Lessons from Nature: Bioinspired Mechanically Durable and Self-healing Superliquiphobic/philic Surfaces

with Self-cleaning, Anti-icing, low drag, Transparency/Antireflectivity, Anti-fogging, Anti-biofouling, and Oil-water separation/water purification

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30 min

Superliquiphobicity/philicity

The commonly used terms for wetting states are "hydrophobic" and "hydrophilic".

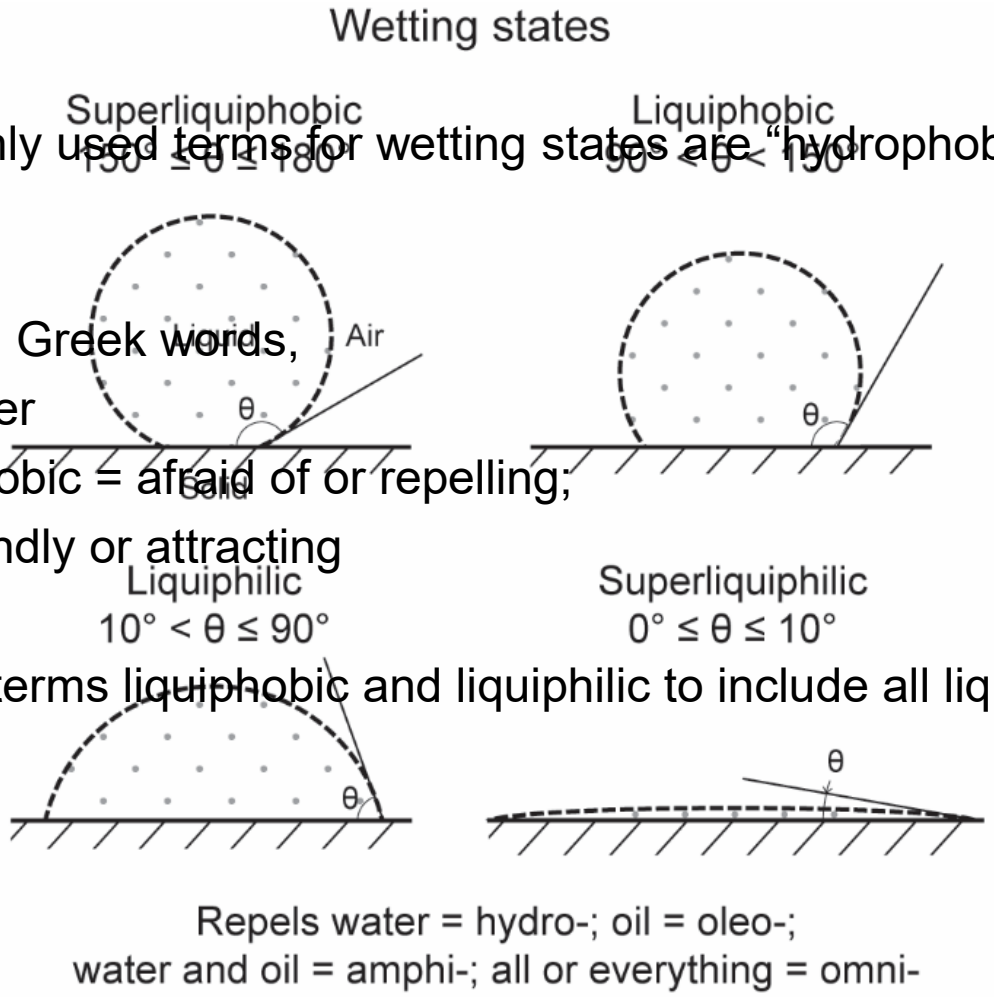
Derived from Greek words,

hydro- = water

Suffixes, -phobic = afraid of or repelling;

-philic = friendly or attracting

I coined the terms liquiphobic and liquiphilic to include all liquids (2016).



Schematic of liquid droplets in contact with superliquiphilic/phobic solid surfaces

B. Bhushan, *Biomimetics: Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology*, second ed., Springer (2016)

Introduction

Living Nature is not only beautiful and magical; it is also a great teacher.

Look deep into nature and you will understand everything. **Albert Einstein**

- Nature has gone through evolution over 3.8 billion years. It has evolved species with desired functionality using commonly found materials and routine fabrication methods.

(In nature,) Nothing is lacking and nothing is superfluous – ***Leonardo da Vinci***

Nature always tends to act in the simplest way. **Bernoulli**

- Nature has a limited toolbox and can still provide multifunctional properties. To provide functionality, biological materials generally have hierarchical structure with dimensions of features ranging from the macroscale to the nanoscale.

M. Nosonovsky and B. Bhushan, *Multiscale Dissipative Mechanisms and Hierarchical Surfaces: Friction, Superhydrophobicity, and Biomimetics*, Springer (2008); B. Bhushan, *Biomimetics: Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology*, third ed., Springer (2018); B. Bhushan, *Phil. Trans. R. Soc. A* **367**, 1445-1486 (2009); B. Bhushan, *Springer Handbook of Nanotechnology*, Fourth ed., Springer (2017)

- **In our research**, we look to living nature and select species, which provide functionality of commercial interest.

- We characterize the species to understand how nature provides functionality.
- We fabricate structures in the lab *using nature's route to verify our understanding.*

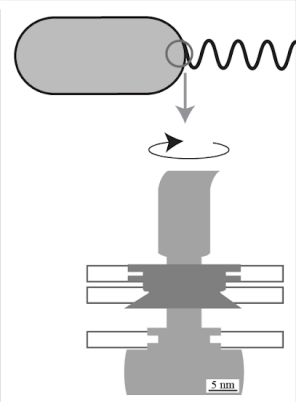
- For our applications, we model the structures and develop optimal designs. Biology works on *"the principle of good enough".*
- We then fabricate bioinspired, structured surfaces using smart materials and modern manufacturing processes *in a more sustainable and environmentally friendly manner.*

- This field of research, is called biomimetics. It is derived from a Greek word "biomimesis" which means mimicking biology or nature. Another word commonly used is biomimicry.
- Bioinspiration would be a more appropriate term for the field, as we do not copy nature but are inspired to develop designs of commercial interest.

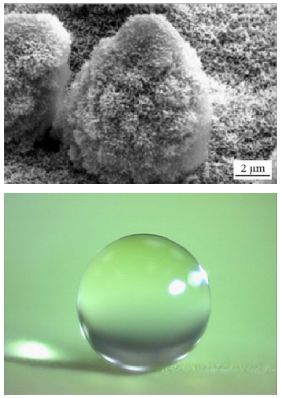
Lessons from Living Nature

About 1.7 million living organisms are known to exist (Barthlott et al., 2017).

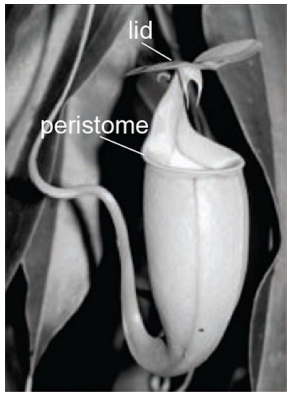
There are a large number of flora and fauna with properties of commercial interest.



flagellum motor

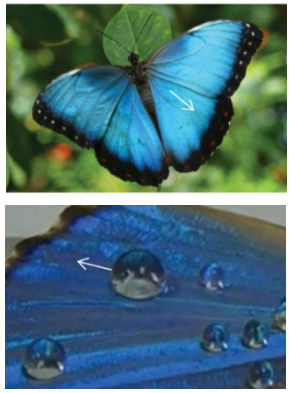


lotus leaf

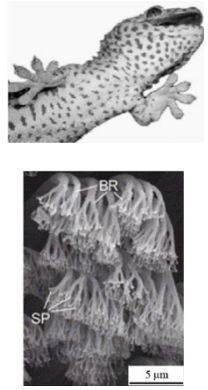


pitcher plant

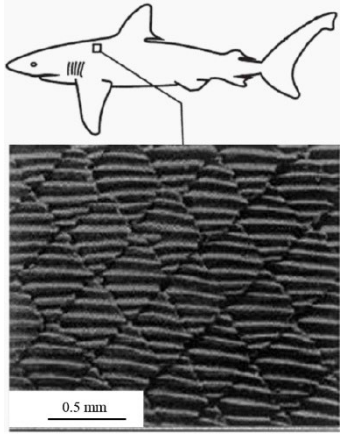
water strider



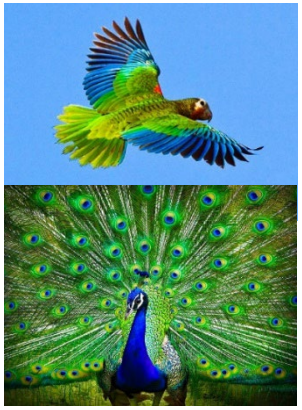
butterfly wings



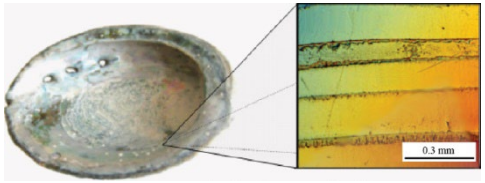
gecko feet



shark skin



bird & peacock



nacre of abalone shell

sensory aid devices: ear and eye

moth eye

self-healing

spider web

Nelumbo nucifera (Lotus leaf)

