Institute for Research in Fundamental Sciences

Molybdenum Sulfide as a New Gateway to Technology Development

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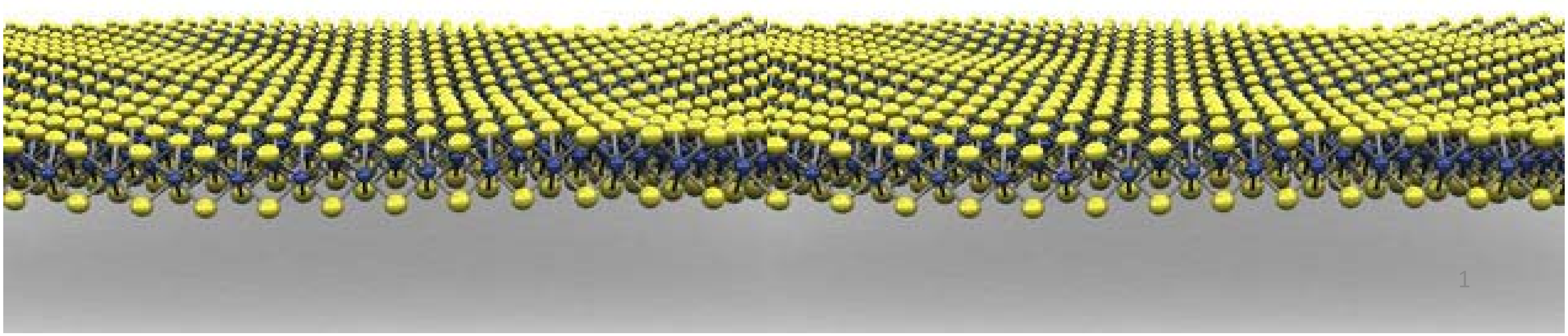
School of Physics-IPM



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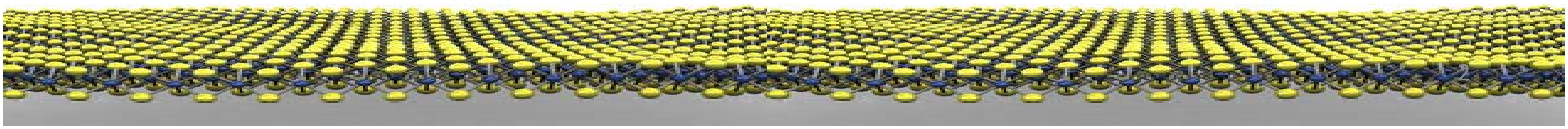
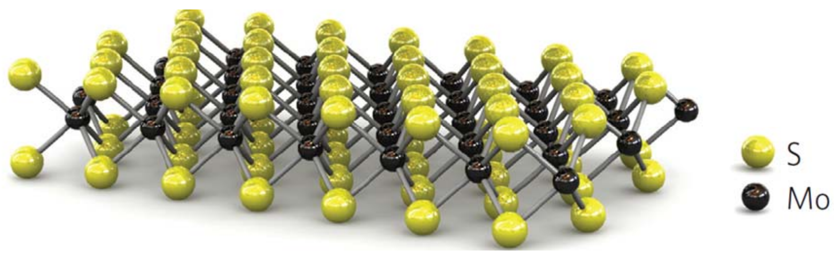
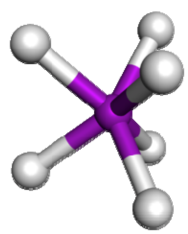
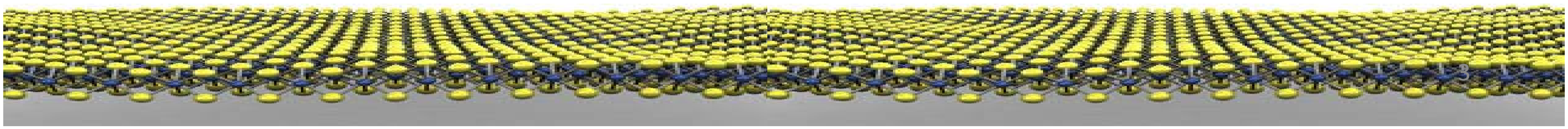


Two Dimensional MoS_2

- High effective surface area in layered systems
- Tunable band gap energy depend on the system's thickness (1.2-1.9 eV)
- Catalytic active edges in reactions
- Desirable mechanical properties (comparable with graphene)
- Chemical stability as compared with other low gap sulfides







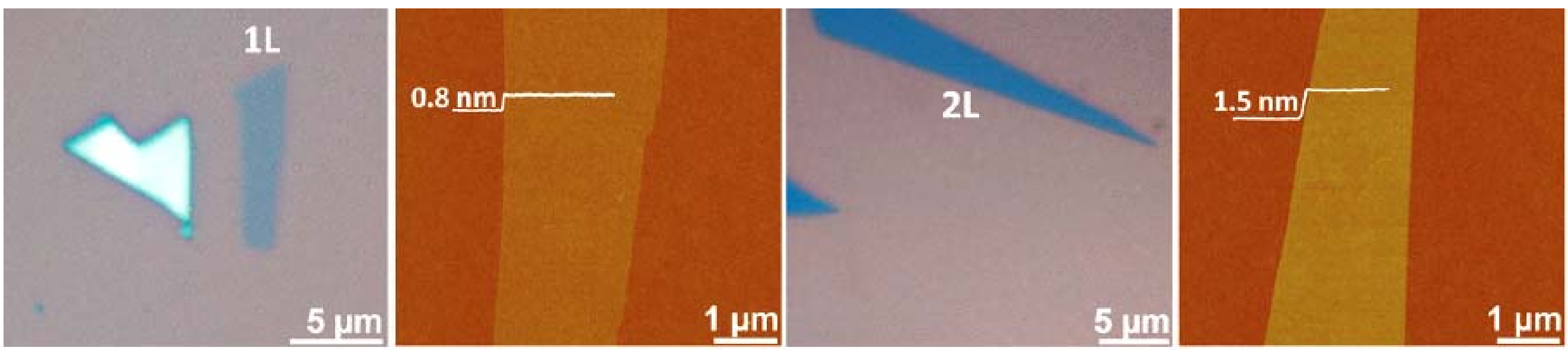
Top-down Synthesis Methods

- Mechanical cleavage
- Exfoliation
- Lithium intercalation
- Laser thinning

Micromechanical Cleavage

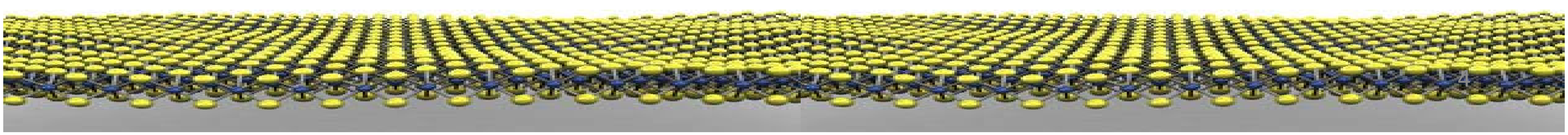
Rubbing a fresh surface of a layered crystal against a target surface (e.g. Si/SiO_2), flakes of the rubbed crystal were detached and adsorbed onto the target surface.

Limited fabrication amount & Low reproducibility



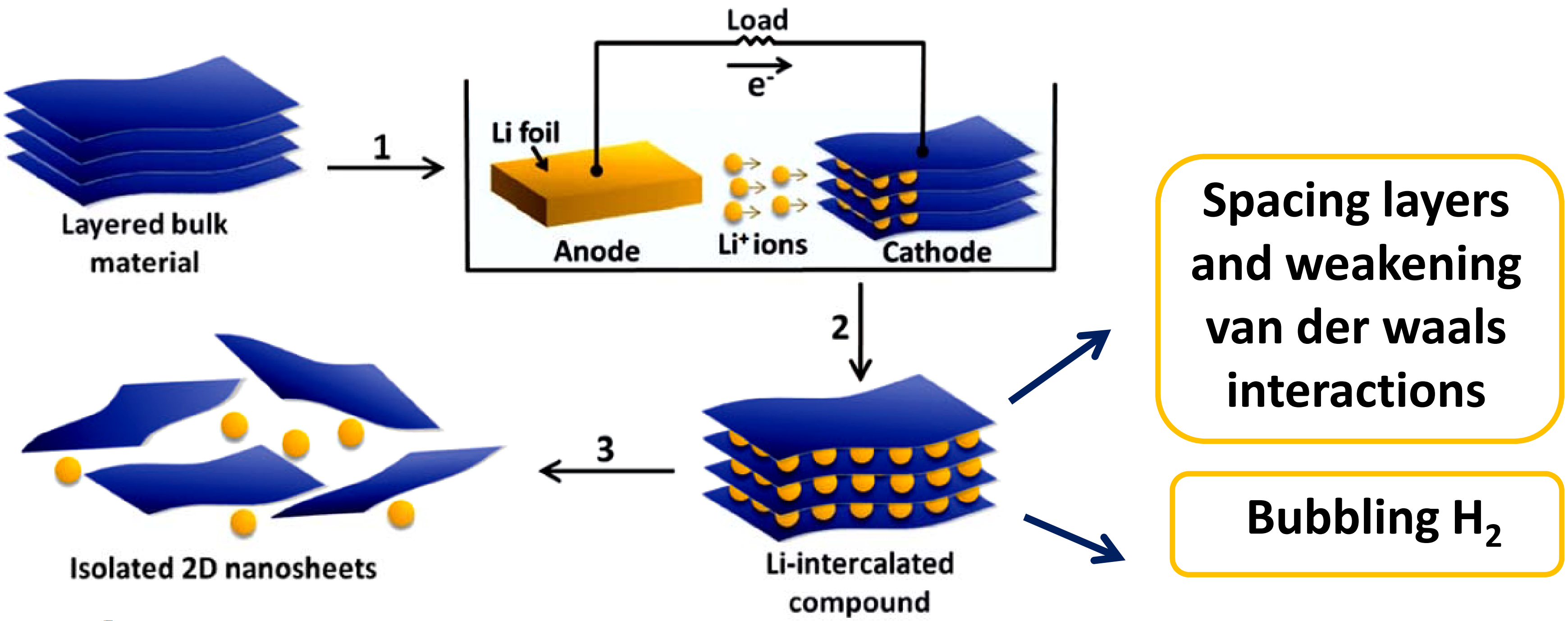
Small, 2012, 8, 63.

Nature Nanotechnology, 2011,6,147.



Top-down Synthesis Methods

Lithium Intercalation



$$2Li^0_xMoS_2 + 2xH_2O \rightarrow 2(MoS_2) \text{ exfoliated layers} + 2xLiOH + xH_2$$

- **Almost >92% are single layer**
- **Possible at room temperature in a short while**
- **Expensive**
- **Controlling mount of inserted Li ions**

Angew. Chem., Int. Ed., 2011, 50.

Top-down Synthesis Methods

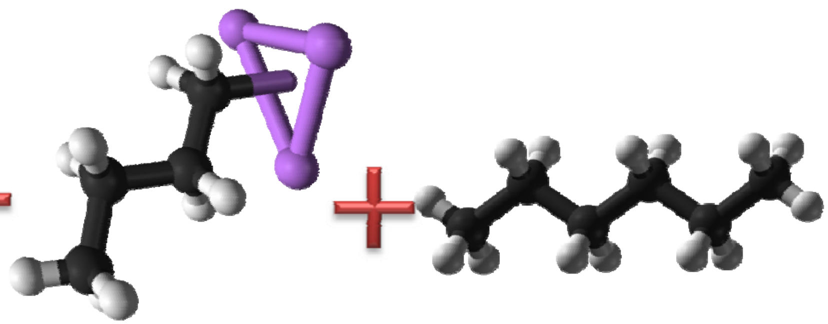
Chemical Lithium Intercalation

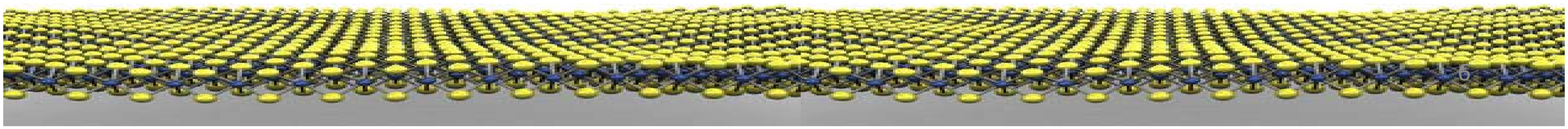
SINGLE-LAYER MoS_2

Mat. Res. Bull. 1986, 21, 457

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

Bulk MoS_2 + **N-buthyl Li** + **hexane** + **In Ar /glove box for 48 hours**

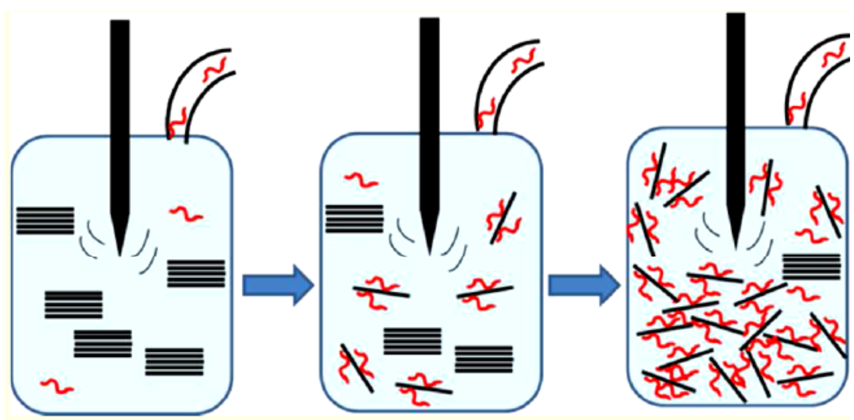




Top-down Synthesis Methods

Sonication-Exfoliation

When the surface energy of the solvent matches with that of the layered material, the enthalpy of exfoliation is minimized. For MoS_2, solvent like *N-methyl-pyrrolidone (NMP)*, with a surface energy of ~70 mJ /m^2, gave the best dispersity.



