

Surfaces with Extreme Wettability

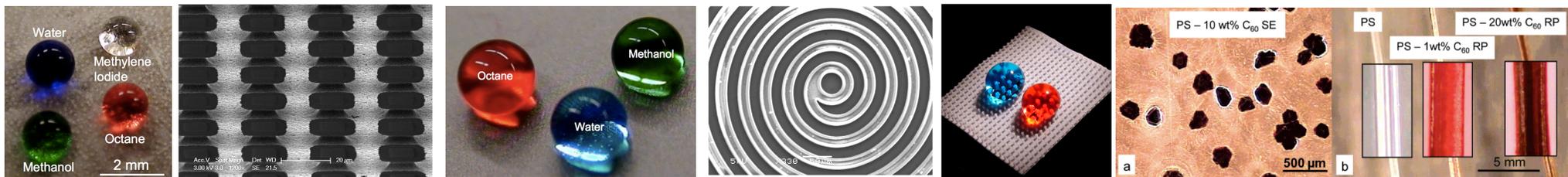
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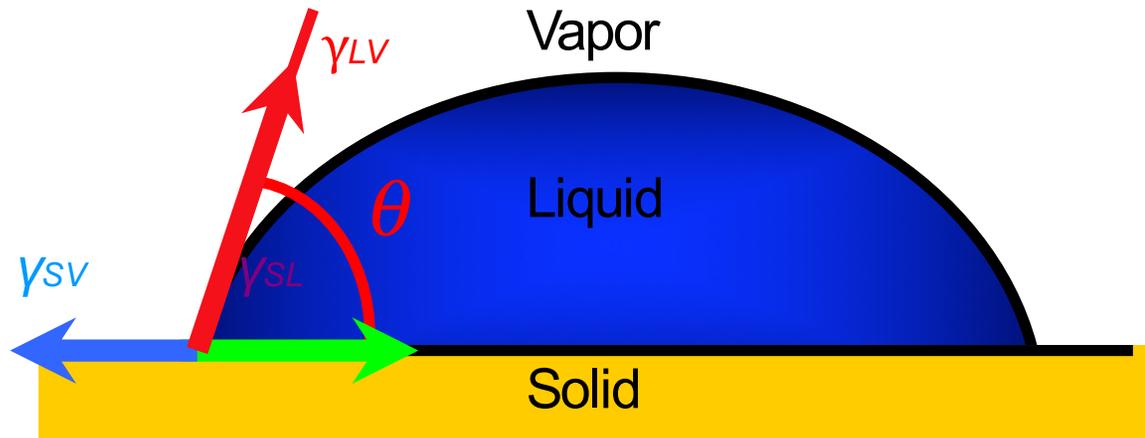
Department of Chemical Engineering, University of Michigan

Polymers, Surfaces and Interfaces (PSI - ψ) group



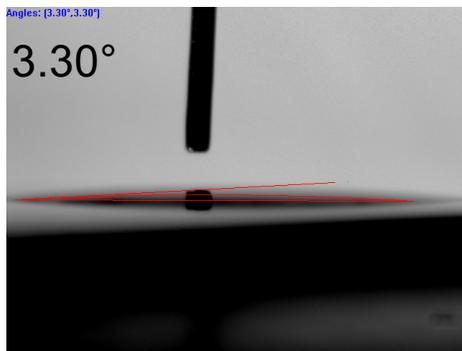
Superoleophobic surfaces

Young's Equation (1805)

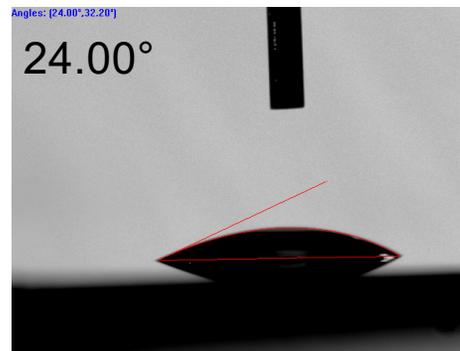


$$\gamma_{SV} = \gamma_{LV} \cos \theta + \gamma_{SL}$$
$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

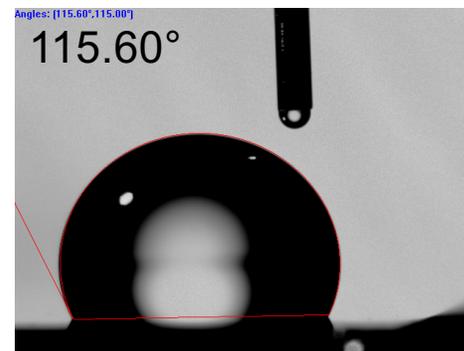
Contact angles with water:



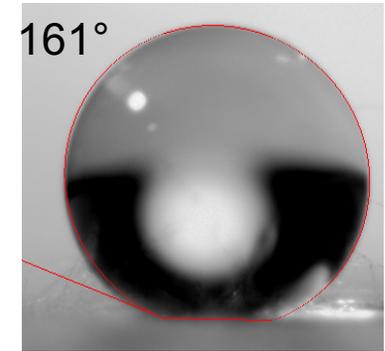
Superhydrophilic
 $\theta \sim 0^\circ$



Hydrophilic
 $0^\circ < \theta < 90^\circ$



Hydrophobic
 $\theta > 90^\circ$

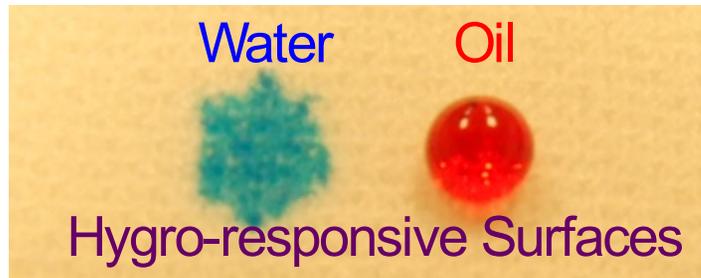


Superhydrophobic
 $\theta^* > 150^\circ$, low hysteresis

Similarly, superoleophobic surfaces display contact angles $\theta^* > 150^\circ$ and low hysteresis with oils or alkanes

The wettability landscape

Superhydrophilic
and Superoleophobic



Contact angles with oil

$$\theta_{oil} = 180^\circ$$

Superhydrophobic
and Superoleophobic



$$\theta_{water} = 0^\circ$$

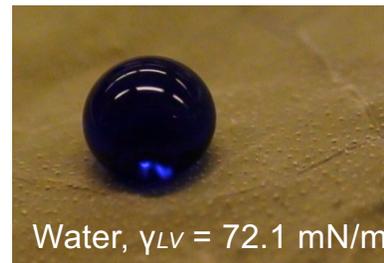
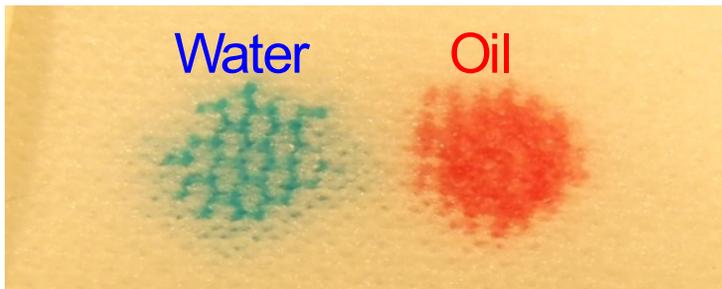
$$\theta_{water} = 90^\circ$$