Blue Morpho didius (Butterfly)

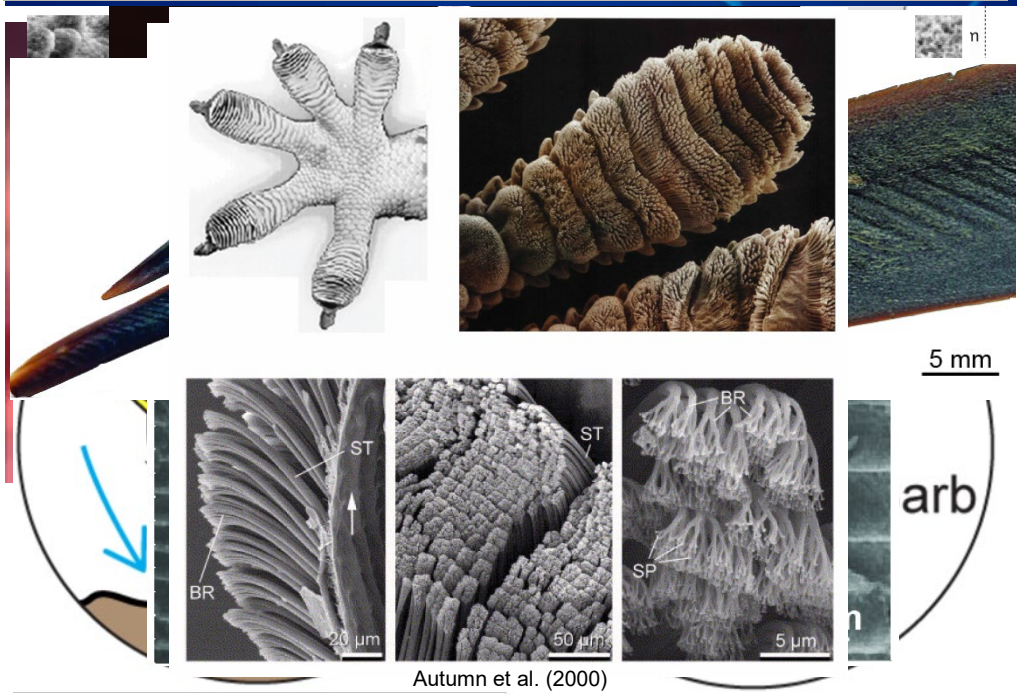
Opuntia microdasys (Cactus)

Isurus oxyrinchus (Shark)

Rynchops (Skimmer bird)

Gekko gecko (Tokay gecko)

Aedes vexans (Mosquito)



Autumn et al. (2000)

Applications

Lessons from species can be used in commercial applications.

- Lotus leaf and Butterfly Wings Inspired Self-cleaning Surfaces are of interest for various applications, e.g., self-cleaning windows and textiles (my lab).

- Cactus Inspired Surfaces can be used to collect and provide Safe Drinking Water in dry regions. Even the Southwest U.S. has experienced drought for many years and could benefit from this technology. We have designed large water harvesting towers covered with cones which can be used to collect water.

- Shark Skin and Skimmer Bird Inspired Low Drag Surfaces are of interest in both internal and external fluid flow applications. Major applications are in transportation such as aircraft skin (my lab).

- Gecko Feet Inspired Reversible Adhesion property can be used to develop climbing robots, and organic-free reversible adhesion surfaces, such as in surgical masks (my lab).

- By using Mosquitoes Piercing Design, we have developed painless microneedles, which can be used for the flu shots, drug delivery, and other biomedical applications.

Objective

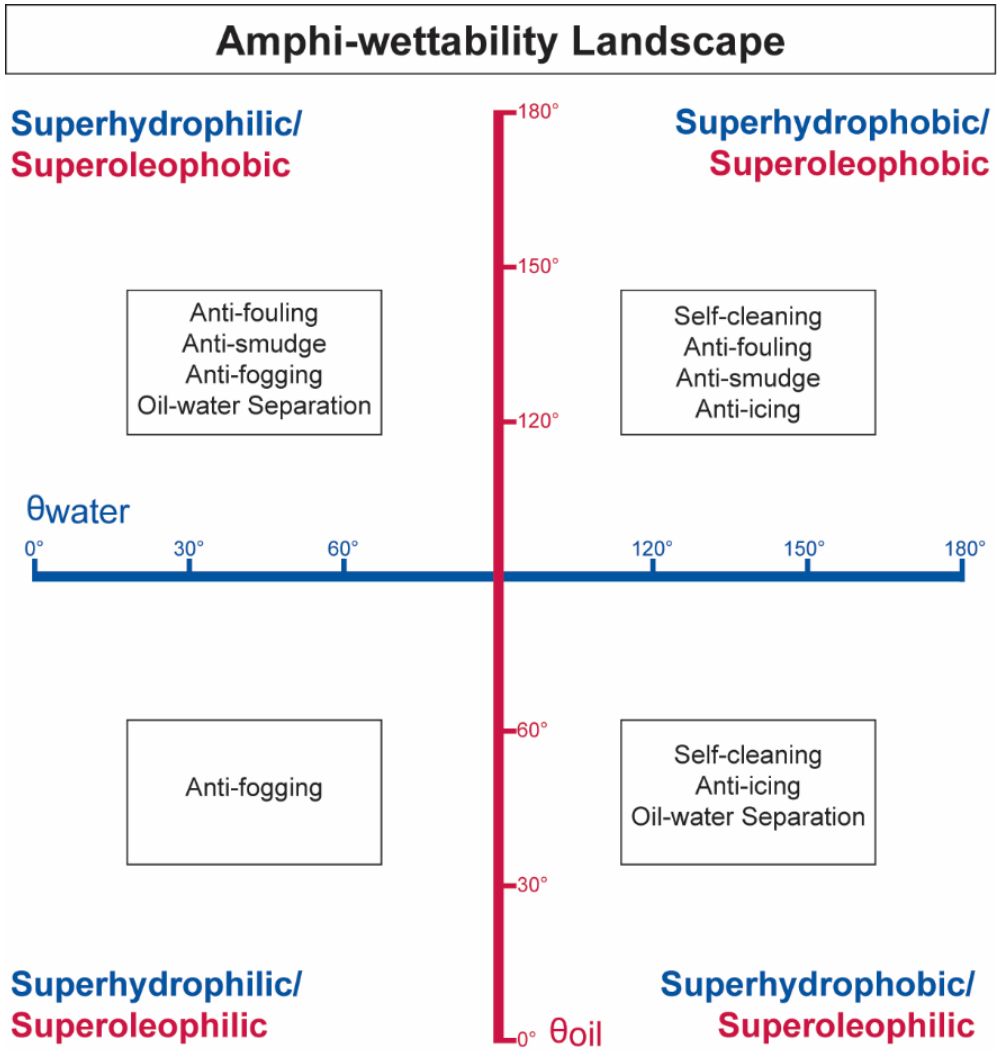
- Develop *mechanically durable, self-healing*, roughness-induced *superliquiphobic/philic and self-cleaning surfaces* for various applications.

- Other properties of interest are anti-icing, low drag, transparency/anti-reflectivity, anti-fogging, anti-biofouling, and oil-water separation/water purification.

M. Nosonovsky and B. Bhushan, *Multiscale Dissipative Mechanisms and Hierarchical Surfaces: Friction, Superhydrophobicity, and Biomimetics*, Springer (2008); B. Bhushan, *Biomimetics: Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology*, third ed., Springer (2018); B. Bhushan, *Phil. Trans. R. Soc. A* **367**, 1445-1486 (2009); B. Bhushan, *Springer Handbook of Nanotechnology*, Fourth ed., Springer (2017)

Superliquiphobic/philic Surfaces

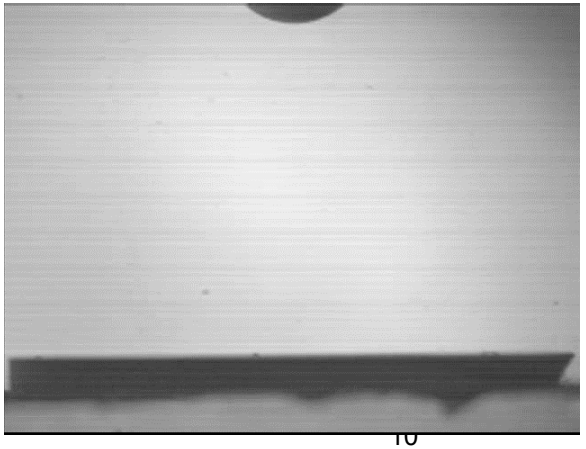
To design surfaces with various functionalities, various combinations of water and oil repellency and affinity are desired.



