

# TENTATIVE LECTURE SCHEDULE

	Date	Topic
1.	Wed 07.09.	Course Introduction & Short Review of the Elements
2.	Fri 09.09.	Periodic Properties & Periodic Table & Main Group Elements (starts)
3.	Mon 12.09.	Short Survey of the Chemistry of Main Group Elements (continues)
4.	Fri 16.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
5.	Mon 19.09.	Transition Metals: General Aspects & Pigments
6.	Wed 21.09.	Redox Chemistry
7.	Fri 23.09.	Crystal Field Theory (Linda Sederholm)
8.	Mon 26.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
9.	Wed 28.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
10.	Fri 30.09.	Mn, Fe, Co, Ni, Cu & Magnetism & Superconductivity
10.	Mon 03.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
11.	Fri 07.10.	Lanthanoids + Actinoids & Luminescence
12.	Mon 10.10.	EXTRA
14.	Wed 12.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
15.	Fri 14.10.	Inorganic Materials Chemistry Research

**EXAM: Oct. 18, 9:00-12:00**



## **QUESTIONS: Lecture 9**

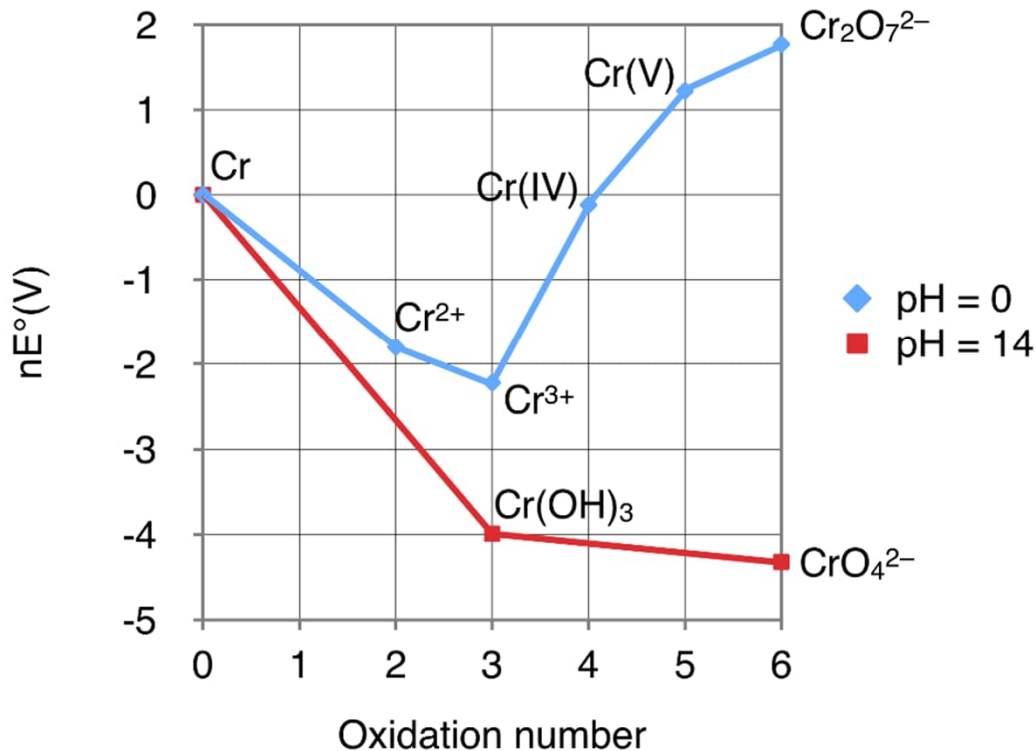
Name your file Exe-9-Familyname; Return by noon next day into MyCourses drop-box

- 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.**

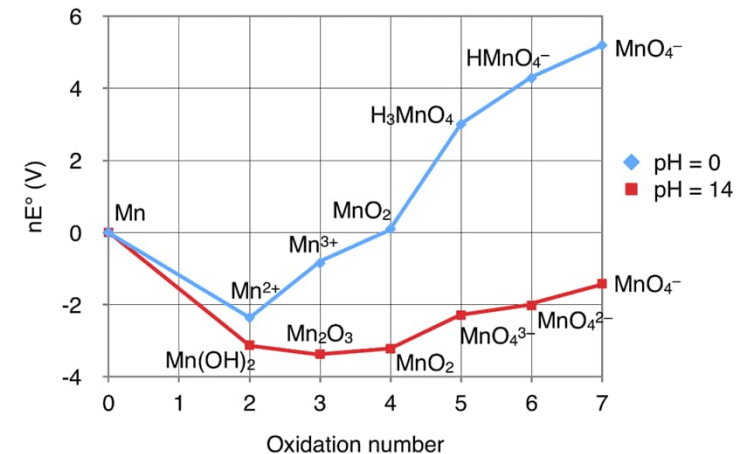
# CHROMIUM (ref. Mn): OXIDATION STATES

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

Frost diagram for chromium

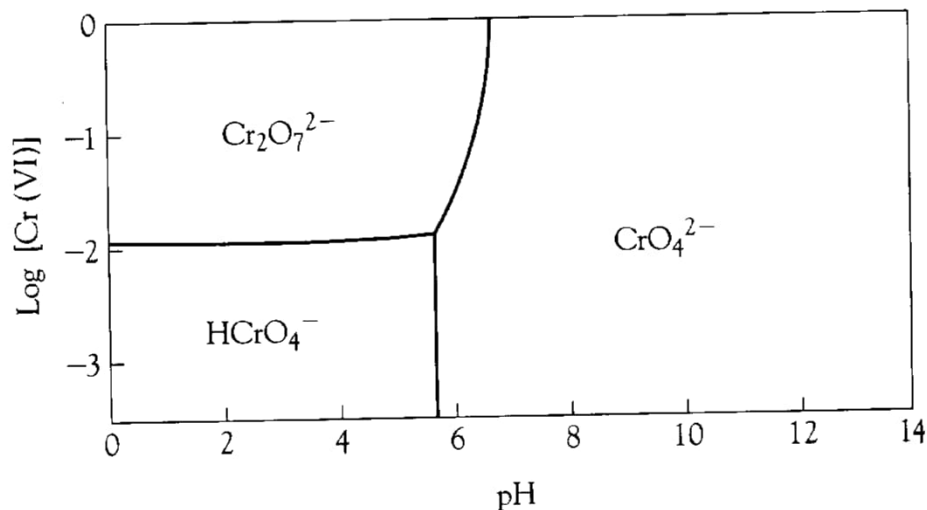
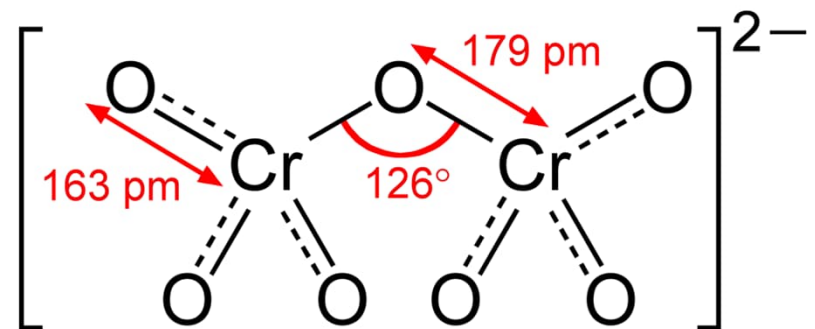
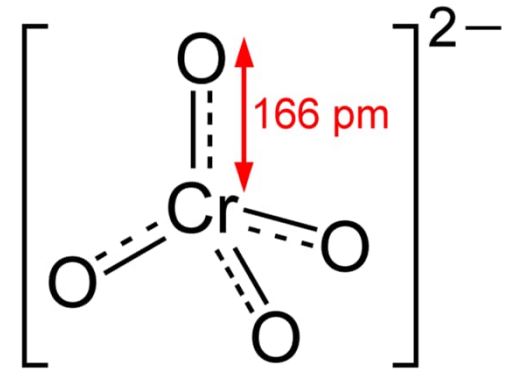


Frost diagram for manganese



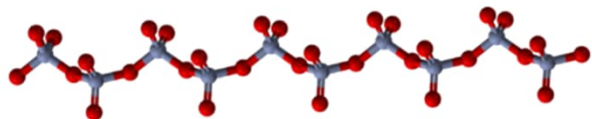
# CHROMATE

- potassium chromate  $\text{K}_2\text{CrO}_4$
- lead chromate  $\text{PbCrO}_4$
- strong oxidizers, carcinogens
- Reason for the colour?
- **Electron transfer reaction:**  
 $\text{Cr(VI)-O(-II)} \rightarrow \text{Cr(V)-O(-I)}$
- $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$



## Chromium trioxide

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



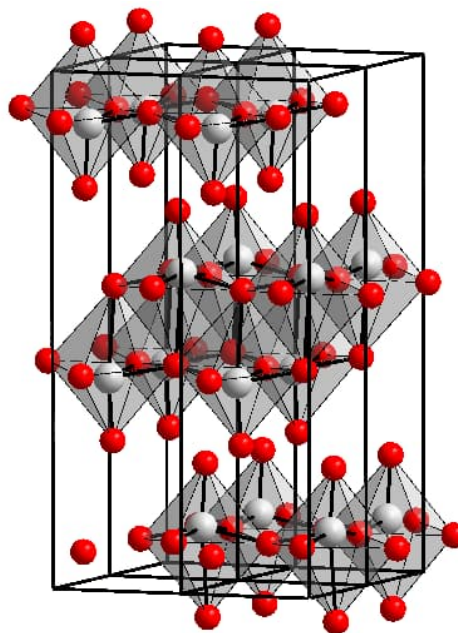
## OXIDES

**"Halfmetal" for SPINTRONICS:  
Electrical conductor & ferromagnet**

Oxidation state:	+6	Intermediate	+4	+3
Cr	<b>CrO<sub>3</sub></b>	Cr <sub>3</sub> O <sub>8</sub> , Cr <sub>2</sub> O <sub>5</sub> , Cr <sub>5</sub> O <sub>12</sub> , etc.	<b>CrO<sub>2</sub></b>	Cr <sub>2</sub> O <sub>3</sub>
Mo	<b>MoO<sub>3</sub></b>	Mo <sub>9</sub> O <sub>26</sub> , Mo <sub>8</sub> O <sub>23</sub> , Mo <sub>5</sub> O <sub>14</sub> , Mo <sub>17</sub> O <sub>47</sub> , Mo <sub>4</sub> O <sub>11</sub>	MoO <sub>2</sub>	—
W	WO <sub>3</sub>	W <sub>49</sub> O <sub>119</sub> , W <sub>50</sub> O <sub>148</sub> , W <sub>20</sub> O <sub>58</sub> , W <sub>18</sub> O <sub>49</sub>	WO <sub>2</sub>	—

