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Graphene Oxide (GO) and Transition Metal Dichalcogenides (TMDs) for gas sensing applications

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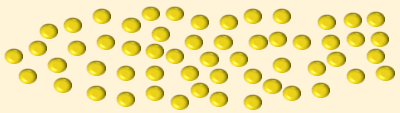
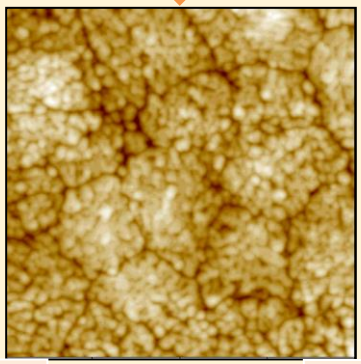
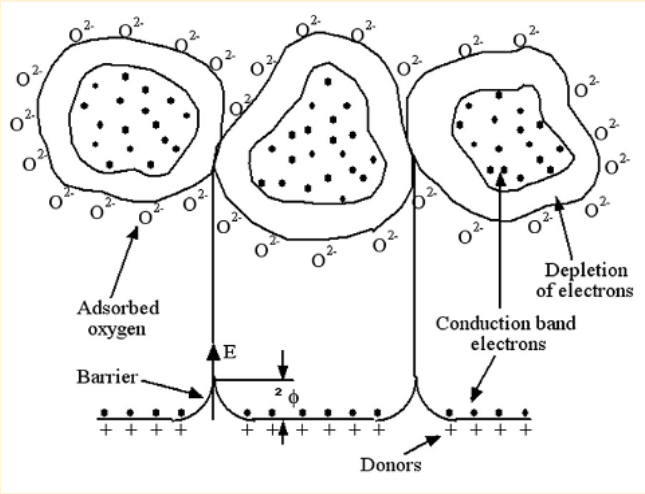
Why 2D-Materials for gas sensing applications?

Metal Oxide Porous sensors



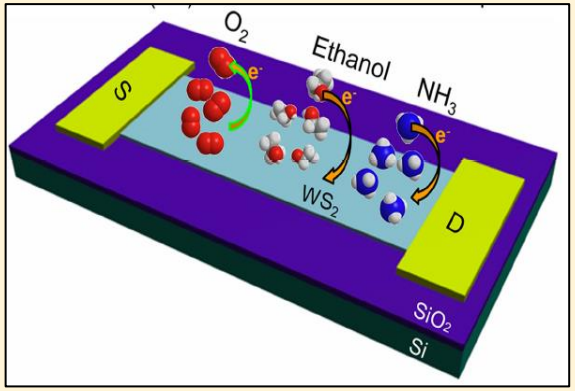


0 500 nm

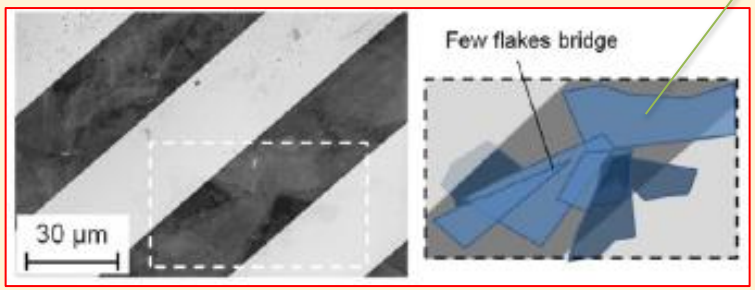


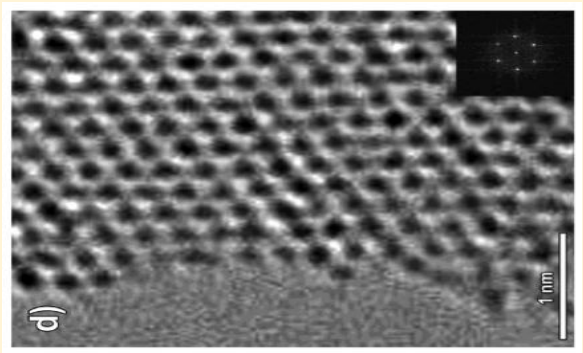
C. Cantalini et al. Sens. Act. B 179 (2013) 107-113

