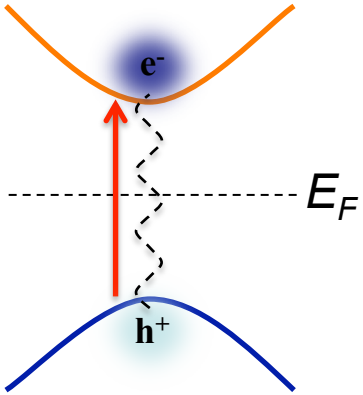
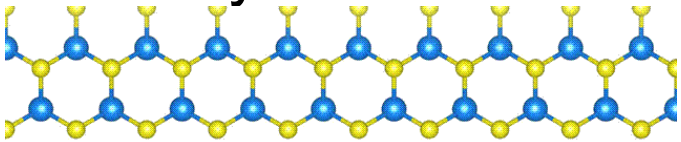
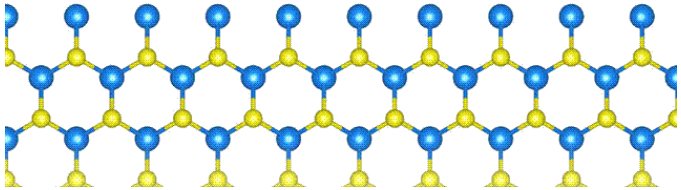
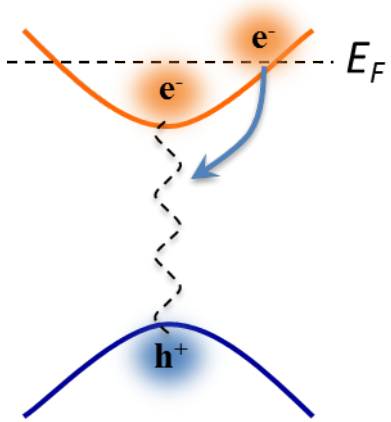
Tailoring properties of 2D transition metal dichalcogenides: looking beyond graphene

Talat S Rahman,
University of Central Florida









Physics Colloquium, University of Virginia, February 12, 2016

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Are we alone?

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Quantum computation
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Nanomagnetism
Atomic vibrational dynamics

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Biomolecular Fluorescence
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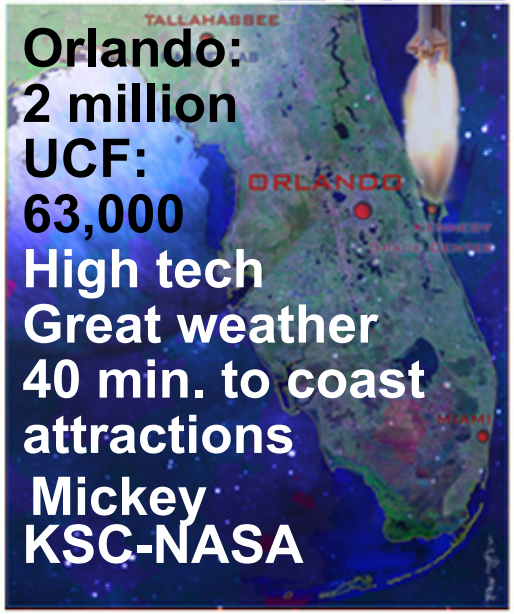

Orlando:
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Two other programs of interest

- Comprehensive PhysTEC Site
- APS Bridge Program Site

Both are funded by the American Physical Society and UCF

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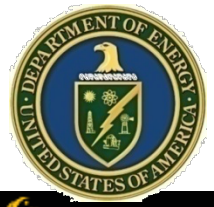
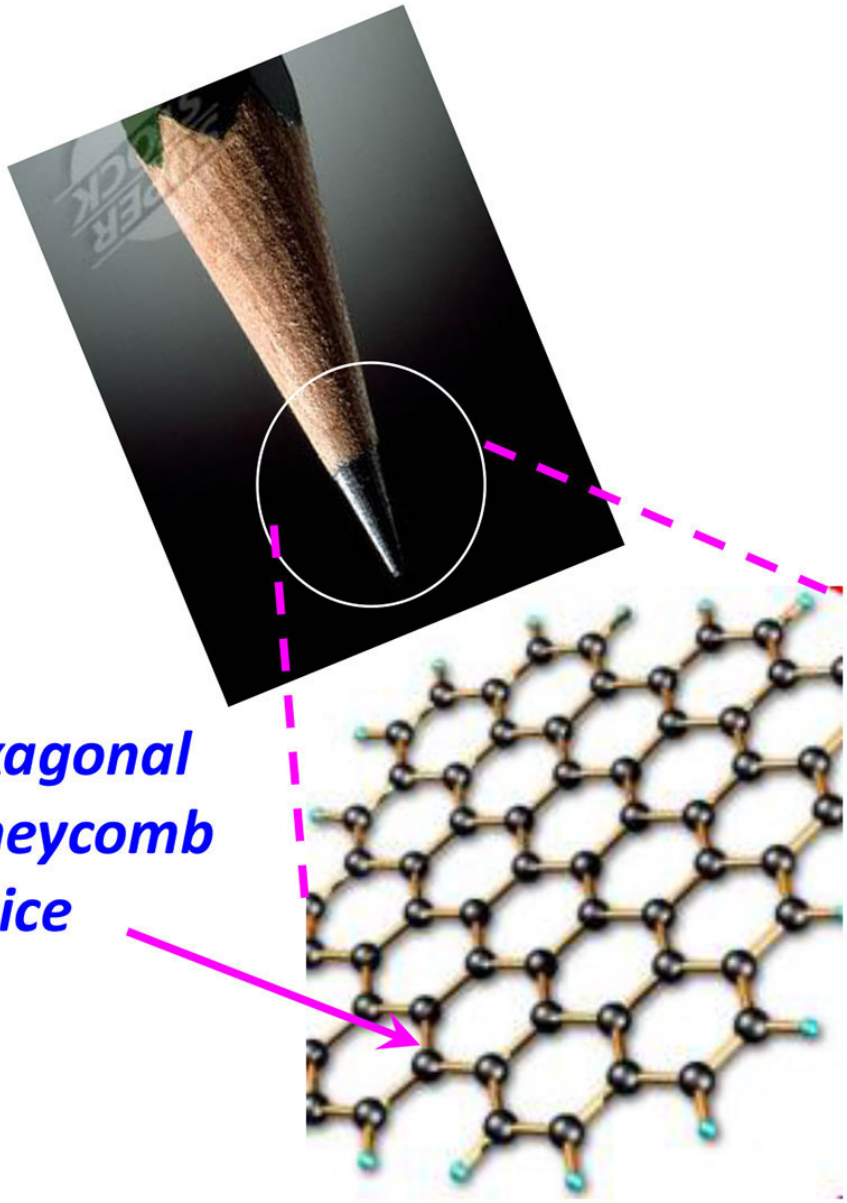
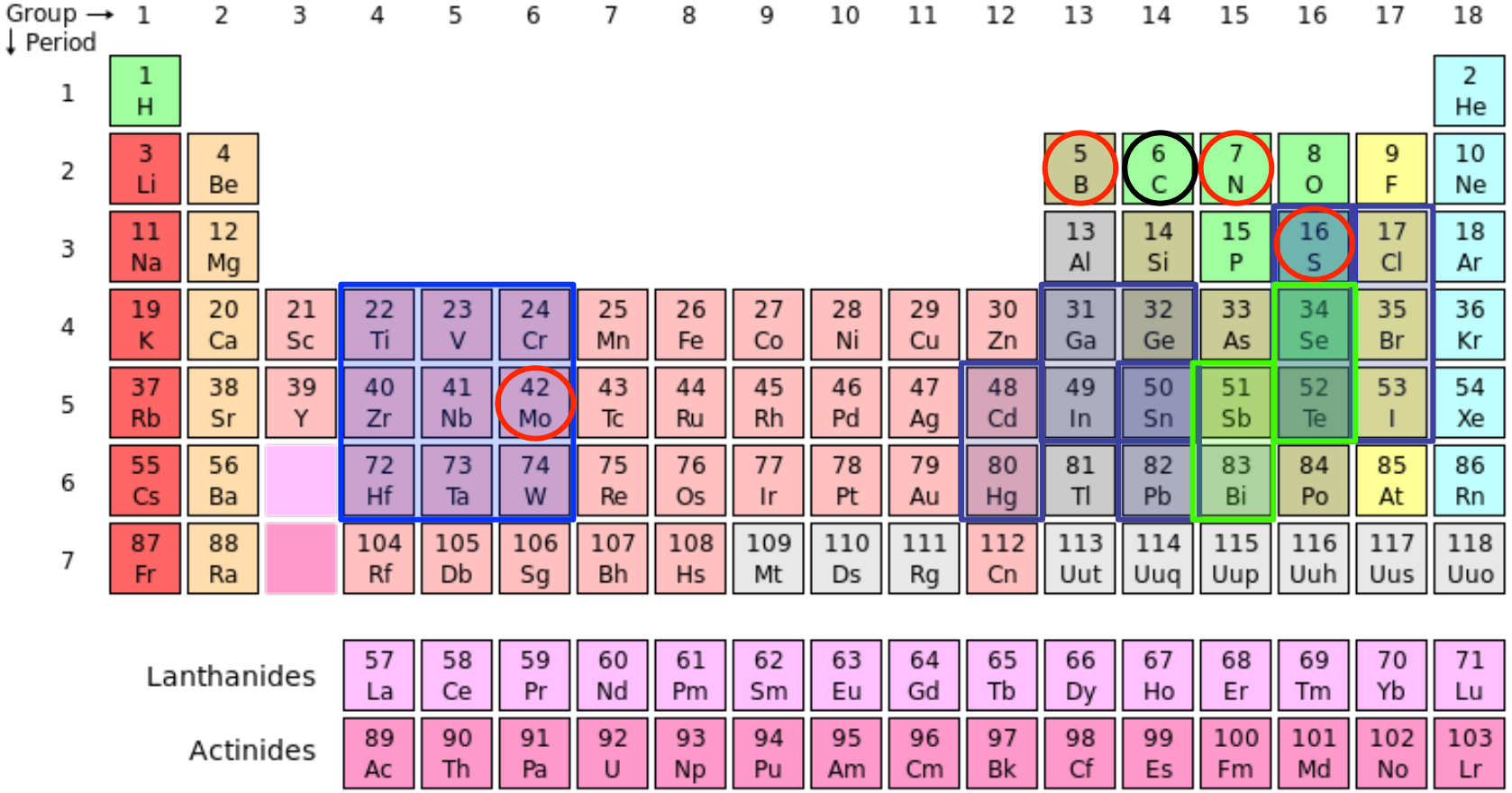


Could a pencil revolutionize science?



Lots of atomically thin materials



Transition-metal chalcogenides

- Semiconductors
- Semimetals (CDW)
- Metals (CDW, superconductivity)

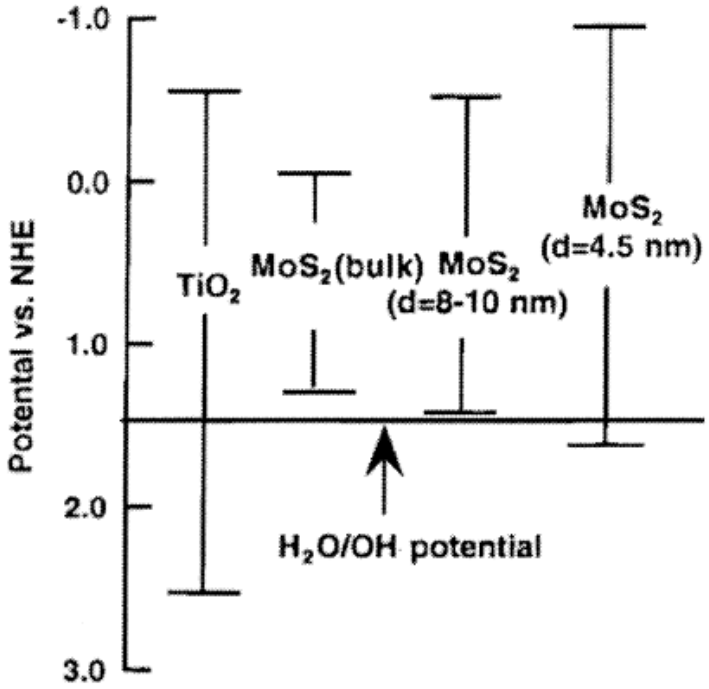
Outline

- Motivation
- **Growth** of single-layer MoS_2 is nontrivial
  Moiré Patterns on fcc(111)
- **Joint edges** of SL MoS_2: 1-D magnetism?
- Controlling properties through **defects**
  Band gap engineering: vacancy, doping
- **Manipulation** of chemical properties
  defect-laden MoS_2, on Cu(111),
  MoS_2- supported Ag/Cu/Au Nanoparticles
- Enhanced Coulomb interaction
  Excitons & Trions
- Concluding Remarks

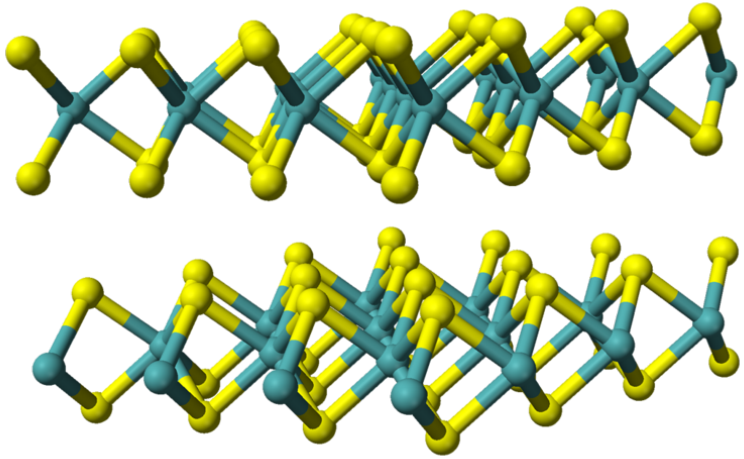
Bulk MoS_2: already in much use

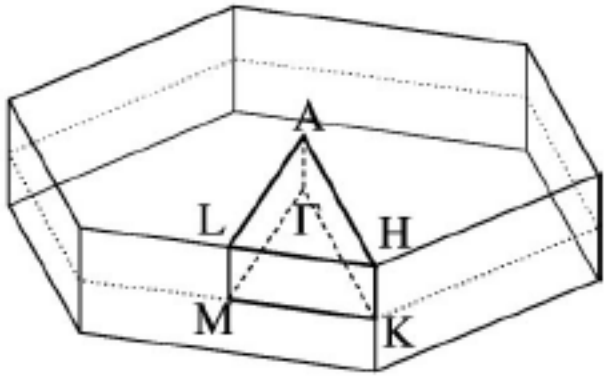
Lubricants

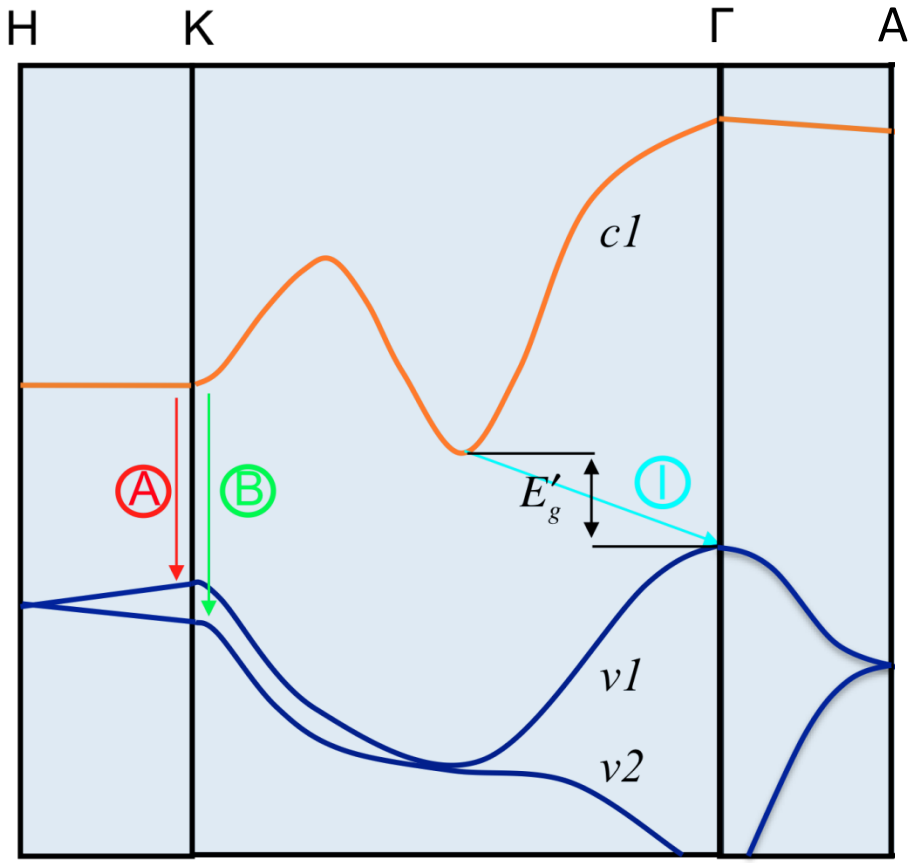
Catalysis/photocatalysis



Bulk MoS_2: band structure



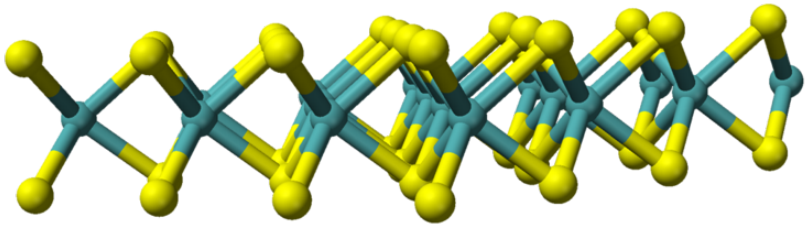




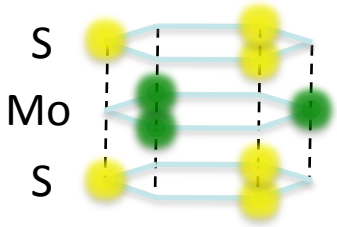
Indirect gap semiconductor

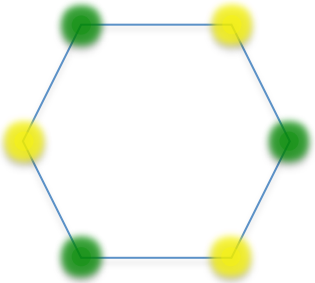
Negligible PL quantum yield

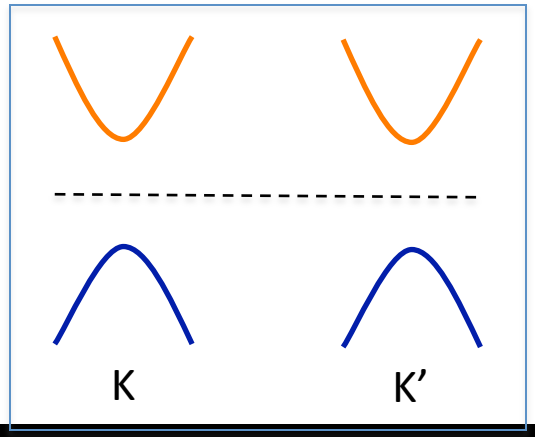
Single layer MoS_2



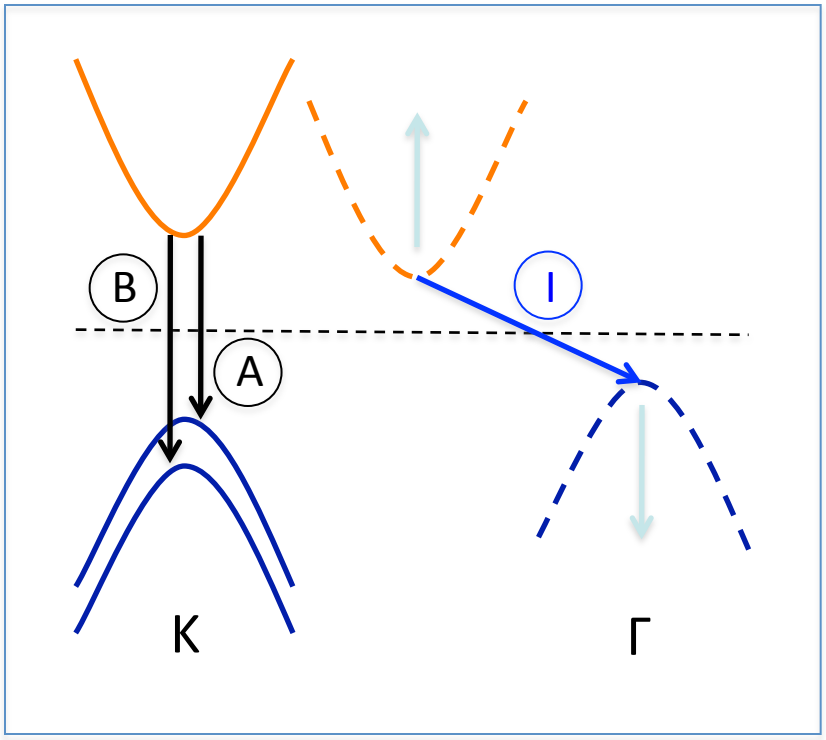
Honeycomb lattice with
broken sublattice symmetry

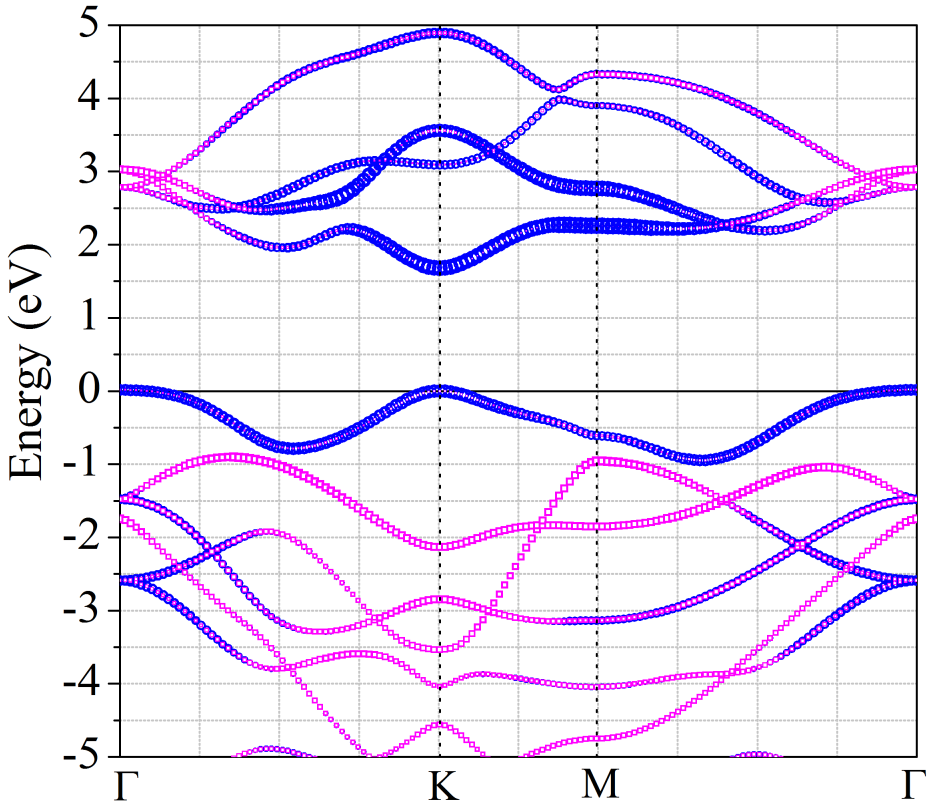






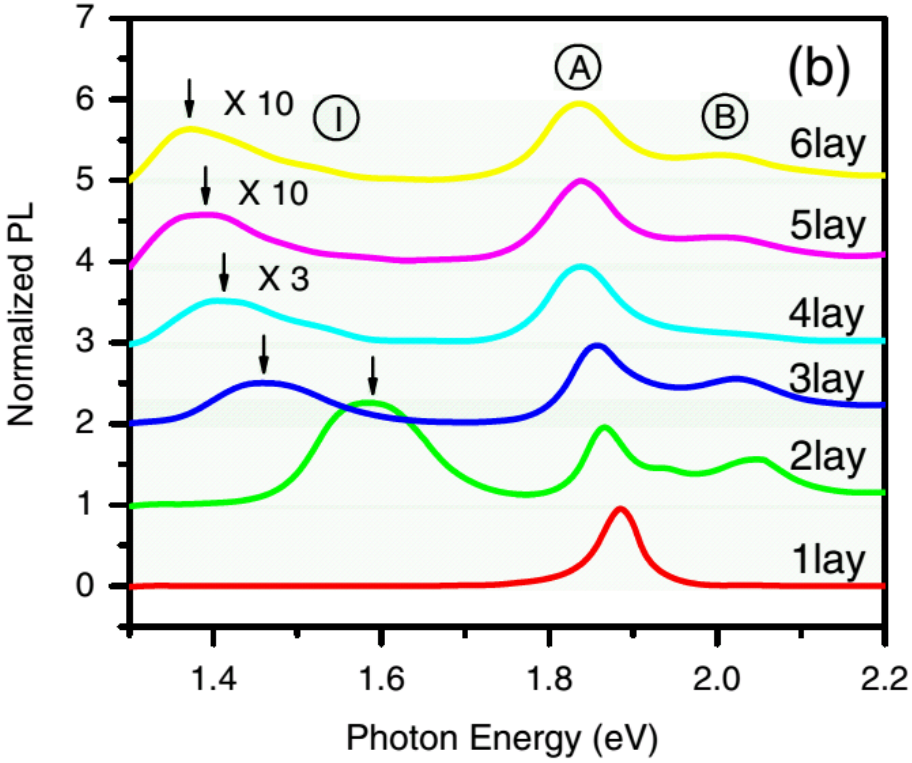
Indirect-Direct Band Gap Transition

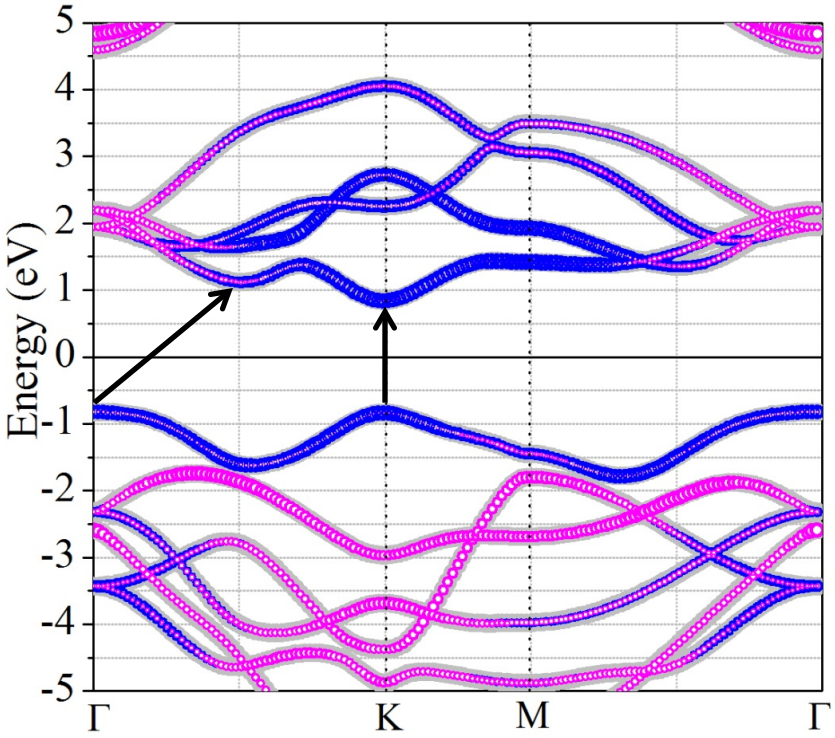




Blue: Mo orbitals
Magenta: S orbitals
(Le et al, 2012)

Band-gap transition

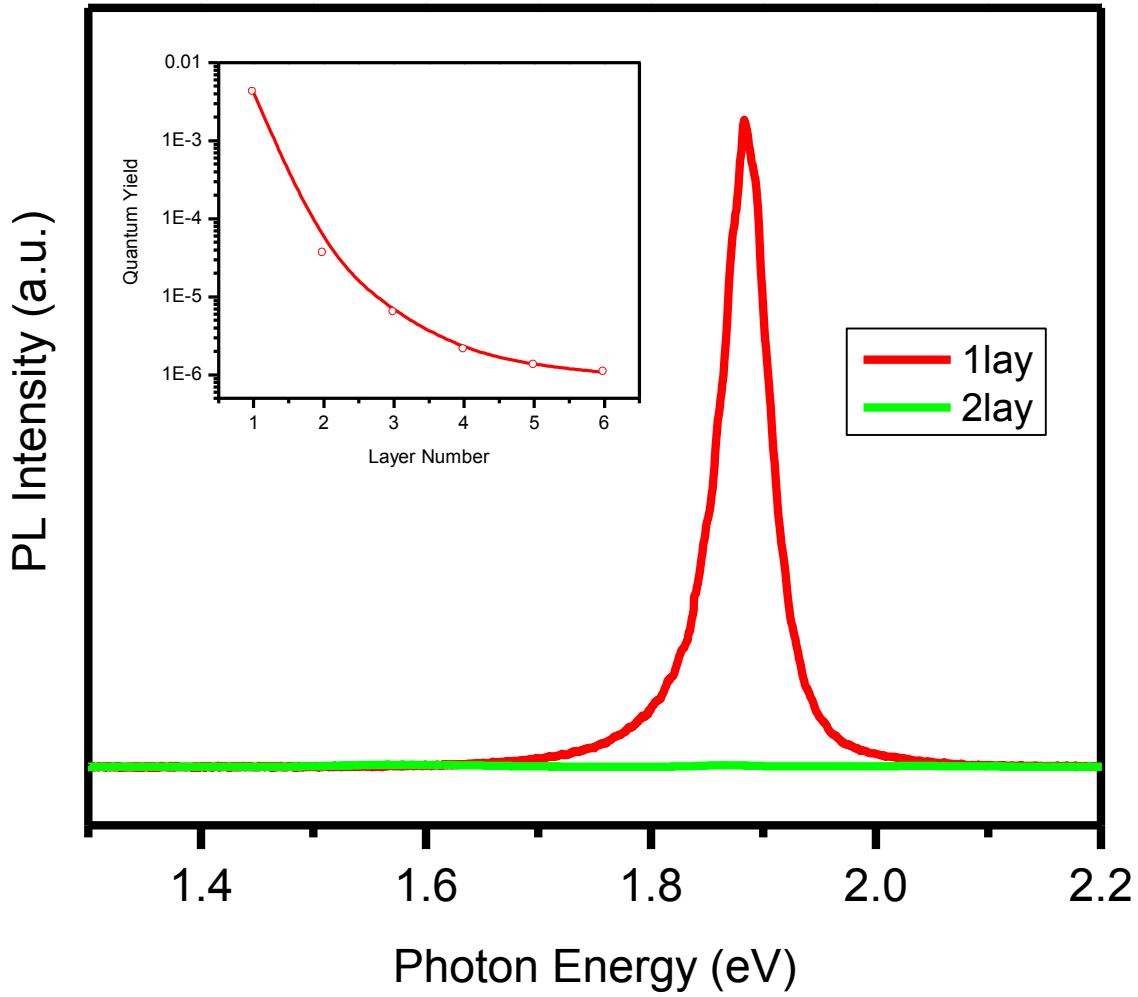




Mak et al., PRL (2010)

- Positions of indirect transitions are strongly affected by number of layers, while that of direct transitions are not.
- Can be explained by theoretical color-coded band structure: at K, states are d-like, localized at Mo atoms (blue) while at indirect transition points the states are affected by S states (magenta).

