Hongkonk, 15th May 2018

Wetting – a multiscale phenomenon

Max Planck Institute for Polymer Research

Hans-Jürgen Butt

Wetting – a multiscale phenomenon


Vollmer


Steffen


Kappl


Encinas

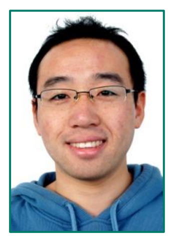

Paven


Geyer


Gao


Wooh


Papado-
poulos

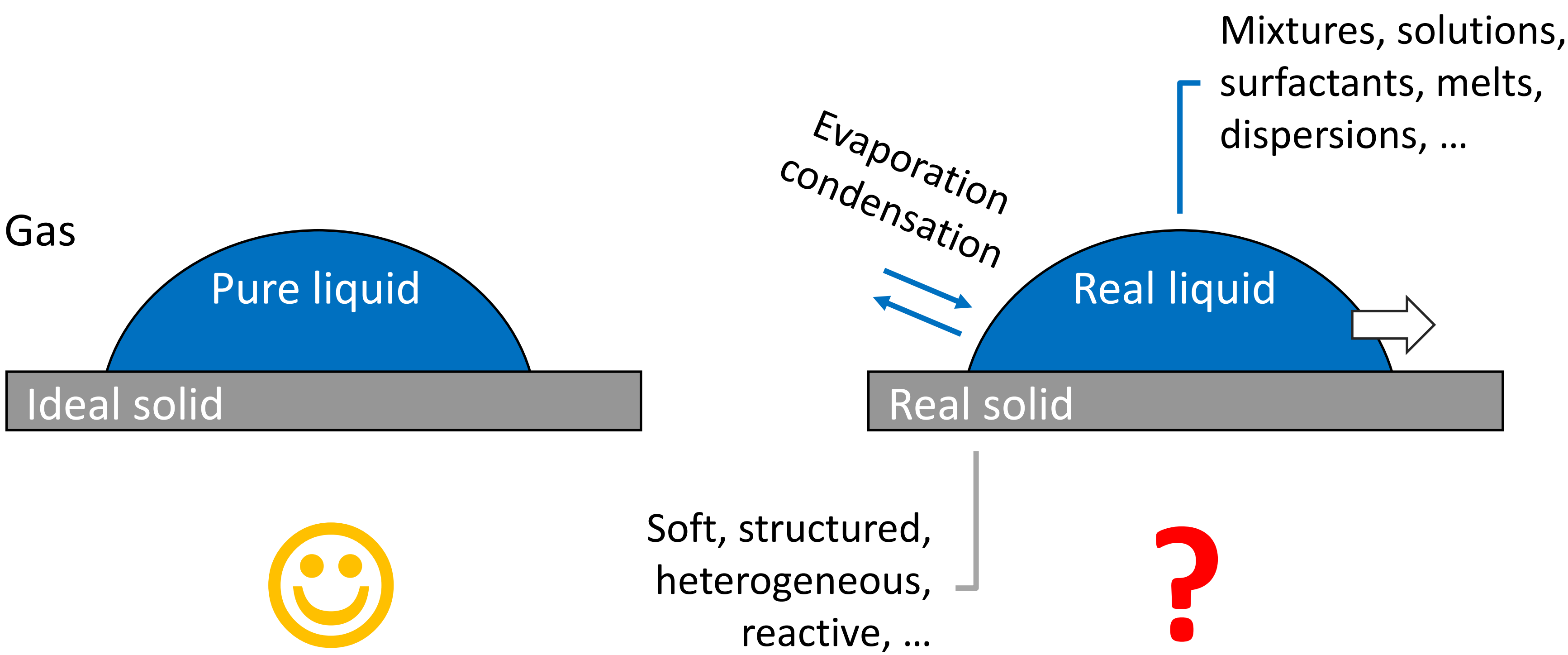

Deng


Schellen-
berger


D'Acunzi

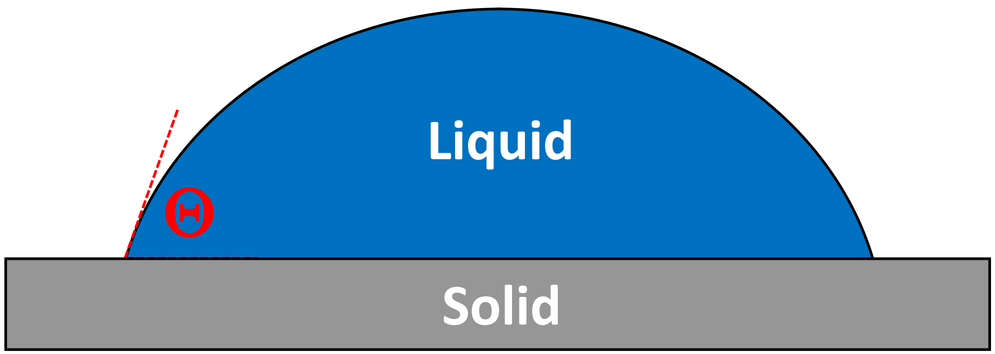

Berger

Wetting



Aim: Understand and control wetting

Young equation



$$\gamma_L \cos\Theta = \gamma_S - \gamma_{SL}$$

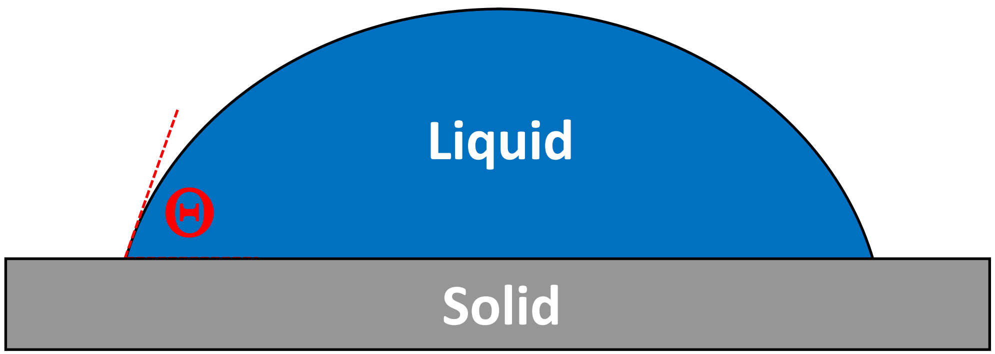
Surface tension liquid (γ_L)

Interf. energy solid/vapor (γ_S)

Interf. energy solid/liquid (γ_{SL})

T. Young, *Phil. Trans. Roy. Soc. London* **1805,** *95*, 65

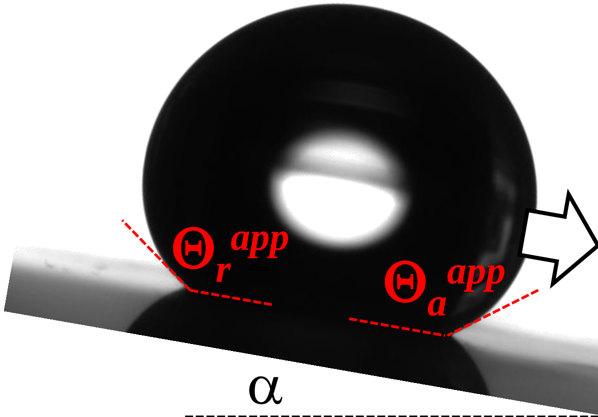
Contact angle hysteresis



$$\gamma_L \cos\Theta = \gamma_S - \gamma_{SL}$$

$$\text{Advancing} \quad \Theta_a^{app} \geq \ldots \geq \Theta_r^{app} \quad \text{receding}$$

Contact angle hysteresis



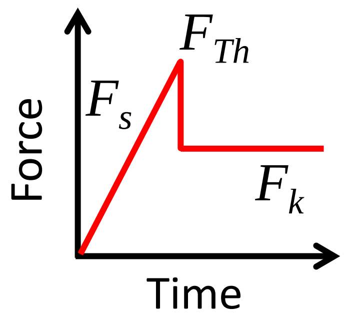
$$\gamma_L \cos\Theta = \gamma_S - \gamma_{SL}$$

$$\text{Advancing} \quad \Theta_a^{app} \geq \ldots \geq \Theta_r^{app} \quad \text{receding}$$

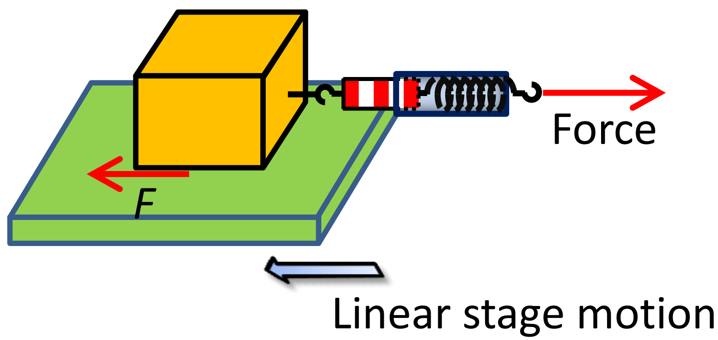
➡ Contact angle hysteresis is of fundamental importance

Furmidge, *J. Colloid Sci*. **1962**, *17*, 309; Yoshimitsu et al., *Langmuir* **2002**, 18, 5818; Furmidge, J. Colloid Sci. **1962**, *17*, 309; ElSherbini & Jacobi, *J. Colloid Interface Sci*. **2006**, 299, 841; Antonini, Carmona, Pierce, Marengo & Amirfazli, *Langmuir* **2009**, *25*, 6143.