Few layers 2D-Material



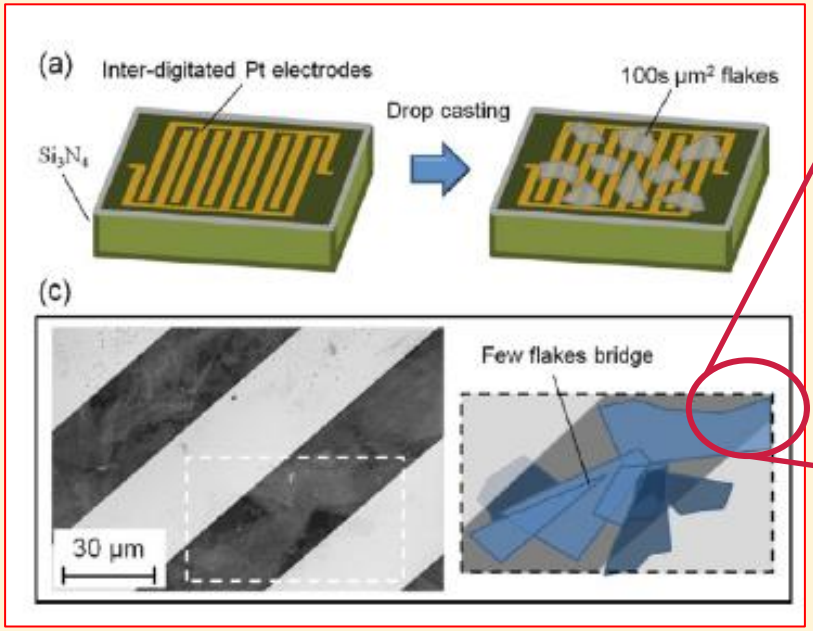
Single Layer

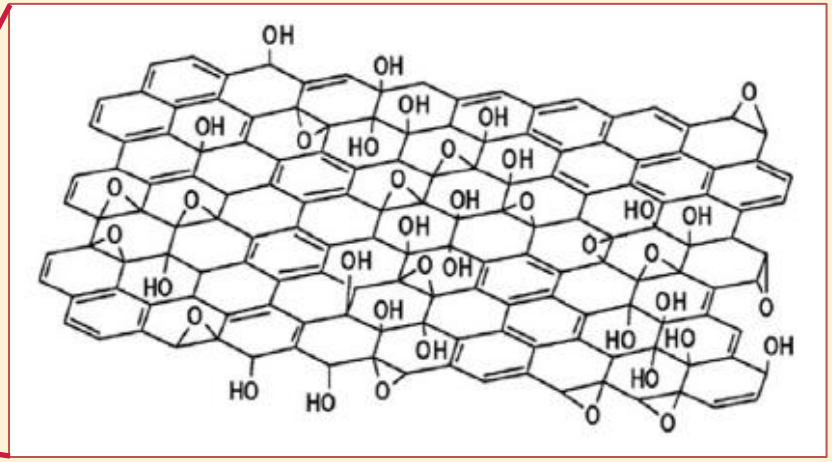




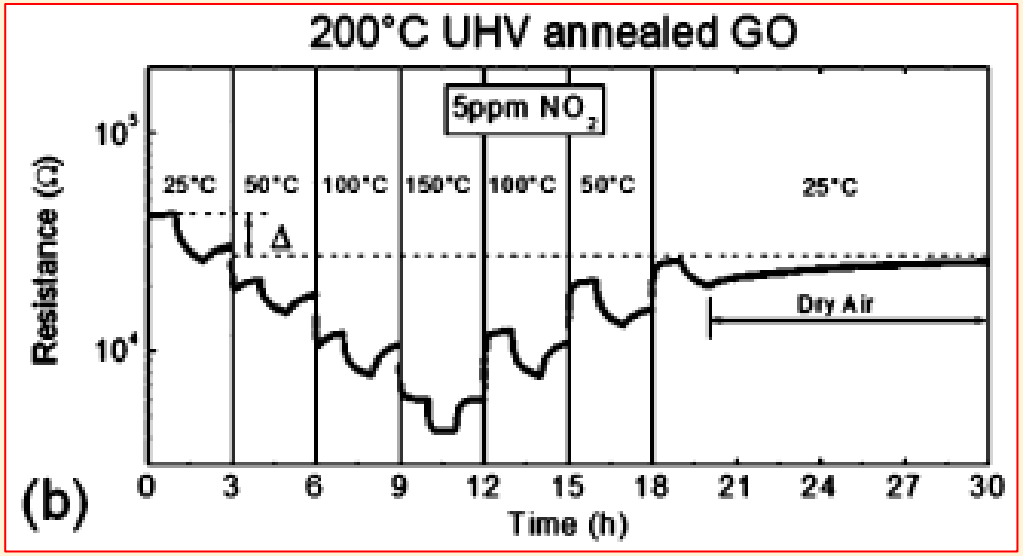
S. Prezioso et l., J. Phys. Chem. C , 2013, 117, 10683

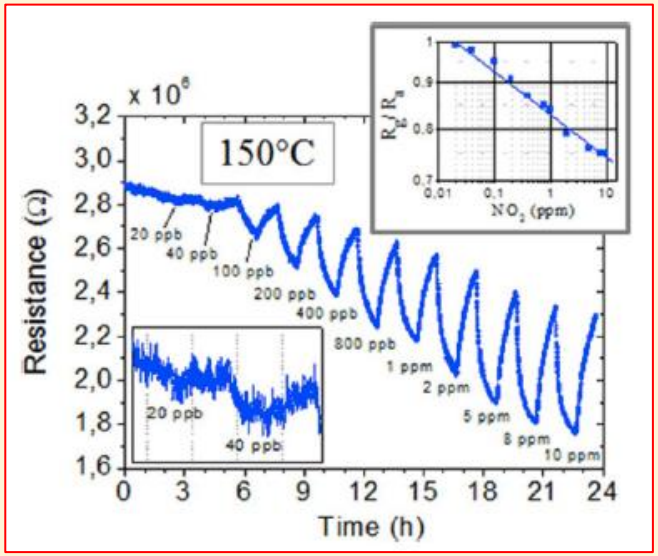
GO- Graphene oxide





H. He, . S. Klinowski et al. Chem. Phys.Lett (1998), 287, 53





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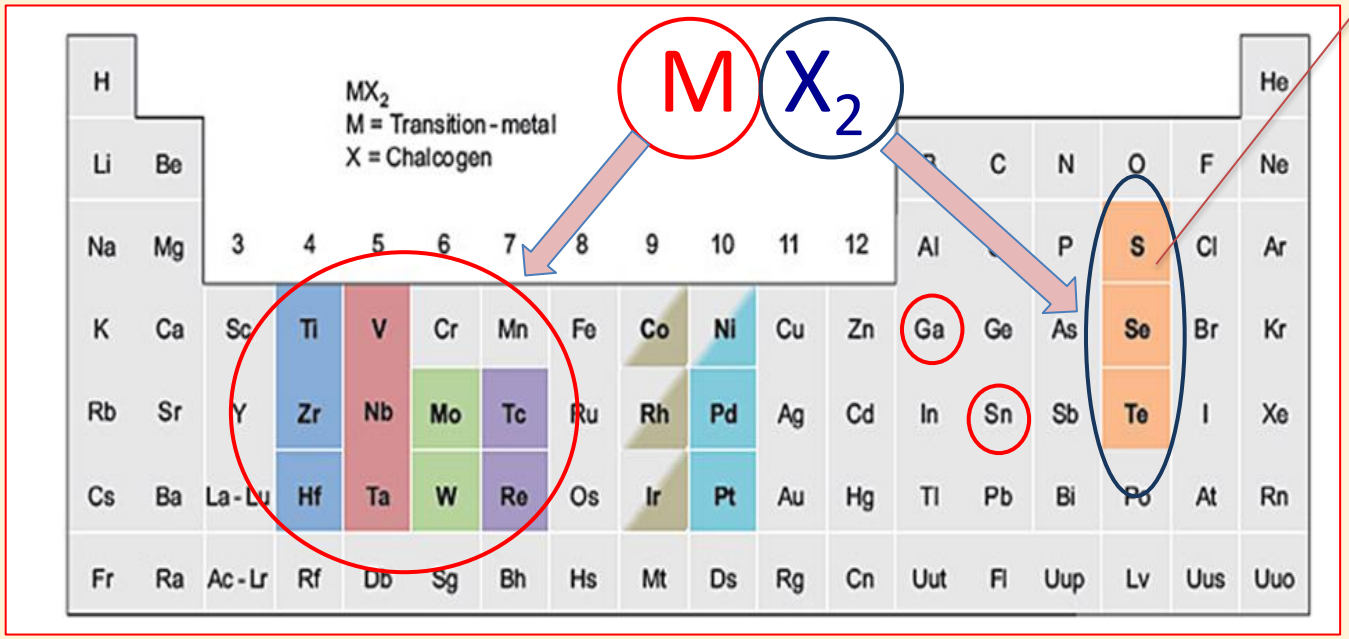
2D Transition Metal Dichalcogenides (TMDs)



Character

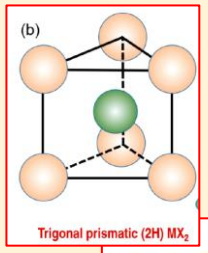
- semiconductors (MoS_2, $MoSe_2$, WS_2, WSe_2)
- semimetals (e.g., WTe_2, $TiSe_2$),
- true metals (e.g., NbS_2, VSe_2)
- superconductors (e.g., $NbSe_2$, TaS_2)

