First-principles Study of 2D van der Waals Heterojunctions

Jinlong Yang

Email: jlyang@ustc.edu.cn

Hefei National Laboratory for Physical Sciences at Microscale,
University of Science and Technology of China

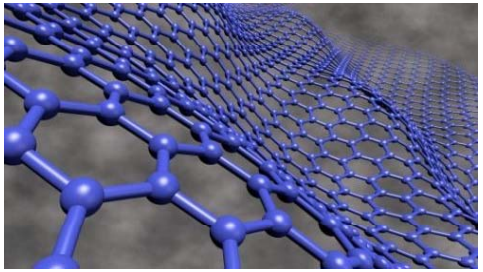
Outline

- Introduction
- Our works
  - Graphene/Silicene, g-ZnO, BP, MoS_2
  - g-C_3N_4/MoS_2, C_2N
  - Phosphorene nanoflake heterojunctions
- Conclusions

Introduction

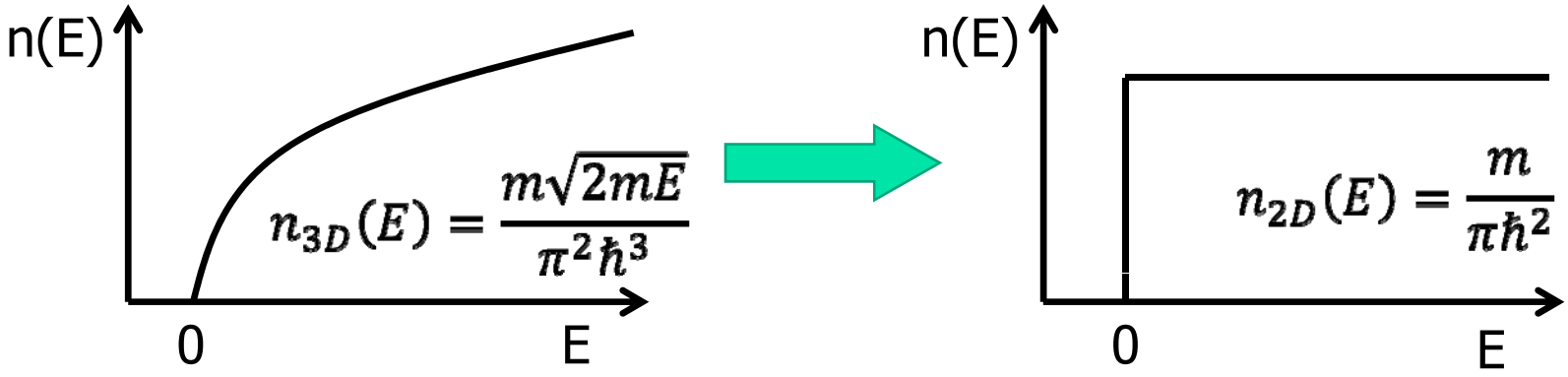
- From 3D to 2D materials

monocrystalline silicon

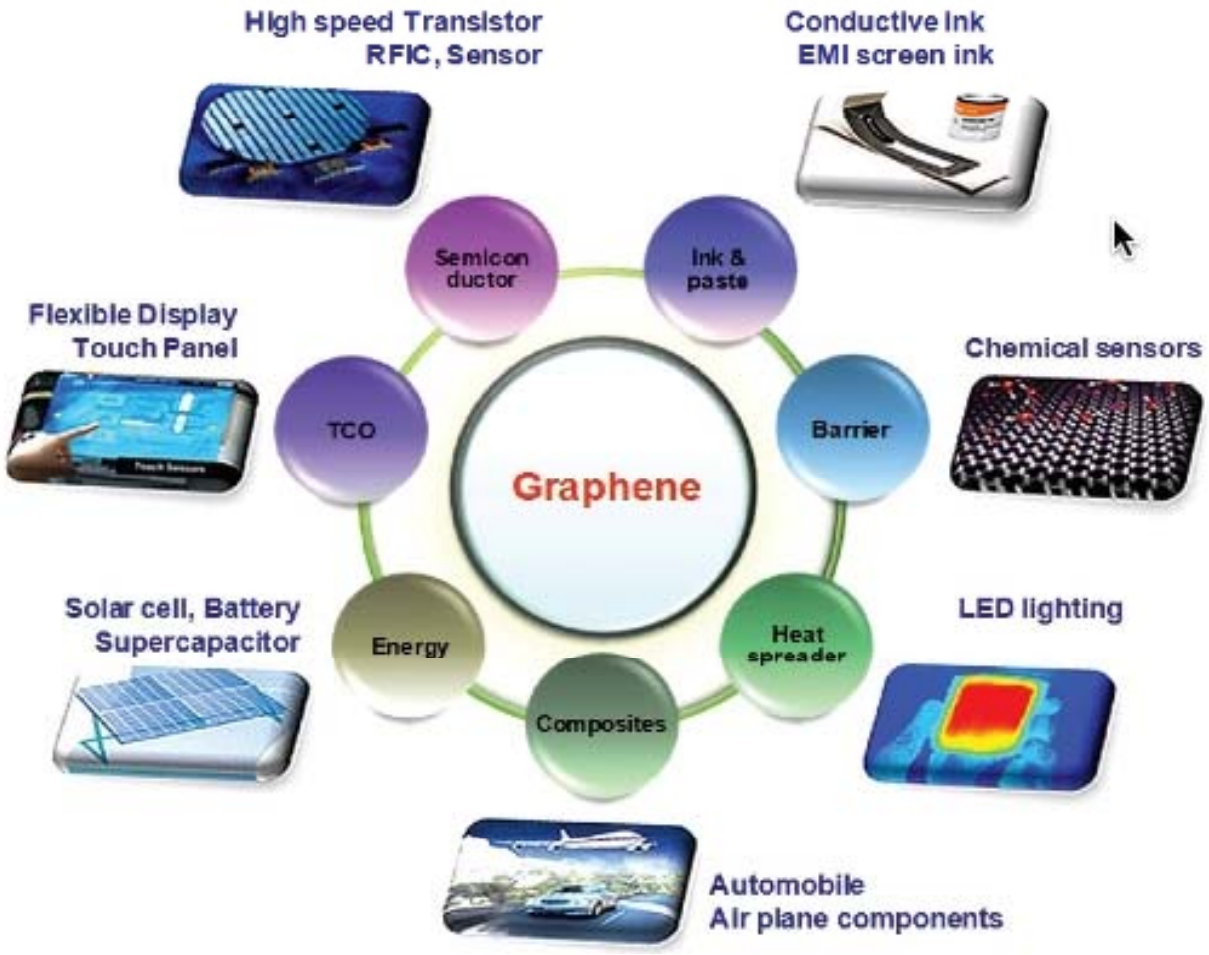


graphene

- Free electron DOS (per volume) in 2D and 3D

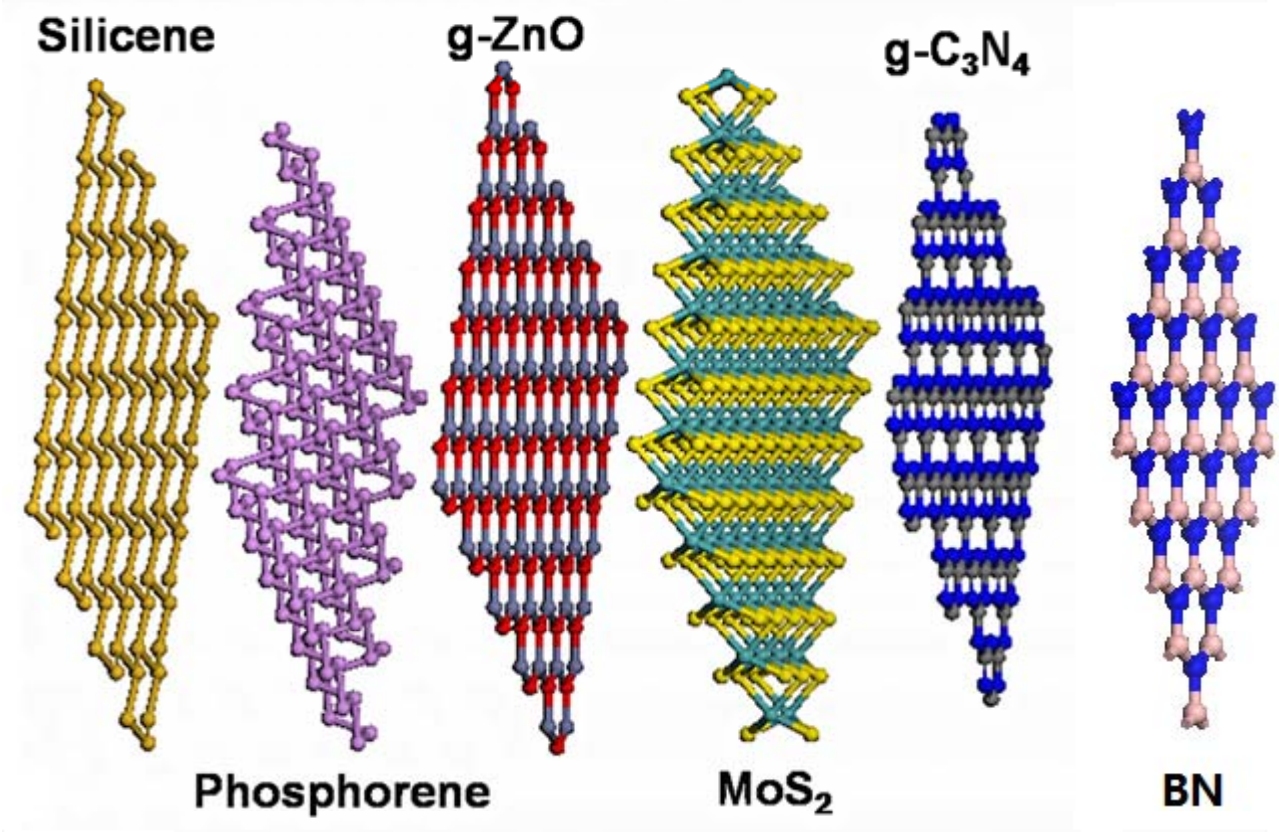


Superiority of graphene



Nature 2005, 438, 7065; *Phys. Rev. Lett.* 2006, 96, 136806; *Nature* 2007, 448, 571; *Nature Mater.* 2007, 6, 183; *Science* 2008, 320, 5881; *Science* 2008, 321, 385; *Nano Lett.* 2008, 8, 902; *Phys. Rev. B* 2009, 80, 245406; *Adv. Funct. Mater.* 2009, 19, 3077; *Science* 2013, 340, 6139.

Other 2D materials



[1] *Phys. Rev. Lett.* 2012, 108, 155501;
[2] *Nature Nanotech.* 2014, 9, 372;
[3] *Phys. Rev. Lett.* 2007, 99, 026102;
[4] *Phys. Rev. Lett.* 2010, 105, 136805;
[5] *Nature Mater.* 2009, 8, 76;
[6] *Nature Mater.* 2004, 3, 404.

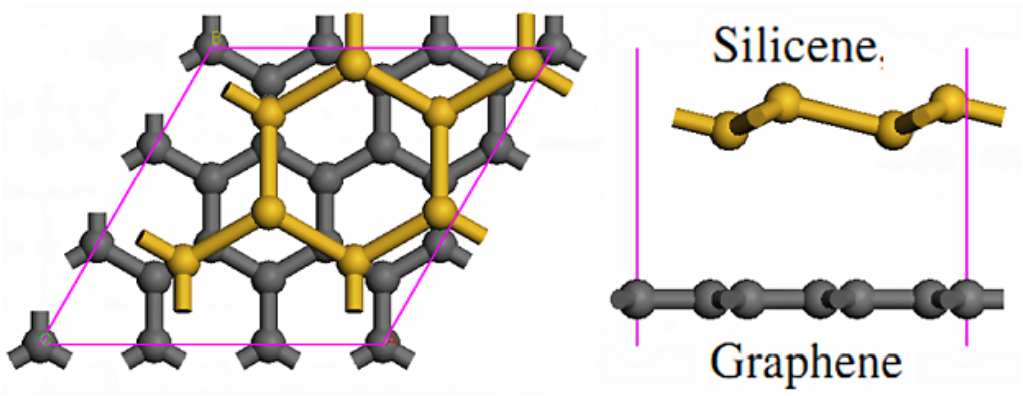
Why 2D van der Waals heterojunctions?

