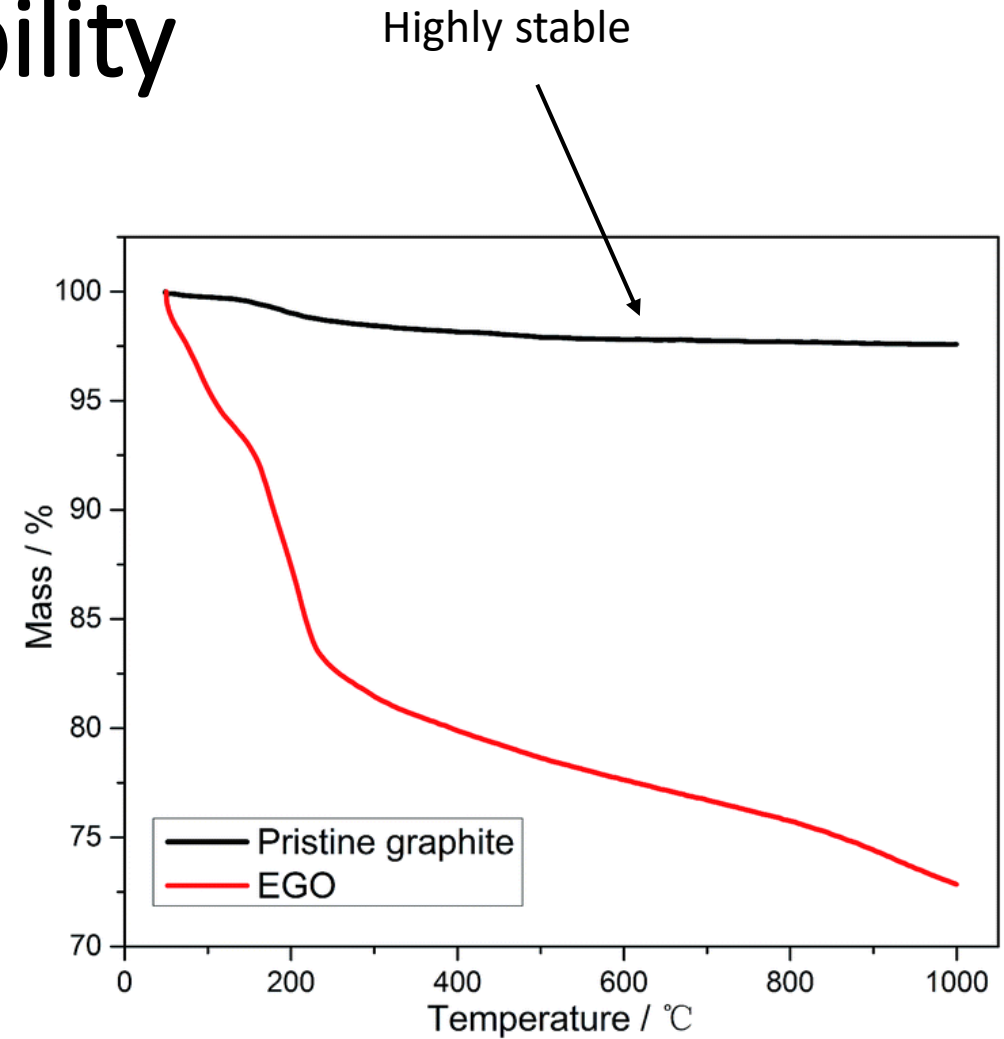
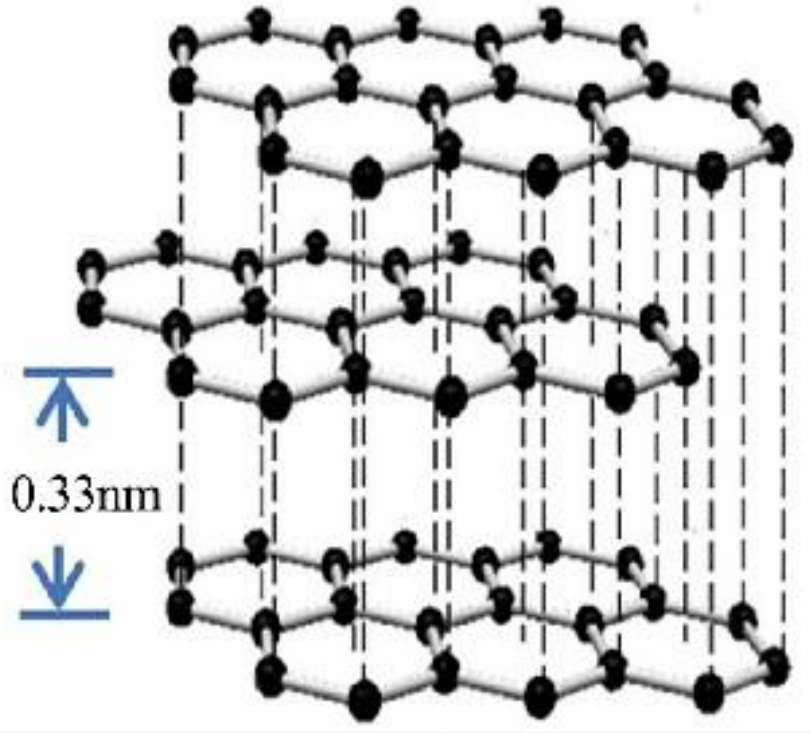


2D Materials and Applications

Unit - 2

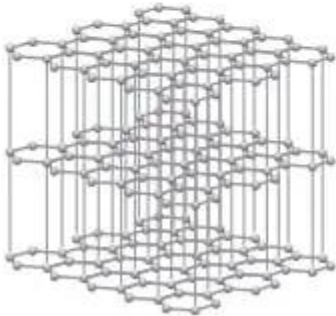
Graphite and thermal stability



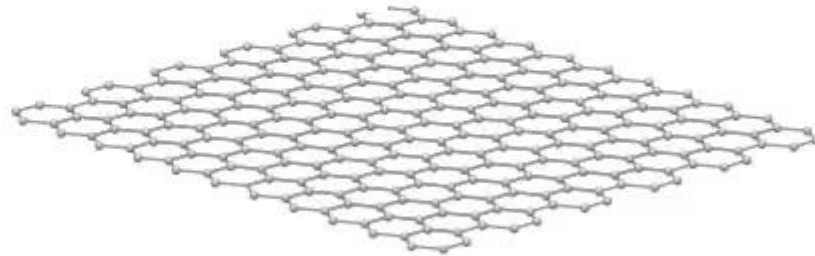
Melting Point, 3950 degree centigrade

Graphite to Graphene

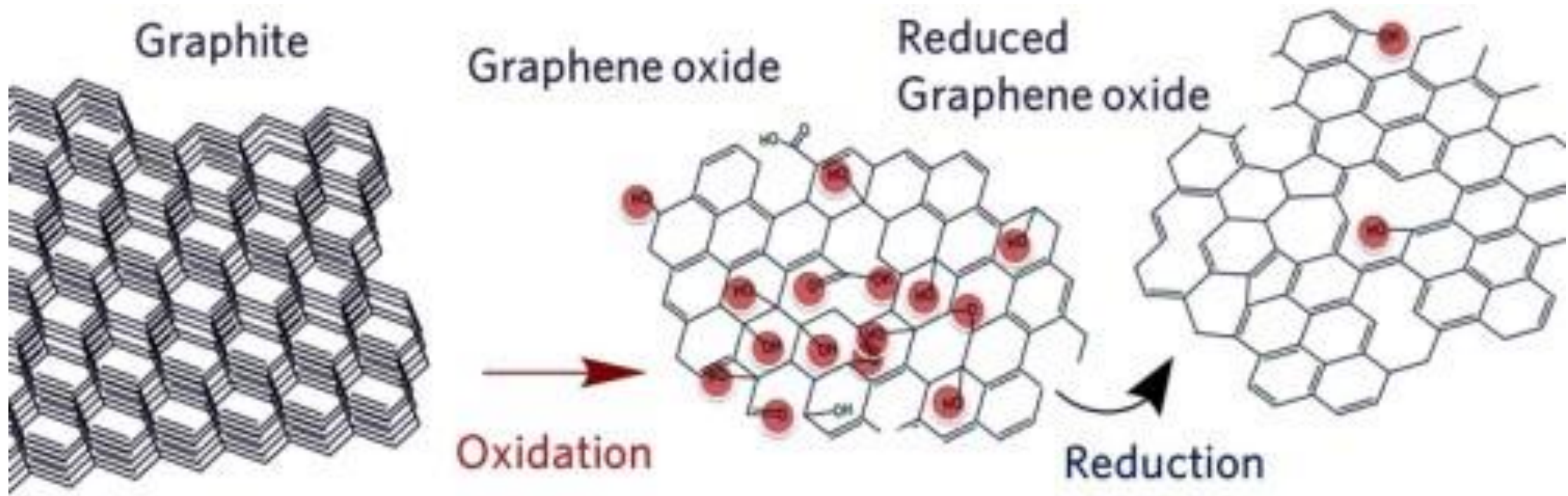
graphite



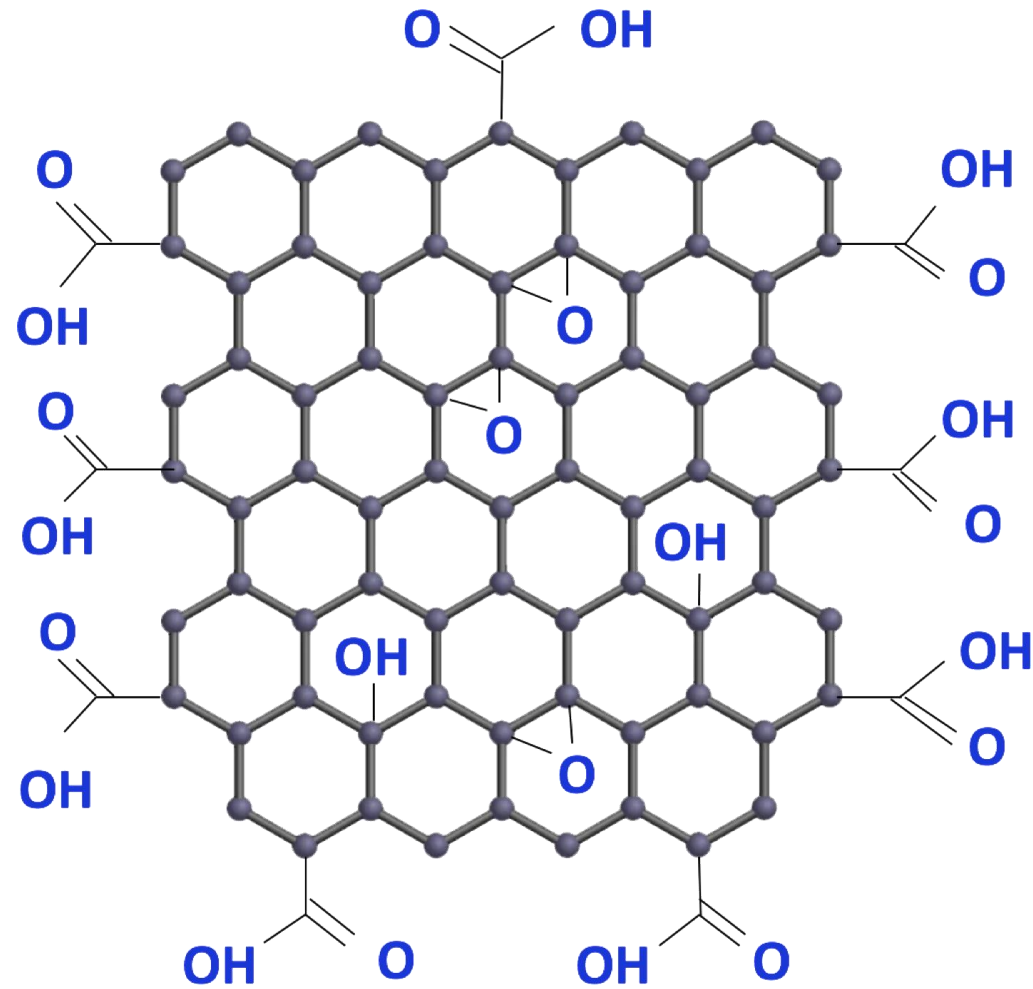
graphene



Graphite – Graphite oxide – Graphene

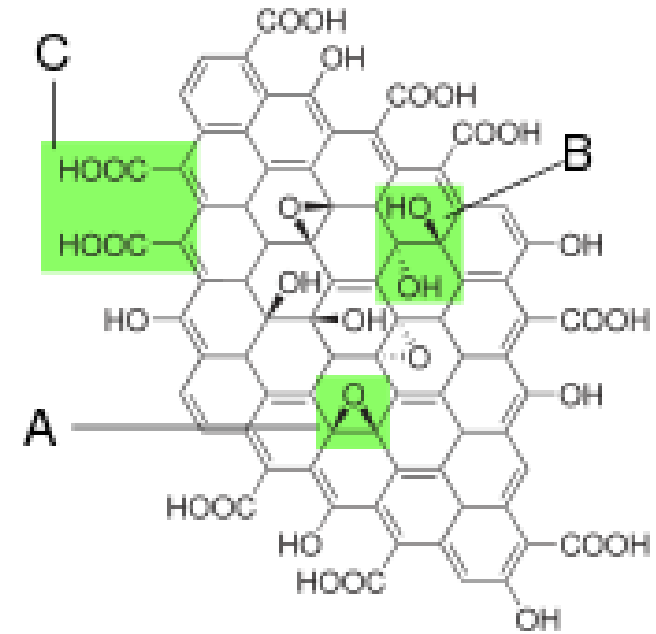


Graphite oxide



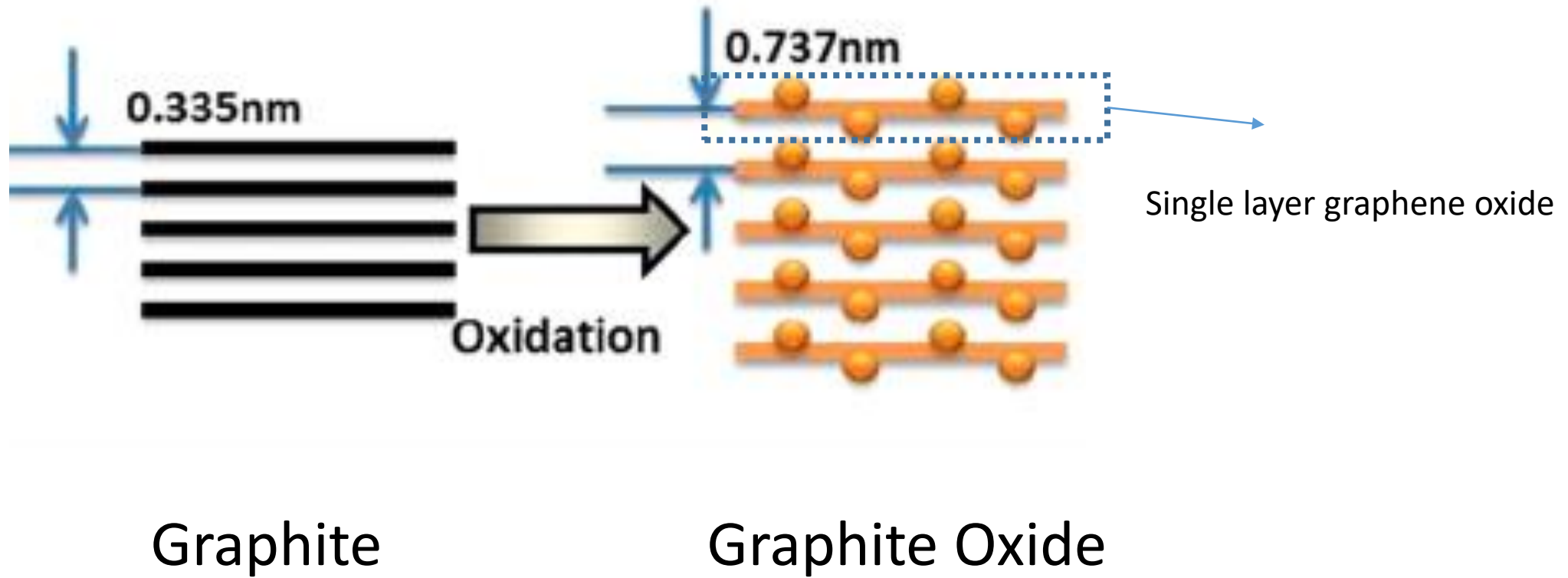
Properties of Graphite oxide

- It is a compound of carbon, oxygen and hydrogen in variable ratios.
- It is obtained by treating with strong oxidizers.
- The maximally oxidized bulk product is a yellow solid with C:O ratio between 2.1 and 2.9, that retains the layer structure of graphite but with a much larger and irregular spacing.



Structure proposed in 1998[1] with functional groups. A: Epoxy bridges, B: Hydroxyl groups, C: Pairwise carboxyl groups.

