TENTATIVE LECTURE SCHEDULE

		Date	Topic
1.	Mon	13.09.	Course Introduction & Short Review of the Elements
2.	Wed	15.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	17.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Mon	20.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Wed	22.09.	Transition Metals: General Aspects & Pigments
6.	Mon	27.09.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
7.	Wed	29.09.	Redox Chemistry
8.	Mon	04.10.	Crystal Field Theory
9.	Wed	06.10.	V, Nb, Ta & Metal Complex & POM, MOF, MLD
10.	Fri	08.10.	Cr, Mo, W & 2D materials
11.	Mon	11.10.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
12.	Wed	13.10.	EXTRA
13.	Fri	15.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Mon	18.10.	Lanthanoids + Actinoids & Luminescence (Down/Upconversion)
15.	Wed	20.10.	Inorganic Materials Chemistry Research

EXAM: Thu Oct. 28, 2021

QUESTIONS: Lecture 10

Name your file Exe-10-Familyname; Return by noon next day into MyCourses drop-box

1. **Explain why K_2CrO_4 is colorful even though hexavalent Cr does not have d electrons. Give another example of the same phenomenon.**

2. **Give three examples of interesting 2D materials; motivate your choices.**

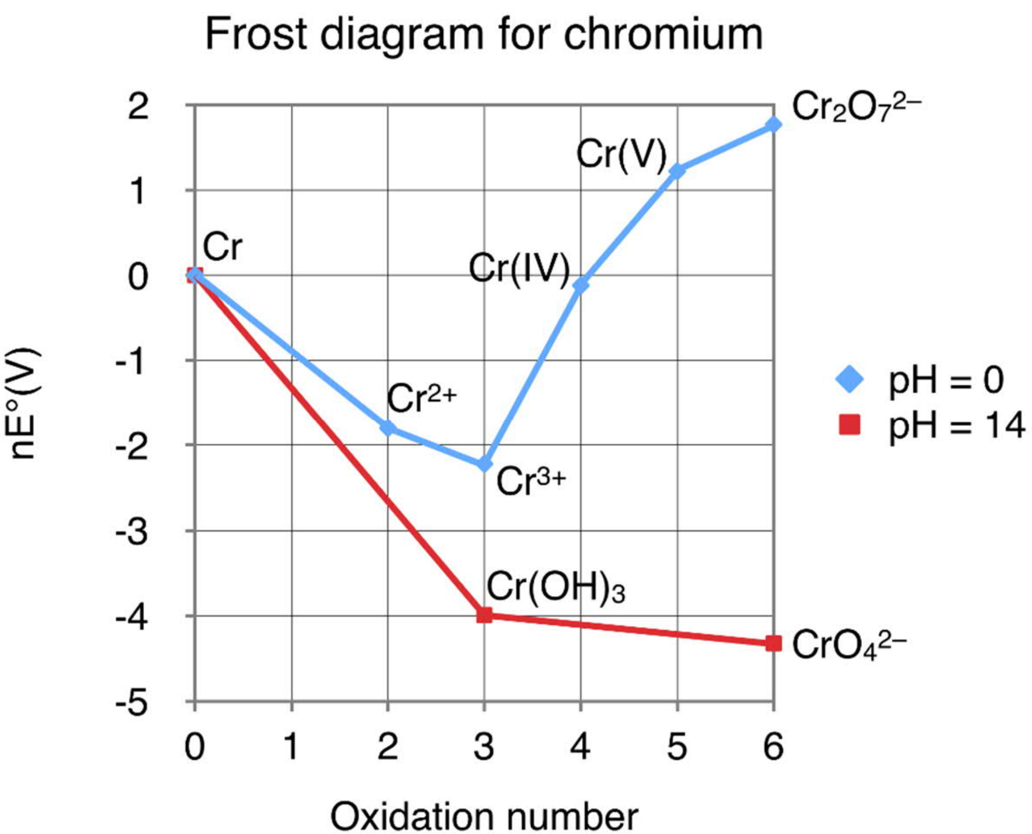
3. **From your opinion, what is the main advantage of the ALD/MLD technique over conventional solution-based techniques in precise “layer-engineering” of inorganic-organic multi-layer structures? Please elaborate your answer with few sentences of explanation.**

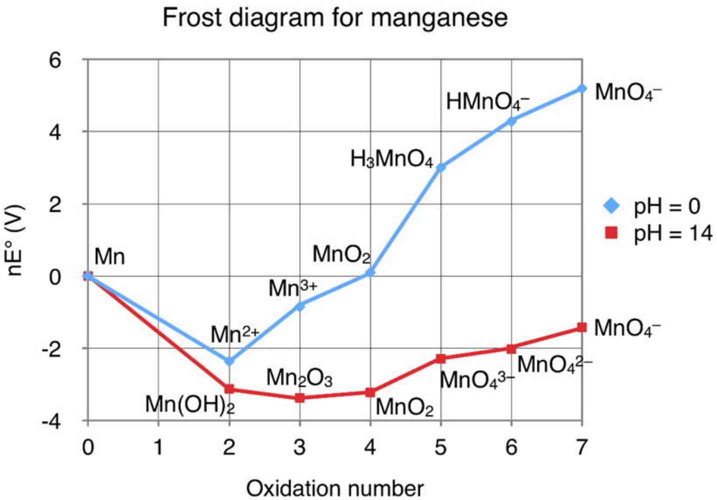
PRESENTATION TOPICS/SCHEDULE

Wed	06.10.	Nb:	Toivonen
Fri	08.10.	Mo:	Ahmed, Shamshad
Mon	11.10.	Mn:	Majaniemi, Thakur, Ahkiola
		Ru:	Ichanson, Locqueville, Olsio
Wed	13.10.	Co:	Ekholm, Olander, Syväniemi
		Cu:	Kolawole, Nguyen, Munib
Fri	15.10.	In:	Kovanen, Ogunyemi, Svinhufvud
		Te:	Huhtakangas, Wallin, Kaarne
Mon	18.10.	Eu:	Sonphasit, Tuisku
		Nd:	Jussila, Siuro, Perttu
		U:	Sinkkonen, Wennberg, Partanen

CHROMIUM (ref. Mn): OXIDATION STATES

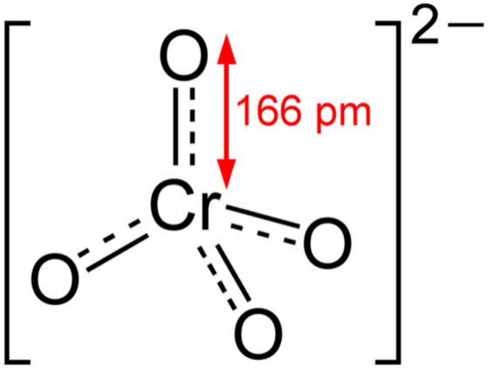
- **Chromium:** **VI: stable (chromate and tendency towards polychromates)**
  V and IV: unstable (disproportionate)
  III: most stable
  II: strong reducing agent

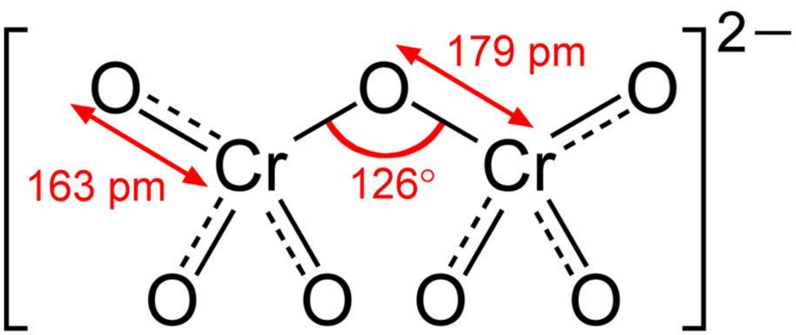


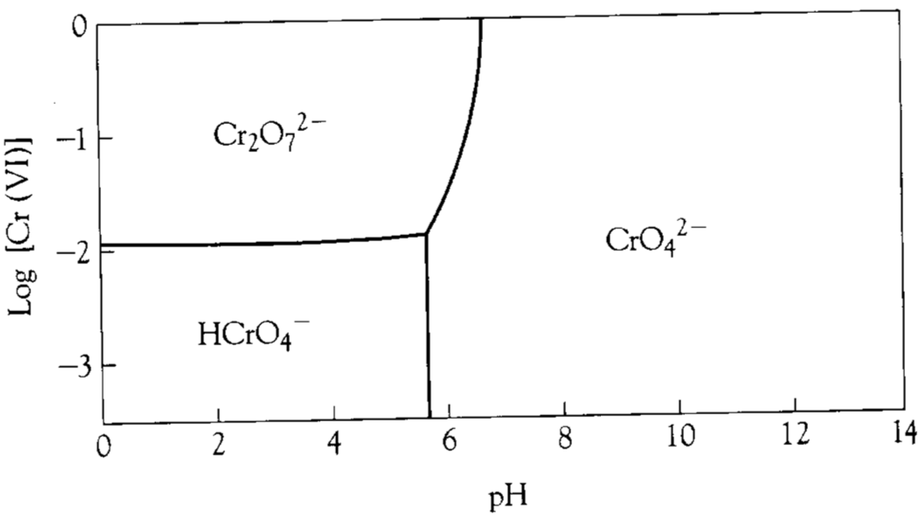


CHROMATE

- potassium chromate K_2CrO_4
- lead chromate $PbCrO_4$
- strong oxidizers, carcinogens
- Ehat is the reason for the colour?
- Electron transfer reaction: Cr(VI)-O(-II) → Cr(V)-O(-I)
- $2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$

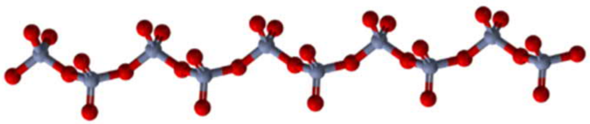






Chromium trioxide

- Strong oxidizer (oxygen source)
- Carcinogen
- Used for chrome plating
- 1D chain structure
- CN(Cr) = 4