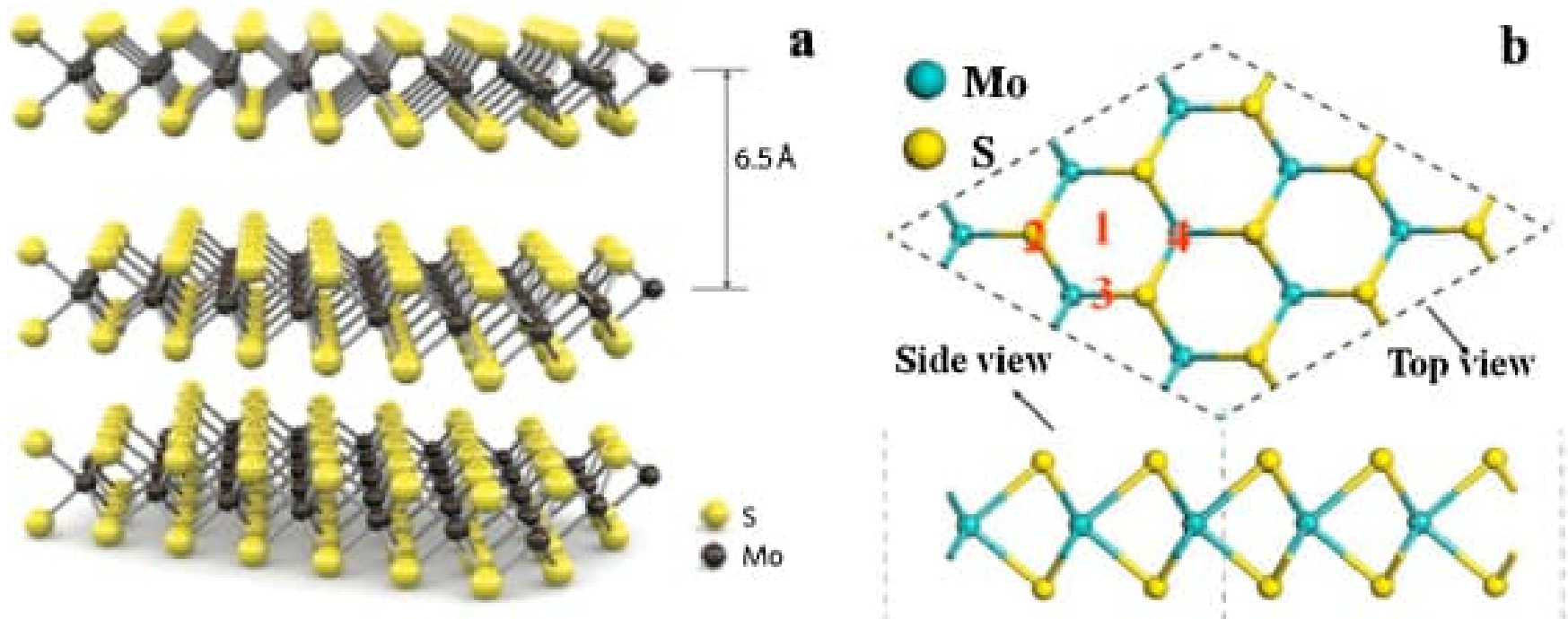
## Molybdenum trioxide

- Mineral molybdenite is of MoO<sub>3</sub>
- Important industrial catalyst
- 2D structure → **Van der Waals gap**
- $CN(Mo) = 6$

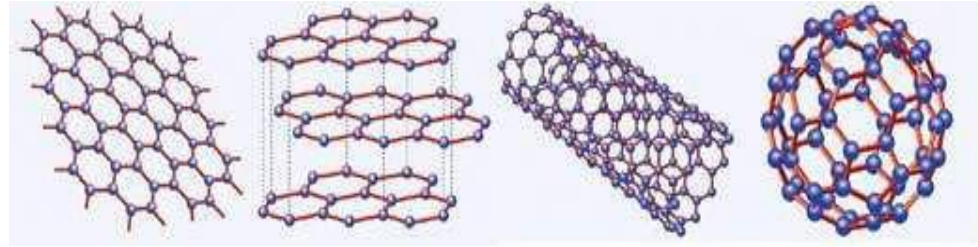


## Another 2D Structure: CHALCOGENIDES (S, Se, Te)

- Natural mineral molybdenite  $\text{MoS}_2$  (similar to e.g.  $\text{TiS}_2$ )
- Trigonal prismatic (CN = 6) coordination around Mo
- Semiconductor (somewhat similar to graphite)



# GRAPHENE



- Monolayer of graphite or a giant PAH molecule

(*polycyclic aromatic hydrocarbon*;  
the largest known PAH molecule consists of 10 C<sub>6</sub>-rings)

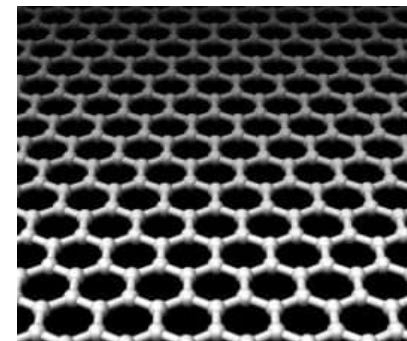
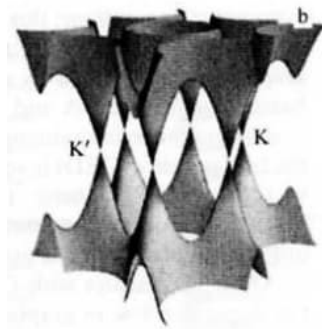
- sp<sup>2</sup>-hybridization, C-C bond length 1.42 Å
- Thinnest (but strongest) material known
- Best electrical conductor (at room temperature)
- Electrons in graphene:
  - behave like wave motion
  - move like having zero mass
  - move faster than in any other material
  - do not scatter from impurities
- 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

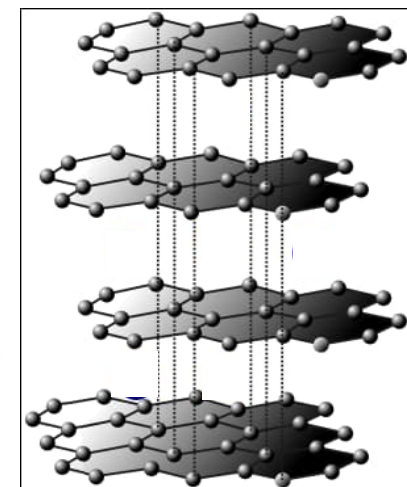
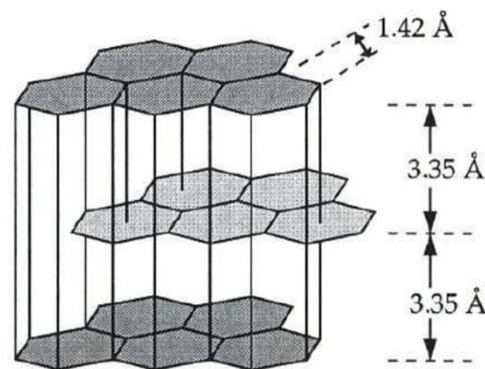
- Unusual electronic properties