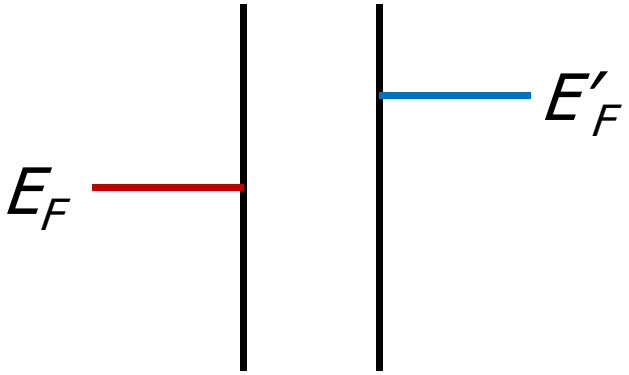
- Simplest junction. Interface is clean and controllable
  - Junction -> element of devices
- Extend properties of 2D materials
  - Bandgap opening, electric field response
- New phenomena and applications
  - Schottky and ohmic contacts, tunable self-doping
  - Water splitting, solar cells

Classification

- Metal/Metal
  - Graphene/Silicene
- Metal/Semiconductor
  - Graphene/Phosphorene, Graphene/g-ZnO, Graphene/MoS_2
- Semiconductor/Semiconductor
  - g-C_3N_4/MoS_2, Bi-layer blue phosphorus
  - Phosphorene Nanoflake Heterojunctions

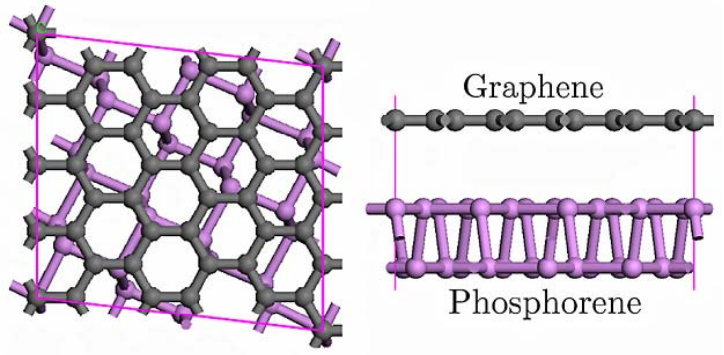
Metal/Metal

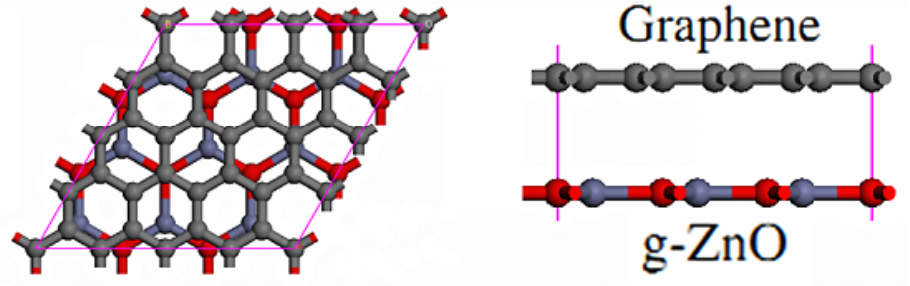


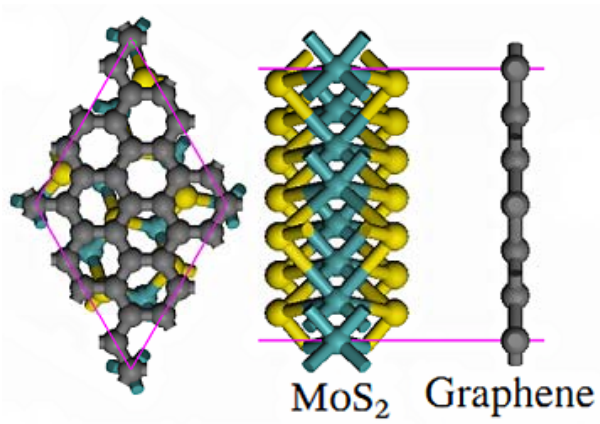


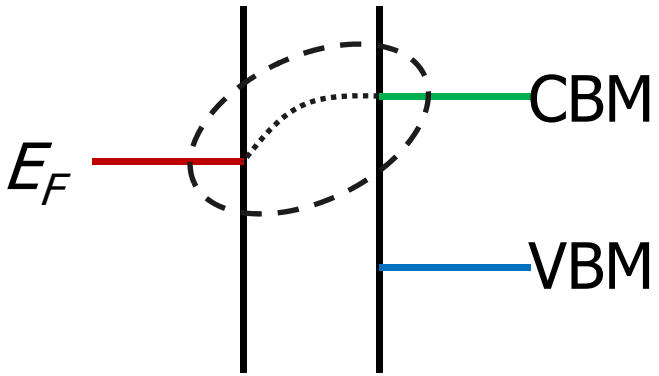
- Charge transfer
- Self-doping

Metal/Semiconductor



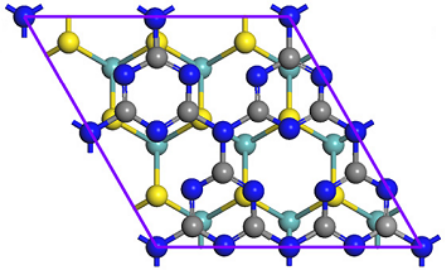


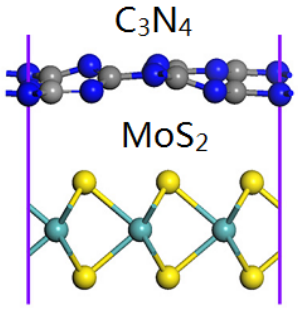


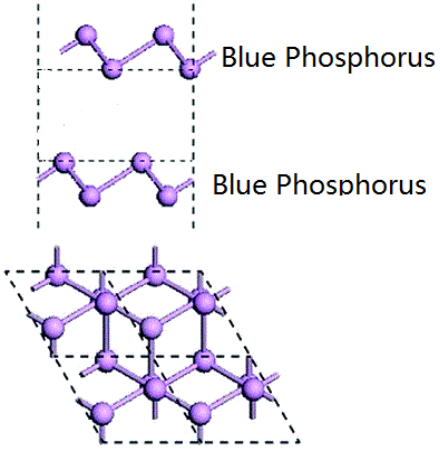


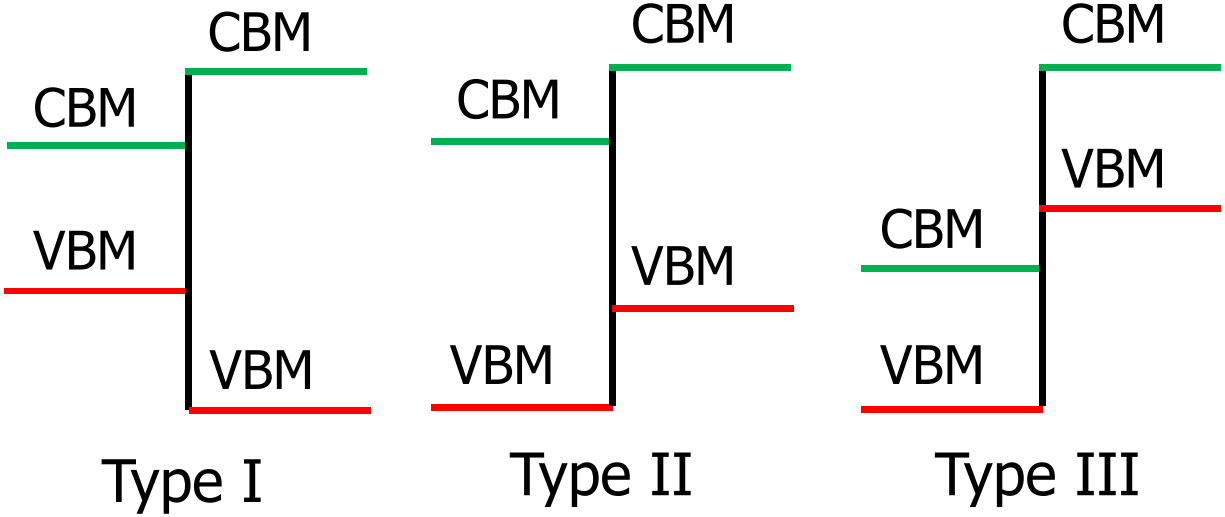
- Charge transfer
- Schottky or ohmic contact

Semiconductor/Semiconductor





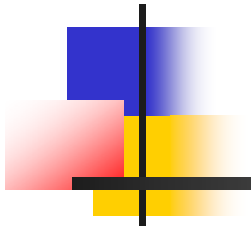




➢ Energy level alignment

Our works

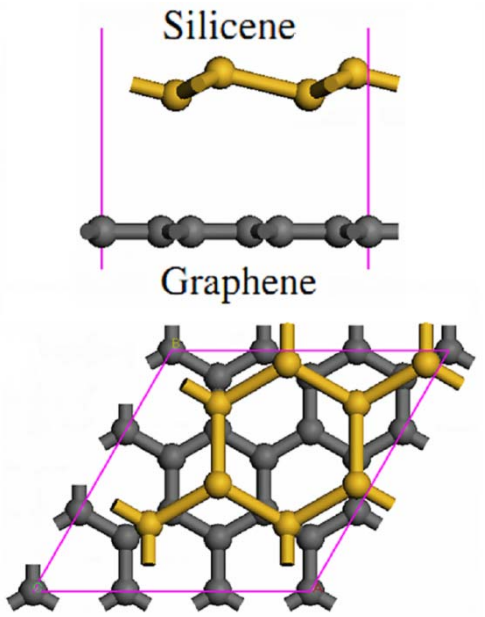
- Graphene/Silicene, g-ZnO, BP, MoS_2
  - Tuning properties of Graphene
- g-C_3N_4/MoS_2, C_2N
  - Visible light-driven water splitting
- Phosphorene nanoflake heterojunctions
  - Highly efficient solar cells

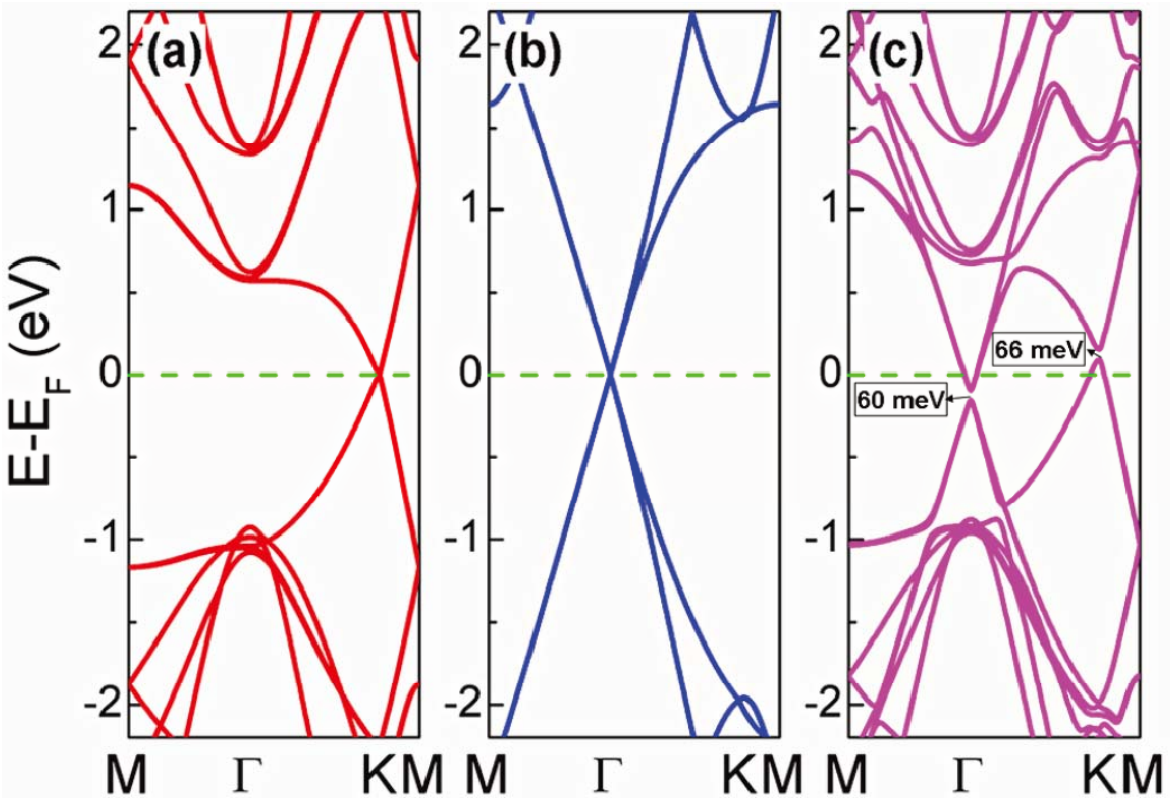


I. Tuning properties of graphene

- Graphene/Silicene
- Graphene/g-ZnO
- Graphene/Black phosphorus
- Graphene/MoS_2

