# Pulsed laser annealed $VO_2$ thin films for smart windows and gas sensing applications

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[4] University of Padua, Physics and Astronomy Department
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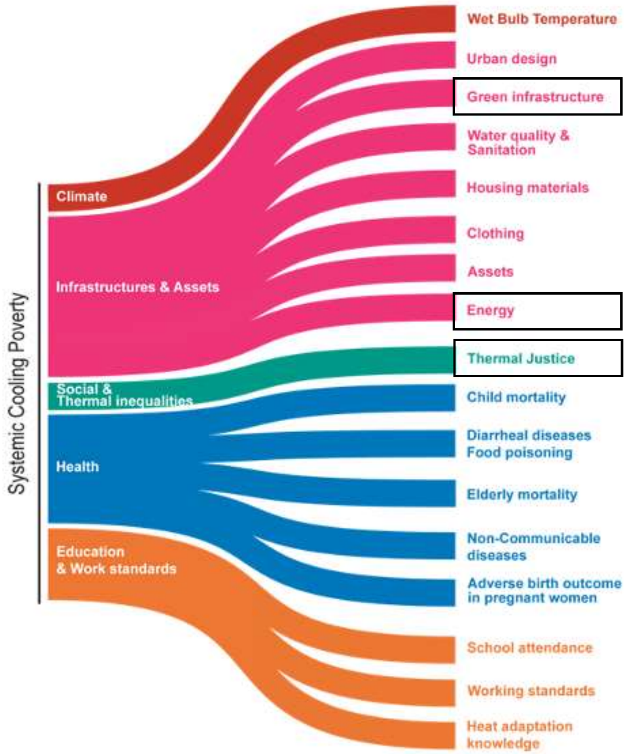
# Energy equality

Systemic energy poverty ➡

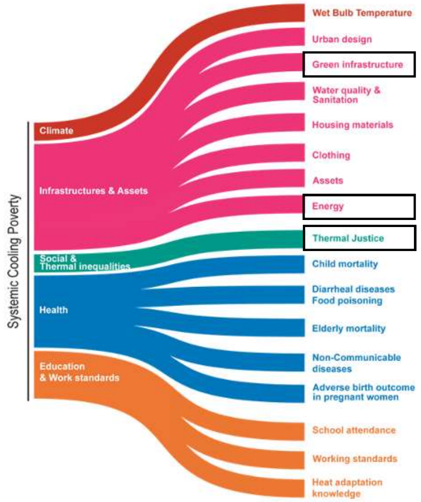



Over 1.5 billion people suffer from energy poverty, including 40 million Europeans

Mazzone, A. *et al*. Understanding systemic cooling poverty. *Nature Sustainability,* 2023.

# Energy equality

Systemic energy poverty




Smart windows

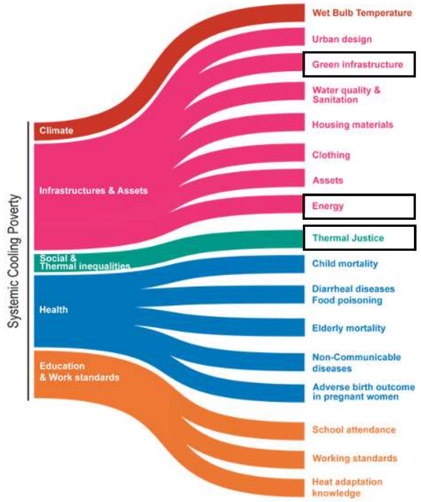
$H_2$ gas sensors

Vanadium dioxide ($VO_2$)

Mazzone, A. *et al*. Understanding systemic cooling poverty. *Nature Sustainability,* 2023.

# Energy equality

Systemic energy poverty




Smart windows

$H_2$ gas sensors

Vanadium dioxide ($VO_2$)

Mazzone, A. *et al*. Understanding systemic cooling poverty. *Nature Sustainability,* 2023.

# 1st Application: Smart Windows

> 40% global energy consumption related to heat exchange through buildings' windows ➡ ~~HVAC systems (Heat, Ventilation, Air Conditioning)~~ ➡ Alternatives required

Cao *et al*. *Matter*, Volume 2, Issue 4, 2020

# 1st Application: Smart Windows

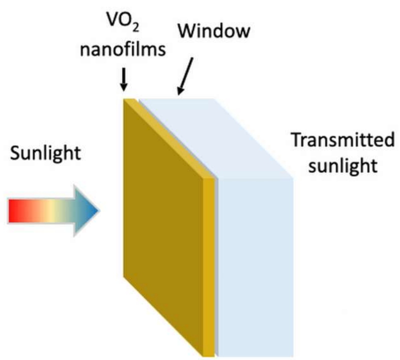
> 40% global energy consumption related to heat exchange through buildings' windows ➡ ~~HVAC systems (Heat, Ventilation, Air Conditioning)~~ ➡ Alternatives required

⬇

## Thermochromic smart windows

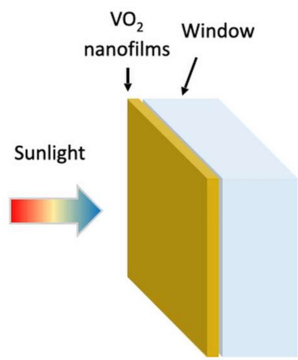
⬇

Winter
T < 30°C




⬅ Modulation of solar radiation in function of external temperature ➡

Summer
T > 30°C




Cao *et al*. *Matter*, Volume 2, Issue 4, 2020

# Vanadium dioxide ($VO_2$)

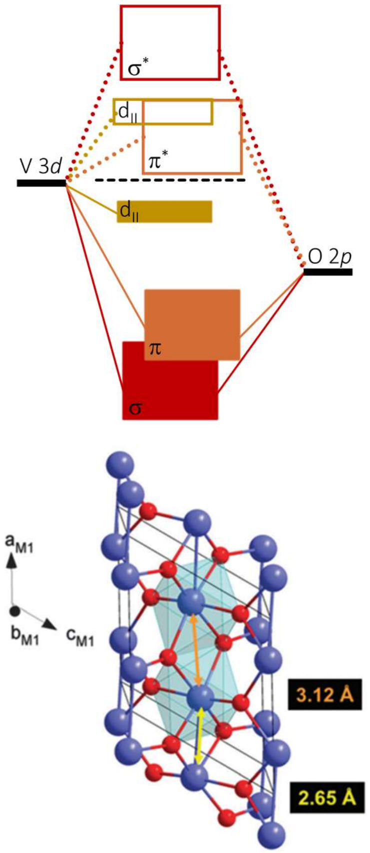
## Properties

*Metal-insulator* transition ($T_c$ = 68°C):

- *Electrical* change

- *Structural* change

Monoclinic

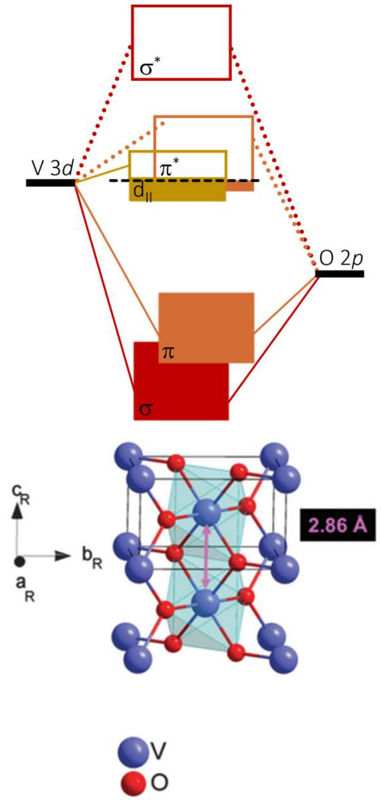



Reversible

T > $T_c$

T < $T_c$

Rutile




*Phys. Chem. Chem. Phys.*, 2014, 16, 17705

# $VO_2$ thin films for Smart Windows

Challenges

1. *Environmental friendliness*
2. *Flexible fabrication for multi-field application*
3. *Improved thermochromic performance*
4. Improved stability for long-term service
5. Lower transition temperature
6. Improved color

