

Literature Seminar

–2D materials–

M2 T. Sawazaki
190110

CONTENTS

2D materials

graphene (2004–)

introduction

TMD (2005–)

MXene (2011–)

...

beyond graphene

their application

hot reports

for future

practical using

hot reports

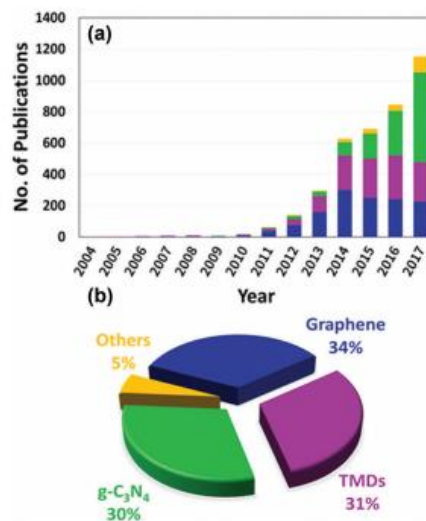


Fig. 2 (a) The number of publications on composite 2D/SC materials applied to water splitting by photocatalysis and PEC processes between 2004 and 2017 (from Scopus) and (b) the contribution of each 2D material to the publication activity.

Energy Environ. Sci., **2019**, Advance Article. (IF 30.0)



Editorial

pubs.acs.org/journal/apchd5

New Discoveries and Opportunities from Two-Dimensional Materials

Victor W. Brar,[†] Andrew R. Koltonow,[‡] and Jiaying Huang[‡]

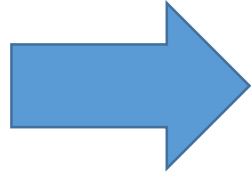
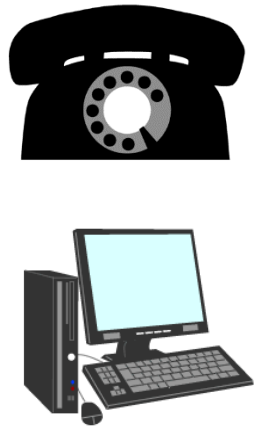
[†]Department of Physics, University of Wisconsin–Madison, Madison, Wisconsin 53711, United States

[‡]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States

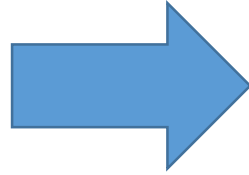
ACS Photonics, **2017**, *4*, 407. (IF 6.9)

(virtual issue; <http://pubs.acs.org/page/vi/2Dmaterials.htm>)

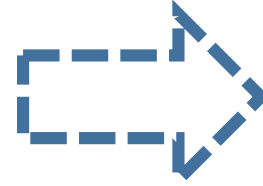
INTRODUCTION (0)



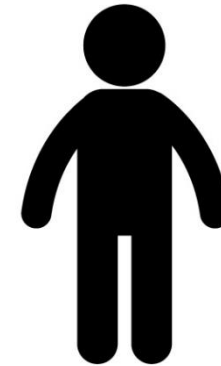
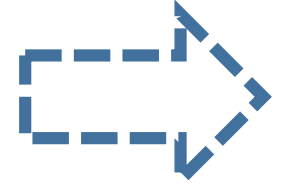
portable



wearable



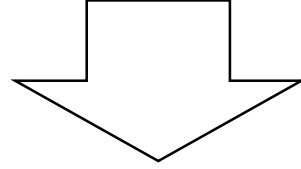
implantable



“nanotechnology”

INTRODUCTION (1)

“The atom is the smallest unit of a substance.”



The atomic size is the theoretical smallest one.

·first isolation of atomic-size compound

Nobel Prize in Physics in 2010

"for groundbreaking experiments regarding the **two-dimensional material** graphene."



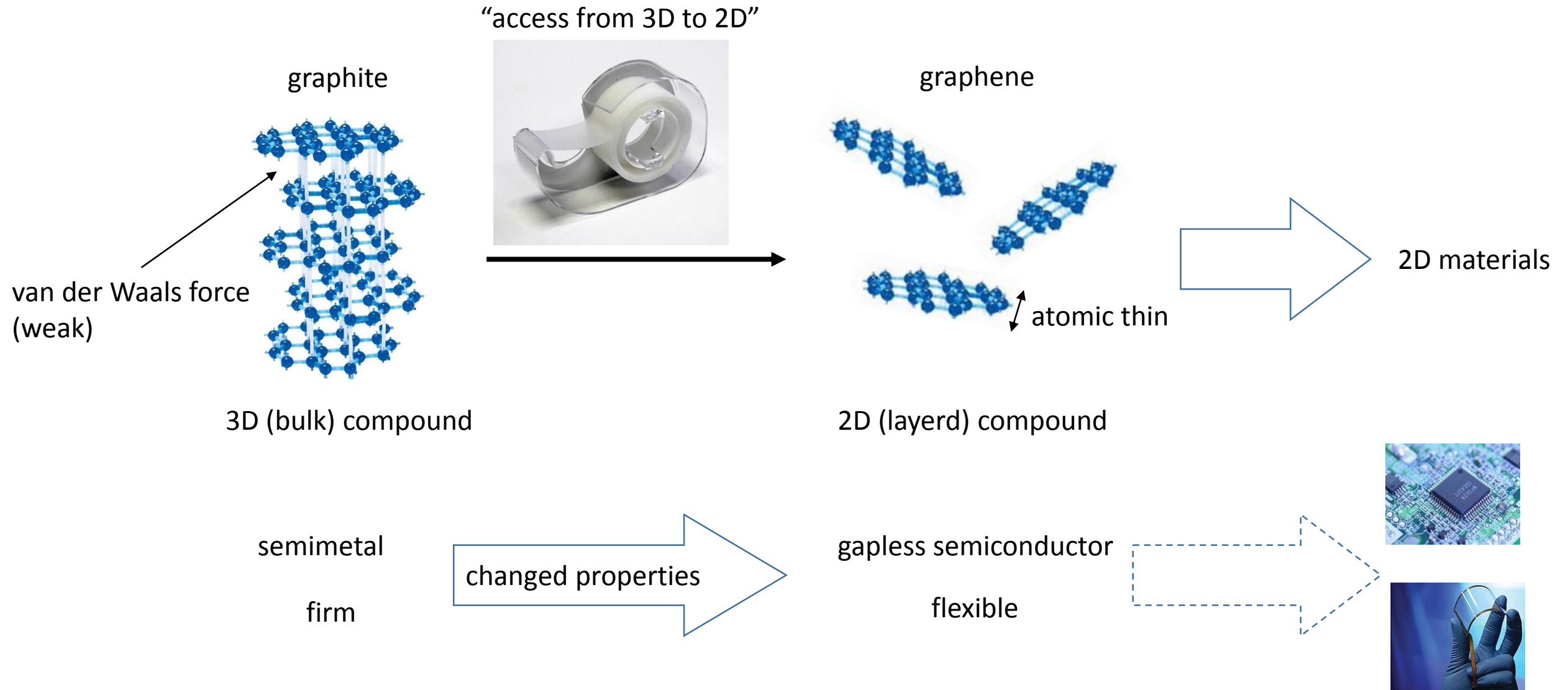
Andre Geim



Konstantin Novoselov

Science, **2004**, 306, 666.

ISOLATION OF GRAPHENE



PROBLEM OF GRAPHENE

the (practical) example

Vollebak launches first graphene jacket that acts as a radiator



Augusta Pownall | 16 August 2018 | [Leave a comment](#)

Innovative clothing manufacturer Vollebak has produced a jacket made with graphene that can conduct power, store body heat and repel bacteria.

The reversible item outwardly resembles a regular raincoat. One side it is constructed from a new fabric made from graphene blended with polyurethane and nylon, while the other is made from matte black high-stretch, high-strength nylon.



The graphene-hybrid material can store and conduct the wearer's body heat and transfer it equally around the body. It can also theoretically store an unlimited

cf \$695



high cost

difficulty of mass production

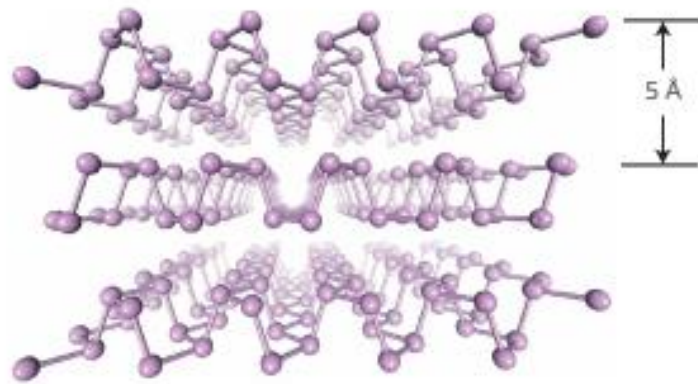
difficulty of big-size production

no band gap

Ref. <https://www.dezeen.com/2018/08/16/vollebak-graphene-jacket-radiator-conduct-power-clothing-design/>

BEYOND GRAPHENE (1)

black phosphorus
(phosphorene)



Nat. nanotech. **2014**, *9*, 372.

Metal Halide Perovskite

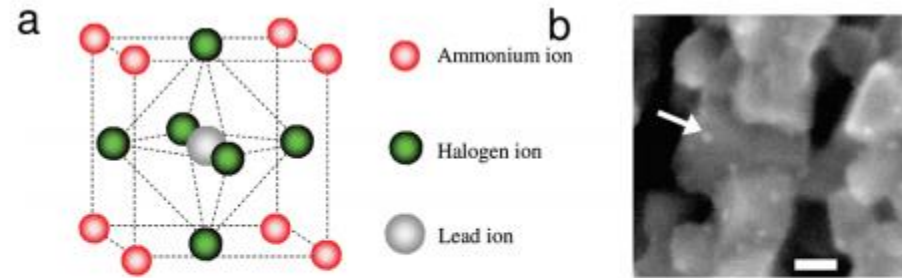
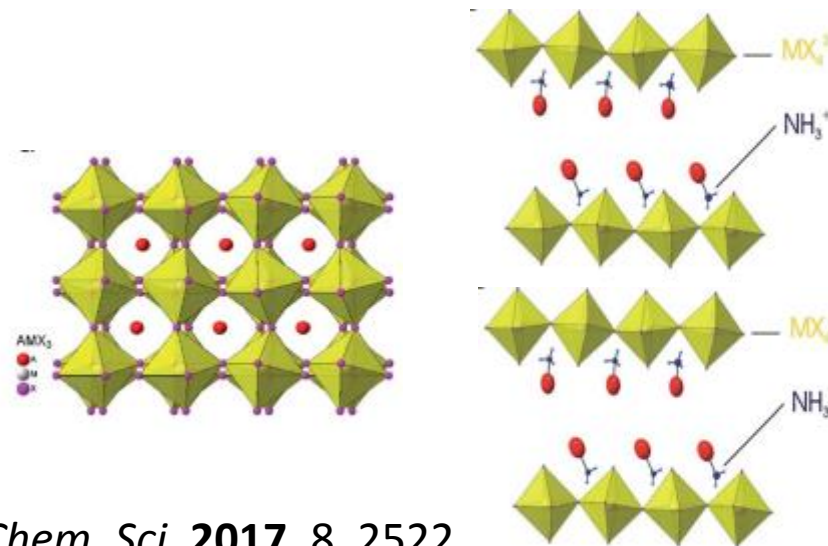


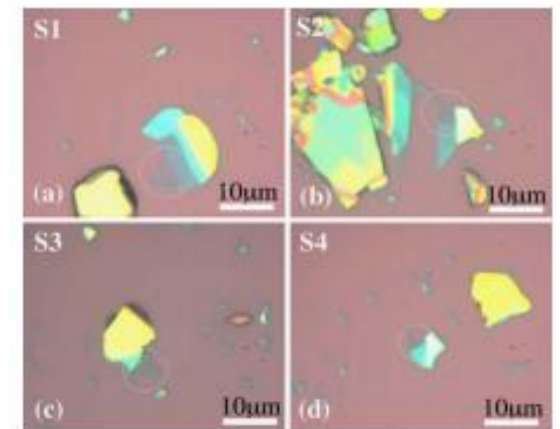
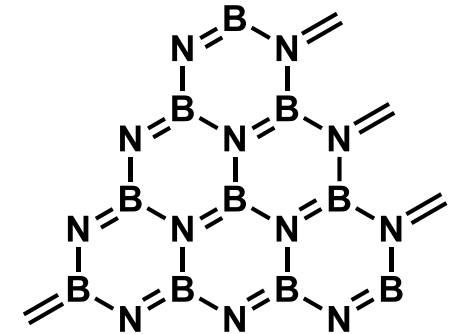
Figure 1. (a) Crystal structures of perovskite compounds. (b) SEM image of particles of nanocrystalline $\text{CH}_3\text{NH}_3\text{PbBr}_3$ deposited on the TiO_2 surface. The arrow indicates a particle, and the scale bar shows 10 nm.

J. Am. Chem. Soc. **2009**, *131*, 6050.



Chem. Sci. **2017**, *8*, 2522.

h-BN



Appl. Phys. Lett. **2008**, *92*, 722.

BEYOND GRAPHENE (2)

Transition Metal Dichalcogenide MX_2

chalcogen

Transition metal

1 H Hydrogen 1.008																	2 He Helium 4.002602						
3 Li Lithium 6.94	4 Be Beryllium 9.0121831																	5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998403153	10 Ne Neon 20.1797
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305																	13 Al Aluminium 26.9815385	14 Si Silicon 28.085	15 P Phosphorus 30.973761998	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955909	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798						
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293						
55 Cs Caesium 132.90545196	56 Ba Barium 137.327	57 - 71 Lanthanoids	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.227	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.592	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)						
87 Fr Francium (223)	88 Ra Radium (226)	89 - 103 Actinoids	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (264)	108 Hs Hassium (265)	109 Mt Meitnerium (276)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (282)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (289)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)						

57 La Lanthanum 138.90547	58 Ce Cerium 140.12	59 Pr Praseodymium 140.90766	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93033	68 Er Erbium 167.259	69 Tm Thulium 168.93422	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.0377	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)

COMBINATION OF TMD

MX_2
 M = Transition metal
 X = Chalcogen

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Nat. Chem., **2013**, *5*, 263.

