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

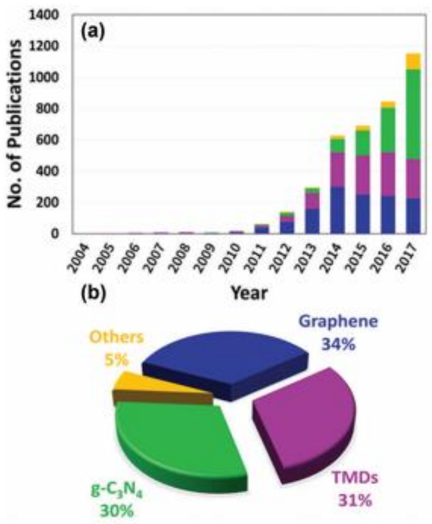

Fig. 2 (a) The number of publications on composite 2D/SC materials applied to water splitting by photocatalysis and PEC processes between 2004 and 2017 (from Scopus) and (b) the contribution of each 2D material to the publication activity.

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

ACS Photonics

Editorial

pubs.acs.org/journal/apchd5

New Discoveries and Opportunities from Two-Dimensional Materials

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[‡]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)

“nanotechnology”

INTRODUCTION (1)

"The <u>atom</u> is the smallest unit of a substance."

The atomic size is the theoretical smallest one.

·first isolation of atomic–size compind

Nobel Prize in Physics in 2010

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

Andre Geim

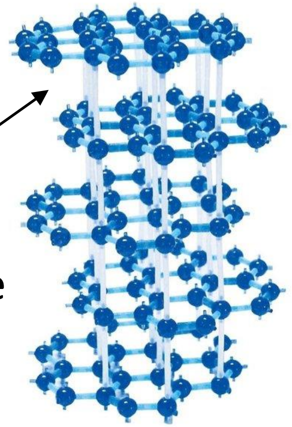
Konstantin Novoselov

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

ISOLATION OF GRAPHENE

"access from 3D to 2D"

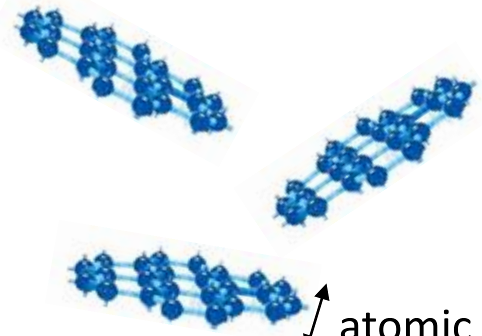
graphite



van der Waals force
(weak)

3D (bulk) compound

graphene



atomic thin

2D (layerd) compound

2D materials

semimetal

firm

changed properties

gapless semiconductor

flexible

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

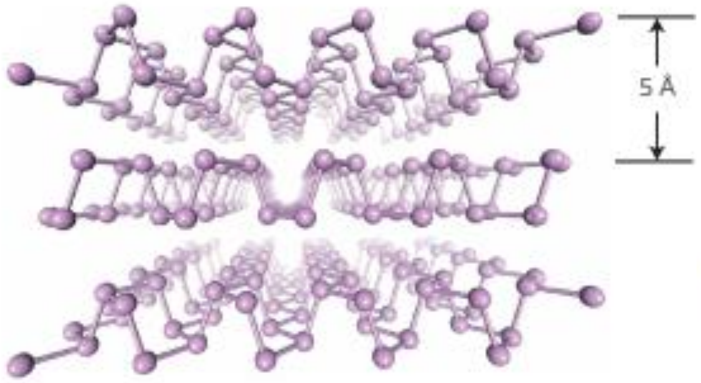
cf $695

- 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

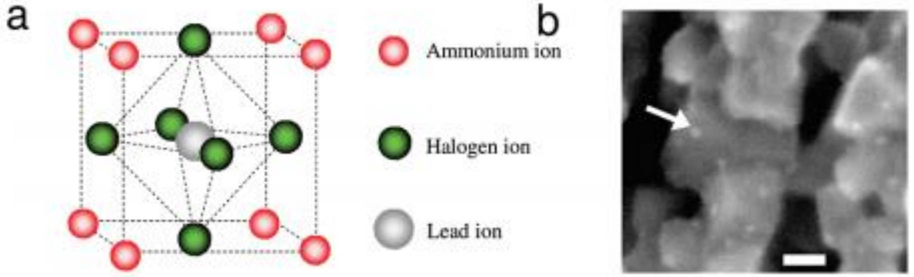
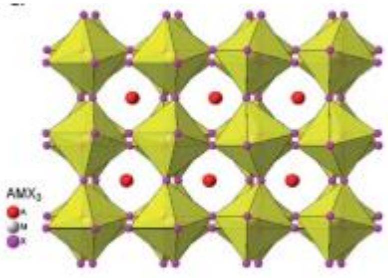
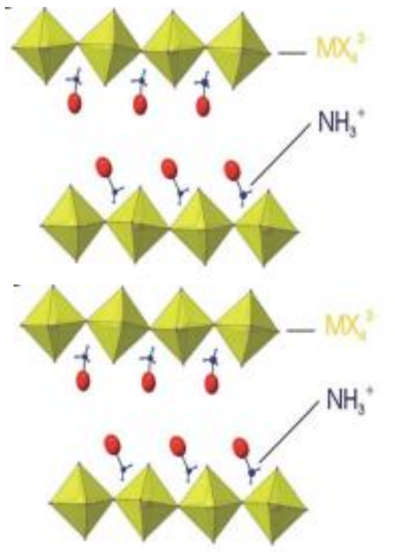


Figure 1. (a) Crystal structures of perovskite compounds. (b) SEM image of particles of nanocrystalline $CH_3NH_3PbBr_3$ deposited on the TiO_2 surface. The arrow indicates a particle, and the scale bar shows 10 nm.

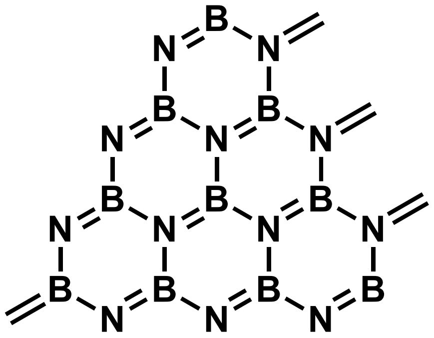
J. Am. Chem. Soc. **2009**, *131*, 6050.

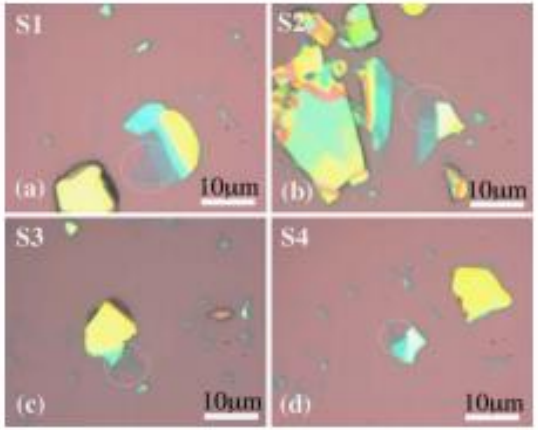




Chem. Sci. **2017**, 8, 2522.

h–BN

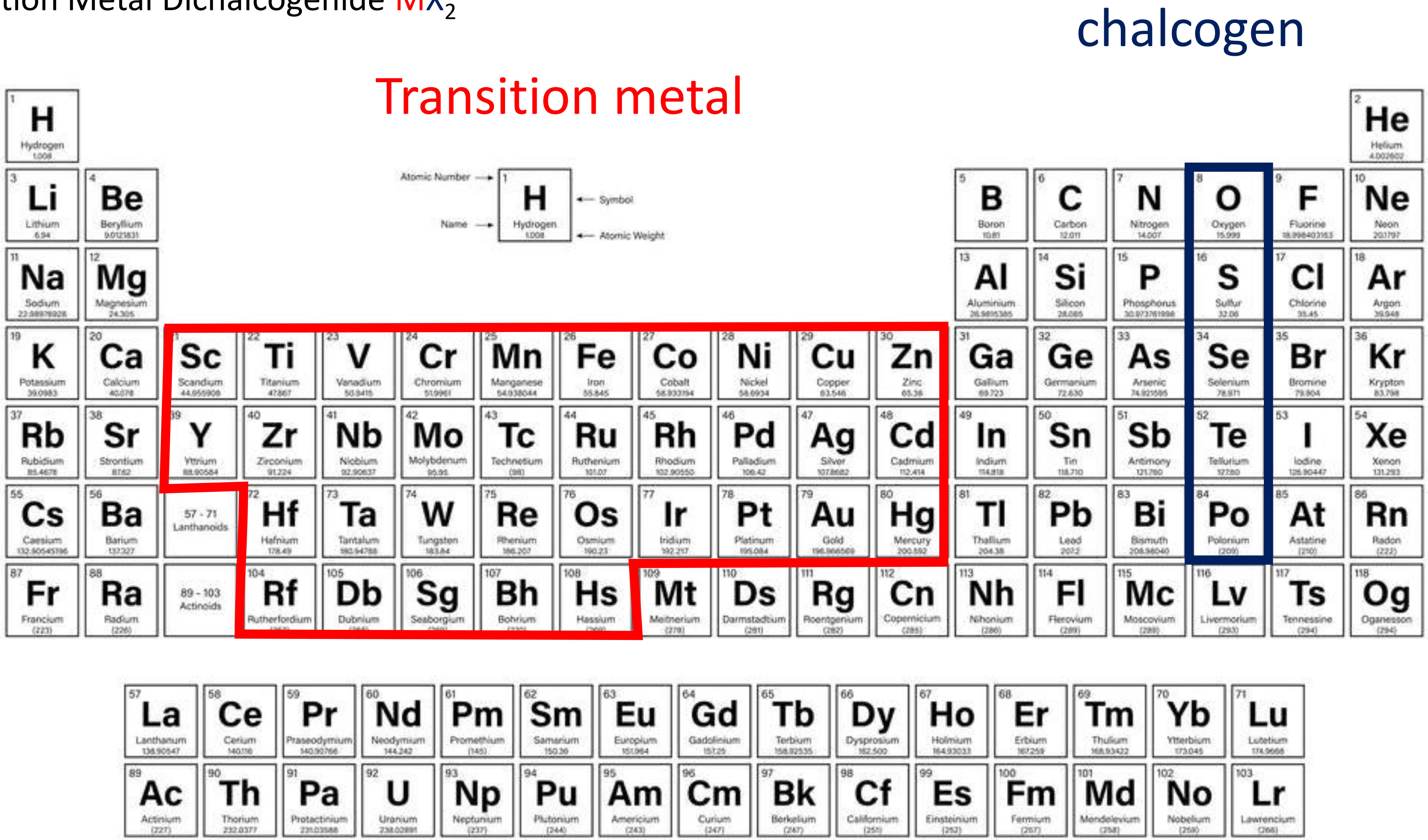




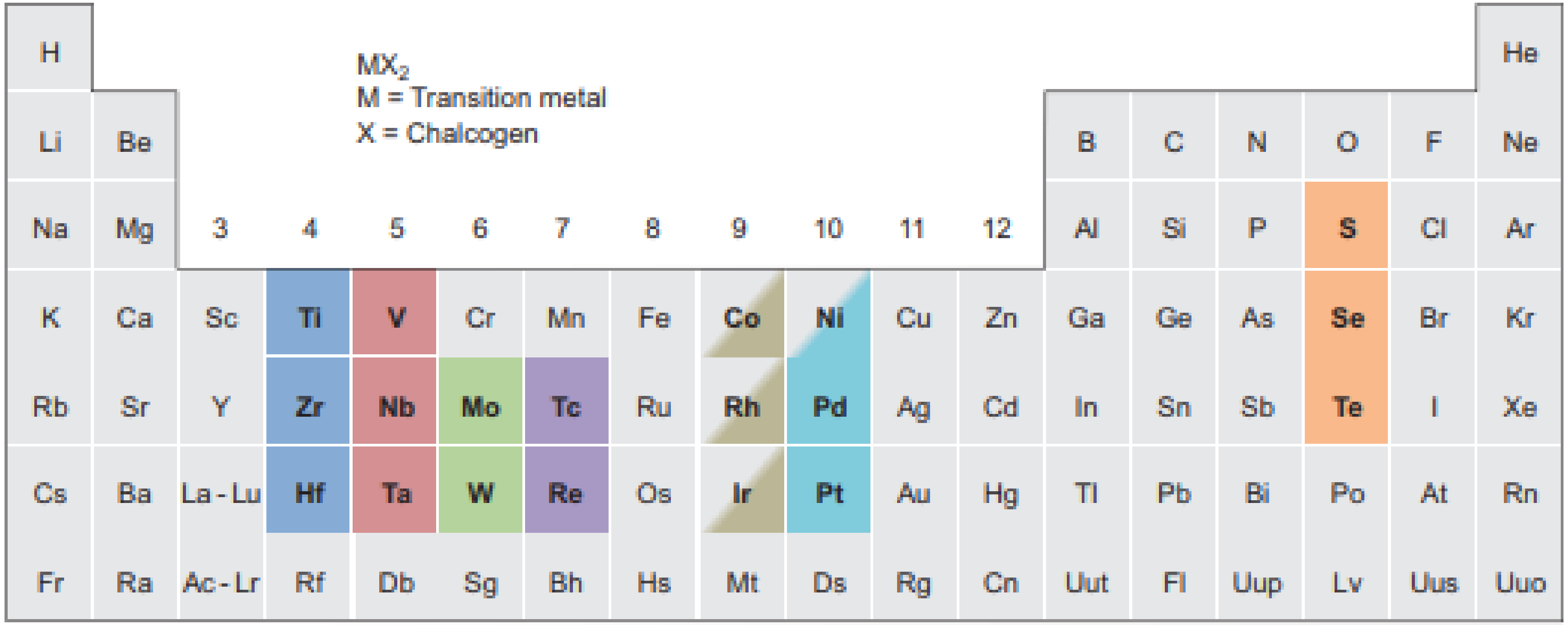
Appl. Phys. Lett. **2008**, *92*, 722.