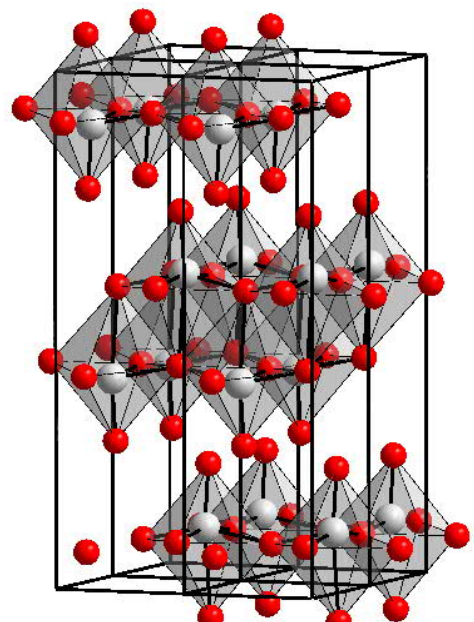
"Halfmetal" for SPINTRONICS: Electrical conductor & ferromagnet

OXIDES

Oxidation state:	+6	Intermediate	+4	+3
Cr	CrO_3	Cr_3O_8, Cr_2O_5, Cr_5O_{12}, etc.	CrO_2	Cr_2O_3
Mo	MoO_3	Mo_9O_{26}, Mo_8O_{23}, Mo_5O_{14}, $Mo_{17}O_{47}$, Mo_4O_{11}	MoO_2	—
W	WO_3	$W_{49}O_{119}$, $W_{50}O_{148}$, $W_{20}O_{58}$, $W_{18}O_{49}$	WO_2	—

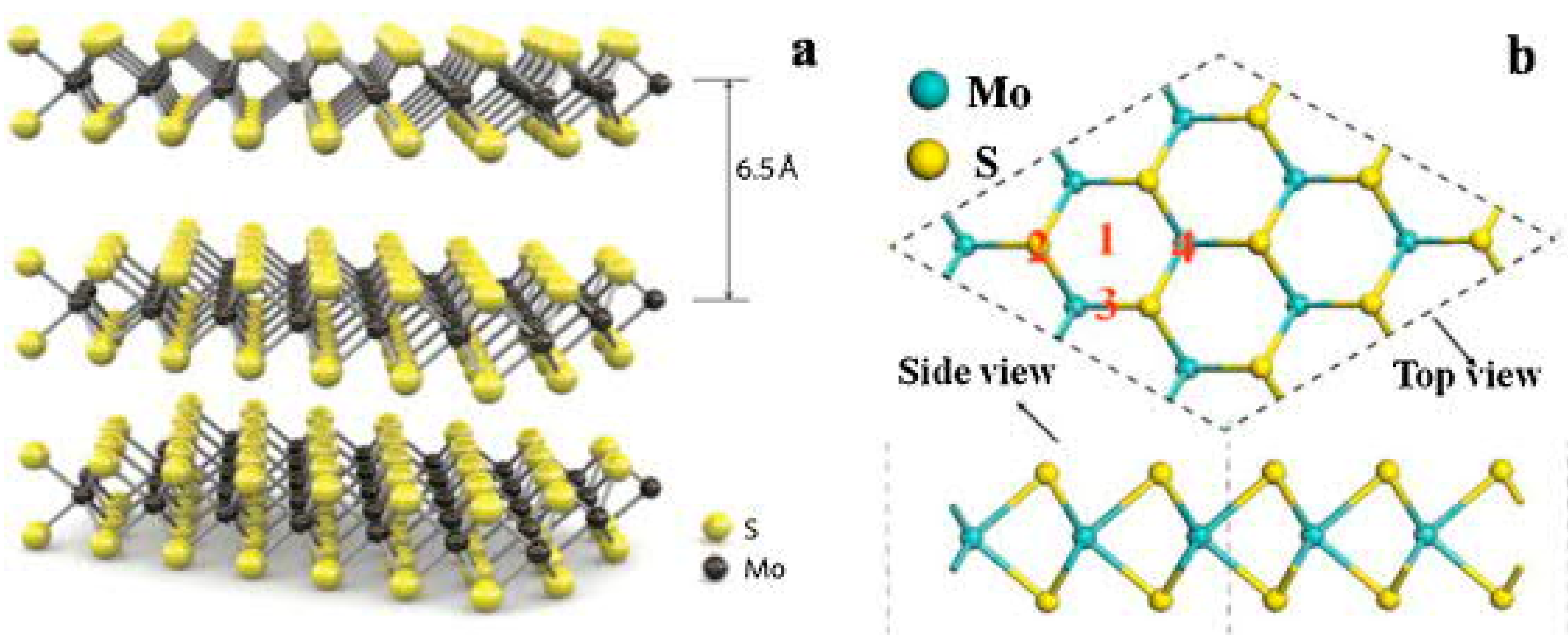
Molybdenum trioxide

- Mineral molybdite is of MoO_3
- Important industrial catalyst
- 2D structure → **Van der Waals gap**
- CN(Mo) = 6

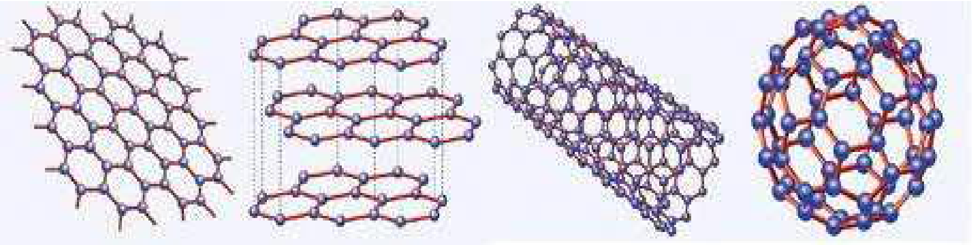


Another 2D Structure: CHALCOGENIDES (S, Se, Te)

- Natural mineral molybdenite MoS_2 (similar to e.g. TiS_2)



GRAPHENE



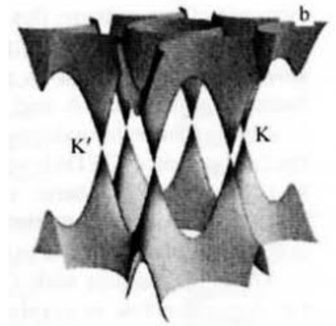
- **Monolayer of graphite or a giant PAH molecule**
  (*polycyclic aromatic hydrocarbon*; the largest known PAH molecule consists of 10 C_6-rings)
- **sp^2-hybridization, C-C bond length 1.42 Å**
- **Thinnest (but strongest) material known**
- **Best electrical conductor (at room temperature)**
- **Electrons in graphene:**
  - **behave like wave motion**
  - **move like having zero mass**
  - **move faster than in any other material**
  - **do not scatter from impurities**

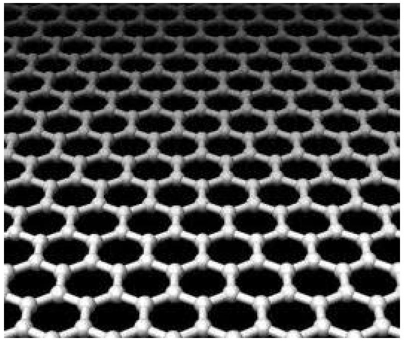
  → is graphene going to replace silicon in next-generation electronics ?
- **The unique properties of graphene were predicted already before it was first prepared in 2004** [Novoselov, Geim, *et al*., *Science* 306, 666 (2004)]; **Nobel 2010**

Graphene

- **Unusual electronic properties**

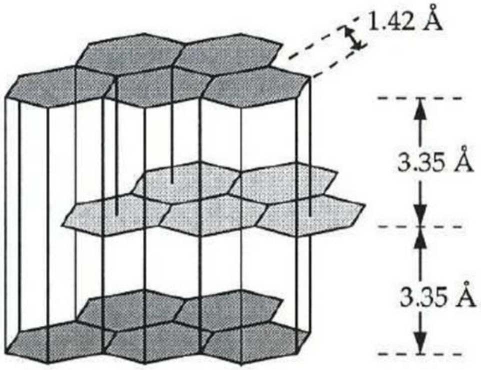
band-structure of graphene

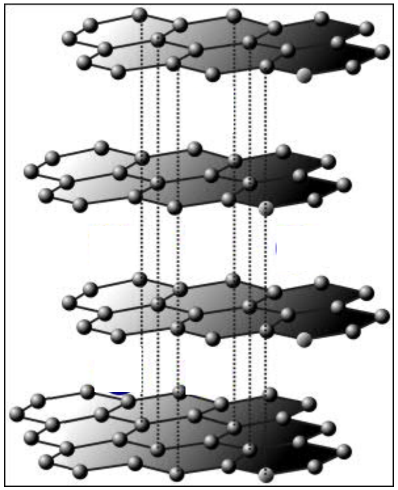




Graphite

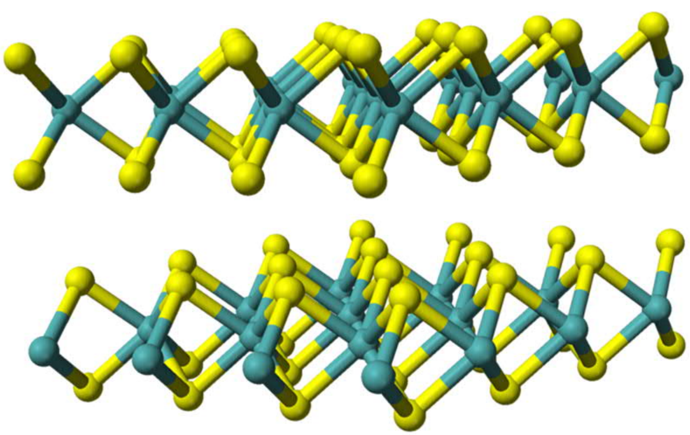
- **Weak (van der Waals) bonds between the layers**
- **Solid lubricant**



