

Using of modified supercritical carbon dioxide for the preparation of TiO_2 nanocrystalline photocatalyst-thin films and aerogels

M. Cerhová¹, M. Sajfrtová¹, L. Matějová², V. Dřínek¹, Stanislav Daniš³, V. Jandová¹



¹Institute of Chemical Process Fundamentals of the CAS, v.v.i., Rozvojová 135, 165 02 Prague 6, Czech Republic

²Institute of Environmental Technology, VŠB-Technical University of Ostrava, 17.listopadu 15/2172, 708 33 Ostrava, Czech Republic

³Department of Condensed Matter Physics Faculty of Mathematics and Physics, Charles University in Prague Ke Karlovu 5, 121 16 Prague 2, Czech Republic

Group of supercritical fluid extraction

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Ing. Martin Topiař

Ing. Marie Sajfrtová, Ph.D.

Ing. Marie Cerhová

Ing. Zdenka Zachová

Ing. Helena Sovová, CSc.



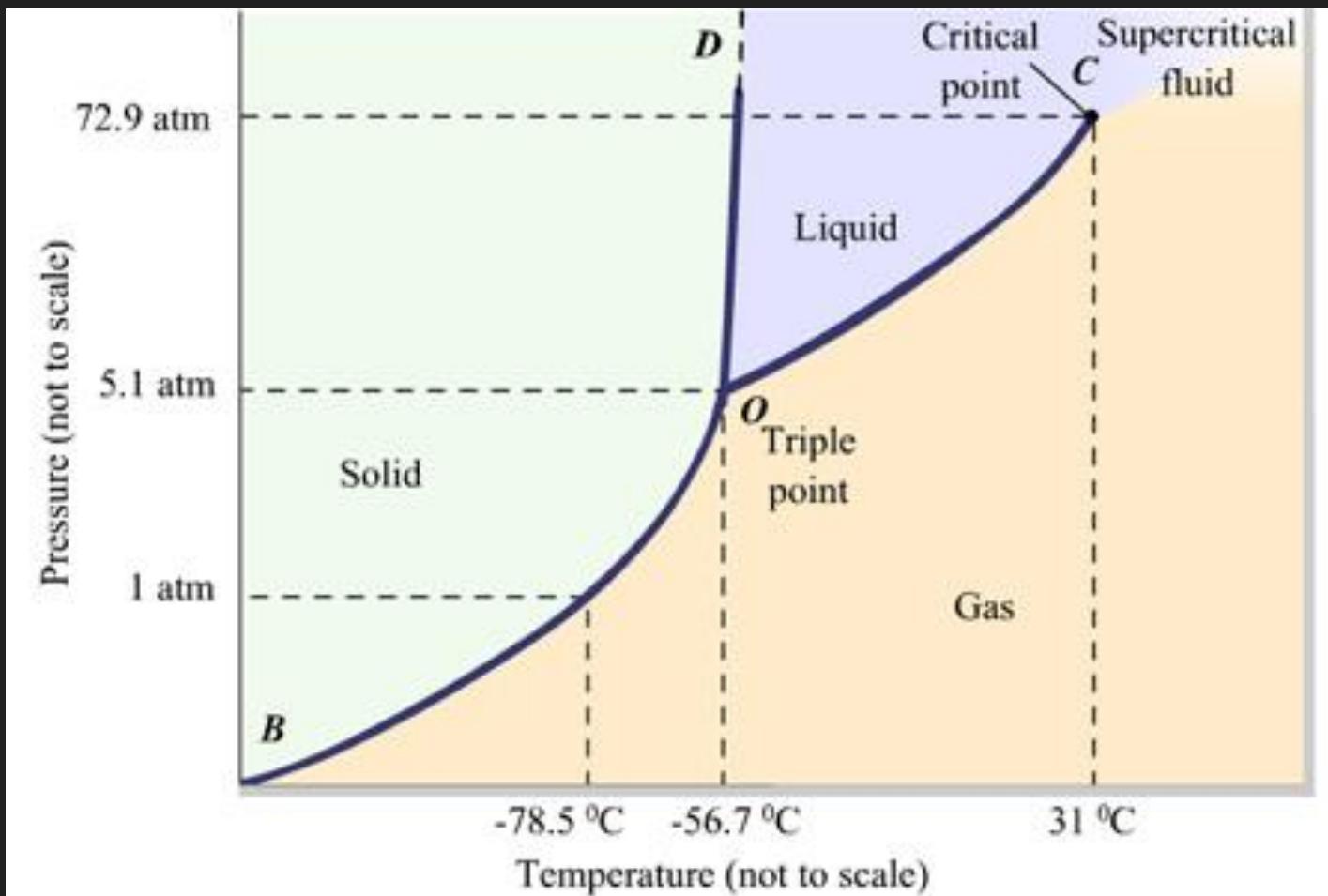
INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS OF THE ASCR
GROUP OF SUPERCRITICAL FLUID EXTRACTION

ING. MARIE CERHOVÁ

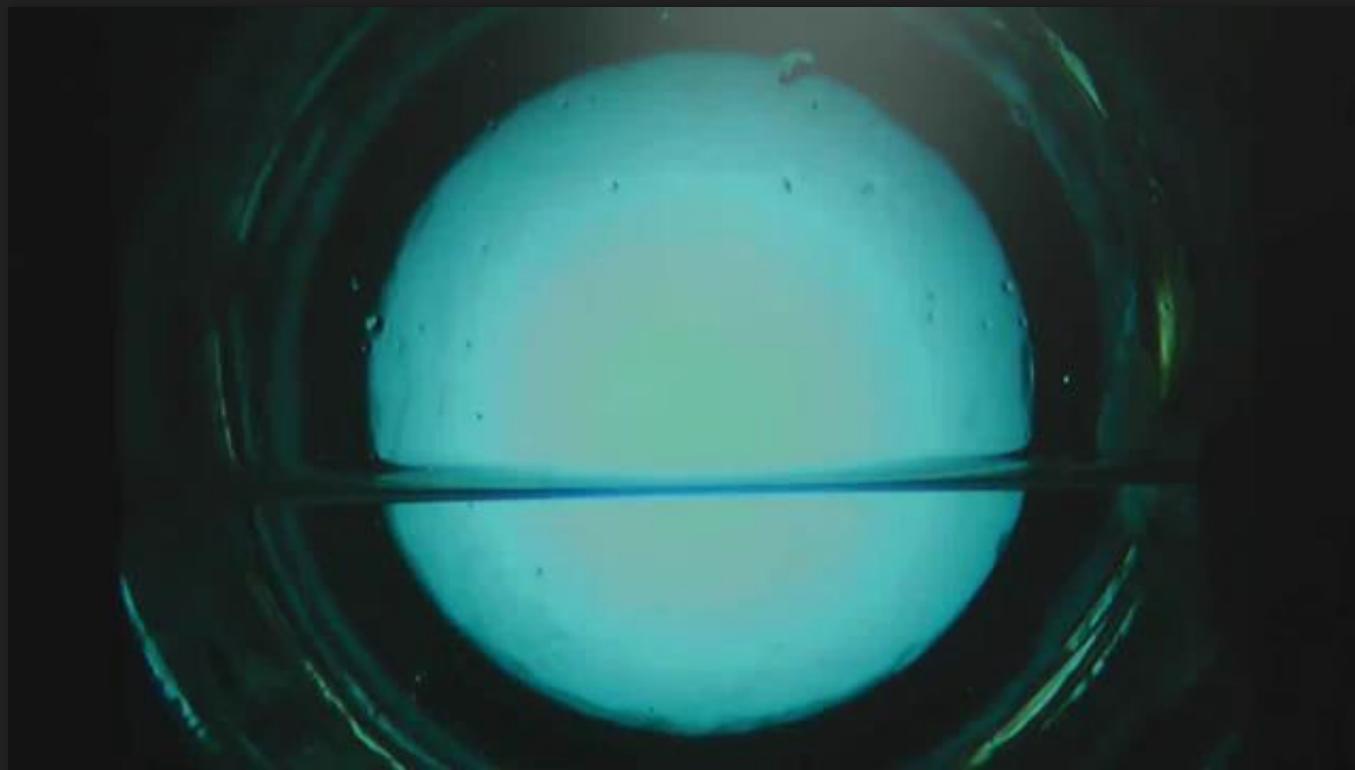


CO_2

$$\begin{aligned}T_c &= 31 \text{ }^{\circ}\text{C} \\P_c &= 7,4 \text{ MPa} \\d_c &= 468 \text{ kg/m}^3\end{aligned}$$



Supercritical CO₂



scCO₂

Density, viscosity .. between gas and liquid

Dependence of properties on p and T

Solubility increases with density and T

Low viscosity – high diffusivity

Low interphase tension

Easy separation of gaseous CO₂

Non-flammable, non-explosive, low cost, high purity

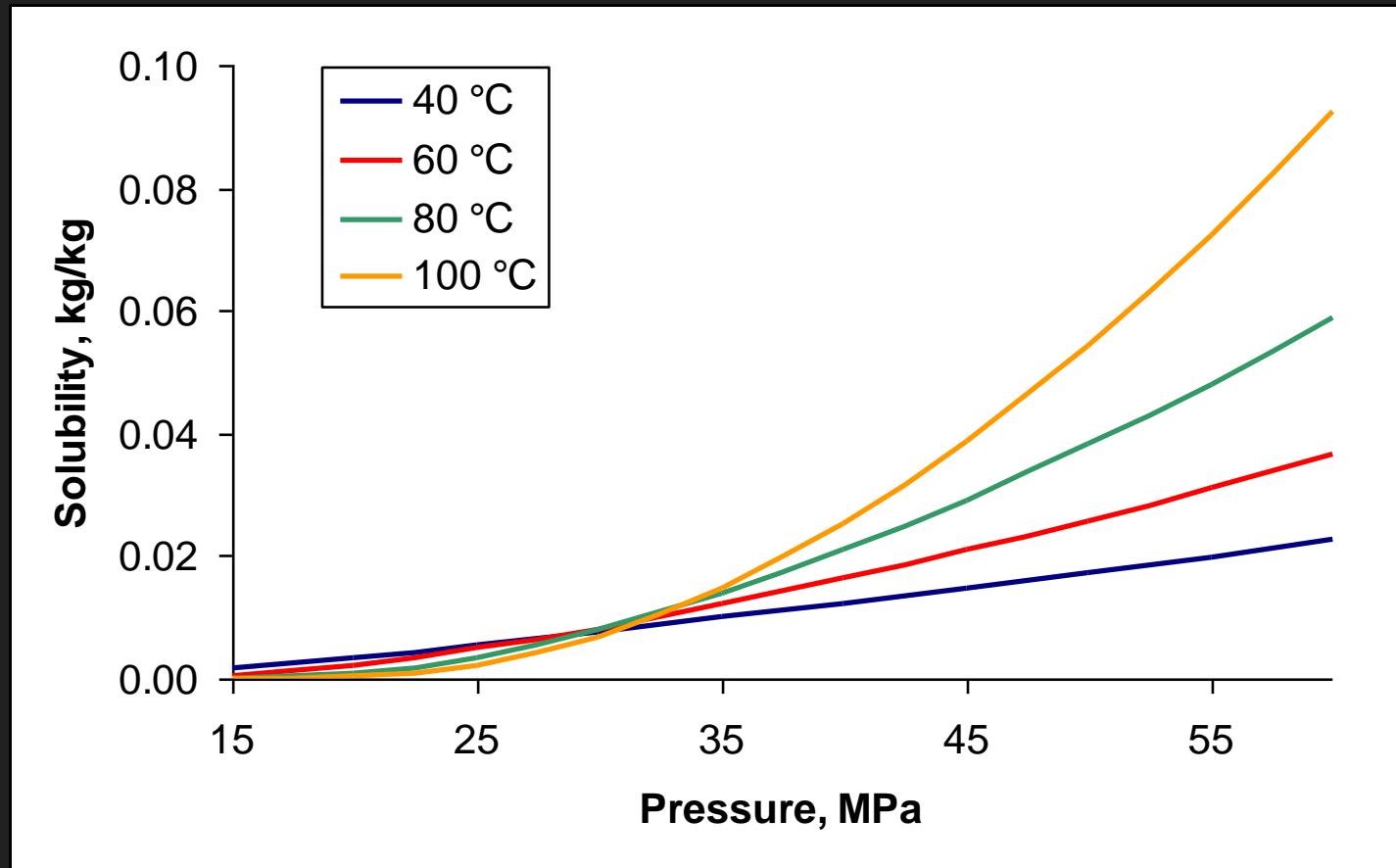
Non-toxic, inert, low critical temperature

