

# 仿生多功能表面之結構設計與應用

國立清華大學材料科學工程系  
陳柏宇 副教授

## Biological & Bio-inspired Materials Laboratory



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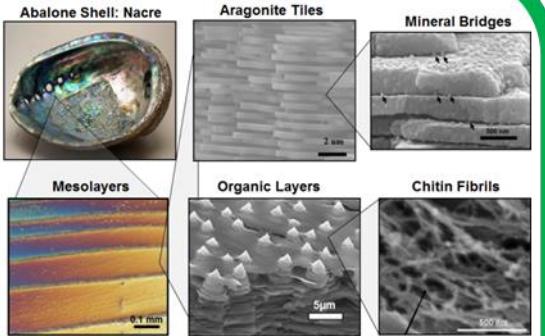
### Research Interests/Expertise:

- Biological (Natural) Materials
- Bio-inspired (Biomimetic) Materials
- Bio-medical Materials
- Bio-mechanics/Biomineralization
- Surface Science & Coating Technologies

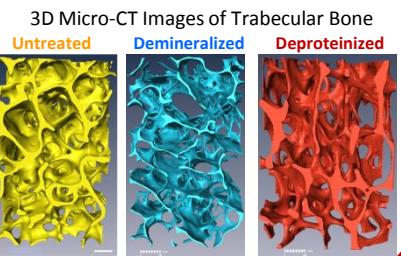
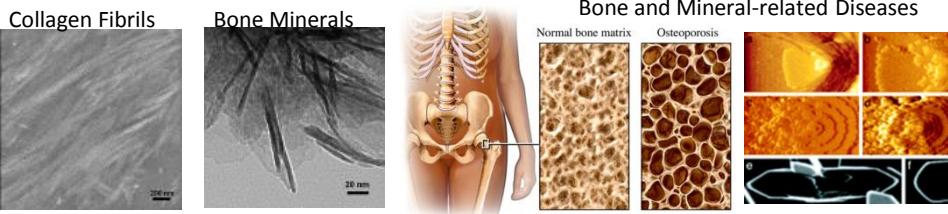


### Structural Biological (Natural) Materials

- Mollusk Shells
- Teeth & Tusks
- Natural Armors
- Avian Materials

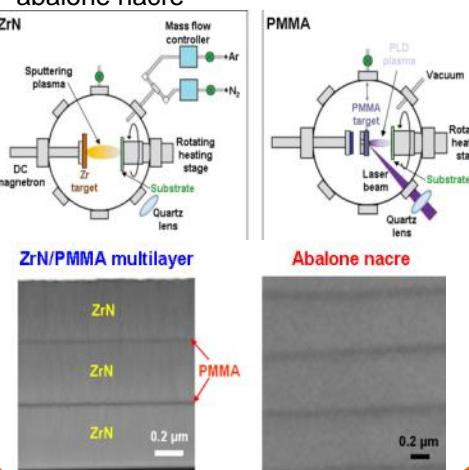


### Bone & Mineralized Tissues/ Biomedical Materials



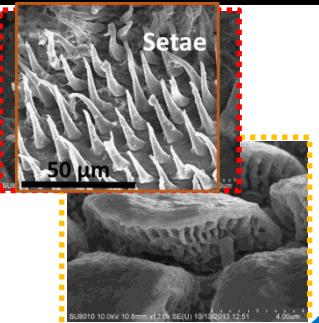
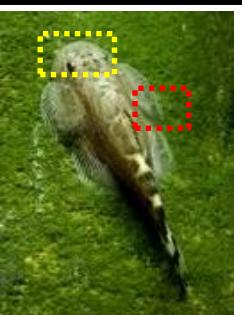
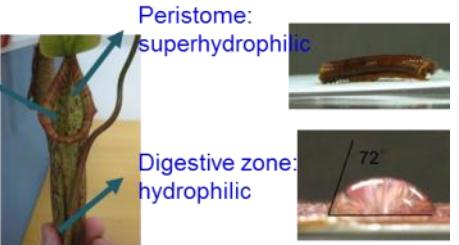
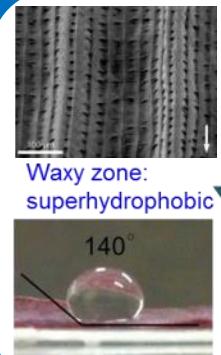
### Bio-inspired Composites/Coatings

Tough inorganic/organic multilayer composites inspired from the design of abalone nacre



### Biological Adhesives & Multi-Functional Surfaces

Multifunctional Surfaces Controlled by Wettability



# Water Collection: Our Approach - Dam

Hoover Dam (USA)



石門水庫洩洪



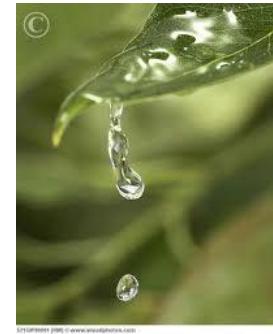
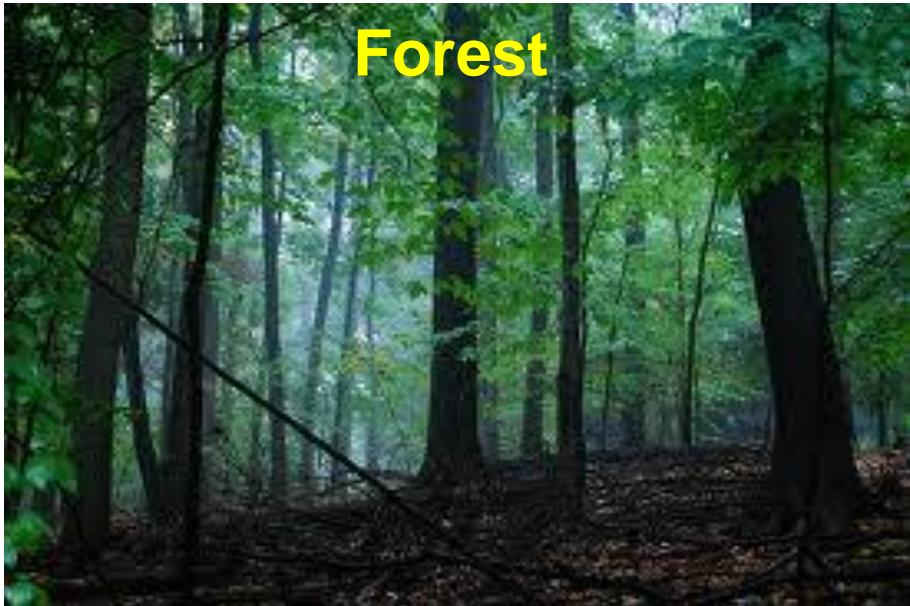
長江三峽大壩



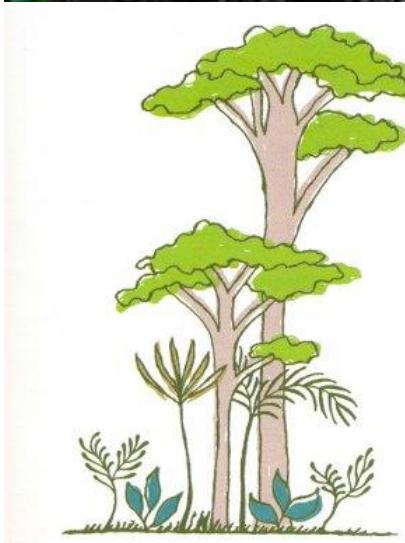
石門水庫淤積



# Water Collection: Nature's Approach

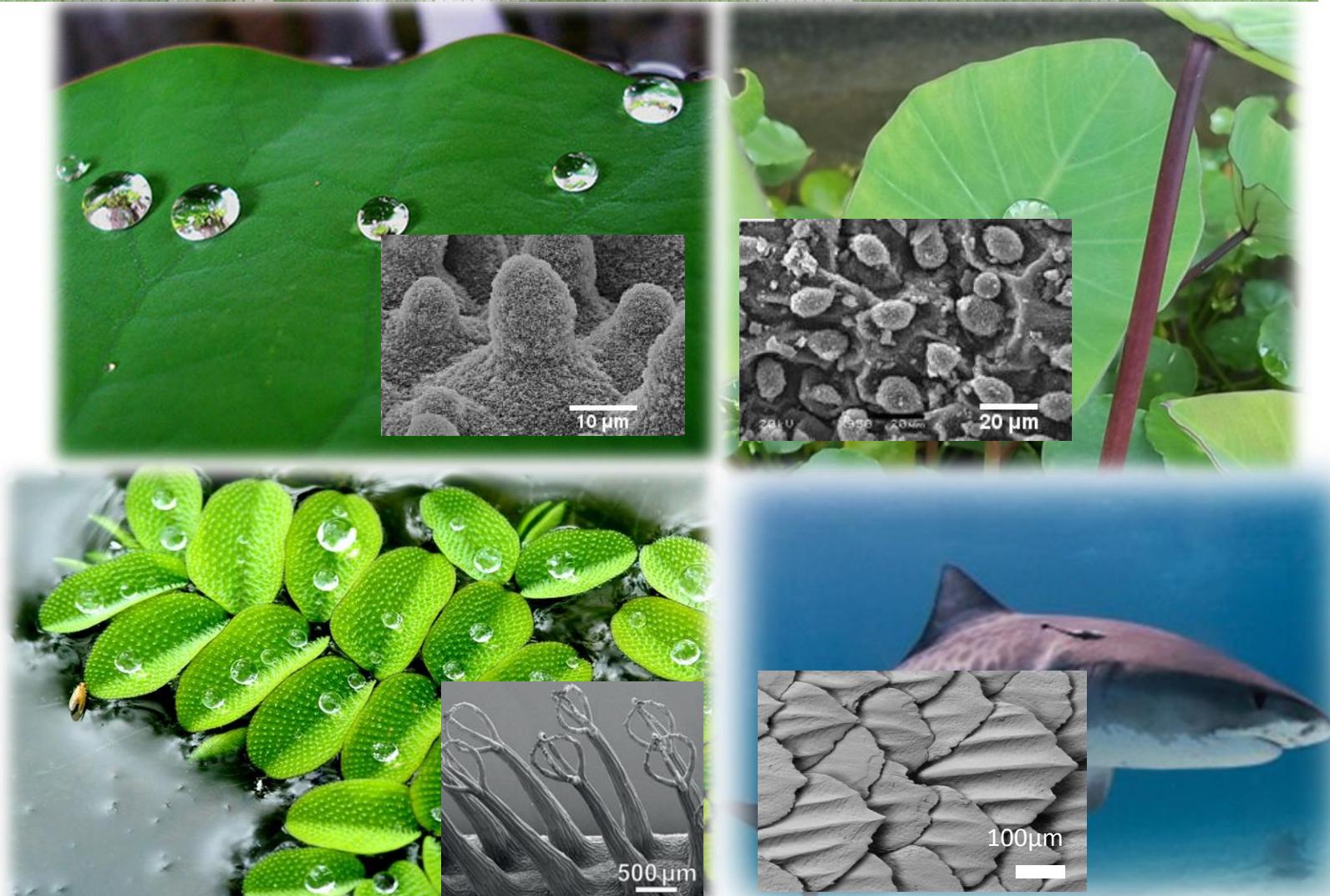


**Plants on the forest floor**



**Root systems**

# Multifunctional Surfaces in Nature



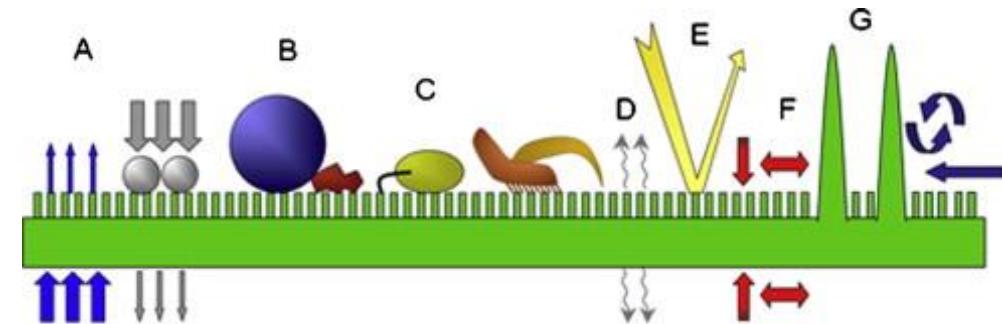
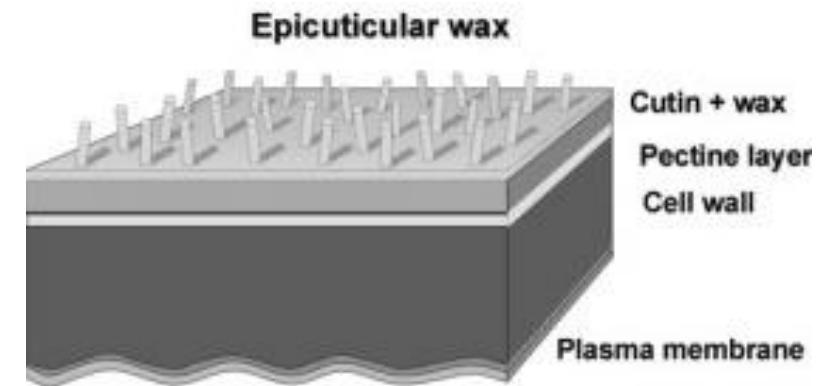
<http://ocean.si.edu/ocean-photos/biomimicry-shark-denticles>

Y.Y. Yan et al. *Advances in Colloid and Interface Science* 169 (2011) 80–105  
Barthlott, Wilhelm, et al. *Advanced Materials* 22.21 (2010): 2325-2328.