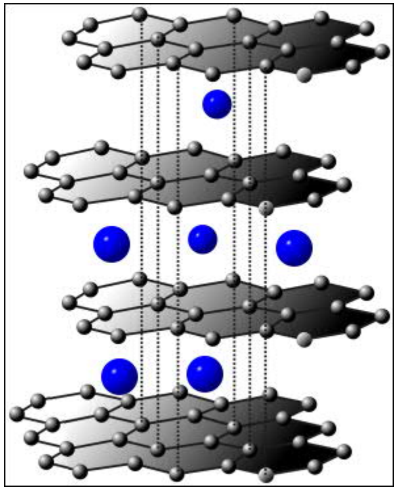


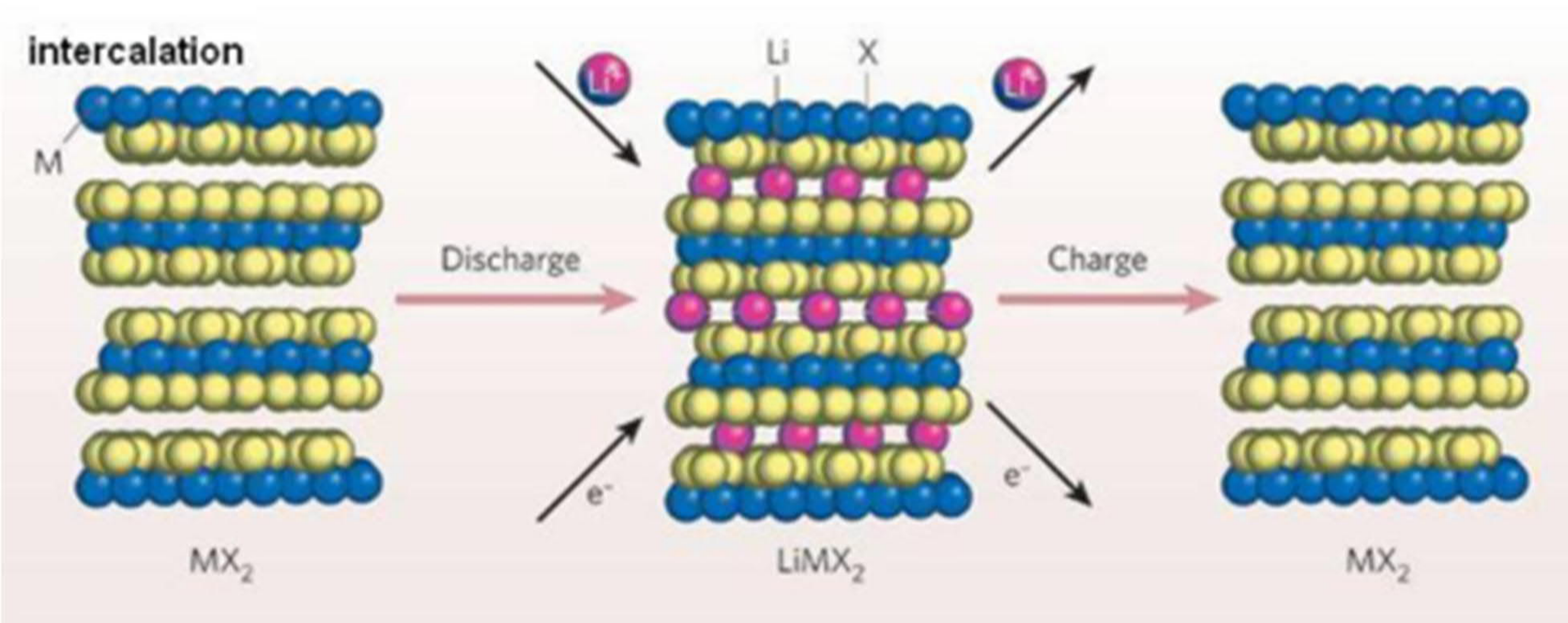
MoS_2

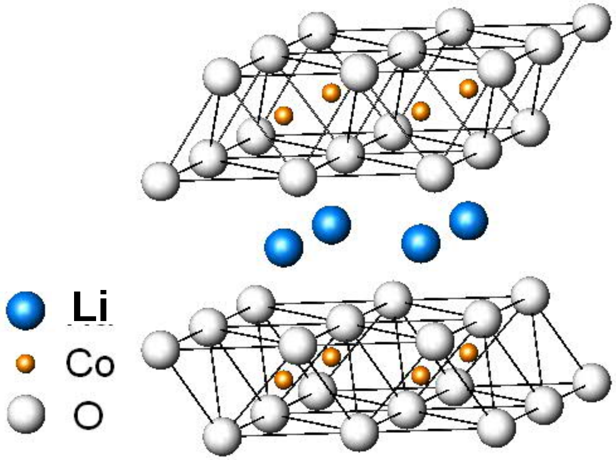
- **Similar to graphite**
- **Band-gap**
- **Solid lubricant**



INTERCALATION




intercalation
M
Discharge
Li
X
e⁻
Charge
MX2
LiMX2
MX2



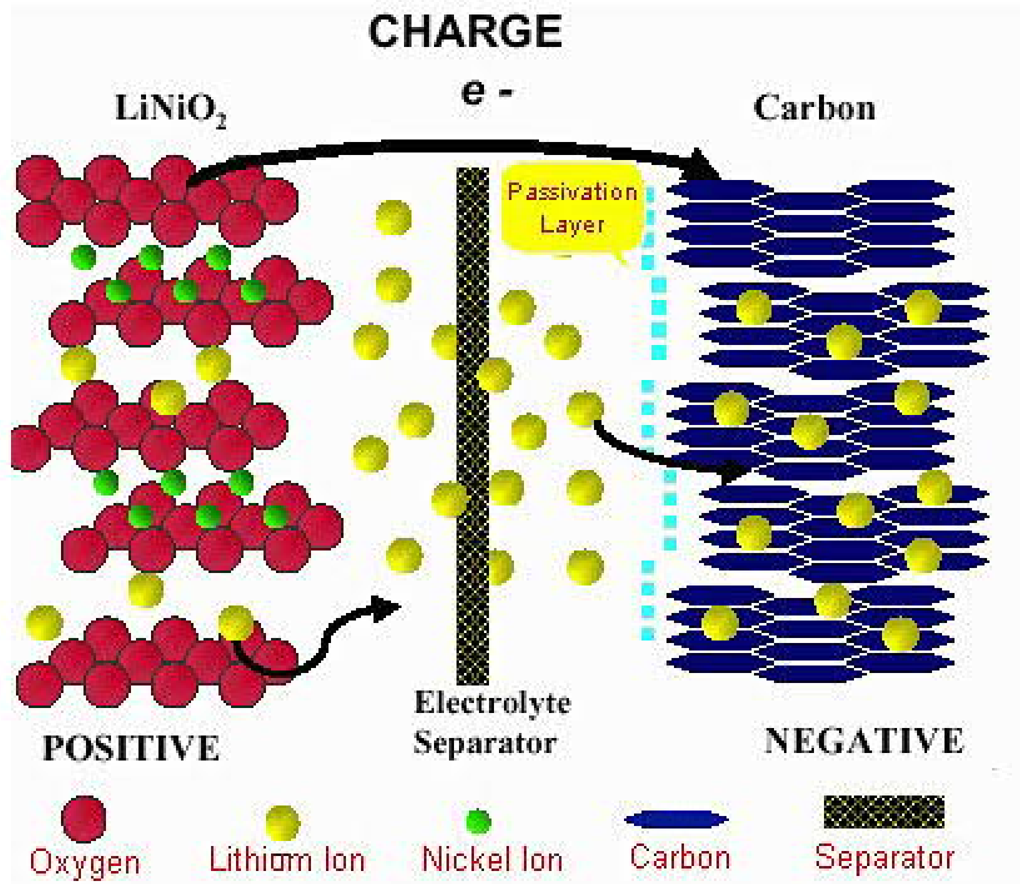
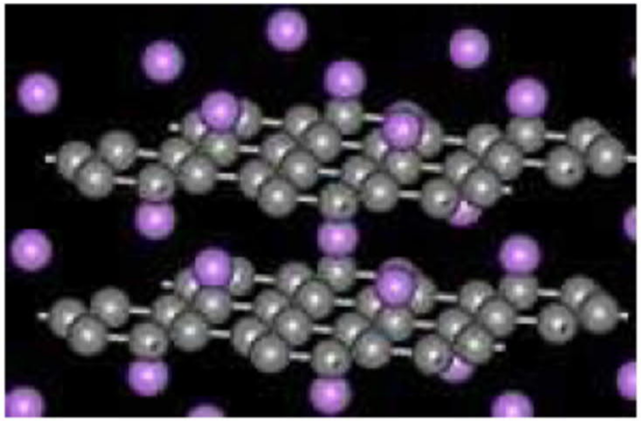


Photo Courtesy of SAFT America

Calcium graphite: CaC_6

The graphite interlayer distance increases upon Ca intercalation from 3.35 to 4.524 Å, and the carbon-carbon distance from 1.42 to 1.444 Å.



Among the superconducting graphite intercalation compounds, CaC_6 exhibits the highest critical temperature Tc = 11.5 K, which further increases under applied pressure (15.1 K at 8 GPa)

