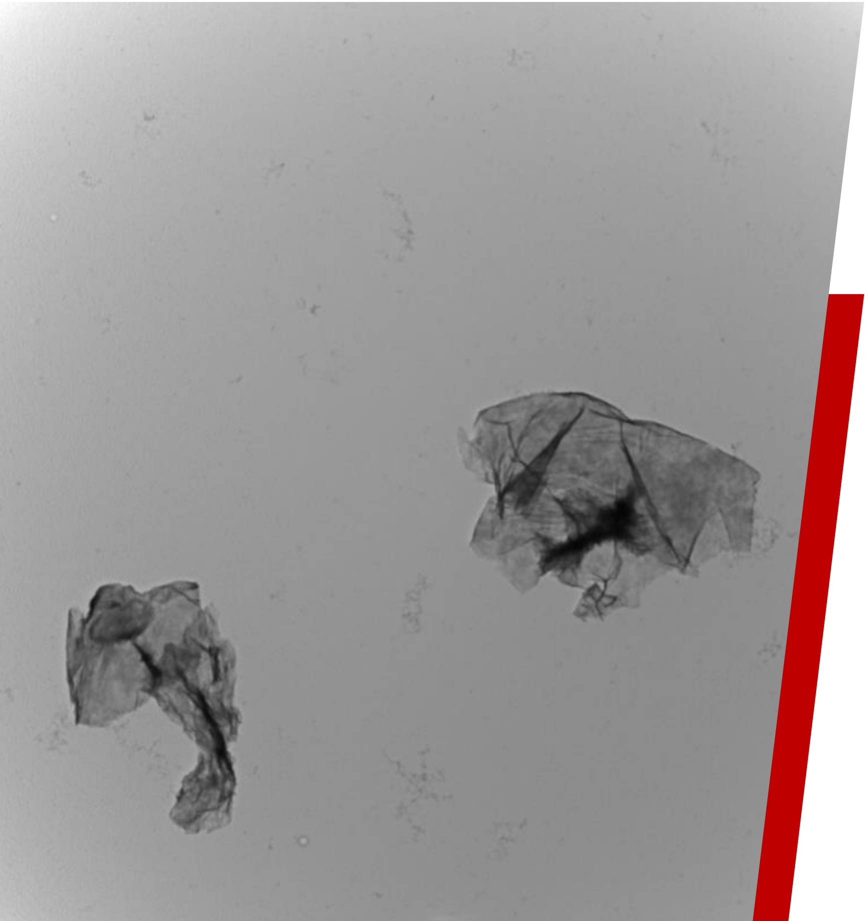
Empa
Materials Science and Technology



Challenges in the synthesis and characterization of 2D materials (Part 1)

Dr. Giacomo Reina

20.08.24 Visp

Outline

- 2D Nanomaterials: Timeline
- 2D Nanomaterials: Who are they?
- Synthetic Methods: Bottom-up
- Synthetic Methods: Top-Down
- Overview and Questions

2D Nanomaterials: Timeline

2000

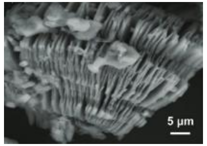
2004

Prof. A. Geim & K. Novoselov

KUNGL. VETENSKAPS-AKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

2010

2011



Pro. Y. Gogotsi et al.

