LECTURE SCHEDULE

	Date		Topic
1.	Wed	28.10.	Course Introduction & Short Review of the Elements
2.	Fri	30.10.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Fri	06.11.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Wed	11.11.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
5.	Fri	13.11.	Redox Chemistry
6.	Mon	16.11.	Transition Metals: General Aspects & Crystal Field Theory
7.	Wed	18.11.	Zn, Ti, Zr, Hf & Atomic Layer Deposition (ALD)
8.	Fri	20.11.	V, Nb, Ta & Metal Complexes and MOFs
9.	Mon	23.11.	Cr, Mo, W & 2D materials
10	Wed	25.11.	Mn, Fe, Co, Ni, Cu & Magnetism and Superconductivity
11.	Fri	27.11.	Resources of Elements & Rare/Critical Elements & Element Substitutions
12.	Mon	30.11.	Lanthanoids + Actinoids & Pigments & Luminescence & Upconversion
13.	Wed	02.12.	Inorganic Materials Chemistry Research

EXAM: Thu Dec 10, 9:00-12:00 (IN ZOOM)

PRESENTATION TOPICS/SCHEDULE

Wed	18.11.	Ti: Ahonen & Ivanoff
Mon	23.11.	Mo: Kittilä & Kattelus
Wed	25.11.	Mn: Wang & Tran
		Ru: Mäki & Juopperi
Fri	27.11.	In: Suortti & Räsänen
		Te: Kuusivaara & Nasim
Mon	30.11.	Eu: Morina
		U: Musikka & Seppänen

QUESTIONS: Lecture 9

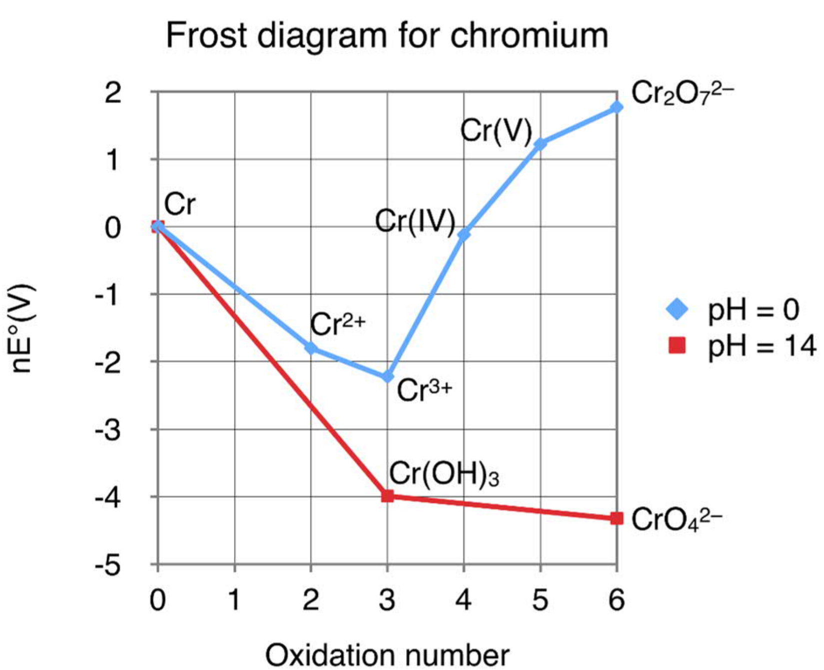
1. Explain why K_2CrO_4 is colorful even though hexavalent Cr does not have d electrons. Give two other examples of the same phenomenon.

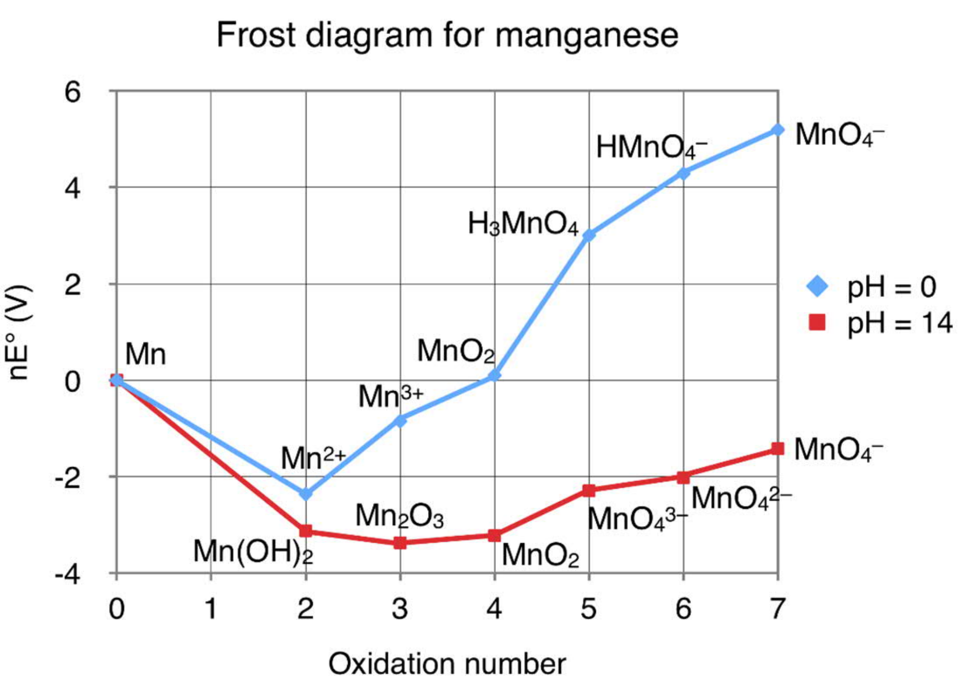
2. Give three examples of typical 2D materials.

3. Explain the concept of “layer-engineering”.

CHROMIUM (ref. Mn): OXIDATION STATES

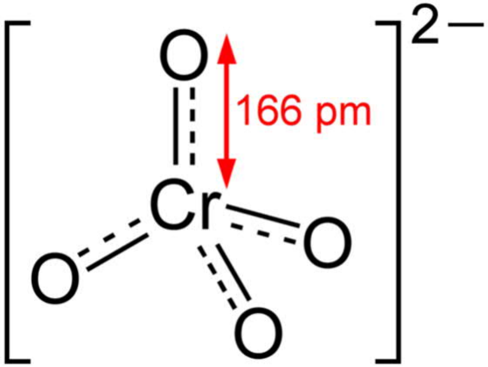
- **Chromium:** **VI: stable (chromate and tendency towards polychromates)**
  V and IV: unstable (disproportionate)
  III: most stable
  II: strong reducing agent

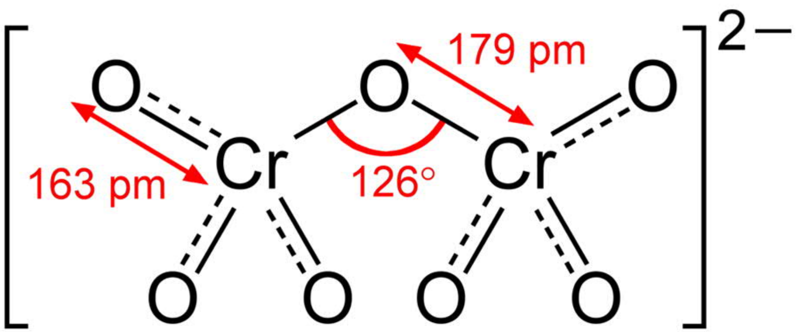


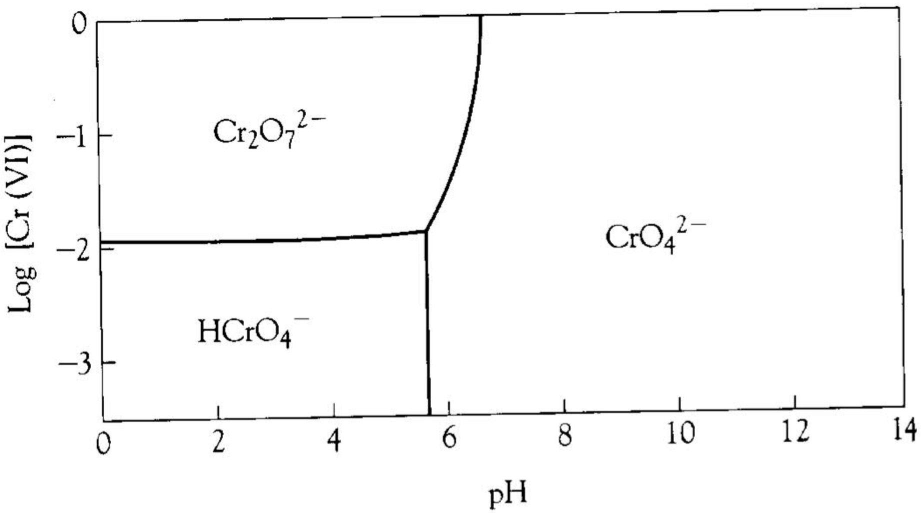


CHROMATE

- potassium chromate K_2CrO_4
- lead chromate $PbCrO_4$
- strong oxidizers, carcinogens
- Electron transfer reaction:
  Cr(VI)-O(-II) $\rightarrow$ Cr(V)-O(-I)
- $2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$
- $CrO_4^{2-} + H_2O \rightleftharpoons HCrO_4^- + OH^-$

