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Phosphorene under exotic conditions - in search for pathways to novel materials and physics

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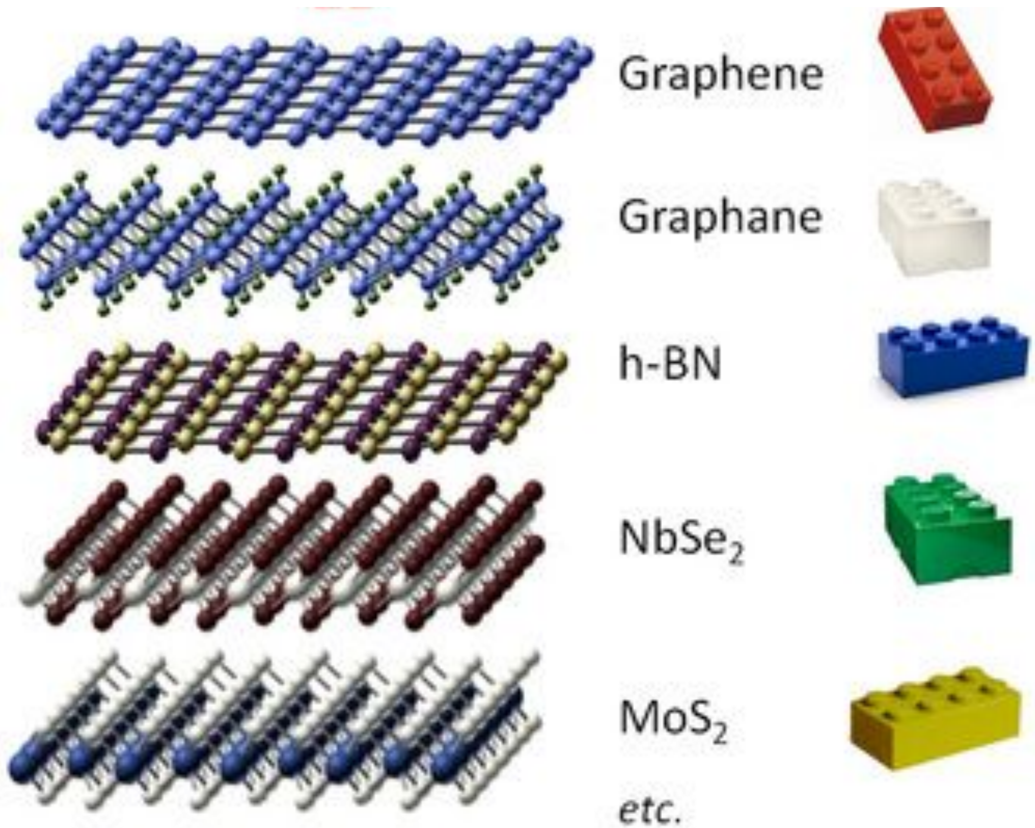
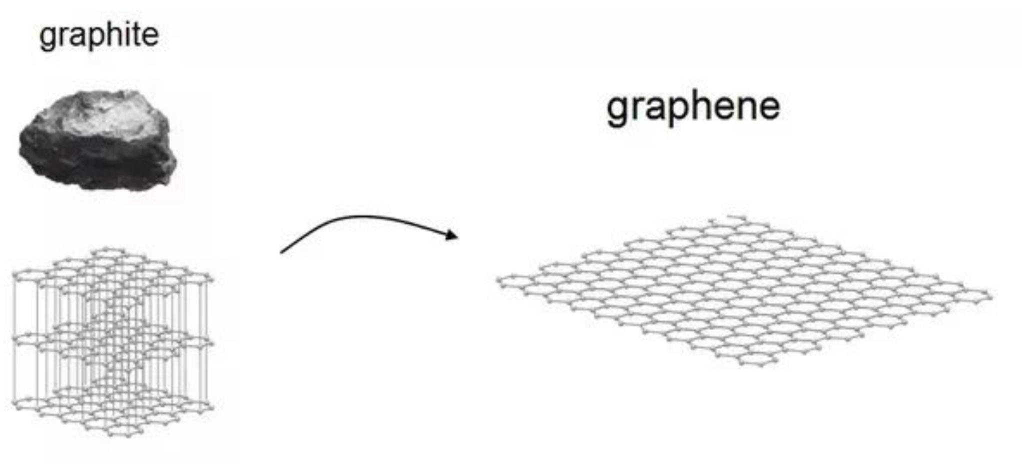
Synthesis and Processing Science Program & EPSCoR Program

2D Materials



https://sites.google.com/site/sarahnaharchowdhury/research/2d-materials

2D Materials - Graphene



The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov

The Nobel Prize in Physics 2010
Andre Geim
Konstantin Novoselov

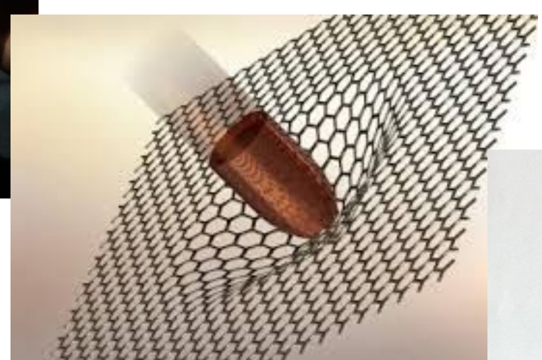
Photo: Sergeom, Wikimedia Commons

Andre Geim

Photo: University of Manchester, UK

Konstantin Novoselov

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*



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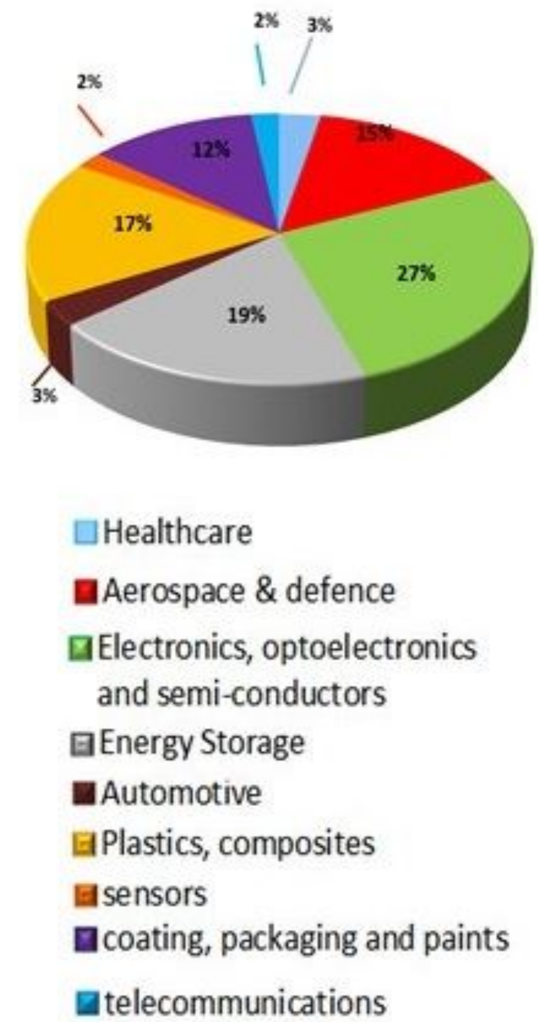
Applications of Graphene



A. Ferrari et al, Nanoscale, 2015, 4597-5062

https://ecms.adelaide.edu.au/graphene-research-hub/about-graphene/applications/

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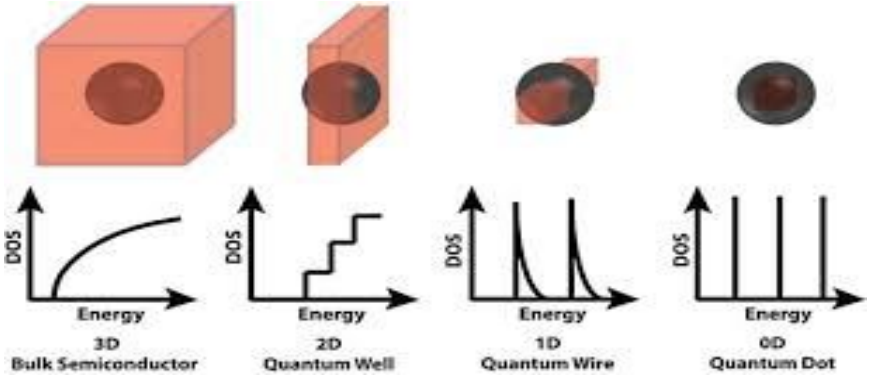
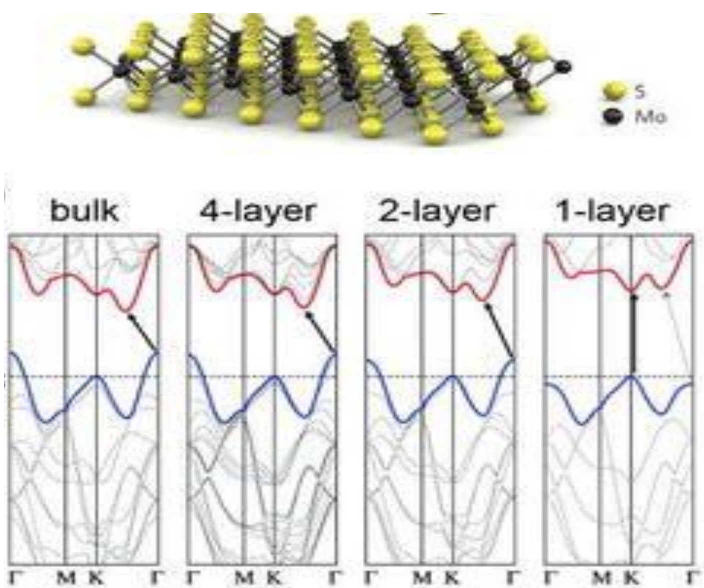
Why 2D Materials?

Quantum Size Effects

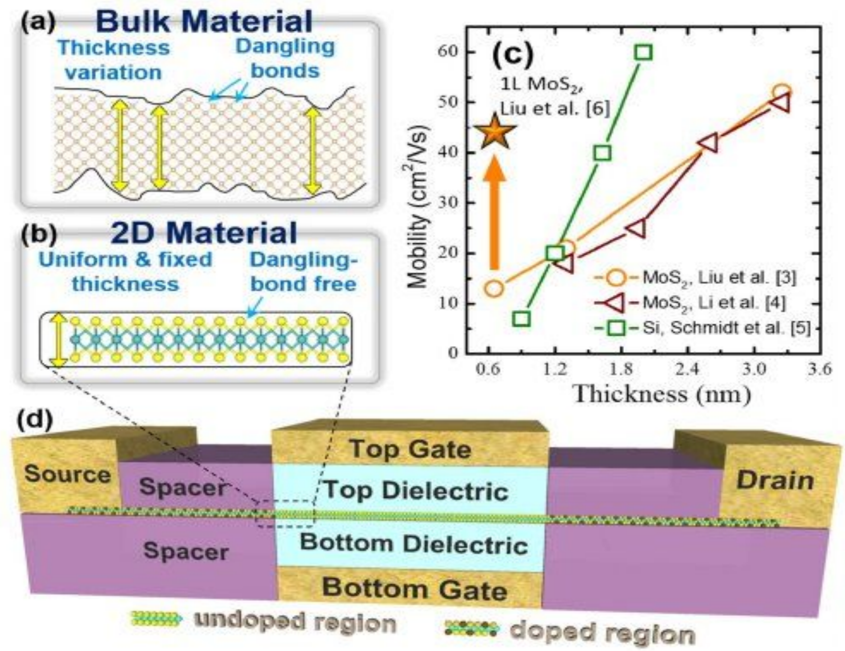


Ease of Band Structure Tunning



Sun et al. " *Applied Physics Reviews* 4, no.1, 011301, 2017.

Sharp Interfaces & Interesting Physics



Cao et al., IEEE Transactions on Electron Devices, 62, 3459-3469 (2015)

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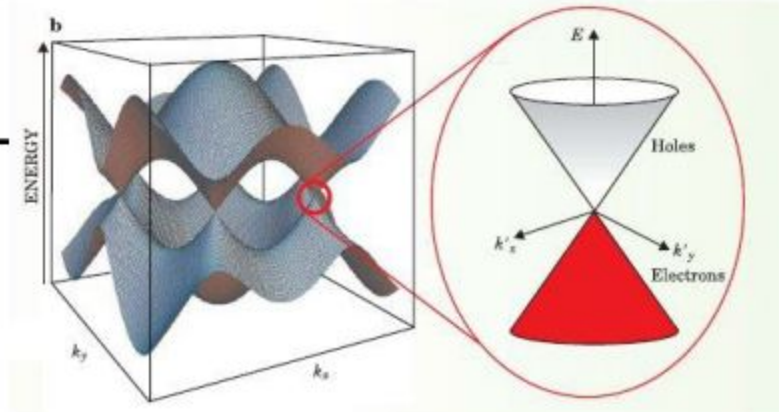
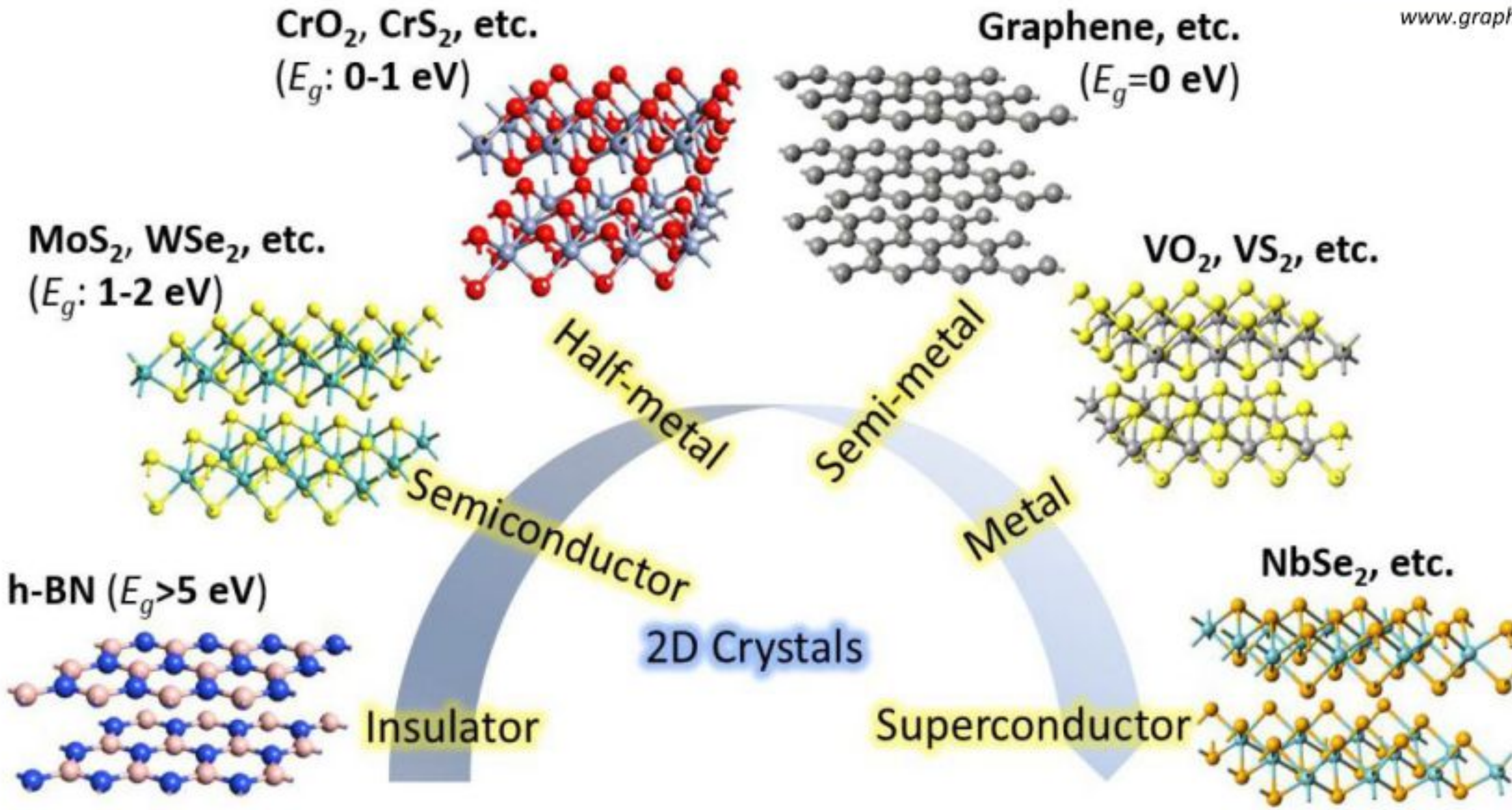
2D Materials

2D materials have been the focus of extensive research since the discovery of graphene in 2004