GRAPHENE FLAGSHIP

2013

2018

Huawei Mate P30 Pro

Intel 3D Stacked Transistors Based on TMDs g. length below 10nm

2023

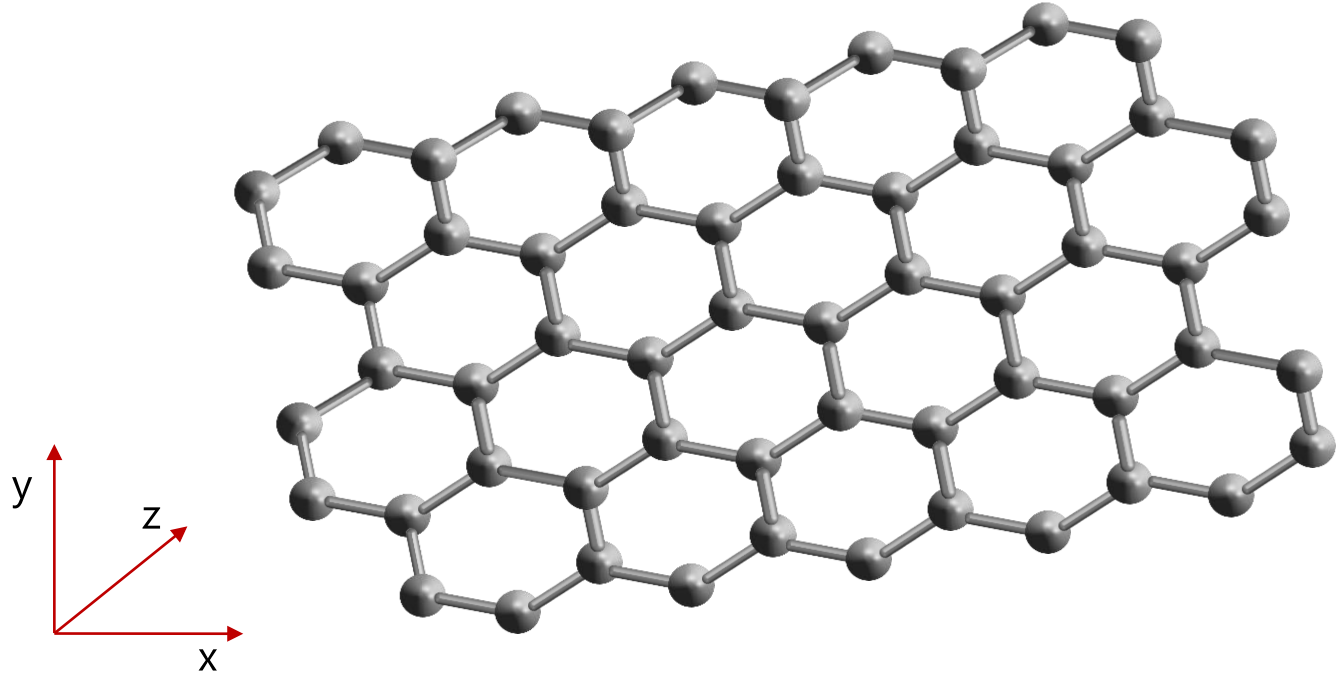
2024

Source: Wikipedia
Naguib et al. Advanced Materials 2011

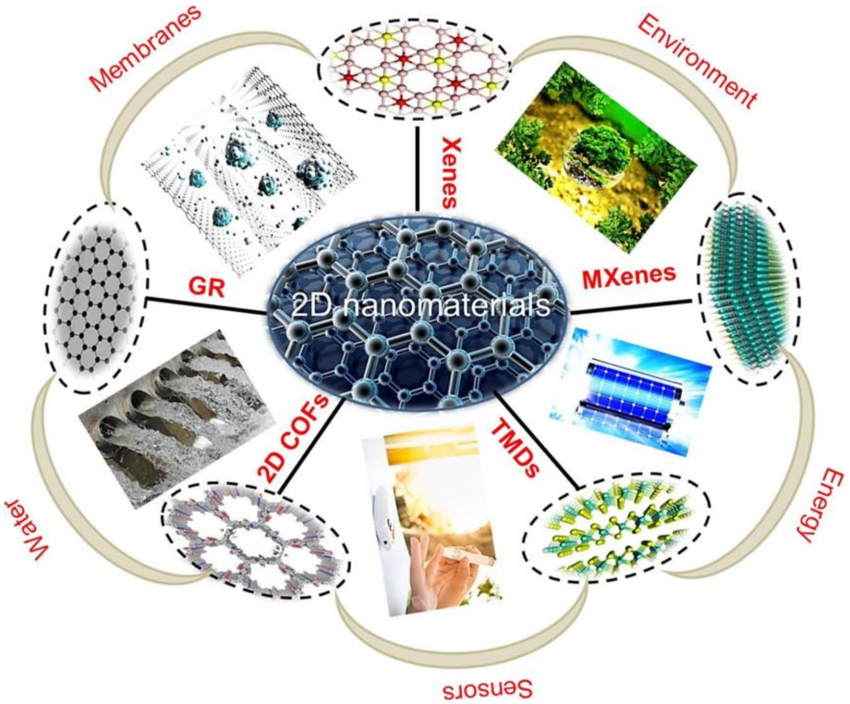
2D Nanomaterials: Who are they?

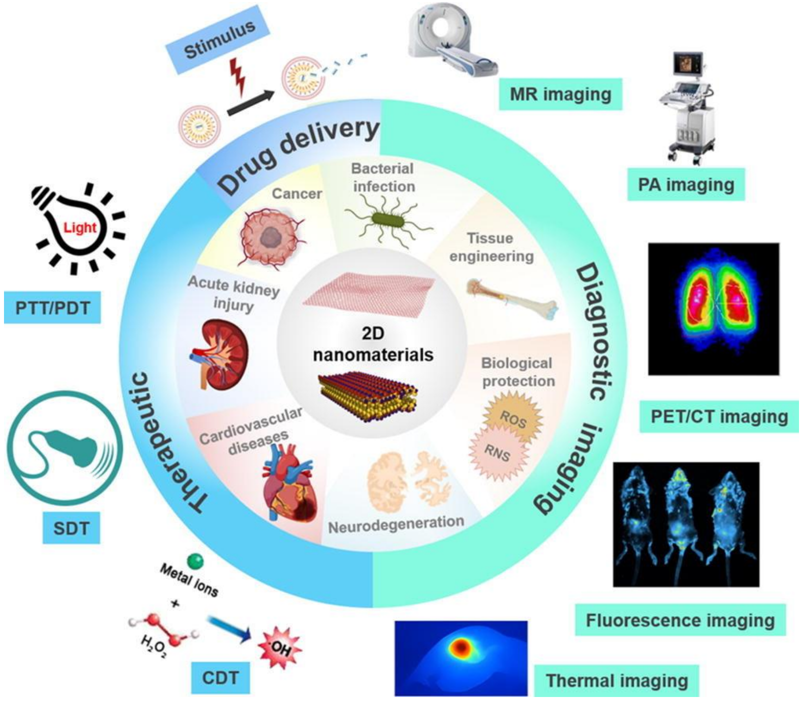
2D Nanomaterials are 2D nanocrystals

Morphologically the are characterized by a lateral size (x, y) and a number of layers (z)



2D Nanomaterials: Who are they?



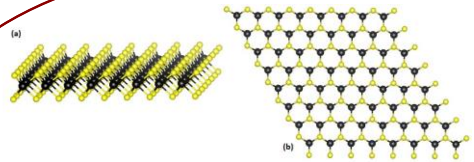


Baig et al. Composites Part A: Applied Science and Manufacturing 2023
Ouyang et al. Advanced Drug Delivery Reviews 2022

2D Nanomaterials: Who are they?

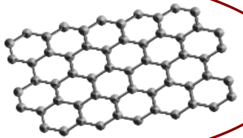
2D Nanomaterials are a family of different compounds

Depending on the composition they have different names



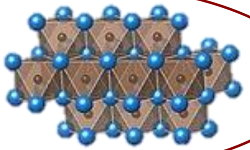
Transition Metals Dichalcogenides (TMDs)

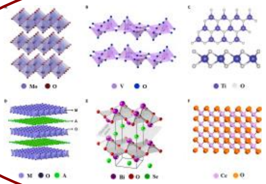
XEnes



2D Nanomaterials

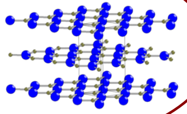
MXenes



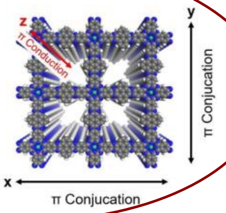


Metal Oxides

h-BN



Organic

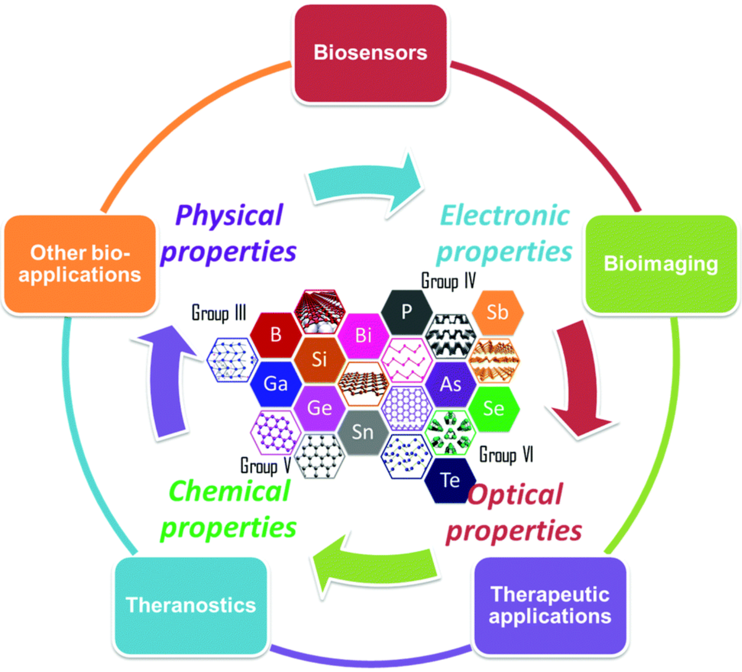


Xie et al. iScience 2022

2D Nanomaterials: Who are they?

