Layered Compounds

2D = Two-dimensional layers

Graphite and Graphene

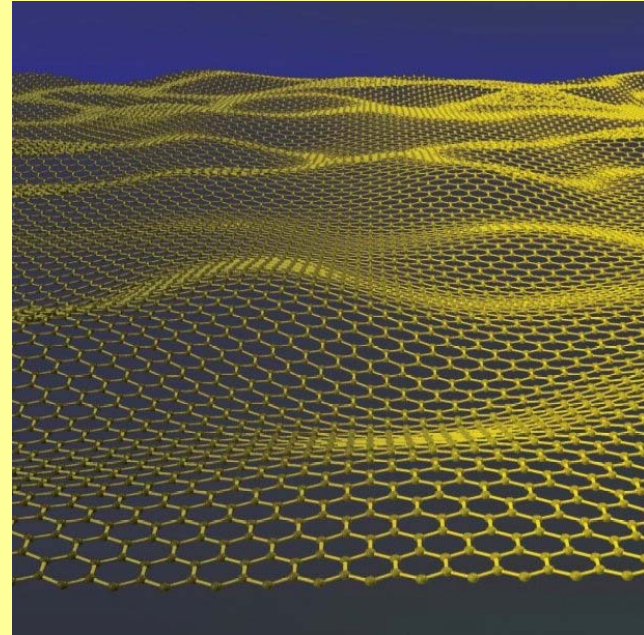**Clay Minerals, Mica**

Layered Double Hydroxides (LDHs)

Layered Zirconium Phosphates and Phosphonates

Layered Metal Oxides

Layered Metal Chalcogenides - TiS_2, MoS_2, WS_2, MPS_3 (M = Ti, V, Mo, W, Mn, Fe, Co, Ni, Zn)
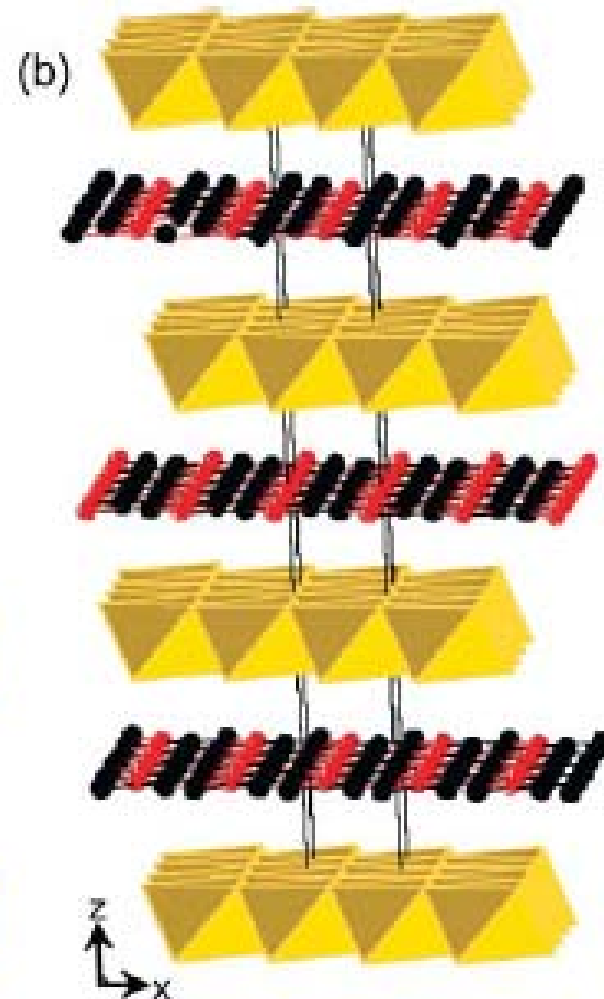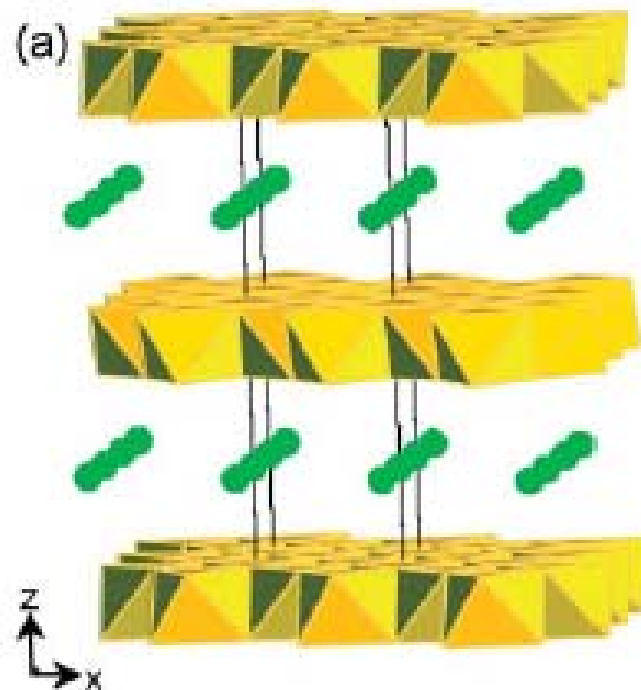
Alkali Silicates and Crystalline Silicic Acids

Layered Compounds
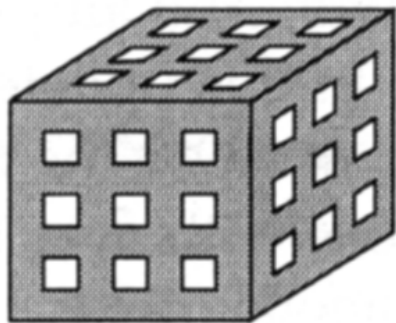
Intralayer bonding - strong (covalent, ionic)

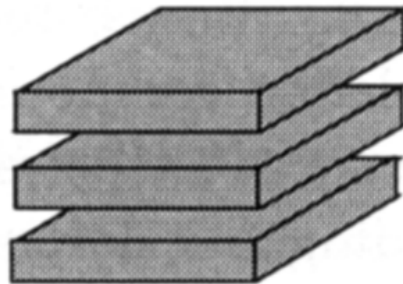**Interlayer bonding - weak (H-bonding, vdWaals)**
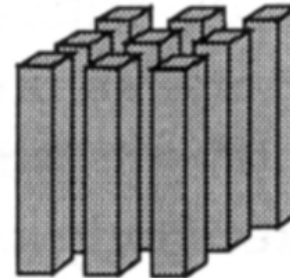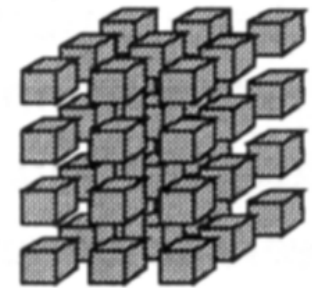
Host-Guest Structures

Host dimensionality
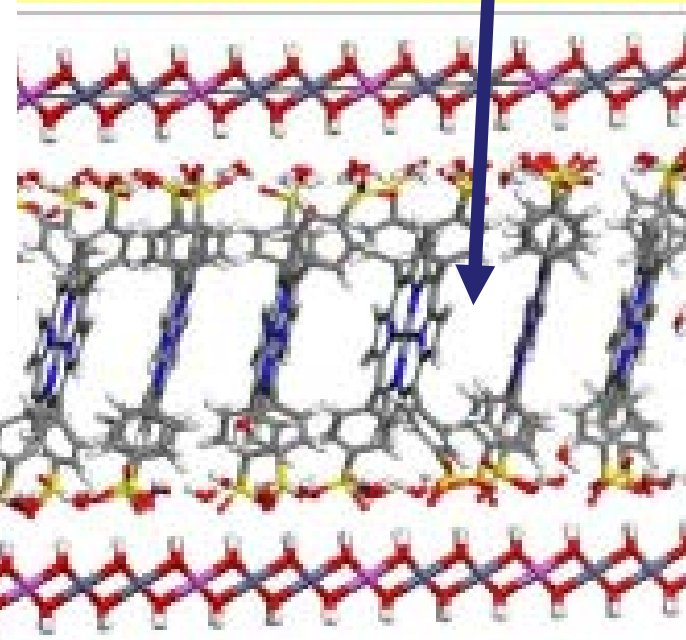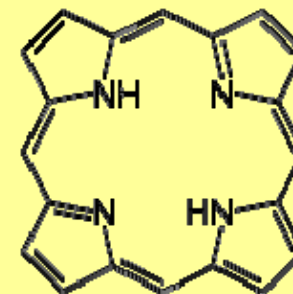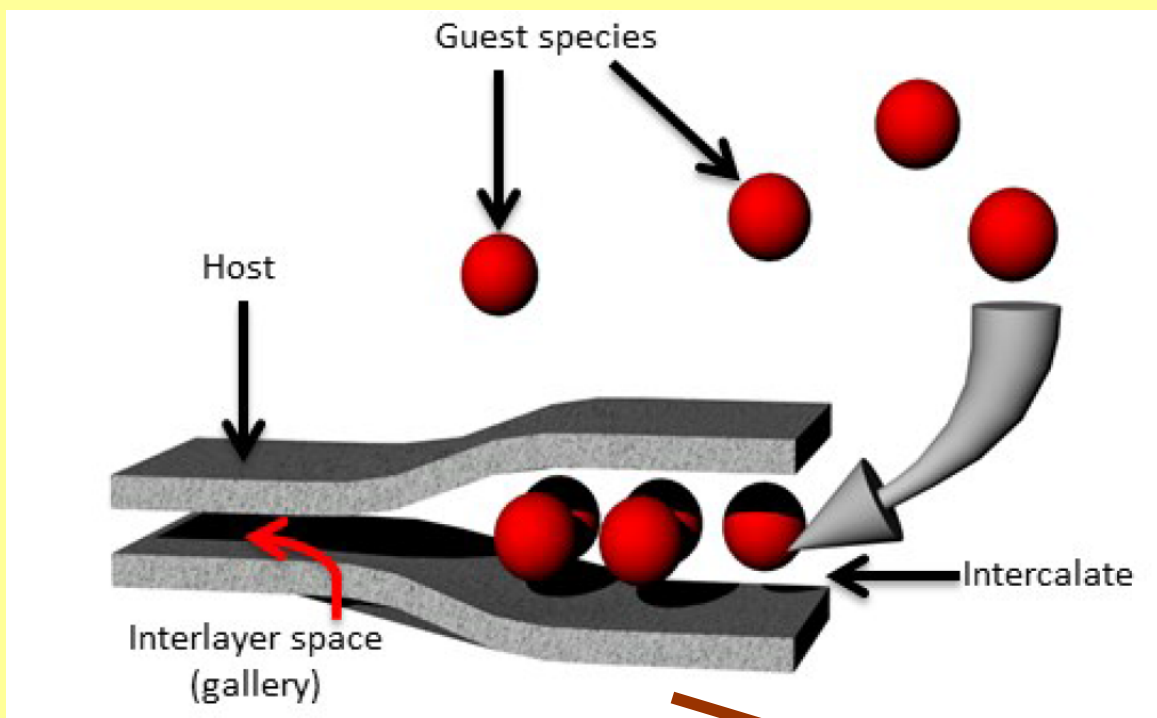

3D   **2D**   **1D**   **0D**

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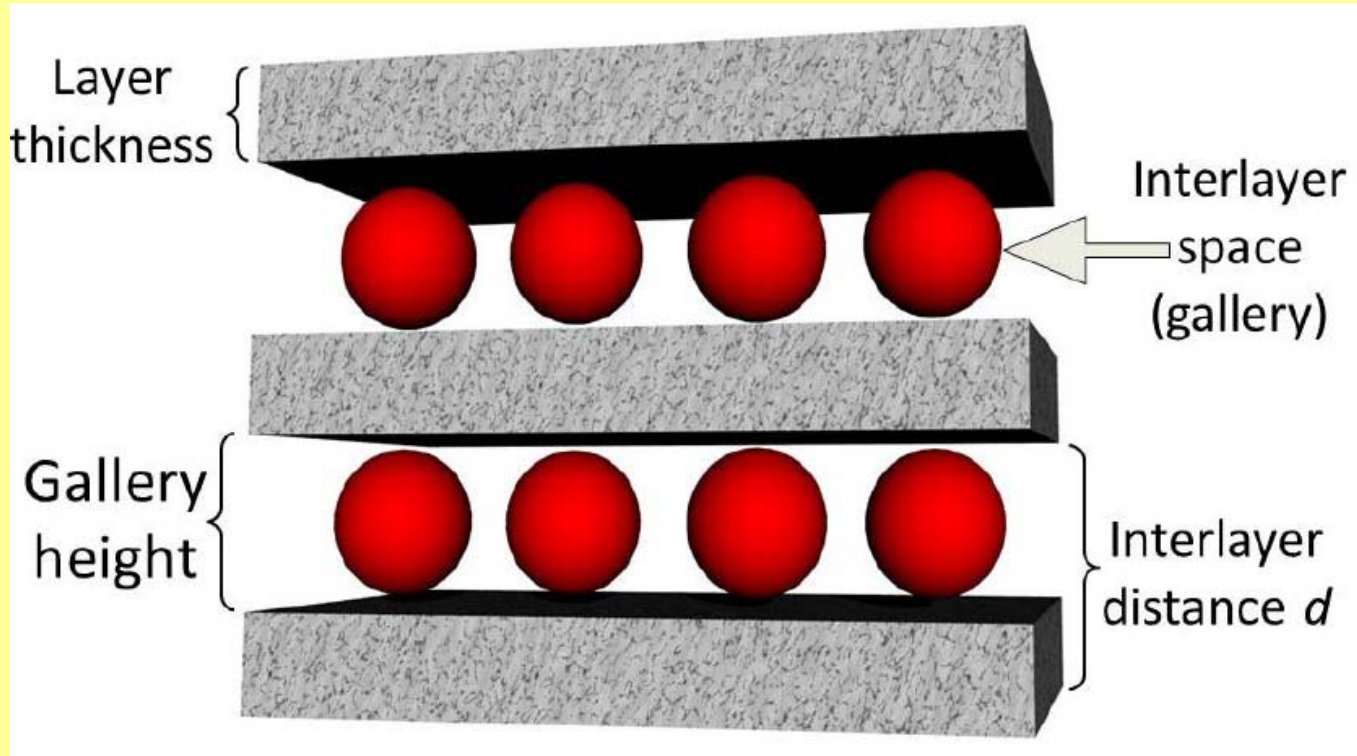
Intercalation

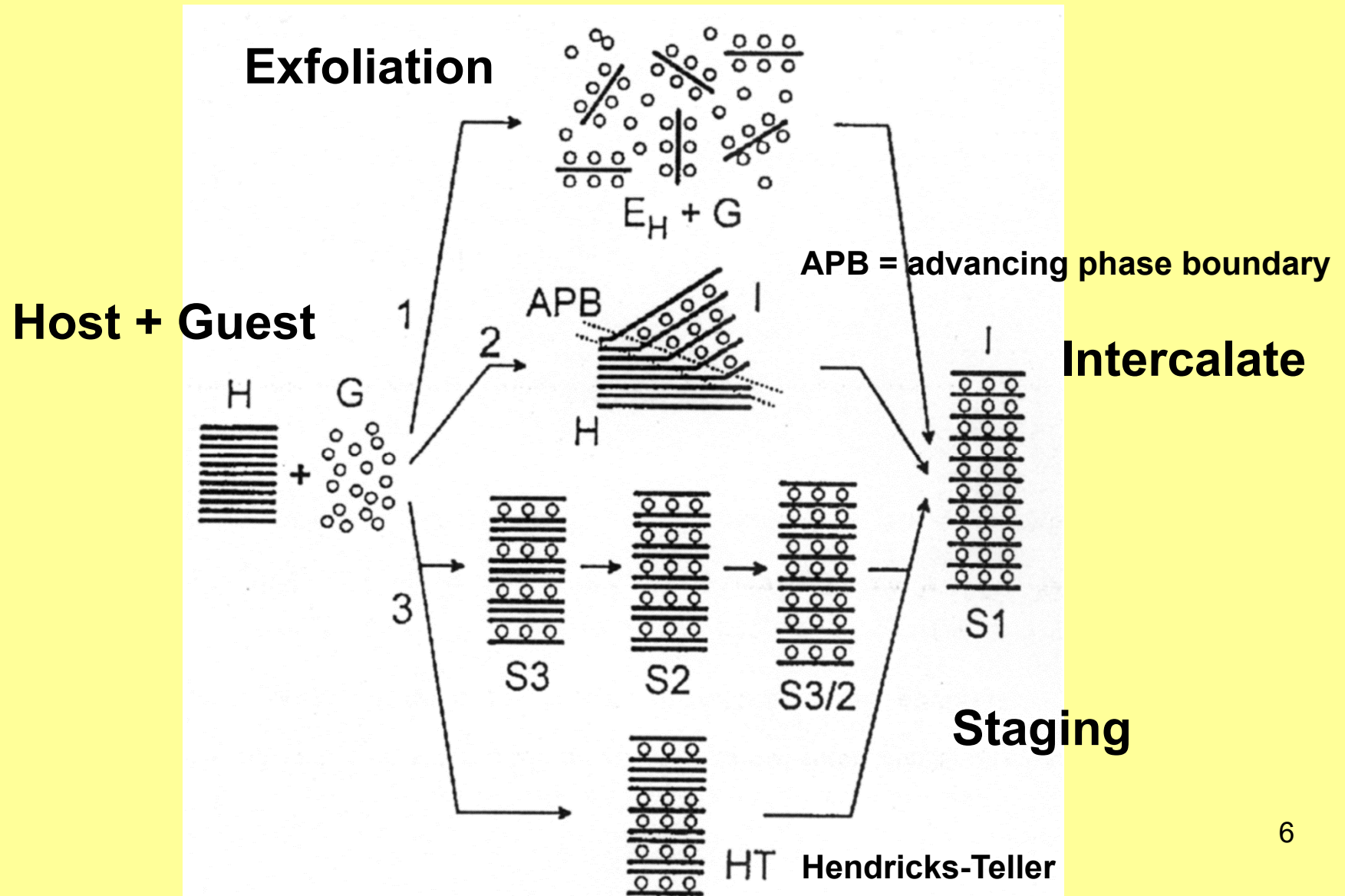**Intercalation**   **Insertion of molecules between layers**
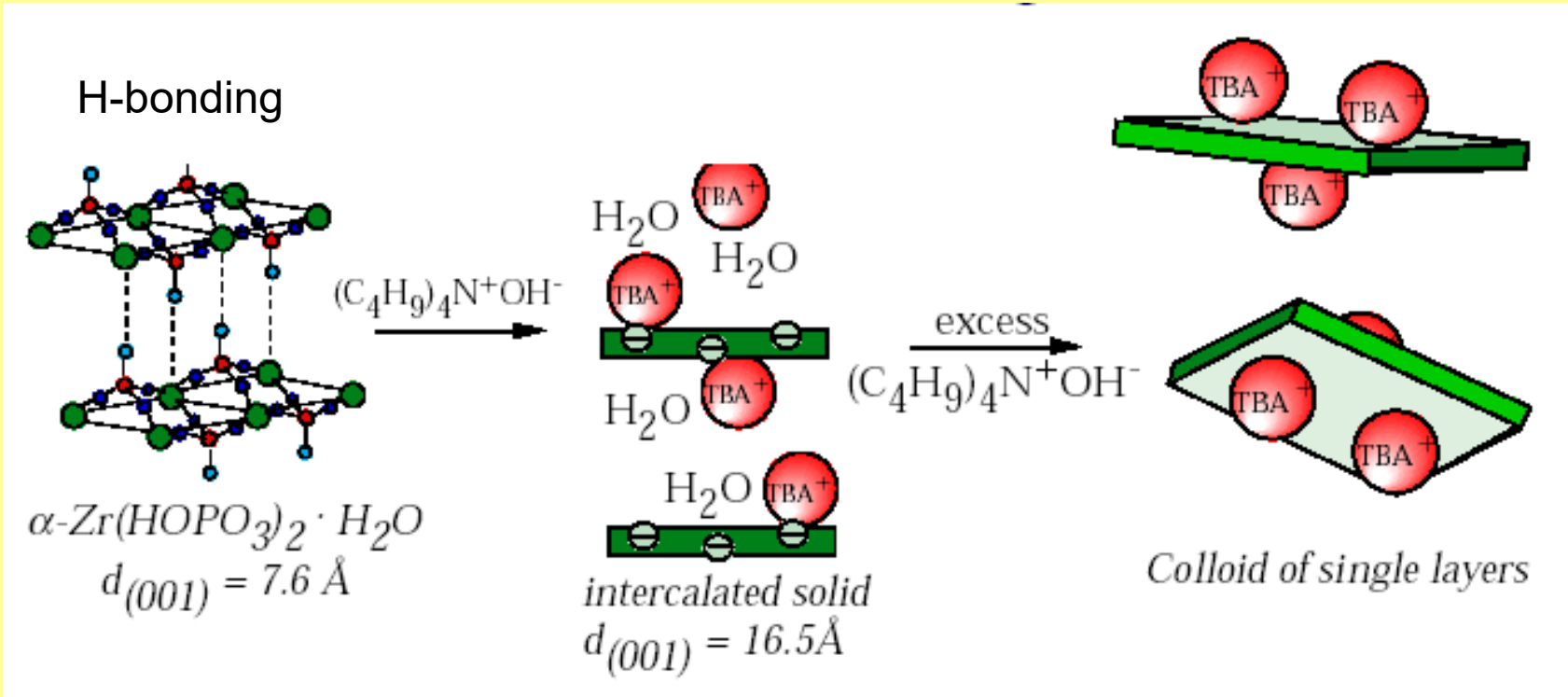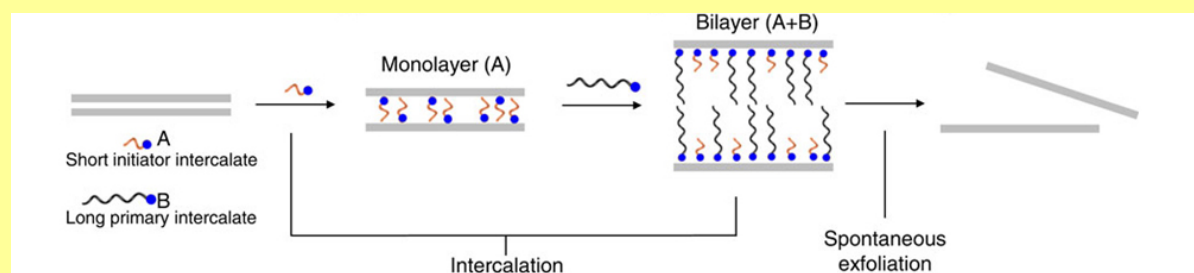
Intercalation

Intercalation

Exfoliation

$E_H + G$

APB = advancing phase boundary

Host + Guest

APB

I

Intercalate

H + G

1

2

3

H

S3

S2

S3/2

S1

Staging

HT   Hendricks-Teller

6

Exfoliation

**Decrease attractive forces between layers
Separate layers**

H-bonding

α-Zr(HOPO$_3$)$_2 \cdot$ H$_2$O
$d_{(001)}$ = 7.6 Å

$(C_4H_9)_4N^+OH^-$

H$_2$O
H$_2$O
TBA$^+$
TBA$^+$
H$_2$O TBA$^+$
H$_2$O TBA$^+$

intercalated solid
$d_{(001)}$ = 16.5Å

excess
$(C_4H_9)_4N^+OH^-$

TBA$^+$
TBA$^+$
TBA$^+$
TBA$^+$
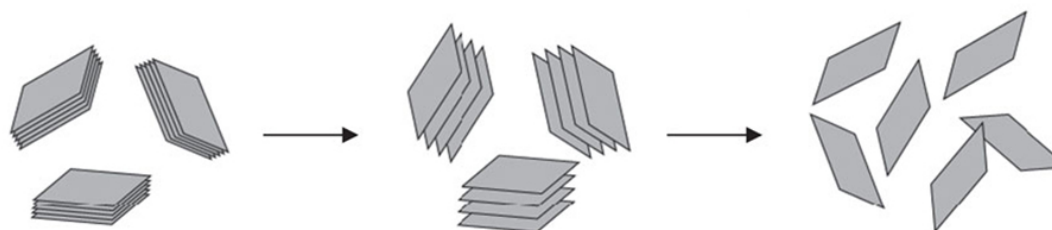TBA$^+$

Colloid of single layers

Tandem Molecular Intercalation

Lewis base short initiator first intercalates to open up the interlayer gap, and the long molecules then bring the gap to full width and overcome the interlayer attractive force resulting in spontaneous exfoliation
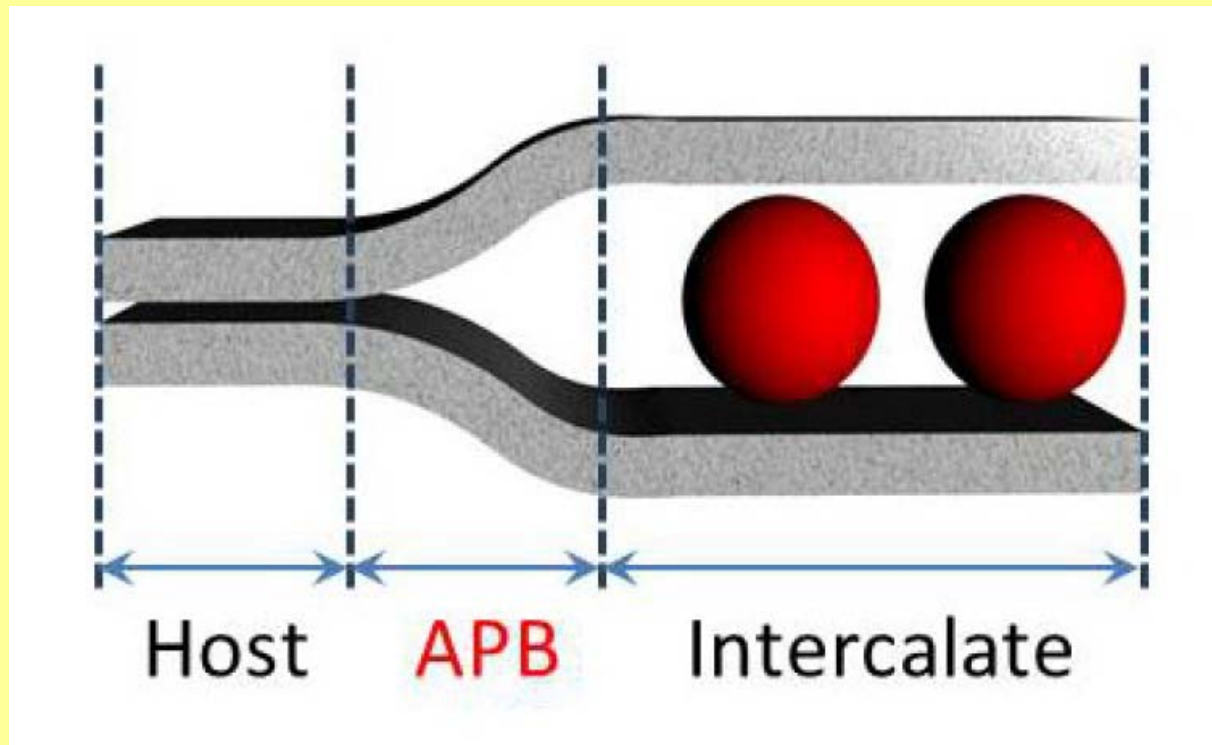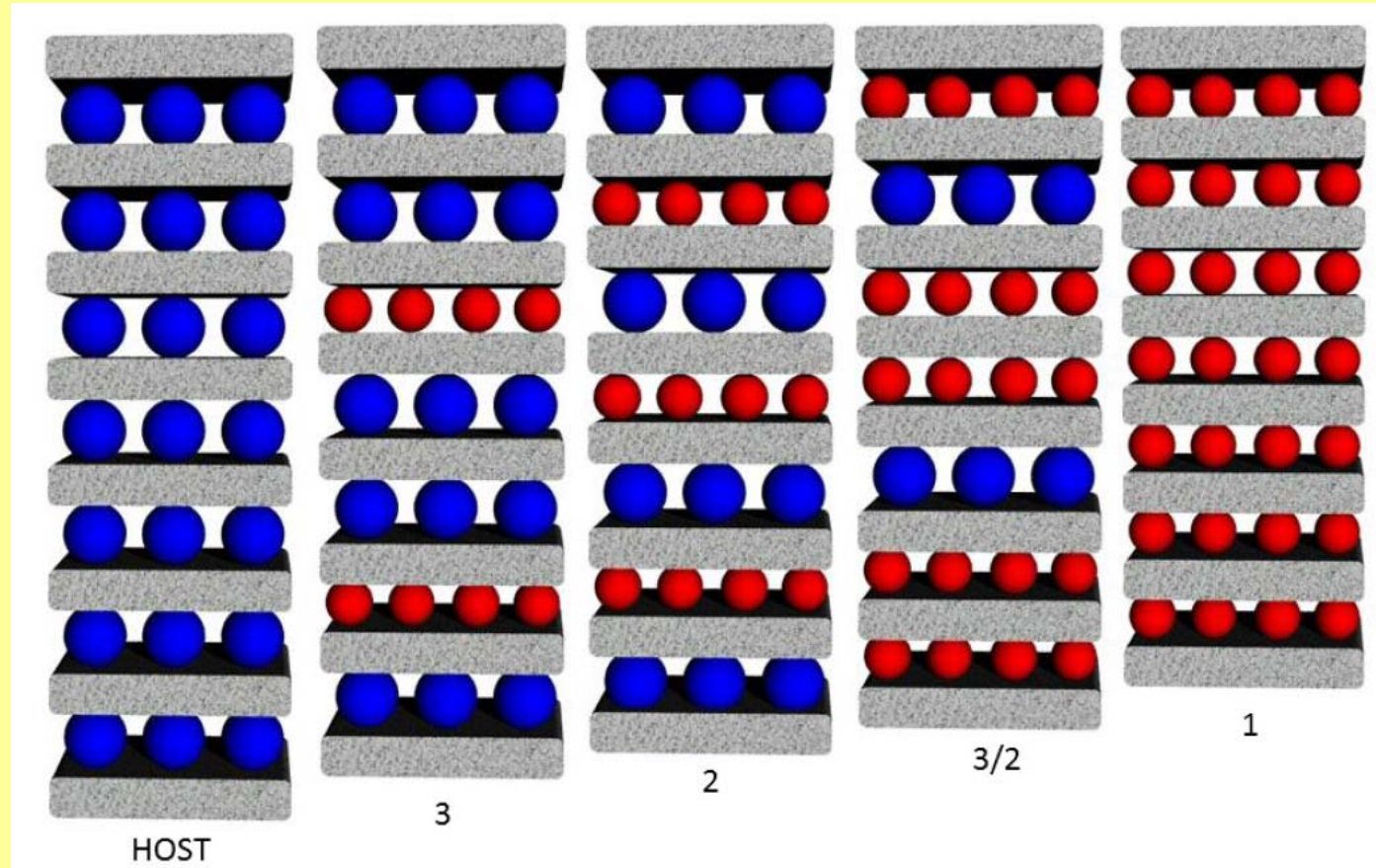
Transition-Metal Chalcogenides

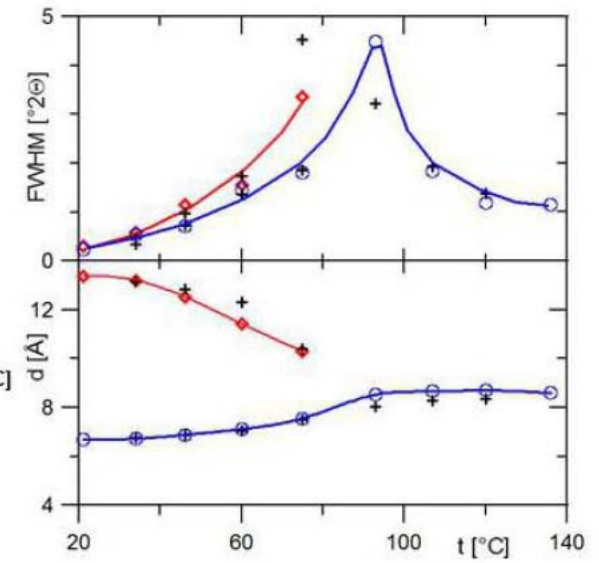Nat. Commun. 2015,6, 5763, Jan. 9, 2015

APB = Advancing Phase Boundary

APB = advancing phase boundary
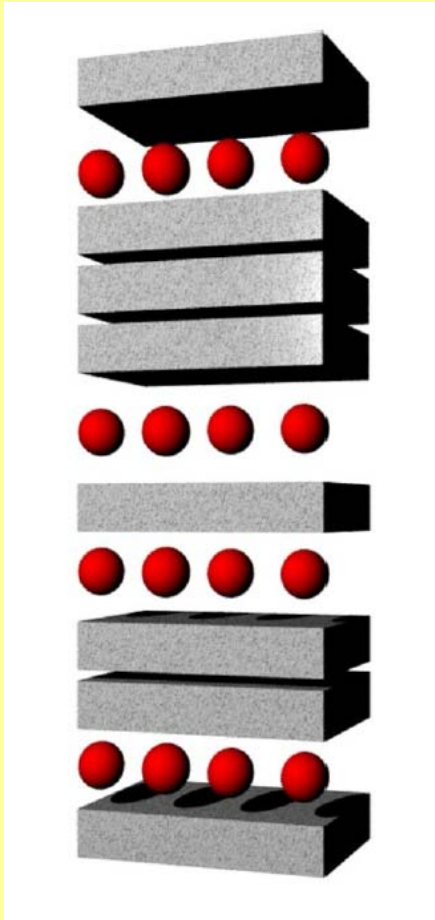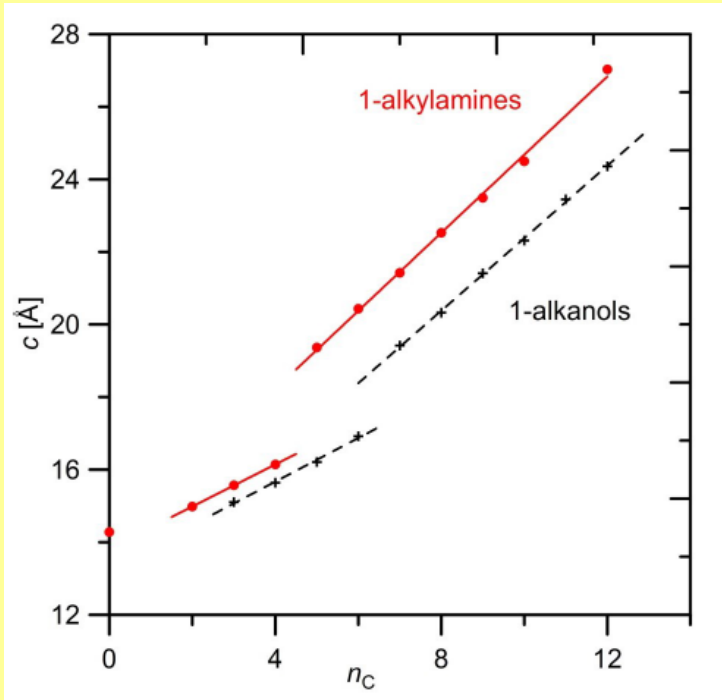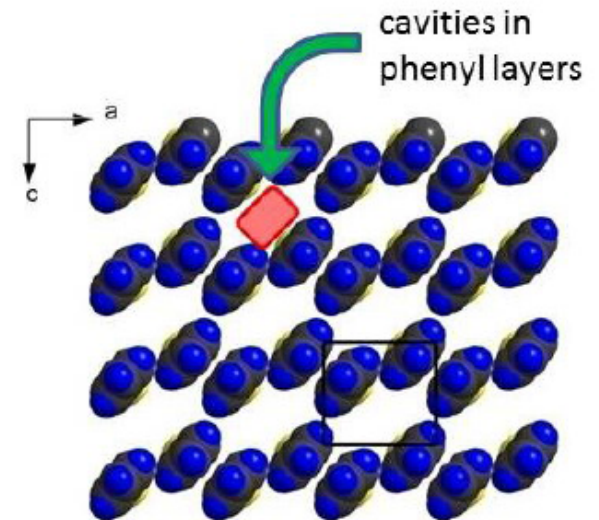
Staging