<http://organic-gardening.site27.com/lotus-plant-benefits/lotus-leaf/>  
Guo, Z. and W. Liu, *Plant Science*, 2007. **172**(6): p. 1103-1112.

# Multifunctional Surfaces of Plants

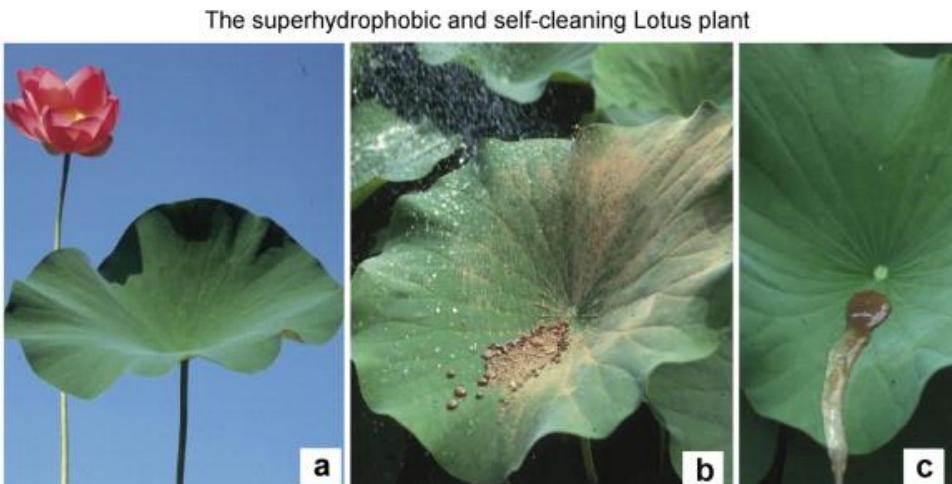
- Stratification of plant epidermis
  - Cuticle: cutin + wax
  - Pectine layer
  - Cell wall
  - Plasma membrane
- Epicuticular waxes are important for the functionality
- Multi-functionality:
  - (A) transport barrier
  - (B) surface wettability
  - (C) anti-adhesive, self-cleaning
  - (D) signaling, sensing
  - (E) optical properties: protection against harmful radiation
  - (F) mechanical properties
  - (G) reduction of surface temperature by increasing turbulent air flow



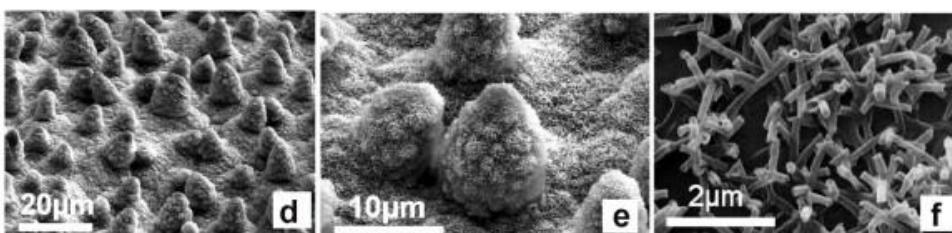
K. Koch, B. Bhushan, W. Barthlott, Prog Mater Sci 54 (2009) 137-178

# Water and wetland plants: experts in water repellent and self-cleaning

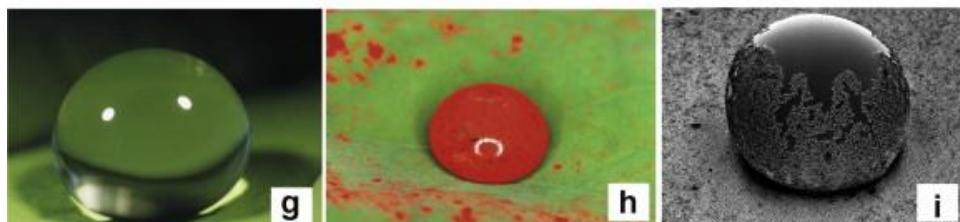
- Why water plants develop water repellent surface?
- CO<sub>2</sub> diffuses 10,000 times more slowly through water than air; water layers on leaves reduce the uptake of CO<sub>2</sub>
- The growth of microorganisms (bacteria and fungi) is limited by water shortage on plant surface



The lotus plant (*Nelumbo nucifera*) (a); removement of dirt particles from the leaves by water (b,c)



SEM figures of the lotus leaf microstrucutre (d) with papillose cells (e) and wax tubules (f) on it



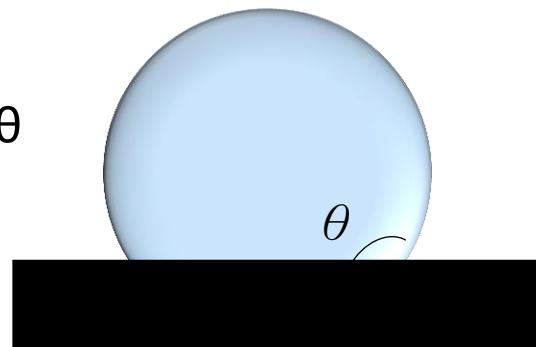
Water droplet on a Lotus leaf (g), and removement of lipoidic particles (sudan red) by water (h,i)

# Definition of Wettability

## Smooth surface

$$\gamma_{S/G} - \gamma_{S/L} = \gamma_{L/G} \cos\theta$$

$\theta$  : Contact angle



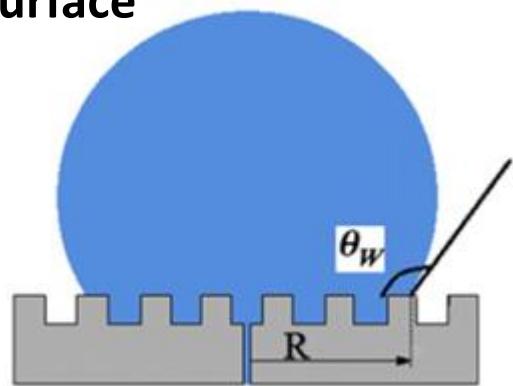
$CA < 10^\circ \Rightarrow$  Super-hydrophilic

$10^\circ \leq CA < 90^\circ \Rightarrow$  Hydrophilic

$90^\circ \leq CA < 150^\circ \Rightarrow$  Hydrophobic

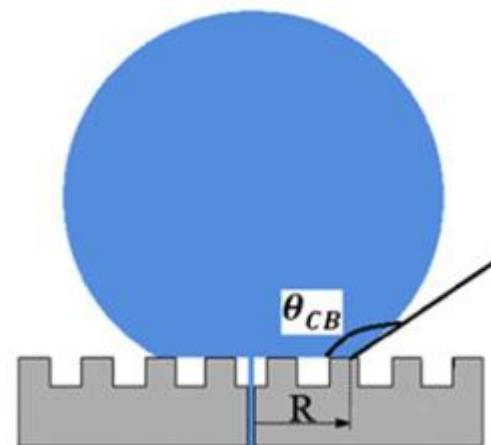
$CA \geq 150^\circ \Rightarrow$  Super-hydrophobic

## Rough surface



**Wenzel Model**

$$\cos\theta_W = r \cos\theta$$



**Cassie-Baxter Model**

$$\cos\theta_{CB} = f(\cos\theta + 1) - 1$$

Yan, Y.Y., N. Gao, and W. Advances in Colloid and Interface Science, 2011. 169(2): p. 80-105.

Young, T., Philosophical Transactions of the Royal Society of London, 1805. 95: p. 65-87.

Wenzel, R.N. Industrial & Engineering Chemistry, 1936. 28(8): p. 988-994.

Cassie, A. and S. Baxter, Transactions of the Faraday Society, 1944. 40: p. 546-551.

# Lotus Leaf

The surface of the lotus leaf has small pillars covered by a smaller scale protrusions covered with wax.

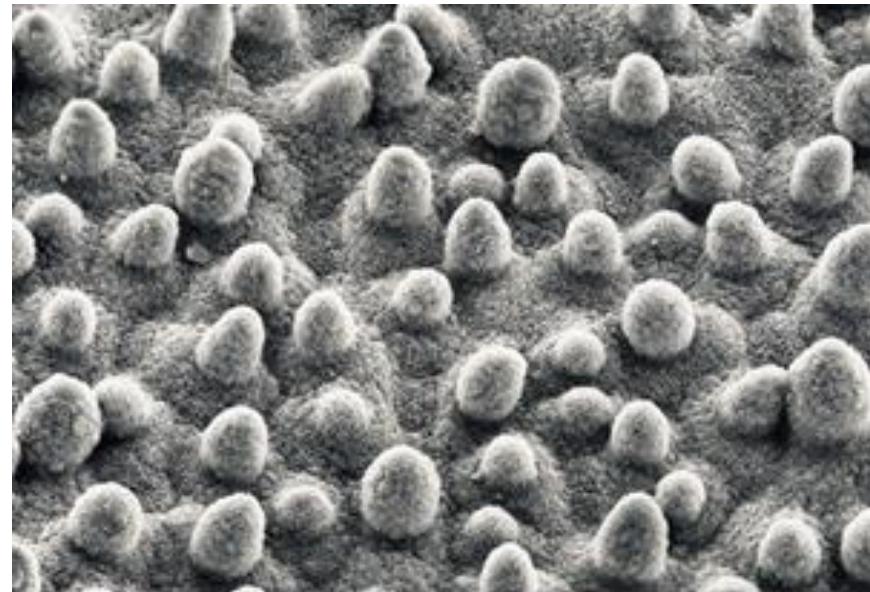
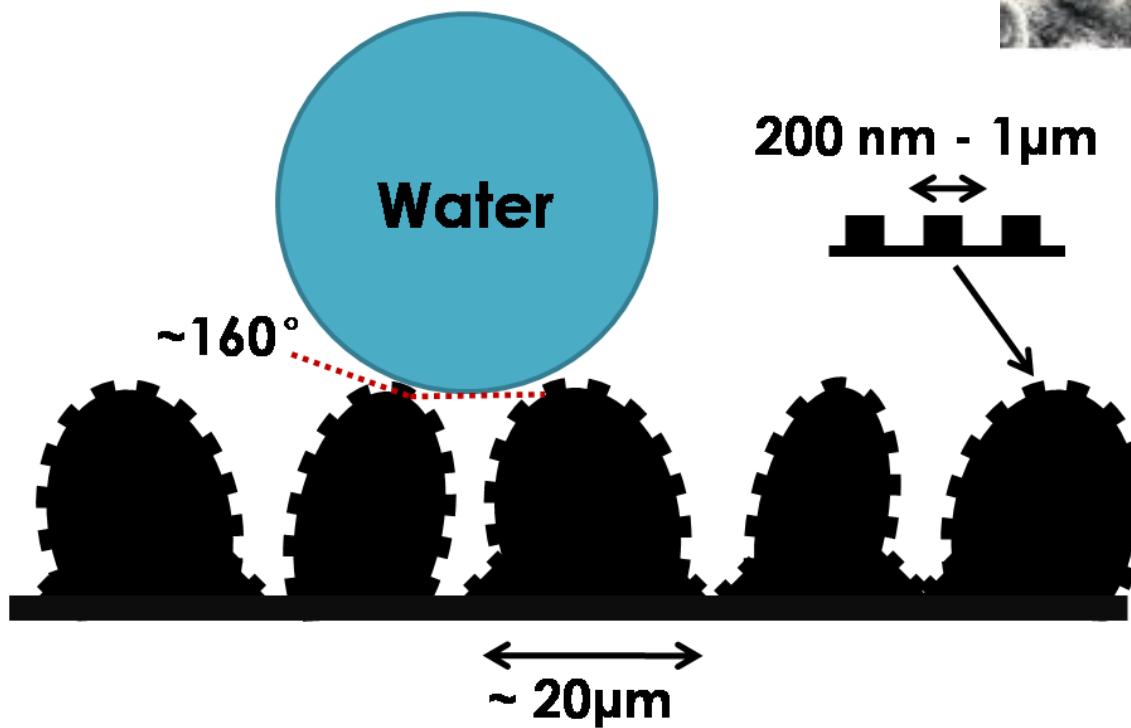


Image credit: W. Barthlott



Hydrophilic surfaces have contact angles below 90°.

