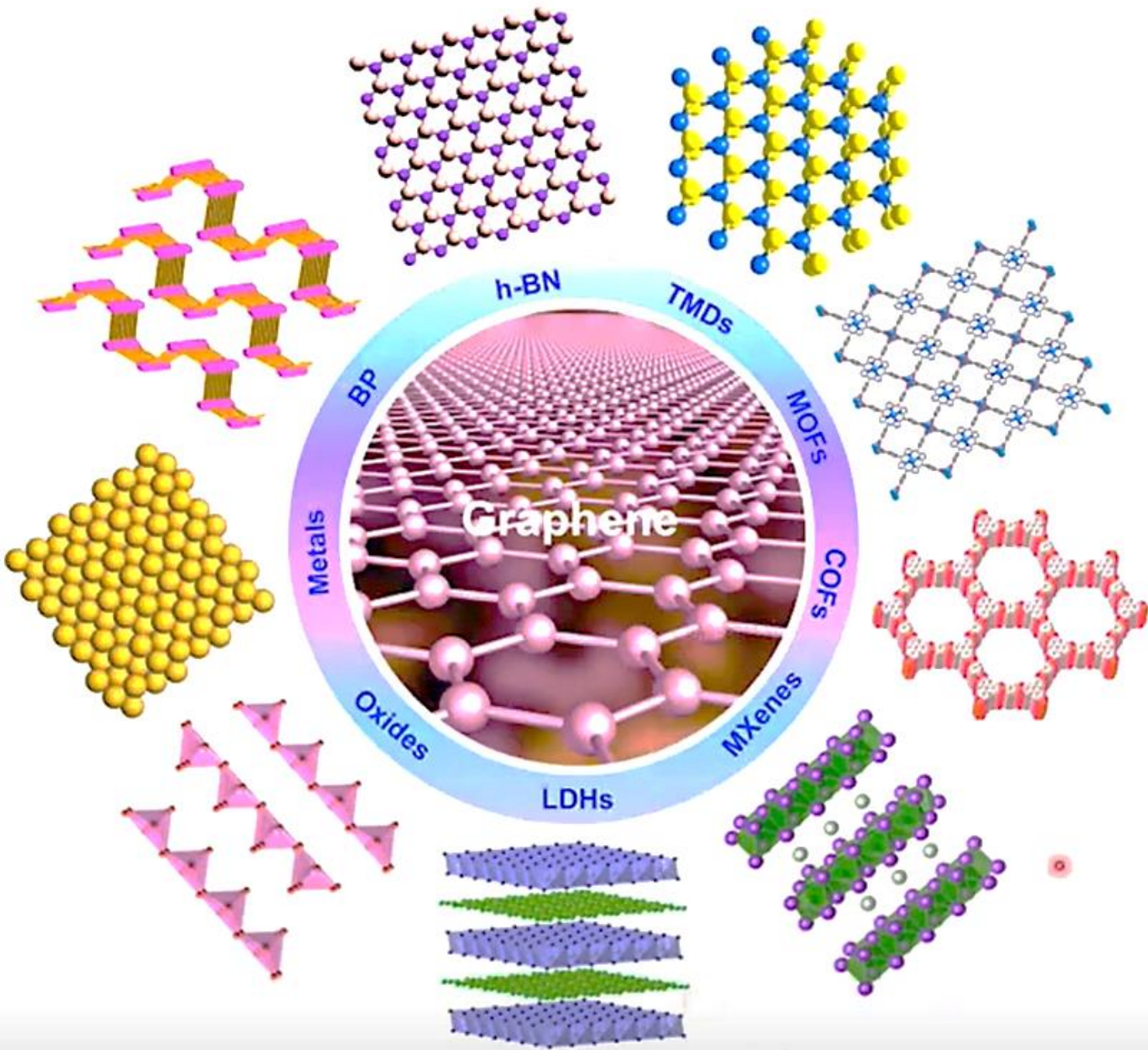


**MXenes'
Structure
Design & Modification
for
Photocatalysis**

Yue He



Two Dimensional Materials

1. Why graphene can be planar?

VASPER MODEL (Valence-Shell Electron-Pair-Repulsion)

Rules for determining molecular shape:

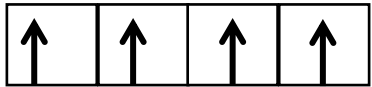
Equal Bond Energies imply **Equal Spatial Dispositions**



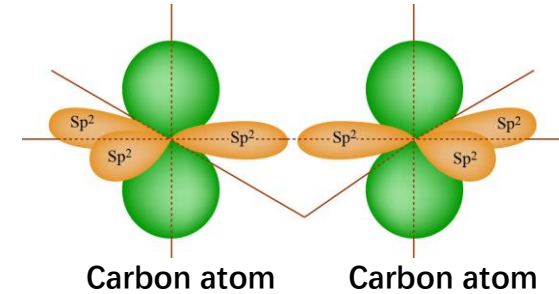
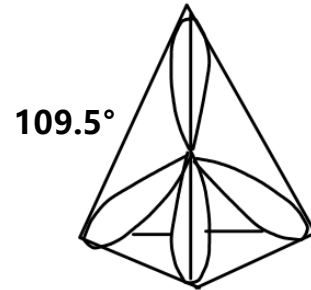
Two carbon atoms share 4 electron-pairs (Octet (8 electrons) Stability) to form covalent bonds.

Need Orbital Hybridization

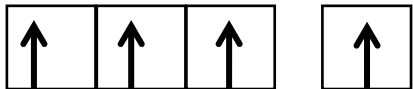
sp³ orbital hybridization



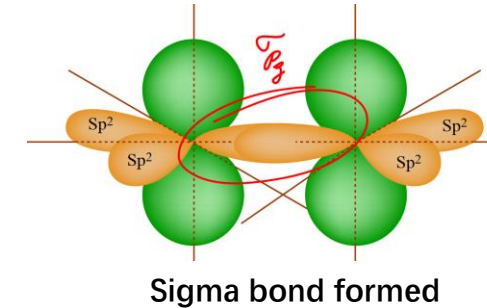
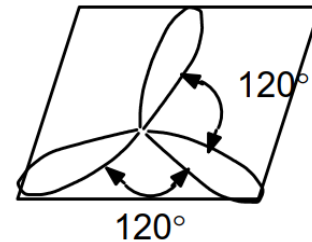
4 sp^3 orbital
4 Sigma bond



sp² orbital hybridization



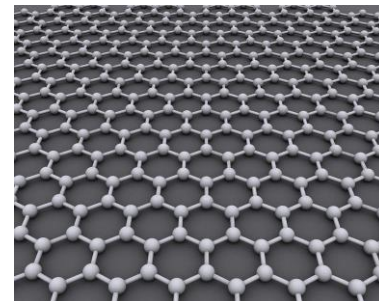
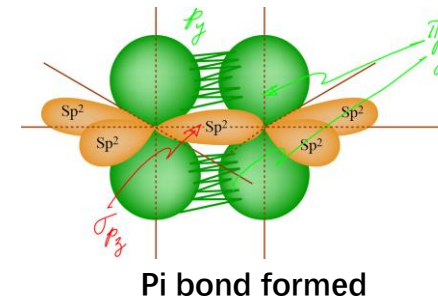
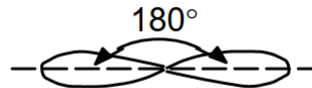
3 sp^2 + 1 p orbital
3 Sigma bonds + 1 Pi bond




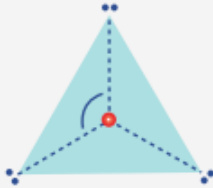
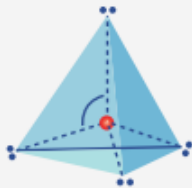
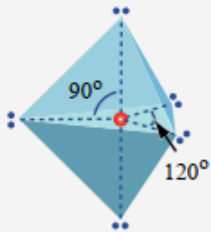

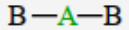
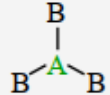
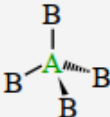
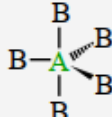
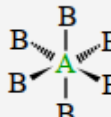
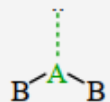
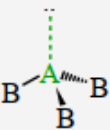
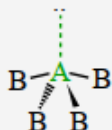
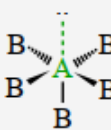
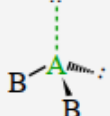
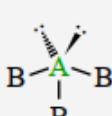
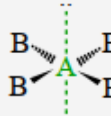
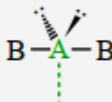
sp orbital hybridization



2 sp + 2 p orbital
2 Sigma bonds + 2 Pi bonds



Electron Pairs Geometry vs. Molecular Geometry

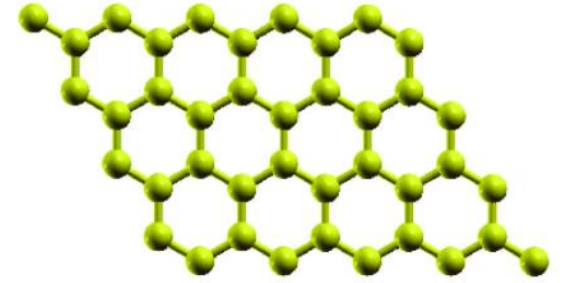
Overview of molecular geometries					
Electron pairs	2	3	4	5	6
Electron pairs geometry					
	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Molecular geometry: Zero lone pairs	 Linear AB ₂	 Trigonal planar AB ₃	 Tetrahedral AB ₄	 Trigonal bipyramidal AB ₅	 Octahedral AB ₆
Molecular geometry: One lone pair		 Bent (V-shaped) AB ₂	 Trigonal pyramidal AB ₃	 Seesaw AB ₄	 Square pyramidal AB ₅
Molecular geometry: Two lone pairs			 Bent (V-shaped) AB ₂	 T-shaped AB ₃	 Square planar AB ₄
Molecular geometry: Three lone pairs				 Linear AB ₂	

By the way,

This model is classical,
not take quantum mechanics,
but still useful.