Non-polar solvent (modifying)

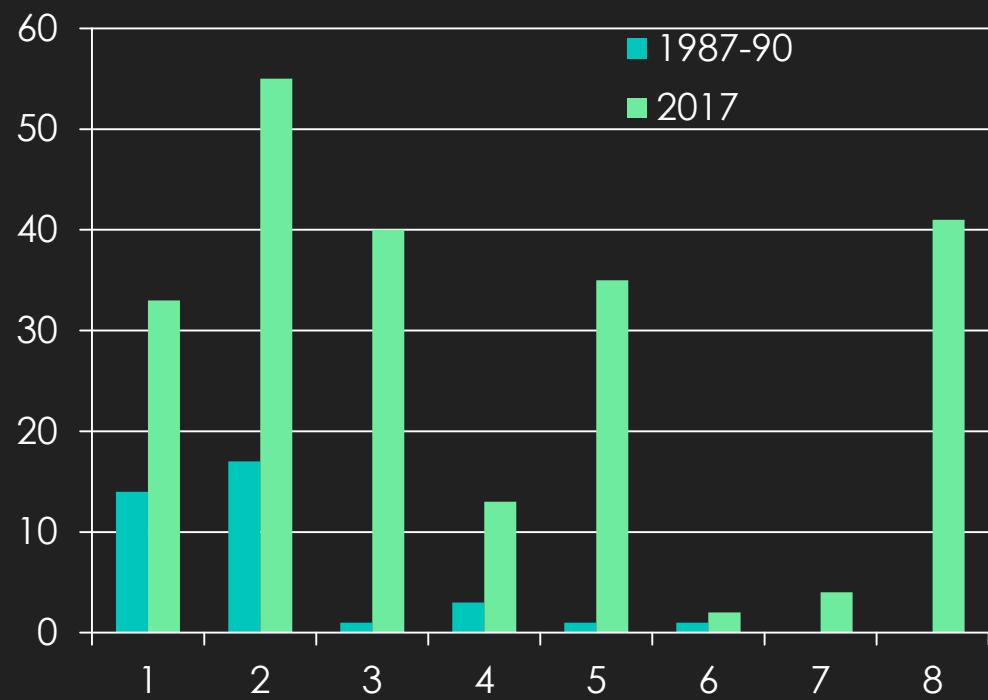


Dependence of properties on p and T

Vegetable oil - solubility in scCO₂



Research



- 1 Properties, solubility/equilibrium
- 2 SFE, cleaning, recycling
- 3 Nanostructures, drying
- 4 Reactions
- 5 Technique
- 6 Chromatography
- 7 Impregnation, polymers
- 8 Sequestration, oil extraction



2 Supercritical Fluid Extraction



Author: ChemViews

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Weinheim

This year marks the 50th anniversary of the first patent describing the use of supercritical fluid extraction by Kurt Zosel, Max Planck Institute for Coal Research, Mülheim an der Ruhr, Germany. It also marks the 40th anniversary of Zosel's US patent of the use of supercritical fluid extraction in the decaffeination of coffee.



2 Flavex



2 Cleaning

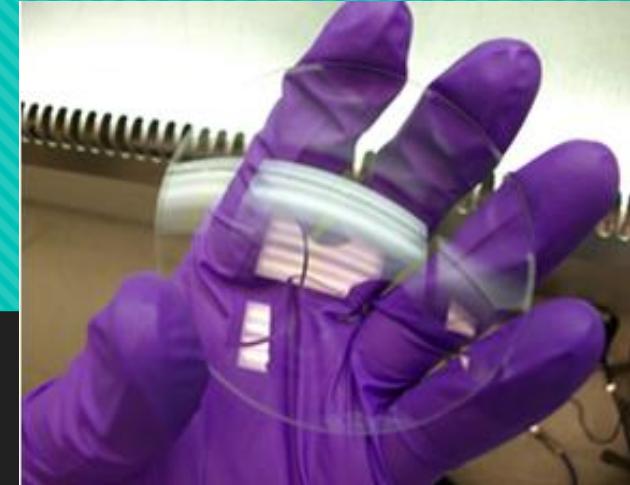


Figure 6: Assorted Medical Devices Extracted with Supercritical CO₂.

2 Cleaning

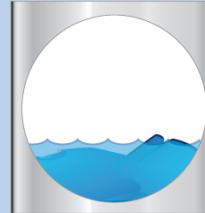
How Solvair® works:



Clothes are placed in the Solvair machine.



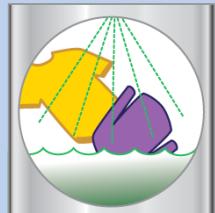
Biodegradable cleaning liquid removes stains and dirt.



Cleaning liquid takes dirt with it as it is drained. Clothes are damp and ready for drying.



The machine is pressurized. CO₂ turns from a gas to a liquid under pressure.



Cold liquid CO₂ rinses cleaning liquid from the clothes.



Pressure is reduced. CO₂ converts to a gas and clothes are instantly dry.



Cleaning liquid and CO₂ are purified & reused.



Clothes are clean, bright & odor free.

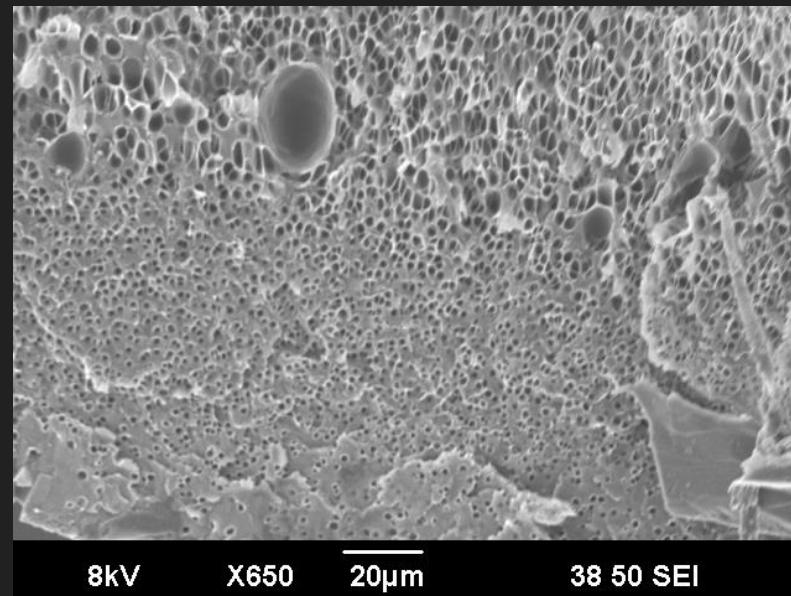
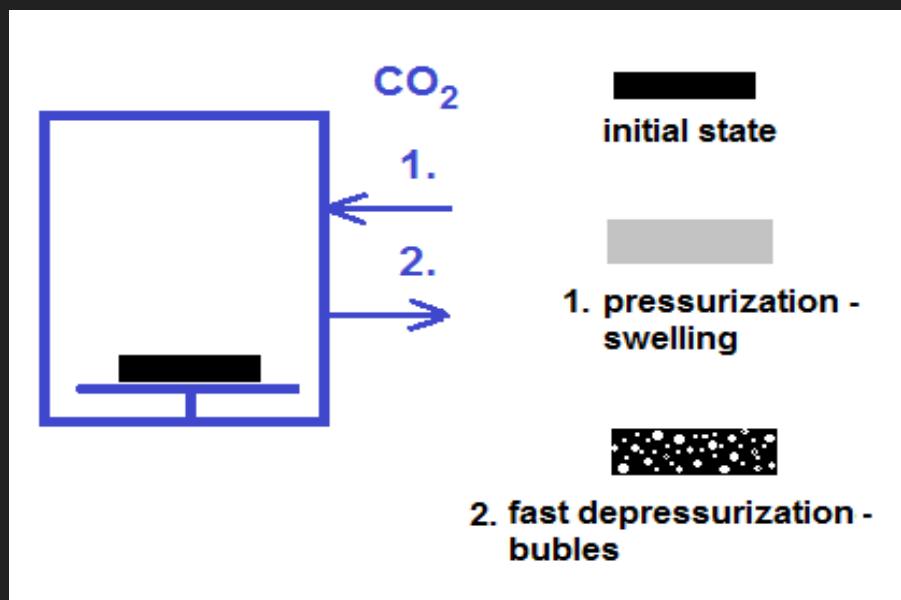
Solvair
greenclothingcare.com

Truly Unique™

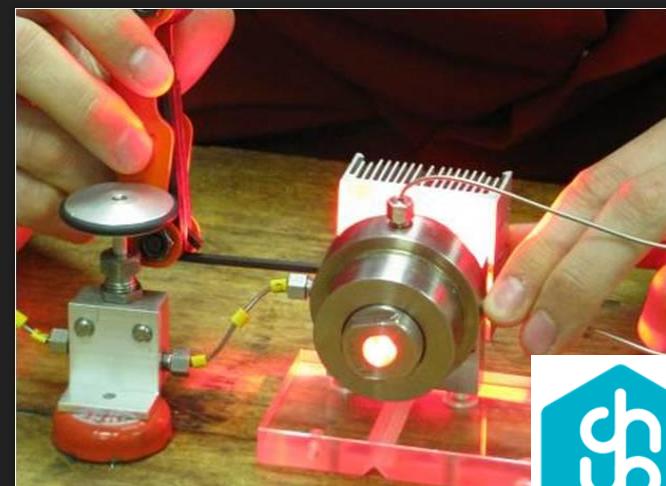
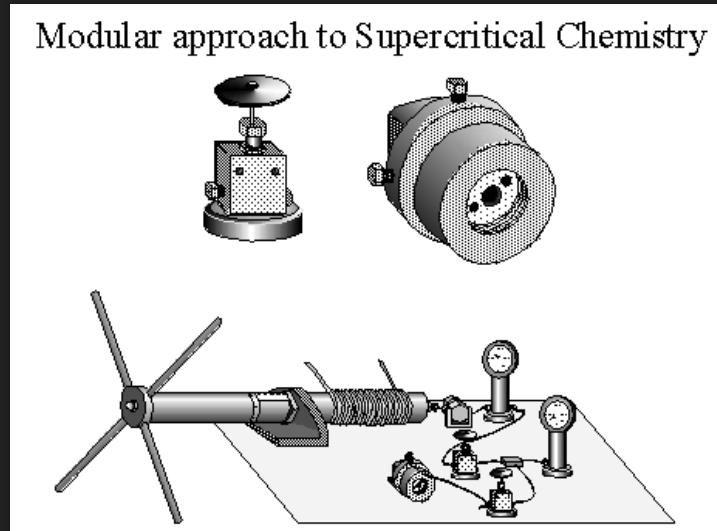
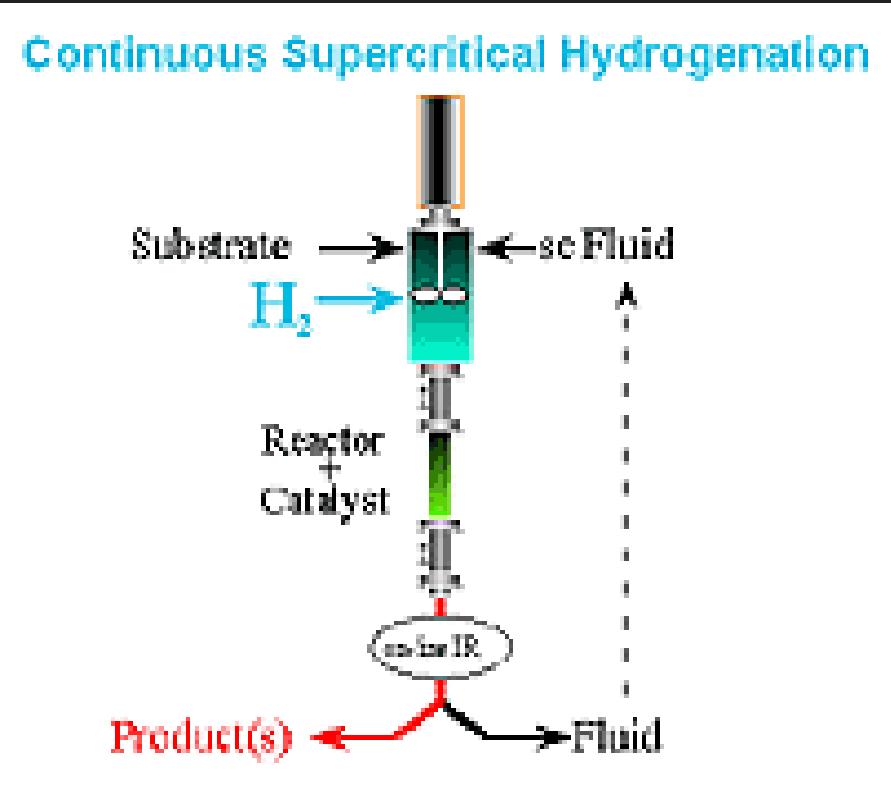
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3 Foams