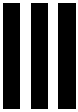


a variety of combination

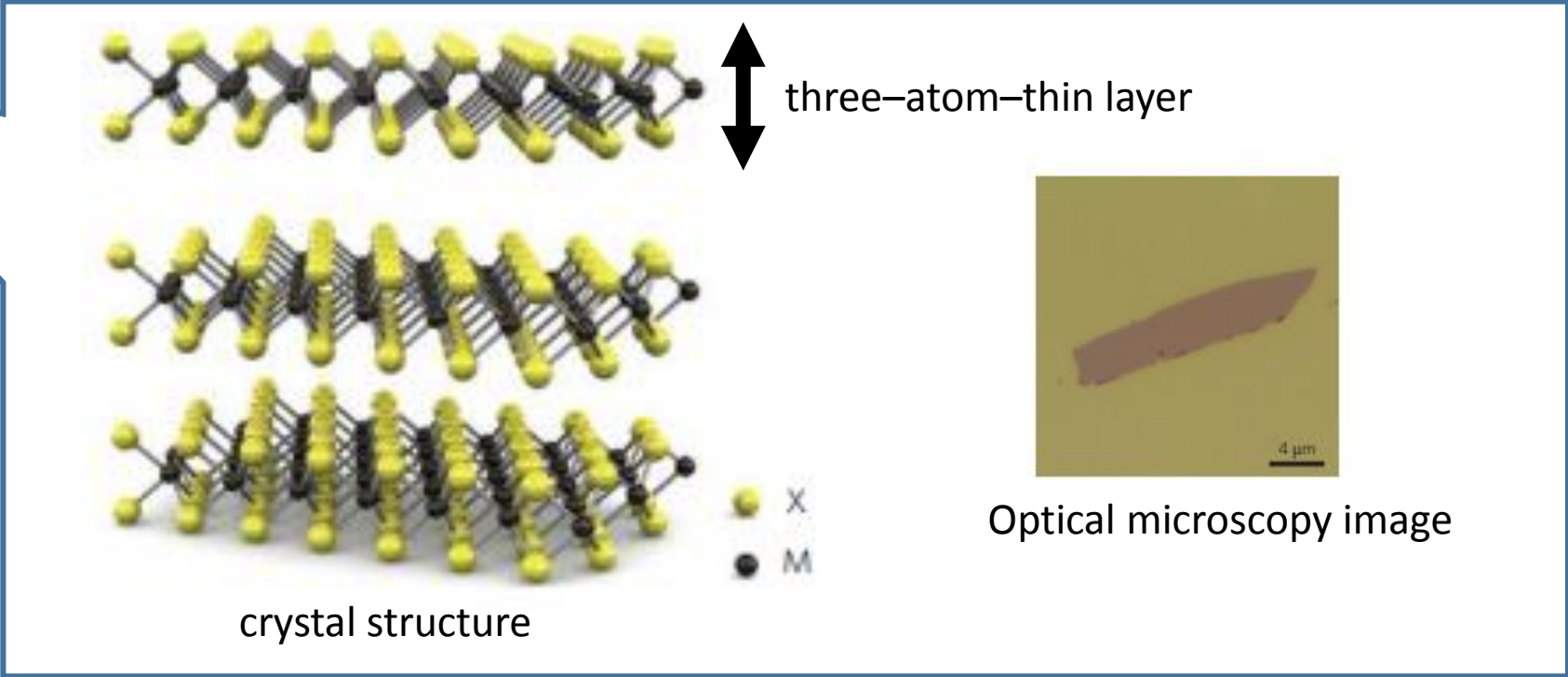
EXAPMLE OF TMD



bulk crystal MoS₂

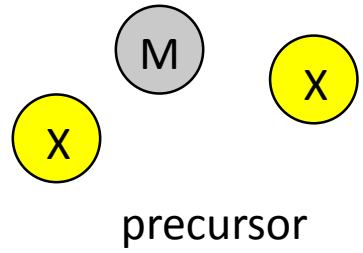


For lubrication
Ampere cop



Nat. Nanotechnol. **2012**, 7, 699.

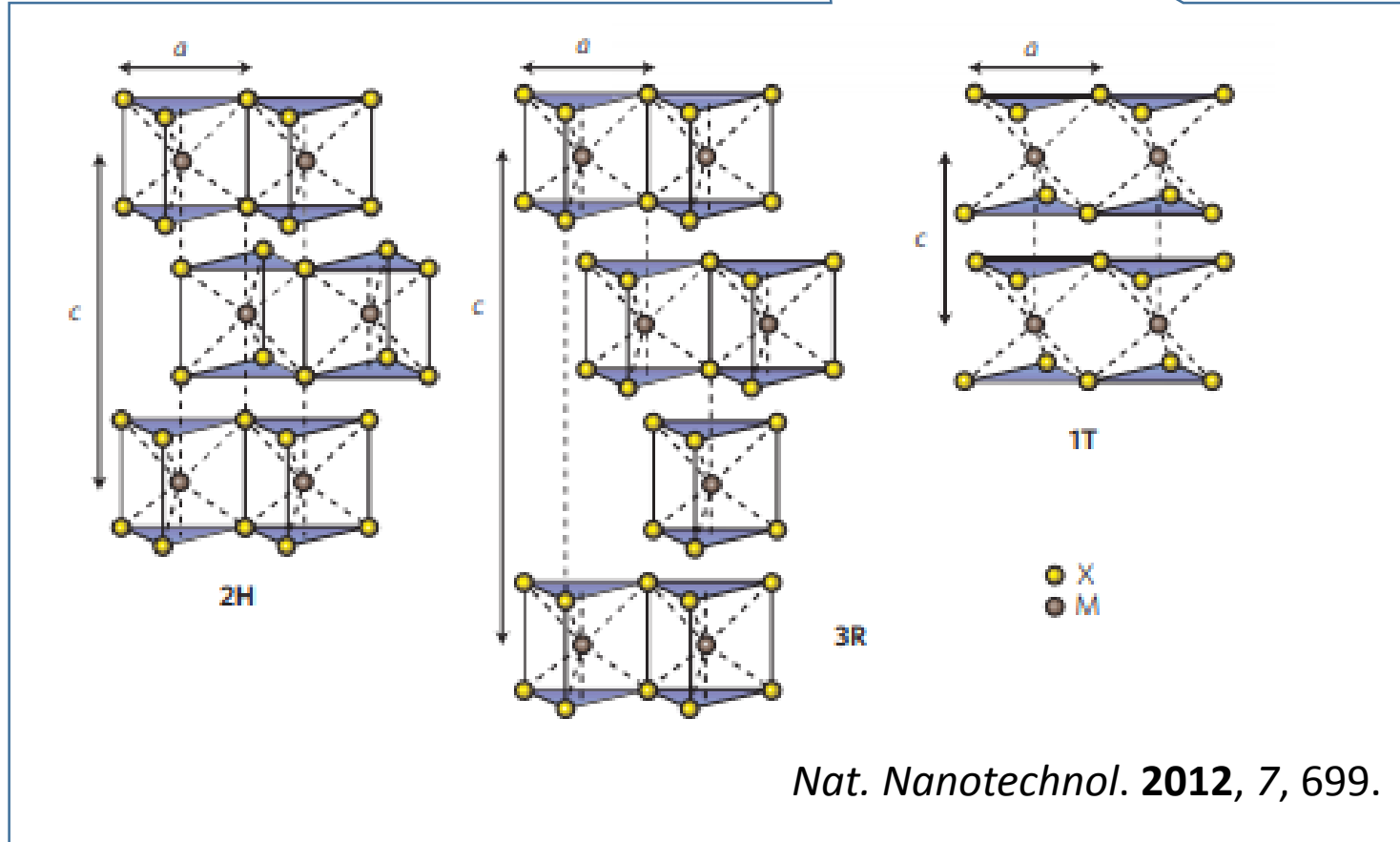
STRUCTURE OF TMD



bulk TMD

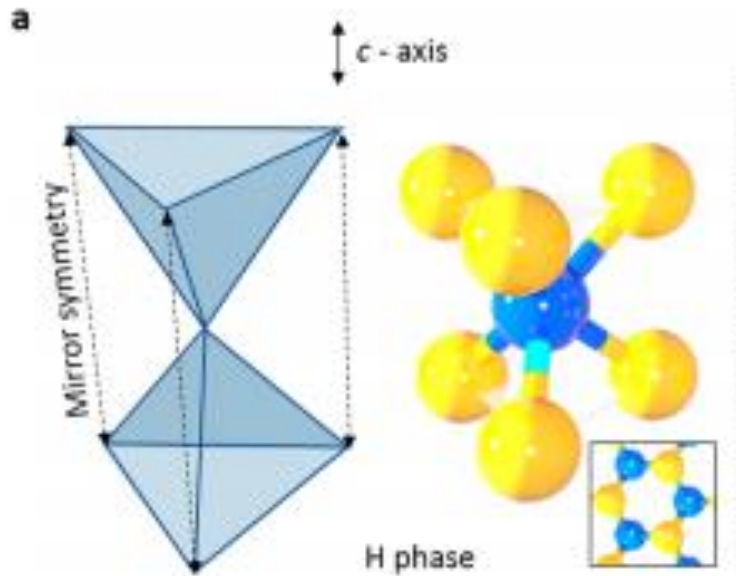
exfoliation

layerd TMD

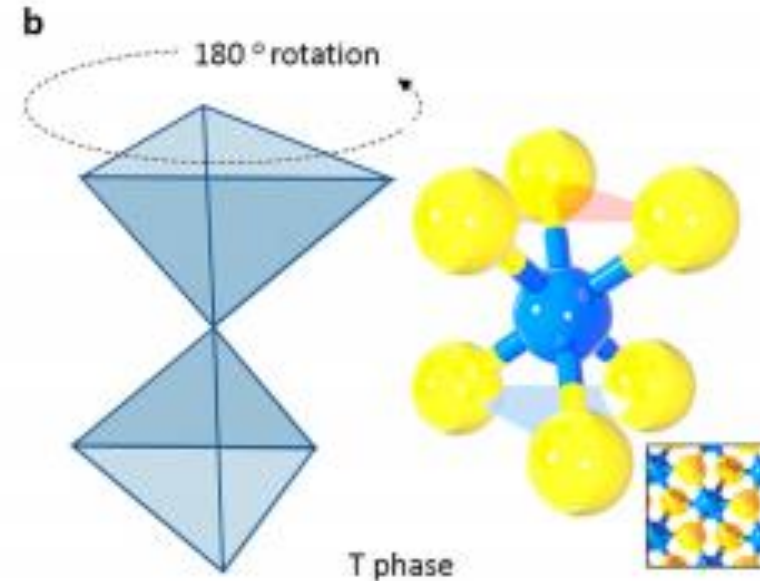


H / T ...??

STRUCTURE OF LAYERED TMD (1)



trigonal prismatic



octahedral

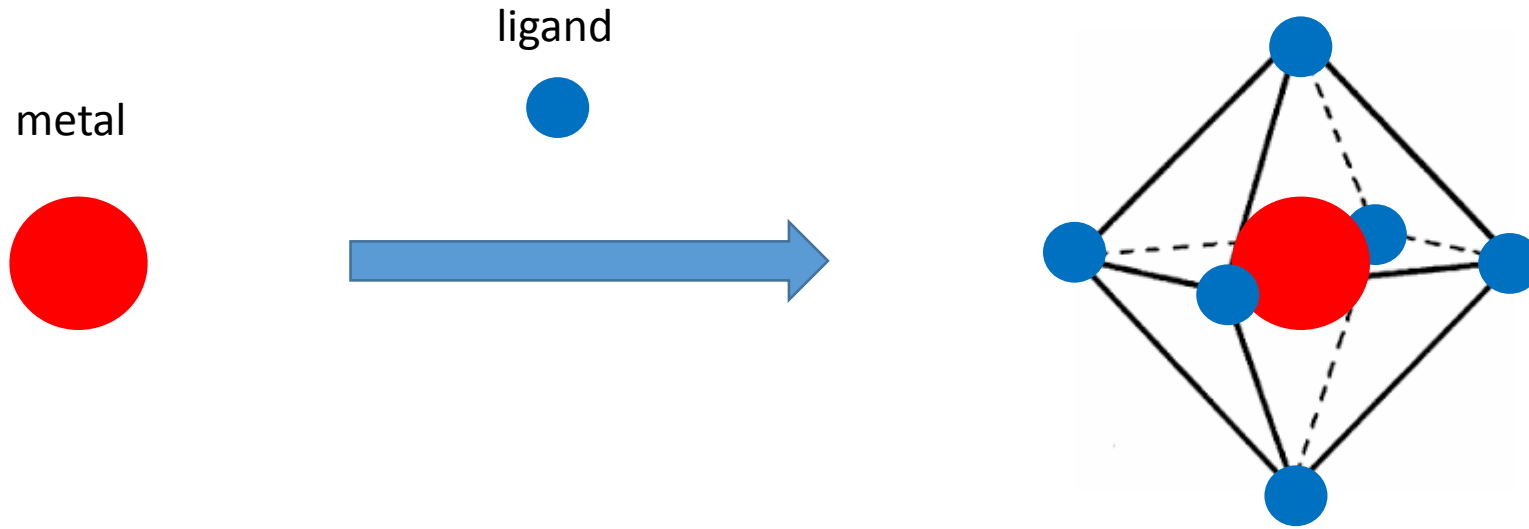


Chem. Rev. **2018**, *118*, 6297.

