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EXCELENCIA SEVERO OCHOA 2017 - 2021 · AGENCIA ESTATAL DE INVESTIGACIÓN

Nano-engineered (Multi)functional Surfaces

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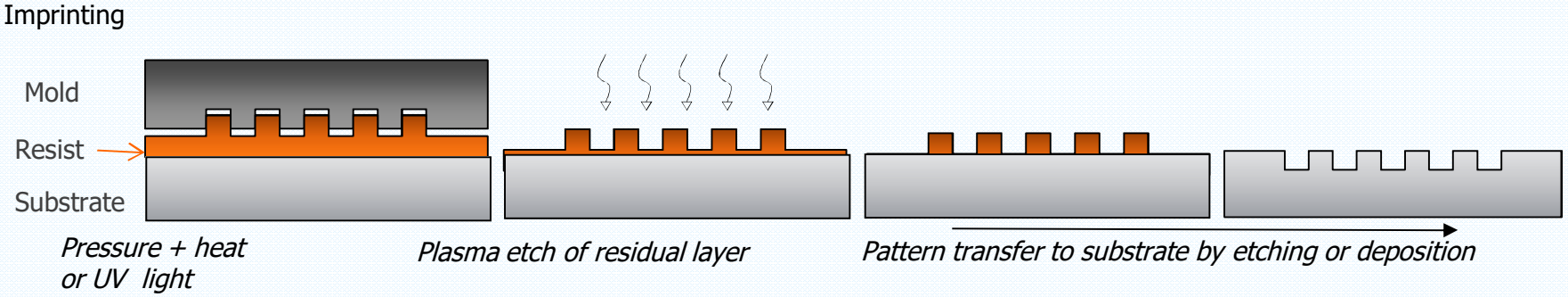
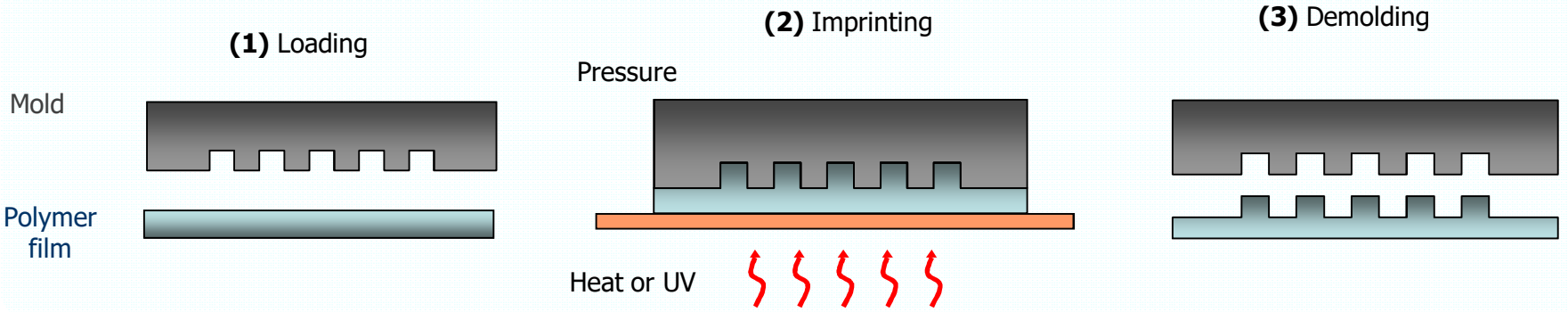
Nanoimprinting: A replication process

Pattern transfer by mechanical deformation of a resist material

➢Nanoimprint lithography (NIL) ~ UV - Thermal

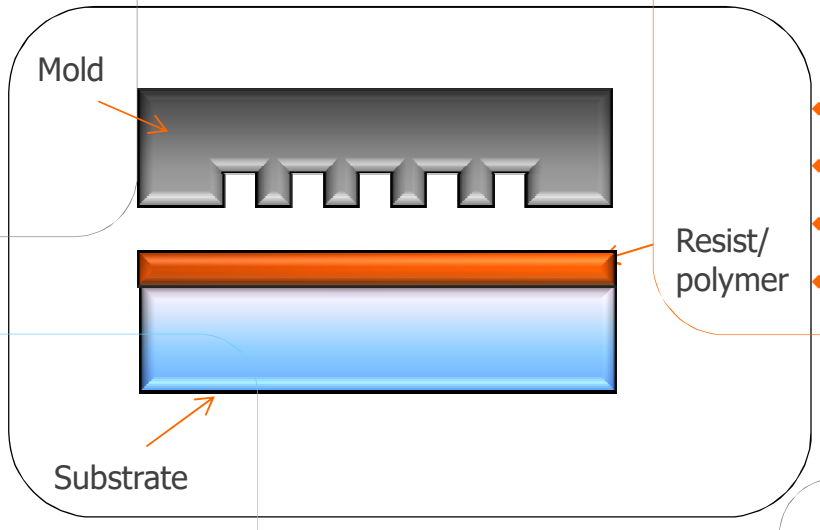


➢Nanoimprint technology (NIT) ~ UV - Thermal



Nanoimprinting tool box

- Silicon
- Quartz
- Nickel
- Oxides
- Carbides
- Polymers



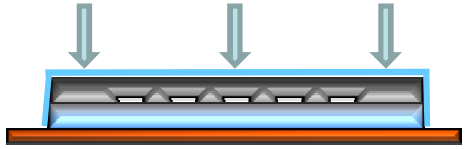
- Thermoplastic polymers:
  PMMA, PC, PS, PP, PES..
- Liquid monomers
- Biopolymers
- Semiconducting polymers
- Sol gel materials

- Silicon
- Quartz, silica
- Polymers
- Textiles, paper..
- No substrate

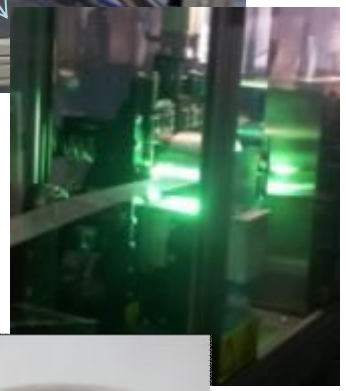
Equipment - press
- Thermal
- UV
- Batch
- R2R