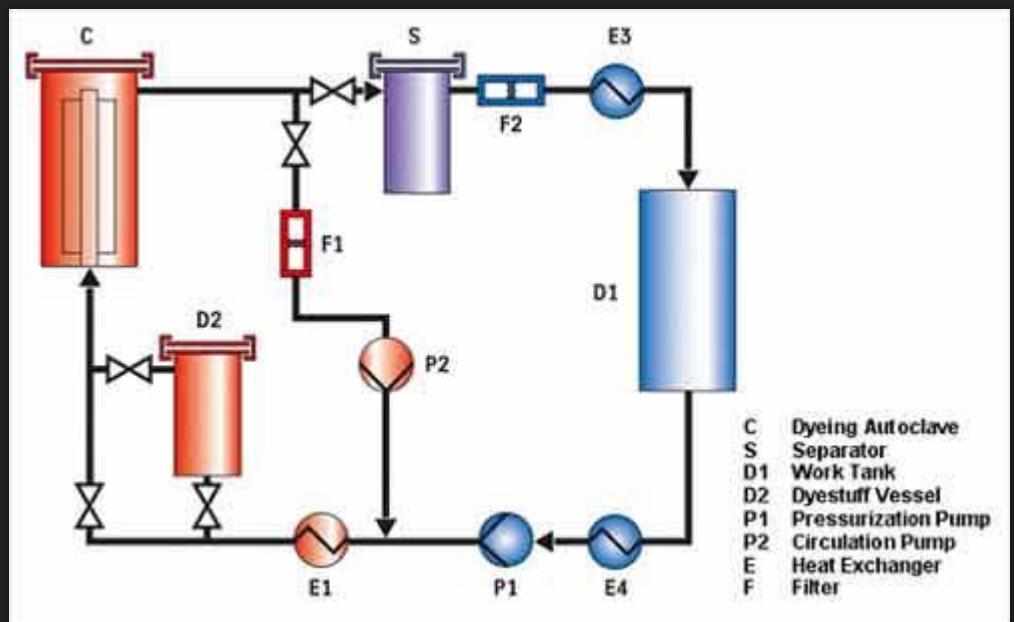
4 Reactions - University in Nottingham



7 Wood impregnation (Sweden)

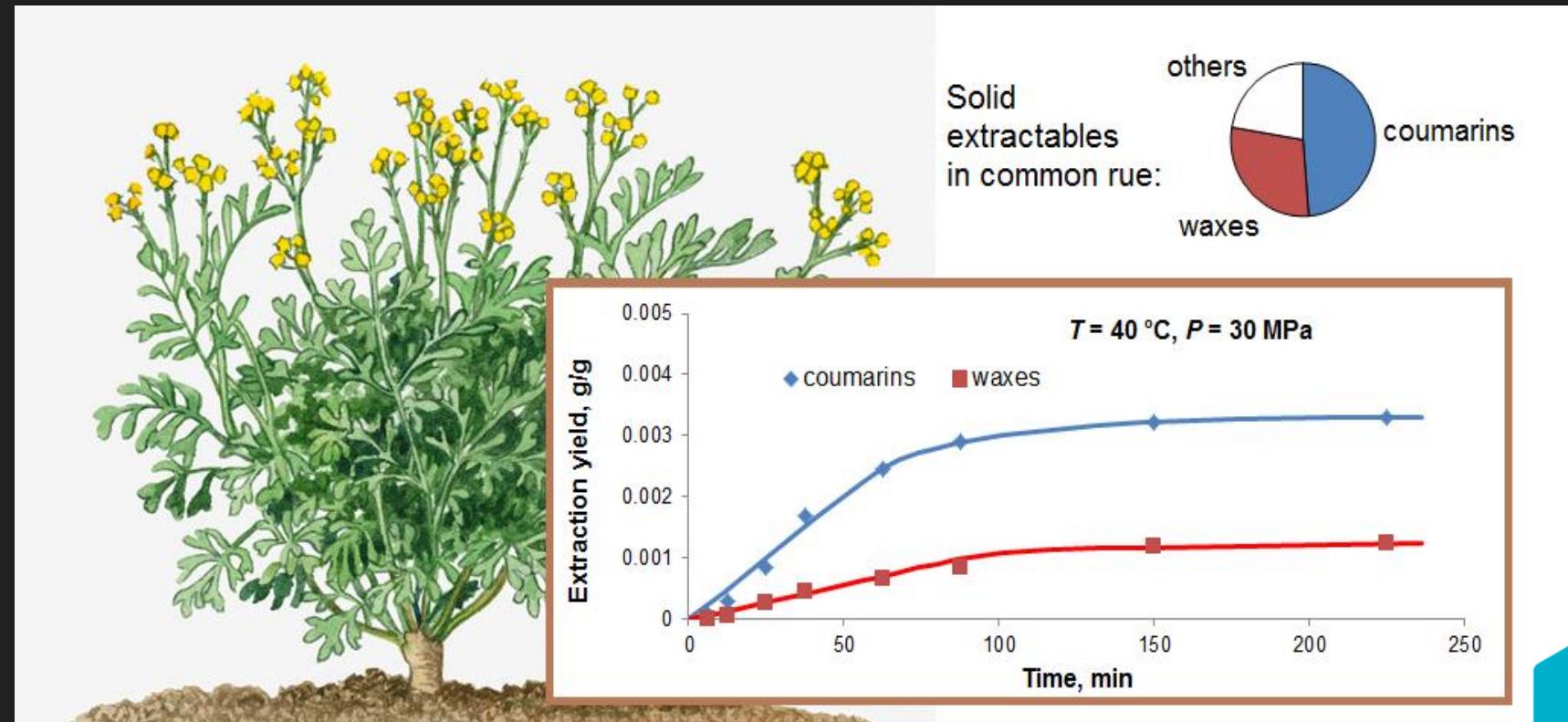


7 Textile dyeing

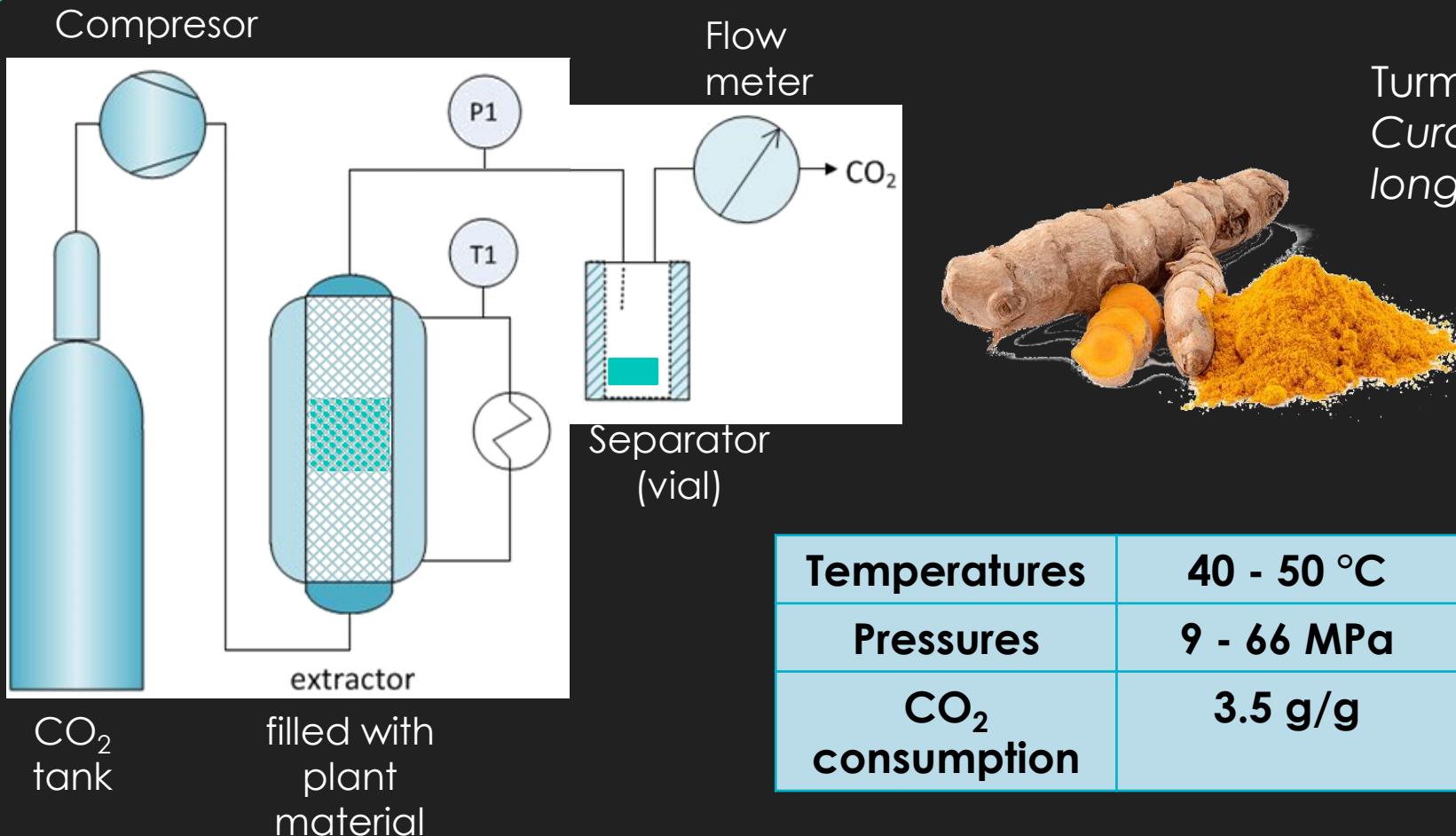


Extraction – botanical insecticides

common rue (*Ruta graveolens*), savory (*Satureja hortensis*)