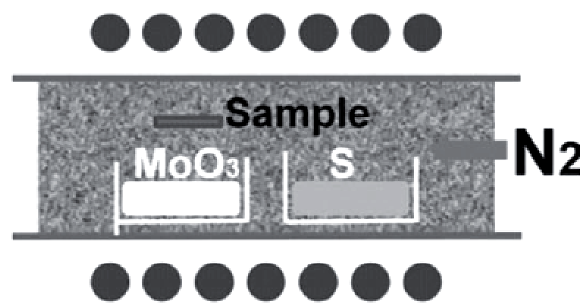
- **Easy and safe process**
- **Low yield for single layers**
- **Expensive (except water-ethanol solvent)**

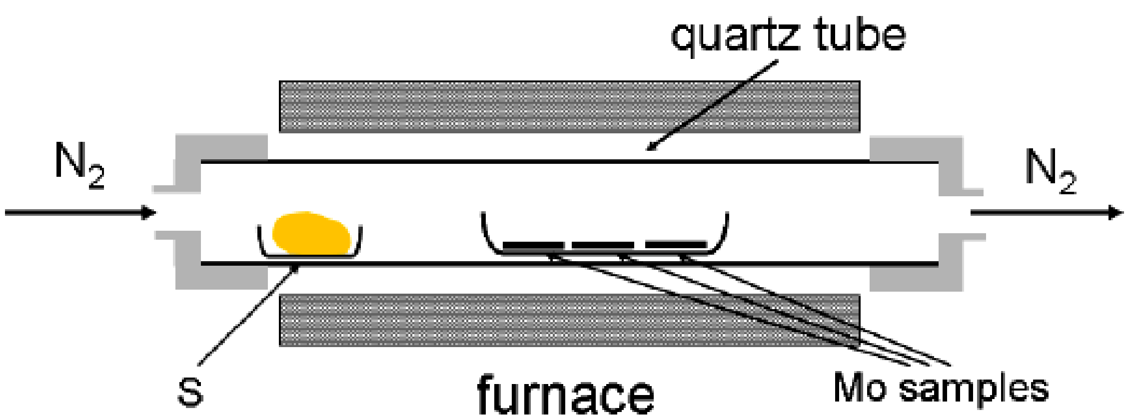
Coleman et al. Science, 2011, 331, 568
Notely, Langmuir 2012, 28, 14110.

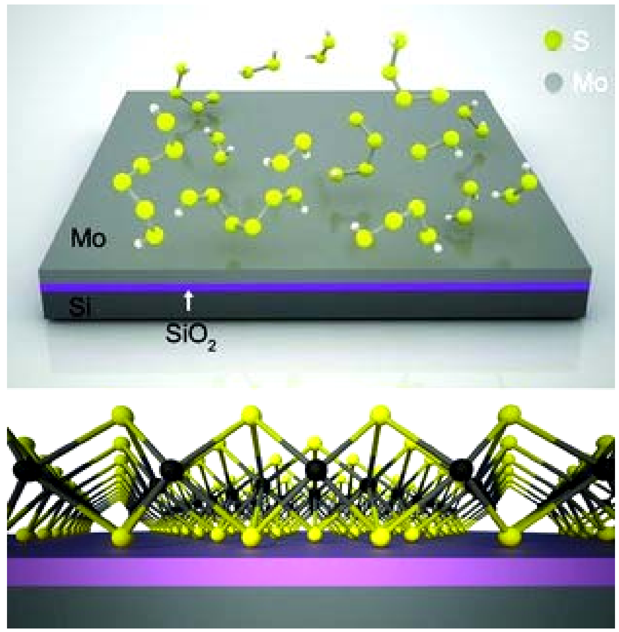
Bottom-up Synthesis Methods

CVD growth

$$S_2 + MoO_{3-x} \rightarrow MoS_2 + SO_2$$







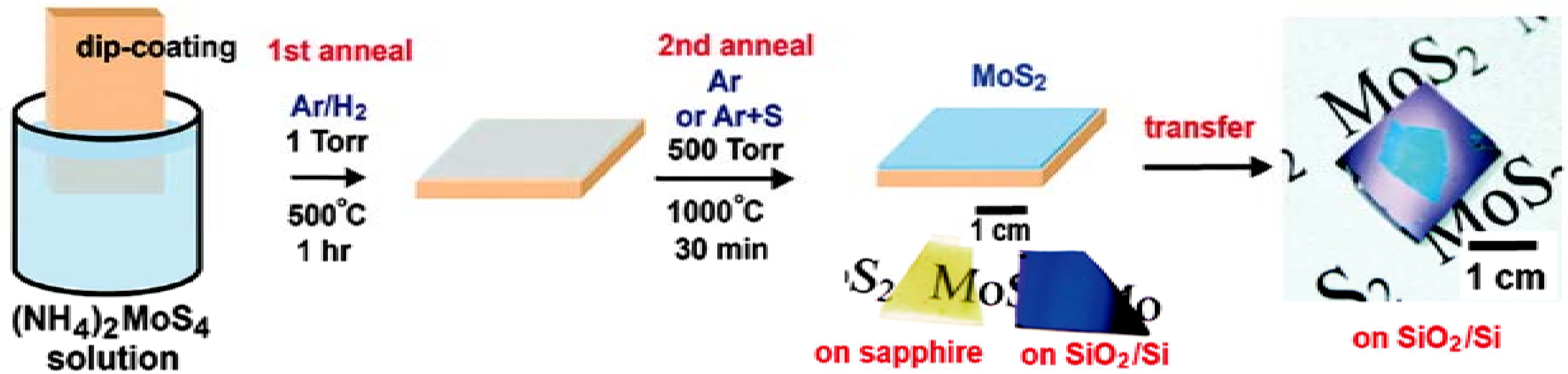
T_o > sulfur melting point ……… T_r ~ 750^{o}C
~ 113^{o}C, N_2

Zhan et al. Small 2012, 8, 966.
Lin et al. Nanoscale, 2012, 4, 6637.

Bottom-up Synthesis Methods

CVD growth

Thermal decomposition of ammonium thiomolybdate



$$(NH_4)_2MoS_4 \rightarrow 2NH_3 + H_2S + MoS_3$$

120-360 °C

$$MoS_3 \rightarrow MoS_2 + S$$

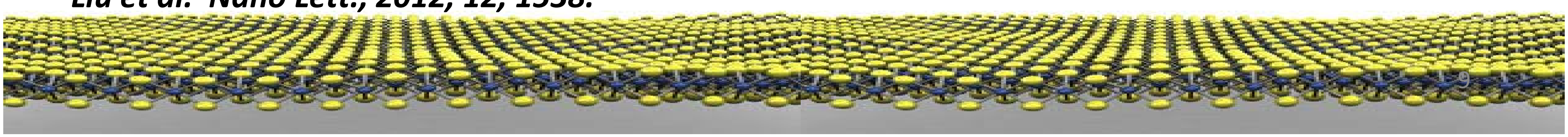
800 °C

$$(NH_4)_2MoS_4 + H_2 \rightarrow 2NH_3 + 2H_2S + MoS_2$$

450 °C

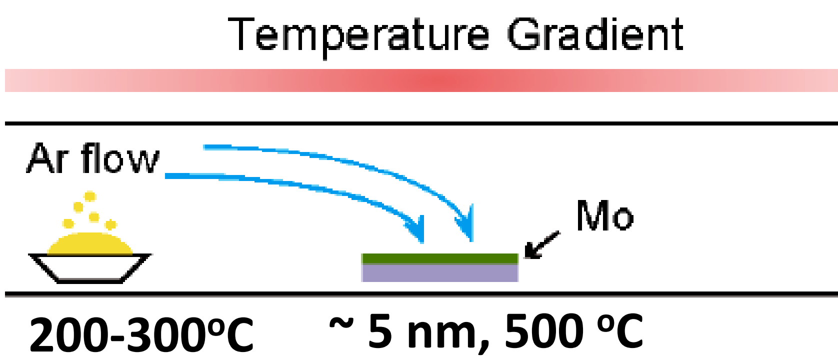
- **Transferring to desirable substrate**
- **Hybrids (rGO/MoS_2)**
- **Defects hinders charge mobility**

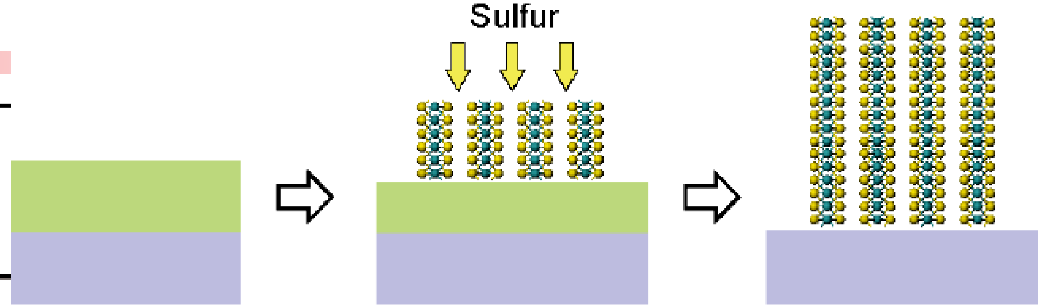
Liu et al. Nano Lett., 2012, 12, 1538.

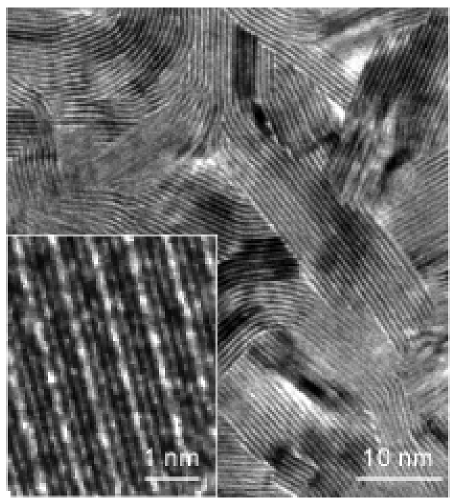


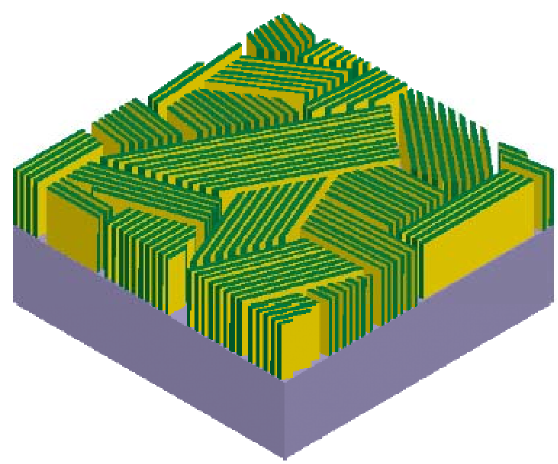
Bottom-up Synthesis Methods

Aligned growth : Rapid CVD









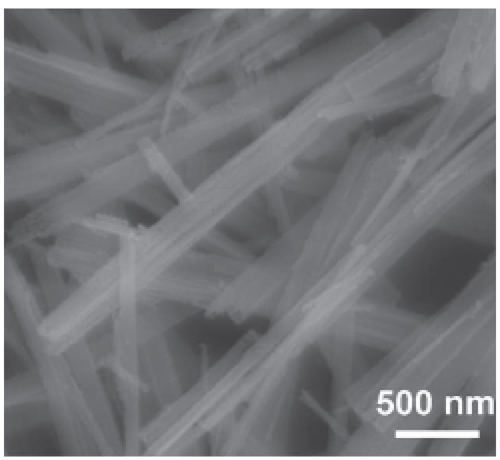
Kong et al. Nano Lett. 2013, 13, 1341.