band-structure of graphene



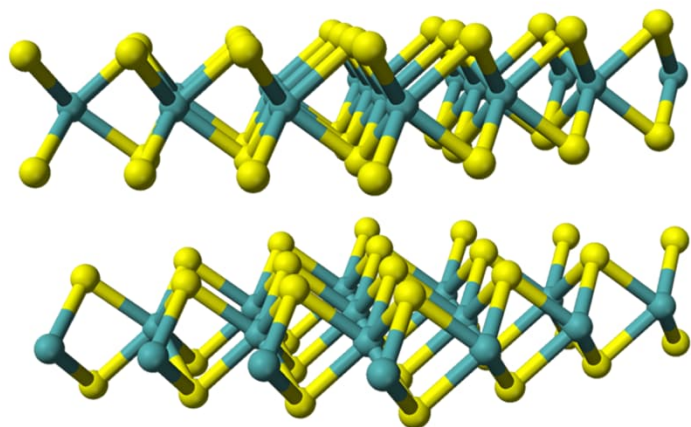
## Graphite

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

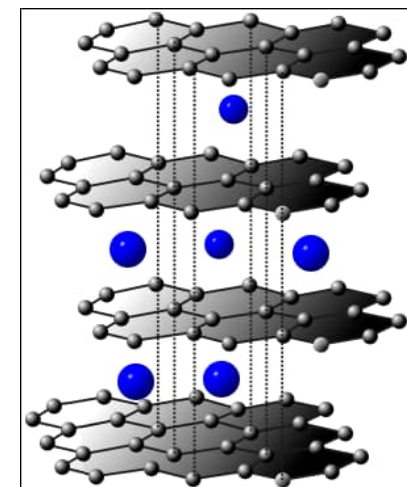


## MoS<sub>2</sub>

- Similar to graphite
- Band-gap
- Solid lubricant



INTERCALATION



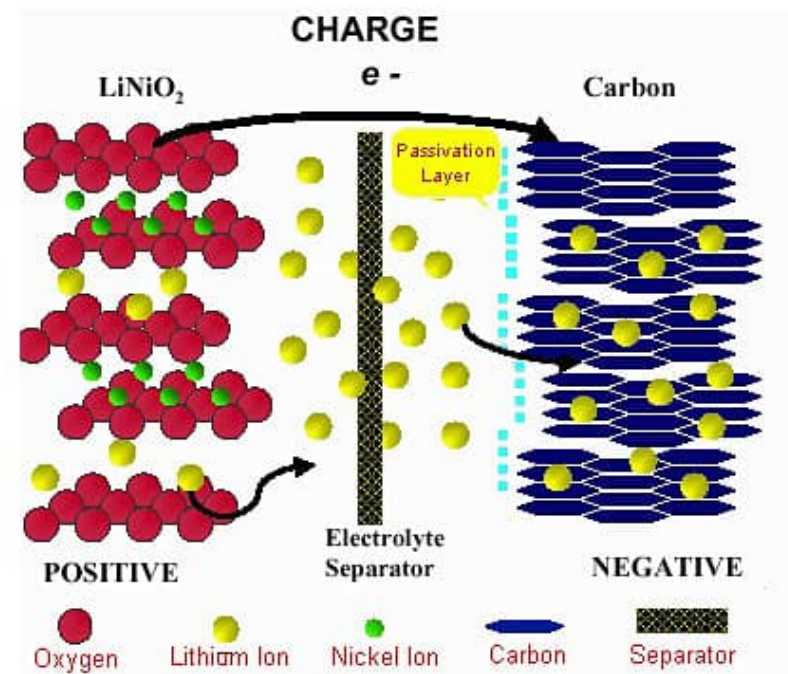
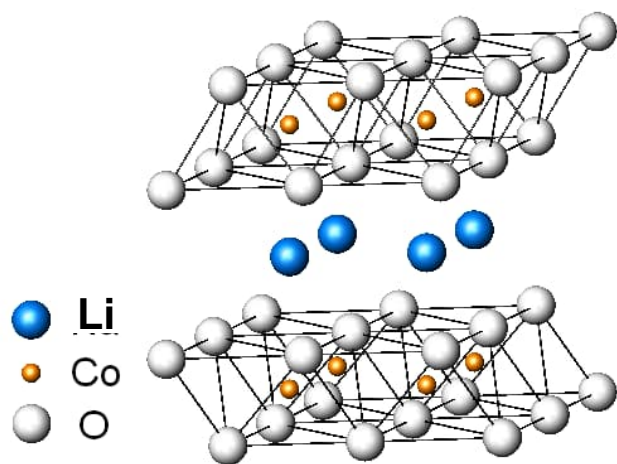
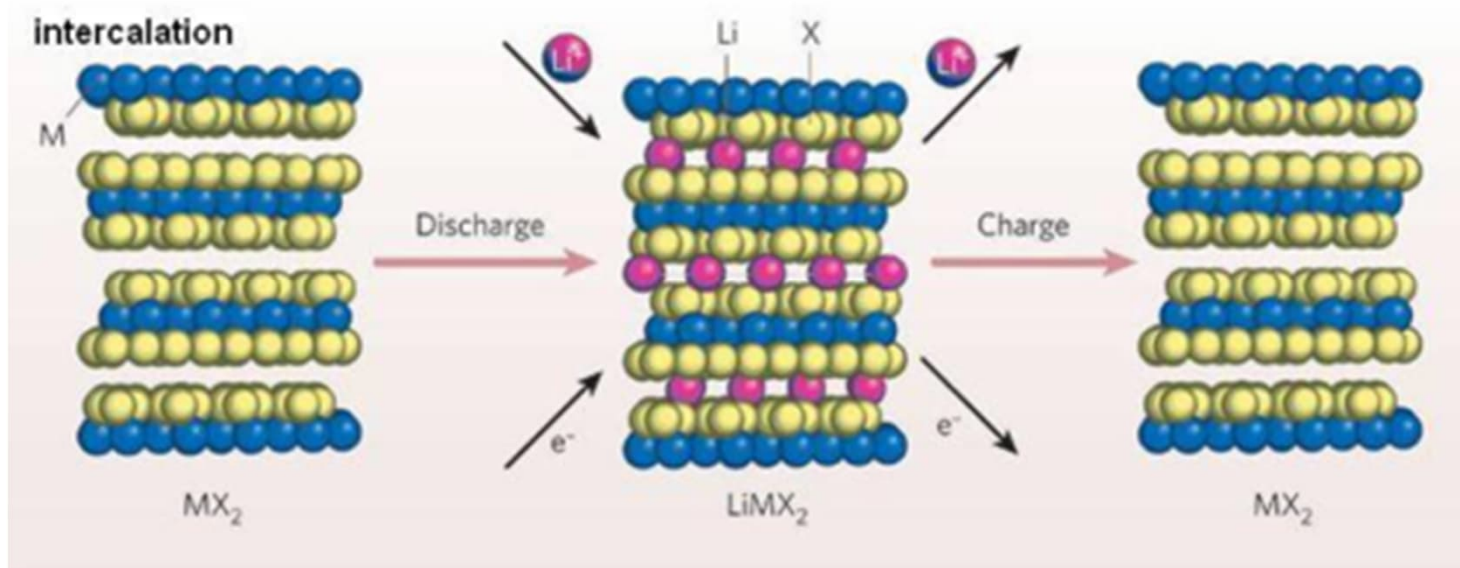
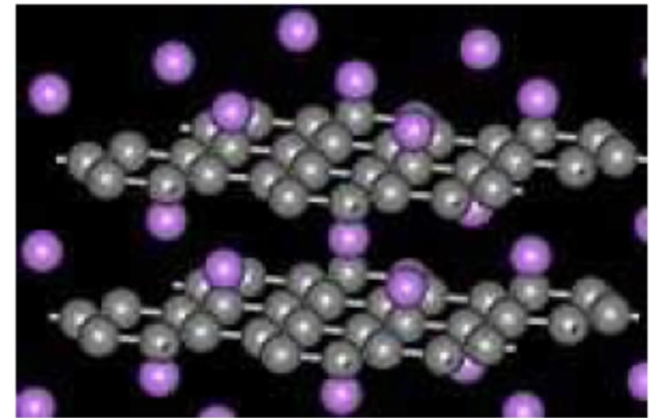


Photo Courtesy of SAFT America

## Calcium graphite: CaC<sub>6</sub>

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<sub>6</sub> exhibits the highest critical temperature  $T_c = 11.5$  K, which further increases under applied pressure (15.1 K at 8 GPa)

## Superconductivity in 2-layer graphene with different intercalants

	$\lambda\omega_D/\epsilon_F$	$T_c$ (K)	$\Delta(0)$ (meV)	$2\Delta(0)/k_B T_c$
C <sub>6</sub> KC <sub>6</sub>	0.079	8.2	1.38	3.91
C <sub>6</sub> CaC <sub>6</sub>	0.081	14.0	2.46	4.08
C <sub>6</sub> RbC <sub>6</sub>	0.093	5.5	0.87	3.67
C <sub>6</sub> SrC <sub>6</sub>	0.062	8.5	1.41	3.85



