

Ceramic and Colloidal Processing

Surface Tension, Wettability and Hydrophobic Surfaces

Dr. Ing. Matteo Donati
Lausanne, 07 October 2025

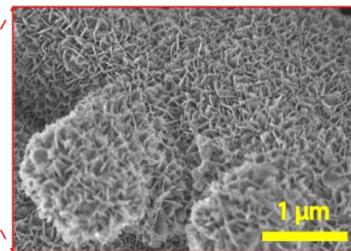
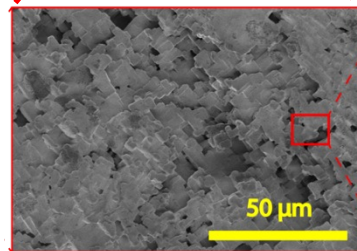
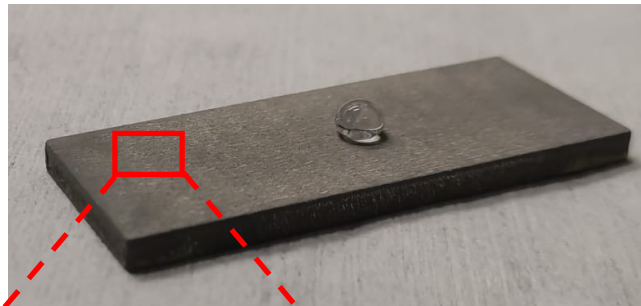
About Me (Dr. Ing. Matteo Donati)

- Bsc. and Msc. in mechanical engineering (ETH Zürich)
- Doctorate (ETH Zürich)
- Development of robust and scalable hydrophobic/superhydrophobic (water repellent) surfaces for efficient condensation heat transfer
- Micro-/nanotopography design and surface chemistry modification
- Currently postdoc (PSI)
- Research on wettability of rare-earth oxides (second lecture part)

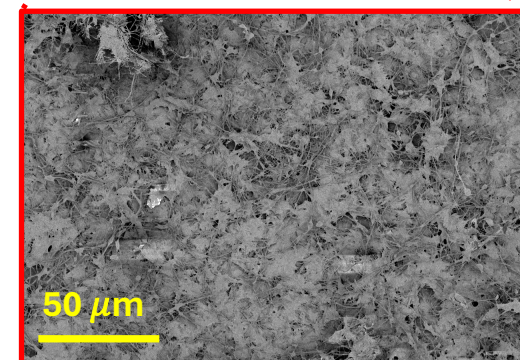
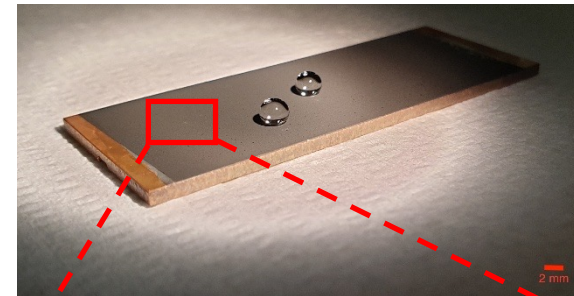


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Hierarchically-structured
superhydrophobic surface on aluminum



Sprayable superhydrophobic
nanocomposite



References

- References:
- 1) Matteo Donati et al., Metal Surface Engineering for Extreme Sustainance of Jumping Droplet Condensation, *Langmuir*, 2023
 - 2) Matteo Donati et al., Sprayable Thin and Robust Carbon Nanofiber Composite Coating for Extreme Jumping Dropwise Condensation Performance, *Advanced Materials Interfaces*, 2020
 - 3) Abhinash Tripathy et al., Ultrathin Durable Organic Hydrophobic Coatings Enhancing Dropwise Condensation Heat Transfer, *Langmuir*, 2022

Objectives

- Define and explain the concepts of **surface tension** and **interfacial tension**
- Mention **examples of experimental methods** for the measurement of surface tension of liquids
- Explain the physical principles behind surface wettability (**Young's equation, Wenzel and Cassie–Baxter models**)
- Distinguish between **hydrophilic** and **hydrophobic** surfaces
- Explain **how we can measure contact angles on surfaces using a goniometer**
- Define and explain **superhydrophobicity**
- Understand the difference between **static contact angle, advancing contact angle, receding contact angle** and **contact angle hysteresis**
- Mention **examples of application fields of superhydrophobic surfaces**
- Discuss **engineered approaches** to design superhydrophobic surfaces and the respective **challenges**
- Summarize the state of the art on **wettability of rare-earth oxides**
- Discuss the **potential of rare-earth oxides as hydrophobic coating material**, as well as **examples of scalable deposition techniques**

Outline

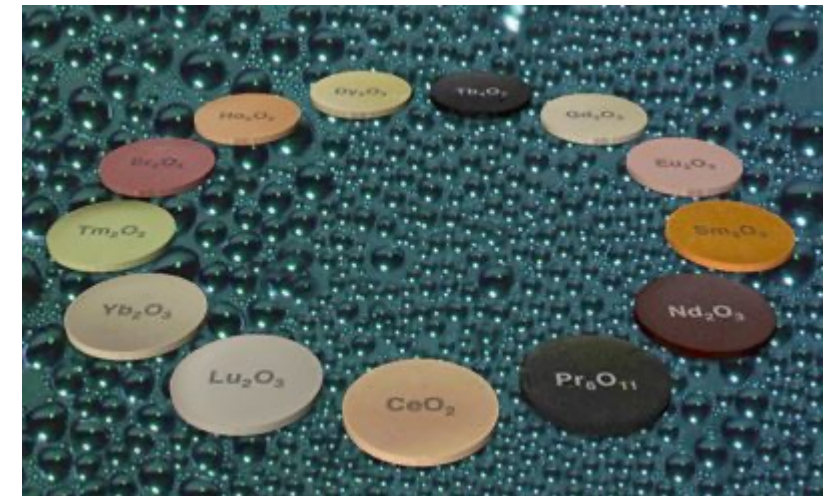
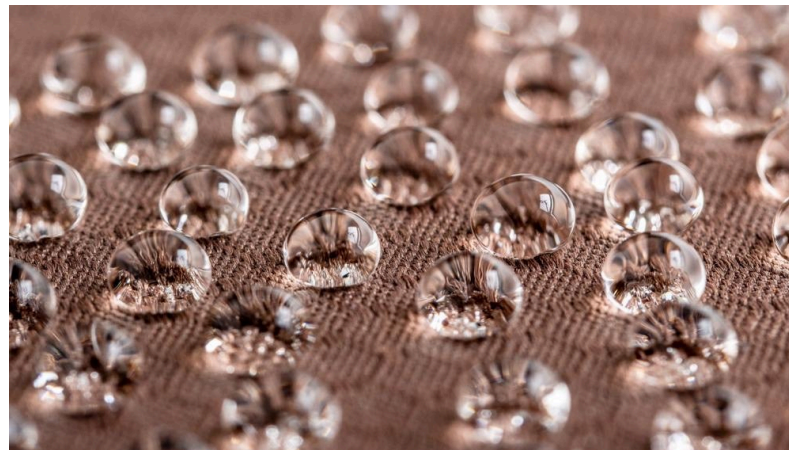
1. Theory and Fundamentals

2. Superhydrophobic Surfaces

3. Hydrophobicity of Rare-Earth Oxides

a) State of the Art

b) Experimental Results



Outline

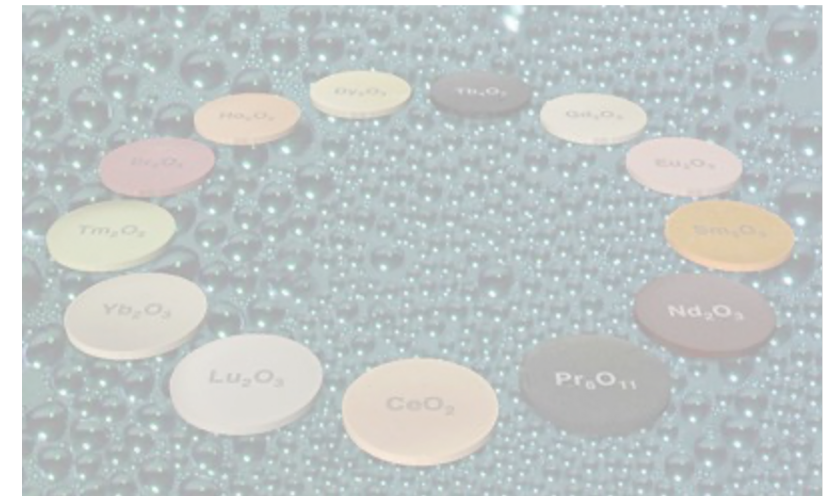
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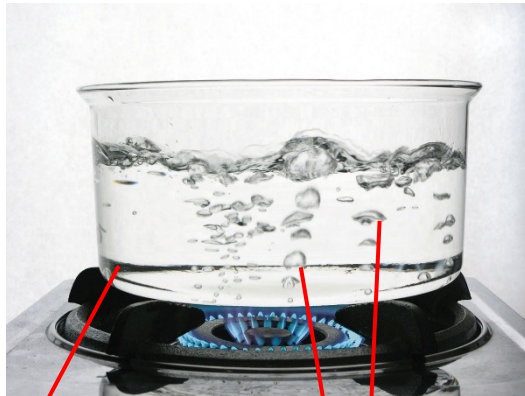
a) State of the Art

b) Experimental Results

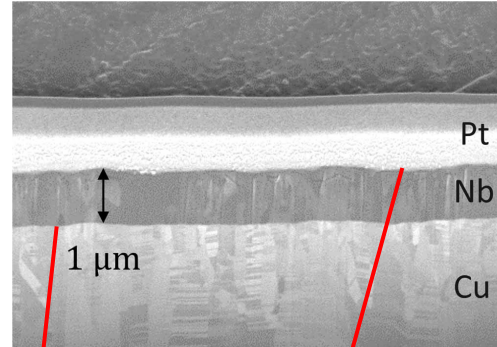


Interface: Definition and Examples

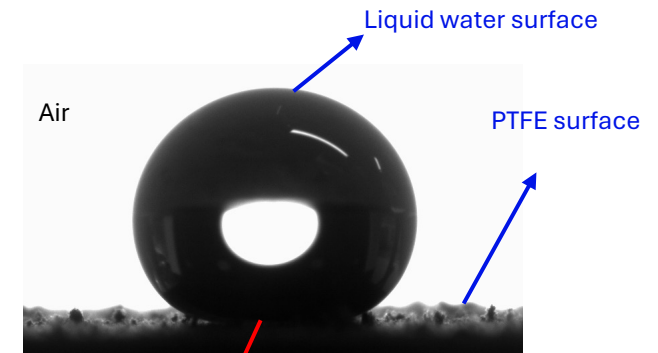
- **Interface** = Boundary between two spatial regions occupied by different matter, or by matter in different physical states
 - Example 1: boiling water in glass beaker
 - Example 2: stack of different thin metal films
- **Surface** = interface, where one of the two phases is air or vacuum
 - Example 3: water droplet sitting on solid polytetrafluoroethylene (PTFE) surface



Interface water vapor (bubbles) – liquid water
Interface glass – liquid water



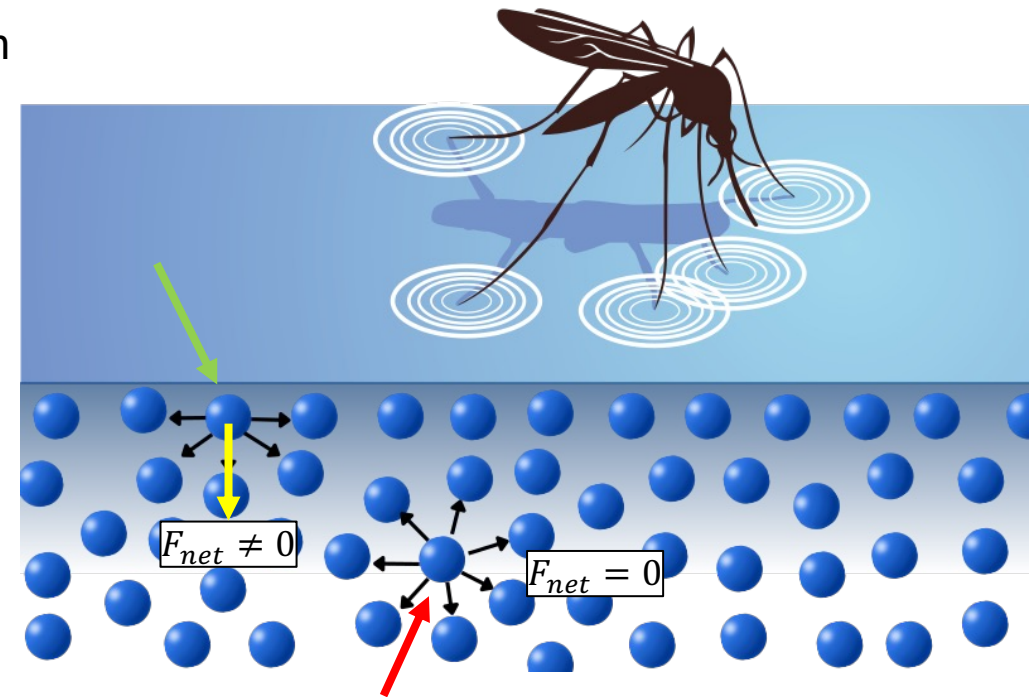
Interface copper – niobium
Interface niobium - platinum



Interface liquid water - PTFE

Origin of Surface Tension

- Surface tension is the tendency of a liquid to assume the shape that minimizes its surface area and therefore its energy
- Matter property arising from the cohesive forces between molecules such as van der Waals forces and hydrogen bonds
- **Molecule in the midst of a liquid:** energetically favorable state (sum of cohesive forces with all molecules in its neighborhood is zero). Equal attraction in all directions
- **Molecule located at the surface:** is not equally pulled in all directions, in fact it loses half of the cohesive interactions with its neighboring molecules, resulting in a non-zero net force pointing towards the liquid
- Result: molecules at the liquid surface are pushed together and are able to resist an external force, like for example the weight of a water spider on water



Surface Tension: Physical Derivation

- Surface tension is a property of an interface which is associated with the energy required to form the interface (work of transferring a molecule to the surface)
- Let's consider a homogeneous bulk material consisting of molecules A
- Bulk cohesive energy per mole $E_{A,b}$:

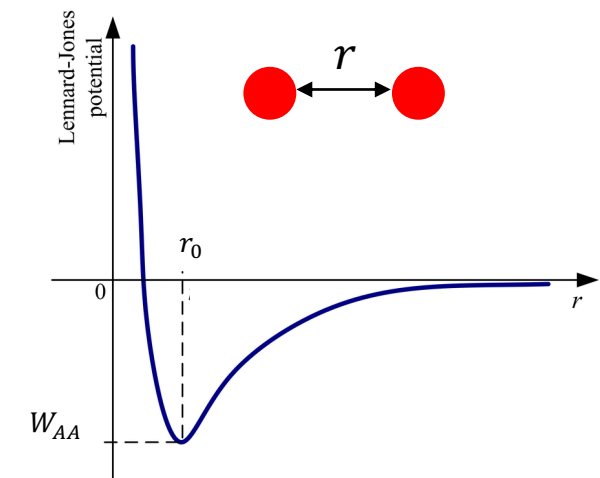
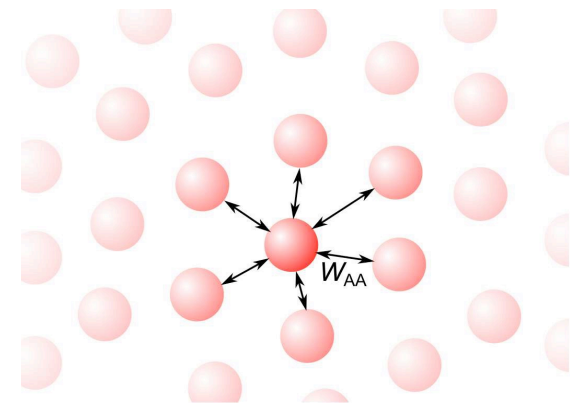
$$E_{A,b} = \frac{1}{2} \cdot W_{AA} \cdot N_A \cdot Z_b$$

W_{AA} : interaction energy between two molecules A at equilibrium distance r_0

N_A : Avogadro constant

Z_b : average number of neighboring molecules to a molecule A in the bulk

- W_{AA} is estimated from the Lennard-Jones model: description of intermolecular forces
- $W_{AA} < 0 \Rightarrow E_{A,b} < 0 \Rightarrow$ formation of bulk material energetically favored!