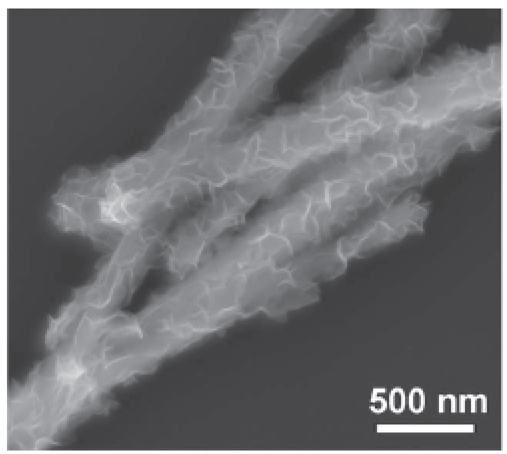
Bottom-up Synthesis Methods

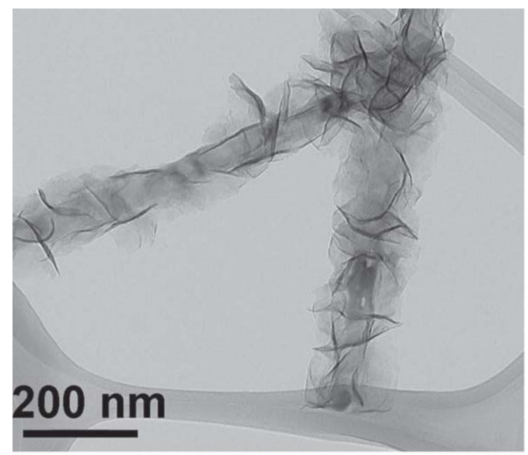
Hydrothermal growth

Reaction between Mo & S included salts under controlled temperature and pressure on the conventional film/substrate

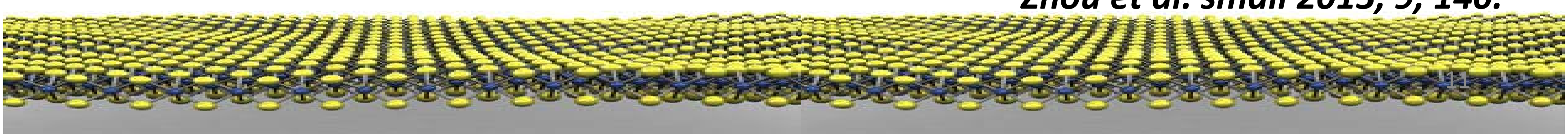
Sodium molybdate ($Na_2 MoO_4 \cdot 2H_2O$) + Thioacetamide (C_2H_5NS) were dissolved in DI water with TiO_2 nanobelts in autoclave + heated an electric oven at 200°C for 24 h. → Centrifuging + drying





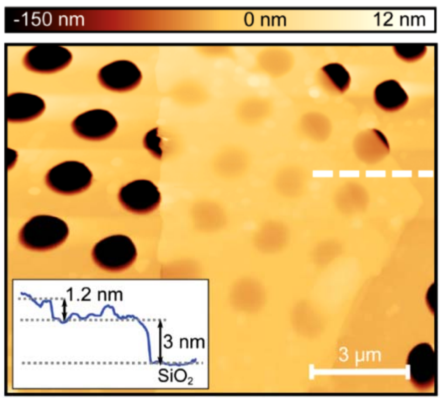


Zhou et al. small 2013, 9, 140.

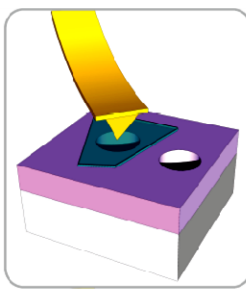


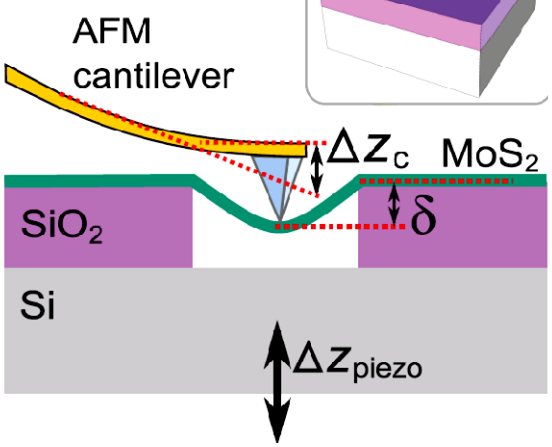
Characterizations

Mechanical Properties

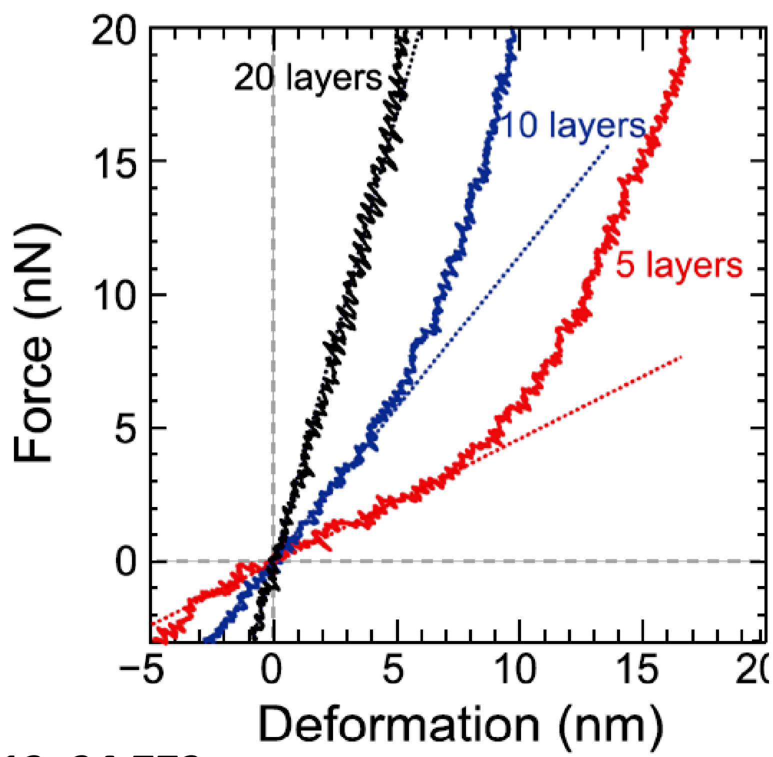


5-7 layers
By Cleavage





$$F = \left[\frac{4\pi E}{3\,(1-\nu^2)} \cdot \left(\frac{t^3}{R^2}\right)\right]\delta + (\pi T)\,\delta + \left(\frac{q^3 E t}{R^2}\right)\delta^3$$



$$\delta = \Delta z_{piezo} - \Delta z_c$$

$$F = k_c \cdot \Delta z_c$$

Y (TPa)	
Thick	0.4
10L	0.35
5L	0.35

Gomez et al. Adv. Mater. 2012, 24,772.

Characterizations

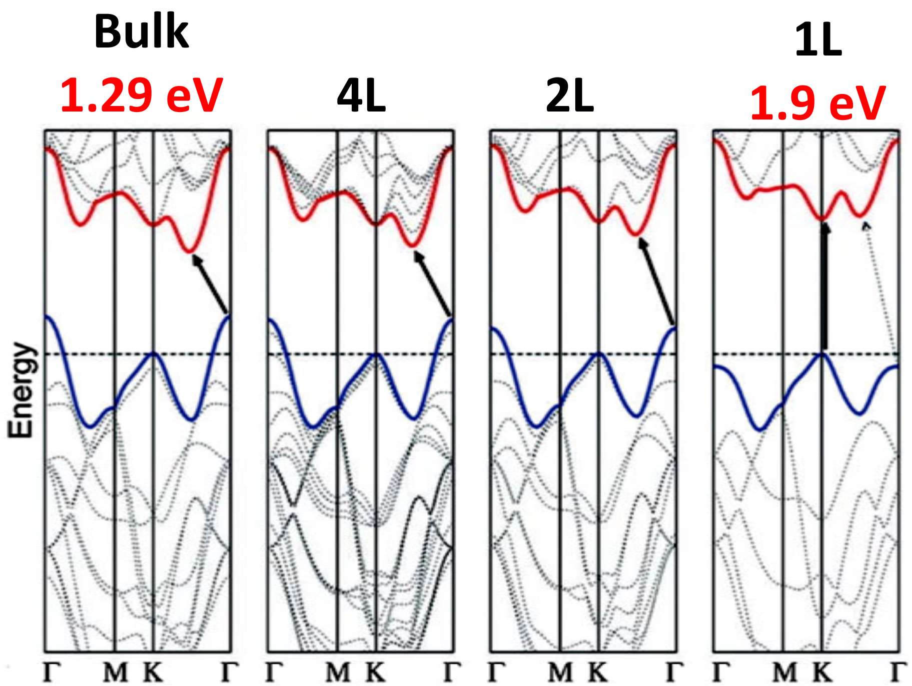
Mechanical Properties

material	Young's modulus E_{Young} (GPa)	breaking strength σ_{max}^{eff} (GPa)	strength/Young's modulus (%)
stainless steel ASTM-A514	205	0.9	0.4
molybdenum	329	0.5—1.2	0.15—0.36
polyimide	2.5	0.231	9
PDMS	0.3—0.87	2.24	2.5
Kevlar 49	112	3	2.6
monolayer MoS_2	270	16—30	6—11
bulk MoS_2	238		
WS_2 nanotubes	152	3.7—16.3	2.4—10
carbon nanotubes	1000	11—63	1.1—6.3
graphene	1000	130	13

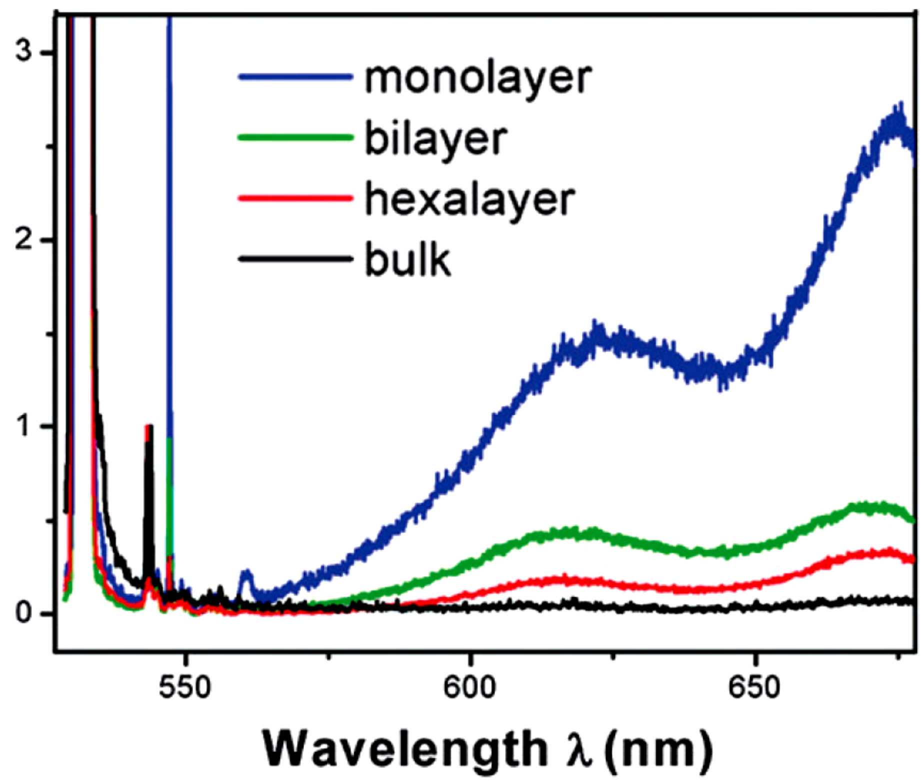
Bertolazzi et al. ACS Nano, 5,2011,9703.