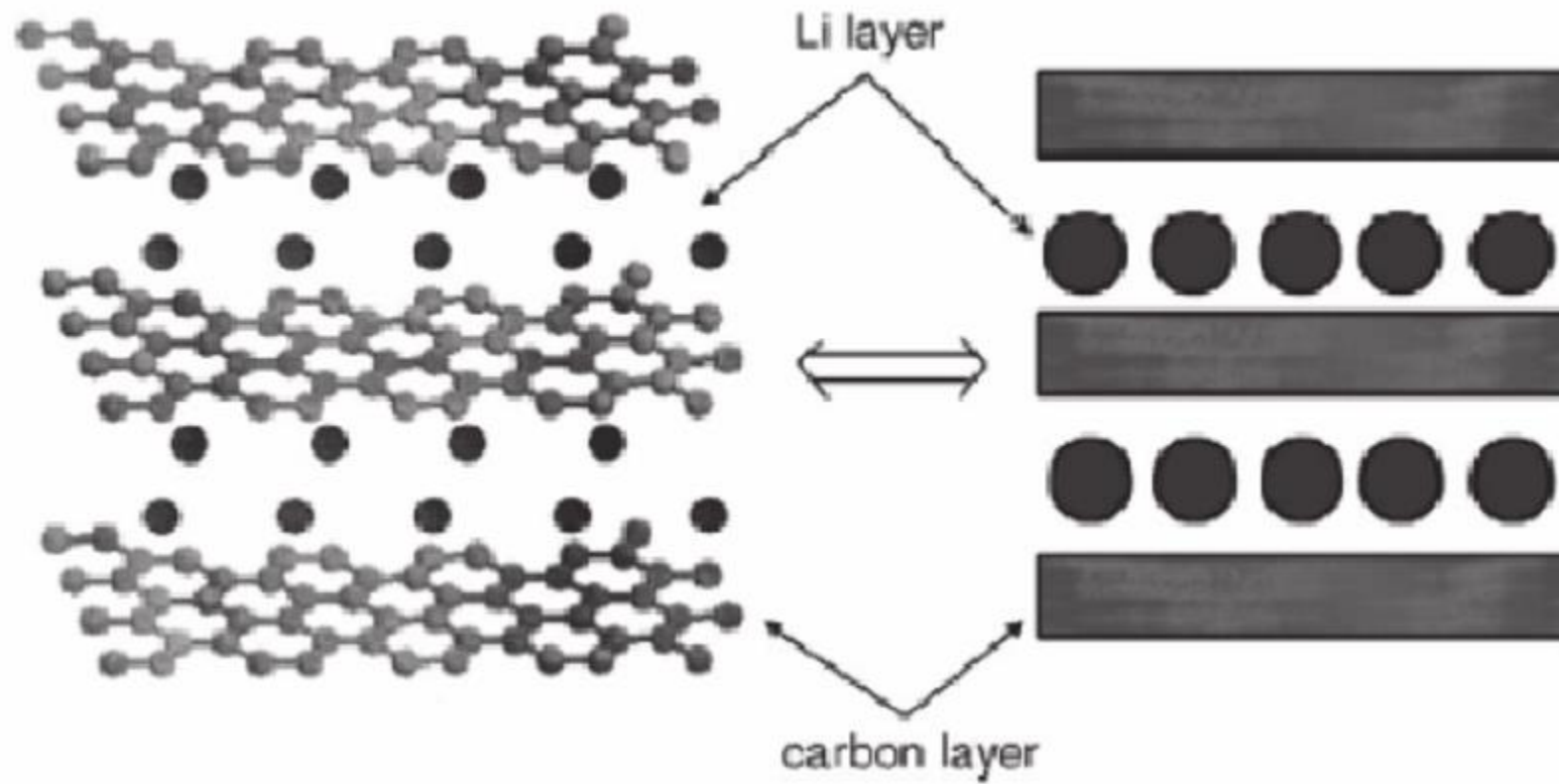
Interlayer spacing



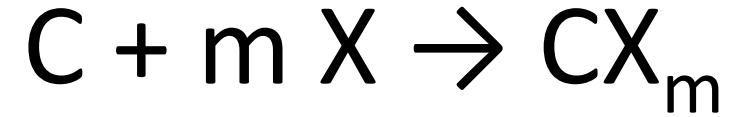
Properties of Graphite oxide

- The edges of each layer of graphite oxide terminate with carboxyl and carbonyl groups.
- It easily get dispersed in water
- It is hydrophilic in nature.
-
- Electrical insulator due to the disruption of conjugated networks.

Graphite intercalant compounds



These GLC materials are prepared by treating graphite with a strong oxidant or a strong reducing agent:



The reaction is reversible.

The host (graphite) and the guest X interact by charge transfer. An analogous process is the basis of commercial lithium-ion batteries.

In a graphite intercalation compound not every layer is necessarily occupied by guests. In so-called stage 1 compounds, graphite layers and intercalated layers alternate and in stage 2 compounds, two graphite layers with no guest material in between alternate with an intercalated layer. The actual composition may vary and therefore these compounds are an example of non-stoichiometric compounds. It is customary to specify the composition together with the stage. The layers are pushed apart upon incorporation of the guest ions.

Graphene composites

- Graphene polymer composites
- Graphene metal composites
- Graphene ceramic composites
- Graphene-bio composites

Composites of Graphene

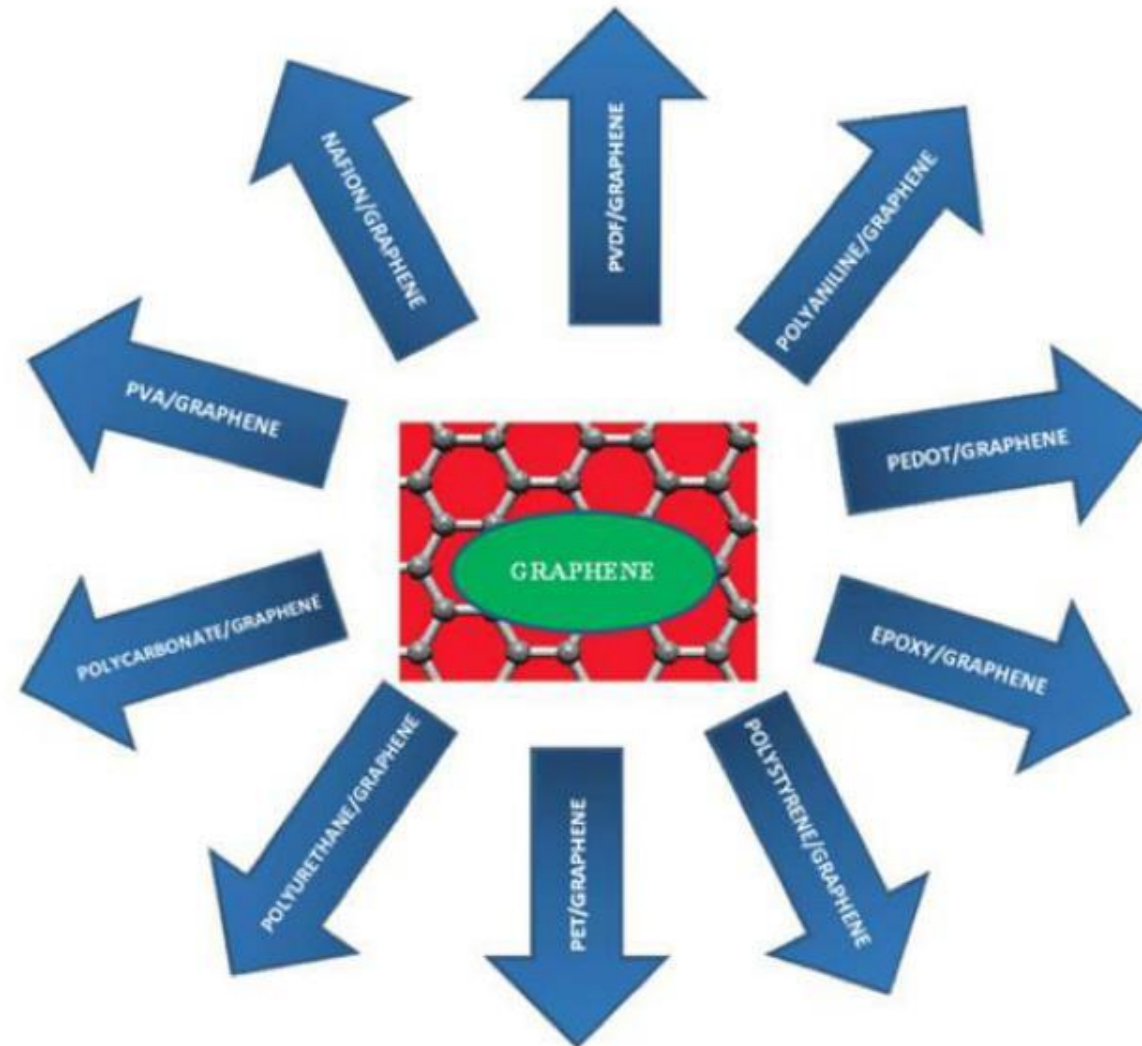
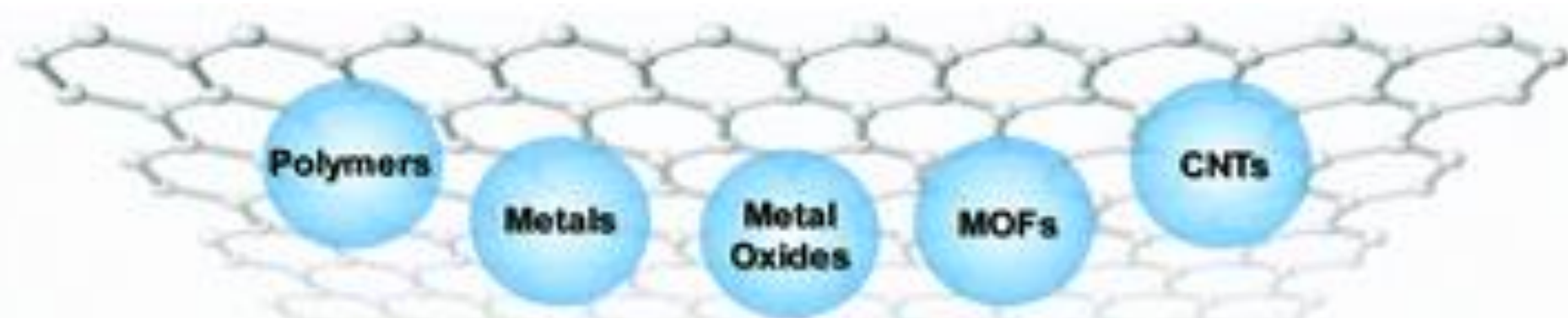
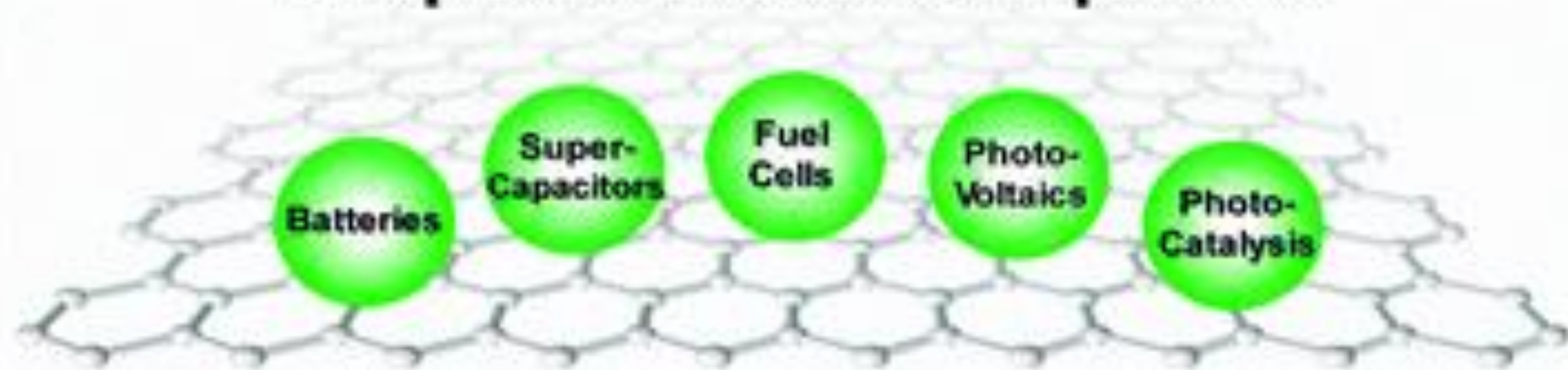


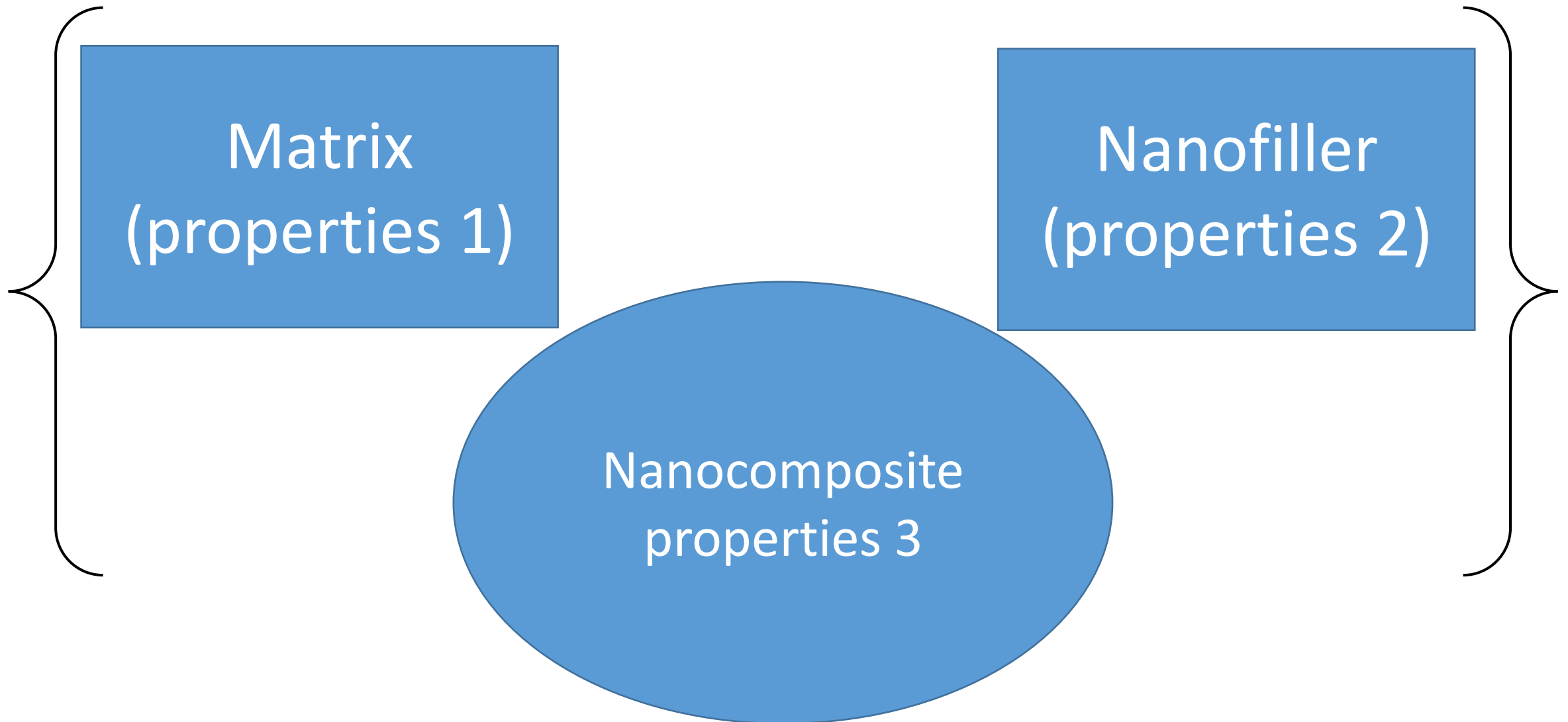
Figure: Polymer-Plastics Technology and Engineering, 52: 319–331, 2013



Graphene-Based Composites



What is a composite



Effects of Adding Graphene to Common Polymers

- ***Epoxy/Graphene-***

Composite strengthens the thermal conductivity of the common adhesive Epoxy.