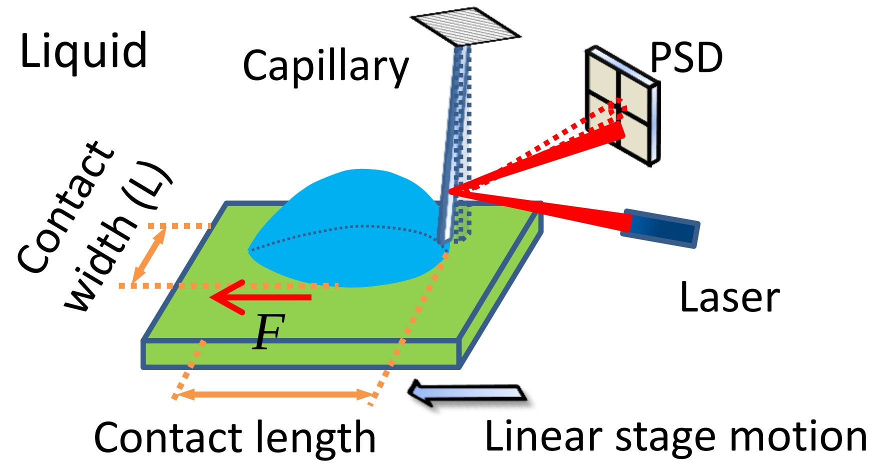
Friction



Solid

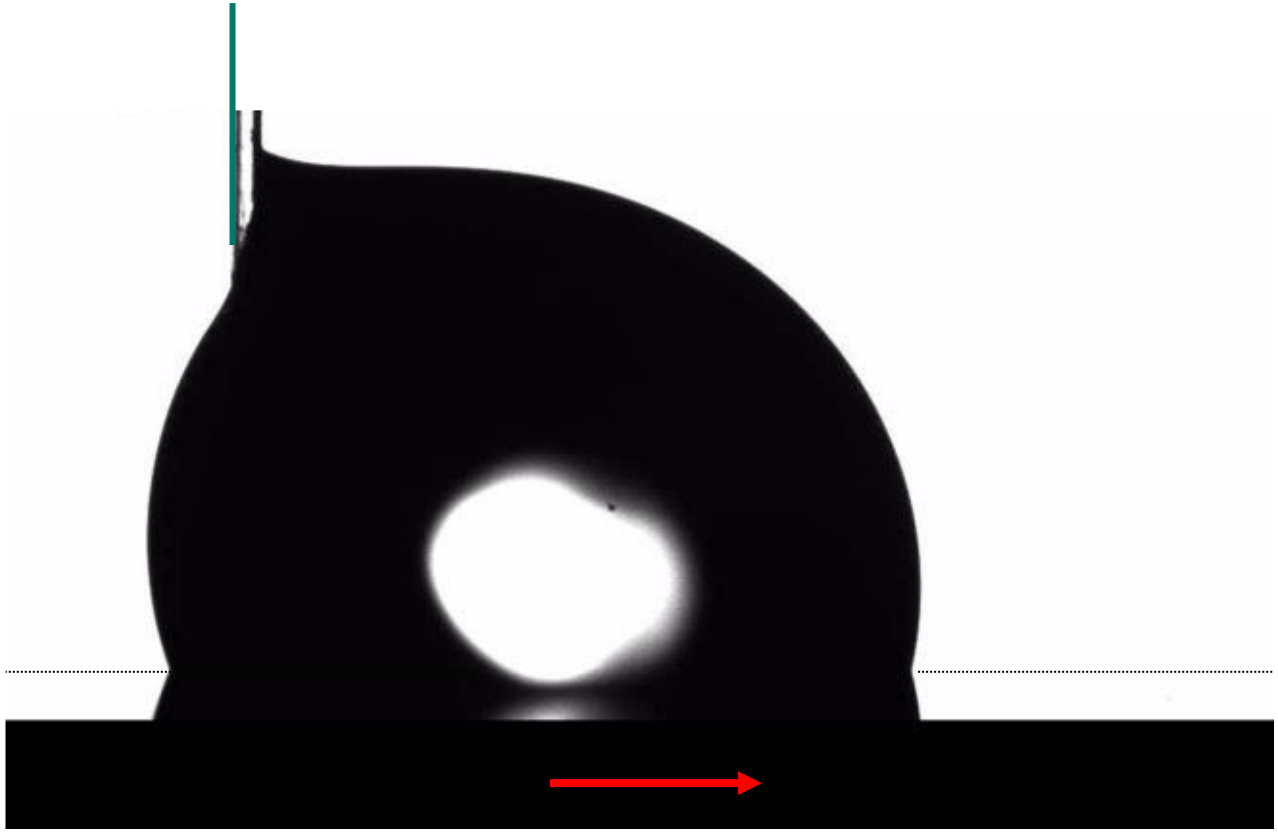


Liquid



Langmuir **2012,** *28*, 16812

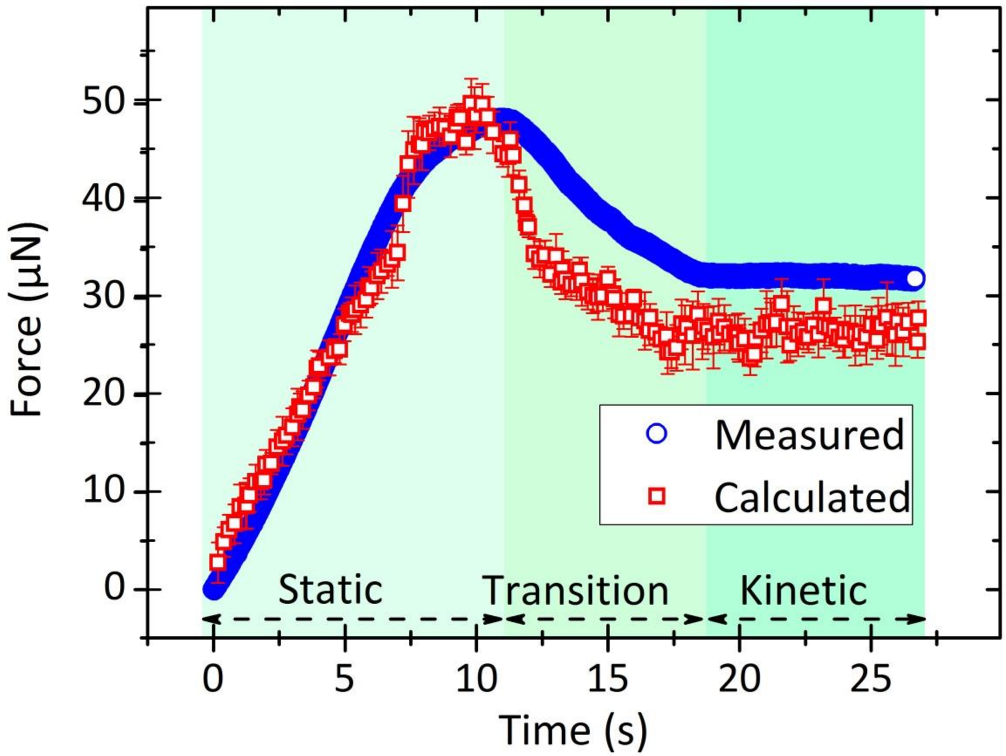
Lateral adhesion of drops



1.5 µL ionic liquid on a fluorinated silicon wafer at 0.2 mm/s

1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide

Lateral adhesion of drops



1.5 µL ionic liquid on a fluorinated silicon wafer at 0.2 mm/s

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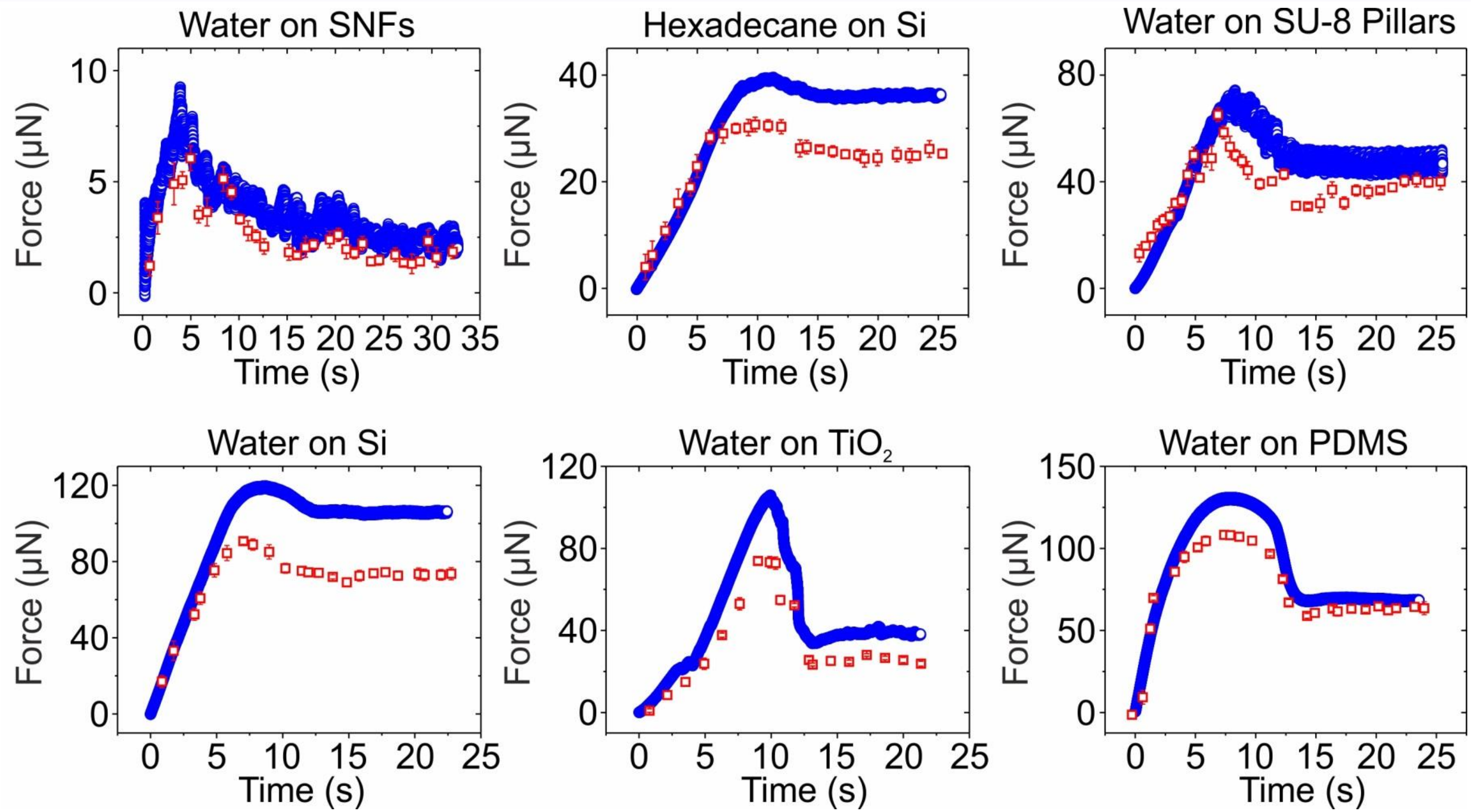
Nature Phys. **2017**, *14*, 191

Lateral adhesion of drops



➡ Distinguish between static and kinetic friction

Nature Phys. **2017**, *14*, 191

Liquid repellency

Superhydrophobic

Ras & Marmur, 2017: *Non-wettable Surfaces: Theory, Preparation and Applications*

Superhydrophobic surfaces

ROBERT N. WENZEL 1936
INDUSTRIAL AND ENGINEERING CHEMISTRY

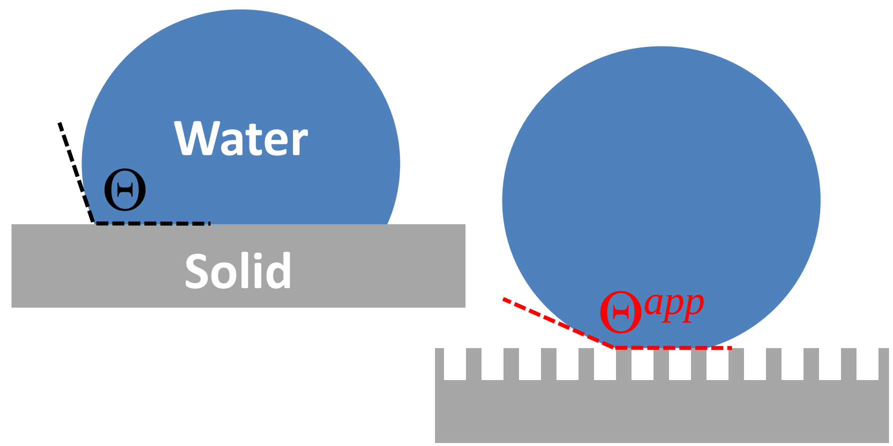
RESISTANCE OF SOLID SURFACES TO WETTING BY WATER

Hydrophobized paper

	Contact Angle		
	Plate 1	Plate 2	Av.
	Degrees		
Mg stearate	145.9	140.6	143.2
Sn stearate	151.6	149.1	150.4
Ba stearate	152.5	157.2	154.8
Th stearate	158.8	159.4	159.1
Cd stearate	162.0	165.2	163.6
Zn stearate	162.9	170.1	166.5
Al stearate	169.4	170.8	170.1

A. B. D. CASSIE NATURE 1945
S. BAXTER.

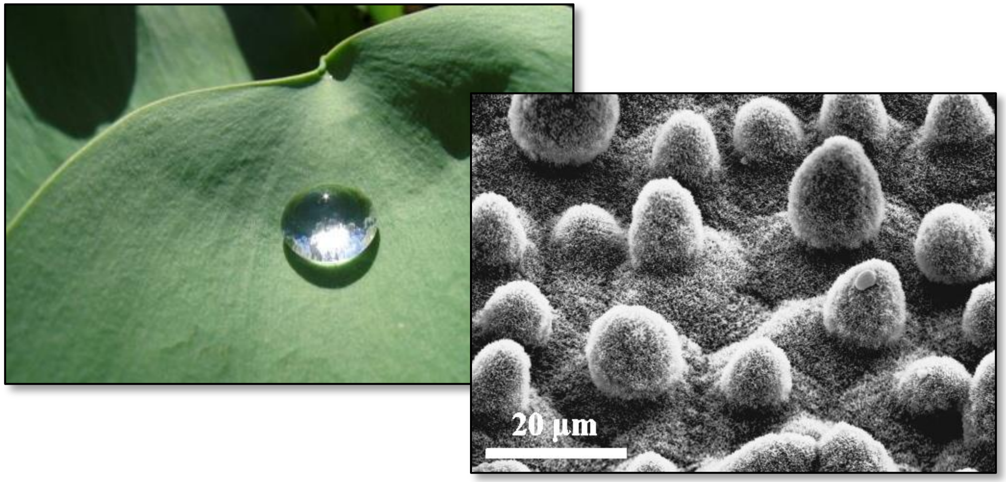
Large Contact Angles of Plant and Animal Surfaces



Roughness

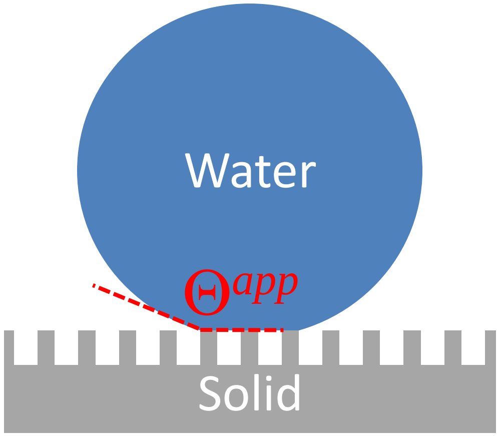
Entrapped air

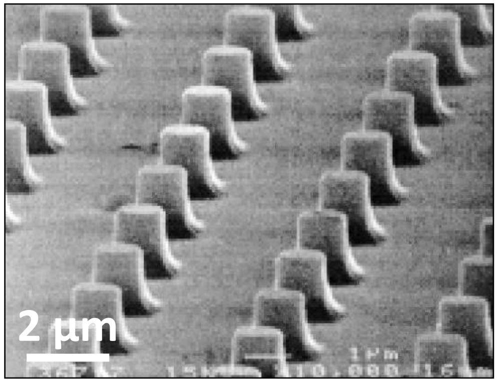
Lotus leaf



Neinhuis & Barthlott, *Planta* **1997**, *202*, 1

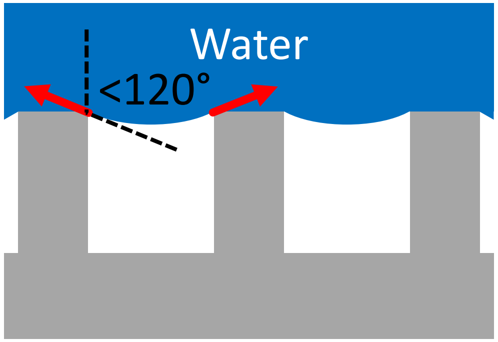
Superhydrophobic surfaces



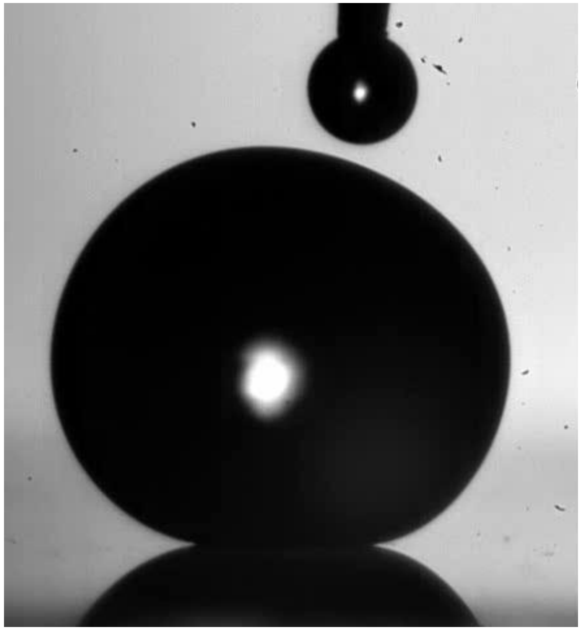


Bico et al., *EPL* **1999**, *47,* 220

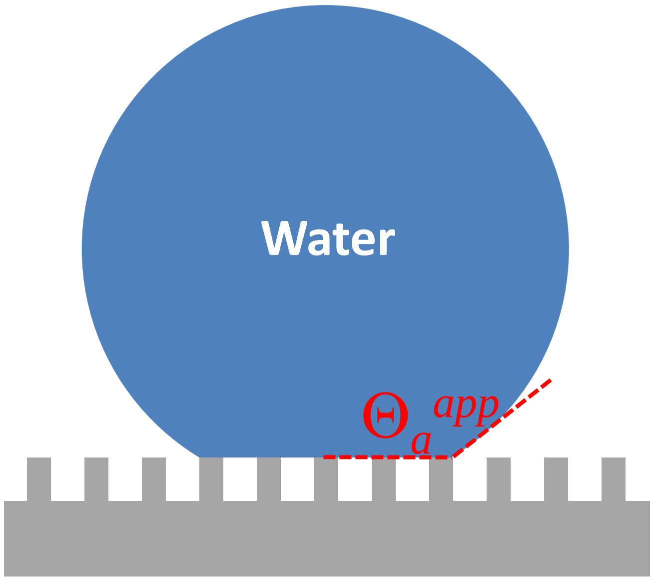
Surface tension



Superhydrophobic surface

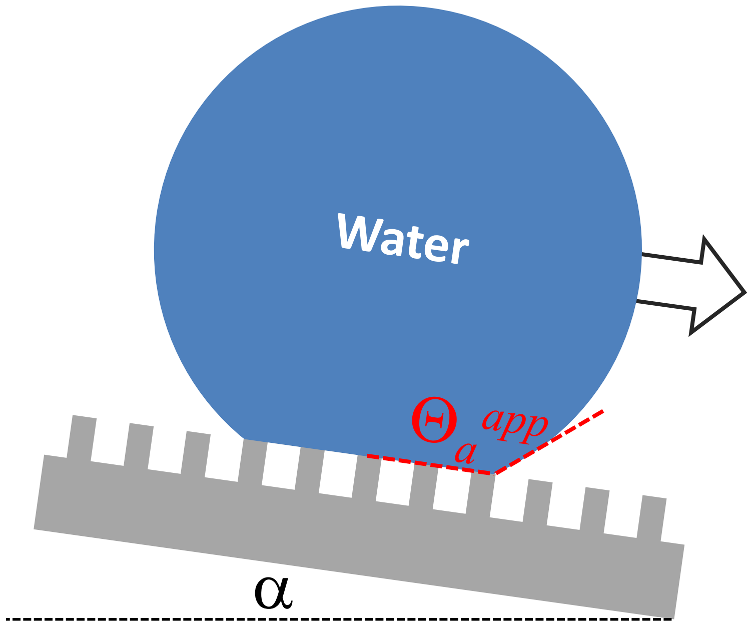


Superhydrophobic surface: Definition



$$\Theta_a^{app} \geq 150°$$

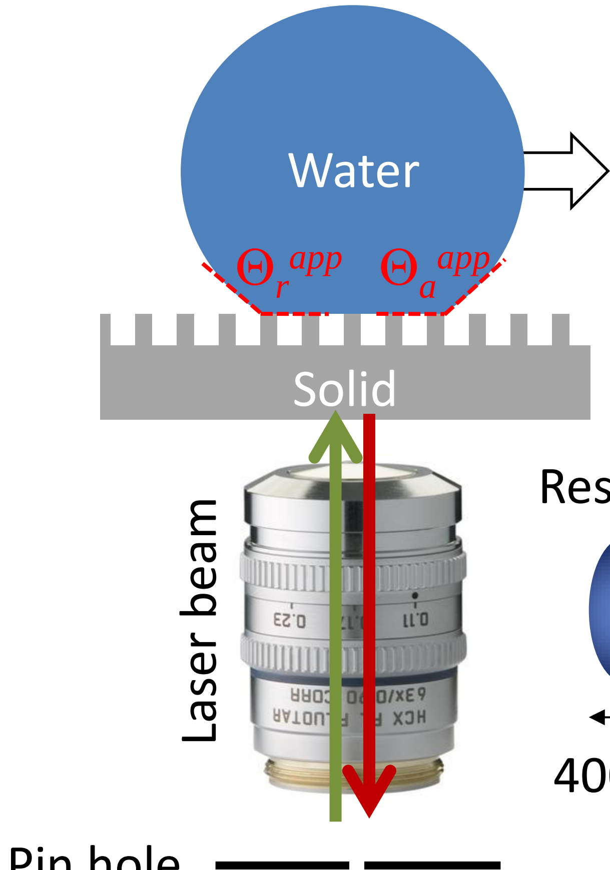
Superhydrophobic surface: Definition



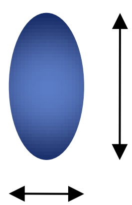
$$\Theta_a^{app} \geq 150°$$

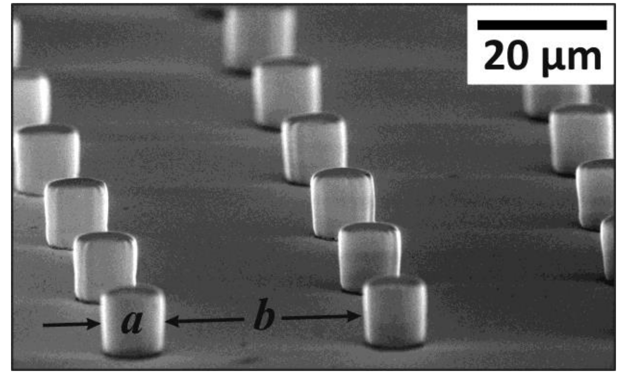
$$\alpha \leq 10°$$

How does a drop advance and recede on superhydrophobic surfaces?