Characterizations

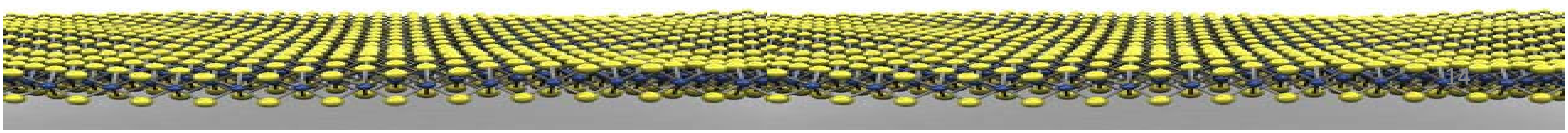
Optical & Electronic Properties



Photoluminescence



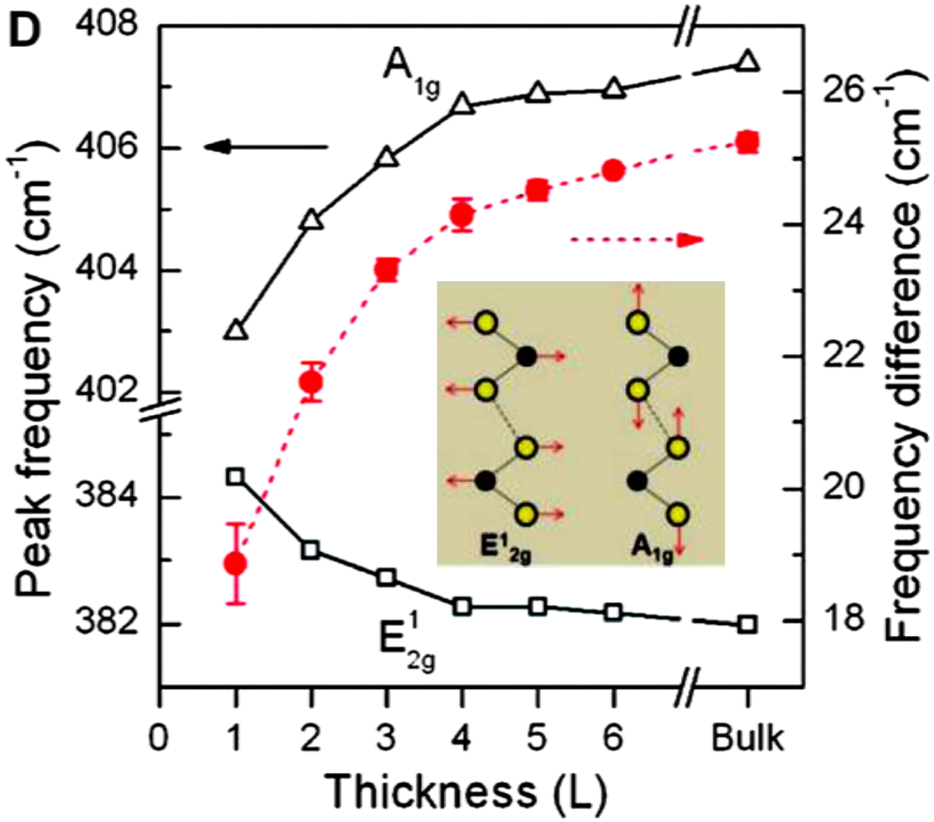
Splendiani et al. Nano Lett., 2010, 10, 1271



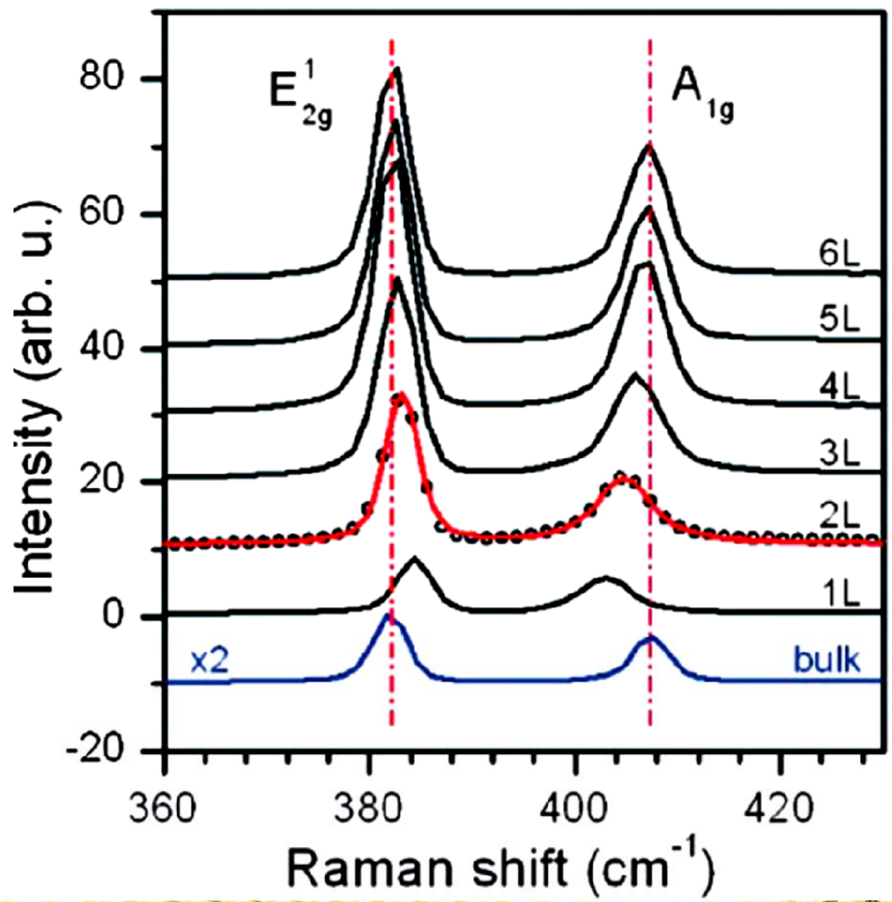
Characterizations

Optical & Electronic Properties

Raman Spectroscopy



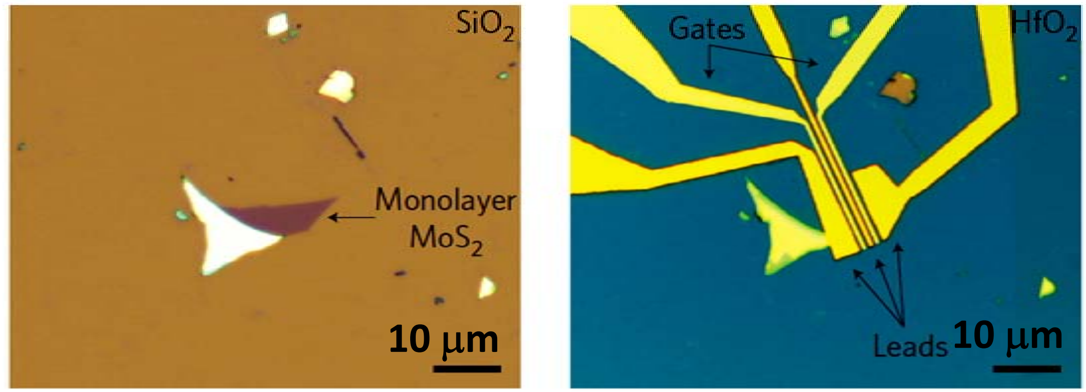
Lee et al. ACS Nano, 2010, 4, 2695.

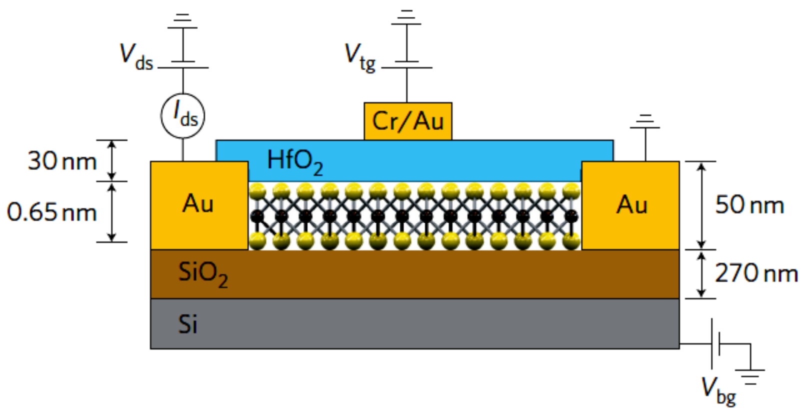


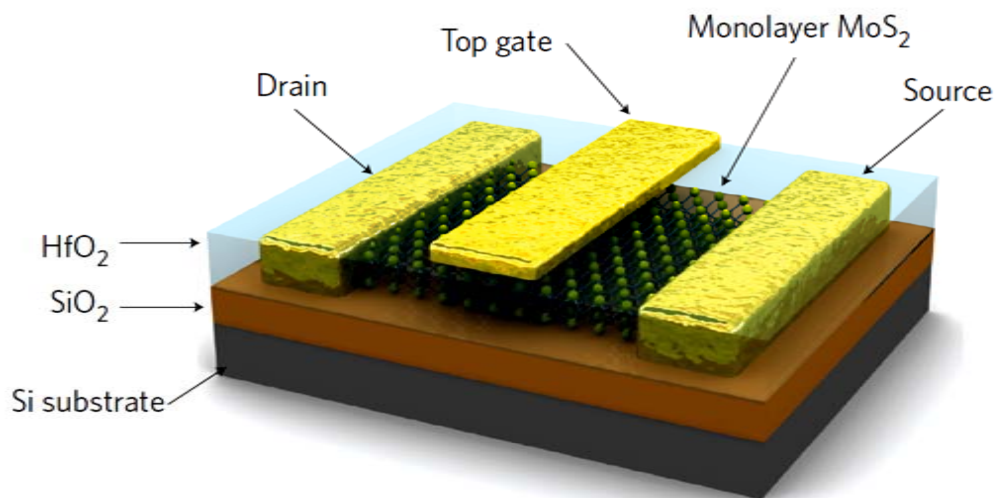
Application : Electronic Devices

- Suitable band gap
- 2D morphology associated electric integrity
- Low charge mobility

Fabricating conduction channel
Thickness ~ 6.5 °A
I_{on}/I_{off} ~ 10^8
Mobility ~200 cm^2/Vs



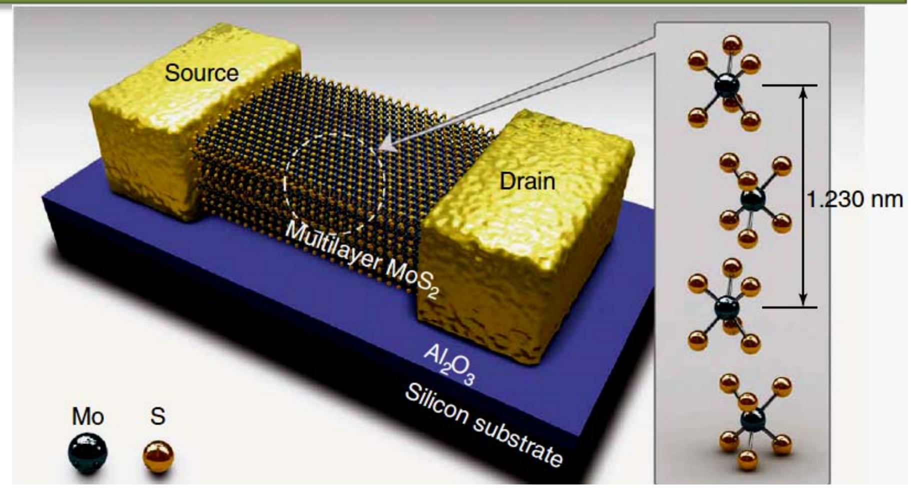




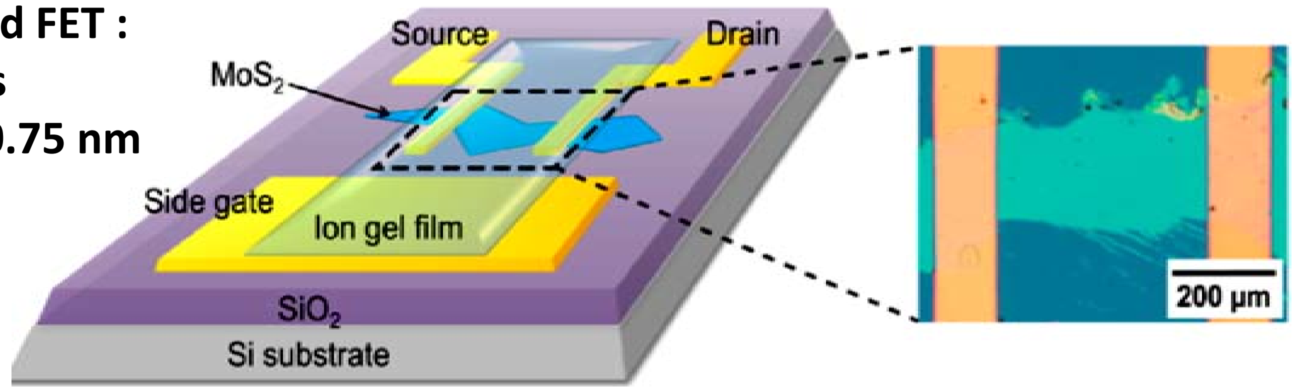
B. Radisavljevic, Nature Nanotech. 2011,