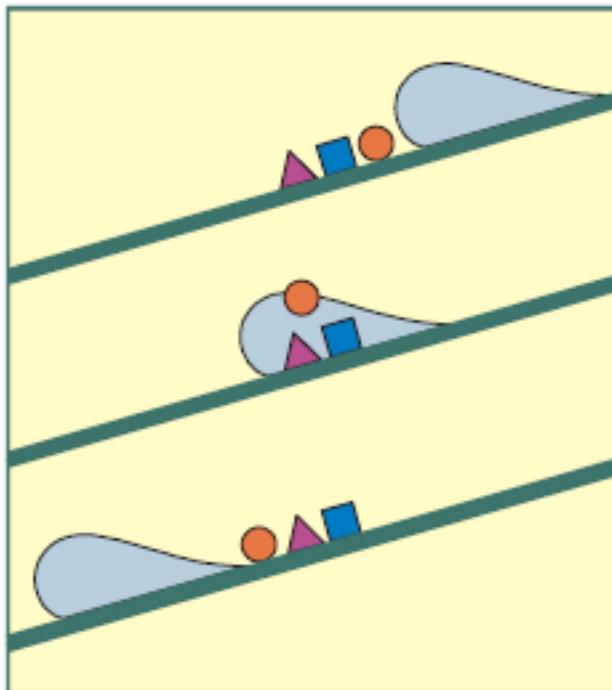
Hydrophobic surfaces have angles above 90°.

For the lotus, this angle can be as high as 160°.

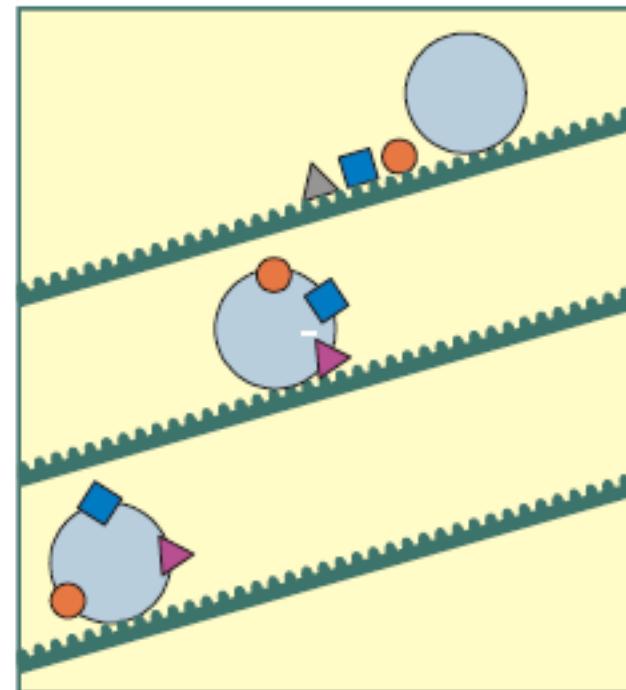
# The Lotus-Effect in action: self-cleaning surfaces

- CA $\geq$ 150°, CAH $\leq$ 10°

- Smooth hydrophobic surface



- Super hydrophobic surface



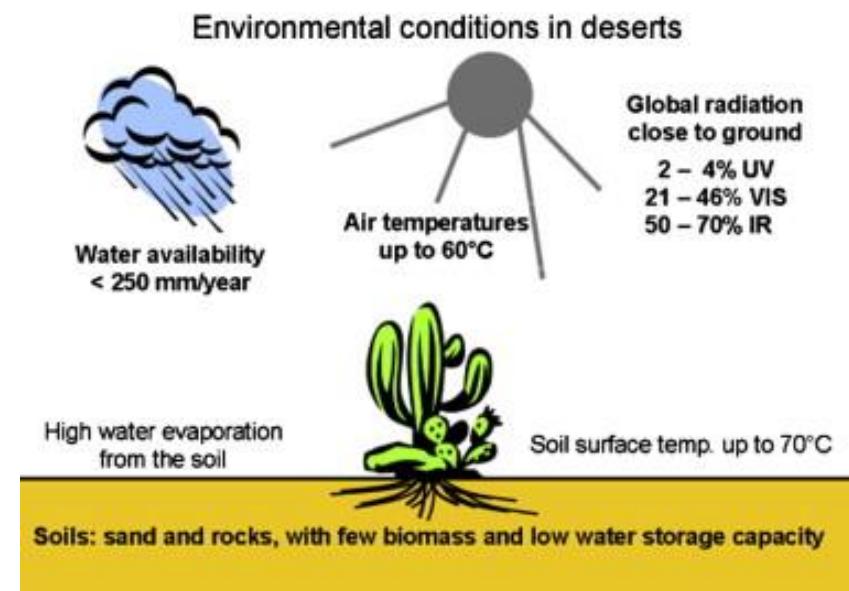
# Lotusan® paint



<http://www.biomimicryinstitute.org/>

# Plants of hot and arid environment: surviving strategies

- Extreme environmental conditions: low water availability, intensive solar radiation, high temperature, sand abrasion, etc.
- Functional surface structures:
  - water absorption
  - water storage
  - reduce water evaporation
  - optical properties:
    - reflection of visible light and UV
    - UV-absorption
  - wear resistant

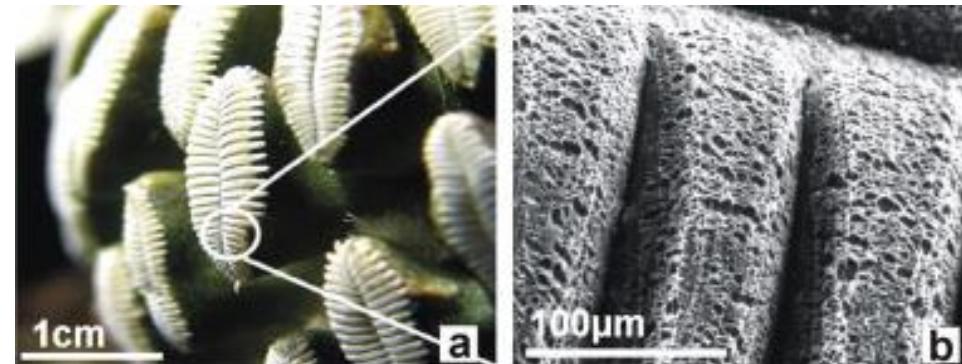


# Water absorption and storage



*Pelecyphora aselliformis*

[http://farm1.static.flickr.com/203/473347954\\_d5bc9d7d00.jpg](http://farm1.static.flickr.com/203/473347954_d5bc9d7d00.jpg)

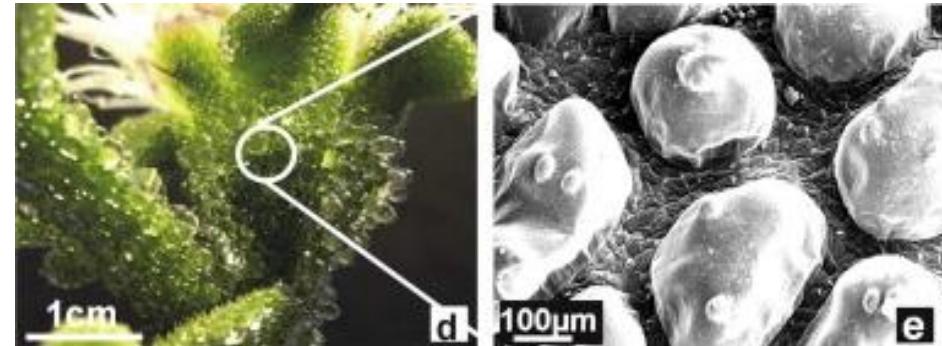


Porous thorns for water absorption



*Mesembryanthemum crystallinum*

[http://www.redescepalcala.org/ciencias1/Flora/imagenes\\_2/mesembryanthemum\\_crystallinum.jpg](http://www.redescepalcala.org/ciencias1/Flora/imagenes_2/mesembryanthemum_crystallinum.jpg)

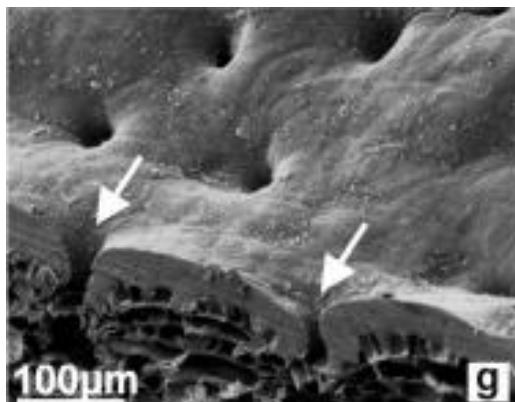


Water storage vesicles

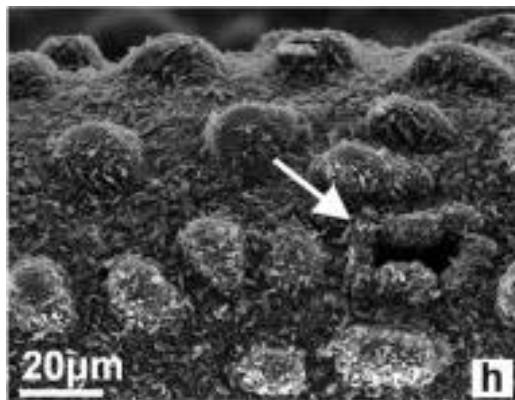
K. Koch, B. Bhushan, W. Barthlott, Prog Mater Sci 54 (2009) 137-178

# Reduction of water loss

**sunken stomata**

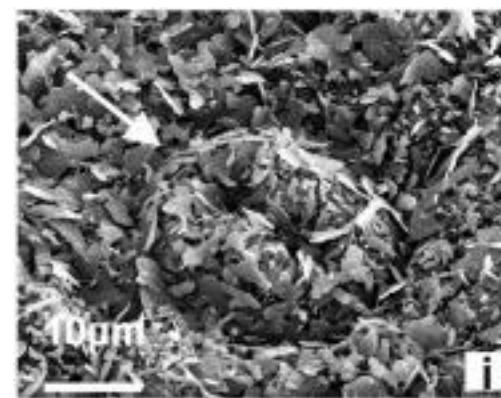


*Rhipsalis spec.*



*Aloe porphyrostachys*

**wax covered stomata**

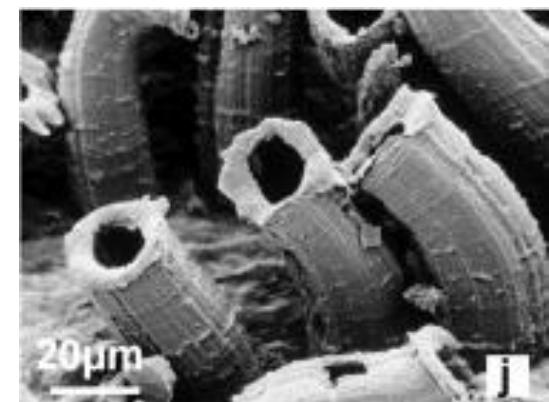


*Aloe vera*



[http://mydnafragrance.com/perfume/images/AloeVeraPlant\\_Full.jpg](http://mydnafragrance.com/perfume/images/AloeVeraPlant_Full.jpg)

**wax chimneys**



*Colletia cruciata*

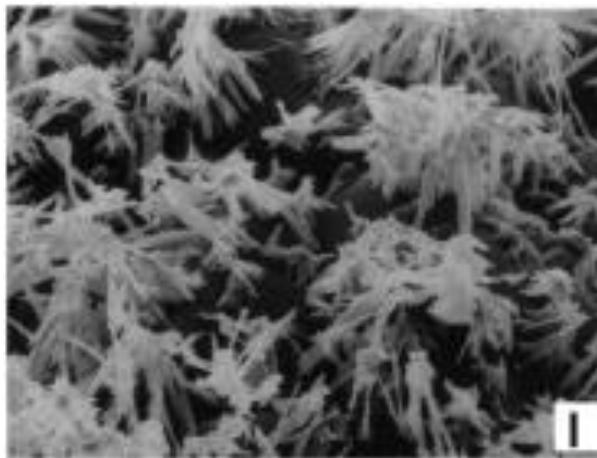


[http://www.strangewonderfulthings.com/Colletia\\_paradoxa\\_cruciata\\_Anchor\\_Tree\\_0007.jpg](http://www.strangewonderfulthings.com/Colletia_paradoxa_cruciata_Anchor_Tree_0007.jpg)