Xenes

Xenes are mono elemental 2D materials apart from graphene the name is given by –ene suffix

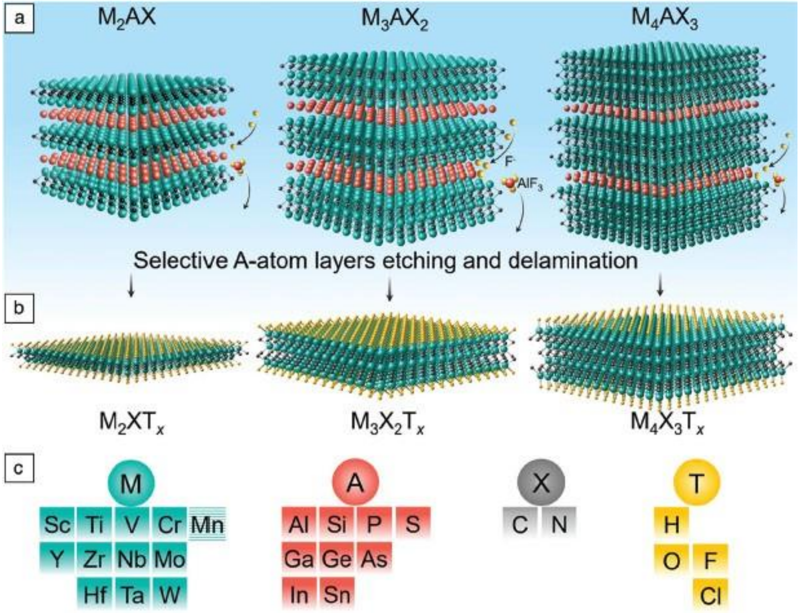


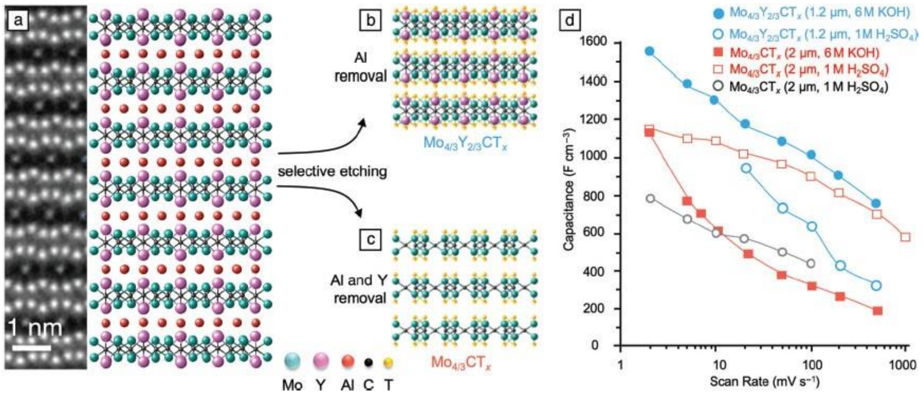
Tao et al. Chem. Soc. Rev. 2019

2D Nanomaterials: Who are they?

MXenes

Mxenes are 2D metal carbides or nitrides



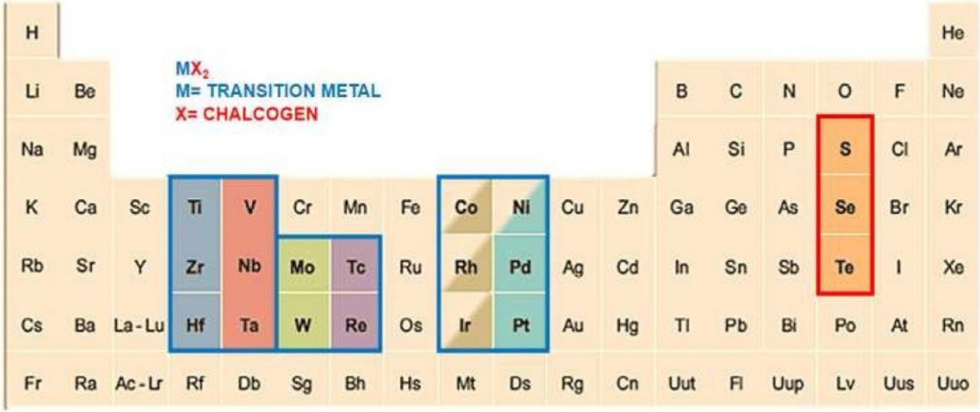


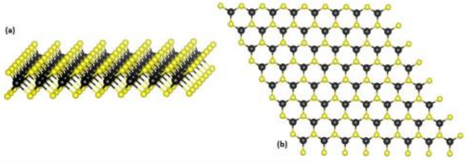
Hong et al. MRS Bulletin 2020

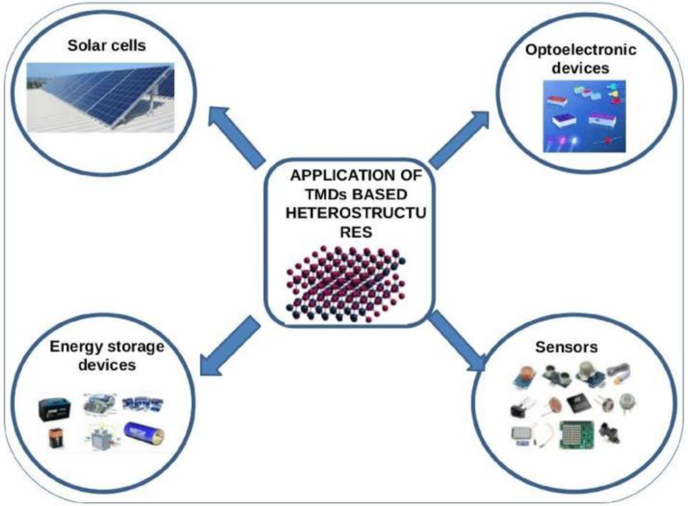
2D Nanomaterials: Who are they?

TMDs

TMDs are bi-elemental 2D materials composed by a transition metal and a chalcogenen (1:2)





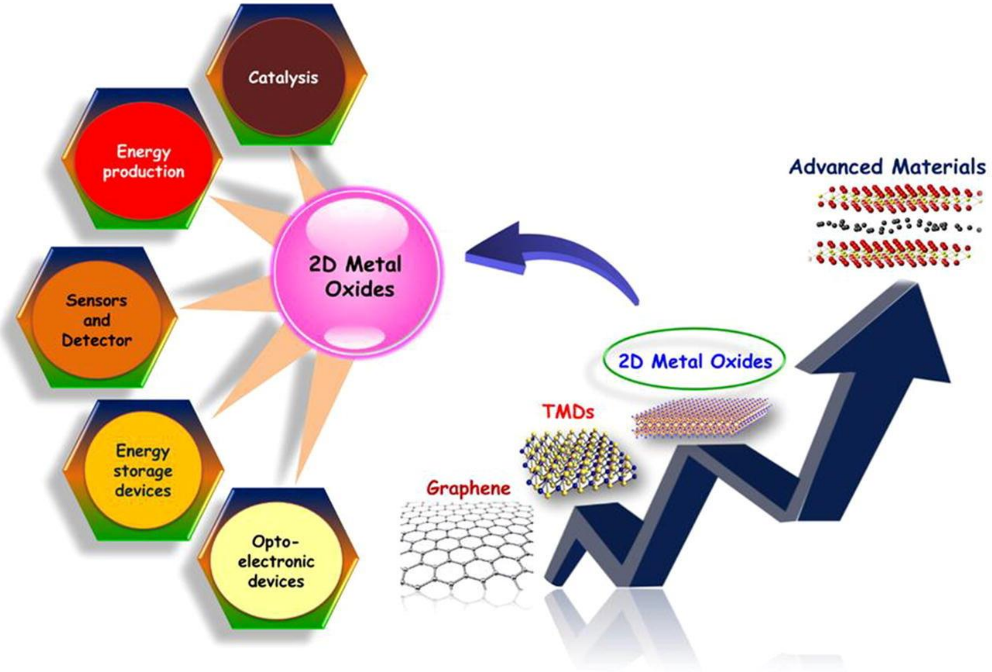


Joseph et al. Materials Chemistry and Physics 2023

2D Nanomaterials: Who are they?

