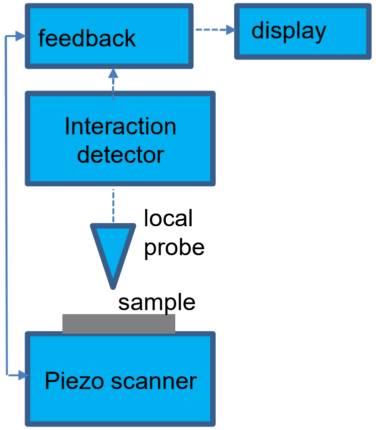
6. Analytical Tools for 2D Materials

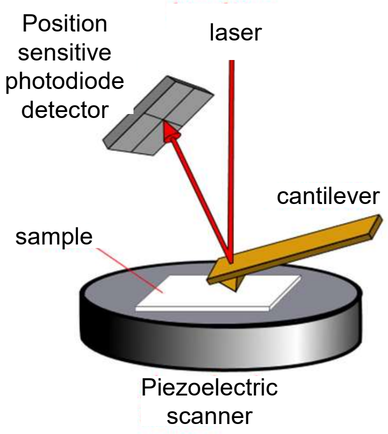
서 울 대 학 교
SEOUL NATIONAL UNIVERSITY

Analytical Tools for 2D Materials: SPM

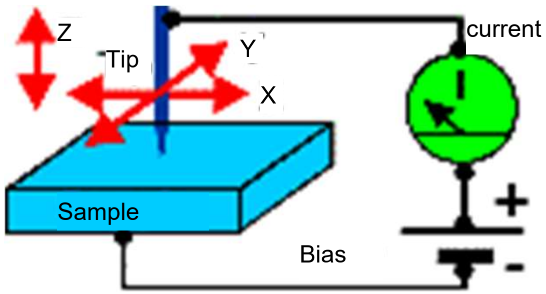
Scanning Probe Microscopy (SPM)



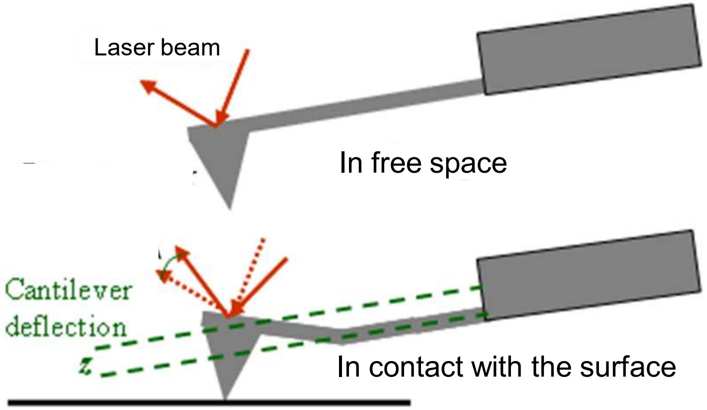
Atomic Force Microscopy (AFM)



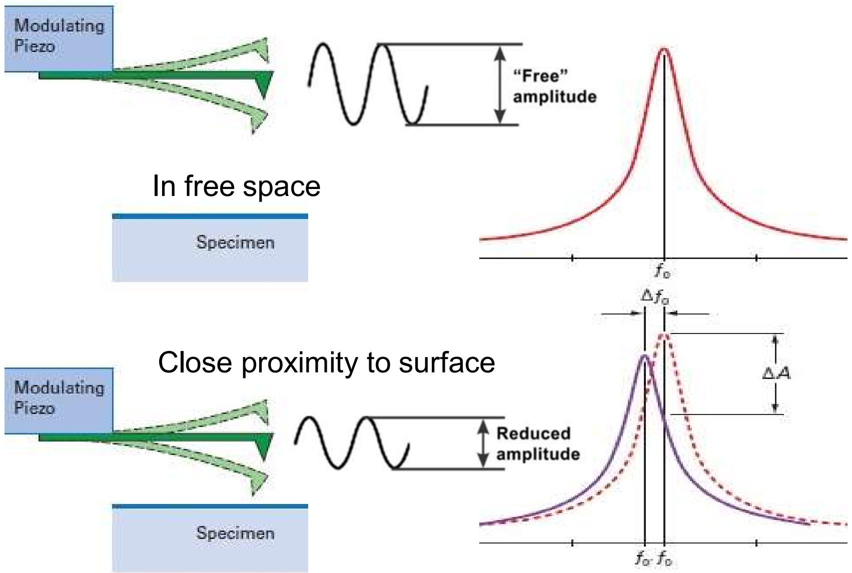
Scanning Tunneling Microscopy (STM)



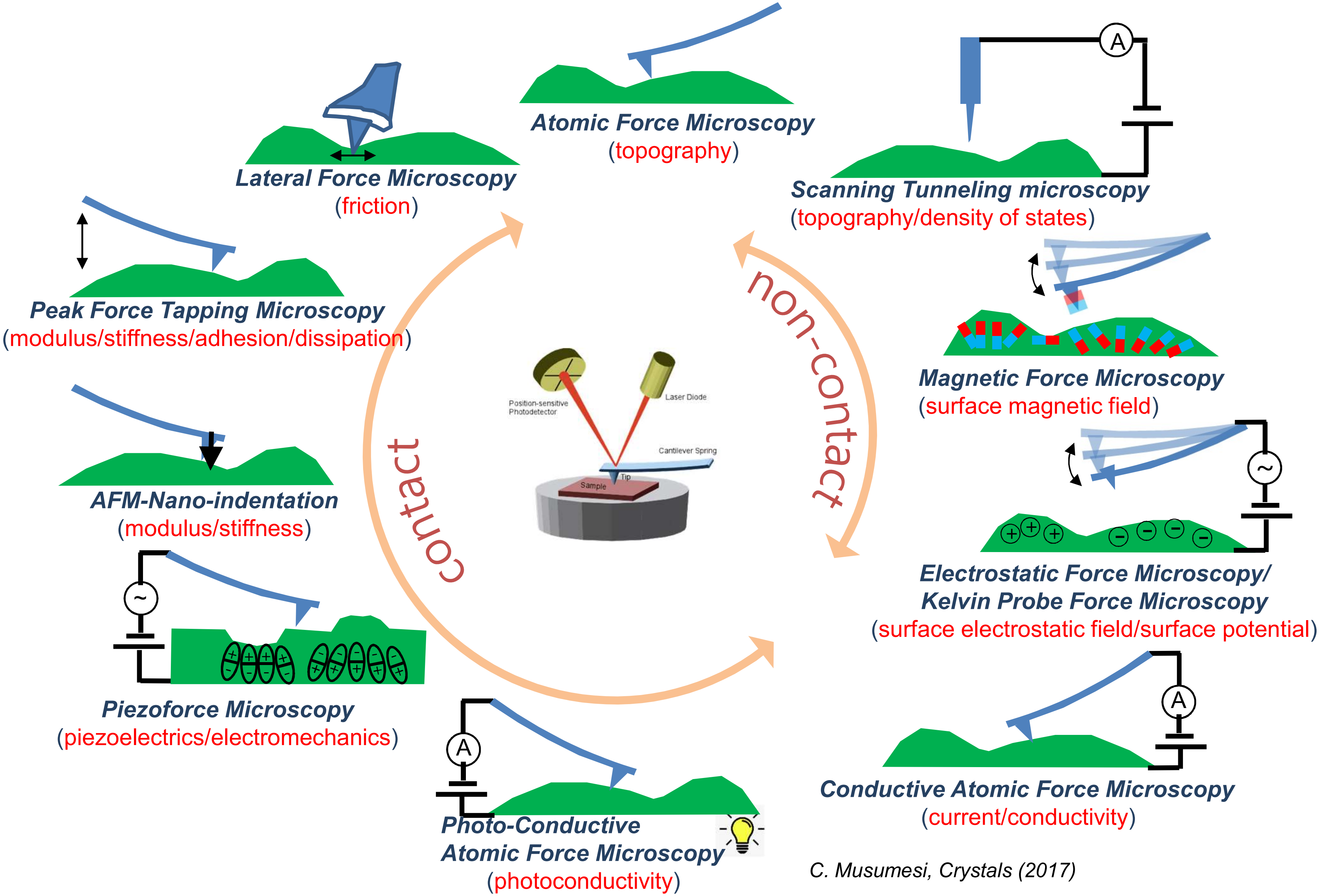
Contact mode AFM



Non-Contact mode AFM



Analytical Tools for 2D Materials: SPM



Atomic Force Microscopy
(topography)

Lateral Force Microscopy
(friction)

Scanning Tunneling microscopy
(topography/density of states)

Peak Force Tapping Microscopy
(modulus/stiffness/adhesion/dissipation)

Magnetic Force Microscopy
(surface magnetic field)

AFM-Nano-indentation
(modulus/stiffness)

Electrostatic Force Microscopy/
Kelvin Probe Force Microscopy
(surface electrostatic field/surface potential)

Piezoforce Microscopy
(piezoelectrics/electromechanics)

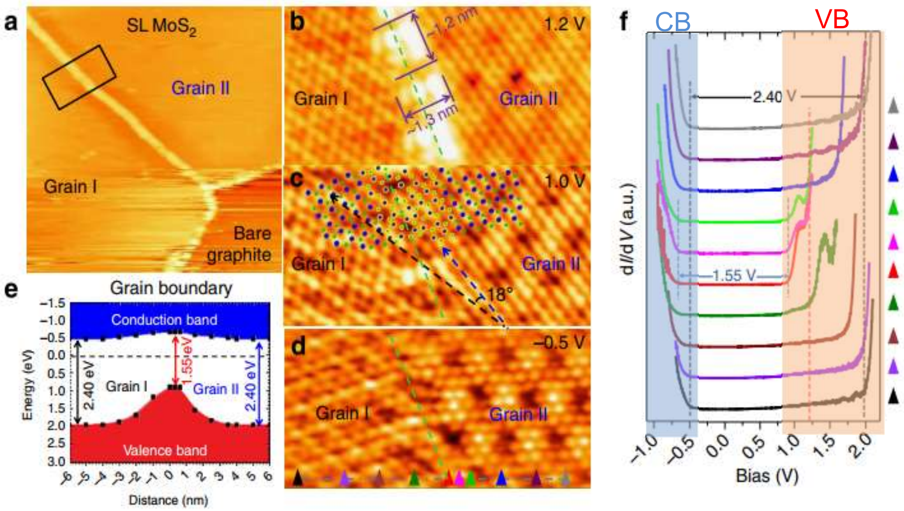
Conductive Atomic Force Microscopy
(current/conductivity)

Photo-Conductive
Atomic Force Microscopy
(photoconductivity)

C. Musumesi, Crystals (2017)

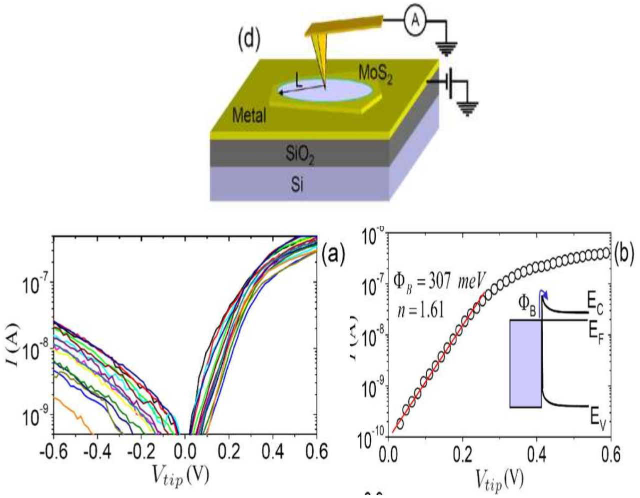
Analytical Tools for 2D Materials: SPM

Scanning Tunneling Microscopy



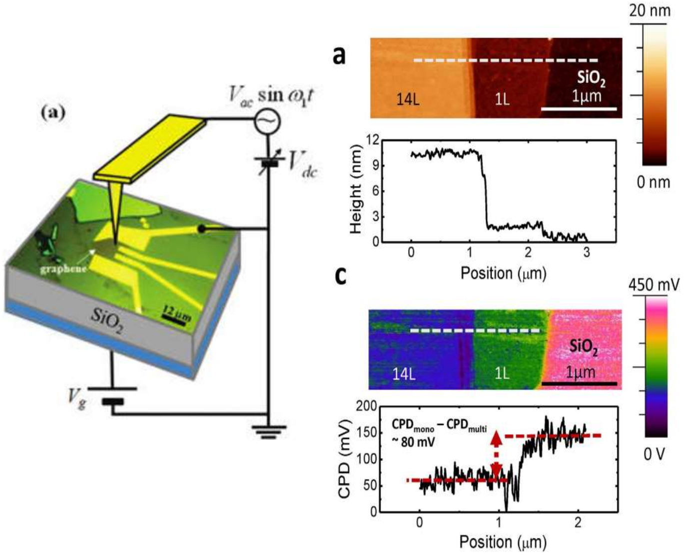
Yu Li Huang et al. Nat.Comm 6, 7298 (2015)

Conductive-AFM



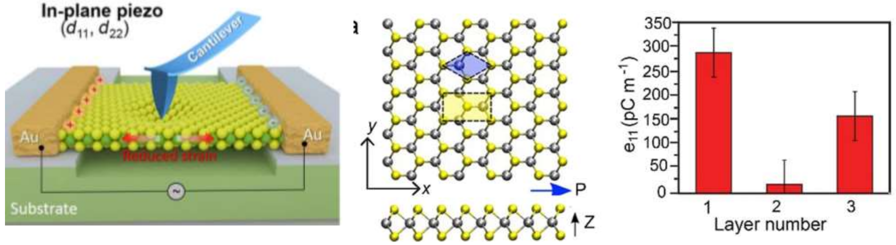
F. Giannazzo et al. PRB 92, 081307 (2015)

