LECTURE SCHEDULE

Mon	(Ke3)	12.15 – 14.00
Wed	(Ke2)	10.15 – 12.00
Fri	(Ke5)	10.15 – 12.00

		Date	Topic
1.	Wed	06.09.	Course Introduction & Short Review on Elements & Periodic Table
2.	Fri	08.09.	Short Survey of Main Group Elements
3.	Mon	11.09.	Zn + Ti, Zr, Hf & Atomic Layer Deposition (ALD)
4.	Wed	13.09.	Transition Metals: General Aspects & Pigments
5.	Fri	15.09.	Redox Chemistry
6.	Mon	18.09.	Crystal Field Theory (Linda Sederholm)
7.	Wed	20.09.	V, Nb, Ta & Perovskites & Metal Complexes & MOFs & MLD
8.	Mon	25.09.	Cr, Mo, W & 2D materials & Mxenes & Layer-Engineering
9.	Wed	27.09.	Mn, Fe, Co, Ni, Cu
10.	Fri	29.09.	Cu & Magnetism & Superconductivity
11.	Mon	02.10.	Ag, Au, Pt, Pd & Catalysis (Antti Karttunen)
12.	Wed	04.10.	Lanthanoids + Actinoids & Luminescence
13.	Fri	06.10.	Resources of Elements & Rare/Critical Elements & Element Substitutions
14.	Fri	13.10.	Inorganic Materials Chemistry Research

EXAM: Tuesday Oct. 17, 9:00-12:00 in Ke2

PRESENTATION TOPICS/SCHEDULE

Mon	25.09.	Mo:	Maryam Jafarishiad & Saara Siekkinen
Wed	27.09.	Mn:	Naomi Lyle & Sanni Ilmaranta
		Ru:	Miklos Nemeszeghy & Timo de Jonge
Fri	29.09.	Cu:	Koshila Hiruni & Kaushalya Poonanoo
Wed	04.10.	Eu:	Binglu Wang & Mari
		Nd:	Patrich Wiesenfeldt & Tomoki Nakayama
		U:	Miikka Viirto & Ashish Singh
Fri	06.10.	Co:	Gabrielle Laurent & Yan Zheng
		In:	Sonja Alasaukko-oja & Katri Haapalinna
		Te:	Sofia Rantala & Roger Peltonen

QUESTIONS: Lecture 8

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

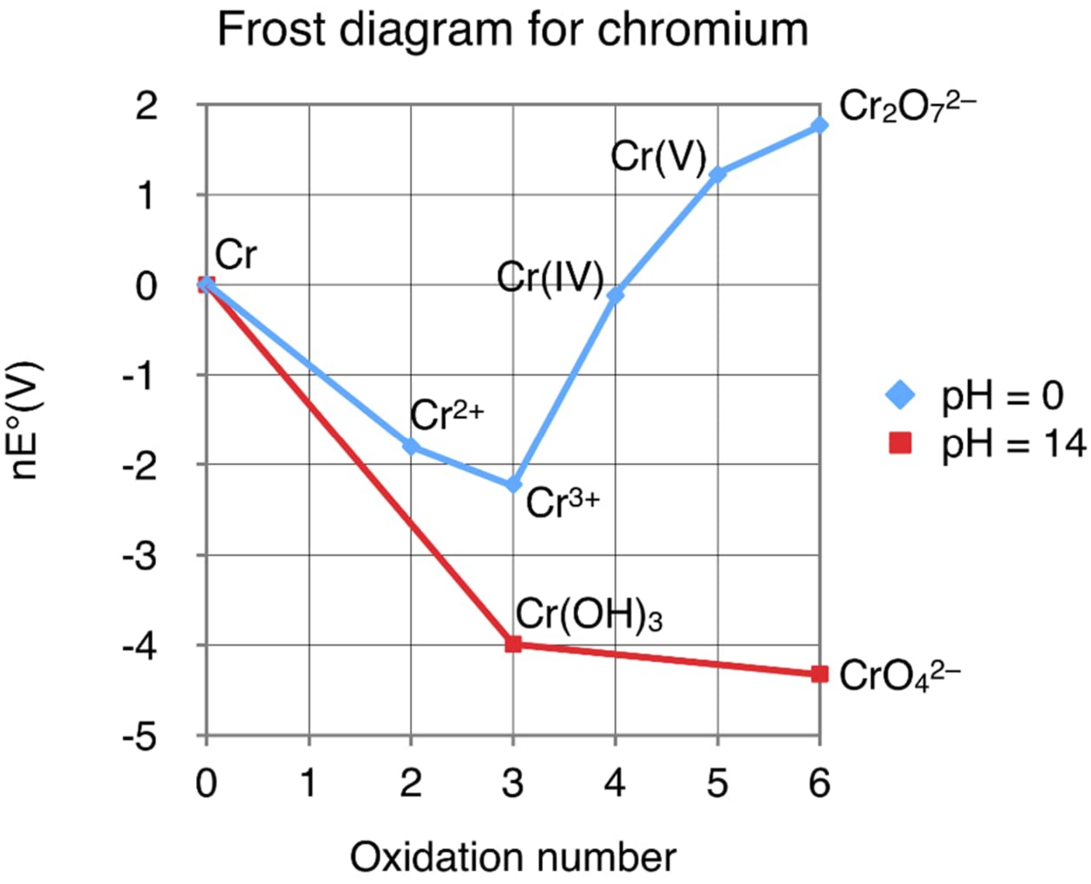
1. **Explain why K_2CrO_4 is colorful even though hexavalent Cr does not have d electrons. Give another example of the same phenomenon.**

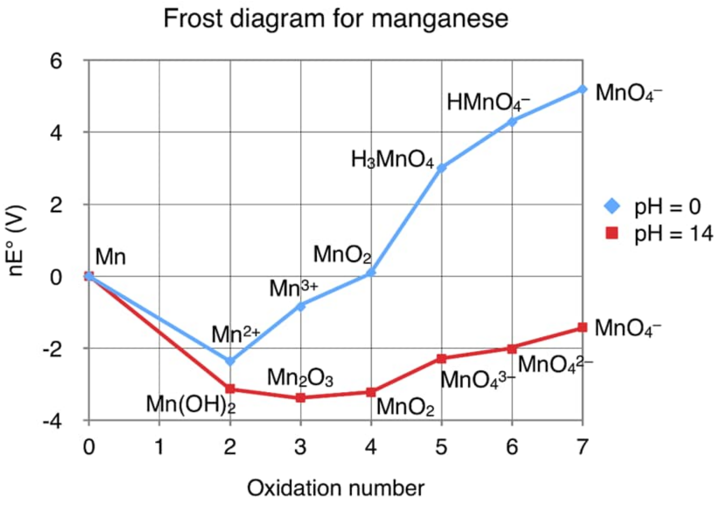
2. **Give three examples of interesting 2D materials; motivate your choices.**

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

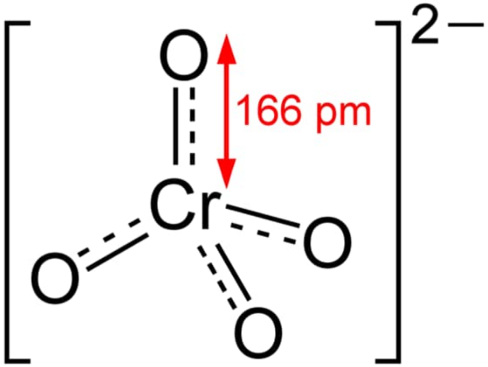
- **Chromium:** **VI: stable (chromate and tendency towards polychromates)**
  V and IV: unstable (disproportionate)
  III: most stable

