Gwangju Institute of
Science and Technology

Non–noble Metal Catalyst Embedded WO_3 Microspheres for Enhancement of NO_2 Gas Sensing

Presenter : Jun-Cheol Park
Advisor : Sanghan Lee

School of Materials Science and Engineering
Gwangju Institute of Science and Technology (GIST)

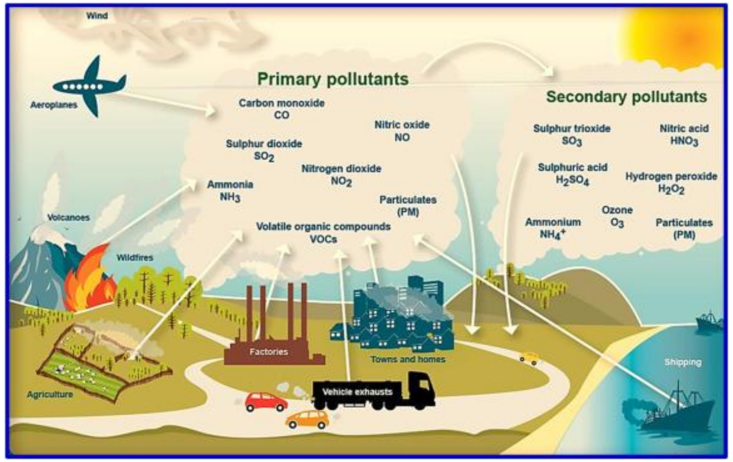
30th Apr. 2024
YF-17 // 09:30 – 09:45

Sustainable Energy and Electronic Devices laboratory

Contents

Demands for Gas Sensor

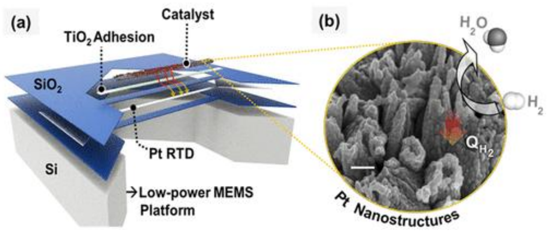
Why the "Gas Sensor" should be studied?



ref. *Sensors International* **2021**, 2, 100116

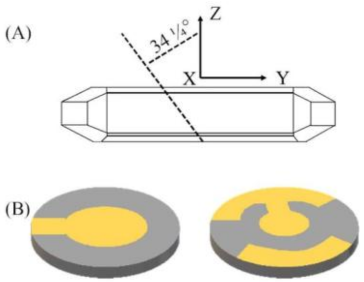
- Presence of toxic gases due to development of industry
- In terms of atmospheric ;
  Acid rain, photochemical smog
- In terms of human life ;
  Respiratory disease, poor lung function

Types of Sensors



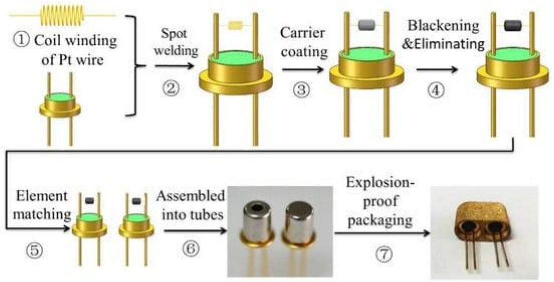
ref. *ACS Appl. Nano Mater.* **2021**, 4, 1, 7-12

< catalytic combustion >



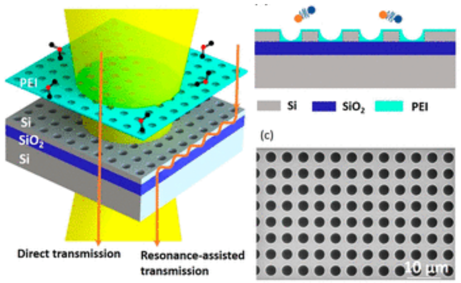
ref. *Chemosensors* **2021**, 9, 7, 153

< quartz crystal microbalance >



ref. *Sensors* **2018**, 18, 7, 2191

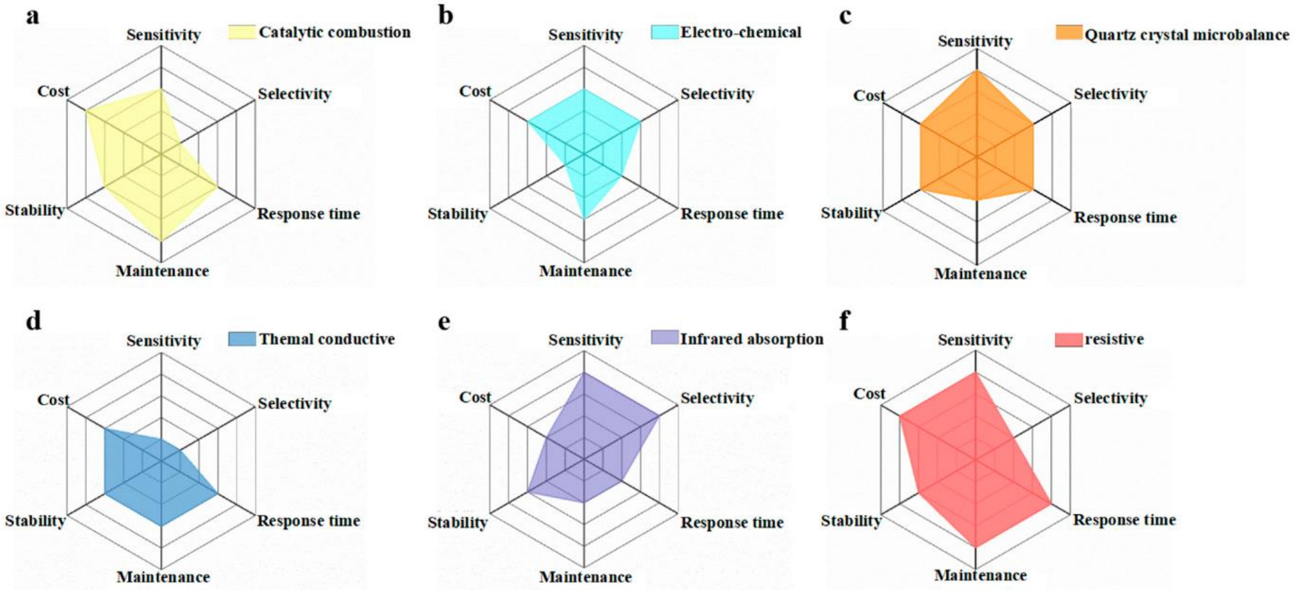
< thermal conductive >



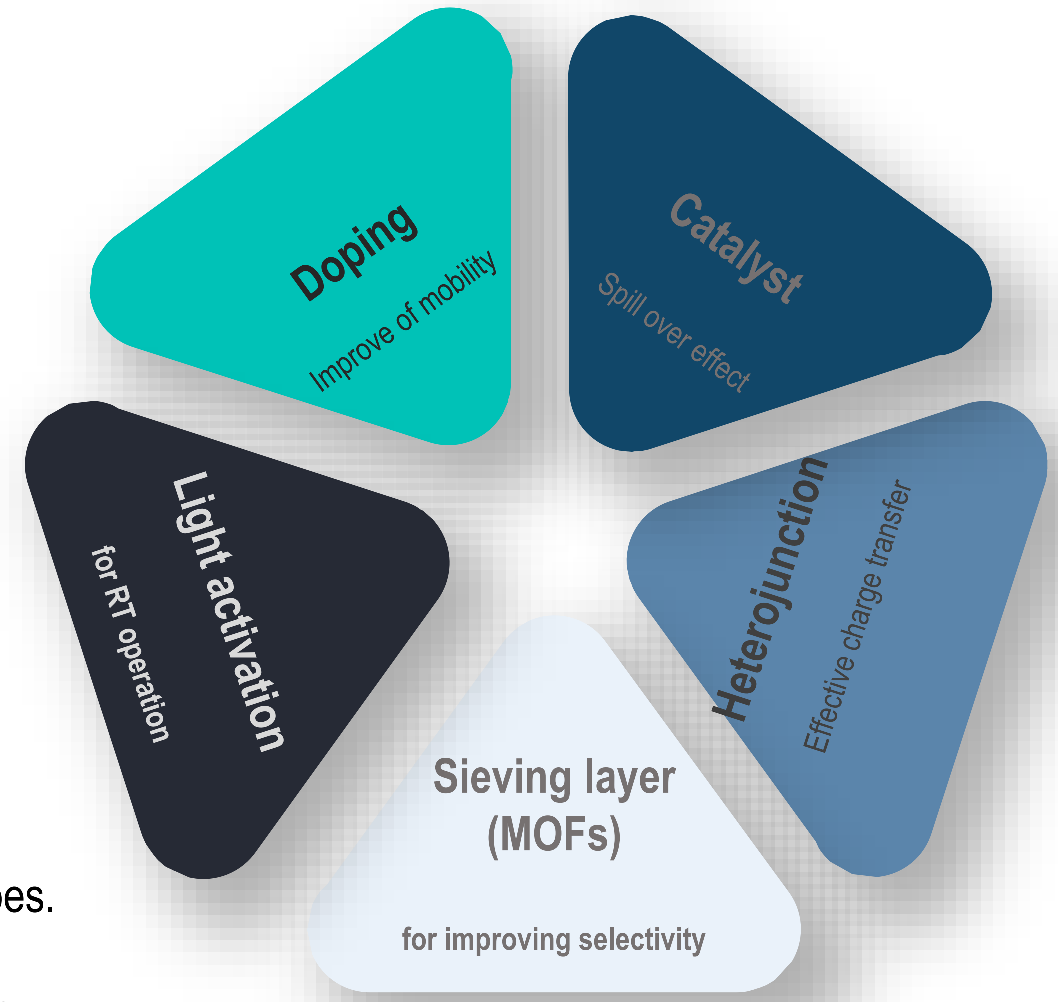
ref. *ACS Appl. Mater. Interfaces* **2018**, 10, 44, 38272-38279

< infrared absorption >

Important parameters for Sensor



ref. *Chemosensors* **2021**, 9, 8, 198



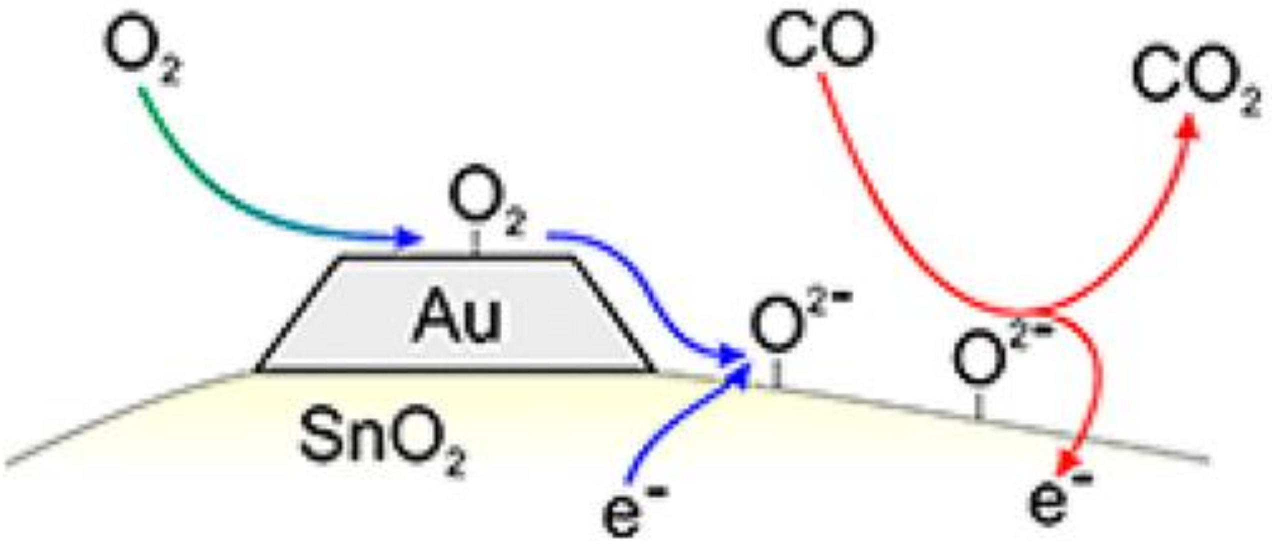
- Key parameters
  Selectivity, Sensitivity, Res/Rec time, stability, etc.