Kelvin Probe Force Microscopy

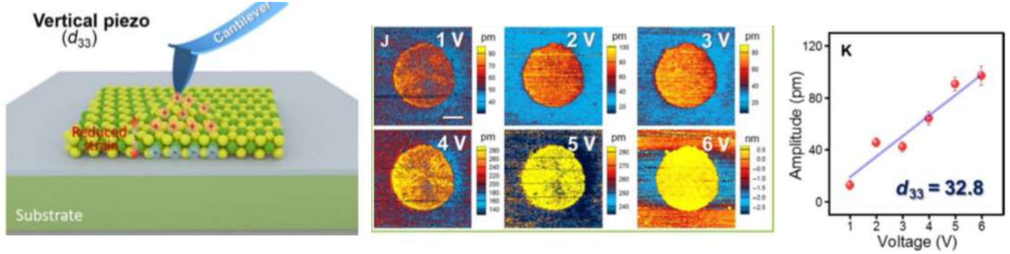


M. Tosun et al. Sci.Rep 5, 10990 (2015)

Piezo Force Microscopy



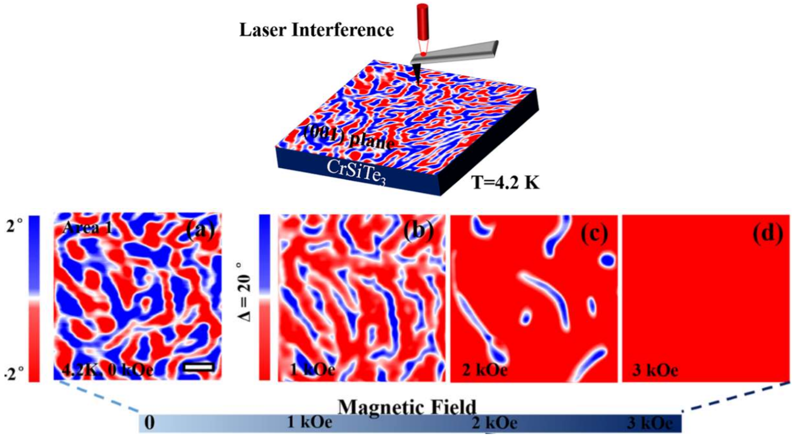
subatomic deformation-induced vertical piezoelectricity of CdS



Zhu, H. et al. Nat. Nanotechnol. 10, 151 (2015)
Wang, X. et al. Sci. Adv. 2, e1600209 (2016)

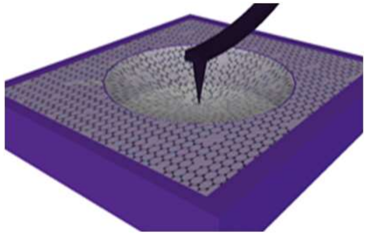
Analytical Tools for 2D Materials: SPM

Magnetic Force Microscopy



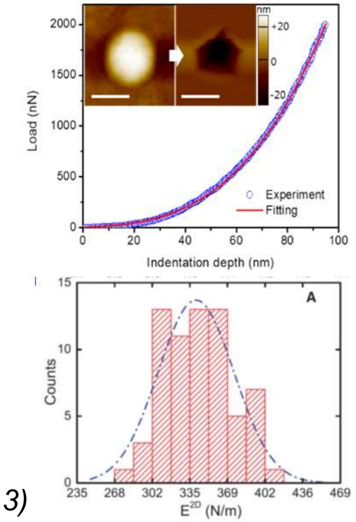
Wu et al. AIP Advances 8, 055016 (2018)

AFM Nano-indentation



$$F = \left(\sigma_0^{2D}\pi\right)\delta + \left(E^{2D}\frac{q^3}{r^2}\right)\delta^3$$

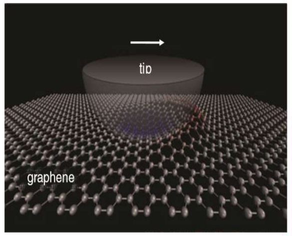
$$\sigma_m^{2D} = \left(\frac{FE^{2D}}{4\pi r_{tip}}\right)^{1/2}$$

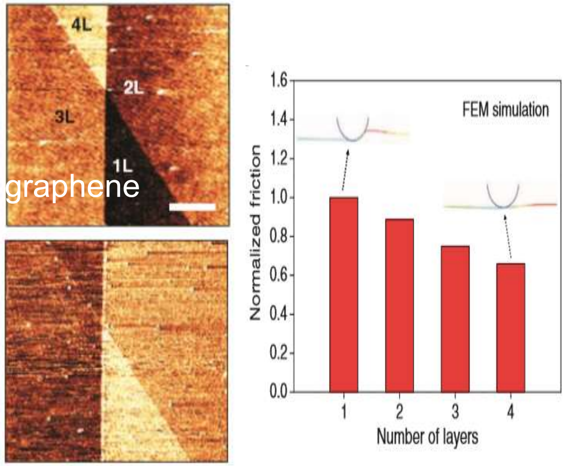


G. Lee et al. Science 340, 1073 (2013)

Friction Force Microscopy

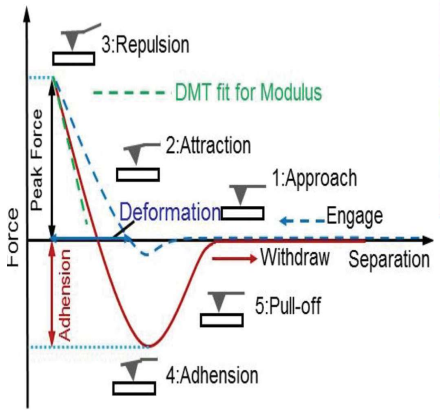
Puckering effect

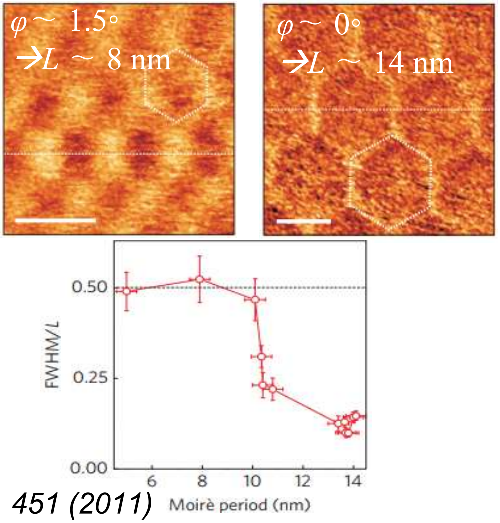




C. Lee et al. Sci. 328, 76 (2010)

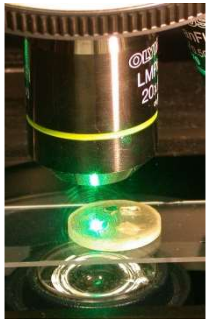
Peak Force Tapping Microscopy

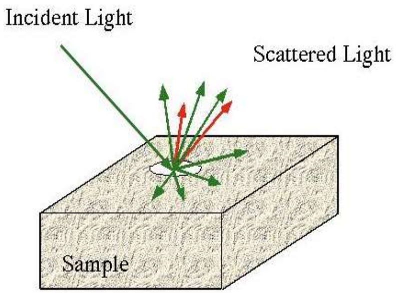




C. R. Woods et al. Nat.Phys. 10, 451 (2011)

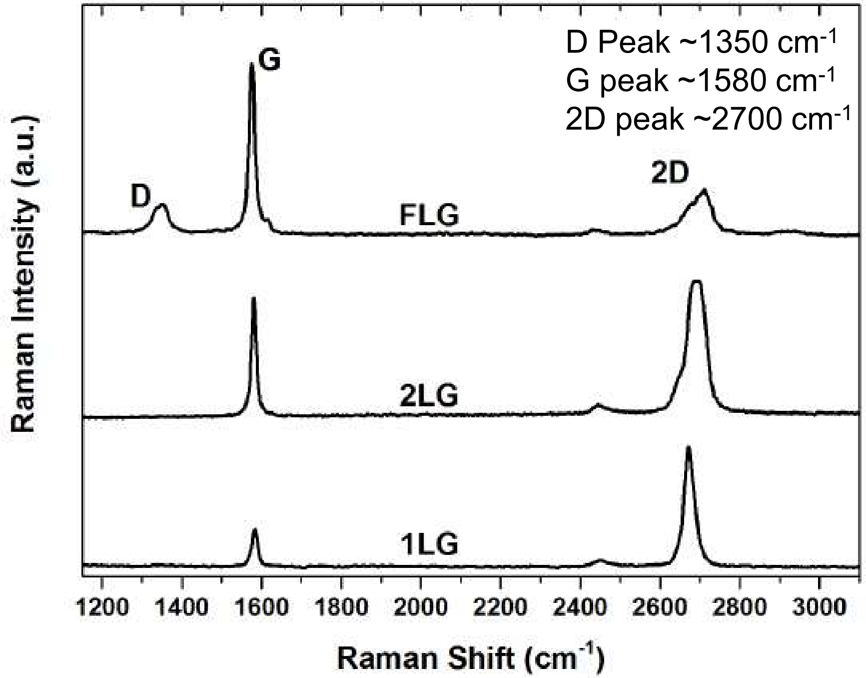
Analytical Tools for 2D Materials: Raman Spectroscopy





Raman is powerful tool to analyze quality of graphene. To avoid damaging the graphene, laser spot power of less than 1 mW must be used for a laser spot diameter of 500 nm or greater and acquisition times of less than 30 seconds and it is recommended to include a range from 1150 cm^{-1} to 3100 cm^{-1}

Raman spectrum of graphene



Disorder of graphene

- The values of I_D/I_G should be recorded as the measurands for the level of disorder of the graphene. For low and moderate defect density, I_D/I_G increases with an increasing defects density**.**

Evidence of monolayer graphene

1. 2D-peak must be a single Lorentzian peak
2. FWHM of 2D of ≤35 cm^{-1}, where $I_D/I_G \leq 0.2$.
3. $I_{2D}/I_G > 2$ (However, this ratio can be reduced by other factors such as the level of disorder and doping and as such it cannot be explicitly used as an indication of single layer graphene.)

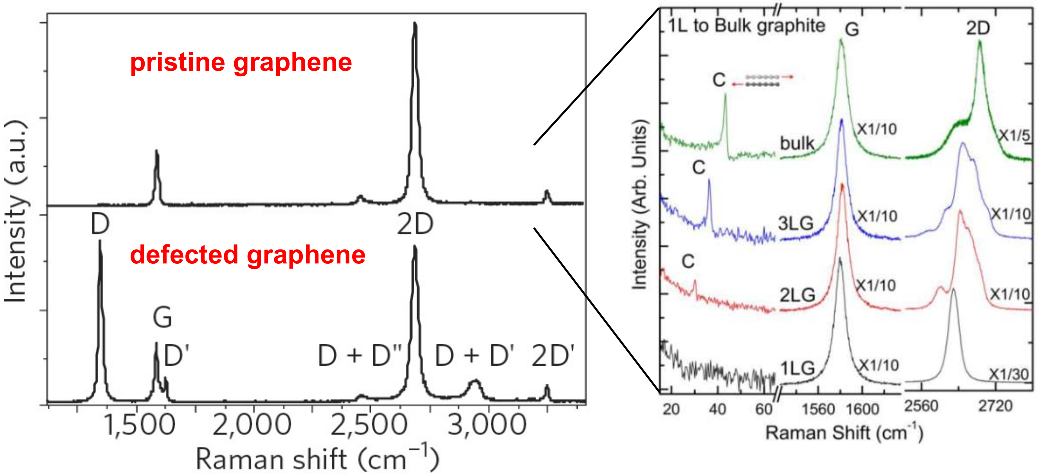
Mismatch of bilayer graphene

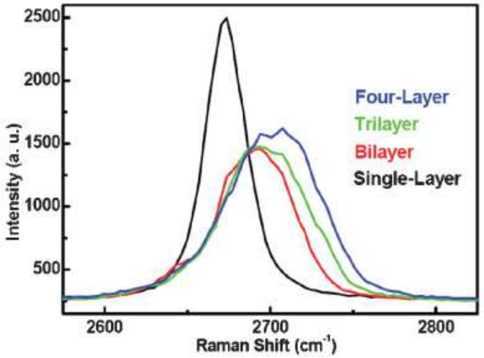
Mismatch angle is low (<5°) : the presence of additional peaks at either 1370~470 cm^{-1} or 1540~1620 cm^{-1} must first be assessed. If these peaks are not observed, the sheet could be single layer or twisted-bilayer with a higher (>5°) mismatch angle between the two layers

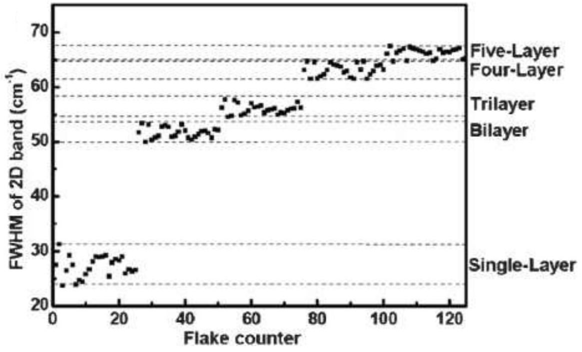
A. J. Pollard et al. "Characterization of the structure of graphene", NPL, (2017)

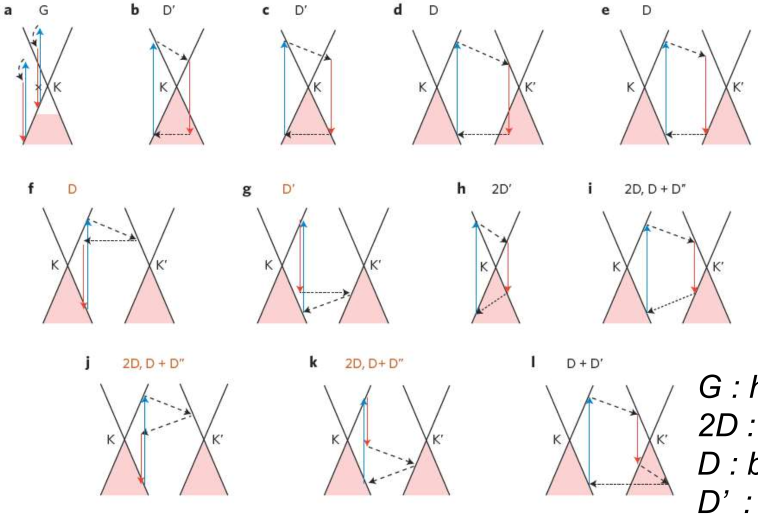
Analytical Tools for 2D Materials: Raman Spectroscopy

