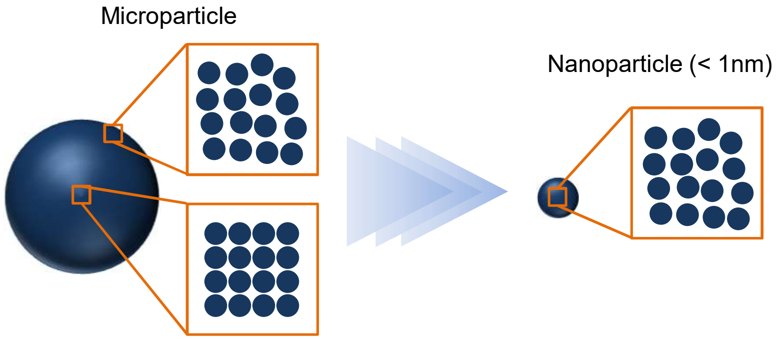
7. Control of Properties in 2D Materials

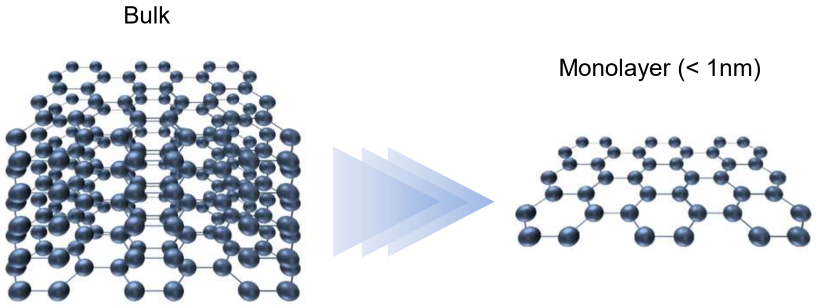
2D Materials vs Conventional Nanomaterials

Conventional nanomaterials
(nanoparticles, thin film, *etc.*)



- Different crystalline structures in nanomaterials: less ordered structure of the surface
- Difficulty in control of size, structure, and phase
- No efficient way to pattern or arrange nanoparticles

2D materials (layered materials)

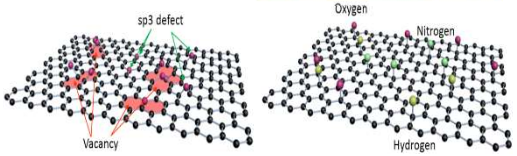


- Maintenance of highly crystalline structure even in monolayer
- Large effect of defect or disorder on the properties
- Easy patterning and stacking for lateral and vertical heterostructures

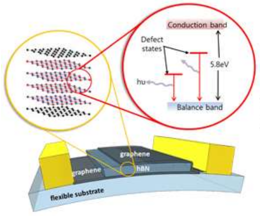
Effect of Shape/Strain/Substrate

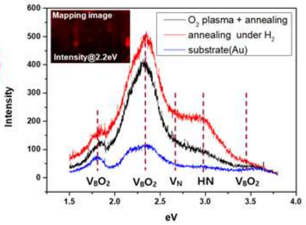
Defect Engineering

Plasma & chemical treatment

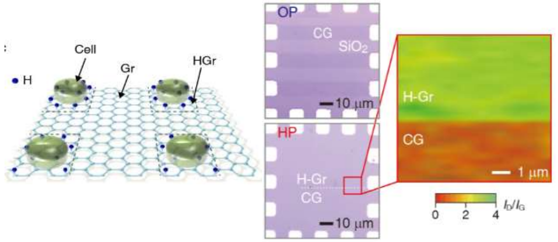


Defect control



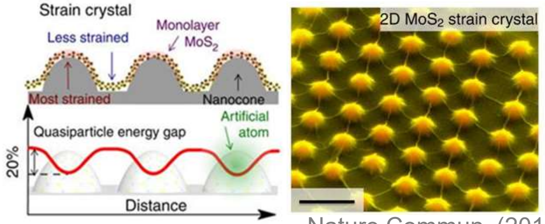


Applications for bio and electronics

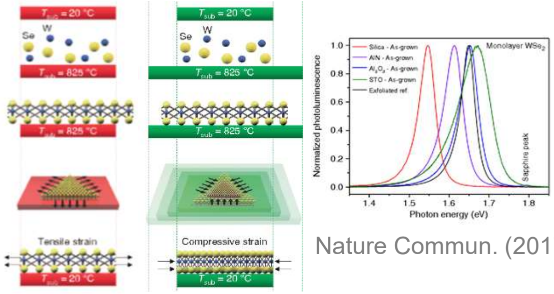


Strain Engineering

Band engineering by strain

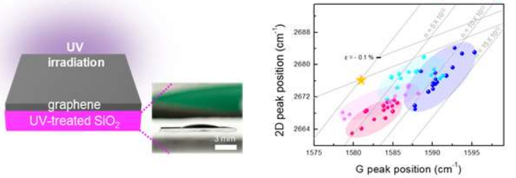


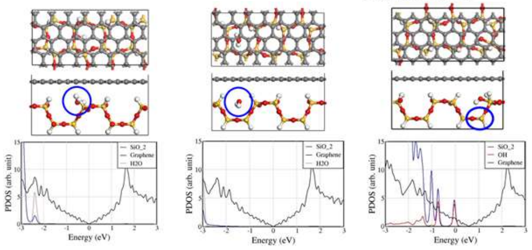
Nature Commun. (2015)



Nature Commun. (2017)

Substrate-induced strain & doping

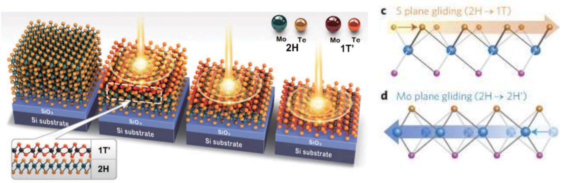




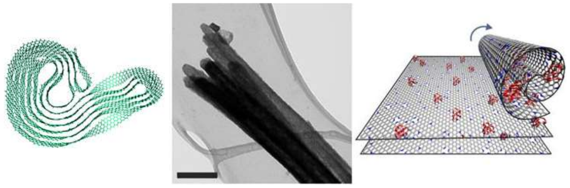
E.J. Ji, G.H. Lee, Carbon (2021)

Phase Engineering

Stimulus-induced phase transition

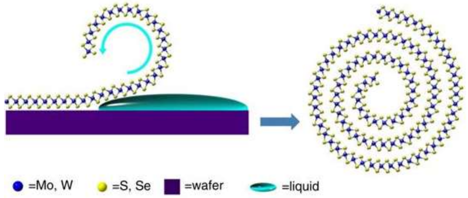


Morphology change



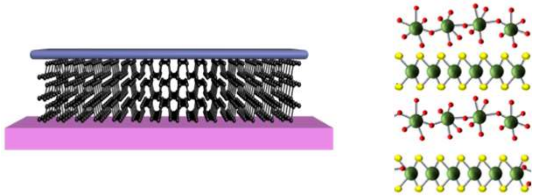
ACS Nano (2010)

Nature Commun. (2013)



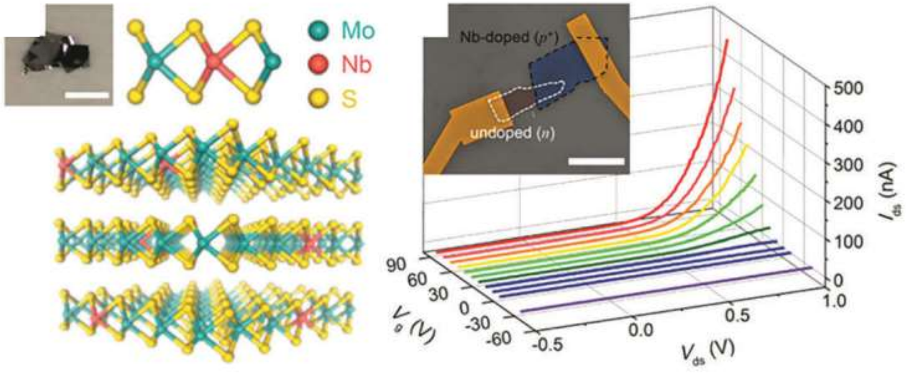
Nature Commun. (2018)

Layer-by-layer oxidation



Control of Properties: Doping

Substitutional doping

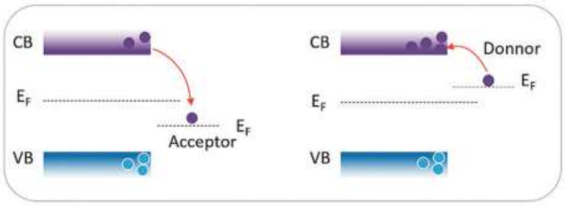


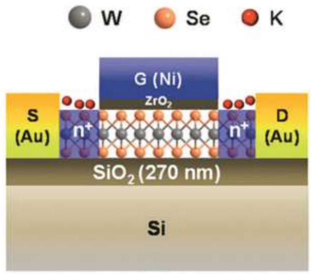
n- type MoS_2 → p^{++} - type $Mo_xNb_{1-x}S_2$ (Nb: covalently bonded dopant)

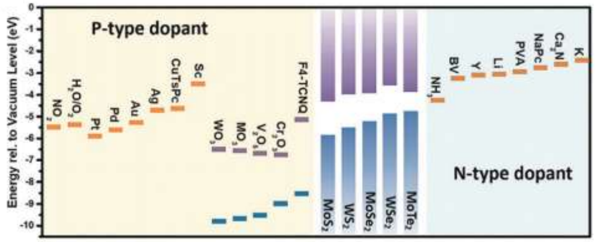
Type conversion

Nano Lett., 2014, 14, 6976–6982.

Charge transfer doping







Work function difference

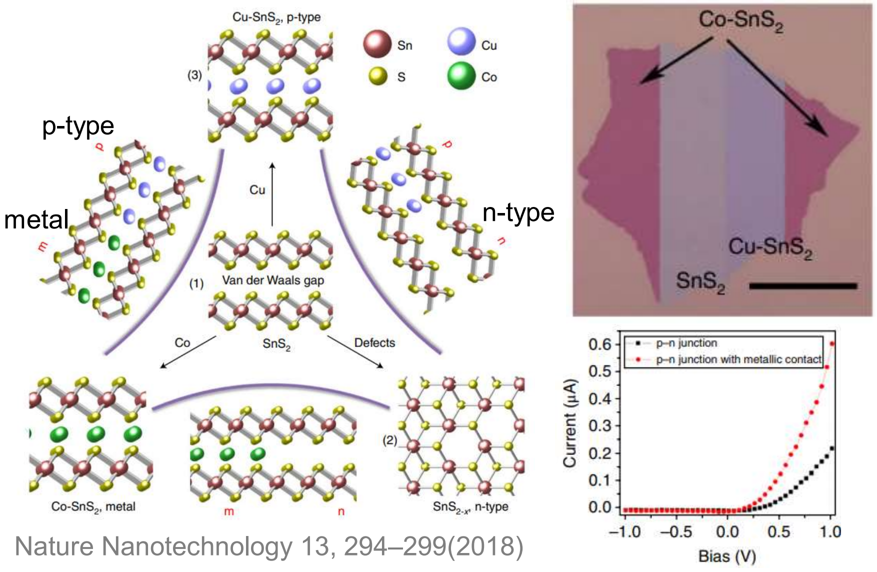
Surface adatoms, ions molecules

No lattice distortion
→ elecrical propertis ↑

Nanoscale Horiz., 2019, 4, 26--51

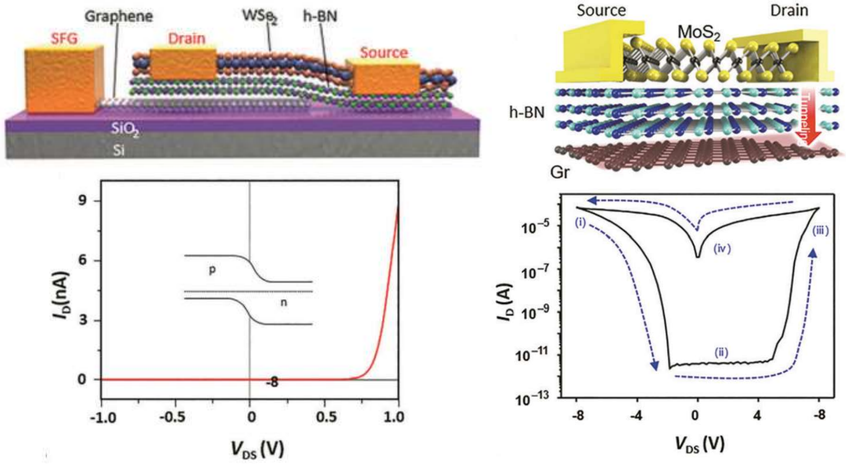
Nano Lett., 2013, 13, 1991–1995

Intercalation doping



Nature Nanotechnology 13, 294–299(2018)

Electrostatic doping



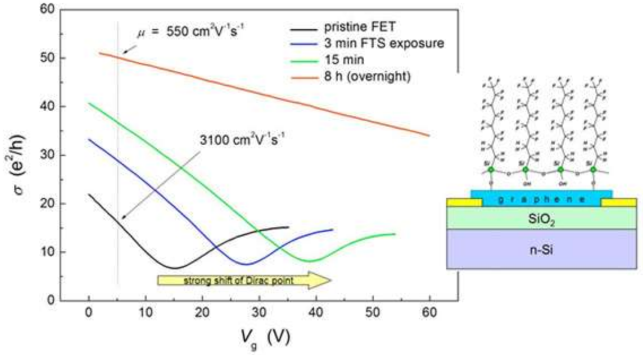
Floating gate, ferroelectric gate, metal-dielectric gate

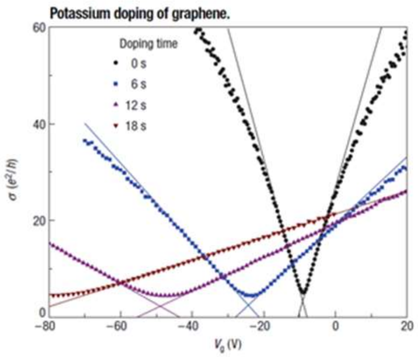
No lattice distortion

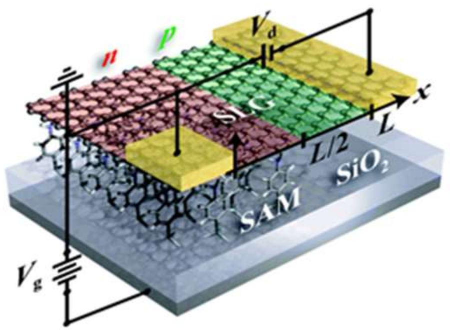
Nat. Nanotechnol., 2017, 12, 901–906.
Nat. Commun., 2016, 7, 12725.

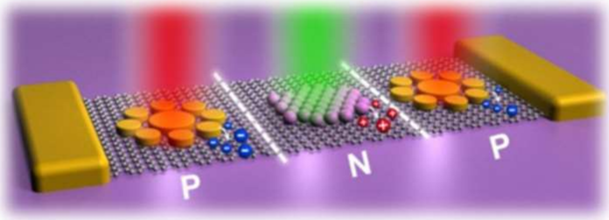
Control of Properties: Doping

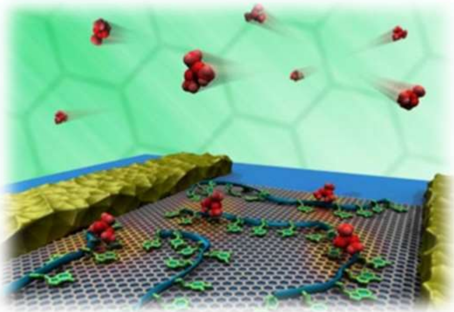
- substitution of atoms
- absorption of molecules
- deposition of self-assembled monolayers
- covalent functionalization
- metal nanoparticles (NPs)
- substrate doping
  - Control of Fermi level
  - Increased conductivity
  - Formation of p-n junctions
  - Chemical sensors

