Electronic and optical properties of functionalized graphene and 2D layered materials

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Graphene: a physicist's/materials scientist's favorite playground since c. 2005 (Geim, Novooselov, Nobel 2010)

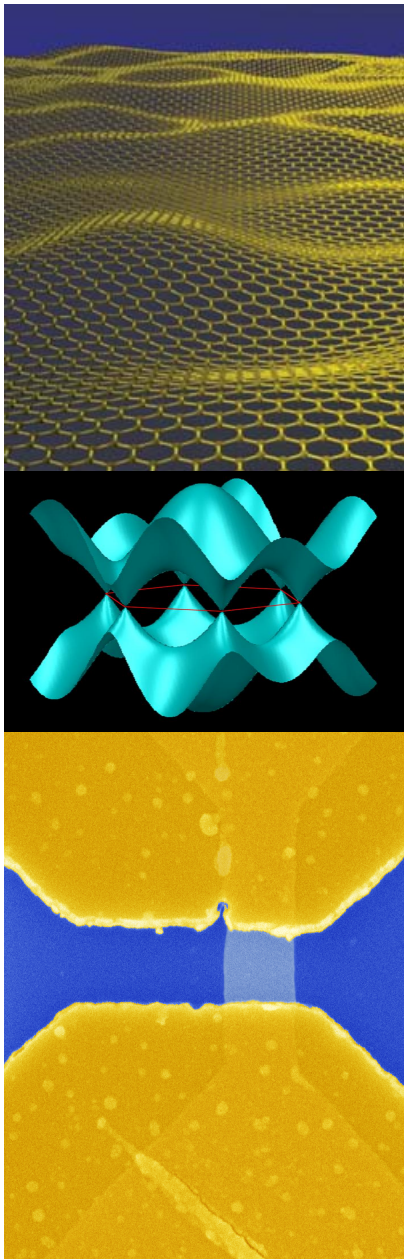
- Quasi-2D crystal: strongest material recorded

  (stiffness: Young's modulus $E \sim 1$ TP)

- Exceptional mobility: as high as 2×10^5 $cm^2V^{-1}s^{-1}$
- Low spin-orbit coupling and hyperfine interaction (1% C^{13})
- Unique band structure: massless quasi-particle
- Other properties: room temperature quantum hall effect

  <u>BUT</u>

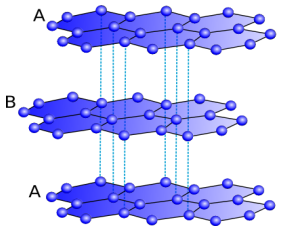
- No band gap
- Difficult contacts

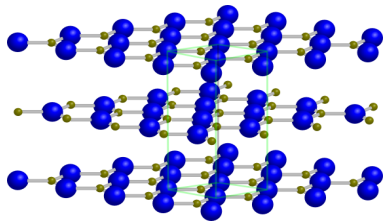


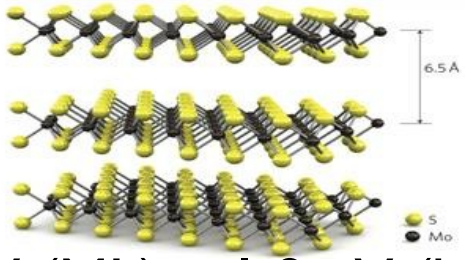
Graphene (single- or few-layered)

h-BN

Transition Metal Di-Chalcogenides (TMDC's)
(WS_2, TiS_2, ZrS_2, $MoSe_2$, MoS_2, ...)



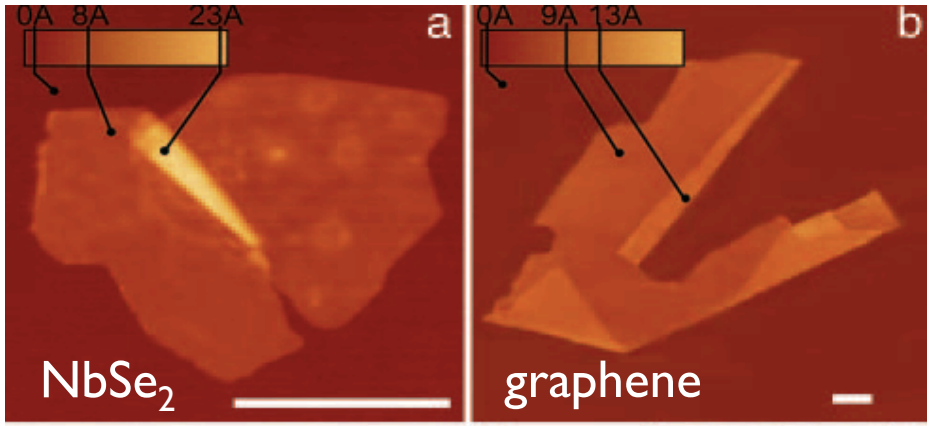


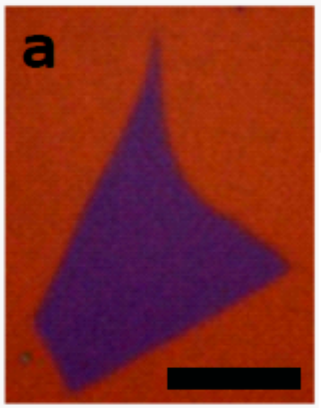


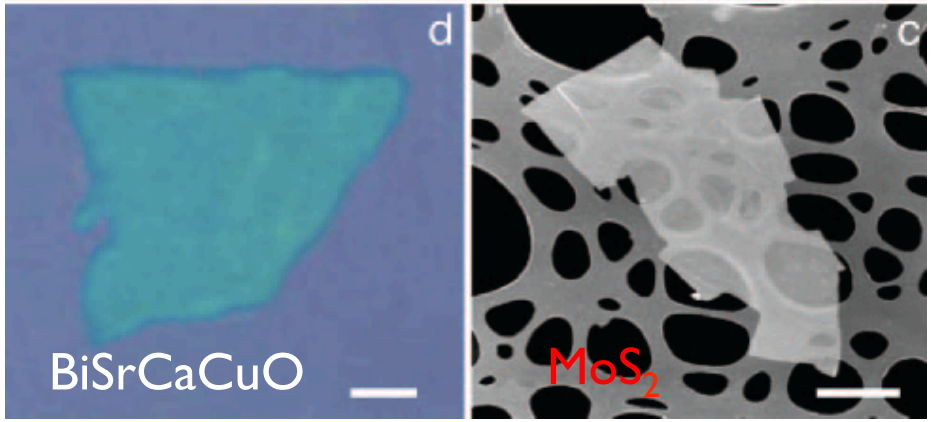
E_{gap} = 0.0 eV

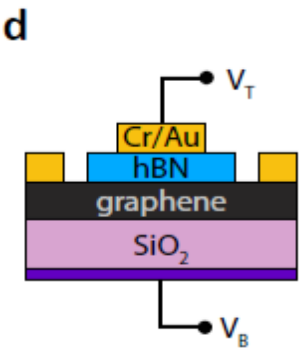
5.0 eV

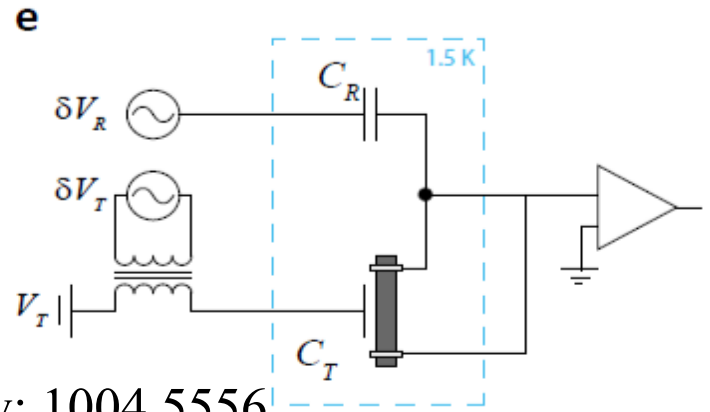
1.2 eV (ML) – 1.9 eV (bulk)





