



UNIVERSITÀ
DEGLI STUDI DI TRIESTE



A.A. 2020-21

Corso «Materiali Naturali e Biomimetici»

- Biomimetic Materials -

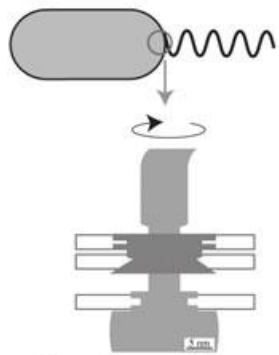
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“In materials processing, Nature replaces the massive use of energy (for example high temperatures or harsh chemical reactions) with the **use of information** (which equates with structure at all levels, molecule to ecosystem).

Indeed, most of the exceptional functionality of biological materials is due to their **complex structure**, driven by their chemical composition and morphology derived from DNA. It is here that the most important aspect of biomimetics emerges, and **it has the power to redesign engineering.**”



flagellum motor



lotus leaf



pitcher plant



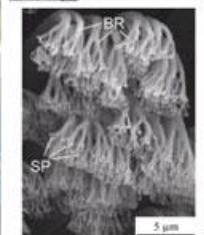
water strider



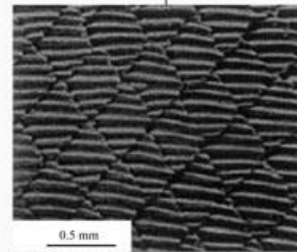
butterfly wings



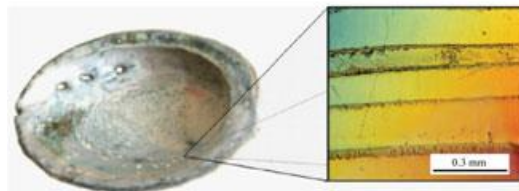
gecko feet



shark skin



bird & peacock



nacre of abalone shell



spider web



mosquito



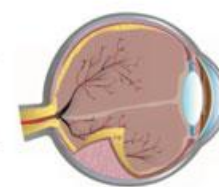
moth eye

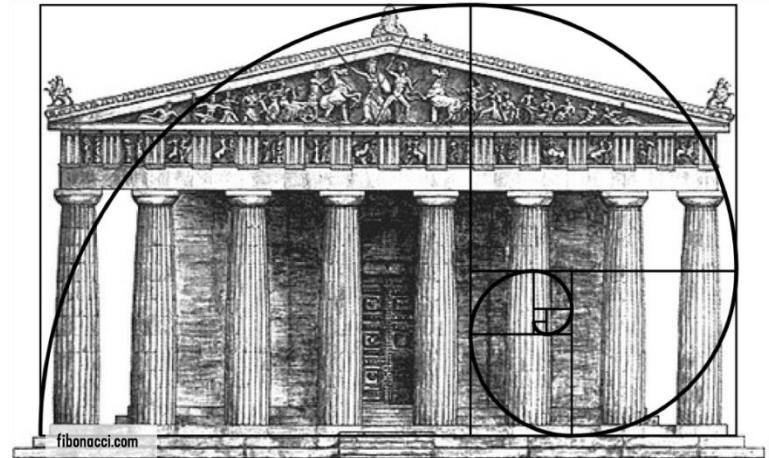
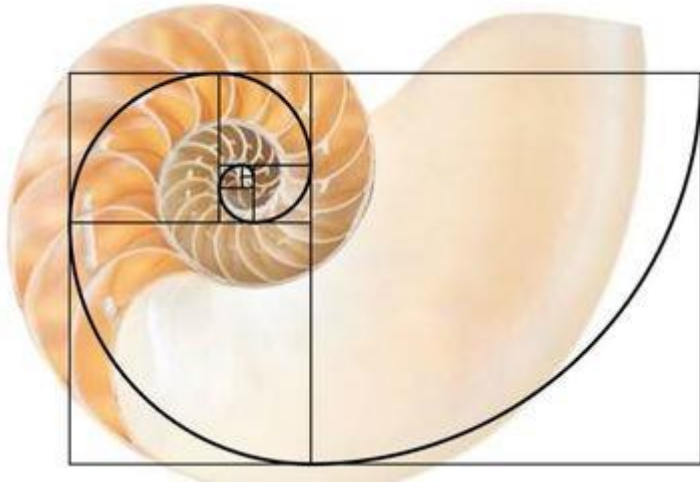
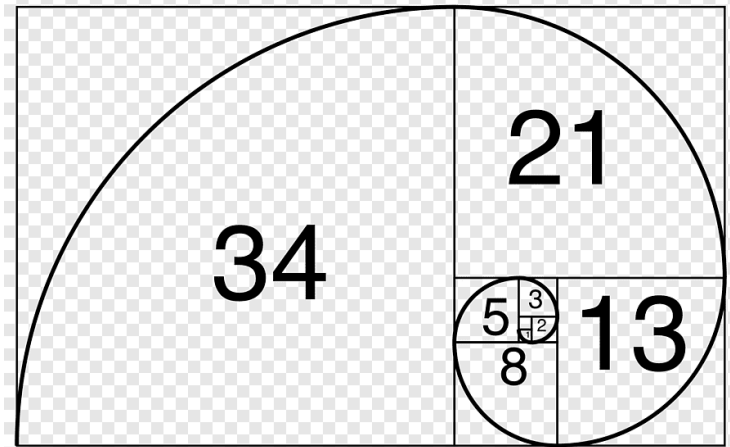
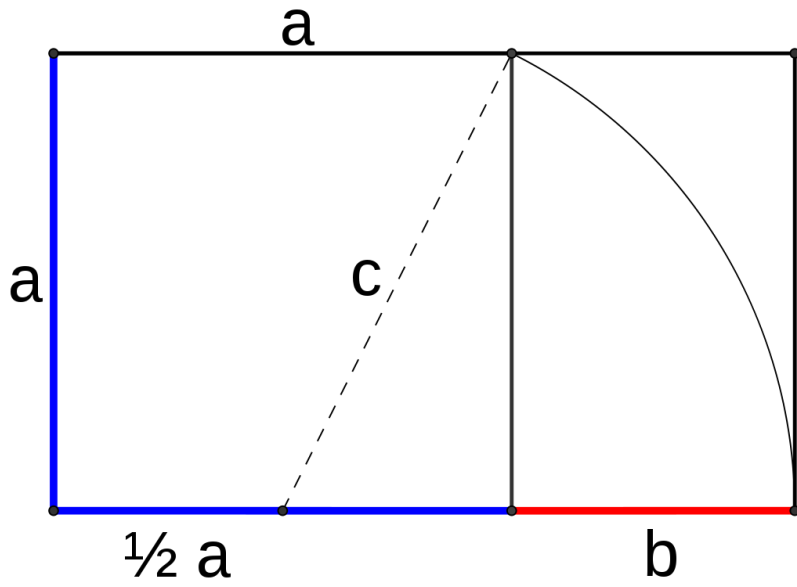


self-healing

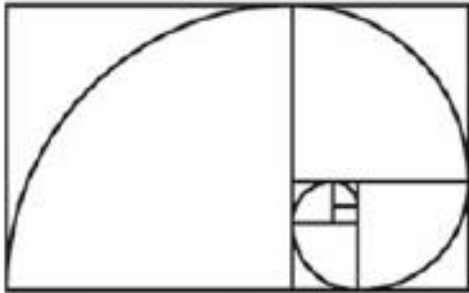


sensory aid devices: ear and eye

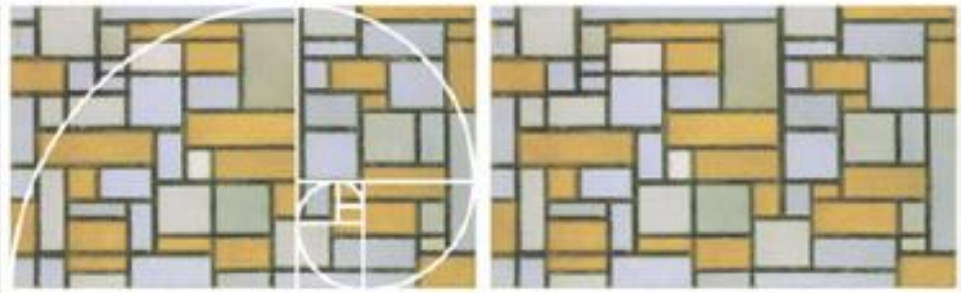




Examples of Bioinspiration in Art



Golden Spiral



Composition in Gray and Light Brown (Mondrian, 1918)



Interior of Bird Bone



Bone Chair and Bone Armchair (Laarman, 2006 & 2008)

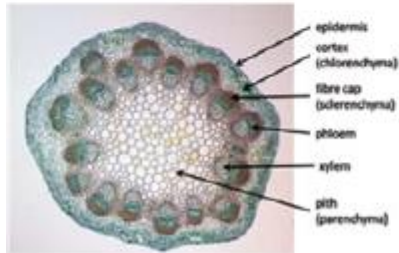
Examples of Bioinspiration in Architecture: Plants, Animals, and Replication



Evergreen Forest



Sagrada Família, Barcelona, Spain (Gaudi, 1882)



Cross section of a dicot stem



Nakagin Tower, Tokyo (Kurokawa, 1972)



Bird wings unfolding



Solar sensitive wings, Milwaukee Art Museum, Wisconsin (Calatrava, 2001)

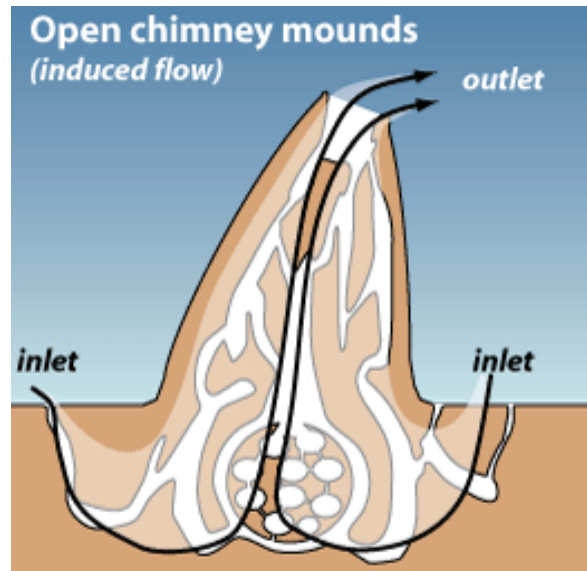


Ribs with intercostal muscles

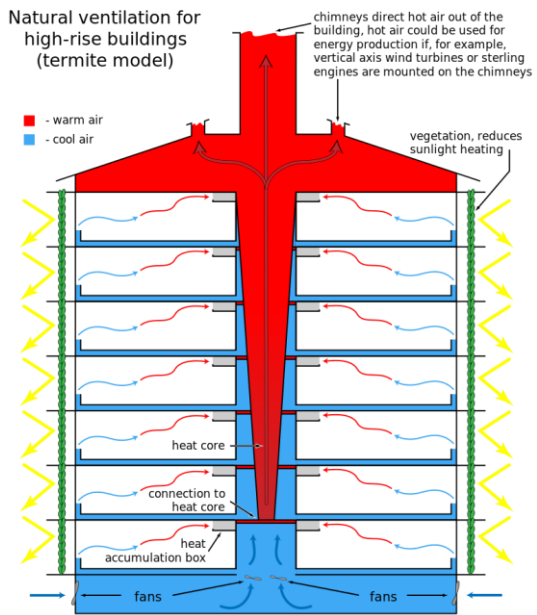


Rib vaulting, Exeter Cathedral, Exeter UK (architect unknown, 1400)





Natural ventilation for high-rise buildings (termite model)



- warm air
 - cool air

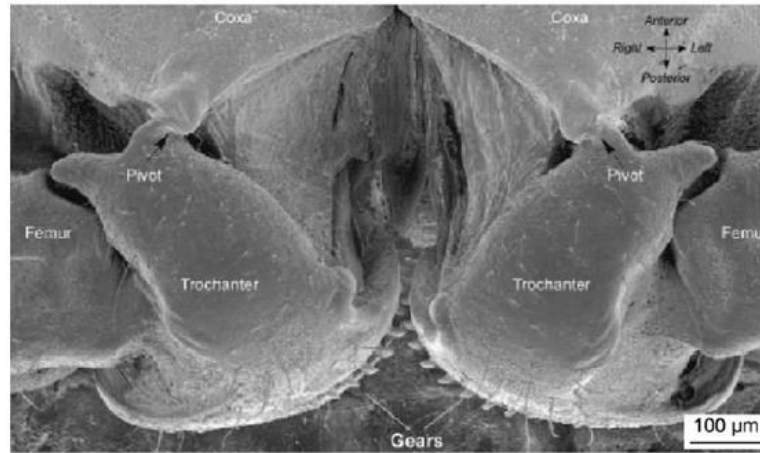
vegetation, reduces sunlight heating

fans

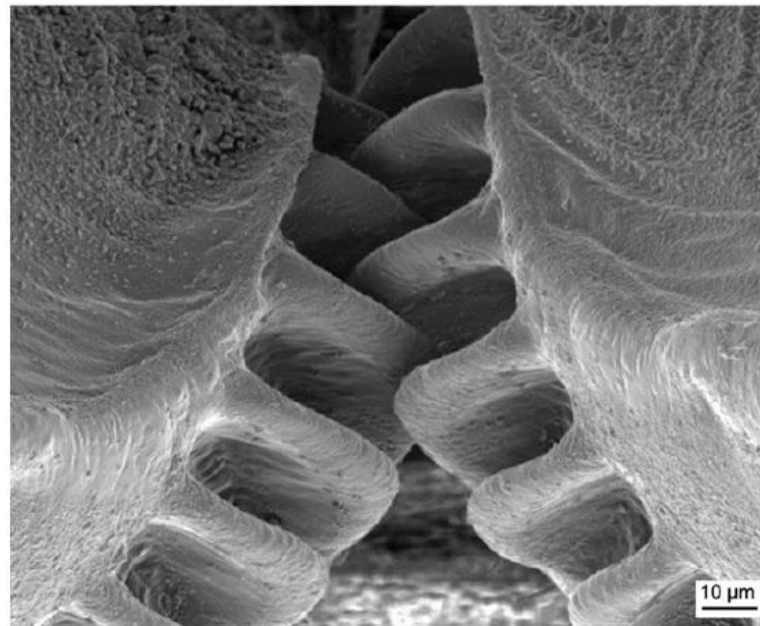
heat core
 connection to heat core
 heat accumulation box

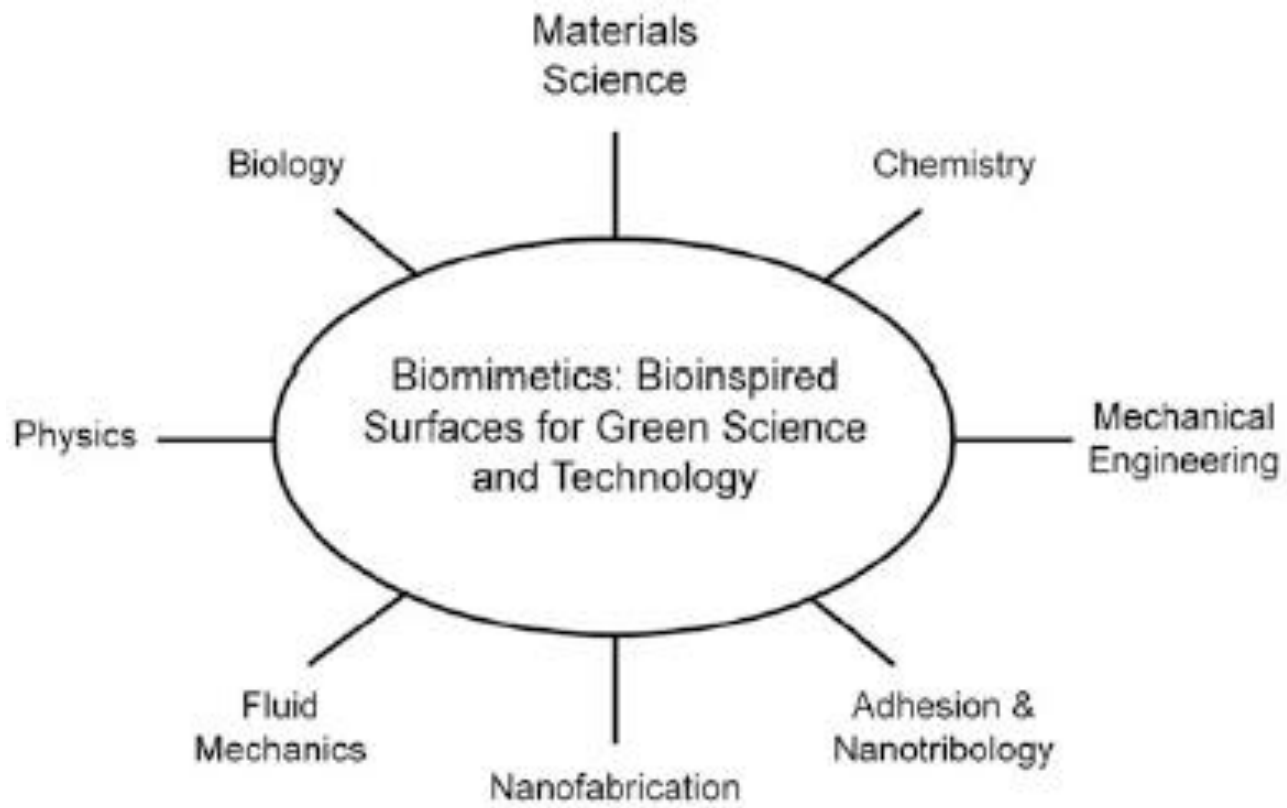
chimneys direct hot air out of the building, hot air could be used for energy production if, for example, vertical axis wind turbines or sterling engines are mounted on the chimneys

Toothed gears on hind legs of insect *Issus coleoptratus*

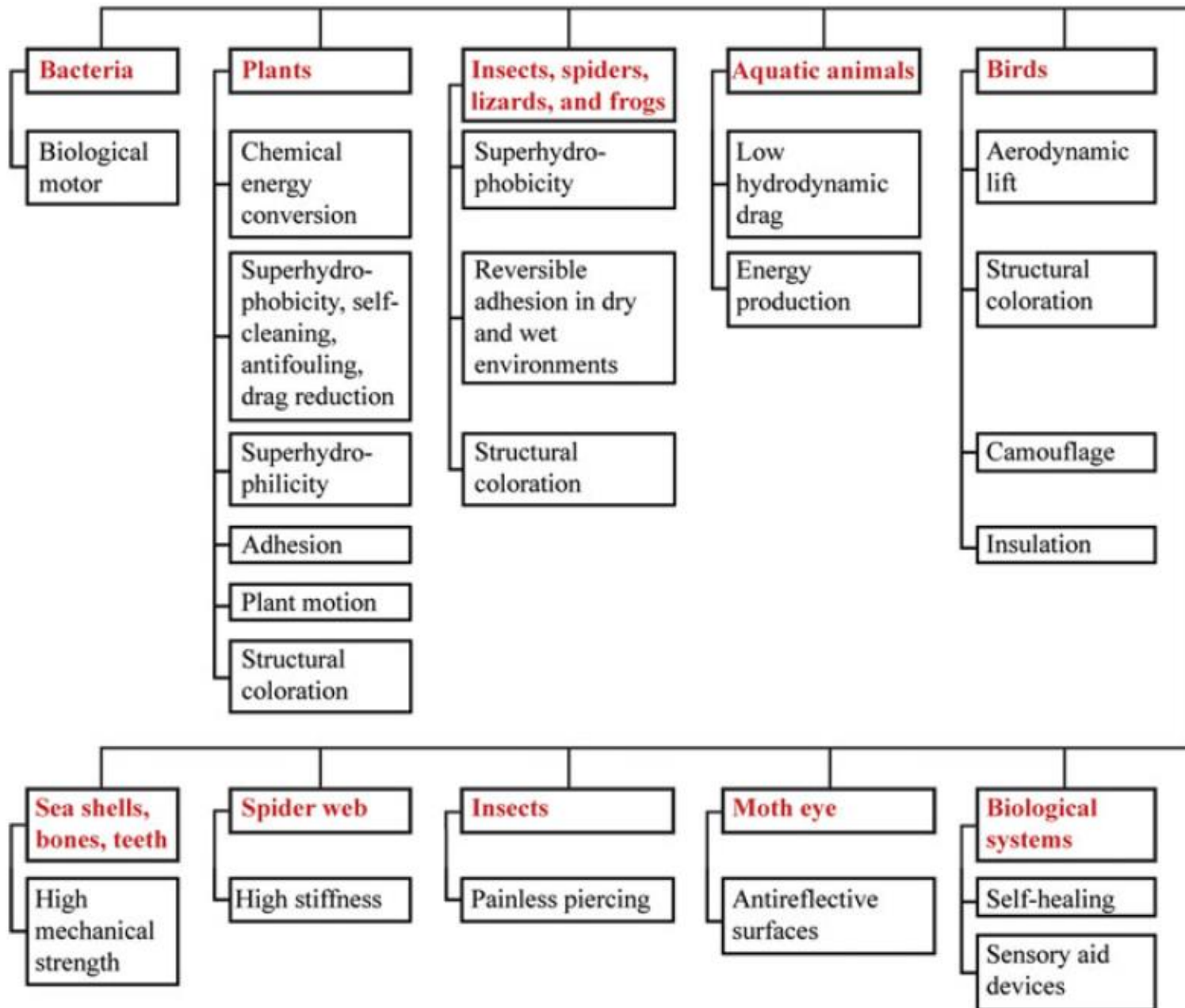


Magnified view of the gears





Overview of Various Species and Objects from Living Nature and Their Selected Functions



Biomimicry

Natural materials are efficient

Little material and energy are used for complex requirements:

- Mechanical: static and dynamic loads
- Thermal and electrical: insulation, transpiration, sensing, actuation
- Sustainable: recyclable, biodegradable



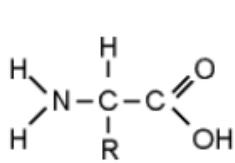
Mimicking these characteristics is a very promising strategy for engineering

Most natural materials are hybrids and composites

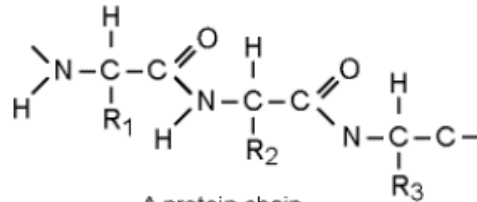
Key role of surfaces!

Building Blocks of Natural Materials

Proteins



An amino-acid

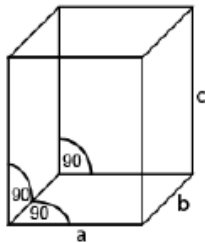


A protein chain

- Natural polymers (collagen, keratin)
- Natural elastomers (elastin, resilin, abductin)

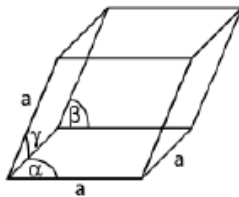
Minerals

Aragonite,
 CaCO_3



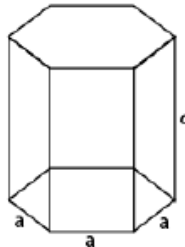
Orthorhombic: $a \neq b \neq c$

Calcite,
 CaCO_3



Trigonal: $\alpha \neq \beta \neq \gamma$

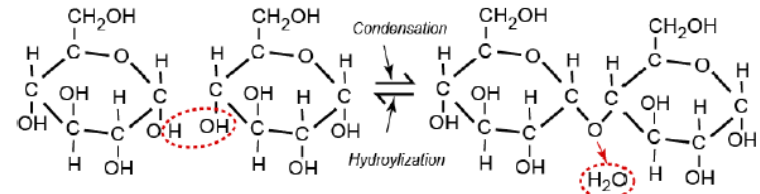
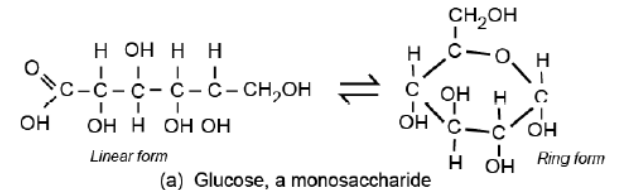
Hydroxyapatite,
 $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$



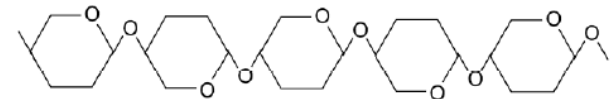
Hexagonal: $a \neq c$

- Also: amorphous bio-silica, SiO_2

Polysaccharides



(b) Condensation of monosaccharides to a polysaccharide

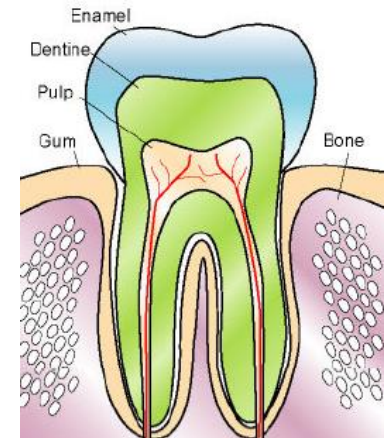
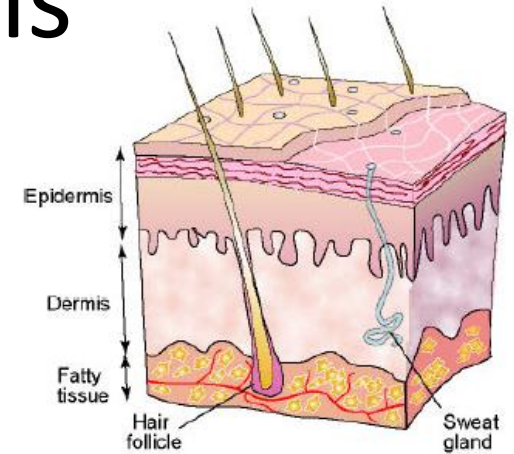


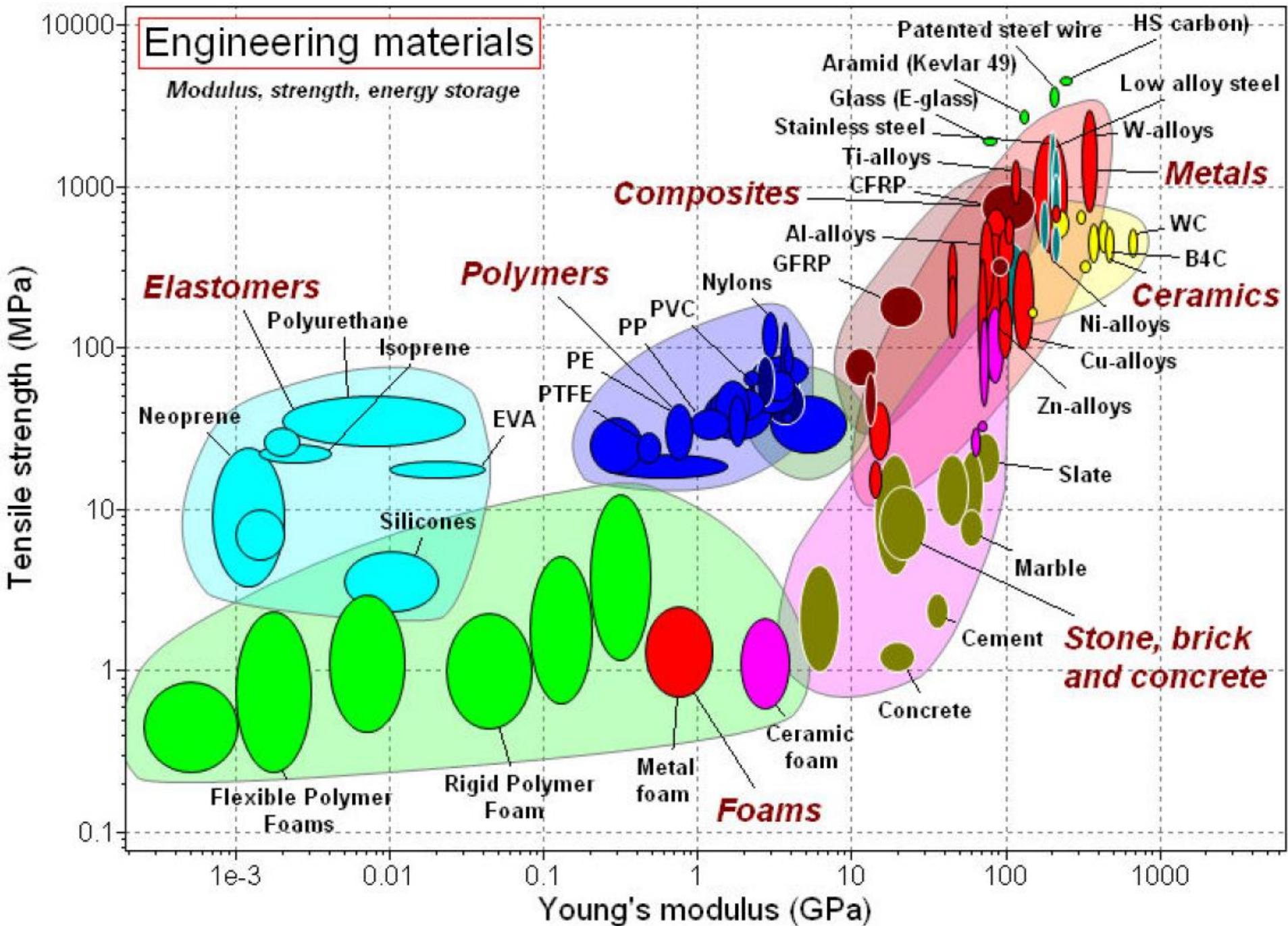
(c) The cellulose molecule in short-hand

- Starch, glycogen (energy storage)
- Coellulose, lignin, chitin (structural)

Natural Materials

- Soft tissue
- Mineralized tissue
- Woods and wood-like materials
- Natural fibers
- Bio-materials

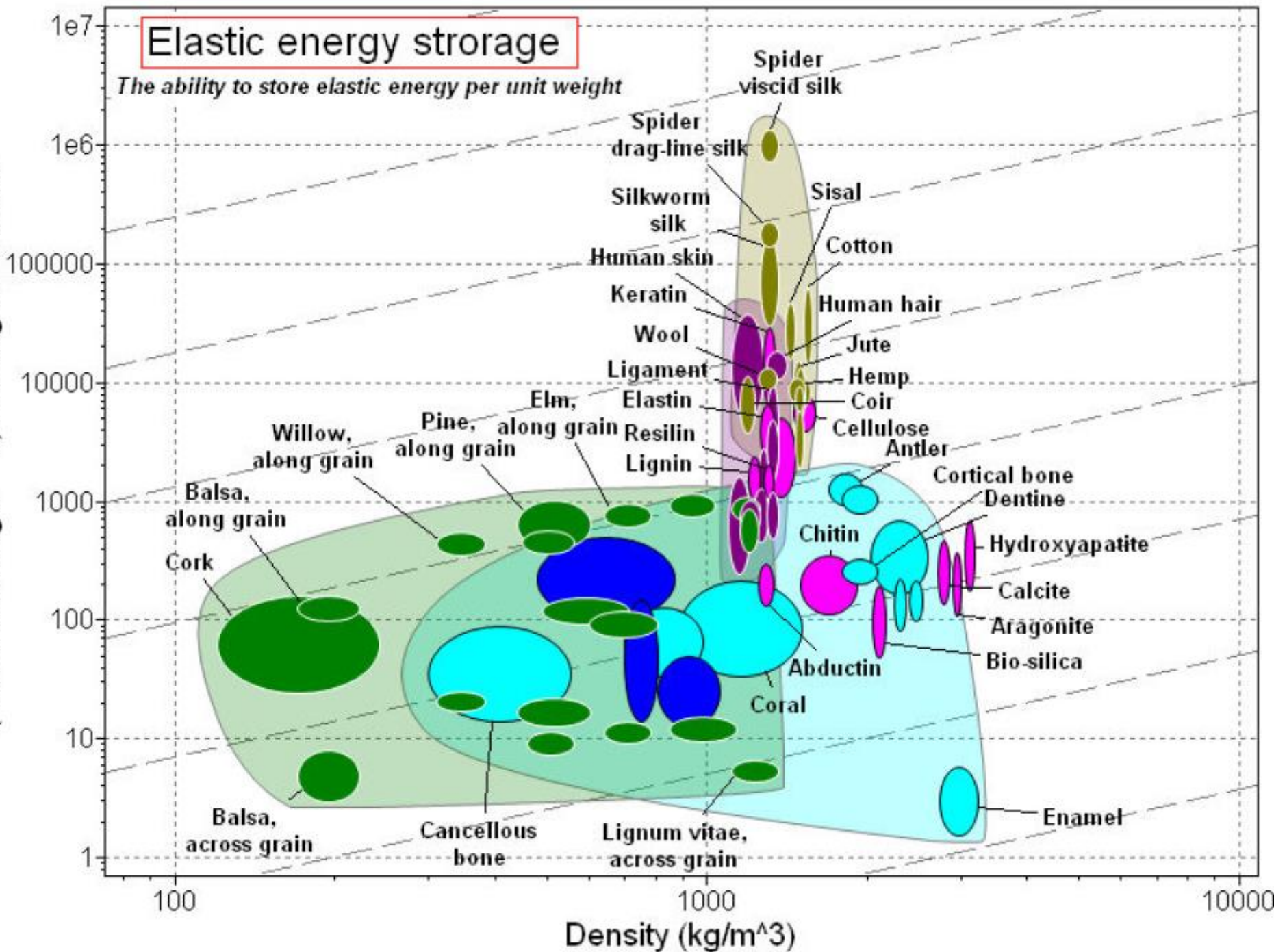




Elastic energy storage

The ability to store elastic energy per unit weight

(Tensile strength \wedge 2)/Young's modulus

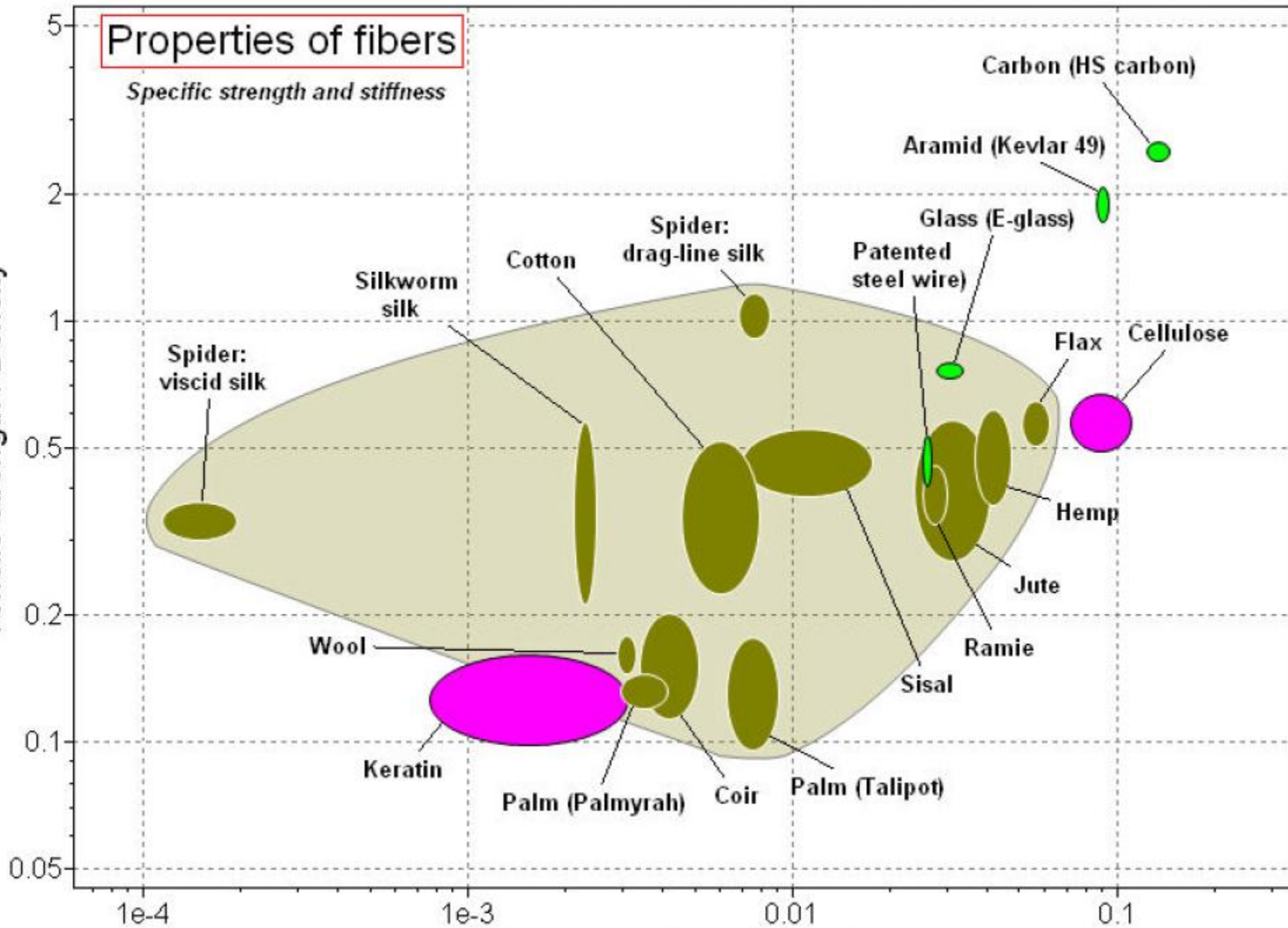


Properties of fibers

Specific strength and stiffness

Tensile strength / Density

Young's modulus / Density



Applications

Objects	Typical materials	Desired properties
<i>(a) Biomedical applications</i>		
Biomedical devices, catheters, drainage tubing, micropumps, microvalves, electronic circuits	PDMS, Polystyrene, PMMA	Superoleophobic, self-cleaning, anti-biofouling
<i>(b) Automotive applications</i>		
Windshield, window glass, side/rear view mirrors, camera lens (back of car)	Glass	Superoleophobic, self-cleaning, anti-finger touch, antifouling, optically transparent/antireflective
Display, headlights	PMMA for smart screens for capacitive touch material, Polycarbonate (head lights)	Superoleophobic, self-cleaning, anti-finger touch, antifouling, optically transparent/antireflective
Dashboard, door liners, seats, carpet, leather	Polyurethane, nylon (dashboard), Polypropylene (door liner), Polyurethane (seats), Leather (natural, synthetic polycarbonate)	Superoleophobic, self-cleaning, anti-finger touch, antifouling
Car body	Painted Steel	Self-cleaning, anti-smudge, low drag
<i>(c) Smart screens for electronic display</i>		
Screens	Soda-lime glass, polyethylene terephthalate, polycarbonate	Superoleophobic, self-cleaning, anti-finger touch, antifouling, optically transparent
<i>(d) Plastic bottles and caps and plastic sheets</i>		
Bottles	High-density polyethylene, polyethylene terephthalate, polypropylene	Superoleophobic, superhydrophobic
Bottle caps	Polypropylene	Superoleophobic, superhydrophobic
Plastic packaging sheets	Polypropylene, acrylic	Superoleophobic, superhydrophobic, anti-fouling