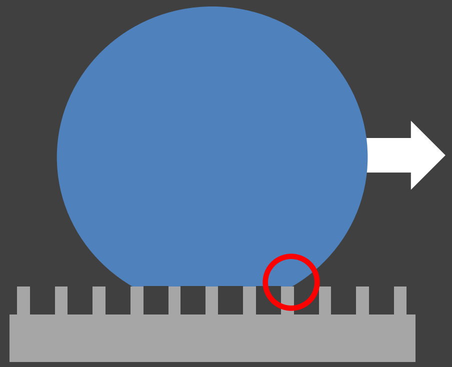
Resolution

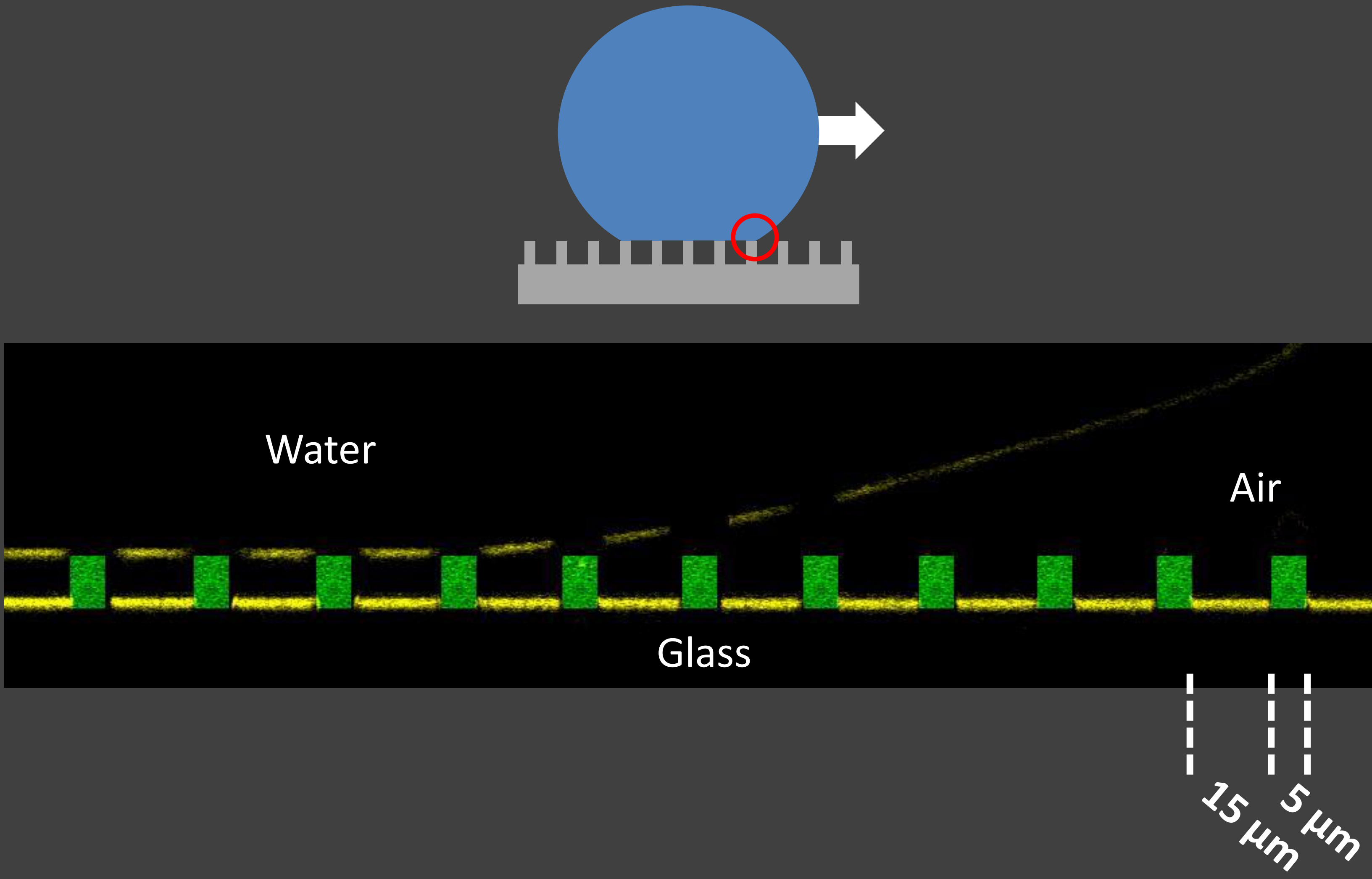




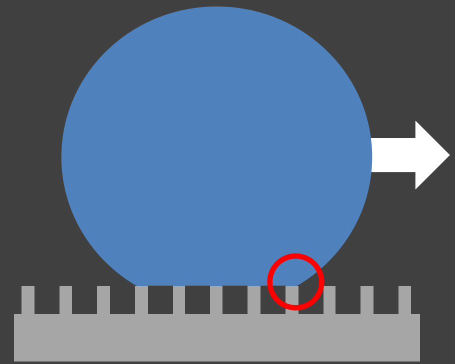
a = 5-25 µm, b = 15-75 µm

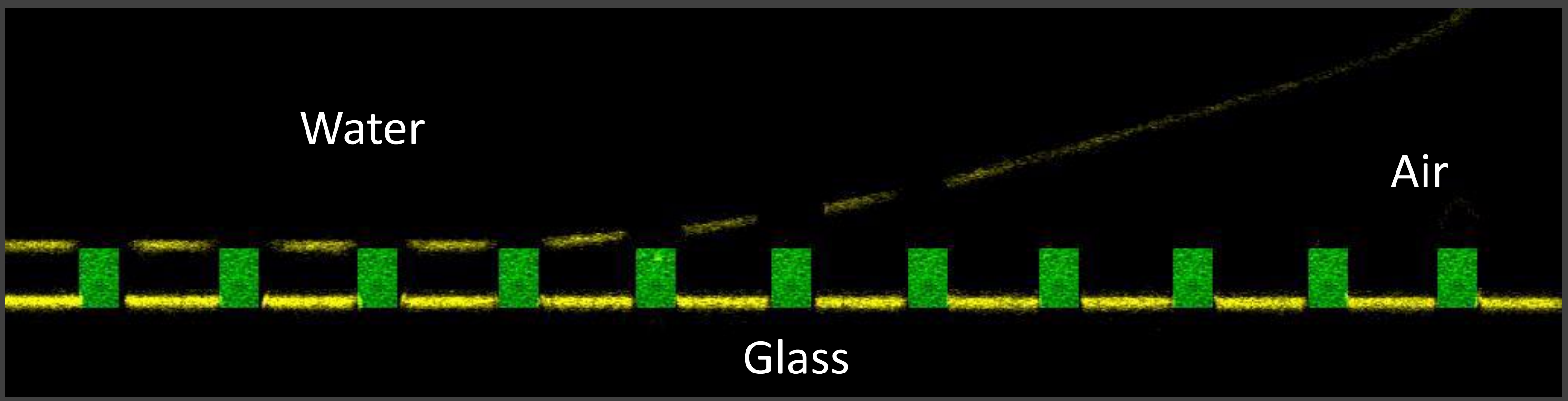
Laser scanning confocal microscope





Laser scanning confocal microscopy

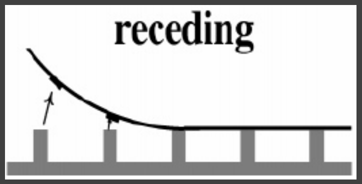


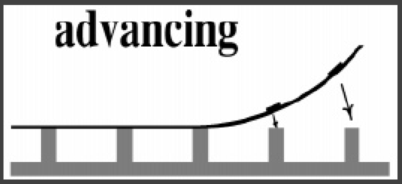


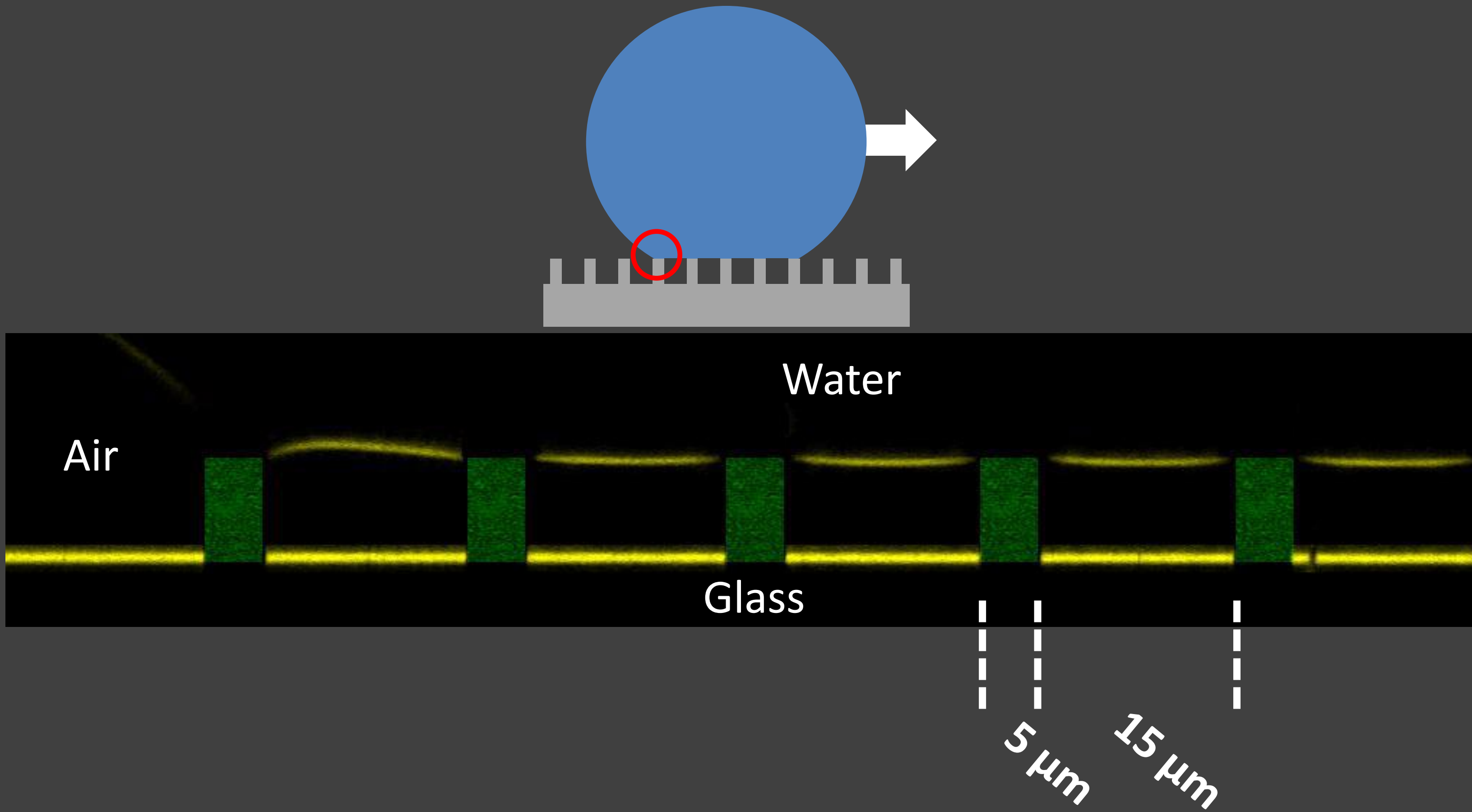
Bartell & Shepard, *JPC* **1953**
Extrand, *Langmuir* **2002**
Gao & McCarthy, *Langmuir* **2006**

Advancement is touch down

$\Theta_a^{app} = 180°$

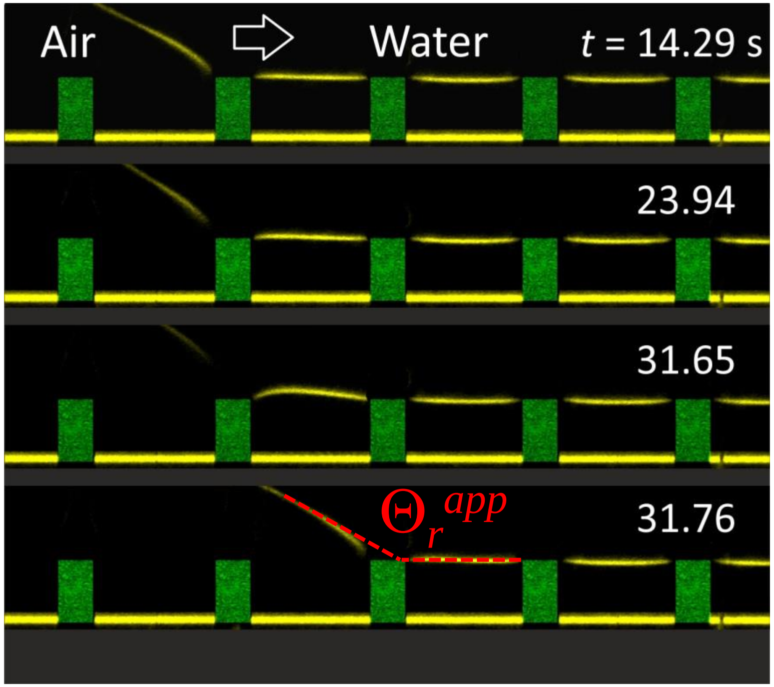


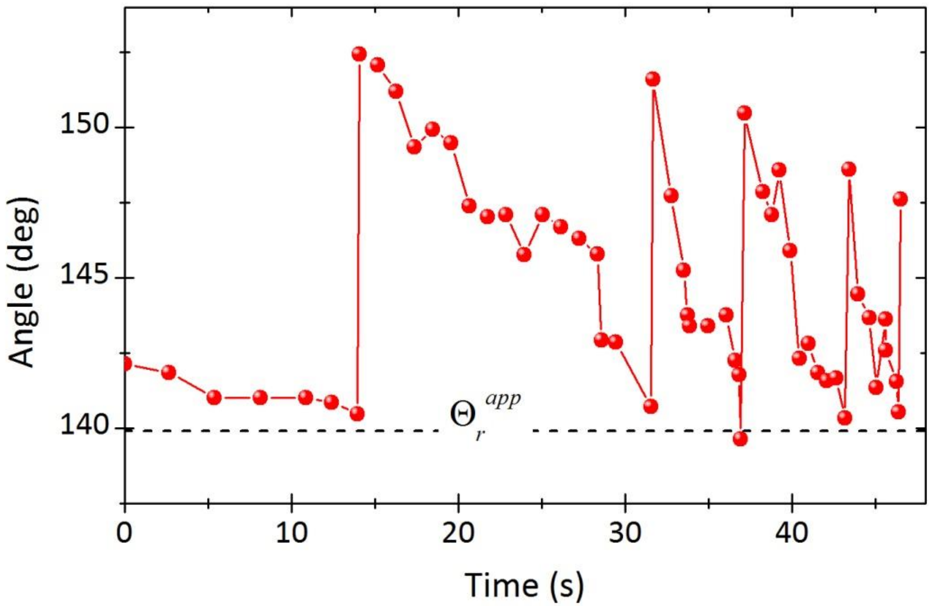




Laser scanning confocal microscopy

Receding water front



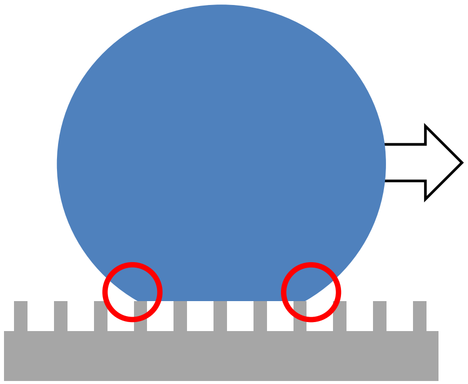


The apparent receding contact angle is defined and characteristic

Phys. Rev. Lett. **2016**, *116*, 096101

Micropillar arrays

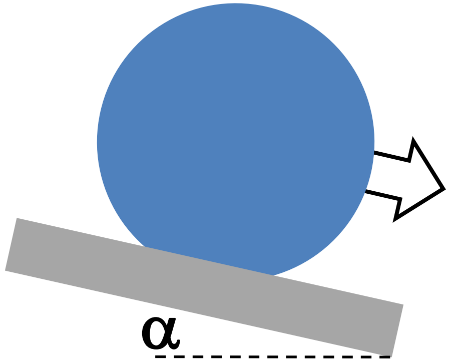
- Drops recede via depinning at defined Θ_r^{app}
- Advancing side touches down, Θ_a^{app} = 180°
- Neither Θ_a^{app} nor contact angle hysteresis characterize superhydrophobicity



- Receding contact angle to measure superhydrophobicity

Korhonen et al., *Langmuir* **2013**, *29*, 3858

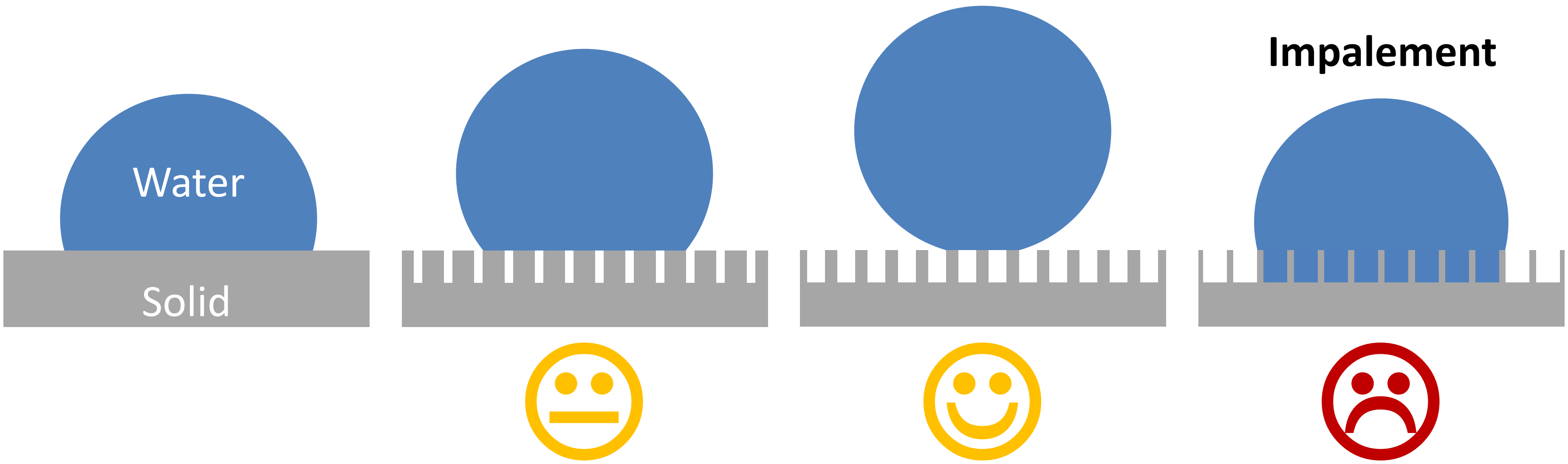
- Sliding angle $\sin\alpha = \frac{k\gamma w}{mg}\left(\cos\Theta_r^{app} + 1\right)$