# NANOSHEET MATERIAL LIBRARY

**BLUE:** stable in air

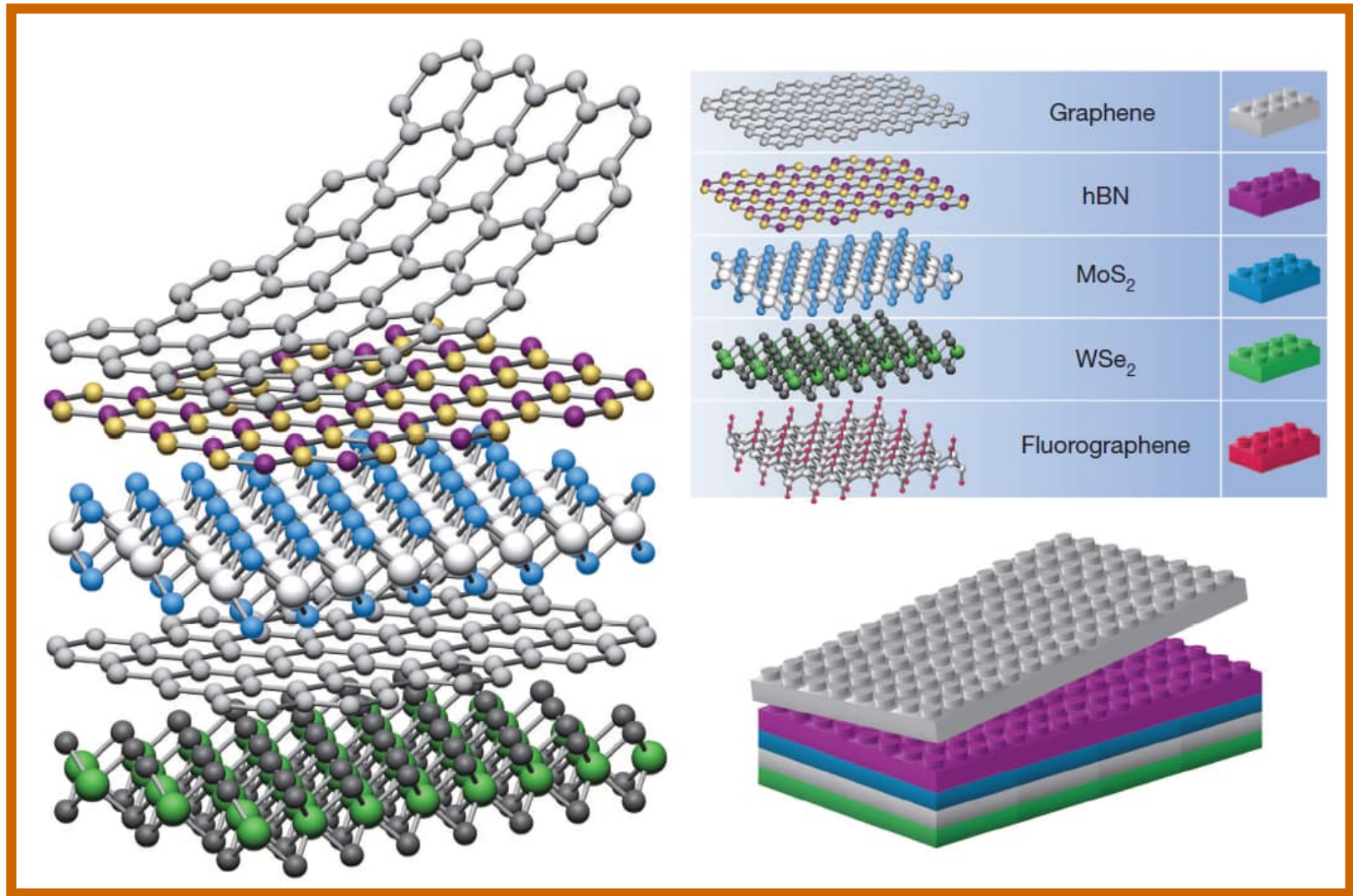
**GREEN:** probably stable in air

**PINK:** unstable in air but stable in an inert atmosphere

**GREY:** made but no other details known

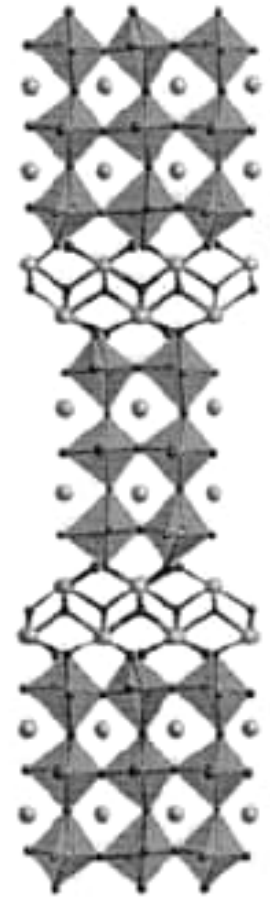
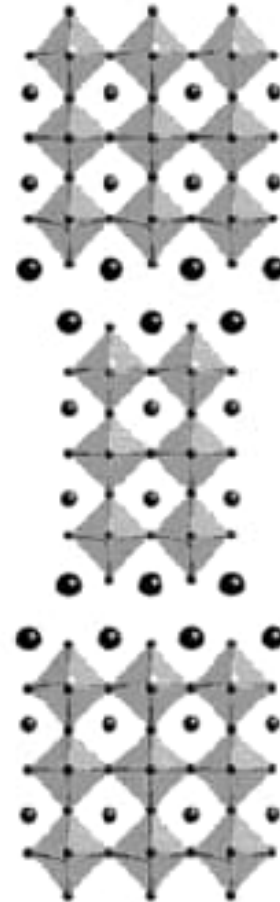
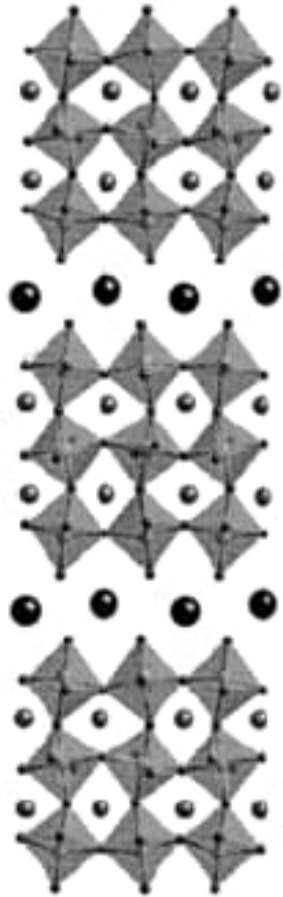
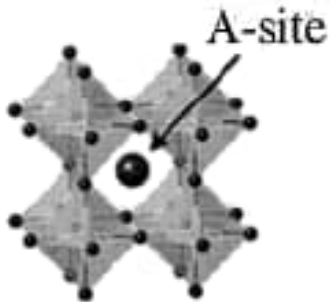
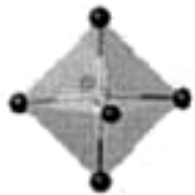
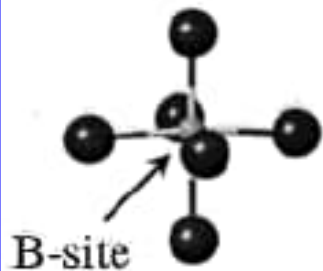
Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenides	MoS <sub>2</sub> , WS <sub>2</sub> , MoSe <sub>2</sub> , WSe <sub>2</sub>	Semiconducting dichalcogenides: MoTe <sub>2</sub> , WTe <sub>2</sub> , ZrS <sub>2</sub> , ZrSe <sub>2</sub> and so on	Metallic dichalcogenides: NbSe <sub>2</sub> , NbS <sub>2</sub> , TaS <sub>2</sub> , TiS <sub>2</sub> , NiSe <sub>2</sub> and so on		
			Layered semiconductors: GaSe, GaTe, InSe, Bi <sub>2</sub> Se <sub>3</sub> and so on		
2D oxides	Micas, BSCCO	MoO <sub>3</sub> , WO <sub>3</sub>	Perovskite-type: LaNb <sub>2</sub> O <sub>7</sub> , (Ca,Sr) <sub>2</sub> Nb <sub>3</sub> O <sub>10</sub> , Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> , Ca <sub>2</sub> Ta <sub>2</sub> TiO <sub>10</sub> and so on		Hydroxides: Ni(OH) <sub>2</sub> , Eu(OH) <sub>2</sub> and so on
	Layered Cu oxides	TiO <sub>2</sub> , MnO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub> , TaO <sub>3</sub> , RuO <sub>2</sub> and so on			Others

# NANO-LEGO GAME



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

# Multilayered oxide structures ...



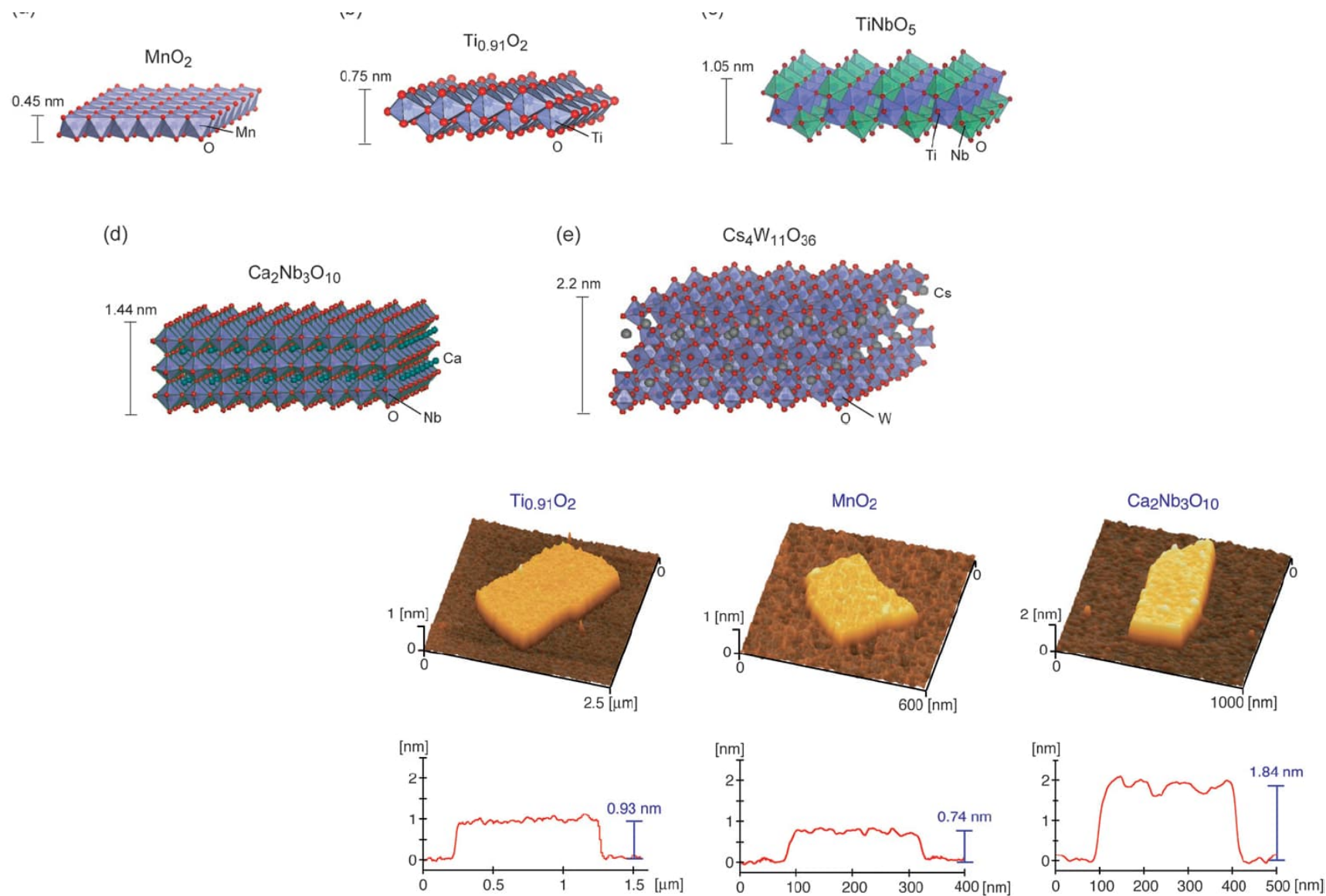
**Perovskite**  
[BaTiO<sub>3</sub>]