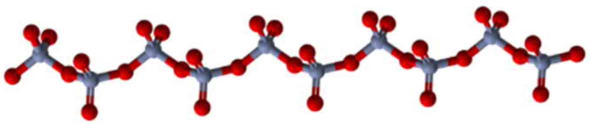






Chromium trioxide

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



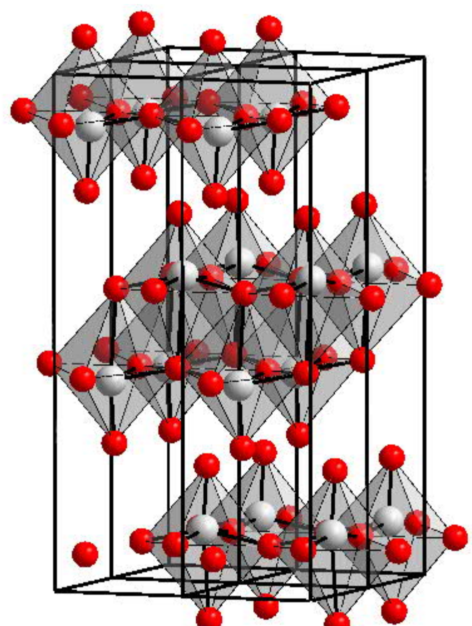
"Halfmetal" for SPINTRONICS: Electrical conductor & ferromagnet

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	—

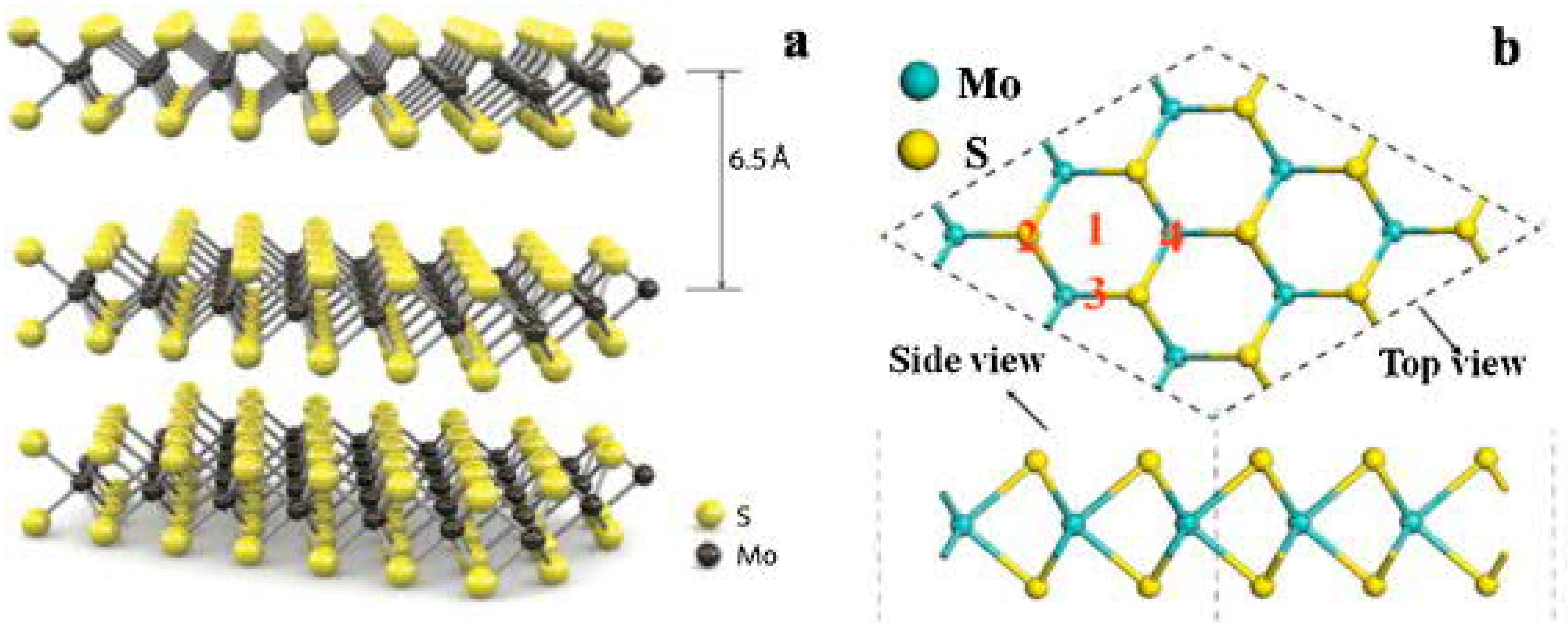
Molybdenum trioxide

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

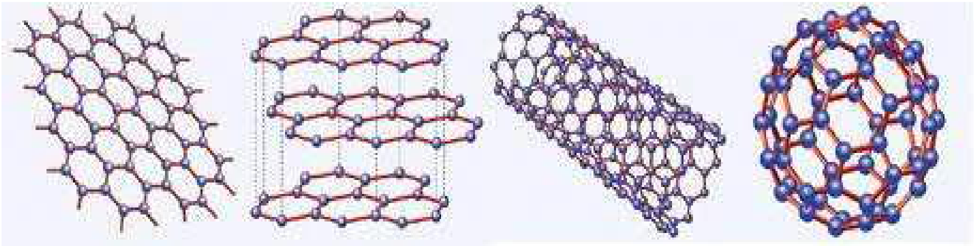


2D CHALCOGENIDES (S, Se, Te)

- **e.g. MoS_2, 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

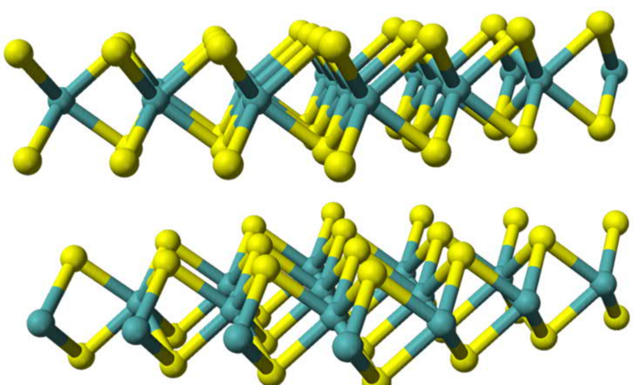
- **Unusual electronic properties**

Graphite

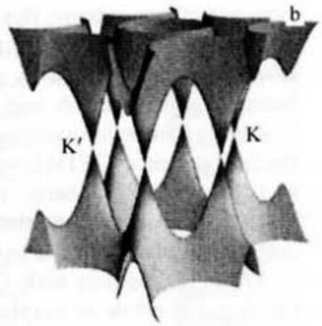
- **Weak (van der Waals) bonds between the layers**
- **Solid lubricant**

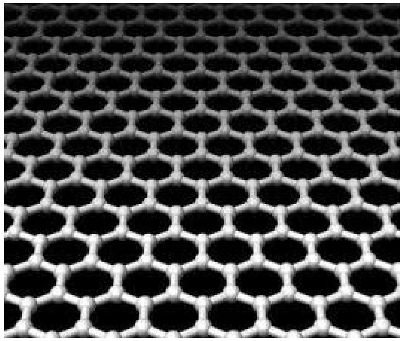
MoS_2

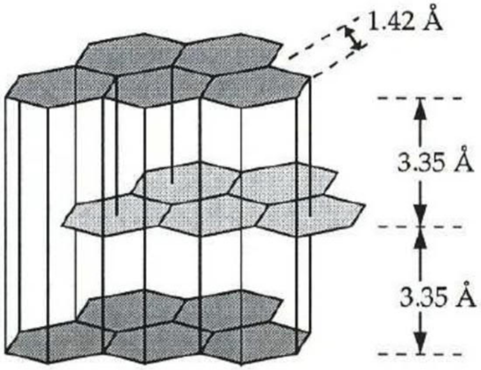
- **Molybdenite (natural mineral)**
- **Solid lubricant (similar to graphite)**
- **Band-gap (ref. graphene)**

