



# 歪み制御化学抵抗性ガスセンサーとその応用

Strain-controlled chemiresistive gas sensors and their applications

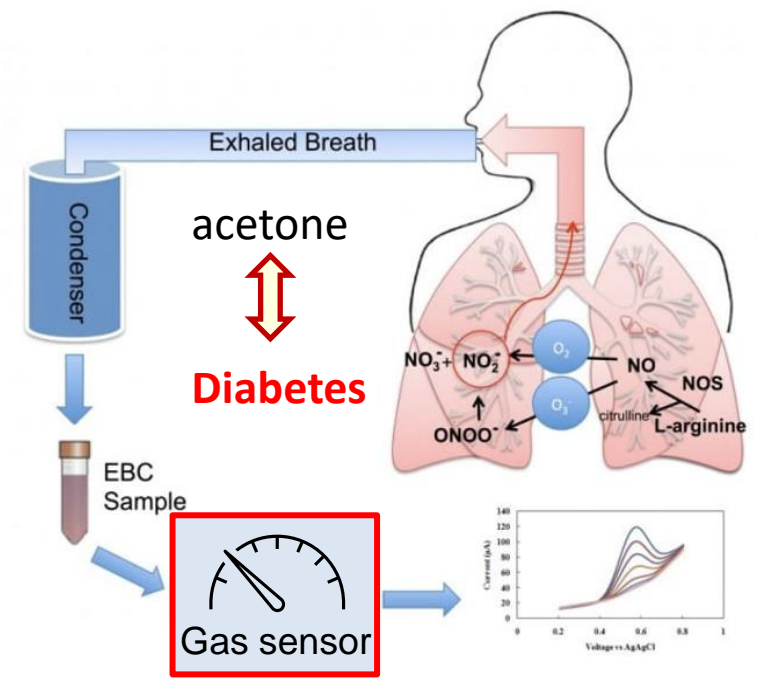
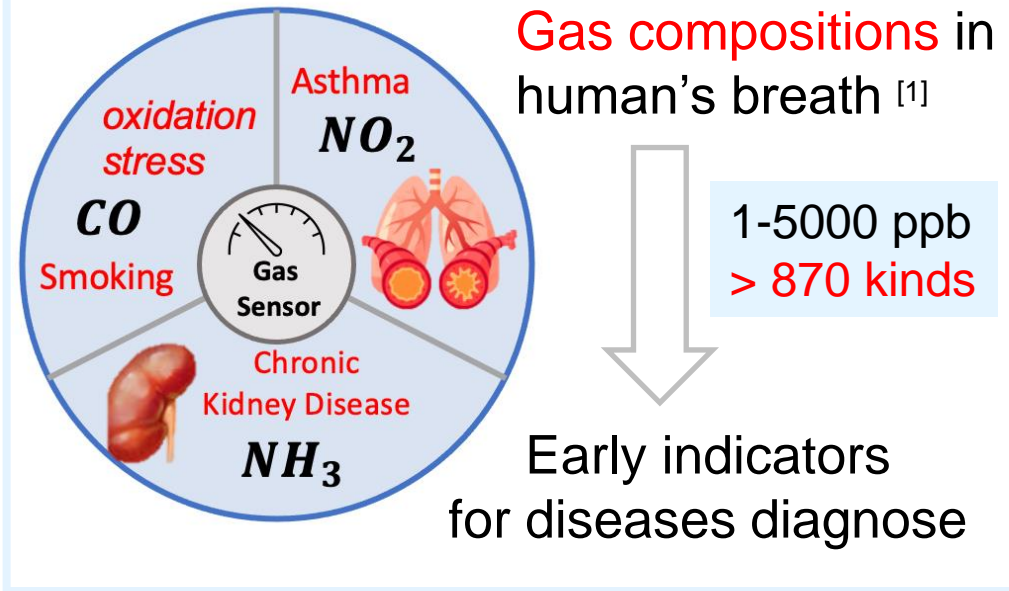
尹 朦

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指導教員: 鈴木 研 教授

◆ **Aged society** → **Rising healthcare burdens** → **Cost-effective medical method**

## Advanced Breath Analysis Method



Electrochemical gas sensing scheme [2]

An ultra-sensitive gas sensing technology with selectivity is required.

[1] X. Zhou et al. *J. Mater. Chem. B*, vol. 8, no. 16, pp. 3231–3248, 2020. [2] Gholizadeh, et al. *Microsyst Nanoeng* 3, 17022, 2017.

# Chemiresistive gas sensors: compact, affordable potential for long-term health monitoring

## Traditional GC-MS

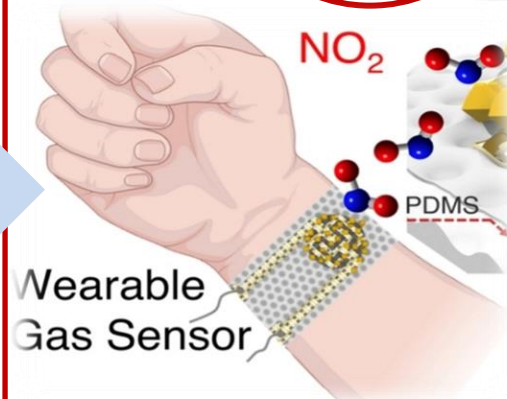
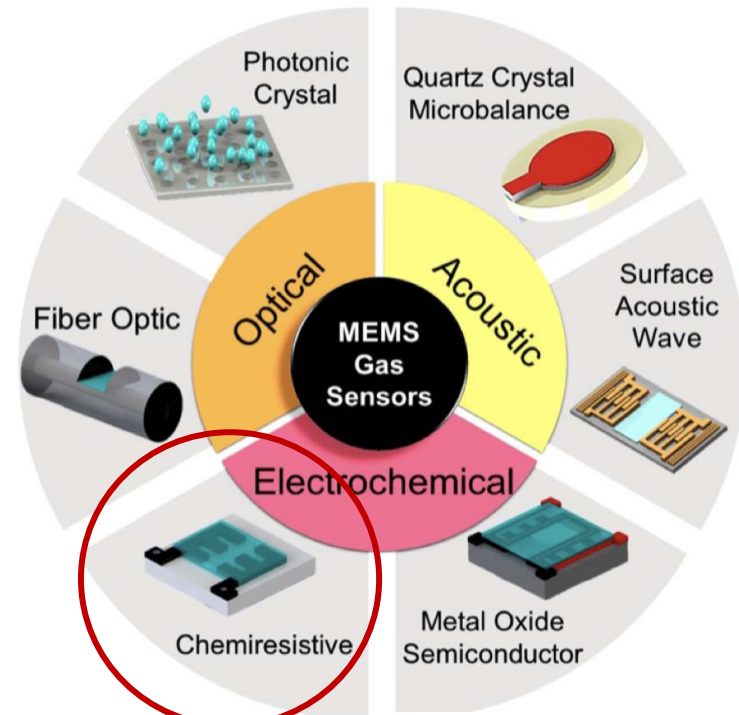


- Good sensitivity & selectivity
- Expensive and bulky
- Requires specialized training

## Chemiresistive gas sensors

- ✓ High sensitivity
- ✓ Cost-effective
- ✓ Compact size
- ✓ Simplicity
- ✓ User-friendly, even for patients

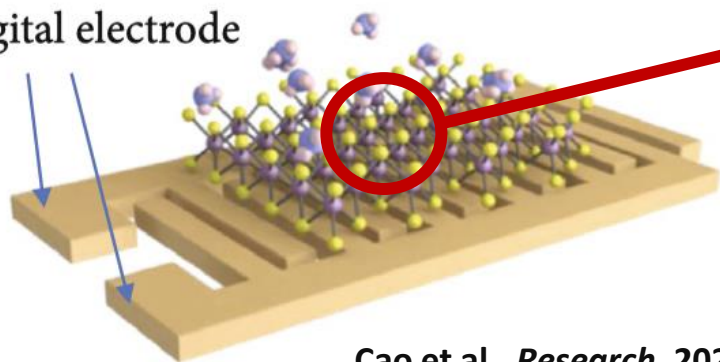
**Make it possible**



Heng et al., Science 385, 954–961 (2024)

# Their sensing mechanism and challenge

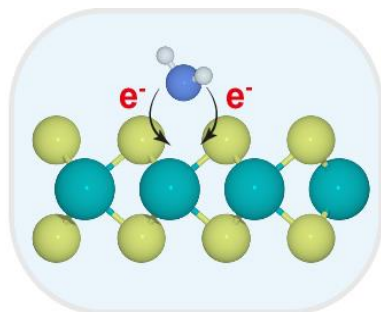
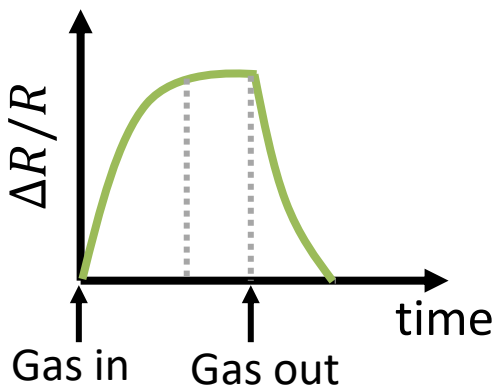
Interdigital electrode



Cao et al., *Research*, 2021.

Chemiresistive gas sensor

**Working principle:** change in electrical resistance due to gas adsorption.



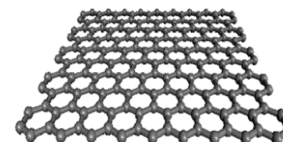
Charge Transfer

*npj Computational Materials*  
| (2024)10:138

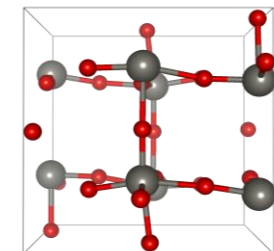
➤ **Sensing material** is the **heart** of a **chemiresistive gas sensor**.

➤ Most used in this filed :

- Carbon-based *Graphene*...



- Metal oxide *WO<sub>3</sub>*...

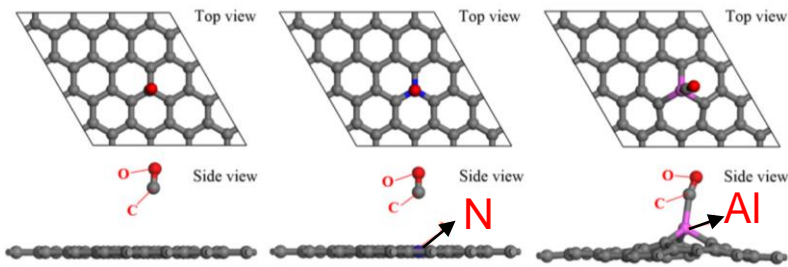


✓ Good sensitivity: 1ppm

☹ No matter which material, the **common challenge** in chemiresistive gas sensor is the **limited selectivity**.

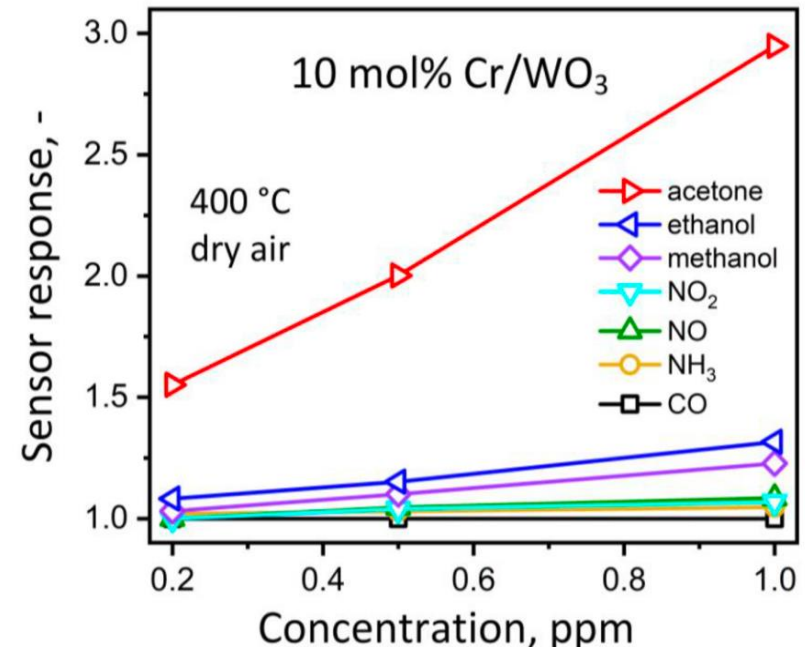
# Previous study on methods to improve sensing performance

❖ Al-doped graphene is more sensitive to CO [1]



Adsorption system	$E_{ad}$ (eV)	$D$ (Å)	$\Delta Q$ (e)
CO on pristine graphene	-0.0102	3.8561	-0.0011
CO on N-doped graphene	-0.0261	3.5540	-0.0027
CO on Al-doped graphene	-2.6928	2.0623	0.2346

❖ Doping Cr to  $WO_3$  and enhanced acetone sensing [2].