Surface Tension: Physical Derivation

- Bulk cohesive energy per molecule $\tilde{E}_{A,b}$:

$$\tilde{E}_{A,b} = \frac{E_{A,b}}{N_A} = \frac{1}{2} \cdot W_{AA} \cdot Z_b$$

$E_{A,b}$: bulk cohesive energy per mole

N_A : Avogadro constant

W_{AA} : interaction energy between two molecules A at equilibrium distance r_0

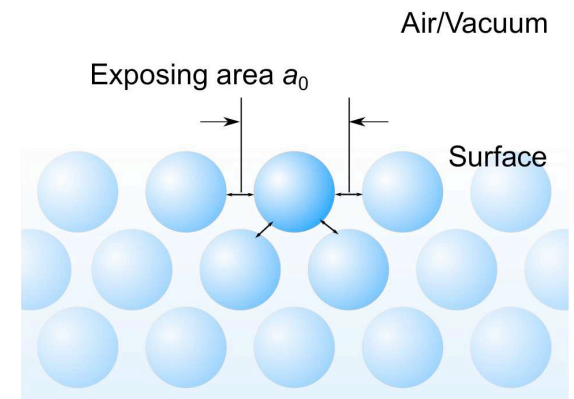
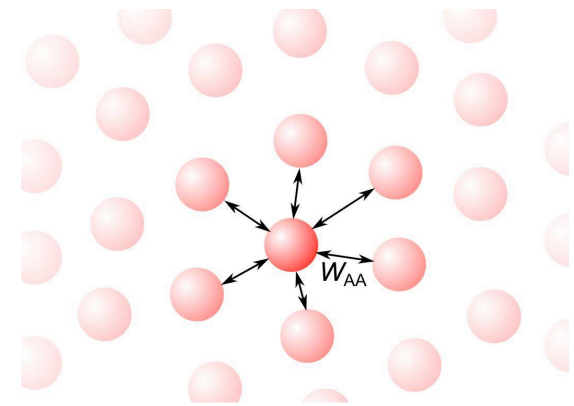
Z_b : average number of neighboring molecules to a molecule A in the bulk

- Surface cohesive energy per molecule $\tilde{E}_{A,s}$:

$$\tilde{E}_{A,s} = \frac{1}{2} \cdot W_{AA} \cdot Z_s$$

Z_s : average number of neighboring molecules to a molecule A at the surface

- Because at the surface we have less molecules interacting compared to inside the bulk ($Z_s < Z_b$) we have that $\tilde{E}_{A,s} > \tilde{E}_{A,b}$
- Energy is required to separate bulk material A and create interface!



Surface Tension: Physical Derivation

- We can now define a new parameter that we call surface tension of material A (γ_A):

$$\gamma_A = \frac{\tilde{E}_{A,s} - \tilde{E}_{A,b}}{a_0} = \frac{1}{2a_0} \cdot W_{AA} \cdot (Z_s - Z_b) > 0$$

$\tilde{E}_{A,s}$: surface cohesive energy per molecule

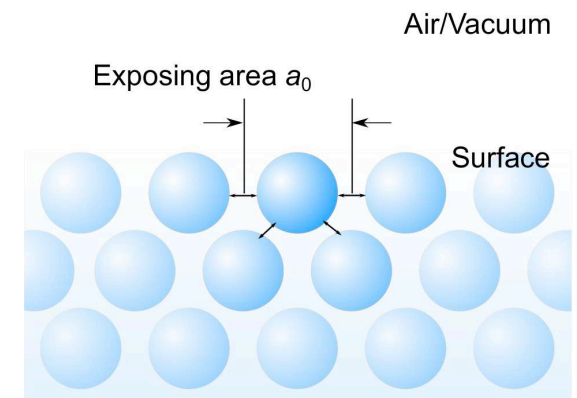
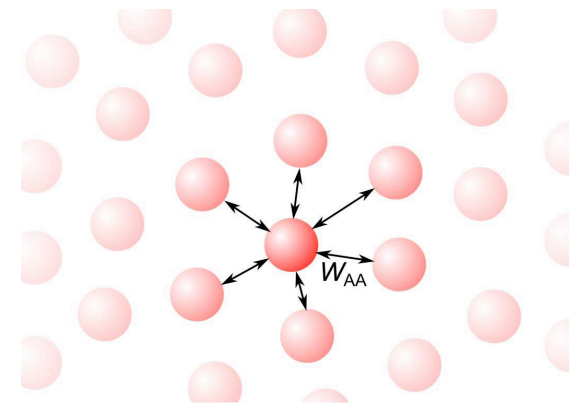
$\tilde{E}_{A,b}$: bulk cohesive energy per molecule

a_0 : area of occupancy of an A molecule at the surface

W_{AA} : interaction energy between two molecules A at equilibrium distance r_0

Z_s : average number of neighboring molecules to a molecule A at the surface

Z_b : average number of neighboring molecules to a molecule A in the bulk



Surface Tension: Two Different Interpretations

1. γ_A can be seen as the amount of energy needed to increase the interface per unit area (surface energy)

- By pulling the string work is applied to the system: increase of soap surface area
- Work is proportional to the number of molecules transferred to the surface
- $dW = \gamma_A \cdot dA$

- Units: $\gamma_A = \left[\frac{\text{energy}}{\text{area}} \right] = \left[\frac{\text{J}}{\text{m}^2} \right]$

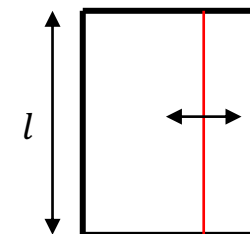
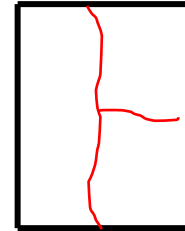
2. γ_A can be seen as a force per unit length (surface tension)

- As soon as the frame is removed from the liquid soap, the mobile string spontaneously moves in the film direction to reduce liquid surface area
- Work done to move the string
- $dW = F \cdot dx = 2 \cdot \gamma_A \cdot l \cdot dx$

- Units: $\gamma_A = \left[\frac{\text{force}}{\text{length}} \right] = \left[\frac{\text{N}}{\text{m}} \right]$

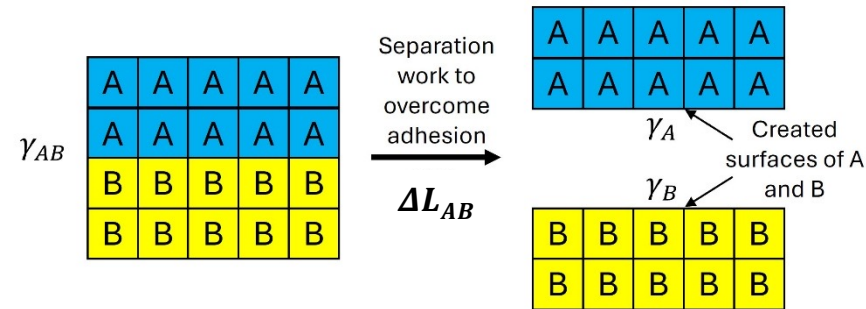
Examples:

- $\gamma_{\text{Water}} (25^\circ\text{C}) \approx 72 \frac{\text{mJ}}{\text{m}^2}$ (polar, hydrogen bond)
- $\gamma_{\text{Ethanol}} (25^\circ\text{C}) \approx 22 \frac{\text{mJ}}{\text{m}^2}$ (less polar, weaker hydrogen bond)
- $\gamma_{\text{Mercury}} (25^\circ\text{C}) \approx 489 \frac{\text{mJ}}{\text{m}^2}$ (metallic bond, strong)



Interfacial Tension: Physical Derivation

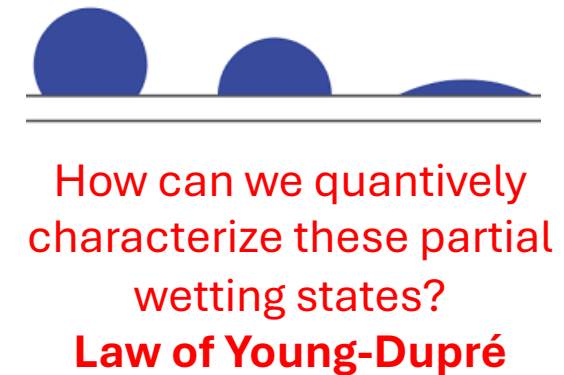
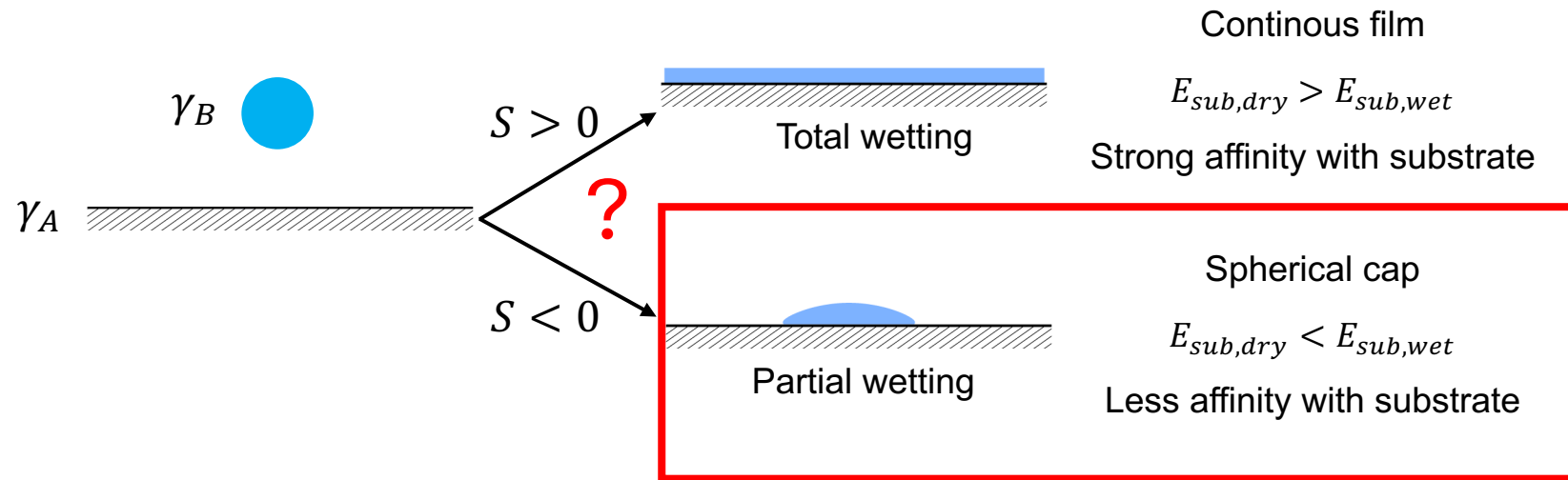
- Until now: surface tension (for surface in vacuum or air)
- Interfacial tension
 - Between two different materials (molecules A and B): γ_{AB}
 - Definition: energy per unit area needed to create new interface between materials A and B



$$\gamma_{AB} = \gamma_A + \gamma_B - \Delta L_{AB}$$


Wetting


- How does a liquid droplet deposited on a solid (or liquid) substrate spread out?



- Spreading parameter
 - Difference between surface energy (per unit area) of substrate when dry and wet

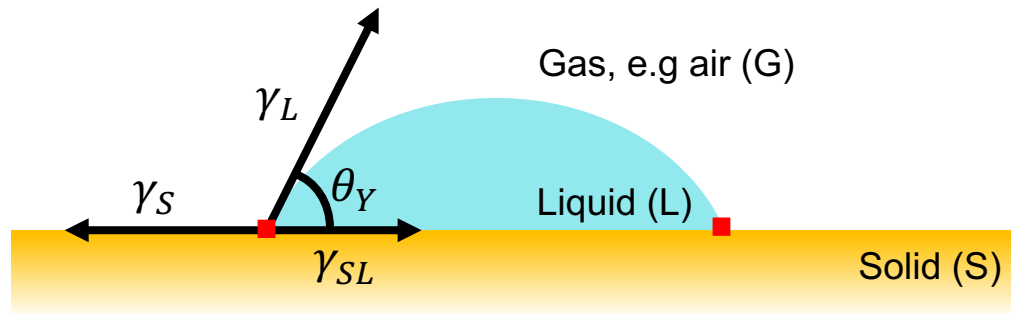
$$S = E_{sub,dry} - E_{sub,wet} = \gamma_A - (\gamma_{AB} + \gamma_B)$$

γ_A


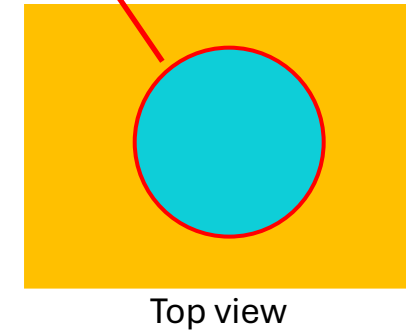
γ_B
 γ_{AB}

- Scenario minimizing total surface energy (more convenient)!
- Valid for smooth, chemically homogeneous substrate surfaces only

The Law of Young-Dupré



Three-phase contact line, triple line



- γ_S , γ_L and γ_{SL} : surface tension of solid, liquid and at the interface solid-liquid acting on triple line
- This partial wetting state is characterized by an equilibrium contact angle with the substrate, called Young's contact angle θ_Y and can be described by the **Young's equation** (derived in 1805)
- Projection of equilibrium forces onto solid plane and balance

$$\gamma_S - \gamma_{SL} - \gamma_L \cos \theta_Y = 0 \Leftrightarrow \boxed{\cos \theta_Y = \frac{\gamma_S - \gamma_{SL}}{\gamma_L}}$$

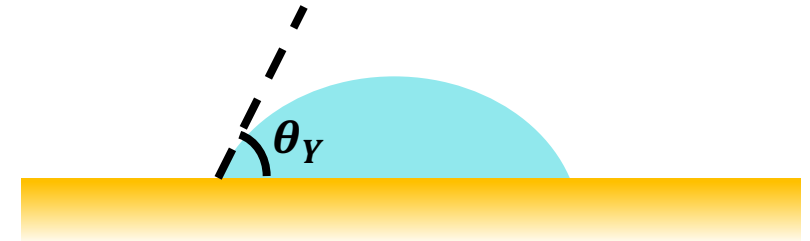
- Valid for smooth, chemically homogeneous substrate surfaces only

The Law of Young-Dupré

- Consider water as liquid
- Depending on the surface wettability we can distinguish between two wettability regimes

$\theta_Y < 90^\circ$: Surface is **hydrophilic**

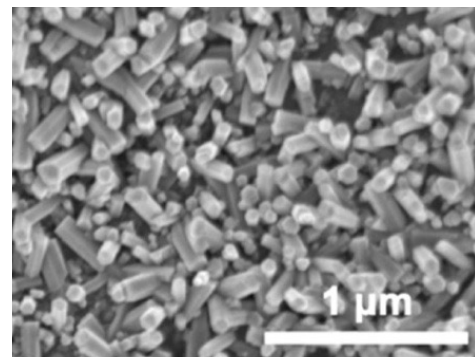
- From ancient greek: hydor (ὕδωρ) = water + philos (φίλος) = love



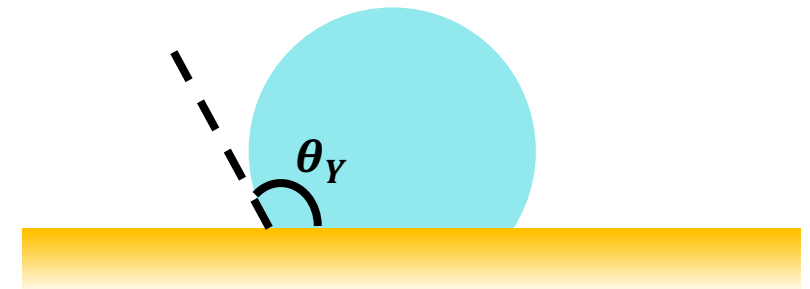
$\theta_Y > 90^\circ$: Surface is **hydrophobic**

- From ancient greek: hydor (ὕδωρ) = water + phóbos (φόβος) = fear
- Max contact angle reported in literature on smooth chemically homogeneous surface: $\approx 120^\circ$
- Higher values reachable only by introducing micro- and/or nanoroughness

- Apparent contact angle
- More details later...