# Protection from harmful solar radiation

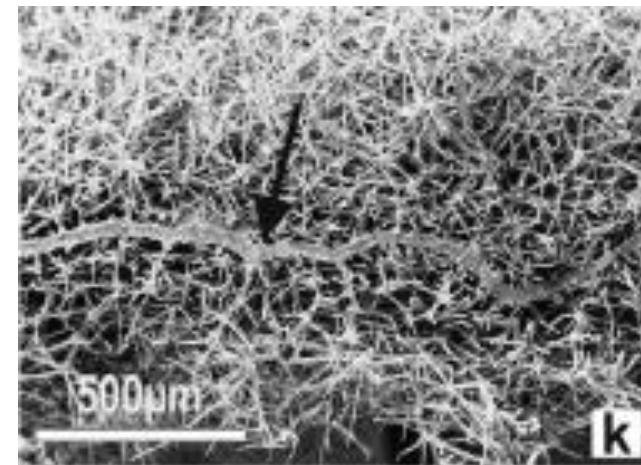
- Visible light/UV reflective structures
  - 3-D structured waxes and wax crusts
  - dense coverage with air-filled hairs
- UV-B absorbing compounds

**3-D structured waxes**



*Kalanchoe pumila*

**Dense layer of hairs**



*Salvia spec.*

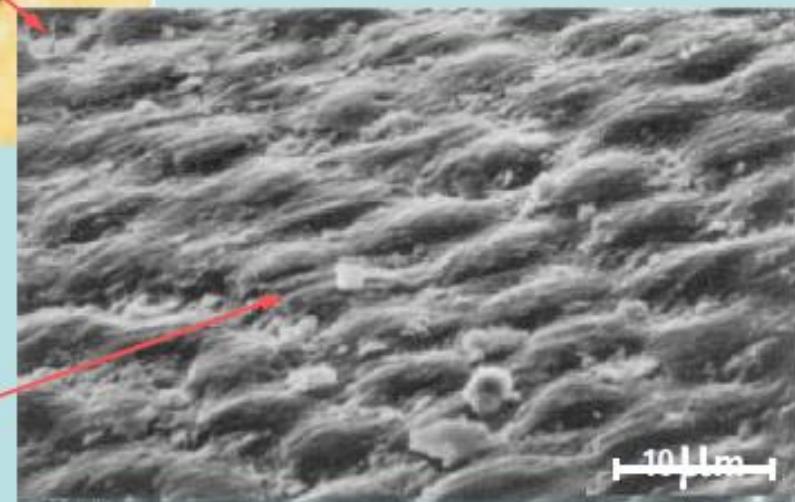
# Water Harvesting Beetle



Hydrophilic peaks

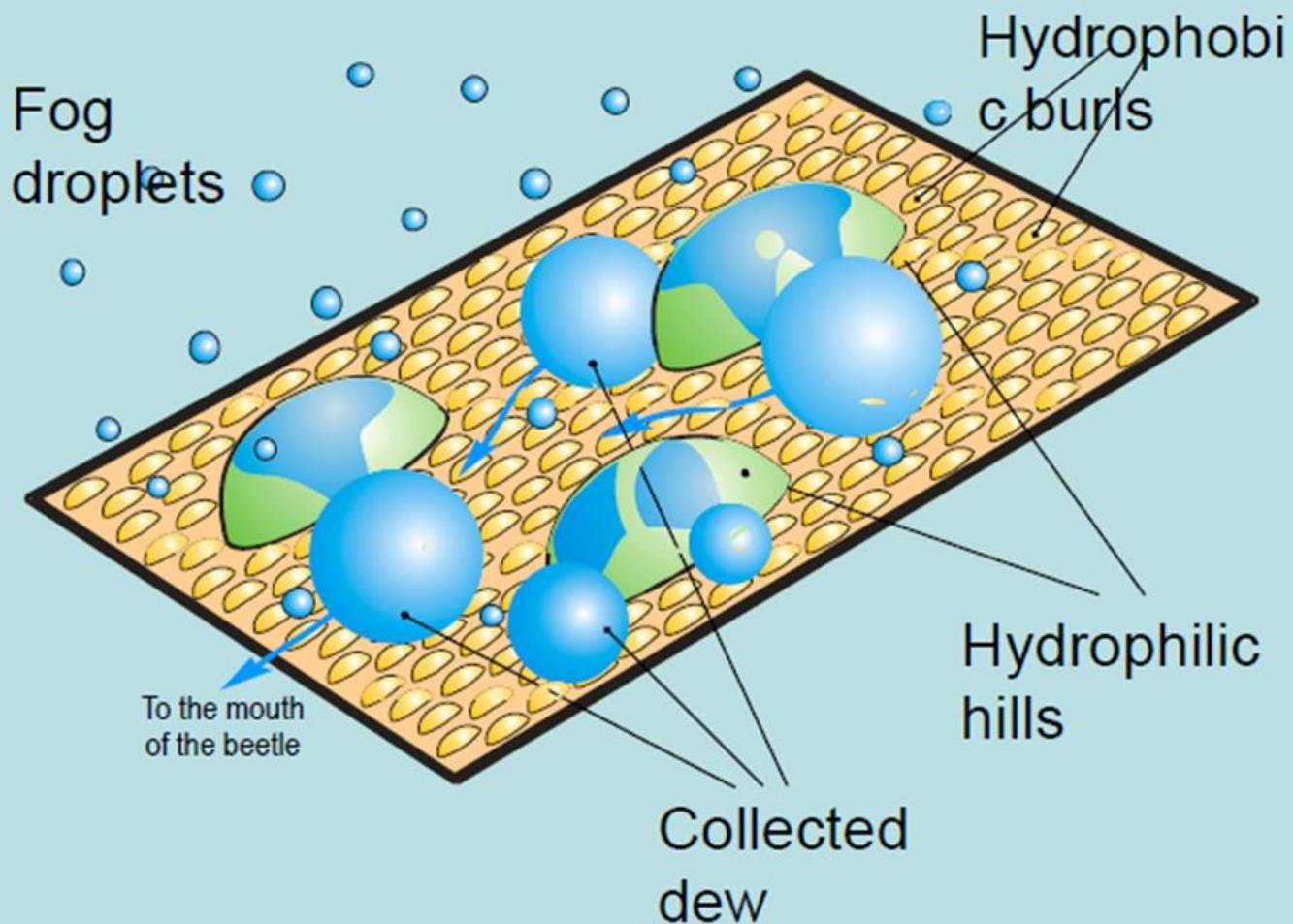
Hydrophobic burled lowland  
similar to the Lotus-Effect®

Darkling beetle of the Namib desert  
(*Stenocara* sp.)

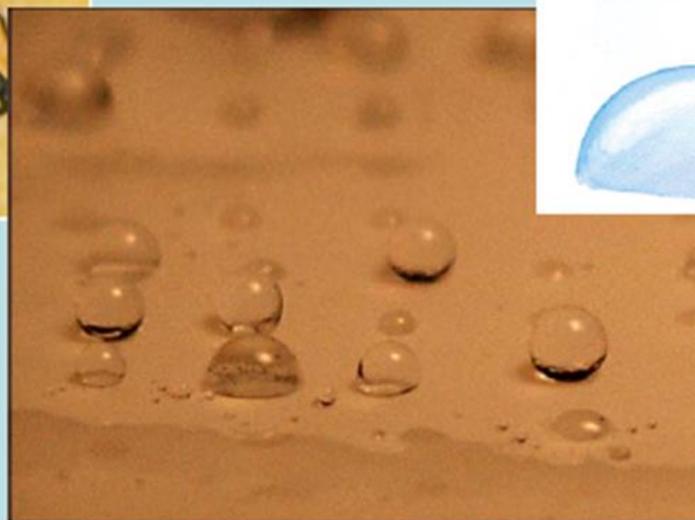


Andrew R. Parker and Chris R. Lawrence

# Water Harvesting Mechanism



# *Beetle-inspired Material for water harvester: the patterning*

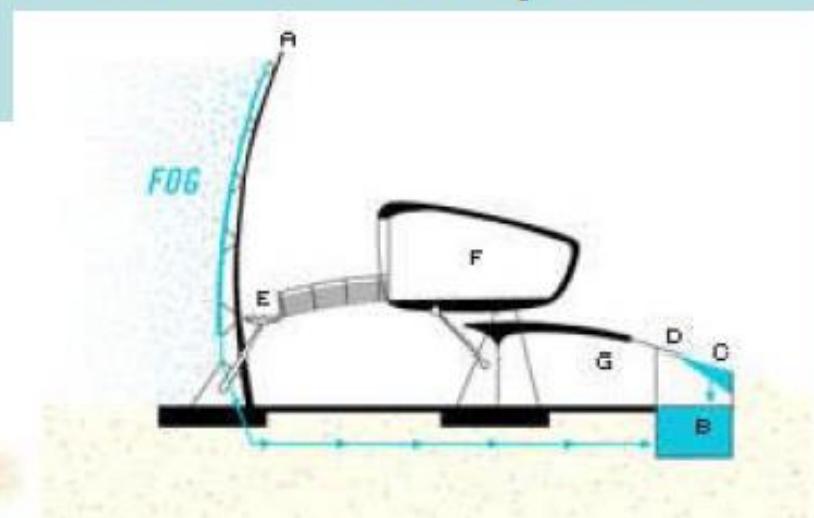


New material that copies the properties of the wing surface of the Namibian desert beetle for collecting precious drinking water from an invisible mist. Inventa Partners: Air Conditioning for recycling water. 2004 (Original research by MIT)

Namib Desert beetle



# Beetle-inspired water harvester: The pose



A nylon-mesh sail (a) collects the fog as it rolls in. As the mesh becomes saturated, gravity feeds the water into an underground tank (b), where it joins pumped-in seawater (c) that has been desalinated using photovoltaic panels (d). A footbridge (e) leads to a classroom pod (f), under which is office space (g).

Photos: Left, courtesy QinetiQ; right, courtesy KSS Architects, Ltd.

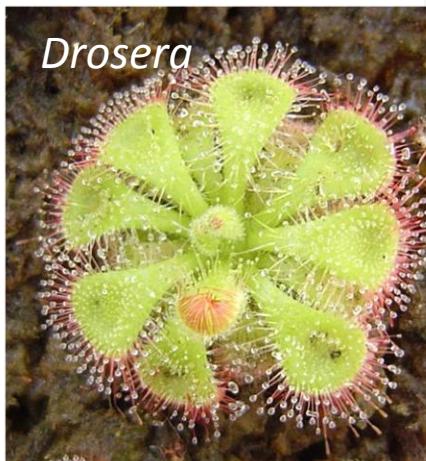
# Carnivorous Plants

- Nutrient-deficient environment (**N, P**)
- Specialized multifunctional surface: attracting, capturing, retaining and digesting

Butterworts



*Drosera*



*Nepenthes*



*Utricularia*



Flytrap



*Sarracenia*



## 豬籠草的誘惑

每當我在臺灣植物保種中心導覽訪客時，一提起豬籠草，大家眼睛都為之一亮，快步跟上。這類跨界生活的熱帶物種就是這麼迷人，瓶口的氣味和蜜汁引來昆蟲，失足落入瓶身，光滑的蠟質內壁讓牠們攀爬不上，只能禁錮在消化液中，最後為這長在貧瘠土壤的特化植物貢獻了氮肥和磷肥。

然而豬籠草的食性並非如此單調，它們之中也有素食者，蘋果豬籠草即是。它的瓶子長在地上，瓶蓋全敞開，內無蠟質壁，收集的是落葉殘渣。食性更怪的是勞氏豬籠草，它的瓶蓋結滿了白糖霜，引來鼴鼯坐在瓶口舔食，鼴鼯的習性是邊吃邊拉，於是瓶身就成了馬桶。嗜糞者還有萊佛士豬籠草，它的瓶子設計是邀來蝙蝠隱身長住，屎尿都成了營養。世間有120種豬籠草，保種中心蒐集了80種，再加上300餘天然及人為雜交種，深得訪客喜愛和玩家覬覦，但我最期盼的是能得到科學

家的青睞，願意深入研究這群已經達到演化顛峰的瀕危物种。

顧客終於上門了，是位仿生學的新秀專家，清華大學材料系的陳柏宇。他想研究捕蟲的豬籠草瓶口何以特別滑不溜丟，連螞蟻都站不住腳，於是率研究生們到保種中心採集各式瓶子，初步結論是：瓶口溝槽狀裙緣上的無數奈米級小突起，把蜜汁和水混成了超親水結構，若是能人工合成類似的材料，那麼吞藥再也不會噎到，大顆的維他命丸就可以咕溜直接滑進胃裡了。陳柏宇在2013年初為《科學》寫了篇回顧專論，〈以大自然為師——仿生材料〉是他為《科學人》讀者寫的普及版，再加上〈夢幻材料真未來〉，就成了我們新春新希望的專題報導了。