Cao *et al.* Challenges and Opportunities toward real applications of $VO_2$ based smart glazing. *Matter*, Volume 2, Issue 4, 2020

# $VO_2$ thin films for Smart Windows

**Challenges**

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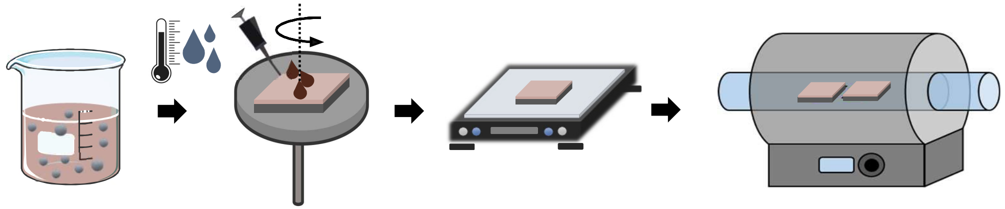
6. Improved color

**Sol Gel process**

Synthesis ➡ Deposition ➡ Drying ➡ Thermal annealing



# $VO_2$ thin films for Smart Windows

Heat-sensitive substrates (e.g., polymers) ✕

⬆

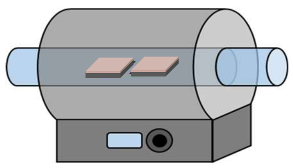
Challenge (2): Flexible fabrication for multi-field application

⬆

Crystallization step:

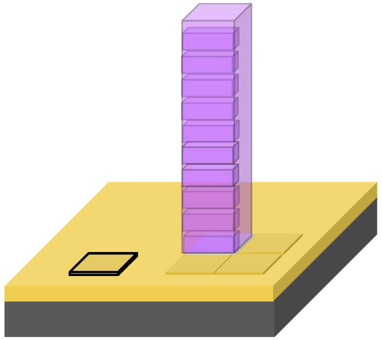
- Crystalline structure required for solar modulation ⬅
- Temperatures > 400°C

Thermal annealing



➡ Alternatives required

# ns Pulsed Laser Annealing



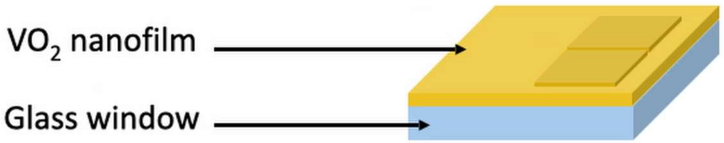
UV ns-pulsed
laser annealing

⬇

- Film heating
- Substrate not involved
- Defined irradiation wavelength
- Fast timescales - ns pulse
- Heating rates > $10^8$ K/s
- Extreme spatial and temporal control of temperature distribution

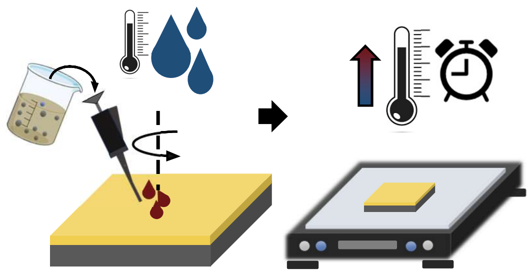
Light absorption

photothermal effects



# ns-PLA of $VO_2$ thin films

Thin film deposition



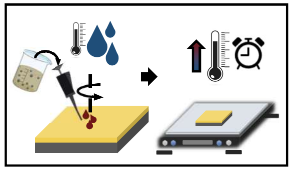
**Step 1** –

Optimized

deposition

Challenges

1. *Environmental friendliness*
2. Flexible fabrication
3. Improved thermochromic performance



# **Step 1** – Optimized deposition

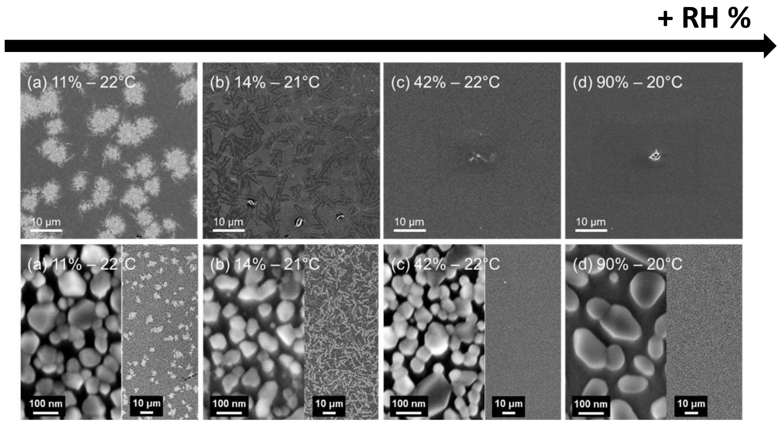
Parameters:

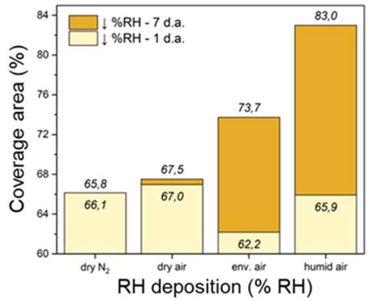
- Humidity during deposition
- Drying temperature
- Film aging before annealing

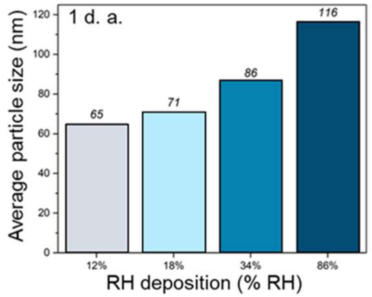
⬇

Influence on:

- Particle coverage area
- Particle size
- Particle size distribution

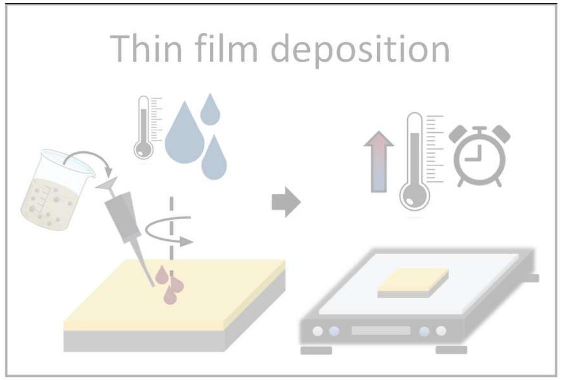


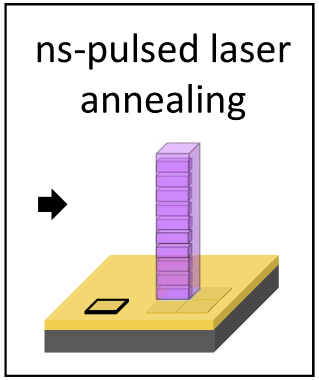




Basso, M., et al. Influence of humidity and aging on the optimization of $VO_2$ sol-gel thin films for thermochromic smart windows. Submitted.