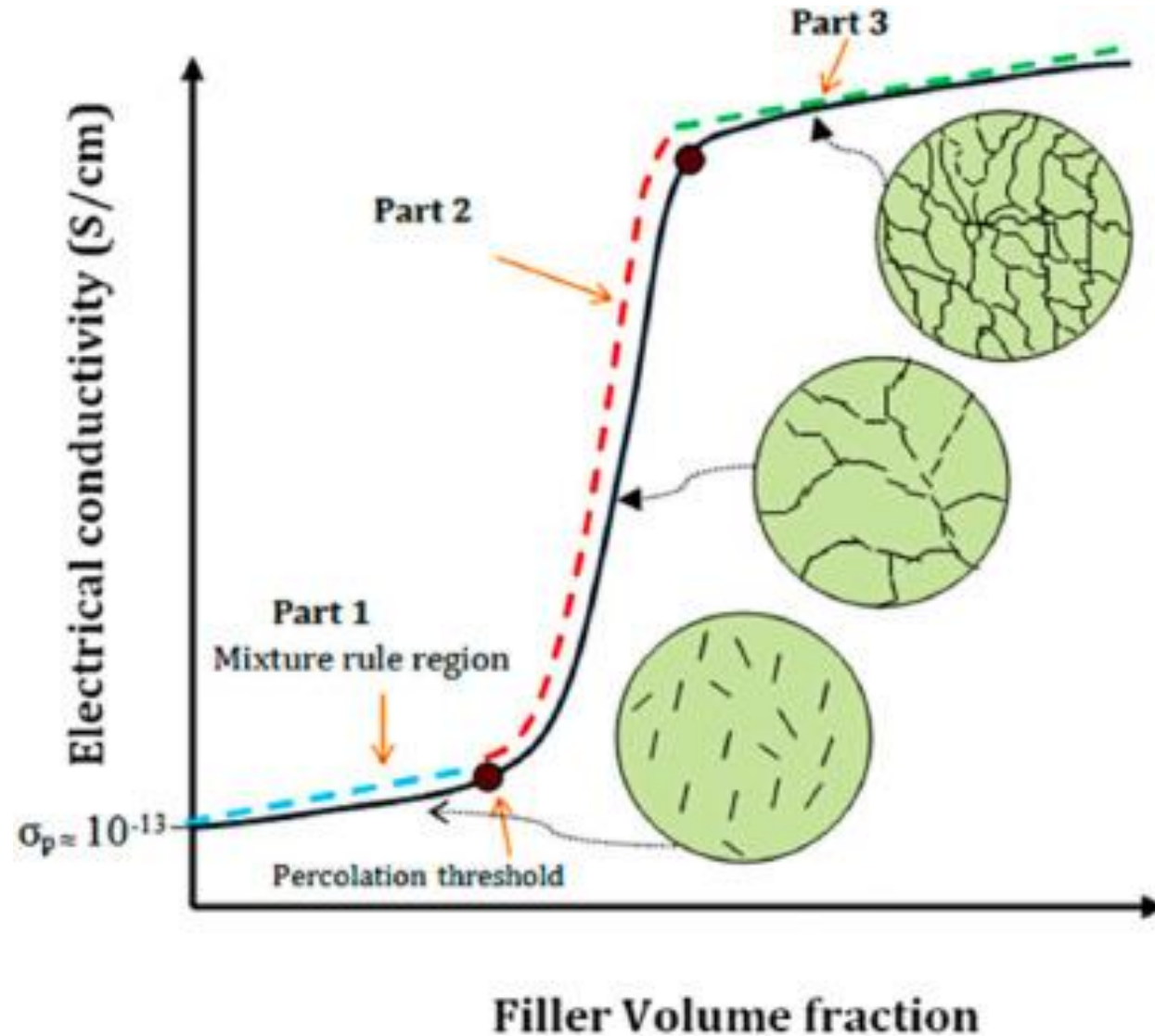
Bolsters abilities to be used as thermal interface

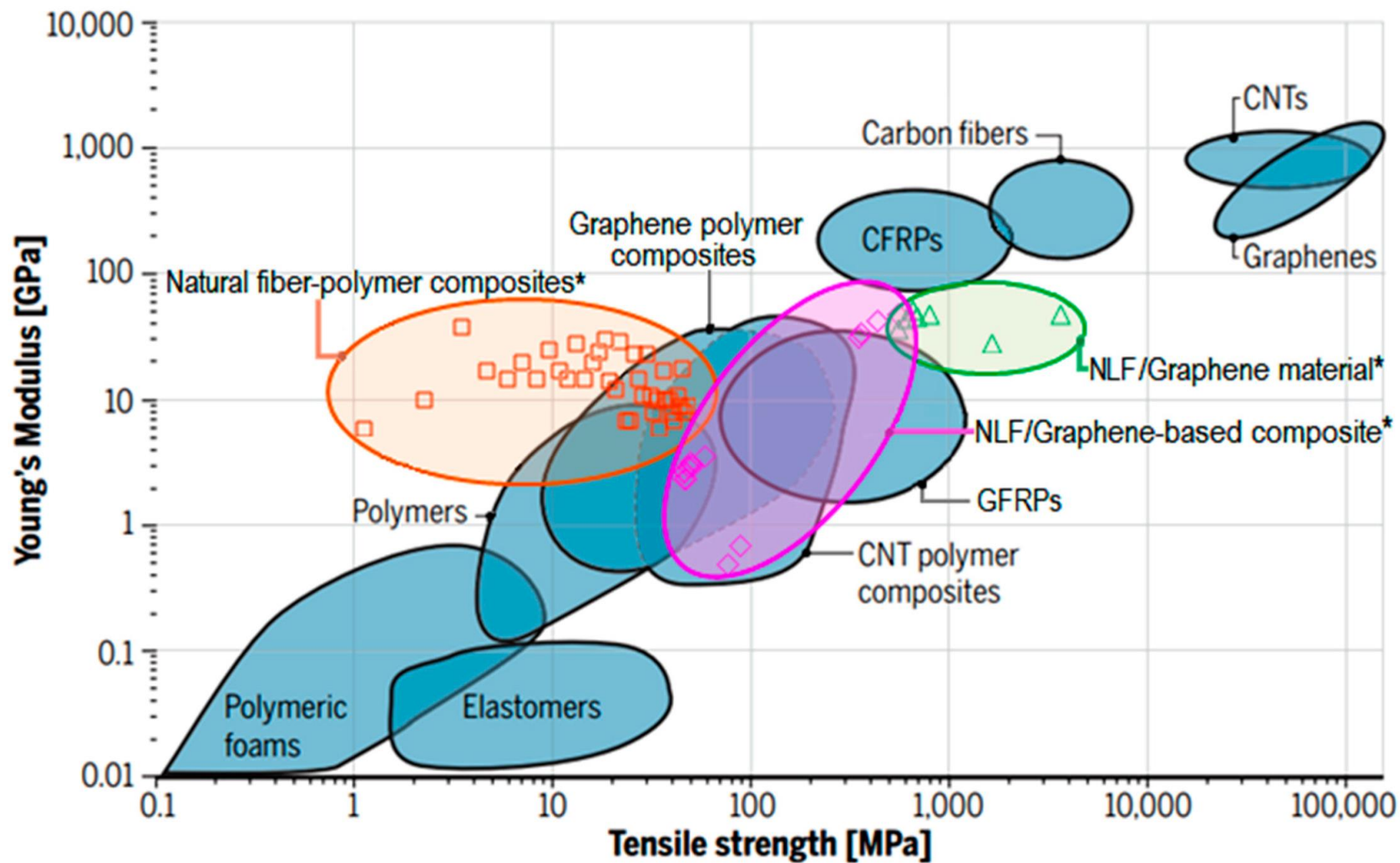
- ***Poly Styrene/Graphene***

Introduction of Graphene improves electrical conductivity and expands uses.



Percolation threshold in graphene polymer composites

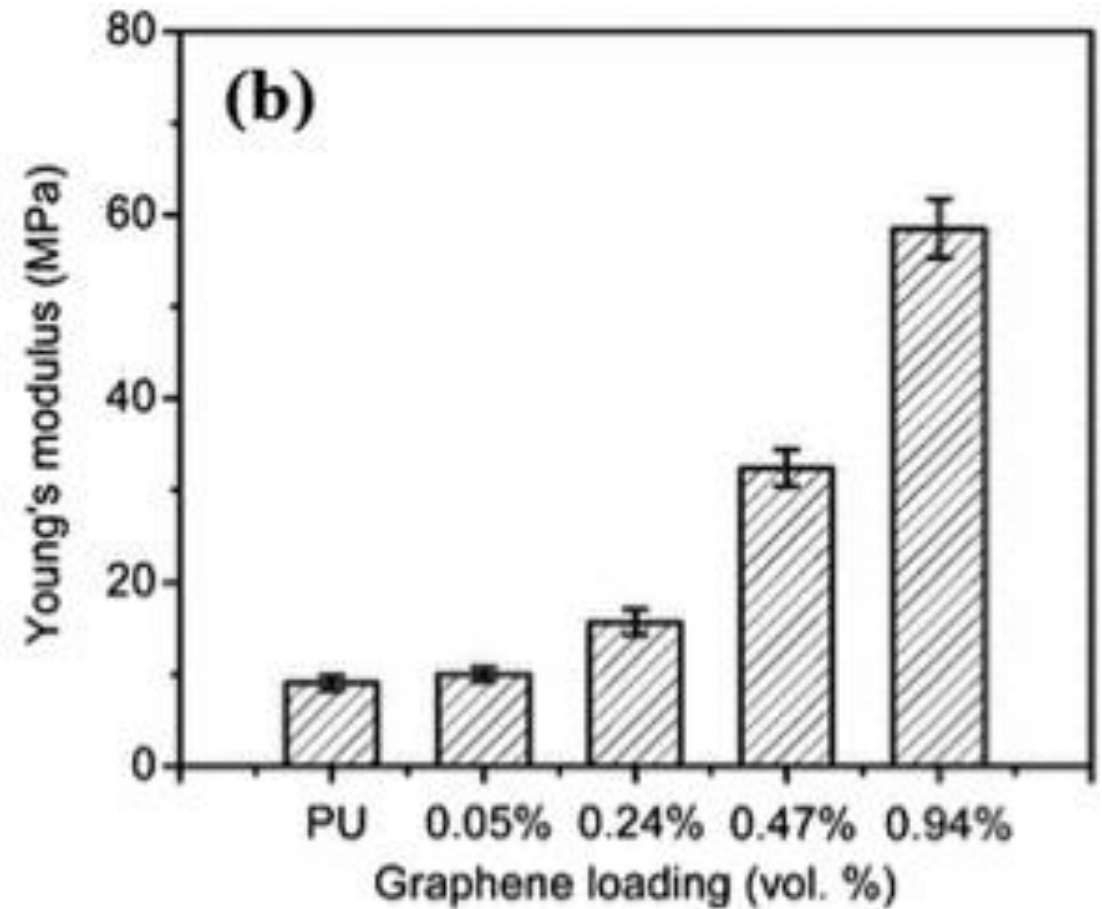
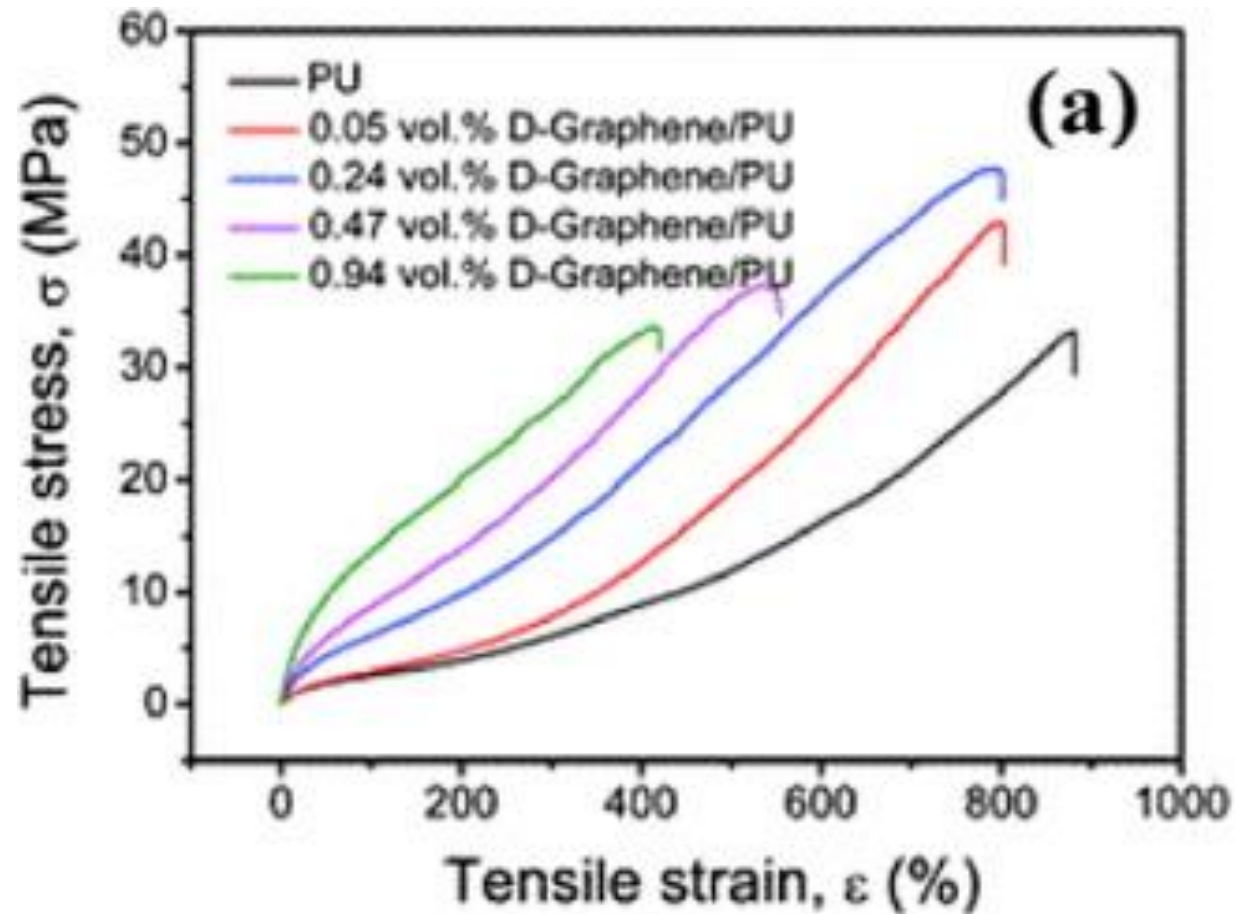




Graphene composites: Improvement in mechanical properties

Filler type and % loading	Matrix	%increase in tensile strength	%increase in elastic modulus
0.7 wt% GO	PVA	76	62
2 wt% GO	PVA	92.2	-
1 wt% <i>in-situ</i> CRGO	PMMA	60.7	-
1 wtt% TRGO	PMMA foam	13	20
0.5 wt% GO	PCL film	77	49
0.5 wt% graphene	PA12	32.2	-
0.05 wt% in-situ TRGO	Polyester	72.2	-
0.54 vol% GO	Epoxy	10	25

Graphene composites: Improvement in mechanical properties

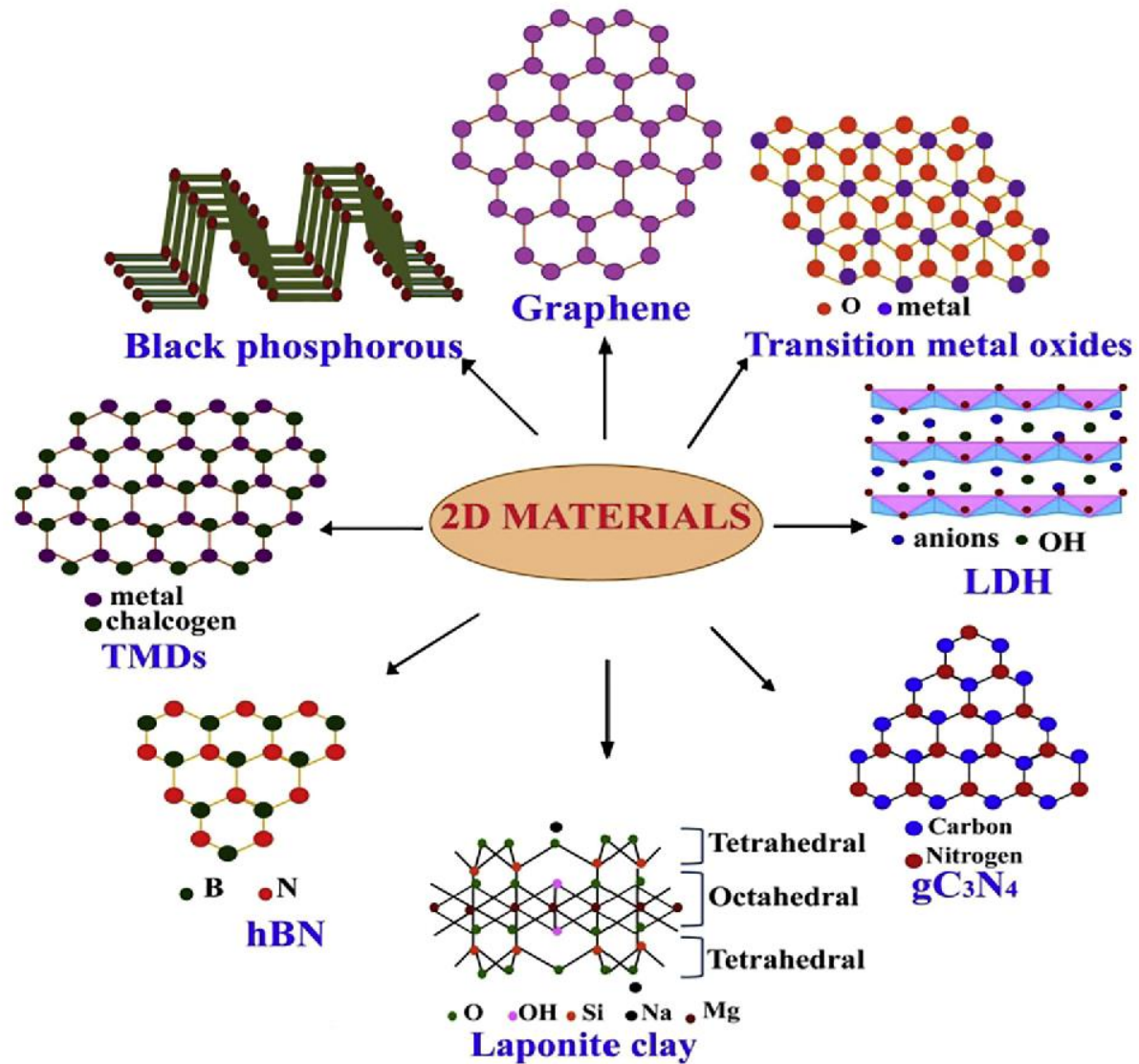


Composite application areas

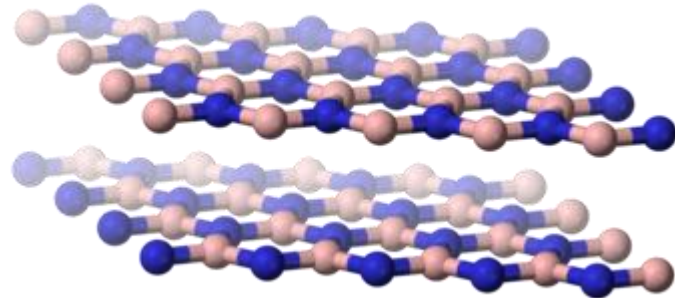
- Automotive
- Rubber
- Plastics
- Aerospace
- 3D printing
- Coating and barrier
- Polymers and epoxies
- Carbon fiber reinforced polymer
- Sports equipment

Read about “ Space elevator
concept using graphene and
Carbon nanotube”