Shows four combinations of water and oil repellency and affinity and their applications.

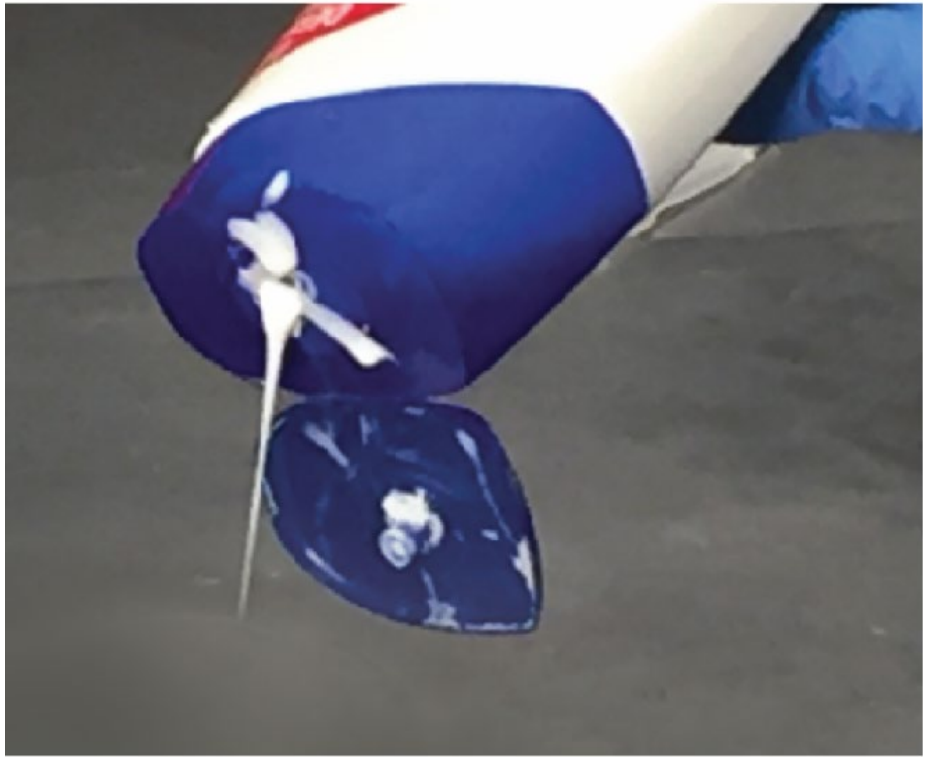
Liquid repellant, Self-cleaning and Low Drag Applications

- *One of our* focus is on liquid repellant, self cleaning and low drag surfaces for various applications, e.g., self cleaning windows, windshields, camera lenses, exterior paints for buildings, roof tiles, textiles, solar panels, and exterior surfaces in transportation – ships and aircrafts.
- They also exhibit anti-biofouling of interest, e.g., in membranes for desalination & water purification, biomedical, food packaging, and various eng. and consumer applications.
- Superhydrophobic surface can also be used for energy conservation and energy conversion.



- In shampoo bottles, caps get contaminated. It is hard to squeeze out the last bit of shampoo.
  Customer loses some liquid, and residual shampoo also makes it to the land fill which is undesirable.
- It is of interest to have self-cleaning bottles.

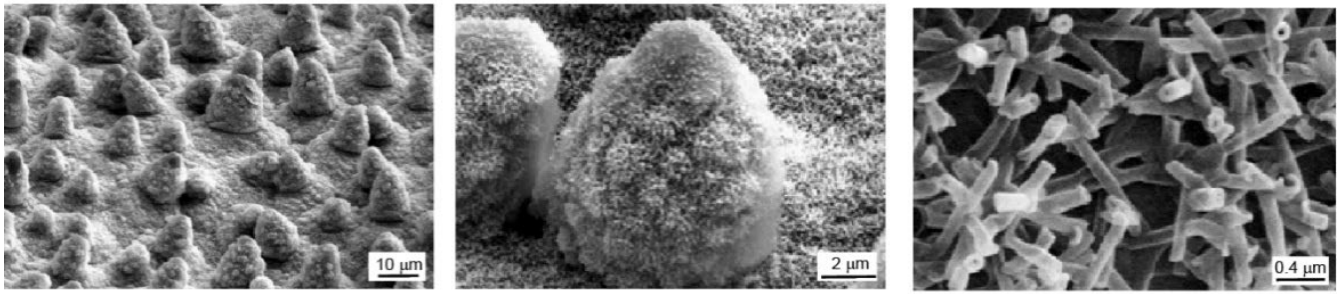
Fouling of shampoo bottle cap



Superhydrophobic & Self-cleaning Example in Nature

A model surface is provided by the Lotus Leaf (Top surface)

Lotus leaf (*Nelumbo nucifera*)



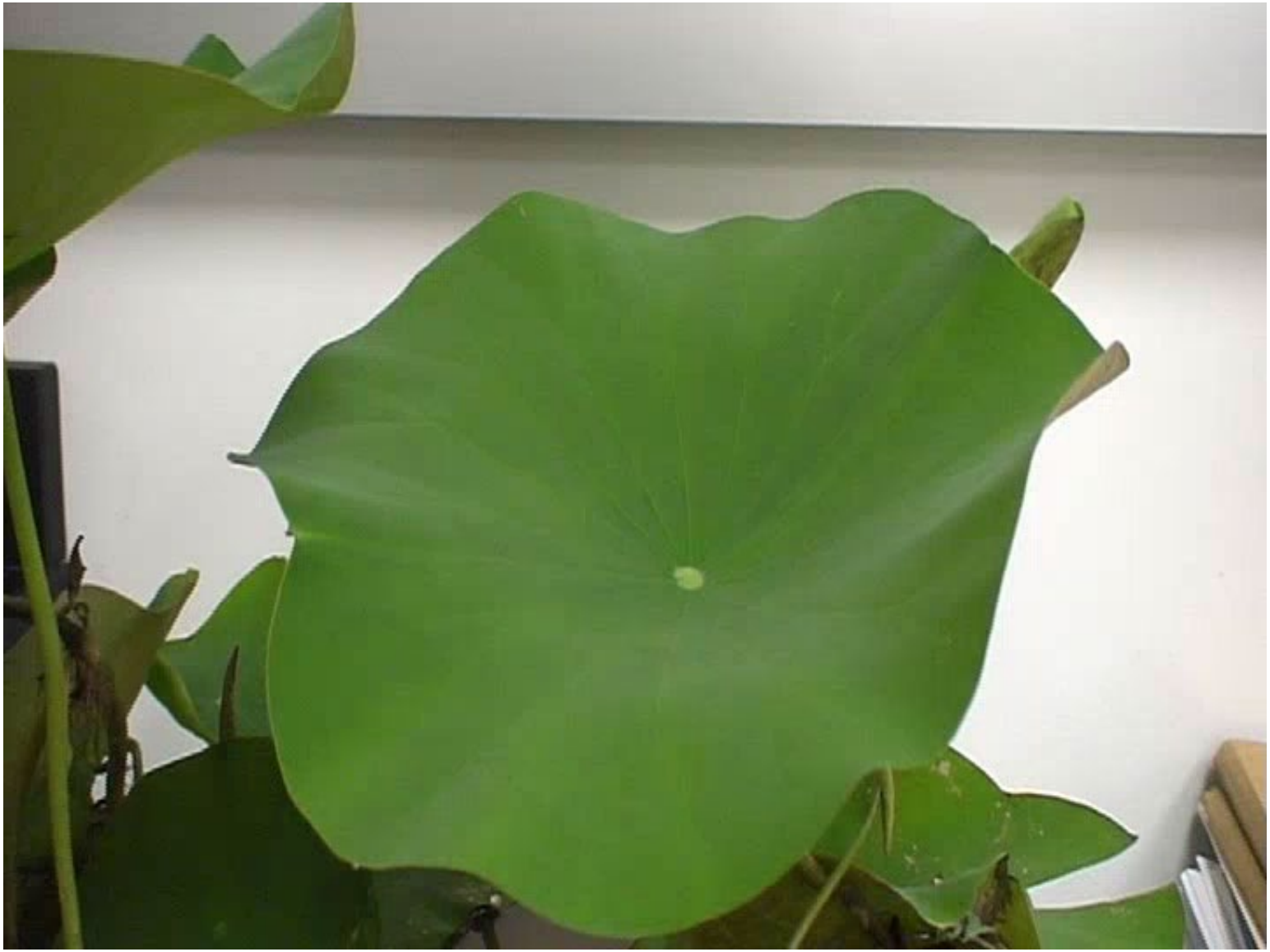
Droplet on a lotus leaf

Lotus Effect (Bhushan, Jung and Koch, 2009)