Nanoimprinting machines

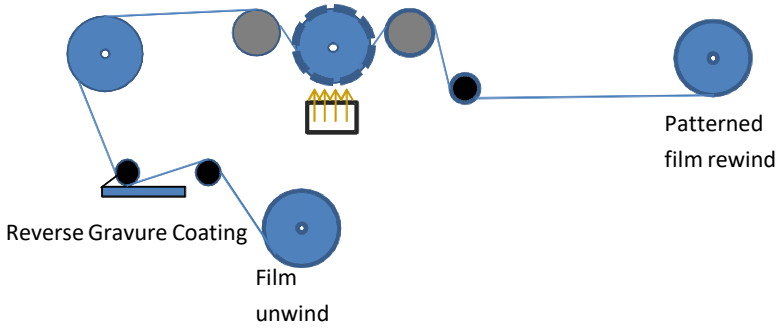
Plate

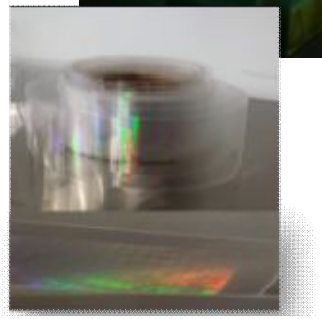


Roll to Roll



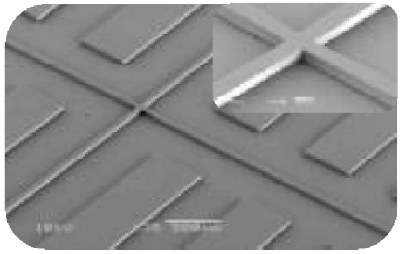
Imprinting



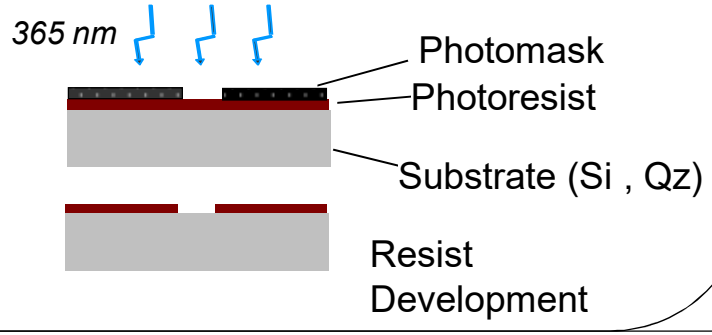


Mold fabrication

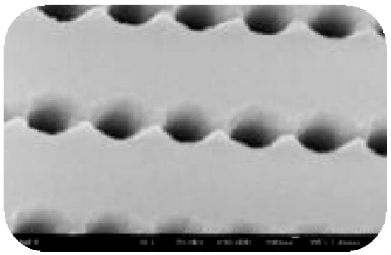
Photo lithography : Micrometer range



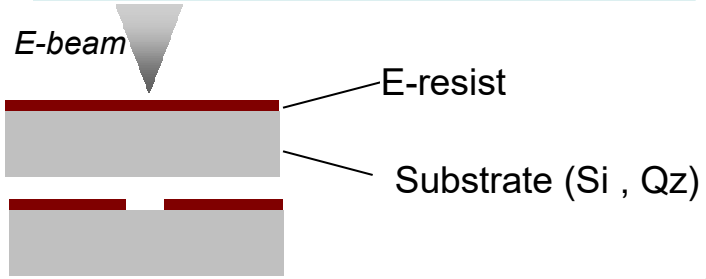
- Limited resolution to 1 μm^2
- Patterned area – 2 - 12”



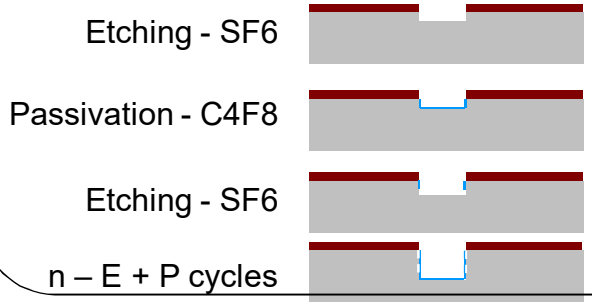
E-Beam lithography: Sub-micron and Nanometer range



- Resolution from 600- 5 nm
- Limited writing area



Deep Si Etching "Bosch“ Plasma process



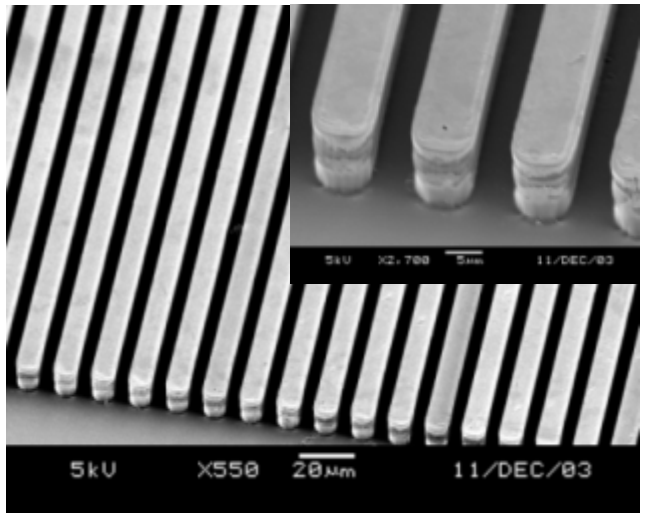
Working mold Replication

Ni Electroplating

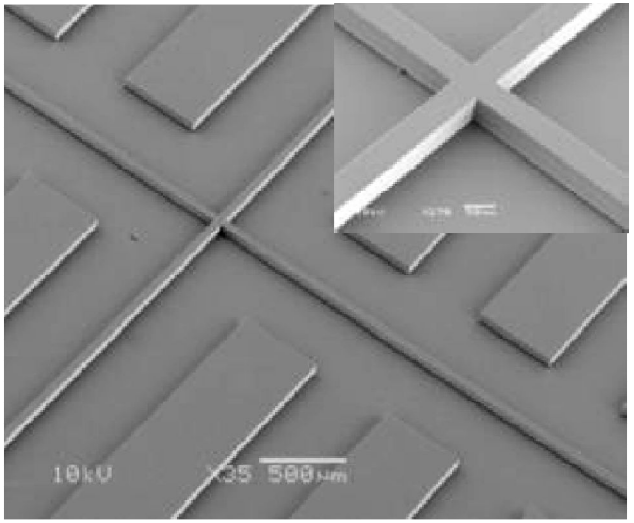
Polymers: PDMS, PTFE …

Molds - stamps

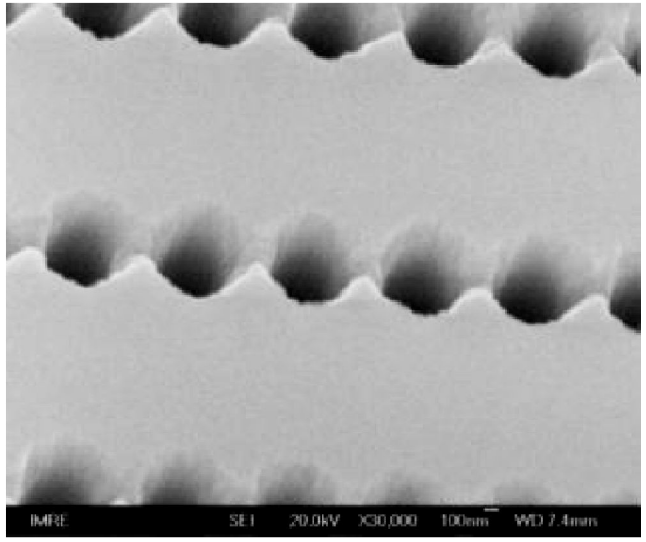
Quartz



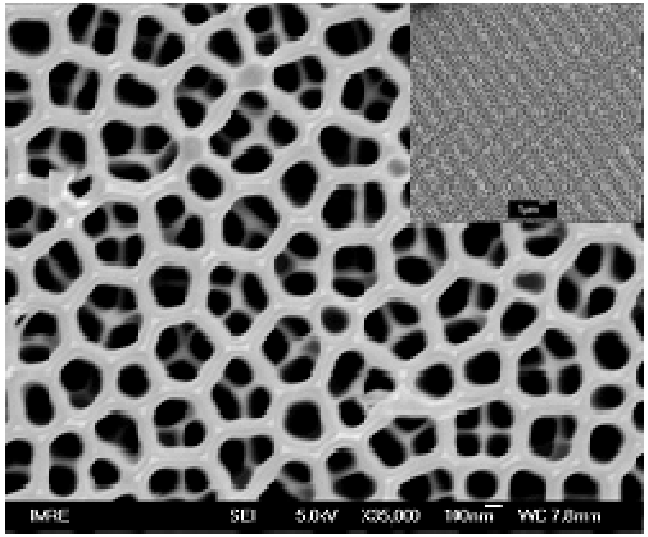
Silicon



PDMS

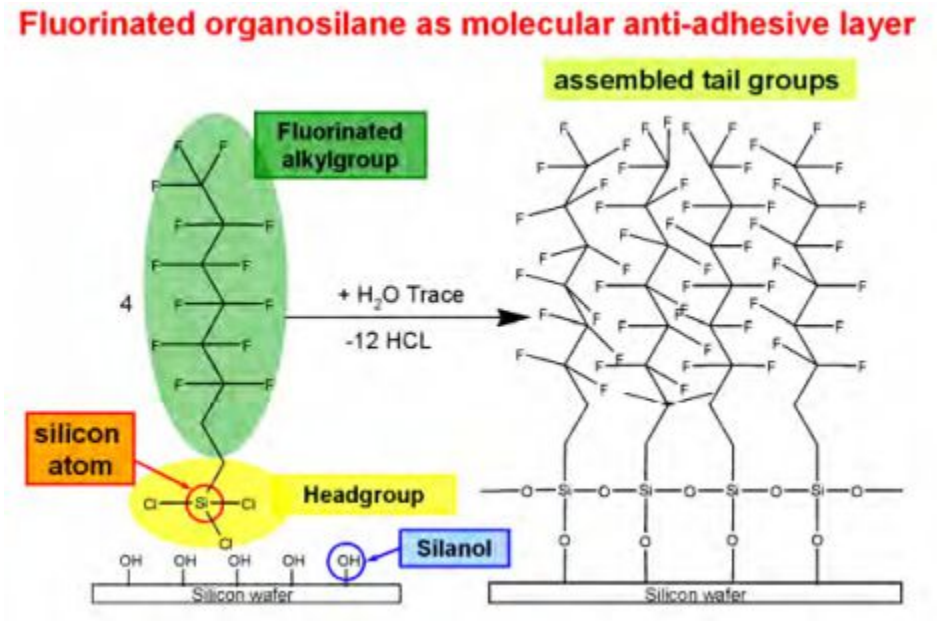


Alumina



Anti-sticking coating

Anti-adhesion surface treatment to reduce the surface energy



Perfluorodecyltrichlorosilane (FDTS)
Heptadecafluoro-1,1,2,2-tetrahydrooctyl)-trichlorosilane (F13-TFS),