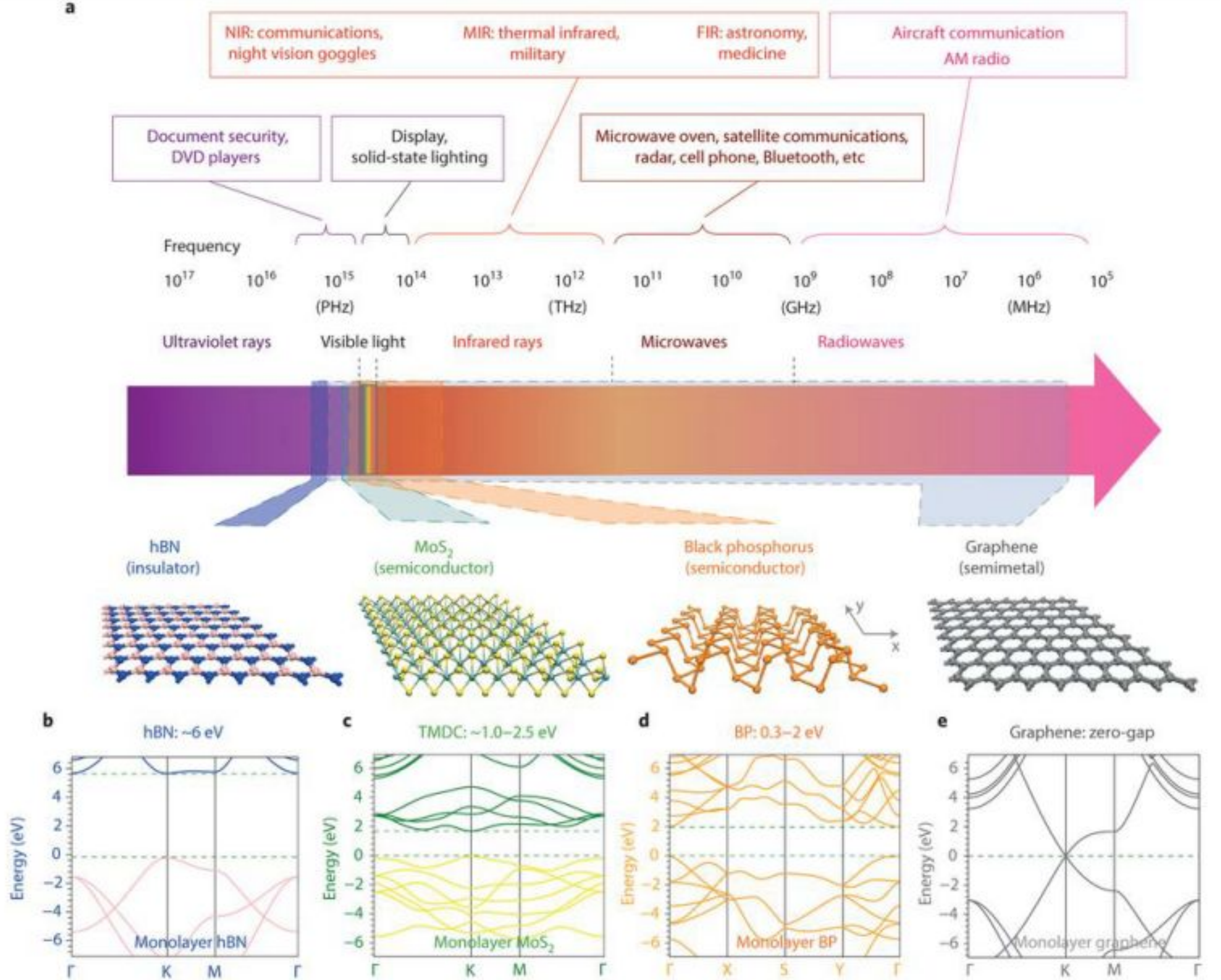


www.graphenea.com



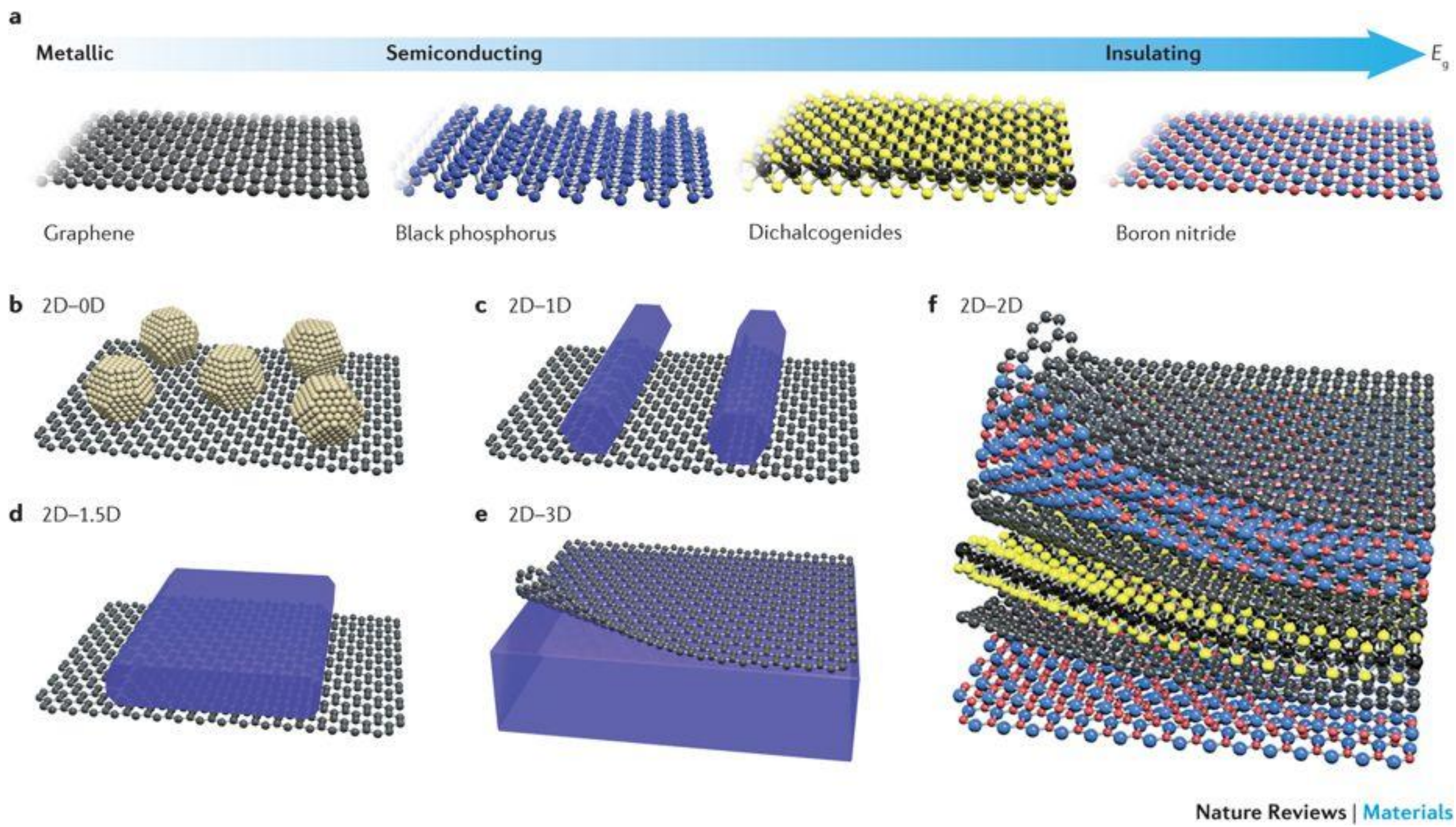
Kang et al., Proc. SPIE, 908305 (2014).

Optical Applications



Xia et al., Nature Photonics 8, 899–907 (2014)

2D Materials as Building Blocks

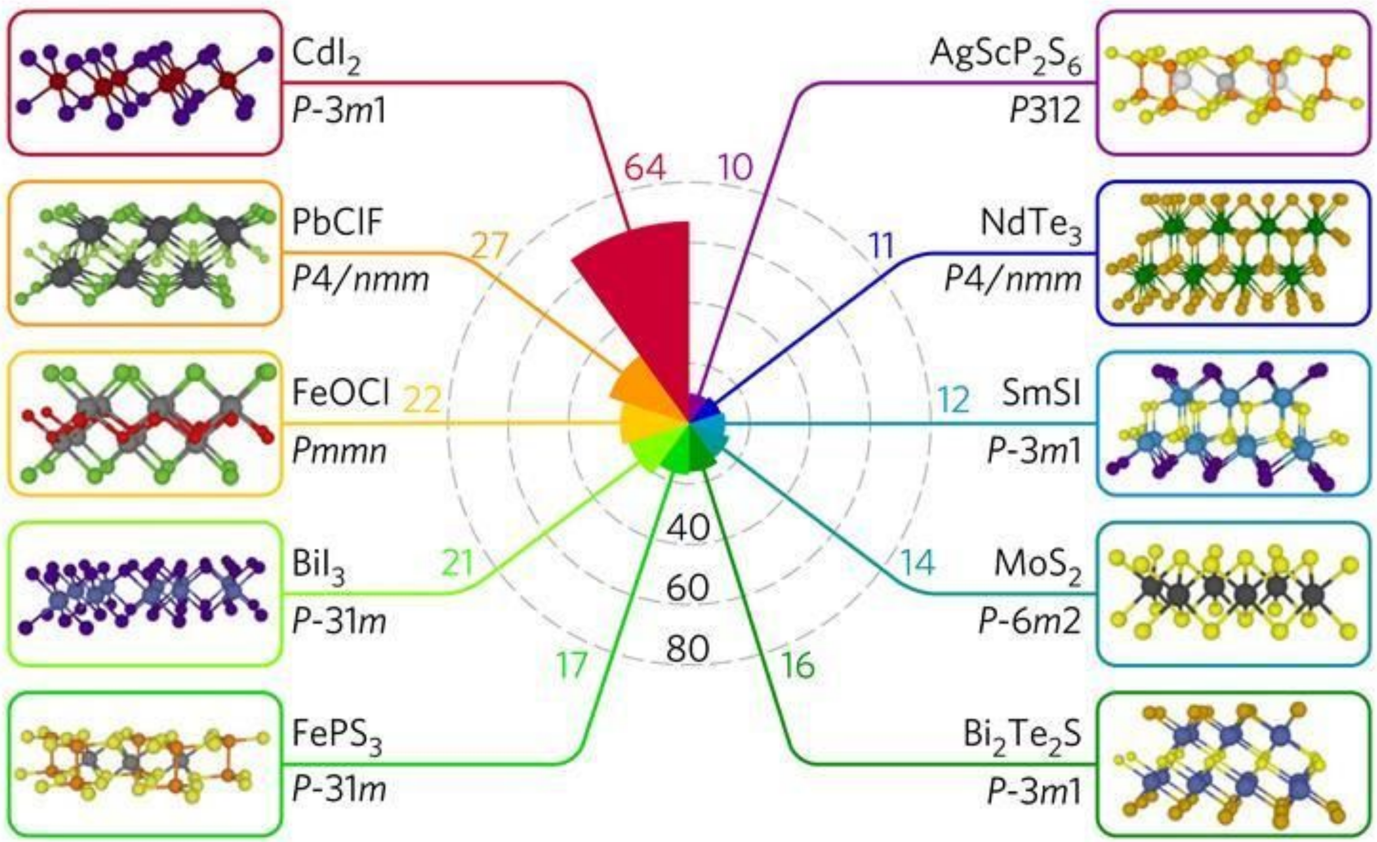


Liu et al., Nature Reviews Materials 1, 16042 (2016)

From 3D to 2D Layered Materials

3D layered compounds can be exfoliated. Ultimately, it should be possible to slough an atomic layer from such materials.

The most common 2D structural prototypes



Source: Macmillan Publishers Ltd

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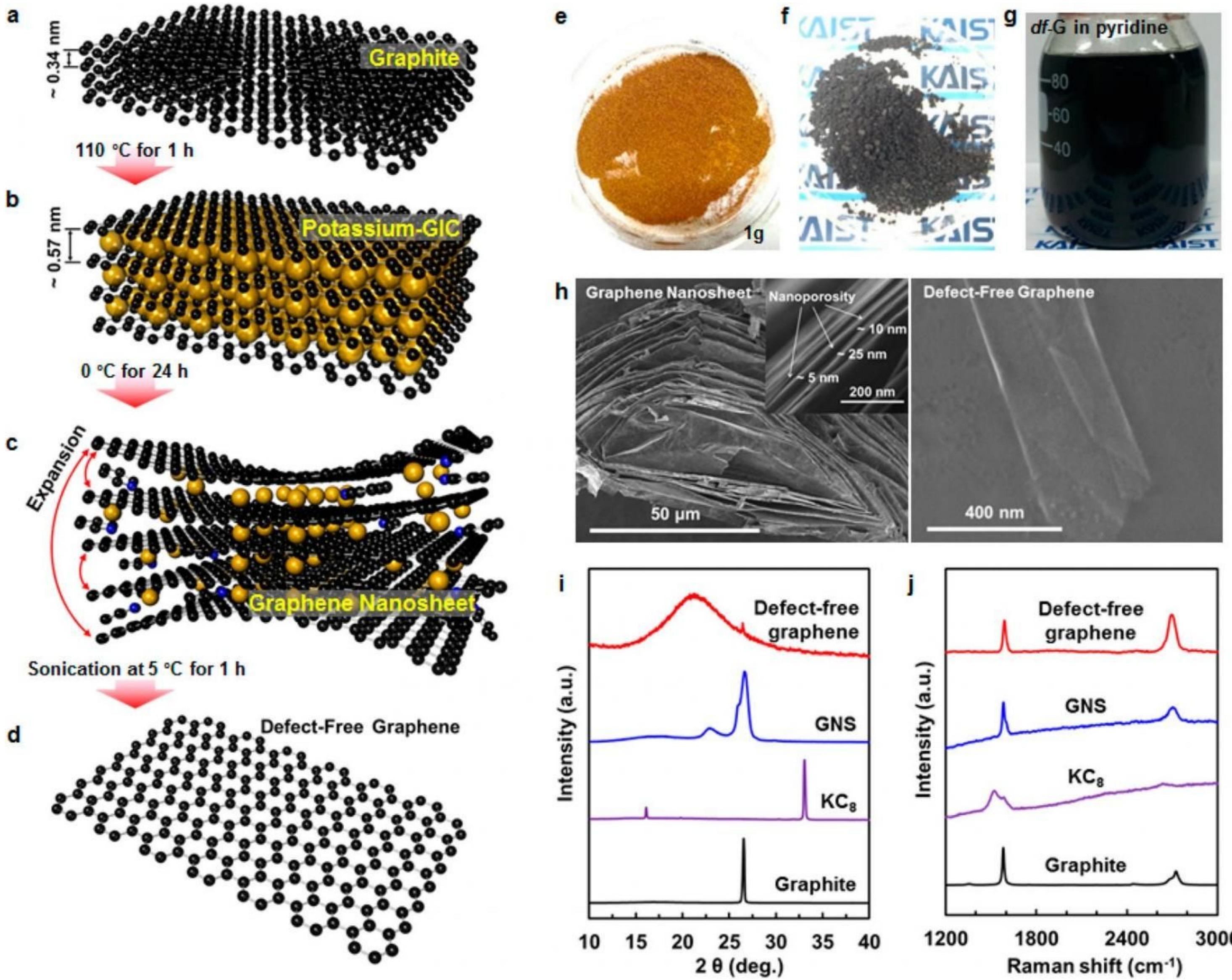
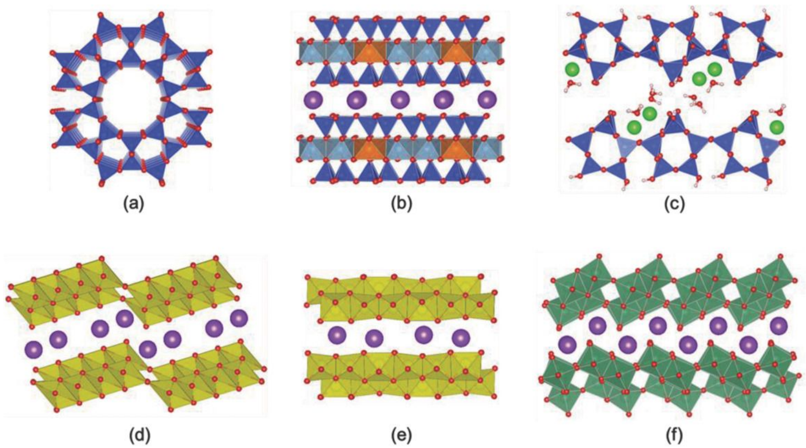
Exfoliation of Layered Materials



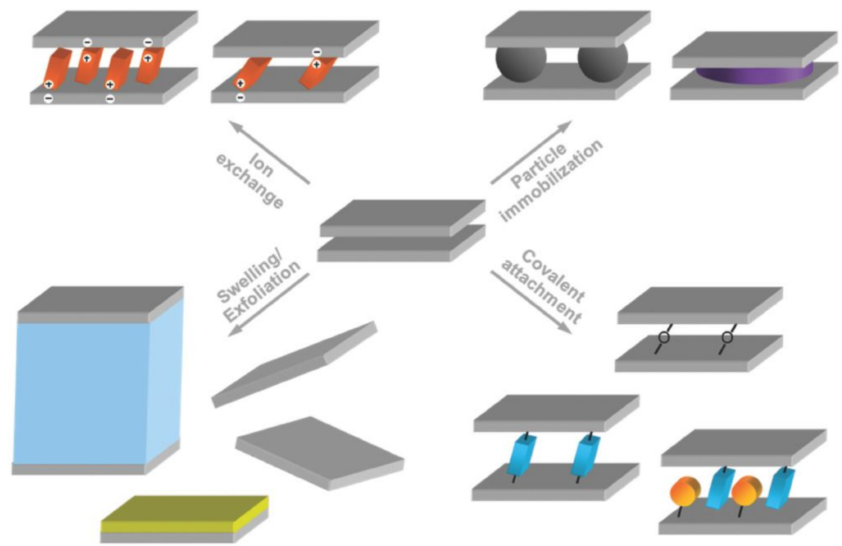
Park et al., Nano Lett. 14, 4306, (2014).

Intercalation of Layered Materials



Schematic structures of typical layered inorganic solids and zeolite. Color coding: blue = Si, red = O, pale blue = Al, orange = Mg, purple = K, green = Na, pink = H, yellow = Ti, dark green = Nb. a) TON-type zeolite showing open micropores. b) A smectite clay, montmorillonite. Pillared layered clays having open micropores can be designed, for example, by replacing original inorganic cations with bulky organic molecules. c) A layered silicate, octosilicate ($Na_2Si_8O_{17}\cdot nH_2O$). The surface silanol group (SiOH) is visible. d) A layered titanate, $K_2Ti_4O_9$. e) A lepidocrocite-type layered titanate, $K_{0.8}Ti_{1.73}Li_{0.27}O_4$. Li, which replaces a part of Ti, is invisible. f) A layered niobate, $K_4Nb_6O_{17}$.

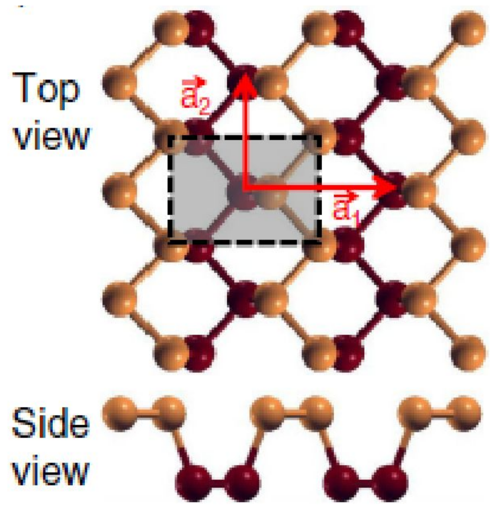
Overview of guest species intercalation into the interlayer space of layered materials via physical or chemical attachments.



Sangian etal, Small 14, 1800551, 2018

Phosphoerene

Black Phosphorene



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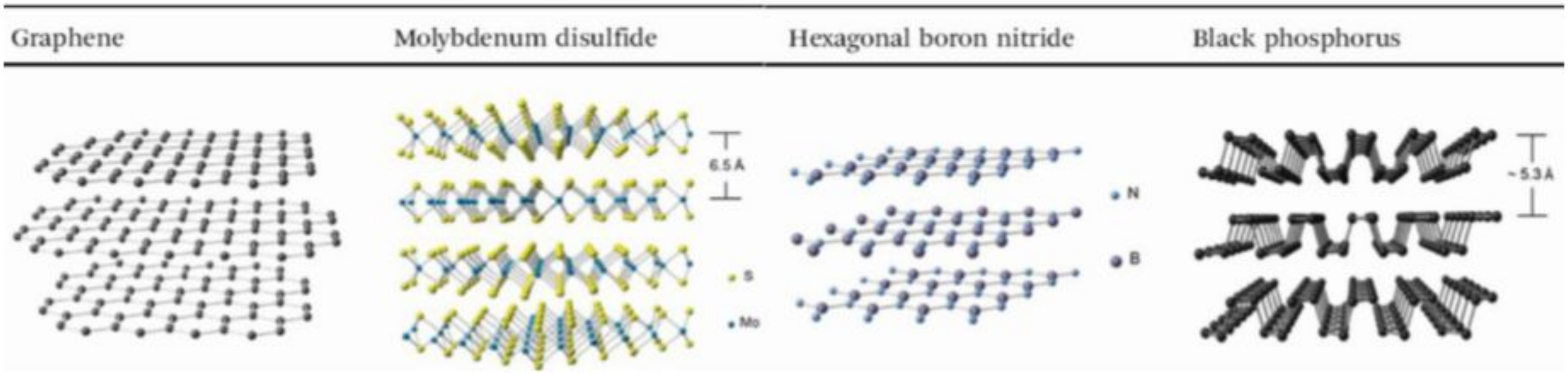
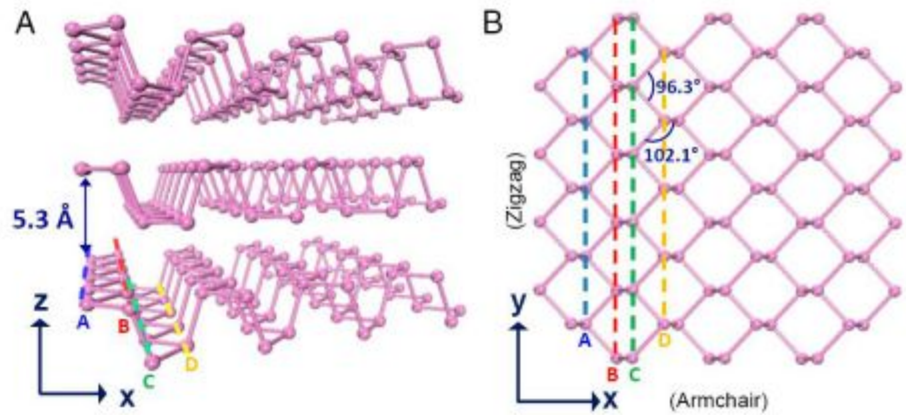
Phosphorene – What's So Special?