- (Chemi)Resistive gas sensor is one of the most attractive gas sensor types.

- Need to overcome some obstacles in terms of gas sensing performances
  Selectivity, operating temperature, recovery times

Motivation – Catalyst

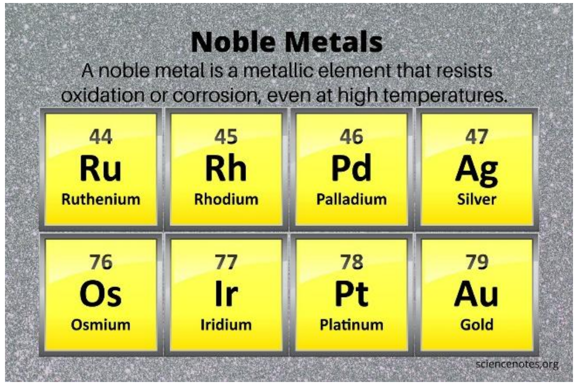
Improving gas sensing performance



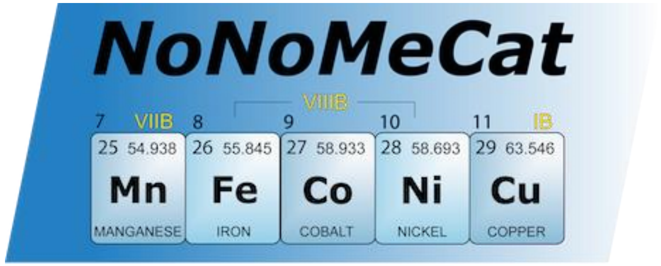
ref. *ACS Sens.* ***2016***, 1, 11, 1322–1329

- Catalysts could be helpful for improving gas sensing performance via inducing **spill-over effect**.
- Spill-over effect occurs when gas molecules are adsorbed onto the catalyst surface, transition to active intermediates on the surface.
- Finally, it could help to **enhance the sensitivity and selectivity**.

Candidates



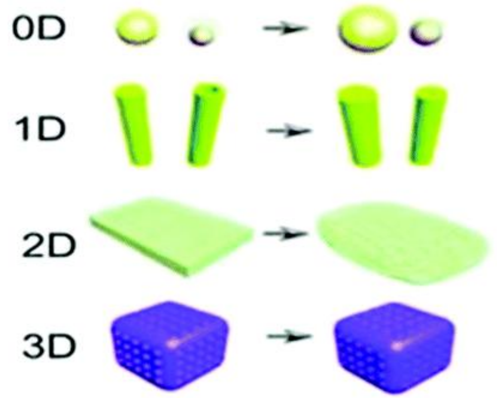
- Generally, noble metals (Au, Pt, Pd, etc) are used.



- Many researchers try to replace non-noble metal catalyst.

Motivation – Transition metal oxides

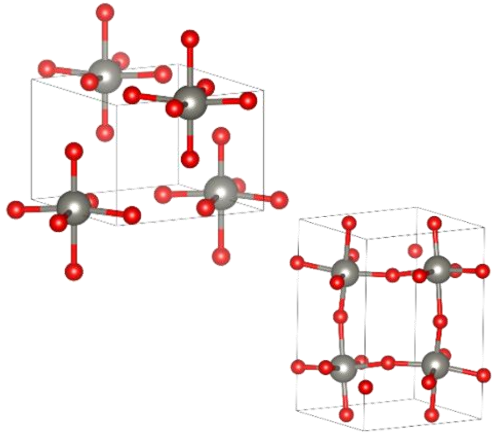
Transition metal oxides (TMOs)



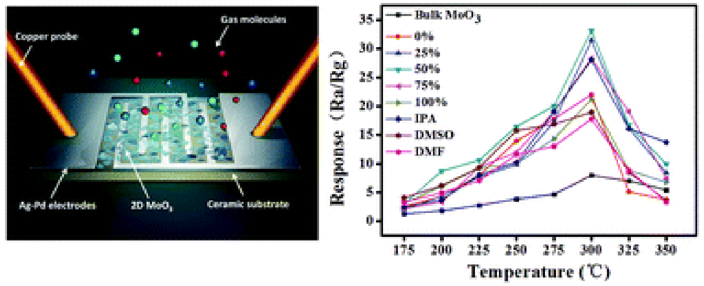
ref. *Mater. Adv.* **2021**, 2, 6839-6884

- Structure or morphology controls are easy to achieve.
- Low cost
- It is suitable for applying catalyst due to its stability in chemical reactions.
- In terms of sensors, it exhibits high sensitivity.

Tungsten oxide (WO_3)

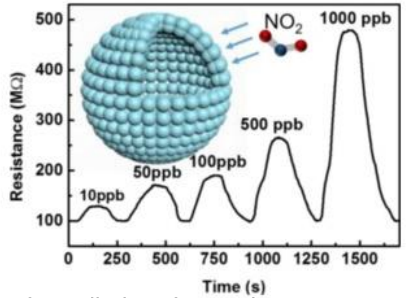


- Need high operating temperature.
- Low response at low concentration
- Improvement in recovery time is needed.
- The selectivity is insufficient.



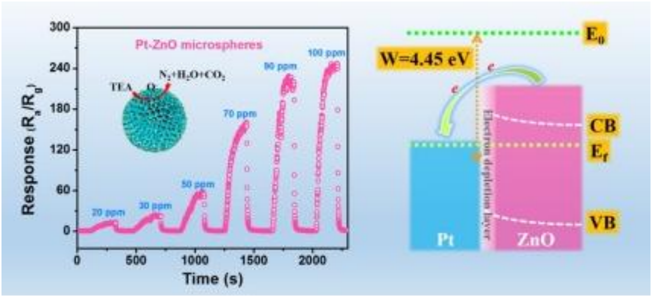
ref. *Nanoscale,* **2016**, 8, 8696-8703

< MoO_3 based >



ref. *Applied Surface Science,* **2018**, 434, 891-897

< WO_3 based >

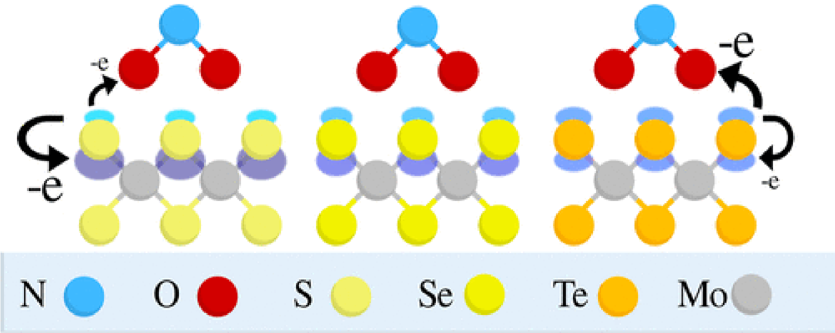


ref. *Sensors and Actuators B,* **2021**, 331, 129425

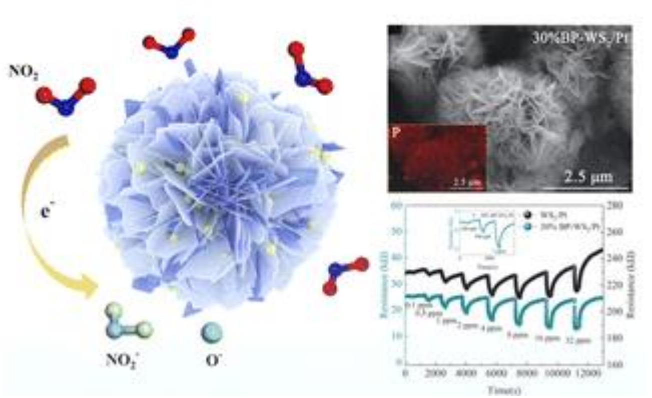
< ZnO based >

Motivation – Sulfurization of TMO

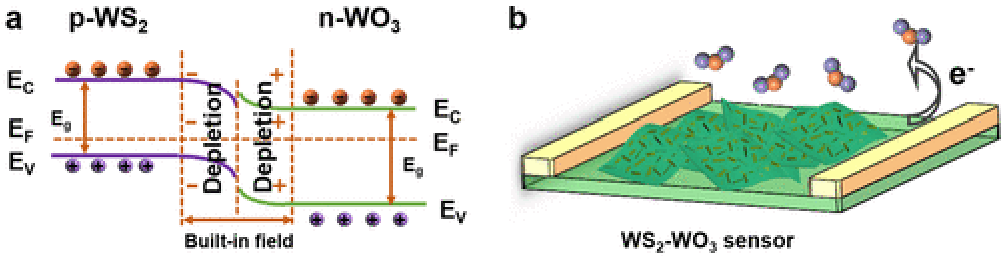
TMDs modification of TMO



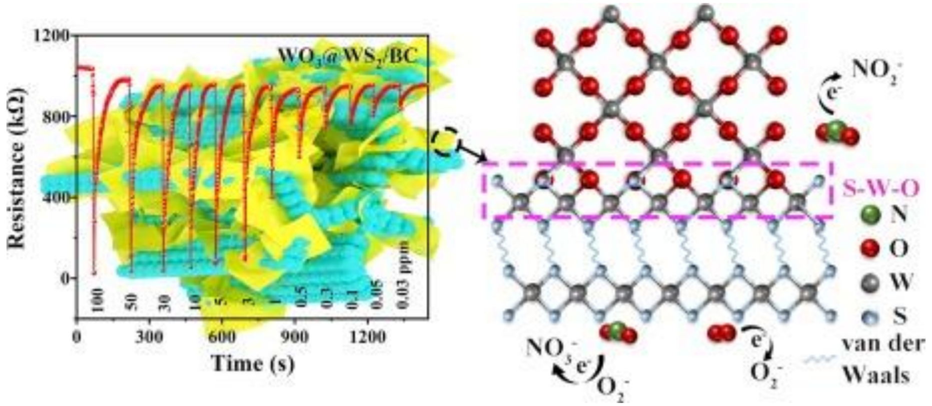
ref. *J. Phys. Chem. C.* ***2023***, *127, 43, 21374-21386*



ref. *Nanoscale*, ***2024***, *16, 2478-2489*



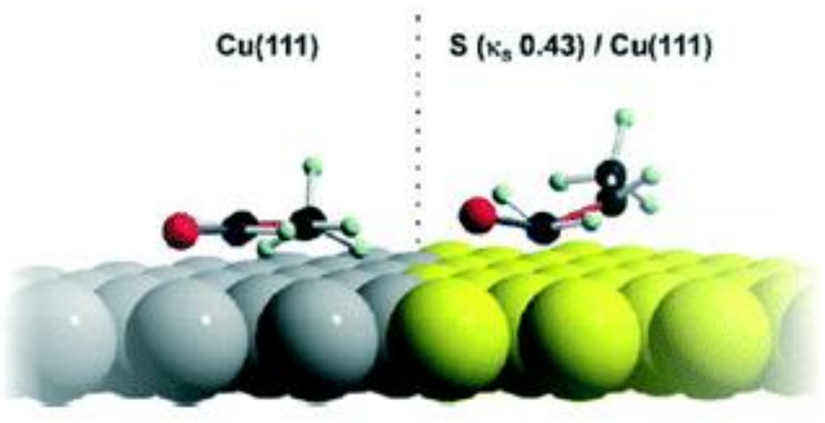
ref. *ACS Appl. Nano Mater.* ***2021***, *4, 2, 1626-163482*



