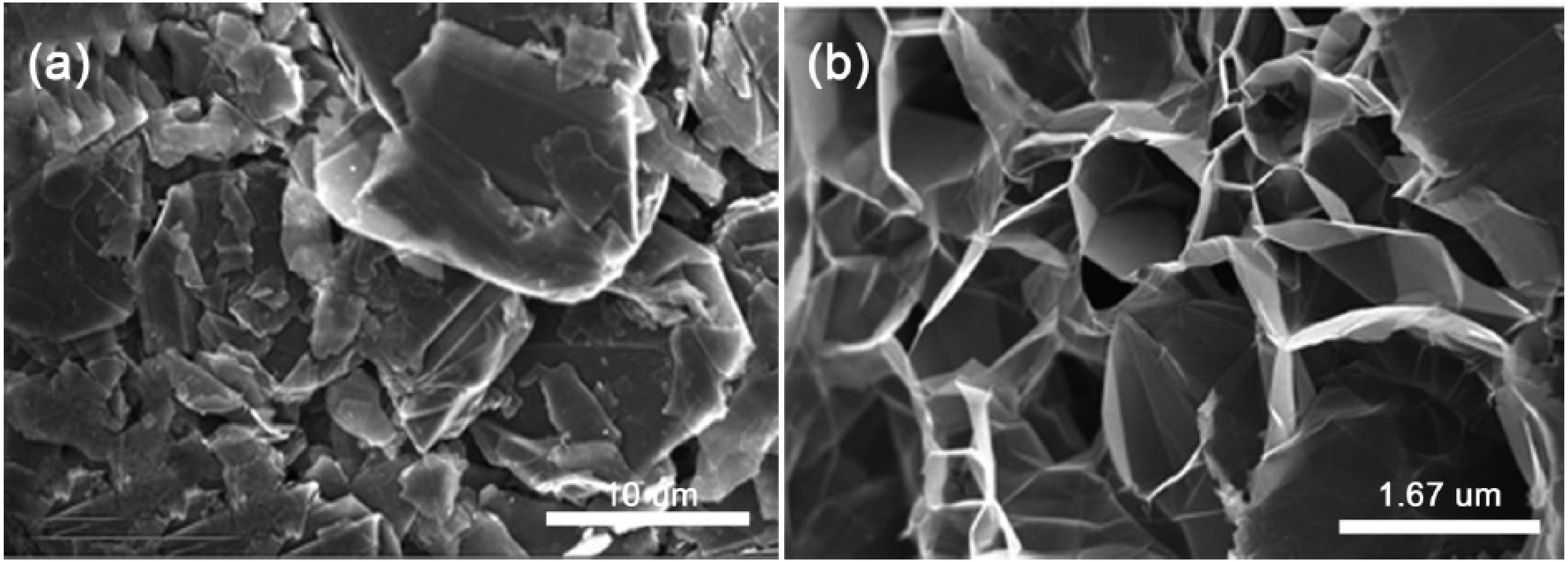




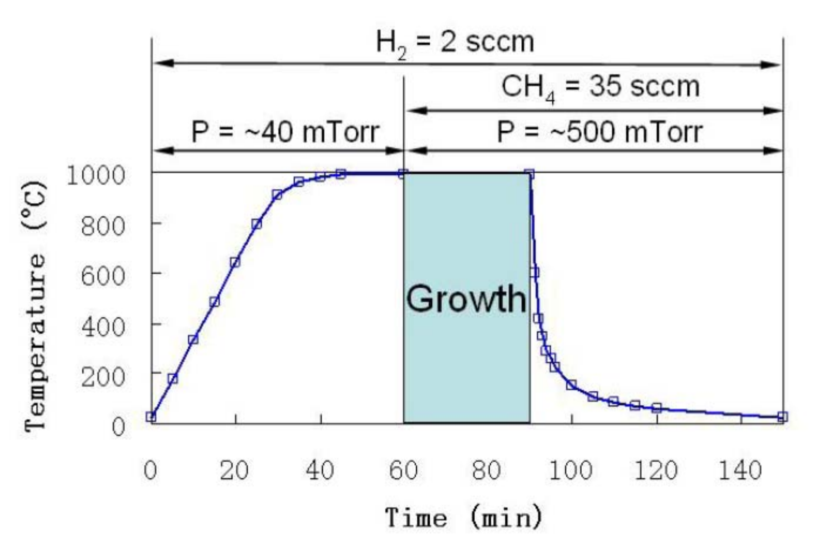
Exfoliation

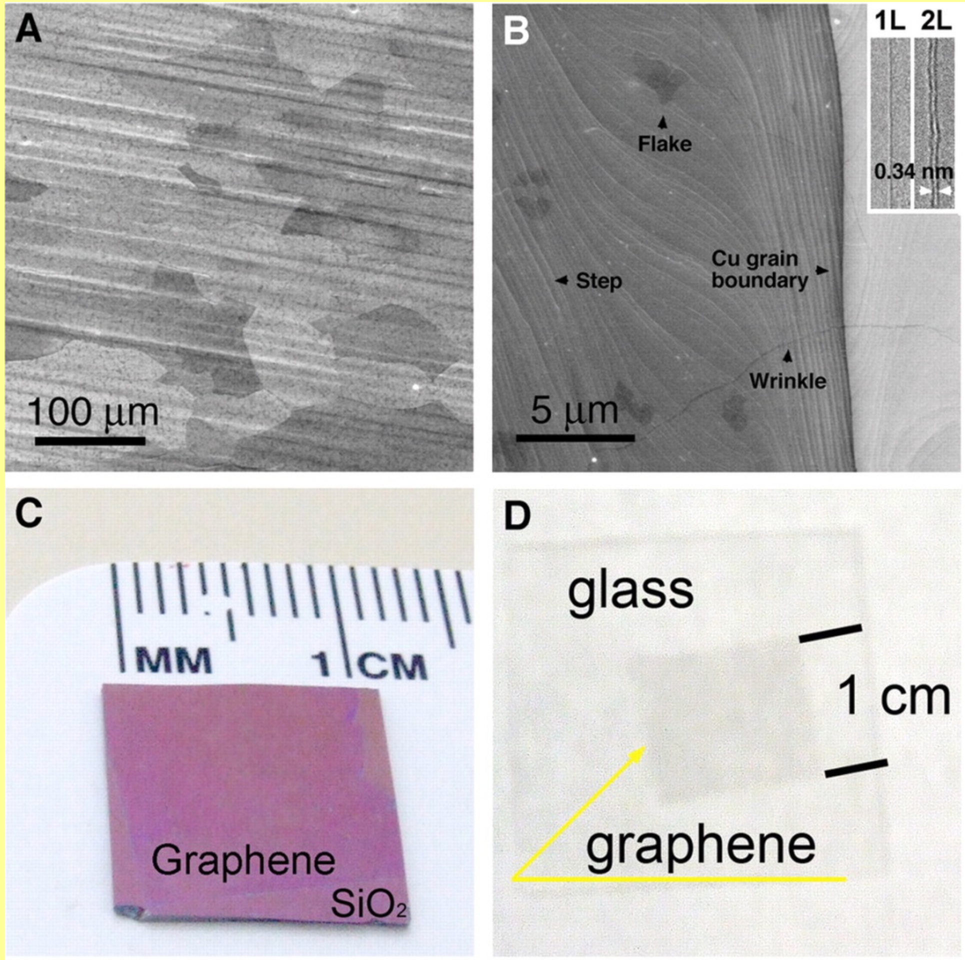
Chemical exfoliation (surfactant)

Sonochemical exfoliation



CVD from CH_4 / H_2 on Metal Surfaces





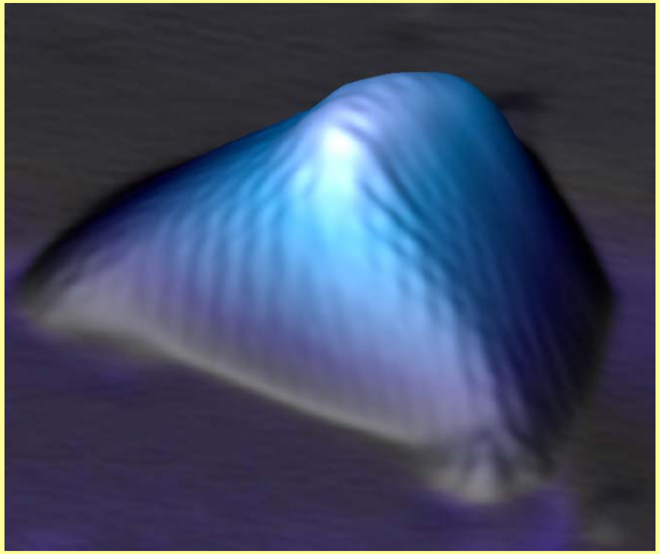
(A) SEM - graphene on a copper foil
(B) High-resolution SEM - Cu grain boundary and steps, two- and three-layer graphene flakes, and graphene wrinkles. Inset (B) TEM images of folded graphene edges. 1L, one layer; 2L, two layers.

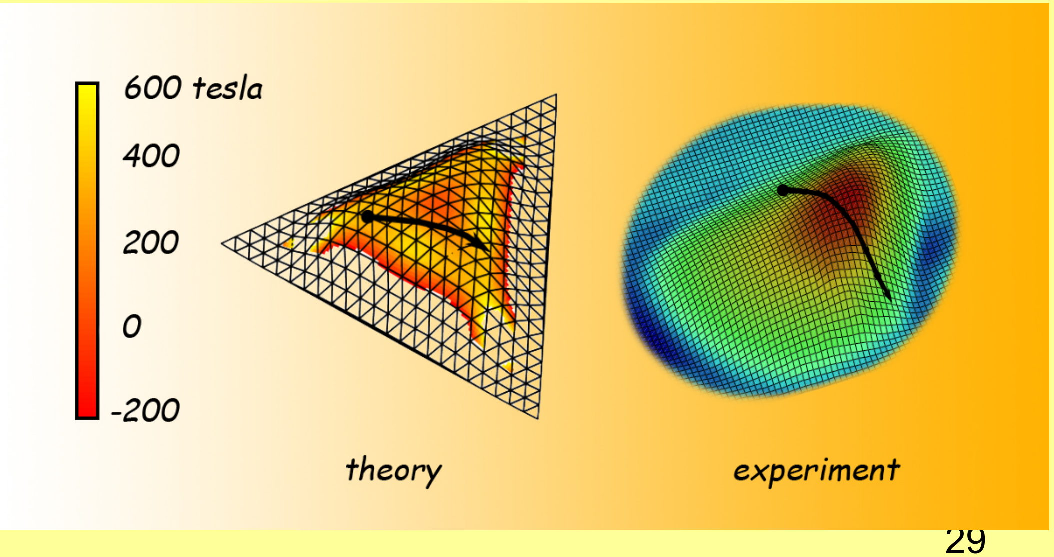
Graphene transferred onto
(C) a SiO_2/Si substrate
(D) a glass plate

Graphene on SiO_2

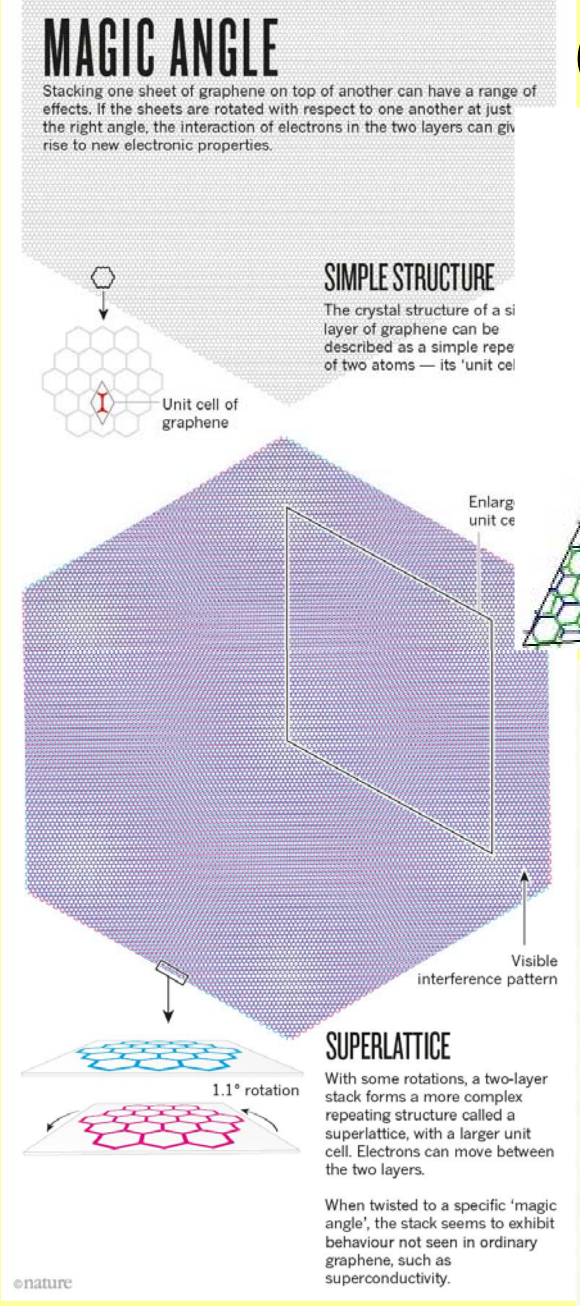
Pseudo-magnetism

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)





d bilayer graphene



MAGIC ANGLE

Stacking one sheet of graphene on top of another can have a range of effects. If the sheets are rotated with respect to one another at just the right angle, the interaction of electrons in the two layers can giv rise to new electronic properties.

SIMPLE STRUCTURE

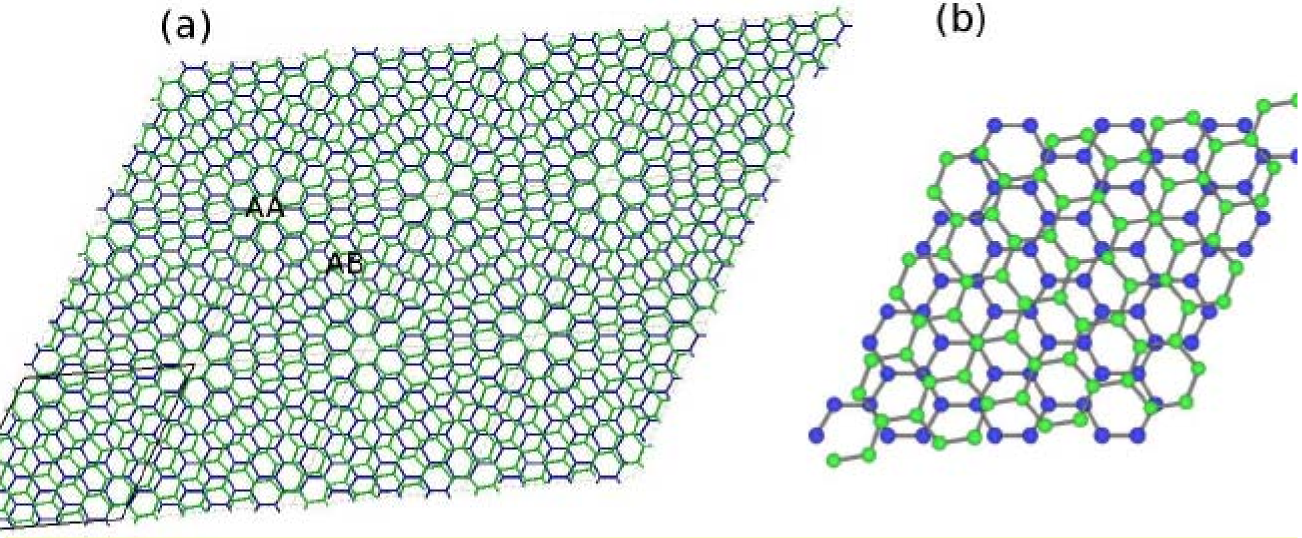
The crystal structure of a si layer of graphene can be described as a simple repe of two atoms — its 'unit cel

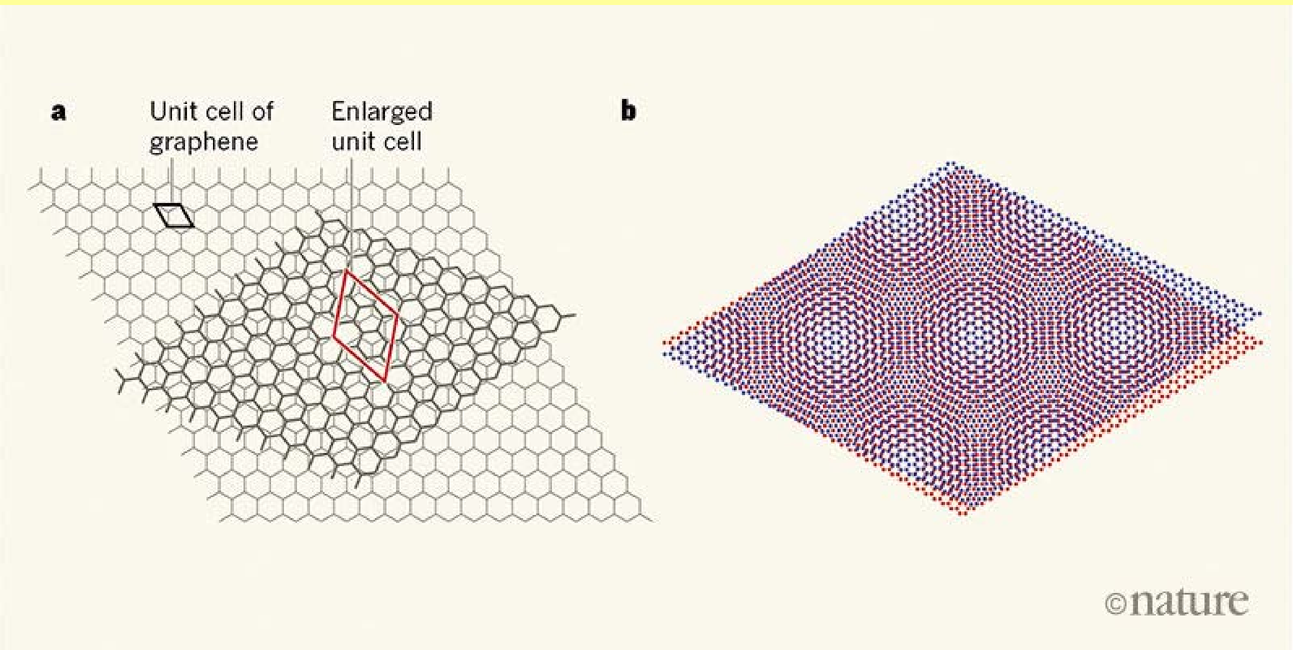
SUPERLATTICE

With some rotations, a two-layer stack forms a more complex repeating structure called a superlattice, with a larger unit cell. Electrons can move between the two layers.