$$\theta_{water} = 180^\circ$$

Contact angles with water

$$\theta_{oil} = 90^\circ$$

The lotus leaf



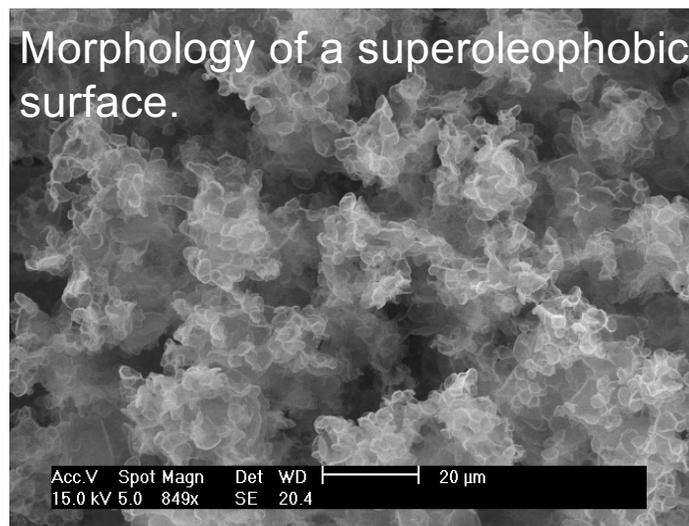
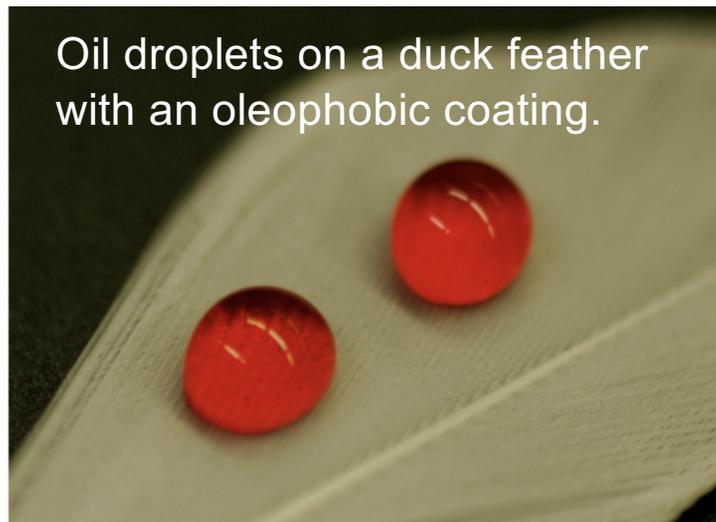
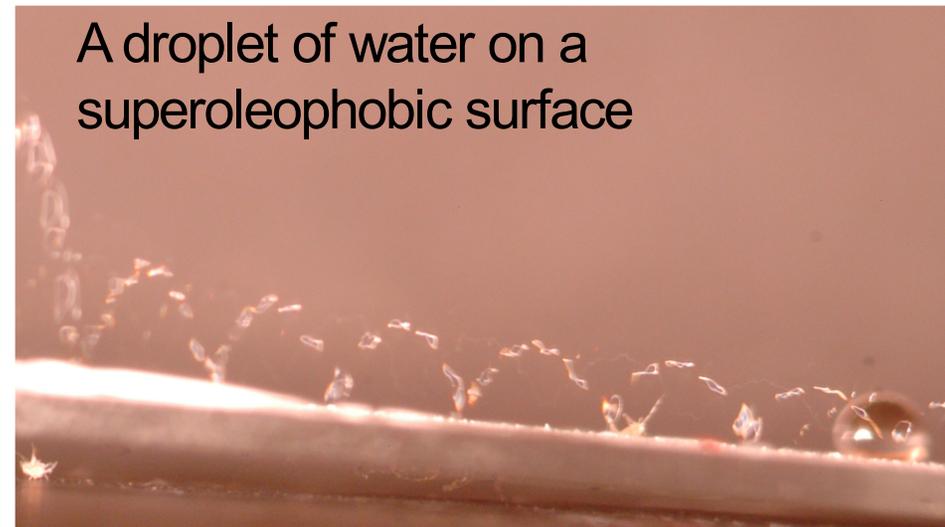
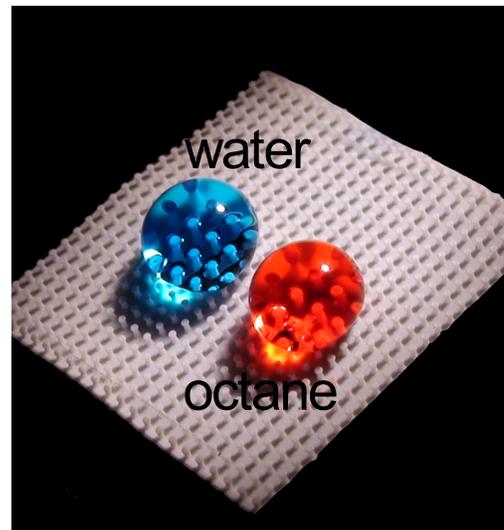
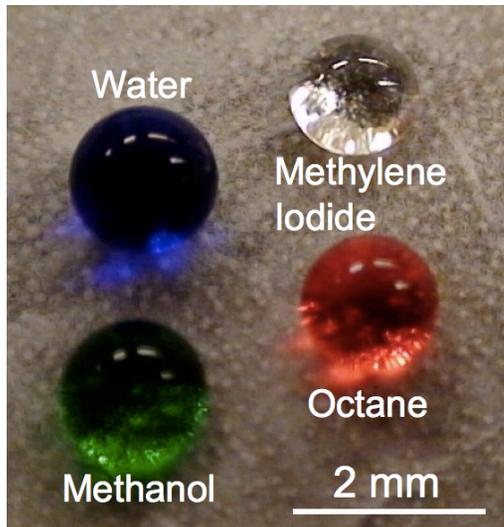
Superhydrophilic
and Superoleophilic

$$\theta_{oil} = 0^\circ$$

Superhydrophobic
and Superoleophilic

Designing superoleophobic surfaces

Superoleophobic Surfaces: Surfaces on which all liquids, including water, oils, alcohols, acids and bases bead up and roll-off the surface. **Applications include chemical and biological protection, fingerprint resistance, stain-resistant textiles, drag-reduction, preventing biofouling, icephobicity.**



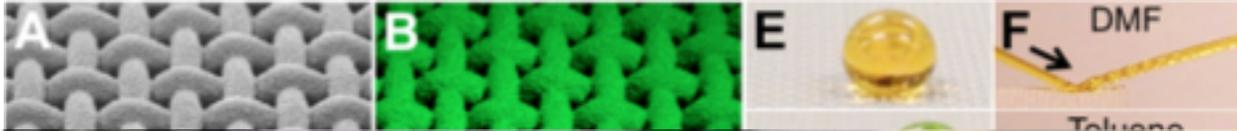
Tuteja et al., *Science*, 2007
Tuteja et al., *PNAS*, 2008
Kota et al., *Advanced Materials*, 2012



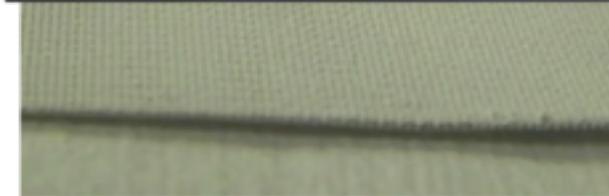
HygraTek

DOW CORNING

Superoleophobic surfaces



In collaboration with Dr. Joe Mabry, Tech Advisor, Propellants branch, Edwards AFB



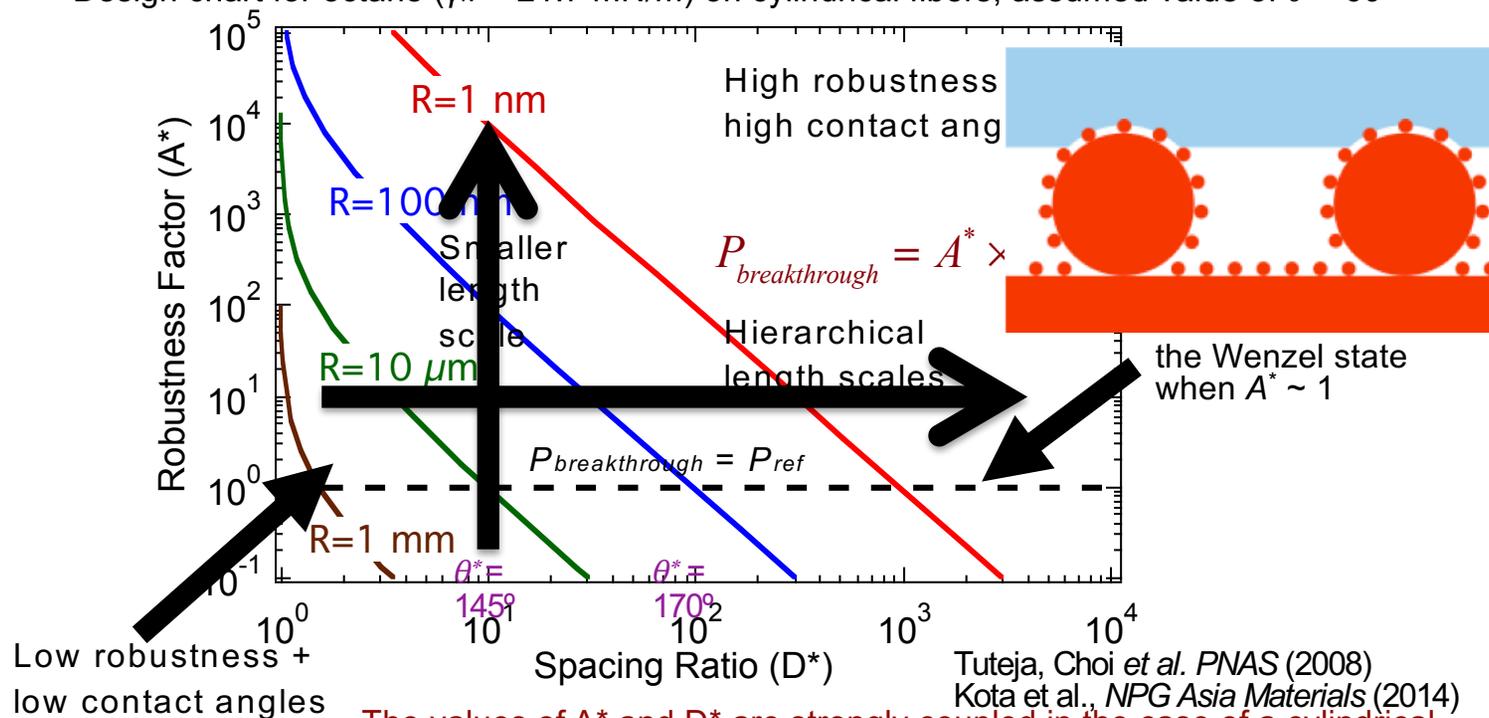
Kota *et al.*, *Advanced Materials*, 2012 ; Pan *et al.*, *JACS*, 2013.

A design chart for a composite interface

$$D^* = (R+D)/R \quad A^* = \left(\frac{R \ell_{cap}}{D^2} \right) \frac{(1 - \cos \theta)}{(1 + 2(R/D) \sin \theta)}$$

Green: Surface properties
 Red: Fluid properties
 Blue: Surface-fluid-vapor interaction