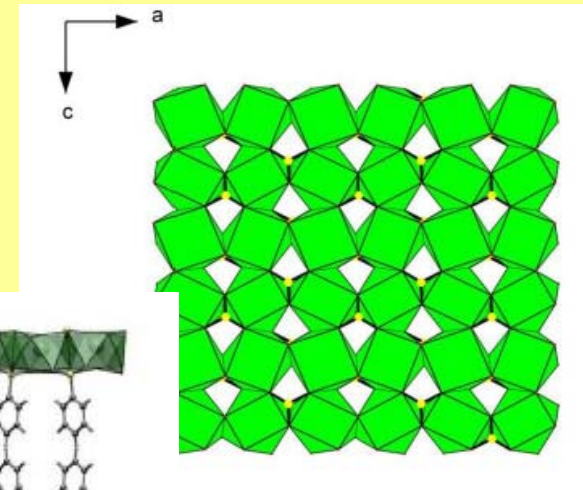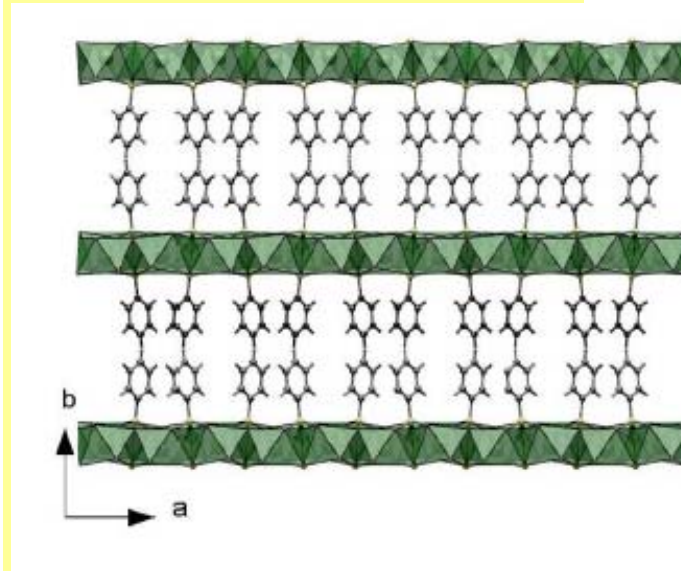HOST   3   2   3/2   1

Hendricks-Teller Effect
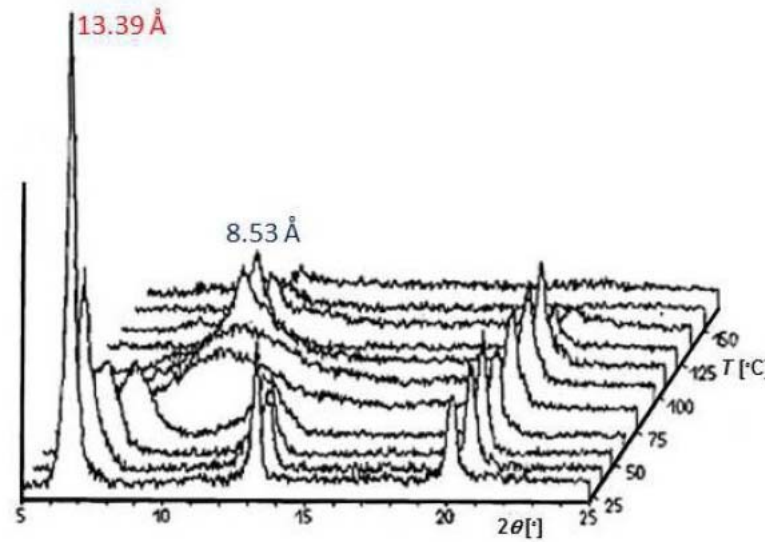
HT = galleries are filled randomly

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 $SrC_6H_5PO_3 \cdot 2H_2O$

cavities in phenyl layers

Graphite

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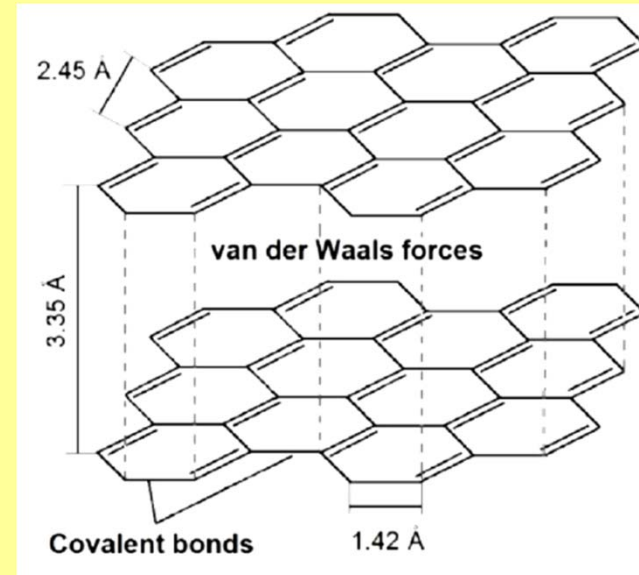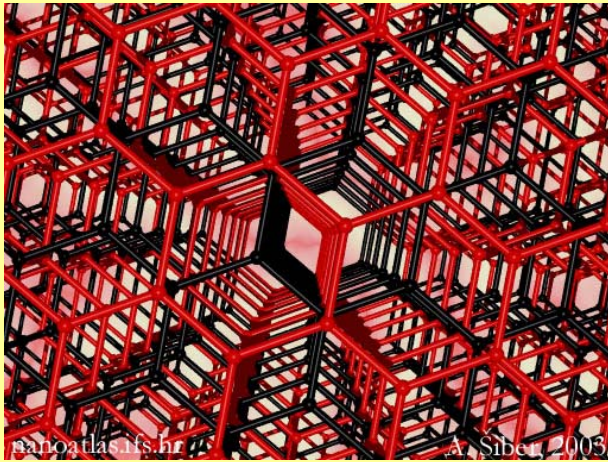
**Graphite sp^2 sigma-bonding in-plane p-p-bonding out of plane
Hexagonal graphite = two-layer ABAB stacking sequence**

**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) $\rightarrow$ C$_8$K (bronze)

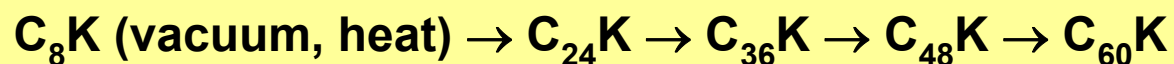**C$_8$K (vacuum, heat) $\rightarrow$ C$_{24}$K $\rightarrow$ C$_{36}$K $\rightarrow$ C$_{48}$K $\rightarrow$ C$_{60}$K**

C$_8$K potassium graphite ordered structure

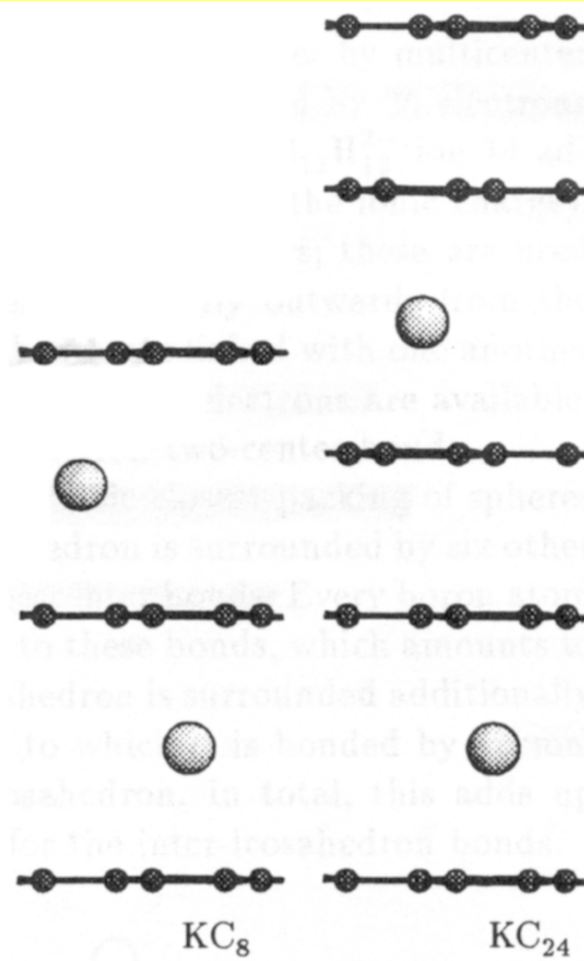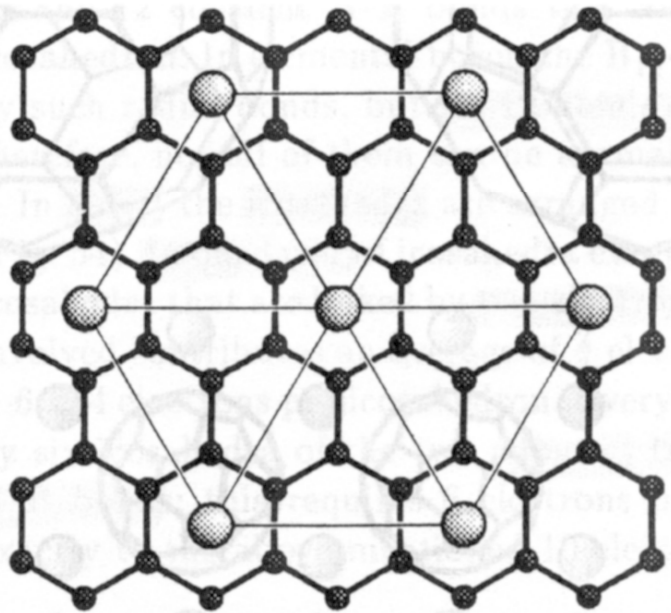**Ordered K guests between the sheets, K to G charge transfer**

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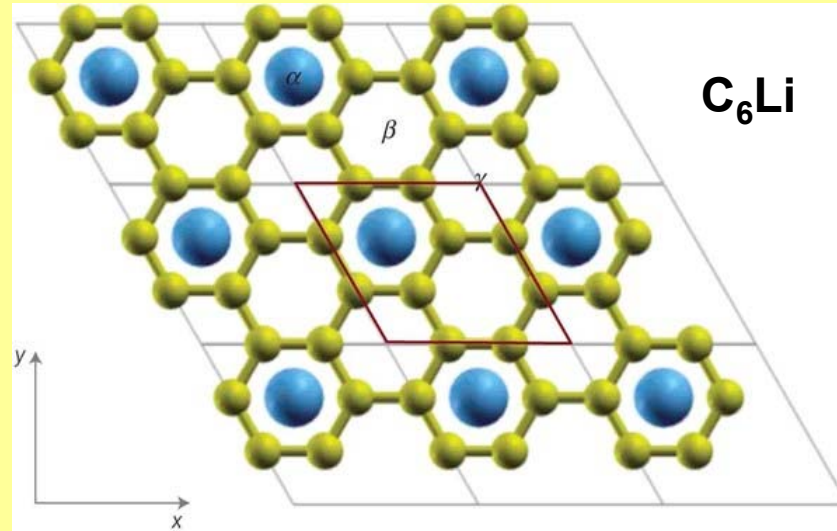**K$^+$ nesting between parallel eclipsed hexagonal planar carbon six-rings**

Graphite

Intercalates

KC$_8$ KC$_{24}$

15

Intercalation in Li-ion Cells

C_6Li

LiFePO$_4$ Charge / Discharge   FePO$_4$

16

Intercalation in Li-ion Cells

Anode
discharge
$$C_6Li_x \rightarrow 6\ C + x\ Li^+ + x\ e^-$$

Cathode
discharge
$$Li_{1-x}Co^{III/IV}O_2 + x\ Li^+ + x\ e^- \rightarrow LiCo^{III}O_2$$
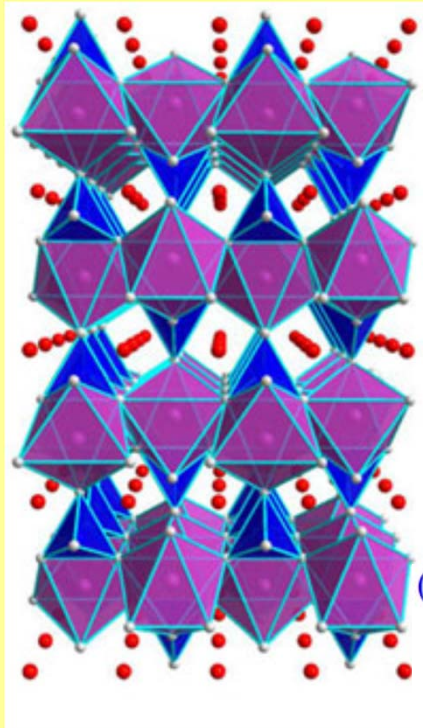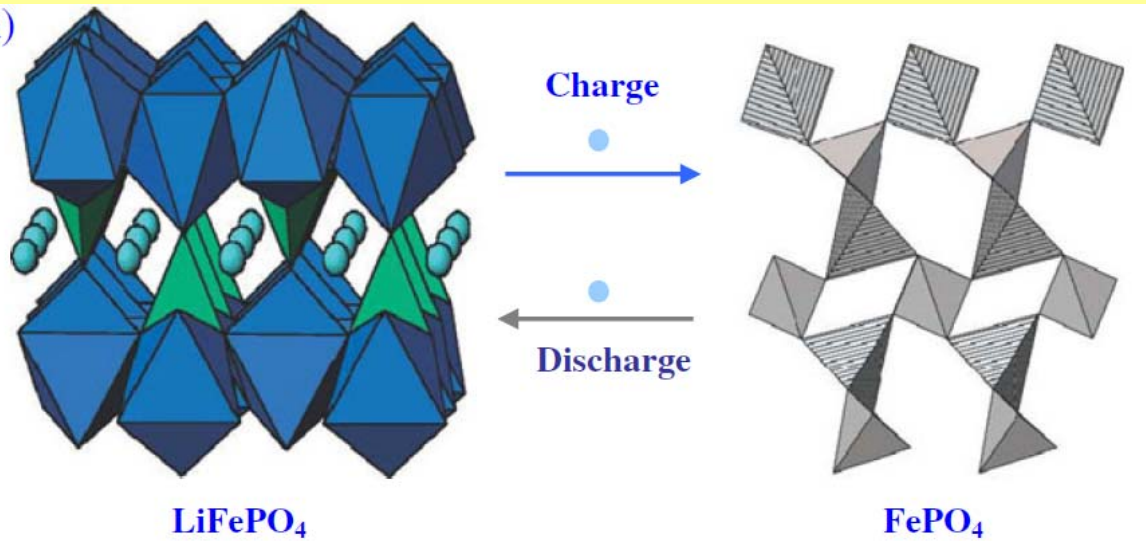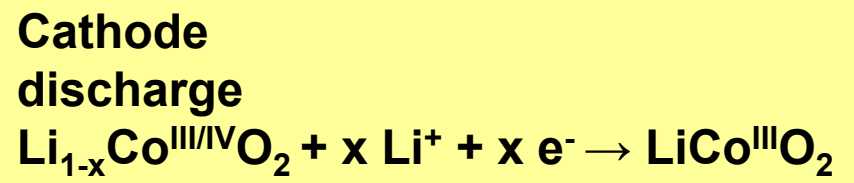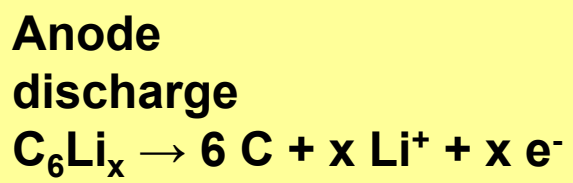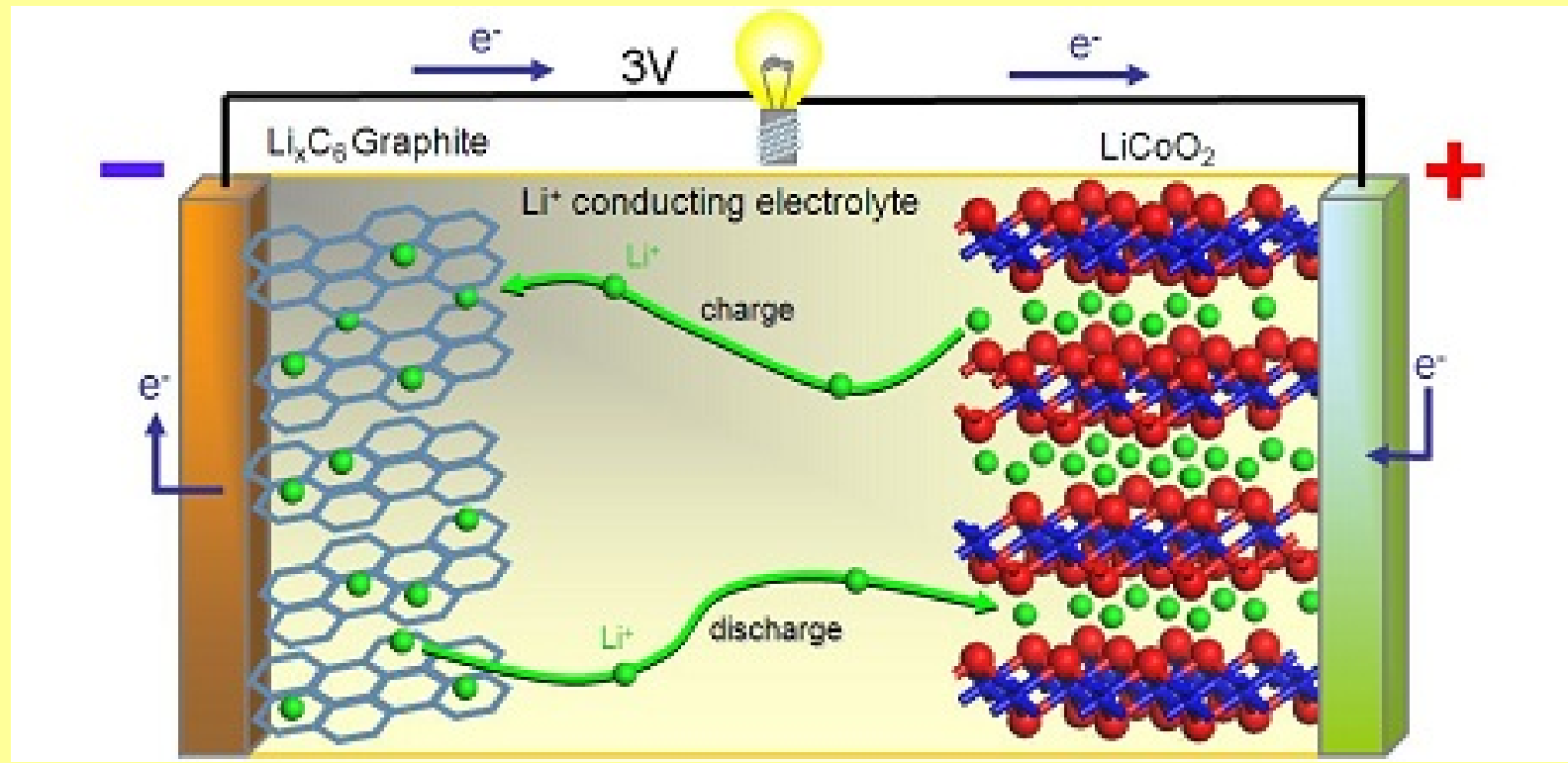
Graphene Family

Graphene

Graphene oxide

h-BN

BCN

Fluorographene

C_3N_4

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**
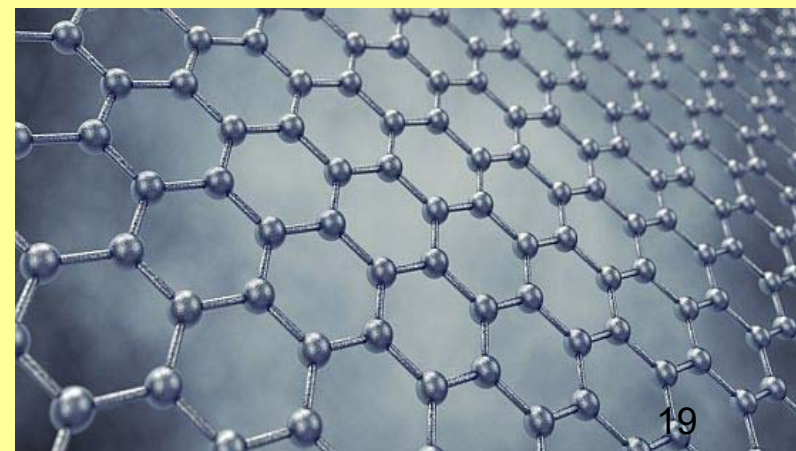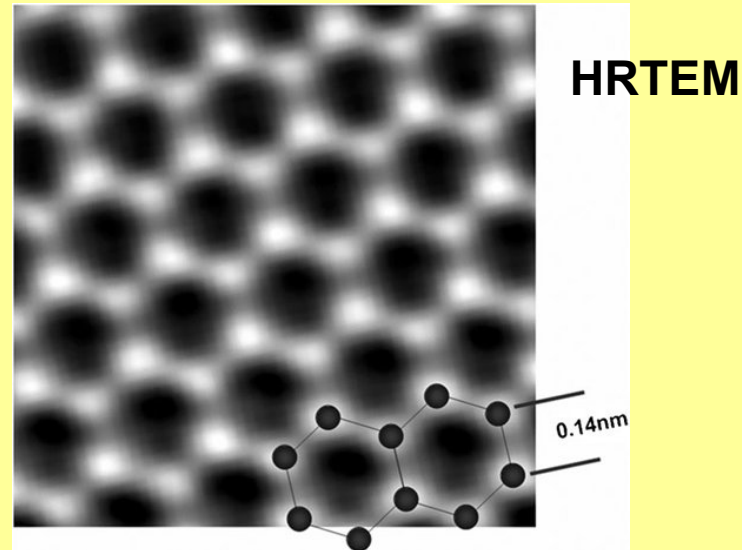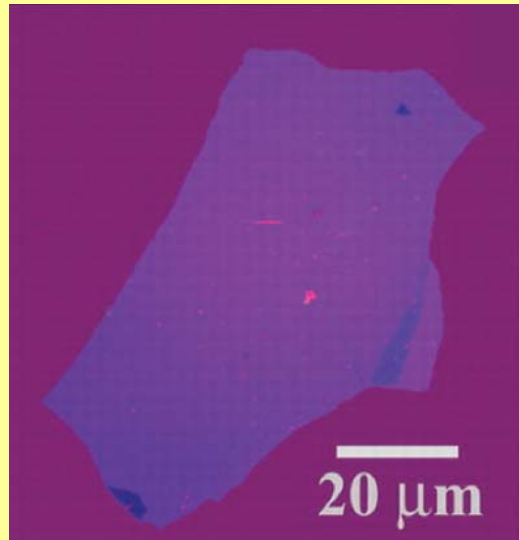 - **Specific surface area (theoretically): 2630 m^{2}g^{-1}**

K. Novoselov **A. Geim**

2010 Nobel Prize in Physics

Graphene

HRTEM

0.14nm

High electric conductivity (metallic, ~20,000 S/cm)
High mobility at low temperature ($2 \cdot 10^5$ cm^2 V^{-1} s^{-1}, Si ~800 cm^2 V^{-1} s^{-1} at r.t.)
Optically transparent (~97.7%) – 1 layer absorbs 2.3% of photons
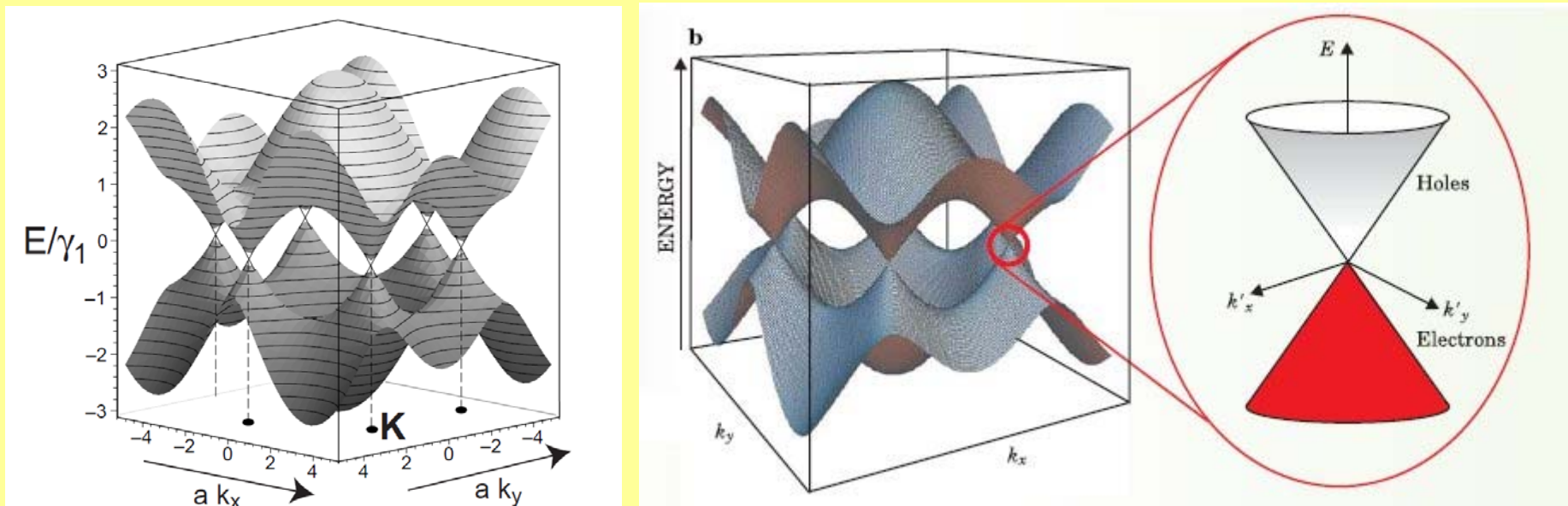Low reflectiveness (<0.1%)
High mechanical strength (E ~ 1 TPa)
High thermal conductivity (K ~ $5 \cdot 10^3$ W m^{-1} K^{-1})
Low anisotropic thermal expansion coefficient
High stability in air atmosphere up to 400 °C

Graphene

LCAO-band structure of graphene

Synthesis of Graphene

Top down

Mechanical exfoliation

Chemical exfoliation (oxidation/reduction)

Dry and/or liquid-phase exfoliation

Unzipping of nanotubes
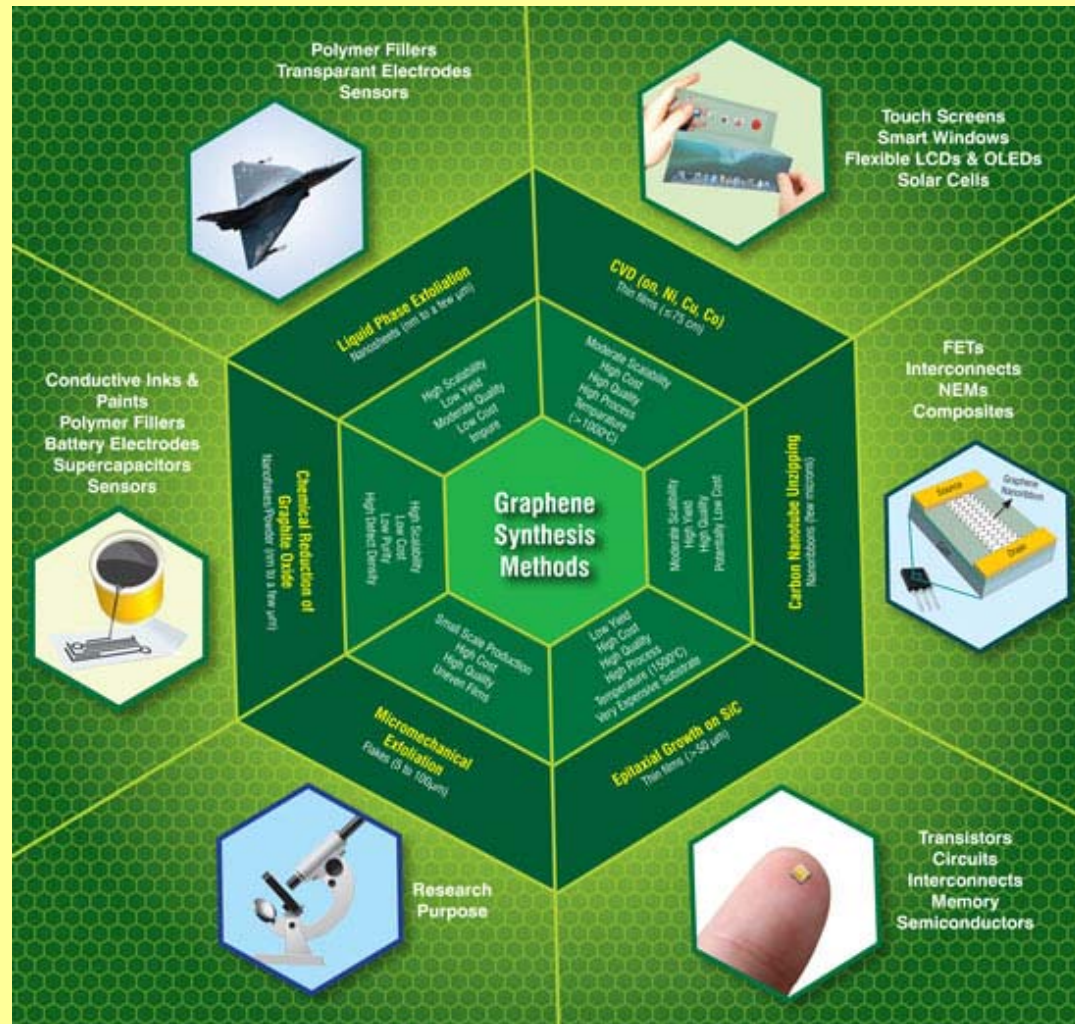
Bottom up

CVD, epitaxial growth, (on SiC and on metals)

Precipitation

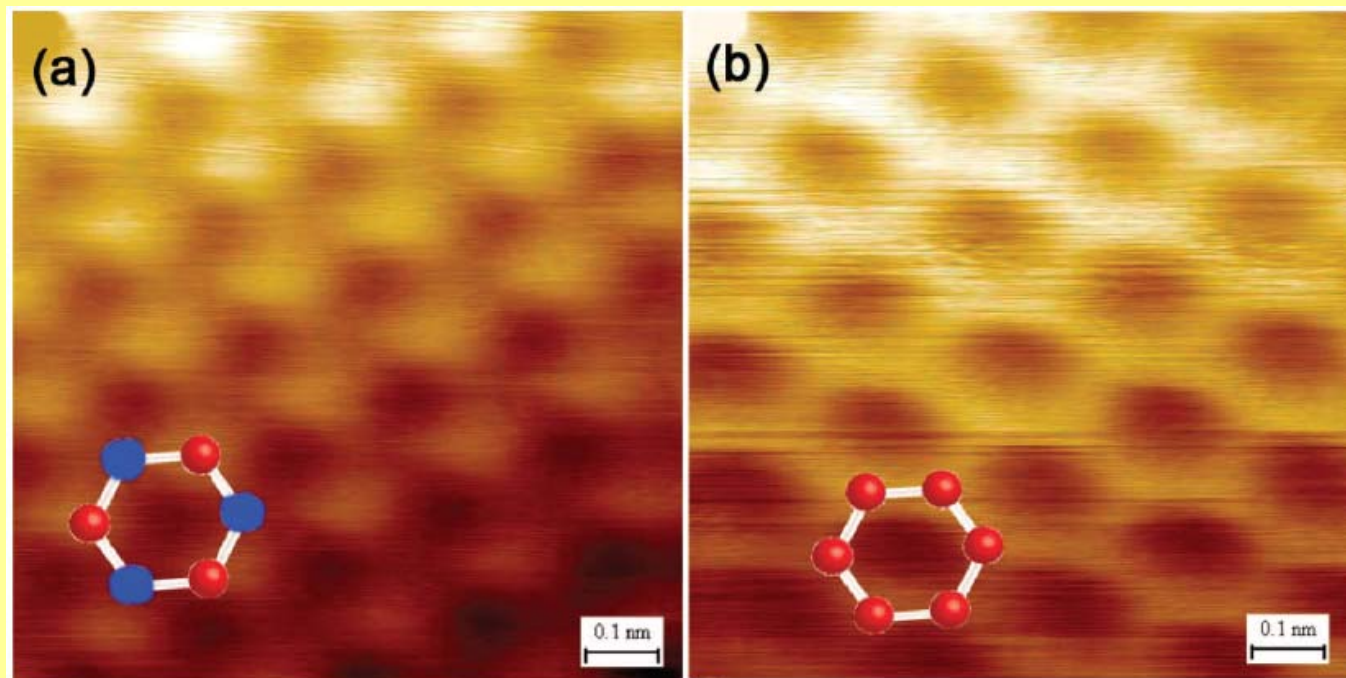**Molecular beam epitaxy**

Synthesis of Graphene

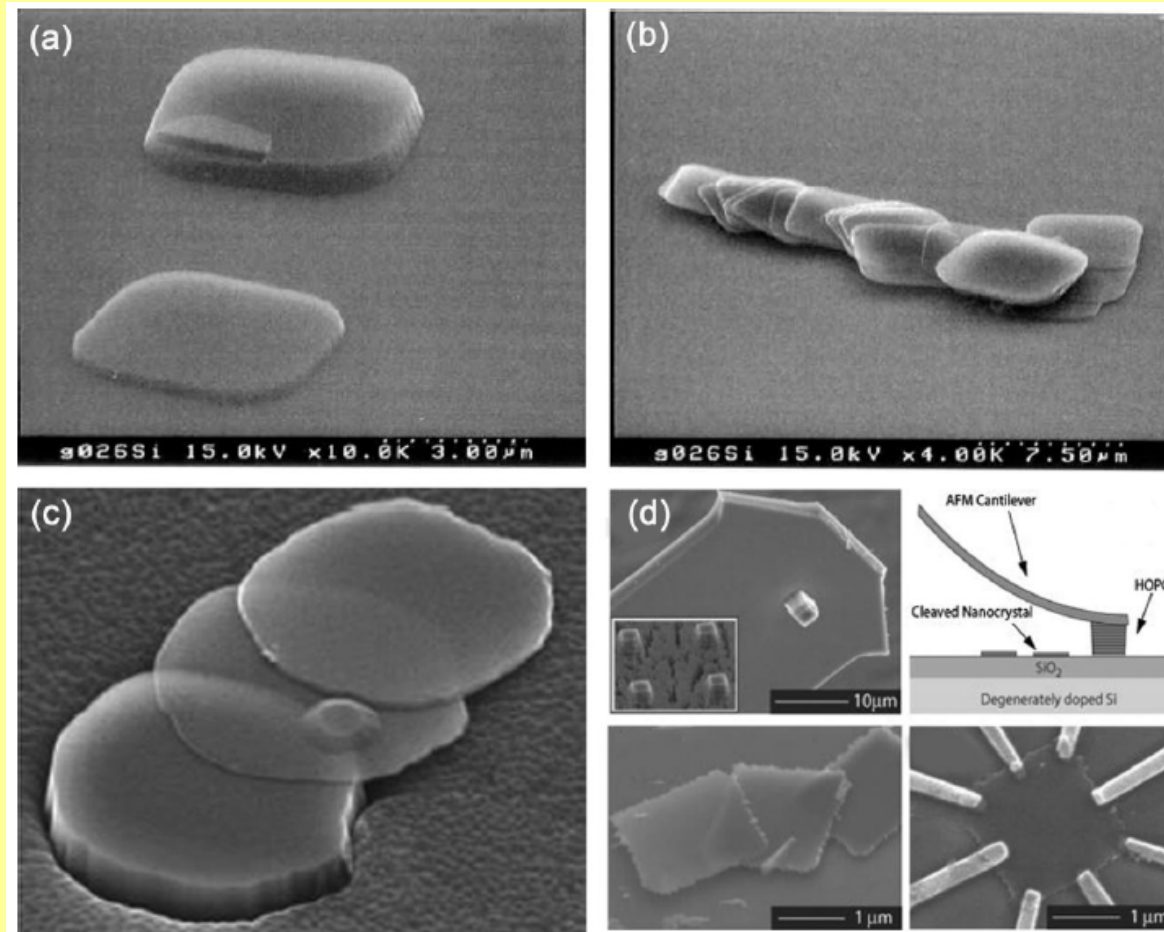http://www.nanowerk.com/what_is_graphene.php