(reversible)
Super-Adhesion

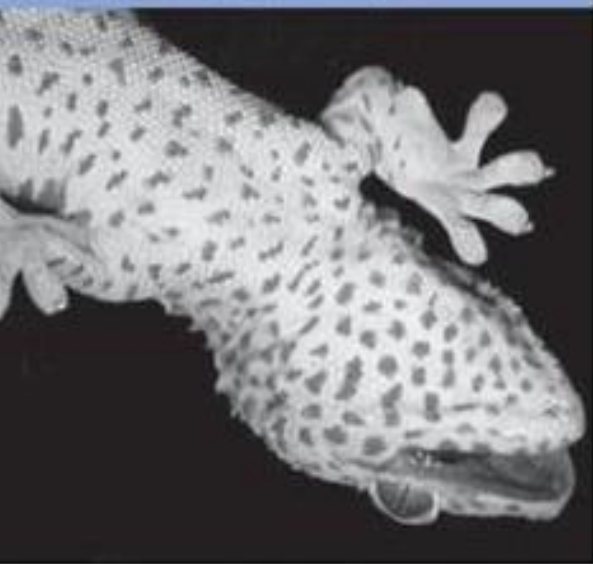








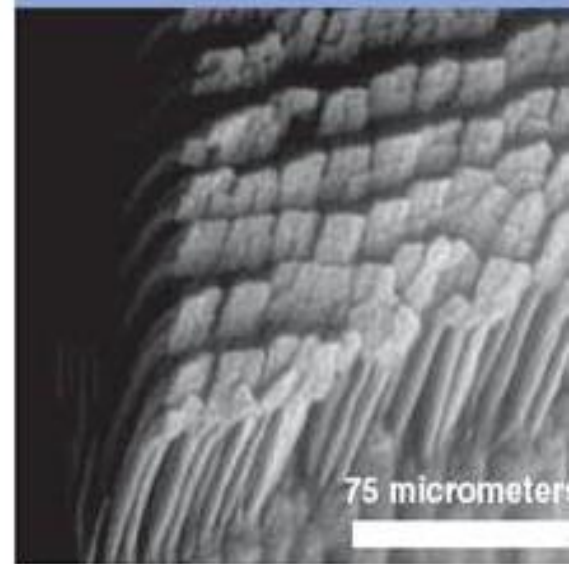
macrostructure



mesostructure

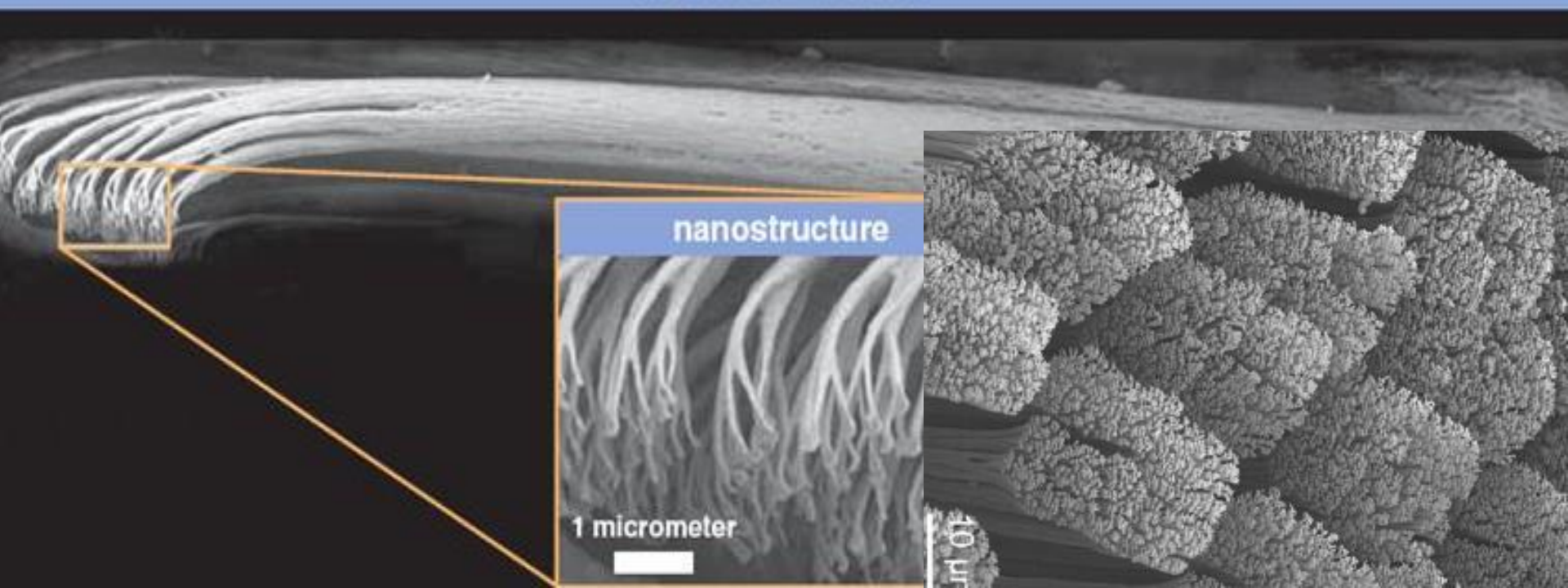


microstructure

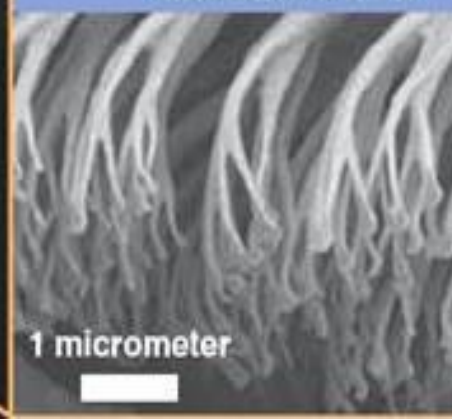


75 micrometers

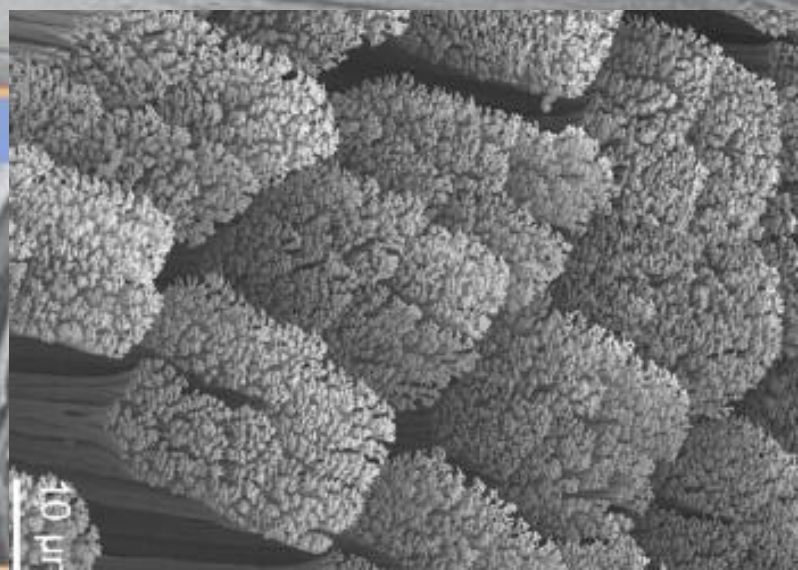
fine microstructure



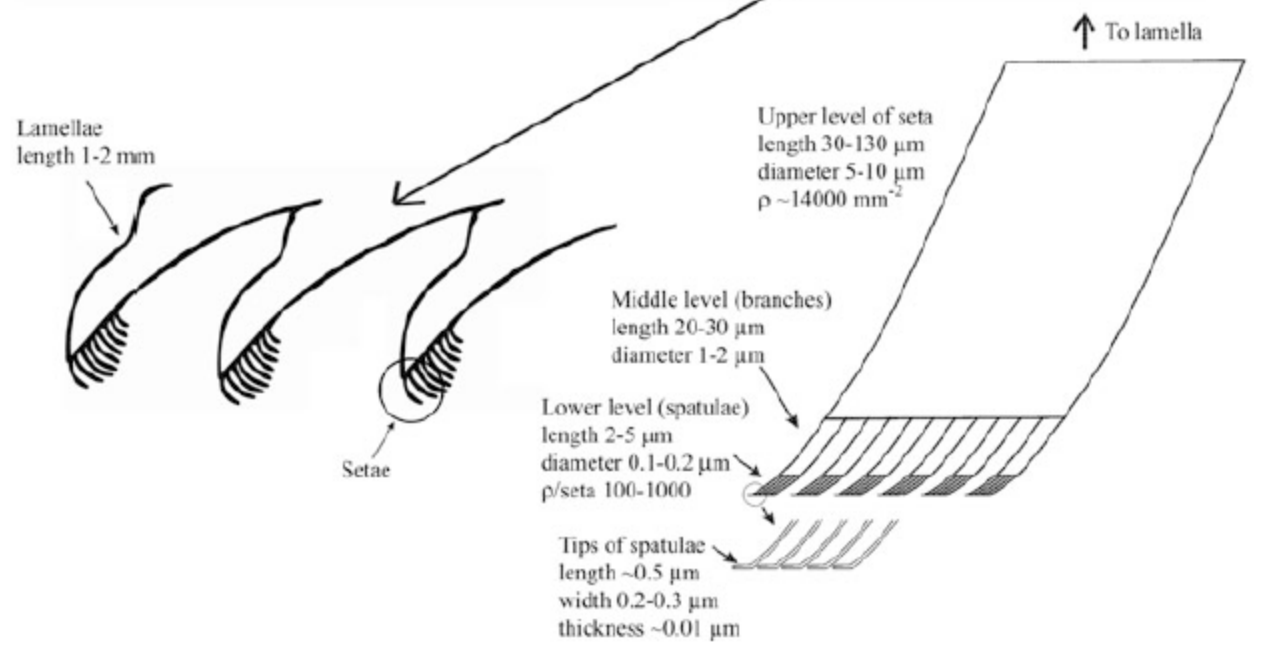
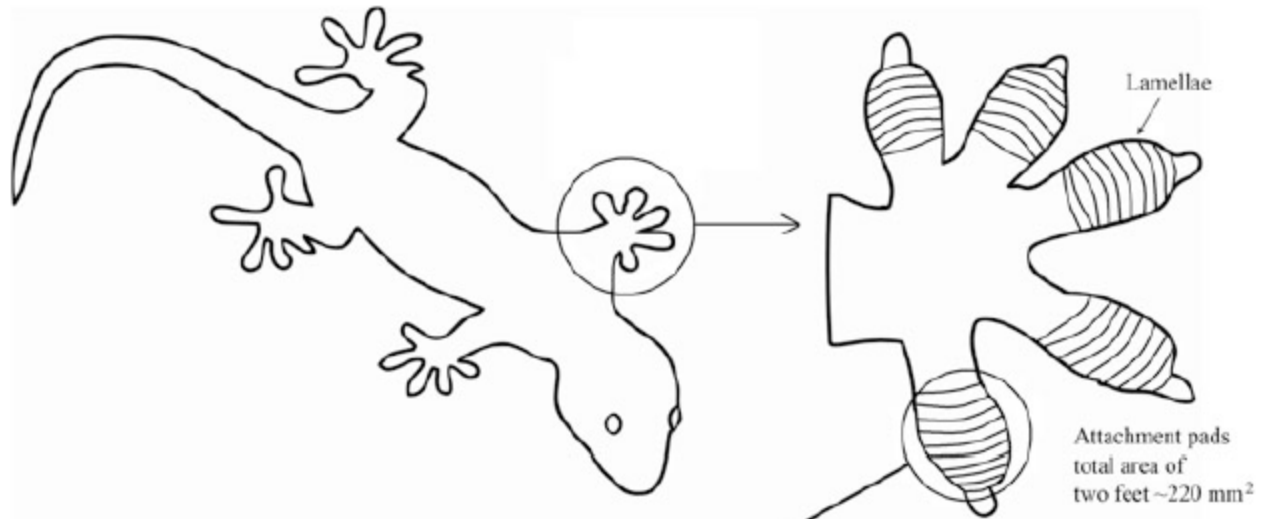
nanostructure



1 micrometer



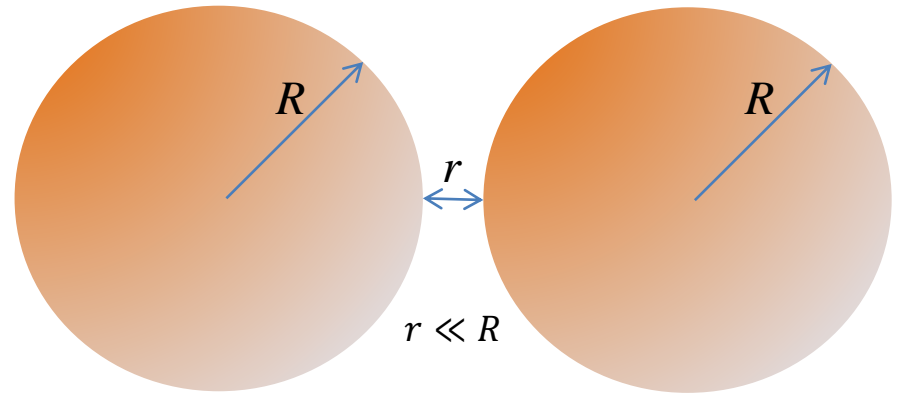
1 micrometer



Van der Waals forces

$$F_{VdW,sphere} \cong A \frac{R}{12r^2}$$

$A \cong 10^{-19} - 10^{-20} \text{ J}$
Hamaker coefficient



VdW forces between "large" (multimolecular and above) objects:

- Are very small
- Grow with the size of the object, R

But...

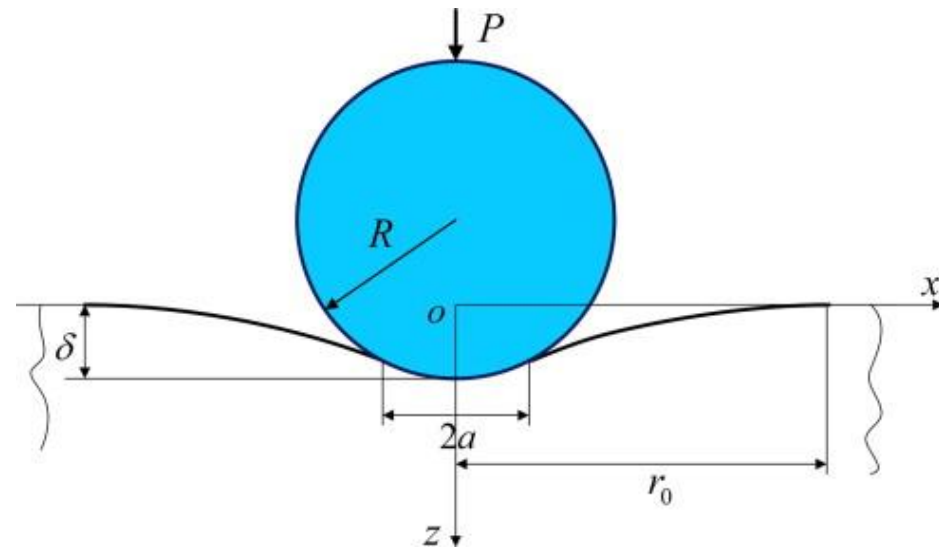
$$\frac{F_{VdW,macro}}{F_{gravity}} \cong A \frac{R}{12r^2} \frac{1}{\frac{4}{3}\pi R^3 \rho g} \cong \frac{A}{16\pi \rho r^2 g} \frac{1}{R^2}$$

VdW forces between "large" (multimolecular and above) objects:

- **Grow** with the size, R , but **slower than volume forces** (gravity, drag, lift...)
 - Become **preponderant at the nanometric scale**
- *Nanosystems tend to aggregate*
- ***Nanostructures can inspire dry, reversible adhesives***

Contact Forces

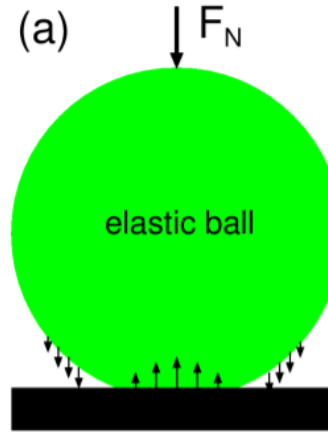
Hertz



No adhesion

DMT

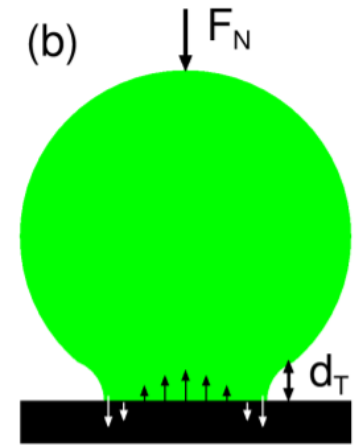
Deryagin
Muller
Toporov



DMT-limit

JKR

Johnson
Kendall
Roberts



JKR-limit

Adhesion

$$F_{ad} = 2\pi W_{ad}R \quad F_{ad} = \frac{3}{2}\pi W_{ad}R$$

Hertz

The contact between two smooth elastic bodies was investigated by Hertz (1896) who demonstrated that both the size and shape of the zone of contact followed from the elastic deformation of the bodies. For two spheres of radius R_1 and R_2 pressed together under a load P_0 (see figure 1a) the radius a_0 of the circle of contact is given by

$$a_0^3 = \frac{3}{4}\pi(k_1 + k_2) \frac{R_1 R_2}{R_1 + R_2} P_0, \quad (1)$$

where k_1 and k_2 are the elastic constants of the material of each sphere; that is

$$k_1 = \frac{1 - \nu_1^2}{\pi E_1} \quad \text{and} \quad k_2 = \frac{1 - \nu_2^2}{\pi E_2}$$

where ν is the Poisson ratio and E the Young modulus of each material. Resulting from local compression near to the contact region, distant points in the two spheres approach each other by a distance δ given by

$$\delta^3 = \frac{9}{16}\pi^2(k_1 + k_2)^2 \frac{R_1 + R_2}{R_1 R_2} P_0^2. \quad (2)$$

Hertz used an optical microscope to measure the contact between glass spheres and so verified his theory experimentally.

JKR

The following elementary analysis shows how surface attraction may be interpreted in terms of surface energy.

Consider two elastic spheres in contact under zero external load. Attractive forces between the surfaces produce a finite contact radius, a , a balance eventually being established between stored elastic energy and lost surface energy. The loss in surface energy U_S is given by

$$U_S = -\pi a^2 \gamma, \quad (3)$$

where γ is the energy per unit contact area (i.e. the two surfaces). The force F_S associated with this energy change is

$$F_S = -dU_S/dx, \quad (4)$$

where x is the movement of the bodies and is approximately the same as δ which is given by the Hertz equations (1) and (2) but cannot be worked out exactly from these because the attractive surface forces disturb the stress distributions in the bodies. Thus we may only write that

$$x \approx a^2(R_1 + R_2)/R_1 R_2 \quad (5)$$

combining equations (3), (4) and (5) gives

$$F_S \approx \pi R_1 R_2 \gamma / (R_1 + R_2). \quad (6)$$

This force acts in addition to the ordinary load P_0 between surfaces and the simple analysis shows that it may be related to the geometry and energy of the contacting surfaces. Further, the surface force will strongly influence the contact size when

$$P_0 \approx \pi R_1 R_2 \gamma / (R_1 + R_2). \quad (7)$$

Suppose $R_1 = R_2 = 2$ cm and $\gamma = 600$ erg cm⁻² (for mica $\gamma \approx 300$ erg cm⁻² per surface) then P_0 is around 2 g.

Surprisingly, perhaps, the force of adhesion F_S between convex surfaces does not depend upon the elastic moduli of the materials. The modulus influences the contact radius, a , but, however, it can be seen from equations (3) and (5) that both the surface energy and the elastic work vary as a^2 , so that the force of adhesion is independent of a and hence of the elastic modulus. The more rigorous analysis which now follows provides the magnitude of the adhesive force but does not change this conclusion.

(dall'articolo originale di JKR!)

Key Adhesion Mechanisms

- **Van der Waals (main mechanism)**
- Capillary forces (secondary mechanism in humid conditions)

1. Fundamental force: Johnson-Kendall-Roberts (JKR)

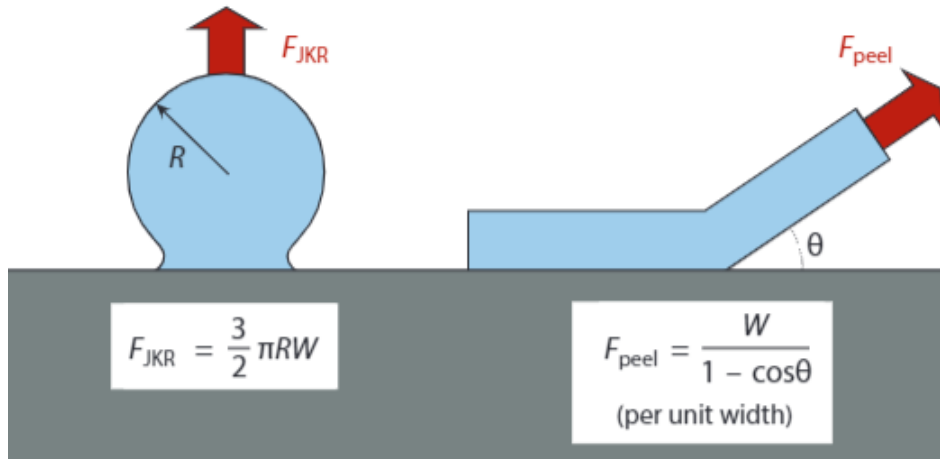
$$F_{ad} = \frac{3}{2} \pi W_{ad} R$$

2. Multiple (n) contacts, constant contact area:

$$F'_{ad} = \frac{3}{2} \pi W_{ad} \left(\frac{R}{\sqrt{n}} \right) \quad n = \sqrt{n} F_{ad}$$

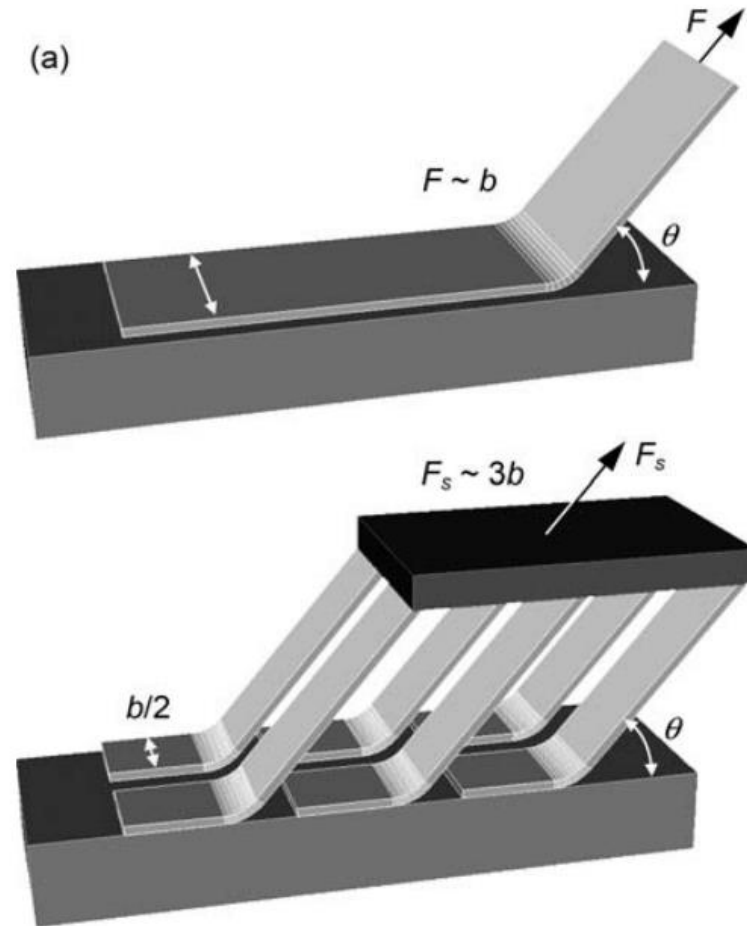
3. More realistic mechanism: peeling

$$F_{peel} \approx \frac{2W_{ad}b\theta}{\pi(1 - \cos\theta)\sin\theta}$$

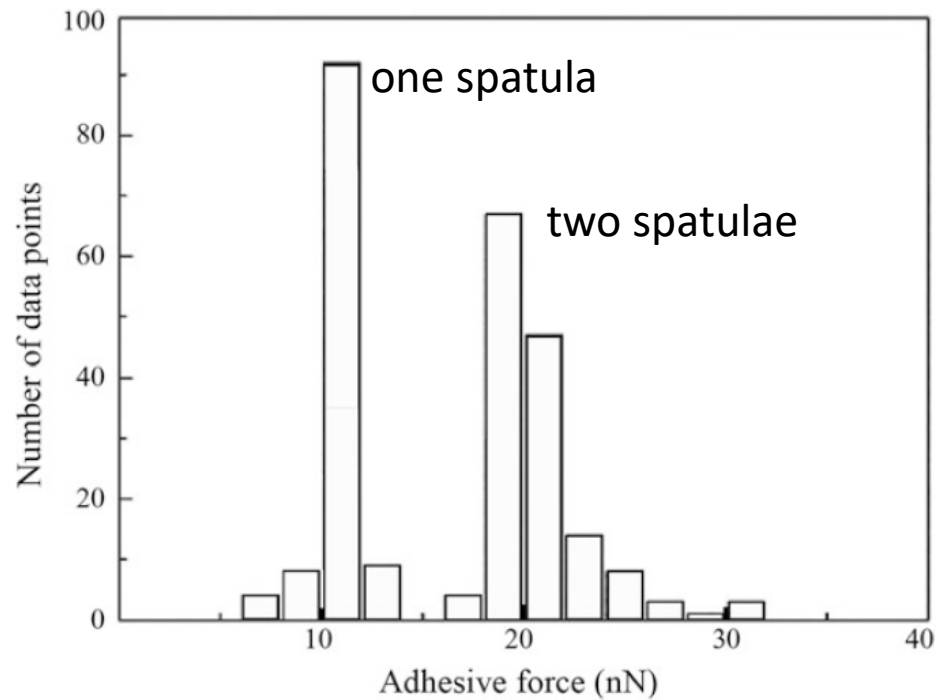


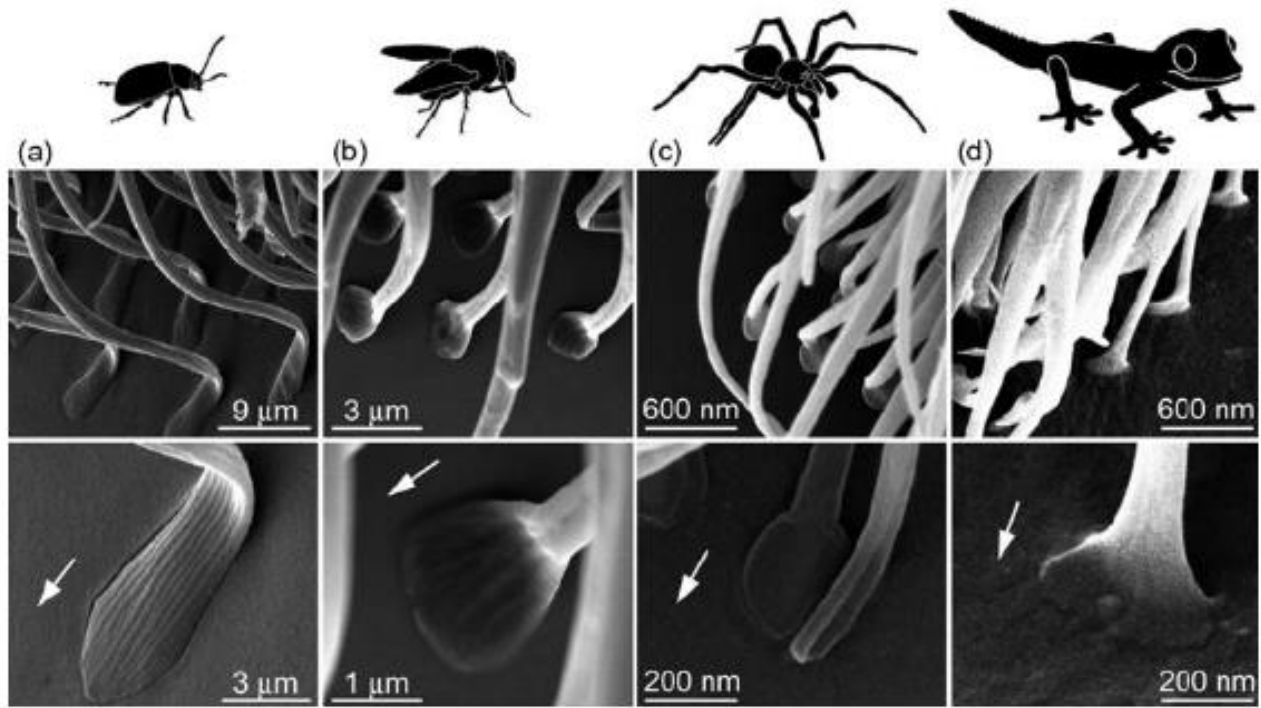
$$W_{ad} \approx 50 \frac{mJ}{m^{-2}}$$

Effect of Multiple Contacts in Peeling

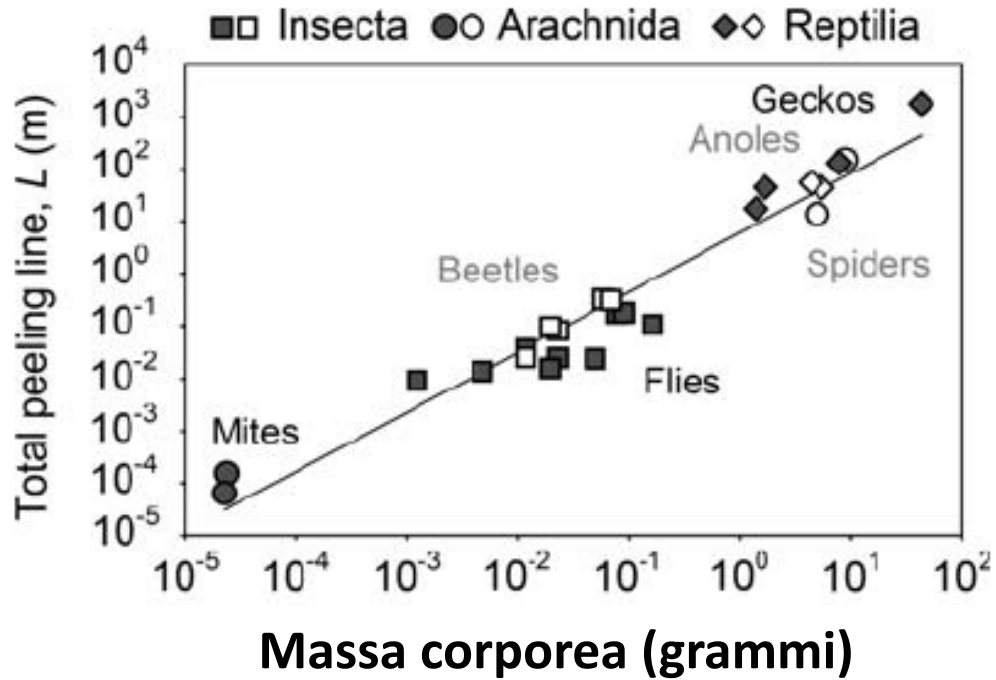


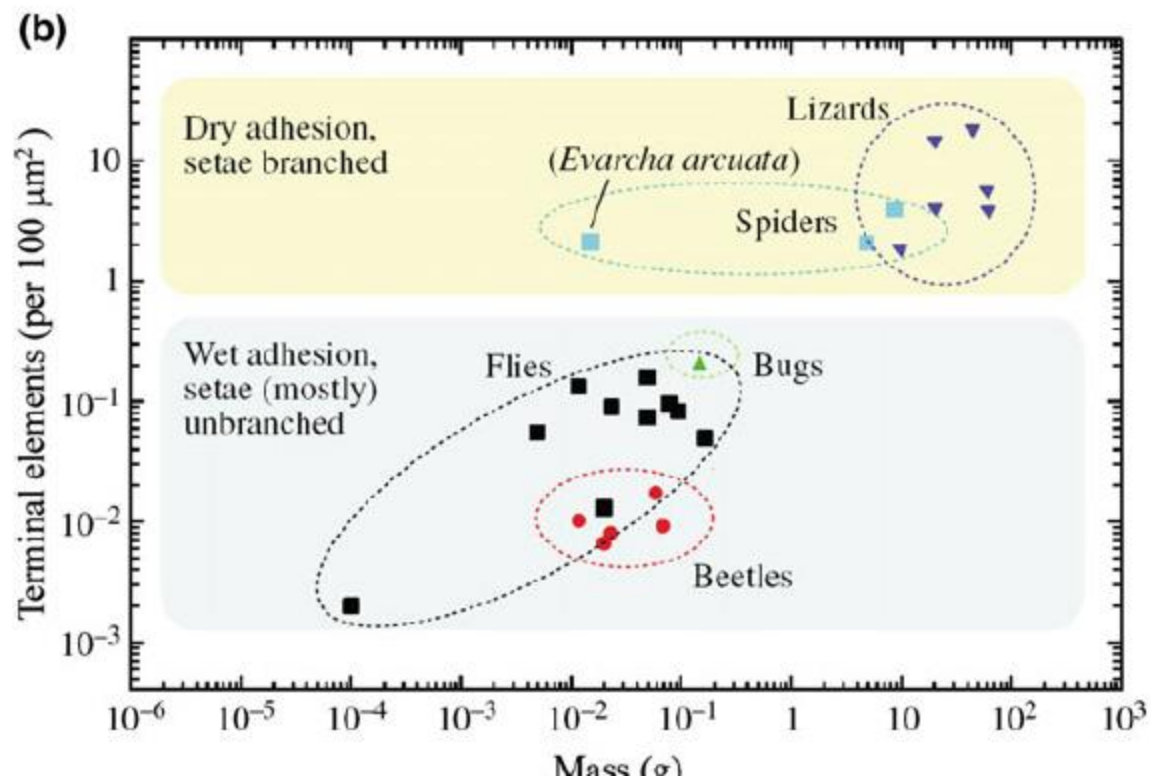
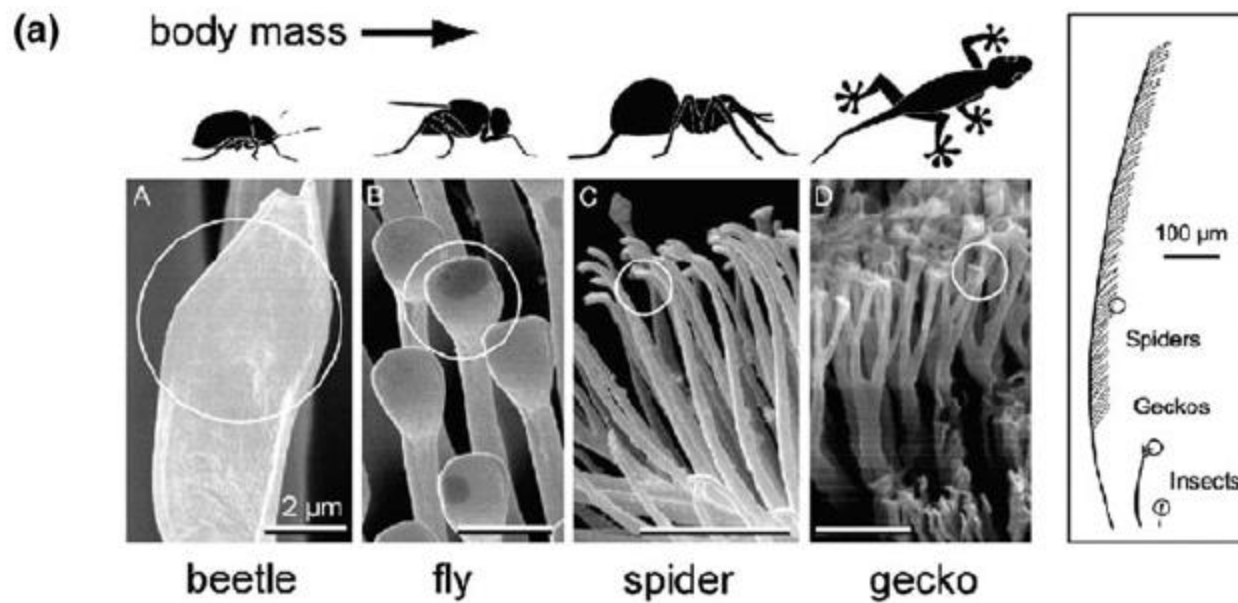
Adhesive Force per Spatula