Photoluminescence from Atomically Thin MoS_2 Layers

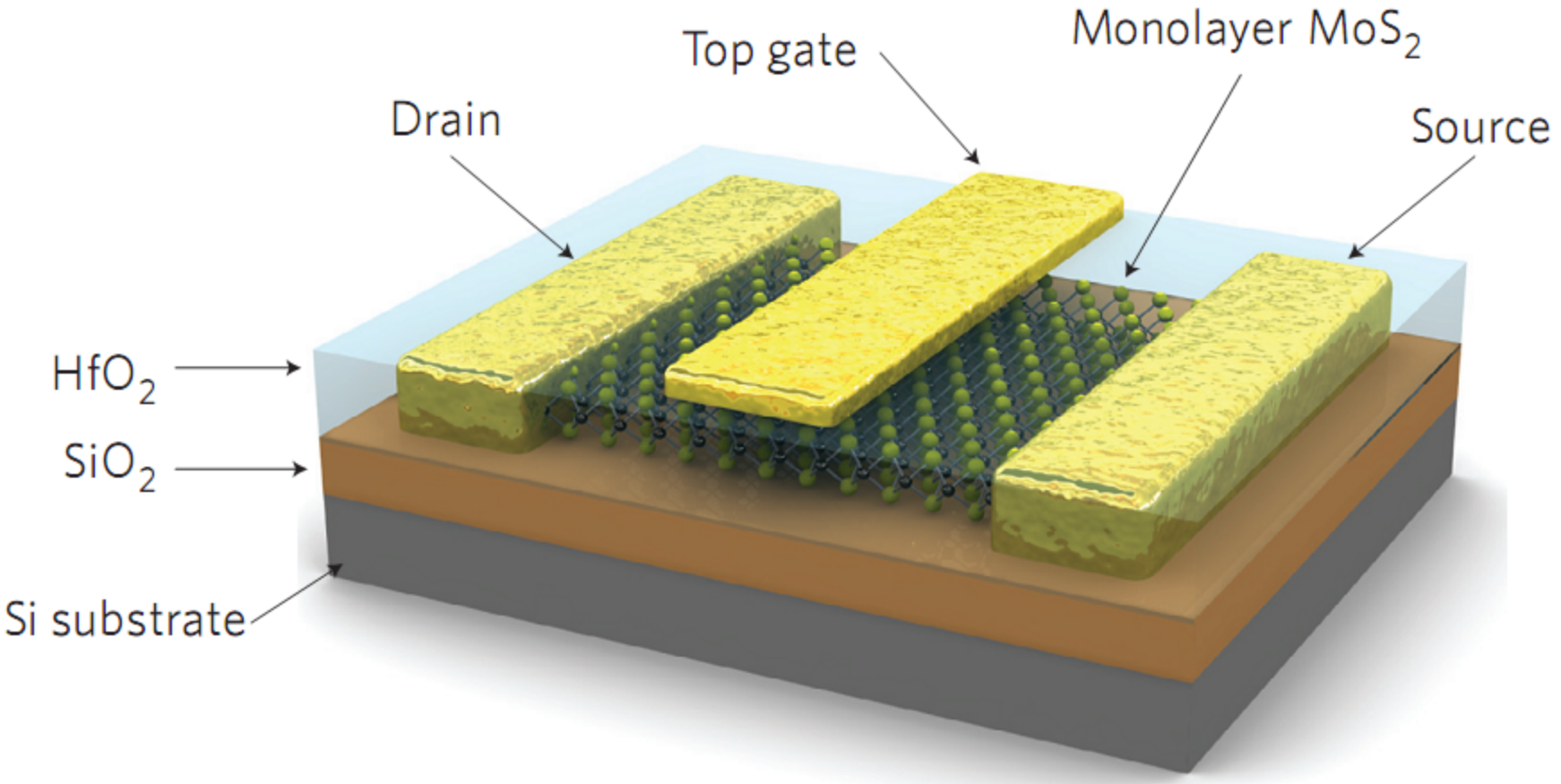


Significant enhancement of PL in *thinner* layers

Nearly 10^4 compared to bulk

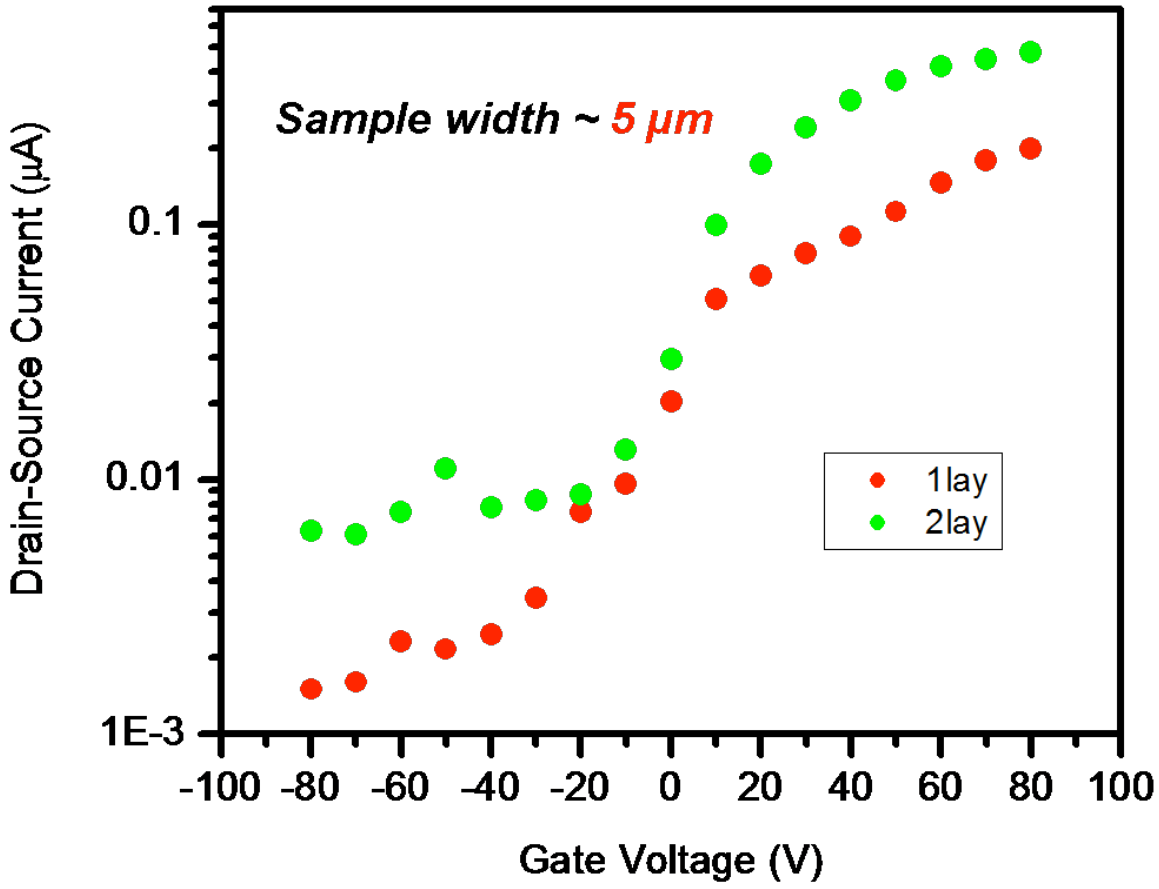
Mak et al. PRL (2010)

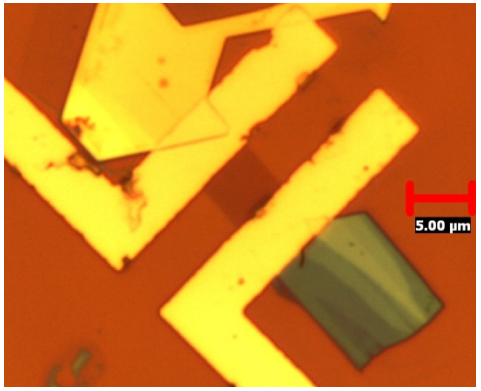
Electronic Application: Field Effect Transistor



Used hafnium oxide gate dielectric to demonstrate a room-temperature single-layer MoS_2 mobility of at least 200 $cm^2V^{-1}s^{-1}$, similar to that of graphene nanoribbons, and produce transistors with room-temperature current on/off ratios of $1x10^8$and ultralow standby power dissipation.
Radisavljevic et al., *Nature nanotechnology (2011).*

Single Layer MoS_2 Field-Effect Transistors

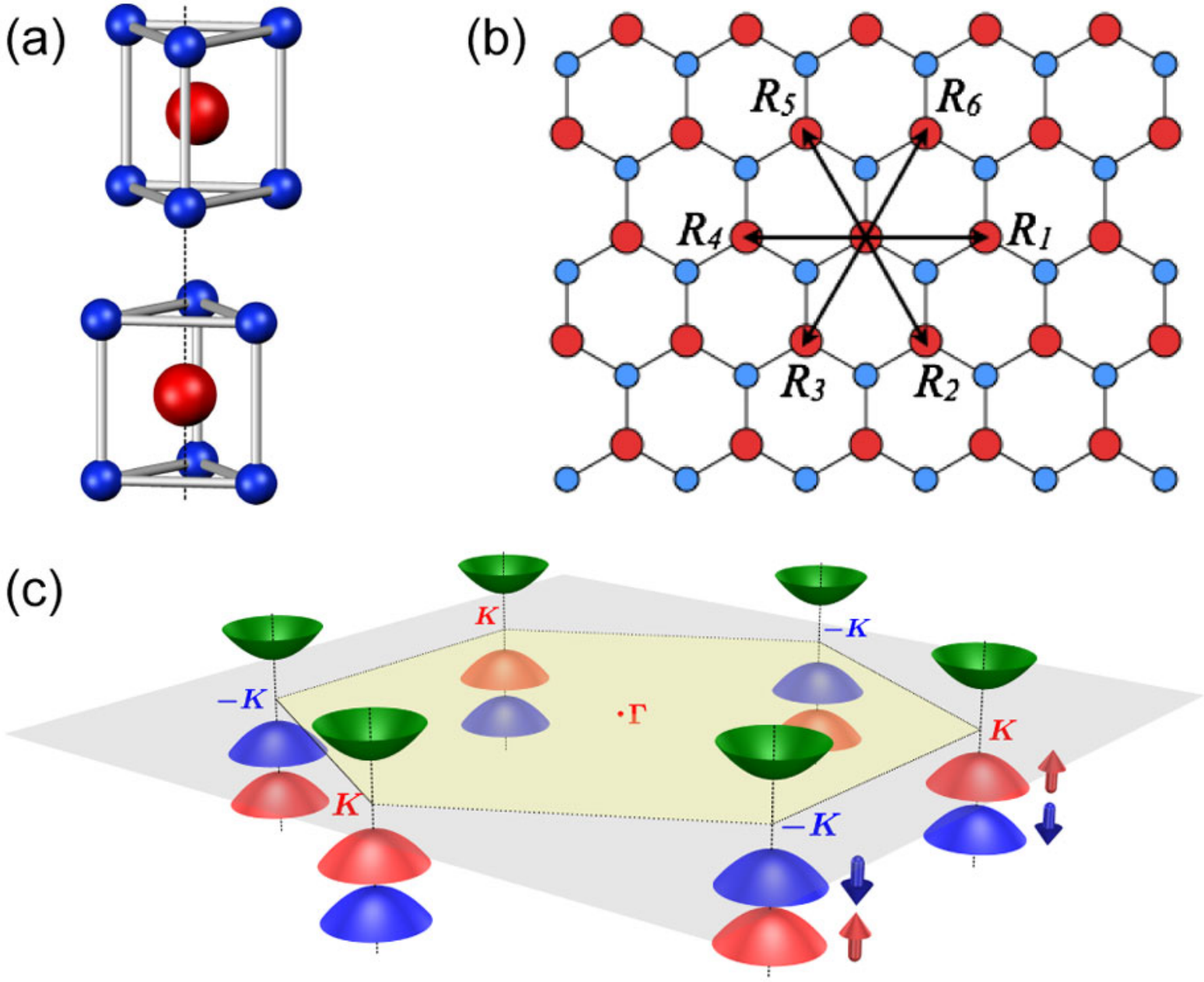




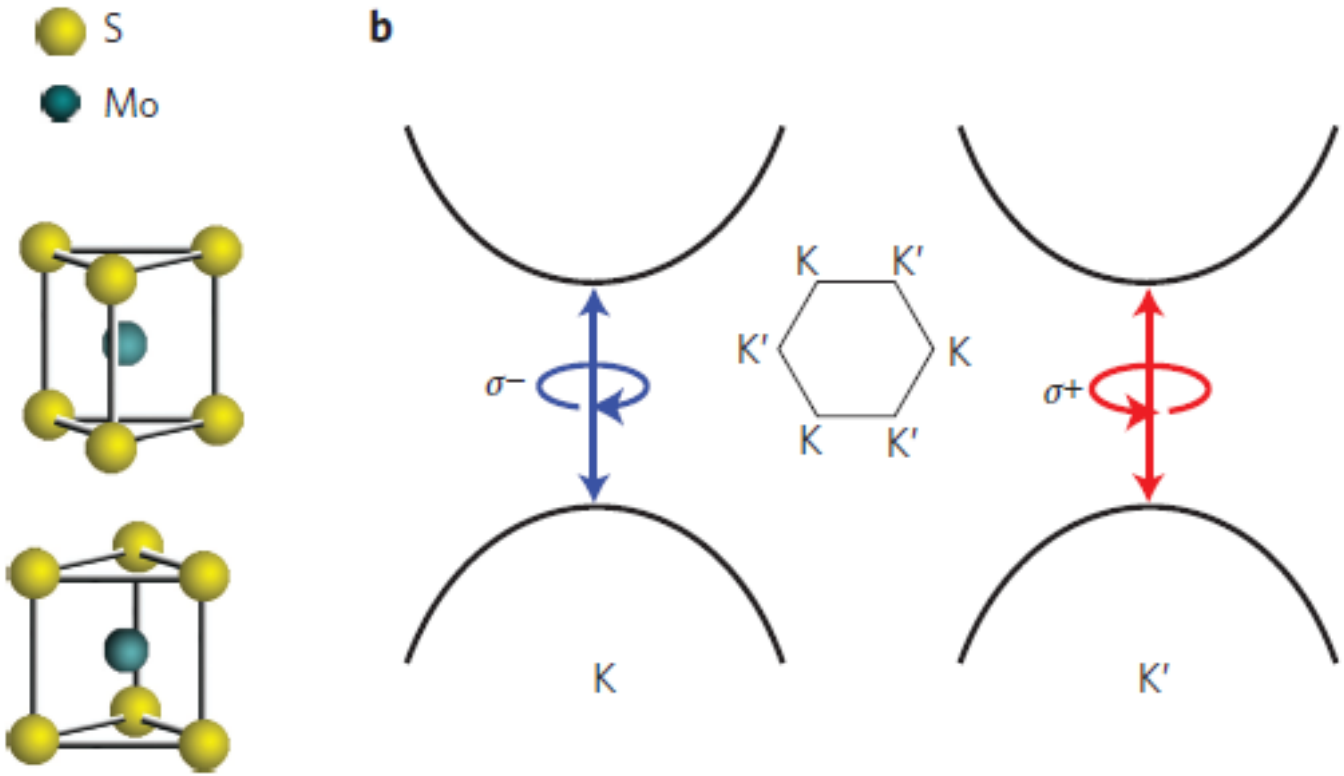
Mak et al. PRL (2010)

A. Kis et al. Nature Nano (2011).

Reminescent of Graphene & Beyond



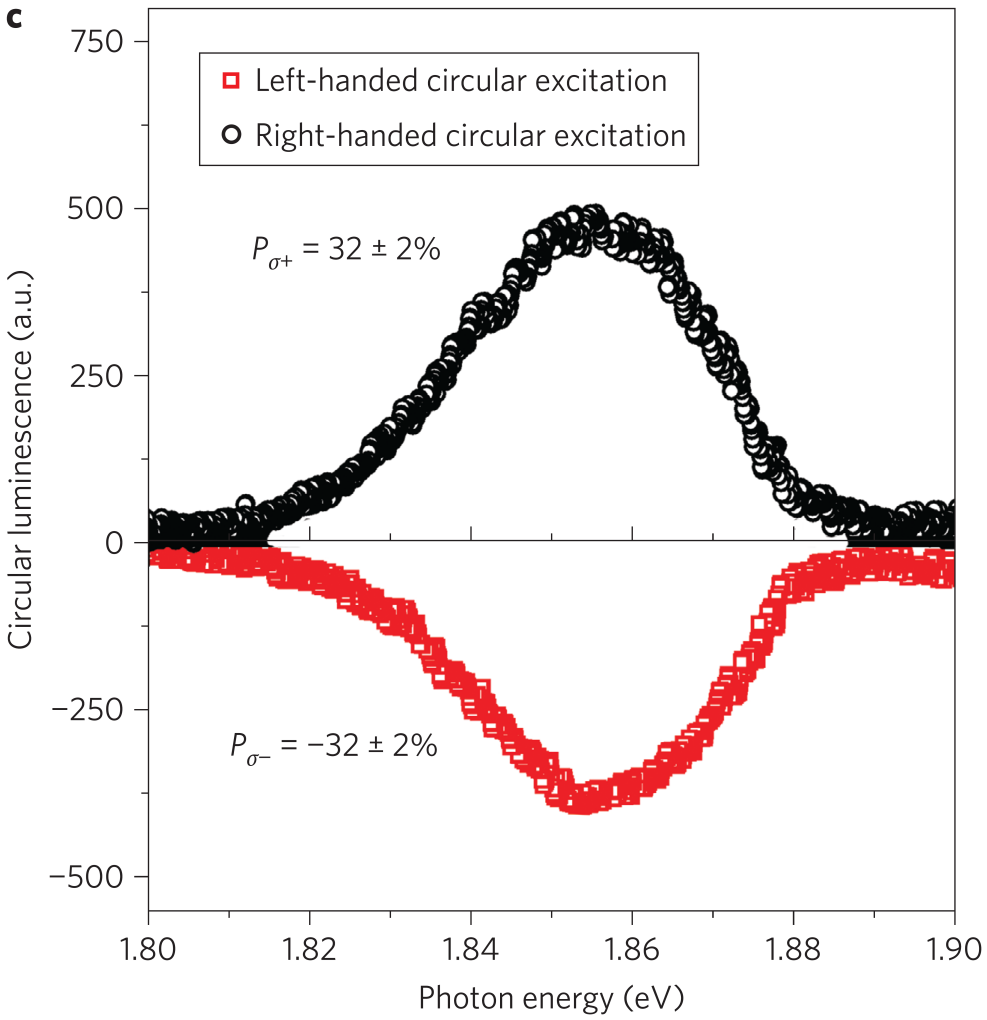
Valley-dependent selection rules at K and K′ points



left (right)-handed circularly polarized light σ^+ (σ^-) only couples to the band-edge transition at K (K′) points for the sake of angular moment conservation and time reversal symmetry

Figure from H. Zeng et al., Nature Nanotech. 7 409 2012)

Luminescence polarization in MoS_2



H. Zeng et al., Nature Nanotech. 7 409 2012

➢Transition Metal Dichacogenides (TMDCs) are among the most studied layered compounds that have been isolated in monolayer form.

	$-S_2$	$-Se_2$	$-Te_2$
Mo-	Semiconducting Optical gap: 1.9 eV	Semiconducting Optical gap: 1.5 eV	Semiconducting Optical gap: 1.1 eV
W-	Semiconducting Optical gap: 2.1 eV	Semiconducting Optical gap: 1.7 eV	Semiconducting Optical gap: 1.1 eV
Ta-	Metal Superconducting Charge Density Wave	Metal Superconducting Charge Density Wave	Metal
Nb-	Metal Superconducting Charge Density Wave	Metal Superconducting Charge Density Wave	Metal

This table was reproduced from Q. H. Wang *et al.*, Nat. Nanotechnol. **7**, 699 (2012).

➢Mo- and W-based TMDCs are the most studied because of their availability and possibility of isolation in single layer form

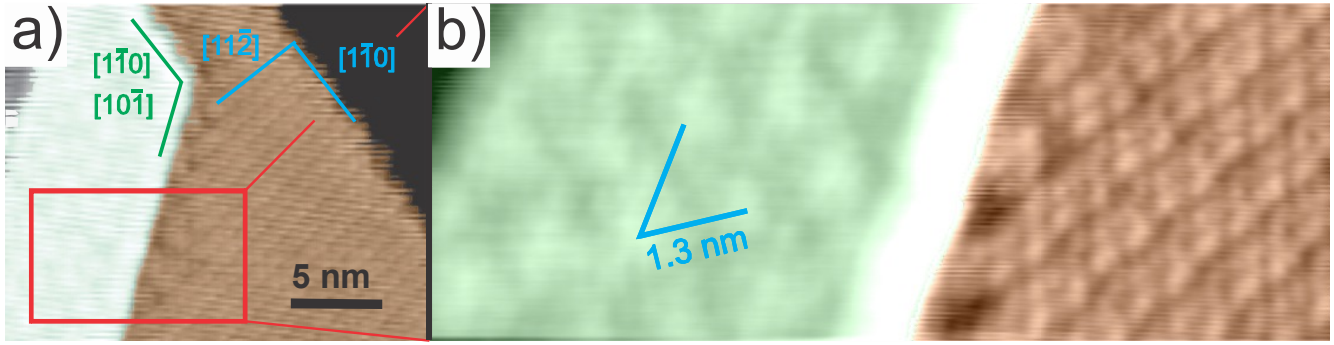
But how do you get 1L TMDC

- Exfoliation
- Chemical Vapor Deposition
- Wet chemistry
- Others?

Growth of Single Layer MoS_2 on close-packed metal surfaces

D. Kim, D. Sun, W. Lu, Z. Cheng, Y. Zhu, D. Le, TSR, and L. Bartels "Toward the Growth of an Aligned Single-Layer MoS_2 Film," Langmuir 27, 11650 (2011).
D. Le, L. Bartels, and TSR and, "Single layer MoS2 on the Cu(111) surface: First-principles electronic structure calculations,"Phys. Rev. B 85, 075429 (2012).

➢Recently, large single layer patches of MoS_2 were grown on Cu(111) which shows a regular Moiré pattern of about 1.3 nm.



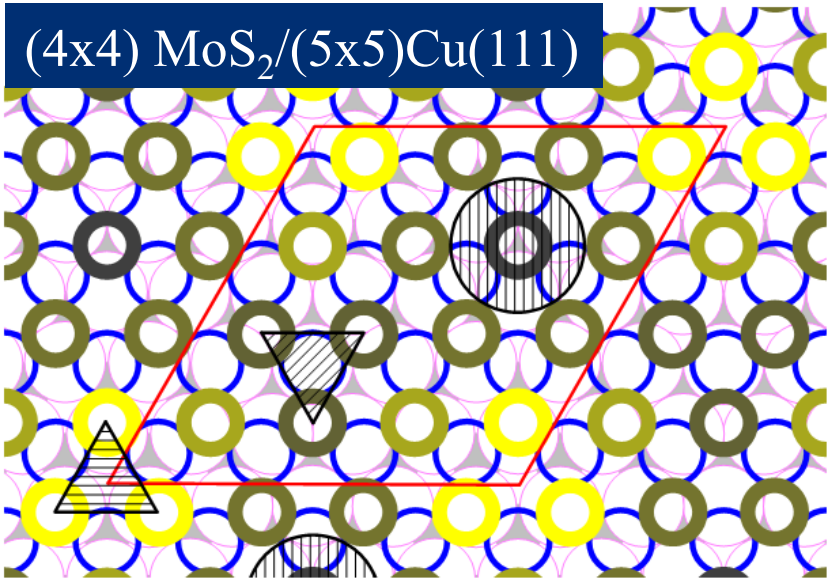
(a) portion of a MoS_2 layer (left, green) on a sulfur terminated Cu(111) terrace with a dislocation step indicating substrate crystallographic axes. (b) Enlarged portion near the MoS2 edge showing angular registry between MoS2 Moiré pattern and straight edge. Image Parameters: Bias: -560 mV, Current: 140 pA [D. Kim *et al*, Langmuir (2011)]

➢ Using DFT with vdW-DF) we have:

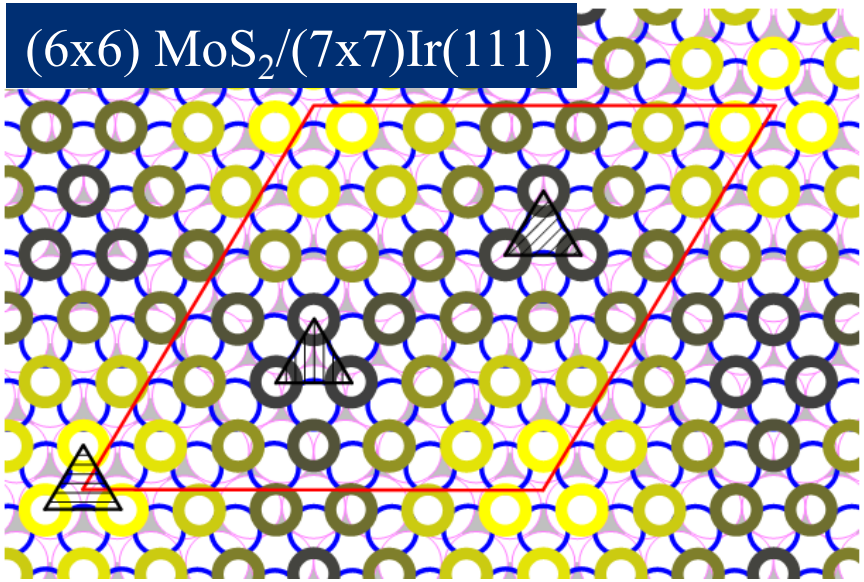
- Confirmed the observed Moiré pattern periodicity on Cu(111)
- Investigated geometry of MoS_2 layer and Cu(111).
- Found the nature of bonding between MoS_2 layer & Cu(111)
- Predicted Moiré patterns on other metal surfaces.

Moiré patterns on metal surfaces

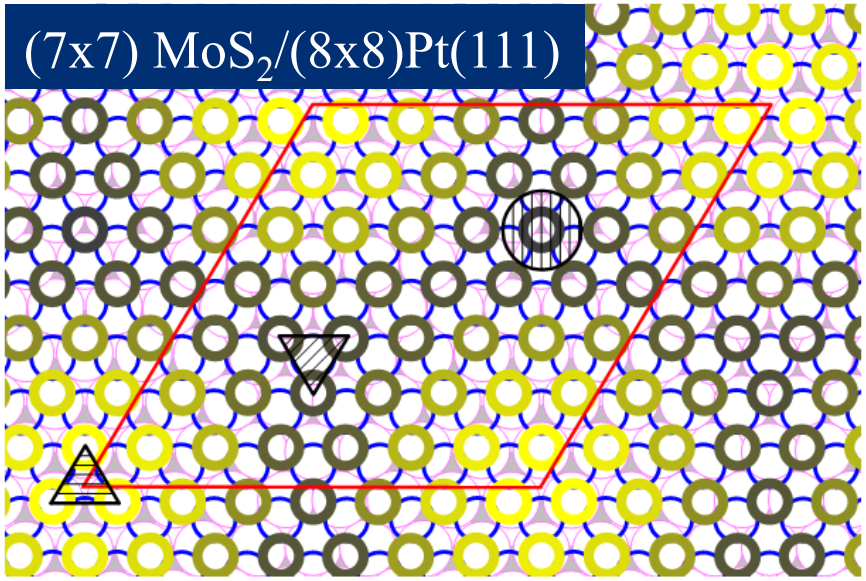
(4x4) MoS_2/(5x5)Cu(111)



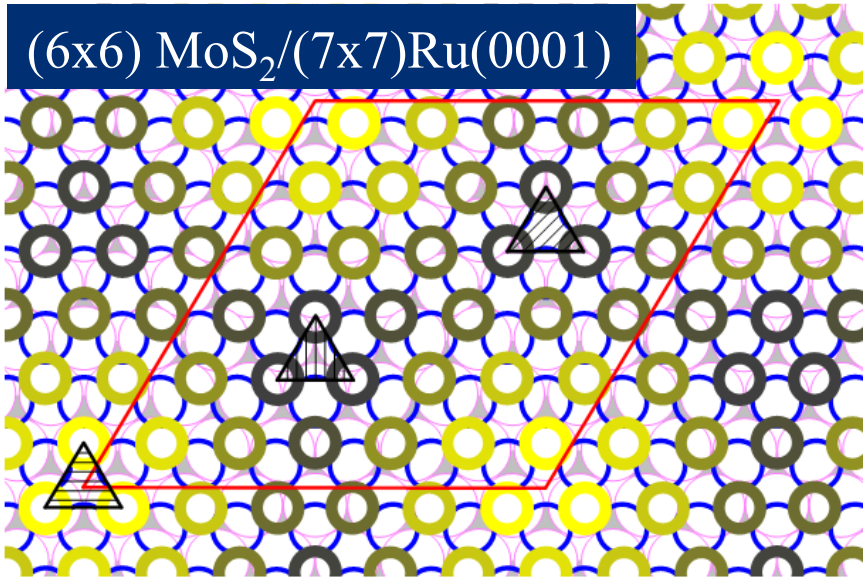
(6x6) MoS_2/(7x7)Ir(111)



(7x7) MoS_2/(8x8)Pt(111)



(6x6) MoS_2/(7x7)Ru(0001)



Moiré pattern periodicities

- Morié pattern is formed if a MoS_2 layer can be grown on close packed metal surfaces.
- It is because of the mismatch between MoS_2 lattice (3.16 Å) and the distance between two three-fold hollow sites.

- If the unit cell of Morié pattern consists of a $(n_1 x n_1)$ MoS_2 and $(n_2 x n_2)$ Metal surfaces, the mismatch m has to be small:

$$m = \frac{n_1 d_S}{n_2 d_M} - 1$$

d_S: S-S distance
d_M: Metal-Metal distance

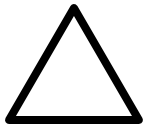
TABLE I. Predicted sizes of MoS_2 Moiré unit cell on several close packed metal surfaces. ($n_2 \leq 20$)

Surfaces	d_M (Å)[a]	n_1	n_2	m (%)
Ag(111)	2.89	10	11	−0.7
Cu(111)	2.55	4	5	−1.0
Ni(111)	2.49			−0.2
				0.2
Pt(111)	2.77			−0.2
Rh(111)	2.69			0.8
				−0.5
		17	20	0.0
Ir(111)	2.72	6	7	−0.2
Re(0001)	2.76	7	8	0.2
Ru(0001)	2.71	6	7	−0.1

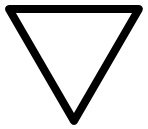
[a] Calculated from experimental lattice parameters

Agree with experimental observation

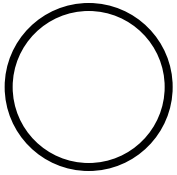
Geometry of MoS_2 on Cu(111) - Registry



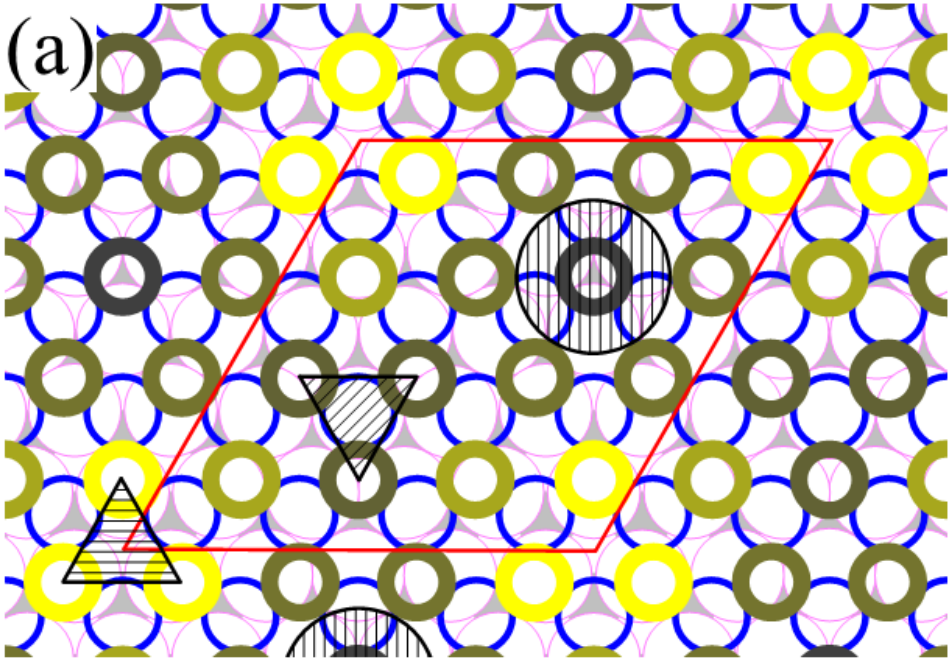
Connect 3 equivalent S without Mo at center



Connect 3 equivalent S with Mo at center



Centered at S atom that is in registry with high symmetry site

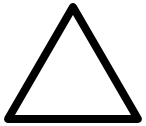


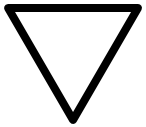
S

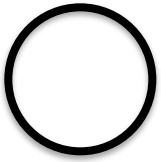
Mo

Cu

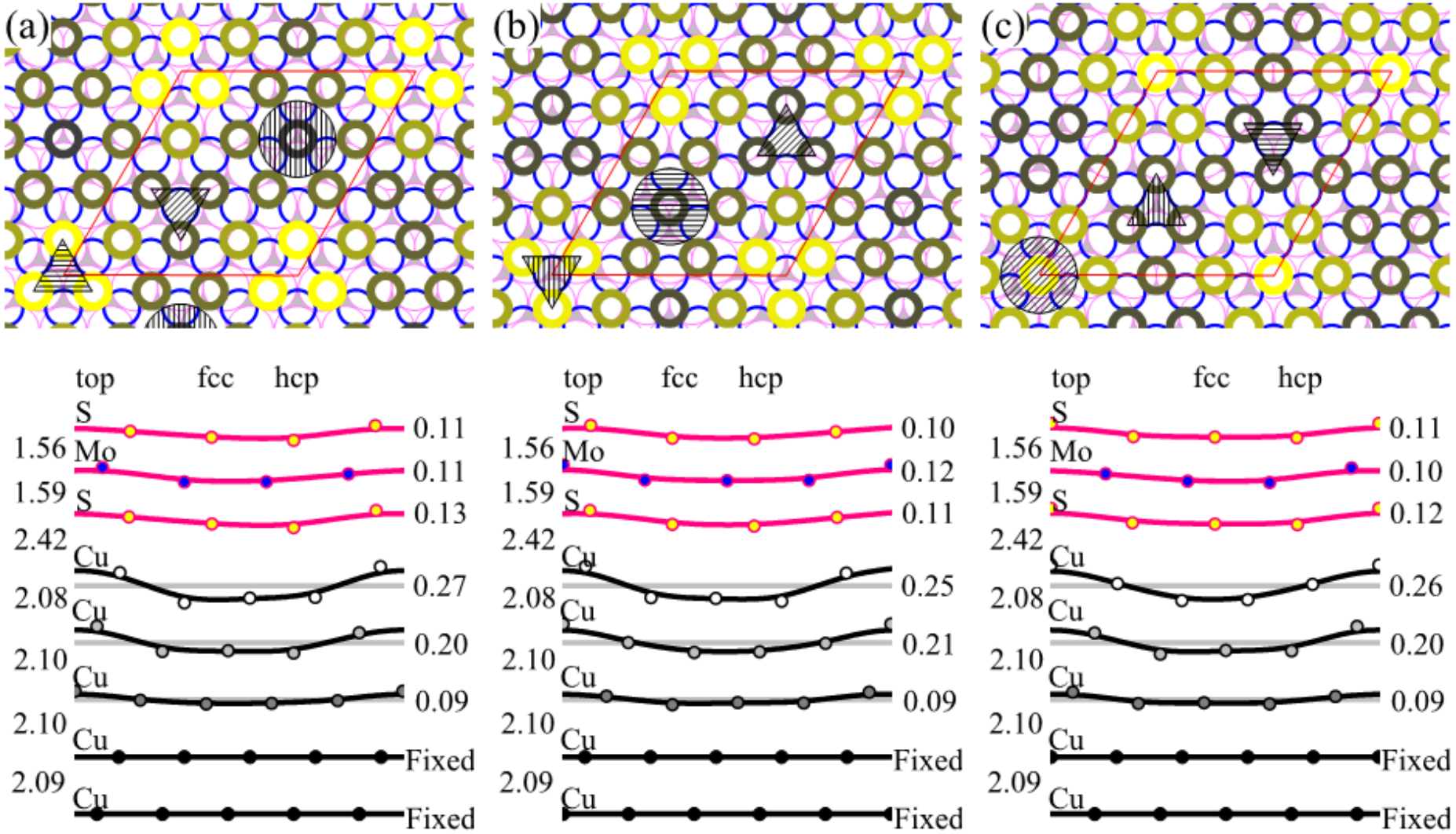
α stacking

Centers of  are in registry with fcc sites

Centers of  are in registry with top sites

Centers of  are in registry with hcp sites

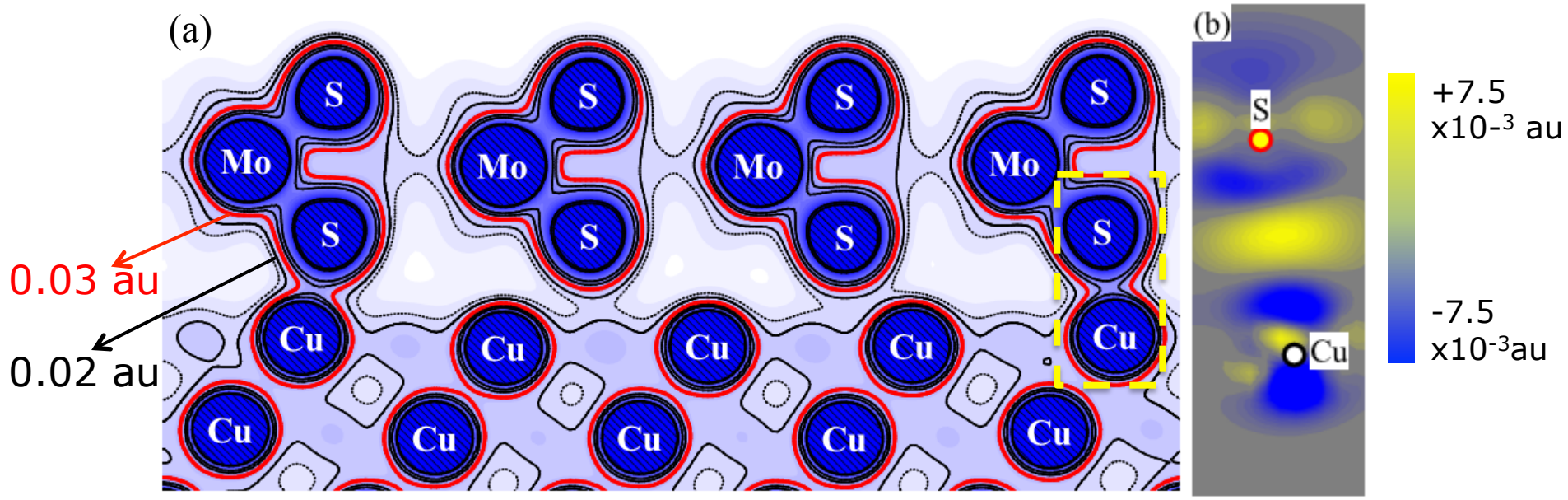
Geometry of MoS_2 on Cu(111) - Buckling



Buckling along the longest diagonal of Moiré unitcell

- S, Mo layers buckling of ~0.1 Å
- Cu surface buckles more ~0.3 Å

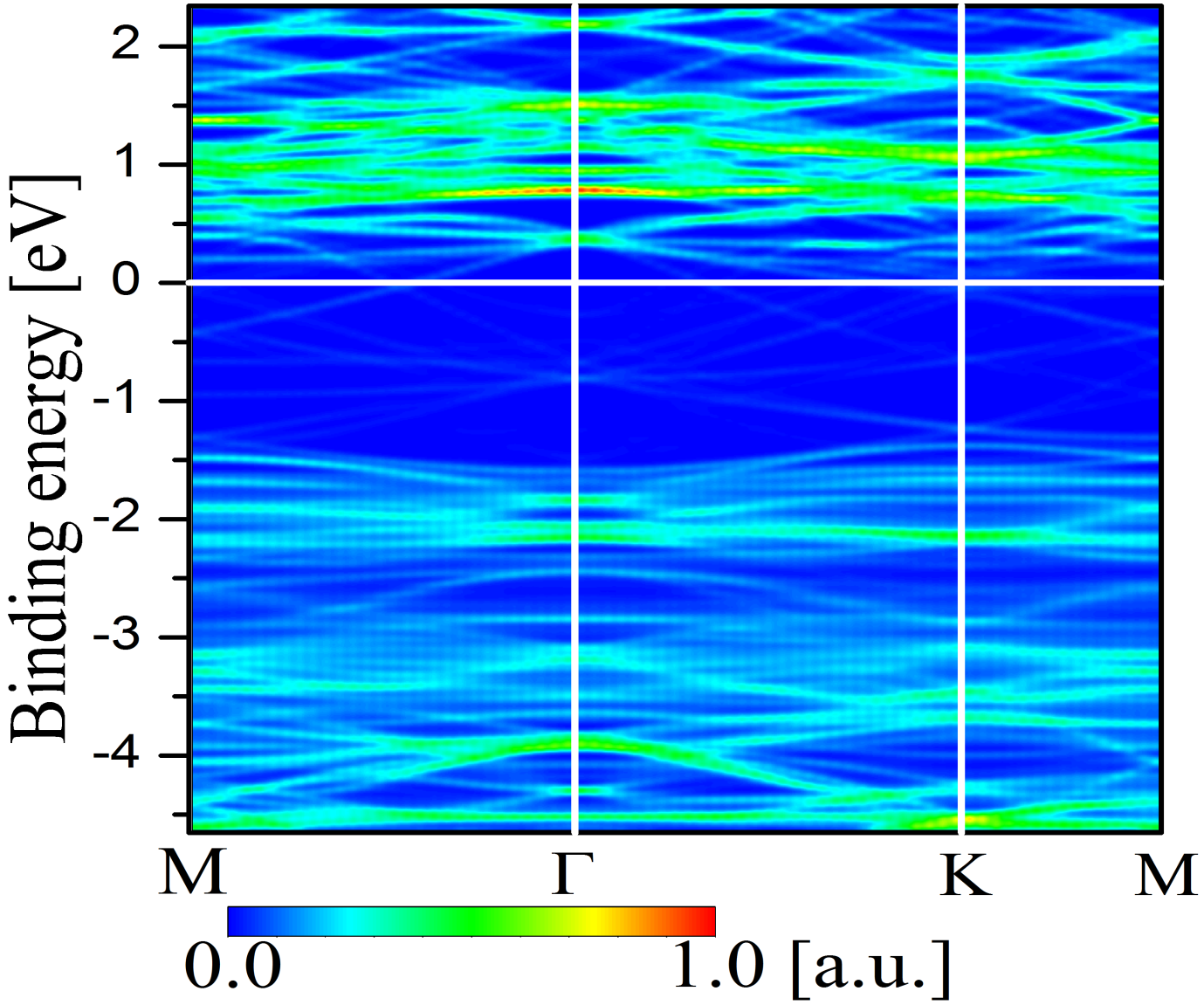
Interaction between MoS_2 layer and Cu(111)