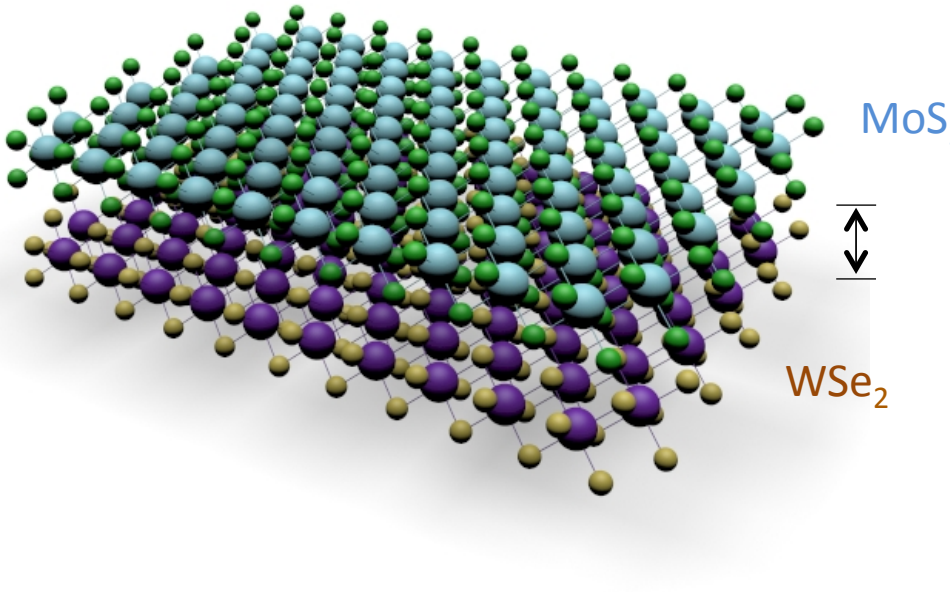


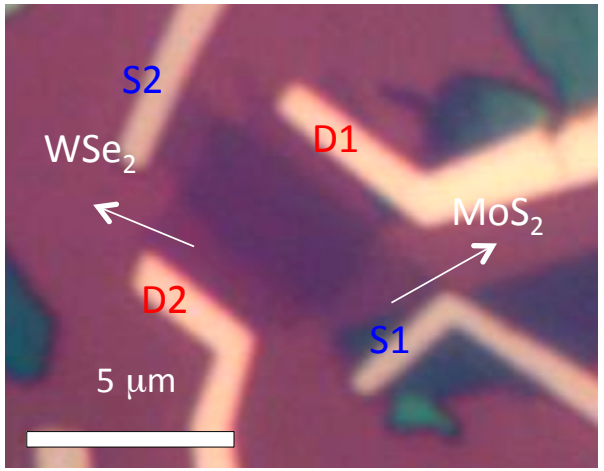


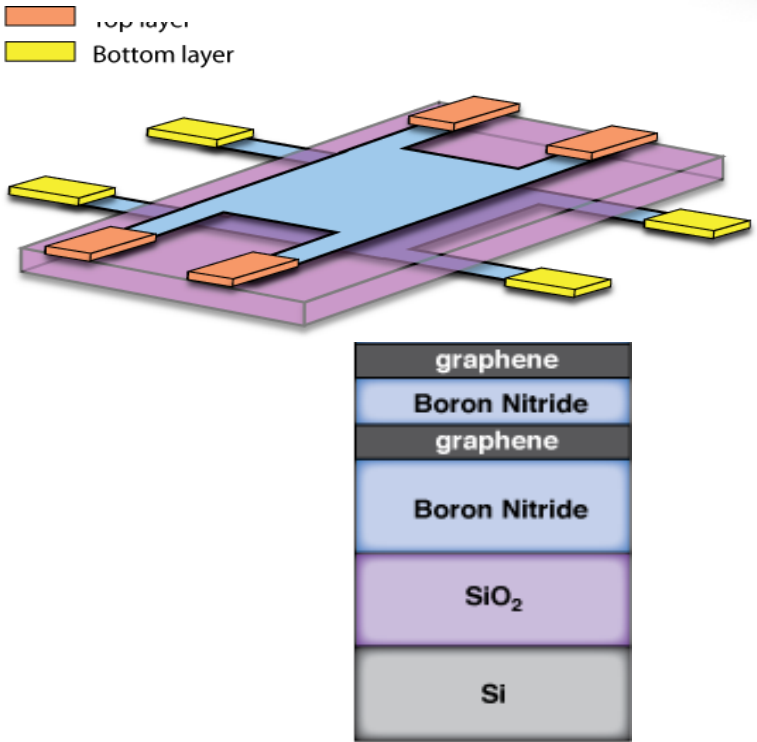


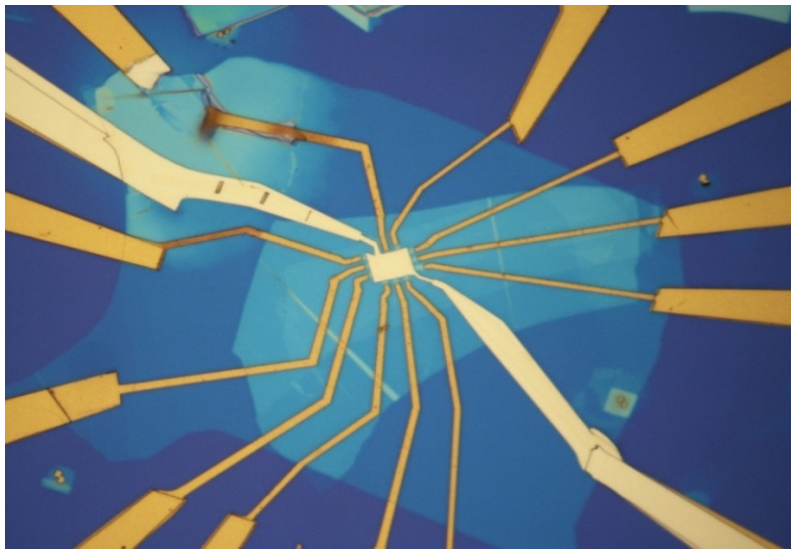
PNAS, **102**, 10451 (2005)

arXiv: 1004.5556



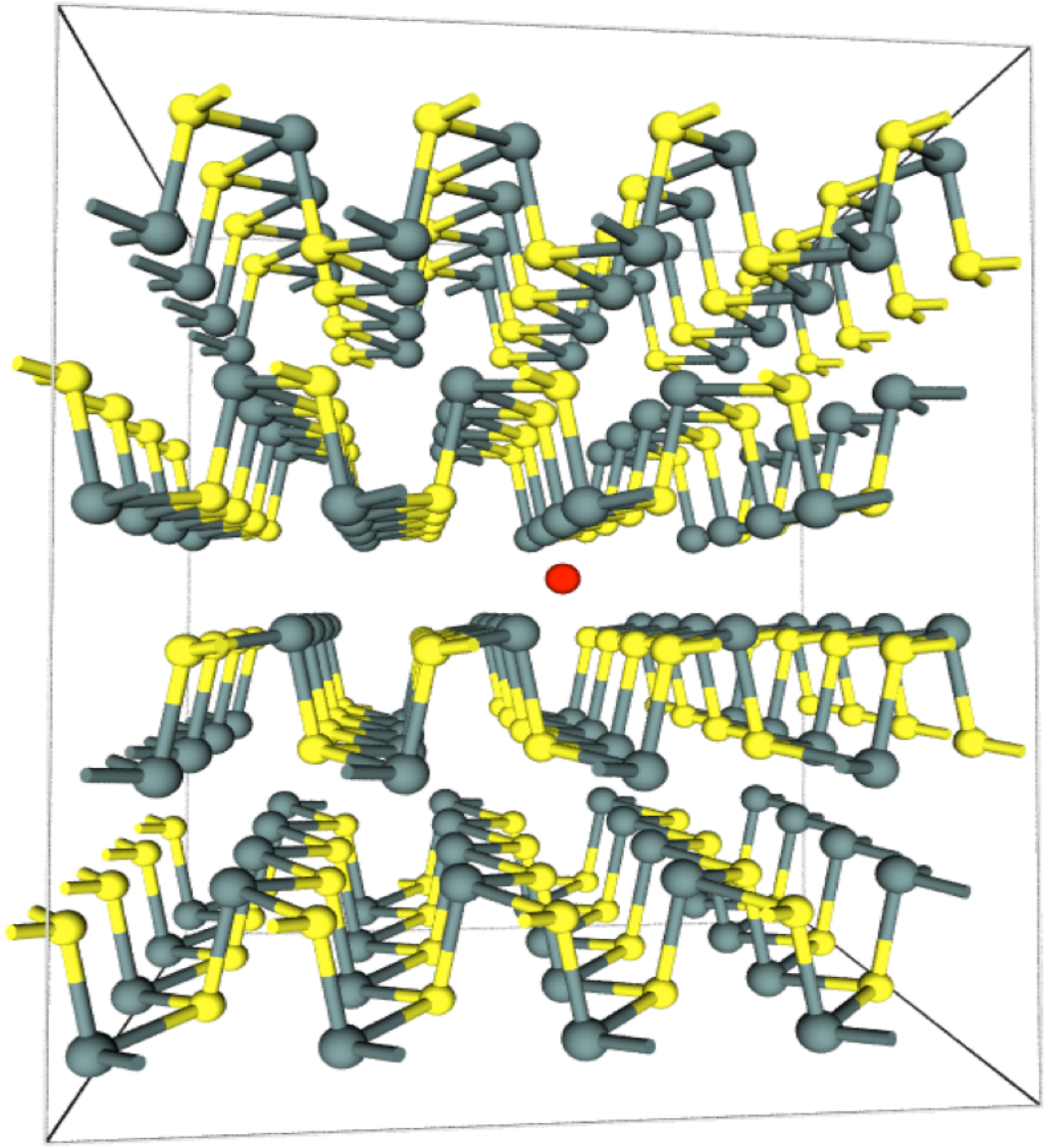






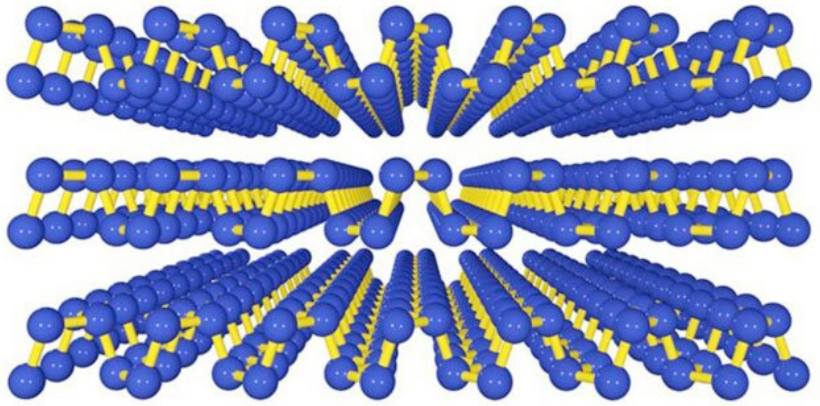
Images from:
Philip Kim,
Physics Dept.
Harvard

Transition metal mono-chalcogenides (TMMC's): SnS, GeS thin films (candidates for PV applications)

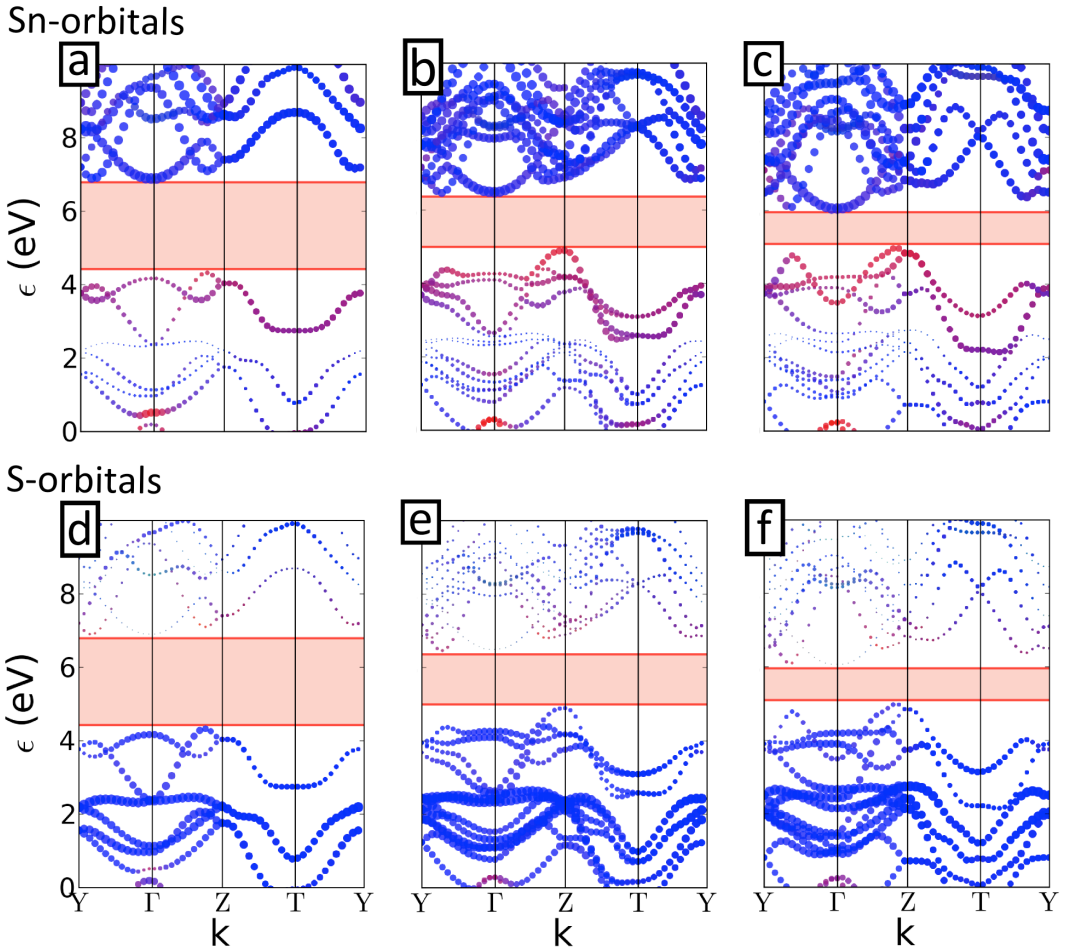


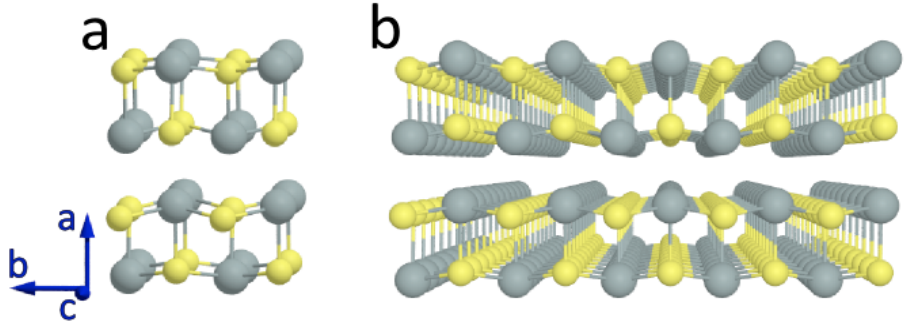
- high absorption ($\alpha > 10^4\ cm^{-1}$)
- suitable band gap (~1.1 – 1.5 eV)
- low-toxicity
- earth–abundant