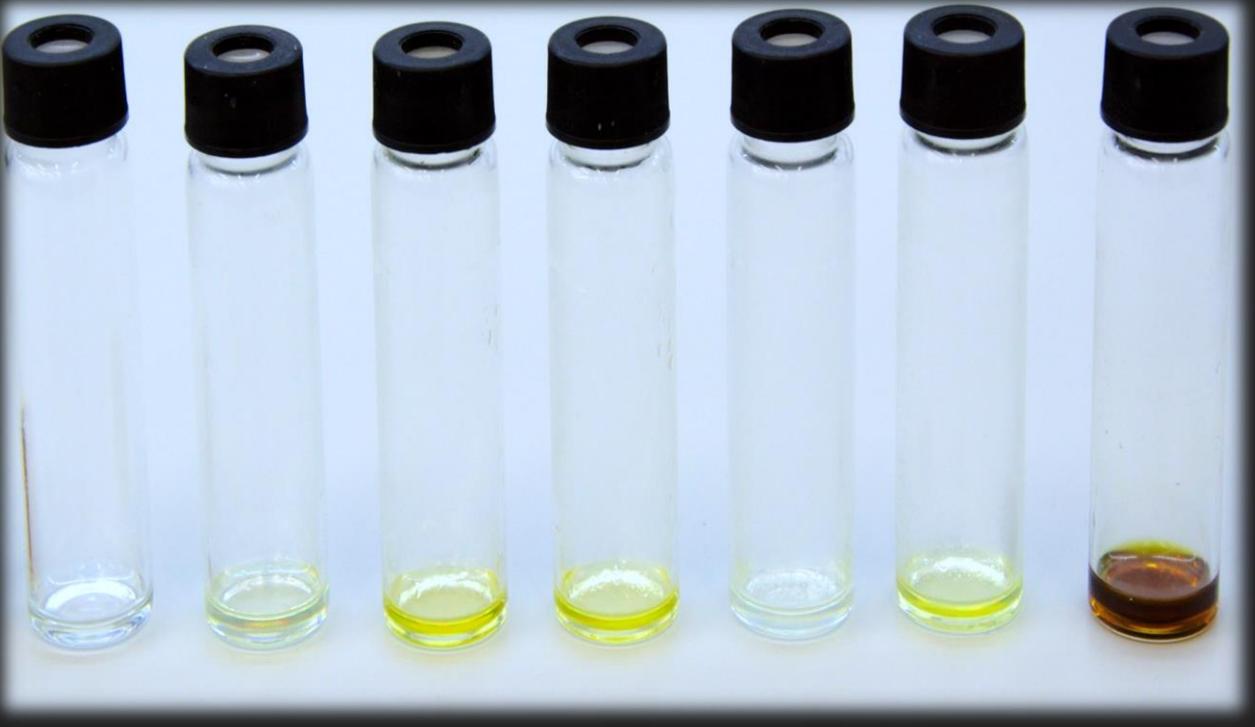


Extraction + separation



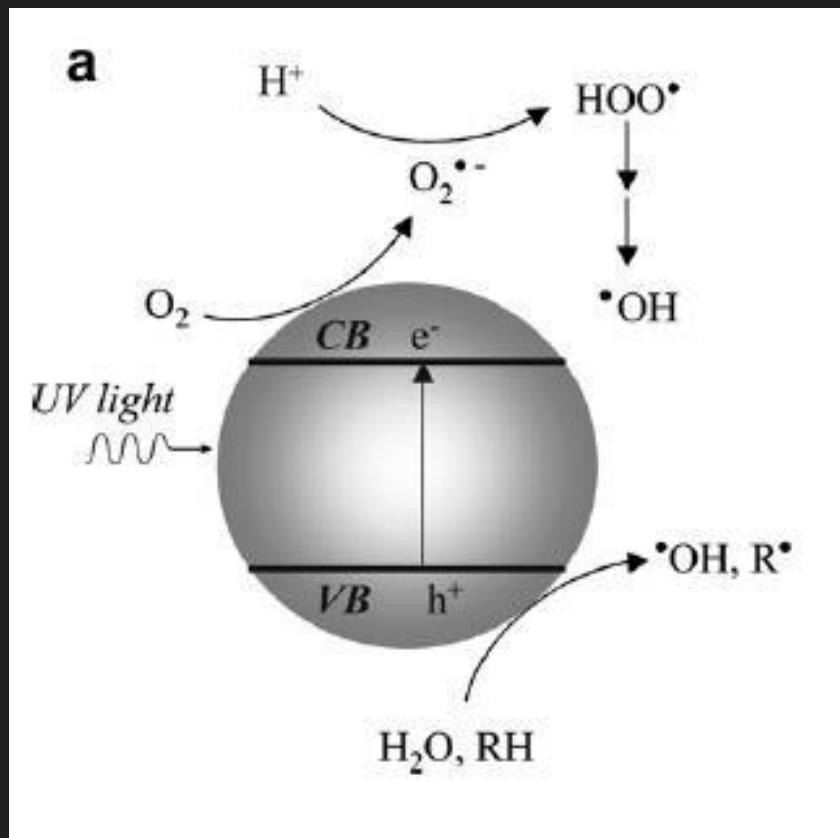


Initial
SFE
isolate



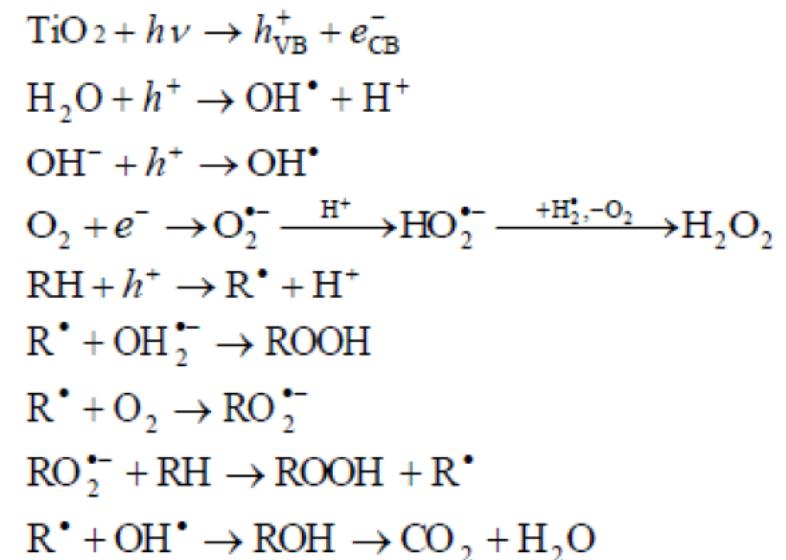
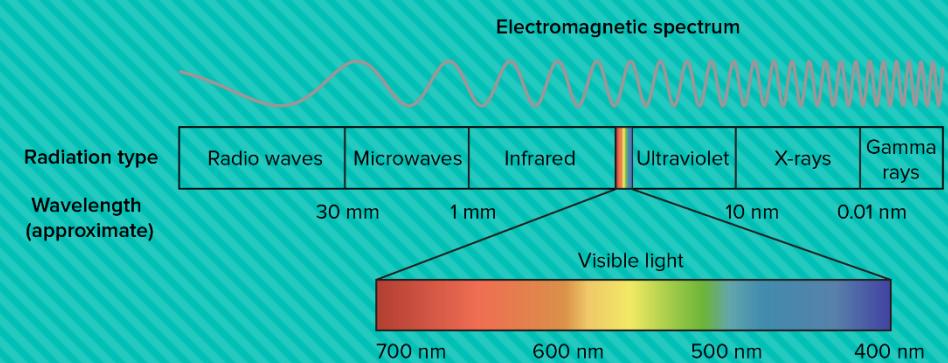
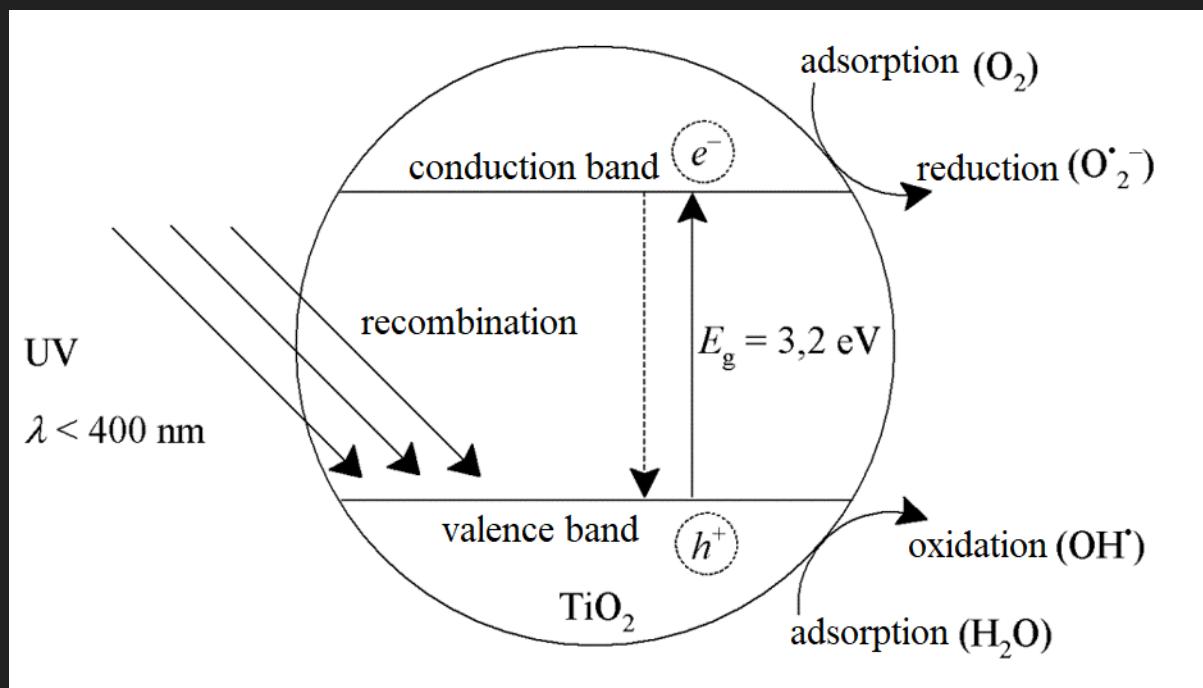
Fractions from supercritical fractionation
process

Photocatalysis

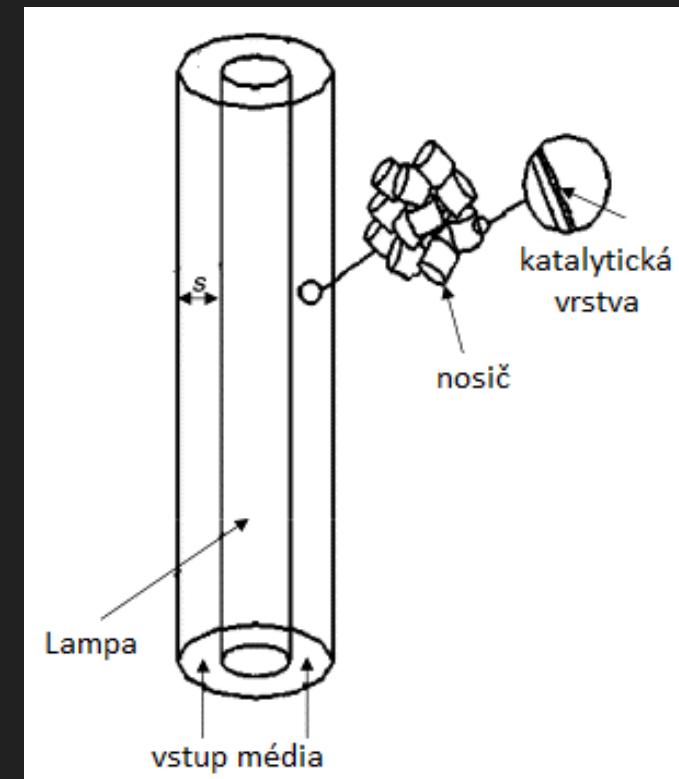
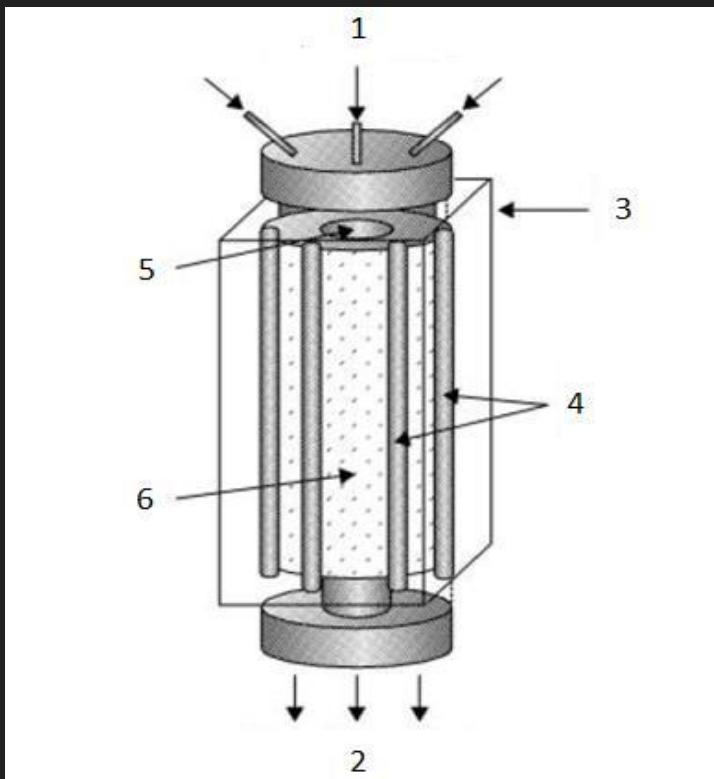