2D Metal Oxide

Similar to TMDs but with oxygen

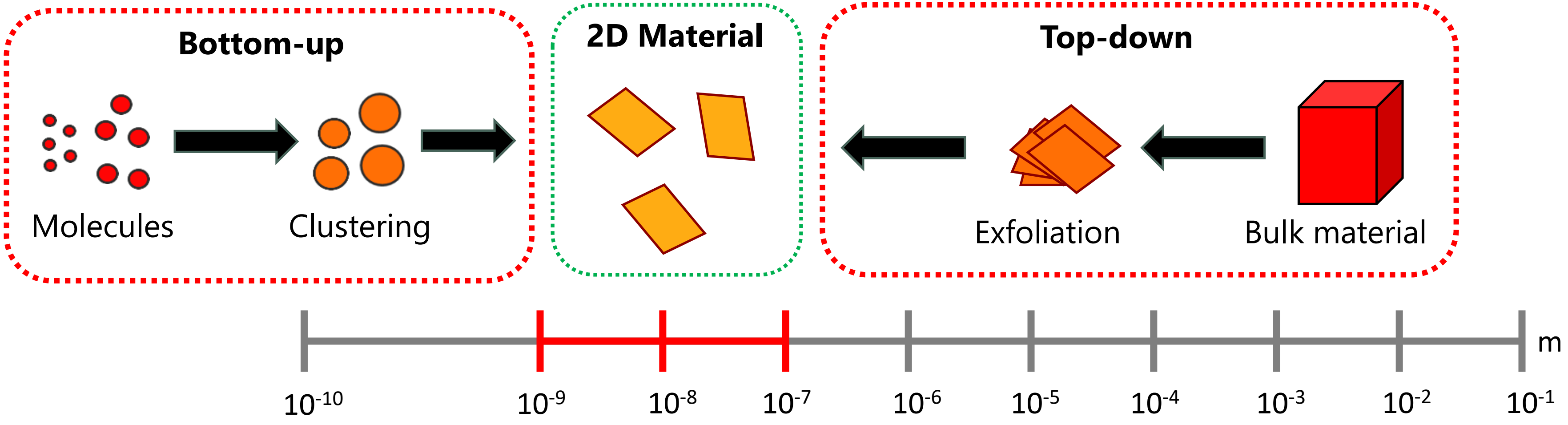


Kumbhakar et al. Materials Today 2021

Top-down vs Bottom-up, Physical vs Chemical

Top-down approaches relies on the controlled fragmentation of the bulk material to form NMs

In **bottom-up approaches** the NMs are formed from their atomic/molecular precursors

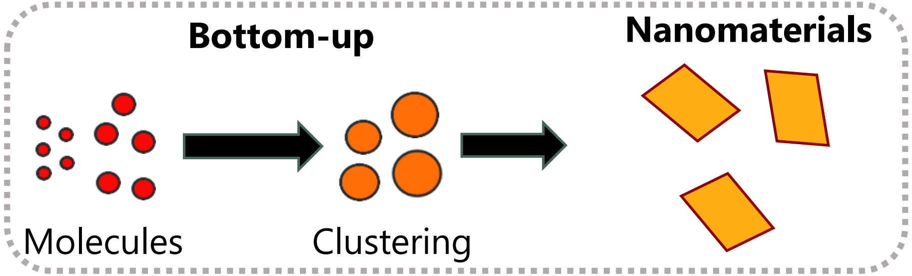


Chemical approaches foresee a chemical reaction for the 2D-NMs synthesis

Physical approaches there is a change on the morphology but not in the chemical composition (no chemical reaction)

Bottom-up Approaches

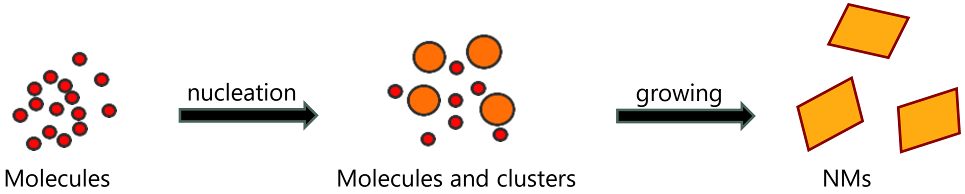
Bottom-up approaches the NMs are formed from their atomic/molecular precursors



Bottom up approaches are genuinely chemical approaches where reagents are converted into NMs

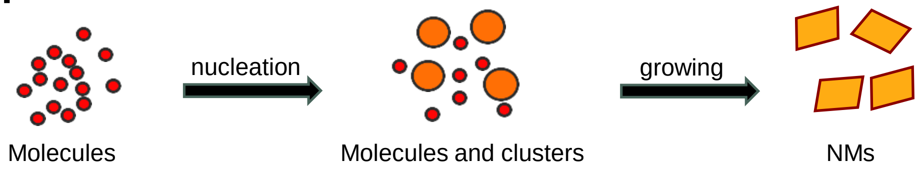
The goal is then to make NMs grow as mush as **WE** want

General Theory: The NM growth in two steps Nucleation (were cluster are formed) and Growth (were particles grow)



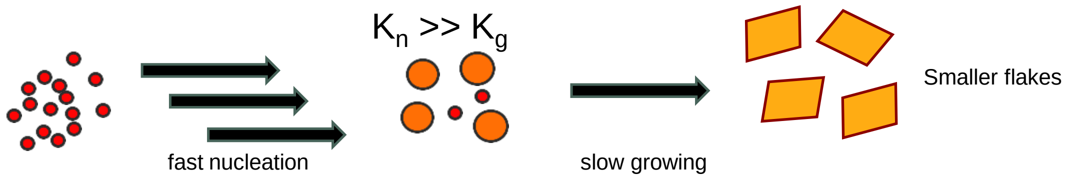
Bottom-up Approaches

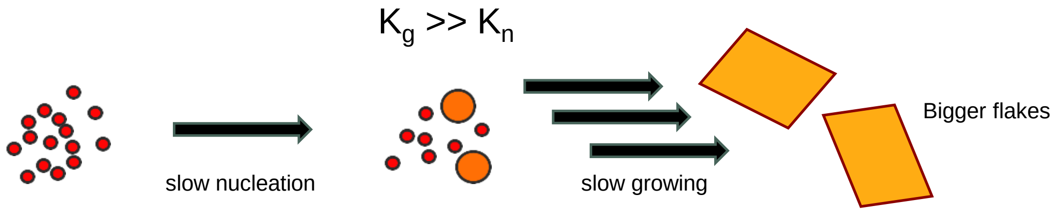
How can we control this process?