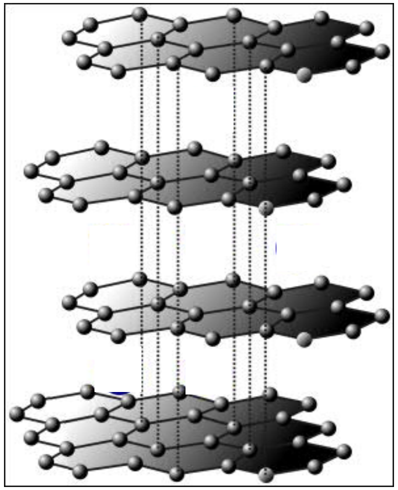


band-structure of graphene

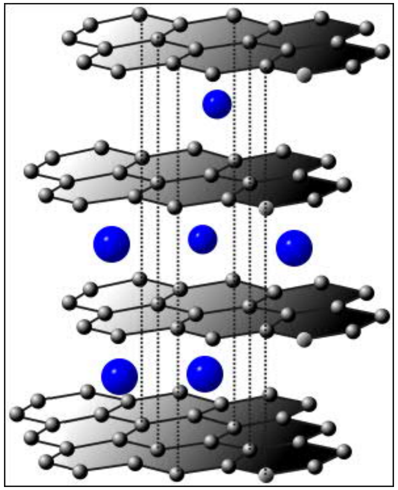


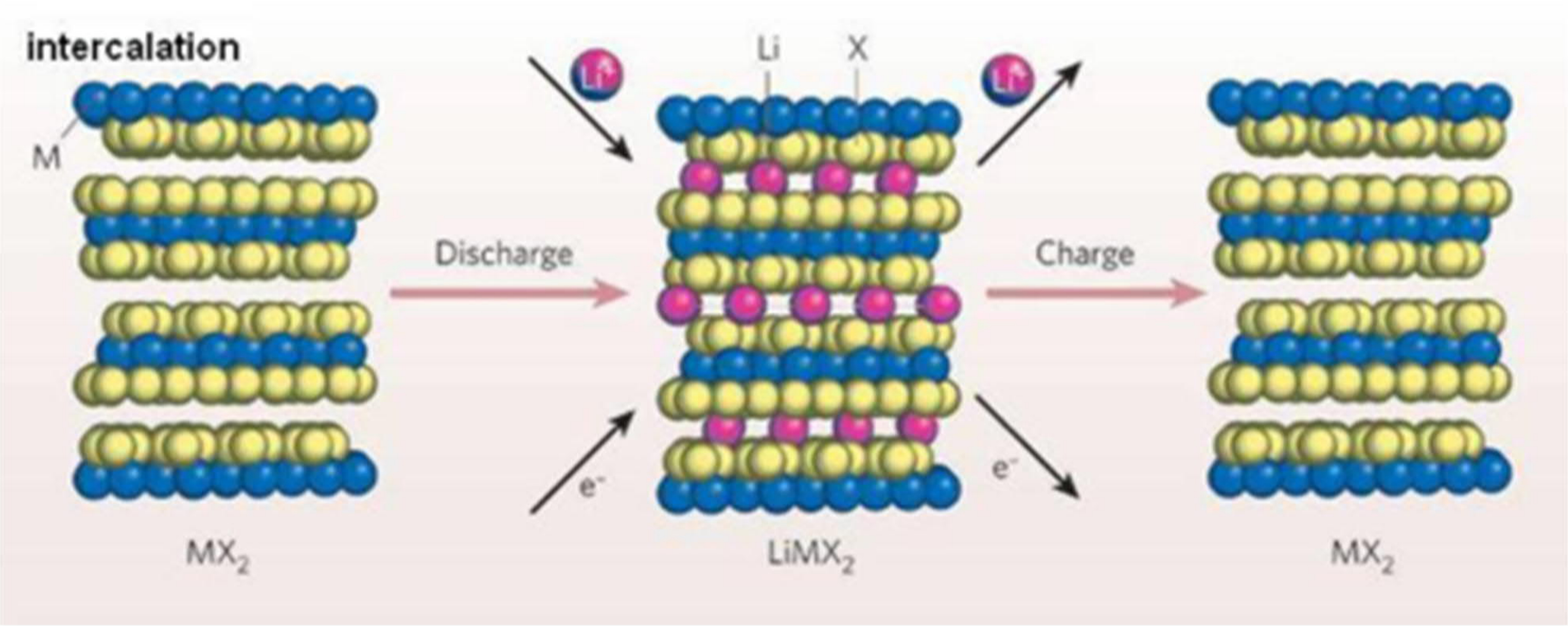


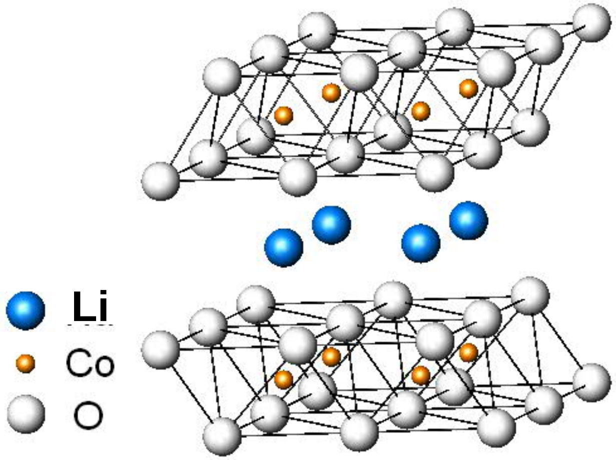




INTERCALATION




intercalation
M
MX2
Discharge
Li+
e-
Li
X
LiMX2
Charge
Li+
e-
MX2



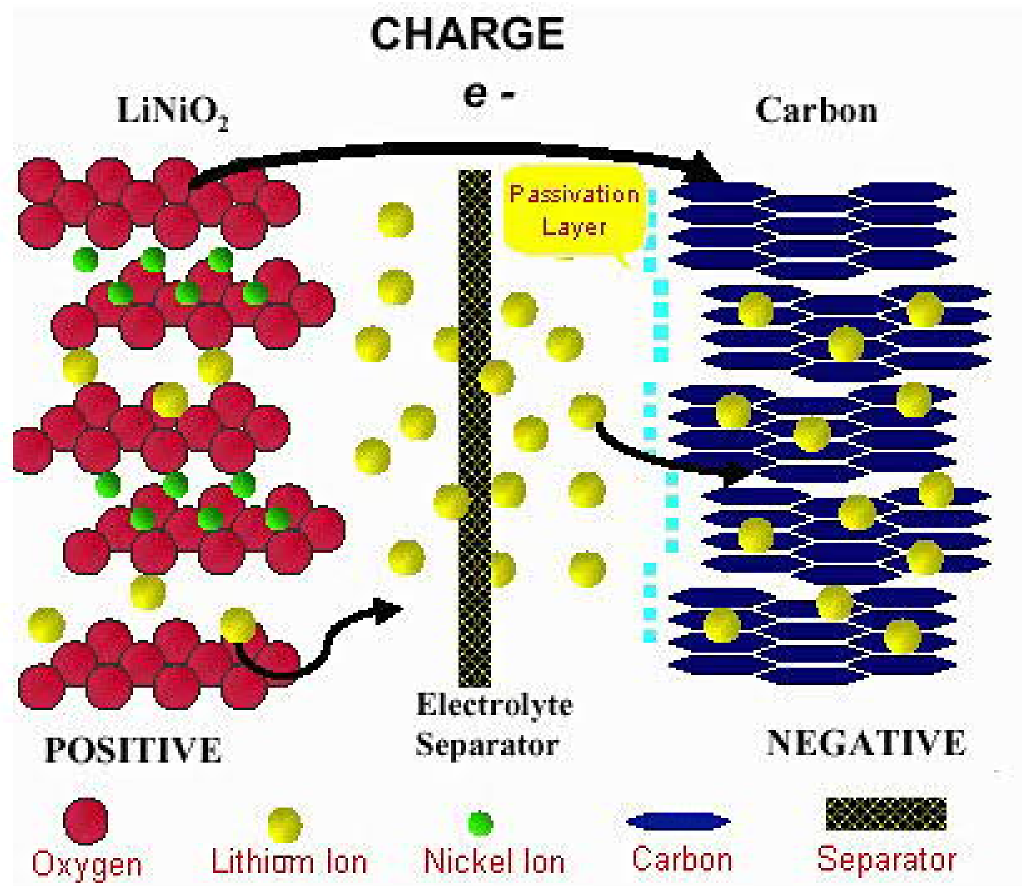
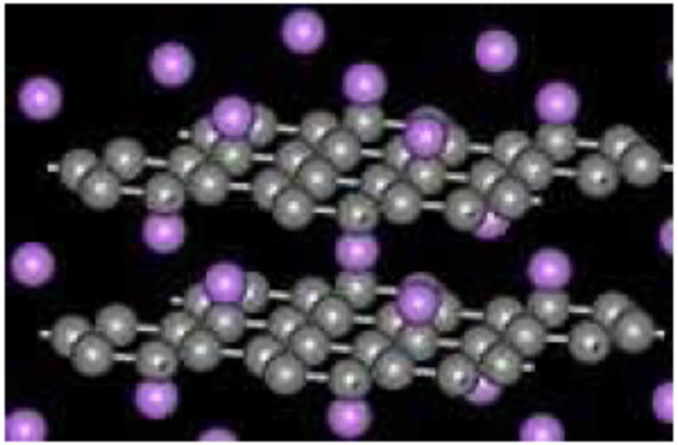


Photo Courtesy of SAFT America

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.



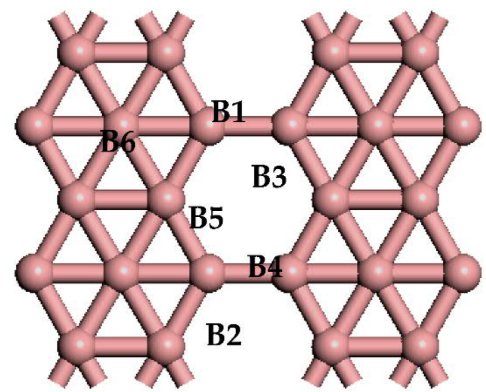
Among the superconducting graphite intercalation compounds, CaC_6 exhibits the highest critical temperature Tc = 11.5 K, which further increases under applied pressure (15.1 K at 8 GPa)

Graphene

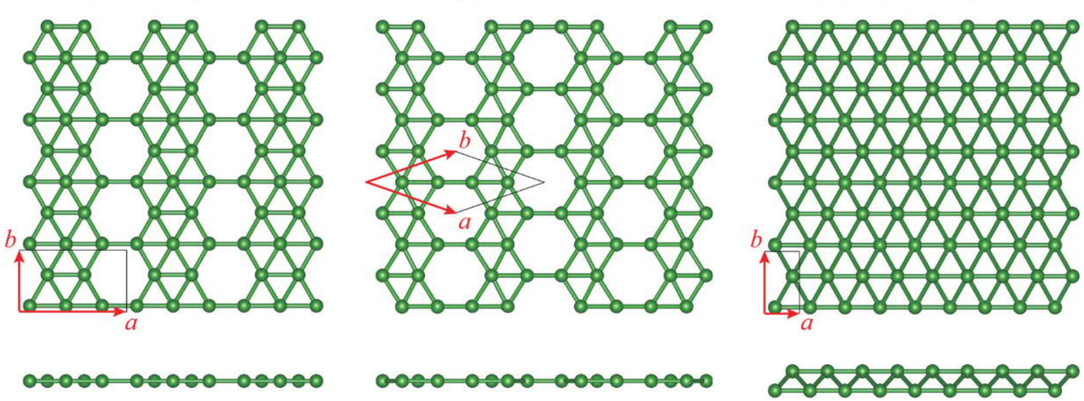
Geim & Novoselov (Univ. Manchester) 2004; Nobel (physics) 2010

Borophene

- 2D structure of boron atom sheets
- two-center and multi-center in-plane bonds
- characteristic buckled or crinkled surface
- in nano-scale B and C very similar,
  even though macroscopic allotropes quite different !
- predicted 1997, synthesized by MBE (on Ag) 2015
- bonded weakly to the silver substrate
- metallic, strong, flexible, highly conducting



(a) β_{12} borophene (b) X_3 borophene (c) striped borophene



I. Boustani, New quasi-planar surfaces of bare boron, Surface Science 370, 355 (1997).

A.J. Mannix, et al., Synthesis of borophenes: anisotropic, two-dimensional boron polymorphs, Science 350, 1513 (2015).