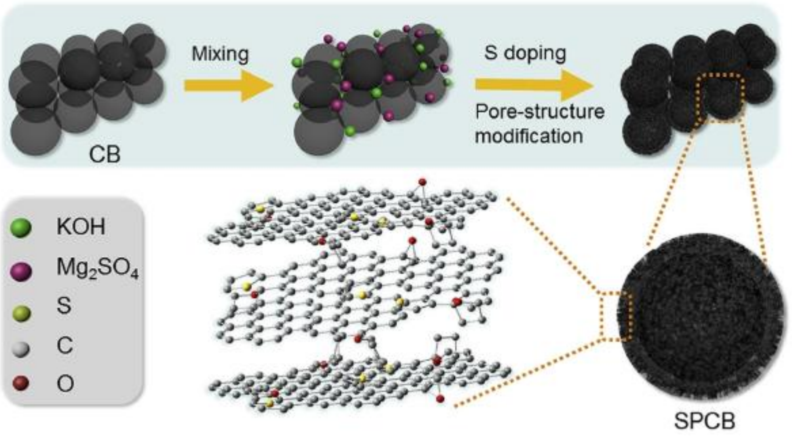
ref. *Applied Surface Science* ***2023***, *615, 156338*

- S-termination plays an essential role in improving gas sensitivity and selectivity.
- Electron transmission speed is accelerated by constructing the “S–W–O” transition layer.
- There are no reports on the intrinsic effects or roles of sulfur.

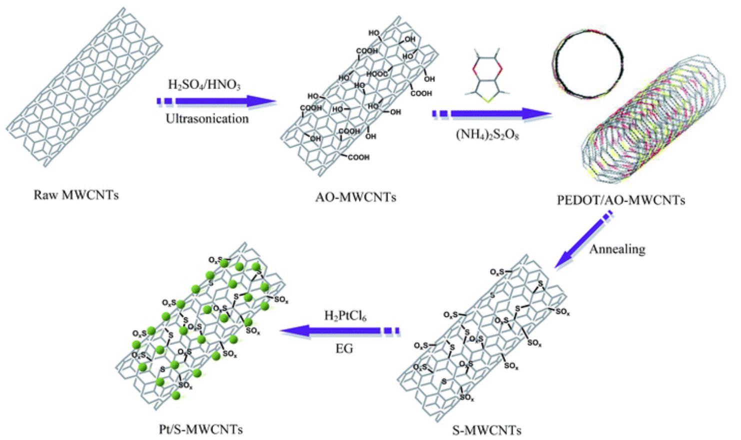
Motivation – Non-noble metal catalyst



ref. *Chem. Commun.* ***2006***, *1283-1285*

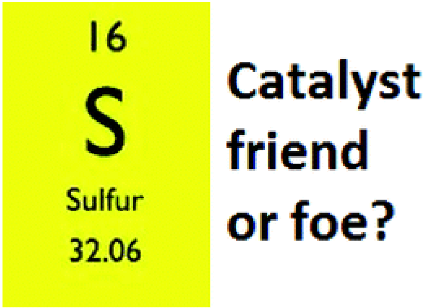


ref. *ChemSusChem* ***2022***, *15, e202101282*



ref. *J. Mater. Chem. A*, ***2017***, *5, 19467-19475*

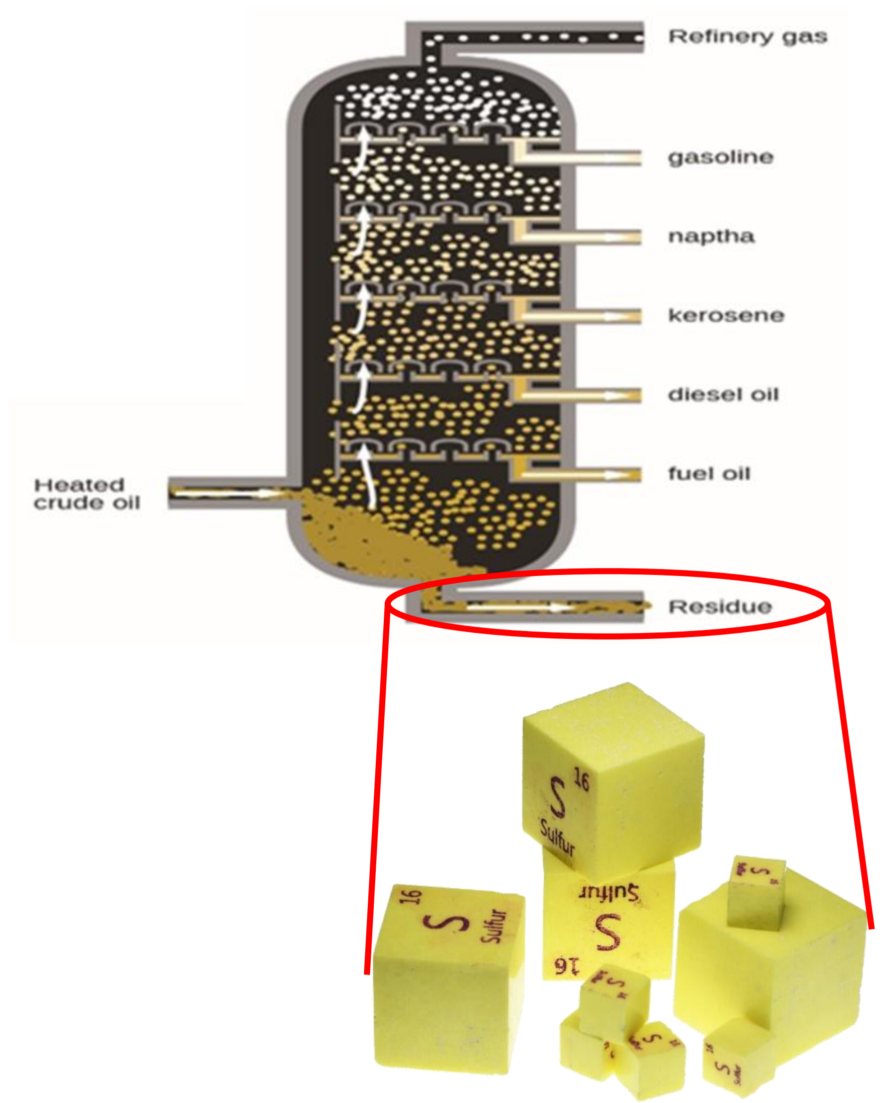
- The possibility of spill–over effect has been observed in various carbon composites.
- Sulfur is much cheaper in prices compared to most metal catalysts.
- Most studies fail to prove the presence of sulfur.
- Sulfur catalysts are rarely applied in gas sensor.