Du et al., *J. Mater. Chem. C*, 2015, 3, 8760--8775

- Like graphene, phosphorene is a **monolayer of a single element (black phosphorous)**
  - Other elemental 2D materials (silicene, germanene, stanine) need substrate
- However, not flat but has a **puckered layer structure**
- It shows a strong **in-plane anisotropy**
- key properties
  - tunable bandgap
  - in-plane anisotropy
  - high carrier mobility



Ling et al., PNAS 112, 4523–4530 (2015).

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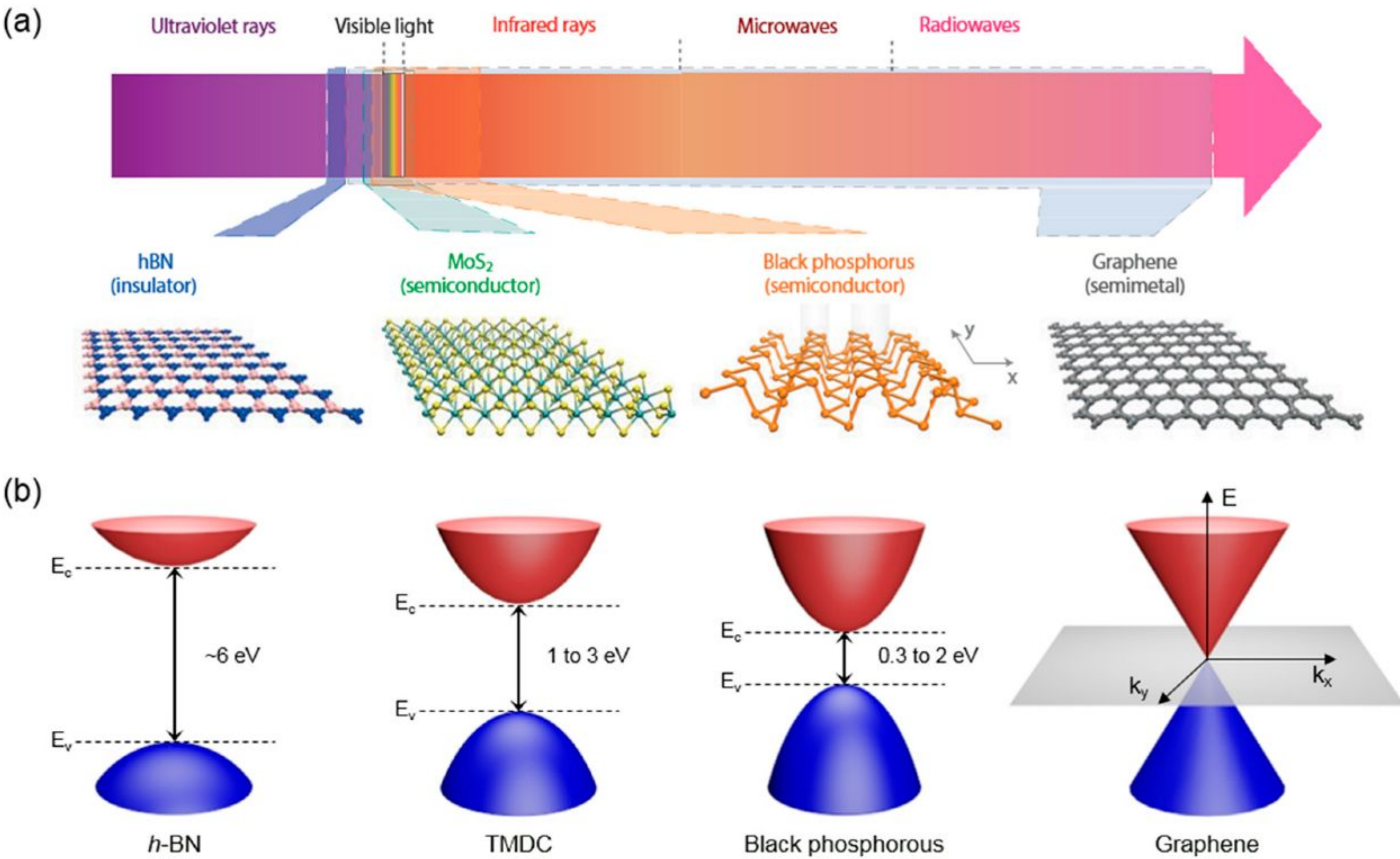
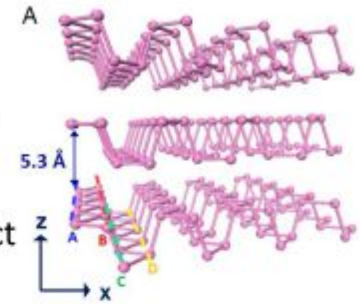
Bandgaps of 2D Materials

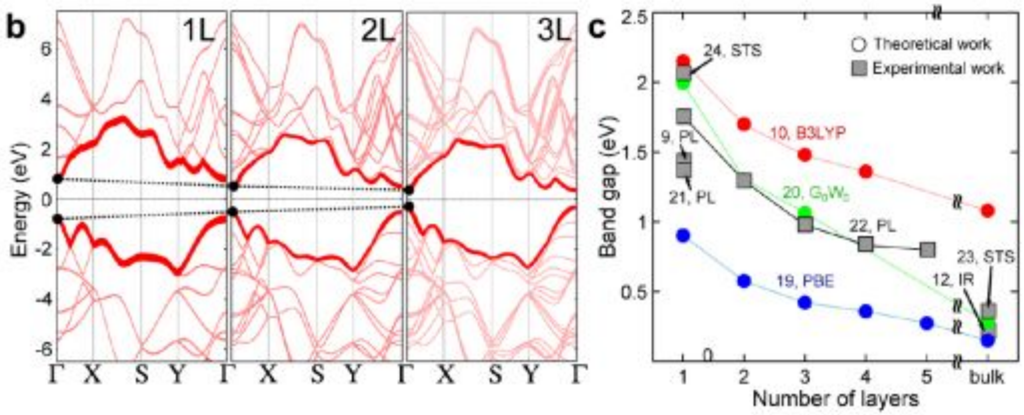


Lee et al., Nanomaterials, 6, 193 (2016)

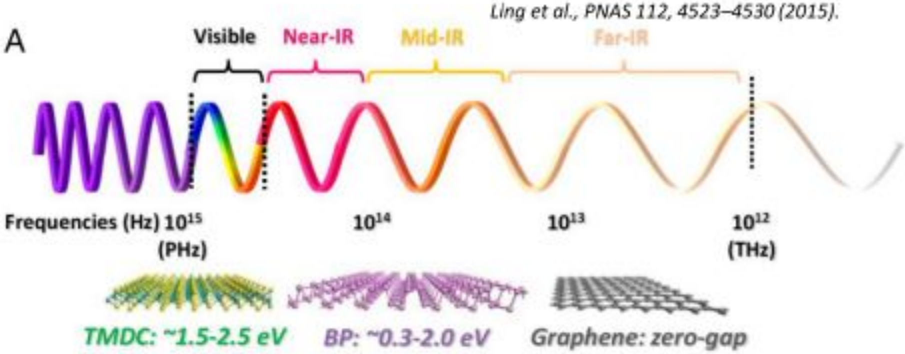
Bandgap Tunability

- The key characteristic of phosphorene is its highly tunable bandgap, between 0.3 eV and 2 eV for different number of layers
  - Unlike MoS_2 phosporene has direct bandgap even for multilayers

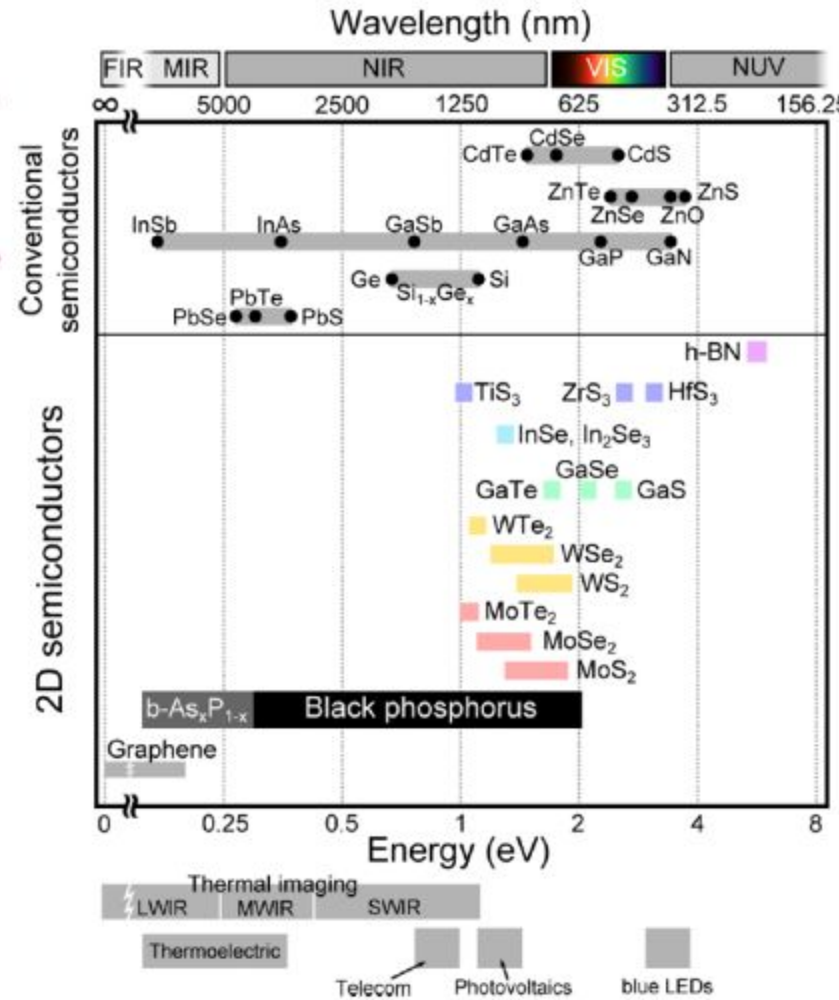




Ling et al., PNAS 112, 4523–4530 (2015).

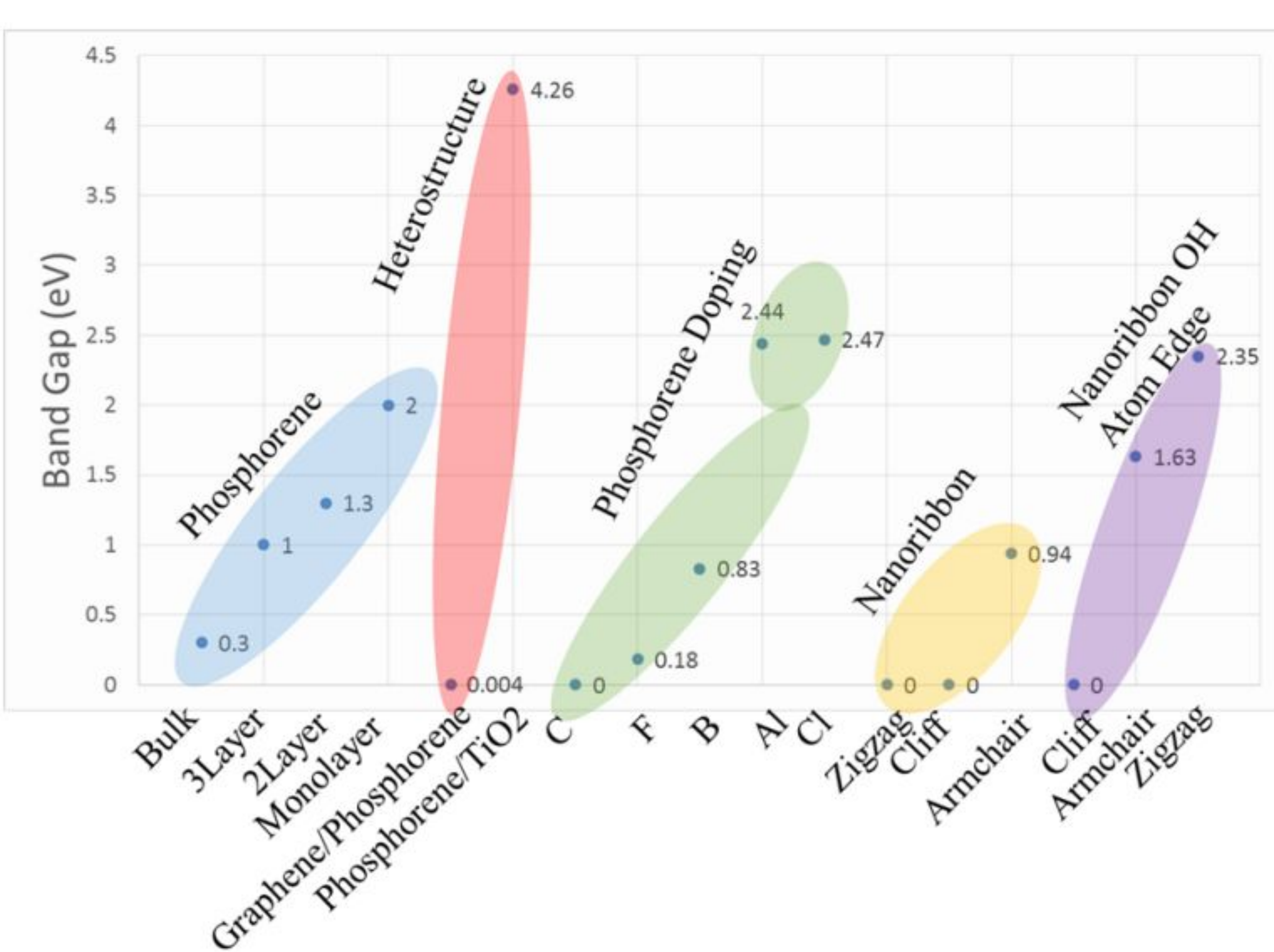


Ling et al., PNAS 112, 4523–4530 (2015).



Castellanos-Gomez, J. Phys. Chem. Lett. 2015, 6, 4280–4291

Bandgap Tunability – Other Factors



Akhtar et al., npj 2D Materials and Applications 1, 5 (2017).

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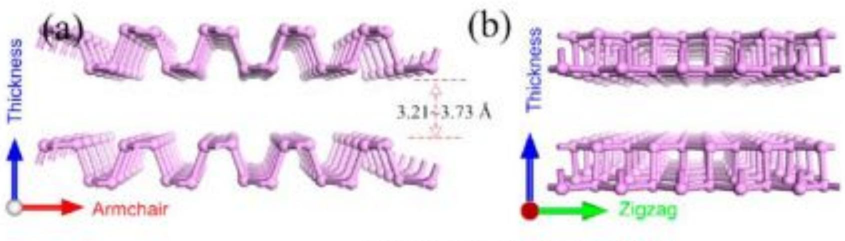
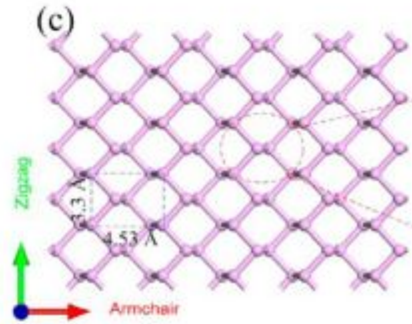
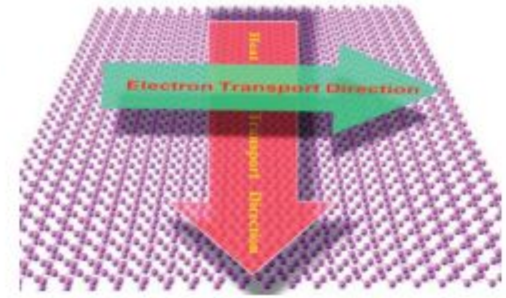
In-Plane Anisotropy

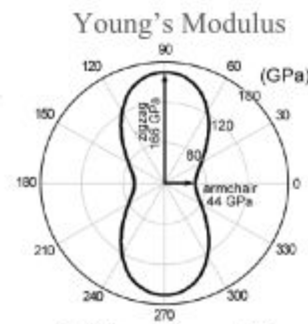


Kou et al., *J Phys Chem. Lett. 2015*

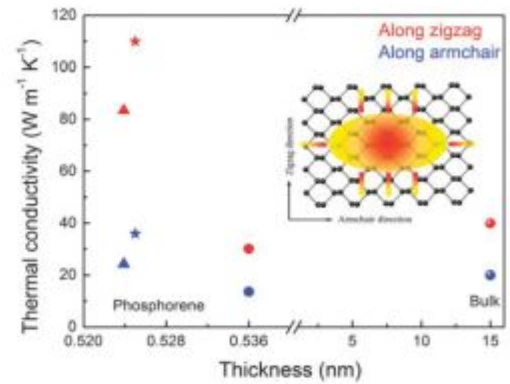




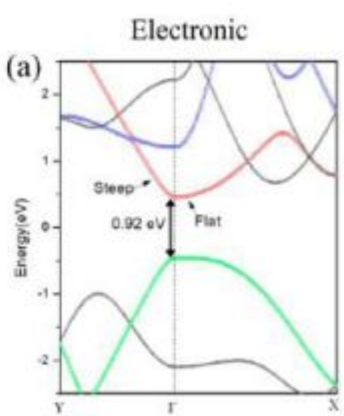
Strong Intrinsic anisotropy is shown in many properties of phosphorene (electronic structure, optical, electrical, mechanical, transport, thermoelectric, etc.).