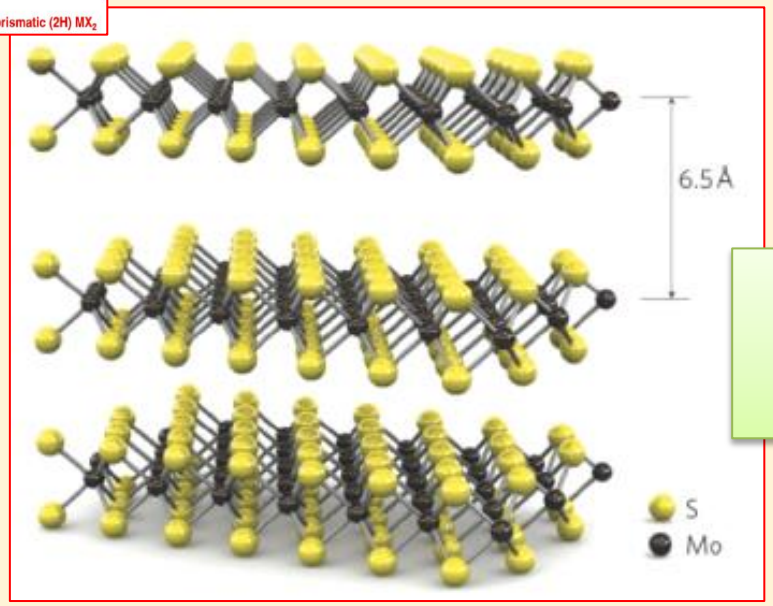
Properties

- PL Photoluminescence
- Photocatalytic H_2 generation
- Photovoltaic response
- Gas sensing applications

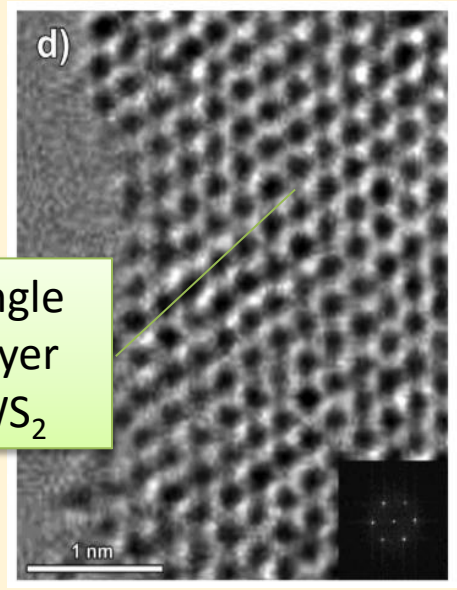
2D - TMD Transition Metal Dichalcogenides

Uncharged - Layered vdW solids

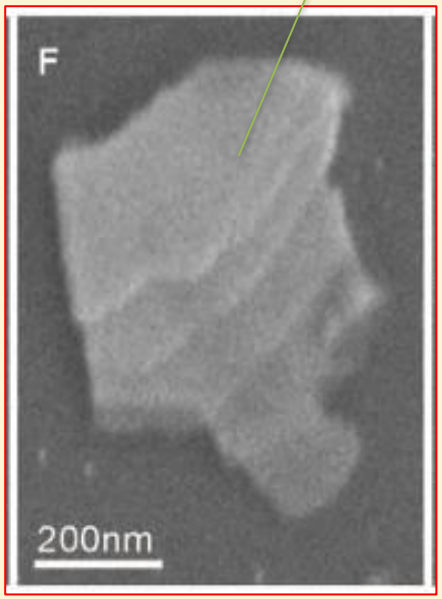




Single Layer WS_2



Few Layers MoS_2



Structure

Each single plane of MoS2 comprises a trilayer composed of a Mo layer sandwiched between two sulphur layers in a trigonal prismatic coordination

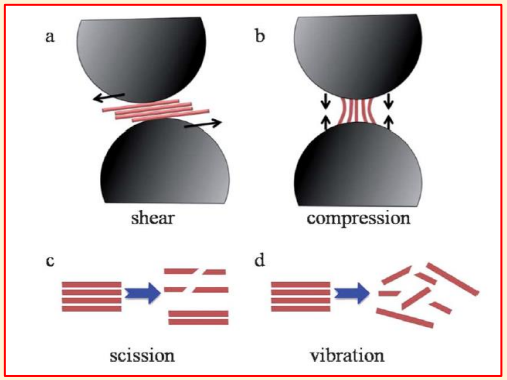
Properties are thickness/size dependant

- MoS_2/WS_2 bulk show indirect bandgap (1.2-1.3 eV).
- 1L-MoS_2/WS_2 shows a direct bandgap (1.8-2.1 eV)
- Reducing number of layers to single layer causes in direct band gap, lower band gap energy and faster gas response and strong photoluminescence

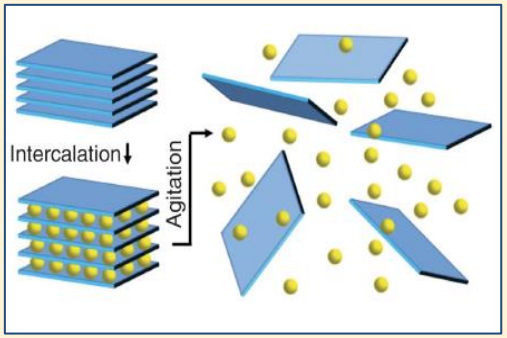
2D - TMD Preparation techniques

Top-Down Route

Mechanical Exfoliation
- Adehesive tape exfoliation
- Grinding and Sonication



Chemical Exfoliation
- Chemical Exfoliation via Lithium/Hydrogen intercalation



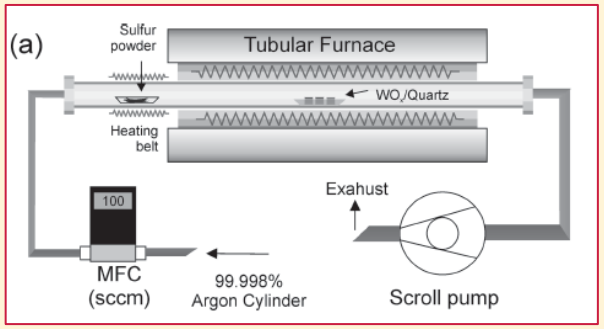
$LiBH_4 + WS_2 = LiWS_2 + ½\ B_2H_6 + ½\ H_2$