2. The “offspring” of “ancestor” graphene

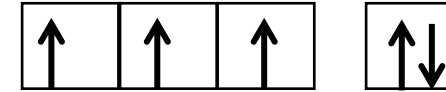
Generalize graphene template to more cases.



1. Phosphorus

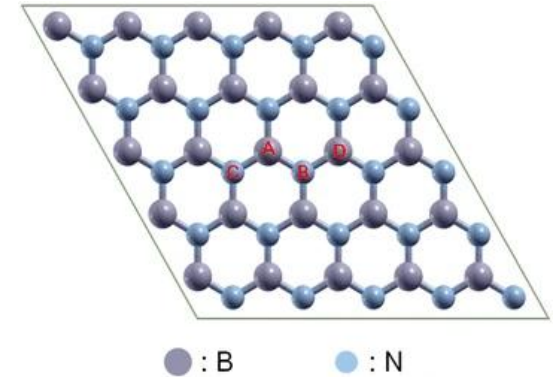
Electron Configuration $3s^2 3p^3$

sp^2 Hybridization



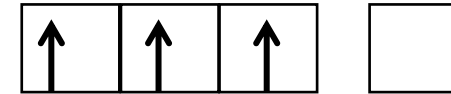
2. III-IV (Boron Nitride, h-BN)

B is an exception of octet stability
(I mean 8 electrons)



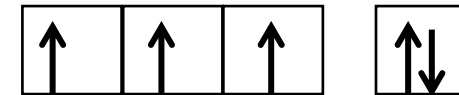
B Electron Configuration $2s^2 2p^1$

sp^2 Hybridization



N Electron Configuration $2s^2 2p^3$

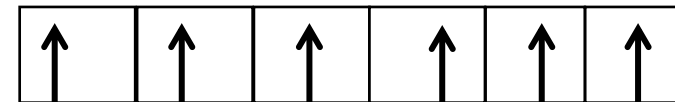
sp^2 Hybridization



3. Transition Metal Compound

Mo Electron Configuration $4d^5 5s^1$

ds Hybridization

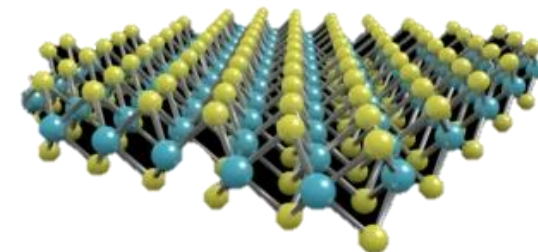


S Electron Configuration $3s^2 3p^4$

spd Hybridization

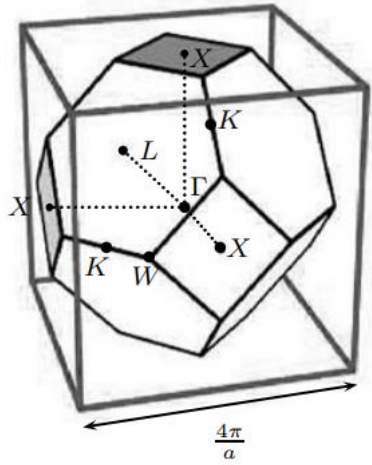


MoS₂



3. Why is two dimensional material so **hot**?

Band Structure (electron/photon)



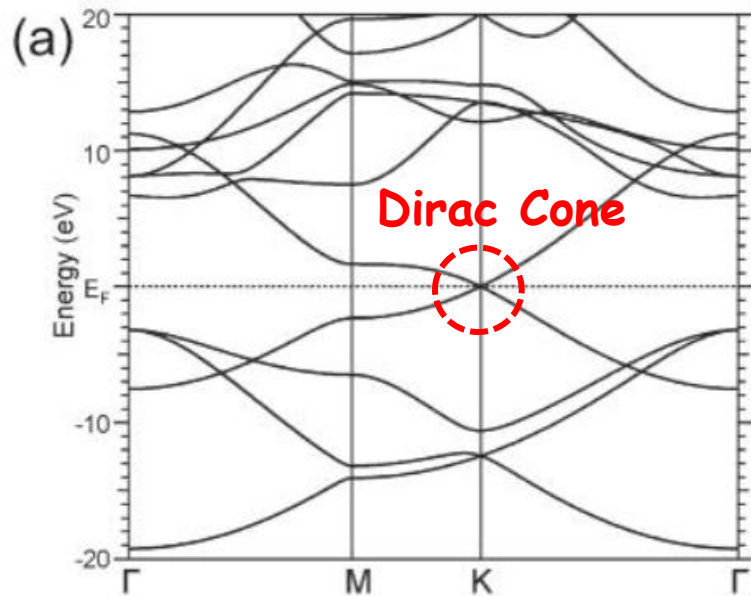
First Brillouin Zone

same shape
as the Wigner-Seitz cell
In Reciprocal Space

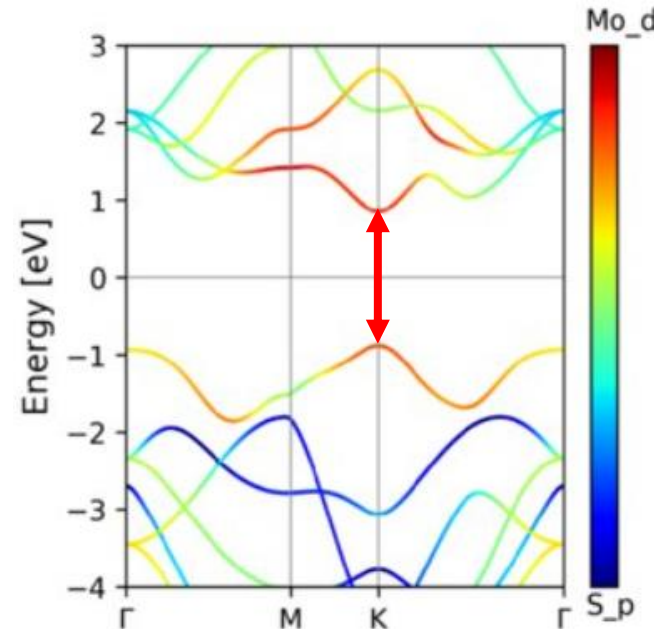
Visible light energy $2\pi\hbar\omega = 1.64\text{-}3.19\text{ eV}$,

So if band gap is larger than 3 eV,
transparent.

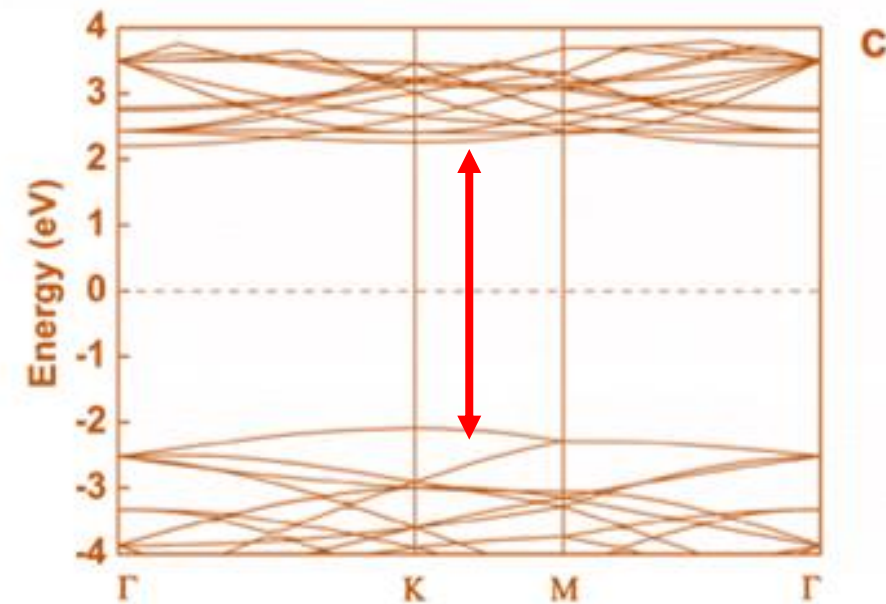
1. Graphene
Band Gap = 0 eV
Metal



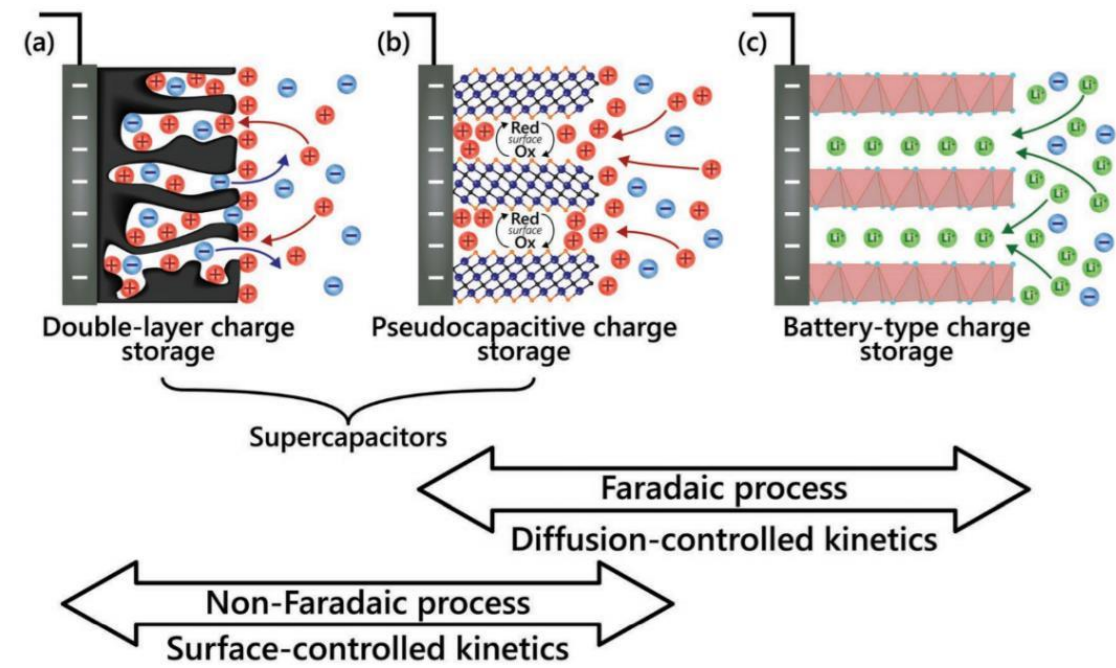
2. Transition Metal Compound
Monolayer MoS2 Band Gap = 1.9 eV
Semiconductor