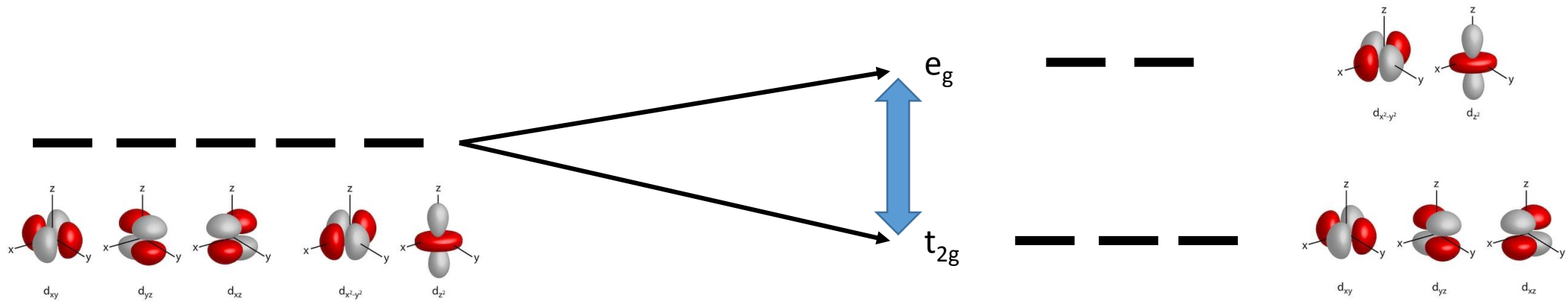
1. What is trigonal prismatic / octahedral?
2. What makes H-phase / T-phase?
3. electronic properties

EXPLANATION (1)

·crystal-field theory



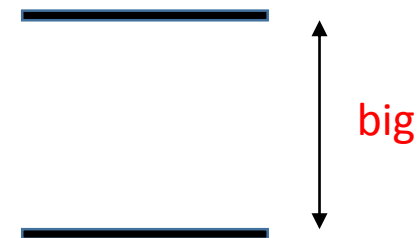
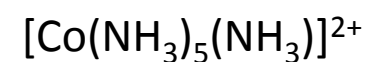
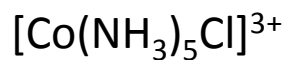
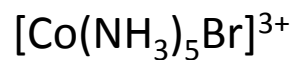
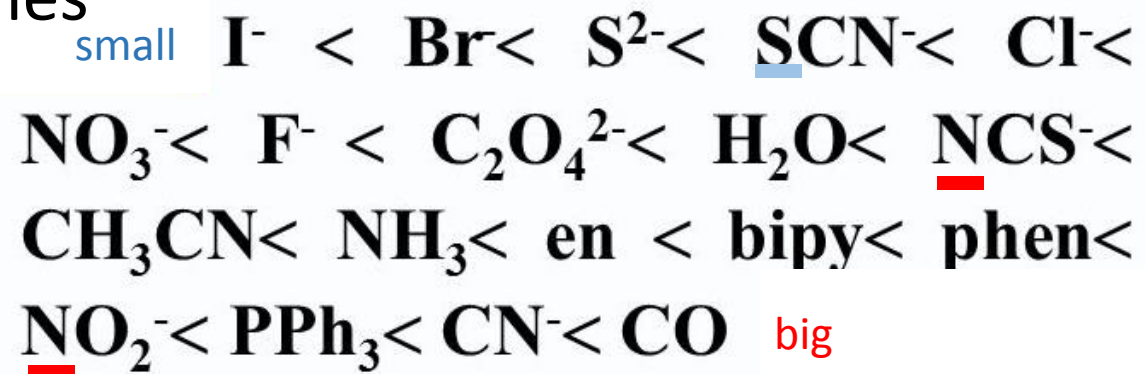
d orbital



“splitting d orbitals”

EXPLANATION (2)

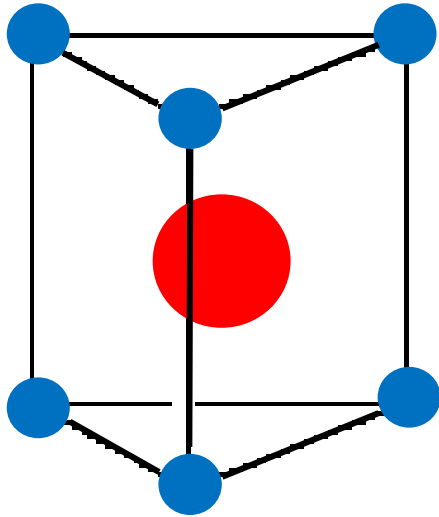
·spectrochemical series



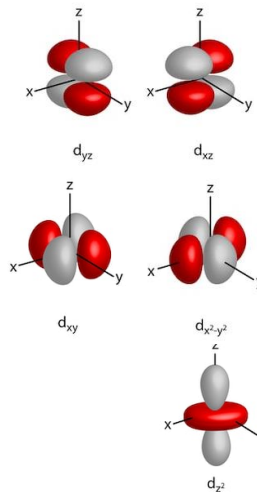
EXPLANATION (3)

·mono-lattice d orbital

trigonal prismatic



d orbital



e''



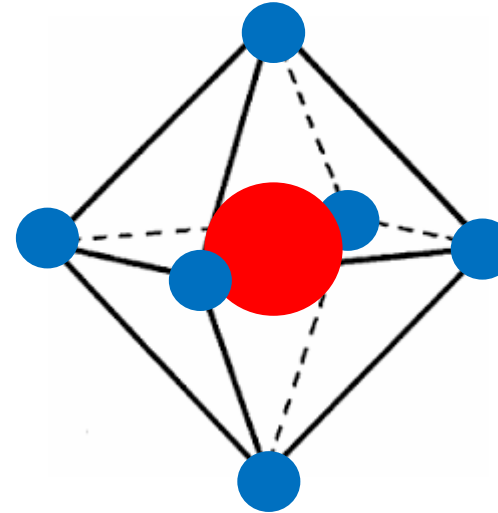
e'



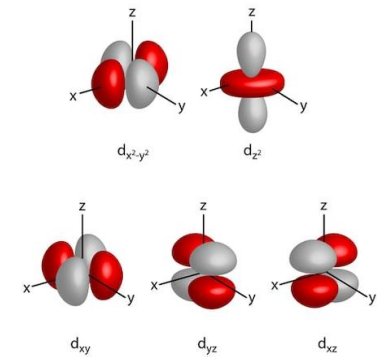
a_1'



octahedral



d orbital



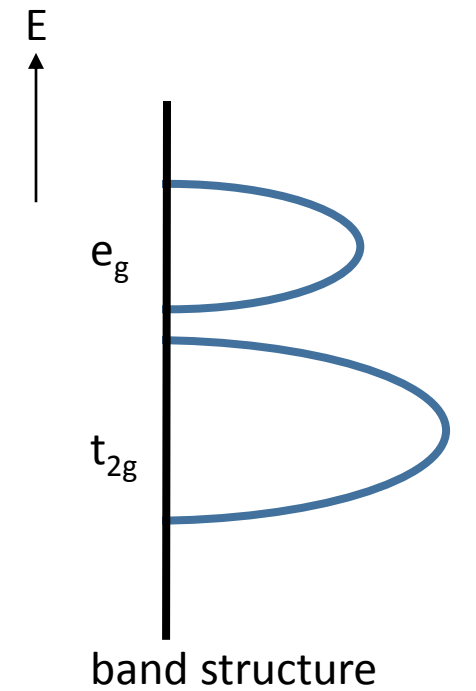
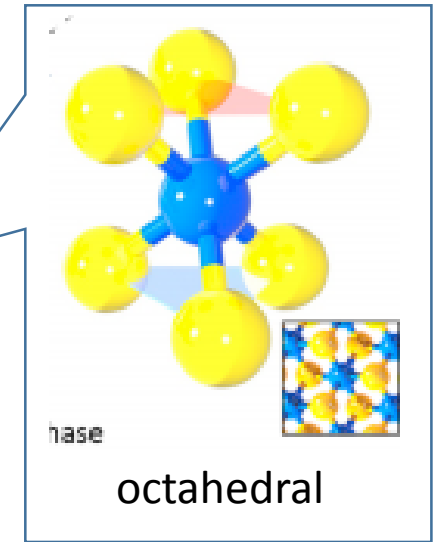
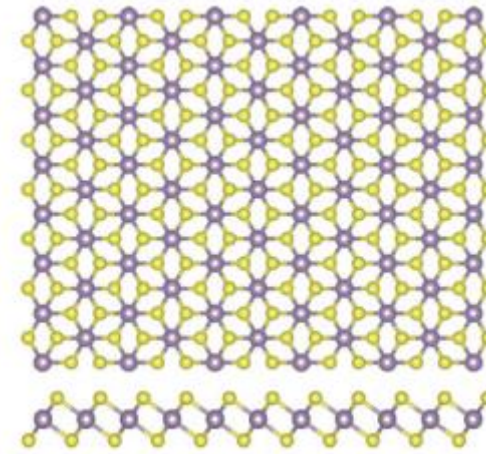
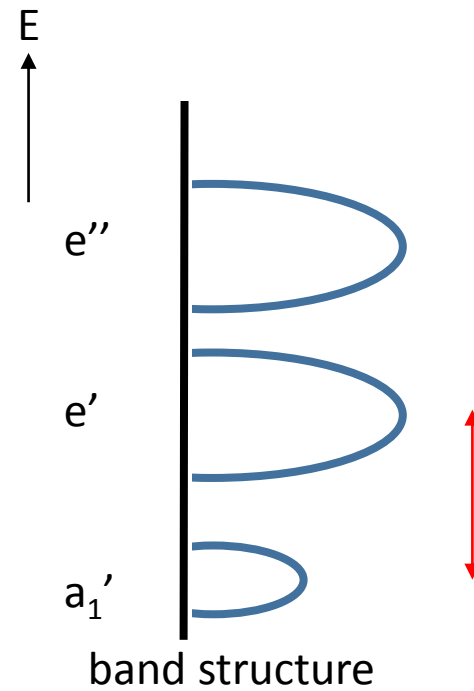
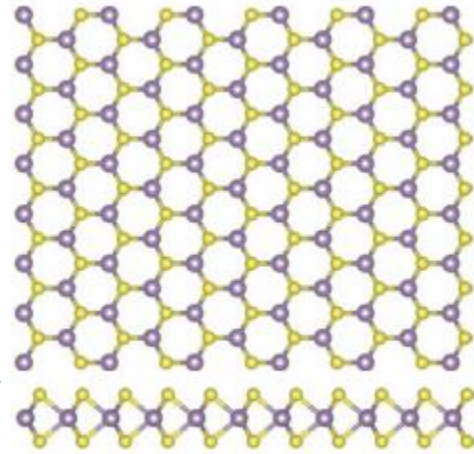
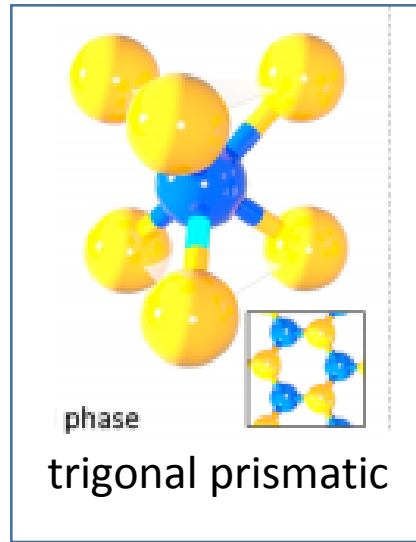
e_g



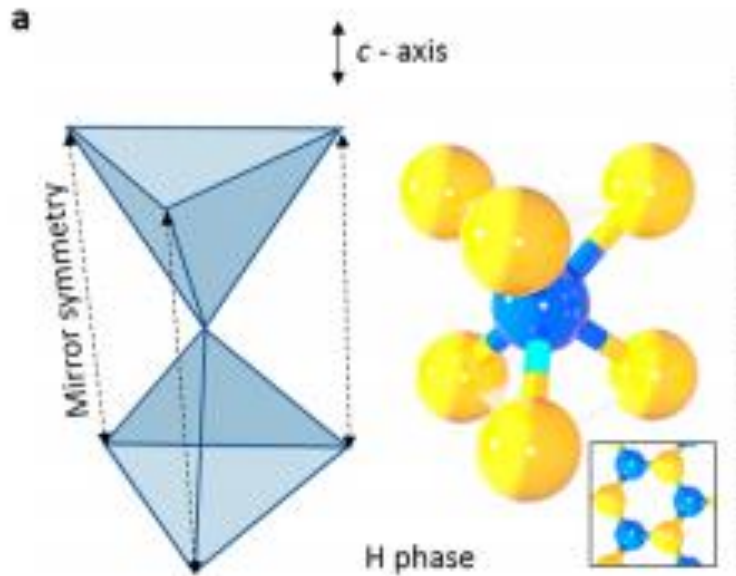
t_{2g}



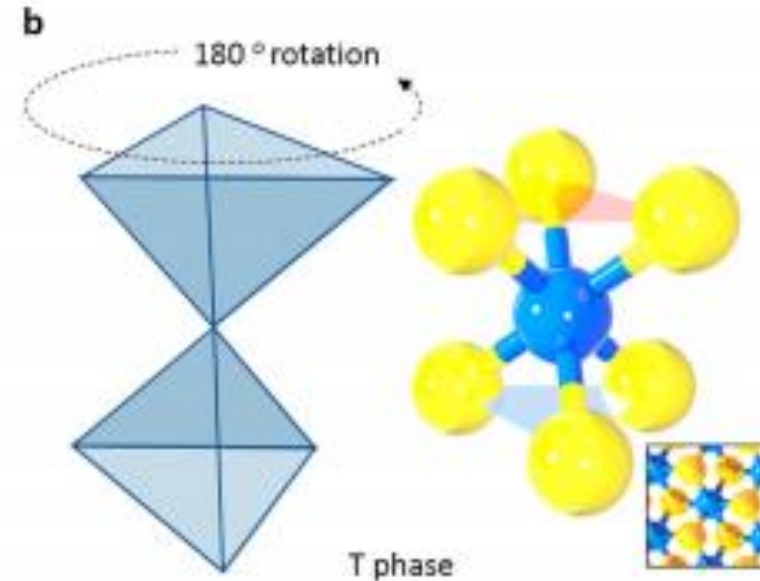
BAND STRUCTURE OF LAYERED COMPOUND



STRUCTURE OF LAYERED TMD (2)