$LiWS_2 + H_2O = WS_2 + LiOH + ½\ H_2$

Bottom-up Route

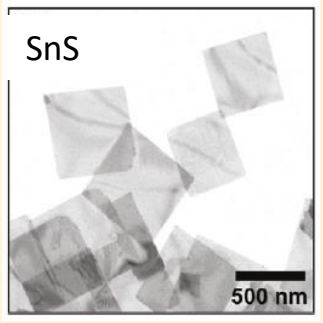
- Chemical Vapor Deposition (CVD)
- Direct Wet Chemical Synthesis (DWCS)

CVD – Chalcogenisation (S)



DWCS

$SnCl_2$ + TOP-Se @ 240 °C



Exfoliation Procedure by Grinding and Sonication

Mixing

Commercial MoS_2/WS_2

ACN- Aceto nitrile

5g MoS2/WS2
12 mL ACN

Grinding

@400 rpm 2h
Drying 30 °C 2h

Mixing

MoS_2/WS_2 GRINDED

Ethanol

Distilled Water

Ethanol + Dist. H_2O 1:1 -150 mL

Sonication

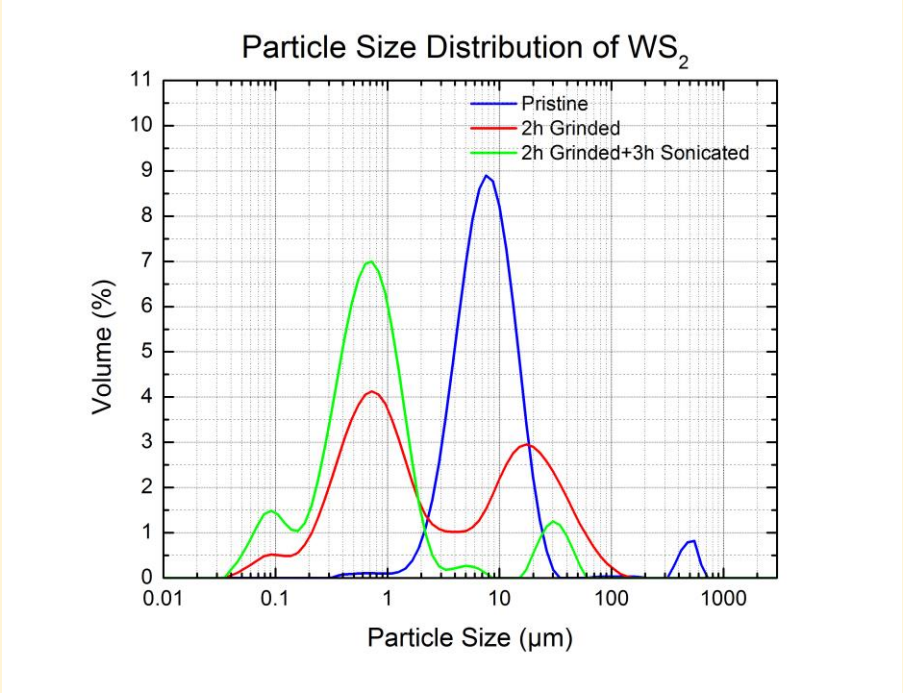
Power 100W – 3h - T = 15 °C

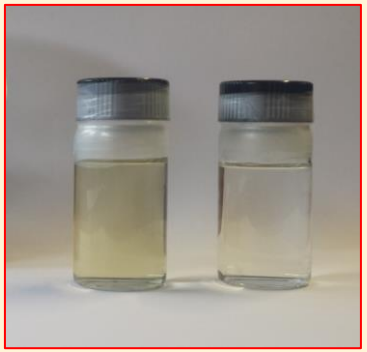
Centrifugation

At 2500-rpm - 1h

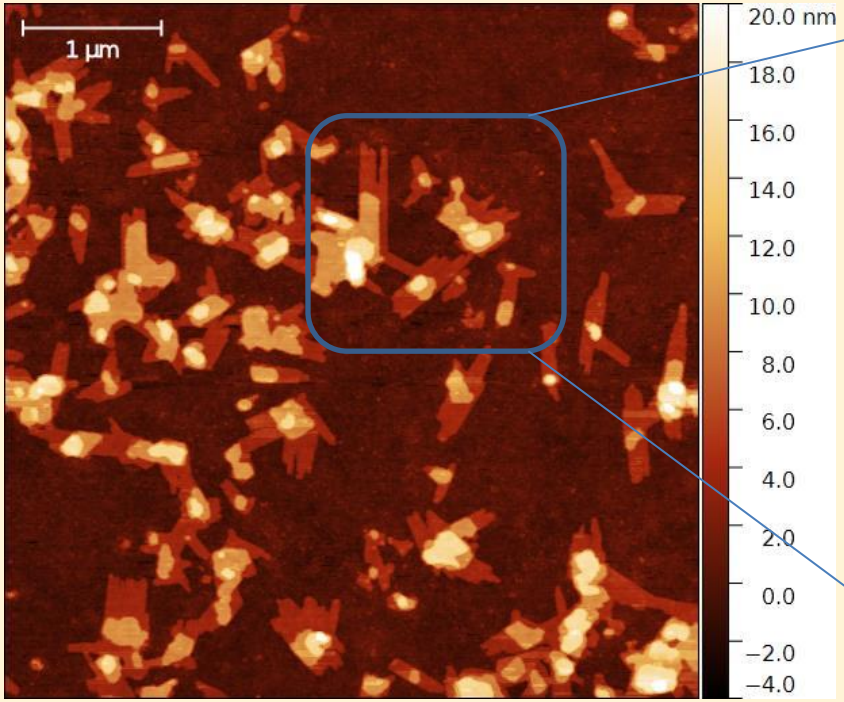
Spin Coating

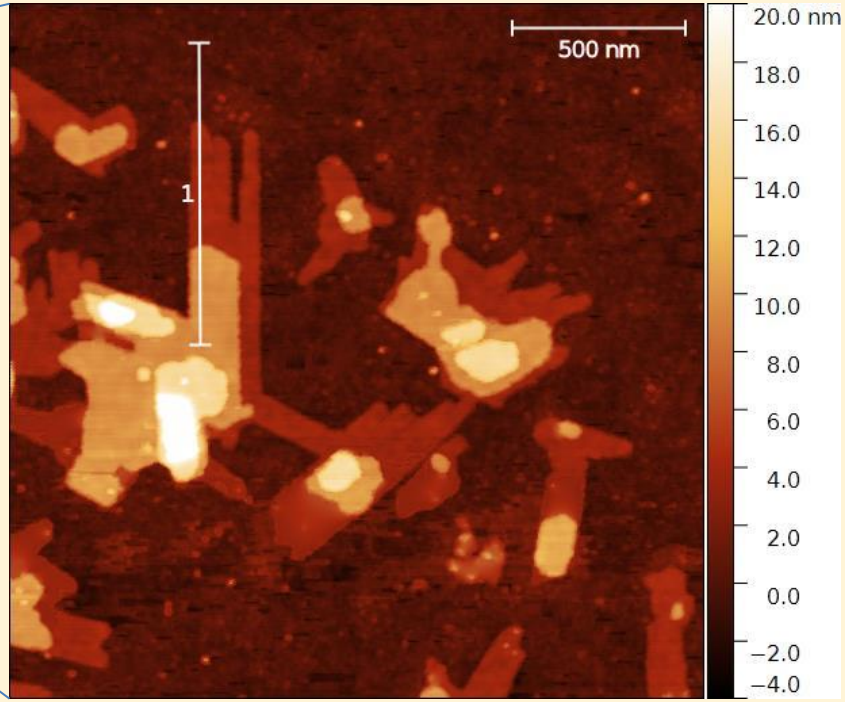
1 drop at 2000 rpm for 30 s

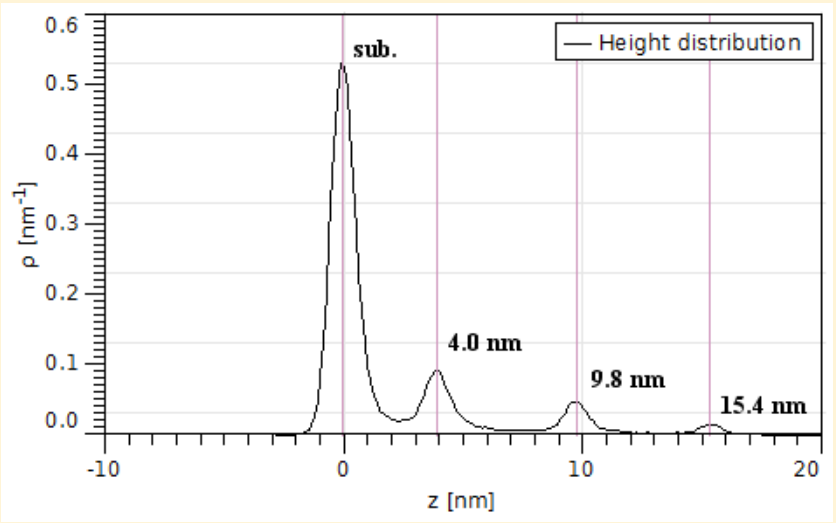


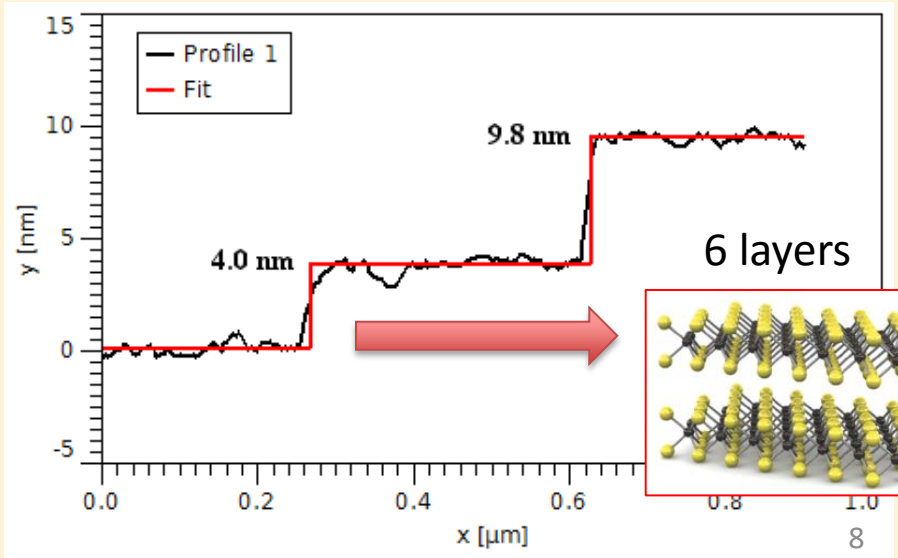


AFM As Deposited WS2