# ns-PLA of $VO_2$ thin films



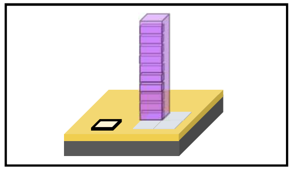




**Step 1 –** Optimized deposition

**Step 2 –** Laser-induced crystallization mechanism

Challenges
1. Environmental friendliness
2. *Flexible fabrication*
3. Improved thermochromic performance

# ns-PLA of $VO_2$ thin films

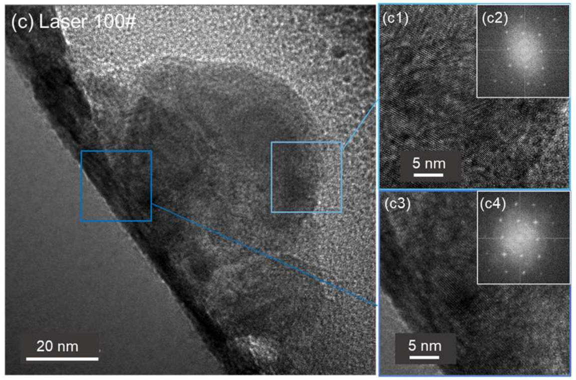


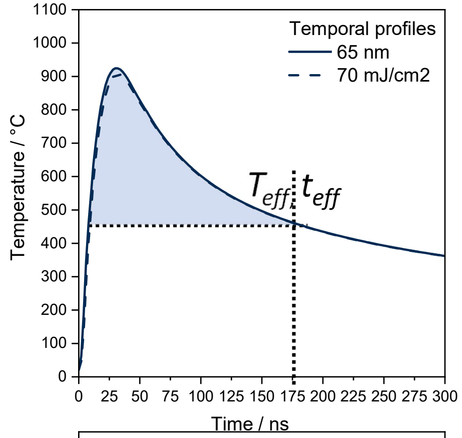
## **Step 2** – Laser-induced crystallization mechanism

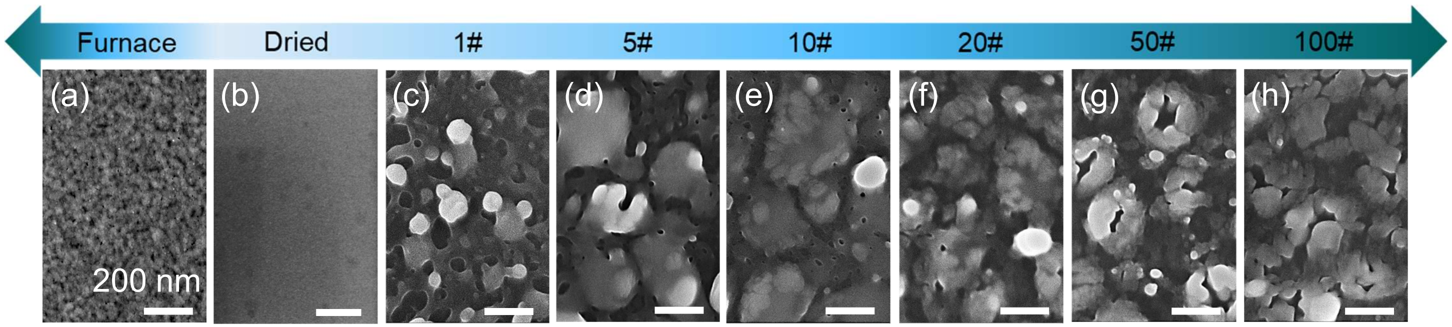
⬇

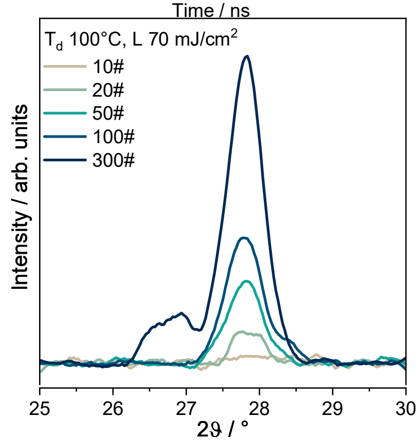
Results:

- Low temperature ($T_{room}$ << $T_{furnace}$~500°C)
- Seconds timescales
- Crystallite formation after 5 pulses
- Effective crystallization time ($t_{eff}$)



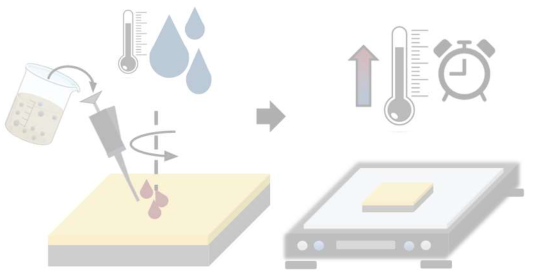



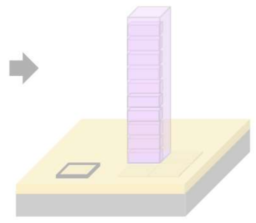

Basso, M., et al. Ultrafast laser crystallization dynamics of thermochromic $VO_2$ thin films by simple moisture-assisted sol-gel. *Chem. Mater*. 2024, 36, 11, 5508–5520

# ns-PLA of $VO_2$ thin films

Thin film deposition



ns-pulsed laser annealing



**Step 1 –** Optimized deposition

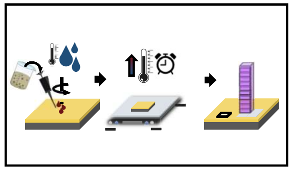
**Step 2 –** Laser-induced crystallization mechanism

**Step 3 –** Combined effect

Challenges

1. Environmental friendliness
2. Flexible fabrication
3. *Improved thermochromic performance*

# ns-PLA of $VO_2$ thin films



## **Step 3** – Combined effect

Parameters:

- Humidity in deposition
- Drying temperature
- Film aging before laser
- Laser pulses
- Energy density