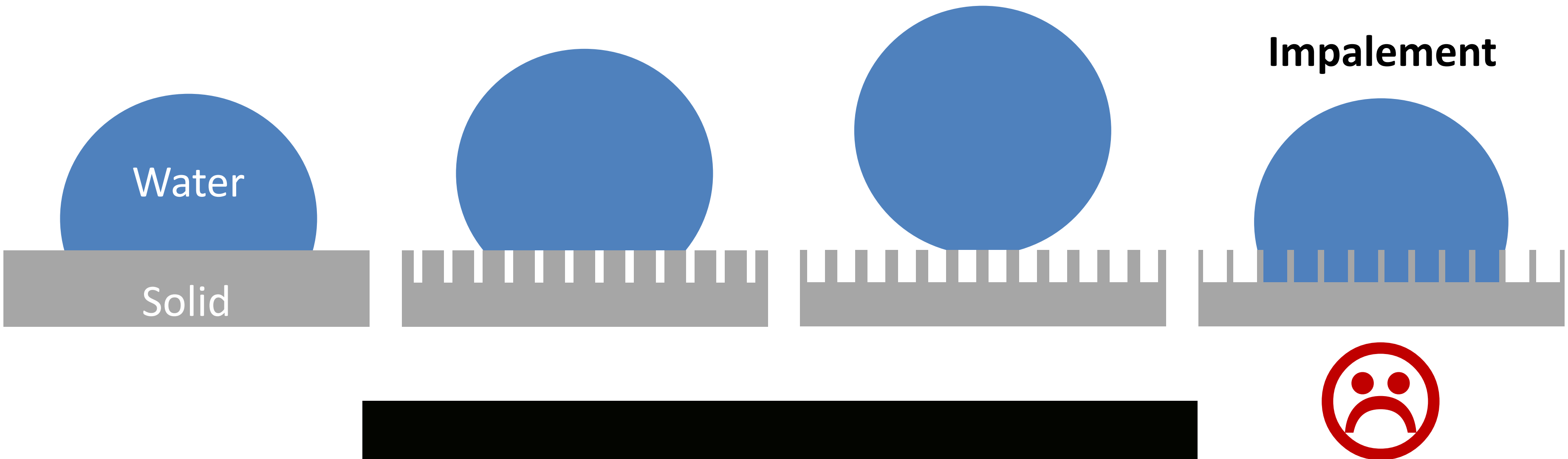
- $\cos\Theta^{app} = f(\cos\Theta + 1) - 1$ not useful

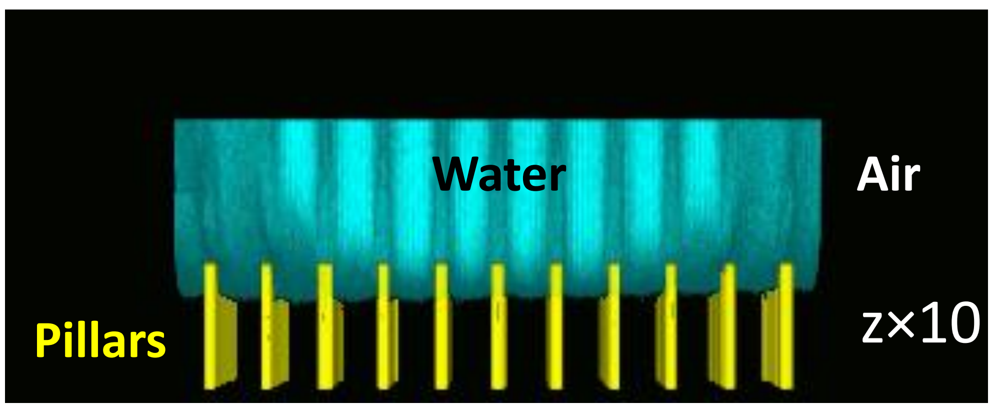
Cassie & Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546

Superhydrophobic surfaces



Superhydrophobic surfaces

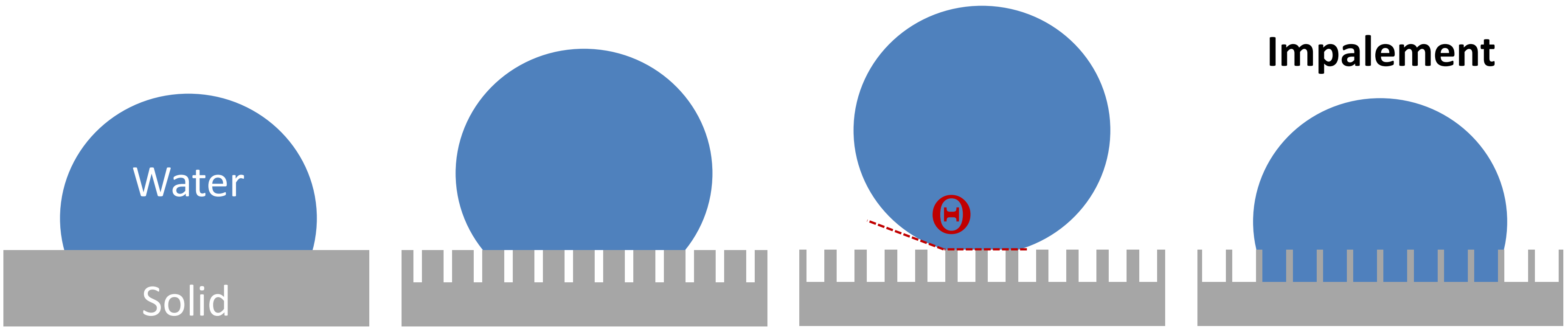




1 frame/s

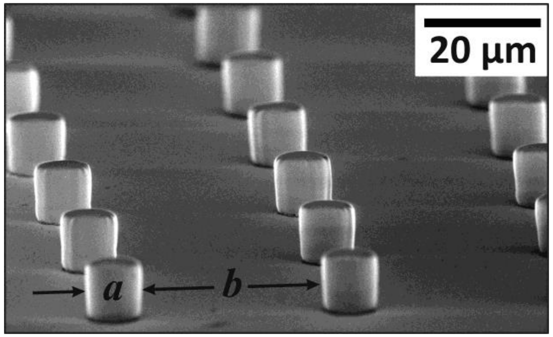
Proc. Natl. Acad. Sci. **2013**, *110*, 3254

Superhydrophobic surfaces



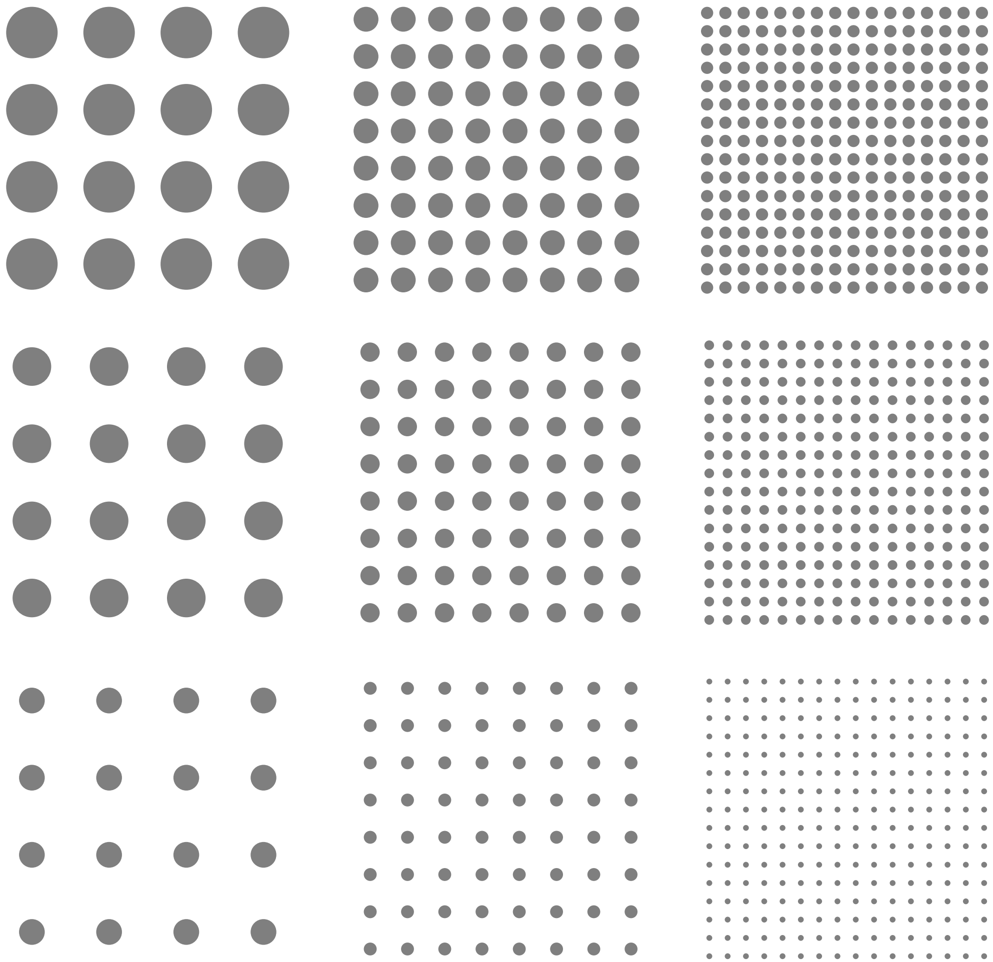
➡ High contact angle **and** high impalement pressure

