Beyond graphene: The amazing world of layered transition metal dichalcogenides (TMDs)

Humberto Terrones

Department of Physics, Applied Physics and Astronomy

Rensselaer

Layered Materials (1959)

What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them… I can hardly doubt that when we have some control of the arrangement of things on a small scale, we will get an enormously greater range of possible properties that substances can have…

R. P. Feynman
There is Plenty of Room at the Bottom
December 29, 1959

Structure of monolayer TMDs

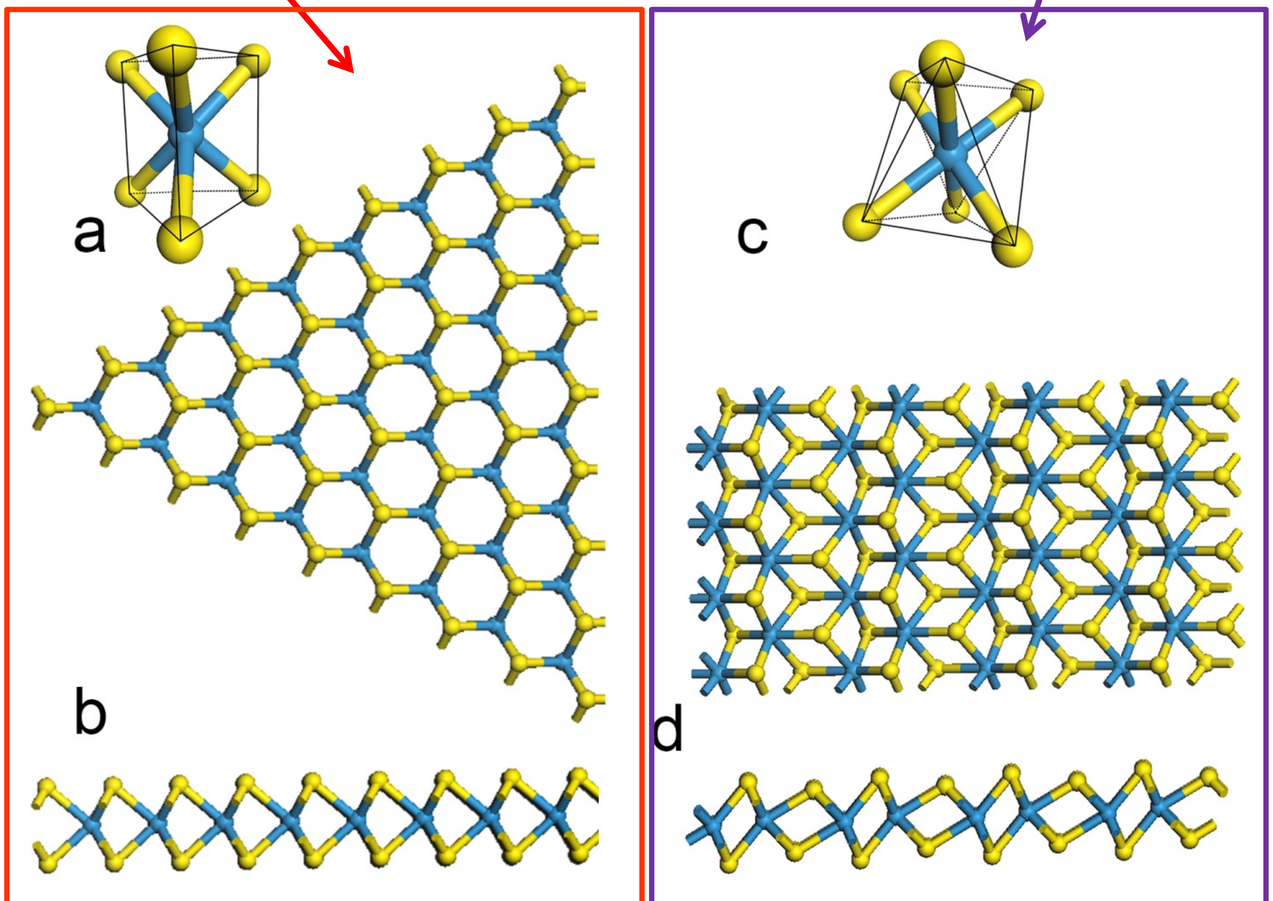
Transition metal dichalcogenides exhibit two main phases:

***Trigonal prismatic (Hexagonal) (P63/mmc)**

***Octahedral ($P2_1/m$)**

Semiconductor:
MoS_2, WS_2, $MoSe_2$, WSe_2

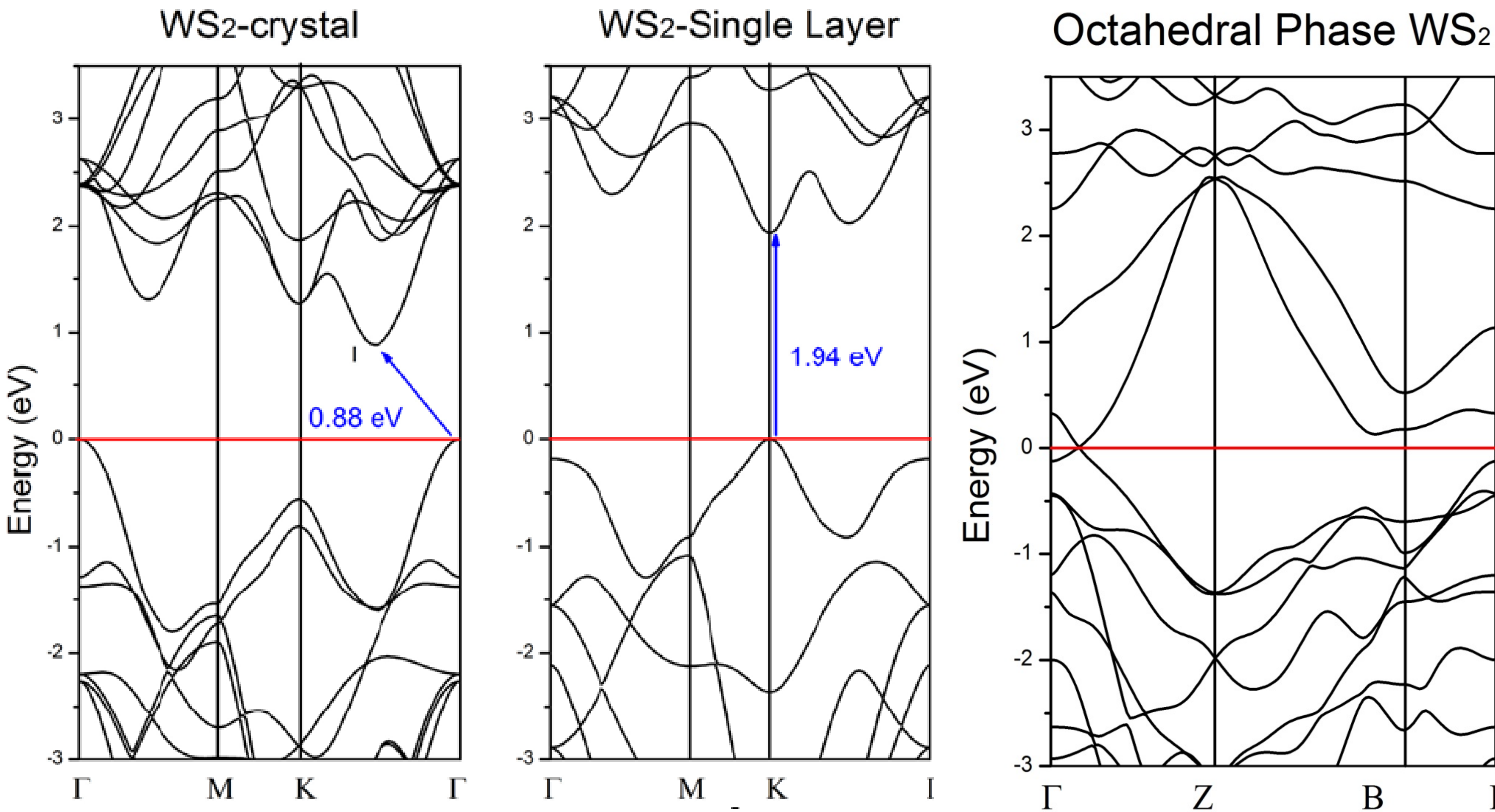
Metal:
NbS_2, $NbSe_2$



Metal:
MoS_2, WS_2, $MoSe_2$, WSe_2

Trigonal prismatic is more stable

Multi layer and Single layer behavior



Indirect band gap **Direct band gap** **Metallic**

Mak, K.F., et al, PRL , 105, 136805 (2010)

DFT-LDA Plane wave calculations

Single Crystals of MoS_2 Several Molecular Layers Thick

R. F. FRINDT*

Physics and Chemistry of Solids, Cavendish Laboratory, Cambridge, England

(Received 24 March 1965; in final form 18 June 1965)

J. Appl. Phys. **37**, 1928 (1966); doi: 10.1063/1.1708627

Early workers on electron diffraction prepared thin fragments of MoS_2 [2,3]; however no direct thickness measurements were made. It is now well known that small MoS_2 crystals thin enough to be transparent in the electron microscope can be prepared by the stripping technique using adhesive tape. Crystals of

The called scotch tape method for exfoliating graphite

SINGLE-LAYER MoS_2

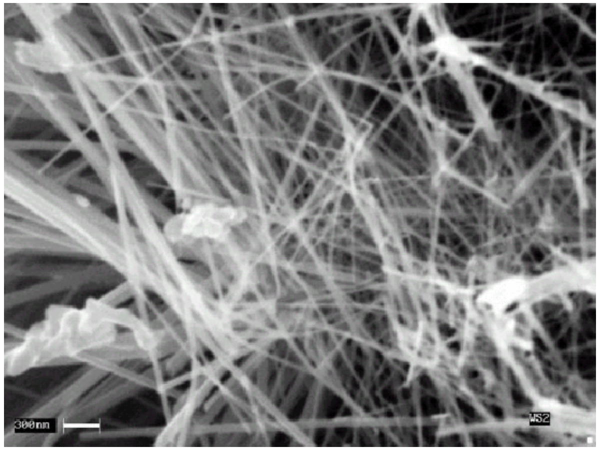
Per Joensen, R.F. Frindt, and S. Roy Morrison
Energy Research Institute
Department of Physics
Simon Fraser University
Burnaby, B.C., Canada V5A 1S6

Mat. Res. Bull., Vol. 21, pp. 457-461, 1986. Printed in the USA.

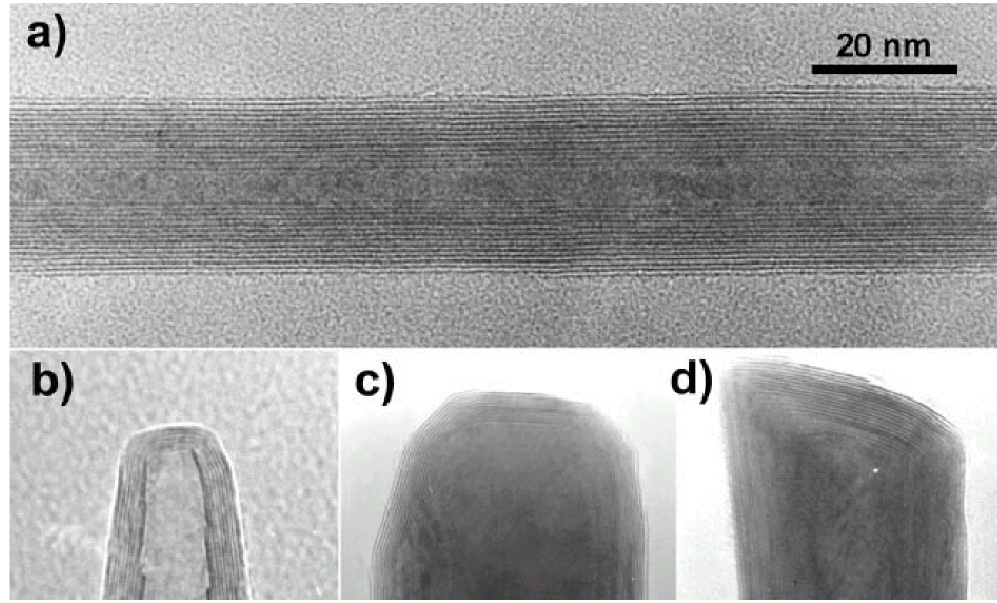
ABSTRACT

MoS_2 has been exfoliated into monolayers by intercalation with lithium followed by reaction with water. X-ray diffraction analysis has shown that the exfoliated MoS_2 in suspension is in the form of one-molecule-thick sheets. X-ray patterns from dried and re-stacked films of exfoliated MoS_2 indicate that the layers are randomly stacked. Exfoliated MoS_2 has been deposited on alumina particles in aqueous suspension, enabling recovery of dry exfoliated MoS_2 supported on alumina.