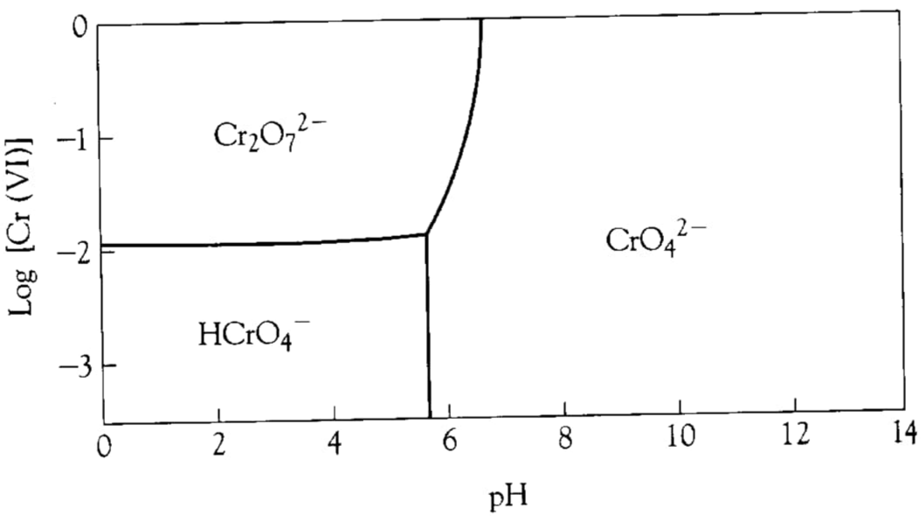


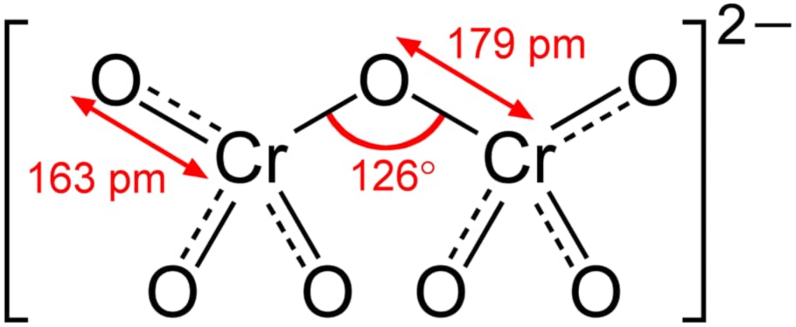


CHROMATE

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

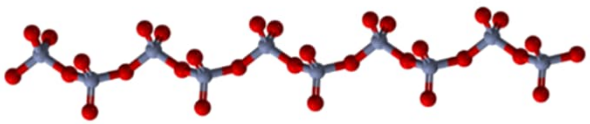






Chromium trioxide

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



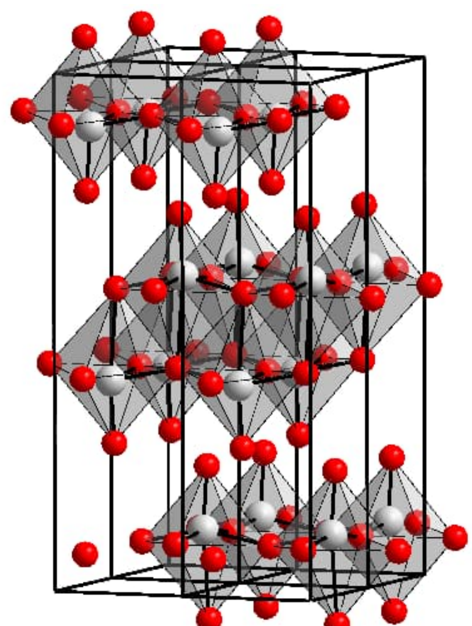
"Halfmetal" for SPINTRONICS: Electrical conductor & ferromagnet

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	—

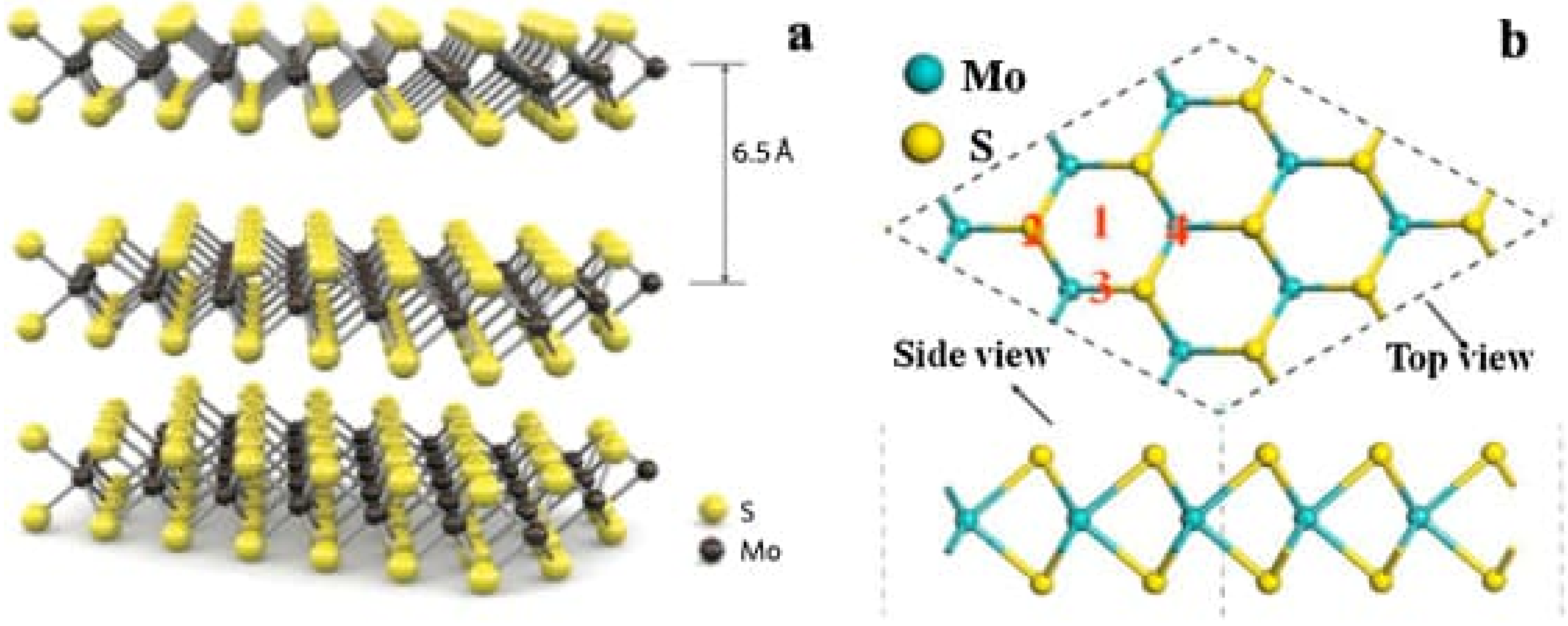
Molybdenum trioxide

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

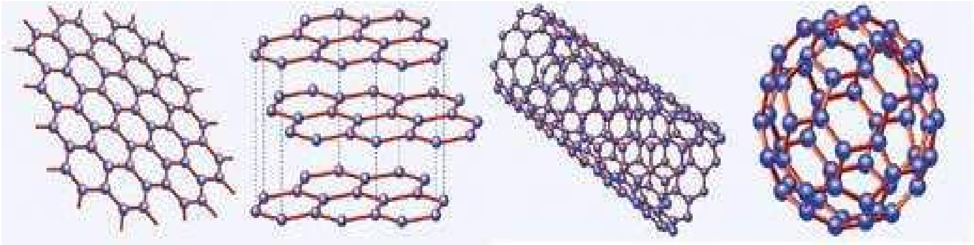


Another 2D Structure: CHALCOGENIDES (S, Se, Te)