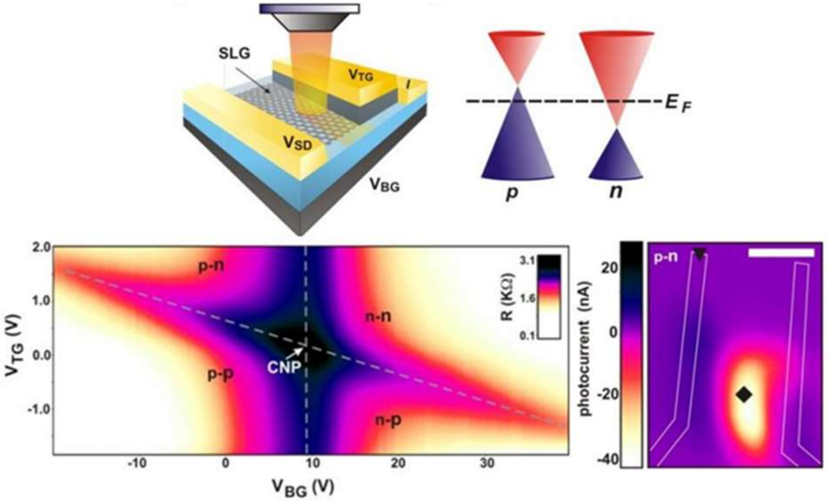


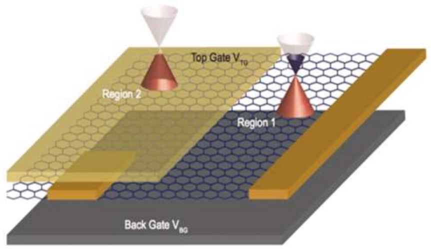


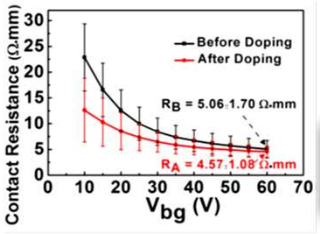


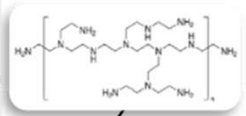


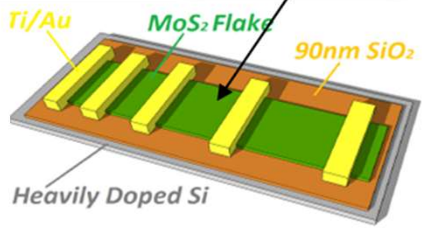








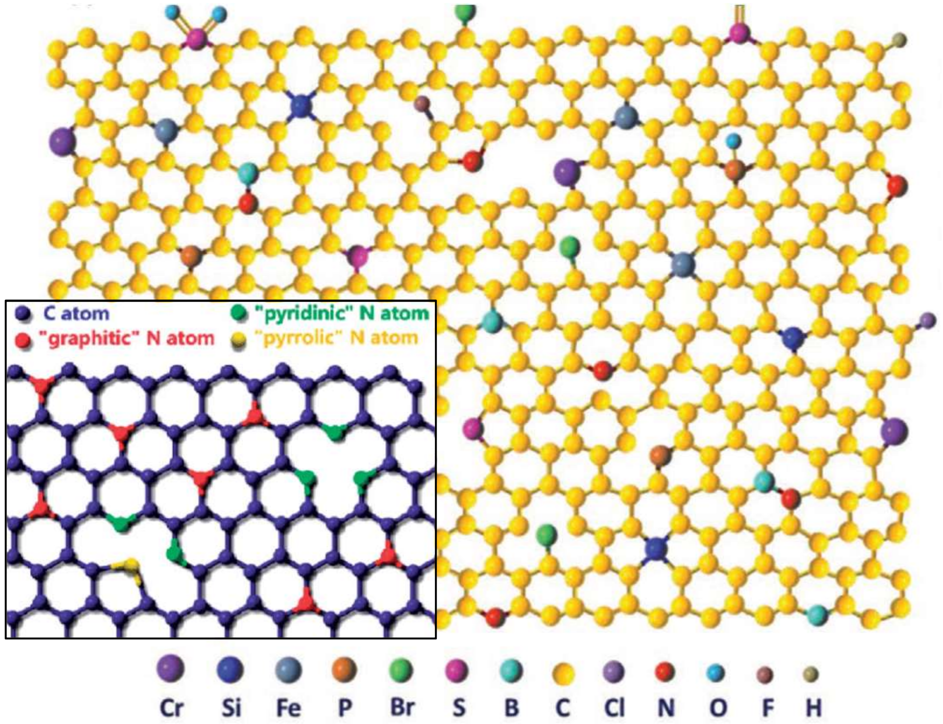




Y. Du et al. IEEE (2013) & Z. Fang et al. ACS Nano (2012) & B. Lee et al. Nano Lett. (2010) & K. Yokota et al. Phys. Chem. Chem. Phys. (2014) & N. M. Gabor et al. Science (2011)

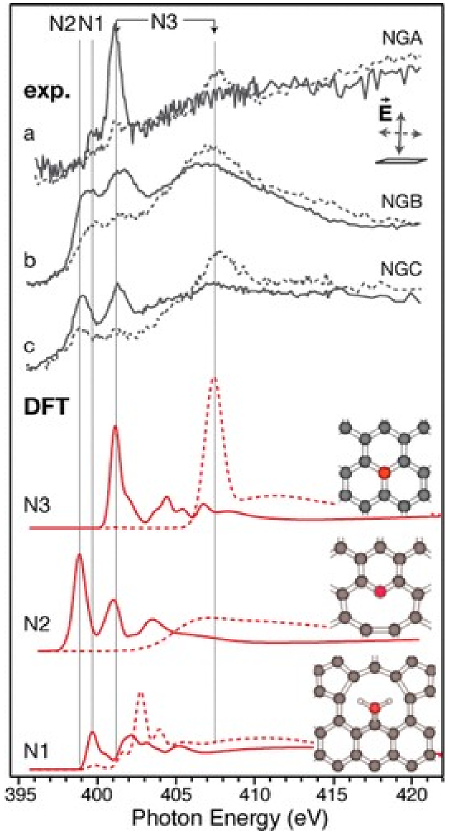
Substitutional doping

Dopant-induced bonding configurations



Adv. Mater. Interfaces 7, 2000999 (2020)

N 1s XAS and DFT-computed spectra



Nitrogen typically forms three types of bonding structures:

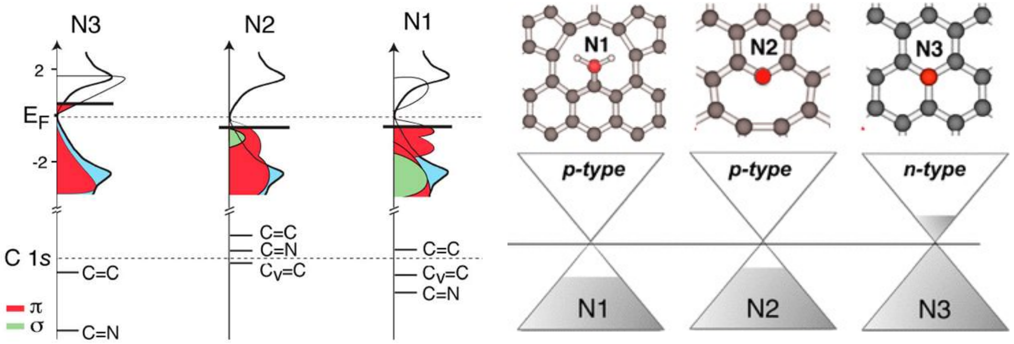
sp^2 hybridization with planar arrangements

1) graphitic, 2) pyridinic

sp^3 configuration with distortion in the planar symmetry

3) pyrrolic

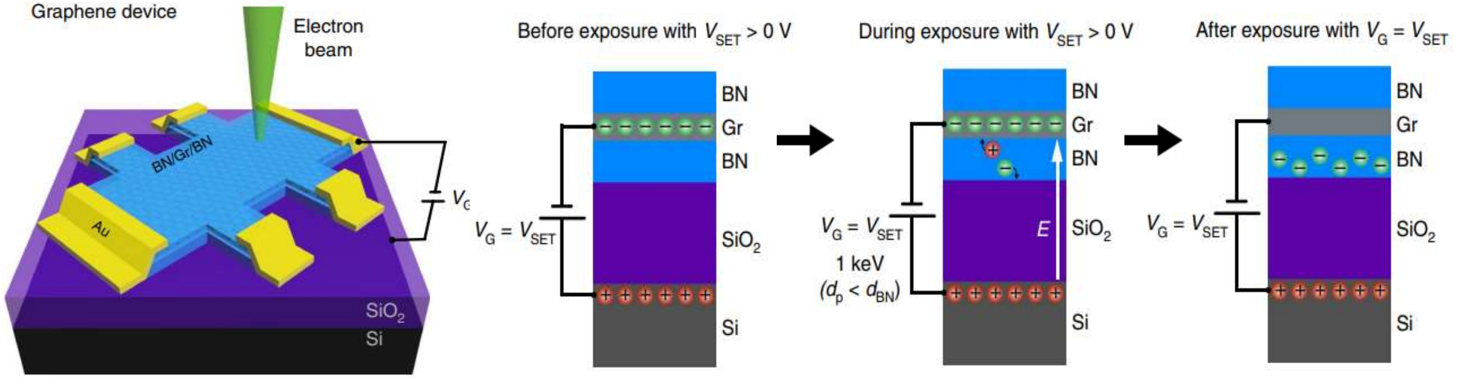
Nanoscale 5, 4541-4583 (2013)

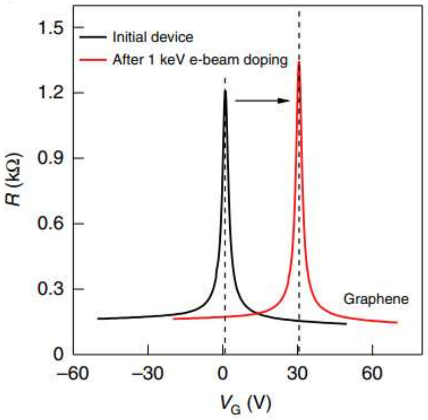


Nano Lett. 12, 4025–4031 (2012)

Charge Trap in Defect States

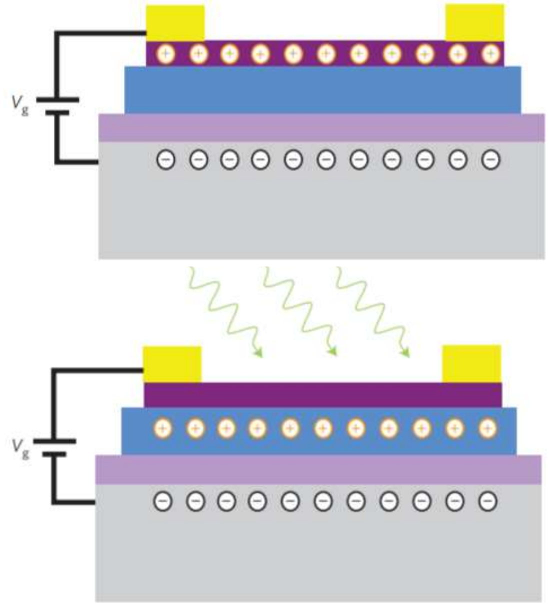
E-beam source doping

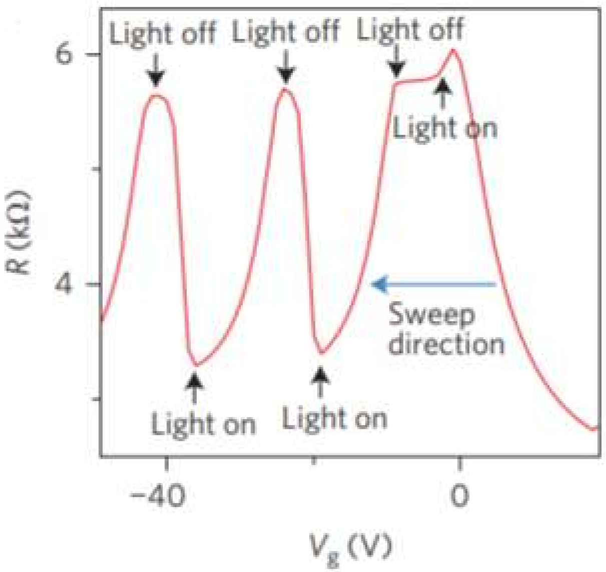


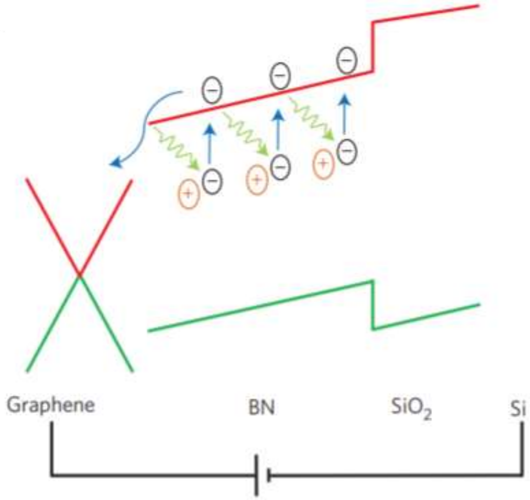


Nature Electronics 3 2020 99-105

Light source doping







Nature Nanotechnology 9, 2014 348–352

Control of Properties: Doping

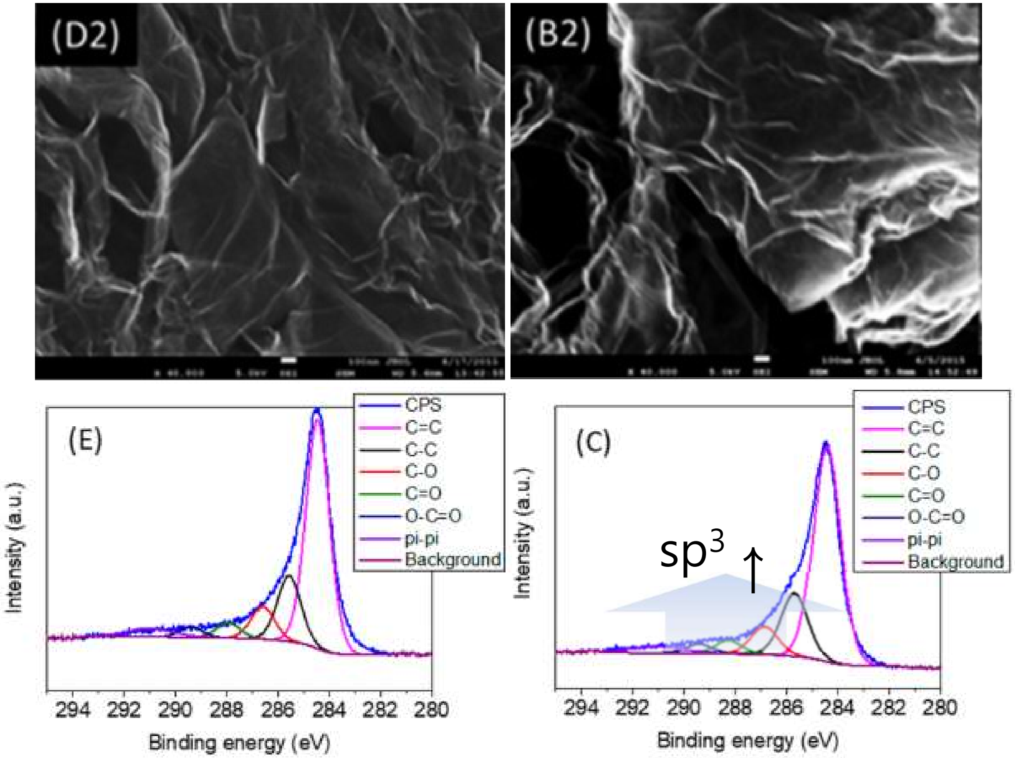
ACS NANO
www.acsnano.org

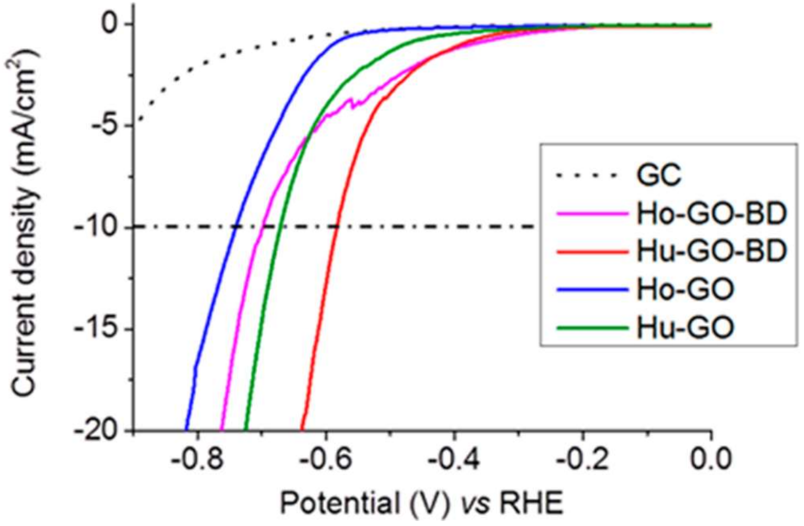
Guano has a great advantage for doping over using synthetic chemicals. It is available at low cost, it contains a plethora of elements (including N, P, S, Cl, etc.)

Will Any Crap We Put into Graphene Increase Its Electrocatalytic Effect?

Lu Wang, Zdenek Sofer, and Martin Pumera*

Non treated *Guano treated*

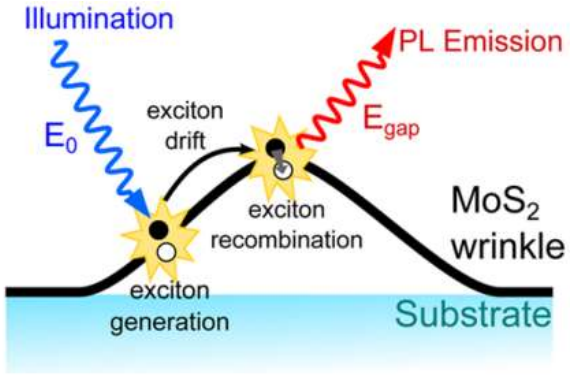


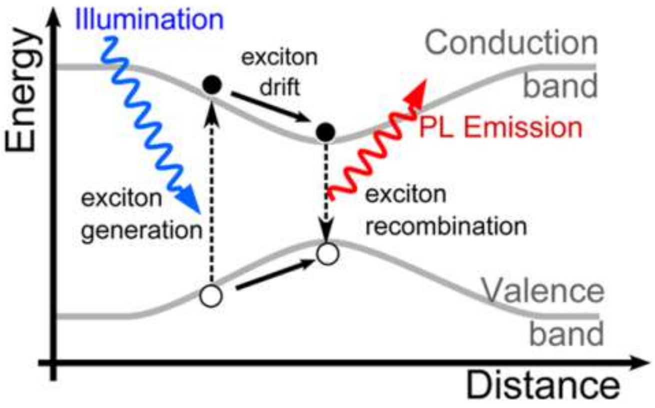


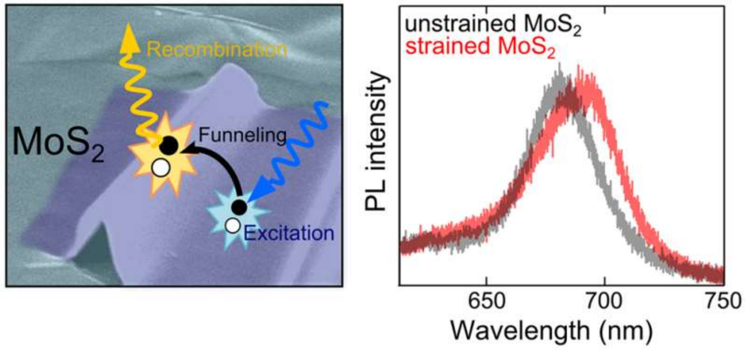
ACS Nano 2020, 14, 21−25

Effect of Strain

Strain - Band engineering (funnel effect)