〈夢幻材料真未來〉介紹的10項科學突破中，我最期待的是能把二氧化碳礦化成岩石的演練。如果成真，地球不再增加溫室氣體，過往的偏差也將深埋地層，瀕危的生態環境當然會因之舒緩。多樣的豬籠草已罕見於原野，保種中心應該只是暫時的庇護所，當它們能重回山林時，才是人與自然的真正和諧。



李家維

影像來源：鄧志忠／攝影室、朱家維

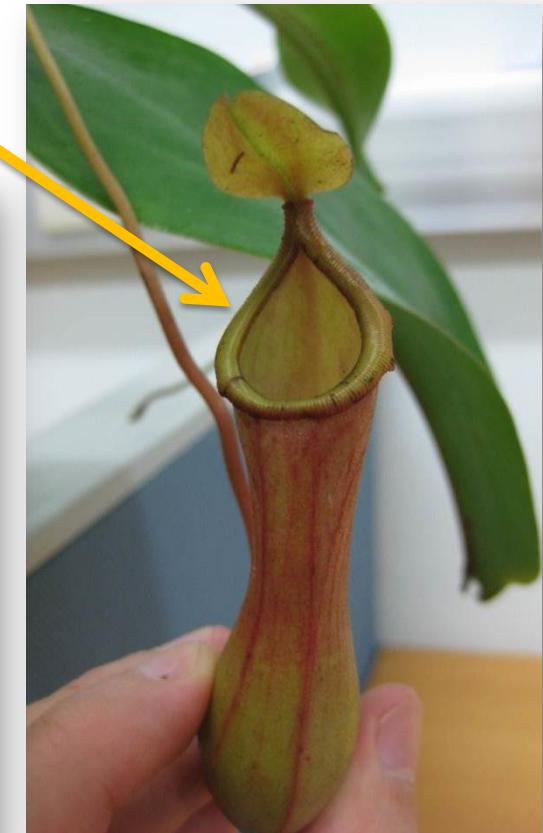
# Nepenthes



*N. x miranda*

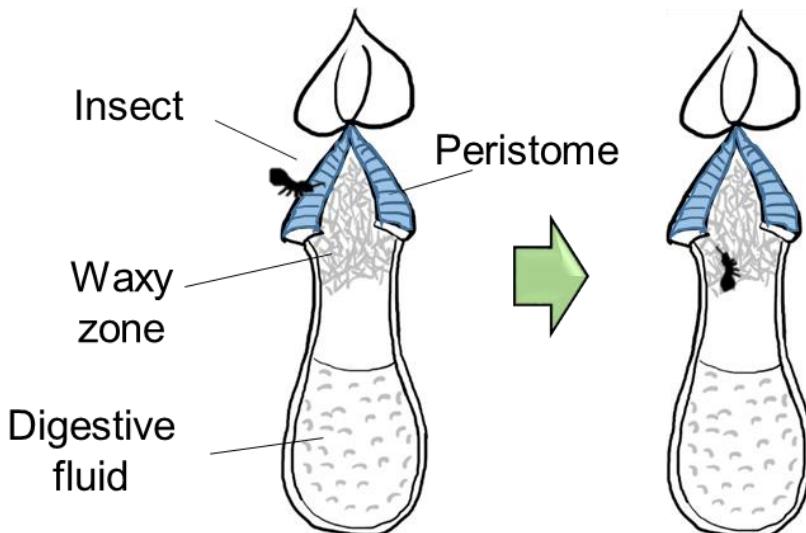


*N. x hookeriana*



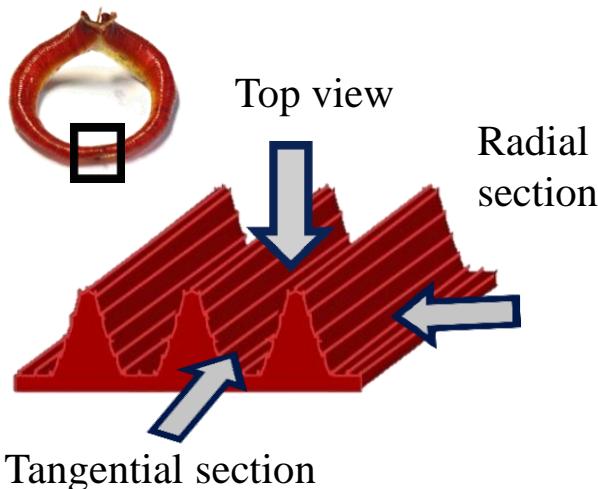
*N. x ventrata*

# Capture Mechanism of Nepenthes-Peristome



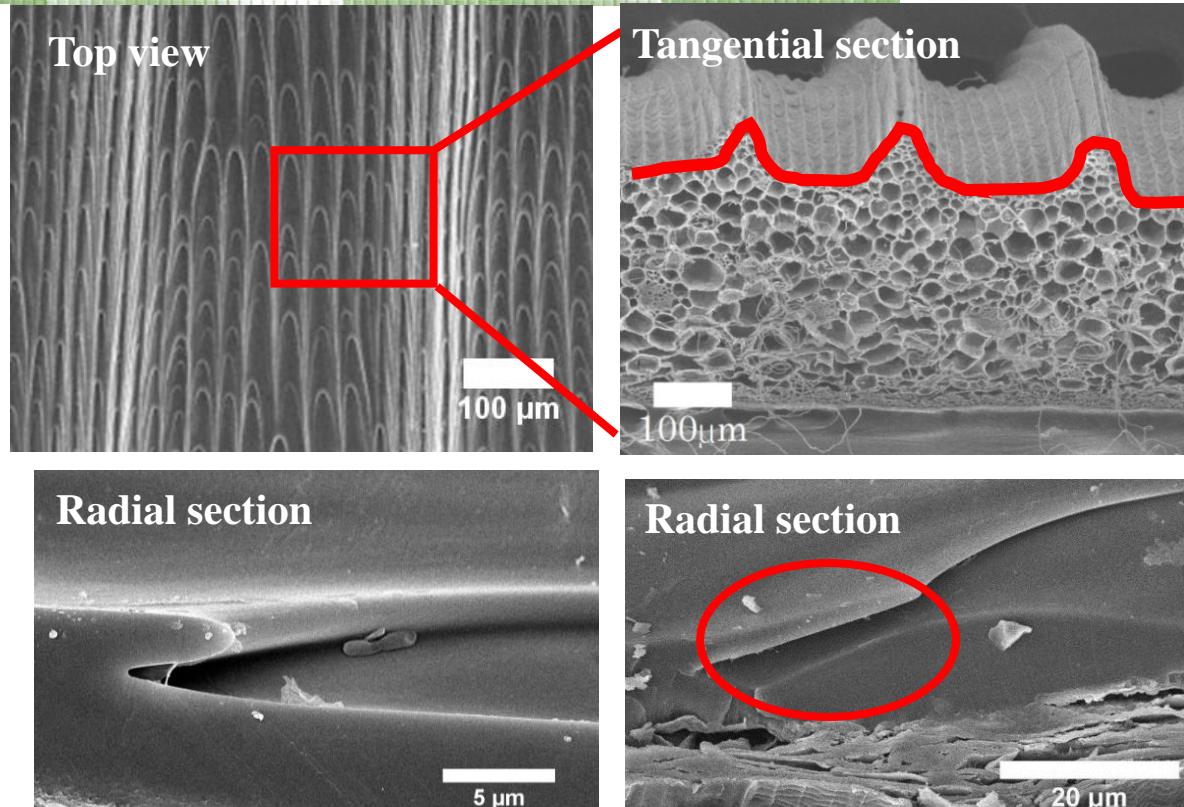
- Nectar attracts insects
- Water film forms in wet and moist environment
- Frictionless and slippery surface
- Efficient trapping mechanism

# Peristome-Microstructure



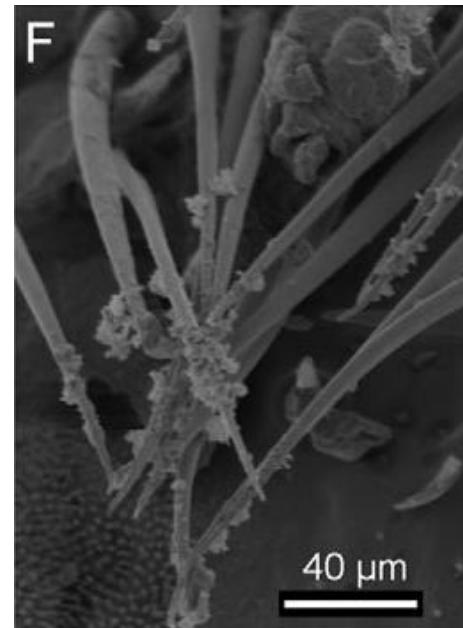
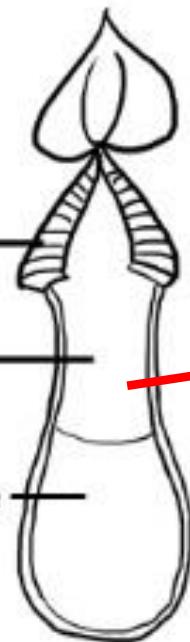
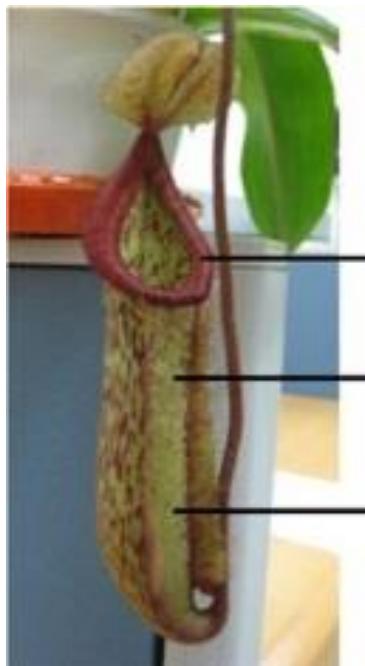
## Hierarchical structure

- Ridge-like stripe
- Large and small grooves
- Epidermal cells cover on the surface
- Radial orientation
- Small cavity



Microstructure	First-order	Second-order
Height	150μm	5μm
Width	250μm	5μm
Spacing	450μm	40μm

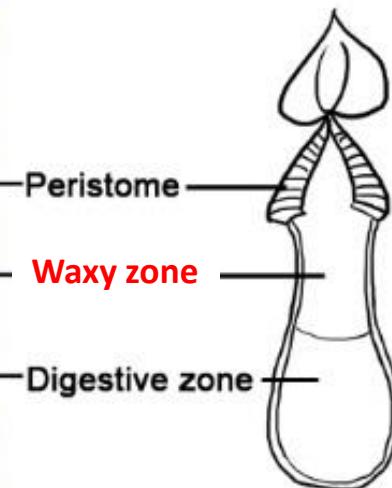
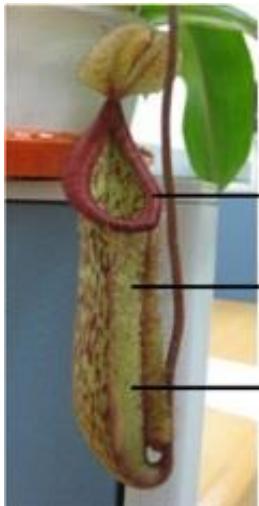
# Capture Mechanism of Nepenthes-Waxy zone