WS_2 Nanotubes: Sulfurization Process

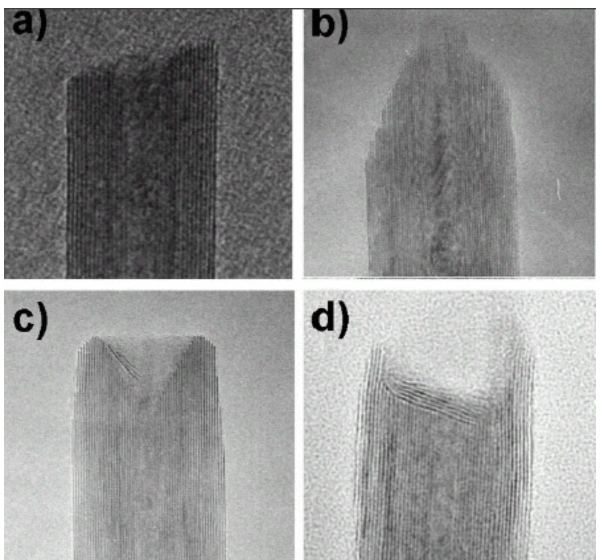


SEM image



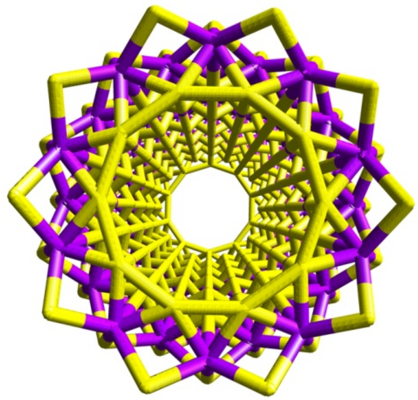
TEM images

Zhu, Y.Q., et al. Chemistry of Materials 12, 1190-1194 (2000); Journal of Materials Chemistry 10, 2570-2577 (2000)

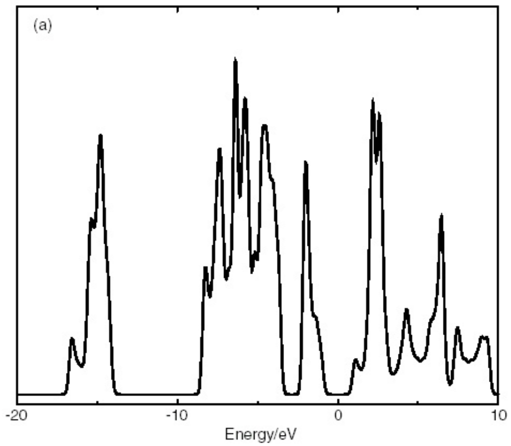


Open Nanotube Caps

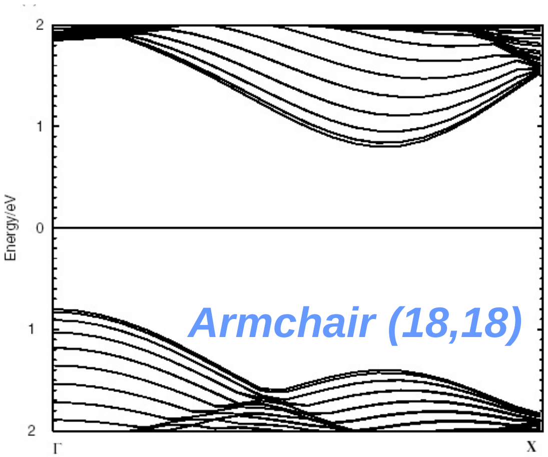
WS$_2$ Nanotubes: Electronic Properties

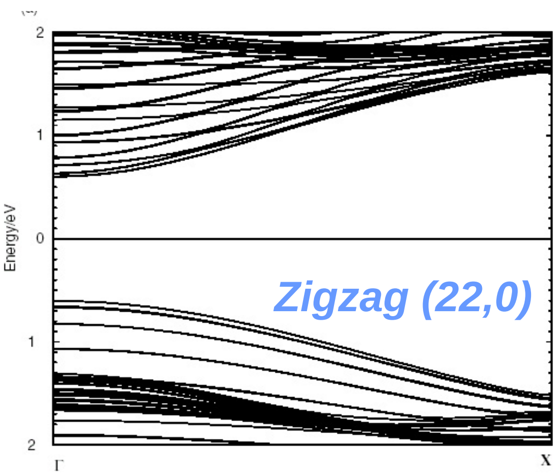


Molecular Model



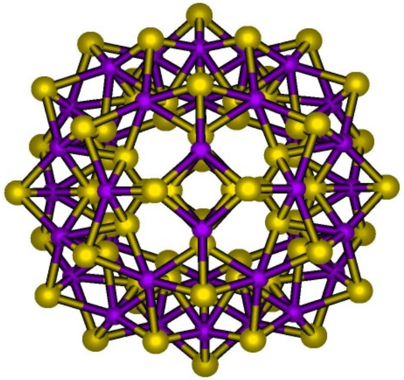
DOS for a (18,18)



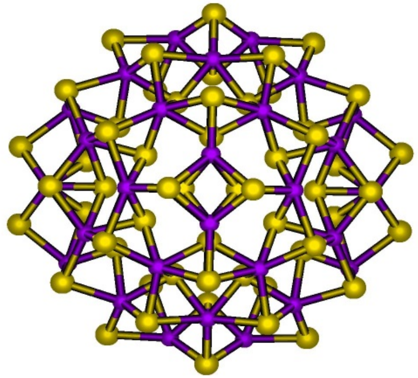


Seifert, G., Terrones, H., Terrones, M., Jungnickel, G., Frauenheim, T. Solid State Communications 114, 245-248 (2000). Seifert, G., Terrones, H., et al., PRL, Vol. 85, 146,(2000).

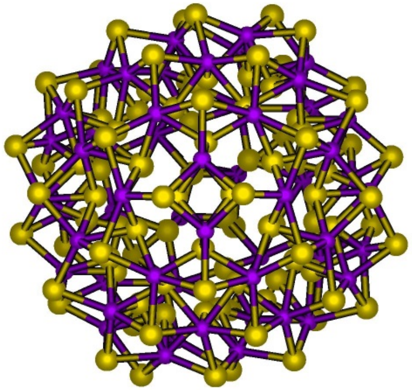
Octahedral Inorganic Fullerenes



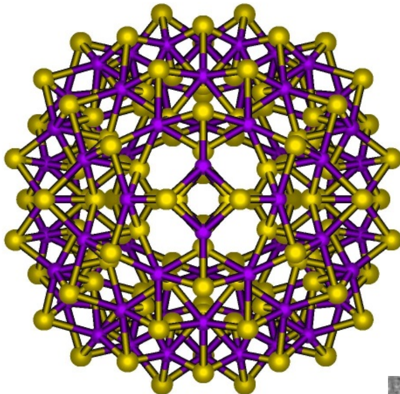
Mo36S72



Mo48S96

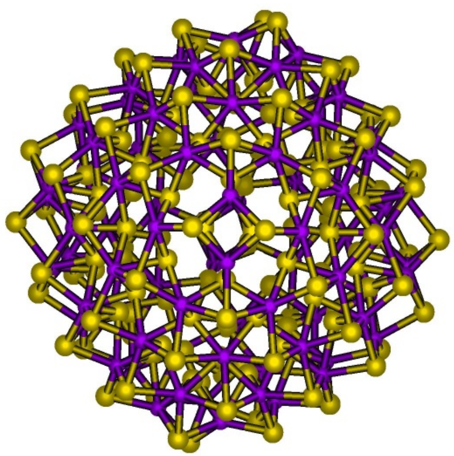


Mo52S104

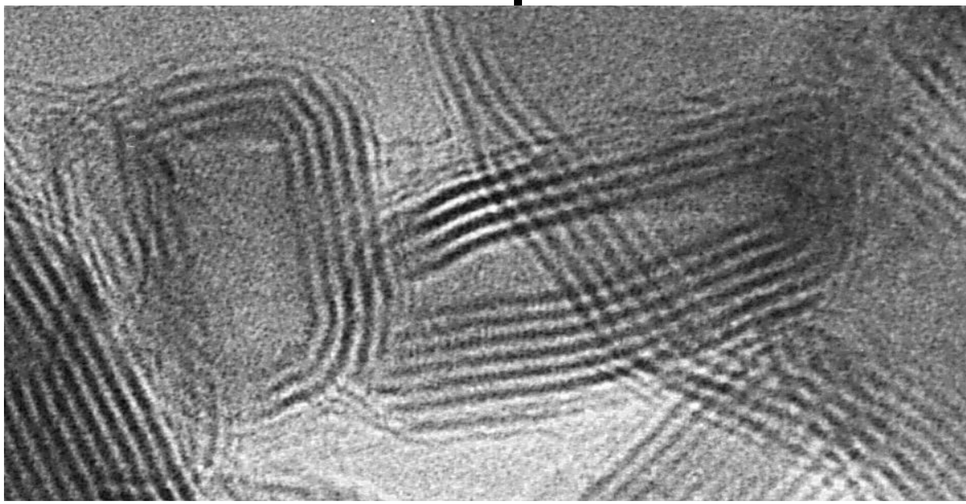


Mo64S128

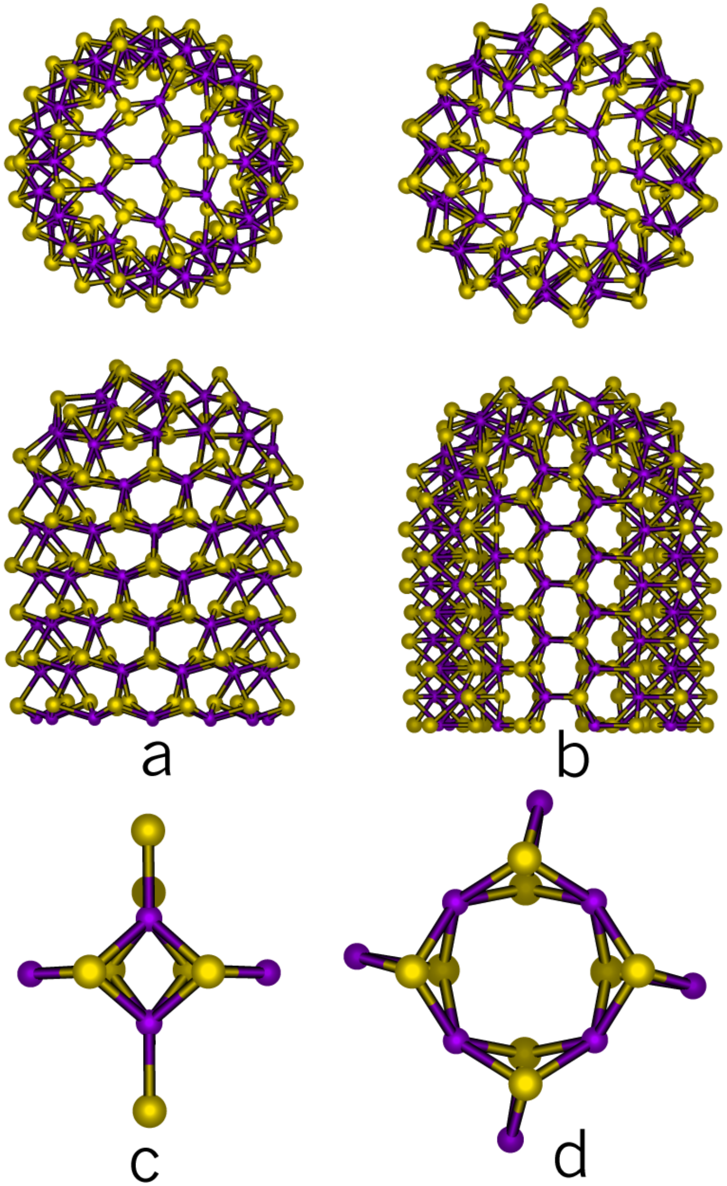
Mo76S152

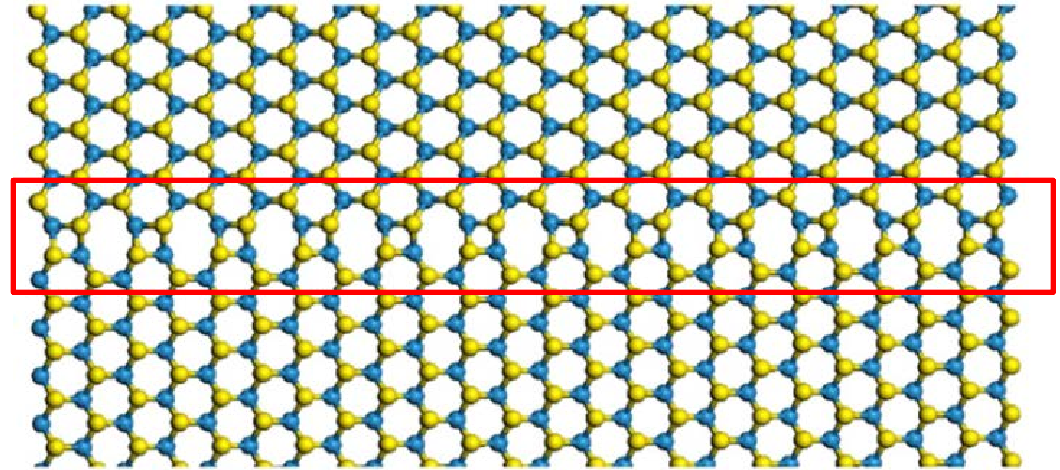


WS_2 nanoparticles

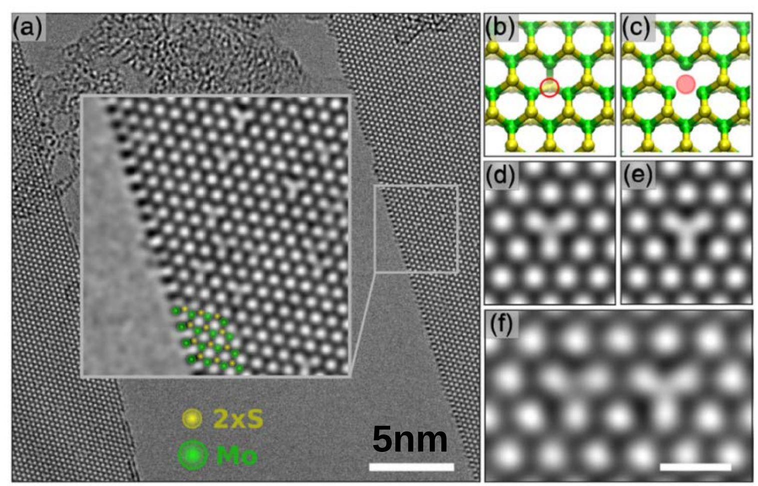


Topological defects and vacancies in TMD





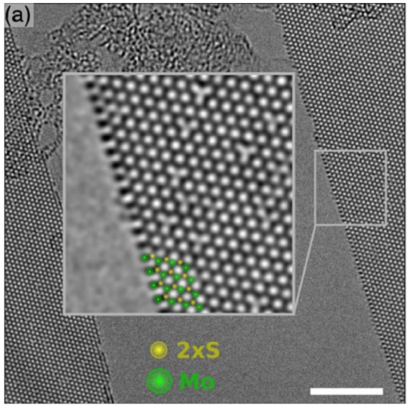
Terrones, H., Ruitao, Lv, Terrones, M., Dresselhauss, M,S., Reports on ProgressIn Physics, Vol. 75, 062501, (2012).