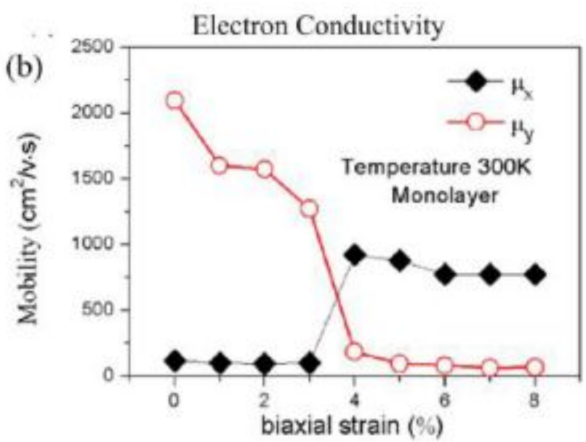


Castellanos-Gomez, J. Phys. Chem. Lett. 2015, 6, 4280−4291

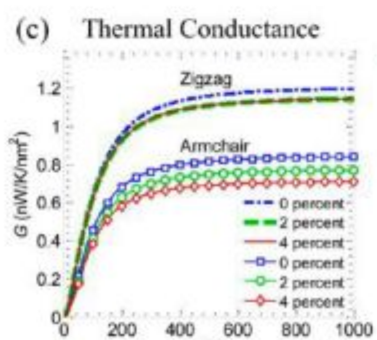


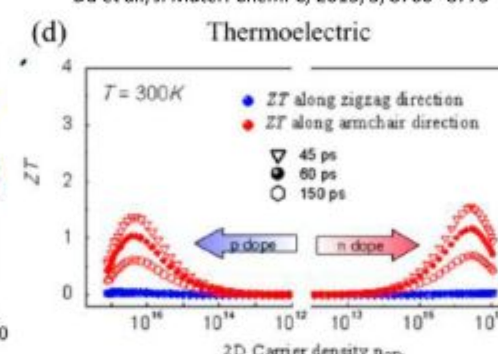
Du et al., *J. Mater. Chem. C*, 2015, 3, 8760--8775





Kou et al., J. Phys. Chem. Lett. 2015, 6, 2794−2805





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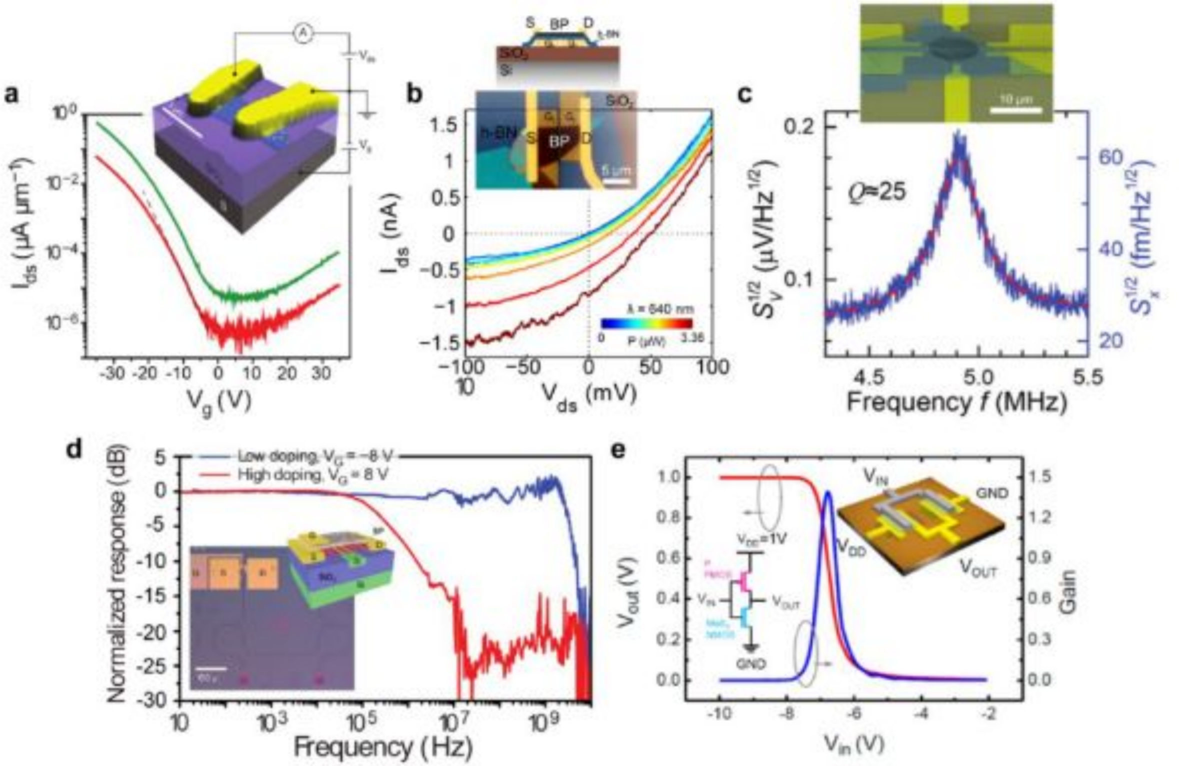
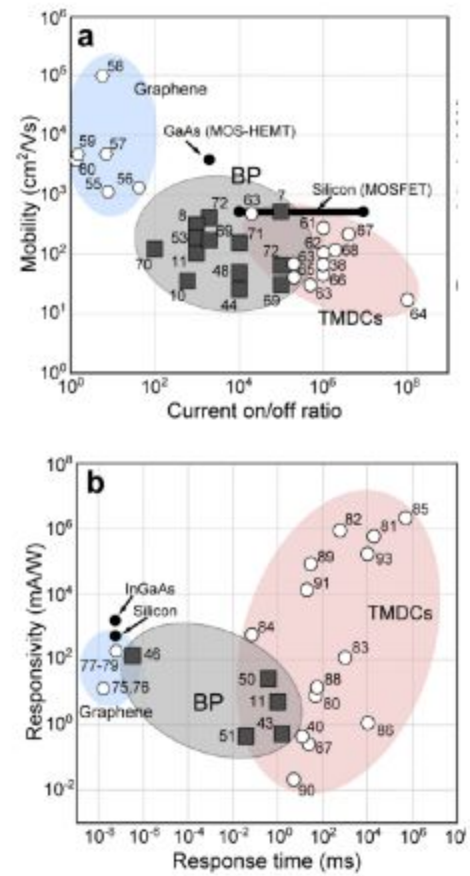
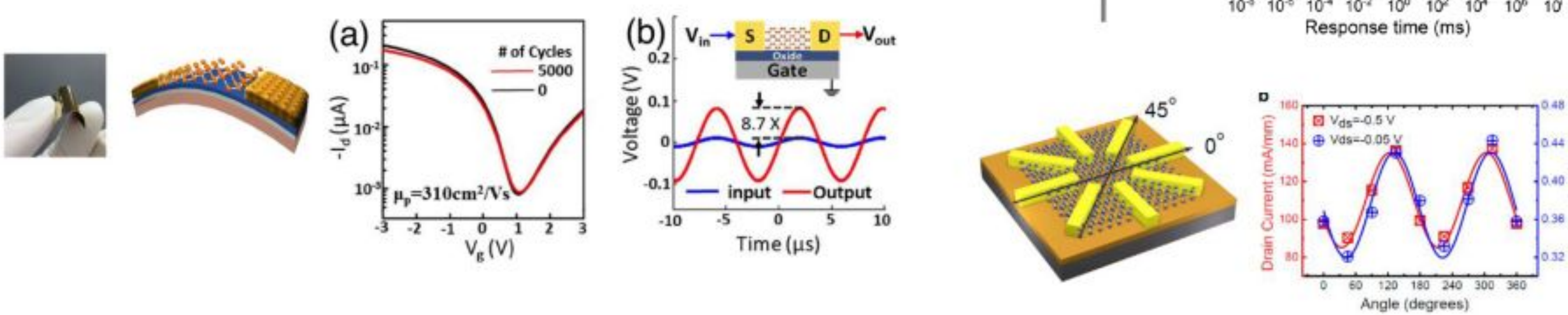
Phosphorene Nanoelectronic Devices



Castellanos-Gomez, J. Phys. Chem. Lett. 2015, 6, 4280–4291





Liu et al. ACS Nano 2015

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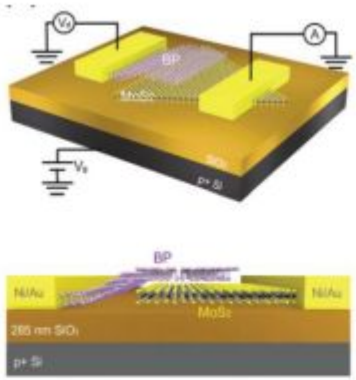
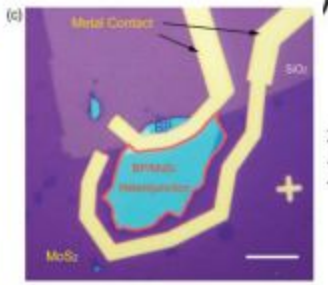
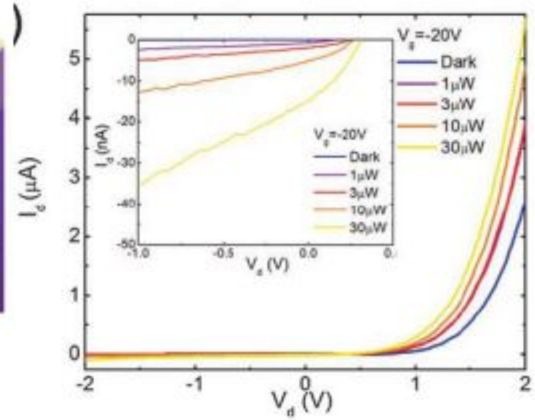
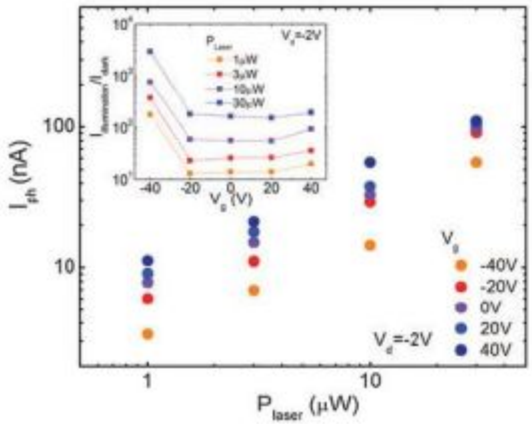
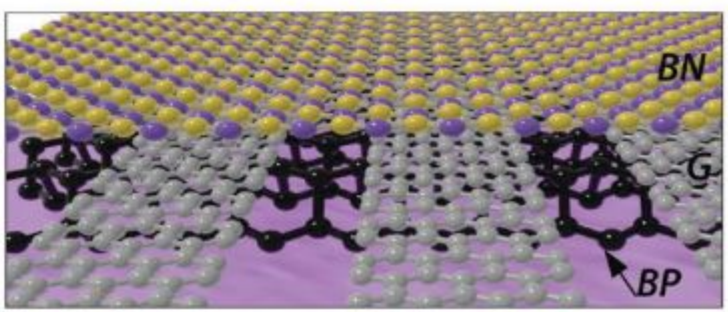
Phosphorene Heterostructure Devices

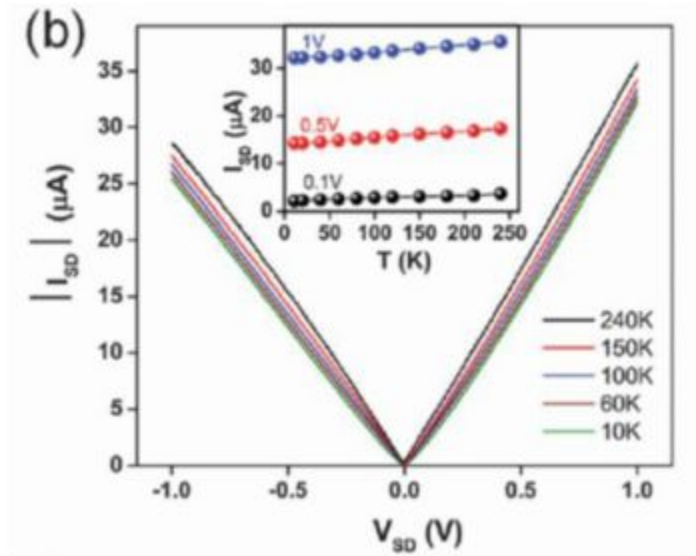








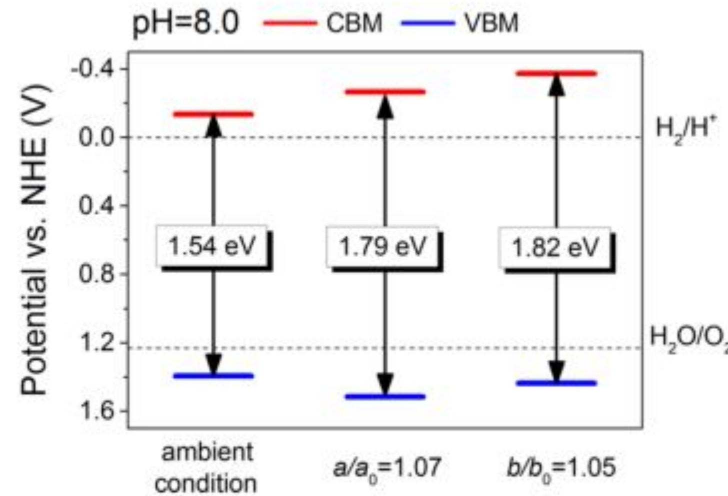




Du et al., *J. Mater. Chem. C*, 2015, 3, 8760--8775

Phosphorene for Photocatalytic Applications

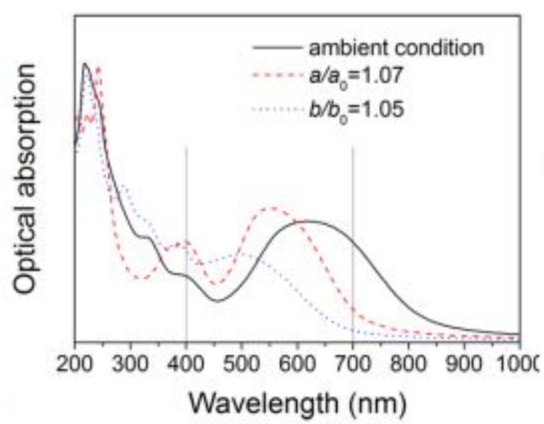
- Recent DFT work proposed ***strain-engineered phosphorene as a photocatalyst for water splitting and hydrogen production***
- Phosphorene lattice is unstable under compression strains and could be crashed however shows good stability under tensile strains. Tunable band gap from 1.54 eV at ambient condition to 1.82 eV under tensile strains
- Appropriate band gaps and band edge alignments demonstrate the potential of phosphorene as efficient photocatalyst for visible light water splitting
- Negative splitting energy of absorbed H_2O indicates the water splitting on phosphorene is energy favorable both without and with strains

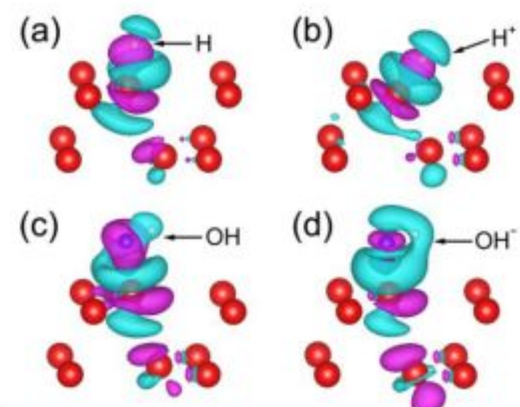


$$E^{\mathrm{OH}}_{\mathrm{splitting}} = E_{\mathrm{OH/phosphorene}} + E_{\mathrm{H}} - E_{\mathrm{H_2O/phosphorene}}$$

Table 3. Calculated Driving Force of the Splitting of Water Molecule on Phosphorene

$E^{\mathrm{M}}_{\mathrm{splitting}}$ (eV)	strain free	a/a_0 = 1.07	b/b_0 = 1.05
$E^{\mathrm{H+}}_{\mathrm{splitting}}$	−4.183	−4.204	−4.278
$E^{\mathrm{OH^-}}_{\mathrm{splitting}}$	−0.704	−1.042	−0.918
$E^{\mathrm{H}}_{\mathrm{splitting}}$	−2.225	−2.470	−2.254
$E^{\mathrm{OH}}_{\mathrm{splitting}}$	−2.458	−2.612	−2.575





Sa et al., J. Phys. Chem. C 2014, 118, 26560–26568

Challenge: Fabrication

- ***Fabrication methods for phosphorene***
  - ✓ **Mechanically Exfoliation**
    - high quality material for research
    - not scalable for industrial applications
  - ✓ **Liquid-Phase Exfoliation**
    - cheap and scalable method
    - material quality might not be high enough for certain electronic or optical applications
  - ✓ **Pulsed Laser Deposition**
    - can be scaled up
    - samples show lack of crystallinity and poor electrical properties

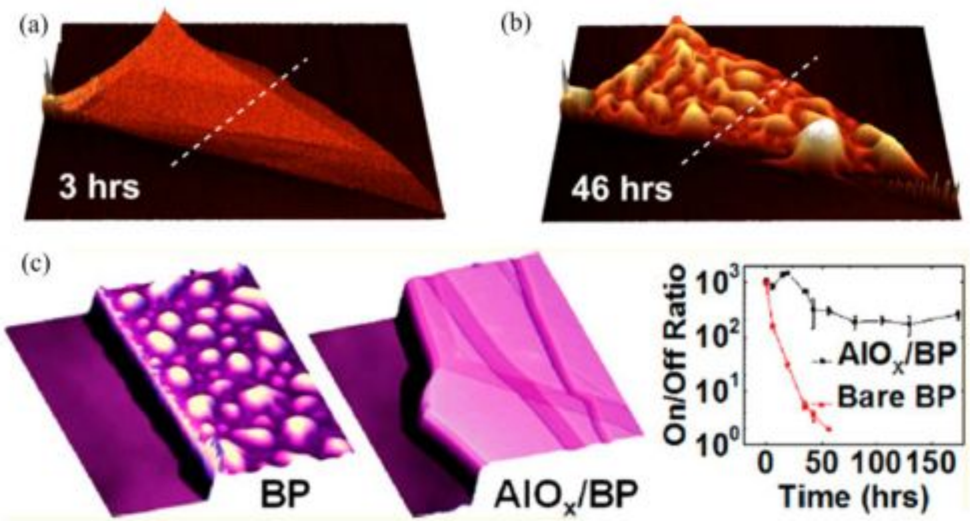
- ***A large-area synthesis method for crystalline phosphorene is needed***

	phosphorene		graphene		TMDC	
	fabrication successful	reference	fabrication successful	reference	fabrication successful	reference
top-down						
cleavage with tape	√	9, 10	√	14	√	14, 16
liquid-phase exfoliation	√	64, 65	√	56, 62	√	62, 63
lithiation	×		√	66	√	66, 67
plasma-assisted fabrication	√	60	√	58	√	59
bottom-up						
CVD growth	×		√	69, 72	√	70, 71
hydrothermal synthesis	×		√	75	√	76