## Problems:

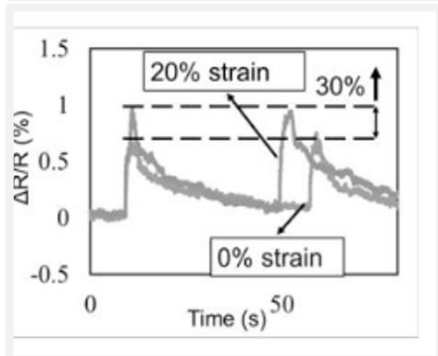
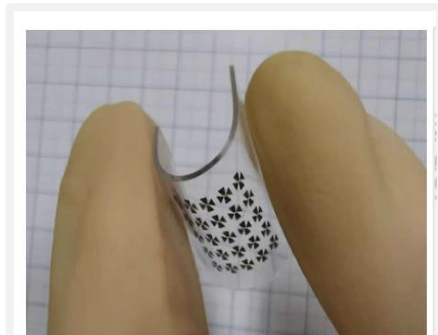
- ❑ Only effective to specific kind of gas
- ❑ Reduce the charge carrier mobility
- ❑ Requires extensive testing for suitable dopants

➔ Demands a high degree of control over functionalization

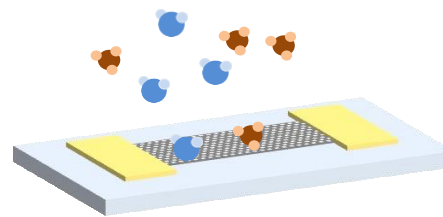
# Previous study on the strain-dependent adsorption behaviour and research gap

- ❖ **Strain engineering** is popular but limited in gas sensing filed.
- ❖ **Our lab** recent work: strain can change the **electrochemical properties** of chemiresistive gas sensor [1~2]

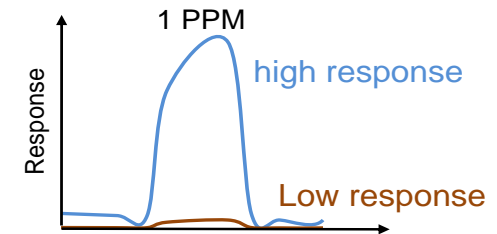
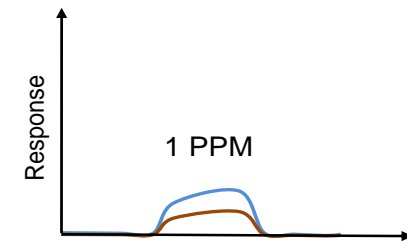
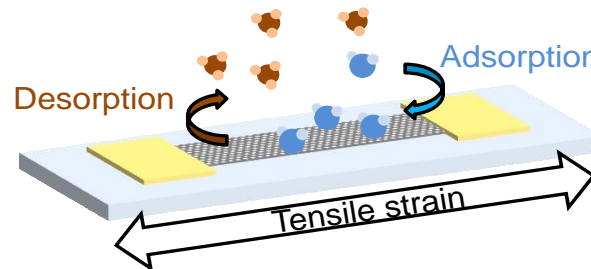
**Hint:** provide the possibility of controlling the gas adsorption behavior on graphene using strain.



- Graphene + H<sub>2</sub>O



It is **difficult to distinguish** the gas type from the similar response



20% strain → Sensitivity  
Improved over 30%

**Gap:** How to understand the **mechanism** of strain modulated adsorption and whether this can be **generalized across different sensing materials** ?

[1] Xiangyu Qiao *et al.* IMECE2020-23581.

[2] Xiangyu Qiao *et al.* IMECE2023-112231.

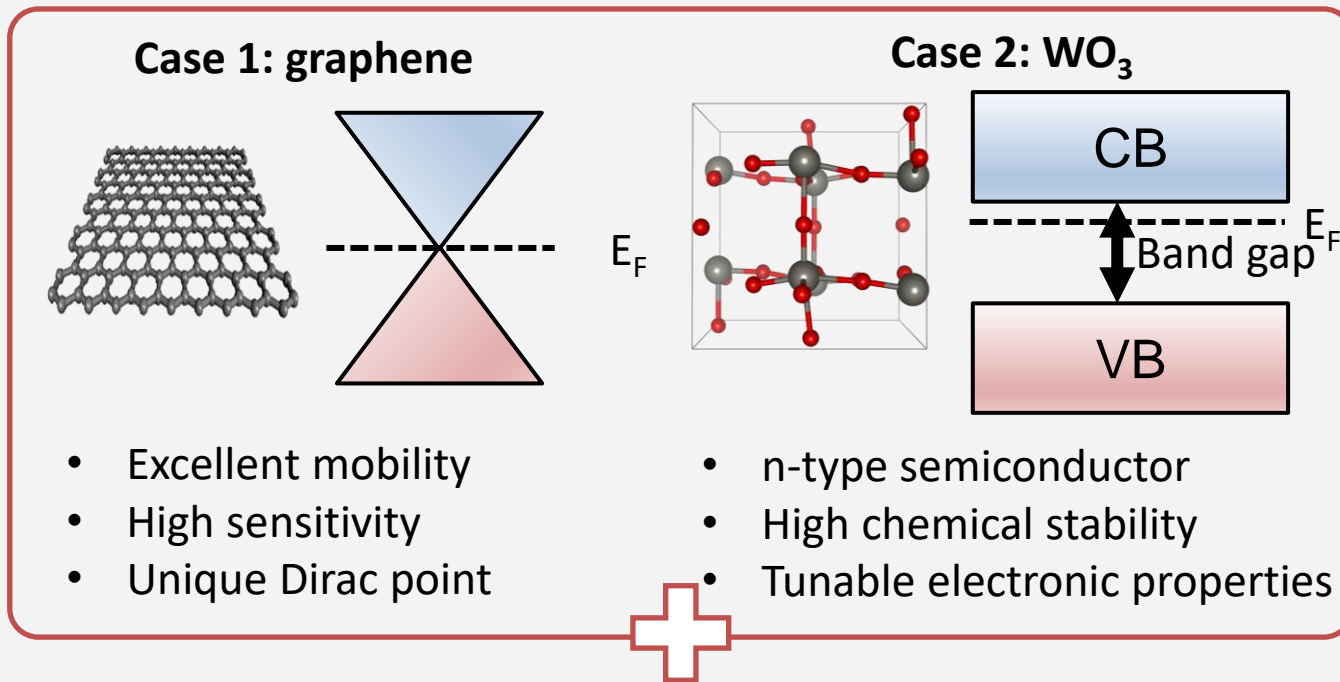
# Proposal for strain-controlled chemoresistive gas sensors from electronic band structure modulation

LUMO

---

HOMO

Donor molecules



LUMO

---

HOMO

Acceptor molecules

+

Strain control

## ❖ My Proposal:

- Strain can modulate materials electronic band structures (Dirac point position of graphene, CB/VB edge of WO<sub>3</sub>)
- Their band alignment with molecular energy levels would be changed
- The gas adsorption on these materials should be tuned

# Objective of this study

Establishment of a design guideline for strain-controlled chemiresistive gas sensors based on first-principles band alignment predictions, focusing on graphene and  $\text{WO}_3$ .

1. Develop an **accurate simulation framework** for understanding strain-controlled gas adsorption systems.
2. Electronic structure analyze the effect of **mechanical strain** on gas adsorption behavior in **graphene**.
3. First-principles investigate how **structure defects** affect gas sensing performance in **strain-modulated graphene**.
4. Extend the exploration of **strain-controlled** approach to  **$\text{WO}_3$** , as well as the effect of **oxygen defects**, comparing them with graphene for broader insights.



# Content

- Chapter 1. Introduction and objective of this study
- Chapter 2. First-principles study of the effect of **strain** on gas adsorption in **graphene**
- Chapter 3. Electronic band structure investigation of the role of **defect** in **strain**-modulated **graphene** gas sensors
- Chapter 4. From graphene to **WO<sub>3</sub>**: exploring the design guideline for **strain-controlled** chemiresistive gas sensors (**on-going...**)
- Chapter 5. Summary and outlook

## Objective

Understand the impact of **mechanical strain** on gas adsorption behavior in **graphene** from first-principles calculation

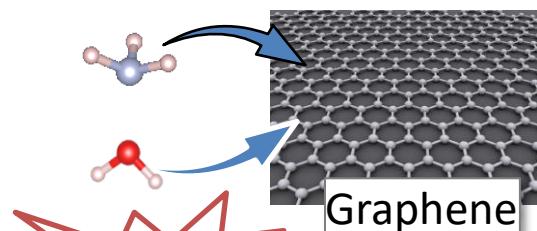
## Key Requirements:

1. Establishing a simulation framework for evaluating the strain-modulated gas adsorption systems
2. Understanding the effect of strain on gas adsorption in graphene
3. Validating strain effects through comparison with experimental results

# Existing issues to develop a strain-controlled chemiresistive gas sensor

## Clarification of the adsorption-induced change of graphene's electrical properties

Adsorption of certain gas

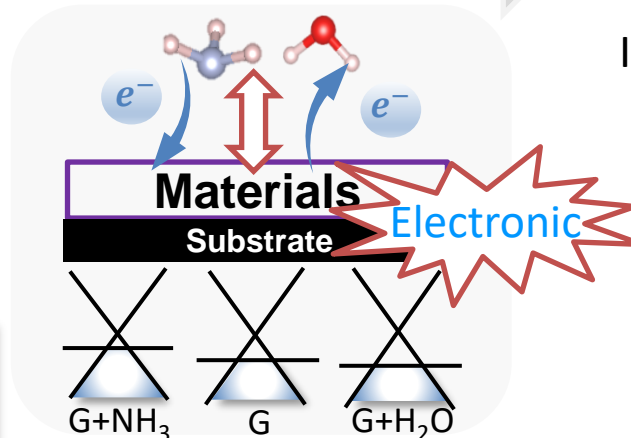


Graphene

Chemical

Original Idea

Charge transfer



Materials Substrate

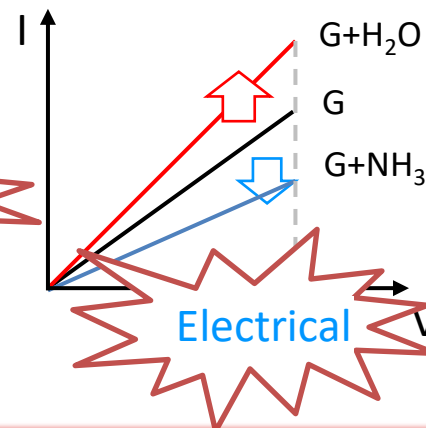
Electronic

G+NH<sub>3</sub>

G

G+H<sub>2</sub>O

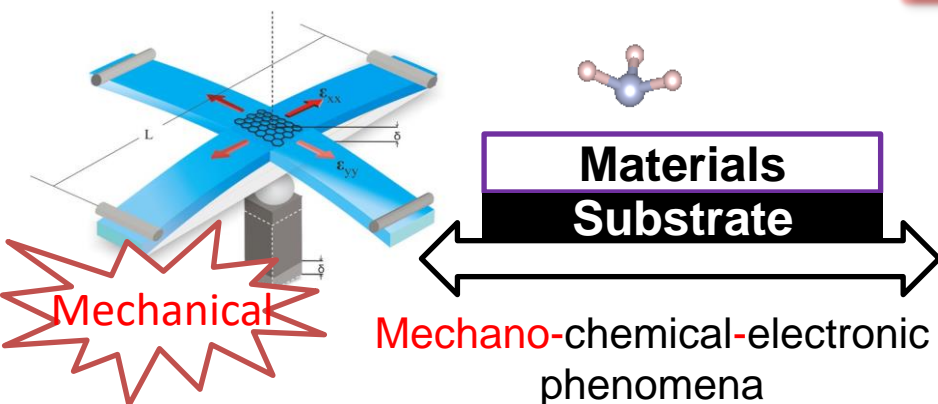
Measured I-V change



Electrical

How to clarify the **strain-induced** change of the adsorption properties of graphene?