Superconductivity in 2-layer graphene with different intercalants

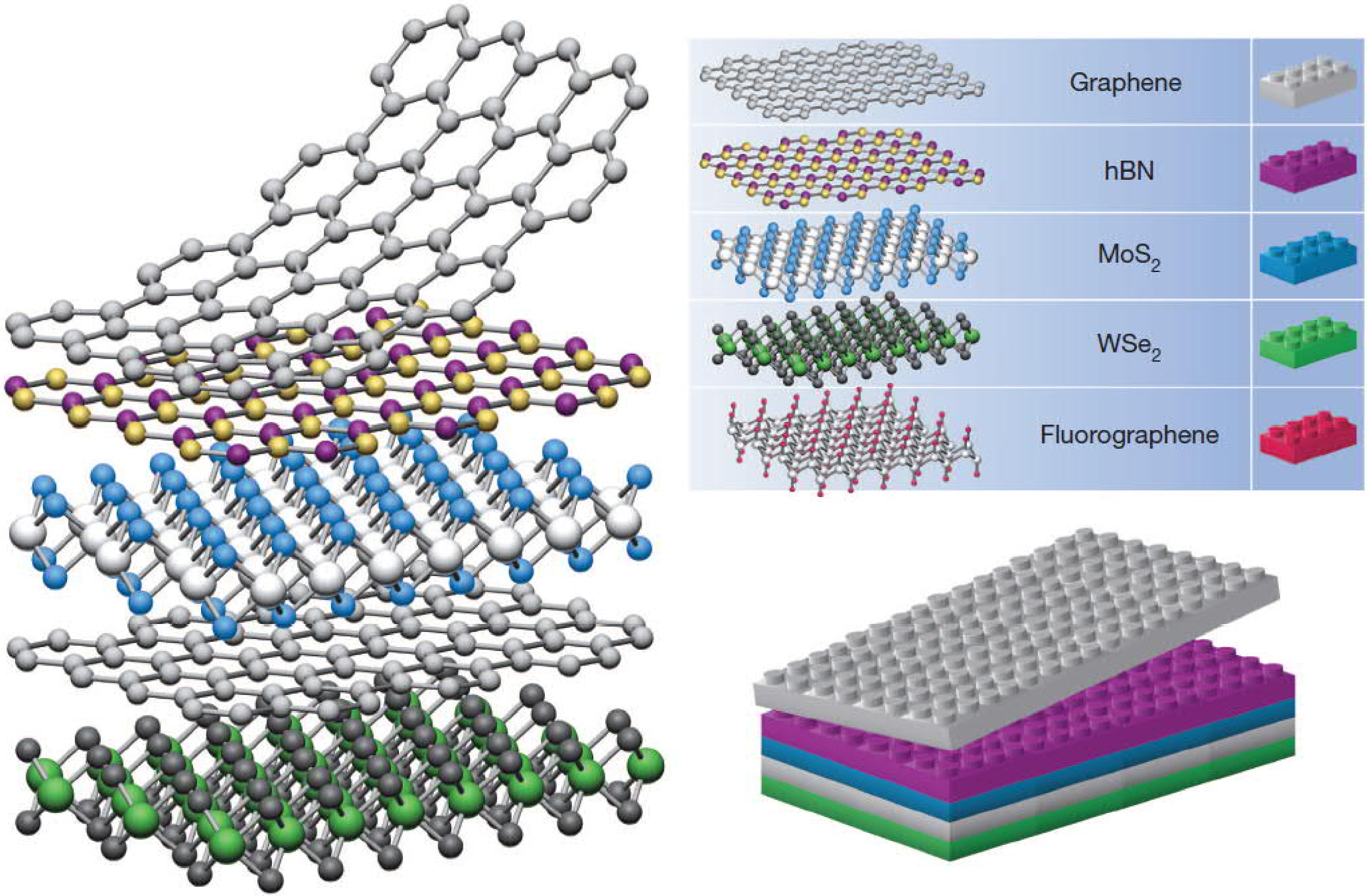
	$\lambda\omega_D/\varepsilon_F$	T_c (K)	$\Delta(0)$ (meV)	$2\Delta(0)/k_B T_c$
C_6KC_6	0.079	8.2	1.38	3.91
C_6CaC_6	0.081	14.0	2.46	4.08
C_6RbC_6	0.093	5.5	0.87	3.67
C_6SrC_6	0.062	8.5	1.41	3.85

NANOSHEET MATERIAL LIBRARY

BLUE: stable in air
GREEN: probably stable in air
PINK: unstable in air but stable in an inert atmosphere
GREY: made but no other details known

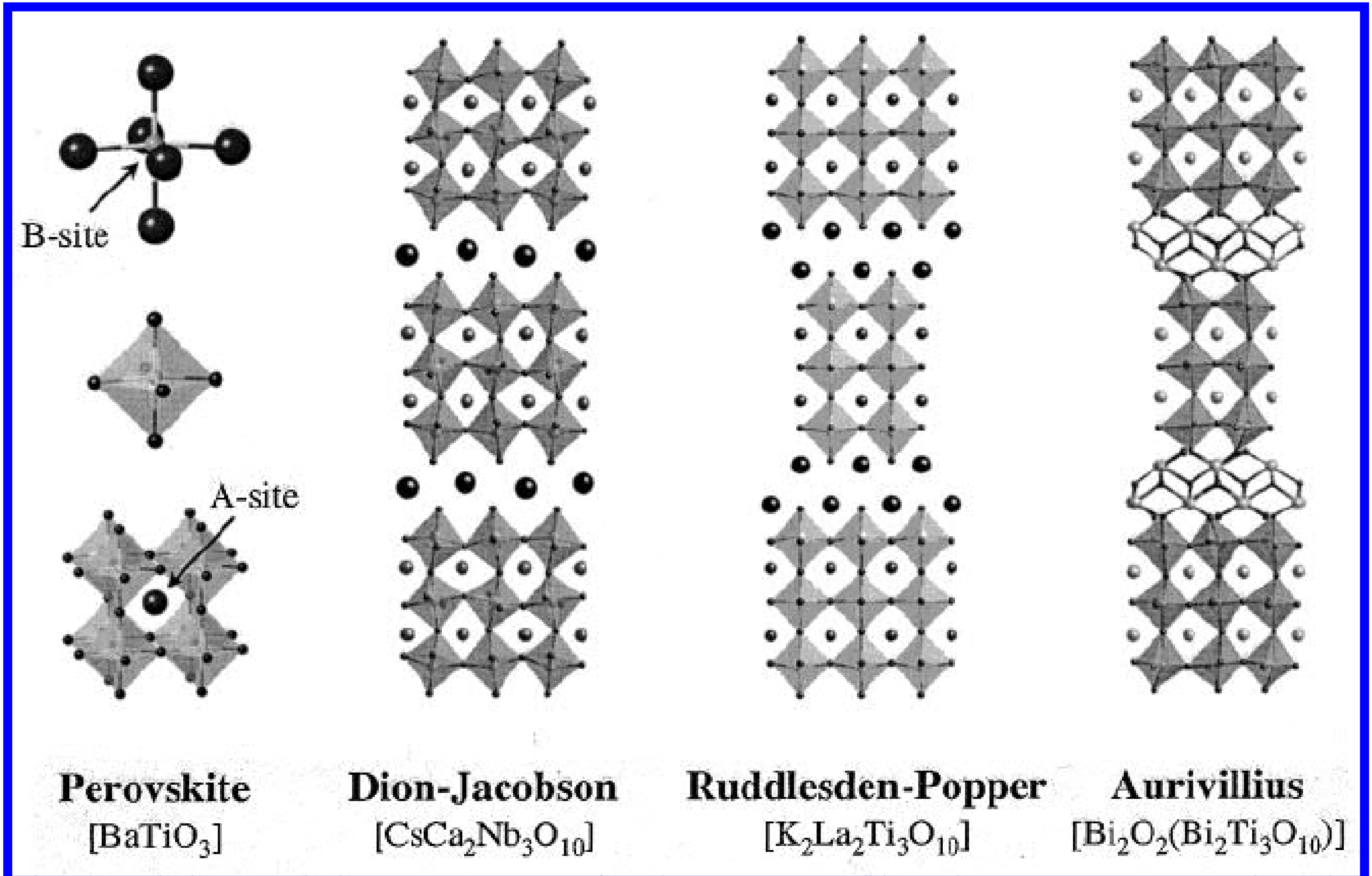
<table>
<tr><td>Graphene family</td><td>Graphene</td><td>hBN ‘white graphene’</td><td>BCN</td><td>Fluorographene</td><td>Graphene oxide</td></tr>
<tr><td rowspan="2">2D chalcogenides</td><td rowspan="2">MoS_2, WS_2, $MoSe_2$, WSe_2</td><td rowspan="2">Semiconducting dichalcogenides: $MoTe_2$, WTe_2, ZrS_2, $ZrSe_2$ and so on</td><td colspan="3">Metallic dichalcogenides: $NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$ and so on</td></tr>
<tr><td colspan="3">Layered semiconductors: GaSe, GaTe, InSe, Bi_2Se_3 and so on</td></tr>
<tr><td rowspan="2">2D oxides</td><td>Micas, BSCCO</td><td>MoO_3, WO_3</td><td rowspan="2" colspan="2">Perovskite-type: $LaNb_2O_7$, $(Ca,Sr)_2Nb_3O_{10}$, $Bi_4Ti_3O_{12}$, $Ca_2Ta_2TiO_{10}$ and so on</td><td>Hydroxides: $Ni(OH)_2$, $Eu(OH)_2$ and so on</td></tr>
<tr><td>Layered Cu oxides</td><td>TiO_2, MnO_2, V_2O_5, TaO_3, RuO_2 and so on</td><td>Others</td></tr>
</table>

NANO-LEGO GAME

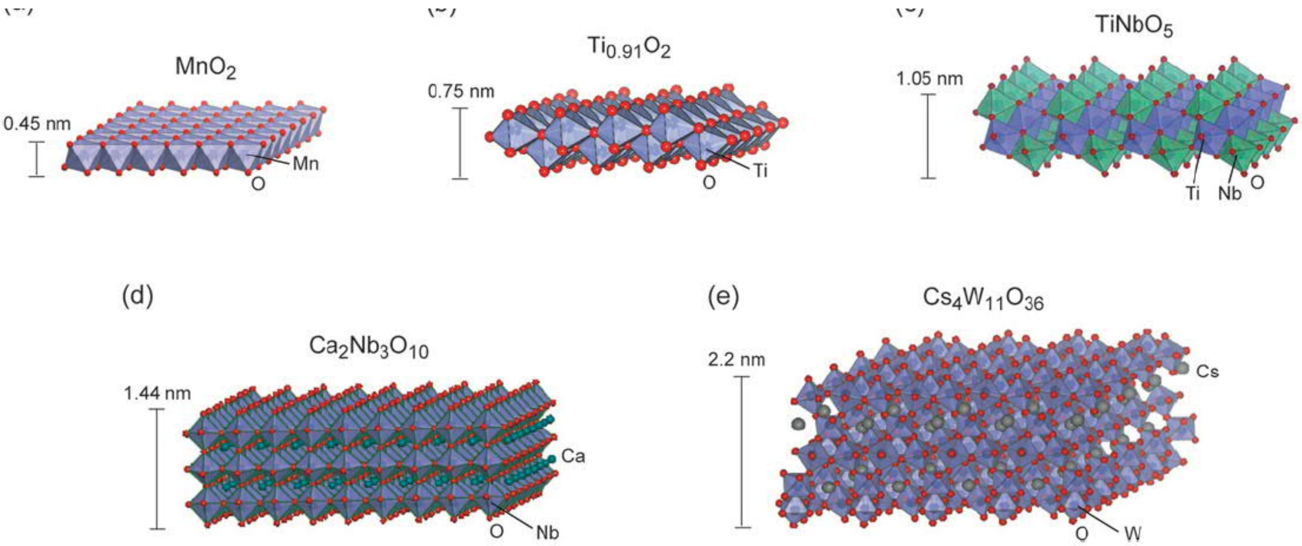


A.K. Geim & I.V. Grigorieva, Van der Waals heterostructures, *Nature* **499**, 419 (2013).