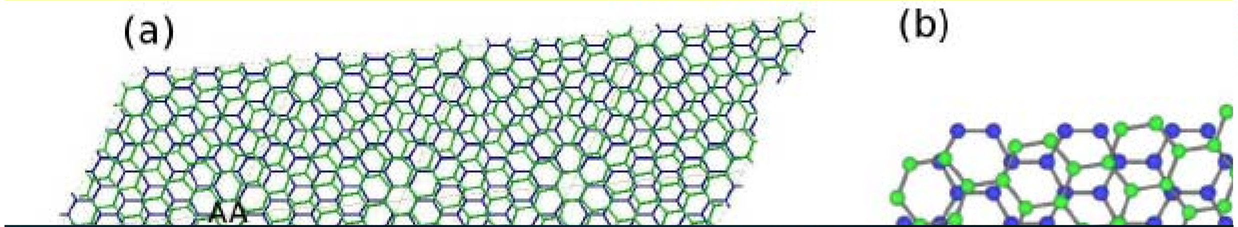
When twisted to a specific 'magic angle', the stack seems to exhibit behaviour not seen in ordinary graphene, such as superconductivity.

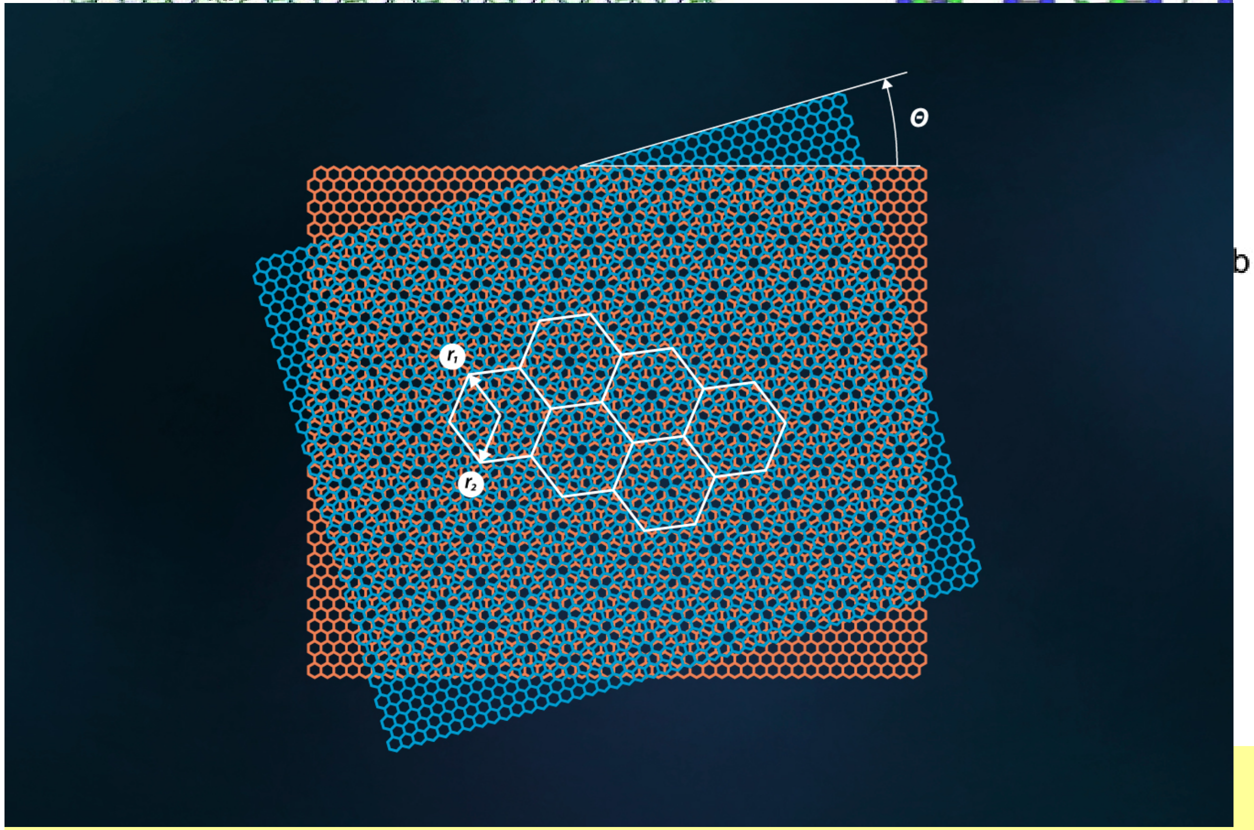
©nature

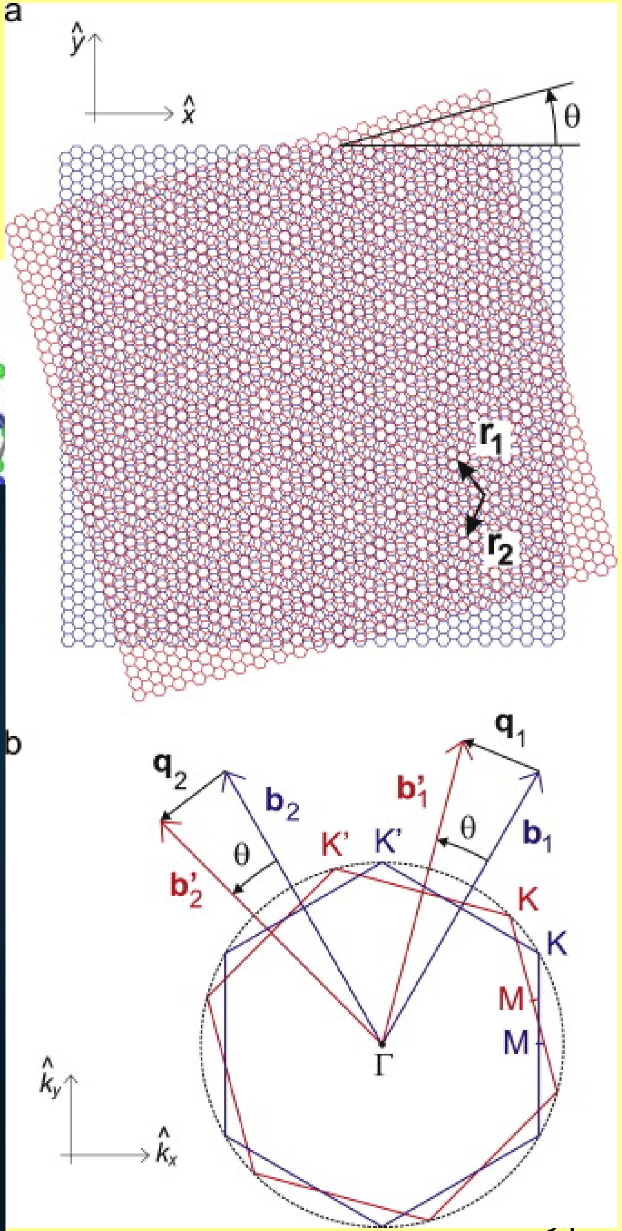




©nature


(a)
AA
(b)


Θ
r1
r2


a
ŷ
x̂
θ
r1
r2
b
q1
q2
b'1
b2
b1
θ
θ
K'
K'
b'2
K
K
M
M
Γ
k̂y
k̂x

Graphene family

Graphene

hBN

BCN

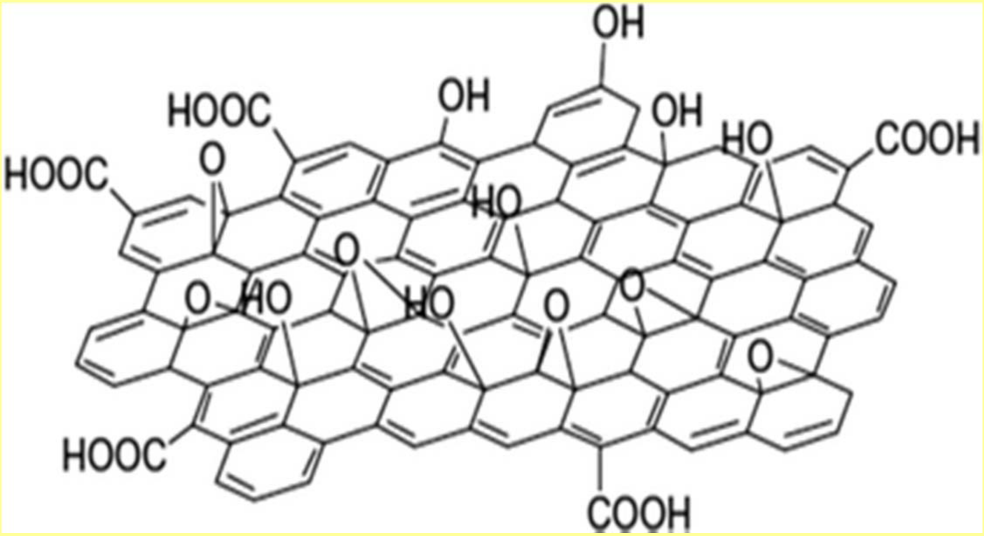
Fluorographene

graphene oxide

C3N4

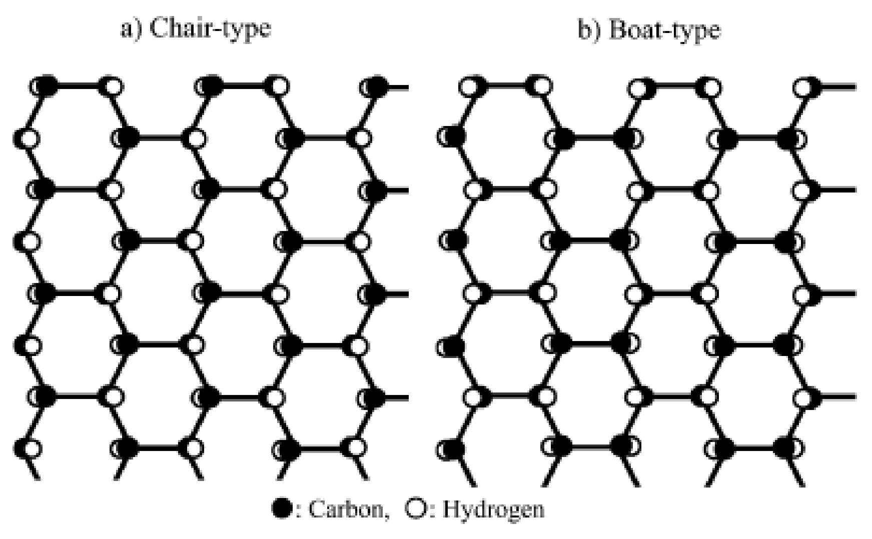
Graphene oxide

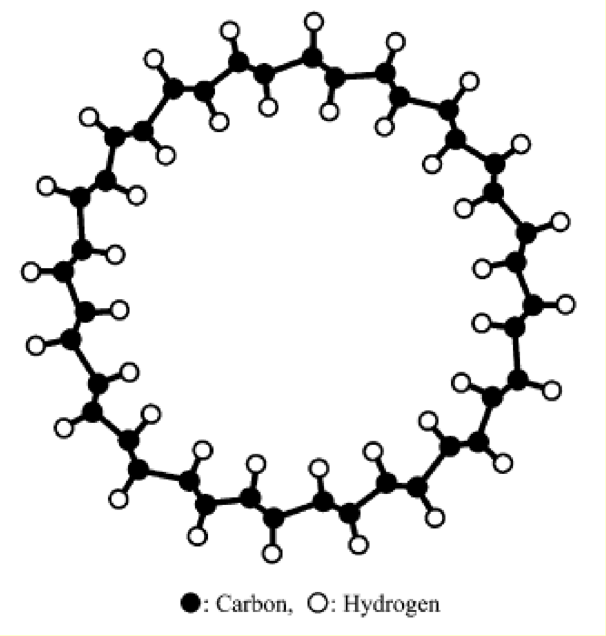
- **More reactive than graphene**
- **Presence of oxygen groups: -OH, -COOH, =O, -O- hydrophilic character**
- **Electric insulator**
- **Specific SA (theoretically): 1700-1800 m^2g^{-1}**
- **Hummers method**



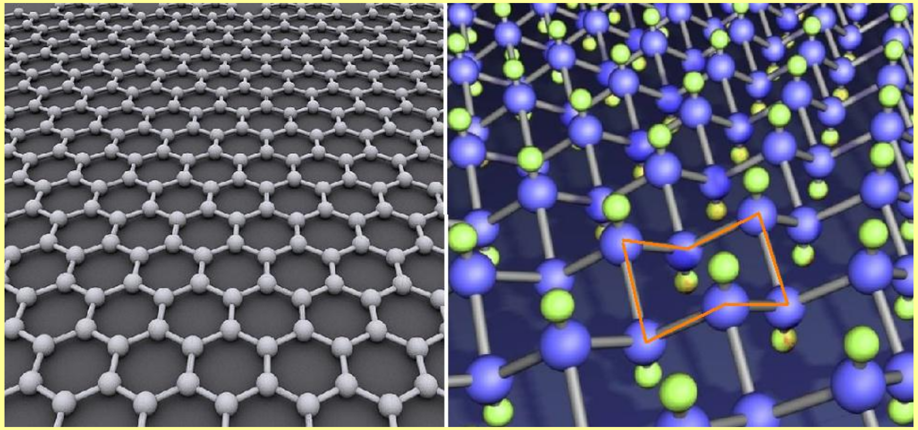
Graphane – hydrogenated graphene

- 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



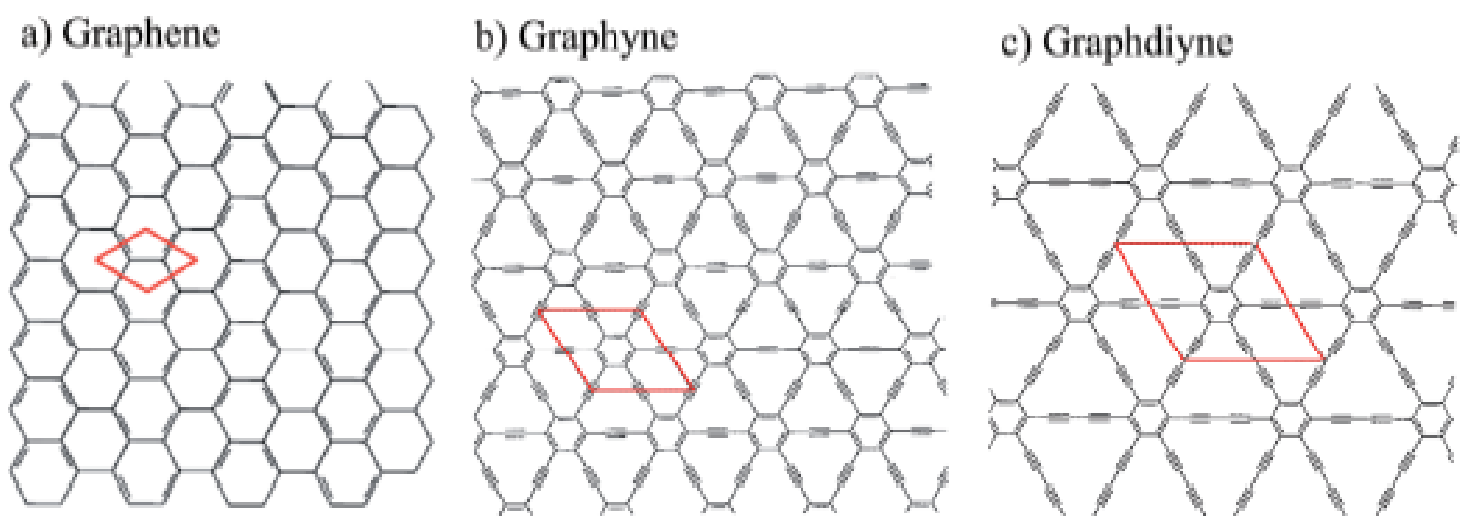


Fluorographene



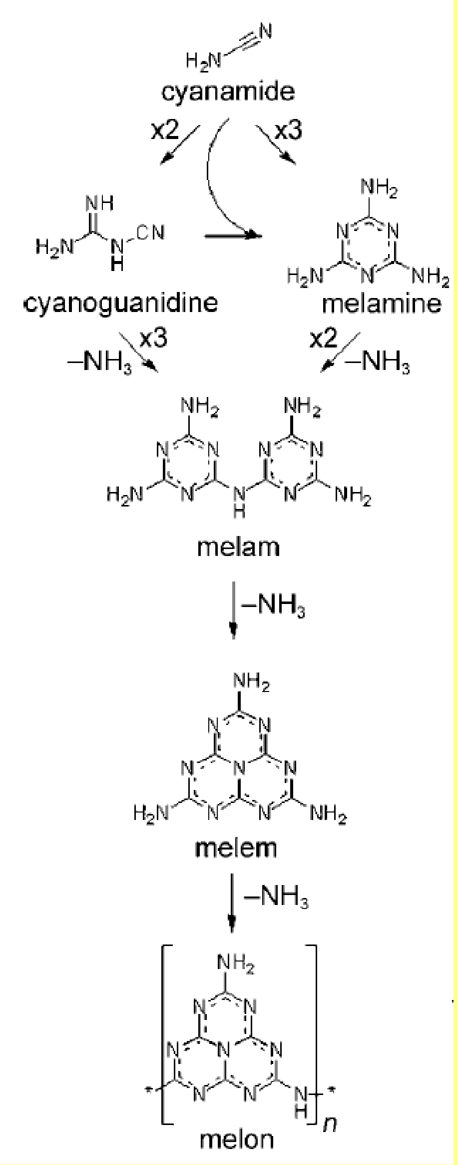
- **Monolayer of graphite fluoride**
- **Chair type x boat type-strong repulsion**
- **Sythesis:**
  - **Graphene + XeF_2/CF_4 (room temperature)**
  - **Mechanical or chemical exfoliation of graphite fluoride**
  - **By heating graphene in XeF_2 gas at 250 °C**
- **Graphene + XeF_2 at 70 °C – high-quality 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**