Selectivity of gas molecules by applied strain



Mechanical

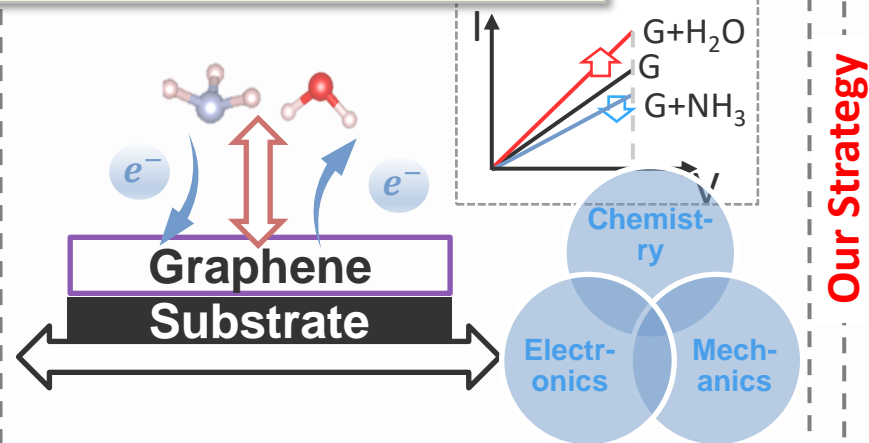
Materials Substrate

Mechano-chemical-electronic phenomena

1. Chemical part:
  - Gas adsorption on graphene
2. Electronic part:
  - Charge transfer among them
3. Electrical part:
  - Change of I-V characteristics
4. Mechanical part:
  - Application of strain

# Strategy and computational method

Mechano-chemical-electronic phenomena



Our Strategy

Step1: Evaluation of gas adsorption behaviors



- Chemical part: Gas adsorption energy
- Electronic part: Charge transfer

Step2: Investigation of the **strain effect** on gas adsorption behaviors



- Strain dependence of **adsorption energy**
- Strain dependence of **charge transfer**
- Strain dependence of **band structures**

Step3: Mechanism discussions

## Density Functional Theory (DFT) Calculations

### Settings

- VASP code
- $E_{xc}$ : GGA-PBE
- Cutoff energy: 500 eV
- EDIFF =  $10^{-5}$  eV
- EDIFFG = 0.01 eV/Å
- K-points:  
4 x 4 x 1 for relaxation  
12 x 12 x 1 for scf

$n(\mathbf{r})$

*Low computational cost*

Kohn-Sham Equation

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\vec{r}) \right) \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$



*Reliable package*

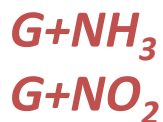
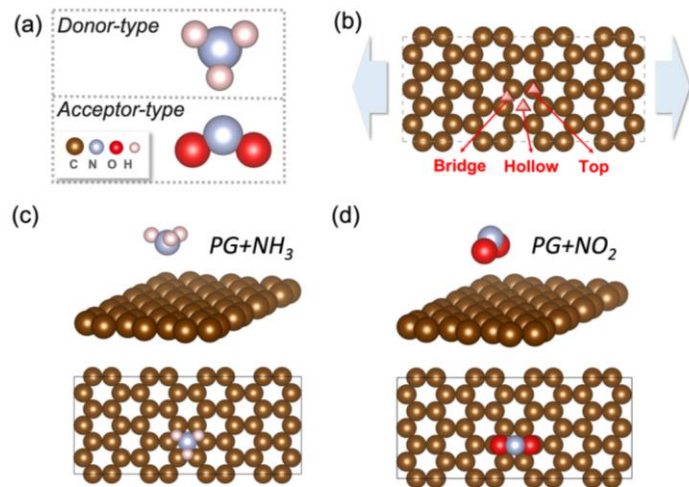
VASP

✓ Electronic/transport properties

(e.g., *Adsorption energy, charge transfer, band structure...*)

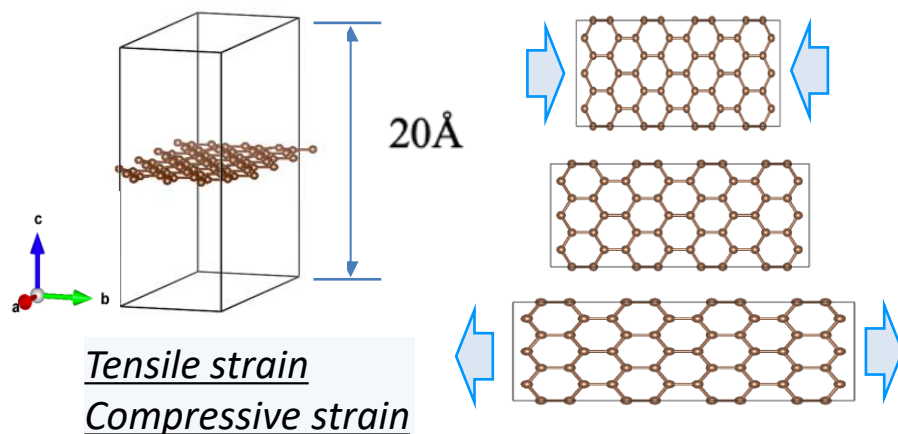
# Computational models and key parameters

## ◆ Possible Gas Adsorption Positions



Molecular  
 Orientations  
 & Sites

## ◆ Application of Uniaxial Strains



## ◆ Key parameters for the evaluation of gas adsorption behavior on graphene

① Adsorption energy,  $E_{ad}$

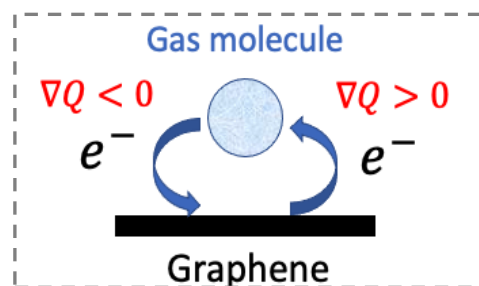
$$E_{ad} = E_{\text{graphene with gas}} - E_{\text{graphene}} - E_{\text{gas molecular}}$$

$$E_{ad} < 0$$

→ adsorption

② Charge transfer,  $\nabla Q$

Bader charge analysis



③ Charge density difference (CDD)

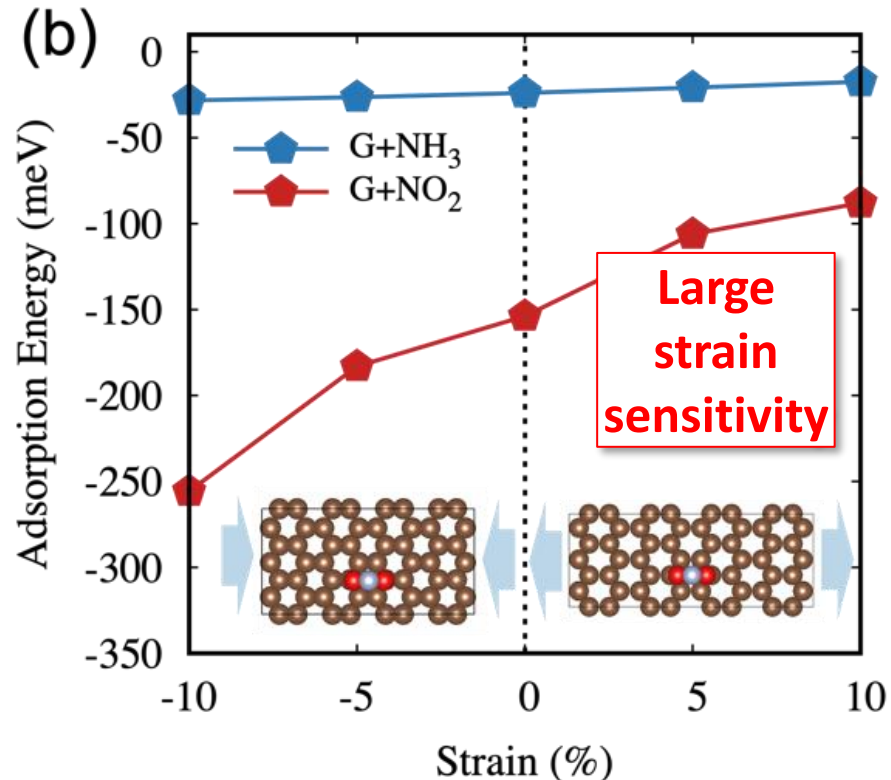
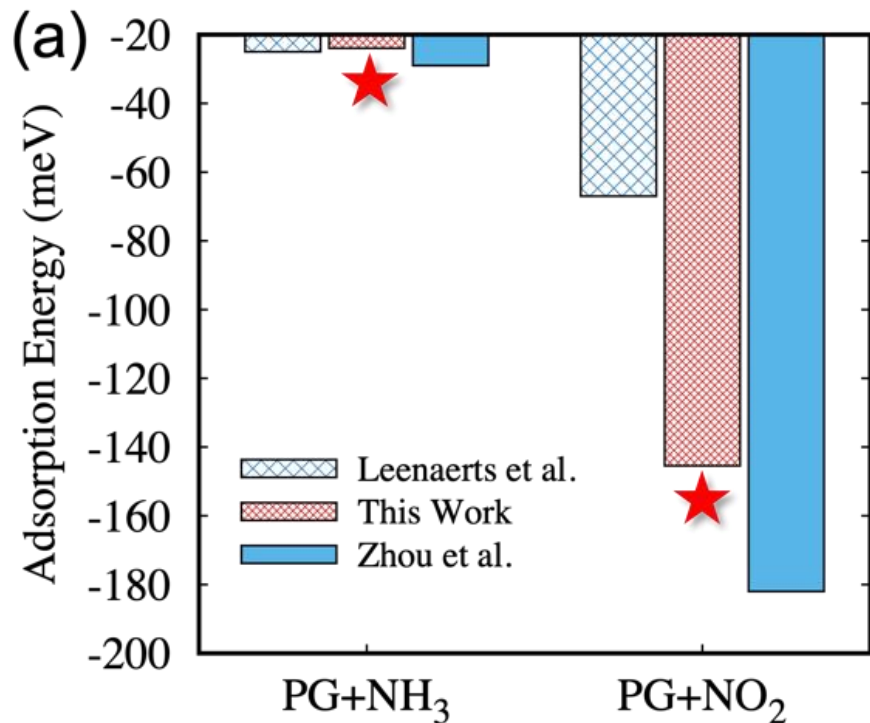
$$\Delta\rho = \rho_{\text{graphene with gas}} - \rho_{\text{graphene}} - \rho_{\text{gas molecular}}$$

From the view of  
 orbital interactions

# Variation of adsorption energy with applied strain

❖ Without strain: good agreement

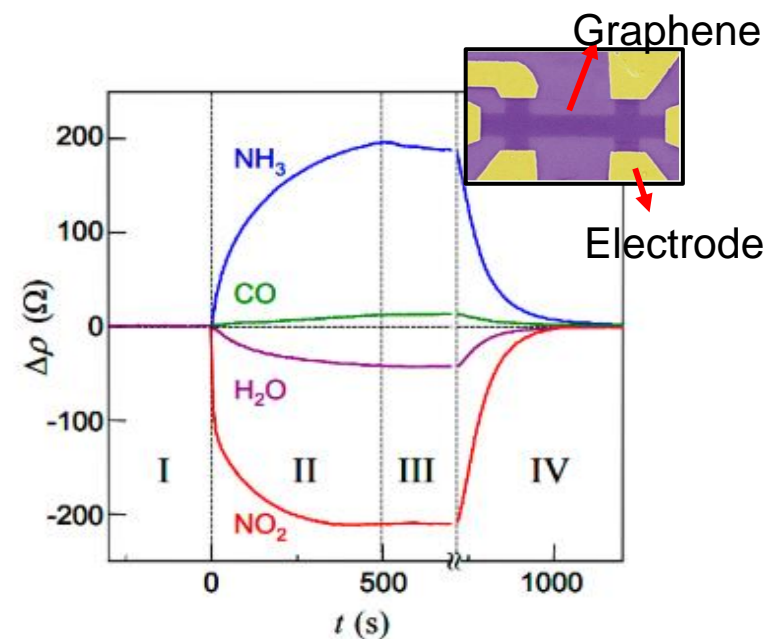
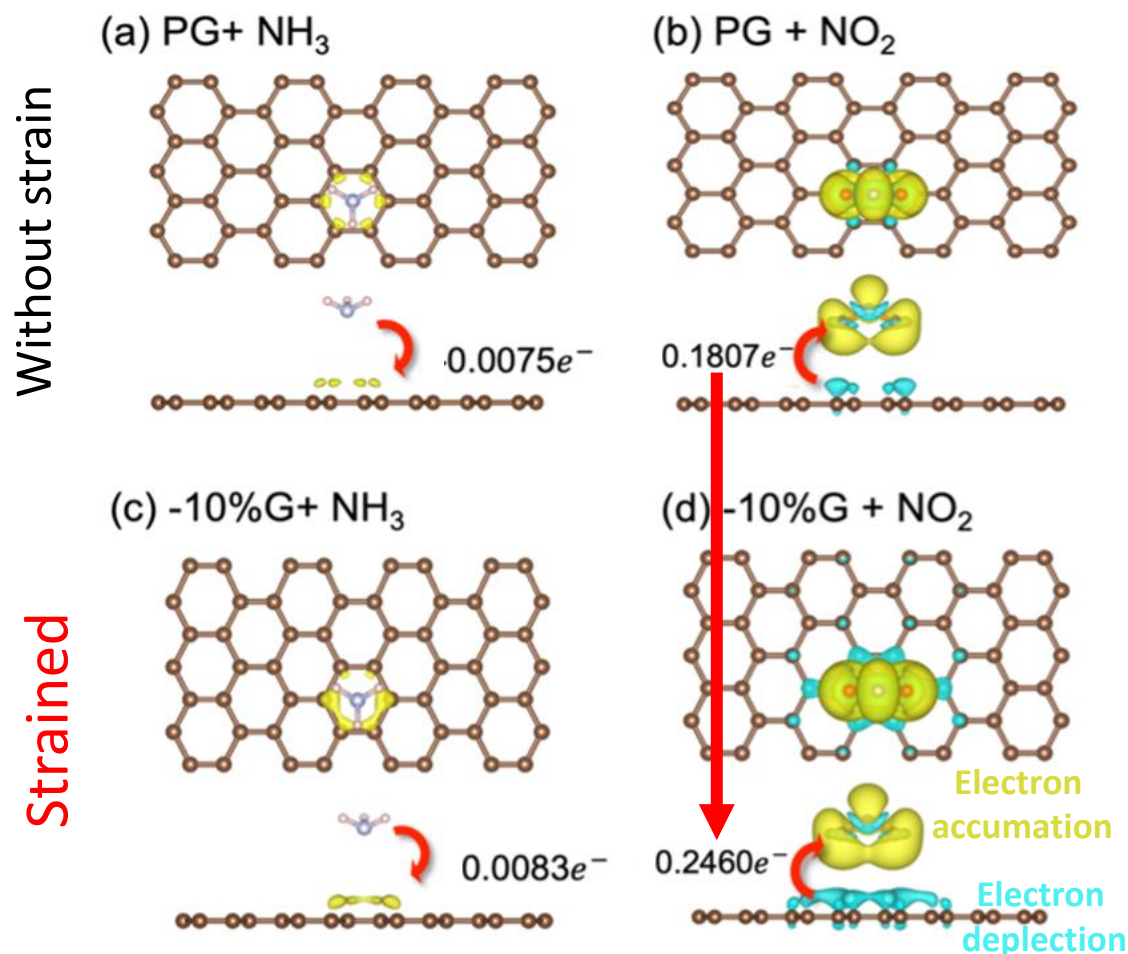
❖ Strain-induced change of  $E_{ad}$