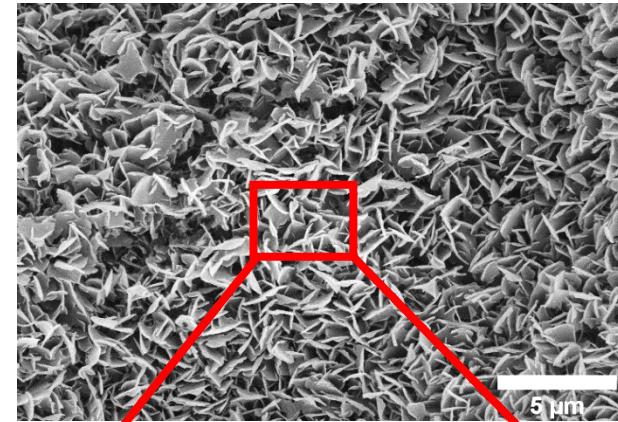
## Fragile wax crystals

- Hamper the locomotion of insect
- stick on the foot of prey

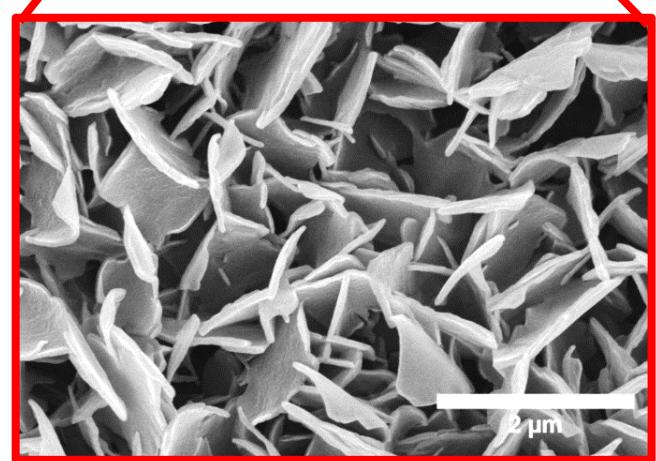
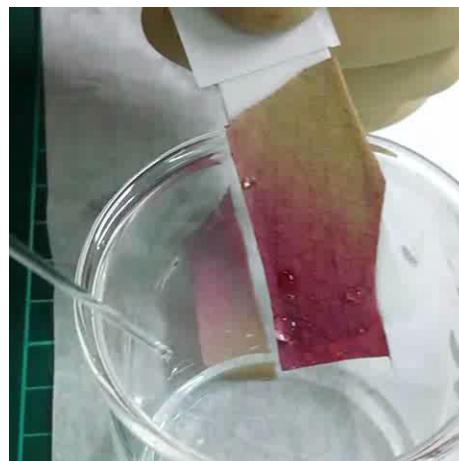
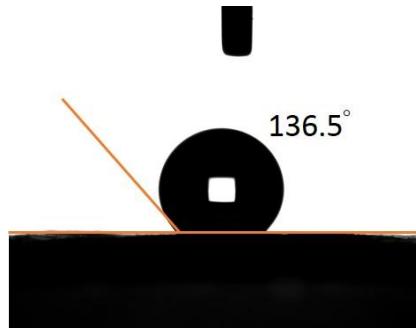
# Waxy zone



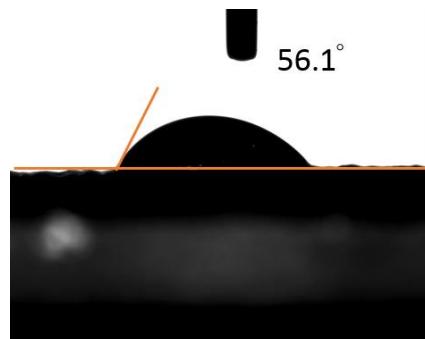
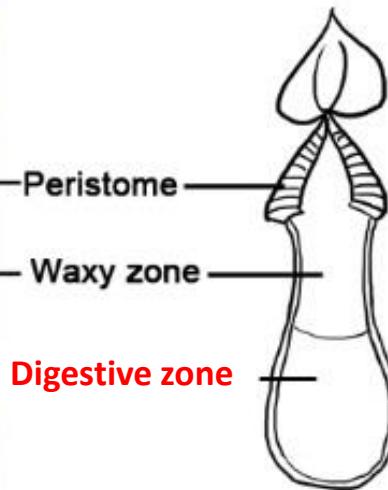
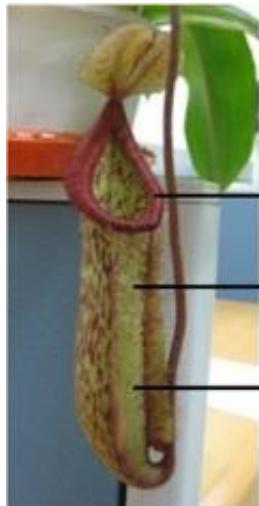
3-D Plate-like wax



- Hydrophobic surface
- Contact angle  $\sim 130^\circ$

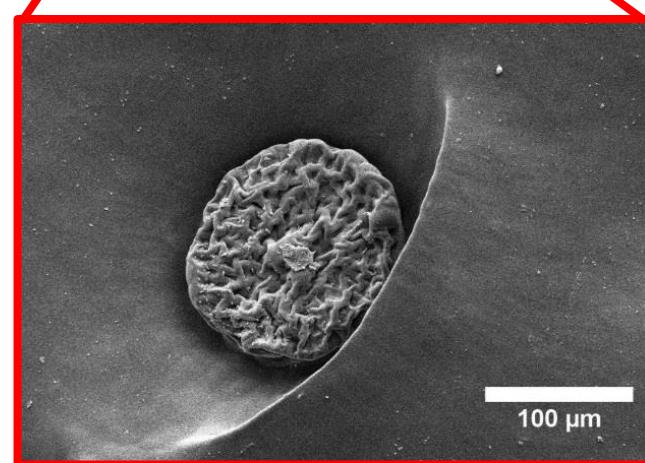
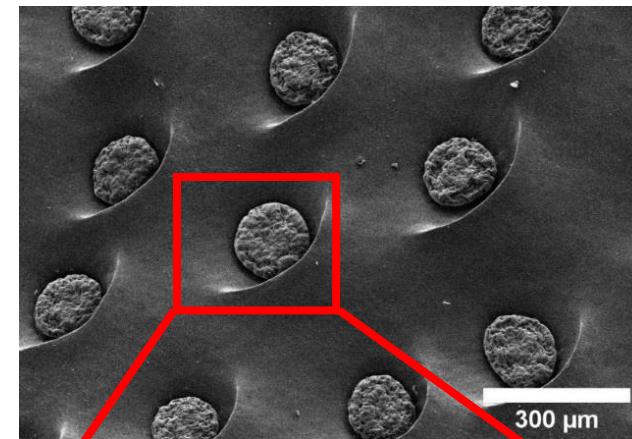