2D Materials



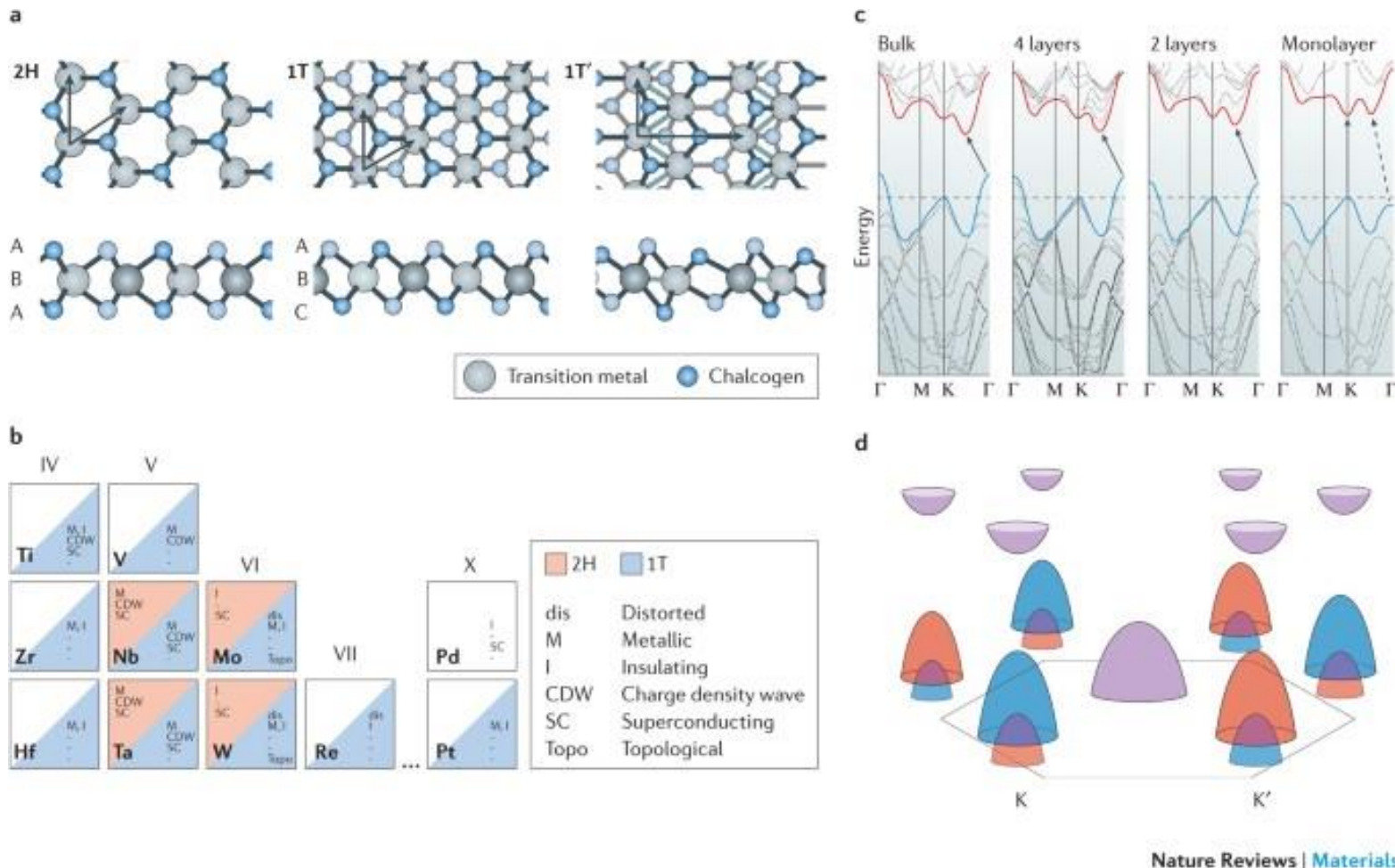
Boron Nitride



Hexagonal form (h-BN)
hexagonal analogous to graphite

Molecular weight	24.83
Density (Theoretical)	2.27 g/cm ³
Crystal Structure	Hexagonal
Color	White
Dielectric Strength	800-1000 volts/mil
Dielectric Constant	4
Coefficient of Friction	0.2-0.7
Electrical Resistivity (at 298 K)	1.7x10 ¹³ ohm-cm
Thermal Expansion (Directional)	0.8-7.5x10 ⁻⁶ /°C; 25-1000°C
Specific Heat (at 298 K)	0.117 cal/g-K
Thermal Conductivity (at 293 K, directional avg.)	est. 0.08 cal/ (cm-sec-K)
Use Temperatures	1800 C Reducing/inert 1400 C Vacuum 1100 C Oxidizing

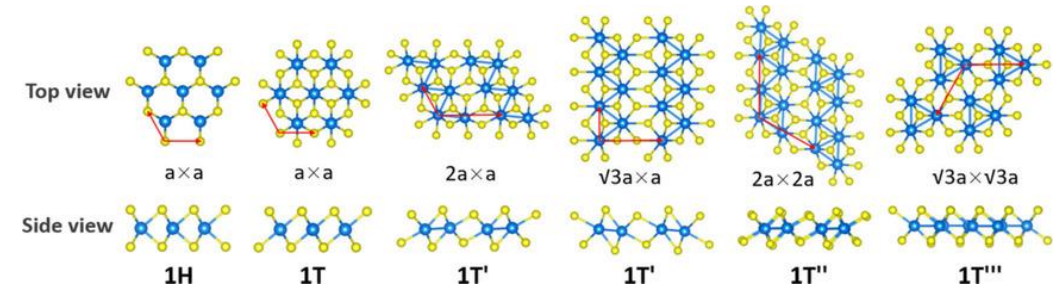
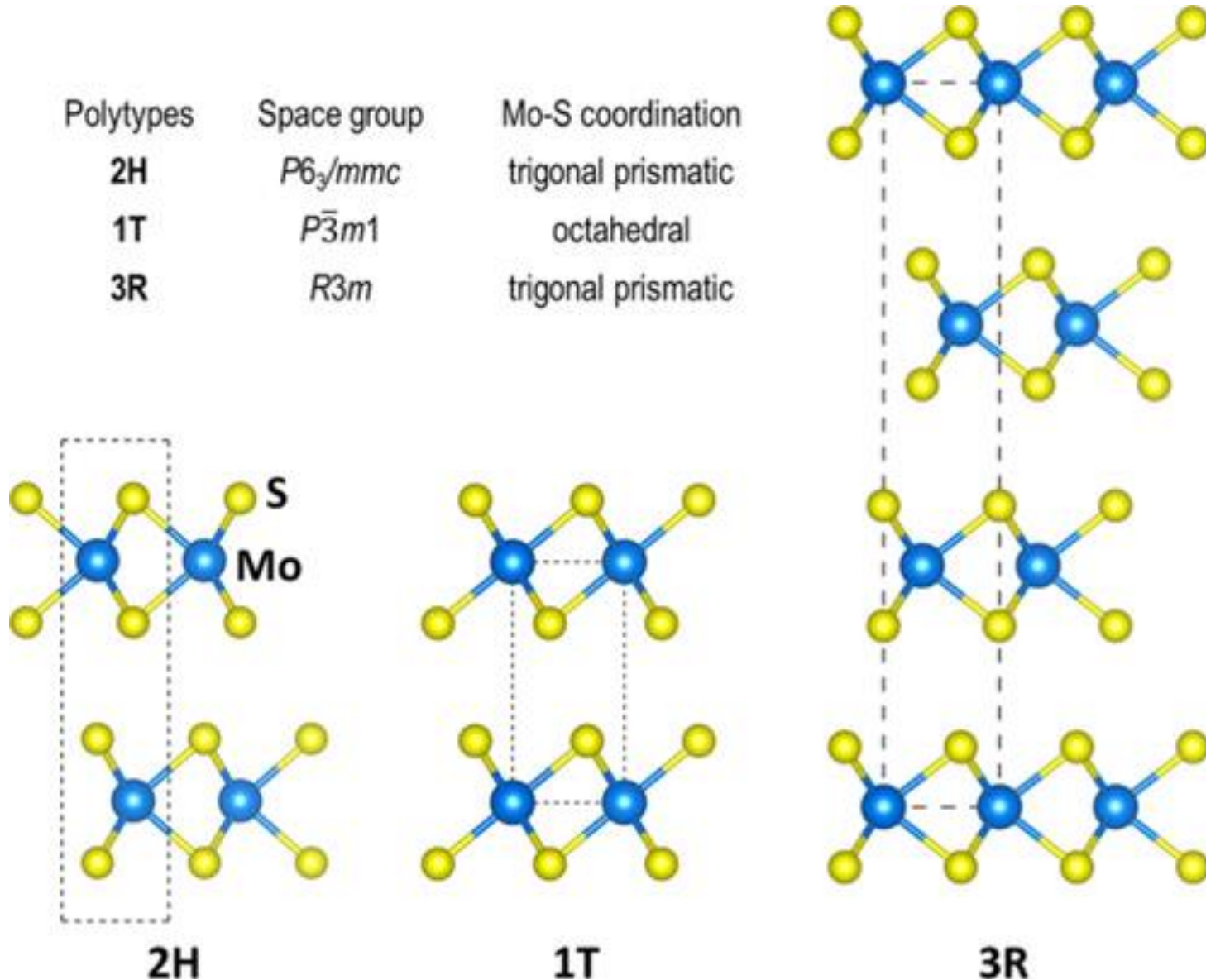
Family of TMDs



Nat Rev Mater **2**, 17033 (2017)

- ❑ Zero electronic bandgap – Graphene
- ❑ stimulated the search for 2D materials with semiconducting character
- ❑ TMDCs exhibit a unique combination properties:
 1. atomic-scale thickness
 2. direct bandgap
 3. strong spin–orbit coupling
 4. favorable electronic and mechanical properties

Crystal structure of MoS₂



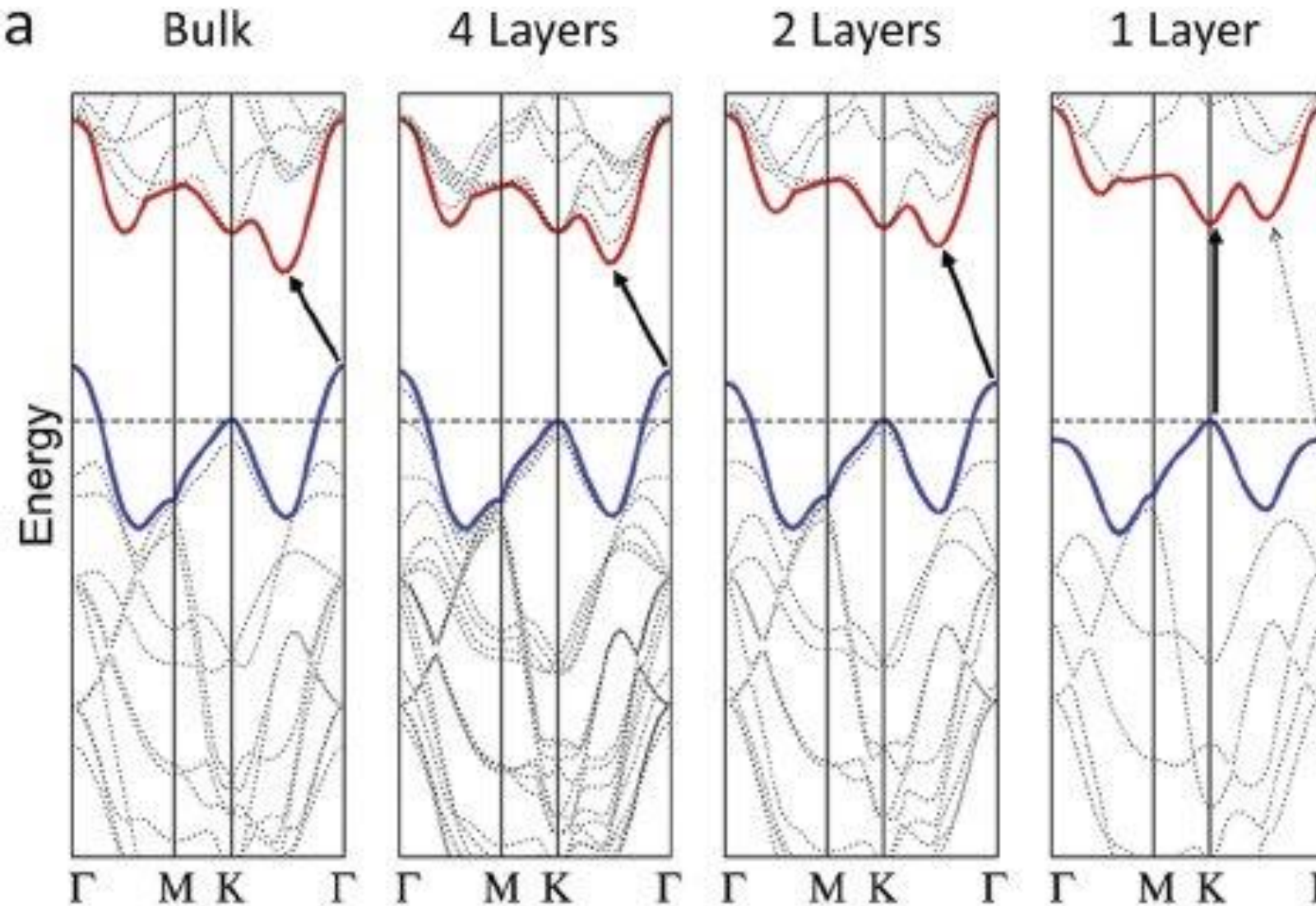
✓ **2H MoS₂ phase :**

- edge-sharing trigonal prisms

✓ **Metastable phases (1T, 1T', 1T'', and 1T'''):**

- ✓ Composed of the edge-sharing octahedra, in which the neighboring Mo-Mo distances differ

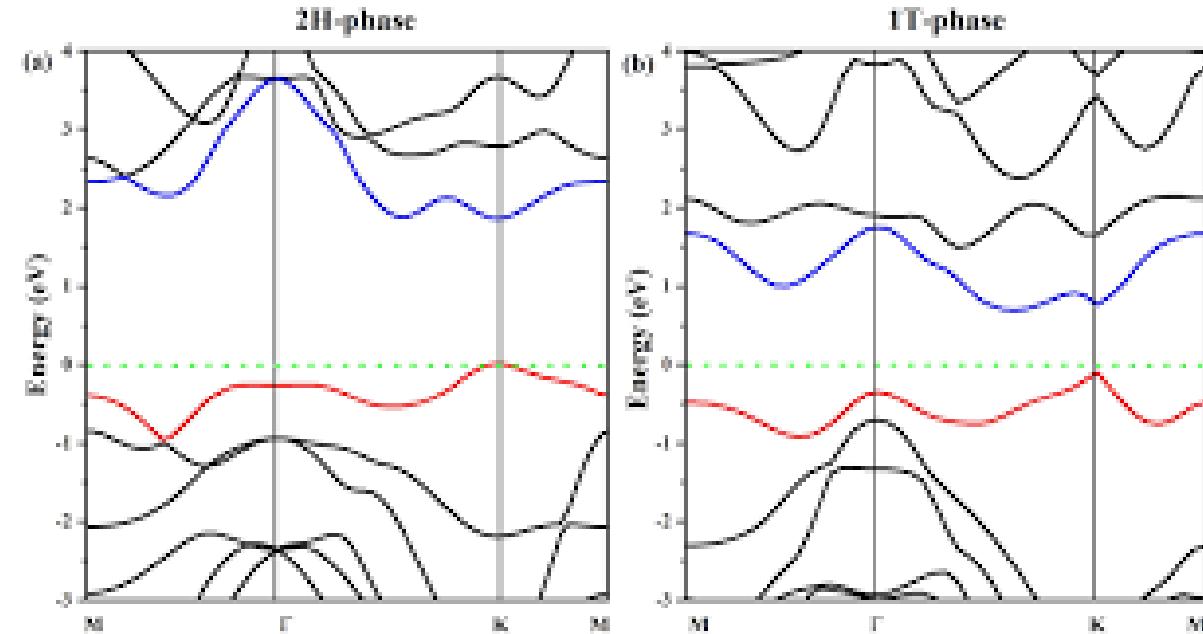
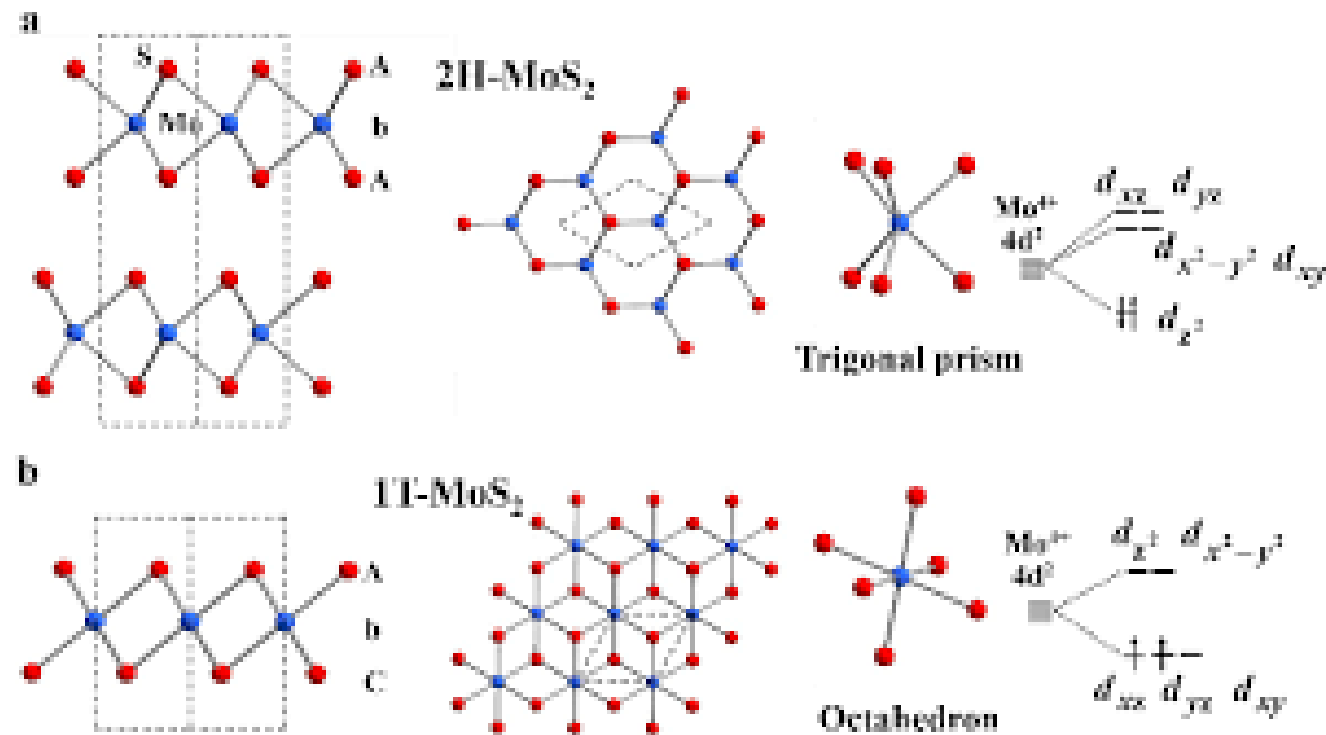
Layer dependent MoS₂ properties