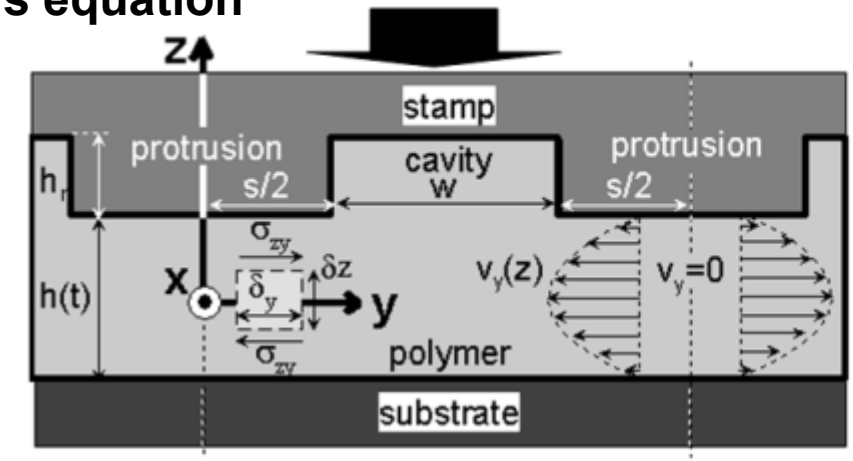
Source: NAPANIL Library process pg 33. Ed. H Shift

Nanoimprinting process

Mechanical displacement of (polymer) material by pressure

The polymer flow into the stamp protrusions - Newtonian flow behavior

- Stefan's equation



- polymer is incompressible
- purely viscous melt
- ideal adhesion of polymer at surfaces
- for s»h(t) the flow is quasi stationary and p = p(y)
- no air trapped in grooves

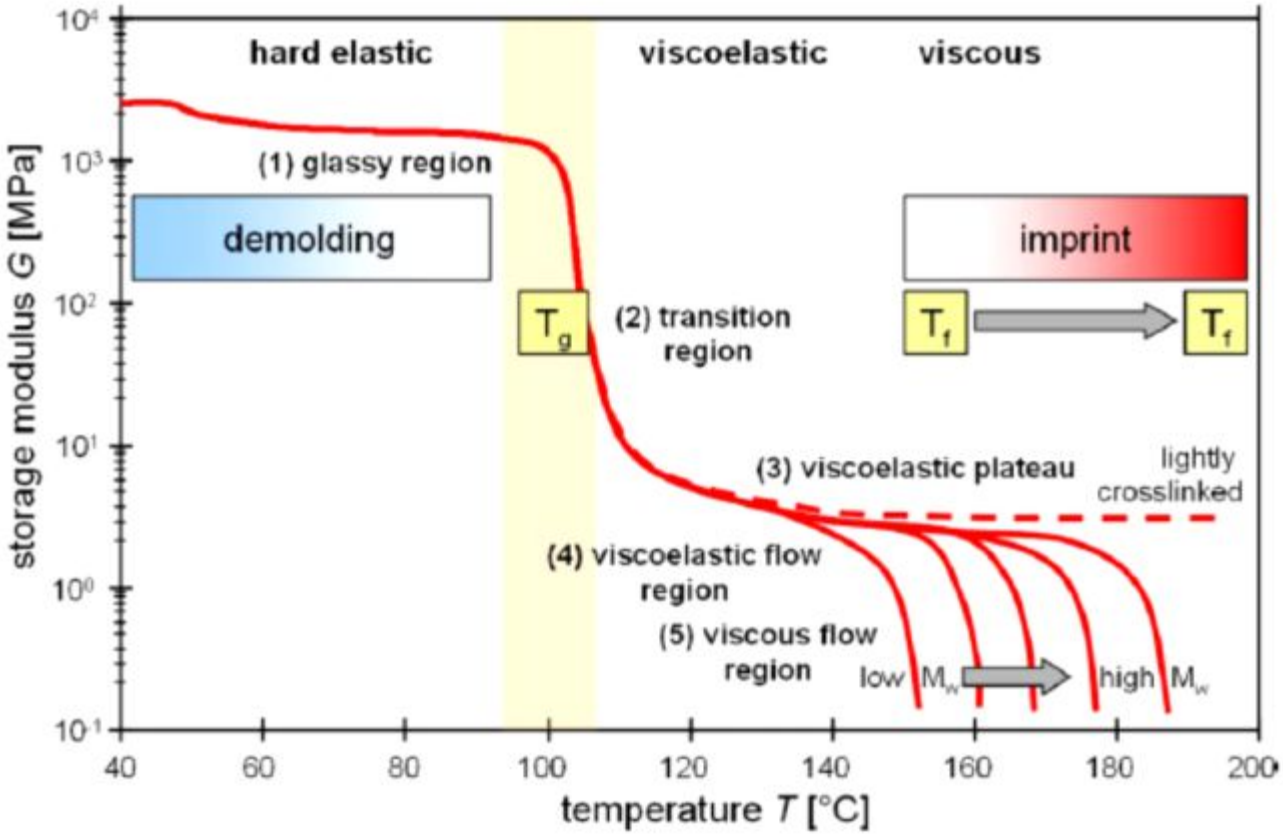
$$t_f = \frac{\eta_0 s^2}{2p}\left(\frac{1}{h_f^2} - \frac{1}{h_0^2}\right)$$

viscosity, stamp width, pressure, initial polymer height, final polymer height

Source: NAPANIL Library process pg 21. Ed H Shift

Choice of process parameters

Mechanical properties change with temperature



$T_f = T_g$ +50 C

Optimum viscosity : 10^3–10^7 Pa s

H. Shift, J. Vac. Sci. Technol. B 2008, 26, 458

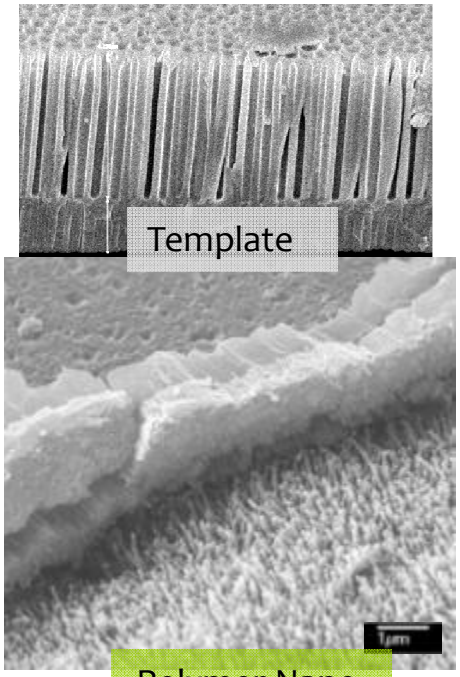
Capillary Nano Imprinting

High Aspect Ratio Polymer Patterning

T = Tm, T >> Tg,

Capillarity action –filling

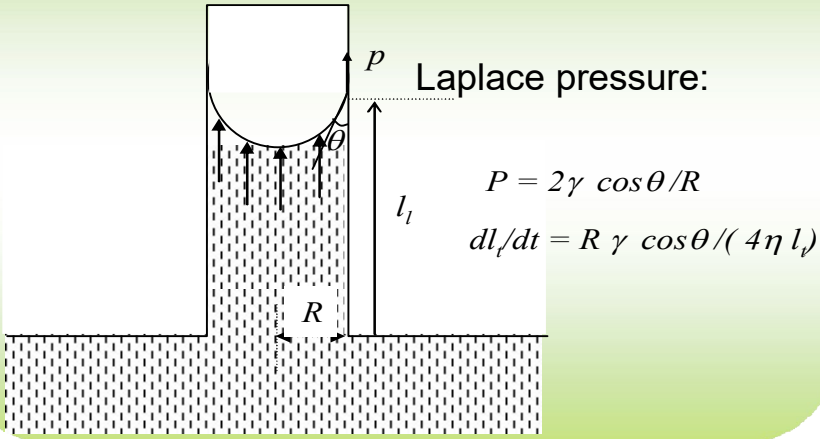
Demolding



1.Polymer is heated above its solidification temperature

2.The pores of templates are wetted and polymer fills-in by capillarity

Capillary action



Laplace pressure:

$$P = 2\gamma \cos\theta / R$$

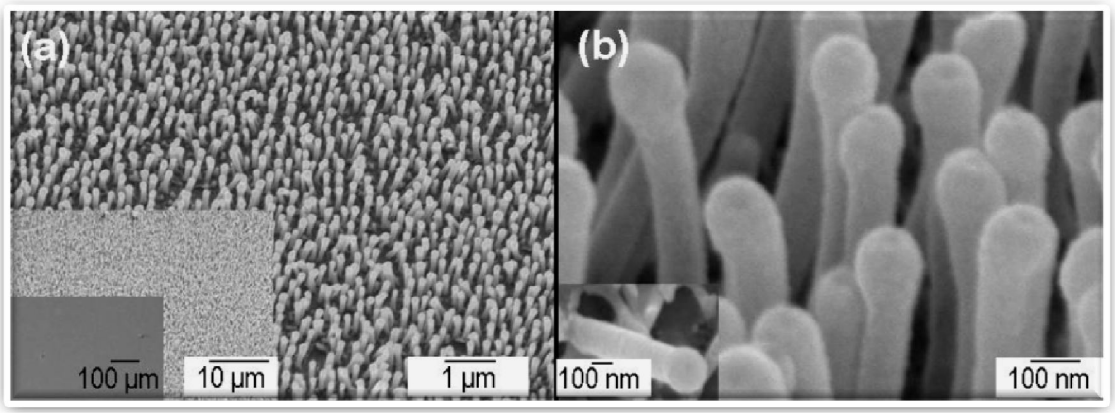
$$dl_l/dt = R\,\gamma\,\cos\theta/(4\eta\, l_l)$$

Features

- High aspect ratio – up to 100:1
- High density
- Sub-100 nm polymer structures

High aspect ratio polymer nano-structures

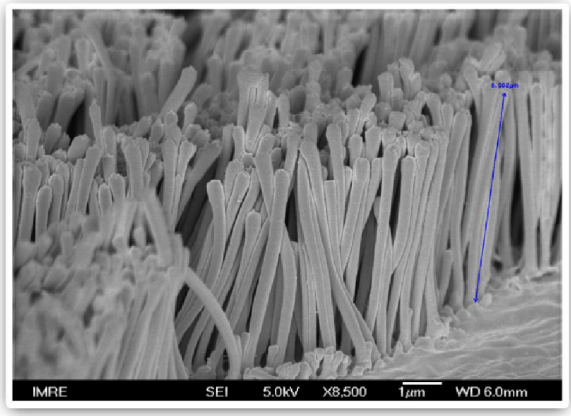
➢**Sub-100 nm.** Pilar size, 80-100 nm; **AR in the range 10:1**



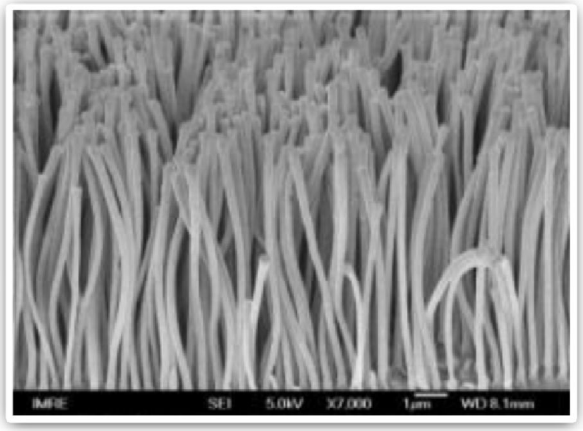
Applications:

- Biomimetic nanophotonics
- Anti reflective, diffractive optics
- Photonic crystals
- Sub wave length optics
- Gecko like dry adhesives
- Substrates for cell biology

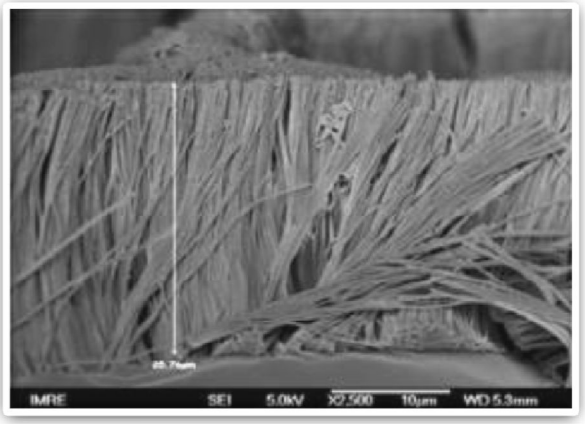
➢**250 nm pillars, AR 24:1**



➢**200 nm pillars, AR 40:1**



➢**270 nm pillars, AR 100:1**



Nanoimprinting facts

- **High-resolution** - Not limited by diffraction but by the mold size (1 nm resolution demonstrated)
- **High-throughput** - Roll to roll scalable, roll to plate
- **Low-cost**
- **Versatility** - Material flexibility
  Process flexibility : UV, thermal
  Feature flexibility : micron- nanoscale
- **Low environmental impact : G**reener - less use of solvent developers

etc.

- Defects, mold patterning and mold wear
- Mechanical resistance of the nanofeatures

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Nanofabrication

Direct writing techniques

E-beam lithography
Ion beam lithography
Scanning probe lithography
Direct Laser Writing Lithography
Two-photon Lithography -3D printing

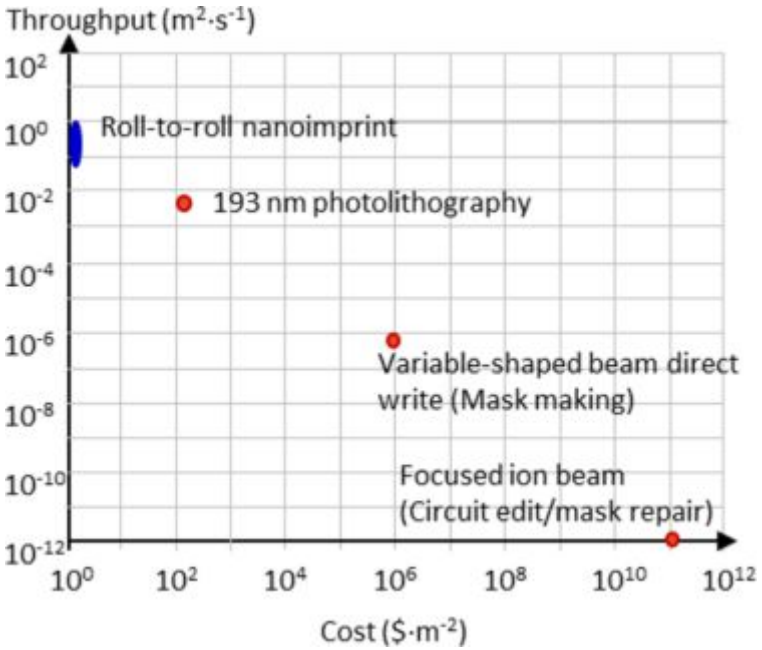
Nanomanufacturing

Replication techniques

mass fabrication processes

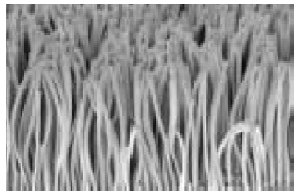
Optical lithography
X-ray lithography
Nanoimprint technology

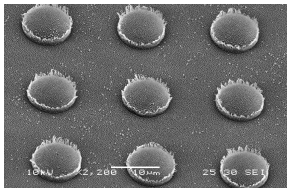
Resolution ~ Throughput – Cost

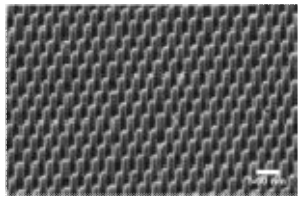


Patterning techniques used in integrated circuit manufacturing.
J. A. Liddle & G. M. Gallatin, Nanomanufacturing: A Perspective ACS Nano 2016, 10, 2995.