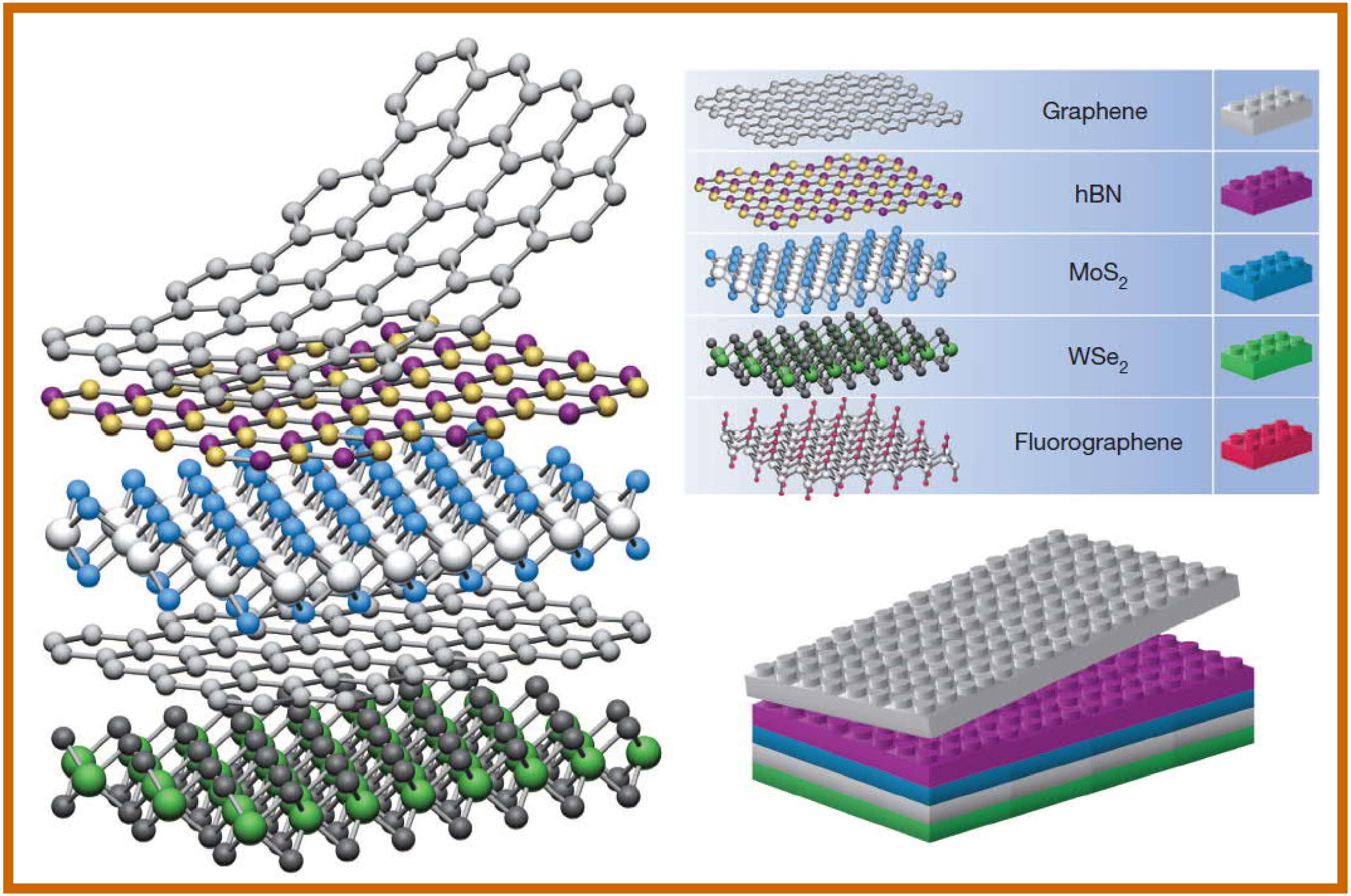
B. Feng, et al., Experimental realization of two-dimensional boron sheets, Nature Chemistry 8, 563 (2016).

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" colspan="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="2">Metallic dichalcogenides:
$NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$ and so on</td></tr>
<tr><td colspan="2">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).

Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides

Hui Fang[a,b], Corsin Battaglia[a,b], Carlo Carraro[c], Slavomir Nemsak[b,d], Burak Ozdol[e,f], Jeong Seuk Kang[a,b], Hans A. Bechtel[g], Sujay B. Desai[a,b], Florian Kronast[h], Ahmet A. Unal[h], Giuseppina Conti[b,d], Catherine Conlon[b,d], Gunnar K. Palsson[b,d], Michael C. Martin[g], Andrew M. Minor[e,f], Charles S. Fadley[b,d], Eli Yablonovitch[a,b,1], Roya Maboudian[c], and Ali Javey[a,b,1]

6198–6202 | PNAS | April 29, 2014 | vol. 111 | no. 17

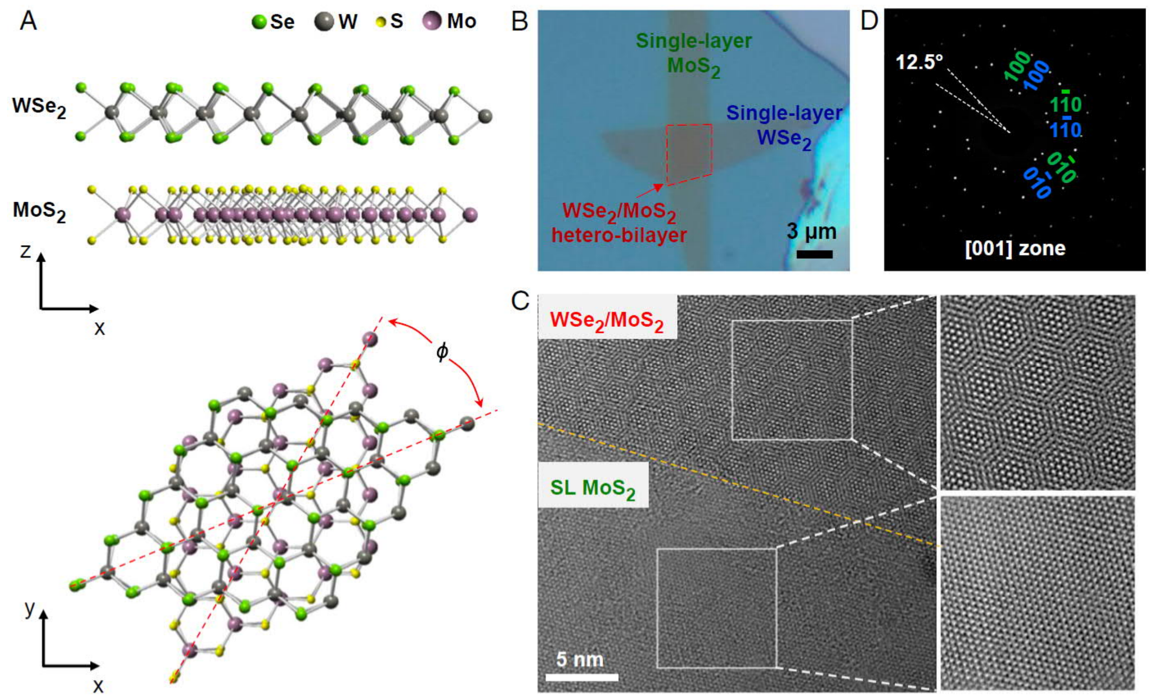
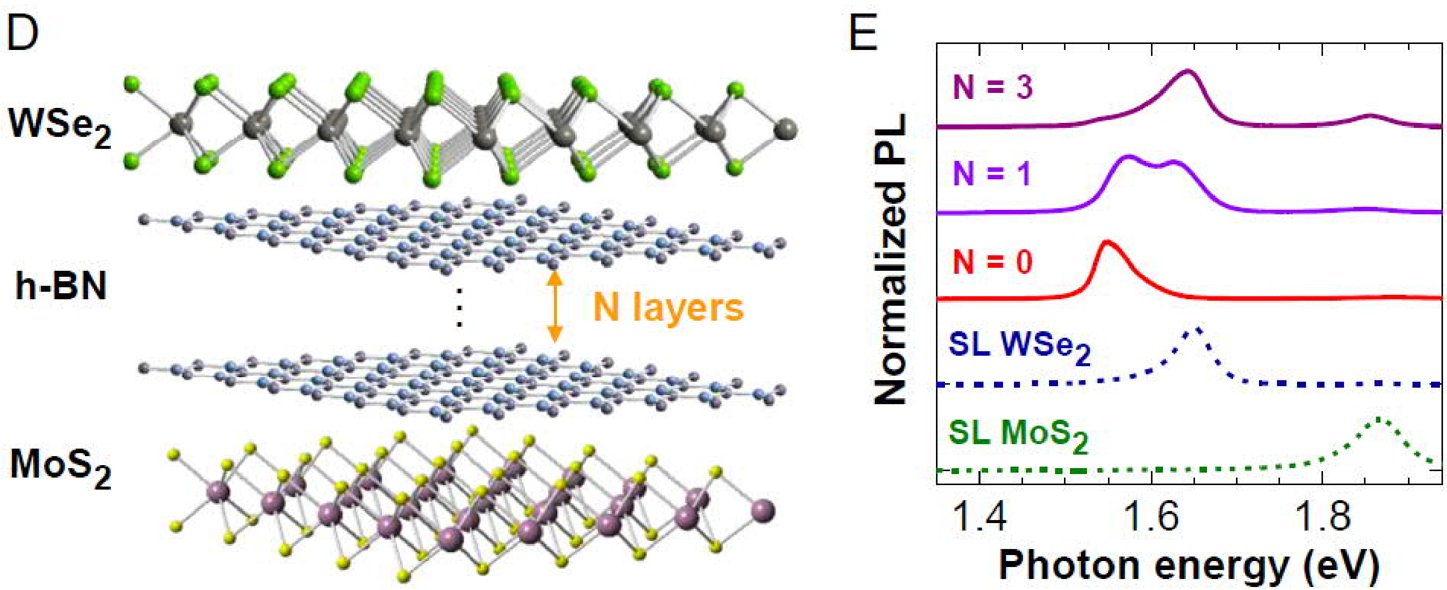