Nano Lett. 2010, 10, 4, 1271–1275

- More than one-layer MoS₂ as indirect bandgap semiconductor with negligible photoluminescence.
- Monolayer, has strong photoluminescence emerges, indicating an indirect to direct bandgap transition in this d-electron system.
- Quantum confinement in layered d-electron materials

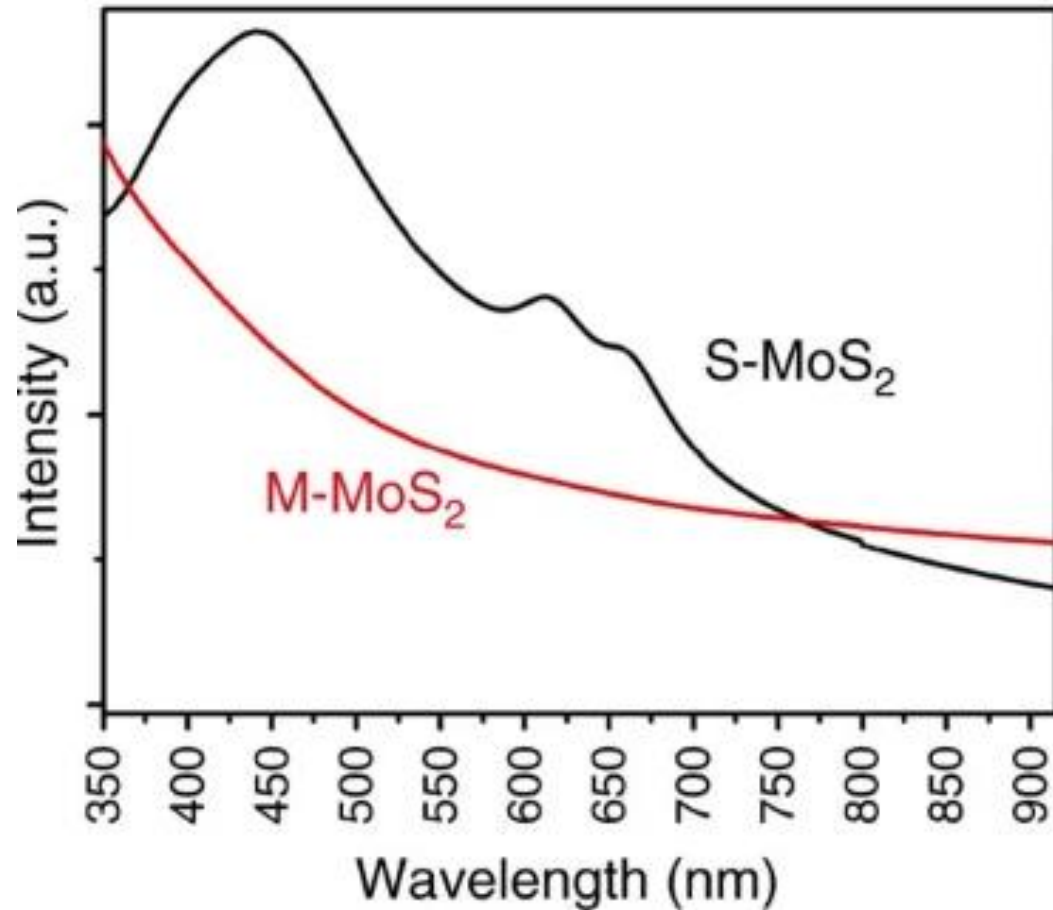
Comparison of 1T and 2H phase MoS₂



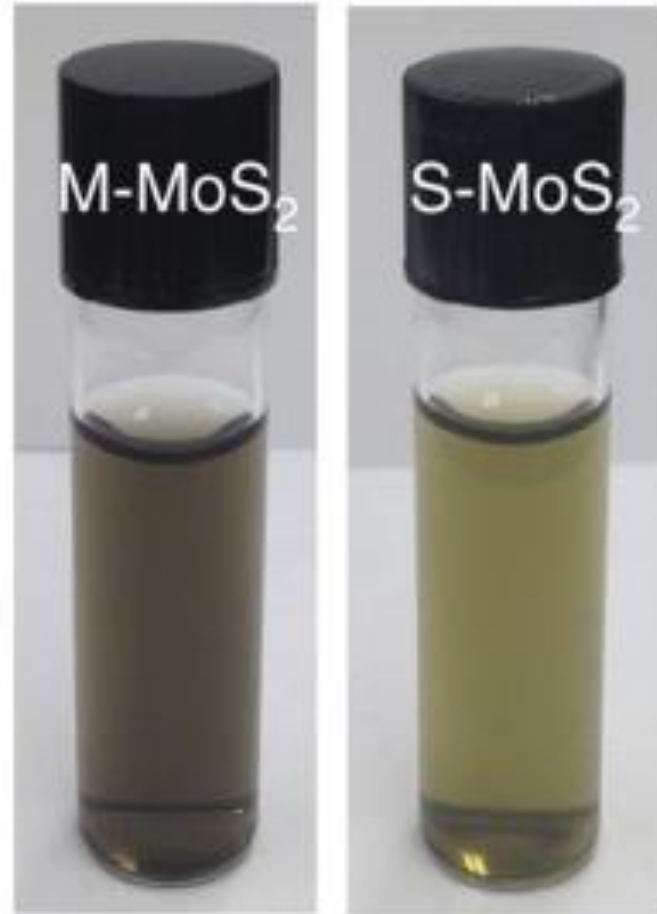
J. Mater. Chem. C, 2019,7, 12312-12320

<https://doi.org/10.1002/anie.201710512>

Optical properties of MoS₂

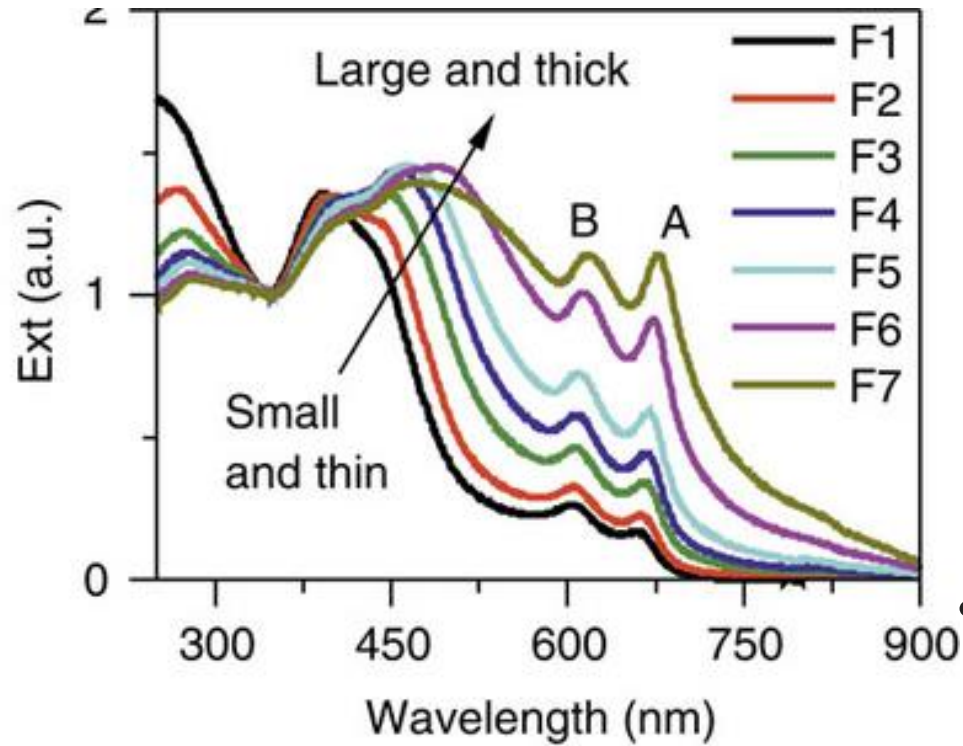


Nat Commun 7, 10672 (2016).

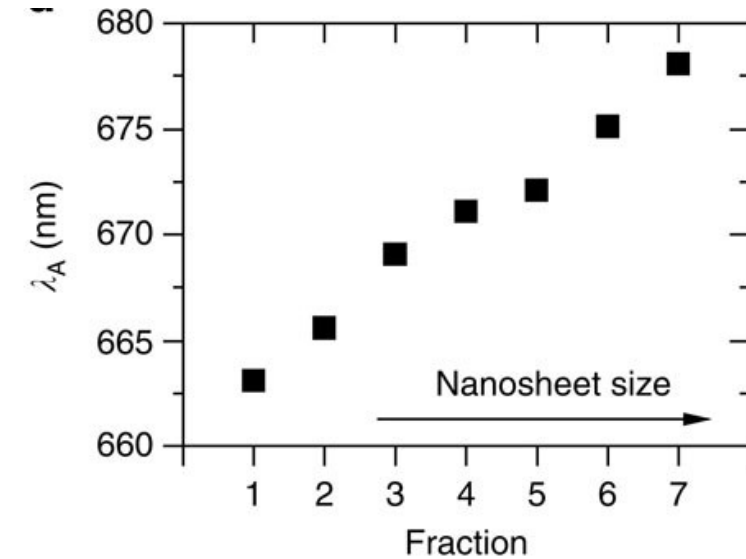
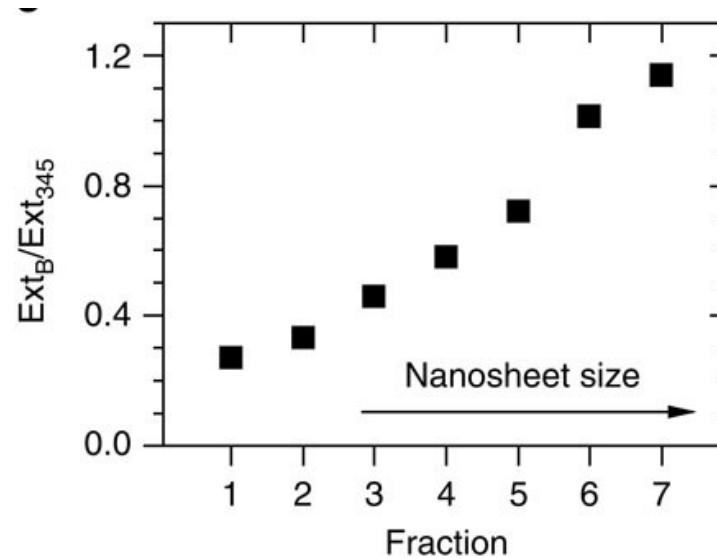


- S-MoS₂ exciton peaks are associated with the energy split from the valence band spin-orbital coupling in S-MoS₂
- M-MoS₂ has no salient absorption bands but a monotonic change that is indicative of its metallic property.

Effect of MoS₂ nanosheets size on optical properties

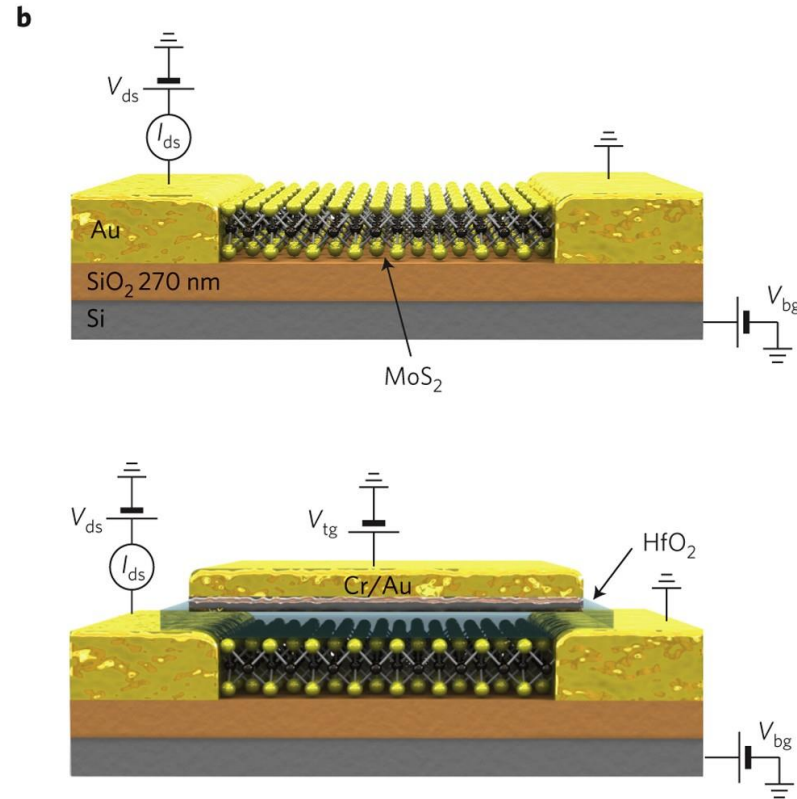
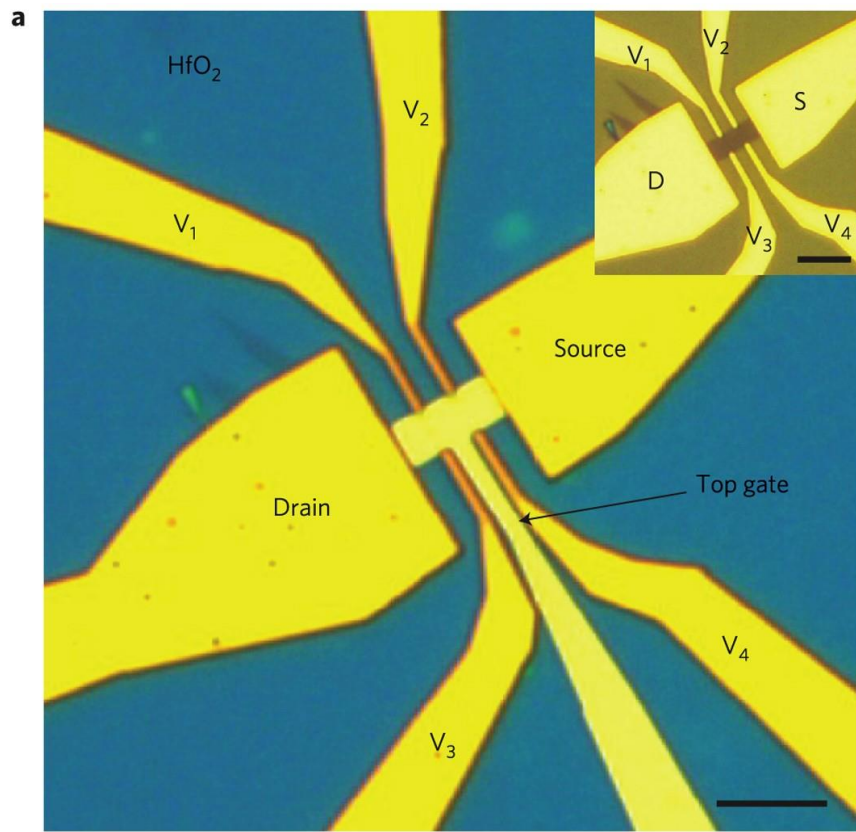


Nat Commun **5**, 4576 (2014)



- A-exciton and the relative intensity of the B-excitonic transition varied systematically with fraction number (that is, with nanosheet size)
- MoS₂ absorbance and extinction spectra variation because of both confinement and nanosheet edges on the electronic structure of the material.