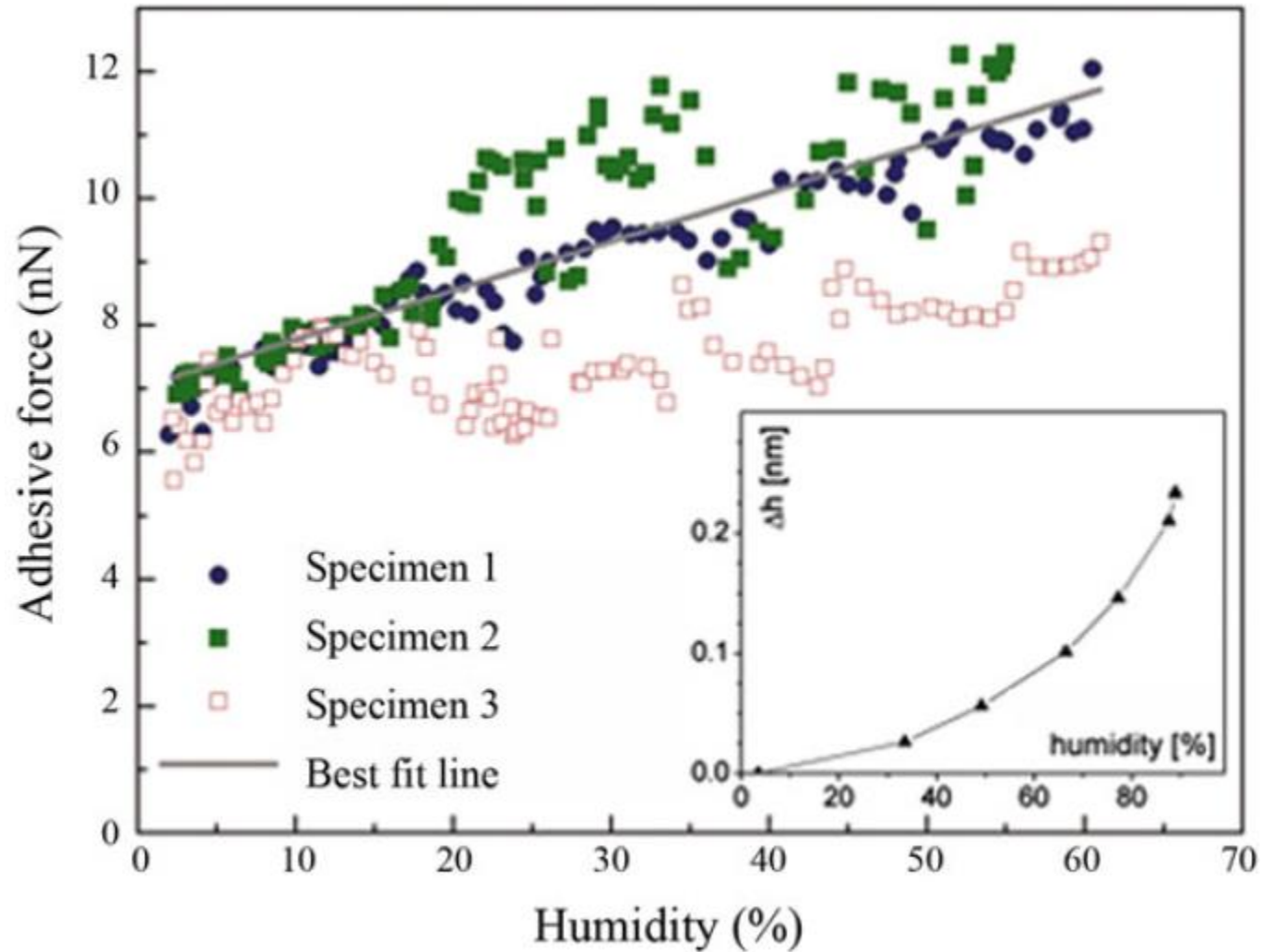


**Numero di elementi di
contatto sulla zampa**



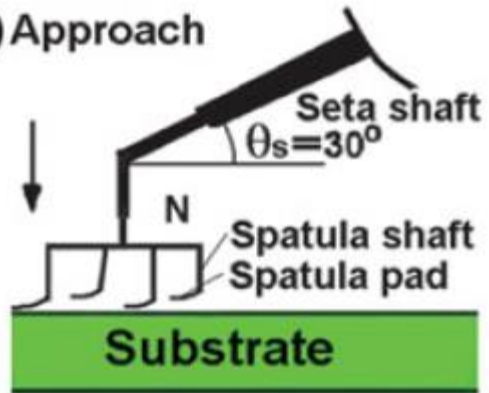


Effect of Humidity

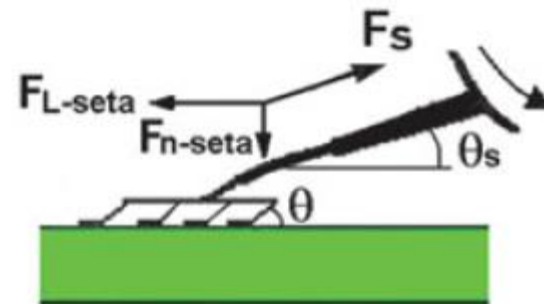


Detachment Mechanism

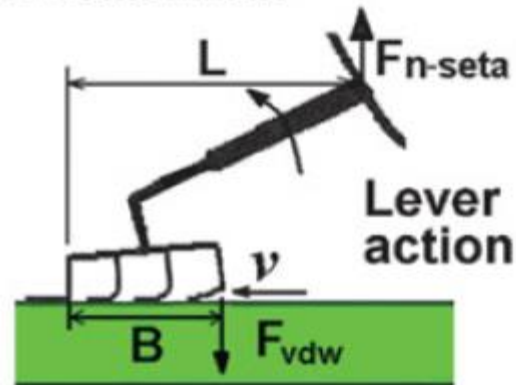
(a) Approach



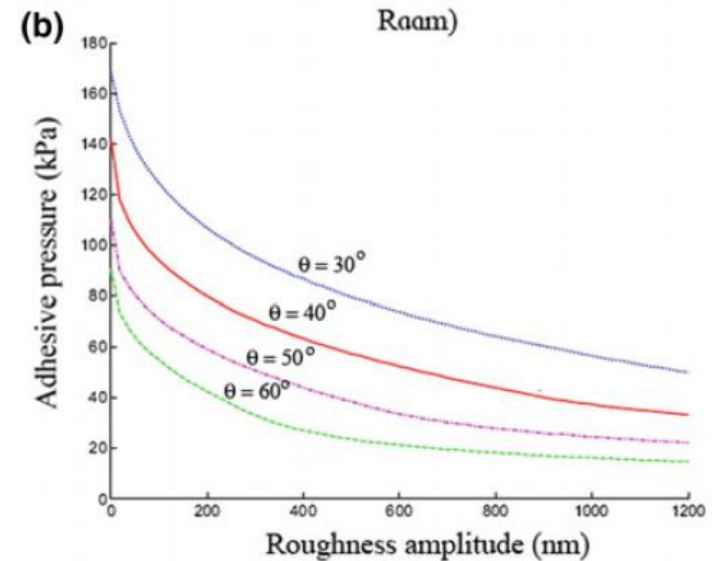
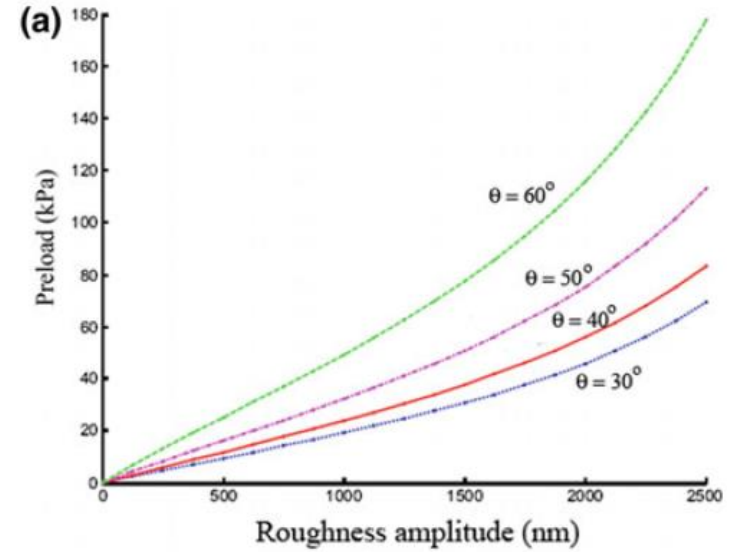
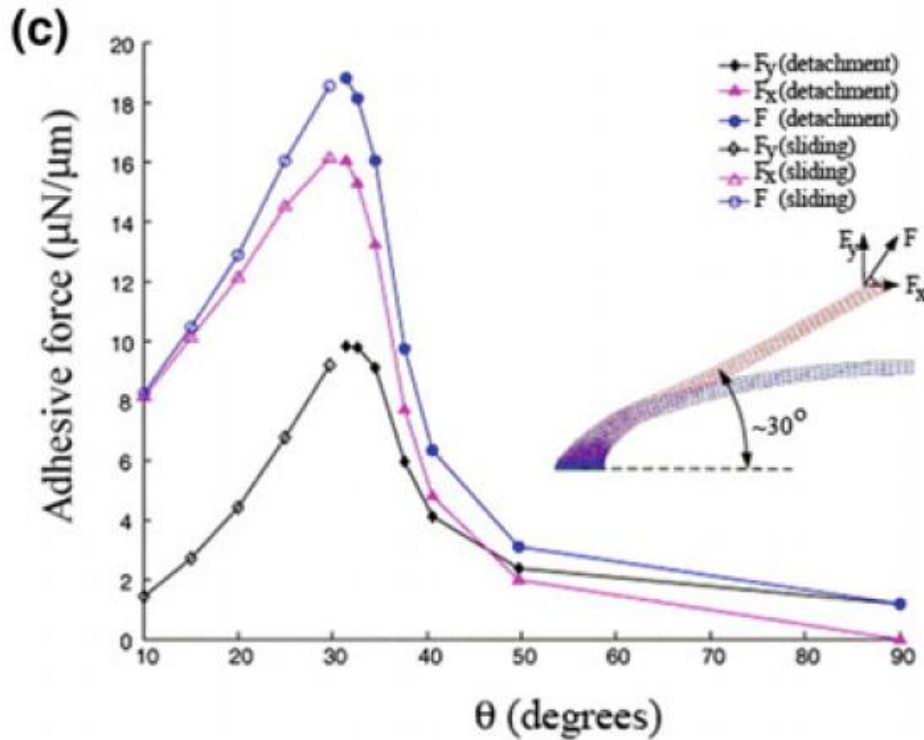
(b) Rolling in Attachment



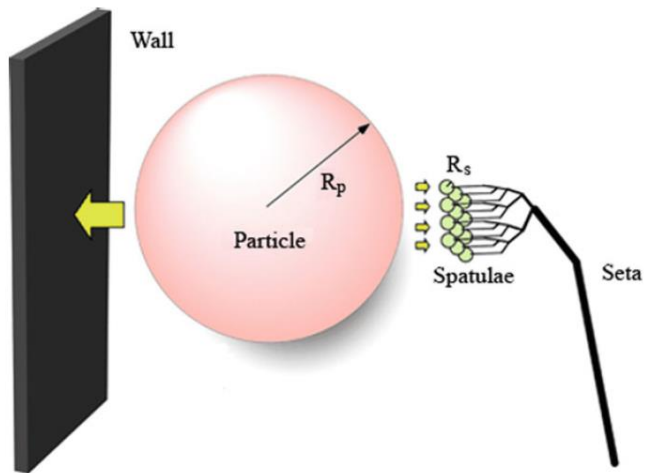
(c) Rolling out Detachment



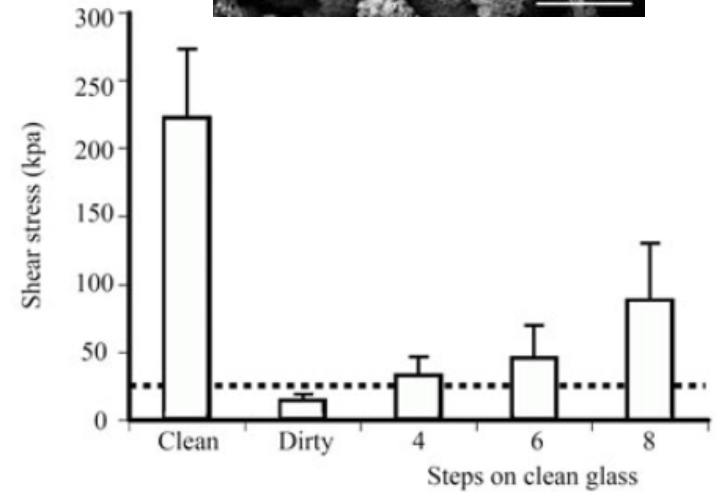
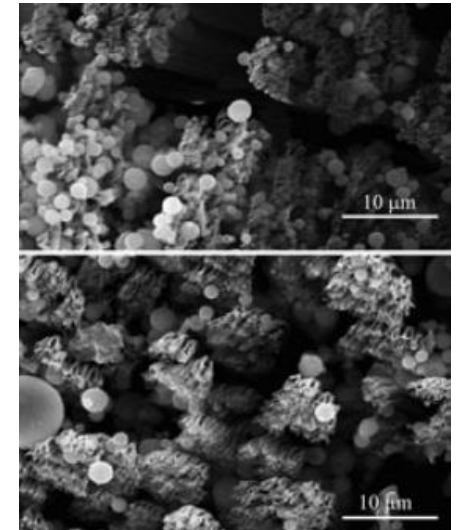
Detachment Mechanism



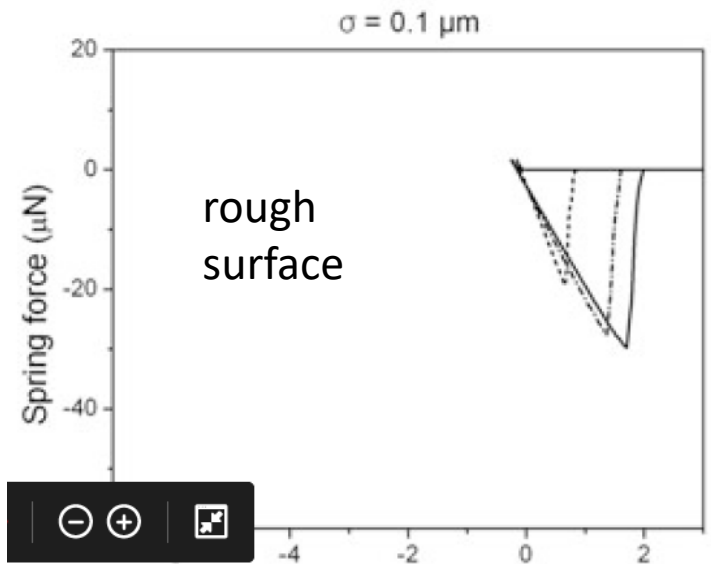
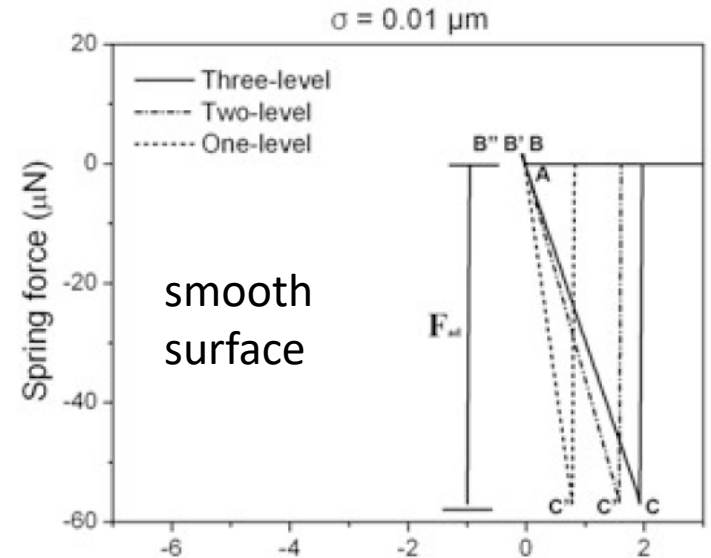
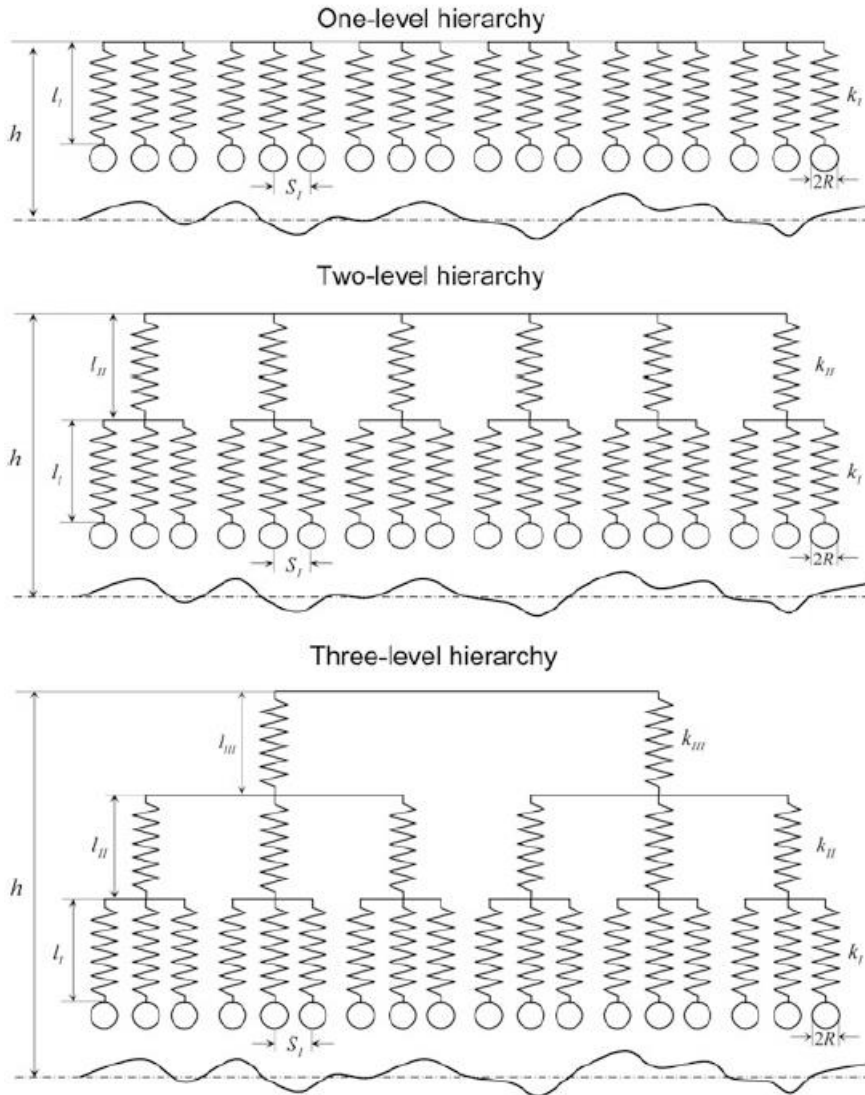
Self-cleaning



$$W_{pw} = \frac{-H_{pw}R_p}{6D_{pw}} \gg W_{ps} = \frac{-H_{ps}R_pR_s}{6D_{ps}(R_p + R_s)}$$



Role of hierarchy



Fabrication of Gecko-like Structures

One-level features

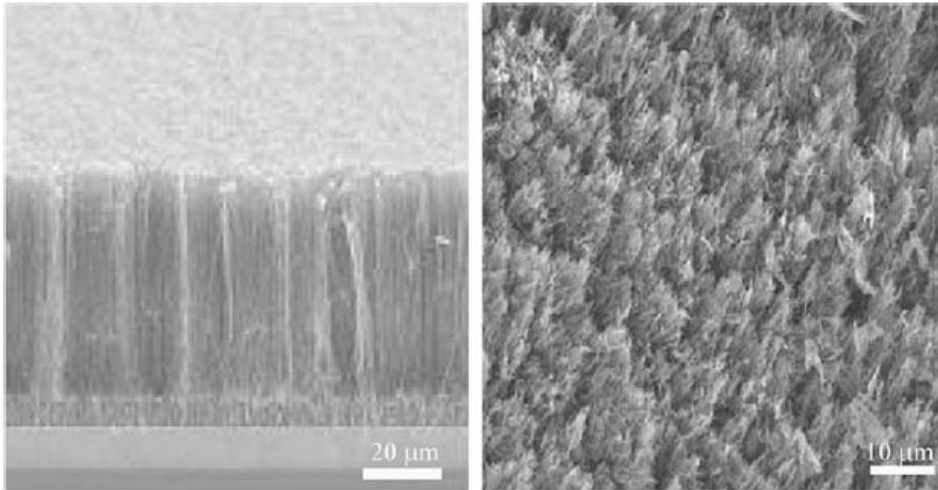


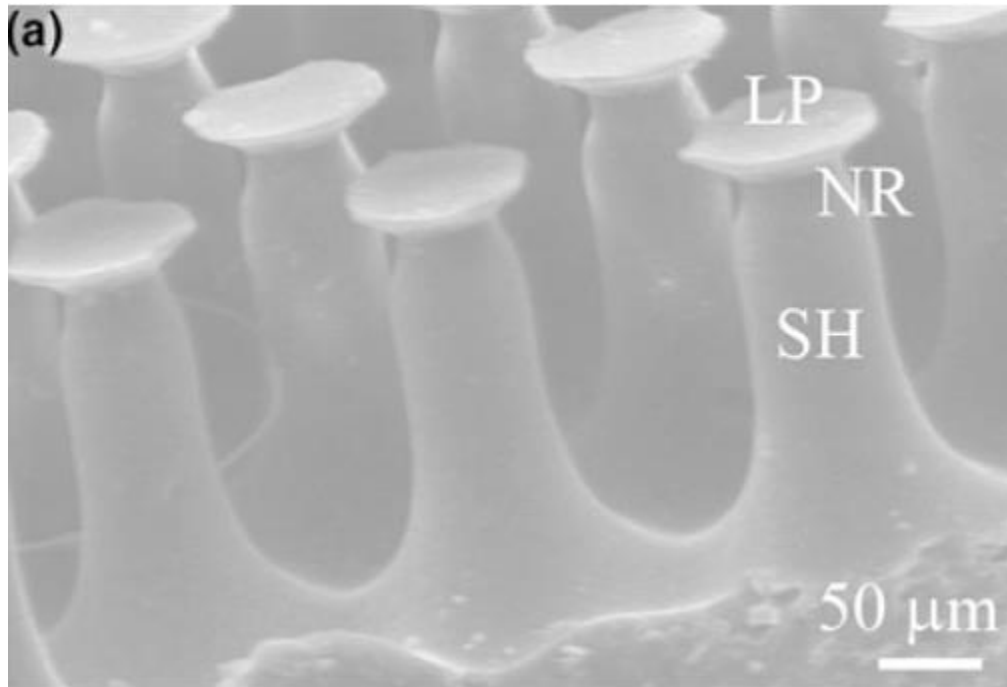
Fig. 19.34 Multi-walled carbon nanotube structures: (left) grown on silicon by chemical vapor deposition, (right) transferred into a PMMA matrix, and then exposed on the surface after solvent etching (Yurdumakan et al. 2005)



Polyimide pillars (before and after use)

Fabrication of Gecko-like Structures

One-level features



Fabrication of Gecko-like Structures

One-level features

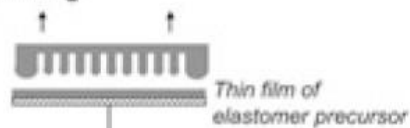
1) Soft moulding (complete filling of master cavities) and curing



2) Demoulding



3) Inking



4) Downwards curing



4) Printing, curing



4) Tilted printing, curing



1) Spin coat a thin film and wait for partial hardening (delay time, t_d)



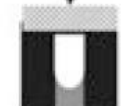
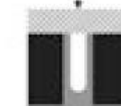
2) Retarded moulding (partial filling)



t_{d1}

$>>$

t_{d2}



Planar contacts

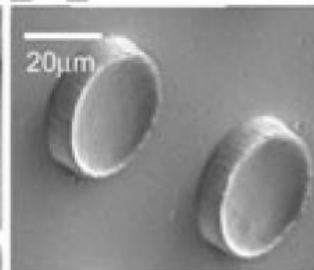
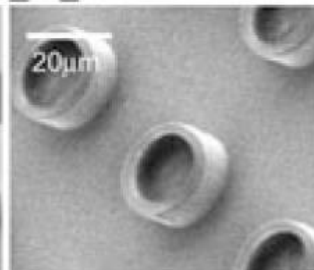
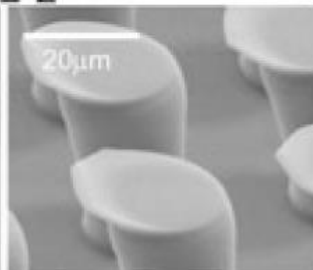
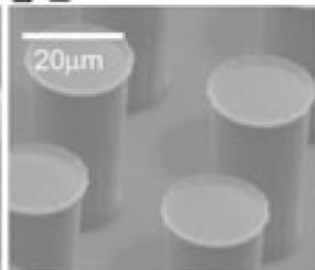
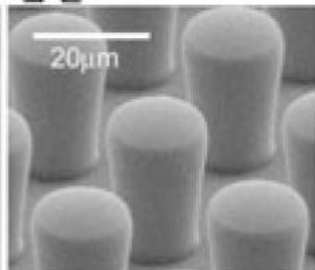
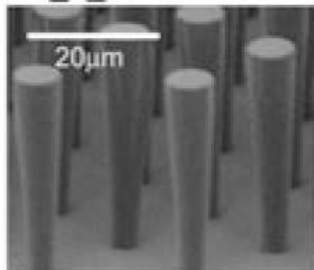
Spherical tips

Symmetric spatulae

Asymmetric spatulae

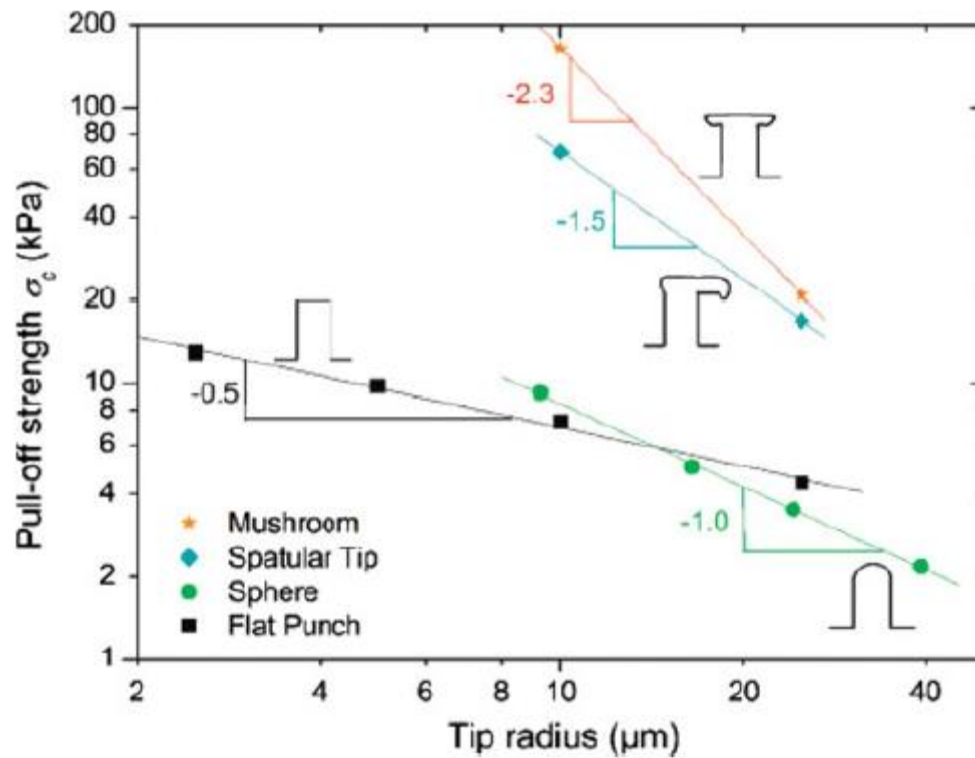
Tubes

Concave tips



Fabrication of Gecko-like Structures

One-level features



Fabrication of Gecko-like Structures

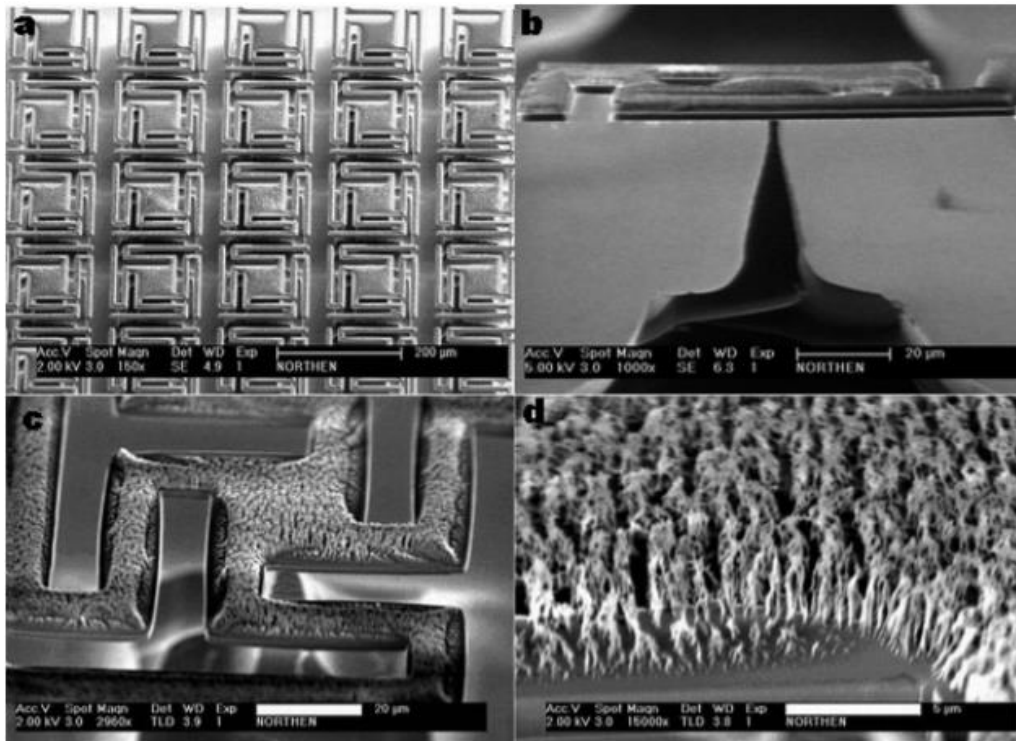
Multi-level features

Nanotechnology 16 (2005) 1159–1166

doi:10

A batch fabricated biomimetic dry adhesive

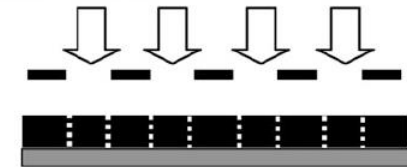
Michael T Northen^{1,3} and Kimberly L Turner²



(1) Spin-coating photoresist



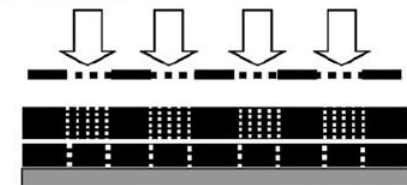
(2) Masked irradiation



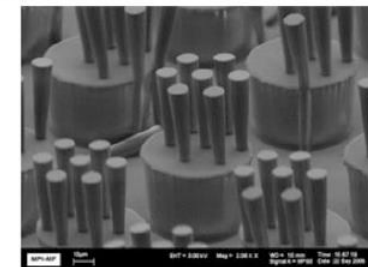
(3) Spin-coat new photoresist layer



(4) Masked irradiation



(5) Development



Fabrication of Gecko-like Structures

ADVANCED
MATERIALS

DOI: 10.1002/adma.200801340

A Gecko-Inspired Reversible Adhesive**

By Michael T. Northen, Christian Greiner,* Eduard Arzt, and Kimberly L. Turner

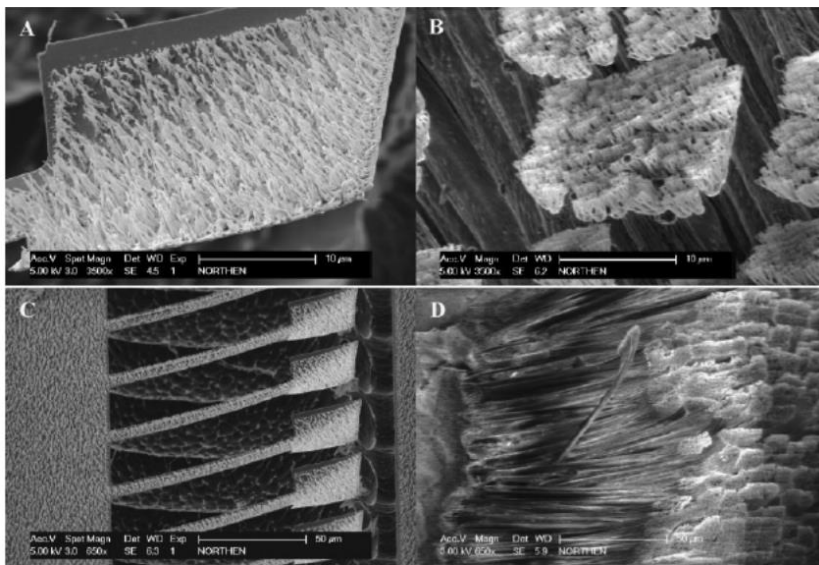
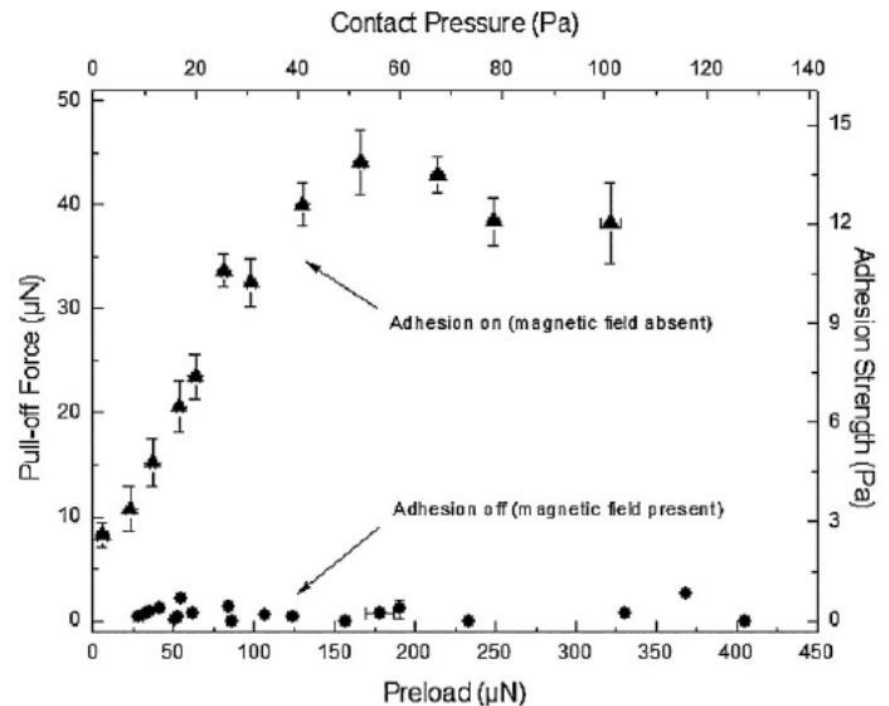
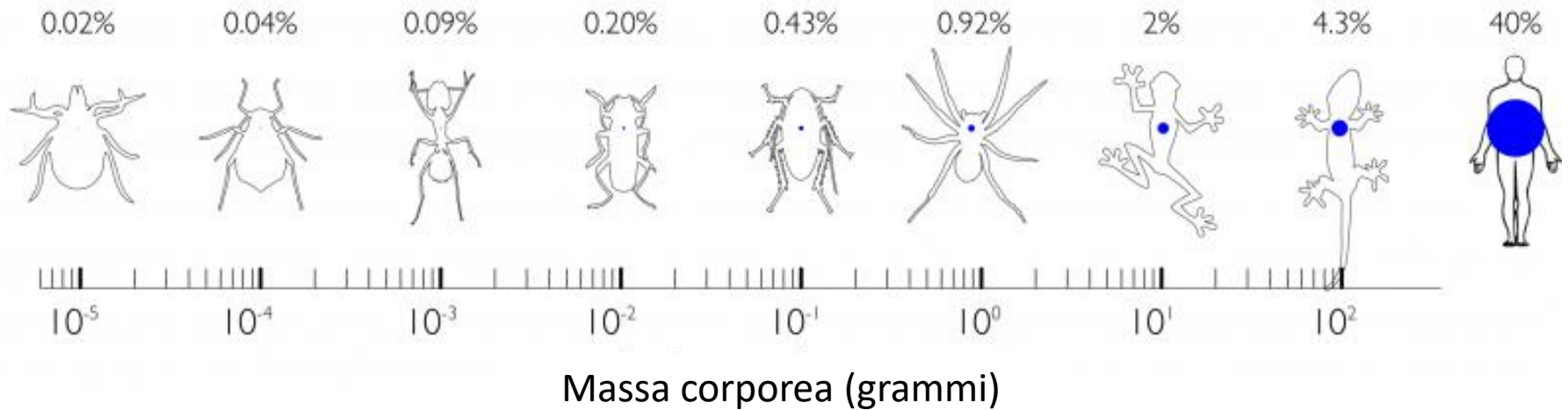


Figure 1. Electron micrographs of synthetic structures (left) and the analogous gecko structures (right), samples from a Tokay Gecko (*Gekko Gekko*). A) Paddle surface coated with evenly spaced uncondensed aligned vertical polymer nanorods (left) and B) the branched terminus of a seta into spatulae (right), same magnification and scale bar 10 μm. C) Freestanding nickel cantilevers and paddles coated with nanorods (left) and an array of setae (D) (right), same magnification and scale bar 50 μm.



Quanta superficie corporea deve essere coperta da elementi adesivi per sostenere il peso del corpo?
per sostenere il peso del corpo?





Love & is
light change
more being needed
and spiritual
might help and

Everything happens
for a reason
I believe in
God's plan
Trusty friend

Love the
Monday after the
the
I love my friends
Kiss

Love the
Monday after the
the
I love my friends
Kiss

Accept of the things
that life brings
be thankful because
you have it all
enjoy each and every
day and do it with love
- 1/23/08

Love
Young!