Different gas species have different **strain sensitivity**

→ Can be used as an **important factor to improve the selectivity**

Take the *compressive strain* for example:



Scheden et.al (2007)

Experiment:

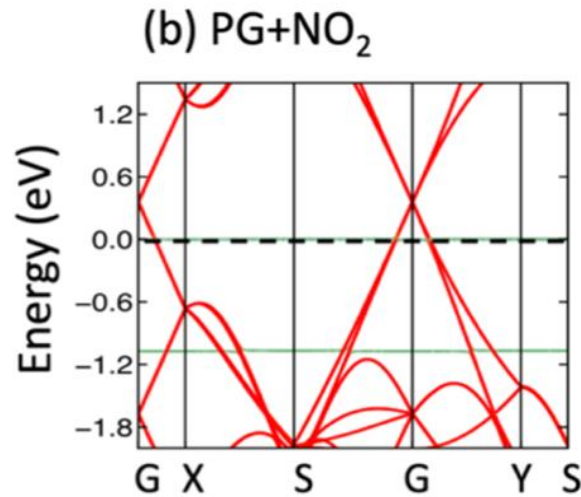
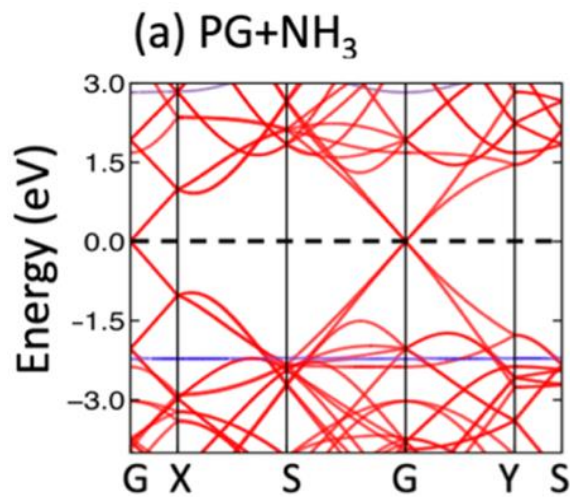
G + NH<sub>3</sub>: resistance increased

G + NO<sub>2</sub>: resistance decreased

Strain-induced change of **charge transfer** between NO<sub>2</sub> and graphene is much larger than that on NH<sub>3</sub>.

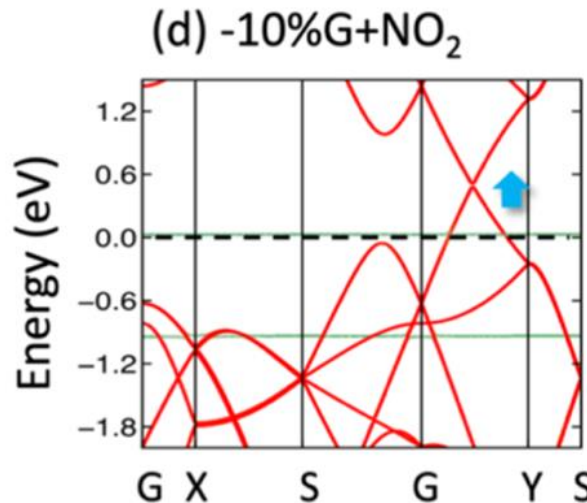
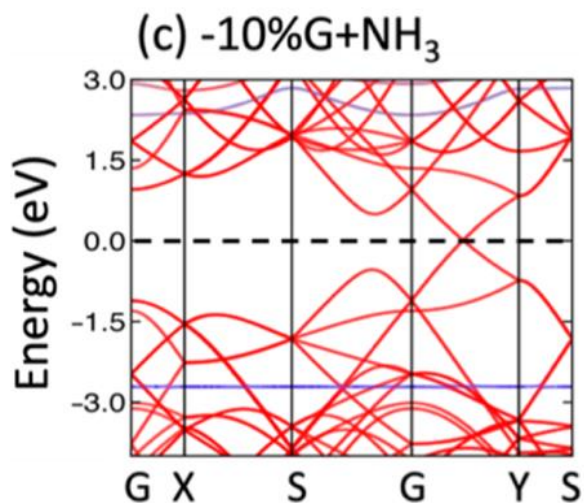
# Variation of band structure under the applied strain


Without strain



NO<sub>2</sub> on **pristine** G  
 → p-type doping

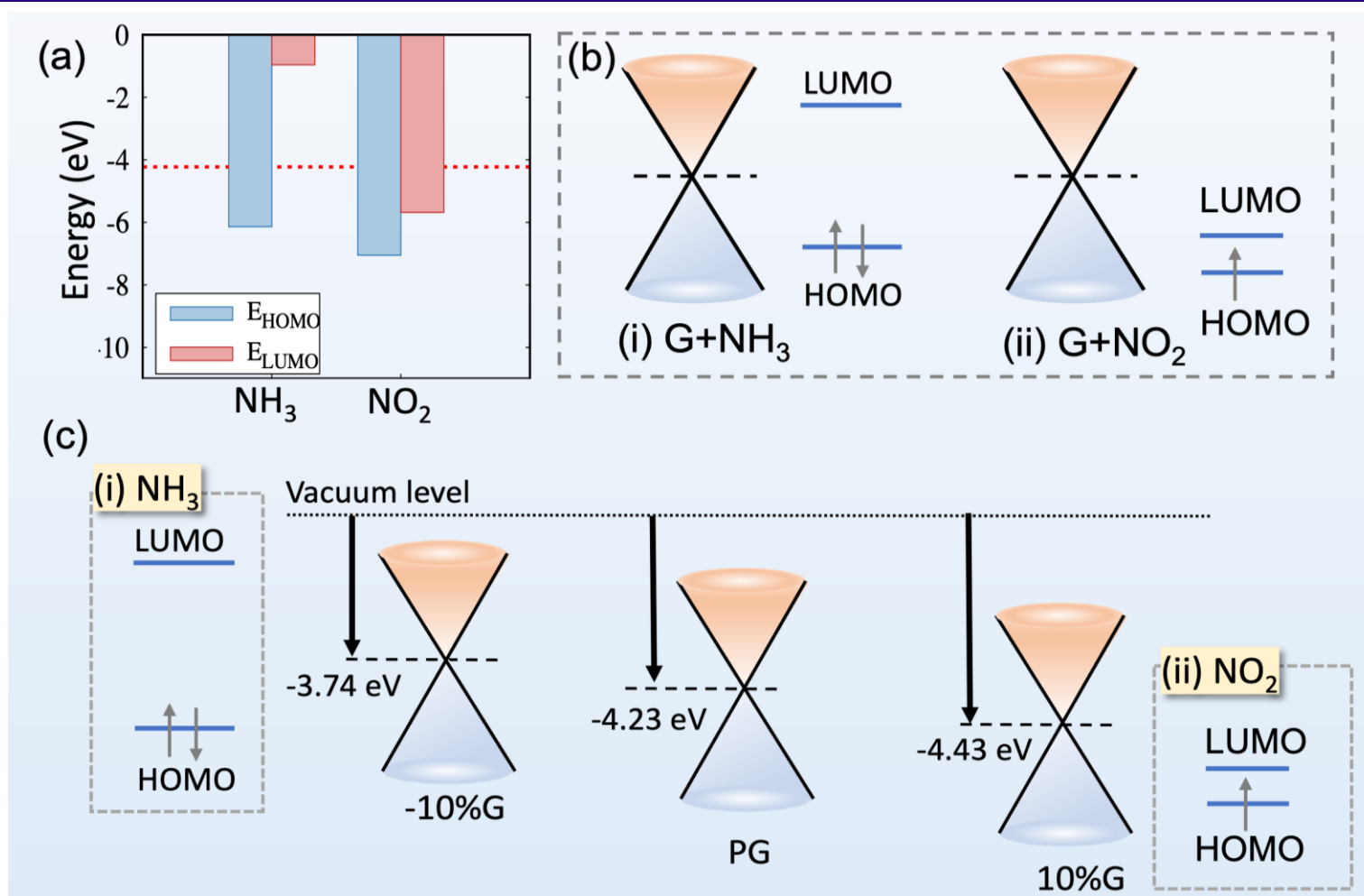
Strained



NO<sub>2</sub> on **strained** G  
 → p-type doping 

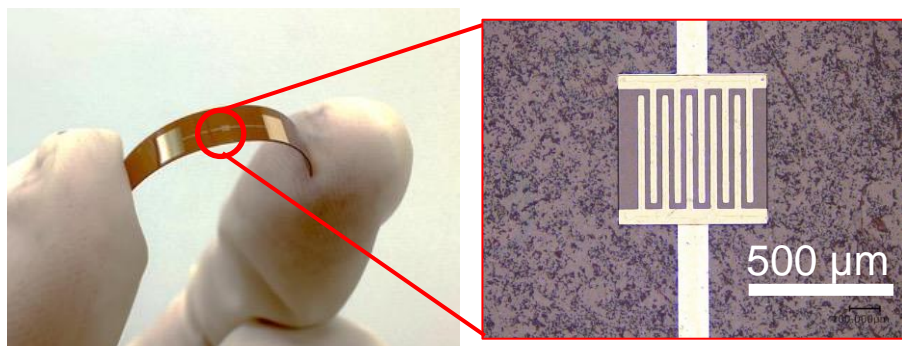
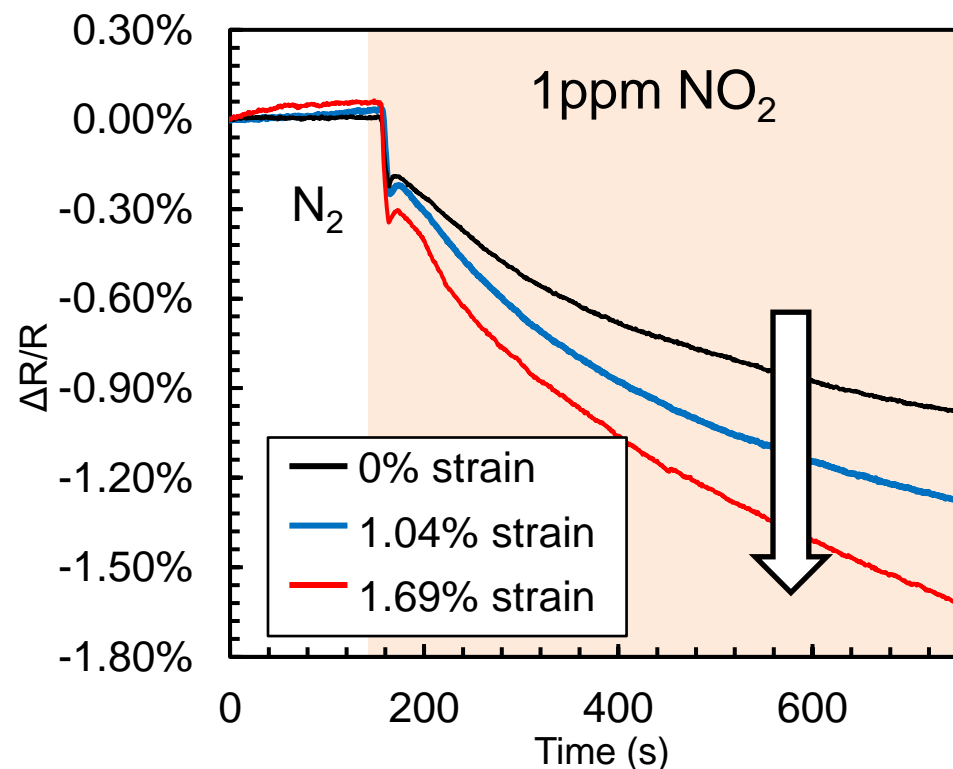
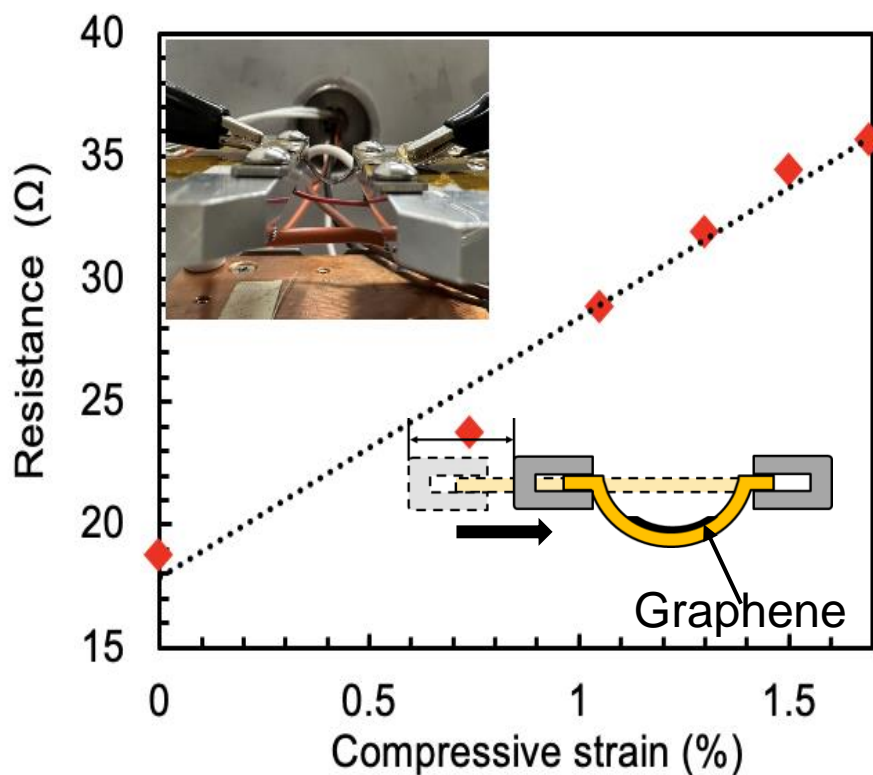
The effect of strain on the **band structure** of NO<sub>2</sub> on graphene is more significant, while the effect on NH<sub>3</sub> is almost neglected.