23

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**
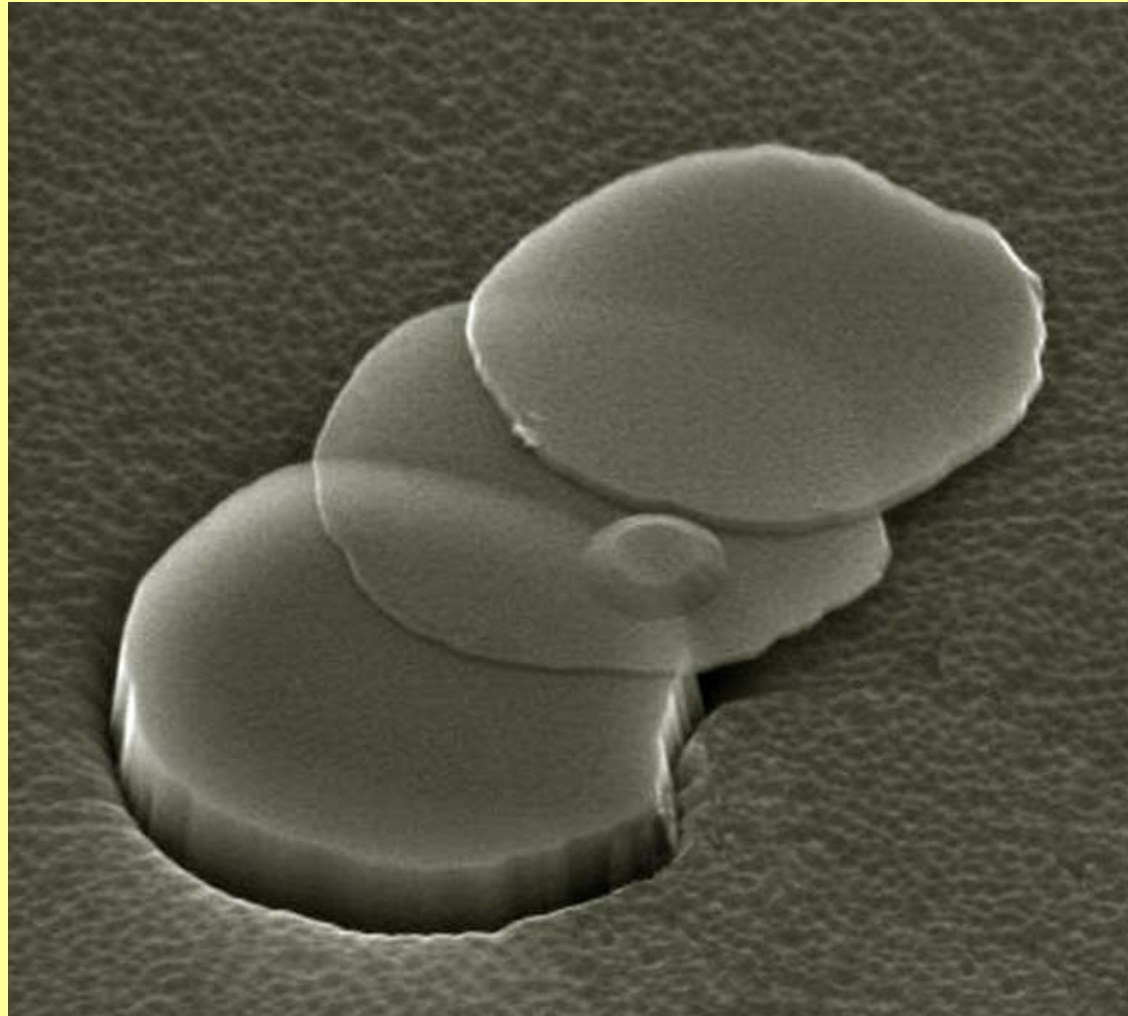

(a)

(b)

0.1 nm
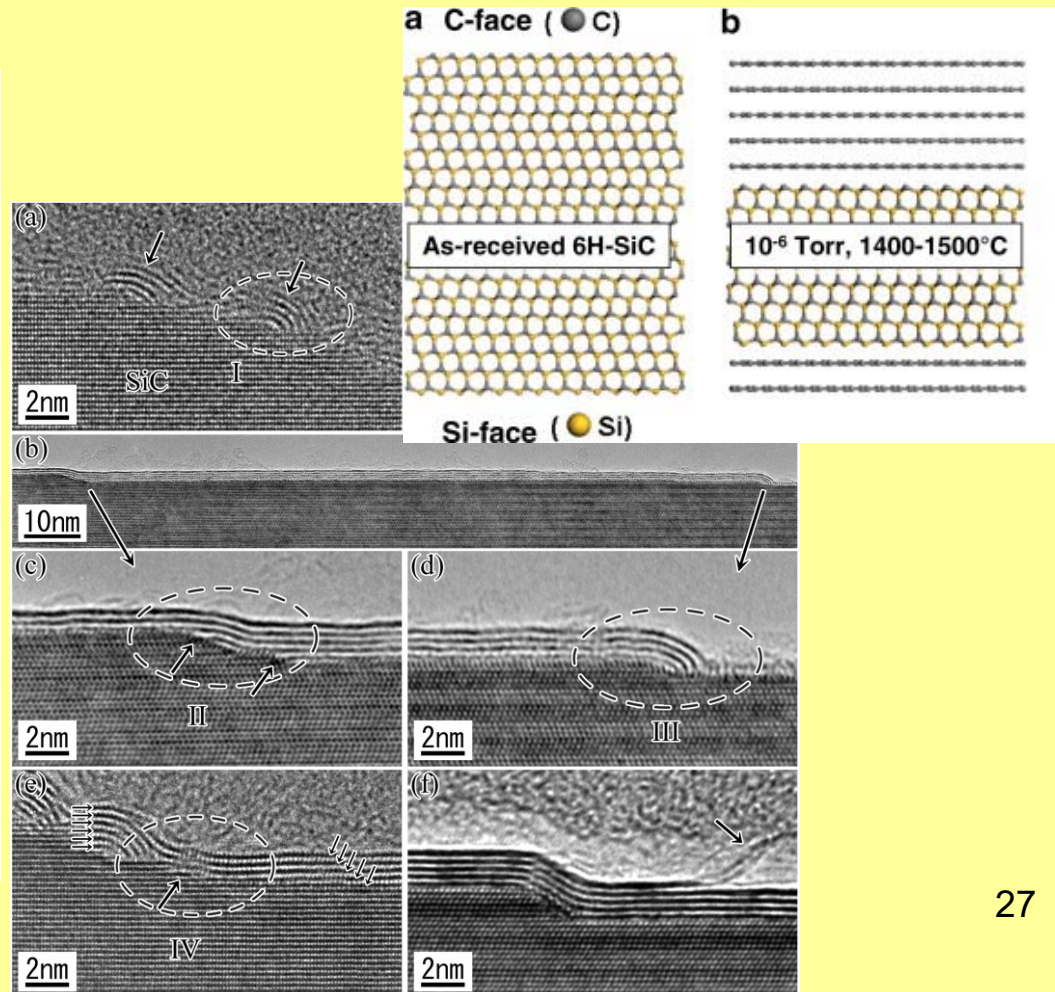
0.1 nm

Scotch Tape – Layer Peeling
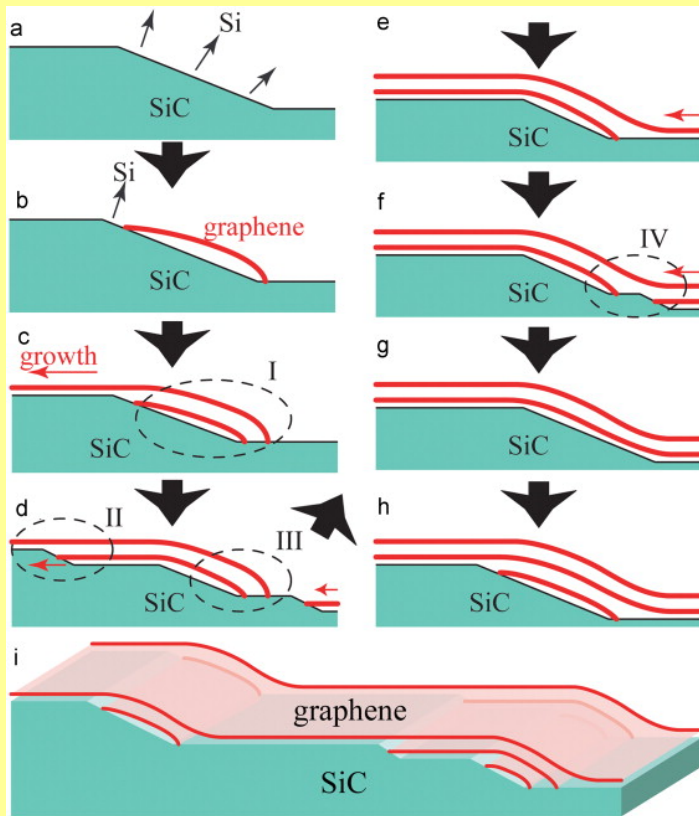
Mechanical exfoliation

Scotch Tape – Layer Peeling
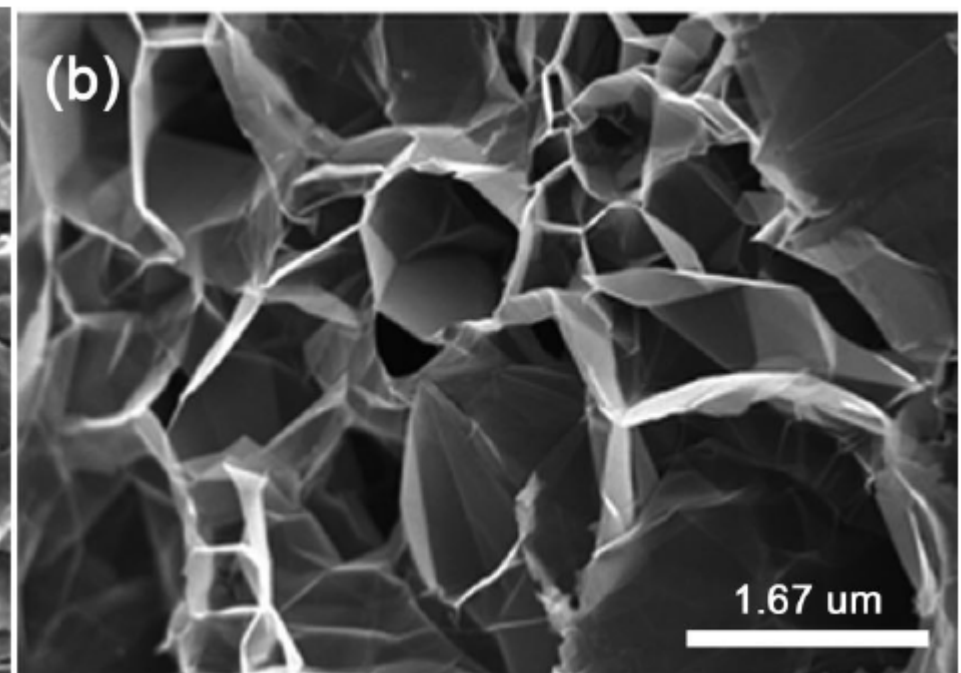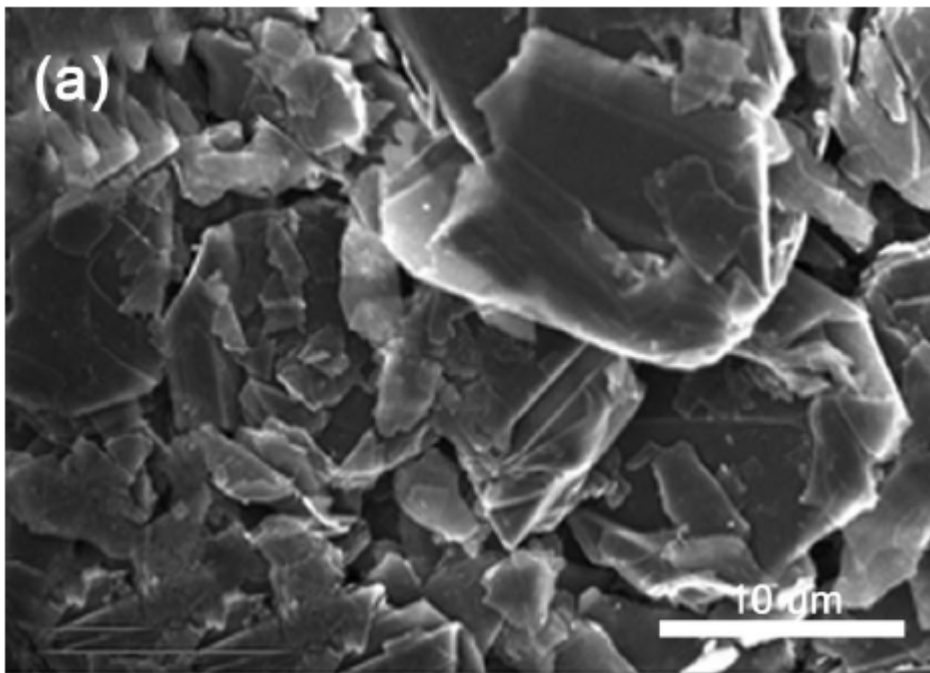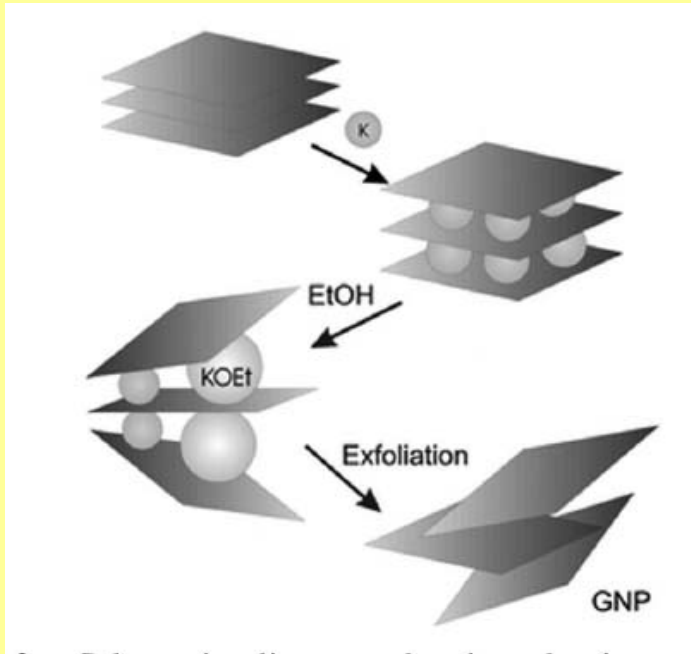
SiC Pyrolysis

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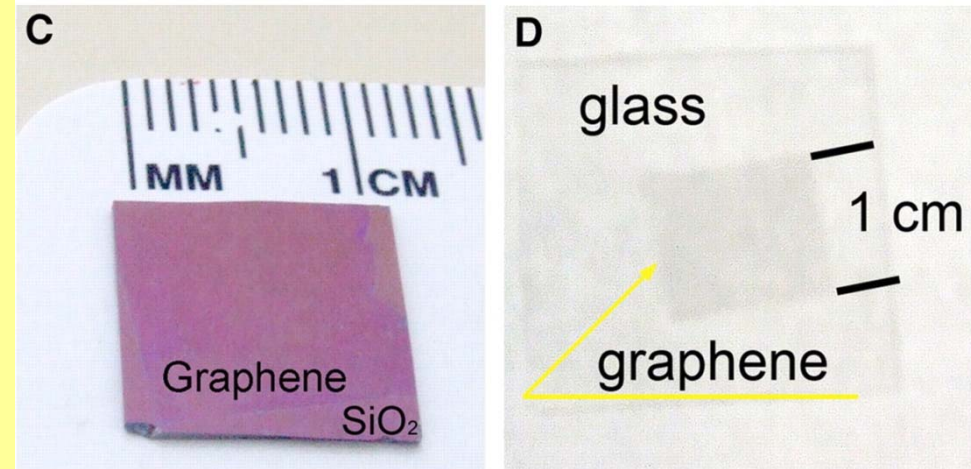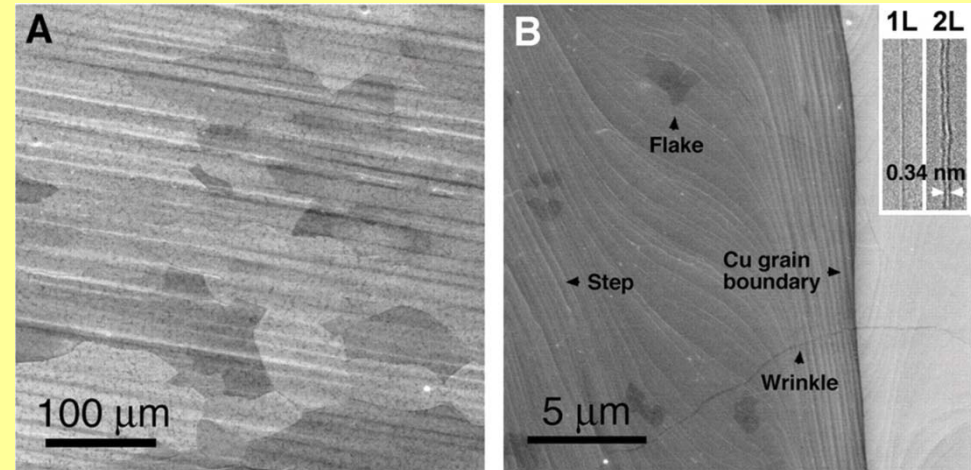- **The formation of graphene layers by the remaining carbon atoms**

Exfoliation

Chemical exfoliation (surfactant)

Sonochemical exfoliation

CVD from CH$_4$ / H$_2$ on Metal Surfaces
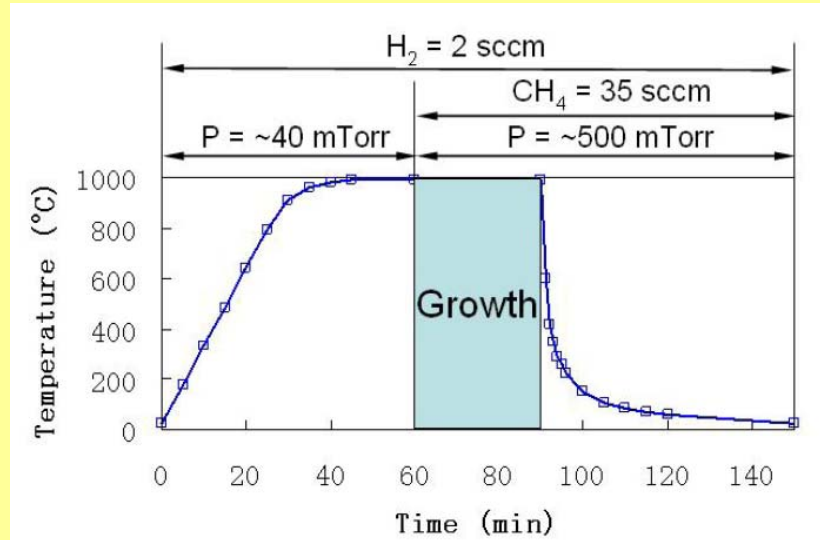
(A) SEM - graphene on a copper foil

(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.
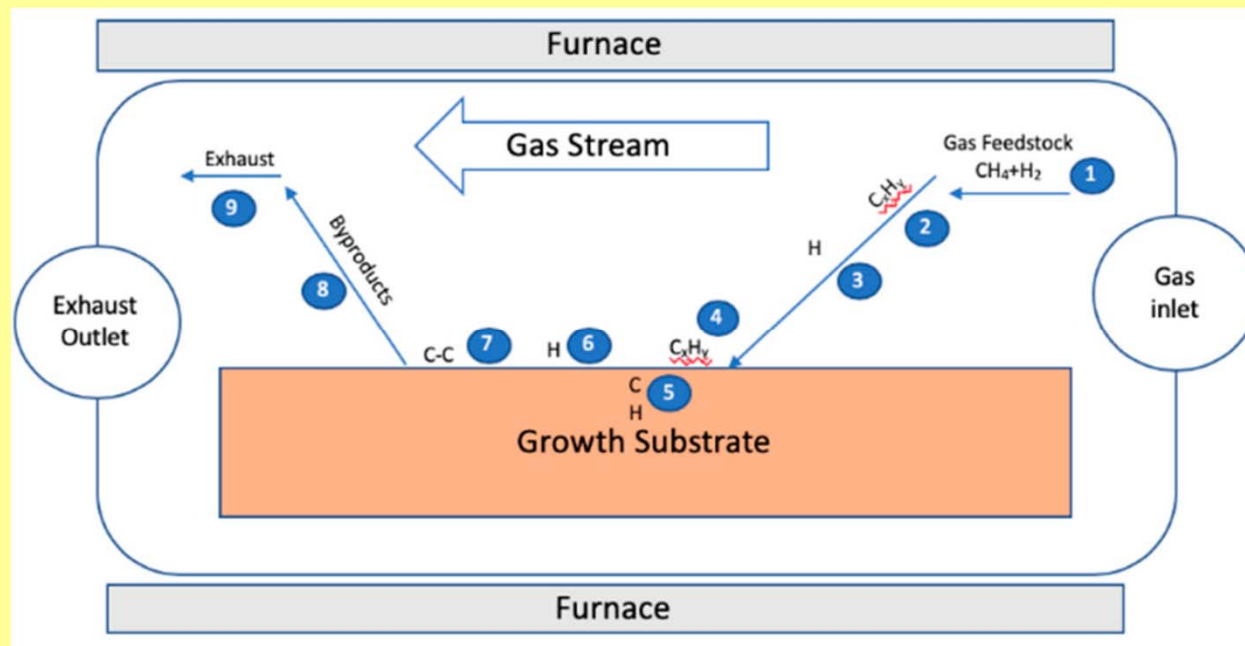
Graphene transferred onto
(C) a SiO$_2$/Si substrate
(D) a glass plate

29

CVD from Hydrocarbons on Metal Surfaces

The first graphene synthesis by CVD
2006 Somani - camphor and nickel substrate

Carbon cannot diffuse into Cu = monolayer graphene

Carbon diffuses into Ni = formation of multi-layered graphene
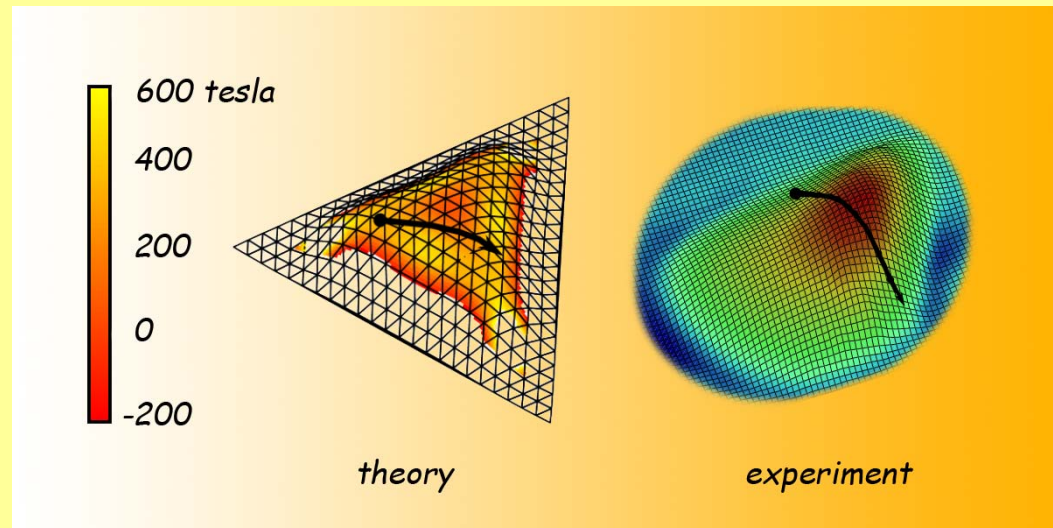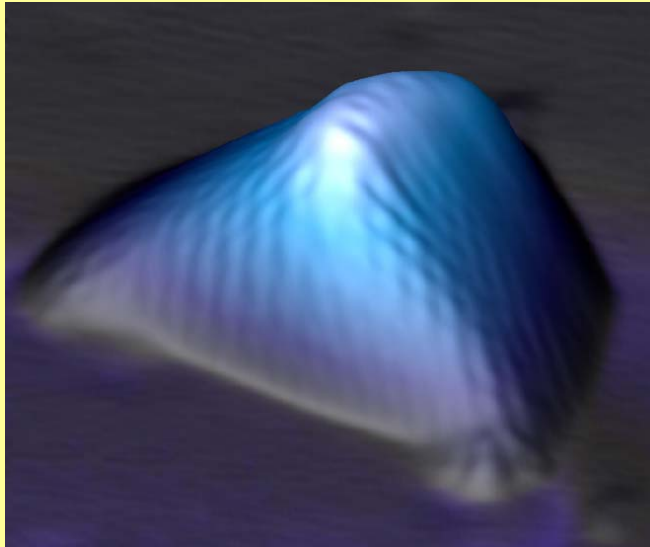

30

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)

theory   experiment

32

Magic-Angle Twisted Bilayer Graphene

Twisted Bilayer Graphene

Graphene Oxide

- **More reactive than graphene**
- **Presence of oxygen groups: -OH, -COOH, =O, -O-**
- **Hydrophilic character**
- **Electric insulator, sheet resistance R_s ~10^{12} Ω/sq**
- **Specific SA (theoretical): ~890 m^2g^{-1} (1700-1800 m^2g^{-1})**
- **Photoluminescence properties**
- **Bandgap from 1.7 to 2.1 eV**
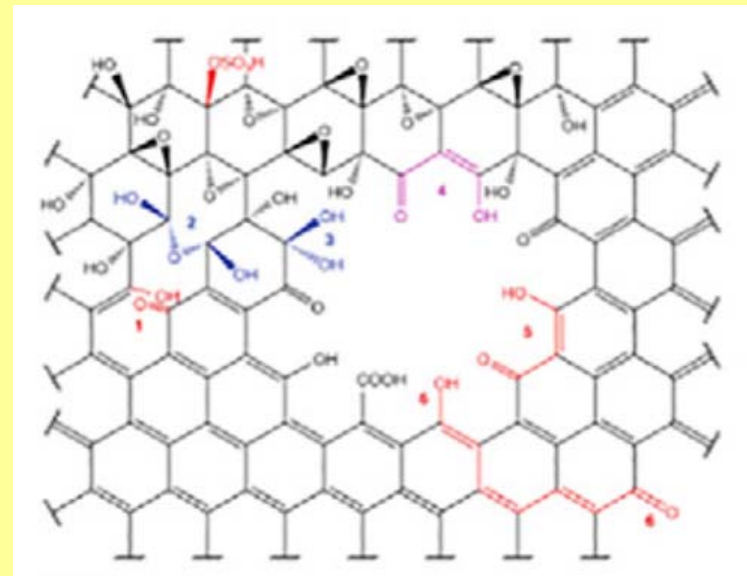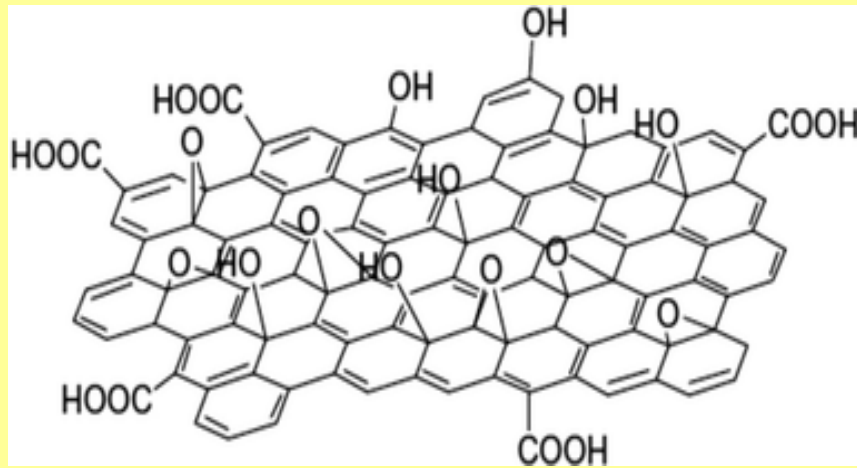
Graphene Oxide

LERF-KLINOWSKI
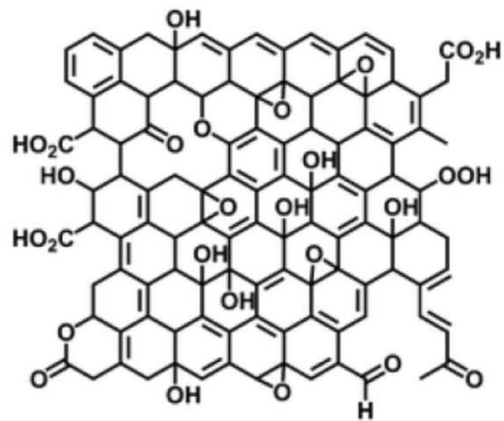
DÉKÁNY

NAKAJIMA-MATSUO

HOFMANN

RUESS

SCHOLZ-BOEHM

Graphene Oxide
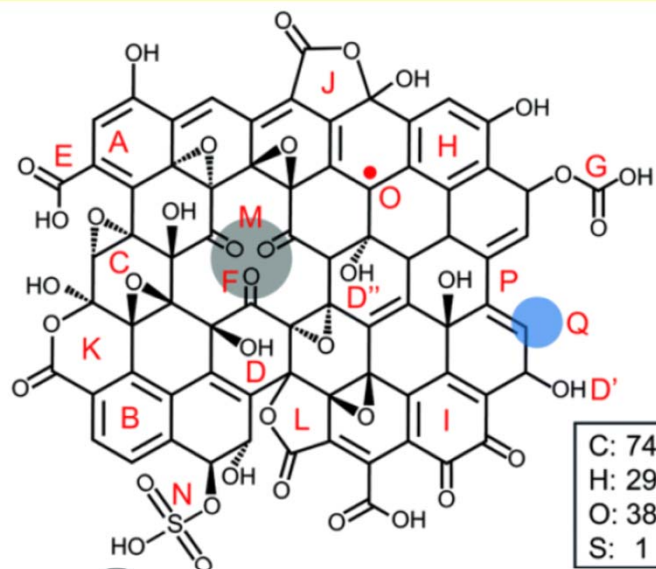
Graphene Oxide

1859 Brodie method

Graphite + KClO₃

Oxidation for 3-4 days at 60°C → +HNO₃ (fuming)

Graphite oxide

4 cycles of oxidation process → +H₂O

Graphite oxide (free of salt and acid)

Vacuum dried at 100°C → Exfoliation

GO

1898 Staudenmaier method

Graphite

Ice bath at 0°C → +H₂SO₄ +HNO₃ (fuming)

Suspension

Oxidation for 3-4 days at room temperature → +KClO₃ (slowly at 0°C)
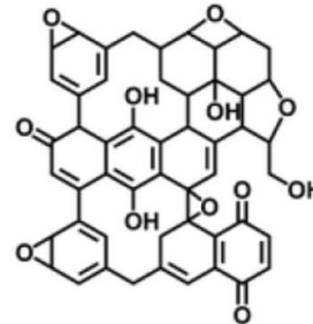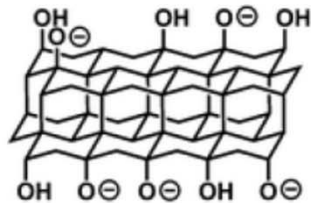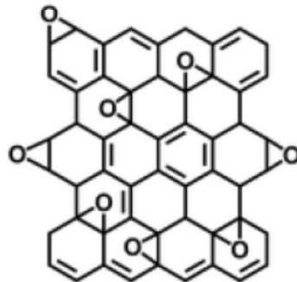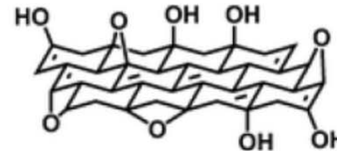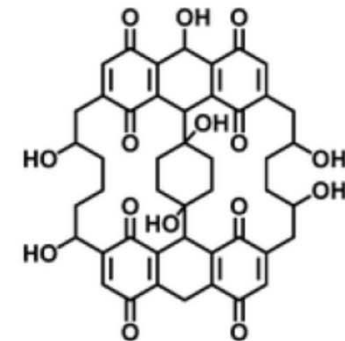
Graphite oxide

→ +H₂O +HCl (remove SO₄²⁻)

Graphite oxide (free of salt and acid)

Vacuum dried → Exfoliation

GO

1937 Hoffman method

Graphite

Ice bath at 0°C → +H₂SO₄ +HNO₃ (non-fuming)

Suspension

Oxidation for 3-4 days at room temperature → +KClO₃ (slowly at 0°C)