Zinc oxide nanorods



Surface Tension Measurement: Capillary Rise

- Insertion of a capillary in a tank filled with wetting liquid
- Level of liquid rises in the capillary until the weight of the liquid column W and the capillary rise force F balance out

$$W = 2\pi r^2 h g \rho_L$$

$$F = 2\pi r \gamma \cos \theta$$

$$W = F \Leftrightarrow 2\pi r^2 h g \rho_L = 2\pi r \gamma \cos \theta \Leftrightarrow \gamma = \frac{r h g \rho_L}{2 \cos \theta}$$

ρ_L : density of liquid

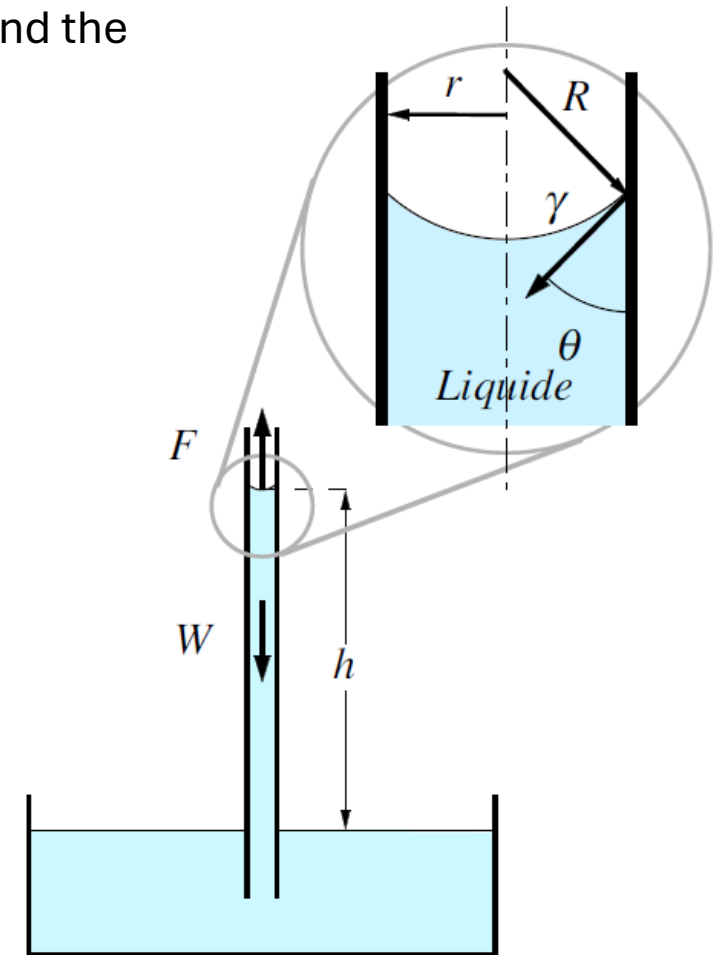
γ : liquid surface tension

g : gravitational acceleration

h : height of capillary rise

r : inner radius of capillary tube

θ : contact angle of liquid in the capillary with the solid surface



Real Surfaces: Effect of Roughness

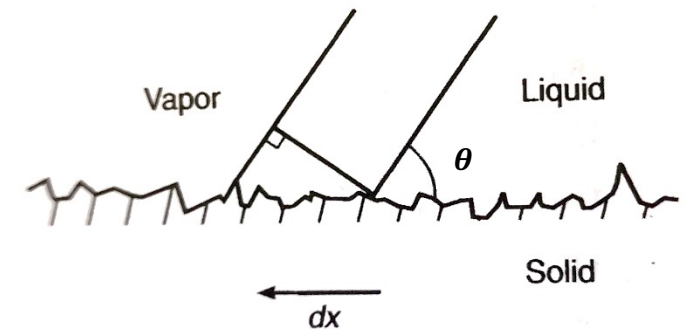
- Real surfaces always present some structural and/or chemical inhomogeneities
- One of first attempts in understanding influence of roughness (f_R) on wettability: Wenzel (1936)

$$f_R = \frac{\text{actual area}}{\text{projected (apparent) area}} \geq 1$$

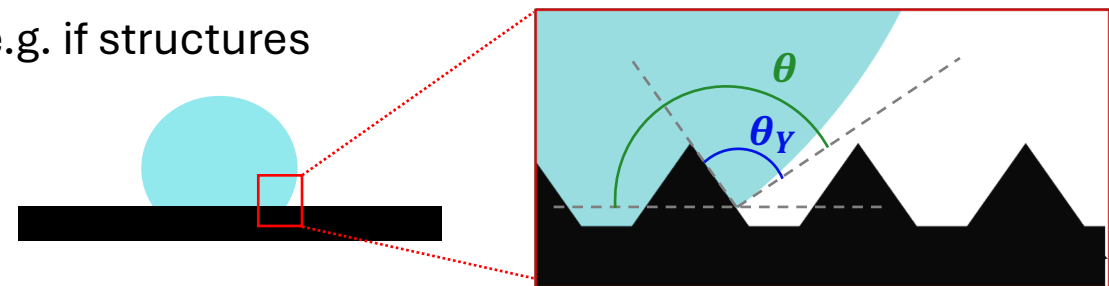
- Assumptions
 - Rough ($f_R > 1$) and chemically homogeneous surface
 - Roughness scale \ll droplet size

$$dE = f_R(\gamma_{SL} - \gamma_S) \cdot dx + \gamma_L \cos \theta \cdot dx$$

- On real surfaces we define θ as apparent (macroscopic) contact angle
 - Contact line not visible (high magnification needed, e.g. if structures dimensions $< 1\mu m$)
 - For simplicity: contact angle (or static contact angle, SCA, commonly used in literature)



θ : apparent contact angle (real surface)
 dx : displacement of contact line
 dE : change of total surface energy
 θ_Y : Young's contact angle



Real Surfaces: Effect of Roughness

$$dE = f_R(\gamma_{SL} - \gamma_S) \cdot dx + \gamma_L \cos \theta \cdot dx \Leftrightarrow \frac{dE}{dx} = f_R(\gamma_{SL} - \gamma_S) + \gamma_L \cos \theta$$

- Minimum of E : equilibrium

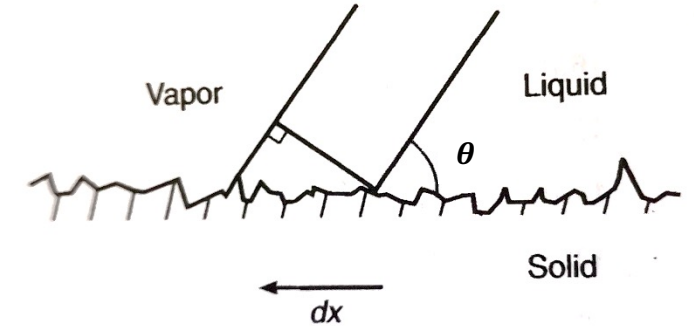
$$\frac{dE}{dx} = f_R(\gamma_{SL} - \gamma_S) + \gamma_L \cos \theta = 0$$

- From Young's equation: $\gamma_{SL} - \gamma_S = -\gamma_L \cos \theta_Y$
- Substitution in previous equation leads to:

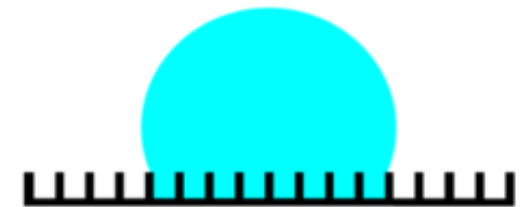
$$-f_R \gamma_L \cos \theta_Y + \gamma_L \cos \theta = 0 \Leftrightarrow \boxed{\cos \theta = f_R \cos \theta_Y} \quad (f_R > 1), \text{ Wenzel's relation}$$

- Observations:
 - If $\theta_Y < 90^\circ \Rightarrow \theta < \theta_Y$
 - If $\theta_Y > 90^\circ \Rightarrow \theta > \theta_Y$

\Rightarrow Surface roughness always magnifies the surface wetting properties!



θ : apparent contact angle (real surface)
 dx : infinitesimal displacement of contact line
 dE : infinitesimal change of total surface energy
 f_R : roughness factor
 θ_Y : Young's contact angle



Wenzel state

- Full contact with substrate
- High Adhesion (large contact area droplet-surface)

Real Surfaces: Effect of Surface Chemistry

- Smooth, chemically heterogeneous surface with n species, where the fractional surface area occupied by a specie i is defined as $\varphi_i = A_i/A_{tot}$

$$dE = \varphi_1(\gamma_{SL,1} - \gamma_{S,1}) \cdot dx + \varphi_2(\gamma_{SL,2} - \gamma_{S,2}) \cdot dx + \dots + \varphi_n(\gamma_{SL,n} - \gamma_{S,n}) \cdot dx + \gamma_L \cos \theta \cdot dx$$

$$= \sum_{i=1}^n [\varphi_i(\gamma_{SL,i} - \gamma_{S,i})] \cdot dx + \gamma_L \cos \theta \cdot dx, \text{ where } \sum_{i=1}^n \varphi_i = 1$$

- Consider 2 species

$$dE = \varphi_1(\gamma_{SL,1} - \gamma_{S,1}) \cdot dx + \varphi_2(\gamma_{SL,2} - \gamma_{S,2}) \cdot dx + \gamma_L \cos \theta \cdot dx$$

$$\Leftrightarrow \frac{dE}{dx} = \varphi_1(\gamma_{SL,1} - \gamma_{S,1}) + \varphi_2(\gamma_{SL,2} - \gamma_{S,2}) + \gamma_L \cos \theta$$

- Minimum of E : equilibrium

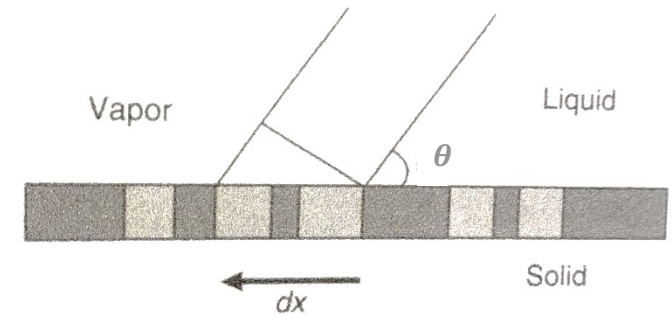
$$\frac{dE}{dx} = \varphi_1(\gamma_{SL,1} - \gamma_{S,1}) + \varphi_2(\gamma_{SL,2} - \gamma_{S,2}) + \gamma_L \cos \theta = 0$$

- From Young's equation: $\gamma_{SL,i} - \gamma_{S,i} = -\gamma_L \cos \theta_{Y,i}$ where $i = 1, 2$
- Substitution in previous equation leads to:

$$-\gamma_L \varphi_1 \cos \theta_{Y,1} - \gamma_L \varphi_2 \cos \theta_{Y,2} + \gamma_L \cos \theta = 0 \Leftrightarrow \boxed{\cos \theta = \varphi_1 \cos \theta_{Y,1} + \varphi_2 \cos \theta_{Y,2}} \quad \text{Cassie-Baxter relation (1944)}$$

- Observations:

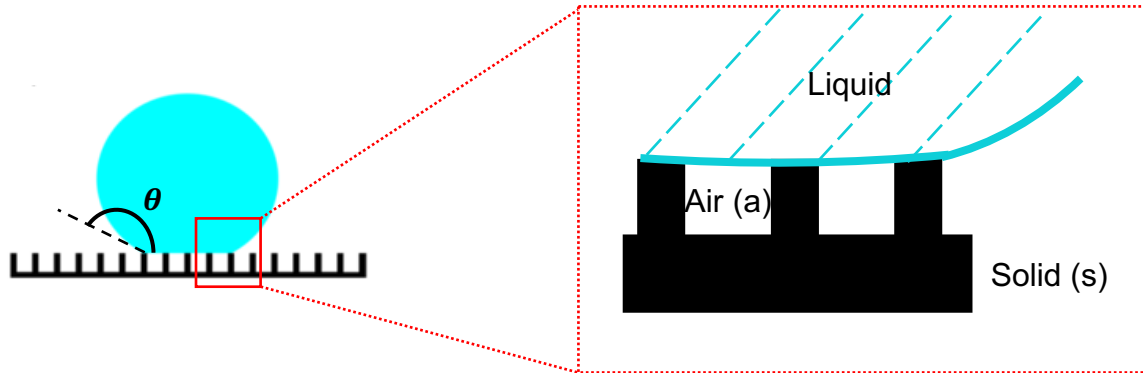
- $\theta \in [\theta_{Y,1}, \theta_{Y,2}]$
- θ is closer to θ_Y on surface consisting of the component with larger φ



θ : apparent contact angle (real surface)
 dx : infinitesimal displacement of contact line
 dE : infinitesimal change of total surface energy
 $\theta_{Y,i}$: Young's contact angle on specie i

Real Surfaces: The Cassie-Baxter State

- Consider case from previous slide (Cassie-Baxter equation), where one of the two species consists of air (Cassie-Baxter state)



- Cassie-Baxter state, fakir state
- Droplet suspended over surface asperities (formation of air pockets)
- Low adhesion
- Surface can be superhydrophobic with low liquid adhesion (extremely water-repellent, later)

Cassie-Baxter relation: $\cos \theta = \varphi_s \cos \theta_{Y,s} + \varphi_a \cos \theta_{Y,a}$

- Define:
 - $\varphi_s = \varphi \Rightarrow \varphi_a = 1 - \varphi$
 - $\theta_{Y,a} = 180^\circ$ (air)
- After substitution in previous equation we get:

$$\begin{aligned} \cos \theta &= \varphi \cos \theta_{Y,s} + (1 - \varphi) \cos 180^\circ \\ \Leftrightarrow \cos \theta &= \varphi \cos \theta_{Y,s} + (1 - \varphi) \cdot (-1) \\ \Leftrightarrow \cos \theta &= \varphi(1 + \cos \theta_{Y,s}) - 1 \end{aligned} \quad \text{(eq 1)}$$

Wenzel to Cassie-Baxter State Transition

- Let's consider now a droplet placed on a rough surface. How can we predict the wetting state (Wenzel or Cassie-Baxter)?



- Given: f_R (roughness), ϕ (solid fraction) and $\theta_{Y,S}$ Young's contact angle
- Wenzel's relation: $\cos \theta = f_R \cos \theta_Y$
- Cassie-Baxter relation with air as one of the components ((**eq. 1**), previous slide): $\cos \theta = \phi(1 + \cos \theta_{Y,S}) - 1$
- Transition point is when the two states have the same surface energy (and therefore same apparent contact angle θ). We can therefore equalize the two equations:

$$f_R \cos \theta_{Y,S} = \phi(1 + \cos \theta_{Y,S}) - 1 \Leftrightarrow \theta_{Y,S} = \cos^{-1} \frac{\phi^{-1}}{f_R - \phi} = \text{const}$$

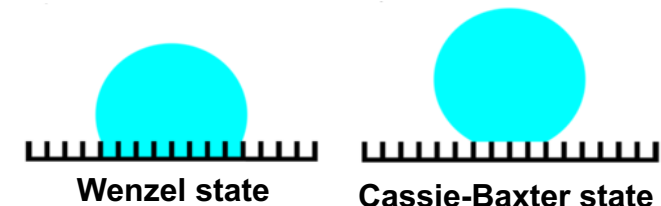
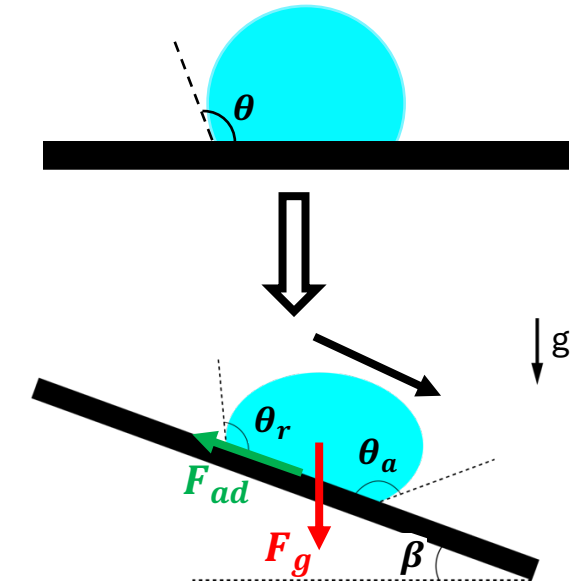
- What is the range of $\theta_{Y,S}$ that leads to Wenzel state and Cassie-Baxter state, respectively?
- At this transition point, we define and use the critical Young's contact angle $\theta_{Y,c}$

$$\theta_{Y,c} = \cos^{-1} \frac{\phi - 1}{f_R - \phi}$$

- Observations
 - If $\theta_{Y,S} < \theta_{Y,c} \Rightarrow$ Wenzel state
 - If $\theta_{Y,S} > \theta_{Y,c} \Rightarrow$ Cassie-Baxter state

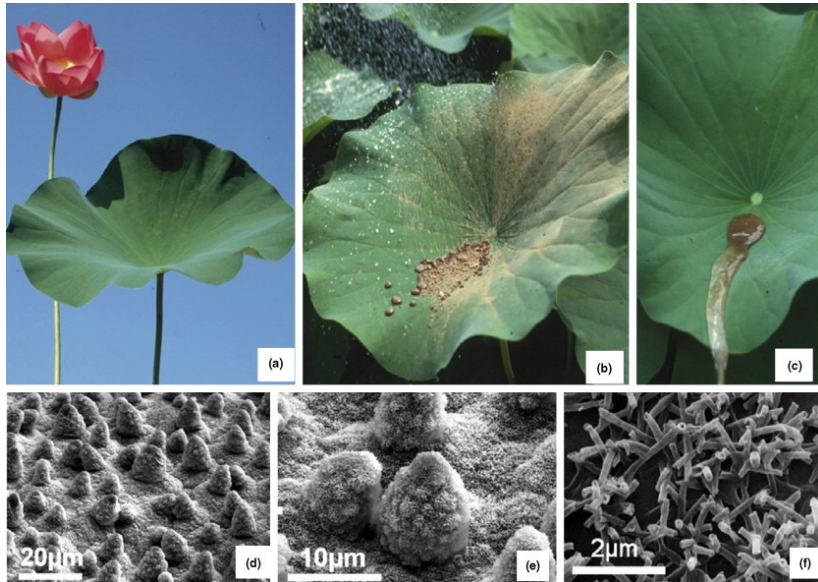
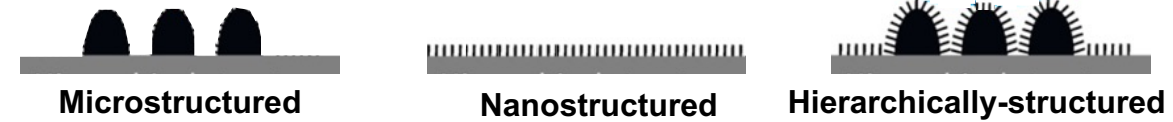
Dynamic Interactions Liquid-Solid on Real Surfaces

- Until now: static interaction droplet-substrate
- What happens when we consider dynamic interactions?
 - Droplet sliding on a tilted plane under effect of gravity (balance: $F_{ad} = F_g \cdot \sin \beta$)
 - Contact angles at the front and back are different (droplet is deformed)
 - Front: advancing contact angle (ACA, θ_a)
 - Back: receding contact angle (RCA, θ_r)
 - Contact angle hysteresis (CAH, $\Delta\theta_h = \theta_a - \theta_r$)
 - $\theta_r < \theta_a, \Delta\theta_h > 0$
- Observations:
 - CAH is the result of surface inhomogeneities (structural and chemical), typical of real surfaces
 - Information on droplet adhesion
 - Adhesion forces $F_{ad} \sim \Delta\theta_h$
 - Contact area (Wenzel vs. Cassie-Baxter states), surface chemistry
 - Low CAH: low adhesion, better droplet mobility and easier droplet removal
 - SCA between RCA e ACA, $\theta \in [\theta_r, \theta_a]$
 - In literature: often only static contact angle, not sufficient, low CAH difficult to achieve