Graphene/Silicene



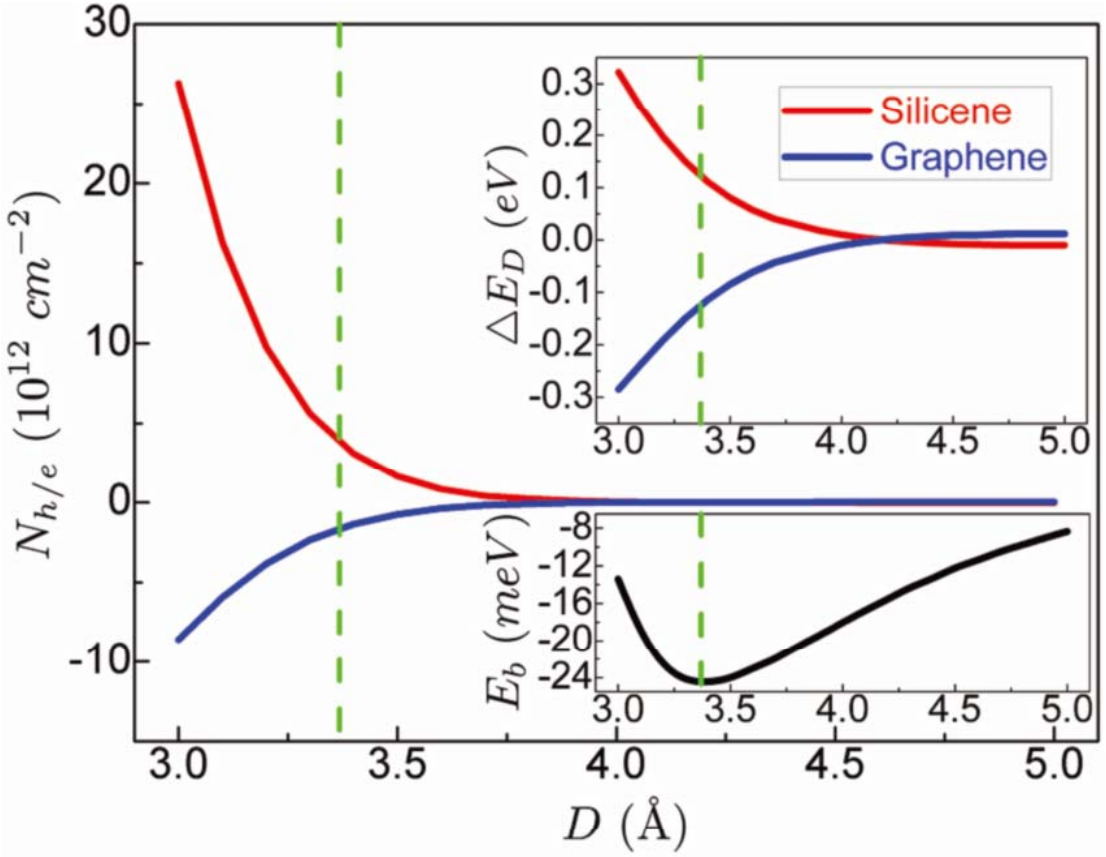


Silicene
W_f = 4.6 eV

Graphene
W_f = 4.3 eV

Silicene p-type doping
Grpahene n-type doping

Graphene/Silicene

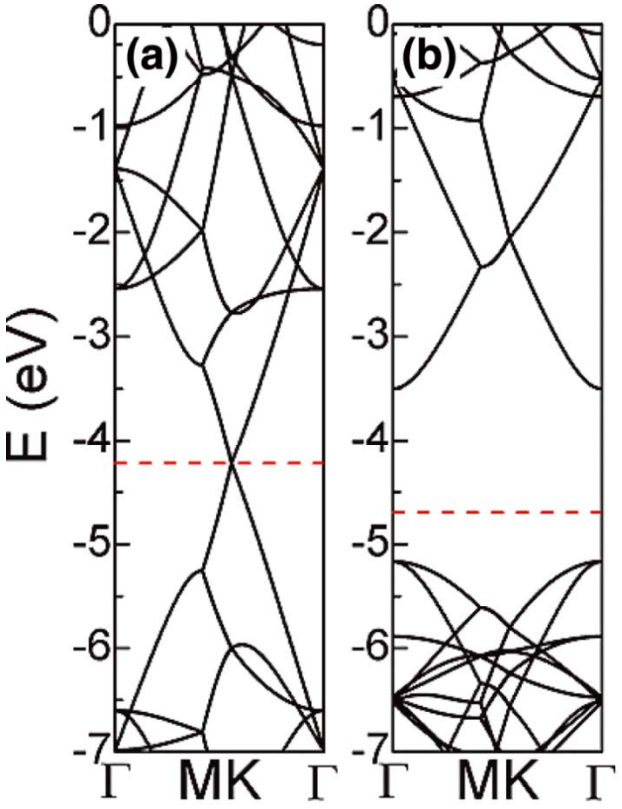


Doping charge carrier concentrations as a function of interfacial distance *D* (Å).

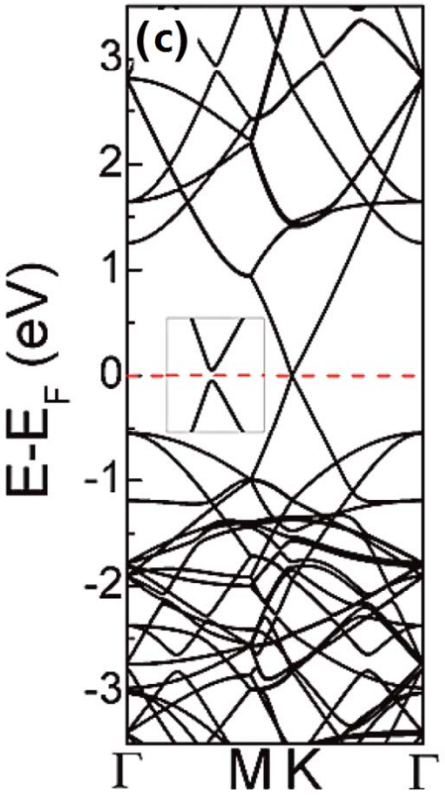
Tunable self-doping with the interfacial distance increases:

- Silicene
  p-type -> n-type
- Graphene
  n-type -> p-type

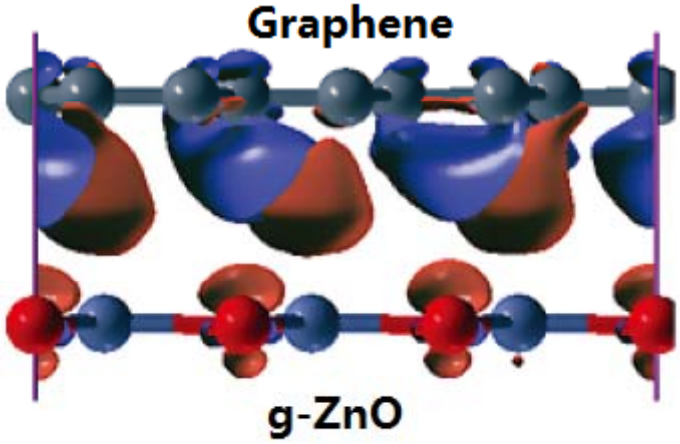
Graphene/g-ZnO



Graphene g-ZnO



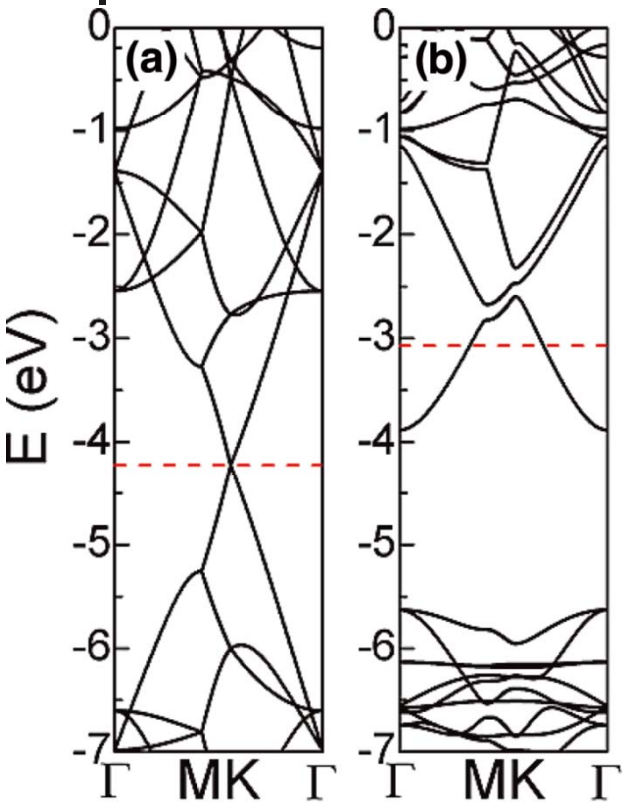
Graphene/g-ZnO



Graphene/Pristine g-ZnO

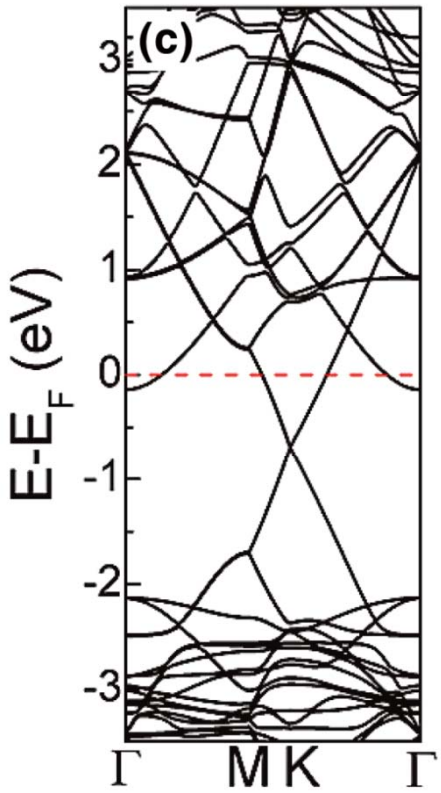
- Fermi level remains in the induced gap
- No charge transfer

Graphene/Al doped g-ZnO

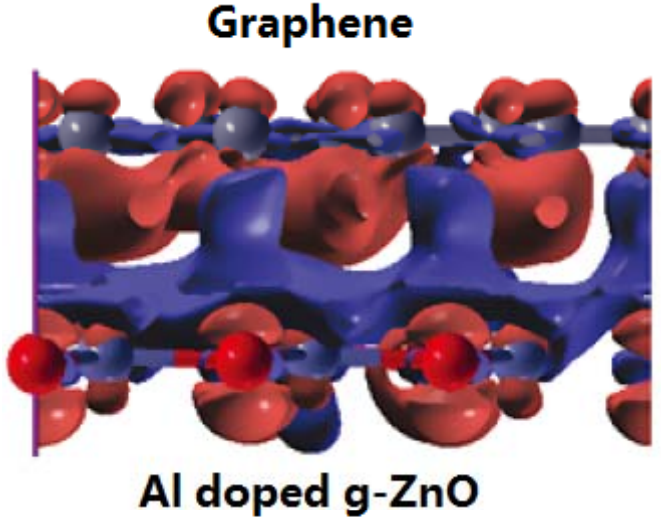


Graphene

Al doped g-ZnO



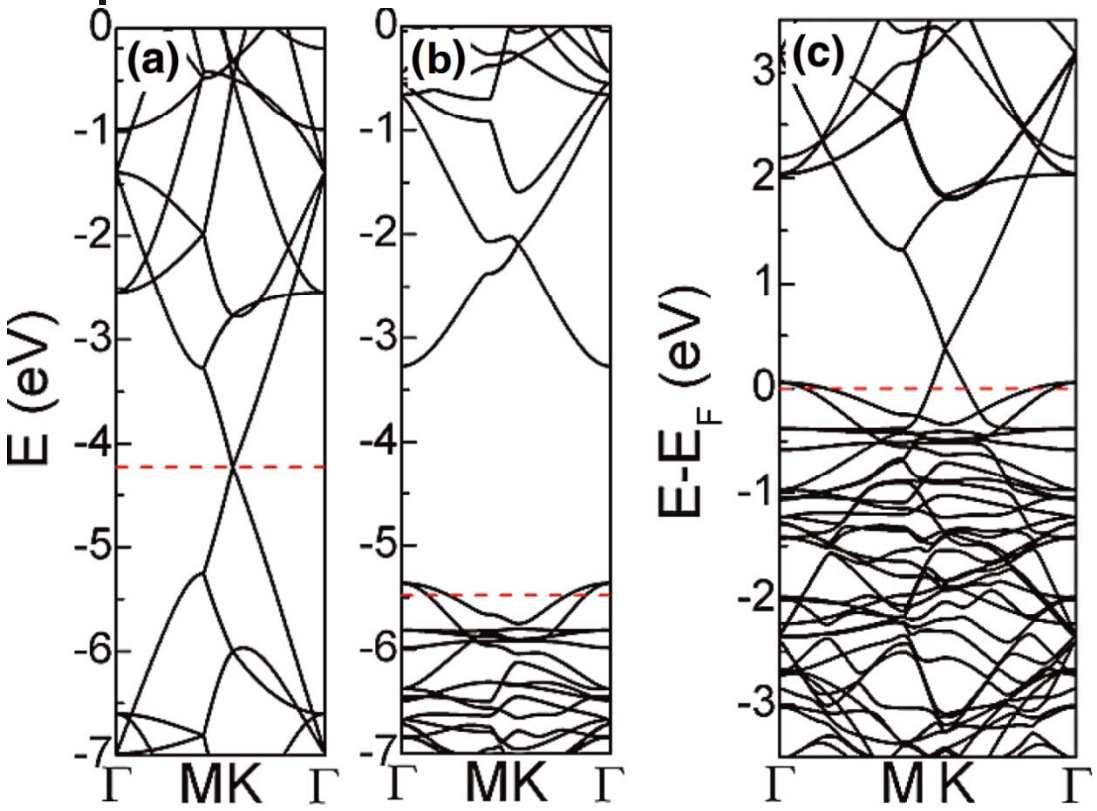
Graphene/ Al doped g-ZnO



Graphene/Al doped g-ZnO

- Al doped n-type g-ZnO
- Dirac point below the Fermi level
- Electron doping in graphene