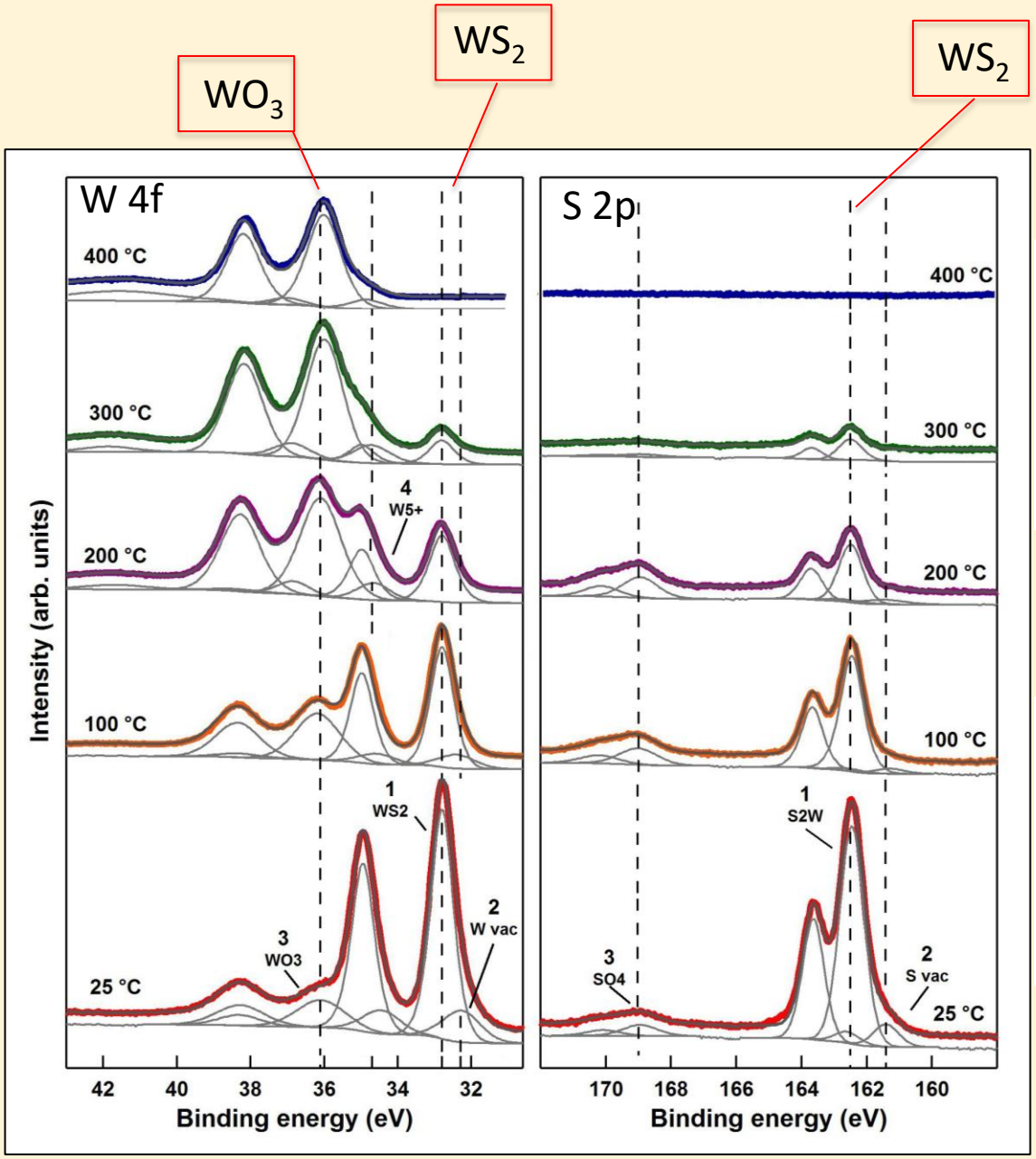








Thermal Stability- XPS as deposited WS_2



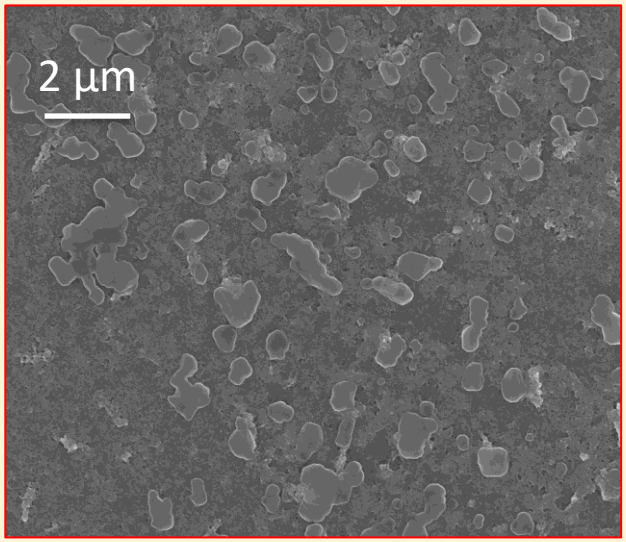
WS_2 -XPS

T (°C)	W-S_2 (%)	W-S_2 def (%)	W-O_3 (%)	W-5+ (%)
25	68	15	17	0
150	53	9	38	0
250	28	0	63	9
350	11	0	77	12
450	**0**	0	**91**	9

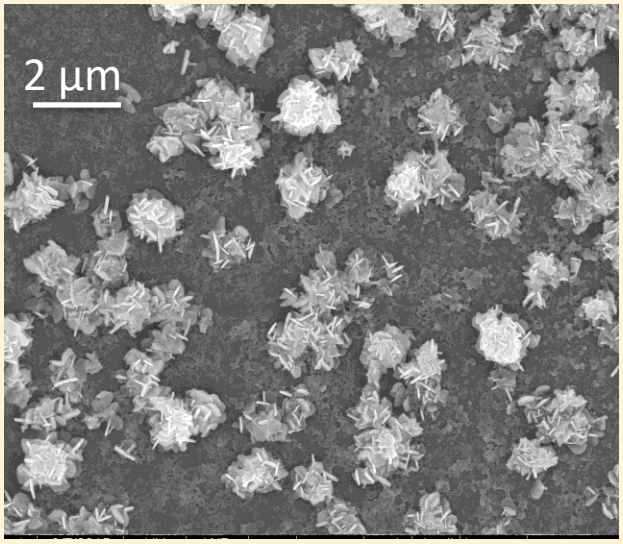
T (°C)	S_2(%) -W	S-O_4 (%)	S_2-W def (%)	S_2-W / W-S_2
25	84	7	9	2.0
150	78	18	4	2.0
250	60	32	8	2.0
350	81	19	0	1.8
450	0	0	0	-