3. III-IV (h-BN)
Band Gap = 6 eV
Insulator



Electrochemical Application-Energy Storage (Capacitor/Battery)



Double layer
Capacitor

Just *electrostatic attraction*
In the interface
between
electrolyte/electr
ode

Power density High
(Energy/Time)
Energy density low

Pseudo
Capacitor

Mixture
of electrostatic
attraction
&
Faradaic reaction

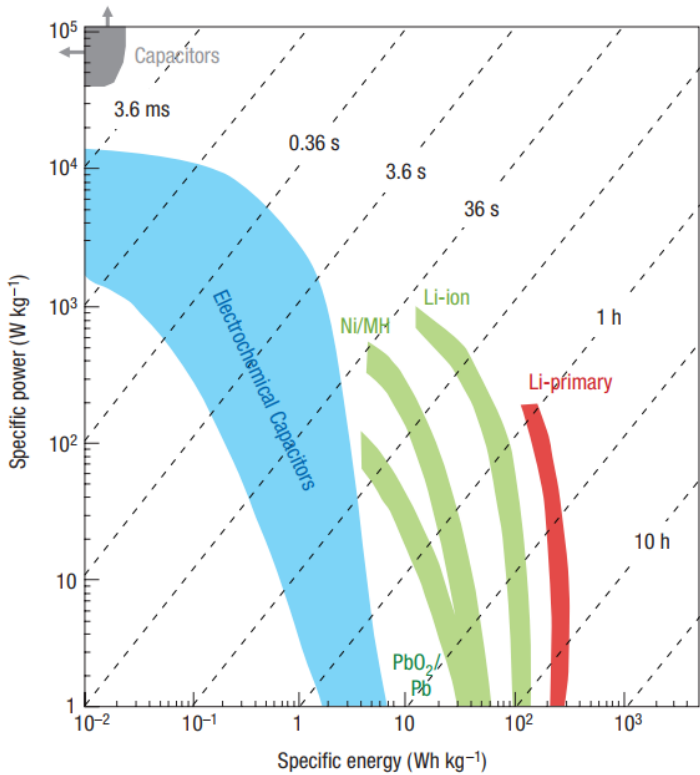
Power density Medium
Energy density Medium

Rechargeable
Battery

Faradaic reaction
which means charge
transfer

But faradic reaction
needs more time to
transfer and the time is
limited.

Power density Low
Energy density High



□ Translate to physical chemistry language,
quantity needs to describe:

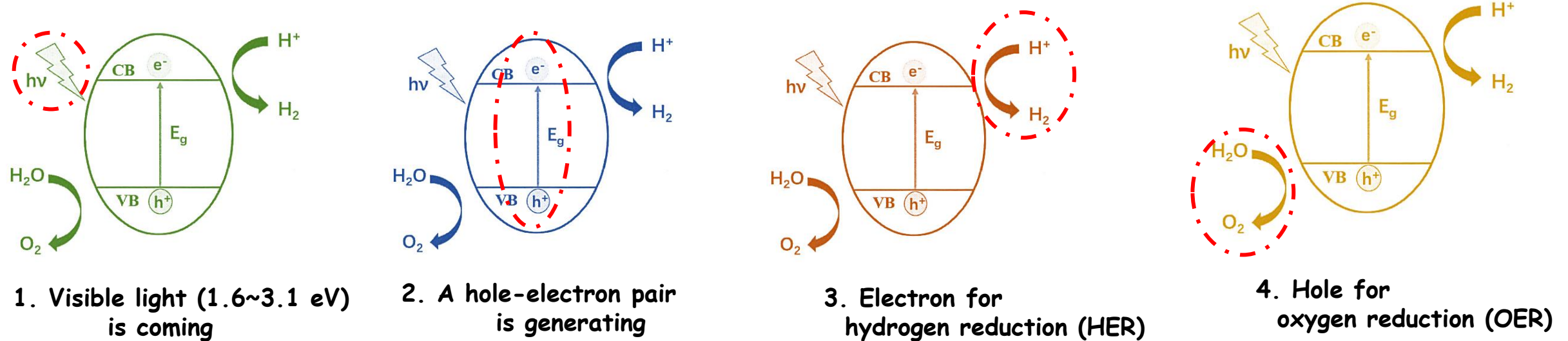
- 1.Charge&discharge characteristics (GCD&CV) ;
- 2.Charge transfer carrier diffusion (EIS) ;
- 3.Power& Energy density;
4. Cycle performance

□ The merit of two dimensional materials:

- ① High conductivity ➞ electron transfer fast
- ② Planar Surface ➞ carrier migrate fast
(ions move in/out fast)
- ③ Functional group ➞ redox active high

Electrochemical Application-Energy Conversion (Photocatalysis)

□ Take Photocatalytic hydrolysis for example



□ The condition of photocatalytic hydrolysis can be functionally operating:

1. A desirable band gap less than $2\pi\hbar\omega = 1.64\text{-}3.19\text{ eV}$
2. Before annihilation, hole and electron have enough time to move to active site, I mean migrate fast.

□ Translate to physical chemistry language, quantity needs to describe:

1. Ideal Band Gap (electronic structure) ;
2. Good Charge distribution;
3. Gibbs free energy for thermodynamics
4. Reaction energy barrier for kinetics

□ The merit of two dimensional materials like say, MoS2:

- | | |
|---|---|
| ① Large specific surface area | ☞ High light absorption / Large amount of active site |
| ② Planar Surface | ☞ Carrier migrates fast |
| ③ Thin thickness | ☞ Small distance of charge moving to active site |
| ④ Gibbs Free Energy for Hydrogen adsorption | ☞ MoS2 (TMDs) \approx Pt |

4. How to play with this kind of material?

Synthesis/Transfer Approaches

□ Top-down

(break Van Der Waals force between layers)

1. Mechanical Exfoliation

Just a Scotch tape



2. Liquid-Phase Exfoliation

Solution mixed with ions, with ultrasonic agitation

□ Down-top

1. CVD

2. Hydrothermal

3. MBE (Molecular Beam Epitaxy)

□ Transfer

1. "pick-up "transfer

2. Wetting transfer

Coating PMMA and etch copper substrate

Materials Characterization

□ Spectroscopy

(molecular energy levels fingerprint)

Raman -Molecular vibrational/rotational energy levels

PL- (Photoluminescence Spectroscopy)

- Electron/hole pair annihilate
- photoluminescence

XPS-chemical bond

□ Morphology (atoms arrangement)

AFM- mechanical/electrics distribution

SEM/TEM-surface morphology

XRD-orientation

Modification

□ Bandgap Engineering

□ Dimensionality Regulation

1D(line)/2D(plane)/3D(cubic)/0D(dots)

□ Strain Regulation

Strain causes lattice constant change

□ Assembly Regulation

The amount of assembly layers

□ Doping Regulation

donor/acceptor energy level in the bandgap

□ Introduce Defects

TiO₂ after hydrogen treatment, white → black,

Ti(4+) → Ti(3+), forming oxygen vacancy,

Bandgap ↓ light adsorption range ↑。

□ Heterojunction (p-n junction)

□ Surface Engineering

□ Surface vacancy

Easy active site formed, easy adsorption

□ Surface functional group

-OH, -F, -O

□ Surface hybridization

Two kinds of materials hybridization on the surface
(ex situ) / (in situ)

□ Surface lattice distortion

5. What is MXenes ?

MXenes' Birth

(Two dimensional transition metal carbon/nitrogen compounds)

Naguib, M. et al. Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 . *Adv. Mater.* 23, 4248-4253 (2011)

2011, Drexel University in the USA

$Ti_3C_2T_x$ (T-termination, Functional Group -F/-OH/-O)