BEYOND GRAPHENE (2)

Transition Metal Dichalcogenide MX_2



COMBINAITON OF TMD



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

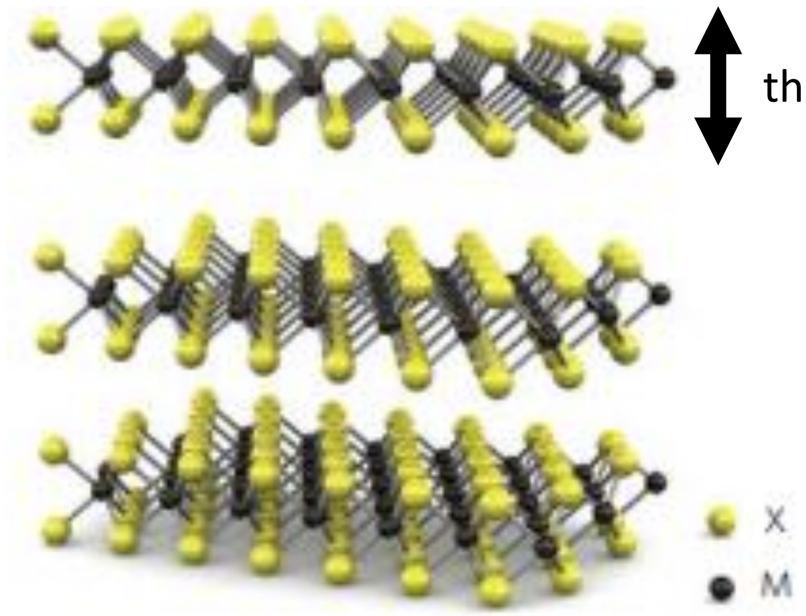
a variety of combination

EXAPMLE OF TMD

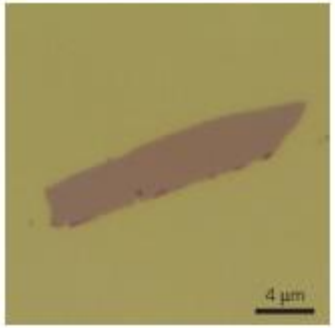
bulk crystal MoS_2

For lubrication

Ampere cop



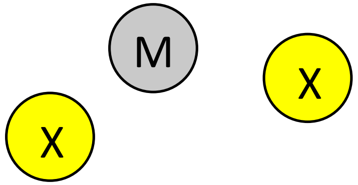
crystal structure



Optical microscopy image

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

STRUCTURE OF TMD

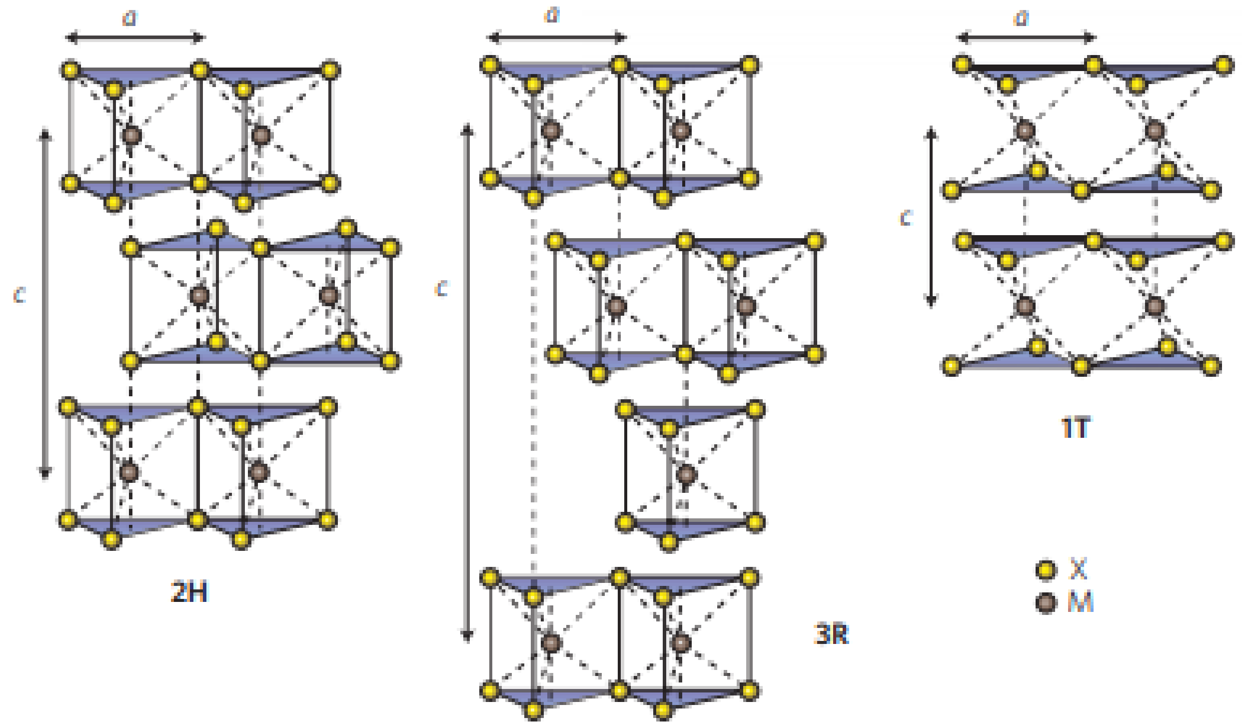


precursor

bulk TMD

exfoliation

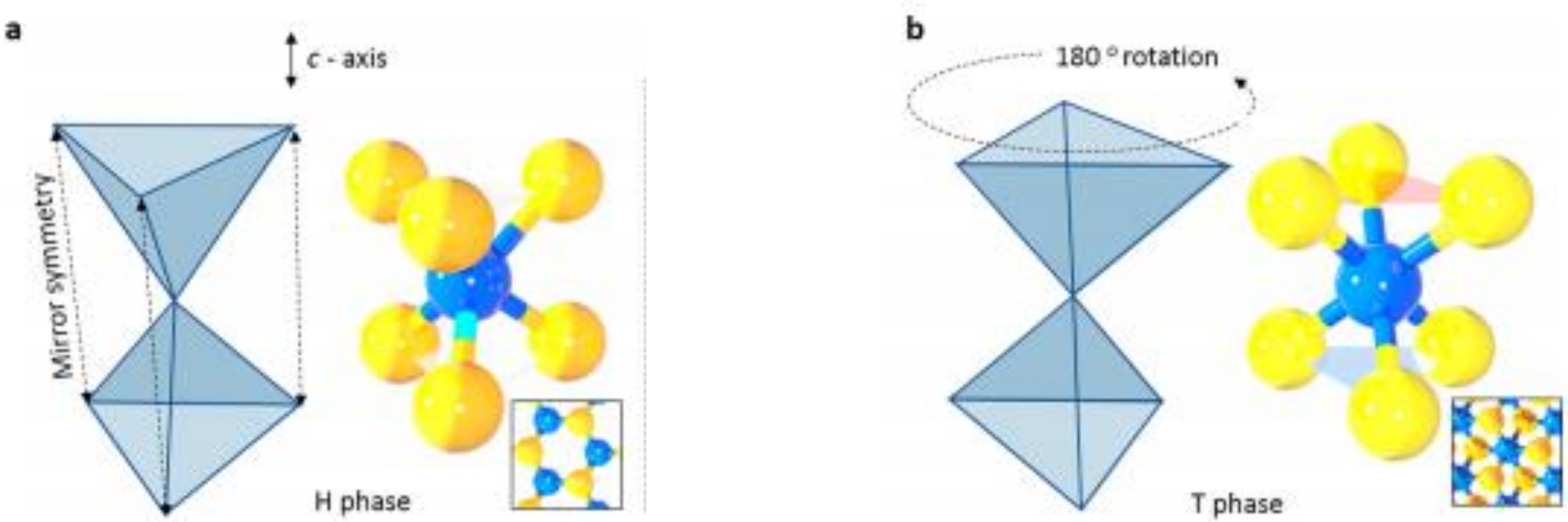
layerd TMD



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

H / T ...??

STRUCTURE OF LAYERED TMD (1)



trigonal prismatic

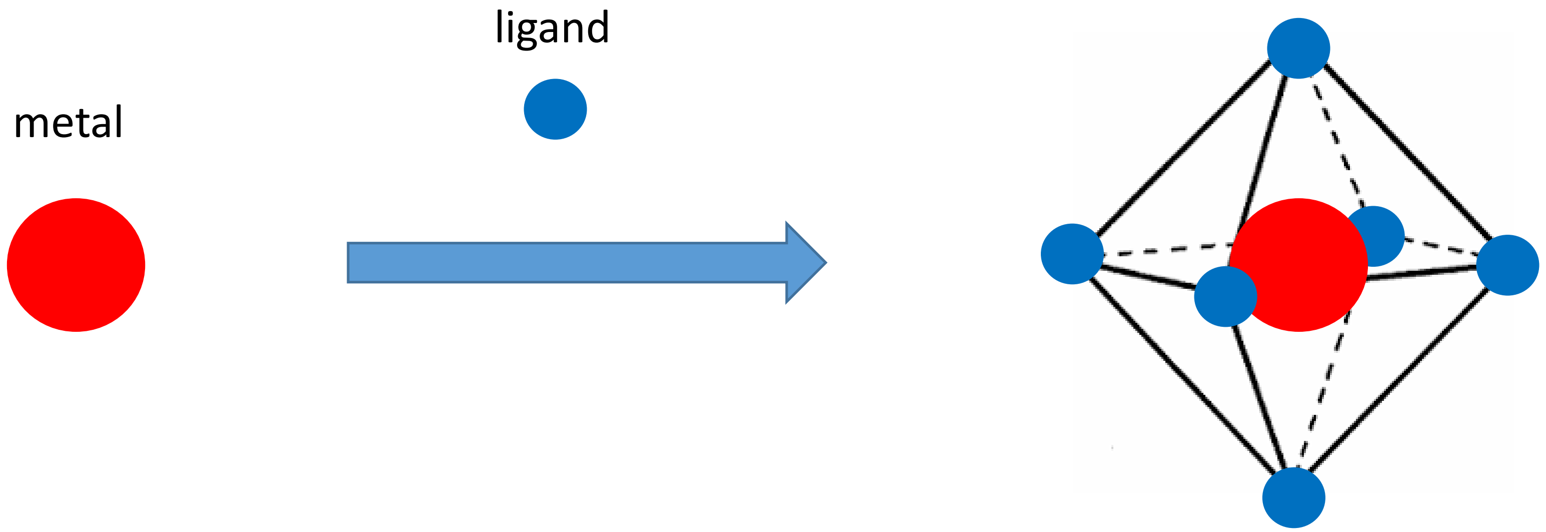
octahedral

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

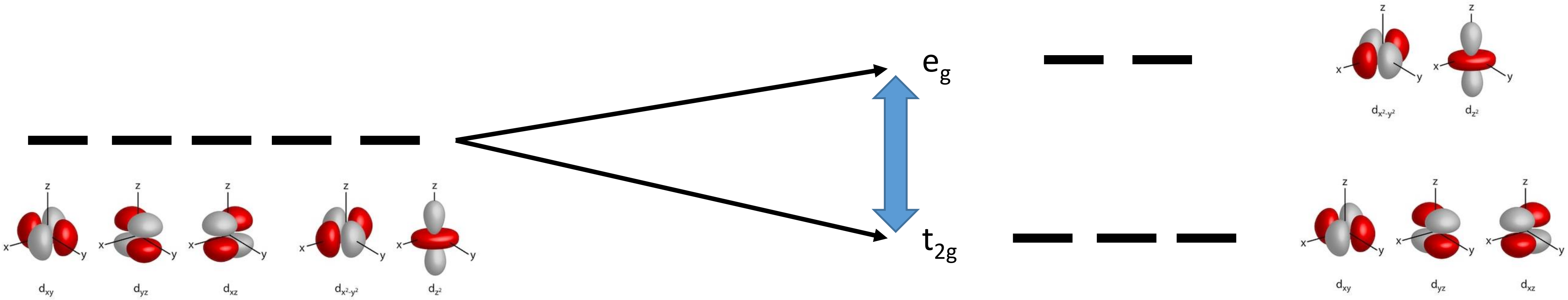
1. What is trigonal prismatic / octahedral?
2. What makes H–phase / T–phase?
3. electronic properties