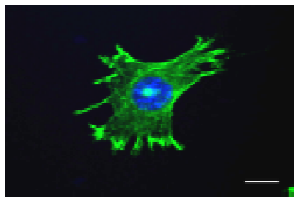
Surface functions & bio-applications

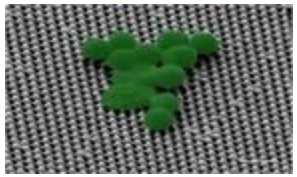






- Gecko like dry adhesives
- Superhydrophobic lotus
- Anti-reflective moth-eye surfaces





- Cell Instructive Patterned Topographies
- Bactericidal Moth Eye Inspired Topography

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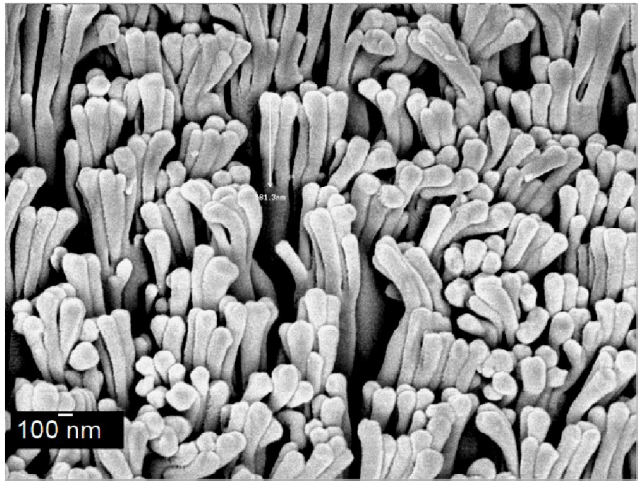
Gecko like dry adhesives

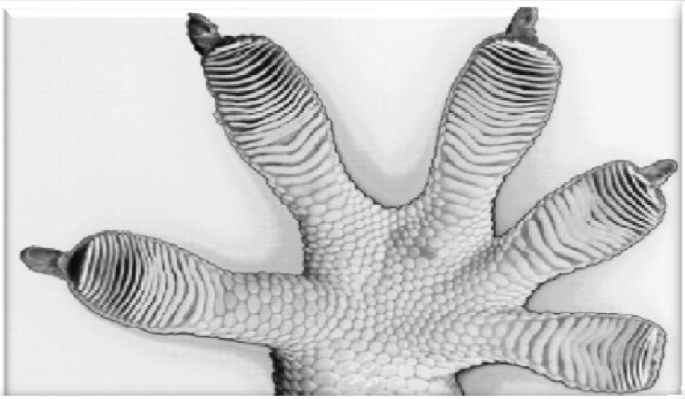
van der Waals adhesion - residue free



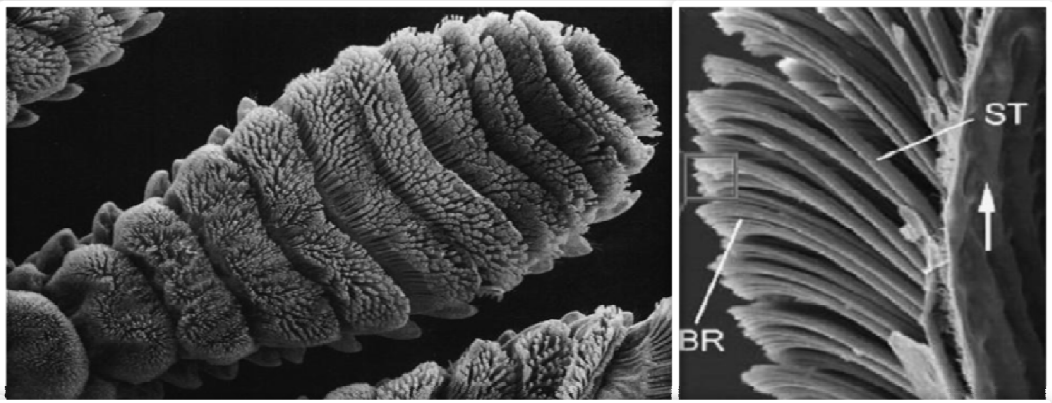
Polymeric hierarchically branched fibrils

Fabrication and Analysis of Gecko-Inspired Hierarchical Polymer Nanosetae, ACS NANO , 5, 1897-1906, 2011

Gecko's Hierarchical Attachment System



Autumn, K., et al., Nature, 2000. **405**(6787): p. 681.



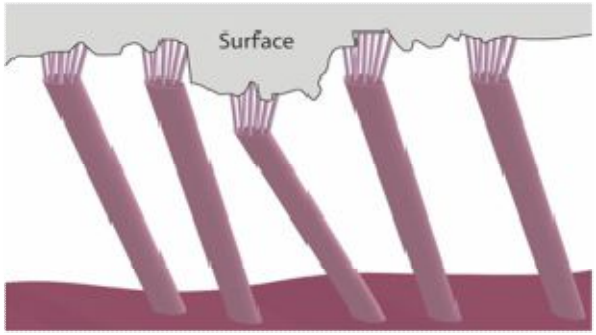
Bhushan, B., J. Adhesion Sci. & Tech., 2007. **21**(12/13): p. 1213.

Hierarchy (β-keratin)	**Name**	**Diameter**	**Height**	**Aspect Ratio**	**Density (#/mm²)**
Level 1	Seta	~ 4 μm	~ 110 μm	~ 25	14×10^3
Level 2	Branch	~ 1 μm	~ 25 μm	~ 25	-
Level 3	Spatula	~ 100 nm	~ 2.5 μm	~ 25	$1.4 - 14 \times 10^6$
End of Level 3	Tip of Spatula	**Width**	**Length**	**Thickness**	
		200 -300 nm	500 nm	10 nm	

Hierarchy allows for conformal contact - Adhesion via van der Waals forces

Gecko adhesive
Hierarchy of compliant structures

Conformational contact to surface roughness



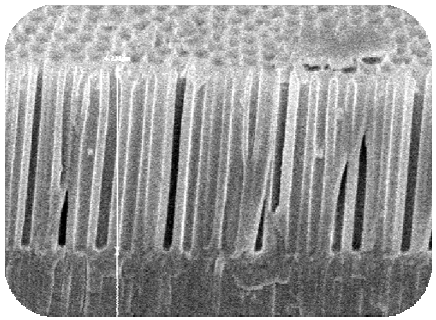
Benchmark functional properties:

1. Anisotropic , directional attachment - shear force adhesion
2. High pull off to preload ratio
3. Low detachment force
4. Material independence / van der Waals adhesion
5. Self-cleaning
6. Anti-self matting
7. Non-sticky in default state

K. Autumn (MRS Bulletin, June 2007)

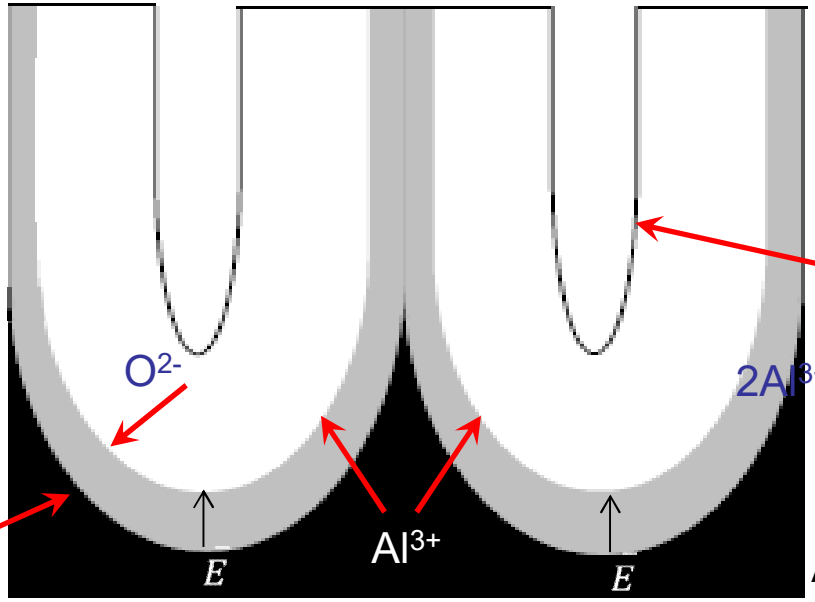
Mold fabrication: Nano porous alumina

Aluminium anodization - Alumina Pore Formation



Platinum as cathode (-)