Graphitic carbon nitride

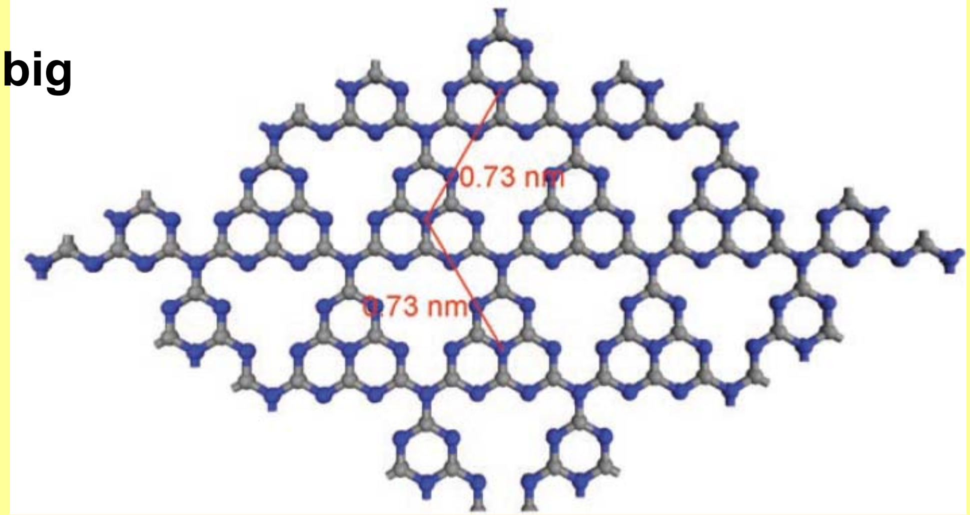


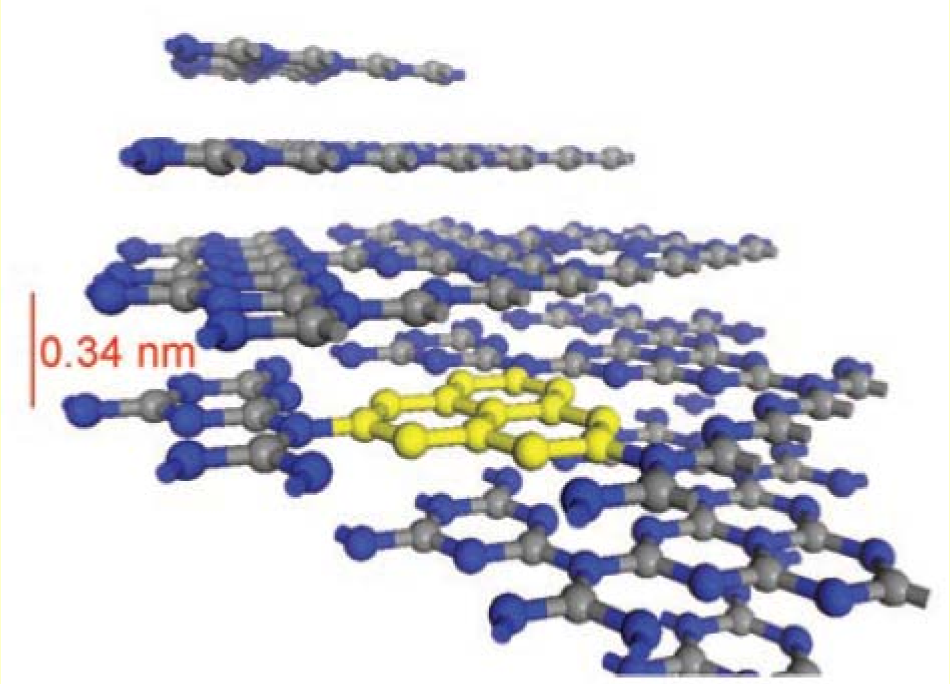
1834 Berzelius, Liebig

Temperature-induced condensation

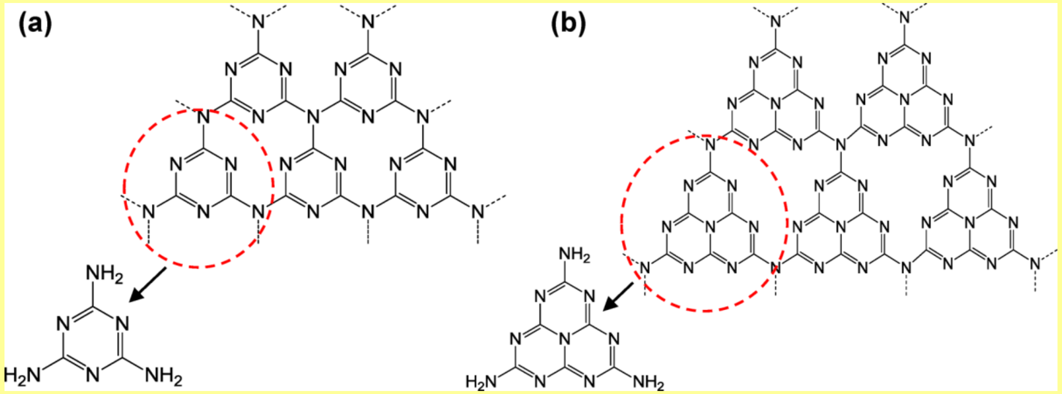
dicyandiamide
$NH_2C(=NH)NHCN$

In a LiCl/KCl melt

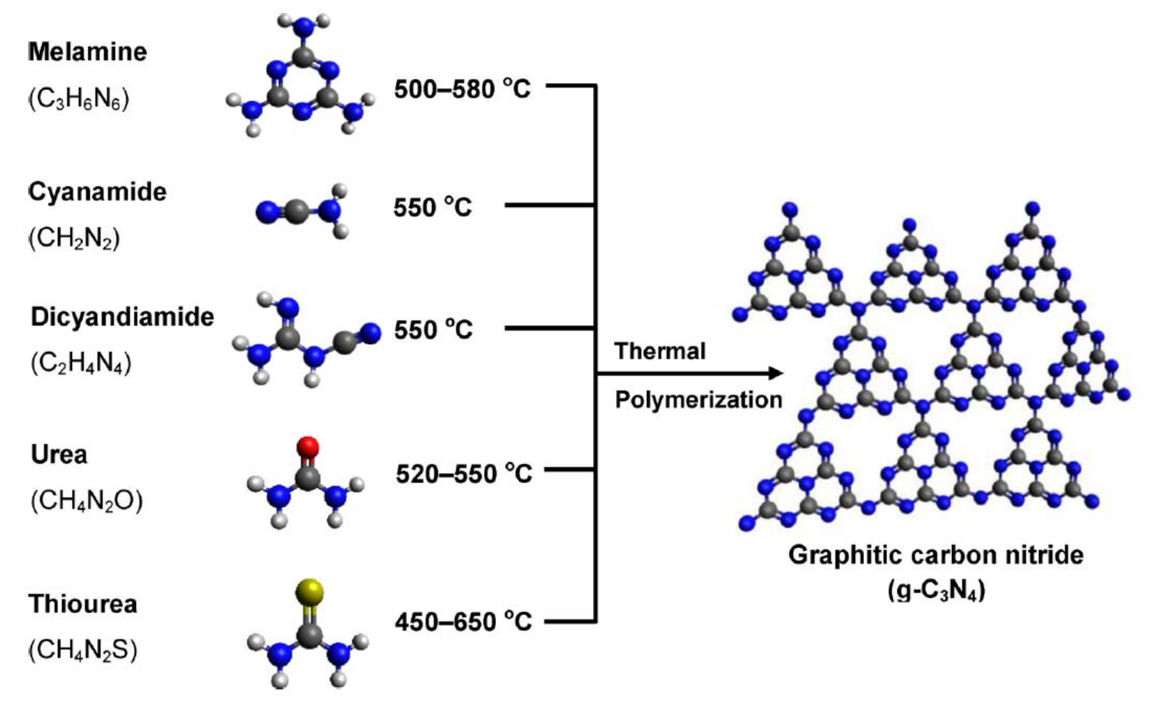




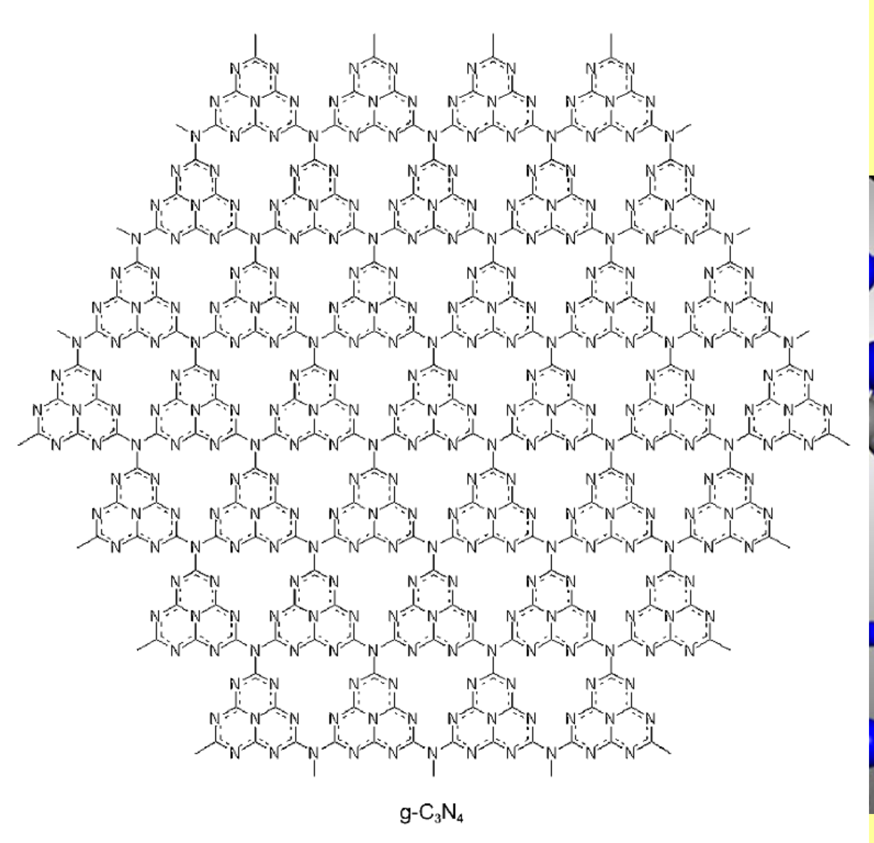
Graphitic carbon nitride



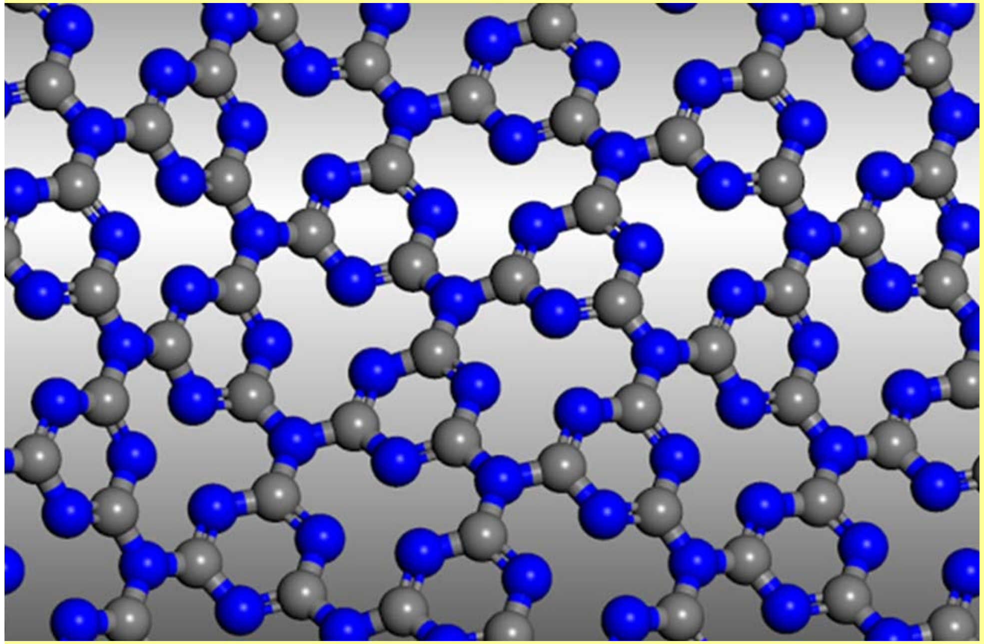
(a) triazine and (b) tri-s-triazine (heptazine)



Graphitic carbon nitride

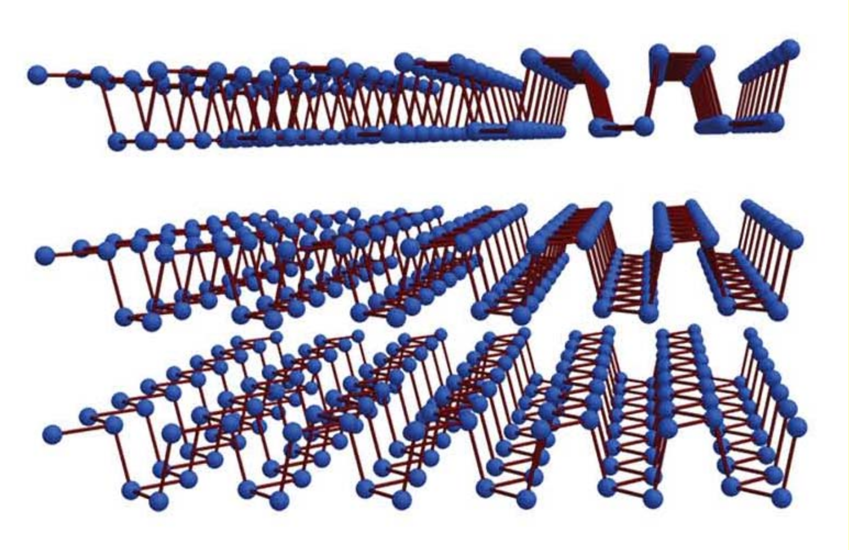

g-C_3N_4

(“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)

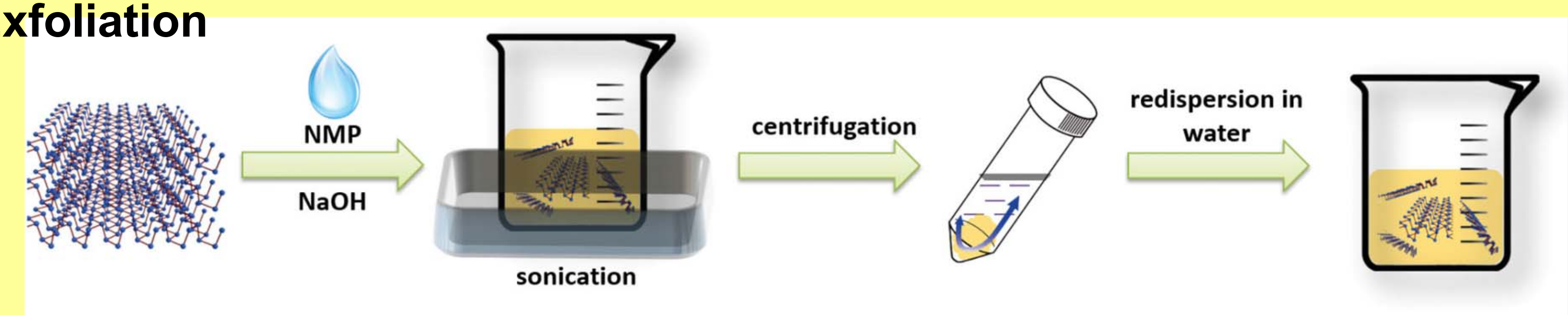
Phosphorene



Black phosphorus

Orthorhombic
a = 3.31 Å, b = 4.38 Å, c = 10.50 Å
$\alpha = \beta = \gamma = 90°$
Space group *Bmab*