Roy Gordon group
Chemistry Dept.
Harvard

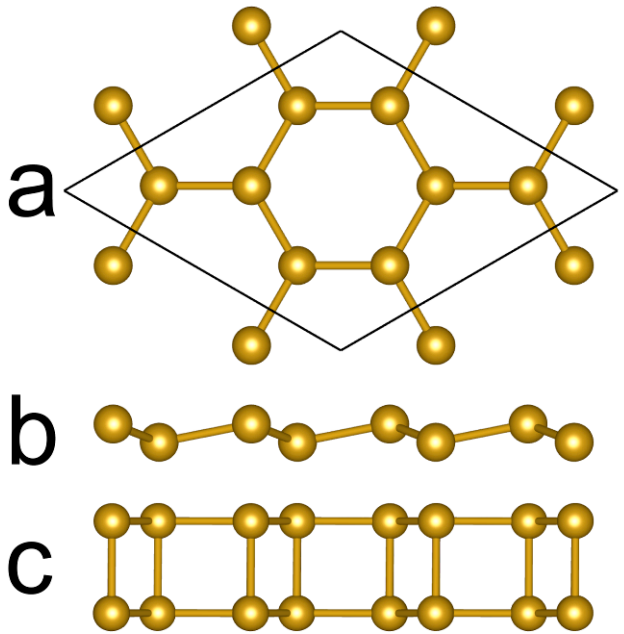


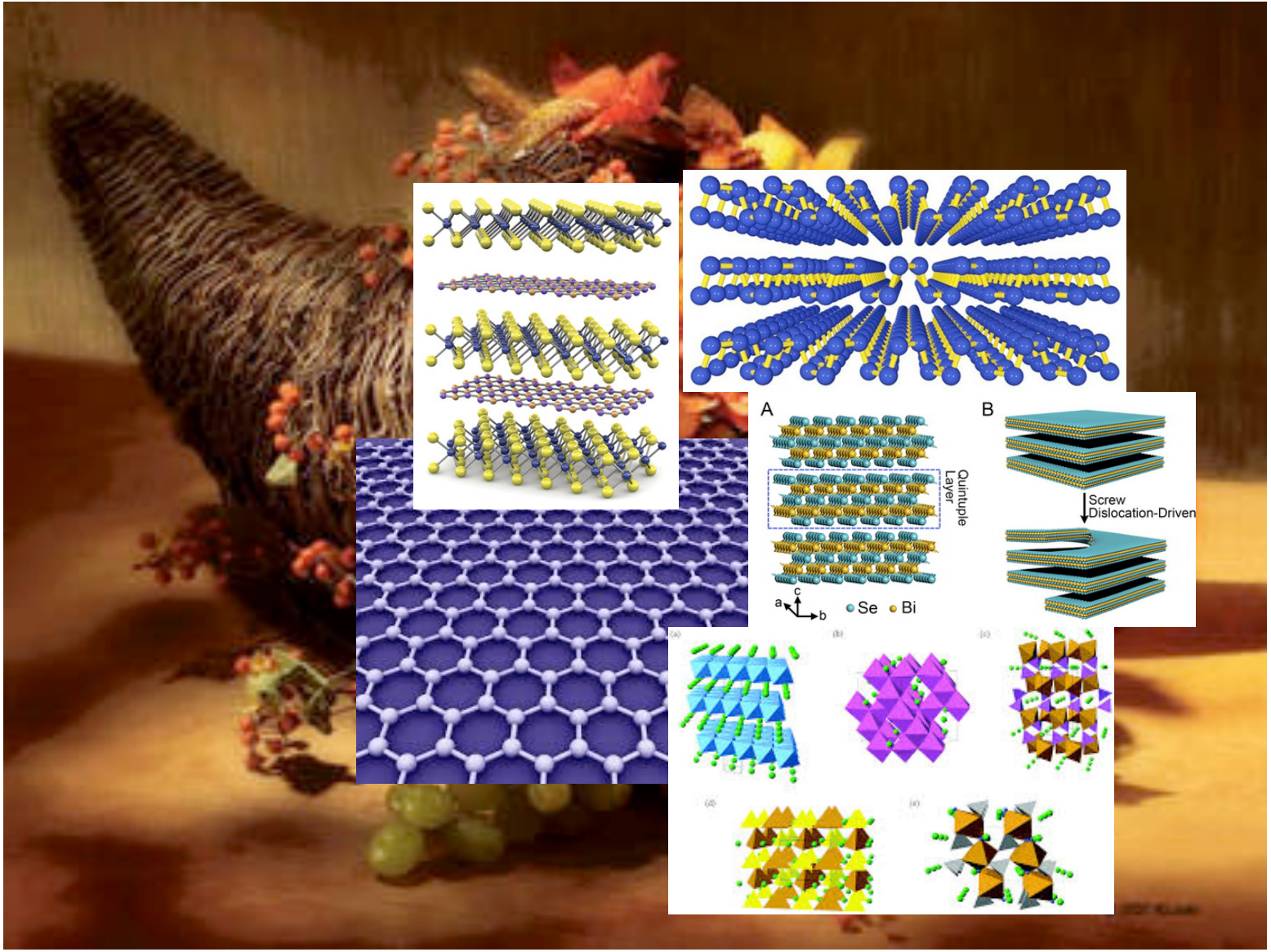
phosphorene





Also: silicene,
germanene,
phosphorene, …





A cornucopia (from Latin *cornu copiae* or horn of plenty) of new materials (2D): how to combine them?

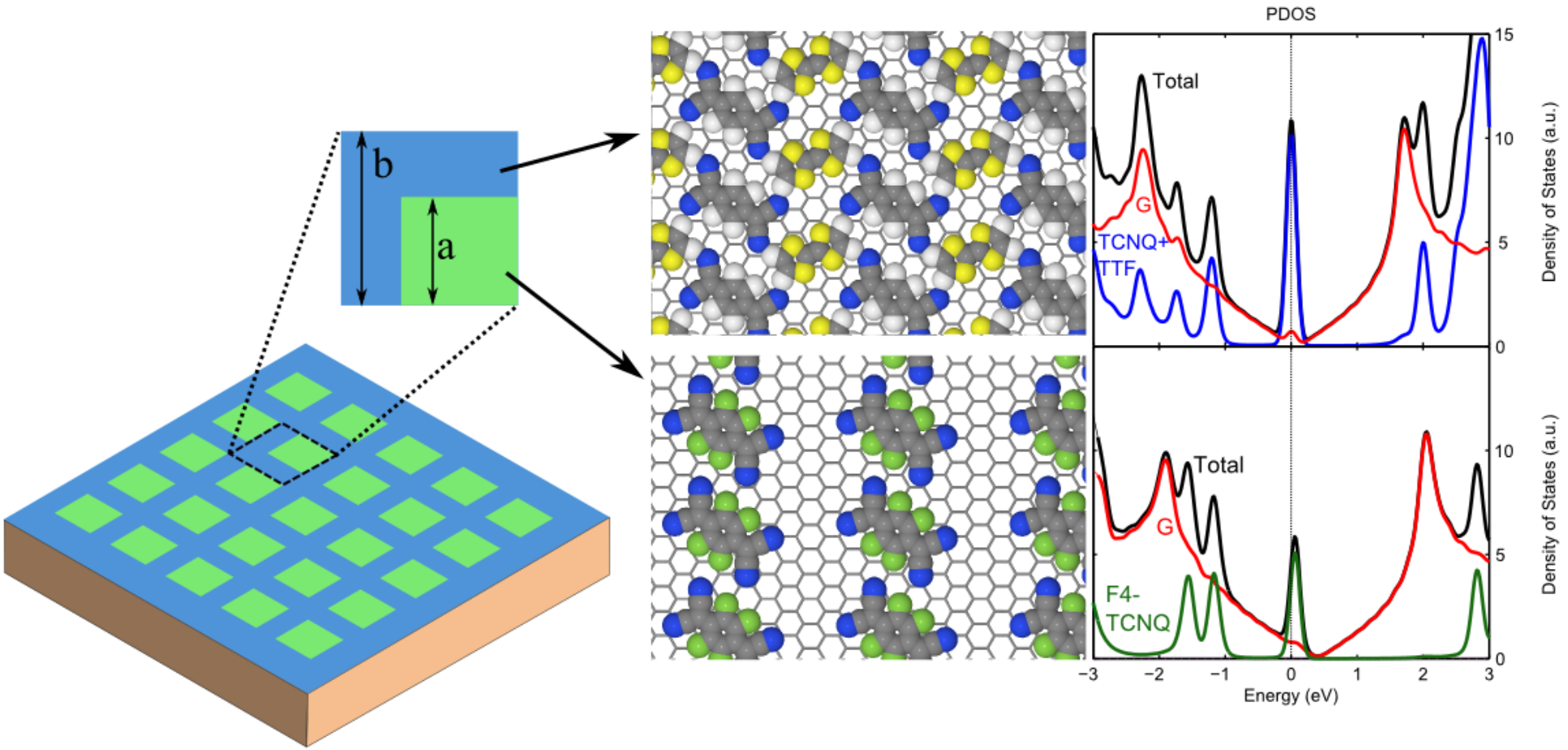
1. Graphene Nano Flakes (GFN's): magnetic properties
2. Ripples in graphene: real-space imaging
3. Functionalized graphene: optical, magnetic properties
4. Graphene and TMDC's: dielectric response in external fields
5. Single-atom chisel for graphene sculpting
6. Graphene as functional substrate: organic PV's
7. TMMC's (SnS, GeS): optical properties for PV applications
8. Silicene, germanene: Li-ion storage

A) Surface Plasmon Engineering in Graphene Functionalized with Organic Molecules: A Multiscale Theoretical Investigation, Jierong Cheng, Wei Li Wang *et al.* NanoLetters 2013.

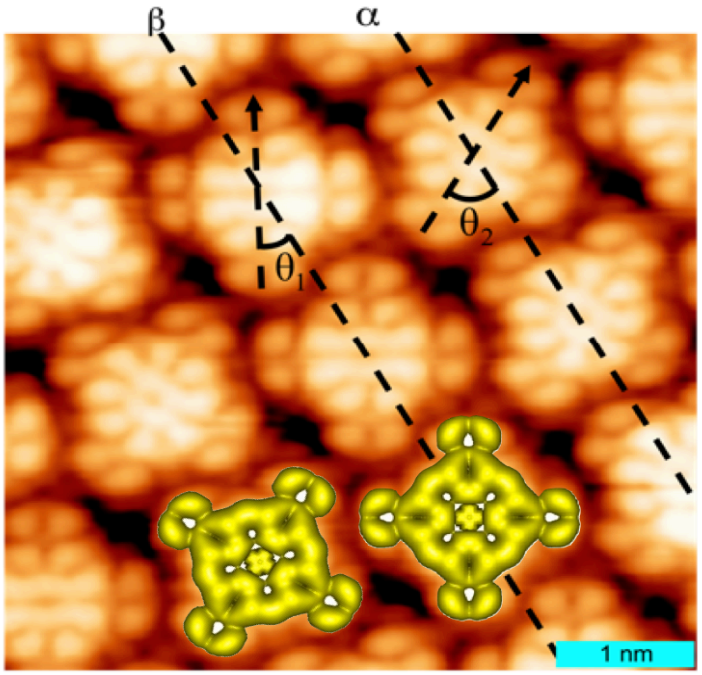
B) Tuning the Electronic and Chemical Properties of Monolayer MoS_2 Adsorbed on Transition Metal Substrates, Wei Chen *et al.*, NanoLetters 2013.

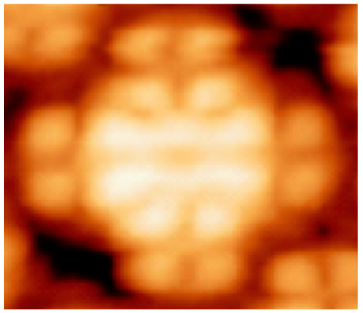
C) Graphene/MoS_2 Hybrid Technology for Large-Scale 2D Electronics, Lili Yu *et al.* (Tomas Palacios group), NanoLetters 2014

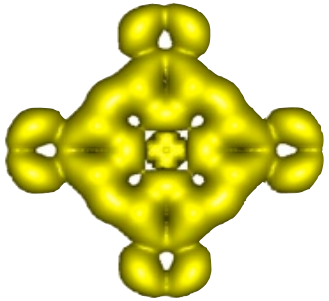
A) Proposal for a graphene-based plasmonic device



F4-TCNQ (blue area) and TCNQ+TTF (green area). Projected DOS shows effects of **doping** and the added molecular signature to the total DOS due to the molecule-graphene interactions.