# Digestive zone

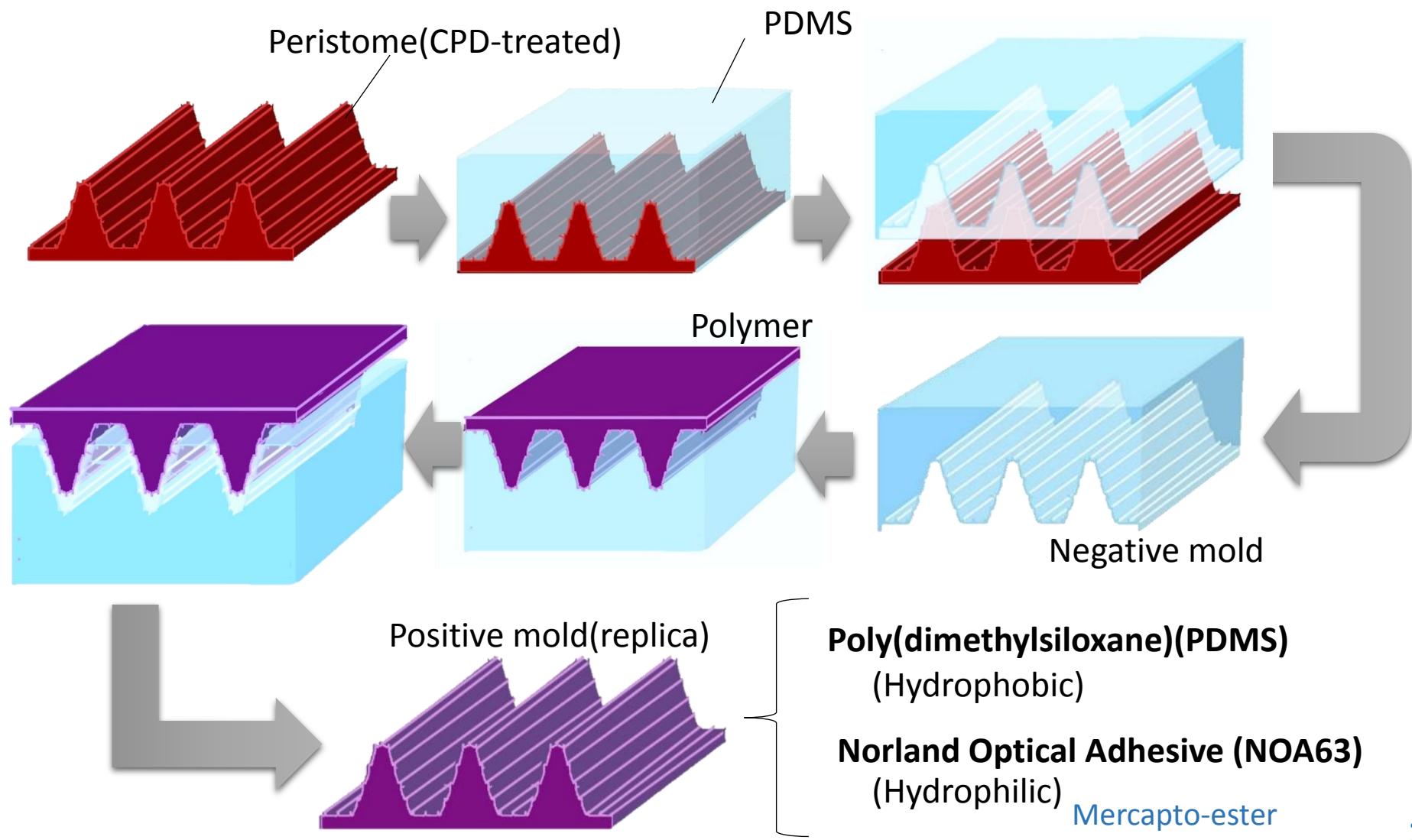


- Hydrophilic surface
- Contact angle  $\sim 56^\circ$

- Glands cover the inner surface



# Replication Process

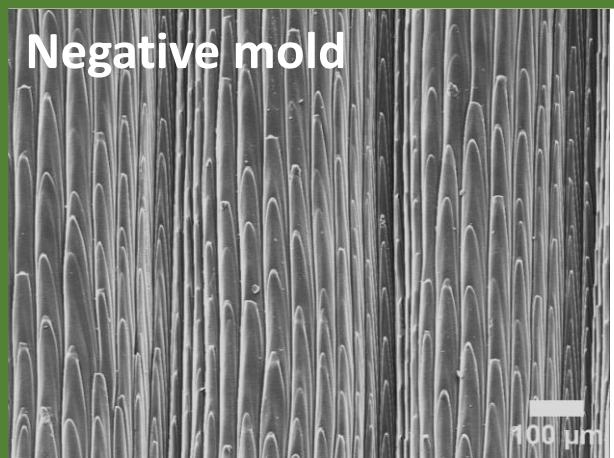


# SEM - Replicas

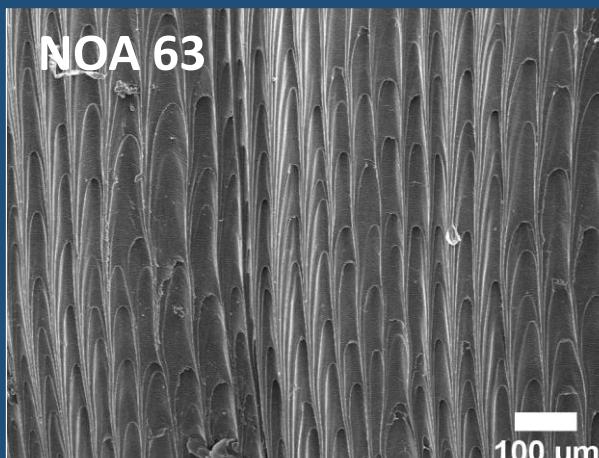


Positive mold

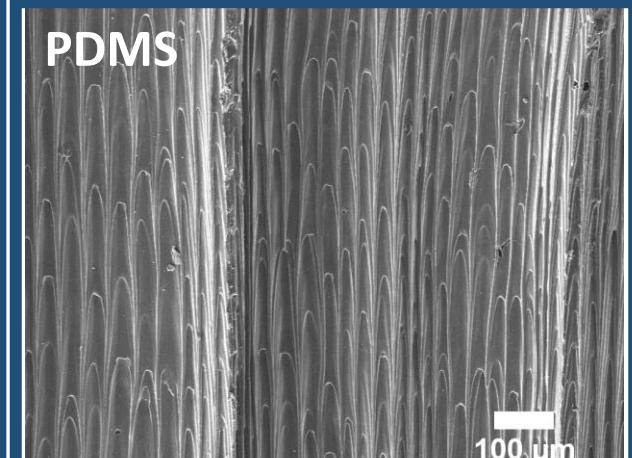
Negative mold



NOA 63

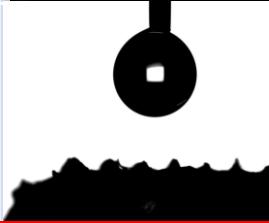


PDMS



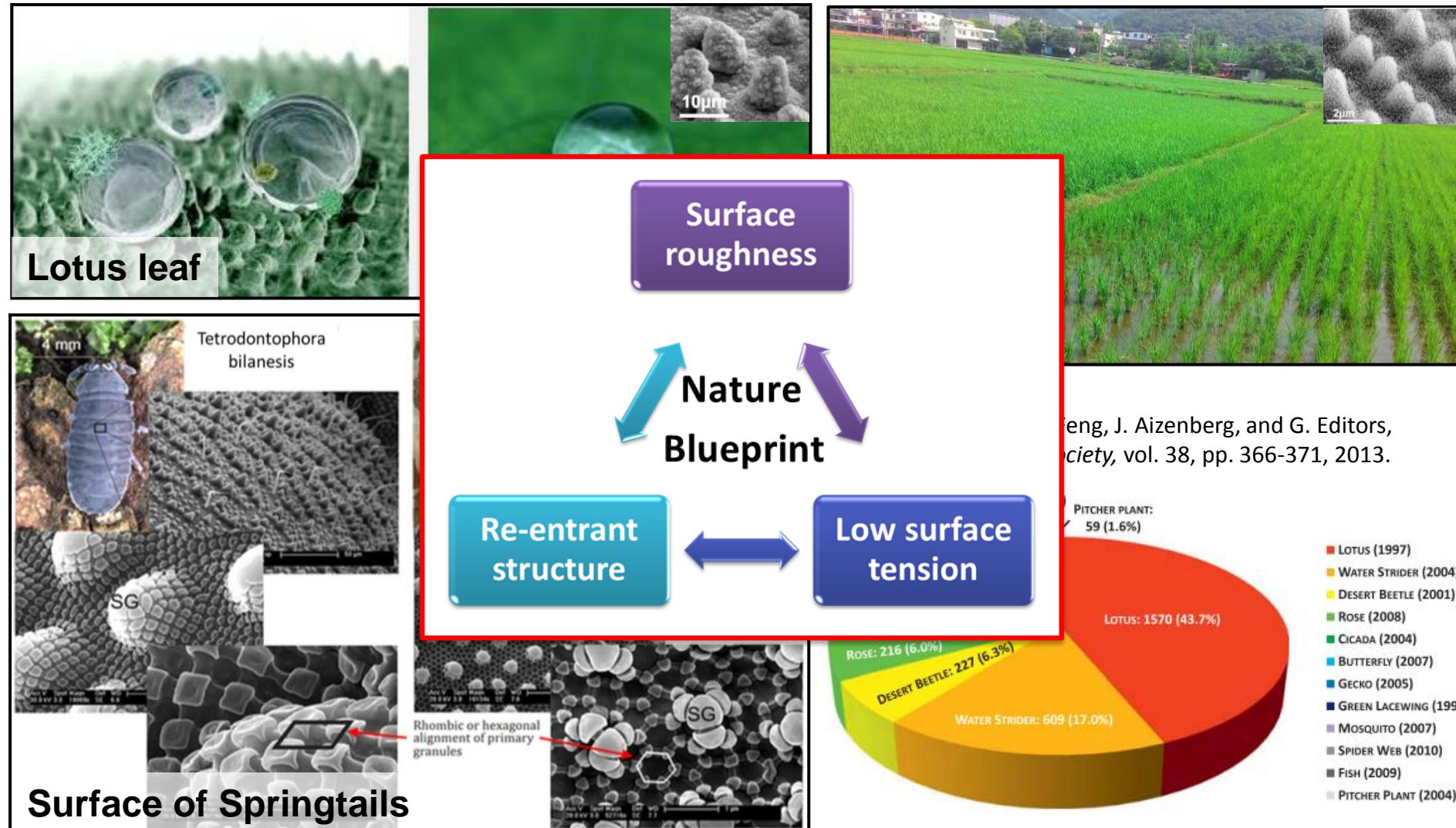
The microstructure is successfully replicated by both polymers

# Contact Angle Measurement of Coated Surfaces

Substrate	Distance	Time(sec)	Original $\theta$	$\theta$ (average)	
Slide	20cm	10	50°	124.5°	
		20		122.6°	
Flat PDMS	20cm	10	110°	135.9°	
		20		133.9°	
PDMS replica		10	140°	Water repellent	
		20			

- Particles provide additional roughness which increases contact angle
- Increasing spray time doesn't affect the value of contact angle
- With the hierarchical microstructure, coated surfaces become water repellent

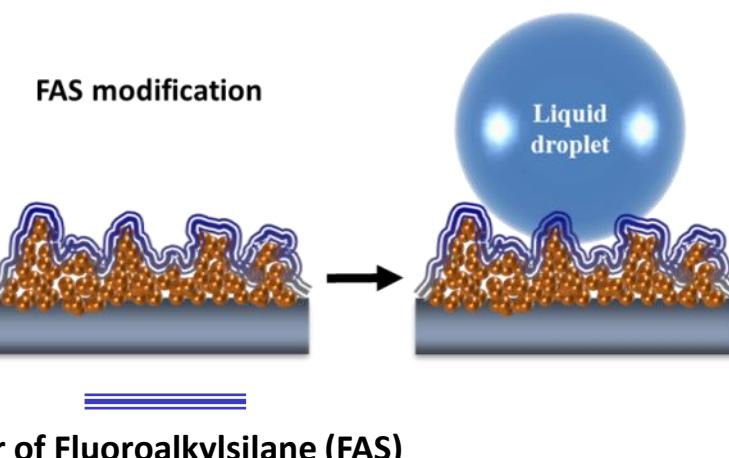
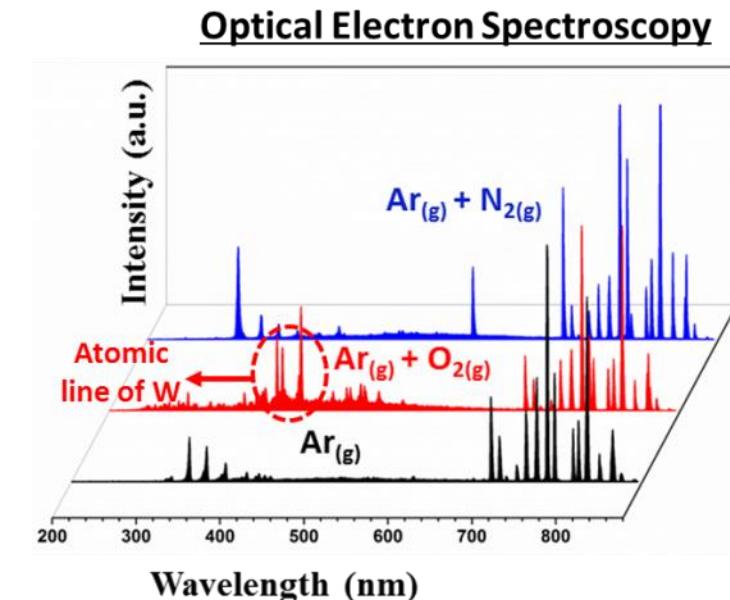
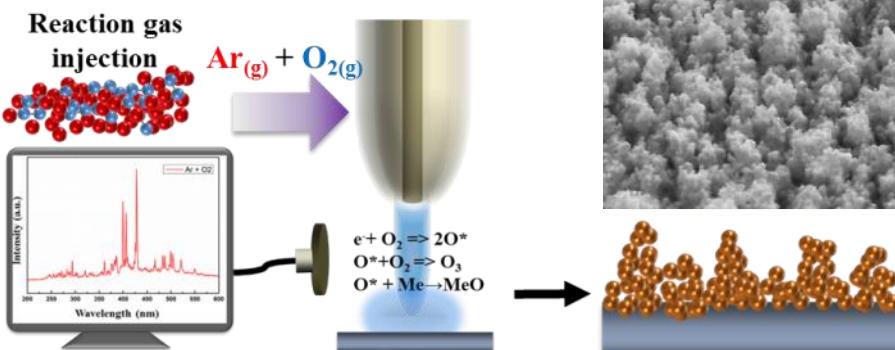
# Superhydrophobic/Oleophobic Surfaces in Nature





# Working Principle of Facile Route for Developing *Omniphobic Surfaces*

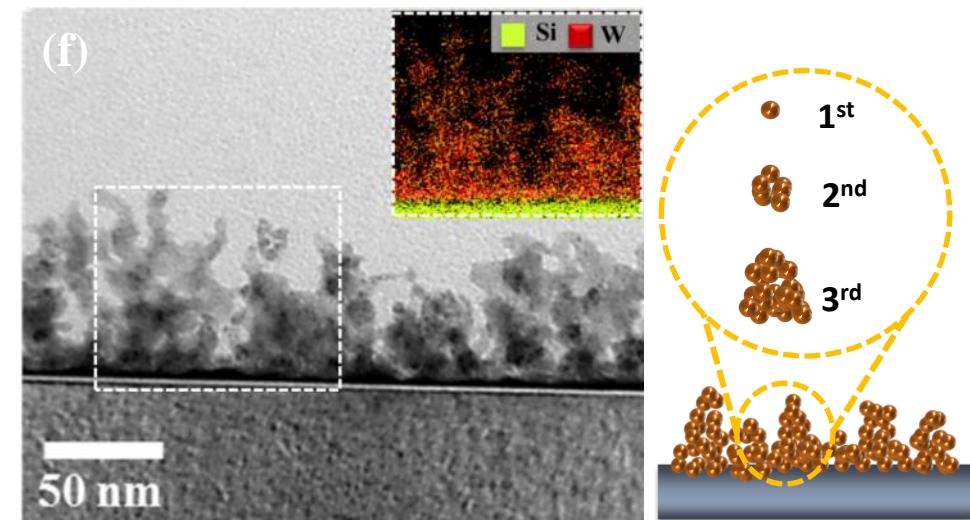
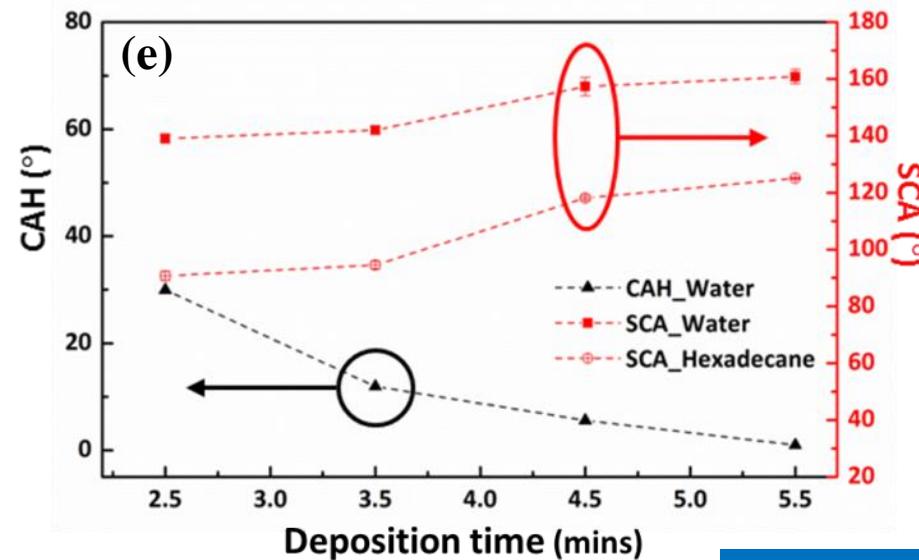
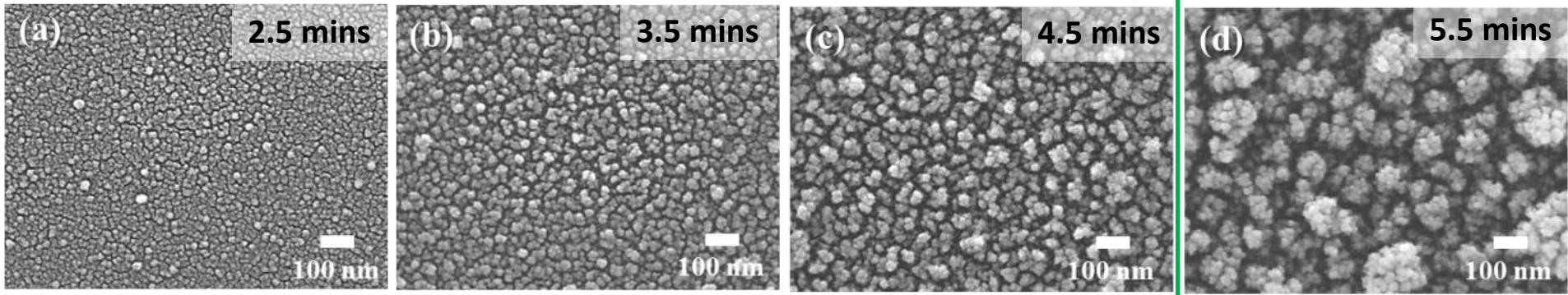
- A two-short-step method.
- The entire process is under atmospheric pressure and room temperature.
- Self-assembly formed porous tungsten oxide coating with submicro- and nanoscaled hierarchical structures.
- Superior liquid repellency toward water and hexadecane.