Take the case of α stacking as an example:

- Large MoS_2--Cu(111) separation (~2.4Å) indicate weak interaction.
- Charge density along vertical plane passing through the longest diagonal of Moiré unit cell (a) shows indeed the formation of S-Cu chemical bonding.
- Charge density redistribution (b) shows noticeable accumulation of charge to the region between S-Cu => Covalent bonding

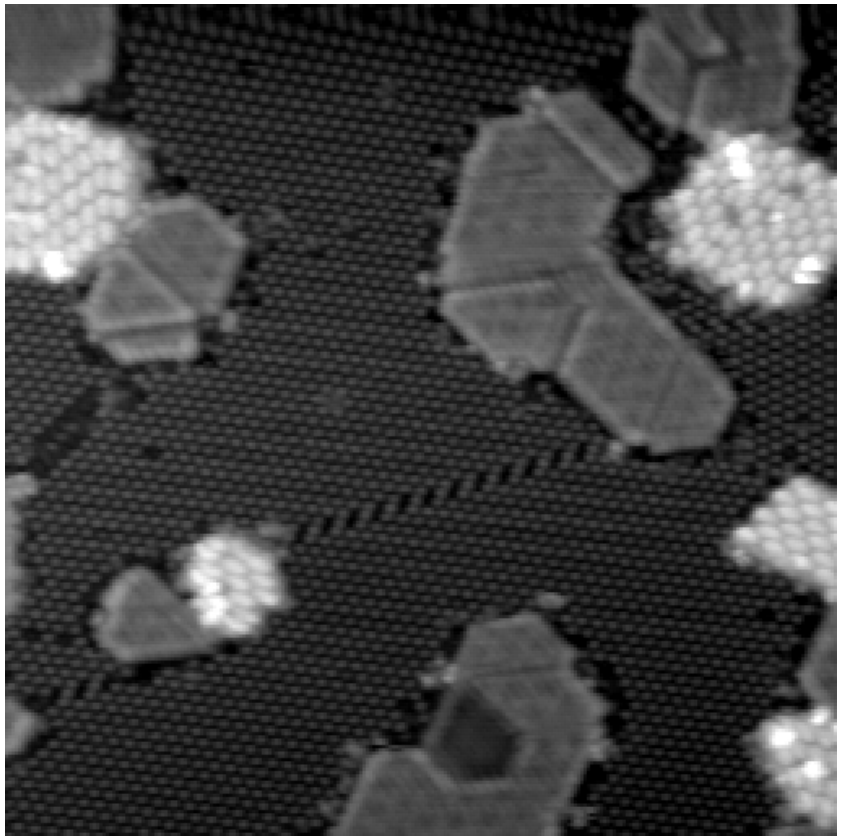
Electronic Structures of MoS_2 and Cu(111)

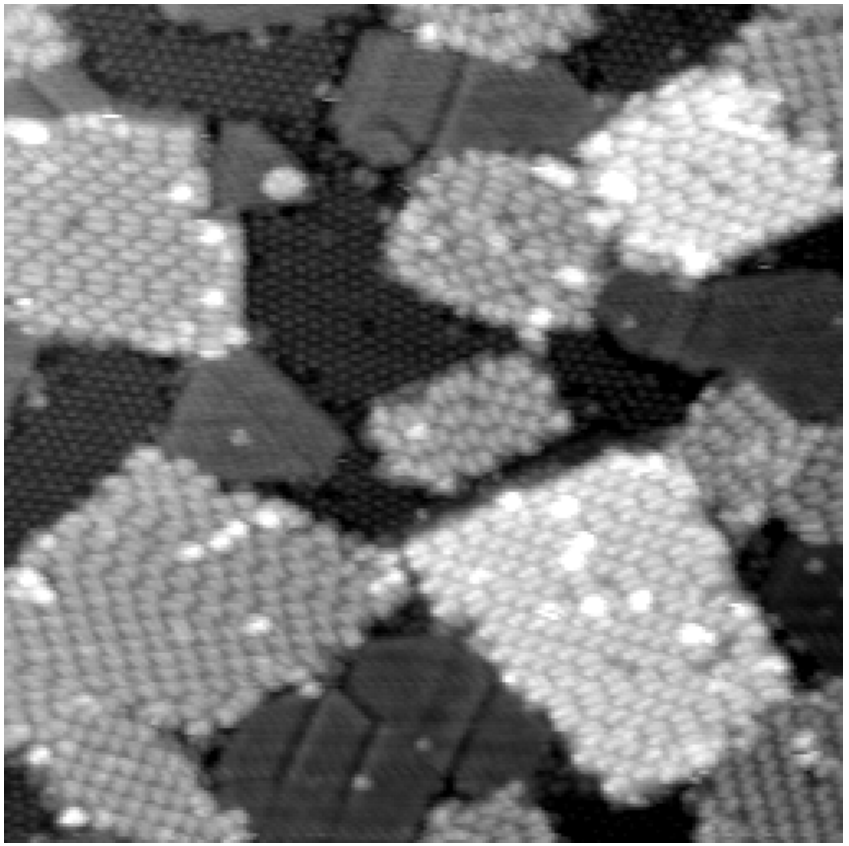


- Appearance of bands inside the gap of MoS_2 from hybridization of MoS_2 and Cu(111) orbitals.
- MoS2 is n-doped

Electronic band structure for (4x4) MoS_2 when grown on Cu(111).

Experiments





Anthraquinone (AQ) tends to adsorb on “square” structures ☺: indicating that this new material is potentially active for chemical reaction.

Summary – Part A

- Our calculated optimum size of the Moiré pattern of (4x4) MoS_2/(5x5) Cu(111) is in agreement with STM observations.
- We predict the size of Moiré patterns for MoS_2 on several close-packed metal substrates.
- Three energetically equivalent stacking types (α, β, γ) of MoS_2 on Cu(111) with distinguishable fingerprints in STM images.
- We find very little corrugation of MoS_2 layer but noticeable rearrangement of the Cu surface atoms.
- MoS_2 overlayer is chemisorbed, albeit weakly, to the Cu surface.

Manipulating joined-edges in 1L MoS_2: 1D Magnetism?

D. Le and T. S. R., "Joined edges in MoS_2: metallic and half-metallic wires," J. Phys.: Condens. Matter 25, 312201 (2013).

The idea

single-layer-MoS_2, distinct from those exfoliated from bulk material.

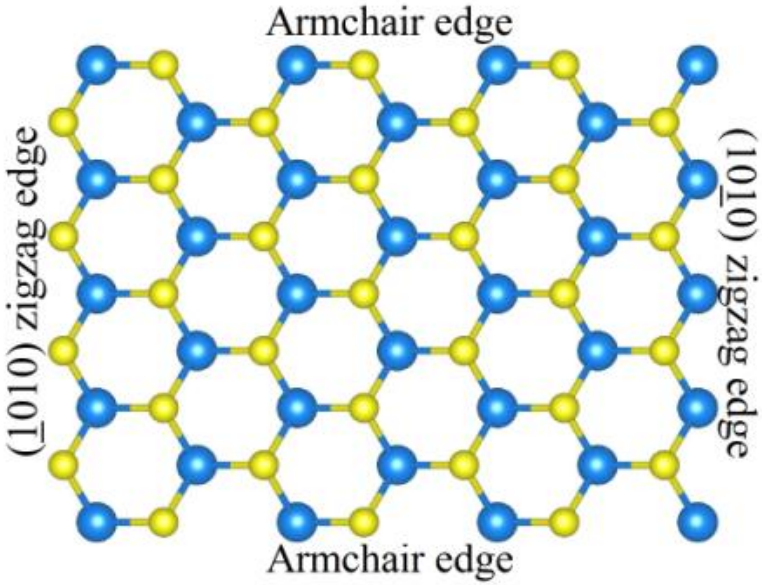
➢During growth the different nucleation centers may lead to the formation of MoS_2 domains of various orientation on substrates.

➢Dislocations and grain-boundaries (GBs) may be formed between MoS_2 domains. [***Najmaei*** *et al.* [arXiv:1301.2812], van der Zande *et al.* [arXiv:1301.1985], [Zou et al., Nano Lett. (2013)]

➢ A possible dislocation in MoS_2 is that formed between the edges of two domains*: joined-edge defect* (JED).

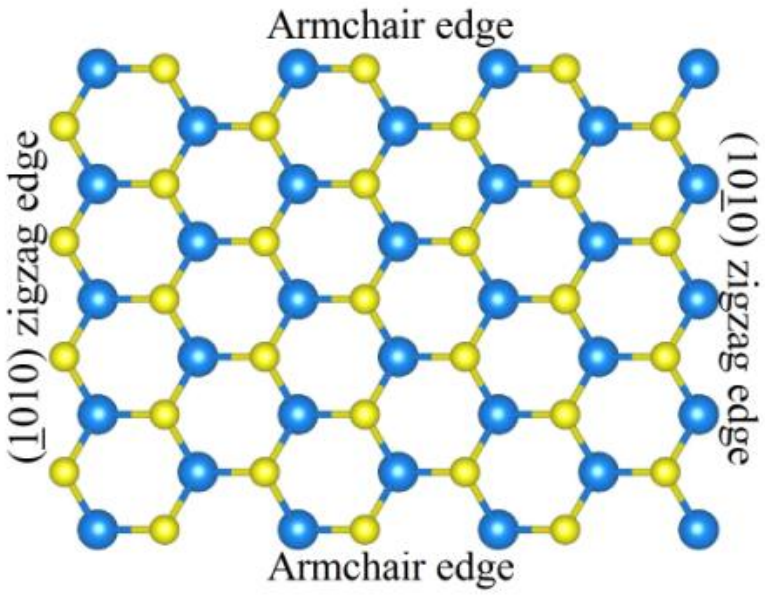
➢The structural and electronic properties of symmetrical JEDs differ from that of MoS_2 layer and other dislocations and GBs.

➢As prototypes: *symmetrical JEDs formed between zigzag edges of two MoS_2 domains by sharing the edge-atoms*.

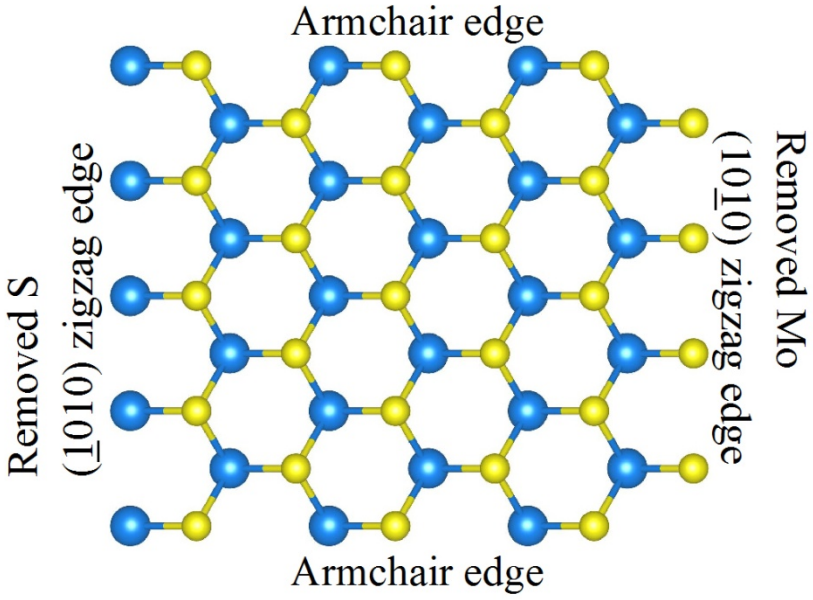


Ball-stick model of armchair and zigzag edges of MoS_2: Blue (Mo) and Yellow

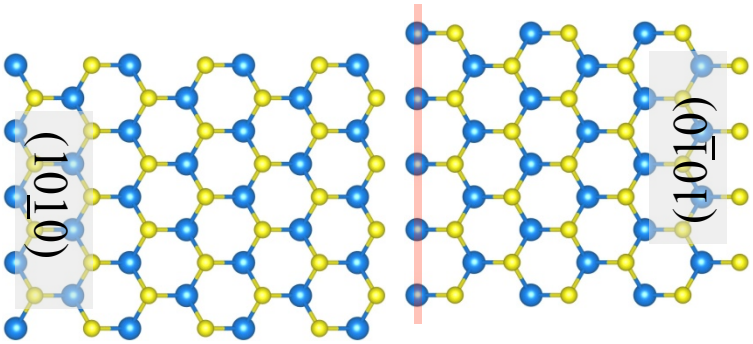
The Edges of Single-layer MoS_2



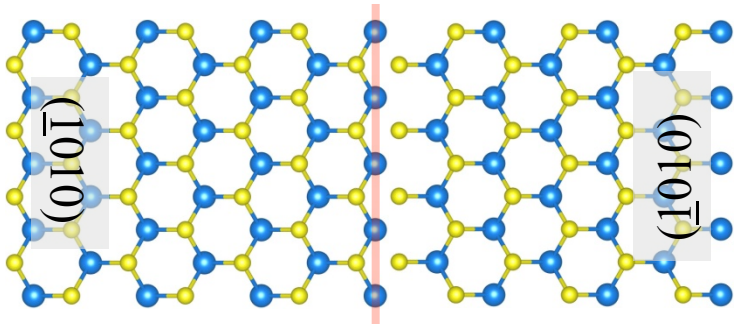
Zigzag and Armchair edges



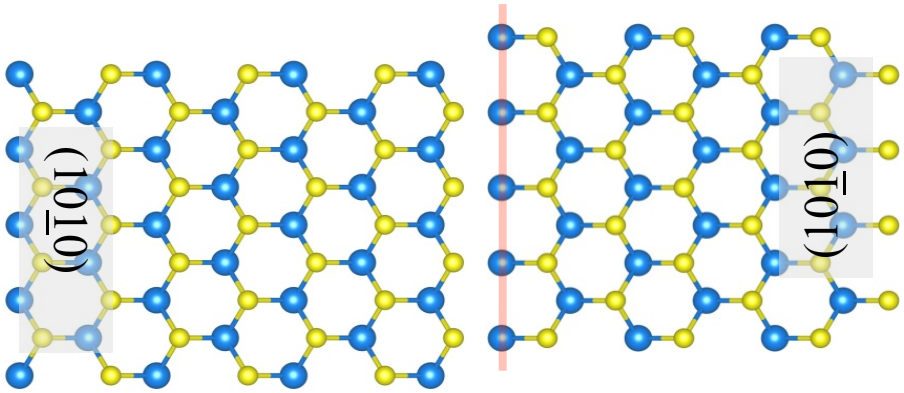
Zigzag edges with outer atoms removed



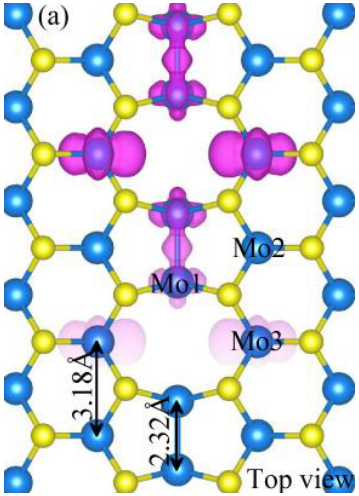
Mo-JED_1



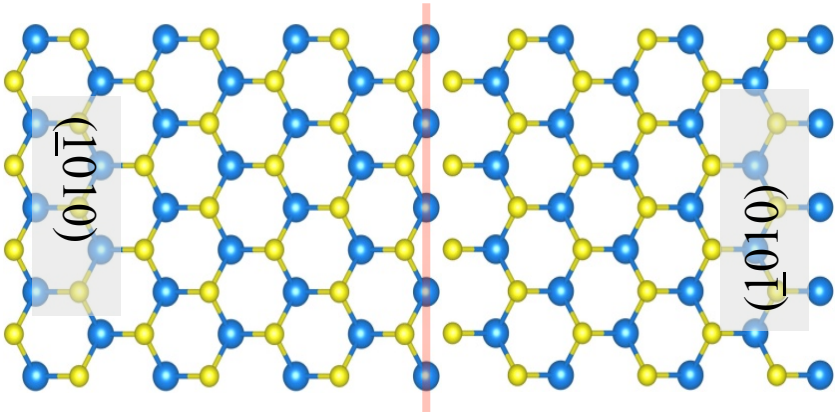
Mo-JED_2



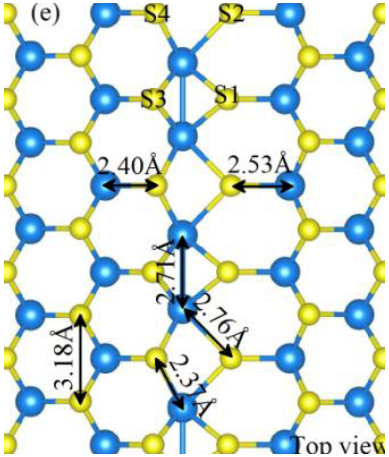
Mo-JED$_1$unrelaxed



Mo-JED$_1$ relaxed

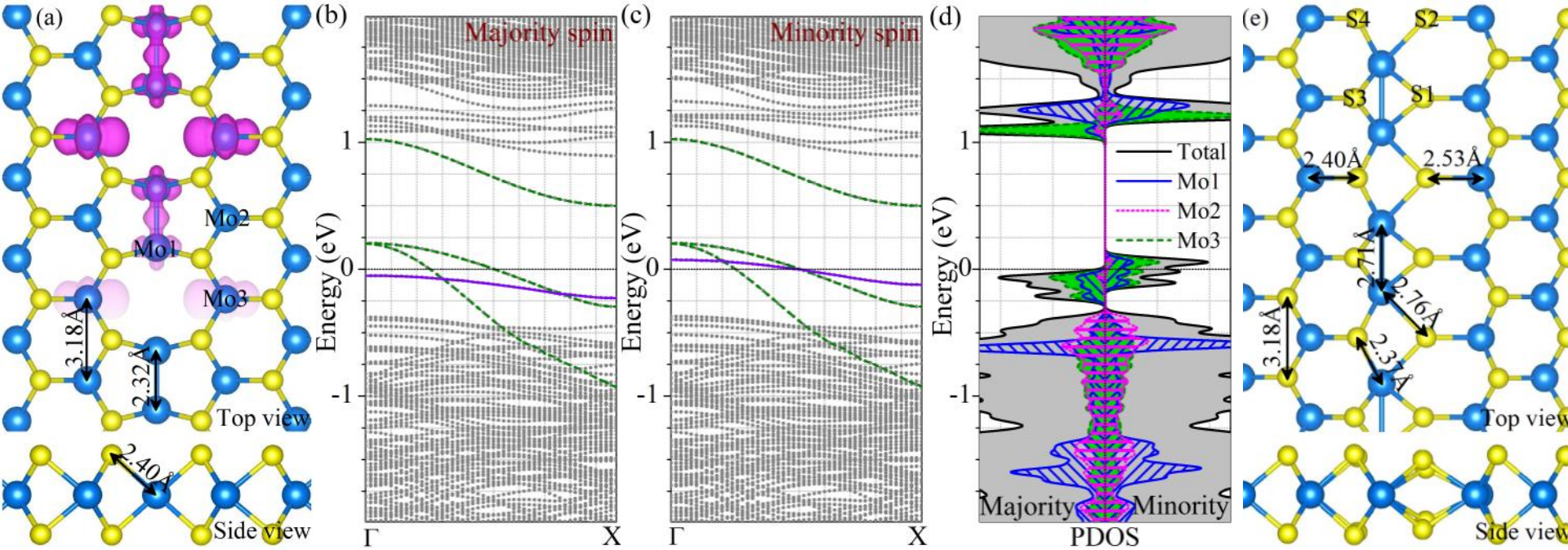


Mo-JED$_2$ unrelaxed



Mo-JED$_2$ relaxed

Electronic Structure & Spin Distribution



- (a) Structure of Mo-JED$_1$ with spin-distribution (iso-surface of 0.006 μ_B/Å^3) --top.
- (b) Majority spin electronic band structure near the Fermi level (0 eV).
- (c) Minority spin electronic band structure near the Fermi level
- (d) PDOS onto orbitals of atoms near Mo-JED$_1$ (Total) and Mo1, Mo2, Mo3 as in (a).
- (e) Structure of Mo-JED$_2$

Violet (Olive) lines highlight mid-gap states of Mo-JED$_1$(Mo-JED$_2$); Gaussian

Summary

- Four candidates for symmetrical JEDs between two MoS_2 domains.
- We find three of them (Mo-JED_1, S-JED_1, and S-JED_2) are mirror-symmetrical.
- We show that Mo-JED_1 (formed between ($\underline{1}$010)-Mo edges of two MoS_2 domains), and S-JED_2 (formed between (10$\underline{1}$0)-Mo edges of two MoS_2 domains) undergo (2 × 1) reconstruction.
- **We predict/discover the half-metallic behavior for Mo-JED_1 and metallic for S-JED_1 and S-JED_2.**
- These results suggest the possibility of using the JEDs as material for 1D transport or spin-transport (Mo-JED_1) and raises questions about the effect of such defects on MoS_2-based applications.

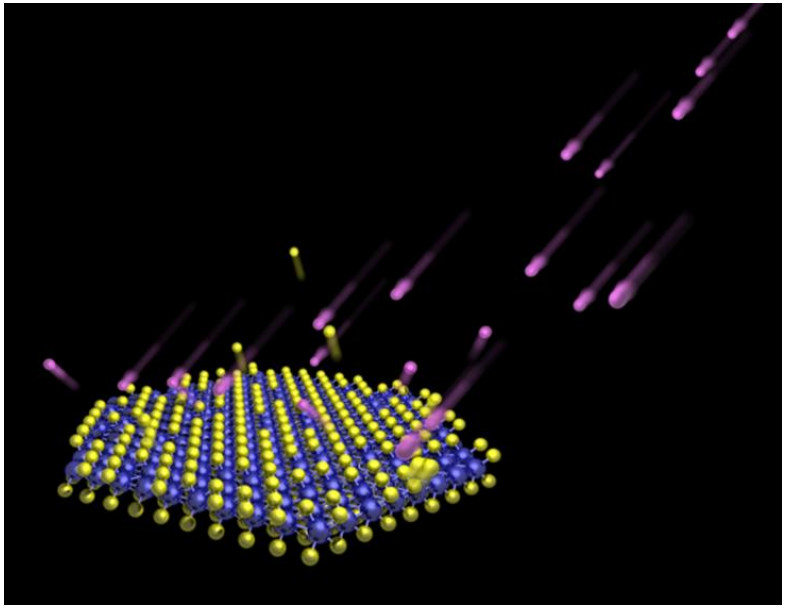
Band Gap Engineering of 1L MoS_2

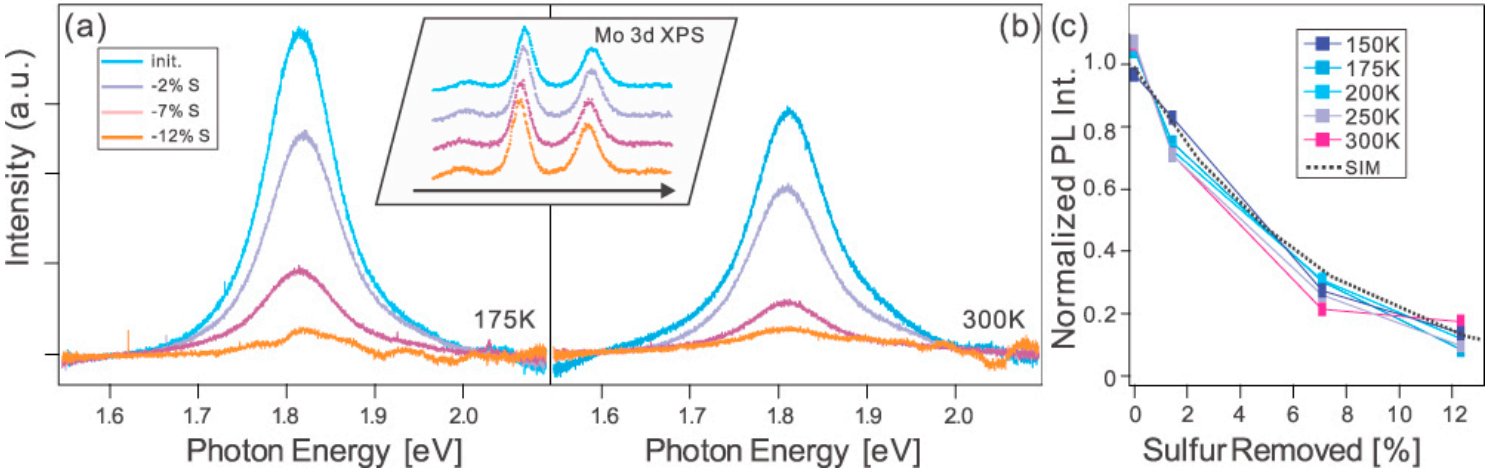
- Alloying
- Alkali Doping
- Hydrogenation
- Vacancies

Vacancies & Alloying: $MoS_{2(1-x)}Se_{2x}$ Tunable Direct Band Gaps

J. Mann, et al. 2014

Creation of Sulfur vacancies





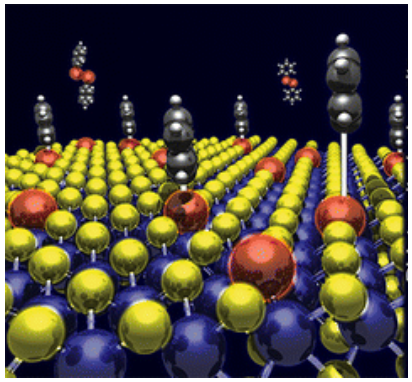
Controlled Argon Beam-Induced Desulfurization of Monolayer Molybdenum Disulfide

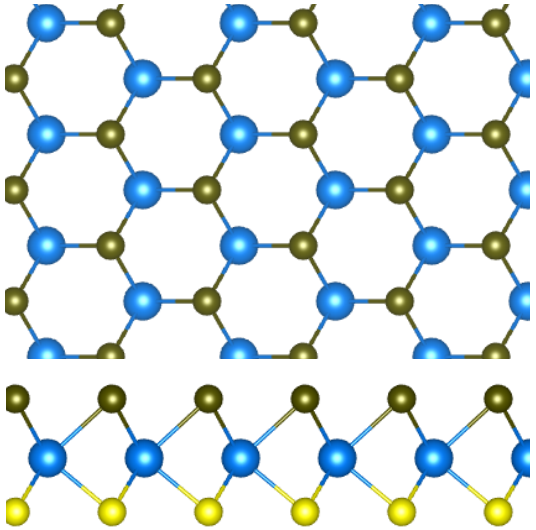
Q. Ma *et al.*, JPCM **25**, 252201 (2013).