Graphite oxide

→ +H₂O +HCl (remove SO₄²⁻)

Graphite oxide (free of salt and acid)

Vacuum dried → Exfoliation

GO

1958 Hummers method

Graphite + NaNO₃

Ice bath at 0°C → +H₂SO₄

Suspension

→ +KMnO₄ (below 20°C)

Graphite oxide

Increase temperature to 98°C → +H₂O

Graphite oxide (free of salt and acid)

→ +H₂O₂ (remove MnO₄⁻ and MnO₂)

Clean Graphite oxide

Vacuum dried at 40°C → Exfoliation

GO
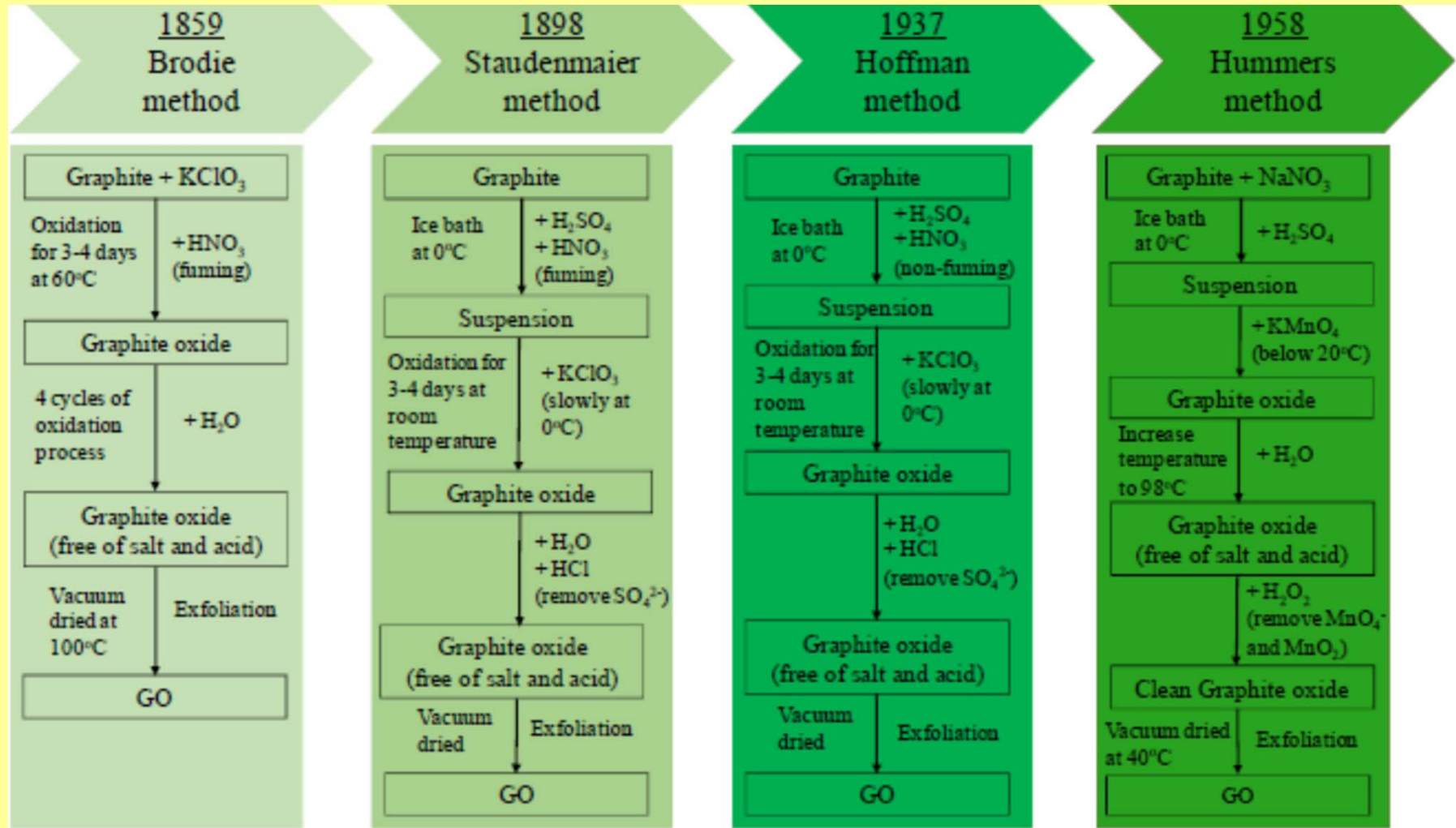
Hummers Method
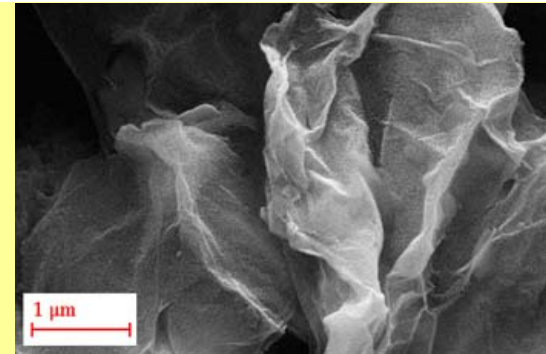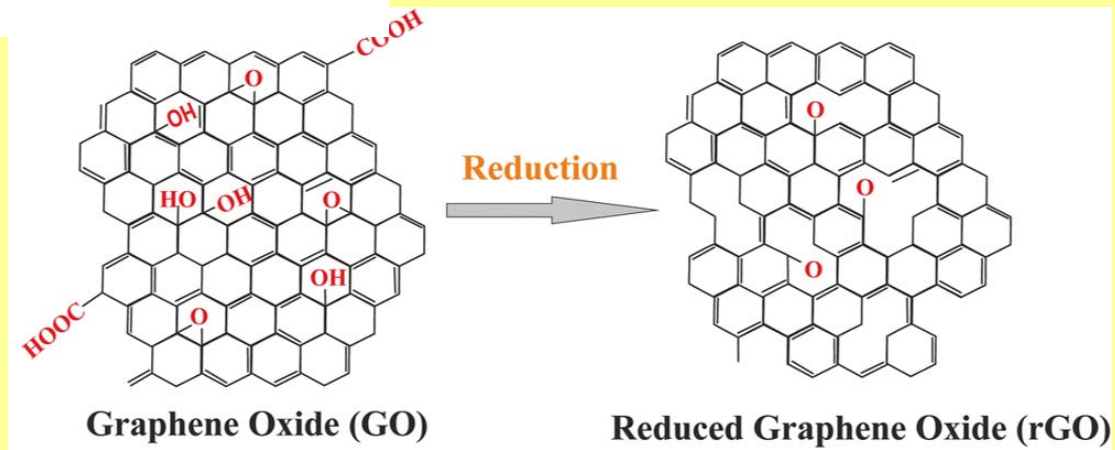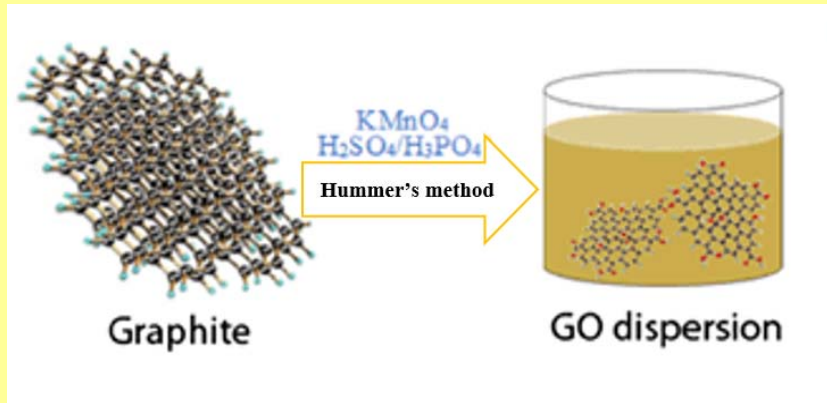
Graphene Oxide Characterization

Well oxidized GO: C/O = 2.1 - 2.9

UV-vis:

~227-231 nm (arom. C=C, $\pi \rightarrow \pi*$)

~300 nm (C=O, $n \rightarrow \pi*$)

C 1s XPS spectrum (eV)

C–C/C=C	284.6
C–O	286.6
C=O	287.8
O–C=O	289.0

40
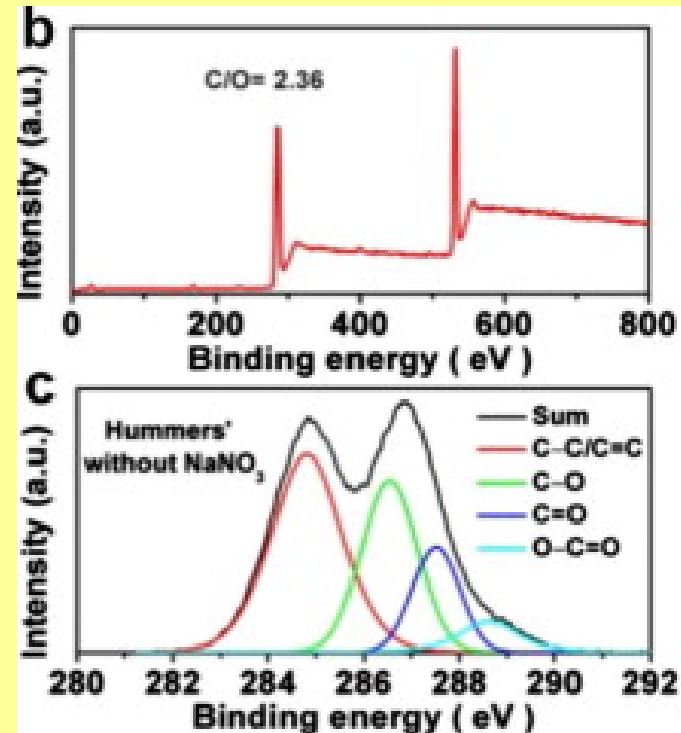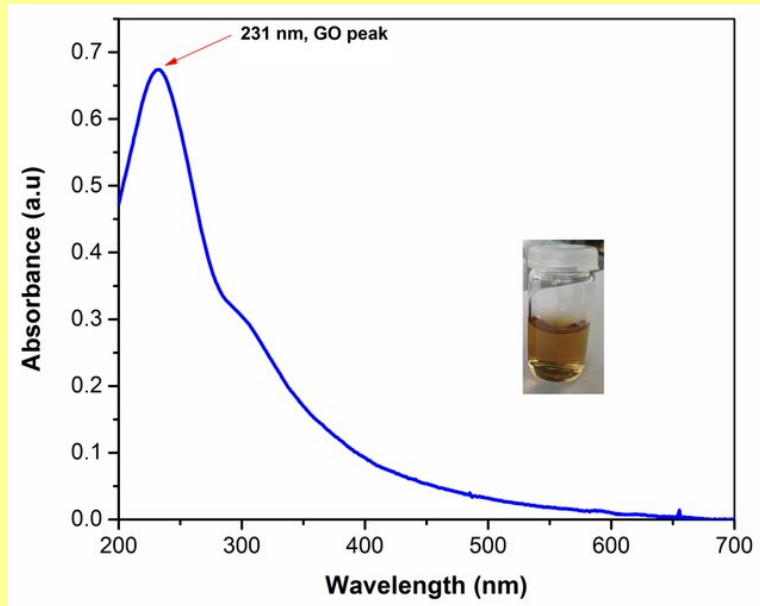
Graphene Oxide Characterization

Zeta potential: -44 mV
aqueous dispersions
0.05 mg/ml
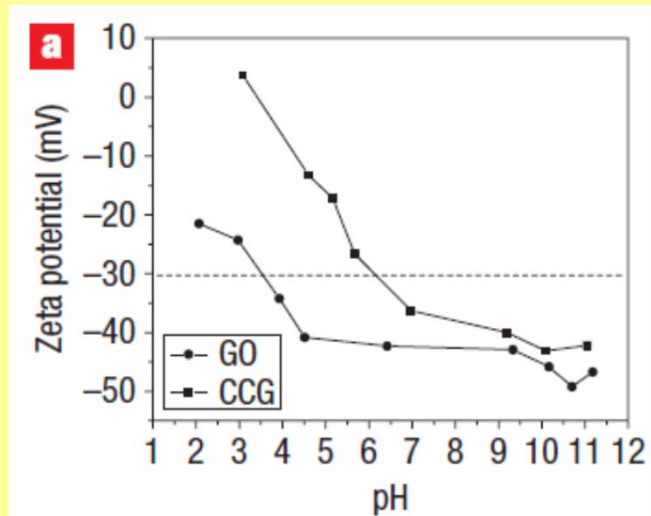
Raman, cm^{-1}
G-band 1590
D-band 1350
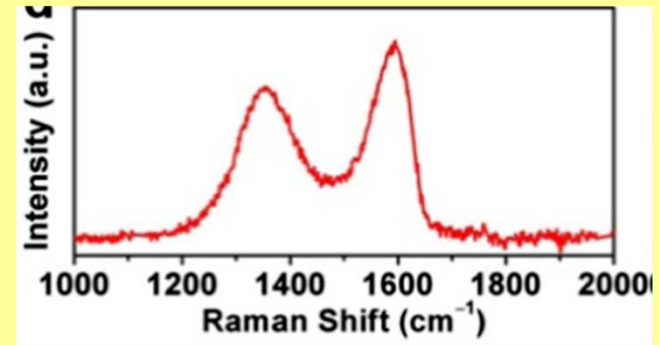
FTIR ATR spectra, cm^{-1}
C-O-C 1000, C-O 1230, C=C 1590-1620,
C=O 1740–1720, O-H stretching 3600–
3300
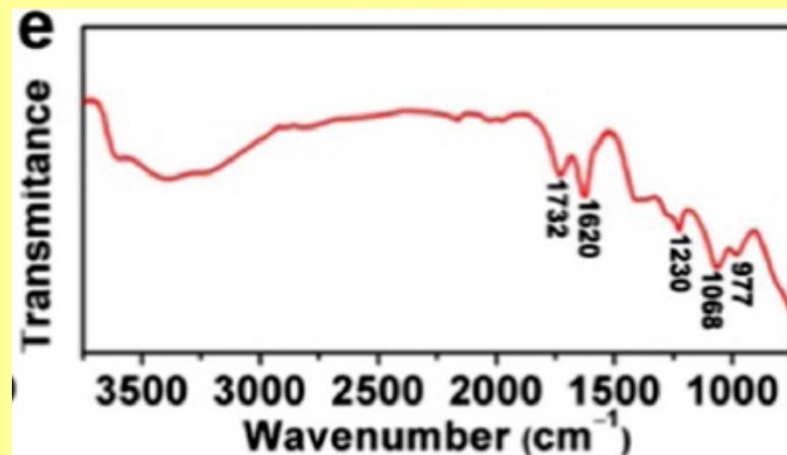
Graphene Oxide Characterization

Solid-state ^{13}C NMR, ppm

Ketone carbonyls	190
Ester and lactol carbonyls	164
Graphitic sp^2 carbons	131
Lactols O-C(sp^3)-O	101
Alcohols	70
Epoxides	61

The measure of oxidation

The ratio between the alcohol/epoxide signal and graphitic sp^2 carbon signal
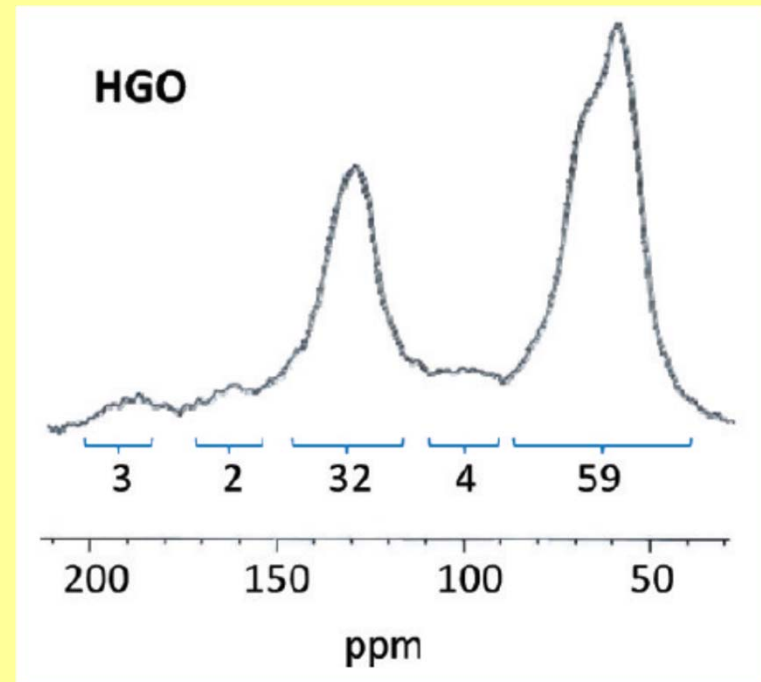
Graphane – Hydrogenated Graphene

- 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

a) Chair-type   b) Boat-type

●: Carbon, ○: Hydrogen

●: Carbon, ○: Hydrogen
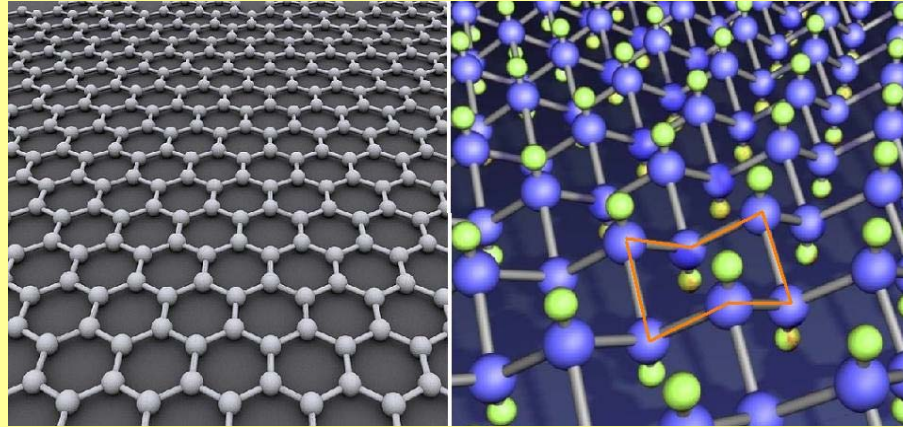
Fluorographene

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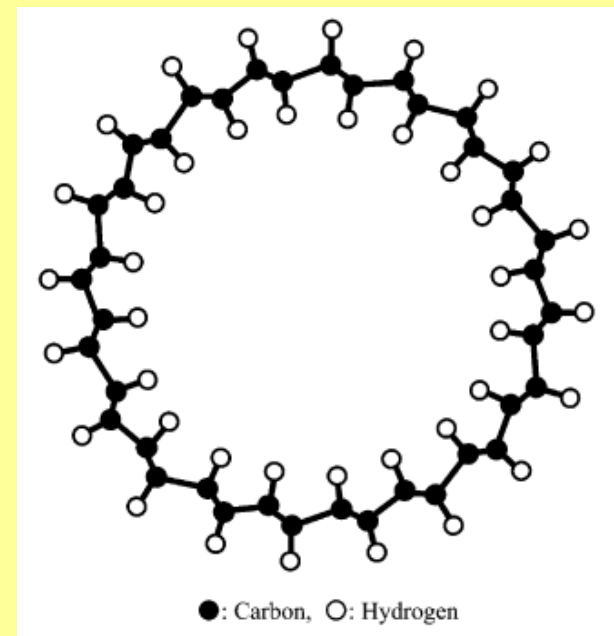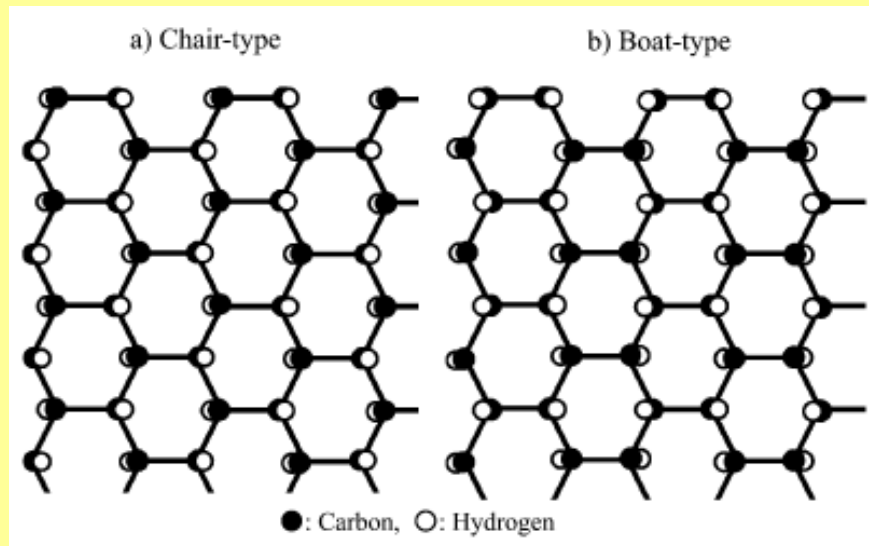- **Sythesis:**
  - **Graphene + XeF_2/CF_4 (room temperature)**
  - **Mechanical or chemical exfoliation of graphite fluoride**
  - **By heating graphene in XeF_2 gas at 250 °C**
- **Graphene + XeF_2 at 70 °C – high-quality insulator, stable up to 400 °C (resemblence with teflon)**

Graphyn, Graphydiyn

a) Graphene   b) Graphyne   c) Graphdiyne
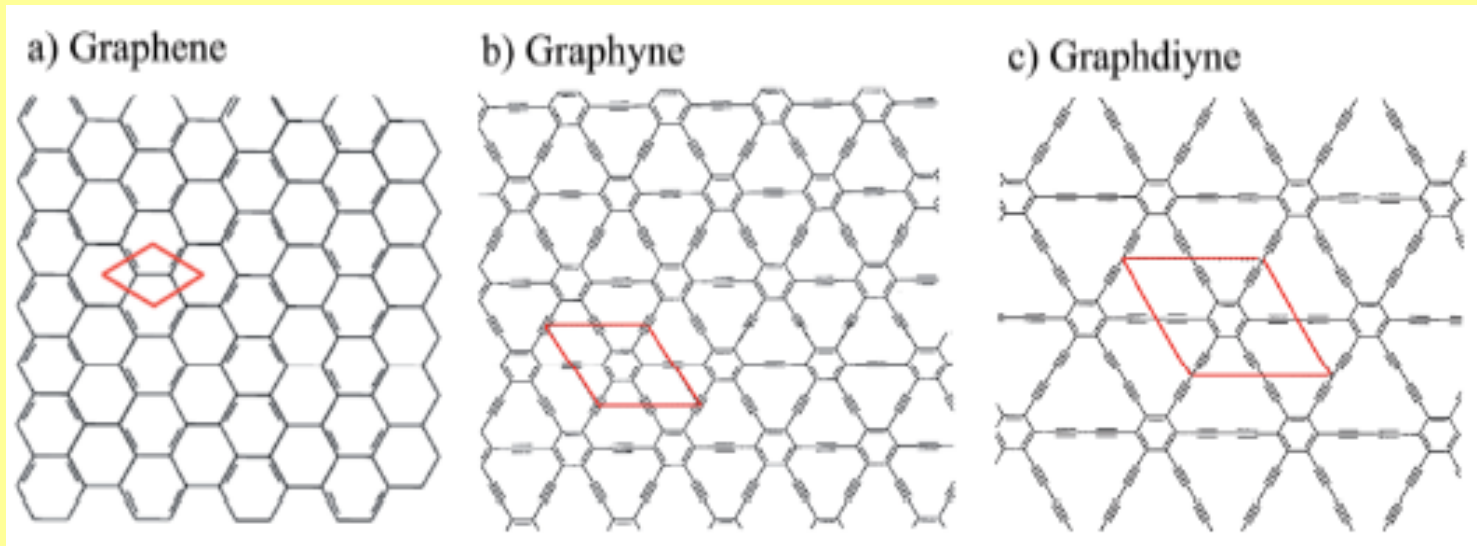
- **Predicted**
- **"Non-derivatives" of graphene**
- **Semiconductors**
- **Movement of electrons as in graphene but only in one direction**

Graphydiyn

Synthesis

Graphitic Carbon Nitride
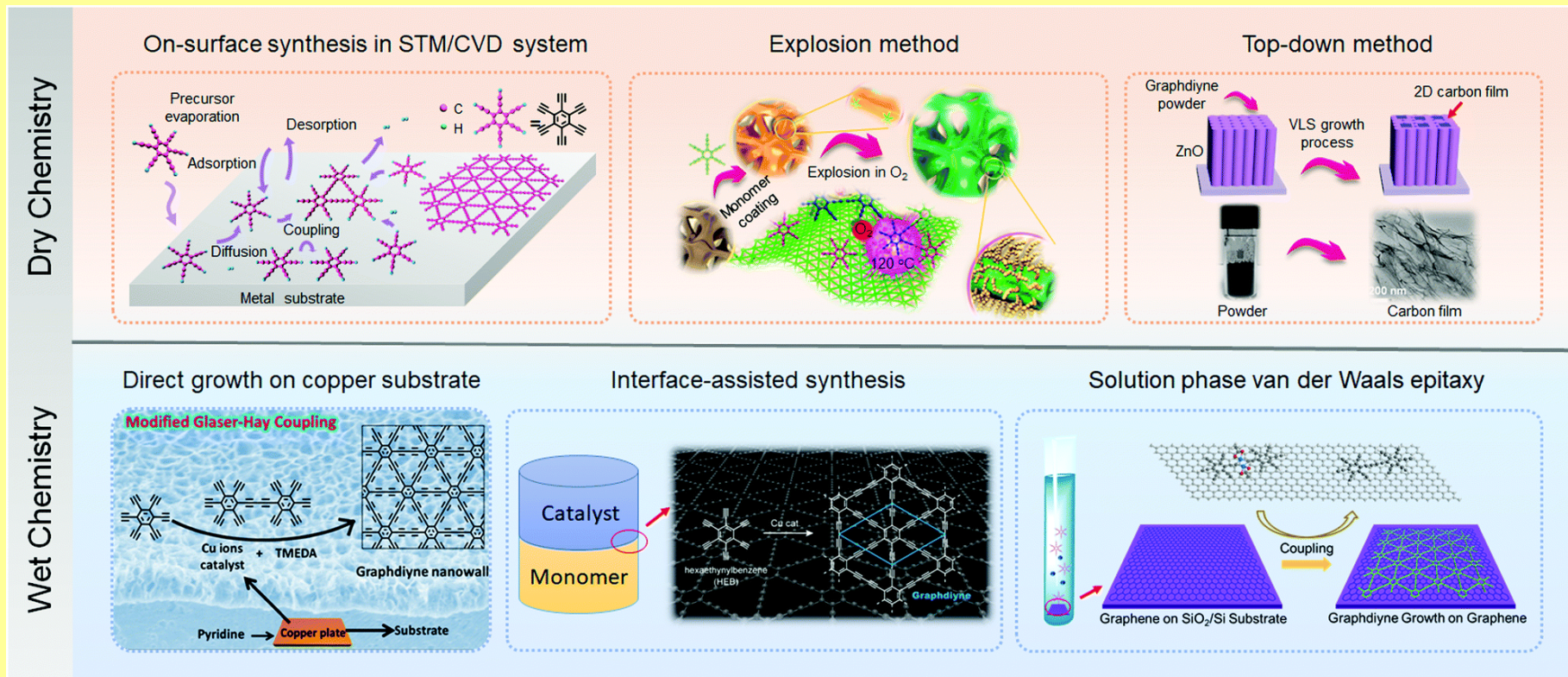

1834 Berzelius, Liebig
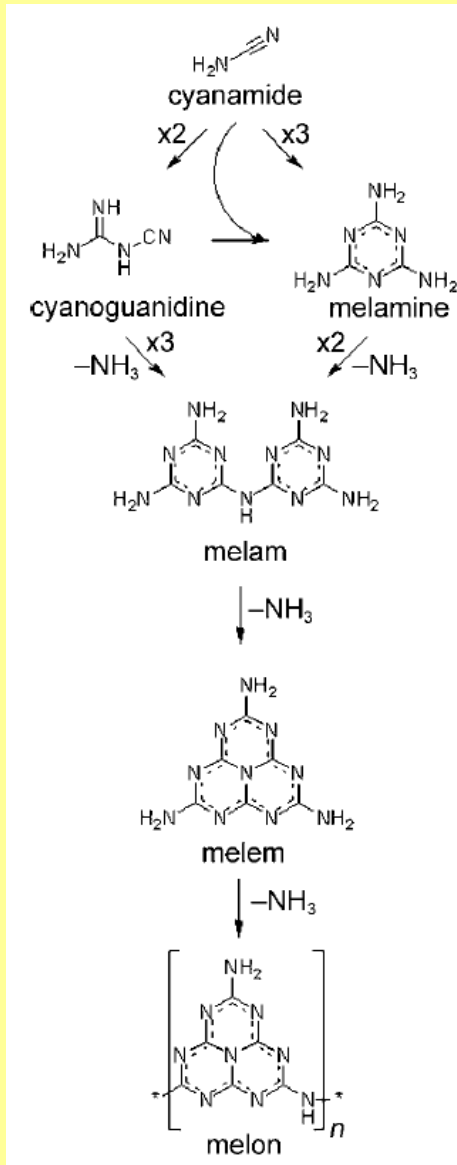
Temperature-induced condensation

dicyandiamide $NH_2C(=NH)NHCN$

In a LiCl/KCl melt
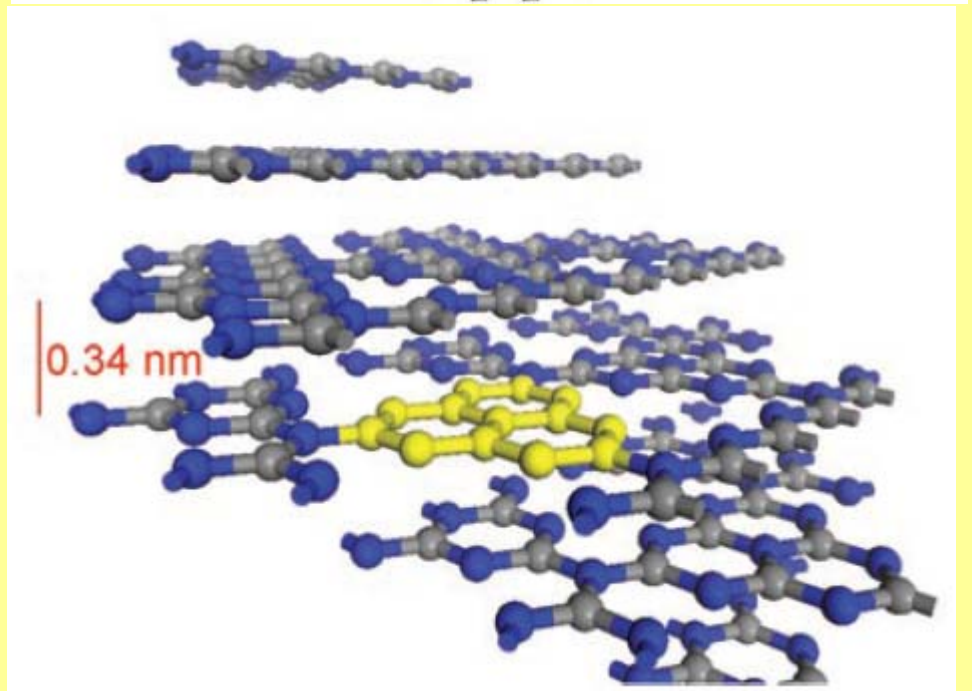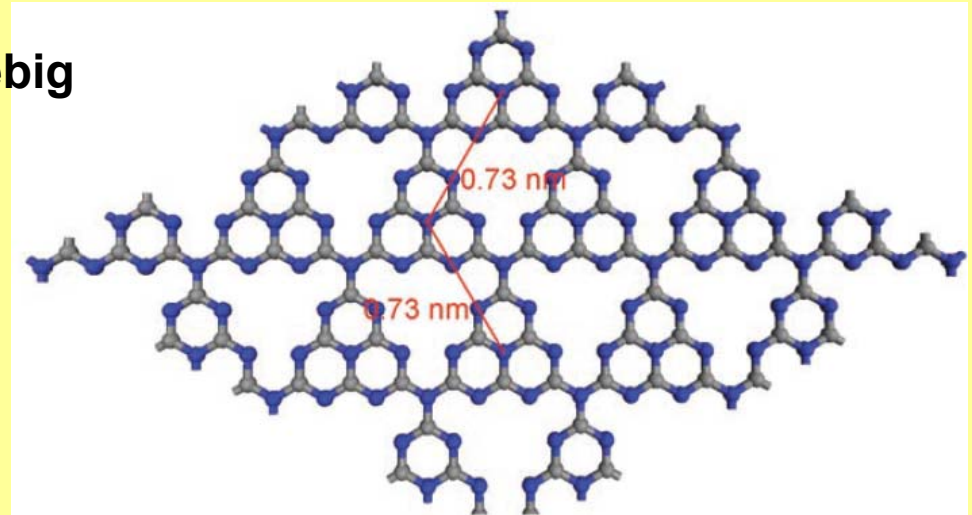
Graphitic Carbon Nitride
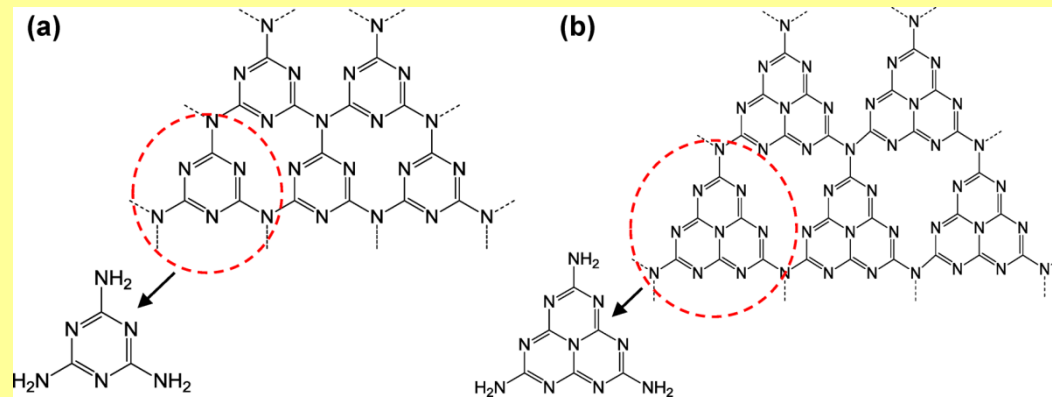
(a) triazine and (b) tri-s-triazine (heptazine)
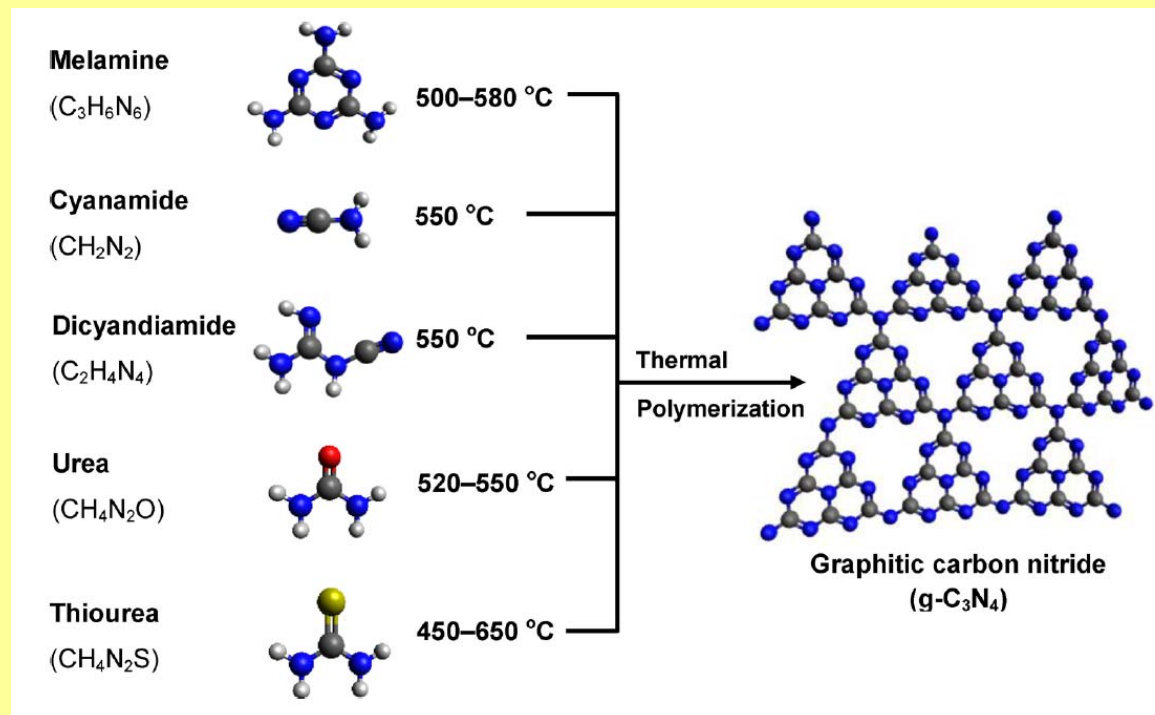
Graphitic Carbon Nitride
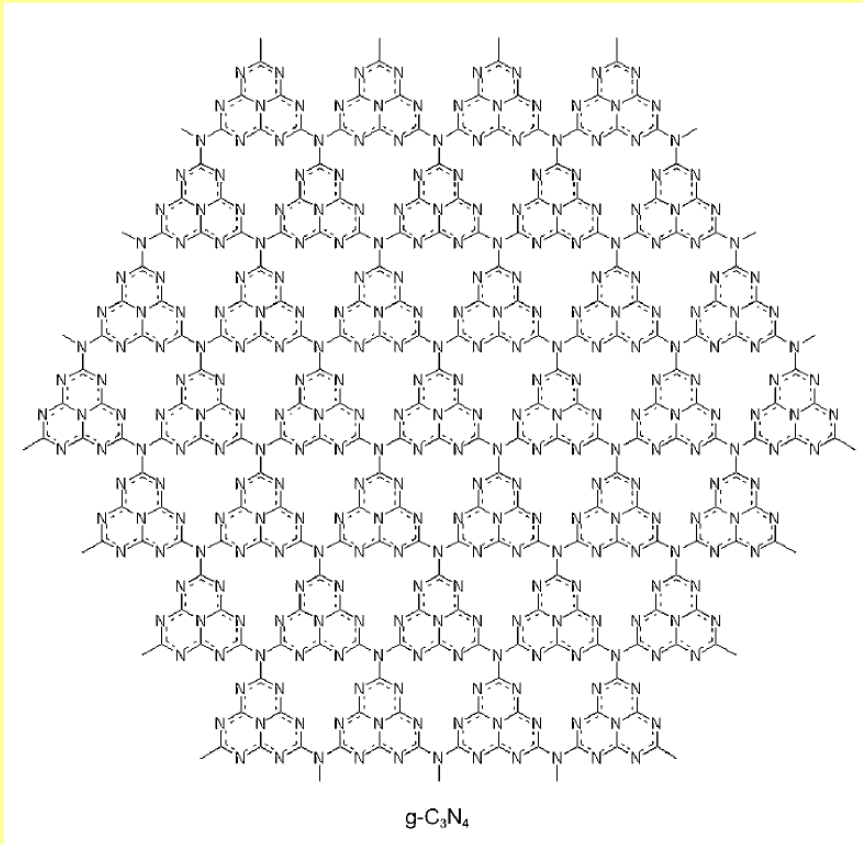
("g-C_3N_4")