Design of superhydrophobic surfaces

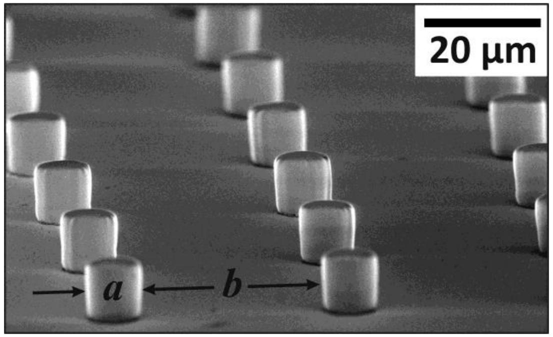


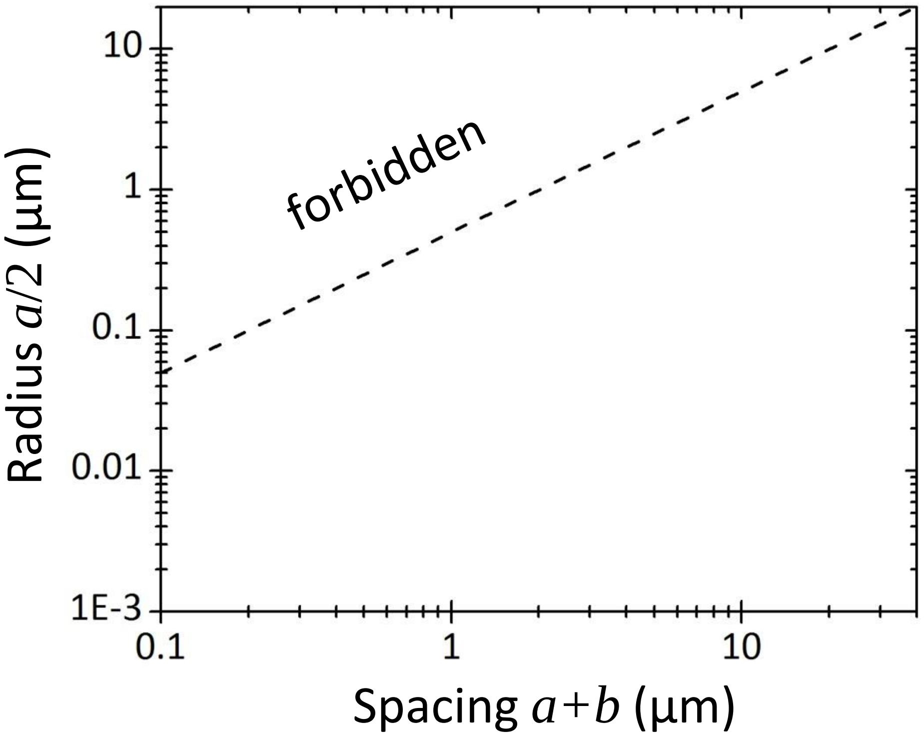
Splitting, area fraction constant →

Radius, number constant ↓



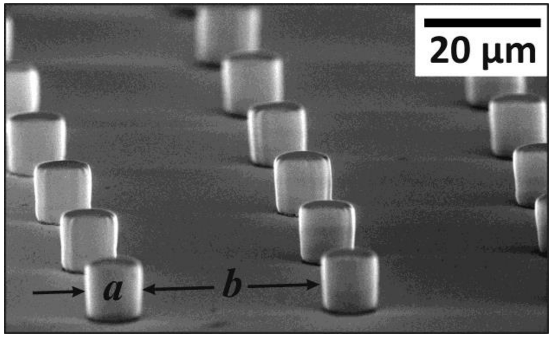
Design of superhydrophobic surfaces

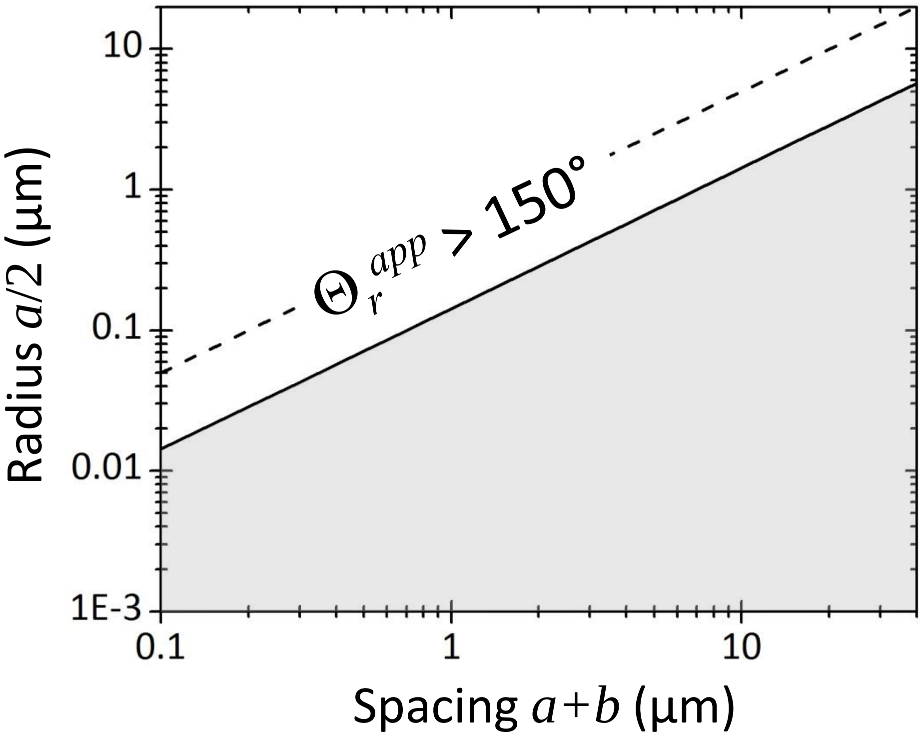




$\Theta_a = 120°, \Theta_r = 100°$

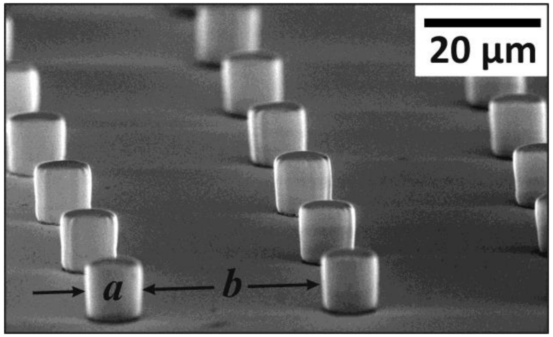
Design of superhydrophobic surfaces

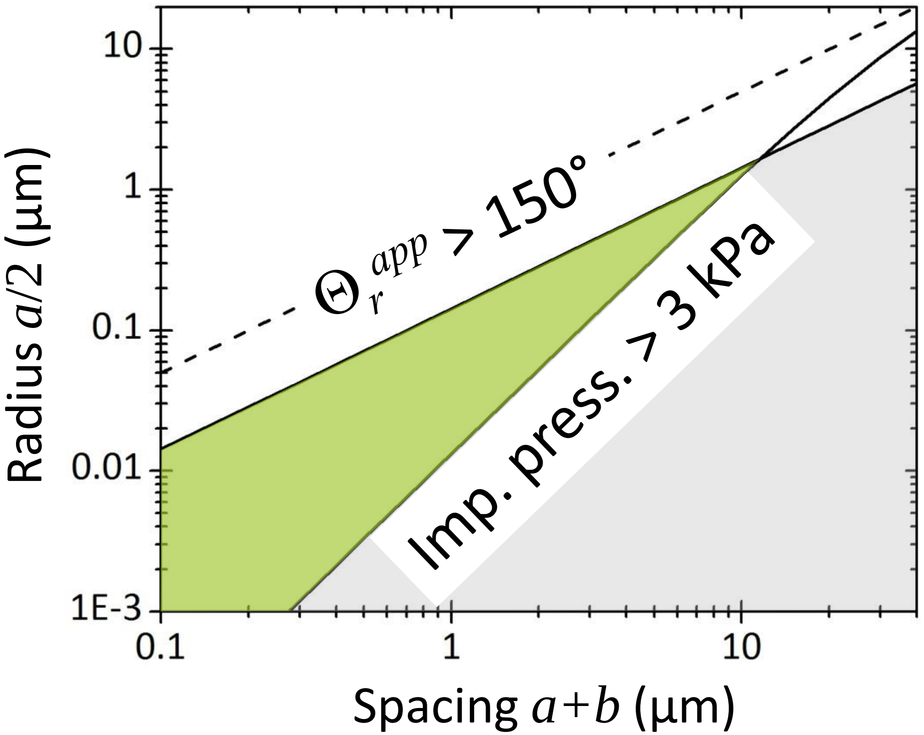




$\Theta_a = 120°$, $\Theta_r = 100°$

Design of superhydrophobic surfaces





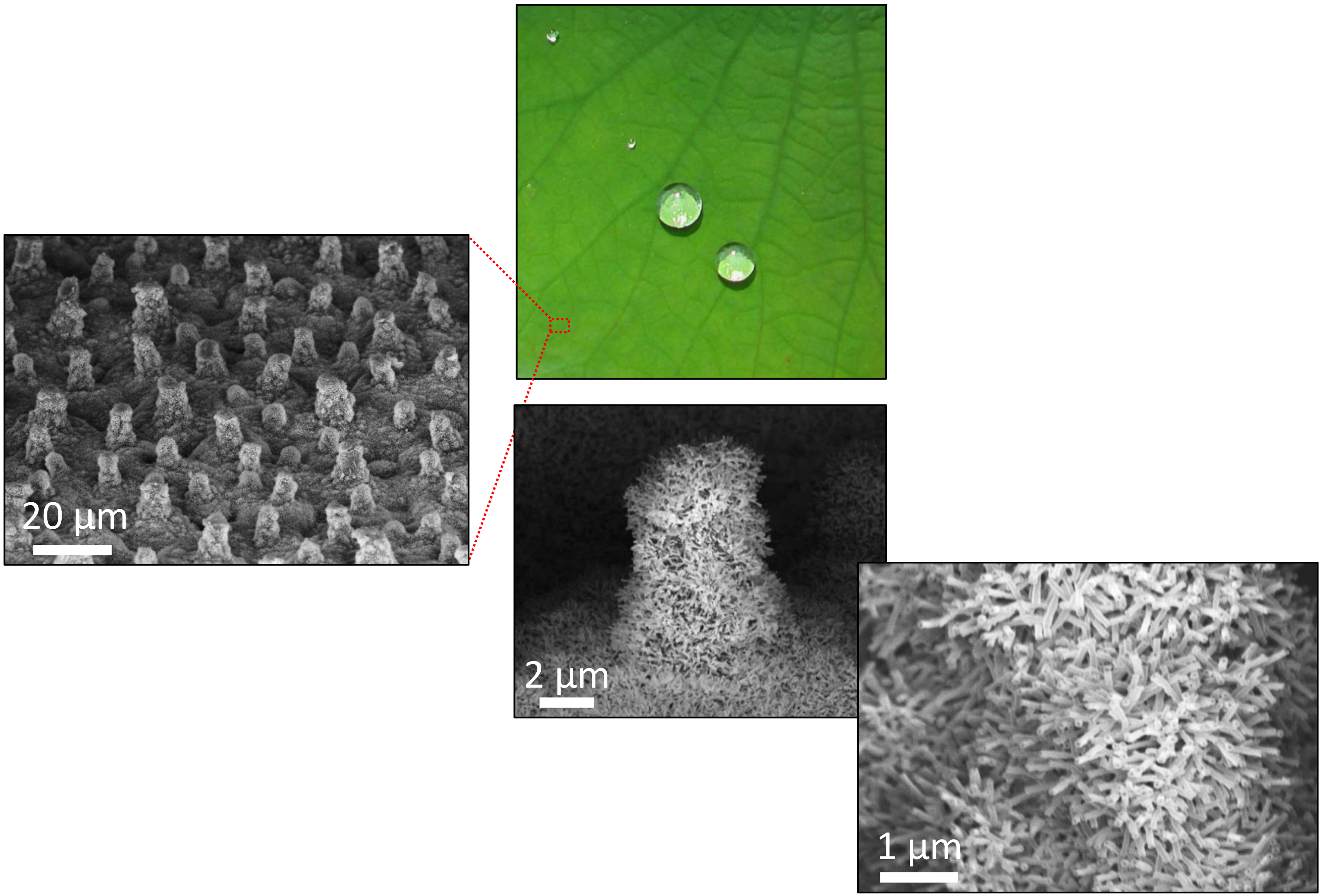
➡ Superhydrophobic structures should be as small as possible

Adv. Colloid Interface Sci. **2015**, *222*, 104

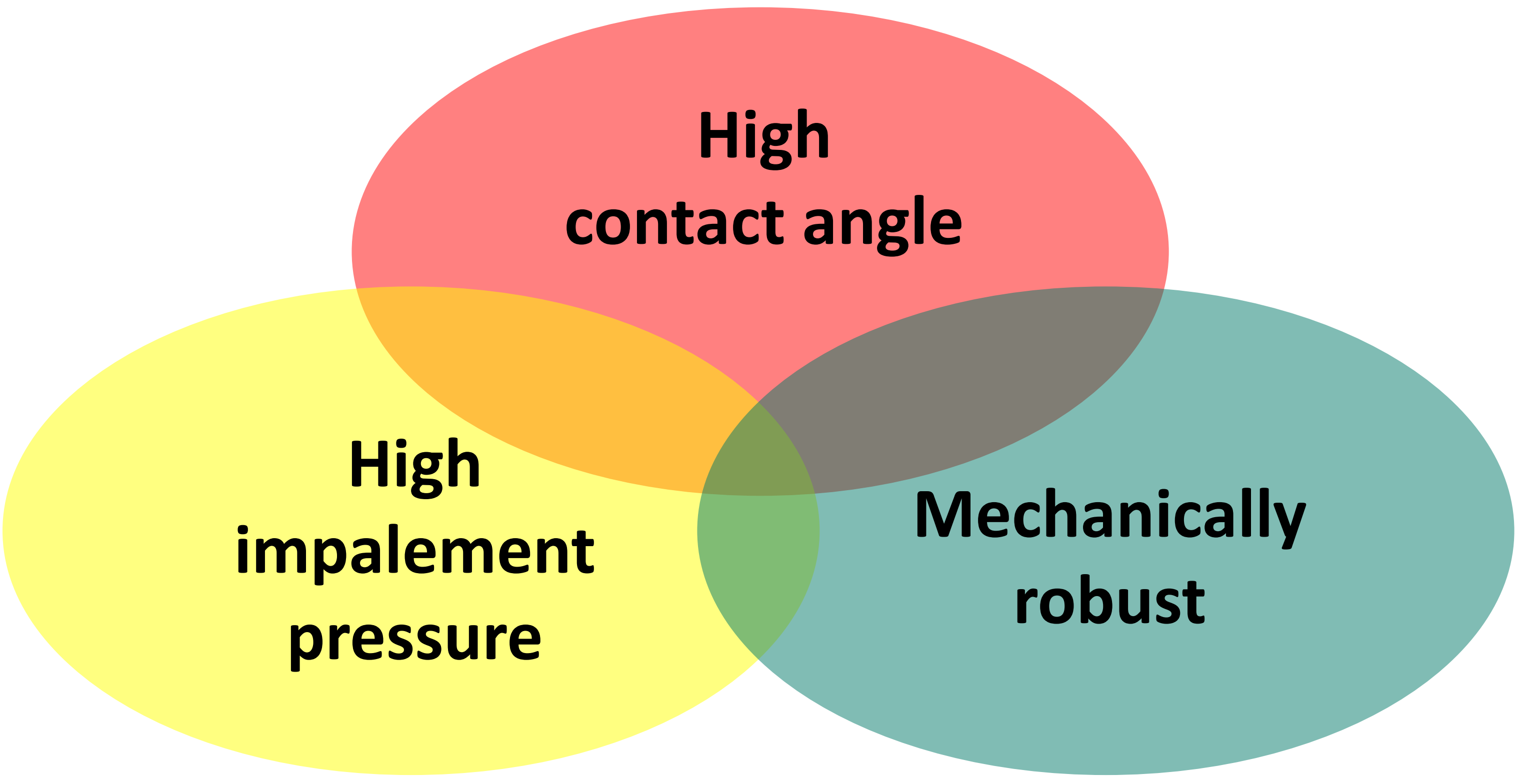
Extrand, *Langmuir* **2006**, *22*, 1711

Θ_a = 120°, Θ_r = 100°

Lotus leaf

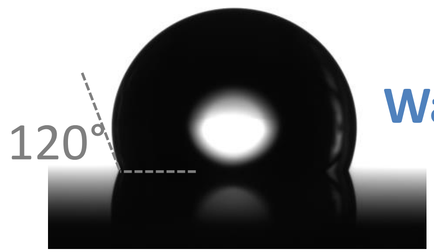


Challenge


High
contact angle
High
impalement
pressure
Mechanically
robust

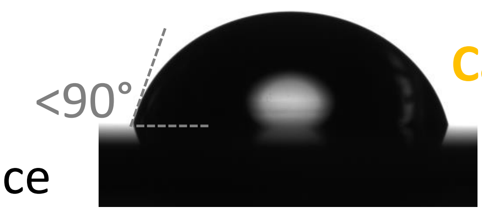
Superoleophobic surfaces

Superoleophobic surfaces



Water

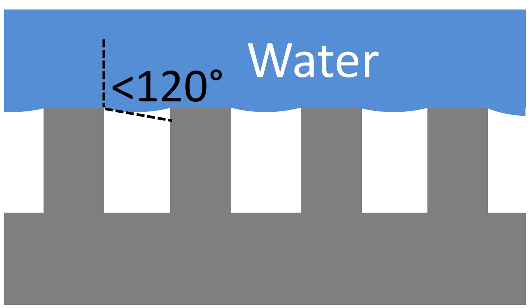
Low energy surface

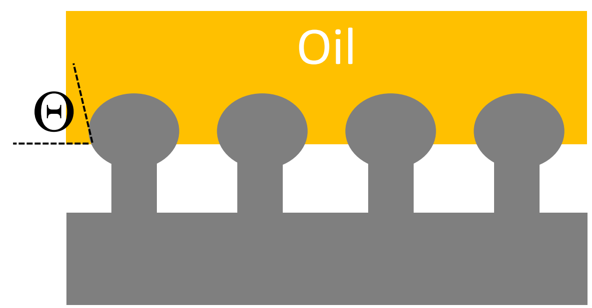


Castor oil

Superhydrophobic

Superoleophobic





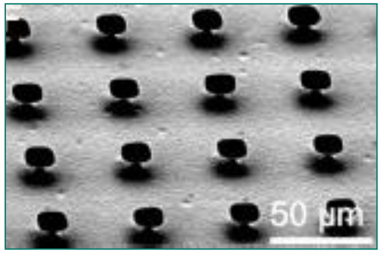
Roughness

Overhangs

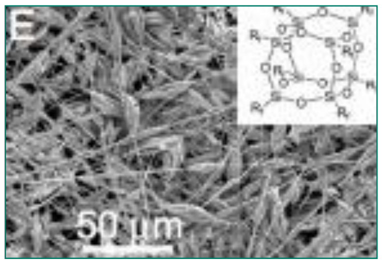
Herminghaus, *EPL* **2000**, *52*, 165; Tuteja, McKinley & Cohen, *Science* **2007**, *318*, 1618

Superoleophobic surfaces

Lithography

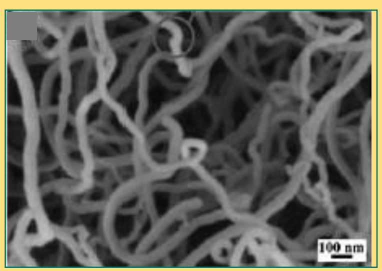


Electrospun fibres

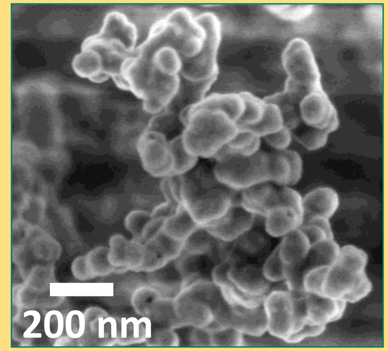


Tuteja et al., *PNAS* **2008**, *105*, 18200

Nanofilaments

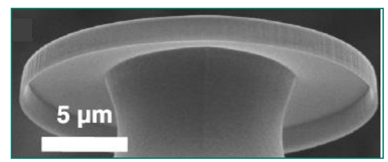


Zhang & Seeger, *Angew. Chem.* **2011**, *50*, 6652



Soot-templated

Science **2012**, *335*, 66



Tables with overhanging rim

Liu & Kim, *Science* **2014**, *346*, 1096

Liquid flame spray

Teisala et al., *Adv. Mater*. **2018**, in press

Superamphiphobic membranes for blood oxygenation

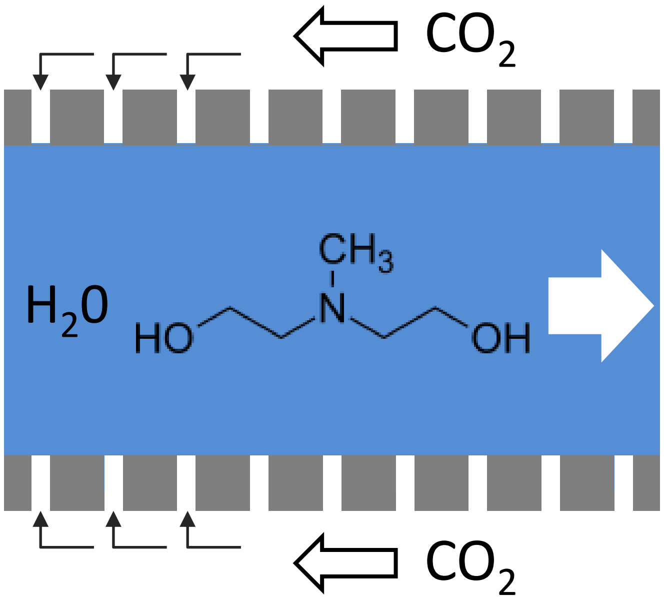
Human blood stabilized by heparin as anticoagulant
after 24 h incubation at 37°C