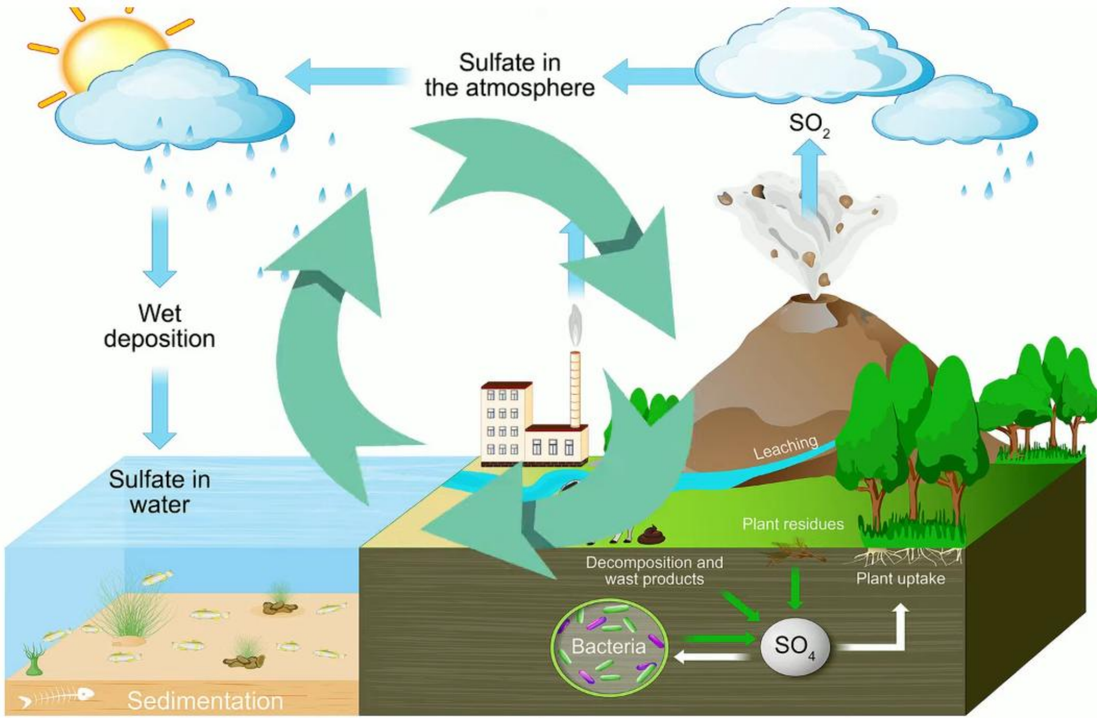


ref. *Catal. Sci. Technol.* ***2014***, *4, 272-294*

Pt	**₩ 28,594**
Au	**₩ 43,316**
Pd	**₩ 35,362**
S	**₩ 66**

Motivation – Upcycling of sulfur

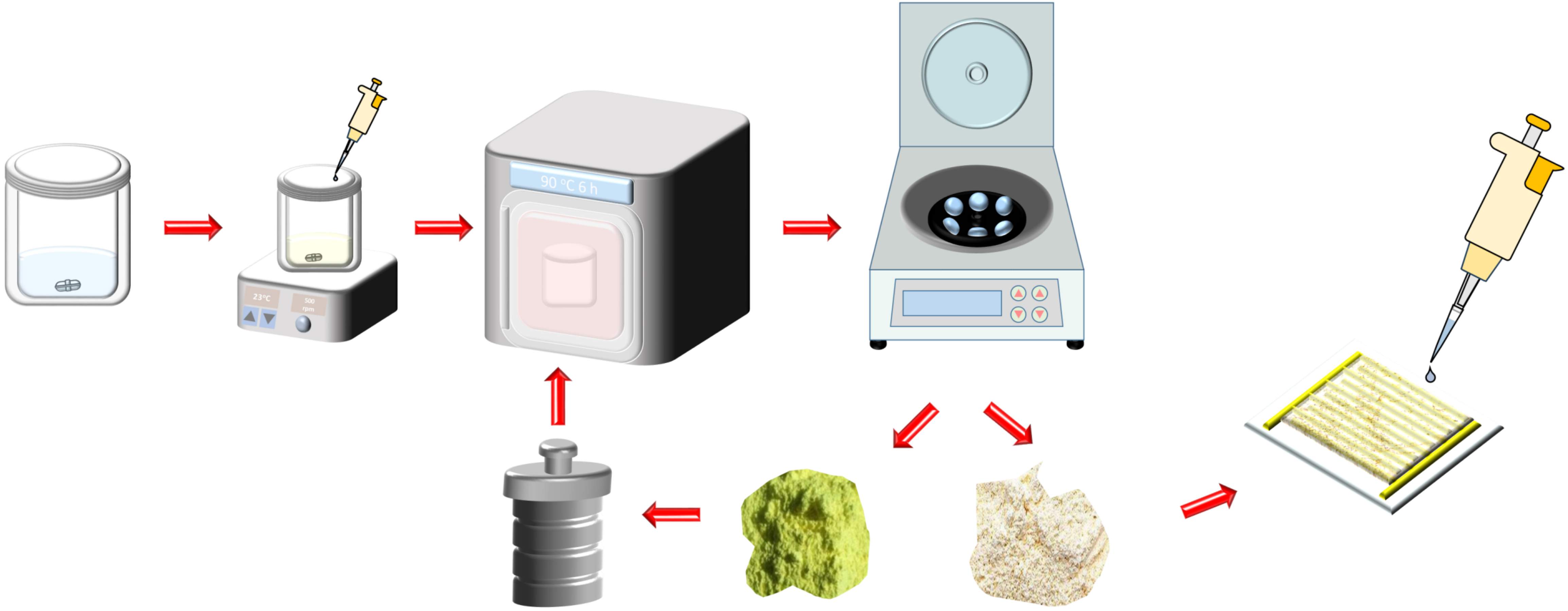




- Sulfur is produced as a byproduct during the process of refining crude oil.
- In nature, the formation of sulfur compounds occurs continuously and cyclically.
- In this terms, various methods are required to handle sulfur.

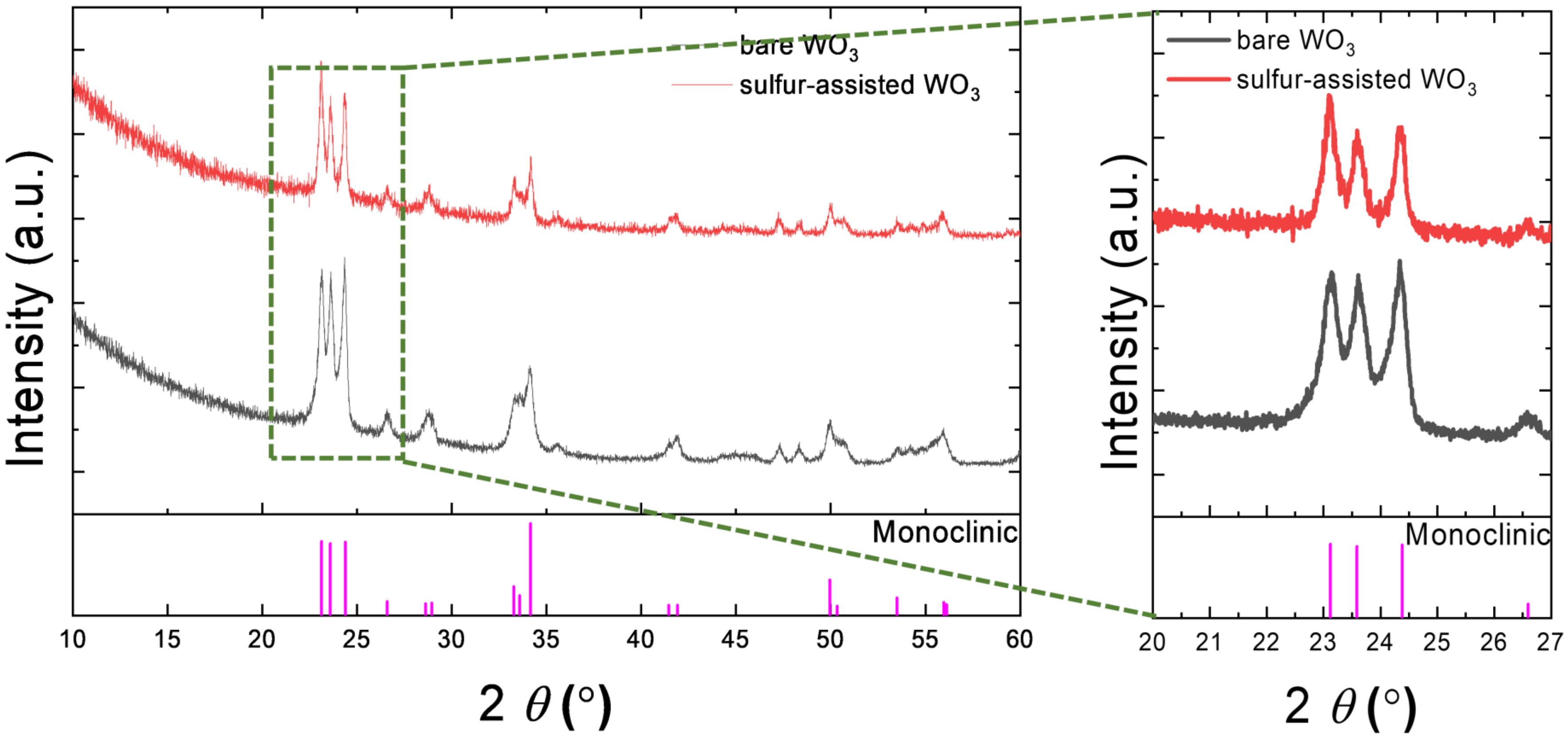
Experimental Setup

Two step hydrothermal process for bare WO_3 and sulfur-assisted WO_3 synthesis



Results – Crystalline analysis

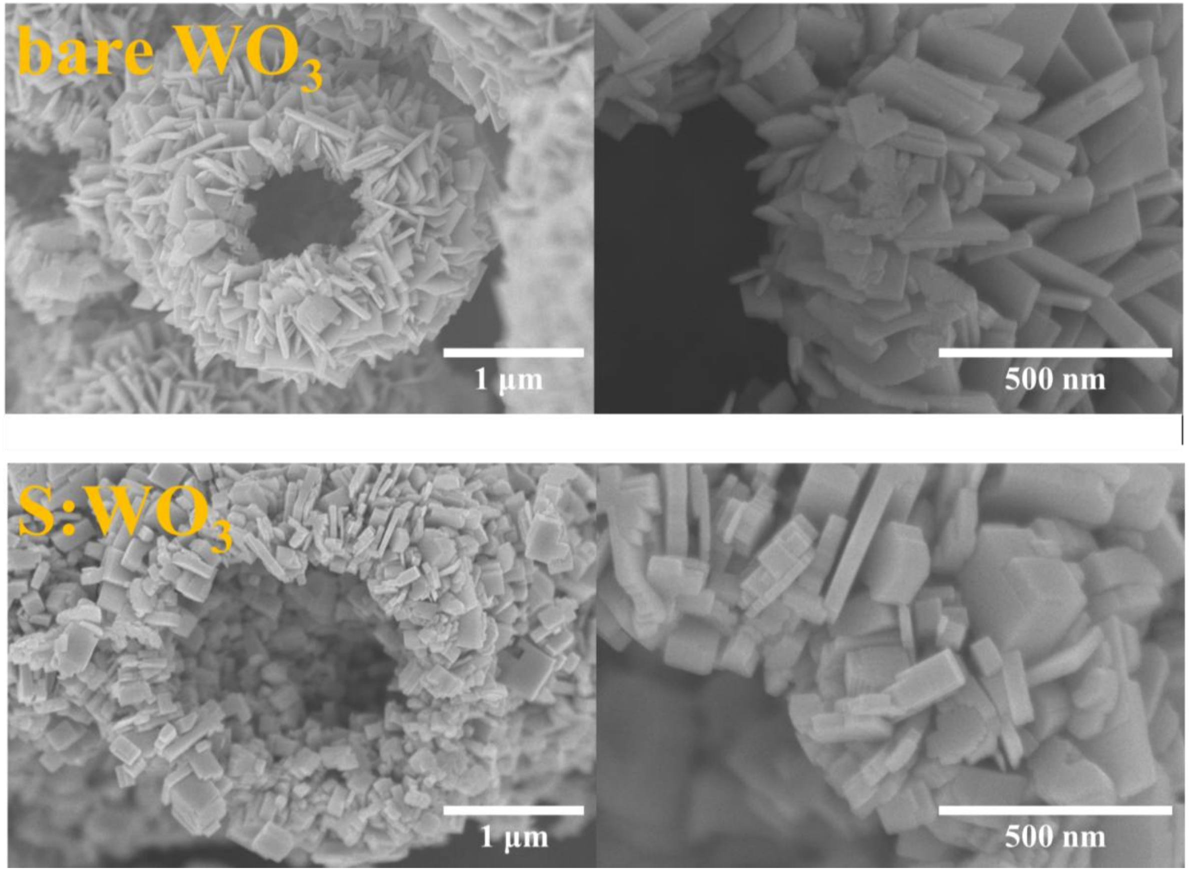
- XRD



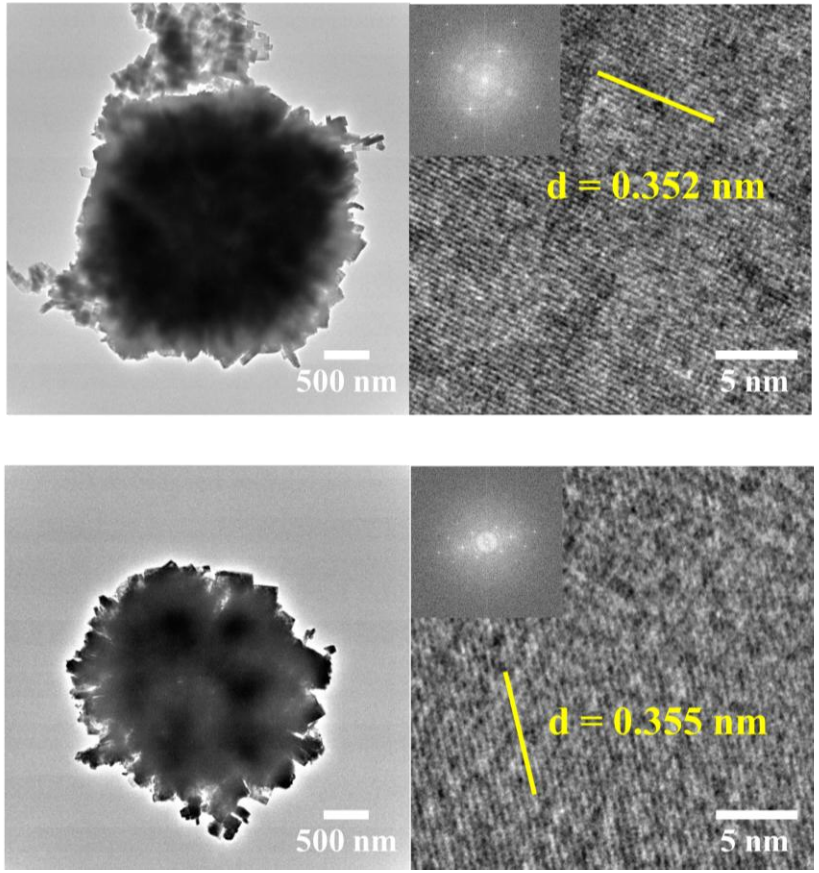
- XRD analysis revealed monoclinic phase of both WO_3 samples.
- The loading of sulfur did not have a significant effect on the crystallinity of WO_3.