trigonal prismatic



octahedral



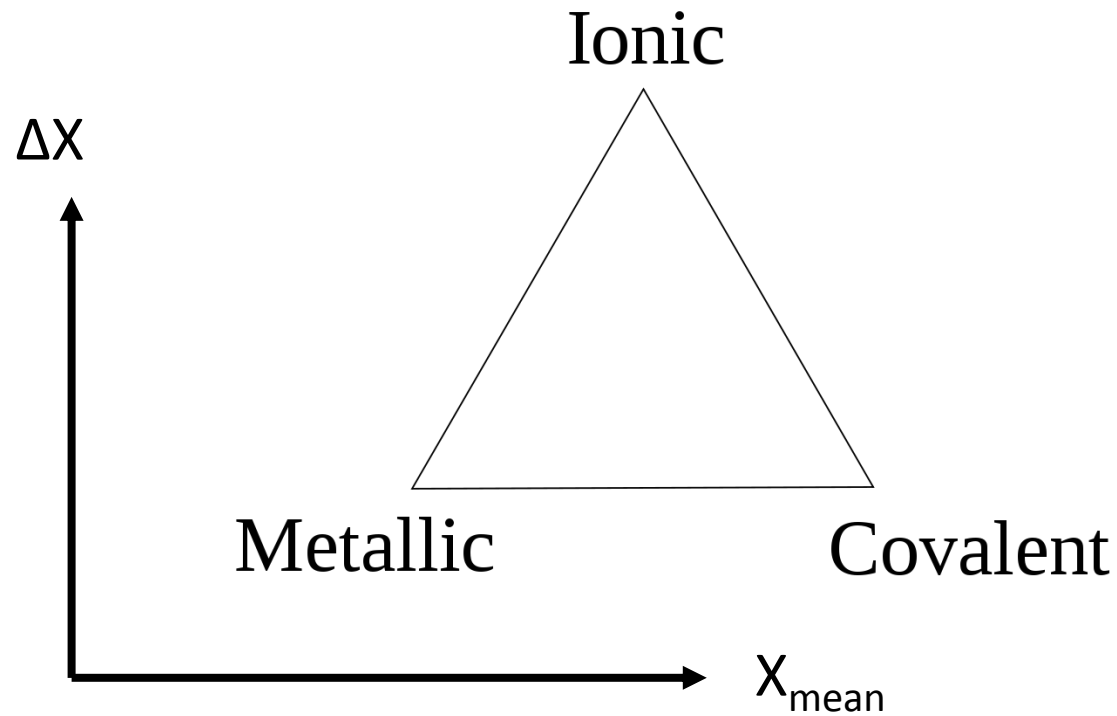
Chem. Rev. **2018**, *118*, 6297.

1. What is trigonal prismatic / octahedral?
2. What makes H-phase / T-phase?
3. electronic properties

© dak

EXPLANATION (4)

•Ketelaar triangle



The order of electronegativity (X)

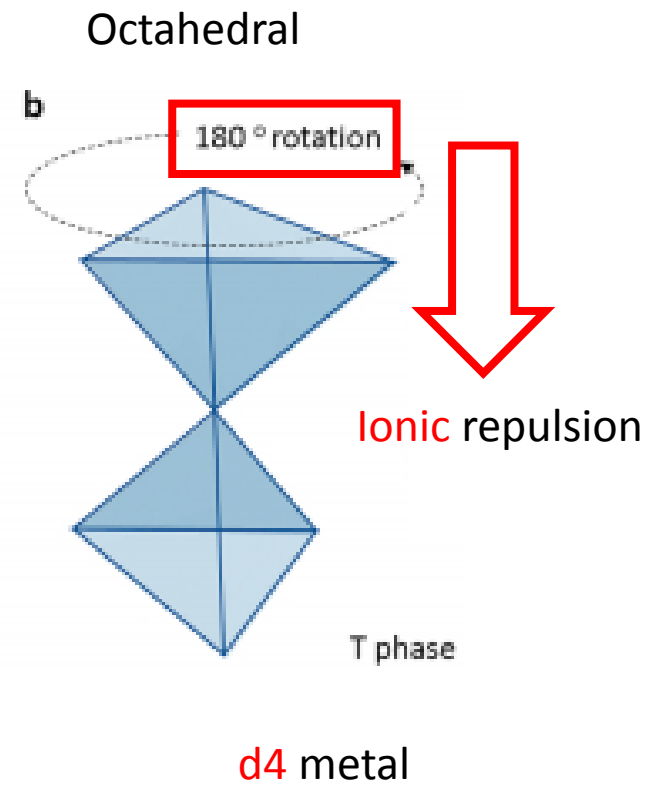
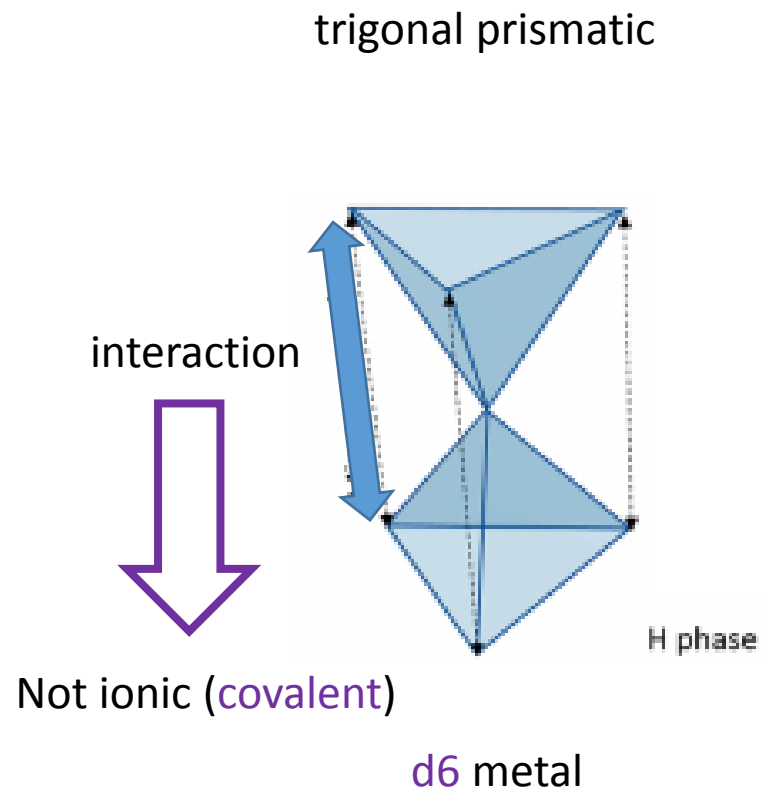
$$4 < 5 < 6 < 16$$

MX_2
M = Transition metal
X = Chalcogen

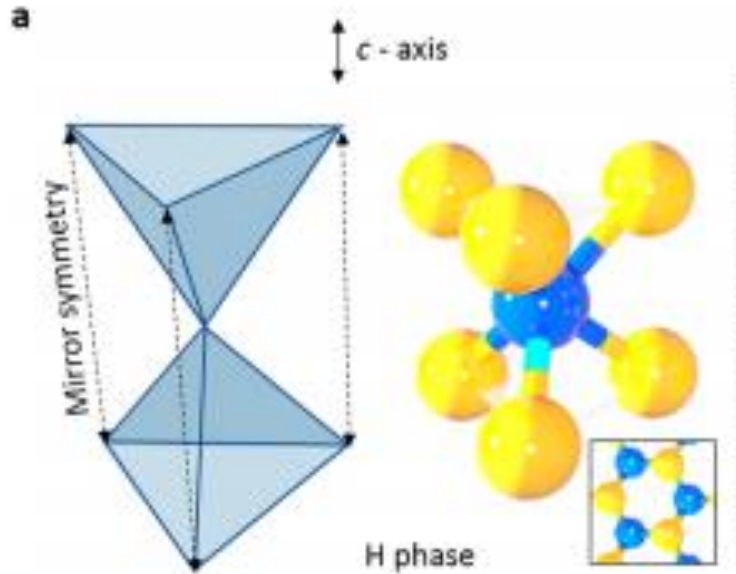
H																			He
Li	Be													B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12		Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		In	Sn	Sb	Te	I	Xe	
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn		Uut	Ff	Uup	Lv	Uus	Uuo	

d6-Ch: covalent
d4-Ch: metallic

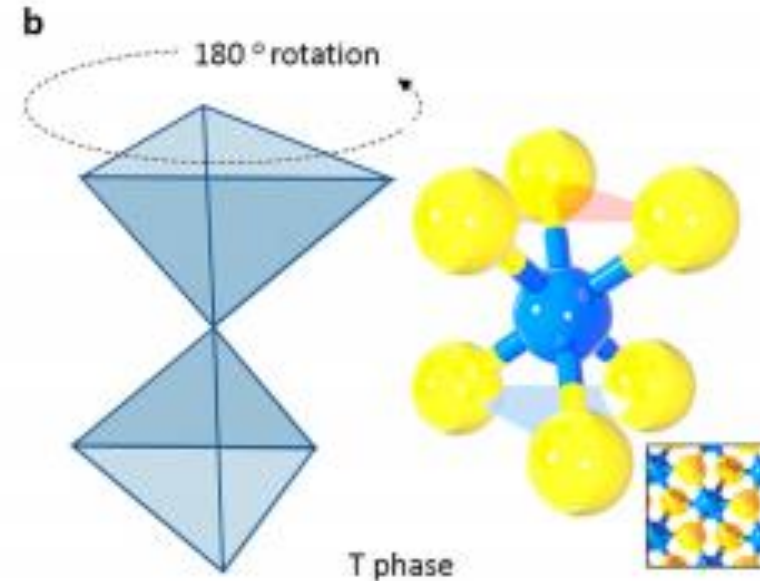
TREMENDACE BETWEEN METAL AND PHASE



STRUCTURE OF LAYERED TMD (3)



trigonal prismatic
d6metal



Octahedral
d4metal

Chem. Rev. **2018**, *118*, 6297.

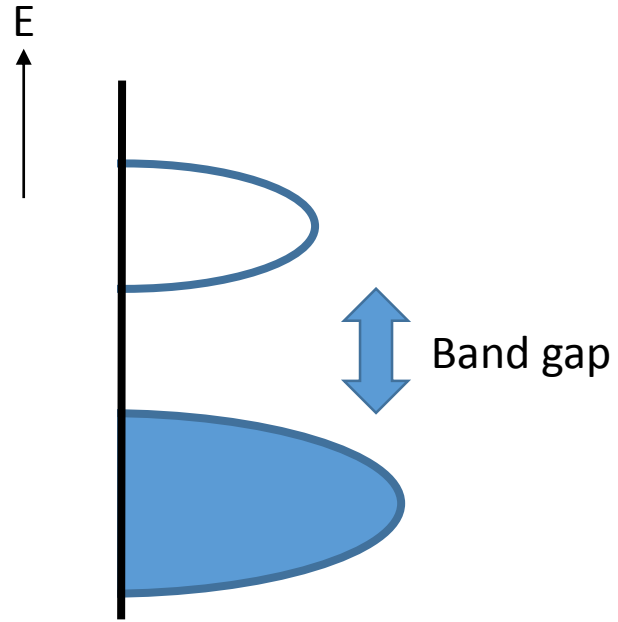


1. What is trigonal prismatic / octahedral?
2. What makes H-phase / T-phase?
3. electronic properties

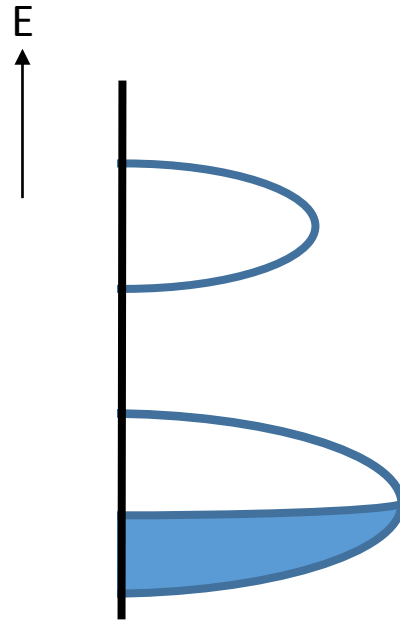
© dak

EXPLANATION (5)

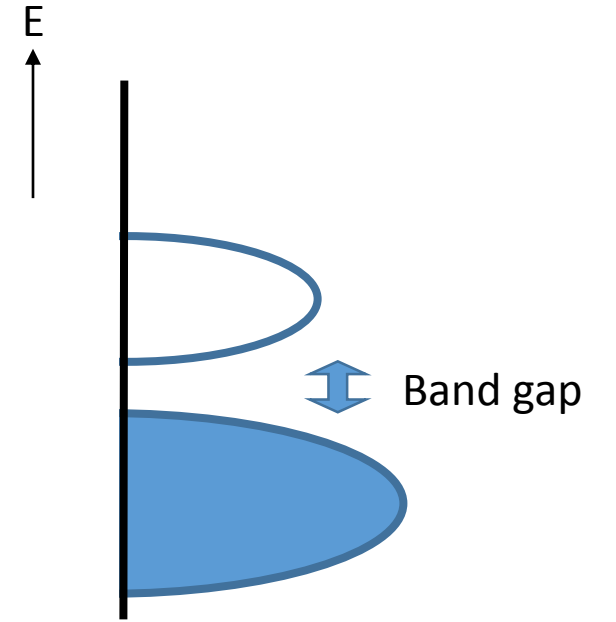
·electronic properties



insulator



metal



semiconductor



EXAMPLE OF METALLIC TMD

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	

Legend:
S (Yellow)
Se (Green)
Te (Red)