• Don't quit
• Never give up
• Don't make more of life as you
live
• Love your name and number
of the book
The Passion Project

Who will love
the life with
God
to the
New year

Enjoy your days
Because one day
you will be gone
So enjoy each day
to the max

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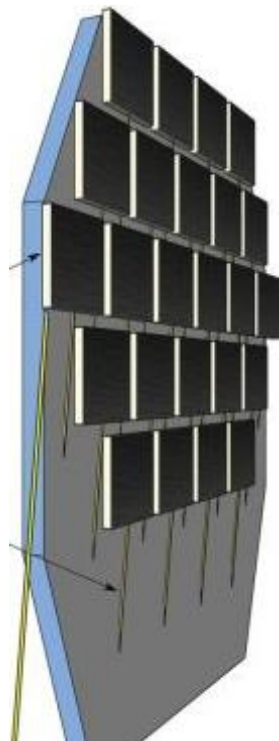
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Superliquiphobicity
($\theta > 150^\circ$)





Most prominent functions of the boundary layer on a hydrophobic plant surface
(Koch et al., 2009)

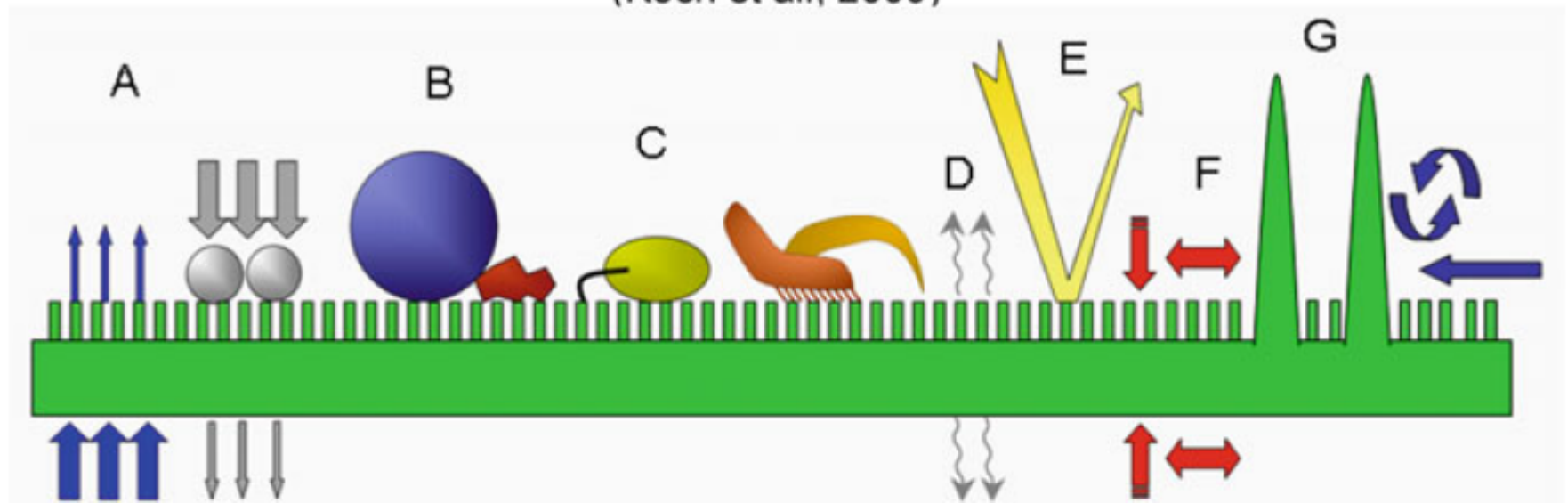
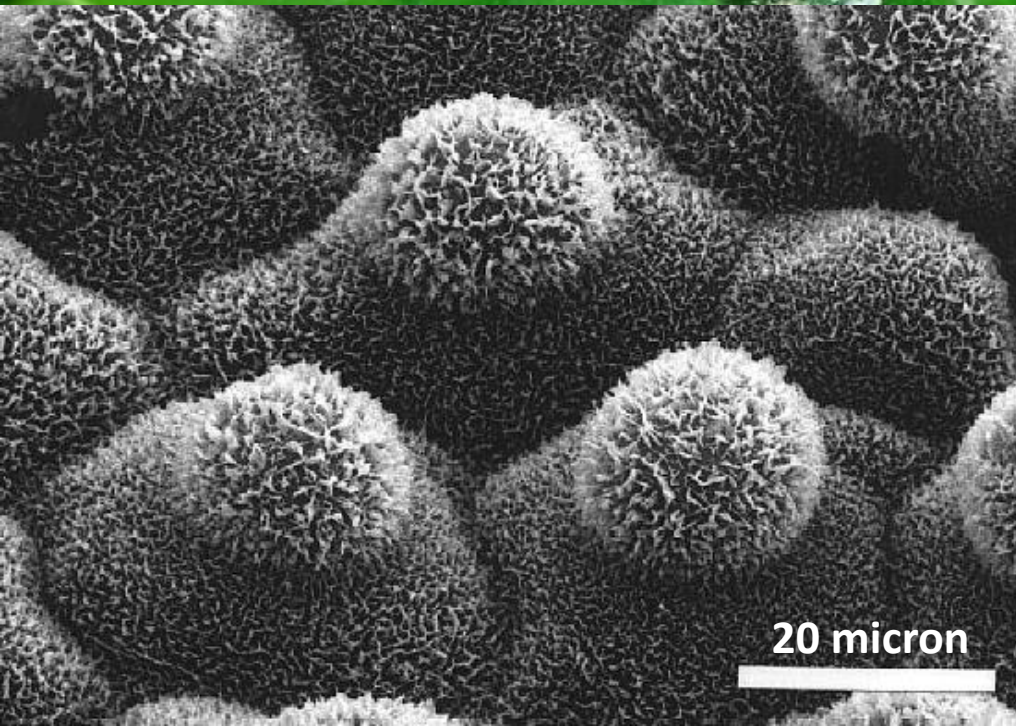
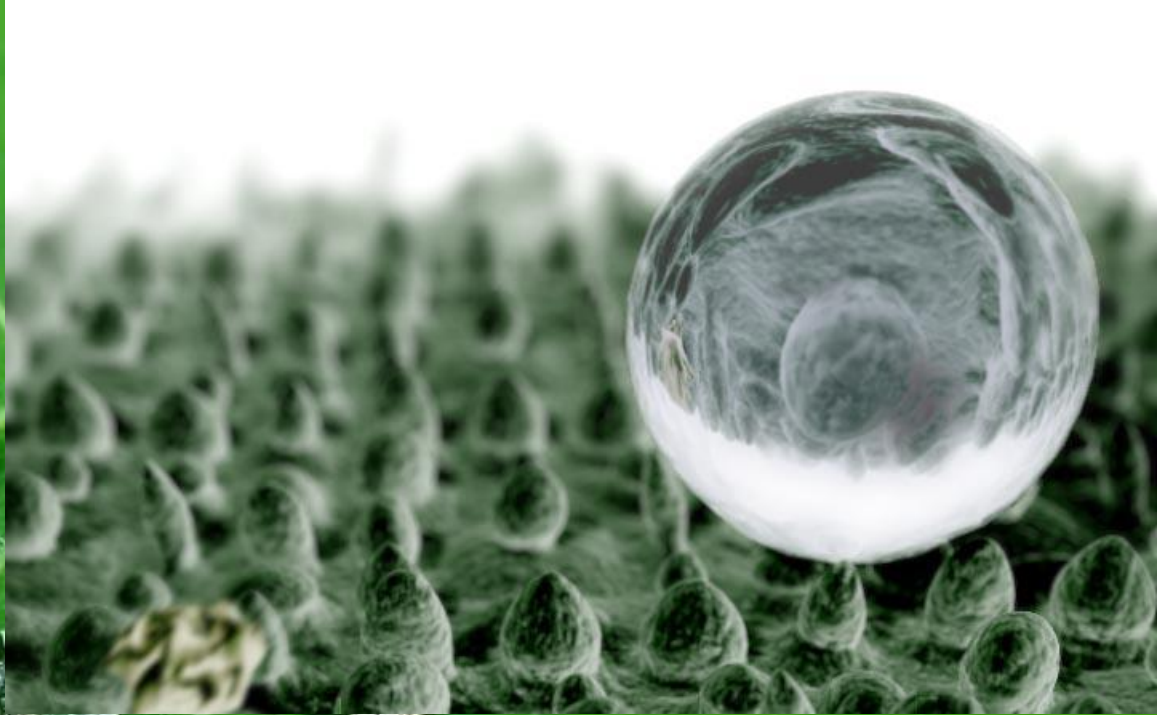


Fig. 4.1 Schematic of the most prominent functions of the boundary layer on a hydrophobic microstructured plant surface. (A) Transport barrier limitation of uncontrolled water loss/leaching from interior and foliar uptake, (B) surface wettability, (C) anti-adhesive, self-cleaning properties: reduction of contamination, pathogen attack and reduction of attachment/locomotion of insects, (D) signaling: cues for host-pathogens/insect recognition and epidermal cell development, (E) optical properties: protection against harmful radiation, (F) mechanical properties: resistance against mechanical stress and maintenance of physiological integrity, and (G) reduction of surface temperature by increasing turbulent air flow over the boundary air layer (adapted from Koch et al. 2009a)

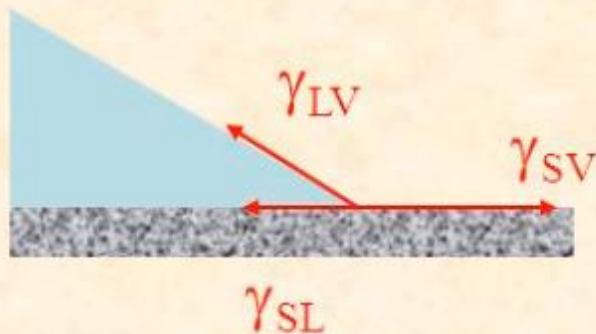


Fundamentals of Wetting

γ_{SL} : solid-liquid surface tension

γ_{SV} : solid-vapor surface tension

γ_{LV} : liquid-vapor surface tension



partially wetting liquid : $\theta < 90^\circ$



non wetting liquid : $\theta > 90^\circ$

equilibrium contact angle :
Young Dupré relation

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



perfect wetting liquid : $\theta = 0^\circ$

Wetting of a Rough Surface

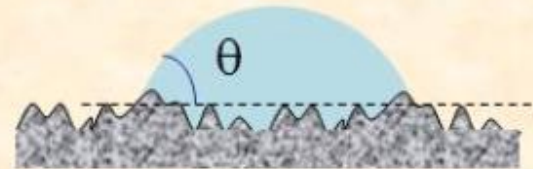
Young's law on rough surface:

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

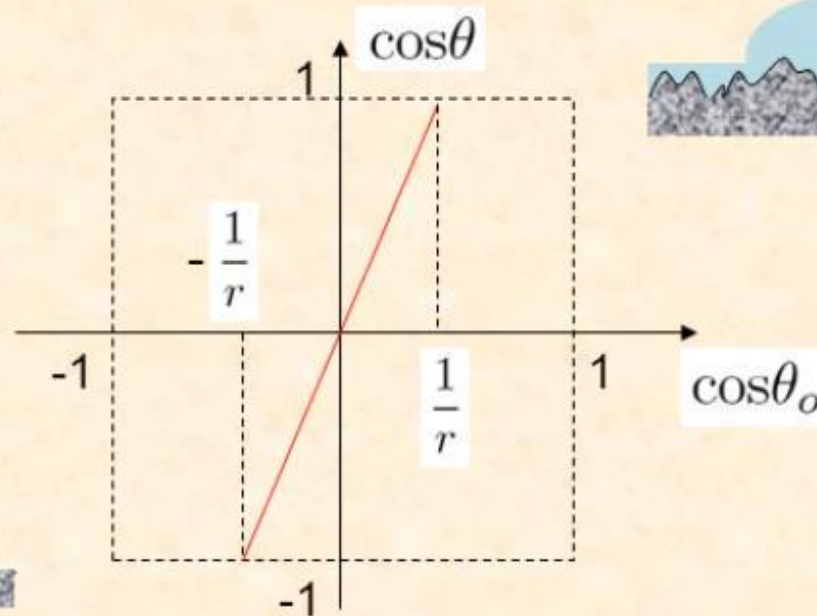
$$\cos\theta = r \cos\theta_o$$

θ_o : contact angle on flat chemically same surface

Wenzel law



$$r = \frac{\text{real area}}{\text{projected area}} > 1$$



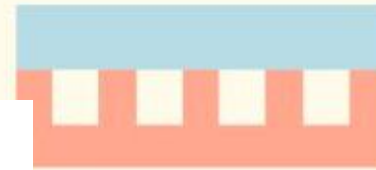
Wetting States

$$r = 1 + 2\pi nah > 1$$

$$\phi = n\pi a^2 < 1$$



Wenzel state



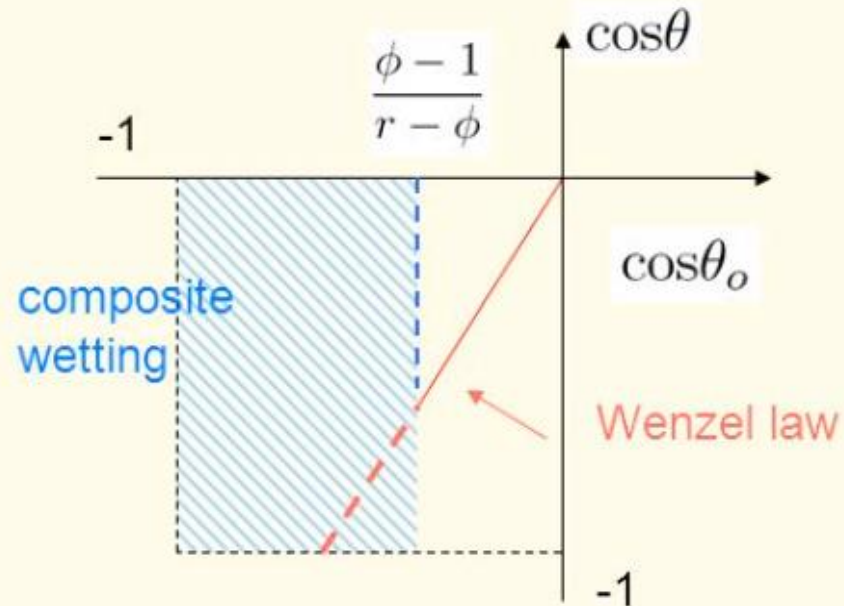
Cassie Baxter state


$$\phi\gamma_{SL} + (1 - \phi)(\gamma_{LV} + \gamma_{SV}) + (r - 1)\gamma_{SV}$$

Trapped air is favorable if

$$(1 - \phi)\gamma_{LV} < (r - \phi)(\gamma_{SL} - \gamma_{SV})$$

$$\cos\theta_o < \frac{\phi - 1}{r - \phi}$$

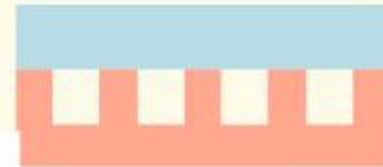


 Liquid must be non-wetting

Transition between wetting states



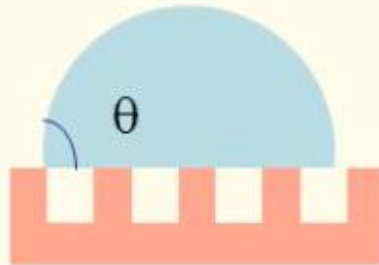
décompresseur TIFF (non compressé)
sont requis pour visionner cette image.



Only the TIFFs
décompresseur TIFF (non compressé)
sont requis pour visionner cette image.

$$\phi\gamma_{SL} + (1 - \phi)(\gamma_{LV} + \gamma_{SV}) + (r - 1)\gamma_{SV}$$

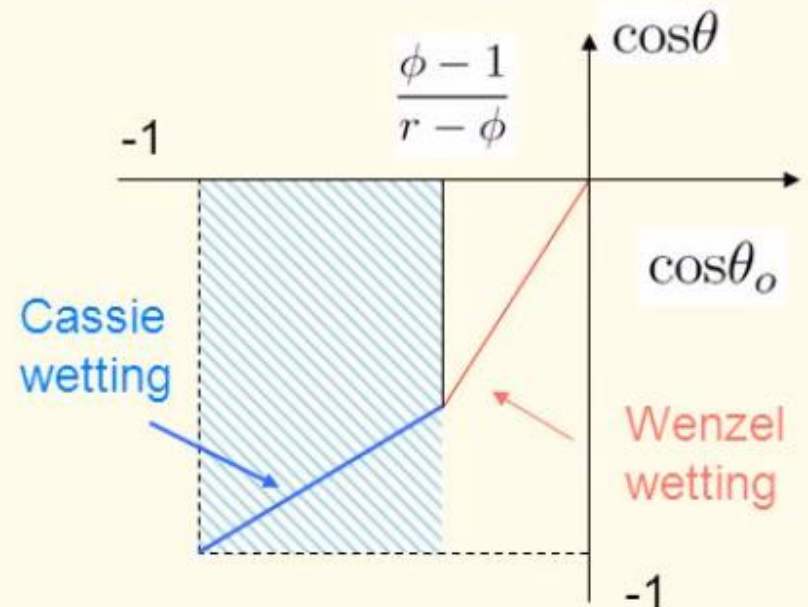
Young's law for
Cassie wetting:



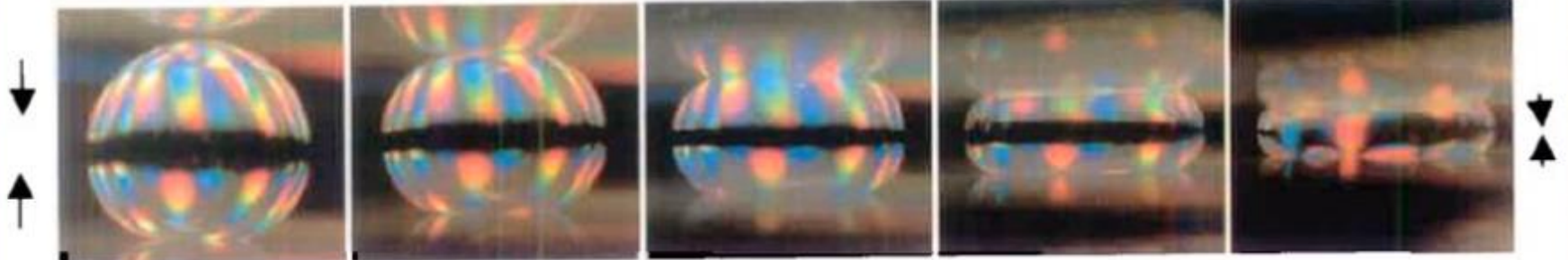
$$r\gamma_{SV} - \gamma_{SL,composite} = \gamma_{LV}\cos\theta$$

$$\cos\theta = \phi\cos\theta_o + \phi - 1$$

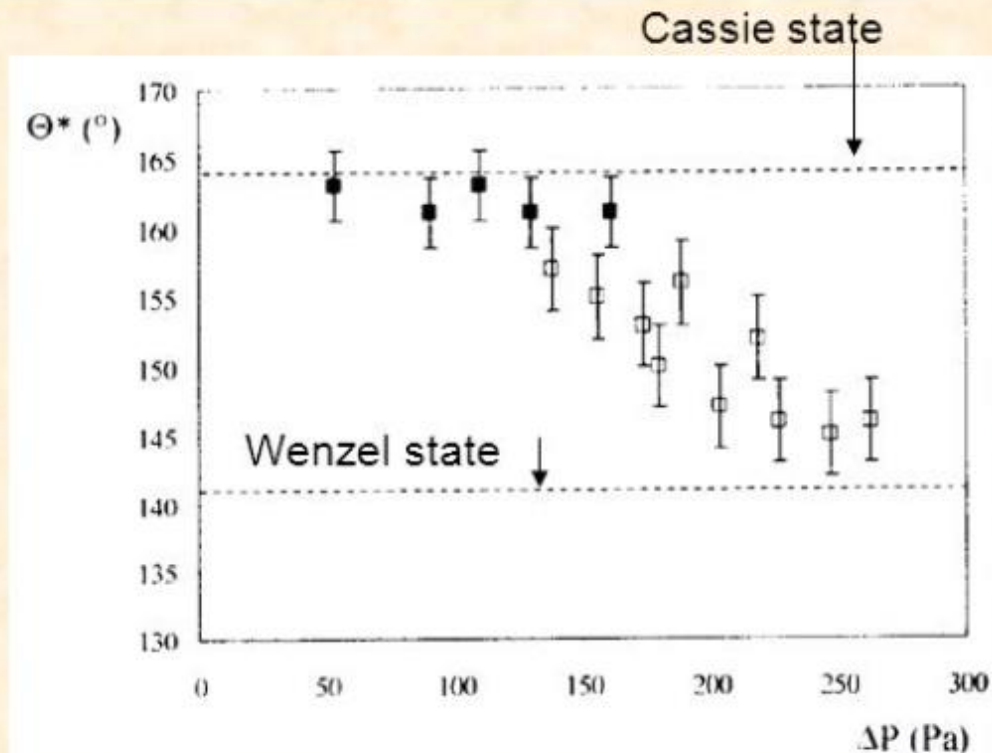
Cassie-Baxter's law



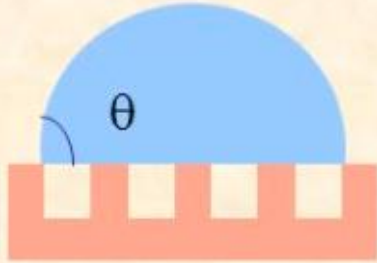
Metastability of Wetting States



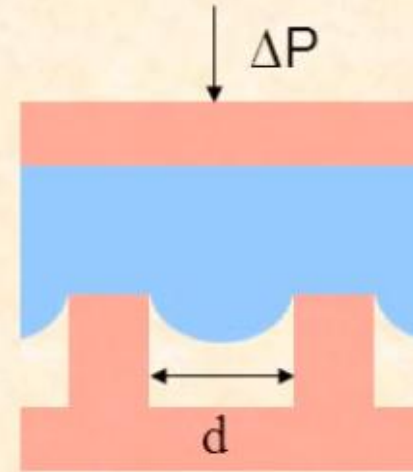
Compression of a water drop between two identical microtextured hydrophobic surfaces. The contact angle is measured as a function of the imposed pressure.



Metastability of wetting states

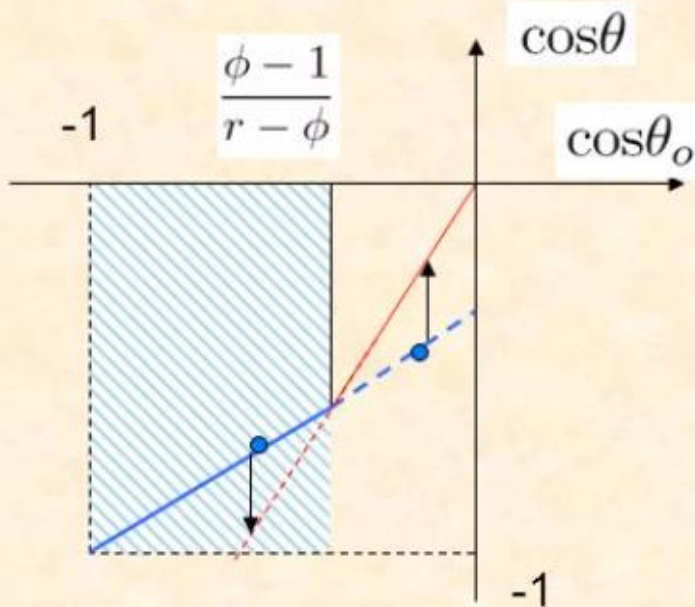


prepared in Cassie state



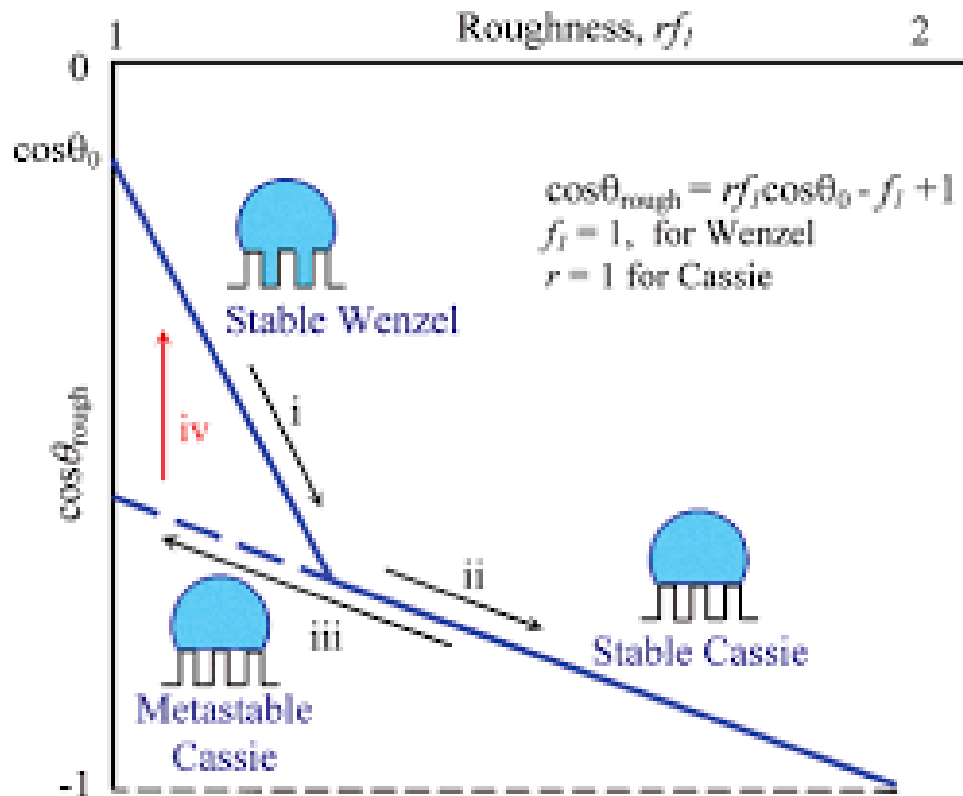
Transition to Wenzel state at

$$\Delta P \leq P_{cap} \sim -\frac{\gamma_{LV} \cos \theta}{d}$$



Robust Cassie state requires small scale and deep holes

Metastability and irreversibility

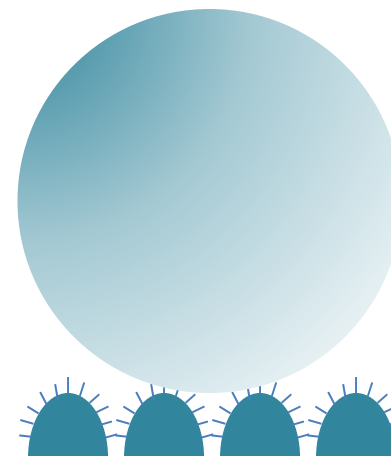




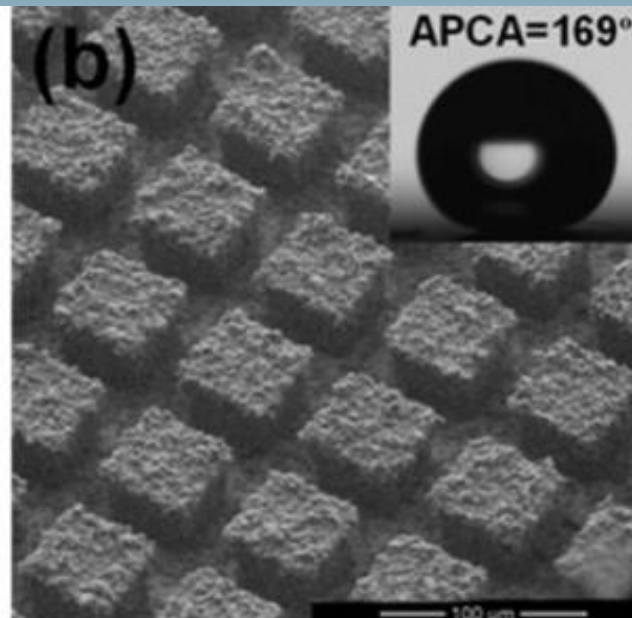
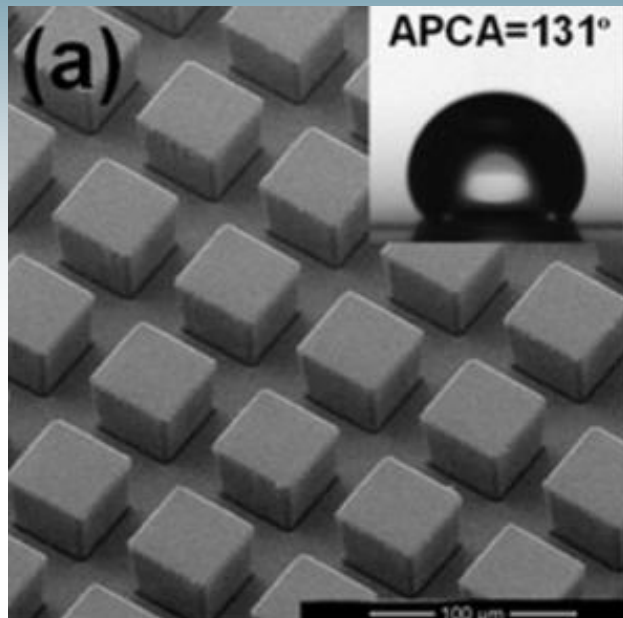
Superficie liscia



Rugosità micrometrica

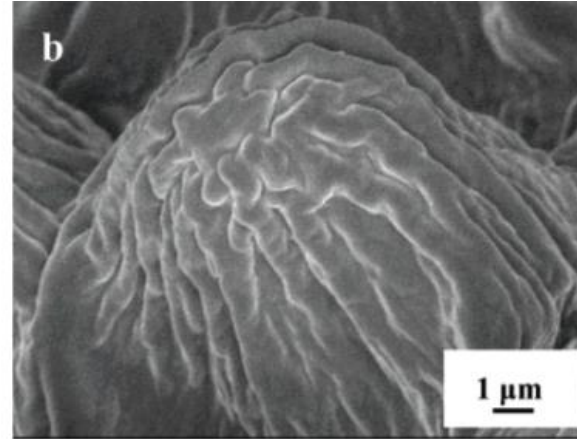
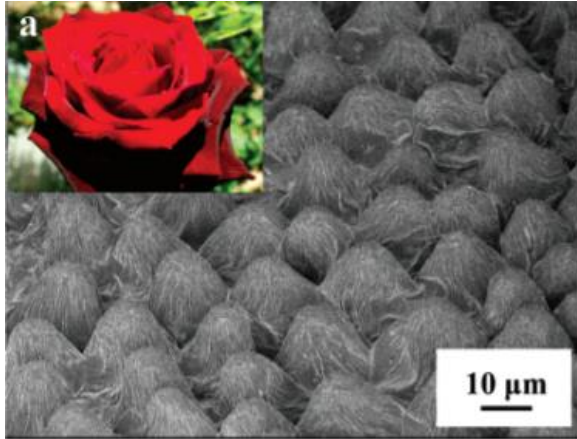


Rugosità nanometrica
e gerarchica

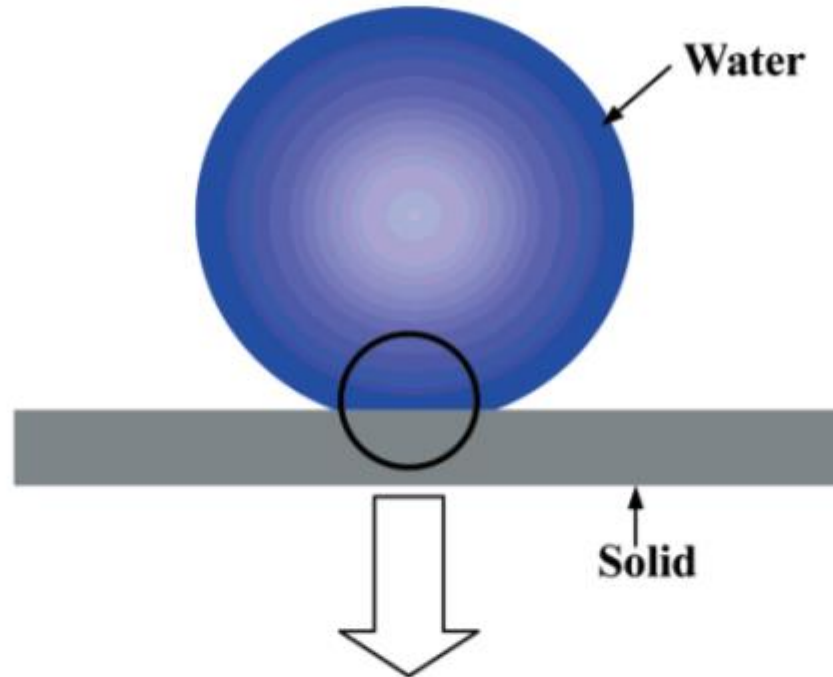




Petal Effect



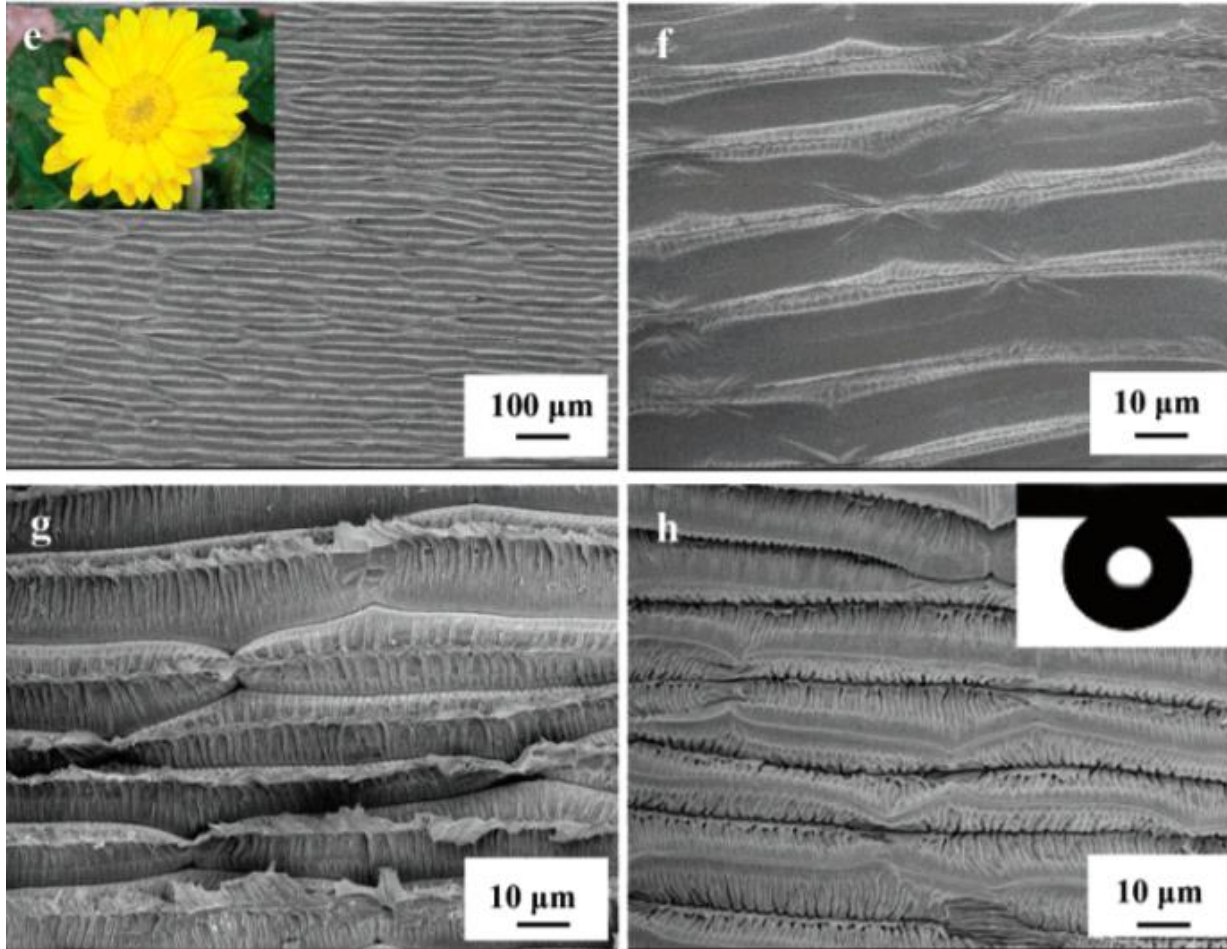
Petal Effect



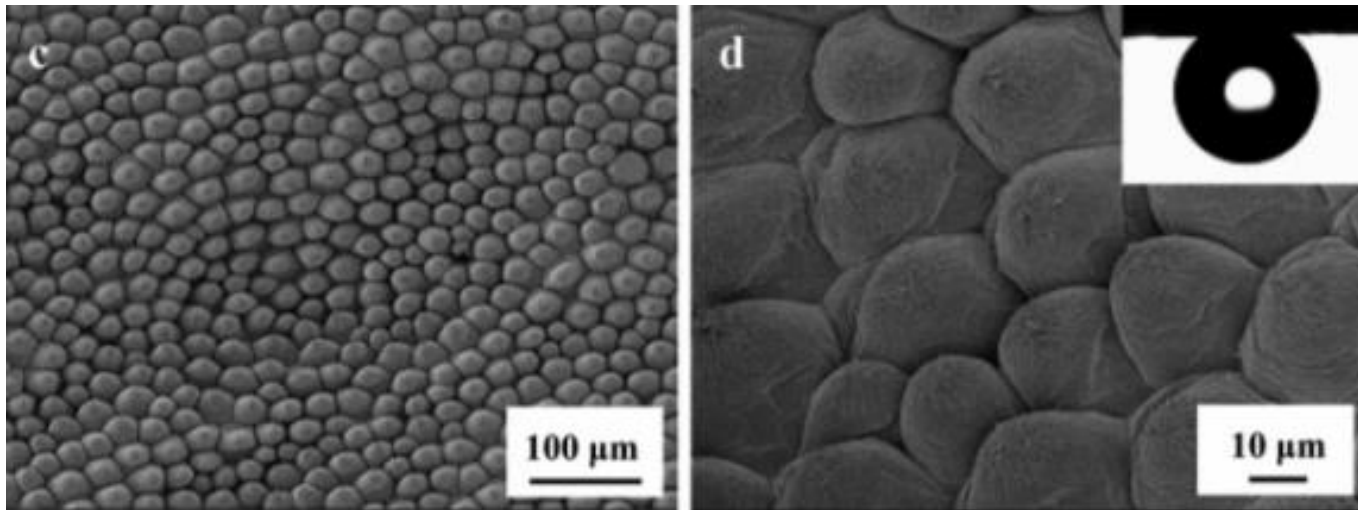
Petal (Cassie impregnating wetting state)

Lotus (Cassie's state)

Petal Effect

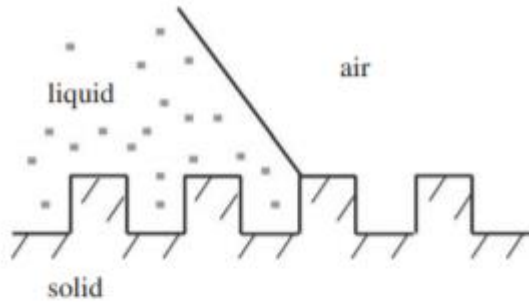


Petal Effect



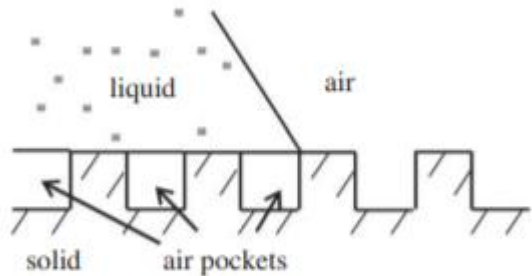
PS Replica

Modes of Superhydrophobicity



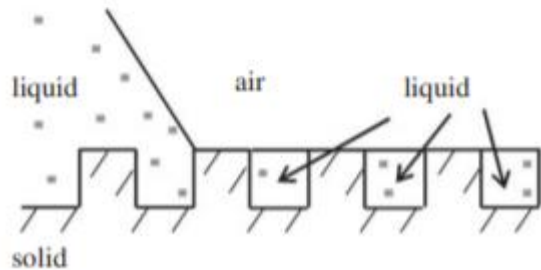
Wenzel

$$\cos \theta = R_f \cos \theta_0$$



Cassie-Baxter

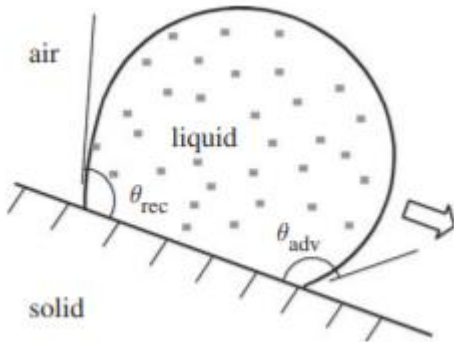
$$\cos \theta = R_f f_{SL} \cos \theta_0 - 1 + f_{SL}$$