- Natural mineral molybdenite MoS_2 (similar to e.g. TiS_2)
- Trigonal prismatic (CN = 6) coordination around Mo
- Semiconductor (somewhat similar to graphite)



GRAPHENE



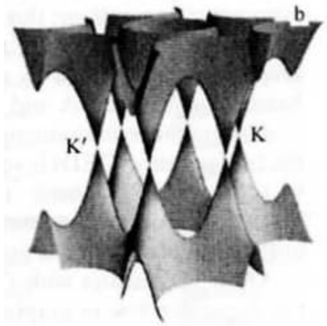
- **Monolayer of graphite or a giant PAH molecule**
  (*polycyclic aromatic hydrocarbon*; the largest known PAH molecule consists of 10 C_6-rings)
- **sp^2-hybridization, C-C bond length 1.42 Å**
- **Thinnest (but strongest) material known**
- **Best electrical conductor (at room temperature)**
- **Electrons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

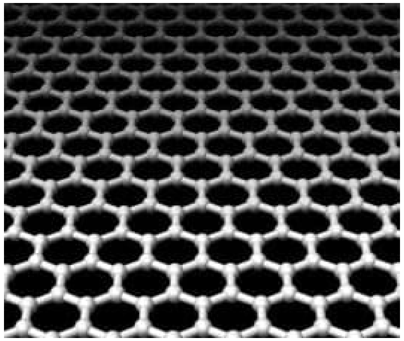
  → is graphene going to replace silicon in next-generation electronics ?
- **The unique properties of graphene were predicted already before it was first prepared in 2004** [Novoselov, Geim, *et al*., *Science* 306, 666 (2004)]; **Nobel 2010**

Graphene

- **Unusual electronic properties**

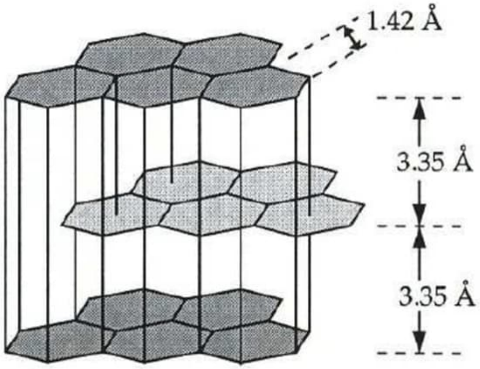
band-structure of graphene

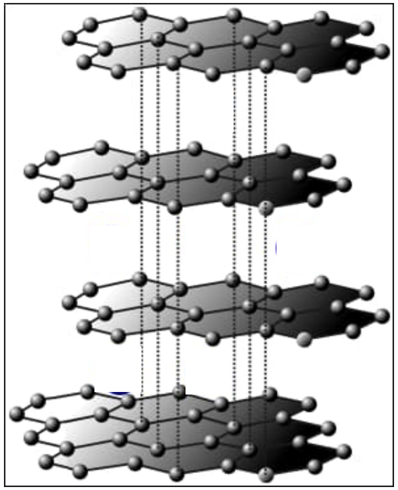




Graphite

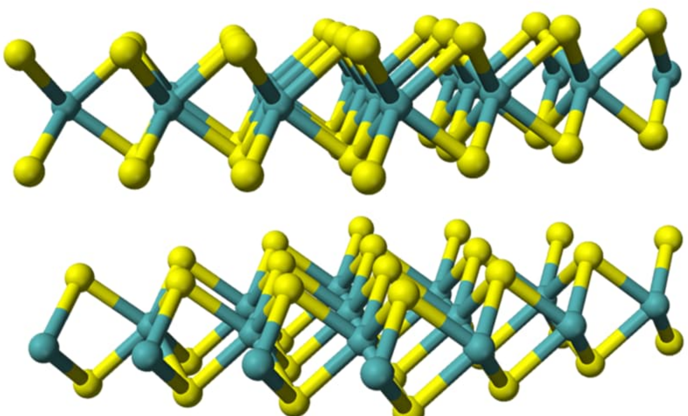
- **Weak (van der Waals) bonds between the layers**
- **Solid lubricant**



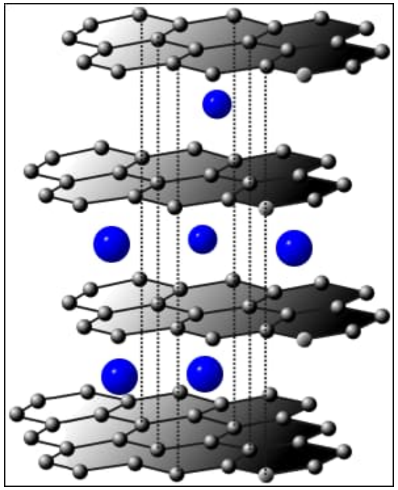


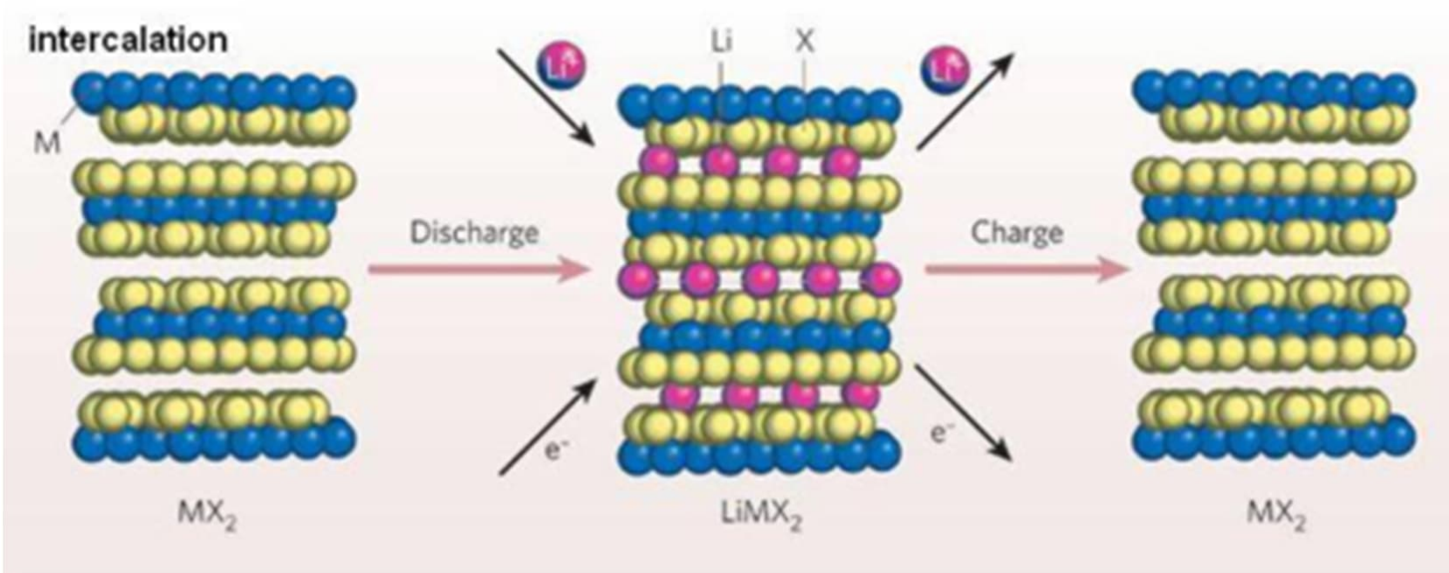
MoS_2

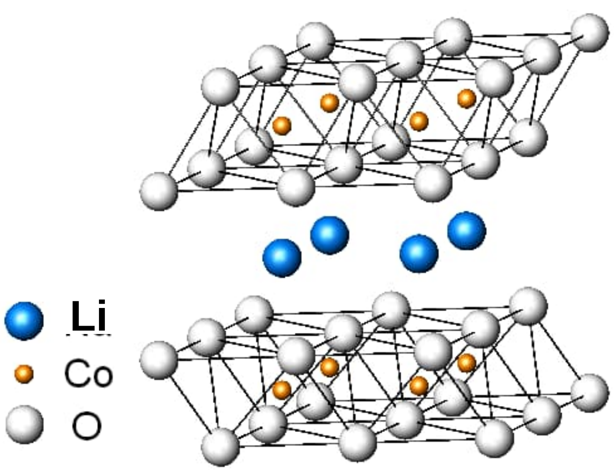
- **Similar to graphite**
- **Band-gap**
- **Solid lubricant**