Multilayered oxide structures …



OXIDE NANOSHEETS



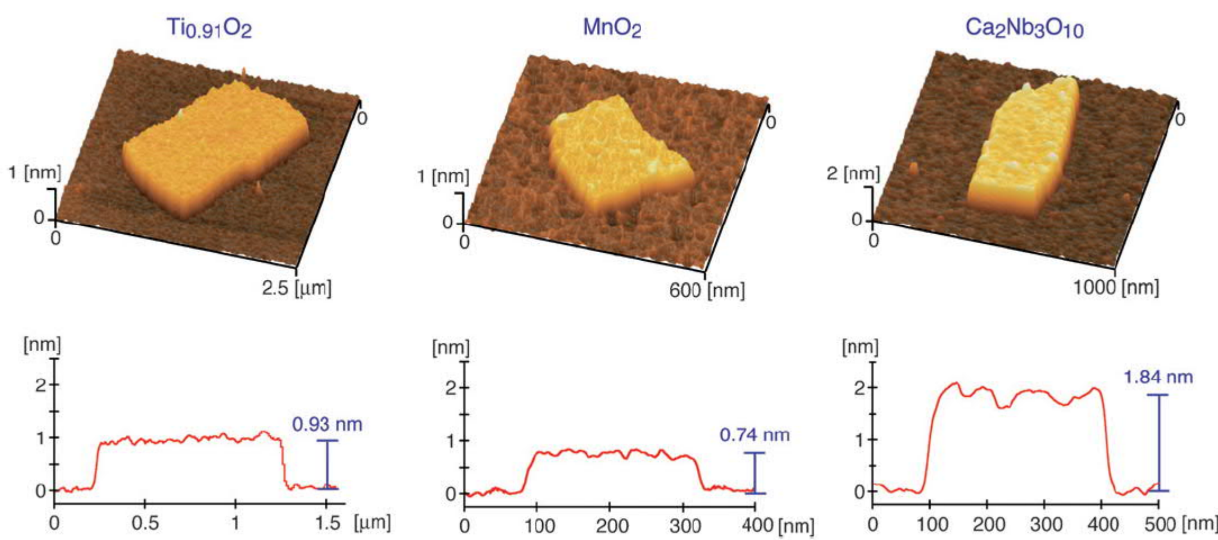
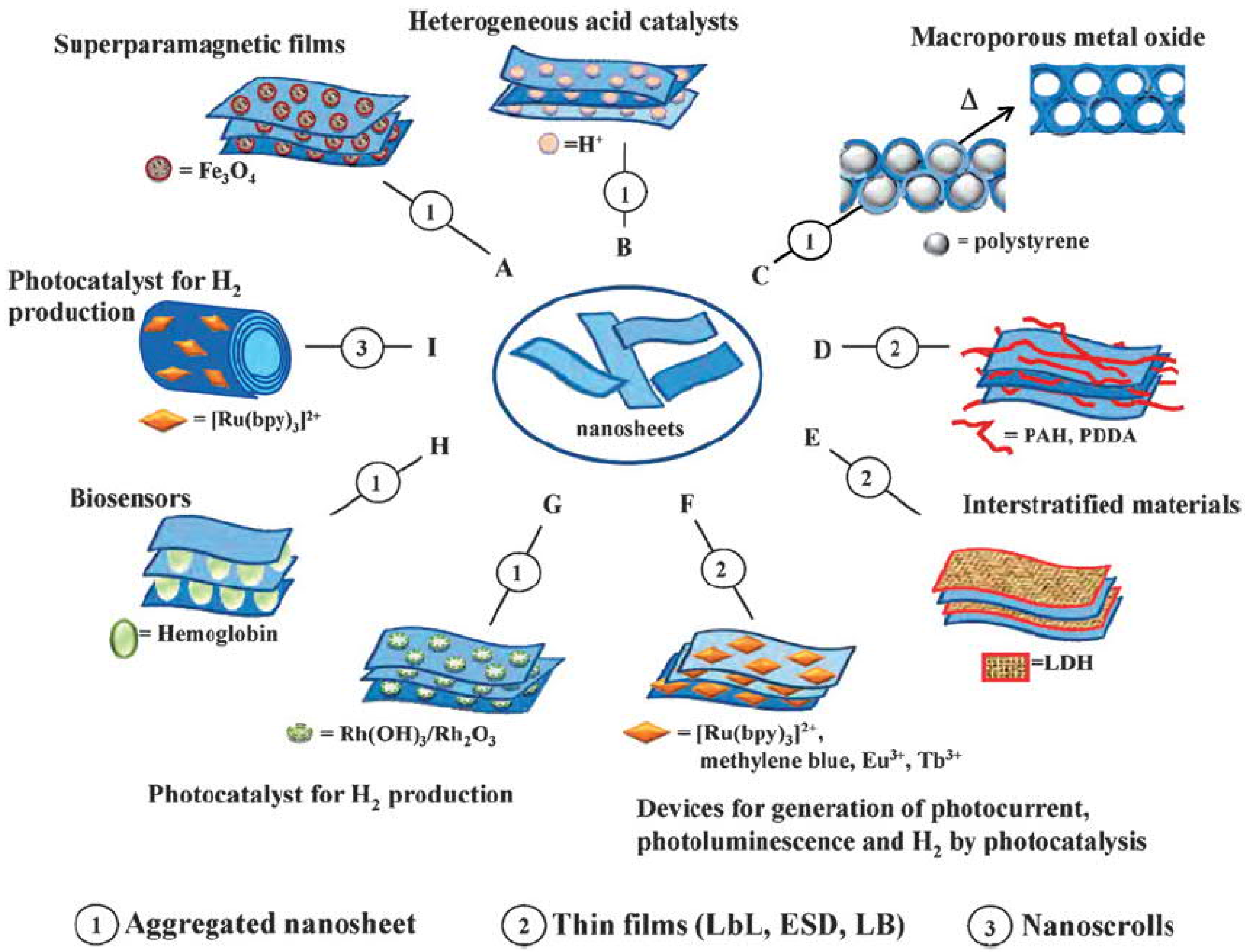
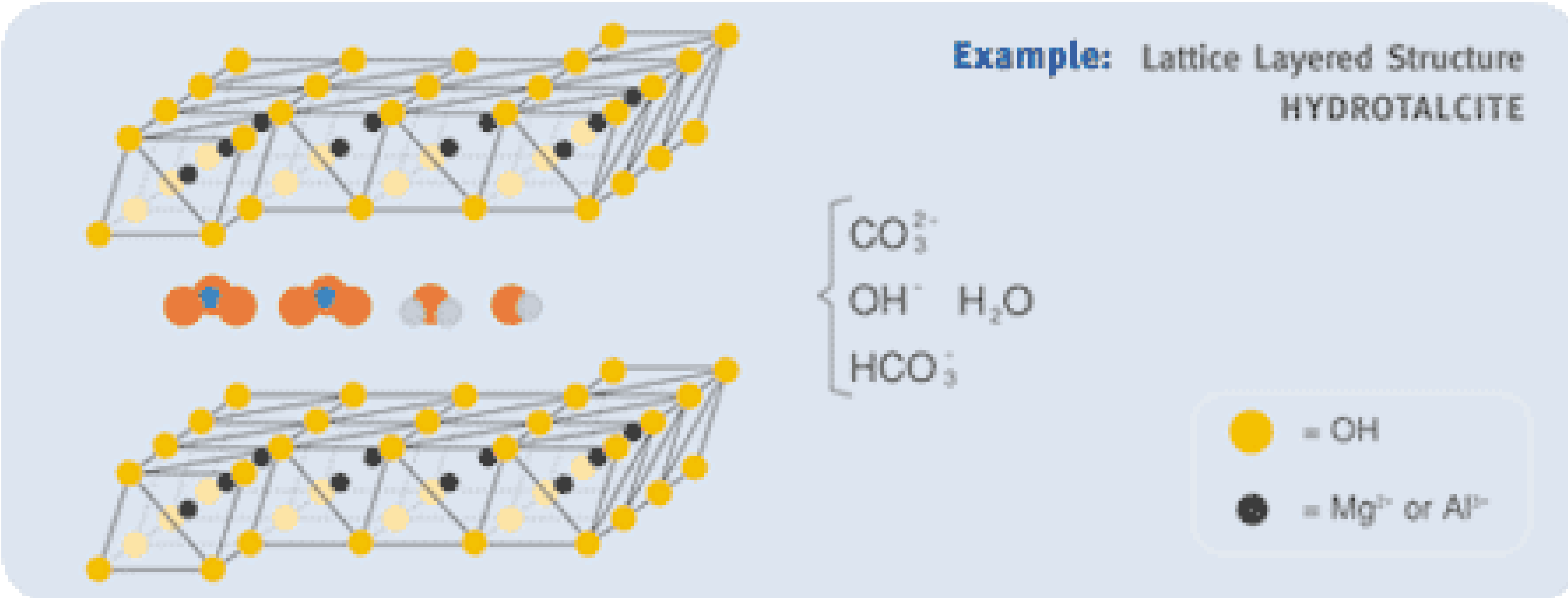


Fig. 2 AFM images of $Ti_{0.91}O_2$, MnO_2 and $Ca_2Nb_3O_{10}$ nanosheets. A tapping-mode AFM (SII nanotech E-Sweep) in vacuum conditions was used to evaluate the morphology of the nanosheets on Si substrates. Height profiles are shown in the bottom panels.



Scheme 1 Niobate nanosheets as building blocks for materials assembly (reproduced from the Feature Article of Bizeto, Shiguihara and Constantino).