Impregnating Cassie

$$\cos \theta = 1 + f_{SL} (\cos \theta_0 - 1)$$

Hysteresis



$$\cos \theta_{adv} - \cos \theta_{rec} = R_f(1 - f_{LA})(\cos \theta_{adv0} - \cos \theta_{rec0}) + H_r$$

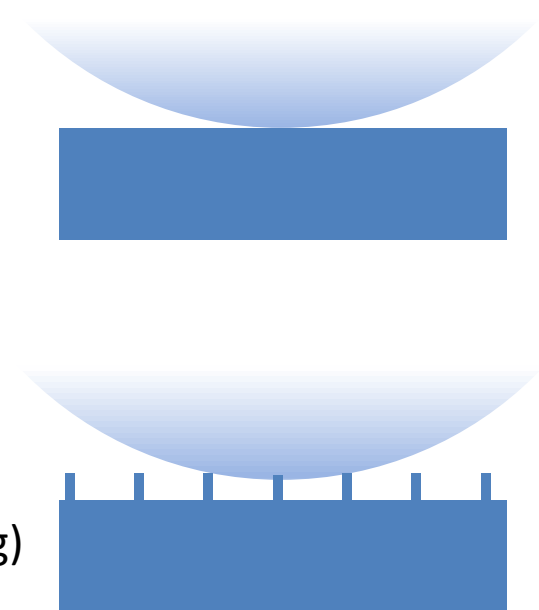
Homogeneous surface*

$f_{LA} \rightarrow 0$ Hysteresis increases with R_f

Composite surface*

$f_{LA} \rightarrow 1$ large CA and low Hysteresis (good for self-cleaning)

**under the droplet!*



Modes of Superhydrophobicity



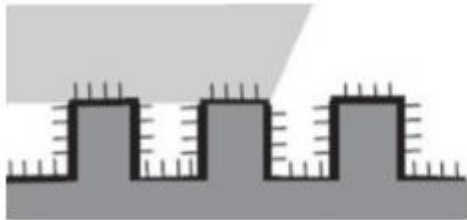
lotus



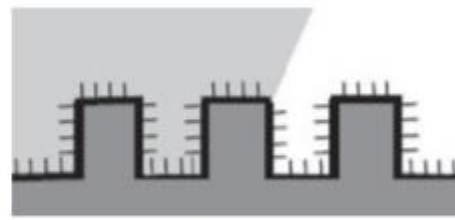
rose



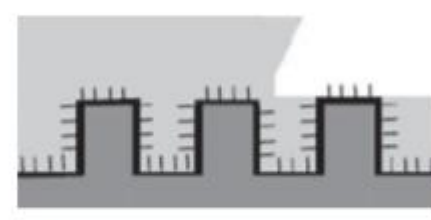
rose filled microstructure



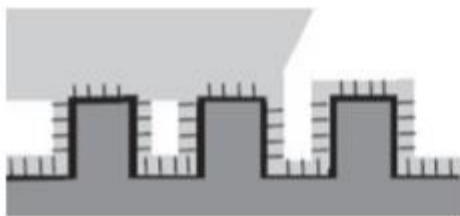
Cassie



Wenzel



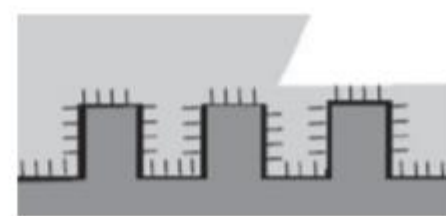
Wenzel filled microstructure



Cassie filled nanostructure

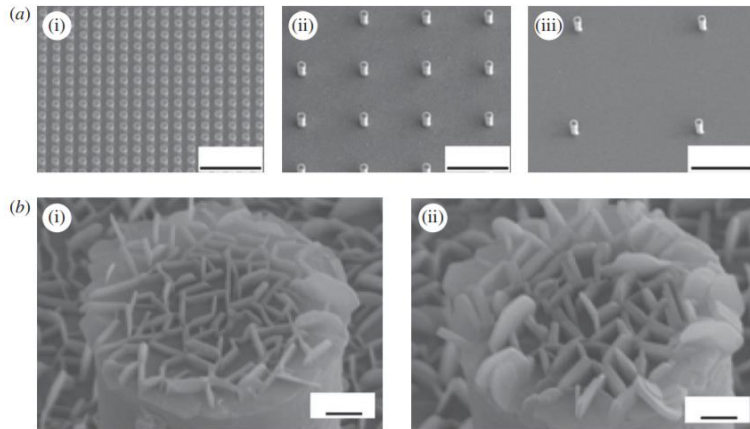


Wenzel filled nanostructure

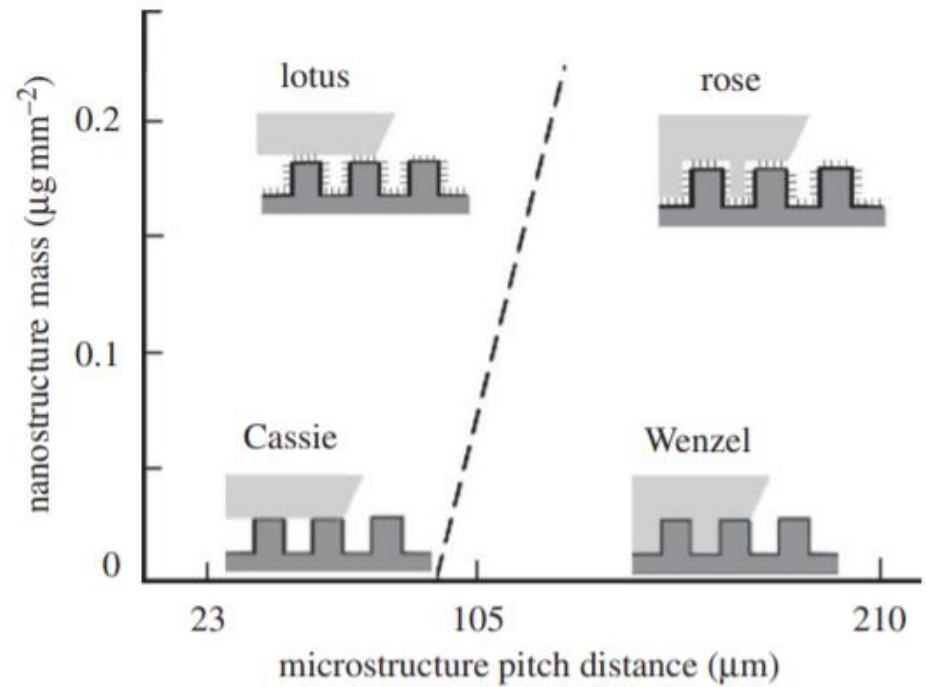
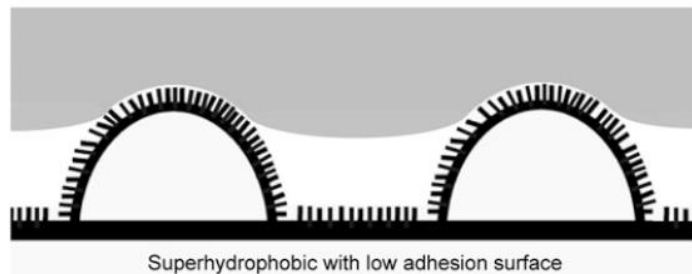
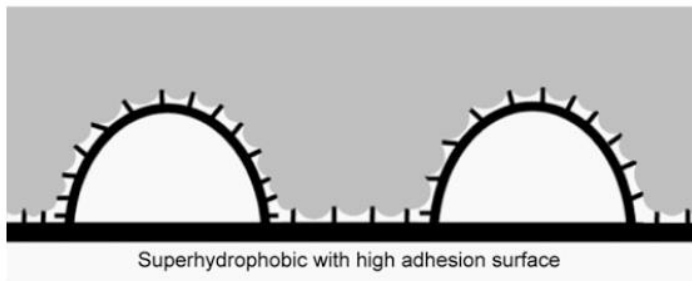


Wenzel filled micro/nanostructure

Modes of Superhydrophobicity



Scale bars, (a) 100 μm and (b) 2 μm .



Modes of Superhydrophobicity

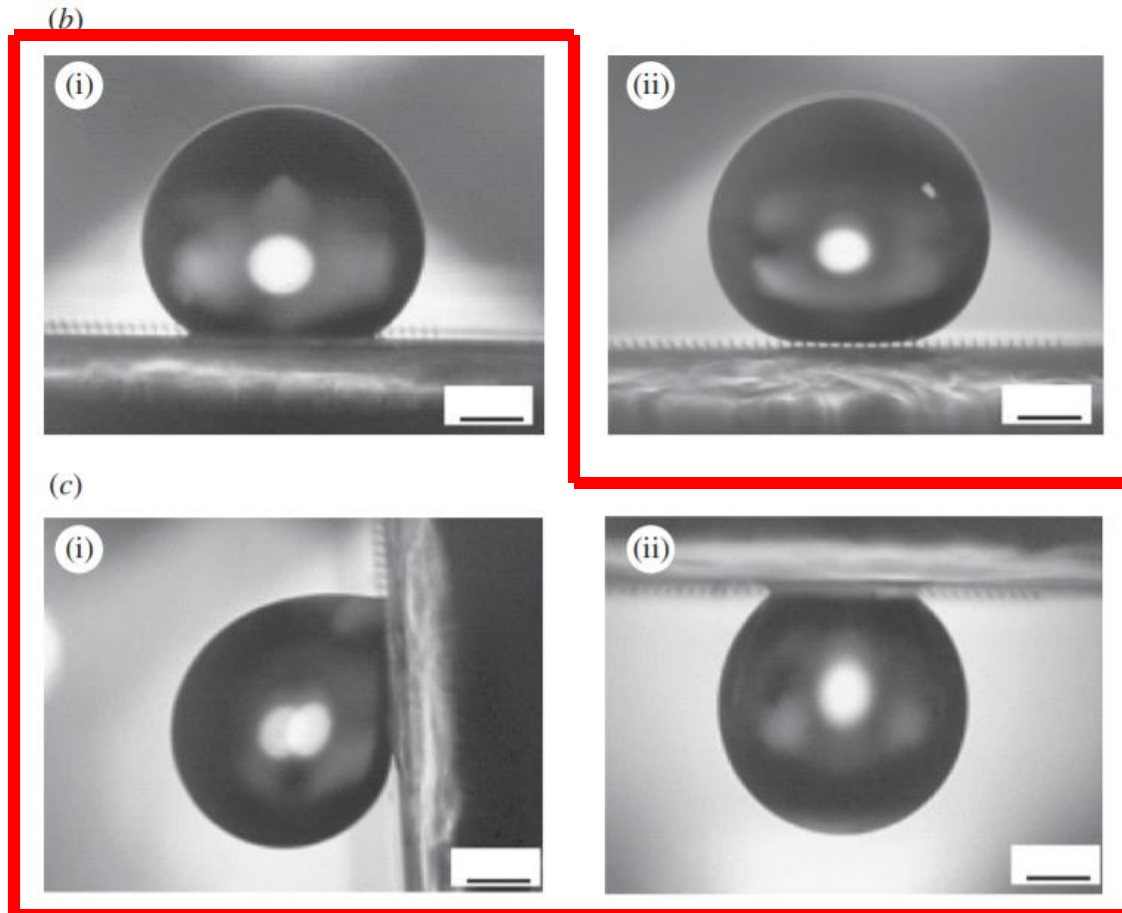


Figure 7. Shapes of droplets on various hierarchical structures. (a) Droplet on a horizontal surface of hierarchical structure with $23\ \mu\text{m}$ pitch and $0.1\ \mu\text{g}\ \text{mm}^{-2}$ *n*-hexatriacontane, showing air pocket formation. (b) Droplet on a horizontal surface of hierarchical structure with $105\ \mu\text{m}$ pitch and (i) $0.1\ \mu\text{g}\ \text{mm}^{-2}$ and (ii) $0.2\ \mu\text{g}\ \text{mm}^{-2}$ *n*-hexatriacontane, showing (i) no air pocket and (ii) air pocket formation, respectively. (c) Droplet on inclined surfaces of hierarchical structure with $105\ \mu\text{m}$ pitch and $0.1\ \mu\text{g}\ \text{mm}^{-2}$ *n*-hexatriacontane, showing that droplet is still suspended when (i) vertical and (ii) upside down. Adapted from Bhushan & Her (2010). Scale bars, all $500\ \mu\text{m}$.

Modes of Superhydrophobicity

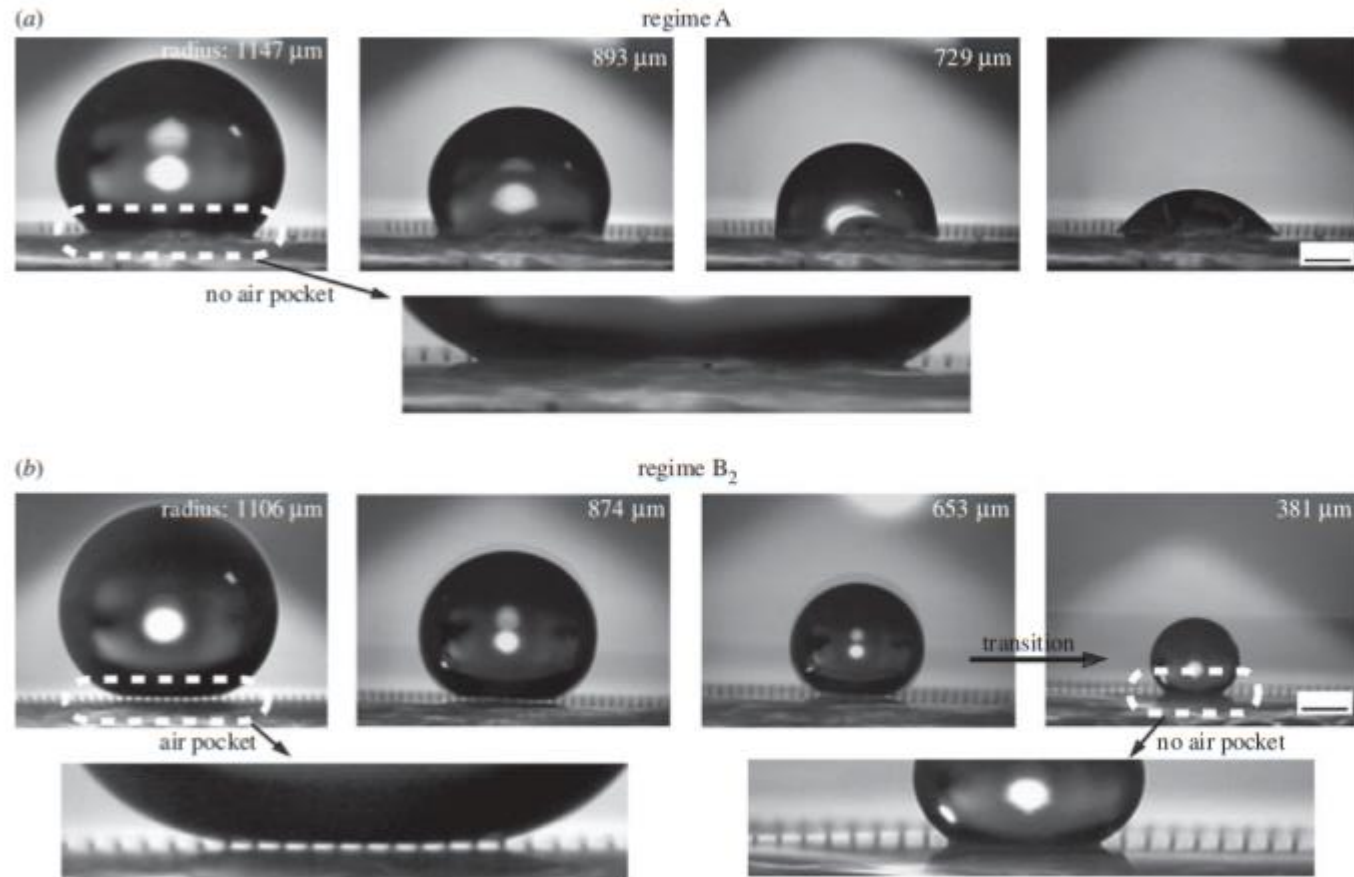
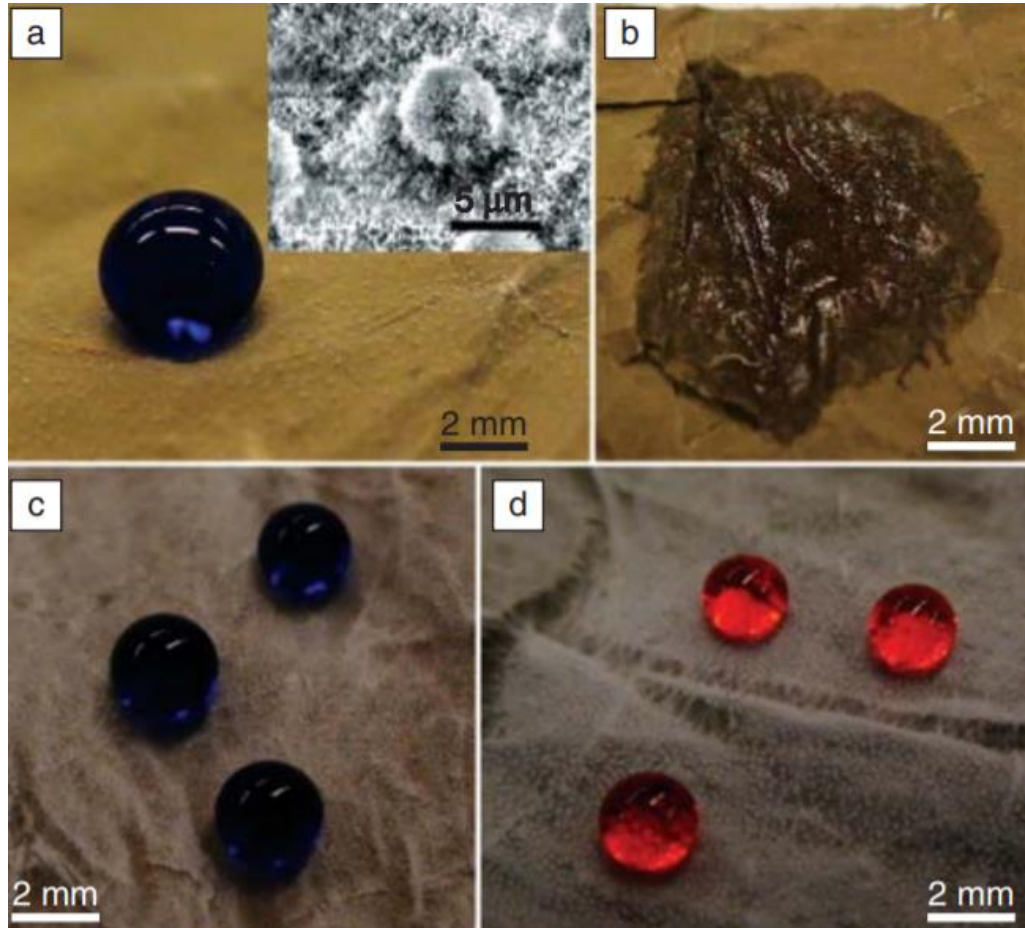


Figure 8. Optical micrographs of droplet evaporation on hierarchical structured surfaces with 105 μm pitch value and (a) 0.1 μm mm⁻² or (b) 0.2 μm mm⁻² n-hexatriacontane. (a) The 0.1 μm mm⁻² n-hexatriacontane coated sample has no air pocket formed between the pillars in the entire contact area until evaporation was complete. (b) The 0.2 μm mm⁻² n-hexatriacontane coated sample has an air pocket, and then transition from the lotus regime to the 'rose petal' regime occurs. Adapted from Bhushan & Her (2010). Scale bars, both 500 μm.

Design of general liquiphobic surfaces



- The matter of superhydrophobic surfaces is solved
- A fundamental problem in designing superoleophobic surfaces remains:

$$\cos\theta_c = \frac{(\phi_s - 1)}{(r - \phi_s)}$$

Critical angle for transition Wenzel-Cassie

➡ $\theta_c > 90^\circ$

➡ $\theta_0 > \theta_c > 90^\circ$

BUT there are no materials with surface energy low enough to guarantee $\theta_0 > 90^\circ$ with alkanes and other oily liquids

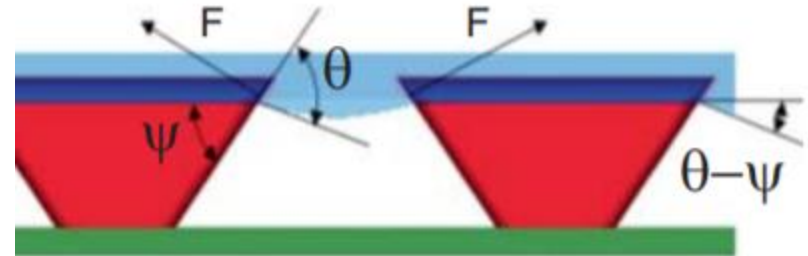
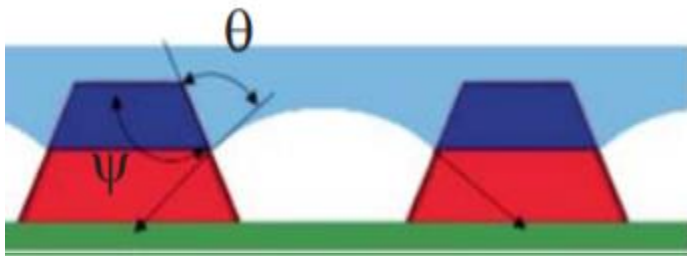
How to overcome this limitation?

HINT: Note that the wax on the lotus leaf is only weakly hydrophobic $\theta_0 = 74^\circ$, so there must be a strong structural reason for superhydrophobicity!

Key Engineering Parameters

- Surface Energy
- Roughness
- Geometry

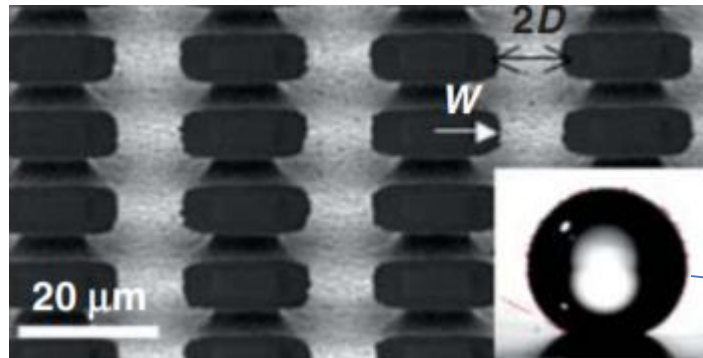
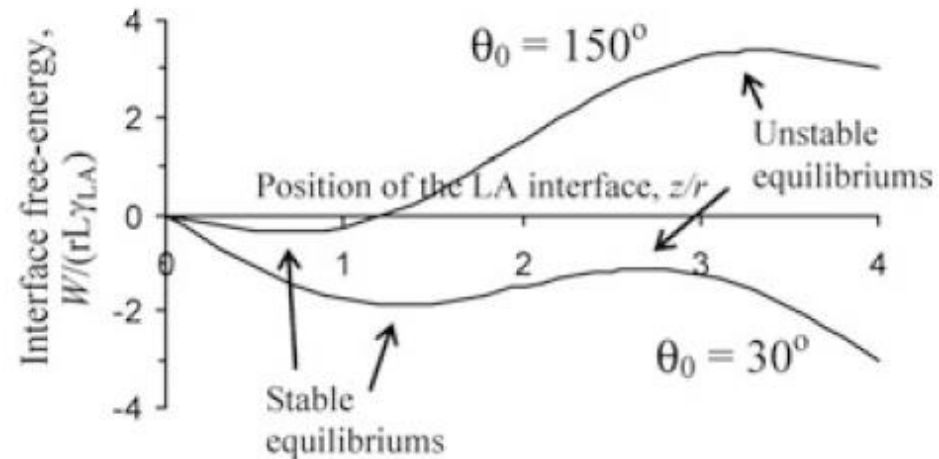
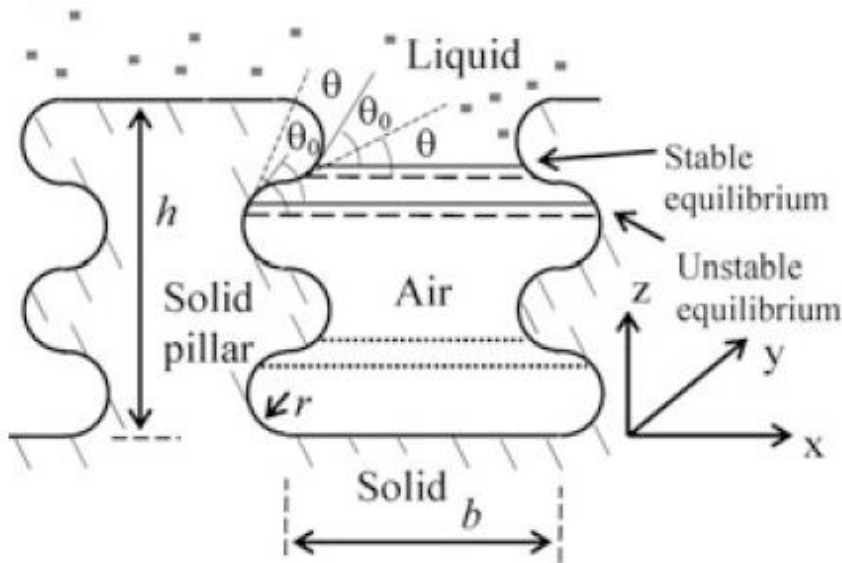
Role of re-entrant geometry



$$\theta_0 > \theta_c > 90^\circ$$

Key Engineering Parameters

Variable angle structures: composite surface with any contact angle



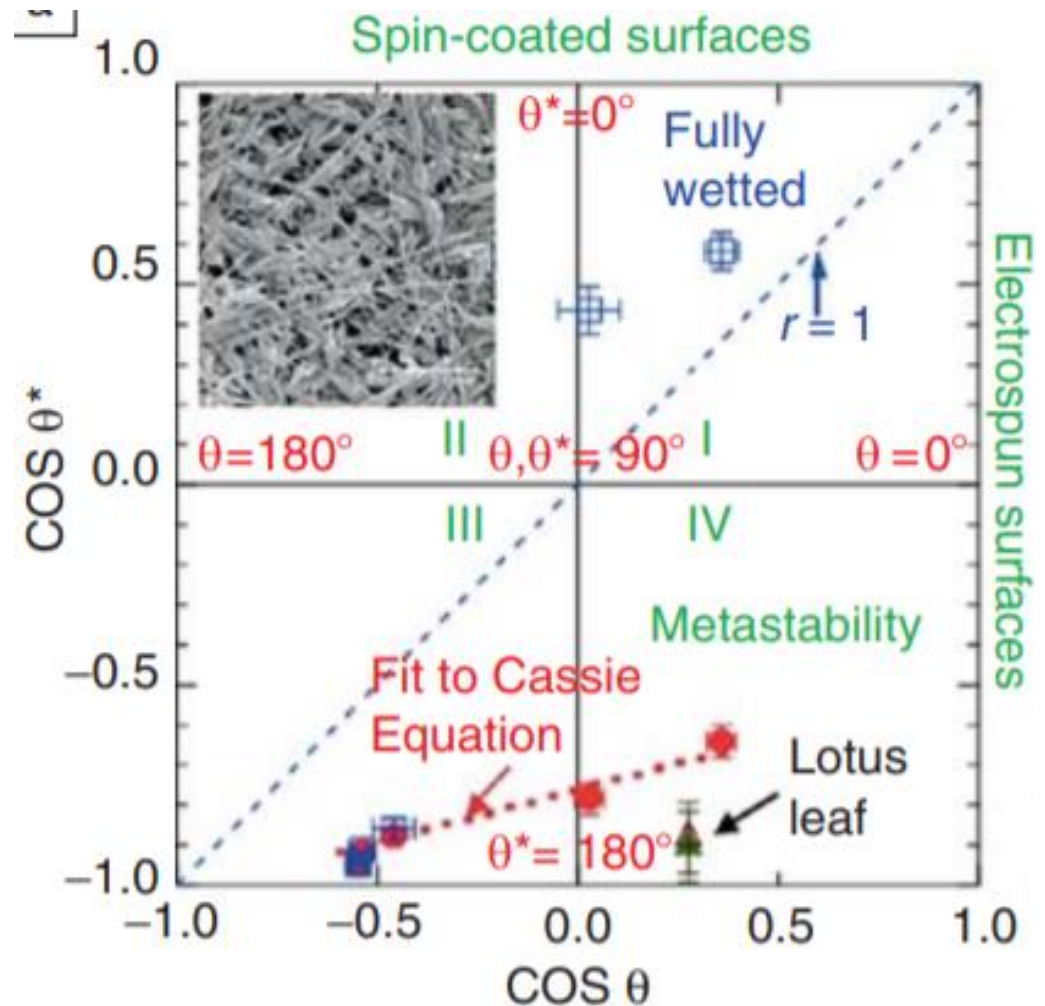
octane!!!

Key Engineering Parameters

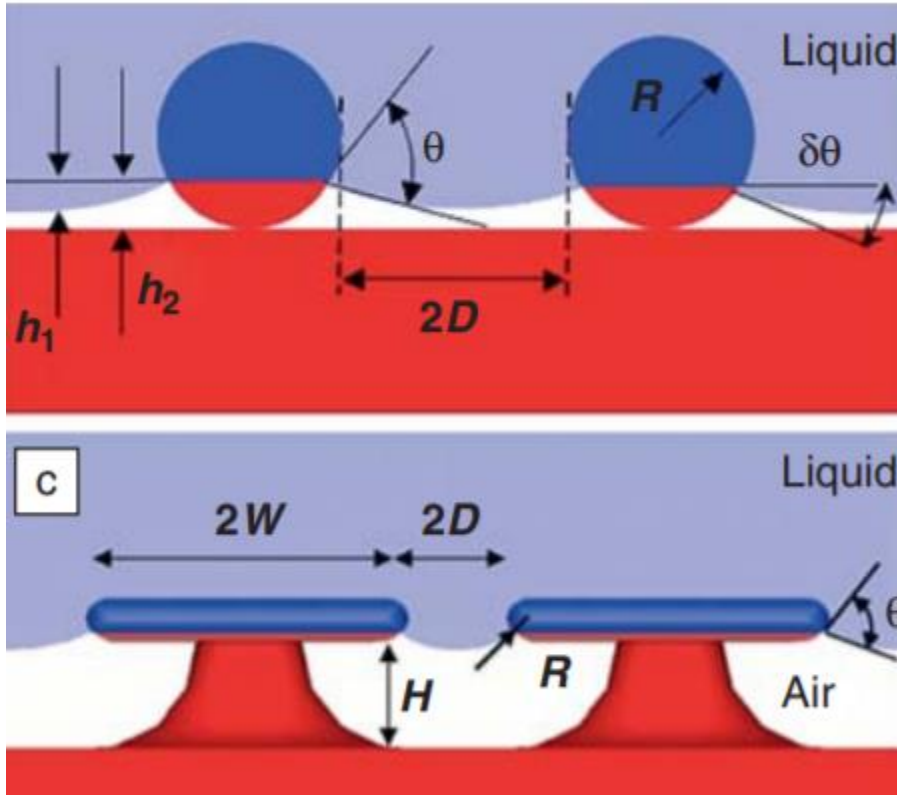
Variable angle structures: composite surface with any contact angle

Use of a mixture of PMMA and fluoroPOSS to systematically change the contact angle

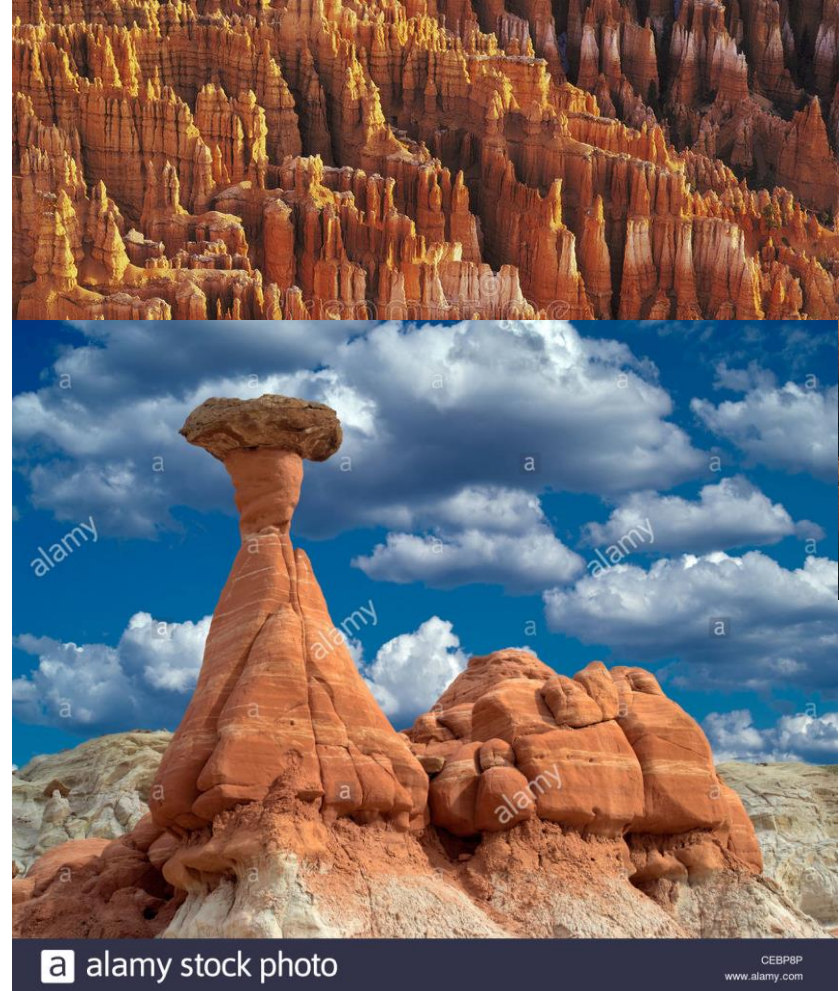
Plot *adv* and *rec* angles for smooth vs rough (reentrant) surfaces



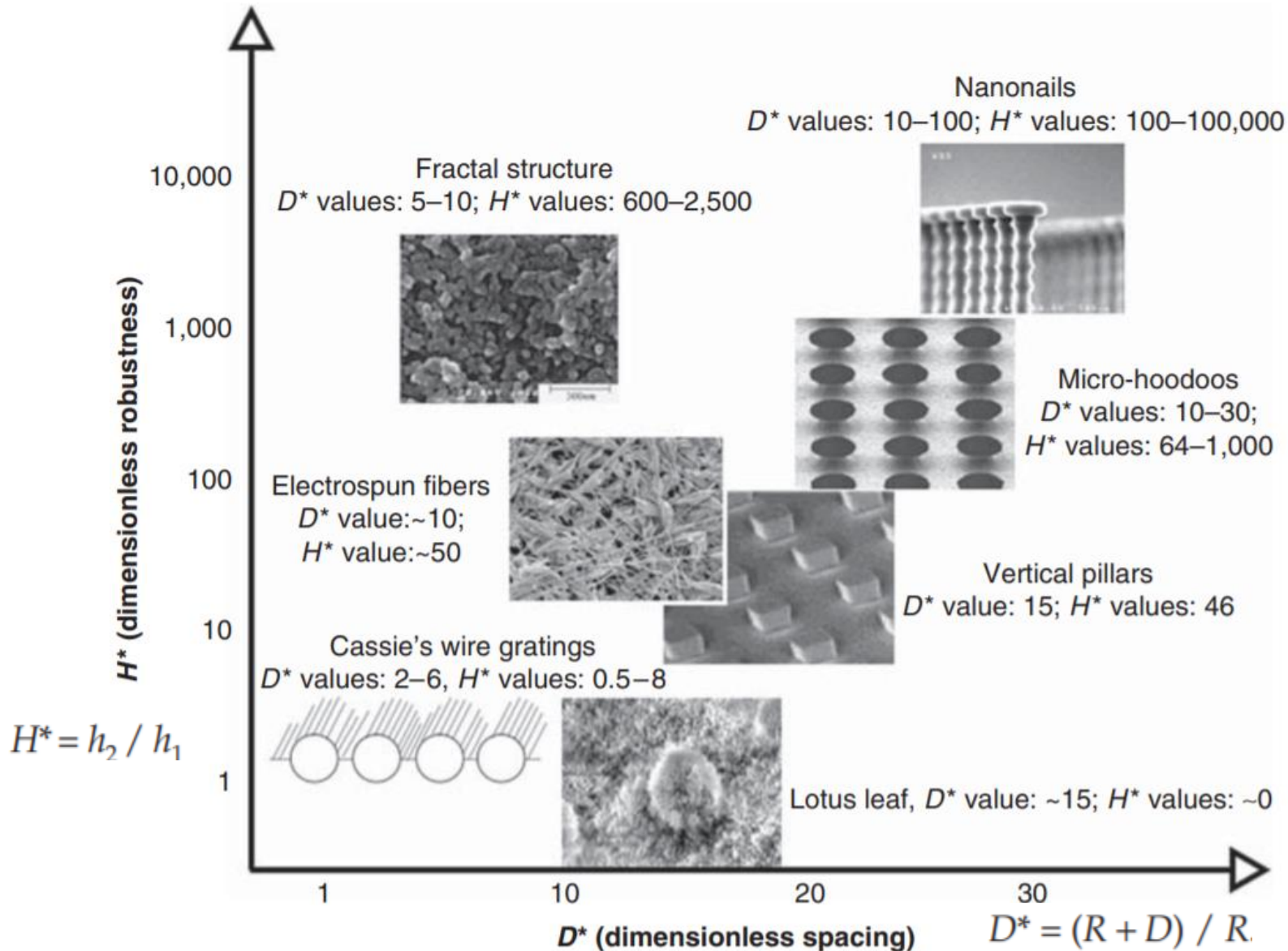
Robustness



Hodoos



Engineering Surfaces for Liquiphobicity



Engineering Surfaces for Liquiphobicity

Table I: Values of the Apparent Contact Angles (θ^*) with Water and Octane and Corresponding Values of the Robustness Parameter H^* for Various Natural and Artificial Surfaces Discussed in the Literature.

	Water			Octane		
	θ^* (deg)	H^*	$\theta - \psi^a$ (deg)	θ^* (deg)	H^*	$\theta - \psi^a$ (deg)
Vertical pillars ²³	~160	~70	30	0	~50	-30
Fractal structure ^{8 b}	~165	740–3,800	75	0	600–2,500	0
Cassie's wire gratings ¹⁹	~150	3.4–34	105	NA ^d	0.5–8	45
Electrospun fiber surface ⁶	~165	~210	120	~140	~50	60
Lotus leaf ^c	~155	~180	~15	0	~0	NA ^d
Micro-hoodoos ⁶	~165	95–1,500	120	140–165	64–1,000	60
Nanonails ¹⁰	~150	150–150,000	120	130–150	100–100,000	60

^aAny liquid for which $\theta - \psi < 0^\circ$ will immediately yield a fully wetted interface.