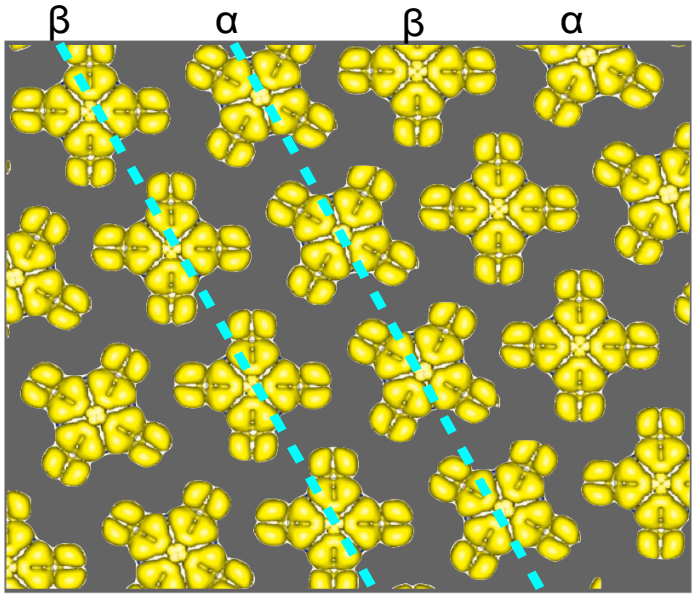


Properties of copper (fluoro-) phthalocyanine layers deposited on epitaxial graphene

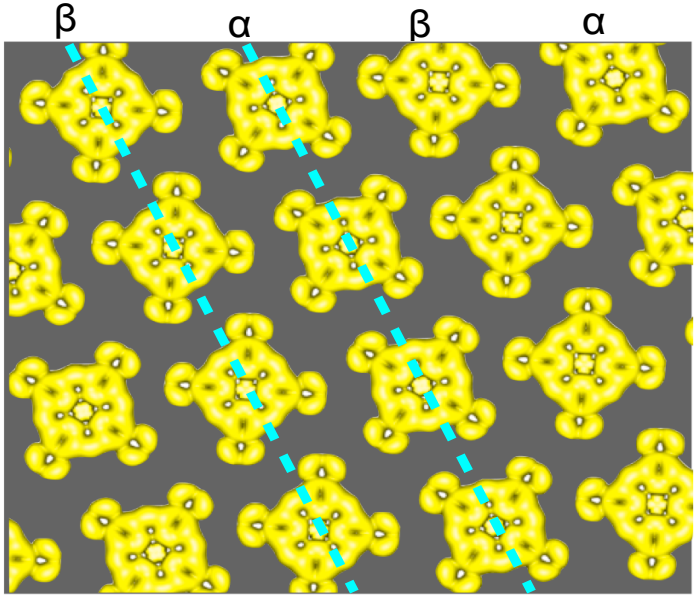
Jun Ren, Sheng Meng, Yi-Lin Wang, Xu-Cun Ma, Qi-Kun Xue, and Efthimios Kaxiras

JOURNAL OF CHEMICAL PHYSICS **134**, 194706 (2011)