Filling S vacancies with Se

➢It is possible to insert Se into S vacancy -> forming $MoS_{2(1-x)}Se_{2x}$

By using organic Se source (diseleno-diphenyl)





➢Possible applications:

- Heterogeneous junction
- Band gap tuning
- *Possibly new physics for polar metal dichalcogenide?*

"Post-Growth Tuning of the Bandgap of Single-Layer MoS_2 Films by Sulfur/ Selenium Exchange"

Q. Ma *et al.*, ACS Nano **8**, 4672 (2014)

Questions:

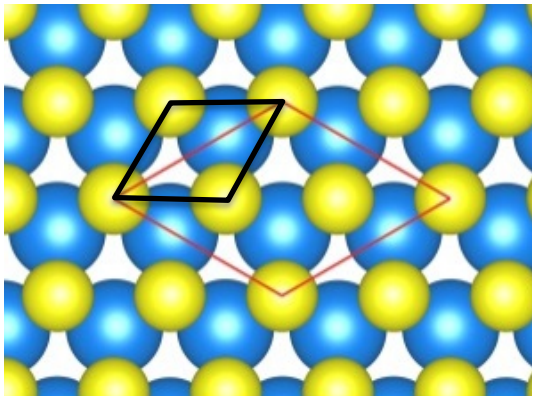
➢Band gap as function of Se concentrations

➢Stability

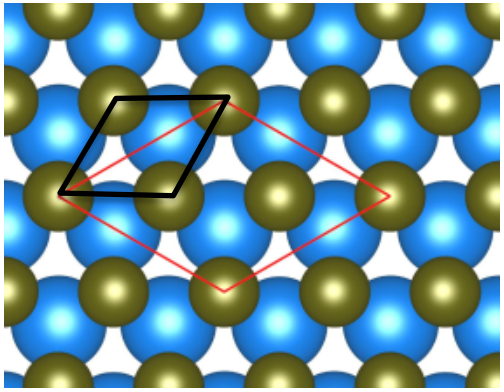
Band-gap engineering

➢ $MoS_{2(1-x)}Se_{2x}$ alloy: allows tuning of band-gap over a short range

MoS_2

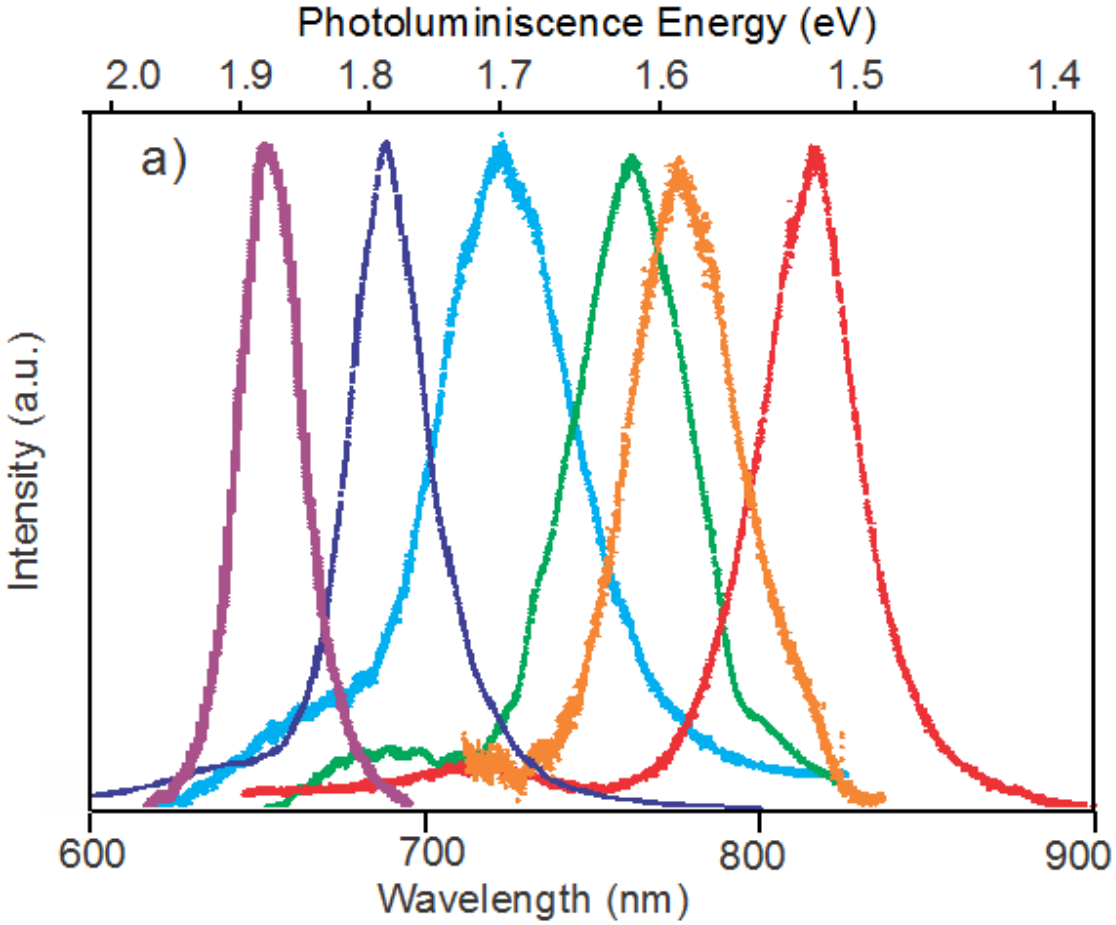


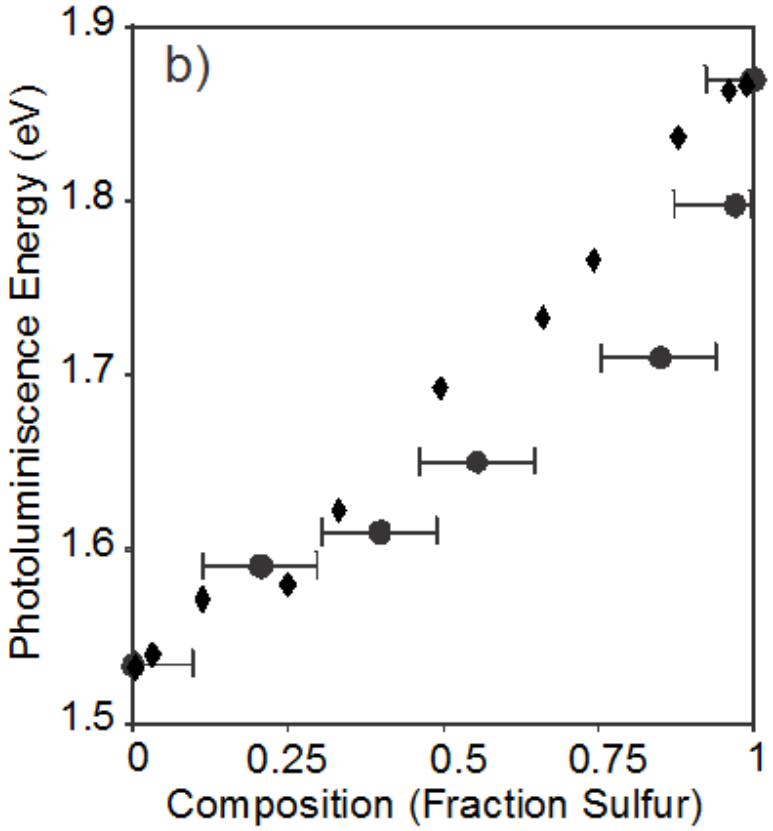
$MoSe_2$



	MoS_2	$MoSe_2$
DFT - PBE Band gap	**1.68 eV**	**1.45 eV**
Experimental PL peak	**1.87 eV**	**1.54 eV**

$MoS_{2(1-x)}Se_{2x}$: experimental data & theory



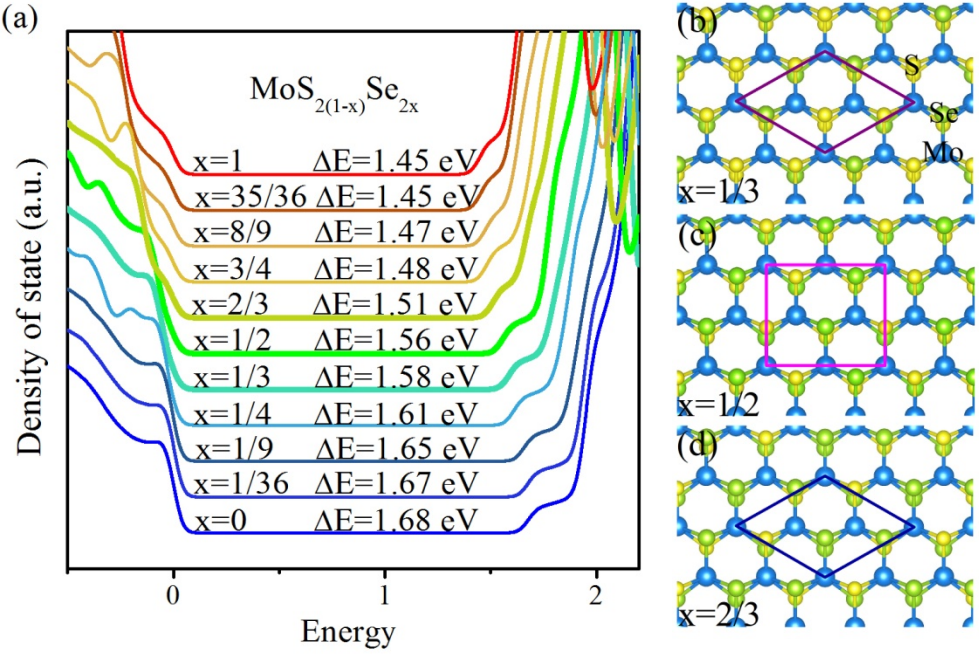


a) Normalized RT PL spectra on $MoS_{2(1-x)}Se_{2x}$ films of different composition.
b) Variation of the PL photon energy with composition (XPS).

black diamond: indicate theoretical predictions of the bandgap (scaled).

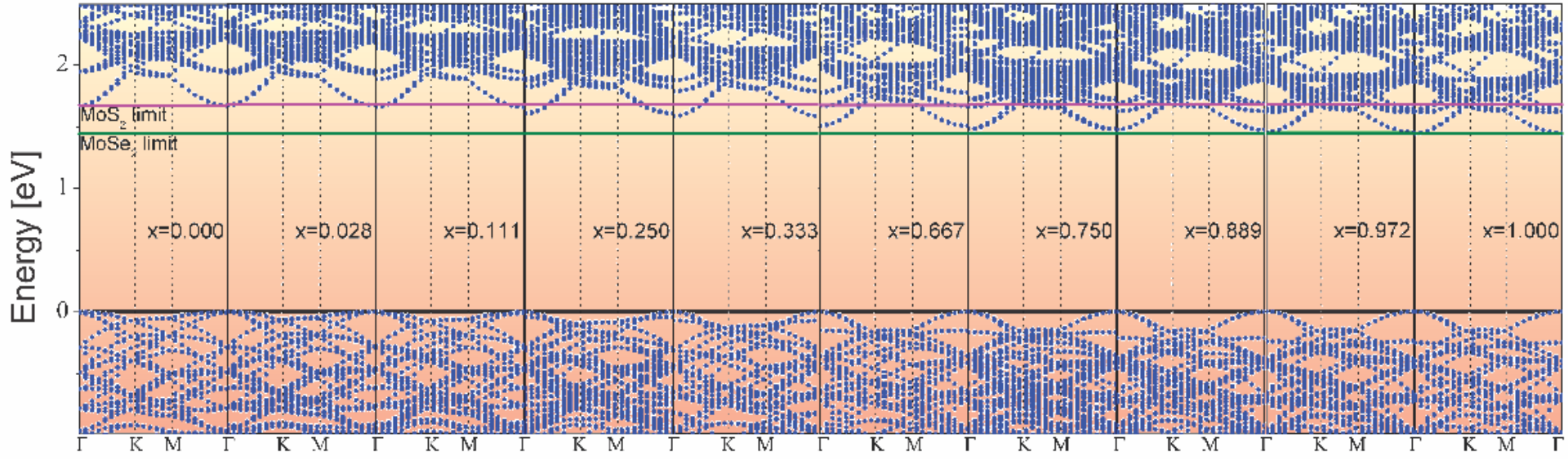
J. Mann *et al.*, Adv. Mater. **26**, 1399 (2014).

$MoS_{2(1-x)}Se_{2x}$: calculated energy bands

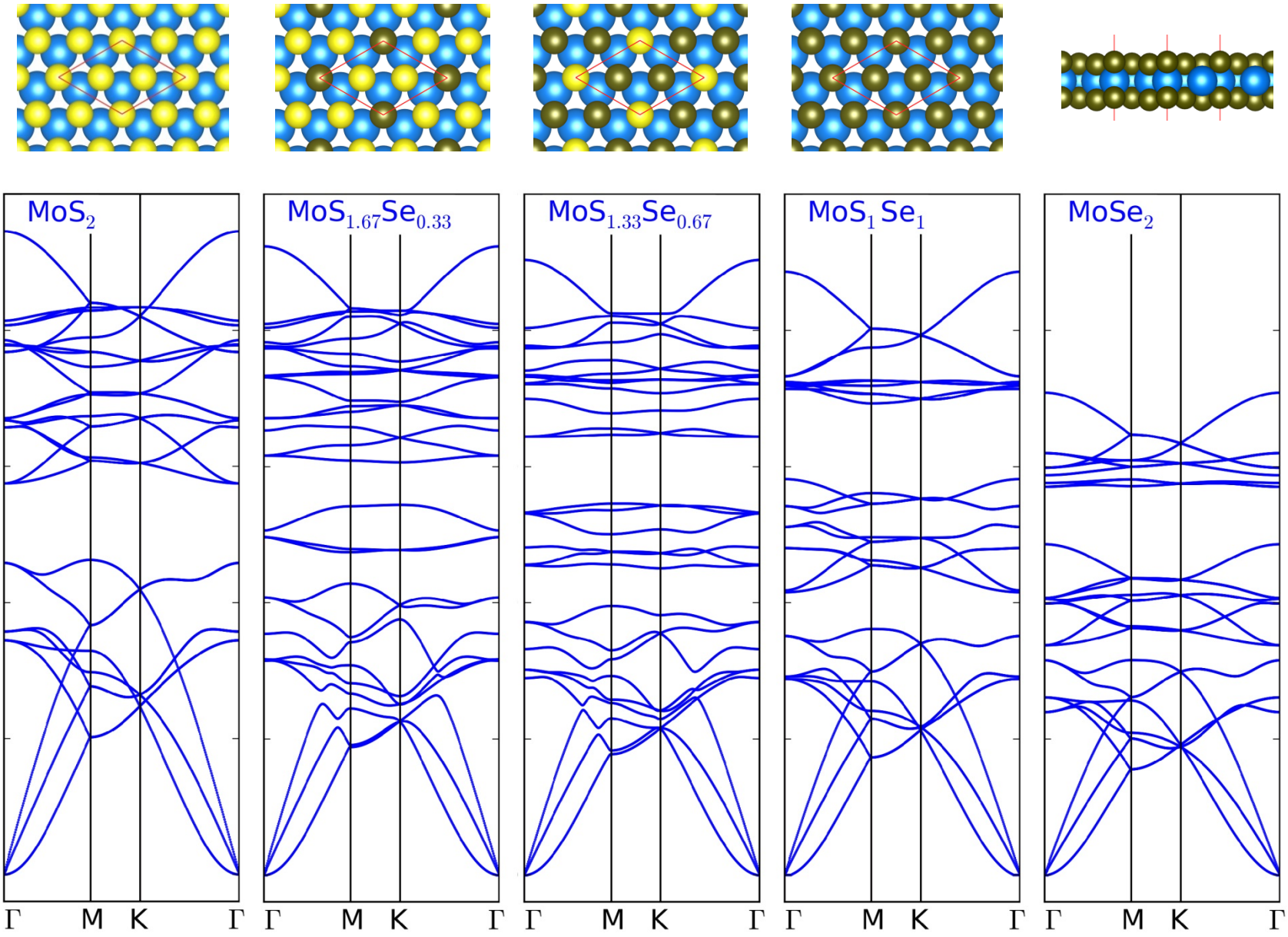


(a) Evolution of density of state of $MoS_{2(1-x)}Se_{2x}$. (b-d) Structures with x = 1/3, ½, and 2/3.

Below is the evolution of band structures of (6x6) supercell

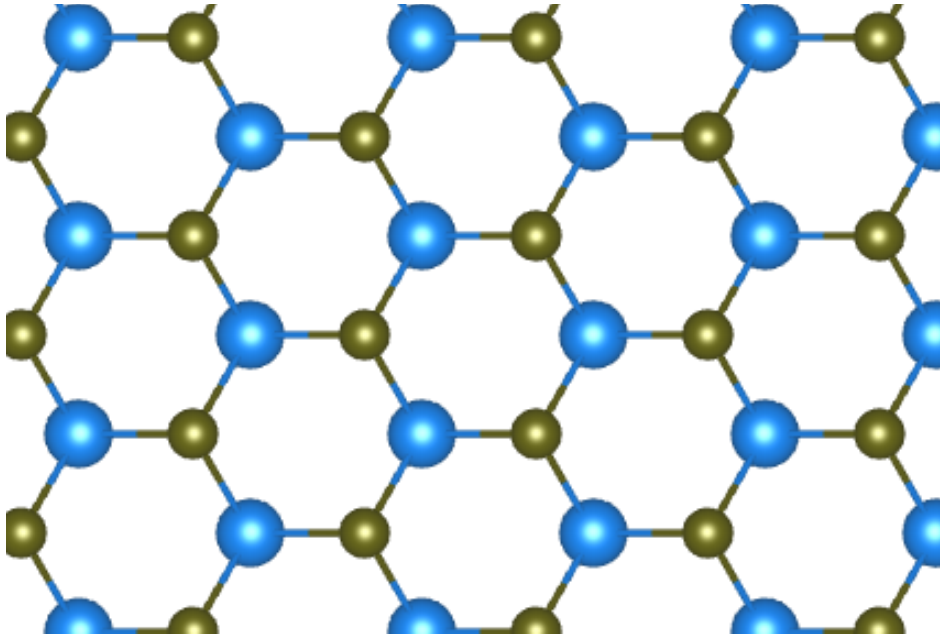


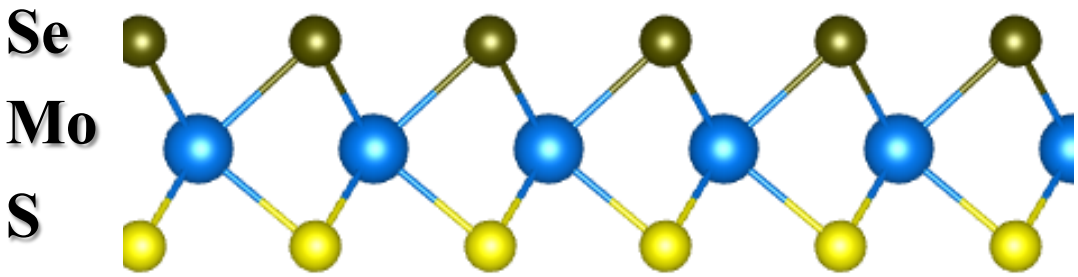
Stability of $MoS_{2(1-x)}Se_{2x}$



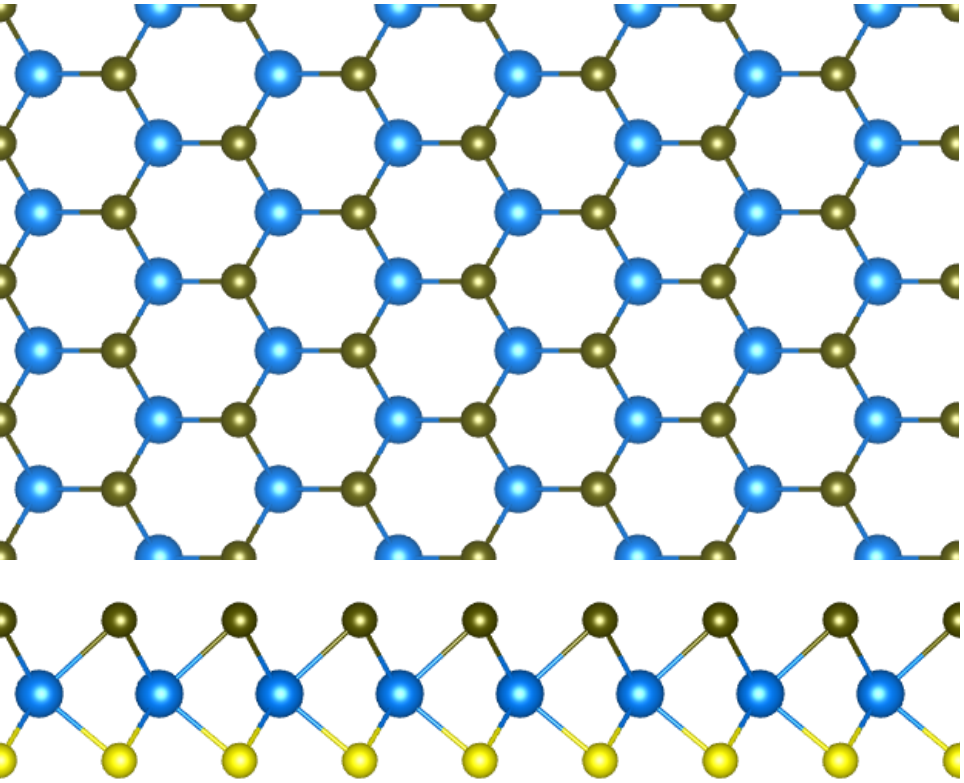
Interesting question

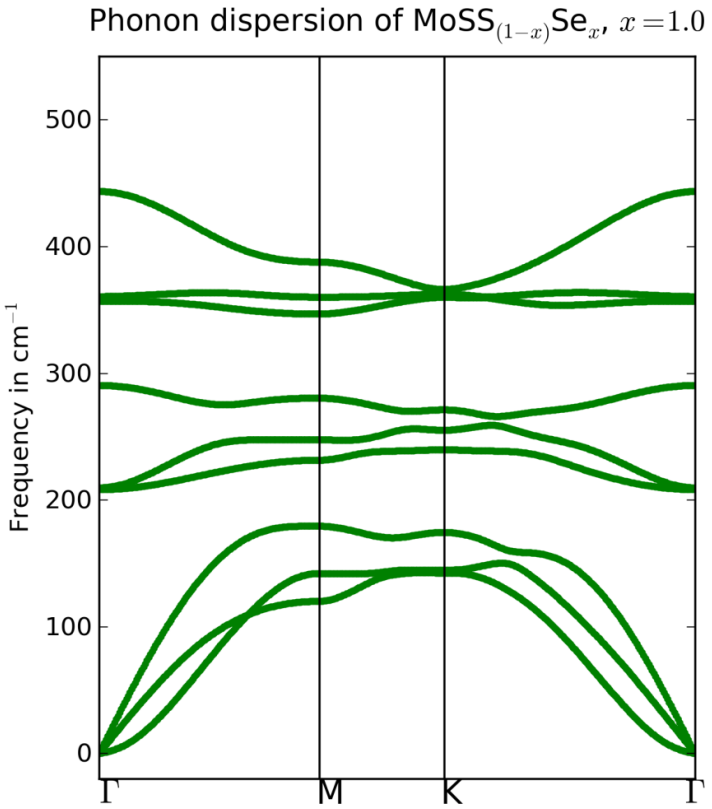
Can one make $MoS_{2(1-x)}Se_{2x}$ alloys in which Se present only **on the top layer**?





Stability of MoSSe



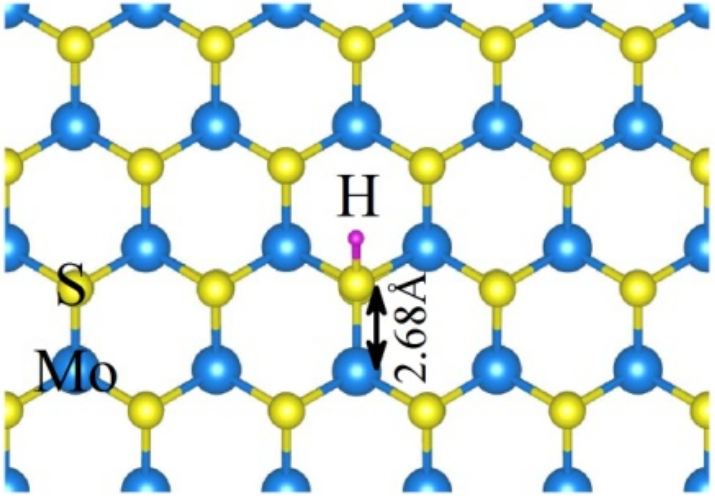


Phonon dispersion calculated with DFPT using 12x12x1 q-mesh.

Highlights

- Isotropic $MoS_{2(1-x)}Se_{2x}$ has tuneable band-gaps
- Band-gap of polar $MoS_{2(1-x)}Se_{2x}$ linearly varies with respect to Se concentrations.
- Variation of band-gap of polar $MoS_{2(1-x)}Se_{2x}$ is the results of the competition between the effect of strain and that of Se concentration.
- Phonon dispersions are calculated for various $MoS_{2(1-x)}Se_{2x}$. We found no imaginary mode suggesting the stabilities of the material.

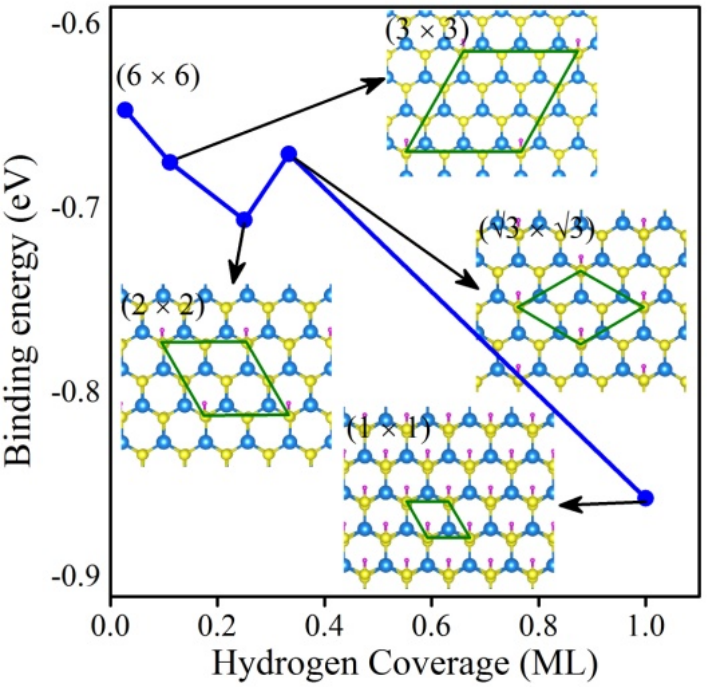
Hydrogenation/Flourination
(with Ishigami group, UCF)

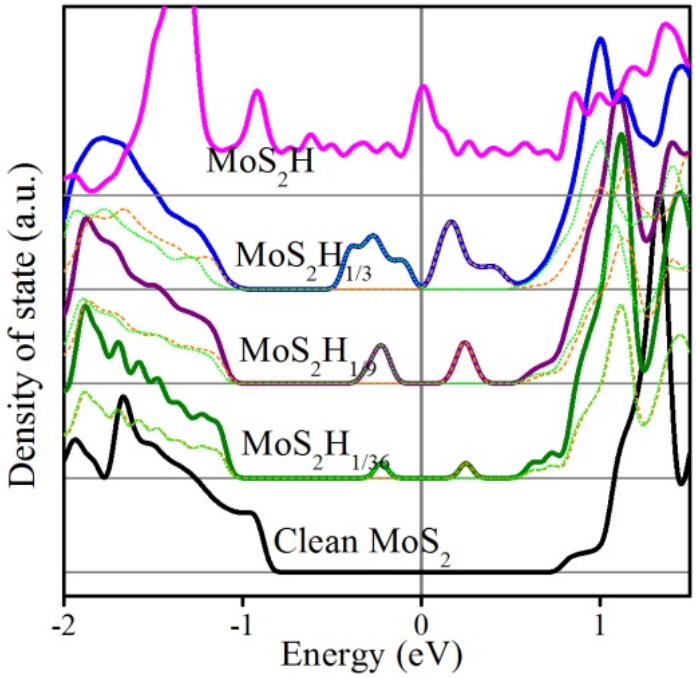


➢S-H bonds prefer to be tilted an angle β with respect to the normal direction. The tilt angle is: β=46°. This adsorption configuration is preferred over the reported configuration) by 140 meV.

➢ the adsorption of H causes the deformation of MoS_2. Mo-S bondlengths at the adsorption site increase from 2.41 Å (without H adsorption) to 2.44 Å and 2.68 Å, indicating the weakening Mo-S bond at the adsorption site.

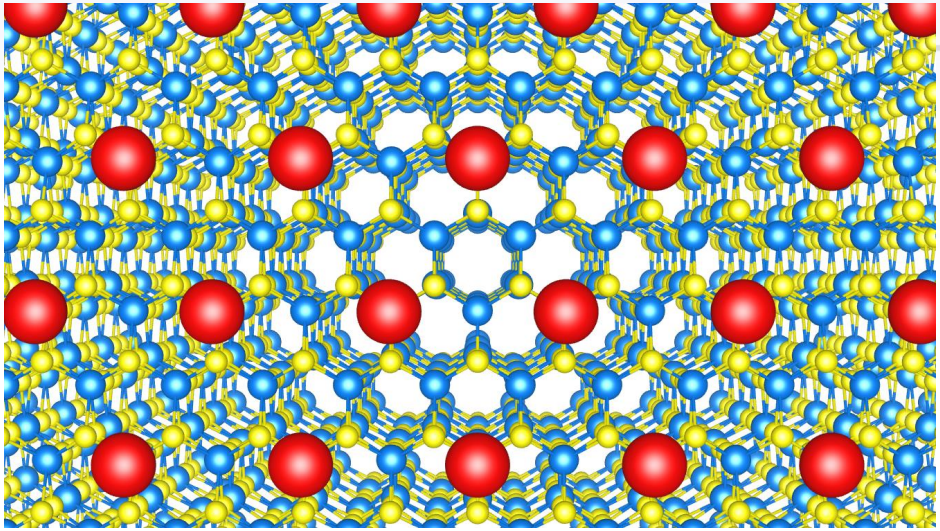
➢ At low coverage (< 100%) The binding energy of an atomic H on MoS_2 is the lowest (most preferable) at ¼ coverage (left figure below). However, the binding energy of H on MoS_2 is the lowest when (1×1) structure formed (Will discuss about this later). The evolution of density of electronic states as increasing H coverage is shown in the right figure below. Note that, in the case of $MoS_2H_{1/36}$, $MoS_2H_{1/9}$, and $MoS_2H_{1/3}$, the mid-gap states are spin-polarized: spin-up is occupied and spin down is un-occupied (dot and dash lines, respectively).





Na doping of MoS_2
ARPES & DFT

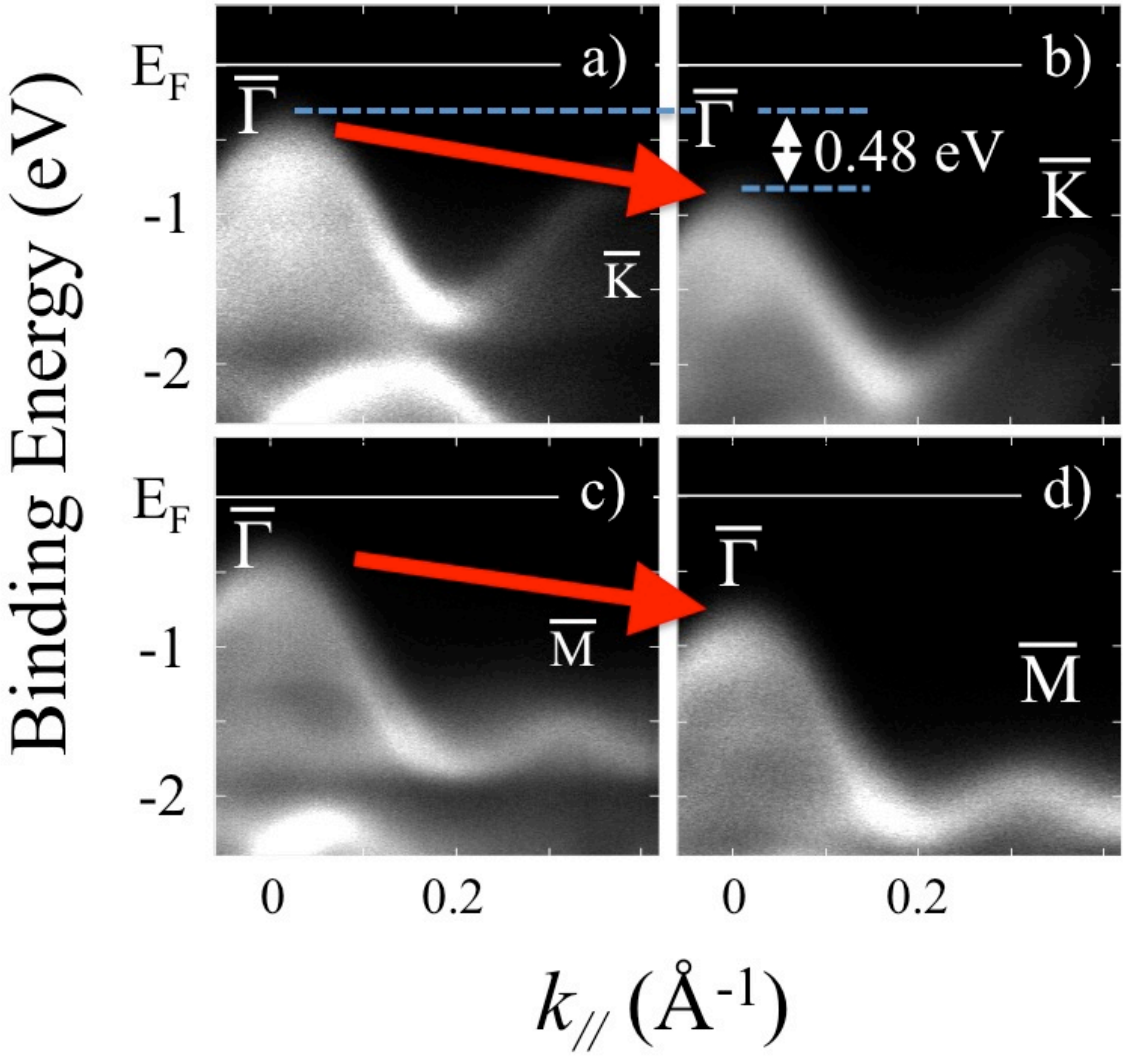
(With Peter Dowben group, U Nebraska)



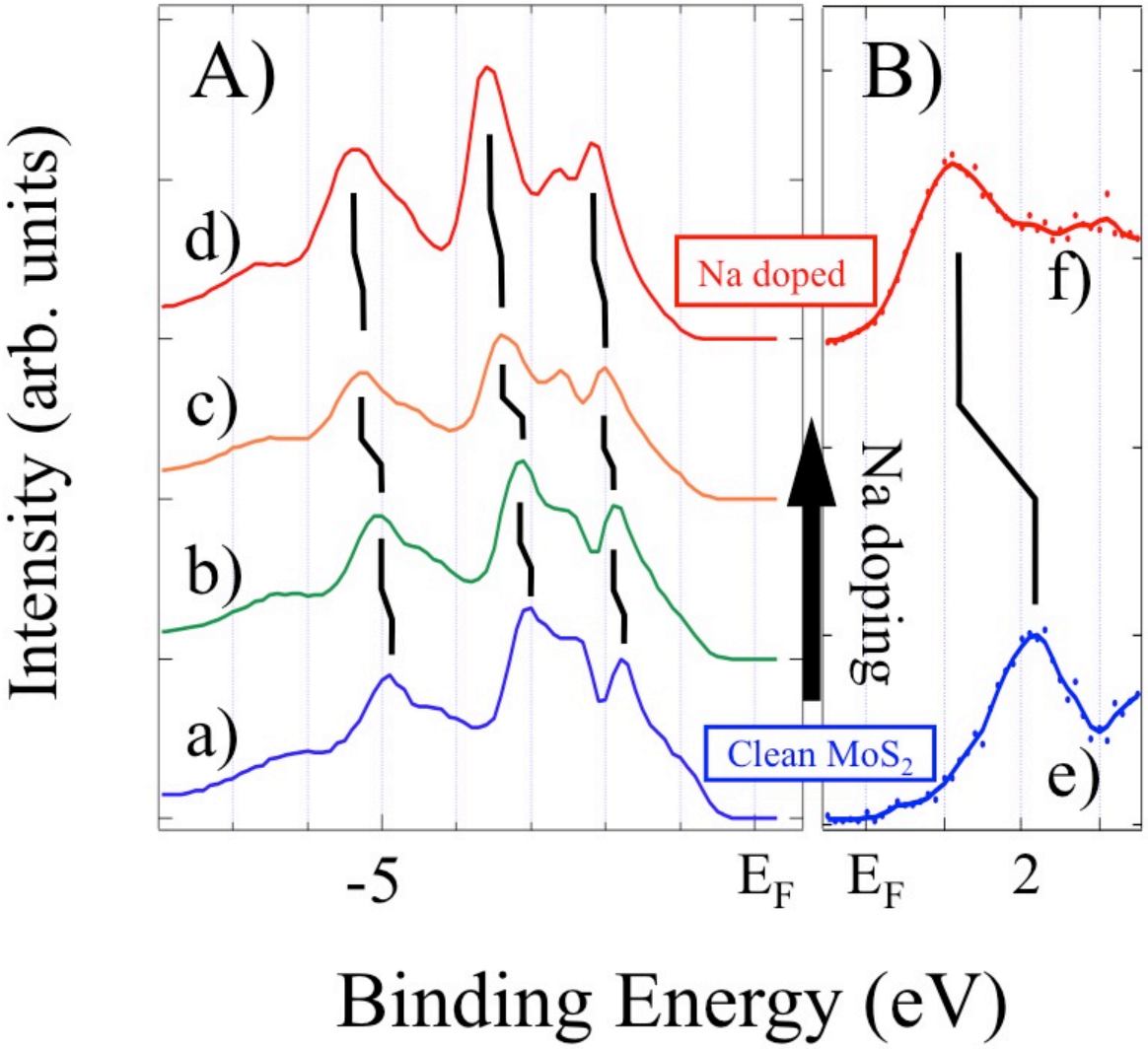
METHODS

- Theory: DFT with van der Waals interaction
- Experiment:
  - High-resolution angle-resolved photoemission spectroscopy (ARPES) (HiSOR, Japan)
  - Unoccupied state spectra were acquired in separate ultrahigh vacuum systems equipped with the inverse photoemission (IPES), low energy electron spectroscopy (LEED) and x-ray photoemission spectroscopy (XPS).