**Dion-Jacobson**  
[CsCa<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub>]

**Ruddlesden-Popper**  
[K<sub>2</sub>La<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>]

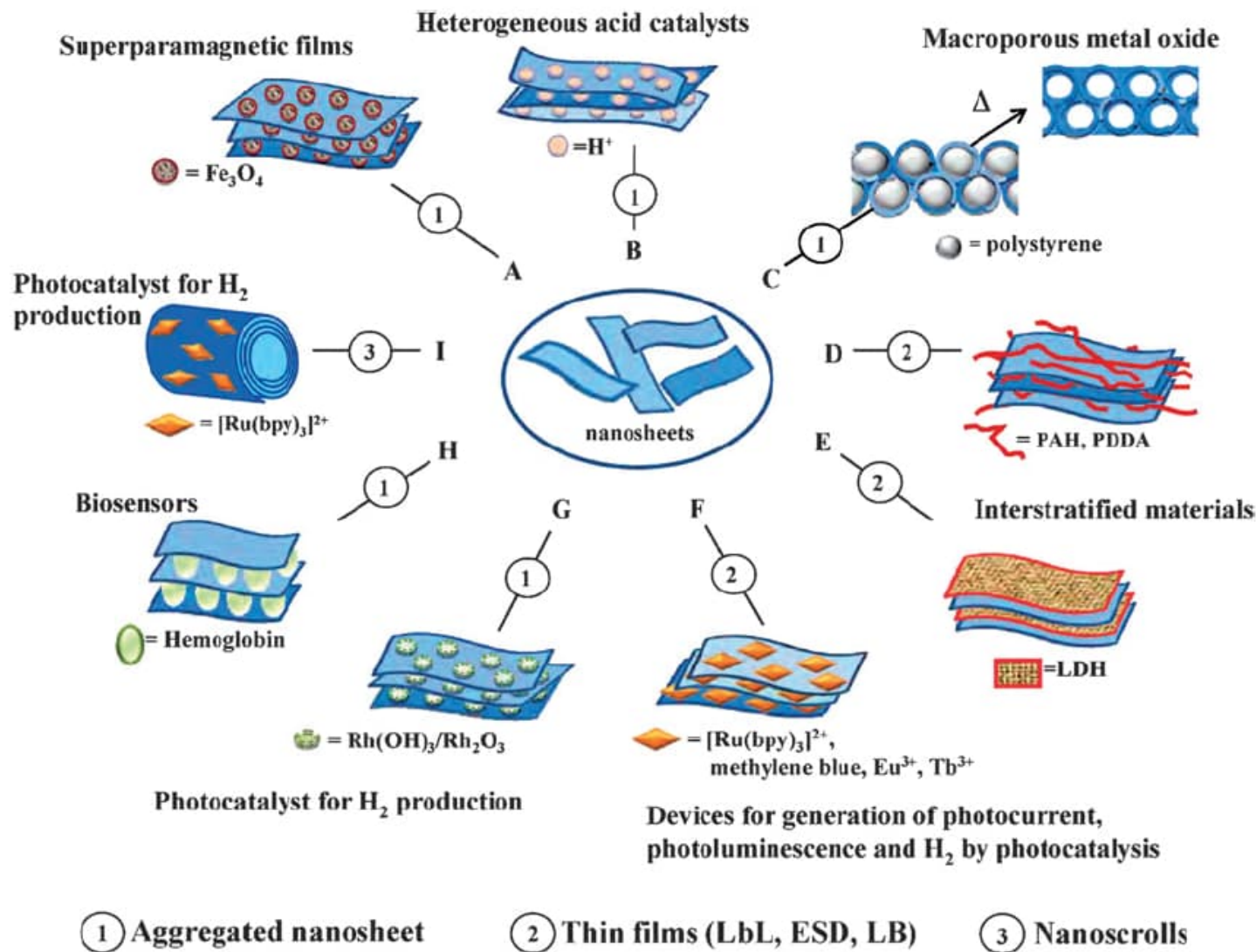
**Aurivillius**  
[Bi<sub>2</sub>O<sub>2</sub>(Bi<sub>2</sub>Ti<sub>3</sub>O<sub>10</sub>)]

# OXIDE NANOSHEETS



**Fig. 2** AFM images of Ti<sub>0.91</sub>O<sub>2</sub>, MnO<sub>2</sub> and Ca<sub>2</sub>Nb<sub>3</sub>O<sub>10</sub> 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.

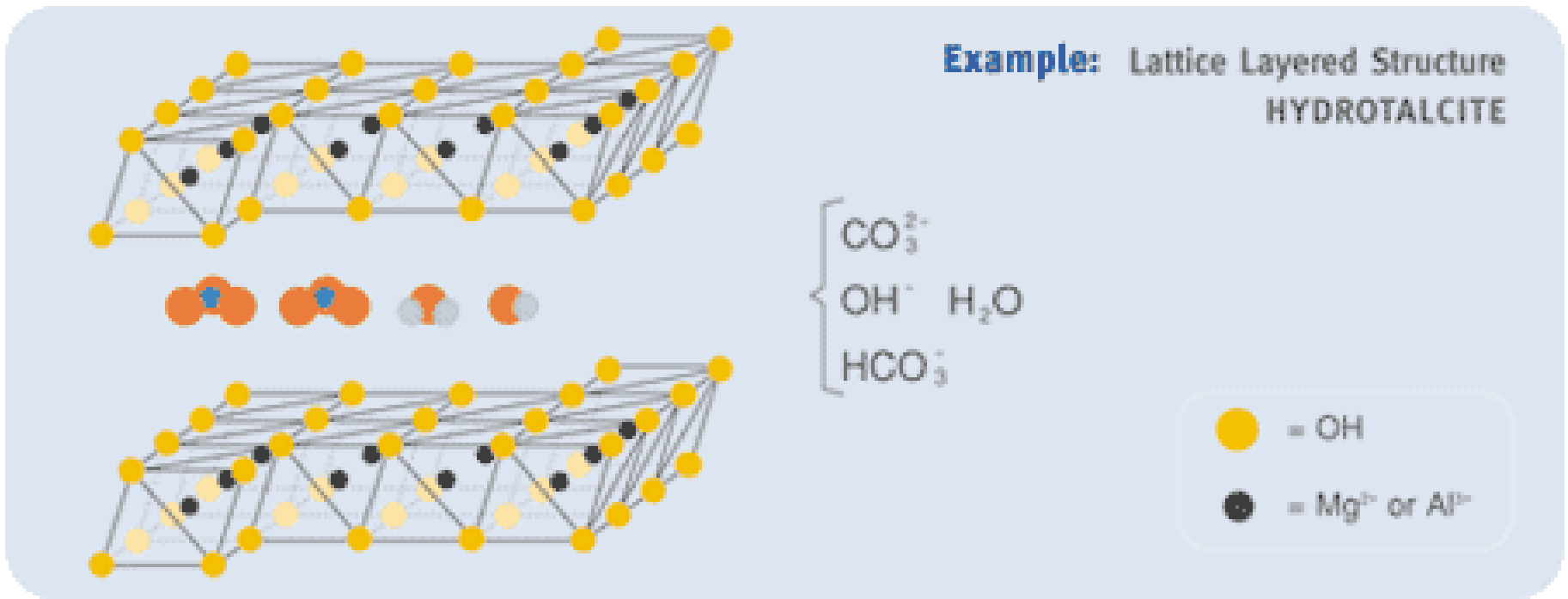




**Scheme 1** Niobate nanosheets as building blocks for materials assembly (reproduced from the Feature Article of Bizeto, Shiguihara and Constantino).