❖ Strain could shift graphene Dirac point, changing the energy difference between molecular HOMO/LUMO and Graphene's E-Fermi, thus tuning the binding between gas and graphene.

# Validation by experiments



- ✓ CVD graphene was transferred onto a **flexible PI substrate**, and different **strains** were applied through **bending**.
- ✓ Under 1 ppm  $\text{NO}_2$ , strain was confirmed to **enhance its sensitivity**.

# Summary of chapter 2.

## Objective

Understand the impact of **mechanical strain** on gas adsorption behavior in **graphene** from DFT calculation

1. Without strains, the calculated results show good consistent with both simulation and experiment work, **confirming the reliability of the established simulation framework.**
2. The **strain effect** was found to be **gas-species dependent**, with a **significantly larger effect on NO<sub>2</sub>** compared to NH<sub>3</sub>, explained by band structure analysis.
3. **Our experimental validation** further **supports** the simulated trend/prediction.

# Role of defects in strain-modulated graphene gas sensors

## Objective

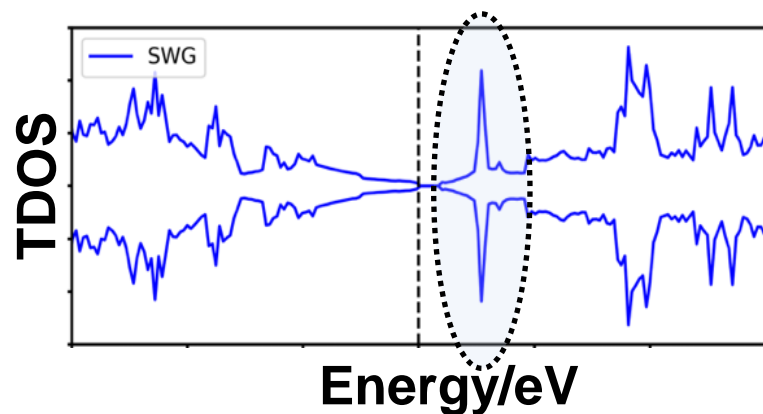
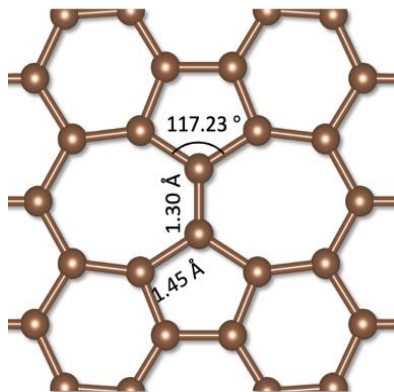
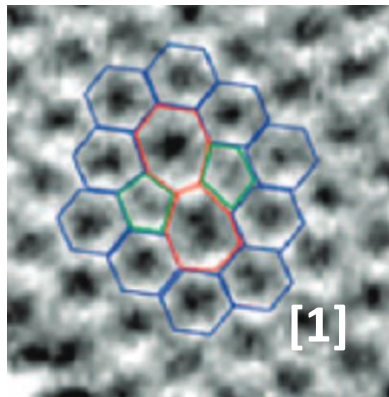
Investigate how **defects** influence **strain-modulated** gas sensing performance in **graphene**

## Key Requirements:

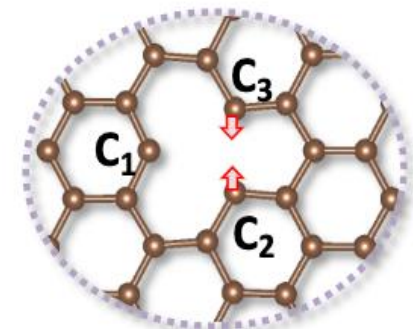
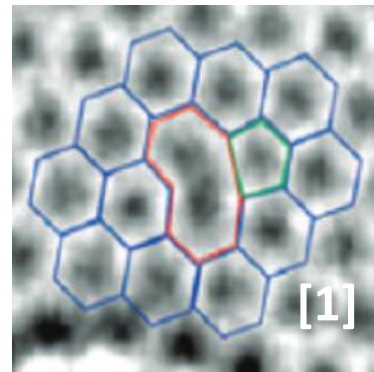
1. Understanding the effects of common **structure defects** (Stone-wales, Single vacancy) on **graphene**.
2. Analyze the gas adsorption behaviour of graphene **in the presence of these defects**.
3. Elucidation of mechanism of gas adsorption underlying considering **both strain and defects**.

# Effect of SW and SV defects on graphene's properties

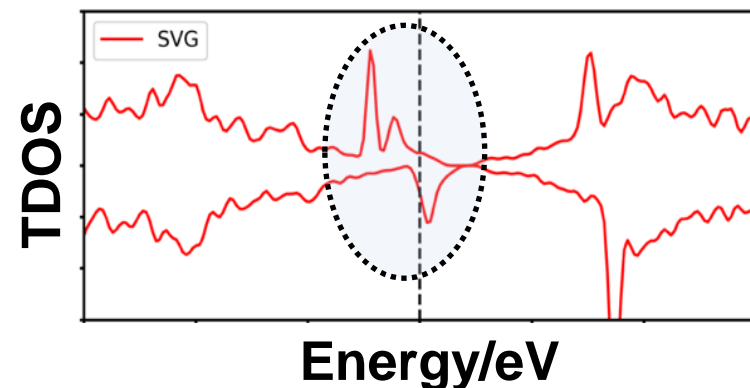
## Stone-Wales Graphene (SWG)



## Single Vacancy Graphene (SVG)

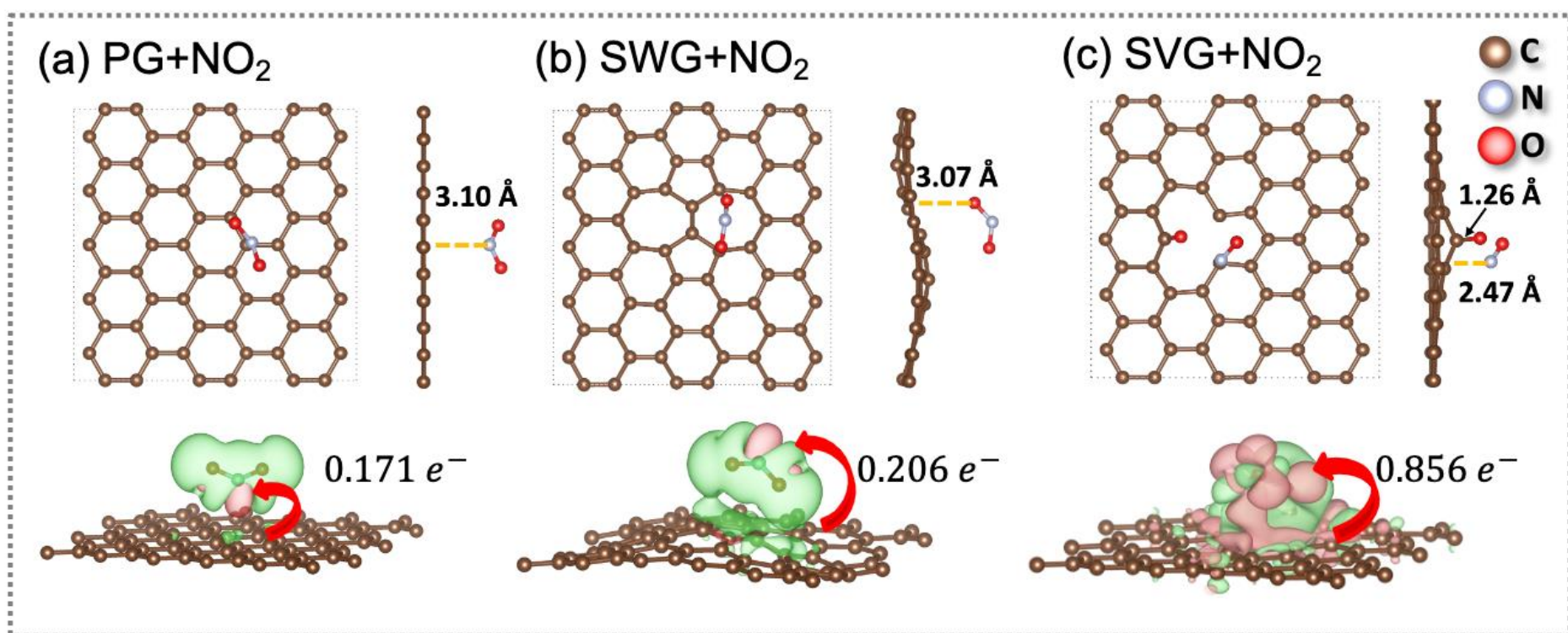


*Jahn-Teller distortion*



SW defect introduce states above  $\sim 0.5$  eV near E-Fermi, while SV graphene exhibit more pronounced defect states at E-Fermi.

# Enhanced NO<sub>2</sub> adsorption on defective graphene



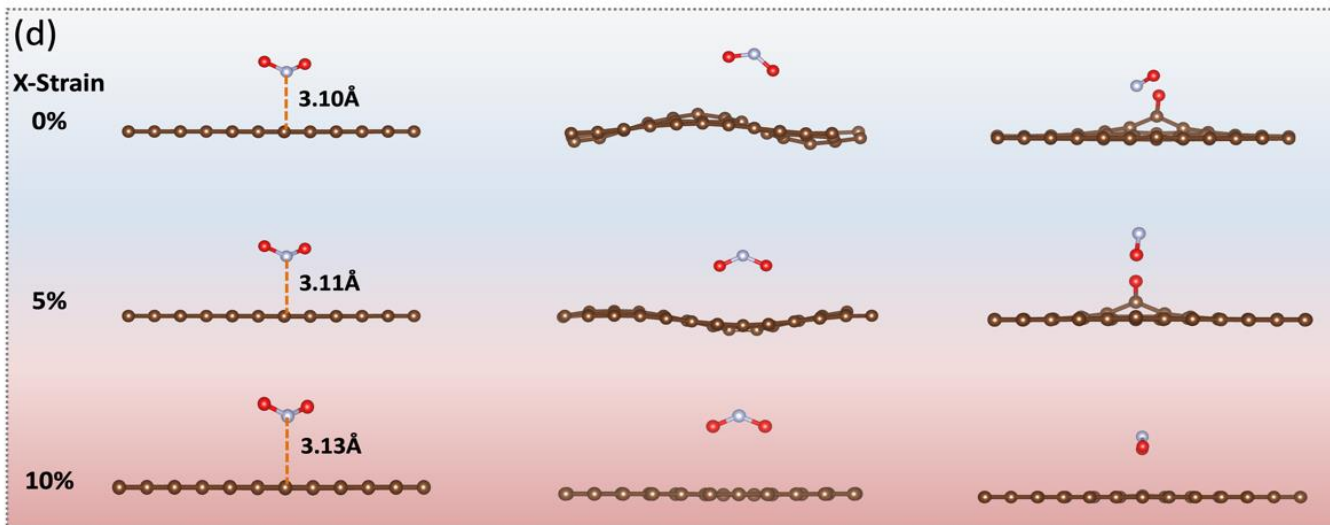
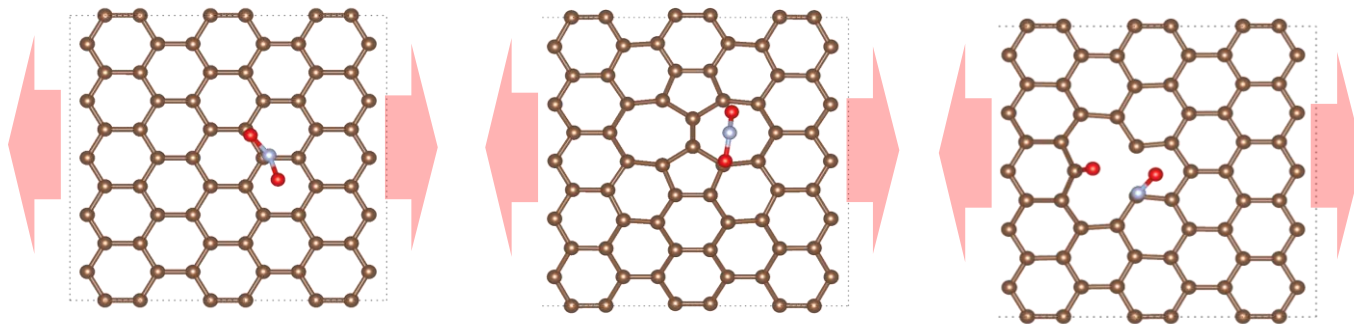
## ❖ Adsorption energy

$$E_{ad} = E_{total} - E_{DG} - E_{gas}$$

Systems	E <sub>sys</sub> /eV	E <sub>slab</sub> /eV	E <sub>gas</sub> /eV	E <sub>ad</sub> /eV
PG+NO <sub>2</sub>	-574.147	-555.518	-18.372	-0.257
SWG+NO <sub>2</sub>	-569.142	-549.719	-18.372	-1.050
SVG+NO <sub>2</sub>	-559.355	-538.613	-18.372	-2.370