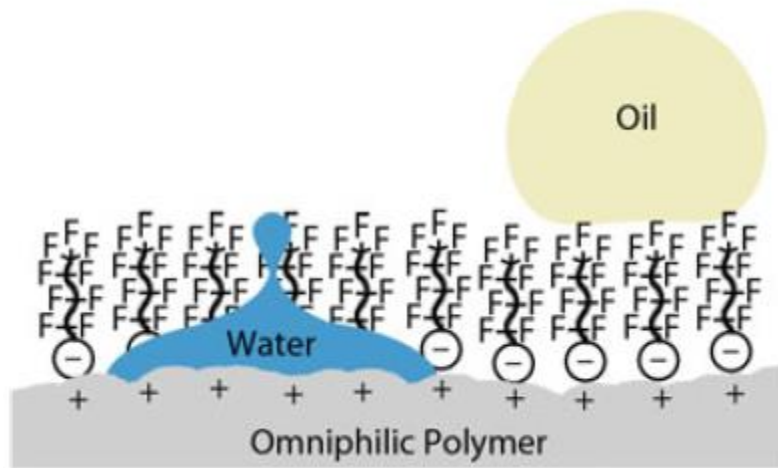
^bThe reentrant angle ψ is hard to measure on randomly shaped textures. On these fractal-like structures, ψ is expected to be $\sim 45^\circ$ as octane penetrates into the surface texture.

^cThe geometry of the lotus leaf has been estimated through the inspection of various published scanning electron microscopy (SEM) images and is possibly prone to error.

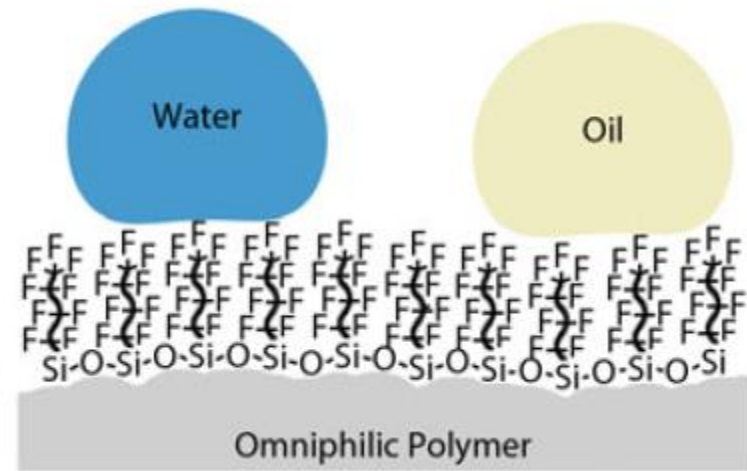
^dNot available.

Engineering surfaces for selective liquiphobicity

Schematic of "flip-flop" surface properties



Schematic of "non-flip-flop" surface properties

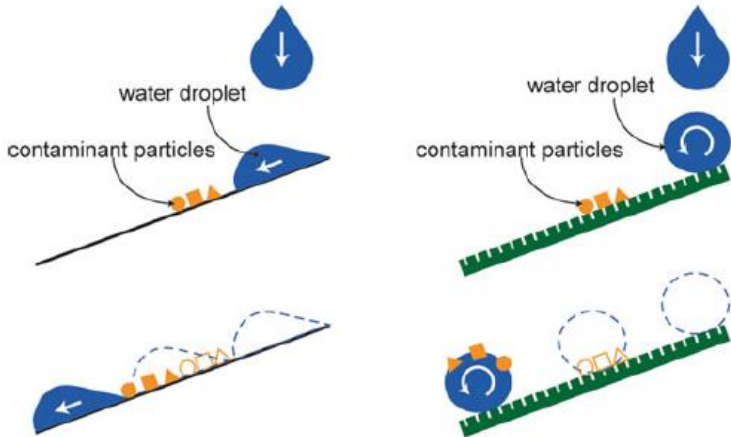


Self-cleaning

Liquid droplets on contaminated smooth and lotus-like surfaces

Smooth surface

Lotus-like surface

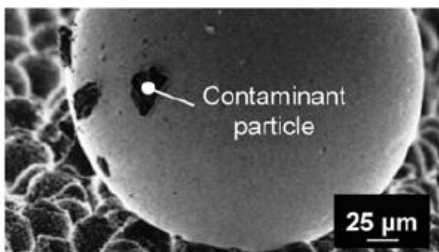


(a)

Water droplet cleaning Lotus leaf

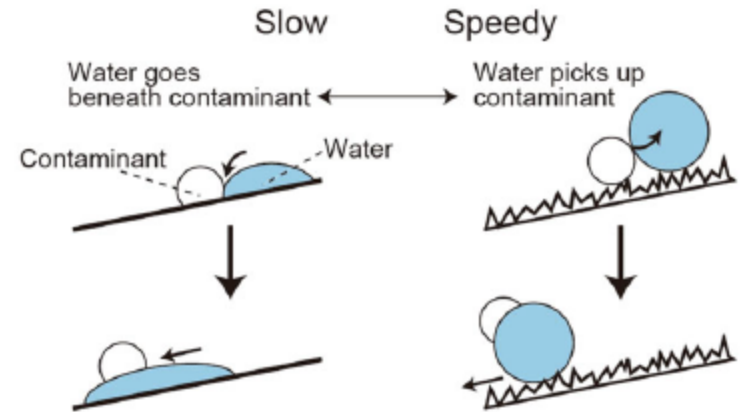


Mercury droplet cleaning Taro leaf



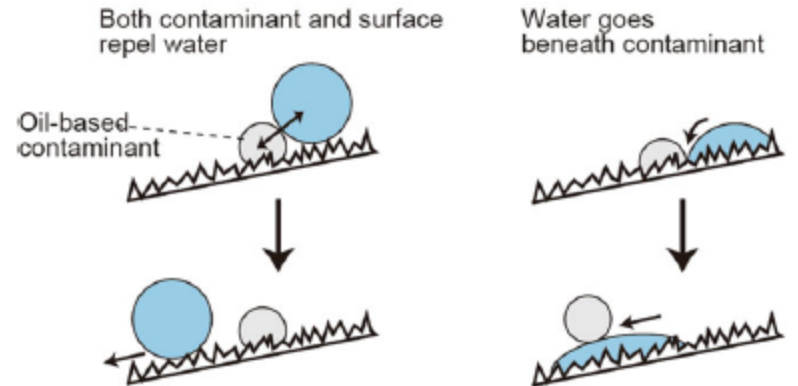
(a) Superhydrophilic surface

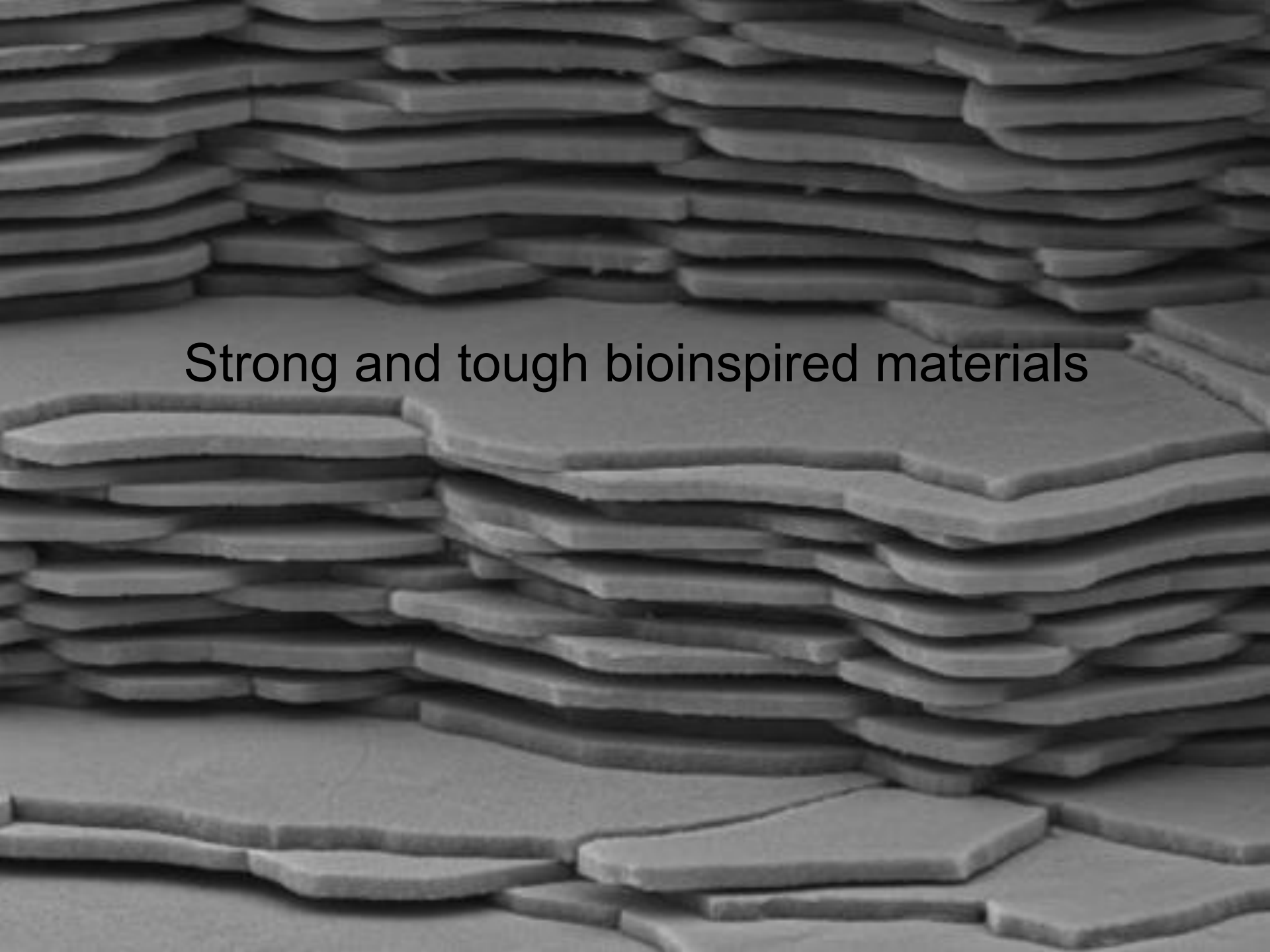
(b) Superhydrophobic surface



(c) Superhydrophobic surface with oil-based contaminant

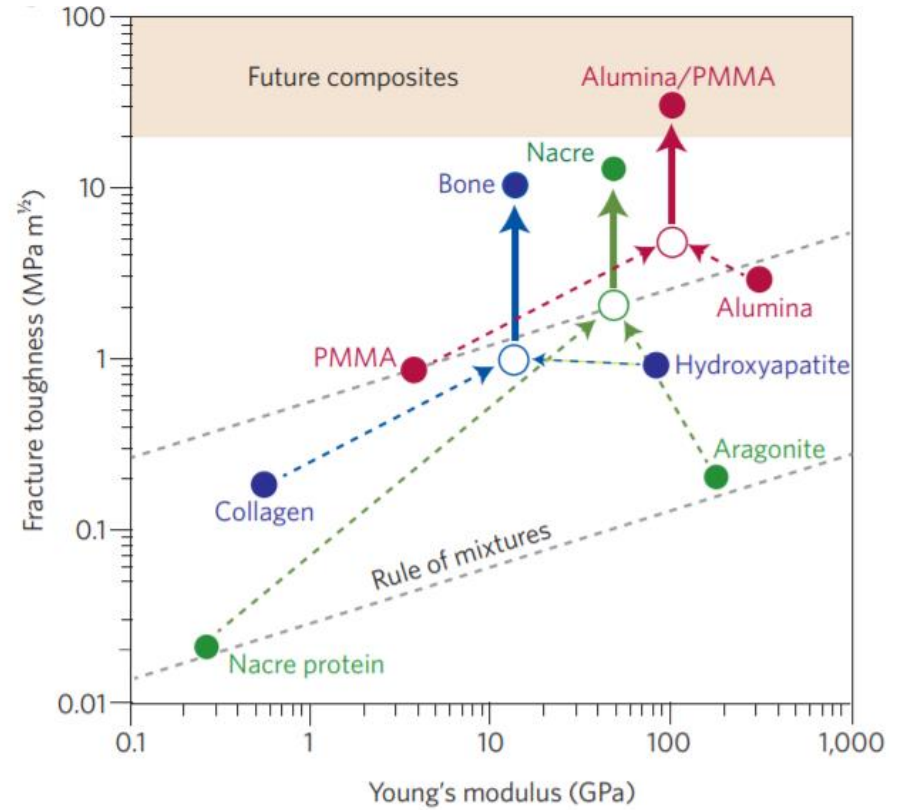
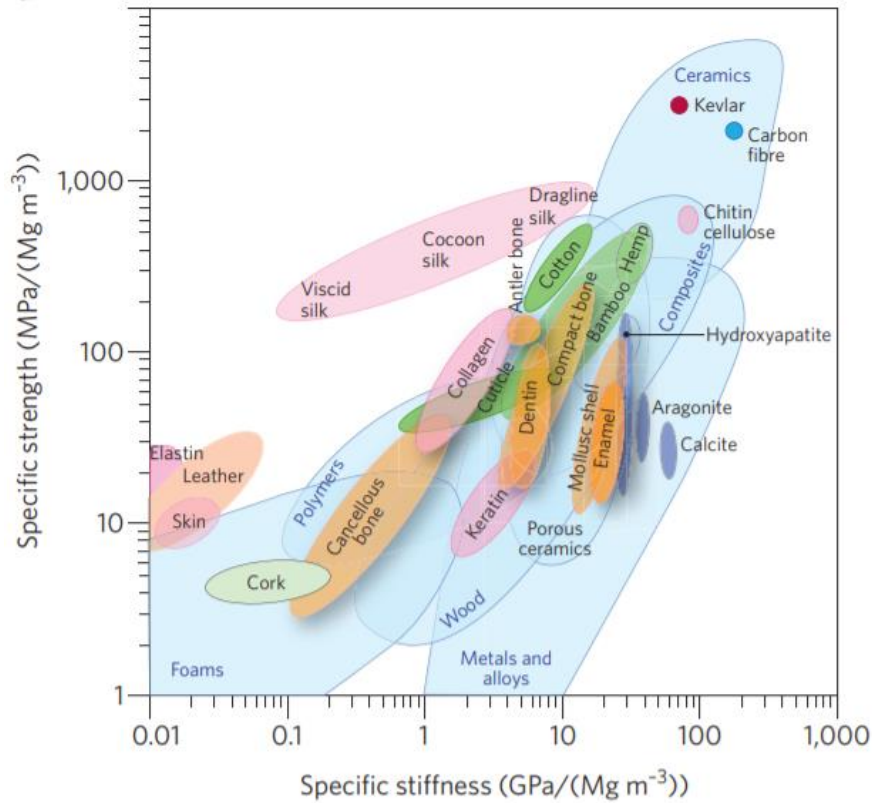
(d) Hydrophilic and superoleophobic (in water) surface with oil-based contaminant





Strong and tough bioinspired materials

Structural Materials



Biopolymers

Microstructure and mechanical properties

Unfurling and straightening

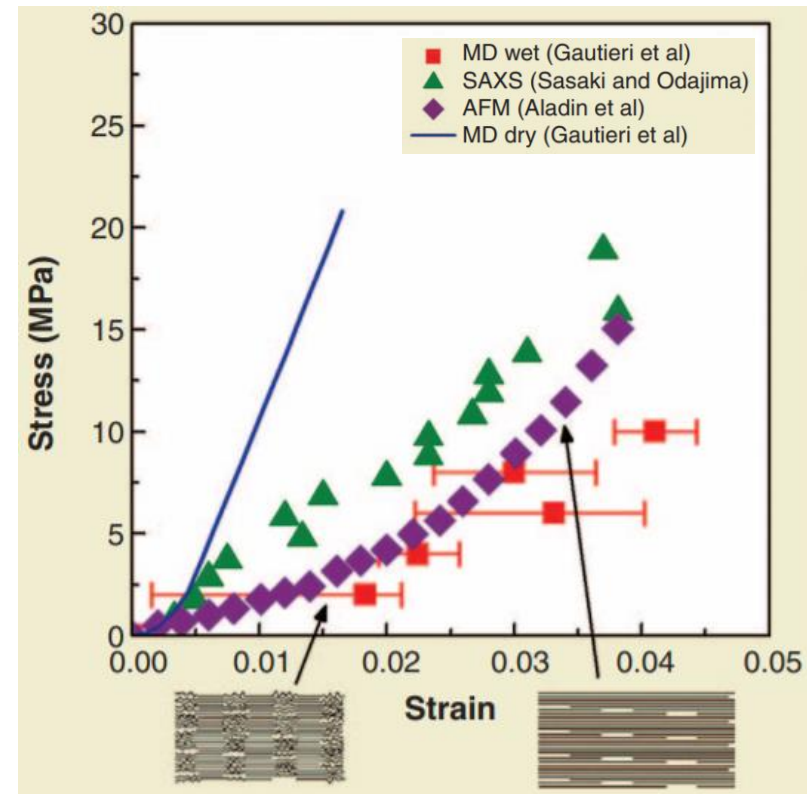
$$\frac{d\sigma}{d\varepsilon} \propto \varepsilon^n \quad (n > 1)$$

Chain bone stretching

$$\frac{d\sigma}{d\varepsilon} \propto E$$

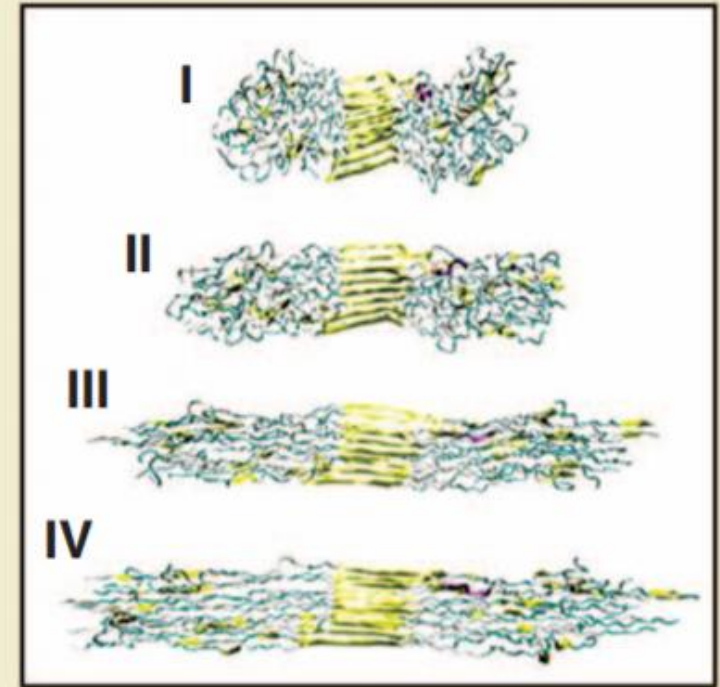
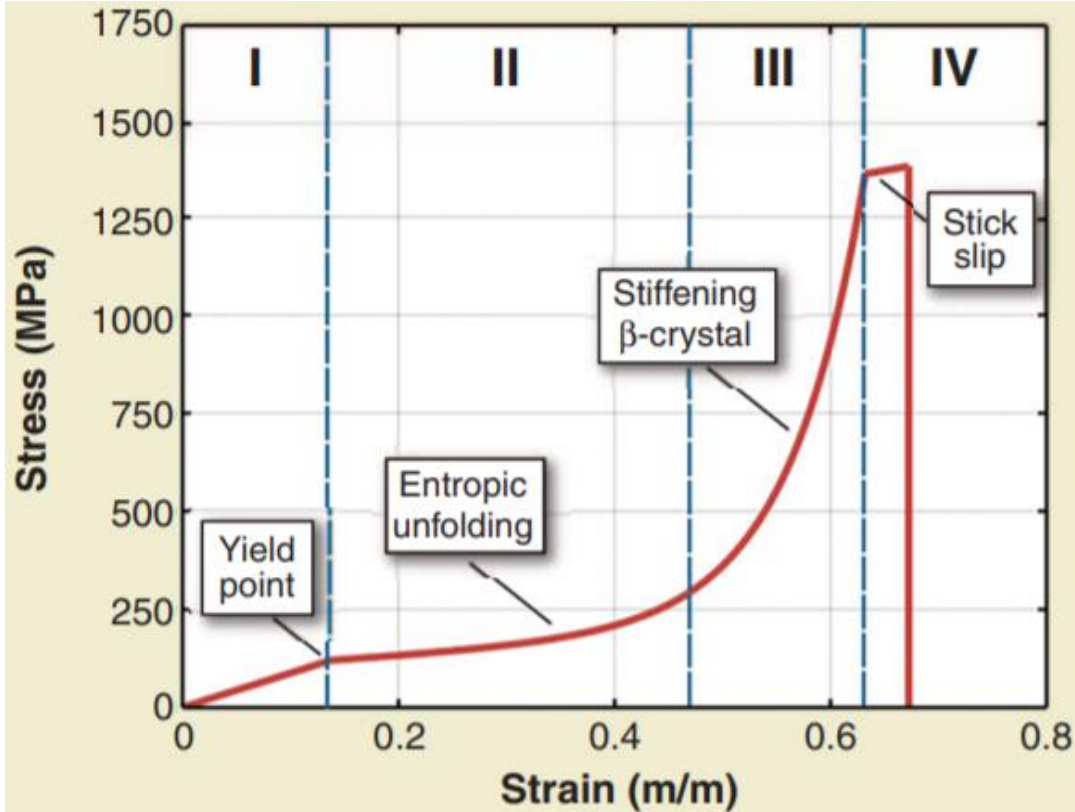


$$\sigma = k_1 \varepsilon^{n+1} + H(\varepsilon_c)E(\varepsilon - \varepsilon_c)$$

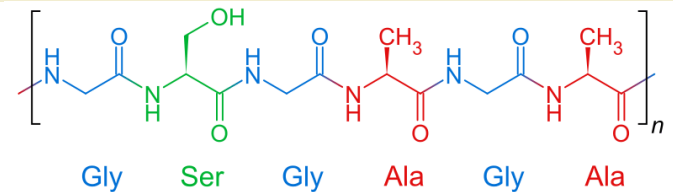


Biopolymers

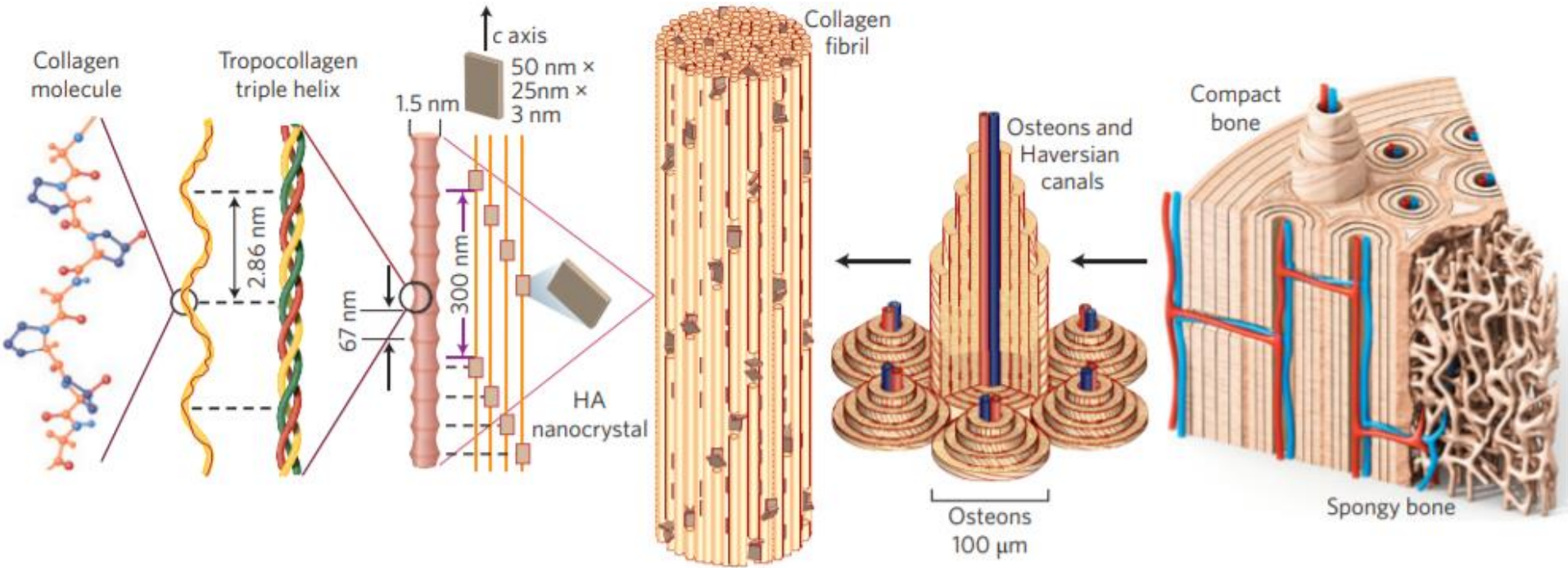
Spider silk



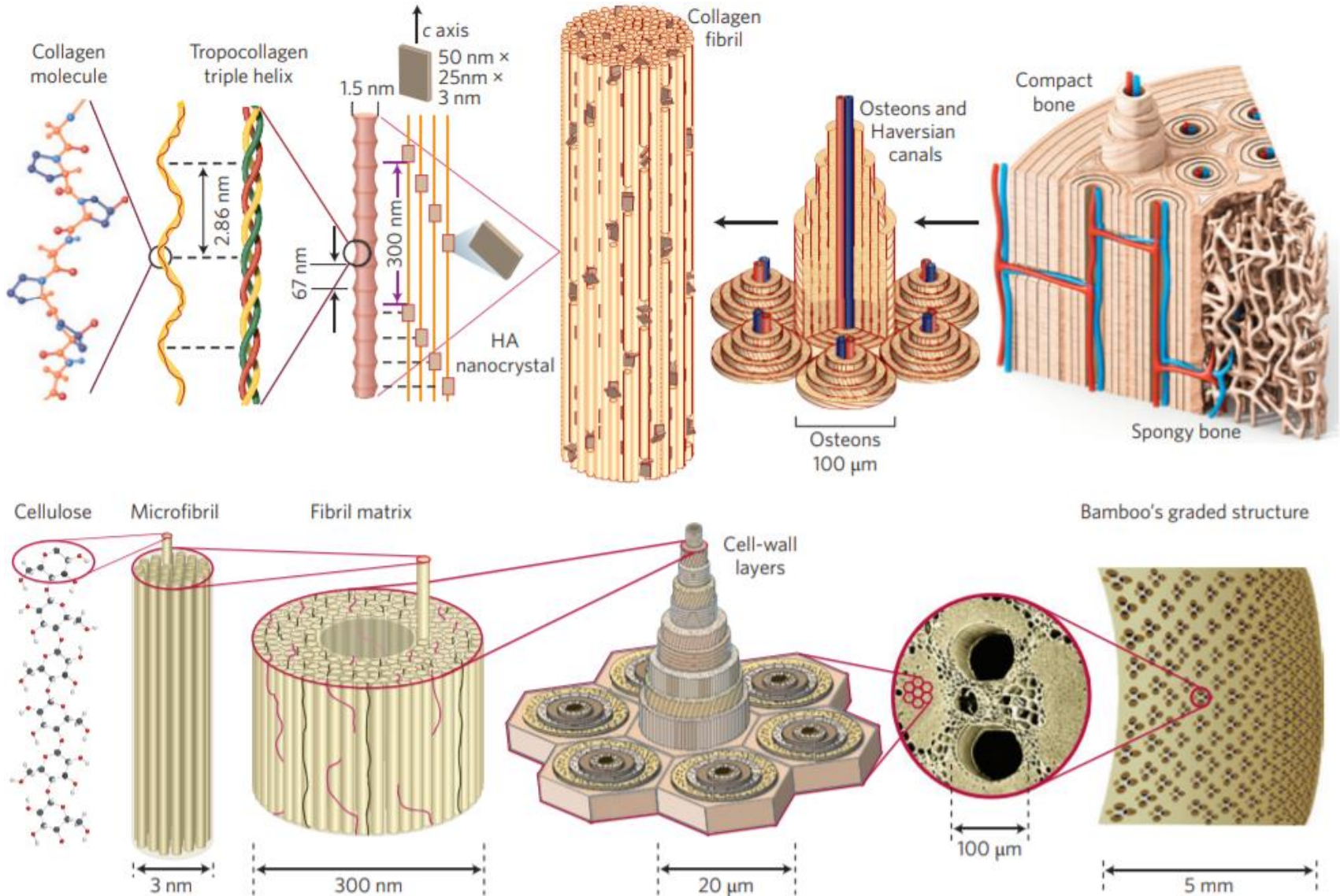
Fibroin stretching mechanism



Bone

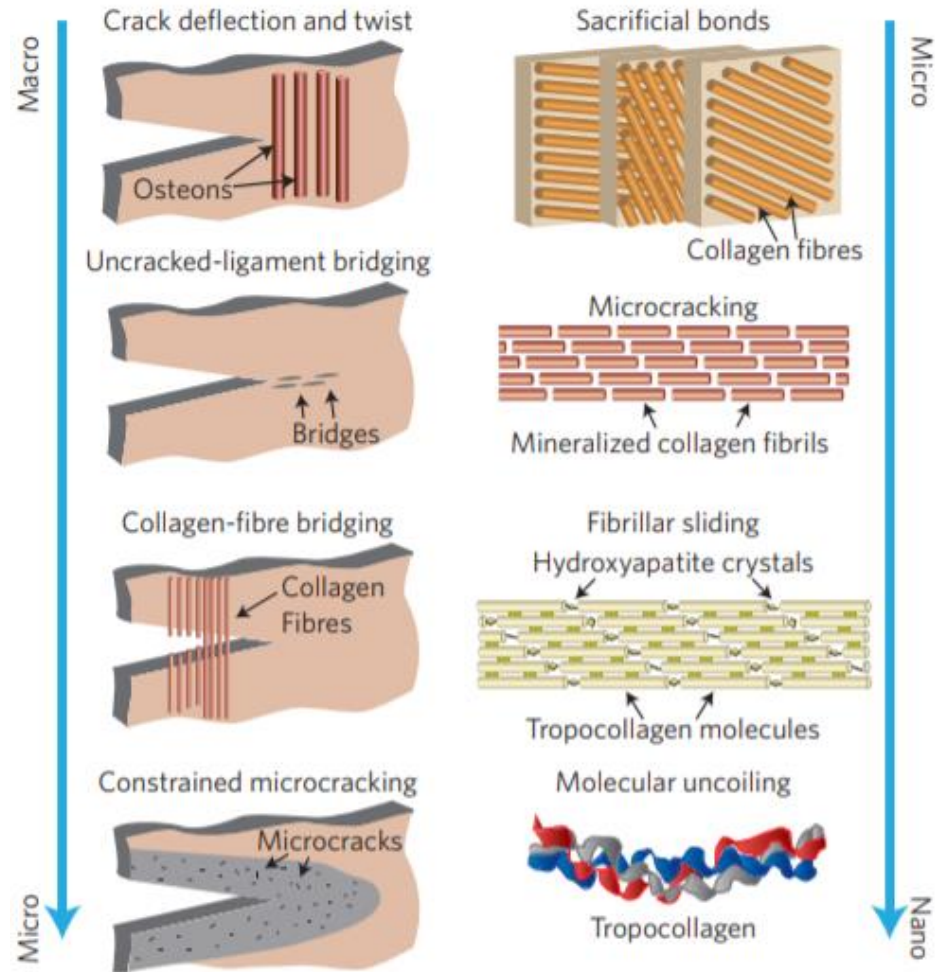
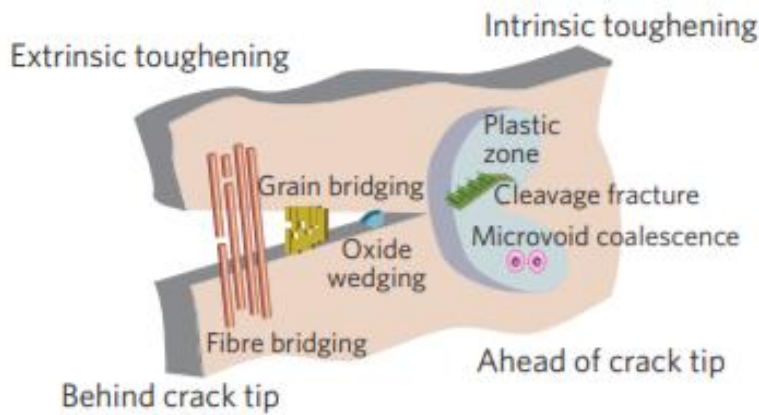


Similarity between bone and bamboo

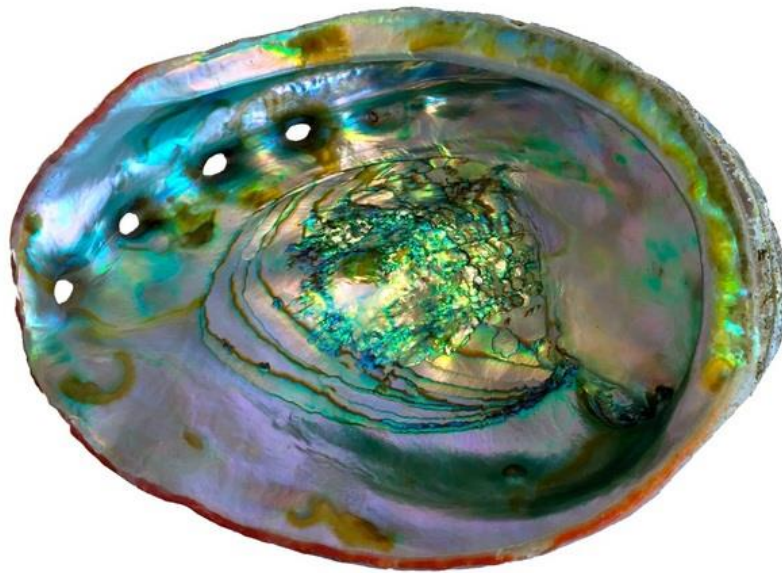


Bone

Toughening mechanisms



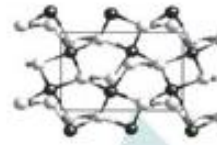
Nacre



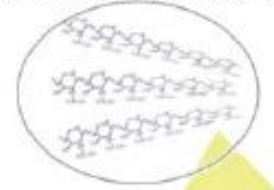
Level

I

Calcium carbonate unit cell

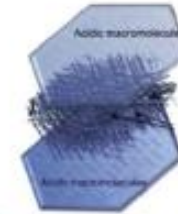
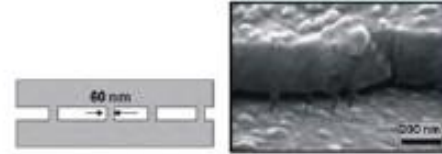


Chitin molecular chains

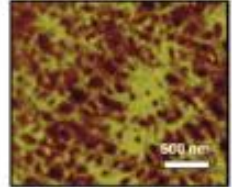


II

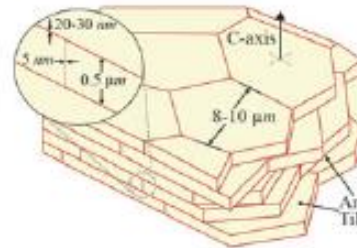
Mineral bridges



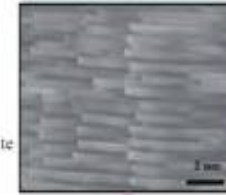
Chitin matrix



III



Tiles

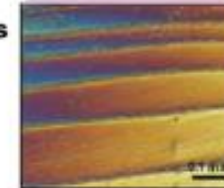


Organic layers



IV

Mesolayers



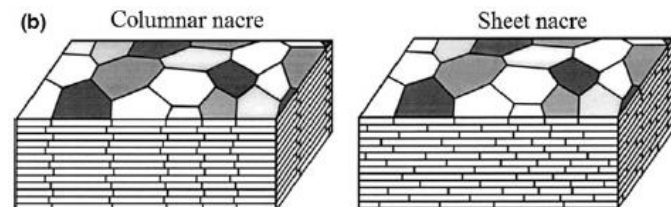
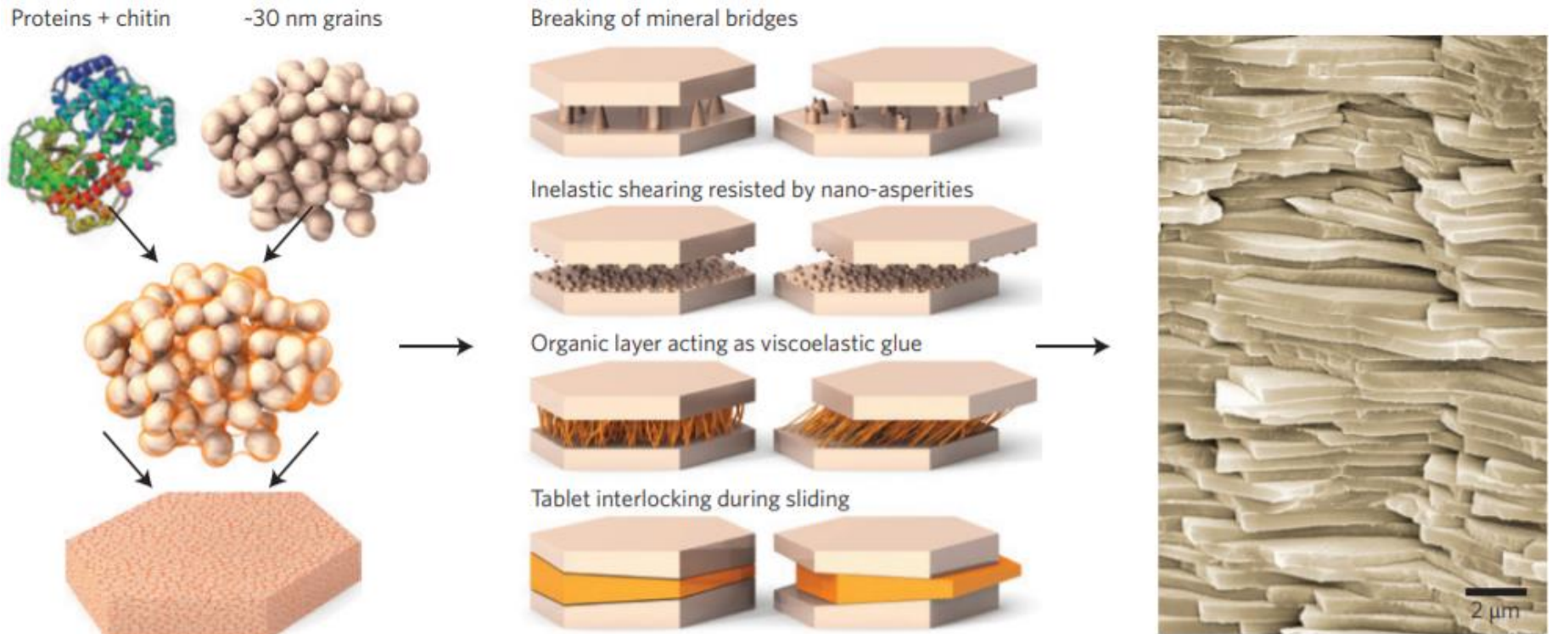
V