Kou et al., J. Phys. Chem. Lett. 2015, 6, 2794–2805

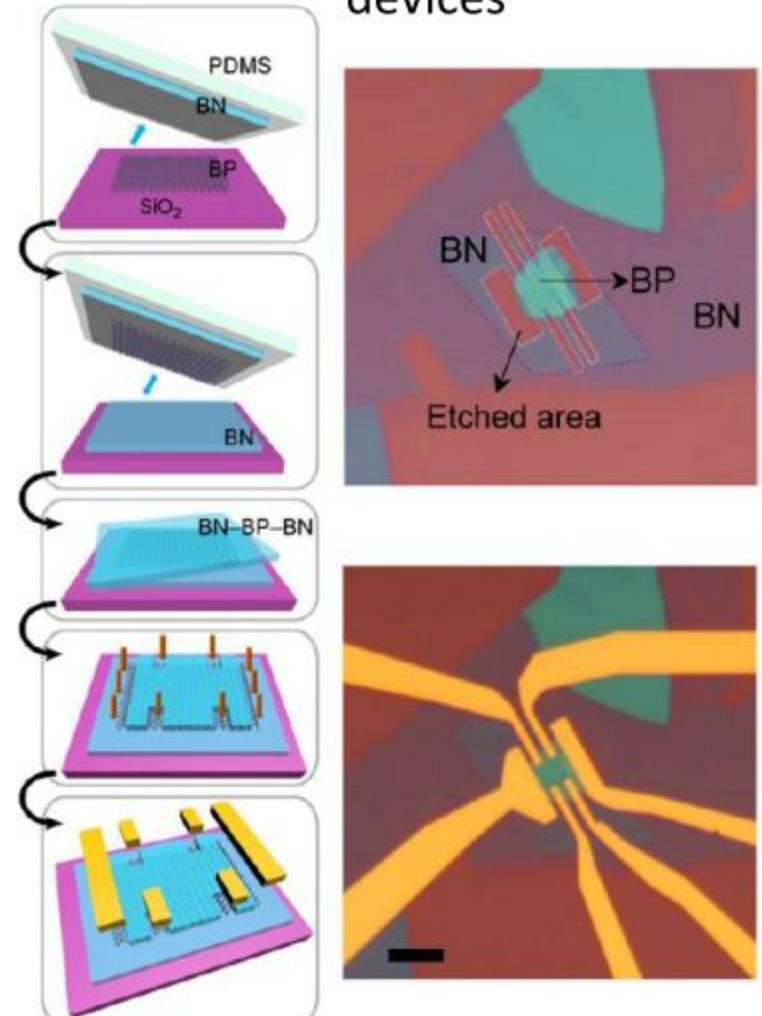
Challenge : Environment-induced degradation and protective encapsulation

Degradation of phophorene and protective encapsulation of BP FET with AlO_x overlayer



Kou et al., J. Phys. Chem. Lett. 2015, 6, 2794–2805

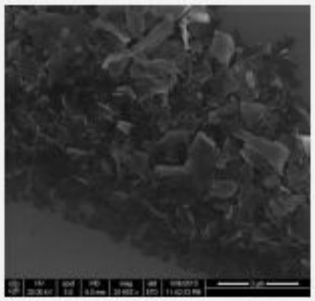
Sandwiching between h-BN fakes to fabricate high quality encapsulated devices

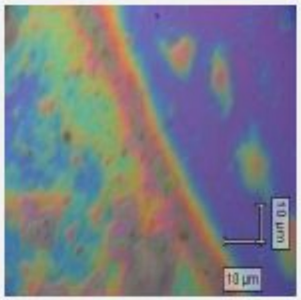


Castellanos-Gomez, J. Phys. Chem. Lett. 2015, 6, 4280–4291

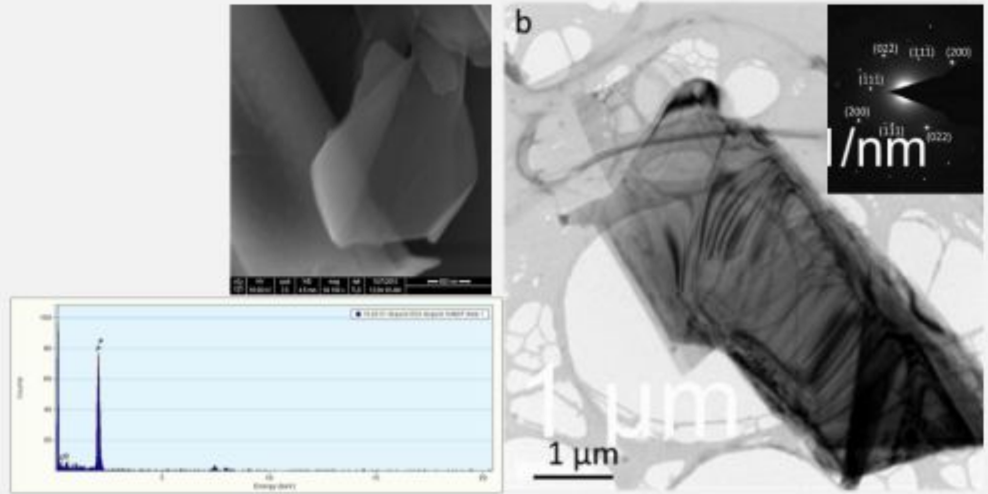
Fabrication and Characterization

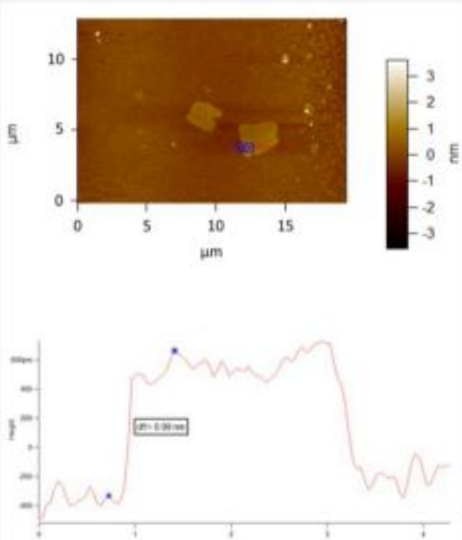
Liquid exfoliation





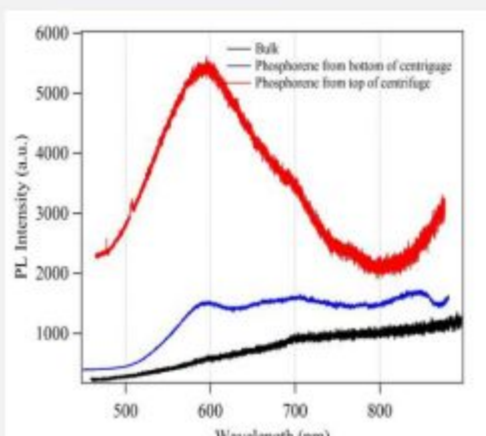
Morphology and crystallinity

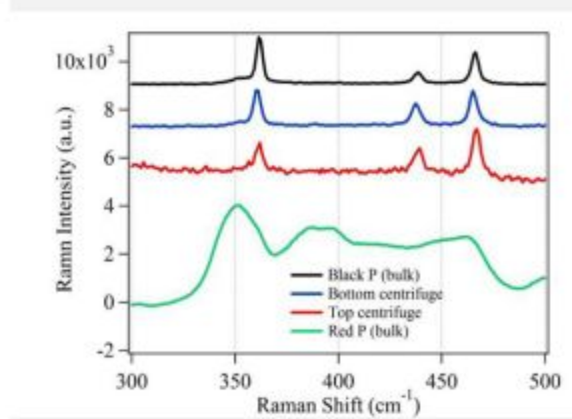


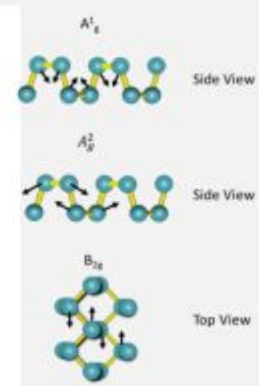


E_g = 2.09 eV

Number of layers







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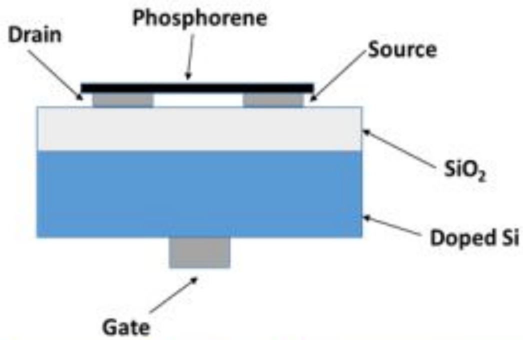
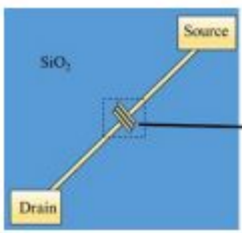
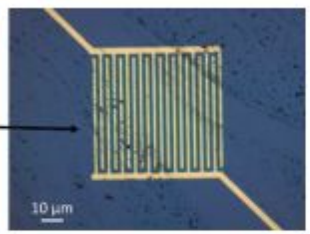
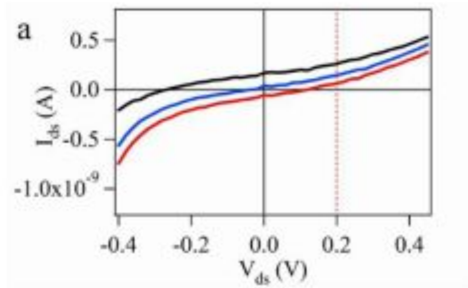
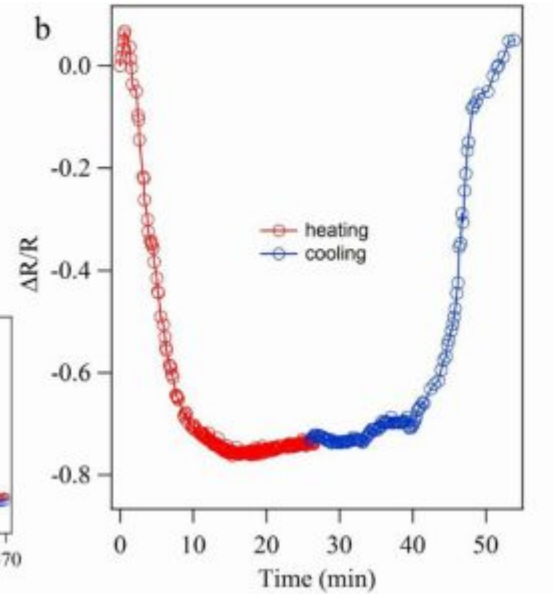
Transport Properties

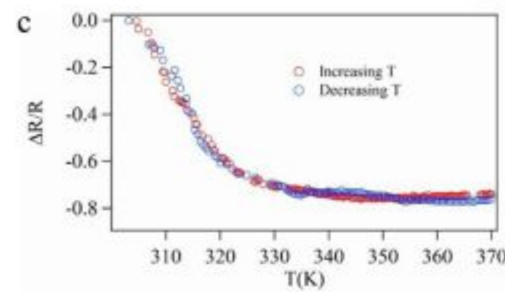


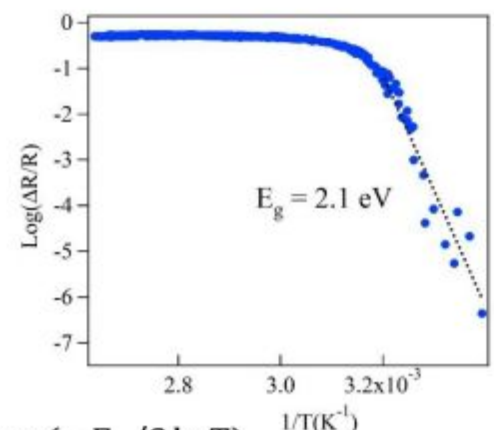


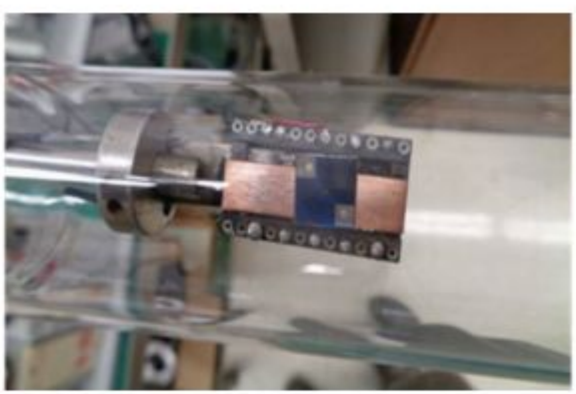


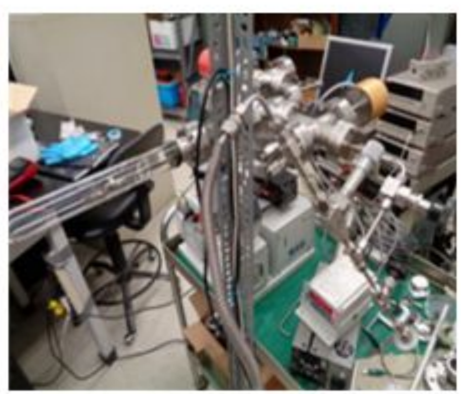












$$n \propto \exp(-E_g/2k_bT)$$

$$\downarrow$$

$$R \propto \exp(E_g/2k_bT)$$

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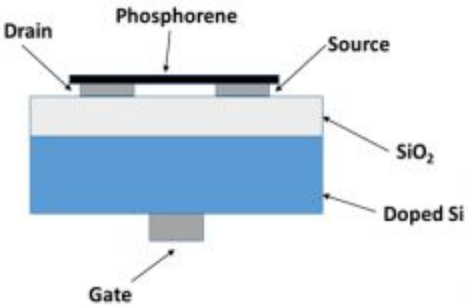
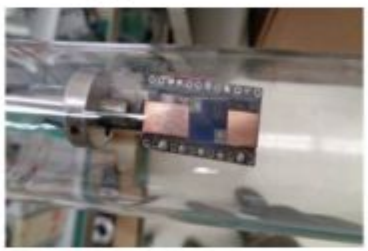
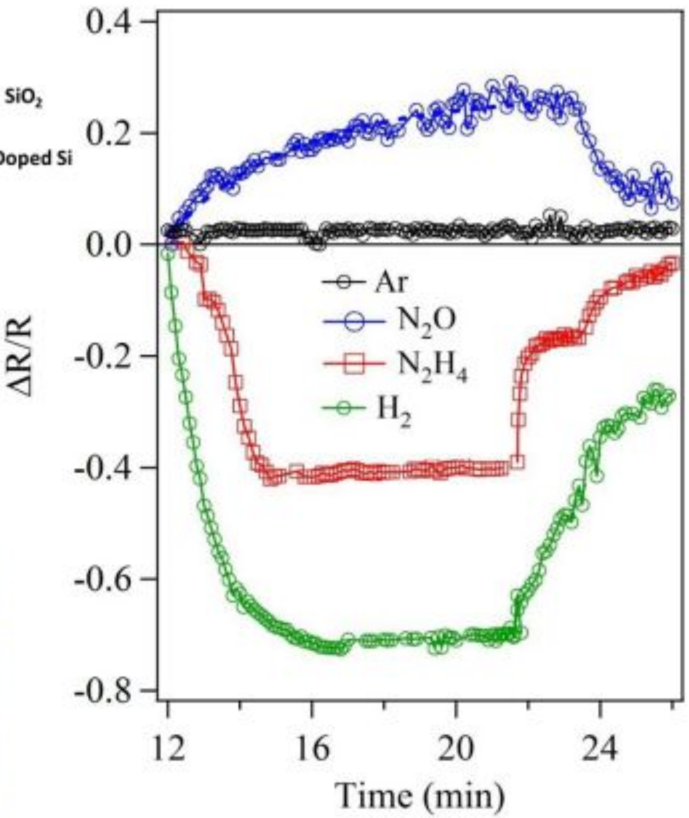
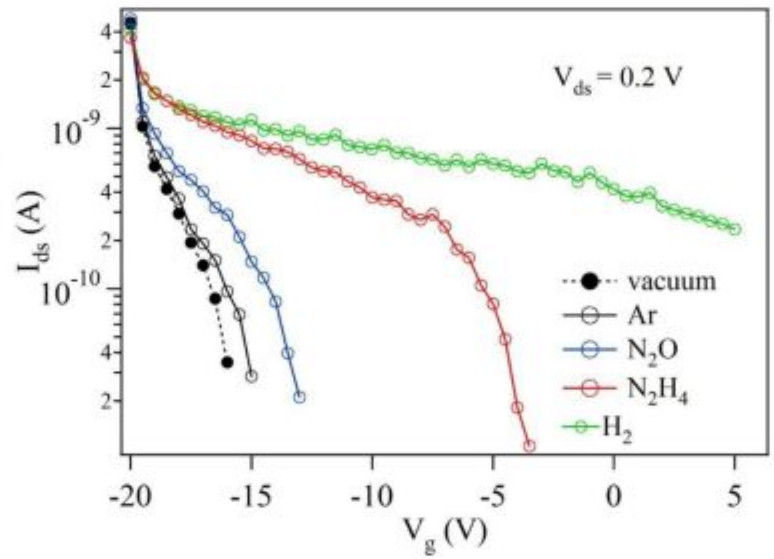
In-situ Exposure to Different Gases









