Invited Talk, IWCE 2015

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ARL

Electronic and Vibrational Properties of 2D Materials from Monolayer to Bulk: Opportunity Unlimited

Mahesh R. Neupane

U.S. Army Research Laboratory, Macromolecular Science & Technology Branch (MSTB), Materials & Manufacturing Science Division (MMSD), Weapons & Materials Research Directorate (WMRD)

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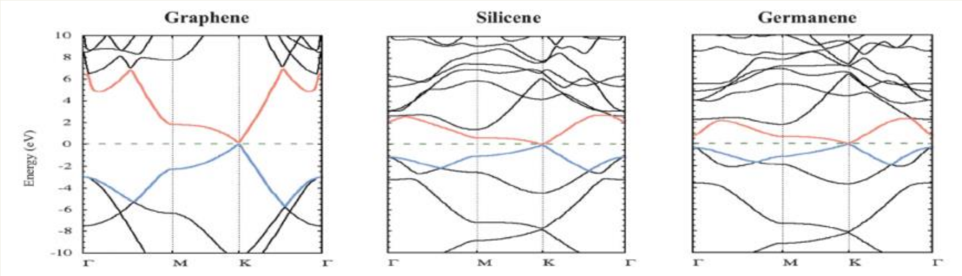
Monolayer 2D: Graphene, h-BN …..

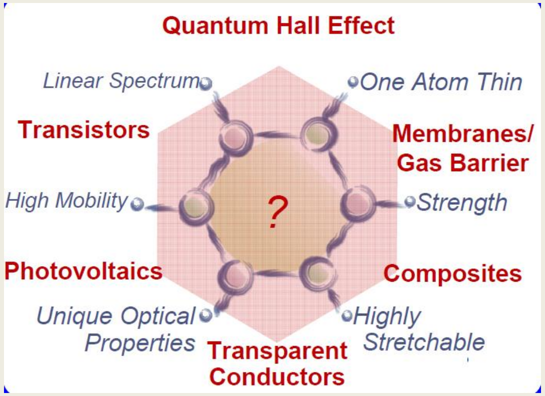
ARL

Pioneer in the 2D materials research:

And others……

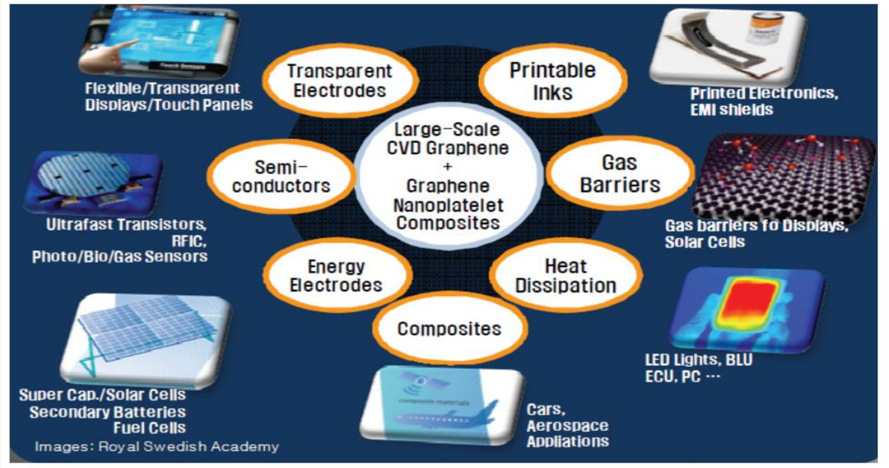


Prof. Andrea C. Ferrari
Cambridge Univ.

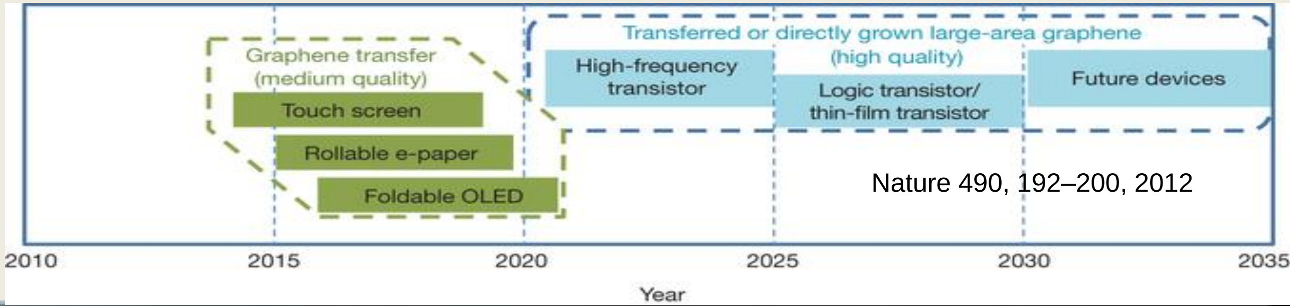


Graphene Properties

Prof. Tomás Palacios, MIT



- ✓ Graphene has become a commercial 2D materials
- ✓ Complementary materials for other 2D materials



Nature 490, 192–200, 2012

Chem. Soc. Rev., 2014, 43, 6537--6554

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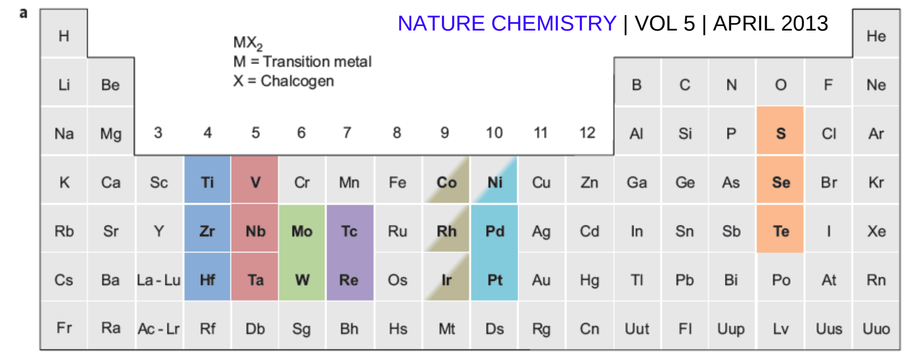
Tetra-layer 2D: TMDC

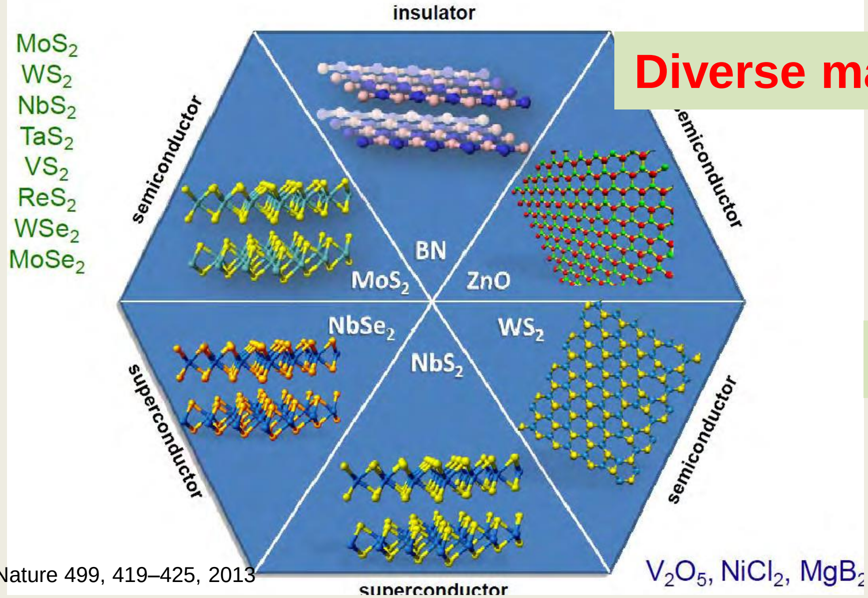
Transition Metal Dichalcogenides - MX_2

Large database

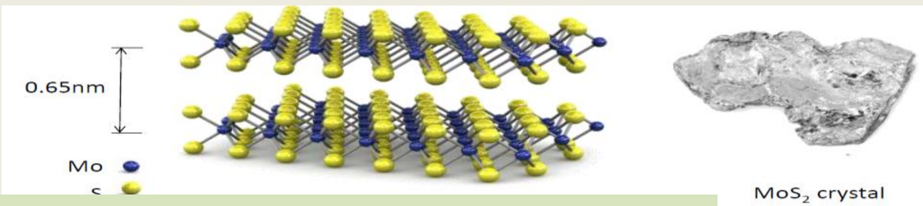
- ✓ 88 compositions possible, but theory predicts 44 stable choices.
- ✓ Depending on column of transition metal, can get wide range of properties: metallic, semiconducting, superconducting, insulating.