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

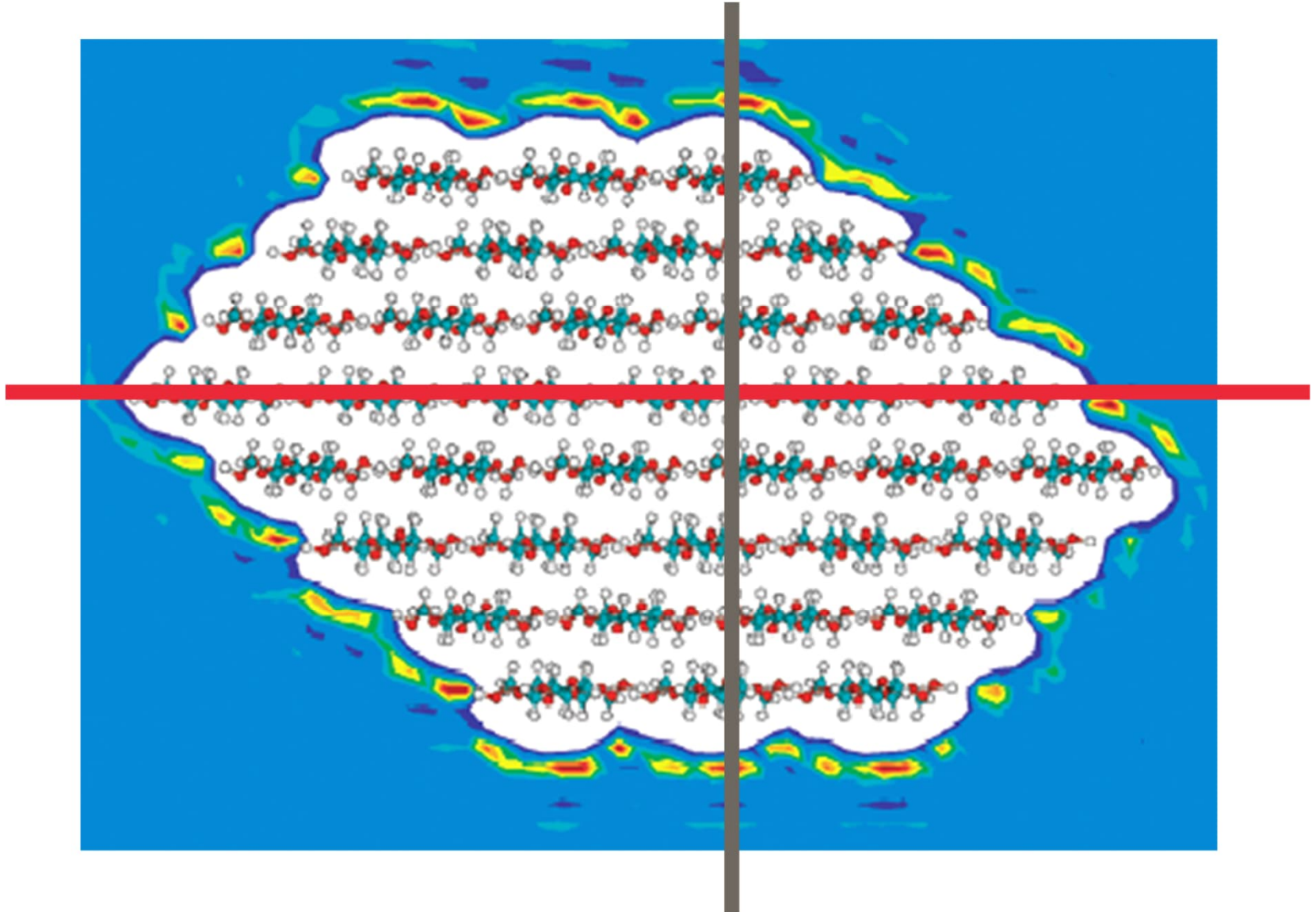


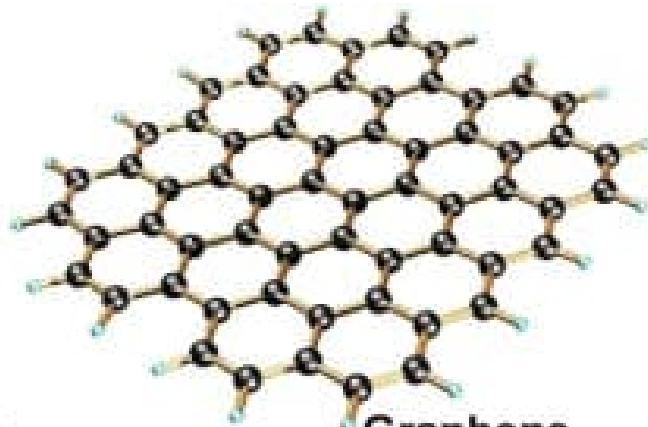


## Hydrotalcite $\text{Al}_2\text{Mg}_6(\text{OH})_{16}\text{CO}_3 \cdot x\text{H}_2\text{O}$

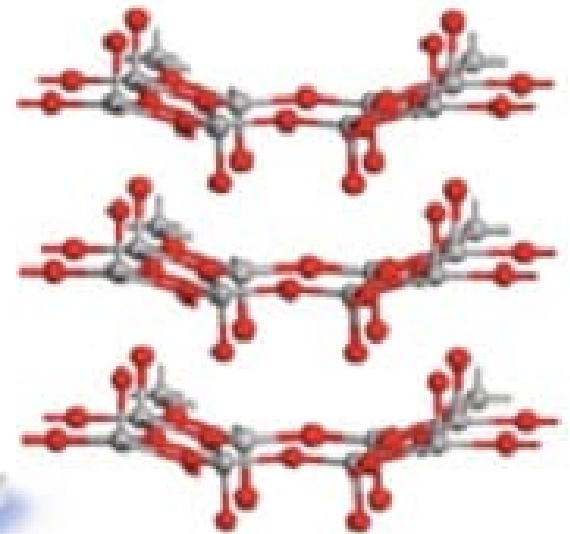
- Multilayered crystal structure
- **Natural clay**
- Name derived from its resemblance with talc and its high water content
- Reacts rapidly with gastric acid even in the presence of pepsin and proteins
- Variety of pharmaceutical applications