WS2/WO3 mixed structure after annealing

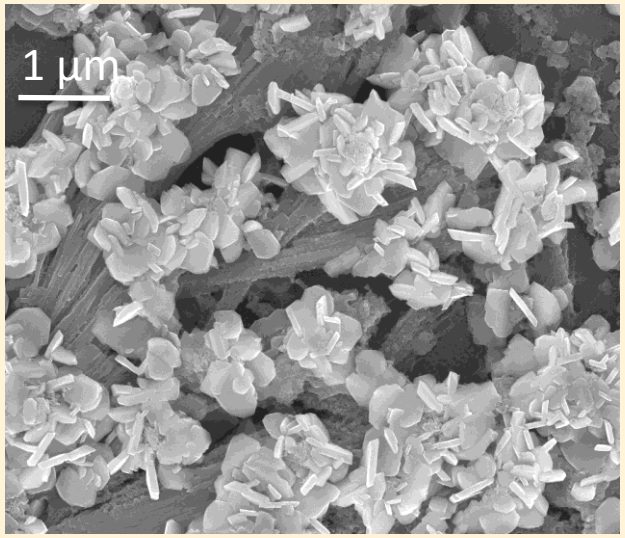
Annealed at 150°C



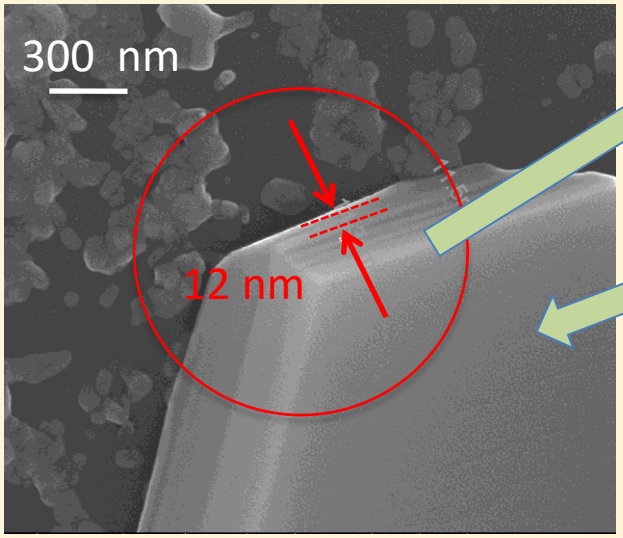
Annealed at 250°C

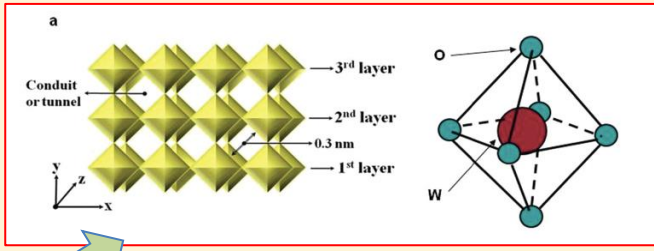


Annealed at 300°C



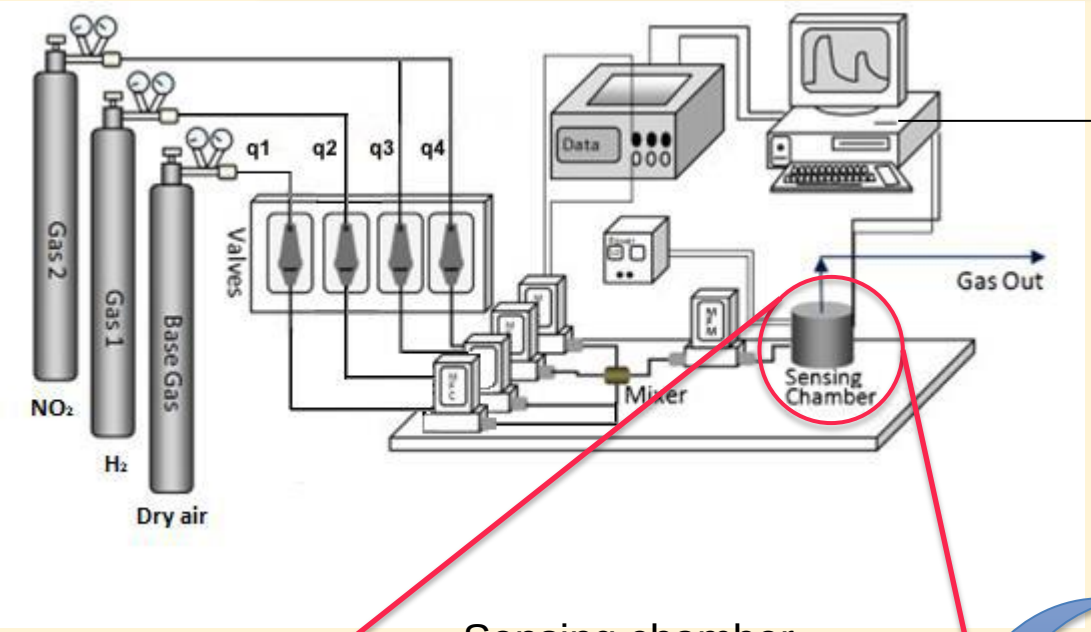
Annealed at 350°C

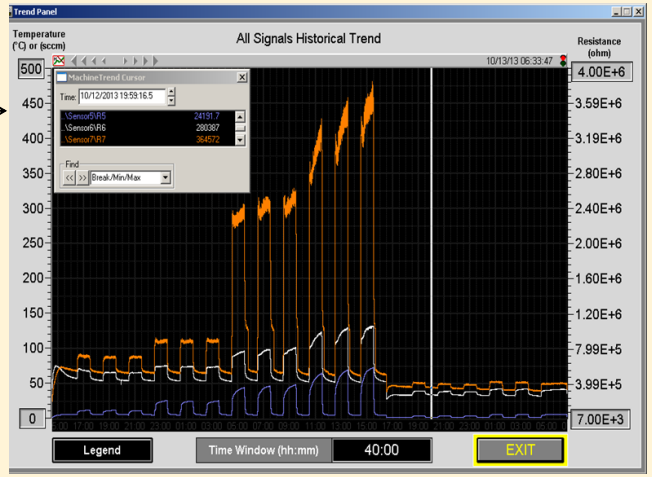




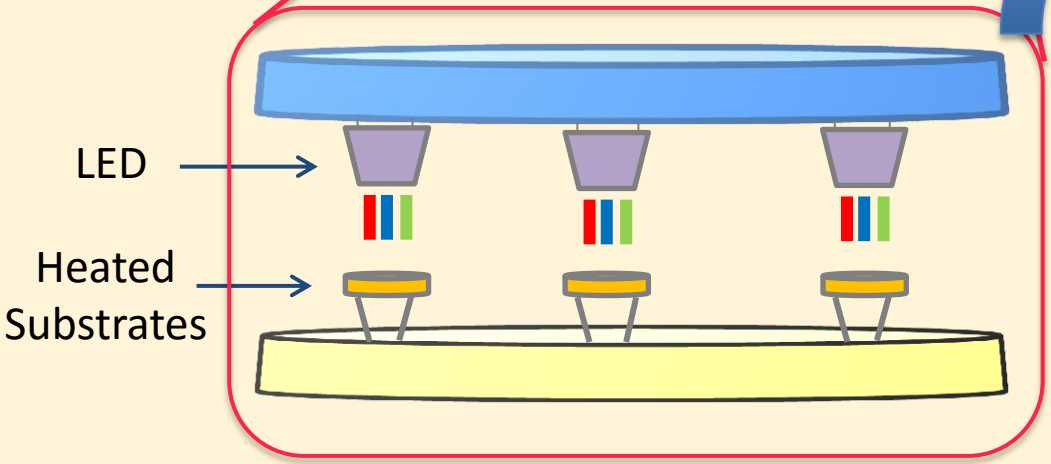
Layered WO_3 sheets ?