Graphene







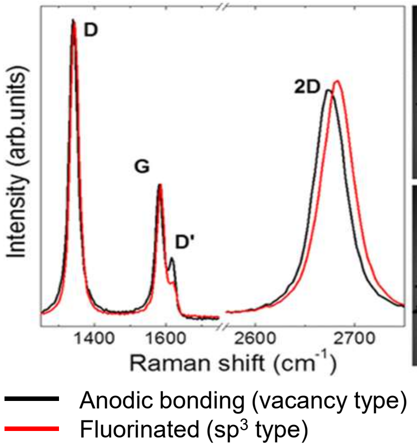


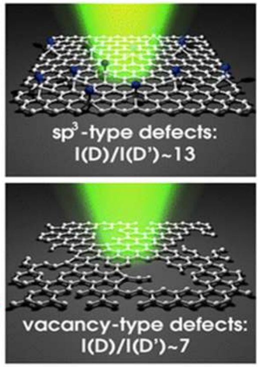
G : high-frequency E_{1g} phonon, stretching of the C-C bond. highly sensitive to strain.
2D : two phonons with opposite momentum in the highest optical branch near the K.
D : breathing modes of rings, degree of defects
D' : double resonance
C : interlayer coupling (direct probe of N)

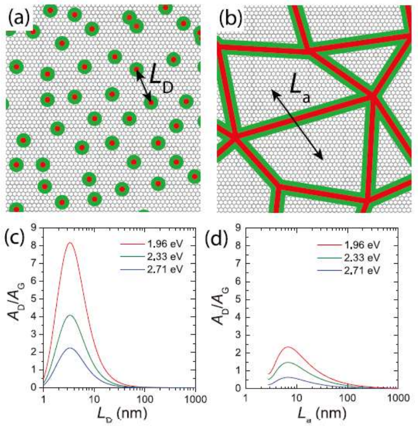
A. C. Ferrari et al. Nature nanotechnol. (2013) & Y. Hao et al. Small (2009)

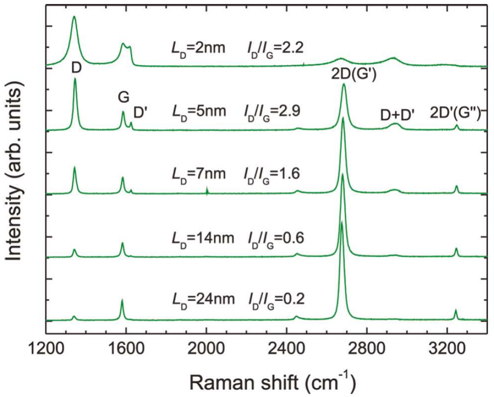
Analytical Tools for 2D Materials: Raman Spectroscopy

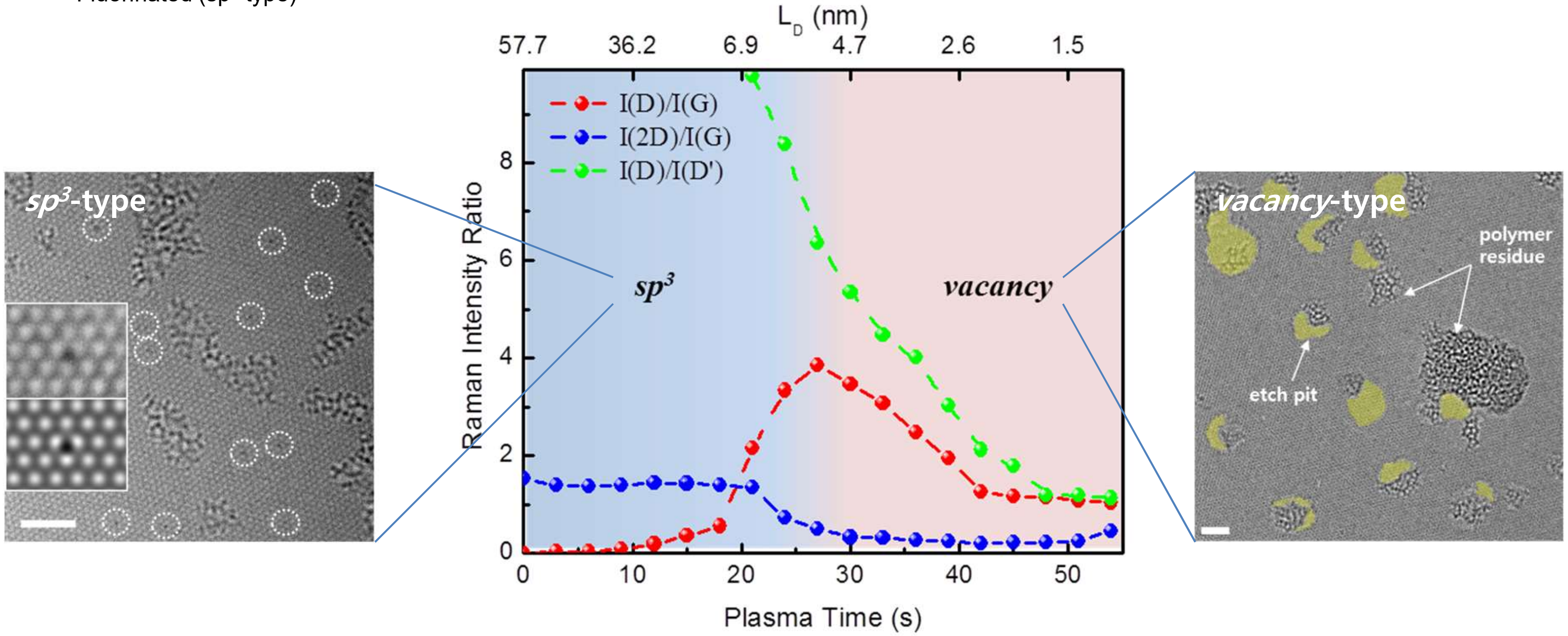
Graphene defect







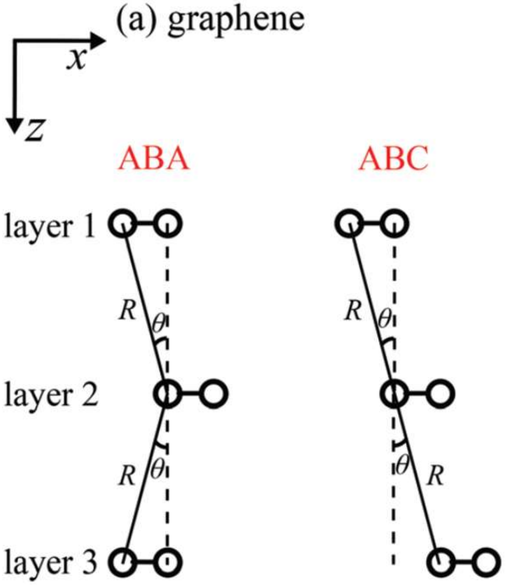


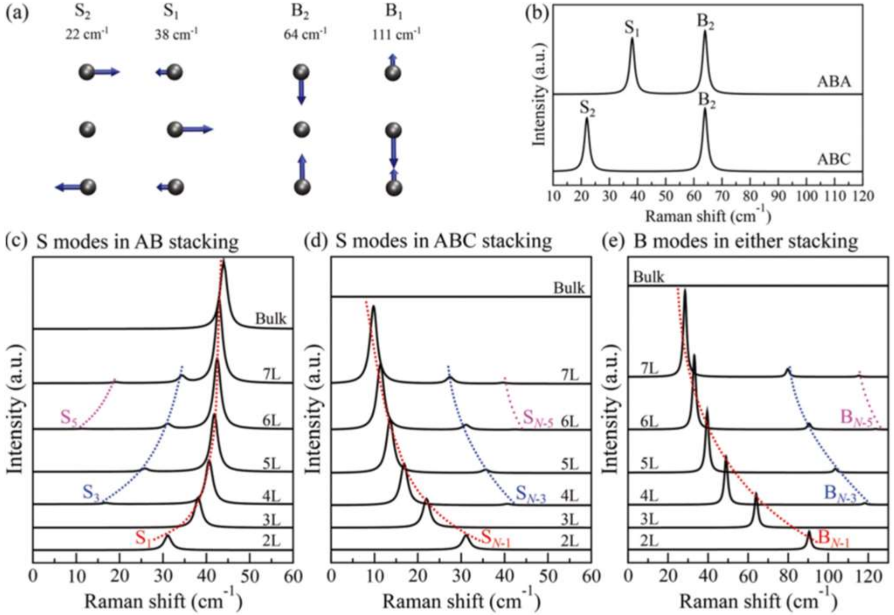


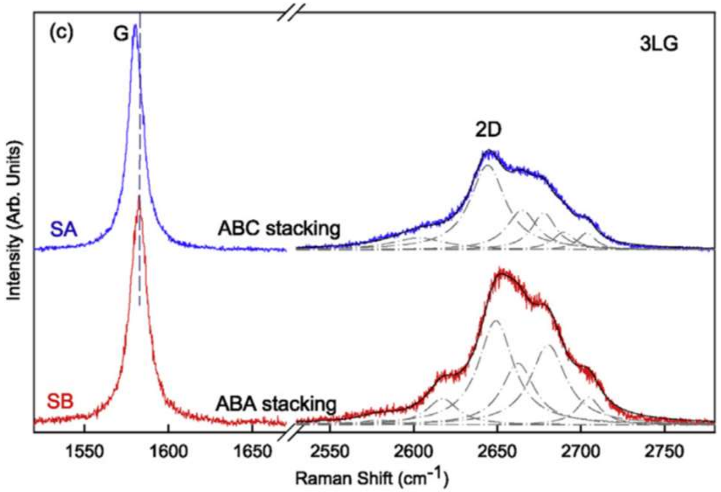
A. Eckmann et al. Nano Lett. (2012) & L.G Cancado et al. Nano Lett. (2011) & L. G. Cancado et al. 2D Mater. (2017) & G.H. Lee Nature Comm (2014)