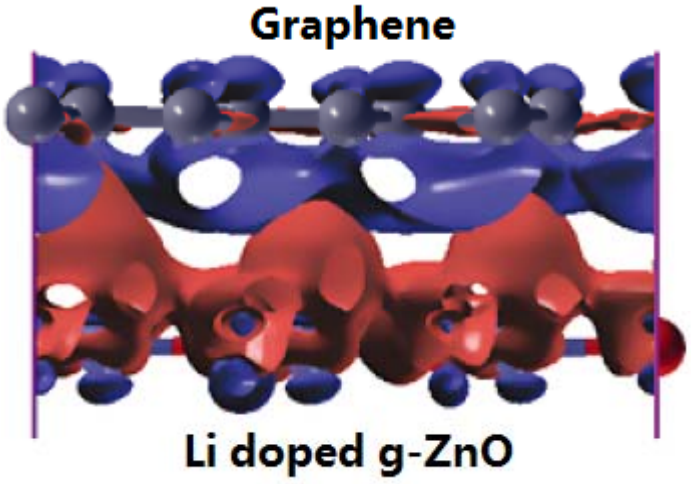
Graphene/Li doped g-ZnO



Graphene

Li doped g-ZnO

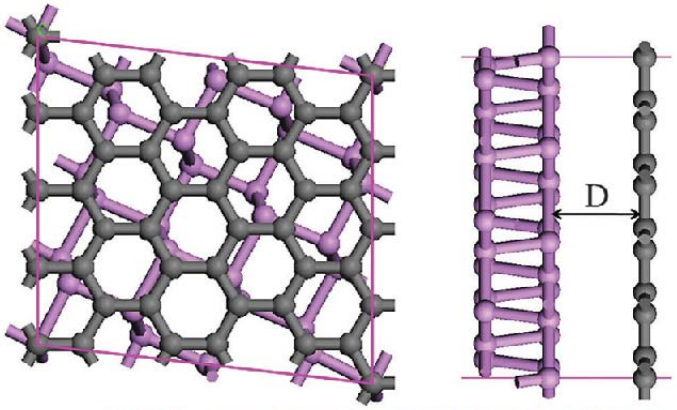
Graphene/ Li doped g-ZnO

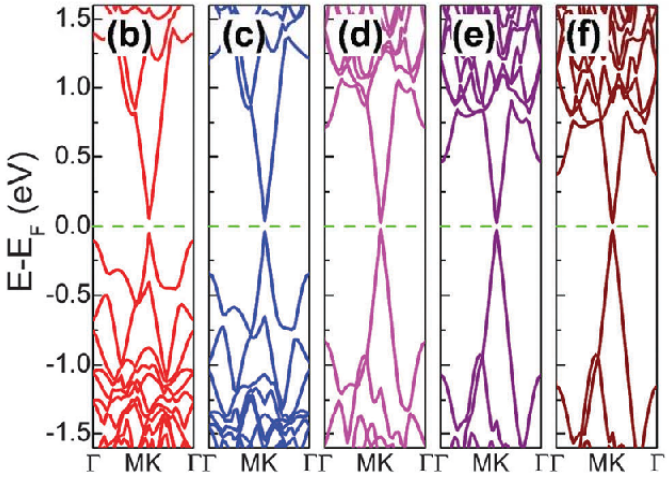


Graphene/Li doped g-ZnO

- Li doped p-type g-ZnO
- Dirac point above the Fermi level
- Hole doping in graphene

Graphene/Phosphorene



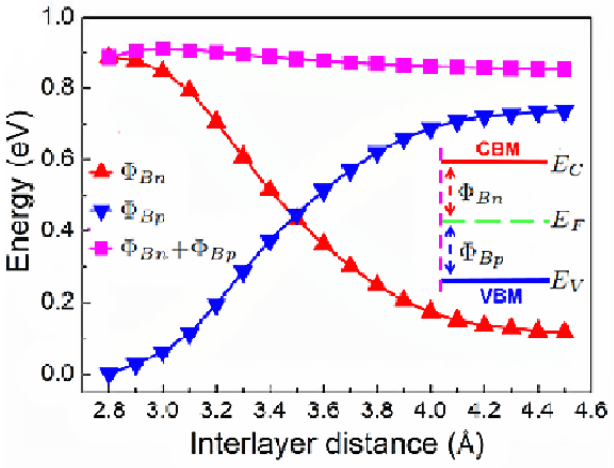


D = 2.8 3.0 3.5 4.0 4.5 (Å)

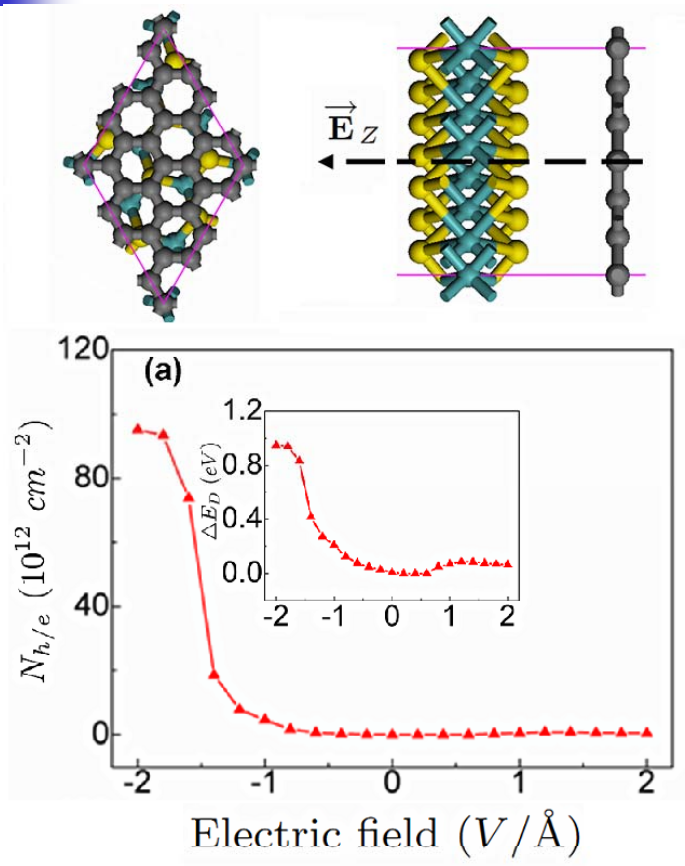
Tunable Schottky barriers with the interlayer distance increases:

- *D* < 3.5 Å, p-type Schottky contact
- *D* > 3.5 Å, n-type Schottky contact

Φ_{Bn}: n-type Schottky barrier
Φ_{Bp}: p-type Schottky barrier

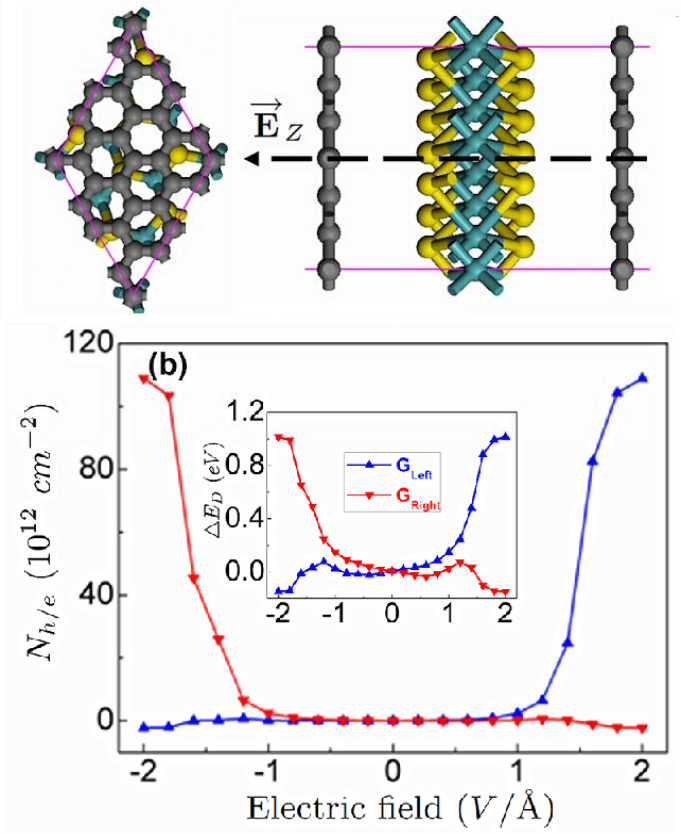


Graphene/MoS_2



Applying electric fields perpendicular to graphene/MoS_2, tunable p-type doping of graphene is very easy to achieve.

Graphene/MoS_2/Graphene



Applying electric fields perpendicular to graphene/MoS_2/graphene, tunable p-type doping of graphene is very easy to achieve, while graphene on the other side is weak n-type doped.

Summary

- Tunable self-doping can be obtained in graphene/silicene by
  - Interlayer distance

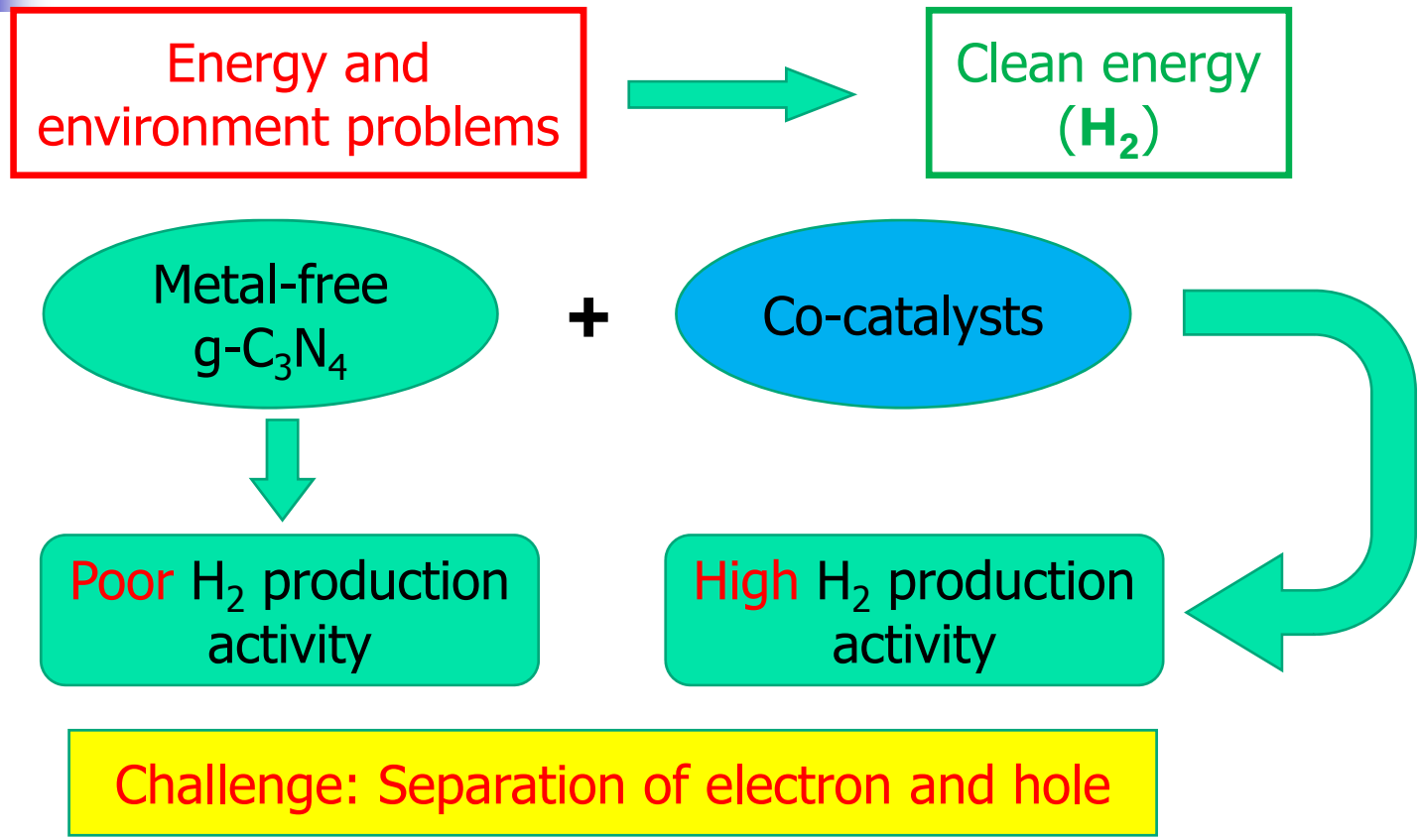
- Tuning properties of graphene can be achieved in graphene/semiconductor composites by
  - Doping type of semiconductor
  - Interlayer distance
  - Vertical electric fields

Review: Hu-Yang, Comput. Mat. Sci. 112, 518 (2016)

II. Visible light-driven water splitting

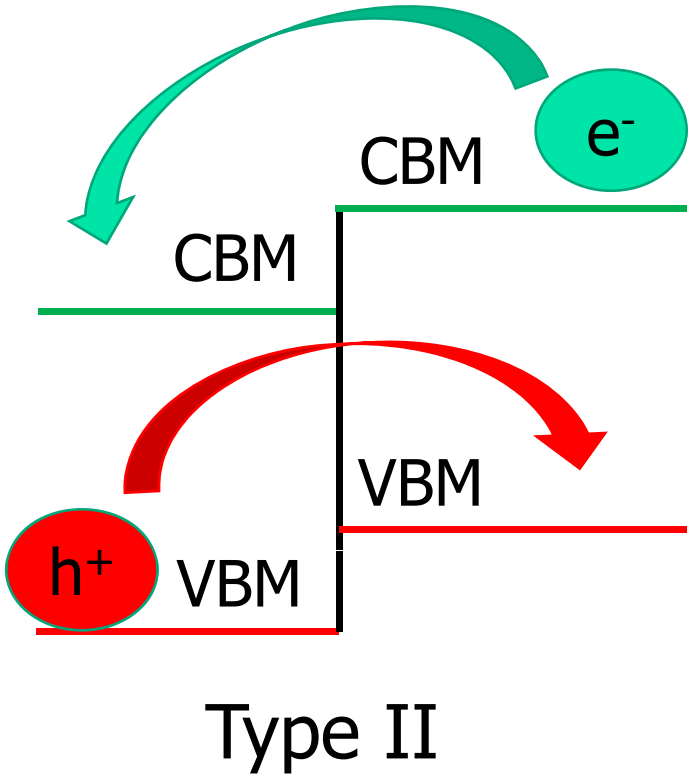
- $g\text{-}C_3N_4/MoS_2$
- $g\text{-}C_3N_4/C_2N$