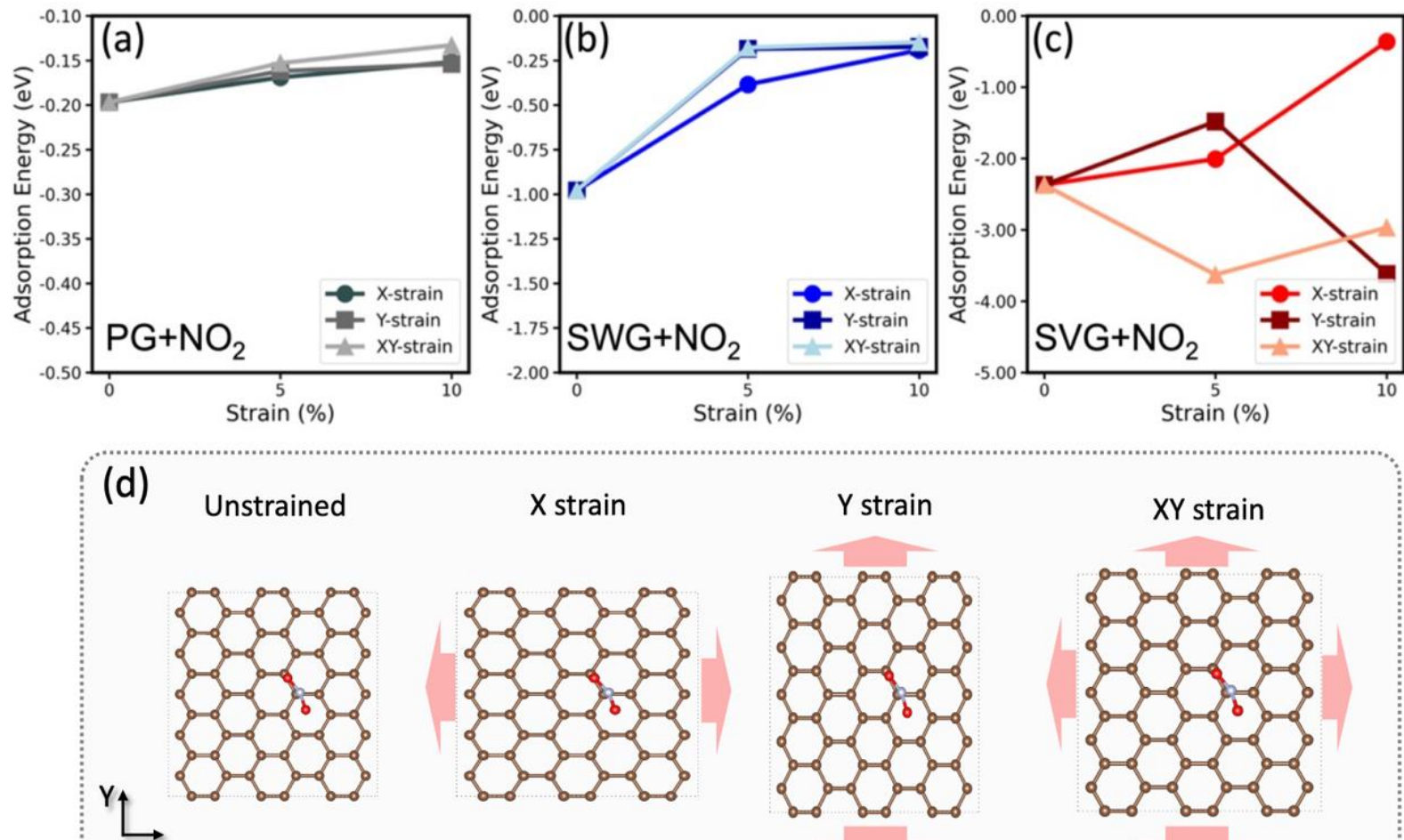
- Both SWG and SVG exhibit **enhanced NO<sub>2</sub> adsorption** than that on PG.
- On SVG, **NO<sub>2</sub> → NO+O** due to the presence of dangling bonds.

## ❖ X-strains on PG/SWG/SVG+ $\text{NO}_2$



Under tensile strain along the X-direction,  $\text{NO}_2$  binding was weakened on all surfaces, with SVG transitioning from dissociative to molecular adsorption.

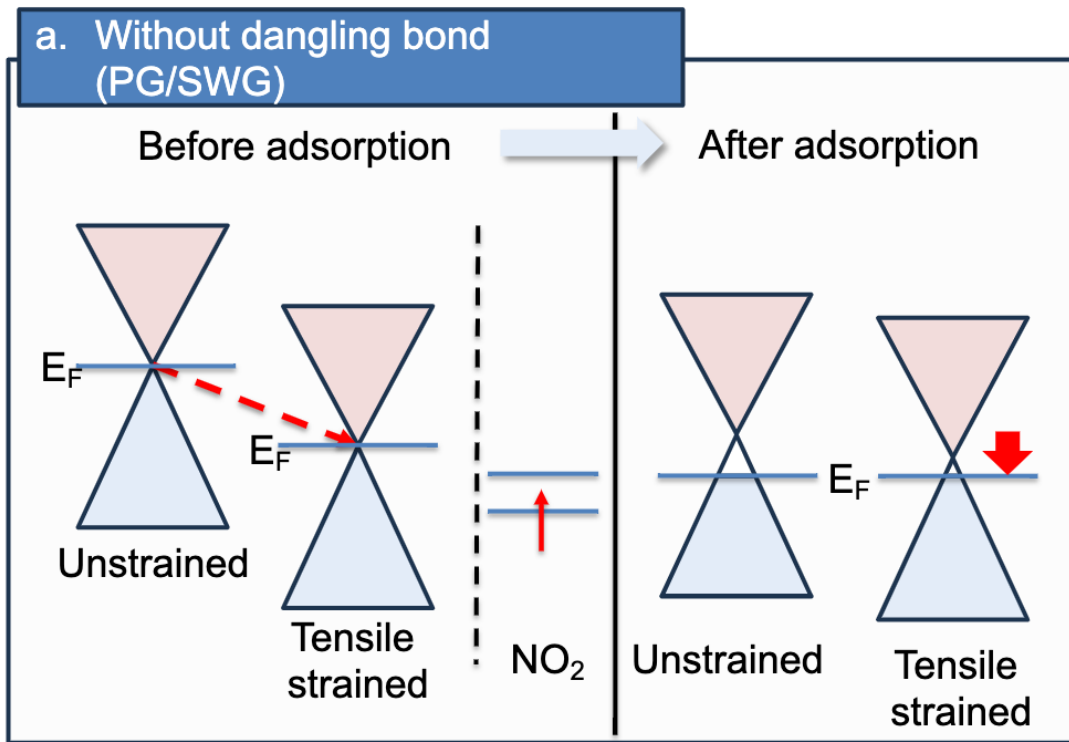
# Variation of $\text{NO}_2$ adsorption on defective graphene under different strains



The adsorption of  $\text{NO}_2$  on PG and SWG shows a similar trend in response to strain, while **SVG** exhibits a **dependence on the direction** of the applied **strain**.

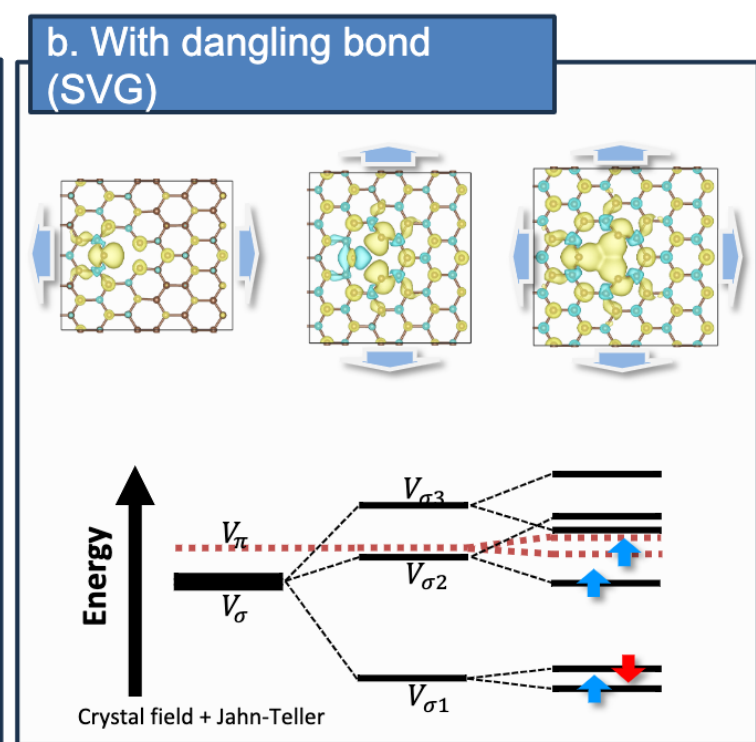


# Mechanism discussions



Principle 1:

Relative position between molecular energy level and graphene's fermi level.



Principle 2:

Depends on the strain direction and strain-induced change in split  $\pi$  bonds.

- The strain effect on  $NO_2$  adsorption is influenced by dangling bonds at defect sites, with **PG/SWG following the Chap. 2 mechanism**.
- While **SVG exhibits strain-dependent spin density** variations, affecting its sensing capabilities.

# Summary of chapter 3.

## Objective

Investigate how **defects** influence **strain-modulated** gas sensing performance in **graphene**

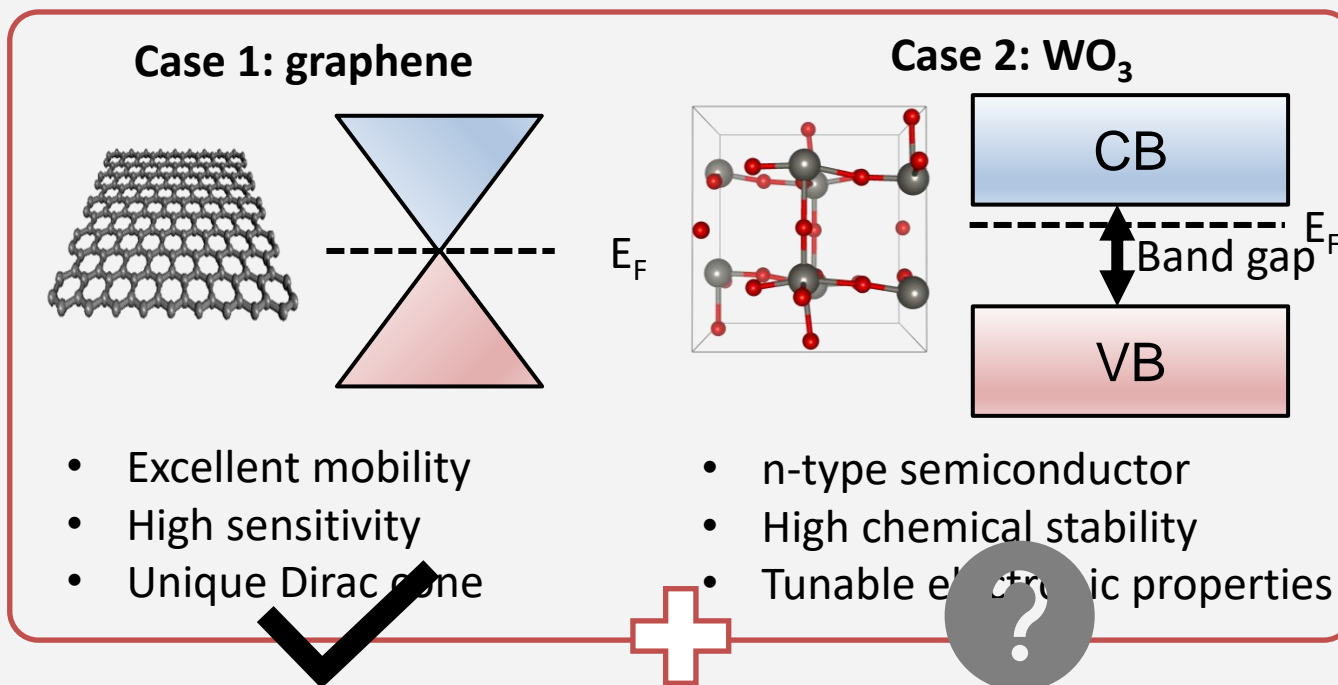
1. Both Stone-Wales (SW) and single-vacancy (SV) defects enhance  $\text{NO}_2$  sensing, with SVG facilitating  $\text{NO}_2$  dissociation due to dangling bonds.
2. Strain effects were systematically studied, showing similar trends for PG/SWG but direction-dependent behavior for SVG.
3. The strain-controlled gas sensing mechanism for graphene was refined and extended based on the model proposed in Chapter 2.