Analytical Tools for 2D Materials: Raman Spectroscopy

Stacking sequence



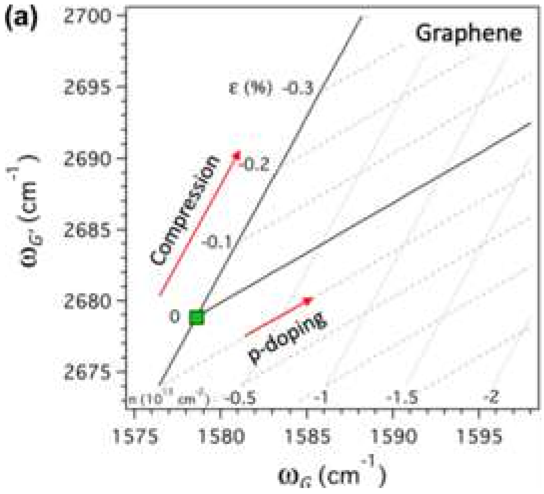


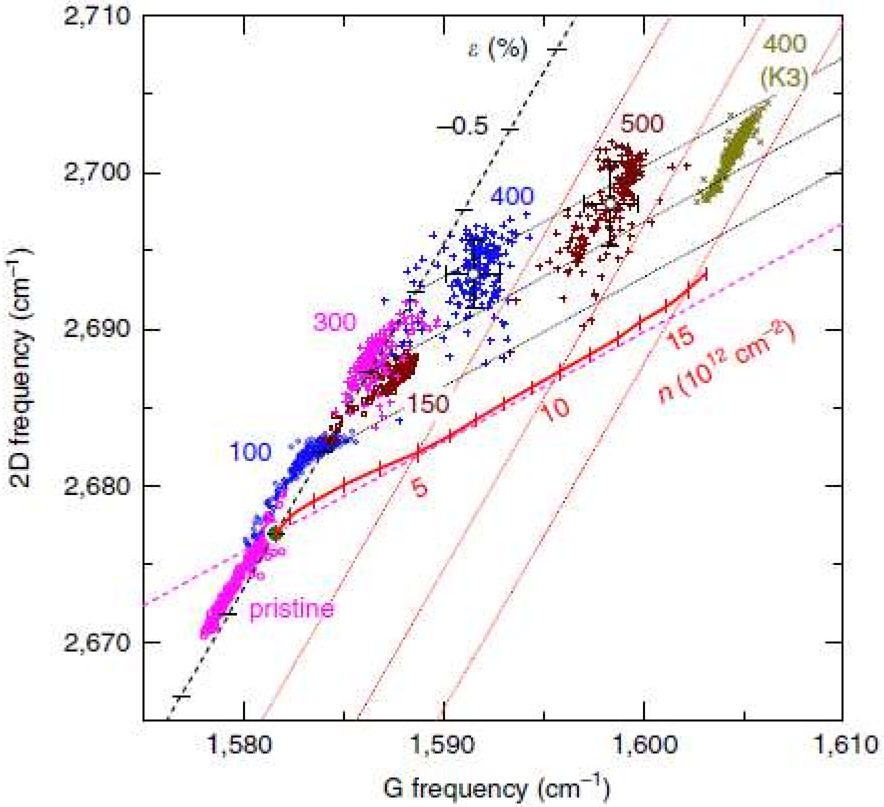


L. Liang et al. Nanoscale (2017) & X. Zhang et al. Carbon (2016)

Analytical Tools for 2D Materials: Raman Spectroscopy

Doping and strain of graphene

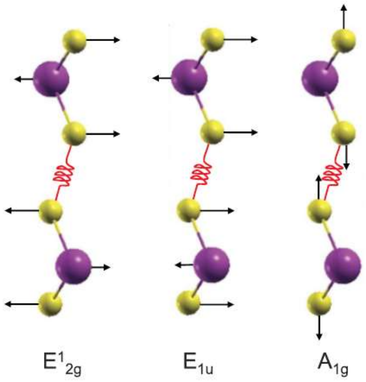




J. E. Lee et al. Nat. Comm. (2012) & R. Rao et al PRB (2019)

Analytical Tools for 2D Materials: Raman Spectroscopy

MoS_2

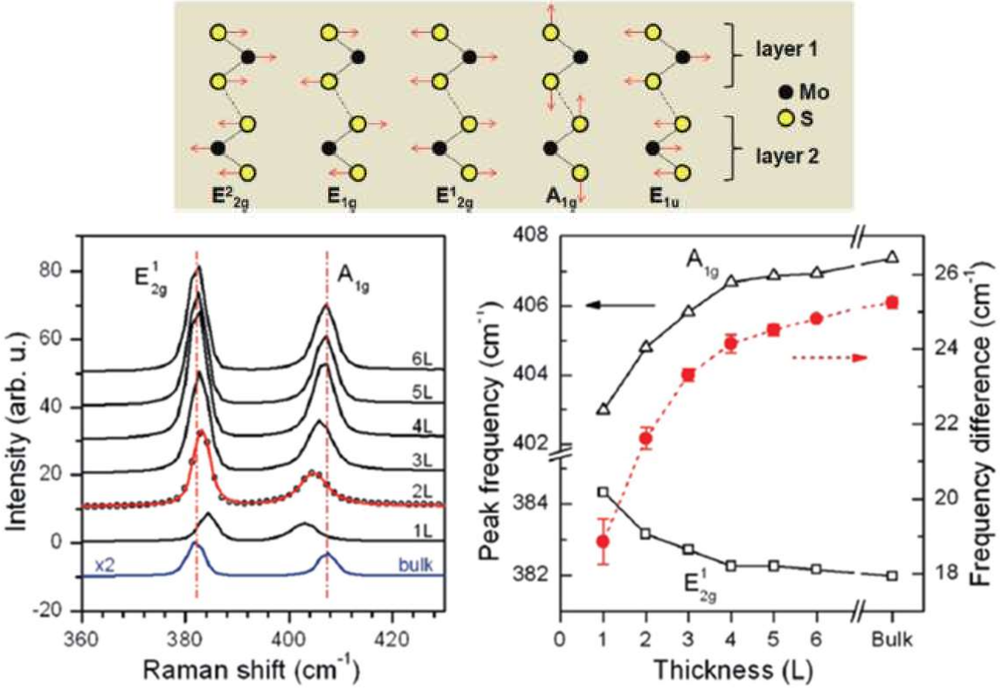


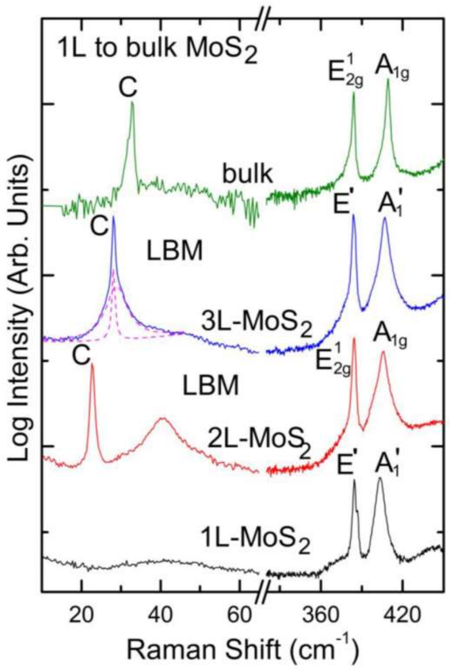
Out-of-plane A_{1g} mode

- *The interaction between sulfur atoms of neighboring layers can influence the frequency.*
- *single layer → double layer, adds an additional spring (binding force) leads to an increase of the A_{1g}-mode frequency with increasing number of layers.*
- *Binding force leads to an increase of frequency the weak interlayer interaction.*

In-plane E^1_{2g} mode

- *The self-interaction terms for Mo and S influence to decrease the frequency with increasing number of layers. (opposite to the result of A_{1g} mode)*
- *Change in frequency is associated to the differences in the lattice constant and interatomic distances in bulk and the single layer, respectively.*
- *The decrease of the E^1_{2g} phonon frequency is associated with a stronger dielectric screening of the long-range Coulomb interaction in few-layer and bulk MoS_2.*

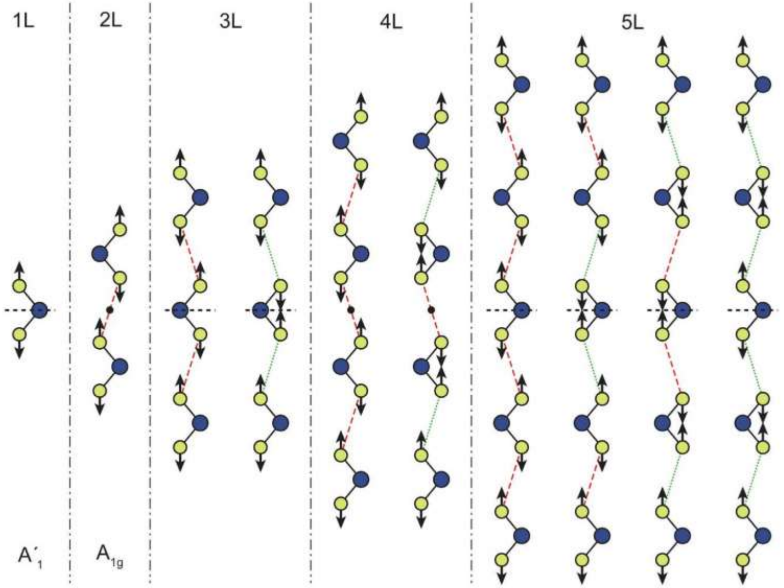




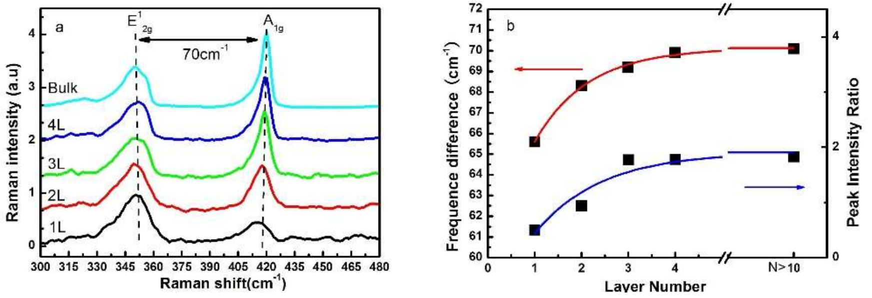
A. C. Ferrari et al. Nature nanotechnol. (2013) & F. Bonaccorso et al. ACS Nano (2013) & C. Lee et al. ACS Nano (2010)

Analytical Tools for 2D Materials: Raman Spectroscopy

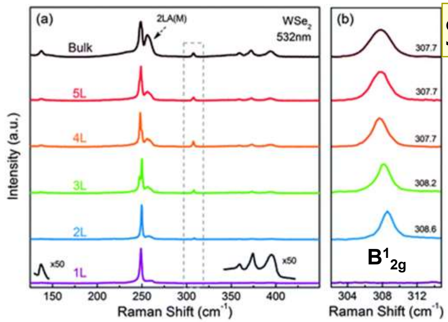
Layer dependence



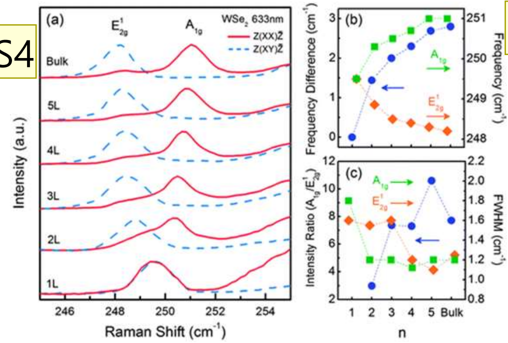
WS$_2$



WSe$_2$

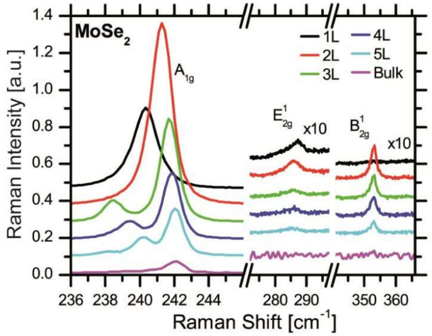


S4



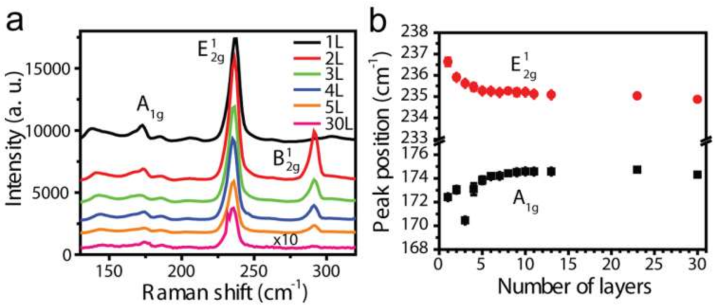
S5

MoSe$_2$



S6

MoTe$_2$



P. Tonndorf et al. Optics Express (2013) & Yamamoto et al, ACS Nano (2014) & Zeng et al. Sci. Rep. (2013) & W. Zhao et al. Nanoscale (2013)

슬라이드 12

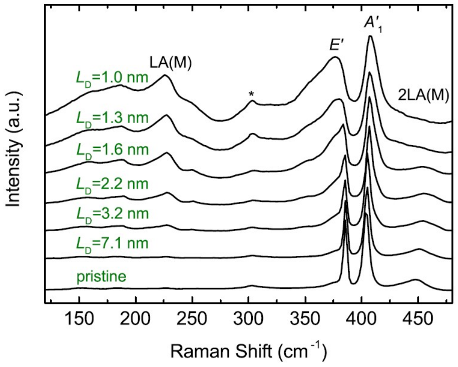
S4 peak간 간격, B12g peak으로 layer 판별
Sojung_NCML, 2020-05-18

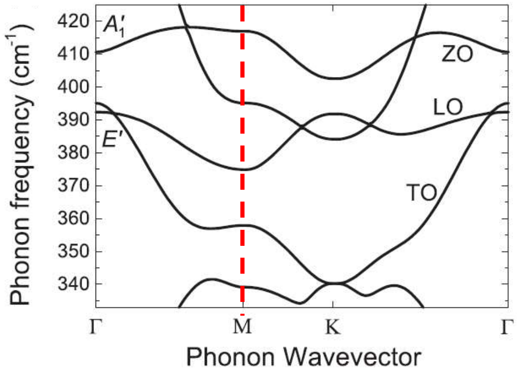
S5 polarized Raman
Sojung_NCML, 2020-05-18

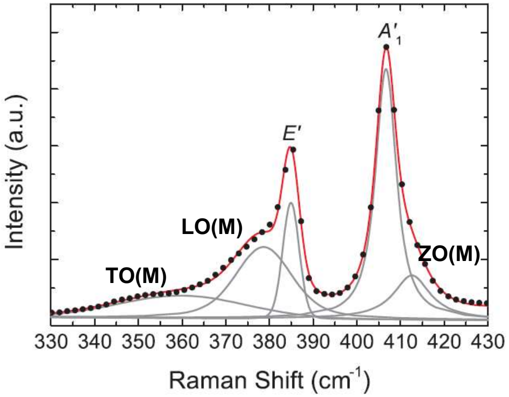
S6 A1g가 점점 커지면서 동시에
1-2L에서는 single line
3-4L에서는 2개, 5L에서는 3개로 split됨 (Davydov split) B12g는 1L에 없고, 2L에서 가장 prominent함
Sojung_NCML, 2020-05-18

Analytical Tools for 2D Materials: Raman Spectroscopy

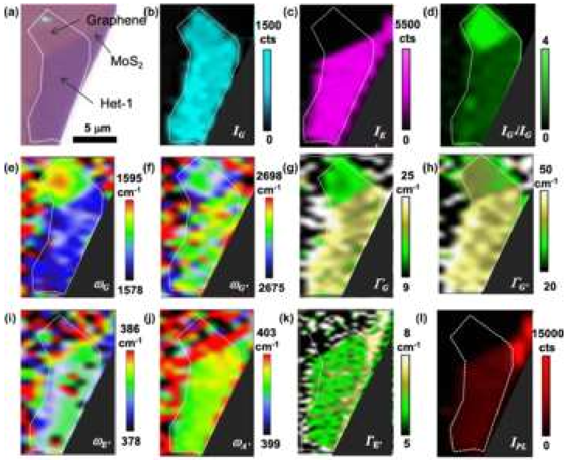
Defect induced Raman

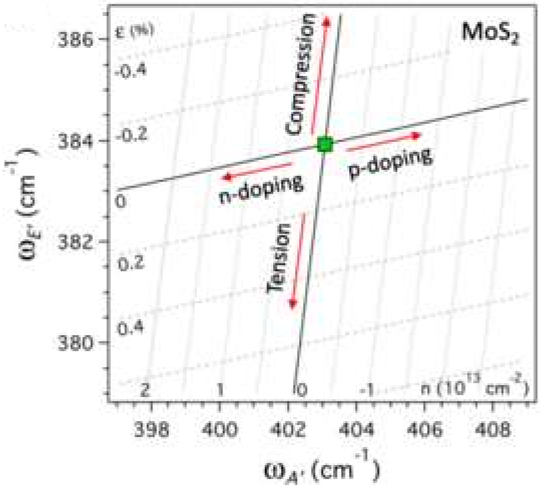


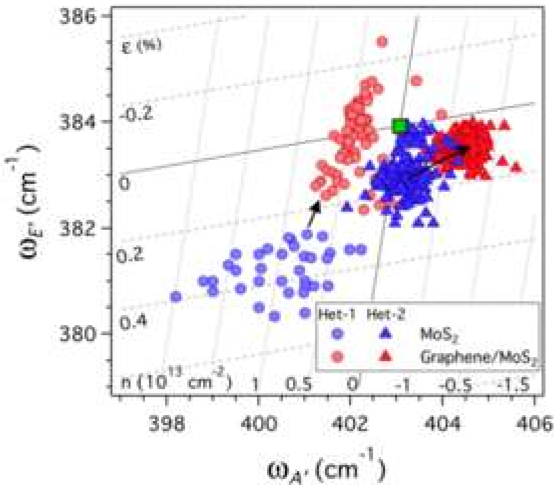




Doping and strain



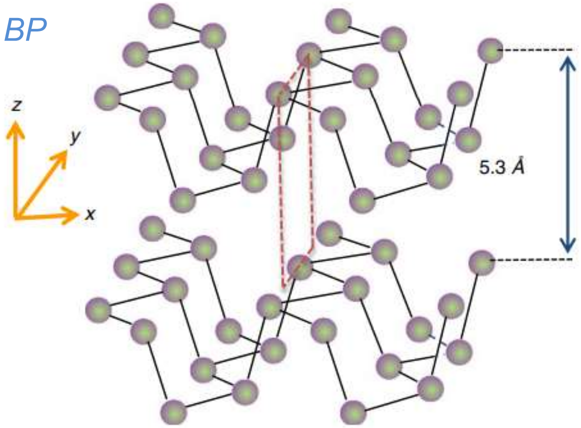


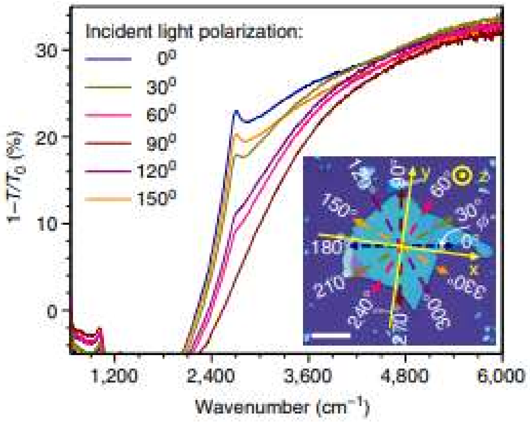


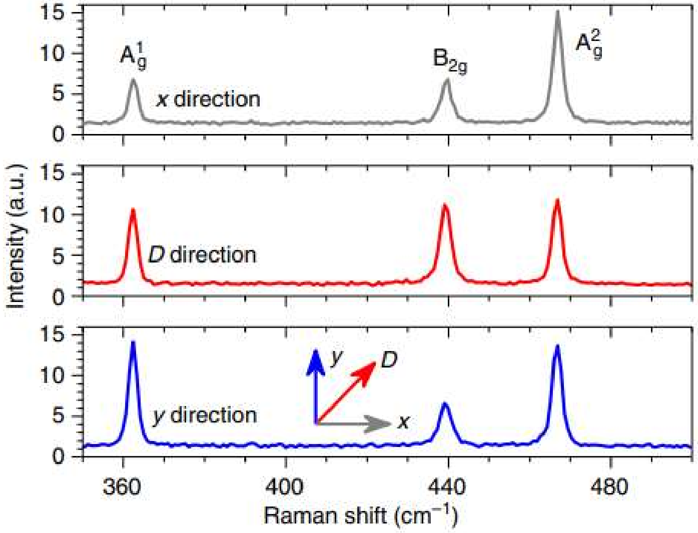
S. Mignuzzi et al. PRB (2015) & R. Rao et al PRB (2019)