Diverse material properties

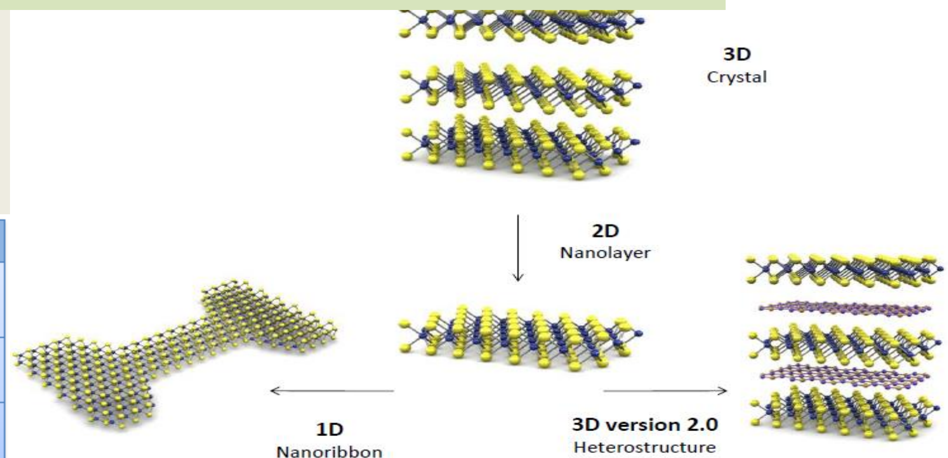


Nature 499, 419–425, 2013



Wide range of geometries

Prof. Andras Kis



Electrical property	Material	Possible Role
metallic, CDW, superconducting	$NbSe_2$, NbS_2, $NbTe_2$ TaS_2, $TaSe_2$, $TaTe_2$	interconnects, Josephson junctions, SC qubits
semimetallic	$TiSe_2$, graphene	interconnects
semiconducting	MoS_2, $MoSe_2$, WS_2, WSe_2	transistors, switches, sensors

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Tetra-layer 2D: Design space

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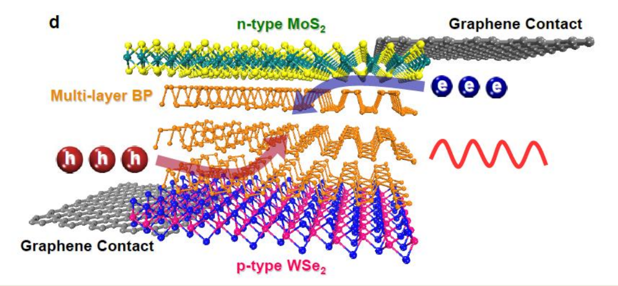
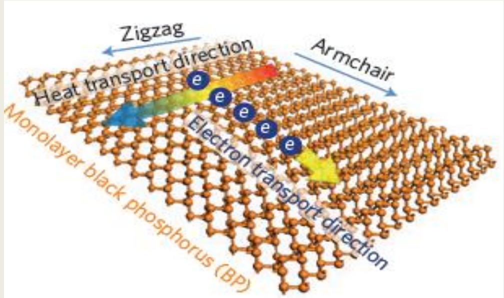
Stack



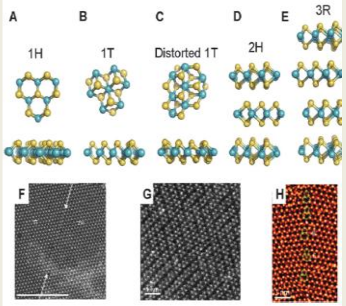
Inter-layer coupling

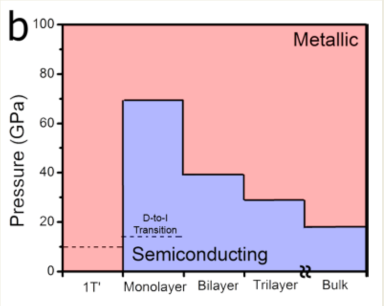
Etch



Edge + Chemical functionalization

Pressure



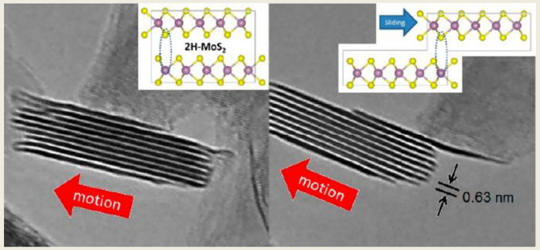


Chem. Soc. Rev., **44** 2702-2712

Mechanical + Orbital chemistry

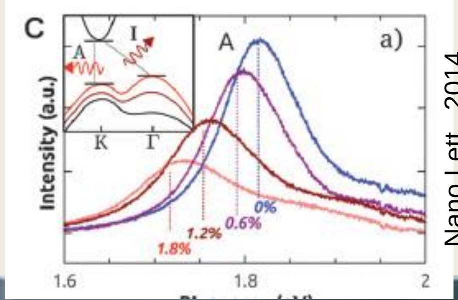
Slide

ACS Nano, Article ASAP
DOI: 10.1021/nn506052d



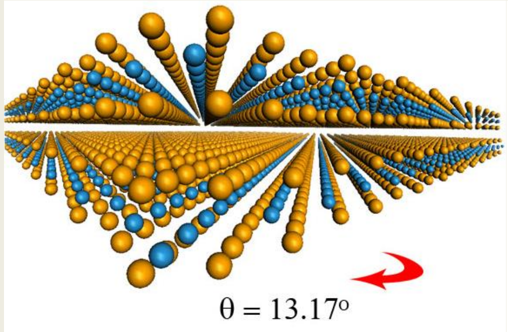
Mechanical coupling

Strain

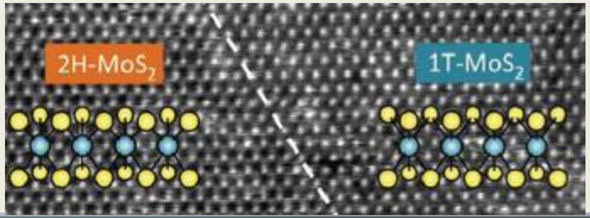


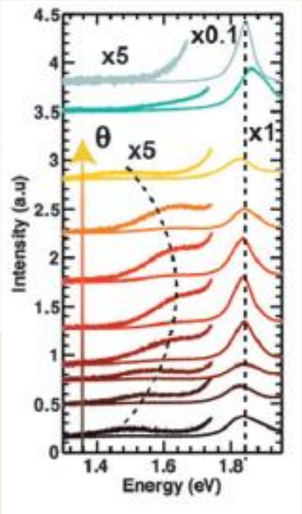
Nano Lett., 2014, 14, 3869–3875

Rotate



Electromechanical
Voiry et al, Nat. Mat. (2013).





Chemistry

True Interdisciplinary

Using

- ➢Chemistry
- ➢Physics
- ➢Surface science
- ➢Mechanics
- ➢Engineering
- ➢More……

Limitless opportunity

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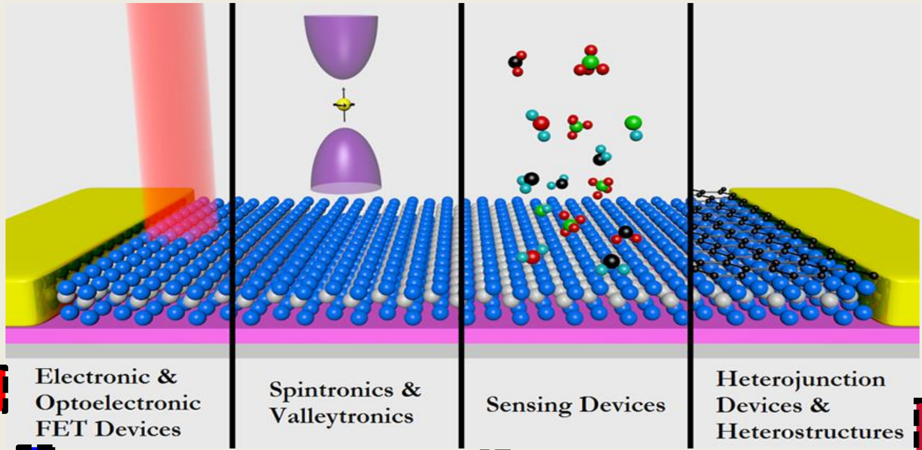
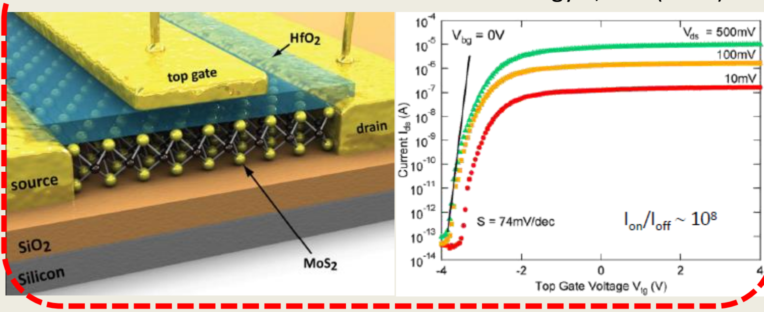
Solution: Application Domain