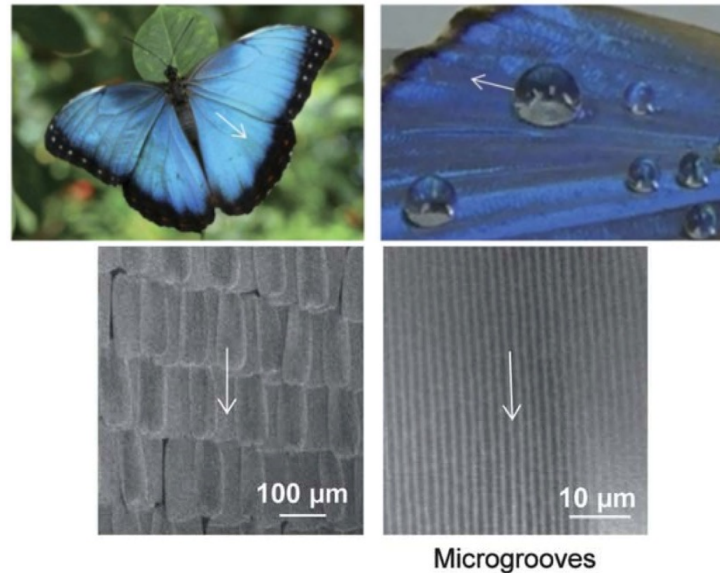


Superhydrophobic Surfaces

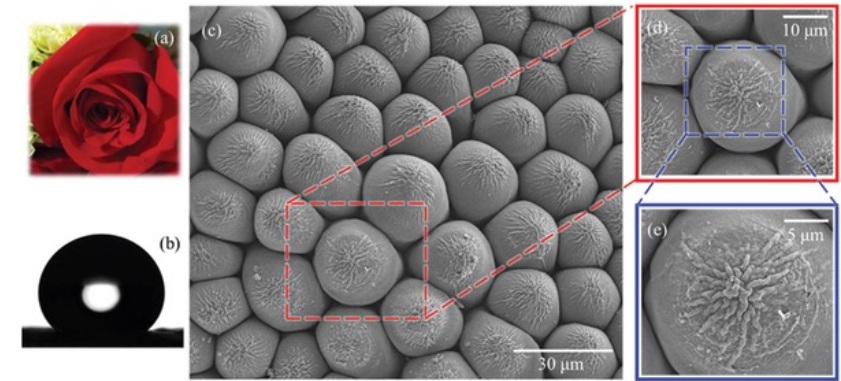
- Superhydrophobic surfaces: extreme water repellency
 - Definition of superhydrophobic surface: $\theta > 150^\circ$
 - Only possible with micro- and/or nanoroughness
 - High $\Delta\theta_h$: high adhesion
 - Small $\Delta\theta_h$: low adhesion
- Examples from nature



Lotus leaf, hierarchical, low CAH, self-cleaning



Butterfly wing (*Blue Morpho Didius*), hierarchical, low CAH, self-cleaning

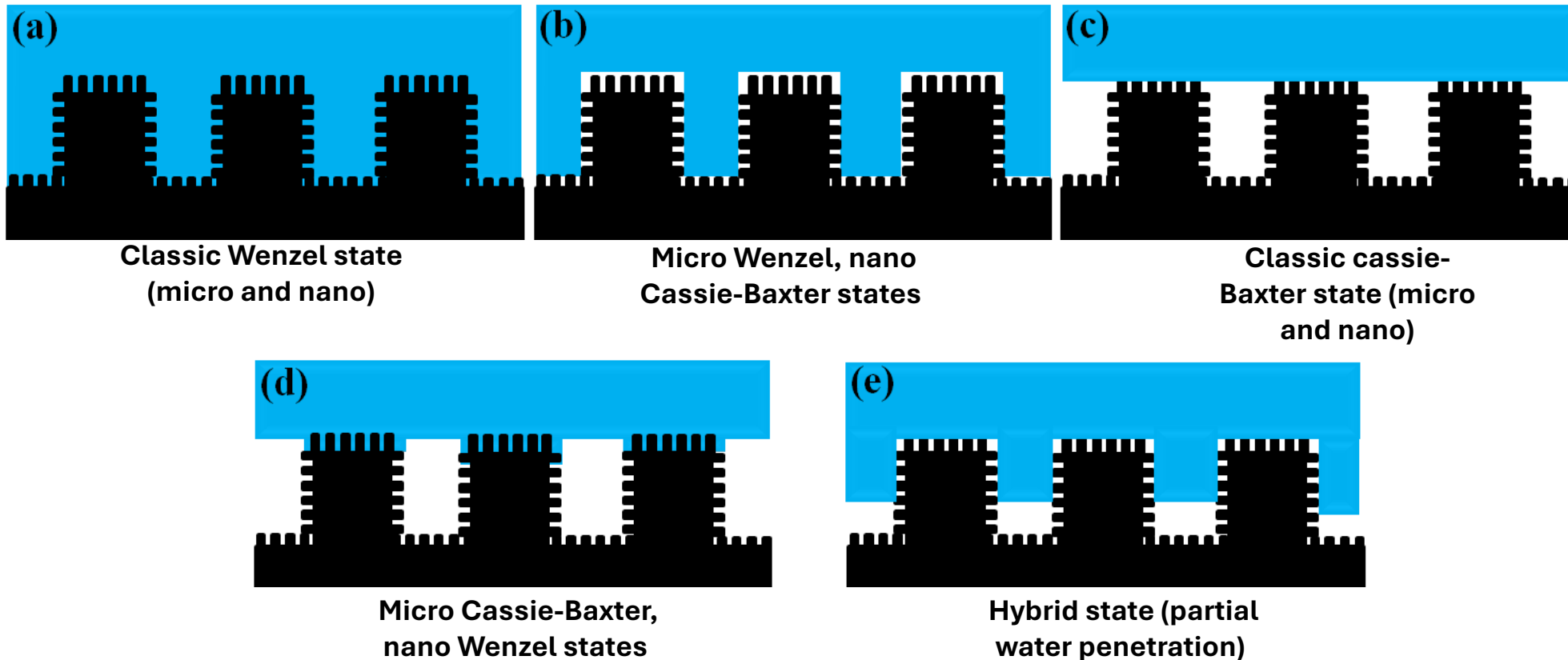


Rose petal, hierarchical, high CAH (low Nanostructures density)



Real Surfaces: Wetting States of Hierarchically-Structured Surfaces

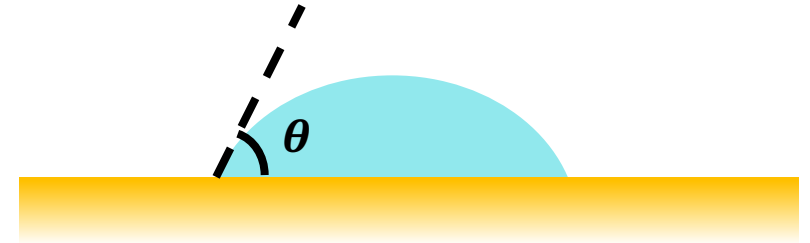
- Possible wetting states on surfaces with combined micro- and nanostructures
 - Water adhesion can be tuned depending on the application



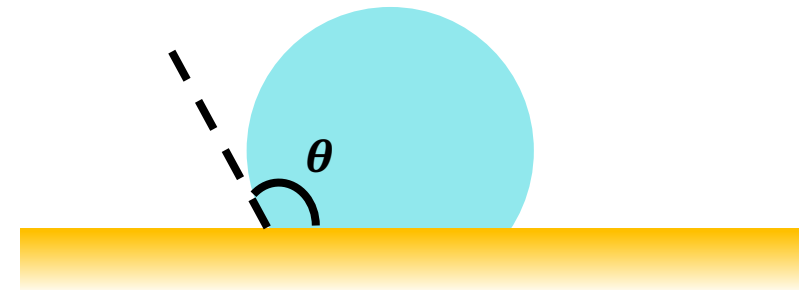
Surface Wettability of Real Surfaces: Summary

- Consider water as liquid
- Depending on the surface wettability we can have four different scenarios

$\theta < 90^\circ$: Surface is hydrophilic

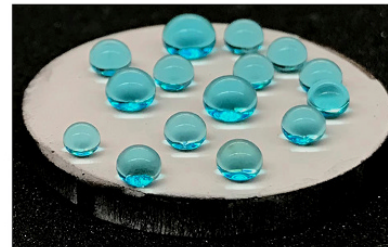


$\theta > 90^\circ$: Surface is hydrophobic

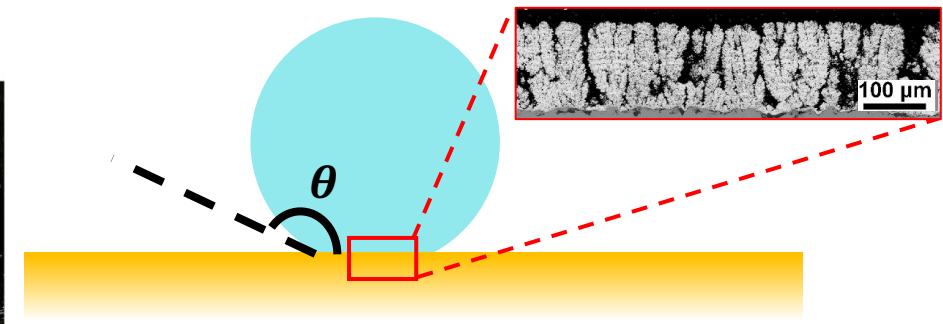


$\theta > 150^\circ$: Surface is superhydrophobic

- Micro- and/or nanoroughness necessary

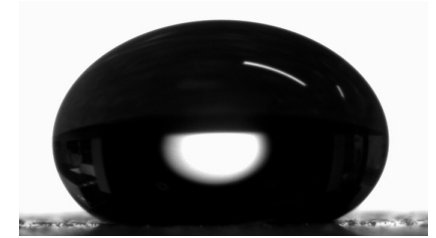


Superhydrophobic yttria coating



Measurement of Contact Angles: Static Contact Angle θ

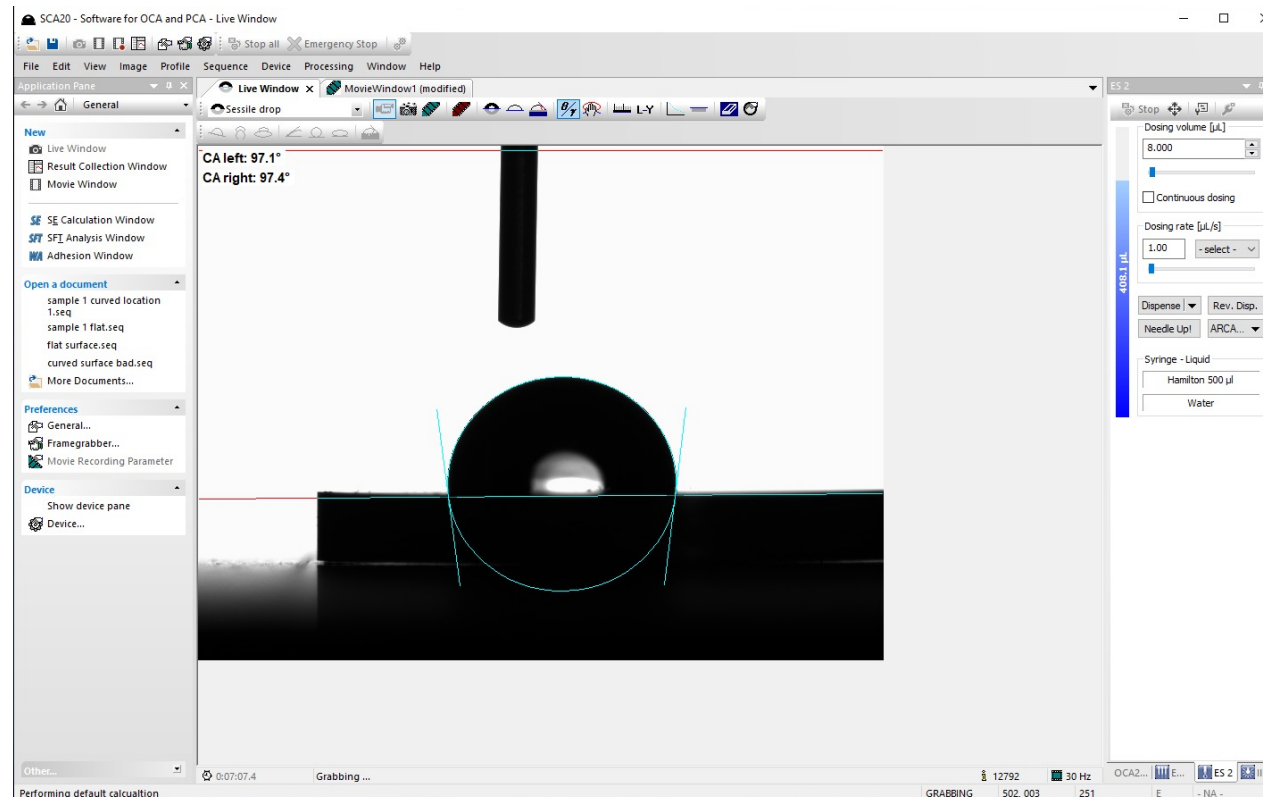
- Procedure
 - Place sample on stage
 - Dispense a water volume of 5 – 10 μL
 - If too much: risk of droplet deformation under effect of gravity and measure wrong values, especially for superhydrophobic surfaces
 - Place base line at correct position (height and inclination)
 - Manual or automatic measurement θ with software



Too much water

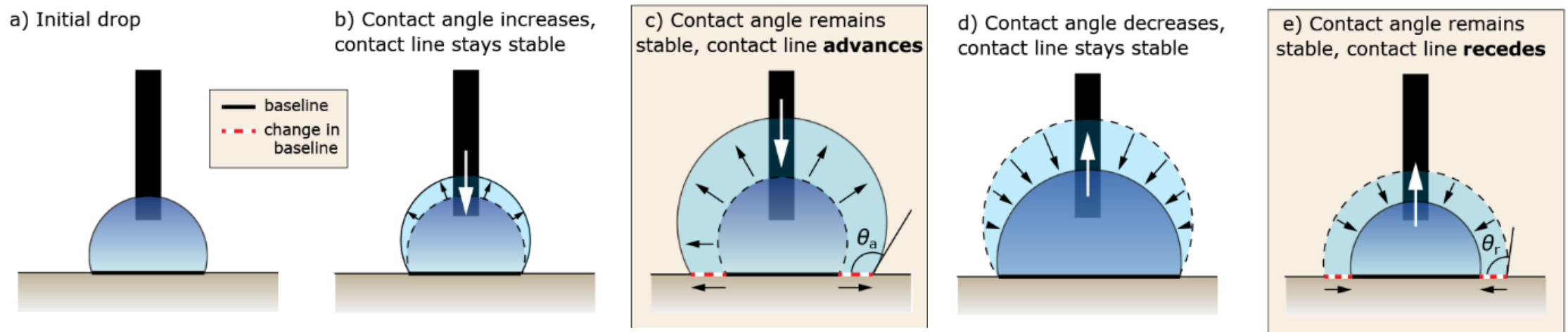


Correct amount of water



Measurement of Contact Angles: Advancing Contact angle, Receding Contact Angle and Contact Angle Hysteresis

- Procedure
 - Sample on stage
 - Video acquisition start
 - Follow steps shown on picture below
 - Video acquisition stop
- From video: manual or automatic evaluation of ACA θ_a and RCA θ_r (same procedure as for SCA θ)
- CAH calculation ($\Delta\theta_h = \theta_a - \theta_r$)



Outline

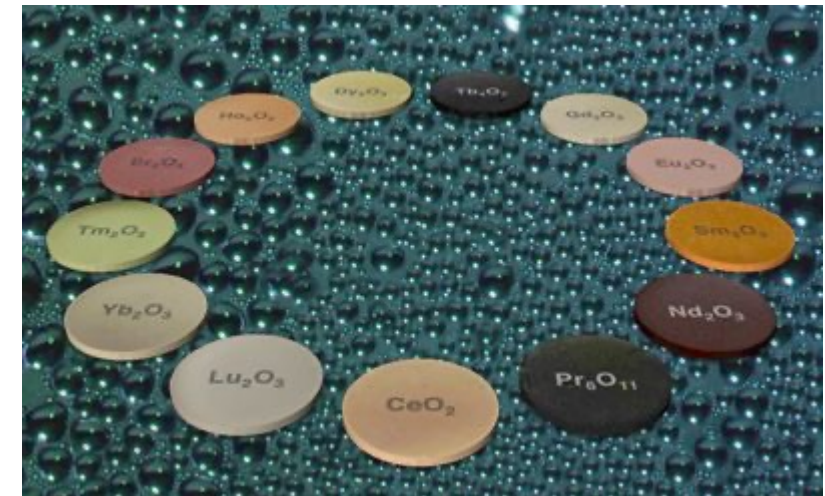
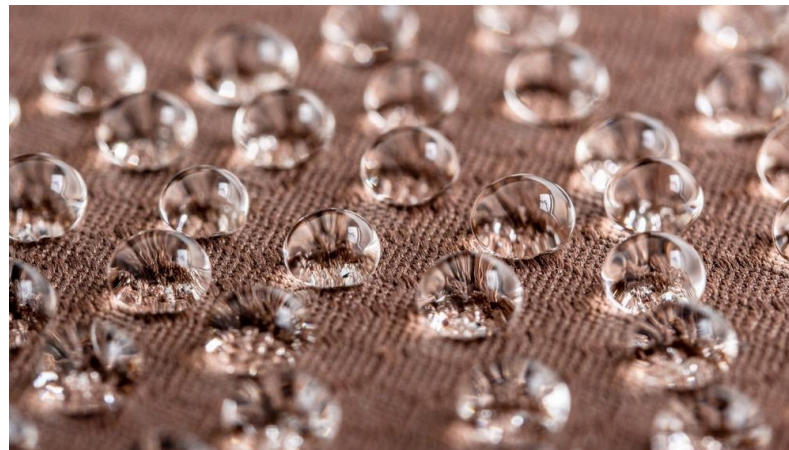
1. Theory and Fundamentals