Results – Morphology

- SEM



- HRTEM

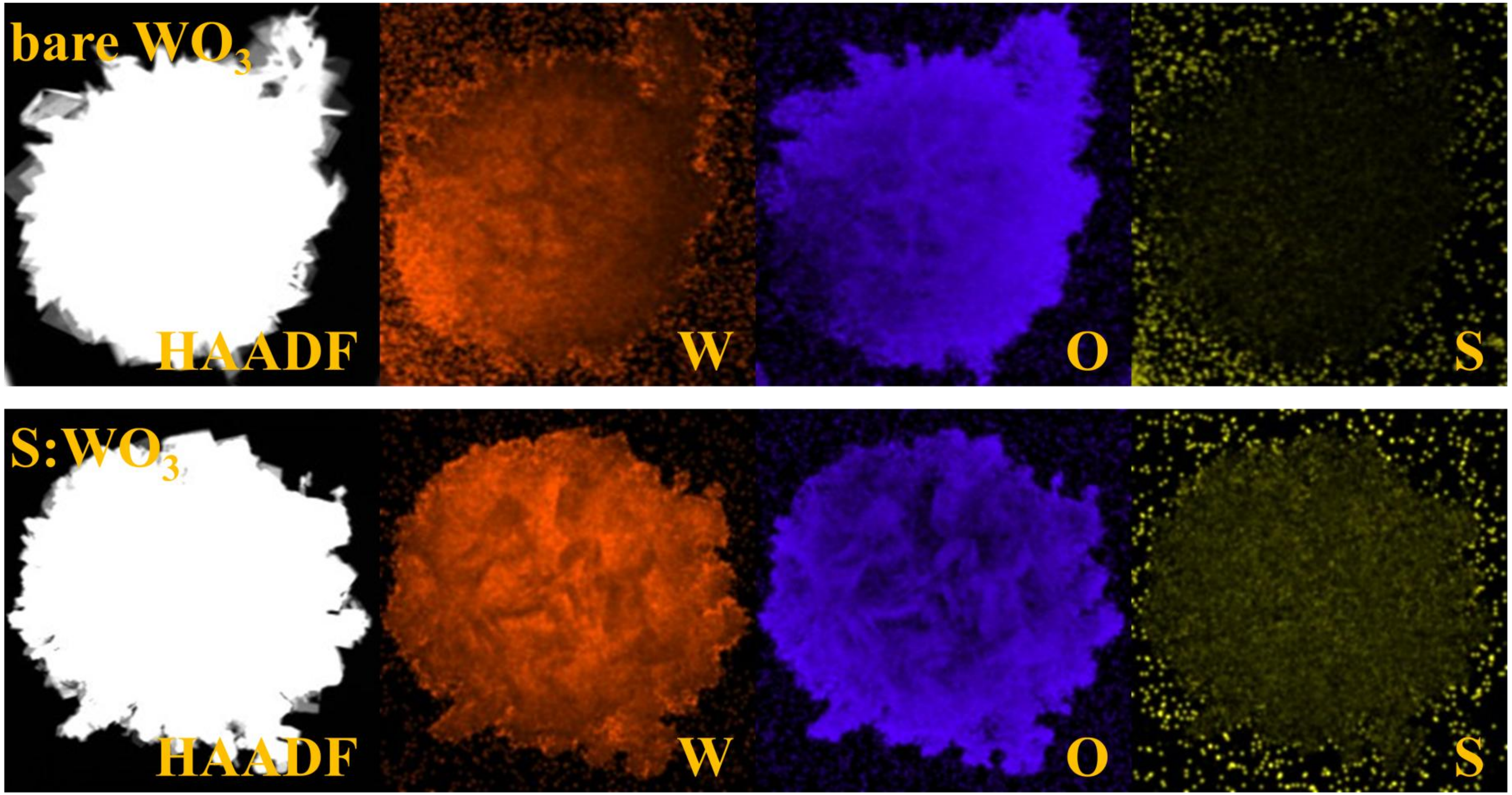


☑ There were no significant changes observed in the overall morphology.

☑ In HRTEM, no change observed in the d-spacing

Results – Morphology

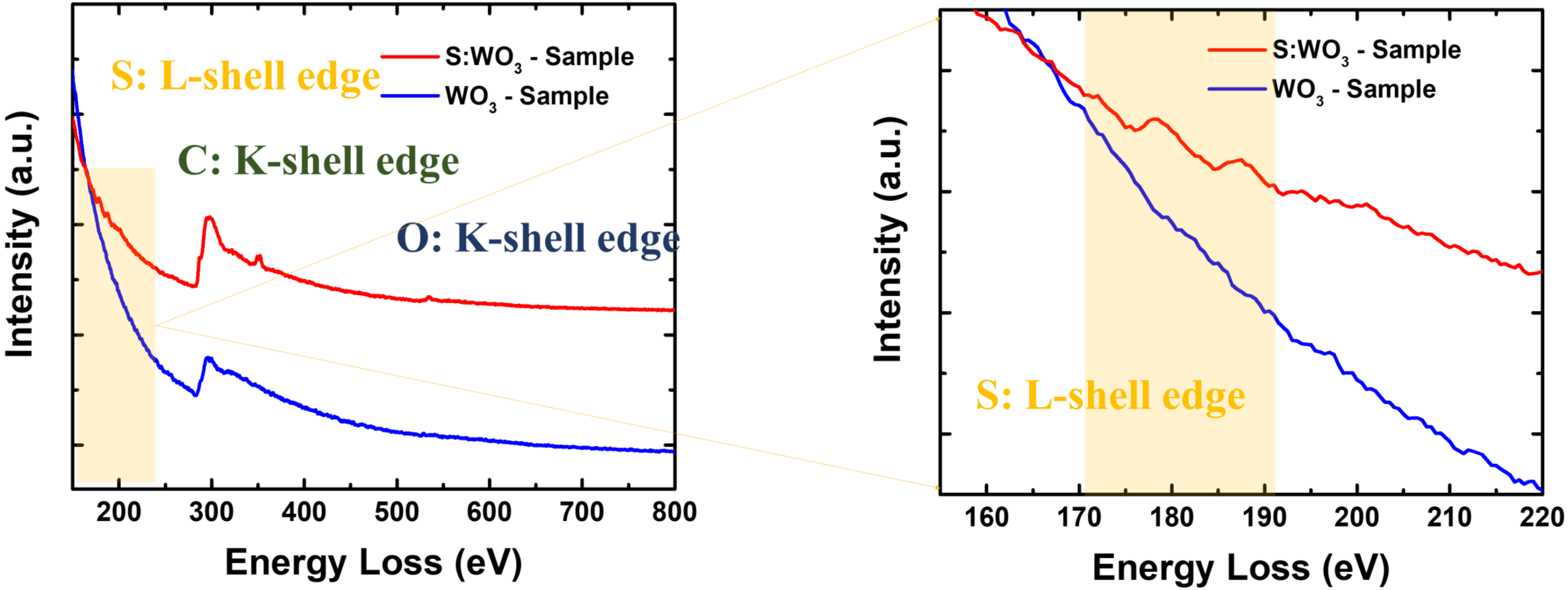
- STEM – EDX



S:WO3 was verifying about presence of sulfur from STEM–EDX(2 at% of sulfur)

Results – Element analysis for sulfur

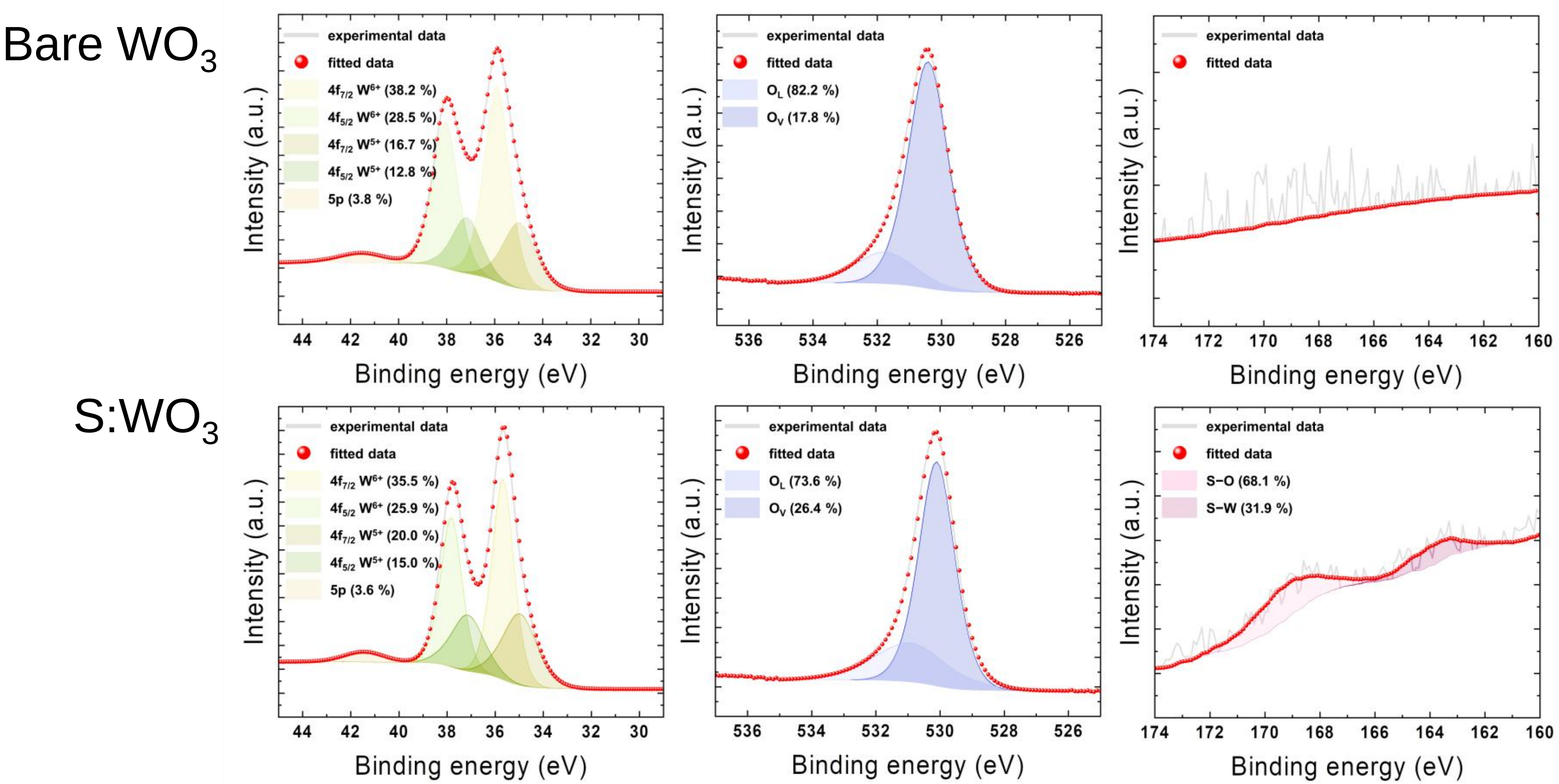
- EELS



- Sulfur resides not within the WO_3 matrix as an internal dopant.
- In addition to the EDX results, the presence of sulfur on the WO_3 microsphere surface was confirmed.