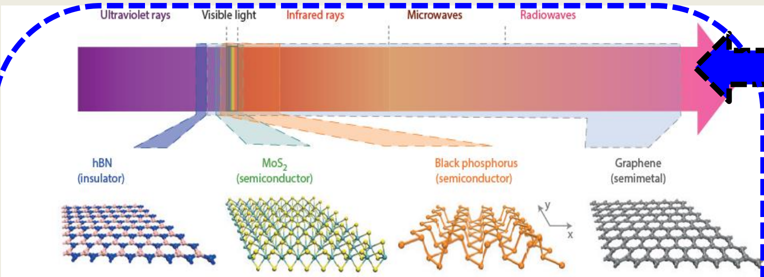
ARL

Physics/Chemistry-based



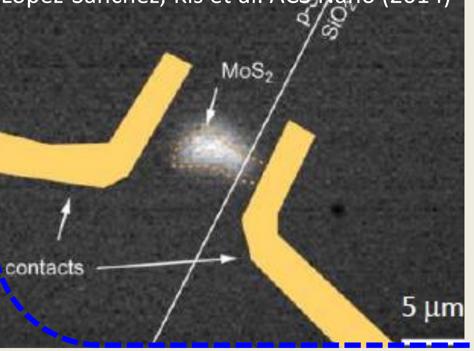
Nature Nanotechnology 6, 147 (2011)

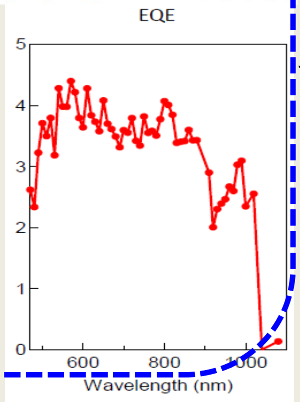


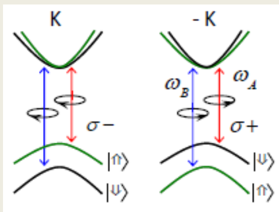


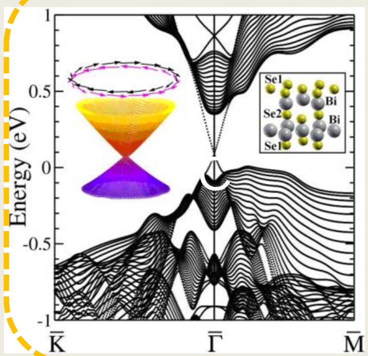
Nature Photonics, 2014

Lopez-Sanchez, Kis et al. ACS Nano (2014)

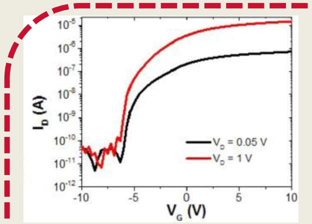




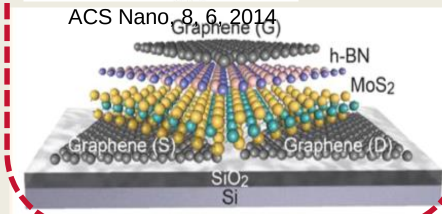


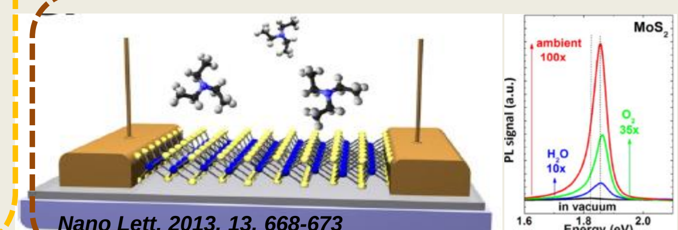


Cao et al., Nature Physics 9, 499 (2013)



ACS Nano, 8, 6, 2014





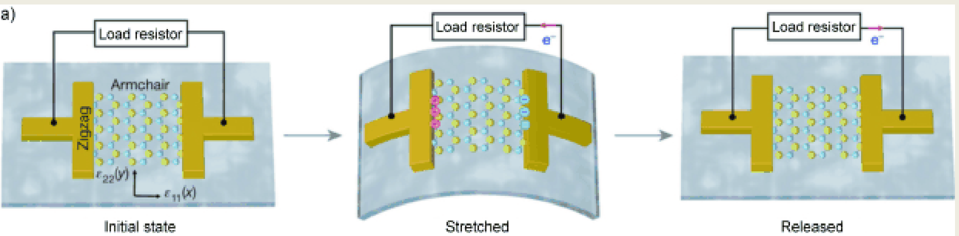
Nano Lett. 2013, 13, 668-673

The Nation's Premier Laboratory for Land Forces

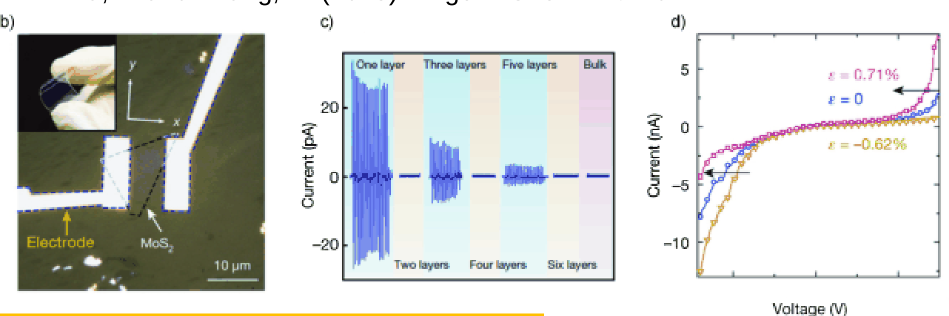
Solution: Application Domain

Energy Generation and Harvesting

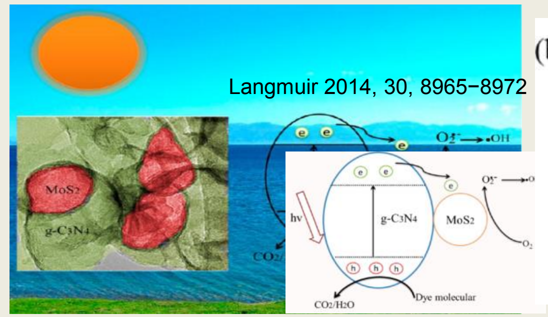
Mechatronics

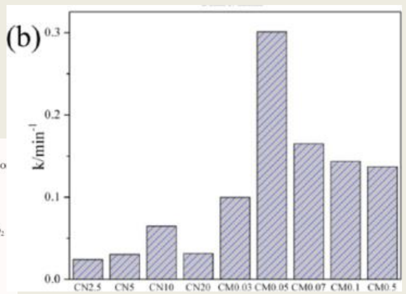


Wu, T. and Zhang, H. (2015). Angew. Chem. Int. Ed..



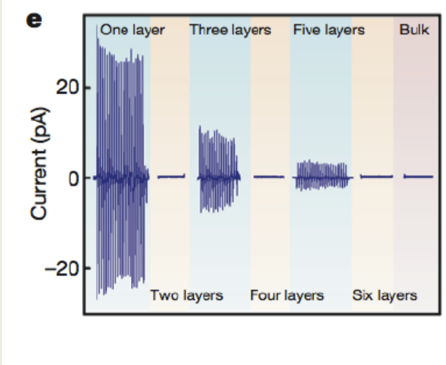
Catalysis





Electron−hole pairs lifetime increases, resulting in the improvement of photocatalytic degradation efficiency

Piezoelectricity

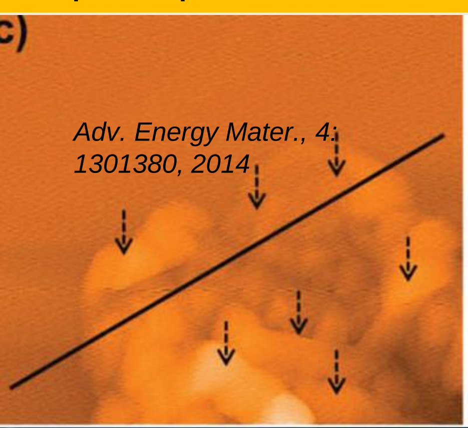


J. Phys. Chem. Lett. 3, 2871 (2012).

Piezo-coefficients of trigonal prismatic TMD structures are comparable to bulk wurtzite structures

Nature (2014).