Fig. 1. WSe_2/MoS_2 hetero-bilayer illustration, optical image, and TEM images. (*A*) Atomistic illustrations of the heterostructure of single-layer (SL) WSe_2 on SL MoS_2 with their respective lattice constants and a misalignment angle ϕ. (*B*) Optical microscope image of a WSe_2/MoS_2 hetero-bilayer on a Si/SiO_2 substrate (260-nm SiO_2). (*C*) HRTEM images of a boundary region of SL MoS_2 and the hetero-bilayer, showing the resulting Moiré pattern. (*D*) The electron diffraction pattern of the hetero-bilayer shown in *B*, with the pattern of MoS_2 and WSe_2 indexed in green and blue colors, respectively.



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

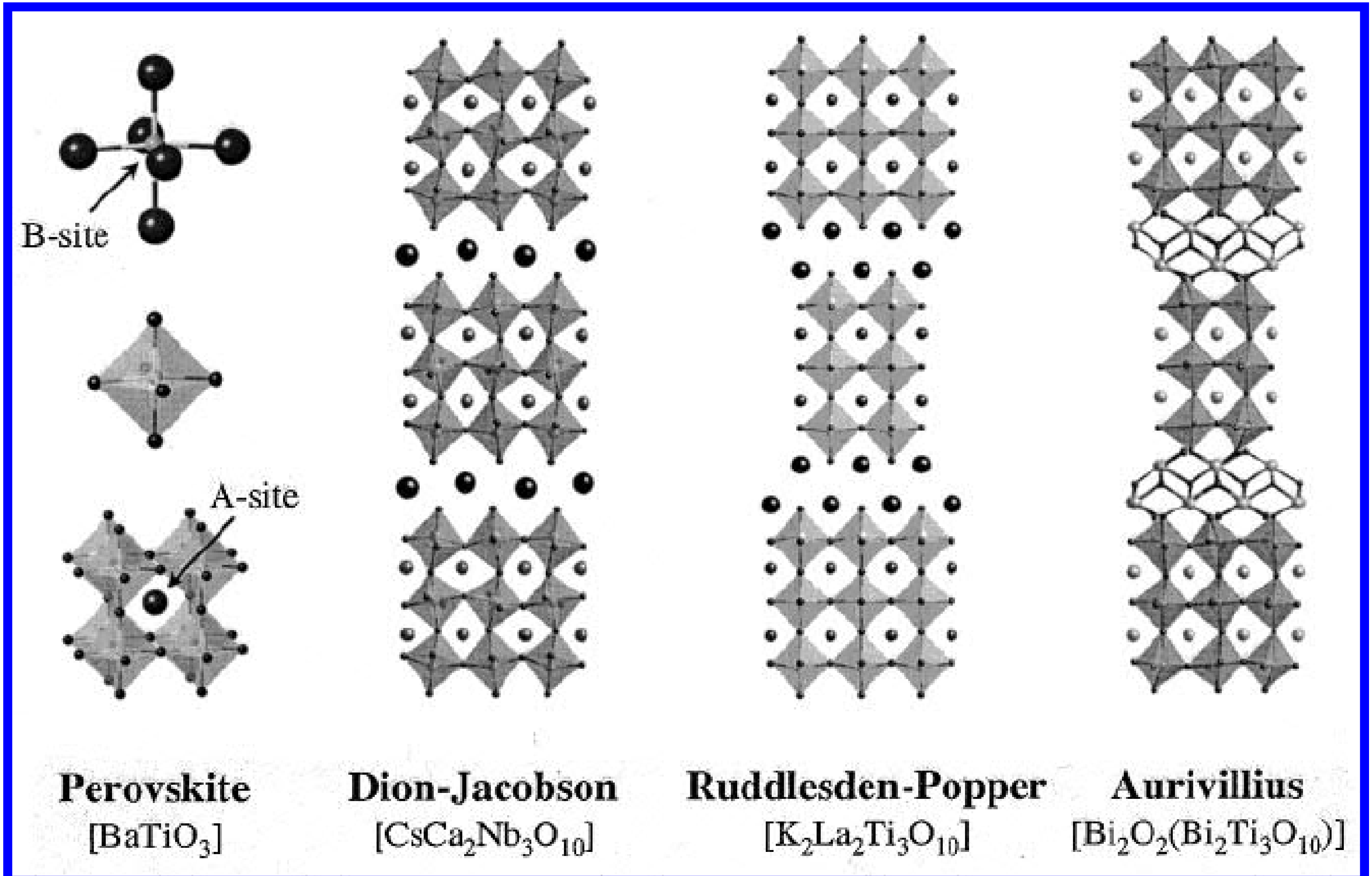
Nonlayered materials

- Growing from gas phase on a proper substrate

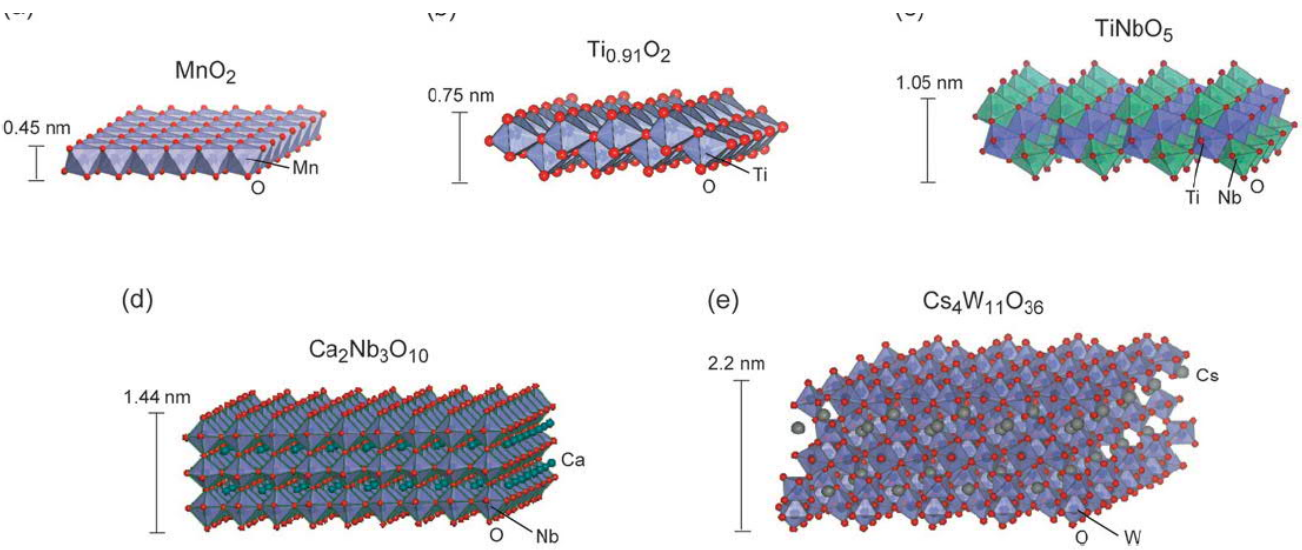
HOW TO VERIFY THE NANOSHEETS

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

Multilayered oxide structures …



OXIDE NANOSHEETS



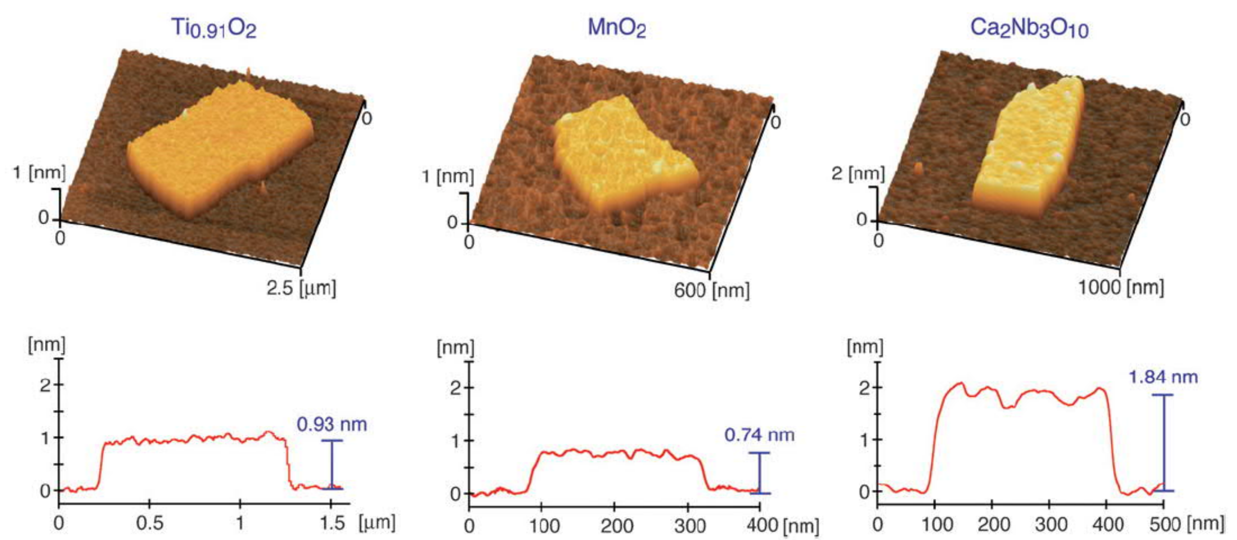
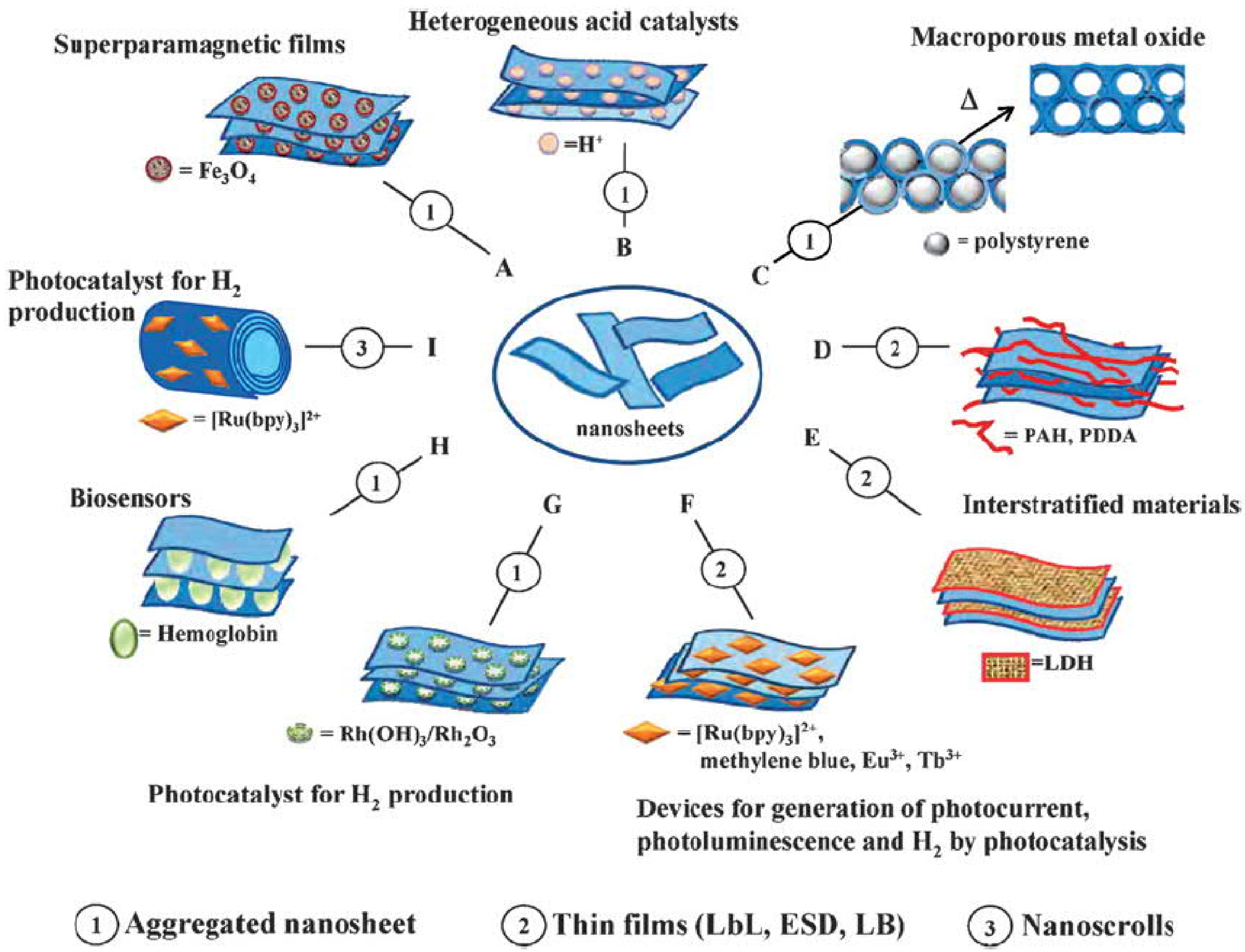
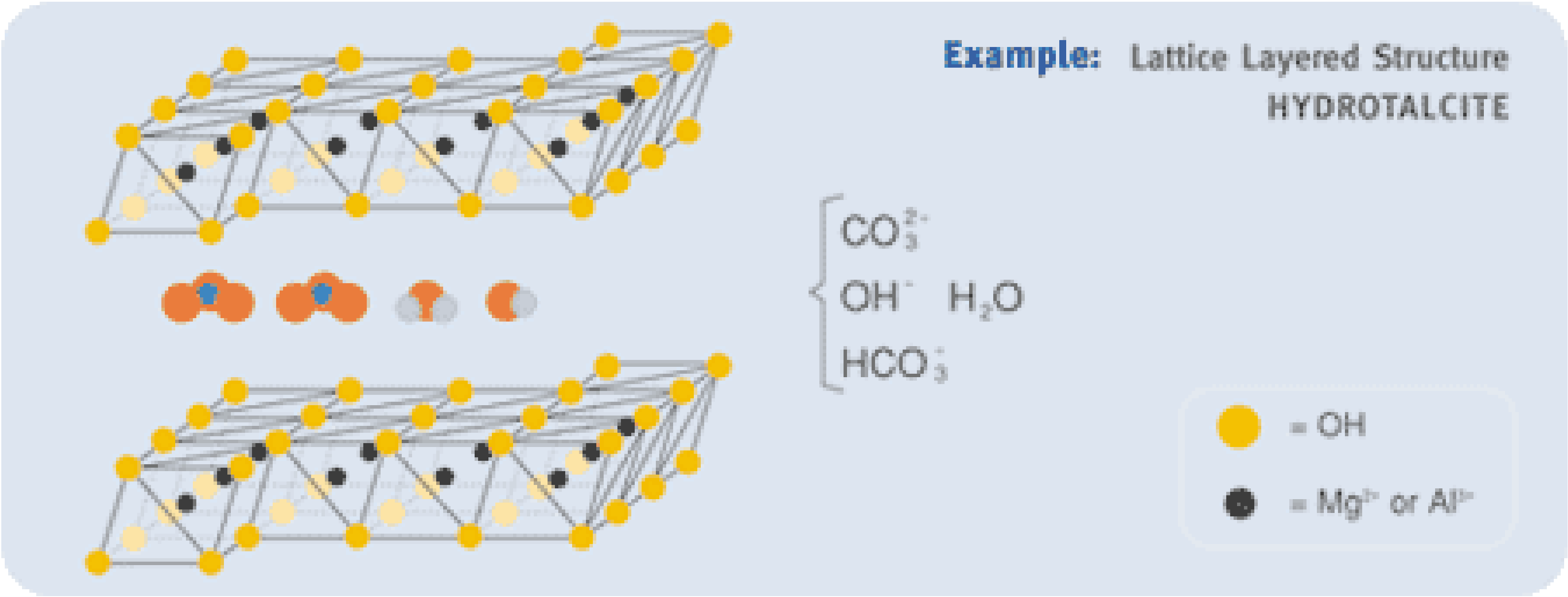


Fig. 2 AFM images of $Ti_{0.91}O_2$, MnO_2 and $Ca_2Nb_3O_{10}$ nanosheets. A tapping-mode AFM (SII nanotech E-Sweep) in vacuum conditions was used to evaluate the morphology of the nanosheets on Si substrates. Height profiles are shown in the bottom panels.