g-C_3N_4
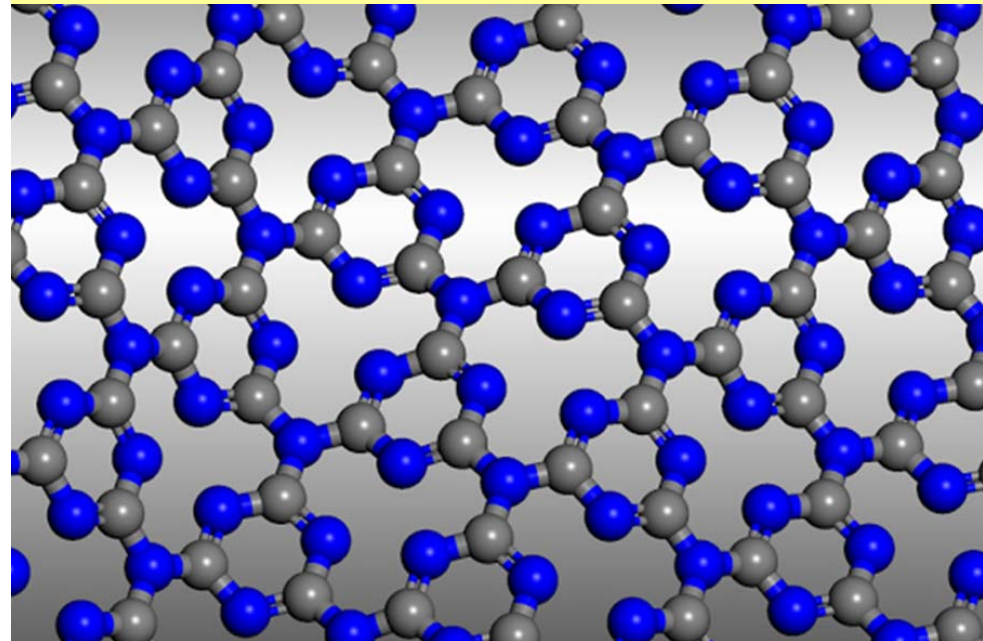
Band gap 1.6 - 2.0 eV
Small band gap semiconductors
Si (1.11 eV), GaAs (1.43 eV), and GaP (2.26 eV)

Porphene

Surface-constrained oxidative coupling of metalloporphyrins (zinc porphyrin) at the air/water interface
A bilayer is formed
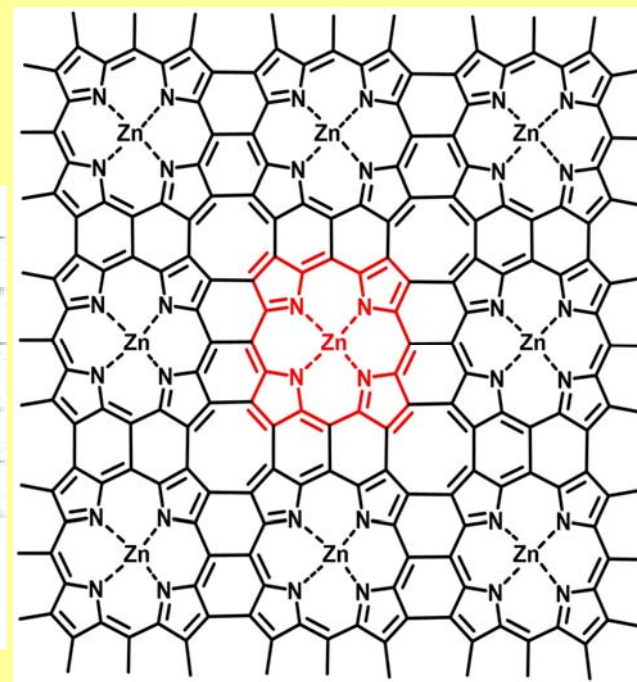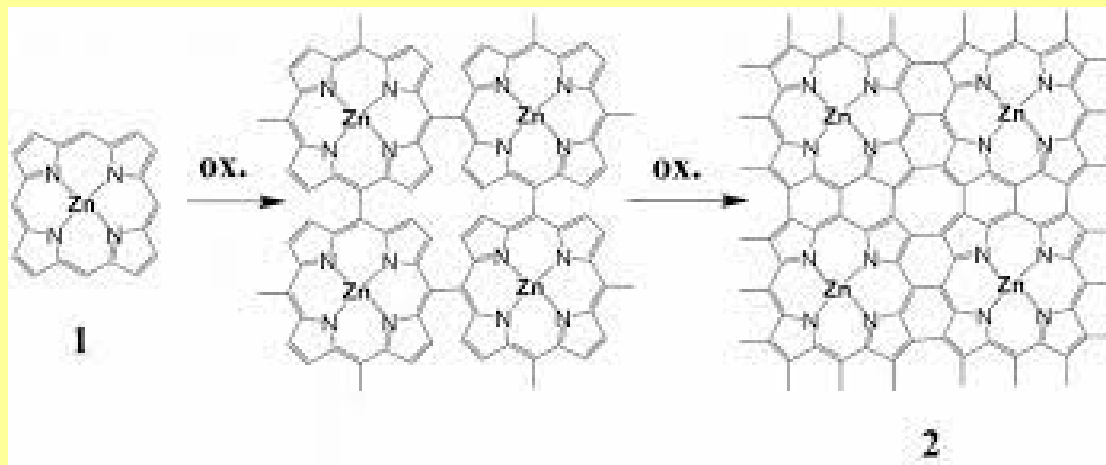
Fully conjugated
Antiaromatic
Semiconductor
Rectangular unit cell P2mm
Family of 2-dimensional polymers
Changing metal, up to two substituents

Phosphorene
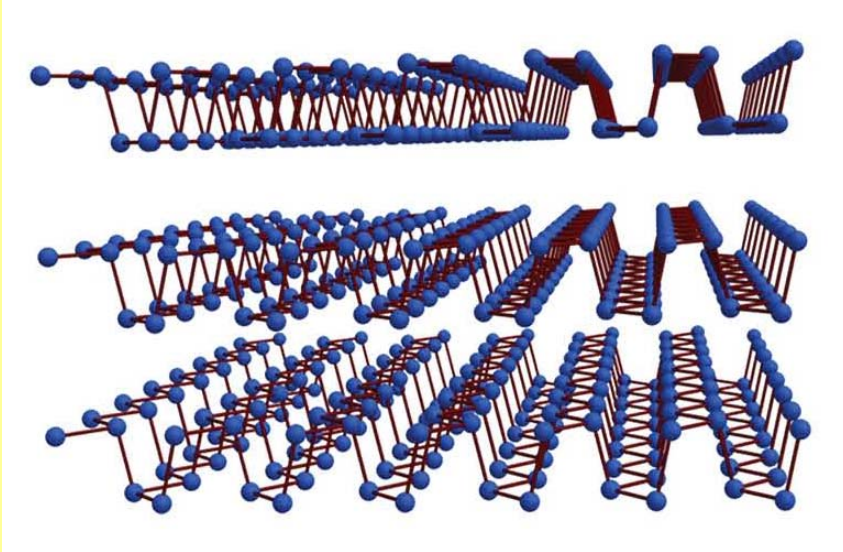
Black phosphorus

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

Exfoliation
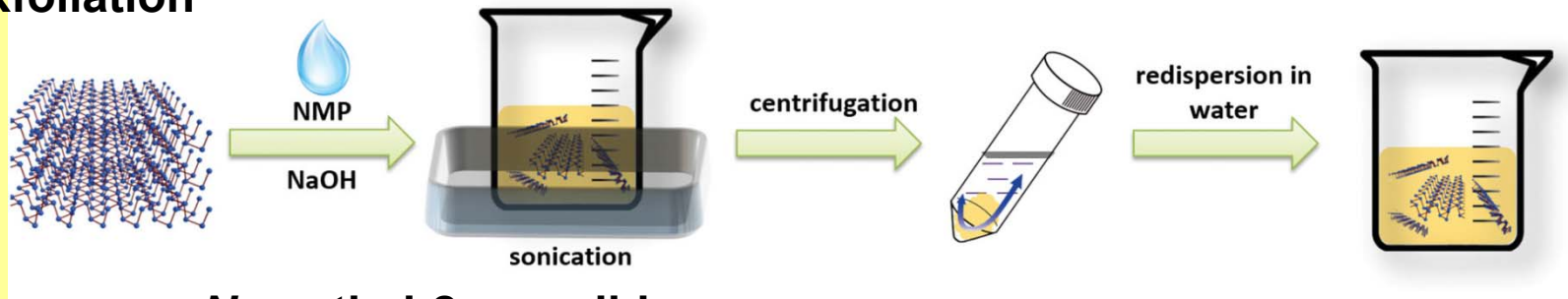
N -methyl-2-pyrrolidone

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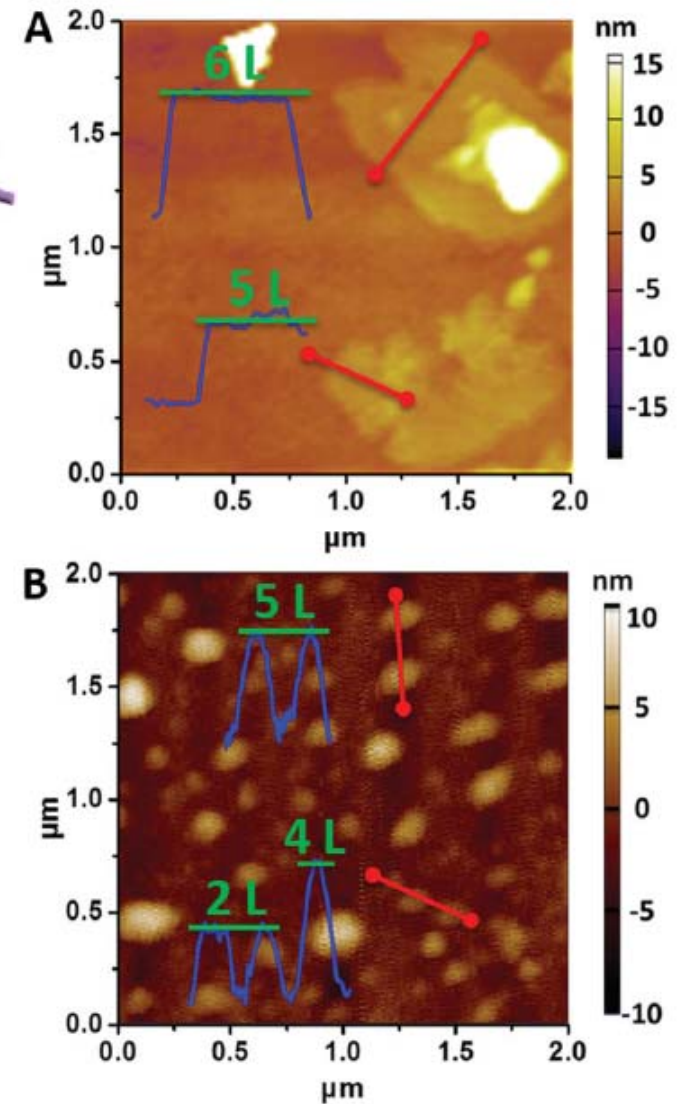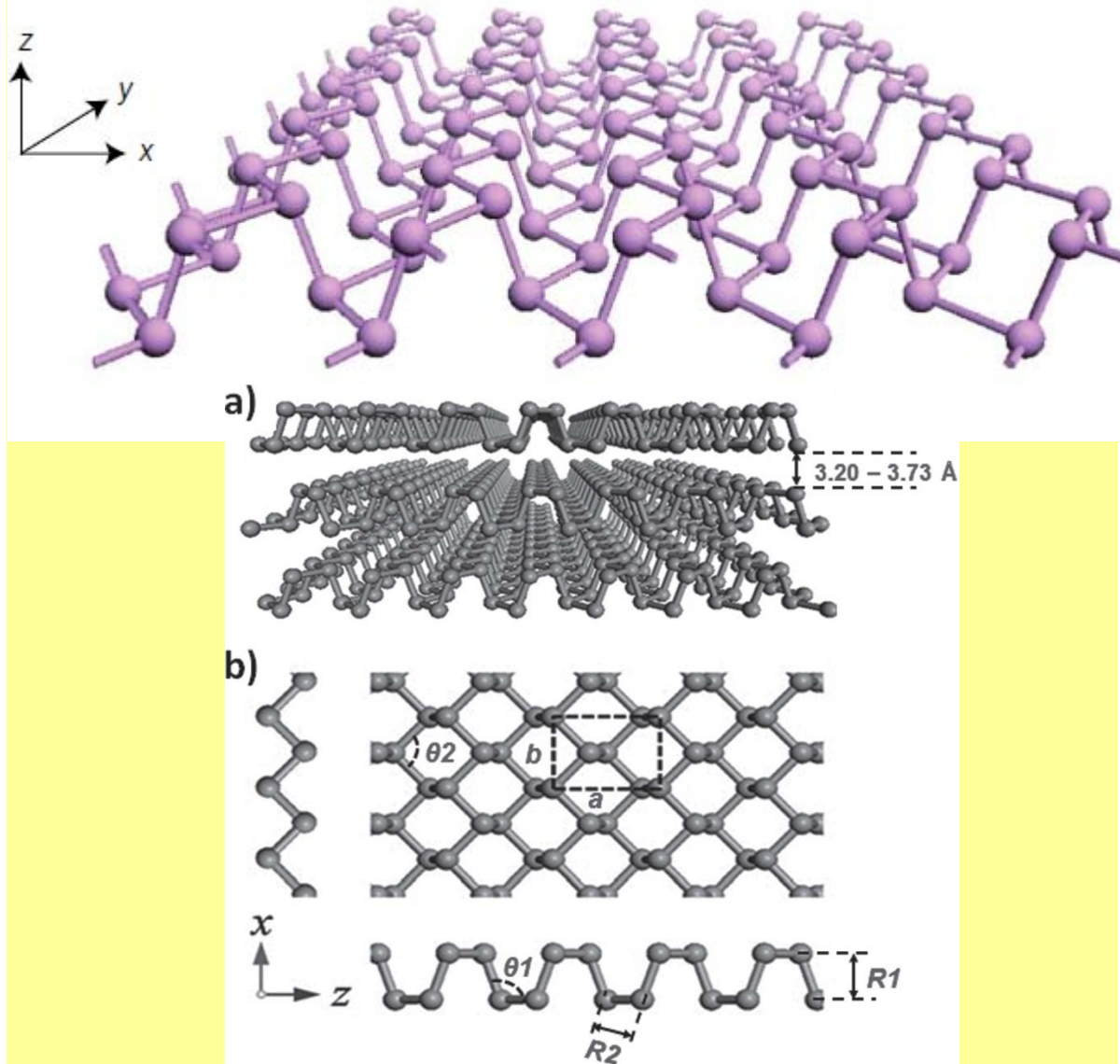
Phosphorene
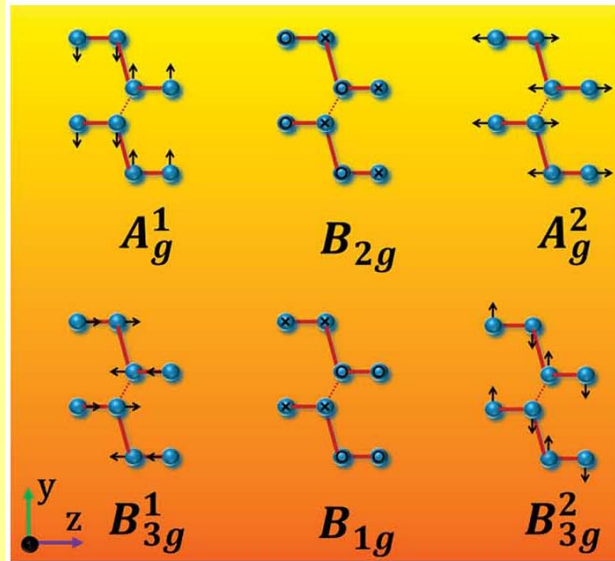
Black phosphorus
12 lattice vibrational modes
6 Raman active modes
3 vibrational modes A^1_g, B_{2g}, and A^2_g can be detected when the incident laser is perpendicular to the layered phosphorene plane: 361 cm^{-1}, 438 cm^{-1}, 465 cm^{-1}

As the number of phosphorene layers increases, the three Raman peaks red-shift
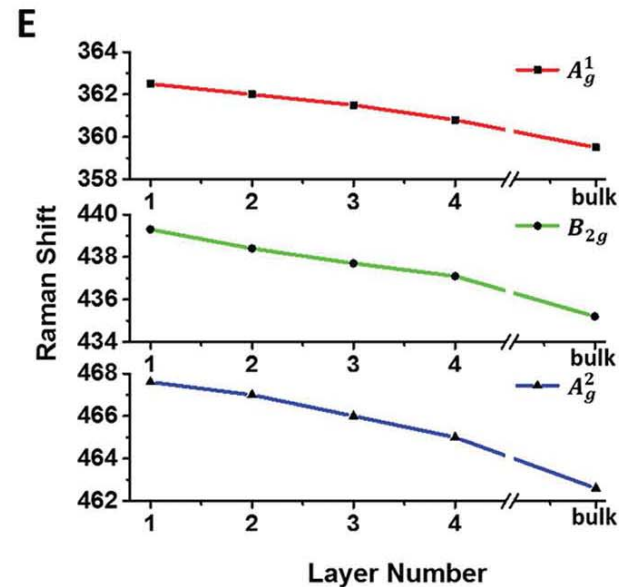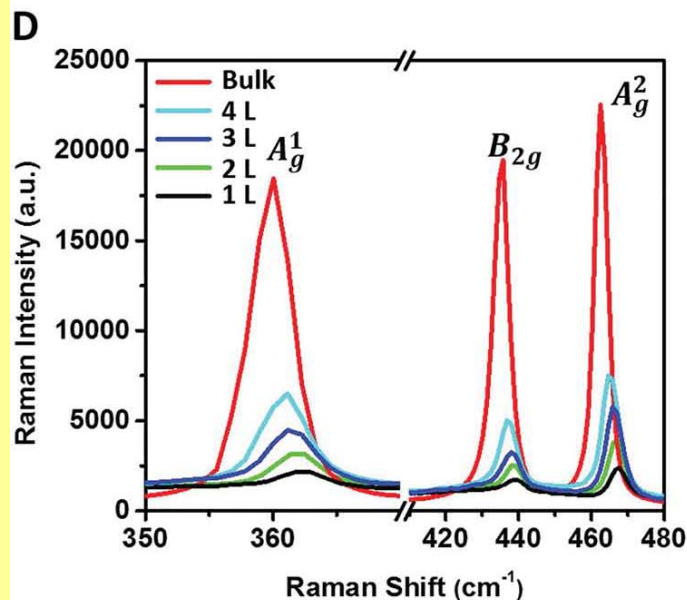
Zirconium Phosphates
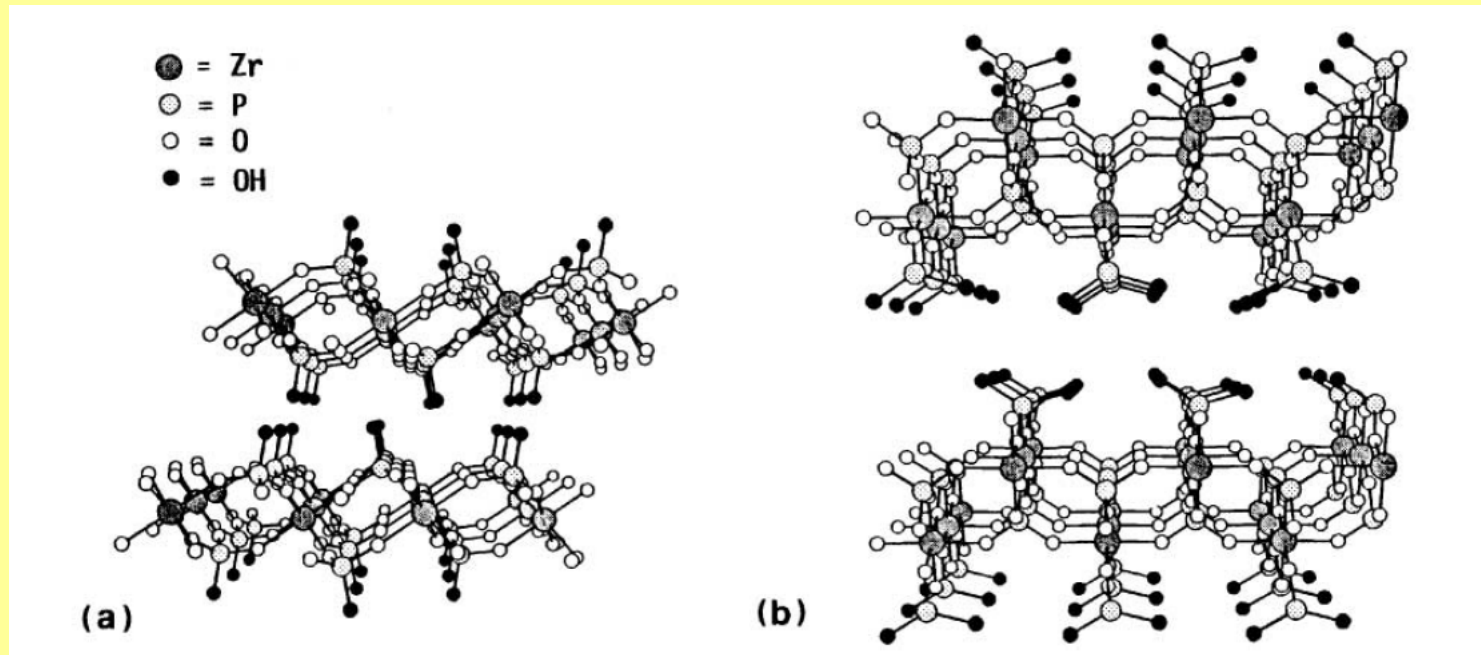
(a) α-zirconium phosphate = $Zr(HPO_4)_2 \cdot H_2O$
interlayer spacing 7.6 Å

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

Zirconium Phosphates
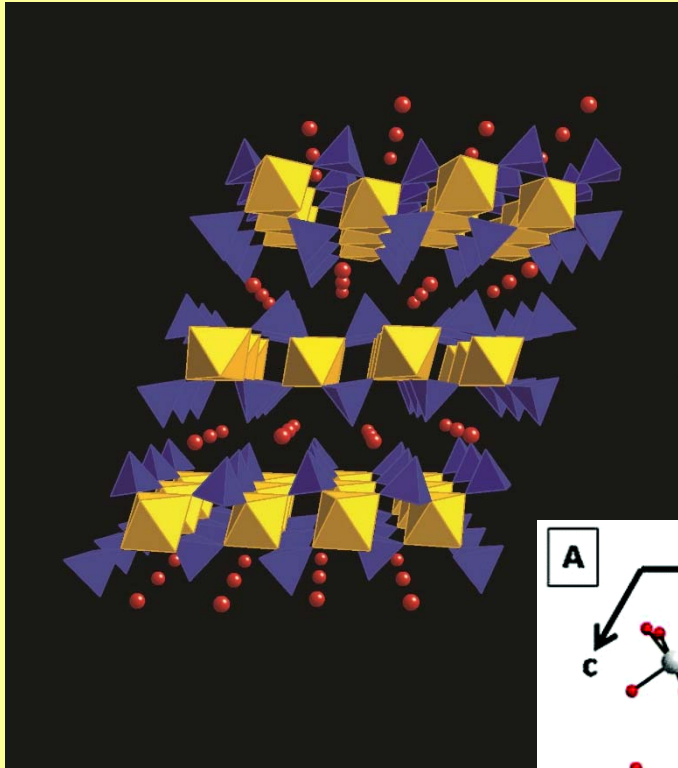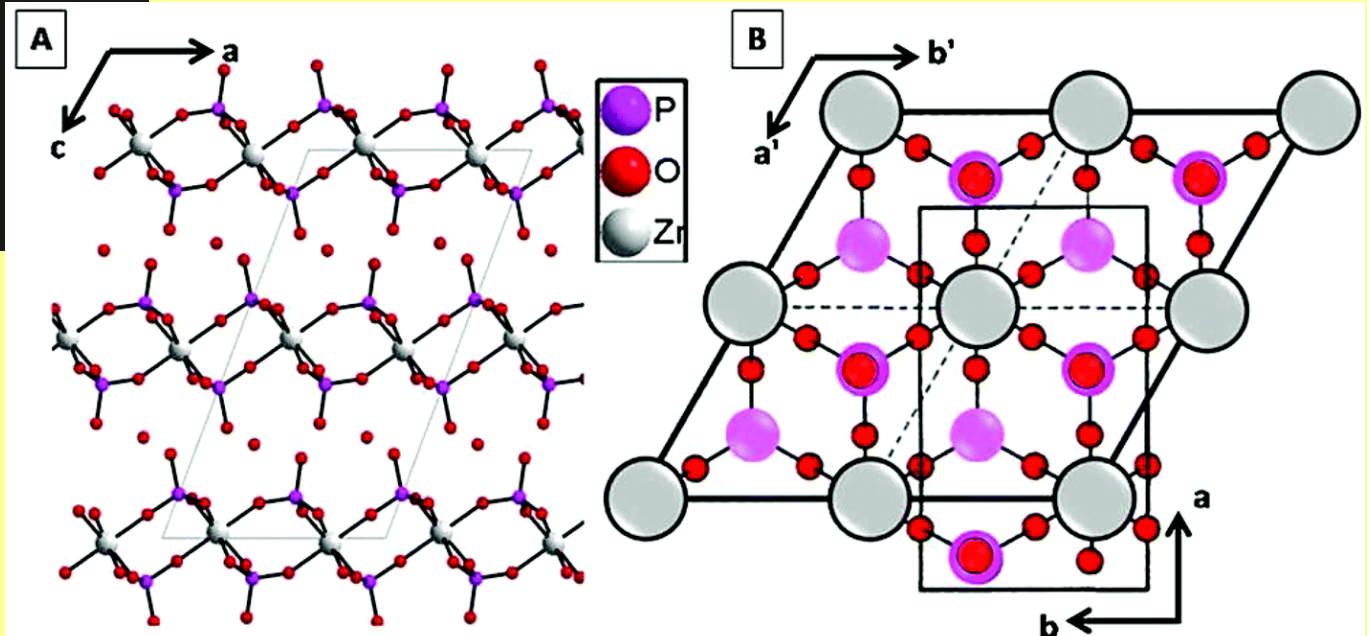
α-zirconium phosphate

$Zr(HPO_4)_2 \cdot H_2O$

interlayer spacing 7.6 Å

Zirconium Phosphates
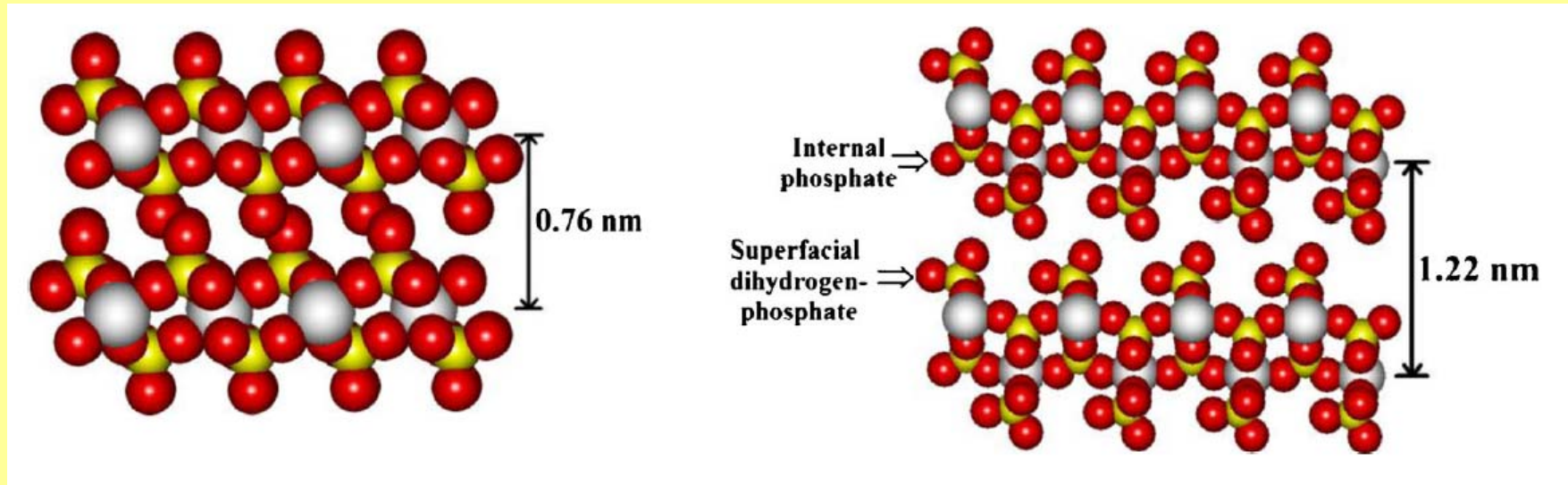
Internal phosphate →