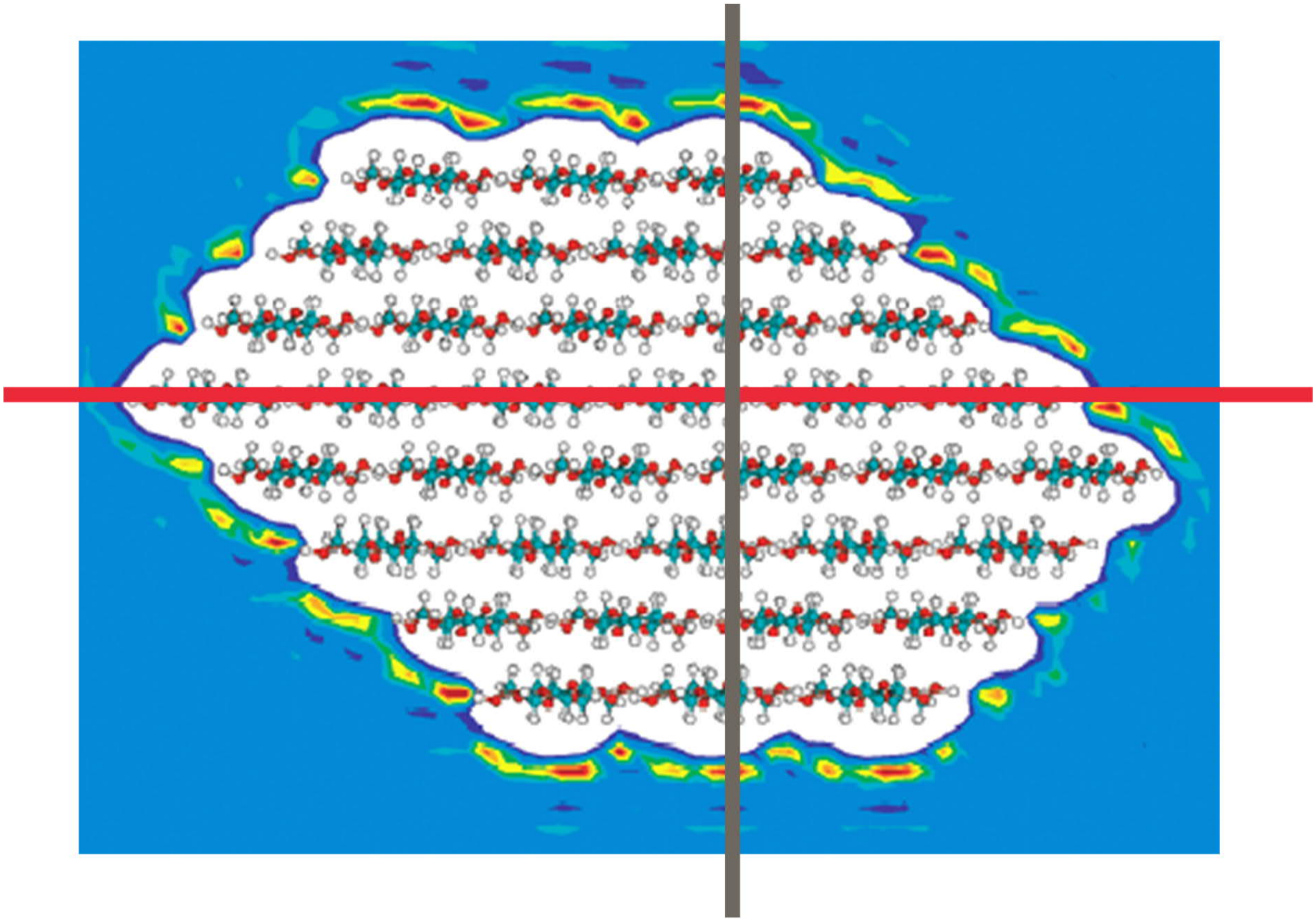
L. Wang & T. Sasaki, Titanium oxide nanosheets: graphene analogues with versatile functionalities, *Chem. Rev.* 114, 9455 (2014).

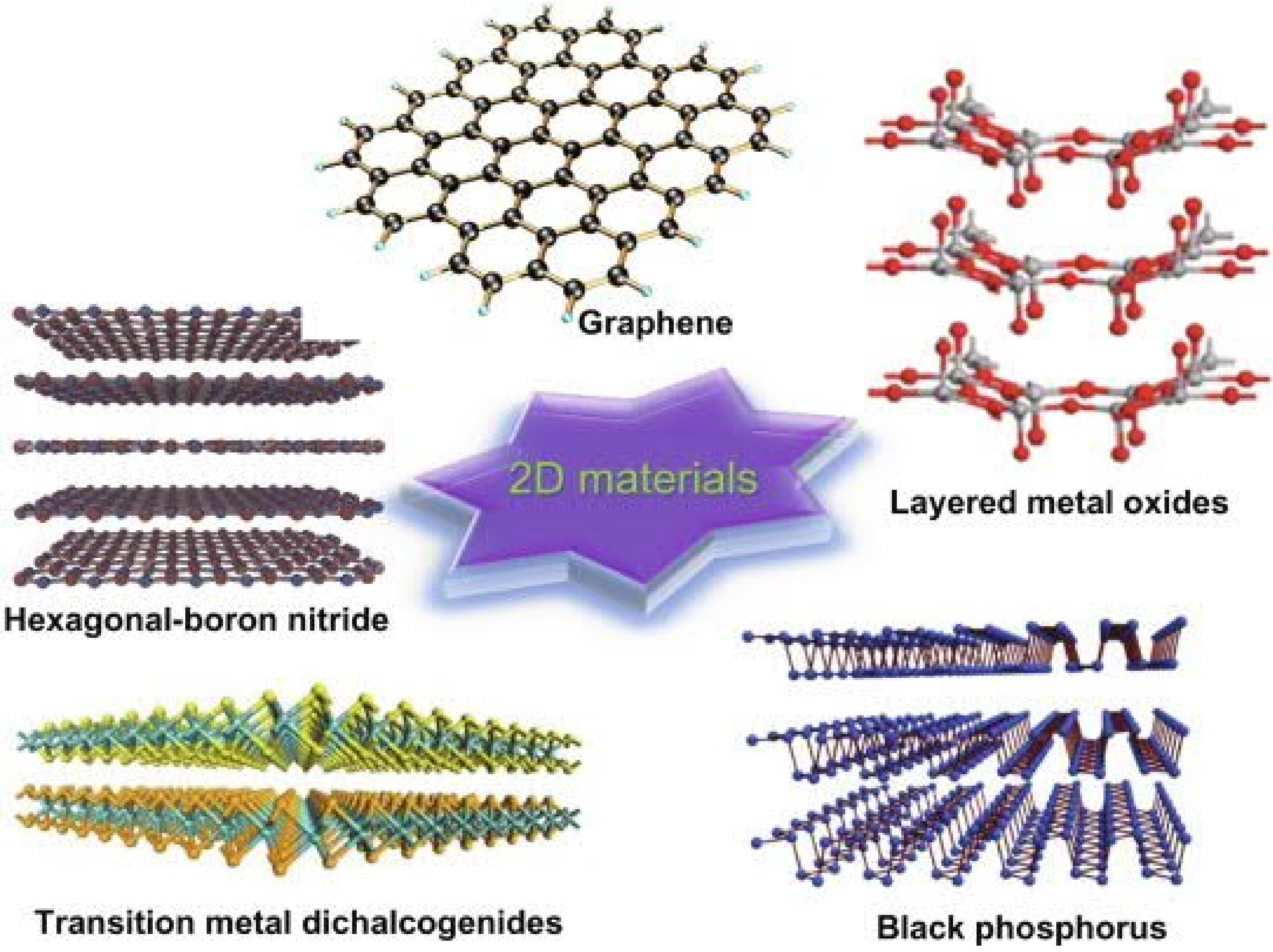


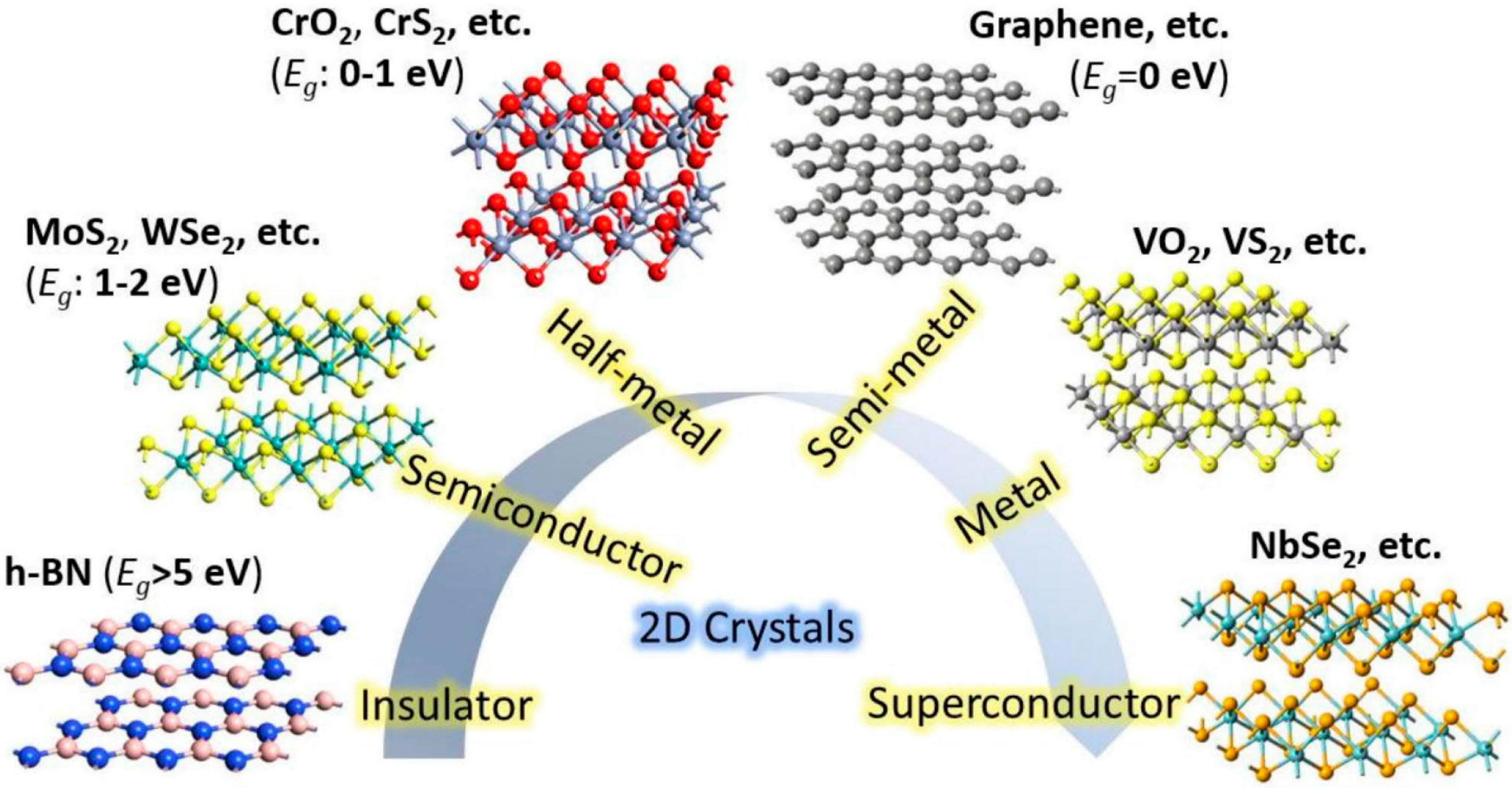
Hydrotalcite $Al_2Mg_6(OH)_{16}CO_3 \cdot x H_2O$