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

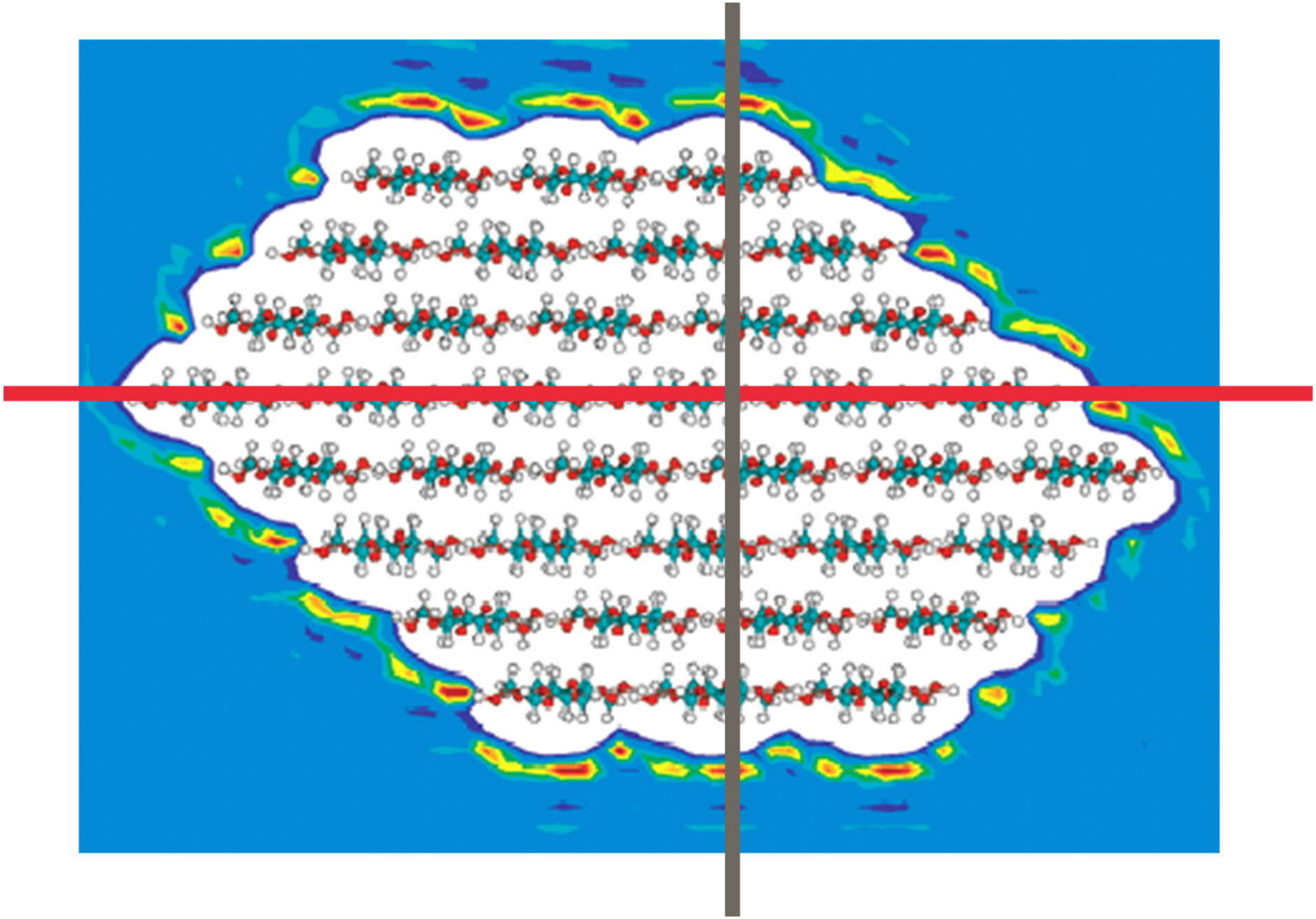
L. Wang & T. Sasaki, Titanium oxide nanosheets: graphene analogues with versatile functionalities, *Chem. Rev.* 114, 9455 (2014).

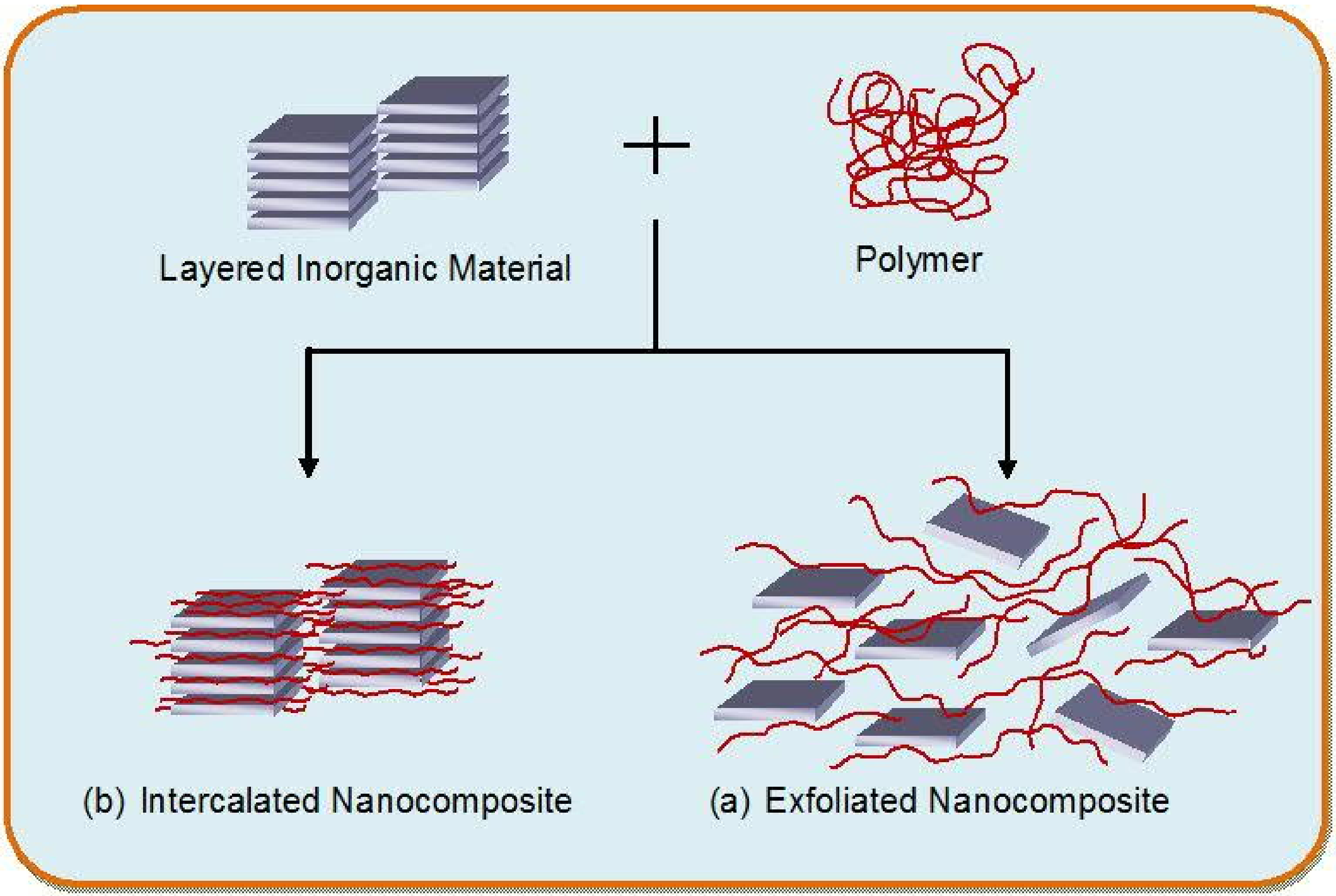


Hydrotalcite $Al_2Mg_6(OH)_{16}CO_3 \cdot xH_2O$

- 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)




Layered Inorganic Material
Polymer
(b) Intercalated Nanocomposite
(a) Exfoliated Nanocomposite

Multilayered Inorganic-Organic Hybrids

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

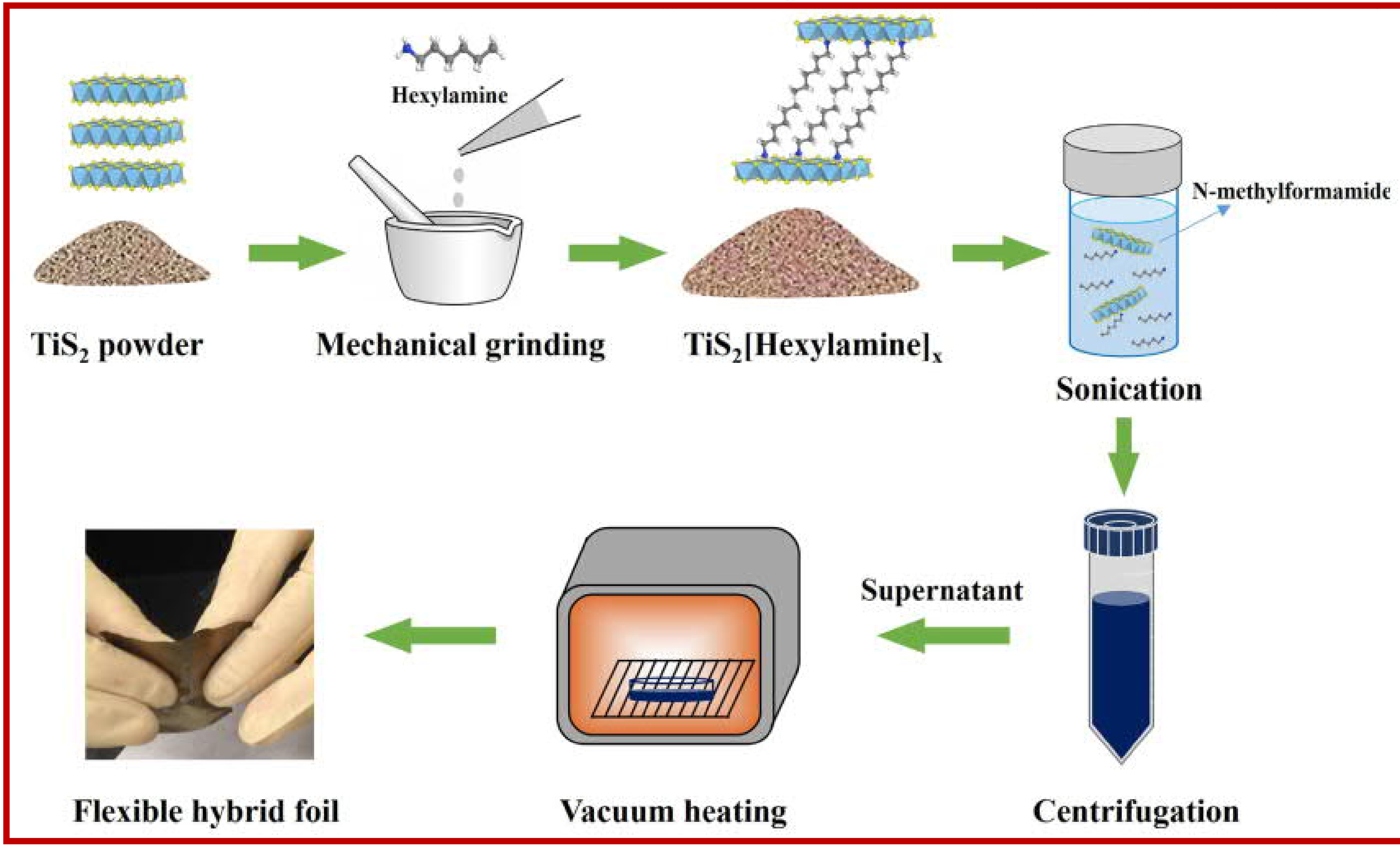
Flexible thermoelectric foil for wearable energy harvesting