Exfoliation

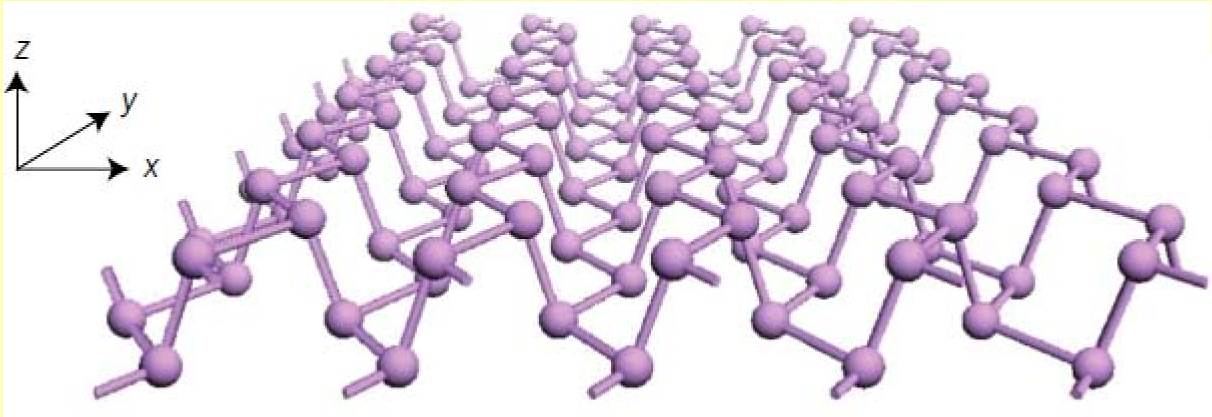


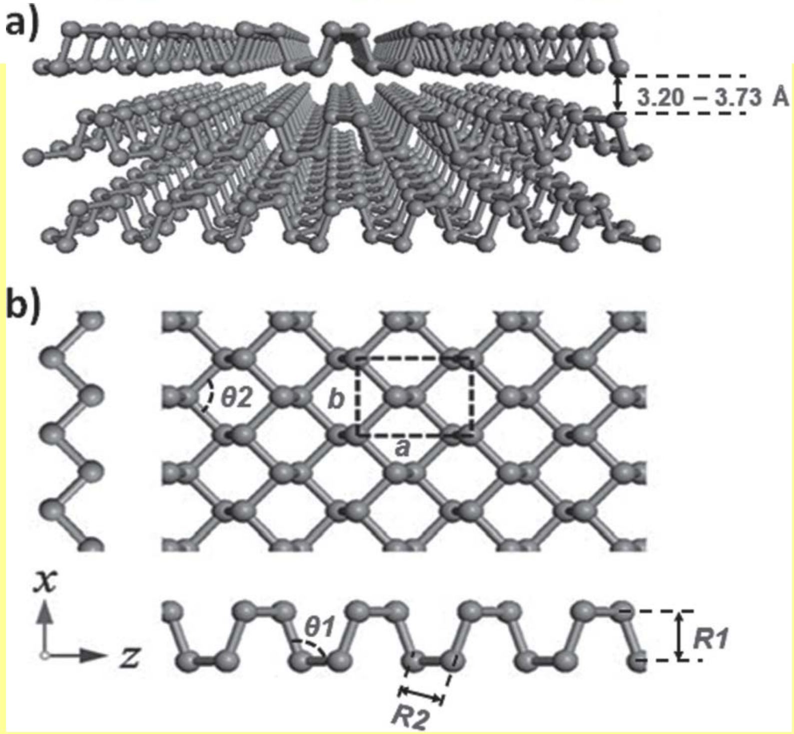
N **-methyl-2-pyrrolidone**

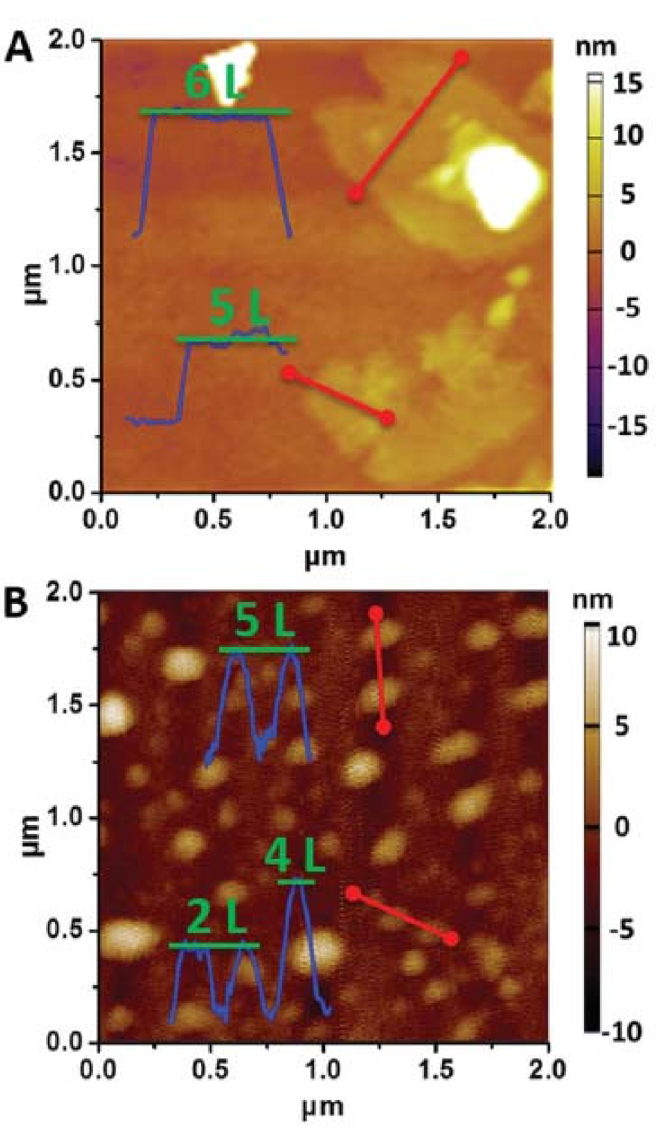
Semiconductor - direct band gap
bulk BP 0.3 eV
monolayer phosphorene 1.5 eV

Phosphorene

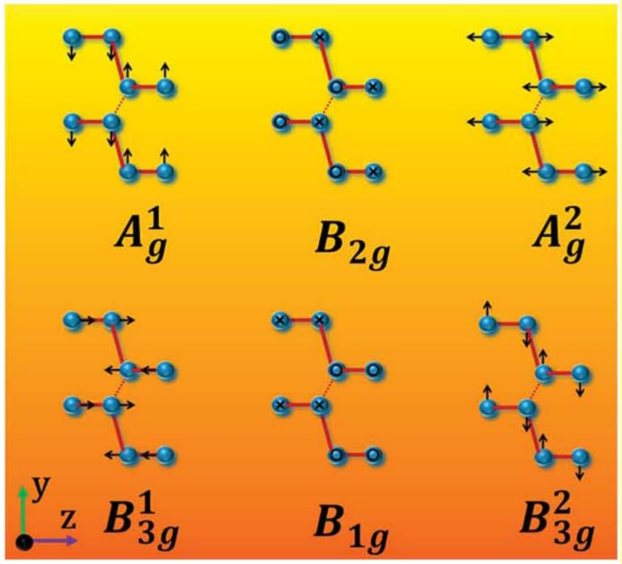
Height-mode AFM images
single-layer phosphorene
ca. 0.9 nm





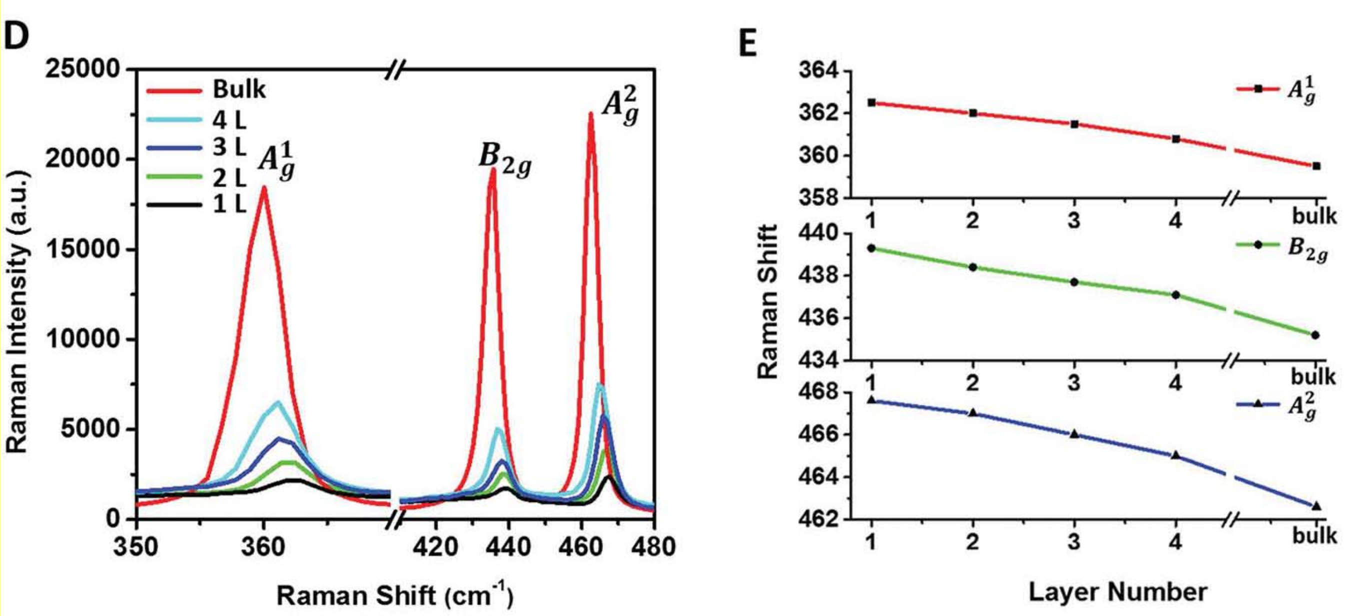


Phosphorene

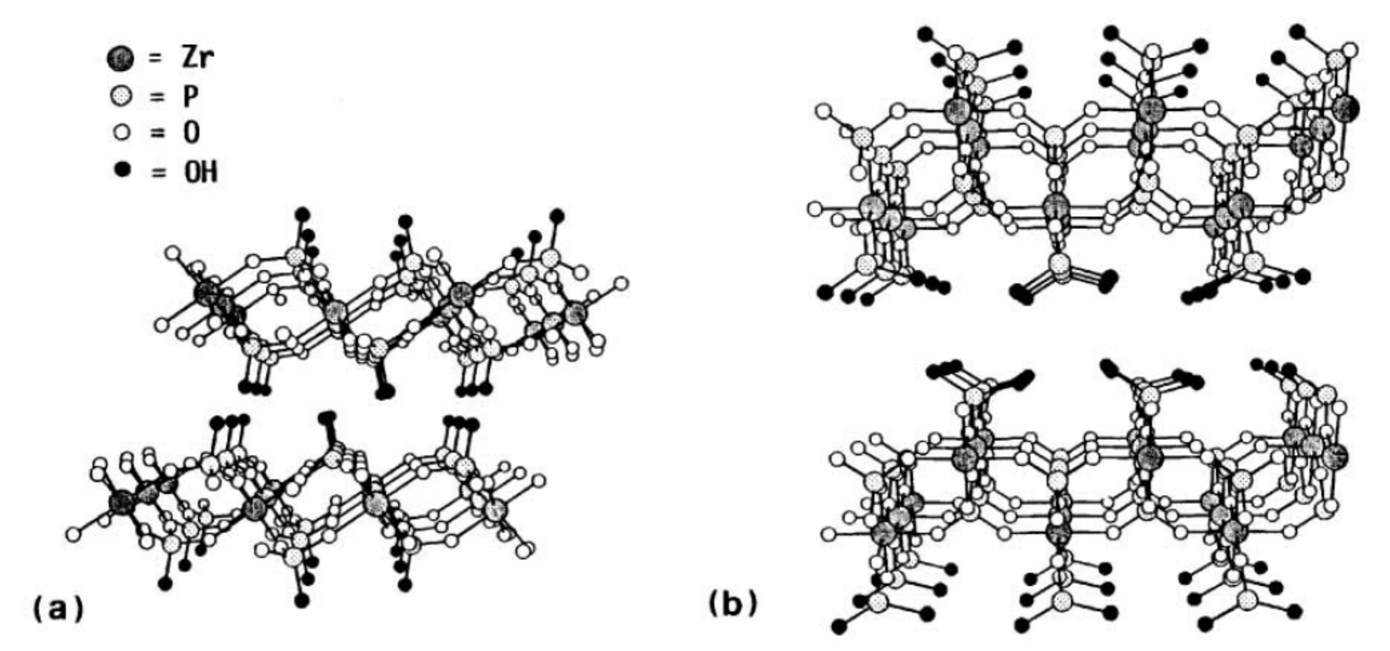


Black phosphorus
12 lattice vibrational modes
6 Raman active modes
3 vibrational modes $A^1{}_g$, B_{2g} , and $A^2{}_g$ can be detected when the incident laser is perpendicular to the layered phosphorene plane: 361 cm^{-1}, 438 cm^{-1}, 465 cm^{-1}

As the number of phosphorene layers increases, the three Raman peaks red-shift



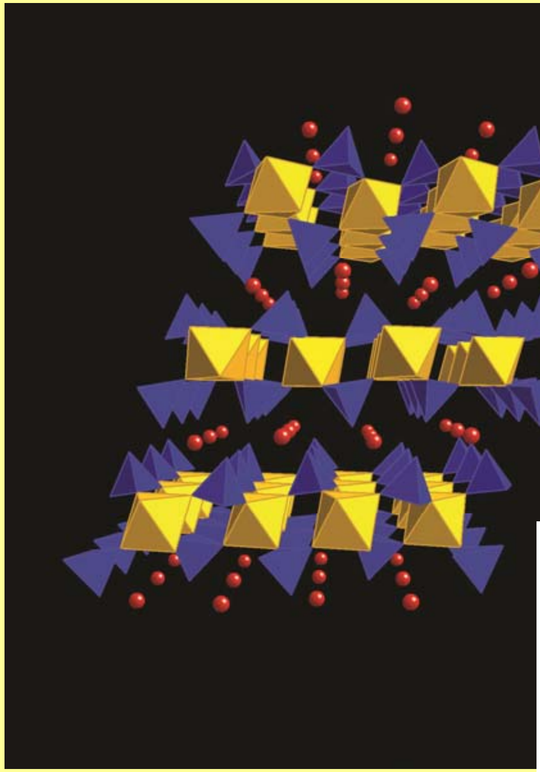
Layered Compounds - Zirconium Phosphates



(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

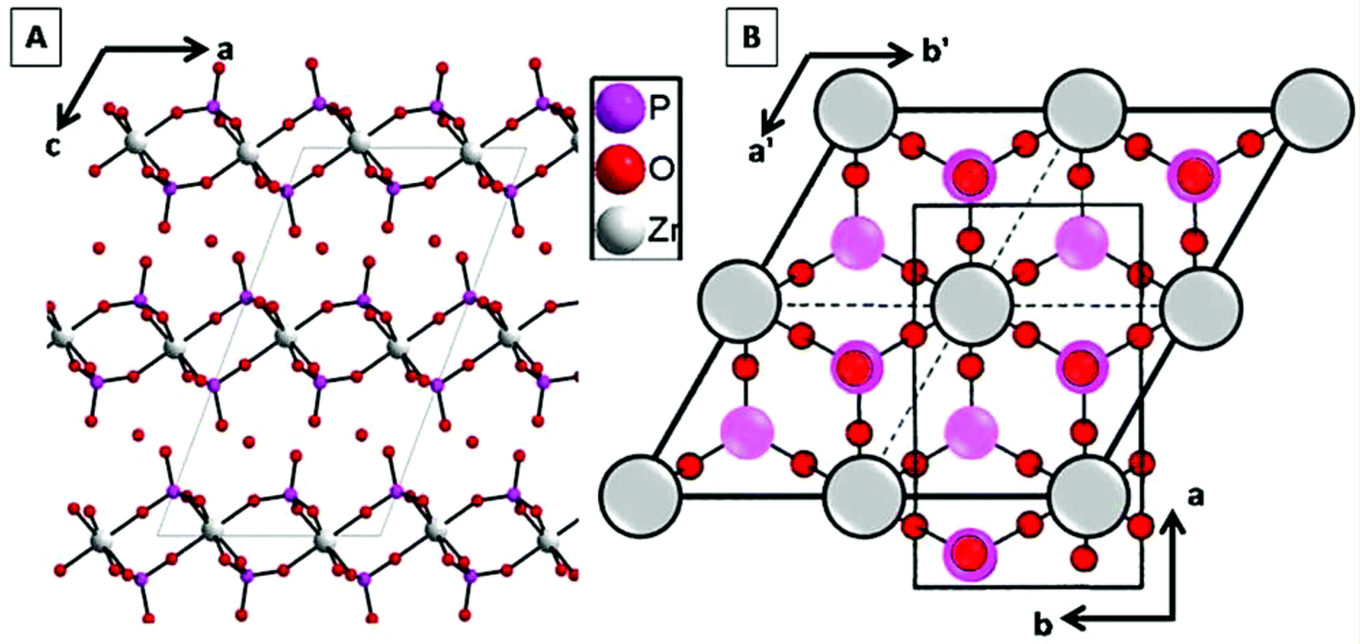
Layered Compounds - Zirconium Phosphates



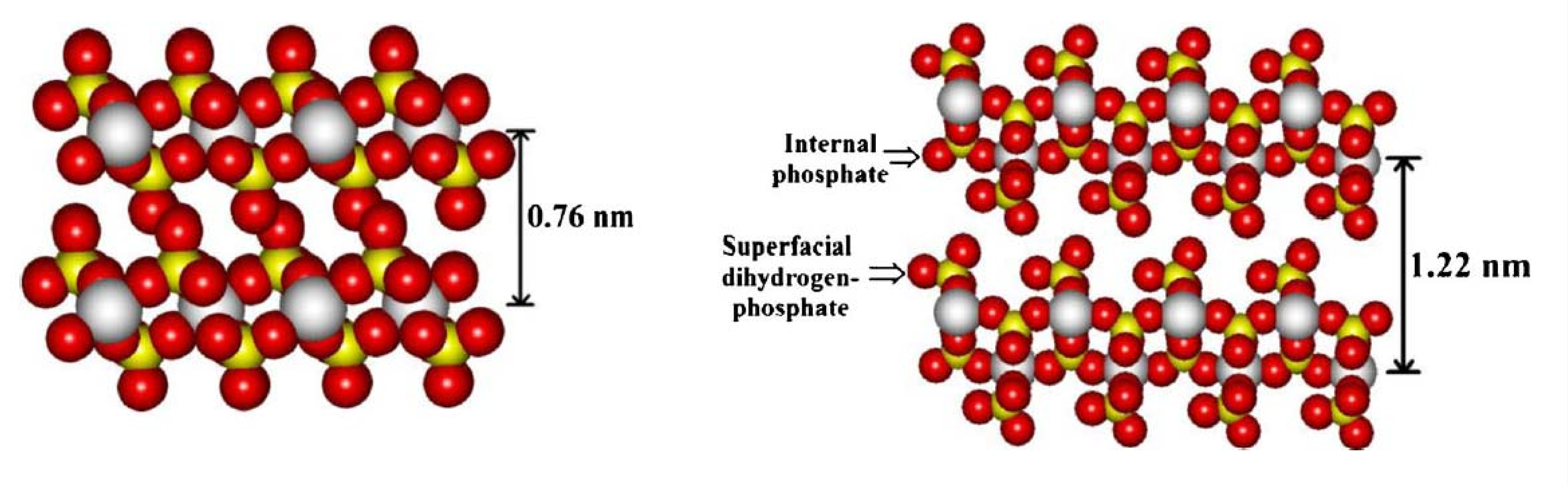
α-zirconium phosphate

$Zr(HPO_4)_2.H_2O$

interlayer spacing 7.6 Å



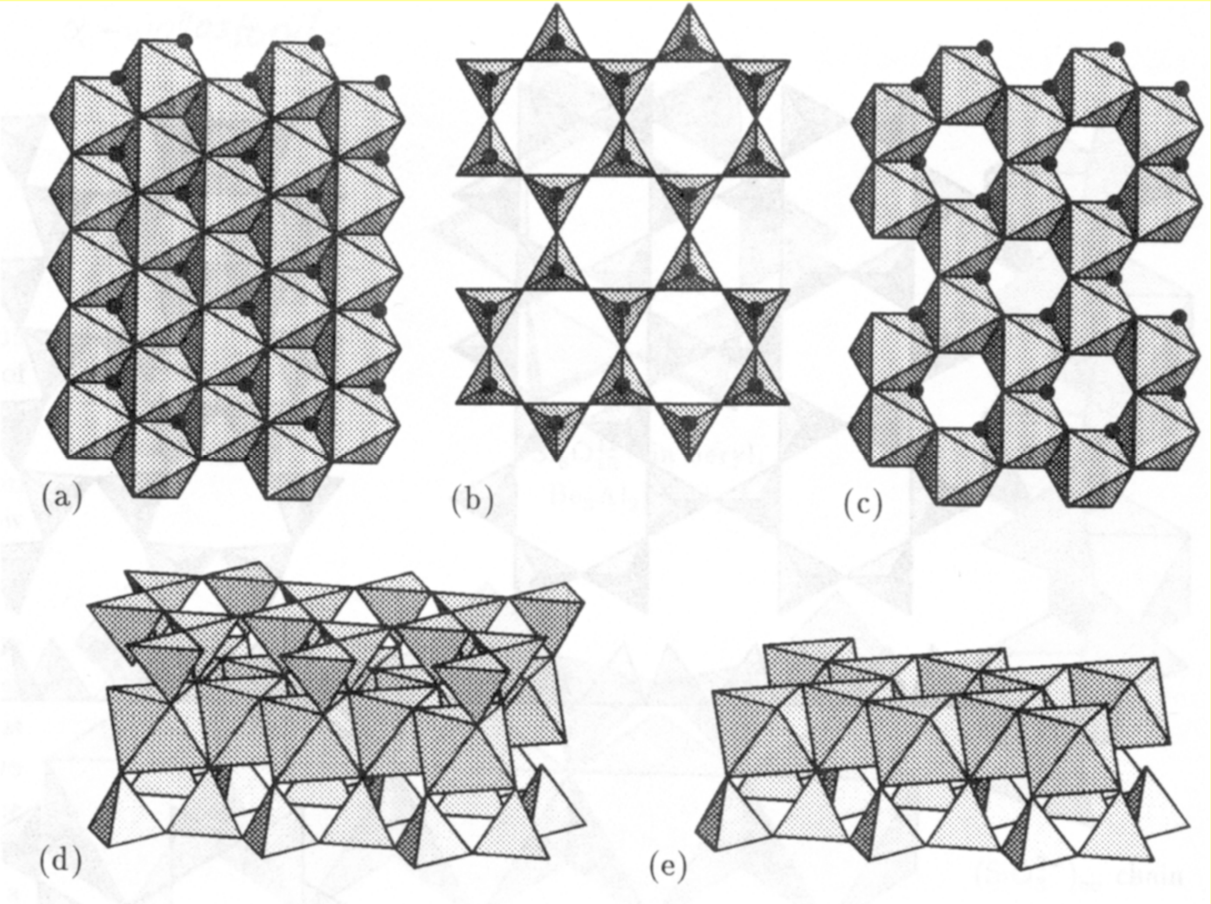
Layered Compounds - Zirconium Phosphates