Abalone



Nacre

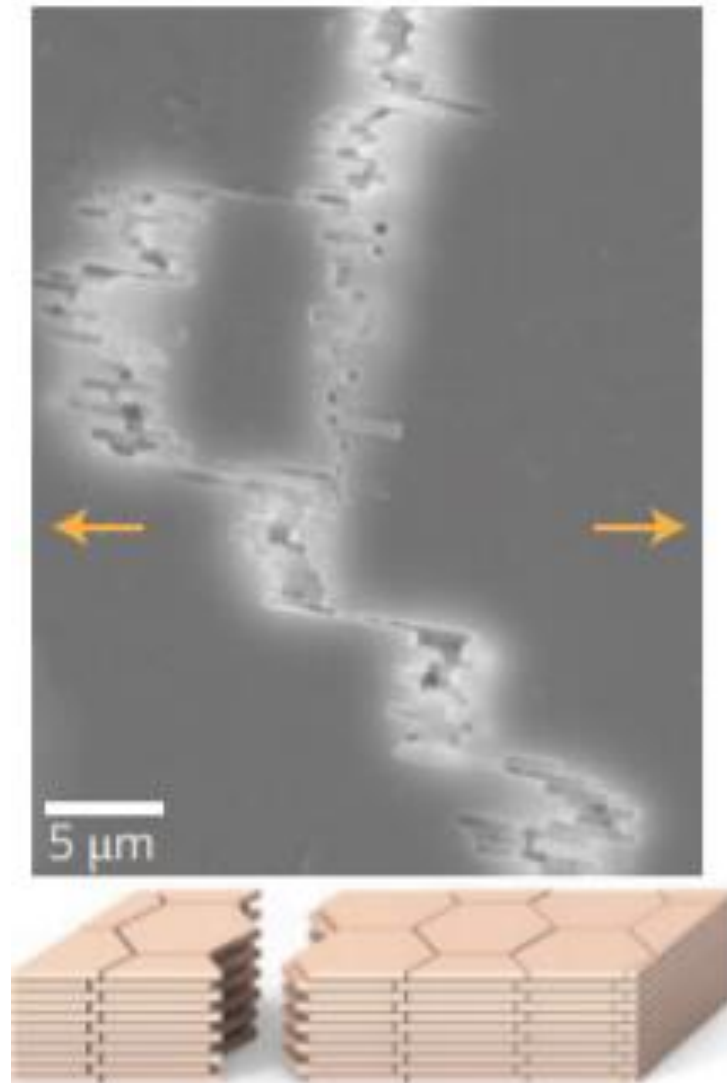
Hierarchical architecture and selected toughening mechanisms



Nacre

Toughening mechanisms

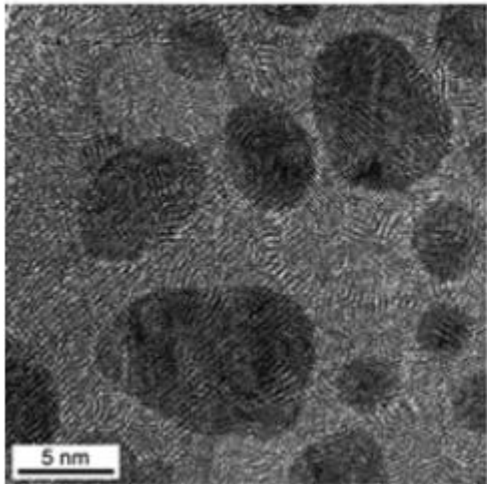
- Crack deflection at soft interlayers
- Crack bridging
- Breaking of mineral bridges
- Viscoelastic behavior of organic component
- Tablet interlock
- Plastic deformation ahead of the crack
- Crack blunting
- Nanograin rotation



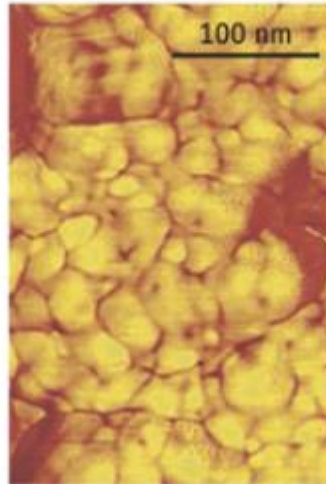
Nacre

Toughening mechanisms: nano grain rotation

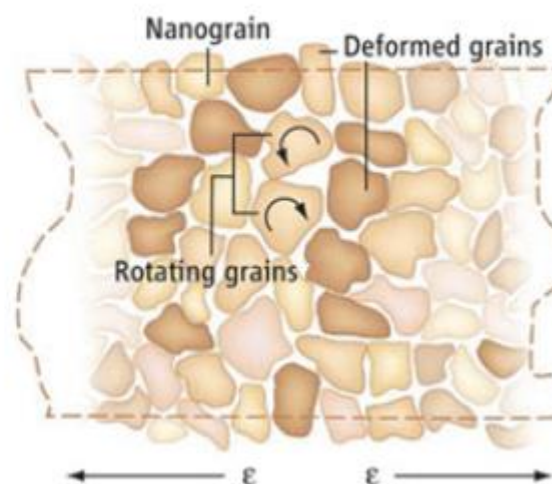
Nanograins



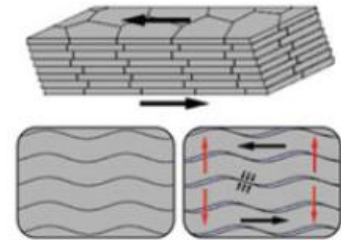
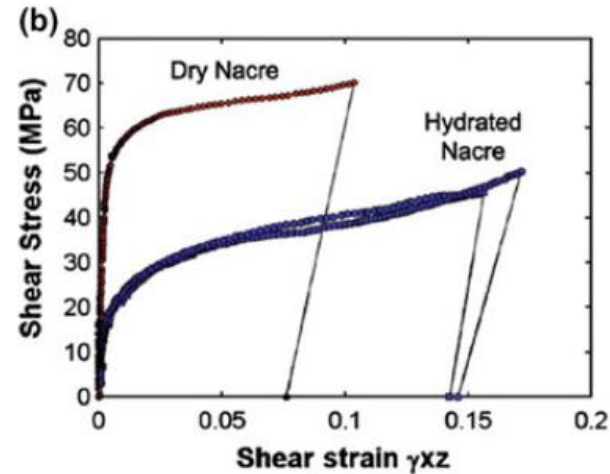
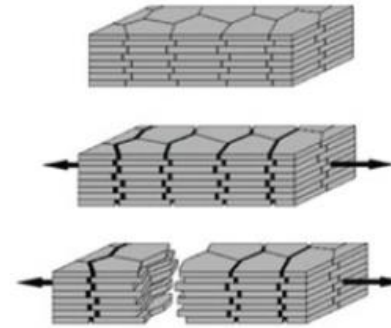
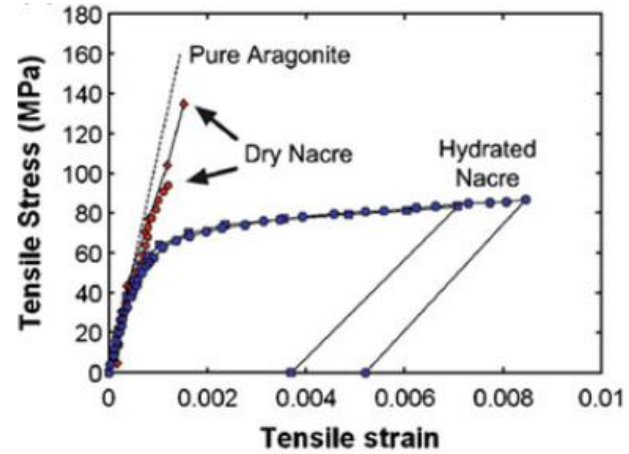
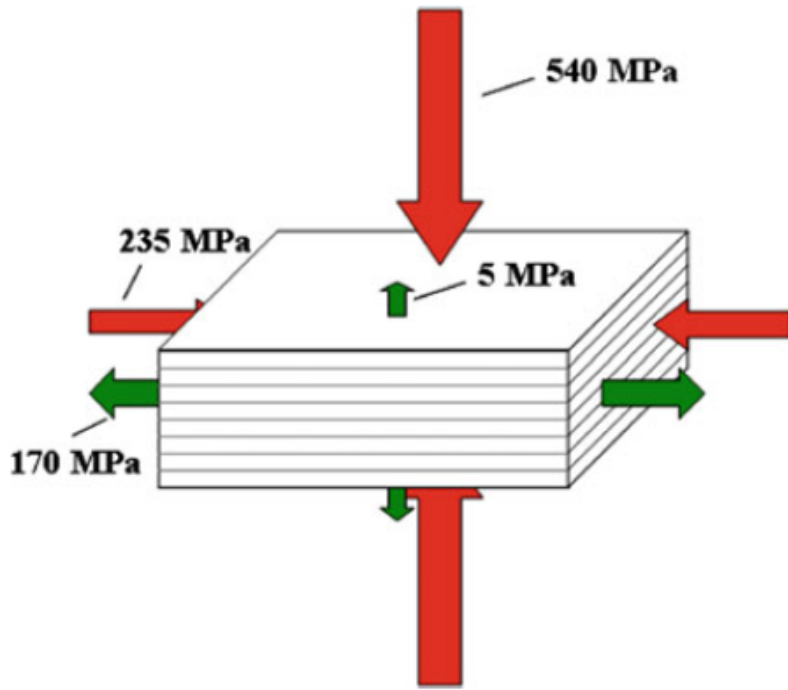
Surface of a tablet



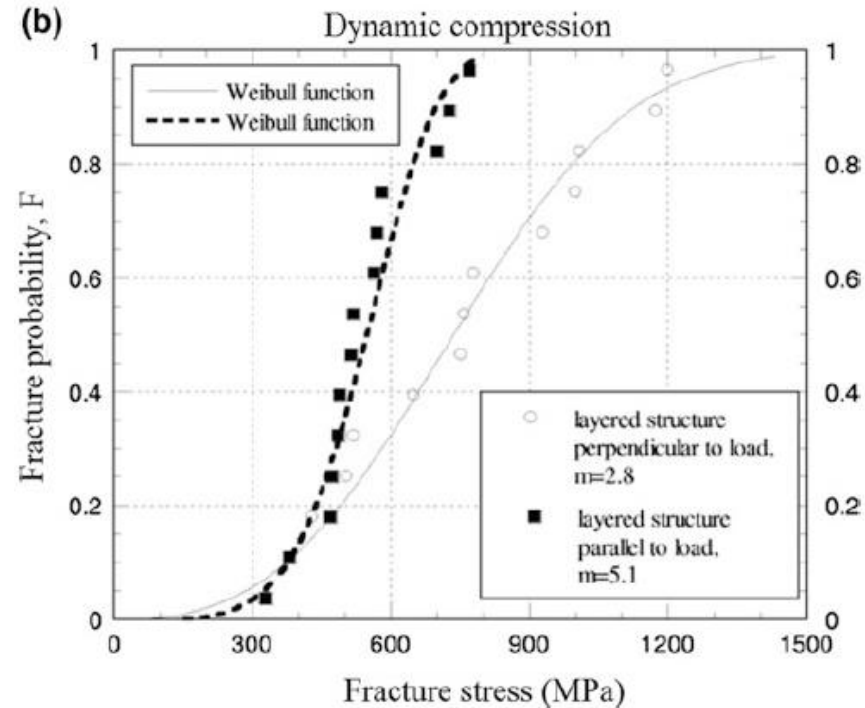
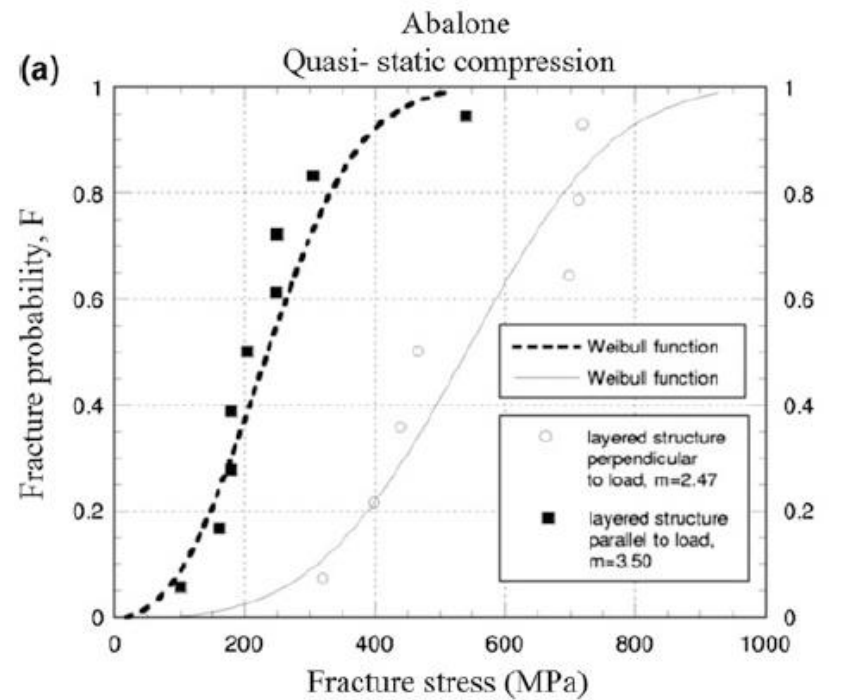
Nacre tablet under tension



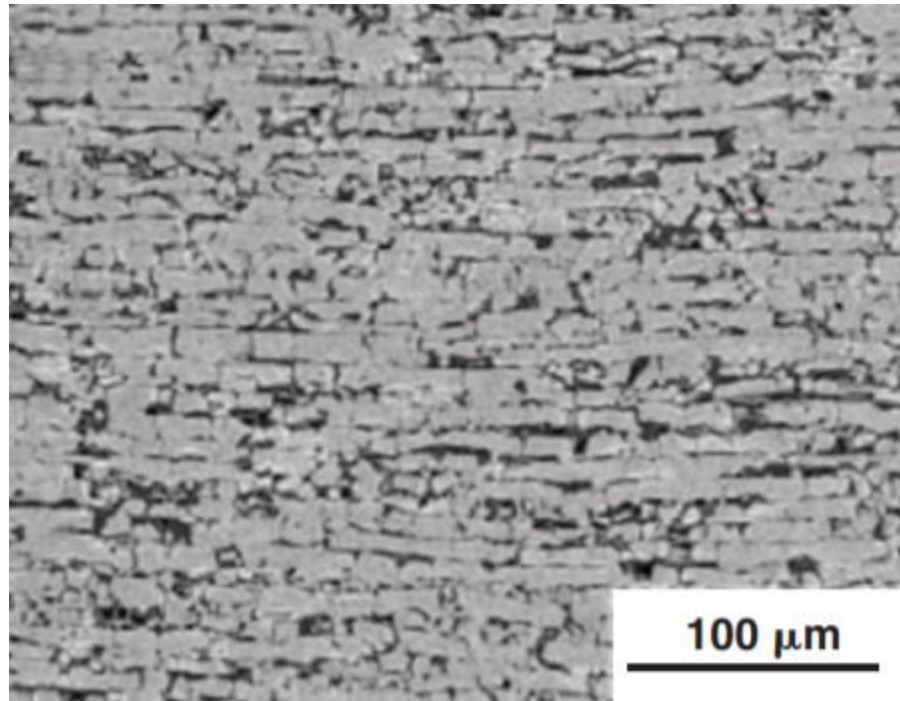
Nacre: mechanical properties



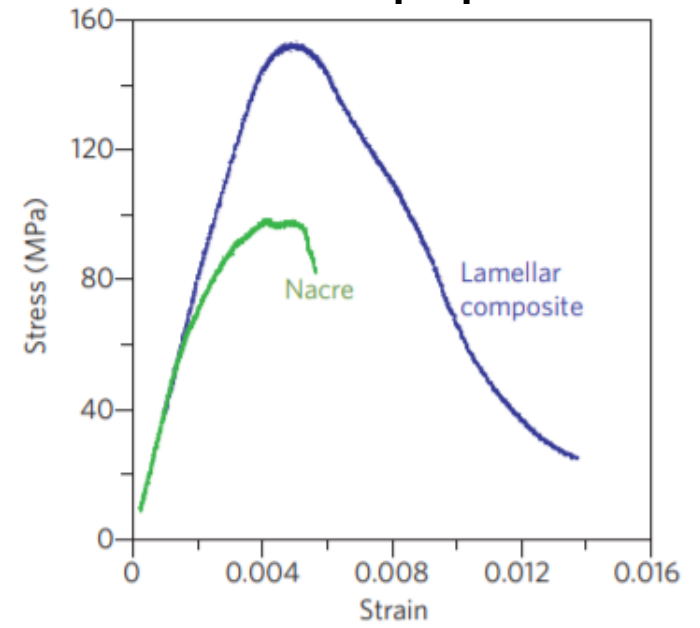
Nacre: mechanical properties



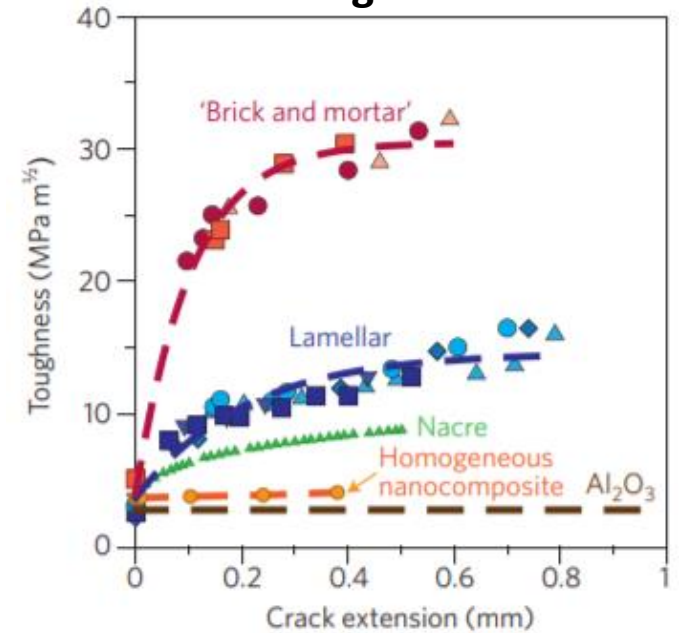
Nacre-like hybrids



Mechanical properties

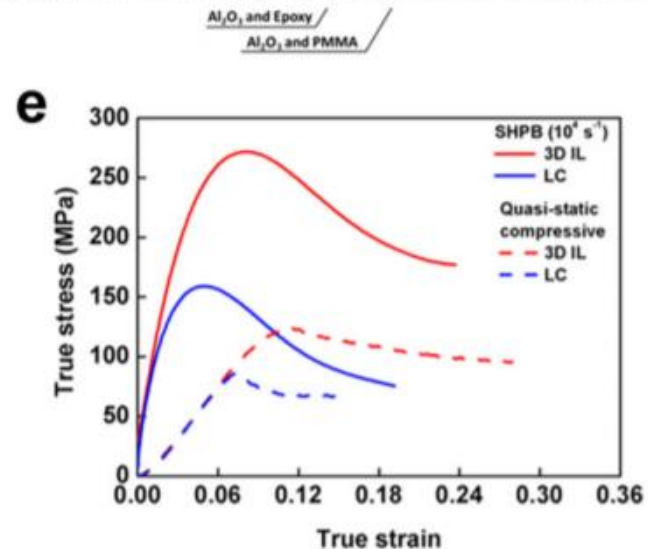
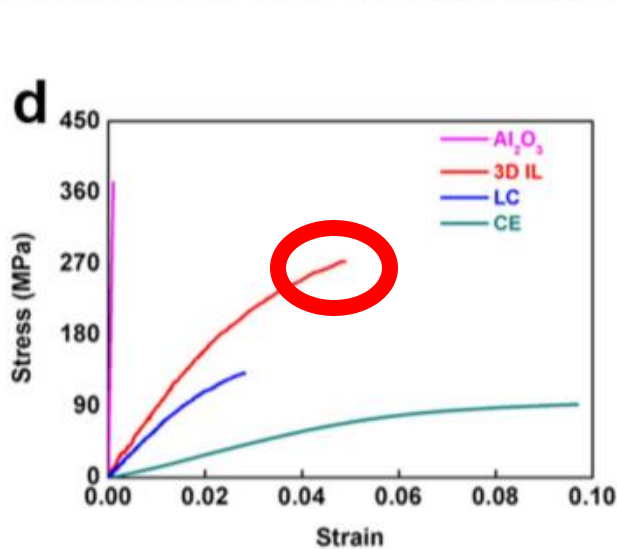
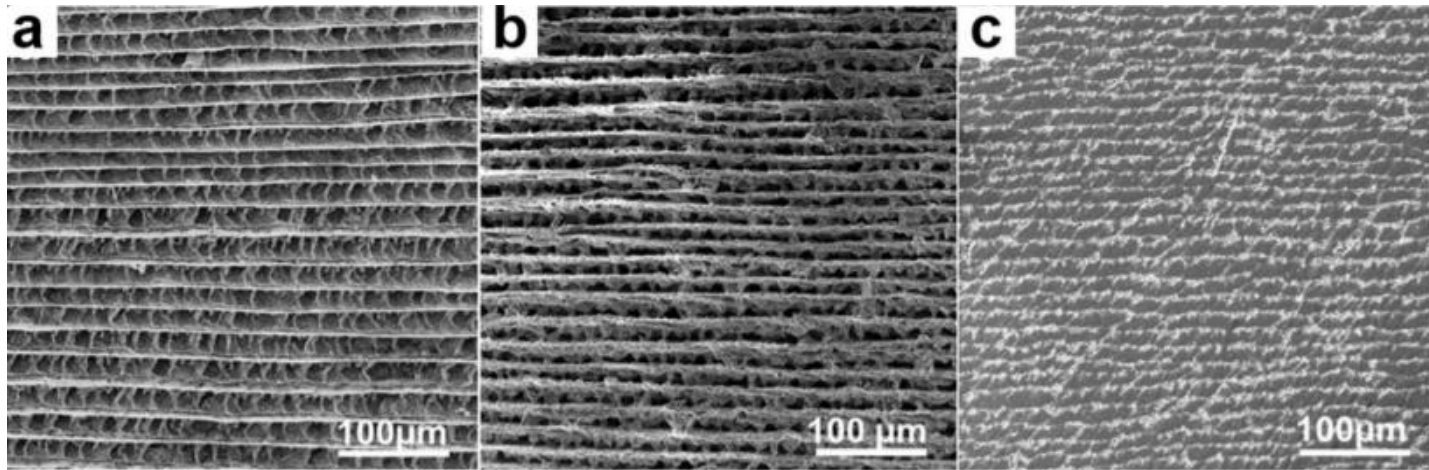


Toughness



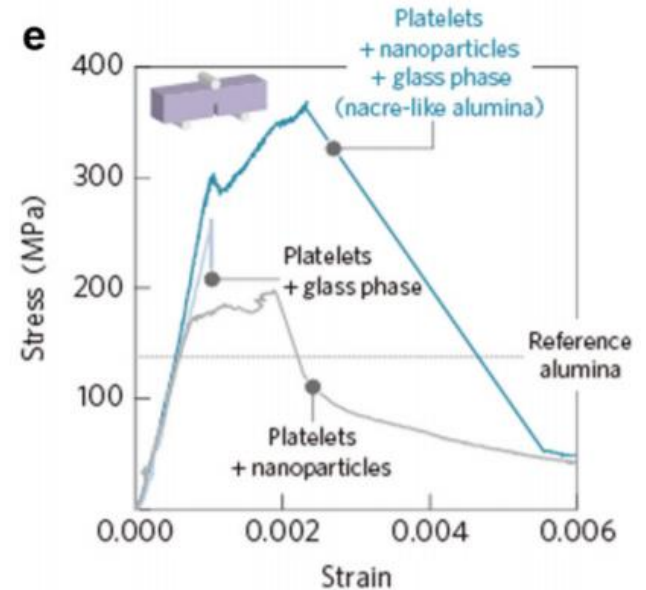
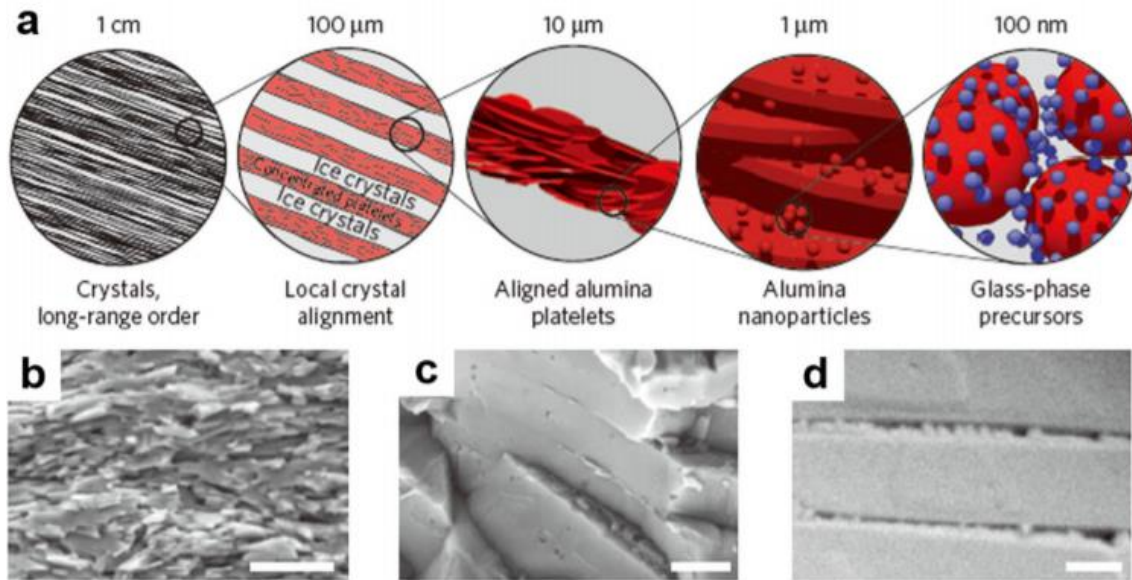
Nacre-inspired structures

Alumina / Cyanate Ester Composite (freeze casting + CE infusion)



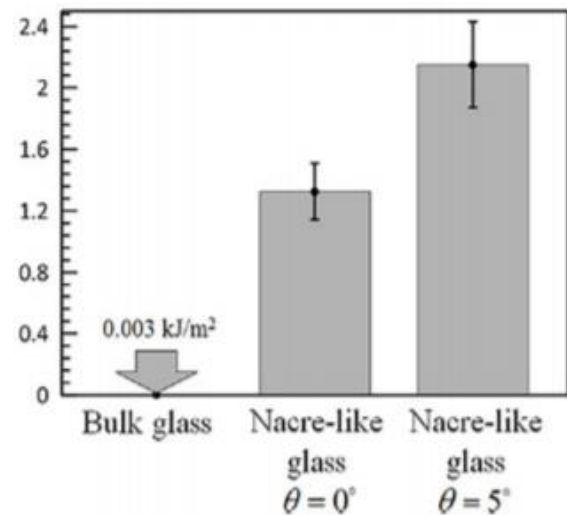
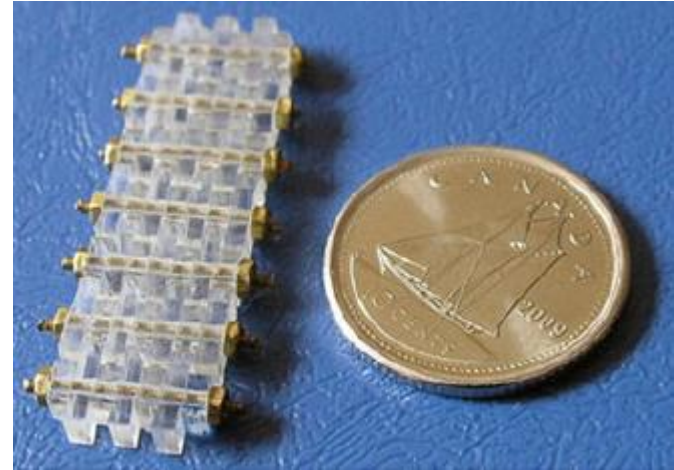
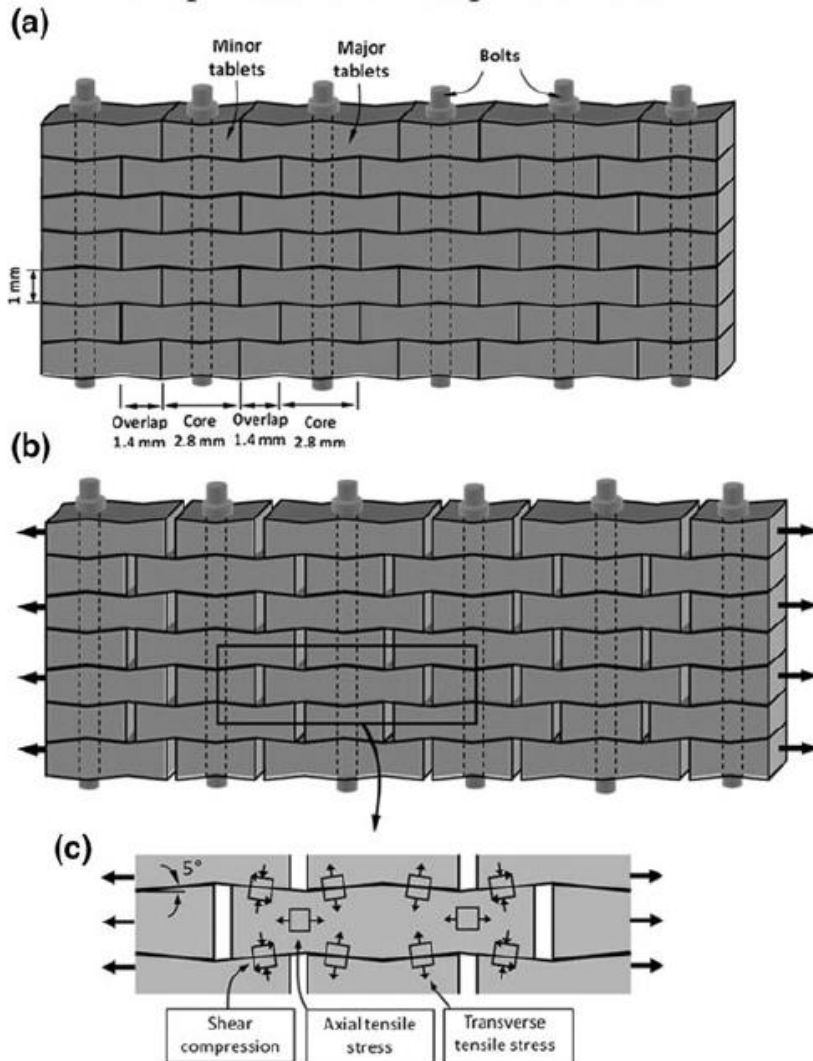
Nacre-inspired structures

High content Alumina (98%) + silica-calcia glassy phase



High strength (480 MPa) and high fracture toughness (22 MPa m^{0.5})

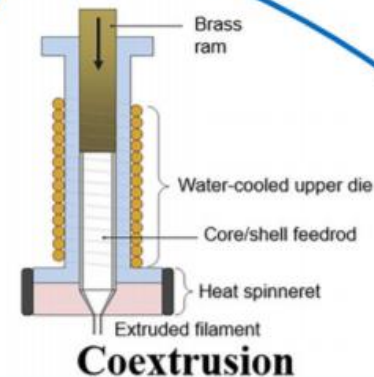
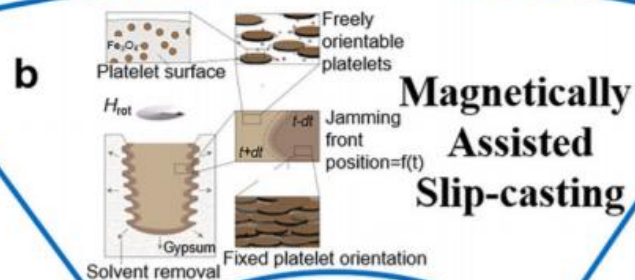
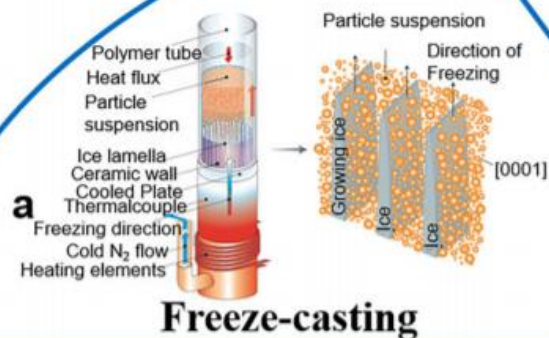
Nacre-inspired structures



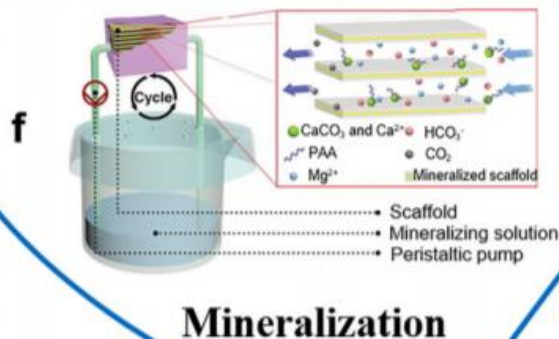
Nacre-inspired structures

Bioinspired nacre structural materials	Scale	Fracture toughness (MPa $\sqrt{\text{m}}$)
Al/Al-Si	μm	5.5–10
Al ₂ O ₃ /Al-Si	μm	40
Al ₂ O ₃ /PMMA ^a	μm	30
Al ₂ O ₃ /TiO ₂	mm	12
SiC/Al ₂ O ₃ -Y ₂ O ₃	mm	14
Si ₃ N ₄ /BN	mm	28

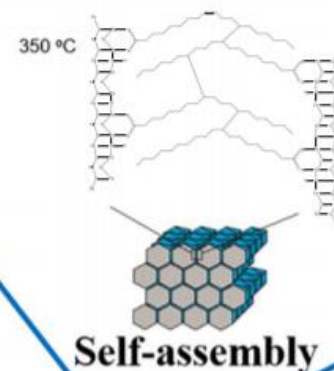
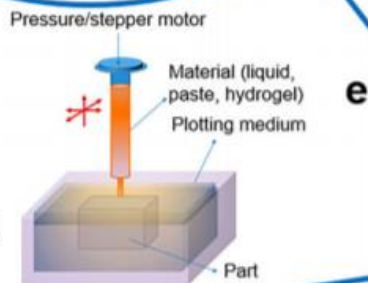
Fabrication of nacre-like materials



3D Nacre-inspired Bulk Materials

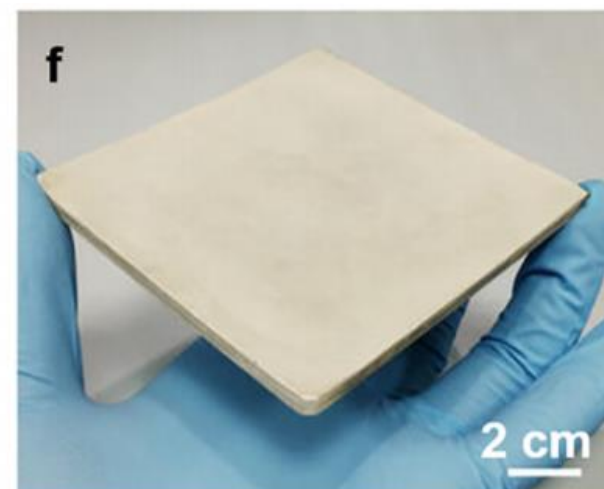
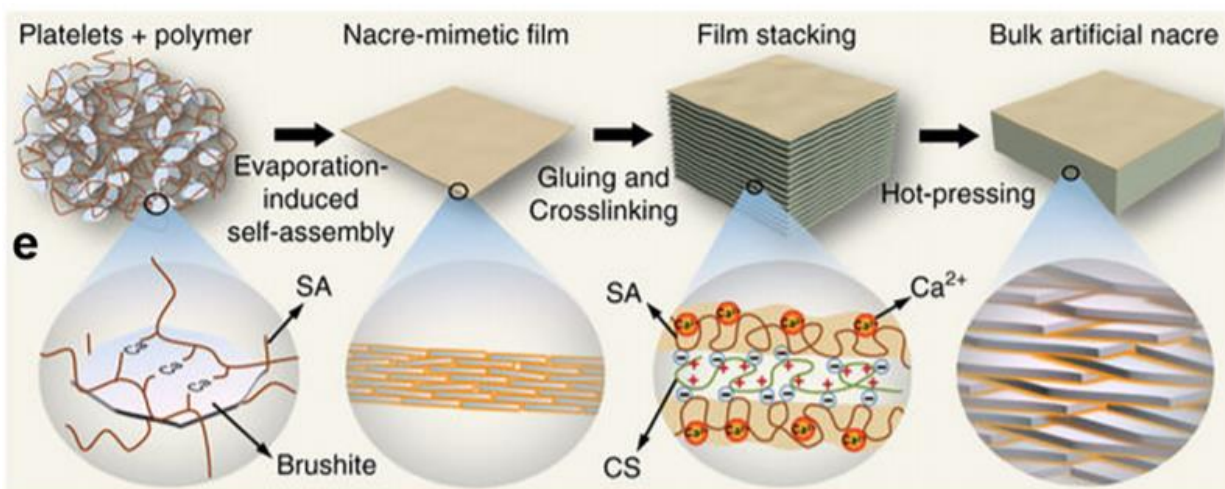