Superhydrophobic, self-cleaning, low adhesion, anti-fouling

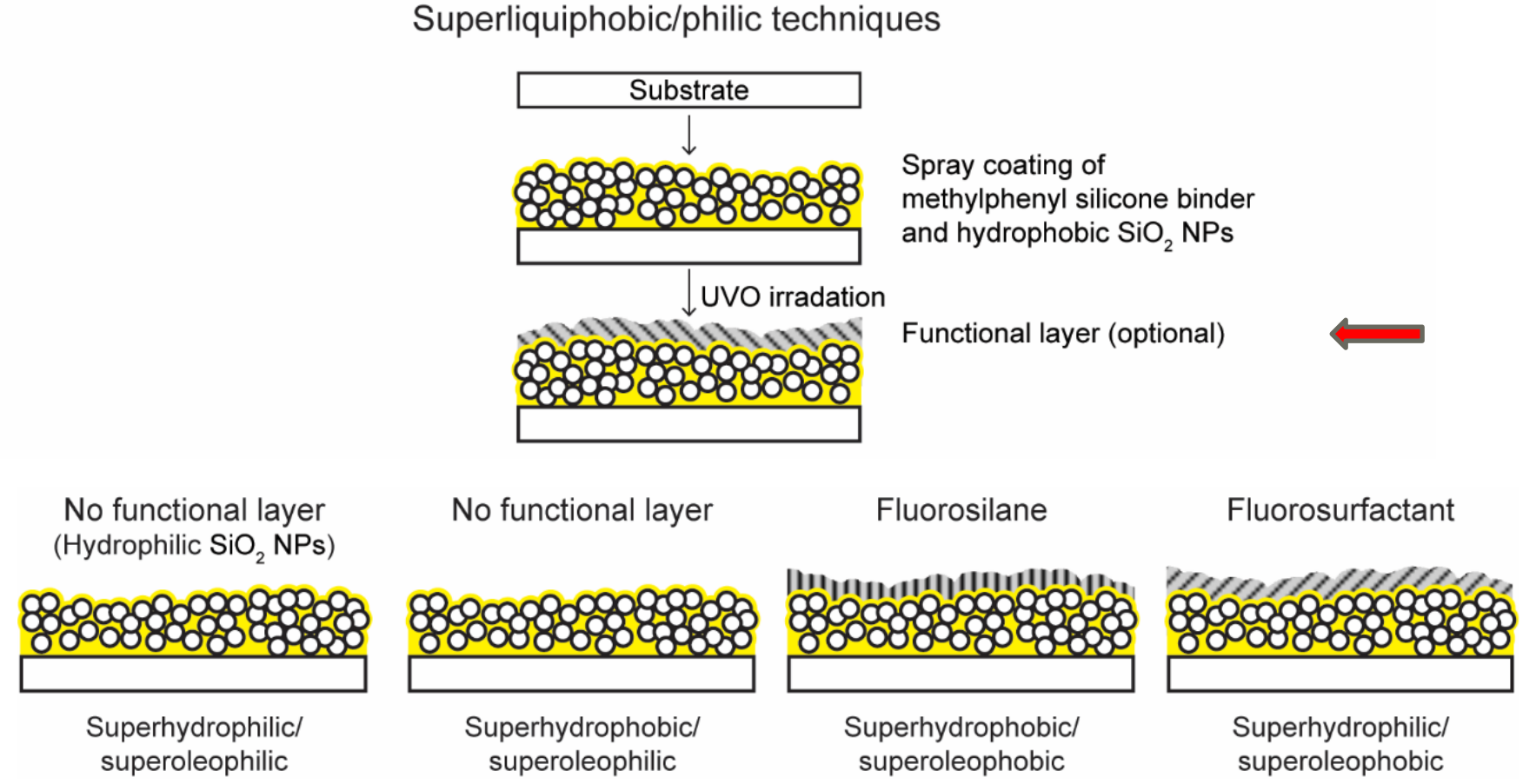
- *The leaf surface consists of microbumps formed by convex papilla epidermal cells, covered with a 3-D epicuticular wax which self-assembles as nanotubules.*
- Presence of wax makes the surface hydrophobic (CA~104º) and hierarchical structure of the rough surface makes it superhydrophobic. CA ~ 164º, CAH ~ 2º

B. Bhushan, *Phil. Trans. R. Soc. A* **367**, 1445-1486 (2009); B. Bhushan, *Biomimetics: Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology*, third ed., Springer (2018).



Rolling off liquid droplet over superhydrophobic Lotus leaf with self cleaning ability

Facile Nanoparticle/binder Technique for Fabrication of roughness-induced Superliquiphobic/philic Surfaces (to cover four quadrants of amphi-wettability landscape)



B. Bhushan, *Biomimetics: Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology*, third ed., Springer (2018); B. Bhushan, "Lessons from Nature for Green Science and Technology: An Overview and Superliquiphoboc/philic Surfaces," *Phil. Trans. R. Soc. A* **377**, 20180274 (2019).

Characterization

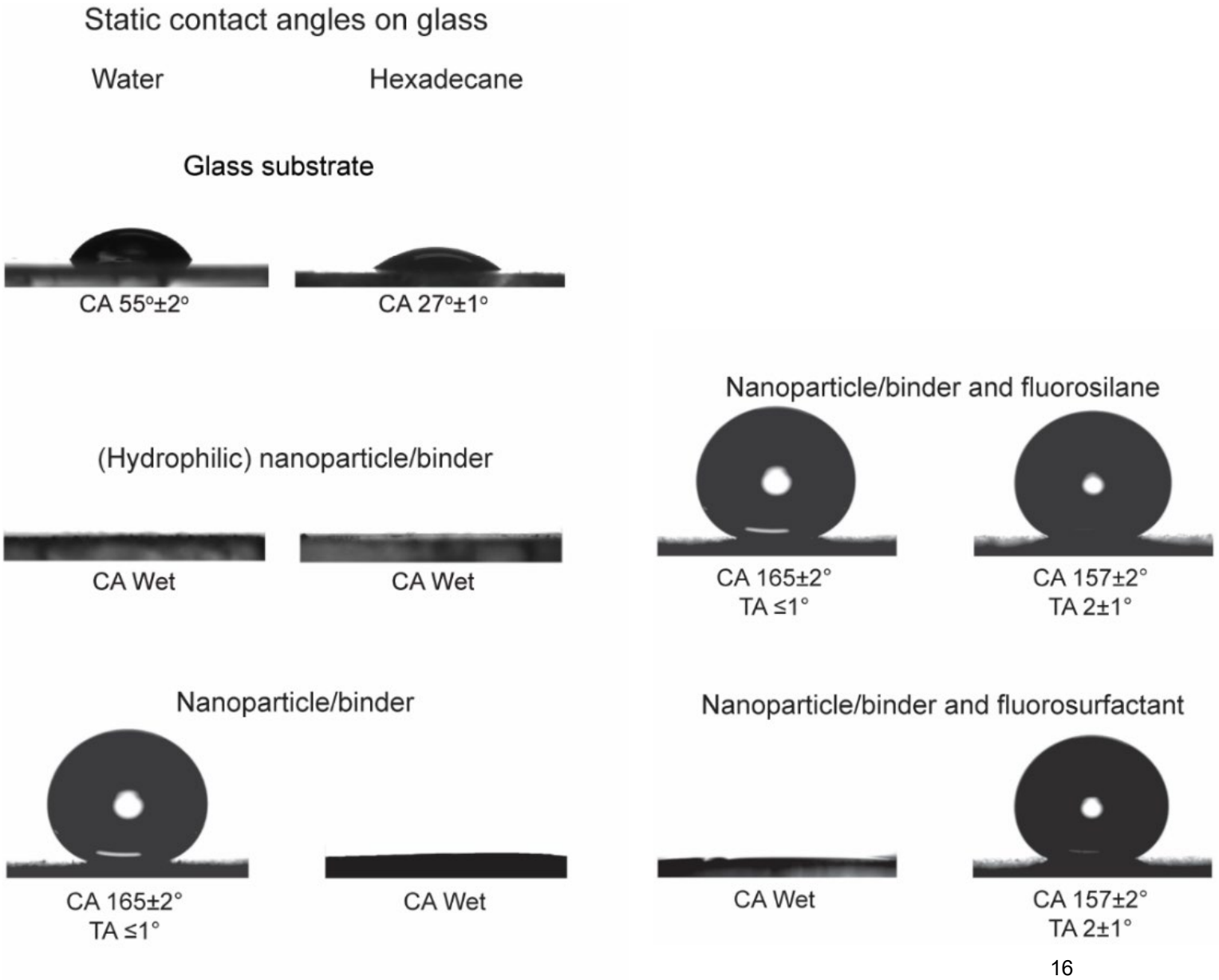
- Wettability - Contact angle (CA), tilt angle (TA) or contact angle hysteresis (CAH)

- Properties of interest –
  Repulsion of water, oils, shampoos and detergents, Self-cleaning, Anti-icing, Low drag, Transparency/reflectivity, Anti-fogging, and Anti-biofouling Properties,
  Oil-water separation/ water purification

- Wear resistance (mechanical durability)

B. Bhushan, *Biomimetics: Bioinspired Hierarchical-Structured Surfaces for Green Science and Technology*, third ed., Springer (2018); B. Bhushan, "Lessons from Nature for Green Science and Technology: An Overview and Superliquiphoboc/philic Surfaces," *Phil. Trans. R. Soc. A* **377**, 20180274 (2019).