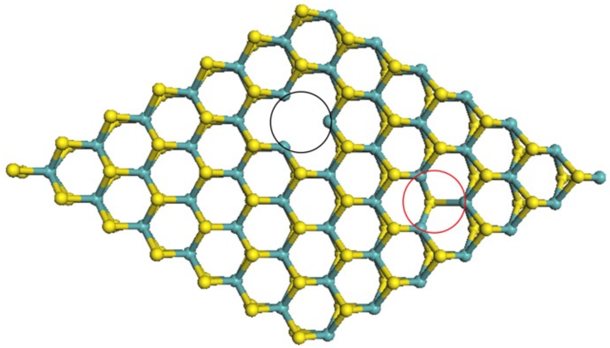


Komsa, H.P., et al., PRL, 109, 035503 (2012).

Seifert, G., Terrones, H., et al., Physical Review Letters, Vol. 85, 146(2000).

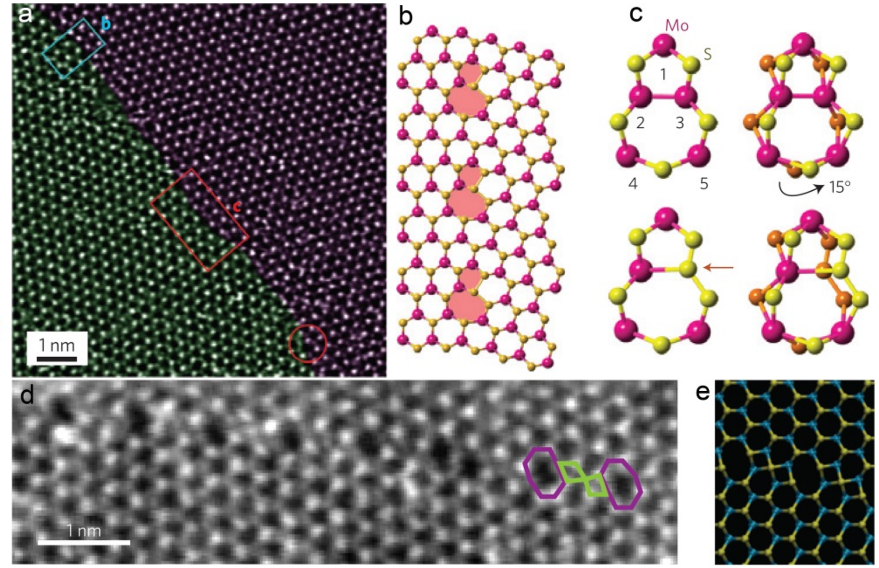
Defects in monolayer TMDs





Point defects: vacancies, divacancies

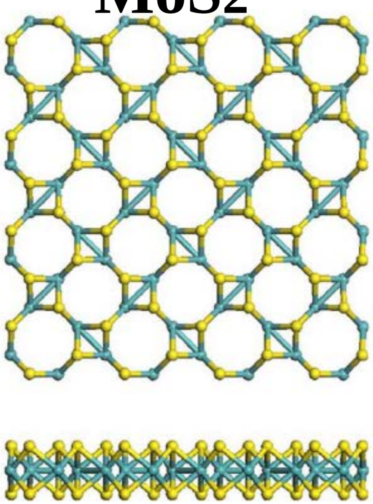
Komsa et al., PRL, Vol.109, art. 035503 (2012)



Grain boundaries

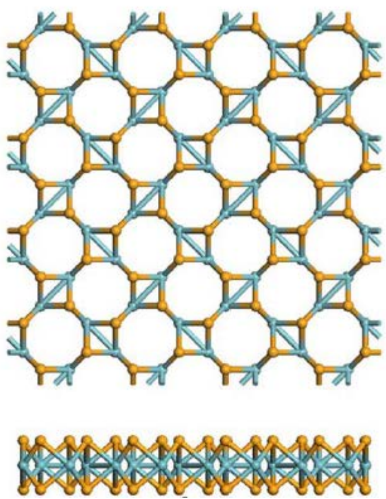
Najmaei,S., et al., Nat. Mat., Vol. 12, 754 (2013)
Van der Zande, et al., Nat. Mat. Vol. 12,554 (2103)

MoS_2



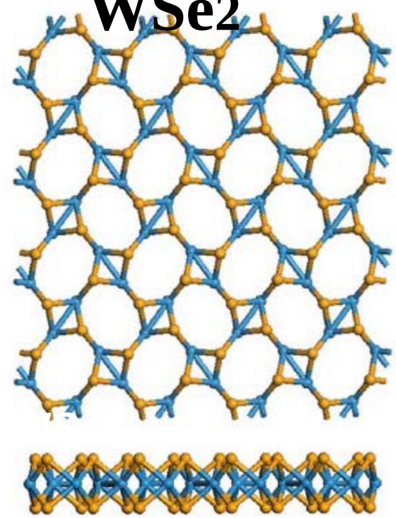
Semimetal

$NbSe_2$



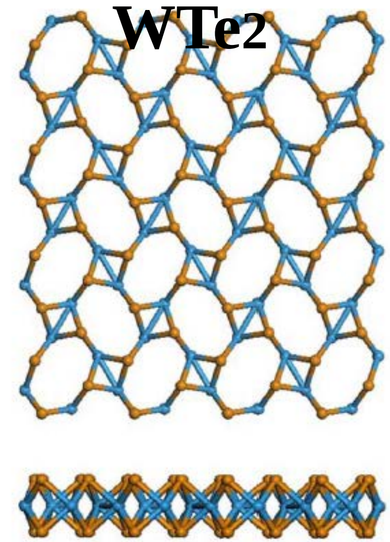
Semiconductor

WSe_2

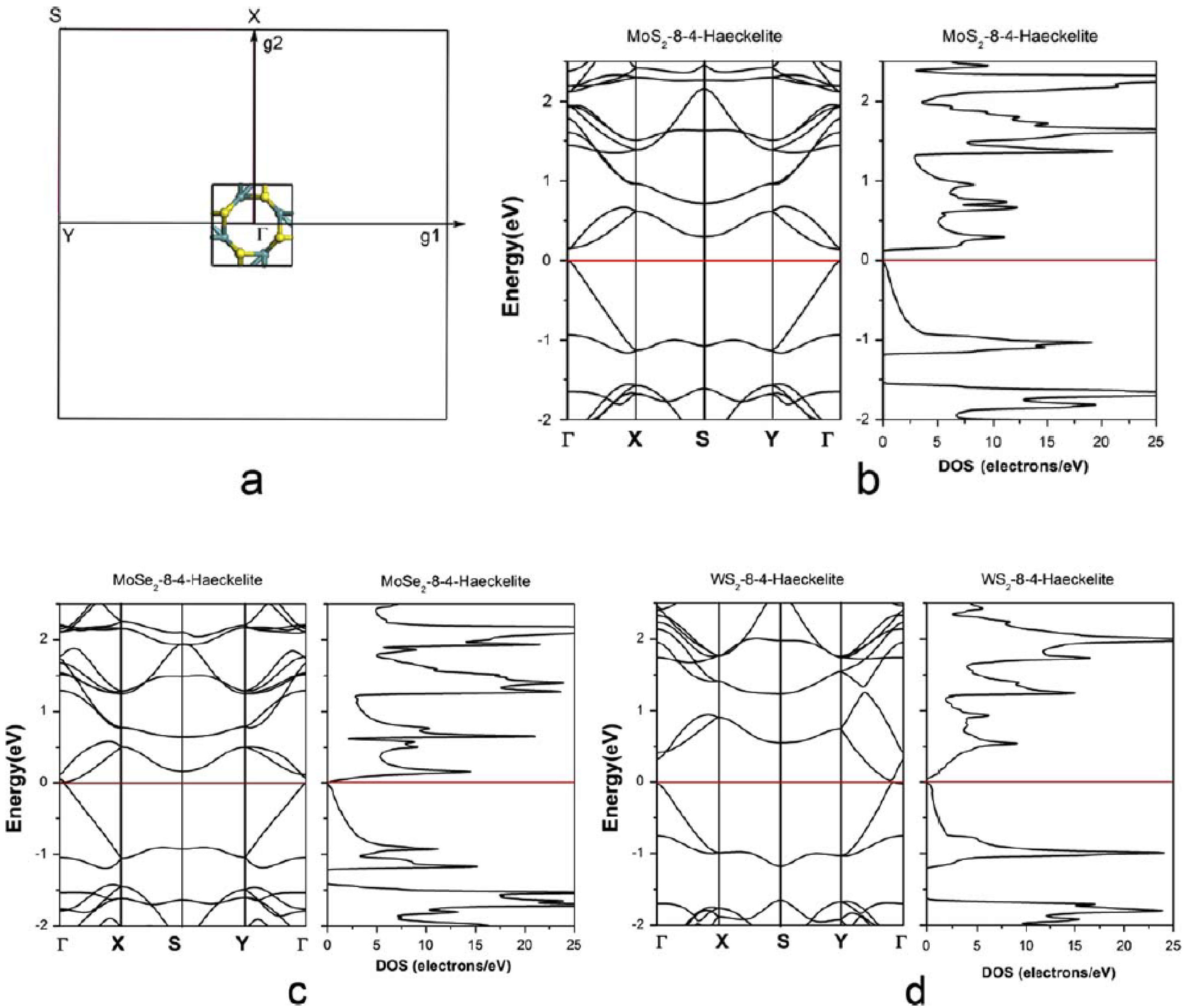


Semimetal

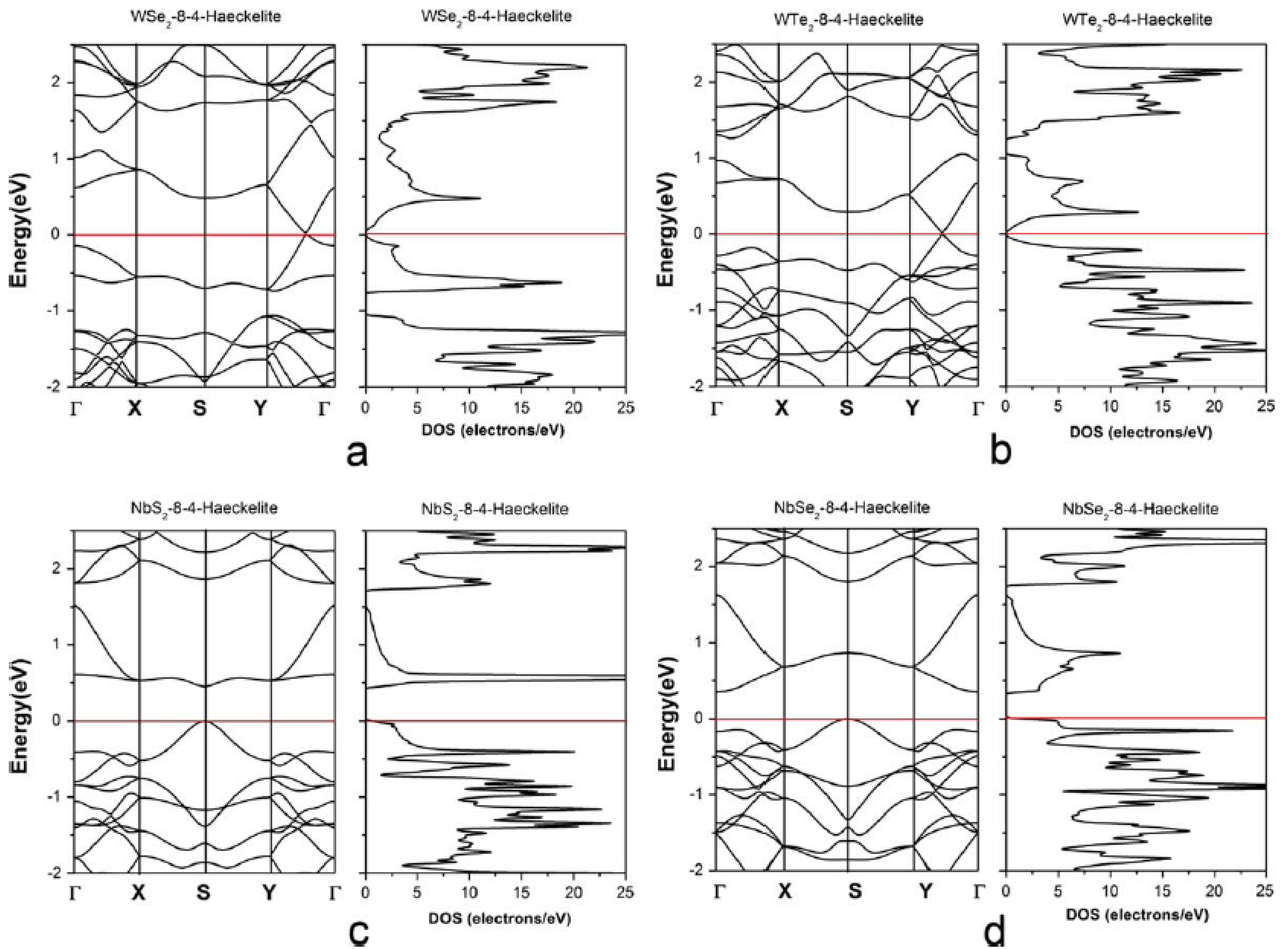
WTe_2



Semimetal



Terrones, H., and Terrones, M., 2-D Materials, Vol.1, 011003 (2014)



Terrones, H., and Terrones, M., 2-D Materials, Vol.1, 011003 (2014)

Monolayer MoS_2 by exfoliation

PRL **105**, 136805 (2010) PHYSICAL REVIEW LETTERS week ending 24 SEPTEMBER 2010

Atomically Thin MoS_2: A New Direct-Gap Semiconductor

Kin Fai Mak,[1] Changgu Lee,[2] James Hone,[3] Jie Shan,[4] and Tony F. Heinz[1,*]

NANO LETTERS
pubs.acs.org/NanoLett

Vol. 10, 1271,(2010).