Superfacial dihydrogen-phosphate →

0.76 nm

1.22 nm

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

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

Brucite - Mg(OH)$_2$
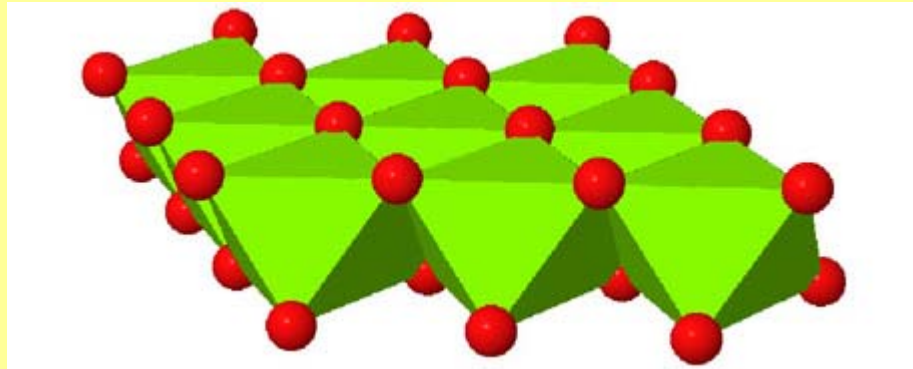
CdI$_2$ hexagonal
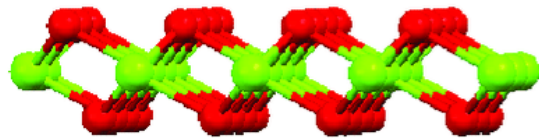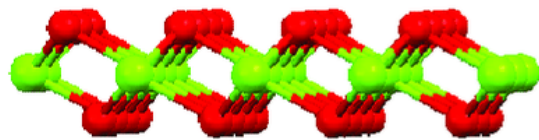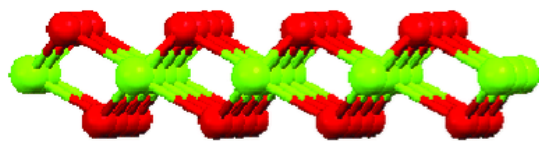
Side view
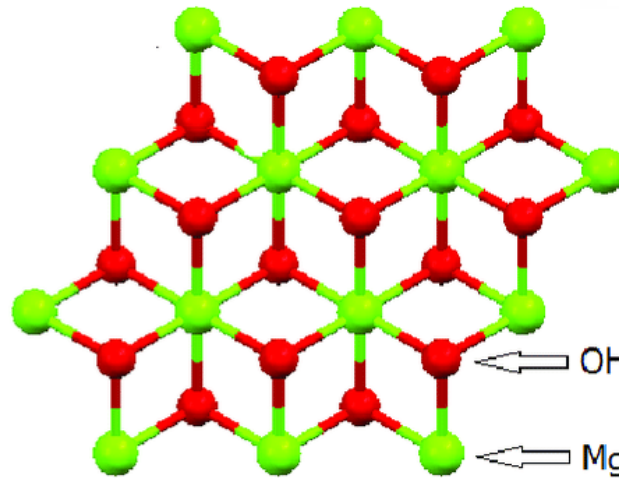
Top view

trioctahedral
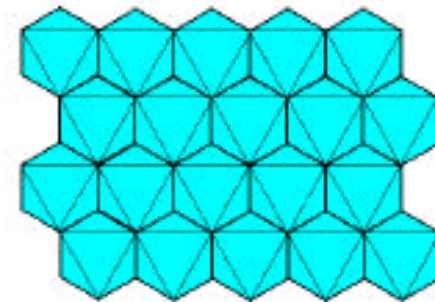
Bayerite and Gibbsite - Al(OH)$_3$
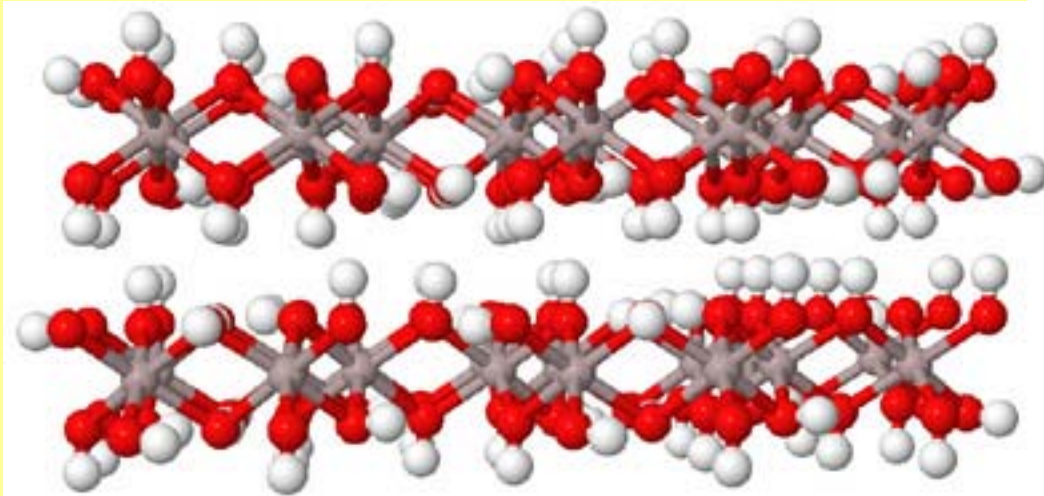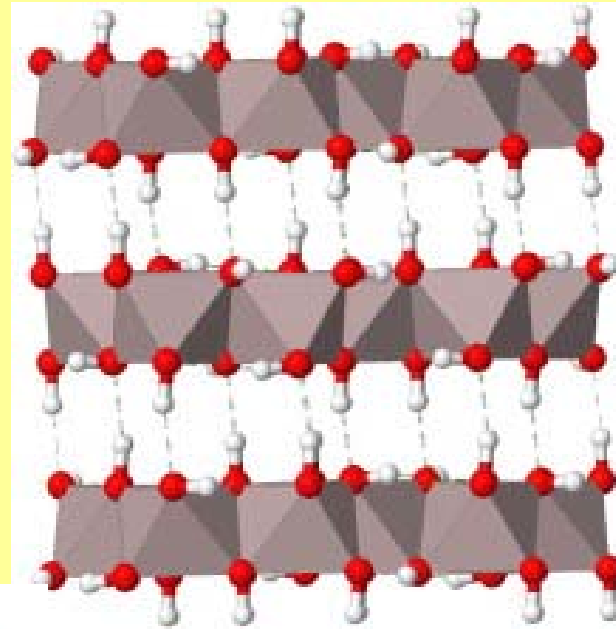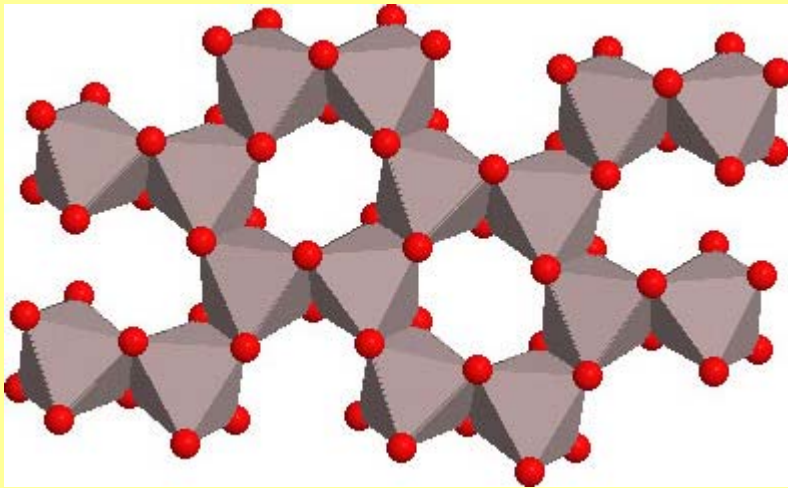
dioctahedral
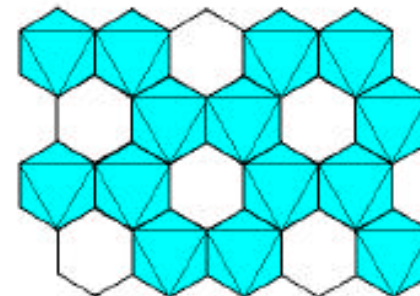
Bayerite and Gibbsite - Al(OH)$_3$
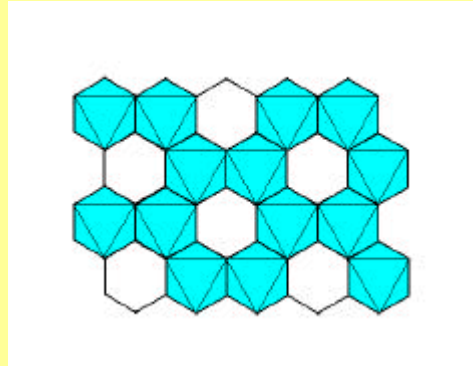
Opposite faces of a single layer Al(OH)$_3$ (A and B sides, respectively)

59
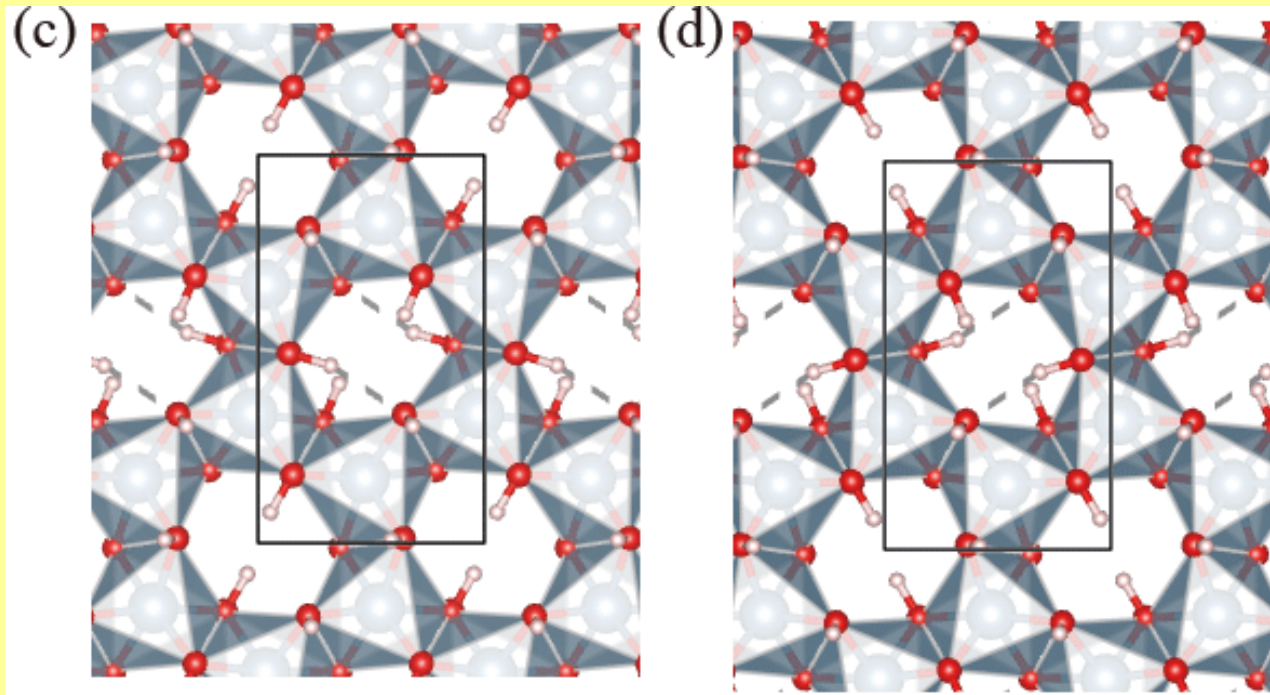
Bayerite and Gibbsite - Al(OH)$_3$

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

60
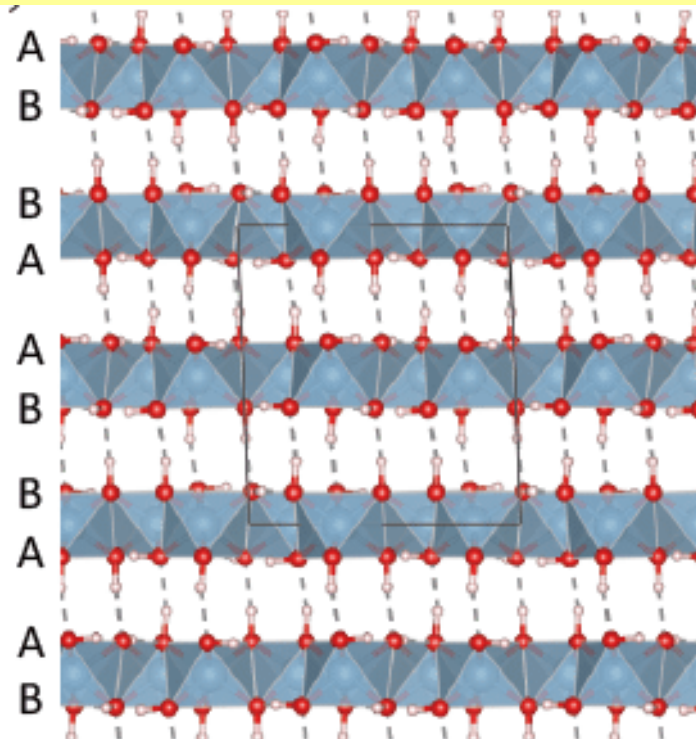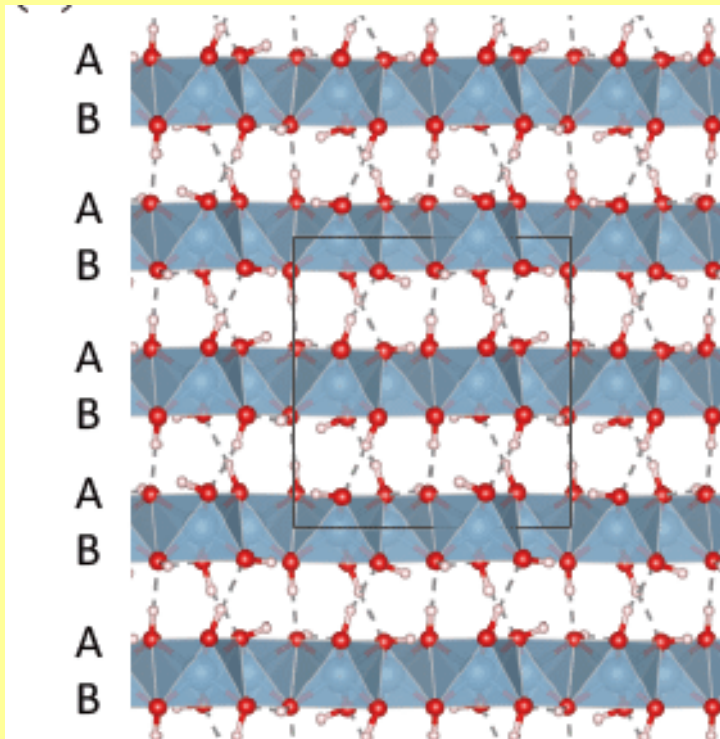
Clay Minerals

$[Si_4O_{10}]^{4-}$ tetrahedral sheet

$[Mg_6O_{12}]^{12-}$ trioctahedral sheet of octahedral units

$[Al_4O_{12}]^{12-}$ dioctahedral sheet

(a) (b) (c)

(d) (e)
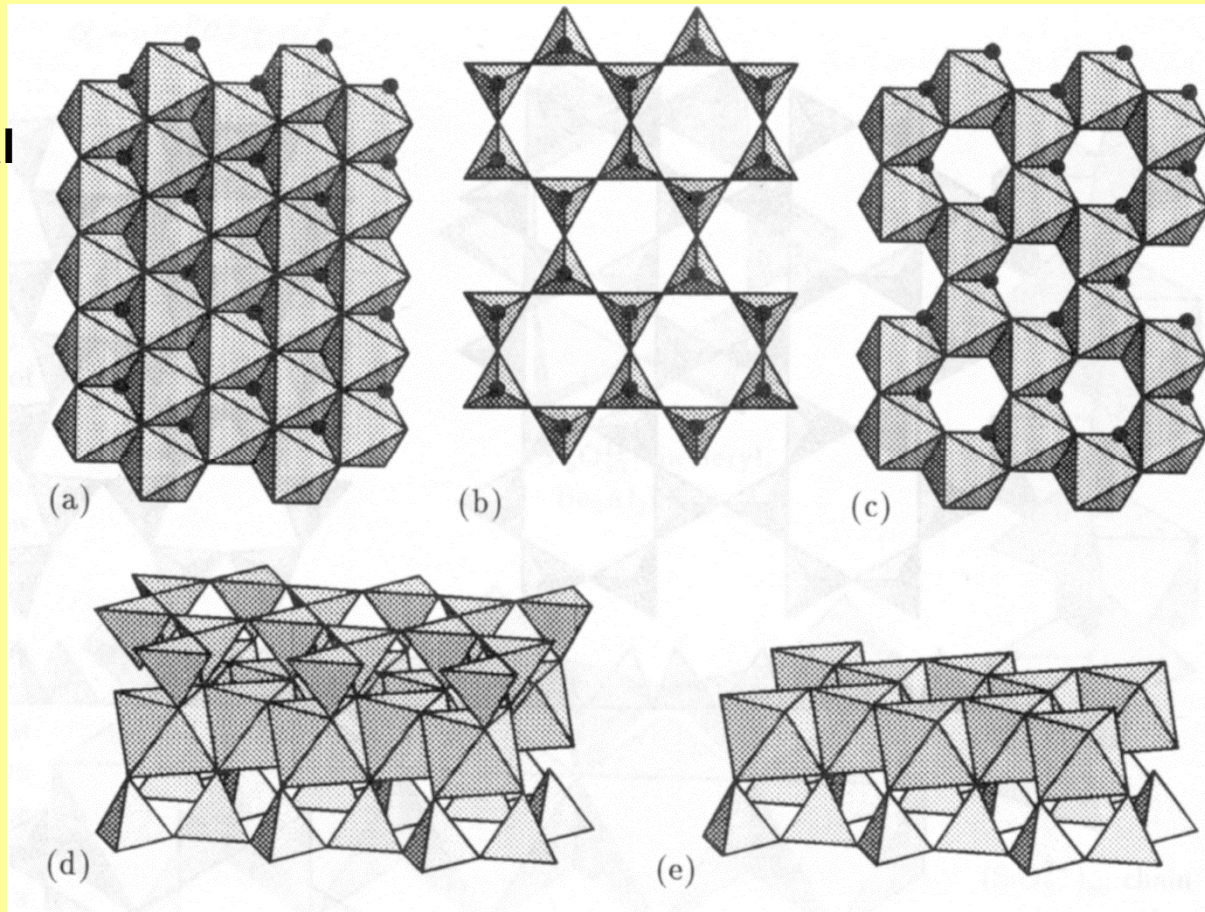
2:1

montmorillonite

1:1

kaolinite

61

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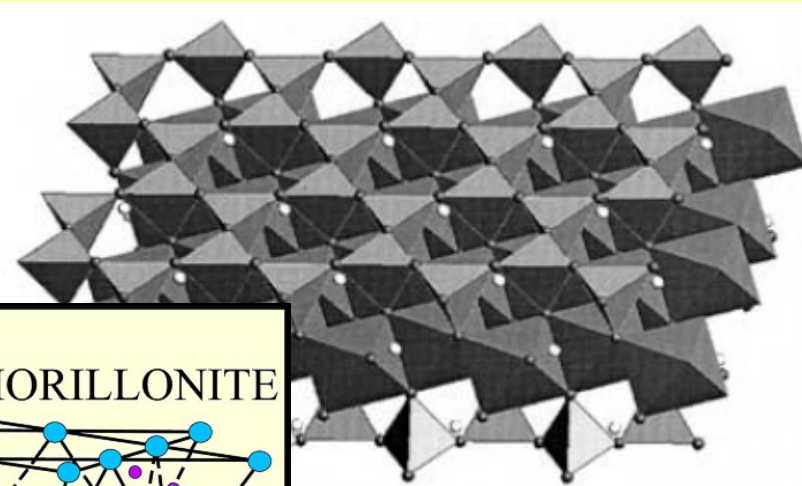
- *Dioctahedral clay mineral*
- T_d-O_h-T_d sandwich
- Isomorphous substitution

O_h: Al^{3+} by Mg^{2+}
T_d: Si^{4+} by Al^{3+}
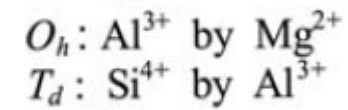
⟶ **Net negative charge**
⟶ **Interlayer cations**

STRUCTURE OF MONTMORILLONITE

- O
- OH
- Si, Al
- Al, Fe, Mg

EXCHANGEABLE CATIONS
n H_2O

MODIFIED FROM GRIM (1962)

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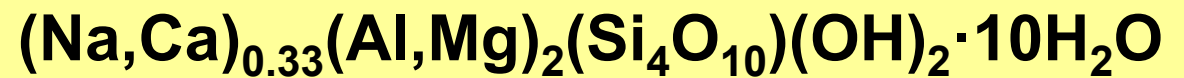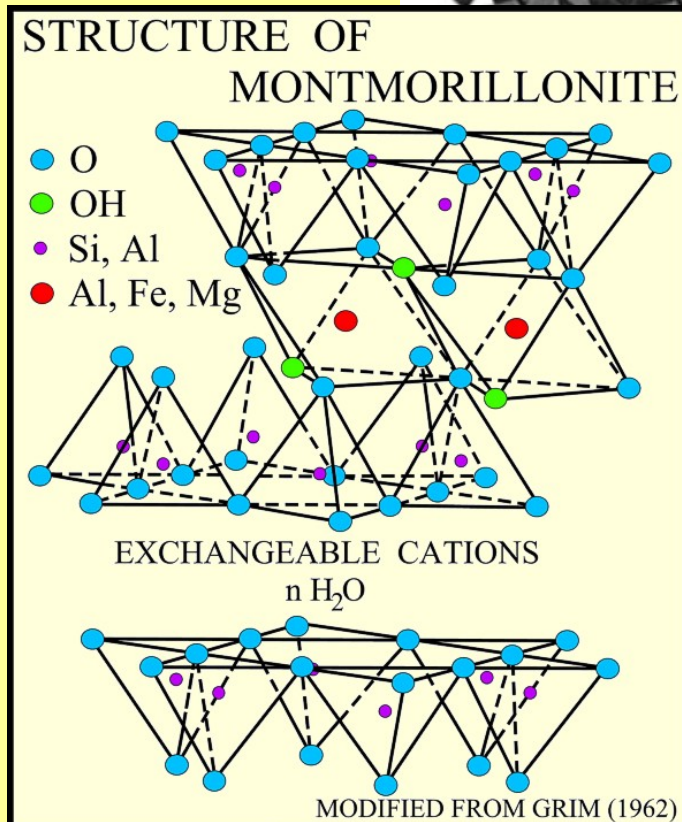
Phyllosilicate Minerals

Structure	Interlayer Charge	Trioctahedral (Y^{2+})	Dioctahedral (Y^{3+})
O	~0	Brucite	Gibbsite
TO	~0	Serpentine	Kaolinite
TOT	~0	Talc	Pyrophyllite
TOT O TOT	~0	Chlorite	
TOT (X^+, X^{2+}, H_2O) TOT expandable clay	~0.2-0.6	Saponite (smectite)	Montmorillonite (smectite)
	~0.6-0.9	Vermiculite	
TOT (X^+, X^{2+}) TOT non-expandable clay	~0.5-0.75	-	Illite
TOT X^+ TOT true mica	1	Phlogopite, Biotite	Muscovite, Paragonite
TOT X^{2+} TOT brittle mica	2	Clintonite	Margarite
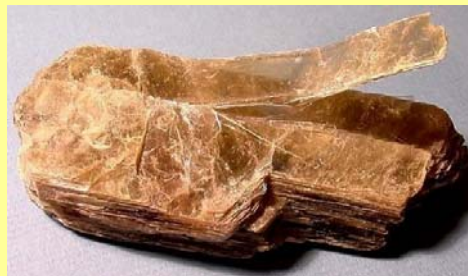
63

Phyllosilicate Minerals
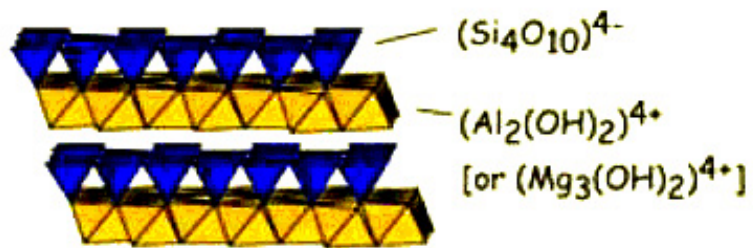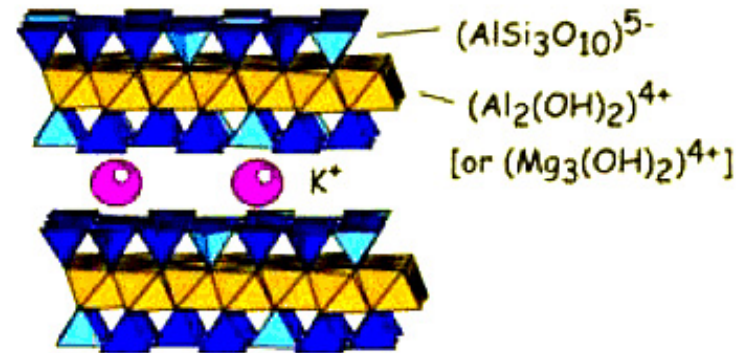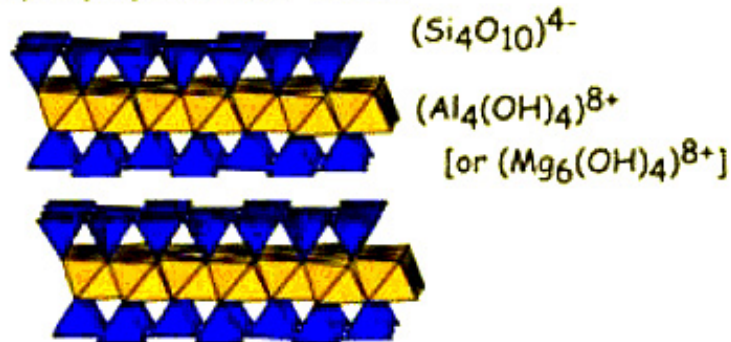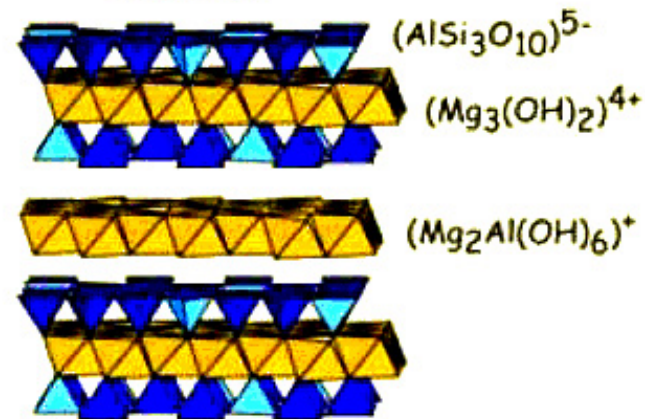
Clay Minerals

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
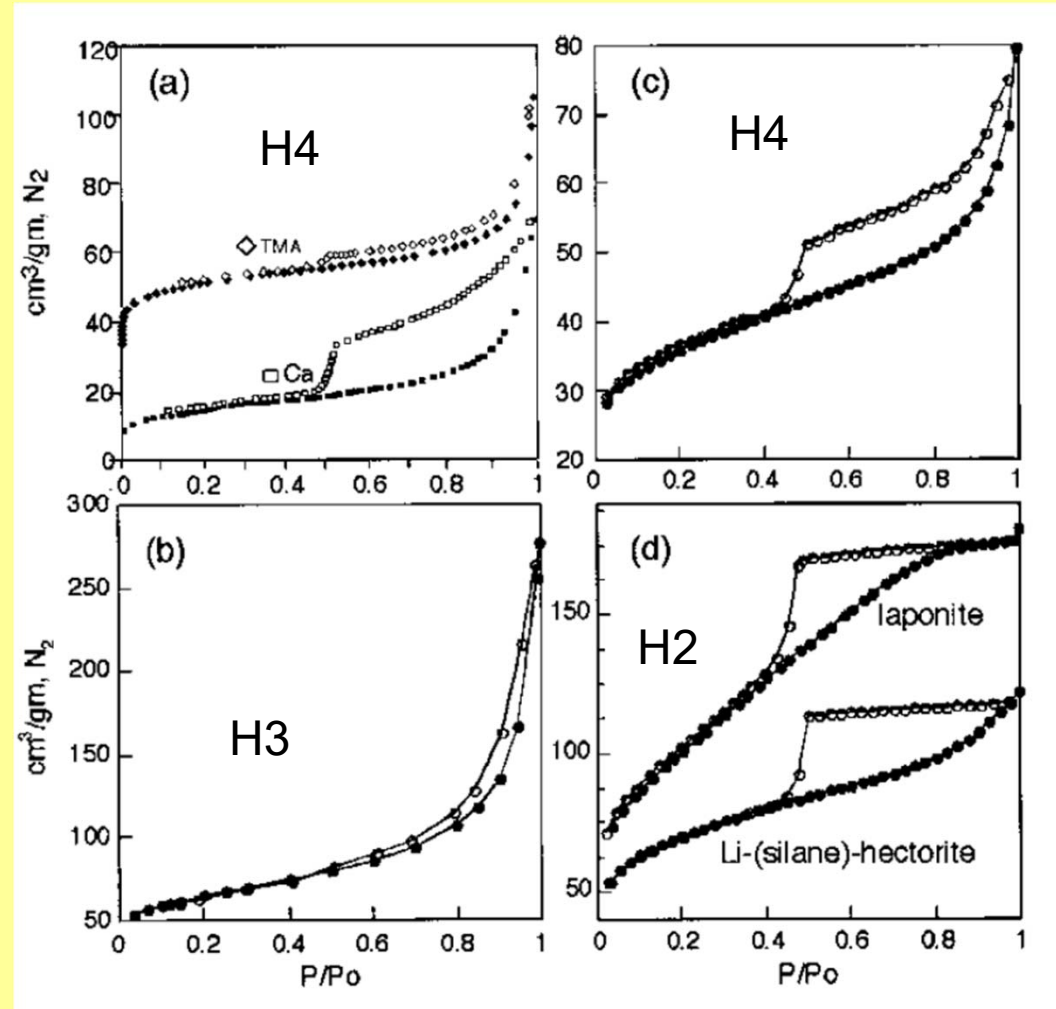
Surface Area

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

66

Layered Double Hydroxides

LDH = layered double hydroxides
HT = hydrotalcites

Brucite-like $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$ layer

basal spacing, d

interlamellar space, l

Intercalated anions

M^{2+}/M^{3+} cation

H_2O OH^- Cl^- NO_3^- CO_3^{2-}

67
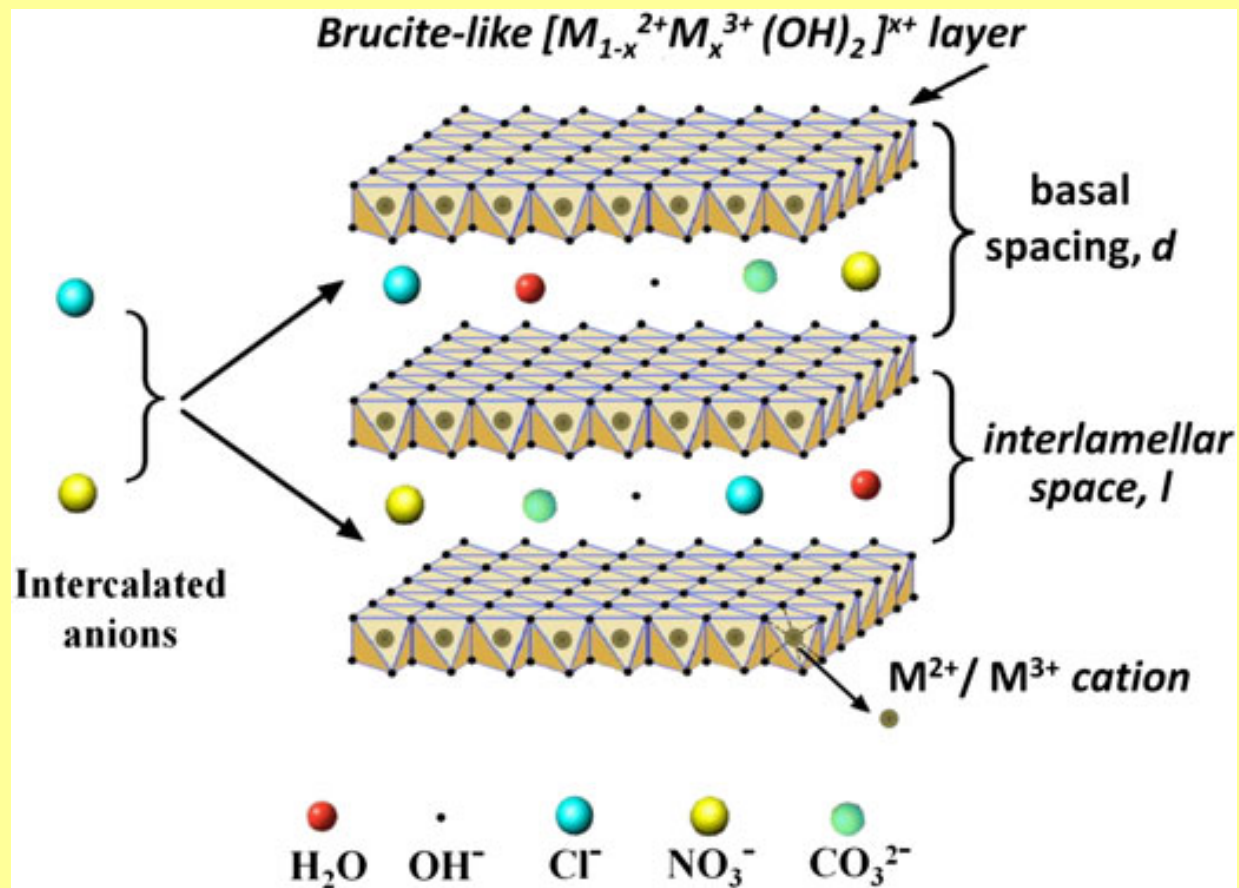
Layered Double Hydroxides

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

OH
M^{2+}, M^{3+}
OH

Layer thickness

Basal spacing

H_2O

A^n

gallery height = 0.280 nm

Interlayer spacing
d(003) = 0.760 nm
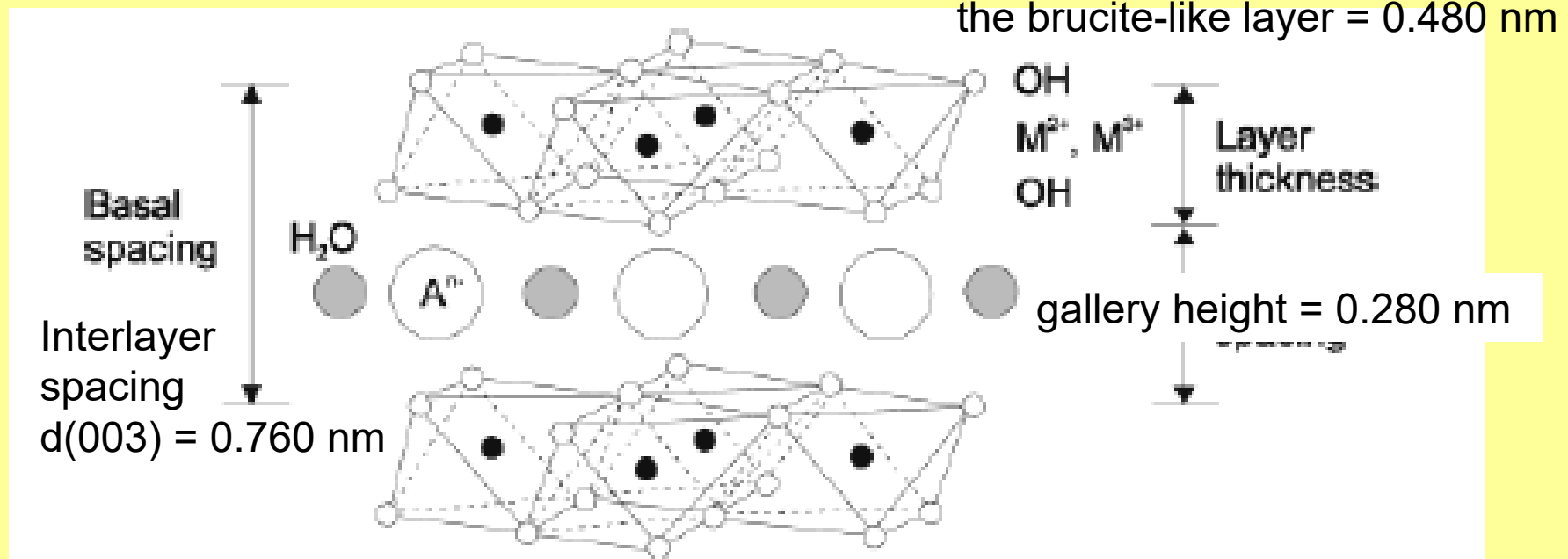
Hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$