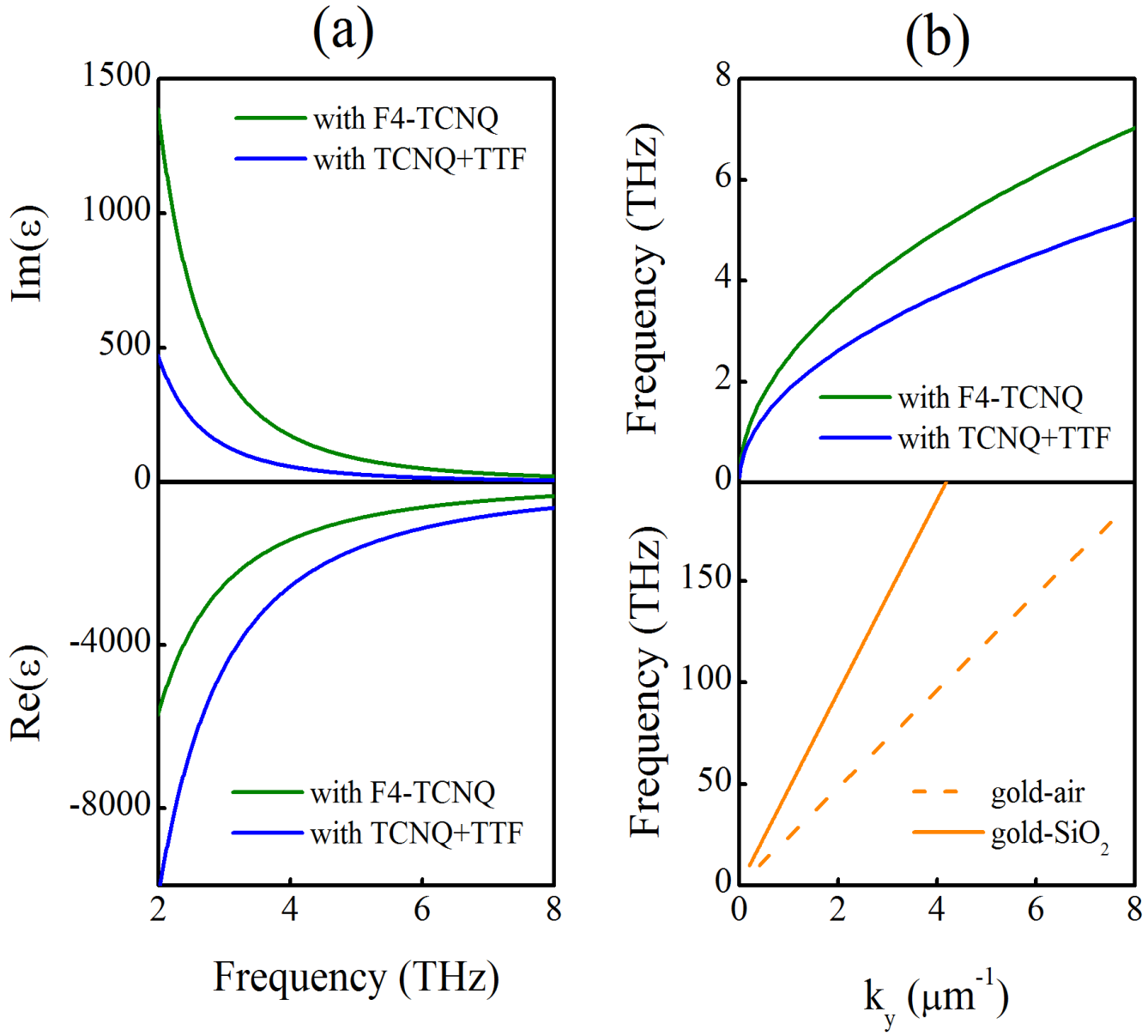
HOMO

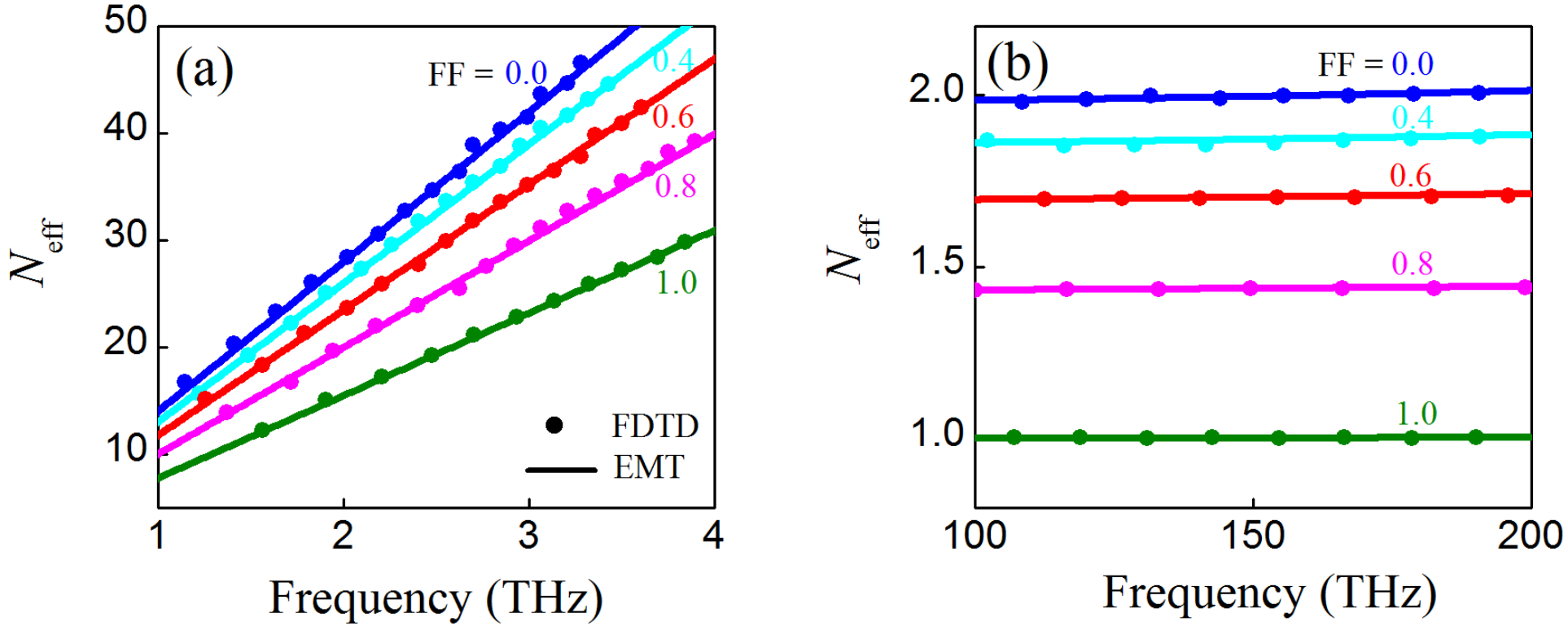


LUMO



Spatially resolved dielectric function

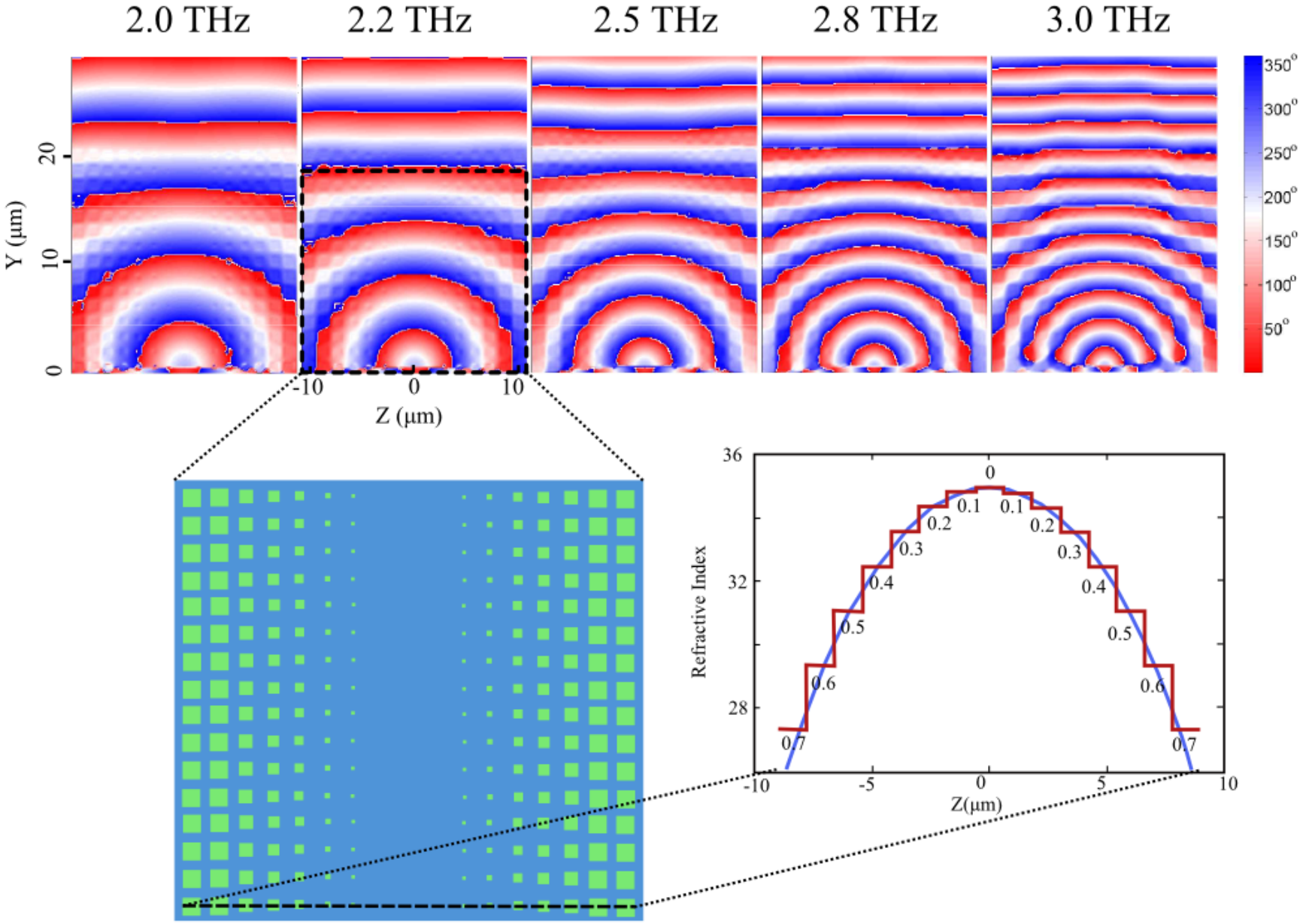




Refractive indices of metamaterials made of: (a) patterned graphene, (b) a gold film on top of Gradient Refractive Index dielectric substrate.

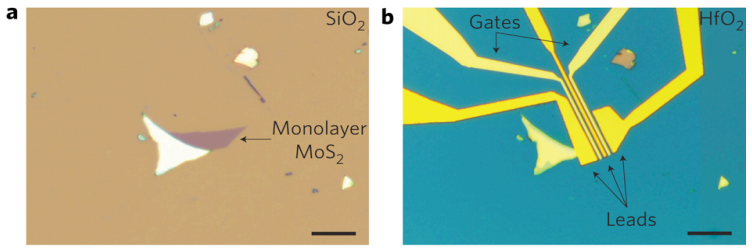
[dots: full-wave FDTD simulation; lines: EMT with filling factor (FF) ranging from 0.0 to 1.0]

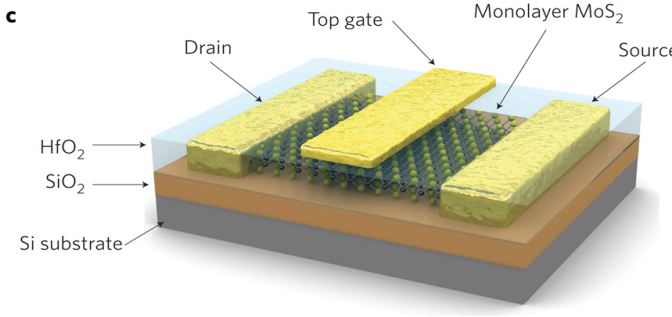
Selfoc lens: collimating EM waves

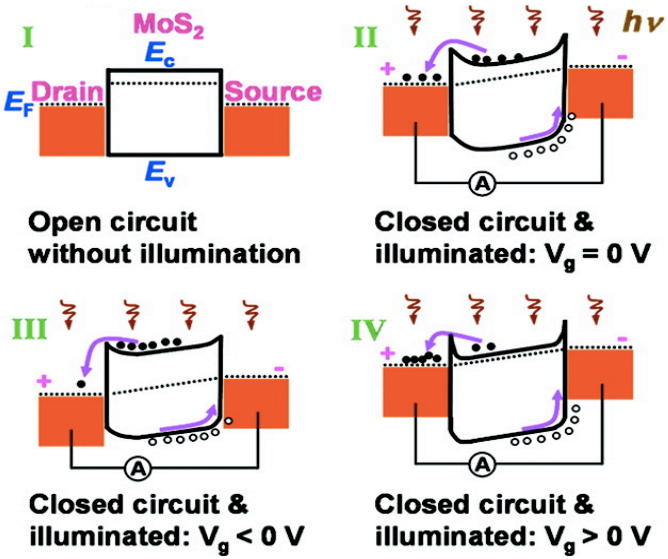


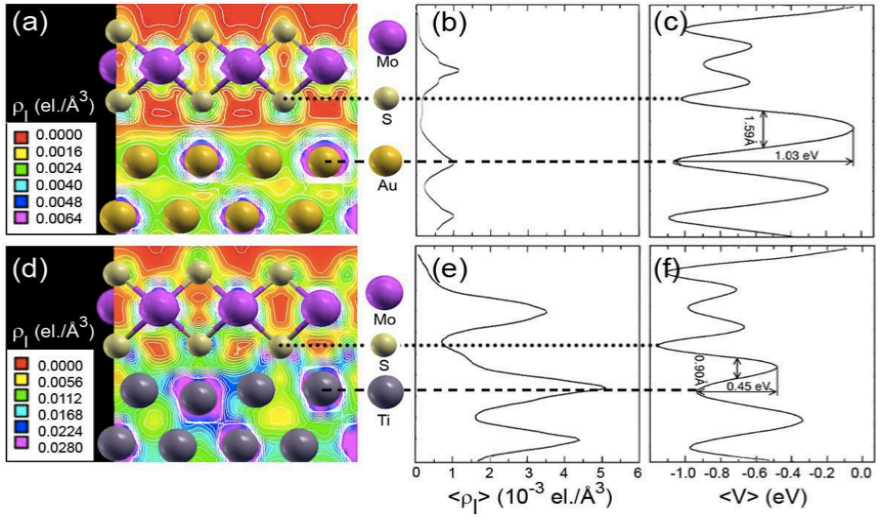
Spherical waves propagate through the lens region (box) and turn into PW's.

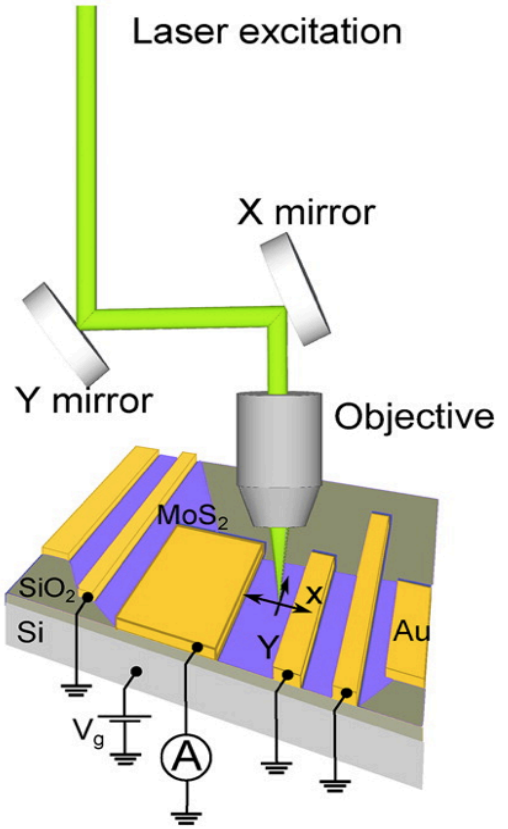
B) MoS_2-based Electronics: metal contacts











"**Single-Layer MoS_2 Transistors**", B. Radisavljevic *et al.*, *Nat. Nanotechnol.* (2011)

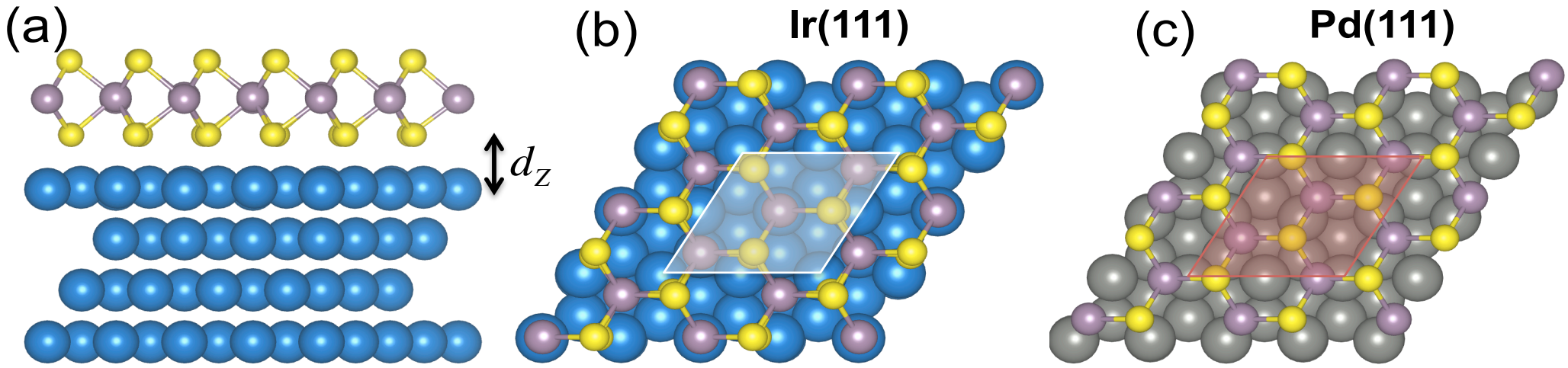
"**Single-Layer MoS_2 Phototransistors**", Z. Yin *et al.*, *ACS Nano* (2012)

"**Large and Tunable Photothermoelectric Effect in Single-Layer MoS_2**", M. Buscema *et al.*, *Nano Lett.* (2013)

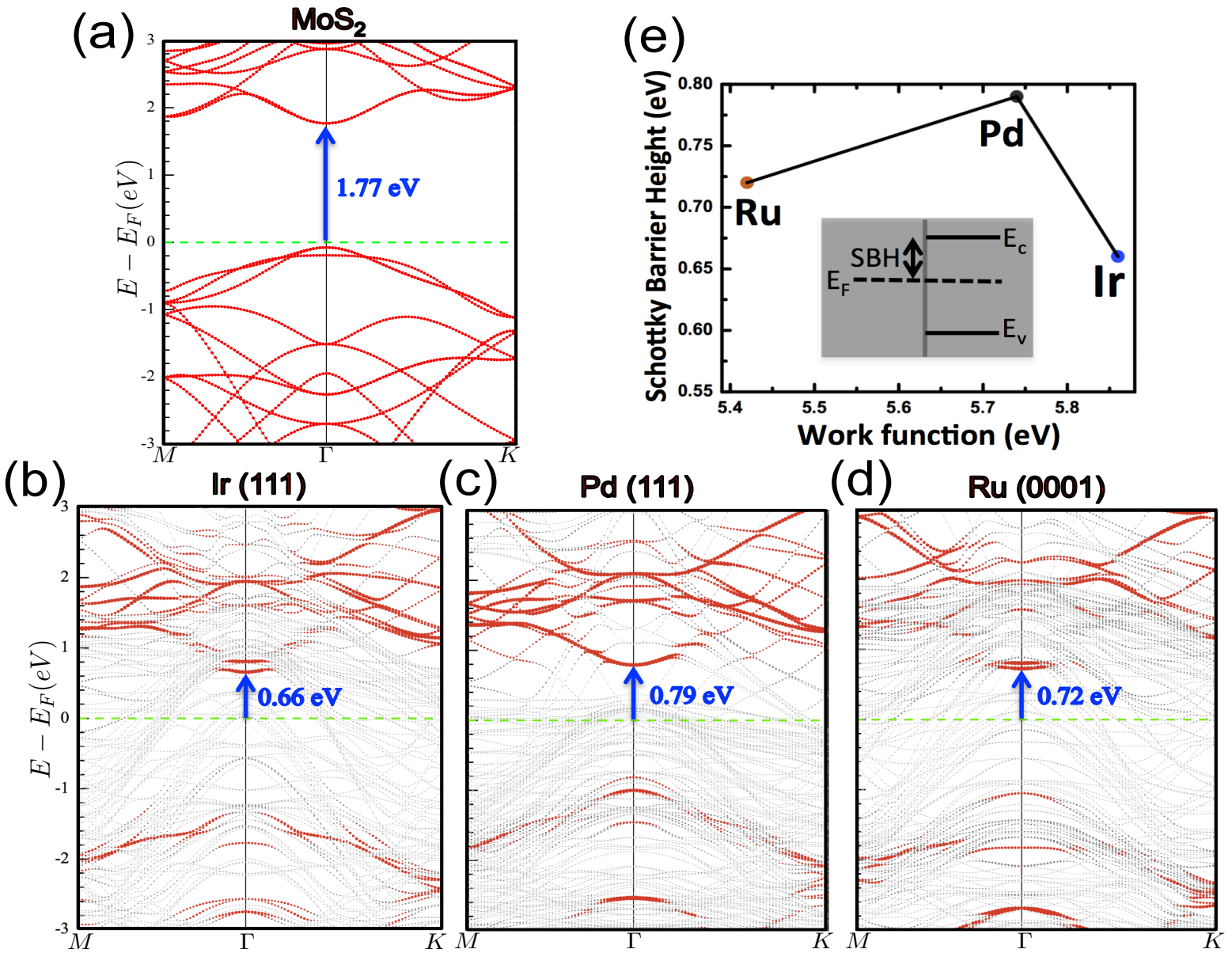
"**Designing Electrical Contacts to MoS_2 Monolayers: A Computational Study**", I. Popov *et al.*, *Phys. Rev. Lett.* (2012)