K_n = kinetic constant of the nucleation reaction

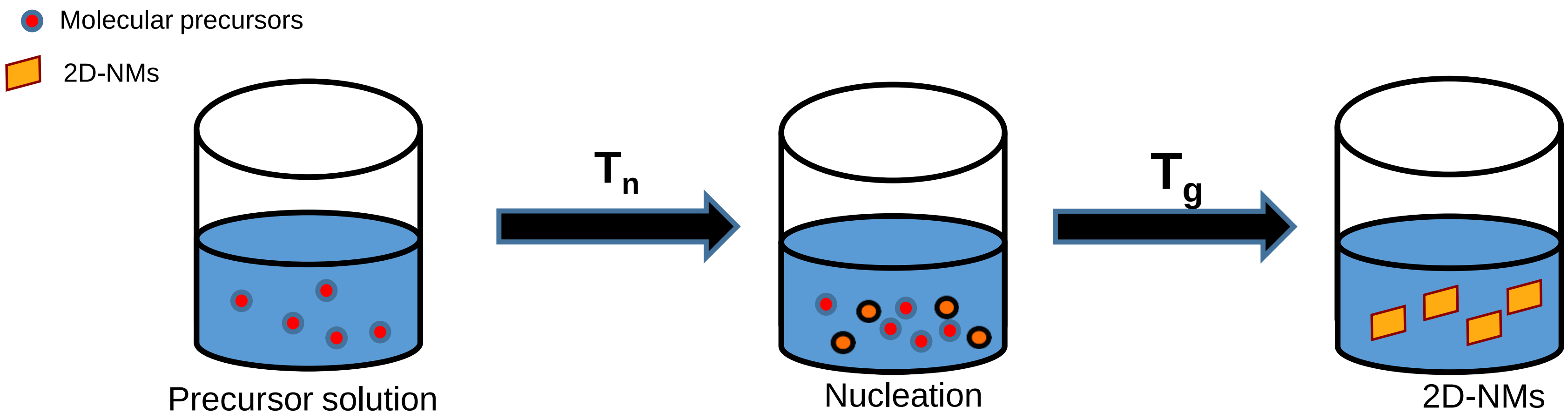
K_g = kinetic constant of the growing reaction





Concentration and Temperature, are the main factors we can control

SolvoThermal



Solvothermal is a synthetic strategy at high temperature (> 100 °C)

The reaction vessel is first heated at a nucleation temperature (T_n)

After seeding, NMs are grown at the growth temperature (T_g)

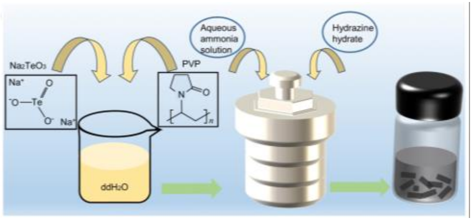
Water can also be used as solvent (Hydrothermal) in that case, high pressure is required so a steel pressure vessel is used

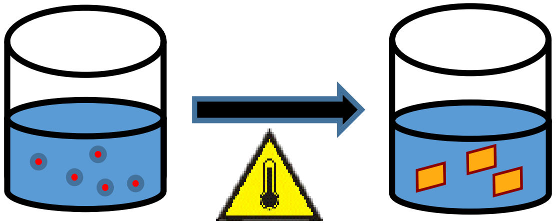
Microwave can be also implied

Solvothermal is an easy strategy to obtain small nanoparticles (<10 nm).

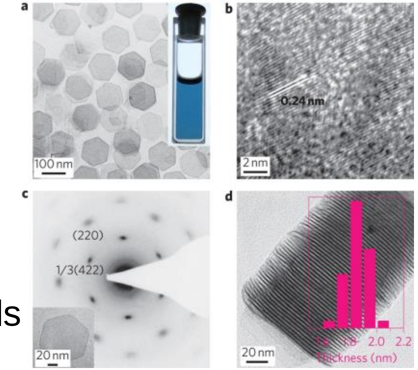
SolvoThermal

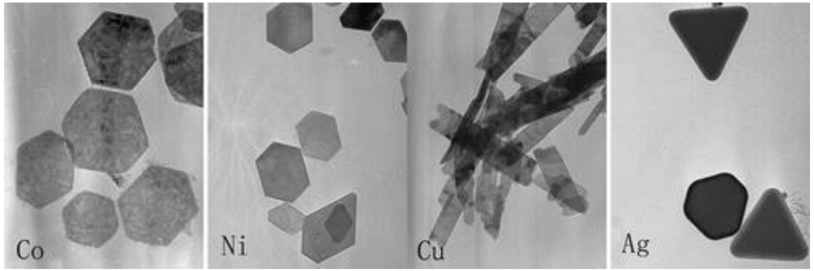
Important parameters:





- Temperature
- Pressure (hydrothermal)
- Reaction time
- Solvent type





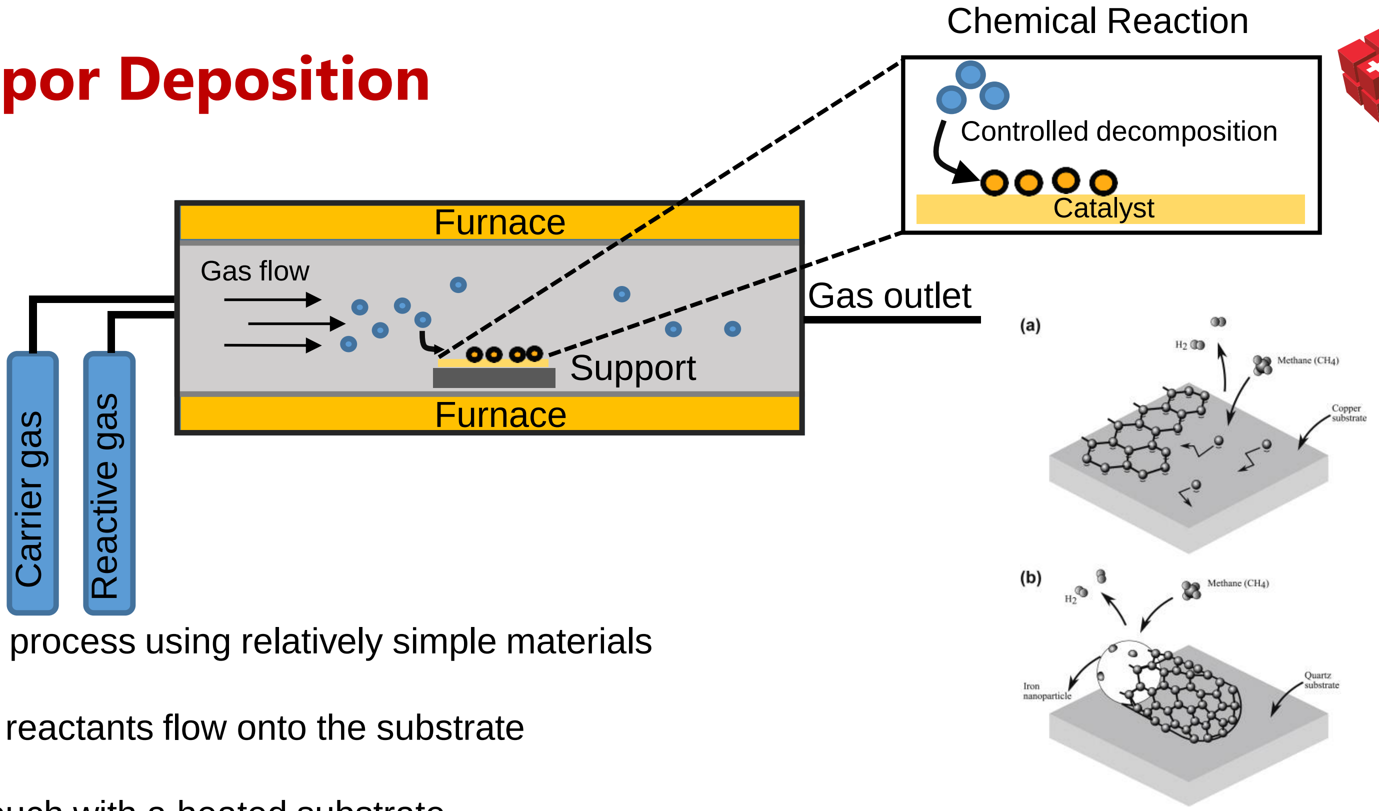
Applications: Ideal for many 2D Metals

Pros
- Scalable
- Precise control of size NPs.
- Produce nanocrystal with high crystallinity