Supercapacitors



- ✓ **Stable covalently bonded MoS_2/RGO heterostructure**
- ✓ **Nearly four fold increment in the capacitance**

One application/device every week

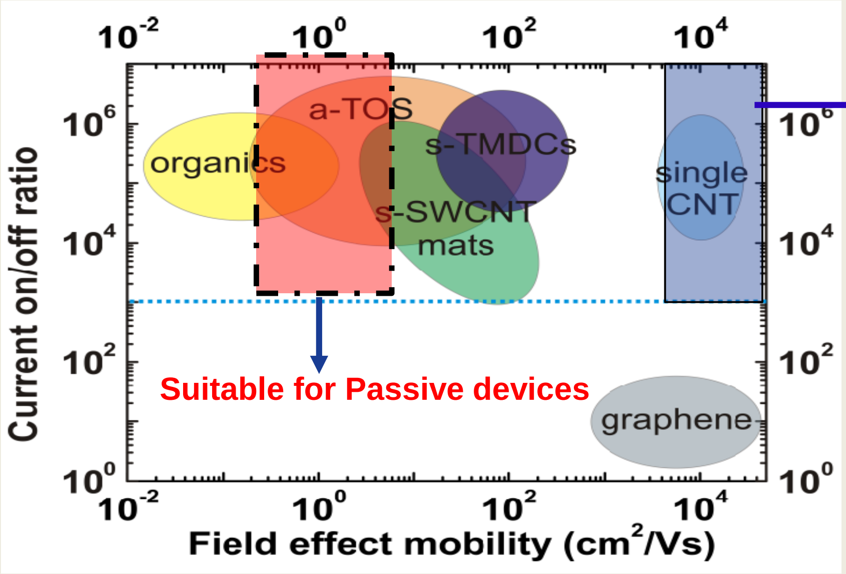
Ann J Materials Sci Eng 1(3): id1014 (2014)

Limitations

- ✓ Interfaces problem –
  - ✓ Difficulty forming an ohmic contact
  - ✓ Exfoliated materials may not be pristine enough to lead to complete electronic coupling
- ✓ Immune to intercalated contamination- Hard to control
- ✓ Growth of Large crystal- Bottleneck for industry-standard electronics
- ✓ Low mobility and higher contact resistivity- Far from bulk Si
- ✓ Uncontrolled chemical doping- Oxidation problem
- ✓ Low optical quantum yield- Indirect gap for FL-system
- ✓ Integration issues exists-Strain mismatch between substrate and TMD
- ✓ Stacking of 2D multilayers- Uncontrolled sliding and twisting

In the last 10 years, 2D materials research had made a huge stride by "Scotch Tape governed" to "Sandwich governed"

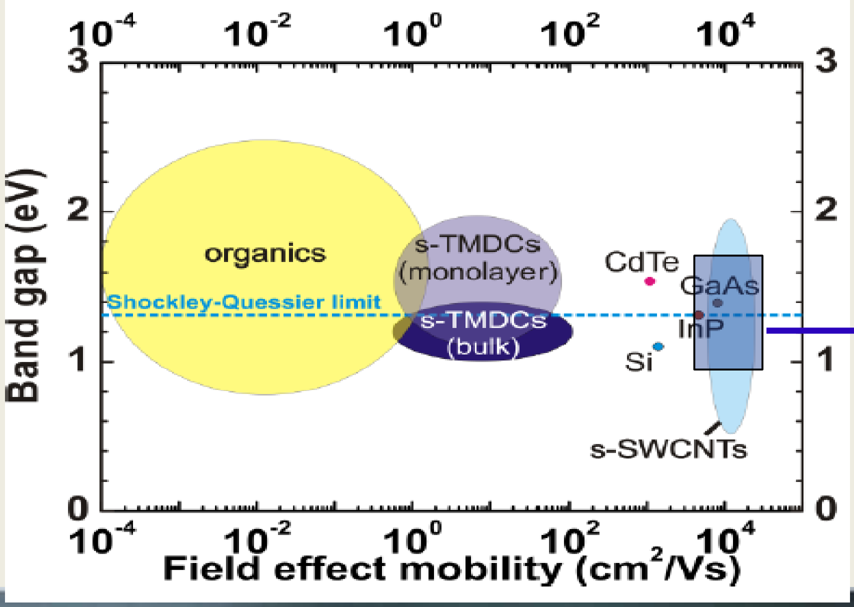
Are we there yet?



- ✓ Suitable for Active devices
- ✓ High mobility and Large on/off ratio

Current Status:

- ✓ 10-200 cm^2/Vs
- ✓ On/Off ratio:10^4-10^6
- ✓ Subthreshold swing (75-100 mV/Decade)



Current Status:

- ✓ Gap between 0.6 eV to 2 eV
- ✓ Direct-to-indirect transition for > 1ML

- ✓ Suitable for high efficiency photovoltaic devices
- ✓ High mobility and medium gap

On par with the Si-technology!!!

Solutions

- Advanced synthesis technique for large area growth

Experiment

- Efficient characterization technique to understand the atomistic details

Experiment +Theory

- Suitable and accurate theory and modeling exploring electronic, photonic and magnetic properties to support and guide experimental process

Theory + Modeling

Role of Modeling

Can complement experimental efforts by being:

- Complementary
  - By providing theoretical reasoning for experimental findings
- Predictive
  - By venturing rich but unexplored chemistry and physics

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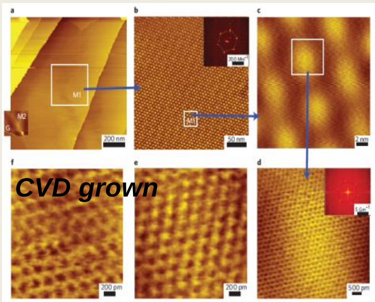
Complementary Modeling

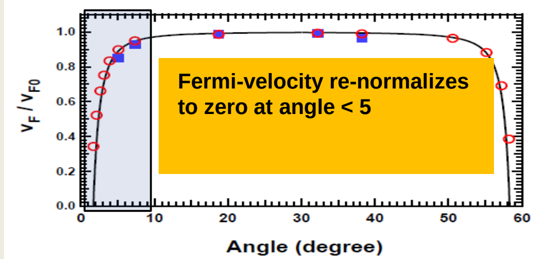
Experimentally observed commensurate Graphene material systems

Misorientation in common in multilayer vdW materials



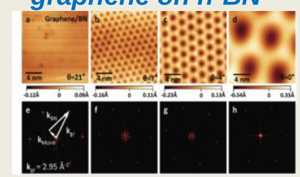
Li et al., Nat. Phys. 2010

PRL 109, 236604 (2012)

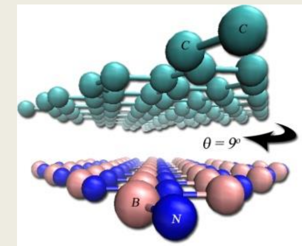


Graphene/h-BN

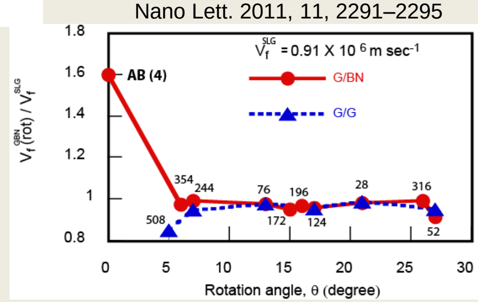
graphene on h-BN

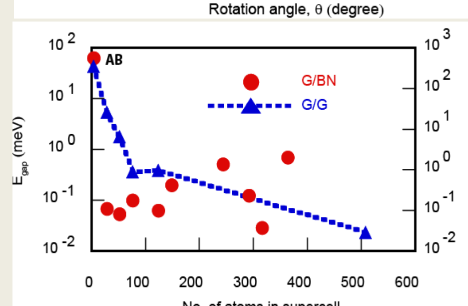


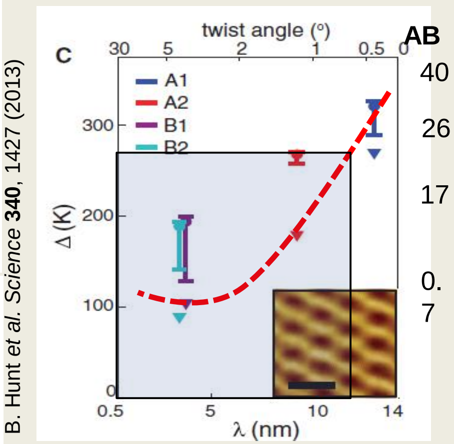
DFT-PBE



Nano Lett. 2011, 11, 2291–2295





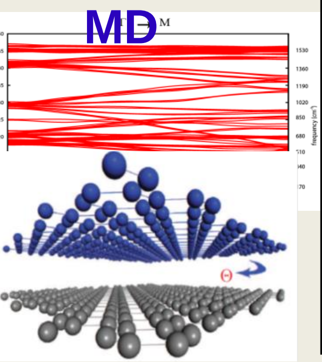


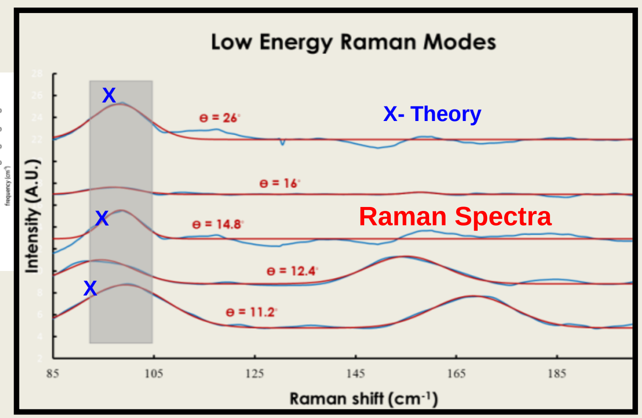
B. Hunt *et al. Science* **340**, 1427 (2013)

Graphene/Graphene

Experimentally observed misoriented Graphene systems is interesting θ <10º

MD





To be published

- ✓ BZ-folding in the commensurate supercell contributes to the low-energy modes, consistent with experiment.
- ✓ Folded phonons attributes to the phonon scattering channels at the zone-center.