$6H^+ + 6e^- \rightarrow 3H_2$



Oxide/Electrolyte Interface

$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+$

Metal/Oxide Interface

$2Al + 3O^{2-} \rightarrow Al_2O_3 + 6e^-$

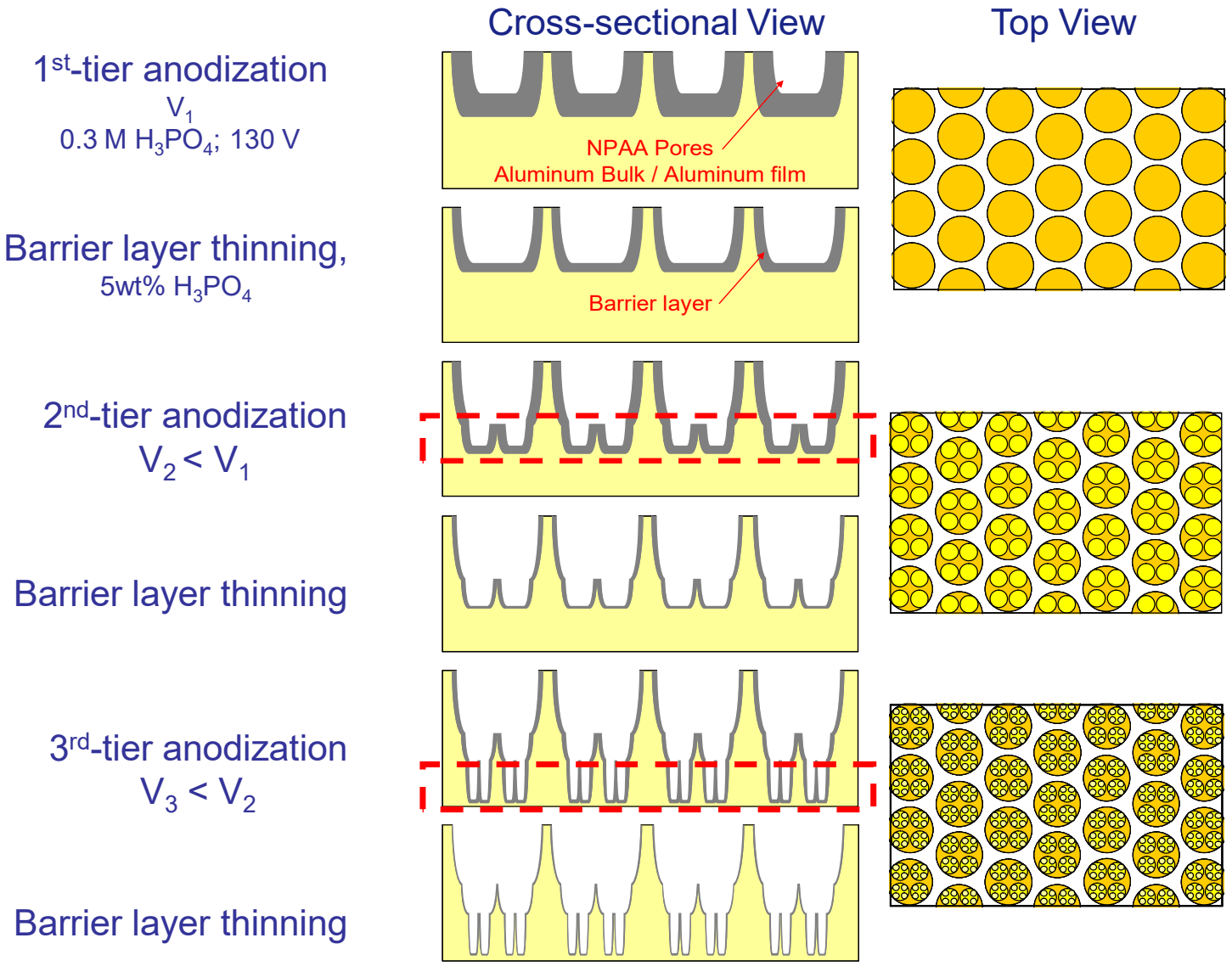
$2Al \rightarrow 2Al^{3+} + 6e^-$

Aluminum as anode (+)

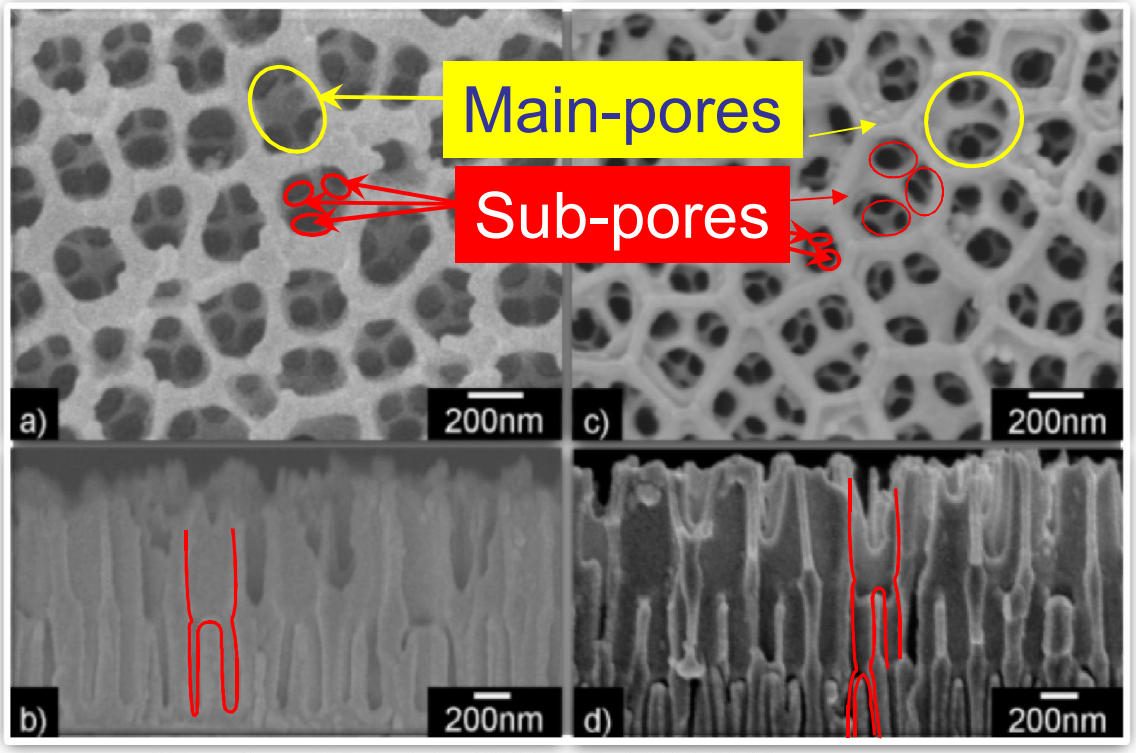
Overall anodization reaction: $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

Fabrication of hierarchical PAA template

Anodization reaction: $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$



Branched Porous Alumina Template



Advanced Functional Materials 2008, 18, 2057-2063.