Cons
- Expensive autoclave
- Use of organic solvents
- Challenging temperature control

Huang et al. Nature Nanotechnology 2011
Xu et al. Crystal Growth 2007
Li et al- Meterial advances 2022

Chemical Vapor Deposition



NMs are created with this process using relatively simple materials

A thin coating of gaseous reactants flow onto the substrate

The gas reacts when in touch with a heated substrate

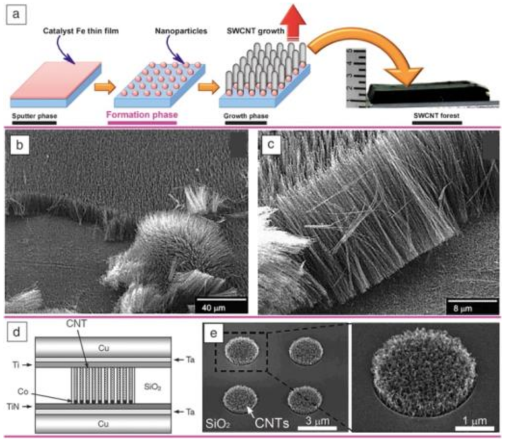
From this reaction 2DNMs are formed

Can you suggest alternative ways to heat to start the reaction?

Different kids of CVD apparatus have been developed depending on the chamber pressure and the energy source

Loos, Marcio. *Carbon nanotube reinforced composites: CNT Polymer Science and Technology*. Elsevier, 2014.

Chemical Vapor Deposition

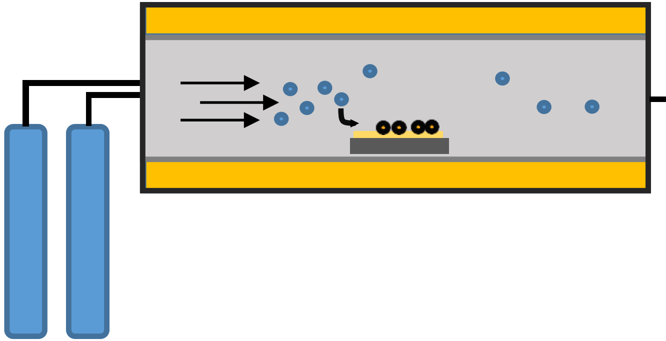


https://www.youtube.com/watch?v=VyULskYuGvg

Substrate Fe and Gd (2021)

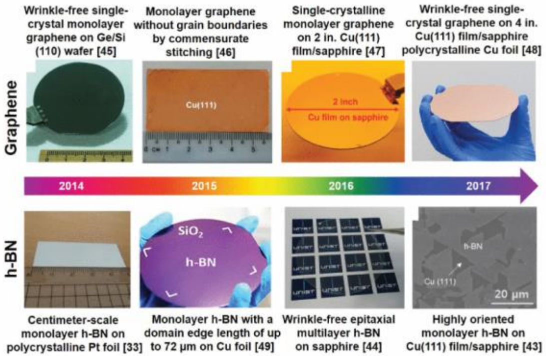
Chen, Guohai, et al. *MRS Bulletin* 42.11 (2017): 802-808.

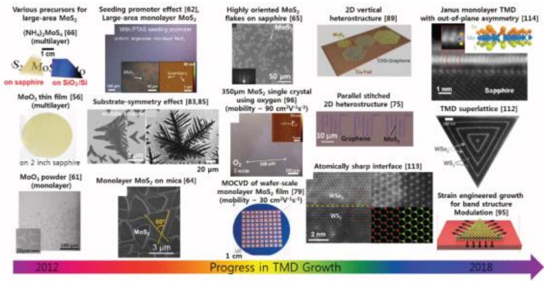
Chemical Vapor Deposition



Important parameters:

- Pressure: lower pressure -> Higher quality, slower process
- Catalyst
- Temperature between 300 °C and 1000 °C





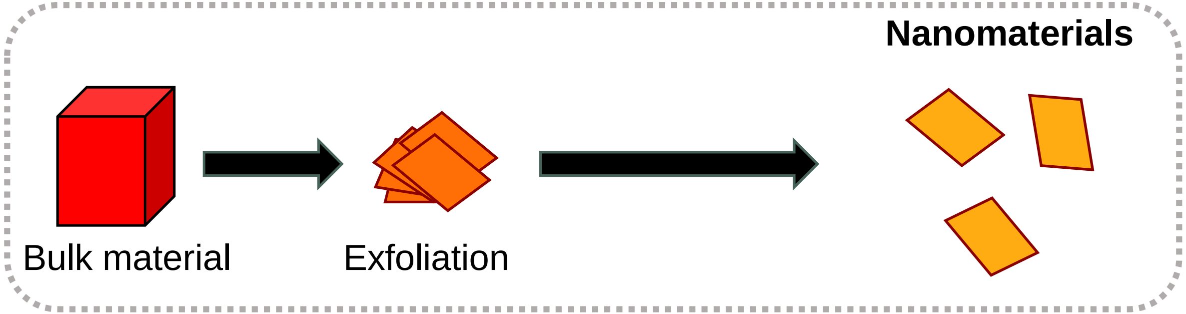
Applications: Most of 2D nanomaterials

Pros
- Scalable (Standard technique in electronics)
- High control and purity
- Reproducibility
- Uniform coating

Cons
- Precursors are poisonous, flammable, or explosive and few are quite costly.
- Fabrication costs.

Shen et al. *IEEE 2018*

Top Down Strategies



Top Down approaches rely on the **controlled etching** of the bulk materials

For those reasons **high energies** are generally required

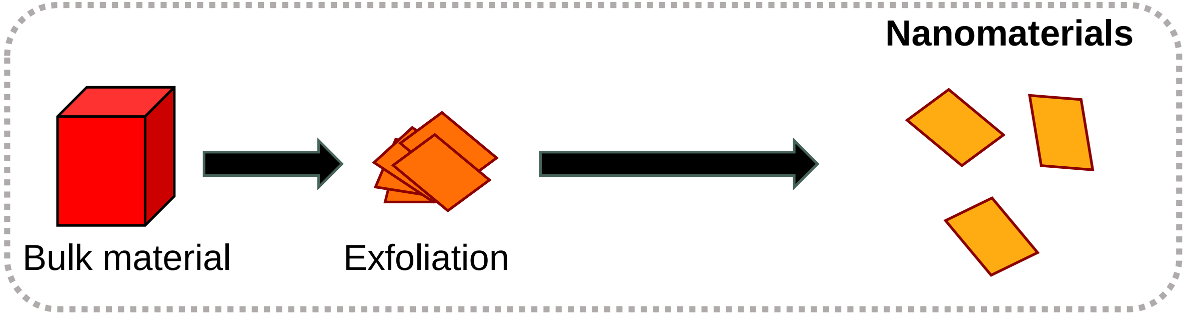
Each process is called **according to the energy source used**.