Emerging Photoluminescence in Monolayer MoS_2

Andrea Splendiani,[†,‡] Liang Sun,[†] Yuanbo Zhang,[†] Tianshu Li,[§] Jonghwan Kim,[†] Chi-Yung Chim,[†] Giulia Galli,[§] and Feng Wang*[,†,||]

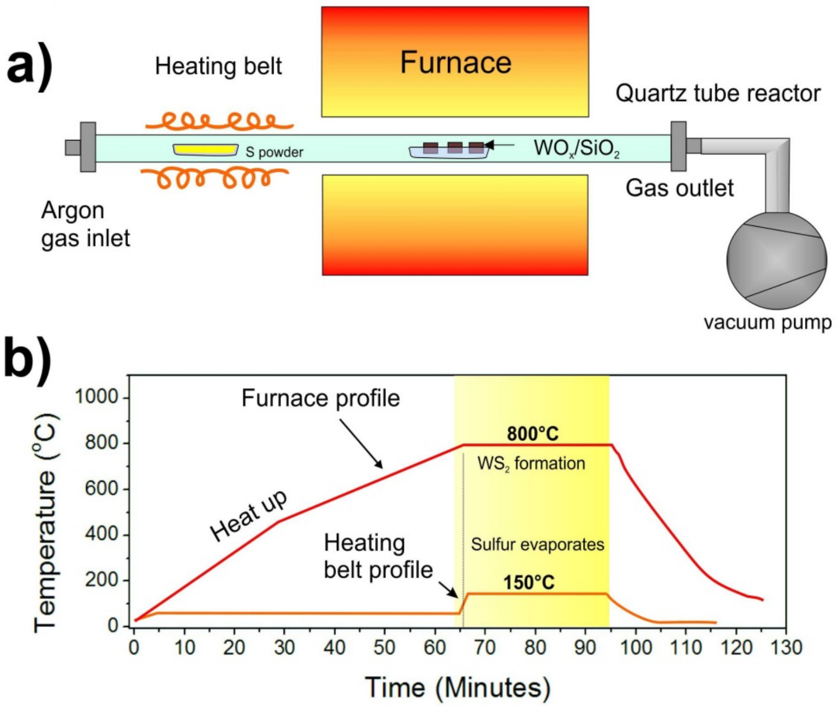
NANO LETTERS
LETTER
pubs.acs.org/NanoLett

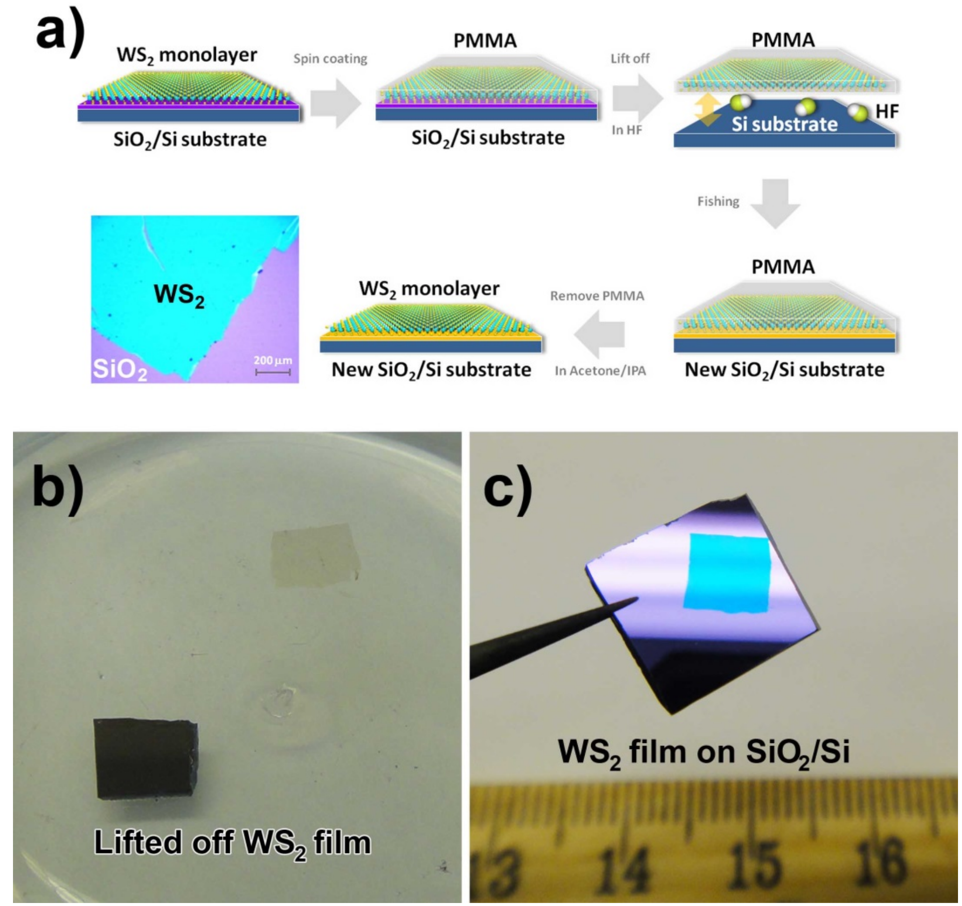
Vol. 11, 5111,(2011).

Photoluminescence from Chemically Exfoliated MoS_2

Goki Eda,[*,†,⊥,#] Hisato Yamaguchi,[‡,#] Damien Voiry,[‡] Takeshi Fujita,[§,||] Mingwei Chen,[§] and Manish Chhowalla[‡]

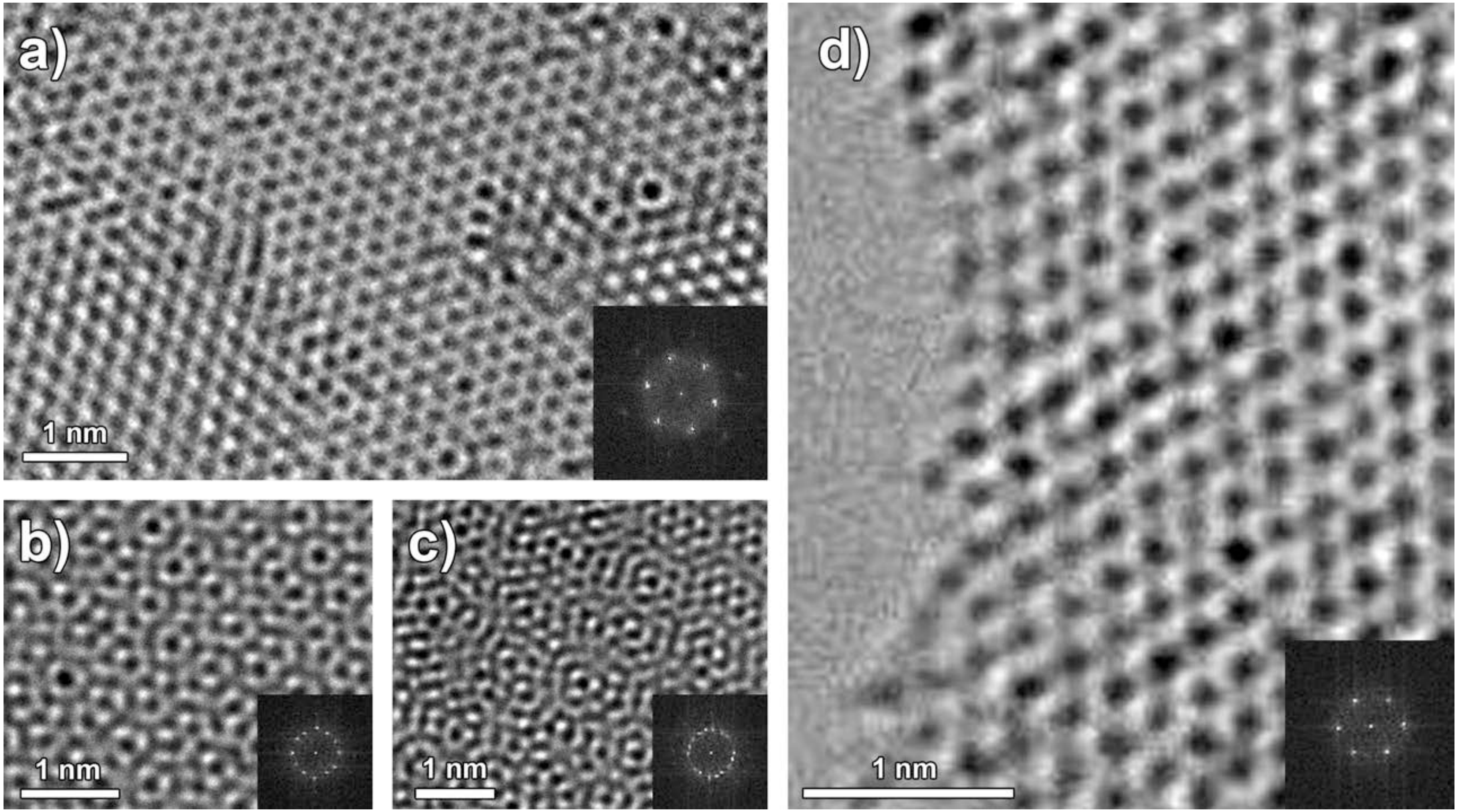
WS_2 synthesis by CVD





Elias, A.L., et al., ACS Nano, Vol. 7, 5235 (2013)

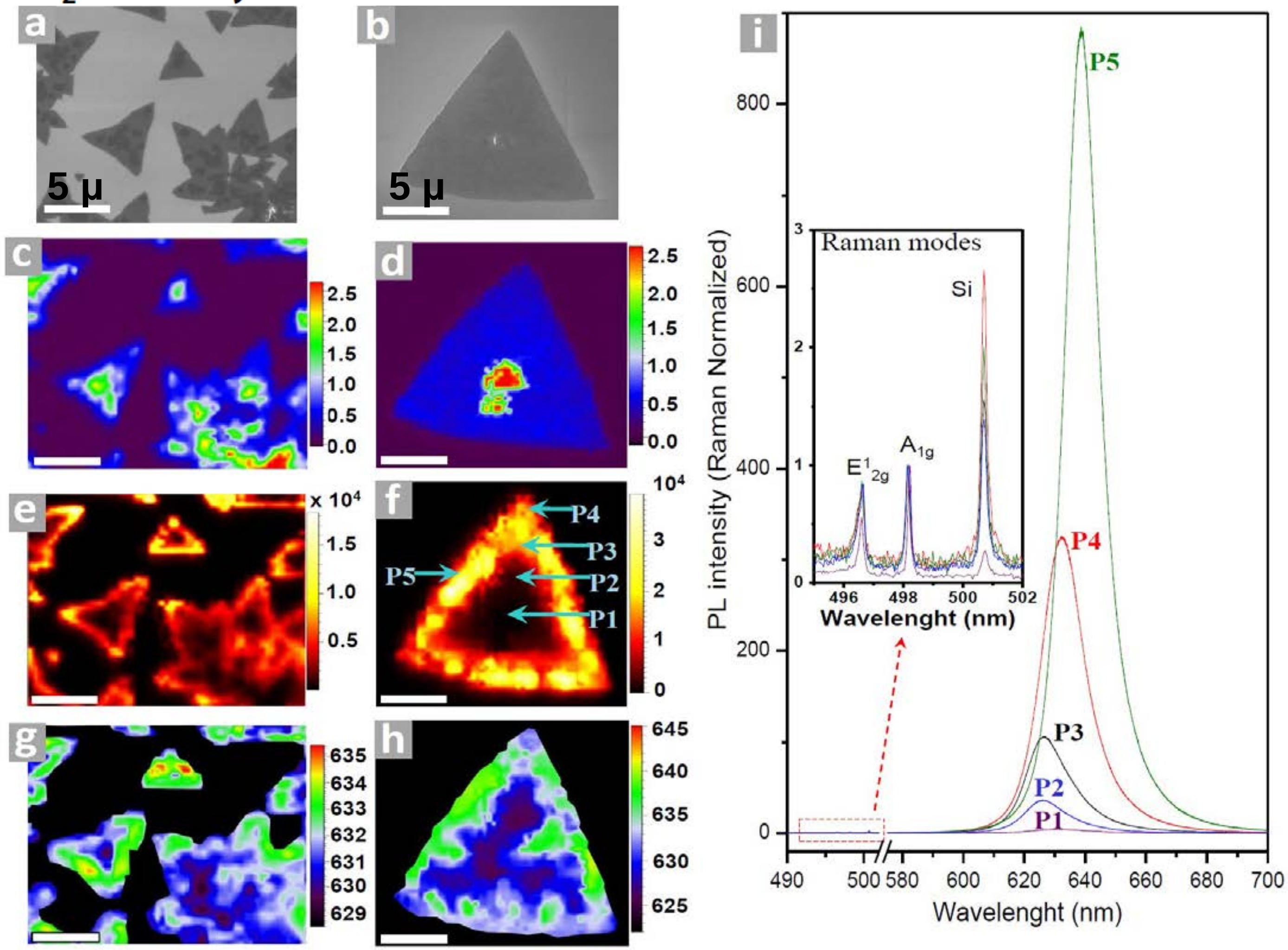
WS_2 Monolayer synthesis



Elias, A.L., et al., ACS Nano, Vol. 7, 5235 (2013)