Application : Electronic Devices

ML MoS_2 based FET :
higher DOS, more derived current and multiple conducting channel



Electrical double layer based FET :
Flexible electronic devices
Minimum bending radius : 0.75 nm



Pu et al. NanaLetters. 2012, 12, 4013

Yoon et al. Nanoletters 2011,11,3768

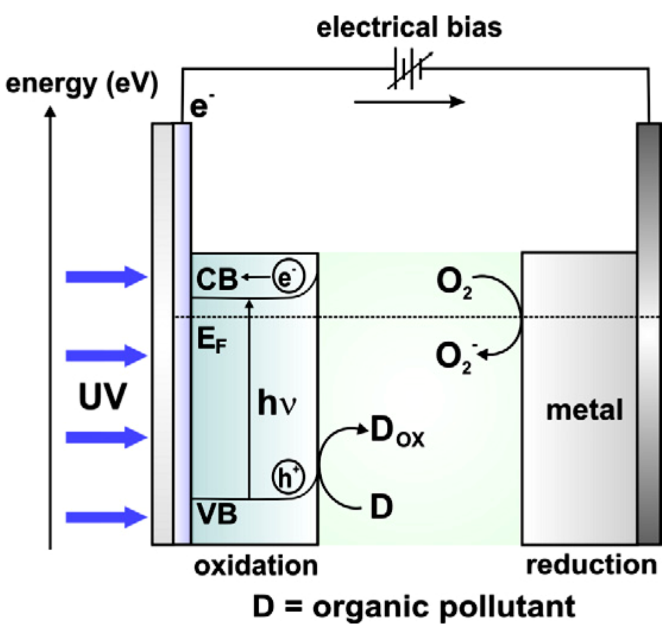
Kim et al. NatureComm. 2012, 3, 1011

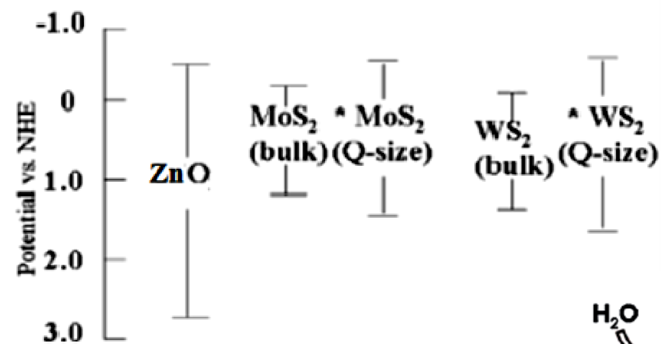
	L_{ch} (nm)	max I_{ON}/I_{OFF}
$In_{0.7}Ga_{0.3}As$ quantum-well FET (ref 22)	75	312
monolayer MoS_2 FET	75	1.4×10^7

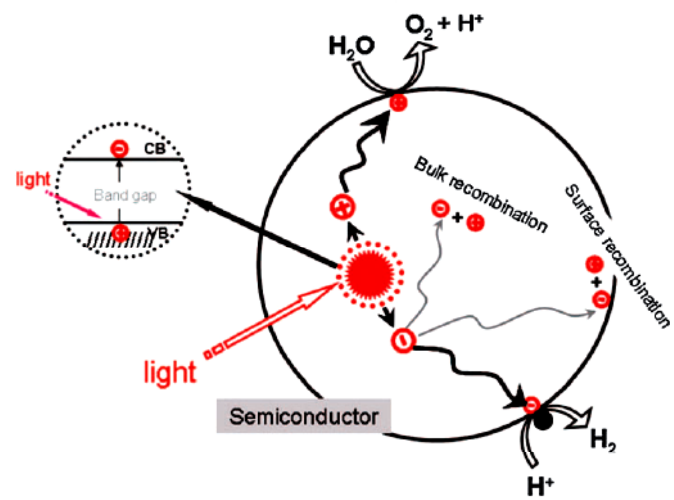
Application : OE and PEC Devices

Phototransistors (Single-1.82 eV, double-1.65eV, three-1.35eV layers)
As an electrode in OLEDs (As an anode in solution process able OLED)

Photoelectrode in Solar Energy Conversion Systems

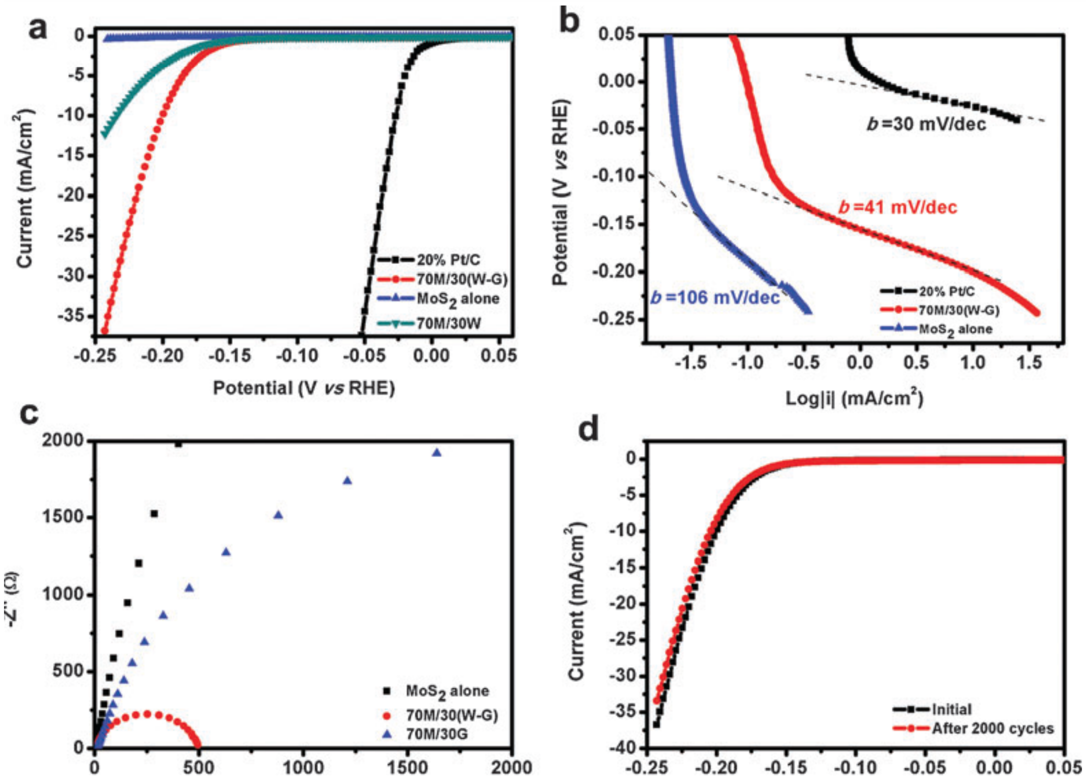


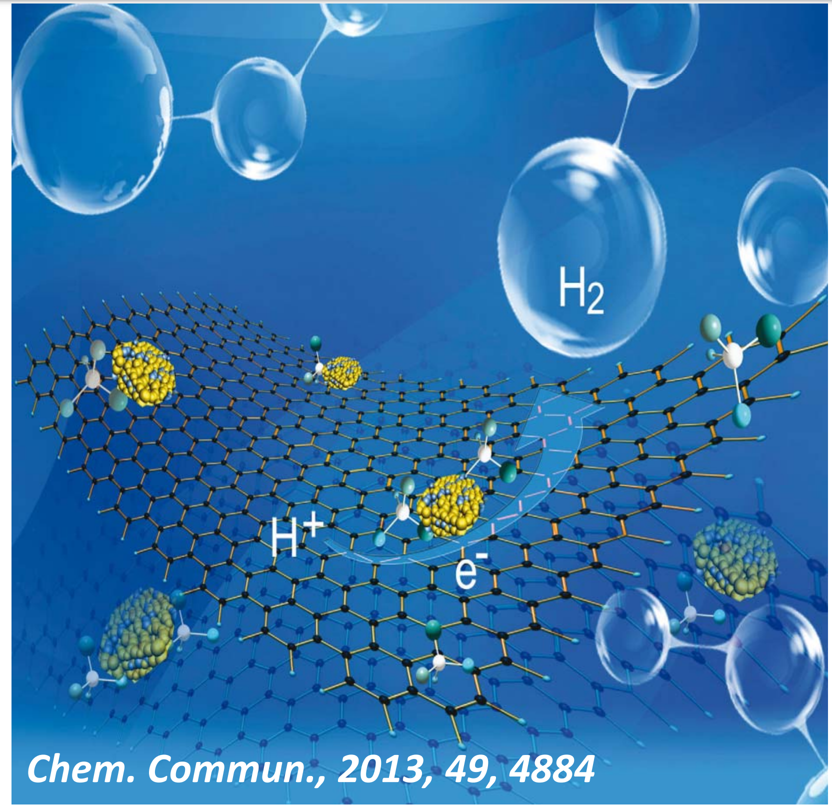




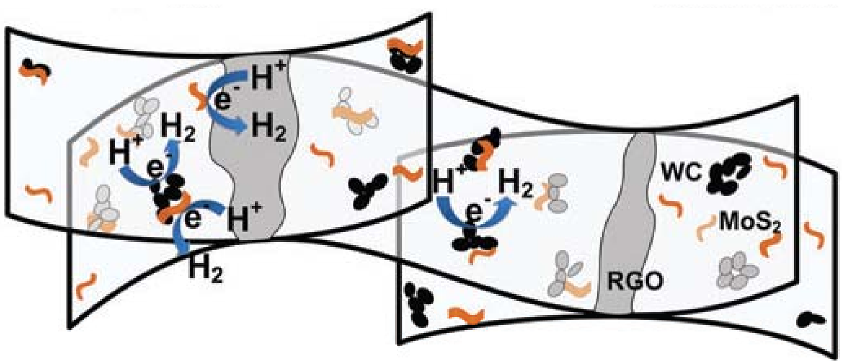
Nano Lett., 2012, 12, 3695.
J. Am. Chem. Soc., 2003, 125, 5998

Photoelectrochemical Performance

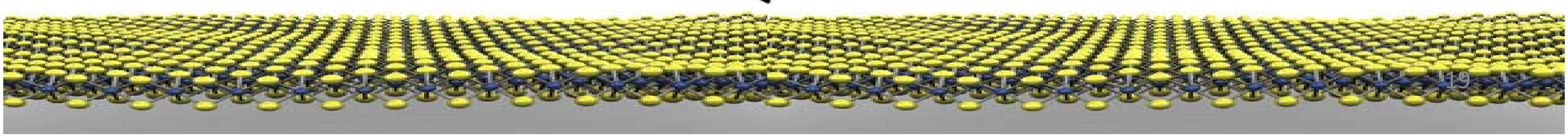




Chem. Commun., 2013, 49, 4884

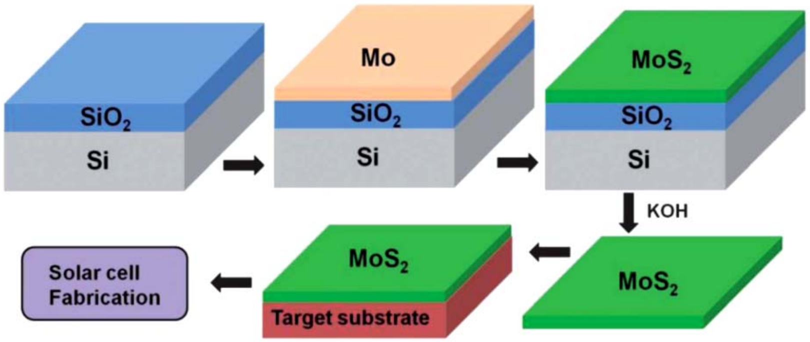


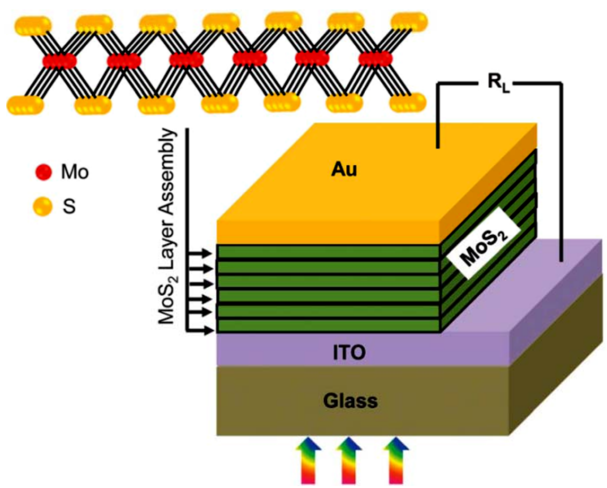
- WC can act as a good conductive dispersant
- Substitute noble-metals as catalysts for HER
- Highly active layered MoS_2 with increased edges