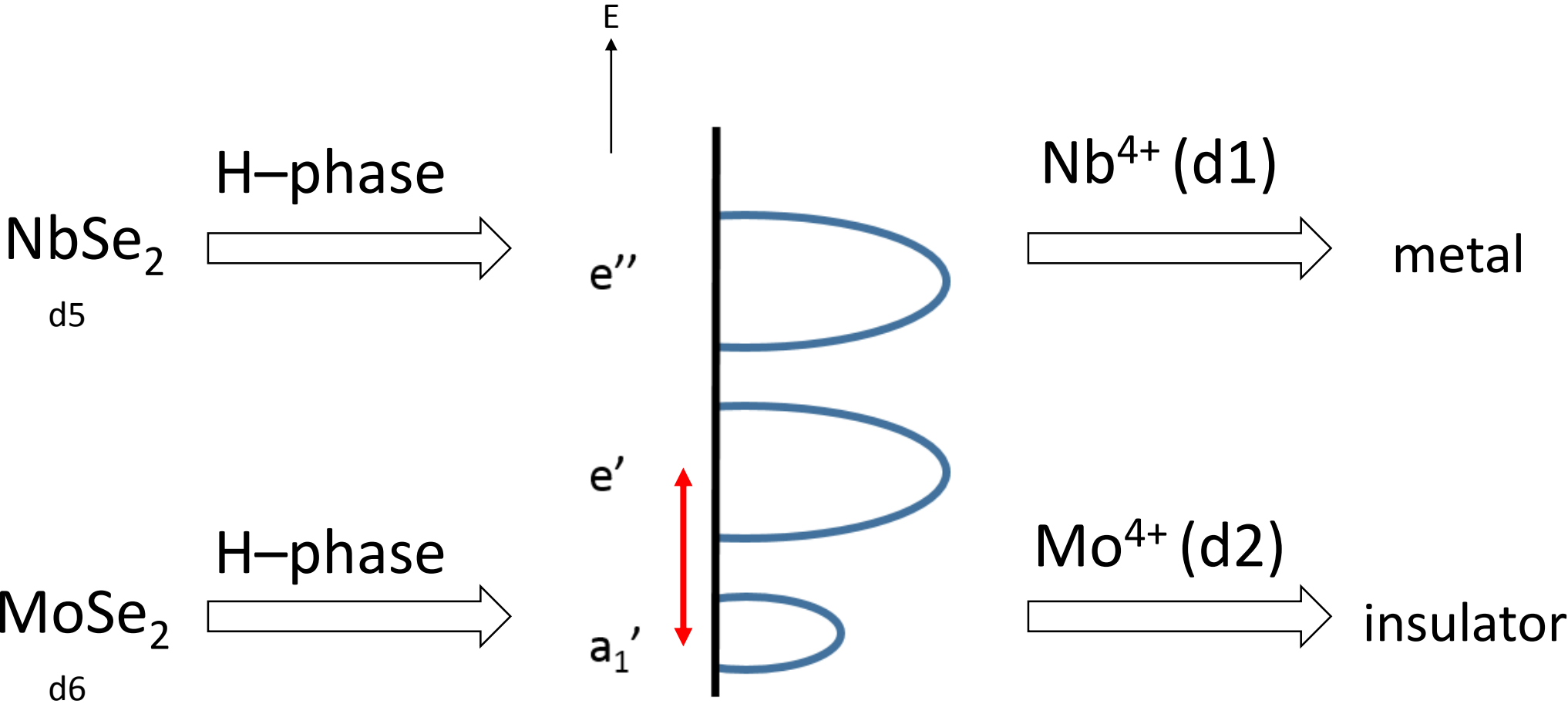
Figure 1. Types of metals involved in layered dichalcogenides. Blue color indicates transition metals for currently developed **metallic-layered dichalcogenides (m-LTMDCs)**, and yellow, green, and red small rectangles are S, Se, and Te compounds. White rectangles for chalcogen are unreported or nonexist phase in m-LTMDCs.

Chem. Rev. **2018**, *118*, 6297.

NOTE

NbSe₂ metal / MoSe₂ not metal

EXPLANATION OF TMD PROPERTIES



SHORT SUMMARY

3D materials
(bulk)

graphite

Transition Metal Dichalcogenide

2D materials
(layered)

graphene

Transition Metal Dichalcogenide

number of the example

1

over 30

constructing atoms

carbon

transition metal and chalcogen

structure

1 type

hexagonal

2 types

trigonal prismatic
octahedral

material properties

gapless semiconductor

semiconducting TMDs (*Nat. Nanotechnol.* **2012**, 7, 699.)

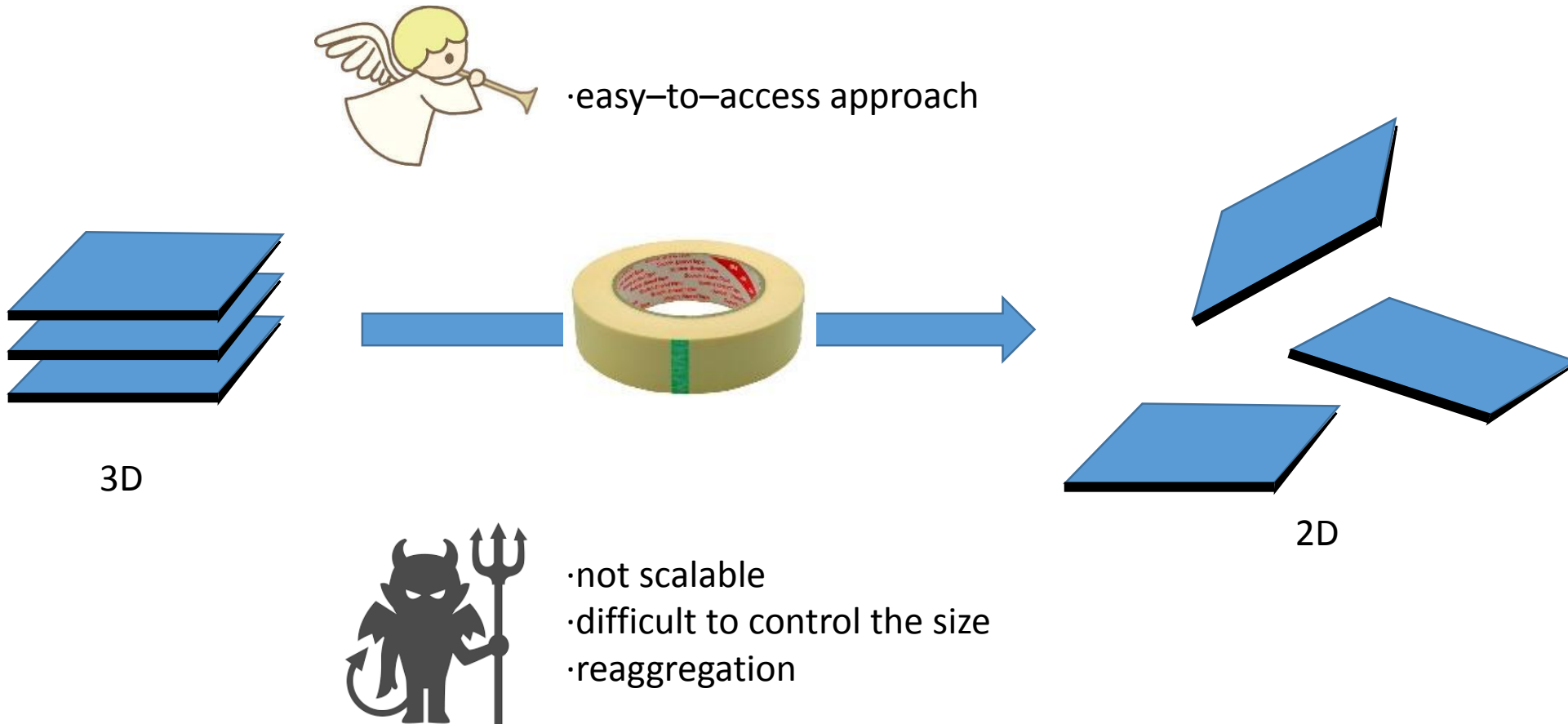
metallic TMDs (*Chem. Rev.* **2018**, 118, 6297.)

SYNTHESIS METHOD (1)

·mechanical exfoliation

top down approach-1

first report; *Science*, **2004**, 306, 666.

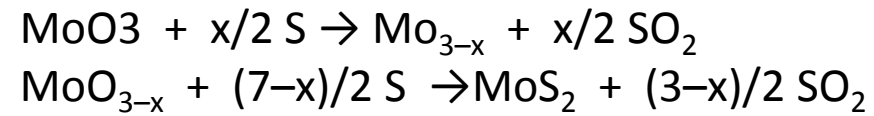
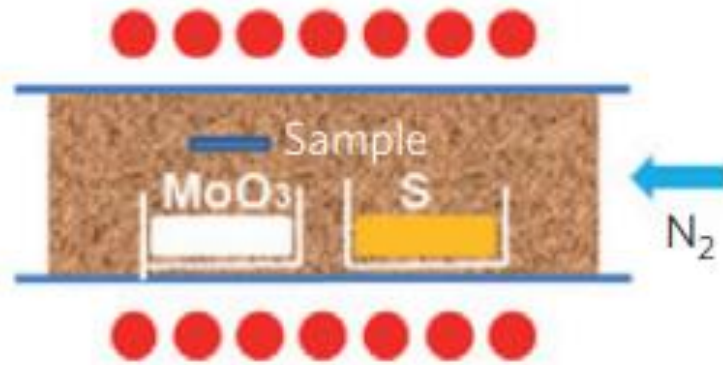


SYNTHESIS METHOD (2)

·Chemical Vapor Deposition

bottom up approach-1

often used for industrial method



Adv. Mater. **2012**, 24, 2320.



·large scale



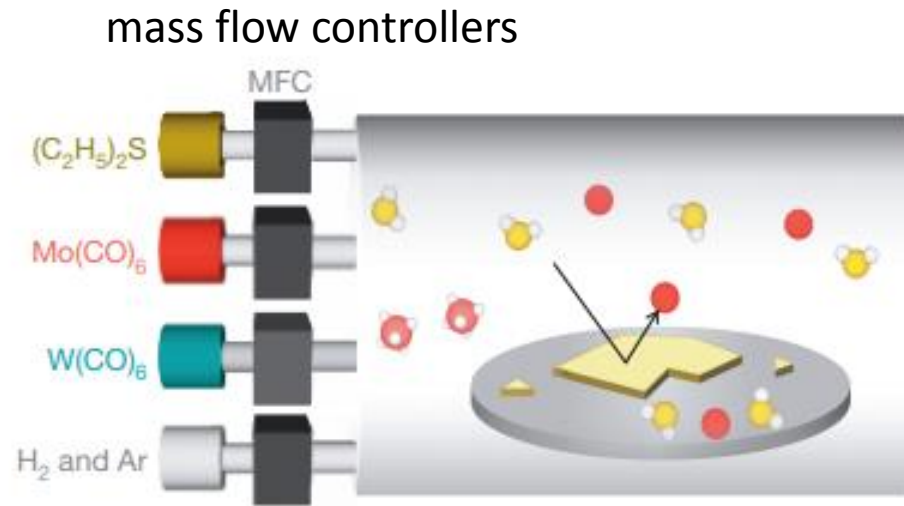
·difficult to control the number of the layer
·poor quality

SYNTHESIS METHOD (3)

·Metal–Organic Chemical Vapor Deposition

bottom up approach–2

first report; *Nature* **2015**, 520, 656.



- homogeneity
- low decomposition temperature of the precursor

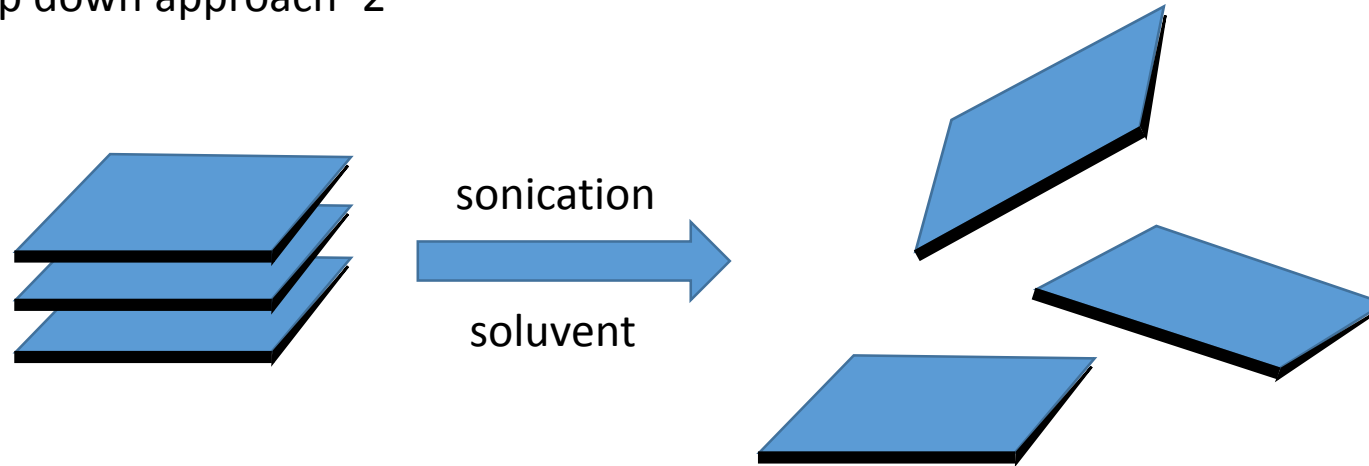


- limited examples (not yet for metal TMD)
- still relatively small (4–inch)
- toxic gas

SYNTHESIS METHOD (4)

·liquid phase exfoliation/mechanical approach

top down approach-2



organic

NMP or IPA (*Science*, 2011, 331, 568.)

ethanol/water (*ACIE*, **2011**, 50, 10839.)

aqueous surfactant

a sodium cholate solution (*Adv. Mater* **2011**, 23, 3944.)

polymer

J. Phys. Chem. C, **2012**, 116, 11393.



·stabilizing against the reaggregation



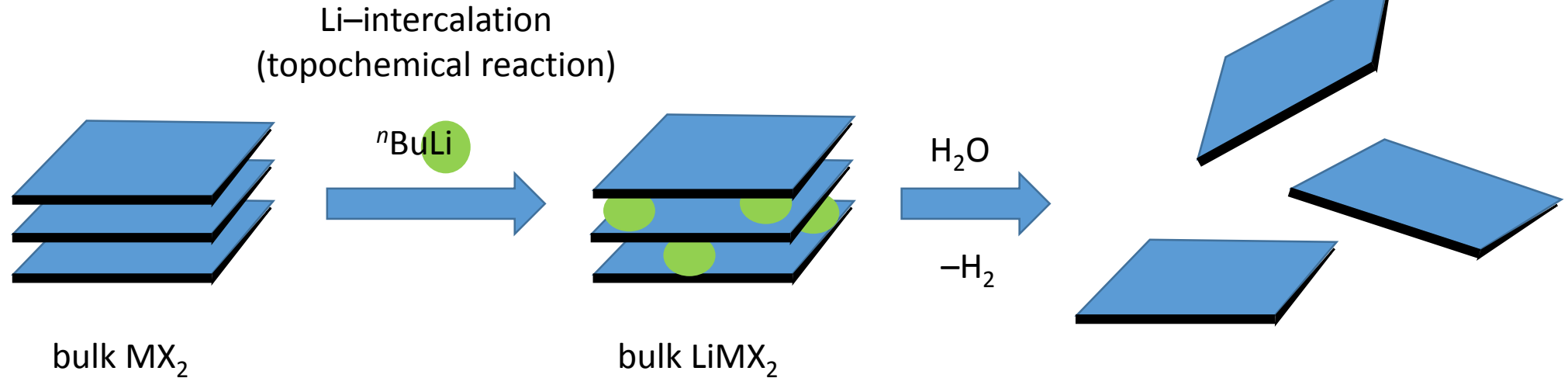
·few hundred nanometers in size

SYNTHESIS METHOD (5)

·liquid phase exfoliation/chemical approach

top down approach-3

first report; *Mater. Res. Bull.* **1986**, 21, 457.