- ✓ Gap of (~56 meV) in the perfectly aligned AB-G/BN system vanishes with the a slight misorientation
- ✓ No velocity renormalization in the linear region of bandstructure.

Submitted

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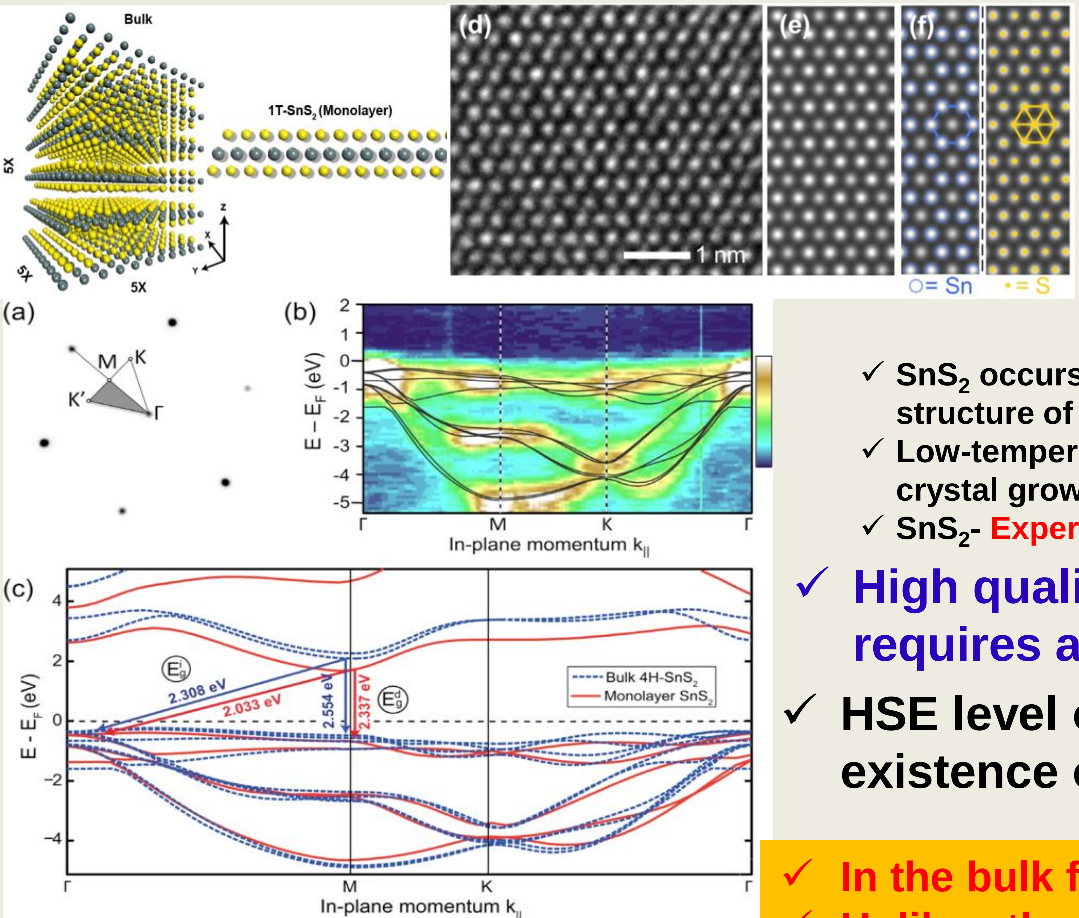
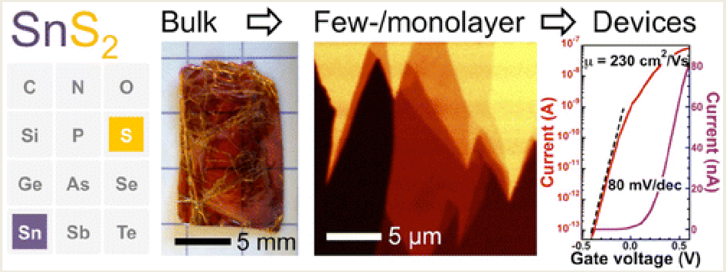
Complementary Modeling

ARL

Identification of structure topology

SnS_2 – An Emerging 2D Material





- ✓ SnS_2 occurs in different polytypes (1T, 2H, and 4H) with the same structure of the S-Sn-S layers but different interlayer stacking
- ✓ Low-temperature synthesis produces the 2H-polytype, while crystal growth at temperatures above 800 C tends to give 4H
- ✓ SnS_2- Experimental ambiguity exist

✓ **High quality mapping of ARPES band structure requires accurate theory**

✓ **HSE level of theory correctly predicted the existence of 4H-topology in the bulk SnS_2**

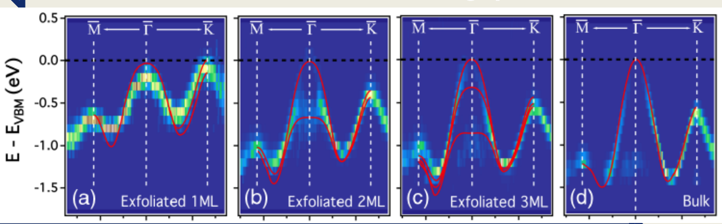
✓ **In the bulk form, SnS_2 exists in the 4H topology**

✓ **Unlike other TMDC, SL-SnS_2 has indirect bandgap**

Y. Huang, E. Sutter, J. T. Sadowski, M. Cotlet, O .L .A. Monti, D. A. Racke, M. R. Neupane, D. Wickramaratne, R. K. Lake, B. Parkinson, and P. Sutter.. ACS Nano, 2014

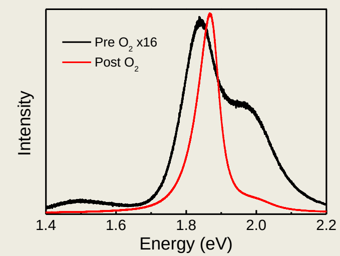
Validation of optical behavior in ML-MoS_2

Indirect-to-direct bandgap

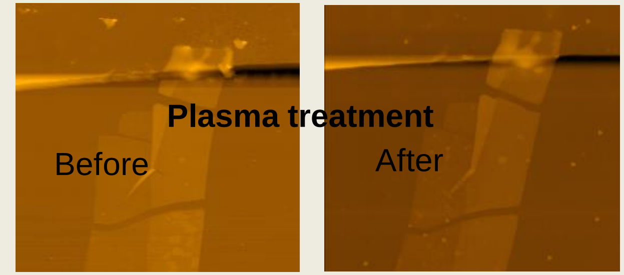


Increasing layer-thickness

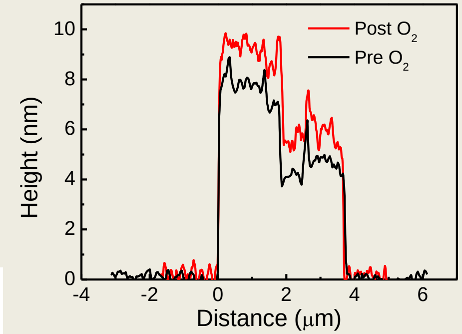
PRL 111, 106801 (2013)



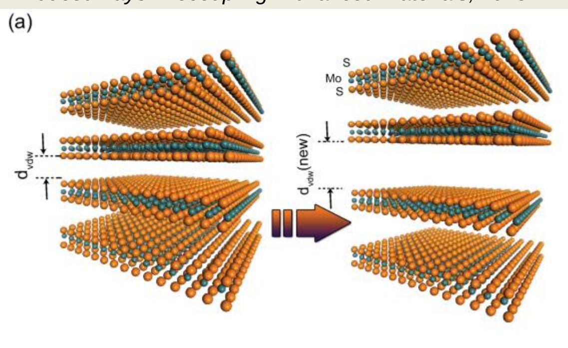
Enhanced PL intensity shows indirect to direct transition



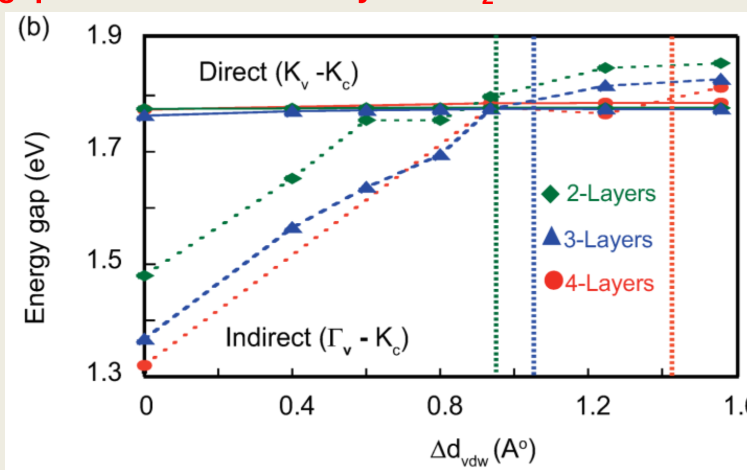
20% Increment in the flake thickness



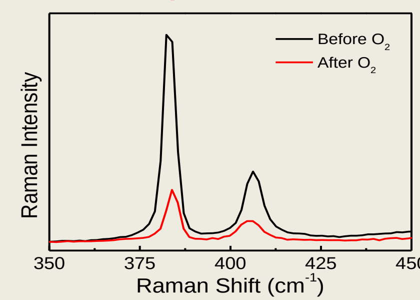
Rohan Dhall, **M. R. Neupane**, D. Wickramaratne, M. Mecklenburg, Z. Li, C. Moore, R. K. Lake, and S. Cronin. *Bulk Direct Band Gap MoS2 by Plasma Induced Layer Decoupling. Advanced Materials, 2015*



DFT (HSE) correctly predicts the indirect-to-direction bandgap transition in Multilayer MoS_2



No significant shift in the Raman peaks



- ✓ For 4L-MoS_2, indirect to direct cross over occurs at Δ (vdW gap) of 1.45 Å
- ✓ The gap is nearly equivalent to the symmetric distribution of 20% increases in layer thickness in the experiment.