Controlling the parameters of the process allows the tailor 2D-NMs’ size and morphology

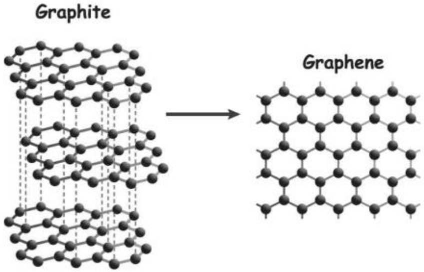
Pros
In general Top-down **processes are scalable**
High quantity of material produced
Easy protocols

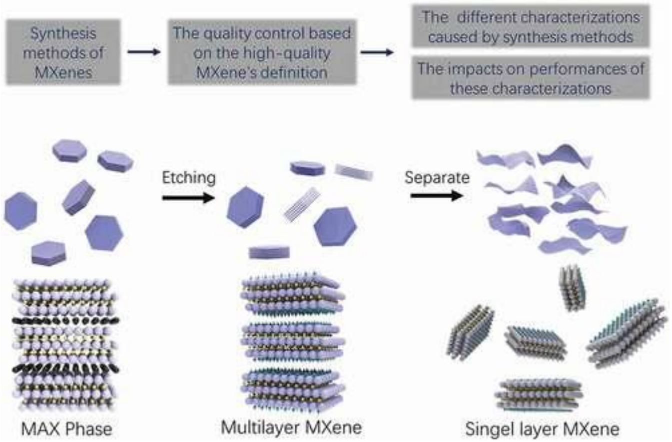
Cons
Wide size of materials are produced
Purification step may be complex
Ineffective on small particles

Top Down Strategies



Depending on the bulk material we can use different protocols





Chen et al. *Energy Materials 2021*

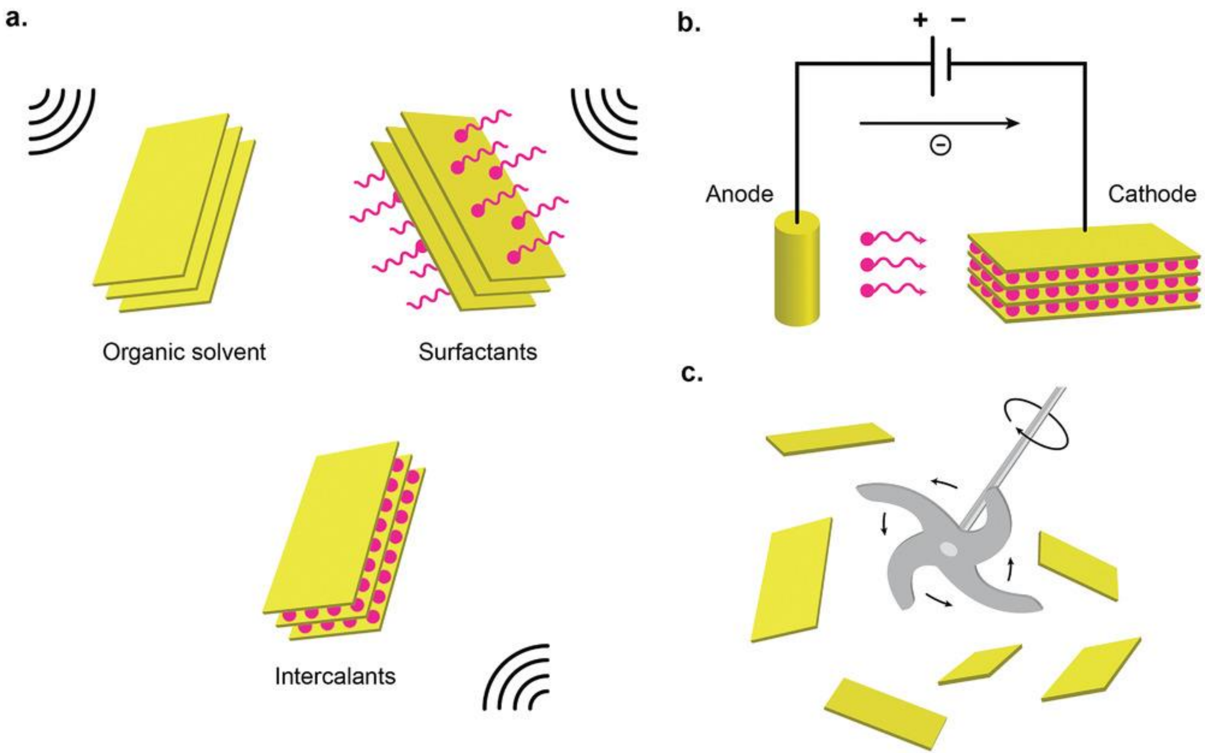
Liquid Exfoliations

Energy can be given by:

Sonication

Electric energy

Mechanical



Azakia et al. *Advanced Science 2021*

Quiz

- Is Phosphorene a MXene?
- What are the scalable ones?
- What are the main technologies to make a film?
- How would you make a Xene?
- How would you produce Platiun Nanoplatelets?

Purification

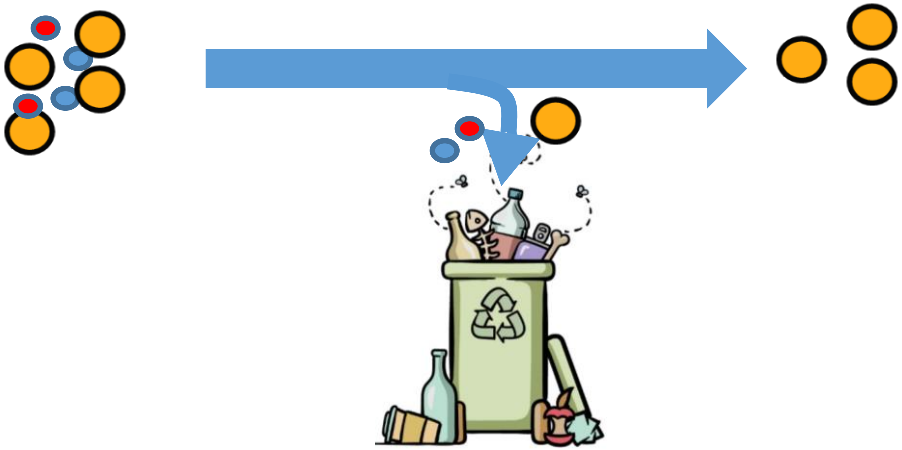
No reaction is 100%, the crude will contain reagents, and byproducts from side reactions

Purification is necessary considering two main factors:

- The quality range needed (e.g., bio grade, technical grade)

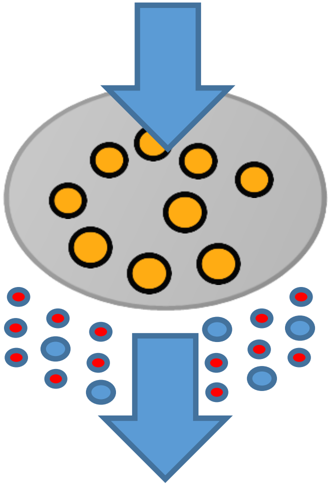
- Each purification step will decrease the yield of the reaction