EXPLANATION (1)

·crystal–field theory



d orbital



“splitting d orbitals”

EXPLANATION (2)

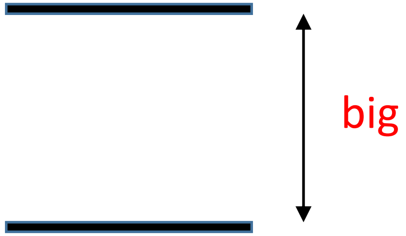
·spectrochemical series

small $I^- < Br^- < S^{2-} < SCN^- < Cl^- <$
$NO_3^- < F^- < C_2O_4^{2-} < H_2O < NCS^- <$
$CH_3CN < NH_3 <$ en $<$ bipy $<$ phen $<$
$NO_2^- < PPh_3 < CN^- < CO$ big

$[Co(NH_3)_5Br]^{3+}$

$[Co(NH_3)_5Cl]^{3+}$

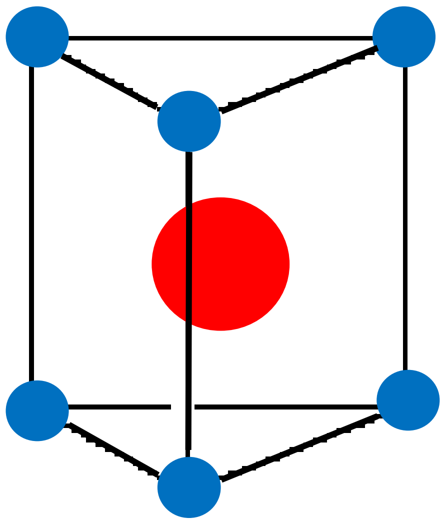
$[Co(NH_3)_5(NH_3)]^{2+}$



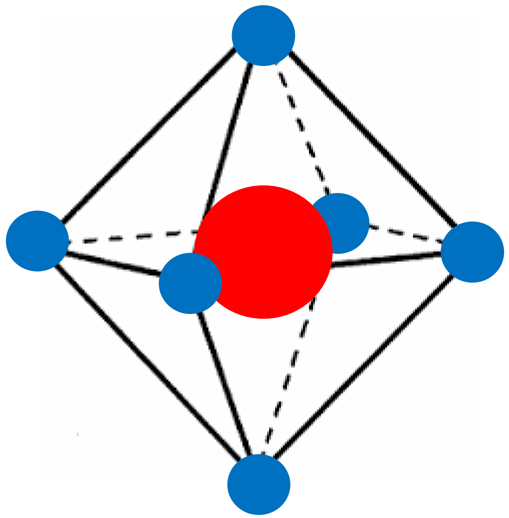
EXPLANATION (3)

·mono–lattice d orbital

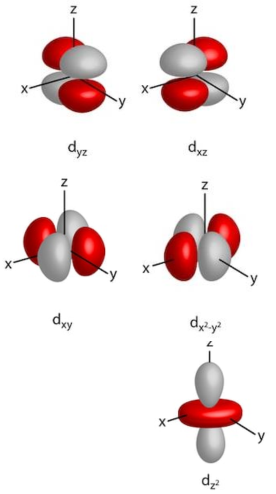
trigonal prismatic



octahedral



d orbital



e’’

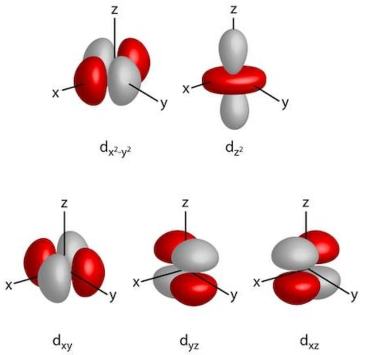
e’

a_1’

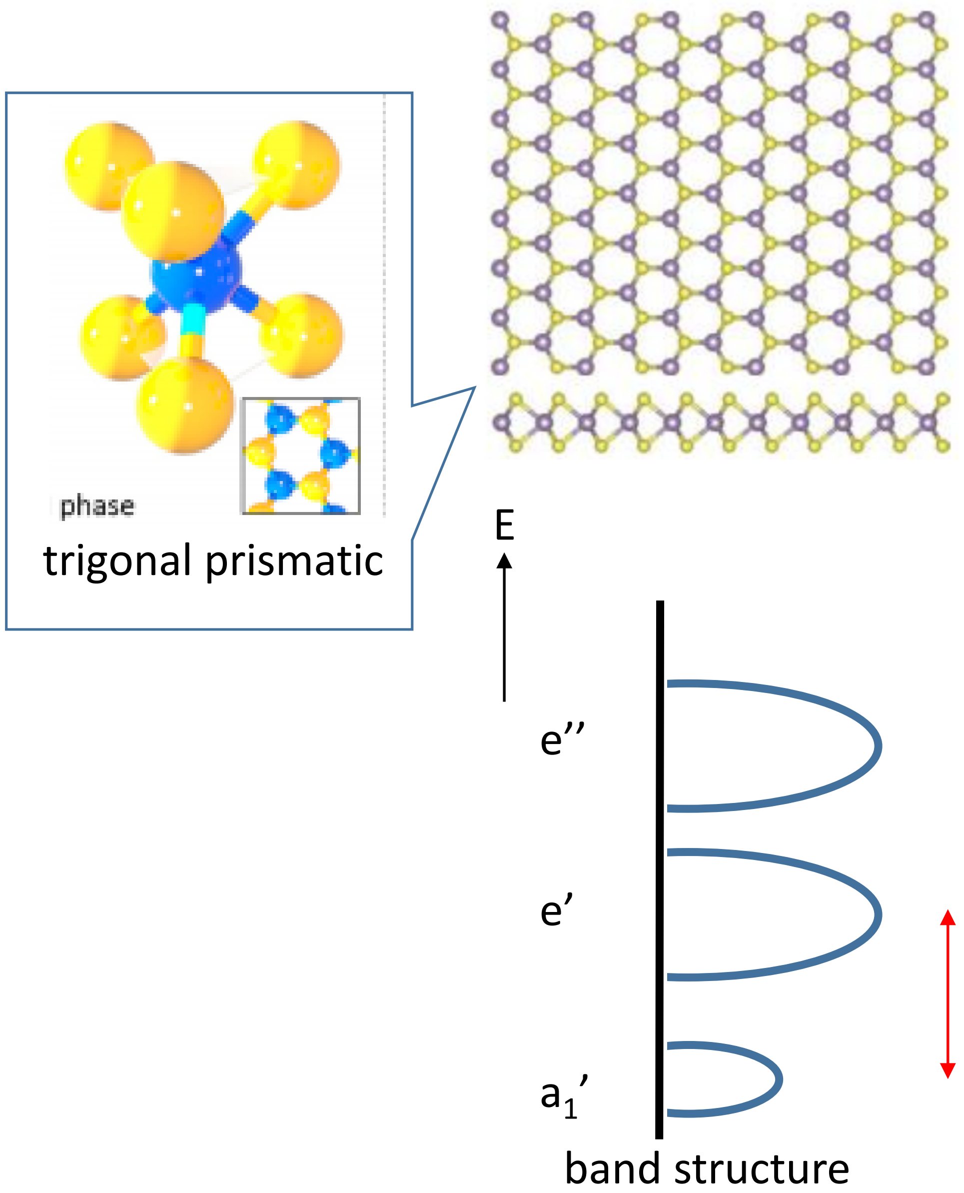
e_g

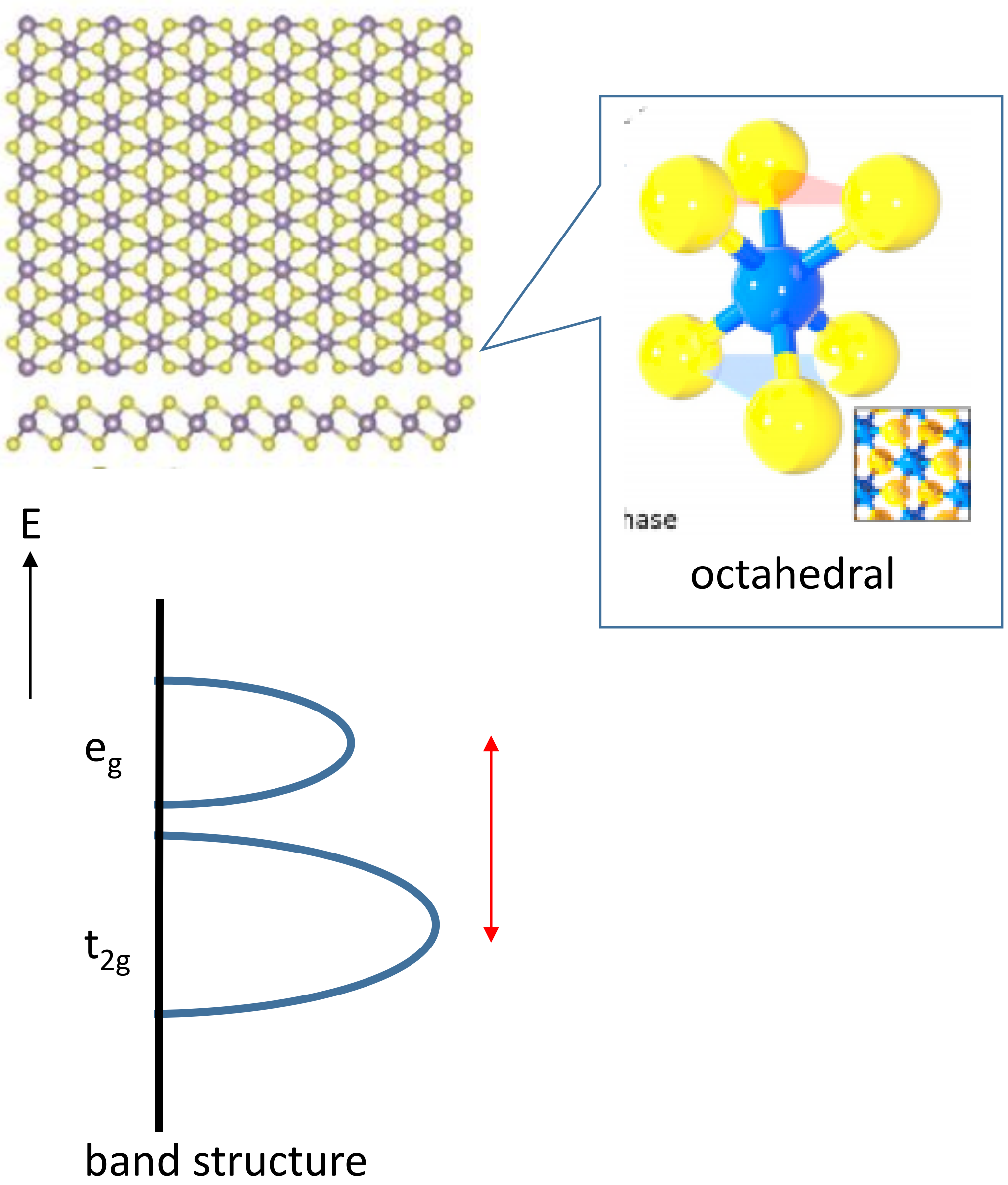
t_{2g}

d orbital

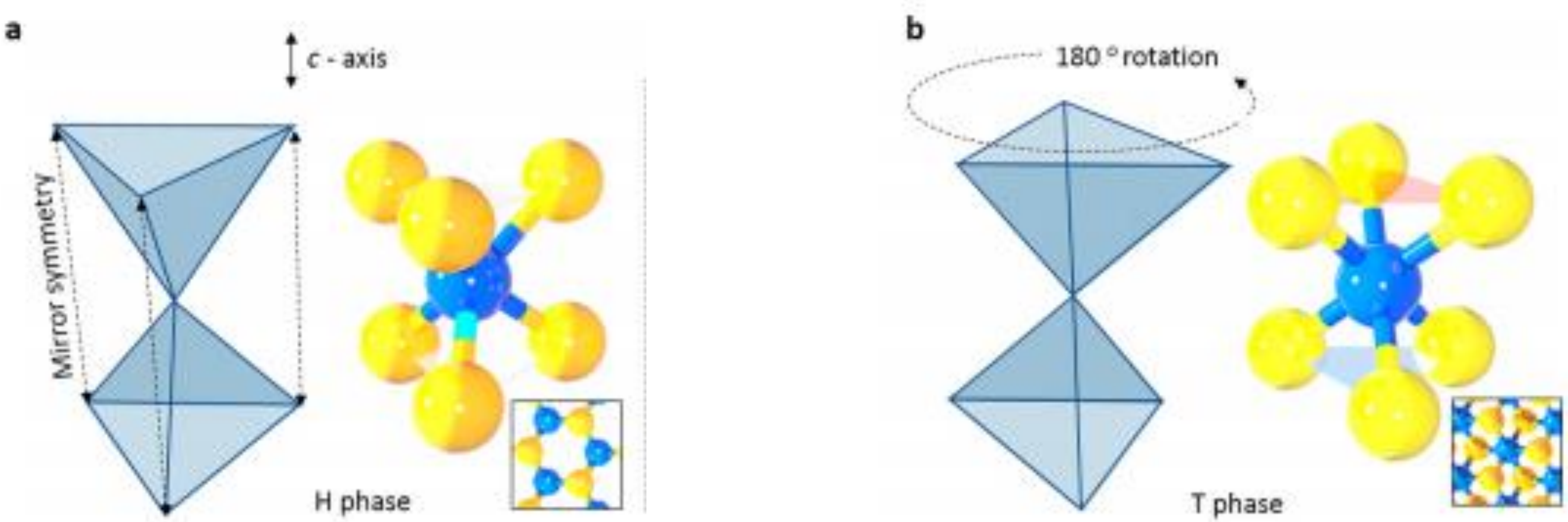


BAND STRUCTURE OF LAYERED COMPOUND





STRUCTURE OF LAYERED TMD (2)