Plasma treatment leads to the modulation of vdW-gap between the layers
New mechanism to turn indirect-direct bandgap tuning ML TMDC

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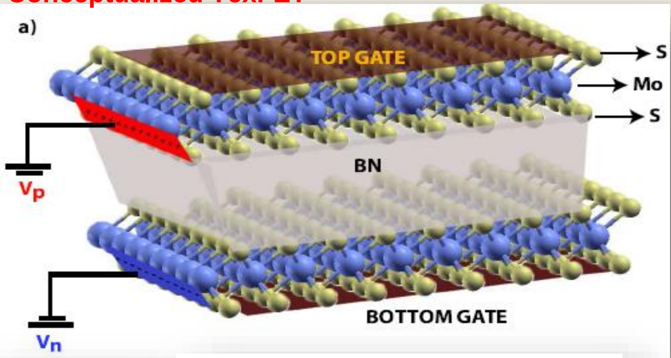
Predictive Modeling

ARL

Excitonic gap

Conceptualized TexFET



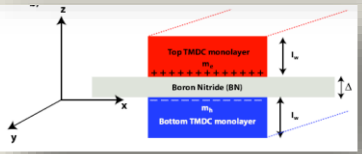
$$E(K.E) = -\frac{\hbar^2}{\mu * \eta^2}$$

$$E_b = min\{E(K.E) + E(Coulomb)\}$$

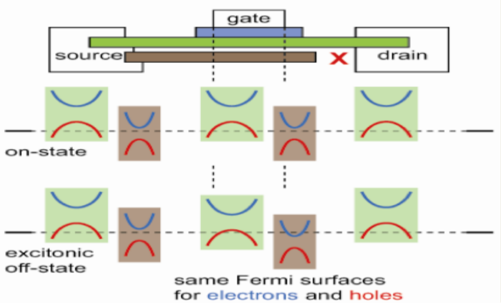
Reduced effective mass

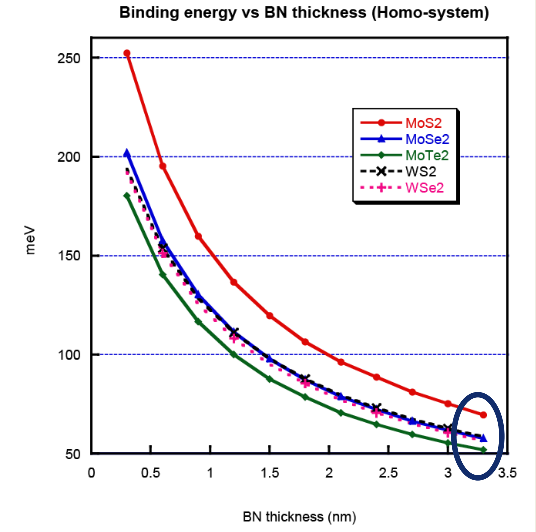
$$E(Coul) = -\frac{e^2}{\kappa}\int\int\int\int[dx\ dy\ dz_e\ dz_h\ N_h^2\ N_e^2 sin^2(\frac{pi * z_h}{l_w})\ sin(\frac{pi * (z_e - l_w - \Delta)}{l_w})$$
$$exp[-\frac{(x^2+y^2)}{2 * \eta}\ \frac{1}{[x^2 + y^2 + (z_e - Z_h)^2]^{1/2}}]$$

Effective dielectric constant



DFT+ Variational principle





Material	ϵ_R	m_e (m_o)	m_h (m_o)	ϵ_{eff}	$E_g(theory)$ (eV)	$E_g(expt)$ (eV)
2H-MoS_2	3.43	0.57	0.66	3.86	1.6	1.9
2H-$MoSe_2$	4.74	0.7	0.55	4.52	1.375	1.66
2H-$MoTe_2$	5.76	0.69	0.66	5.03	0.94	-
2H-WS_2	4.13	0.44	0.45	4.21	1.548	1.95
2H-WSe_2	4.63	0.53	0.52	4.46	1.254	1.64

Mats.	2D Bohr Radius (a_{2D}) (nm)	Effective Bohr Radius (η) (nm)									
		BN thickness (ML)									
		1	2	3	4	5	6	7	8	9	10
MoS_2	0.665	2	2.32	3	3.88	4.31	4.38	5	5.5	5.5	5.6
$MoSe_2$	0.777	1.9	2.50	3.1	3.59	3.81	4.19	4.7	5	5.22	5.37
$MoTe_2$	0.789	1.97	2.52	3.1	3.49	3.8	4.2	4.69	5.2	5.27	5.49
WS_2	1	2.2	2.4	2.78	3.2	3.4	3.7	4	4.3	4.6	4.7
WSe_2	0.9	2.07	2.7	3.15	3.3	3.6	3.9	4.29	4.6	4.78	4.9
Graph.	7.8	10.1	11.7	10.9	-	-	-	-	-	-	-

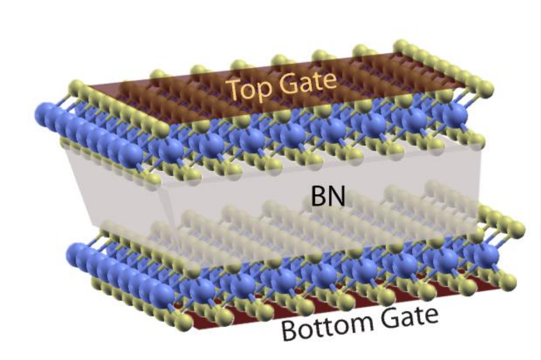
~57 - 70 meV
@ Δ = 3.3 nm (11 ML)

- **In the hetero-TMDC-BN system, the binding energies range from ~59- 63meV at BN thickness of 3.3 nm (~2 -2.5 kT at room temperature).**
- **Effective Bohr radius for the TMDC-BN system ~ 1/3 of the Graphene-BN system**

In collaboration with Prof. Appenzellar

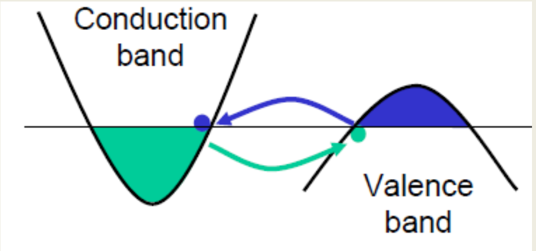
Predictive Modeling

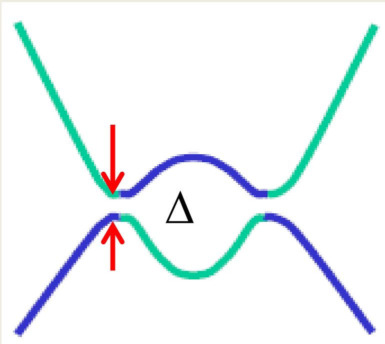
Existence of Suprefluidity

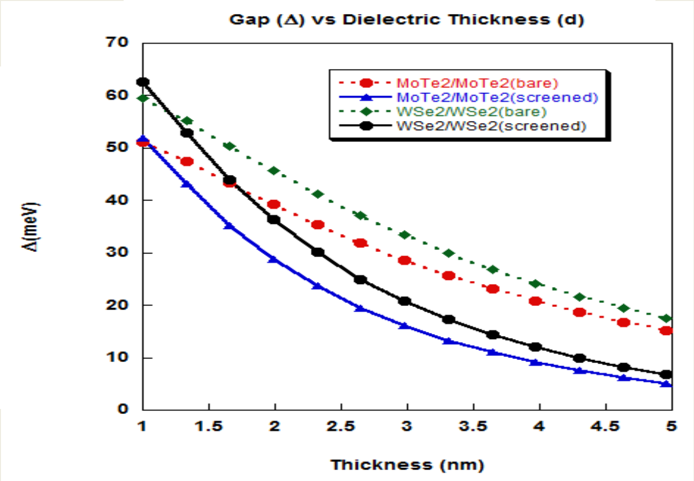


DFT+ Mean-field Approximation

$$\Delta_{k'} = \sum V^{ij}(|k - k'|)\frac{\Delta_k}{2E_{k'}}$$







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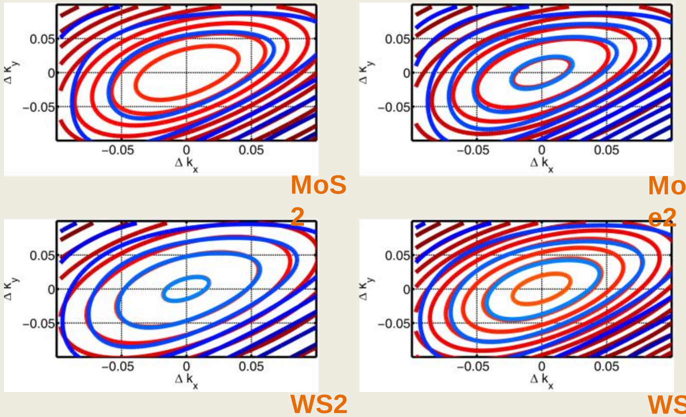
Good Fermi-surface nesting