INTERCALATION







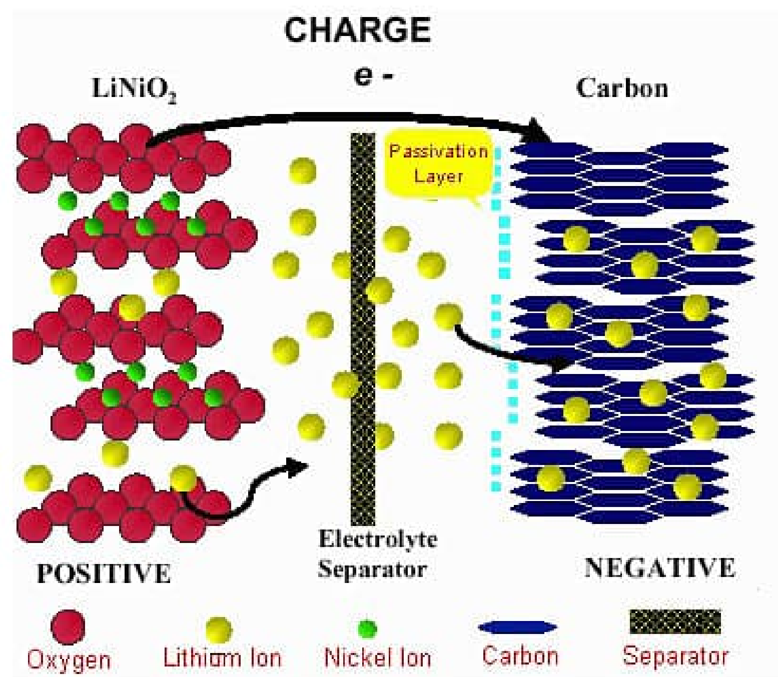
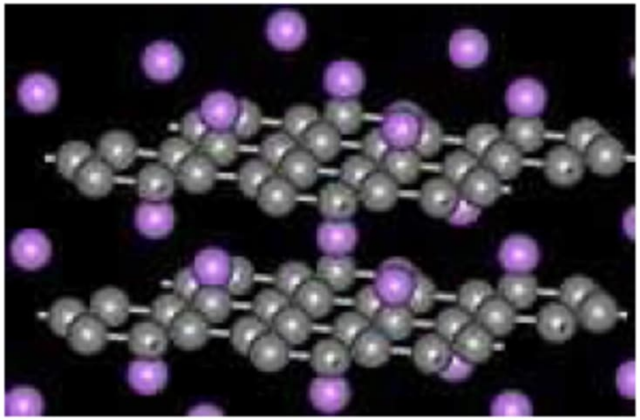


Photo Courtesy of SAFT America

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.

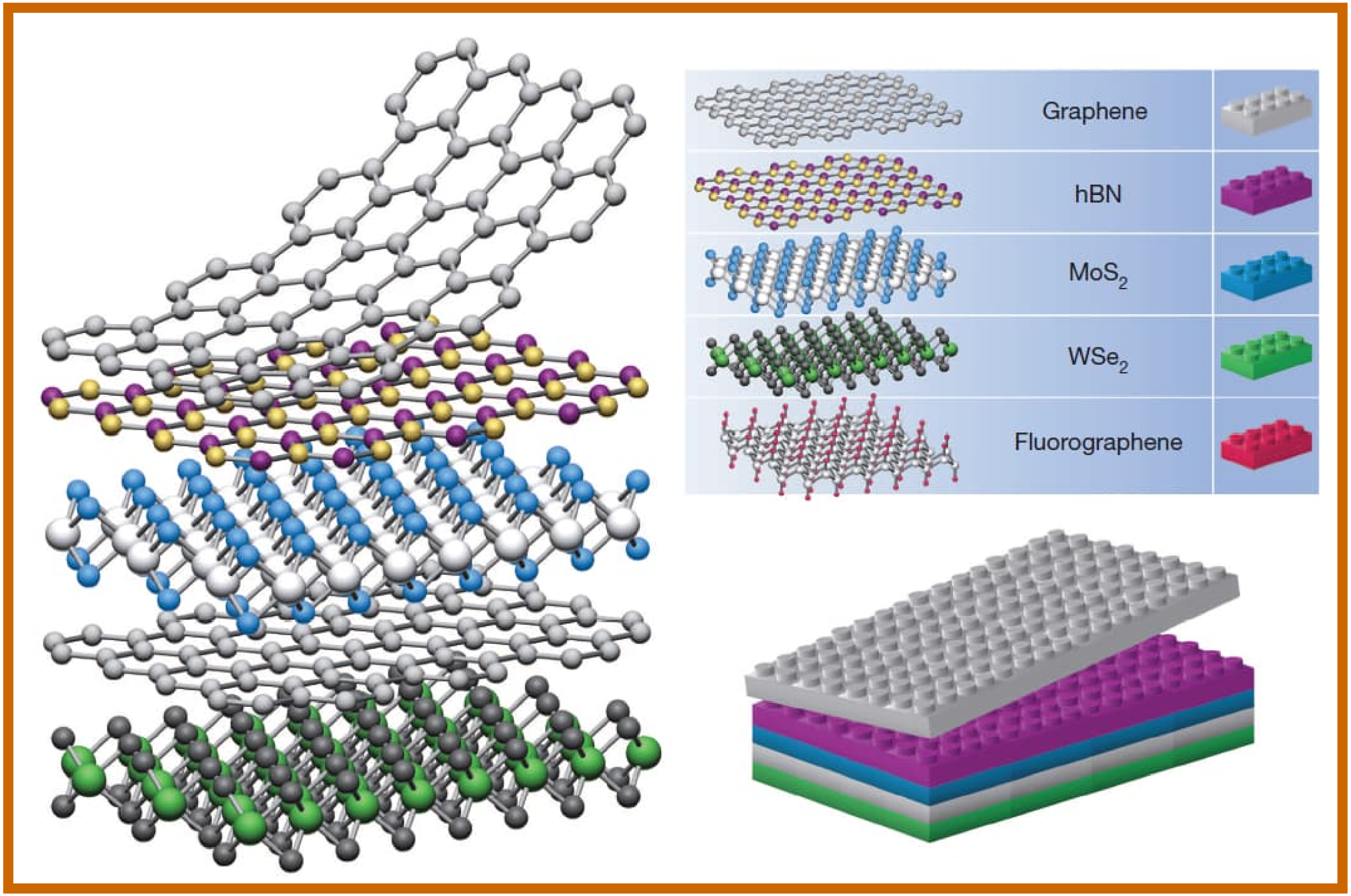


Among the superconducting graphite intercalation compounds, CaC_6 exhibits the highest critical temperature Tc = 11.5 K, which further increases under applied pressure (15.1 K at 8 GPa)