➡

Challenges**:**

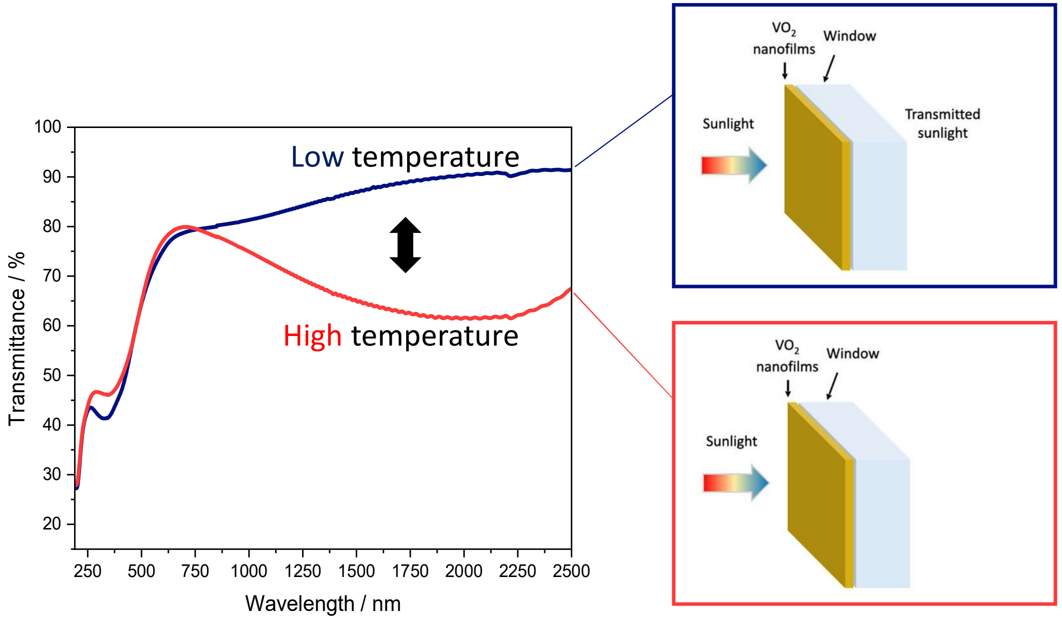
✓ 1. Environmental friendliness

✓ 2. Flexible fabrication

3. Improved thermochromic performance

Basso, M., et al. Ultrafast laser crystallization dynamics of thermochromic $VO_2$ thin films by simple moisture-assisted sol-gel. *Chem. Mater*. 2024, 36, 11, 5508–5520

# Thermochromic performance




⬅ Thermochromic performance

⬇

Solar modulation efficiency:

$$\Delta \mathbf{T_{sol}} = \mathrm{T}_{\mathrm{sol},20°\mathrm{C}} - \mathrm{T}_{\mathrm{sol},90°\mathrm{C}}$$

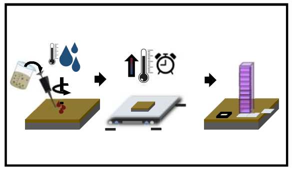
↓

$$\mathrm{T_{sol}} = \frac{\int_{250}^{2500} \phi_{\mathrm{sol}}(\lambda) T(\lambda) \mathrm{d}\lambda}{\int_{250}^{2500} \phi_{\mathrm{sol}}(\lambda) \mathrm{d}\lambda}$$

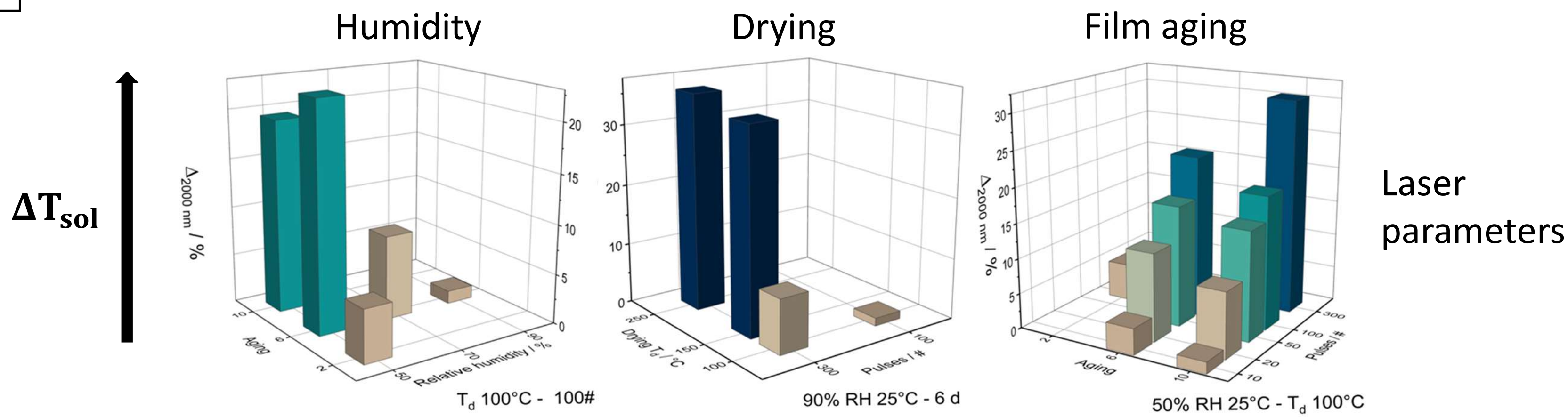
$\phi_{sol}$ = standard solar radiation spectrum for AM 1.5
$\mathrm{T}_{sol}$ = integrated solar transmittance
$T$ = film's transmittance

Basso *et al*. Humidity and aging influence on $VO_2$ sol-gel thin films for thermochromic smart windows. *Journal of Sol Gel Science and Technology* 2025

# ns-PLA of $VO_2$ thin films



## **Step 3** – Combined effect



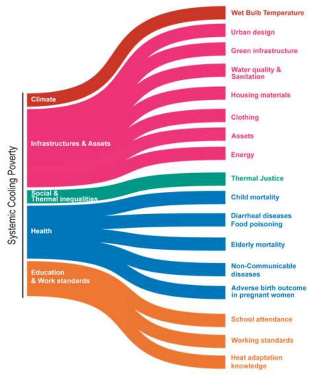

✓ Single-step process: densification, crystallization, film patterning

✓ Versatile process: multiple combinations for high $\Delta T_{sol}$

✓ No inert atmosphere: air processing

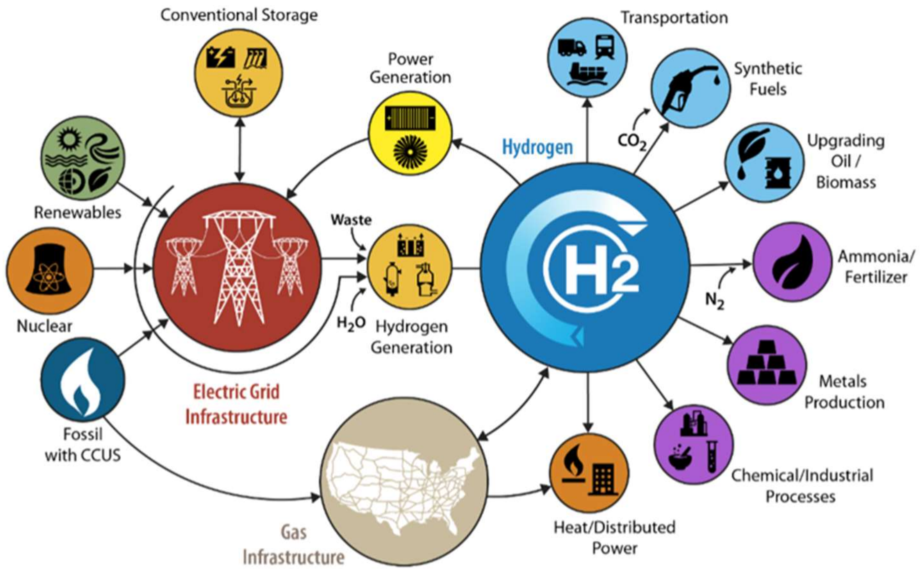
Basso, M., et al. Ultrafast laser crystallization dynamics of thermochromic $VO_2$ thin films by simple moisture-assisted sol-gel. *Chem. Mater*. 2024, 36, 11, 5508–5520

# 2nd Application: $H_2$ Gas Sensors




Energy equality ➡ Hydrogen gas sensors

⬇




https://www.hydrogen.energy.gov/

# $VO_2$ thin films as $H_2$ Gas Sensors

$VO_2$ thin films ⬅ Metal-oxides thin films as gas sensors ⬅ Hydrogen gas sensors

⬇ ⬇

Influence of:

- Crystallinity
- Morphology

Variation of electrical/optical properties upon gas exposure

Basso M. *et al*. Sol-gel Pt-$VO_2$ films as selective chemoresistive and optical $H_2$ gas sensors. *Under revision.*

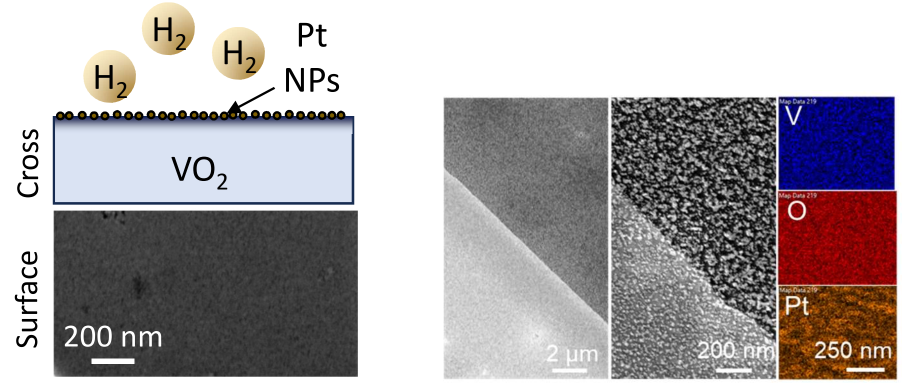
# $VO_2$ thin films as $H_2$ Gas Sensors

## $VO_2$ thin films

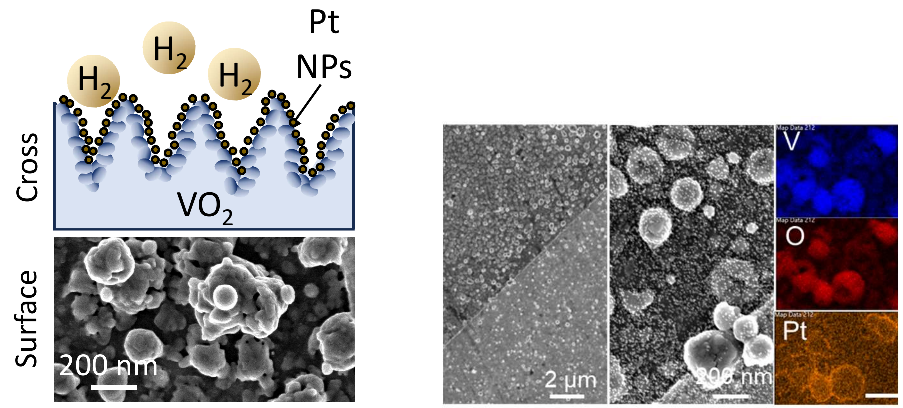
Influence of:

- Crystallinity
- Morphology

### Furnace annealing




### Laser annealing

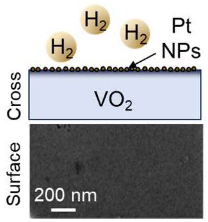


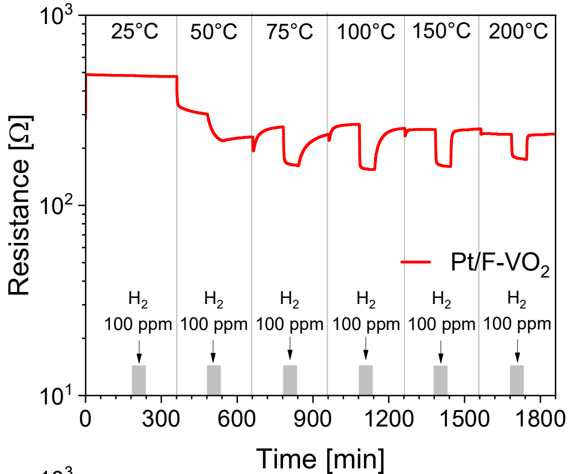

Basso M. *et al*. Sol-gel Pt-$VO_2$ films as selective chemoresistive and optical $H_2$ gas sensors. *ACS Appl. Mater. Interfaces,* 16, 42, 57558–57570 (2024).

# Chemoresistive gas sensors

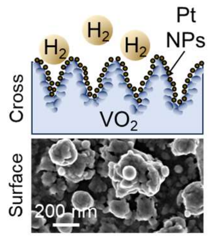
## Static gas sensing

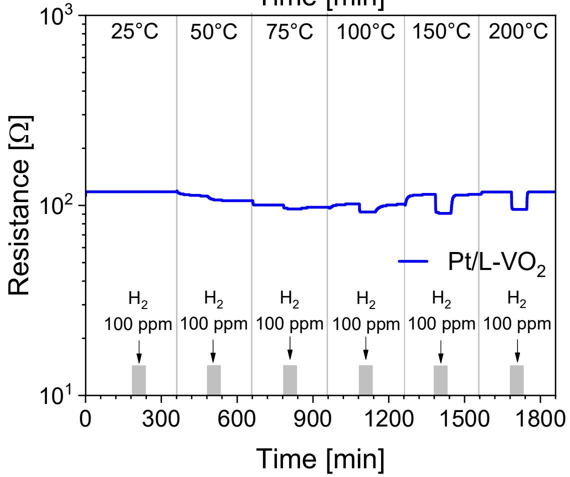
Furnace annealing




Laser annealing




➡ 150°C operating temperature

Basso M. *et al*. Sol-gel Pt-$VO_2$ films as selective chemoresistive and optical $H_2$ gas sensors. *ACS Appl. Mater. Interfaces,* 16, 42, 57558–57570 (2024).

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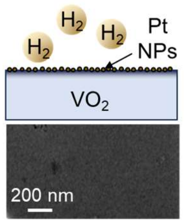
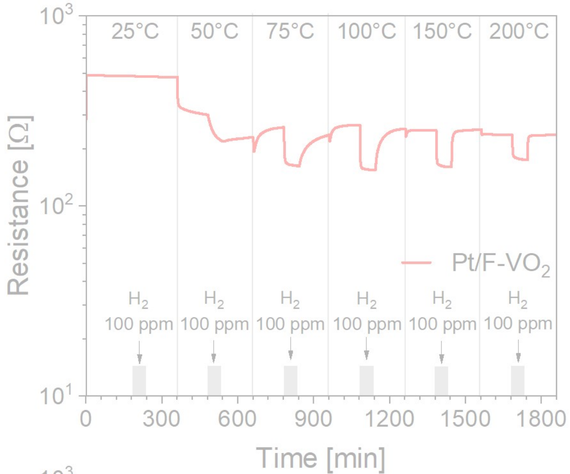
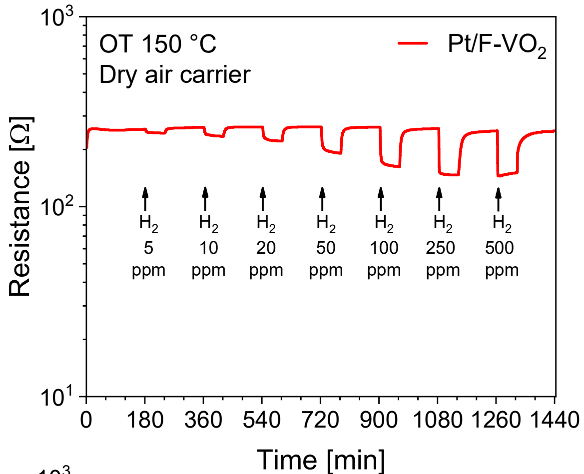
# Chemoresistive gas sensors