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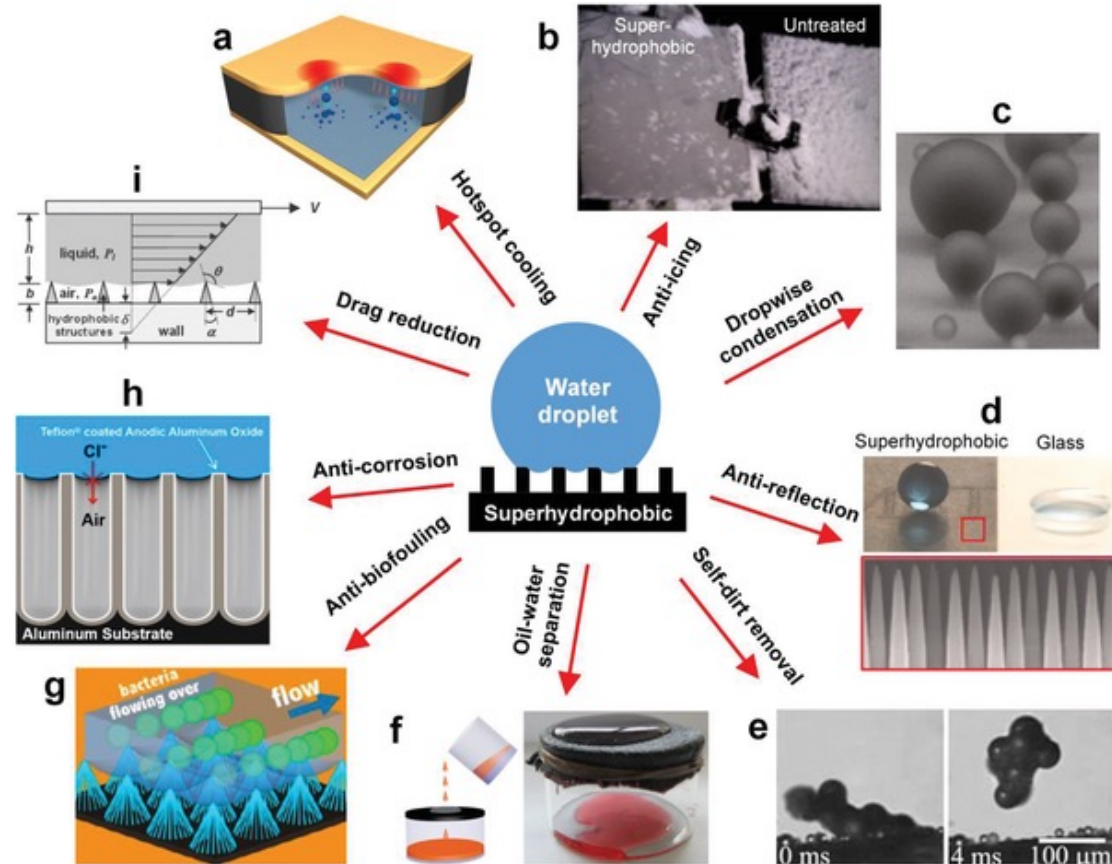
a) State of the Art

b) Experimental Results



Applications of Superhydrophobic Surfaces

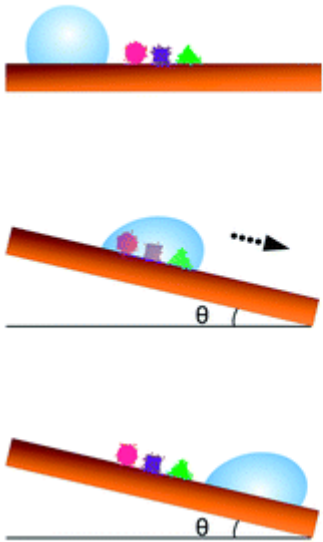
- Self-Cleaning
- Condensation heat transfer
- Anti-icing
- Drag reduction
- Anti-fogging
- Antibiofouling
- Antibacterial
- Anti-corrosion
- Water-oil separation
- ...



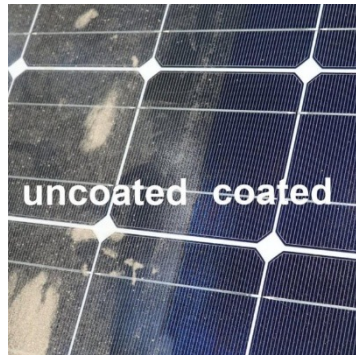
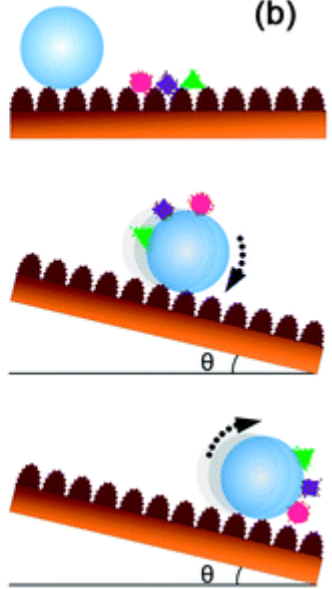
Applications of Superhydrophobic Surfaces: Self Cleaning

- Contact angle $\theta > 150^\circ$ and CAH $\Delta\theta_h < 10^\circ$
- Passive contaminants removal
 - Textiles (tablecloth, spilled liquid doesn't wet surface)
 - Solar panels (dust, increase efficiency)

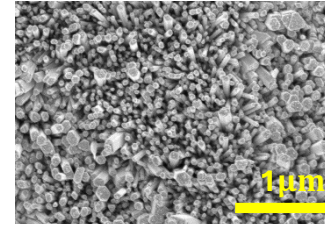
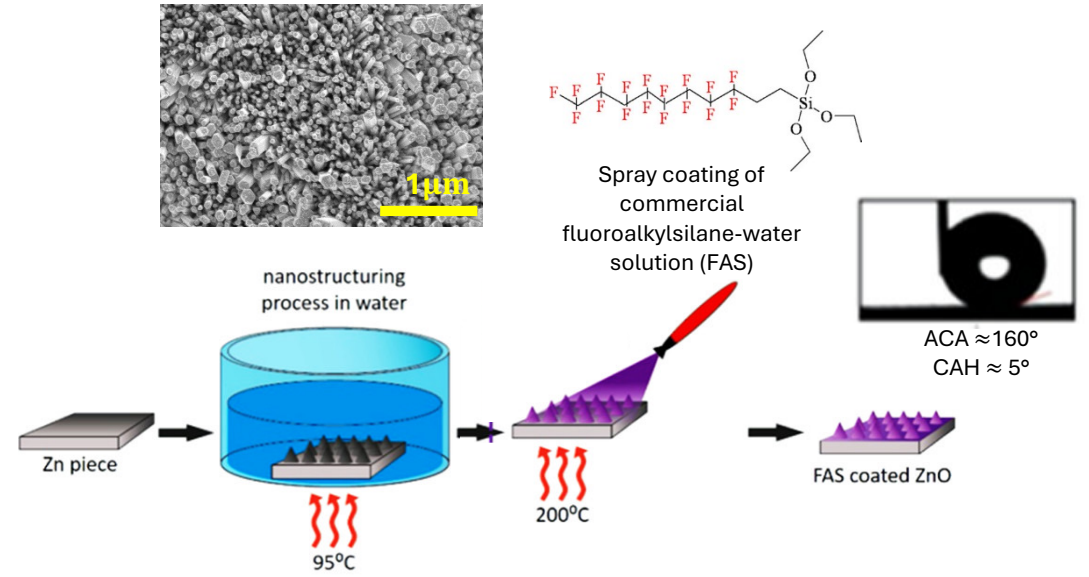
Hydrophobic surface



Superhydrophobic surface (b)



Example: superhydrophobic zinc oxide surface

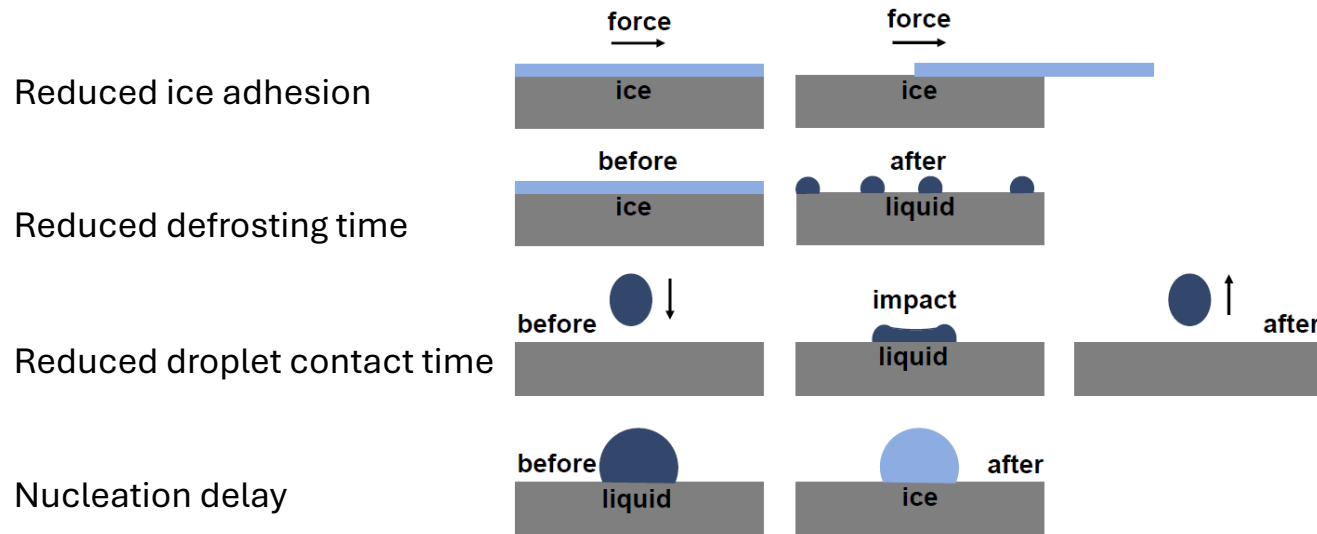


Self cleaning

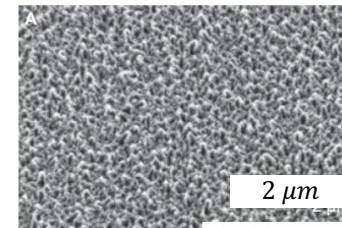
1) https://www.researchgate.net/publication/316014106_A_typical_smooth_surface_and_hydrophobic_effect_due_to_superhydrophobic_film
 2) <https://www.stockphoto.com/search?imagefilter=hydrophobic>
 3) https://www.researchgate.net/publication/316014106_A_typical_smooth_surface_and_hydrophobic_effect_due_to_superhydrophobic_film
 4) https://www.researchgate.net/publication/316014106_A_typical_smooth_surface_and_hydrophobic_effect_due_to_superhydrophobic_film
 5) https://www.researchgate.net/publication/316014106_A_typical_smooth_surface_and_hydrophobic_effect_due_to_superhydrophobic_film
 6) https://www.researchgate.net/publication/316014106_A_typical_smooth_surface_and_hydrophobic_effect_due_to_superhydrophobic_film
 7) https://www.researchgate.net/publication/316014106_A_typical_smooth_surface_and_hydrophobic_effect_due_to_superhydrophobic_film

Applications of Superhydrophobic Surfaces: Anti Icing

- Icing: problem in many sectors
 - Aviation (drop in aerodynamic efficiency, weight increasing, ...)
 - Wind turbines (loss in power output, mechanical damages, ...)
- Current procedure: active ice removal (mostly using de-icing fluids)
- Possible solution: superhydrophobic surfaces (icephobic, *afraid of ice*)
- How can we define icephobicity?



- Example: spontaneous ice removal on nanostructured superhydrophobic glass (coated with perfluorodecyltrichlorosilane)

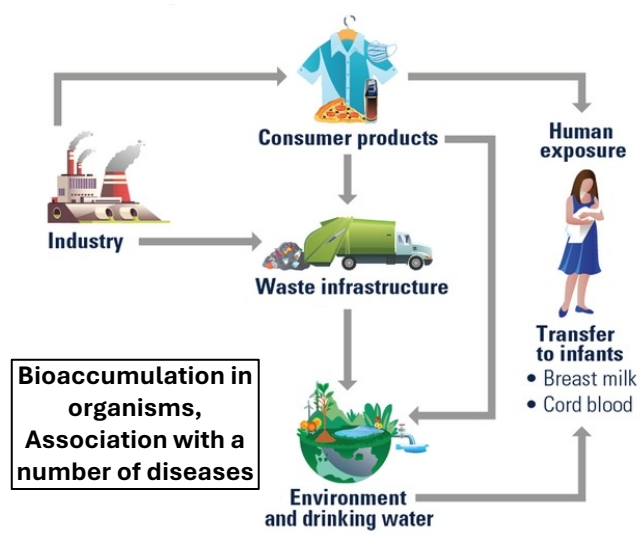
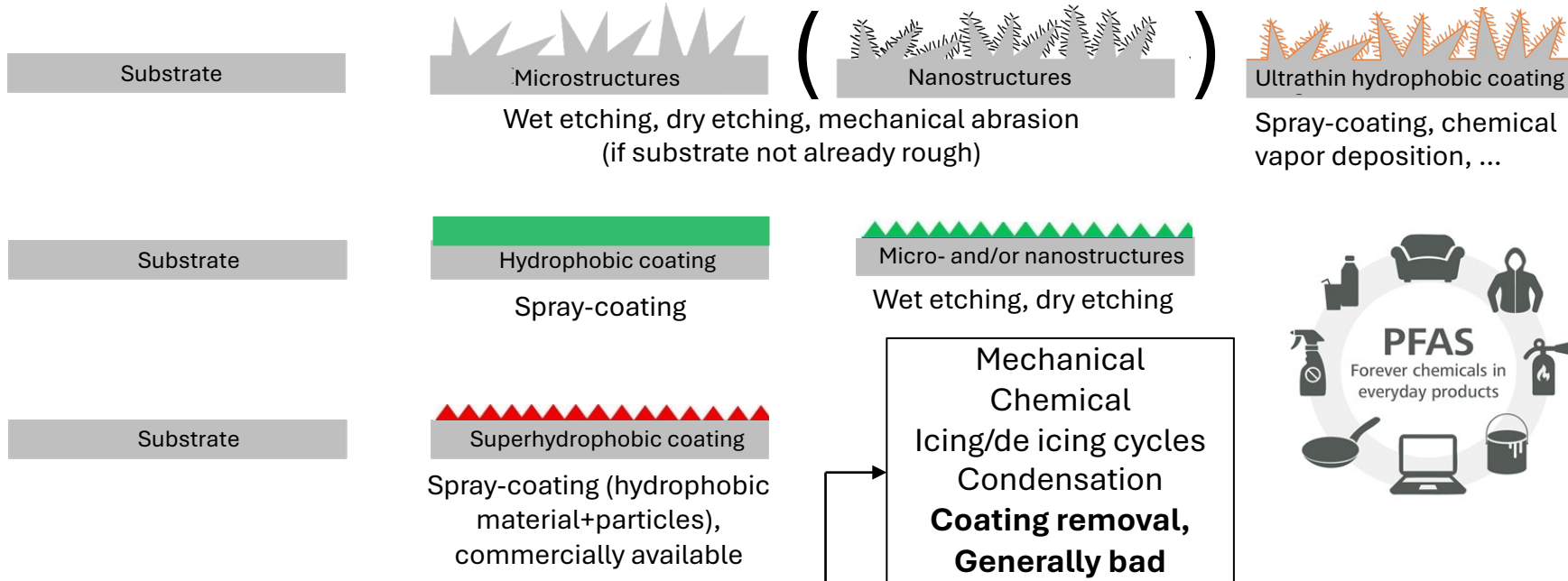


Freezing and self-dislodging of a water droplet on a superhydrophobic surface
 Conditions: $P_{\infty} = 1$ bar; Cold nitrogen flow

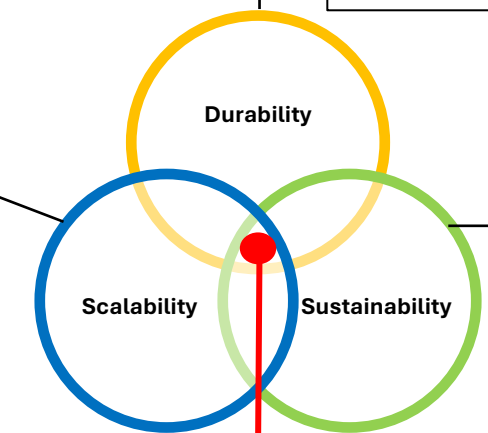


Superhydrophobic Surfaces: Current Challenges

- 3 usual fabrication methods (on **ceramics** and metals, mostly hydrophilic materials)



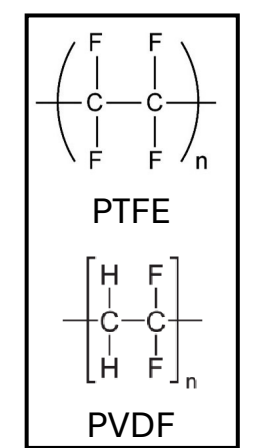
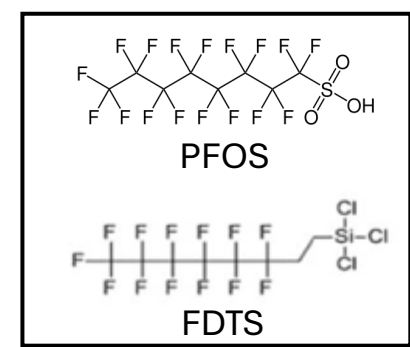
Wet/dry etching
Spraying
Chemical vapor deposition
OK!