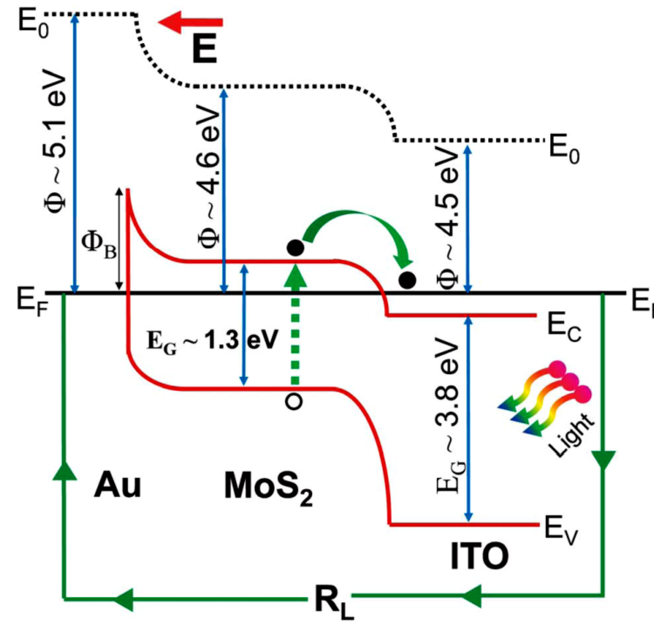


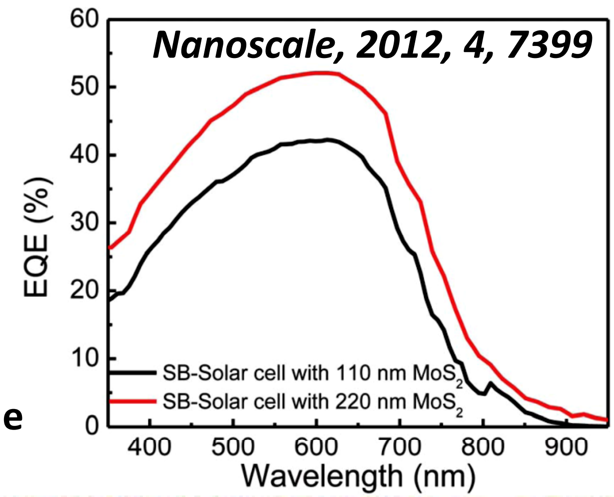
Photoelectrochemical Performance

MoS_2 based solar cell





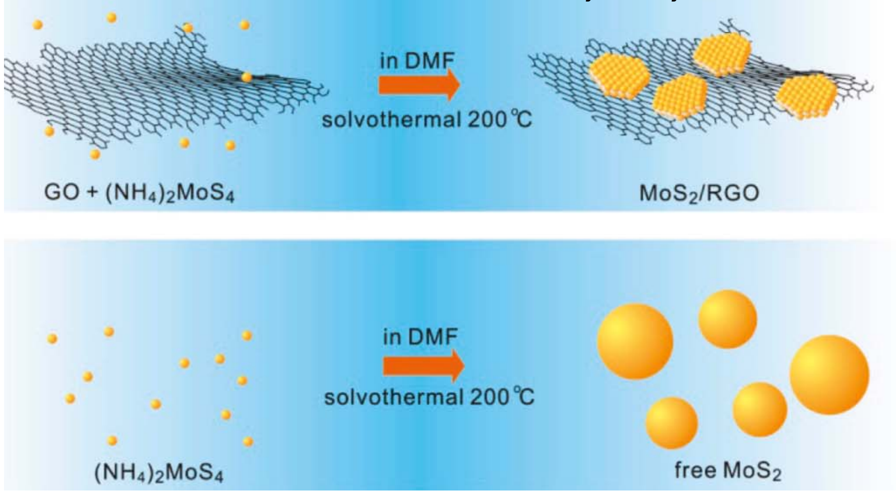


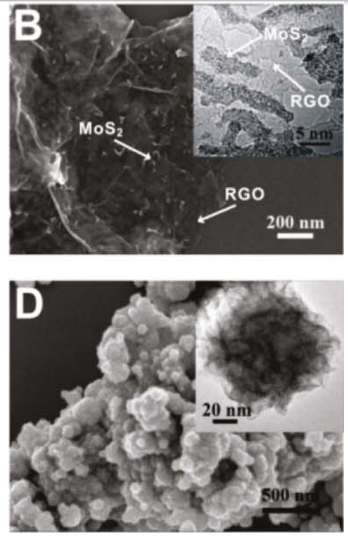


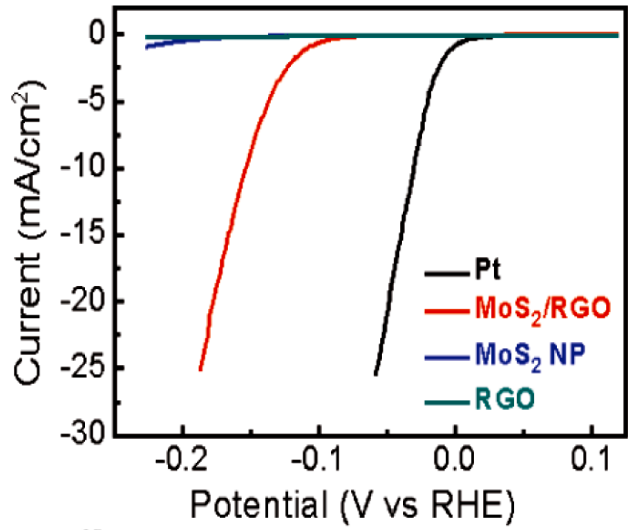
Improvement in solar cell performance is expected through optimizing the growth process, eliminating structural deformation (induced during fabrication), and minimizing the amount of surface defects and impurities

Counter Electrodes in PEC & Solar Cells

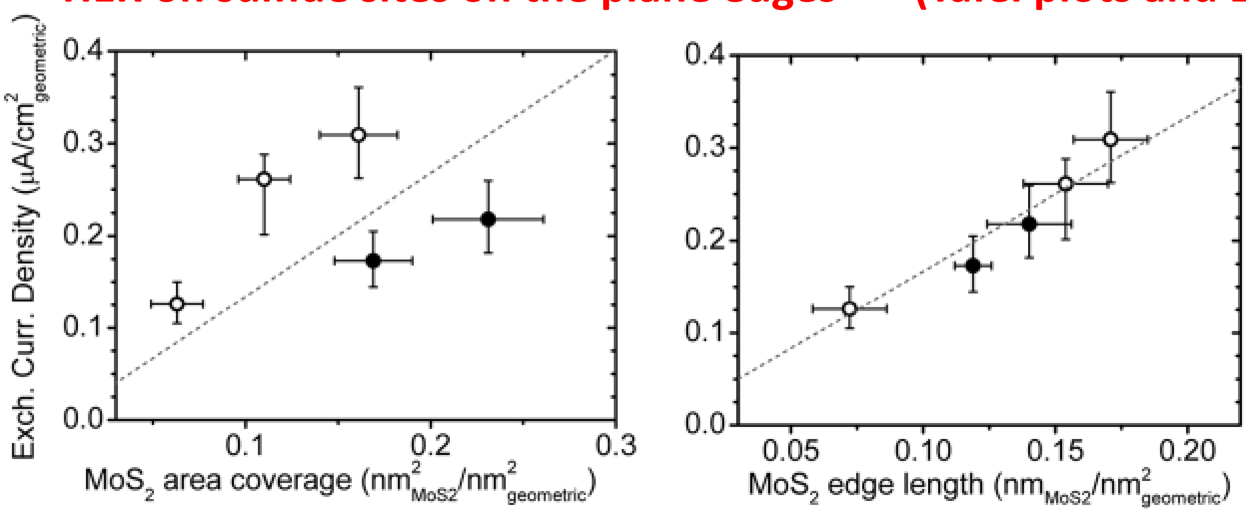
J. Am. Chem. Soc. 2011, 133, 7296

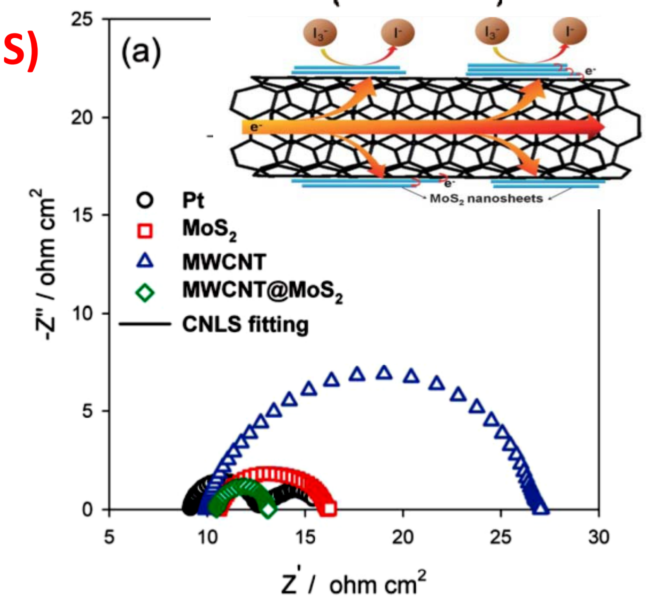






HER on sulfide sites on the plane edges **(Tafel plots and EIS)**





Science 317,2007,101

J. Mater. Chem., 2012, 22, 24753

Application : Sensing Platforms

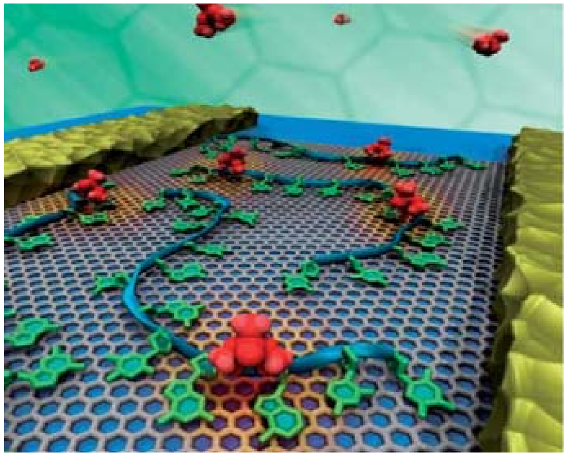
- Chemical, biological and gas sensing by MoS_2 based FET.