Superconductivity in 2-layer graphene with different intercalants

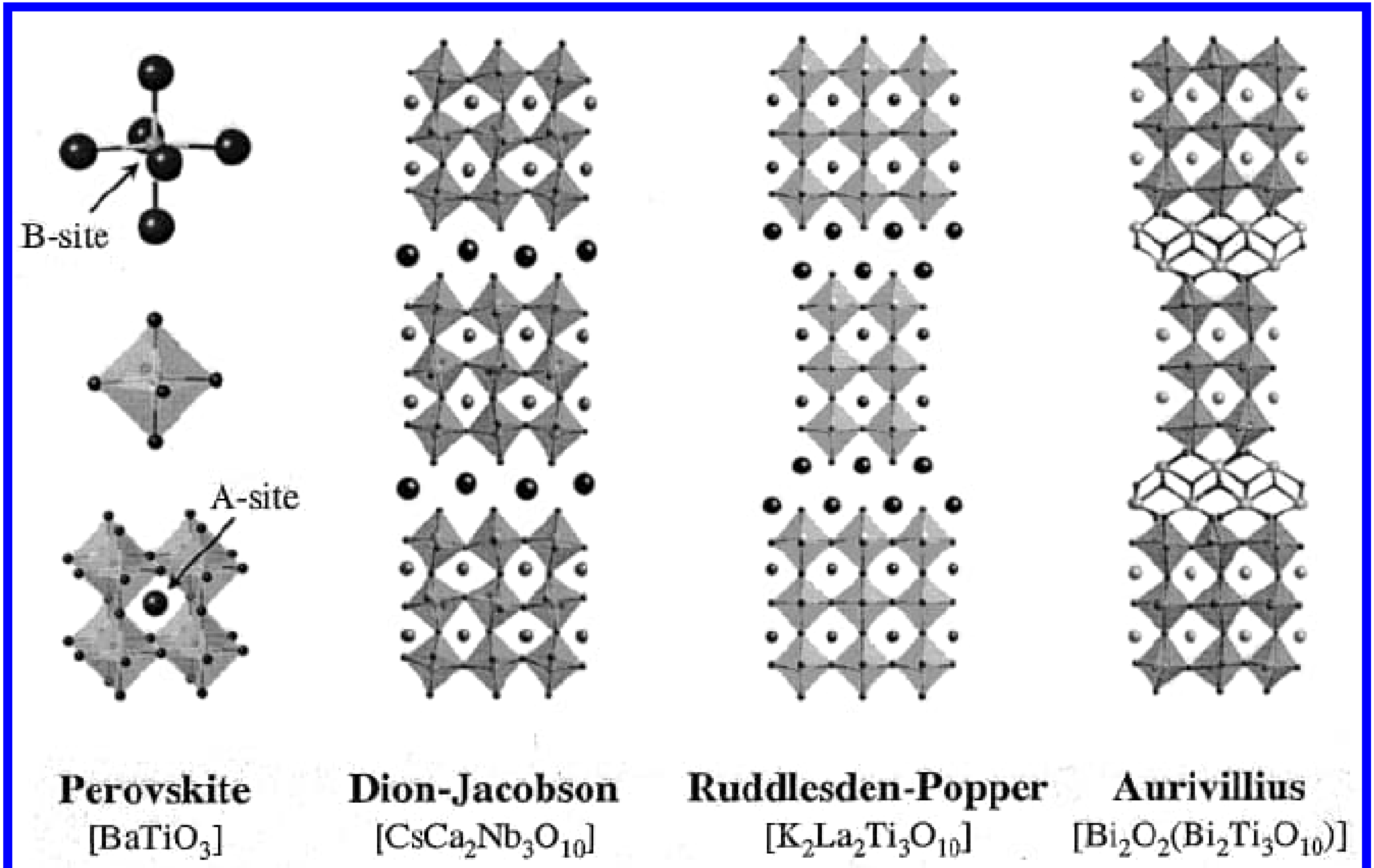
	$\lambda\omega_D/\varepsilon_F$	T_c (K)	$\Delta(0)$ (meV)	$2\Delta(0)/k_BT_c$
C_6KC_6	0.079	8.2	1.38	3.91
C_6CaC_6	0.081	14.0	2.46	4.08
C_6RbC_6	0.093	5.5	0.87	3.67
C_6SrC_6	0.062	8.5	1.41	3.85