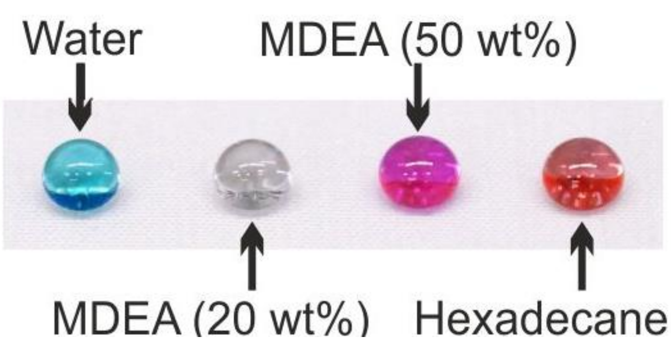
Mailänder

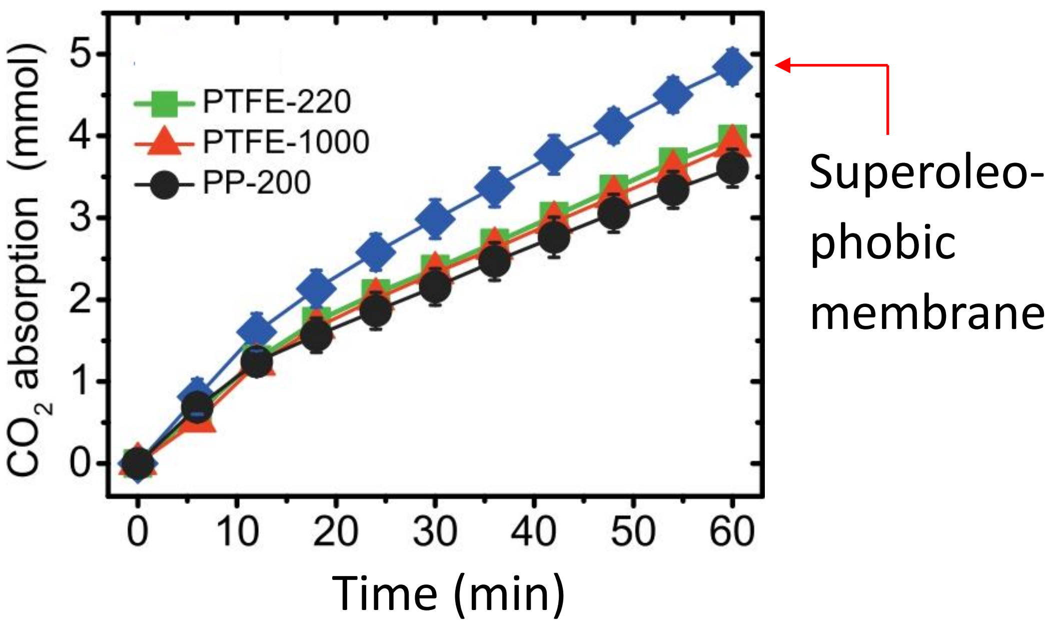
Schöttler

Nature Commun. **2013**, *4*, 2512

Gas membranes for CO_2 capture

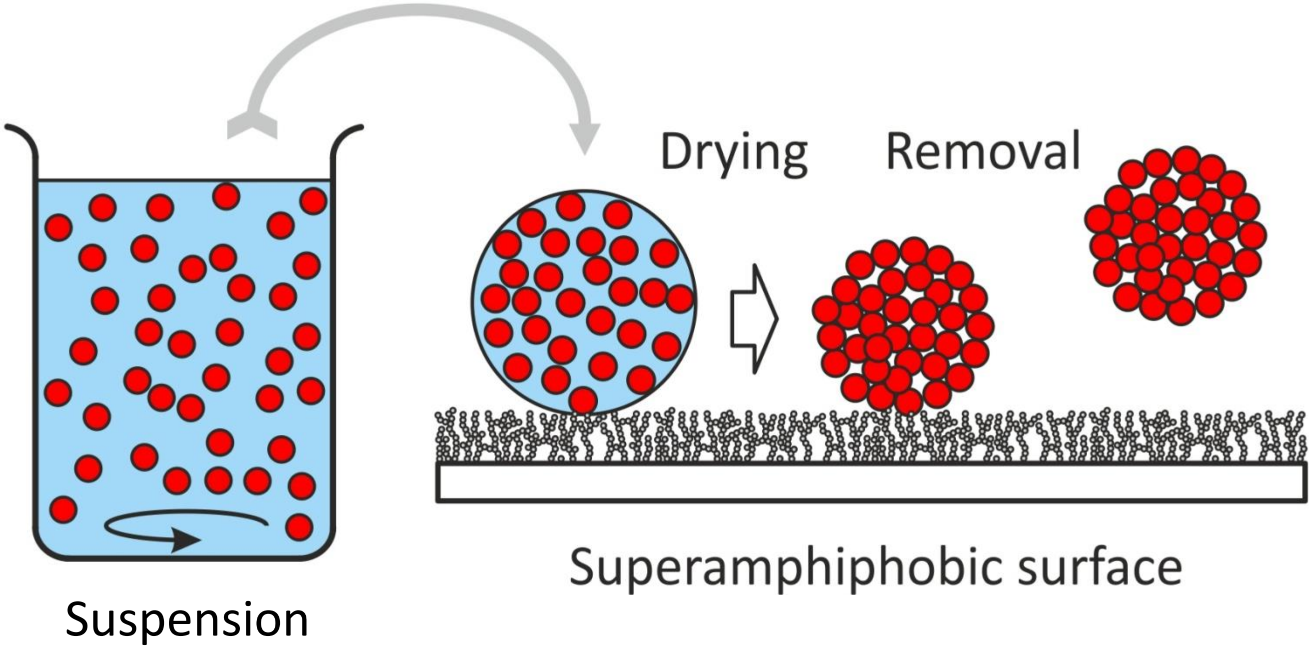




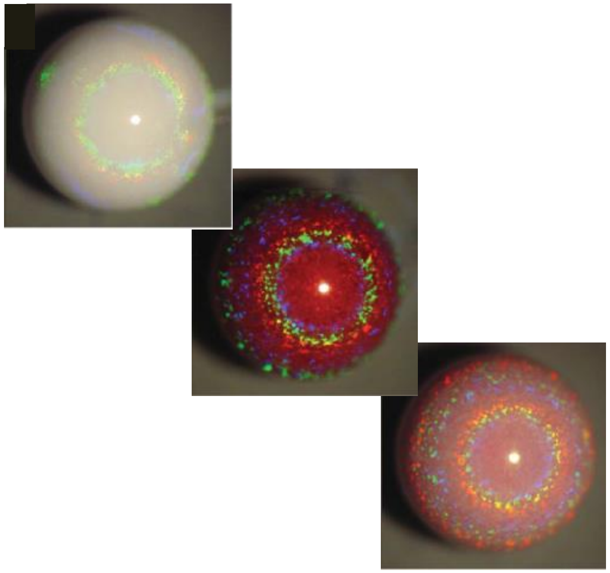


Adv. Mater **2017**, *29*, 1603524

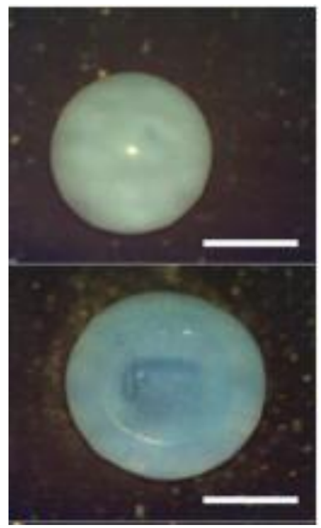
Supraparticles



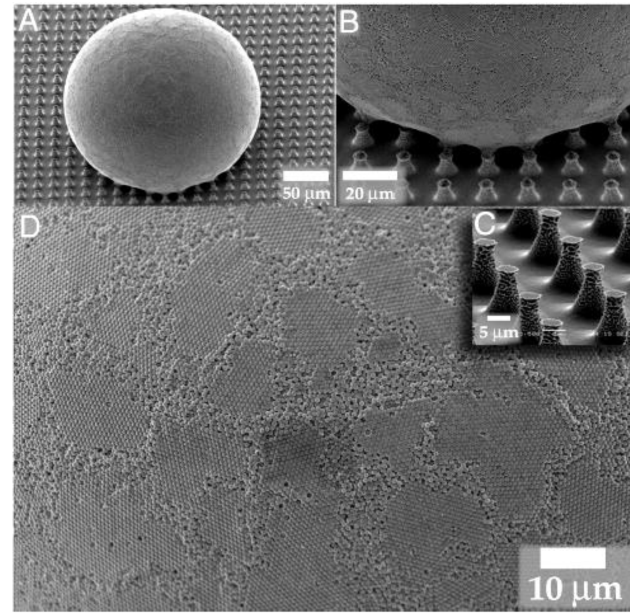
Supraparticles



Rastogi et al., *Adv. Mater.* **2008**, *20*, 4263



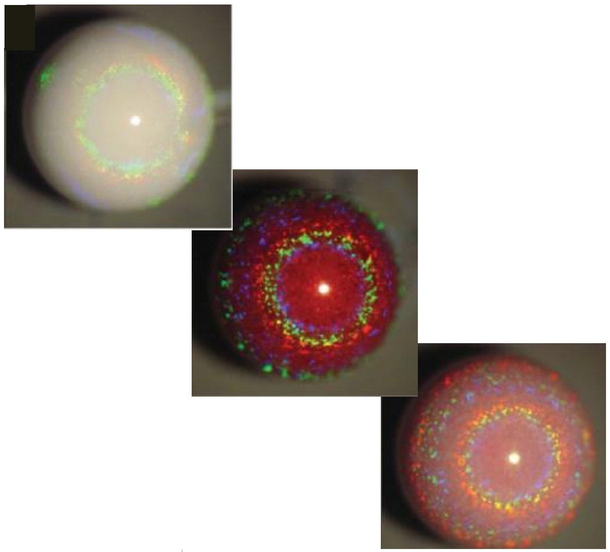
0.5 mm

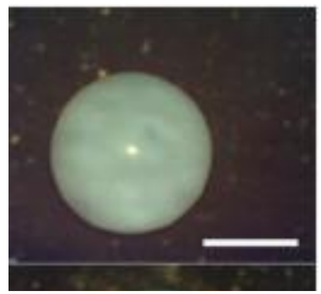


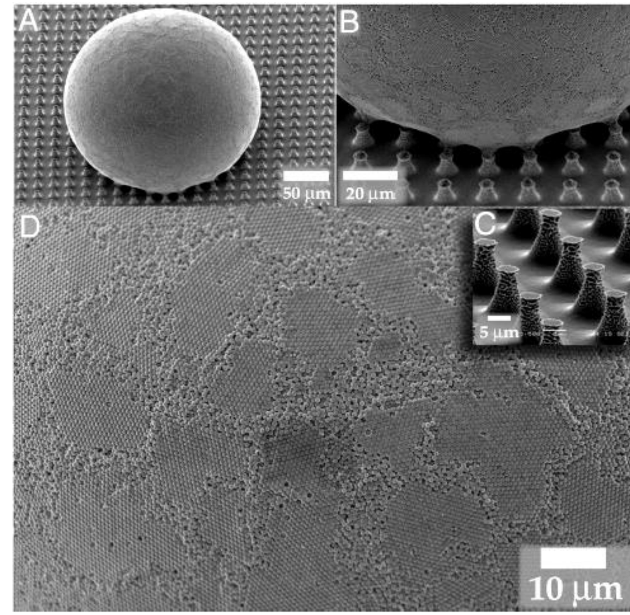
Marín et al., *PNAS* **2012**, *109*, 16455

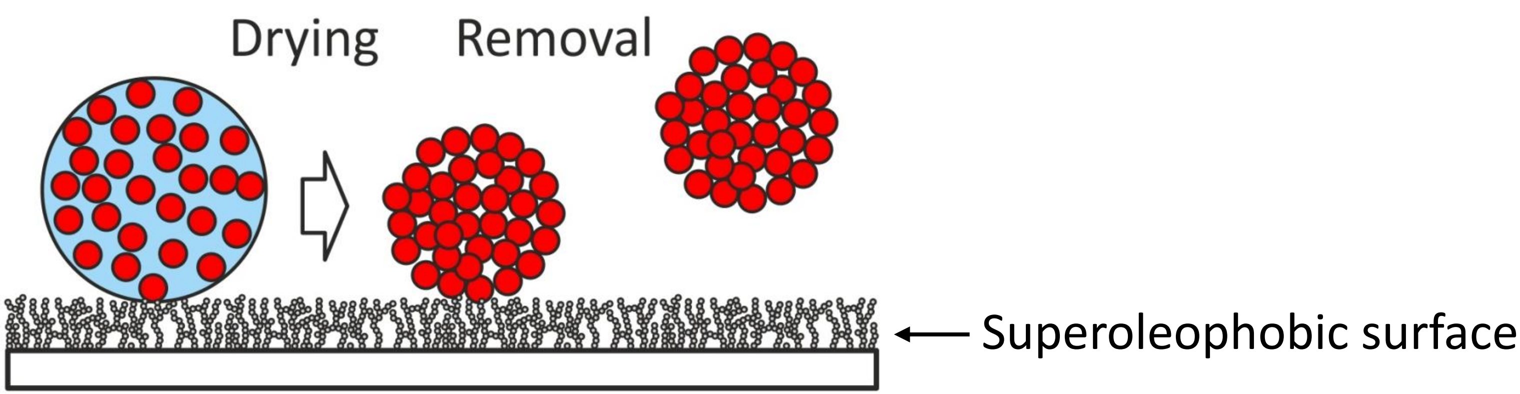
Sperling, Velev & Gradzielski, *Angew. Chemie* **2014**, *53*, 586

Supraparticles



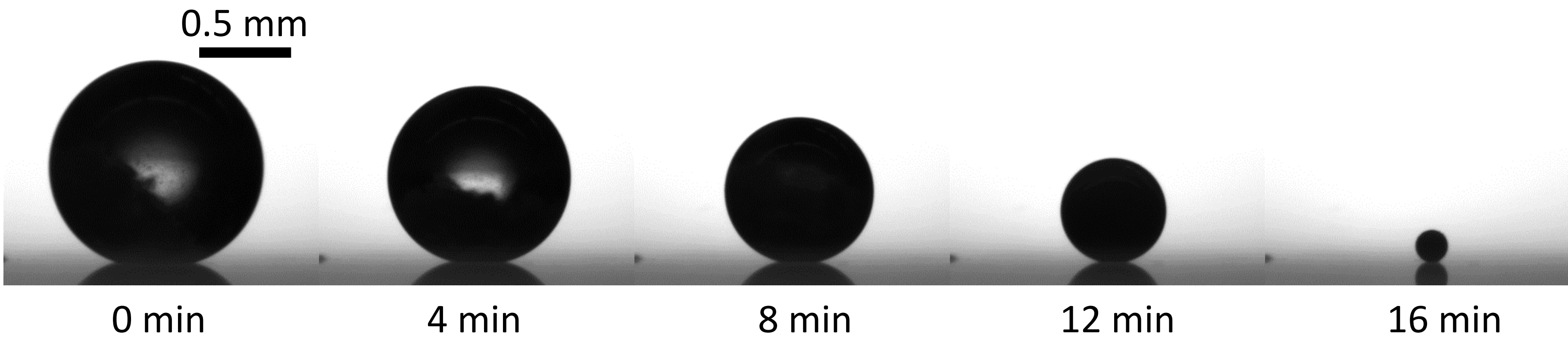




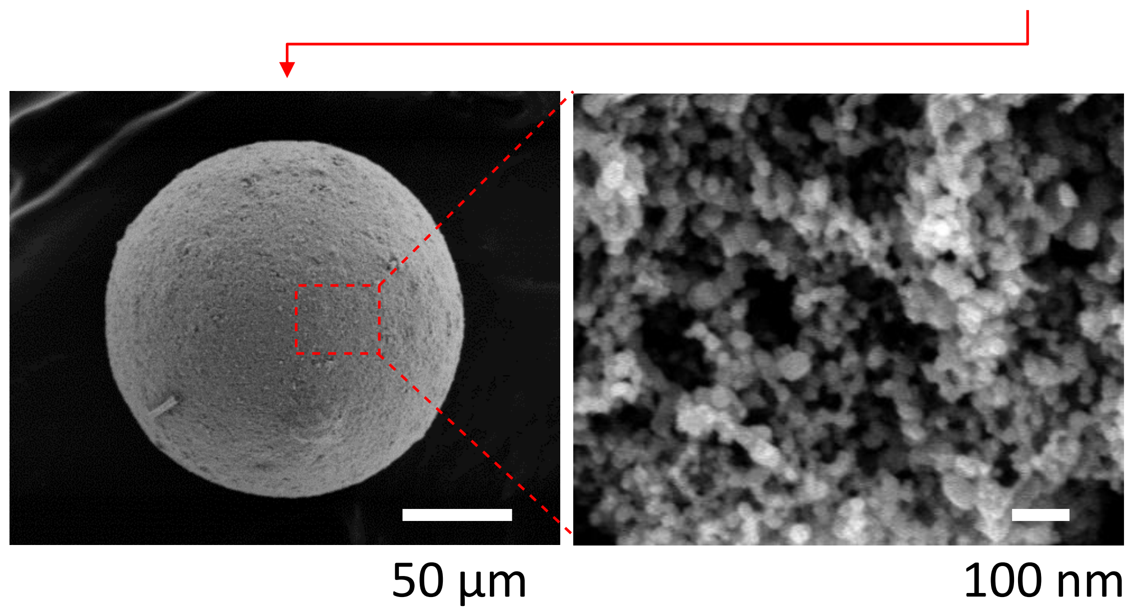


Angew. Chem. Int. Ed. **2013**, *52*, 11286

Mesoporous TiO_2 supraparticles

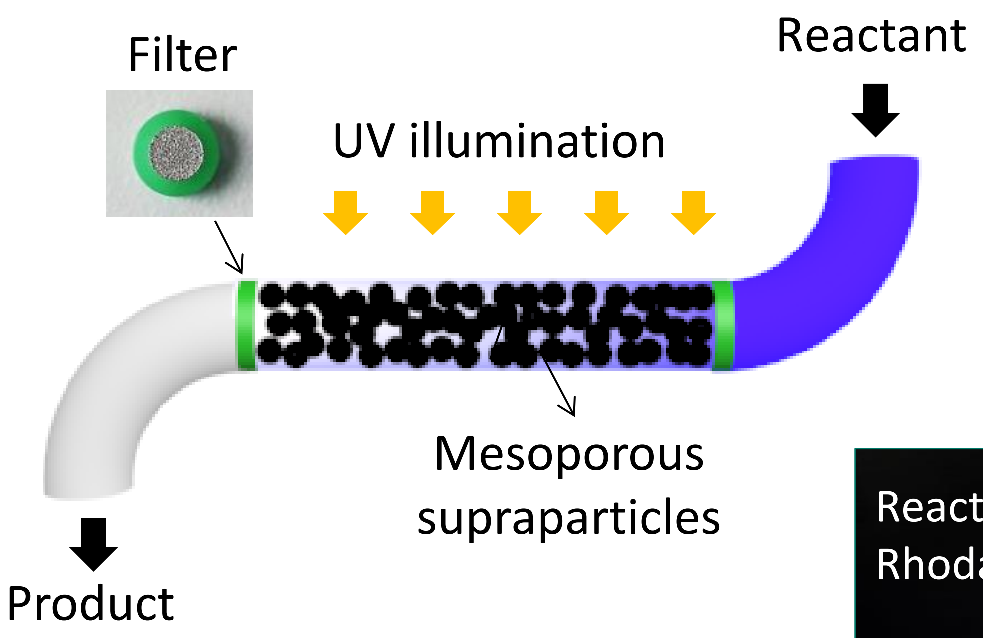


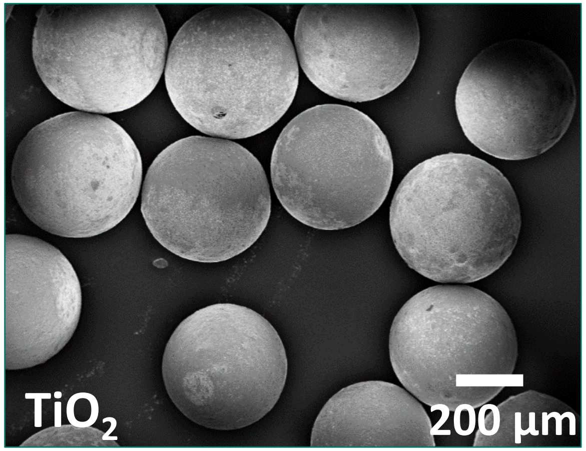
Aqueous 0.1 vol% of TiO_2,
∅ 21 nm, P25 Degussa,
22˚C, 42% RH