Wettability



Video of Liquid Repellency

(Water, hexadecane, shampoo & detergent)

Samples mounted at a 25º incline

Glass substrate

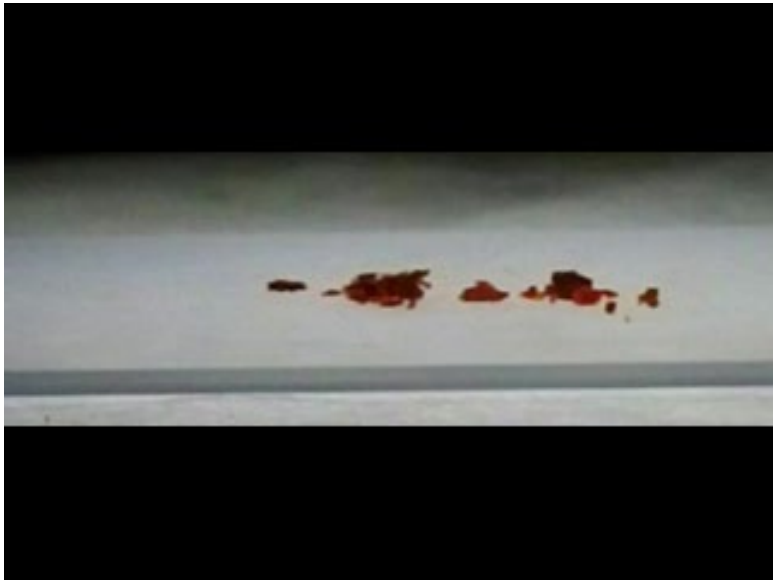
Superliquiphobic surface

Video of Self-cleaning

For superliquiphobic surface with low tilt angle, energy dissipation during flow of liquid droplet is low and droplets roll off the surface and take contaminants with them.

Hydrophilic surface

Superhydrophobic surface with TA~ 2º



Water droplet on tilted and contaminated, hydrophilic surface slid slowly, whereas it rolled over a superliquiphobic surface and taking contaminants with it.

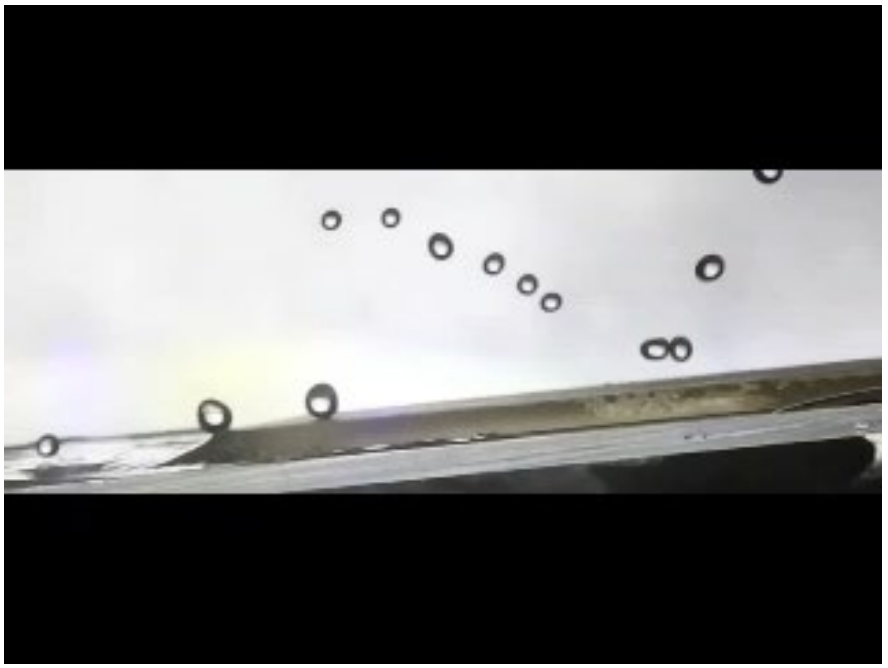
Bhushan, B. and Multanen, V., "Designing Liquid Repellant, Icephobic and Self-Cleaning Surfaces with High Mechanical and Chemical Durability," *Phil. Trans. R. Soc. A* **377**, 20180270 (2019).

Superhydrophobic Surfaces for Anti-icing

Anti-icing surfaces are of interest in app., such as aircraft surfaces.

Glass substrate

Superhydrophobic surface

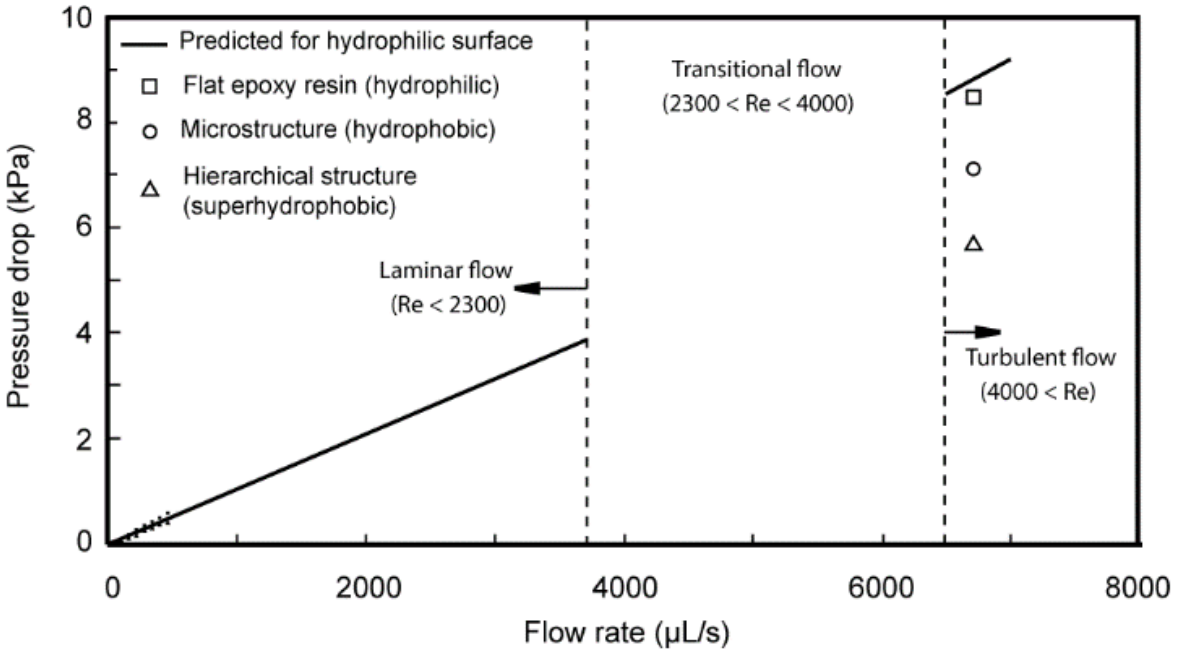


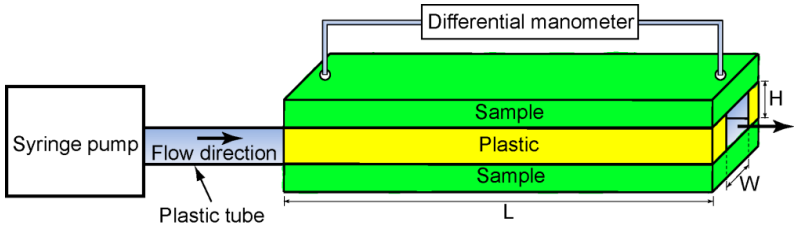
- Supercooled droplets (-18˚C) released onto surfaces in freezer at -60°C, falling from a height of 1 cm.
- On the hydrophilic glass surface, droplets got stuck immediately.
- However, they bounced and rolled off the superhydrophobic surface.

Drag Measurement

Superhydrophobic surfaces with low TA are expected to provide low drag.

Low drag surfaces are of interest in both internal and external fluid flow app.; major application is in transportation, such as aircraft skin.