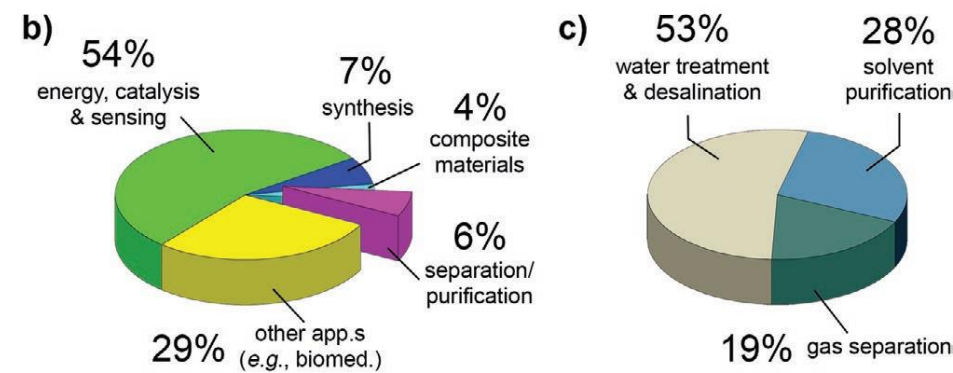
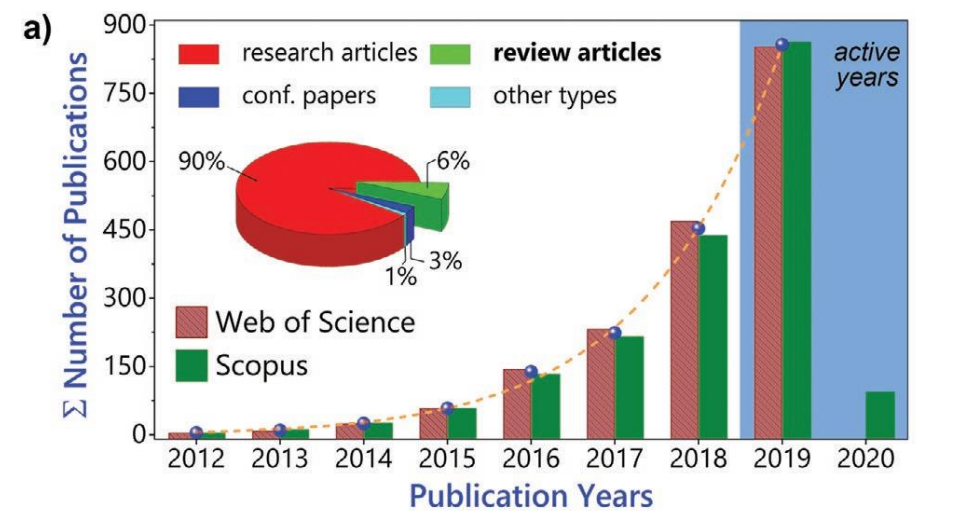
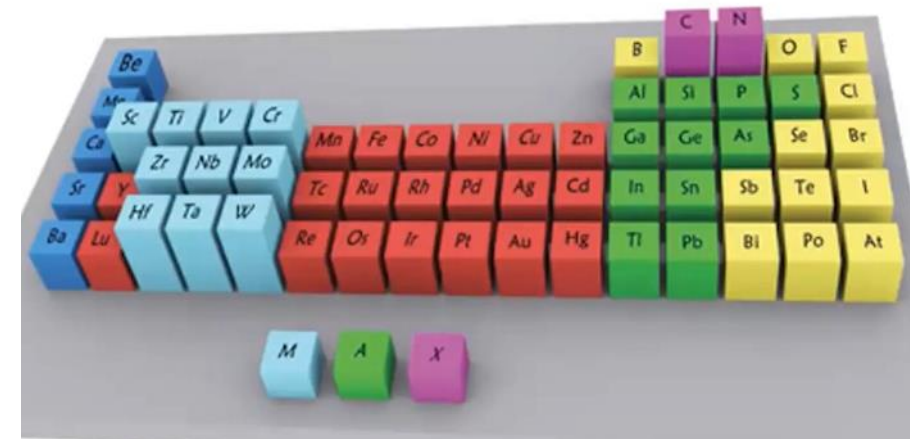
Was found by

Yury Gogotsi
Balak Anandori



Yury Gogotsi

<https://nano.materials.drexel.edu/>



MXenes' Structure and Property

High metallic electrical conductivity (up to 20,000 S/cm)

Hydrophilic, oxide/hydroxide-like polar surface

Strong and stiff (strength 20-30 GPa, $E=300-500$ GPa)

Transparent in thin films

Variety of colors is possible (plasmonic, electrochromic)

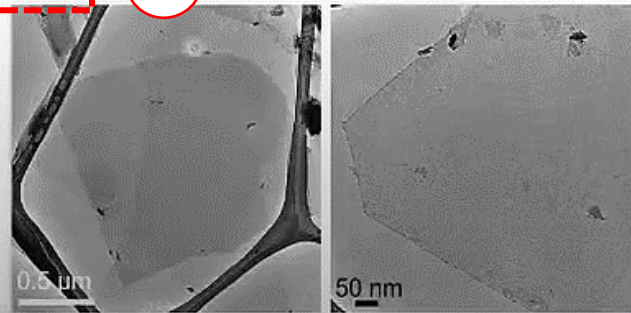
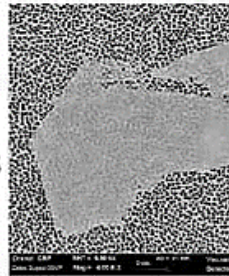
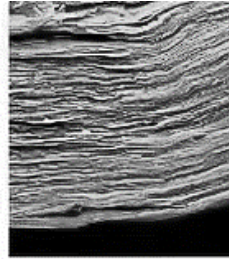
Dispersible in water – easy processing

Can be printed from aqueous solutions with no additives

Efficiently heated by light or EM waves

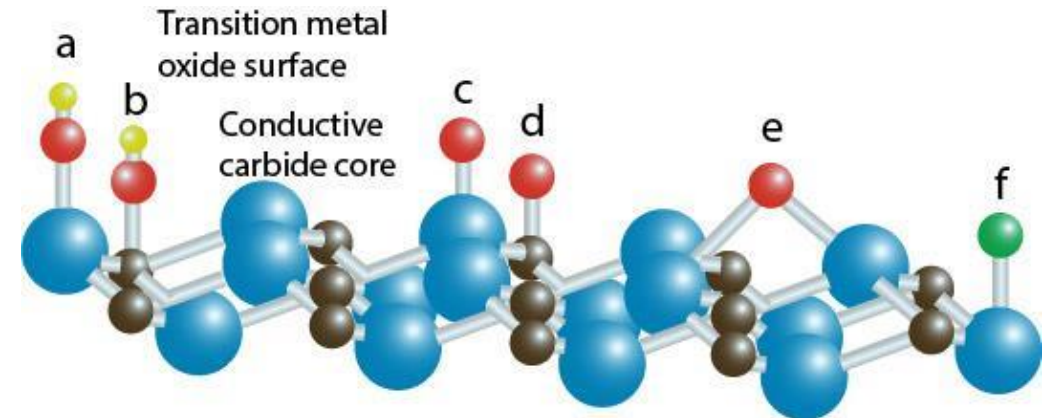
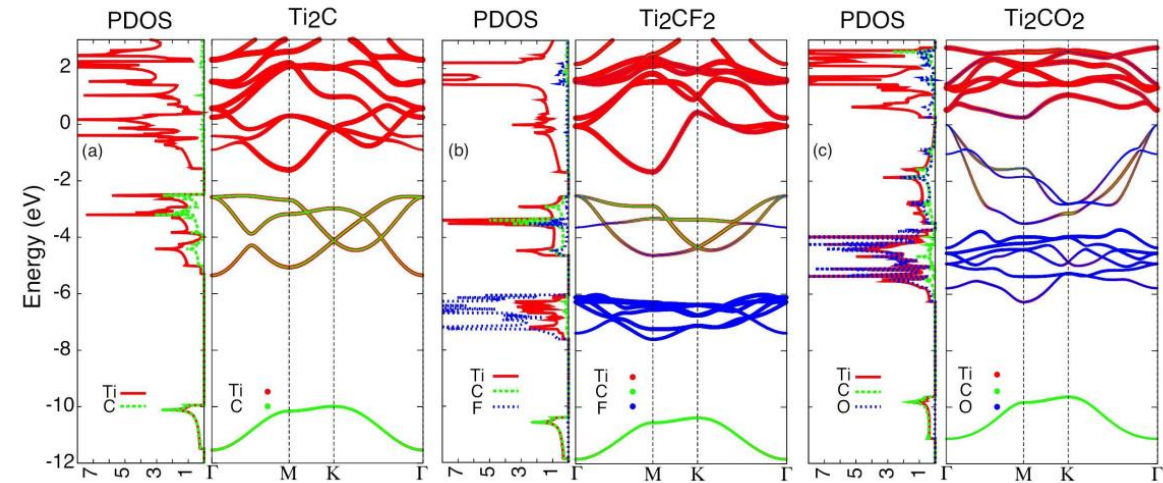
Large electrochemically active surface

Wide control of properties via composition and structure is possible (~100 stoichiometric MXenes and an infinite number of alloys).



1

3



He is the son of father " TiO_2 " + Mother "Graphene"

Merits of Mxenes in Electrochemical Applications

1. Rechargeable Battery

□ Interface Mechanical Performance:

SEI(Solid Electrolyte Interface) break when charge/discharge

Fixed by **Mxenes 3rd strength**

(strength 20-30GPa, elastic modulus 300-500GPa)

□ Li battery storage capacity:

Ti₃C₂ = 320 mAh g⁻¹, Graphene (370 mAh g⁻¹)-----energy density

Li diffusion energy barrier @Mxenes 0.07 eV-----power density

(Graphene 0.3 eV)

2. Supercapacitor (two aspects)

□ In aqueous electrolyte

Surrounded by hydration shell,

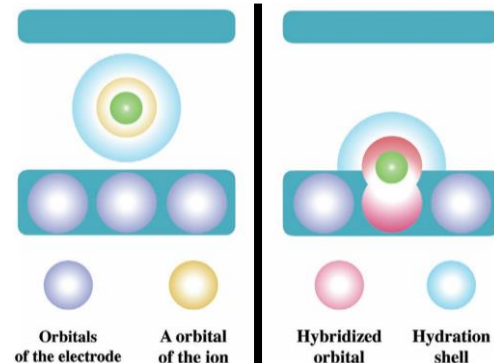
just double-layer capacitor, no charge transfer

□ In non-aqueous electrolyte

No protective layer, pseudo capacitor,

charge transfer and Faradic reaction

happen



Electrochemical Applications of MXenes

- **Electrochemical capacitors** (*Science* 2013; *Nature* 2014, *Nat. Energy* 2017, *Nature* 2018, *Nat. Energy* 2019)
- **Li-ion and Na-ion capacitors** (*Nature Comm.*, 2015; *Nano Energy* 2019)
- **Li⁺, Na⁺, Mg²⁺, Al³⁺, Li-S batteries** (*JACS* 2014, *ACS Nano*, 2014; *Angew. Chemie*, 2015, *Adv. Mater.*, 2019)
- **Hybrid Energy Storage** (*Adv. Energy Mater.* 2018, 2019)
- **On-Chip Energy Storage** (*Energy & Environ. Sci.*, 2016, *Adv. Energy Mater.* 2019)
- **Textile Energy Storage** (*Adv. Funct. Mater.* 2019, *JMC A* 2019)
- **MXene Inks for Supercapacitors** (*Adv. Mater. Techn.* 2019, *Nat. Commun.* 2019)
- **Current Collectors** (*Small* 2018, *Energy Storage Mater.* 2019)
- **Binders for Si or carbon** (*ACS Energy Lett.* 2018, *Nature Commun.* 2019)
- **Capacitive Deionization** (*Desalination* 2020)
- **Electrocatalysis (HER, OER, ORR, CO₂ reduction)** (*ACS Energy Lett.* 2016, *Sci. Rep.*, 2016, *Nature Catalysis*, 2018)
- **Brain Electrodes** (*ACS Nano*, 2019)
- **Electrochromic Devices** (*Adv. Funct. Mater.*, 2019)