# Proposal for strain-controlled chemoresistive gas sensors from electronic band structure modulation

LUMO

HOMO

Donor molecules



LUMO

HOMO

Acceptor molecules

Strain control

✓ In graphene (special Dirac cone structure), strain can modulate the position of Dirac point → achieve molecular orbital matching modulation

□ Now, it is possible to generalize this mechanism to more general semiconductor type electronic structures (WO<sub>3</sub>) ?

## structure driven gas sensors via strain-controlled method

## Objective

Extend the understanding of **strain effects to  $\text{WO}_3$  with oxygen vacancies**, comparing its performance with graphene for **broader insights**.

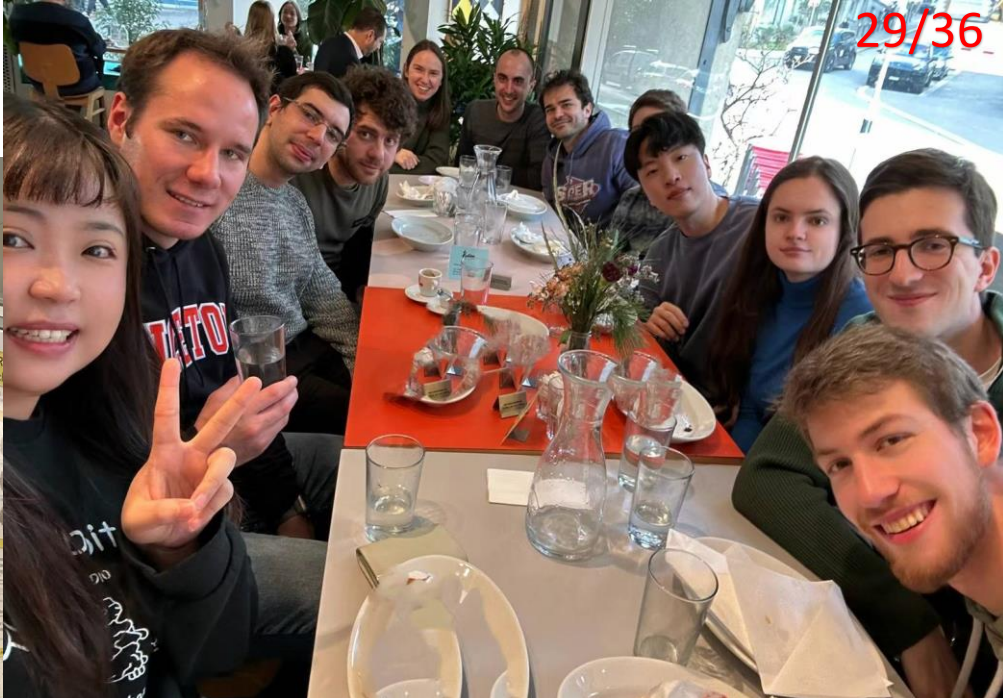
**Experiment**

- **Materials characteriation**
  - Phase composition, XRD
  - Band gap measurement, Uv-vis
  - X-ray absorption fine structures
- **Surface chemistry**
  - In-situ DRIFTS
  - TPD
- **Transduction**
  - Kelvin probe
  - Operando work function measurement

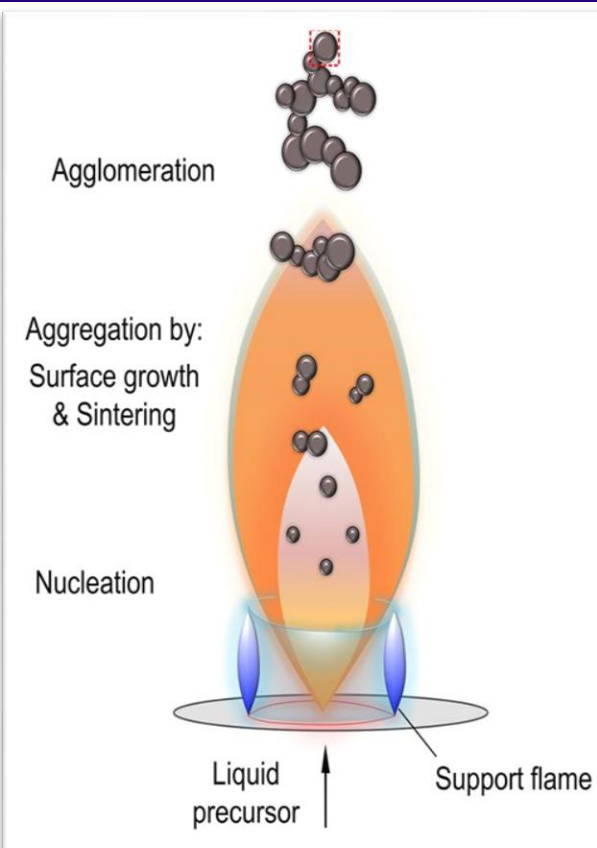
**DFT calculation**

- **Structure properties**
  - Fully relaxed geometry
  - Simulated band structure
- **About surface**
  - Slab model
  - The effect of oxygen vacancy
  - Adsorption energy
- **Electronic properties**
  - Charge density difference
  - Band structure analysis
  - Work function

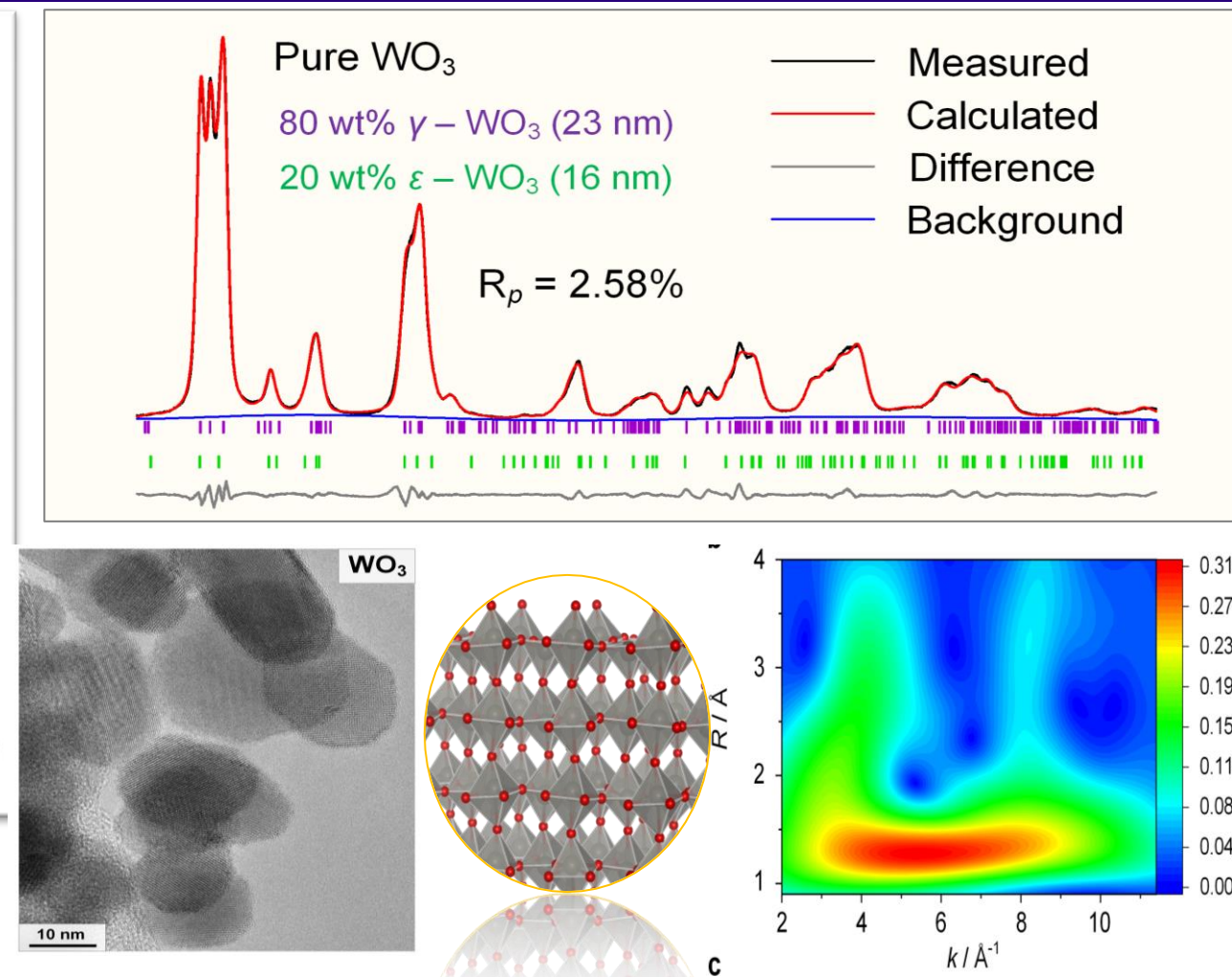
# Collaboration with HSL group at ETH Zurich (9 month visiting and close teamwork)



# Material synthesis and characteristics



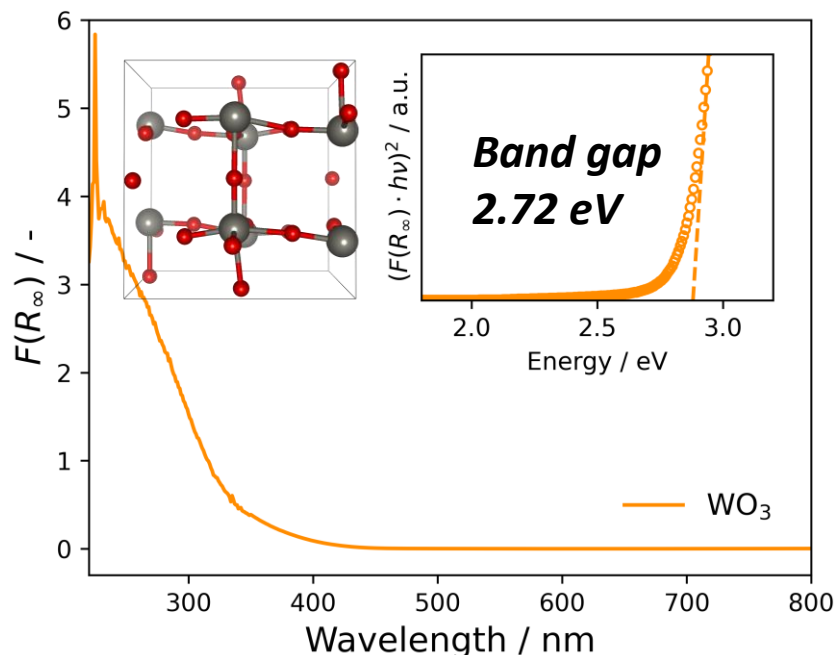
D'Andria, M.; et al.  
*Adv. Sci.* **2024**, *11*, 2308224.



- $\text{WO}_3$  was synthesized using Flame spray pyrolysis (FSP).
- XRD and TEM image indicated the fabricated  $\text{WO}_3$  has high crystallinity.
- X-ray absorption fine structures  $\rightarrow$  a corner-sharing  $\text{WO}_6$  octahedral structure.