Theory of monolayer MoS_2 – Metal Interfaces

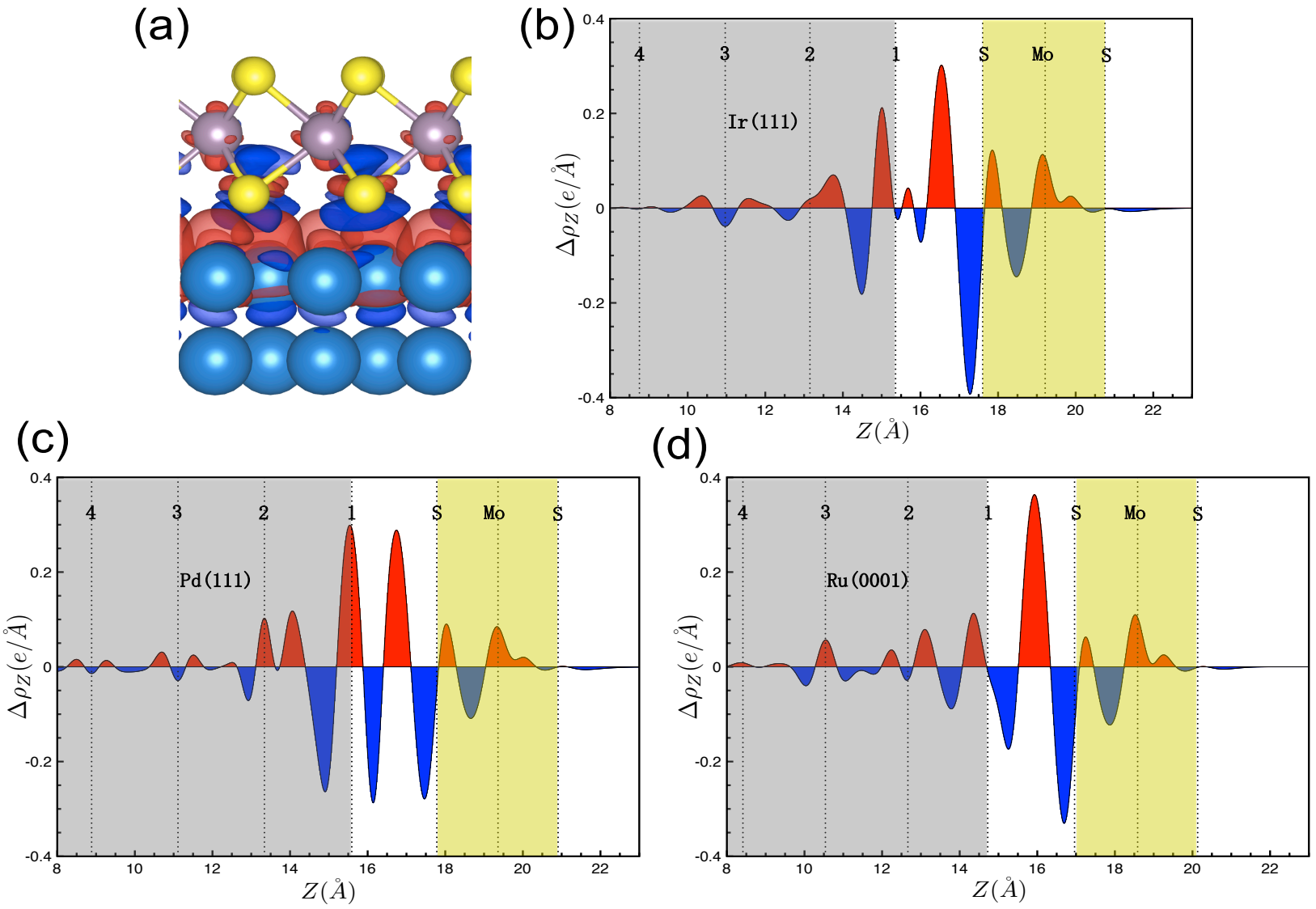
- DFT caclulations: VASP
- Functional: LDA, checked by PBE-vdW
- Supercell: $(\sqrt{3} \times \sqrt{3})$ MoS_2 + (2×2) Metal (mismatch < 1 %)
- Systems: MoS_2-Ru(0001) – d^6, MoS_2-Ir(111) – d^7; MoS_2-Pd(111) – d^8
- Spin-polarized calculations
- Spin-Orbit Coupling (SOC) effect checked



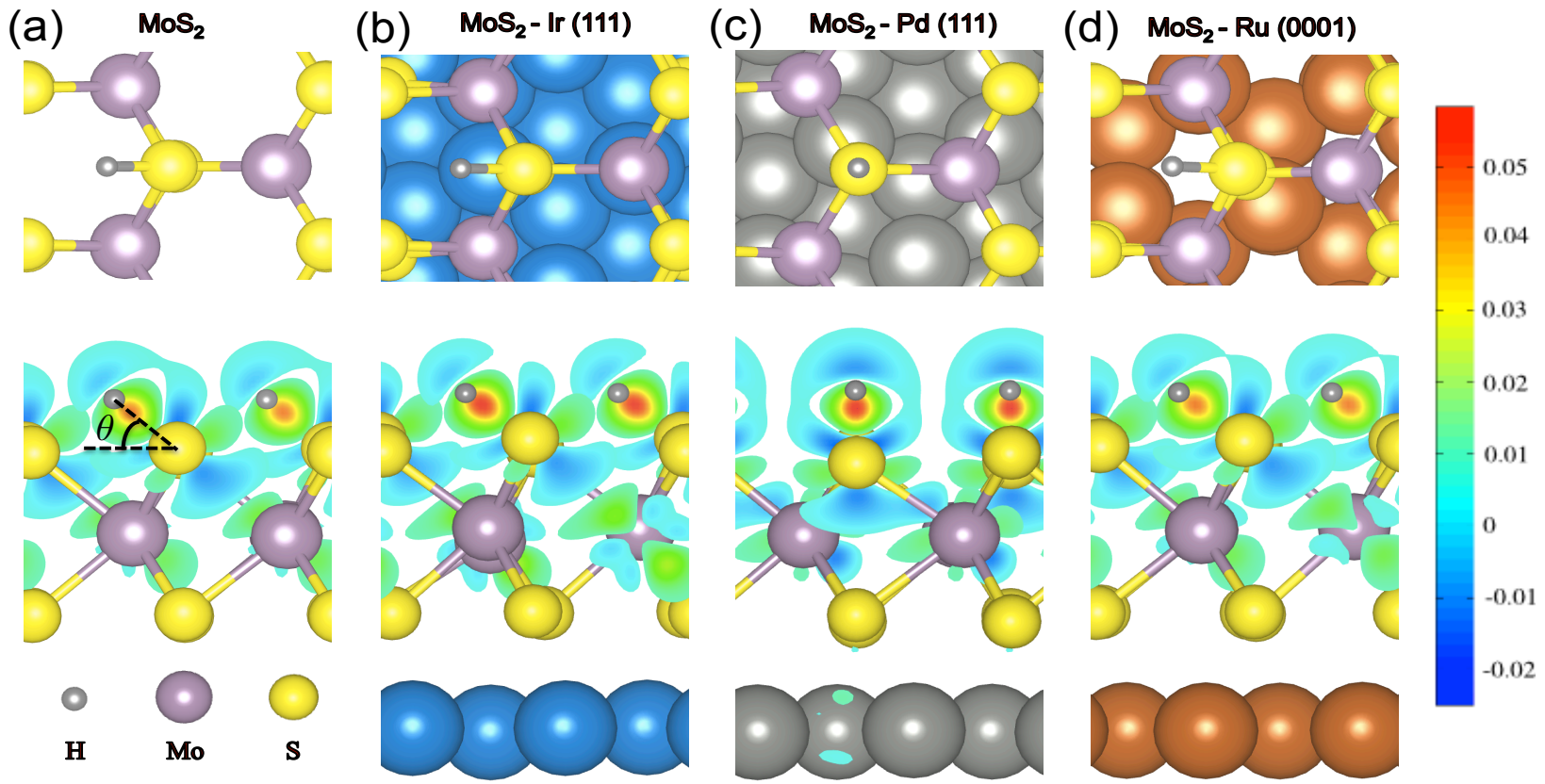
Electronic structures: Schottky barrier heights



Charge redistribution: interface dipole moment



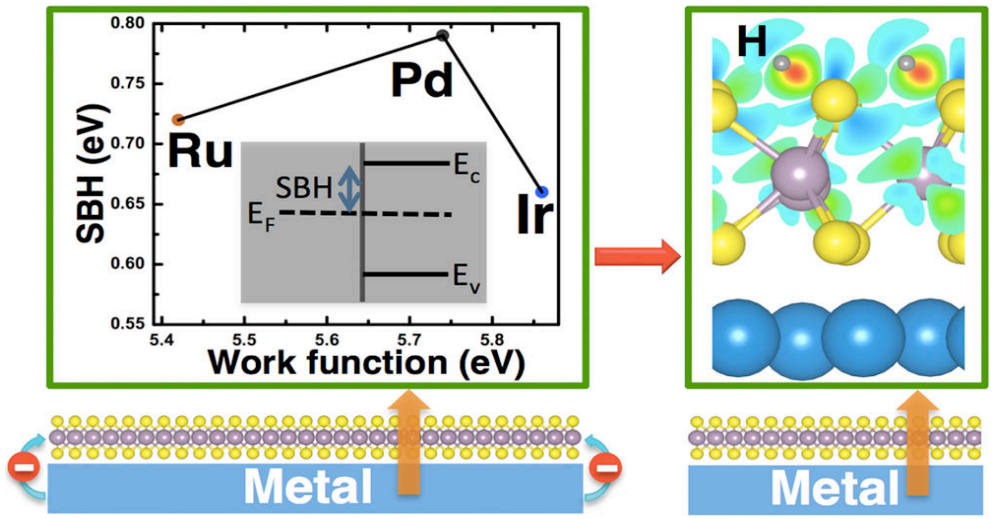
Hydrogen Adsorption: measure of chemical reactivity



	E_b (eV)	d_z^0 (Å)	d_z^H (Å)	E_a (eV)	L_{H-S} (Å)	θ (deg)
free-standing MoS_2				1.07	1.46	40.2
MoS_2/Ir(111)	0.62	2.23	2.20	1.44	1.43	37.2
MoS_2/Pd(111)	0.74	2.17	2.09	1.39	1.39	89.1
MoS_2/Ru(0001)	0.82	2.25	2.20	1.33	1.46	38.2