Background

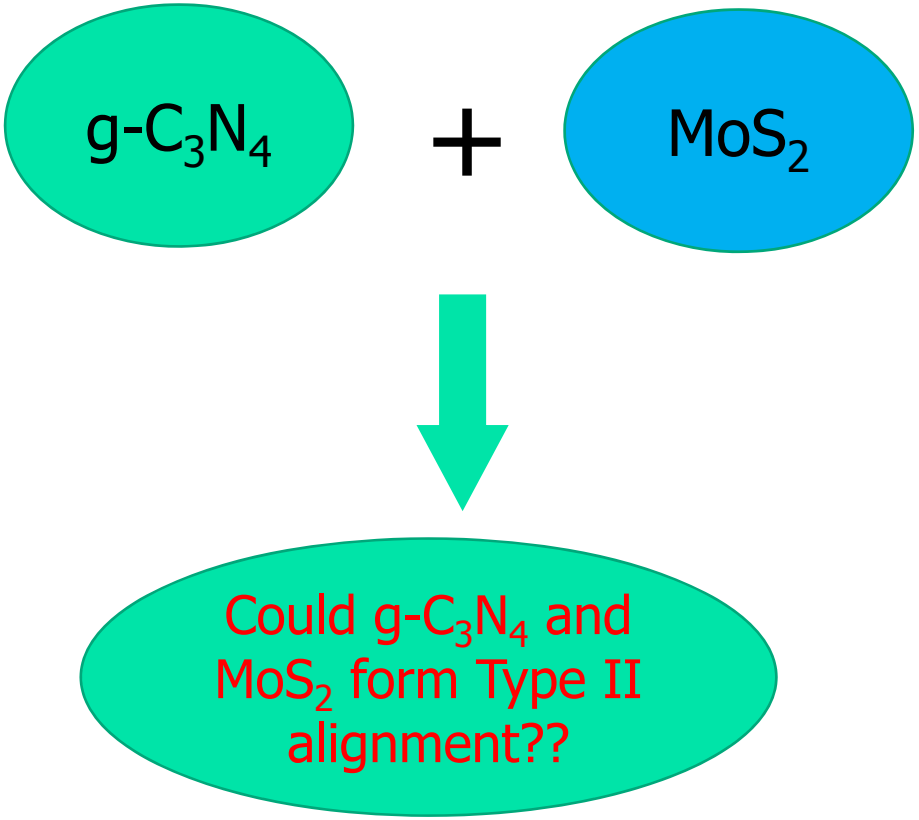


Wang, Maeda, Thomas, et al., *Nat. Mater.* **2008**, *8*, 76; Maeda, Wang, Nishihara, et al., *J. Phys. Chem. C* **2009**, *113*, 4940; Di, Wang, Thomas, Anonietti, *ChemCatChem* **2010**, *2*, 834; Hou, Laursen, Zhang, et al., *Angew. Chem. Int. Ed.* **2013**, *52*, 3621.

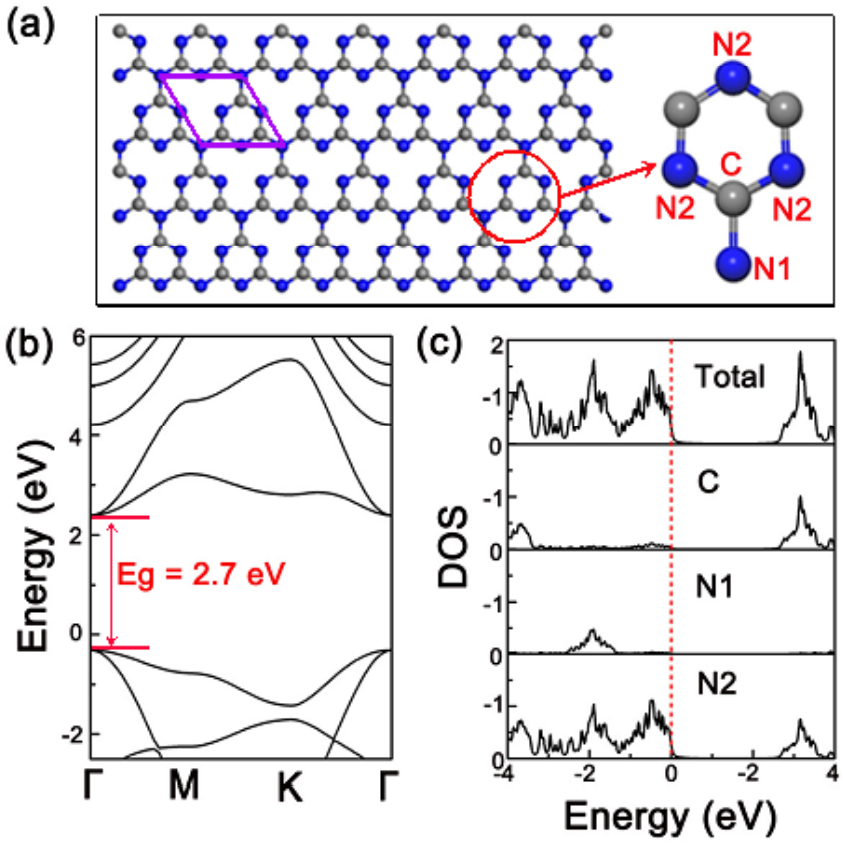
Solution



Type II

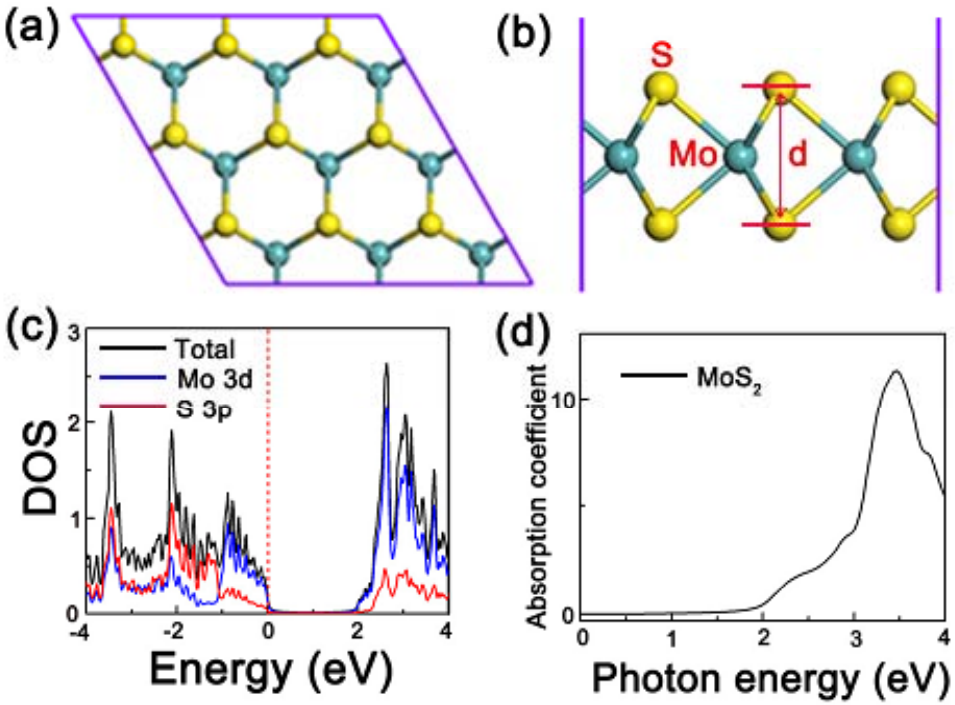


Monolayer of g-C_3N_4



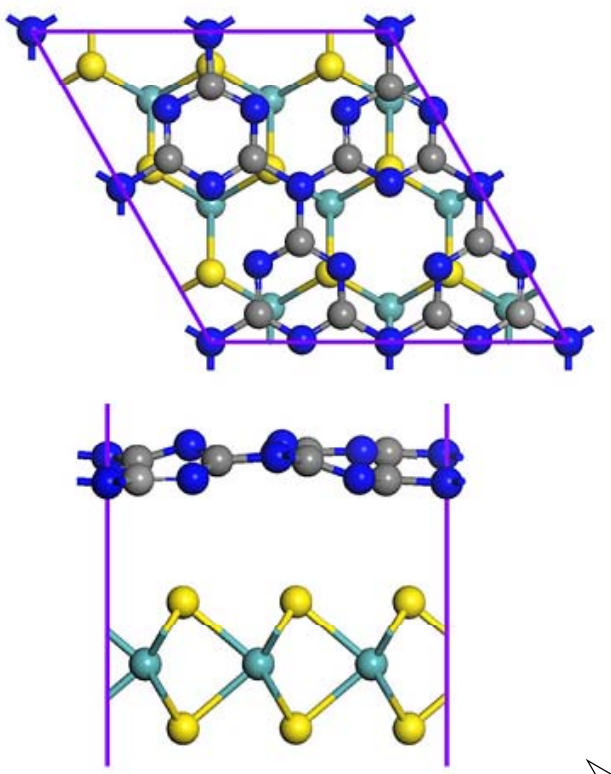
- $d_{C\text{-}N1}$ = 1.47 Å, $d_{C\text{-}N2}$ = 1.33 Å
- Direct band gap of 2.7 eV
- VBM is dominated by N2
- CBM is contributed by C and N2

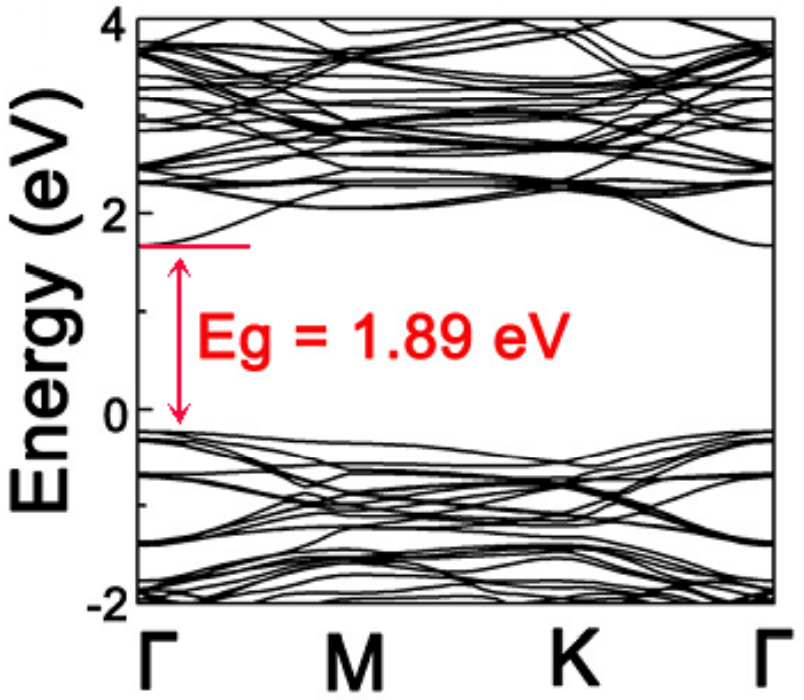
Monolayer of MoS_2



- $d_{Mo\text{-}S}$ = 2.42 Å, $d_{S\text{-}S}$ = 3.13 Å
- Direct band gap of 2.0 eV
- VBM and CBM are all mainly contributed by Mo 4d orbitals and S 3p

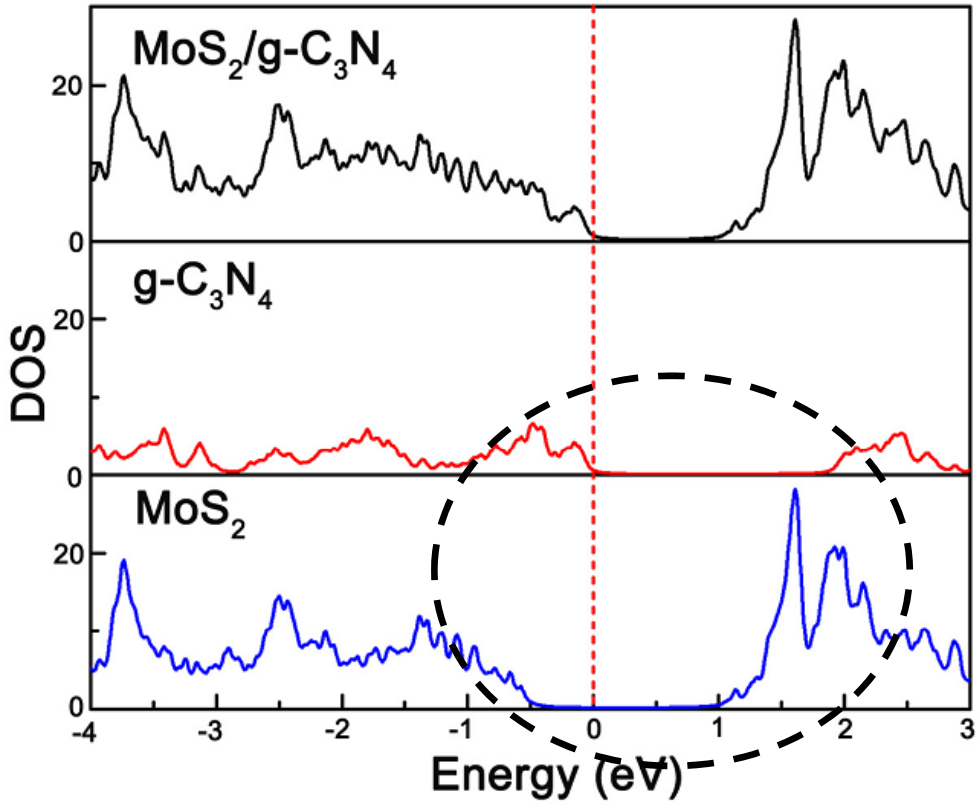
Geometry and band structure





- Interlayer distance is 2.97 Å
- Direct band gap of 1.89 eV at the Γ points

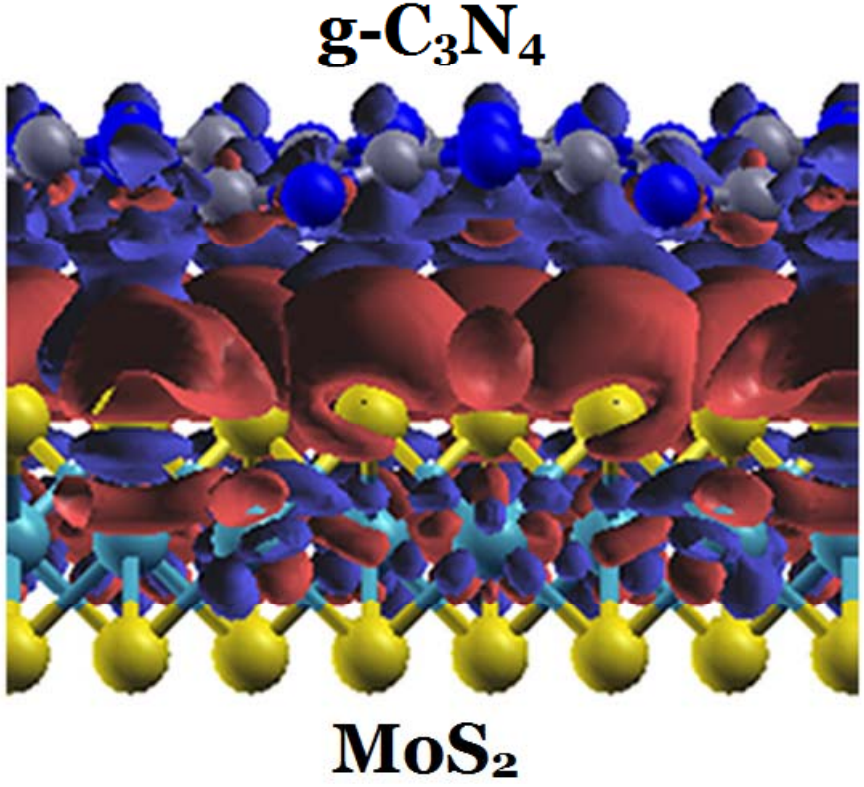
Total and partial DOS



- VBM is mainly contributed by g-C_3N_4
- CBM is dominated by MoS_2

Type II heterostructure is constructed.