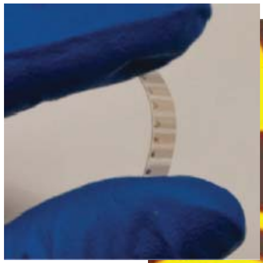
- Low cost high sensitive device
- Simple miniaturization process
- Real time detection

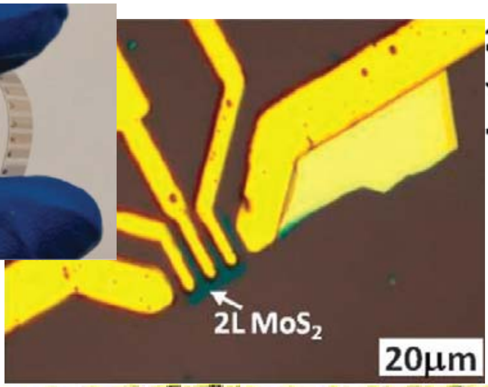
Bulk channels : Restricted interaction with analyte

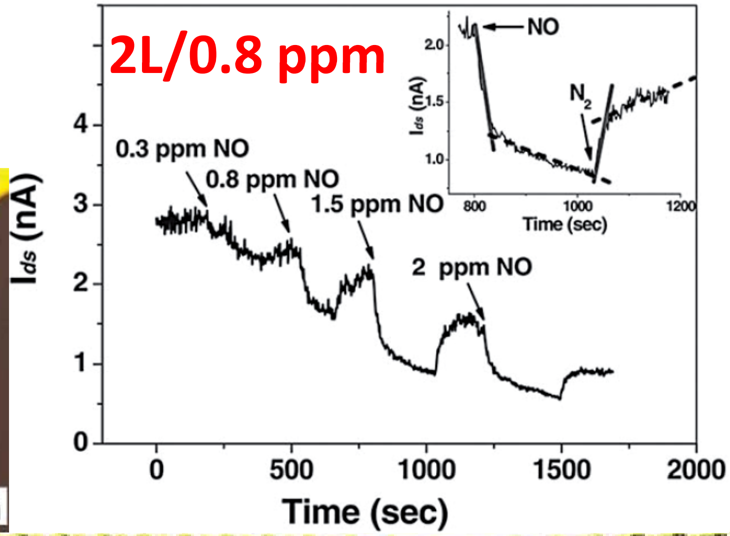
Si NWs, CNTs, Graphene, 2D TMDC

2-4 L MoS_2 : high and stable response
1L MoS_2: rapid but unstable response





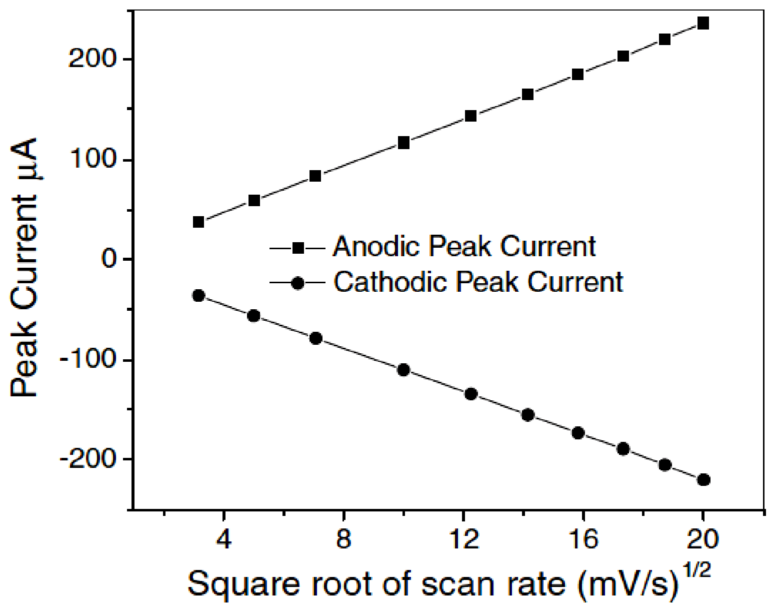


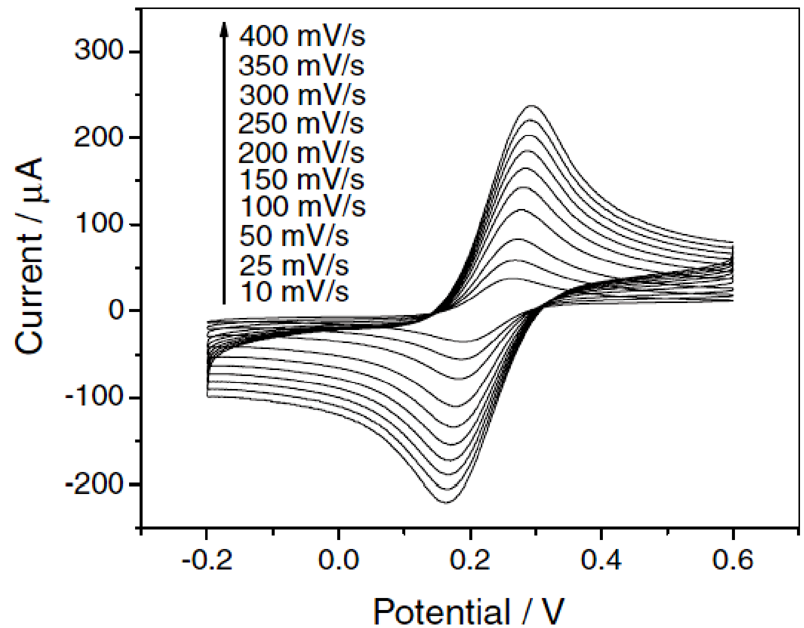


Q. He et al. small 2012, 8, 2994
H Li et al. small 2012, 8, 63

Application : Sensing Platforms

- **Electrochemical sensing: H_2O_2, DNA, glucose, antigen,….**





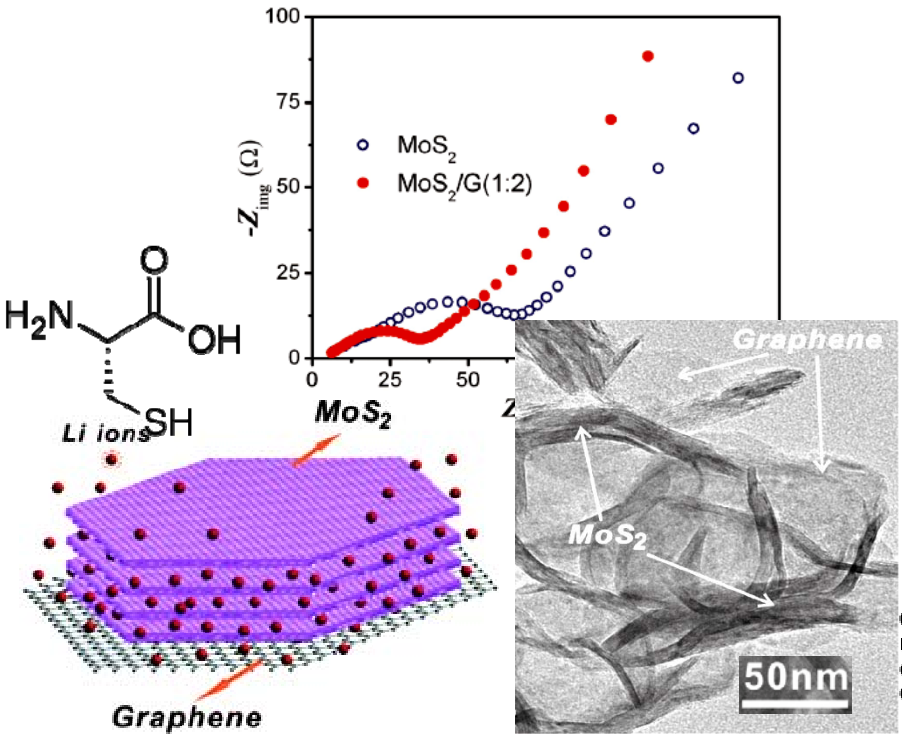
Noble metal nanoparticles for enhancing catalytic behavior of SL MoS_2

Wu et al. small 2012, 8, 2264.

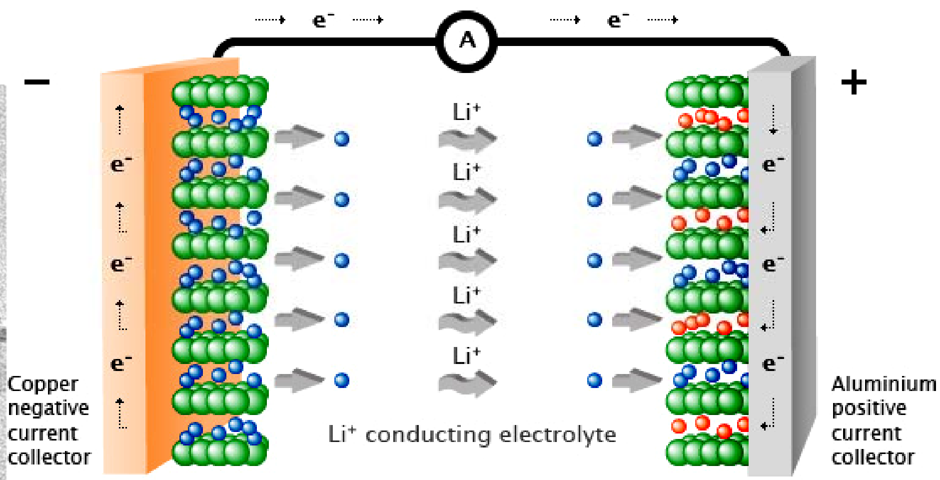
Application : Energy Storage systems

Lithium Ion Batteries

- Restacked MoS_2 has stable high capacity over 50 cycles due to enlarging sheet spacing and improving ionic conductivity.
- Using a polymer (PEO) helps Li^+ accommodation and stabilizes structure.



L-Cystein assisted MoS_2/rGO anode increased charge capacity from 750 to 1100 mAh/gr over 100 cycles.

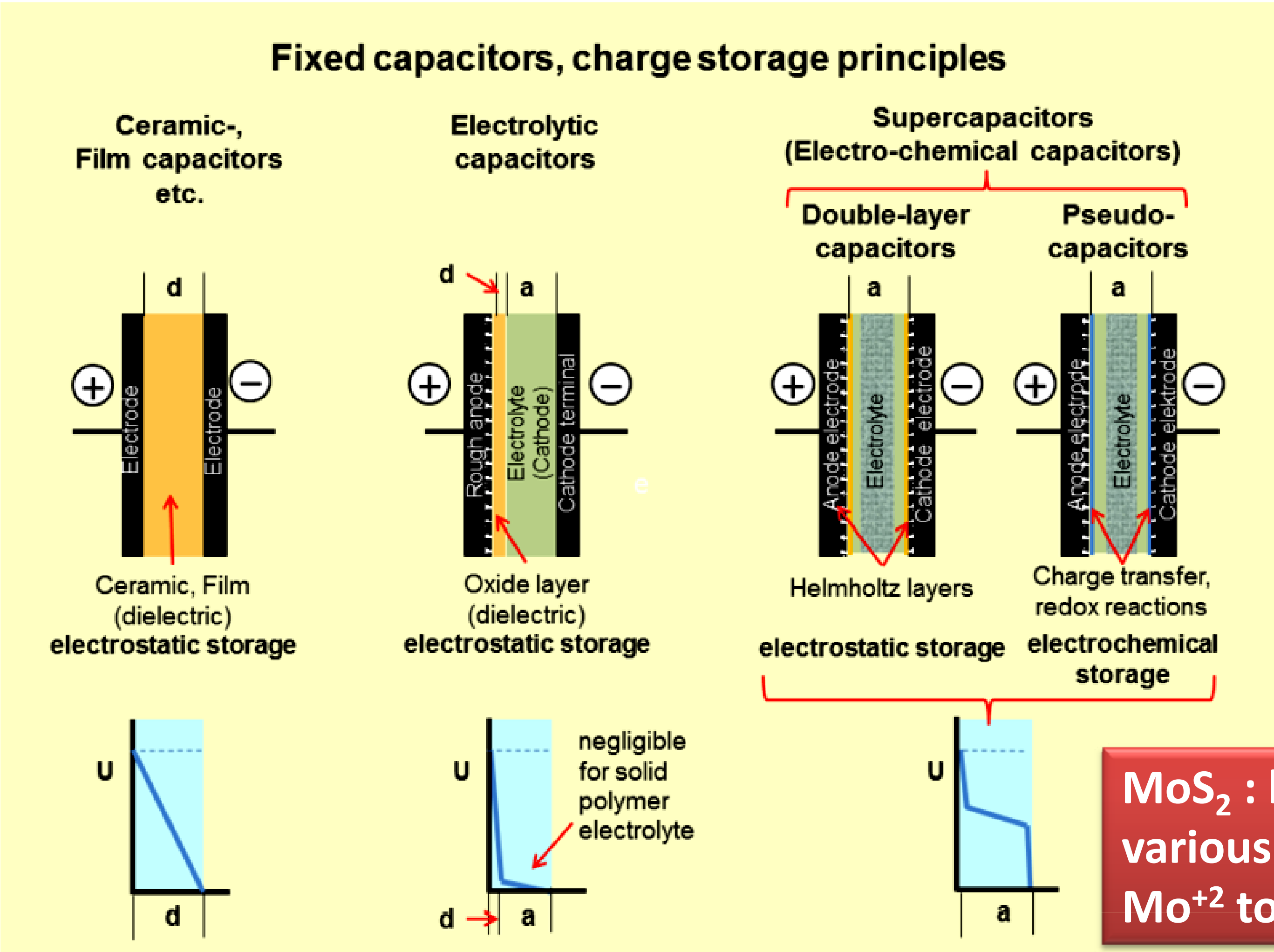


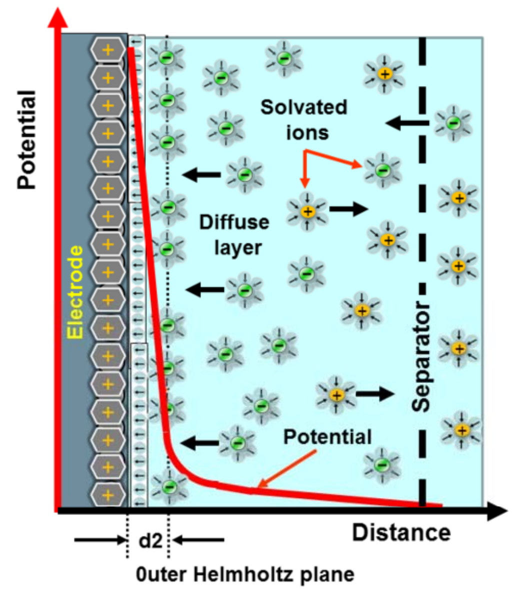
Du et al. Chem. Comm,2010,46, 1106.
Chang et al. ACSNano, 2011,5,4720

$$nLi^+ + ne^- + C \leftrightharpoons Li_nC$$
$$LiCoO_2 \leftrightharpoons Li_{1-n}CoO_2 + nLi^+ + ne^-$$