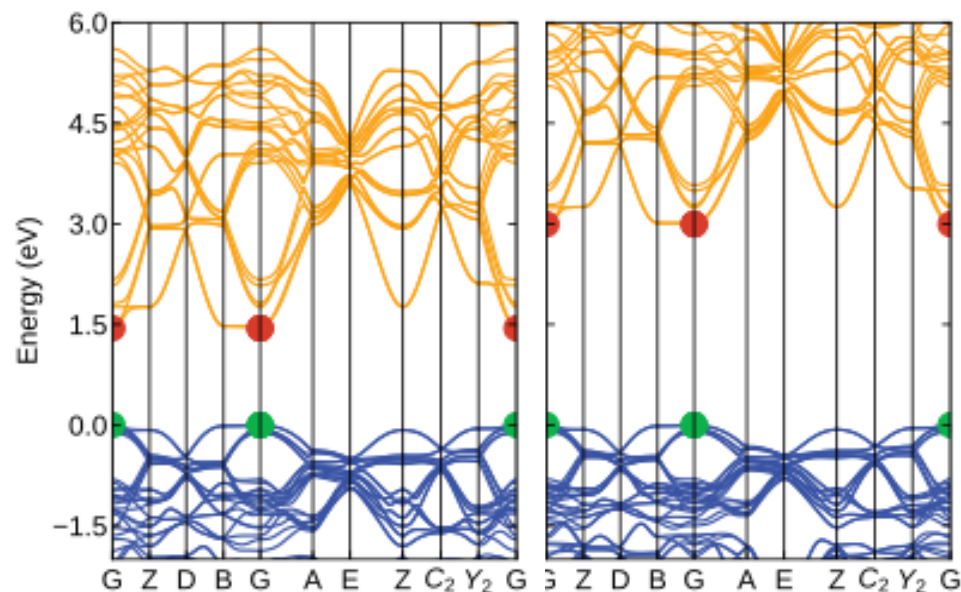
# Measured and DFT-1/2 calculated bandgaps

## Measured band gap of $\text{WO}_3$



- UV-Vis diffuse reflectance spectroscopy
- Analyzing Kubelka-Munk function and Tauc plot → band gap is 2.72 eV

## DFT calculated band structure



DFT  
(GGA-PBE)

$E_g = 1.44 \text{ eV}$

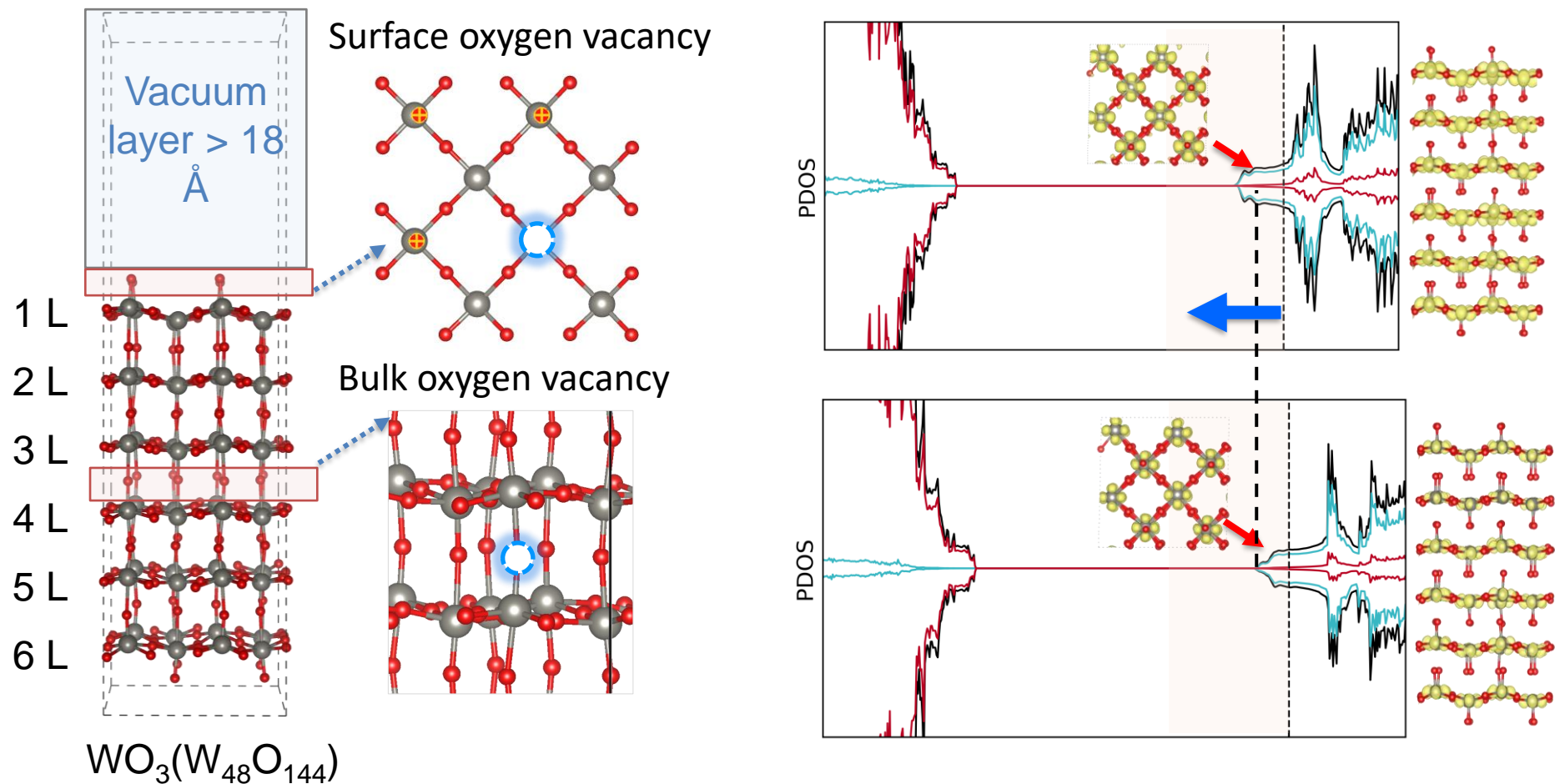
✓ DFT-1/2<sup>[1~2]</sup>  
(GGA-PBE-1/2)

**$E_g = 2.99 \text{ eV}$**



Our measured bandgaps of  $\text{WO}_3$  v.s. DFT calculated

→ Good consistent with previous report, with the range of 2.6~3.2 eV<sup>[3]</sup>.

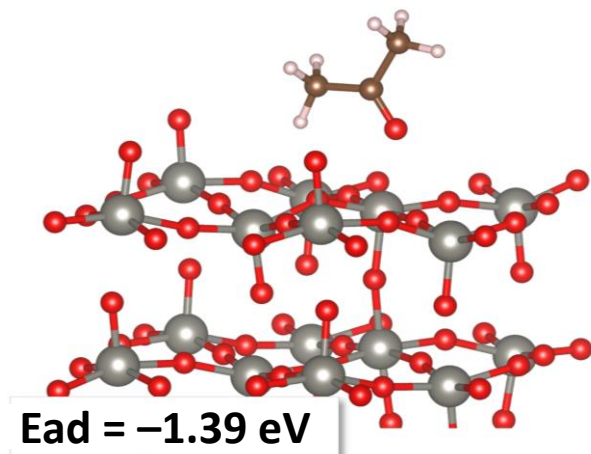
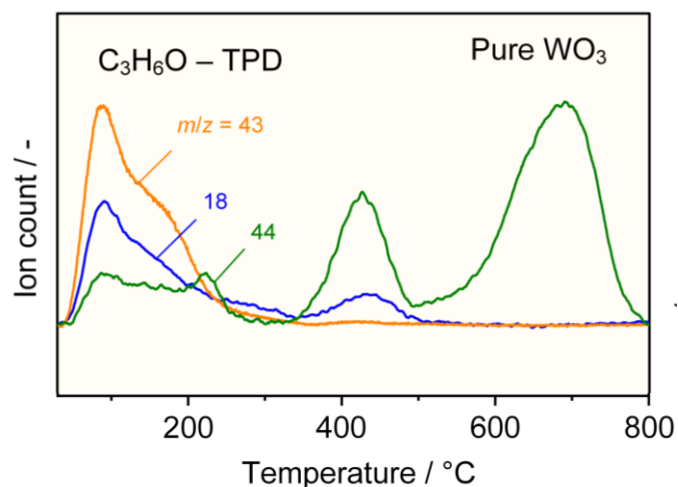


Partial charge density ( $E_{F-1}$  to  $E_F$ ) indicates that the electrons around Fermi level are distributed throughout the system as free electrons rather than localized states.

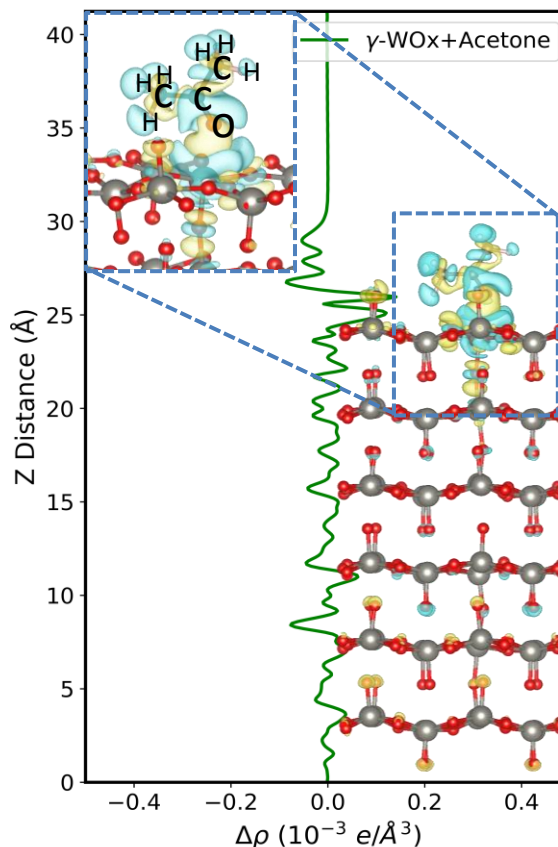


# Surface chemistry

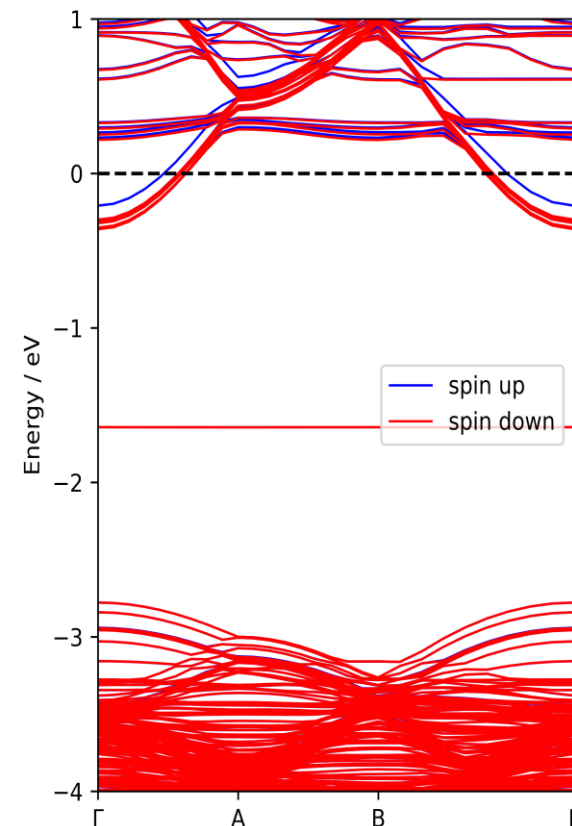
## TPD (Temperature Programmed Desorption) measurement



## Electronic properties analysis



Electron transfer  
between gas and WO<sub>3</sub>



Electronic  
band structure



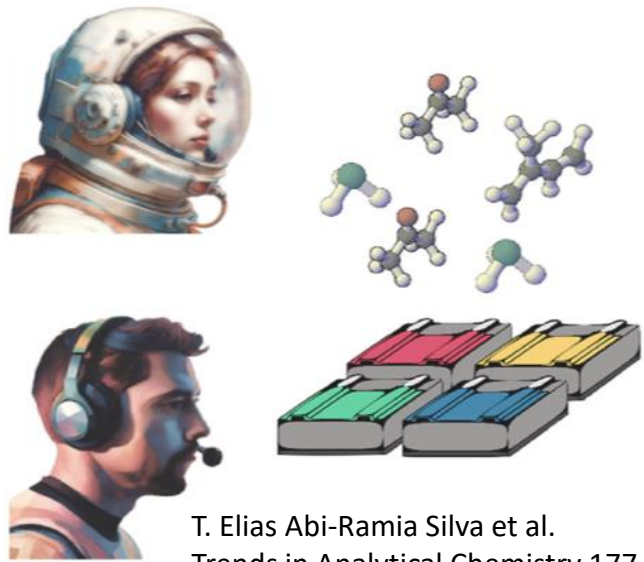
The **binding energy** is **appropriate** and should lead to a **decrease in measured resistivity** when acetone (a reducing agent) interacts with WO<sub>3</sub> (an n-type semiconductor)

Effect of strain on  $WO_3$  and its gas sensing properties and further experimental validations (on-going...)

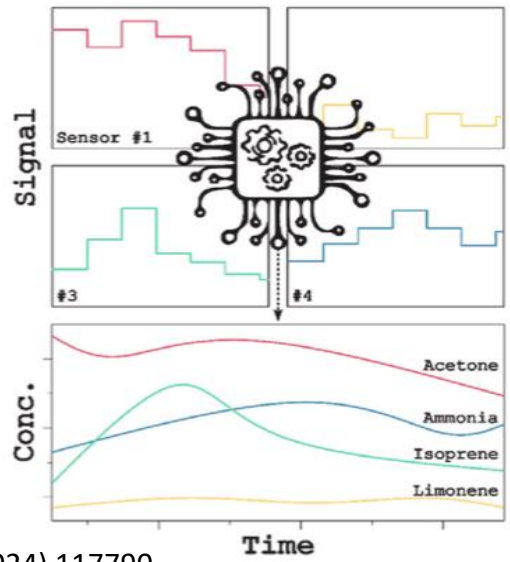
# Further Outlook



Establishment of a design guideline for strain-controlled chemiresistive gas sensors based on first-principles band alignment predictions → Lots of applications from earth to space



T. Elias Abi-Ramia Silva et al.  
Trends in Analytical Chemistry 177 (2024) 117790



# Thank you for your attention!

ご清聴ありがとうございました！

感谢各位的聆听！