3. Photocatalysis

□ Conductivity-carrier migration fast

20,000 S/cm almost like graphene

□ Surface Functional Group-active sites

-OH/-O/-X large electrochemically active surface

6. How to make it crudely ?

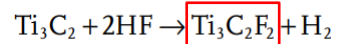
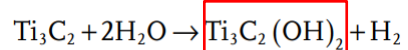
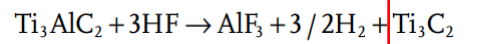
MXenes 'Major Synthesis Idea

Mainstream:

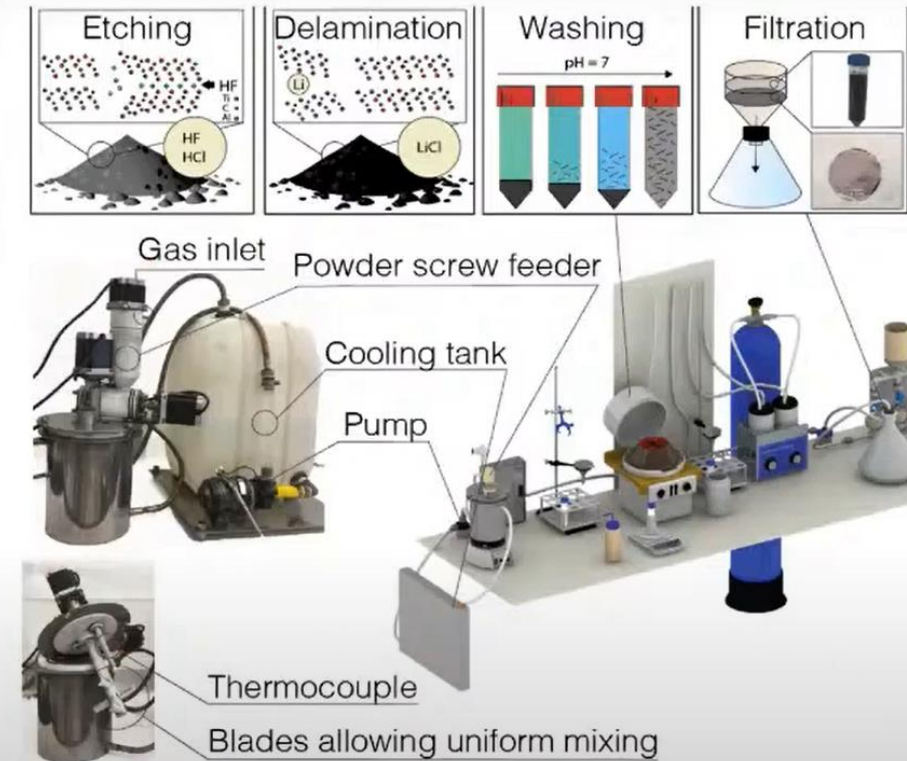
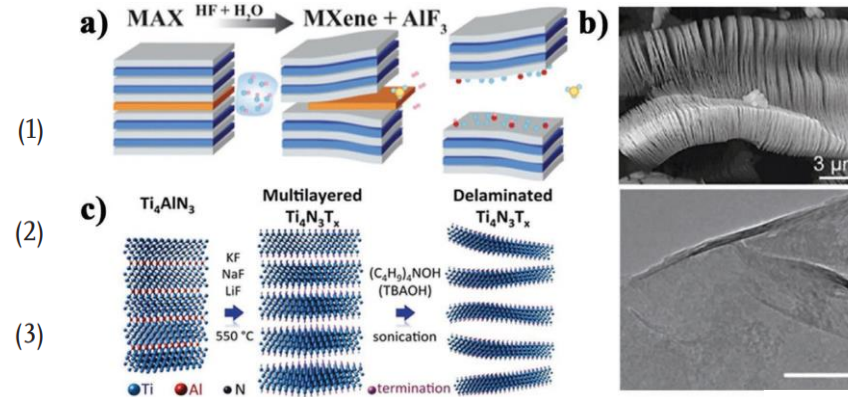
Selectively etch the "A" element of precursor ($M_{n+1}AX_n$)

by using HF solution or corrosive agent,

$Ti_3C_2T_x$ remained



Free-standing $Ti_3C_2T_x$ electrode



But limitation:

1. Random and uncontrollable functional groups are inevitable;



2. Random defects are inevitable;

3. Size is limited.

The potential of CVD shows up:

1. Control functional groups;

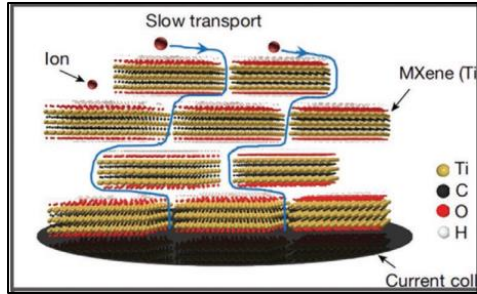
2. High quality with less defects;

3. Large area is possible

Synthesis strategies			Properties	Terminations
Fluorine-containing acid etching	HF etching	HF	1) High defects concentration 2) Accordion-like structure 3) Small flake size	-F, -OH, increasing over time: -O
	In situ HF etching	LiF/NaF/KF+HCl NH ₄ HF ₂	1) Larger flake size 2) Low defects concentration 3) Larger interlayer distance (e.g., Li ⁺ , NH ₄ ⁺) 4) High electrical conductivity	-F, -OH, -O, -Cl; -F, -OH, -O
	Molten fluoride salt etching	LiF+NaF+KF	1) Inferior crystallinity 2) Accordion-like structure	-F, -OH, -O
Fluoride-free etching	CVD		1) Sizeable lateral size 2) Low defect, disorder, impurity 3) Controllable or no surface terminations 4) Limited productivity	Bare
	TMAOH		1) Terminated with -Al(OH) ₄ 2) Strong optical adsorption in the near-infrared	-OH, -Al(OH) ₄
	NaOH		1) Accordion-like structure	-OH, -O
	Electrochemical etching	NH ₄ Cl + TMAOH	1) Larger lateral size 2) Single or bilayer sheets 3) Fluoride free	-OH, -O
	Lewis acidic etching	CuCl ₂	1) Accordion-like structure 2) Low hydrophilicity	-Cl, -O
	Lithiation-expansion-microexplosion	Li ⁺	1) Single or few layer sheets 2) Fluoride free	-OH, -O

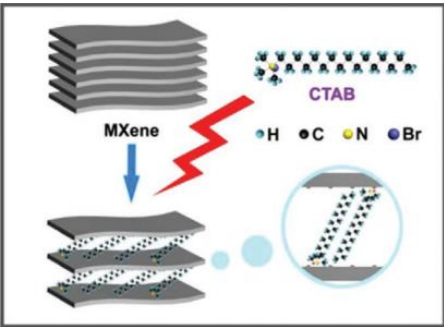
7. How to modify it effectively ?

MXenes 'Structure Design

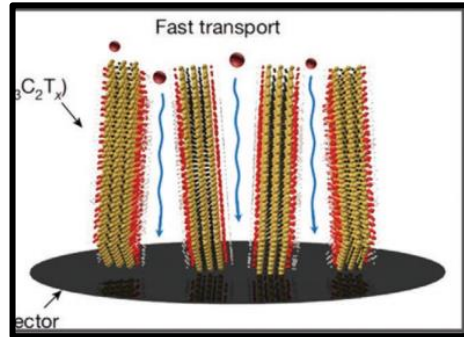


? Self-stacking effect

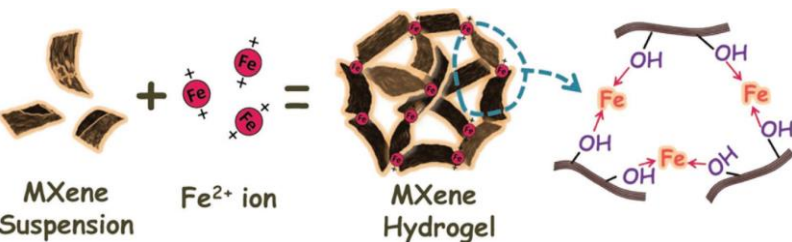
- ❑ Slow transport
- ❑ Decrease active site utilization



1. Enlarge interlayer spacing by intercalation



2. Parallel the orientation with transport direction



3. Build 3D porous structure

4. Make Heterojunctions

- ❑ In situ Oxidation/Phosphorylation/Sulfidation
- ❑ Ex situ Self assembly with others like r-Go etc. by
 - Von der Waals force
 - Hydrogen bond
 - Electrostatic force

MXenes 'Surface Modification

1. Choose Surface functional group

-F/-OH/-O.