# Morphology and Wettability Characterizations

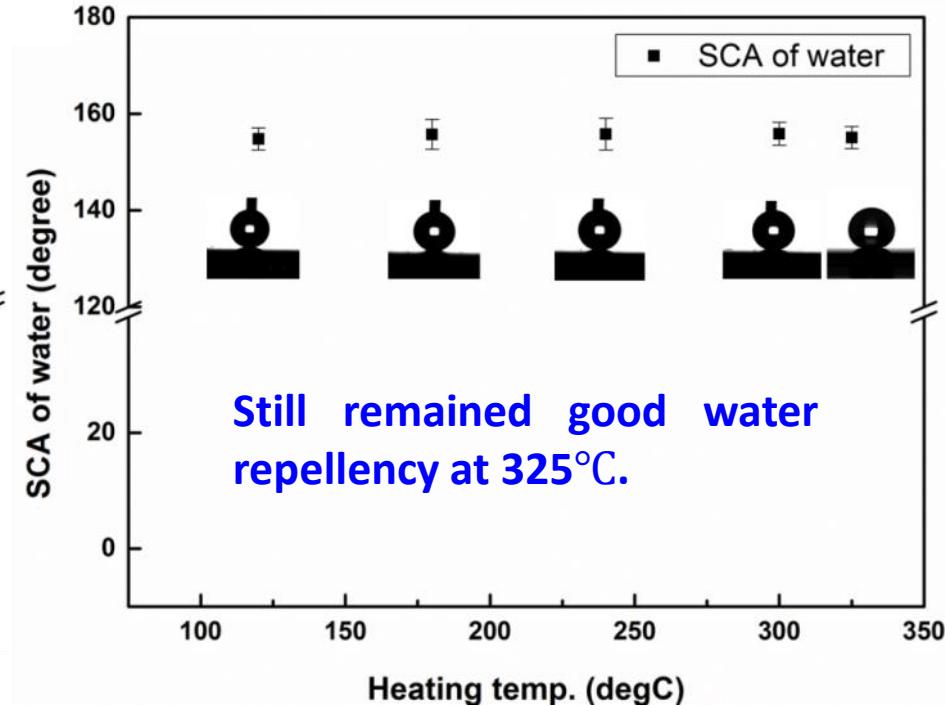
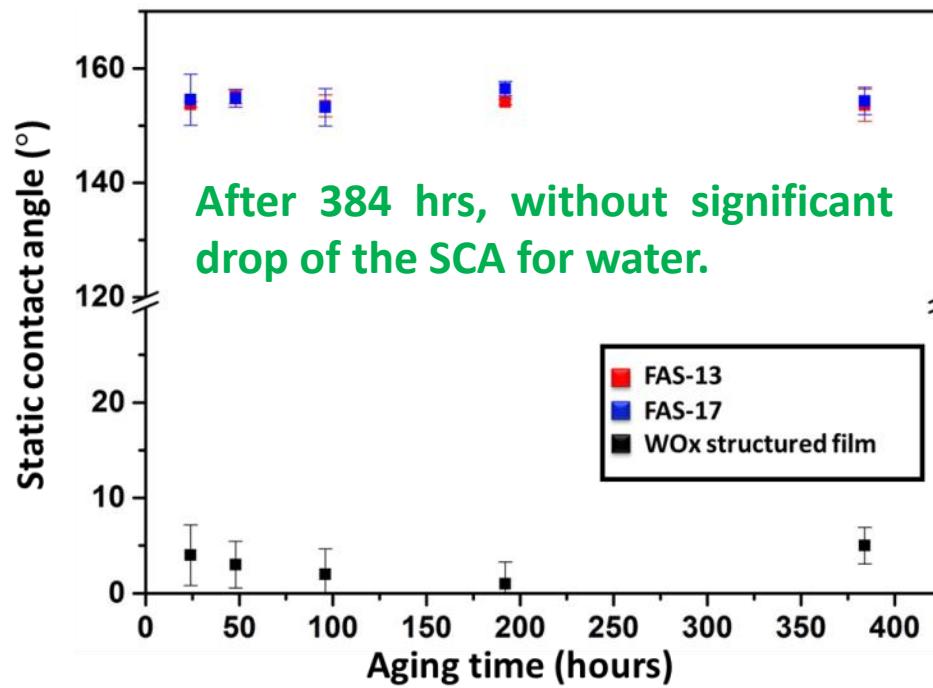
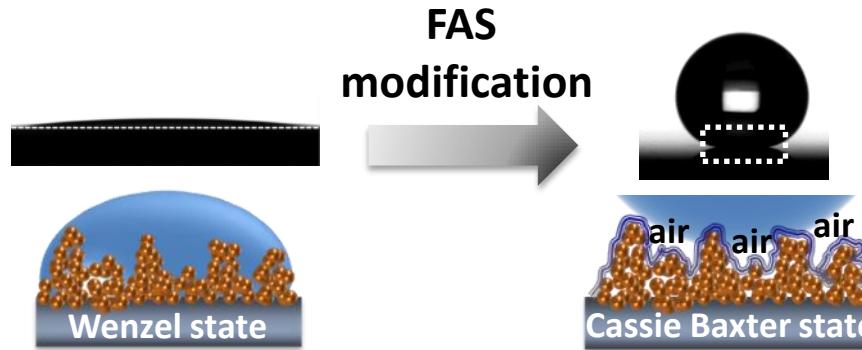
- Tungsten is the major content for the composition of the hierarchical structured coating.
- Roughness of coating increased upon increasing process time.

**Optimized condition**

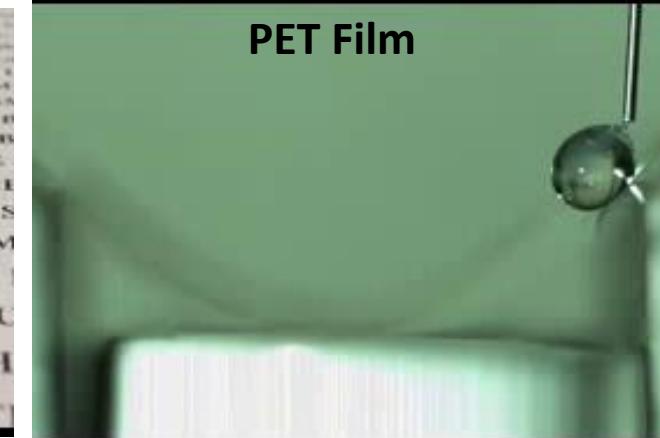
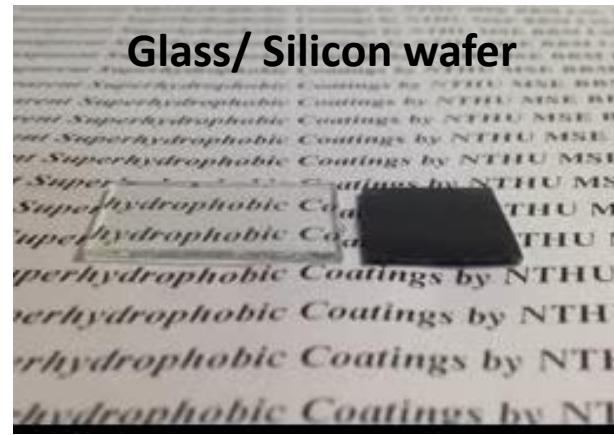
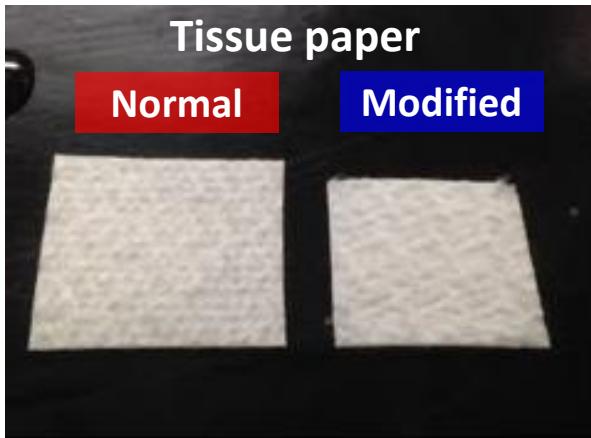


1<sup>st</sup> level: 10-20 nm nanoparticles, 2<sup>nd</sup> level: 50-70 nm clusters, 3<sup>rd</sup> level: 100-200 nm aggregates

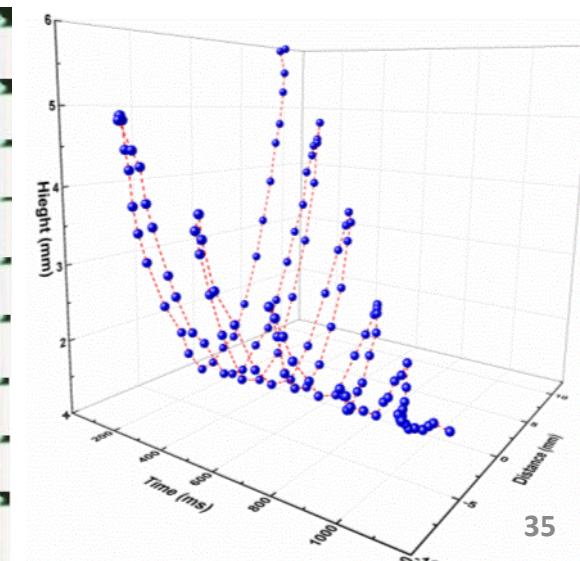
# Superhydrophobicity Stability for Coating



# Dynamic Behavior Observations



- Series of images showing a droplet of PET film in DI water rolling back and forth on the surface bent into a U-shape.
- Trajectory of the water droplet shows that at least four times cycle before it stops.
  - $\Delta E = -15.3\% \text{ for half cycle}$



# 仿生材料之未來展望與應用

- ✓ 表面改質、表面科學
- ✓ 超疏水性、自潔表面
- ✓ 可重複吸附之表面
- ✓ 水中吸附
- ✓ 抗菌表面
- ✓ 低阻抗表面
- ✓ 紡織、功能性布料
- ✓ 航太、汽車工業
- ✓ 新型複合材料
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- ✓ 運動用品
- ✓ 智慧型材料
- ✓ 多功能材料



- ✓ 結構性色彩、光通訊
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- ✓ 再生能源
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- ✓ 仿生綠建築

# 更多訊息與聯絡方式：

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## Structural Biological Materials: Critical Mechanics-Materials Connections

Marc André Meyers,<sup>1,2\*</sup> Joanna McKittrick,<sup>1</sup> Po-Yu Chen<sup>3</sup>

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Biological materials: Functional adaptations and bioinspired designs

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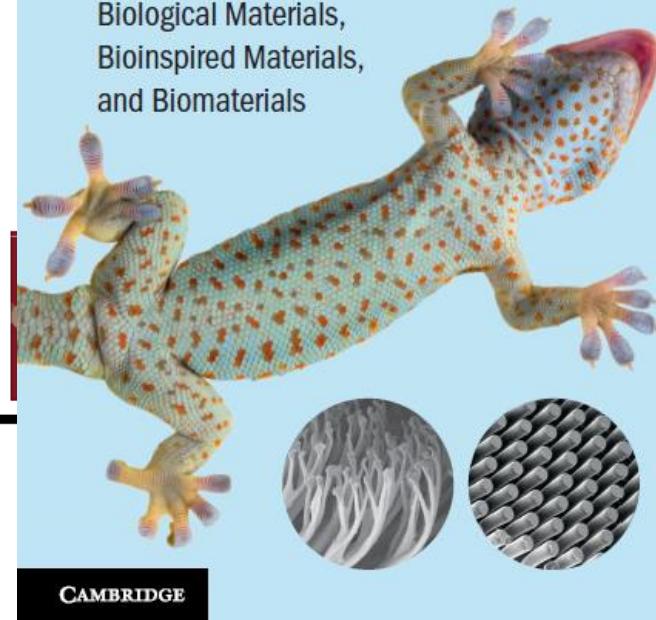
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# Biological Materials Science

Biological Materials,  
Bioinspired Materials,  
and Biomaterials



CAMBRIDGE

Biological materials: Structure and mechanical properties

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  - NTHU MSE, BBML members



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