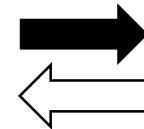


- effective in expanding the layers
- high yield of monolayer



- expensiveness (Li^+)
- structurally and electronically different

for example; MoS_2
trigonal prismatic
(semiconducting)

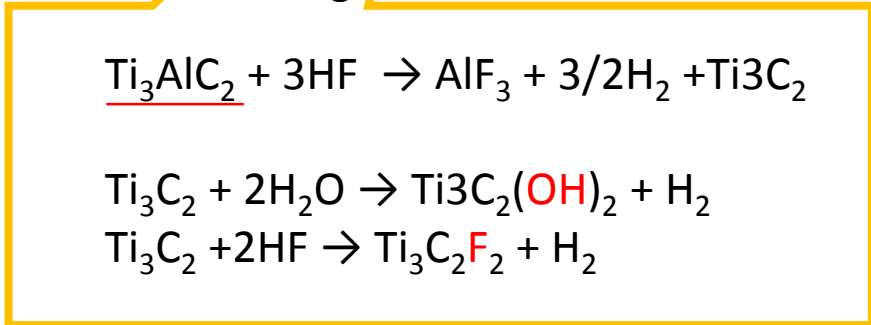
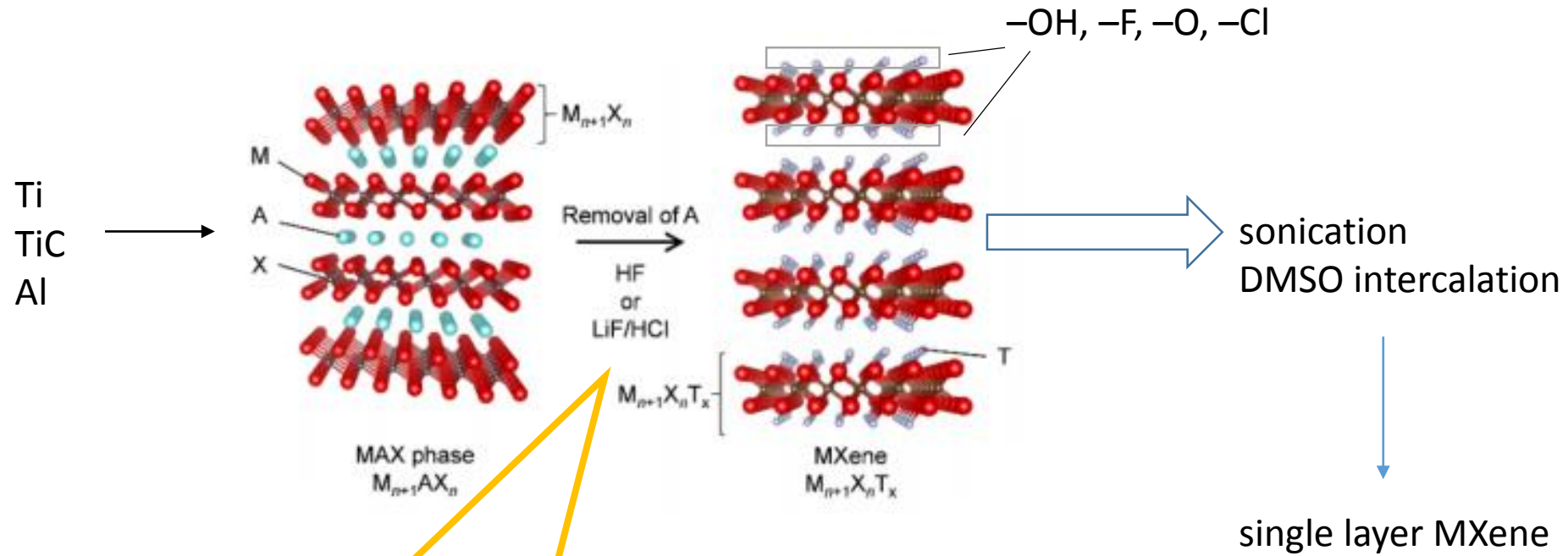


octahedral
(metal)

BEYOND GRAPHENE (3)

MXene

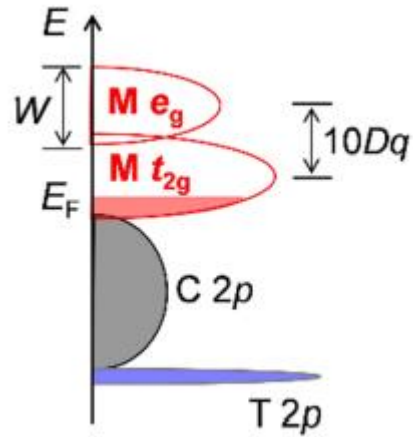
first example; *Adv. Mater.* **2011**, 23, 4248.



Acc. Chem. Res. **2018**, 51, 591.

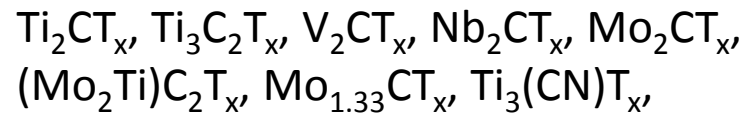
CHARACTERISTICS OF MXene

1. metallic



high electronic conductivity ($2.0 \times 10^4 \text{ S cm}^{-1}$)
(cf. Cu, $5.8 \times 10^5 \text{ S cm}^{-1}$)

2. flexibility of composition

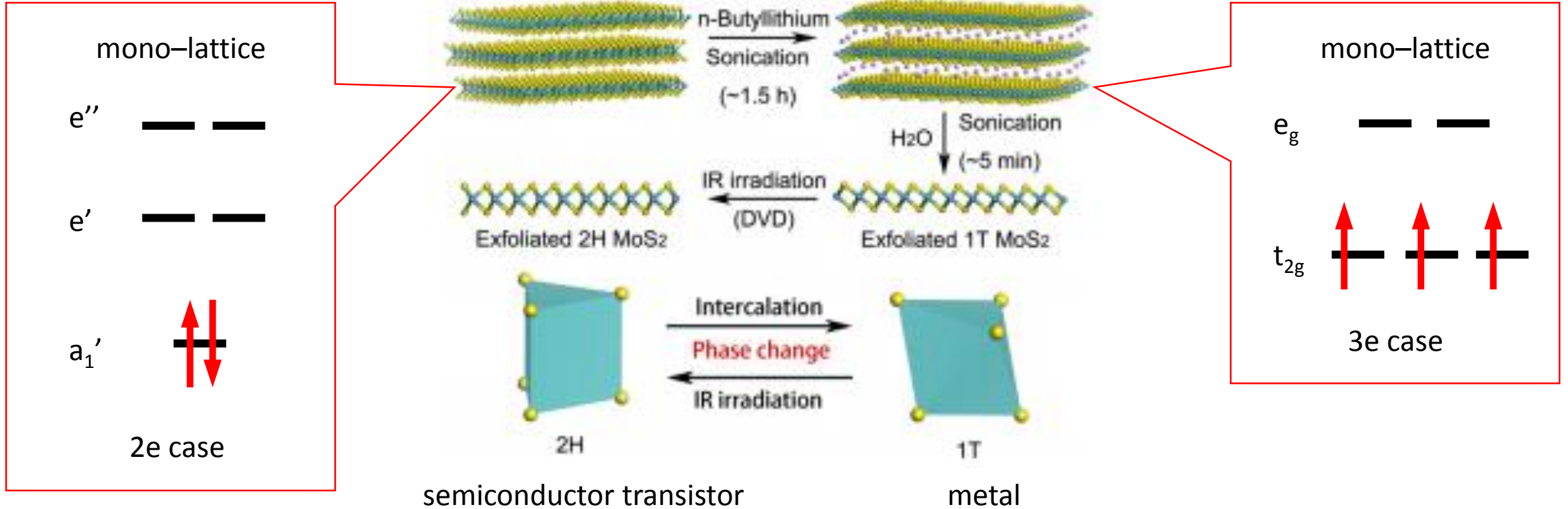


Acc. Chem. Res. **2018**, *51*, 591.

HOT REPORT (1)

·phase engineering

MoS₂ semiconductor to metal transfer



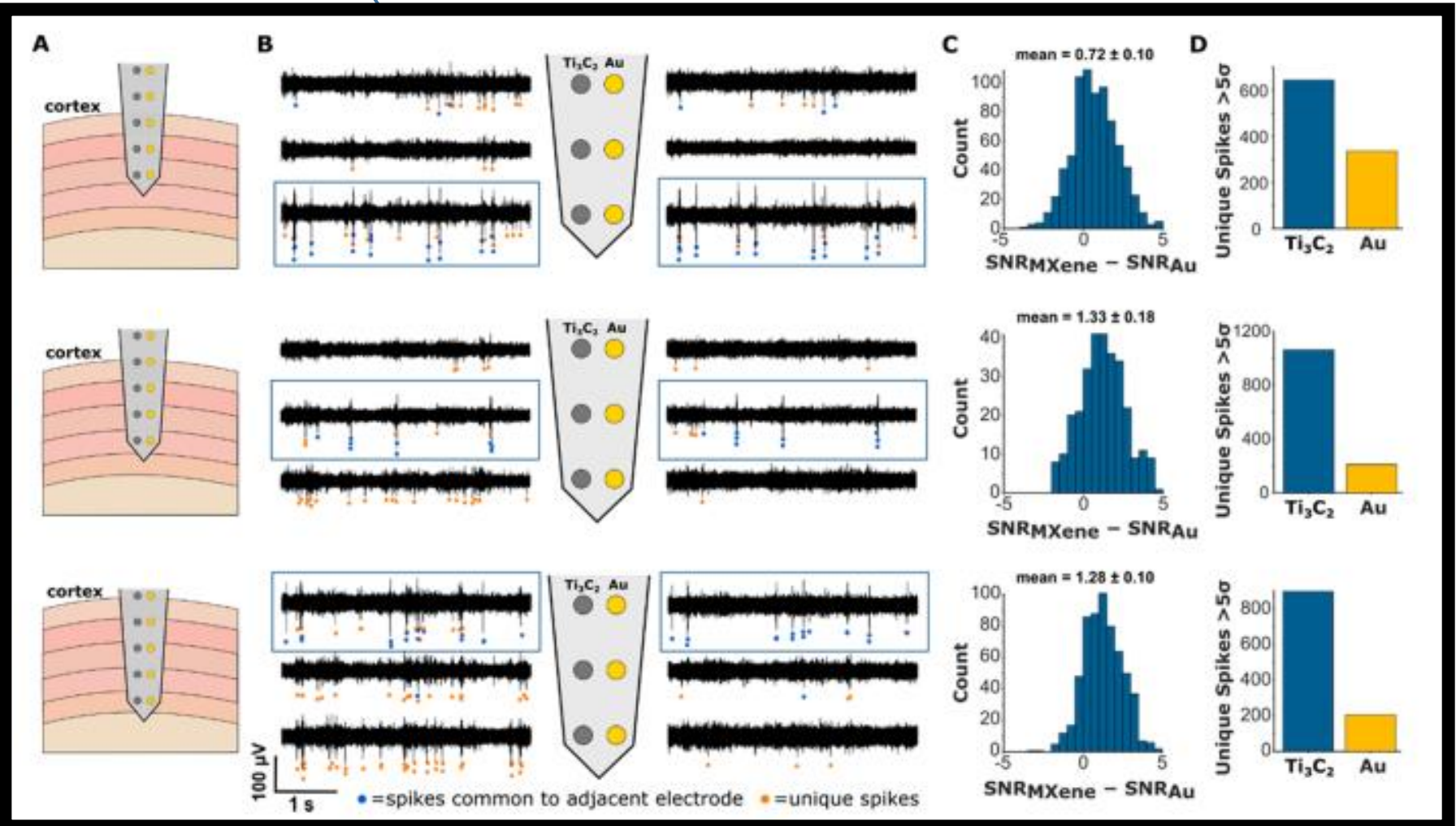
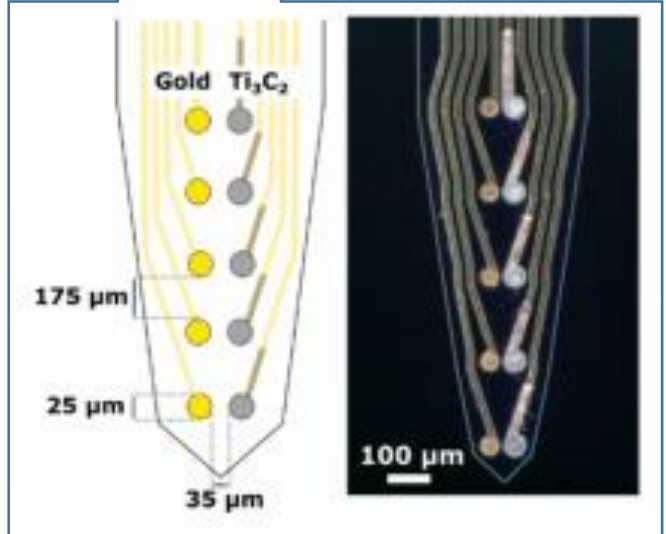
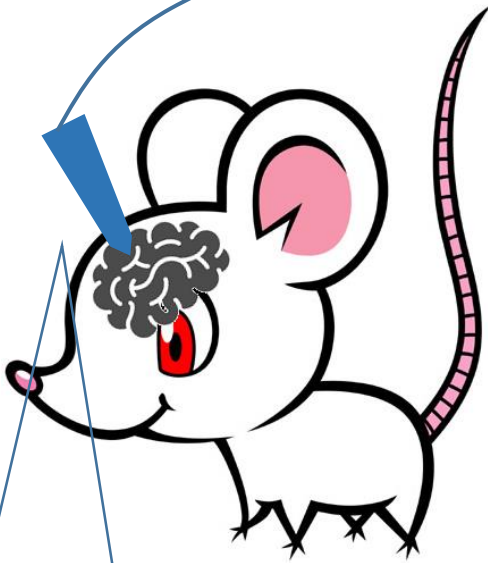
Nano Lett., 2015, 15, 5956.