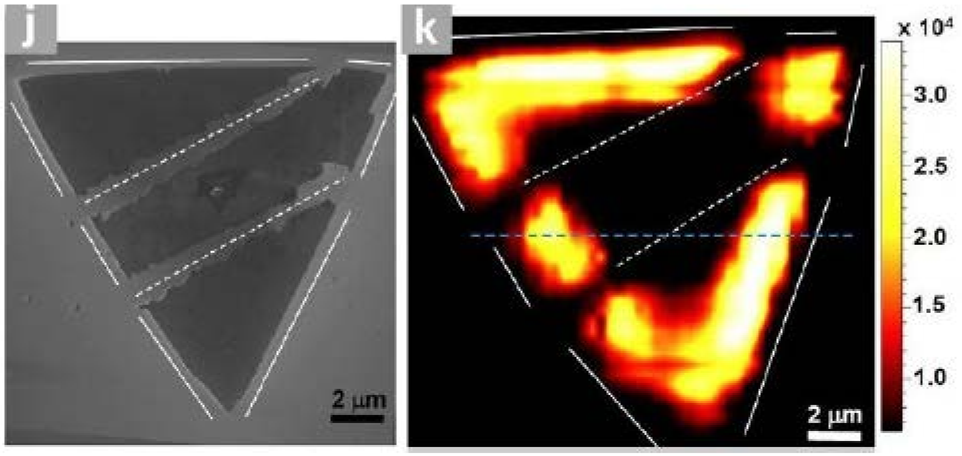
NANO LETTERS
Letter
pubs.acs.org/NanoLett

Extraordinary Room-Temperature Photoluminescence in Triangular WS_2 Monolayers



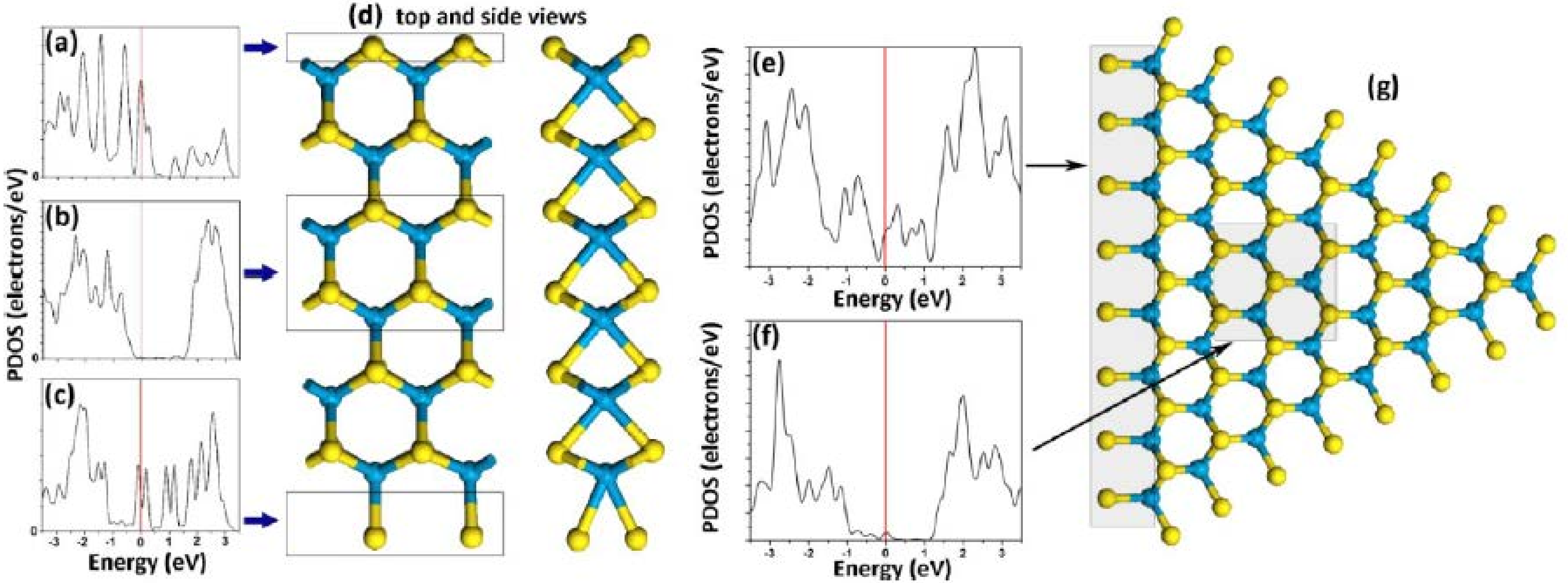
Gutierrez, H.R. et al., Nanoletters, Vol. 13, 3347 (2013)

Edge behavior in WS_2 monolayer



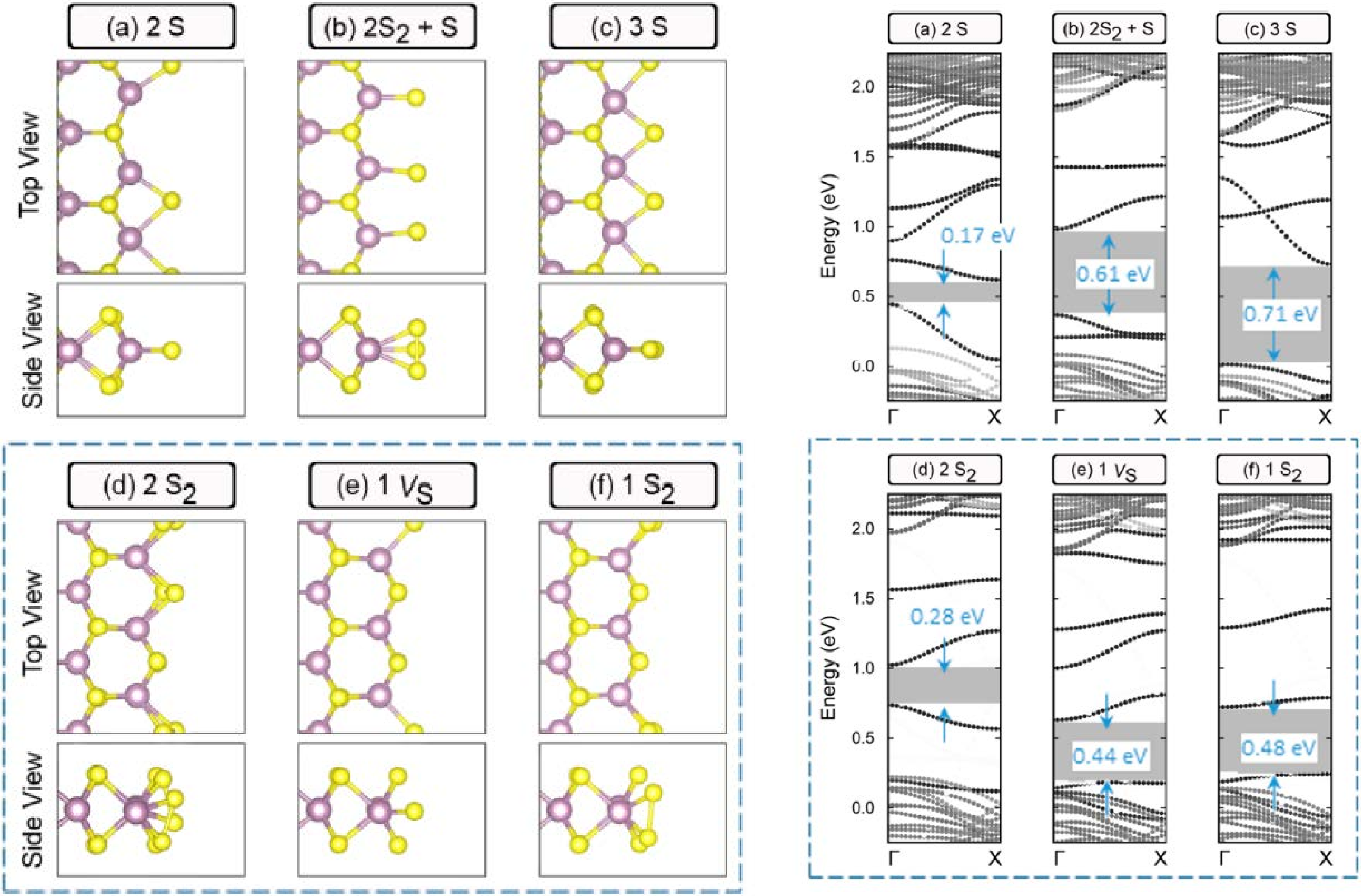
Gutierrez, H.R. et al., Nanoletters, Vol. 13, 3347 (2013)

Sulfur passivation DFT calculations



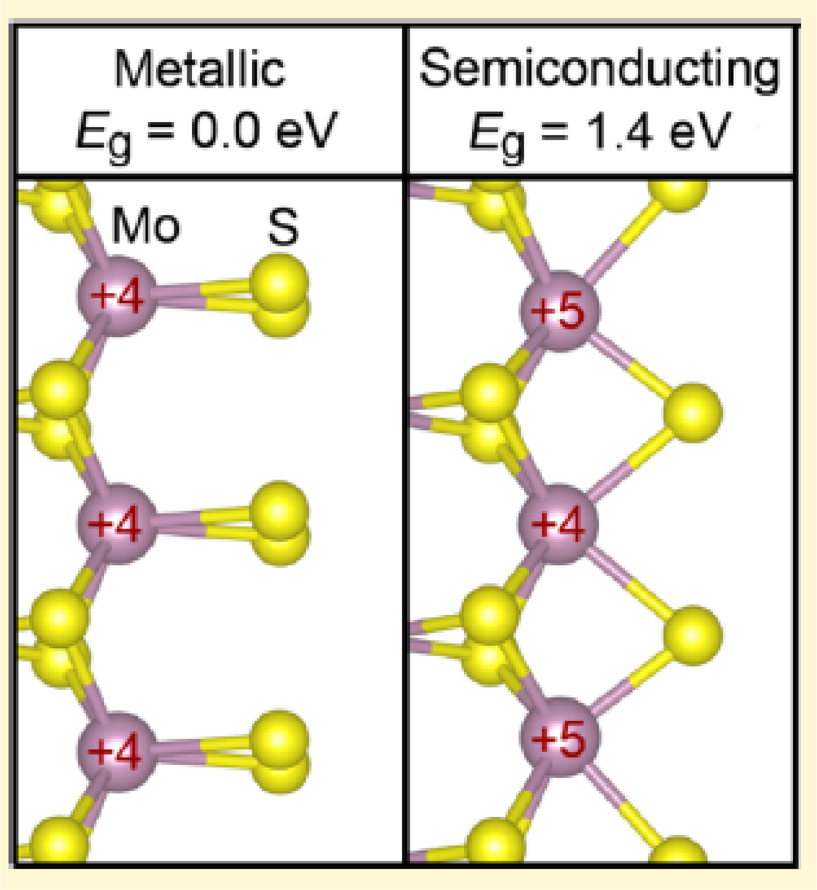
Metallic-like behavior at the edges

Gutierrez, H.R. et al., Nanoletters, Vol. 13, 3347 (2013)



Lucking, M., et al., Chemistry of Materials, Vol. 27, 3326-331 (2015).

Mo Valency change at the ribbon's edge



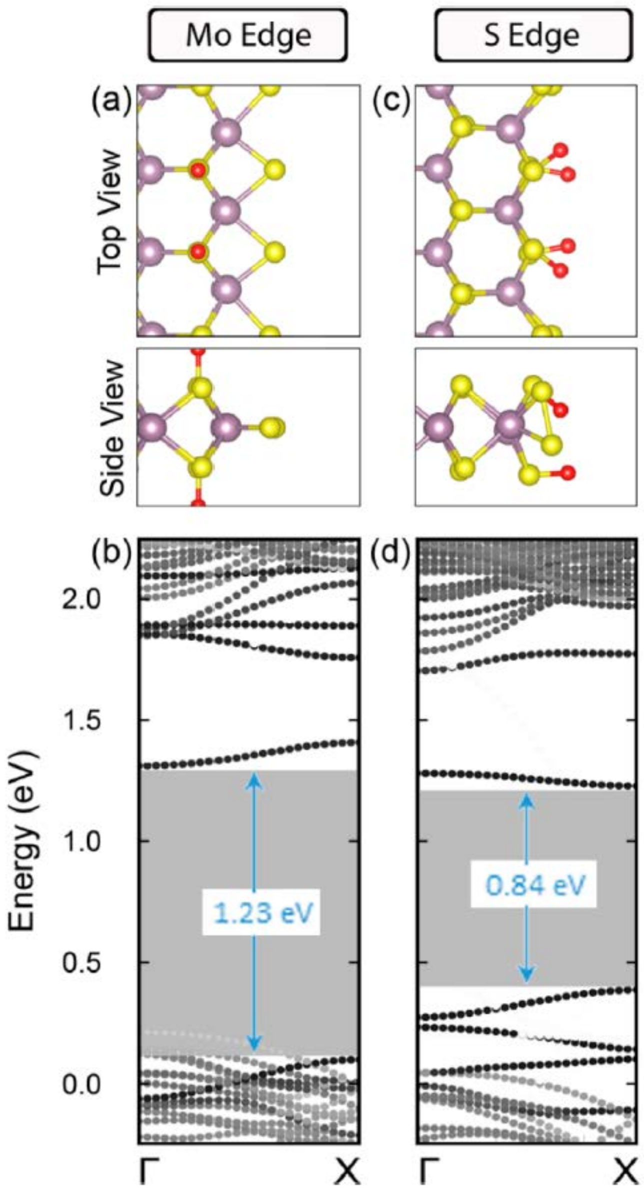
3S case

With HSE hybrid approximation the band gap is 1.4 eV

The band gap with GGA-PBE is 0.71 eV

Lucking, M., et al., Chemistry of Materials, Vol. 27, 3326-331 (2015).