## Static gas sensing / Dynamic gas sensing

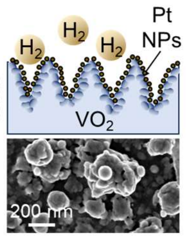
**Furnace annealing**

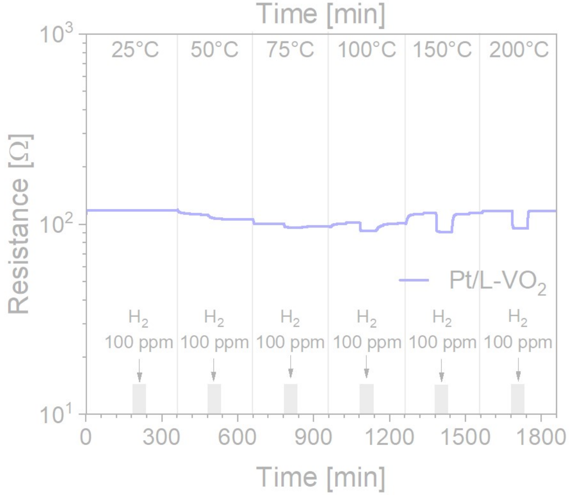


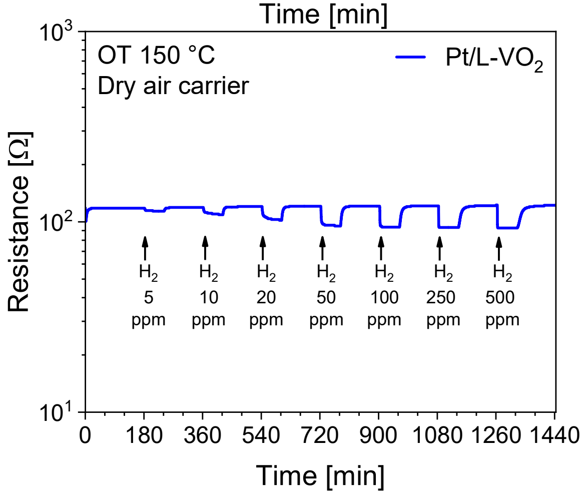




**Laser annealing**



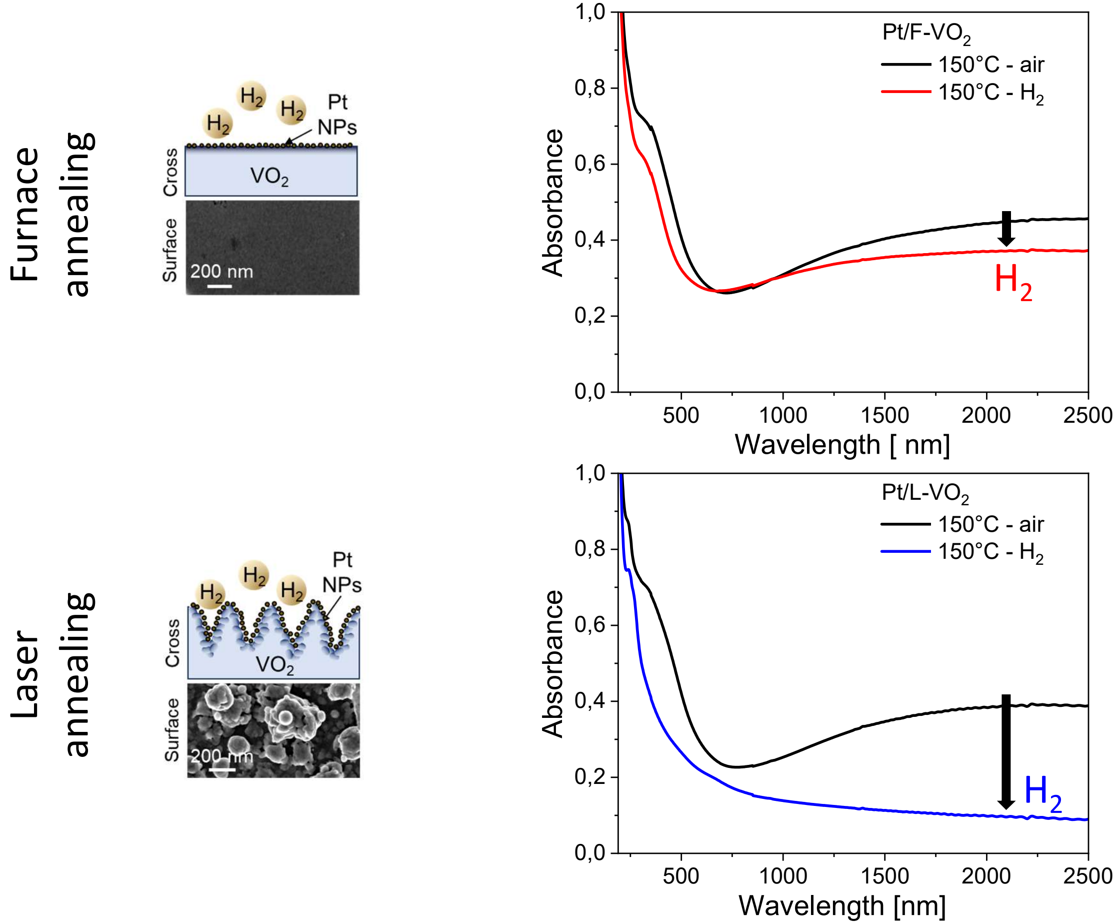




- Excellent baseline recovery
- Limit of detection 2 ppm (furnace) vs 2.9 ppm (laser)


Basso M. *et al*. Sol-gel Pt-$VO_2$ films as selective chemoresistive and optical $H_2$ gas sensors. *ACS Appl. Mater. Interfaces,* 16, 42, 57558–57570 (2024).

# Optical gas sensors

## Static gas sensing

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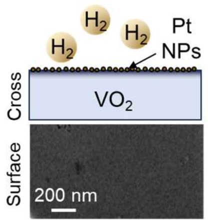
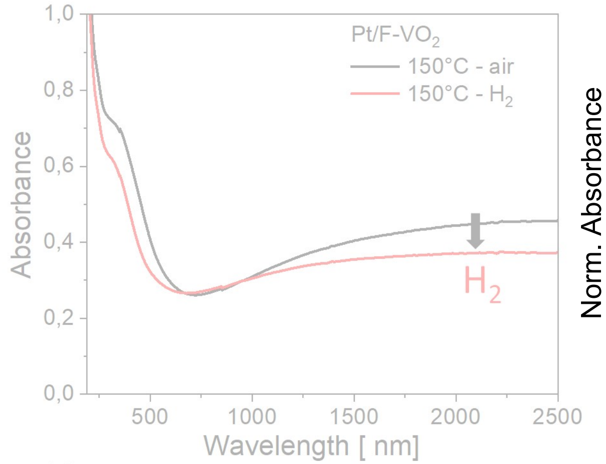
# Optical gas sensors