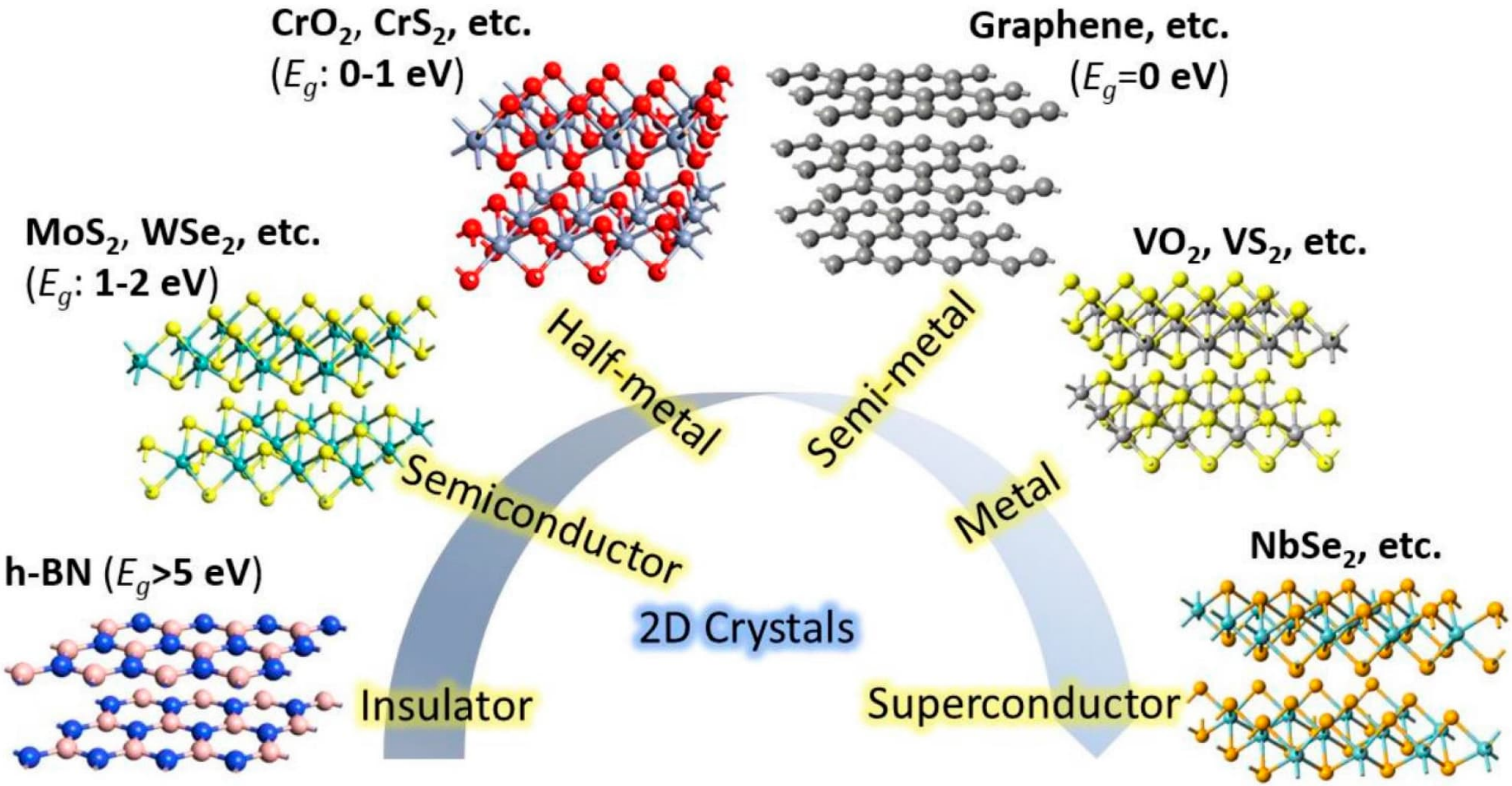
NANO-LEGO GAME



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

Multilayered oxide structures …

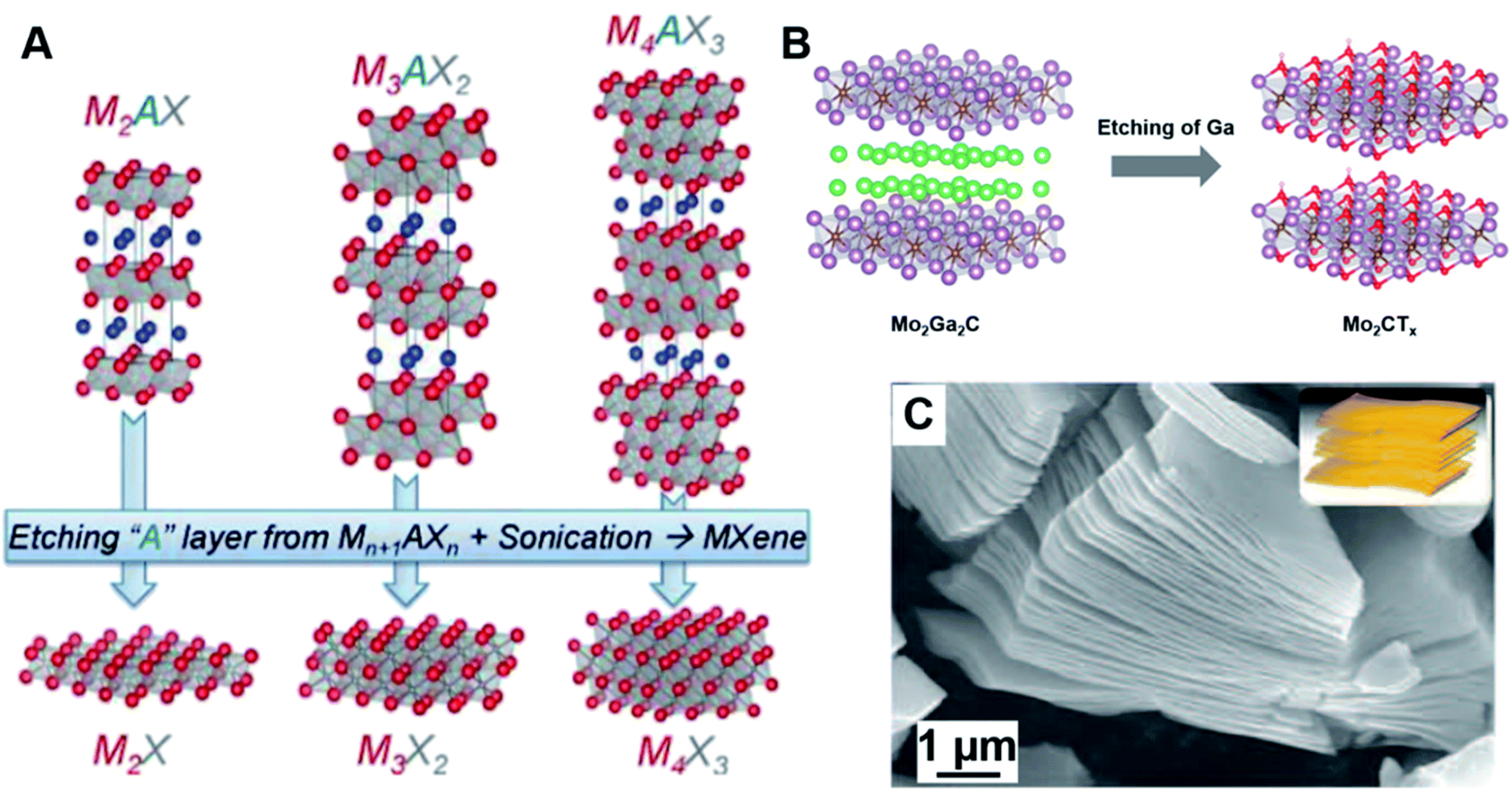




CrO_2, CrS_2, etc.
(E_g: 0-1 eV)
Graphene, etc.
(E_g=0 eV)
MoS_2, WSe_2, etc.
(E_g: 1-2 eV)
VO_2, VS_2, etc.
Half-metal
Semi-metal
Semiconductor
Metal
h-BN (E_g>5 eV)
$NbSe_2$, etc.
2D Crystals
Insulator
Superconductor