Similar electron and hole effective masses

- ➢ **In the hetero-TMDC-BN system, screening effect reduces the Δ by ~1/3 for a thicker BN layer**
- ➢ **Mean field Approximation predicts that the screening issues in the e-hole system is prominent, and it reduces the superconducting gap by an order of magnitude**

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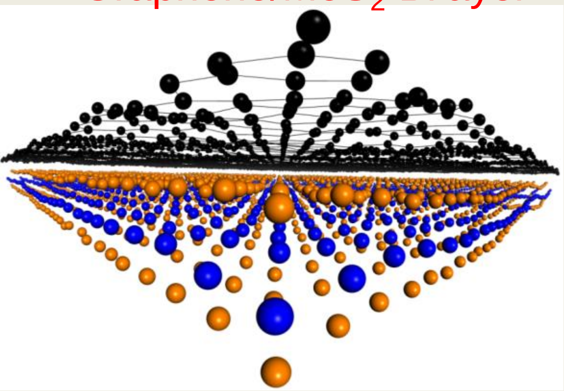
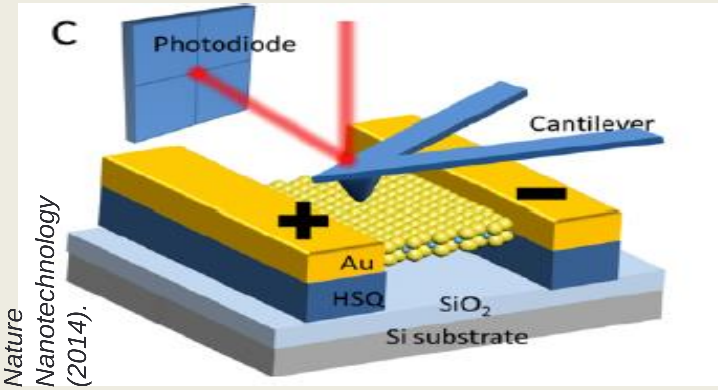
Nanoindentation: Predictive Modeling

ARL

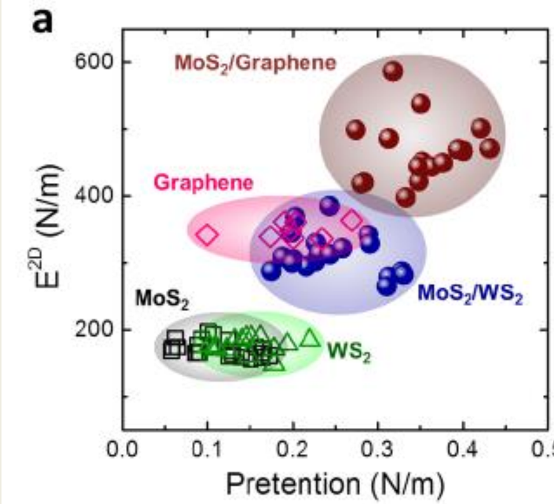
Graphene/MoS_2 Bilayer



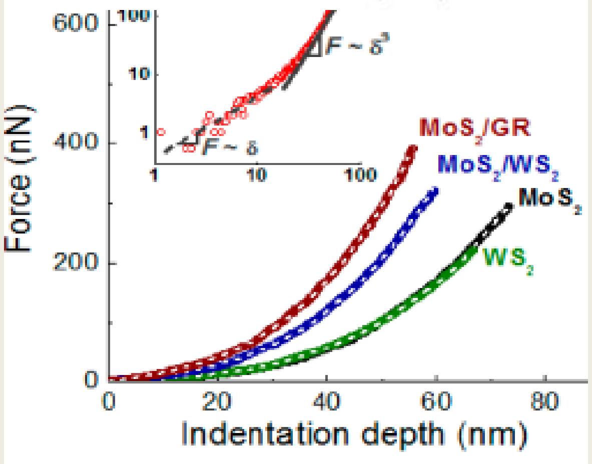


Nature Nanotechnology (2014).

Experiment



Nano Lett. 2014, 14, 5097–5103



Robert M. Elder*, Mahesh R. Neupane*, and Tanya L. Chantawansri, APL, 107, 073101 (2015)

Method:

1. Optimized lattice constants are obtained from DFT calculation using VASP.
2. Nano-indendation simulation was formed in MD simulation using LAMMPS.
3. By examining the maximum of the force-deflection curves, we can calculate the yield stress and ultimate strength of the materials.

Fact:

Graphene is mechanically stronger than steel, with a Young's modulus of 1 TPa, whereas MoS_2 has a Young's modulus of only about 0.25 TPa.

✓ **How does topology (stacking order, number) effect overall mechanical properties of vdW heterostructure?**

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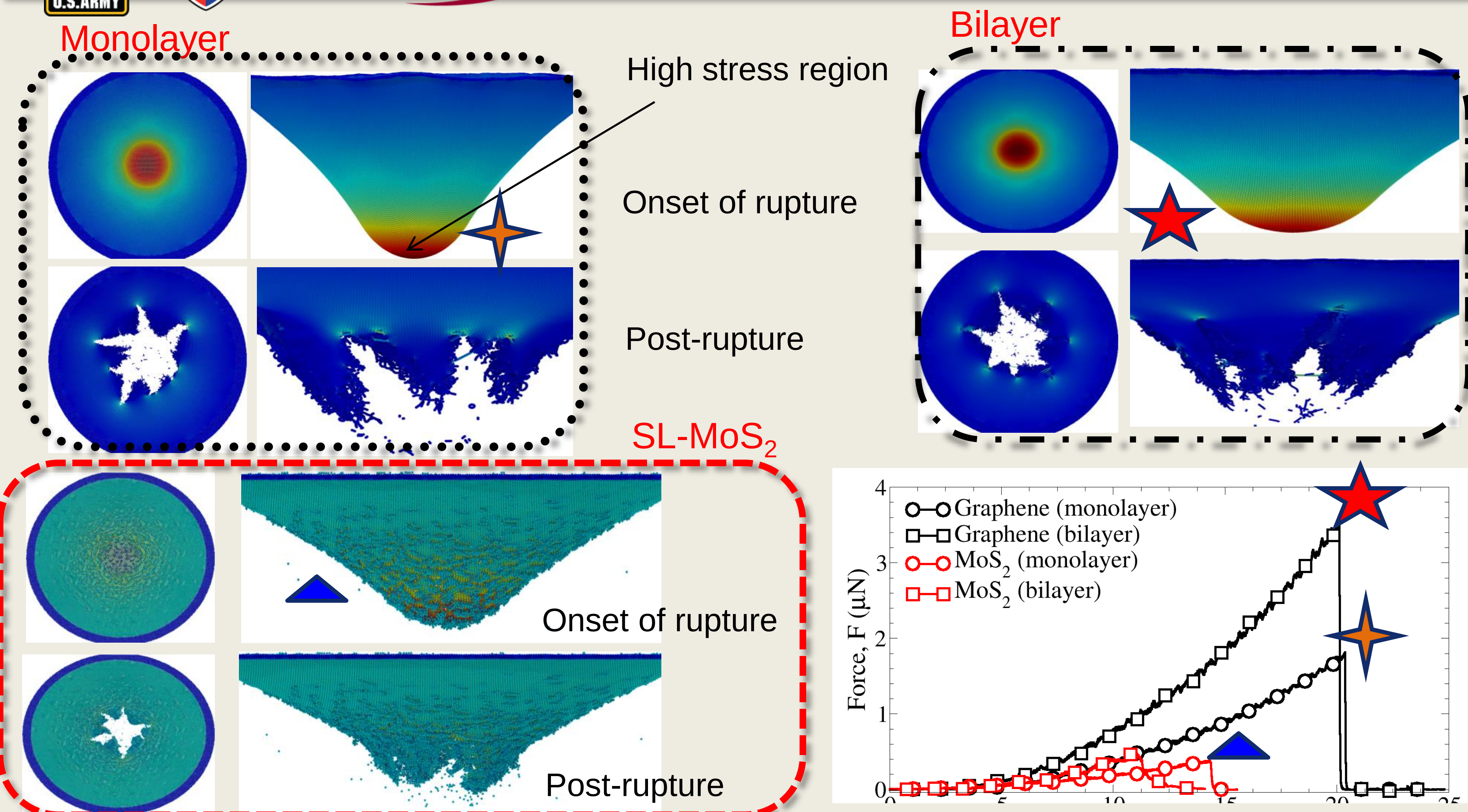
Stress during indentation