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,*]

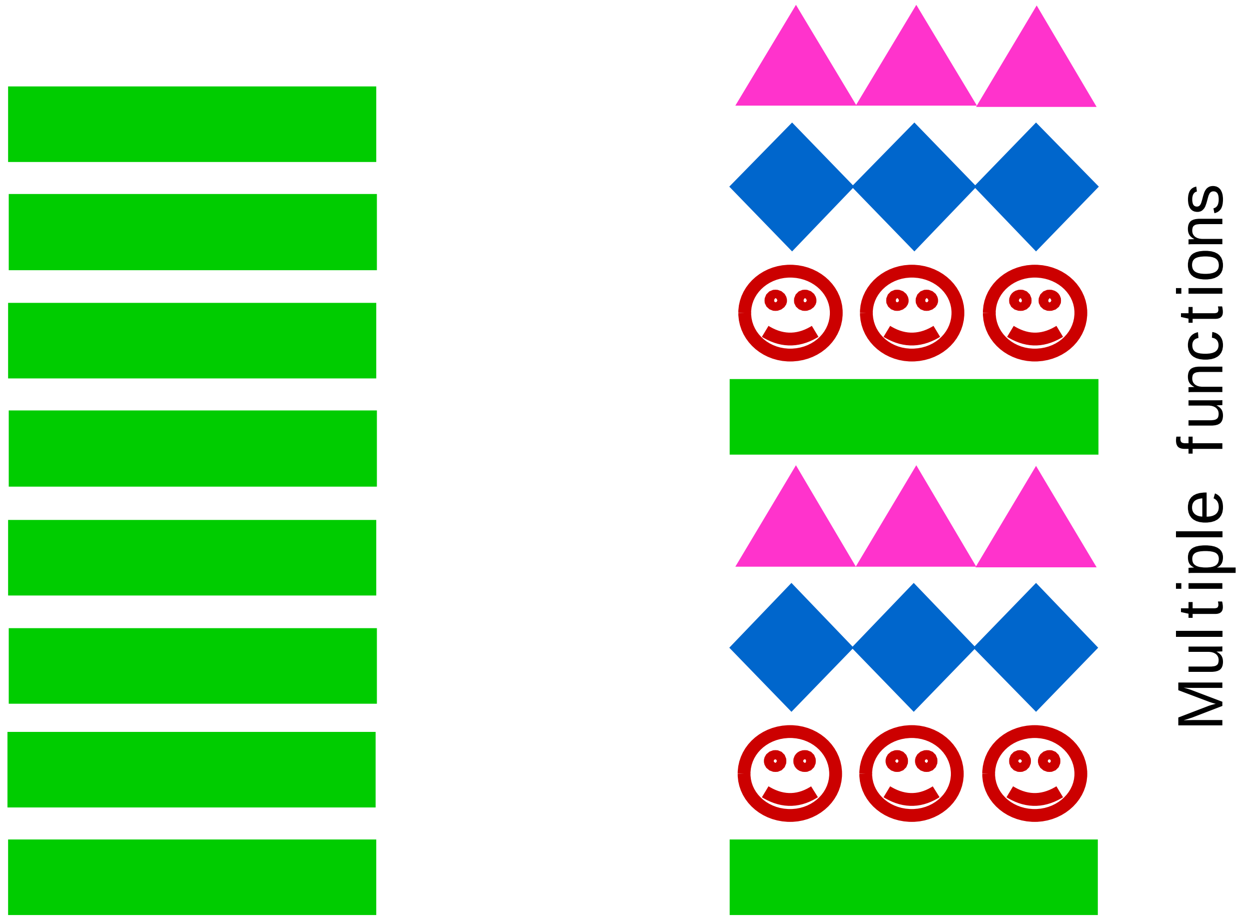
..., Beijing 100084, China

...raki 305-8564, Japan

... Japan



Layer-Engineering

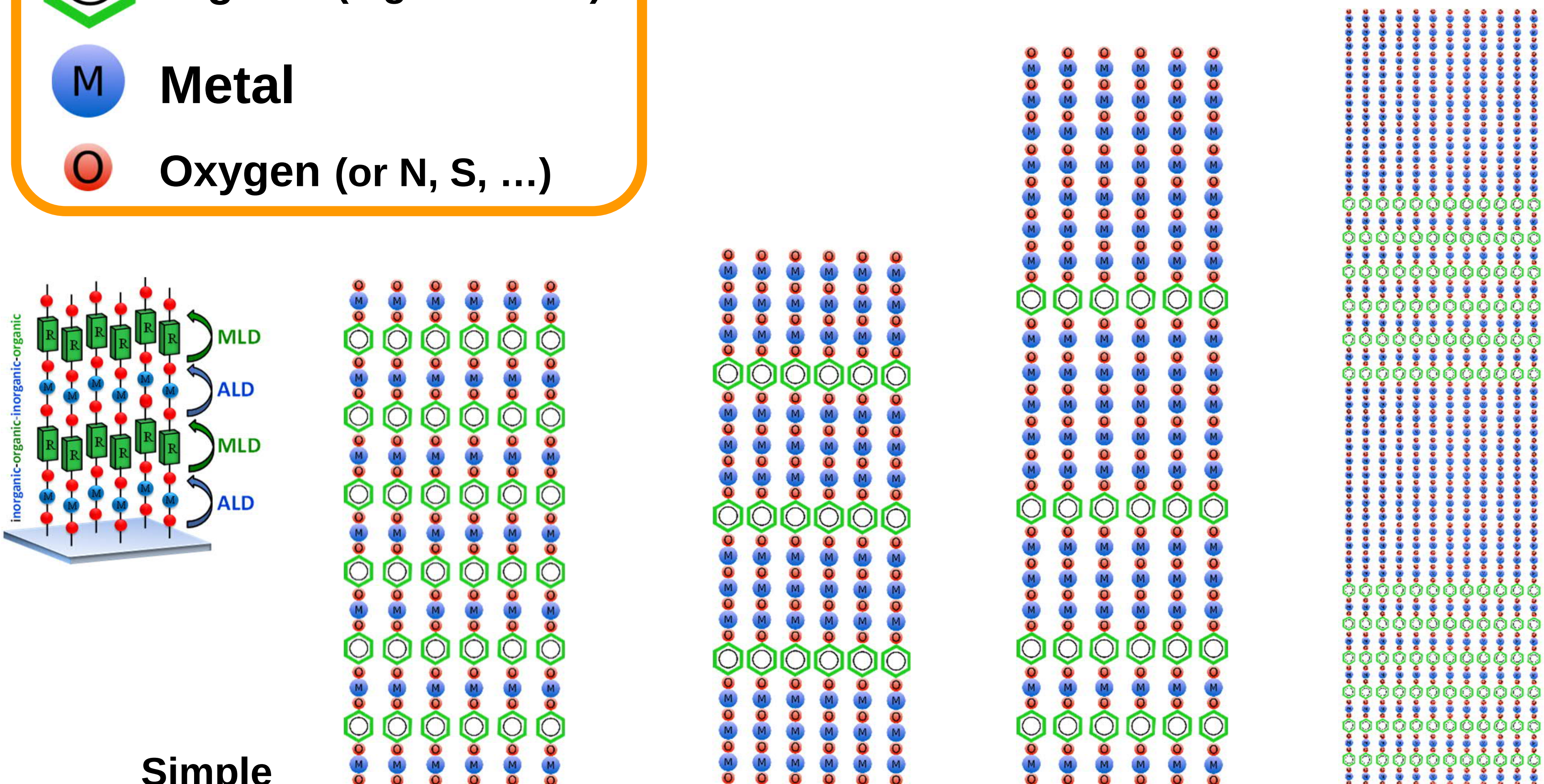


Layered material **Multilayered material**

Organic (e.g. benzene)

Metal

Oxygen (or N, S, …)



Simple
Metal-Organic Network
(amorphous or crystalline)

Superlattice

Gradient hybrid

Nanolaminate

Aalto University
School of Chemical
Engineering

DIFFERENT LAYER SEQUENCES BY ALD/MLD DESIGN