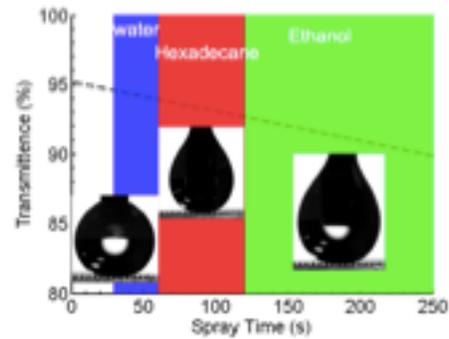
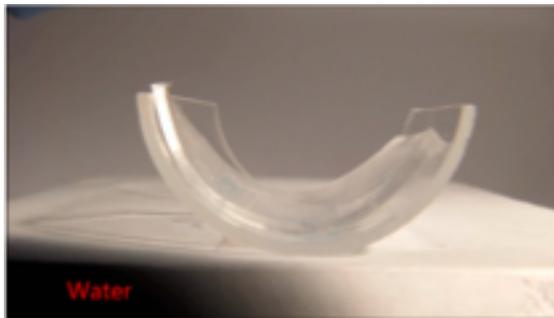
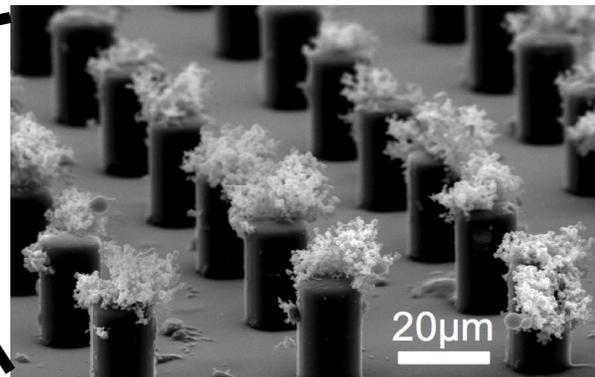
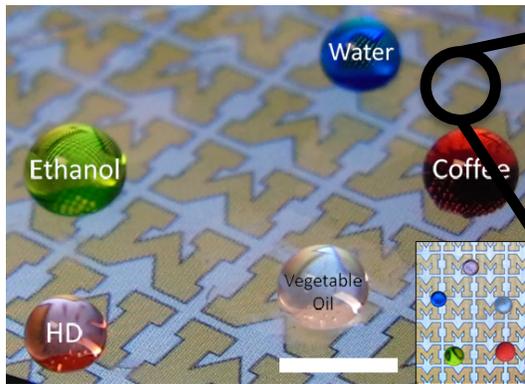
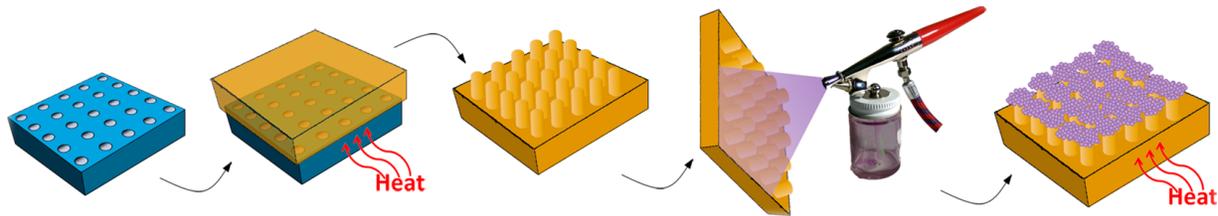
Design chart for octane ($\gamma_{lv} = 21.7$ mN/m) on cylindrical fibers; assumed value of $\theta = 60^\circ$



Tuteja, Choi *et al.* PNAS (2008)
 Kota *et al.*, NPG Asia Materials (2014)

The values of A^* and D^* are strongly coupled in the case of a cylindrical geometry. Typically an increase in D^* will lead to a decrease in A^* .