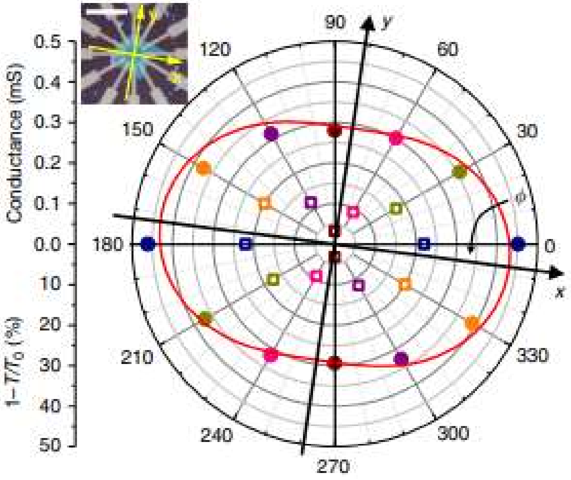
Analytical Tools for 2D Materials: Raman Spectroscopy

Polarized Raman







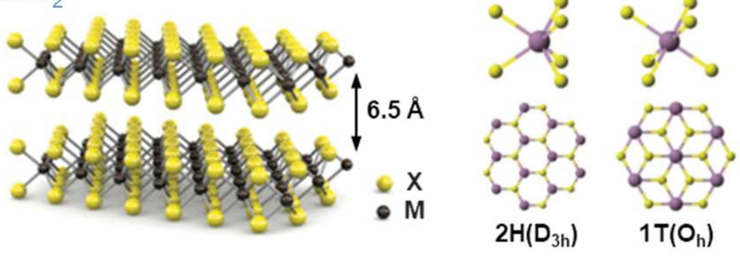


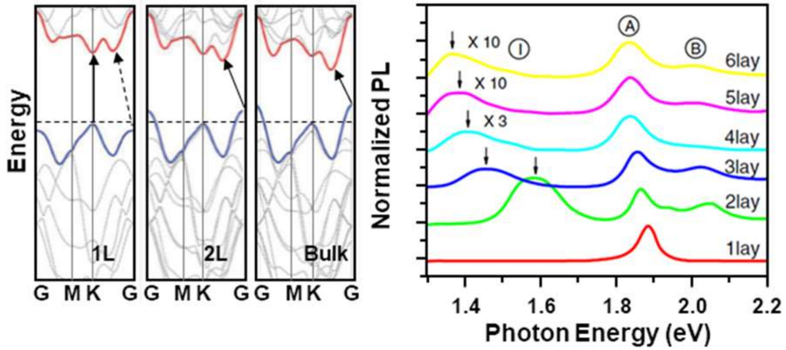
Xia et al. Nat. Comm. (2014)

Analytical Tools for 2D Materials: Photoluminescence

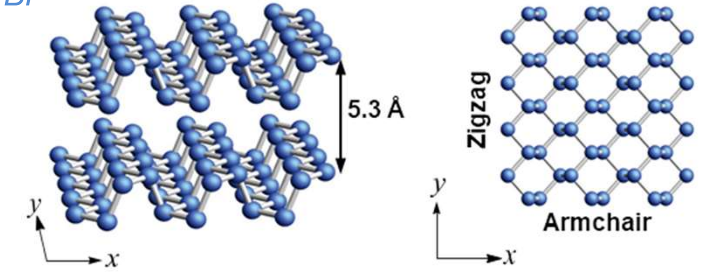
Layer dependent PL

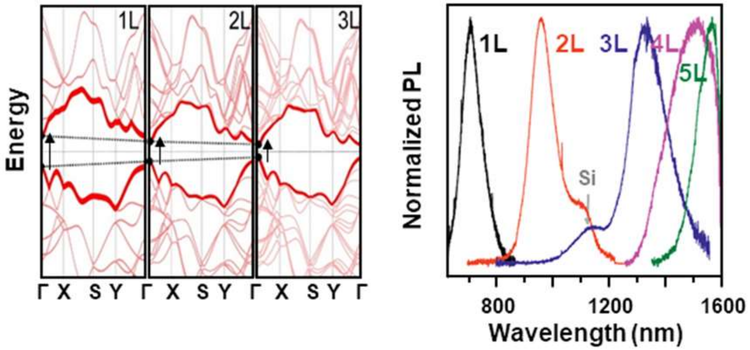
MoS_2



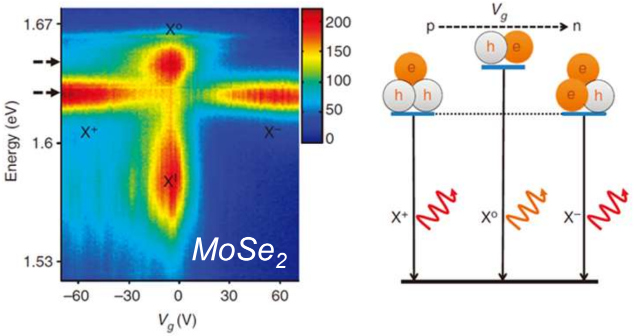


BP

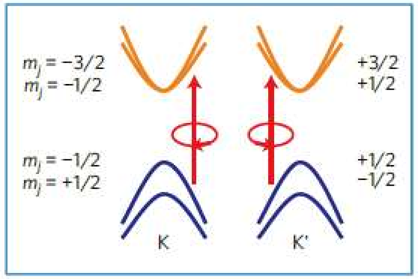




Trion



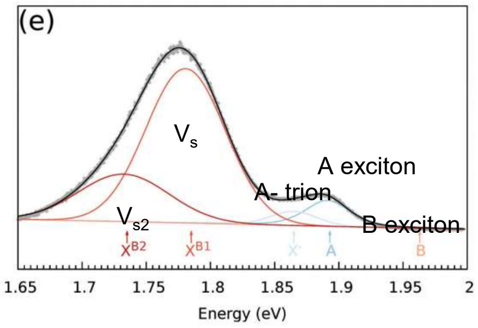
Valley



Mak et al. PRL (2010) & Radisavljevic et al. Nat. Nano (2011) & Splendiani et al. Nano Lett (2010) & Kappera et al Nat. Mater. (2014)
& Tran et al. PRB (2014) & Yang et al. Light Sci. Appl. (2015) & Castellanos-Gomez et al. J. Phys. Chem. Lett. (2015)
& Mak et al. Nat. Mater. (2012) & Ross et al. Nat. Commun. (2013)

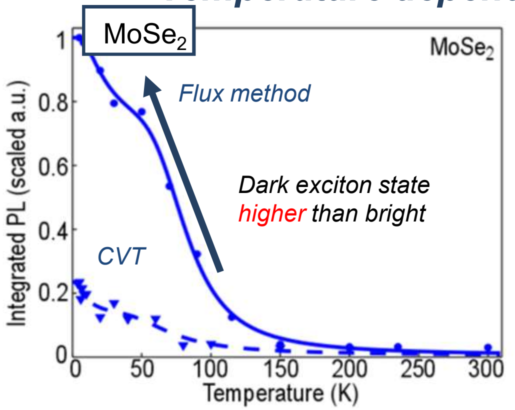
Analytical Tools for 2D Materials: Photoluminescence

Low temperature PL of MoS_2 (50 K)

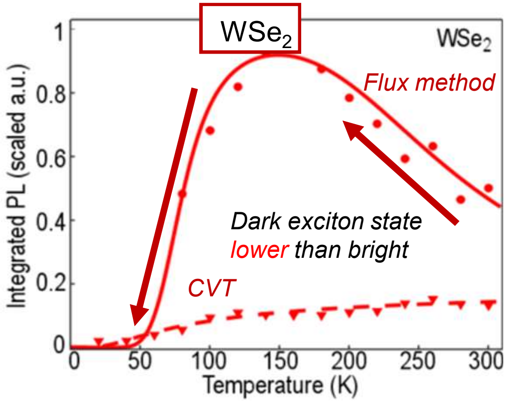


Non-radiative pathway is suppressed because phonon states are less populated at low temperature around bound exciton.

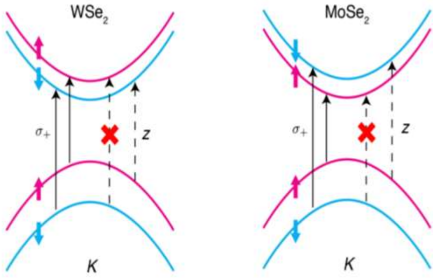
Temperature dependent PL (TDPL)



Dark exciton state higher than bright

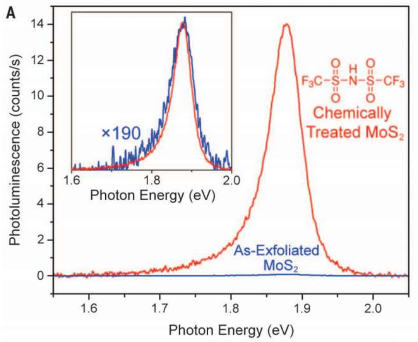


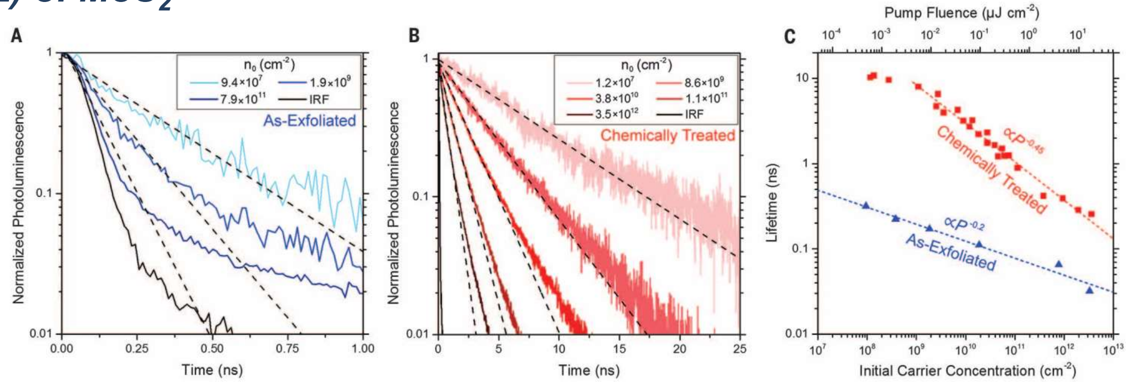
Dark exciton state lower than bright

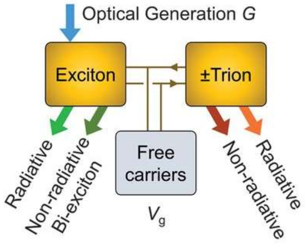


Smaller dark exciton energy than bright exciton for WSe_2
* Dark exciton involves e^- and h^+ in different valleys resulting in momentum-forbidden states, which cannot emit photons

Time-resolved PL (TRPL) of MoS_2



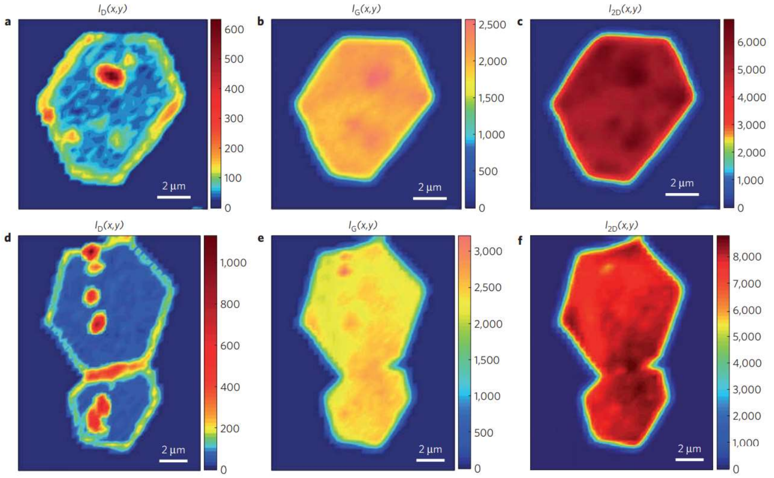




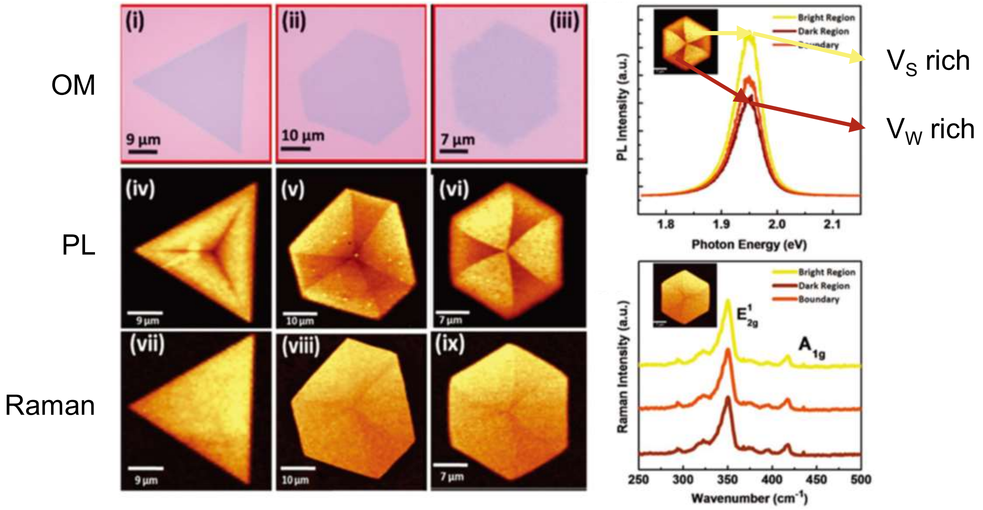
Verhagen et al. Nanoscale (2020) & Edelberg et al. Nano Lett. (2019) & Amani et al. Science (2015)