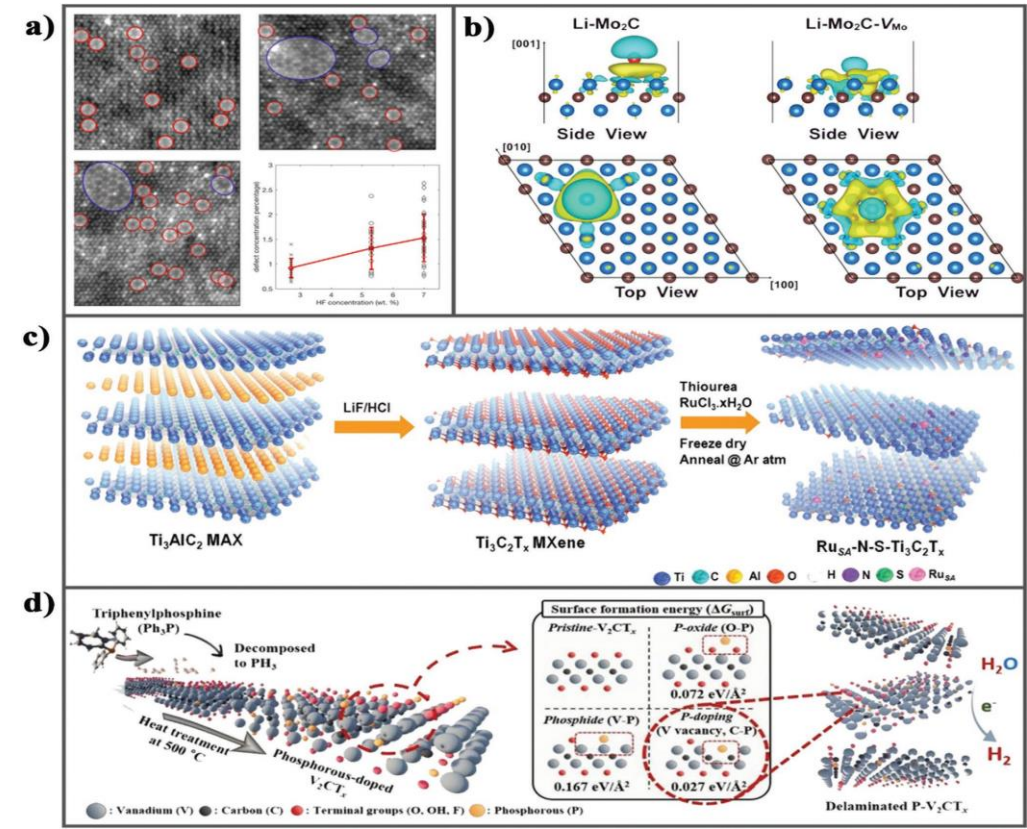
Tuning the content and distribution of surface functional groups

2. Surface Defects

Vacancy cluster/edge lattice

3. Introduce heteroatoms

Like doping N/S/P atoms to increase conductivity



8. What will I do ?

My Objective

I want to make quality but affordable MXenes materials for photocatalysis.
It need to be:

1. Dirt Cheap.

If you want to make something dirt cheap, make it out of dirt.

I will **not take notable metal elements into account** for photocatalysis as much as I can.

2. Big Size.

If you want to use it in real life, it need to be sufficiently big.
So, I will take this factor into my synthesis method.

3. Efficient.

Even without using notable metal, it's still powerful.

So, I take out the periodic table...

Focused on "MAX"

I see a combination of precursor $M_{(n)}AX_{(n+1)}$



After choosing the possible elements,
there are three crucial problems need to be addressed out?

1. How to make it like
semiconductor ?

2. How to make it
surface active ?

3. How to make it
real ?

Commonly, the conventional and conservative methodologies are:

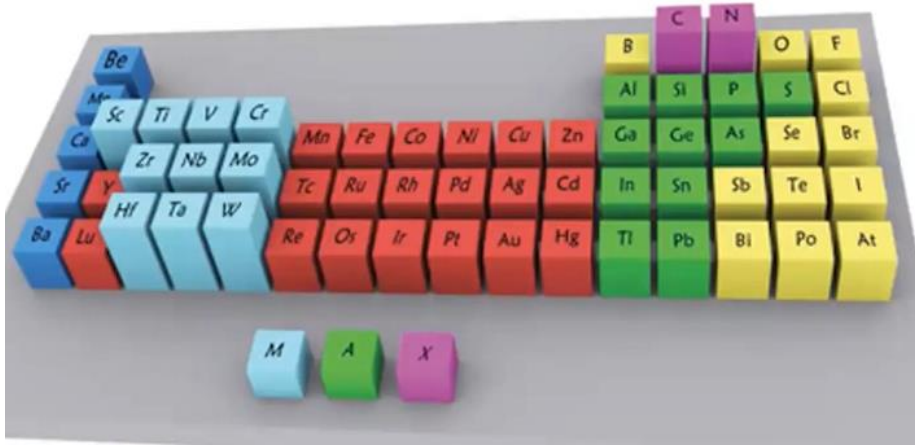
- ① reading tons of papers,
- ② learning ideas for references,
- ③ giving it a shot experimentally by taking chance,
- ④ ultimately figuring out which solution can work.

But ...

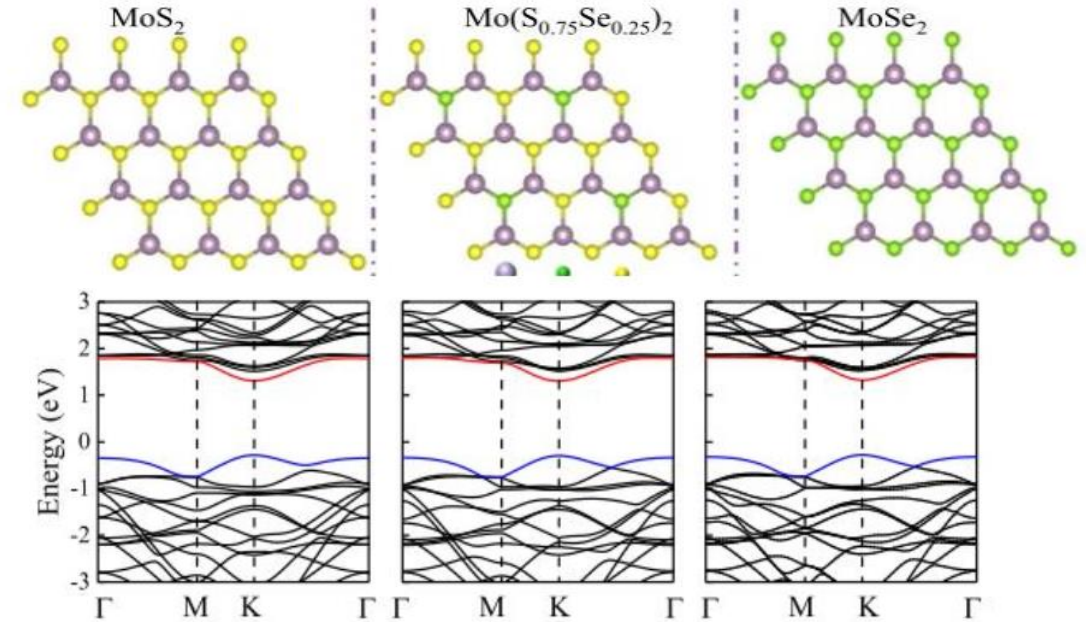
I would like start calculations on computer in advance,
like this...

1. Structure Design for tuning Bandgap in visible light range.

Select element species/content to calculate electronic structure having bandgap $\approx 1.64\text{--}3.19\text{ eV}$ for visible light.

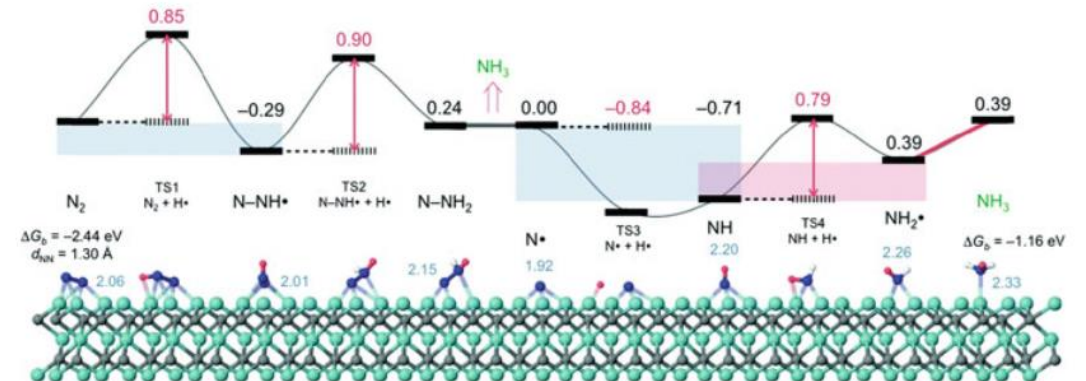
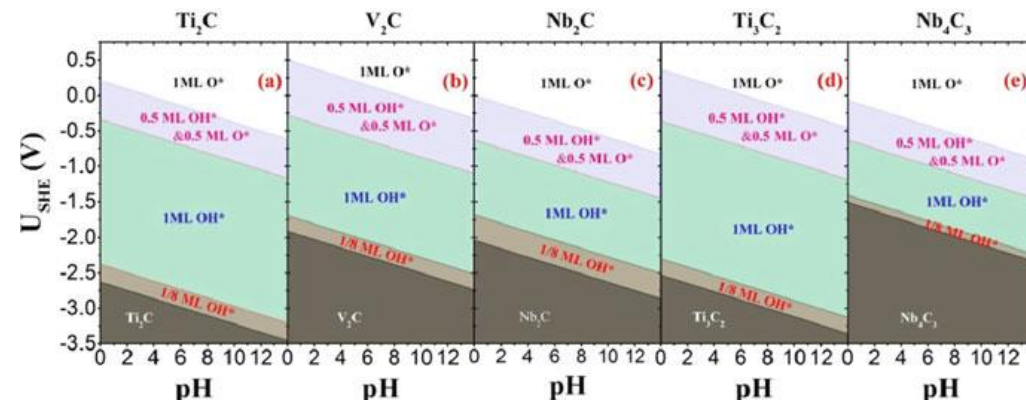


This is my **first** challenge in the future !