Hydrotalcites

Brucite layers, Mg^{2+} substituted partially by Al^{3+}
Layers have positive charge
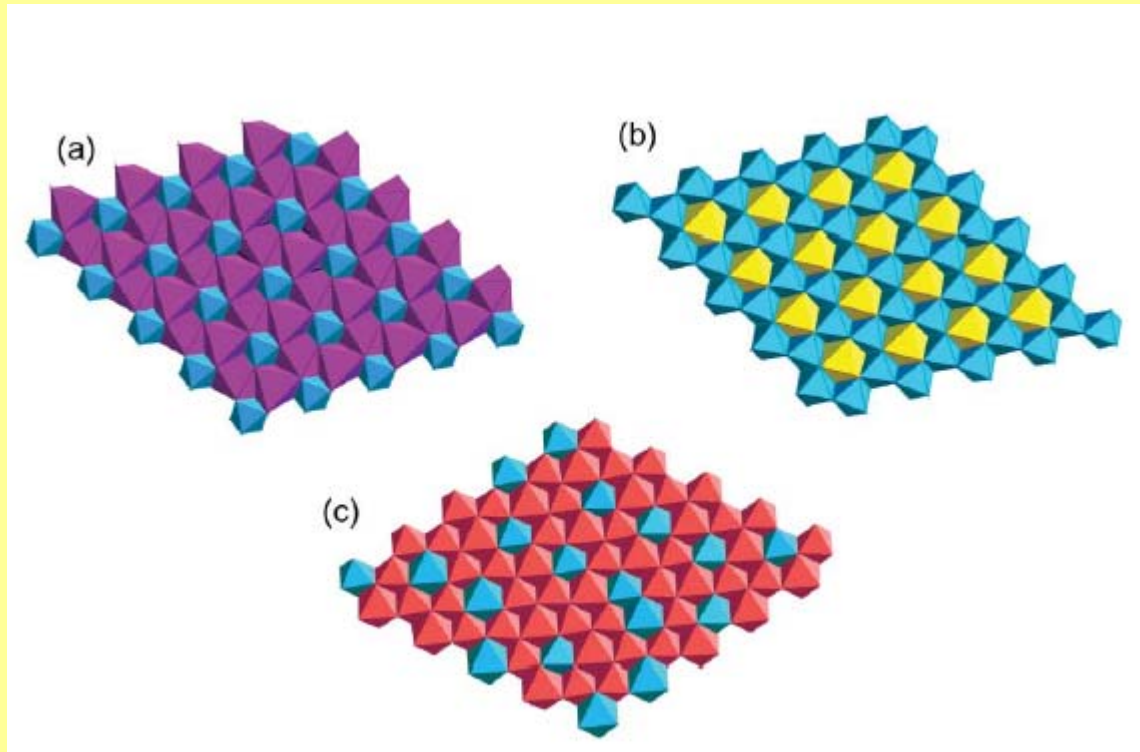
(a) $[Ca_2Al(OH)_6]_2SO_4 \cdot 6H_2O$ (b) $[LiAl_2(OH)_6]Cl$ (c) $[Mg_{2.25}Al_{0.75}(OH)_6]OH$

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 $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ - 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 $Mg(OH)_2$
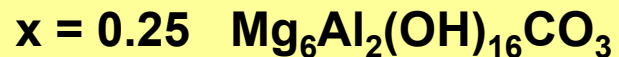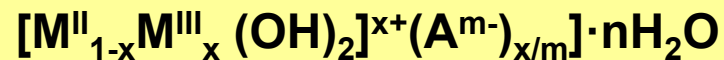
Hydrotalcite

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

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

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

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

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

Hydrotalcite

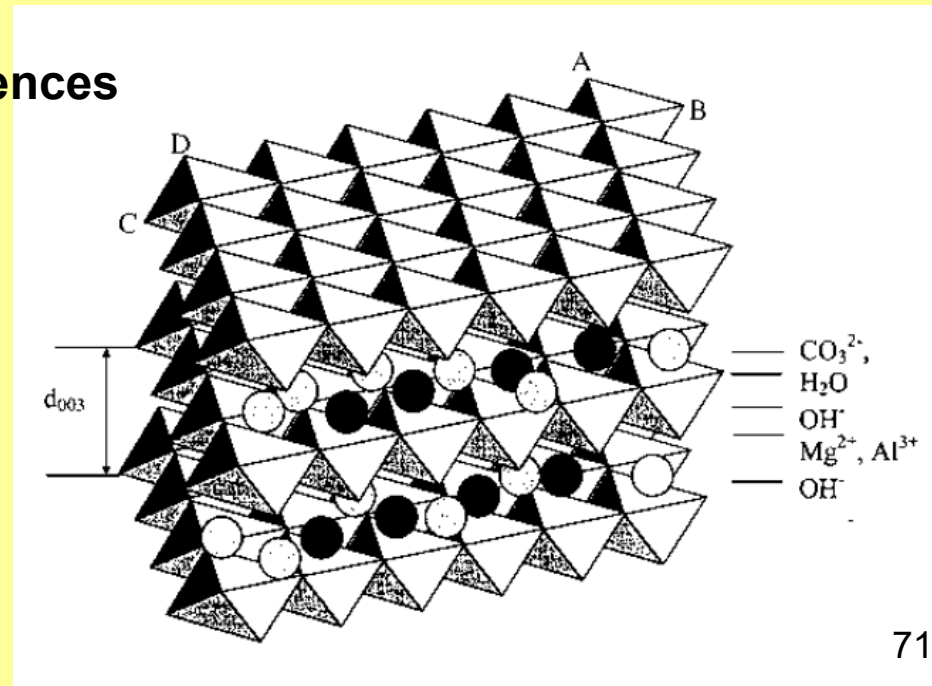Hydrotalcite $Mg_6Al_2(OH)_{16}CO_3.4H_2O$ - 3R stacking

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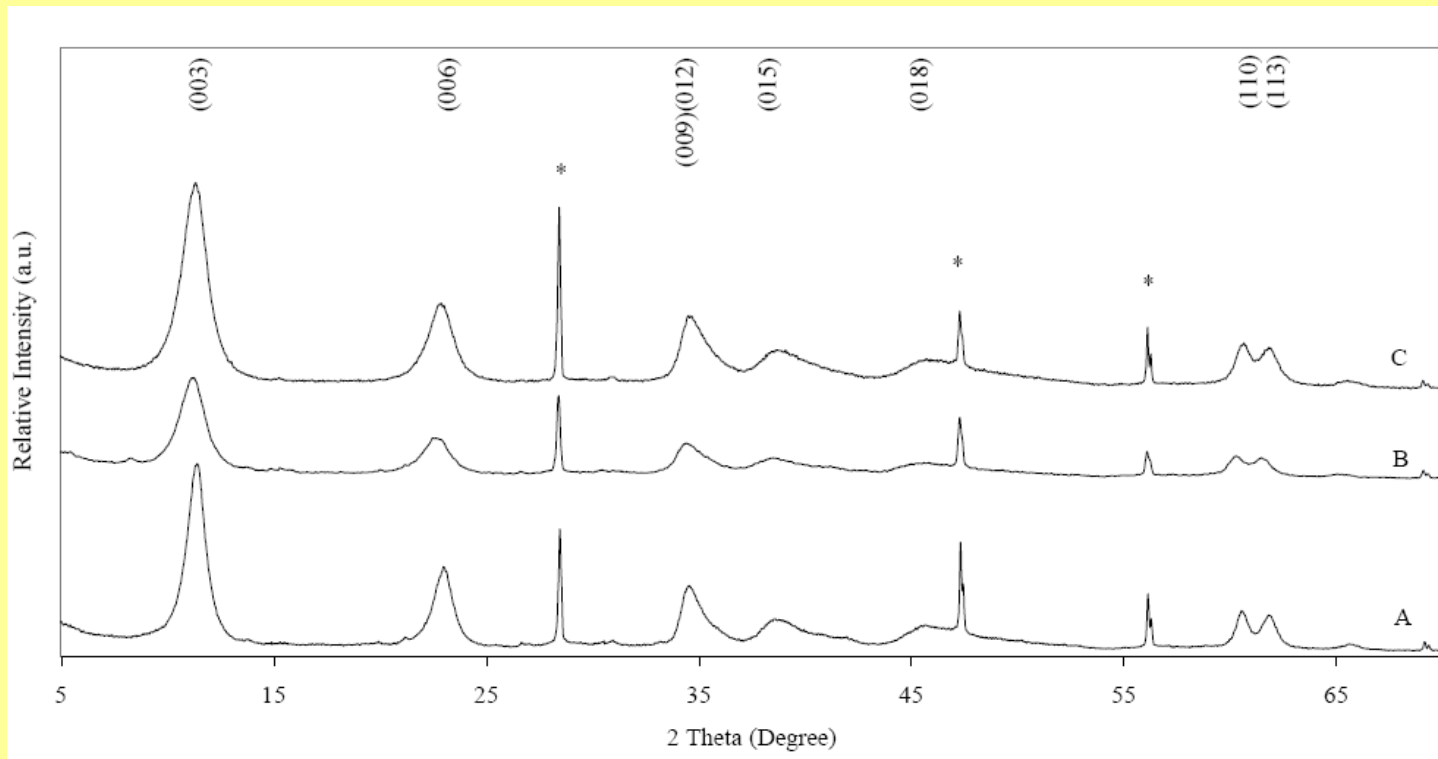
**XRD patterns of layered double hydroxides synthesized by coprecipitation method with various cations composition:
A – Mg/Al; B- Mg/Co/Al; C- Mg/Ni/Al**

* = Reflections from Si crystal used as a reference

XRD Patterns of LDH
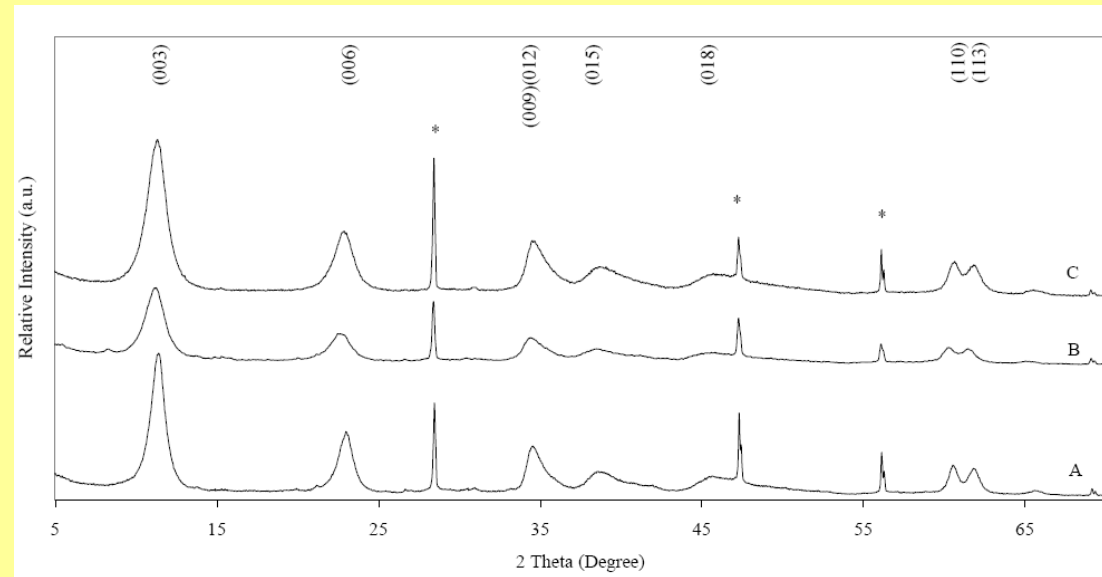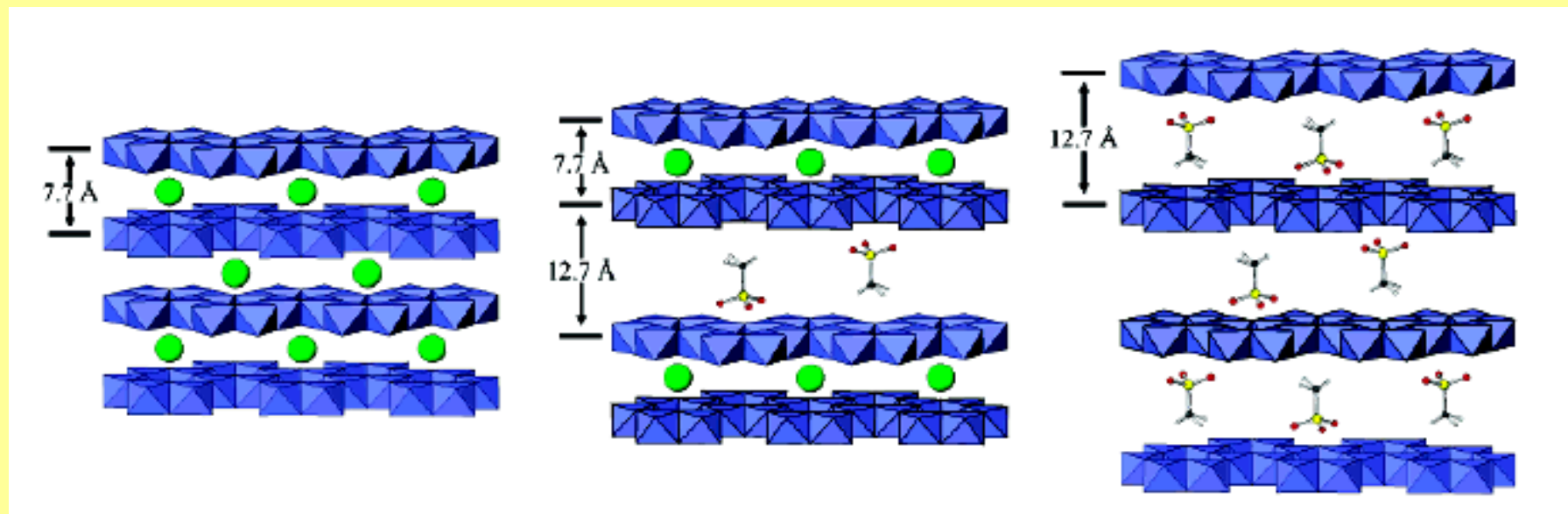

rhombohedral structure
the cell parameters *c* and *a*

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

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

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

Intercalation to LDH

The intercalation of methylphosphonic acid into Li/Al LDH

(a) [LiAl$_2$(OH)$_6$]Cl.H$_2$O
(b) second-stage intermediate, alternate layers occupied by Cl and MPA
   anions
(c) first-stage product with all interlayer regions occupied by MPA

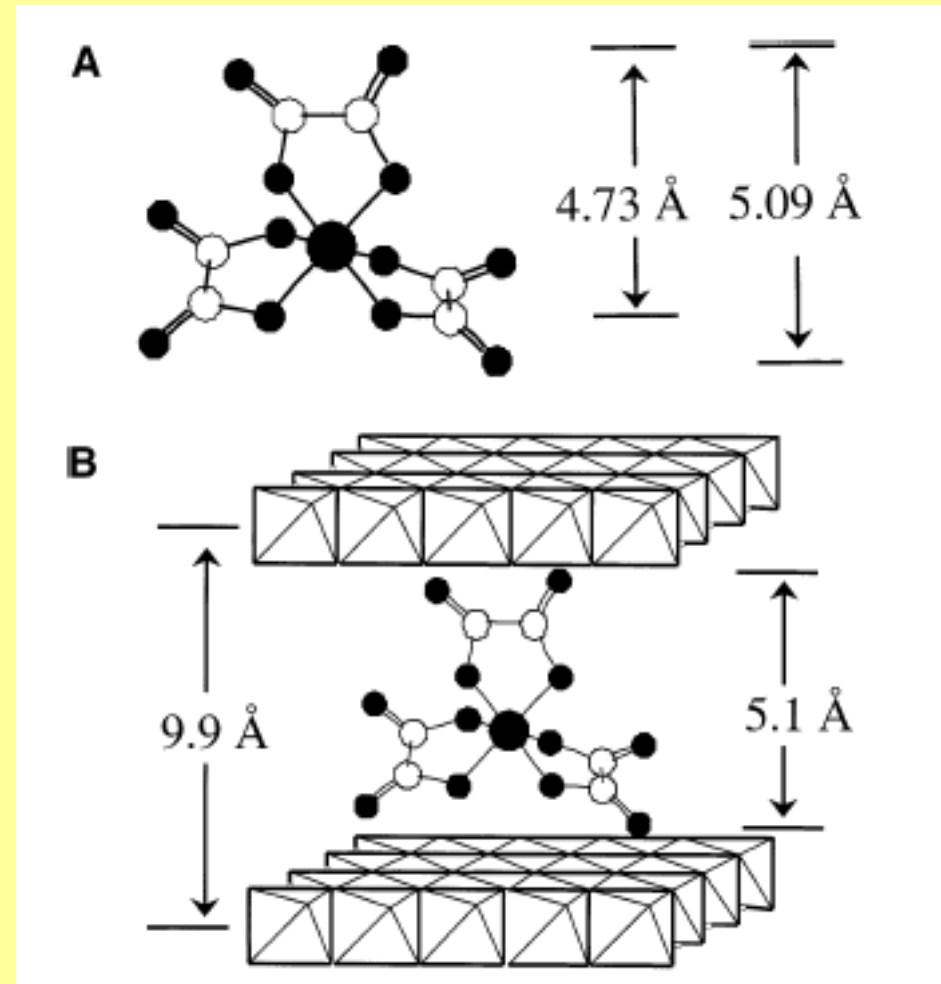# Intercalation to LDH

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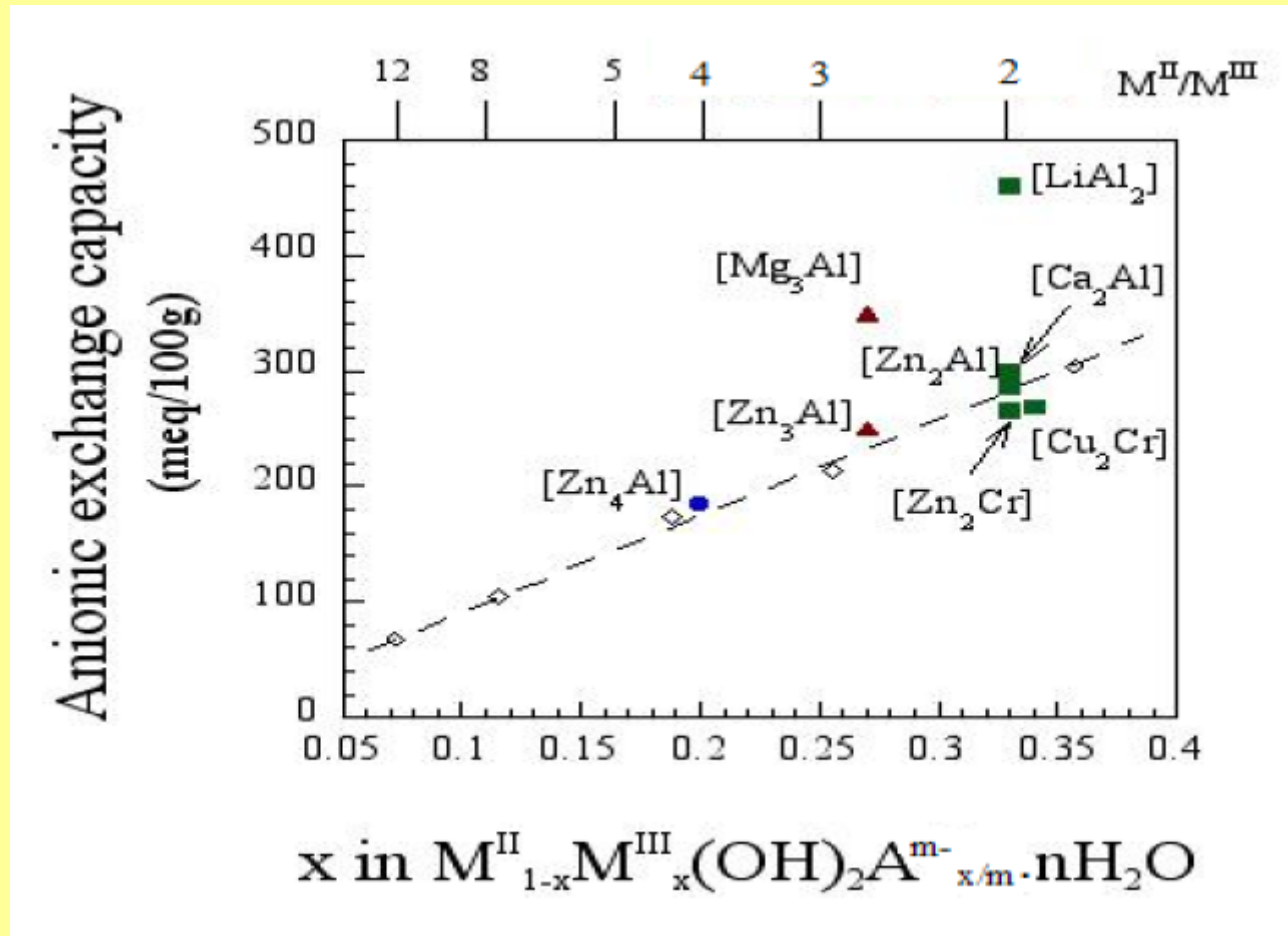
hydrotalcites
mineral $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$

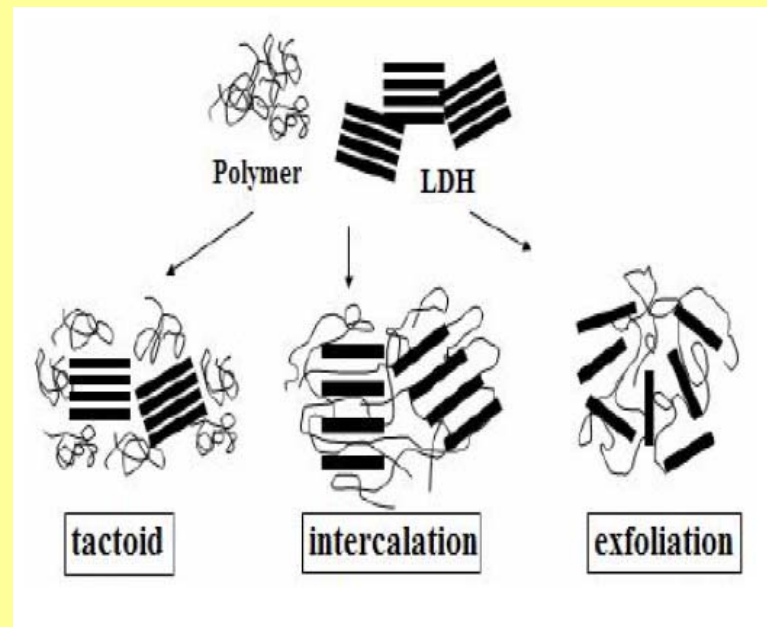Brucite layers, Mg^{2+} substituted partially by Al^{3+}

Layers have positive charge
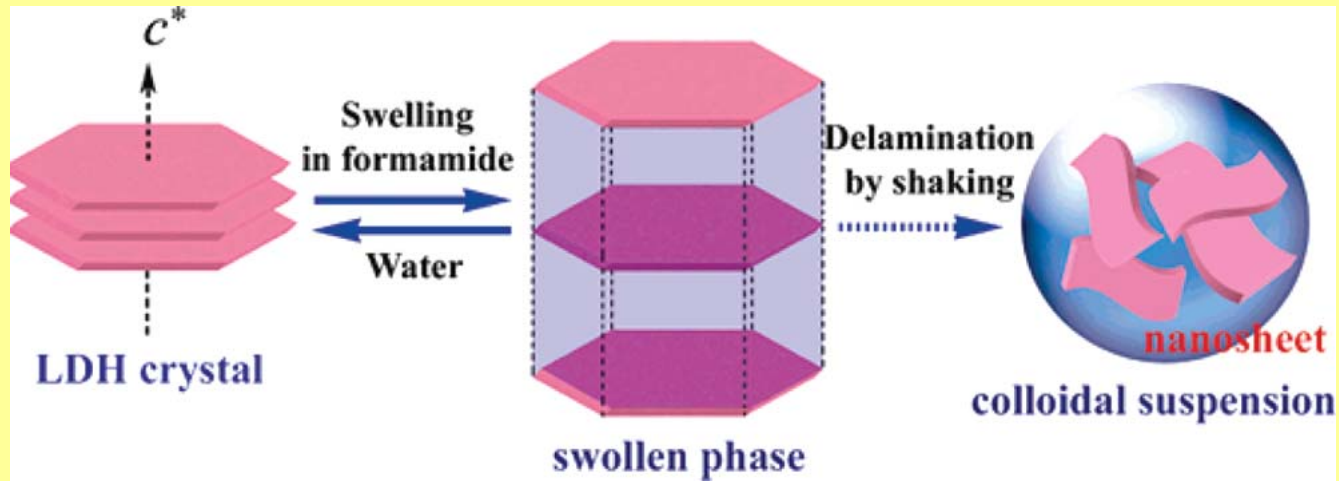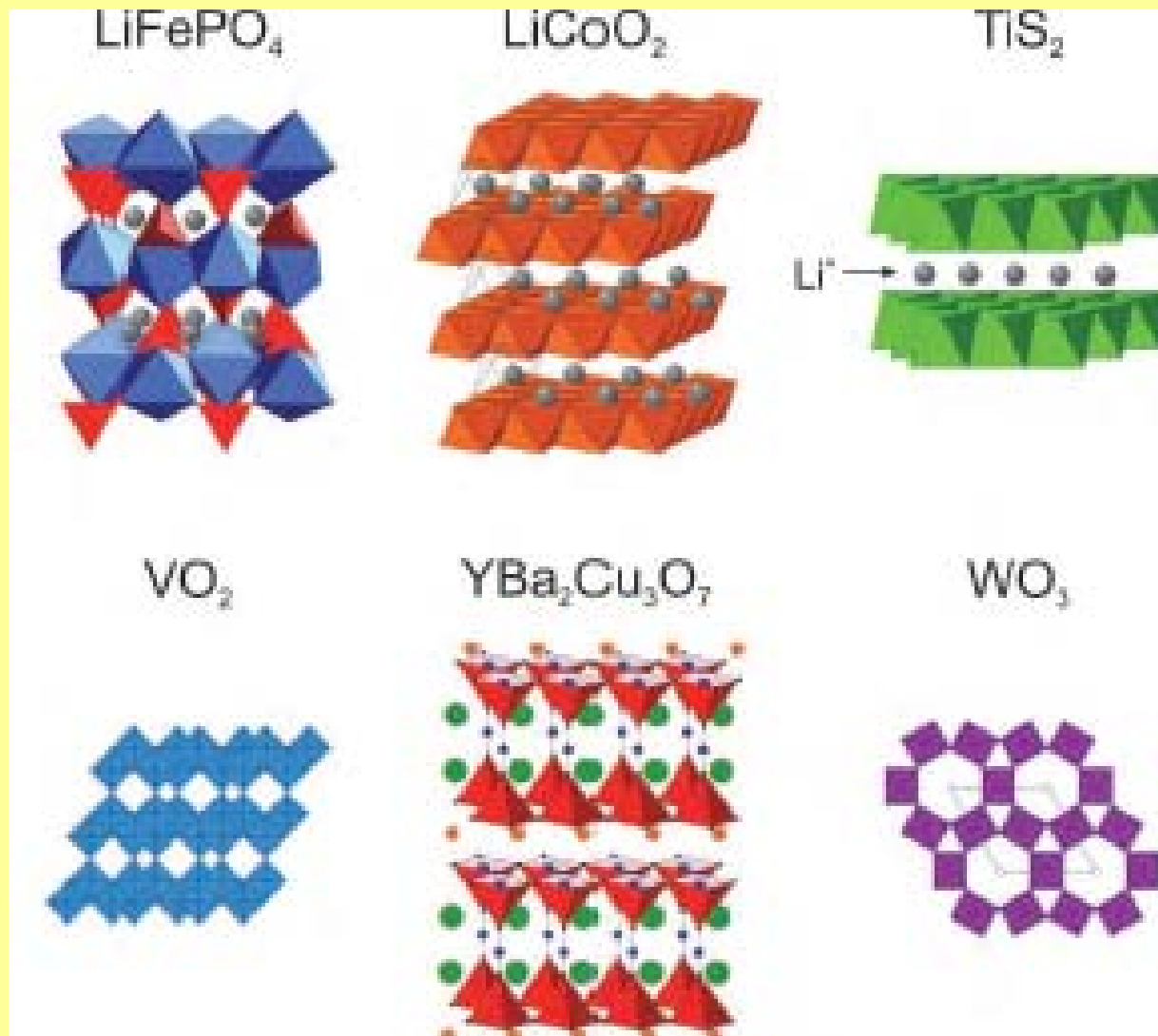
Intercalate anions $[Cr(C_2O_4)_3]^{3-}$

The Anionic Exchange Capacity (AEC)

LDH Composite Structures
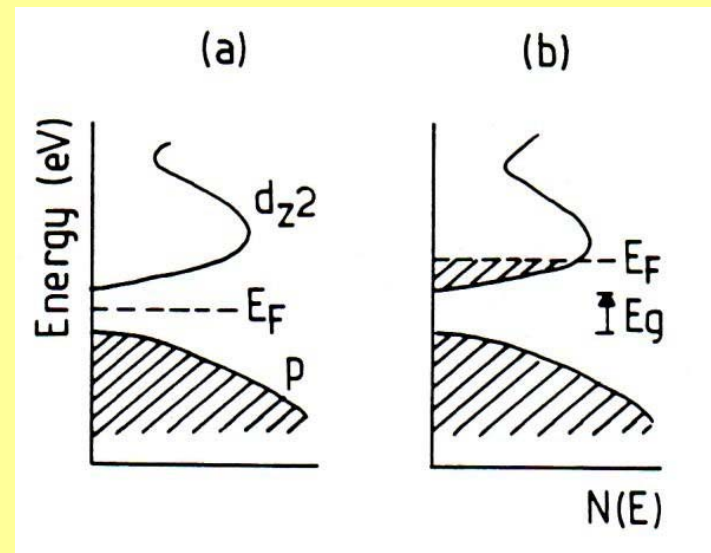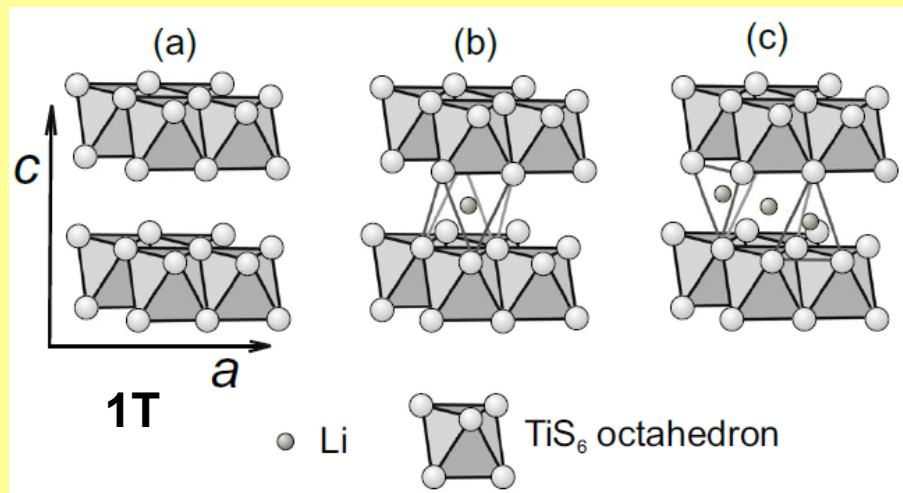
Li Intercalation Compounds

Li Intercalation

x Li + TiS_2 → Li_xTiS_2

titanium(IV) sulfide

Titanium Disulfide

+ Li

Lithium Titanium Disulfide

(a)   (b)   (c)

1T

Li TiS_6 octahedron

d_{z^2}

E_F

p

E_F

E_g

N(E)

Energy (eV)

80

Li Intercalation

FeO$_6$ Octahedron

LiO$_6$ Octahedron

PO$_4$ Tetrahedron

$$LiFe\,PO_4 + 6C \underset{Discharge}{\overset{Charge}{\rightleftharpoons}} Fe\,PO_4 + LiC_6$$