Results – Chemical state & quantitative analysis

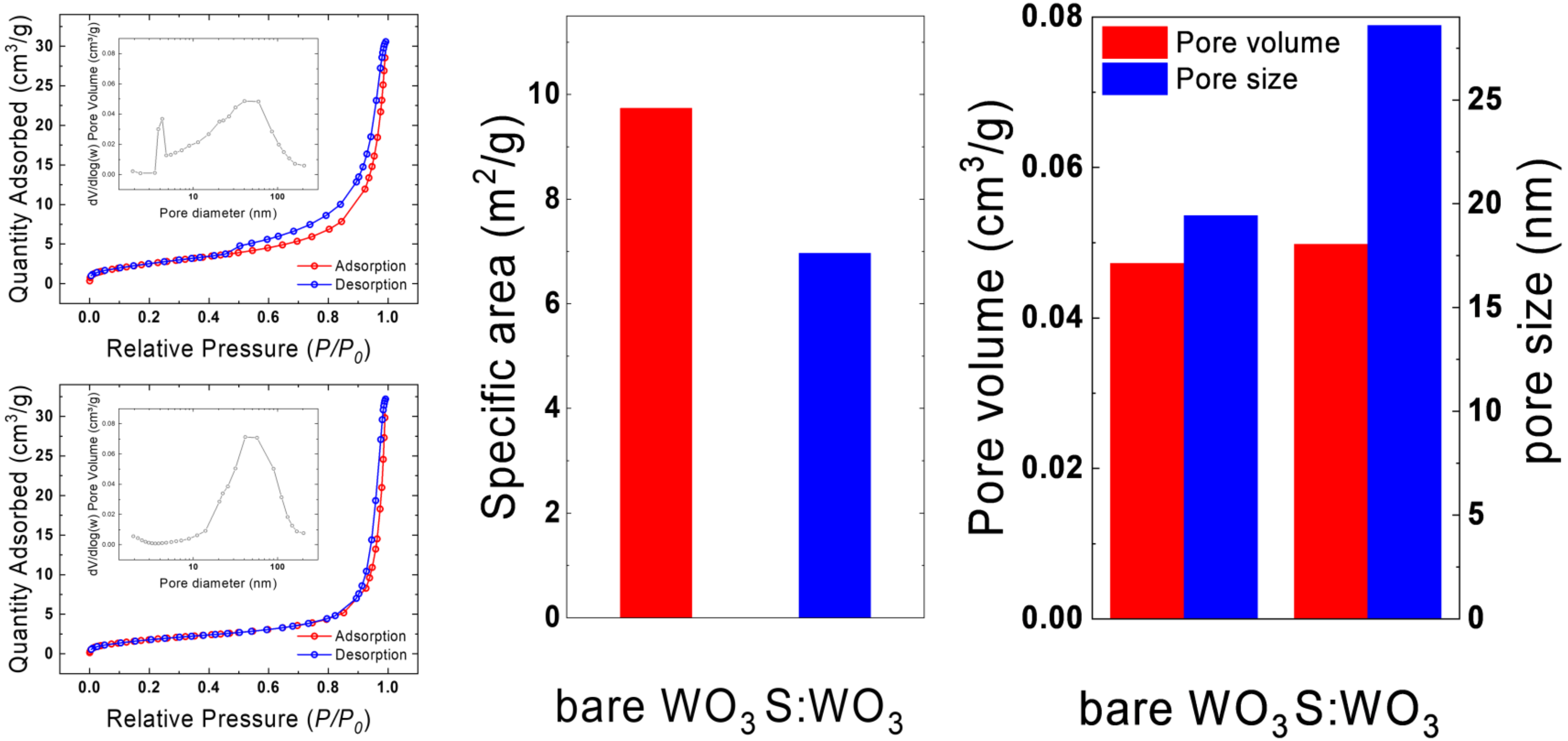
- XPS



The quantitative ratio of sulfur is approximately 2 at%, which is consistent with the EDS results.

The increase in oxygen vacancies in $S:WO_3$ could be attributed to the presence of sulfur.

Results – BET and BJH analysis

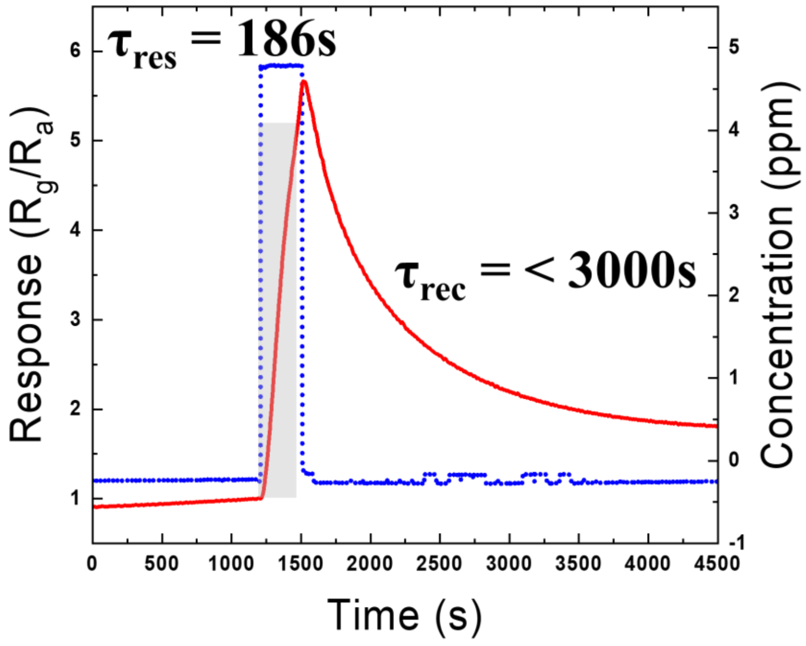


- Both samples have similar micropores with radius of 10 nm
- No relation of BET/BJH results

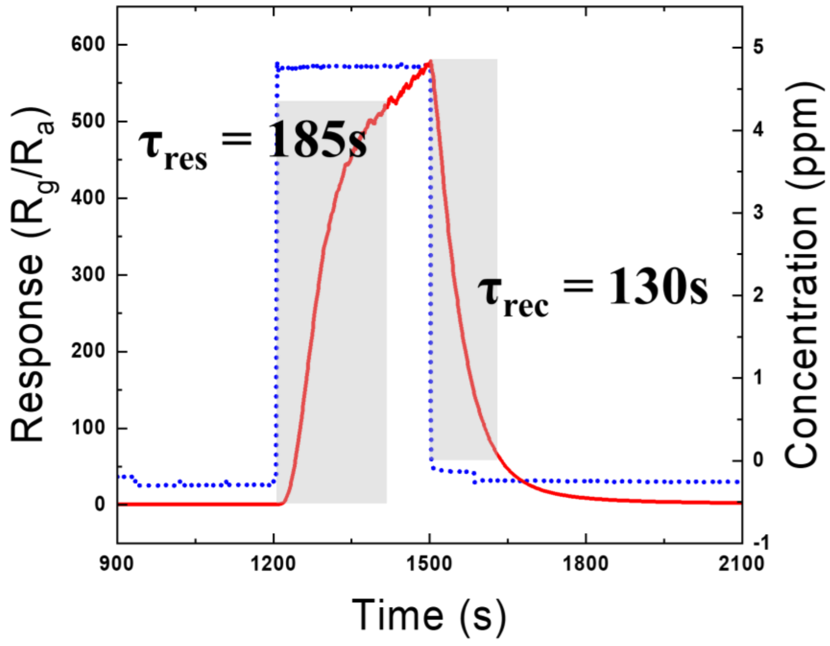
Results – Sensing performance

Gas : NO_2 5 ppm
Operating temperature : 150 °C

- Bare WO_3



- S:WO_3

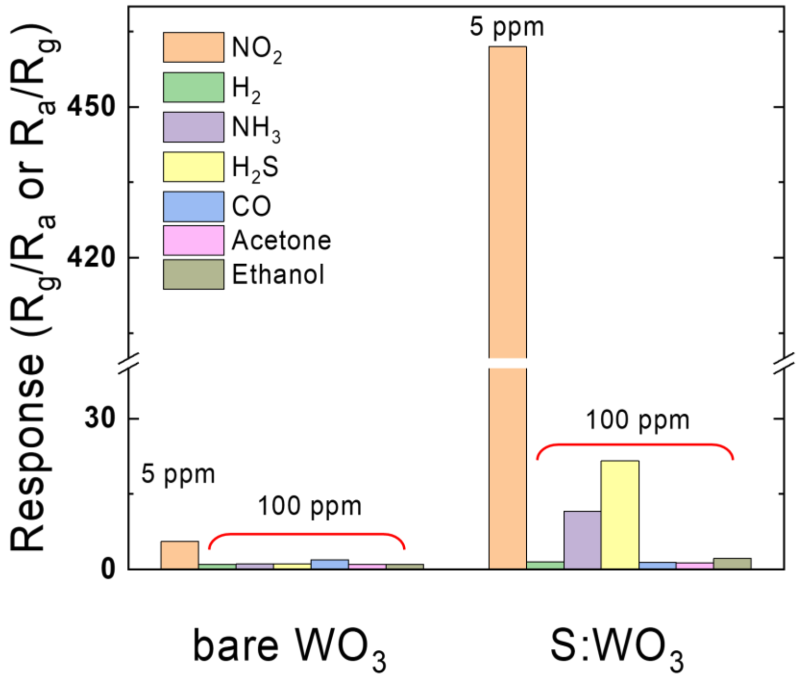


☑ It exhibits an improvement in response by over 100 times compared to the bare WO_3.