trigonal prismatic

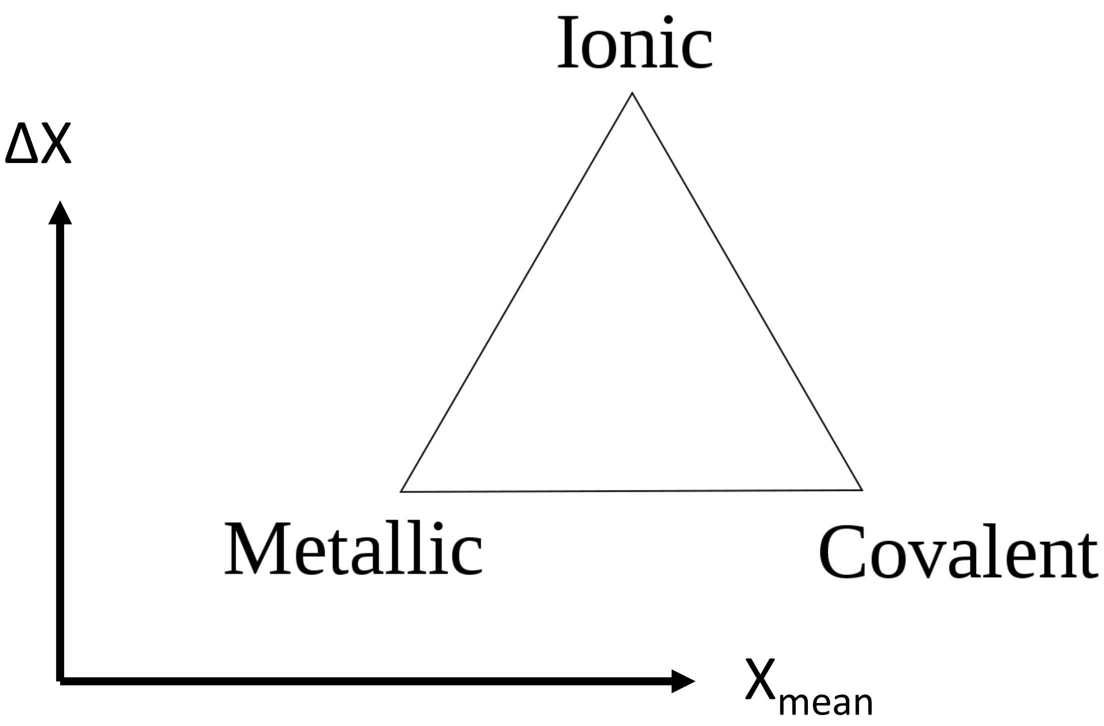
octahedral

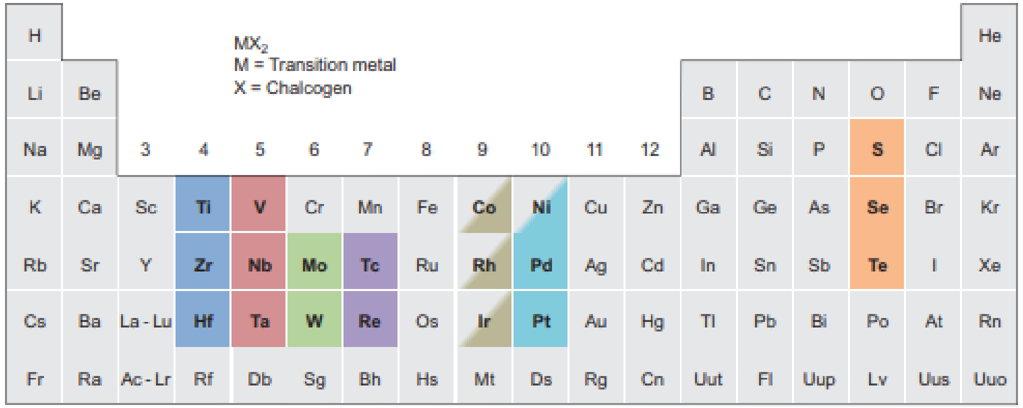
Chem. Rev. **2018**, *118*, 6297.

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

EXPLANATION (4)

- Ketelaar triangle





d6–Ch: covalent
d4–Ch: metallic

The order of electronegativity (X)

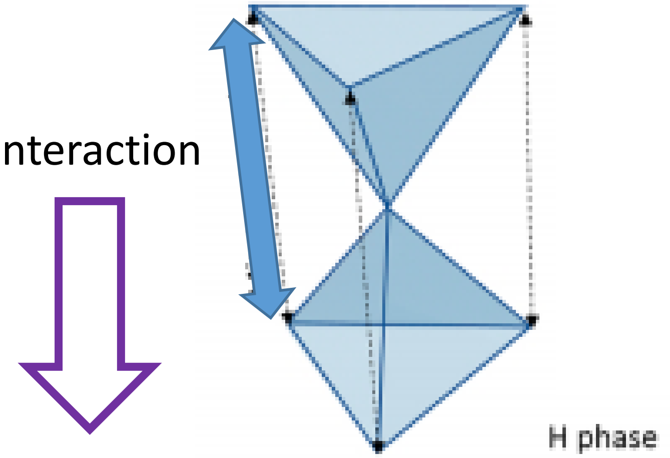
4 <5 <6 <16

TREMENDACE BETWEEN METAL AND PHASE

trigonal prismatic

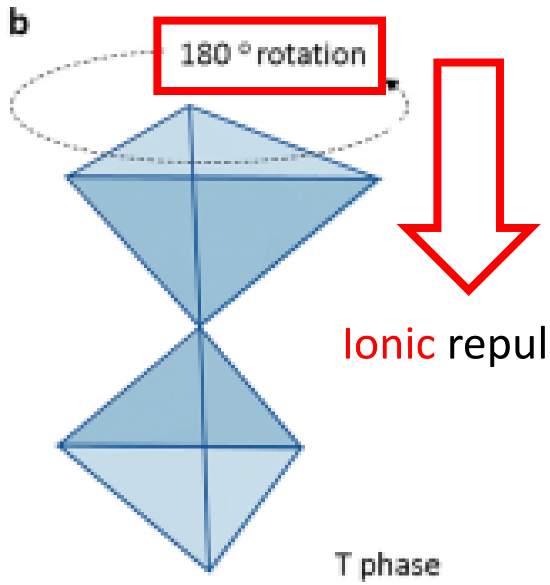
Octahedral

interaction



Not ionic (covalent)

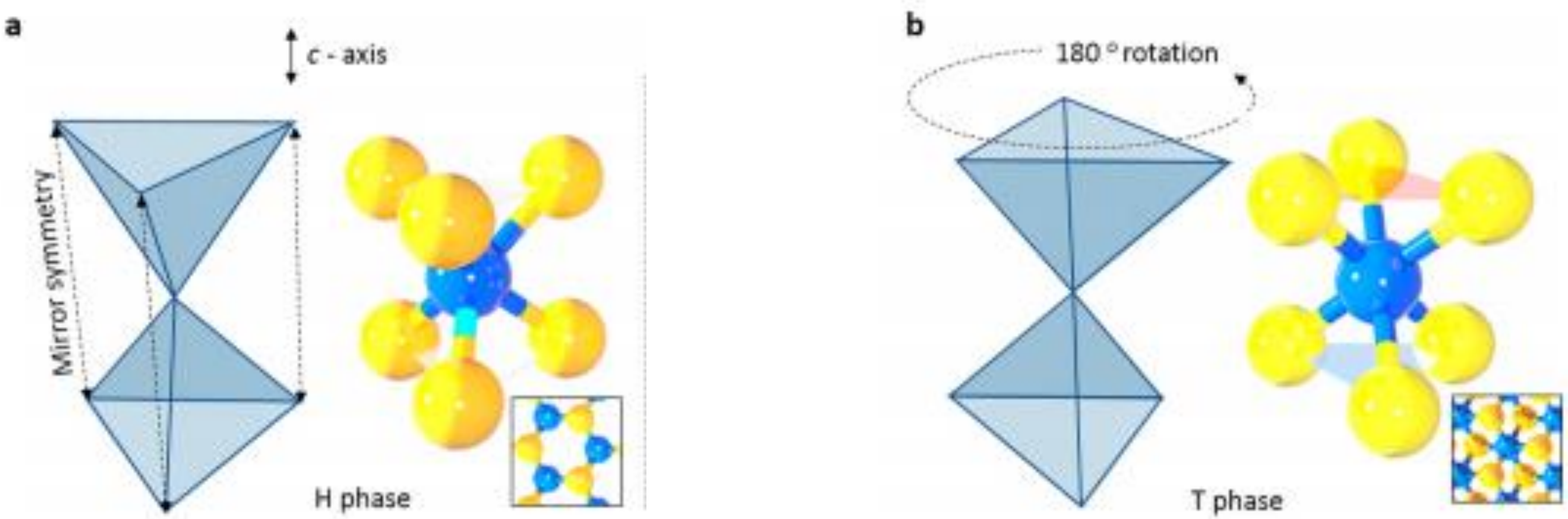
d6 metal



Ionic repulsion

d4 metal

STRUCTURE OF LAYERED TMD (3)



trigonal prismatic
d6metal

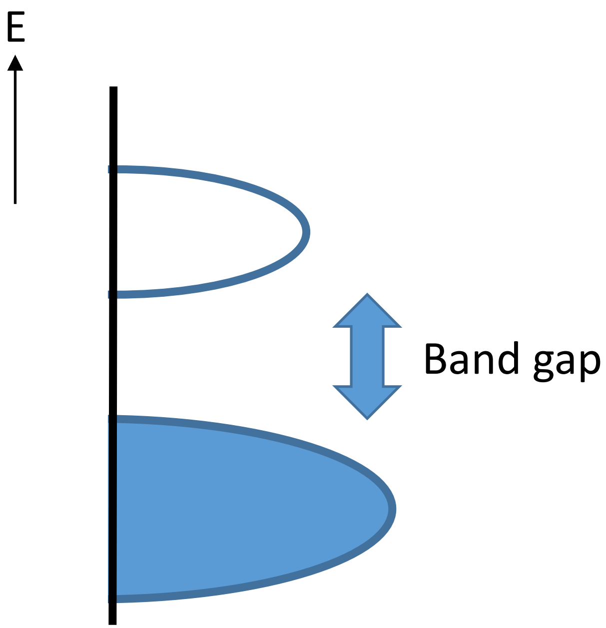
Octahedral
d4metal

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

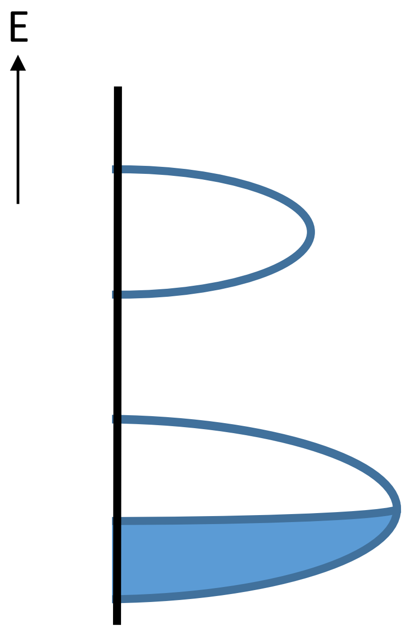
1. What is trigonal prismatic / octahedral?
2. What makes H–phase / T–phase?
3. electronic properties

EXPLANATION (5)