Analytical Tools for 2D Materials: Raman & PL mapping

Raman mapping of CVD-grown graphene



PL mapping of CVD-grown WS_2



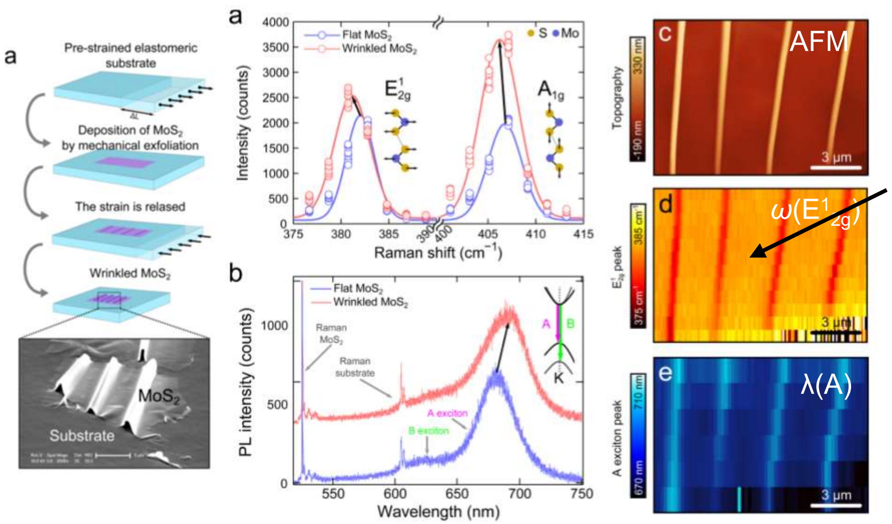
V_S rich

V_W rich

S2

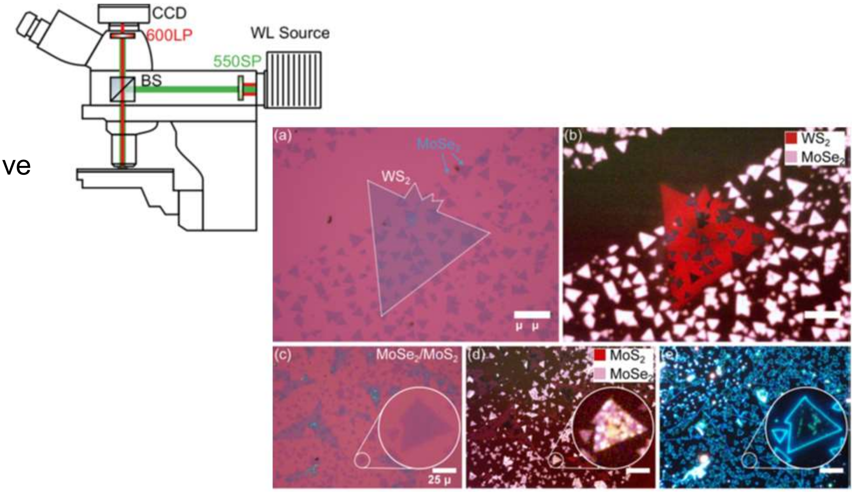
S3

Wrinkled MoS_2



compressive

PL imaging using bright-field optical microscope



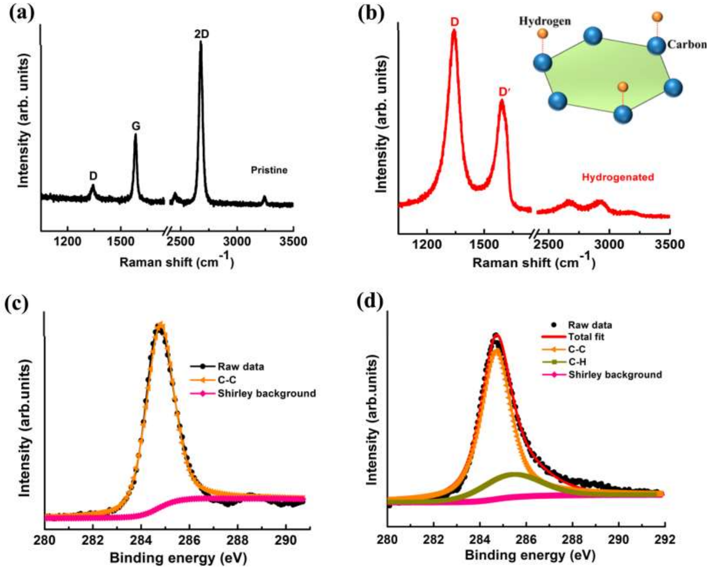
Q. Yu et al. Nat. Mater. (2011) & Zafar et al. Adv. Funct. Mater. (2019)
& Castellanos-Gomez et al. Nano Lett. (2013) & Alexeev et al. Nano Lett. (2017)

S2 sulfur vacancy rich region이 더 밝은 것이 맞습니다.
우리가 평소 생각하는 Vs에 따라 PL이 떨어지는 것은 perfect crystal 대비했을 경우이고, W vacancy가 많으면 deep level 형성되어 pl이 줄어듭니다.
Sojung_NCML, 2020-05-18

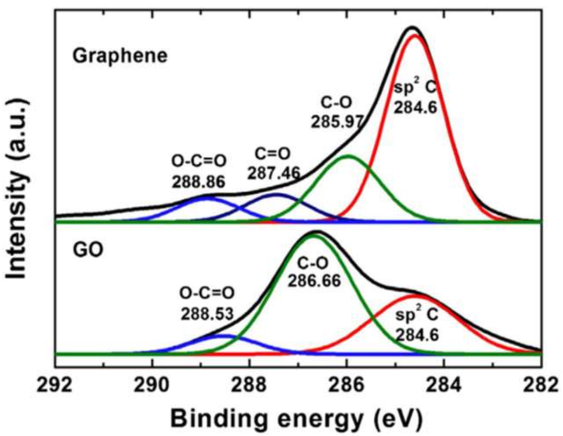
S3 https://onlinelibrary.wiley.com/doi/full/10.1002/adma.201605043
Sojung_NCML, 2020-05-18

Analytical Tools for 2D Materials: XPS

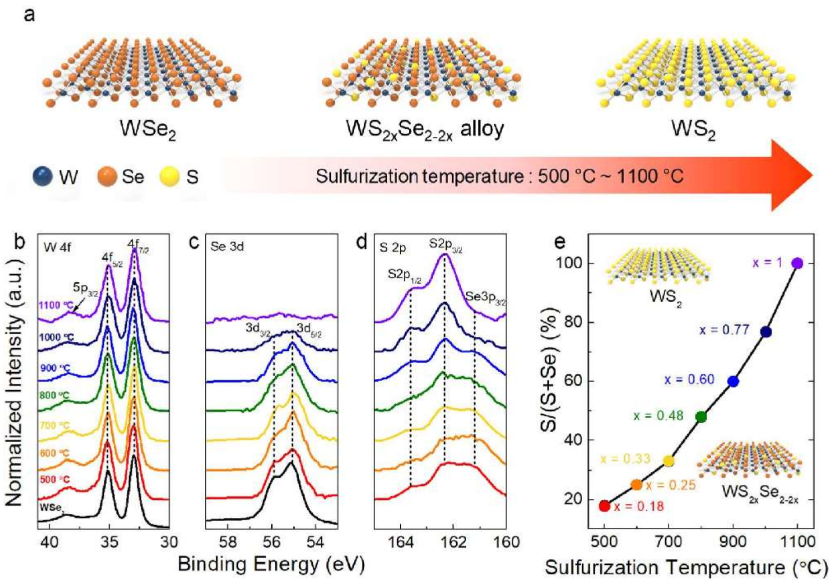
Hydrogenated graphene



Graphene vs GO



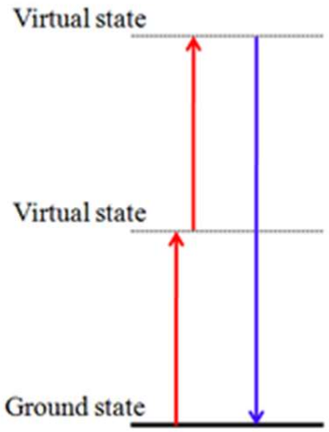
WS_2/WSe_2 alloy



Gowda et al. ACS AMI (2014) & Johra et al. J. Ind. Eng. Chem. (2014)
& Ko et al. ACS AMI (2018)

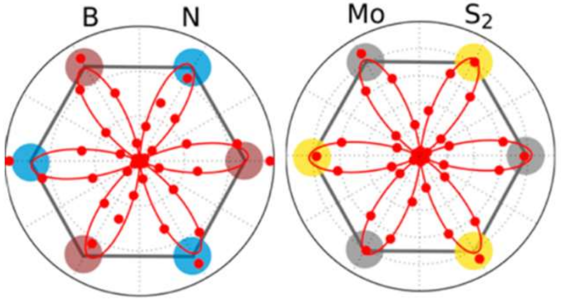
Analytical Tools for 2D Materials: SHG

Second harmonic generation (SHG)

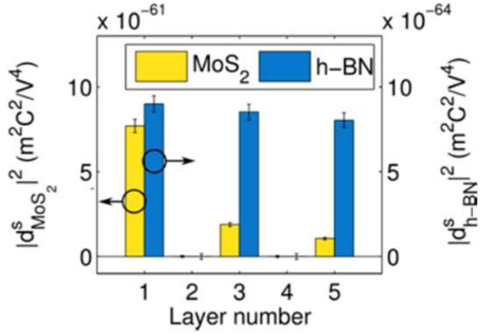


Polarization-resolved SH intensity

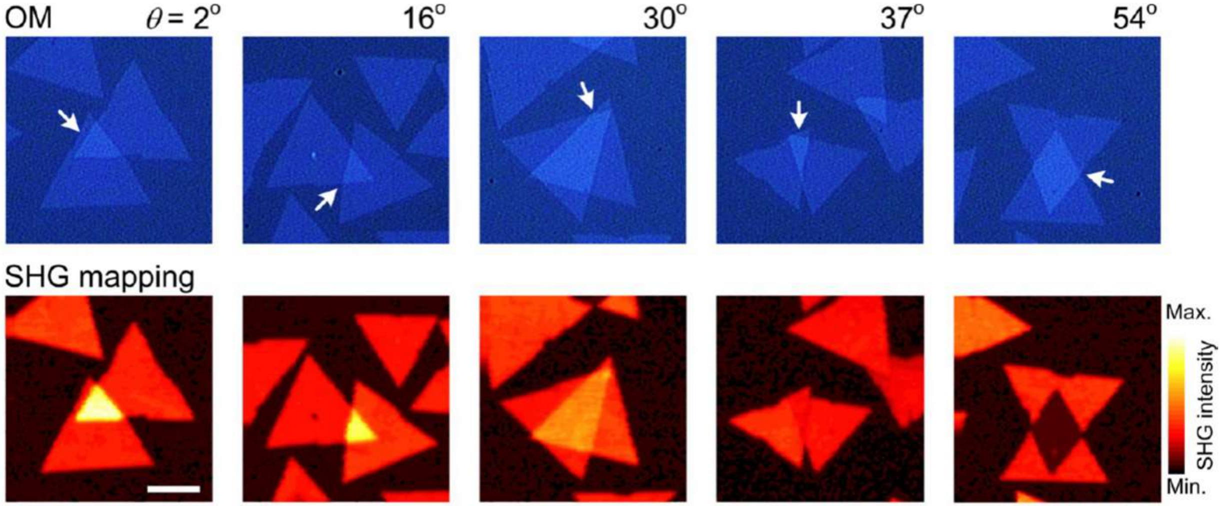
Orientational dependence



Layer number dependence



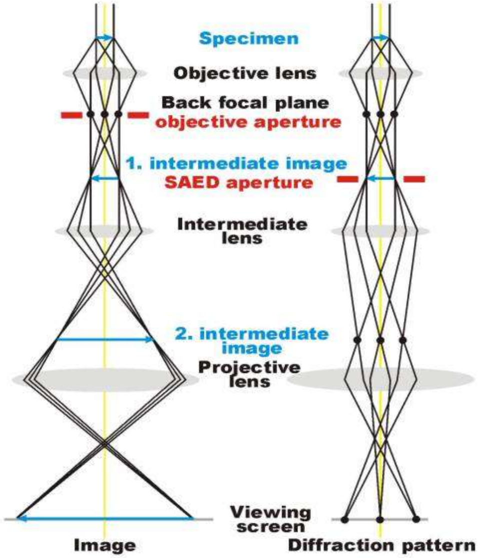
Twisted bilayer MoS$_2$



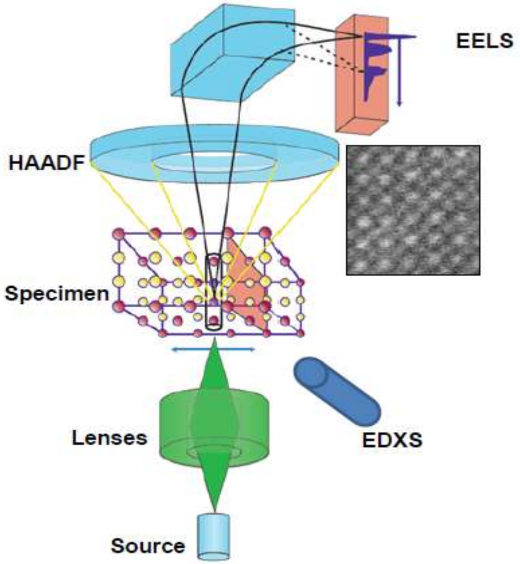
Y. Li et al Nano Lett. (2013) & W.-T. Hsu et al ACS Nano (2014)