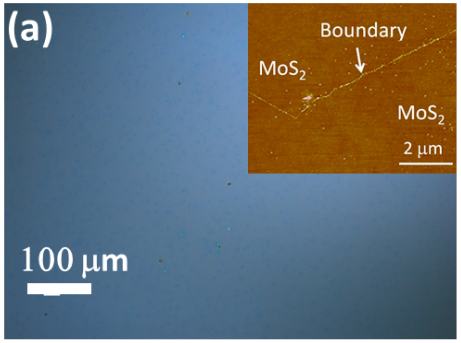
Conclusions

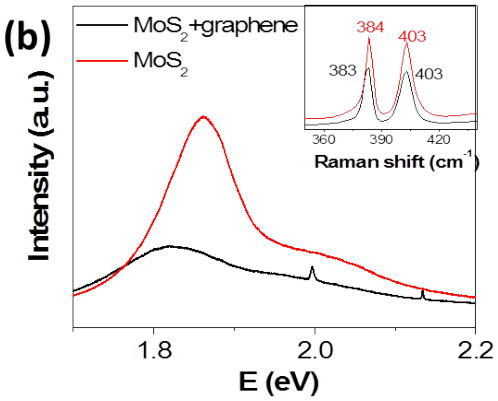
- The nature of the contact is Schottky-barrier type when monolayer MoS_2 is adsorbed on Ir (111), Pd(111), or Ru(0001).
- The dependence of the barrier height on the metal work function exhibits a partial Fermi-level pinning picture.
- Using hydrogen adsorption as a test case, the chemical reactivity of MoS_2 can be substantially altered by the underlying metal substrates.
- Enhanced binding of hydrogen is attributed to enhanced H-S bonding and to a stronger MoS_2-metal interface by H adsorption.

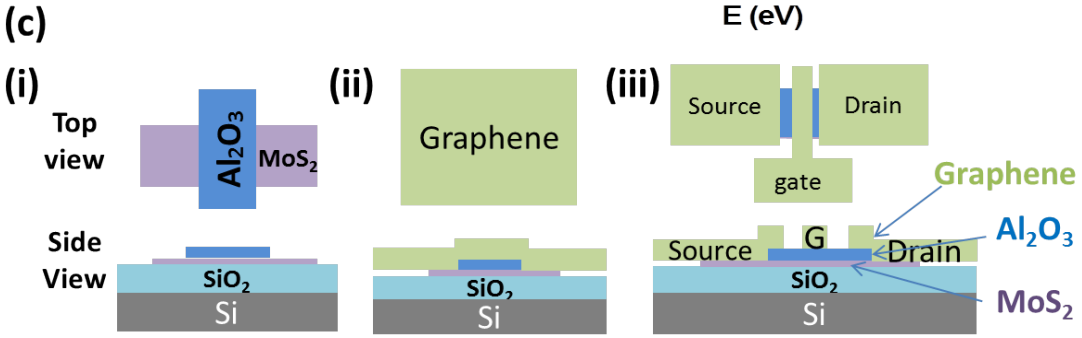


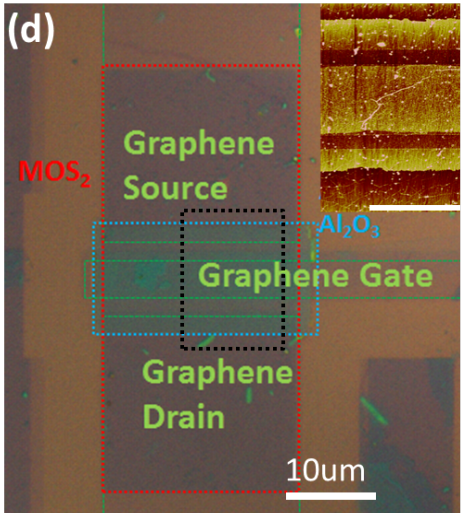
Nano Lett. **13**, 509 (2013)

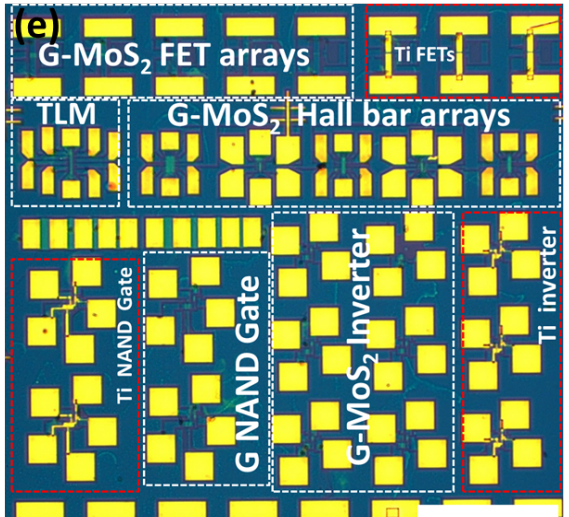
C) MoS_2-based Electronics: graphene contacts



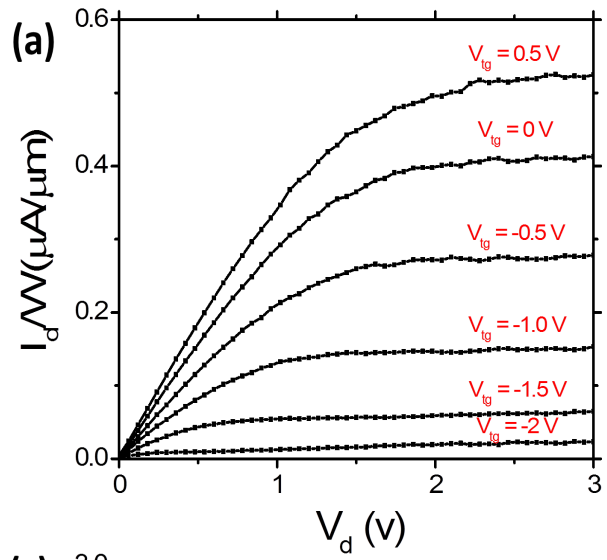


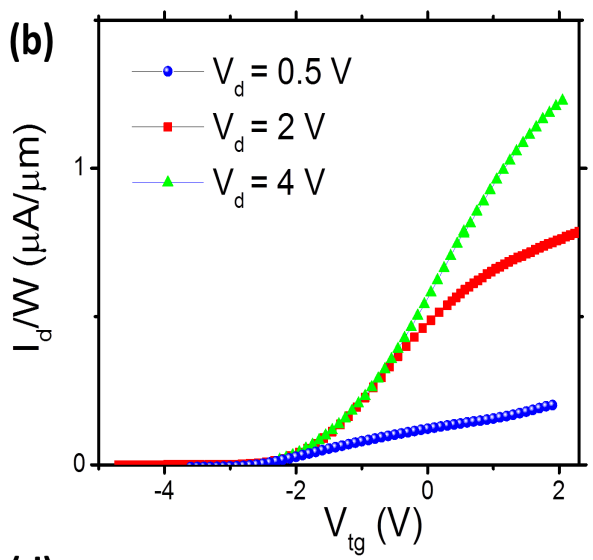




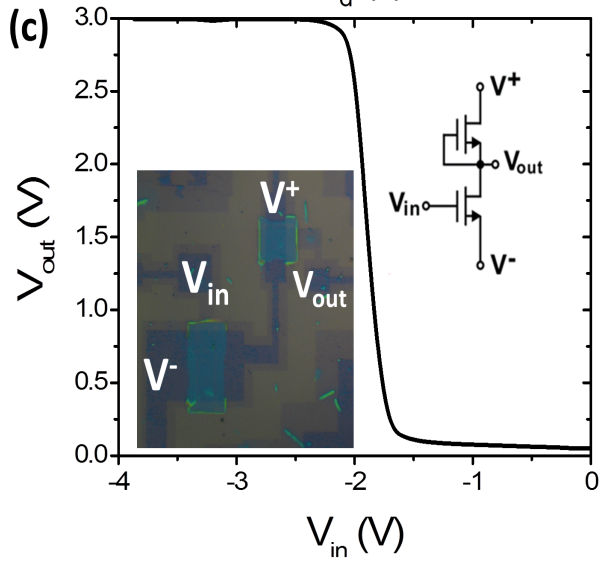


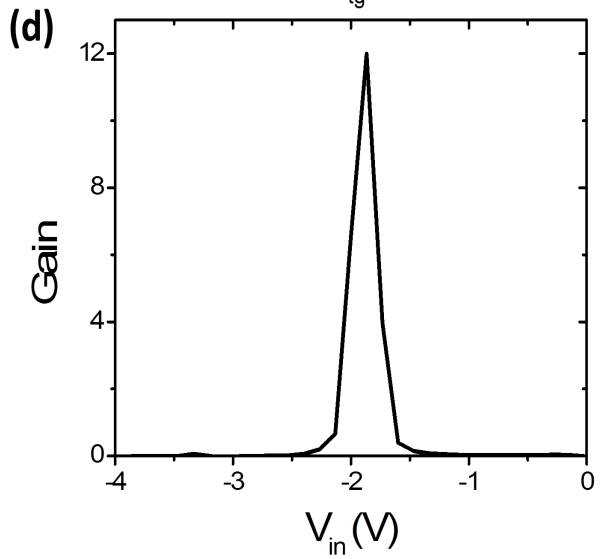
Tomas Palacios group (MIT)



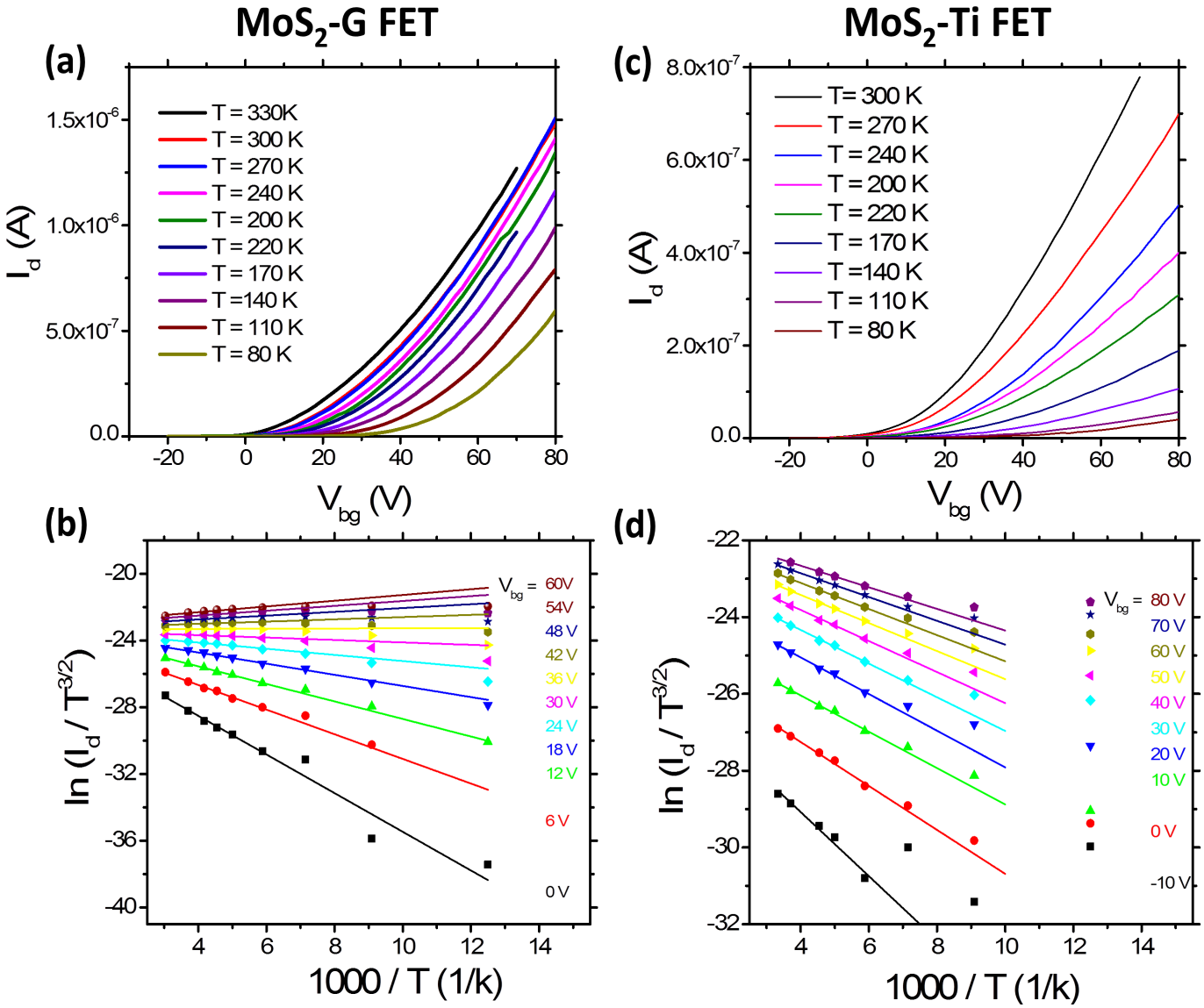


(a) Output (I_d-V_d) and (b) transfer characteristics (I_d-V_{tg}) of top gated MoS_2 transistor with Al_2O_3 as top gate dielectric, graphene as source, drain and gate electrodes.