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

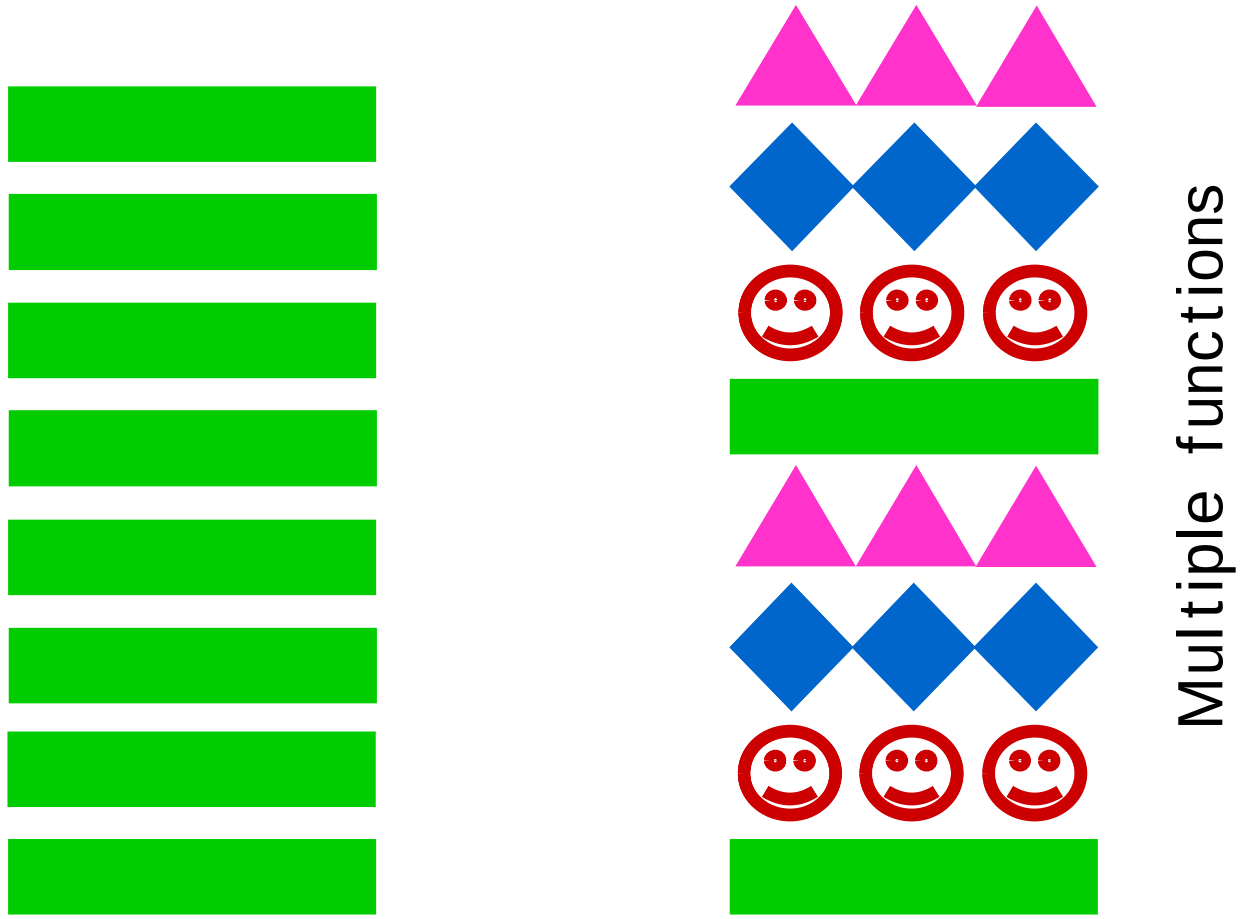
Bottom-up synthesis

- Growing from gas phase on a proper substrate

HOW TO VERIFY THE NANOSHEETS

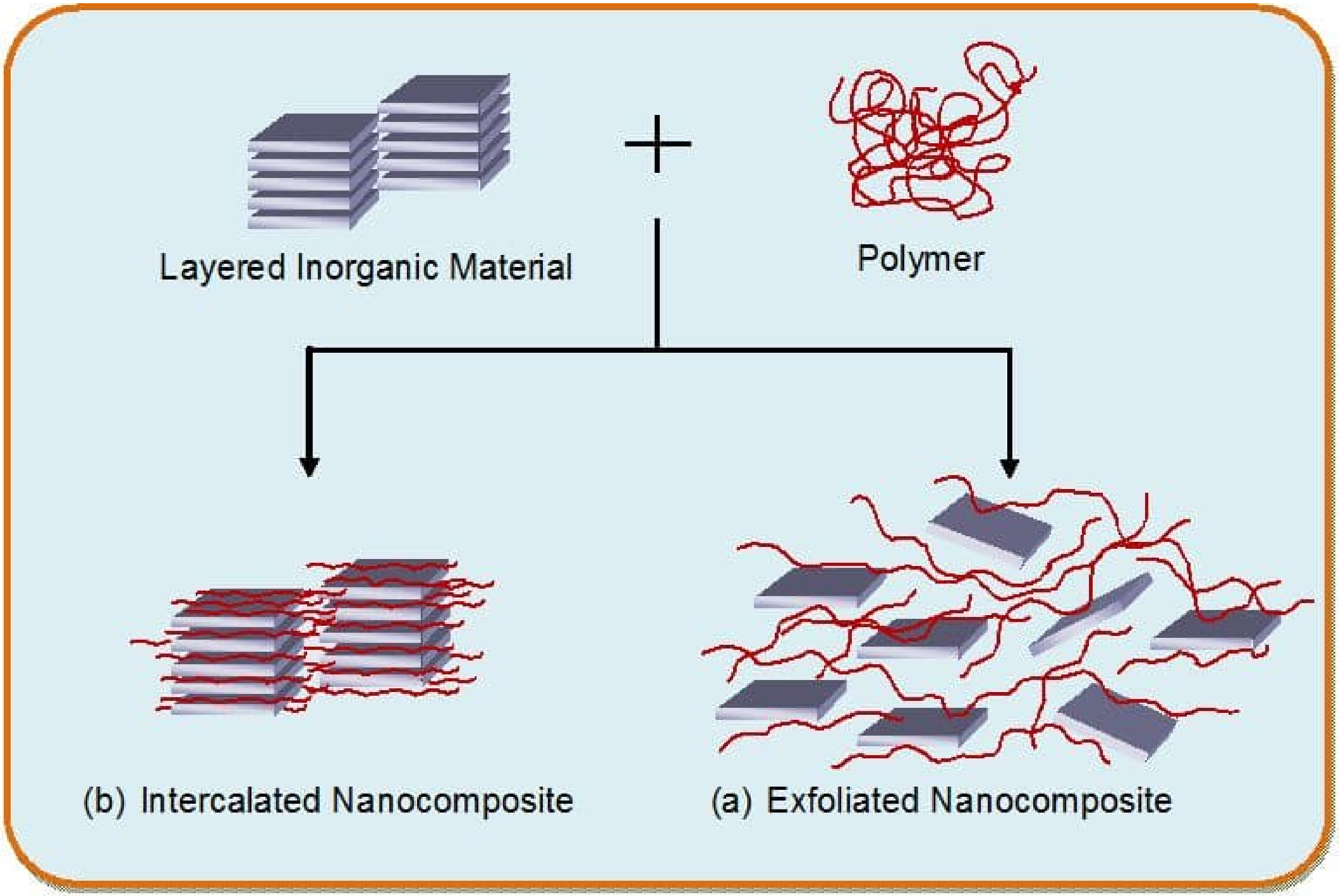
- AFM (Atomic force microscopy)
- Raman spectroscopy
- TEM, STEM, SAXS

Layer-Engineering



Layered material **Multilayered material**

(MULTI)LAYERED INORGANIC-ORGANIC MATERIALS



Multilayered Inorganic-Organic Hybrids

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,*]