Role of Oxygen and Sulfur at the edges



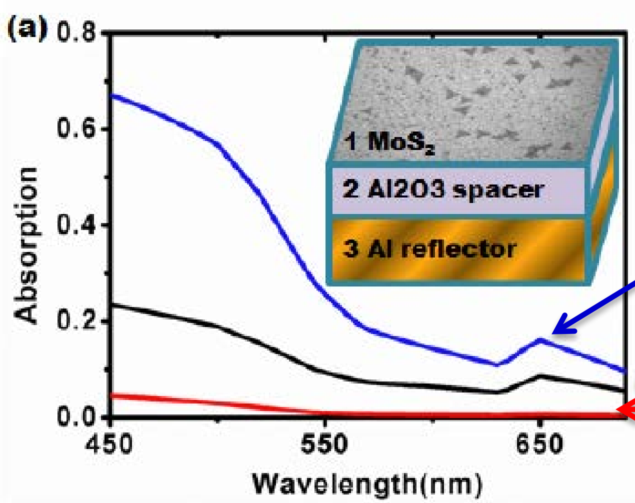
With the HSE hybrid approximation
The gaps become more realistic
and increase

1.23eV → 1.8eV (Mo Edge)
0.84eV → 1.6eV (S Edge)

Lucking, M., et al., Chemistry of Materials, Vol. 27, 3326-331 (2015).

PL of MoS2 monolayers on different nanocavities

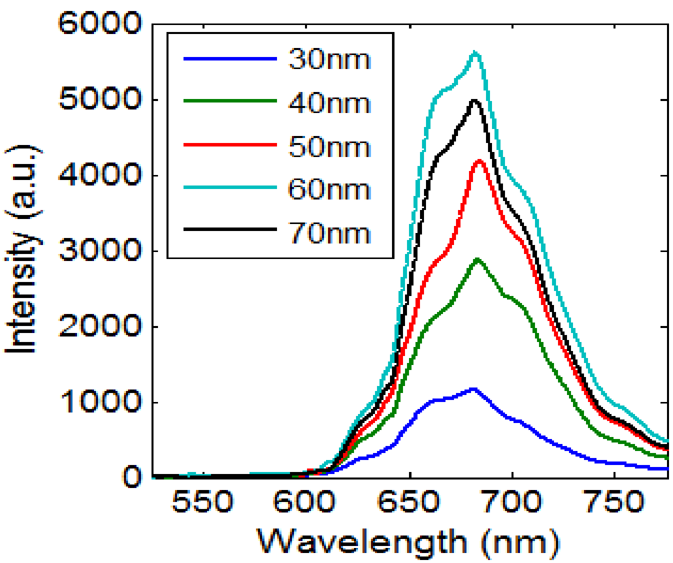
Janish, C. Et al., submitted

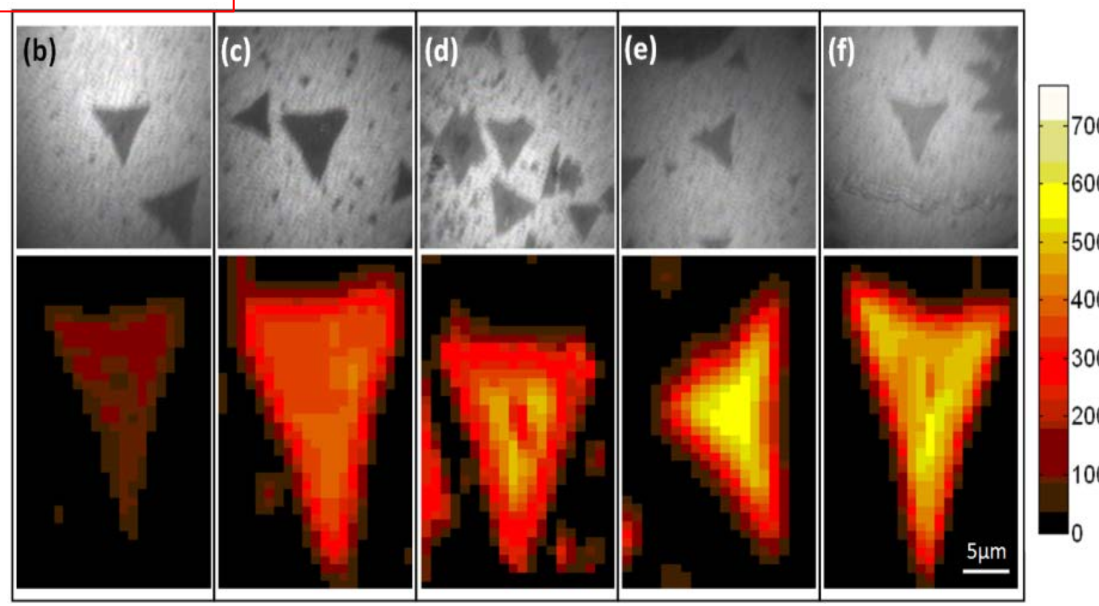


Al$_2$O$_3$/Al nanocavity

Free standing monolayer

Bare Al film



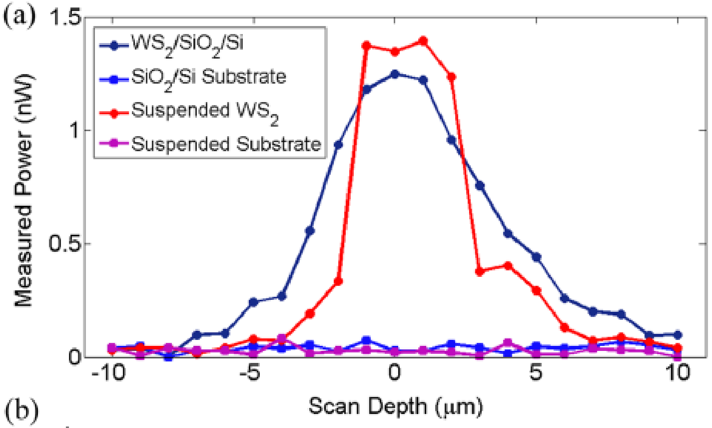


Planar nanocavities can enhance the light-matter interaction:

- **Enhance the exclusive absorption of the 2D materials**
- **Modification of the spontaneous emission rate**

Monolayer trigonal prismatic TMD exhibit no inversion symmetry and show second harmonic generation:

(a)



(b)

Janish, C., et al., Sci. Rep. 4 : 5530 | DOI:10.1038/srep05530; Kumar, N et al., PRB, Vol. 87, 161403 (2013);

nature nanotechnology

LETTERS

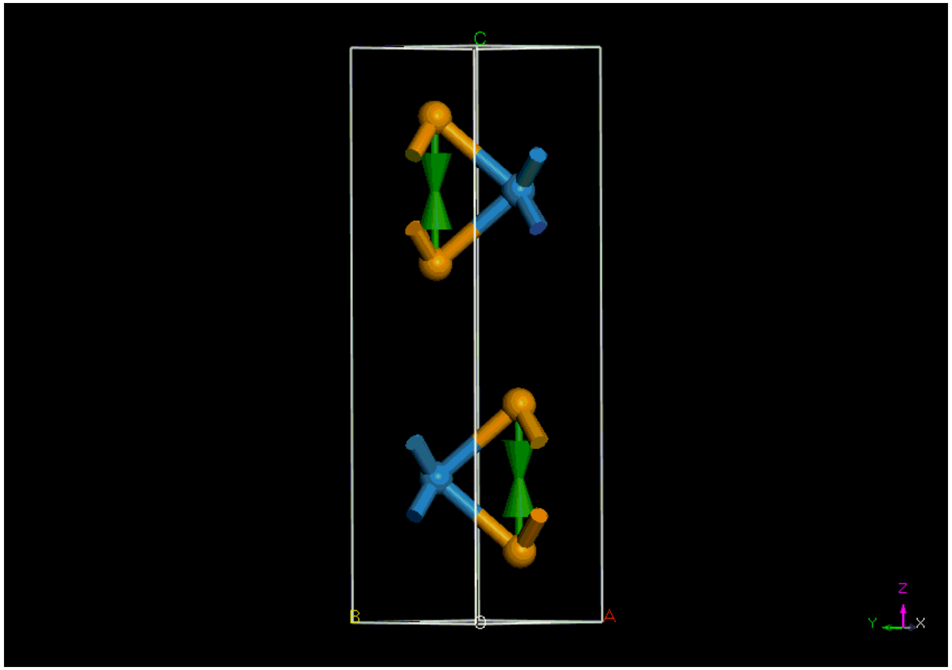
PUBLISHED ONLINE: 20 APRIL 2015 | DOI: 10.1038/NNANO.2015.73

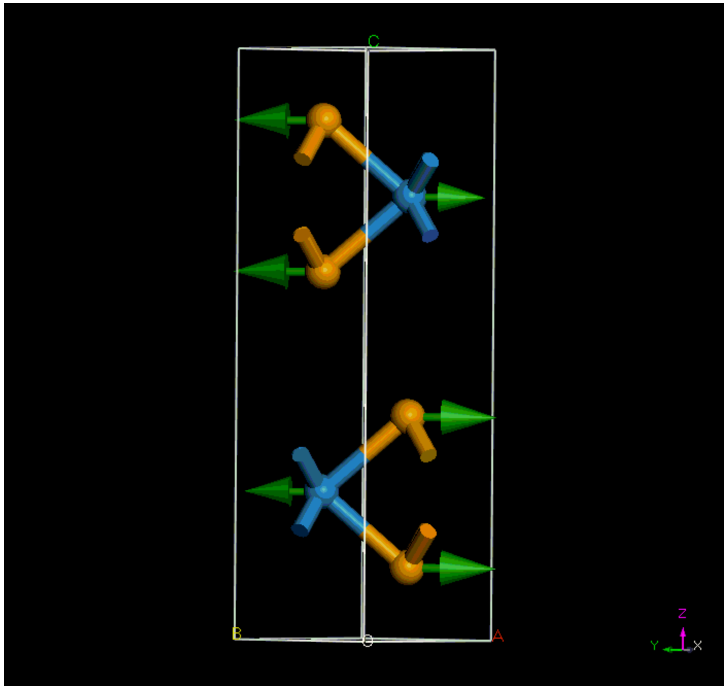
Electrical control of second-harmonic generation in a WSe_2 monolayer transistor

Kyle L. Seyler[1], John R. Schaibley[1], Pu Gong[2], Pasqual Rivera[1], Aaron M. Jones[1], Sanfeng Wu[1], Jiaqiang Yan[3,4], David G. Mandrus[3,4,5], Wang Yao[2] and Xiaodong Xu[1,6]*

Raman Modes in Bulk TMDs

Trigonal prismatic semiconducting TMDs belong to the same space group P63/mmc(194; Nonsymmorphic; Schoenflies notation point group D6h)