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

Li$^+$ + e + FePO$_4$ $\rightarrow$ LiFePO$_4$

anode   electrolyte   cathode
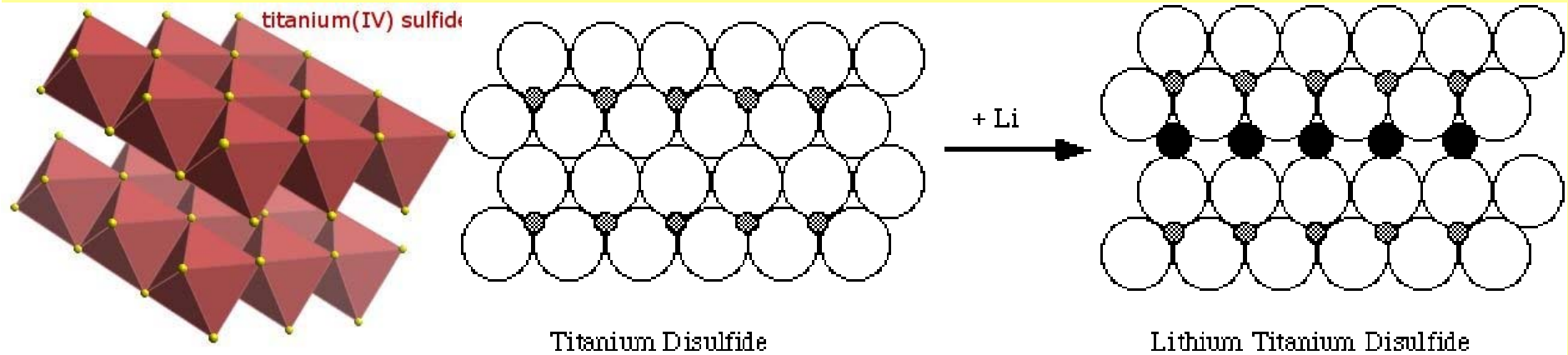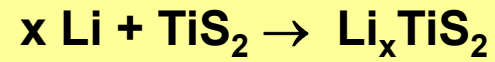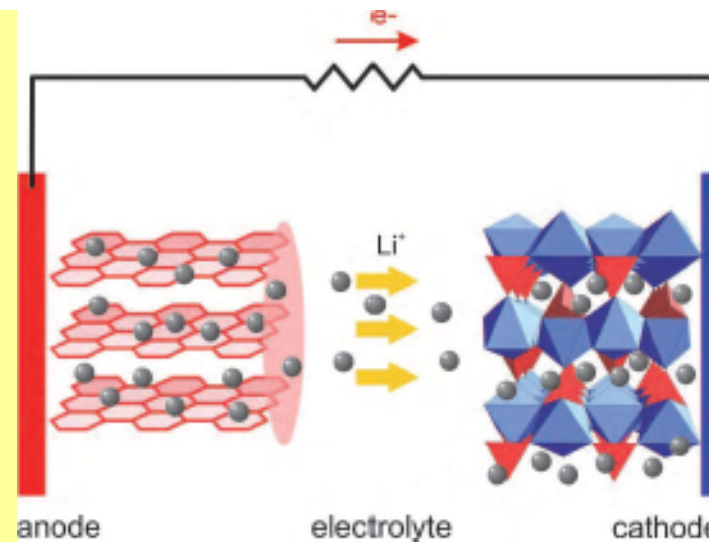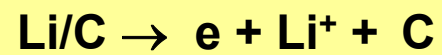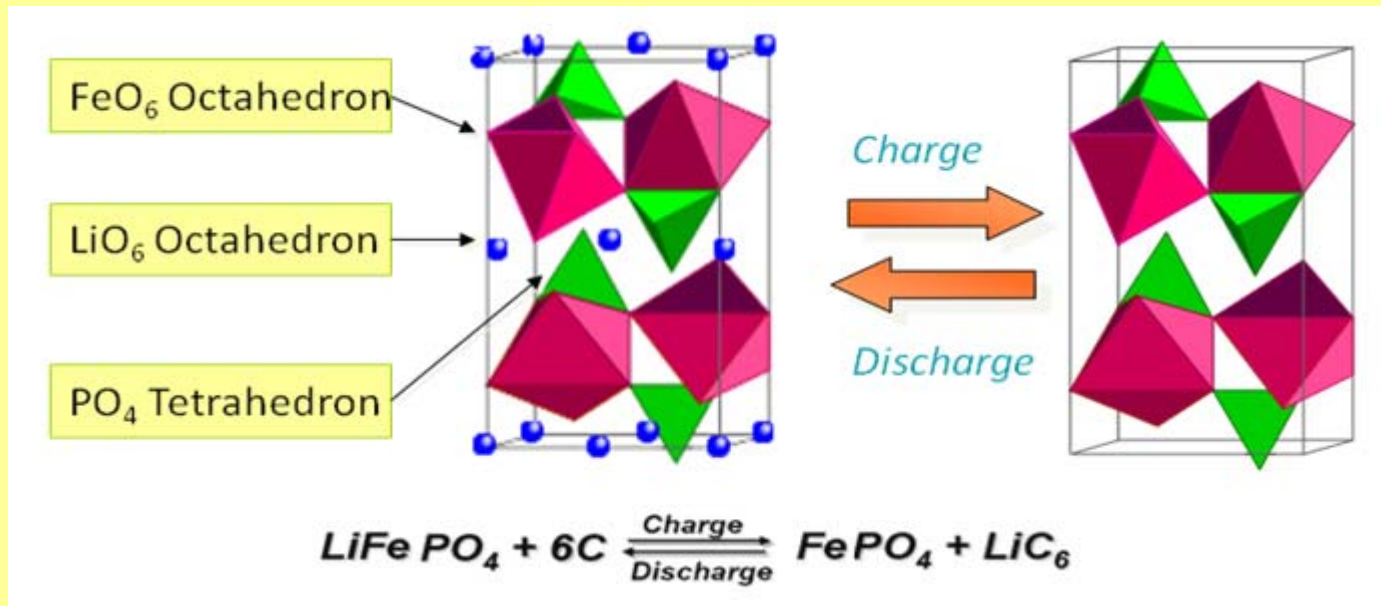
Molybdenum Disulfide (MoS$_2$)

Mineral molybdenite

Hydrodesulfurization catalyst (at edges)

Lubricant

Interlayer spacing 0.62 nm

Free spacing 0.30 nm

● Mo   ● S
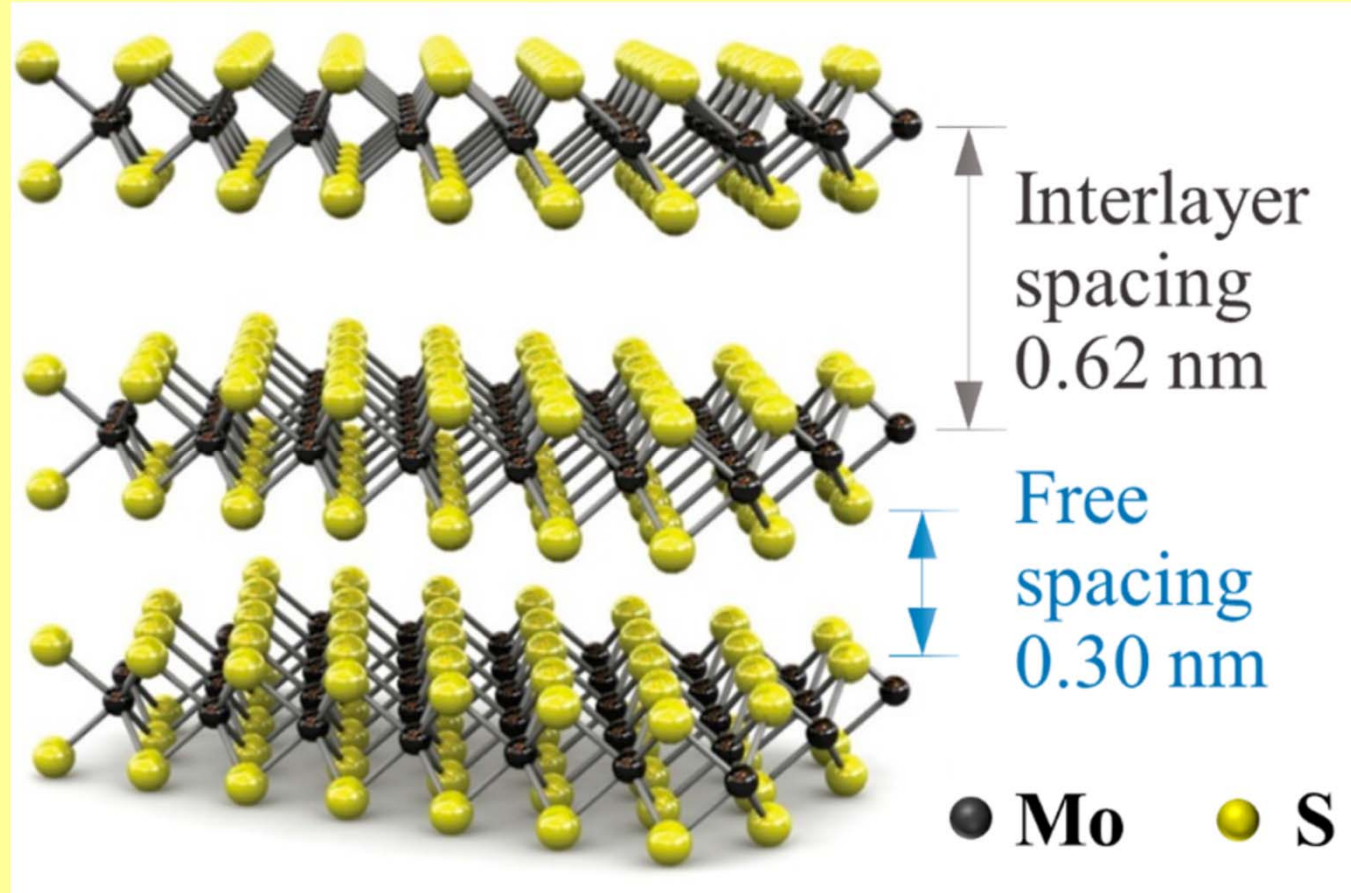
Polymorphs of MoS$_2$

MoO$_6$ trigonal prismatic

MoO$_6$ octahedral

2H

semiconductors

3R

1T

metallic

○ X
○ M
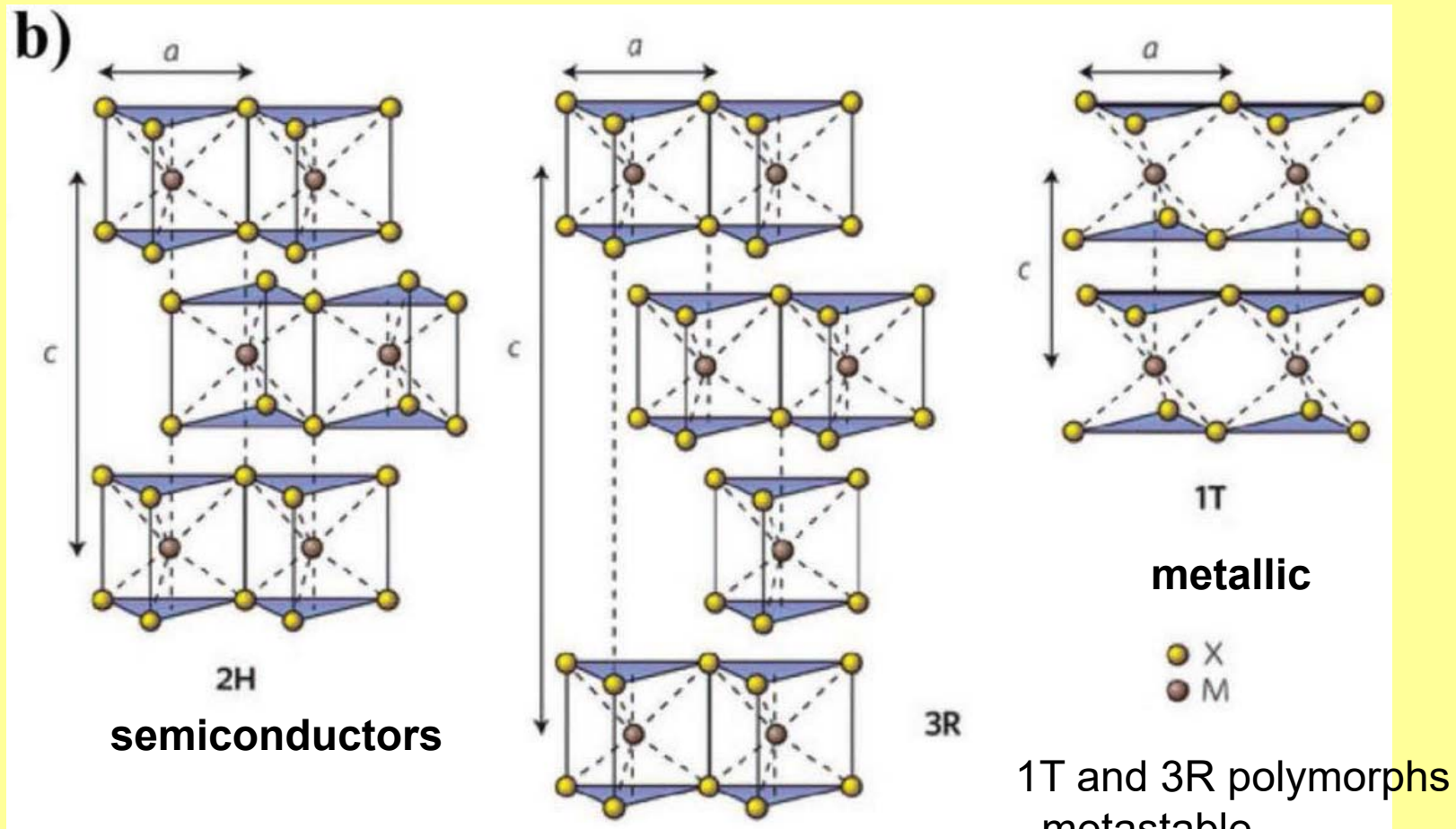
2H phase - thermodynamically stable

1T and 3R polymorphs - metastable

Polymorphs of MoS$_2$

2H - MoO$_6$ trigonal prismatic

semiconductors
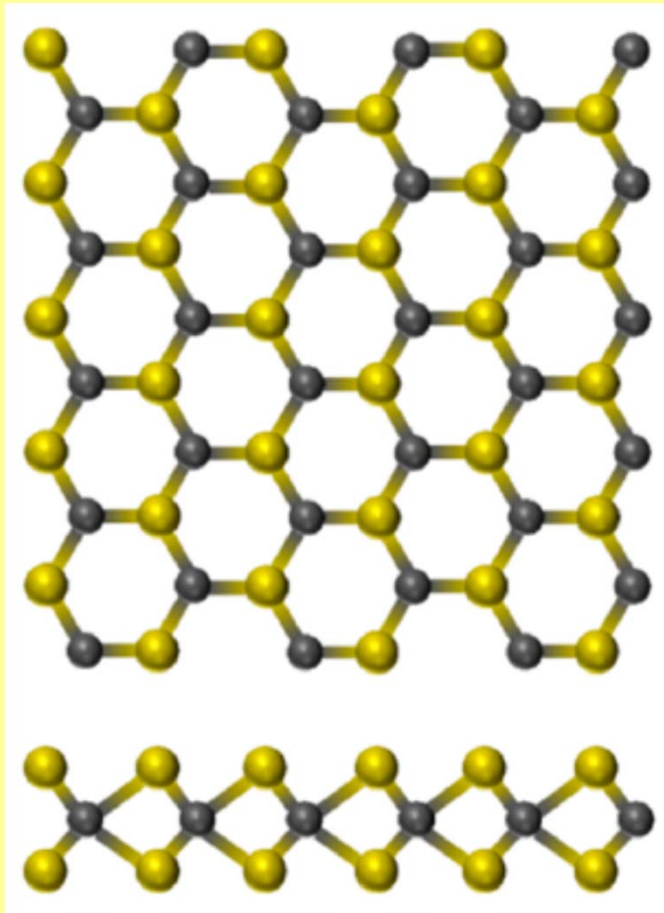
1T - MoO$_6$ octahedral

metallic

Li intercalation (2H to 1T), annealing (1T to 2H)

Polymorphs of MoS$_2$

2H, 3R - MoO$_6$ trigonal prismatic   1T - MoO$_6$ octahedral
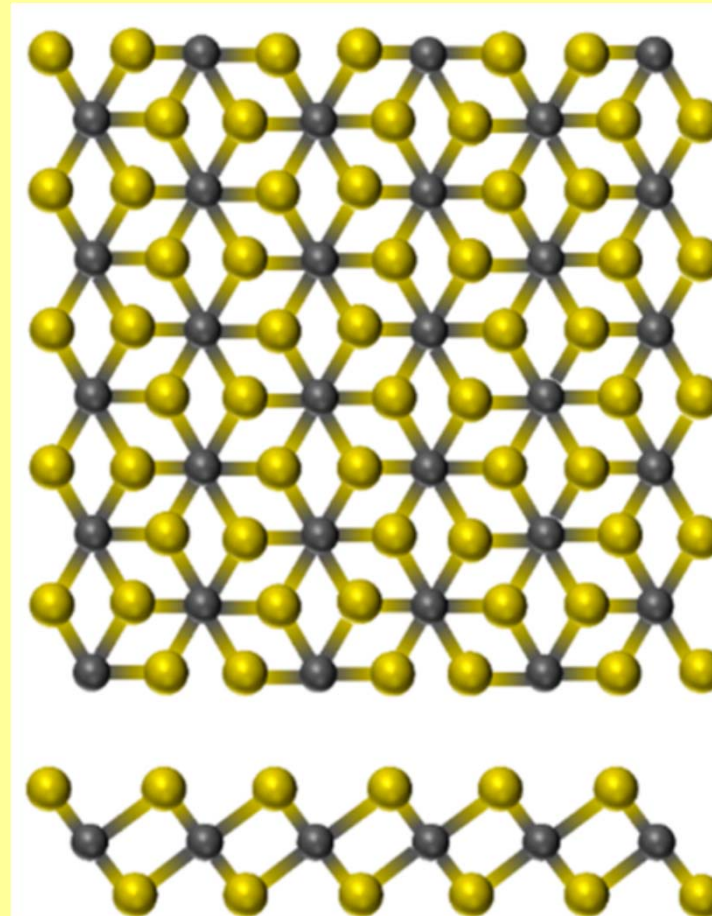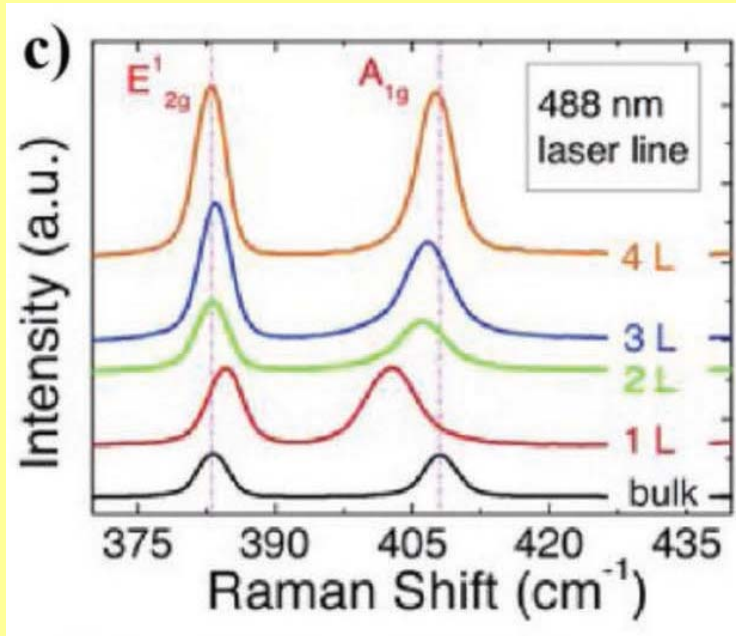
Digit = number of monolayers in the unit cell
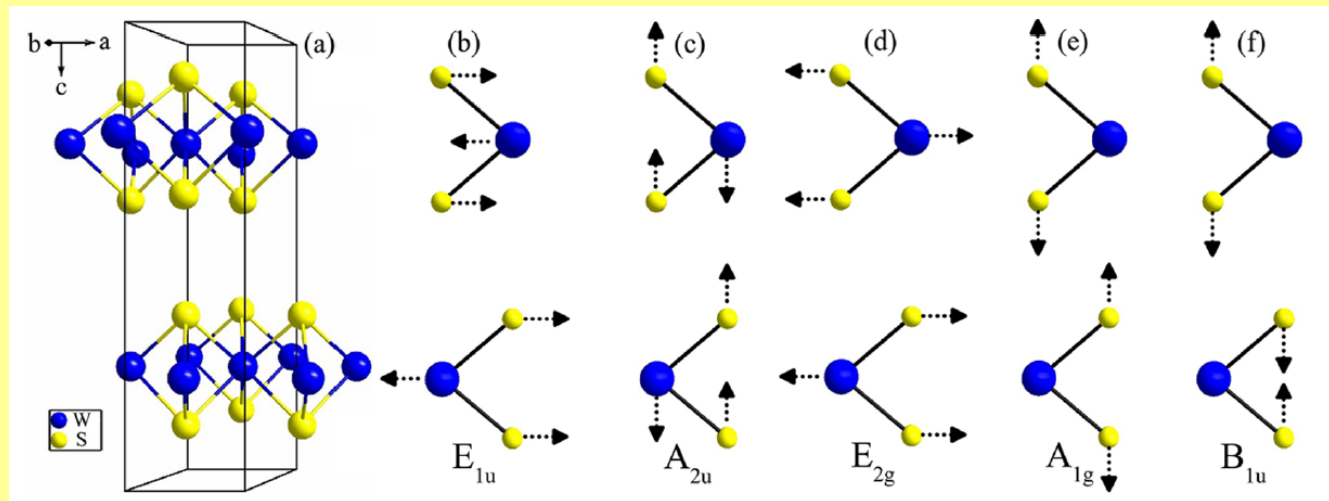the letters T = trigonal, H = hexagonal, R = rhombohedral
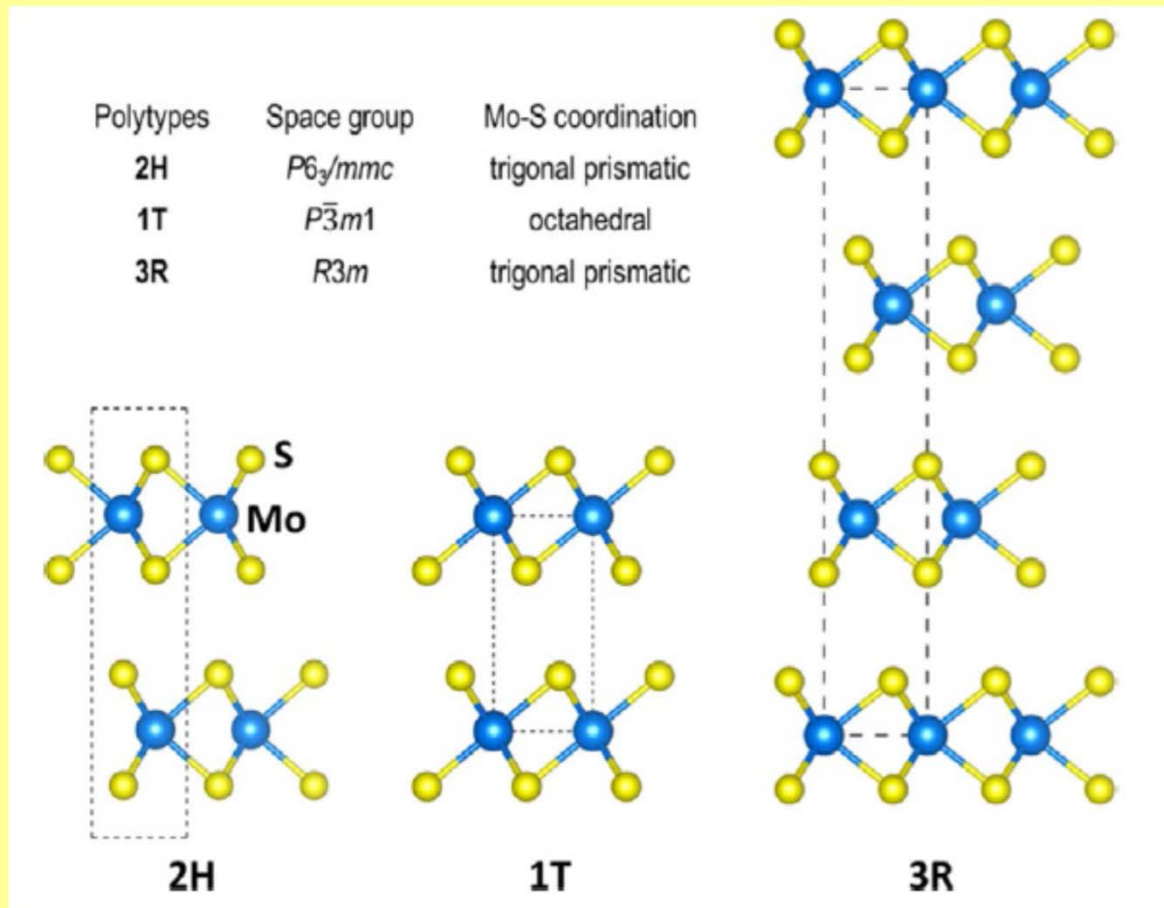
Molybdenum Disulfide (MoS$_2$)

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$_2$)

a) MoS$_2$ bulk — $\Delta = 1.2$ eV

MoS$_2$ monolayer — $\Delta = 1.9$ eV

Conduction band

Fermi level

Valence band

photoluminescence
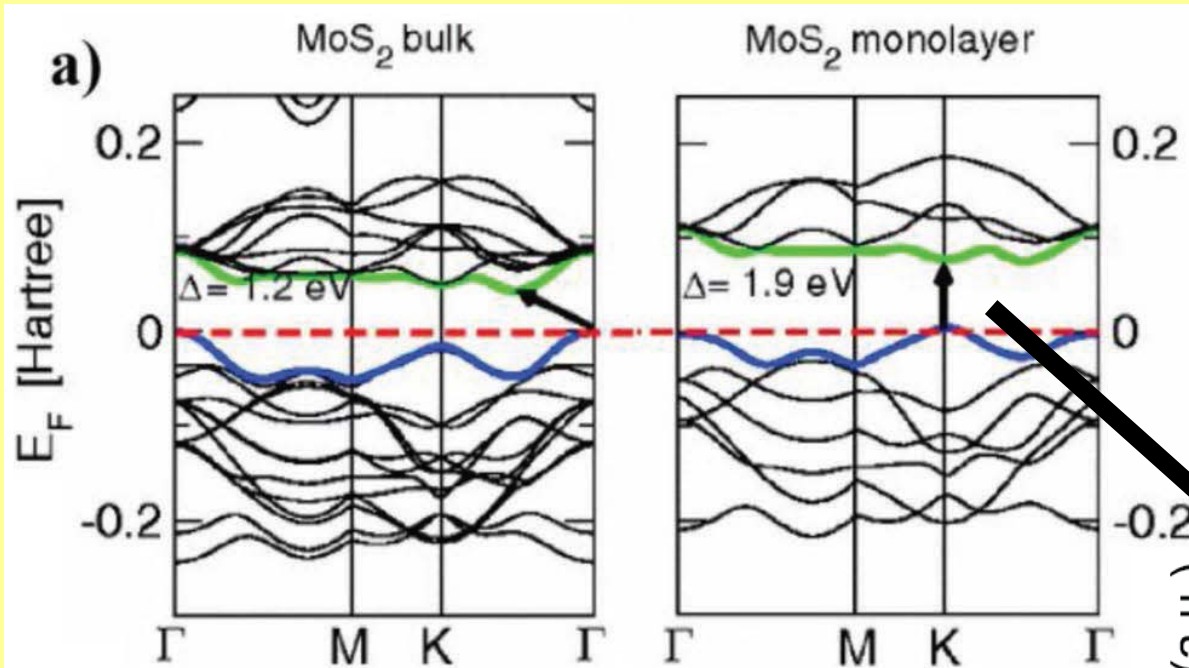
An indirect band gap 1.29 eV

A direct band gap 1.9 eV (2H)

(d) Photoluminescence (a.u.) vs Wavelength (nm)

1 L
2 L
3 L
4 L
bulk

Raman peaks of MoS$_2$

Raman peaks of silicon
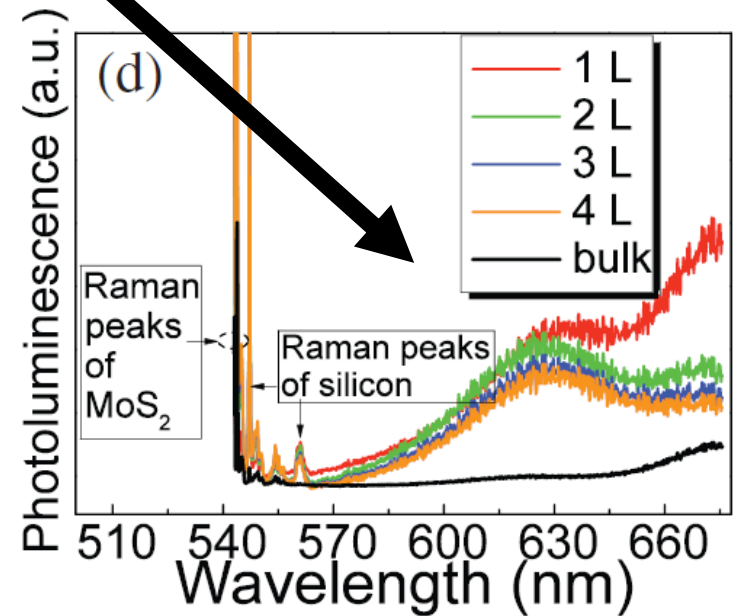
Molybdenum Disulfide (MoS$_2$)
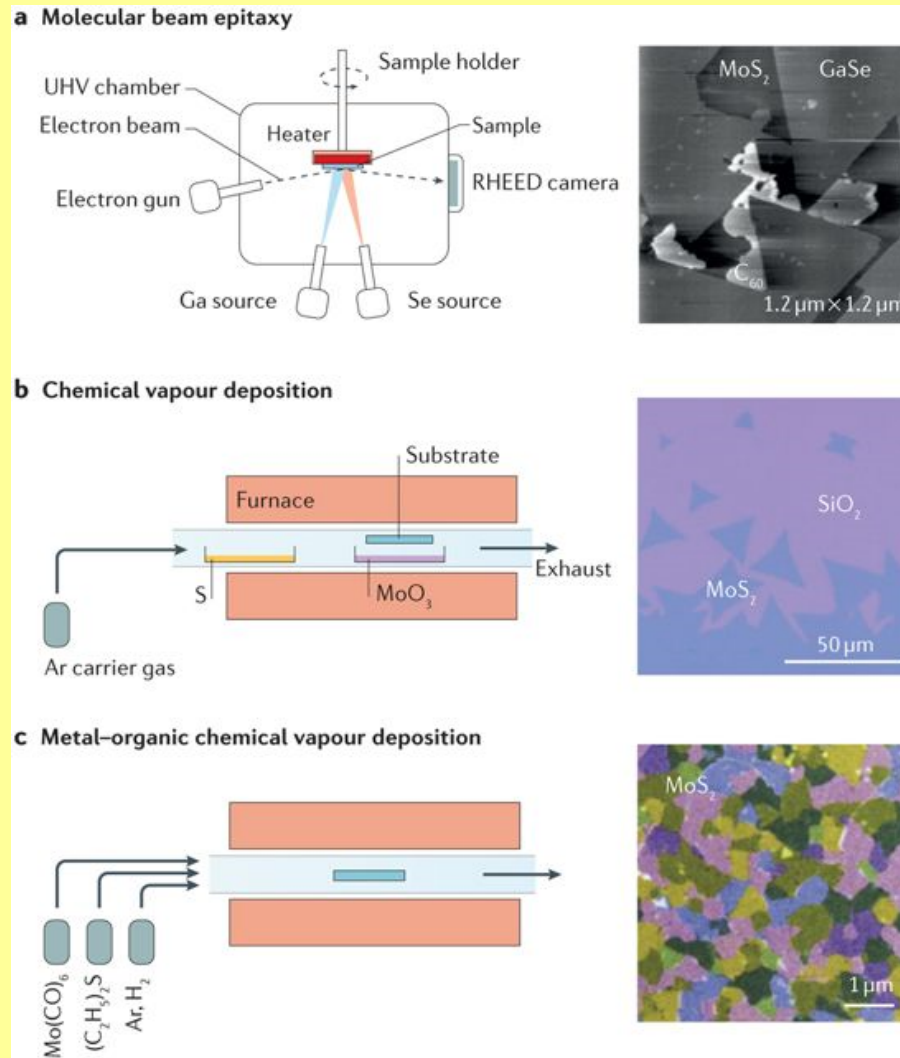
Molybdenum Disulfide (MoS$_2$)

MoS$_2$ nanosheets - all sulfur atoms exposed on surfaces
S = a soft Lewis base - a high affinity for heavy metal ions
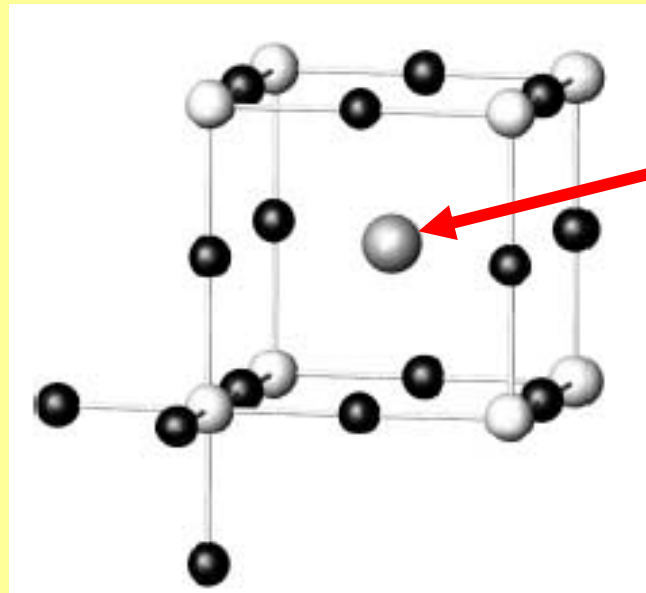(e.g., Hg^{2+} and Ag$^+$) = soft Lewis acids

MoS$_2$ nanosheets
- high adsorption capacity - abundant sulfur adsorption sites
- fast kinetics - easy access to adsorption sites

3D Intercalation Compounds

Cu$_3$N and Mn$_3$N crystallize in the (anti-) ReO$_3$-type structure

the large cuboctahedral void in the structure can be filled
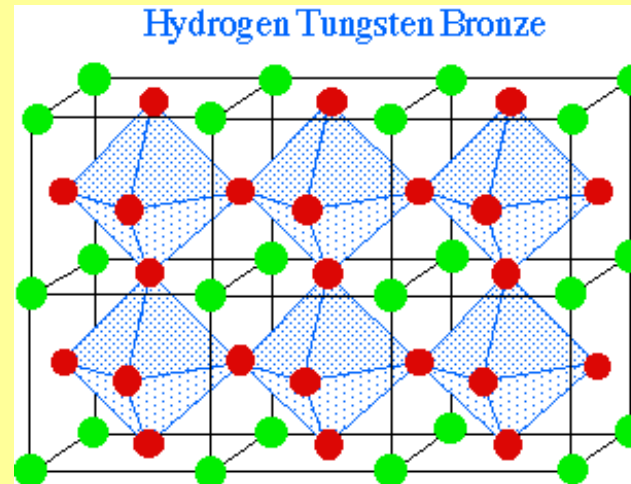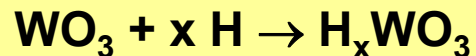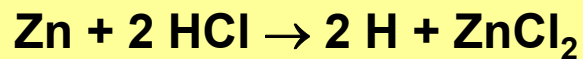
By Pd to yield (anti-) perovskite-type PdCu$_3$N

By M = Ga, Ag, Cu leading to MMn$_3$N

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

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

$$WO_3 + x\ H \rightarrow H_xWO_3$$

Hydrogen Tungsten Bronze

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

$K_3 C_{60}$

K
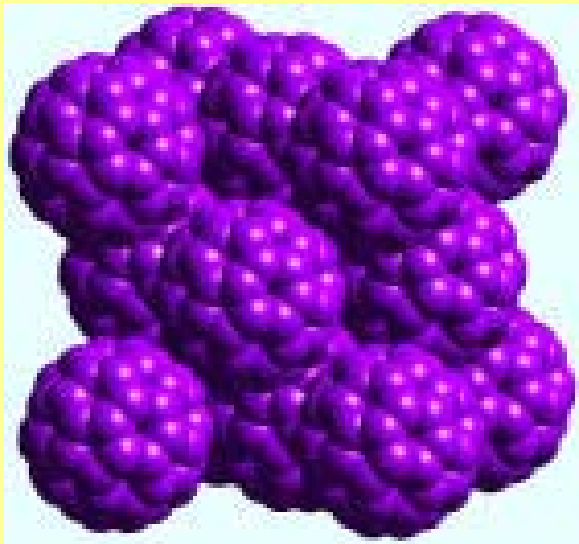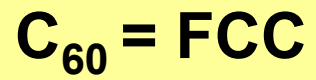
Octahedral voids (N)
Tetrahedral voids (2N)