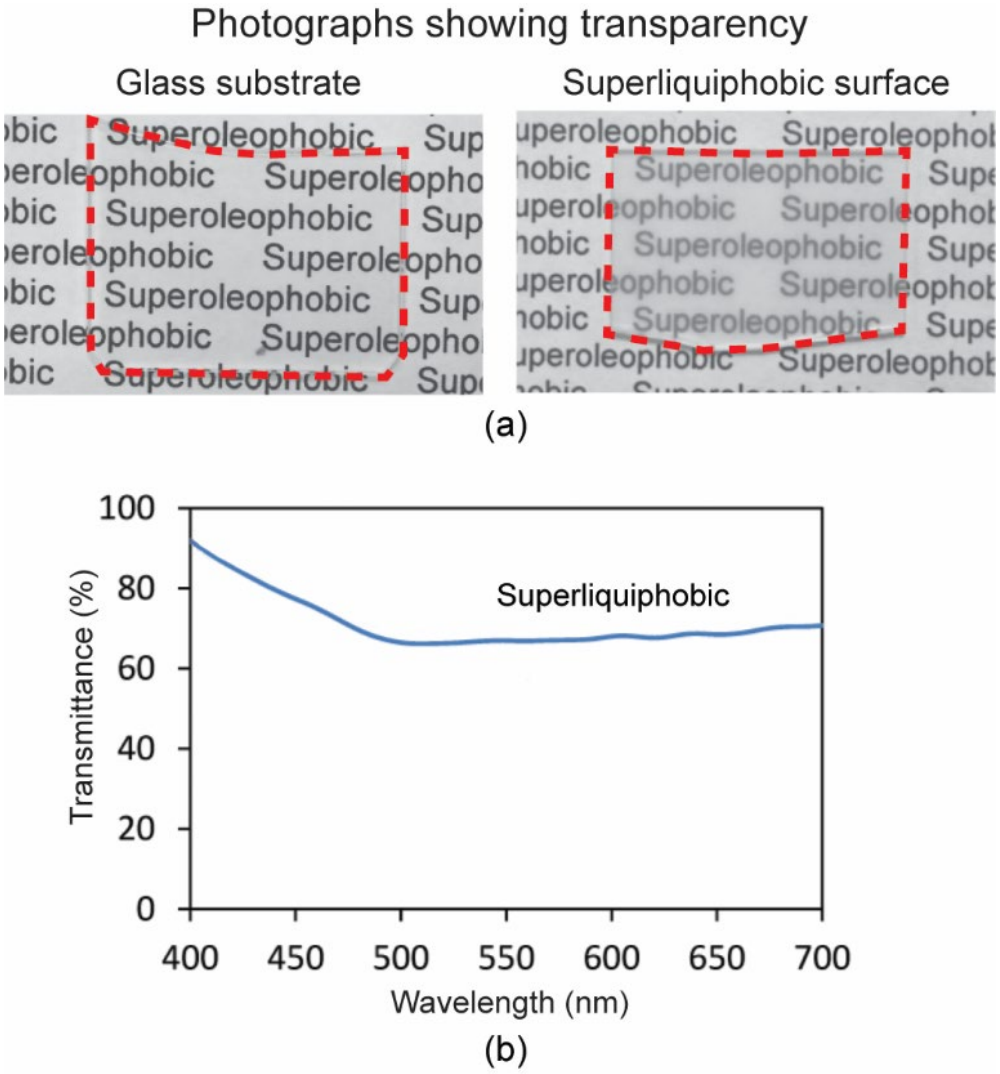
Flow cell connected to a differential manometer

- To measure drag in a closed rectangular channel, pressure drop in a flow cell was measured.
- Lower pressure drop corresponds to lower drag.
- Greatest decrease in pressure drop of ~33% occurs with superhydrophobic surface in turbulent flow.

Y.C. Jung and B. Bhushan, *J. Phys.: Condens. Matt.* **22**, 035104 (2010)

Photographs showing transparency

Electronic mobile devices and many optical applications require coatings to be transparent.



- To test for transparency, text was placed behind samples.
- When text was placed behind the coated glass, the text remained readable suggesting that coating displays transparency.
- The transmission of visible light was measured using a diffraction spectrometer.

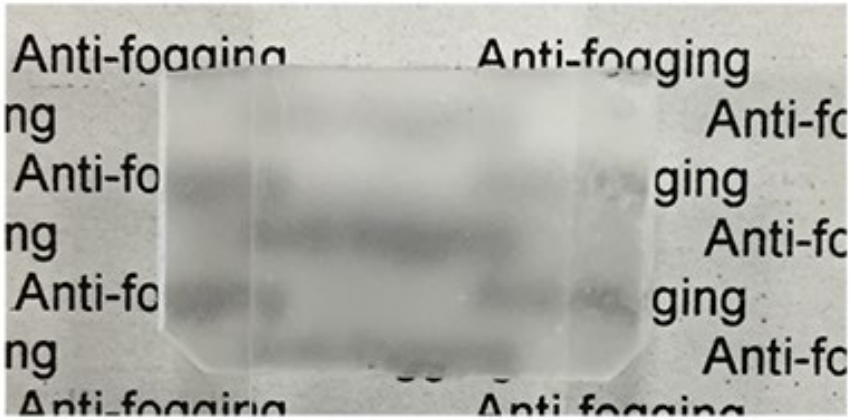
  Percent optical transmittance of the coated glass was 93-70% over visible spectrum.

Superhydrophilic Surfaces for Anti-fogging

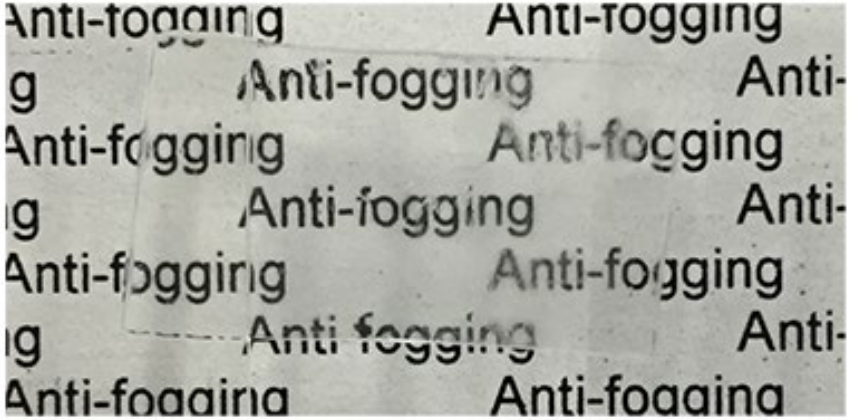
Antifogging properties are of interest in various optical applications, such as optical windows and eyeglasses.

Anti-fogging properties

Glass substrate



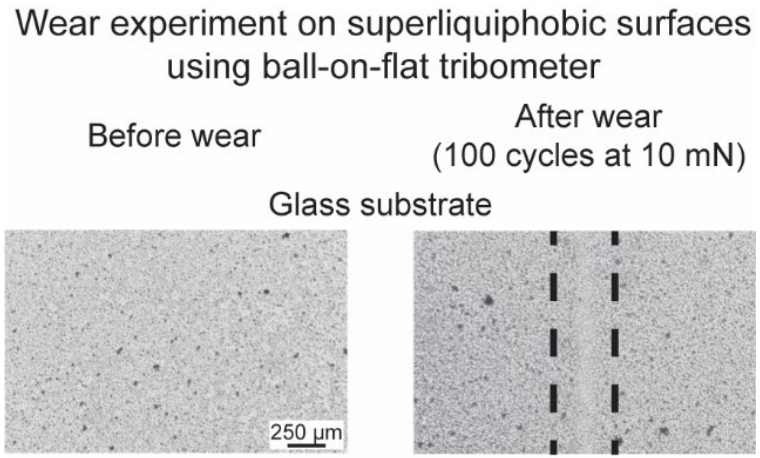
Superhydrophilic surface



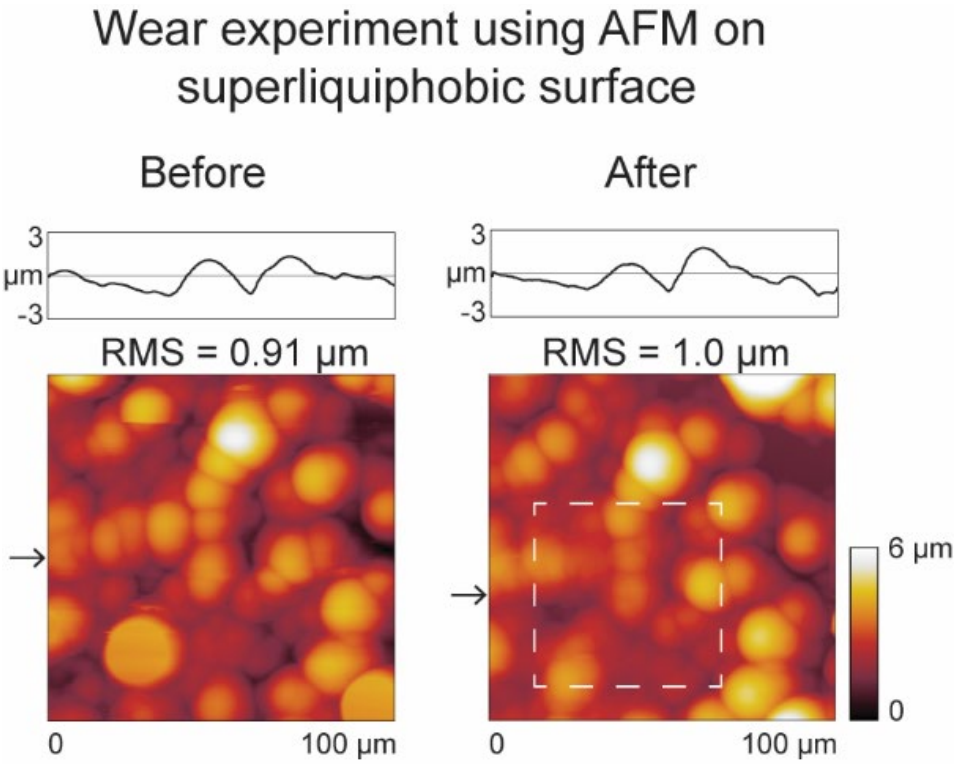
- The samples were placed on top a text, above a source of boiling water for 5 s.
- Glass substrate became opaque. Whereas superhydrophilic surface was found to retain transparency, with text being visible through the condensed water layer.