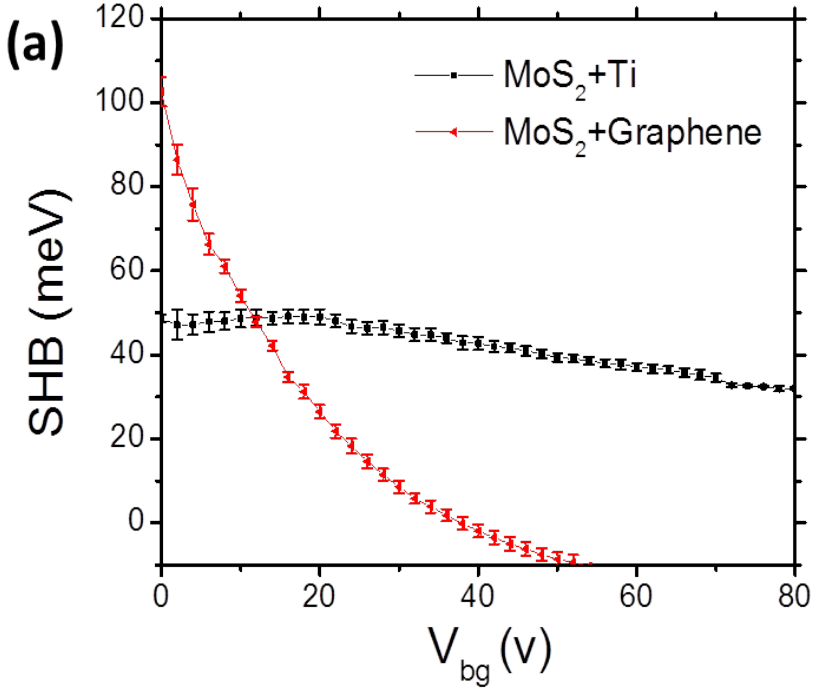


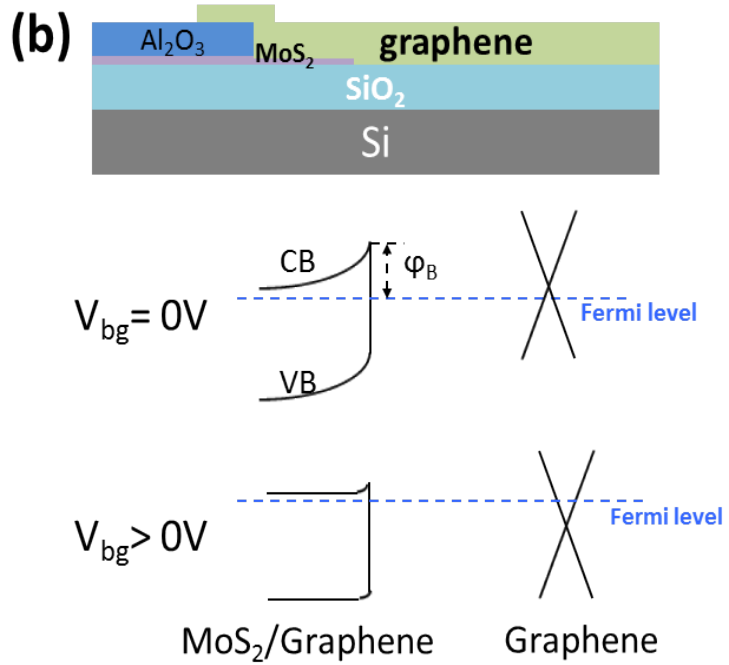


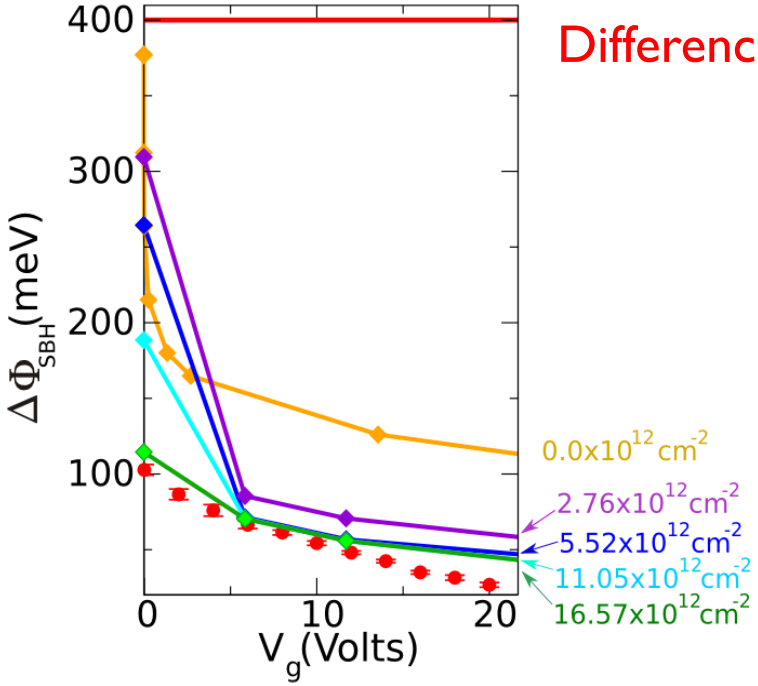
Demonstration of an integrated logic inverter on MoS_2 -G heterostructure
(c) Output voltage as a function of the input voltage, for a MoS_2-graphene logic inverter. Optical image (inset, left down) and schematic of the electronic circuit (inset, right up) for the inverter.
(d) The gain of the inverter is ~12.



$$\ln\left(\frac{I_{\mathrm{d}}}{T^{3/2}}\right) = -\frac{q(\varphi_B - V_{\mathrm{d}}/n)}{k_B T} + \ln(A)$$

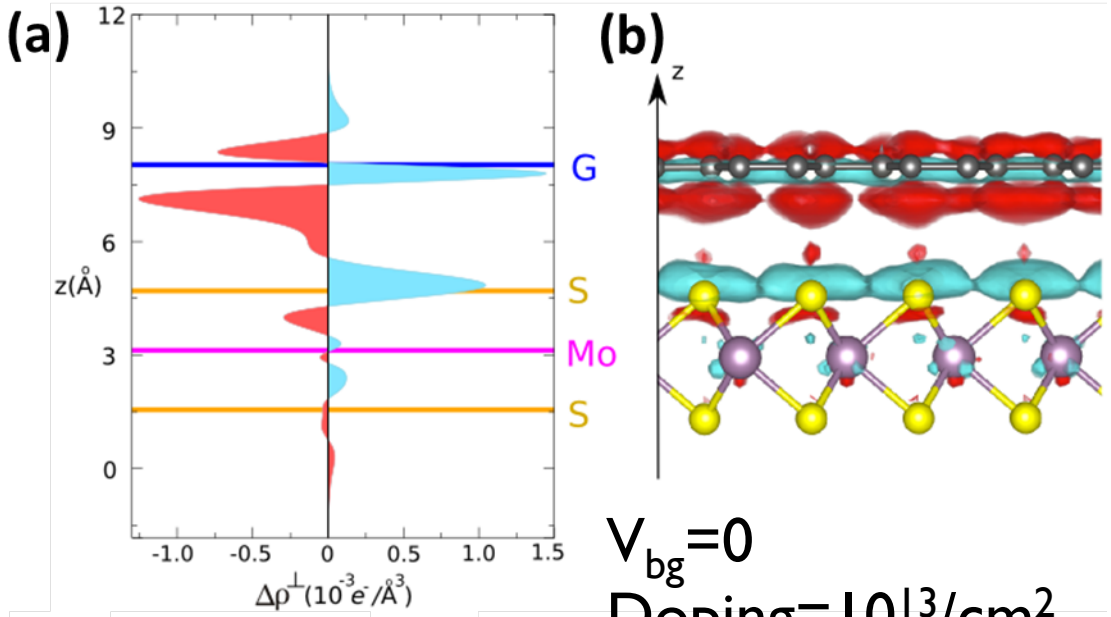






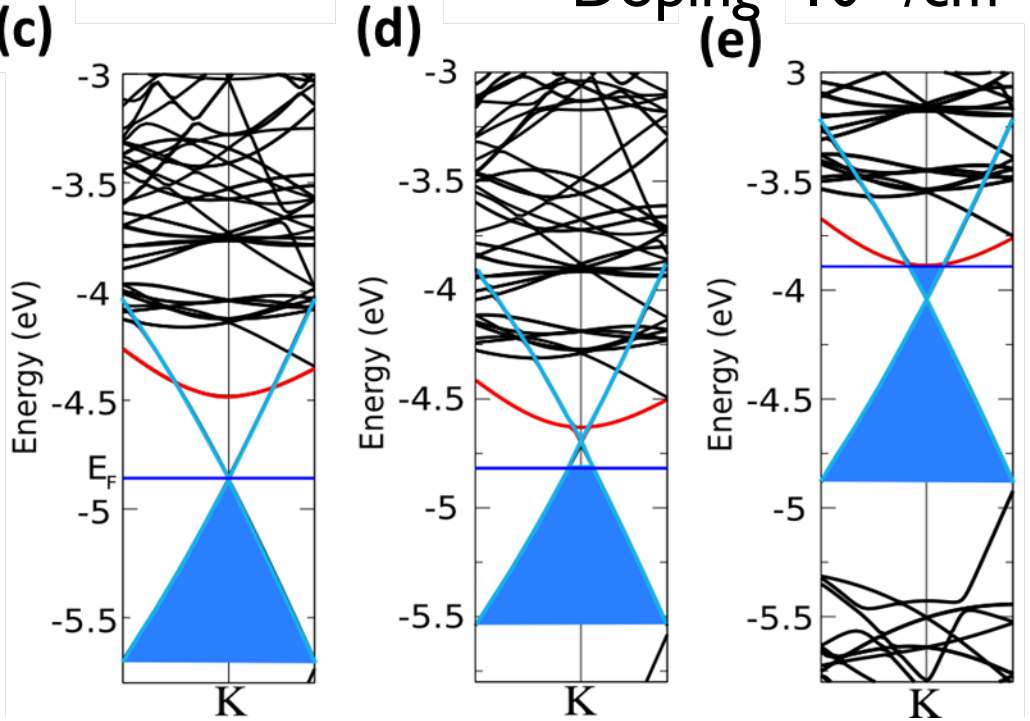
Difference between work function and electron affinity

Theory: DFT-based electronic states, Schottky barrier height



V_{bg}=0
Doping=10^{13}/cm^2

V_{bg}=0
Doping=0



V_{bg}>0
Doping=10^{13}/cm^2

Concluding remarks:

- interesting electronic devices already demonstrated using graphene/2D layered heterostructures

- essential role of theory in exploring possibilities

- we're only at the very beginning of exploiting their potential