HOT REPORT (2)

• application of MXene

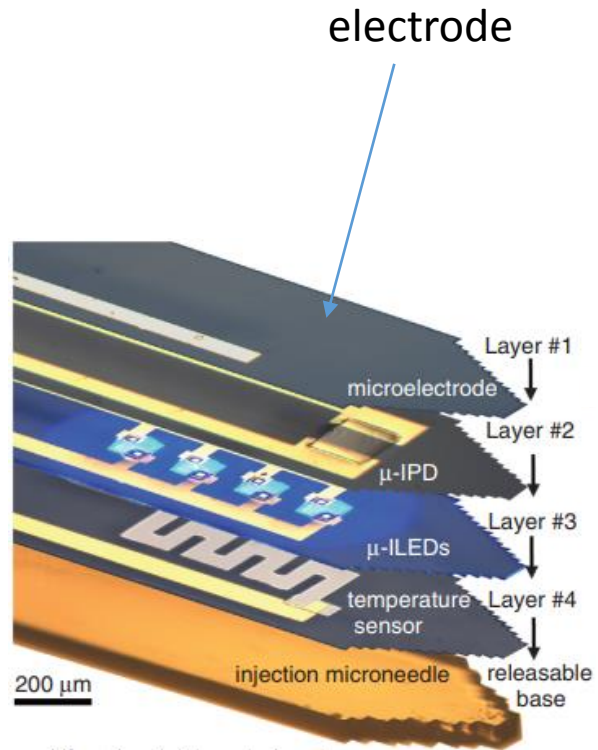
DAQ

ACS Nano 2018, 12, 10419.

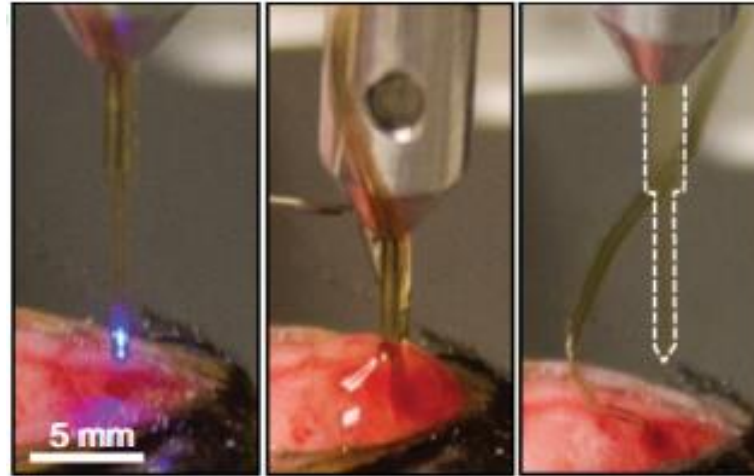


EXPECTED FUTURE

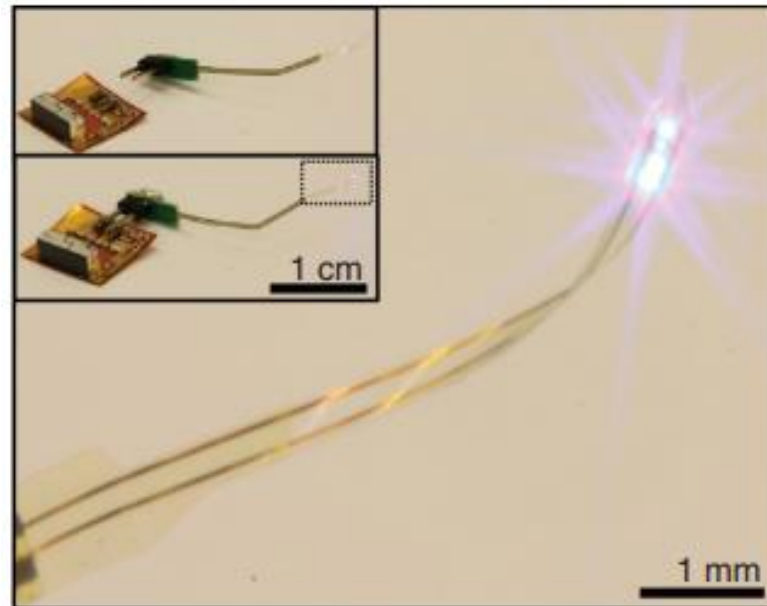
implantable LED



injection and release of the microneedle



wireless power system

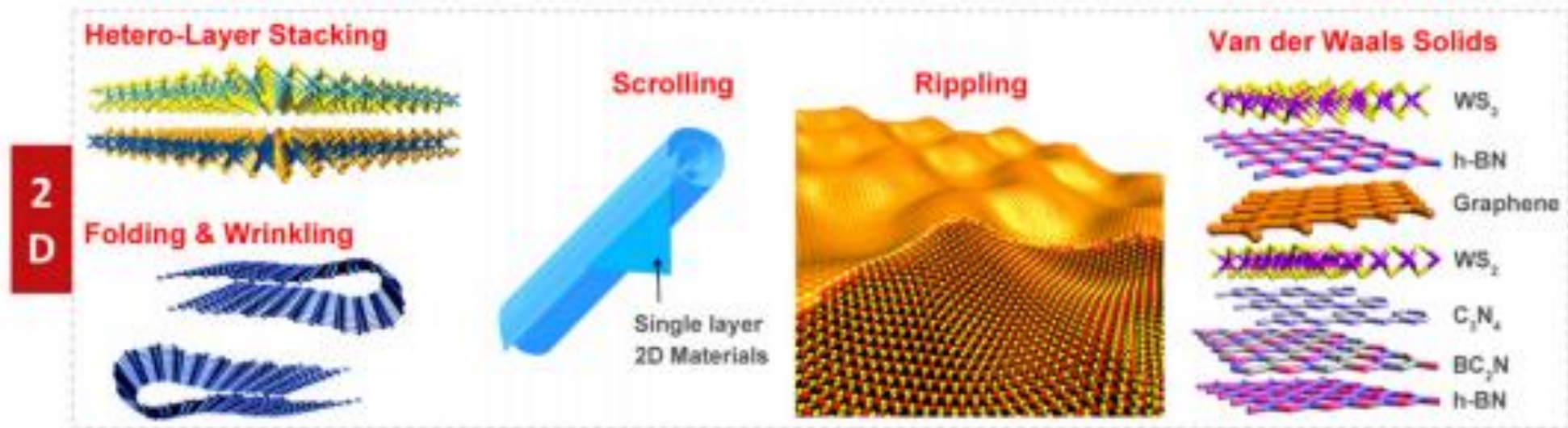


freely moving mice

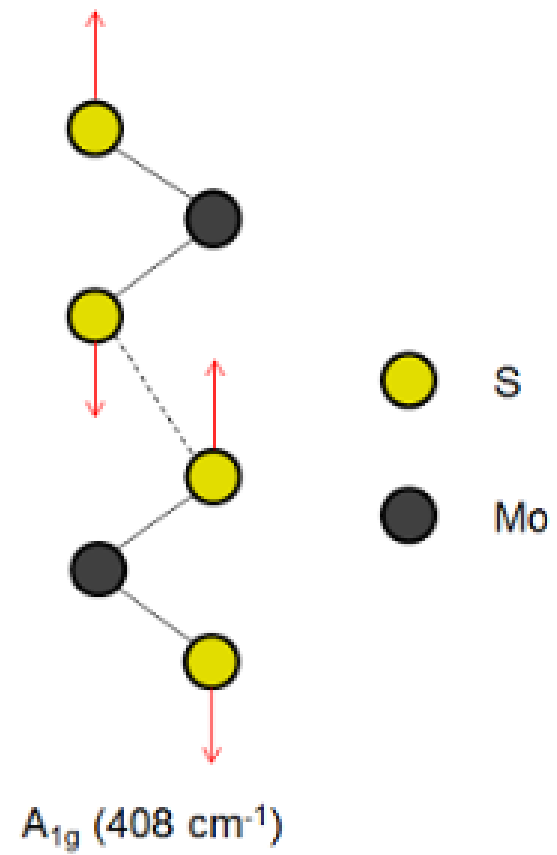
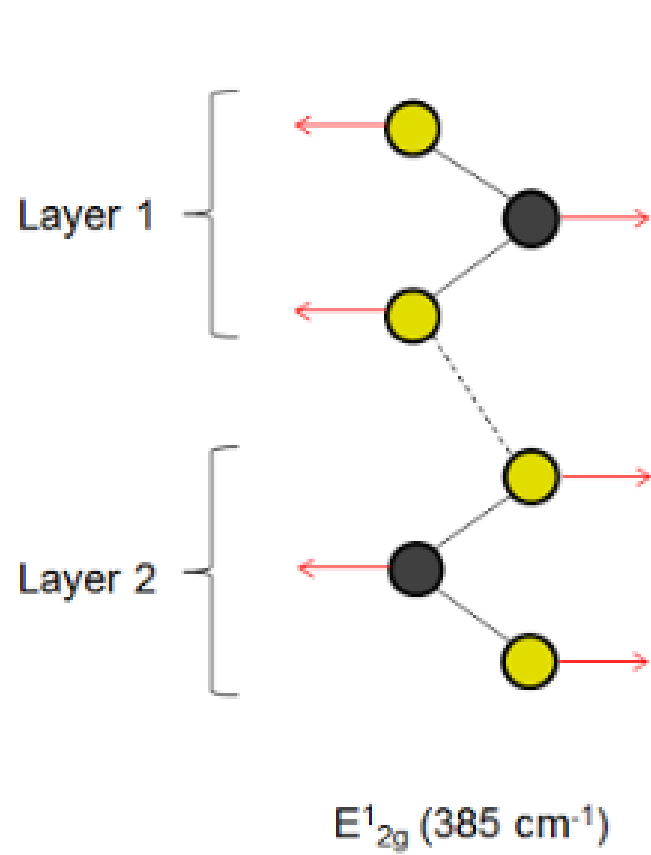


Science **2013**, 340, 211.

CONCLUSION



2D Mater., **2016**, 3, 022002.

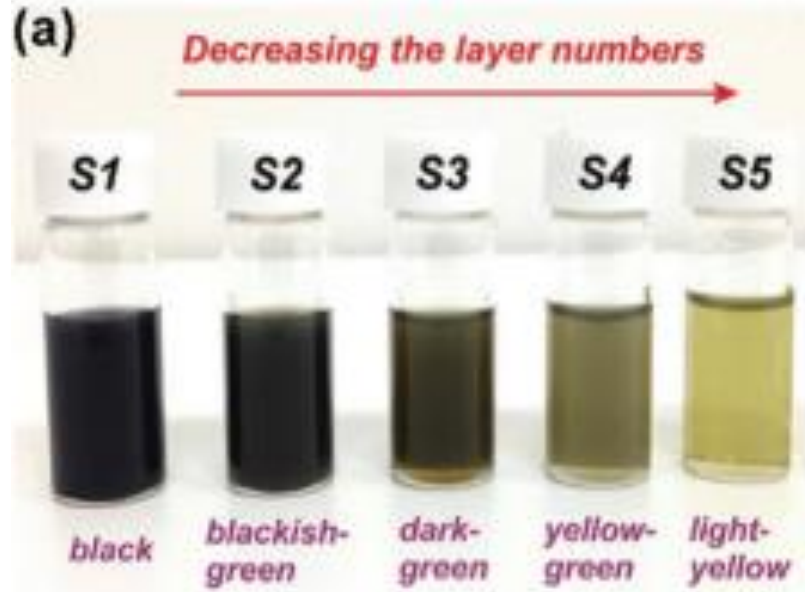


▲ MoS₂の振動モードに対する原子変位

<https://www.nanophoton.jp/applications/30.html>

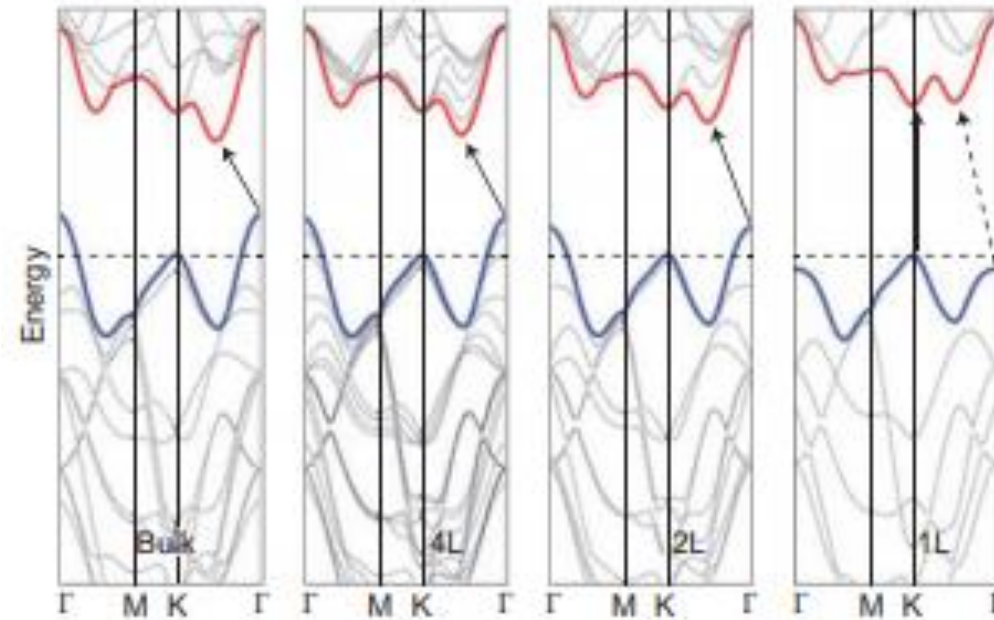
PHYSICAL AND CHEMICAL TUNING (1)

·z direction

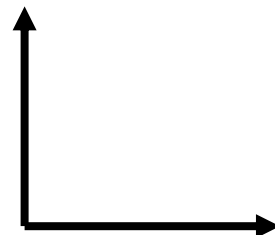


Adv. Energy Mater., **2015**, 5, 1402279.

calculated band structure



$E(k)$



k (electron wavenumber)

Nano. Lett., **2010**, 10, 1272.