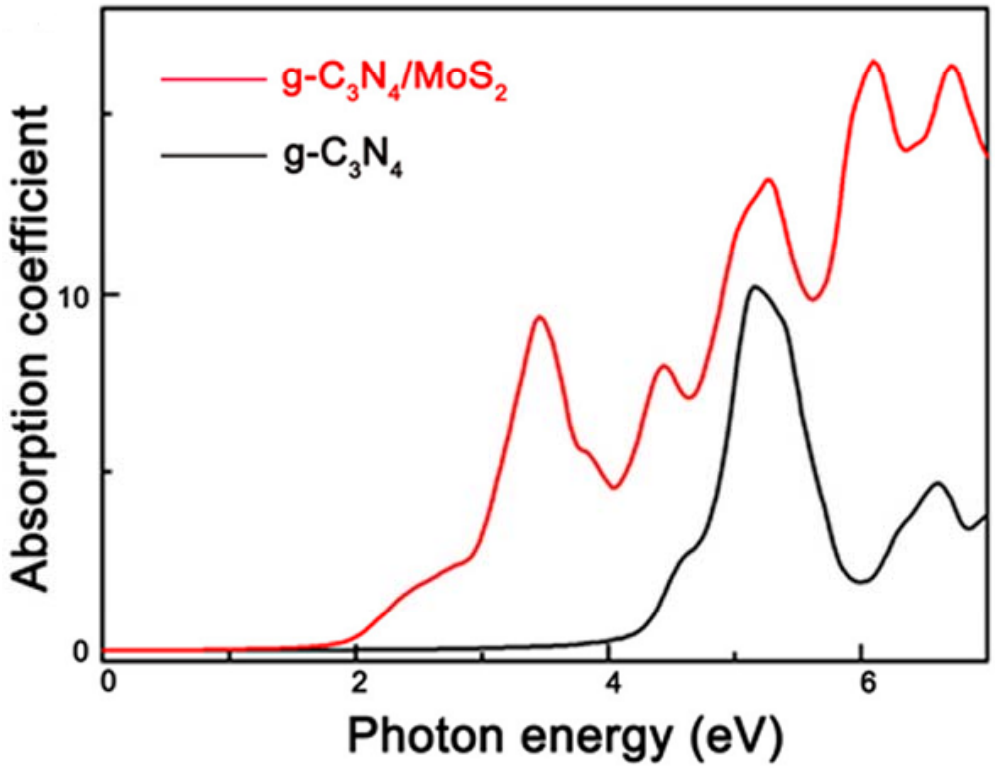
Charge transfer



- Charge transfer from g-C_3N_4 to MoS_2

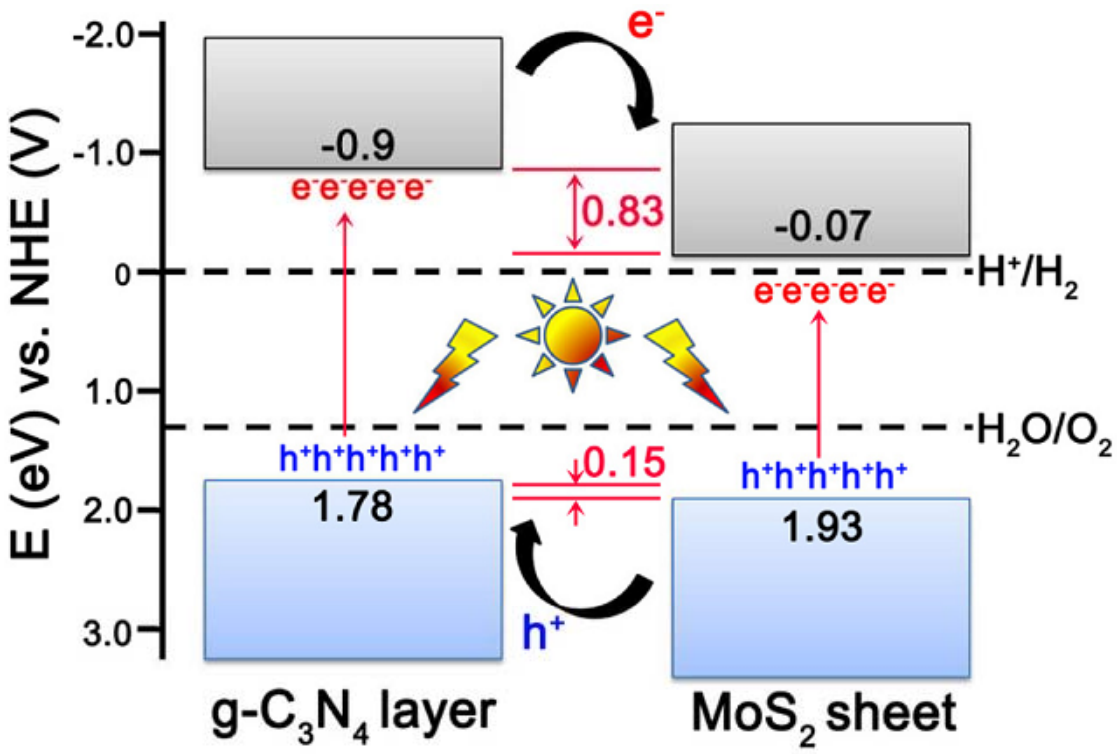
Red and blue regions represent charge accumulation and depletion, respectively.

Optical absorption



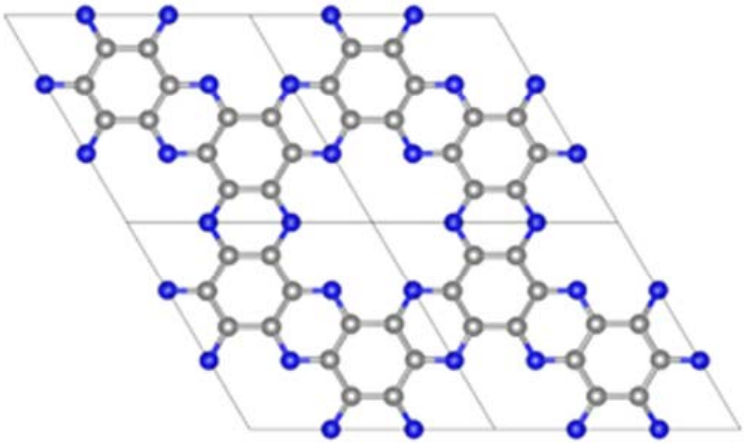
$g\text{-}C_3N_4/MoS_2$ nano-composite exhibits more effective UV absorption and enhanced low-energy visible light response than $g\text{-}C_3N_4$ monolayer.

Carrier transfer and separation

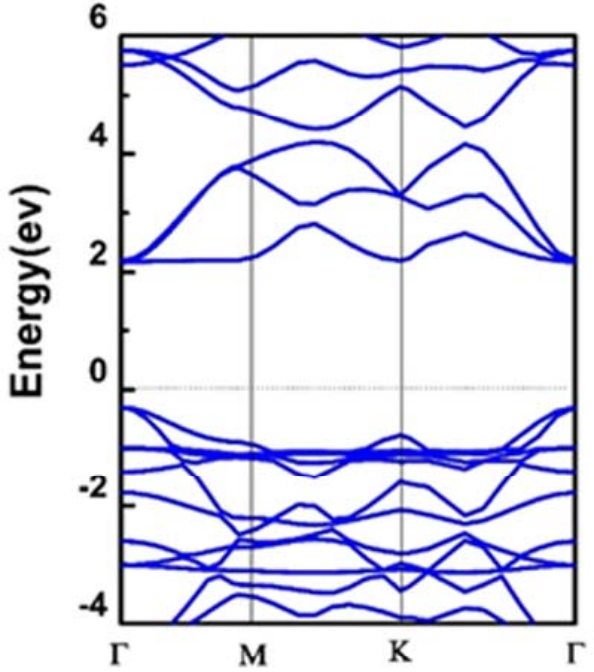


- The VB offset is 0.15 eV
- The CB offset is 0.83 eV
- Electrons transfer from CB of g-C_3N_4 to CB of MoS_2
- Holes transfer from VB of MoS_2 to VB of g-C_3N_4