2. Modification surface for electrochemical active for photocatalysis.

Add appropriate functional groups/defects/heteroatoms/heterojunctions on surface to calculate reaction potential/Gibbs free energy/minimum pathway.



About detailed [synthesis/characterization steps](#), there is an experimental course on web... it's easy to follow the recipe step by step...

Procedure for Synthesis of Ti_3AlC_2 MXene²⁰²⁰

1. Weigh out the precursors TiC:Ti:Al in a 2:1:1 atomic ratio
2. Add alumina balls (2:1 ball:powder weight ratio) to the mixture, and ball mill (50-80 rpm) for 18-24 h
3. Pour the powder into an alumina crucible, then put it into a high-temperature furnace. It should have a heating/cooling rate of 3 °C/min. A temperature set point of 1400 °C, and a holding time of 2 h.
4. Once the sample is cooled, crush the compact into powder. Sieve the powder to the specified size (20-74 µm, for example). Take XRD at this step.
5. Add the powders to 1 M HCl (at least 20 mL/g) and stir overnight. Wash the HCl out by filtration with ample deionized water. Take XRD at this step. Sieve powders.

MXene Course

Learn how to make and characterize MXenes at their birth place from Professor Yury Gogotsi and his team

This certificate course will teach best practices for the synthesis (2-days), characterization (2-days), and electrochemical measurements (1-day) of MXenes

MXENE 2021 Course

Experienced researchers, industry professionals, and students are all welcome to partake in the MXene course.

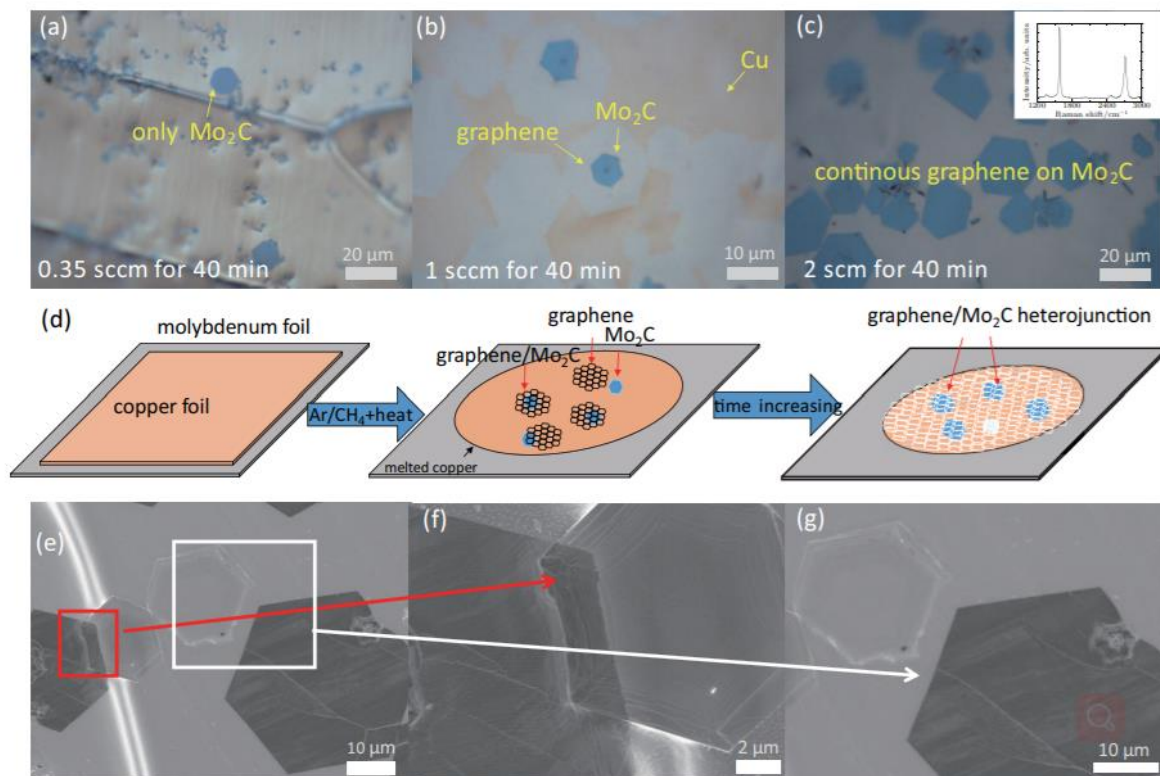
Course date: August 2nd – 6th, 2021

Click to download the MXene Course background for Zoom

<https://nano.materials.drexel.edu/>

This is my **second** challenge in the future !

Synthesis MXenes without using HF !

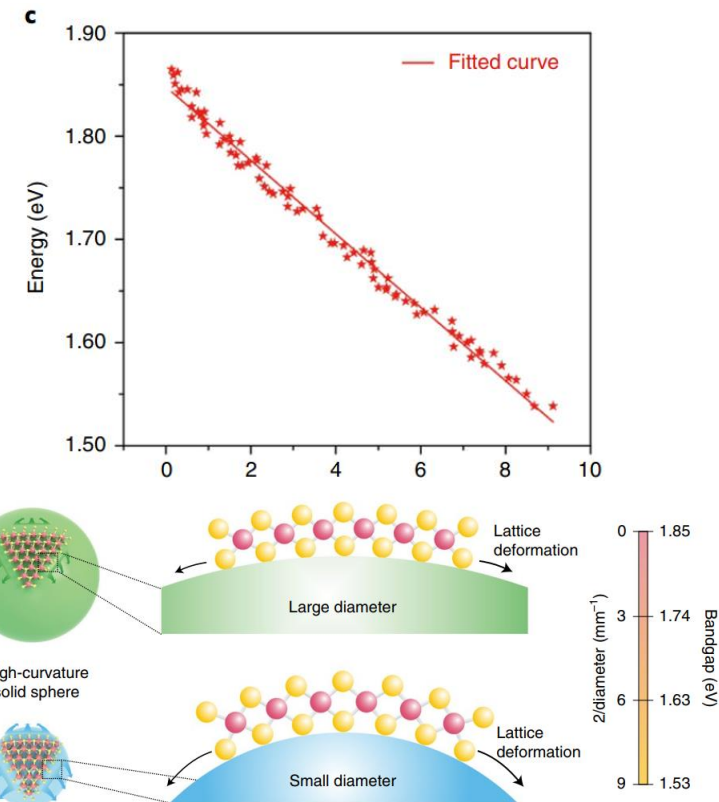


1. Graphene/Mo₂C heterostructure directly grown by CVD

If I put two of them together, what will happen?

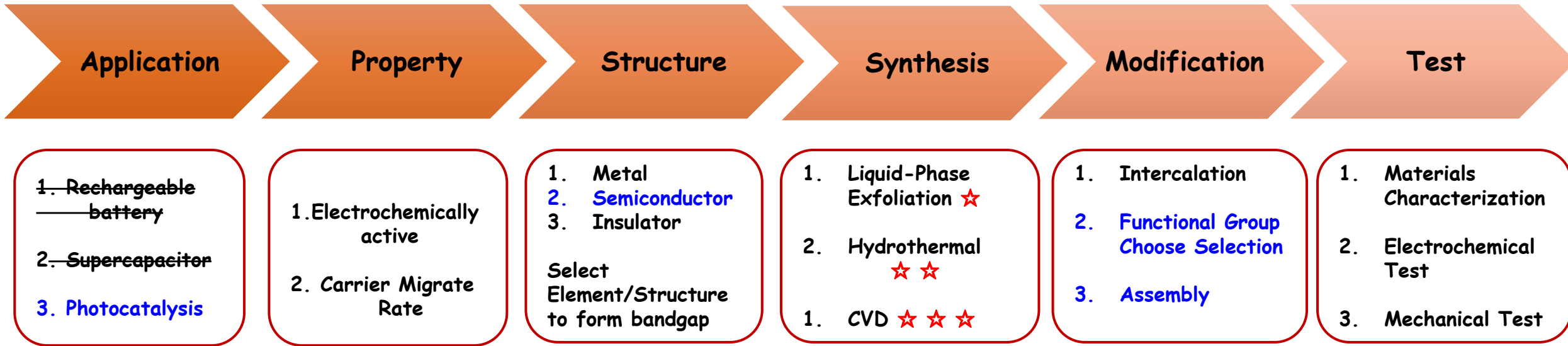
I can get a method to easily and precisely tune a desirable bandgap by CVD MXenes (Mo_2C) on different diameter spheres with graphene substrate.

Bandgap tuning of two-dimensional materials by sphere diameter engineering



2. Glass powders puts on the graphene to form different diameter spheres, causing strains to influence bandgap.

Crude Roadmap



□ Begin with [electronic structure](#) / [adsorption-diffusion](#) calculations:

1. Do electronic structure calculations for selecting element/structure to [form ideal bandgap](#);
2. Do adsorption/diffusion simulations for selecting proper functional group/assembly method to [have active surface](#);



□ My calculation results will determine my experiment plan:

1. Synthesis materials and make surface modifications;
2. Materials characterization, electrochemical test and mechanical test;
3. After finishing a good structure-property model, using machine learning to predict and screen other combinations.