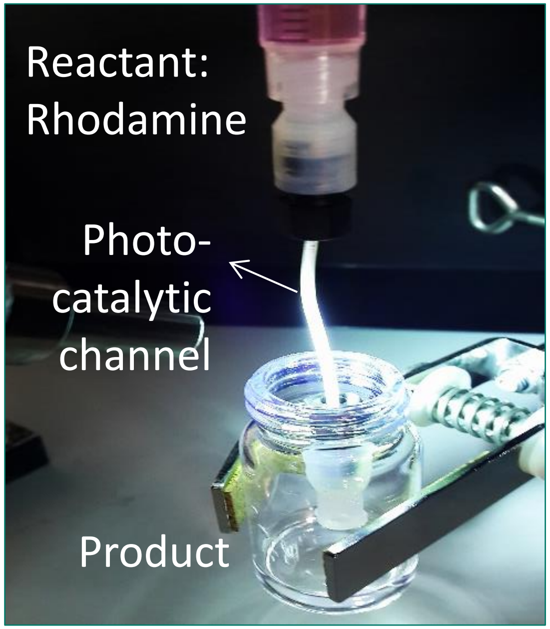


Adv. Materials **2015**, *27*, 7338

Photocatalytically active TiO_2 supraparticles

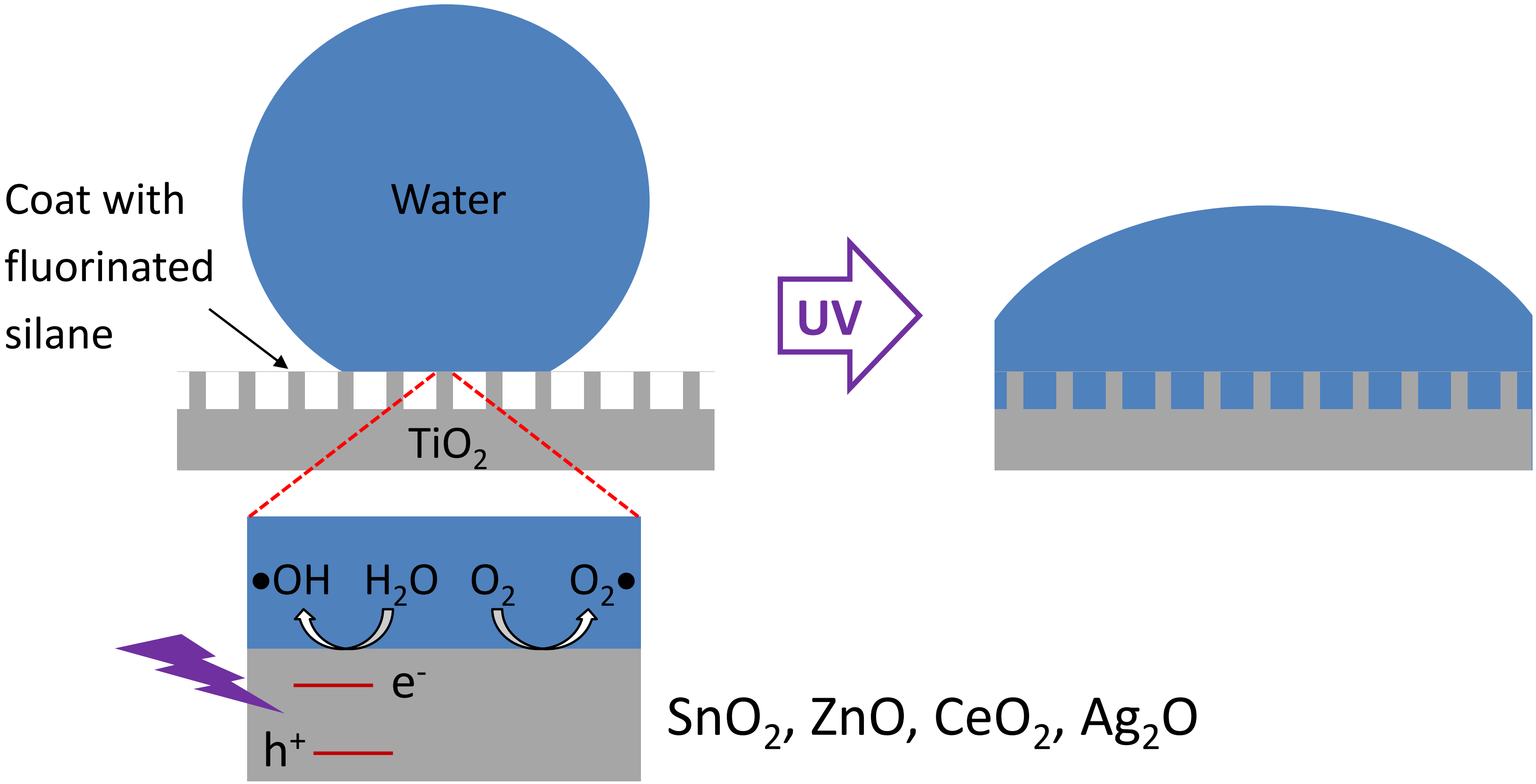






Adv. Materials **2015**, *27*, 7338

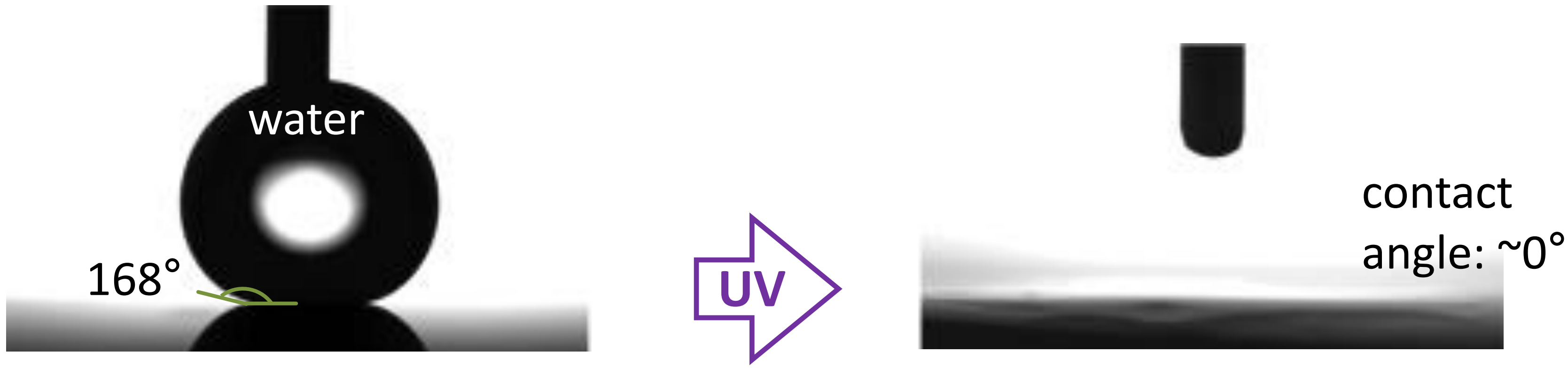
Combine photocatalytic activity & superhydrophobicity



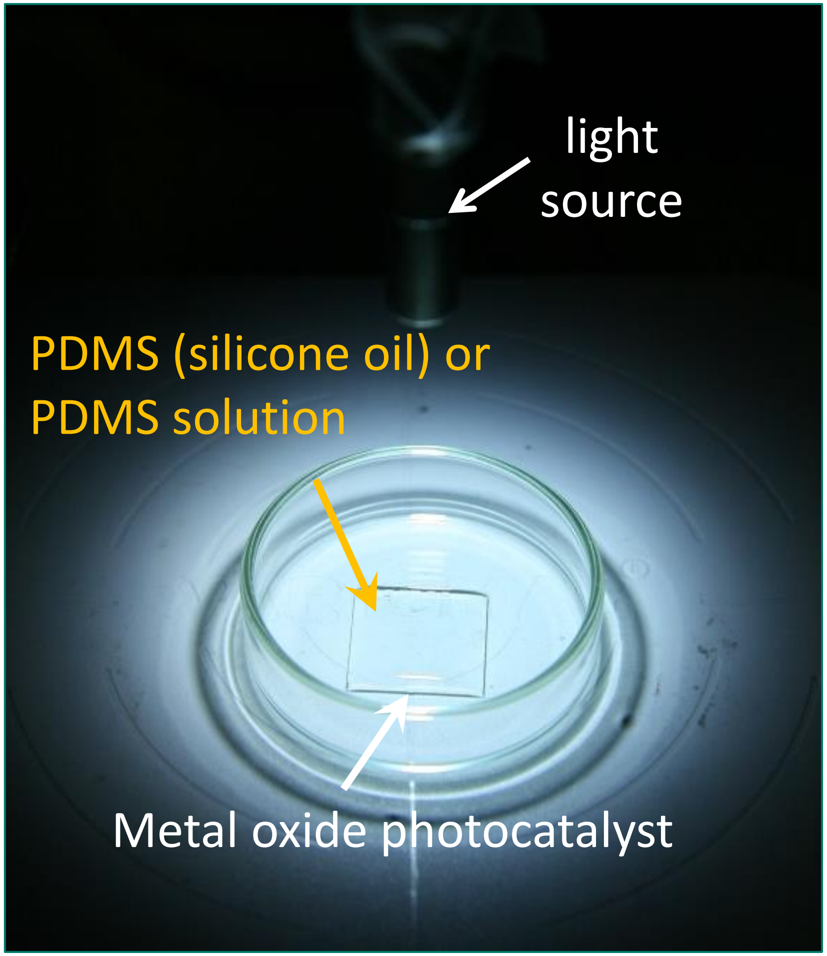
SnO_2, ZnO, CeO_2, Ag_2O

Combine photocatalytic activity & superhydrophobicity

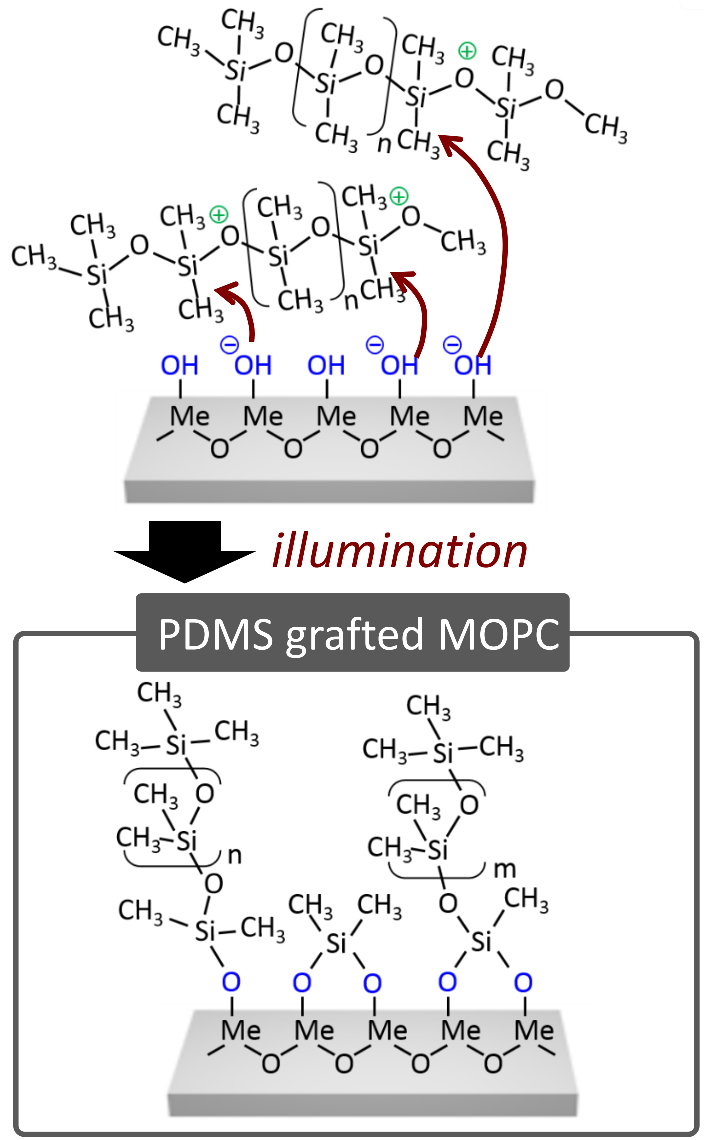
Superhydrophobic etched TiO_2 with octadecylphosphonic acid



Grafting poly(dimethyl siloxane) to metal oxide photocatalyst



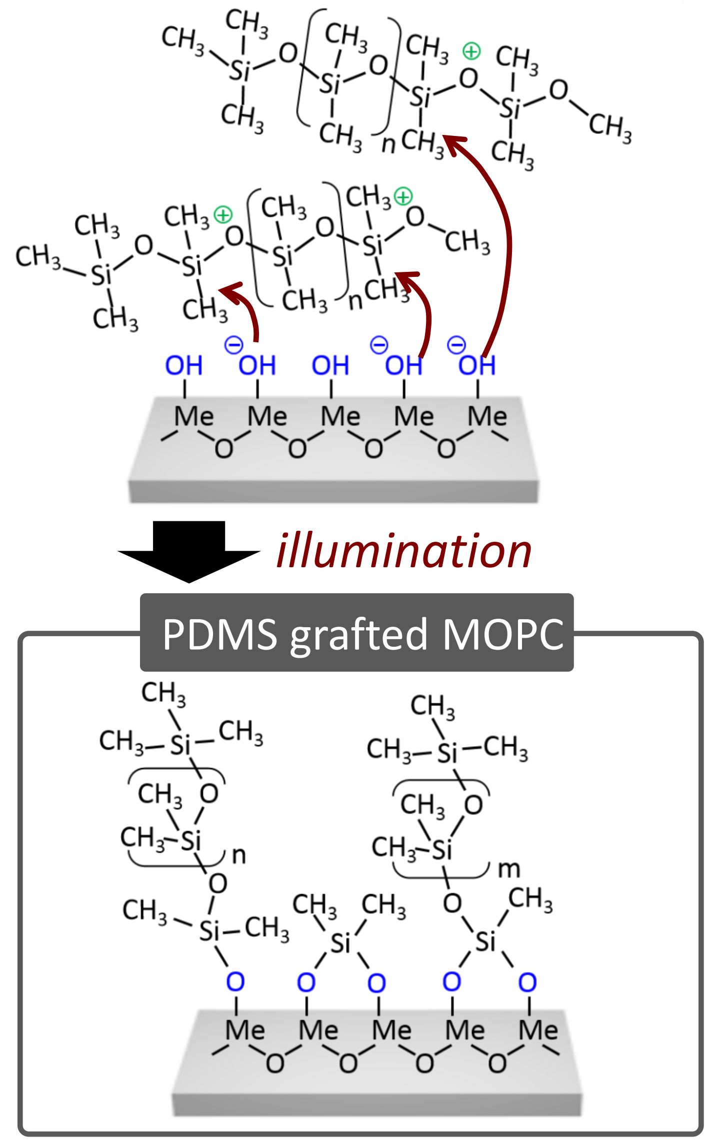
UV-A, 10 mW/cm^2, 10 min



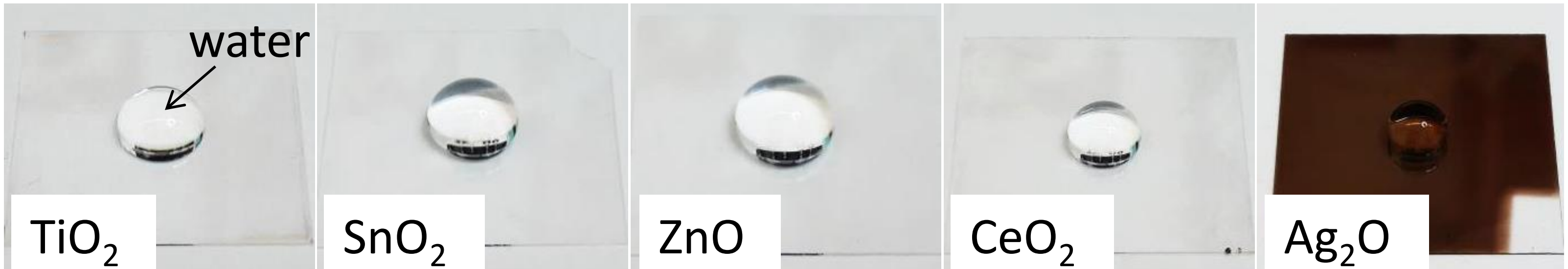
Grafting poly(dimethyl siloxane) to metal oxide photocatalyst