- Condensed droplets spread out into a thin film and evaporate rapidly to maintain transparency, thus providing anti-fogging properties.

Wear Resistance or Durability on Macro- and Microscale



- Macroscale wear test was carried out by sliding a sapphire ball in reciprocating mode. Optical images of samples were taken before and after wear test.
- Burnishing of the coating was observed with no loss of CA.

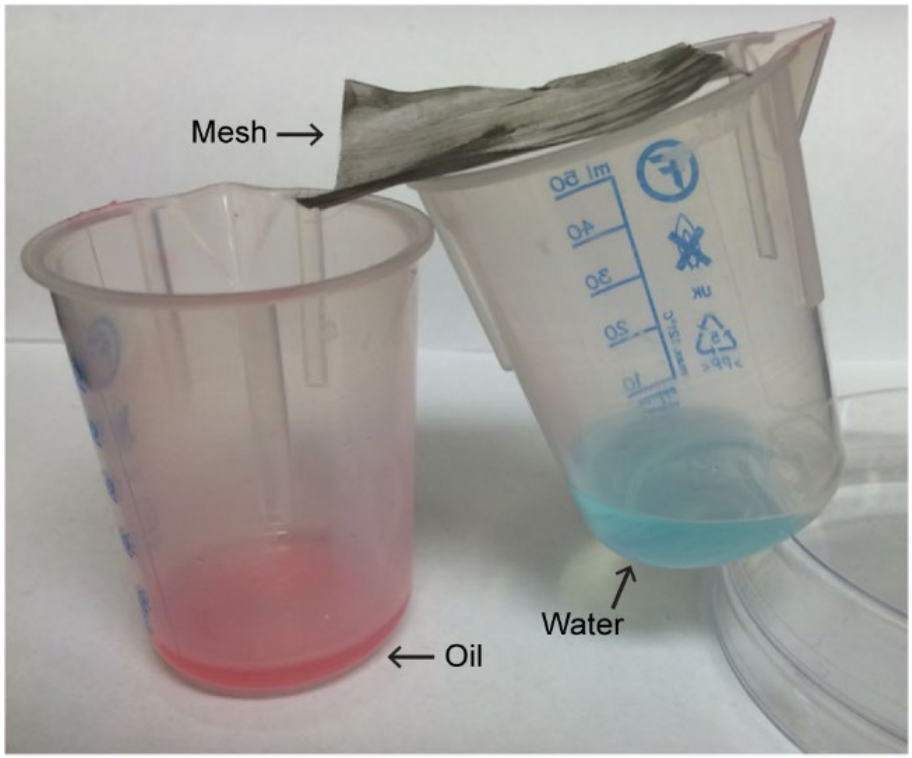


- Microscale wear test was carried out by scanning with an AFM tip using a 15 µm borosilicate glass ball over 50 µm x 50 µm region.
- After the AFM test, there was no burnishing of the coating.

Oil-Water Separators Using Mesh Coated Samples (w/ Dr. Philip Brown)

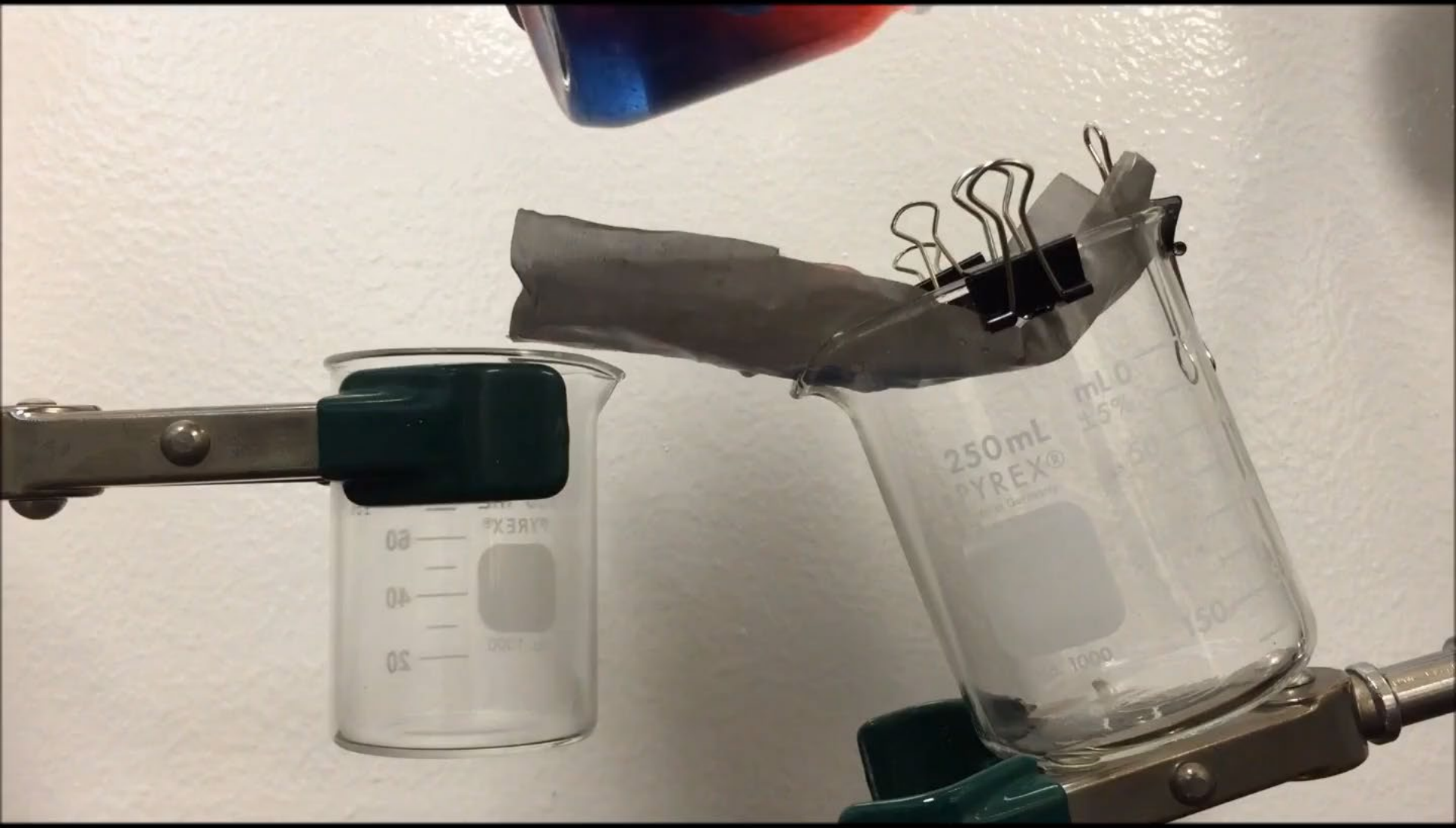
Photograph of oil-water separation
Mesh placed on an inclined plane

Superhydrophilic/Superoleophobic



- To fabricate an oil-water separator, a porous stainless-steel mesh was selected.
- It was spray coated with nanoparticle binder coating with a topcoat of fluorosurfactant by vapor deposition.
- By using a fluorosurfactant layer, we can develop a surface which repels oil and attract water. Superhydrophilic/Superoleophobic nature of coating *means water (dyed blue) passes through mesh whilst oil (dyed red) remains on top*.
- Oil can then be collected continuously from the inclined mesh.

Brown, P. and Bhushan, B., *Scientific Reports – Nature* **5**, 8701 (2015); ibid 14030 (2015)


250mL
PYREX®

- The oil-water separation technology can be used for
  - eco-friendly oil-spill cleanup, and
  - water purification

Brown, P. and Bhushan, B., Phil. Trans. R. Soc. A. ***374,*** 20160135 *(2016)*

- Major offshore oil-spills occur periodically around the world.