(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



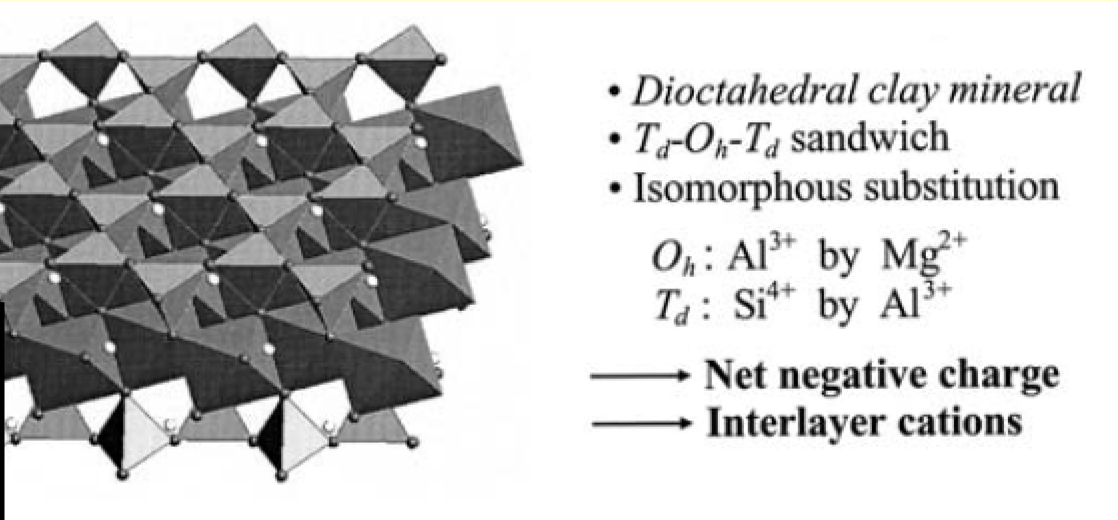
2:1

montmorillonite

1:1

kaolinite

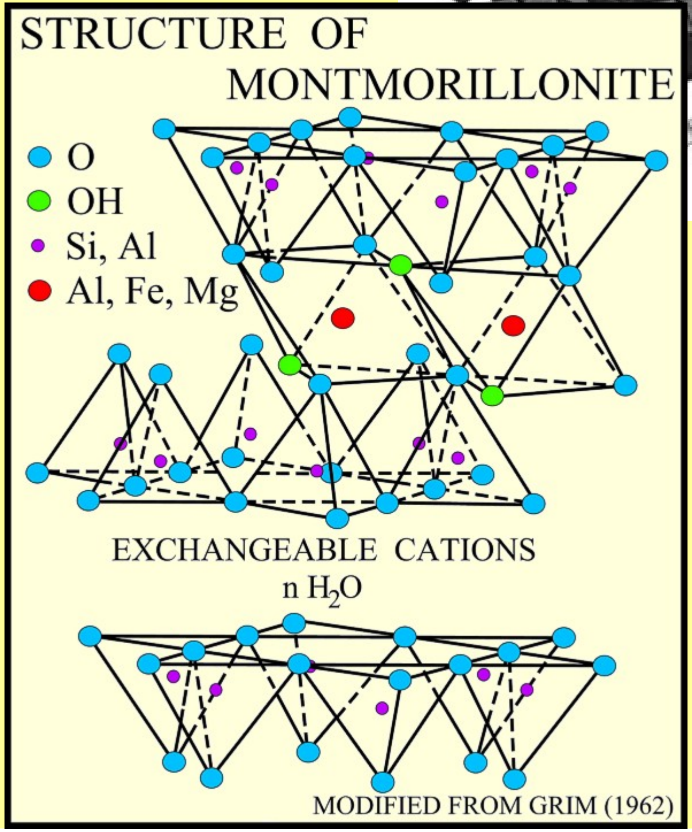
Montmorillonite



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

O_h : Al^{3+} by Mg^{2+}
T_d : Si^{4+} by Al^{3+}

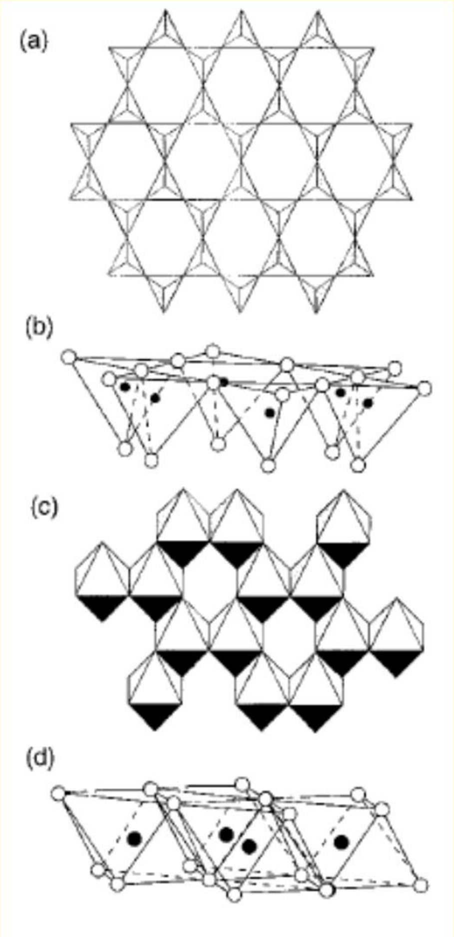
⟶ **Net negative charge**
⟶ **Interlayer cations**



MODIFIED FROM GRIM (1962)

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

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

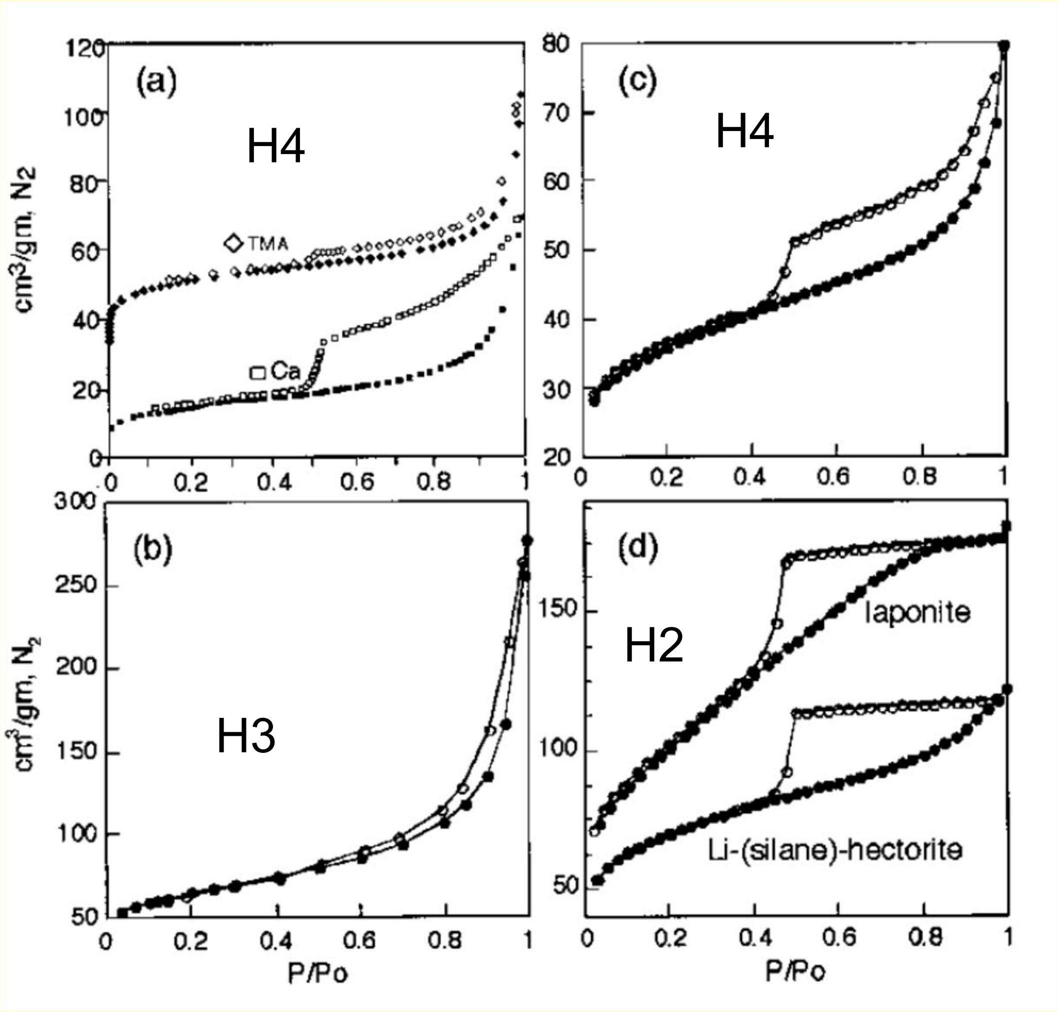
(a) TMA- and Ca-montmorillonite

(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

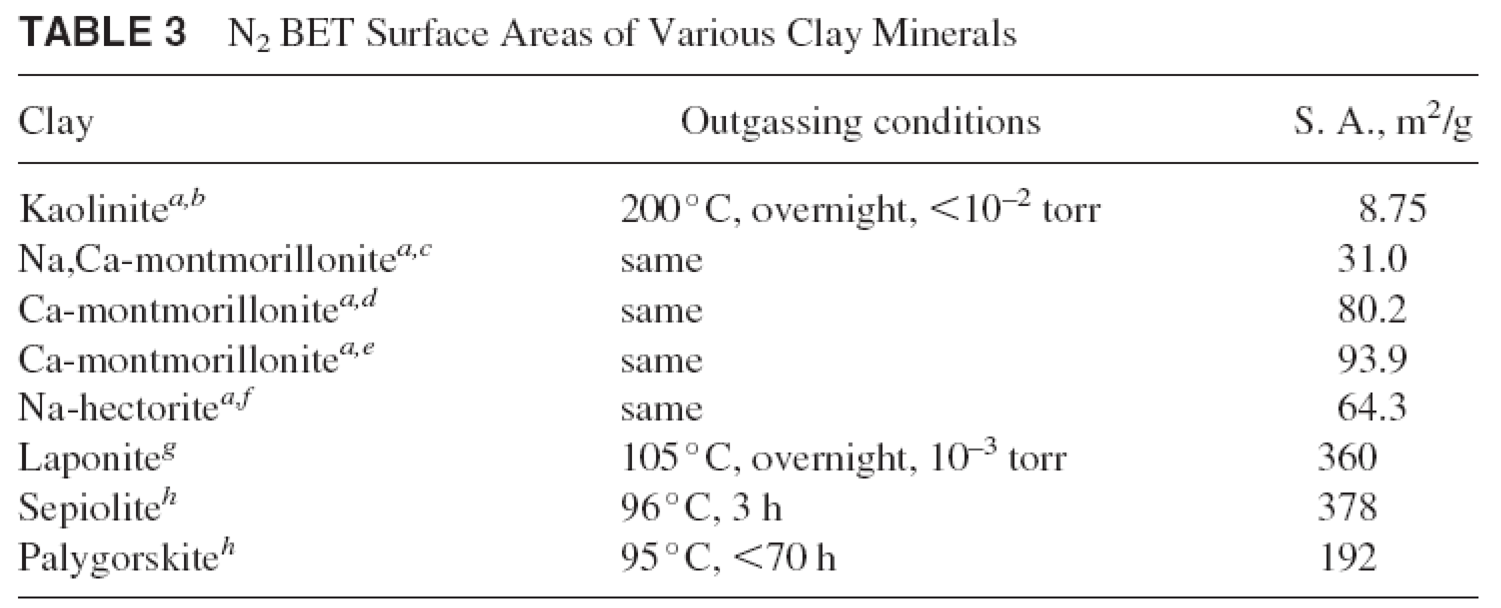


TABLE 3 N_2 BET Surface Areas of Various Clay Minerals

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

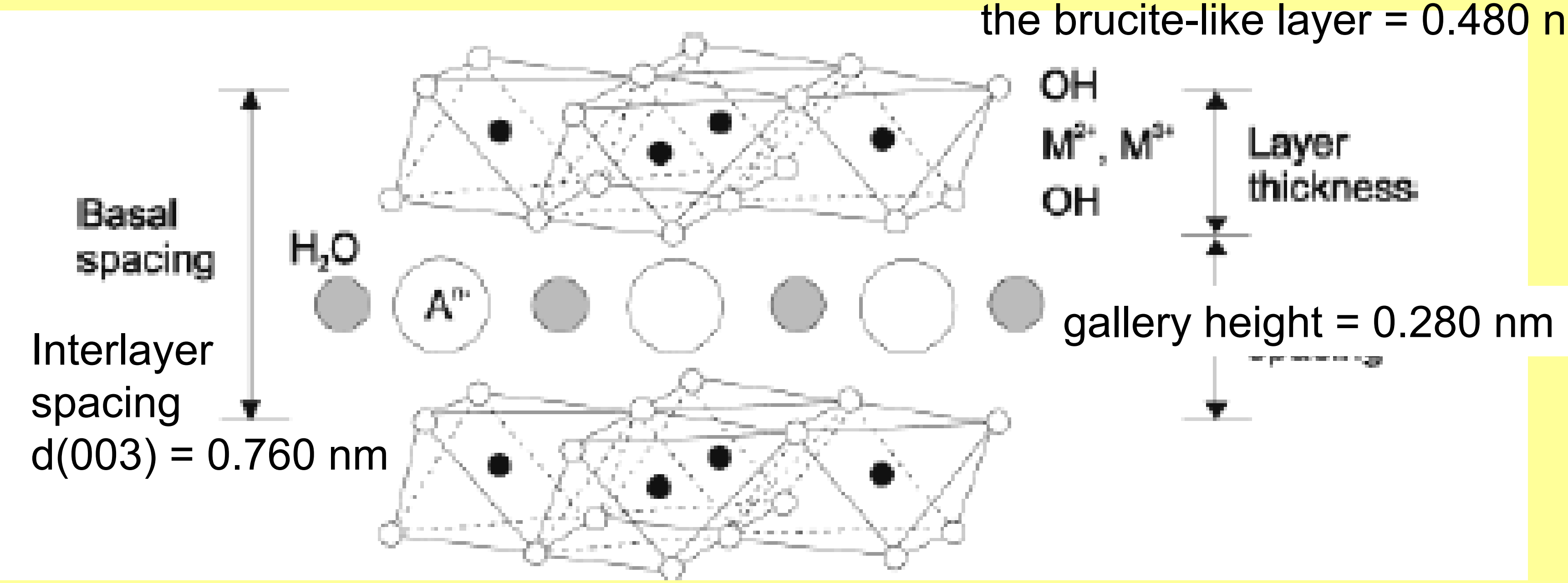
Na^+ forms of smectites and vermiculites – no penetration
larger ions (Cs^+ and NH_4^+ keep the basal planes far enough) - limited penetration