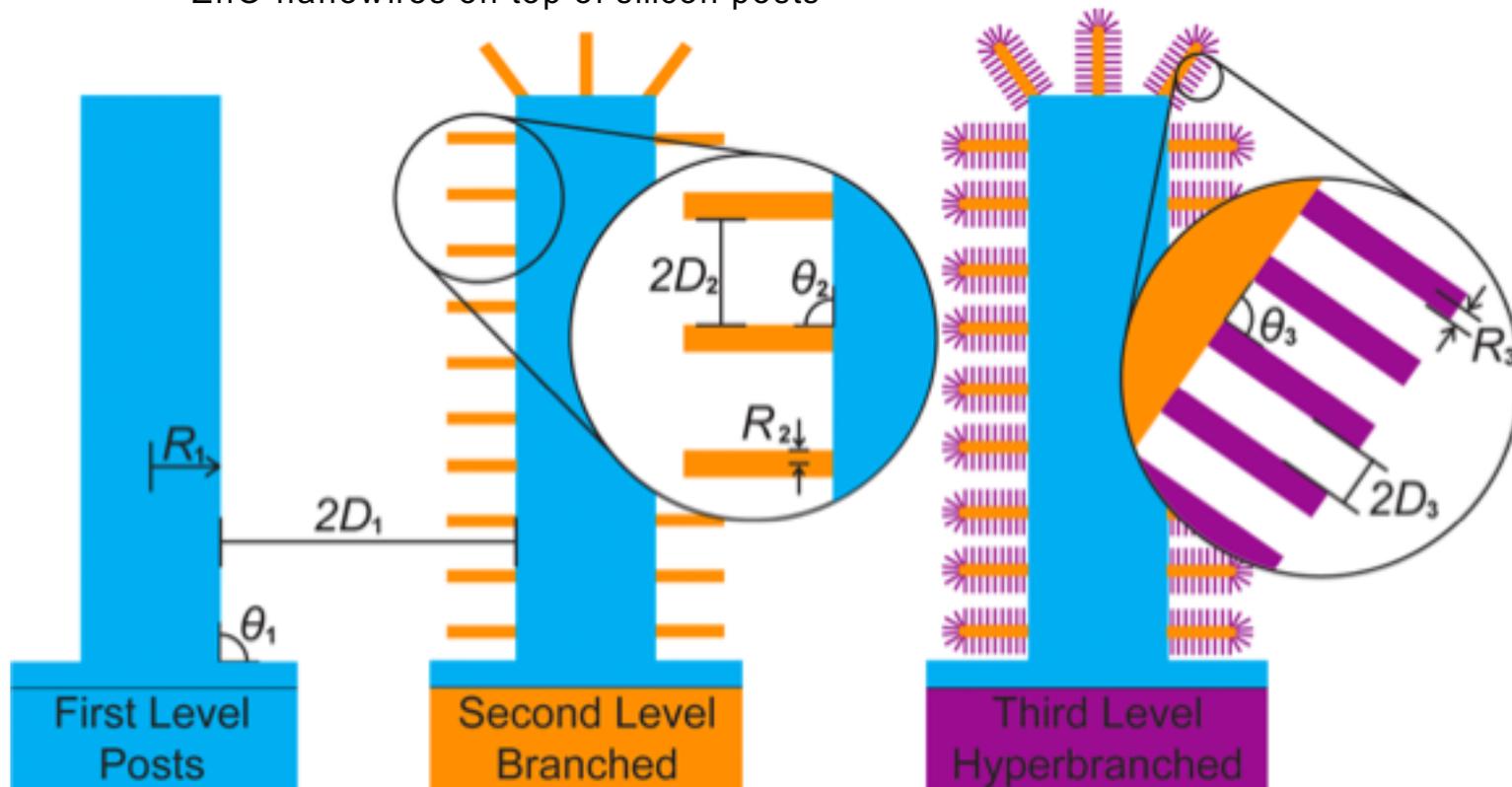
Transparent omniphobic surfaces



Golovin et al.,
Angewandte Chemie, 2013

Three levels of hierarchical texture

ZnO nanowires on top of silicon posts

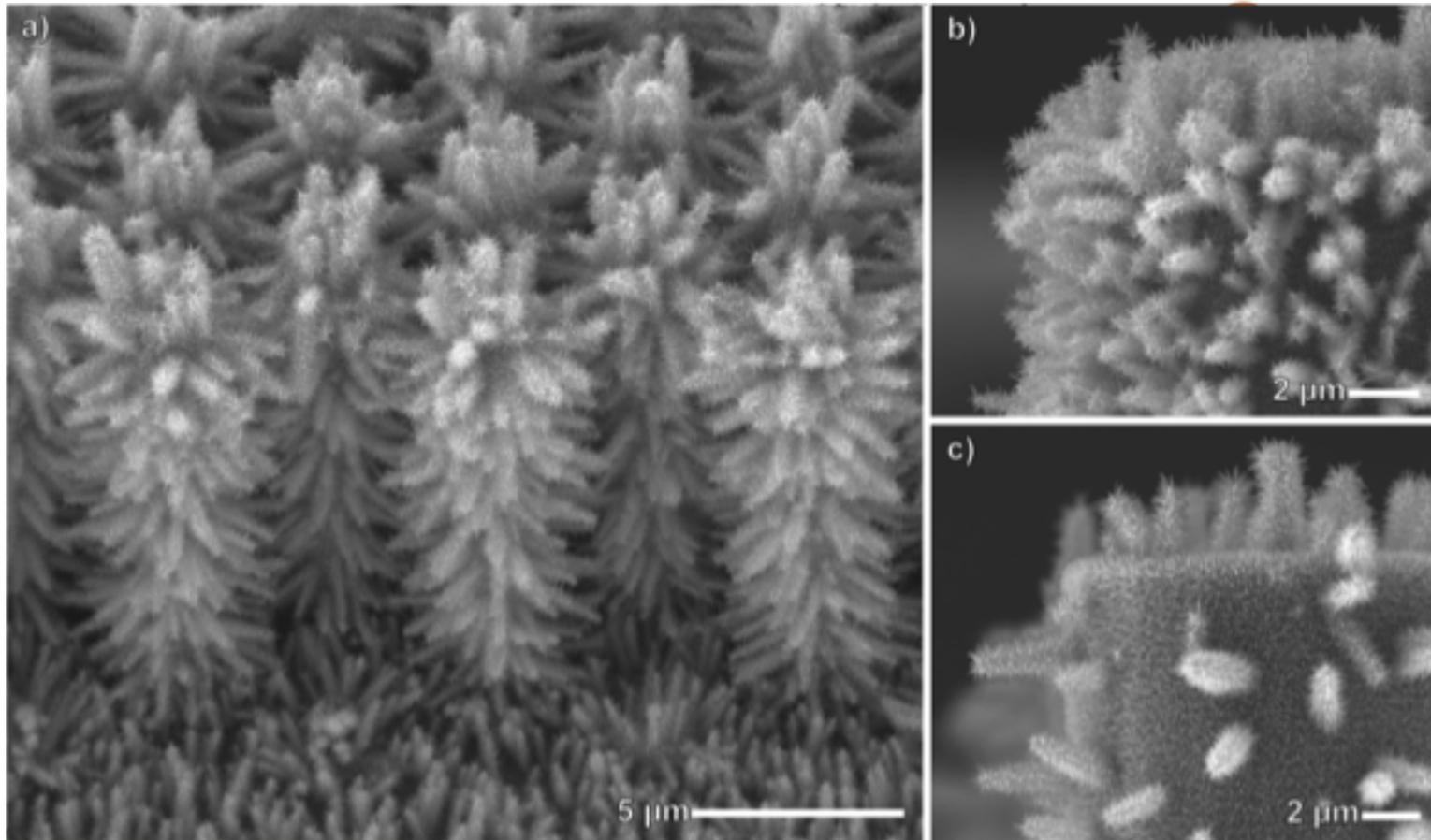


With Neil Dasgupta, Univ. of Michigan

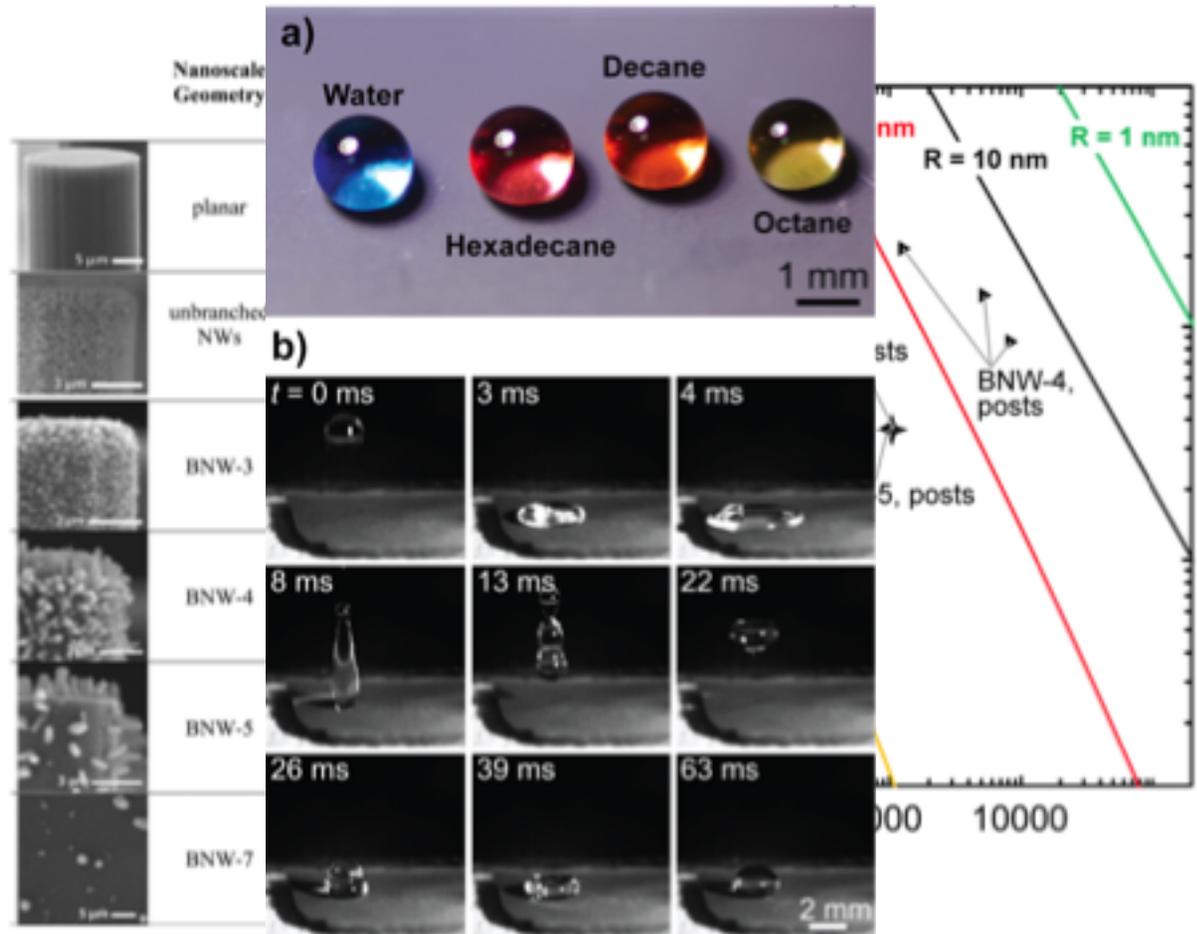
Bielinski *et al.*,
ACS Nano, 2016

ZnO nanowires

a) Low density nanowire growth



Effects on liquids repellency and robustness



Bielinski et al., ACS Nano, 2016

The need for ice-shedding surfaces



The need for ice-shedding surfaces



There is a critical need to develop ice-resistant or ice-phobic coatings for a range of applications. Applications include coatings for automobiles, naval vehicles, aircrafts, wind turbines, refrigeration, power-lines, satellite dishes, off-shore oil drilling platforms. Market size exceeds \$5 Bn / year within North America.

Ice-adhesion strength $\tau_{ice} < 10$ kPa required for airplane wings, power lines and wind turbines.

Ice adhesion strengths vary between 40 kPa – 2200 kPa for different materials.

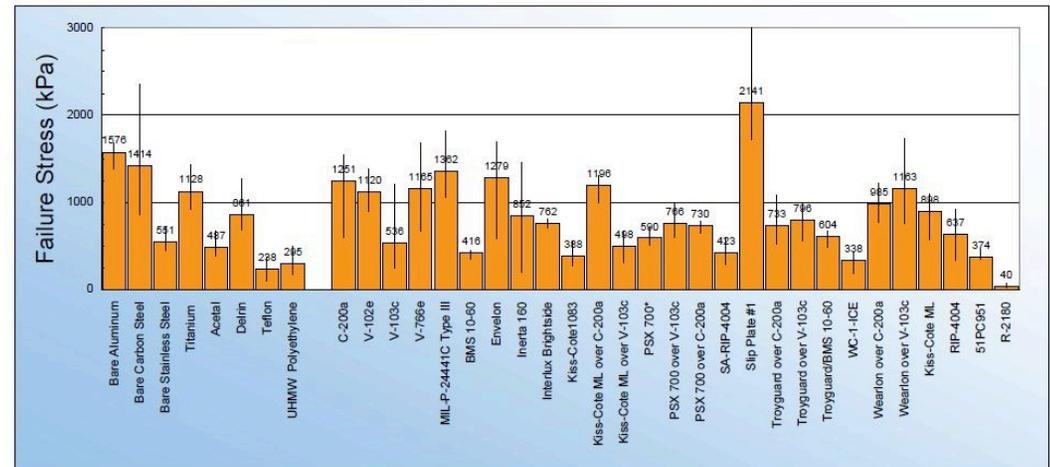


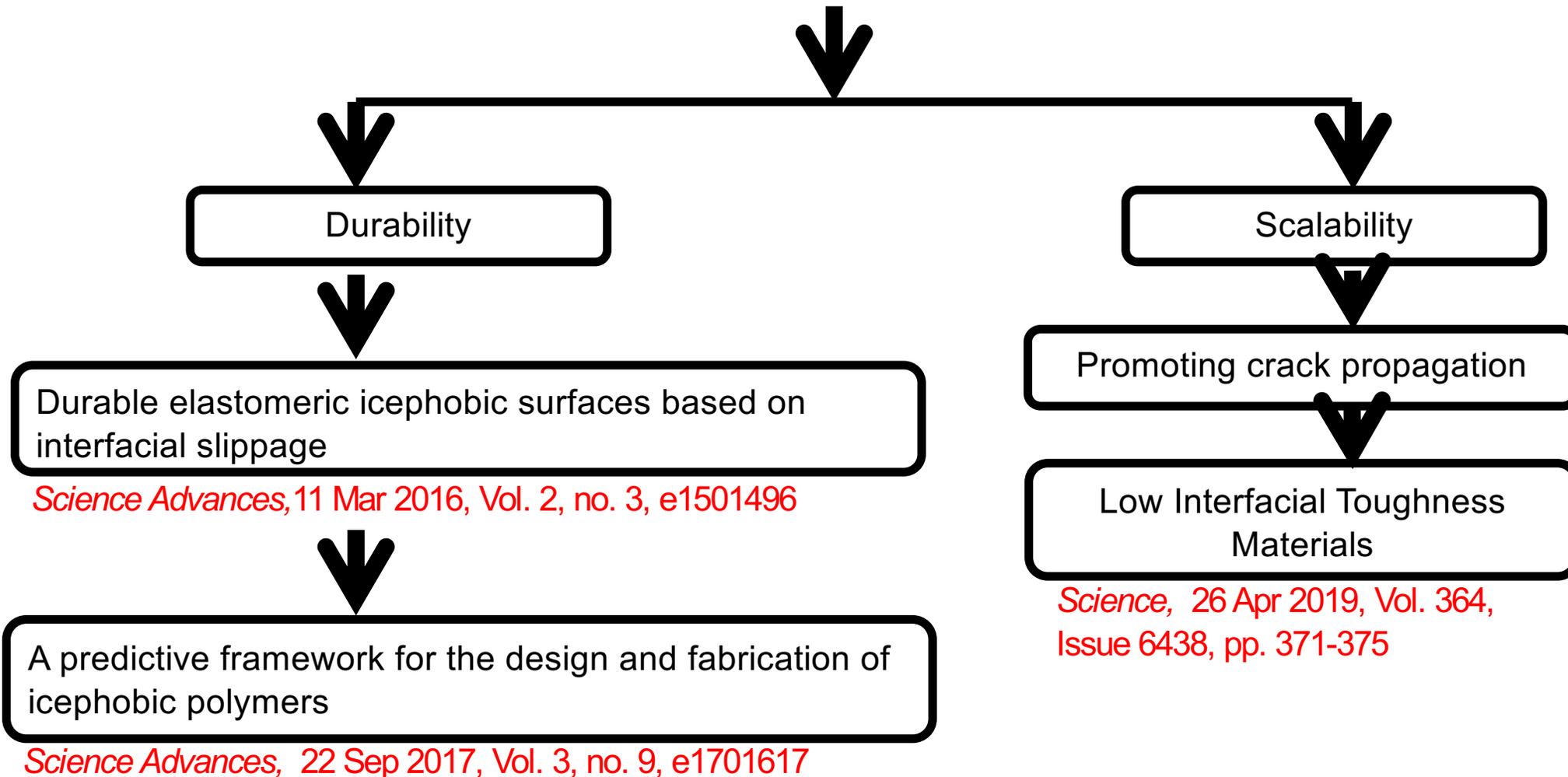
Figure 20-14 Ice adhesion test results for construction materials and commercial coatings. Column heights represent average ice adhesion strength, which is also given as a numerical value on the top of each column. Error bars represent the range in the data.