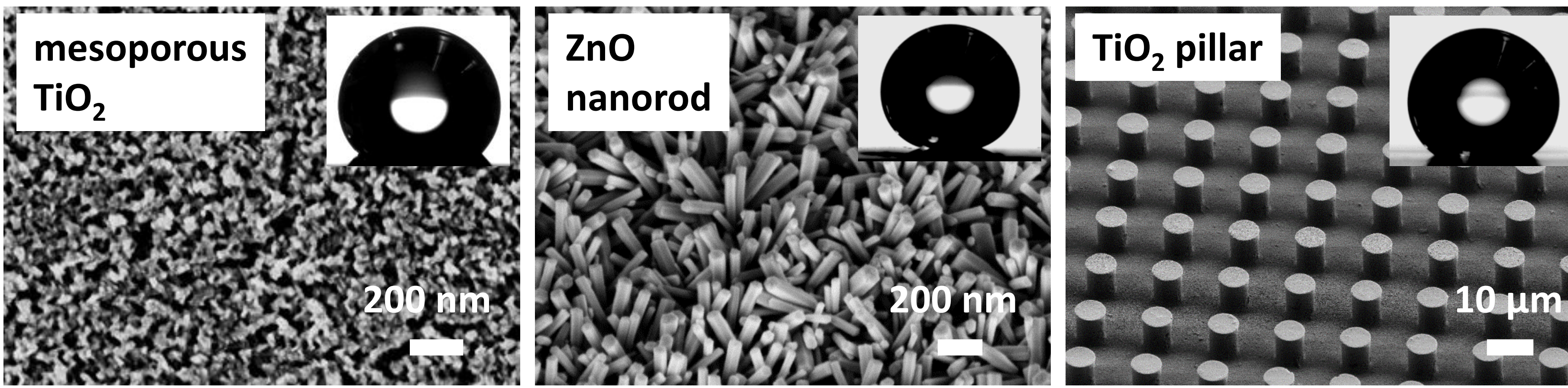
Thermal attachment

Krumpfer & McCarthy , *Langmuir* **2011** , *27* , 11514: 100°C, 24 h
Eifert, Paulssen, Varanakkottu, Baier & Hardt, *Adv. Mater. Interf.* **2014,** *1*, 1300138: 300°C, 3 min



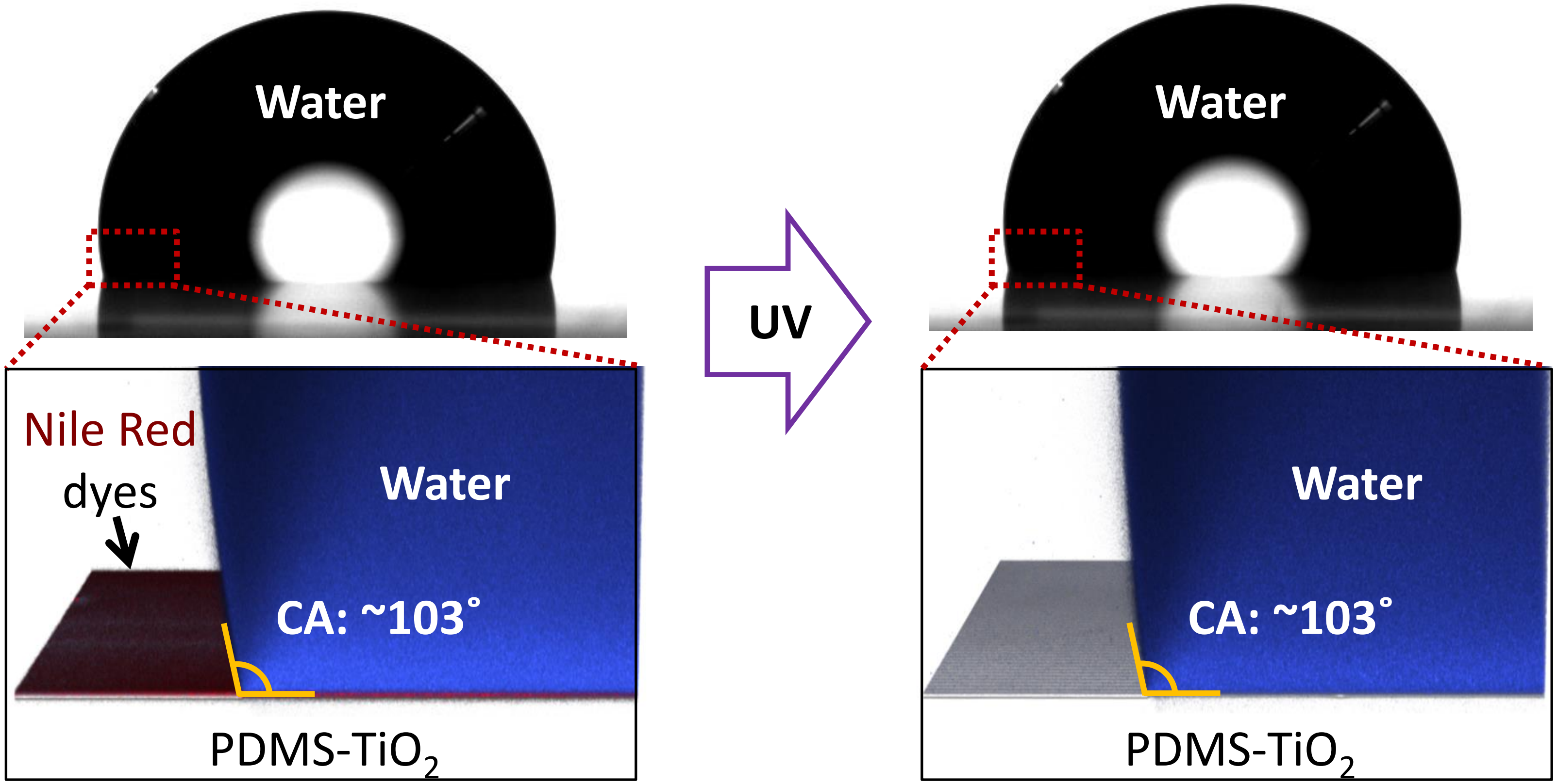
Grafting PDMS to metal oxide photocatalyst





Apparent receding contact angle > 140°

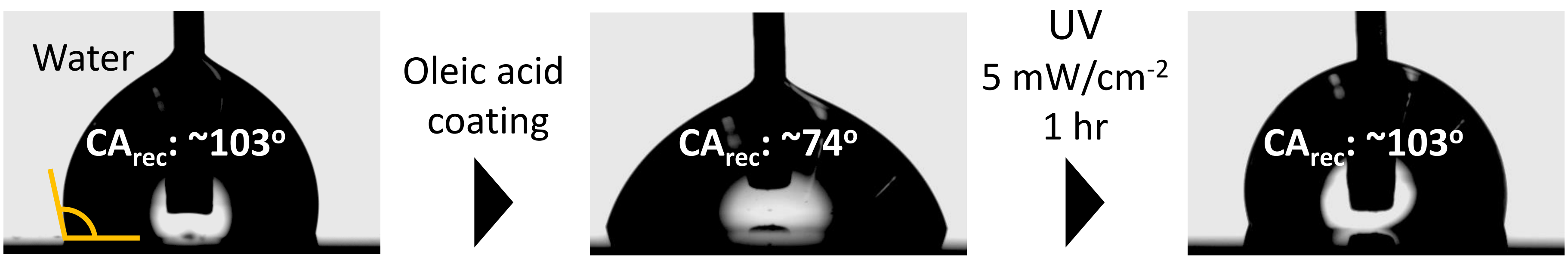
Photocatalytic activity



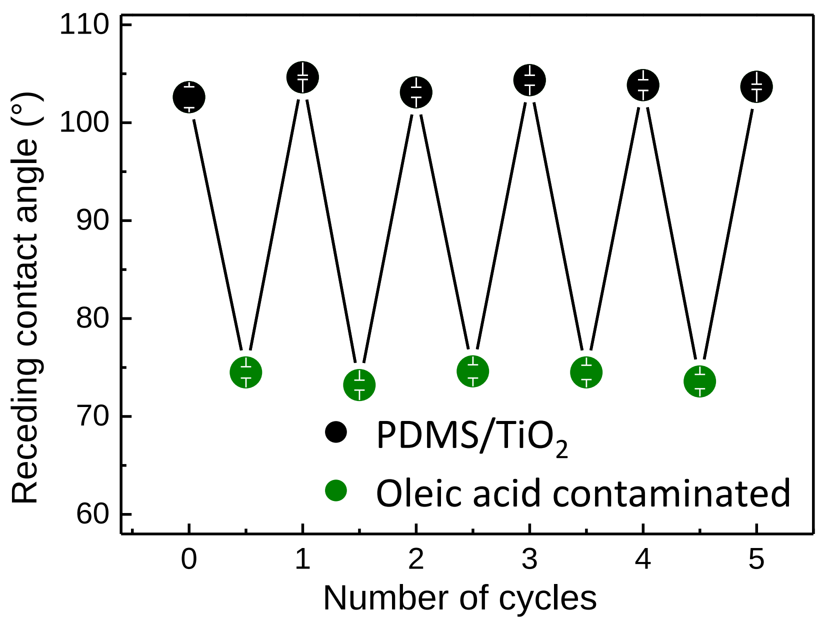
Confocal microscopy to demonstrate photodegradation

Adv. Mater. **2017**, *29*, 1604637; *Angew. Chem. Int. Ed.* **2017**, *56*, 4965

Photodegradation of oleic acid

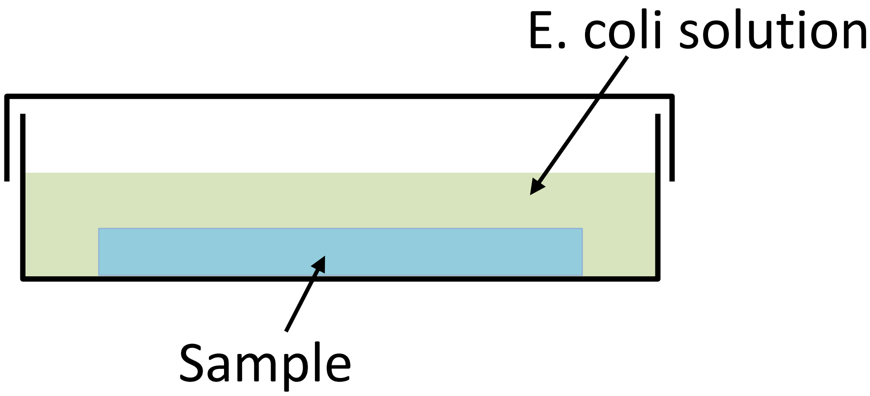


PDMS-TiO_2



Adv. Mater. **2017**, *29*, 1604637; *Angew. Chem. Int. Ed.* **2017**, *56*, 4965

Anti-biofouling surface



Bare TiO_2 & PDMS-TiO_2

Dark & UV illumination

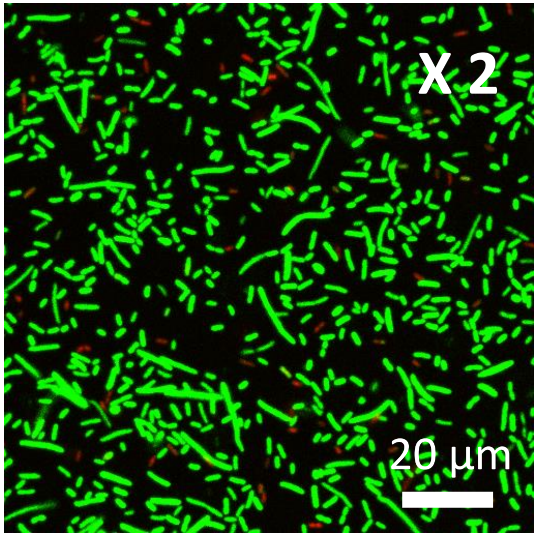
Movements of E. coli

bare TiO_2

Green: living E.Coli

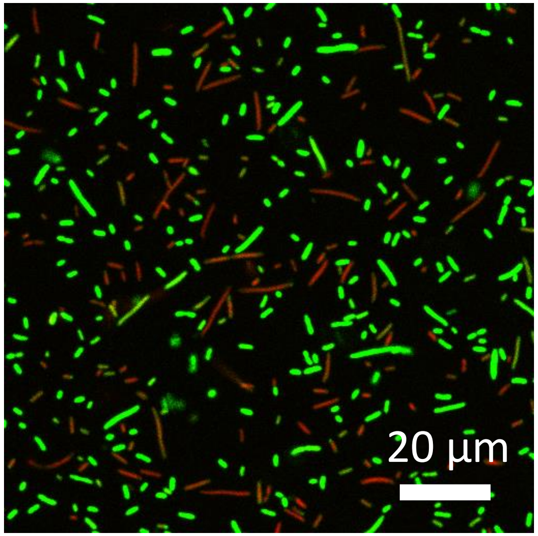
Red: dead E.Coli

Dark



UV-A:

5 mW/cm^2
for 210 min



PDMS-TiO_2 for self cleaning surfaces

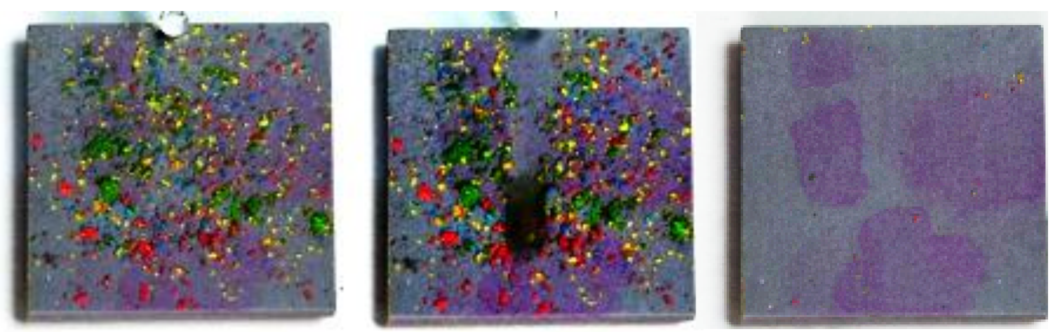
Photocatalytic Superhydrophobic surface
(PDMS-TiO_2 coated etched Al)

(1) contamination w/ Rhodamine B

(2) chalk powder

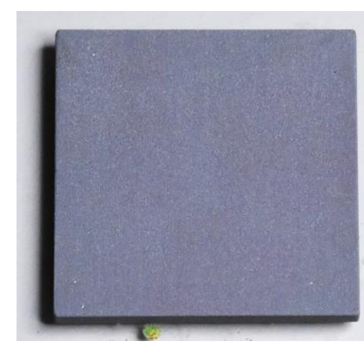
Self-cleaning by combination of

liquid repellency & photocatalytic activity



Cleaning dusts by water drops
superhydrophobicity

UV
5 mW/cm^2
4 h

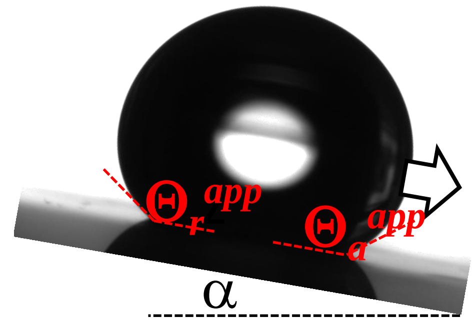


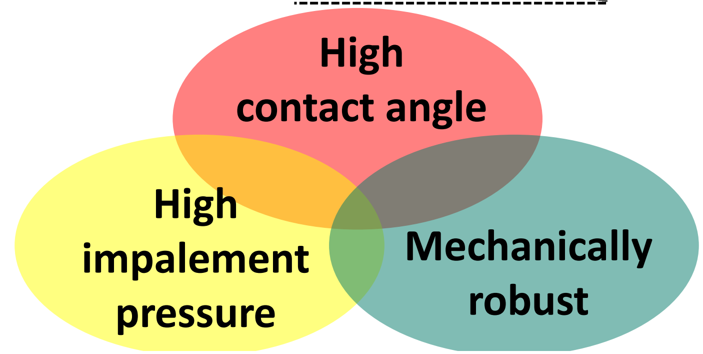
Cleaning organic dyes
by photocatalytic activity

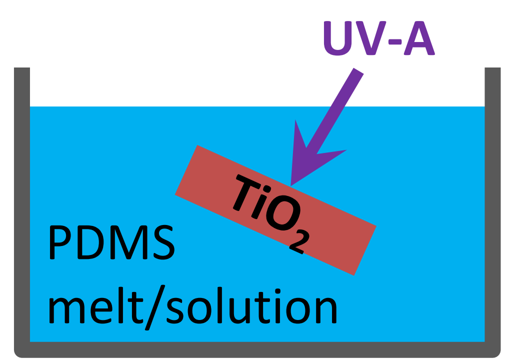
Wetting

- Aim: Understand and control wetting
- Contact angle hysteresis
- Challenges in super liquid-repellency

  & Multifunctional surfaces
- Stable hydrophobic photocatalytically active metal oxides







Thanks

DFG Deutsche Forschungsgemeinschaft

CRC 1194 Interaction between Transport and Wetting Processes

Alexander von Humboldt
Stiftung / Foundation

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European Research Council
Established by the European Commission

complex wetting
Marie Curie Initial Training Network (ITN)

LubISS
Lubricant Impregnated Slippery Surfaces

Thanks for your attention!