- We can recall the Deepwater Horizon in 2010.
  It was the worst disaster in history and spilled some 200 million gallons of oil.

- Partial cle ring cost of some $ olished!

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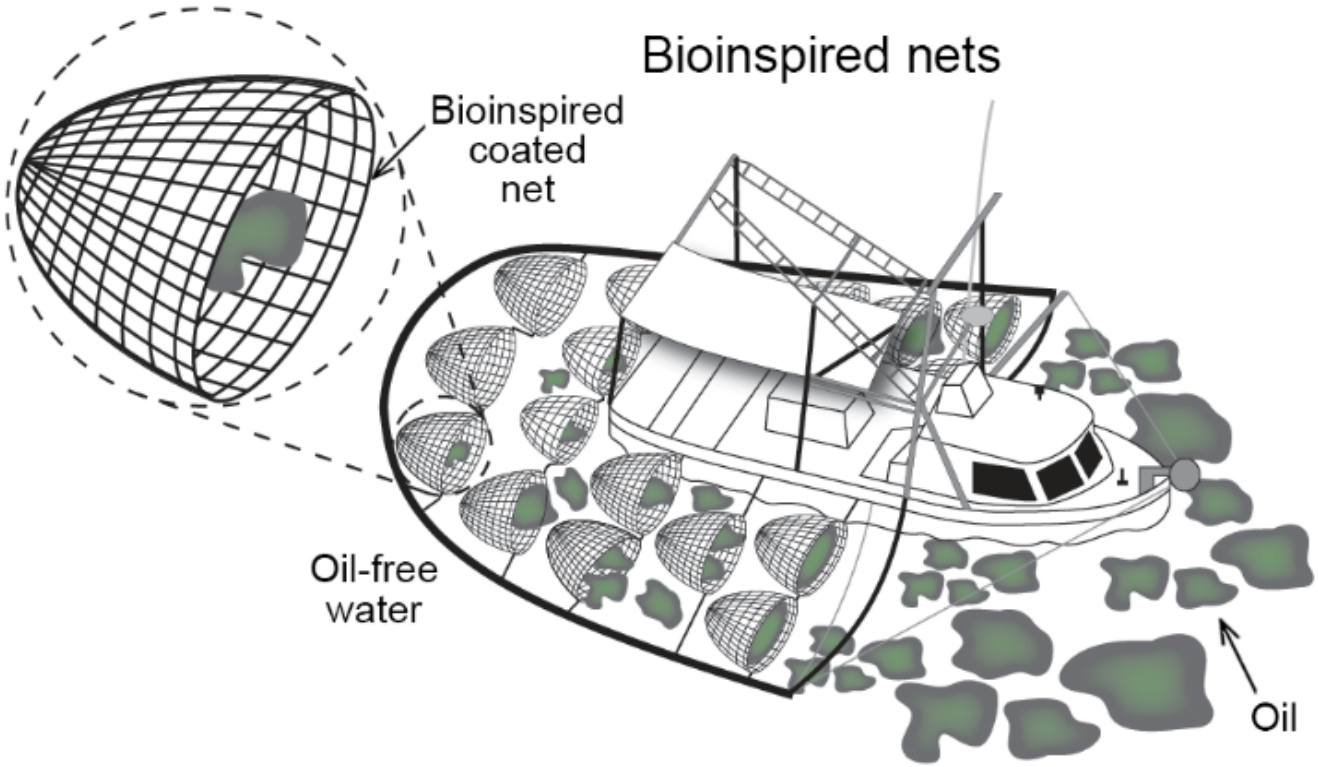
Schematic showing bioinspired nets connected to a boat for oil-spill clean up



Nets featuring bioinspired coated mesh trap oils while allowing passage of water. Oil can easily be recovered from nets via pumping. Oil-repellent nature of mesh reduces need for cleaning.

Water Purification

Water contamination is a major health issue facing the world today. The oil-water separator can be used to remove organic contaminants for water purification.

Licensee - Micron Industrial Solutions Ltd, Gauteng, South Africa, Aug. 2018

The Institution of Chemical Engineers (UK) Global Award, Birmingham, UK, Nov. 5, 2015

Top Ten Science Stories of 2015 – Insight; Top Fifty Stories the Year – Discover, 2015

Summary

- Coatings with various combinations of superliquiphilicity and -phobicity have been developed.

- Coatings demonstrated liquid repellency, self-cleaning, anti-icing, low drag, transparency, anti-fogging, anti-biofouling, and oil-water separation properties.

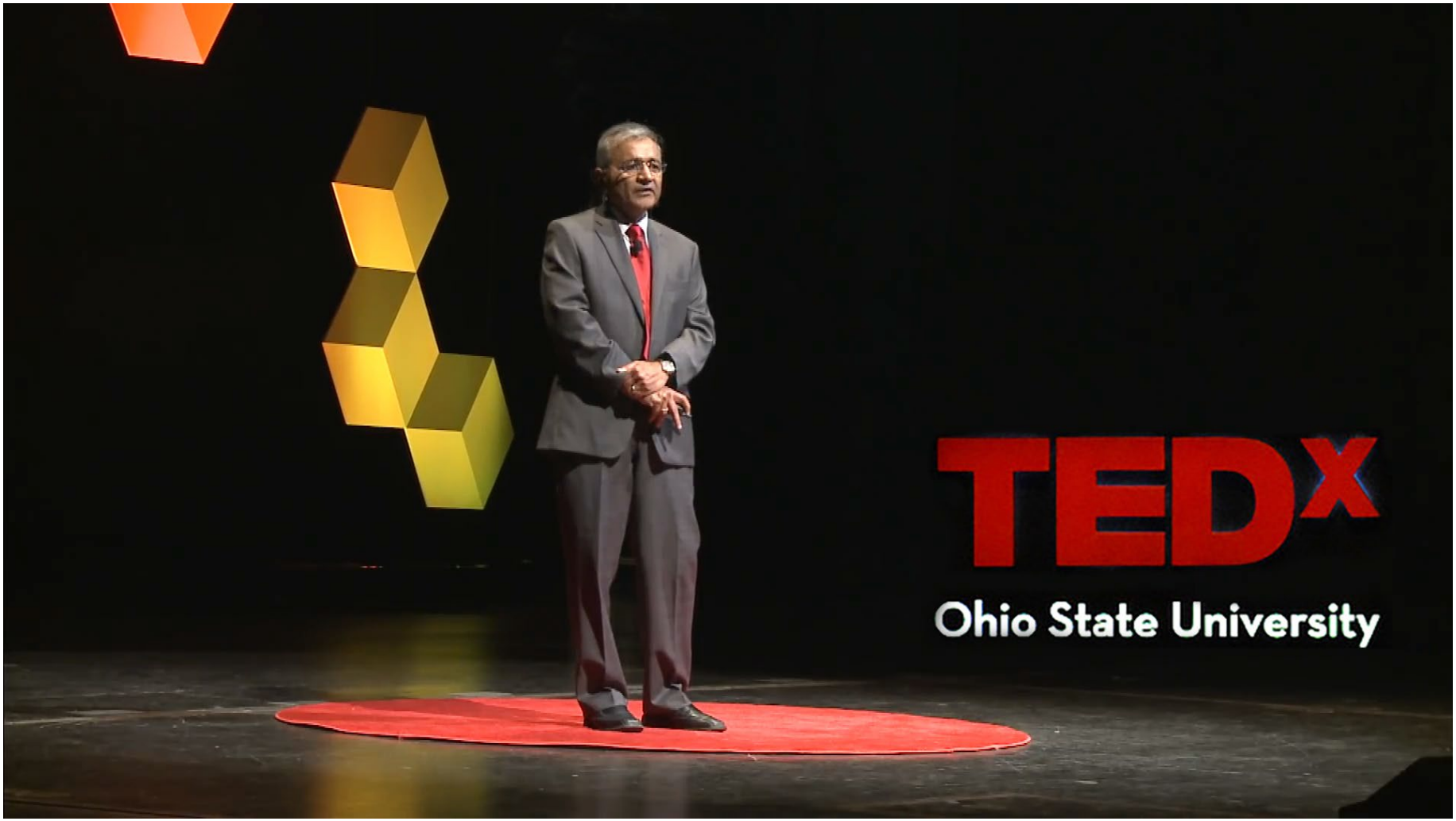
- These coatings are eco-friendly and can be readily used on variety of substrates and are scalable.

The financial support was provided by National Science Foundation, US Navy, Sony Chemical & Info. Dev., Japan, Dexerials Corp, Japan, Honda R&D Americas, Ford, P & G, and Center for Applied Plant Sciences (CAPS).

Concluding Remarks

Nature has learnt to solve its problems,

we can do too by using lessons from nature!



TEDx Fuse Event in Columbus, Ohio on Feb 23, 2019
“Lessons from Nature: Bioinspired Surfaces for Green Technology”
https://www.youtube.com/watch?v=QAH0N328okE

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