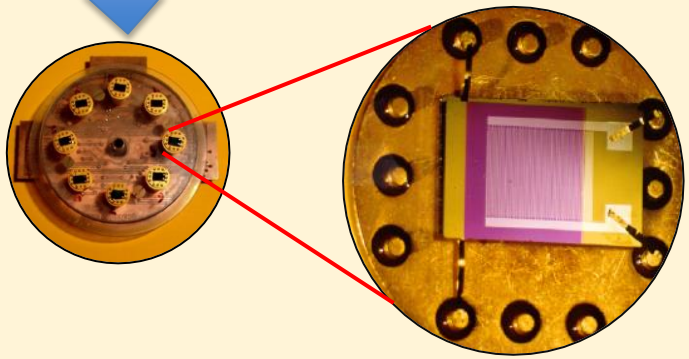
Gas sensing system



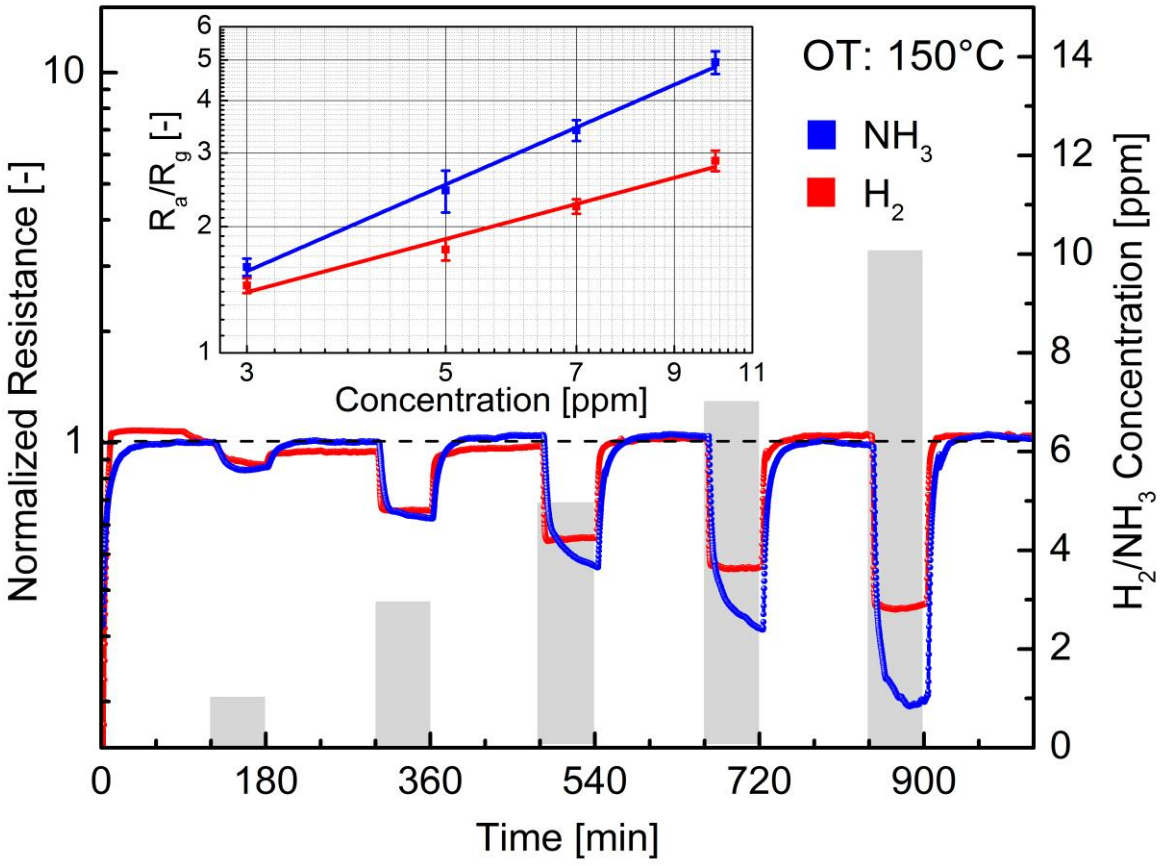


Sensing chamber
Thermal and light activation modes

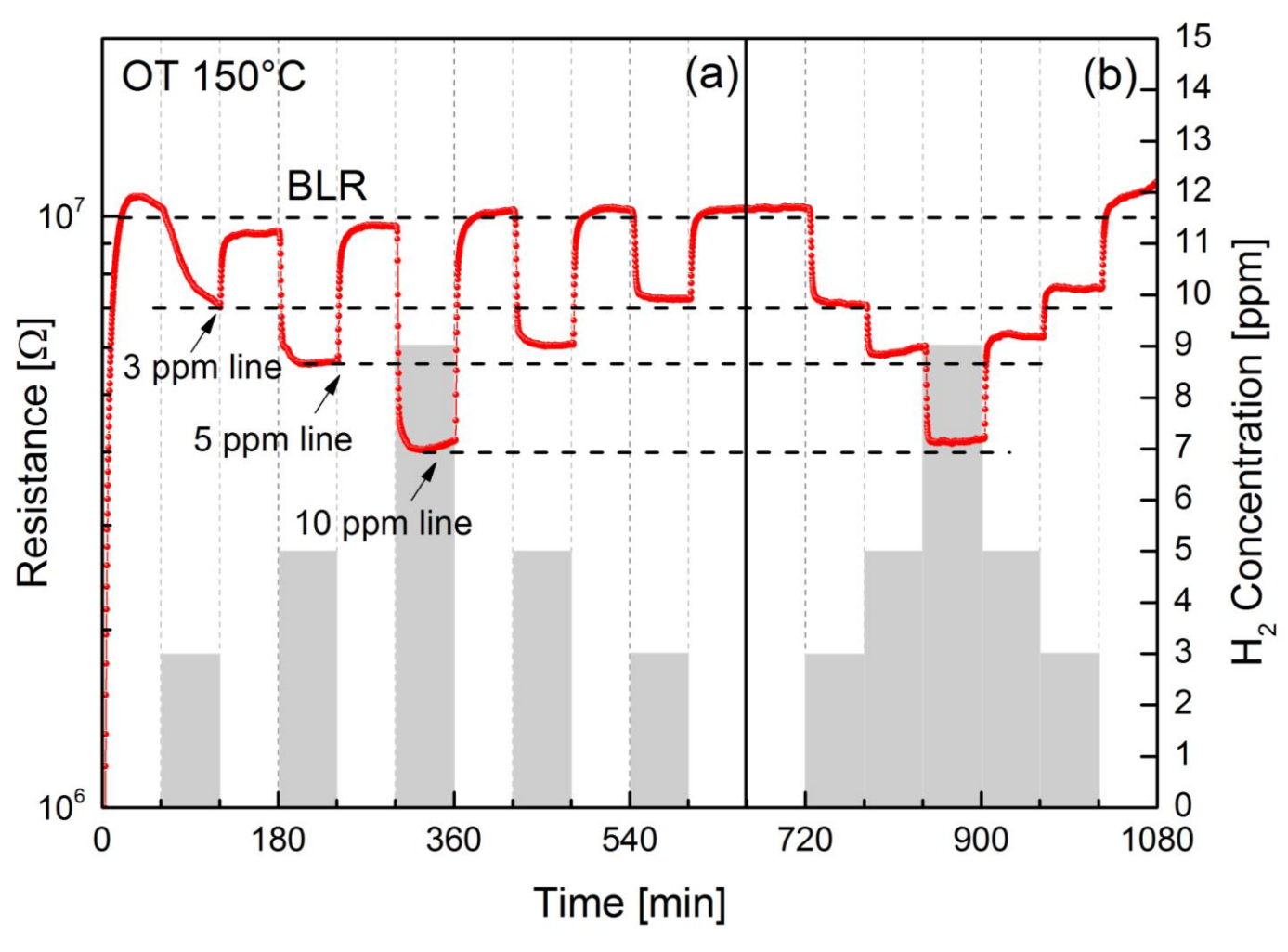




Gas Sensing – detection limit and dynamic response



Gas Sensing - Reproducibility test to H_2



Conclusions

There are plenty of rooms in the 2D world beyond graphene

- Large quantities of exfoliated TMDs can be obtained by a simple grinding and sonication fabrication process.

- TMDs show even better gas sensing properties as respect to GO, opening new perspectives for Hydrogen sensing with reproducible electrical response.


Thank You