Source: CRREL

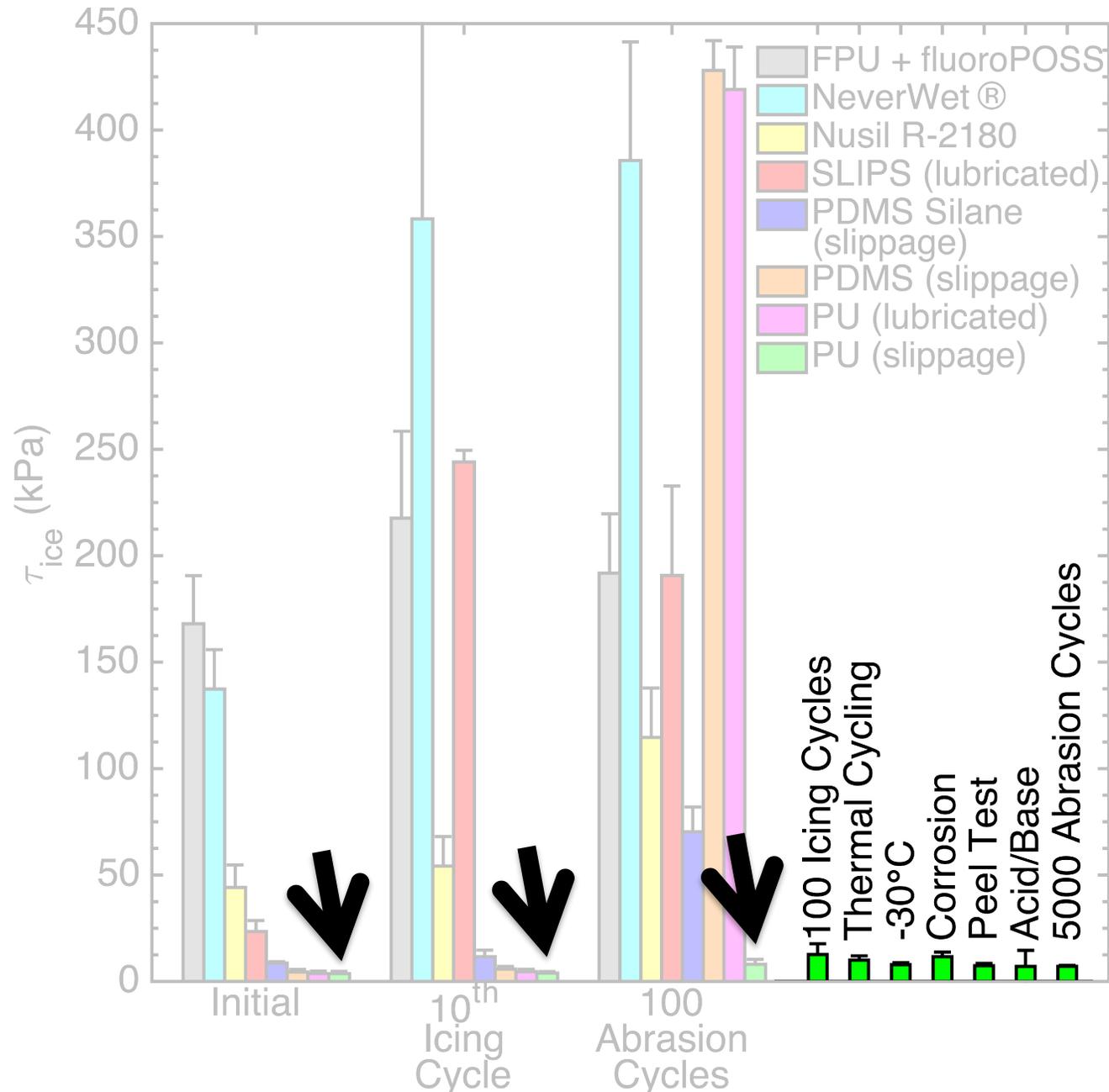
Aluminum: 1600 kPa; Steel: 1400 kPa;
Polyethylene: 300 kPa, Teflon: 240 kPa.

Outline

Two Major Challenges for Ice-Shedding Surfaces



Durable Icephobic Surfaces



Large Scale 2D Testing

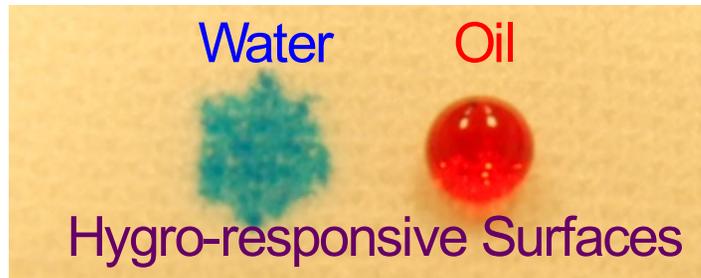


$\tau_{ice} = 0.07 \text{ kPa!}$

$T = -6^{\circ}\text{C}$

The wettability landscape

Superhydrophilic
and Superoleophobic



Contact angles with oil

Superhydrophobic
and Superoleophobic



$\theta_{oil} = 180^\circ$

$\theta_{water} = 0^\circ$

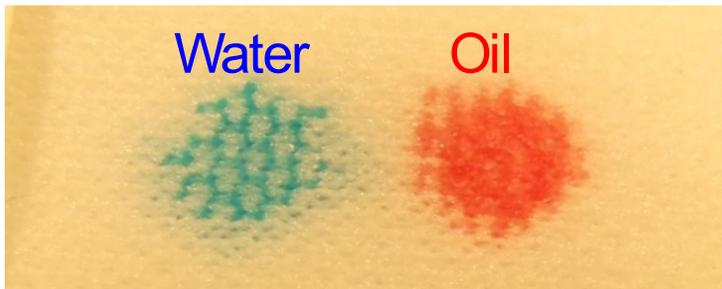
$\theta_{water} = 90^\circ$

$\theta_{water} = 180^\circ$

Contact angles with water

$\theta_{oil} = 90^\circ$

The lotus leaf

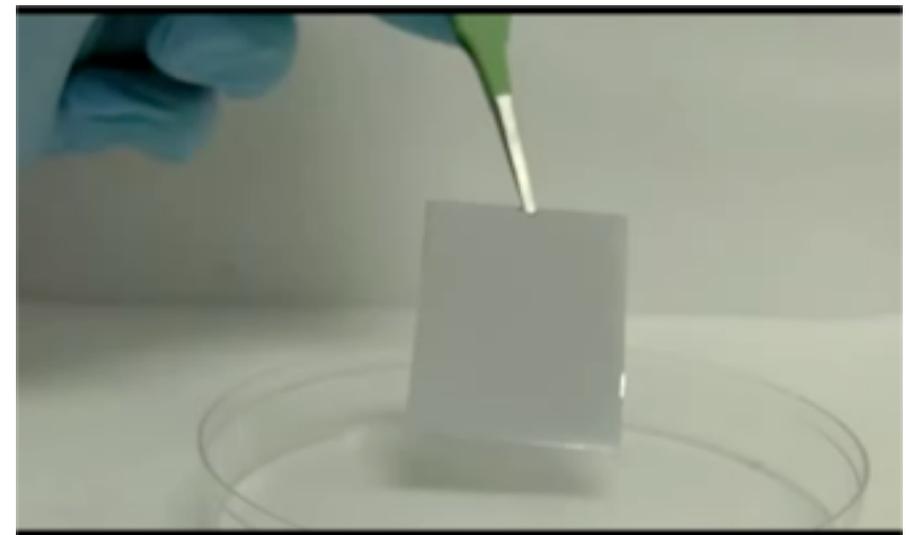
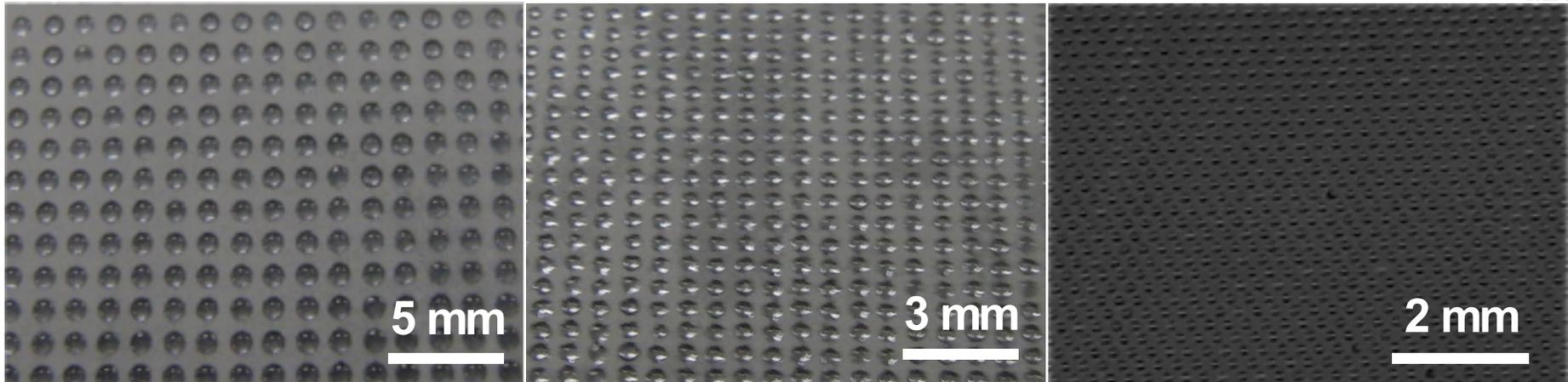