Monolayer of C_2N



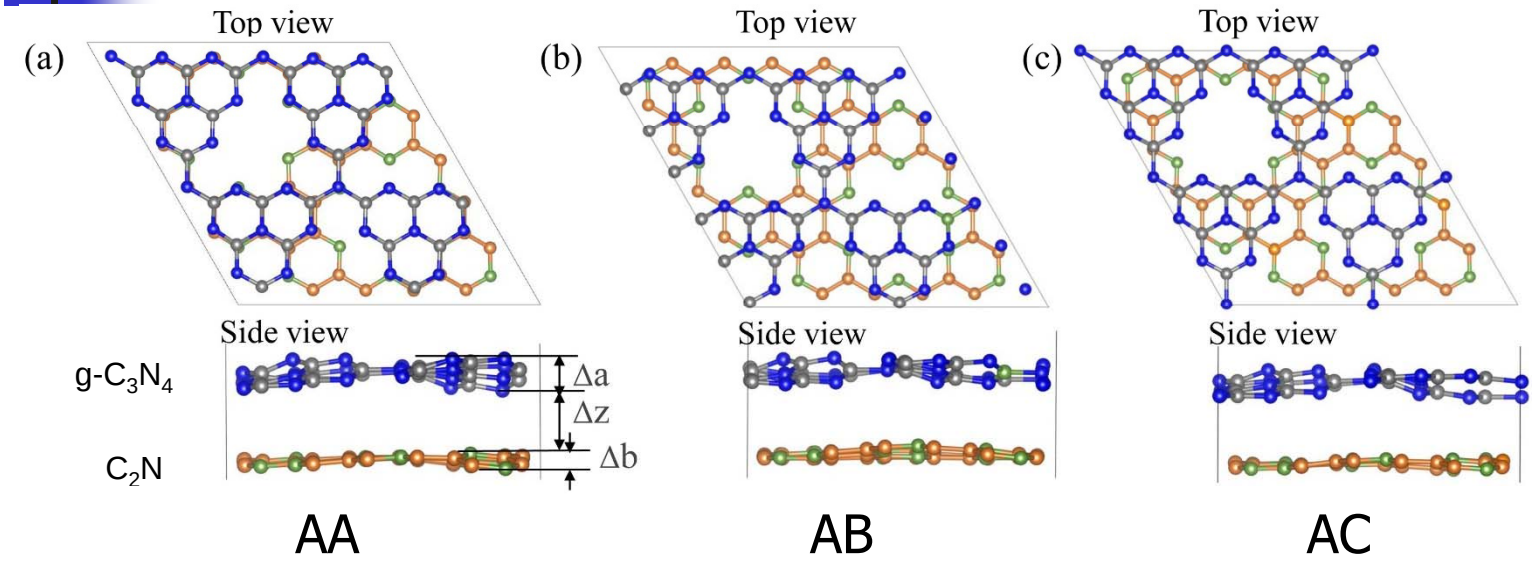
structure



band structure

- Direct band gap of monolayer C_2N is 2.47 eV

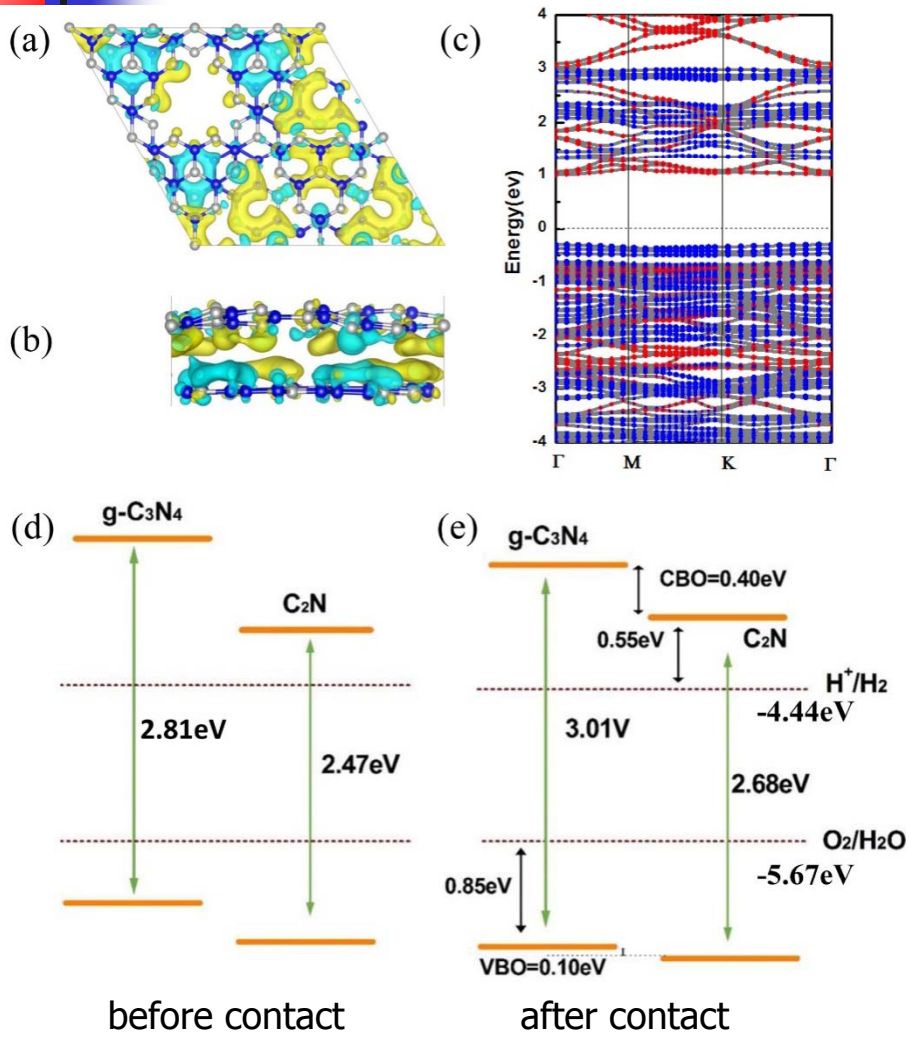
g-C_3N_4/C_2N nanocomposite



Stacking order	Δz (Å)	Δa (Å)	Δb (Å)	E_b (meV/Å^2)
AA	2.66	1.08	0.36	-16.1
AB	2.64	0.98	0.32	-16.2
AC	2.56	0.93	0.28	-16.9

- AC stacking is the most stable
- The buckling of g-C_3N_4

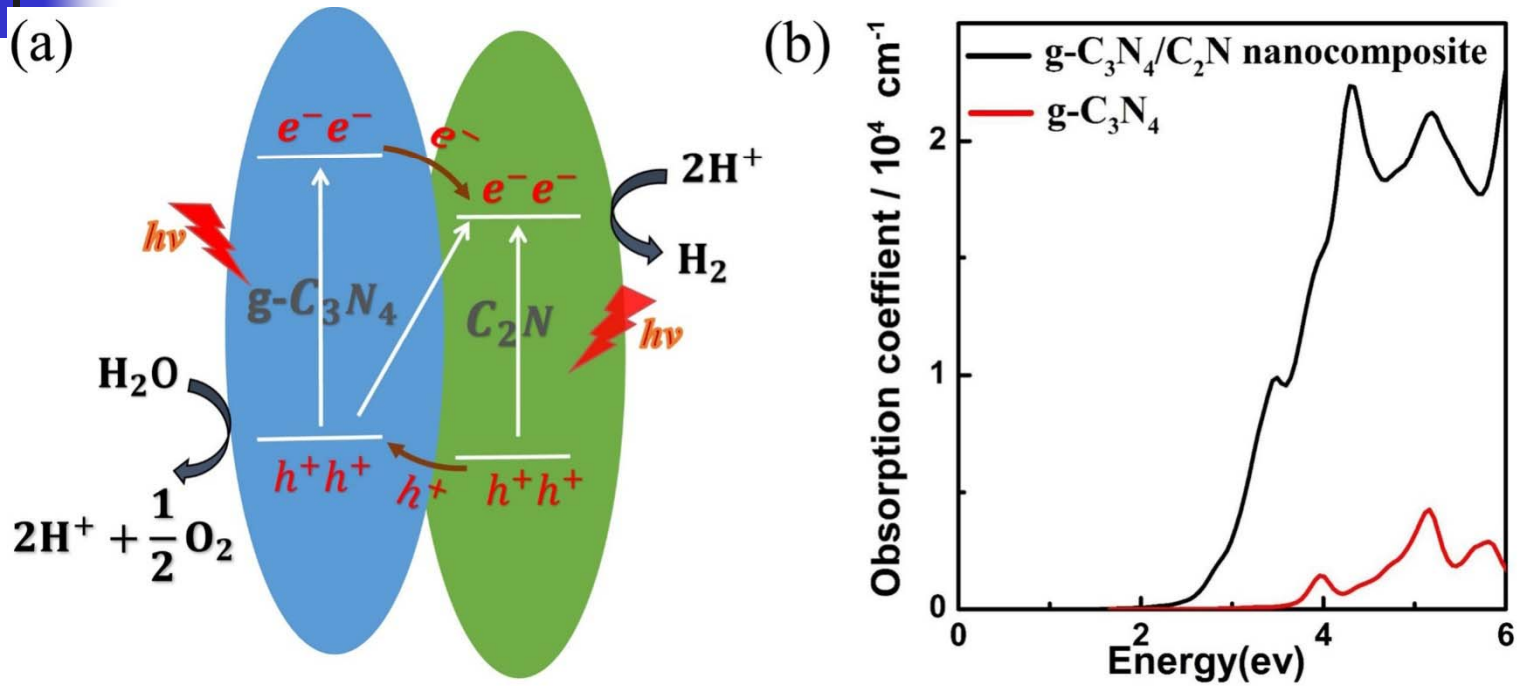
Charge redistribution & band alignment



- g-C_3N_4 layer induces electron-rich and hole-rich regions in the C_2N layer
- VBM is mainly contributed by g-C_3N_4
- CBM is dominated by C_2N

Type II band alignment

Charge separation & Optical absorption



- Three paths of separation: **1)** photo-generated electrons in CBM of g-C_3N_4 migrate to CBM of C_2N, **2)** photo-generated holes in VBM of C_2N transfer to VBM of g-C_3N_4, **3)** electrons in VBM of g-C_3N_4 can be directly excited to CBM of C_2N due to interlayer coupling.

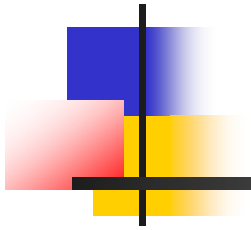
- g-C_3N_4/C_2N nanocomposite exhibits significantly enhanced UV and visible light absorption than g-C_3N_4 monolayer.

Summary

- The g-C_3N_4/MoS_2 (C_2N) nanocomposite constructs type II band alignment heterojunction.

- With the benefit of type II heterojunction, the separation of electron and hole will be more efficient.

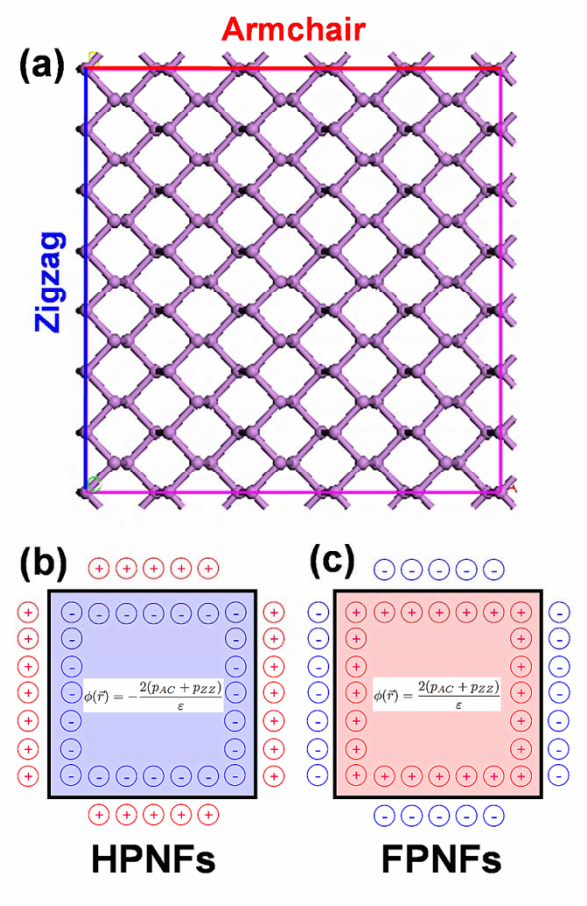
Wang-Guan-Huang-Li-Yang, J. Mater. Chem. A 2, 7960 (2014)
Wang-Li-Yang, ChemPhysChem, 10.1002/cphc.201600209(2016)