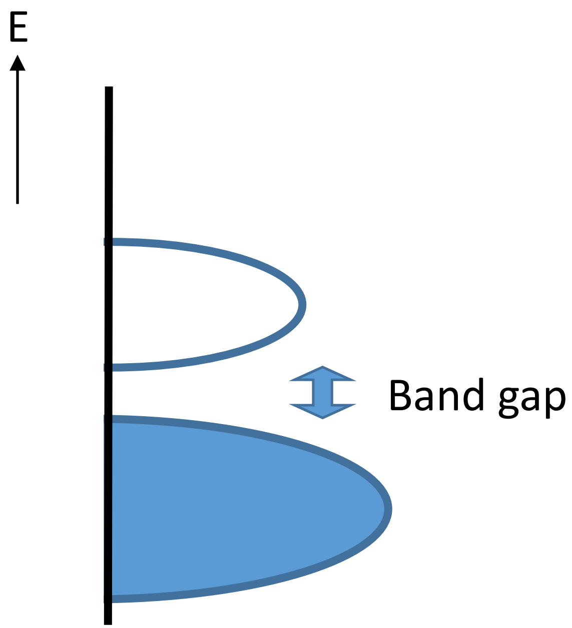
·electronic properties



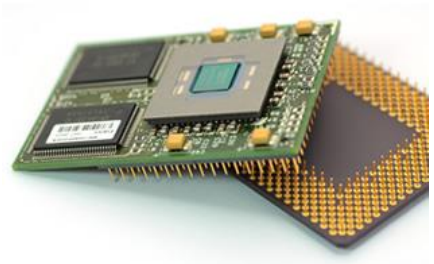
insulator



metal



semiconductor



EXAMPLE OF METALLIC TMD

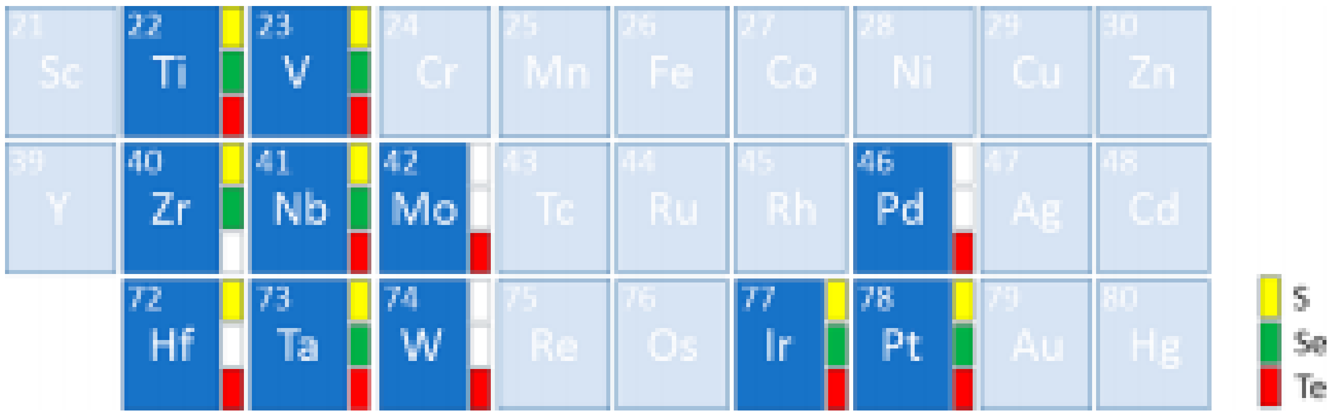


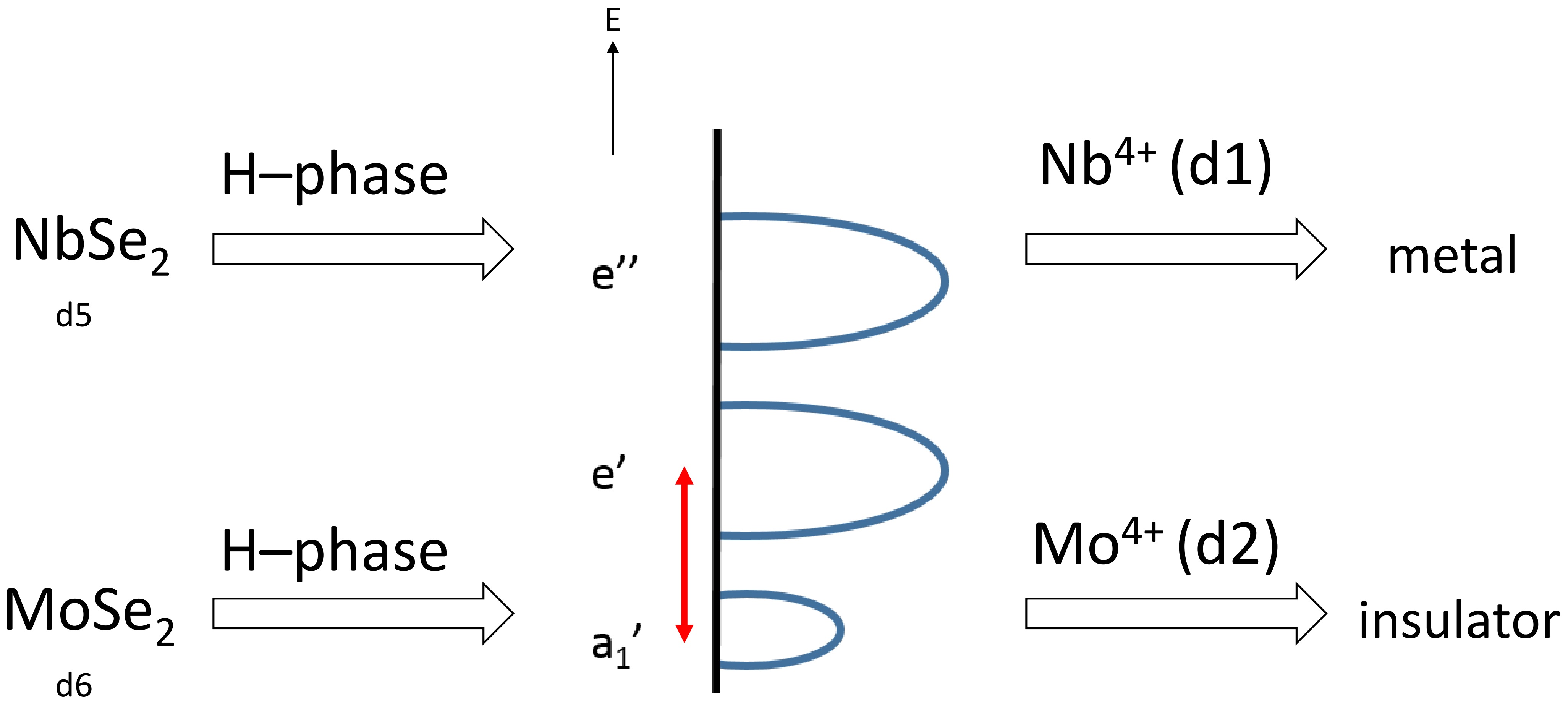
Figure 1. Types of metals involved in layered dichalcogenides. Blue color indicates transition metals for currently developed metallic-layered dichalcogenides (m-LTMdCs), and yellow, green, and red small rectangles are S, Se, and Te compounds. White rectangles for chalcogen are unreported or nonexist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

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

NOTE

$NbSe_2$ metal / $MoSe_2$ not metal

EXPLANATION OF TMD PROPERTIES



SHORT SUMMARY

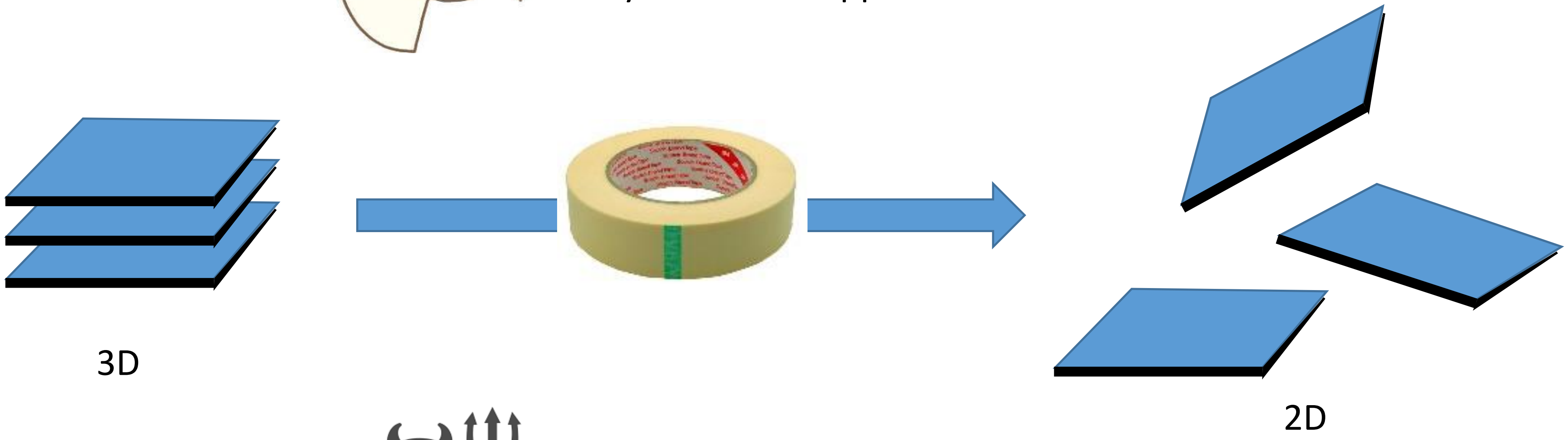
3D materials (bulk)	graphite	Transition Metal Dichalcogenide
2D materials (layered)	graphene	Transition Metal Dichalcogenide
number of the example	1	over 30
constructing atoms	carbon	transition metal and chalcogen
structure	1 type hexagonal	2 types trigonal prismatic octahedral
material properties	gapless 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.

·easy–to–access approach

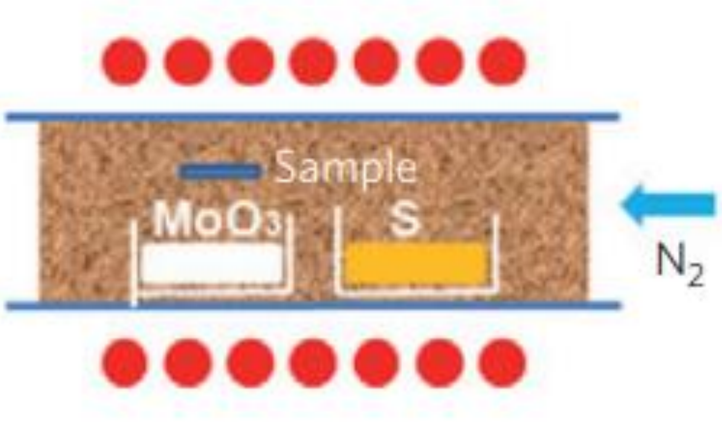


·not scalable
·difficult to control the size
·reaggregation

SYNTHESIS METHOD (2)

·Chemical Vapor Deposition

bottom up approach–1
often used for industrial method



$MoO3 + x/2\ S \rightarrow Mo_{3-x} + x/2\ SO_2$
$MoO_{3-x} + (7-x)/2\ S \rightarrow MoS_2 + (3-x)/2\ SO_2$

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

·large scale

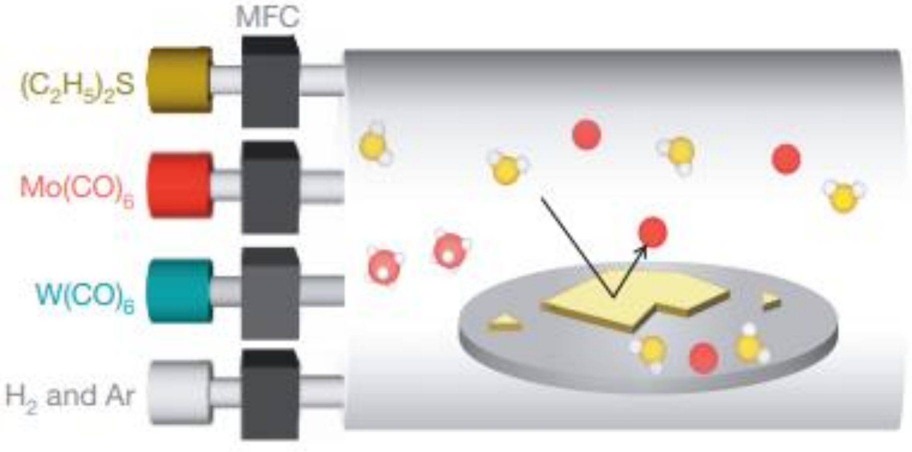
·difficult to control the number of the layer
·poor quality

SYNTHESIS METHOD (3)

·Metal–Organic Chemical Vapor Deposition

bottom up approach–2
first report; *Nature* **2015**, *520*, 656.

mass flow controllers

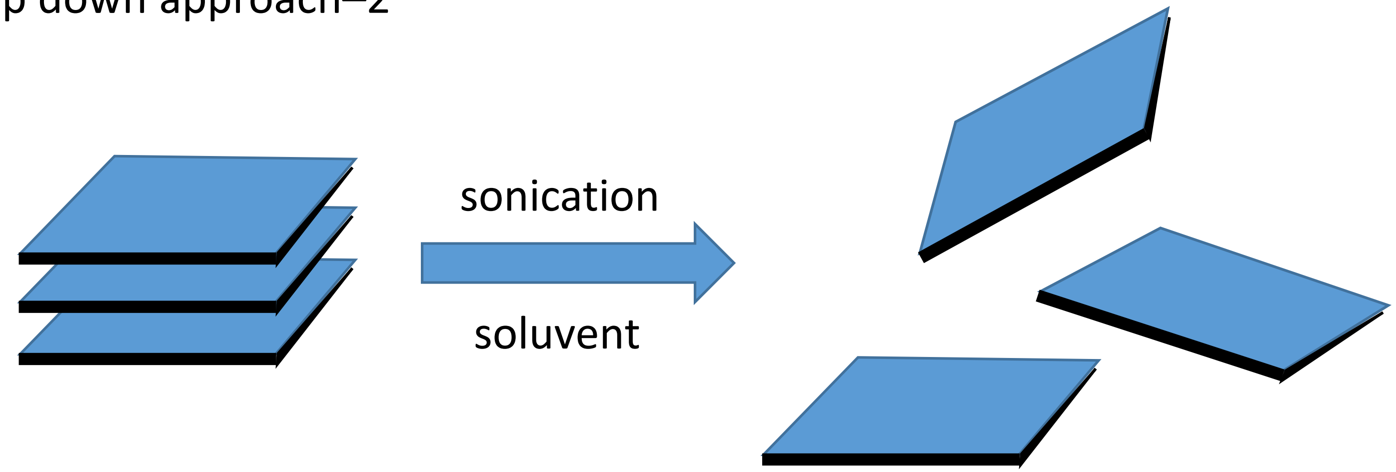


·homogeneity
·low decomposition temperature of the precursor

·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



·stabilizing against the reaggreation

·few hundred nanometers in size

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.