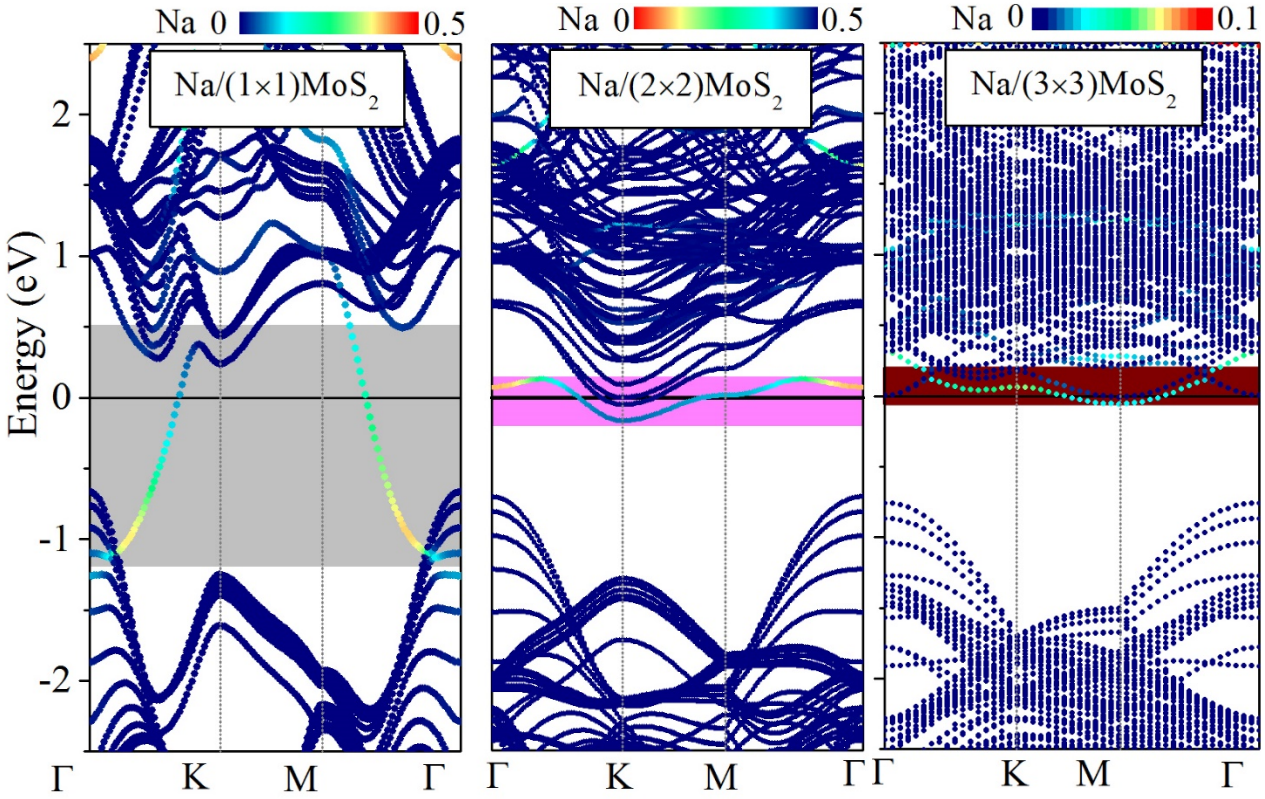
$Na/MoS_2(0001)$: Occupied bands

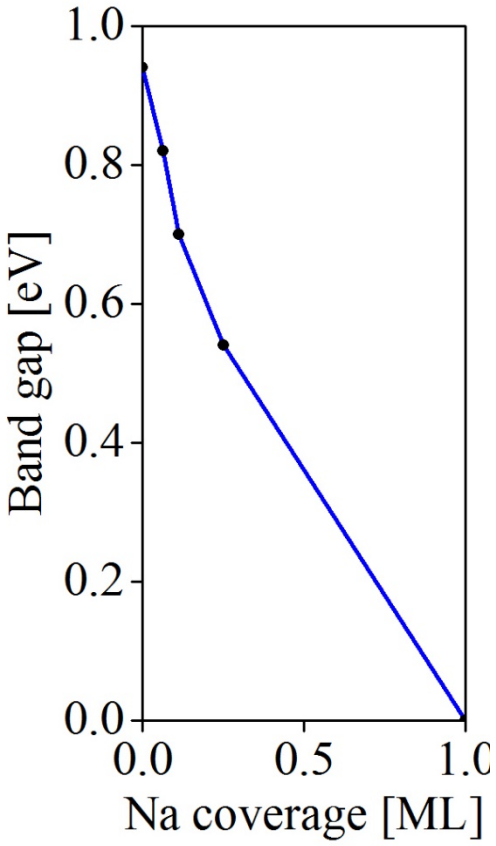


Na Doped MoS_2(0001): Spectra

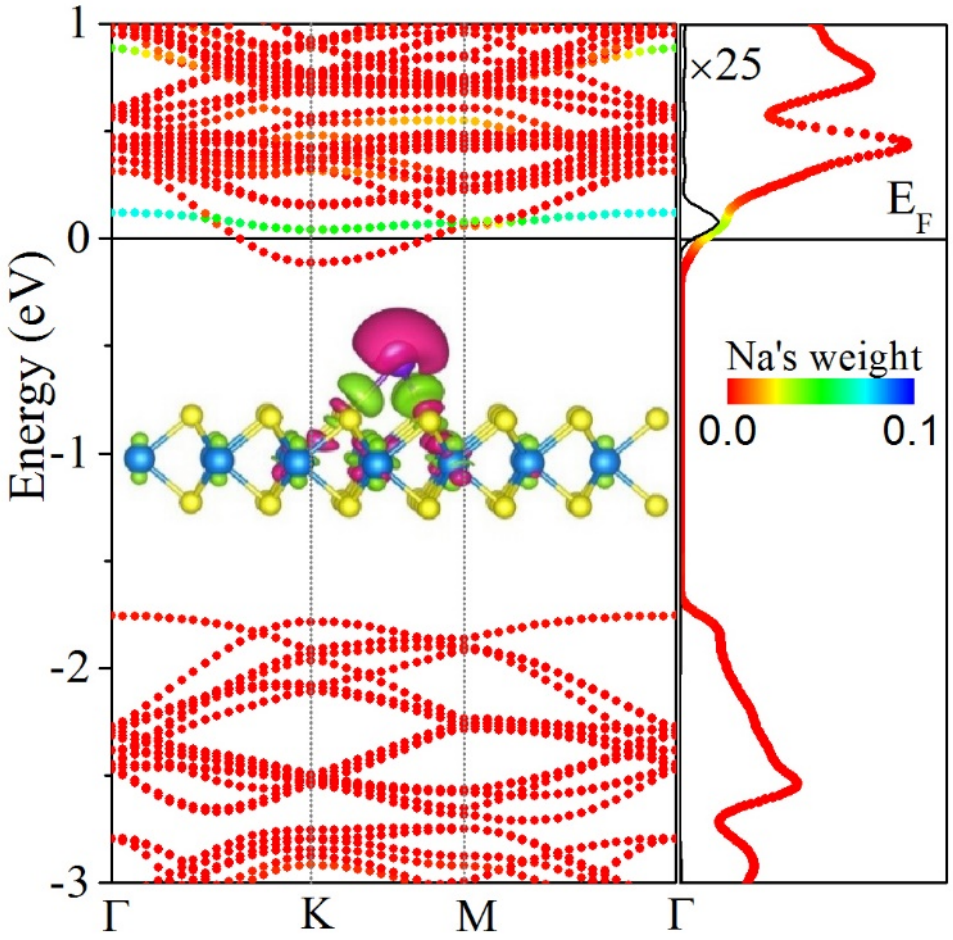


$Na/MoS_2(0001)$: Band Structure

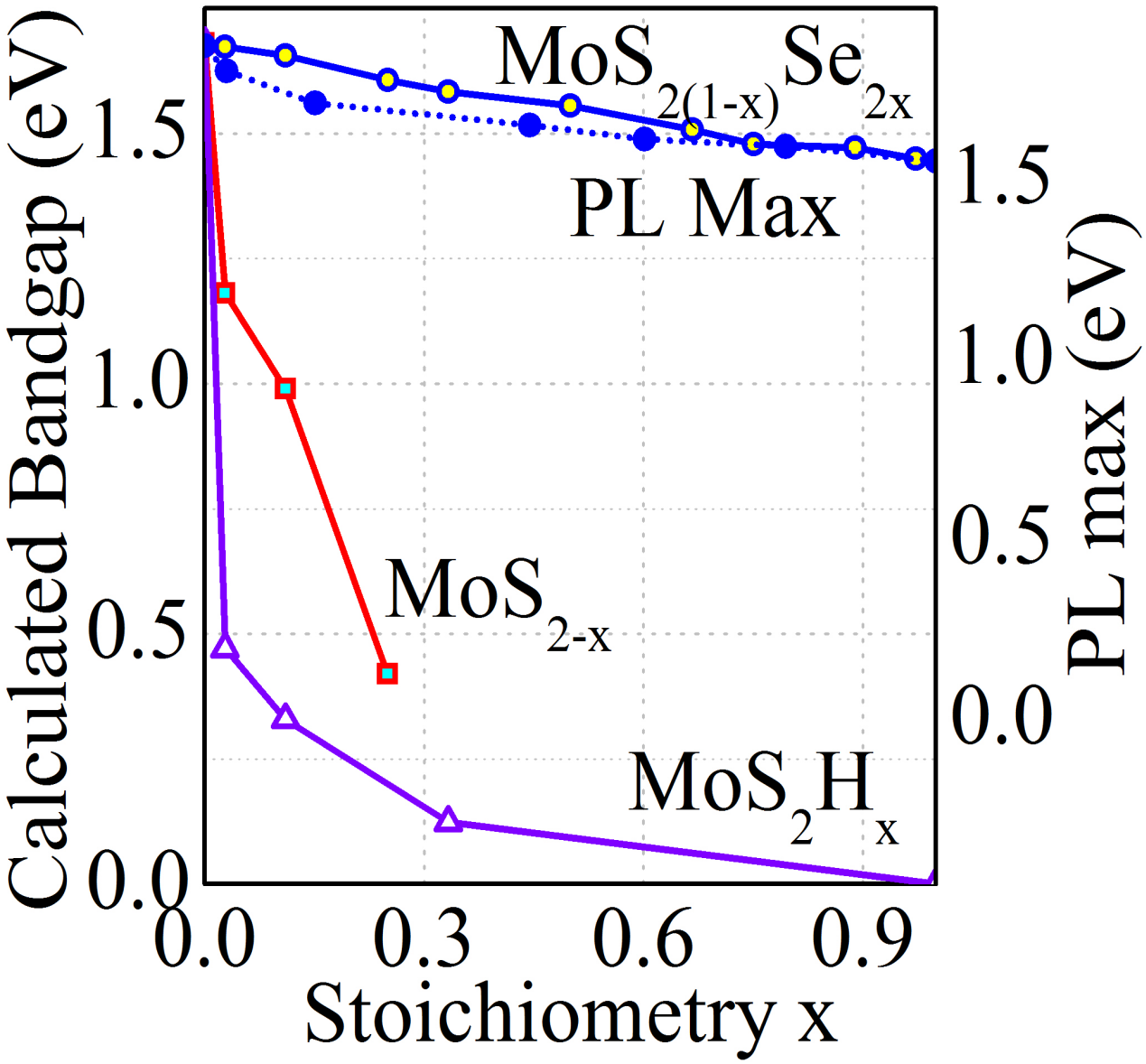




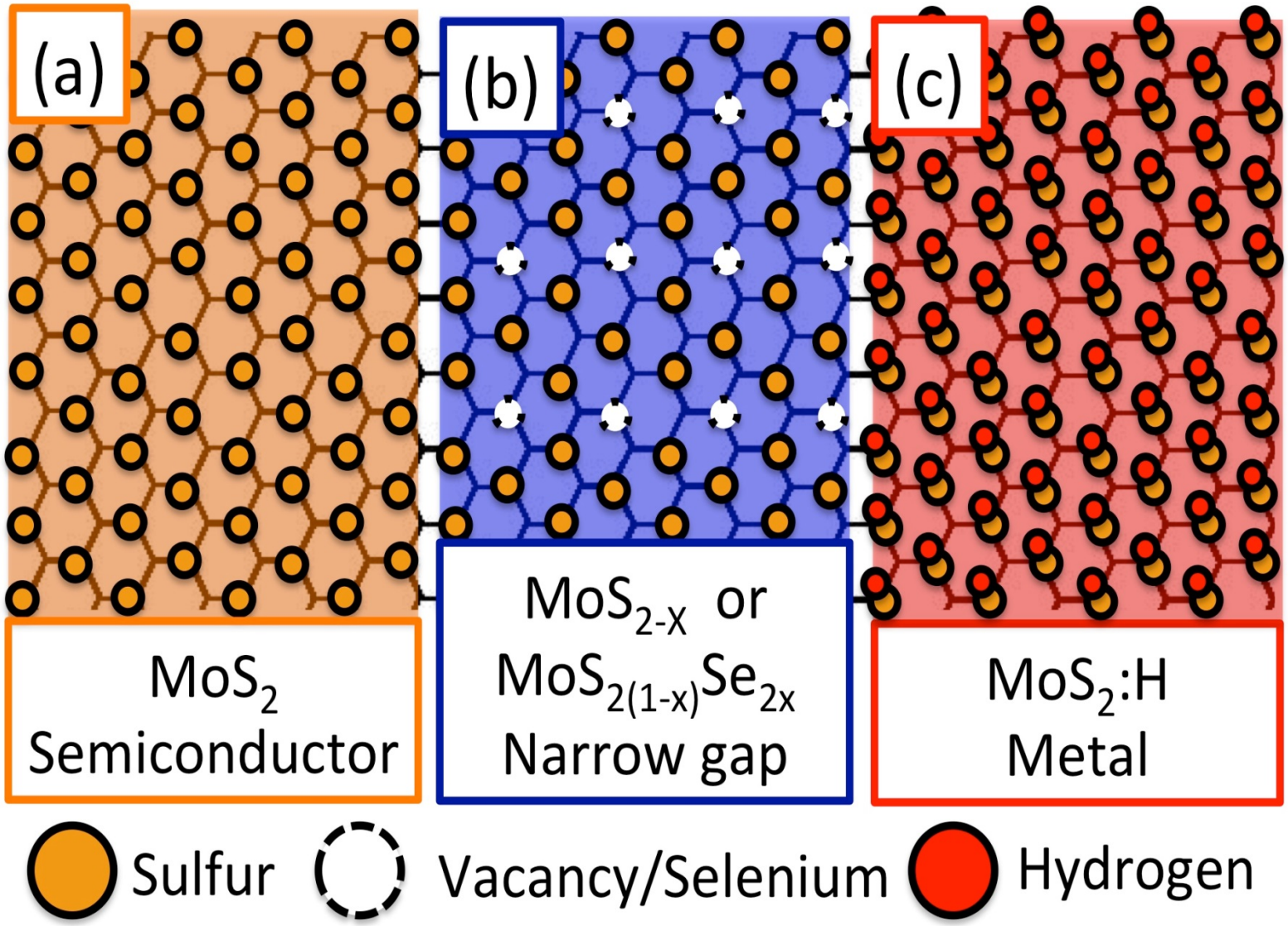
Na/Single Layer MoS_2: Charge transfer



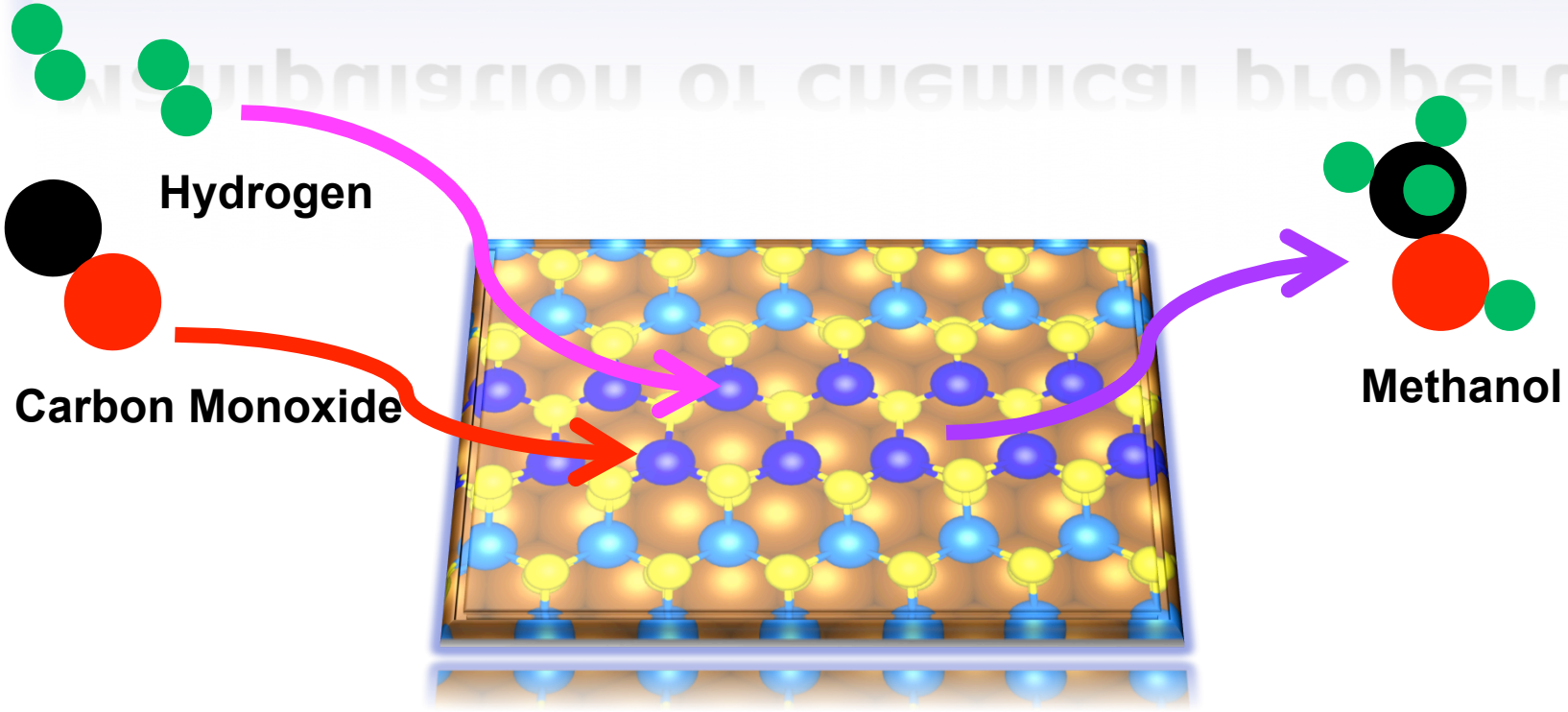
Calculated Band Gaps for Functionalized MoS_2



Summary: Functionalization of Molybdenene

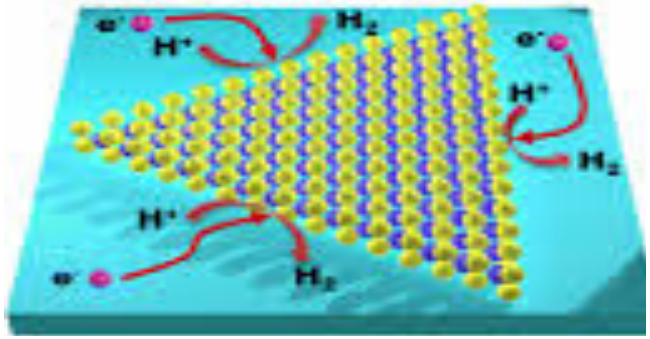


Manipulation of chemical properties

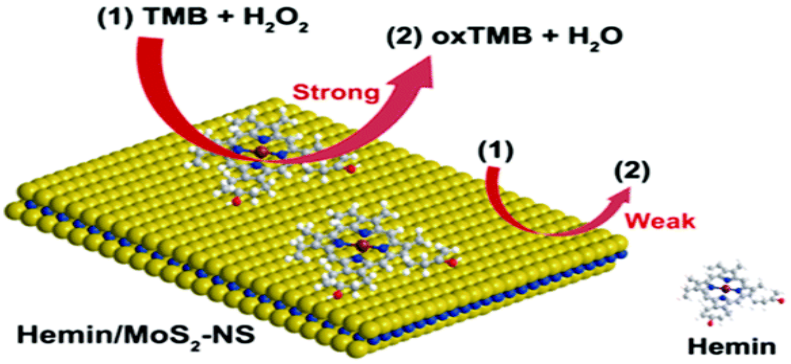


Chemistry on Single-layer MoS_2

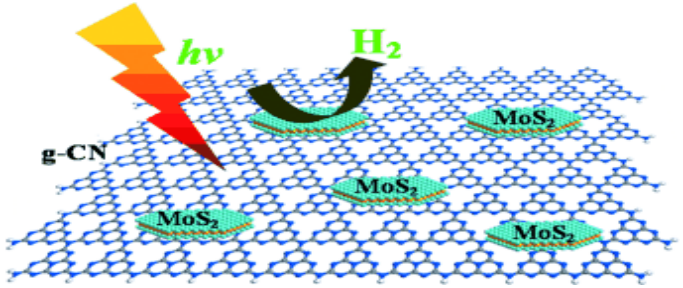
Controllable Growth and Transfer of Monolayer MoS_2 on Au Foils and Its Potential Application in Hydrogen Evolution Reaction, J. Shi et al., *ACS Nano*, **8**, (2014), 10196



Hemin-functionalized MoS_2 nanosheets: enhanced peroxidase-like catalytic activity with a steady state in aqueous solution, B. L. Li, *RSC Adv.*, **4,** (2014) 24256



Layered Nanojunctions for Hydrogen-Evolution Catalysis, H. Yidong et al., *Ang. Chem. Int. Ed.*, **52**, (2013), 3621

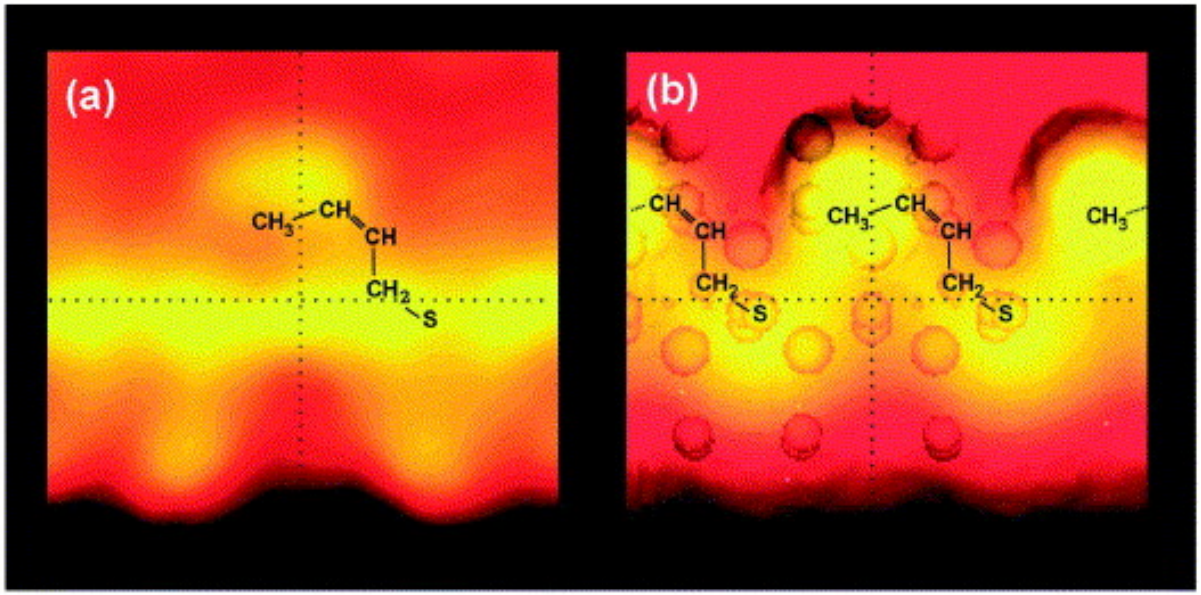


Is it the edge?
Vacancies?
Metallic Support?
Interface with nanoparticle?

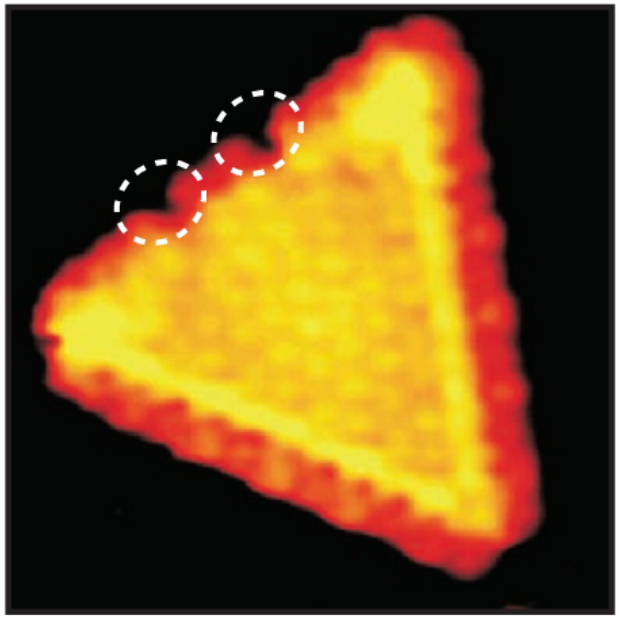
MoS_2 for Hydro-desulfurization

Hydro-desulfurization reaction on MoS_2 nanoclusters:

Edges are the reaction sites

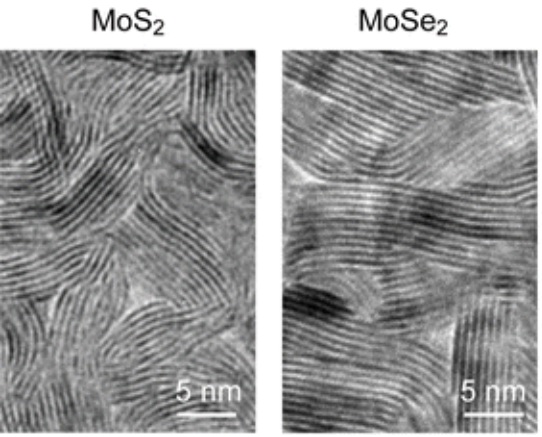


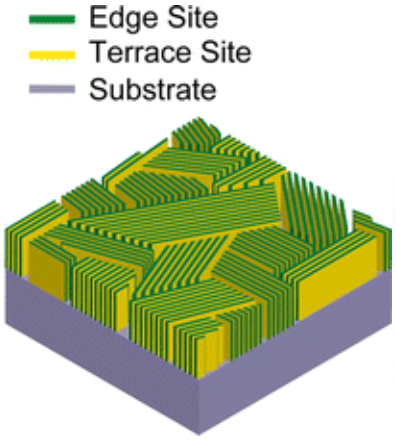
J. V. Lauritsen *et al., J. Catal.* (2004).

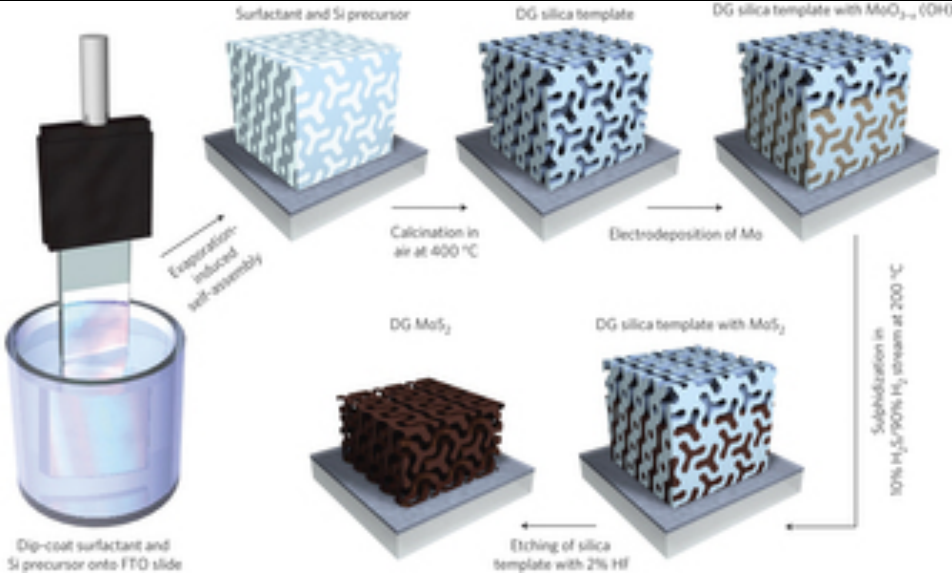


J. Kibsgaard, PhD Thesis (2008)

Create edges for reactions







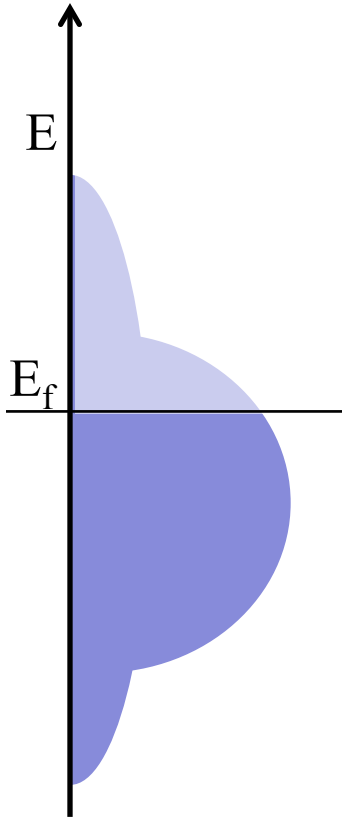
Synthesis of MoS_2 and $MoSe_2$ Films with Vertically Aligned Layers

D. Kong *et al., Nano Lett.* (2013).

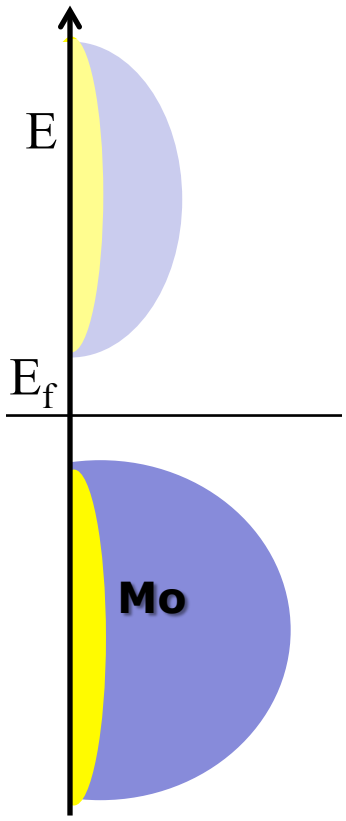
Engineering the surface structure of $MoS_2$to preferentially expose active edge sites for electrocatalysis

J. Kibsgaard *et al., Nature Mater.* (2012).

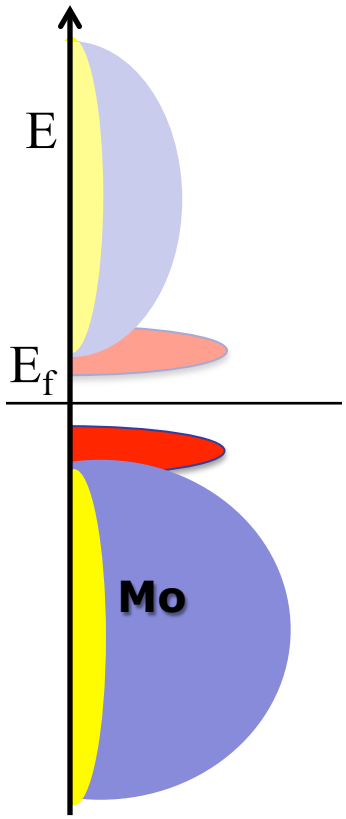
Manipulating Chemical Reactivity



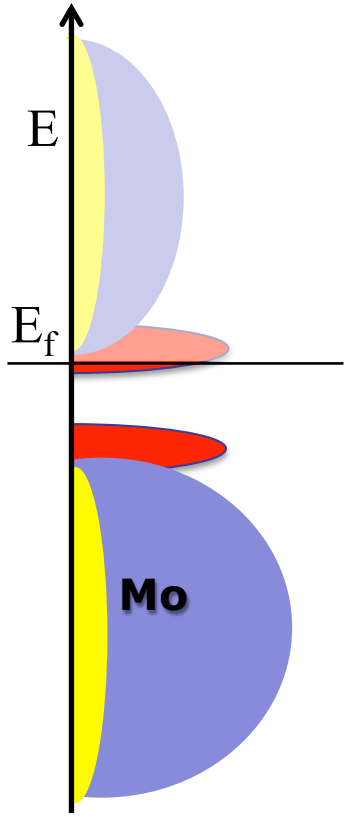
Transition Metal



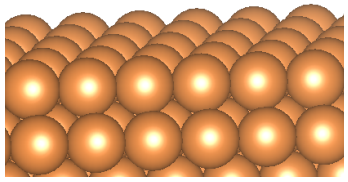
MoS_2

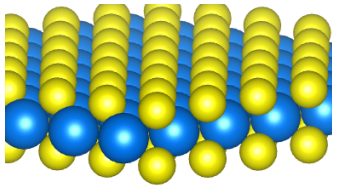


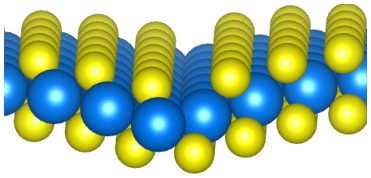
MoS_2 with S vacancy row

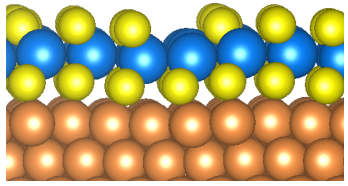


MoS_2 with S vacancy row on Cu(111)



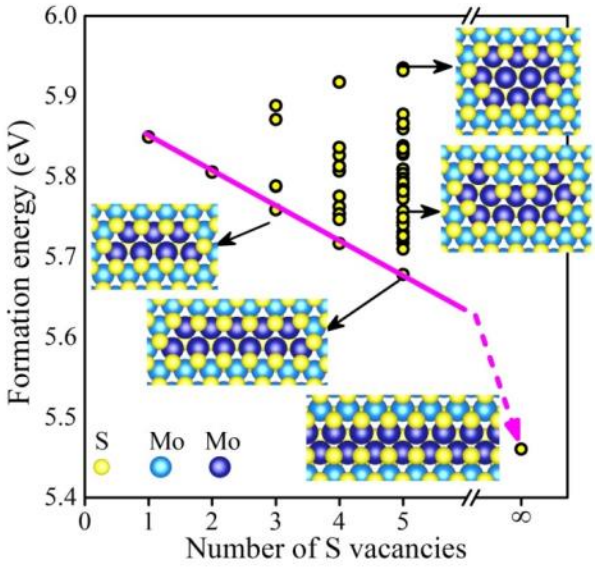


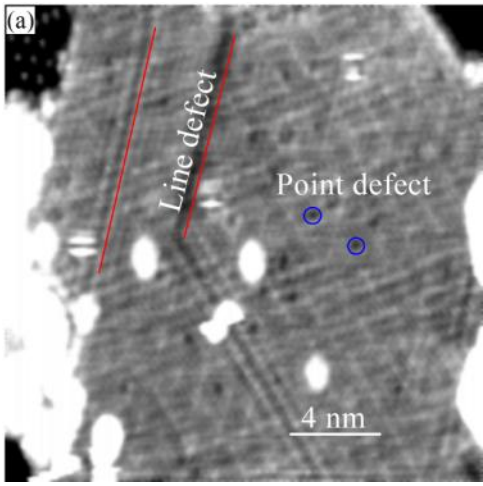




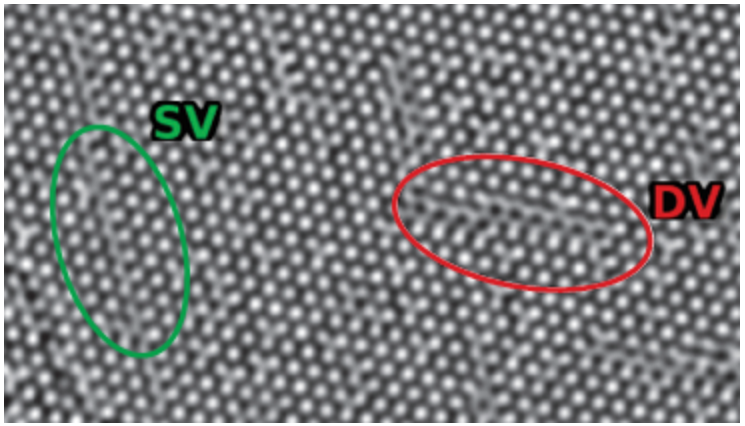
Remarks

- Sulfur vacancies tend to form row structures.
  - Formation energy is lowest when sulfur vacancies form row.
- The longer the row structure , the more stable it is
  - Barrier for diffusion of an nearby S atom to sulfur vacancy row increases as the row elongates.
  - The reversed barrier is always lower.