Mainly per- and polyfluoroalkyl substances (PFAS)

- fluorinated silanes
- fluoropolymers

Bad!



At the moment: still a challenge (especially durability and sustainability)
Possible coating candidates:
Rare-earth oxides (REOs)

Industrial applications

Outline

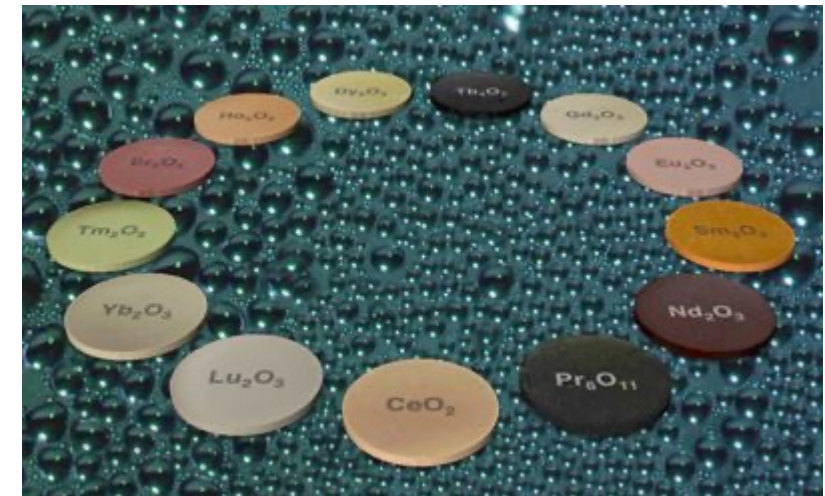
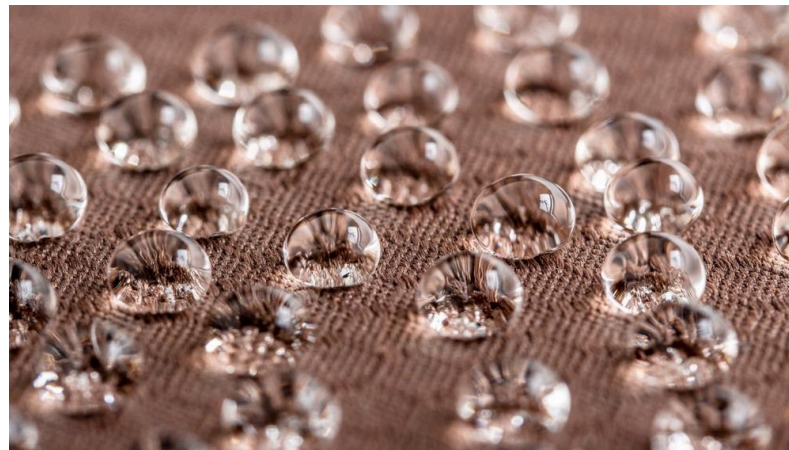
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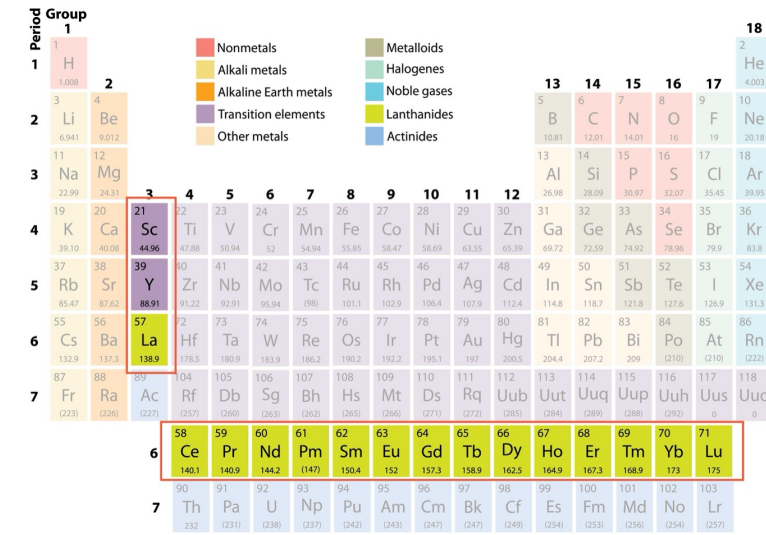
a) State of the Art

b) Experimental Results



Rare-Earth Oxides

- Rare-earth oxides (REOs): class of ceramics
- Advantages
 1. Hydrophobic materials (according to literature)
 2. No need of additional hydrophobic coating (less fabrication steps)
 3. Great mechanical durability
 4. Good thermal stability
 5. Fluorine-free
 6. Easily available as cheap recycled REOs mixtures (electronic industry)
 7. Coating can be applied on a wide range of substrates using scalable methods (sputtering, plasma spraying,)
 8. Self-healing properties



➔ **Still confusion in understanding the mechanism of hydrophobicity of REOs (next slides)**

Why Are Rare-Earth Oxides Hydrophobic?

Possible Explanations (1)

First attempt in explaining the mechanism of hydrophobicity: 2013

Aluminum oxide (common ceramic): water molecules interact with both, oxygen and aluminum atoms (hydrogen bond). We have two bonding sites.

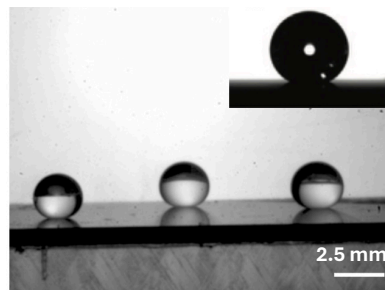
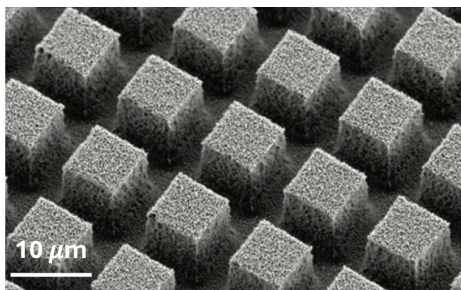
REOs: the empty orbitals (on 4f) are shielded by an electrons octet, minimizing the hydrogen bonding of water molecules with the rare earth atoms. Oxygen atoms are the only bonding sites.



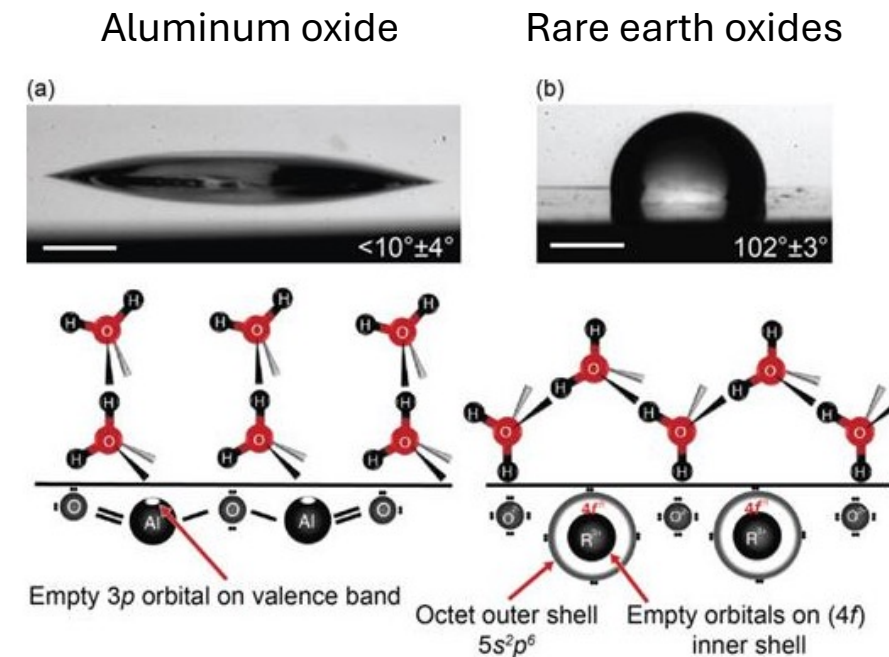
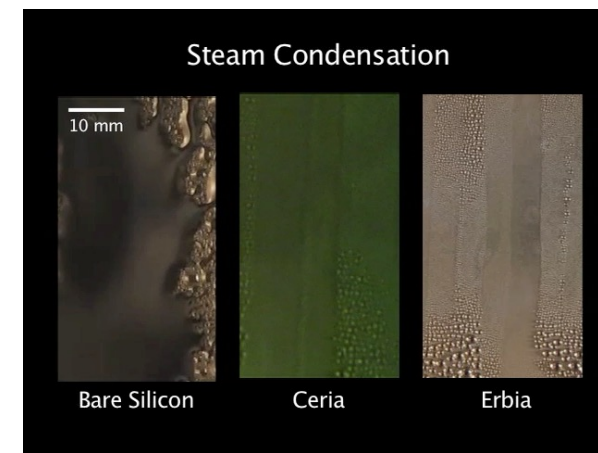
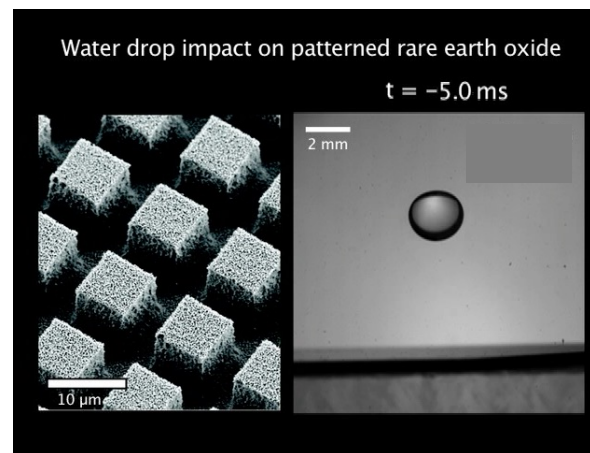
Rare-earth oxides are intrinsically hydrophobic



Hydrophobicity governed by O/RE ratio at the surface



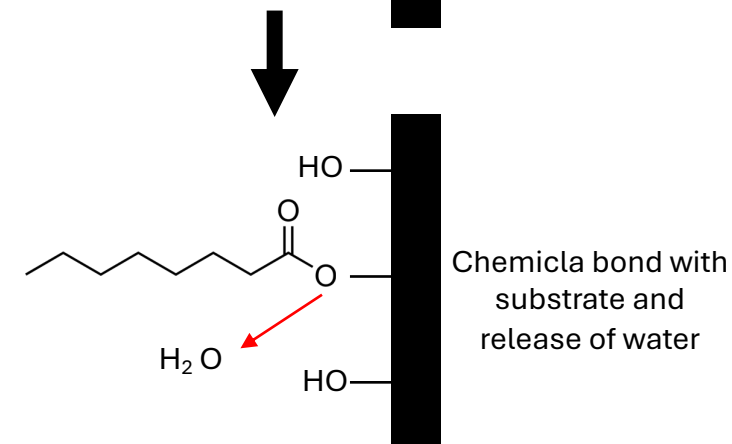
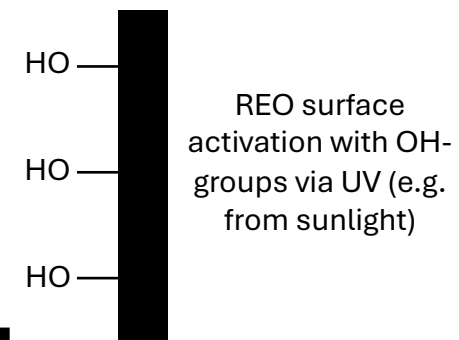
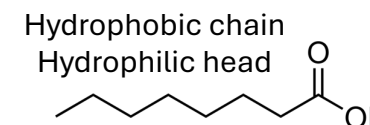
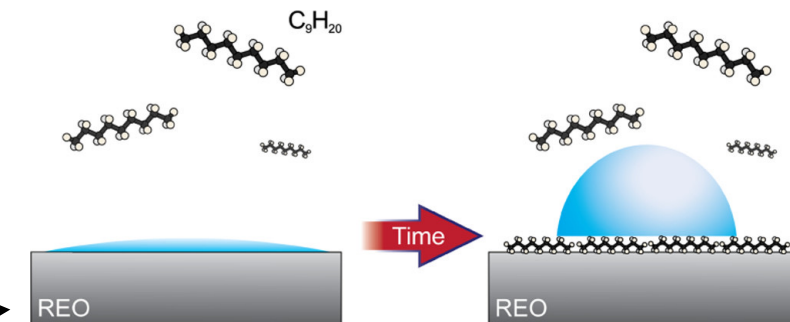
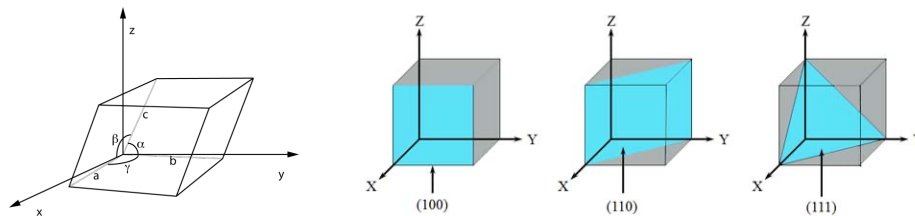
SCA $\approx 160^\circ$
CAH $< 10^\circ$



Why Are Rare-Earth Oxides Hydrophobic?

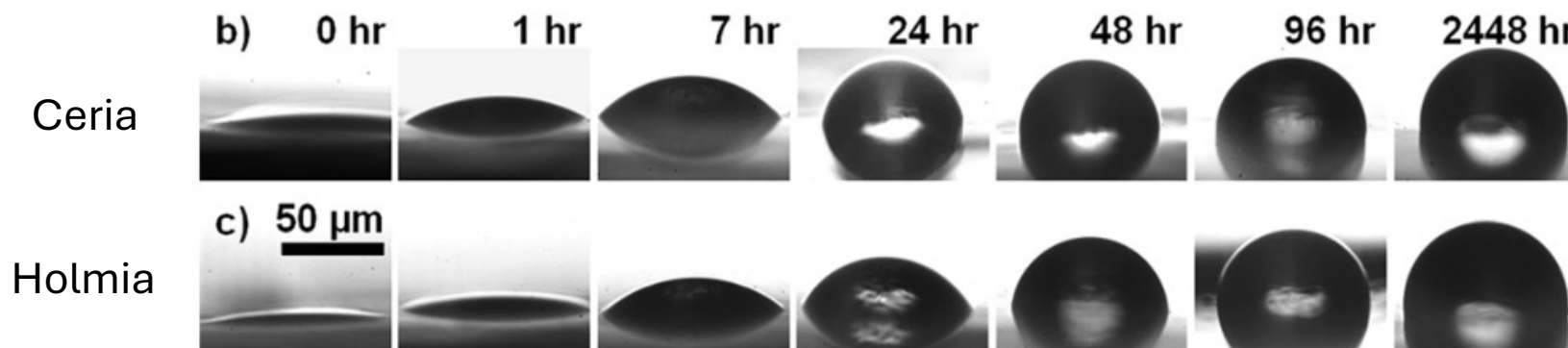
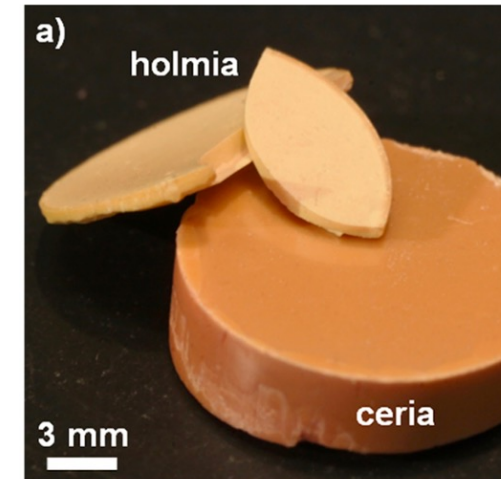
Possible Explanations (2)

- More recent studies: REOs are **inherently hydrophilic**
- The **apparent hydrophobic** nature of these surfaces is due to the gradual adsorption of hydrophobic volatile organic compounds (VOCs) from the environment (contaminants, e.g. from pollution)
 - Long-chain hydrocarbons ($\text{CH}_3(\text{CH}_2)_n\text{CH}_3$)
 - Fatty acids ($\text{CH}_3(\text{CH}_2)_n\text{COOH}$)
 - PFAS?
 - Other?
- Other factors influencing REOs hydrophobicity (research still ongoing)
 - Lattice constants
 - Crystal orientation
 - ...
- In general: still confusion in literature (mechanism not fully understood yet)



Example of Hydrophobic VOCs Adsorption on REOs Surfaces

- Research paper:
 - Ceria and holmia pellets prepared by dry pressing and sintering
 - At $t=0$ surfaces cleaned via argon ion bombardment
 - Both surfaces initially hydrophilic
 - Gradual transition to hydrophobicity via hydrophobic volatile organic compounds absorption
 - Hydrophobicity maintained even after exposure to $\approx 1000^\circ\text{C}$
 - Very stable!