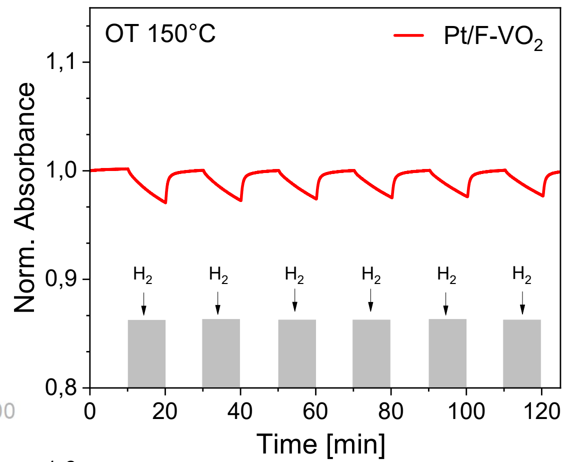
Static gas sensing

Dynamic gas sensing

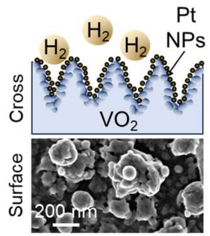
Furnace annealing

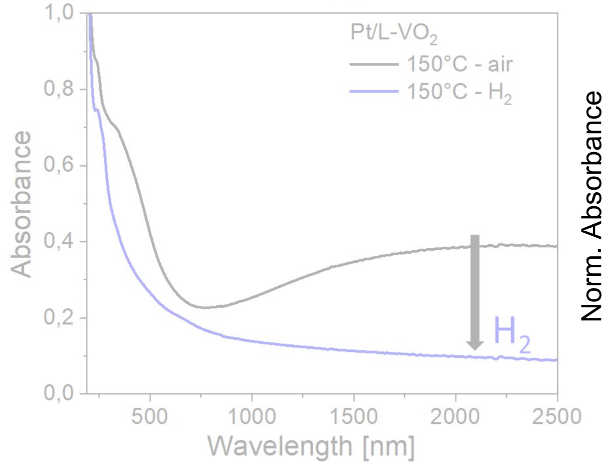


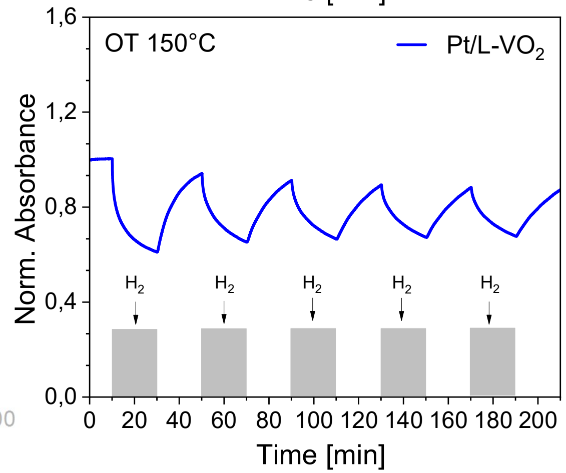




Laser annealing




Laser annealing outperforms furnace annealing

Basso M. *et al*. Sol-gel Pt-$VO_2$ films as selective chemoresistive and optical $H_2$ gas sensors. *ACS Appl. Mater. Interfaces,* 16, 42, 57558–57570 (2024).

# Interaction between $VO_2$ and $H_2$

Structural & Chemical investigation:

1. **In situ** Grazing Incidence X-Ray Diffraction

2. **In operando** X-Ray Photoelectron Spectroscopy

Basso M. *et al*. Sol-gel Pt-$VO_2$ films as selective chemoresistive and optical $H_2$ gas sensors. *ACS Appl. Mater. Interfaces,* 16, 42, 57558–57570 (2024).

# Interaction between $VO_2$ and $H_2$

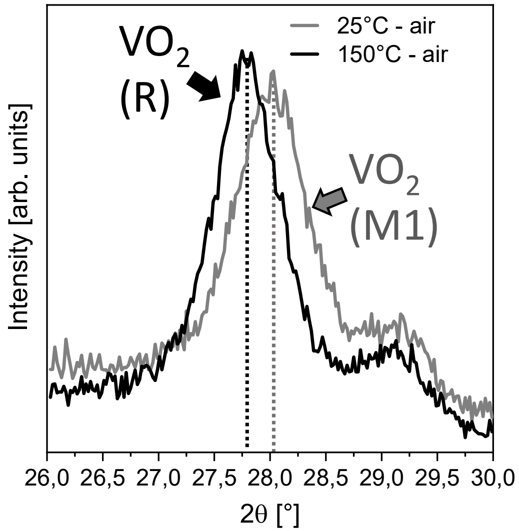
$VO_2$ ***without*** $H_2$ :

1. Structural investigation

➡ Reversible transition

Insulator Monoclinic ⟷ (68 °C) Metallic Rutile

25 °C vs 150 °C




In situ Grazing Incidence X-Ray Diffraction

Basso M. *et al*. Sol-gel Pt-$VO_2$ films as selective chemoresistive and optical $H_2$ gas sensors. *ACS Appl. Mater. Interfaces,* 16, 42, 57558–57570 (2024).

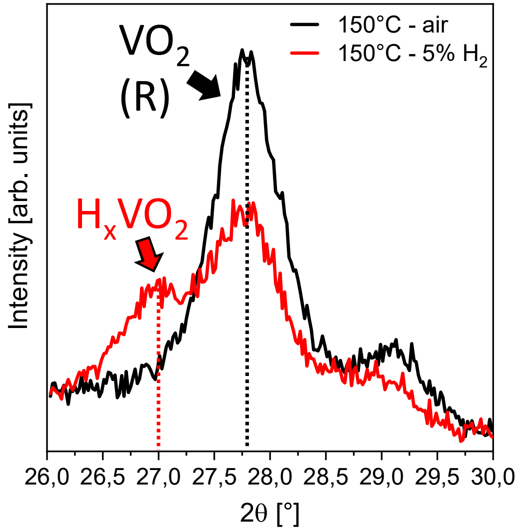
# Interaction between $VO_2$ and $H_2$

$VO_2$ *with* $H_2$ :

1. Structural investigation

➡ Reversible formation of $H_xVO_2$ bronze upon $H_2$ exposure

150 °C




In situ Grazing Incidence X-Ray Diffraction

$$VO_2 + H \leftrightarrow H_xVO_2$$

$$4H_xVO_2 + O_2^- \leftrightarrow 4VO_2 + 2H_2O + e^-$$

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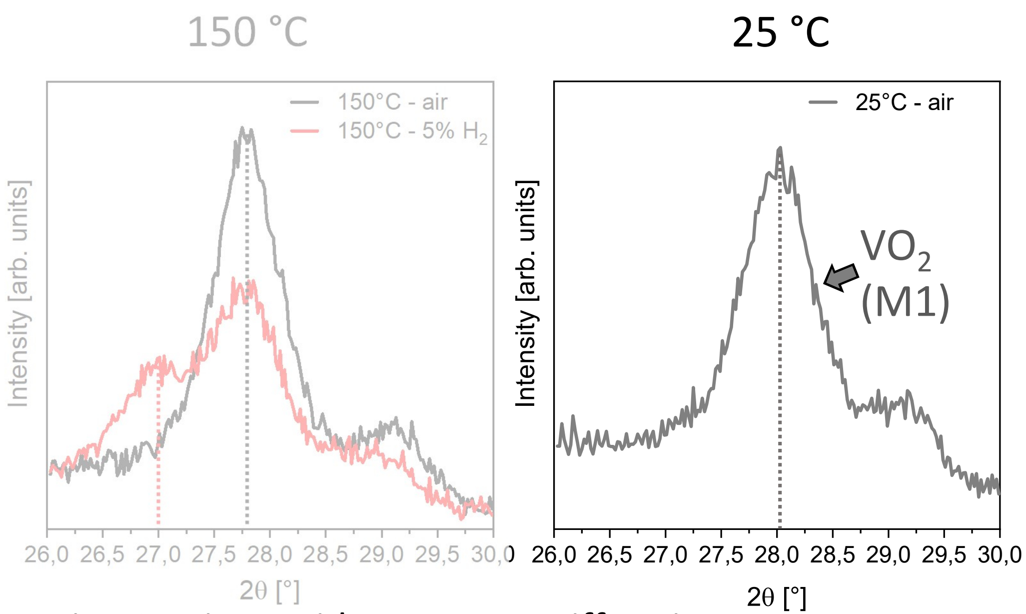