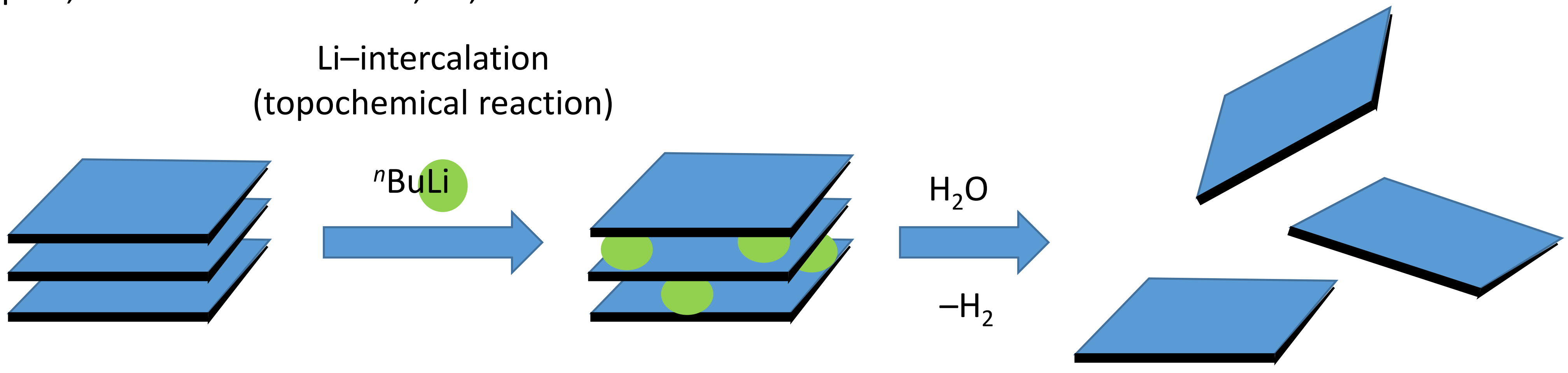
SYNTHESIS METHOD (5)
·liquid phase exfoliation/chemical approach

top down approach–3

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

Li–intercalation

(topochemical reaction)



bulk MX_2 bulk $LiMX_2$

·effective in expanding the layers

·high yield of monolayer

·expensiveness (Li^+)

·structurally and electronically different

for example; MoS_2

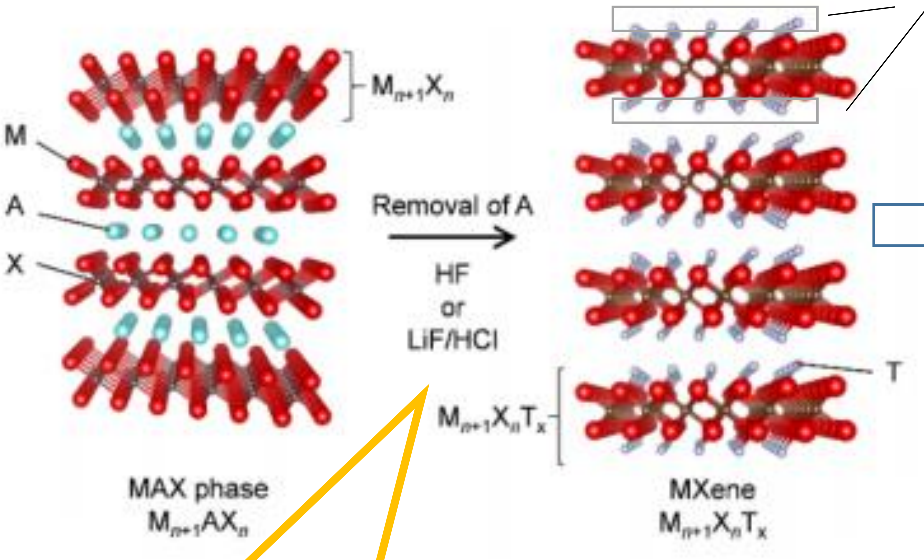
trigonal prismatic (semiconducting) ⇄ octahedral (metal)

BEYOND GRAPHENE (3)
MXene

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

Ti
TiC
Al
→

−OH, −F, −O, −Cl



sonication
DMSO intercalation

single layer MXene

etching

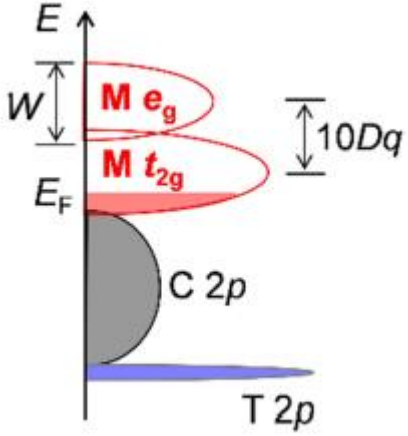
Ti_3AlC_2 + 3HF → AlF_3 + 3/2H_2 +$Ti3C_2$

Ti_3C_2 + 2H_2O → $Ti3C_2(OH)_2$ + H_2
Ti_3C_2 +2HF → $Ti_3C_2F_2$ + H_2

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

CHARACTARISTICS OF MXene

1. metallic



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

2. flexibility of composition

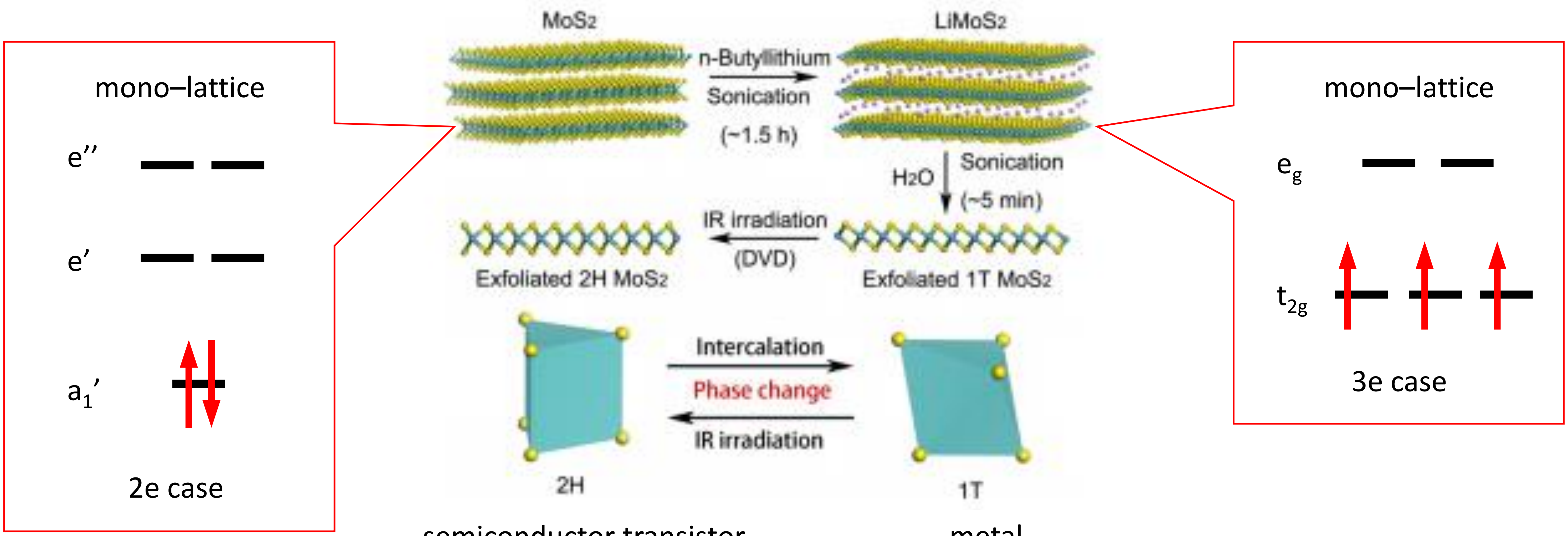
Ti_2CT_x, $Ti_3C_2T_x$, V_2CT_x, Nb_2CT_x, Mo_2CT_x,
$(Mo_2Ti)C_2T_x$, $Mo_{1.33}CT_x$, $Ti_3(CN)T_x$,

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

HOT REPORT (1)

·phase engineering

MoS_2 semiconductor to metal transfer



semiconductor transistor metal

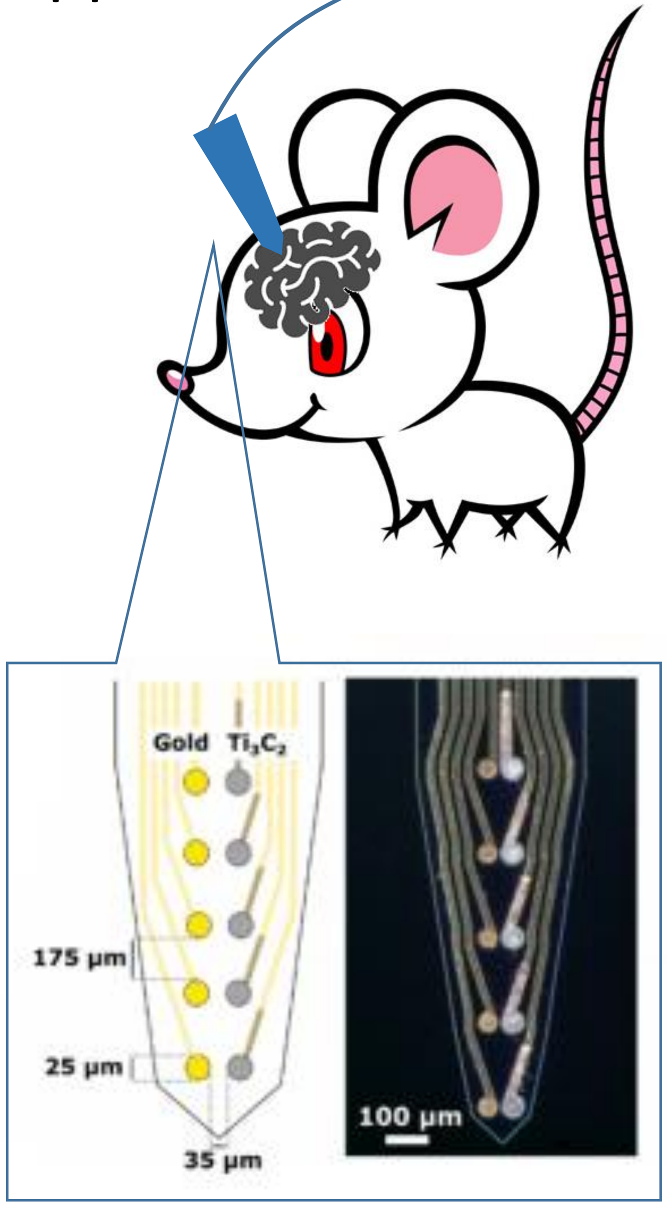
Nano Lett., **2015**, *15*, 5956.