2-3 step aluminum anodization

1st-tier anodization
V_1 (130V)
0.3 M H3PO4
130 V for 35 min

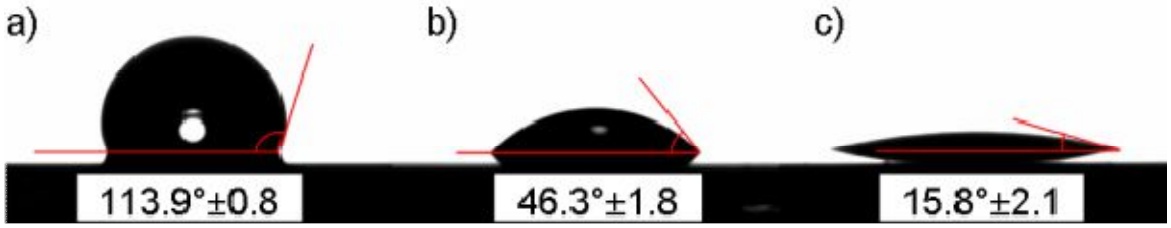
Barrier layer etch
5wt% H3PO4

2nd-tier anodizatio
V2 (80V)
0.15 M C2H2O4
80 V for 3.5 min

Barrier layer etch
5wt% H3PO4

3rd-tier anodization
V3 (50 V)
0.3 M C2H2O4
50 V for 15 min

Barrier layer etch
5wt% H3PO4

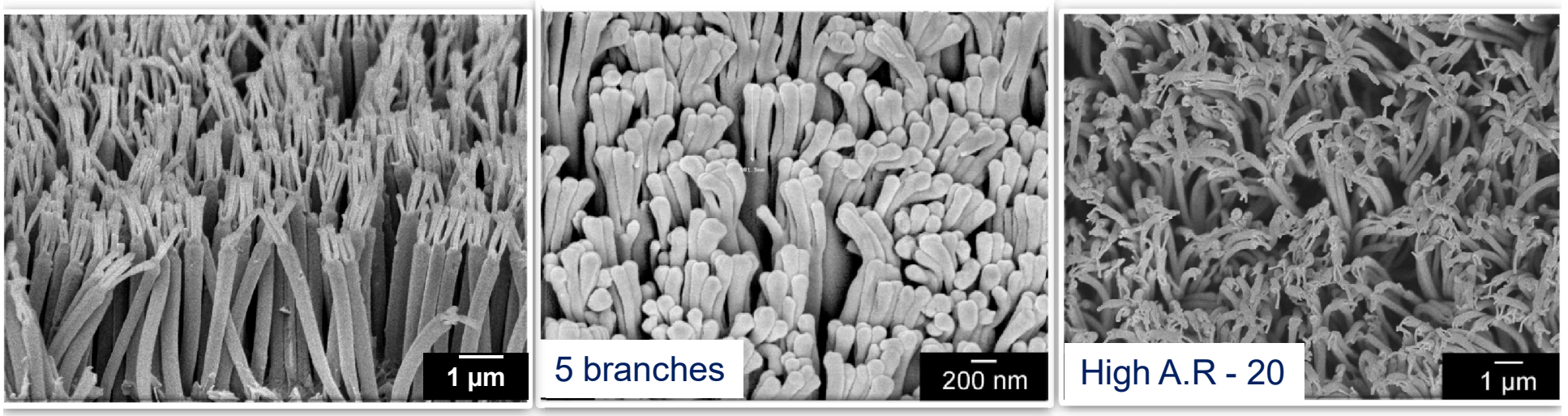


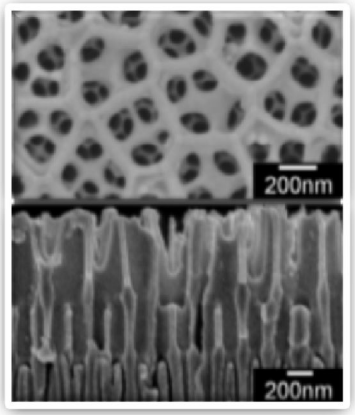
Aluminium | Single tiered PAA | 2 – tiered PAA

Increased wettability ⟶
- filling of the pores

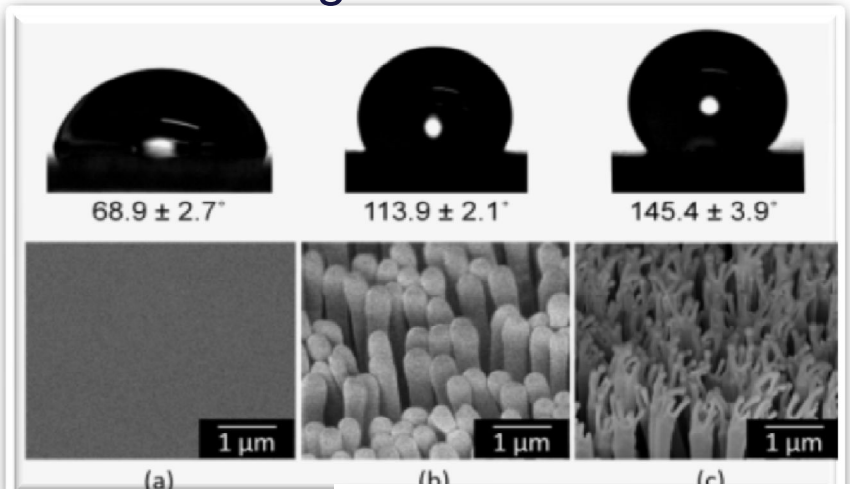
Hierarchical gecko like dry adhesives

Main fibril's Ø: 250 nm , A.R – 10, ρ – 6.2 x 10^6 fibrils/mm^2



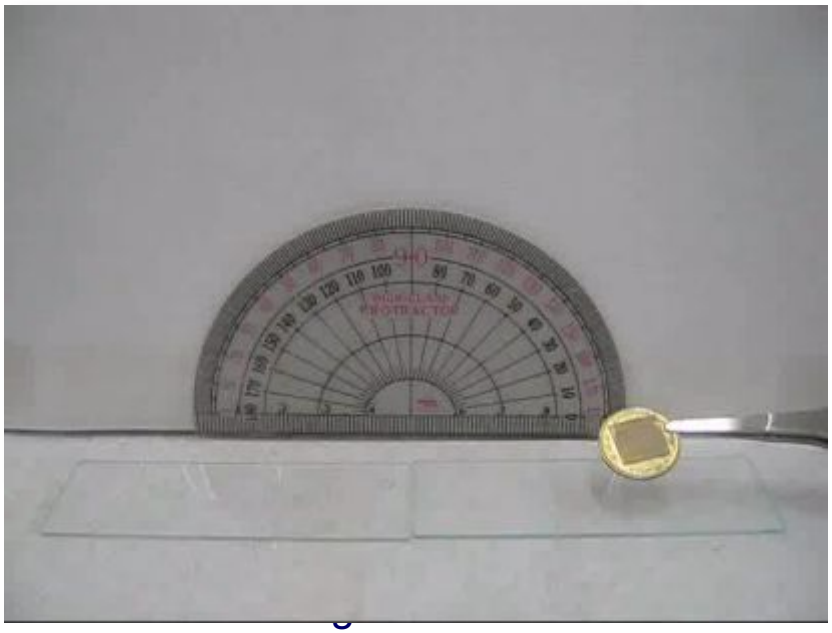


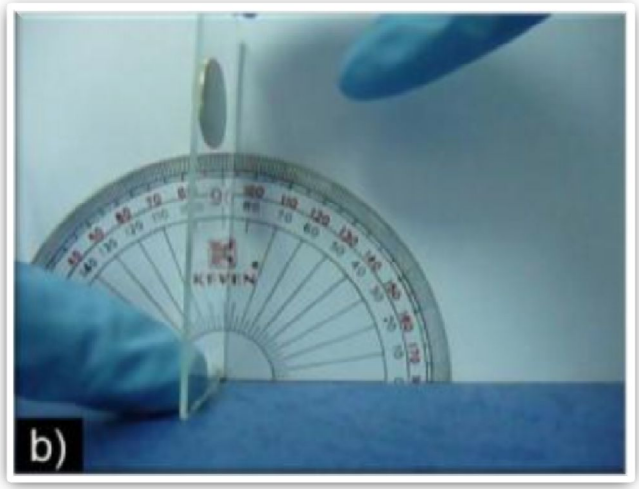
Wetting characteristics



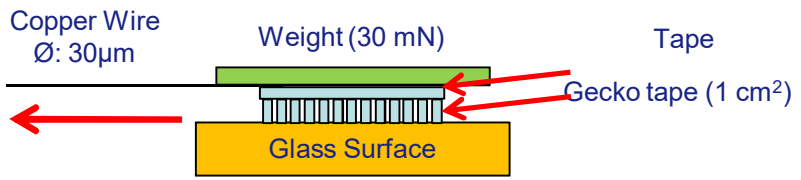
Pristine Polycarbonate Linear pillars Branched pillars