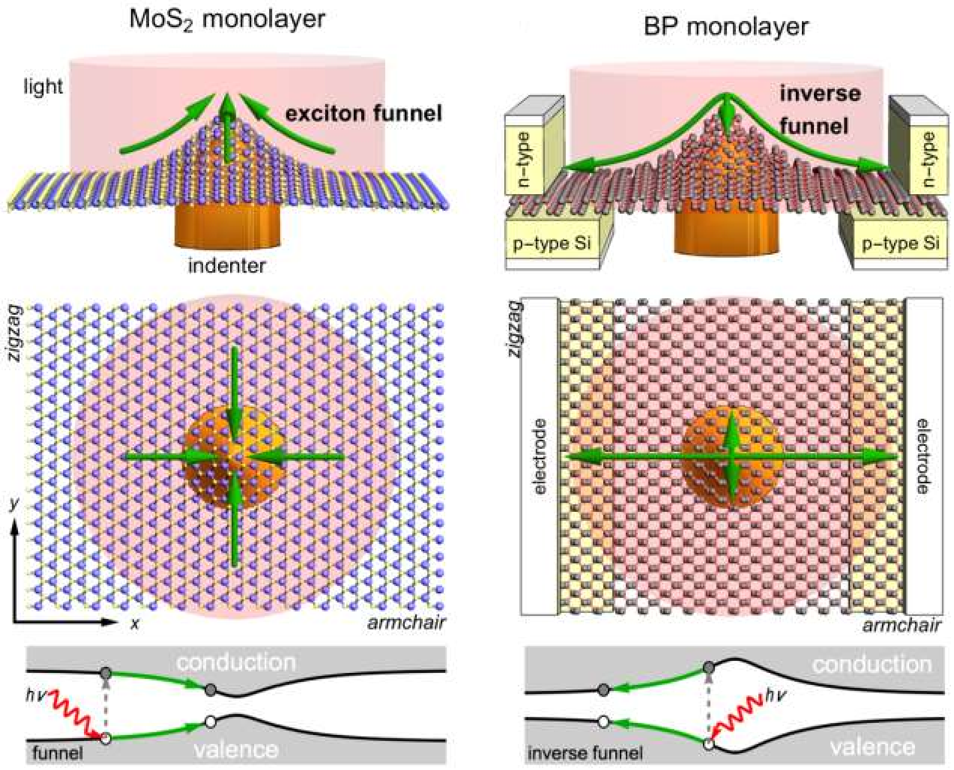






Nano Lett. 2013, 13, 5361−5366

Inverse Funnel Effect in black phosphorus



PHYSICAL REVIEW X 6, 031046 (2016)

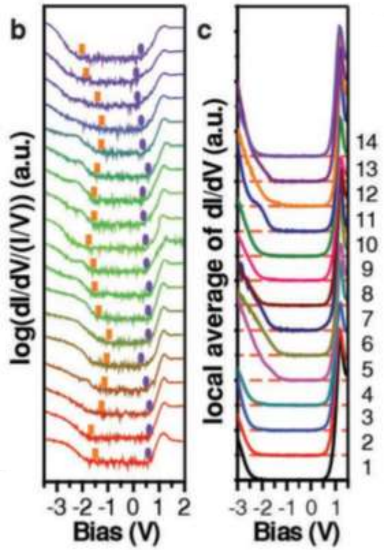
Compressive strain widens band gap of TMDs

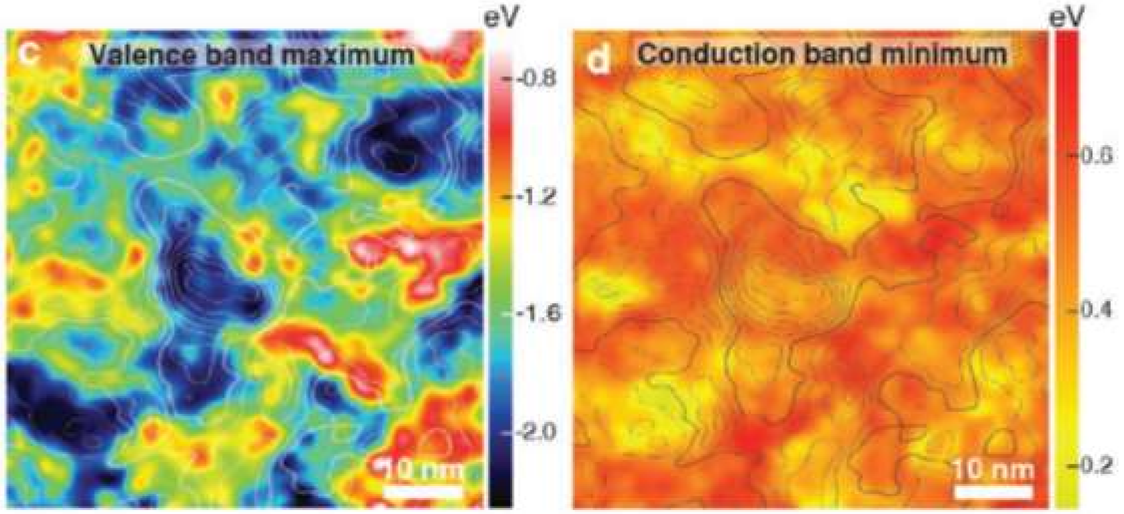
Tensile strain reduces band gap of TMDs

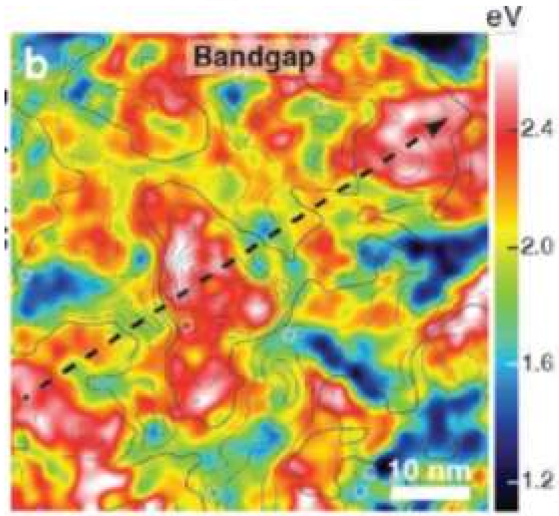
Black phosphorous has reverse funnel effect in contrast to TMDs

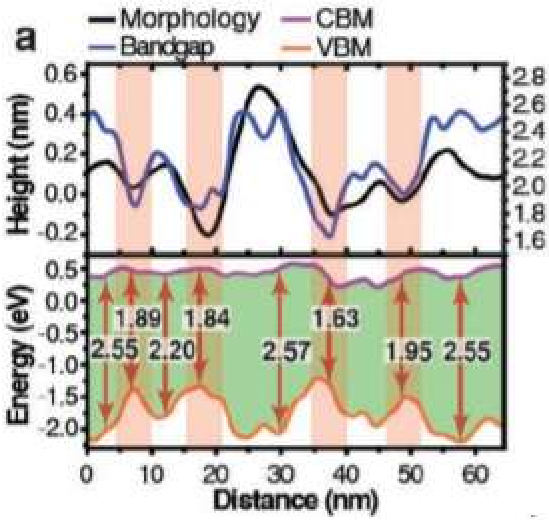
Effect of Strain

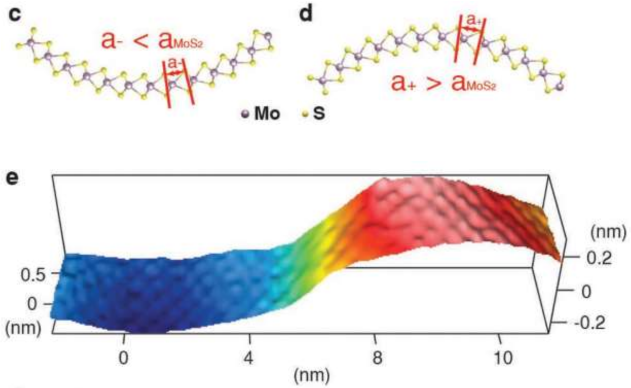
Strain-substrate effect: local band engineering









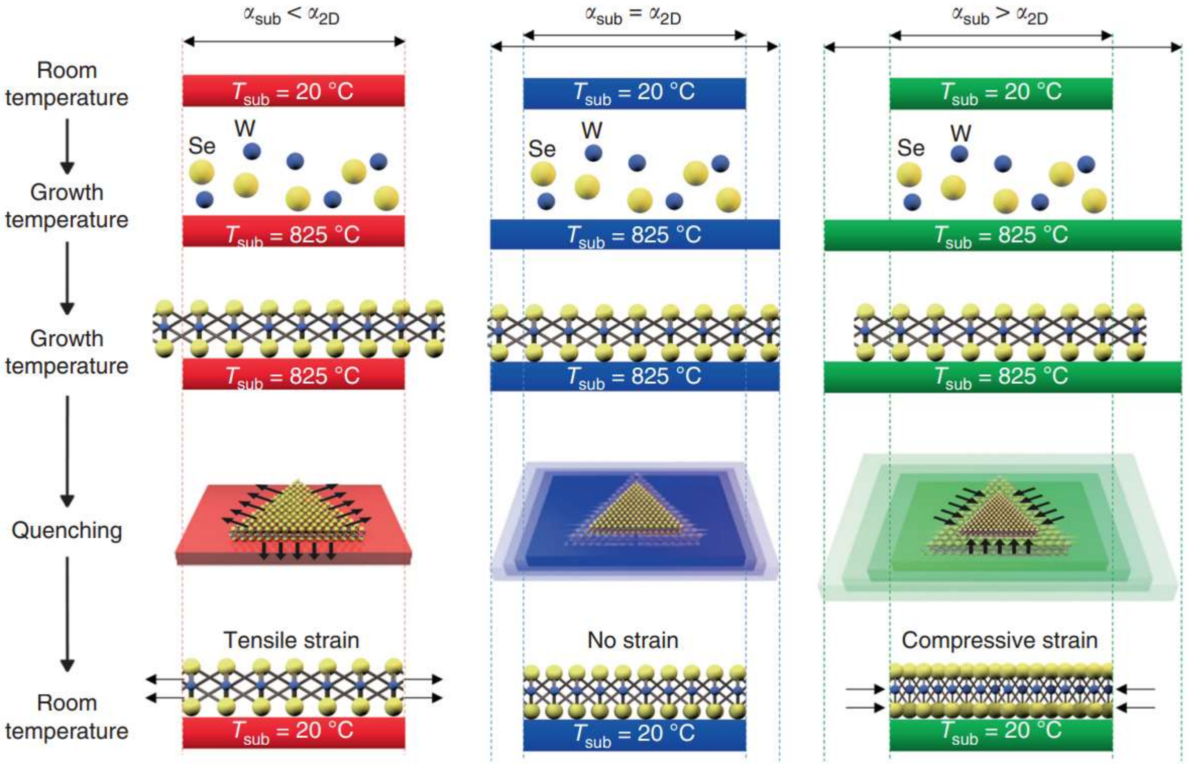


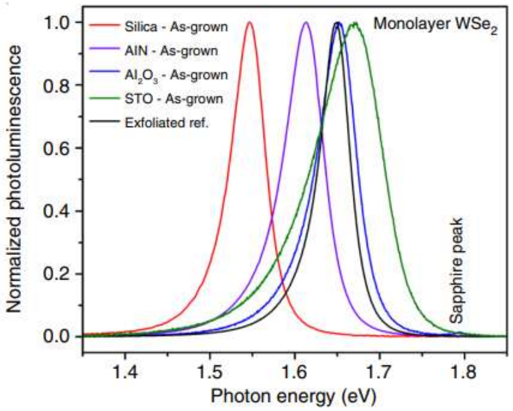
Corrugated surface morphology of the native SiO_2 substrate induces local bending strain varying local band structure.

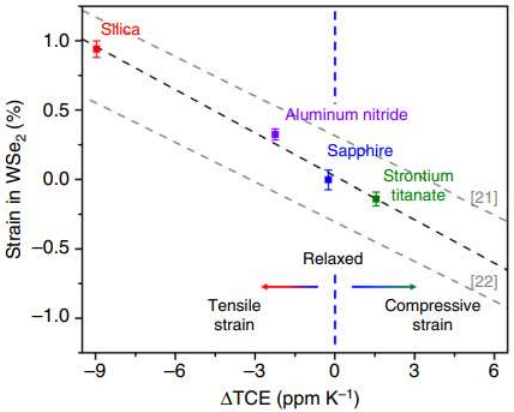
Adv. Mater. 2016, 28, 9378–9384

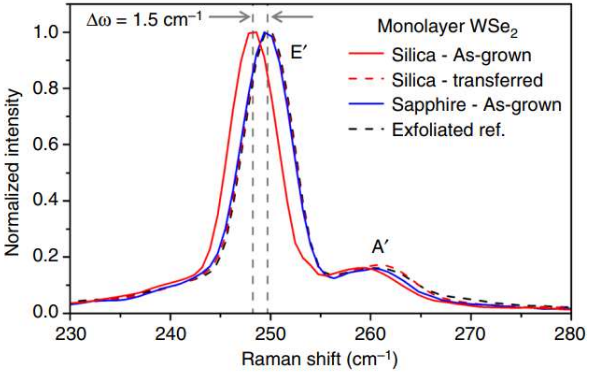
Effect of Strain

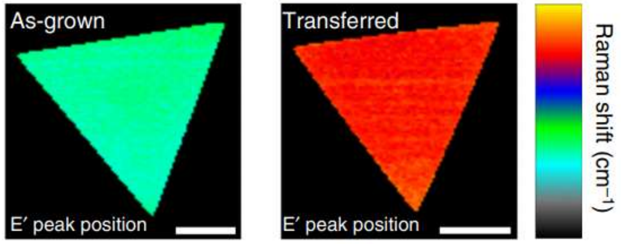
Strain - Growth engineering









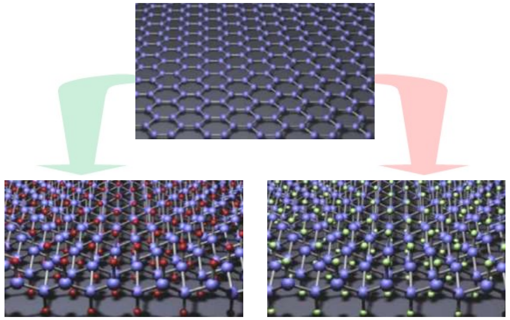


Thermal coefficient of expansion mismatch between the substrate and semiconductor built-in strains ranging from 1% tensile to 0.2% compressive.

Nature Commun. 8, 608 (2017)

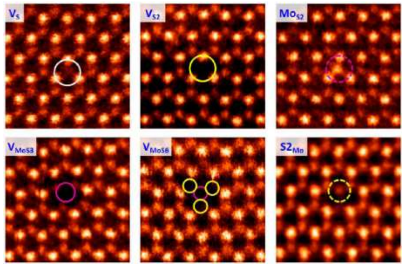
Types of Defects in 2D Materials

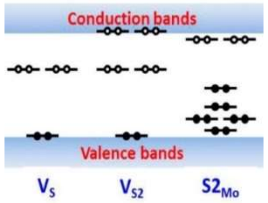
sp^3 bonds



Science (2009) Small (2010)

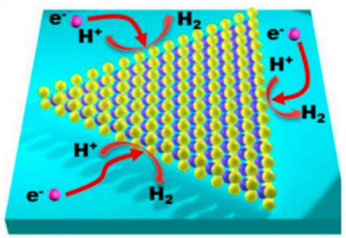
Vacancy



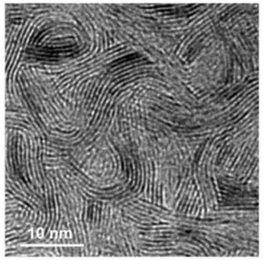


Nano Lett. (2013)

Edge

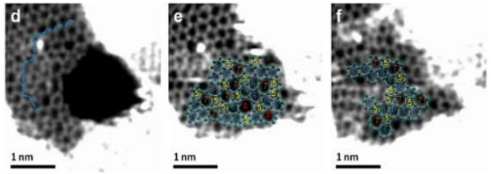


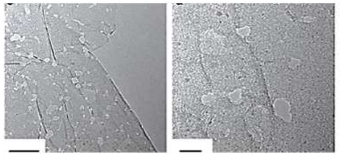
ACS Nano (2014)



Nano Reserch (2014)

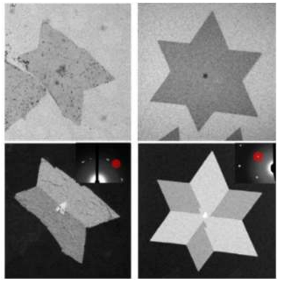
Hole



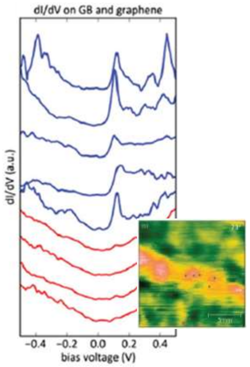


Nano Lett. (2013)

Grain boundary



Nature Mater. (2013)

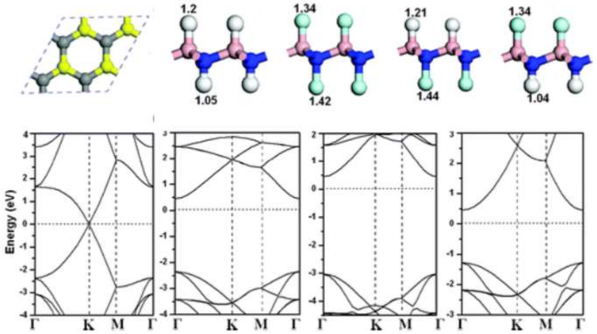


ACS Nano (2014)

- ☐ What are intrinsic characteristics of defects in 2D materials?
- ☐ How can we control of defects?
- ☐ How can we utilize defects for engineering 2D materials?