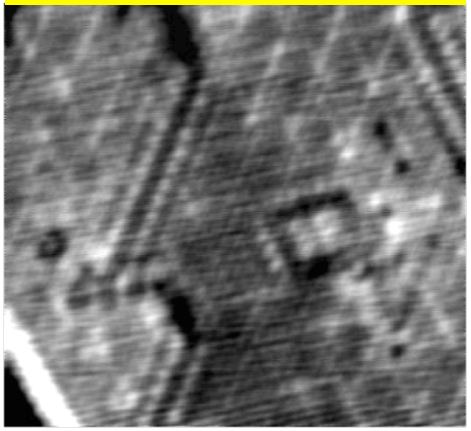
L. Bartels' group



Komsa et al, 2013

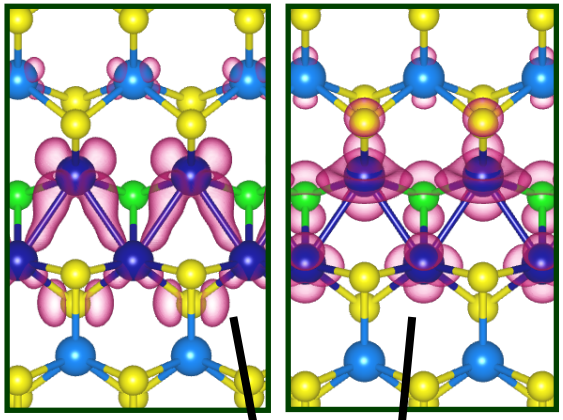
Electronic Structure of Defect-laden MoS_2

MoS_2 on Cu(111)

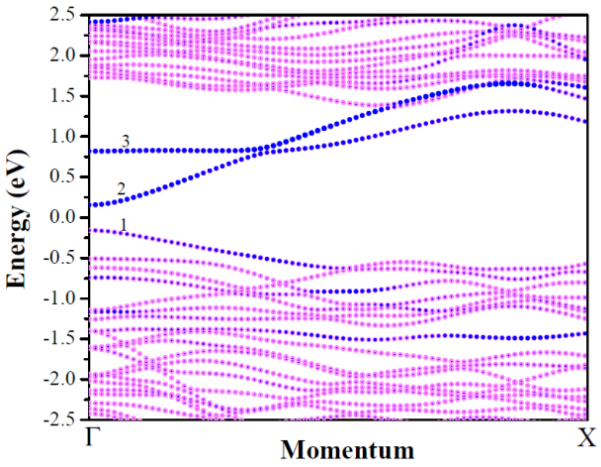


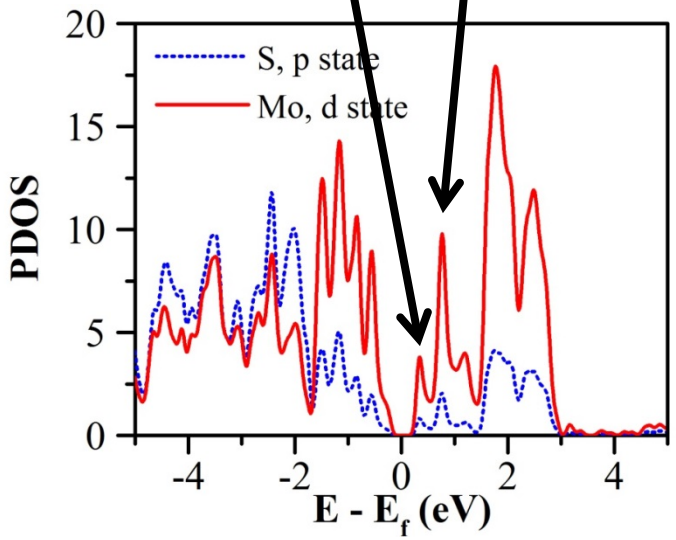
From L. Bartels group

D. Le, T. B. Rawal, T. S. R,
Jour. Phys. Chem C, ***118****, (2014), 5346*

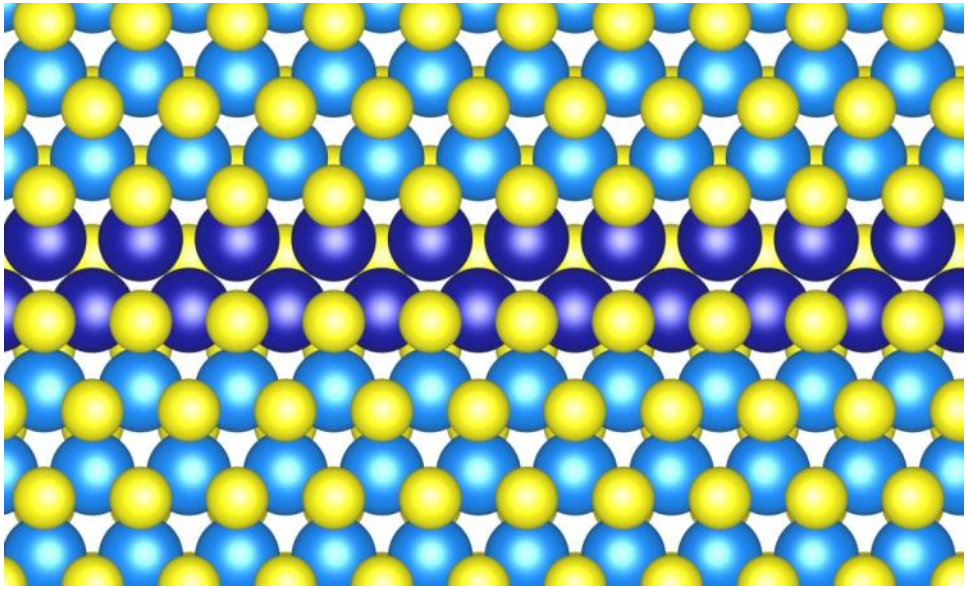


- Both theoretical and experimental findings clearly indicate that line defect (S-vacancy row) forms on MoS_2.
- DFT results show that "defect states" are predominantly Mo d orbitals, that will participate in bonding.



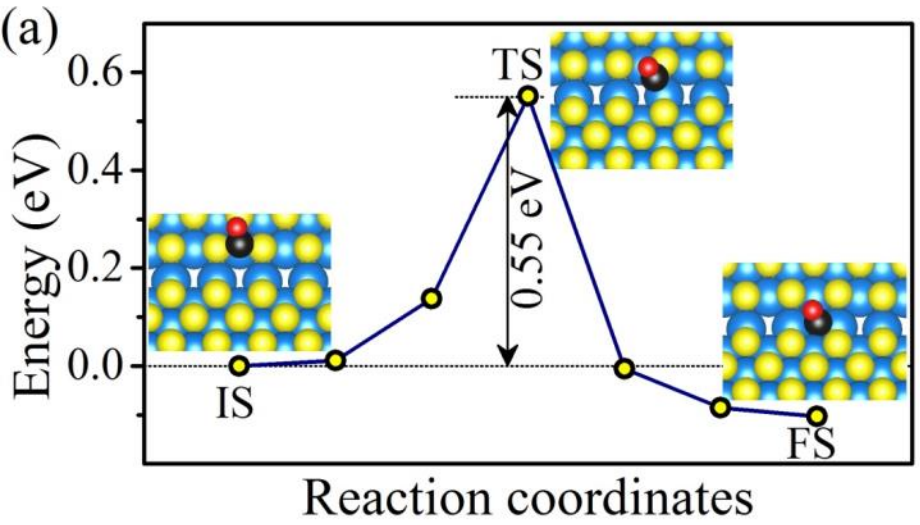


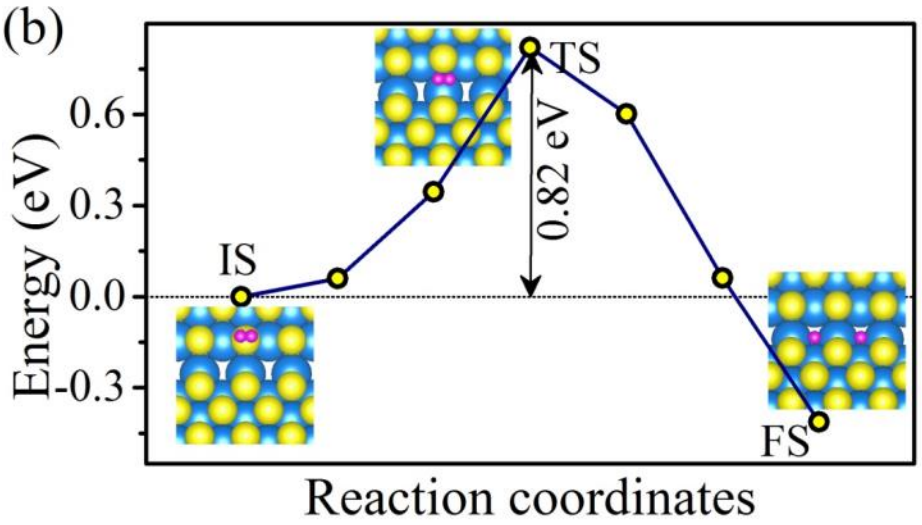
Model system: MoS_2 with S vacancy row

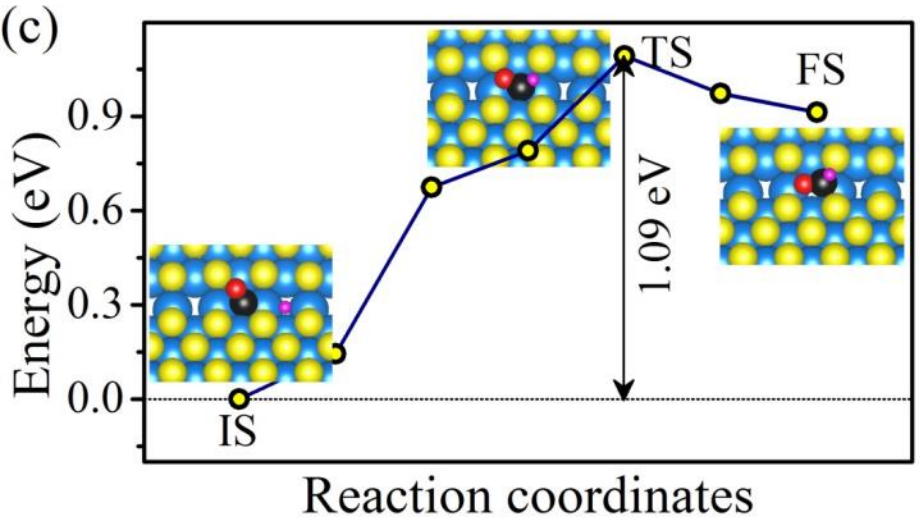


- Sulfur vacancies: Mo atoms and their *d* electrons are exposed to adsorbates.
- Sulfur vacancies: Possible catalyst.
- We examine the CO hydrogenation reaction, as an example.

RESULTS: CO hydrogenation

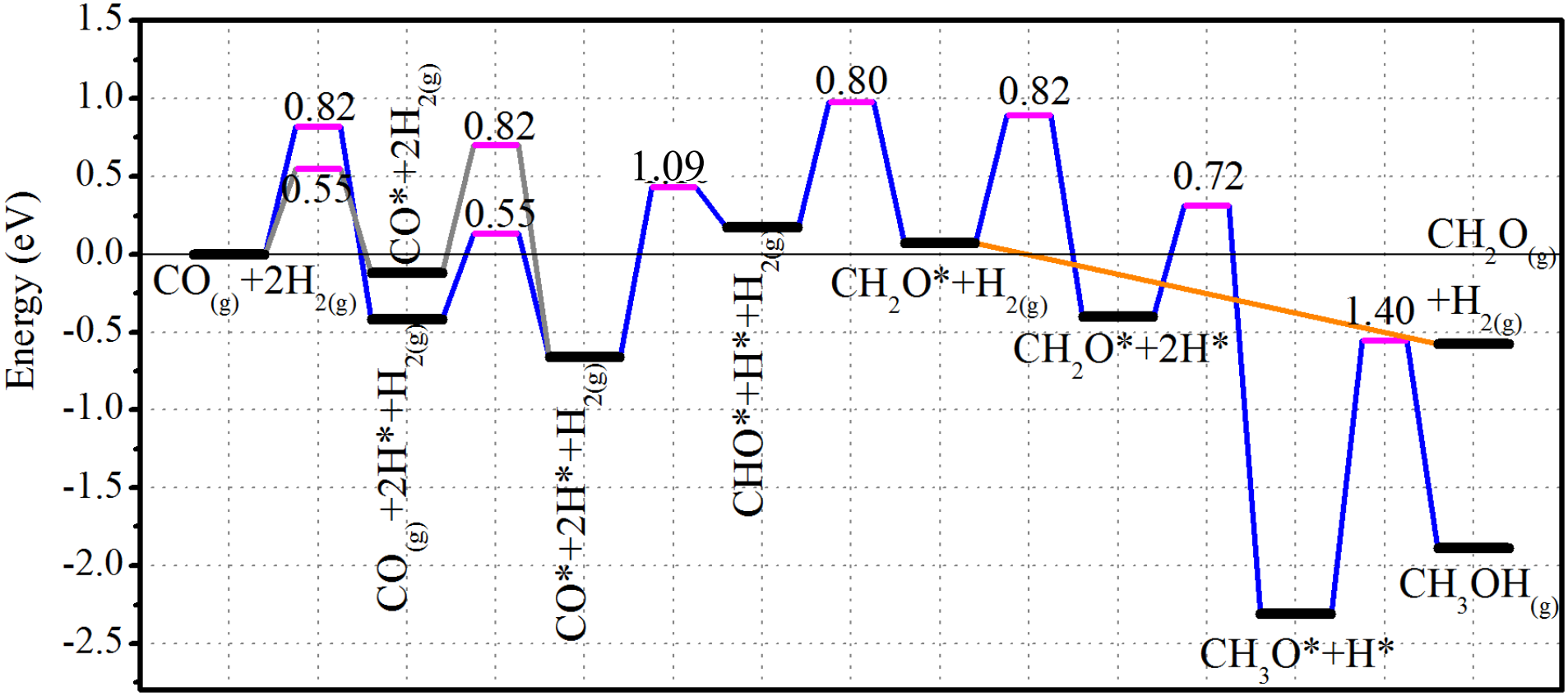


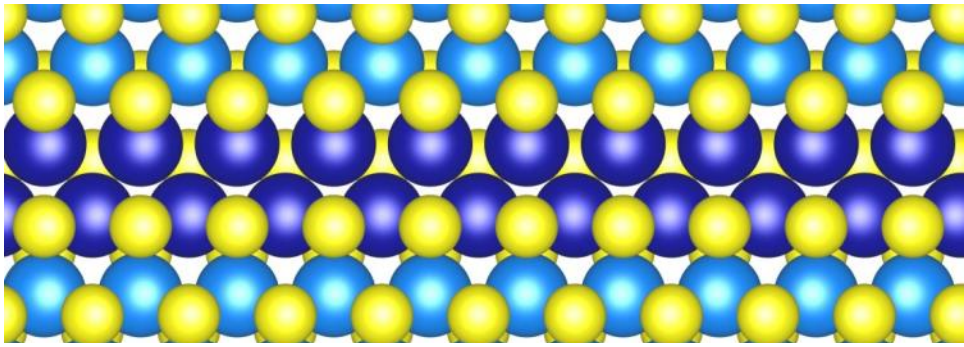




(CI)-NEB results of the adsorption of CO (a), dissociative adsorption of H_2 (b), and the formation of CHO* (c) on MoS_2 with sulfur vacancy row. **Cyan**, **yellow**, **black**, **red**, and **magenta** (smallest) balls represent **Mo**, **S**, **C**, **O**, and **H** atoms, respectively.

RESULTS: CO hydrogenation

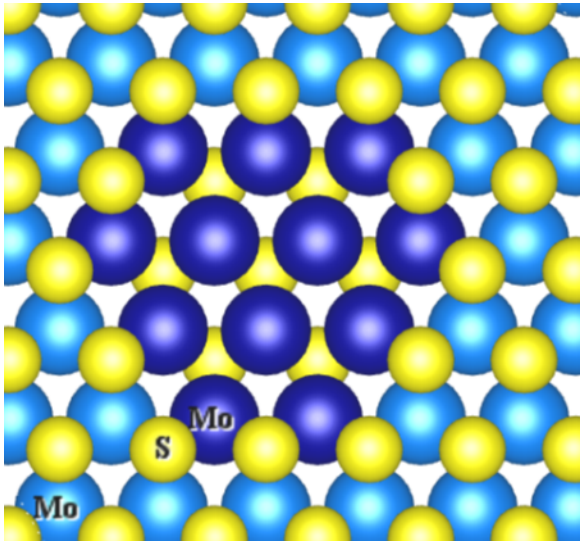




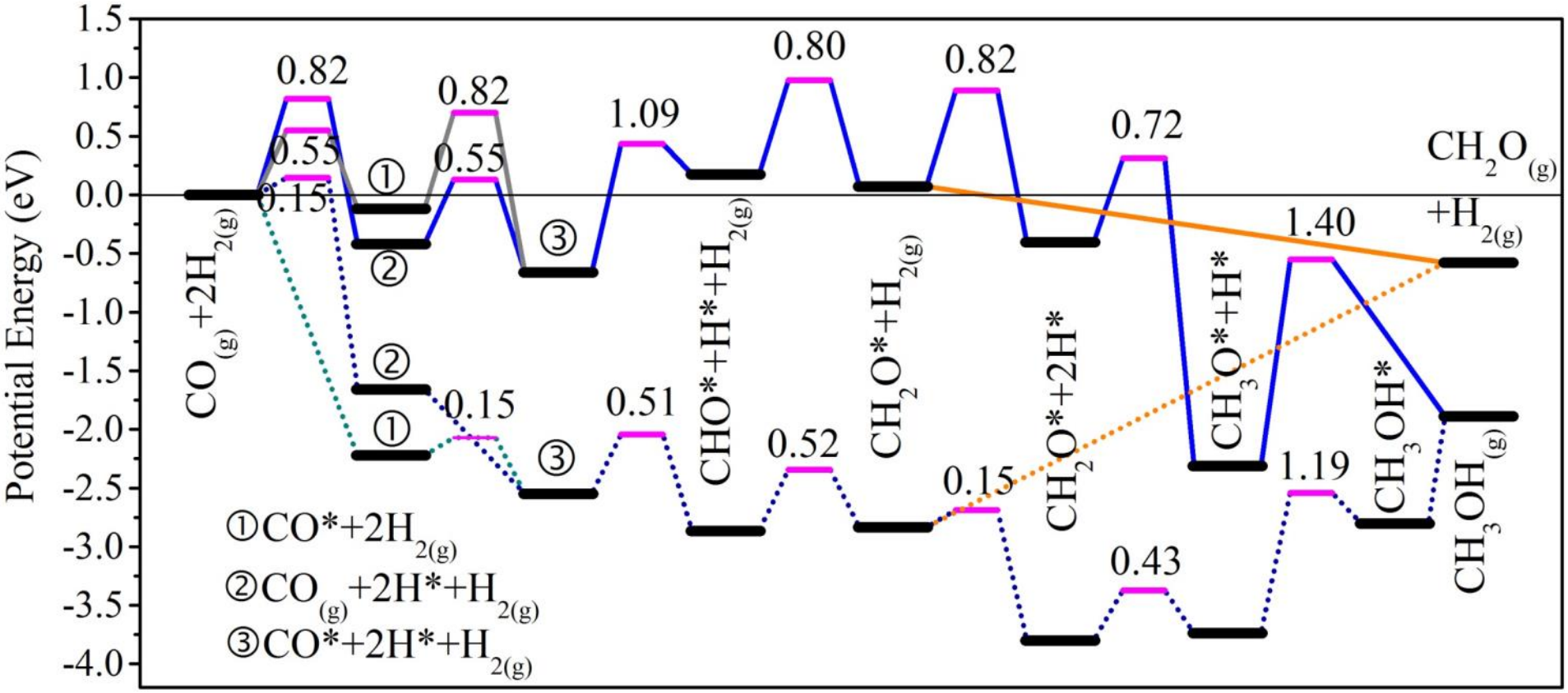
- The barriers are high => S-vacancy row may not be a good candidate for MeOH synthesis from CO and H_2

- Main parameters controlling reaction: Barrier of H diffusion. Most of processes are H defuse to CO, CHO, CH_2O, CH_3O to hydrogenate.

- The high barrier is due to the narrow size of the S-vacancy row => One can manipulate the distribution of S-vacancy for obtaining better results.



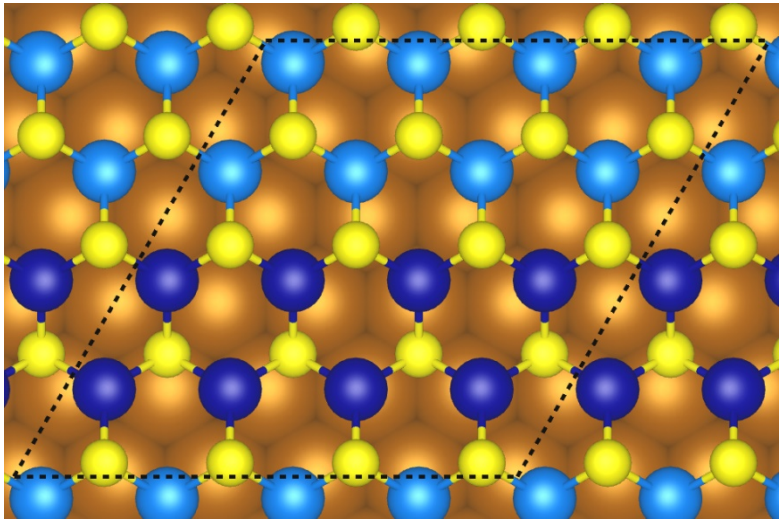
Formation energy of vacancy structures other than row is not much higher than that of row structure => possibility of their existences.



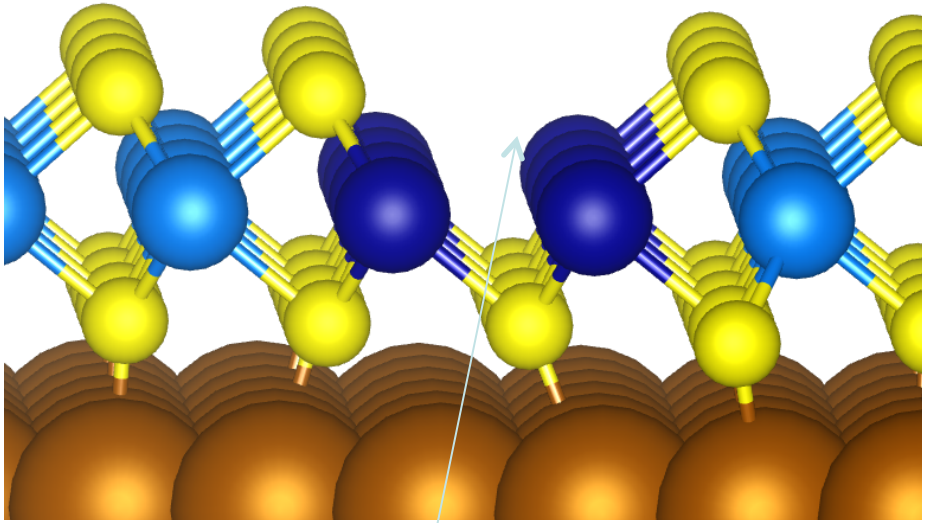
Potential energies along the reaction pathway of the formation of CH_3OH via the CO hydrogenation on MoS_2 with a row of sulfur vacancies (Solid connections) and with a patch of 7 sulfur vacancies (dotted connections). Thicker-longer bars represent the intermediate states while thinner-shorter bars represent transition states. Numbers (in eV) are energetic barriers. Superscript * indicates adsorbed spice. Subscript (g) indicates gas phase.

Model system: MoS_2 with S-vacancy row on Cu(111)

Top View



Side View



Mo atom

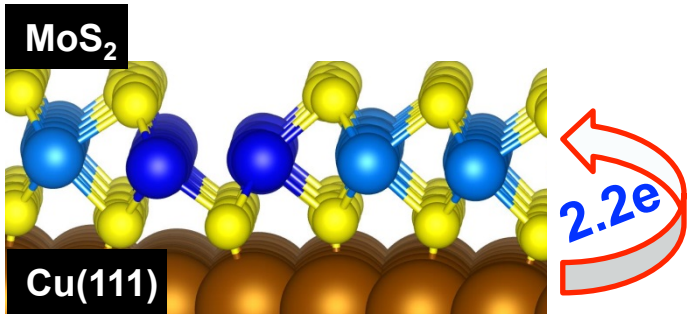
Exposed Mo atom near the S-vacancy

Sulfur atom

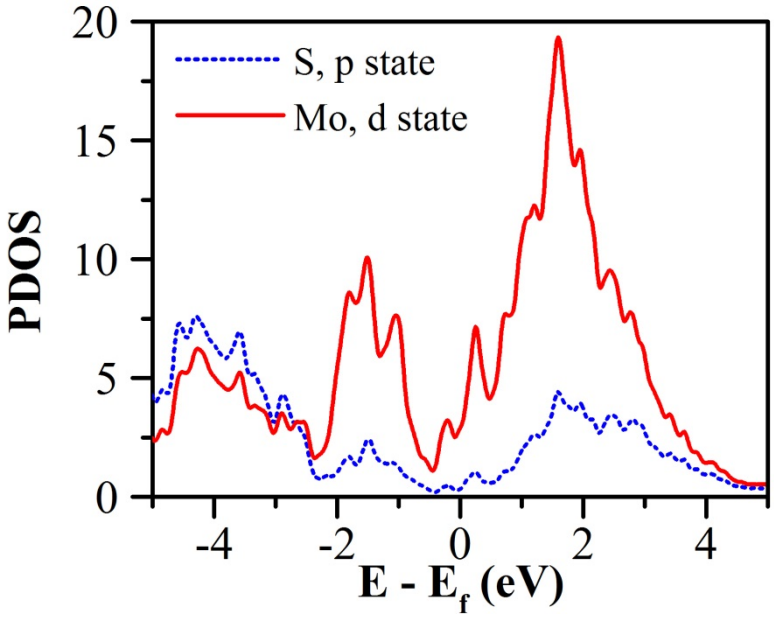
S vacancies

Electronic Structure

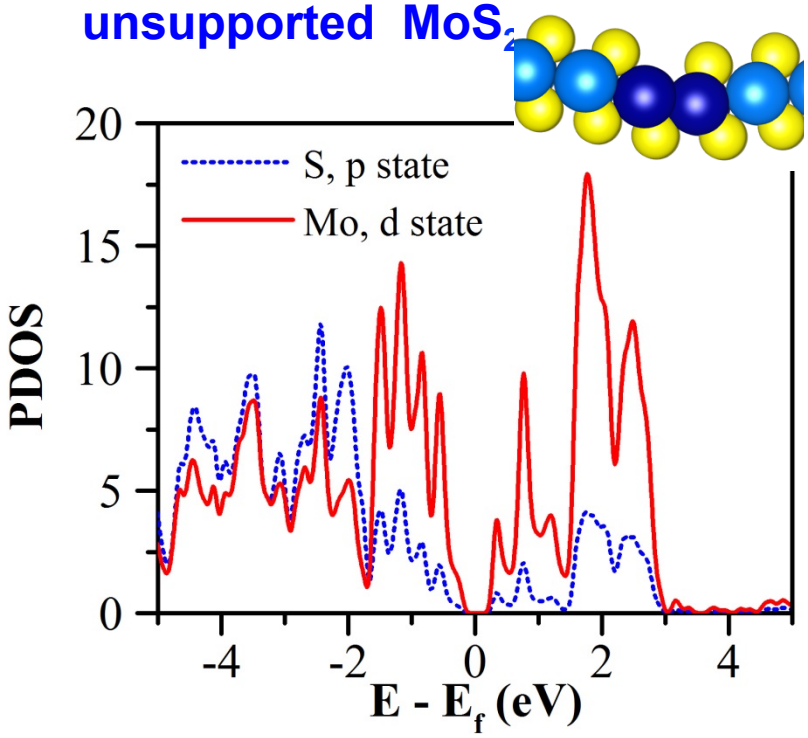
- Charge transfer



- Projected density of states of defect-laden MoS_2/Cu(111)

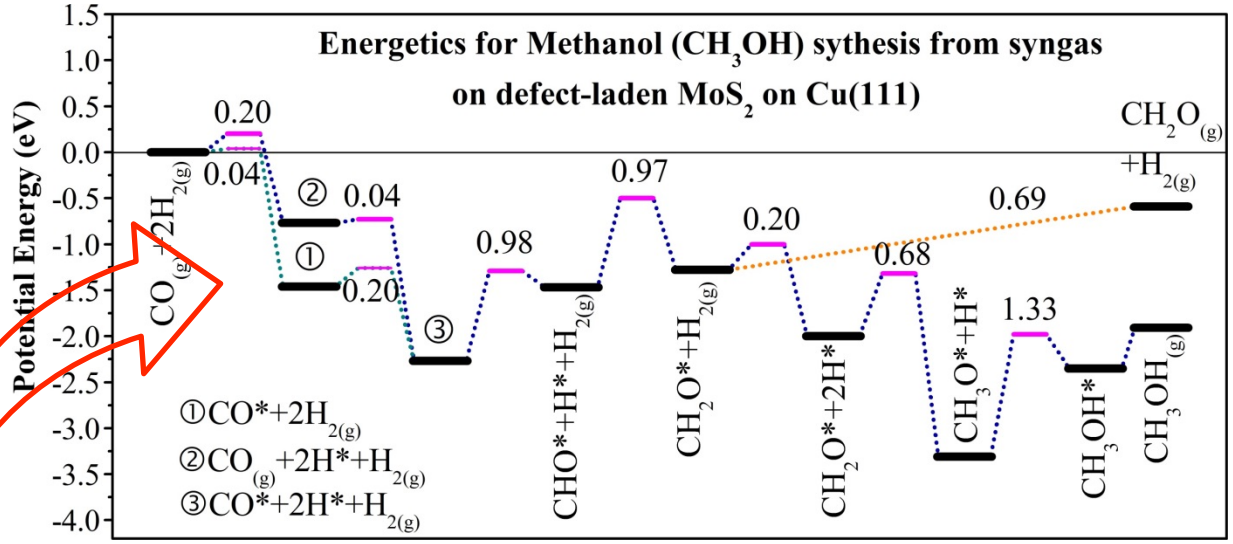


- PDOS of defect-laden, unsupported MoS_2

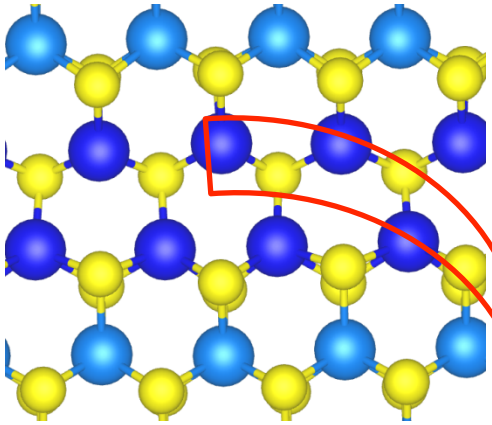


- Because of the **charge transfer** from Cu to MoS_2, and the interaction between MoS_2 and Cu(111), the **frontier orbitals** are shifted towards the Fermi level and hence easily accessible to adsorbates.