Photocatalyst

TiO_2
 ZnO
 WO_3
 SnO_2
 Fe_2O_3
 ZnS



Photocatalytic reactors





anatase

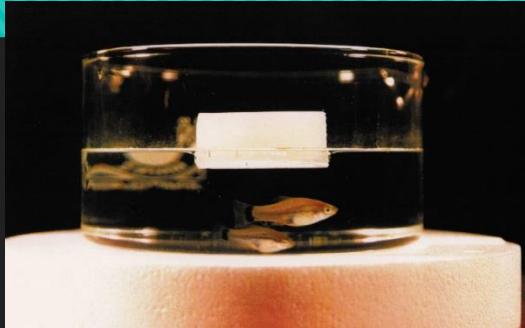


brookite



rutile

TiO_2 - aerogels, thin films

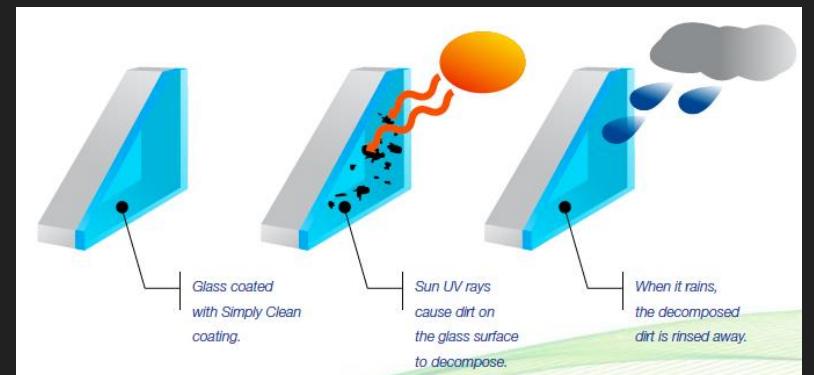


- Low-toxicity
- Good chemical stability
- Catalytic activity
- Sensors
- **Catalyst**

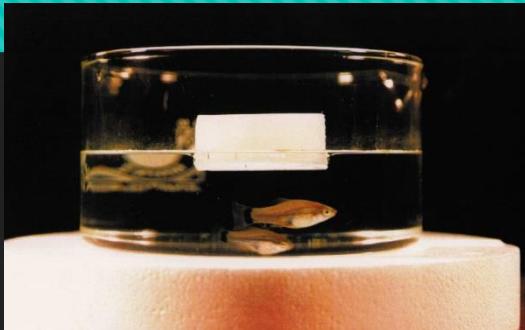


- Low density (up to 95% of volume is air)
- Large open pores
- High specific surface area
- Heat insulation
- Pharmaceuticals
- Biological materials
- Solvent or solute carrier

- Solar cells
- Self-cleaning systems



Methods of preparation of crystalline TiO₂



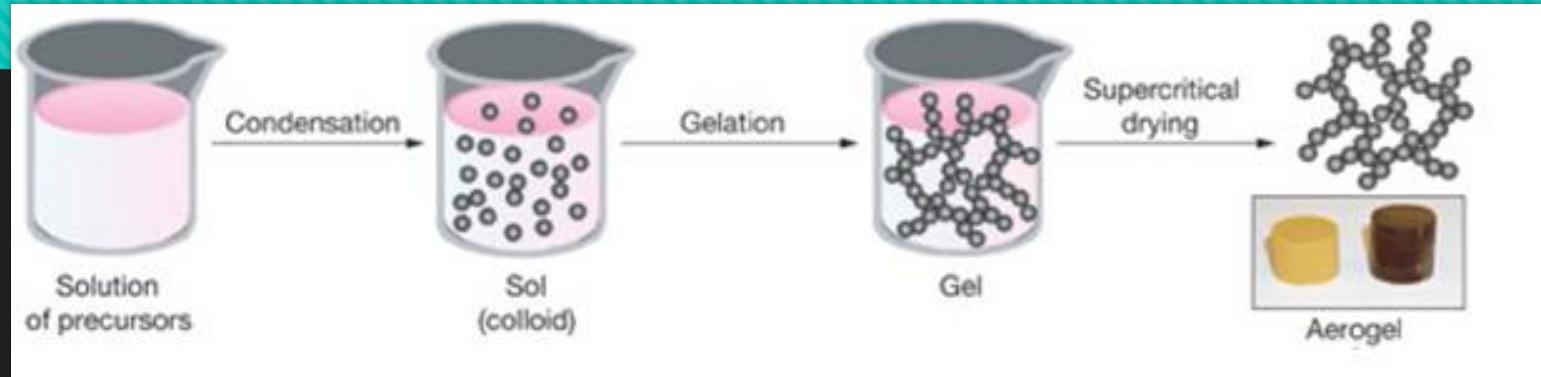
- Ambient drying techniques:
 - solvent removal → the surface tension infers capillary pressure gradient → **collapse the pores**
- Freeze-drying:
 - slow rate & high pressure of sublimation
 - increase of the solvent volume upon crystallization → volume expansion → **powders**
- Thermal treatment (calcination):
 - excessive **sintering**
 - recrystallization
 - cheap and easy
- Supercritical CO₂ + Calcination :
 - ☺ increase the photocatalytic activity
 - ☺ high specific surface area

Preparation: Supercritical fluid crystallization

- No surface tension
- **Gel structure maintains its integrity**
- **Large specific area**
- Control of the solvation power
- Adjusting temperature and pressure= possibility of controlling the structural properties
- low temperature
- Reduced capillary force
- Mild operating temperature
- Easy/no need of solvent separation
- Recycle
- Expensive apparatus
- Cheap operating price



Aerogels



mixture without water



Surfactant (source of TiO₂):
Ti(IV)isopropoxide
HNO₃
hexan

sol-gel process
→
water

wet gel



Thin films

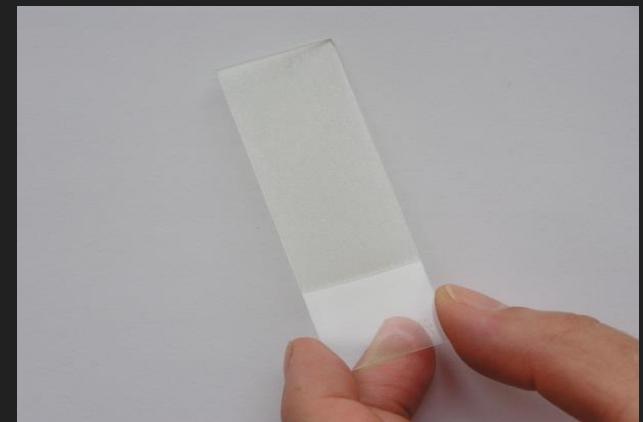
Surfactant (source of TiO₂):
Ti(IV)isopropoxide
HNO₃
Isopropanol
water

solution (sol)