ARL



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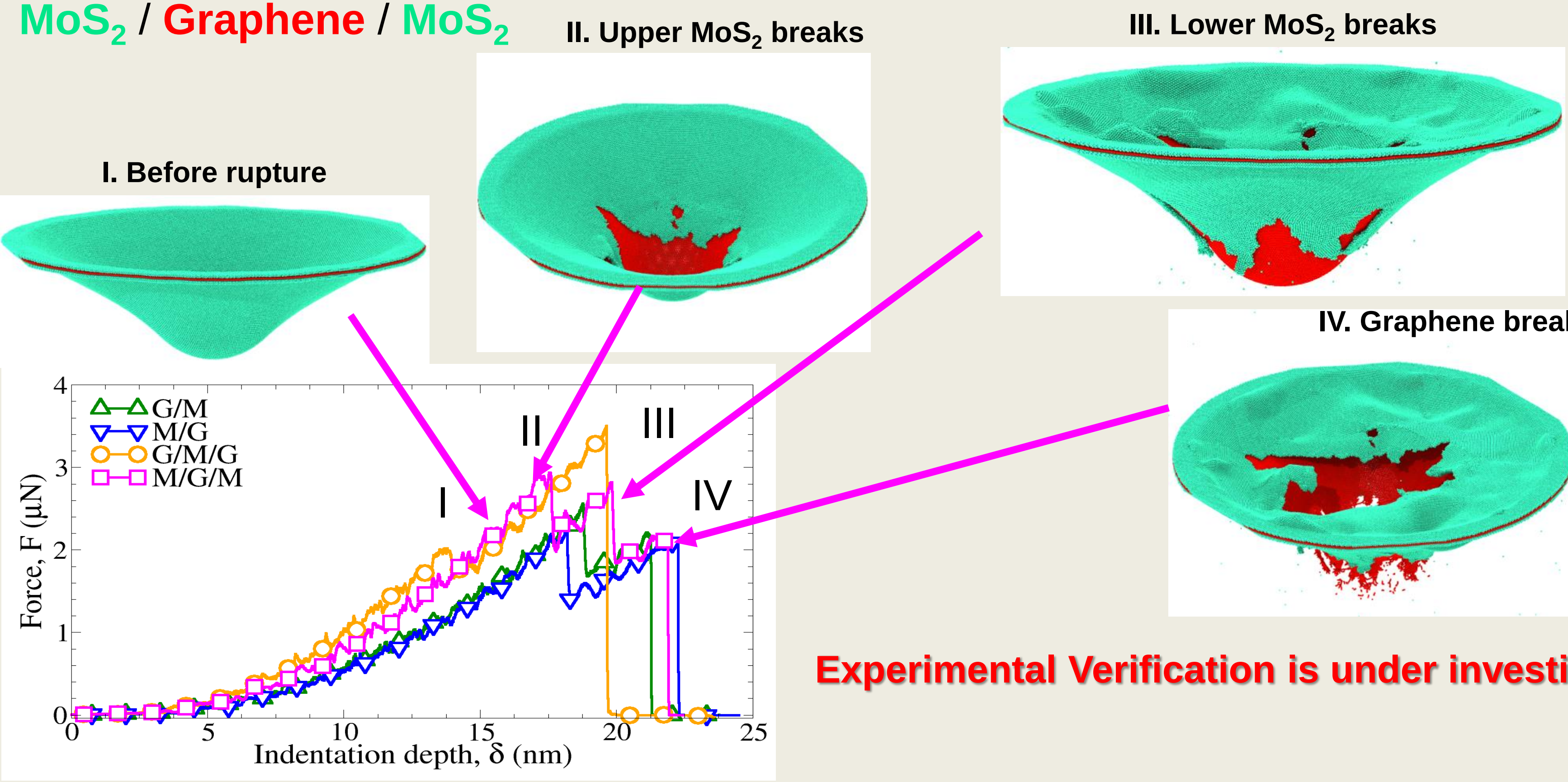
Indentation of vdW Heterostructures

MoS_2 / Graphene / MoS_2



Experimental Verification is under investigation

Key findings:

- The overall mechanical strength of Graphene/MoS_2 heterostructure is ~200% higher than MoS_2 mono and bilayer.
- The Young's modulus of the M/G/M trilayer (0.68 TPa) improving the bending modulus and ultimate strength of mono MoS_2 by an order of magnitude

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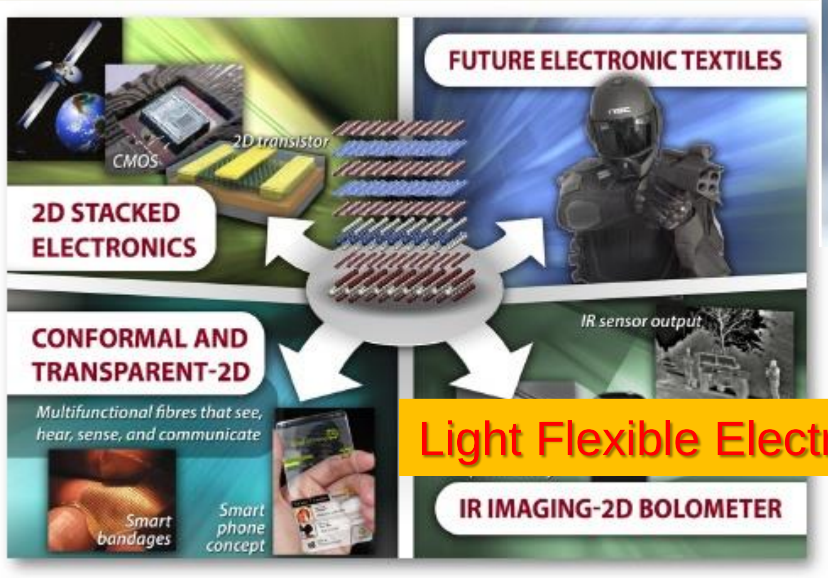
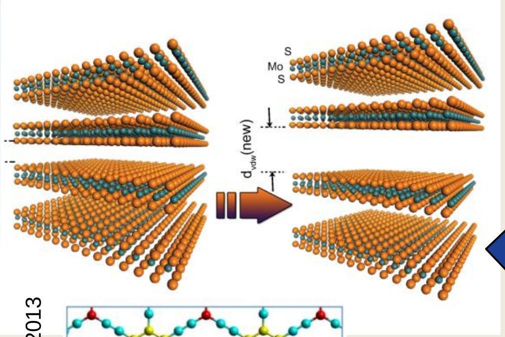
~~Limitations~~ Opportunities

- ✓ ML-TMDC can give a comparable electrical performance to a 10 nm thick organic or amorphous oxide semiconductor
- ✓ Ultrathin TMDCs are particularly well-suited for transparent and flexible electronics

3D materials with 2D properties



Light Flexible Electronics



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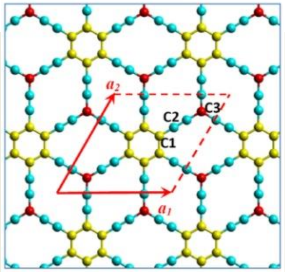
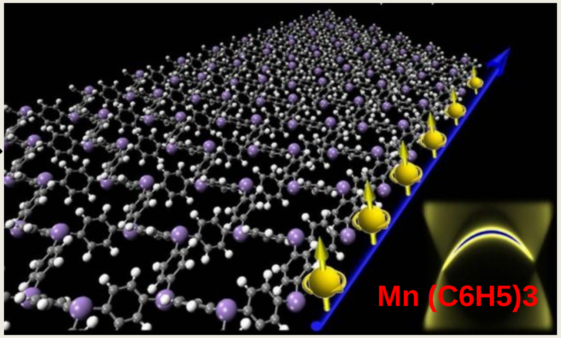


Graphyne

Scientific Reports 3, 3532, 2013

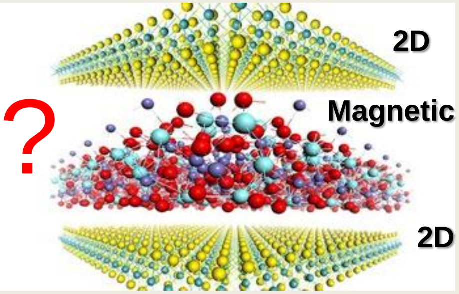
Inorganic/Organic Heterostructure

?



PRL 110, 196801 (2013)

Materials by Design



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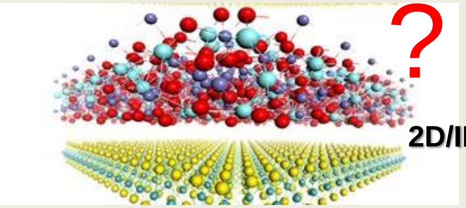

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Computational Modeling could play a significant role

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