Application : Energy Storage systems

Supercapacitors



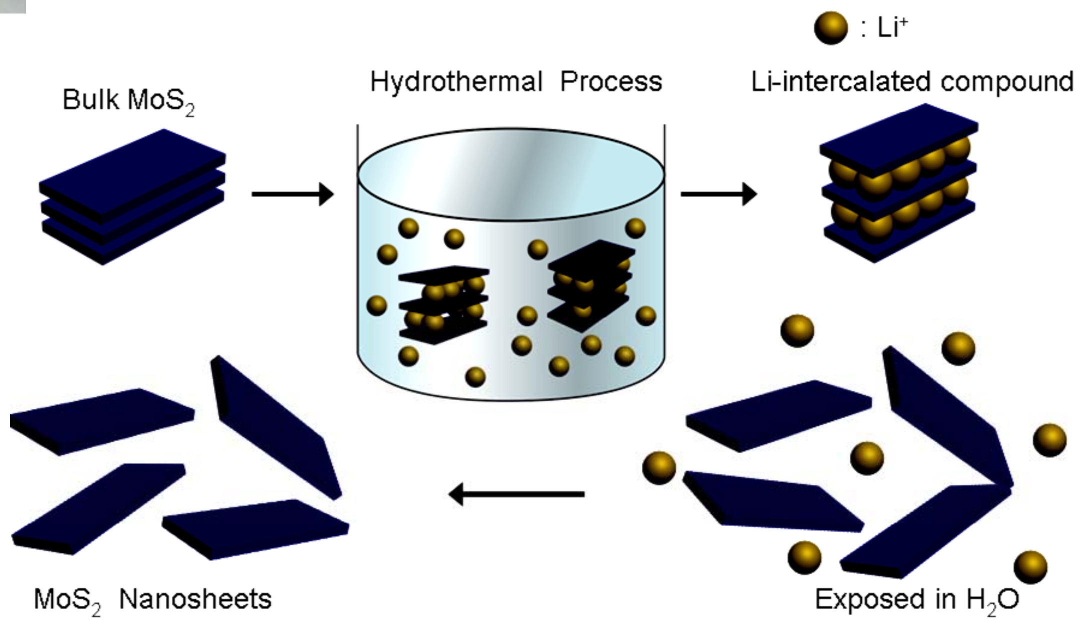


MoS_2 : high surface area and various oxidation states from Mo^{+2} to Mo^{+6}.

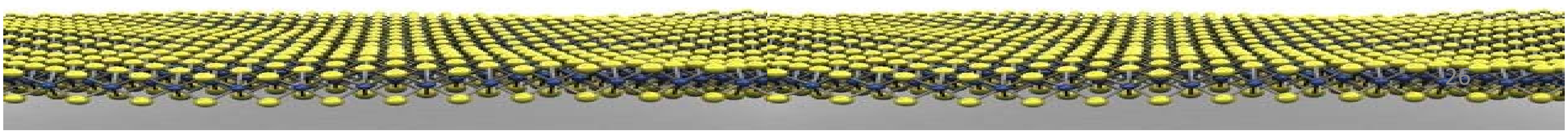
On the synthesis way…

Mohammad Zirak

Prof Alireza Moshfegh

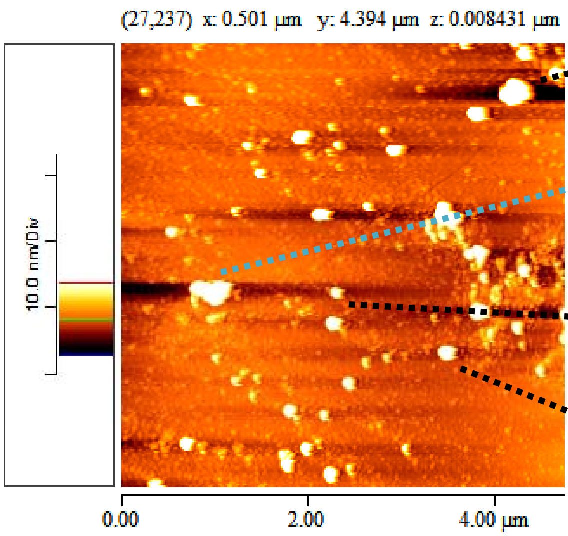


$LiClO_4$ + MoS_2+ EG → **Hydrothermal method at 215 °C for 24 h** → **Sonication & Centrifugation**



On the synthesis way…

2500 rpm



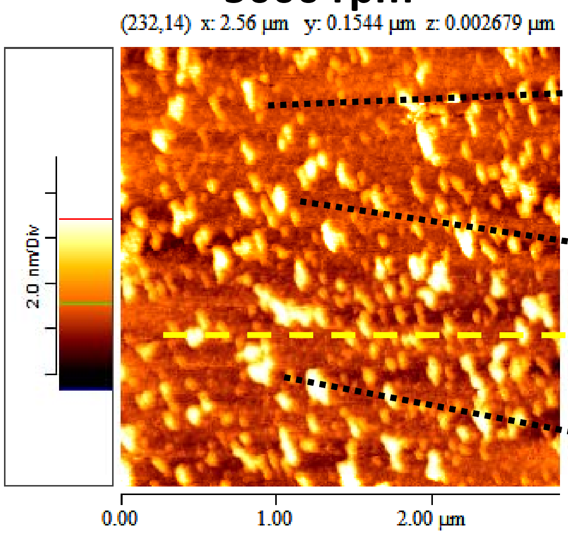
400×20 nm

540×18 nm

170×4 nm

200×9 nm

5000 rpm

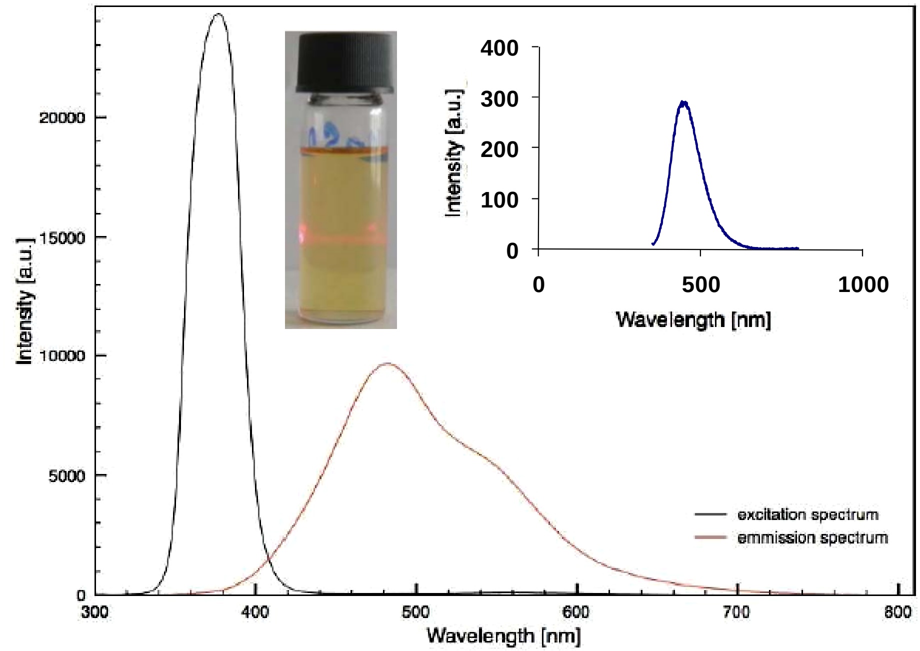


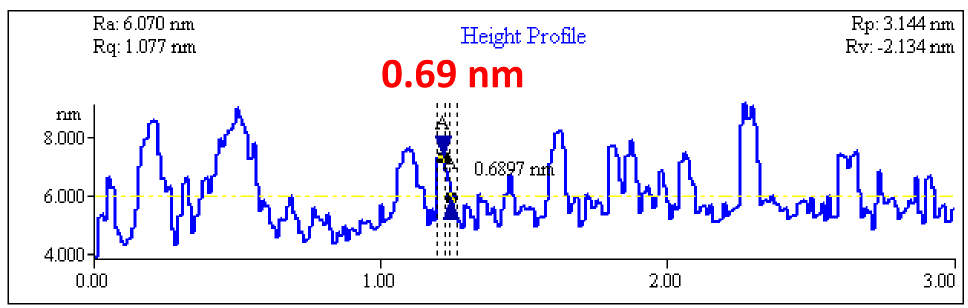
150×2 nm

140×3 nm

210×3 nm

Stengl et al. Nanoscale,2013, accepted.





Outlook

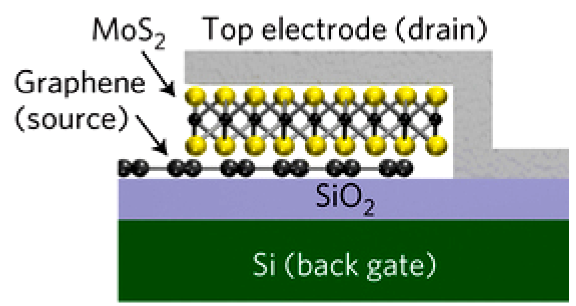
- Scalable production of MoS_2 nanosheets with solution processability is attractive for thin film applications (electronics, sensing and solar energy harvesting) :
  - ***Large size single layers** in a low cost simple way.*
  - ***Soft method** avoiding crystalline deficiencies.*
  - ***Stabilizing** layers on the proper substrate.*

- Mechanical cleavage and CVD methods can generate high-quality MoS_2 films, which are suitable for electronic and optoelectronic devices.

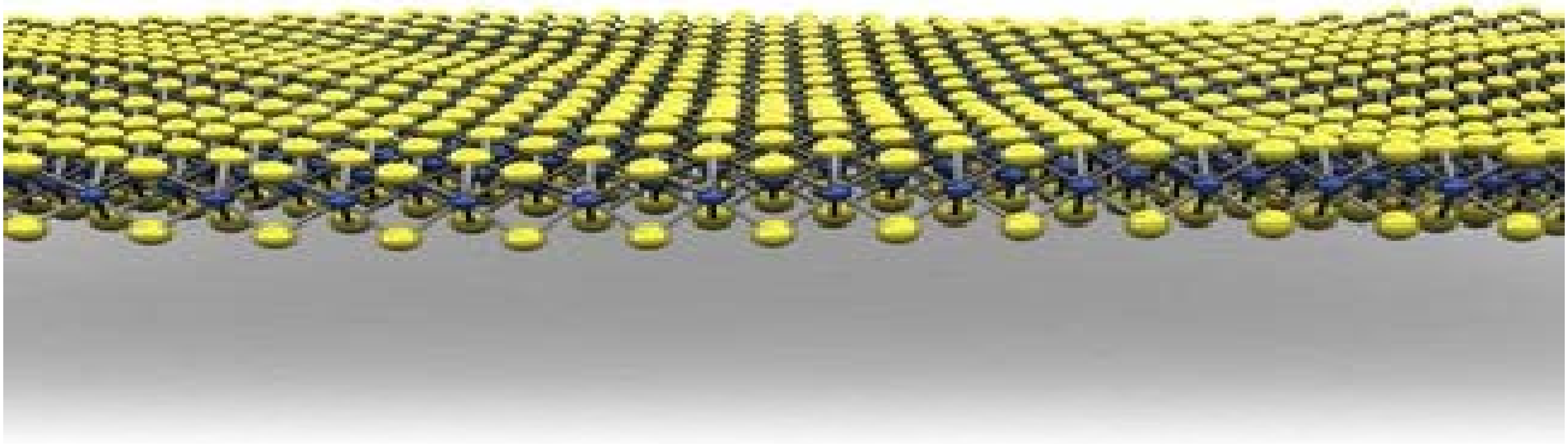
- Through the proper substrate engineering and choice of dielectric environment, further improvement on the FET performance is expected in the near future.

- Stacking of different types of 2D nanomaterials for electronic devices has recently aroused particular interest

- High edge/basal ratio for PC/PEC systems.
  How can applied strain facilitate H^2 evolution?



Duan et al. Nature Mater 2013,12,246.



Thank you!