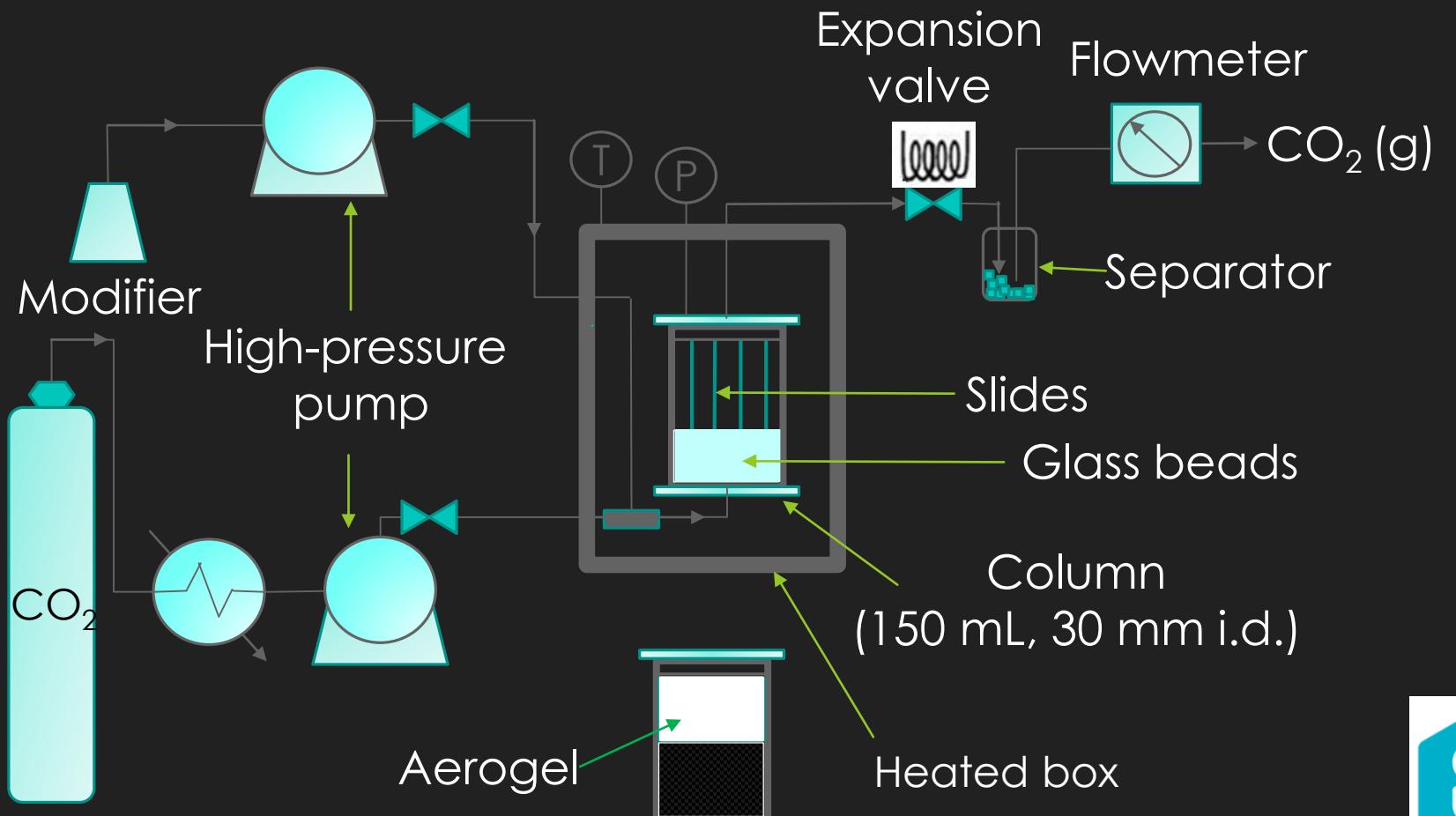


Dip-coating
→

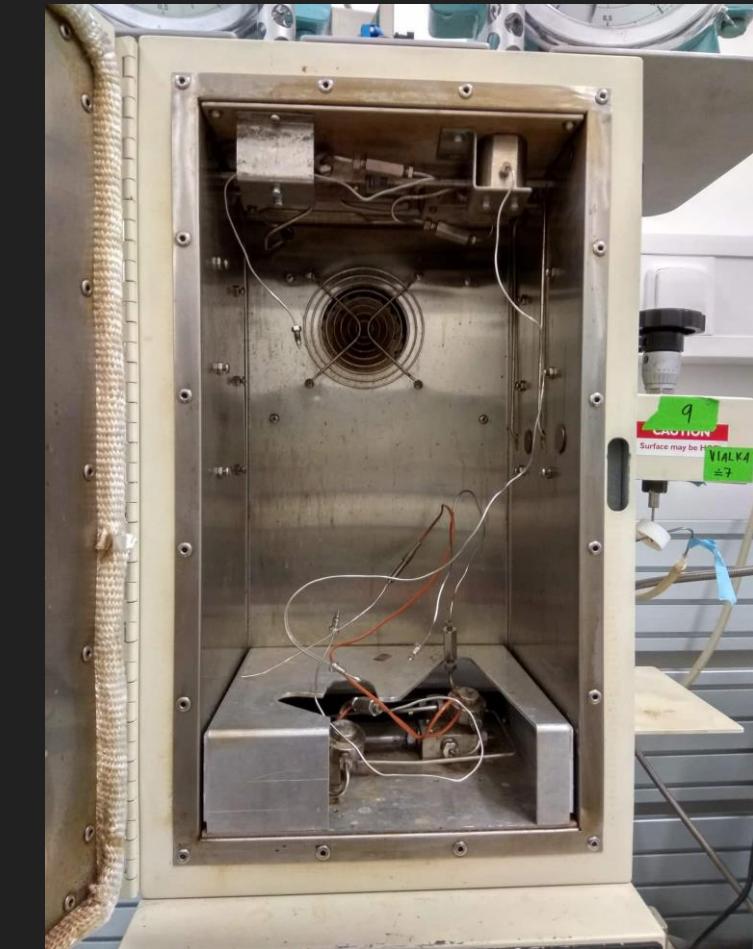
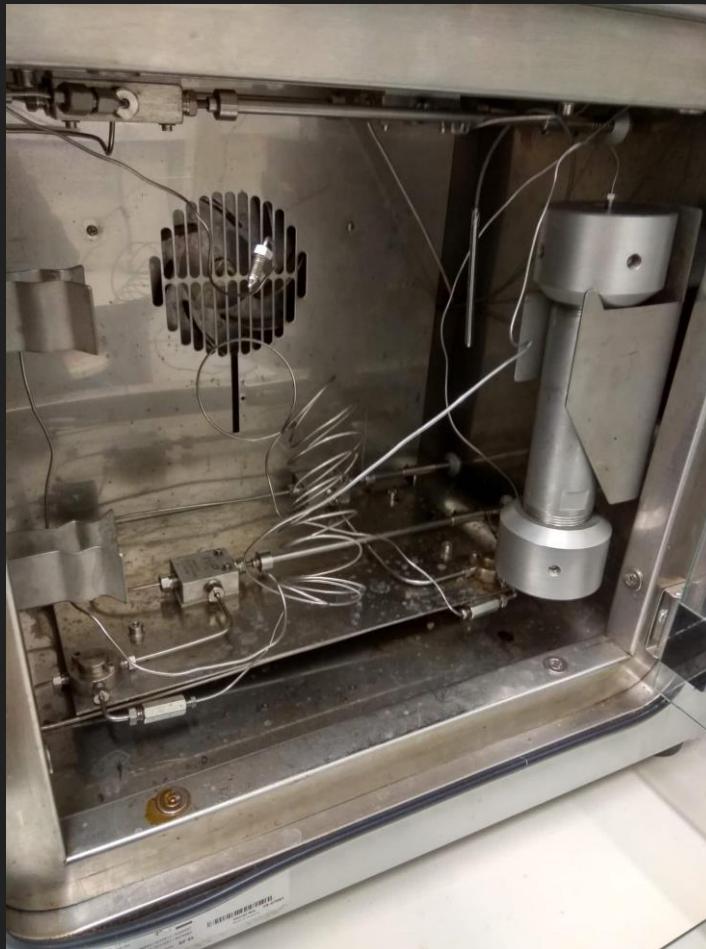
soda-lime slide



Apparatus



Apparatus



Supercritical fluid crystallization

Thin films

| Experimental condition | |
|-----------------------------------------------|-------------------------------|
| Temperature | 40-150 °C |
| Pressure | 10-30 MPa (30 MPa) |
| Amount of CO ₂ | 50-200 g |
| Modifier | water, ethanol, water:ethanol |
| Concentration of water in scCO ₂ | 10-50 wt. % (30 wt.%) |
| Concentration of alcohol in scCO ₂ | 5-80 wt. % (10 wt.%) |
| CO ₂ flow rate | 0.8-1.6 g.min ⁻¹ |

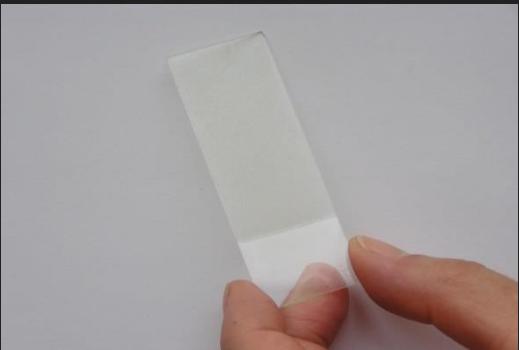
Aerogels

| Experimental condition | |
|-----------------------------------------------|-------------------------------|
| Temperature | 40-100 °C |
| Pressure | 10-30 MPa (30 MPa) |
| Amount of CO ₂ | 50-200 g |
| Modifier | water, ethanol, water:ethanol |
| Concentration of water in scCO ₂ | 5-30 wt. % (5-15 wt.%) |
| Concentration of alcohol in scCO ₂ | 10 wt. % |
| CO ₂ flow rate | 0.8-1.6 g.min ⁻¹ |

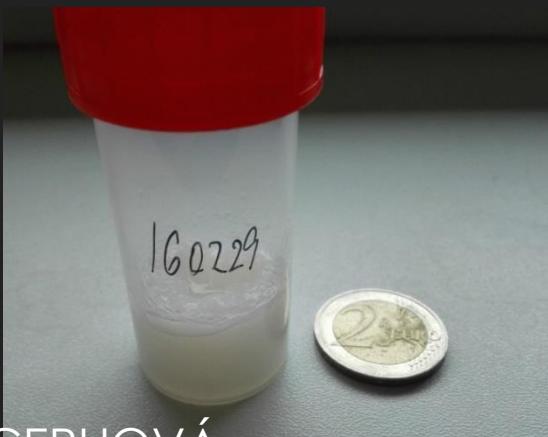


TiO_2 thin films and aerogels after SFC

Deposited
thin film



Aerogel



SFC



Treated thin film



Treated aerogel

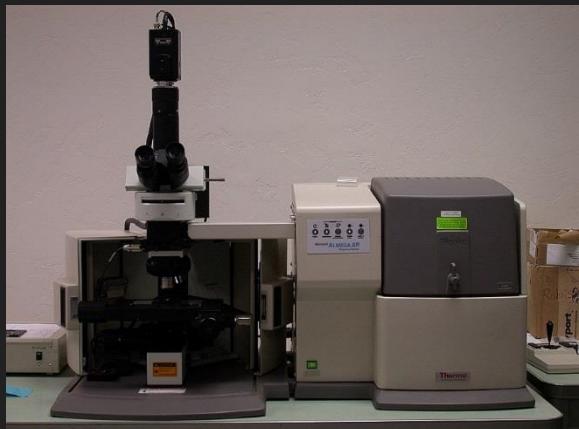


SFC



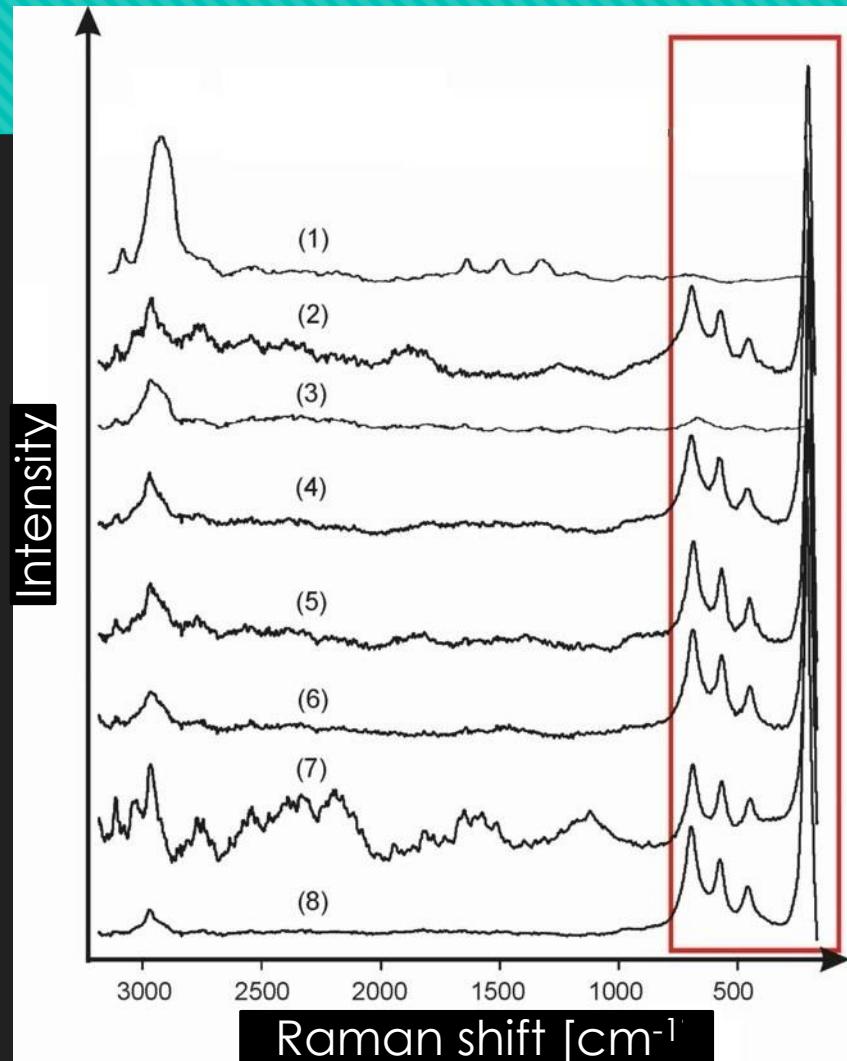
Characterization methods

- Raman spectroscopy: anatase crystalline structure presence and purity
- X-ray diffraction analysis: phase composition and TiO_2 crystal size
- Nitrogen physisorption: specific surface area



Raman spectroscopy Character and purity Thin films

Region of anatase peaks



CO_2 (150 °C)
 $\text{CO}_2 + \text{water}$ (150 °C)
 $\text{CO}_2 + \text{ethanol}$ (150 °C)
 $\text{CO}_2 + \text{water+ethanol}$ (150 °C)