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

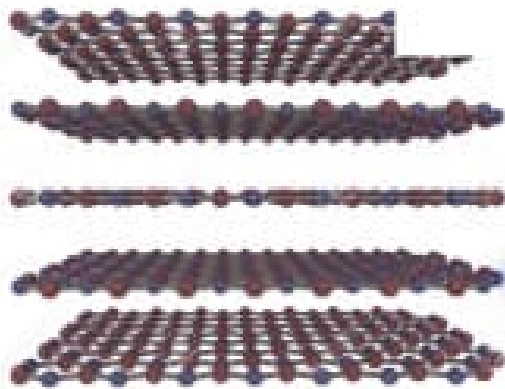




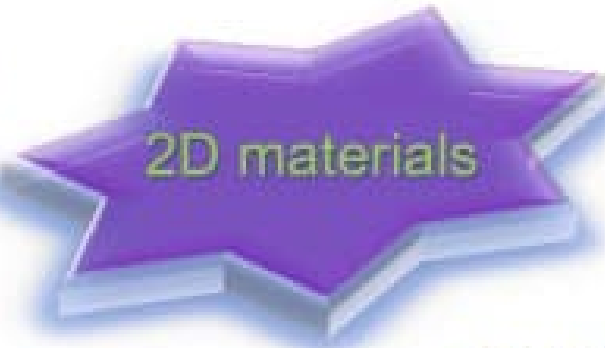
Graphene



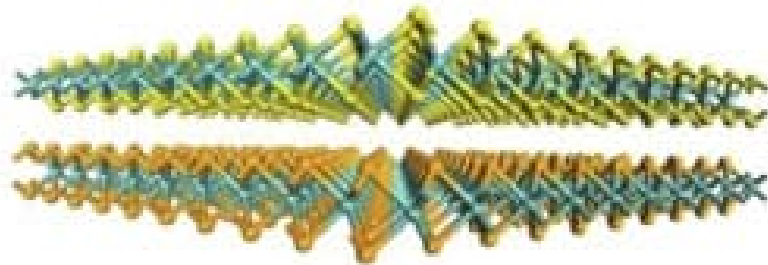
Layered metal oxides



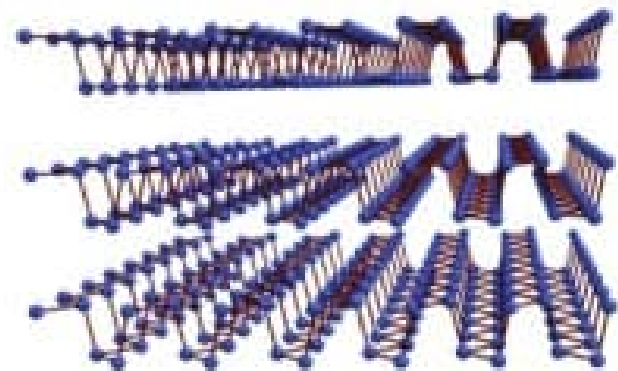
Hexagonal-boron nitride



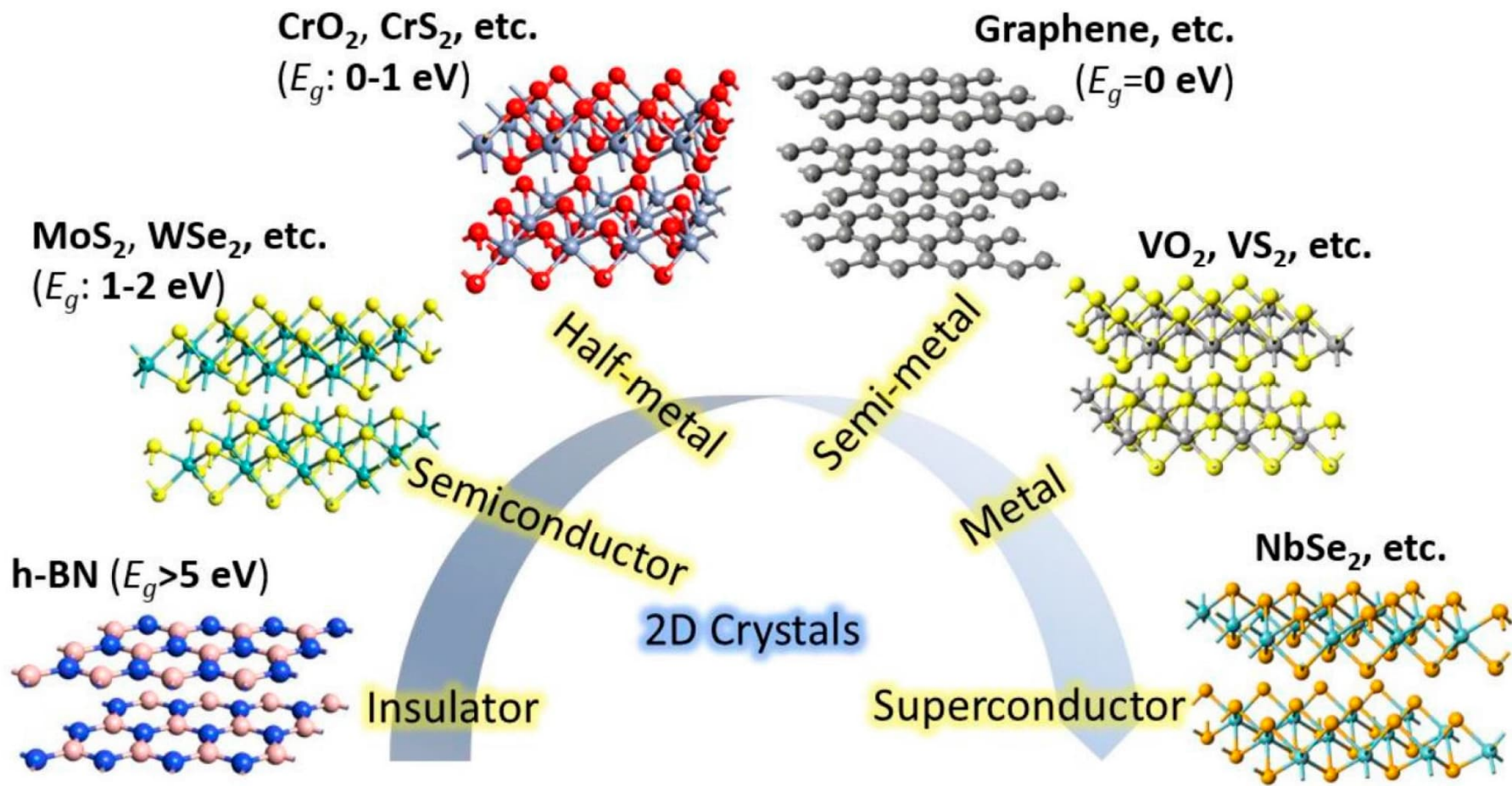
2D materials



Transition metal dichalcogenides



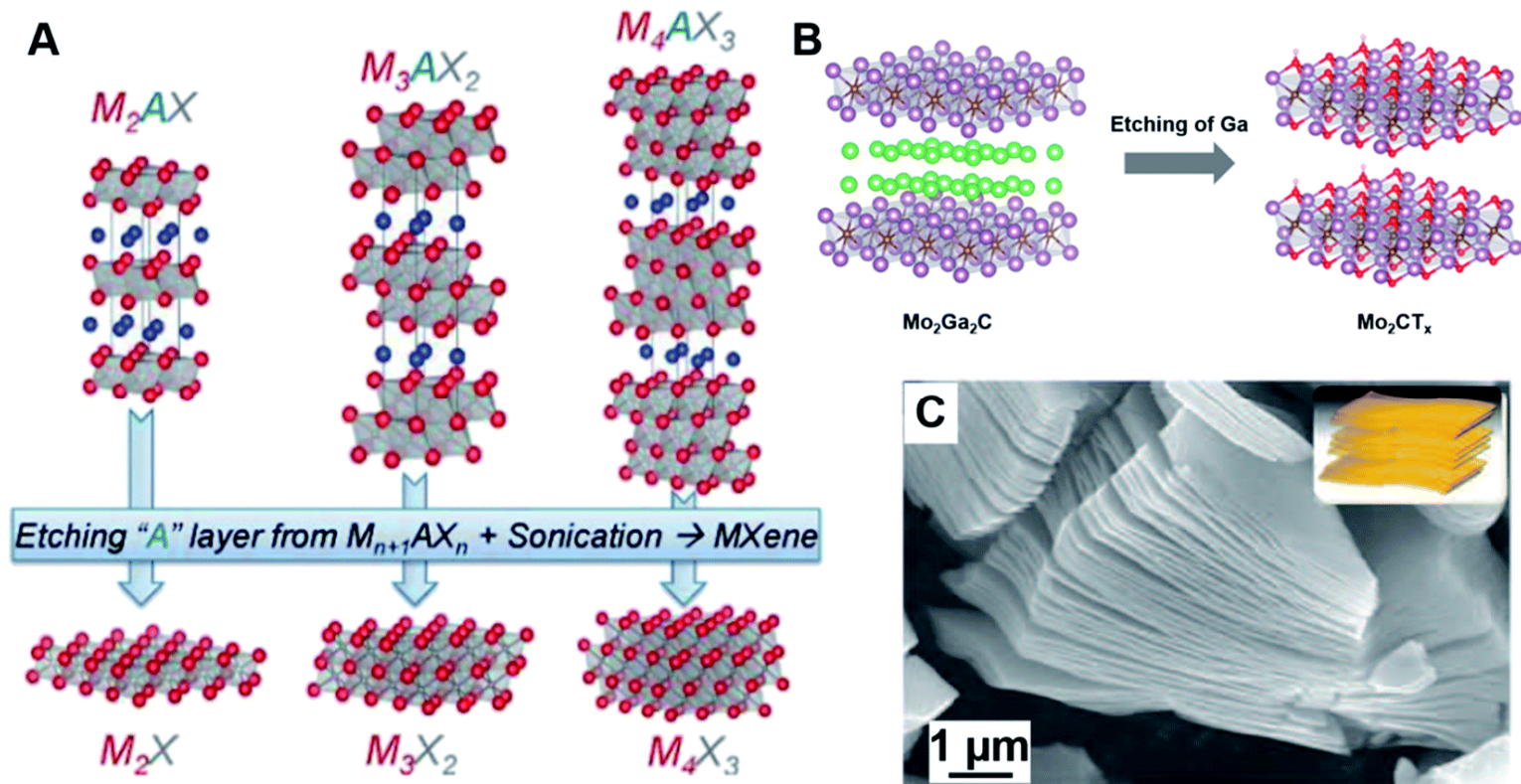
Black phosphorus





# 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

- Exchange of ions with bulky organic ions + dispersion

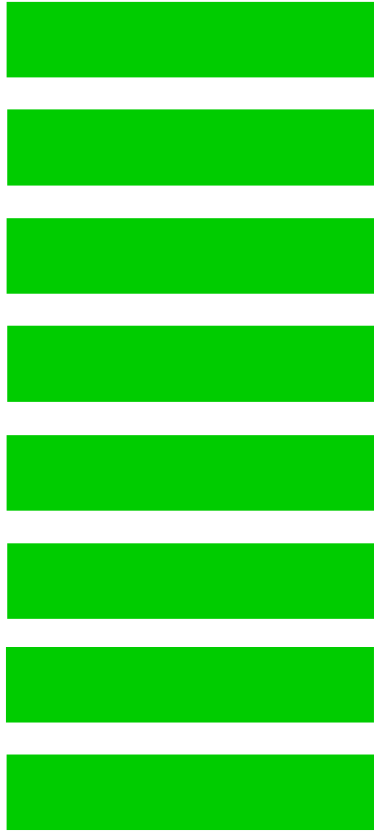
### Bottom-up synthesis

- Growing from gas phase on a proper substrate

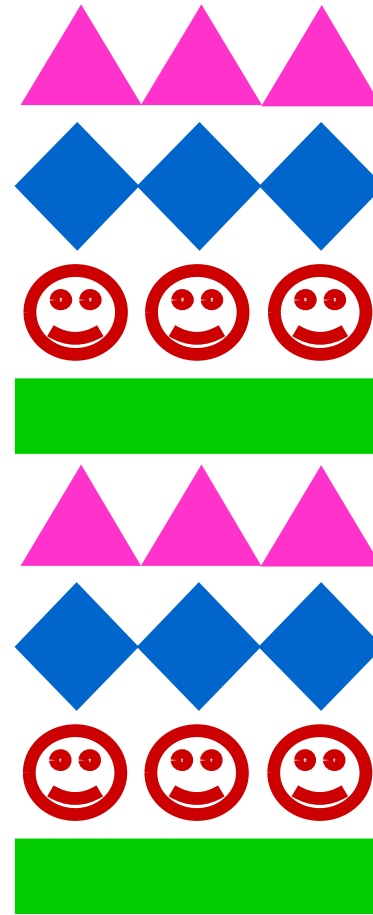
## HOW TO VERIFY THE NANOSHEETS

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

# Layer-Engineering



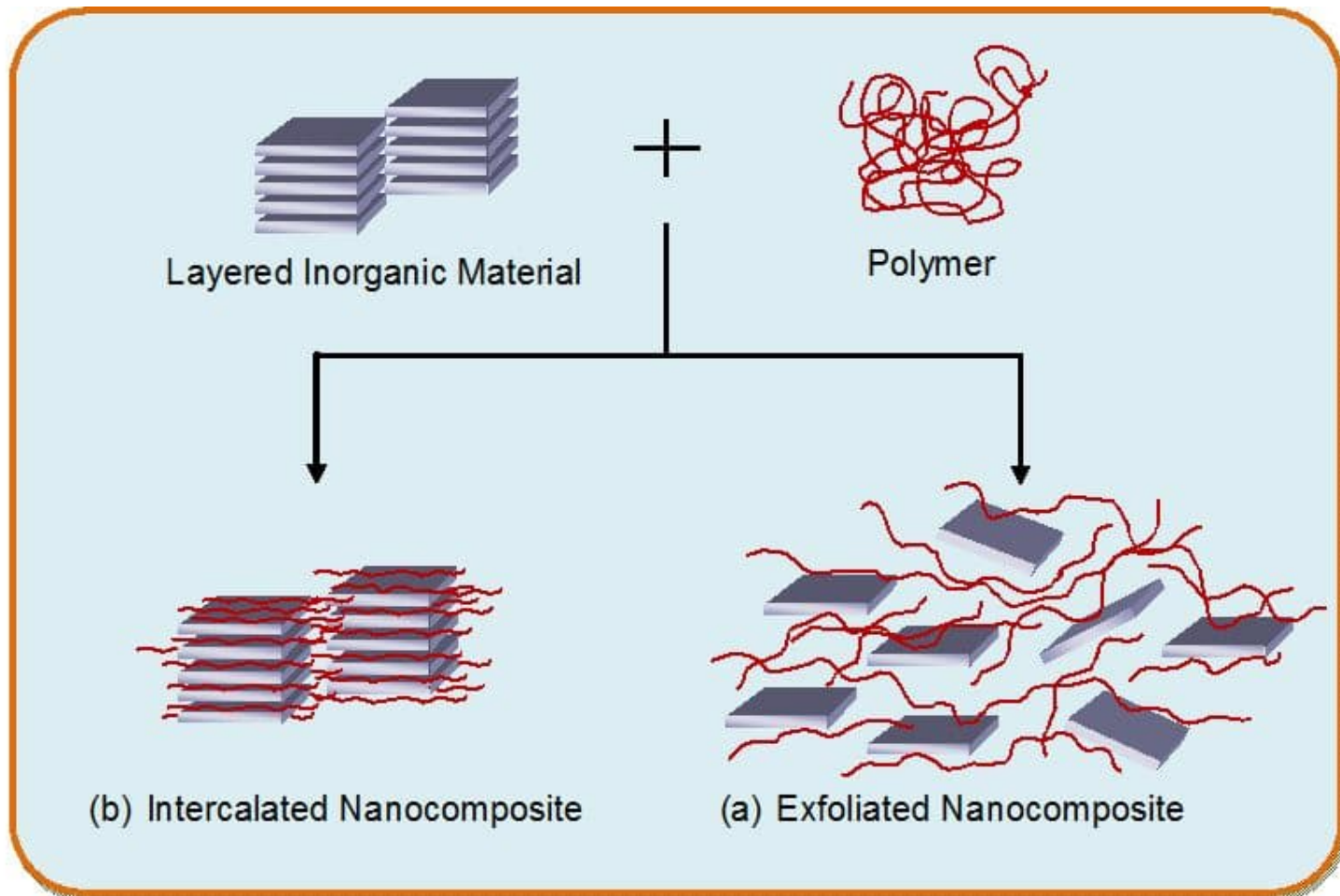
**Layered material**



Multiple functions

**Multilayered material**

# (MULTI)LAYERED INORGANIC-ORGANIC MATERIALS



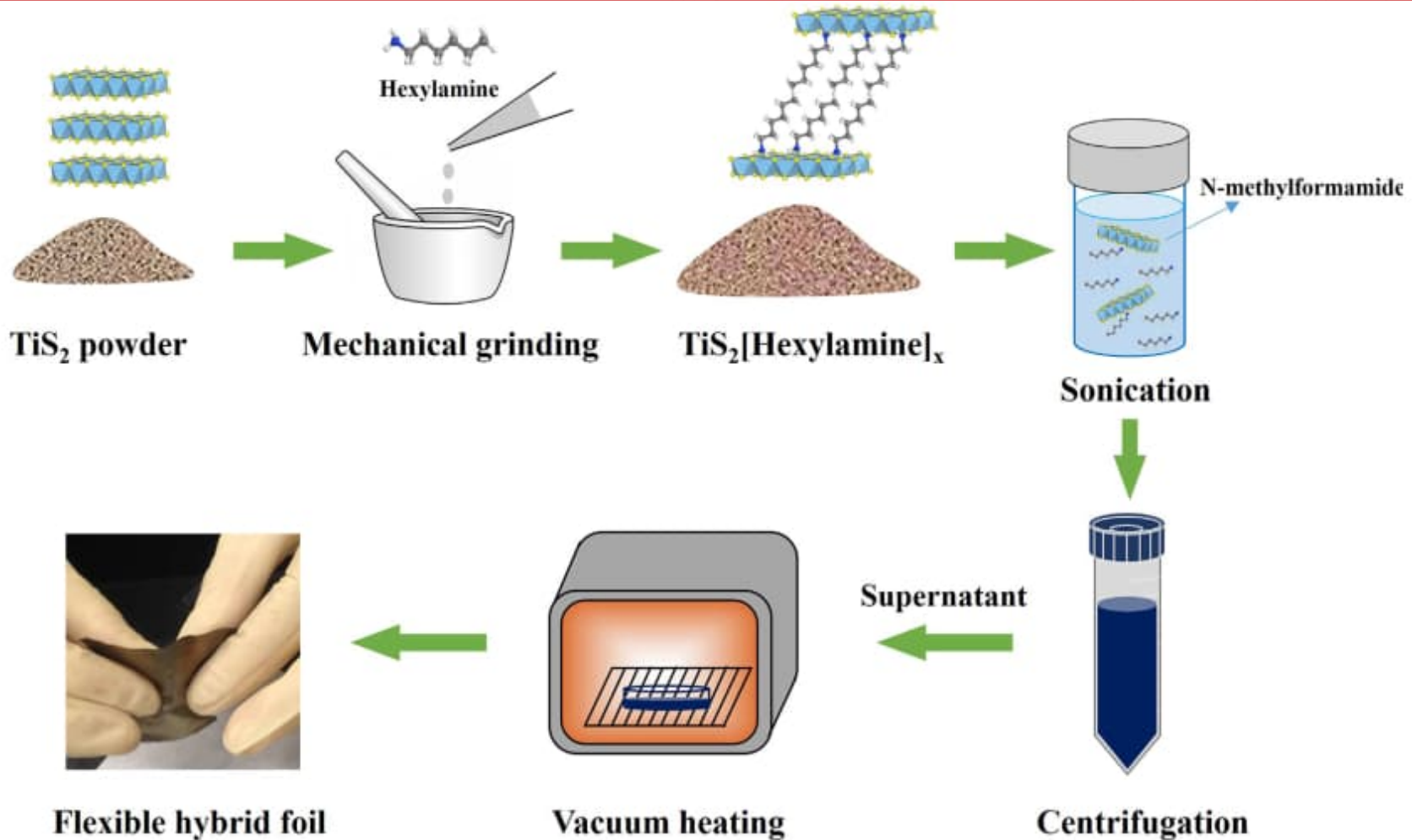