A_{1g}

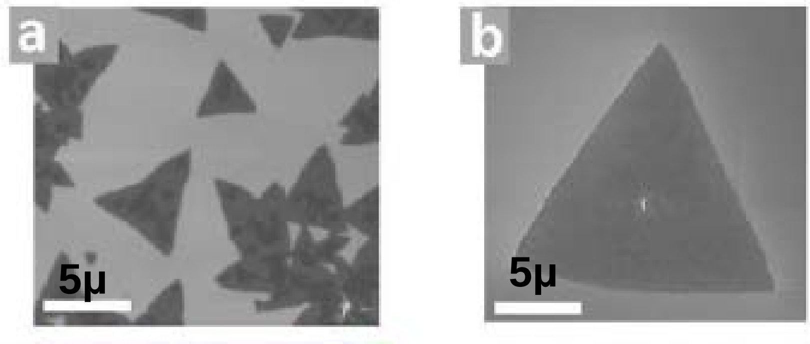
Out of plane

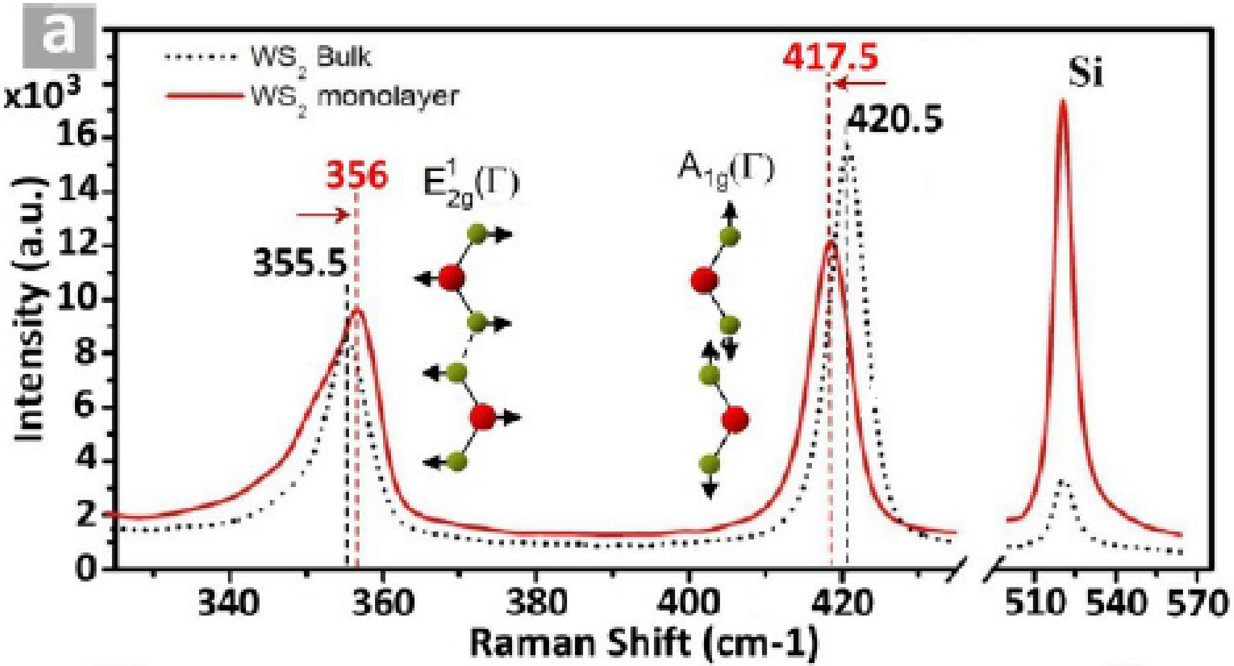
E_{2g}

in plane

25

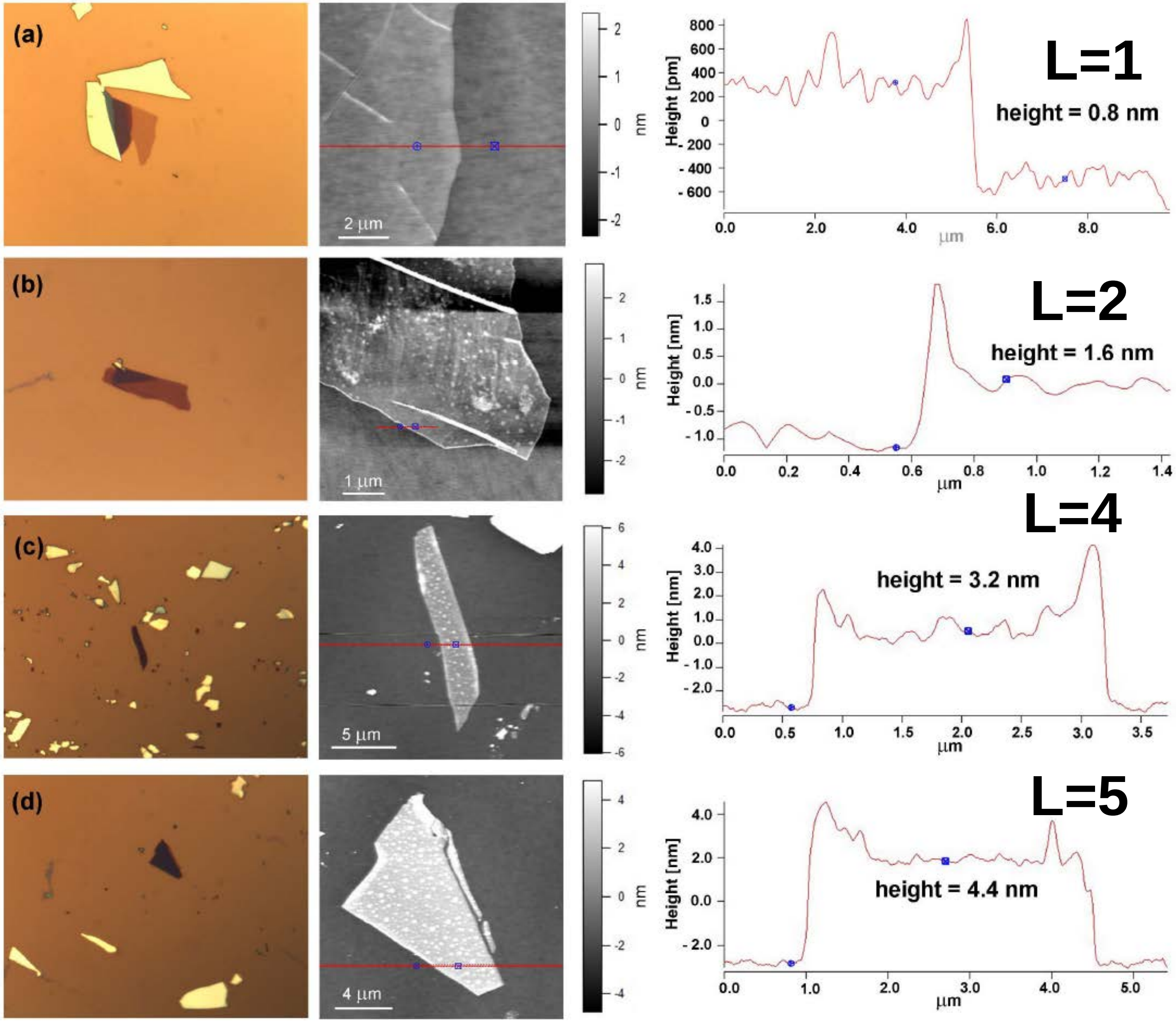
Raman Monolayer WS_2 (CVD)





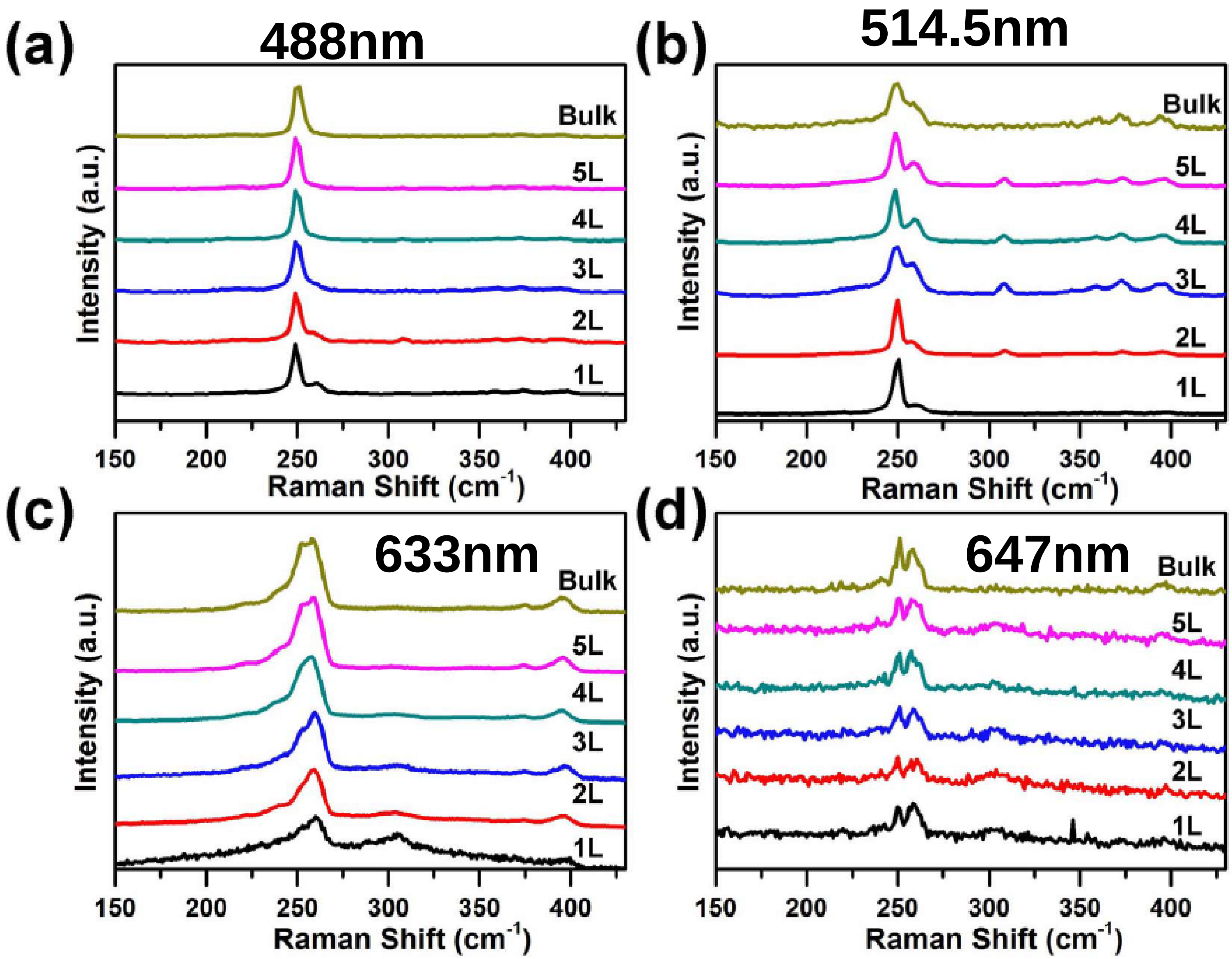
Gutierrez, H.R. et al., Nanoletters, Vol. 13, 3347 (2013)

Layered WSe_2 (CVT) by Mechanical Exfoliation



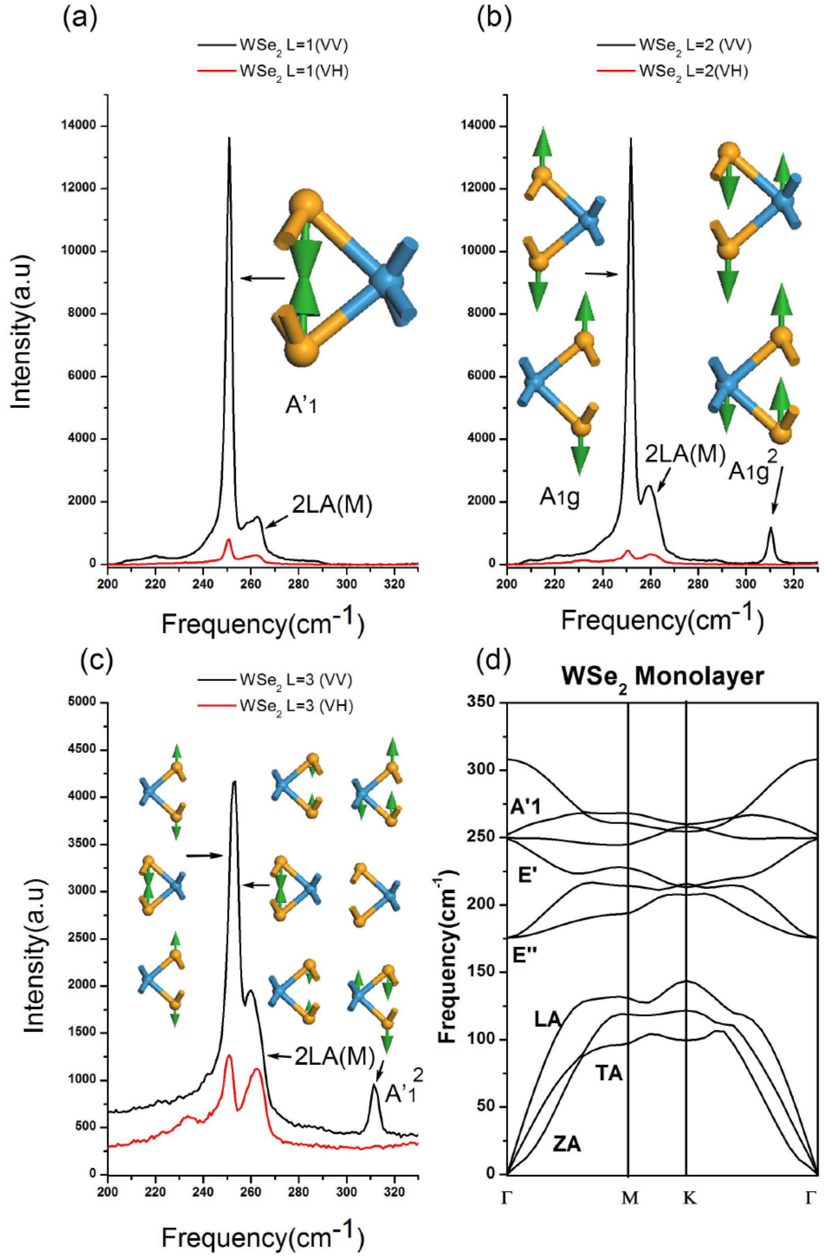
Terrones, H., et al., Scientific Reports, Vol. 4, 4215 (2014)

Layered WSe_2 (CVT) by Mechanical Exfoliation



Terrones, H., et al., Scientific Reports, Vol. 4, 4215 (2014); Zhao, W., et al., Nanoscale, DOI:10.1039/C3NR03052K (2013); Tonndorf, P., et al., Optics Express, Vol. 71, 4908 (2013).