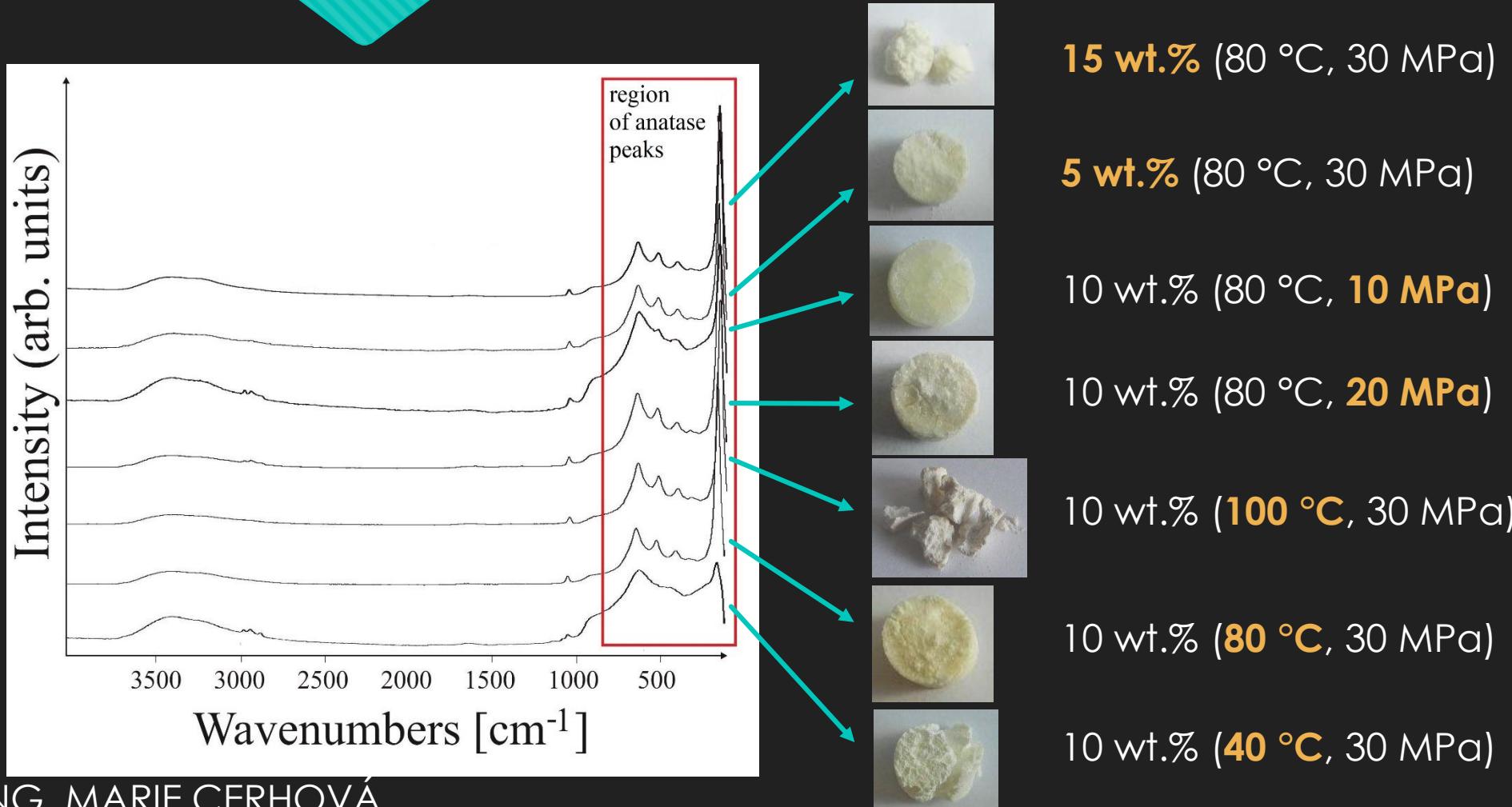
$\text{CO}_2 + \text{water} \longrightarrow \text{CO}_2 + \text{ethanol}$ (40 °C → 150 °C)



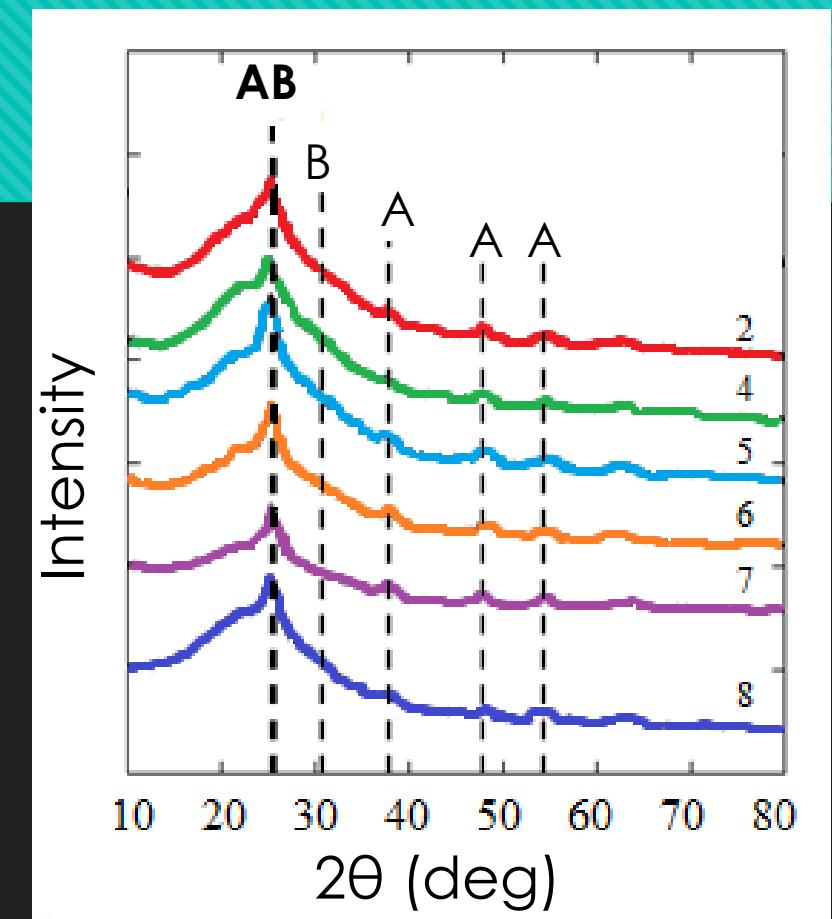
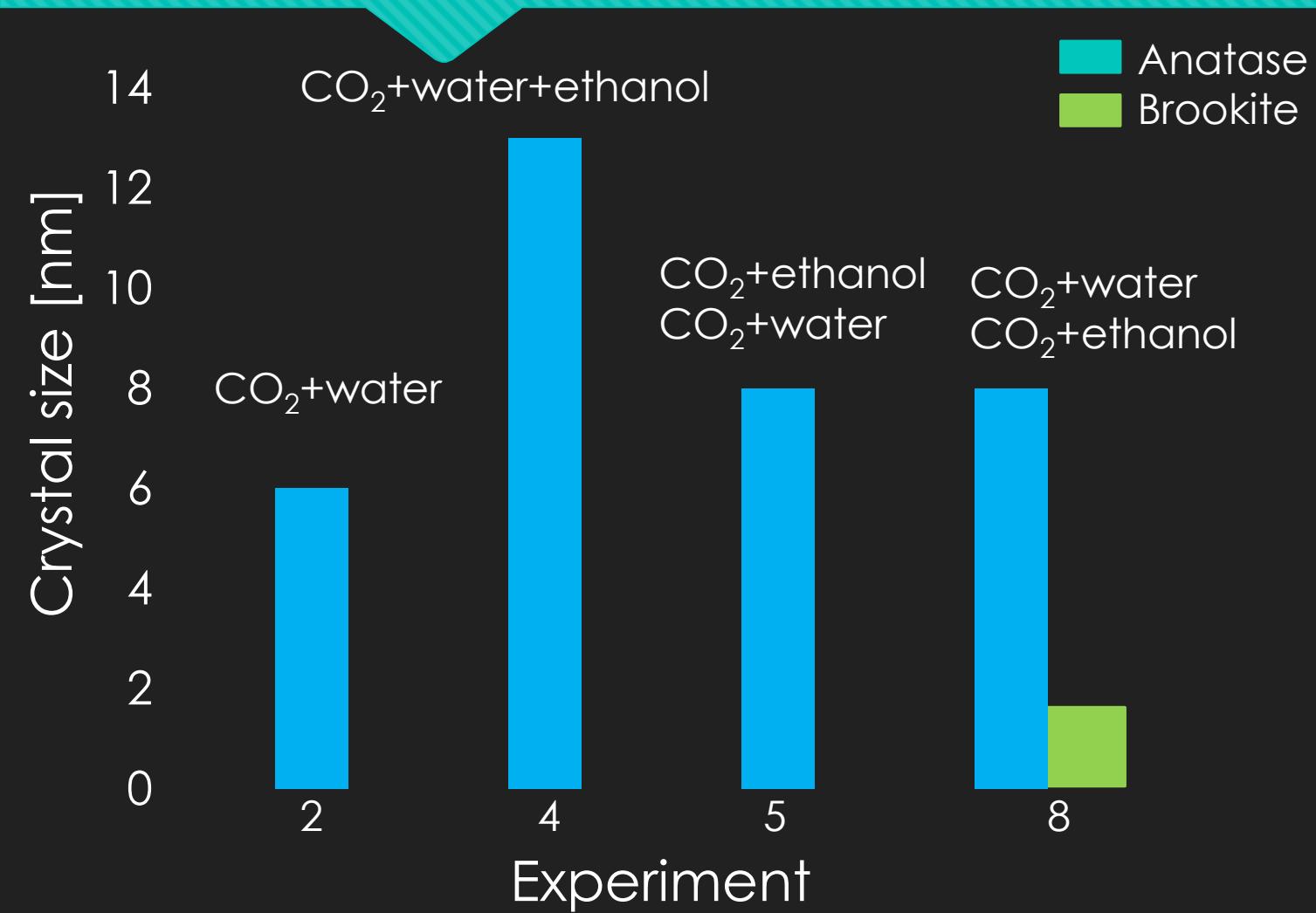
Raman spectroscopy