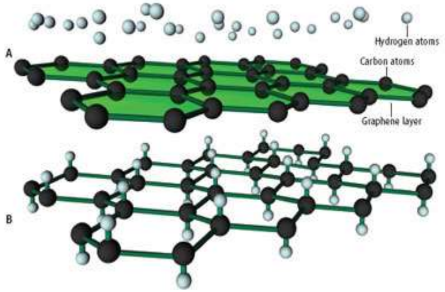
Hydrogenation of Graphene

Functionalization of graphene



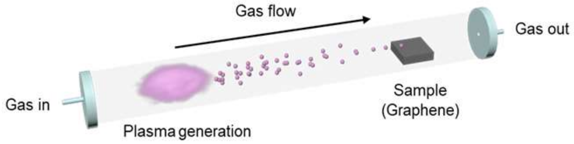
S. Tang. et al. PCCP (2013)

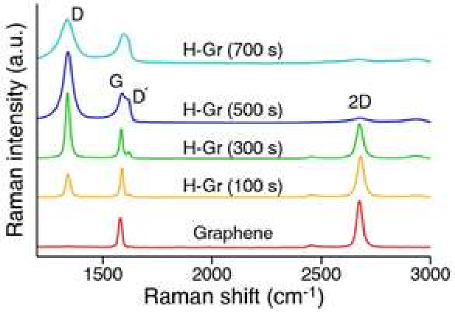
Hydrogenation of graphene

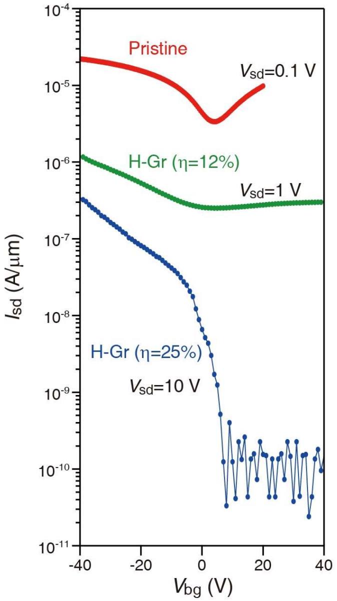


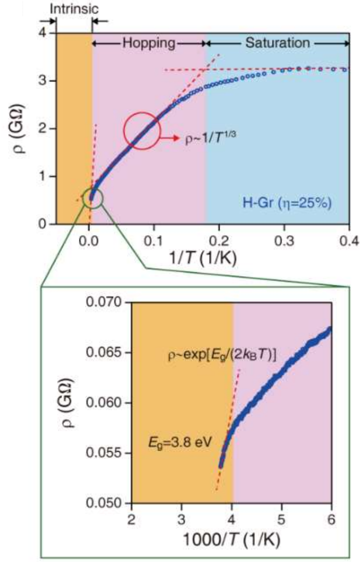
D. C. Elias et al. Science (2009)

Bandgap opening of hydrogenated graphene





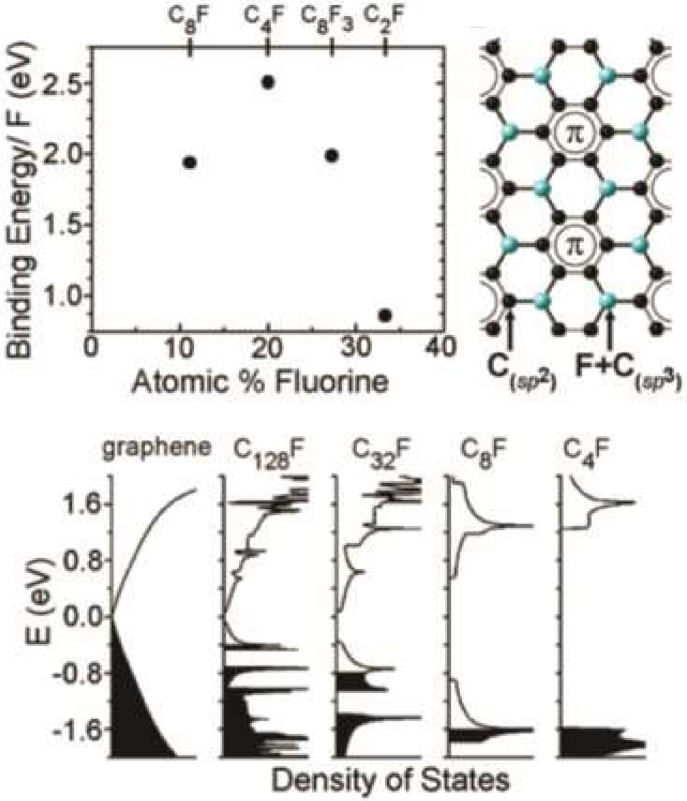




J.Y. Son et al. Nature Comm. (2016)

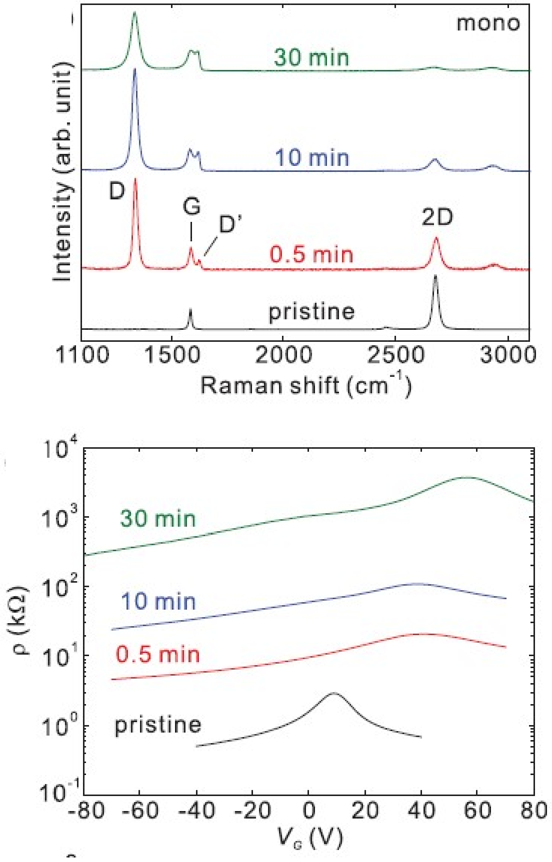
Properties of Fluorinated Graphene

Bandgap opening

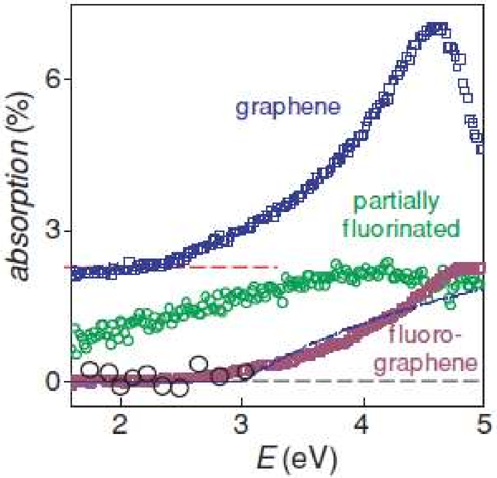


Nano Lett. 10, 3001 (2010)

Properties of fluorinated graphene (FG)



Appl. Phys. Lett. 103, 143106 (2013)

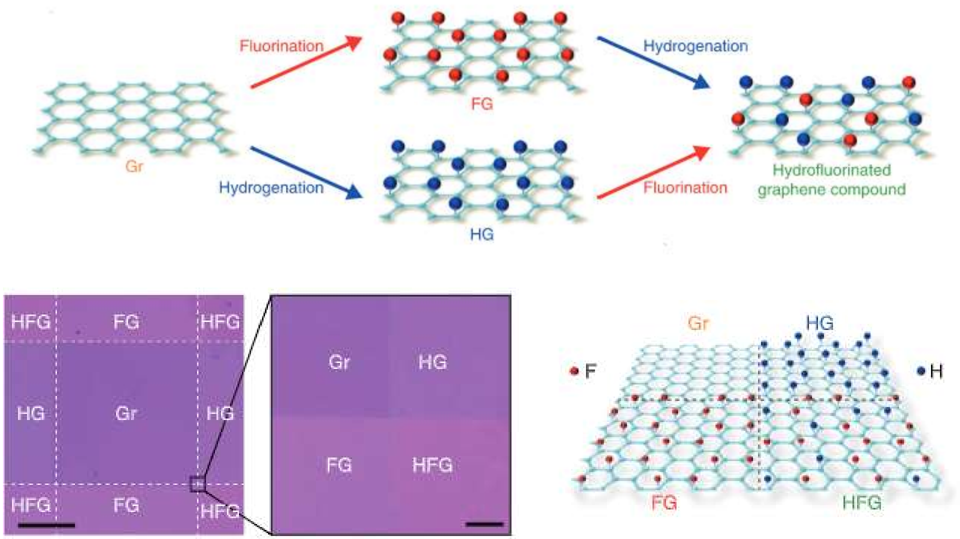


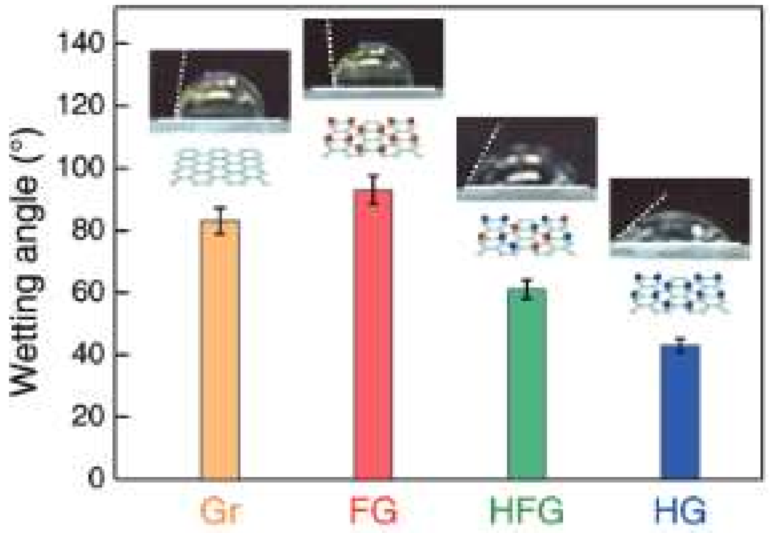
Small 6, 2877–2884 (2010)

- Wide bandgap (bandgap ~ 3 eV)
- High chemical stability
- High room temperature R (>10 GΩ)
- High response to biological signal
- Super-hydrophobicity

Hydrogenation and Fluorination of Graphene

Surface engineering of hydrofluorinated graphene

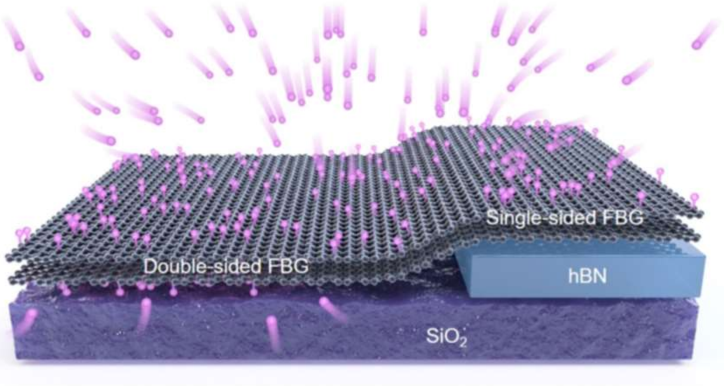


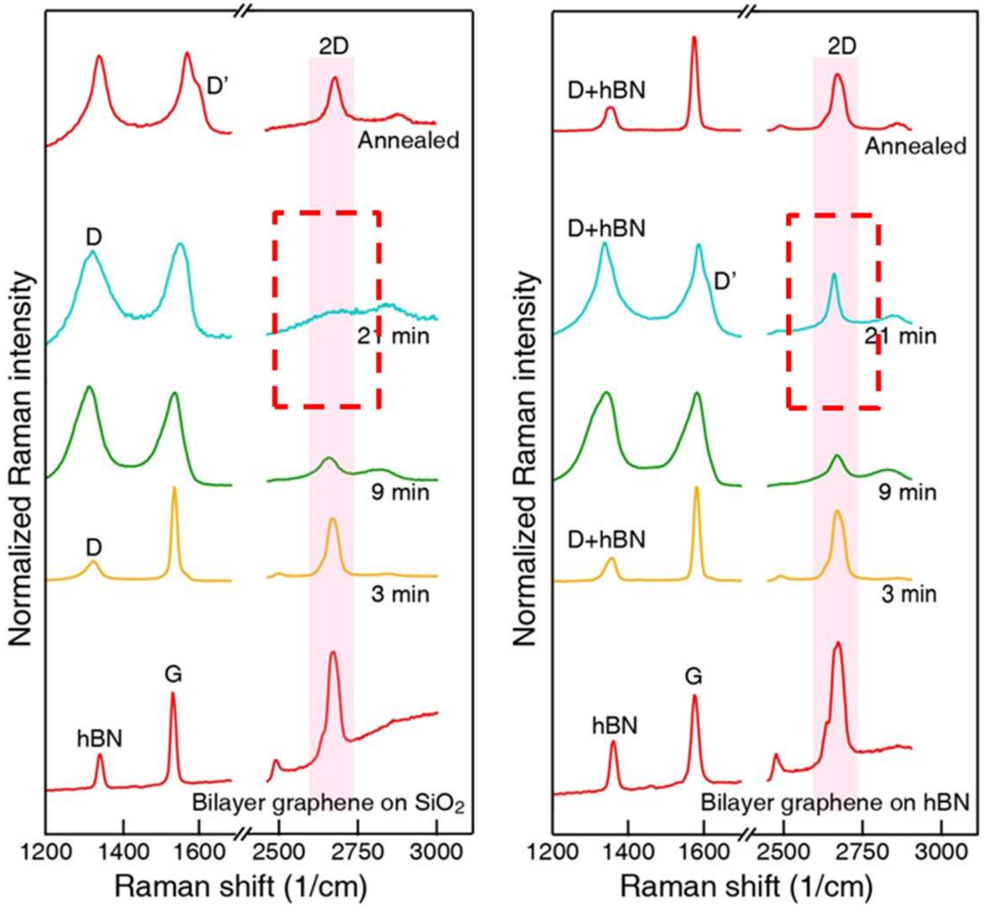


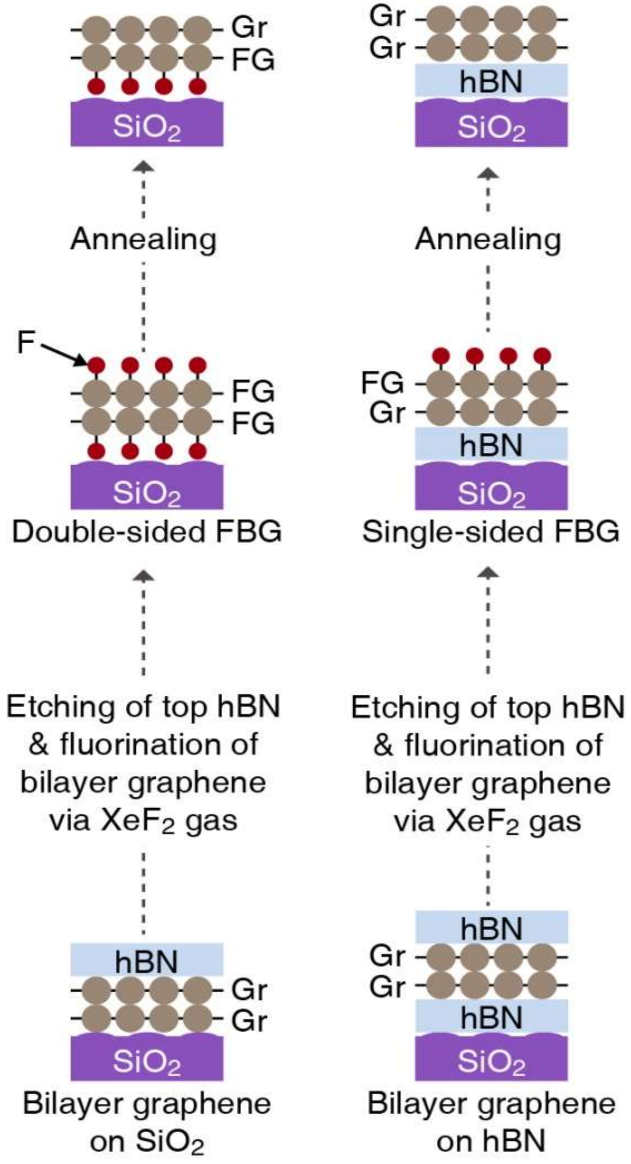
Adv.Mater.2019, 31, 1903424

By synthesis of a hydroflourinated graphene, surface properties such as wettability, friction, and electrical conductivity were tuned.