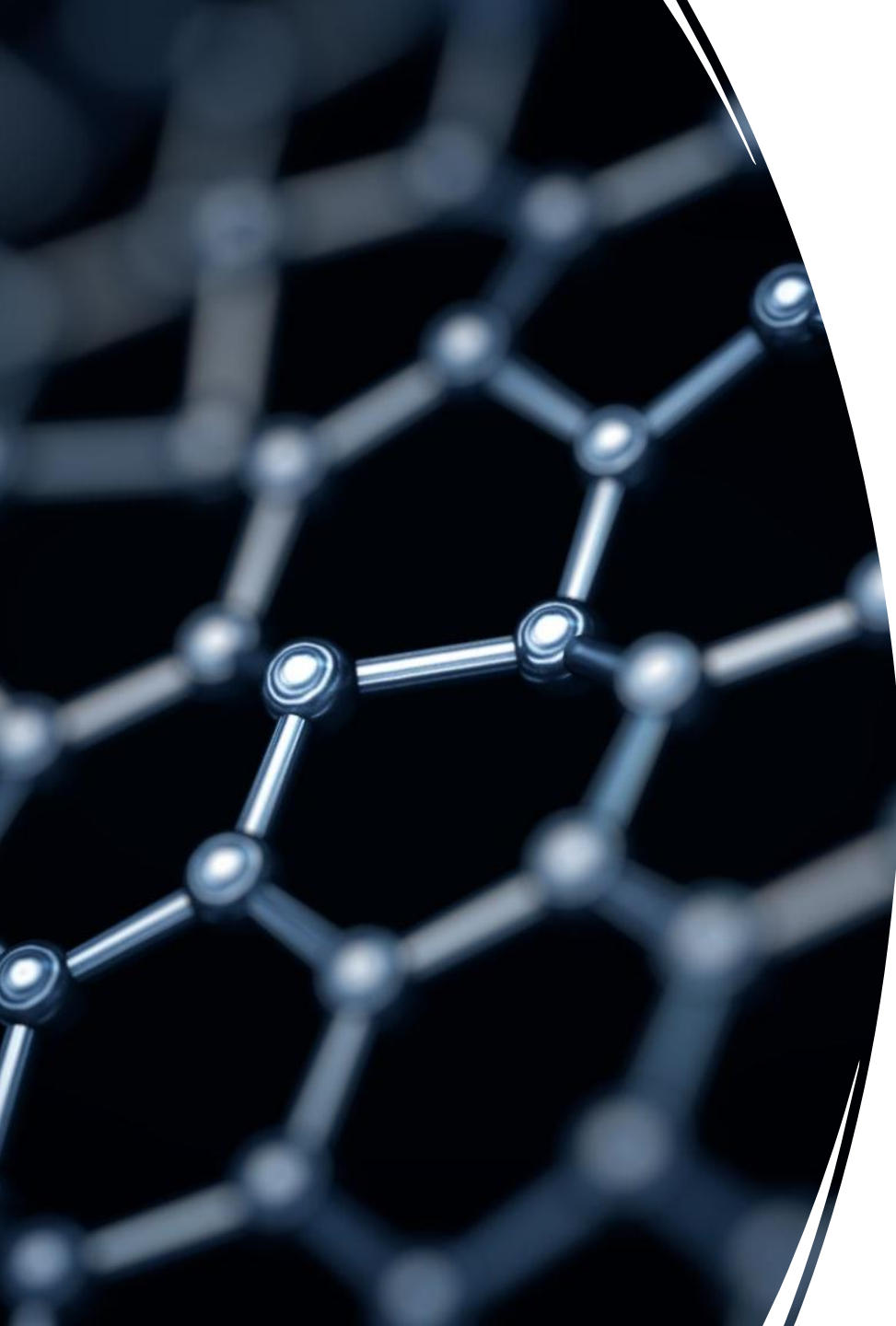
Electronic property of monolayer MoS₂



Nature Mater 12, 815–820 (2013)

Monolayer MoS₂ due to quantum-mechanical confinement allows room-temperature FETs with an on/off ratio exceeding 10⁸.

2D Materials and Applications



Syllabus to cover – Unit 2

- Traps and defects
- Mechanical properties
- Strain effects on electrical and vibrational properties (5 marks assignment, one page)
- Theoretical methods
- Silicene and Germanene
- Properties of Silicene and Germanene (5 marks assignment, one page)
- Last date to submit in GCR by 23rd June 2024
- 2D topological insulator
- Phosphorene: a novel 2D material

2d crystal based heterostructures

A legoland of 2D materials

Handling of 2D heterostructures:
practical issues

Tunnel diodes and Transistors
based on 2D heterostructures

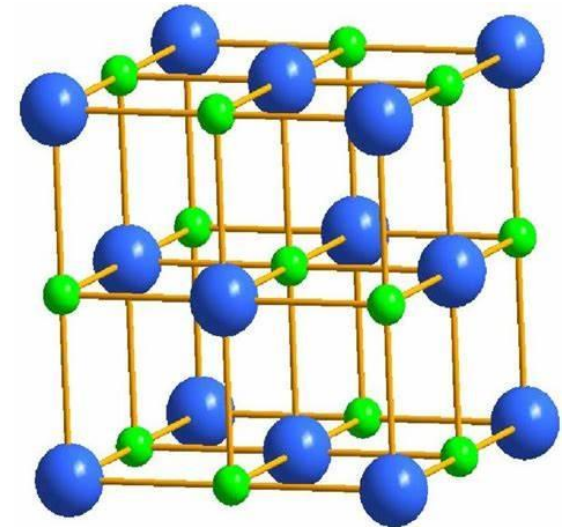
Types of Imperfections

- The concept of a perfect crystal is extremely useful.
- Real crystals are not perfect.
- As the name implies, the most important types of defects are

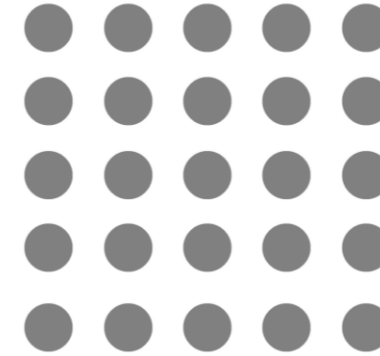
1. Point defects

2. Line defects

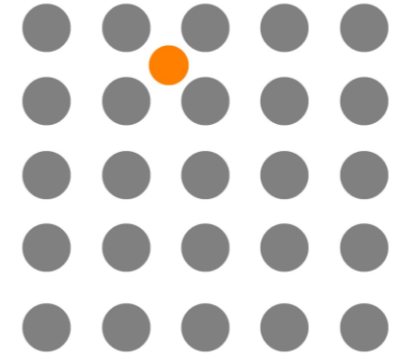
3. Surface defects



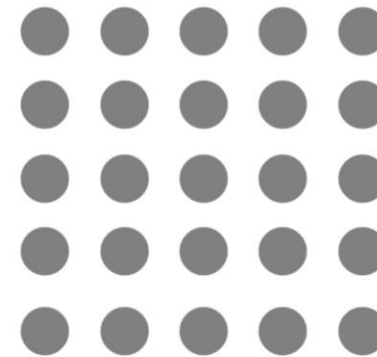
1. **Point defect:** An irregularity in the crystal structure, localized in the lattice.
2. An example is a foreign atom or impurity in the crystal.
3. A crystal usually contains all sorts of impurities that attach themselves to it during crystallization.
4. Particularly small atoms are present in the atmosphere in which the crystal is grown such as oxygen, nitrogen, and hydrogen.
5. An impurity is substitutional if it occupies a lattice site from which the host atom has been expelled.
6. Interstitial if it occupies a position between the host atoms.
7. The region surrounding an impurity is strained. The extent of strain depends on the kind of impurity atom and its location.
8. An appreciable number of substitutional impurities may be present only if the size of impurity is not far from that of host atom otherwise strain energy required would be prohibitive.



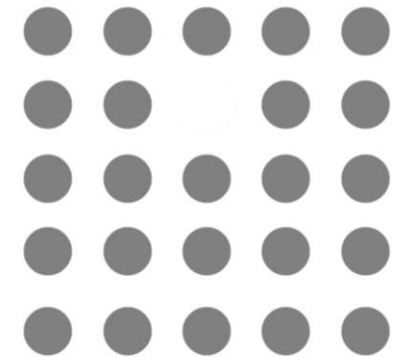
Perfect crystal



Interstitial atom



Perfect crystal



Missing atom

Point defect: Similarly, only small atoms can exist in large numbers as interstitial impurities because the space between host atoms is small.

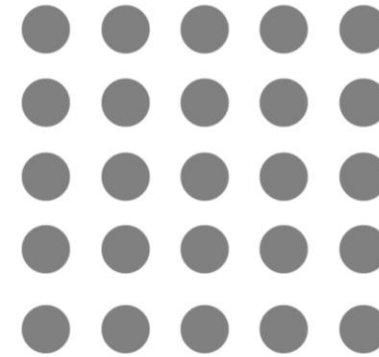
-Atoms are tightly packed in metals.

Vacancy: An empty lattice site from which regular atom has been removed.

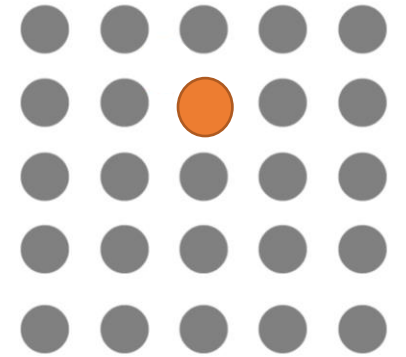
In metals, as in other solids vacancies are created by thermal excitation provided temperature is very high as the atoms vibrate around, some atoms require enough energy to leave the site permanently.

When the regular atom leaves, the region surrounding vacancy is distorted because lattice relaxes.

This contributes to the irregularity of the lattice.



Perfect crystal

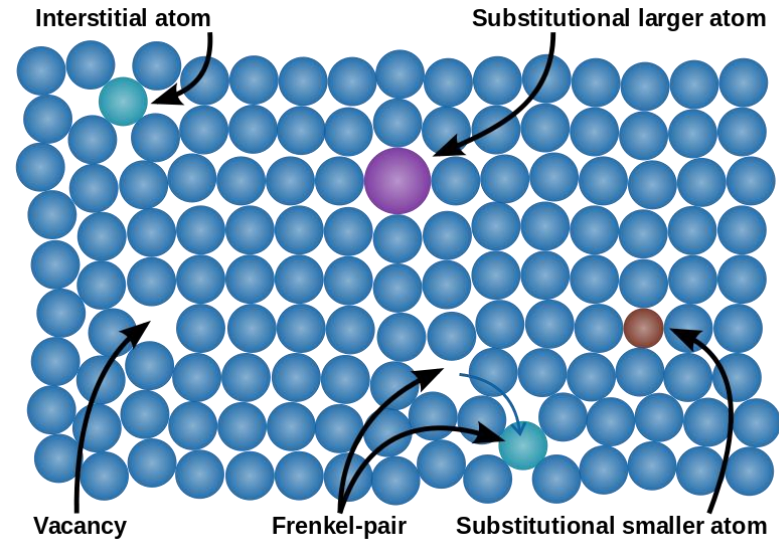


Substitutional atom

Point defect: A regular atom in an interstitial position: Considerable energy is needed to pull an atom from a regular to an interstitial position.

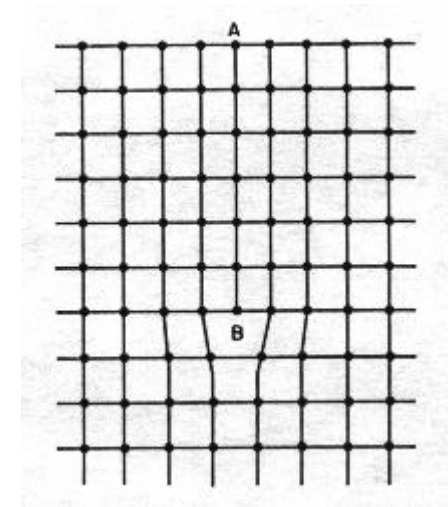
-This type of defect is created thermally only at temperatures near the melting point of solid.

-One can also create this kind of defect by irradiation.

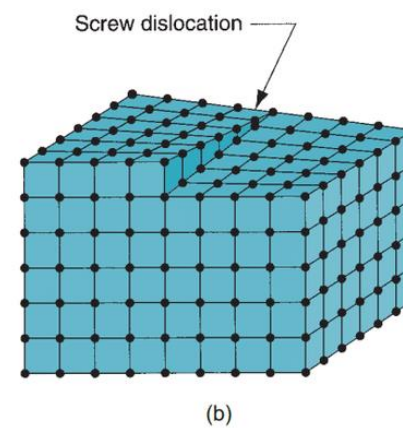
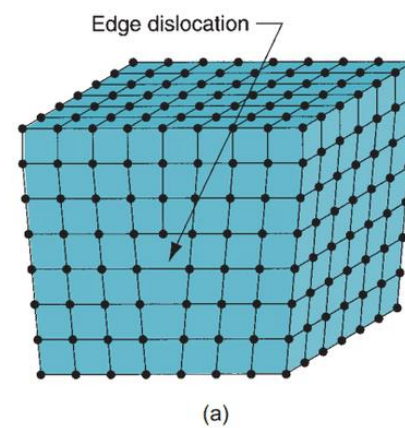
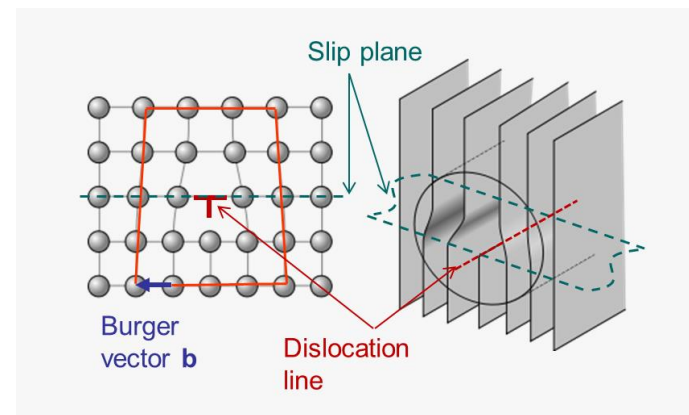
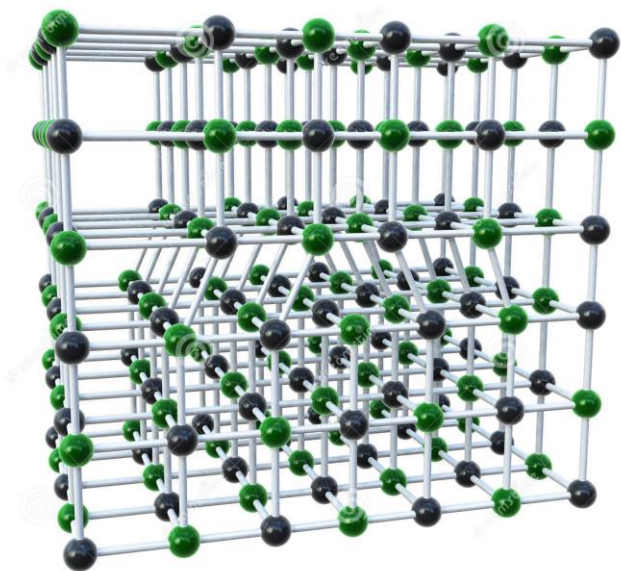
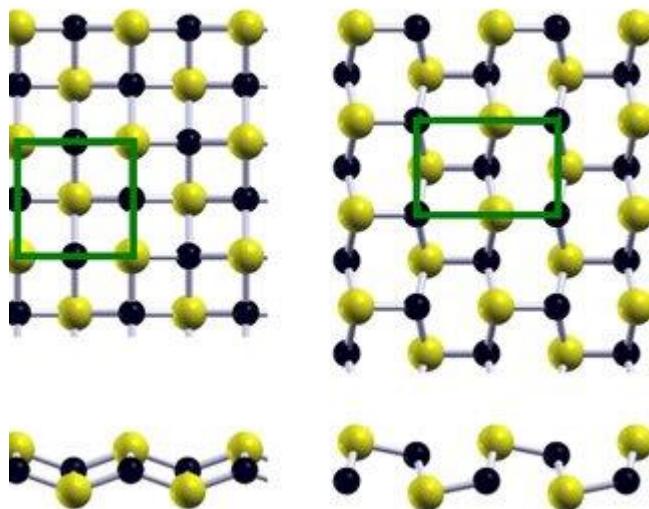


Line defect: A line defect is also called as dislocation. Linear array of misplaced atoms extending over a considerable distance inside the lattice.

Surface defect: In a surface defect, the crystalline irregularity extends in two dimensions. Most solids are not single crystals but polycrystals in which a sample is composed a large number of single crystals called **grains**.