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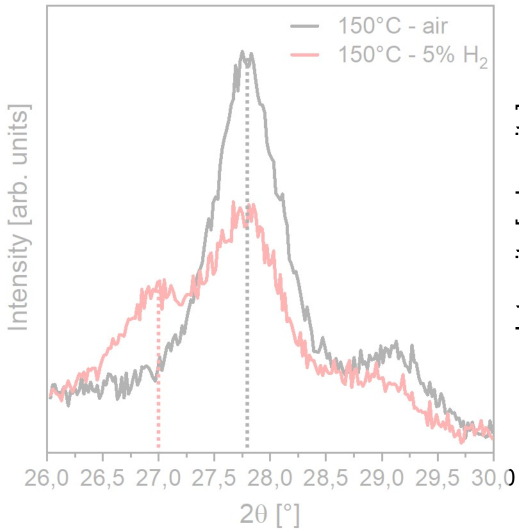
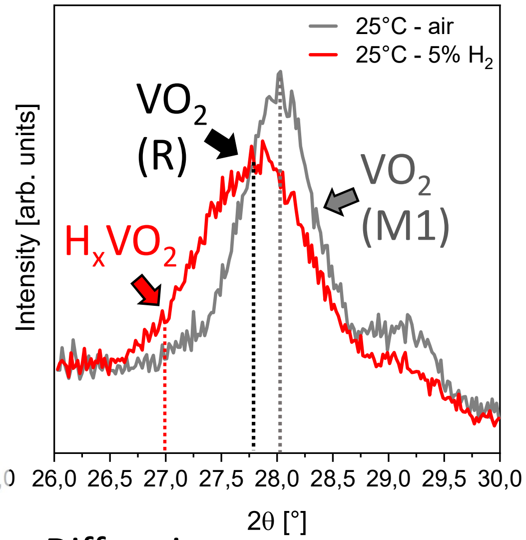



25 °C




In situ Grazing Incidence X-Ray Diffraction

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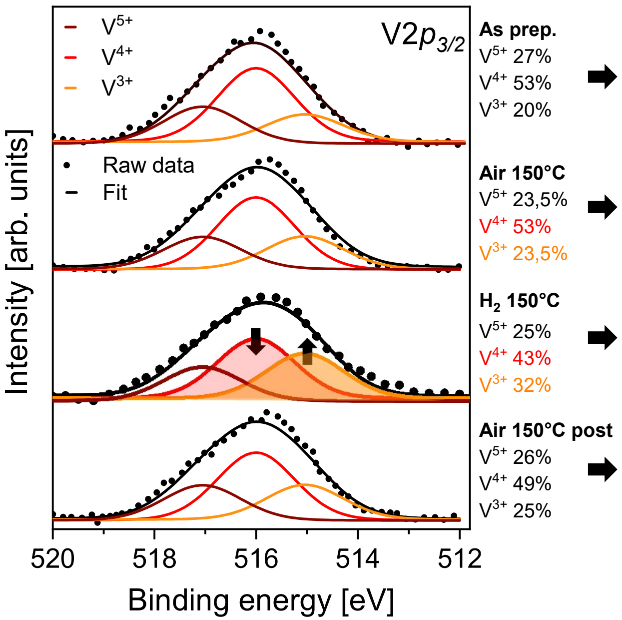
# Interaction between $VO_2$ and $H_2$

$VO_2$ *with* $H_2$ :

2. Chemical investigation (V) ➡

Reversible variation of
**V oxidation state**
upon $H_2$ exposure




➡ Air, 25 °C

➡ Air, 150 °C

➡ $H_2$, 150 °C

➡ Air, 150 °C

In operando X-Ray Photoelectron Spectroscopy

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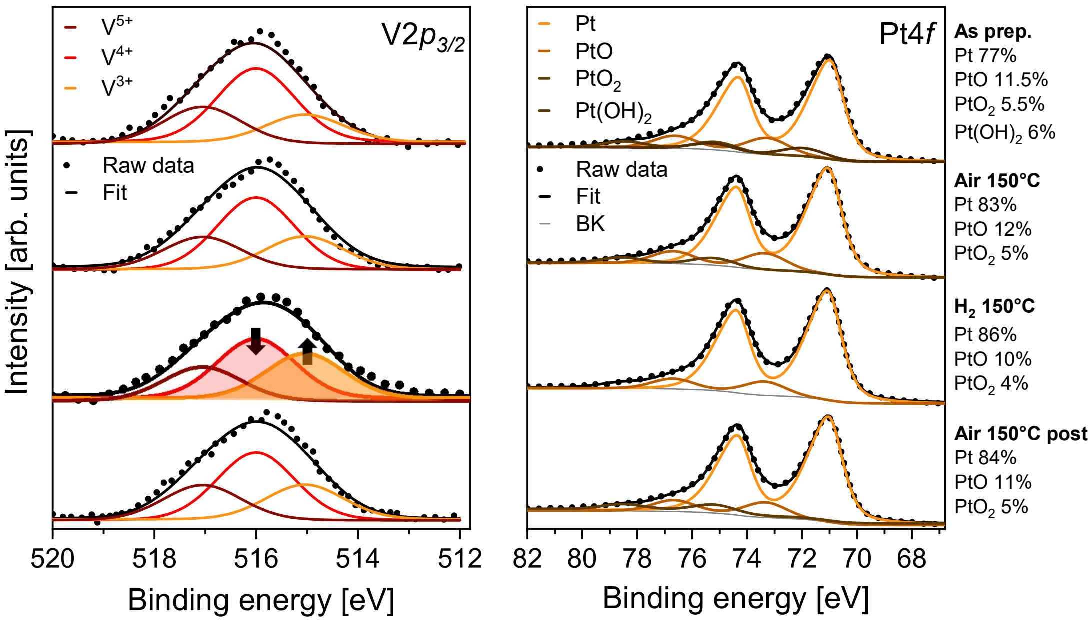
# Interaction between $VO_2$ and $H_2$

$VO_2$ *with* $H_2$ :

2. Chemical investigation (Pt) ➡ **No** variation of Pt oxidation state upon $H_2$ exposure




In operando X-Ray Photoelectron Spectroscopy

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# Conclusions

## Sol-gel + ns-PLA:

Sol-gel method + laser annealing offer high versatility:

- Air processing → No protected atmosphere required
- Industrially scalable + Ultrafast processing → Seconds timescales + Single-step
- Low temperature laser crystallization

## Applications:

- Smart windows ➡
  - Higher visible transmittance
  - Comparable thermochromic performance with literature
  - Air stability
- $H_2$ gas sensors ➡
  - Dual mode: optical and resistive sensors
  - $H_2$ LOD 2 ppm and $H_2$ selectivity
  - Reversible $H_xVO_2$ formation and $V^{5+/4+}$ reduction upon $H_2$ exposure

MONASH University

UNIVERSITÀ DEGLI STUDI DI PADOVA

UNIVERSITÀ DEGLI STUDI DELL'AQUILA

# Thank you
# for the attention

nano ENG RESEARCH GROUP


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