PHYSICAL AND CHEMICAL TUNING (2)

·z direction

PtSe₂




ARTICLE

DOI: [10.1038/s41467-018-03436-0](https://doi.org/10.1038/s41467-018-03436-0)

OPEN

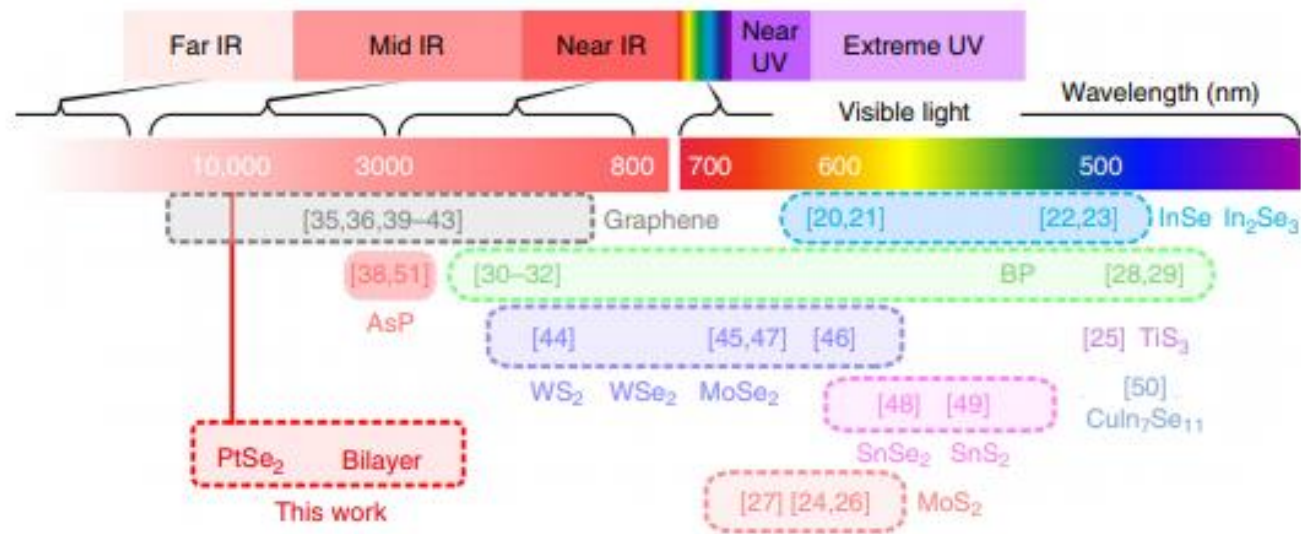
Thickness-modulated metal-to-semiconductor transformation in a transition metal dichalcogenide

Alberto Ciarrocchi ^{1,2}, Ahmet Avsar^{1,2}, Dmitry Ovchinnikov^{1,2} & Andras Kis^{1,2}

Nat. Commun., **2018**, 9, 919.

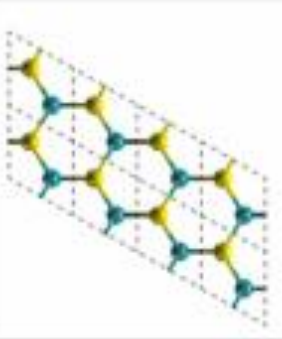
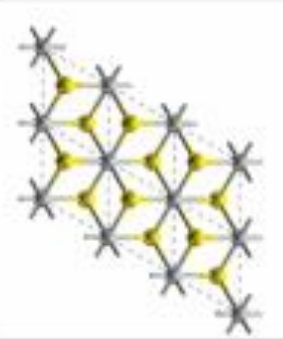
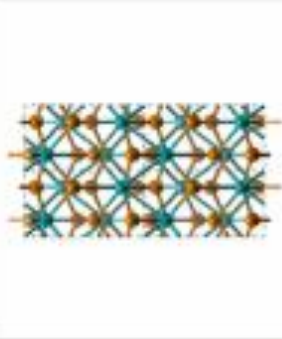
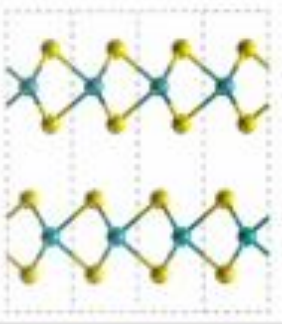
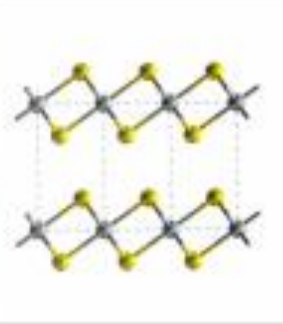
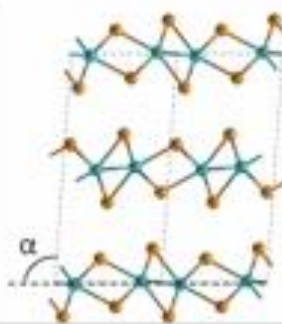
PHYSICAL AND CHEMICAL TUNING

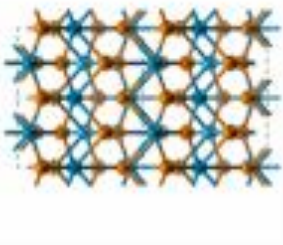
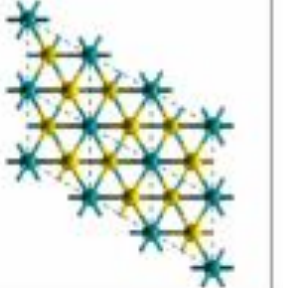
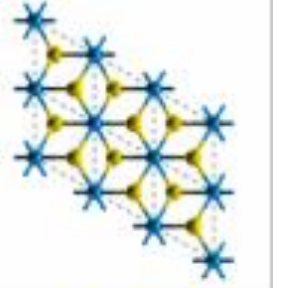
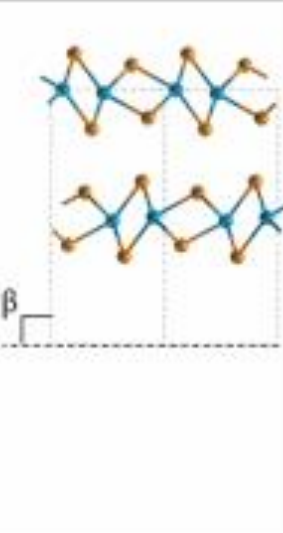
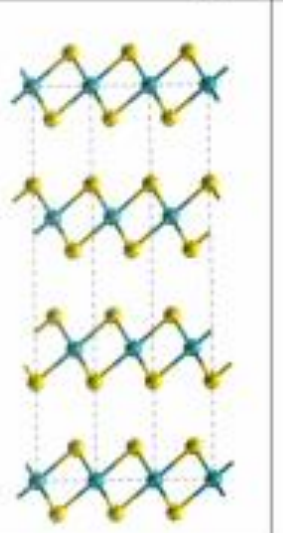
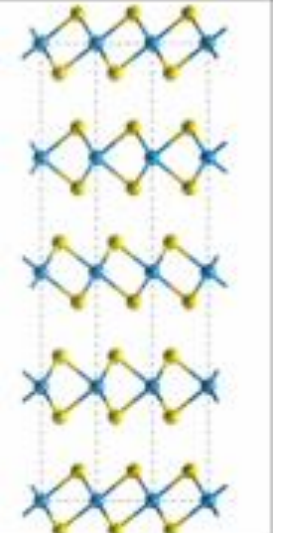
•z direction



Nat. Commun., **2018**, 9, 1545.

STRUCTURE PATTERNS OF BULK TMD

	2H	1T	1T'
Group & Structure	<ul style="list-style-type: none"> $P6_3/mmc$ Hexagonal (Trigonal prismatic) 	<ul style="list-style-type: none"> $P\bar{3}m1$ Hexagonal (Octahedral) 	<ul style="list-style-type: none"> $P2_1/m$ Monoclinic
Top View			
Side View			

	T_d	3R	4H
Group & Structure	<ul style="list-style-type: none"> $Pmn2_1$ Orthorhombic 	<ul style="list-style-type: none"> $R3m$ Rhombohedral 	<ul style="list-style-type: none"> $P6_3/mmc$ Trigonal prismatic
Top View			
Side View			

FIRST EXMAPLE OF TMD

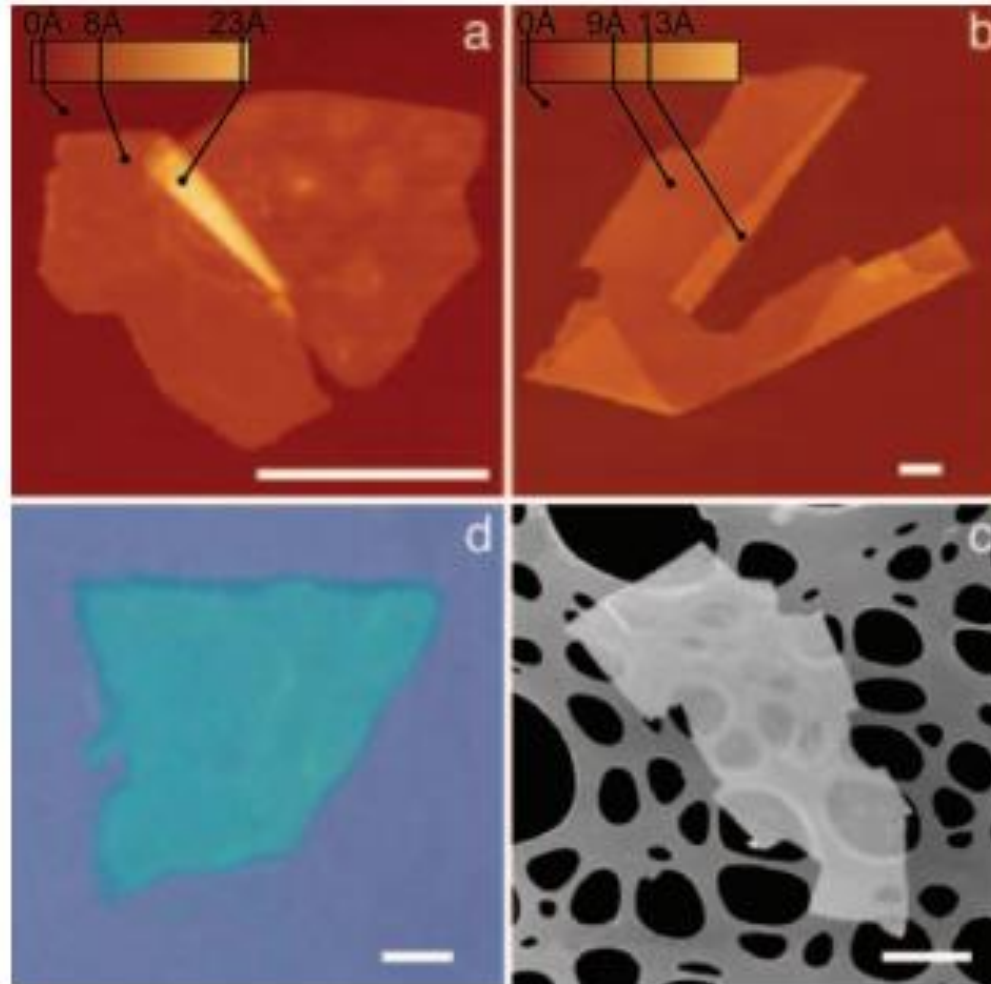


Fig. 1. 2D crystal matter. Single-layer crystallites of NbSe₂ (a), graphite (b), Bi₂Sr₂CaCu₂O_x (c), and MoS₂ (d) visualized by AFM (a and b), by scanning electron microscopy (c), and in an optical microscope (d). (All scale bars: 1 μm.) The 2D crystallites are on top of an oxidized Si wafer (300 nm of thermal SiO₂) (a, b, and d) and on top of a holey carbon film (c). Note that 2D crystallites were often raised by an extra few angstroms above the supporting surface, probably because of a layer of absorbed water. In such cases, the pleated and folded regions seen on many AFM images and having the differential height matching the interlayer distance in the corresponding 3D crystals help to distinguish between double-layer crystals and true single sheets such as those shown here.

PNAS, 2005, 102, 10451.