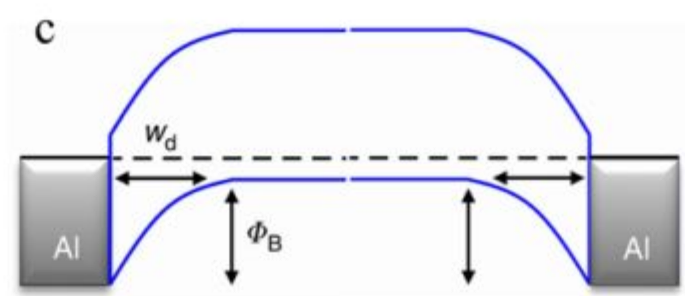


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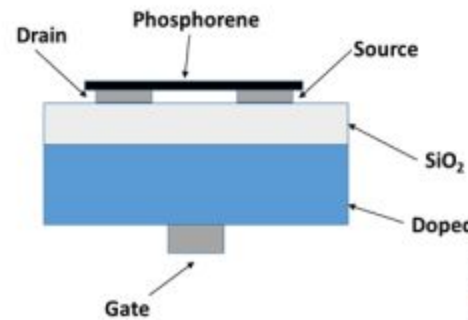
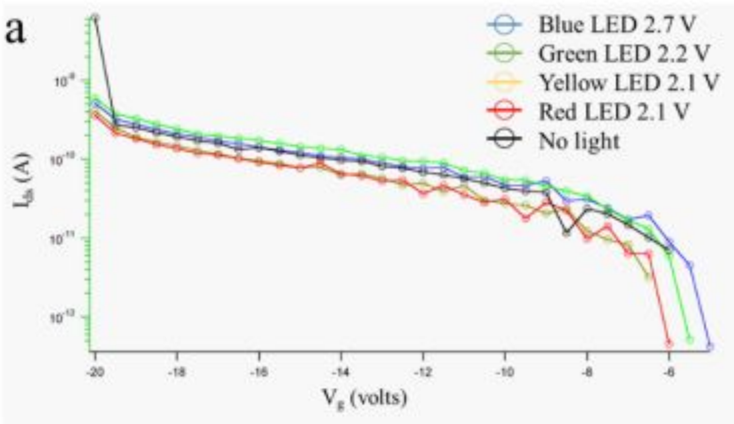
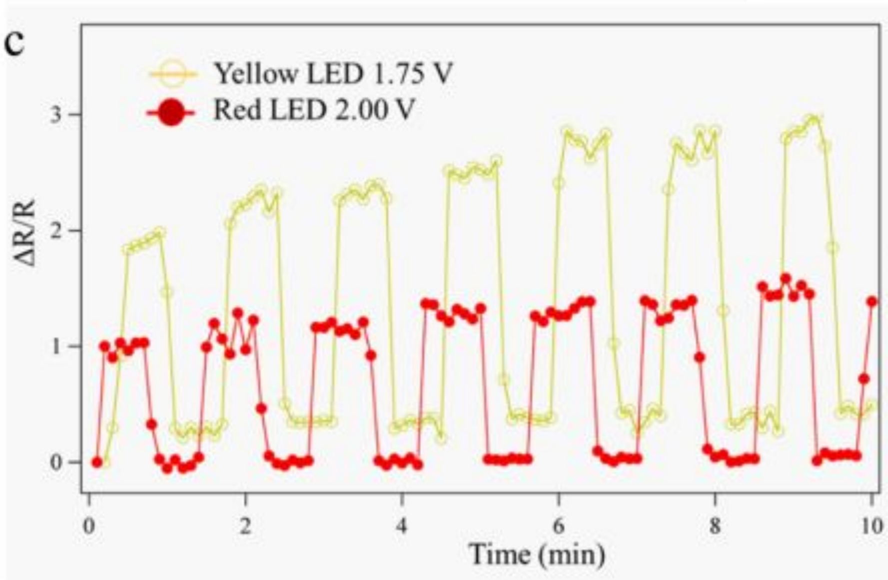
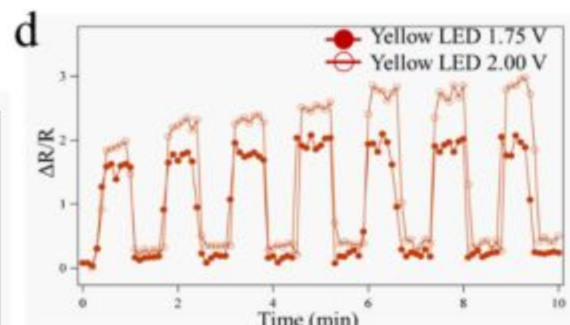
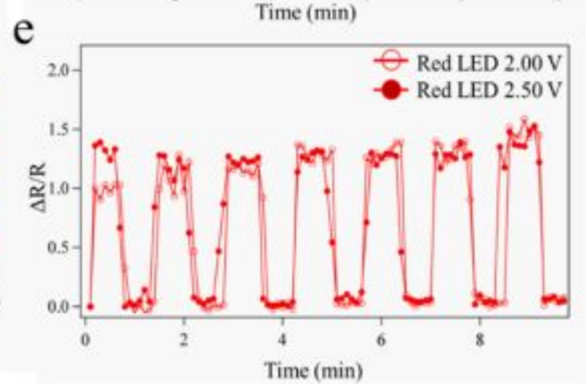
Photo-Response





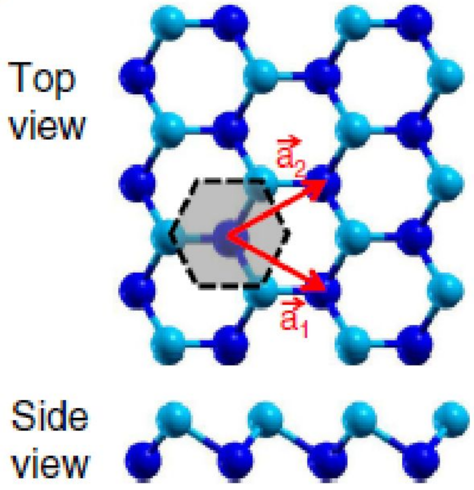






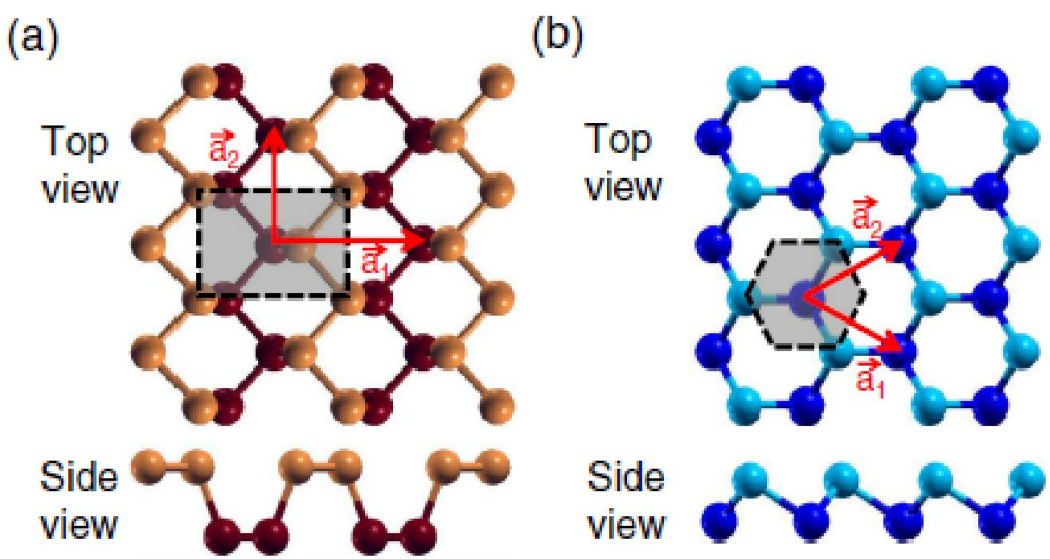
Phosphoerene

Blue Phosphorene



Theoretical Prediction of Layered Blue Phosphorus

Zhen Zhu and David Tománek, PRL, 112, 176802 (2014)



Layered black phosphorus **Layered blue phosphorus**

➢ **Structural properties**

✓ Space group of R-3m

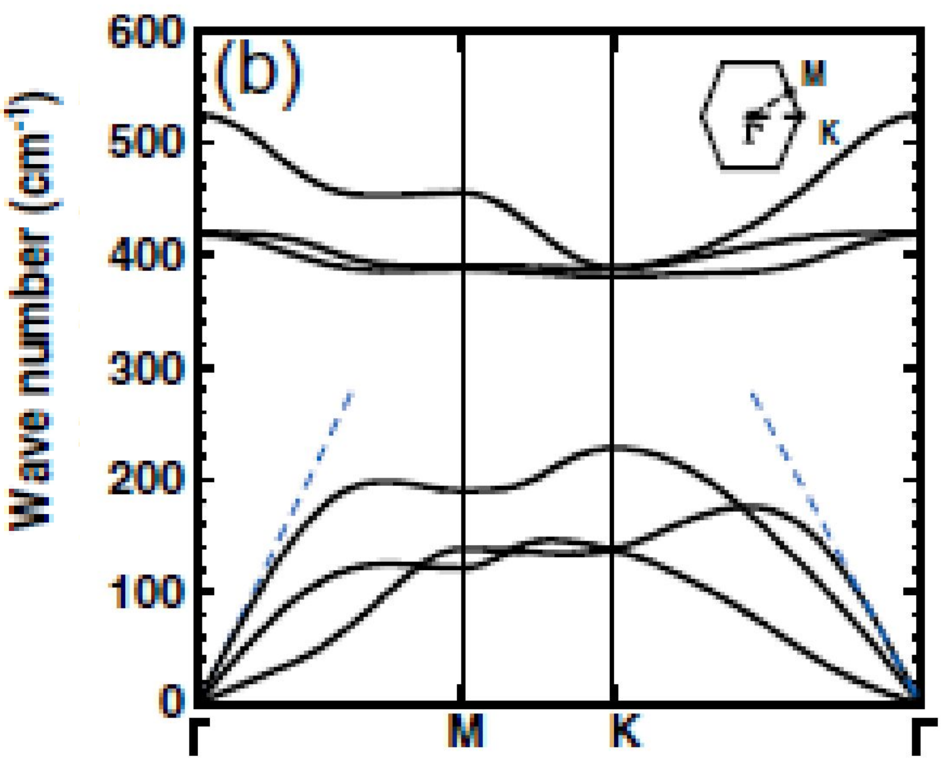
✓ Layers of six-membered rings linked in trans-decalin (zigzag puckering)

✓ AB hexagonal stacking with interlayer distance of ~ 5.63 Å

✓ Nearly as stable as black phosphorene (~ 1 meV/atom difference)

Theoretical Prediction of Layered Blue Phosphorus (cont.)

Zhen Zhu and David Tománek, PRL, 112, 176802 (2014)



Vibrational band structure of a monolayer of blue phosphorus

➢ Vibration spectrum properties

✓ Nearly isotropic in-plane elastic response

✓ High in-plane rigidity of free-standing monolayer (D=0.84 eV)

✓ High speed of sound (vs= 7.7 km/s) and in-plane stiffness

✓ High vibration frequencies of optical modes at Γ point (420 cm^{-1} and 520 cm^{-1})

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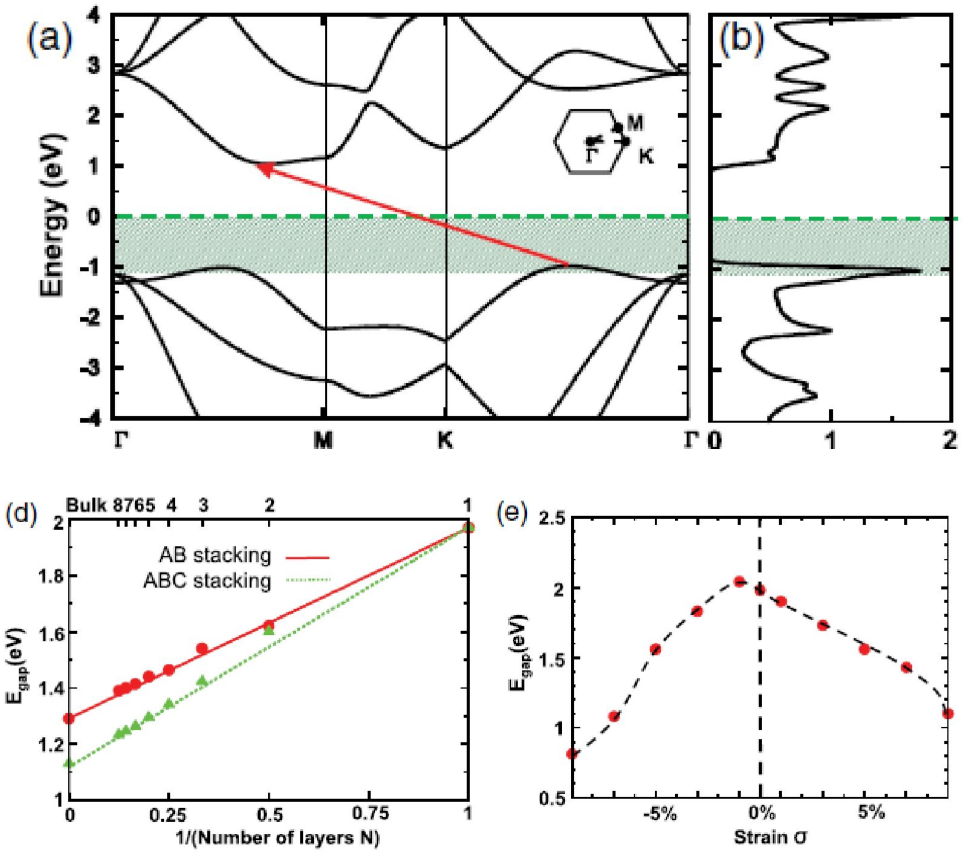
Theoretical Prediction of Layered Blue Phosphorus (cont.)

Zhen Zhu and David Tománek, PRL, 112, 176802 (2014)

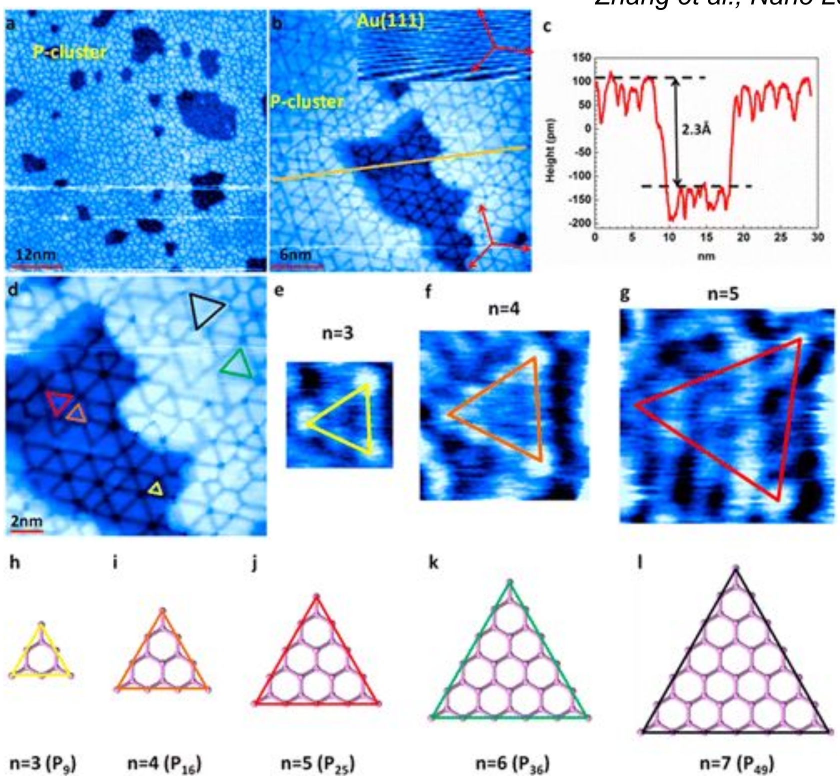


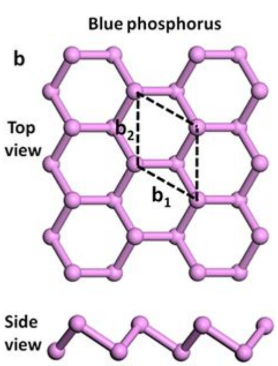
➢ Unique electronic properties

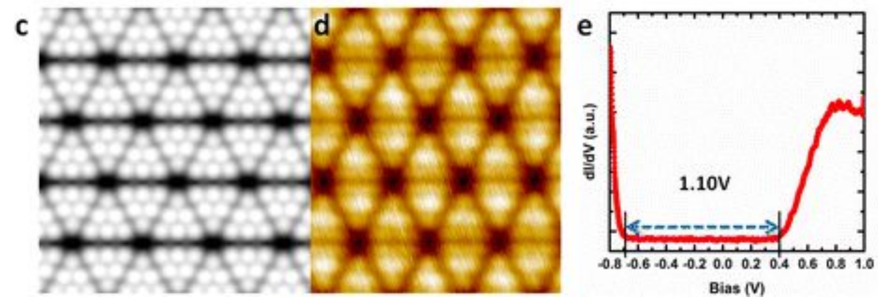
- ✓ Wide indirect wide band gap
- ✓ Layered-dependent tunable bandgap: ~2 eV at monolayer and ~ 1.4 eV (AB stacking) at bulk.
- ✓ Semiconducting-semimetal transition under in-layer strain
- ✓ Possible high carrier mobility
- ✓ A promising candidate as a BCS-superconductor after proper intercalation with some alkali metals such as Li, Na, and K
- ✓ Exhibit the charge-density-wave (CDW) phase due to periodic distortion of the atomic lattice in this layered 2D material under proper intercalation and high pressure.

Epitaxial Single Layer Blue Phosphorene

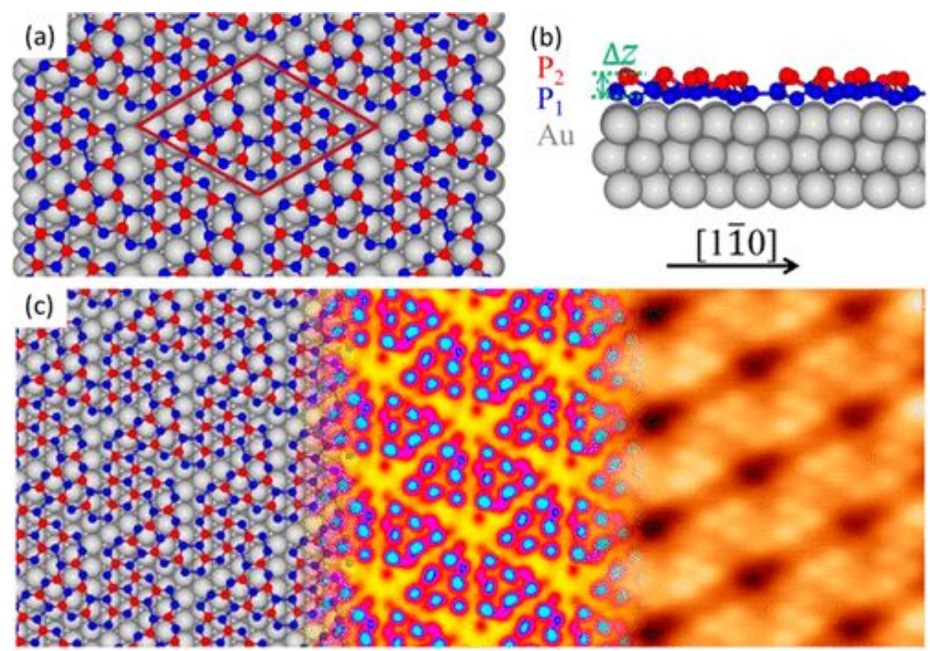
Zhang et al., Nano Lett., 2016, 16 (8), pp 4903–4908







Zhunag et al., ACS Nano, 2018, 12 (5), pp 5059–5065



A New Pathway for Synthesis of Layered Blue Phosphorus from Black Phosphorus by Li Intercalation