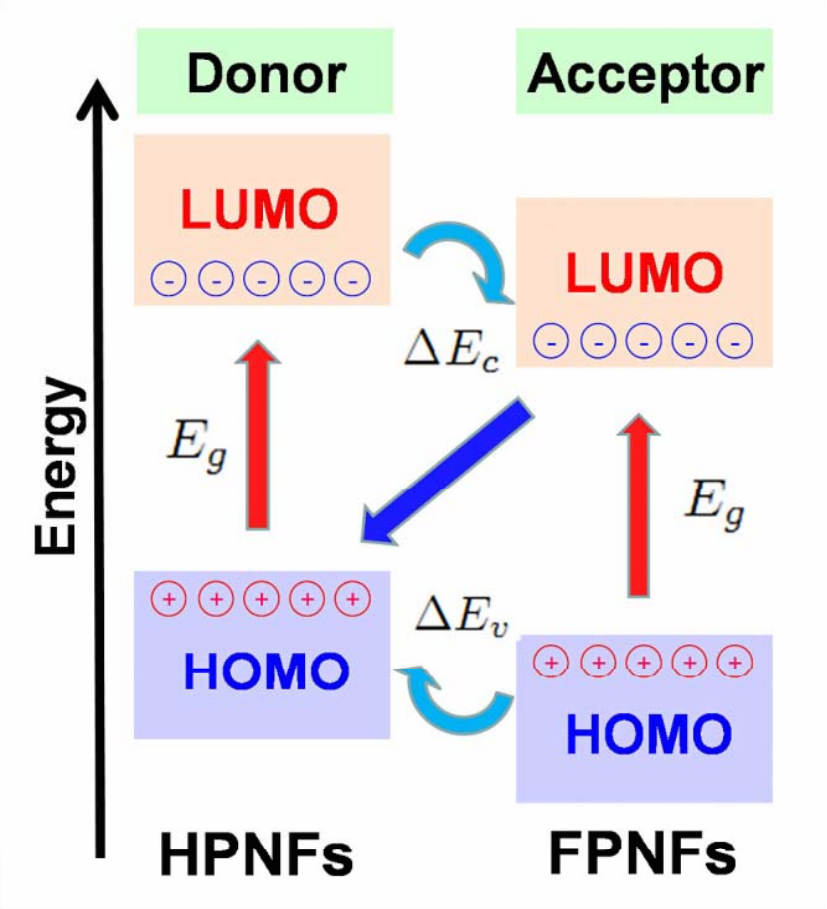
III. Highly efficient solar cells

- Phosphorene nanoflake heterojunctions

Edge-modified PNF heterobilayer



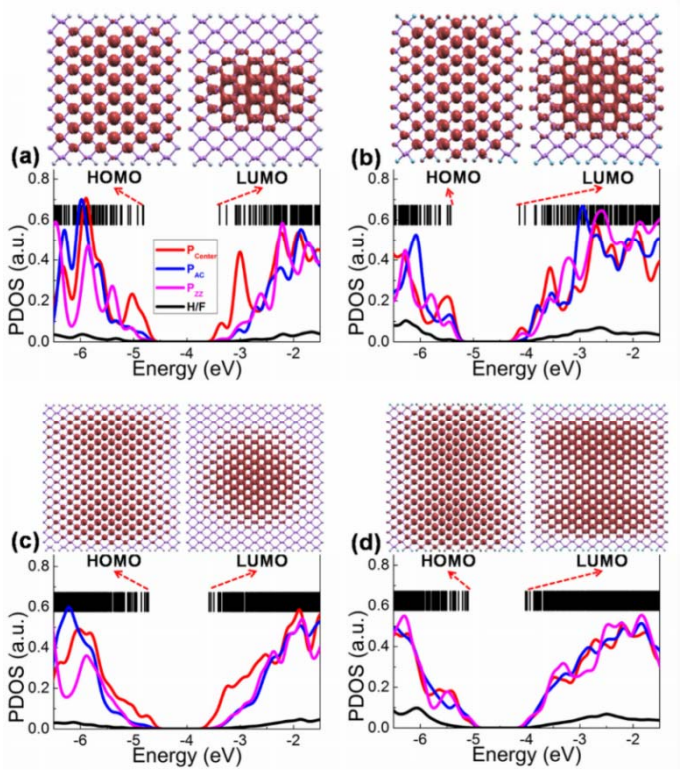
Edge dipole induced potential shift

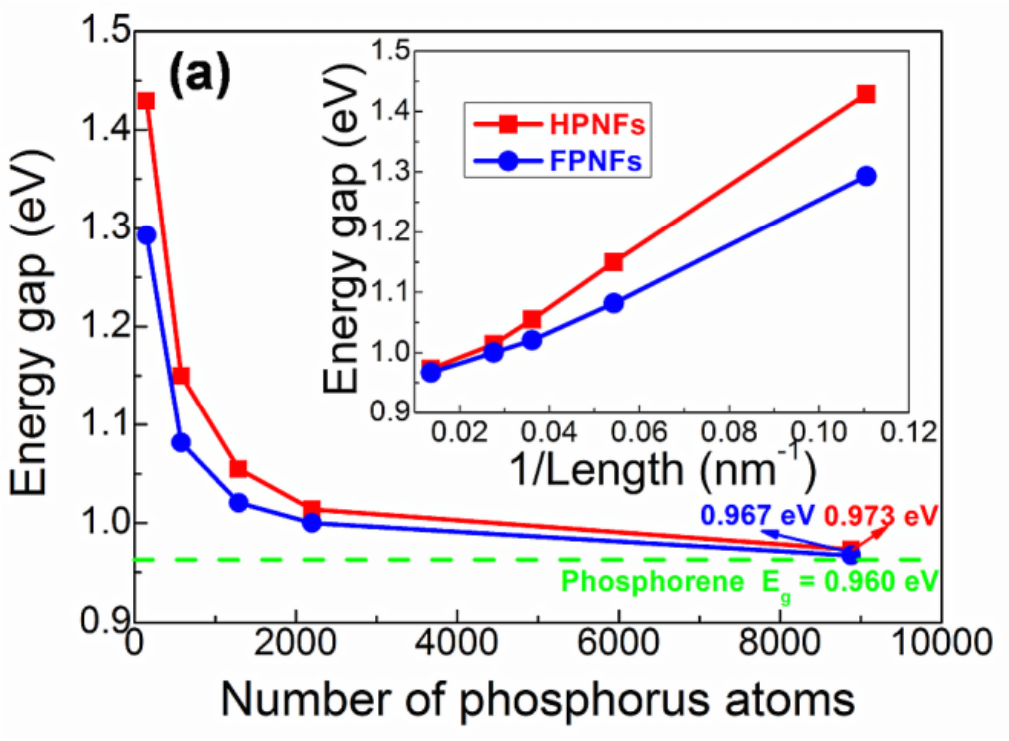


Type-II band alignment

Edge states and energy gaps

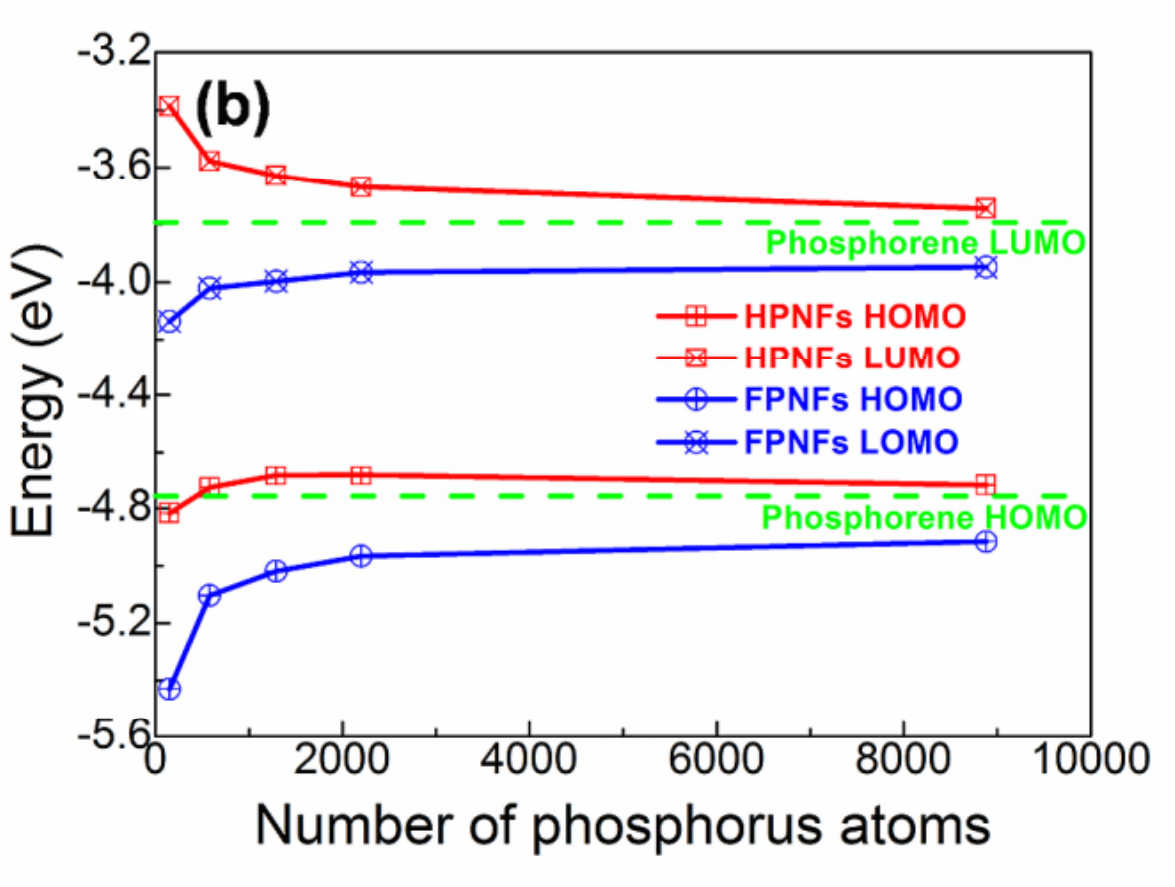
- No edge states in HOMO/LUMO in PNFs
- Edge decoration has little effect on gaps





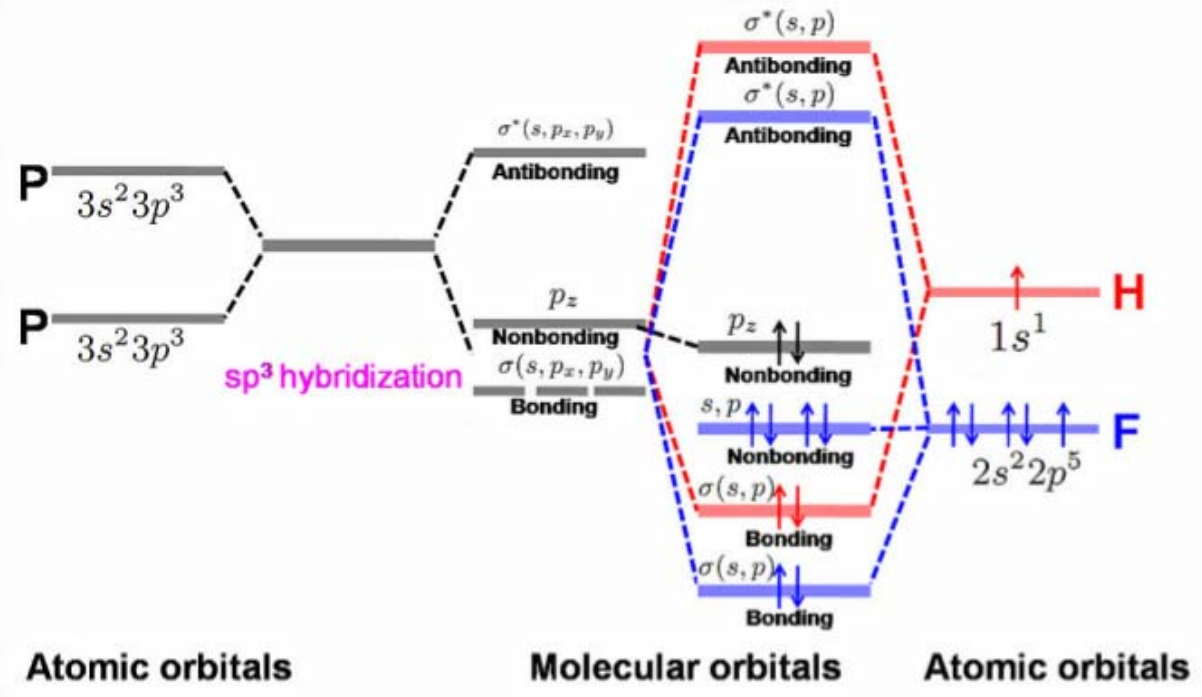
HOMO/LUMO energy

- Edge decoration has strong effect



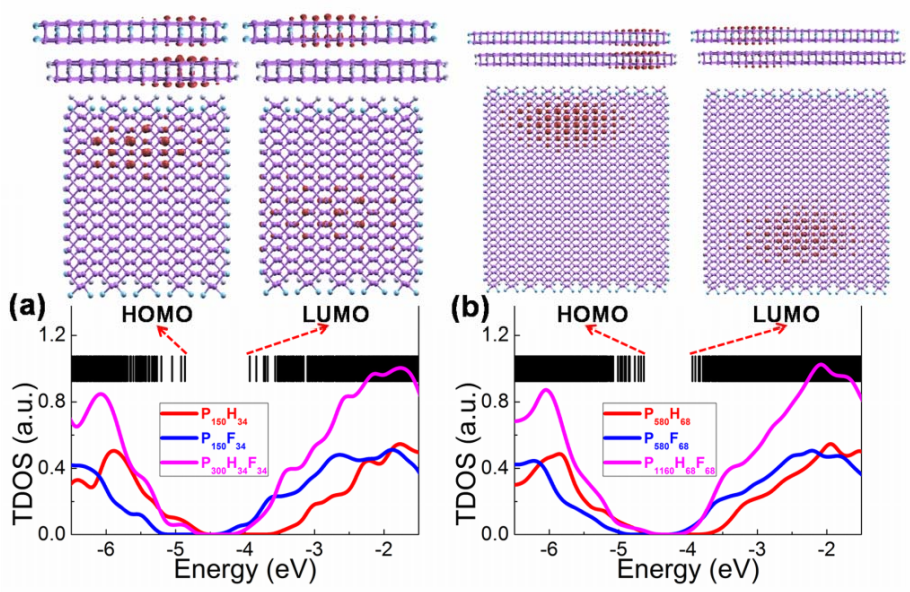
Hybrid molecular orbital diagram

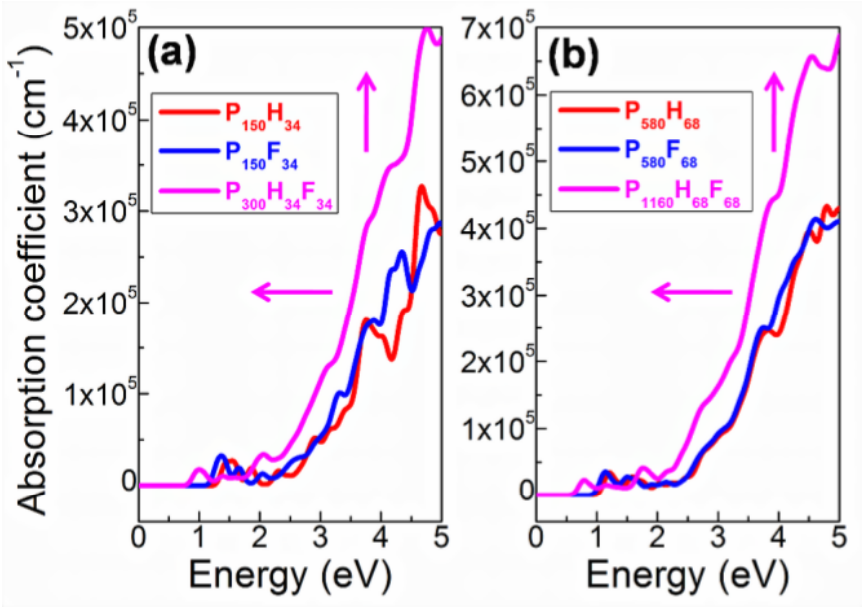
- P-H and P-F bonds are more stable
- HOMO/LUMO states are from inner P atoms



HPNF/FPNF heterobilayer

- Small HOMO/LUMO energy gaps
- Separated HOMO/LUMO states
- Enhanced light absorption





PNF heterojunction solar cells

- Power conversion efficiency ~ 20%

  Energy gap (1.5 eV) and conduction band offset (0.15 eV)

$$\eta = \frac{0.65(E_g - \Delta E_c - 0.3)\int_{E_g}^{\infty} \frac{P(\hbar\varpi)}{\hbar\varpi} \mathrm{d}(\hbar\varpi)}{\int_0^{\infty} P(\hbar\varpi)\mathrm{d}(\hbar\varpi)}$$

- Phosphorene/MoS_2 (16-18%)
- PCBM/CBN (10-20%)
- g-SiC_2 (12-20%)

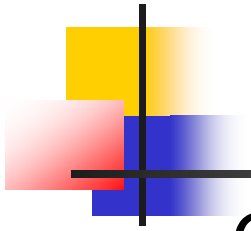
Summary

- Propose edge-modified PNFs as donor and acceptor heterojunction solar cells
- No edge states in HOMO/LUMO in PNFs
- Edge decoration has little effect on gaps
- Small HOMO/LUMO energy gaps
- Separated HOMO/LUMO states
- Enhanced light absorption

Hu-Lin-Yang-Dai-Yang, Nano Lett. 16, 1675 (2016)

Conclusions

- Weak interlayer van der Waals interactions in 2D heterojunctions can induce new properties and phenomena:
  - Bandgap opening, charge transfer and new optical absorption;
  - Self-doping, Schottky and ohmic contacts and electric field response.
- With excellent structural, electronic, electrical and optical properties combined, 2D van der Waals heterojunctions are expected to be applied in efficient electronic, electrochemical, photocatalytic, photovoltaic, photoresponsive and memory devices.



Acknowledgement

Collaborators:

- W. Hu, T. Wang, J. Wang, Z. Guan, L. Hu, H. Wang
- Profs. Zhenyu Li, Jin Zhao, Qunxiang Li

Supports:

- NSFC, MOST, MOE, CAS
- USTCSCC, SCCAS, Tianjin and Shanghai Supercomputer Centers

THANK YOU!

谢谢！