Superhydrophilic
and Superoleophilic

$\theta_{oil} = 0^\circ$

Superhydrophobic
and Superoleophilic

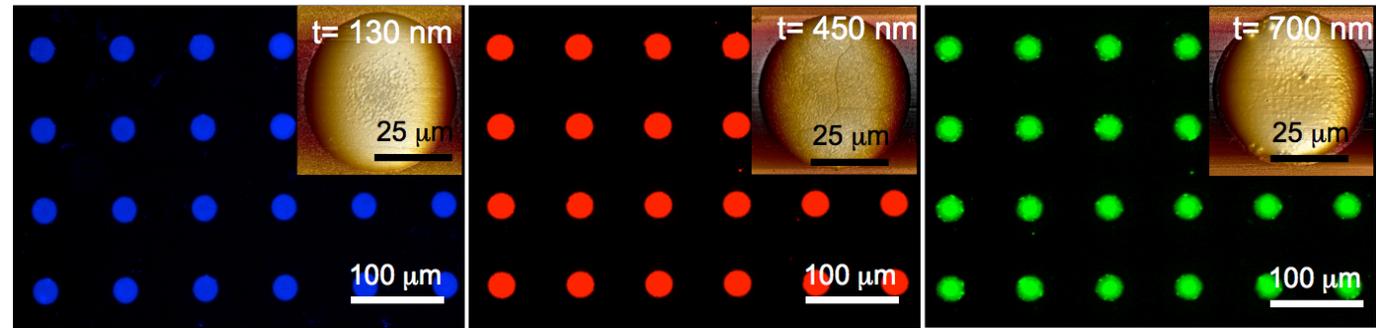
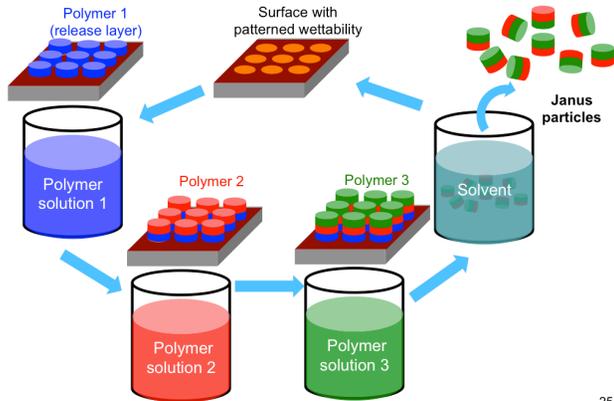
Patterned superoleophobic / superoleophilic surfaces



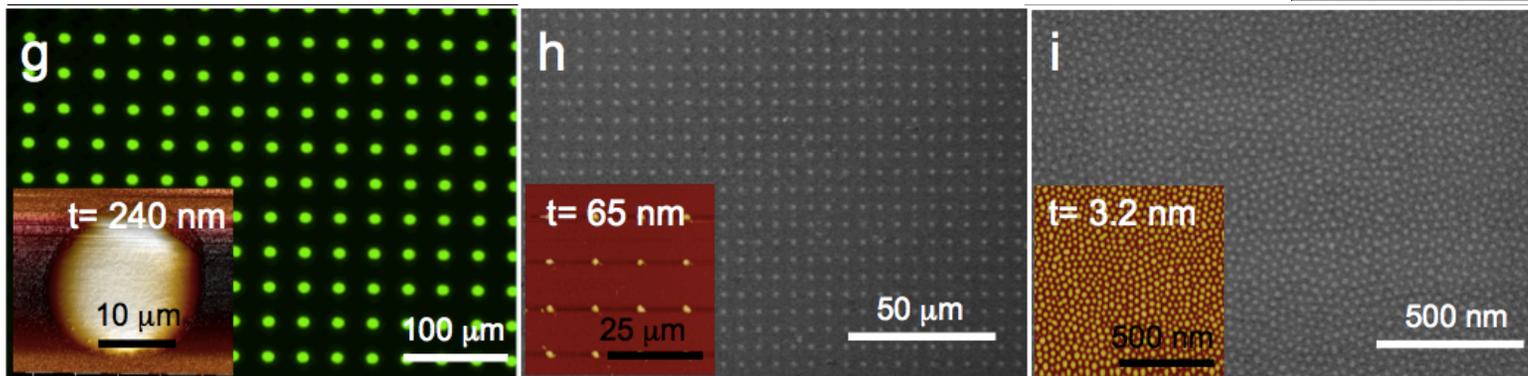
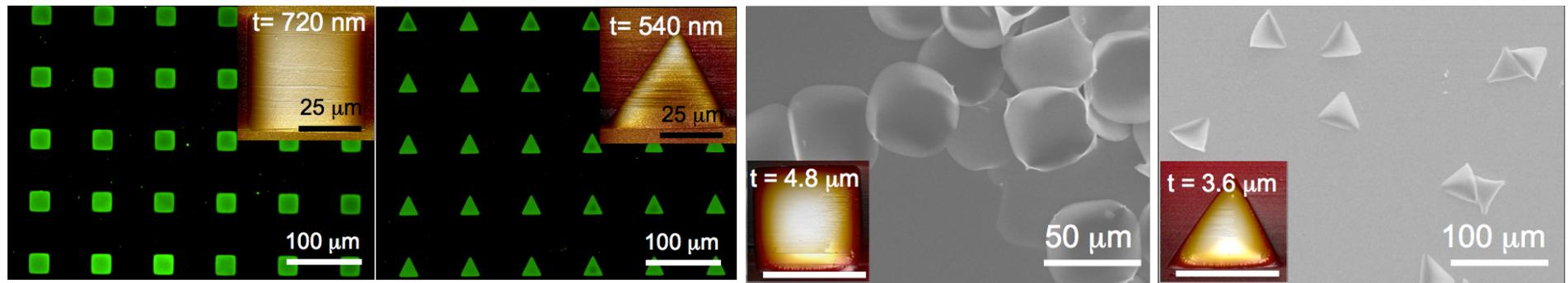
We have developed the first-ever patterned superoleophobic – superoleophilic surfaces. Superoleophilic surfaces are essentially wet by all liquids, while superoleophobic surfaces repel all liquids.