y, Beijing 100084, China

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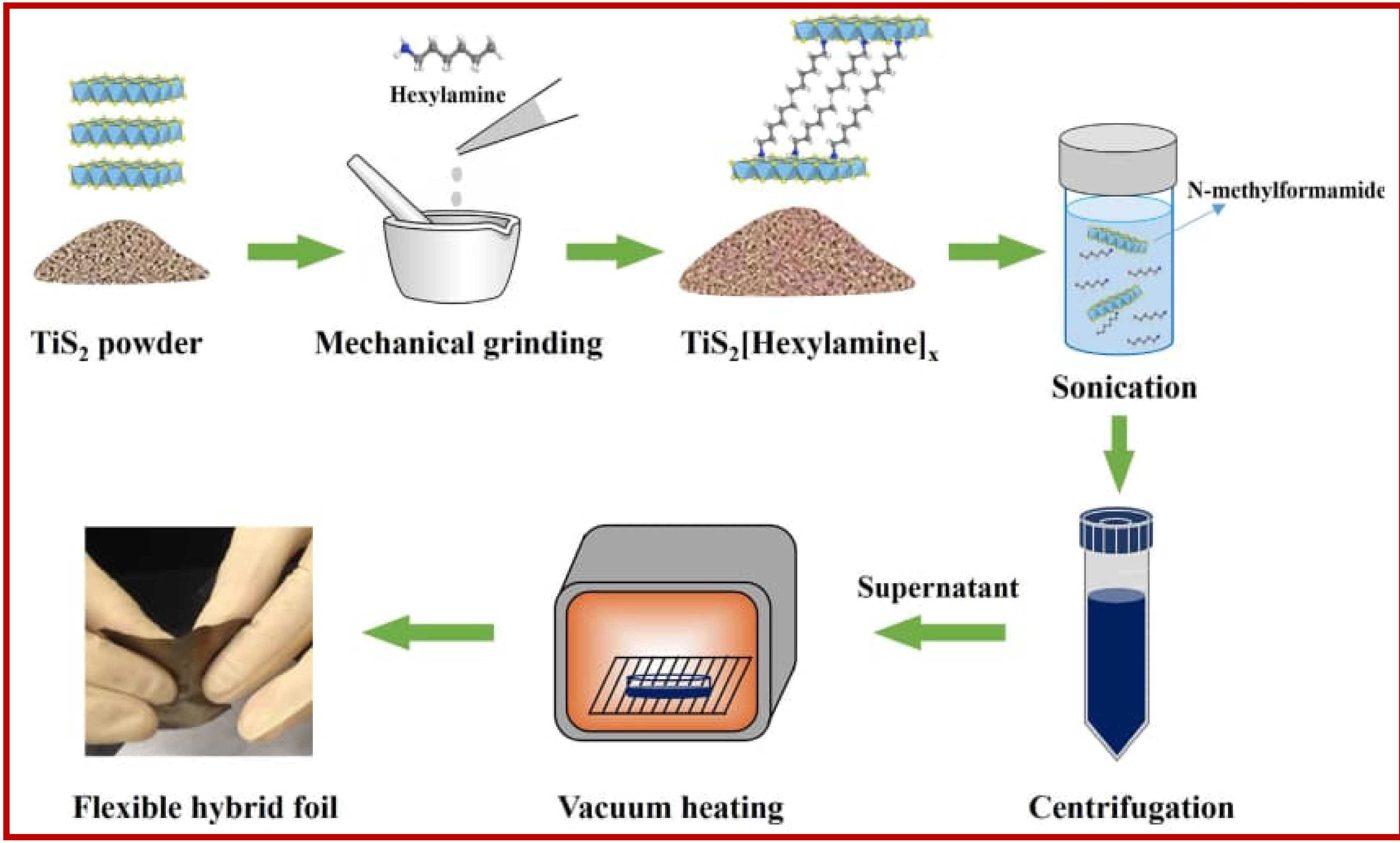
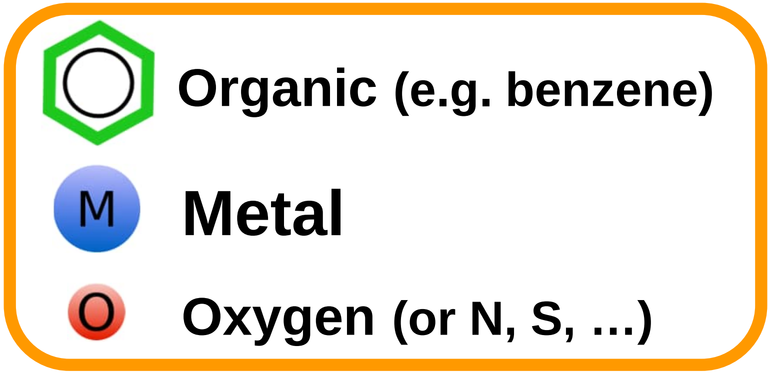
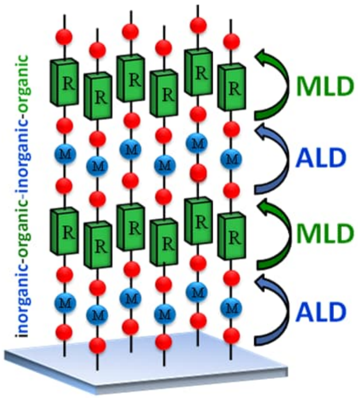
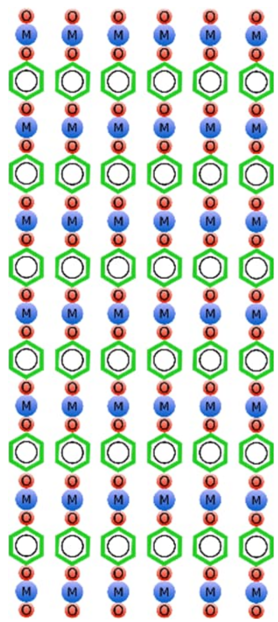
Japan

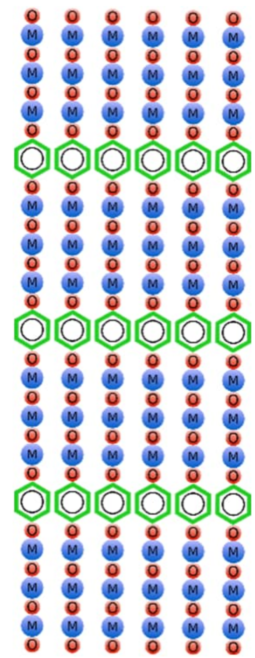




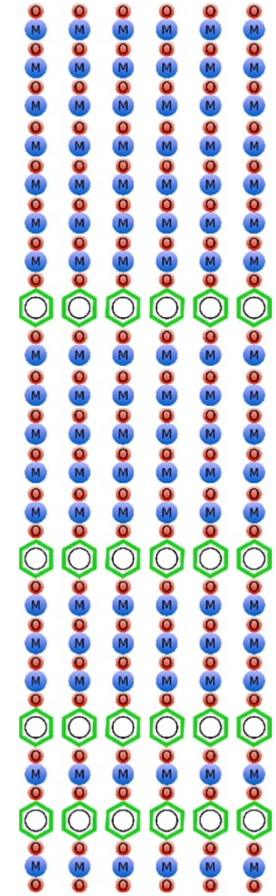




Simple
Metal-Organic Network
(amorphous or crystalline)



Superlattice

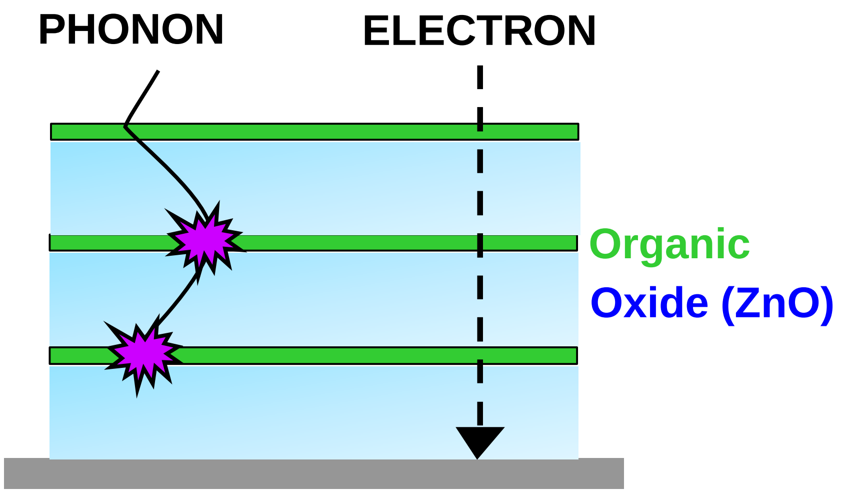


Gradient hybrid

Aalto University
School of Chemical
Engineering

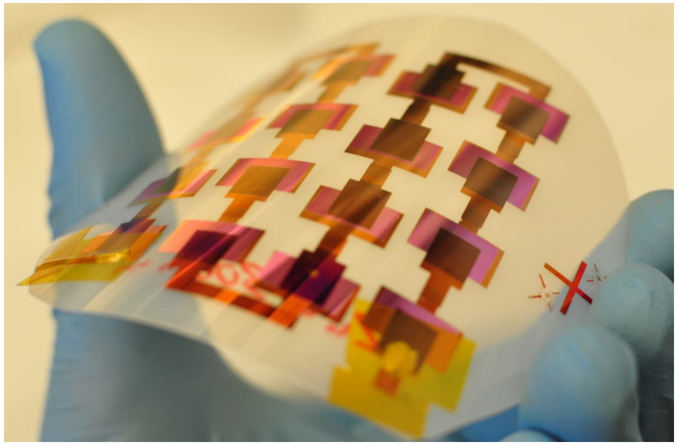
DIFFERENT LAYER SEQUENCES BY ALD/MLD DESIGN

FLEXIBLE THERMOELECTRICS by ALD/MLD



Organic layers in ZnO:org superlattices reduce thermal conductivity (into 1 / 50) without lowering electrical conductivity

T. Tynell, A. Giri, J. Gaskins, P.E. Hopkins, P. Mele, K. Miyazaki & M. Karppinen, *J. Mater. Chem. A* 2, 12150 (2014).



G. Marin, R. Funahashi & M. Karppinen, *Adv. Eng. Mater.* 22, 2000535 (2020).