Selective Functionalization of Graphene







Annealing

Annealing

Double-sided FBG

Single-sided FBG

Etching of top hBN & fluorination of bilayer graphene via XeF_2 gas

Etching of top hBN & fluorination of bilayer graphene via XeF_2 gas

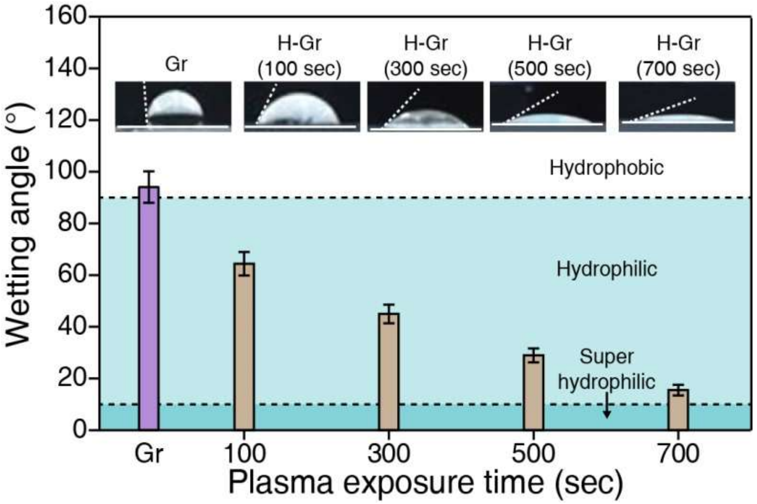
Bilayer graphene on SiO_2

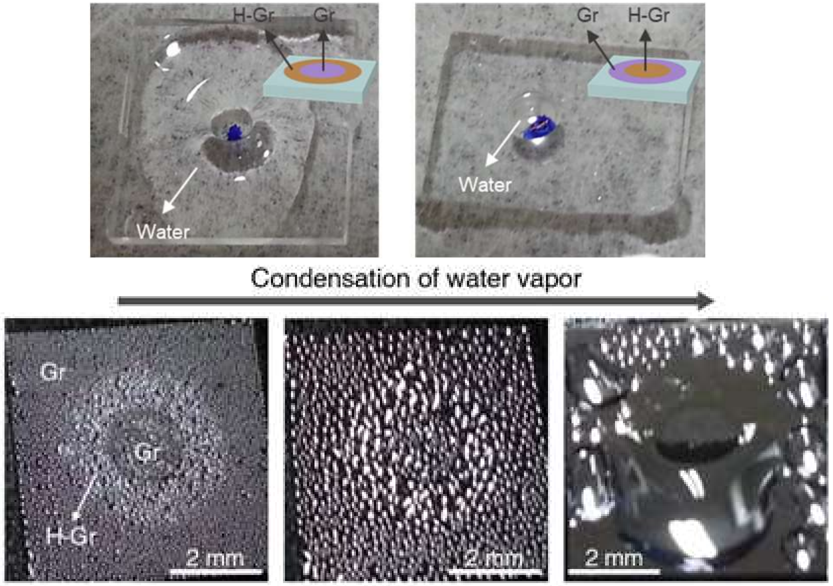
Bilayer graphene on hBN

J.Y. Son, A. van der Zande, G.H. Lee *Nano Lett. (2020)*

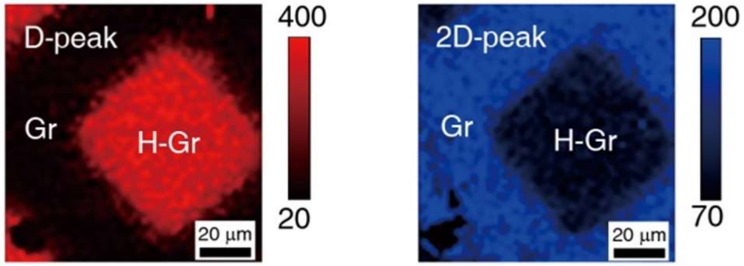
Selective Functionalization of Graphene

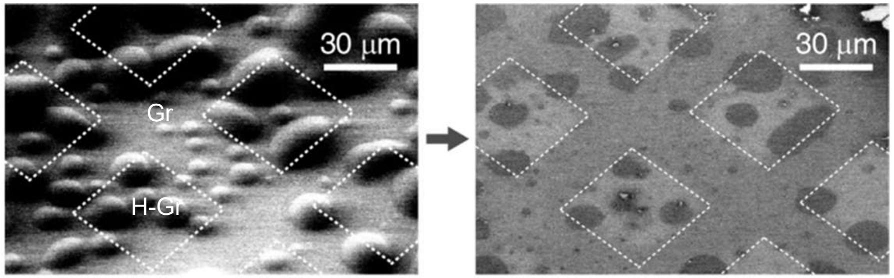
Hydrophilic hydrogenated graphene





Microscale patterning



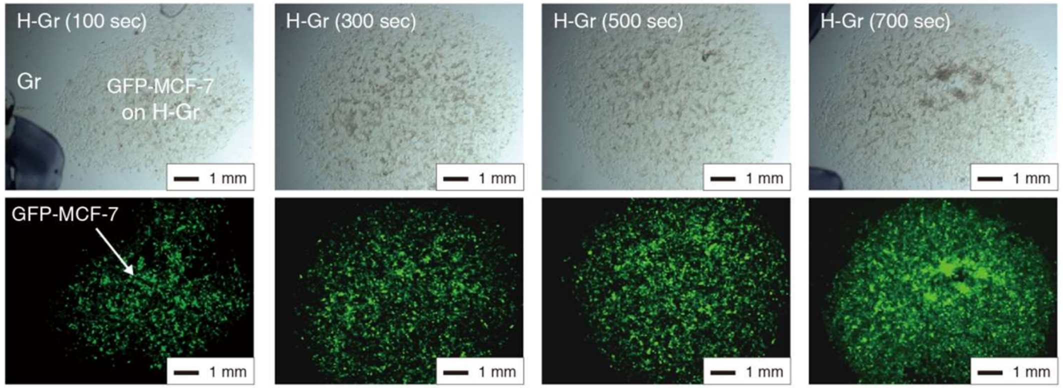


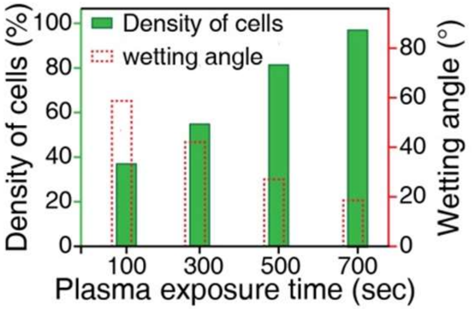
- CVD graphene shows super-hydrophilicity after hydrogenation.
- Wettability of graphene is controlled in microscale through hydrogenation patterning.

J. Son, J.Y. Lee, G.H. Lee*, J. Hong* ***Nano Lett.*** (2020)

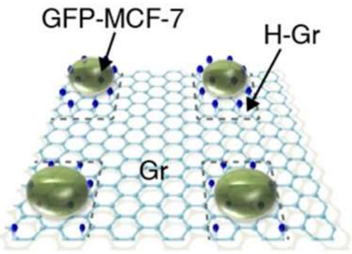
Selective Functionalization of Graphene

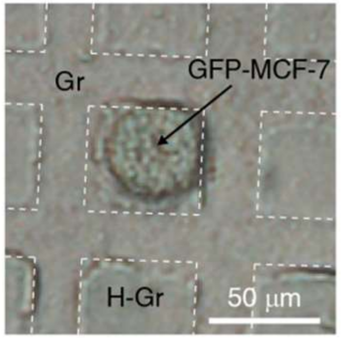
Cancer cell adhesion on Gr/H-Gr

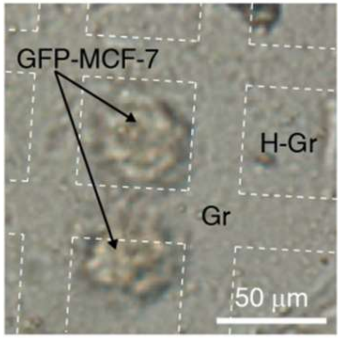




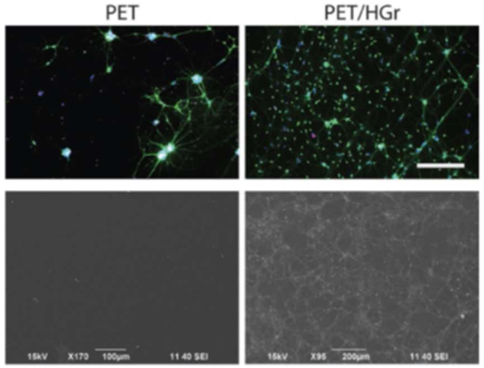
Selective cell sorting







Neuron culturing



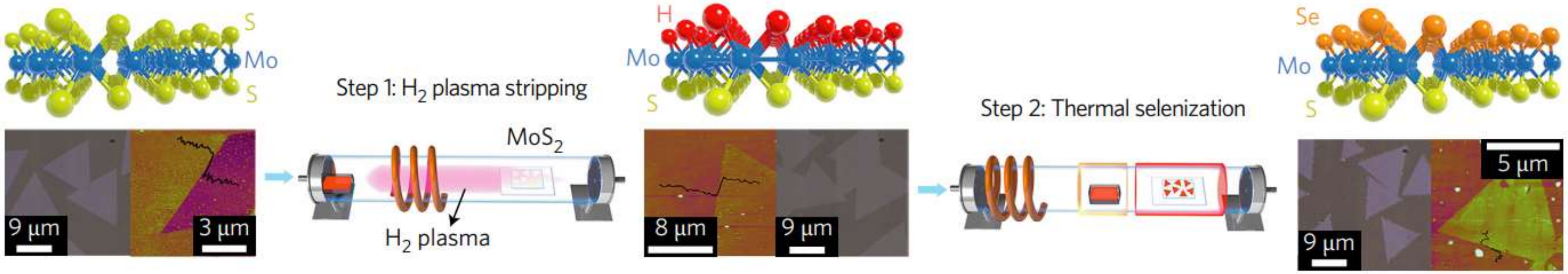
- ☐ Cancer cells attractively attached on hydrophilic H-Gr area.
- ☐ Cell can be sorted individually on precisely patterned H-Gr square.
- ☐ Hydrophilic H-Gr acts as atomically-thin template for studying cell and neuronal biology.

J. Son, J.Y. Lee, G.H. Lee*, J. Hong* *Nano Lett.* (2020)
M. Moschetta, J.Y. Lee, M. Bramini*, A. Capasso* *Adv. Biol.* (2021)

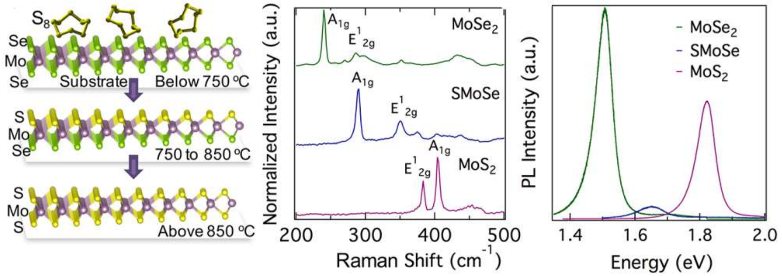
Properties of Janus TMD

Fabrication of junus TMD 1L

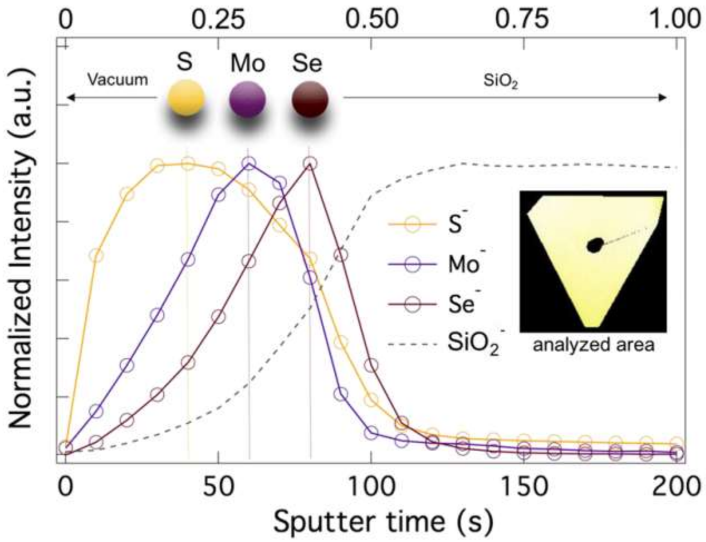
Method 1: H_2 plasma



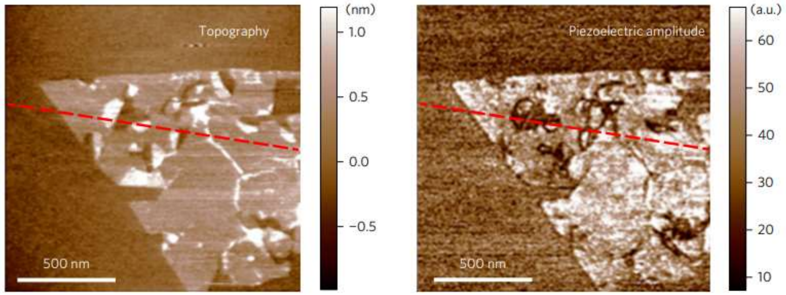
Method 2: Sufurization



Atomic configuration of Janus TMD



Piezoelectric properties of janus TMD 1L



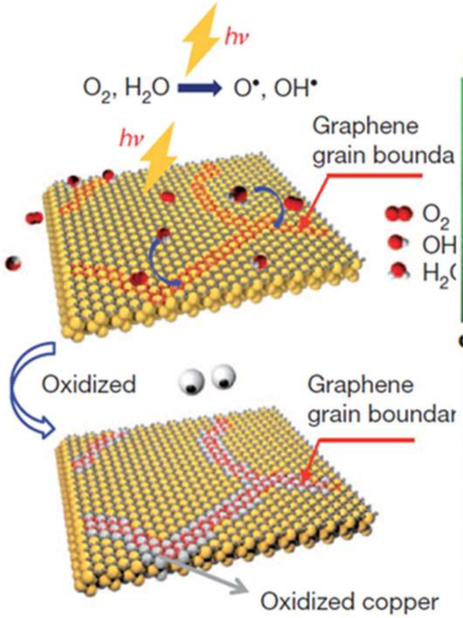
Soft H_2 Plama strips top atomic layer in 1L TMD, and then janus 1L TMD be synthesized by followed calcogenization process.

Janus 1L TMD has piezoelectric properties from intrinsic dipole moment.

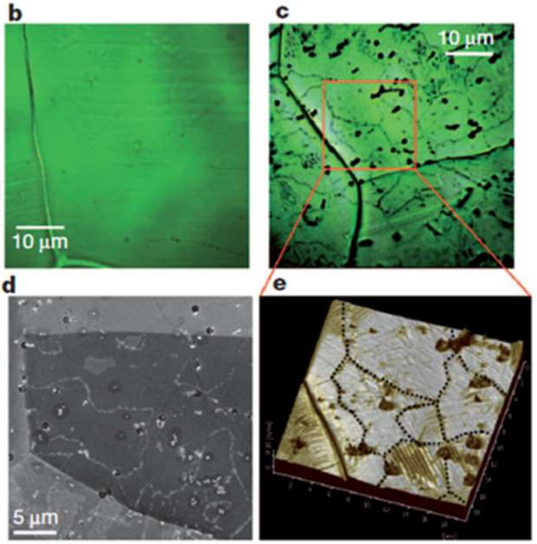
Nature Nanotechnol. 12, 744–749 (2017)

ACS Nano 11, 8192−8198 (2017)

Observation of Grain Boundaries

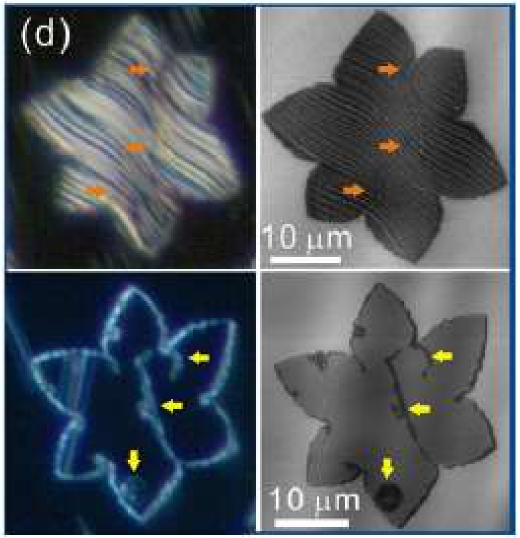


Local Oxidation of GBs



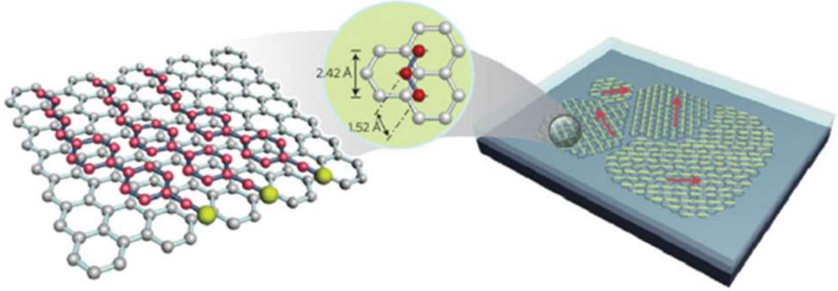
D. L. Duong et al. Nature (2012)