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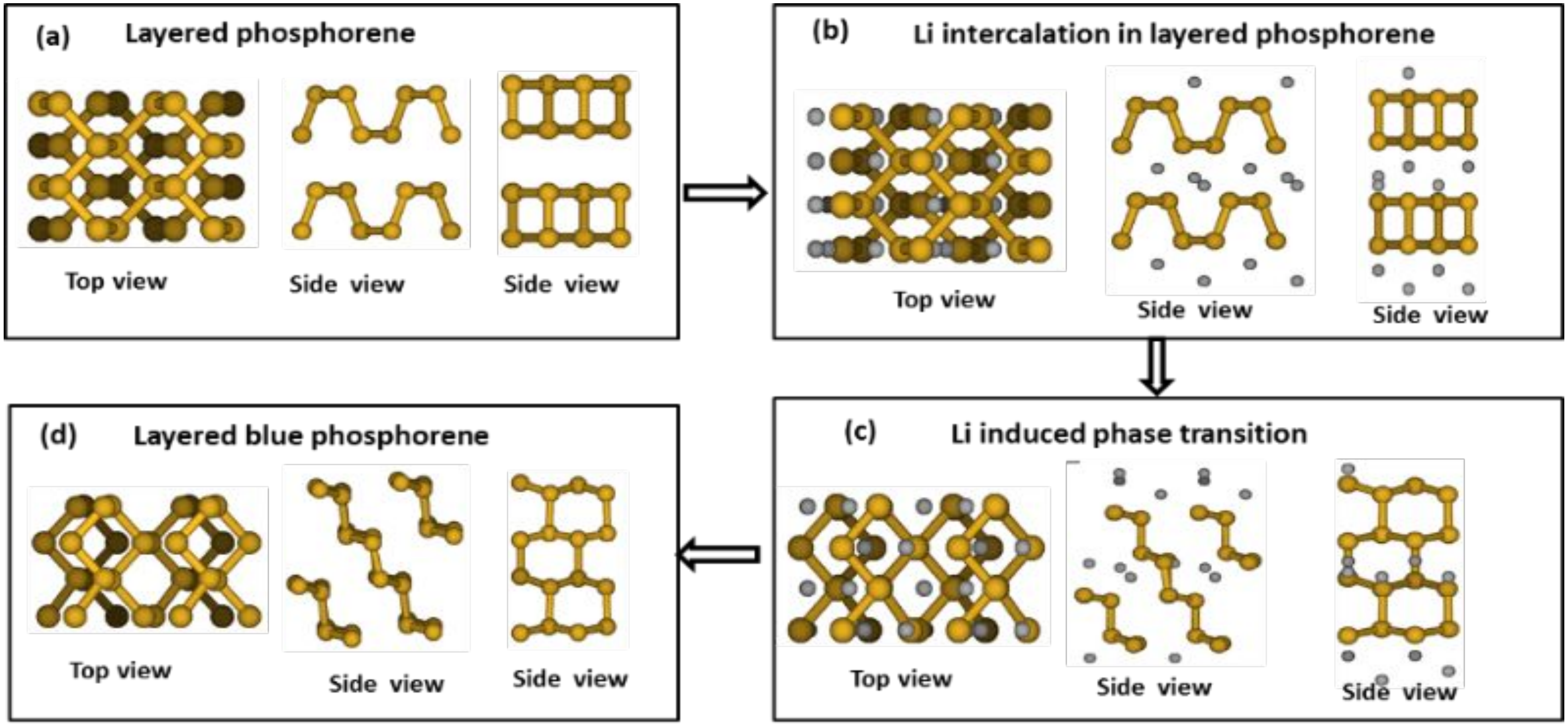
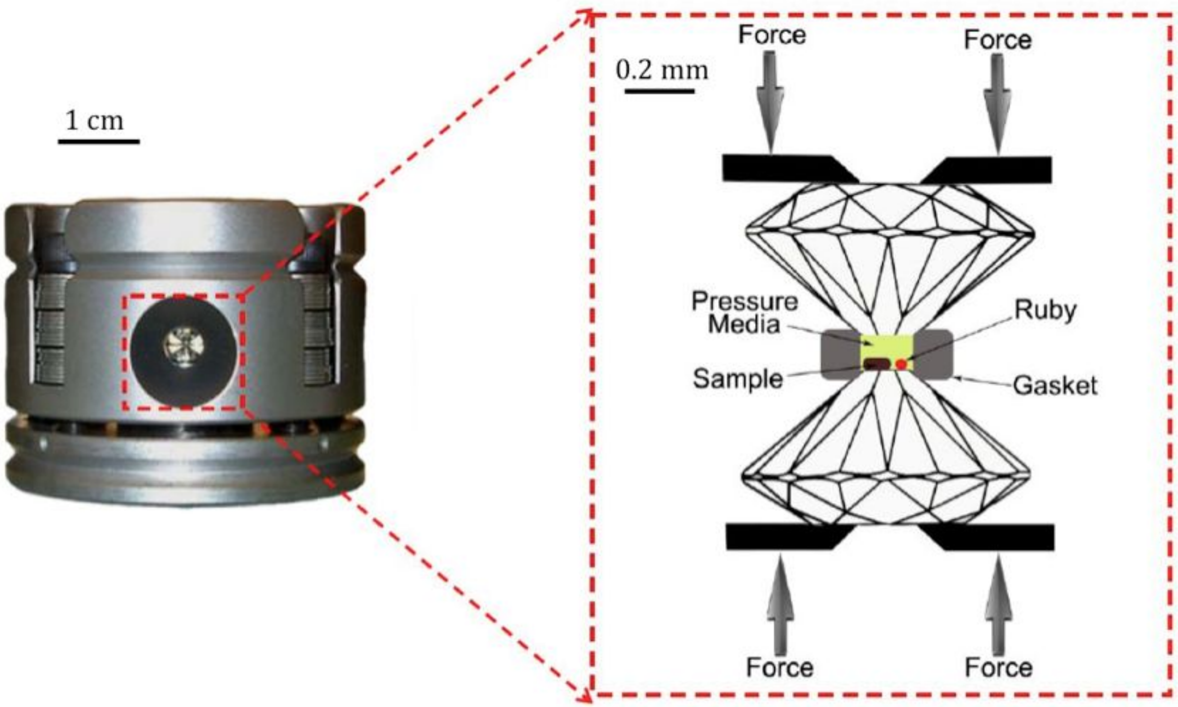
➢ **Preliminary study by Congyan Zhang and Ming Yu, Dept. of Phys. and Astronomy, UofL (2018)**



(a) layered black phosphorene; (b) Li intercalation in the layered black phosphorene; (c) Li induced structural phase transition during the relaxation; and (d) layered blue phosphorene after Li removal, respectively. The arrows show the direction of the flow of the transition induced by the Li intercalation.

High Pressure Experiments



Yang, S. and Zhaohui, D. (2011) Novel pressure-induced structural transformations of inorganic nanowires, in "Nanowires – Fundamental Research", ed. Abbass Hashim, InTech, Rijeka, Croatia.

Diamond Anvil Cell (DAC)

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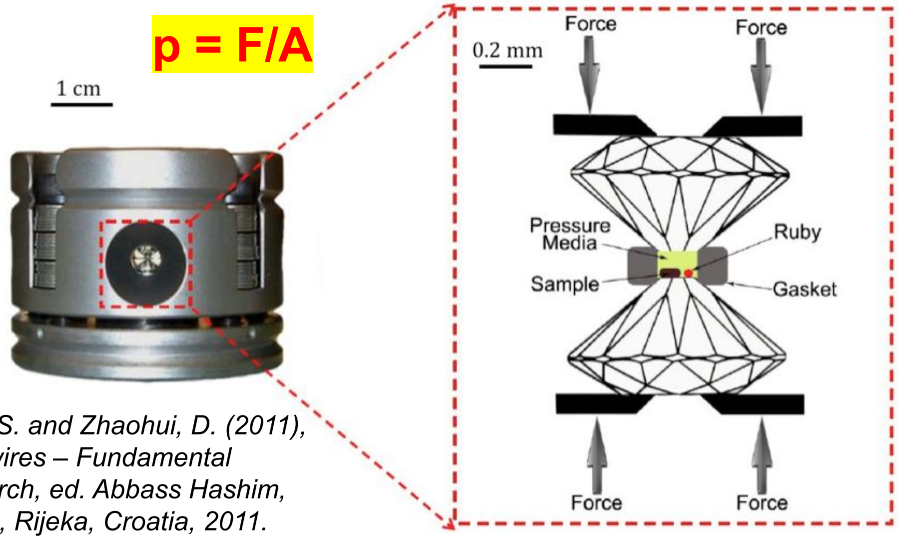
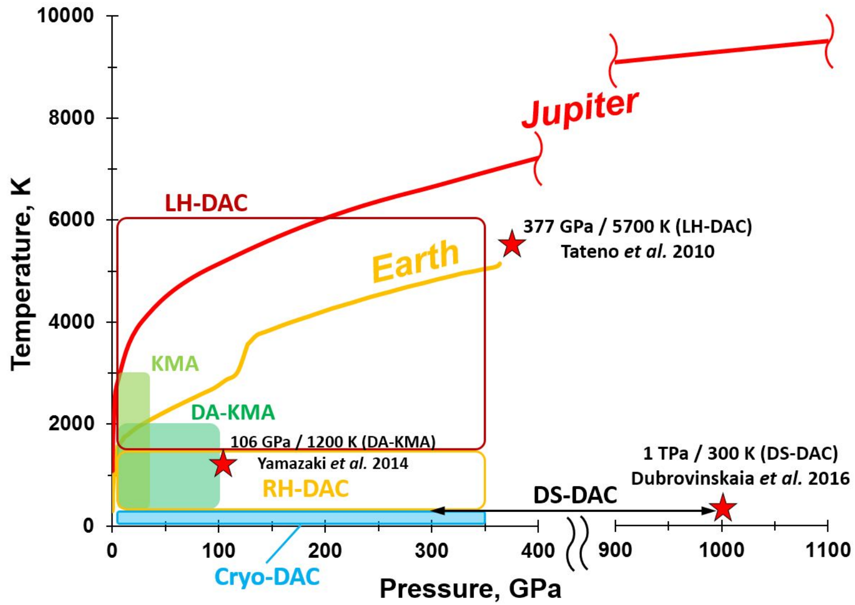
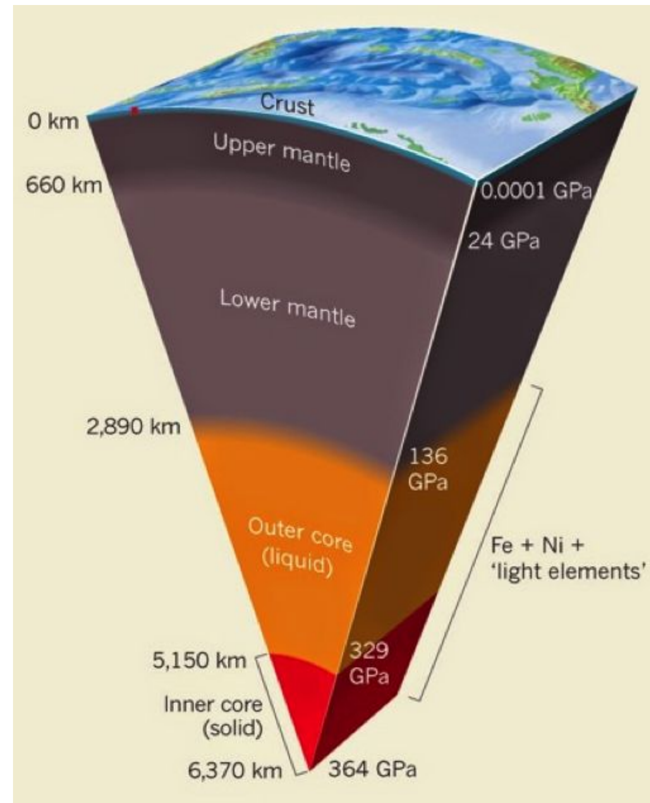
p = F/A



Yang, S. and Zhaohui, D. (2011), Nanowires – Fundamental Research, ed. Abbass Hashim, InTech, Rijeka, Croatia, 2011.



https://en.wikipedia.org/wiki/Diamond_anvil_cell



T.S.Duffy, Nature, 479, 480-481 (2011).

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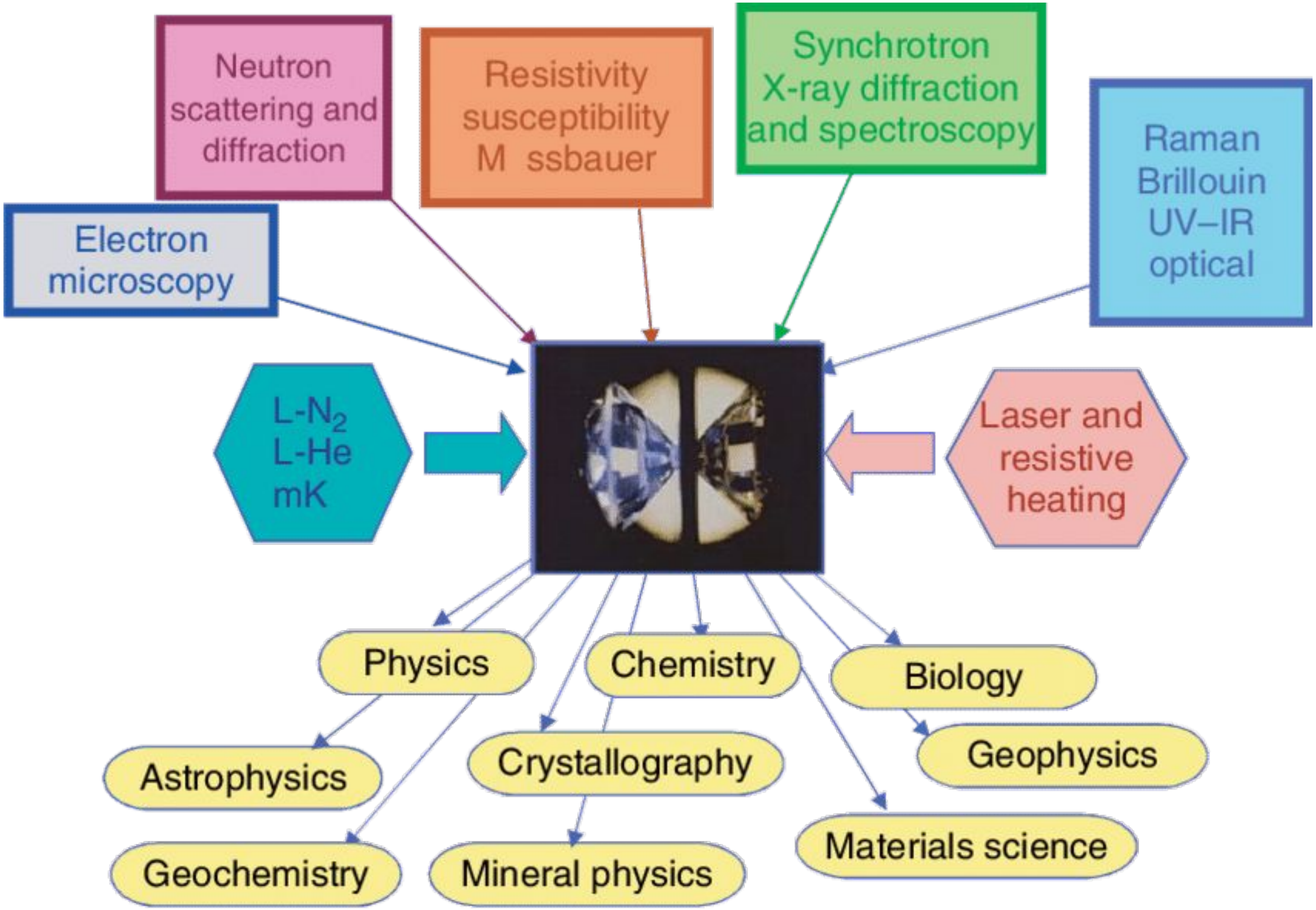
High Pressure Experiments in DAC



H.-K.Mao, W.L. Mao, Treatise on Geophysics 2, 231-267 (2007)

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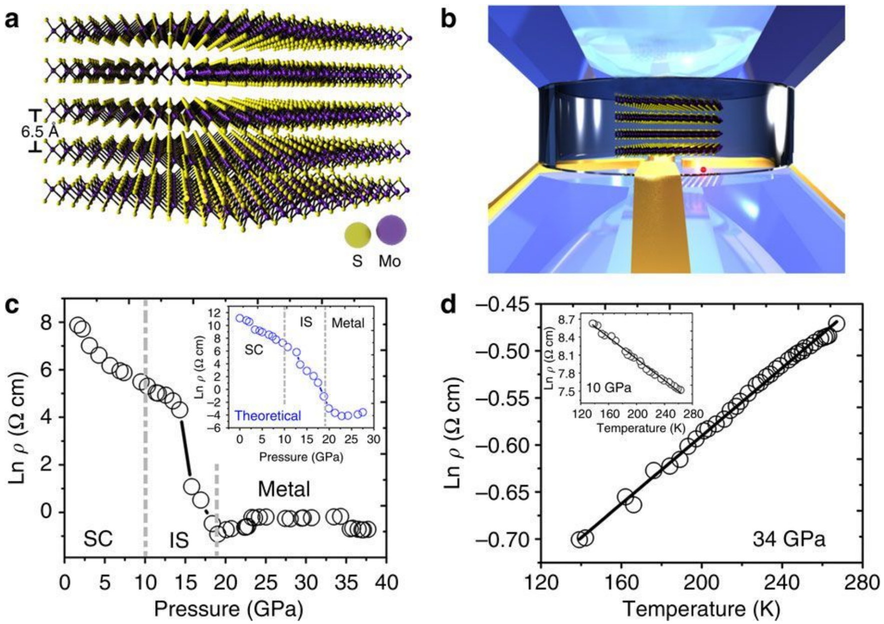
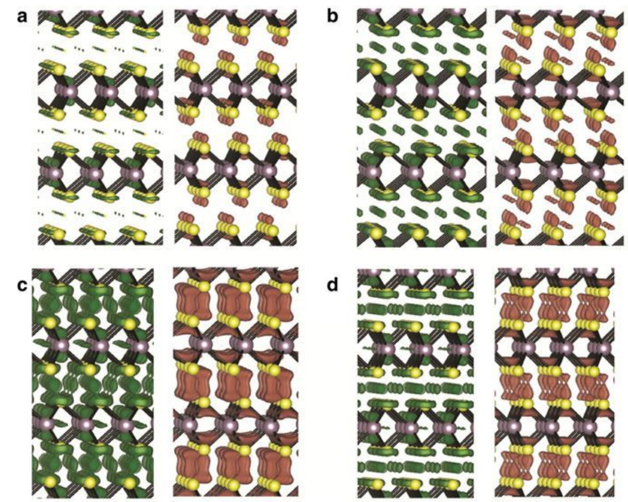
DAC Studies of 2D Materials

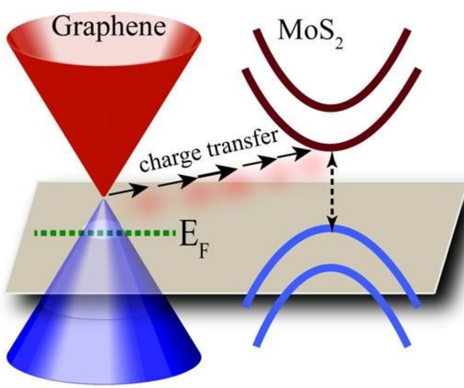
Nayak et al, Nature Comm. 5, 3731 (2014)

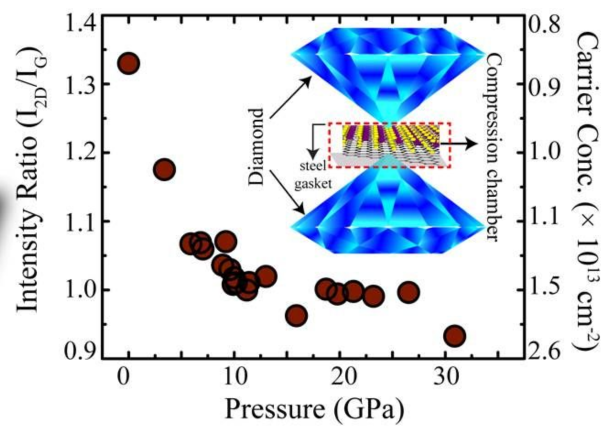




Charge accumulation (green) and depletion (orange) at the various in-plane and out-of-plane strains.