Layered WSe_2 (CVT) by Mechanical Exfoliation

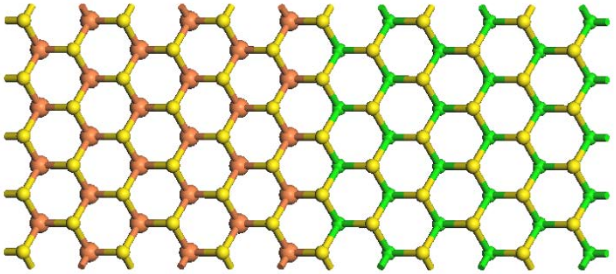


Density functional perturbation theory Using the code CASTEP

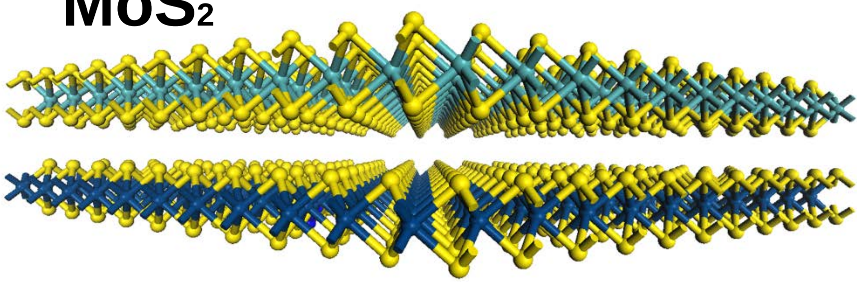
Terrones, H., et al., Scientific Reports, Vol. 4, 4215 (2014)

Heterostructures of TMDs

Can we mix layers or have different types of atoms in one layer? Yes

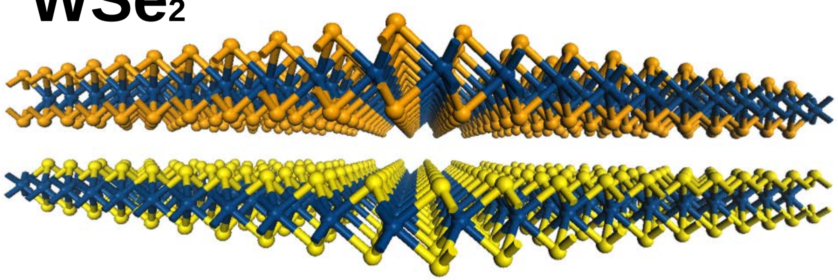


MoS_2



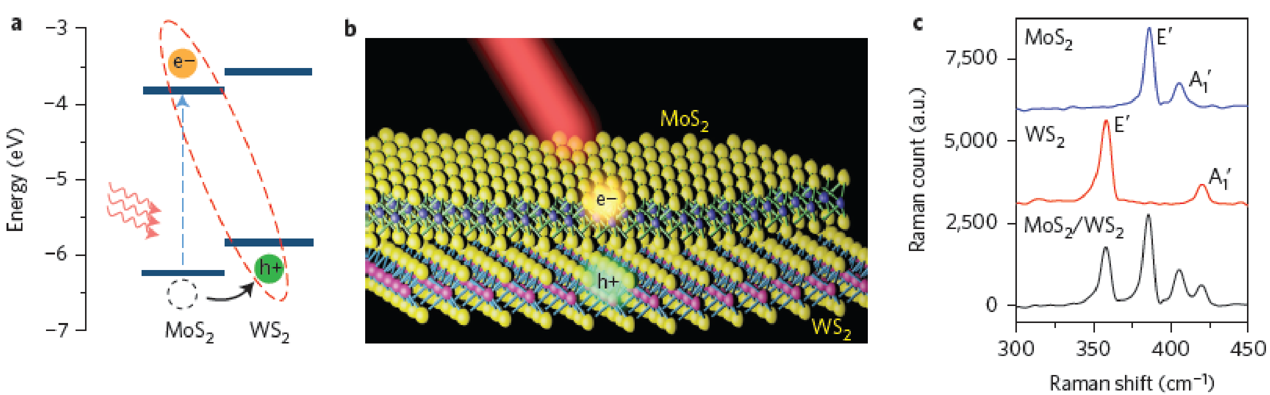
WS_2

WSe_2



WS_2

Terrones, H., et al., scientific Reports, Vol. 3, 1549 (2103)

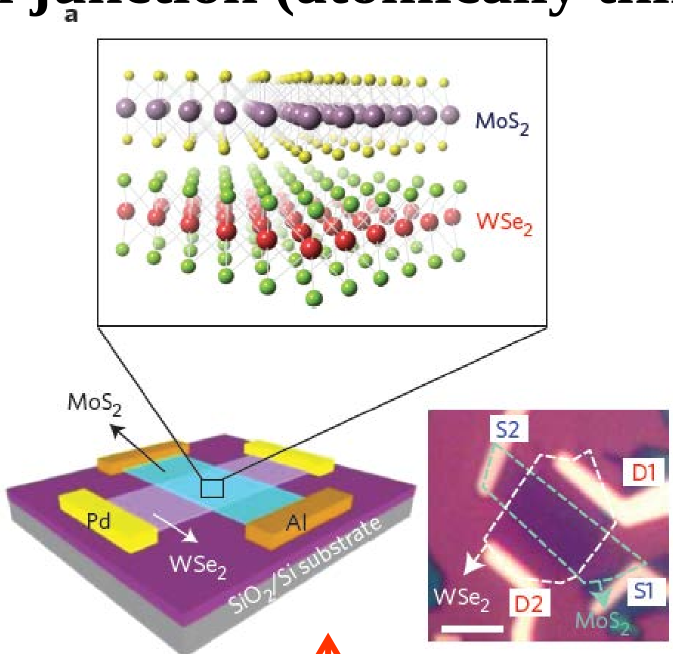


Ultra fast charge transfer $50X10^{-15}$ sec after optical excitation

Xong, X., et al ., Nature Nanotechnology, Vol. 9, DOI: 10.1038/NNANO.2014.167 **2014**

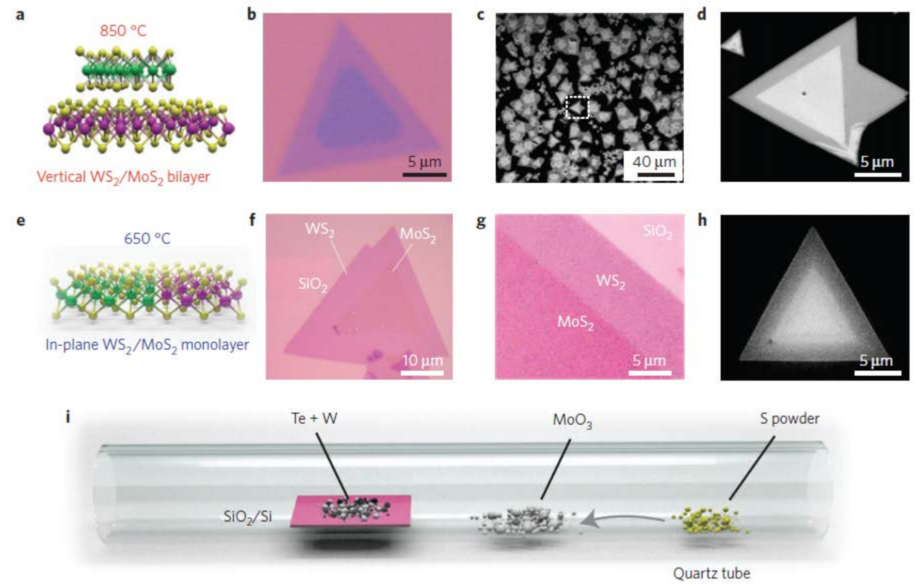
Heterostructures of TMDs

p-n junction (atomically thin)



By mechanical exfoliation (scotch tape)

Lee, C-H., et al., Nature nanotechnology, Vol.10 DOI: 10.1038/NNANO.2014.150 (2104)

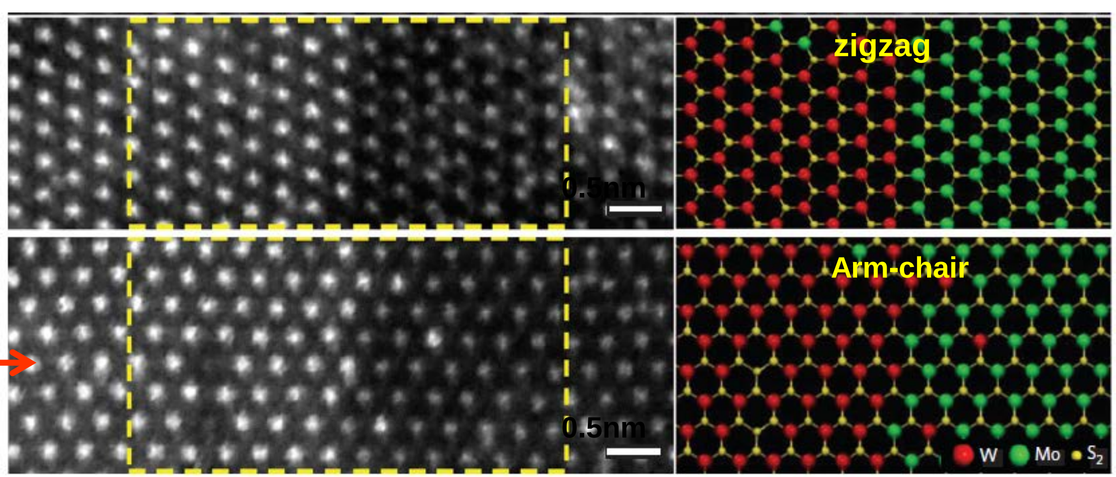


By CVD

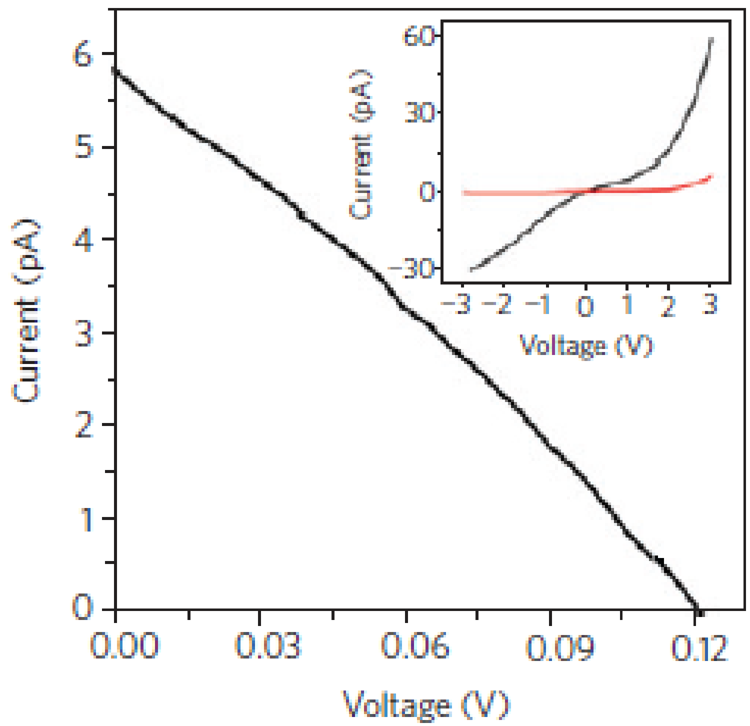
Gong, J., et al, Nature Materials, PUBLISHED ONLINE: 28 SEPTEMBER 2014 | DOI: 10.1038/NMAT4091

Atomic resolution z-contrast STEM

Gong, J., et al, Nature Materials, PUBLISHED ONLINE: 28 SEPTEMBER 2014 | DOI: 10.1038/NMAT4091

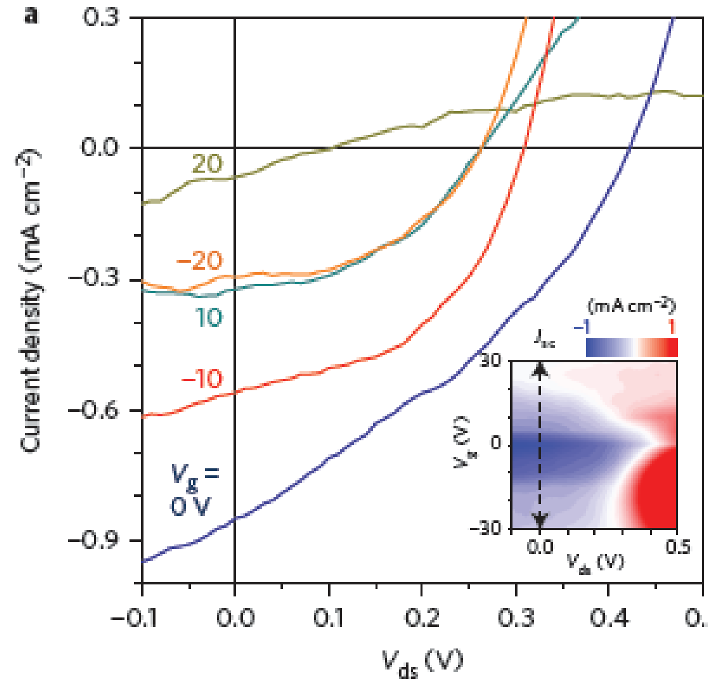


Heterostructures of TMDs



Photovoltaic effect of the in plane heterojunction (MoS_2/WS_2) open-loop voltage of 0.12 V and close-loop current of 5.7 pA

Gong, J., et al, Nature Materials, PUBLISHED ONLINE:28 SEPTEMBER 2014 | DOI: 10.1038/NMAT4091



Photovoltaic effect in MoS_2/WSe_2 bilayer heterojunction

Lee, C-H., et al., Nature nanotechnology, Vol.10 DOI: 10.1038/NNANO.2014.150 (2104)

Challenges:

- **Mass production of single layers**
- **Control of defects, doping and grain boundaries**
- **Control of stacking**
- **Contacts with metals or other TMDs**

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NSF (EFRI-1433311), U.S. Army Research Office MURI grant W911NF-11-1-0362,Penn State Center for Nanoscale Science Seed grant on 2-D Layered Materials (DMR-0820404).

Thank you