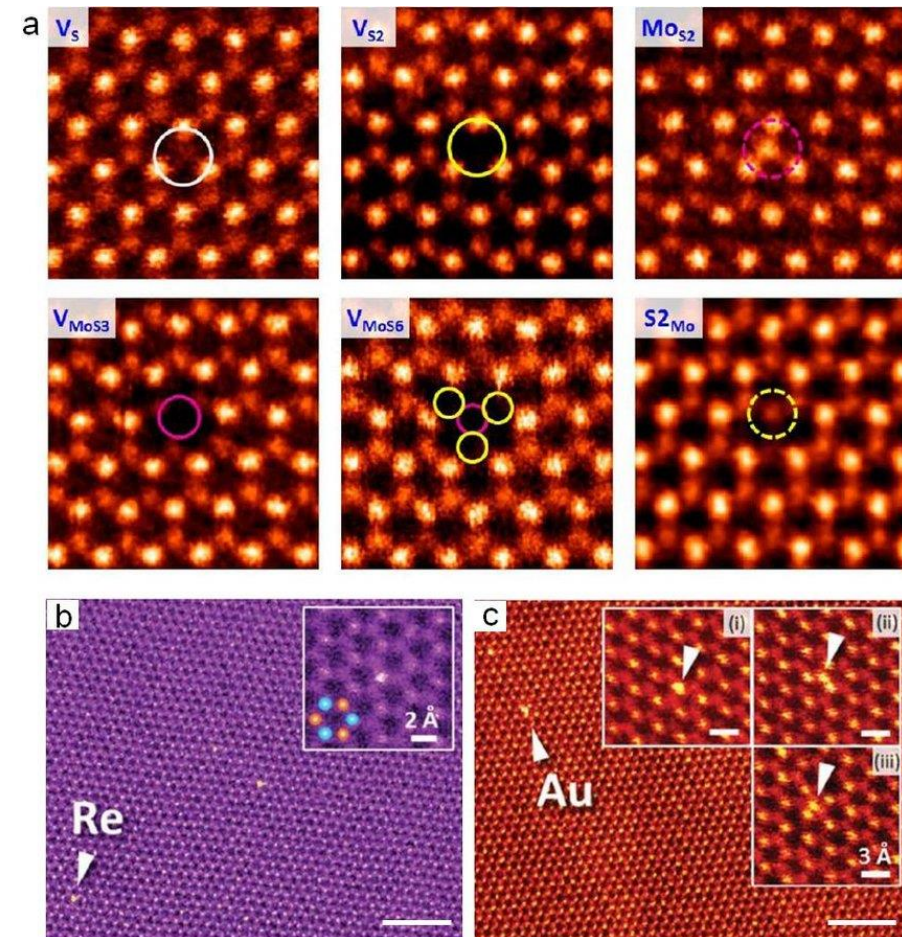


7 (0.224) δ 0.206 (0.252) κ



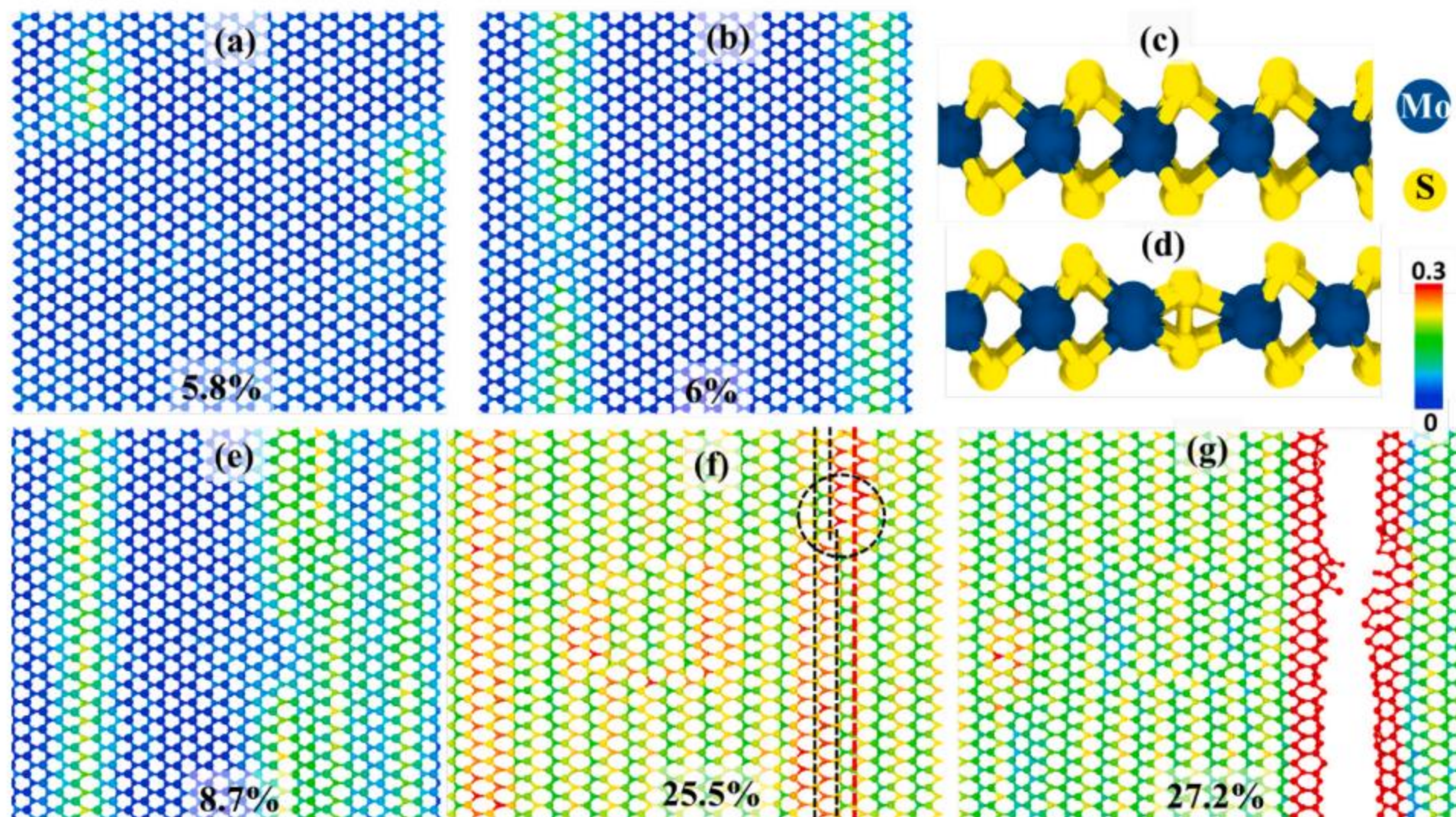
Defects in MoS₂

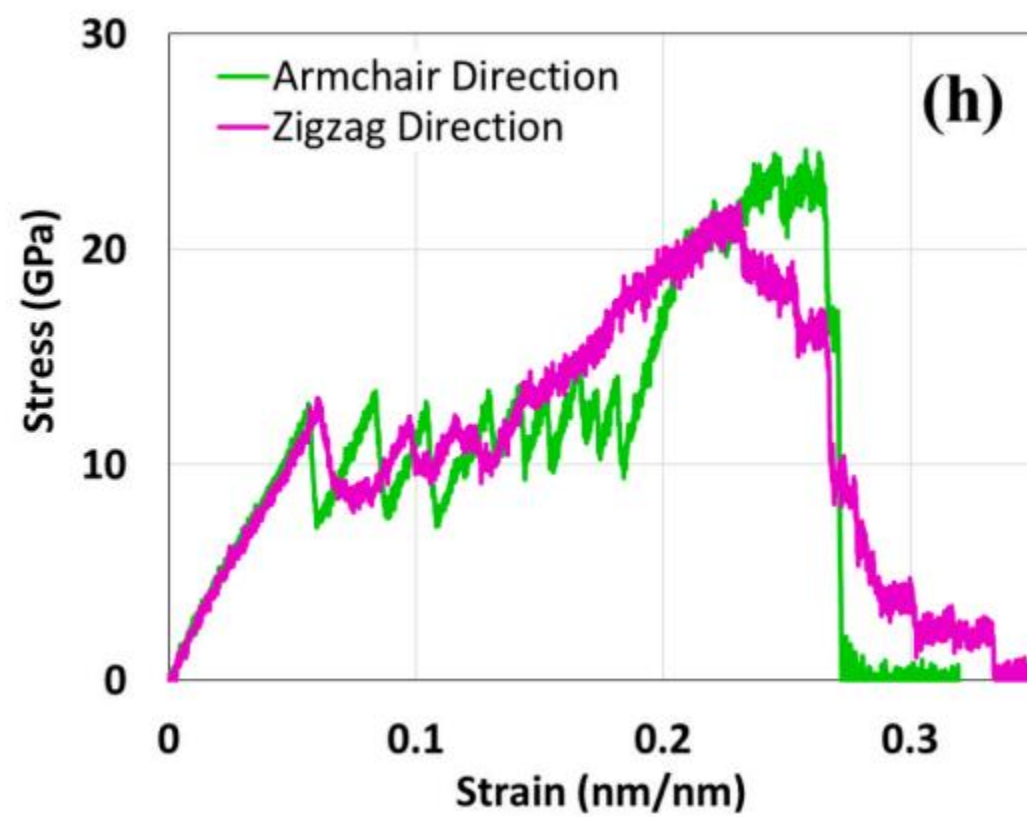
- Defects can cause major changes in the properties of a material, leading to either desirable or unwanted effects. For example, the petrochemical industry has long taken advantage of the catalytic activity of MoS₂ edges, characterized by the presence of a high concentration of defects, to produce petroleum products with reduced sulfur dioxide (SO₂) emissions.
- On the other hand, having a pristine material is a must in electronics. Currently, silicon rules the industry, because it can be prepared in a virtually defect-free manner.



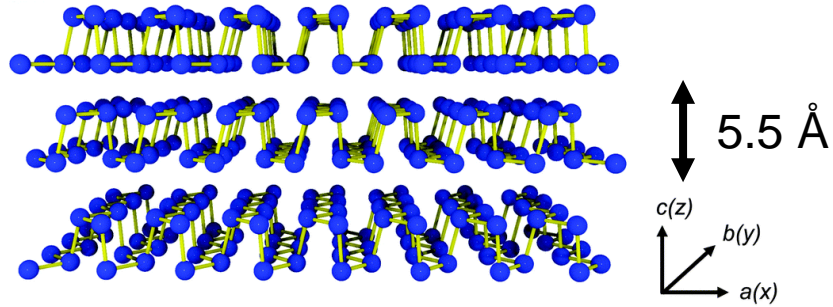
Defects in MoS₂

- In the case of MoS₂, its suitability for electronic applications is currently limited by the presence of naturally occurring defects.

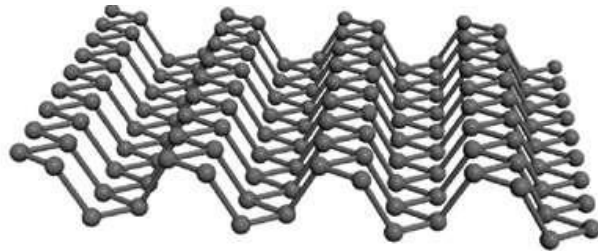




Black Phosphorus



Side view



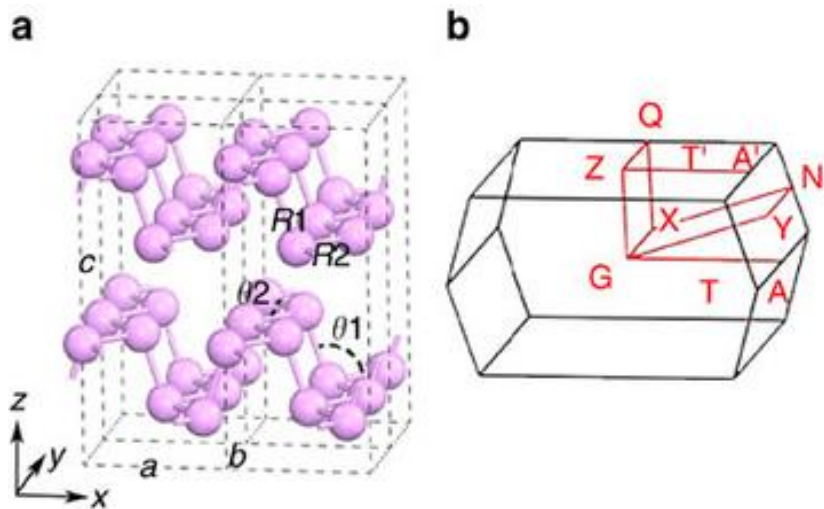
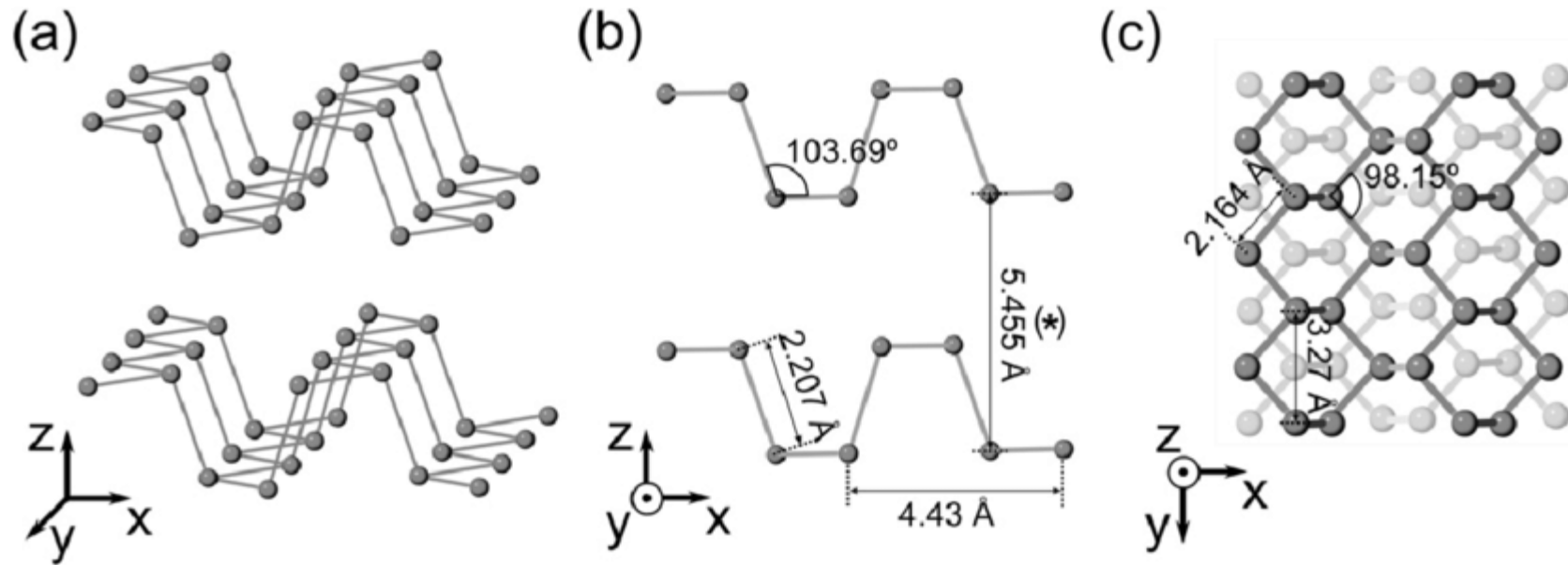
BP (Black phosphorus)

Schematic diagram of the crystal structure of black phosphorus

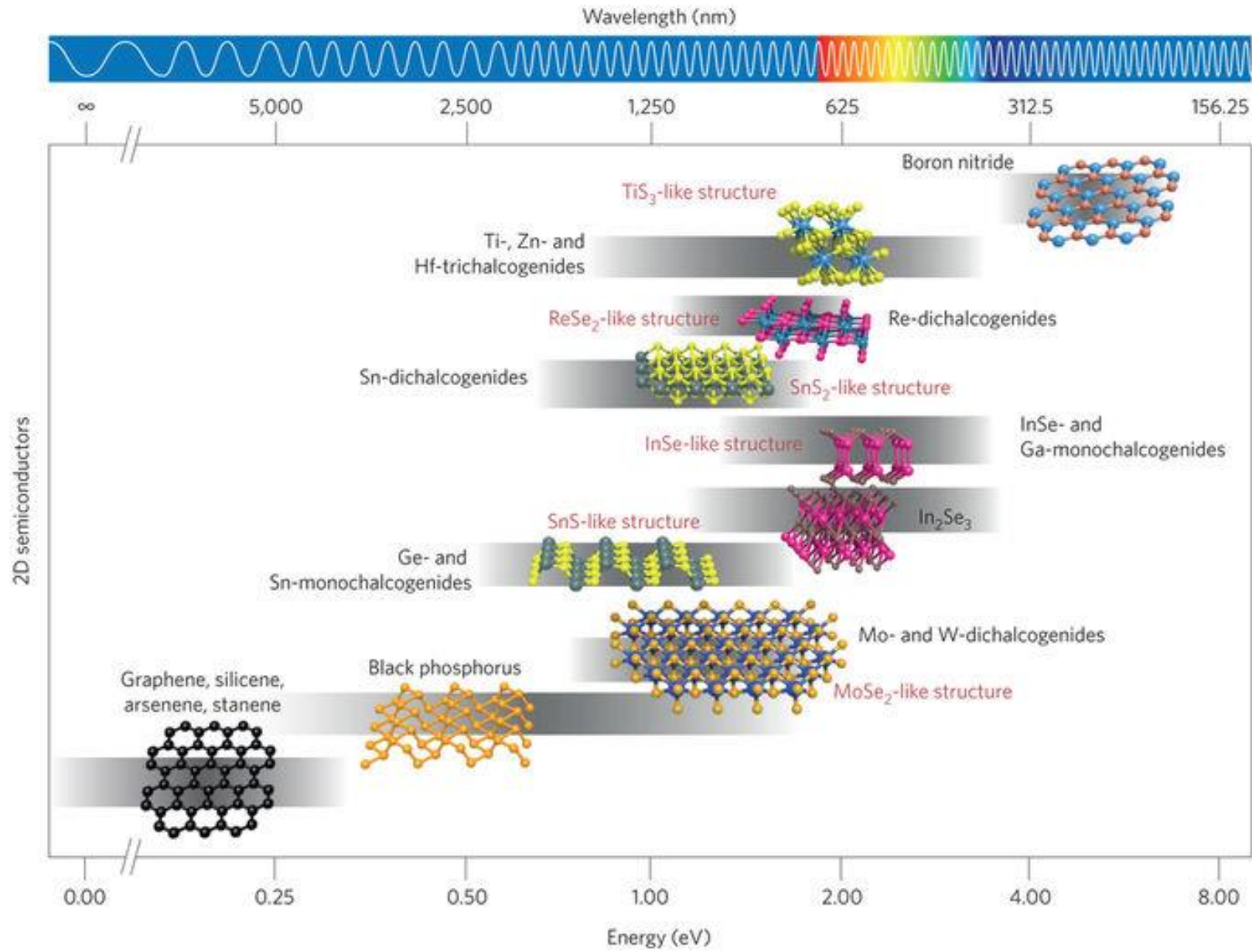
- Least reactive allotrope
- Orthorhombic structure
- Interlinked six membered rings
-
- Each P atom is bonded to three other P atoms
- Puckered honeycomb network
- Individual layers are bonded through van Der Waals interactions

Phonons, photons, and electrons in layered black phosphorus structures behave in a highly anisotropic manner within the plane of layers due to structure