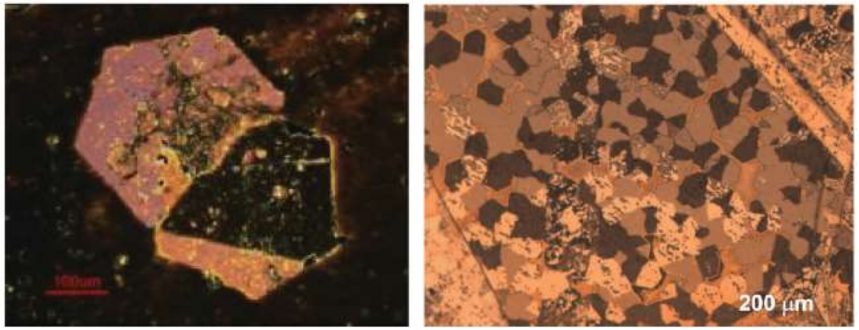
Dark Field Optical Microscopy



X. H. Kong et al. Appl. Phys. Lett. (2013)

Liquid Crystal Deposition for Grain Detection

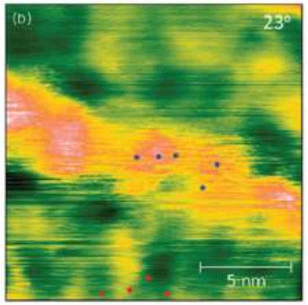


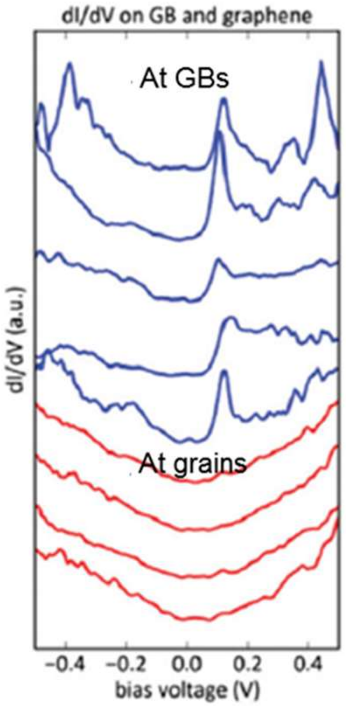


J. H. Son et al. Nature Commun. (2014)
D. W. Kim et al. Nature Nanotechnol. (2012)

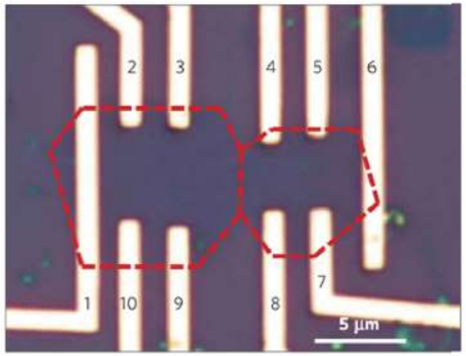
Effect of Defects in Graphene

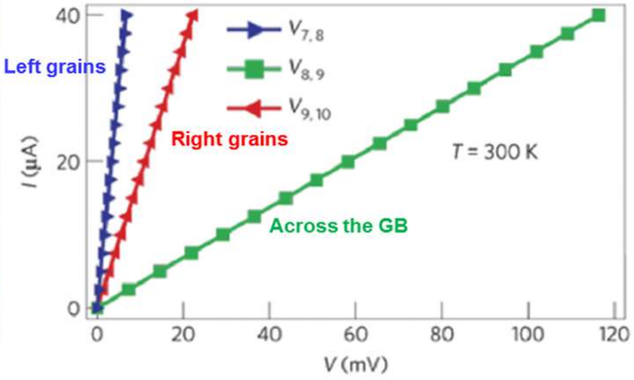
Local Scattering at GBs



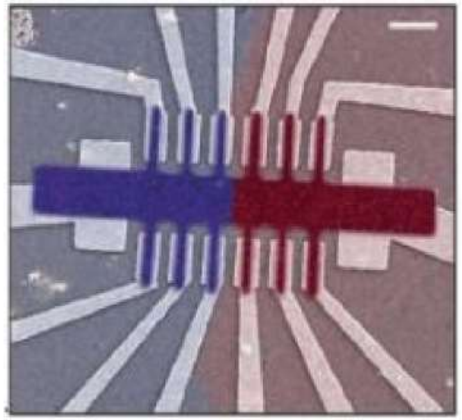


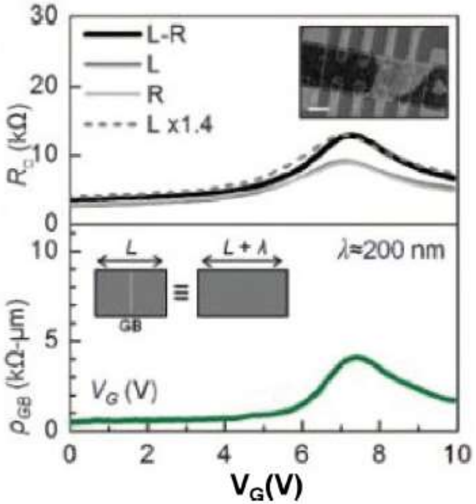
Conductivity across Supported GBs





Conductivity across Suspended GBs

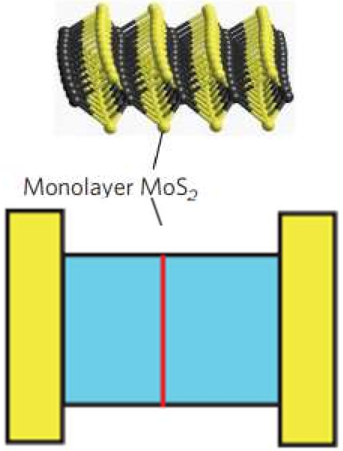


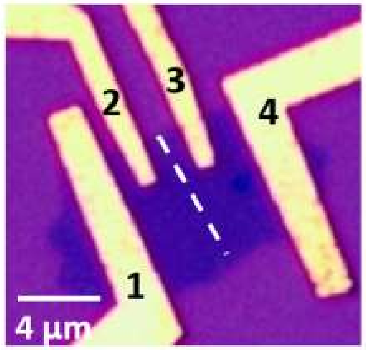


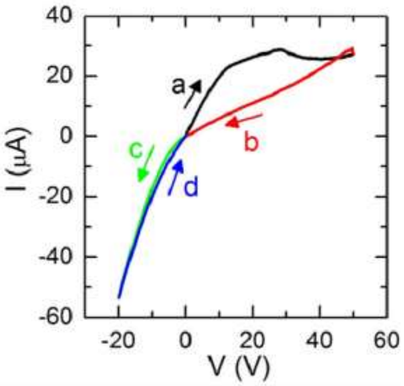
G. H. Lee et al. Science (2013) & A. van der Zande et al. Nature Mater. (2013) & D. W. Kim et al. Nature Nanotechnol. (2012) & J. H. Son et al. Nature Commun. (2014) & Wei et al. Science (2013) & Nature Mater. (2012) & D. L. Duong et al. Nature (2012) & R. Ionescu et al. Chem. Commun. (2014) & W. Zhou et al. Nano Lett. (2013)

Defect-induced Memristive Properties

MoS_2 memristive device using grain boundary



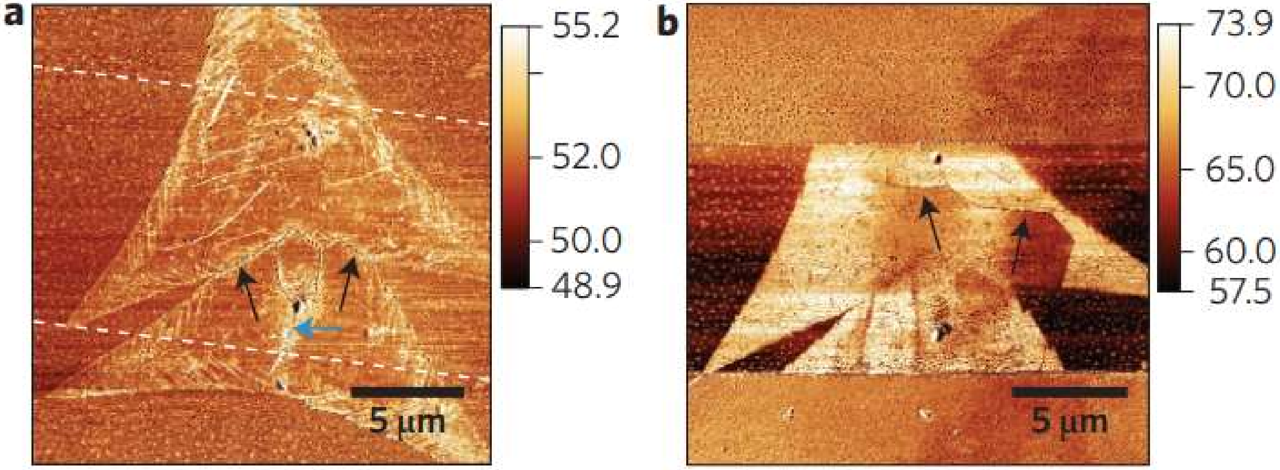




Schottky barrier formation near the contacts via motion of extended defects under contact area by lateral electrical field induces memristive electrical properties.

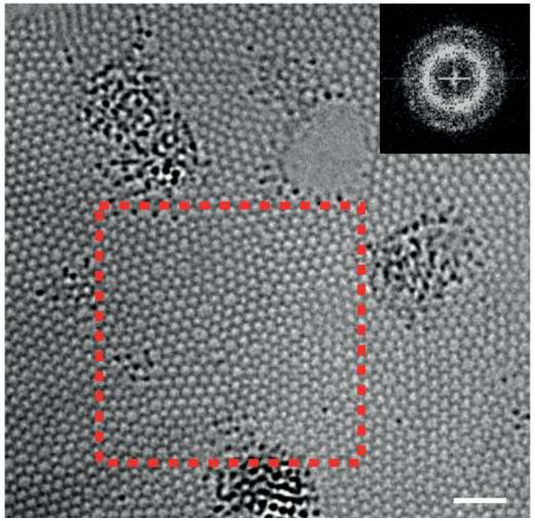
Defects occupied in grain boundary sites.

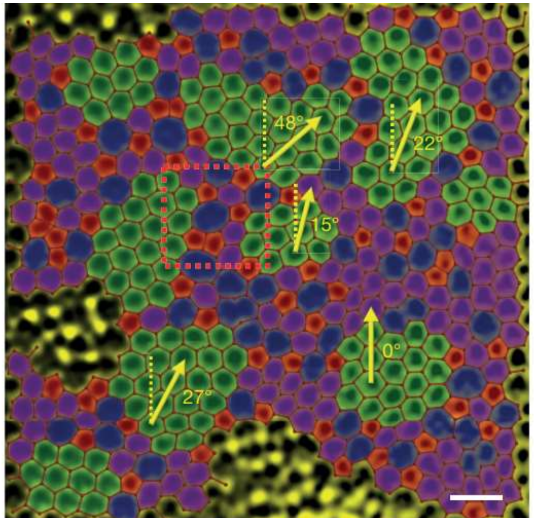
Nature Nanotech 10, 403–406 (2015)

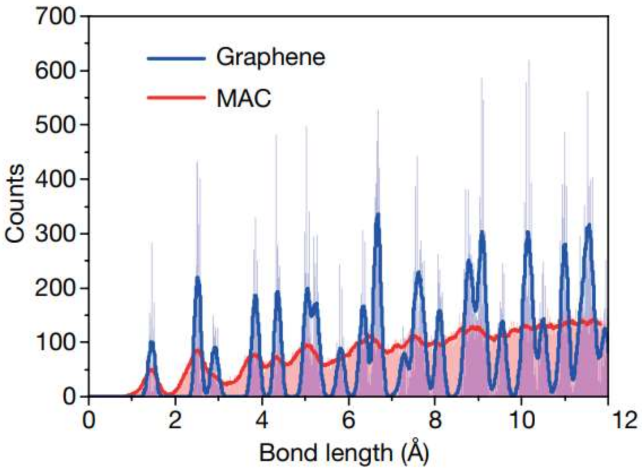


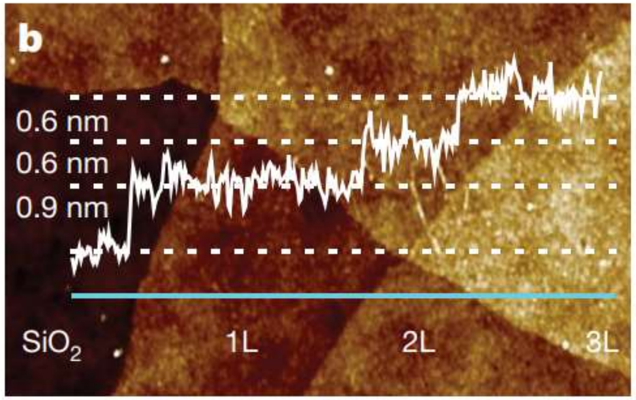
Mechanical Properties of Monolayer Amorphous Carbon

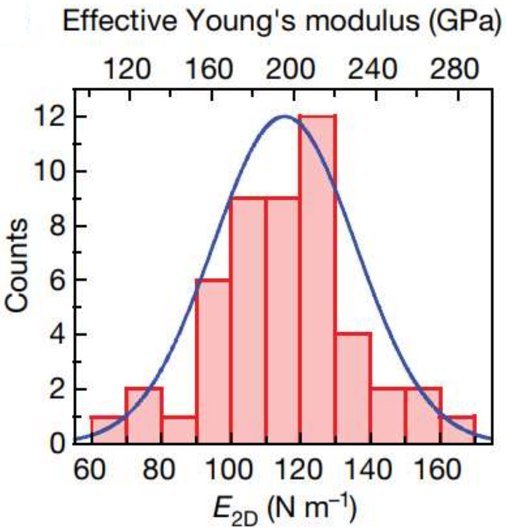
Amorphous carbon synthesized by laser-assisted CVD at 200℃

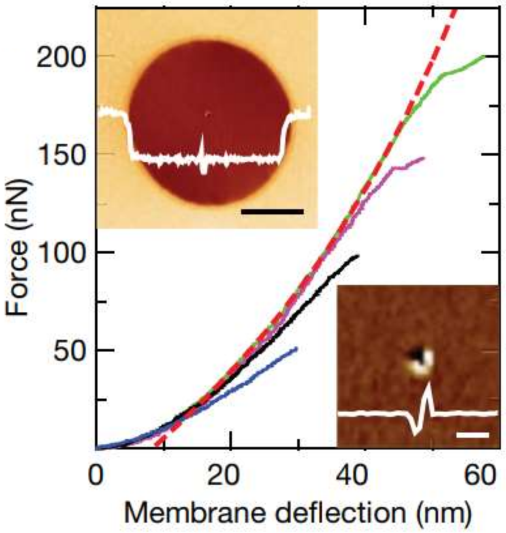










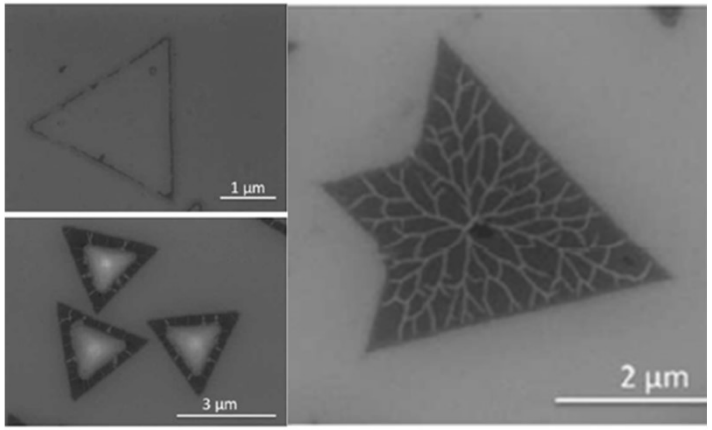


Furthermore, we obtain a breaking strength of 22 N m^{-1}, more than half the strength of single-crystal graphene. We note that indentation rupture is restricted and does not propagate, in contrast to similar experiments with crystalline graphene that result in catastrophic failure by rapid crack propagation.

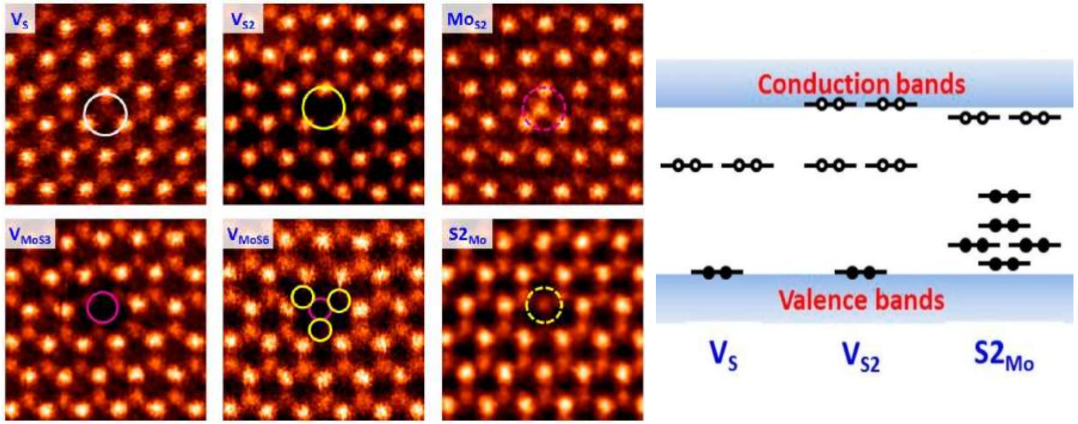
Nature 577, 199–203(2020)

Effect of Defects in MoS_2

Plasma Etching of MoS_2

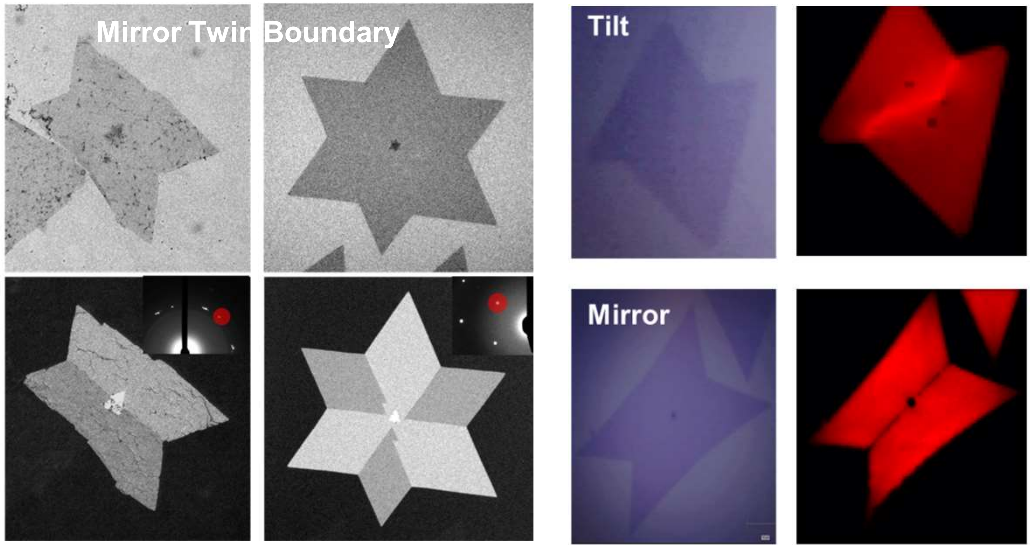


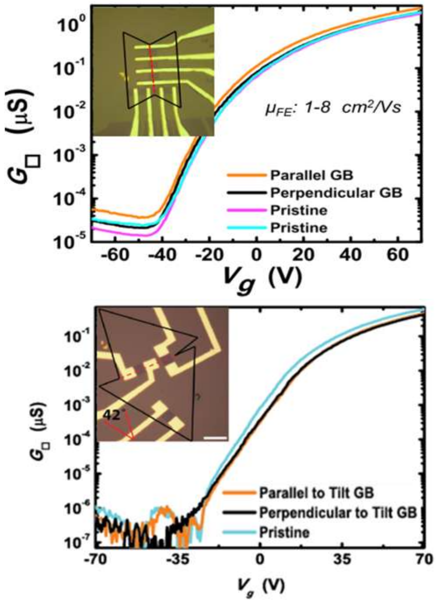
Sulfur Vacancies in MoS_2



W. Zhou et al. Nano Lett. (2013)

Electrical and Optical Properties of GBs in MoS_2

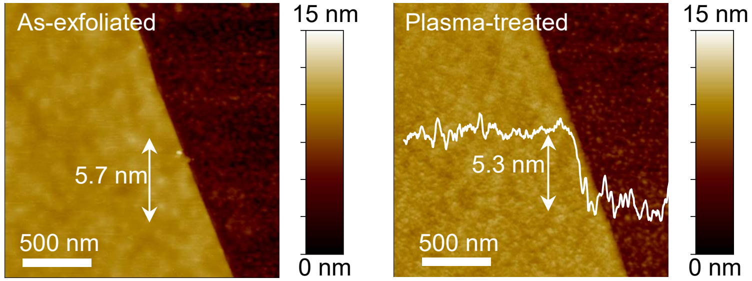


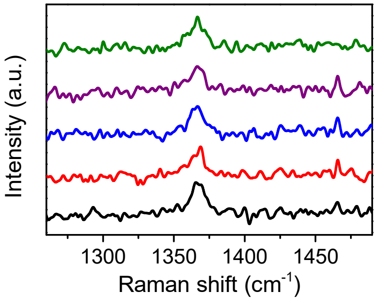


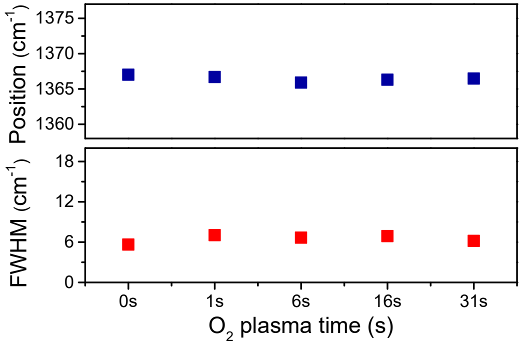
A. van der Zande et al. Nature Mater. (2013)