Kobaku et al. Angewandte Chemie, 2012

Fabrication of mono-, bi-, tri- and multi-phasic particles

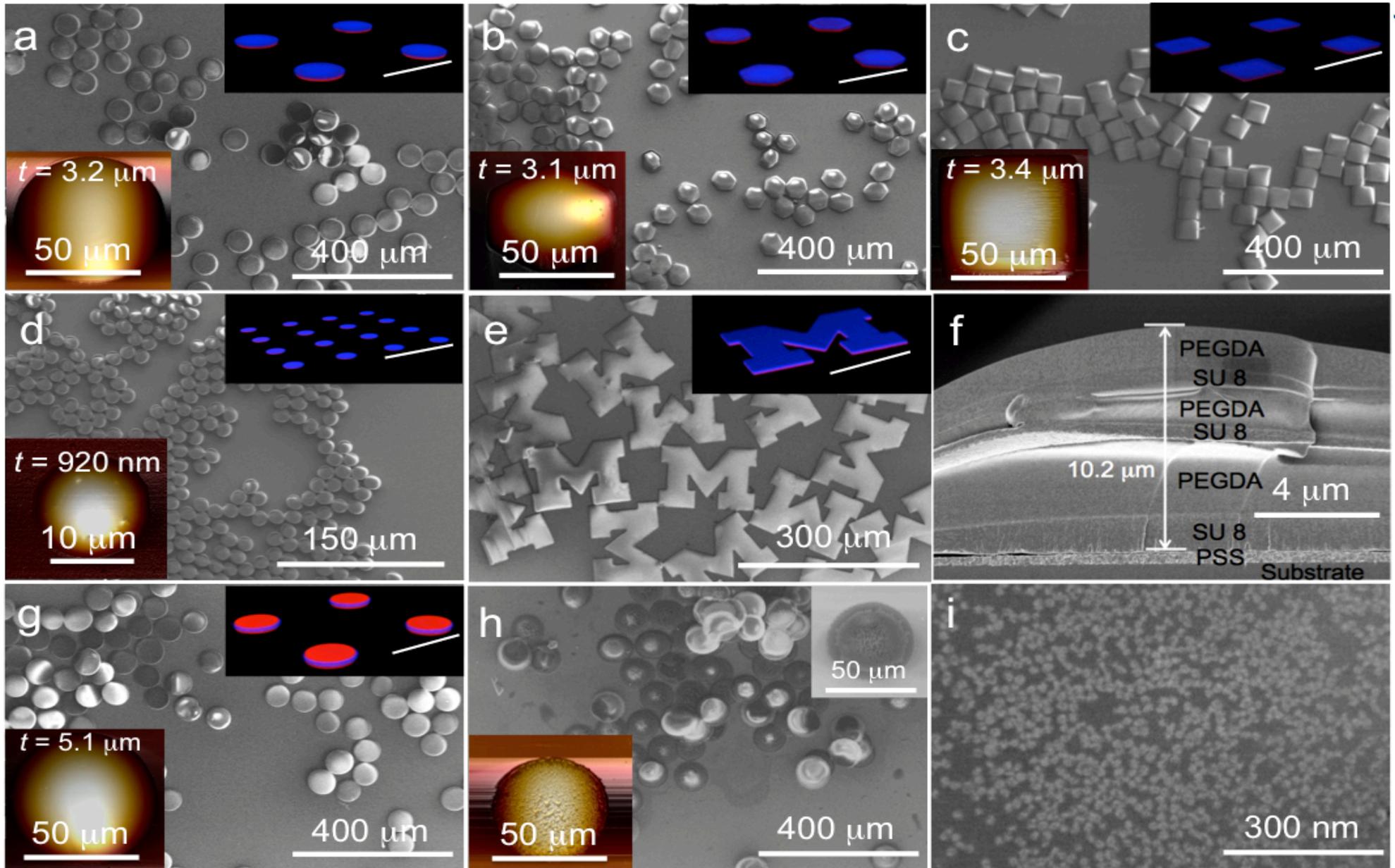


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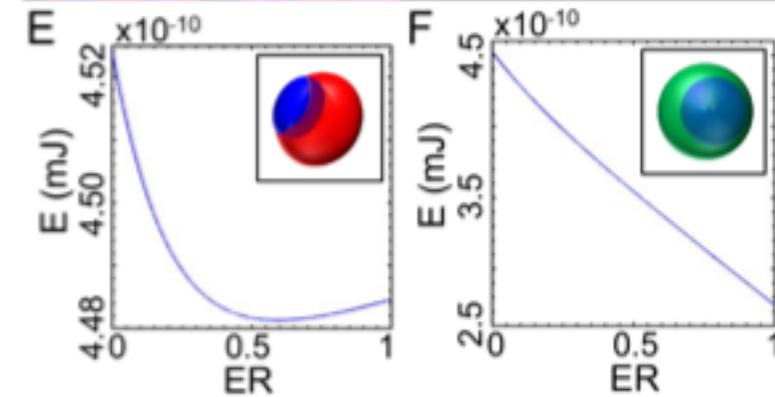
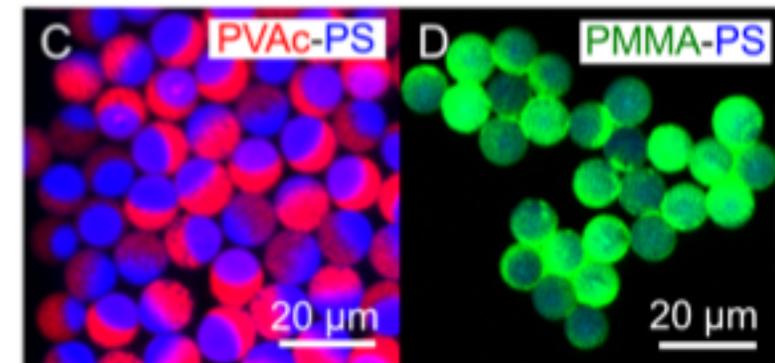
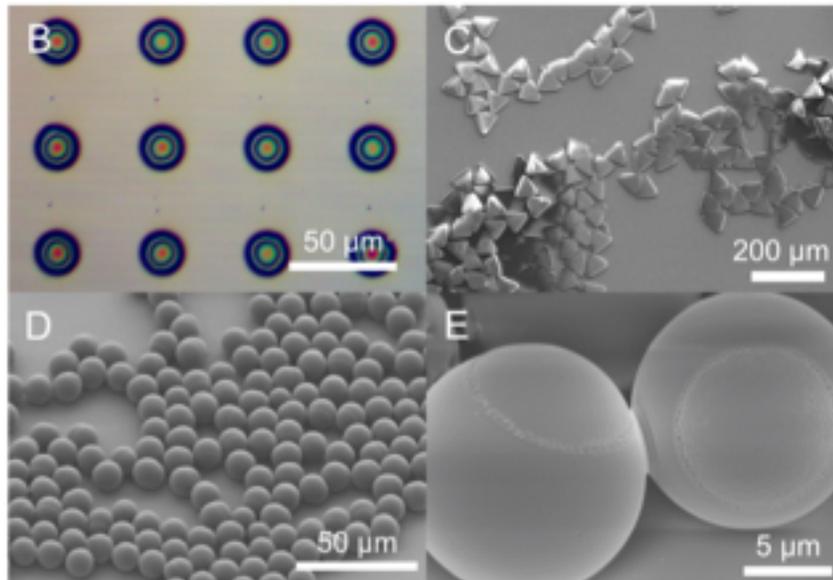
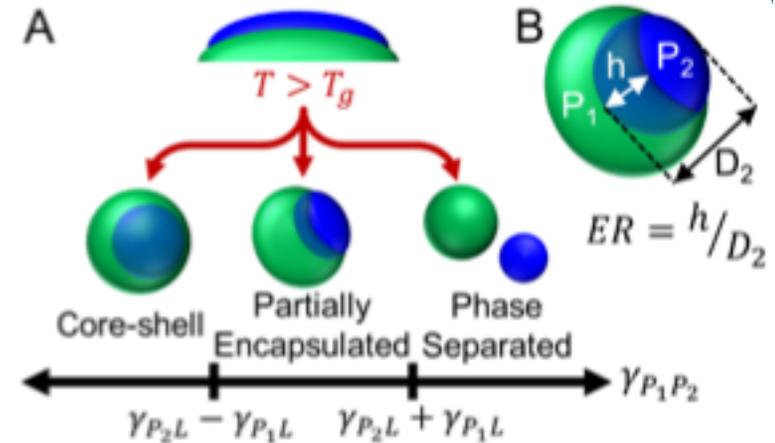
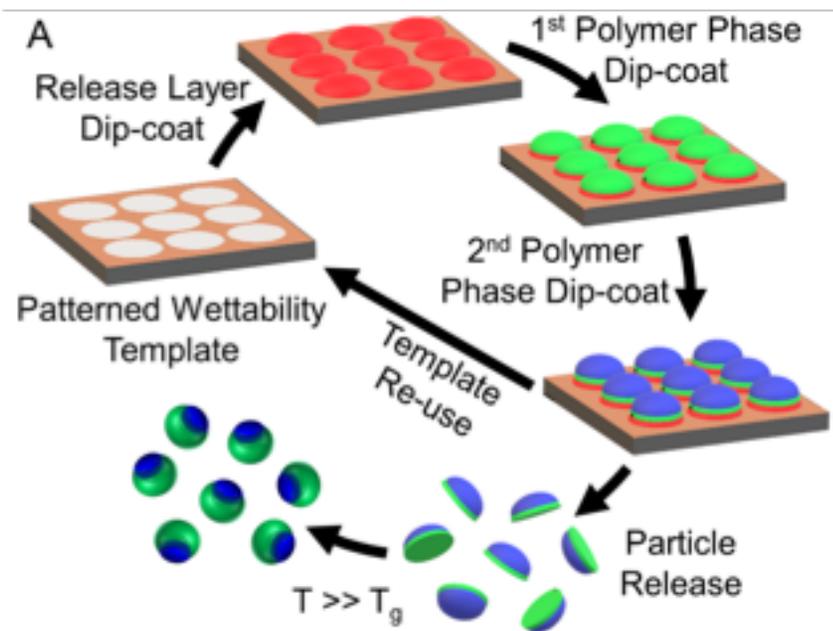
Unprecedented ability to manufacture on a large scale particles of any size, shape or chemistry. Particle shape and size can be used to engineer bio-distribution, skin or lung uptake, intra-cellular localization and cell response.