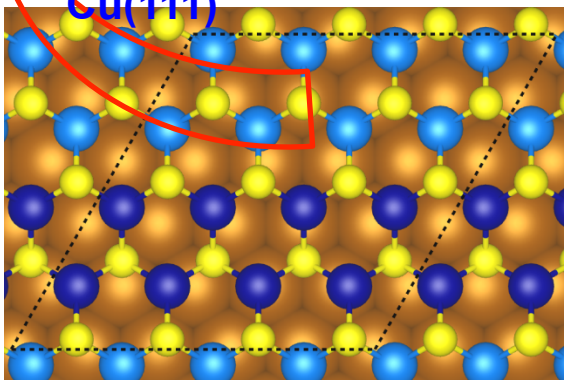
Comparison of energetics

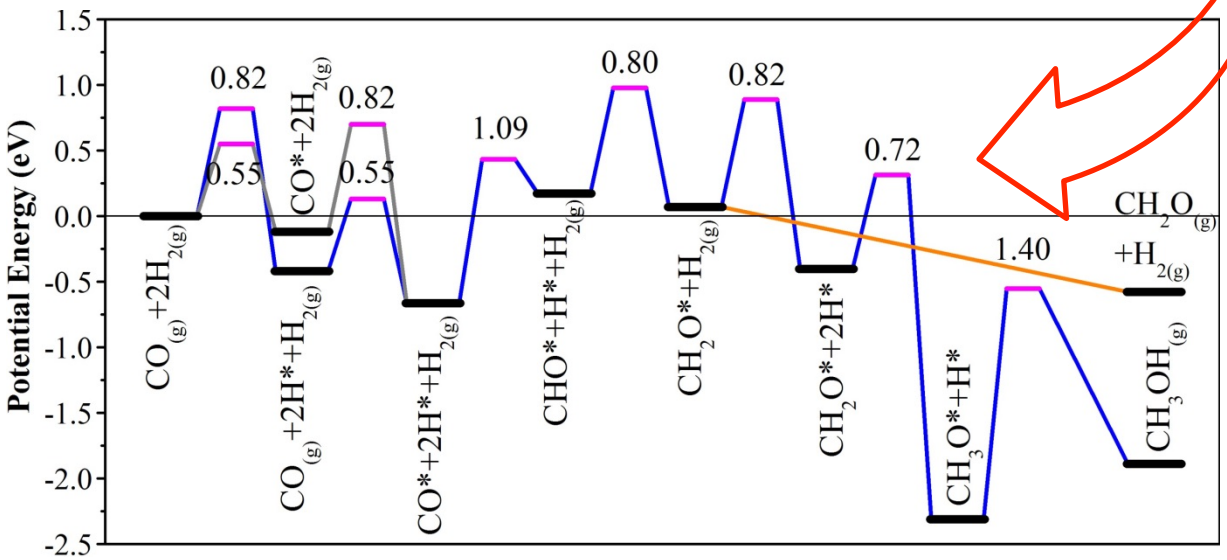


Defect-laden unsupported MoS_2



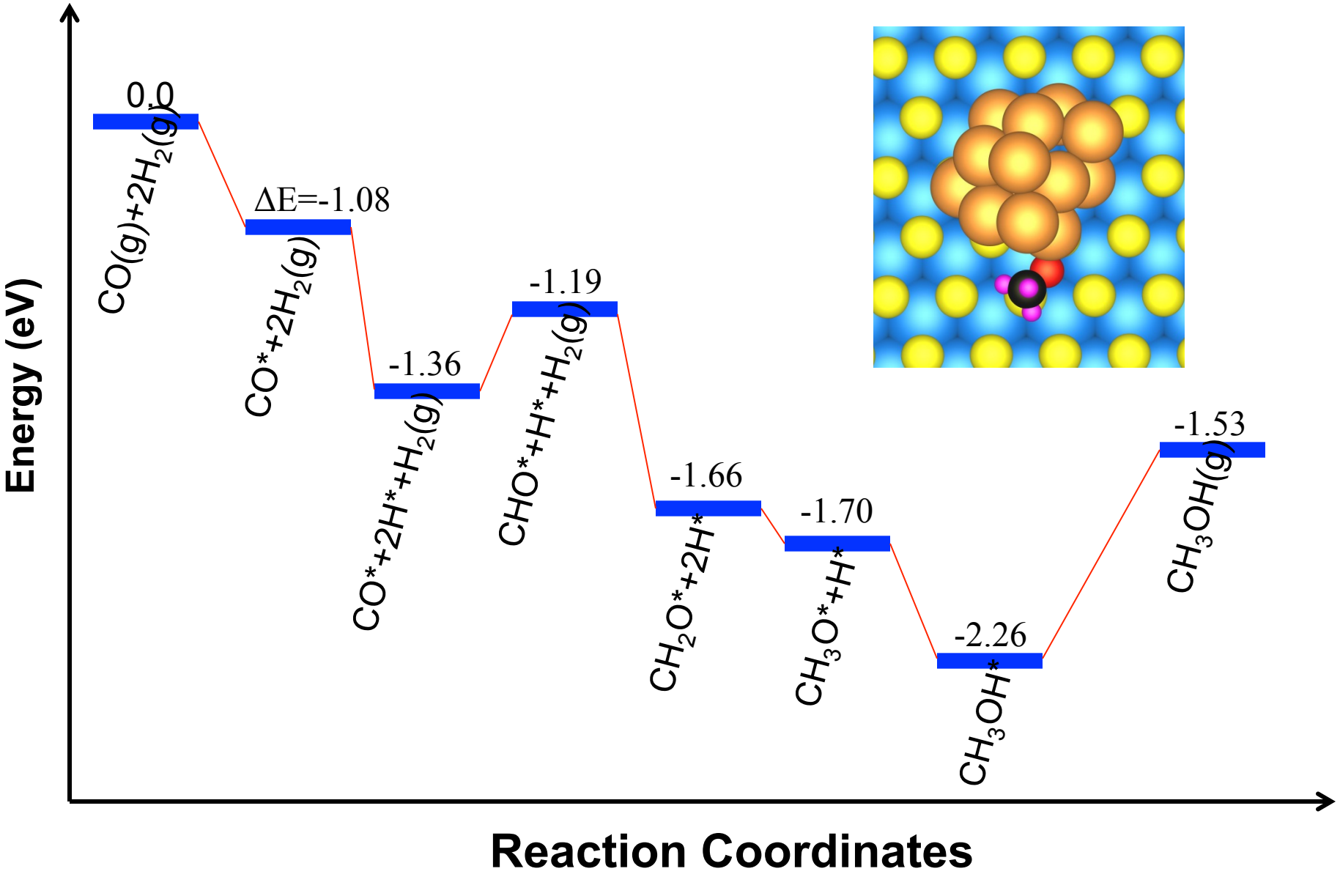
Defect-laden MoS_2/ Cu(111)



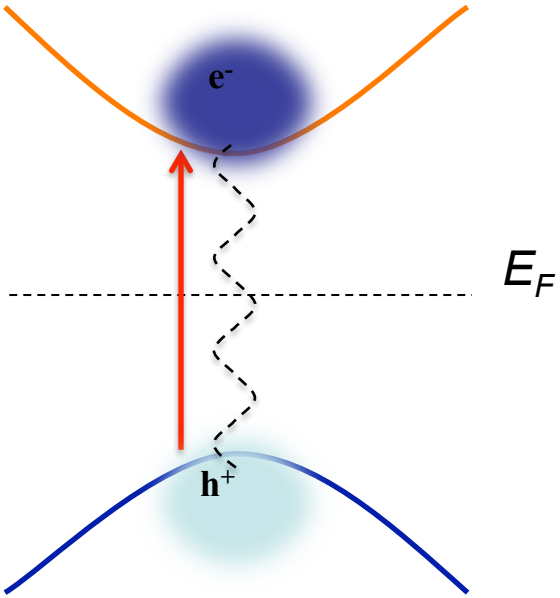


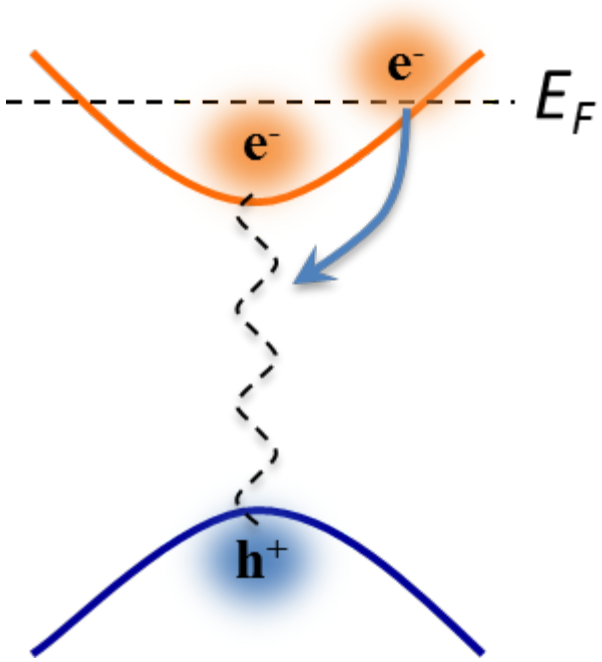
*D. Le, T. B. Rawal, T. S. Rahman, Jour. Phys. Chem C, **118**, (2014), 5346*

Methanol formation on Au_{13} NPs@MoS_2



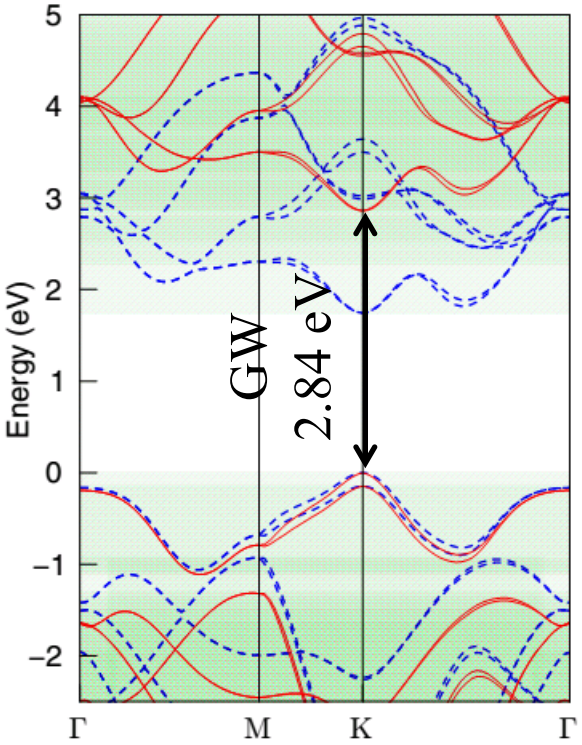
Questions about fundamental band-gap of TDMCs: Excitons & trions

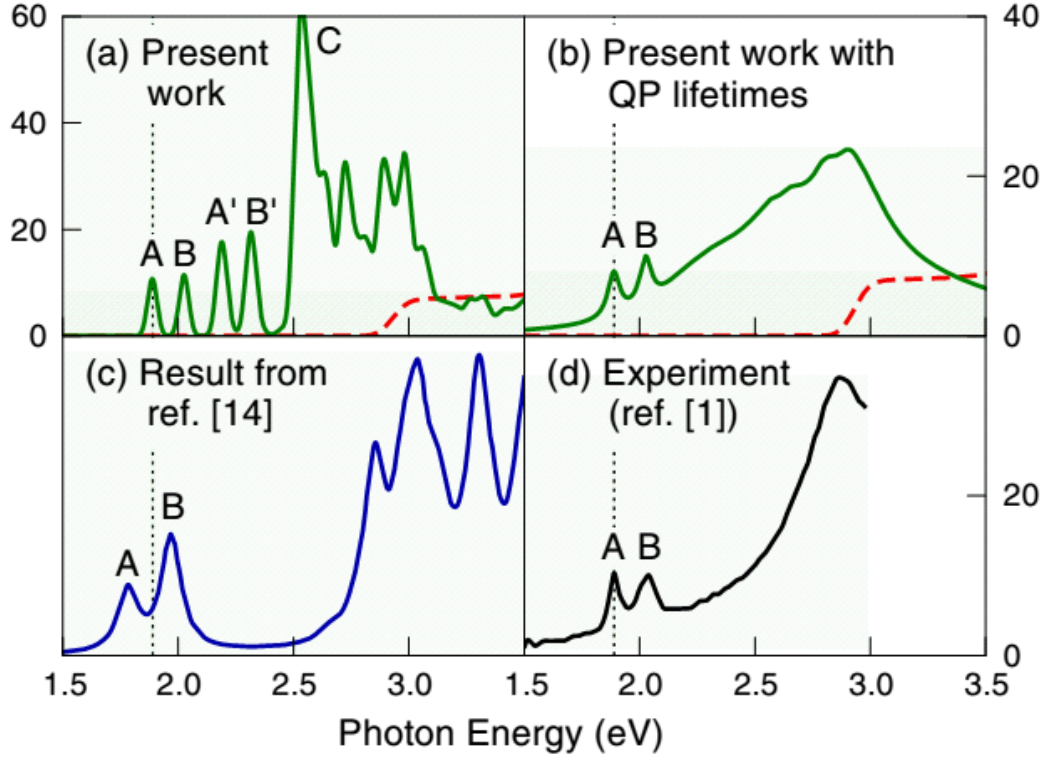




Binding energy of exciton

- There used to be confusions about optical band gap and fundamental band gap because the experimental PL peaks are very close to DFT band-gap.
- DFT underestimates band-gap (for sure, every one knew)
- GW + Bethe-Salpeter equation: resolve very large binding energy of exciton. But they are too large. So is GW band gap.





From: D. Y. Qiu, F. H. da Jornada, and S. G. Louie, Phys. Rev. Lett. **111**, 216805 (2013).

Binding energy of exciton

➢ Binding energy of trions in MoS_2 is about 18 meV (K. F. Mak *et al.*, Nat Mater **12**, 207 (2013))

➢ Binding energy of exciton should be about 10 times as large (theoretical estimation for isotropic 2D semiconductor with similar electron and hole masses).

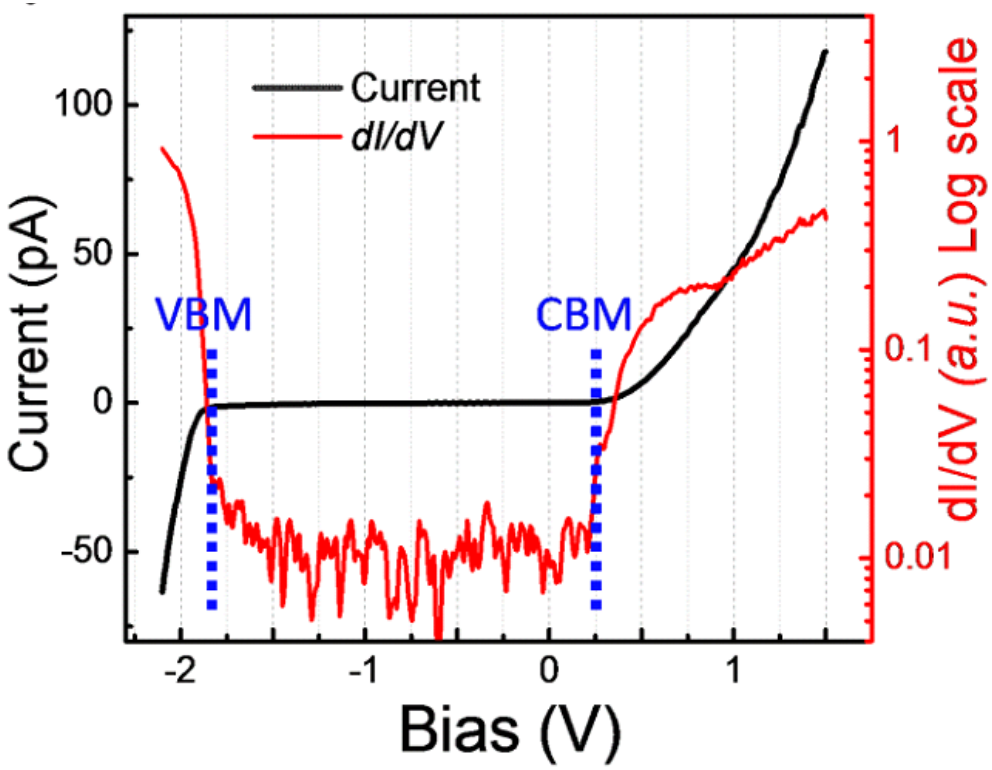
➢ Recent experiment:

- Using STS to measure band-gap of MoS_2: ~2.1 eV

Too small in comparison with GW. Little bit large vs. DFT

- Comparing with PL peak, binding energy of exciton: 220 meV

Too small VS. BSE



C. Zhang *et al.*, arXiv:1401.5100

➢Need to find better theory for accurate prediction.

Outline

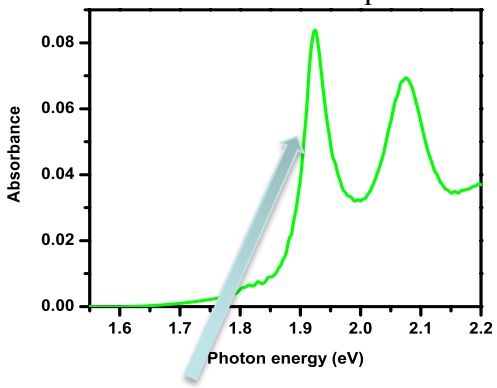
- Motivation
- Density-Matrix TDDFT
- Excitons: in 1L vs. 2L systems
- Trions and biexcitons
- Ultrafast inter-layer hole transfer
- Ultrafast collective charge response
- Concluding Remarks

Motivation

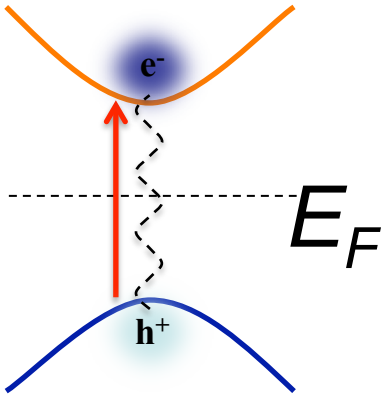
Excitons and the absorption spectrum in 1L MoS2

K.F. Mak et al., Nature Mat. 12, 207 (2013).

Exciton – bound electron-hole pair

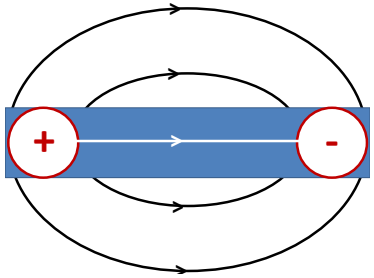


Excitonic peak in the undoped MoS2



Material	Exciton energy, meV
GaAs	3.27
α−GaN	20.4
β−GaN	26.0
CdS	28
CdSe	15

Exp.: Parenteau et al., J. Appl. Phys. 71, 3747 (1992); As et al., APL 70, 1311(1997); Muth et al., APL, 71, 2572 (1997); Jacobson et al., J. Crys. Growth 138, 225 (1994); Voight et al., Phys. Stat. Sol. B 91, 189 (1979).



Binding energy, ~0.2-0.6eV, is extremely large even for systems with reduced dimensionality and low screening.

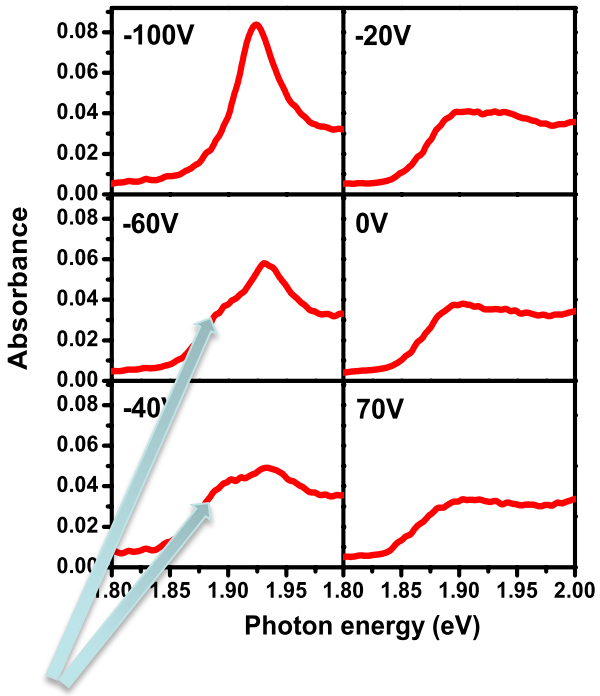
It is an order of magnitude larger than the values for "standard" bulk semiconductors, including the sulfur and selenium compounds.

Excitons, trions & absorption spectrum

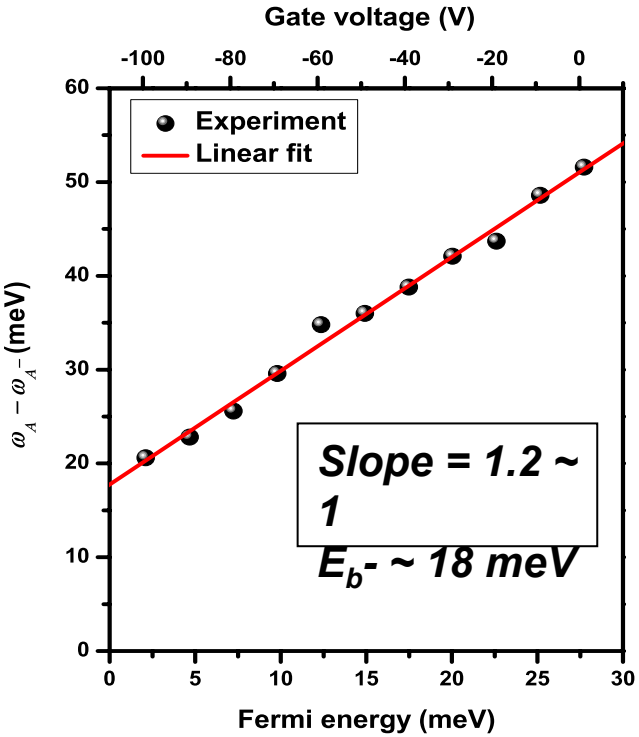
Single Layer MoS_2

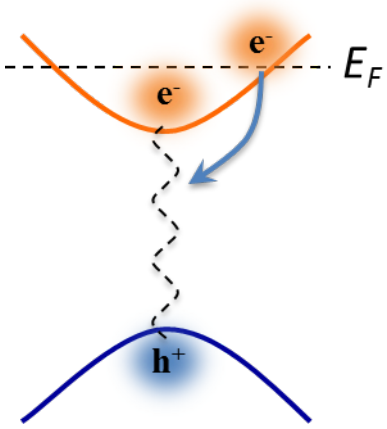
K.F. Mak, K. He, C. Lee, G.H. Lee, J. Hone, T.F Heinz, and J. Shan, Nature Mat. 12, 207 (2013).

Trion – bound state of exciton and electron (hole)
Binding energy – energy necessary to separate them



Trion features below excitonic peak in doped MoS2





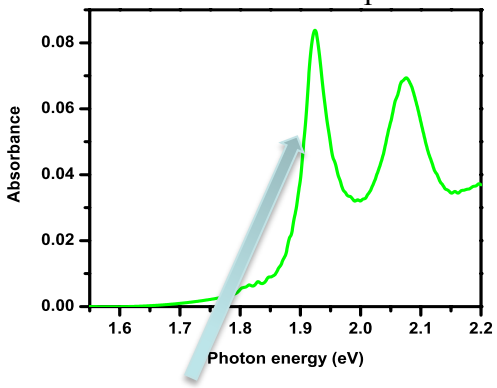
Bound energy ~20meV
Trion effects must be pronounceable at room temperature!

Motivation

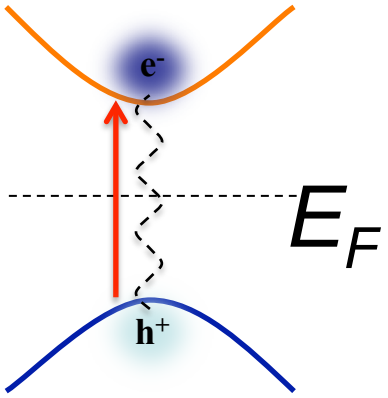
Excitons in the absorption spectrum of 1L MoS_2

K.F. Mak et al., Nature Mat. 12, 207 (2013).

Exciton – bound electron-hole pair

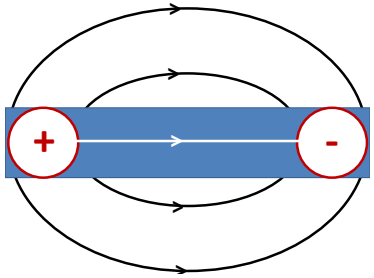


Excitonic peak in the undoped MoS_2



Material	Exciton Binding energy (meV)
GaAs	3.27
α−GaN	20.4
β−GaN	26.0
CdS	28
CdSe	15

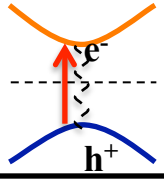
Exp.: Parenteau et al., J. Appl. Phys. 71, 3747 (1992); As et al., APL 70, 1311(1997); Muth et al., APL, 71, 2572 (1997); Jacobson et al., J. Crys. Growth 138, 225 (1994); Voight et al., Phys. Stat. Sol. B 91, 189 (1979).

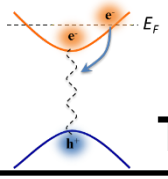


Binding energy ~0.2-0.6eV, is extremely large even for systems with reduced dimensionality and low screening.

It is an order of magnitude larger than the values for "standard" bulk semiconductors, including the sulfur and selenium compounds.

Experimental Observations of excitations in 1L TMDC





	Excitons:	Trions:	Biexcitons:
MoS_2	K.F. Mak at al., PRL. **105**, 136805 (2010). F. Wu et al., PRB **91**, 075310 (2015) **(220-570 meV)**	K.F. Mak et al., Nature Mat. 12, 208 (2013) C. H. Lui, PRL 113, 166801 (2014) C. Zhang et al., PRB **89**, 205436 (2014) **(18-40 meV)**	E.J. Sie at al., **92**, 125417 (2015) **(40-60 meV)**
$MoSe_2$	J. S. Ross at al., Nat. Commun. **4**, 1474 (2013). Y. Li, PRL 113, 266804 (2014). G.Wang et al., arxiv:1504.06333 (2015) A. Arora et al., arxiv:1509.06439 (2015) **(500-550 meV)**	J. S. Ross at al., Nat. Commun. **4**, 1474 (2013). Y. Li, PRL 113, 266804 (2014). A.Singh at al., arxiv:1507.04463 (2015) **(30 meV)**	?
WS_2	E.J. Sie at al., Nature Mat. 14, 290 (2015) A. Chernikov at al., PRL 115, 126802 (2015) G. Plechinger et al., arxiv:1507.01342 (2015) **(320-700 meV)**	G. Plechinger et al., arxiv:1507.01342 (2015) **(30 meV)**	G. Plechinger et al., arxiv:1507.01342 (2015) **(65 meV)**
WSe_2	A. Srivastava at al., Nature Phys. 11, 141 (2015) A.A. Mitiouglu et al., arxiv:1507.00496 (2015) **(370 meV)**	A. M. Jones et al., arXiv:1303.5318 (2013). A.A. Mitiouglu et al., arxiv:1507.00496 (2015) H.J. Liu et al., 2D Mat. 2, 034004 (2015) **(20-30 meV)**	Y. You et al., Nature Phys. 11, 477 (2015) **(52 meV)**

Most monolayers demonstrate strongly-bound exciton, trion and biexciton

Experimental Observations of excitations in 2L TMDC

Excitons

Homo-stacks:

2L MoS_2
T. Jiang et al., Nature Nanotech. **9**, 825 (2014).
K. Liu et al., Nature Comm. 5, 4966 (2014)
B.R. Carvalho et al, PRL 114, 136403 (2015)
J.-U. Lee et al., arxiv:1501.02525 (2015)
H. Yu et al., arxiv:1504.01215 (2015)
(~100-300 meV)

2L $MoSe_2$
H. Dery et al, PRB 92, 125431 (2015)
A. Arora et al., arxiv:1509.06439 (2015)
H.J. Liu et al., 2D Mat. 2, 034004 (2015)
(160-260 meV)

2L WS_2
Q. Liu, PRL 114, 087402 (2015)
(~100-150 meV)

2L WSe_2
S. Kumar et al., arxiv:1509.01085 (2015)
M. Yankowitz, PRL 115, 136803 (2015)
H. Dery, PRB 92, 125431 (2015)
H.J. Liu et al., 2D Mat. 2, 034004 (2015)
(130-330 meV)

Hetero-stacks:

MoS_2-$MoSe_2$
L.H.G Tizei et al., PRL 114, 107601 (2015)
(~100-400 meV)

MoS_2-WS_2
X. Hong et al., Nature Nanotech. 9, 682 (2014)
Q. Liu et al., PRL 114, 087402 (2015)
(~100 meV)

$MoSe_2$-WSe_2
P. Rivera et al., Nature Comm. 6, 6242 (2015)
(~100-300 meV)

Trions

2L WS_2
B. Zhu, PNAS 111, 11606 (2014)
(45 meV)

2L $MoSe_2$
H.J. Liu et al., 2D Mat. 2, 034004 (2015)
(~28 meV)

Several two-layer systems demonstrate excitonic states
More trions and biexcitons - coming soon ?...

TDDFT: density-matrix formulation

Kohn-Sham equations:

$$H\psi_k^v(r,t) = i\frac{\partial}{\partial t}\psi_k^v(r,t), \qquad n(r,t) = 2\sum_{k\in B.Z.}|\psi_k^v(r,t)|^2$$

$$H = -\frac{1}{2m}\nabla^2 + V_{nucl}(r) + V_{ext}(r,t) + V_H[n](r,t) + V_{xc}[n](r,t)$$

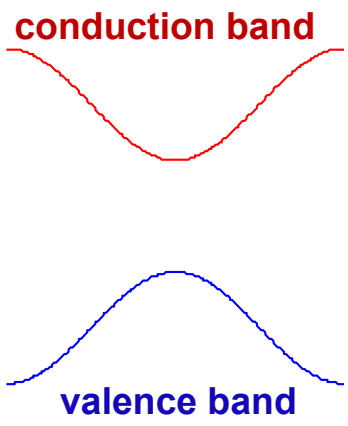
The time-dependent wave function is expanded in terms of the static wave functions $\psi_k^{l(0)}(r)$, that are the solution of the static DFT Kohn-Sham equations

$$H\psi_k^{l(0)}(r) = \varepsilon_k^l\psi_k^{l(0)}(r)$$

In this case:

$$\psi_k^v(r,t) = \sum_l c_k^l(t)\psi_k^{l(0)}(r)$$

Two-band approximation:



TMDC systems: excitons and trions

Monolayers

Slater XC, screening ε

(binding energies in meV)

System	Exciton (exp. in brackets)	Trion (exp. in brackets)
MoS2	361 (220-570)	40 (18-40)
MoSe2	388 (500-640)	43 (30)
WSe2	210 (370-790)	5 (20-30)

Bi-layers

(binding energies in meV)

System	Exciton (exp. in brackets)	Trion (exp. in brackets)
MoS2	204 (~100-300)	27
MoSe2	208 (160-260)	22 (28)
WSe2	133 (130-330)	4

TDDFT results give correct order of magnitude for the excitations in most cases (except trions for WSe2) and correct ratio between different energies:

- Trion energies are ~10 smaller than the exciton ones
- In 2L, the energies are ~ 1/2 that of 1L case

Exp.:
Zhang et al., Nano Lett. **14**, 2443 (2014).
Ugeda et al., arXiv:1404.2331 (2014).
He et al., PRL **113**, 026803 (2014)
Cheiwchanchamnangij et al., PRB **85**, 205302 (2012).
Berkelbach et al., PRB **88**, 045318 (2013).
Liu et al., 2D Mat. 2, 034004 (2015).

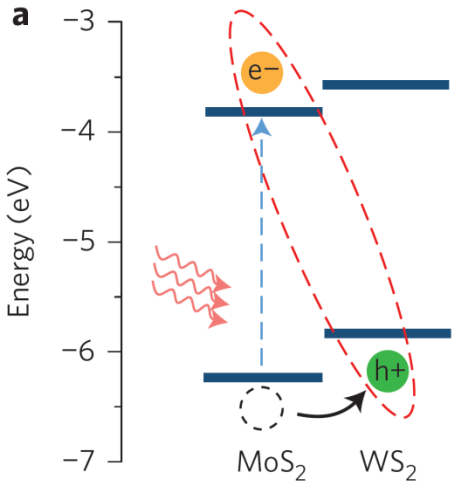
Ultrafast electron-hole separation in bi-layer TMDCs

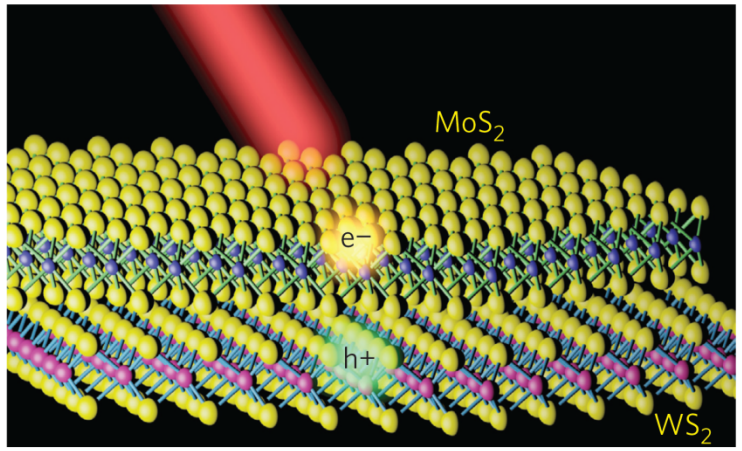
MoS_2-WS_2

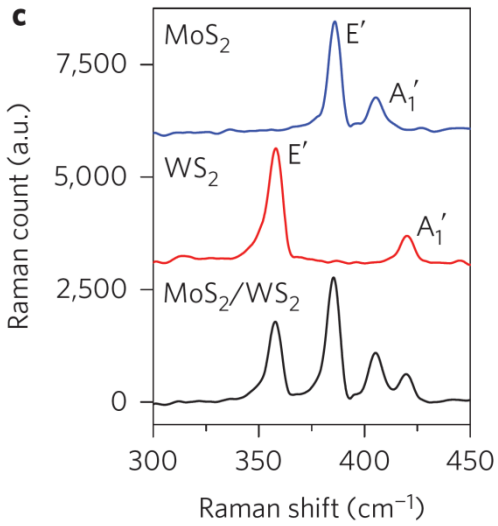
50fs inter-layer hole transfer, unusual for a van der Waals system

Type II Heterojunction

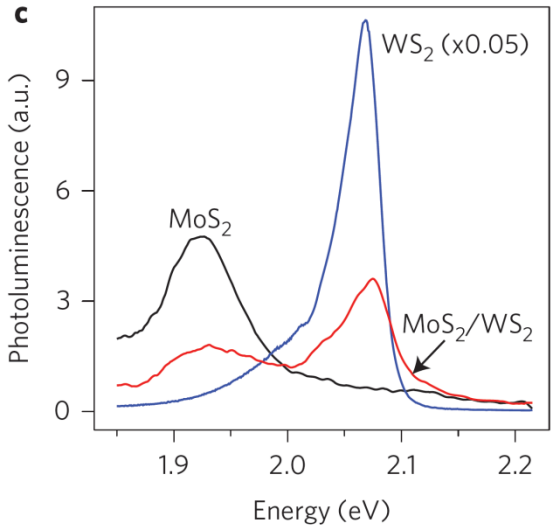
Hong et al., Nature Nano 9, 682 (2014)







Raman spectrum of the coupled layers is practically the sum of the individual layer spectra, suggesting their weak interaction



Quenched exciton luminescence in the coupled system support the hole transfer

Questions

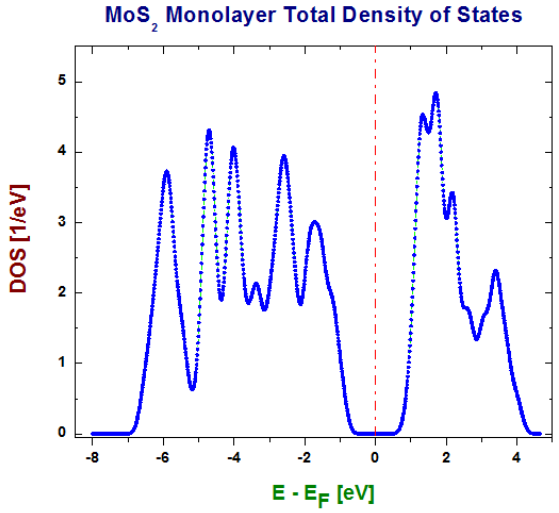
- How do strong electron–electron interactions and excitonic effects affect charge transfer processes?
- How fast can charge transfer take place between van der Waals-coupled layers?