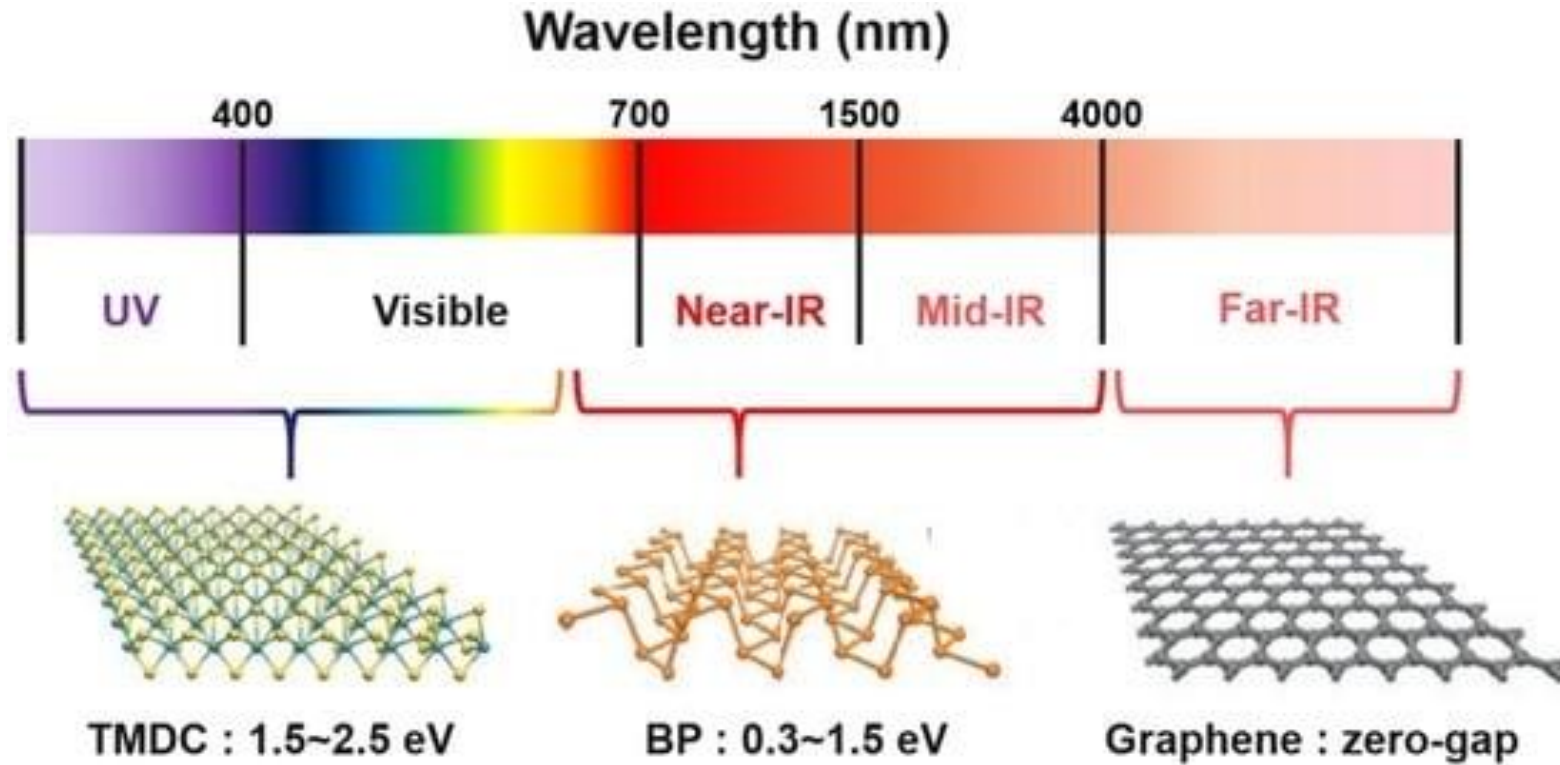
Crystal structure of Black Phosphorus



Bandgap of 2D materials



Band gap of 2D materials



Band structure of Black Phosphorus

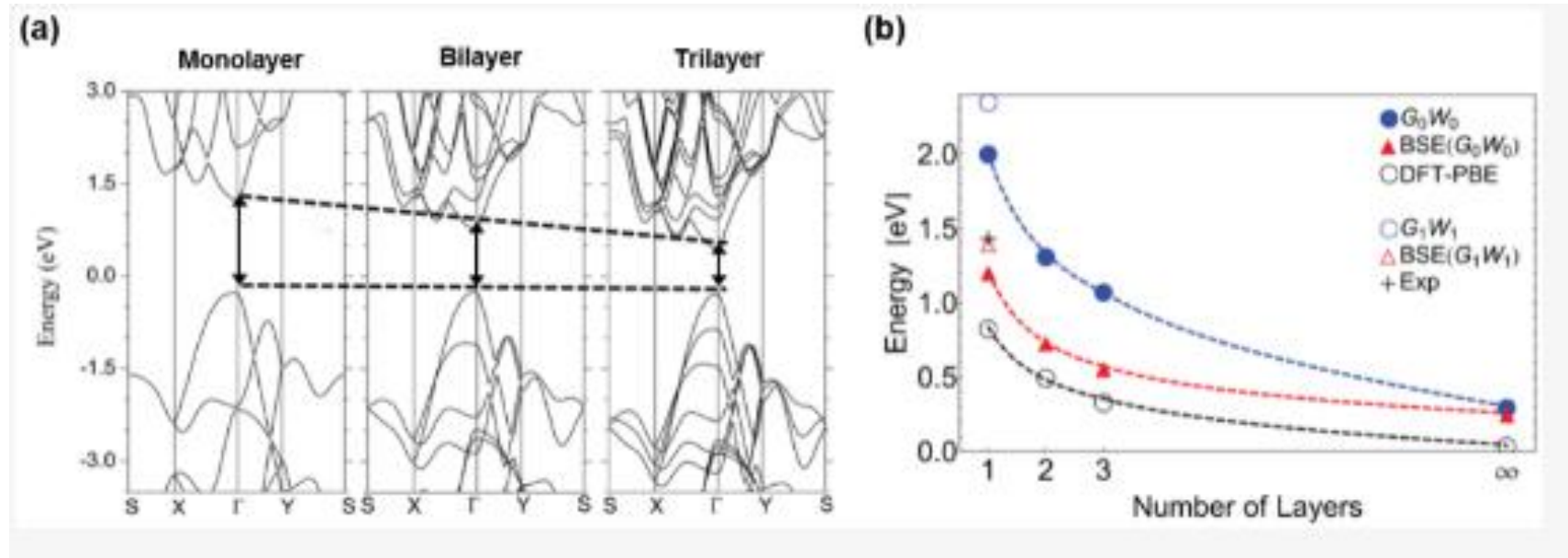


Figure shows the band structures of the monolayer, bilayer and trilayer of black phosphorus constructed by density functional theory calculation with HSE06 hybrid functional.

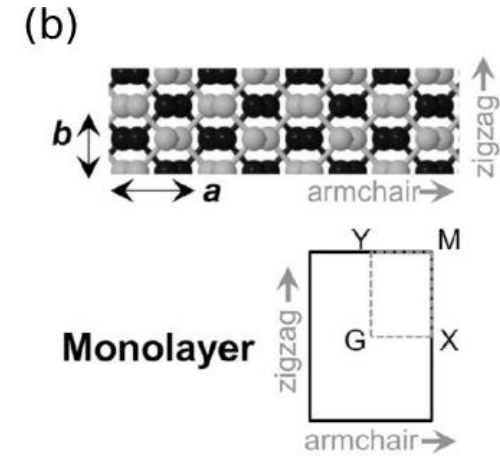
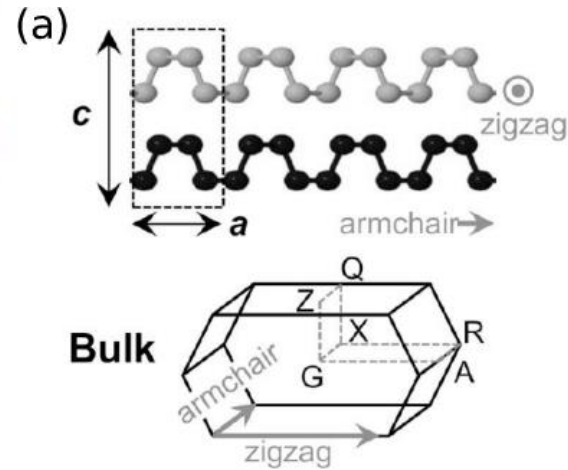
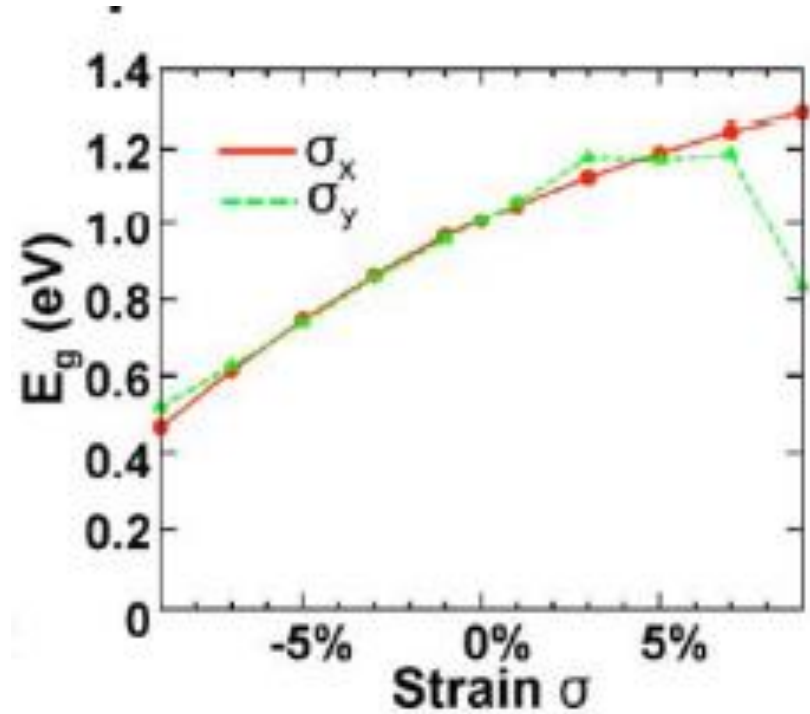
Black phosphorus has a direct band gap at the Γ point of the Brillouin zone regardless of its number of layers.

Properties of Black Phosphorus

- The band gap of black phosphorus varies from 2 eV for monolayer to approximately 0.3 eV for bulk.
- Thickness dependence of the band gap is due to charge carriers' quantum confinement effect, in the out-of-plane direction.
- Electronic properties of black phosphorus are governed intensely by its carrier mobilities and are closely related to effective mass of the carriers.
- Effective mass and mobility of charge carriers with first-principle calculations. Effective masses of both electron and hole decrease when the number of black phosphorus layer increases.
- Hole has the lower effective mass and, thus, the conductivity of the hole surpasses that of electron, making the hole as the major carrier in black phosphorus.

- **Black phosphorus, phosphorene** is one of three different crystal structures that pure phosphorus can adopt.
- White phosphorus is used in making fireworks.
- Red phosphorus is used to make the heads of matches.
- The bandgap is adjusted by varying the number of phosphorene layers stacking one atop another, significantly larger than the bulk value of 0.31- 0.36 eV.
- Much easier to engineer devices with the exact behavior desired.
- **Mobility ~ 600**
- Unstable in air.
- Passivated by Al_2O_3 layer and teflon.
- Harnessing phosphorene's higher electron mobility for making electronic devices.

Strain modulated band gap in graphene

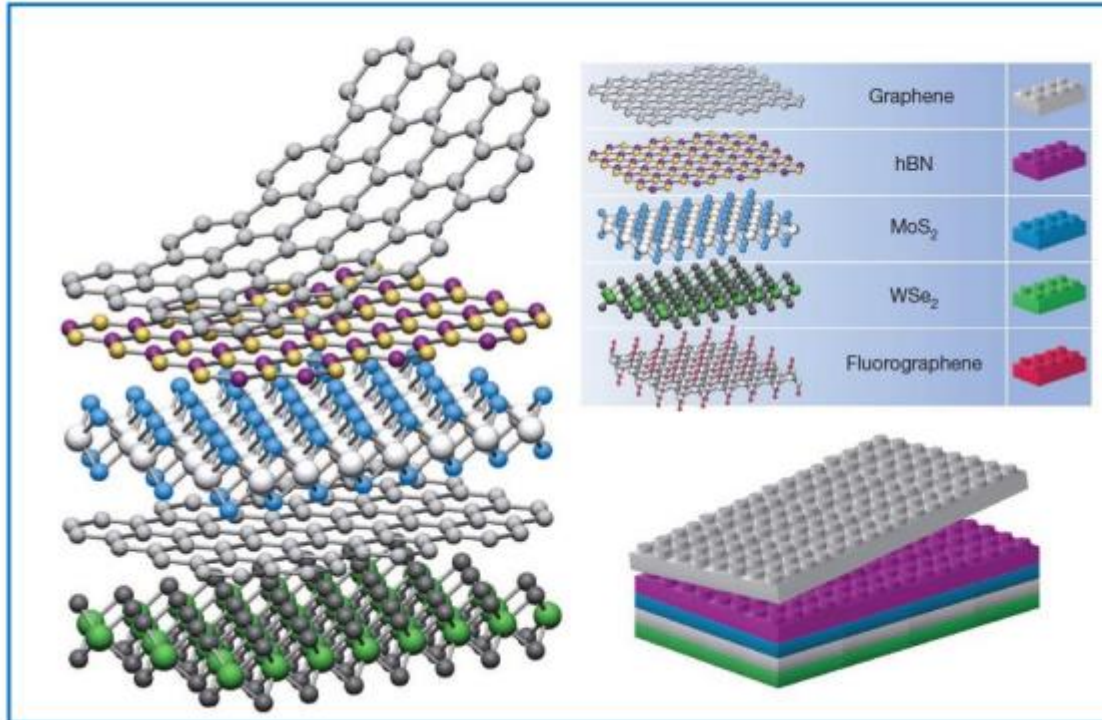


The strain-modulated bandgap significantly alters the density of thermally activated carriers

2D Heterostructures

- ❑ 2-D materials offer stacked like cards in a deck to create the different electronic layers as needed in functional electronic devices. **Van der Waals bonding**
- ❑ Because they do not form tight bonds with the layers above and below.
- ❑ Ye's group at Purdue reported to use both MoS_2 and phosphorene to make ultrathin photovoltaics (PVs).
- ❑ Geim et al reported in Nature Materials to have assembled multiple 2D materials to make efficient thin LEDs.
- ❑ Revolution in electronics and optics just began.
- ❑ Flexible, transparent, temperature stable, and cheap to manufacture

2D Heterostructures



Building van der Waals Heterostructures:

If one considers 2D crystals to be analogous to Lego blocks (right panel), the construction of a huge variety of layered structures becomes possible.

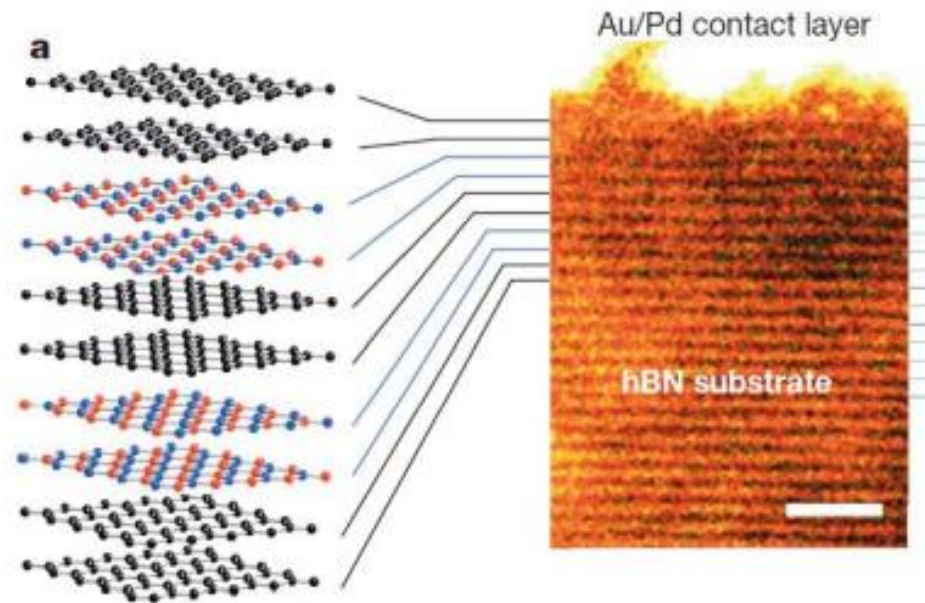
Conceptually, this atomic scale Lego resembles molecular beam epitaxy, but employs different 'construction' rules and a distinct set of materials.

Library of 2D materials

Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenides	MoS ₂ , WS ₂ , MoSe ₂ , WSe ₂		Semiconducting dichalcogenides: MoTe ₂ , WTe ₂ , ZrS ₂ , ZrSe ₂ and so on	Metallic dichalcogenides: NbSe ₂ , NbS ₂ , TaS ₂ , TiS ₂ , NiSe ₂ and so on	
				Layered semiconductors: GaSe, GaTe, InSe, Bi ₂ Se ₃ and so on	
2D oxides	Micas, BSCCO	MoO ₃ , WO ₃	Perovskite-type: LaNb ₂ O ₇ , (Ca,Sr) ₂ Nb ₃ O ₁₀ , Bi ₄ Ti ₃ O ₁₂ , Ca ₂ Ta ₂ TiO ₁₀ and so on		Hydroxides: Ni(OH) ₂ , Eu(OH) ₂ and so on
	Layered Cu oxides	TiO ₂ , MnO ₂ , V ₂ O ₅ , TaO ₃ , RuO ₂ and so on			Others

Ac
Go

Stacked Layers of heterostructures



Graphene–hBN superlattice consisting of six stacked bilayers. On the right its crosssection and intensity profile as seen by scanning transmission electron microscopy are shown; on the left is a schematic view of the layer sequence. The topmost hBN bilayer is not visible, being merged with the metallic contact.