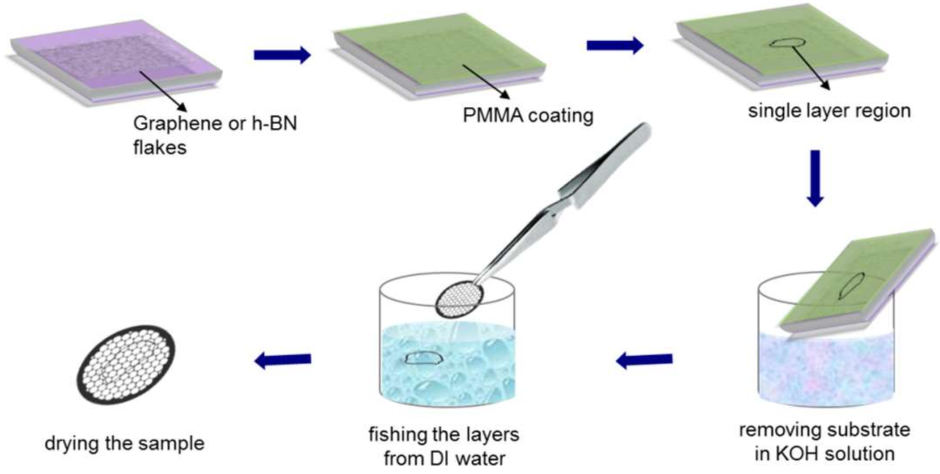
Analytical Tools for 2D Materials: TEM

Transmission Electron Microscope (TEM)



HAASDF-STEM



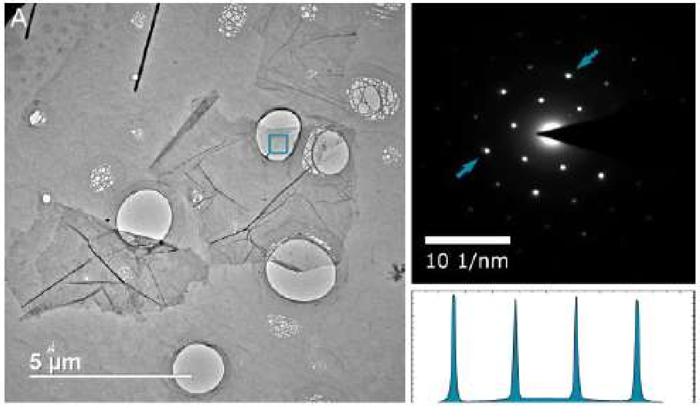


P. Huang et al. Nature (2011) & G. H. Lee et al. Science (2013)

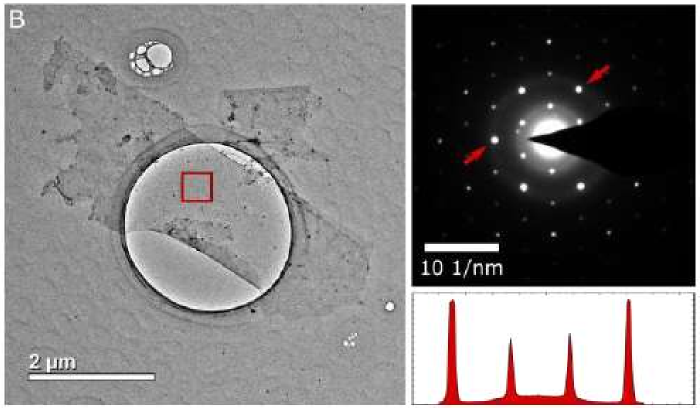
Analytical Tools for 2D Materials: TEM

TEM image of graphene

Monolayer graphene

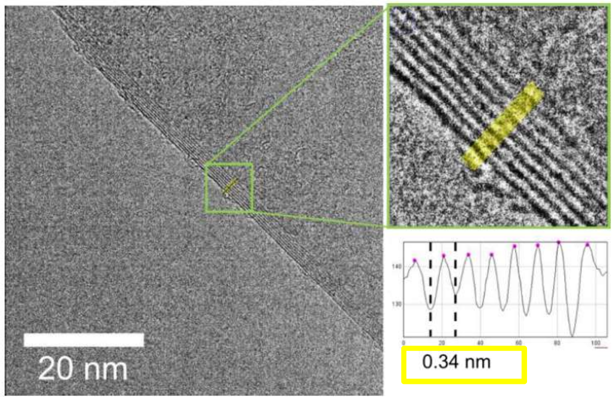


Bilayer graphene

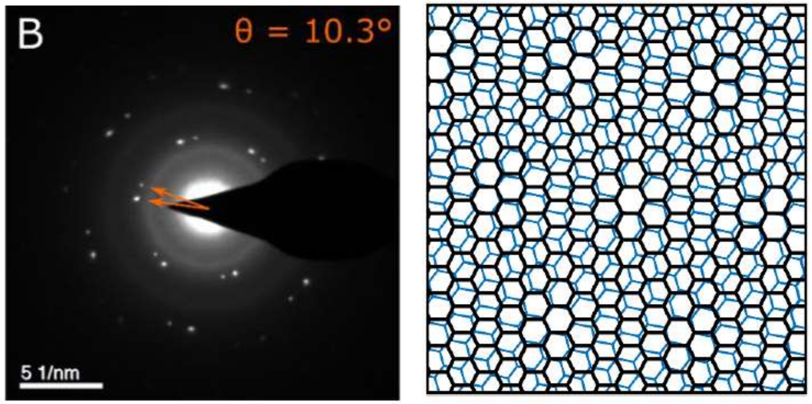


Monolayer graphene the outer hexagon intensity is similar with inner one. On the other hand, bilayer graphene the outer hexagon intensity is greater than the inner one.

Thickness of graphene flakes



Misoriented angle (θ) of graphene layers

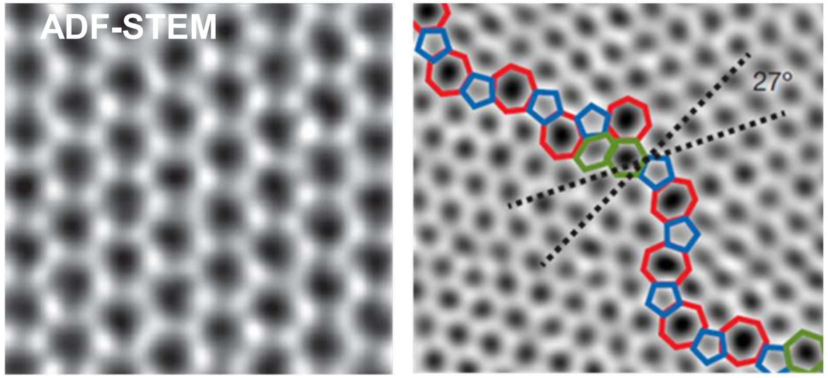


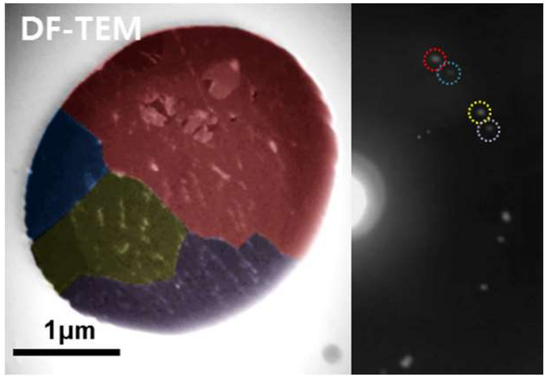
Misoriented bilayer graphene regions are easily identified by the presence of 12 spots in each ring rather than the 6 observed for single layer graphene or AB stacked graphite. The misoriented bilayer graphene also reveals a Moiré pattern.

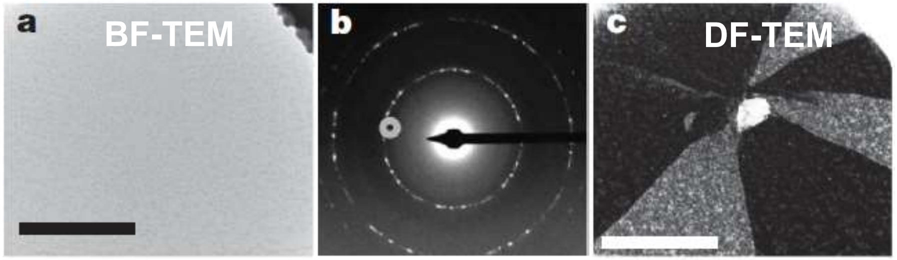
A. J. Pollard et al. "Characterization of the structure of graphene", NPL, (2017)

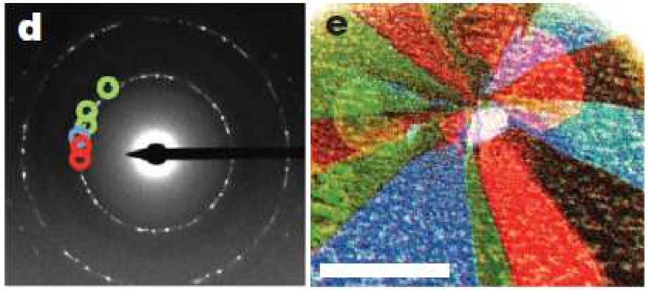
Analytical Tools for 2D Materials: TEM

Crystal Structure of Graphene



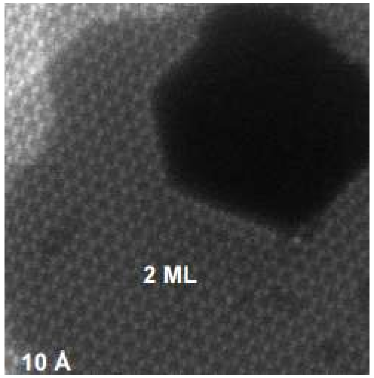




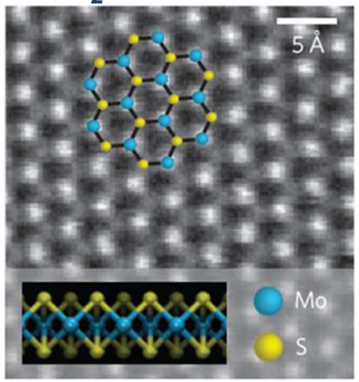


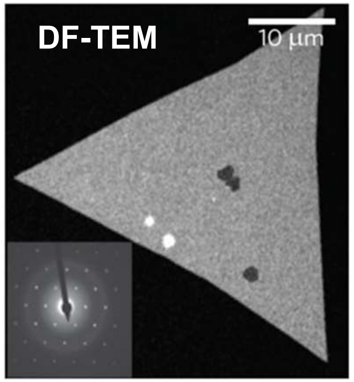
P. Huang et al. Nature (2011) & G. H. Lee et al. Science (2013)

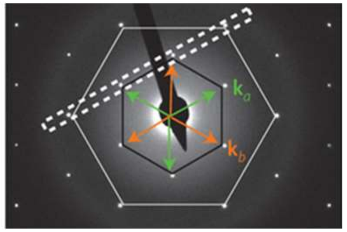
Boron Nitride

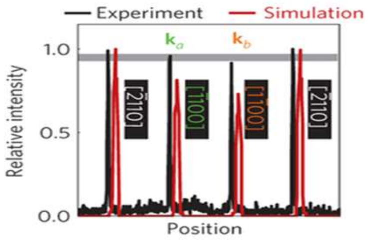


MoS_2







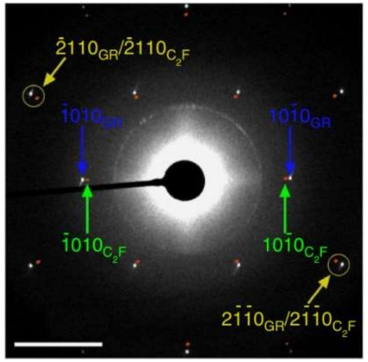


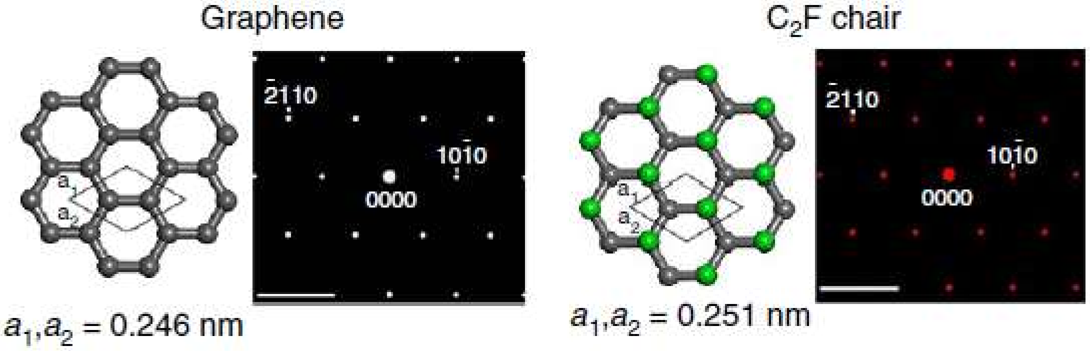
A. van der Zande et al. Nature Mater. (2013)