Outline

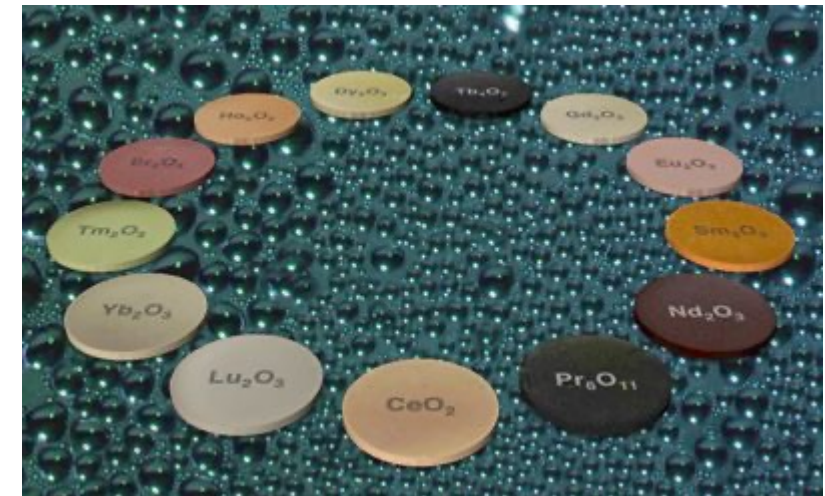
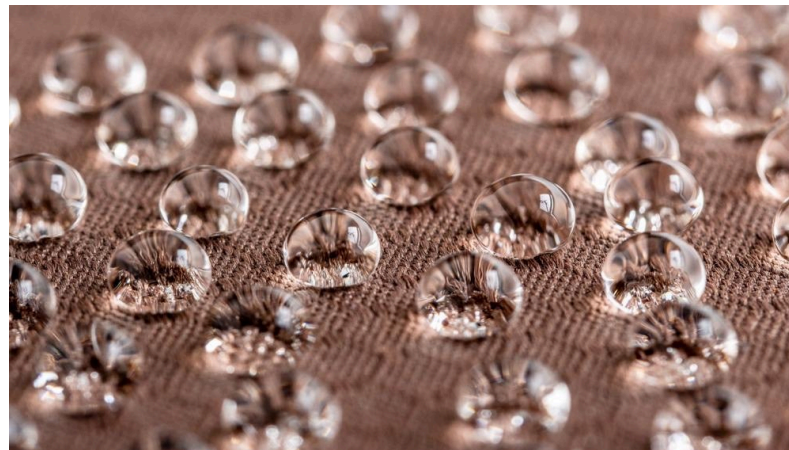
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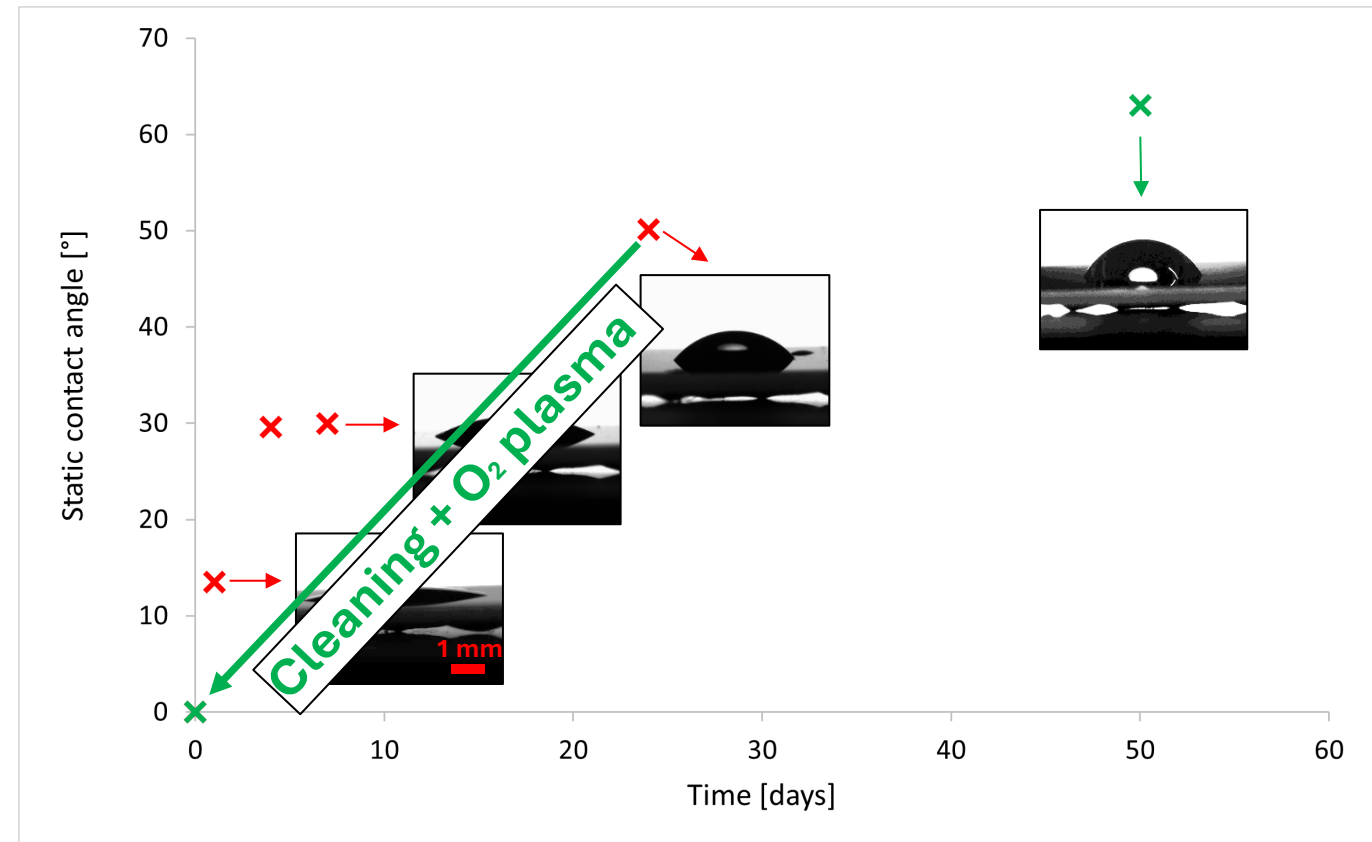
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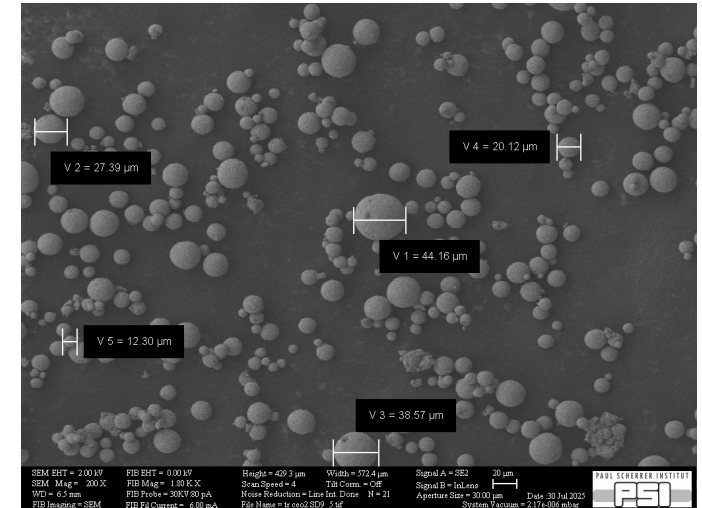
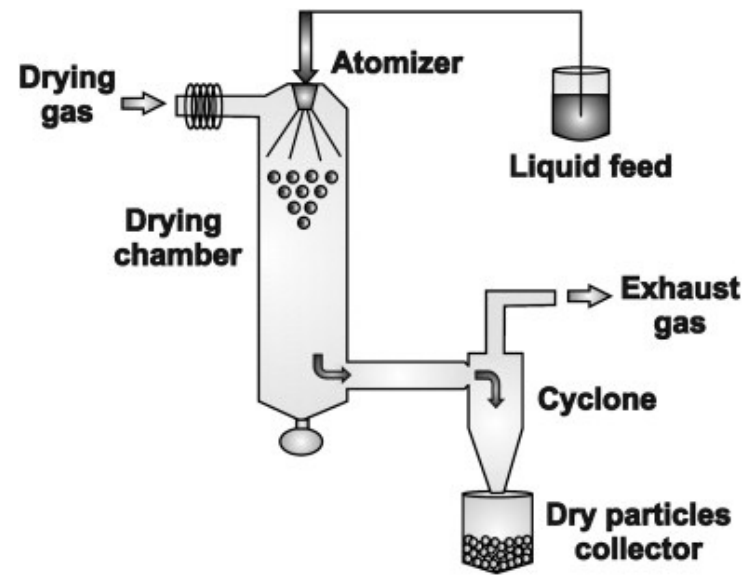
Proof of Concept: Hydrophobic VOCs Adsorption on REOs (CeO₂)

- Sample: smooth sapphire coated with ≈ 20 nm CeO₂ via pulsed laser deposition (no effect of roughness)
 - CeO₂ cheap, known film growth conditions
 - Cristal growth direction [100]
- Exposure to lab environment
- Static contact angle (SCA) increases with time (in agreement with literature)
- Process is reversible and reproduceable (**hydrophobicity self-healing**)
- Hydrophobicity increase quite slow
- Complex process, (most likely) affected by
 - Air contamination
 - Type of contaminants
 - Humidity
 - Temperature



Fabrication Process of CeO₂ Pellets

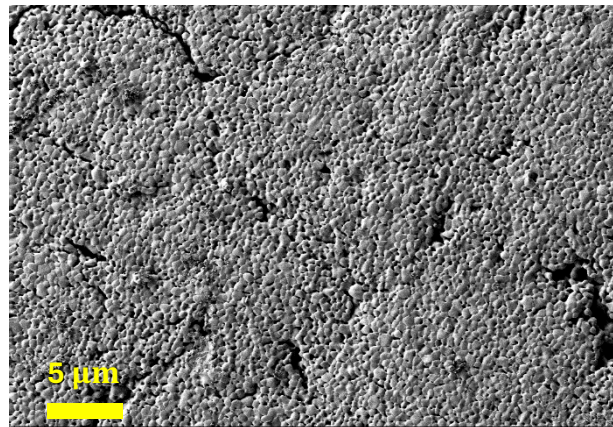
- Starting material: ceria powder, $d_p < 5 \mu\text{m}$, cheap
- Slurry preparation (additives: PVA (5 wt.%), PEG (5 wt.%) and water (50 wt.%))
- Ball milling (particle size reduction)
- Powder preparation by spray drying (spherical particles, good powder flowability)



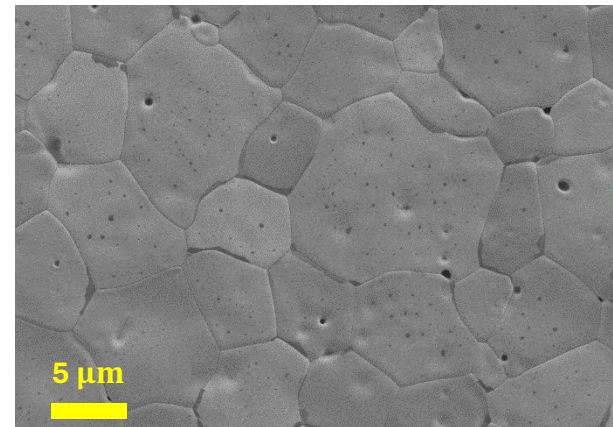
- Limitations of spray dryer (lab scale)
 - Particle size
 - Amount of produced powder

Fabrication Process of CeO₂ Pellets

- Starting material: ceria powder, $d_p < 5 \mu\text{m}$, cheap
- Slurry preparation (additives: PVA (5 wt.%), PEG (5 wt.%) and water (50 wt.%))
- Ball milling (particle size reduction)
- Powder preparation by spray drying (spherical particles, good powder flowability)
- Dry pressing of pellets (diameter: 10 mm, height: 2 mm)
- Calcination and sintering (8h @ 1615 °C)
 - Step optimized by means of thermomechanical analysis
 - Goal: tuning of temperature and time to minimize porosity



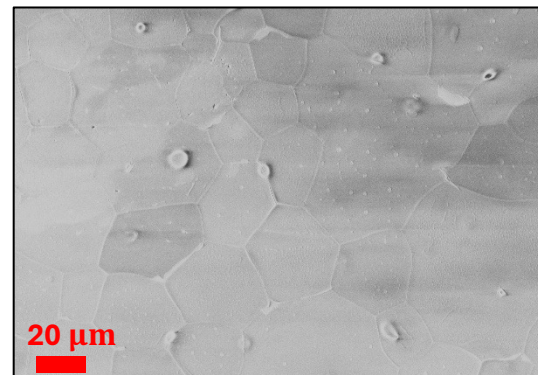
8h @ 1350 °C, open porosity



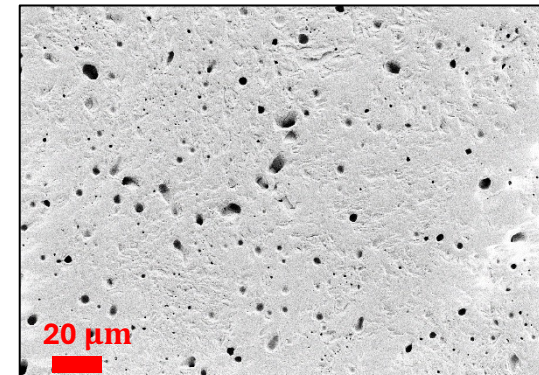
8h @ 1615 °C, closed porosity

Fabrication Process of CeO₂ Pellets

- Starting material: ceria powder, $d_p < 5 \mu\text{m}$, cheap
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 - Step optimized by means of thermomechanical analysis
 - Goal: tuning of temperature and time to minimize porosity
- Polishing: smooth surface, elimination of possible impurities



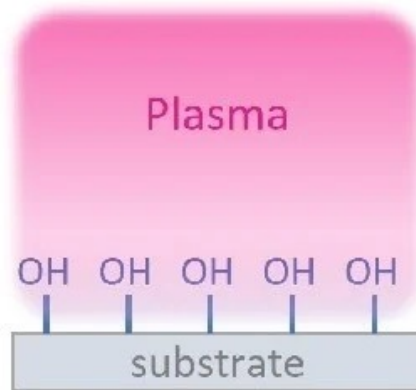
Before polishing



After polishing

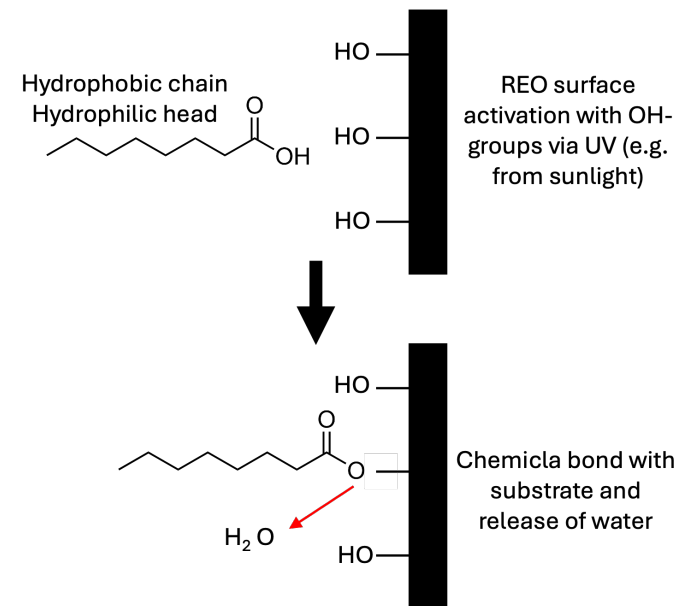
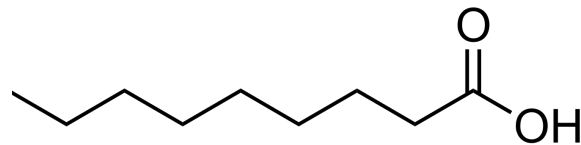
Accelerated Hydrophobic Volatile Organic Compound (VOC) Adsorption Test on CeO₂ Pellets

- From results of surface deposited via PLD: VOCs adsorption is a slow process
- Procedure for accelerated test:
 - Clean surface with acetone, ethanol and water
 - Surface activation via O₂ plasma (similar effect than UV coming from solar light)
 - Promote reactivity with VOCs and better adhesion (higher surface energy)



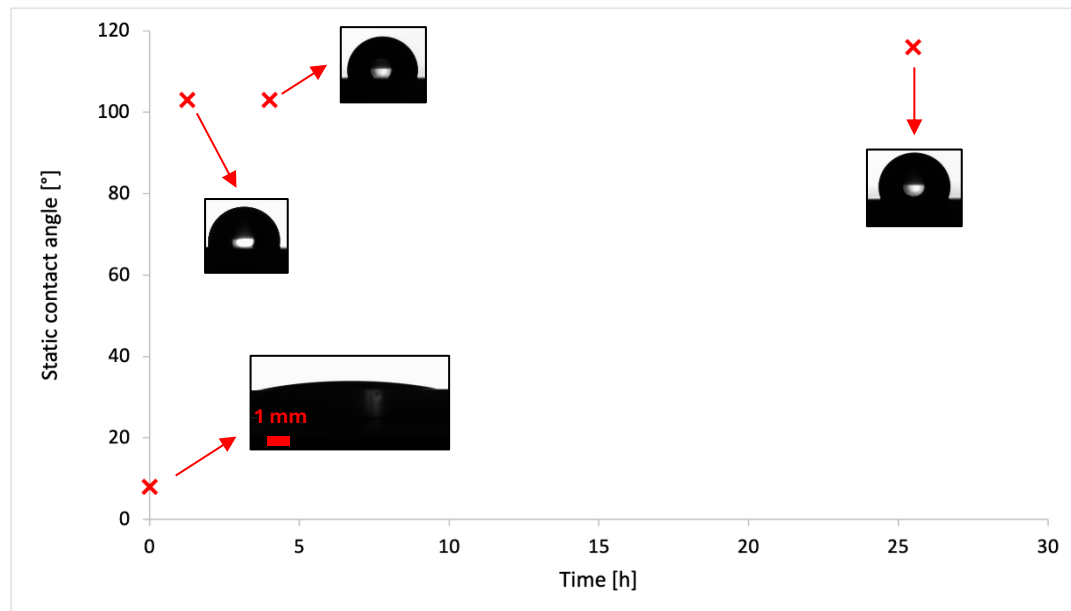
Accelerated Hydrophobic Volatile Organic Compound (VOC) Adsorption Test on CeO₂ Pellets