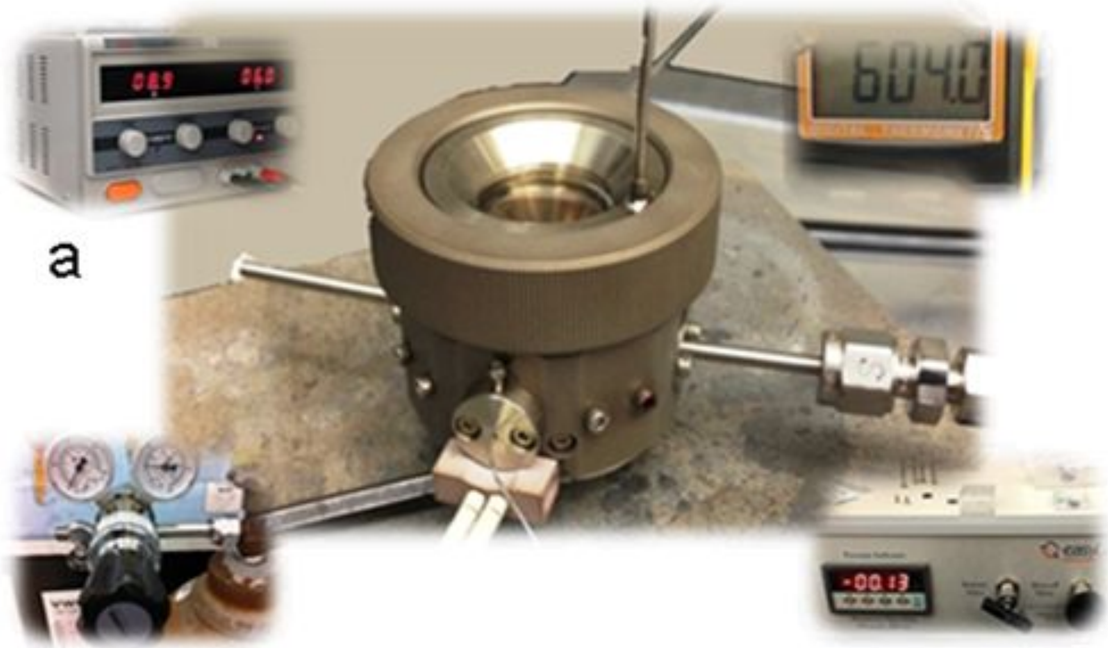
http://hpstar.ac.cn/contents/27/5300.html

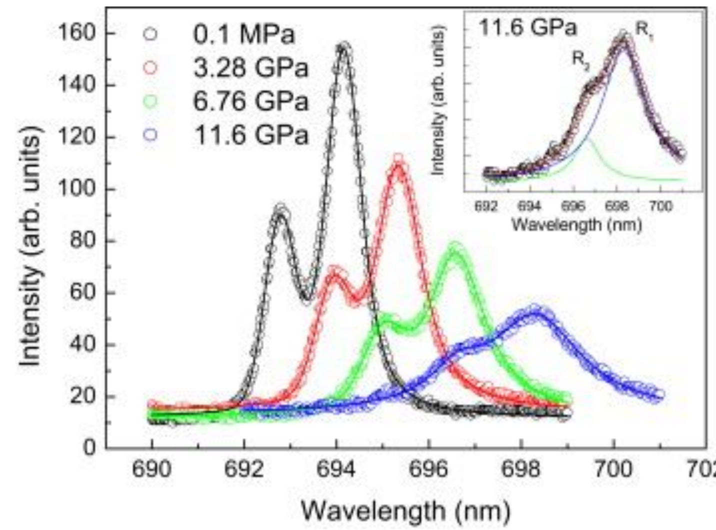




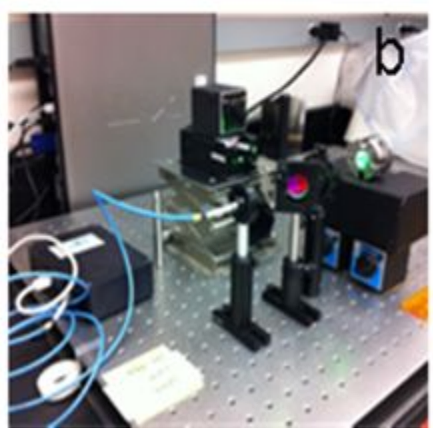
Tuning the carrier mobility and conductivity of heterostructured monolayer grapheme and 2H-MoS2

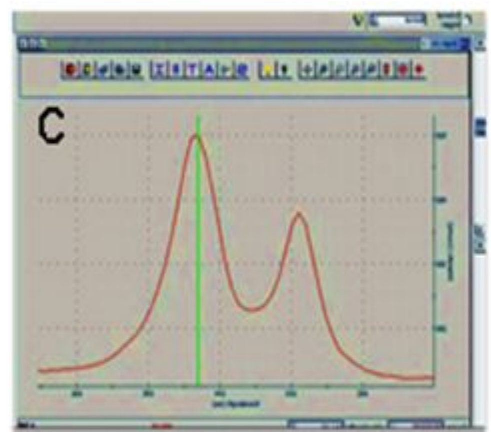
DAC - Experimental Setup





M.-S. Jeong et al., Current Applied Physics 13, 1774 (2013)





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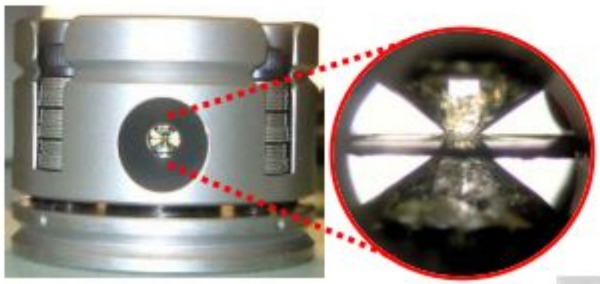
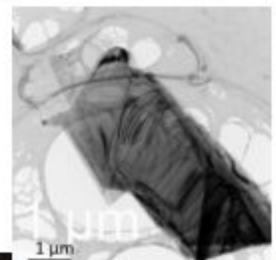
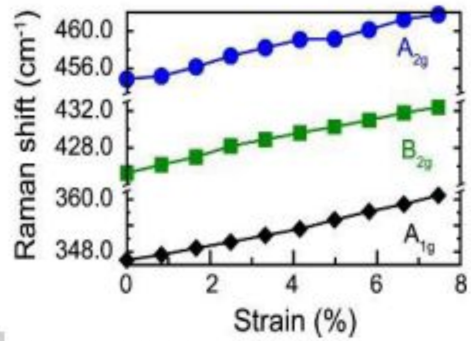
High Pressure Optical Study

Diamond Anvil Cell (DAC)

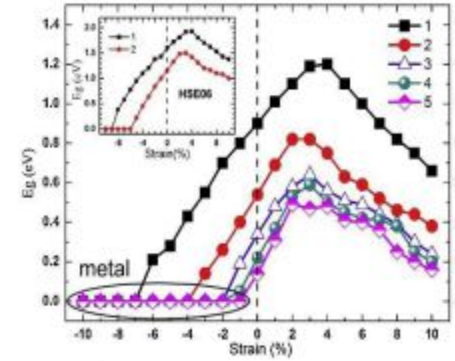


DAC: Pressure → 15 GPa,
Temperature → 1000 °C

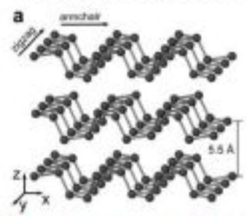




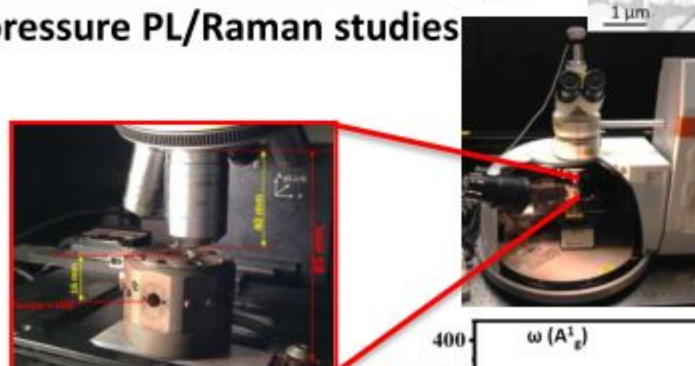
Nanotechnology, 2015. **26**, 075701.

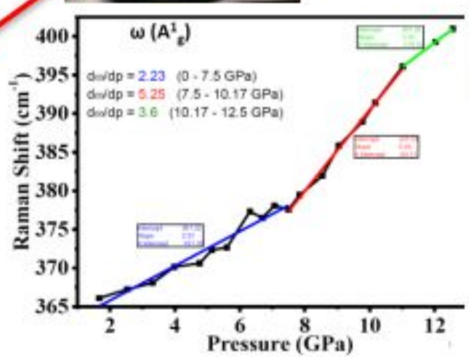


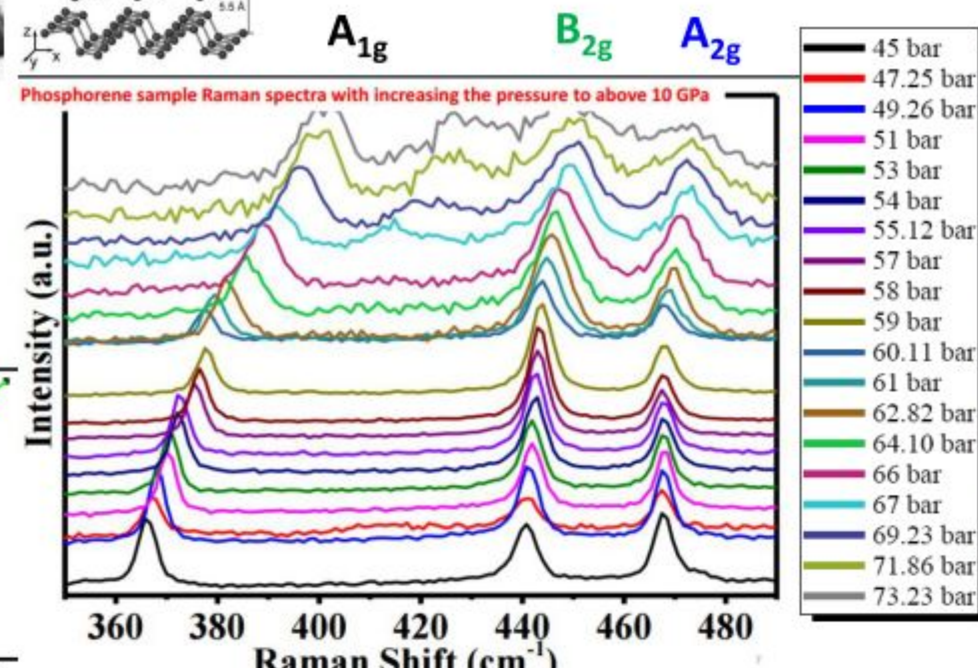
Chem. Phys. Lett., 2015, ***622***, 109.



modified optics for *in-situ* high pressure PL/Raman studies







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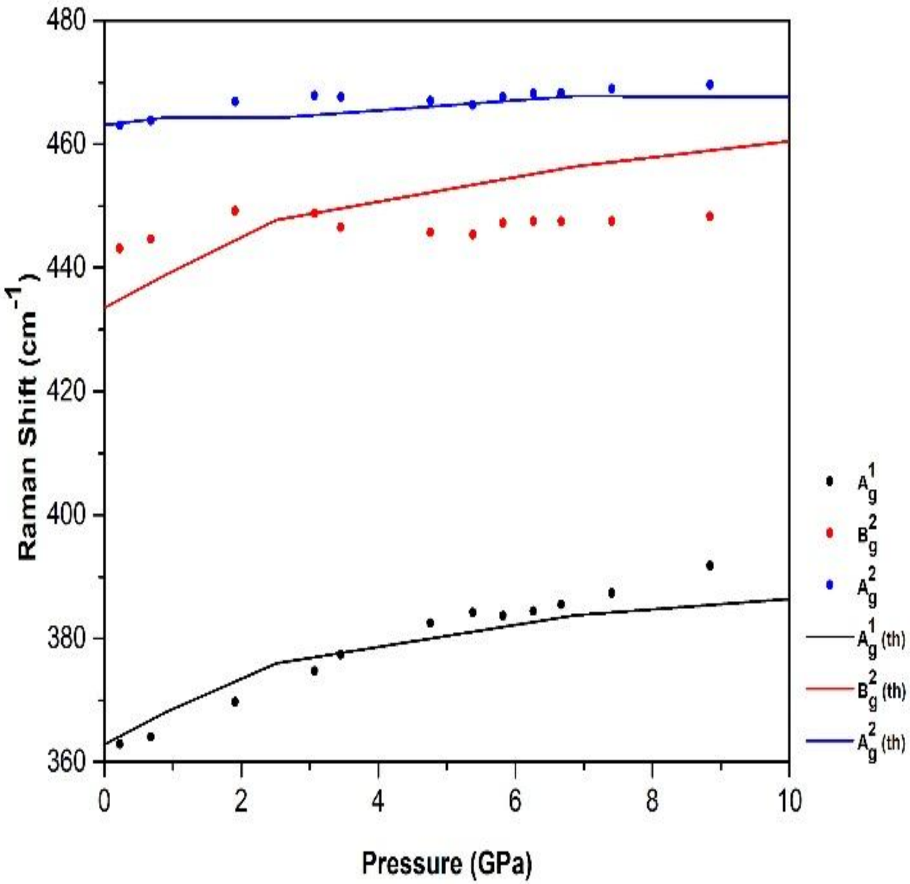
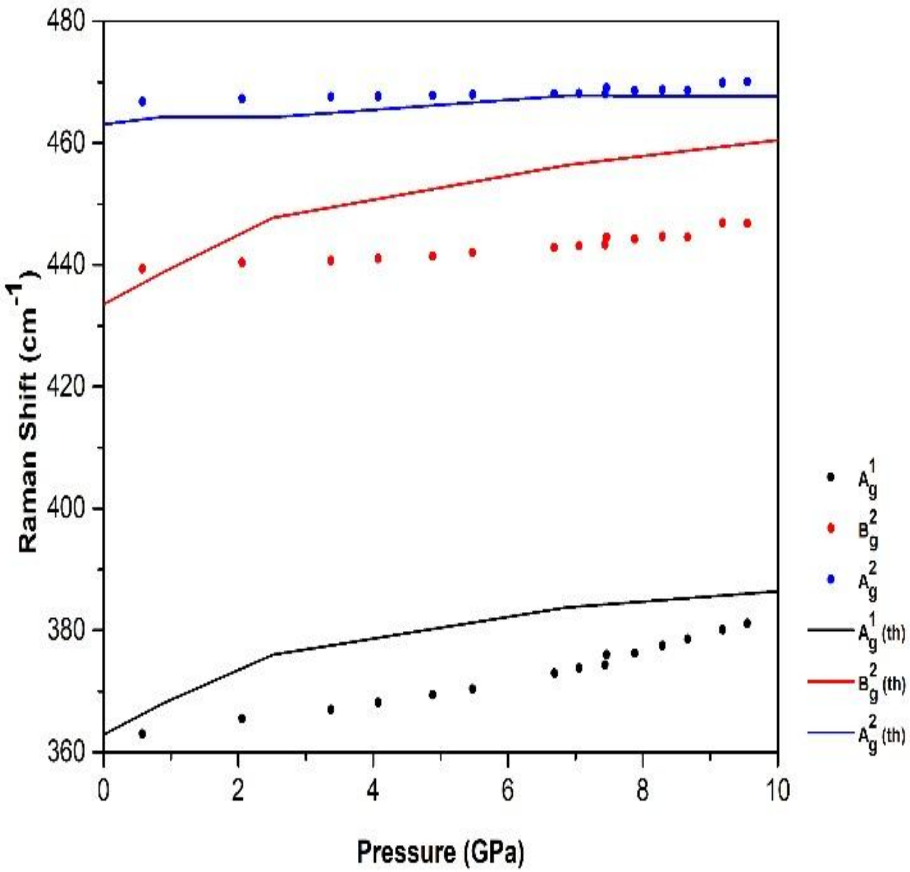
Theory Meets Experiment





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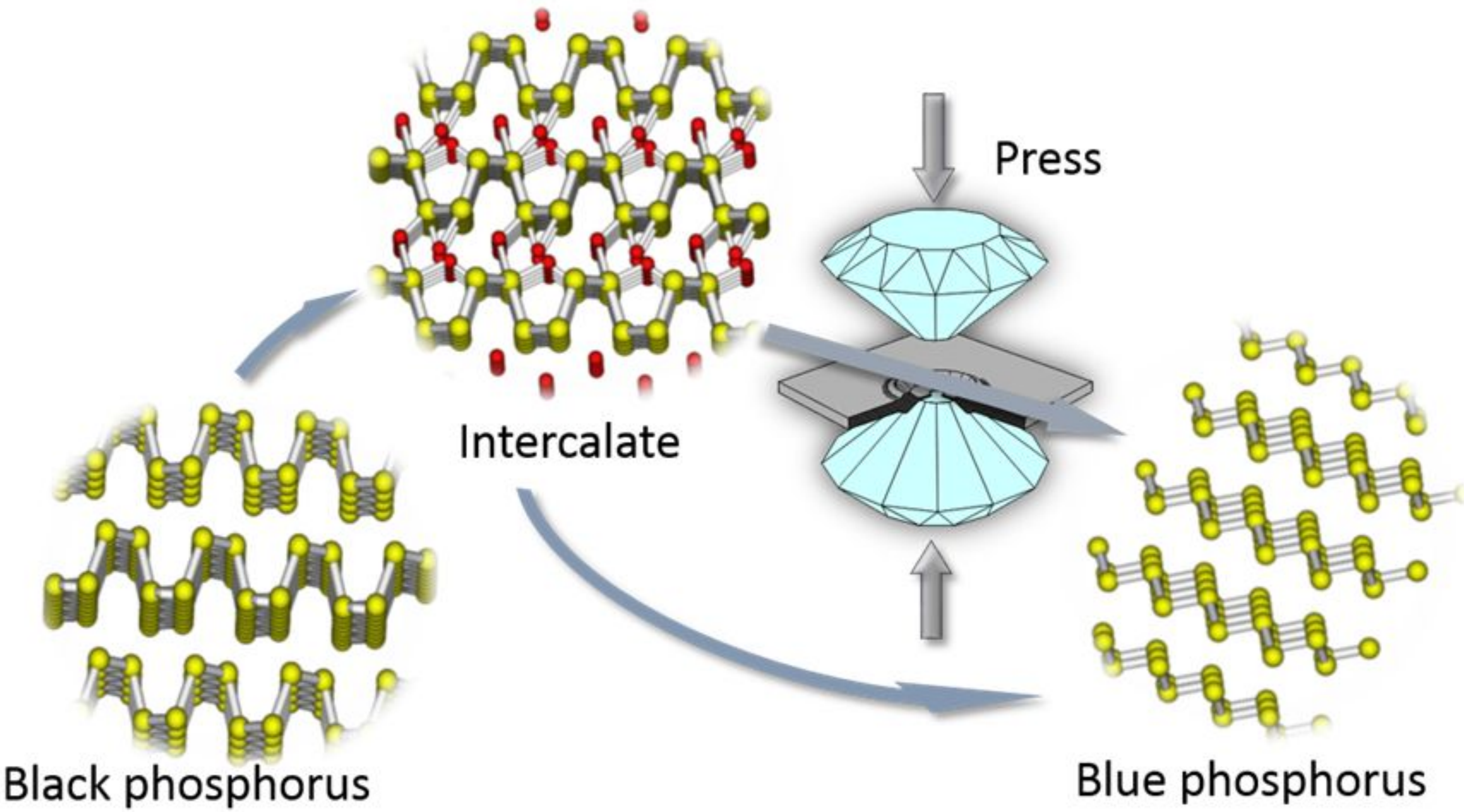
Summary



Thank You