Character and purity

Aerogels

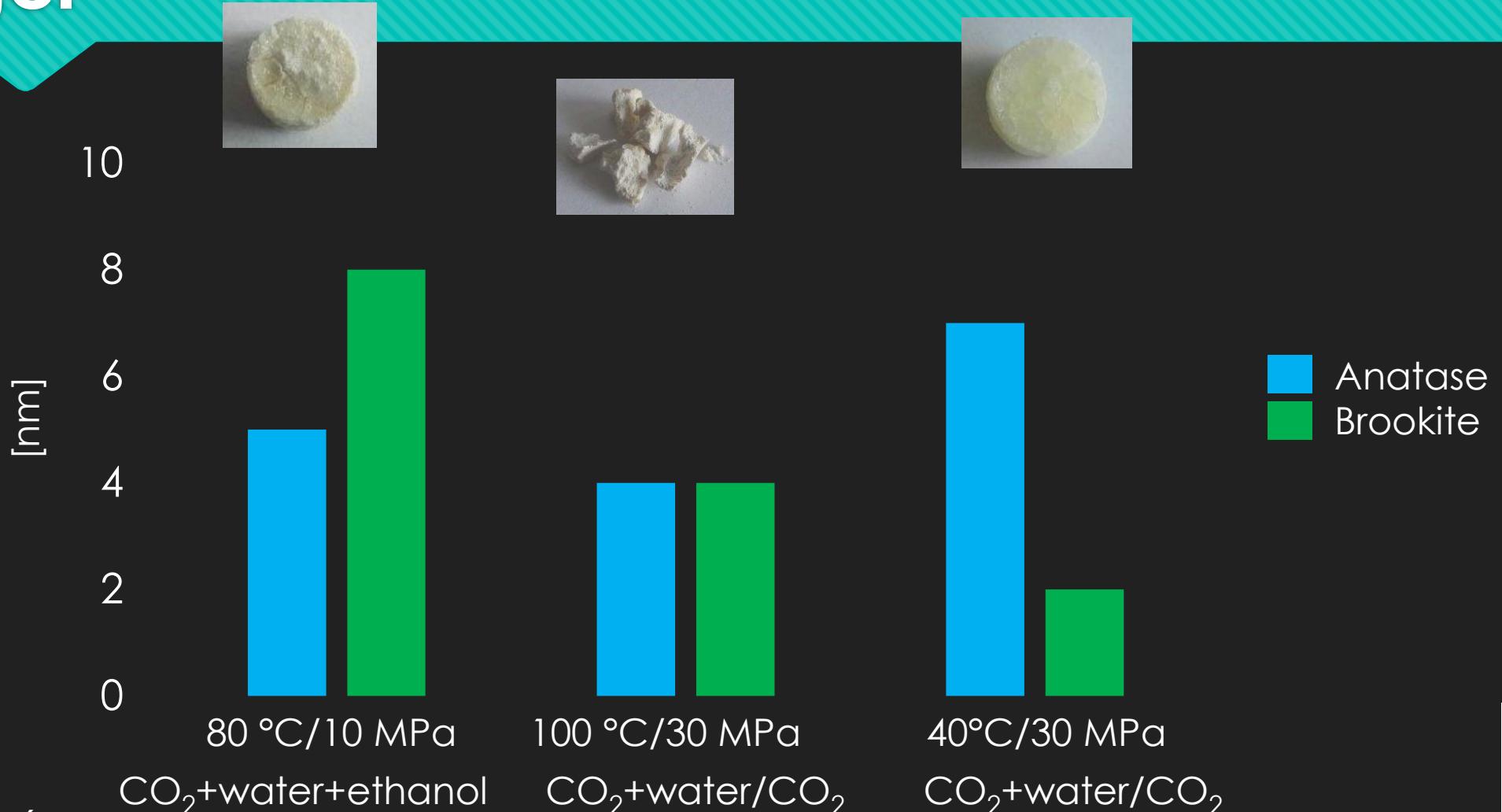


XRD Structure and crystal size Thin films

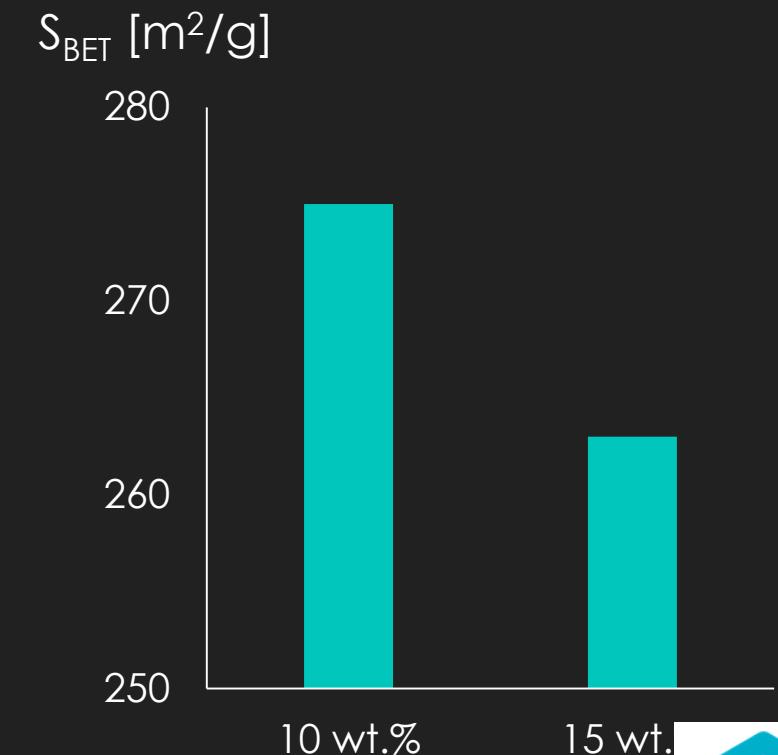
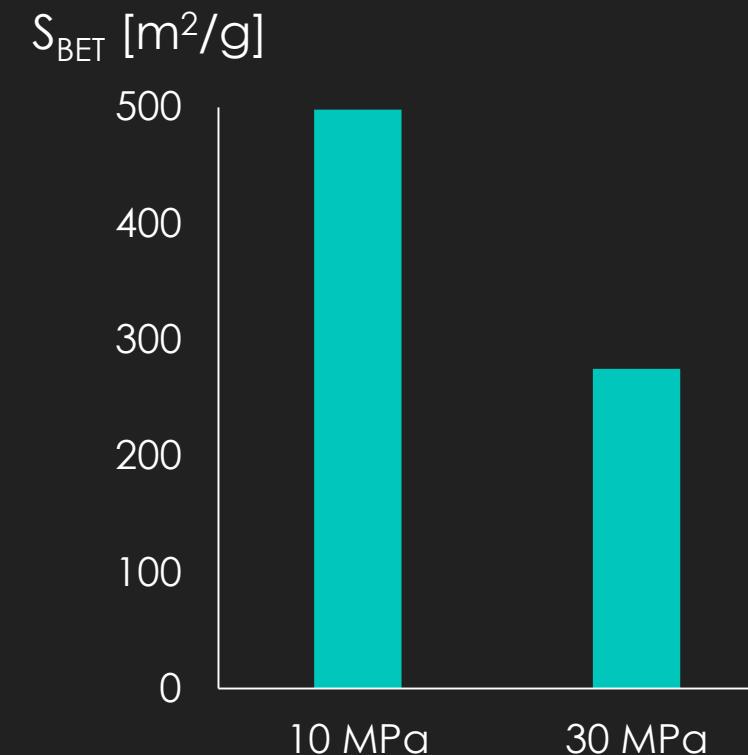
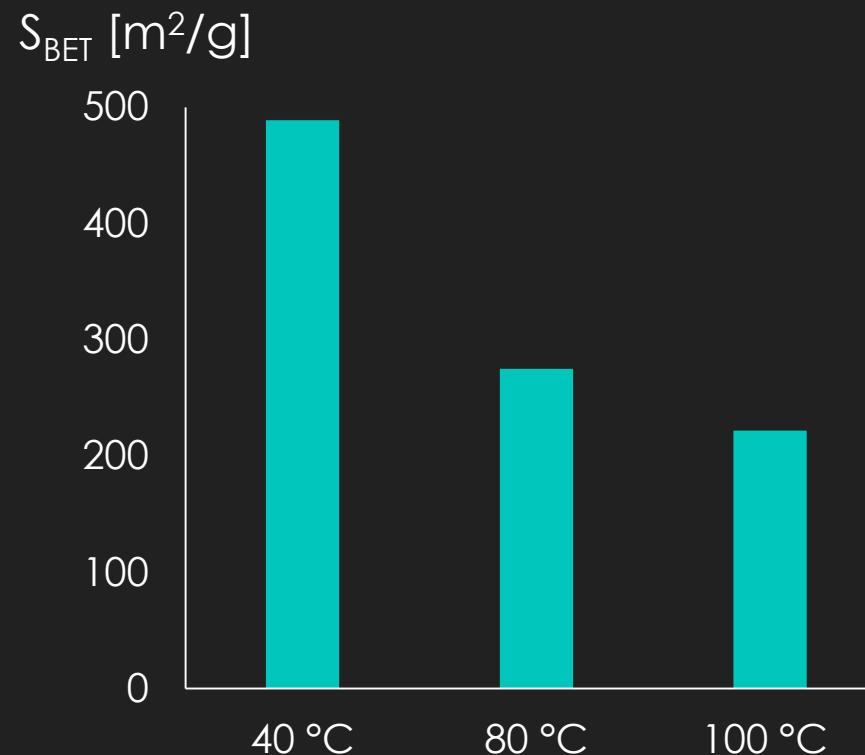


A - anatase
B - brookite
AB - mixture of anatase+brookite

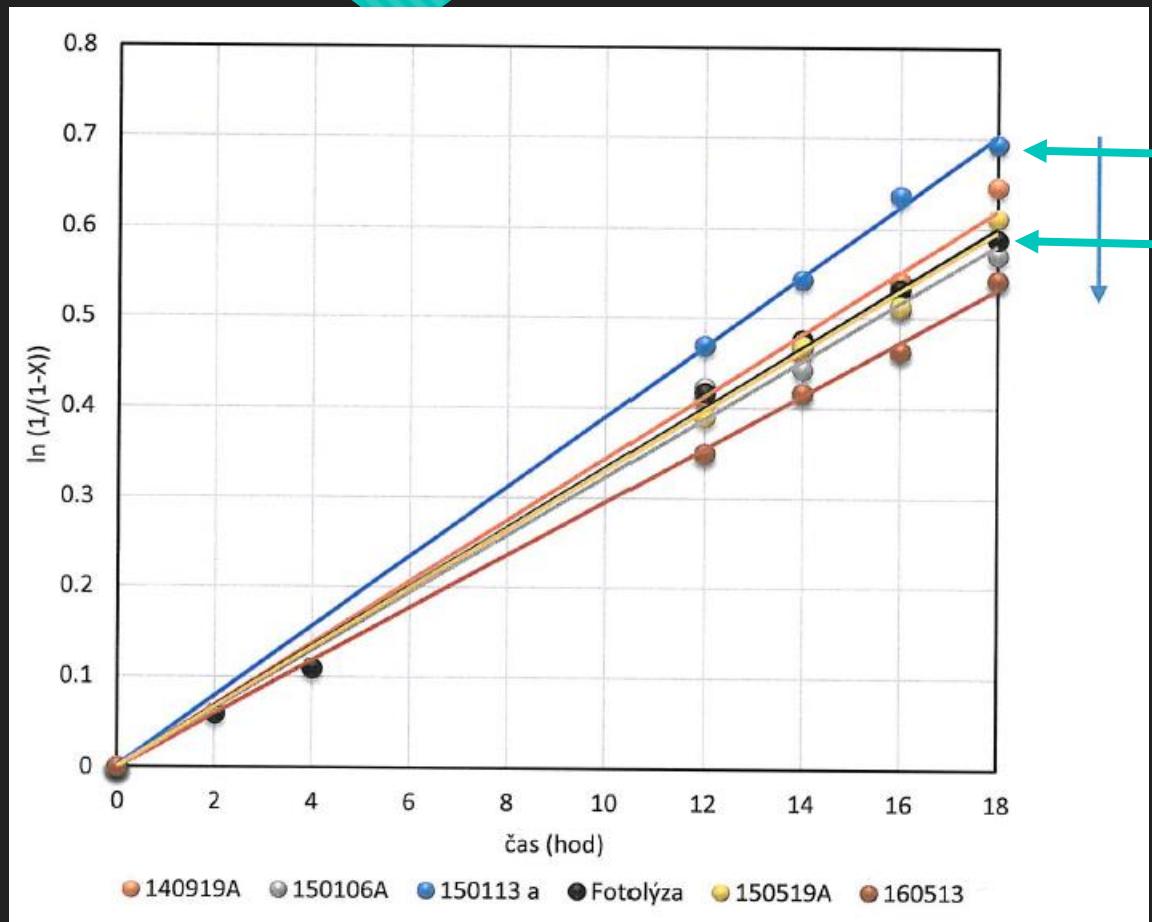
XRD Structure and crystal size Aerogel



N_2 physisorption Specific surface area Aerogel



Photocatalysis N₂O – thin films



| | Kinetic constant [cm ³ .hod ⁻¹] |
|------------|--------------------------------------------------------|
| 150113 | 25.88247 |
| photolysis | 22.09785 |

Conclusion

- Supercritical CO₂ has great properties: **high diffusivity, high solubility power, Non-flammable, non-explosive, low cost, high purity**
- Supercritical CO₂ can be used for: **extractions, cleaning, impregnation, crystallization**
- New method for preparation of crystalline TiO₂ thin films and monolithic aerogels with high surface area (used as photocatalyst in photocatalysis): **Supercritical fluid crystallization**
- **Influence of conditions of modified scCO₂** at the preparation of crystalline TiO₂ aerogels (T, p, amount of CO₂, type of modifier, concentration of modifier in CO₂)
- Modifier of scCO₂: water, ethanol, water:ethanol
- We must be carefull about the conditions
- Using this method we obtained nanocrystalline anatase and brookite in the form of thin films and aerogel, which are photocatalytic active







cerhova@icpf.cas.cz

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