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



the brucite-like layer = 0.480 nm

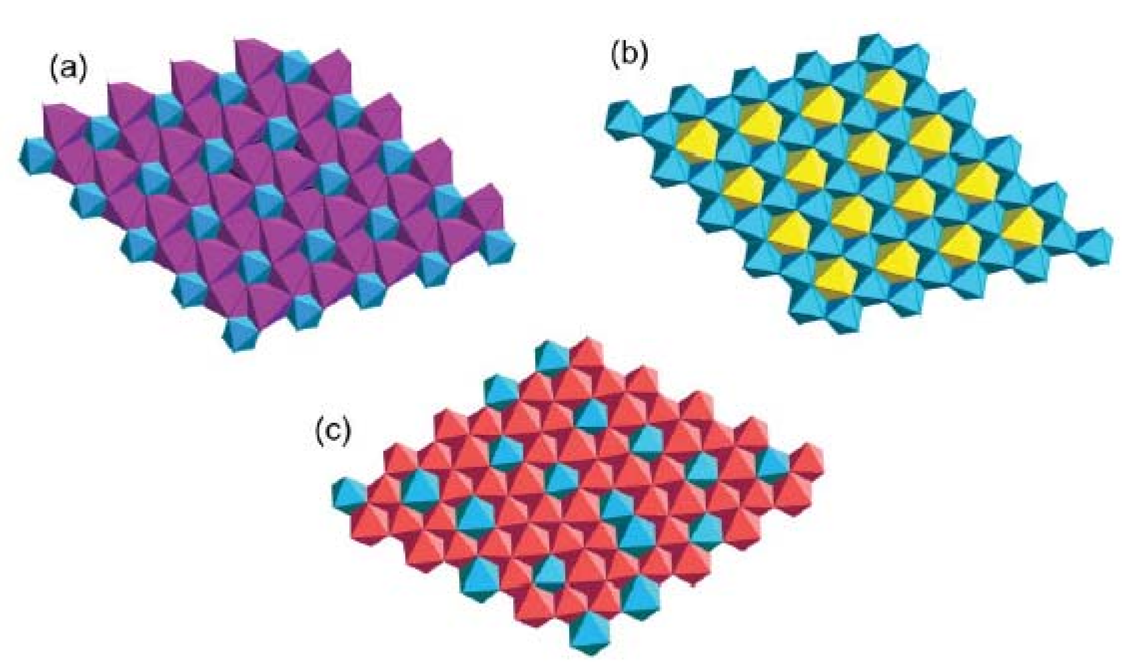
gallery height = 0.280 nm

Interlayer spacing
d(003) = 0.760 nm

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

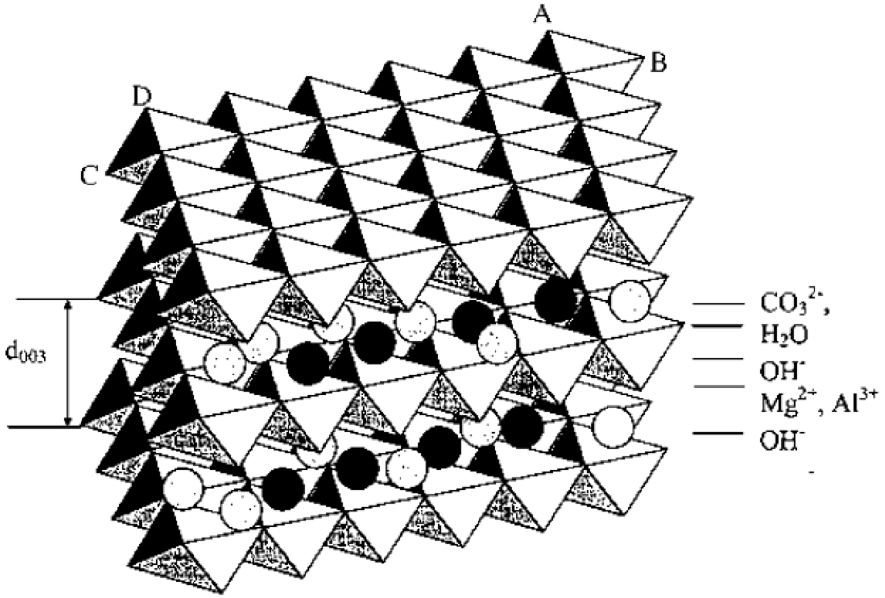
The interlayer spacing c' is equal to $d003$, $2d006$, $3d009$, etc.;

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

The cell parameterc is a multiple of the interlayer spacing c'

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

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



Hydrotalcite

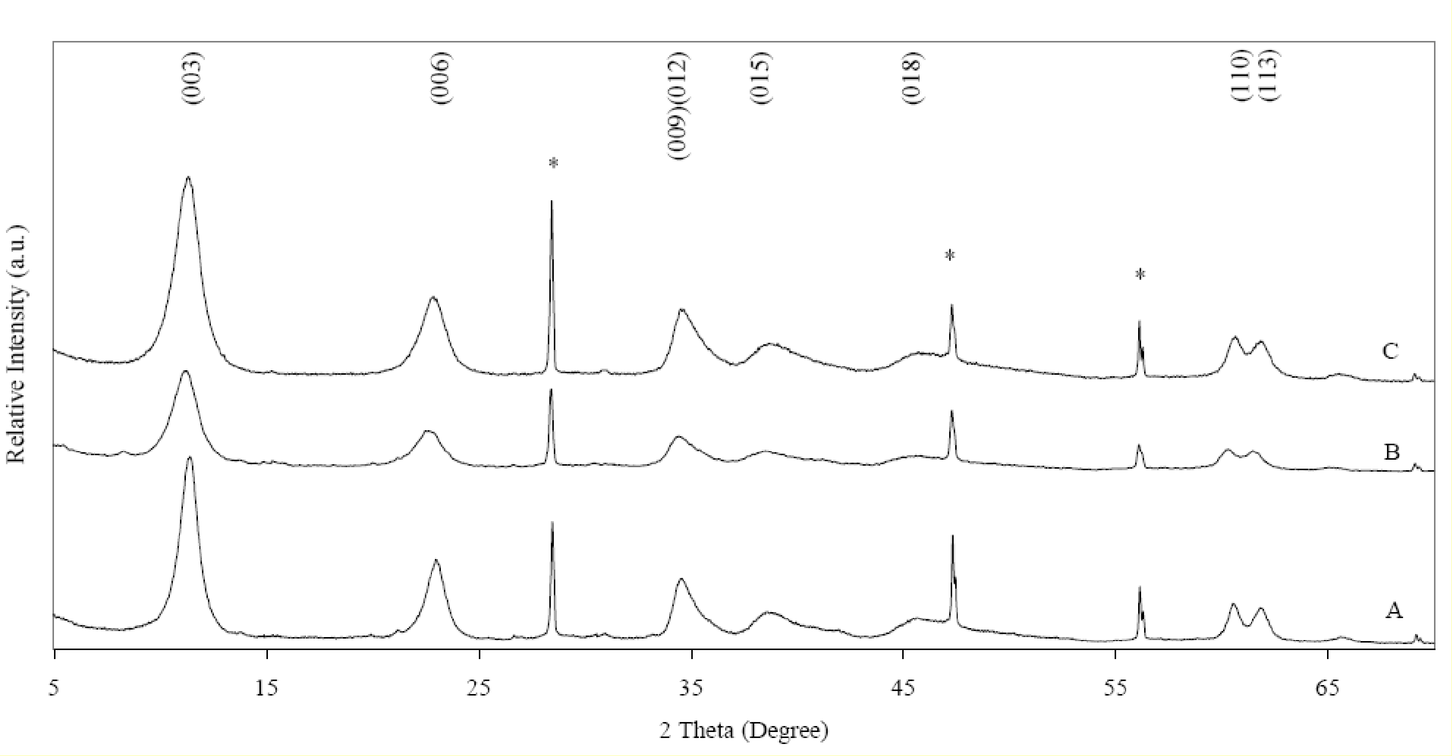
Hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ - 3R stacking

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.

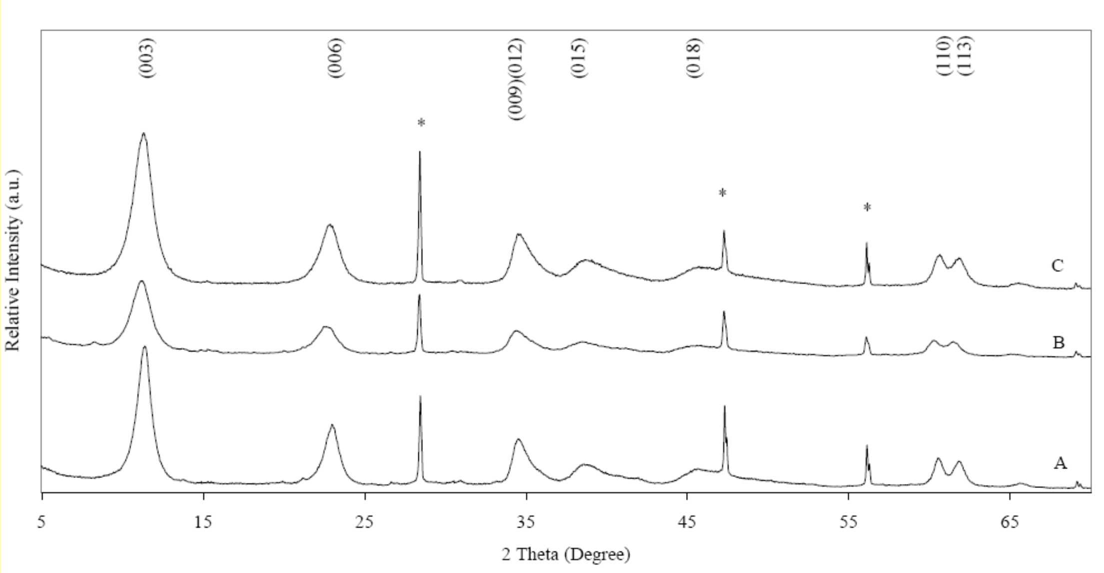
XRD Patterns of LDH



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* = 2*d*(110) corresponds to an average cation–cation distance

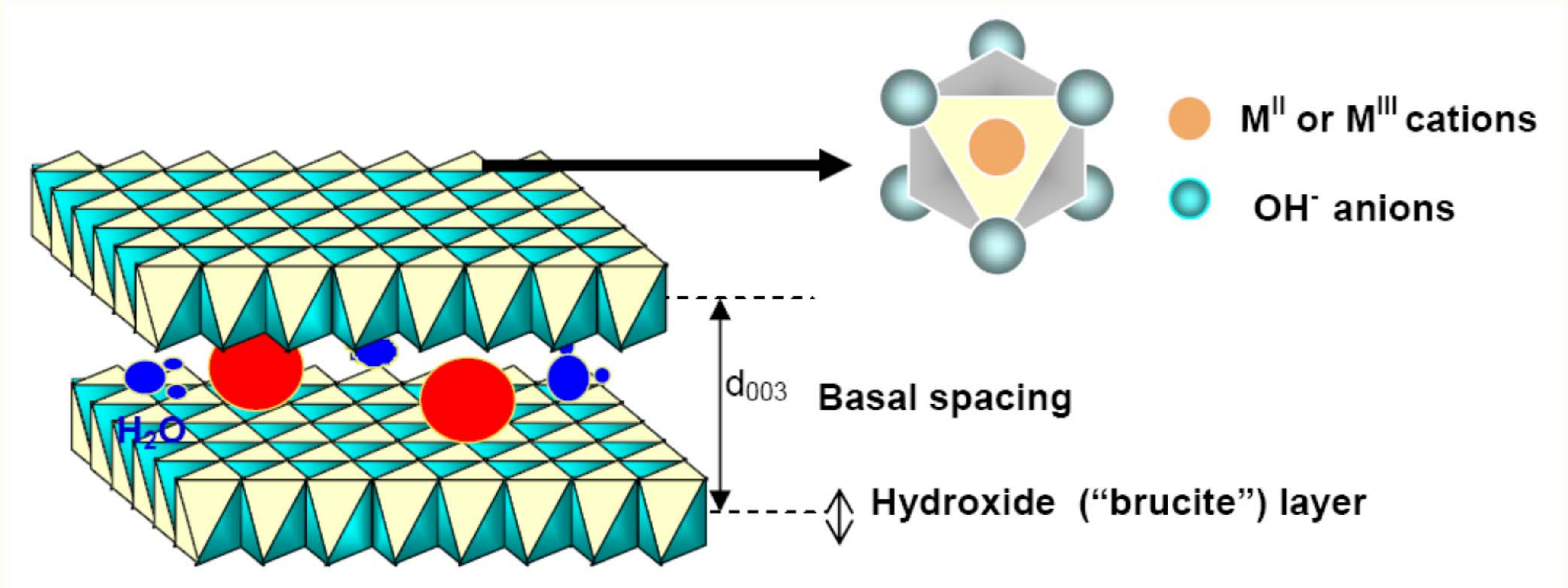
The *c* parameter corresponds to three times the thickness of *d*003

c = 3/2 [*d*003+2*d*006]