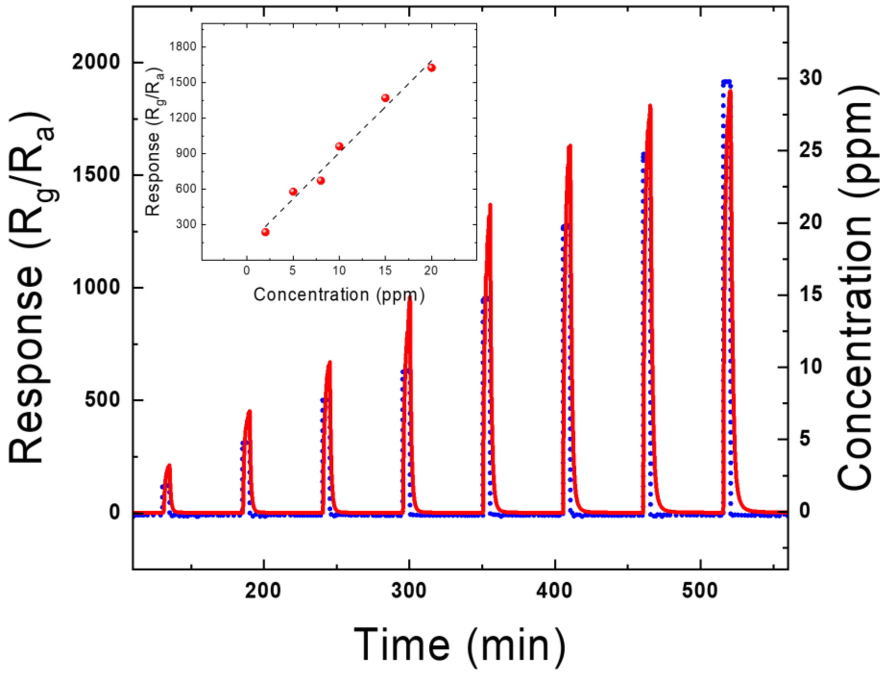
☑ Compared to bare WO_3, which showed no recovery,
the recovery time has been significantly enhanced to around 2 minutes.

Results – Sensing performance

- Selectivity



- Linearity

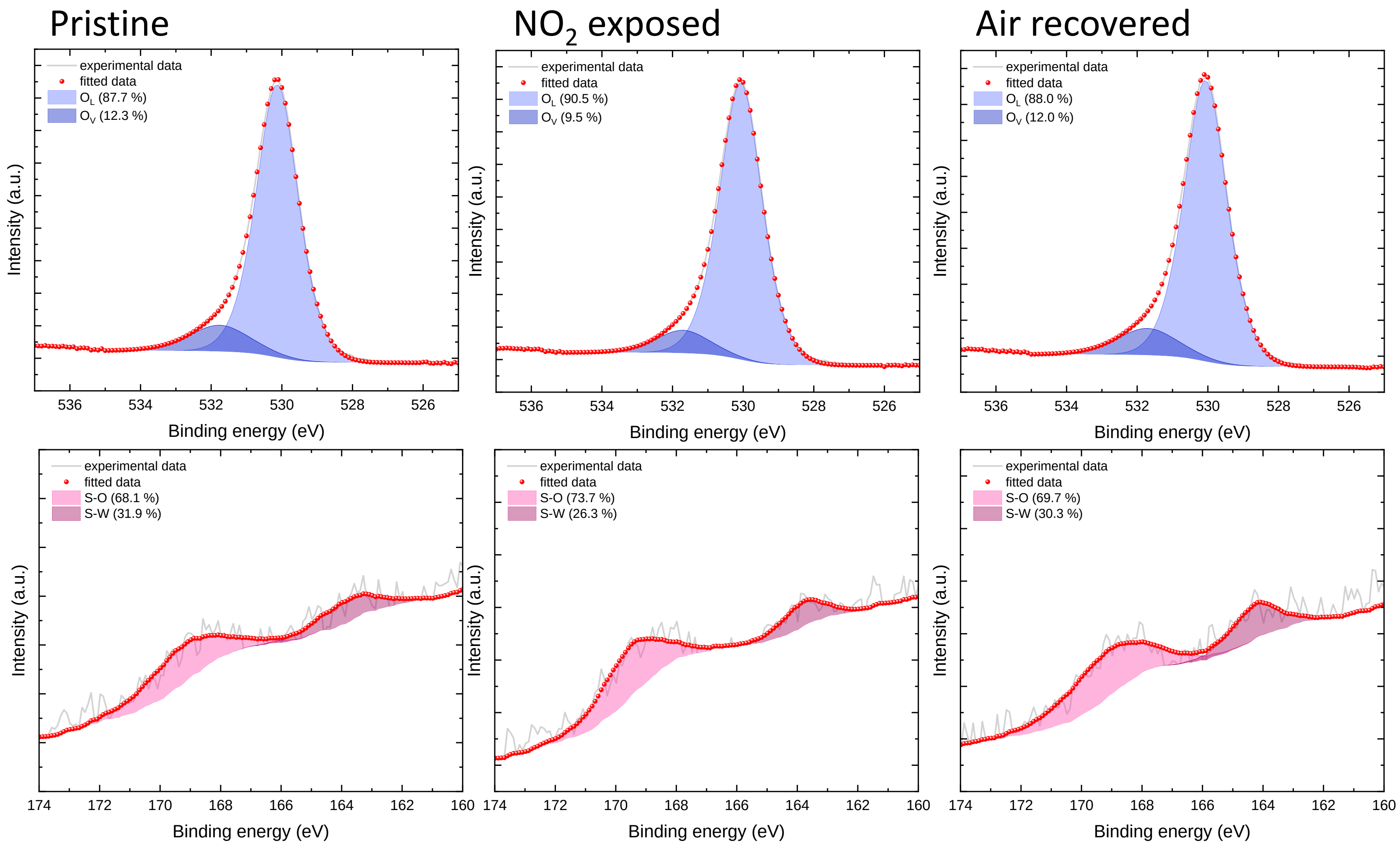


☑ When compared to other reference gases (100 ppm concentration), it shows excellent selectivity.

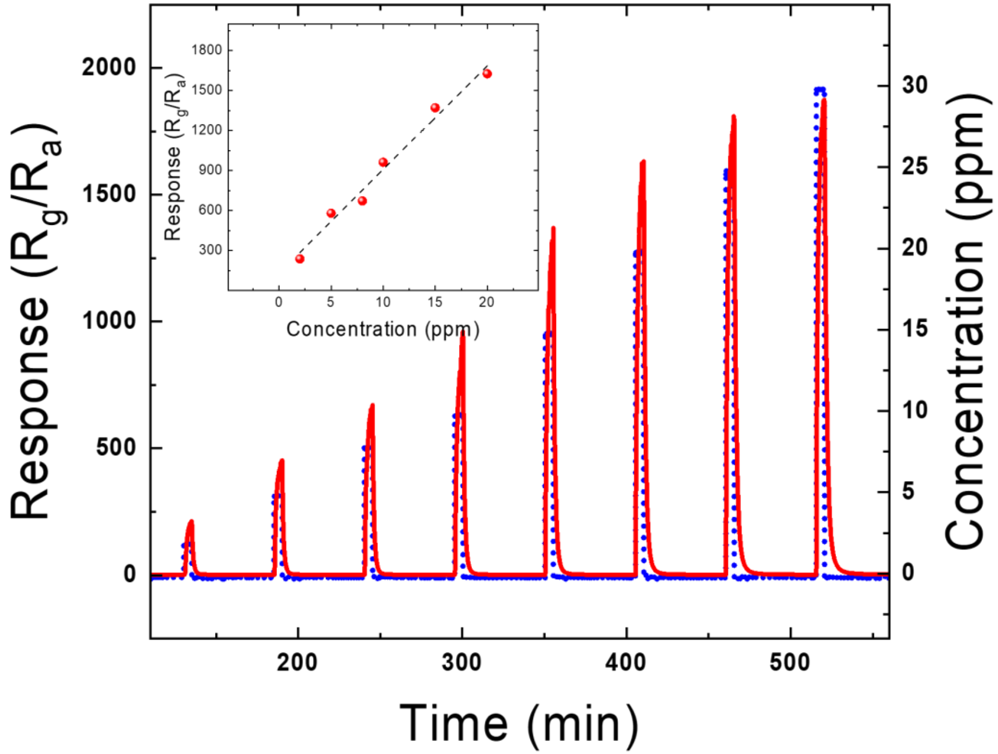
☑ The limit of detection (LOD) of 50 ppb was confirmed through the linearity test.