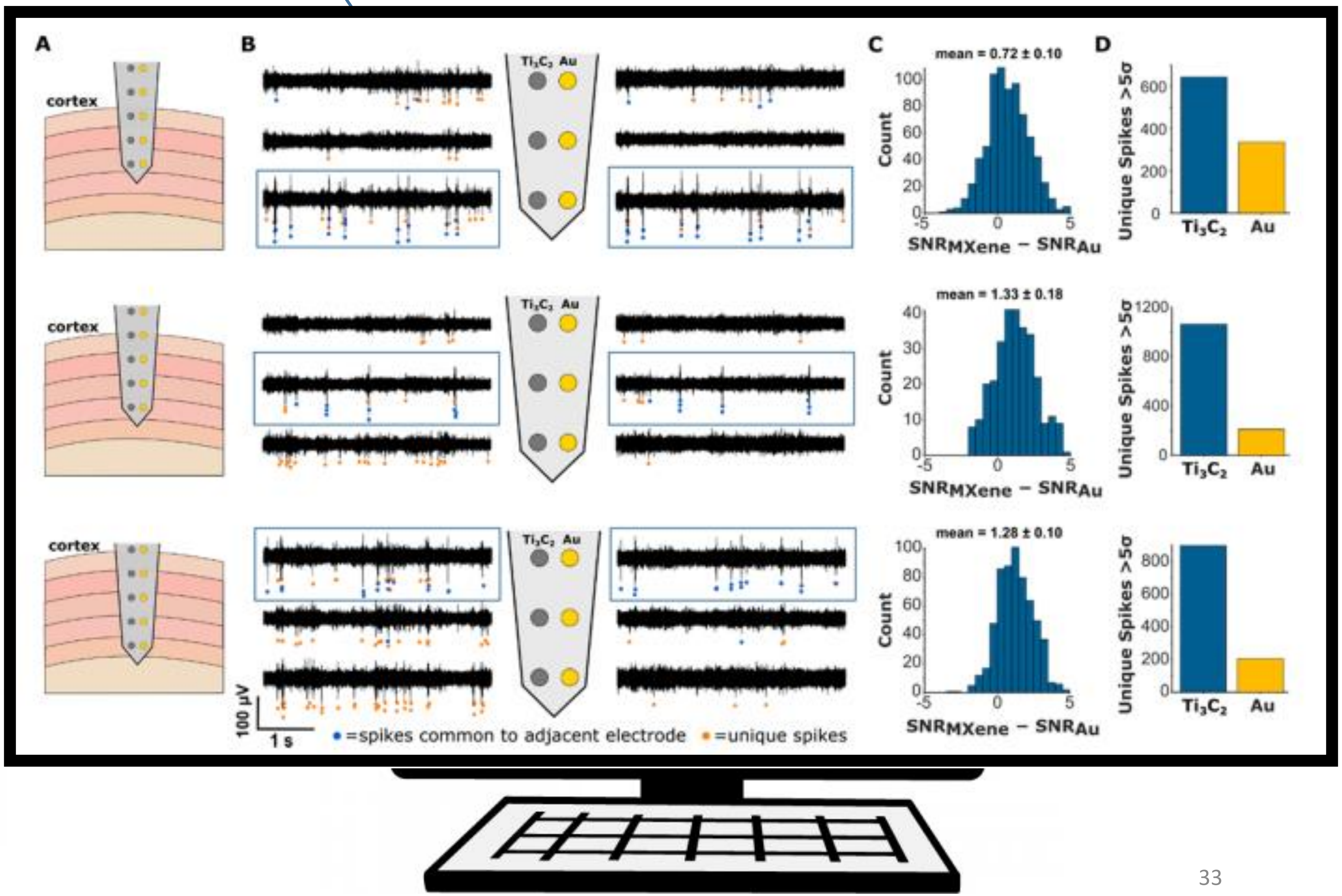
HOT REPORT (2)

·application of MXene

DAQ

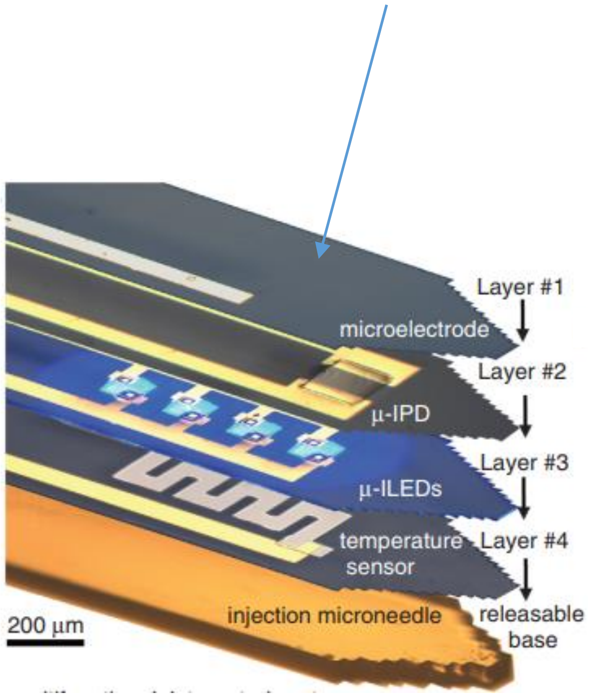
ACS Nano **2018**, *12*, 10419。



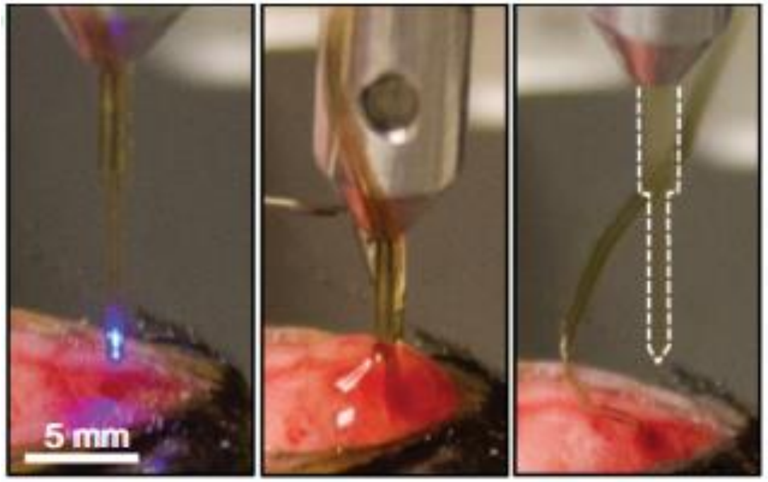


EXPECTED FUTURE

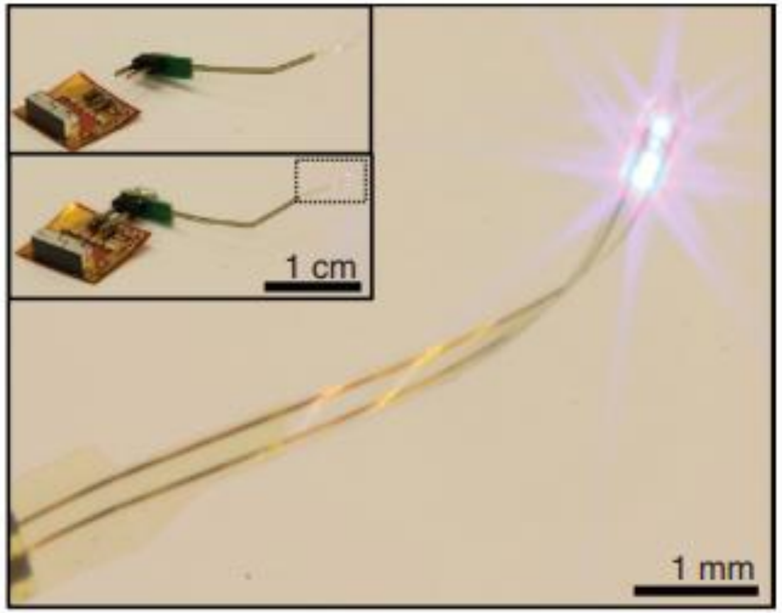
implantable LED



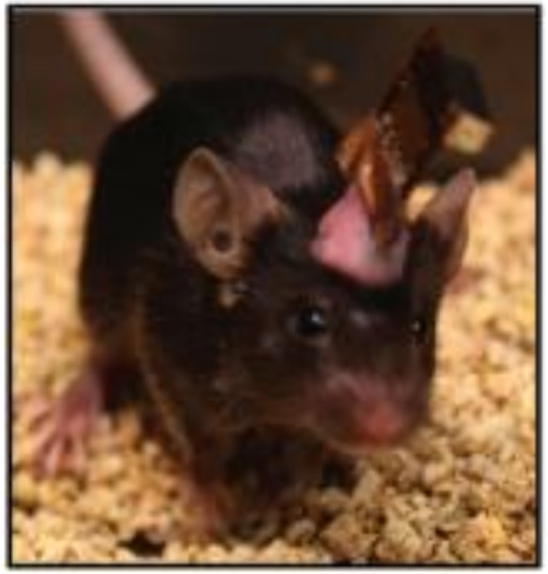
injection and release of the microneedle



wireless power system

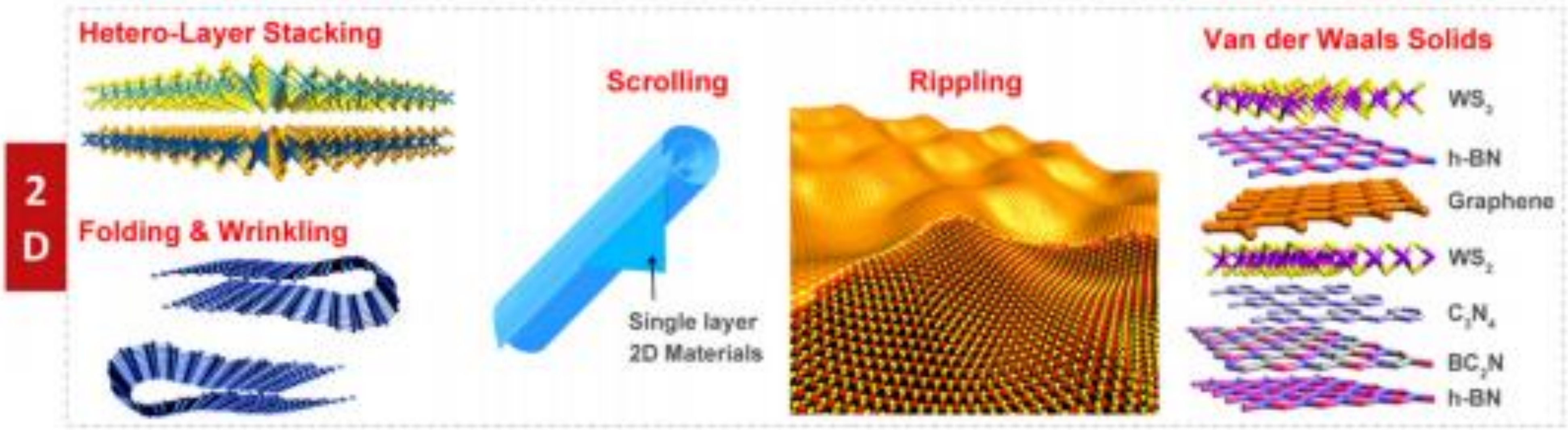


freely moving mice

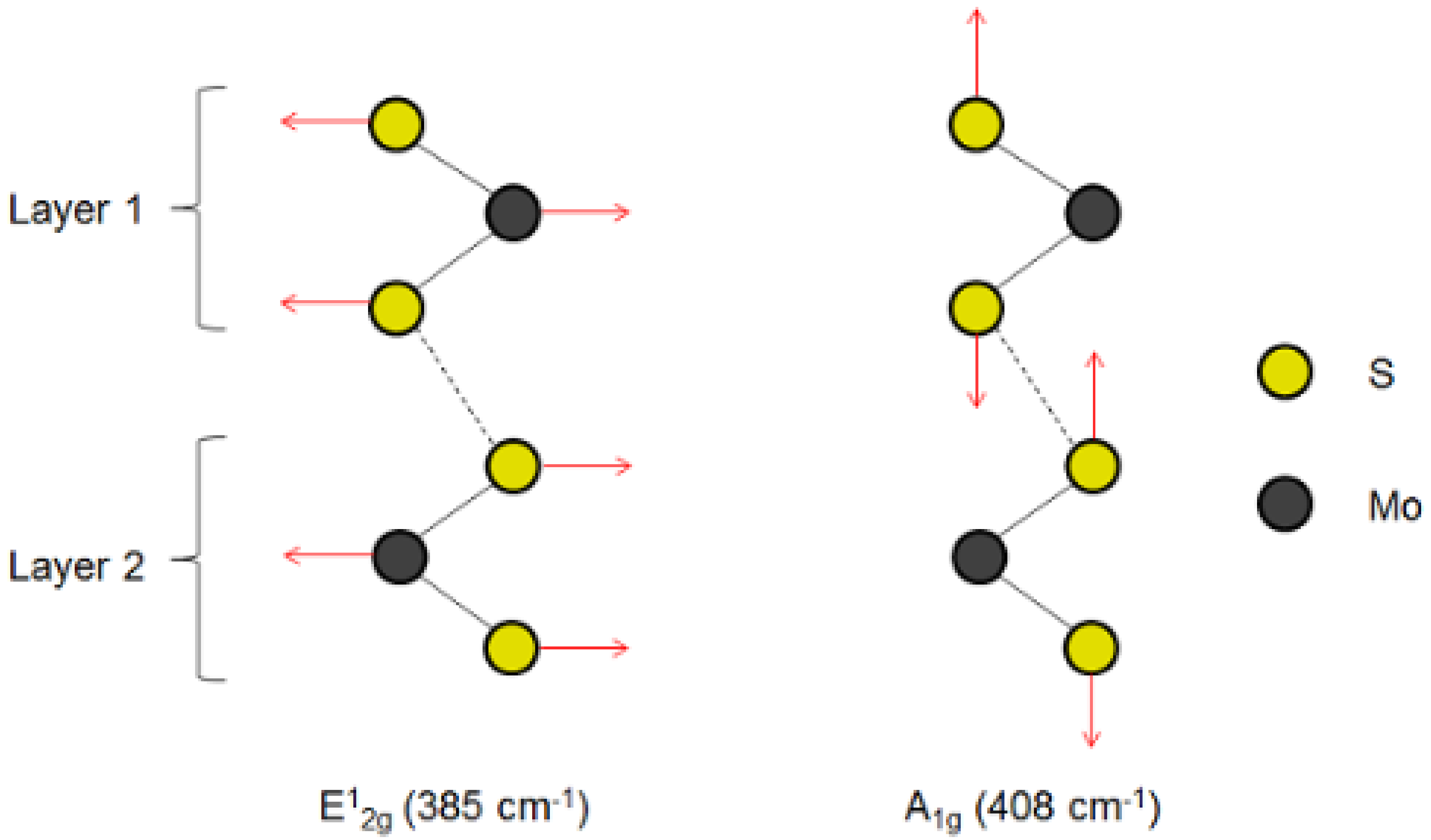


Science **2013**, *340*, 211.