- Multilayered crystal structure
- Natural clay
- Name derived from its resemblance with talc and its high water content
- Reacts rapidly with gastric acid even in the presence of pepsin and proteins
- Variety of pharmaceutical applications

Nanocellulose microfibril shows some analogy to van der Waals solids: strong H-bonds laterally (red), weak van der Waals bonds vertically (brown)



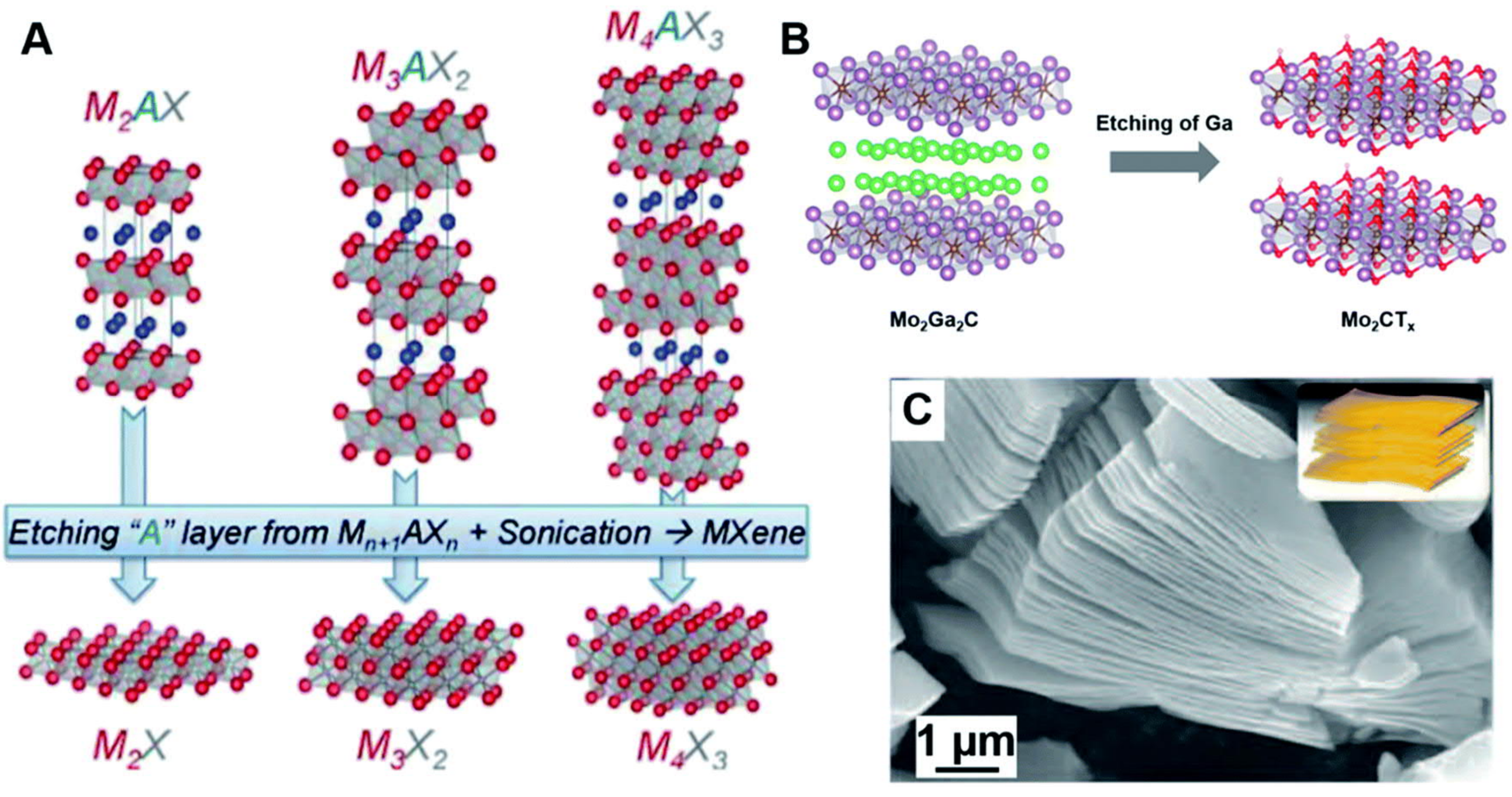

Graphene
Layered metal oxides
2D materials
Hexagonal-boron nitride
Transition metal dichalcogenides
Black phosphorus



CrO2, CrS2, etc.
(Eg: 0-1 eV)
Graphene, etc.
(Eg=0 eV)
MoS2, WSe2, etc.
(Eg: 1-2 eV)
VO2, VS2, etc.
Half-metal
Semi-metal
Semiconductor
Metal
NbSe2, etc.
h-BN (Eg>5 eV)
2D Crystals
Insulator
Superconductor

MXenes

- New (discovered 2011) class of inorganic 2D materials
- Transition metal carbides, nitrides or carbonitrides
- Made from MAX ($M_{n+1}AX_n$) ceramics, e.g. $Ti_3AlC_2 \rightarrow Ti_3C_2$
- Metallic conductivity (from transition metal carbide/nitride) plus specific surface features (due to differently terminated surfaces or grafted functional groups)
- Application potential: batteries, catalysis, water purification, etc.



2D MATERIALS & NANOSHEETS

- Properties of nanosheets different from those of the same material in bulk
- Unusual phenomena due to the confinement of charge and heat transport

HOW TO MAKE NANOSHEETS

Layered van der Waals solids

- Exfoliation
  - Mechanically (Scotch tape technique)
  - Chemically (dispersing in a solvent with surface tension)
  - Through intercalation + dispersion in polar solvent