- From results of surface deposited via PLD: VOCs adsorption is a slow process
- Procedure for accelerated test:
 - Clean surface with acetone, ethanol and water
 - Surface activation via O₂ plasma (similar effect than UV coming from solar light)
 - Promote reactivity with VOCs and better adhesion (higher surface energy)
 - Exposure to VOCs-rich atmosphere
 - Organic compound used (from literature)
 - Decanoic acid



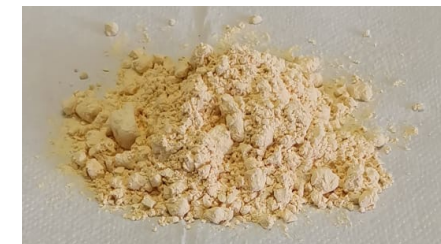
Accelerated Hydrophobic Volatile Organic Compound (VOC) Adsorption Test with Decanoic Acid

- Decanoic acid on CeO₂ pellets

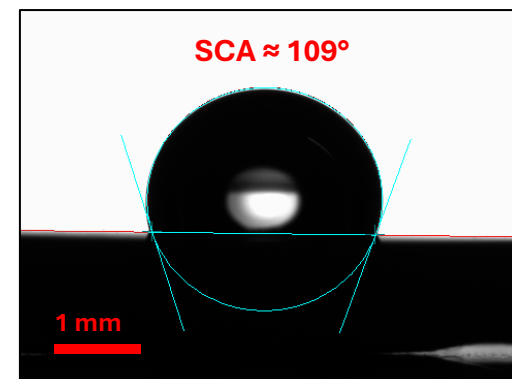


Tests with Recycled REOs Mixture

- Recycled REOs powder mixture (from electronics industry)
 - Low-cost
- Chemical analysis
 - Mainly composed by yttria
 - Presence of other REOs
 - Traces of SO_3
 - Presence of CaO content
- Pellet preparation:
 - Calcination and sintering (2h @ 1490 °C), optimized process
 - Polishing
 - Cleaning (acetone, ethanol, water)
 - O_2 plasma
 - Decanoic acid deposition (1h 15' @ 100 °C)



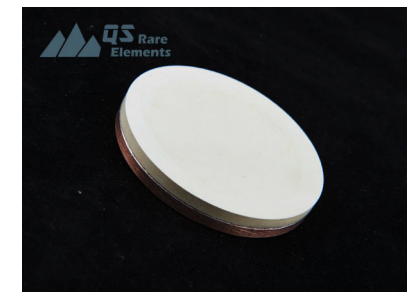
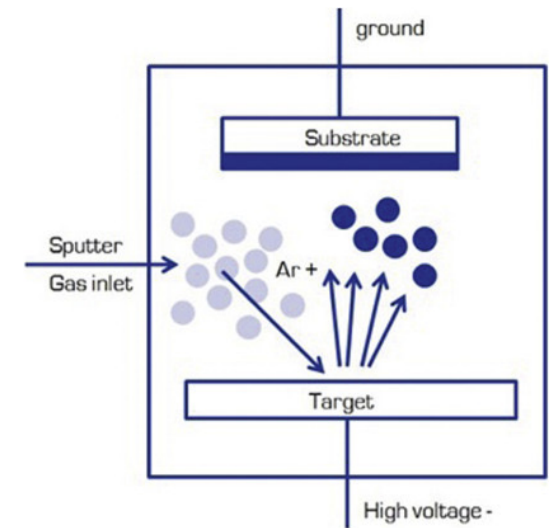
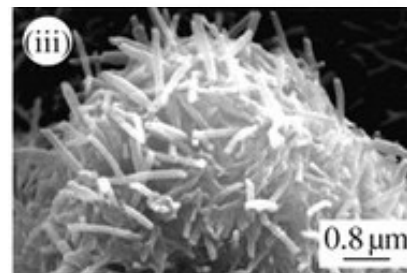
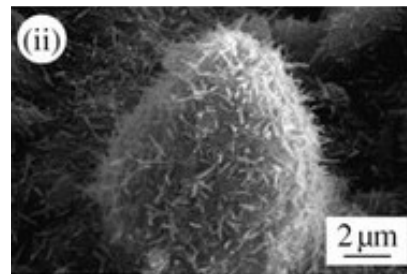
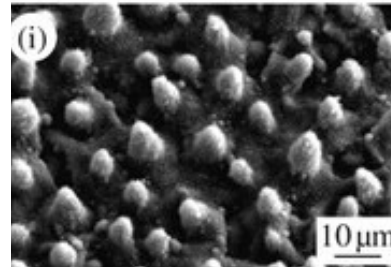
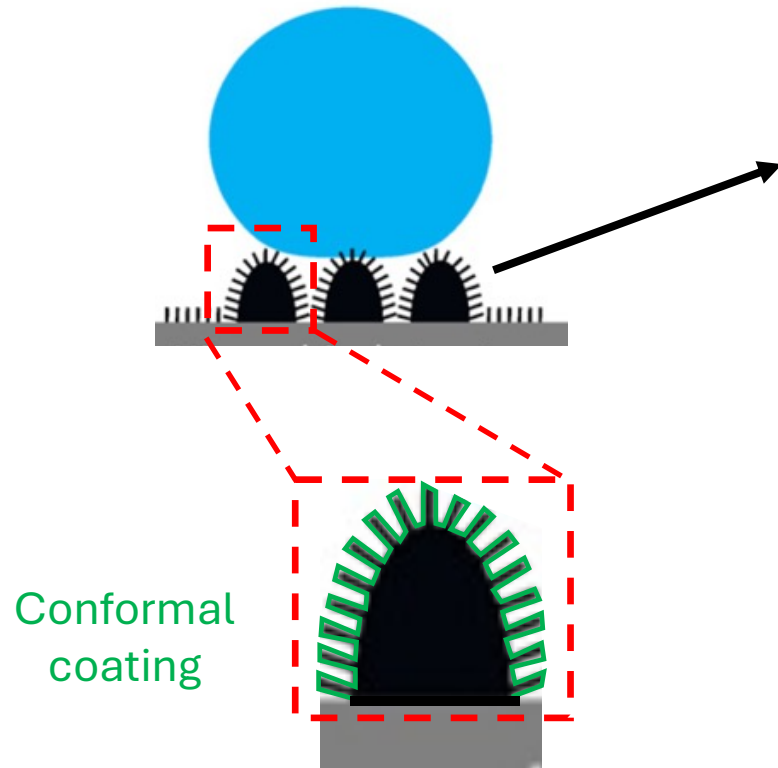
Oxide	Y_2O_3	Eu_2O_3	Ce_2O_3	Gd_2O_3	Tb_2O_3	CaO	SO_3
Wt.%	86.97	4.19	1.43	1.38	0.95	3.71	0.35



Similar wettability
as CeO_2 pellets

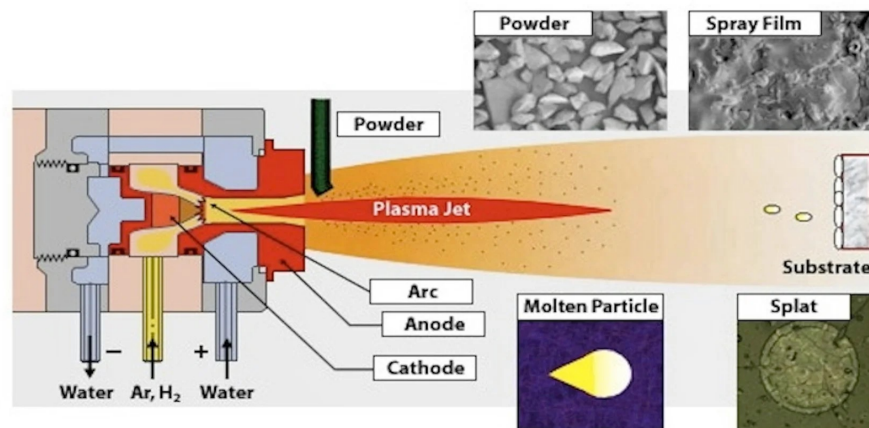
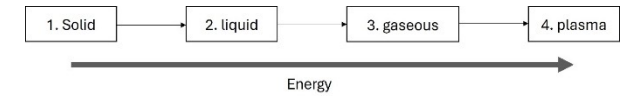
Scalable Deposition Techniques for REOs: Sputtering

- Thin coatings (down to few nm to few μm)
- Allow conformal coating on micro and nanostructures
- Custom-made targets (e.g. made of recycled REOs)
- Not tried yet but experiments are planned



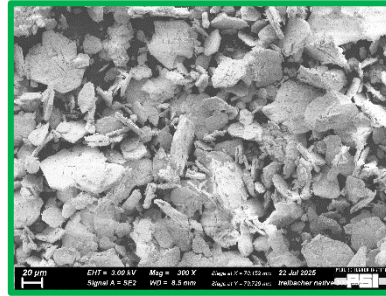
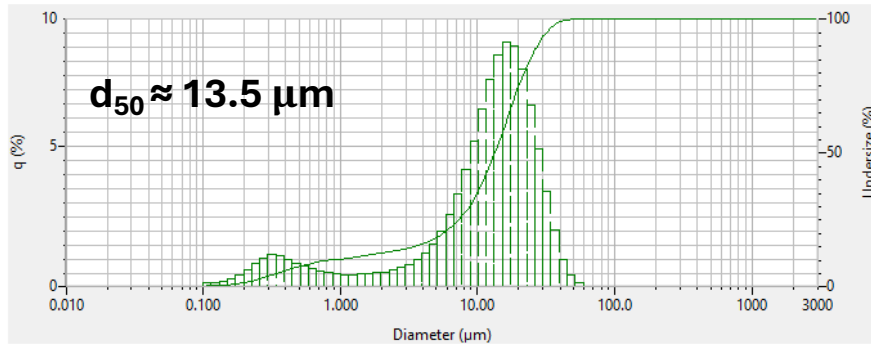
Scalable Deposition Techniques for REOs: Plasma Spraying

- Plasma is the 4th state of matter: ionized gas based on free ions and electrons
- Can be applied on substrates able to withstand high temperatures
- Key points for coating homogeneity (thickness):
 - Constant feeding rate
 - Need of good powder flowability (e.g. particles synthesis via spray drying)
 - Particles should ideally be spherical and not too small ($> 50 \mu m$, reduction of cohesive forces)
 - Working on this technique to deposit REOs
 - Successful deposition on metals, working on ceramics (thermal shocks)

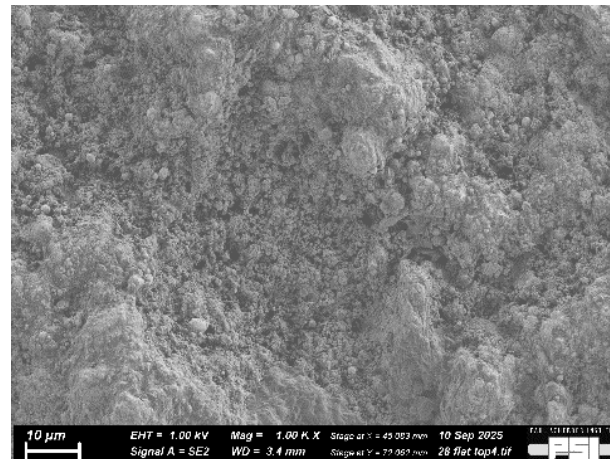
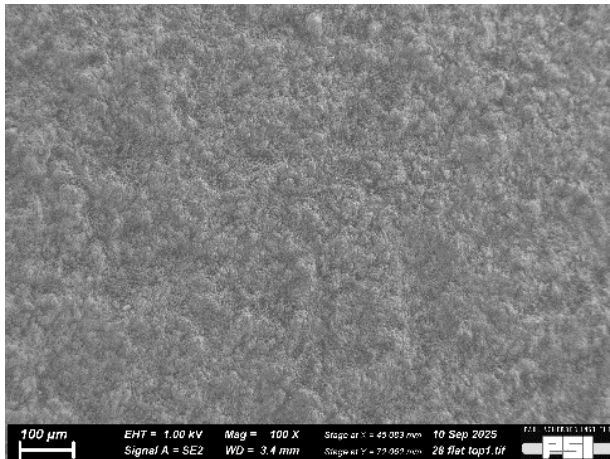


Plasma Spraying: Preliminary Results

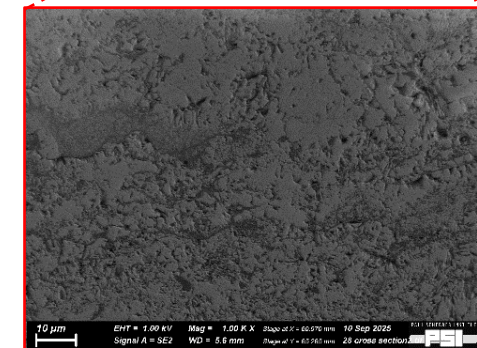
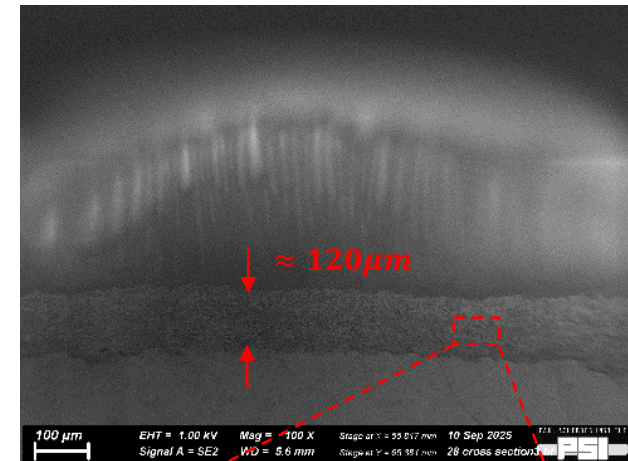
- Powder: native CeO₂ (different from the one used for pellets, cheaper)
- Substrate: Stainless steel



Top view (presence of roughness at different length scales)



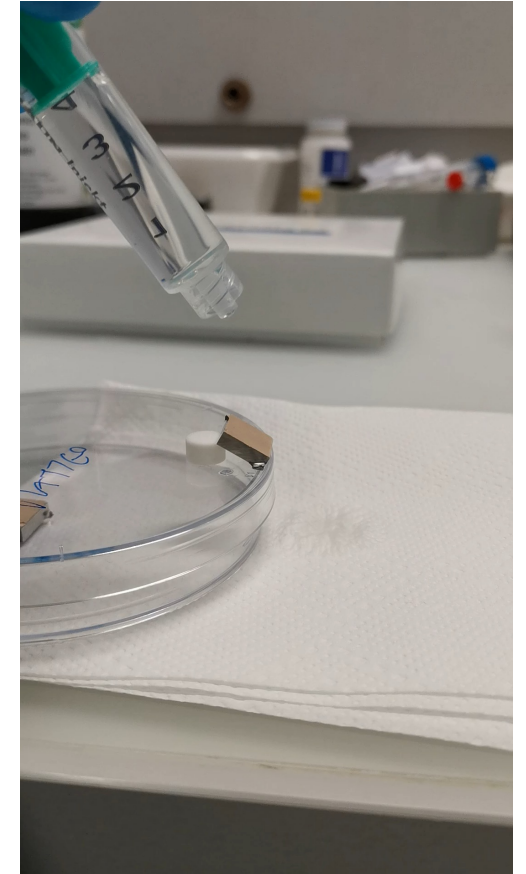
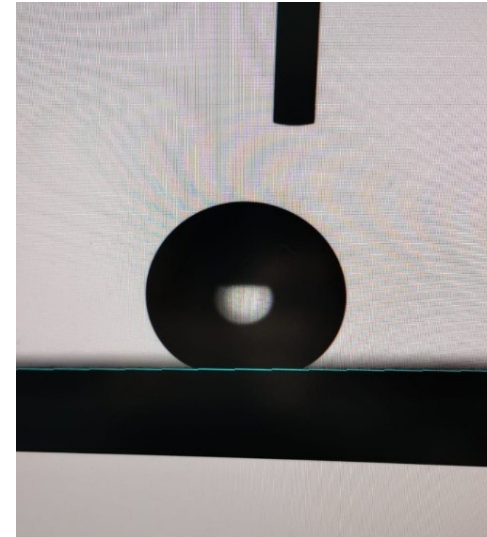
Cross section



Very low porosity, compact 06.10.25

Wettability of Plasma-Sprayed CeO₂ Coating

- Cleaning (acetone, ethanol, water)
- Oxygen plasma activation
- Decanoic acid deposition
- Superhydrophobic regime (contact angle $\approx 155^\circ$)
- Contact angle hysteresis $\approx 25^\circ$
- Rinsing with isopropanol
- No changes in wettability (hydrophobic molecule chemically bonded with substrate)



Observations and Next Steps

- REOs: promising candidate materials to fabricate hydrophobic/superhydrophobic surfaces
 - Cheap (recycled REOs mix powder)
 - Deposition via scalable deposition techniques
 - Environmentally friendly (no PFAS)
- Surfaces can show self healing effects
 - Durability has to be fully evaluated
 - Outdoor tests (ambient exposure, for outdoor applications)
 - Mechanical tests
 - Chemical tests
 - ...
 - Condensation performance
 - Anti-icing performance
 - ...



Thank you for your attention