ADVANCED MATERIALS

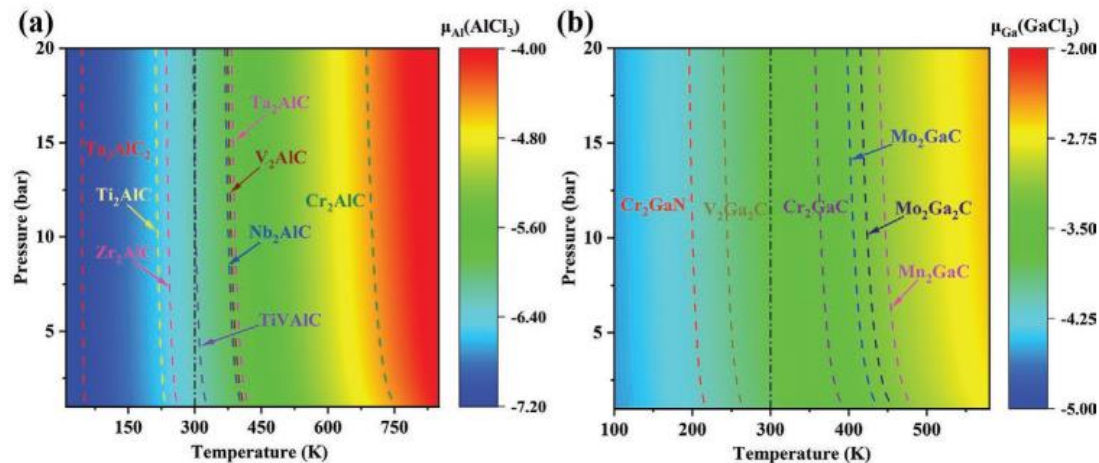
Research Article

HCl-Based Hydrothermal Etching Strategy toward Fluoride-Free MXenes

Changda Wang, Hongwei Shou, Shuangming Chen, Shiqiang Wei, Yunxiang Lin, Pengjun Zhang, Zhanfeng Liu, Kefu Zhu, Xin Guo, Xiaojun Wu, Pulickel M. Ajayan , Li Song 

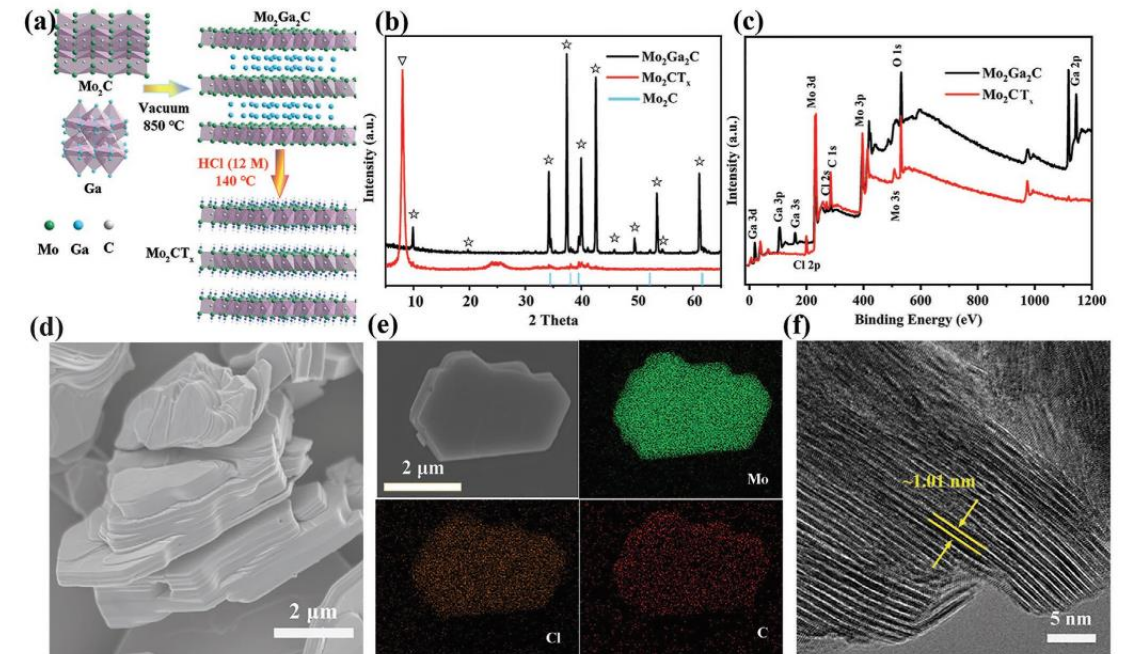
First published 31 May 2021 | <https://doi.org/10.1002/adma.202101015>

Fresh !!!



Simulations of the feasibility of various MAX materials with Al and Ga interlayer elements were performed to predict HCl etching temperature and pressure (T&P)

Someone has used the calculation & experiment methodology ahead of me !



Prepared high quality fluorine-free Mo_2CTX has only Cl- and O- terminal groups

This is my **third** challenge in the future !

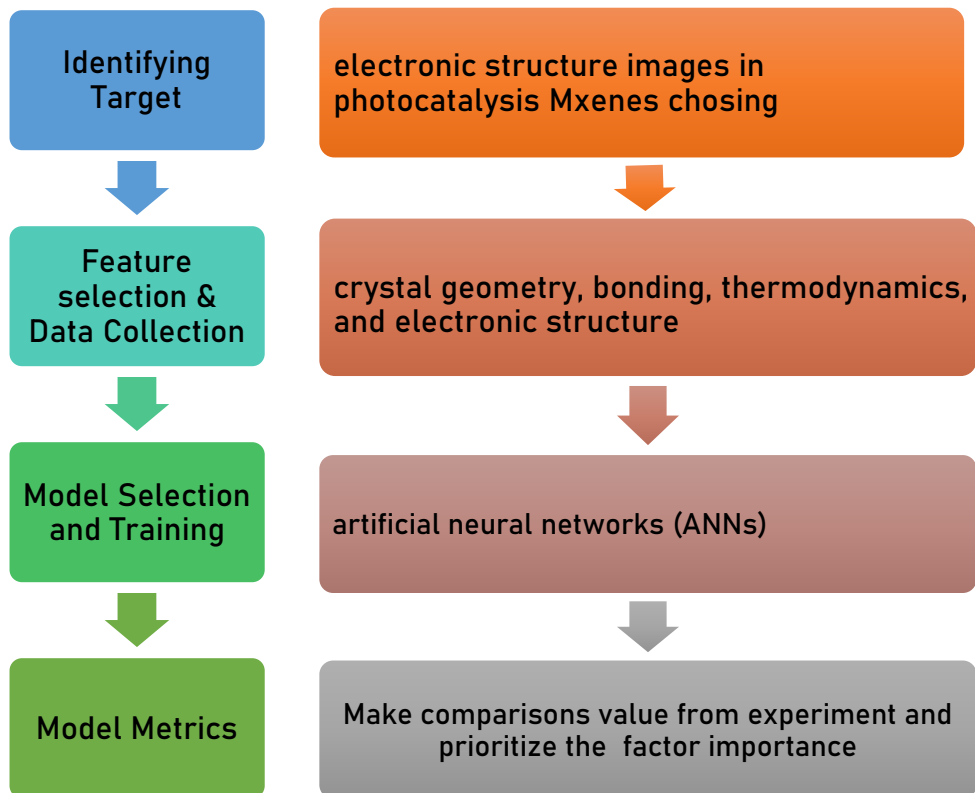
Finally, if it works well, like,

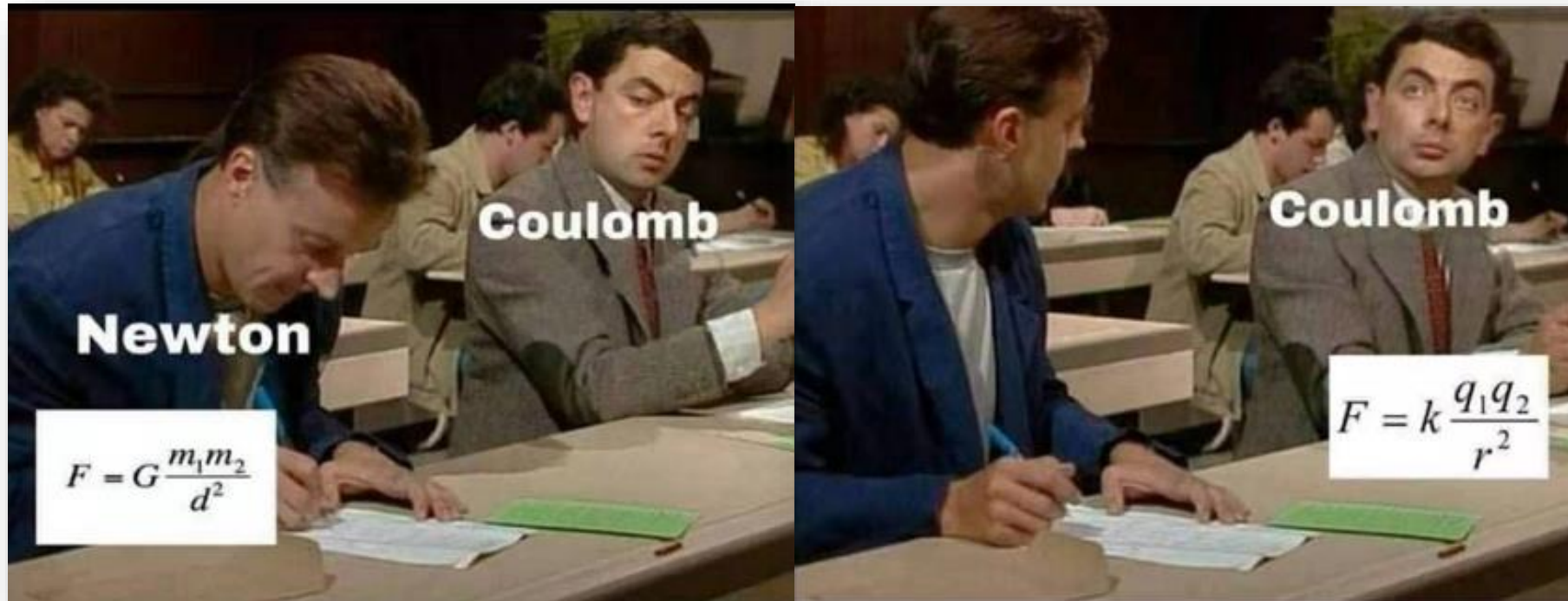
getting a good relationship between structure and property,

I am ready to use machine learning,

to search

other combinations of $M(n)AX(n+1)$ which can be predicted and screened for photocatalysis.





Thanks for your attention.