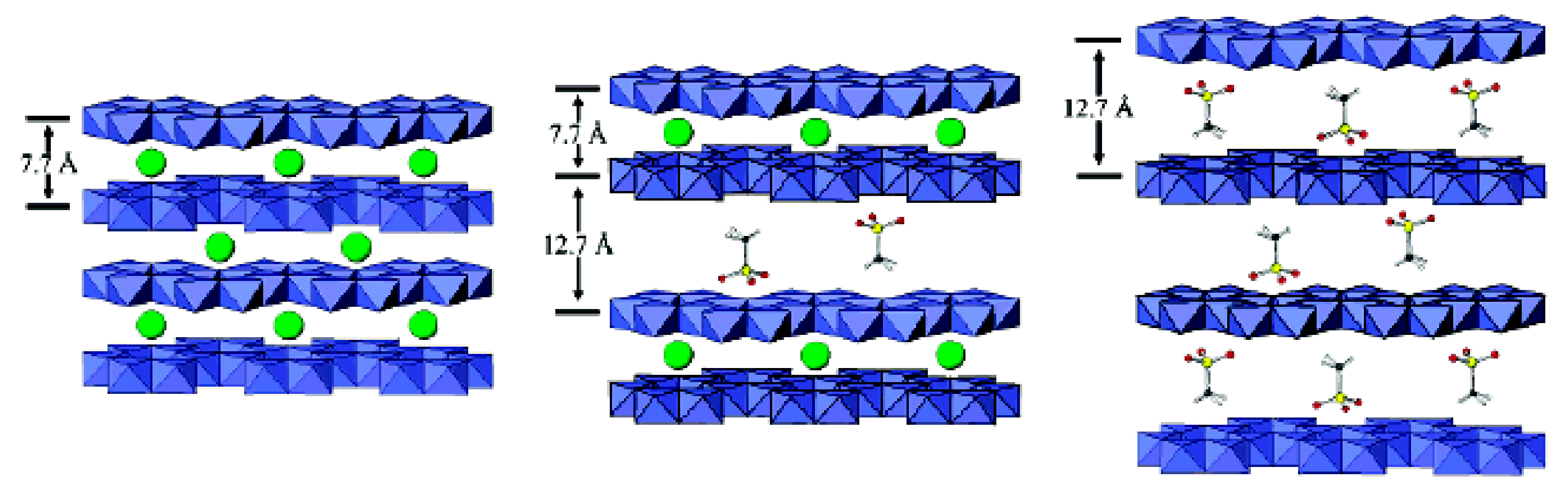
Layered Compounds

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

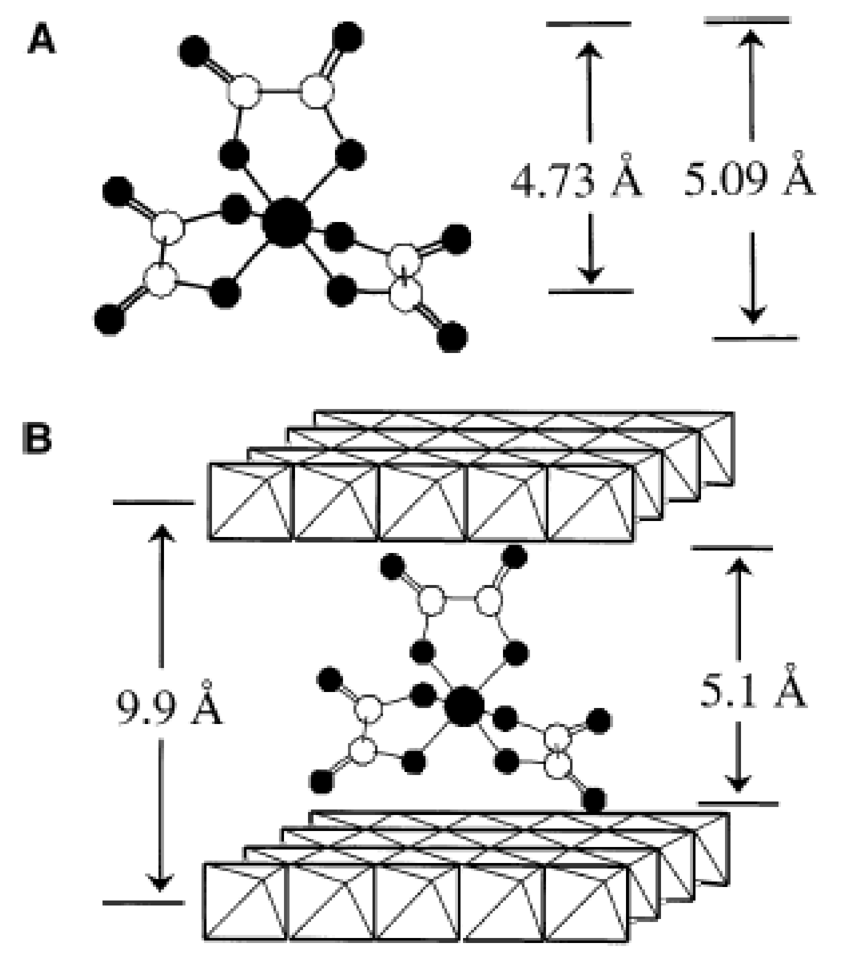
LDH = layered double hydroxides

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

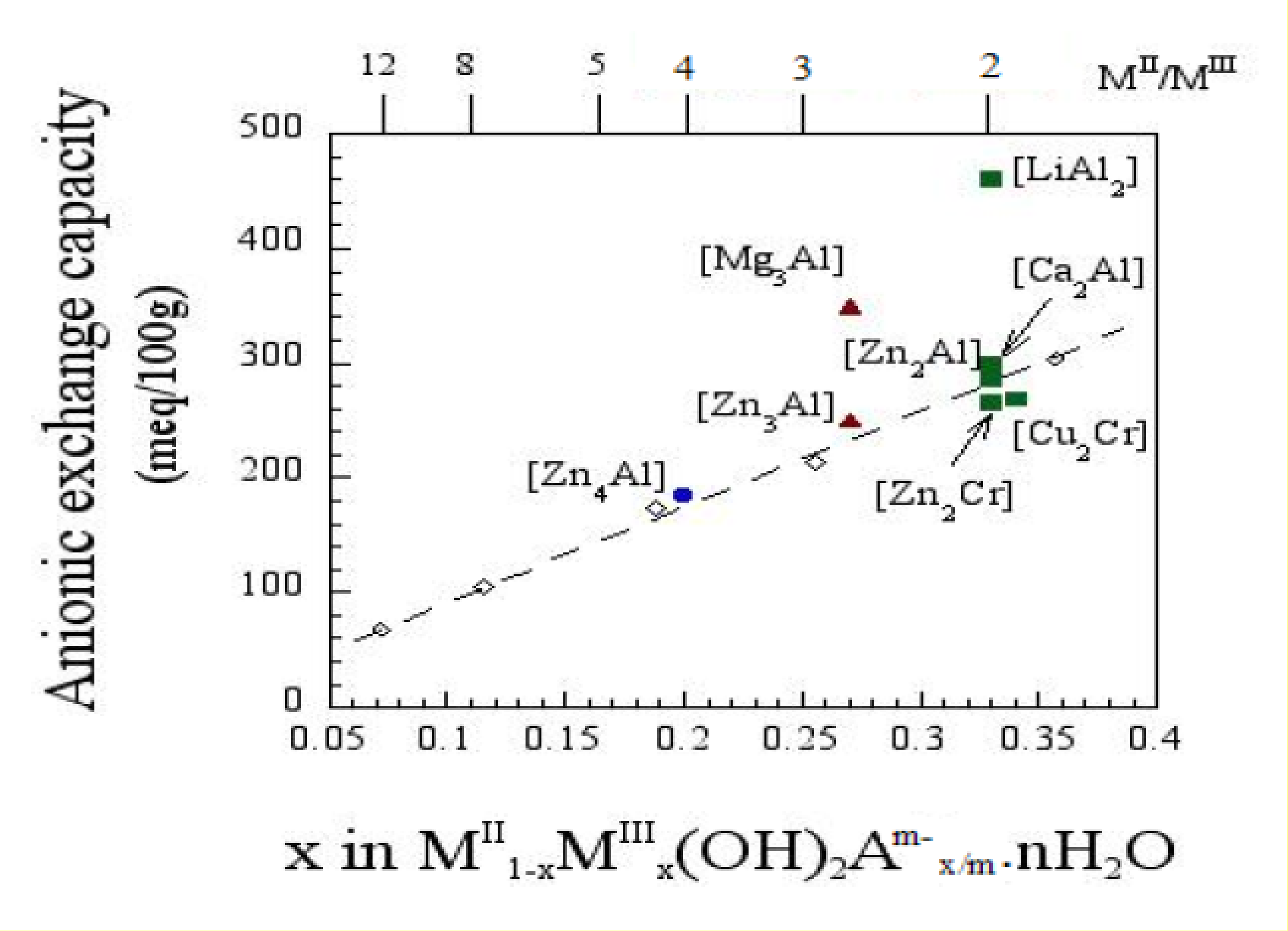
Brucite layers, Mg^{2+} substituted partially by Al^{3+}

Layers have positive charge

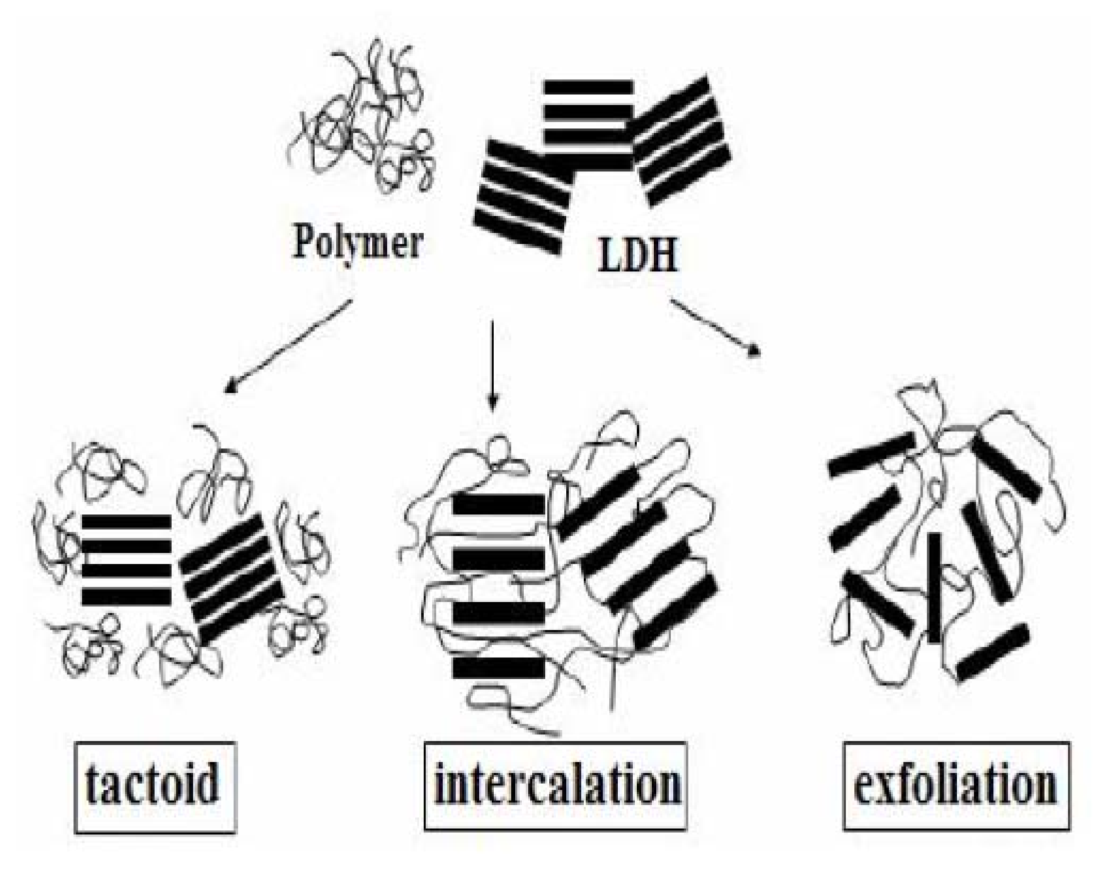
Intercalate anions $[Cr(C_2O_4)_3]^{3-}$



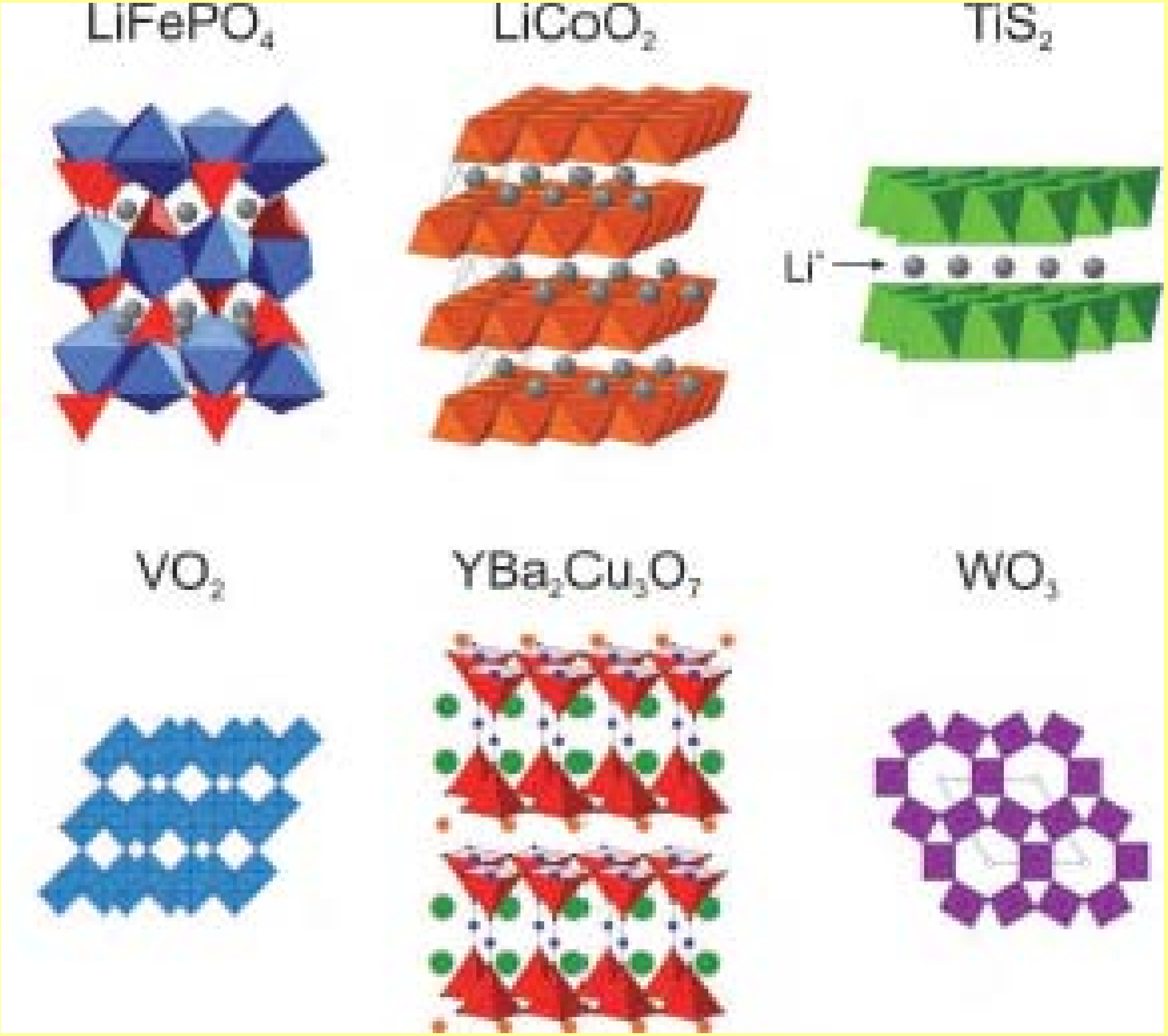
The anionic exchange capacity (AEC)



Types of the composite structures

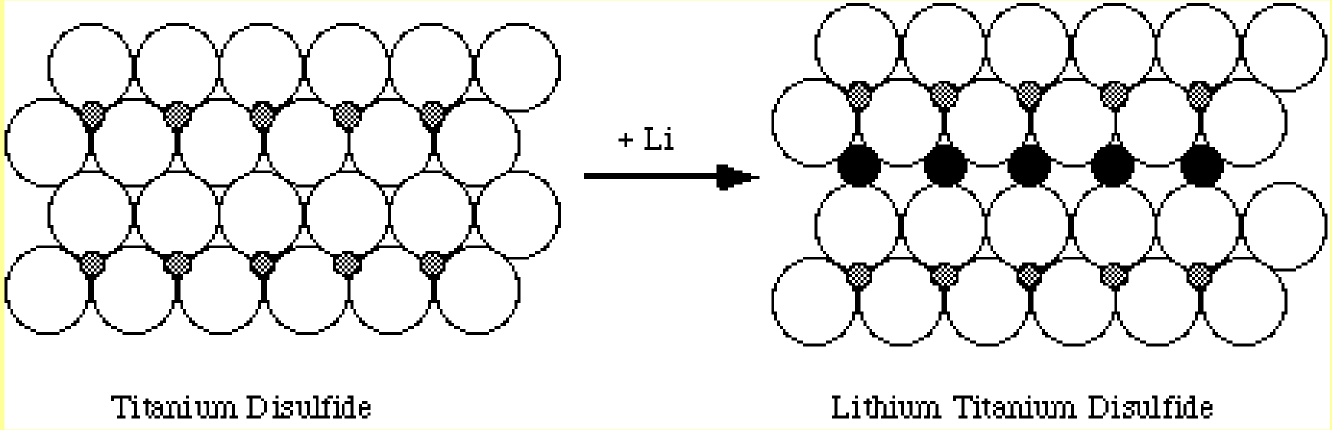


Li Intercalation Compounds

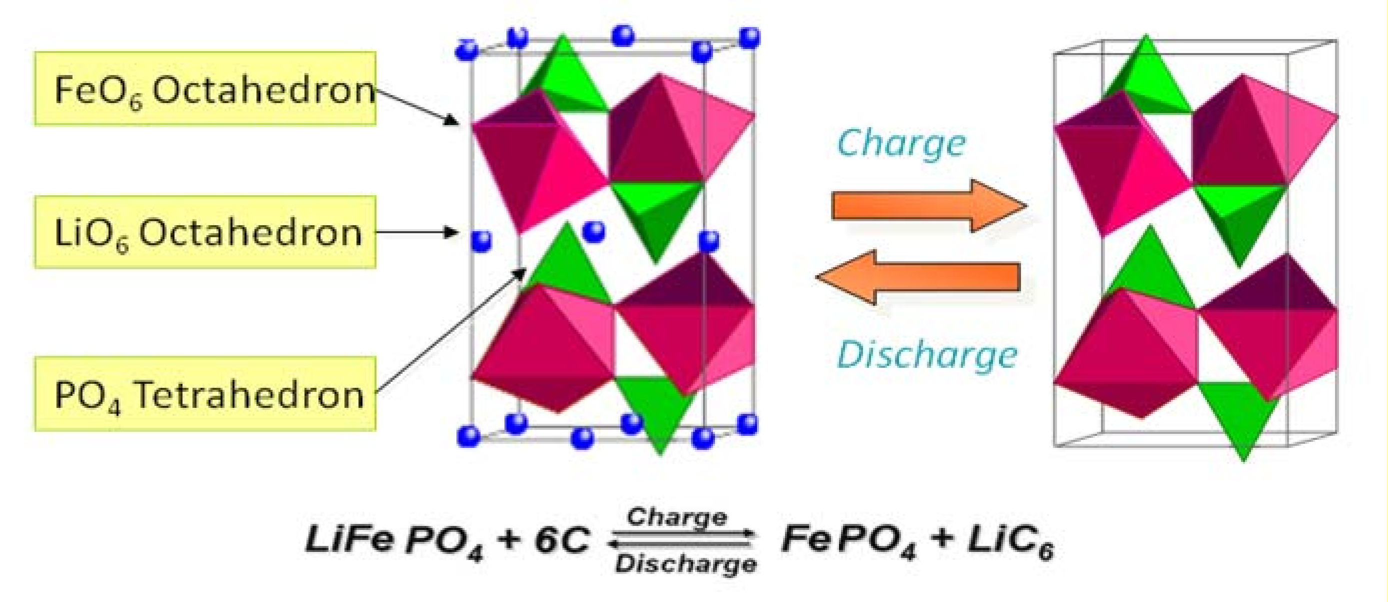


Li Intercalation

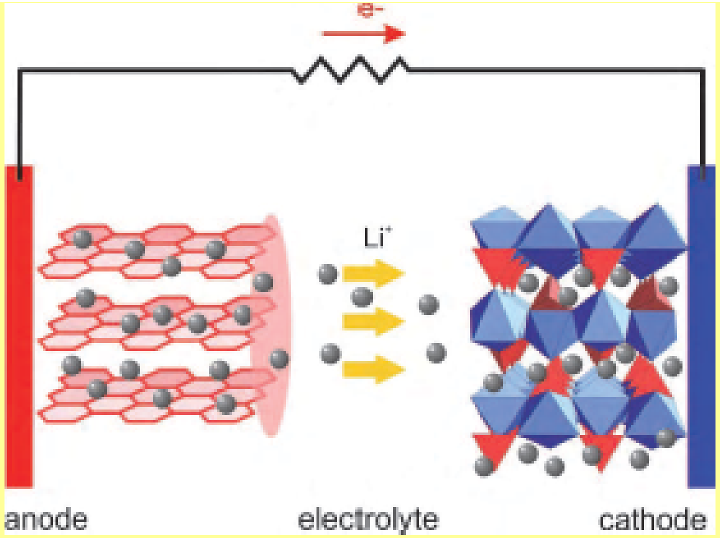
$x\ Li + TiS_2 \rightarrow Li_xTiS_2$



Li Intercalation



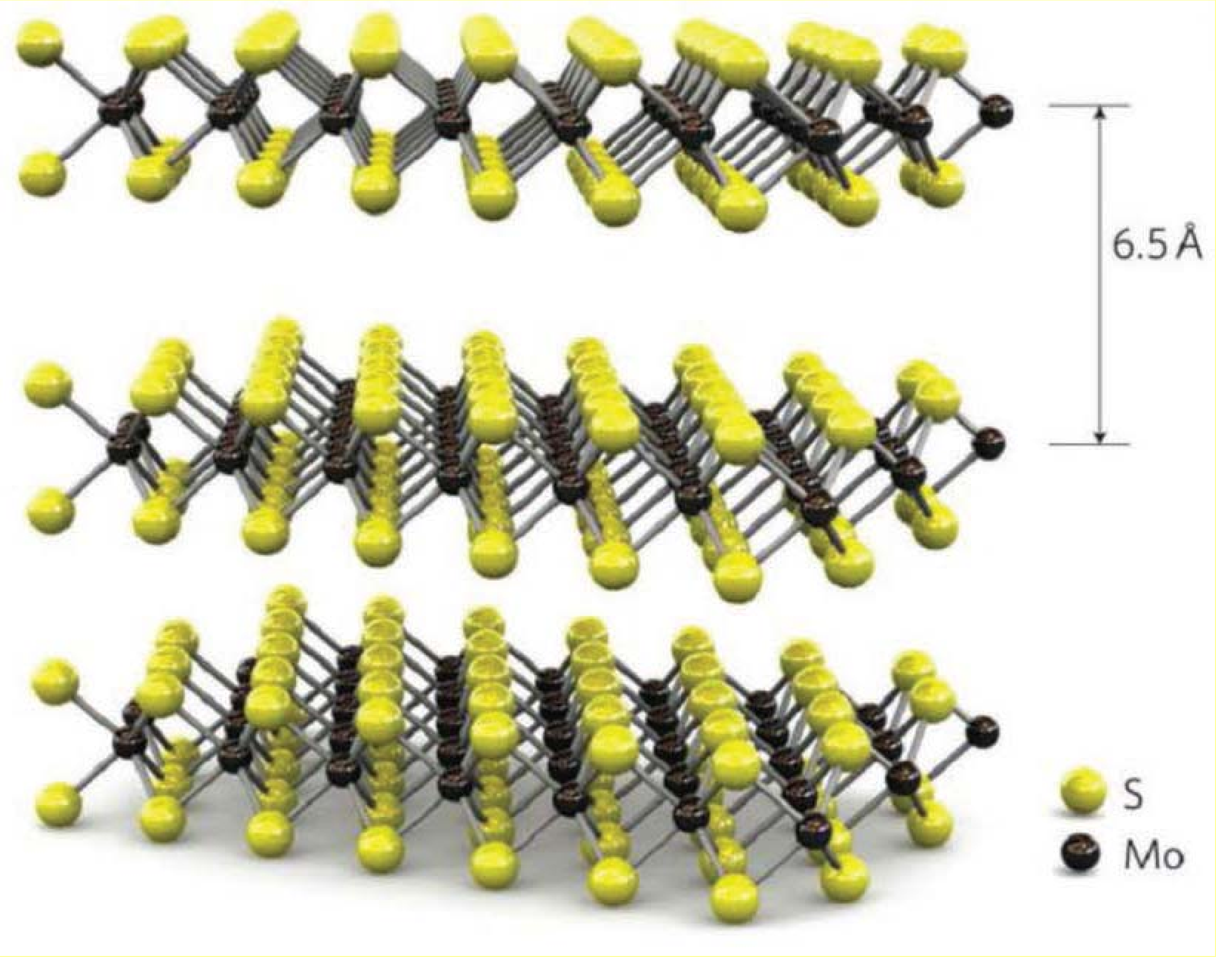
$$LiFePO_4 + 6C \underset{Discharge}{\overset{Charge}{\rightleftharpoons}} FePO_4 + LiC_6$$