Additive Manufacturing



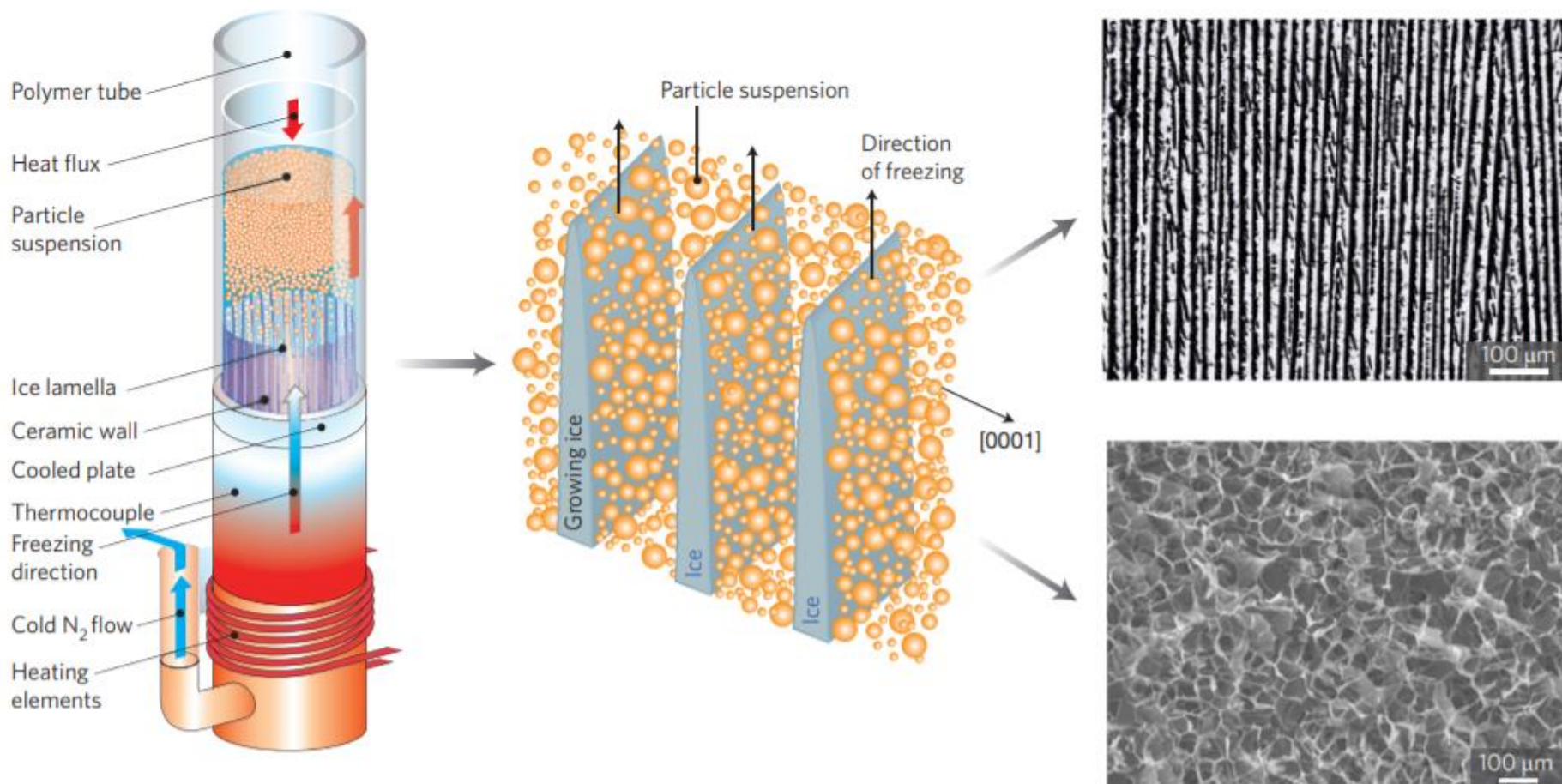
Fabrication of nacre-like materials

An example of scalable fabrication process



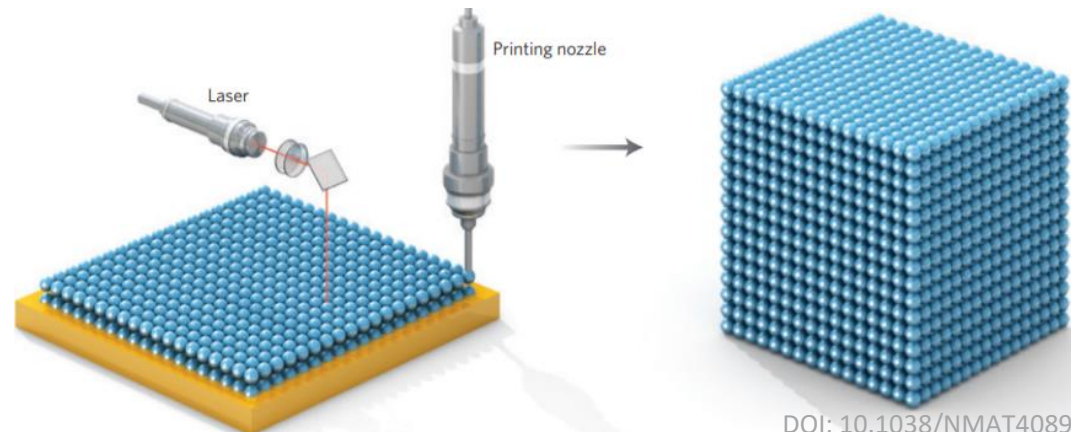
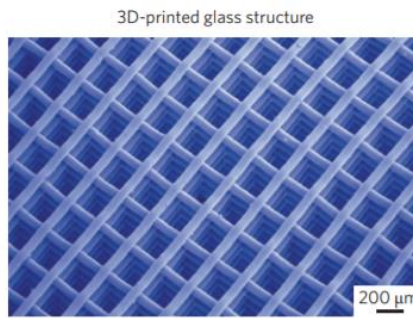
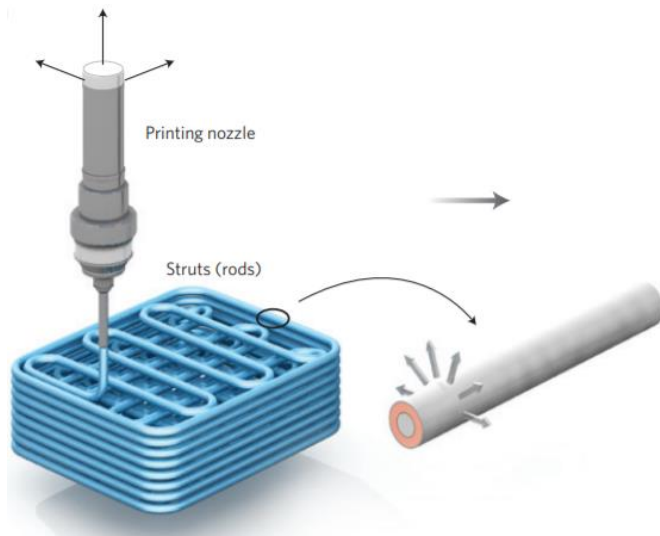
Fabrication of nacre-like materials

Freeze casting

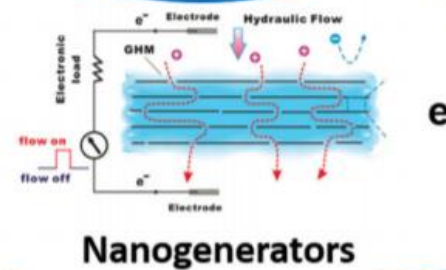
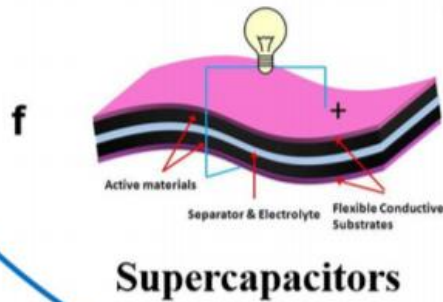
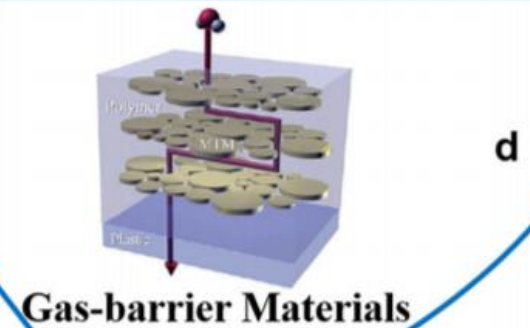
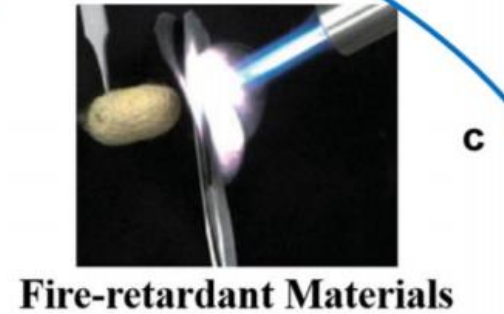
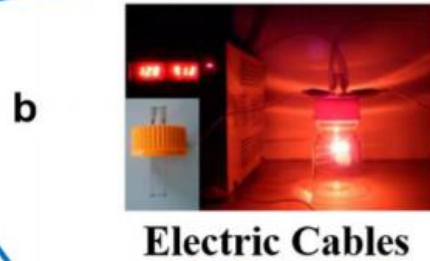


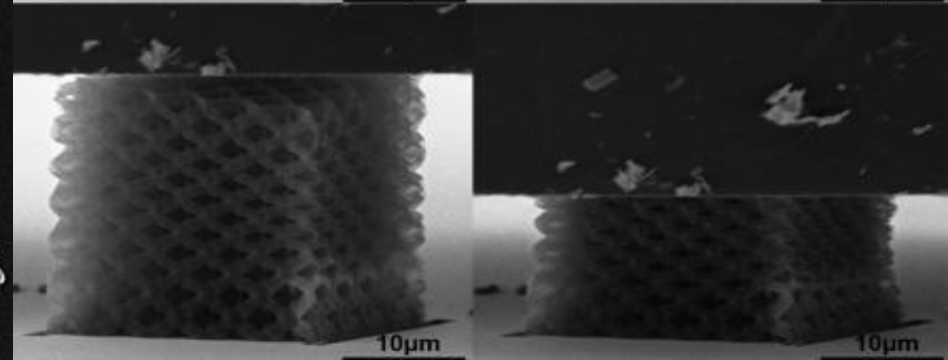
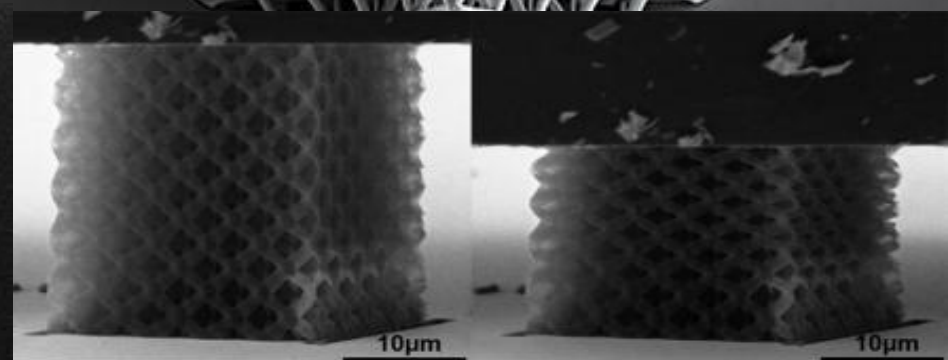
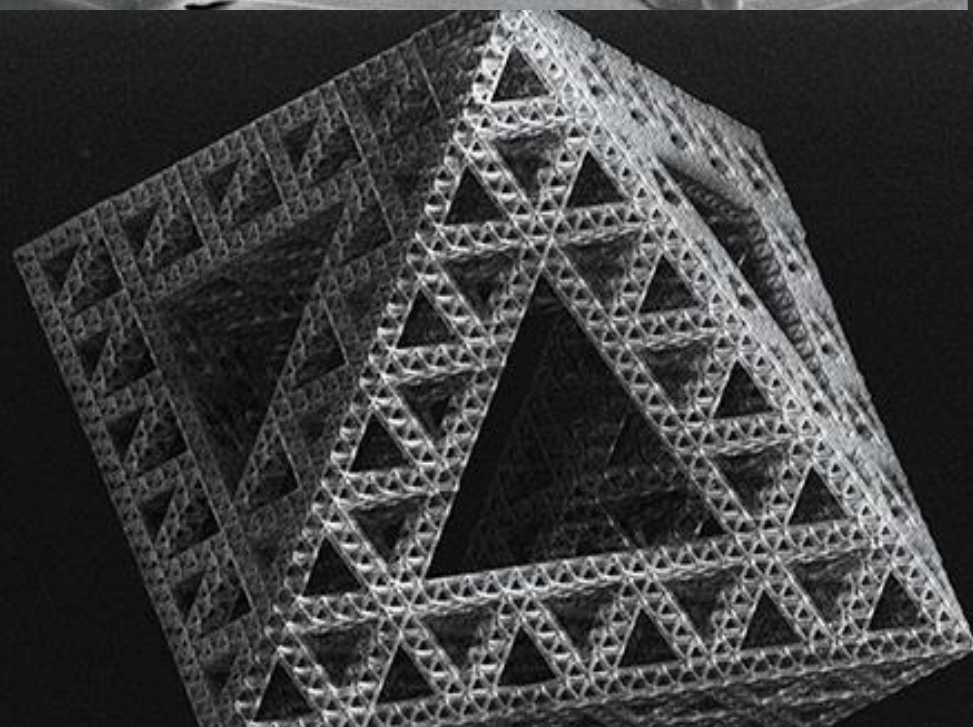
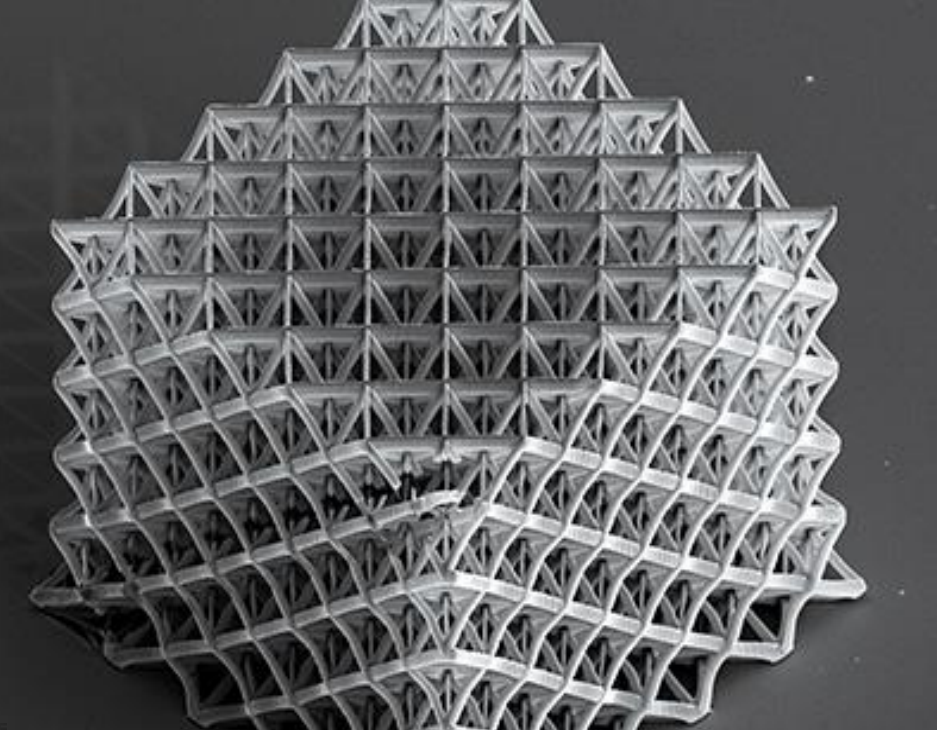
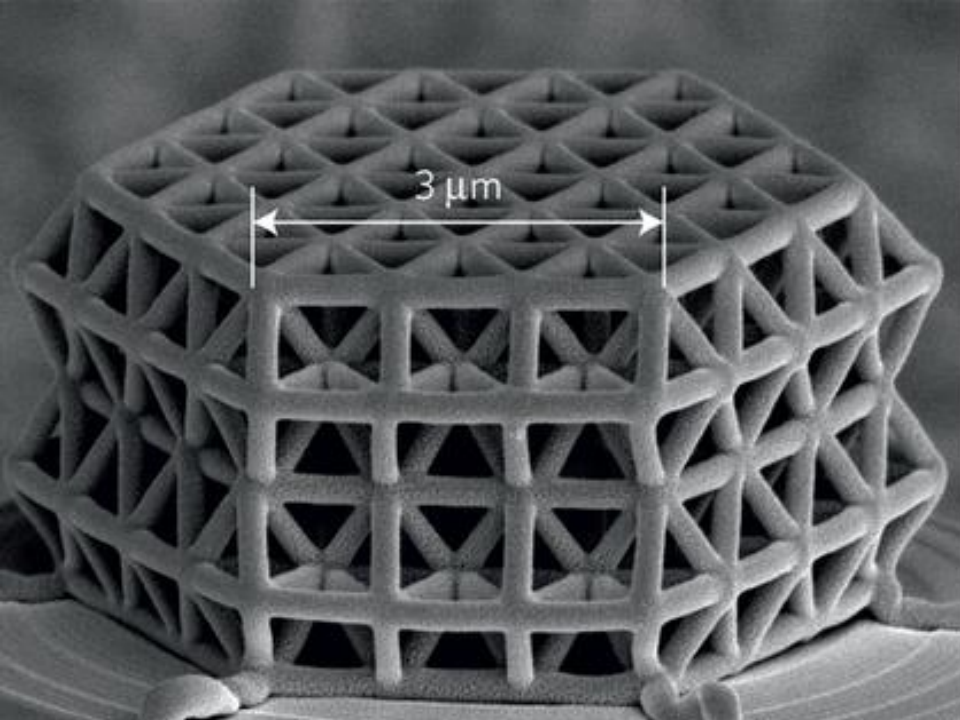
Fabrication of complex, hybrid hierarchical structures

Additive manufacturing

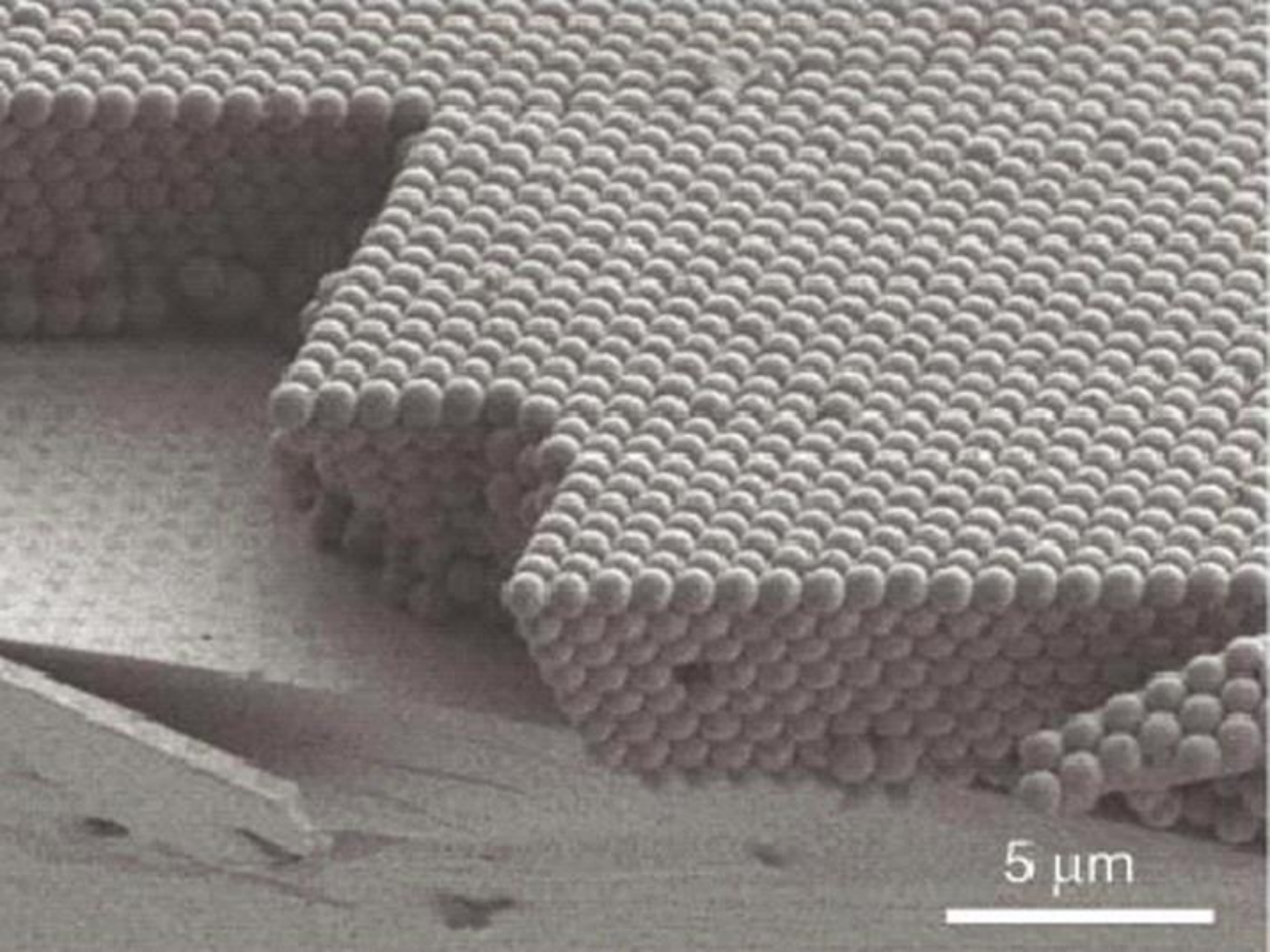


Applications

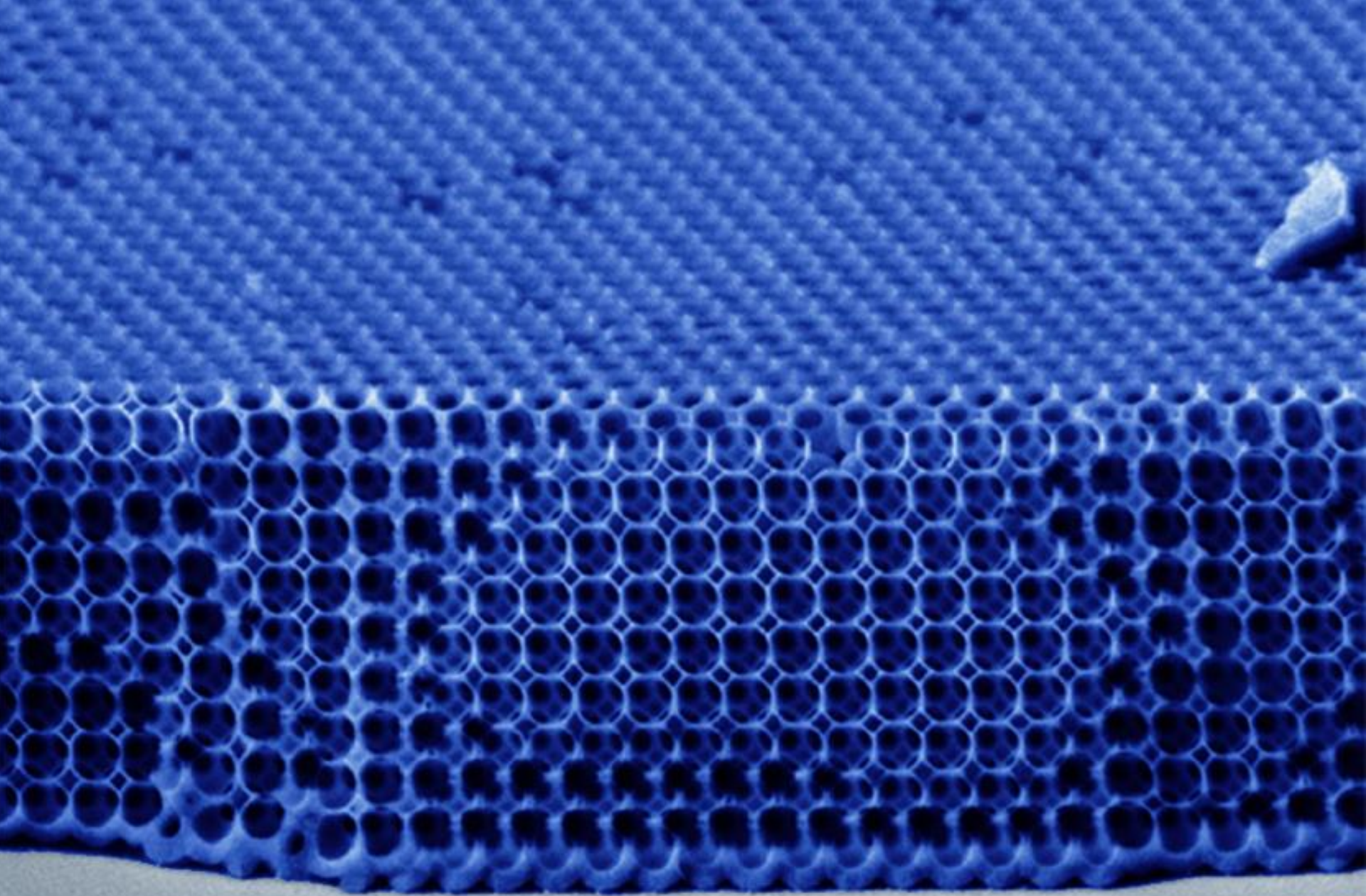




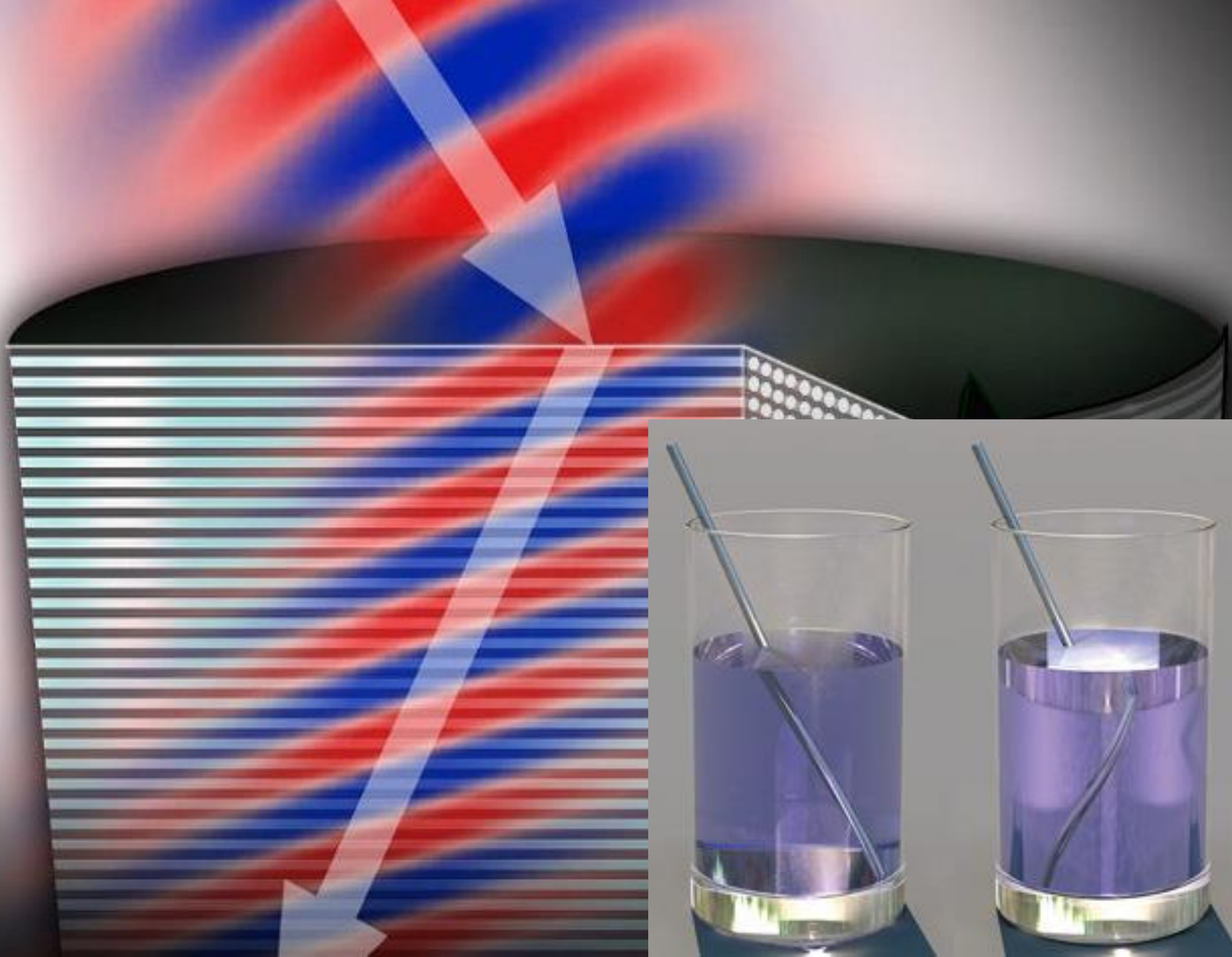


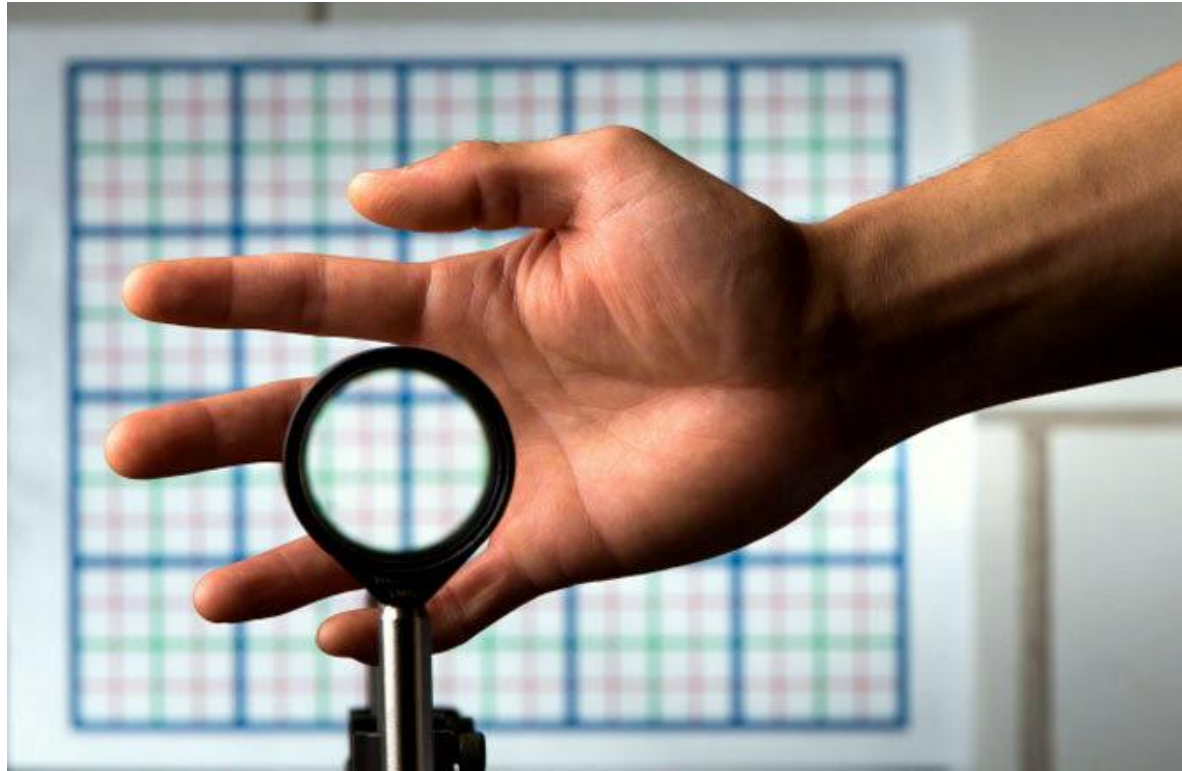
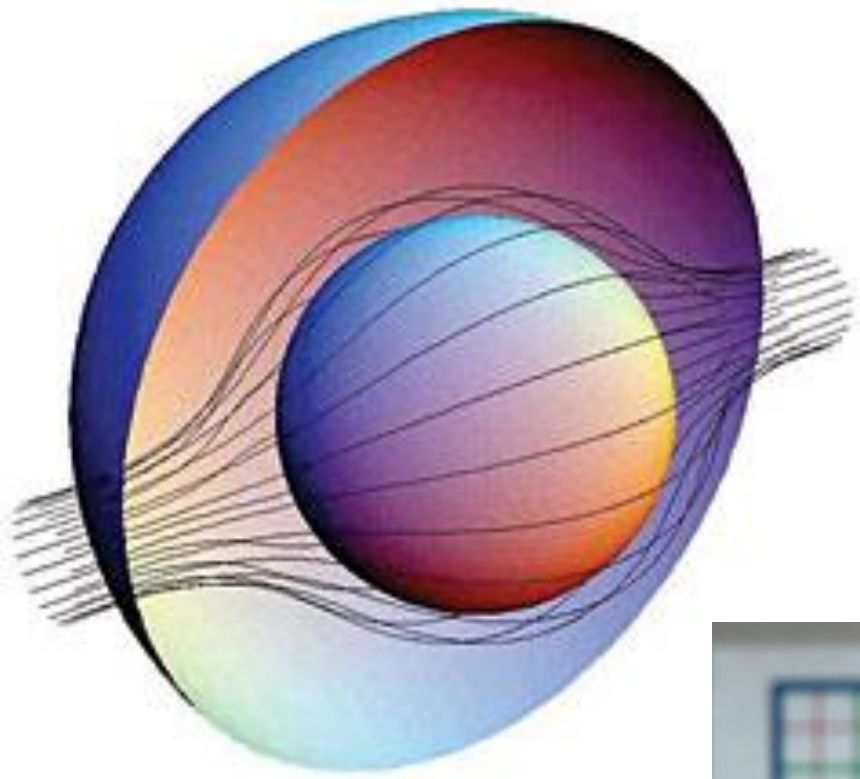


5 μm



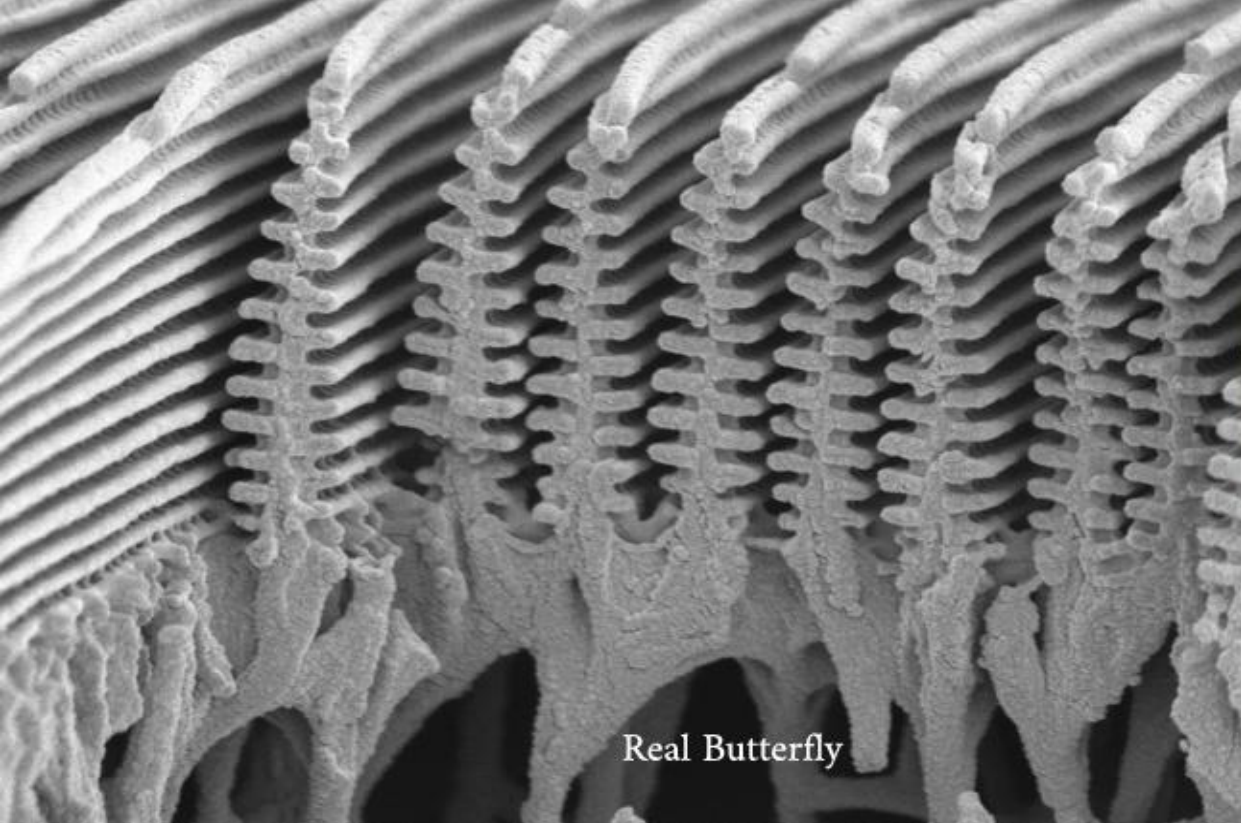
2 μm



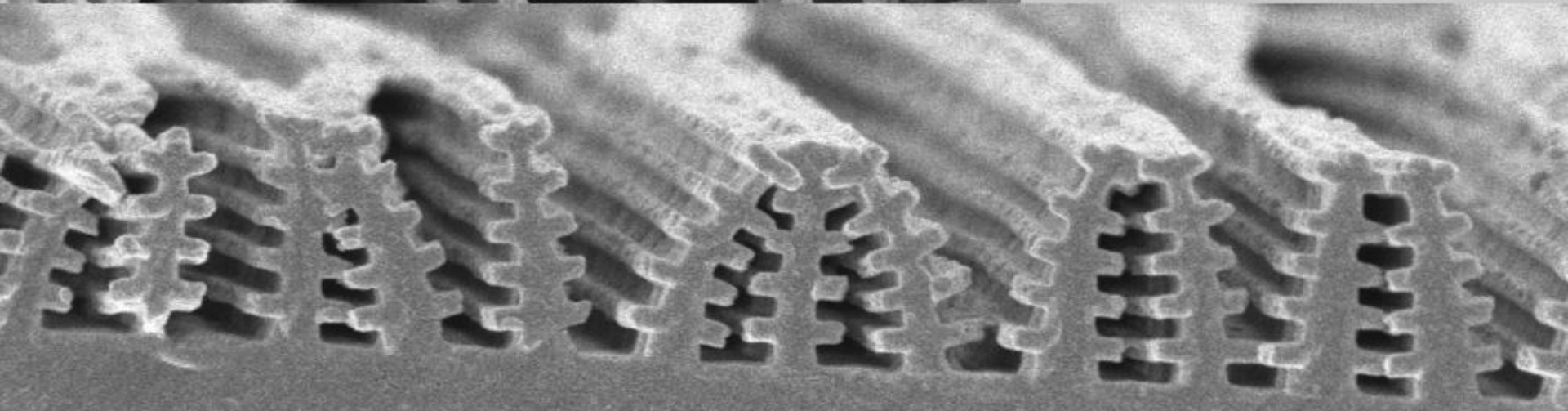








Real Butterfly



Polymer Butterfly

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