# Multilayered Inorganic-Organic Hybrids

Flexible thermoelectric foil for wearable energy harvesting

Chunlei Wan<sup>a,\*</sup>, Ruoming Tian<sup>b</sup>, Azrina Binti Azizi<sup>c</sup>, Yujia Huang<sup>a</sup>, Qingshuo Wei<sup>d</sup>, Ryo Sasai<sup>c</sup>, Soontornchaiyakul Wasusate<sup>c</sup>, Takao Ishida<sup>d</sup>, Kunihito Koumoto<sup>b,\*</sup>

<sup>a</sup>, Beijing 100084, China  
<sup>b</sup>, 305-8564, Japan  
<sup>c</sup>, Japan



Flexible hybrid foil

Vacuum heating

Centrifugation



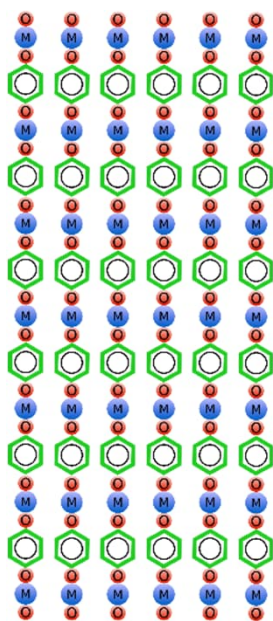
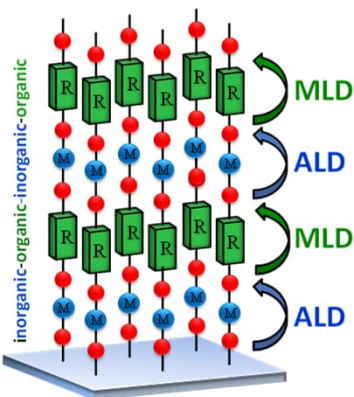
Organic (e.g. benzene)



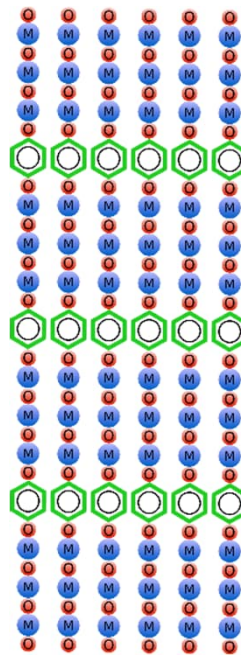
Metal



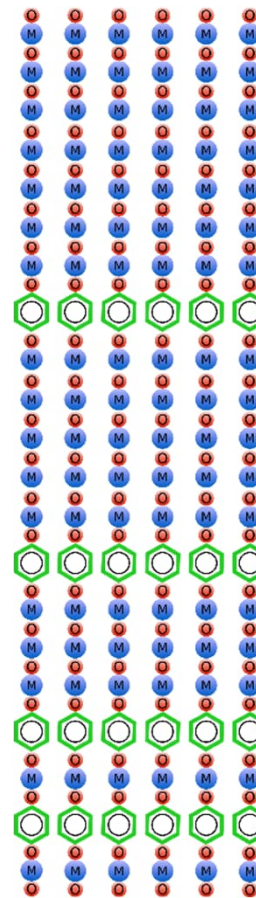
Oxygen (or N, S, ...)



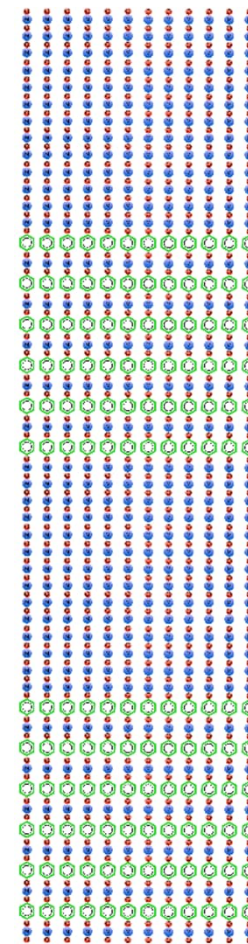
Simple  
Metal-Organic Network  
(amorphous or crystalline)



Superlattice



Gradient hybrid



Nanolaminate

**A!**

Aalto University  
School of Chemical  
Engineering

DIFFERENT LAYER SEQUENCES BY ALD/MLD DESIGN