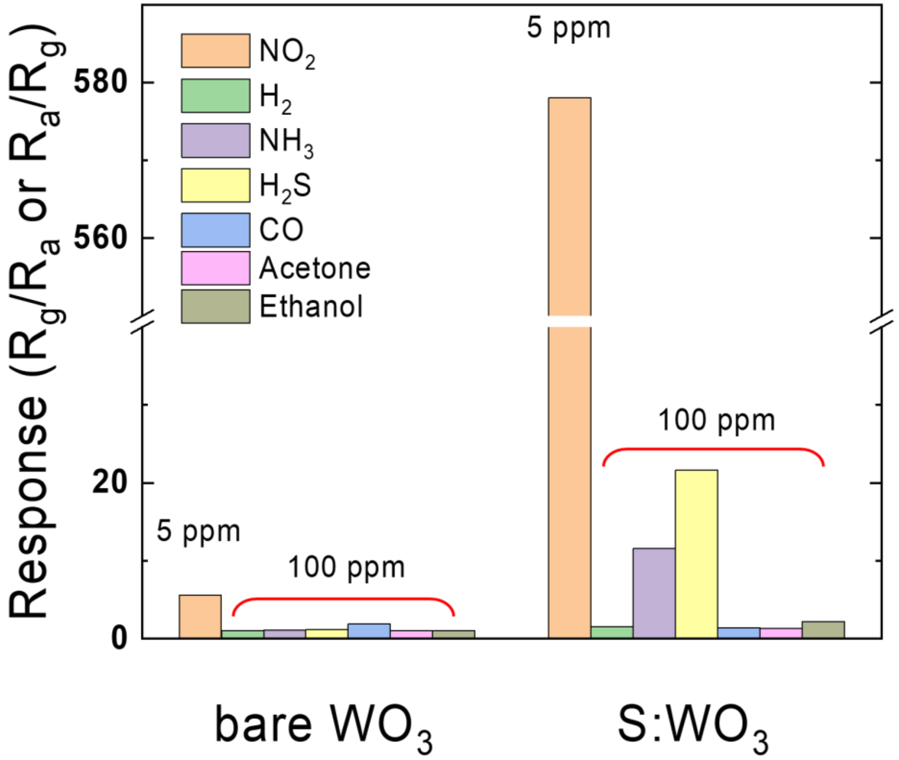
Results – Mechanism

- *ex-situ* XPS



Summary





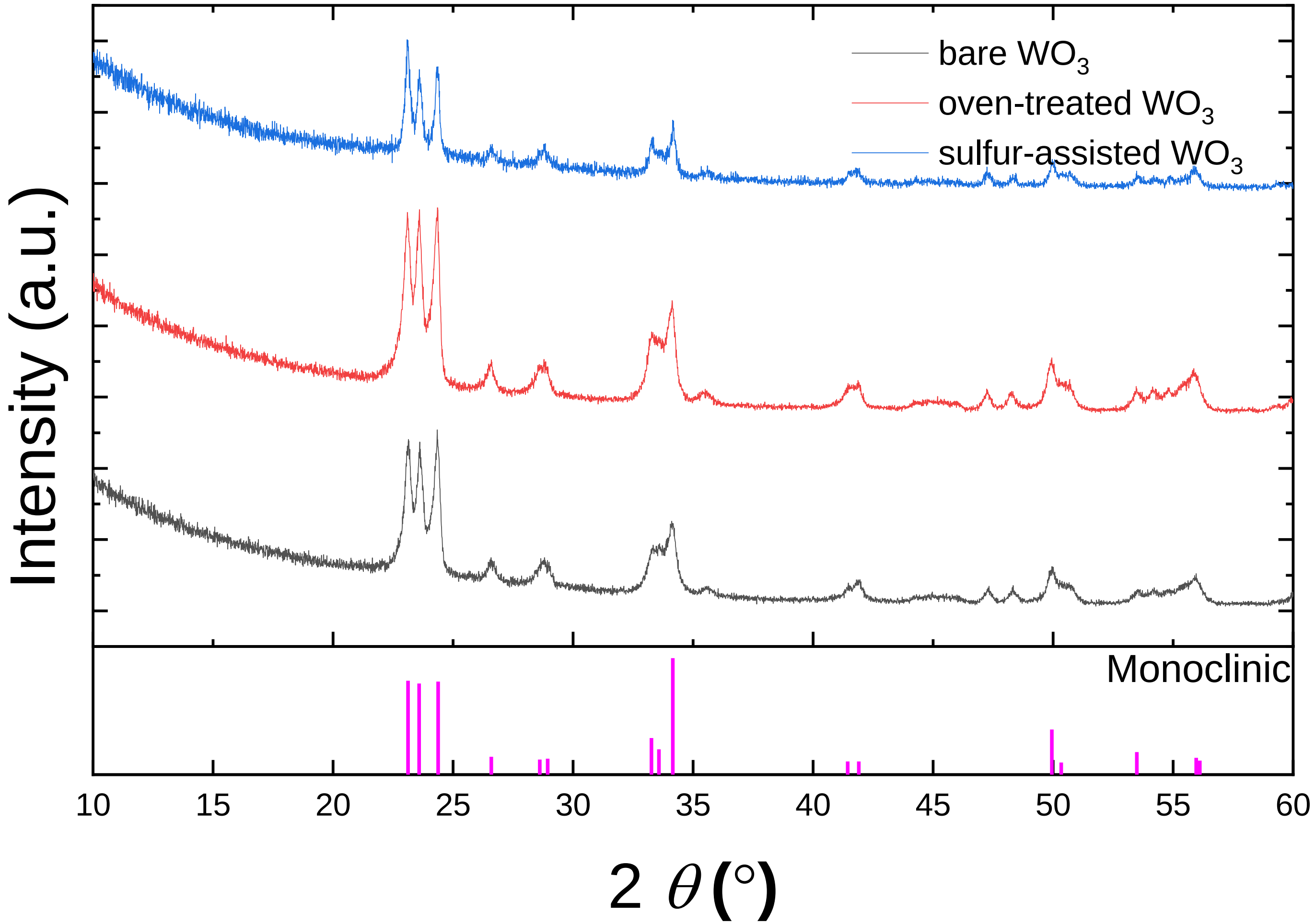
- We successfully fabricated sulfur−assisted WO_3 via two−step hydrothermal synthesis
- S:WO_3 show Superior gas sensor performance with 100 times more than response and about 50 ppb of LOD

Gwangju Institute of
Science and Technology

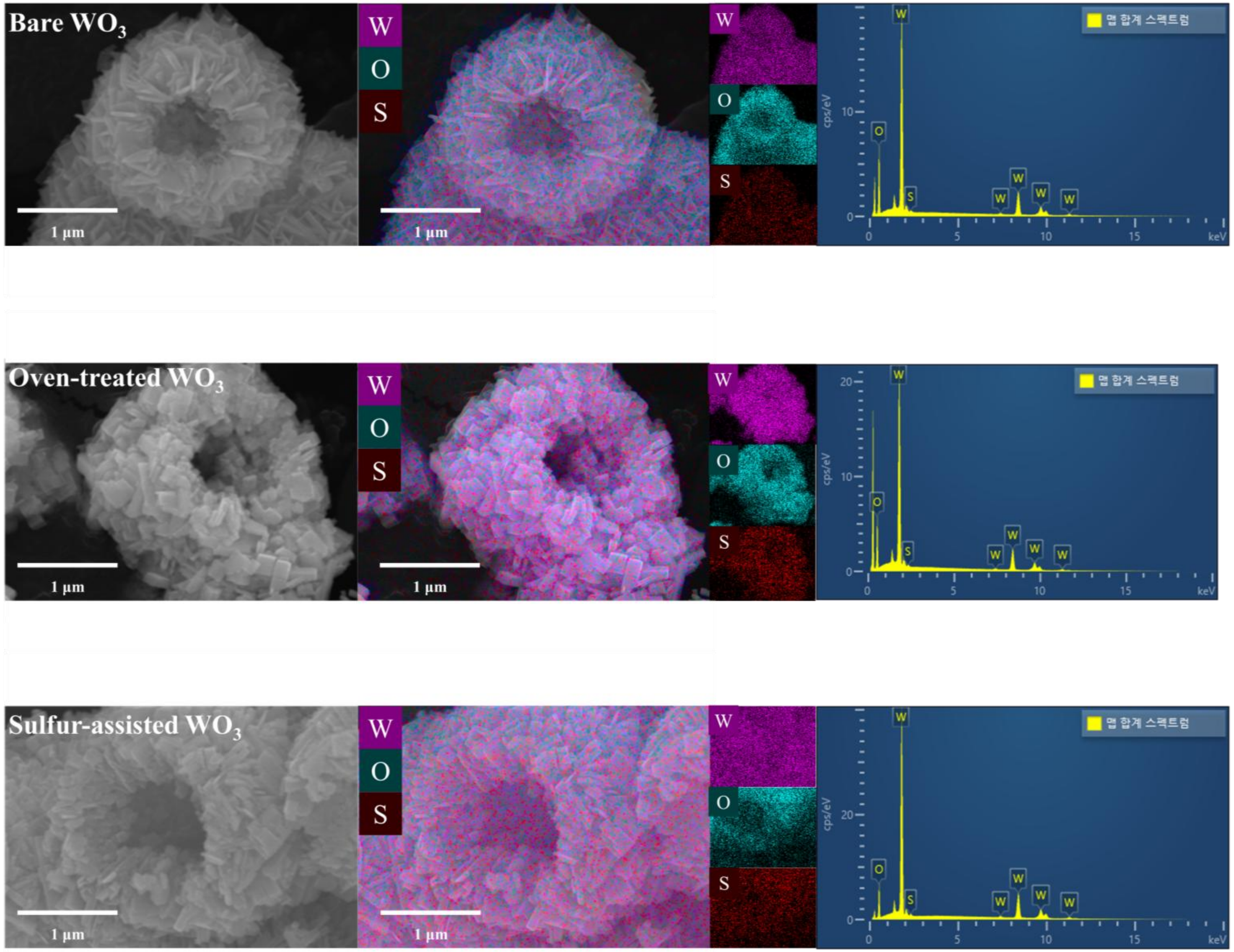
Thank you for your attention

SEED
Sustainable Energy and Electronic Devices laboratory

Supplementary information

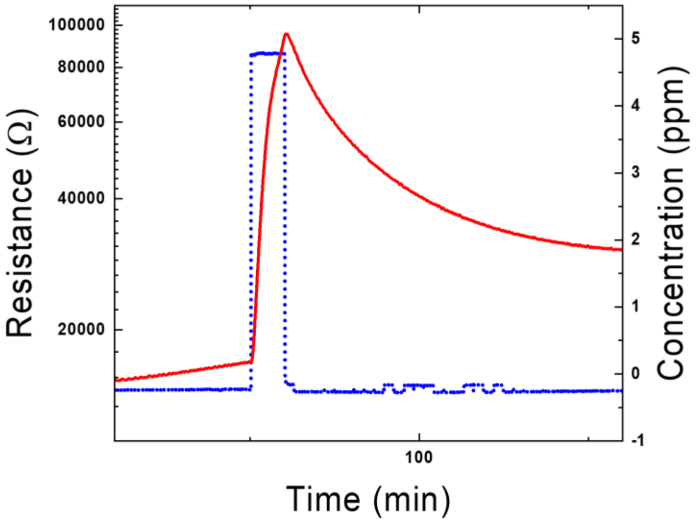


Supplementary information



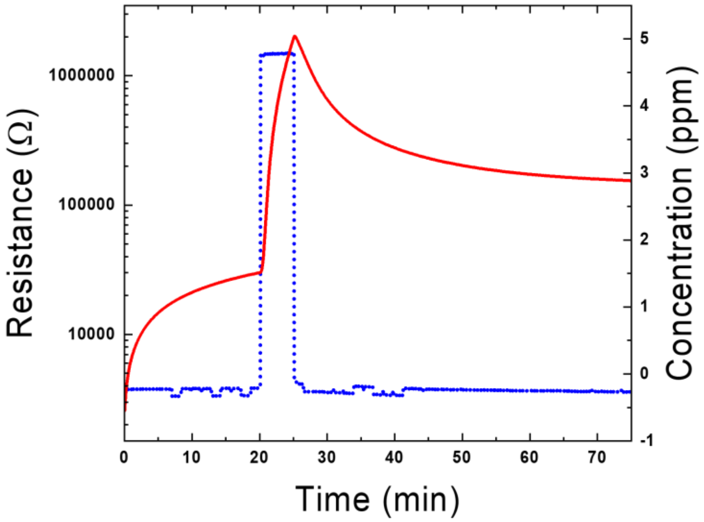
Supplementary information

Bare WO_3



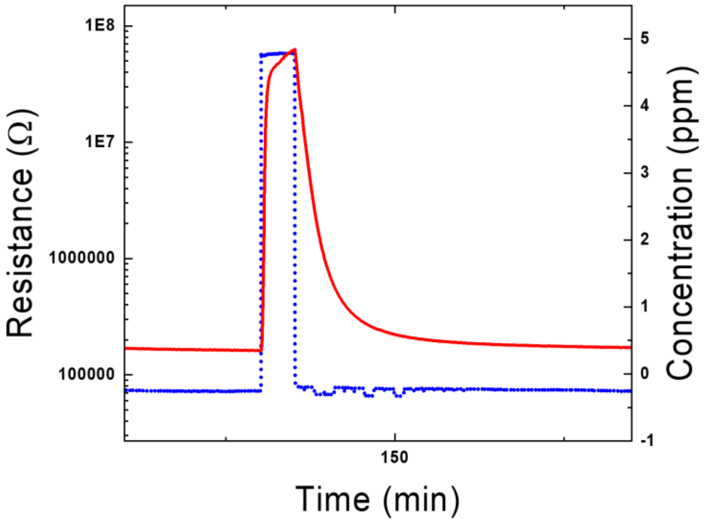
response	5.6
τ_{res}	185s
τ_{rec}	X

Oven-annealed WO_3



response	76.8
τ_{res}	184s
τ_{rec}	1497s

Sulfur-assisted WO_3



response	578
τ_{res}	186s
τ_{rec}	130s

Supplementary information