CONCLUSION



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



▲MoS_2の振動モードに対する原子変位

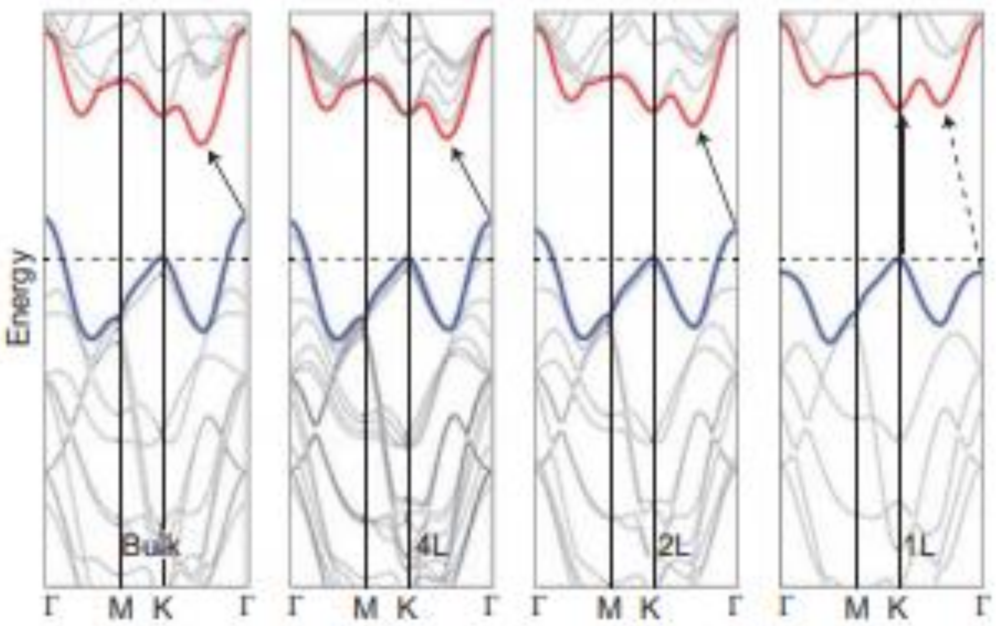
https://www.nanophoton.jp/applications/30.html

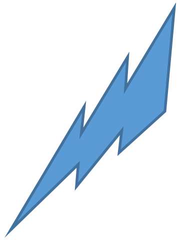
PHYSICAL AND CHEMICAL TUNING (1)

·z direction

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

calculated band structure

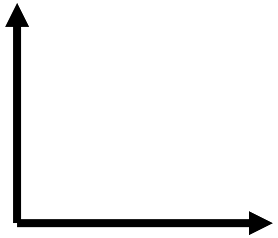




fluorescent

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

E(k)



k (electron wavenumber)

PHYSICAL AND CHEMICAL TUNING (2)

·z direction

$PtSe_2$

nature COMMUNICATIONS

ARTICLE

DOI: 10.1038/s41467-018-03436-0 OPEN

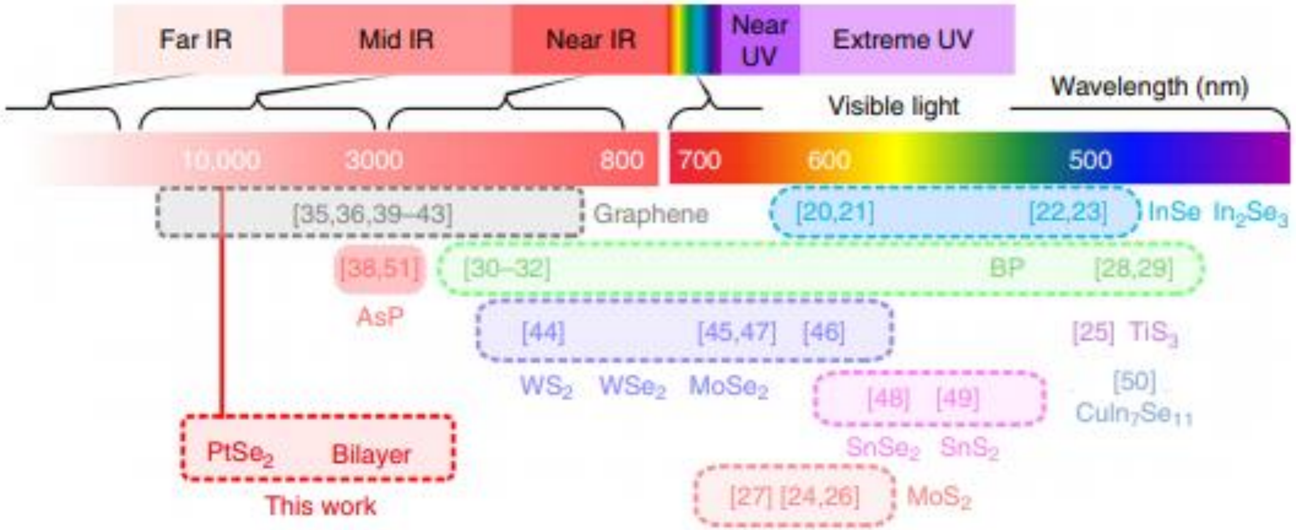
Thickness-modulated metal-to-semiconductor transformation in a transition metal dichalcogenide

Alberto Ciarrocchi[1,2], Ahmet Avsar[1,2], Dmitry Ovchinnikov[1,2] & Andras Kis[1,2]

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

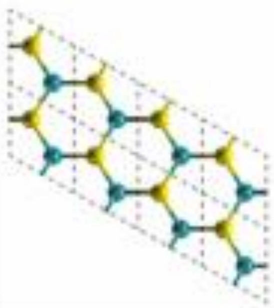
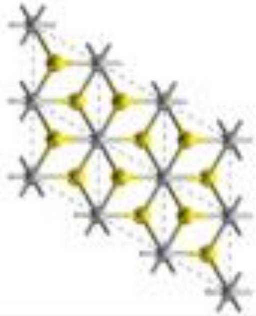
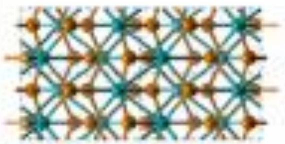
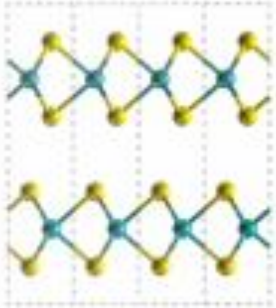
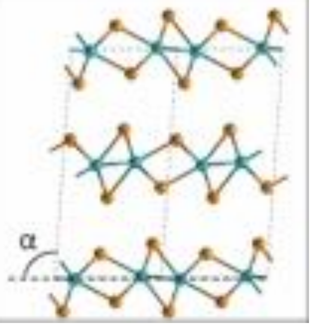
PHYSICAL AND CHEMICAL TUNING

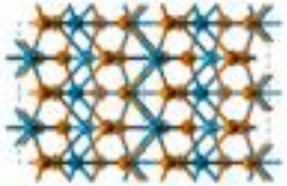
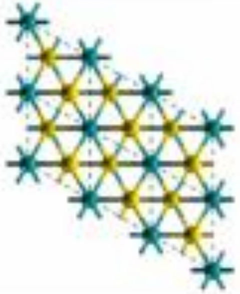
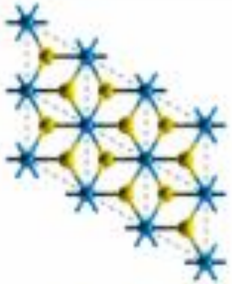
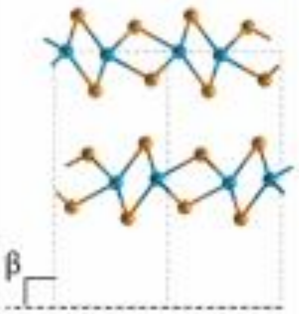
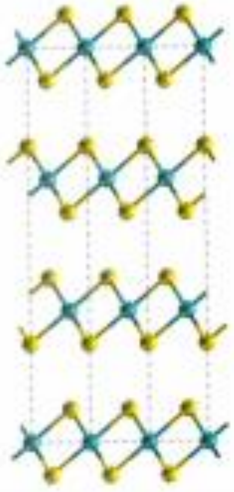
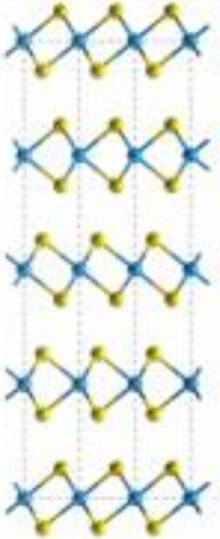
·z direction



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

STRUCTURE PATTERMS OF BULK TMD

	2H	1T	1T'
Group & Structure	• $P6_3/mmc$ • Hexagonal (Trigonal prismatic)	• $P\bar{3}m1$ • Hexagonal (Octahedral)	• $P2_1/m$ • Monoclinic
Top View			
Side View			

	T_d	3R	4H
Group & Structure	• $Pmn2_1$ • Orthorhombic	• $R3m$ • Rhombohedral	• $P6_3/mmc$ • Trigonal prismatic
Top View			
Side View			

FIRST EXMAPLE OF TMD

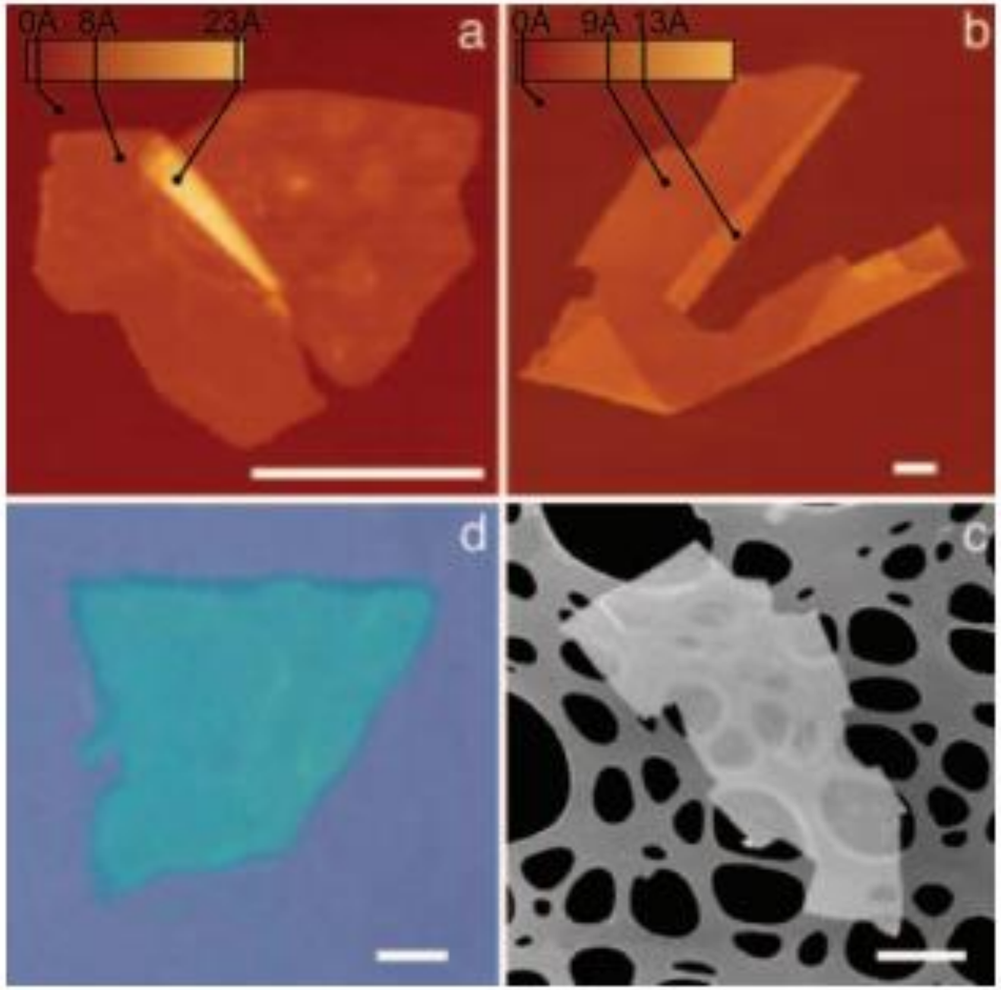


Fig. 1. 2D crystal matter. Single-layer crystallites of $NbSe_2$ (*a*), graphite (*b*), $Bi_2Sr_2CaCu_2O_x$ (*c*), and MoS_2 (*d*) visualized by AFM (*a* and *b*), by scanning electron microscopy (*c*), and in an optical microscope (*d*). (All scale bars: 1 μm.) The 2D crystallites are on top of an oxidized Si wafer (300 nm of thermal SiO_2) (*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.