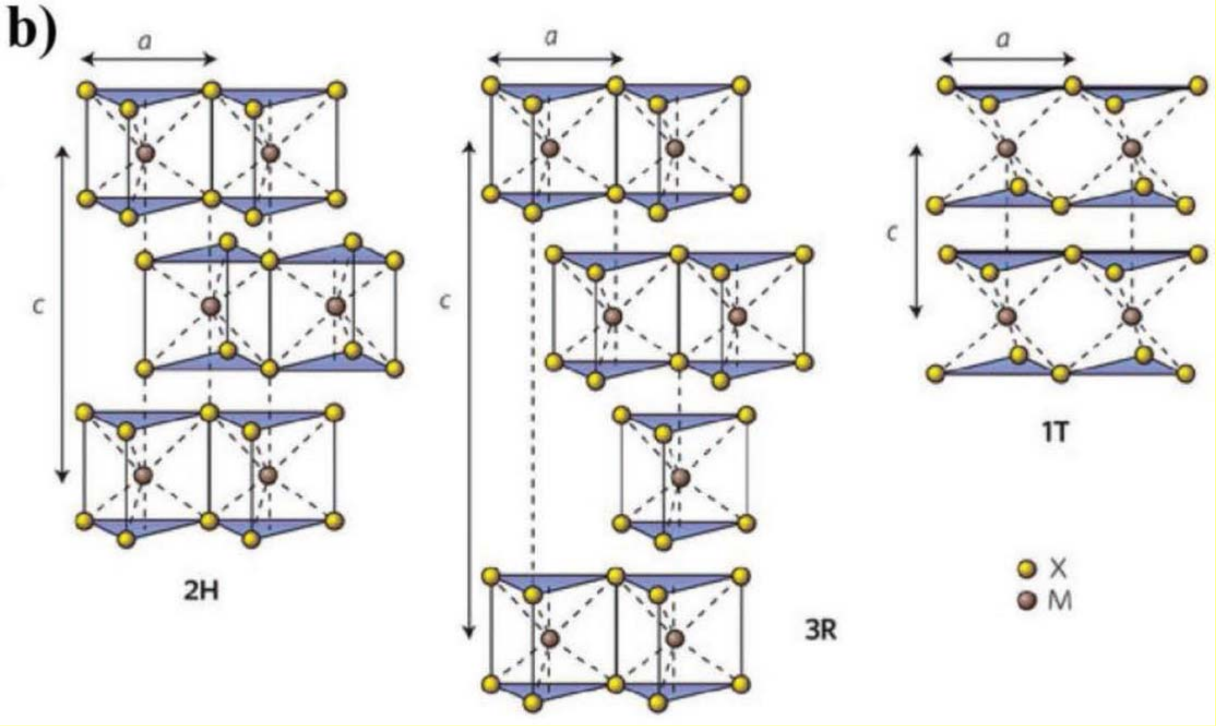
$Li/C \rightarrow e + Li^+ + C$

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

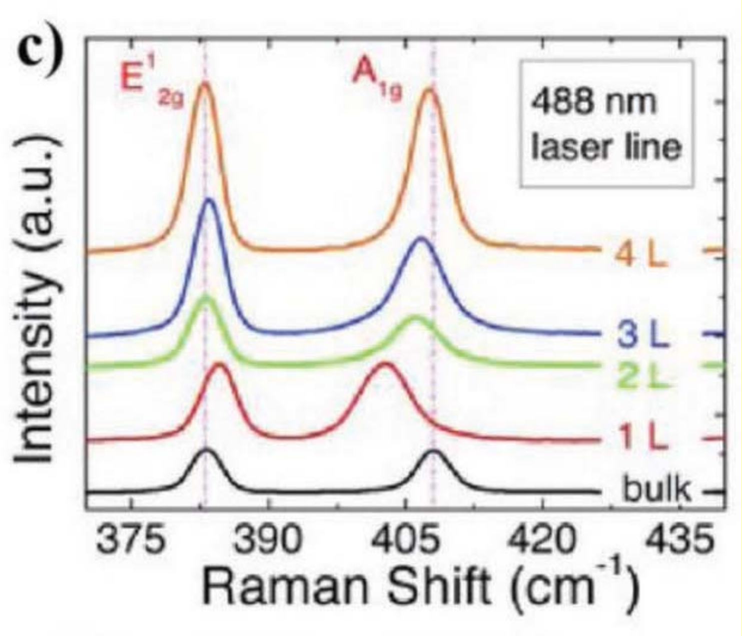
Molybdenum Disulfide (MoS_2)



Molybdenum Disulfide (MoS_2)

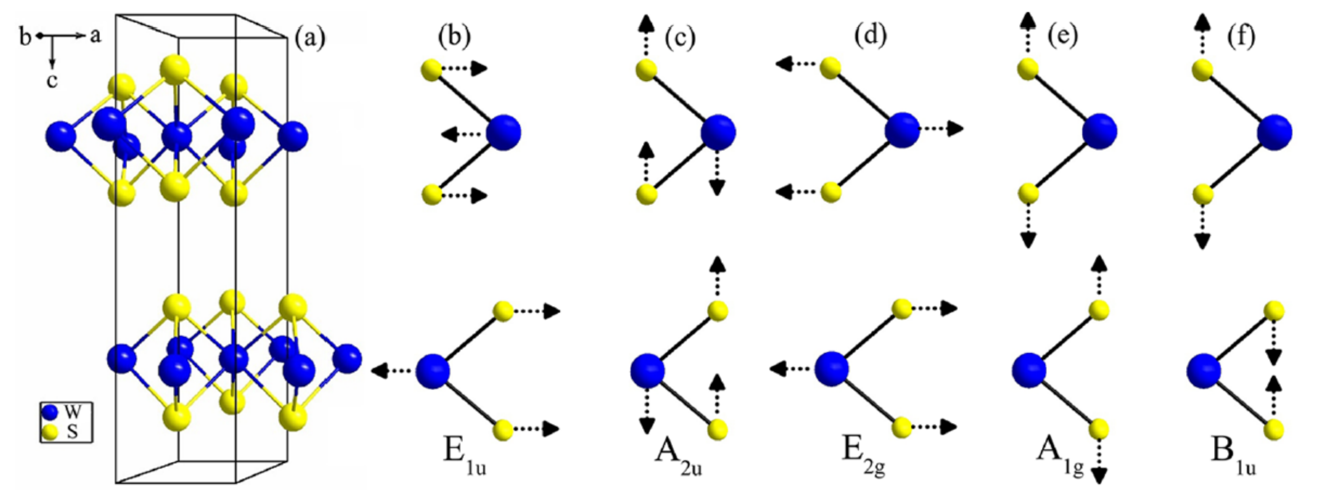


Molybdenum Disulfide (MoS_2)

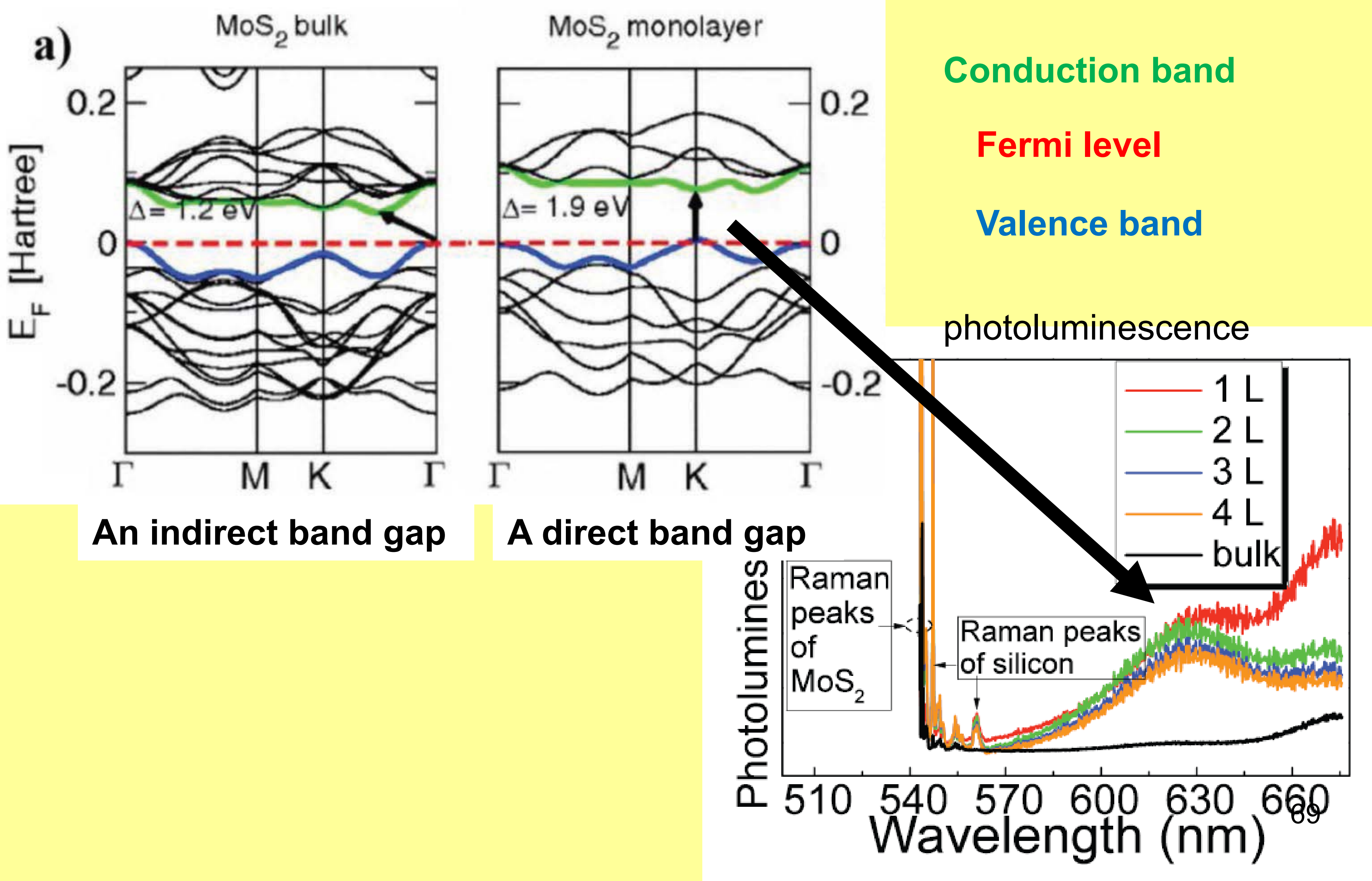


Frequency of A_{1g} band is increasing while that of E^1_{2g} is decreasing with increase in number of layers

(b,c) infraredand (d−f) Raman-active



Molybdenum Disulfide (MoS_2)



An indirect band gap

A direct band gap

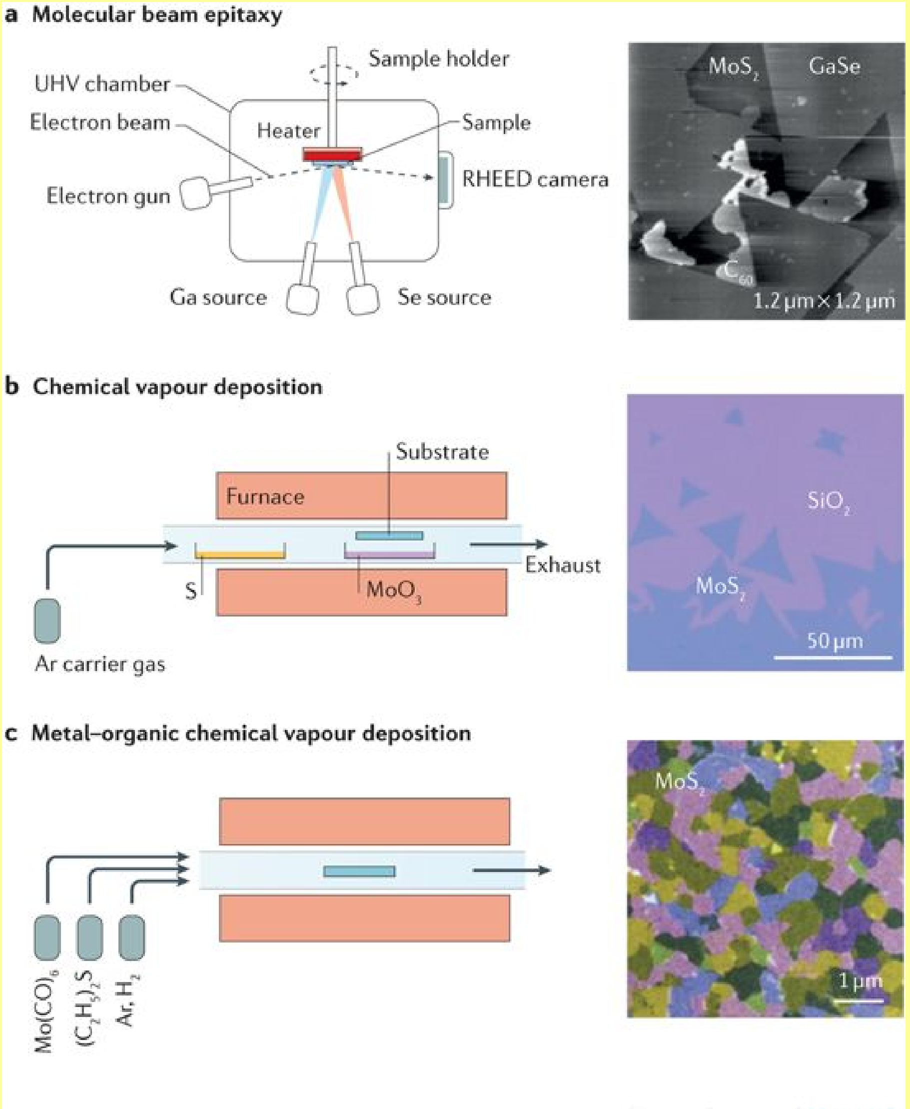
Conduction band

Fermi level

Valence band

photoluminescence

Molybdenum Disulfide (MoS_2)



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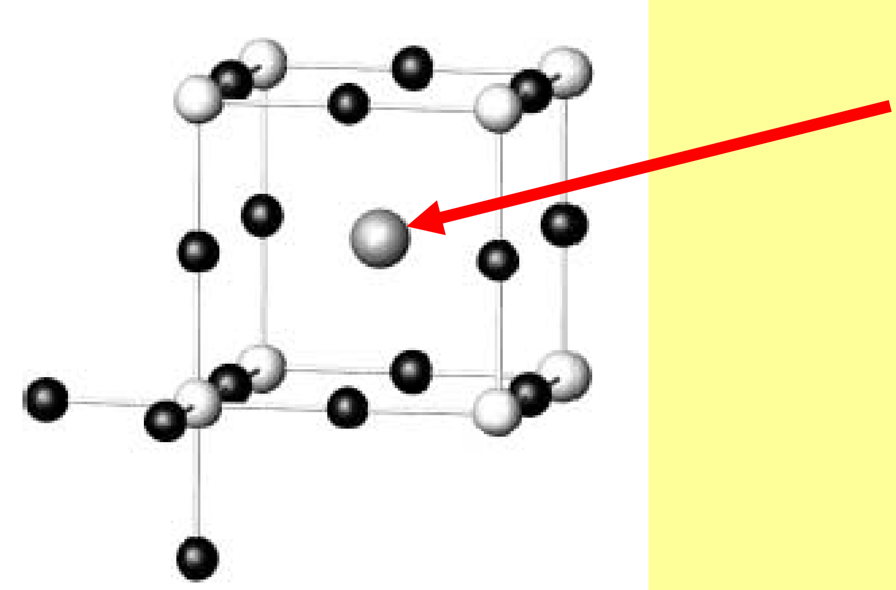
3D Intercalation Compounds

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 $PdCu_3N$

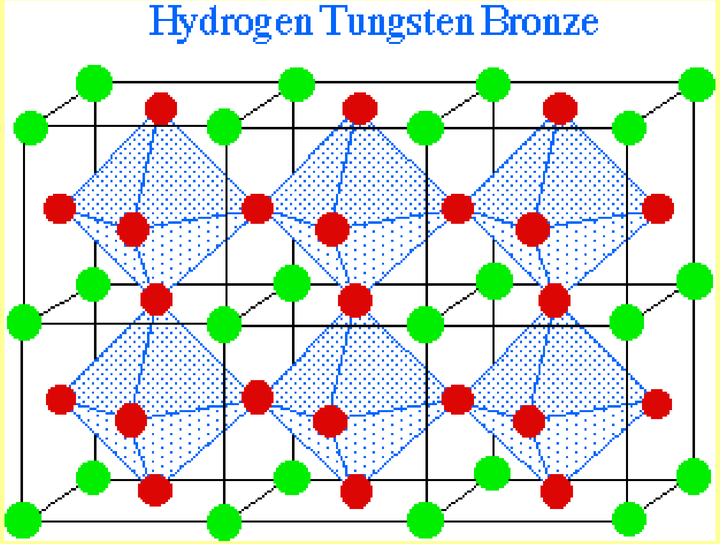
By M = Ga, Ag, Cu leading to MMn_3N

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

$K_3 C_{60}$