Analytical Tools for 2D Materials: TEM

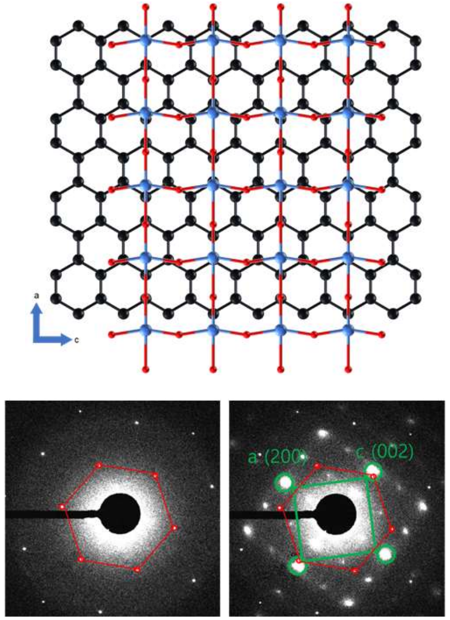
Diffraction pattern

Fluorinated graphene

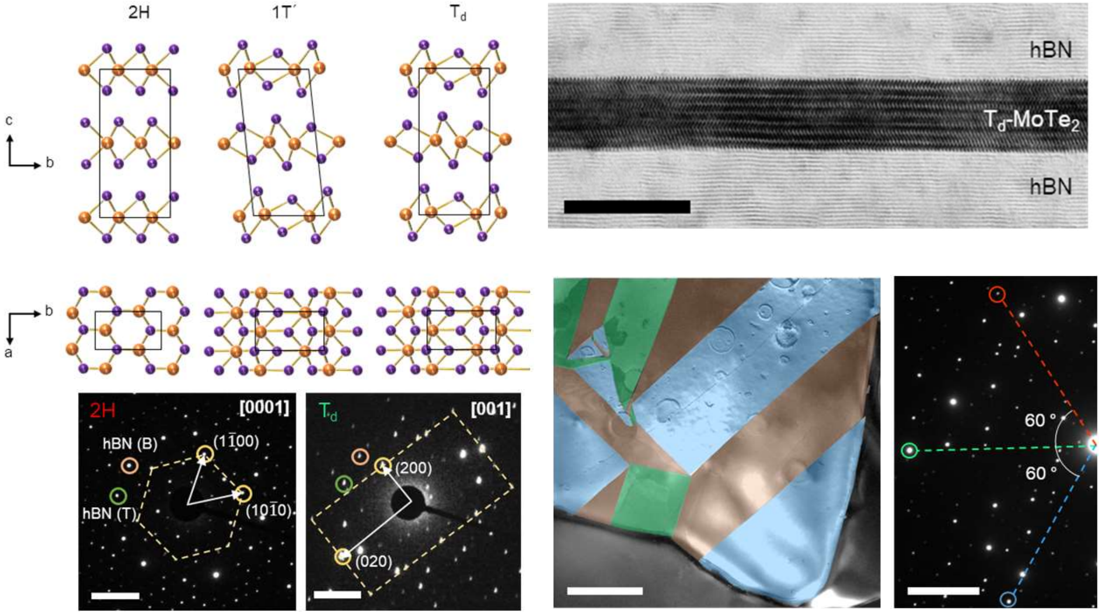




MoO_3/Graphene



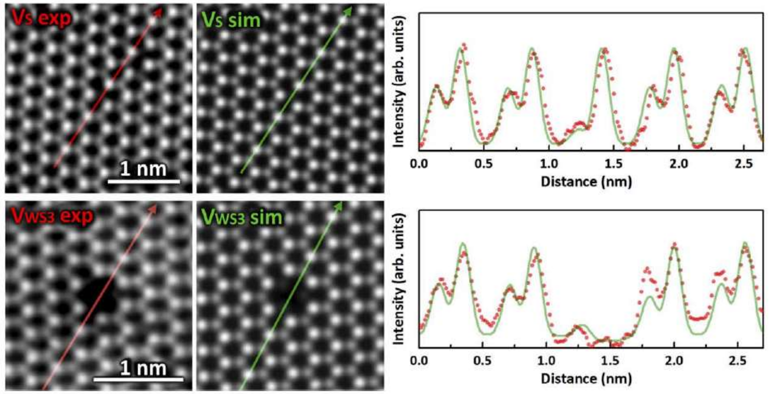
$MoTe_2$ phase transition



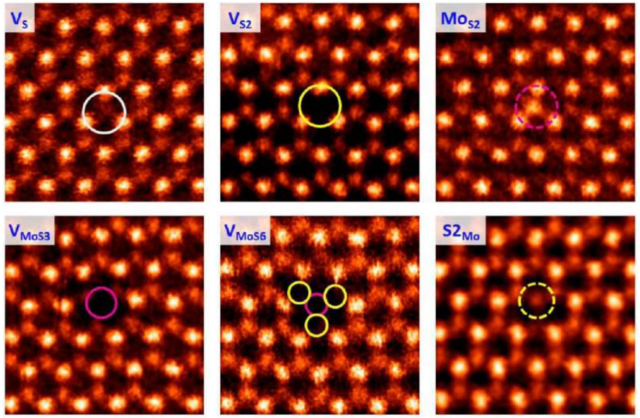
Kashtiban et al. Nat. Commun. (2014) & G.H. Lee et al. in preparation

Analytical Tools for 2D Materials: TEM

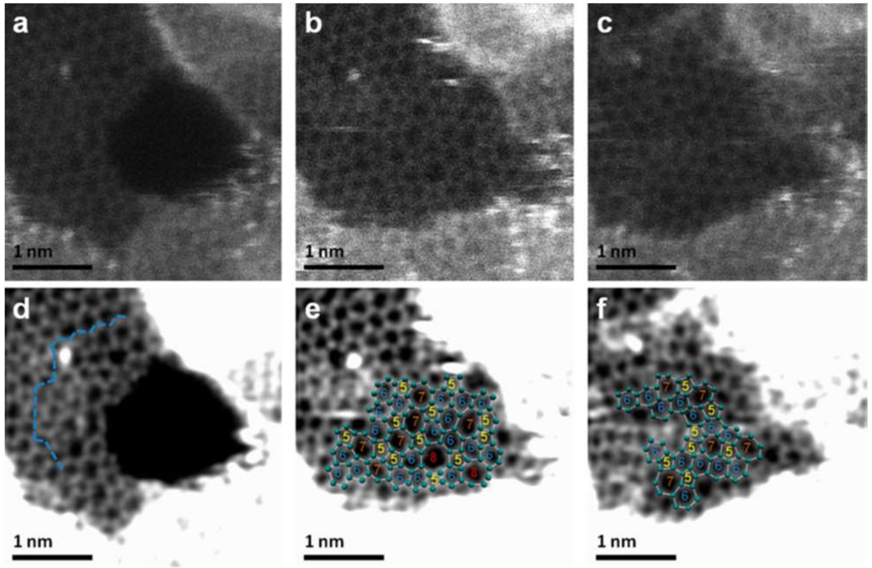
Defect observation of WS_2



MoS_2

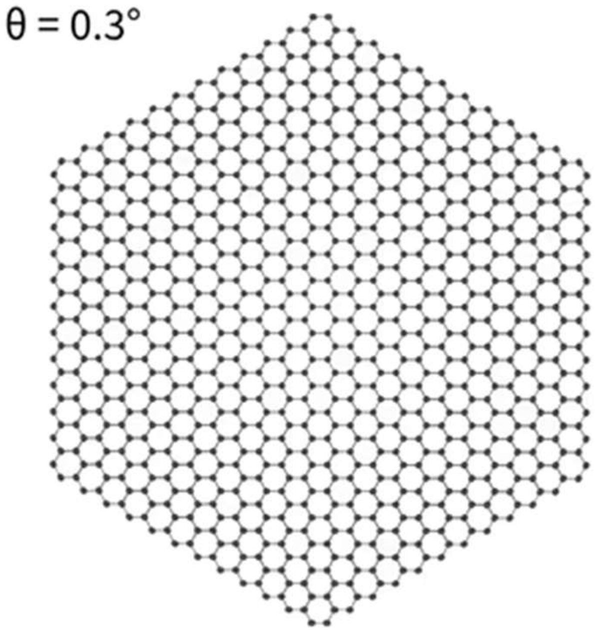


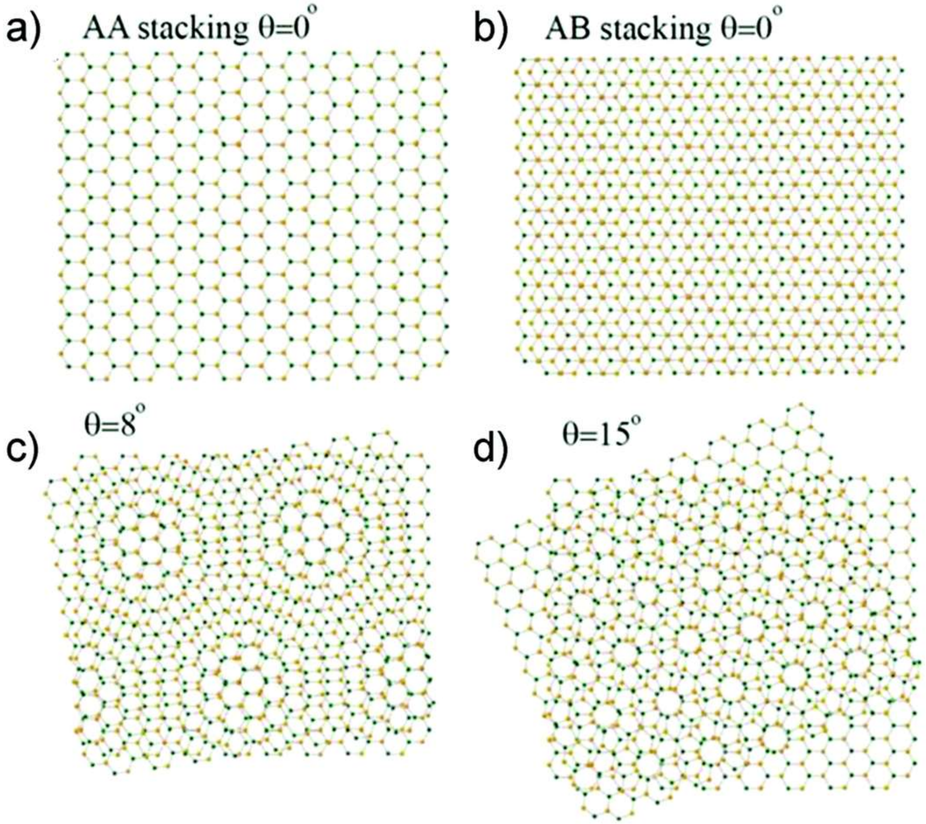
Reknitting graphene



Carozo et al. Sci. Adv. (2017) & Zhou et al. Nano Lett. (2013) & R. Zan et al. Nano Lett. (2012)

Analytical Tools for 2D Materials: TEM

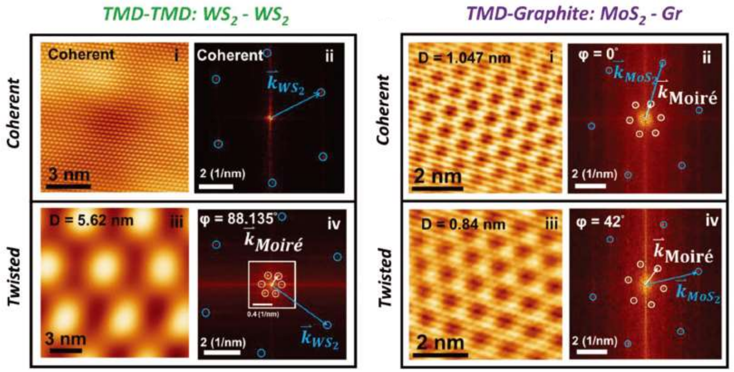




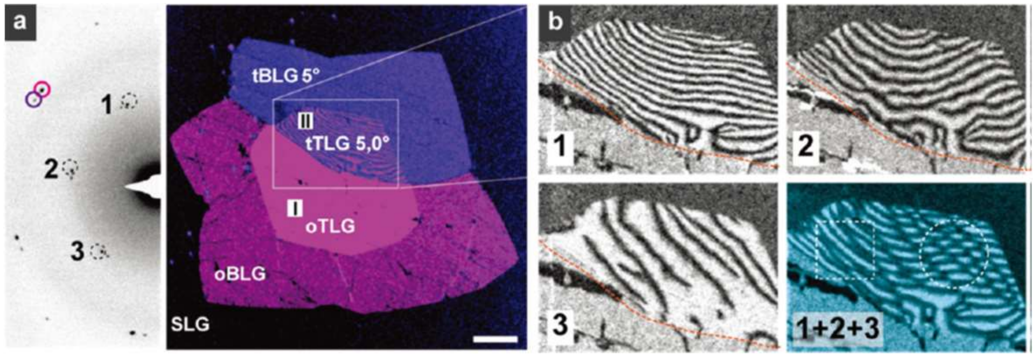
Bottari et al. Chem. Soc. Rev. (2017)

Analytical Tools for 2D Materials: TEM, STM

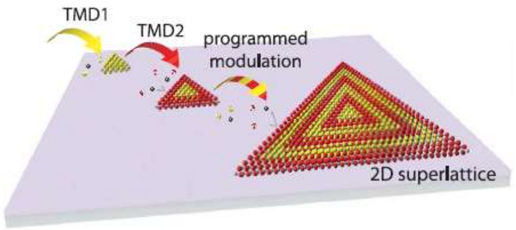
Moiré pattern

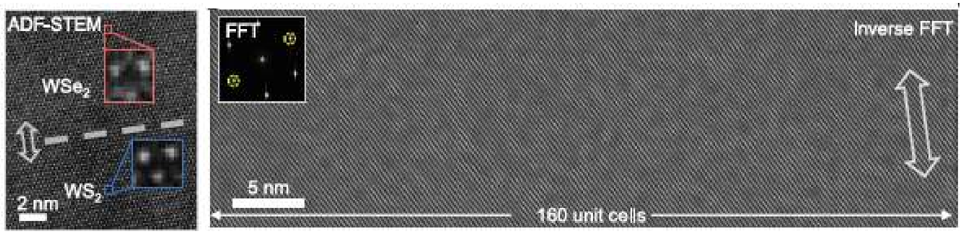


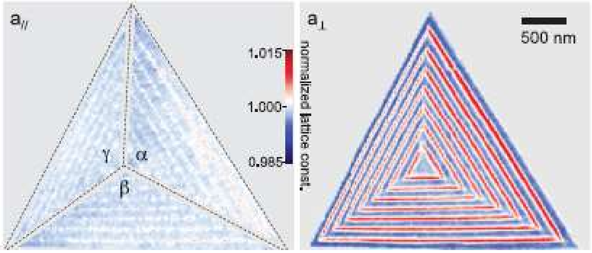
Twisted angle of CVD graphene

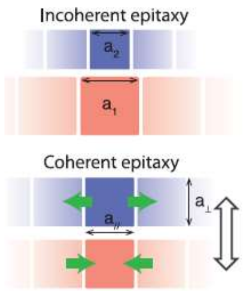


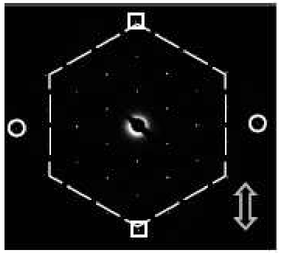
Strain engineered TMD superlattice

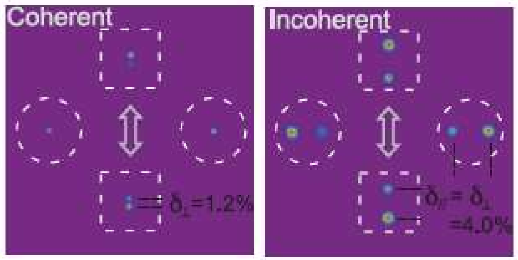












P.-Y. Chen et al. Adv. Mater (2019) & Brown et al. Nano Lett. (2012) & S. Xie et al. Science (2018)