Thus purification protocol is reaction dependent



iHeartCraftyThings.com

Filtration

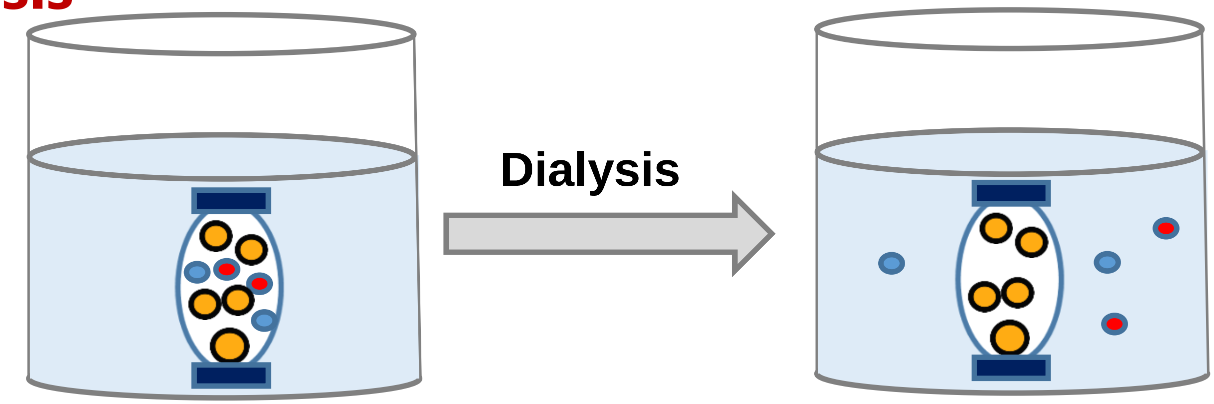


Principle: NMs are dispersed in an appropriate solvent and collected at the filter while molecules pass through.

Pros
- Ease of preparation
- Inexpensive
- Scalable

Cons
- Agglomeration
- Moderate efficacy

Dyalisis

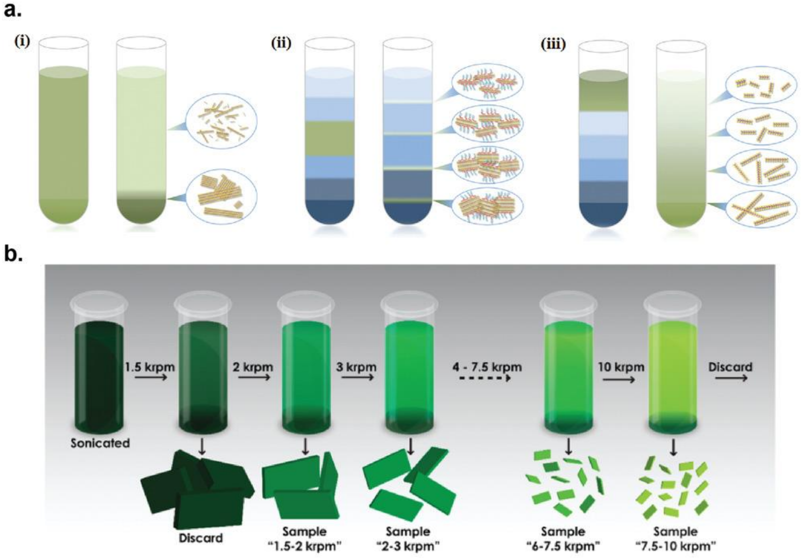


Principle: NMs are enclosed in a dialysis bag and are purified by the osmotic effect.

Pros
- Ease of preparation
- Good separation
- Quantitative
- MW can be tuned

Cons
- Works only in water
- Expensive
- High volumes of water

Centrifugation



i) sedimentation-based separation or centrifugation (SBS),
ii) sedimentation-based density gradient ultracentrifugation (sDGU),
iii) isopycnic density gradient ultracentrifugation (iDGU)

Pros
- Standard procedure
- Fast
- Scalable

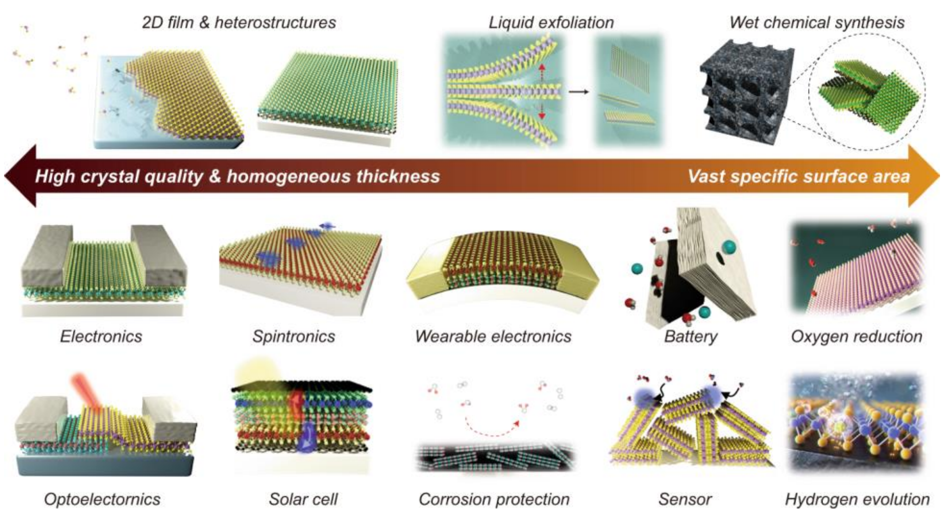
Cons
- Moderate efficacy
- Agglomeration
- High quantities of solvents

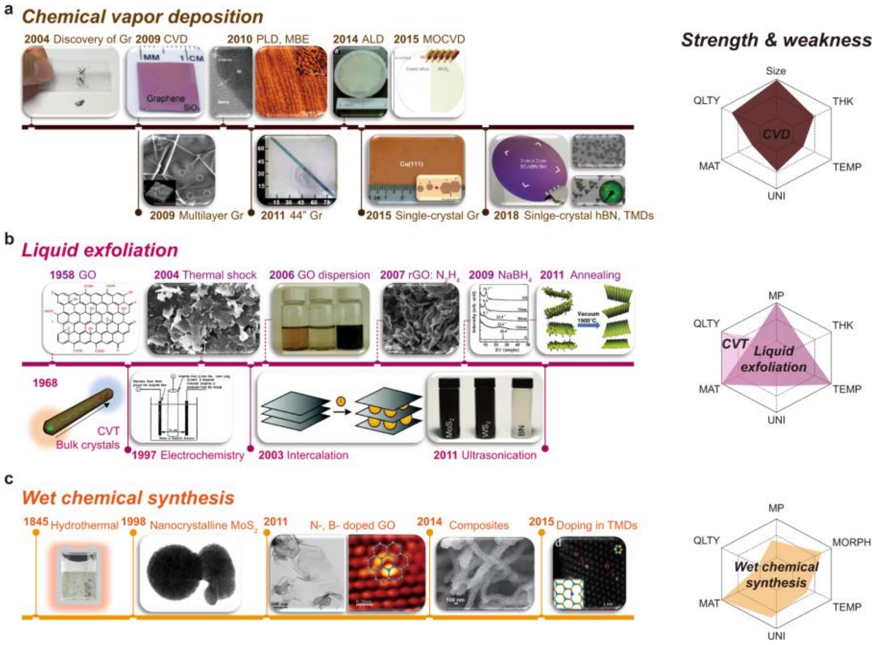
Azakia et al. *Advanced Science 2021*

What is the best synthetic method for industrial applications?

It Depends!

Industrial applications





Mass production (MP), thickness controllability (THK), temperature variation (TEMP), uniformity (UNI), material diversity (MAT), crystal quality (QLTY), morphology (MORPH).

Choi et al. *Advanced Science 2022*