Layered ionic solids

- Exhange of ions with bulky organic ions + dispersion

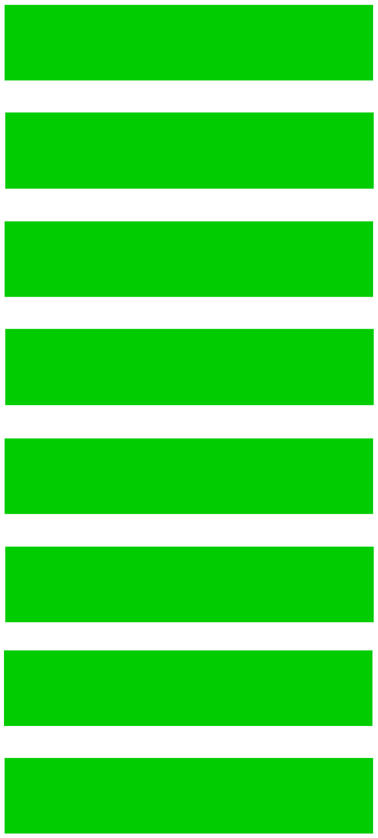
Bottom-up synthesis

- Growing from gas phase on a proper substrate

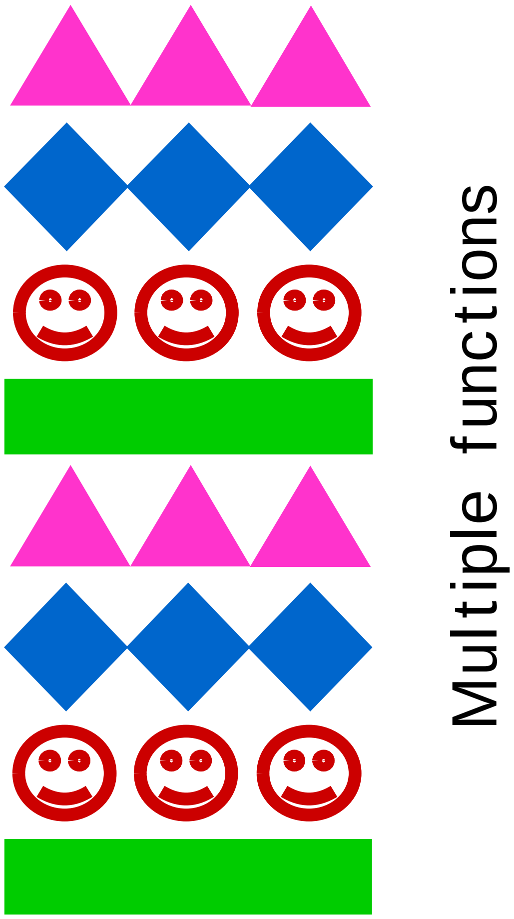
HOW TO VERIFY THE NANOSHEETS

- AFM (Atomic force microscopy)
- Raman spectroscopy
- TEM, STEM, SAXS

Layer-Engineering

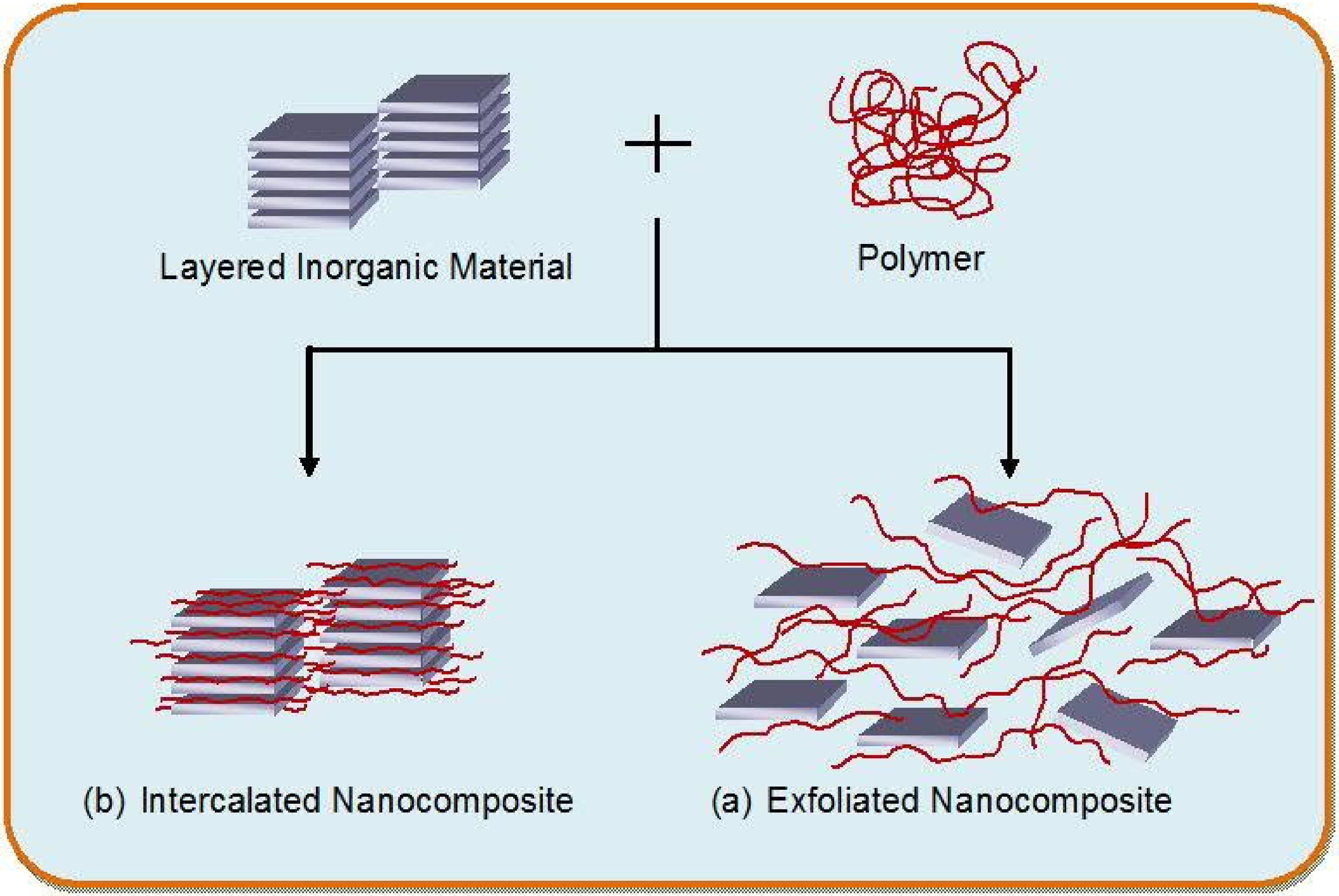


Layered material



Multilayered material

(MULTI)LAYERED INORGANIC-ORGANIC MATERIALS



Multilayered Inorganic-Organic Hybrids

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Flexible thermoelectric foil for wearable energy harvesting

Chunlei Wan[a,*], Ruoming Tian[b], Azrina Binti Azizi[c], Yujia Huang[a], Qingshuo Wei[d], Ryo Sasai[e], Soontornchaiyakul Wasusate[e], Takao Ishida[d], Kunihito Koumoto[b,*]

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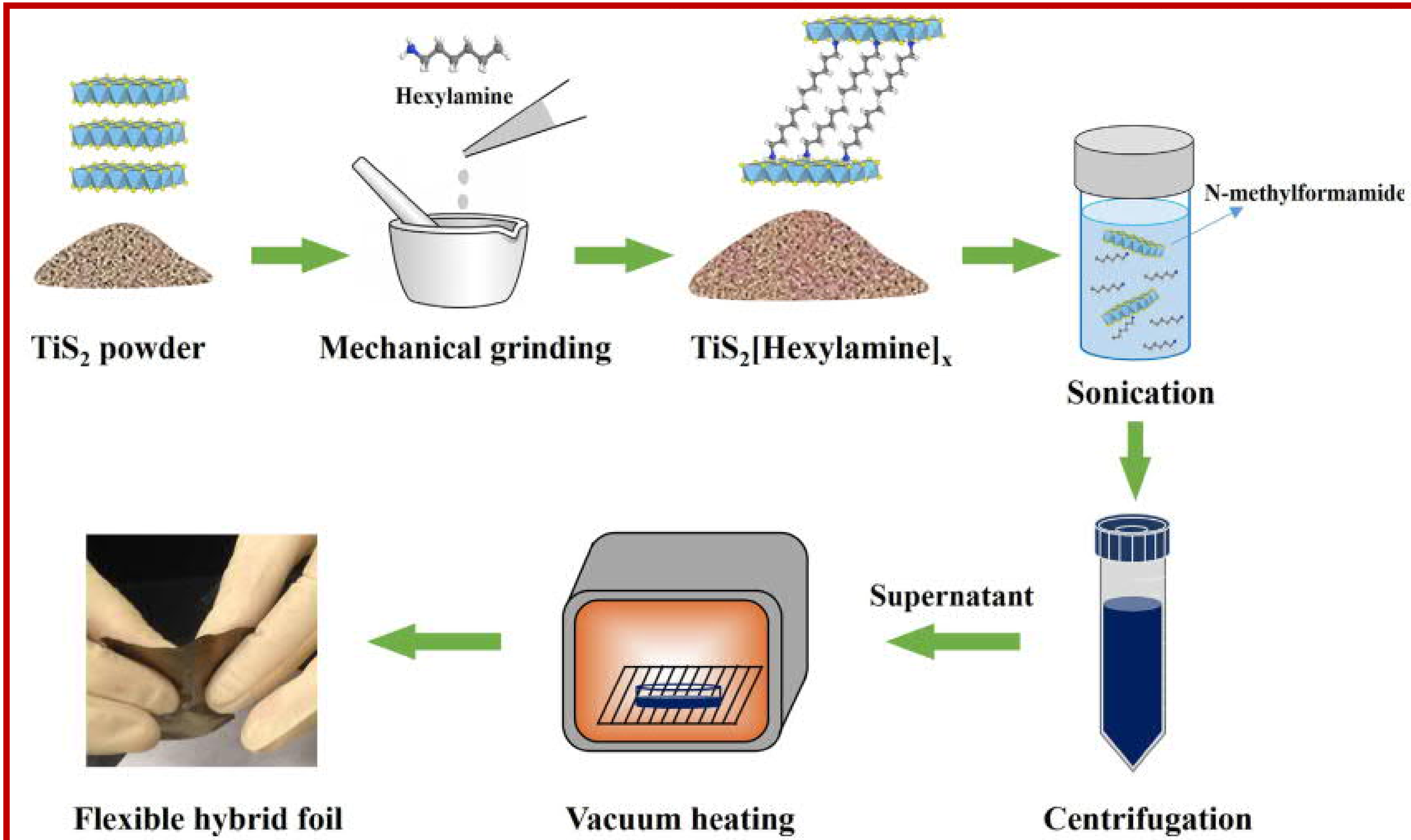

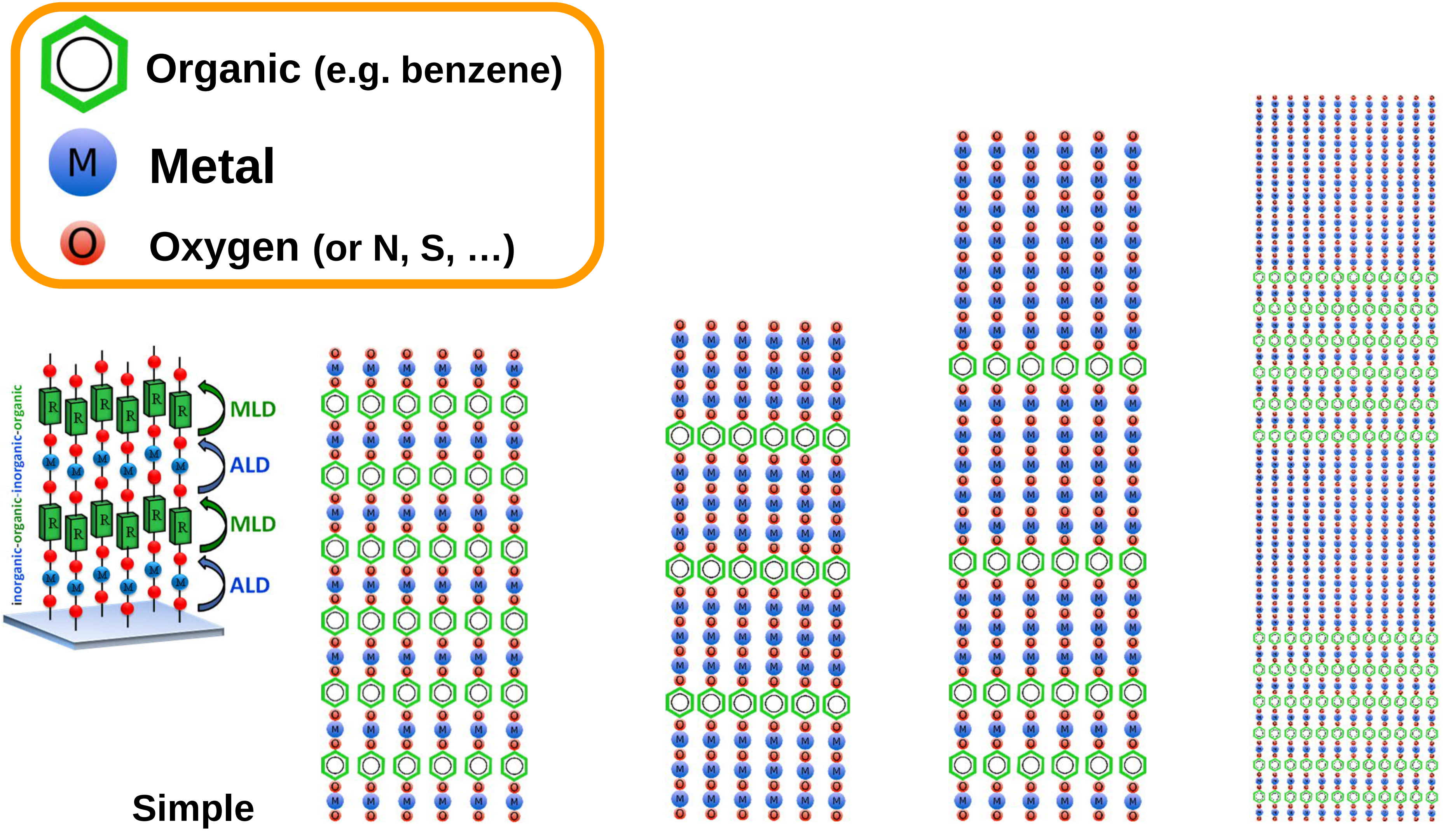

Simple
Metal-Organic Network
(amorphous or crystalline)

Superlattice

Gradient hybrid

Nanolaminate

Aalto University
School of Chemical
Engineering

DIFFERENT LAYER SEQUENCES BY ALD/MLD DESIGN