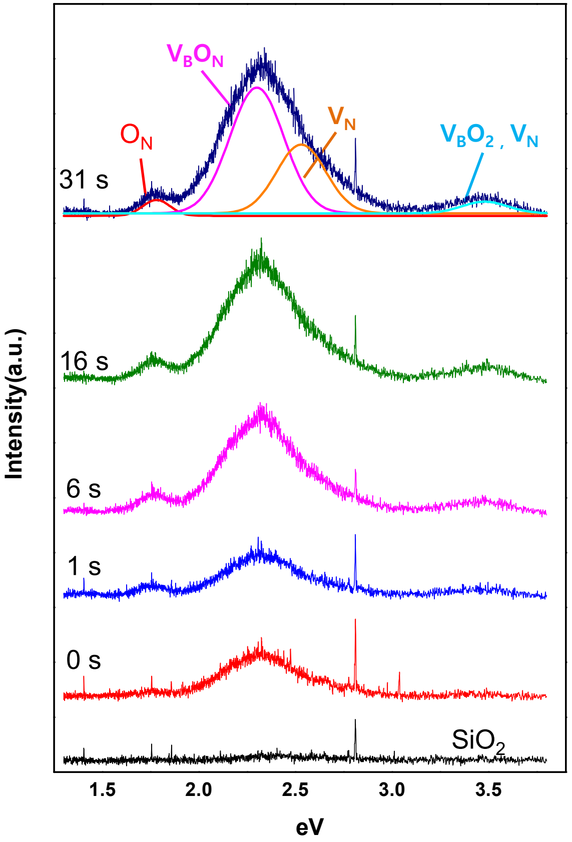
Defect Generation in hBN by Oxygen Plasma

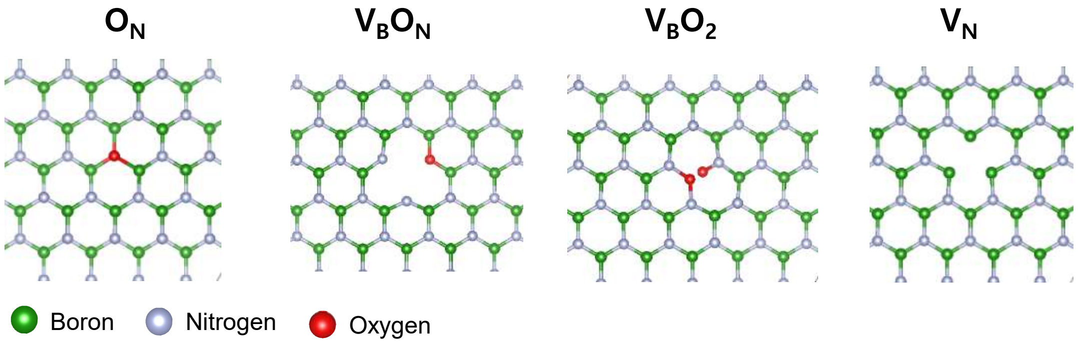
Surface treatment of hBN by mild O_2 plasma

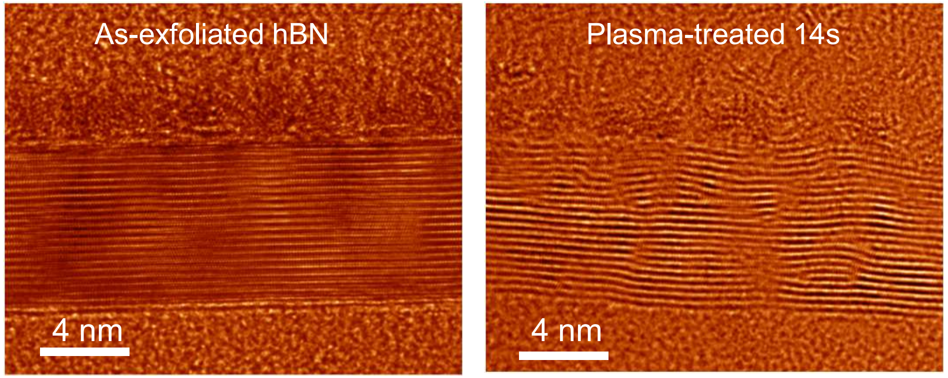








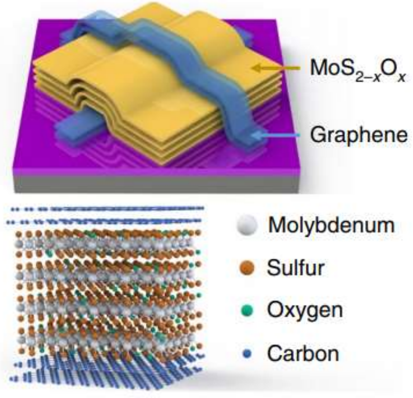


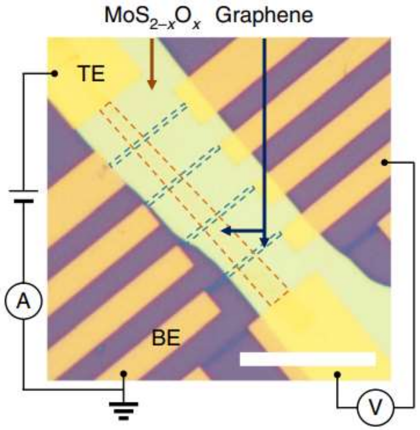


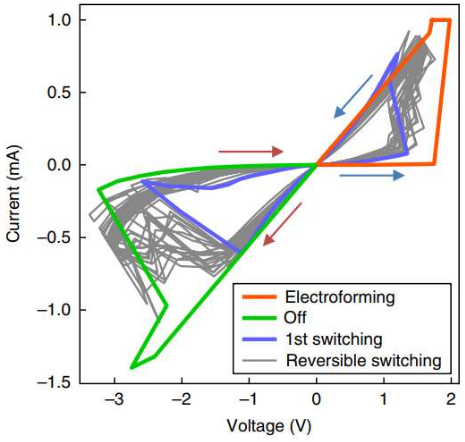
Y. S. Na, G.H. Lee* 2D Materials (2021)

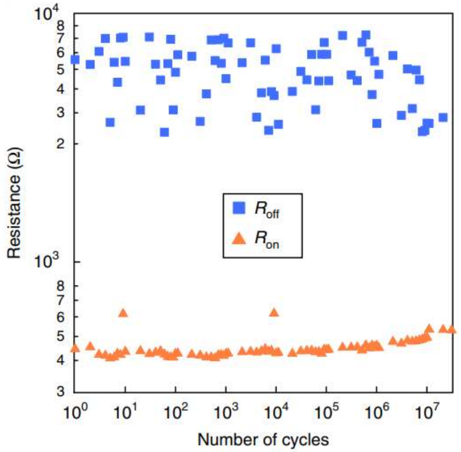
$MoS_{2-x}O_x$-based Memristor Device

Device scheme and electrical properties

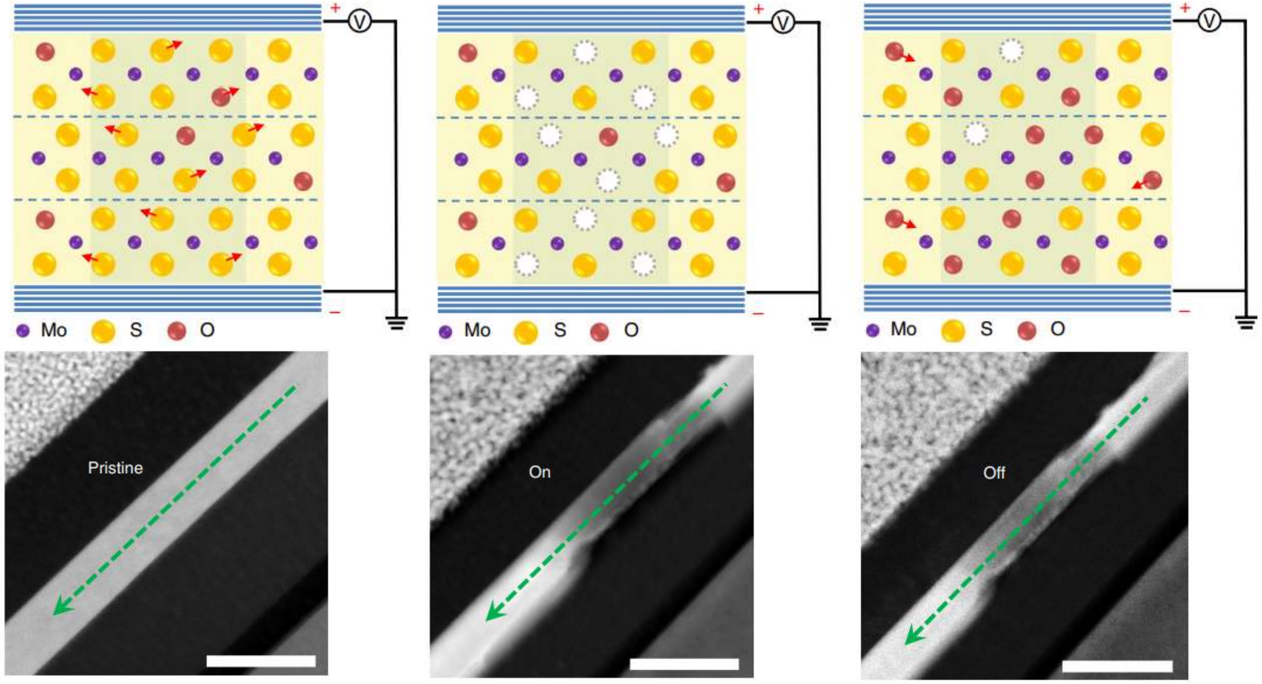








Operation mechanism



Oxdation of MoS_2 film at 160°C for 1.5 hours makes $MoS_{2-x}O_x$ resistive channel.

$MoS_{2-x}O_x$ layer was found to induce the observed high thermal stability after performing high temperature.

Atomically sharp interfaces between Gr and $MoS_{2-x}O_x$ play a crucial role in robustness of the devices.

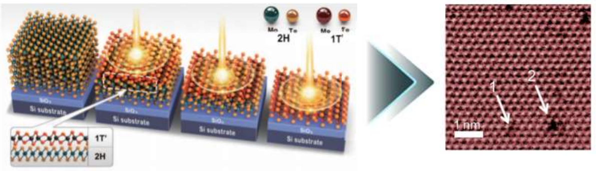
Nature Electronics 1, 130–136 (2018)

Phase Transition of Transition Metal Dichalcogenides

History of phase transition

Laser irradiation

Science(2015)

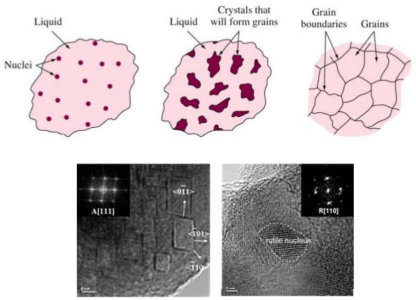


Defective 1T'

Local phase transition of $MoTe_2$ by laser annealing (2H → 1T')

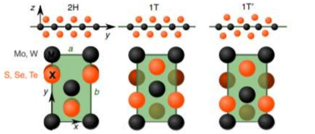
Uniqueness in 2D phase transition

3D phase transition



JACS (2004)

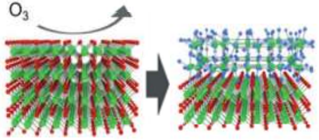
2D phase transition



Nat. Commun. (2014)

Translation of atoms

:Same composition with different crystal structure



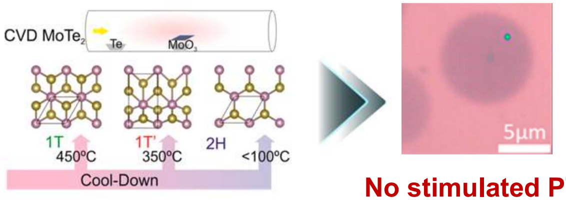
Adv. Mater. (2018)

Chemical reaction

:Different composition and crystal structure

CVD growth

ACS Nano(2016)

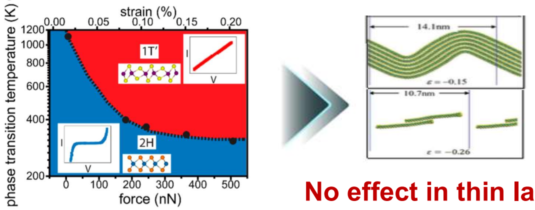


No stimulated PT

Various phase growth of $MoTe_2$ by $T_{cool\text{-}down}$ with CVD (2H/1T'/1T)

Strain

Nano Lett.(2016)

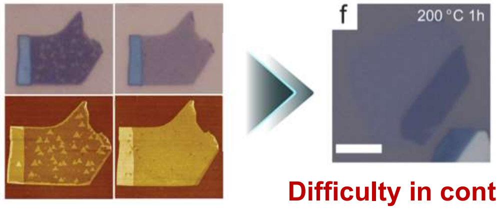


No effect in thin layer

Phase transition of $MoTe_2$ by strain (2H → 1T')

UV Oxidation

Nano Lett.(2015)

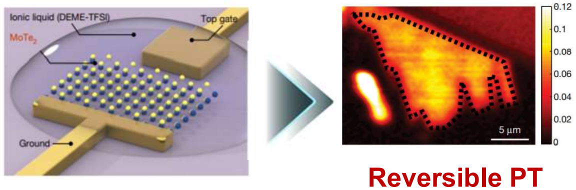


Difficulty in control

Oxidation of WSe_2 by UV irradiation (WSe_2 → WO_X)

Electrostatic doping

Nature(2017)

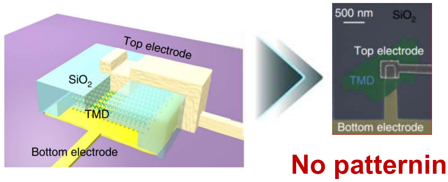


Reversible PT

Phase transition of $MoTe_2$ by electrostatic doping (2H → 1T')

Electrical field

Nat. Mater.(2019)



No patterning

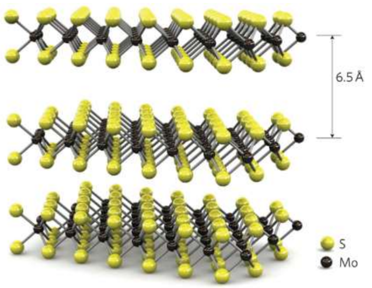
Phase transition of $MoTe_2$ by vertical electric field (2H →$2H_d$)

Need for study in PT

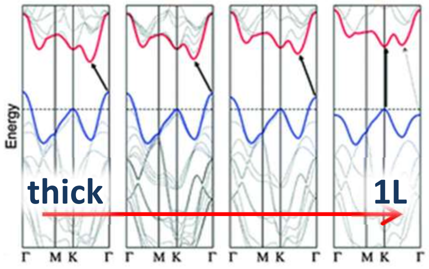
- Structural transition of TMDs
  - New phase in nanoscale
  - Main factors to control PT
- Chemical transition of TMDs
  - Formation of compatible oxides
  - layer-by-layer oxidation

Top-down Approach for Thinning and Phase Transition

Thickness-dependent band structure



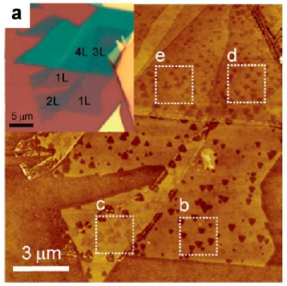
Nature Nanotech. (2011)



Appl. Phys. Lett. (2013)

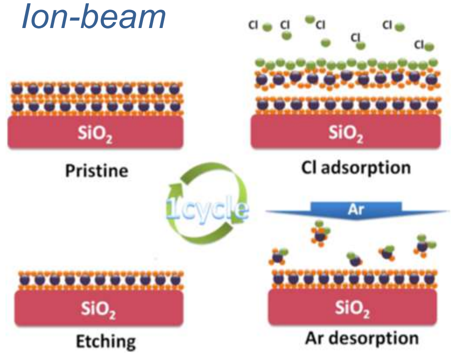
Etching of 2D materials

O$_2$ annealing



J. Phys. Chem. C 11 (2013)

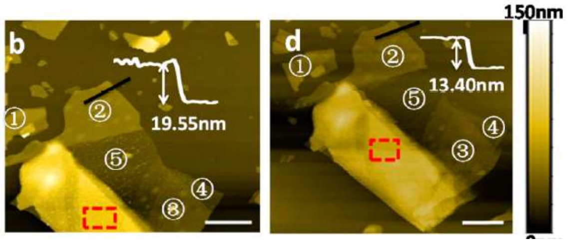
Ion-beam



ACS Appl. Mater. Interfaces (2015)