Multi-phasic particles

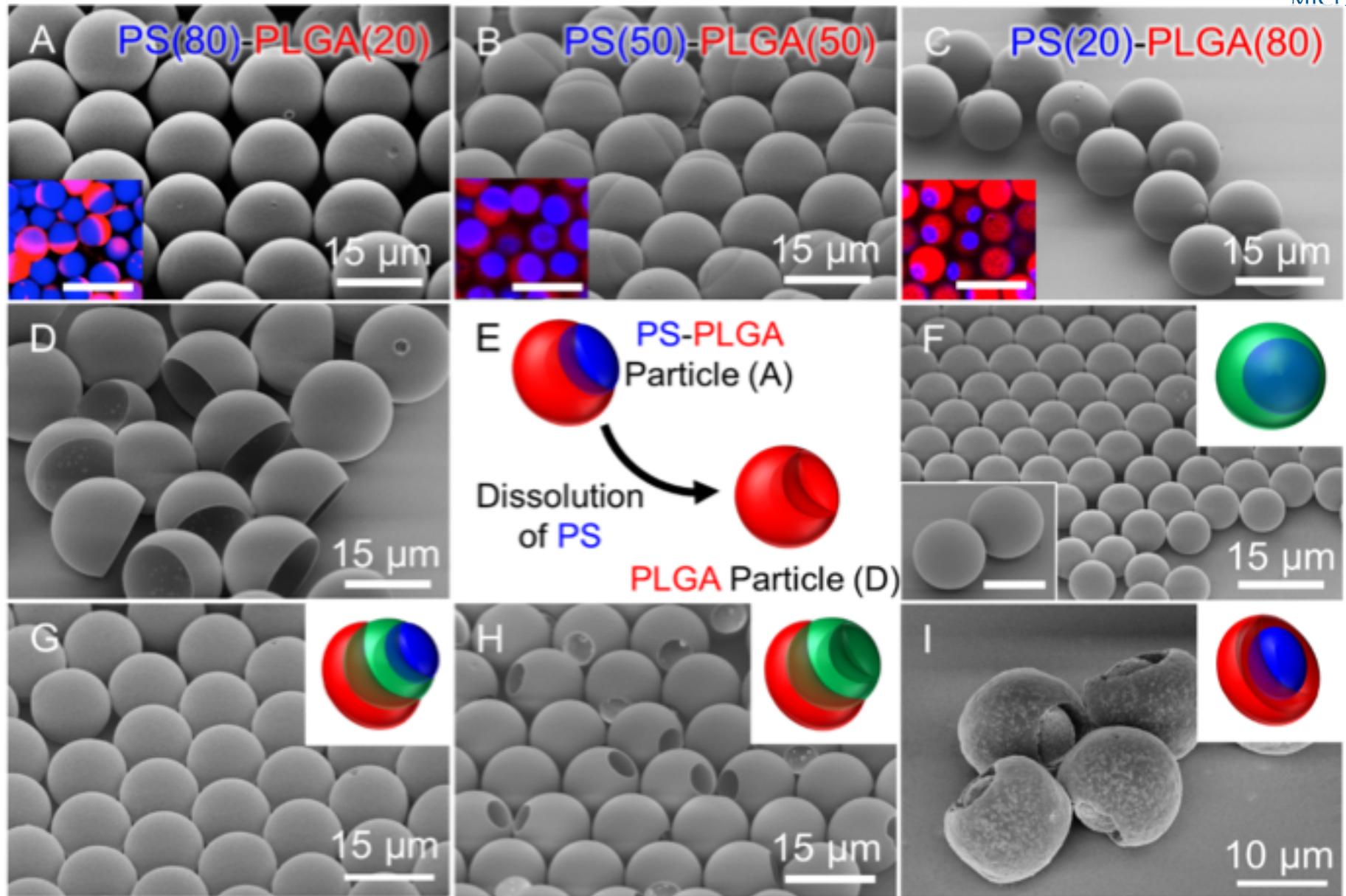


Kobaku *et al.*, *ACS Appl. Mater. Interfaces*, 2015, 7 (7), pp 4075–4080

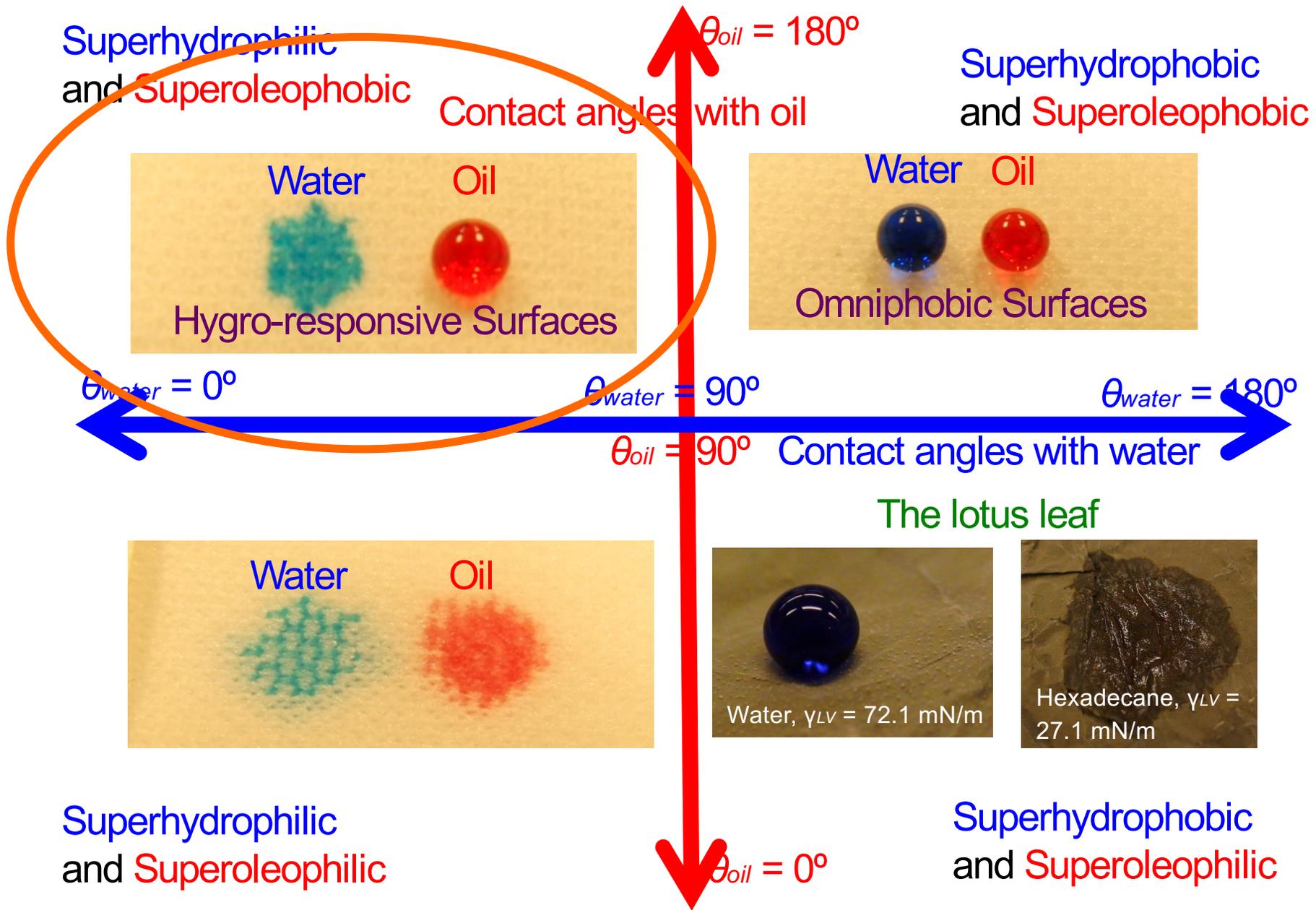
Shape shifting to create spherical particles



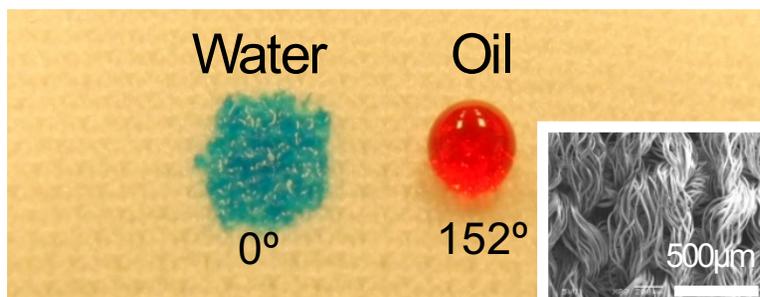
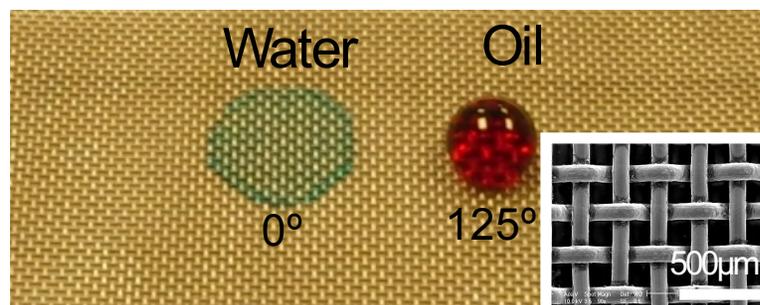
Shape shifting to create spherical particles



The wettability landscape



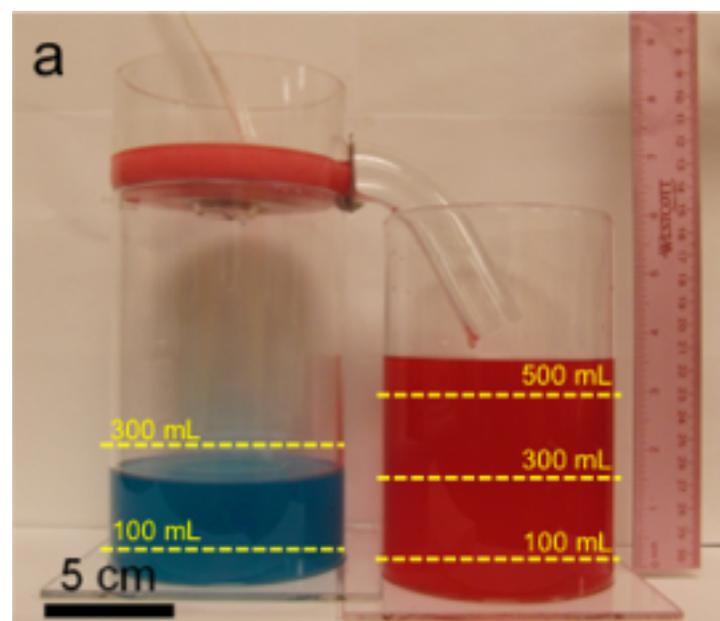
Membranes for oil-water separation



Developed one of the first coatings that counter-intuitively are hydrophilic and oleophobic.

Membranes based on these coatings can allow, for the first time, for the gravity based separation of all kinds of oil-water mixtures.

Applications include clean up of oil-spills, waste-water treatment, emulsion break-up, and oil-extraction.

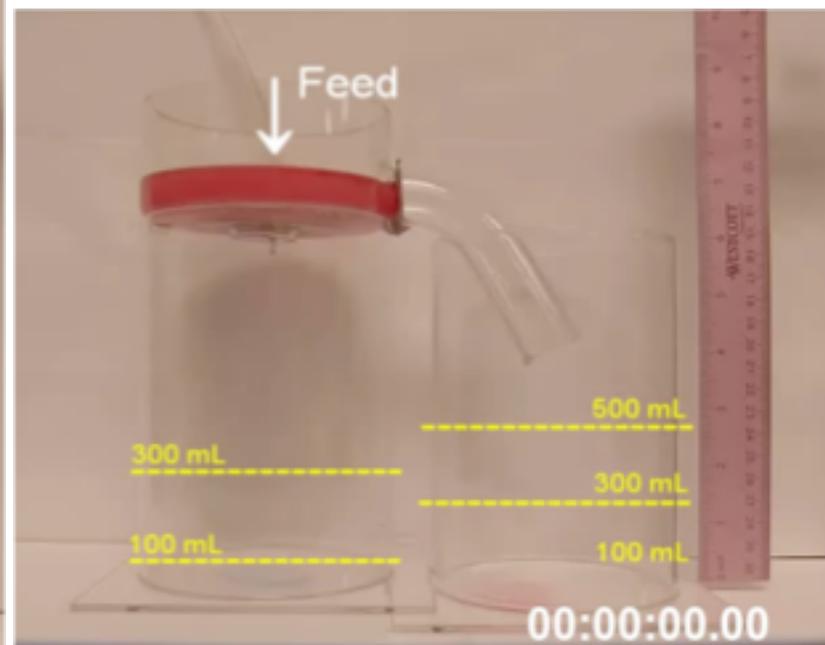
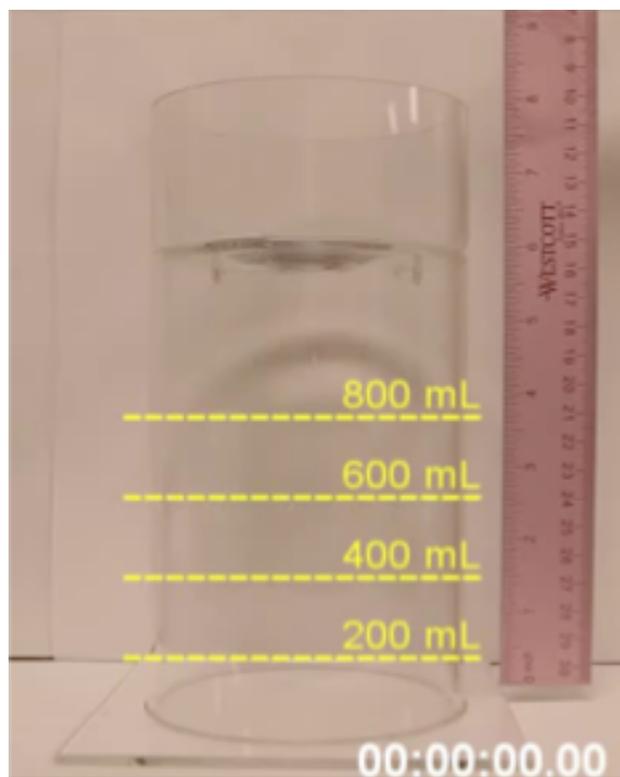


This is the first-ever setup developed for the continuous separation of oil-water emulsions which utilizes only gravity. The membrane separation efficiency exceeds 99.99%.

Kota *et al.* *Nature Communications*, 2012
Kwon *et al.* *Advanced Materials*, 2012

In collaboration with Dr. Joe Mabry, Tech Advisor, Propellants branch, Edwards AFB

Membranes for oil-water separation



Kota *et al.* *Nature Communications*, 2012

Liquid-liquid extraction



CRDF funds for desulfurization of fuels in collaboration with AFRL

Acknowledgements



PSI Group at the University of Michigan



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