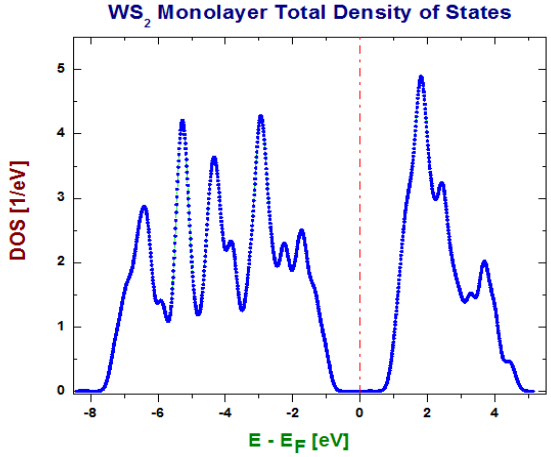
Note that exciton binding energy is larger in the single layer than in the bilayer

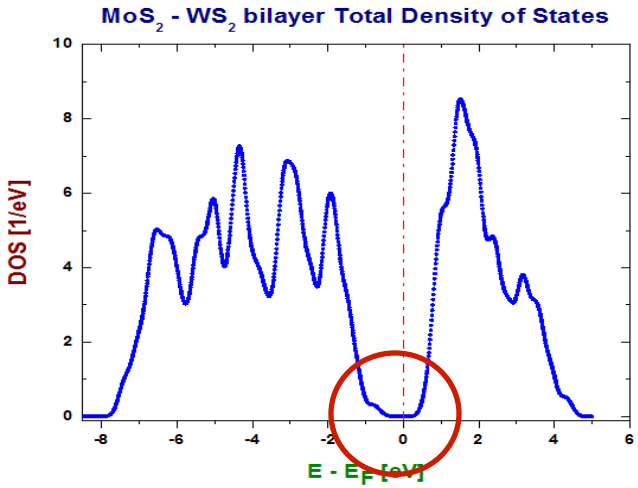
- Will the exciton in the bilayer decay?

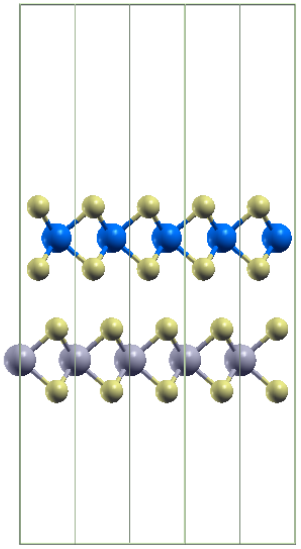
Ultrafast electron-hole separation in MoS2-WS2

DFT DOS





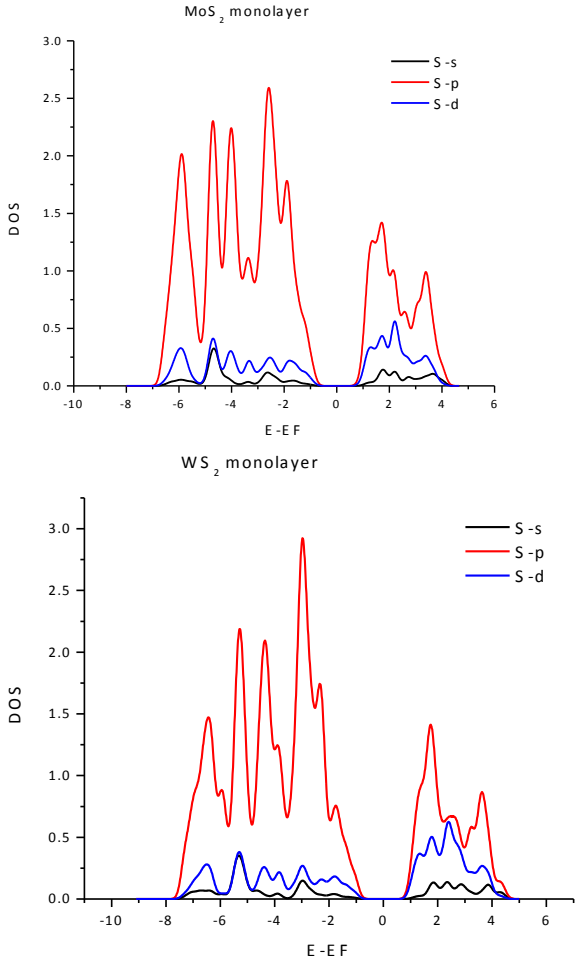


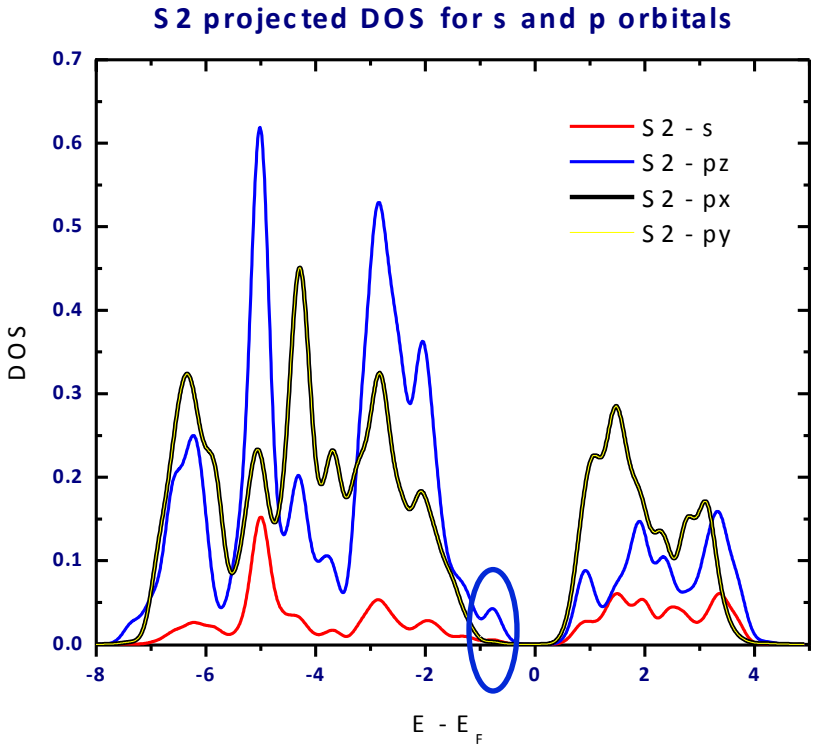


In the coupled system, the valence (hole) bands have significantly different features as compared to the isolated monolayers

Ultrafast electron-hole separation in MoS2-WS2

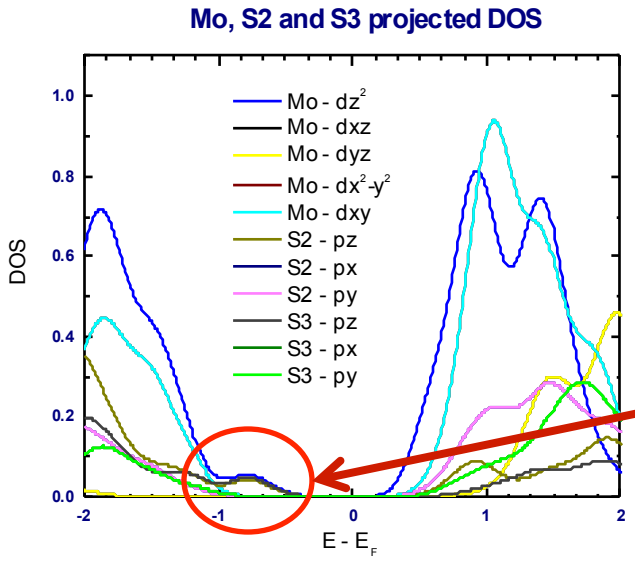
The nature of the hole states

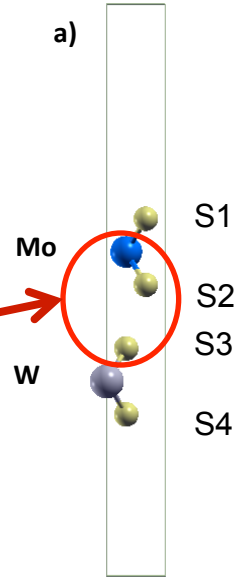


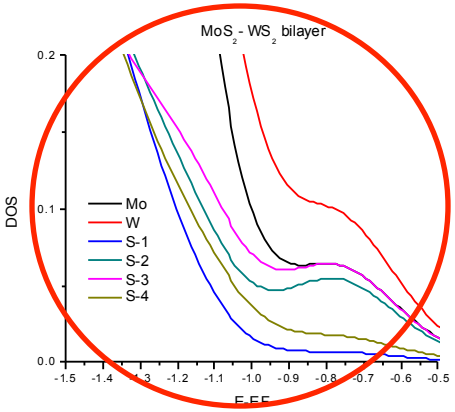


The low-energy holes are mainly formed by p_z-orbital of the sulfur atoms, suggesting their inter-layer hybridized nature

Bi-layer MoS2-WS2: electronic spectrum







DFT calculations demonstrate that, contrary to one-layer MoS2, in the coupled MoS2-WS2 system there is a significant amount of the hole charge in the "internal/central" S layer.

The vicinity of the MoS2 hole charge to the WS2 layer facilitates the inter-layer hole transfer.

Ultrafast electron-hole separation in bi-layer TMDCs

Exciton binding energies (meV)

TDDFT, Slater XC kernel

System	Exciton binding energy
2L MoS2	204
2L MoSe2	208
MoS2-WS2	180

Hole transfer and exciton recombination times (ps)

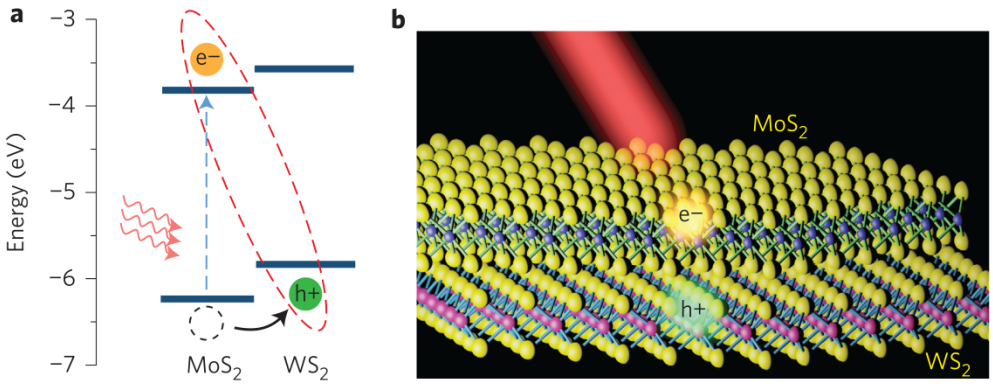
System	Hole transfer time	Exciton lifetime
2L MoS2	0.36	10.0
2L MoSe2	0.42	14.1
MoS2-WS2	0.12	5.4

Lifetimes obtained from the results for the oscillator strength:

$$\tau \sim \frac{1}{|\langle \psi^2 | e\boldsymbol{r} | \psi^1 \rangle|^2}$$

MoS2-WS2

50fs inter-layer hole transfer



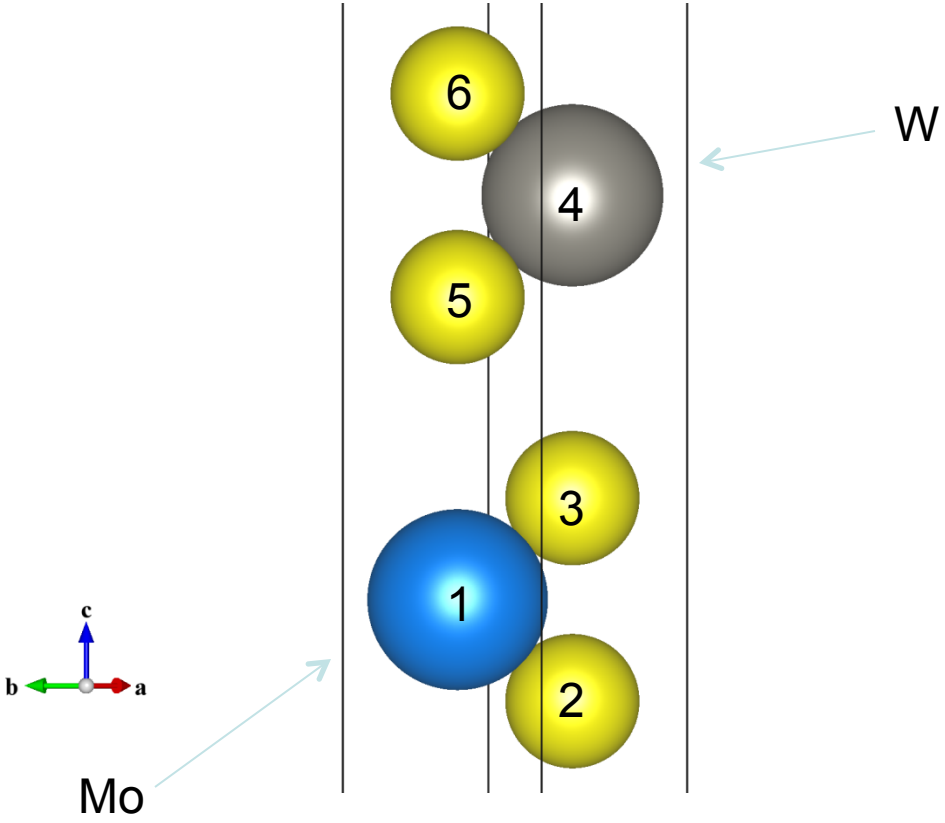
Hong et al., Nature Nano 9, 682 (2014)

For all the systems, the hole transfer times are much shorter than the MoS2 exciton lifetime and are in agreement with the available experimental data for MoS2-WS2.

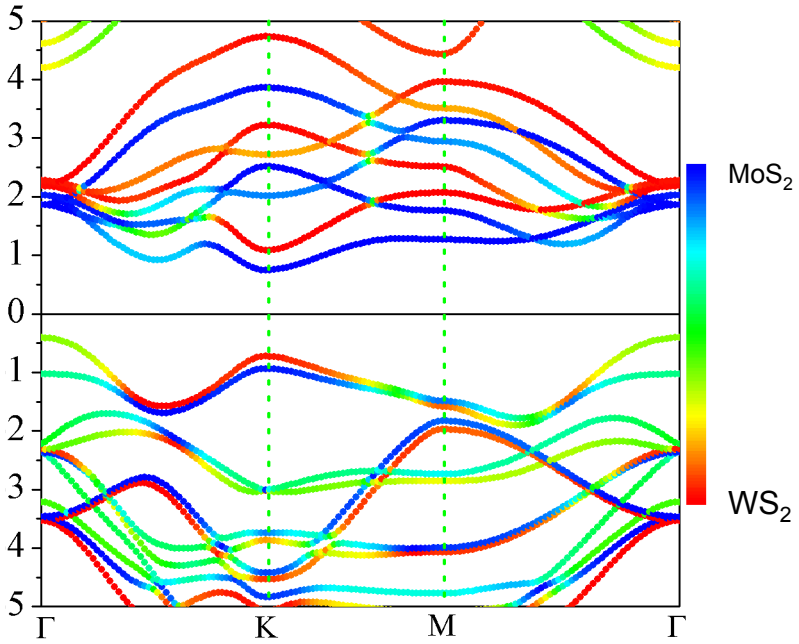
Conclusion

- Single layer MoS_2 is indeed a promising material
- Manipulation of characteristics possible in many ways:
  - Support
  - Defects
  - Edges, joint edges
  - Hydrogenation etc
- Growth of large scale wafers a challenge
- Excitons/trions may have large technological implications
- Probe of ultrafast processes may shed light of interactions
- Much work remains to be done

Thank you for your attention !

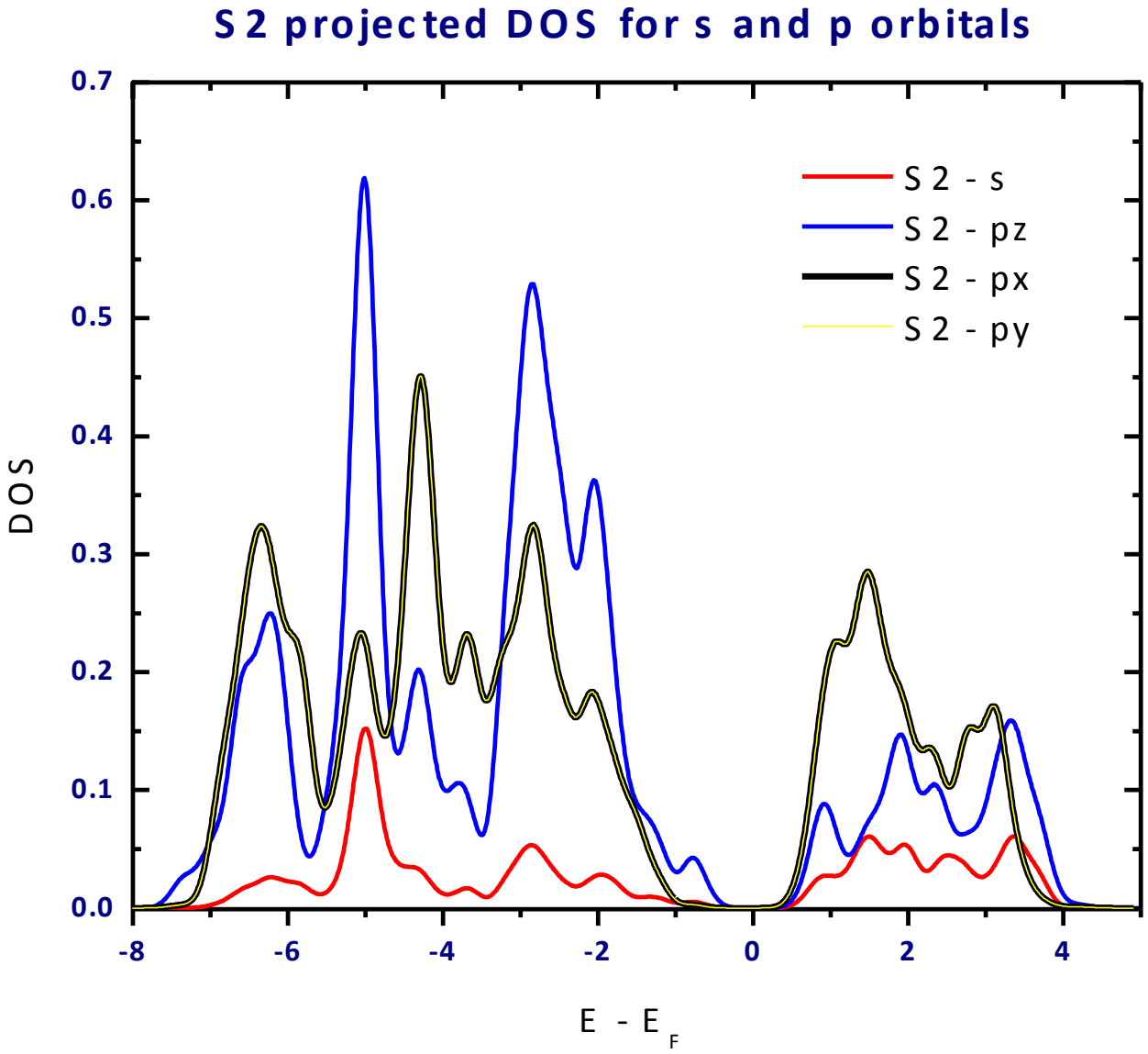


MoS_2/ WS_2 Bi Layer

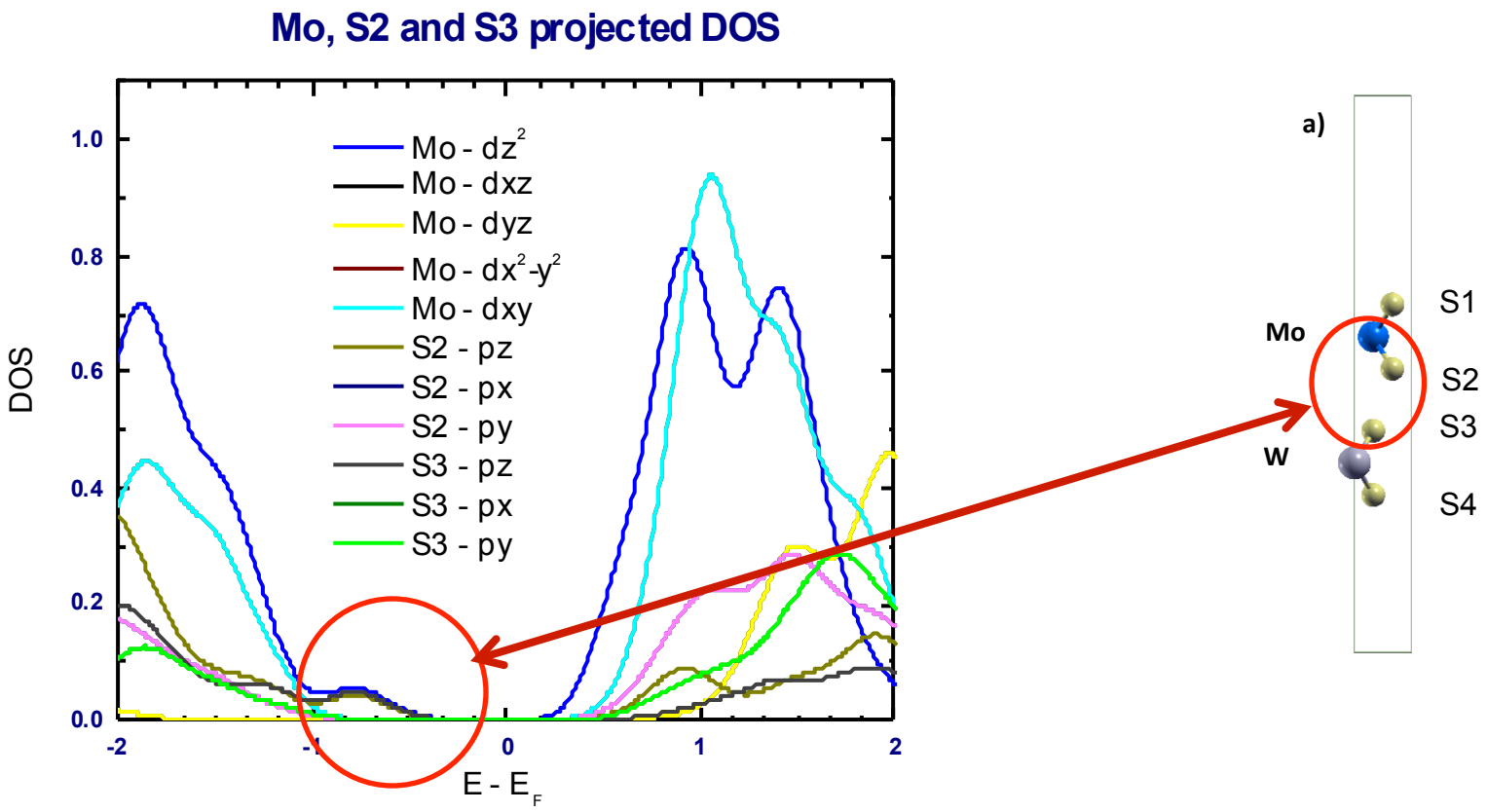


Atom number is a reference for the next slide.

Bi-layer MoS2-WS2: electronic spectrum



Bi-layer MoS2-WS2: electronic spectrum



Strong hybridization of the interlayer charges for the hole excitations, favors its migration to W atoms

Ultrafast electron-hole separation in bi-layer TMDCs

One-layer Exciton binding energies (meV)

TDDFT, Slater XC kernel

System	Exciton binding energy
2L MoS2	204
2L MoSe2	208
MoS2-WS2	180

Hole transfer and exciton recombination times (ps)

System	Hole transfer time	Exciton lifetime
2L MoS2	0.36	10.0
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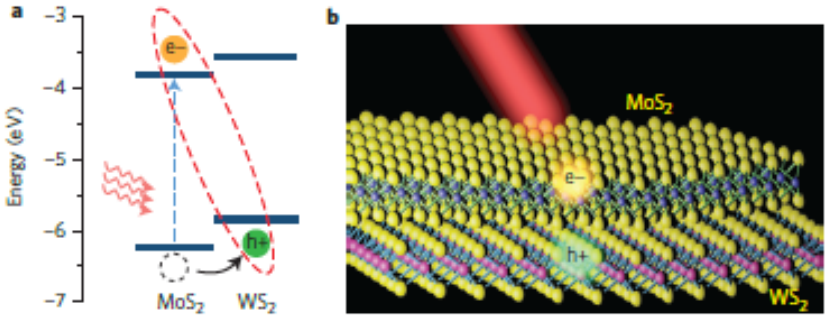
Lifetimes obtained from the results for the oscillator strength:

$$\tau \sim 1/|\langle \psi 2 | e\mathbf{r} | \psi 1 \rangle|^2$$

MoS2-WS2

50fs inter-layer hole transfer



Hong et al., Nature Nano 9, 682 (2014)

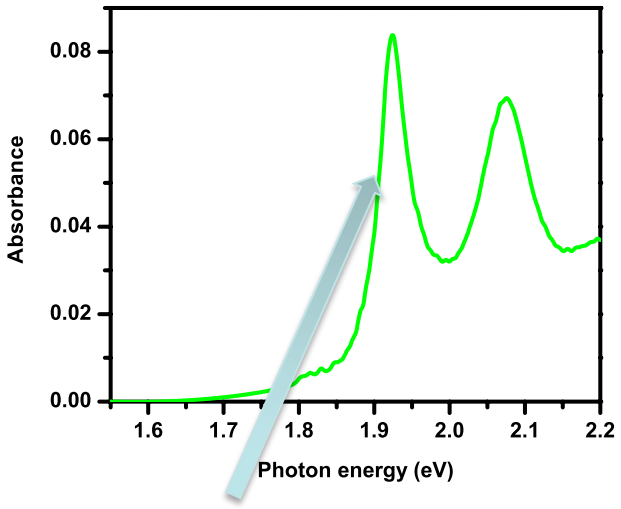
Competition between the inter-layer hole migration and intra-layer e-h recombination times

Part I
MoS_2 trion

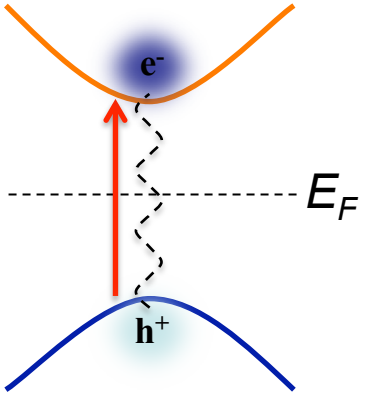
Experimental observation of excitons and trions in doped monolayer MoS2

K.F. Mak, K. He, C. Lee, G.H. Lee, J. Hone, T.F Heinz, and J. Shan, Nature Mat. (in press).

Exciton – bound electron-hole pair



Excitonic peak in undoped MoS2

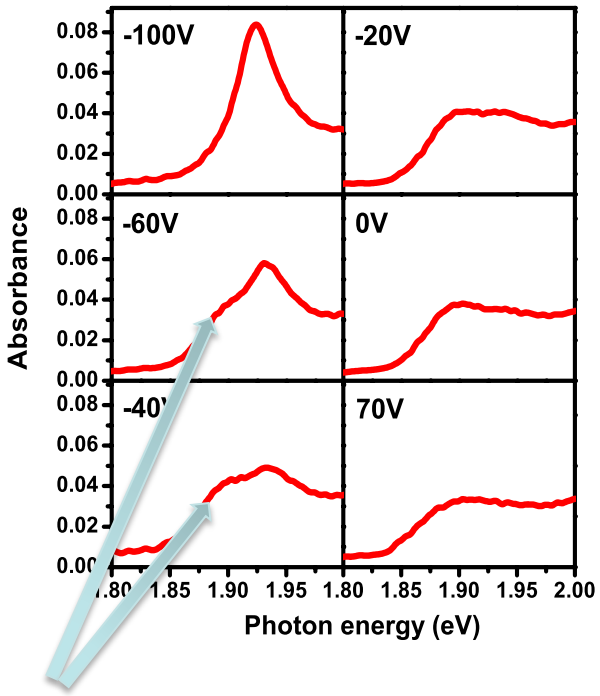


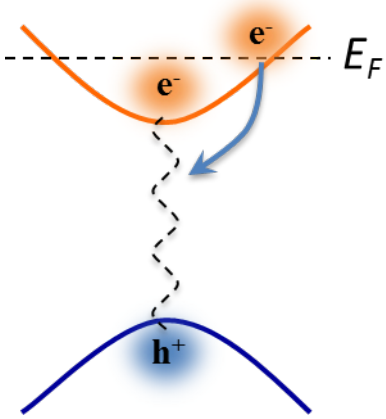
Bound energy ~1eV
extremely large even for systems
With reduced dimensionality!

Experimental observation of excitons and trions in doped monolayer MoS2

K.F. Mak, K. He, C. Lee, G.H. Lee, J. Hone, T.F Heinz, and J. Shan, Nature Mat. 12, 207 (2013).

Trion – bound state of exciton and electron (hole)
Binding energy – energy necessary to separate them





Trion features below excitonic peak in doped MoS_2

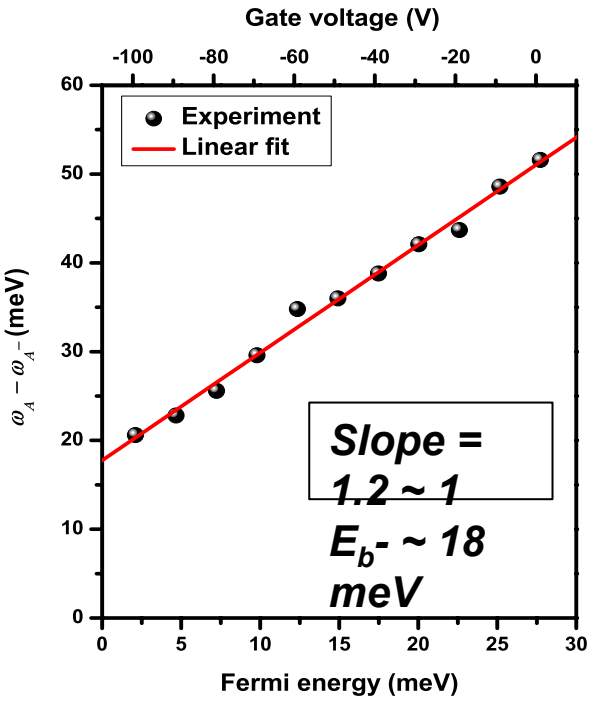
Bound energy ~20meV
Trion effects must be pronounceable at room temperature!

Solutions: adiabatic LDA approximation

$$v_{xc}[n](r,t) = -q^2\left(\frac{3}{\pi}\right)^{1/3} n^{1/3}(r,t)$$

60 independent k-points in the Brillion zone

Excitation	Binding energy	exp
Exciton	312meV	~1000meV
Trion	744meV	~20meV



Trion binding energy is strongly overestimated by LDA since it includes only local electron-hole attraction (almost neglecting e-e repulsion (screened by ε~2.8) when electron is closer to the hole)

Many body Wannier theory predicts correct estimation of the exciton energy

(T. Cheiwchanchamnangij, W.R.L. Lambrecht, Phys. Rev. B 85, 205302 (2012)

Solutions: **three-dimensional long-range kernel**

$$f_{XC}(r,r') = -\frac{1}{|r-r'|}$$

Excitation	Binding energy	exp
Exciton	7meV	~1000meV
Trion	0meV	~20meV

Solutions: **two-dimensional long-range kernel**

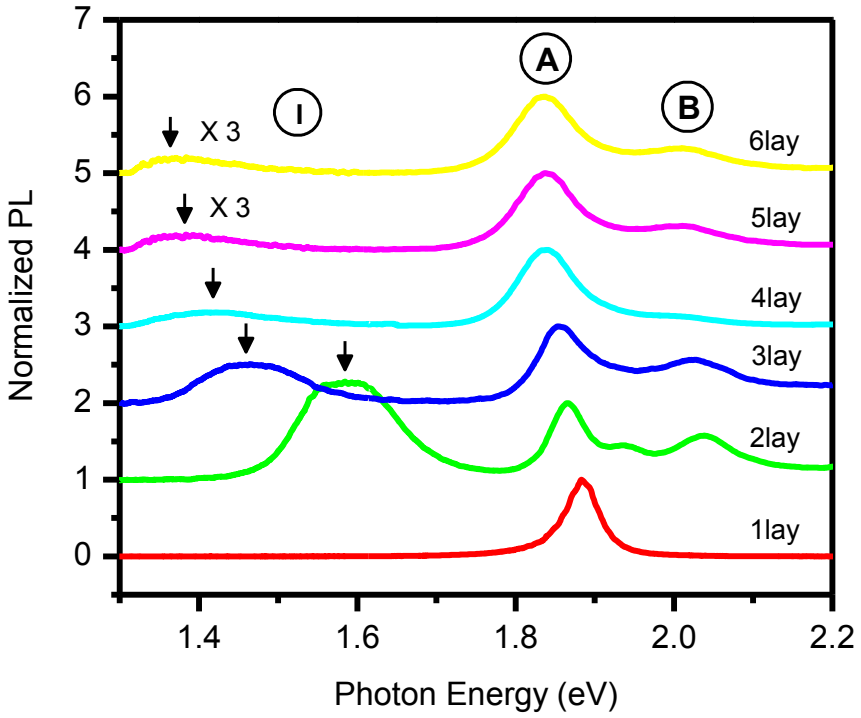
$$f\downarrow XC\,(r,r') = 1/\varepsilon \ln(|r-r'|/L)$$

(solution of 2D Poisson equation, L-dimensionality scale=14Bohr)

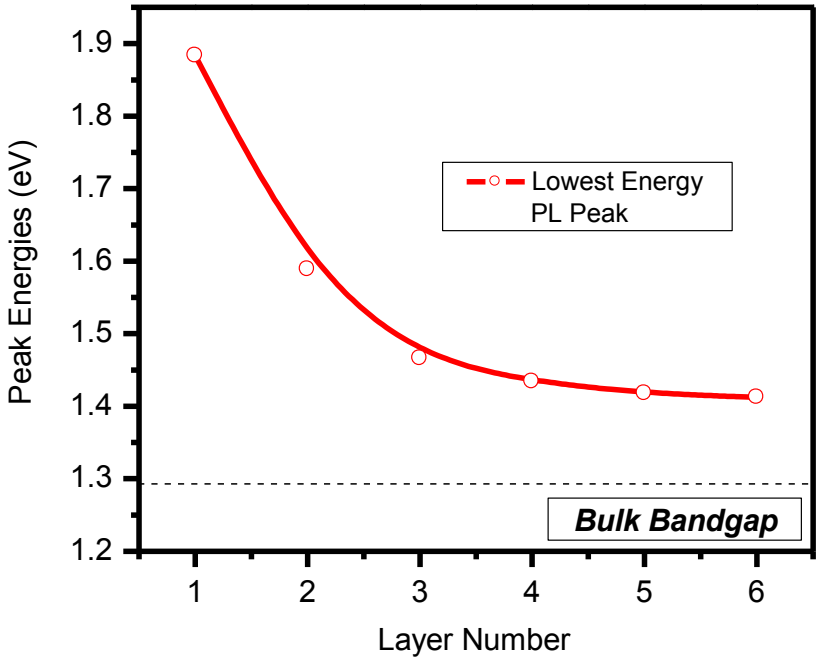
Excitation	Binding energy	exp
Exciton	27meV	~1000meV
Trion	50meV	~20meV

Long-range kernel leads to underestimation of the exciton energy but correct order of magnitude for trions
This is connected with the correct LR nature of the exciton-electron interaction

Band Gap Variation in Few-Layer MoS_2



Band gap decreases as layer number increases



Summary of MoS_2 band gap

Method	Value (eV)	Reference	Note
Photoluminescence	1.8-1.9	[1,2]	Optical band gap
Scanning Tunneling Spectroscopy (STS)	2.15	[3]	
DFT-LDA	1.81	[4]	
DFT-PBE	1.68	[5]	
DFT-optB88-vdW	1.67	[4]	
GW	2.84	[6]	G_1W_0 approximation
DFT-HSE06	2.25	[7]	

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