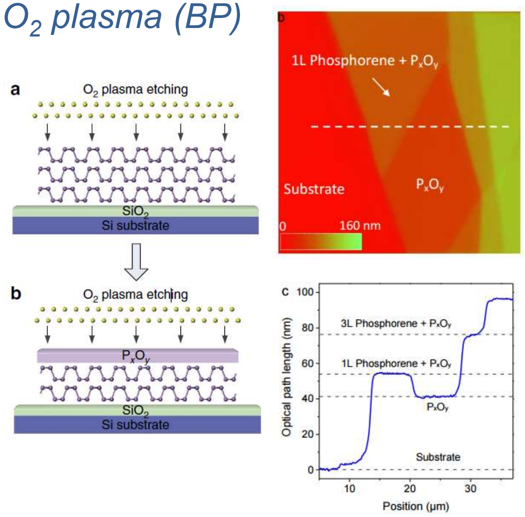
Plasma Treatment on 2D materials

Ar plasma (BP)



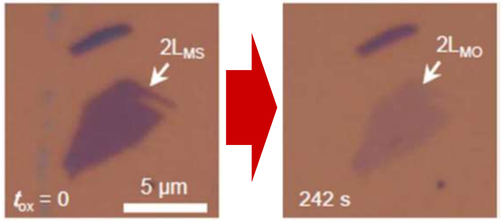
J. Phys. Chem. C (2013)

O$_2$ plasma (BP)

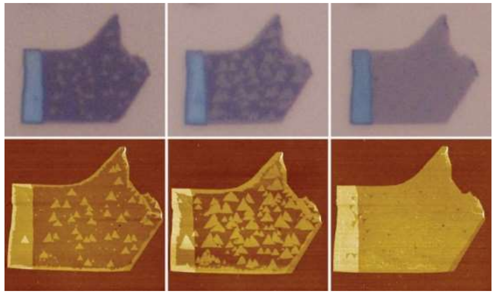


Nature. Commun. (2016)

O$_2$ plasma (MoS$_2$)



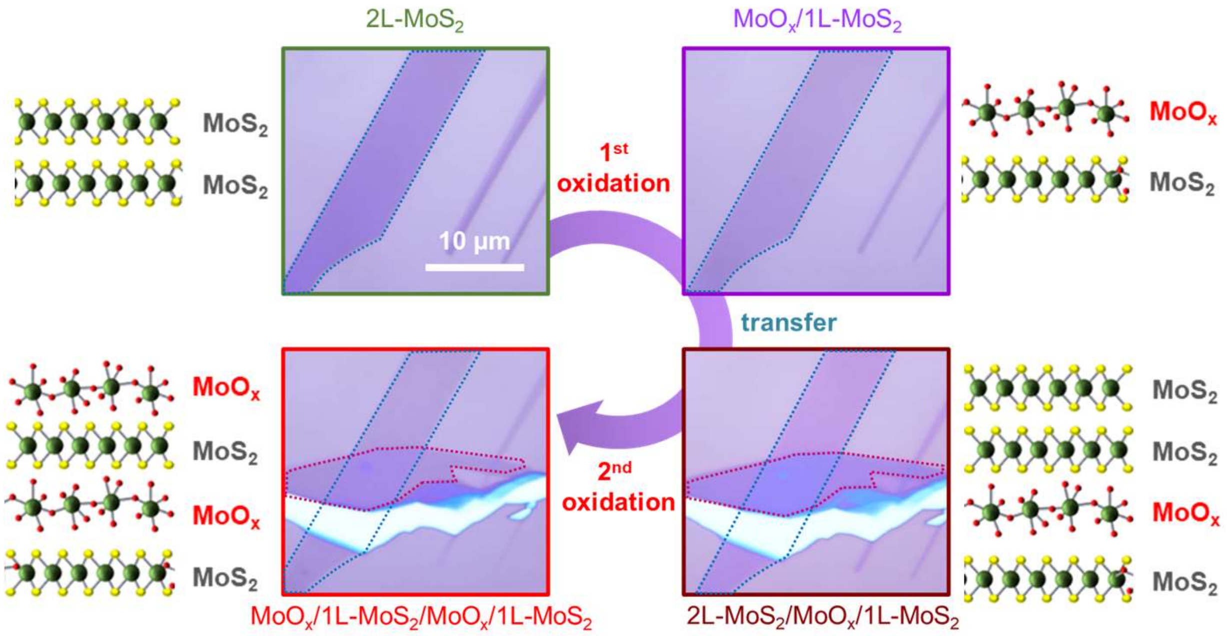
2D Mater (2017)

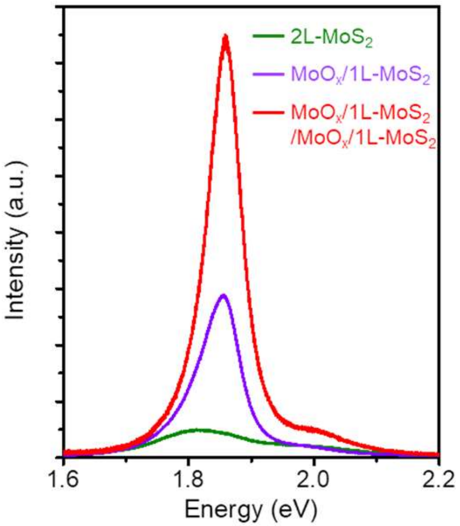


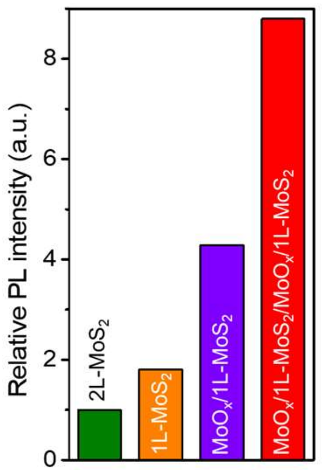
Nano Lett. (2015)

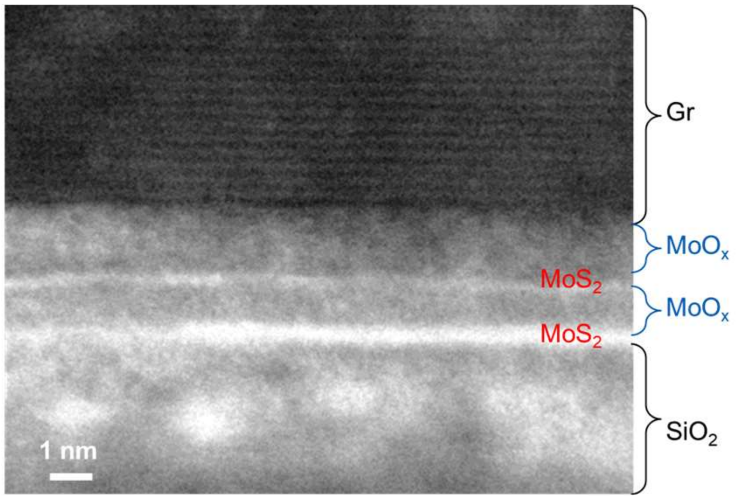
Layer-by-layer oxidation

Fabrication process of $MoO_x/MoS_2/MoO_x/MoS_2$



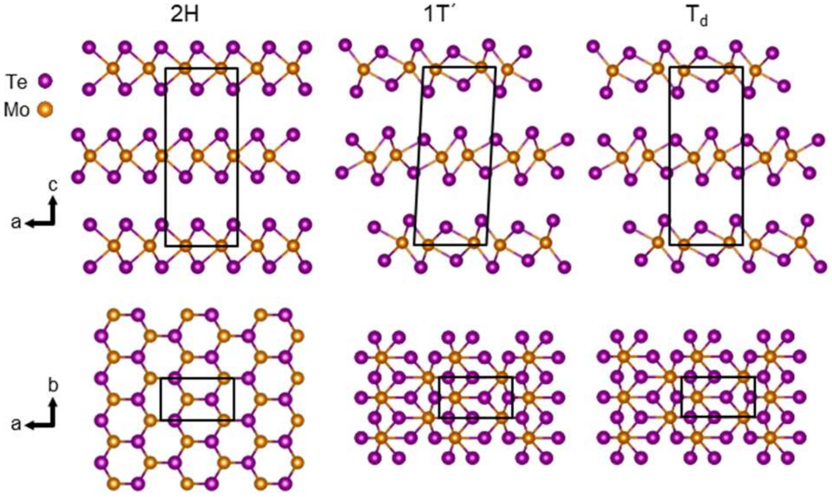


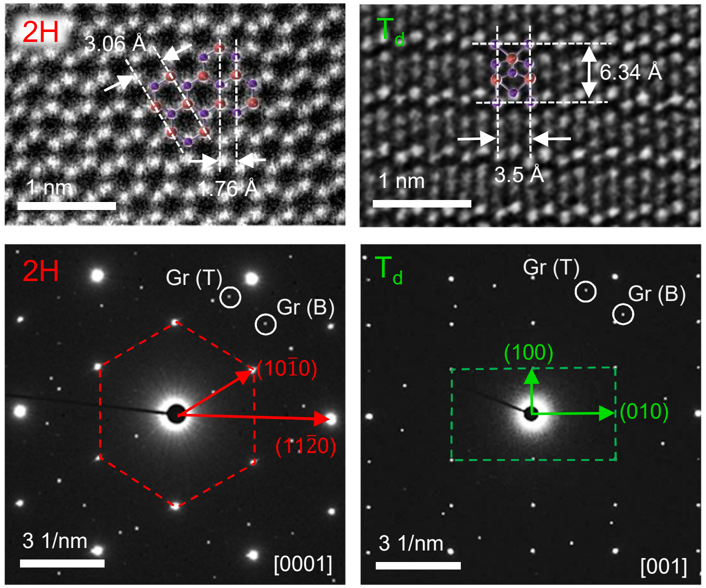




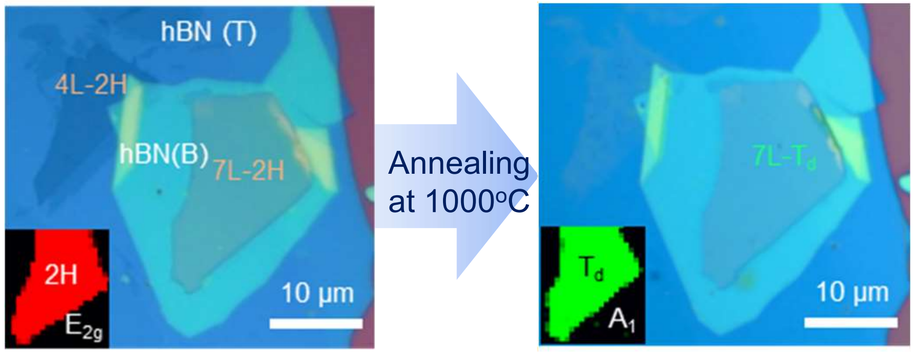
S.J. Kang, Y. Kim, C.H. Lee*, G.H. Lee* ACS Applied Materials & Interfaces (2020)

Phase Transition of MoTe2 by Annealing

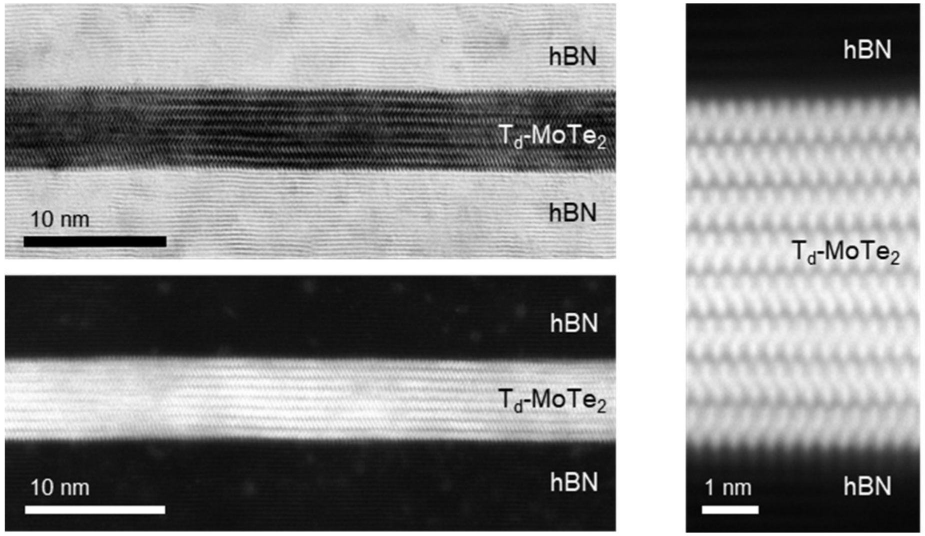




Encapsulation annealing



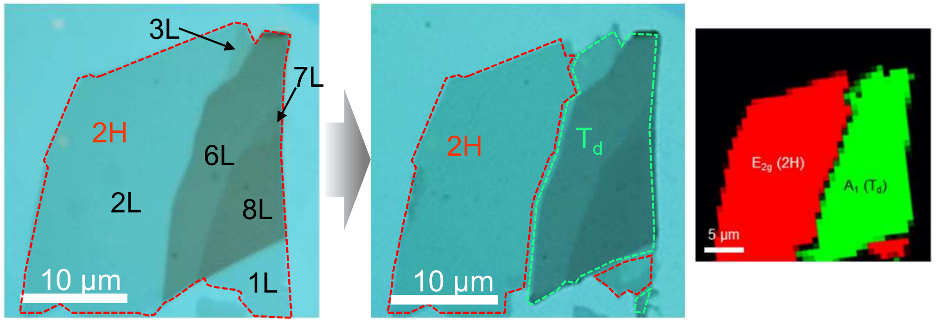
Annealing at 1000°C



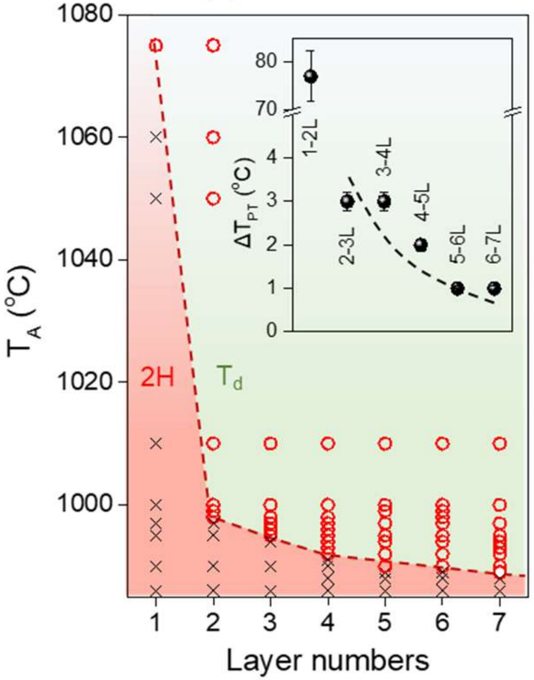
H.J. Ryu, …, K.P. Kim, H. Cheong, Y.W. Son, G.H. Lee, **Advanced Functional Materials (2021)**

Phase Transition of MoTe2 by Annealing

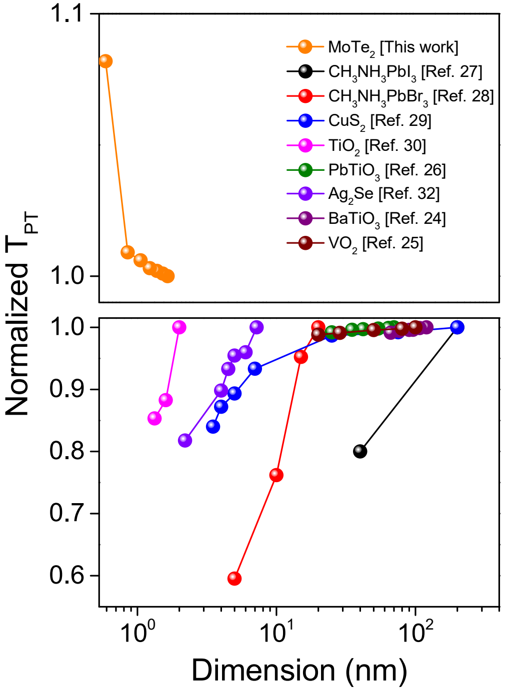
Phase transition of $MoTe_2$ with different thicknesses

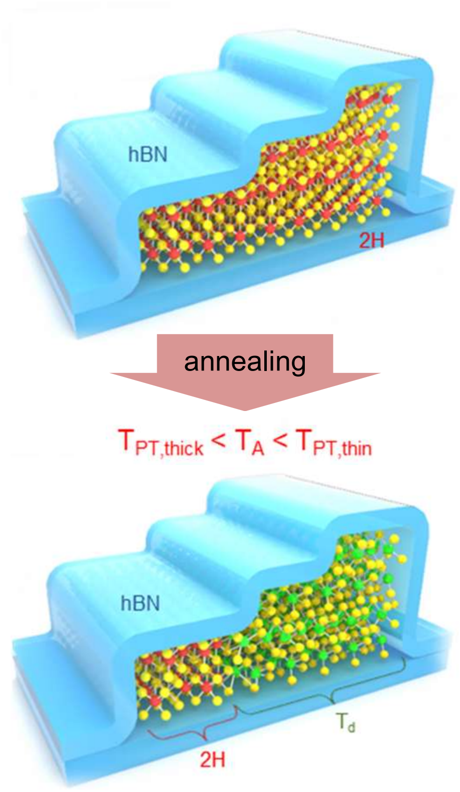


T_{PT} vs. thickness



2D vs. 3D





$T_{PT,thick} < T_A < T_{PT,thin}$

- Phase transition temperature shows step-like increase as the thickness decreases.
- Precise control of phase transition is possible in $MoTe_2$ by using number of layers.

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