Frictional Adhesion Measurements

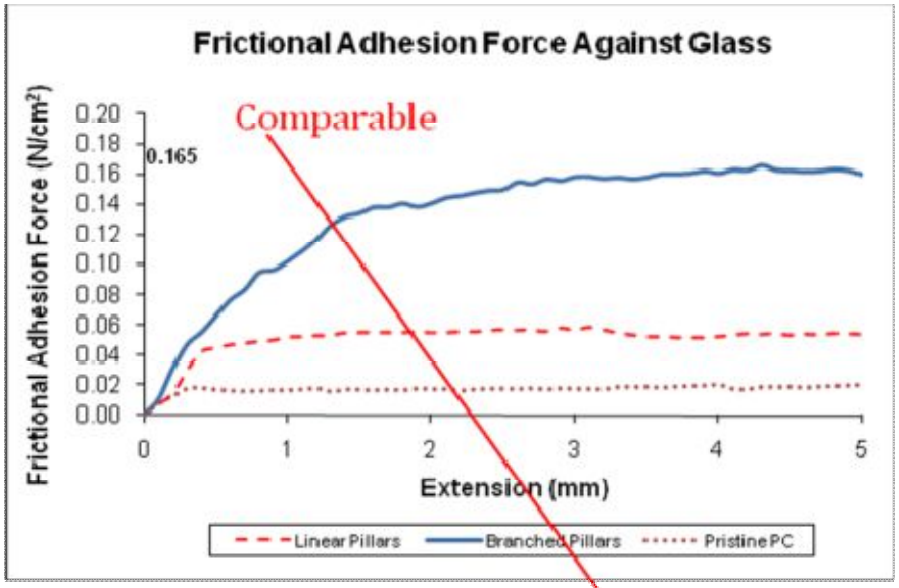




Branched pillared tape on a 5 cents coin remaining on the glass-slide at + 90˚ tilt.



Gecko tape friction test set up



Values by estimating contact region with preload of 0.03 N/sq.cm.

Typical weight of Gekko Gecko : 43.4 ±1.48 g
Pad area : 2.271 ± 0.109 cm²
→ Frictional Adhesion Force : **0.188 N/cm²**

D.J. Irschick et al., Biological *Journal of the Linnean Society* **(1996)**, *59: 21-95.*

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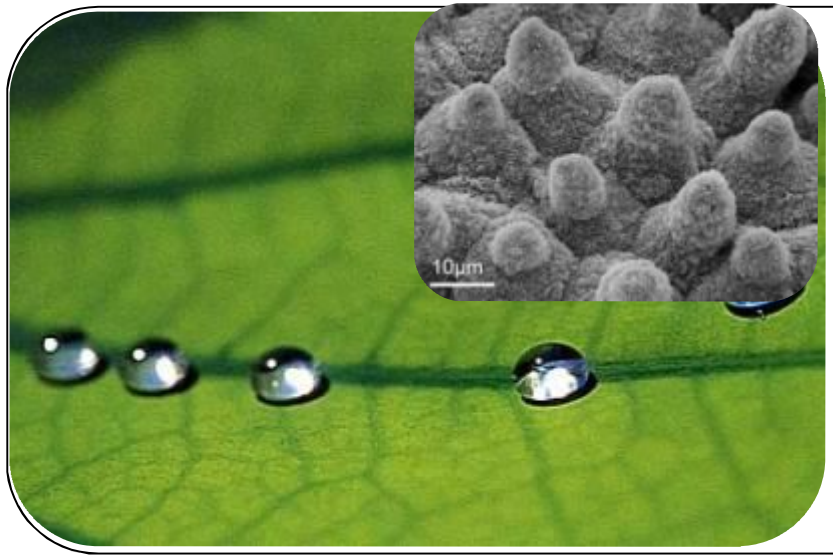
Superhydrophobic, self cleaning lotus leave

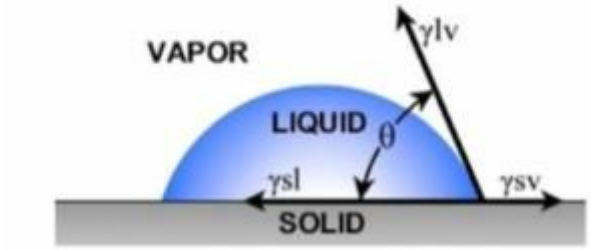


Hierarchical

micro/nano topography

Ho, Audrey et al. Lotus bioinspired superhydrophobic, self-cleaning surfaces from hierarchically assembled templates. Journal of Polymer Science Part B: Polymer Physics, 2014, 52, 603.

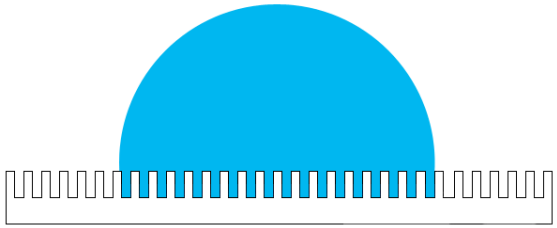
Wetting properties : contact angle



$$\cos\theta_o = \frac{\gamma^{sv} - \gamma^{sl}}{\gamma^{lv}}$$

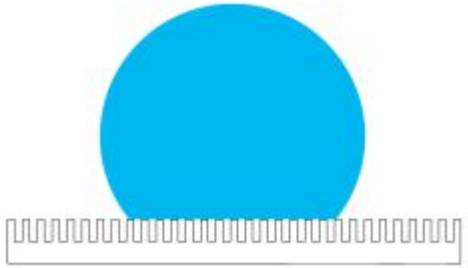
Young's equation

Wenzel state



$$\cos\theta = r\cos\theta o$$

Cassie- Baxter state



$$\cos\theta = rf\cos\theta o - 1 + f$$

Super hydrophobic surfaces

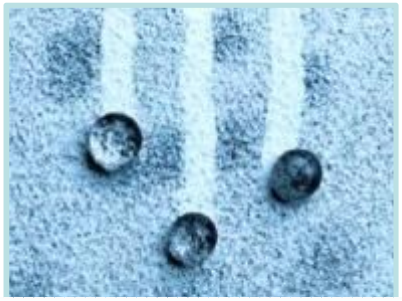
~ Synergy : surface energy + topography ~

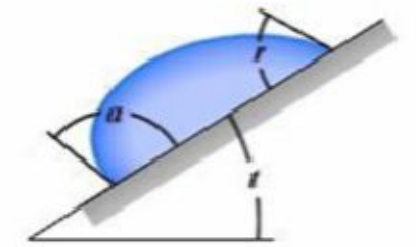
Apparent contact angle (θ) above 150º

160 º

https://en.wikipedia.org/wiki/Ultrahydrophobicity

Self-cleaning surfaces





~ Synergy : surface energy + topography ~

apparent contact angle (θ) above 150º

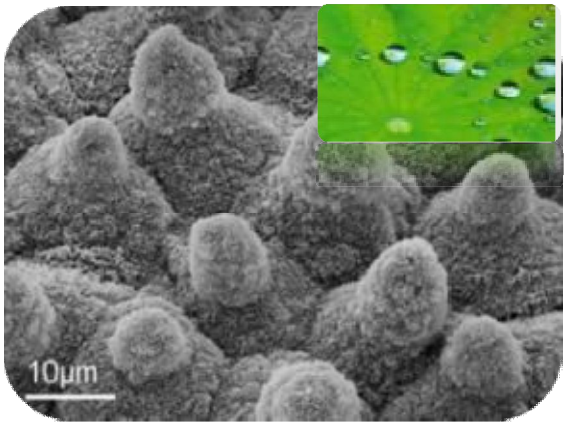
+ contact angle hysteresis below 10 º

$H = \theta_a - \theta_r$

Topography modulated wettability

Self-pinning

Self-cleaning



Petal (Cassie impregnating wetting state)

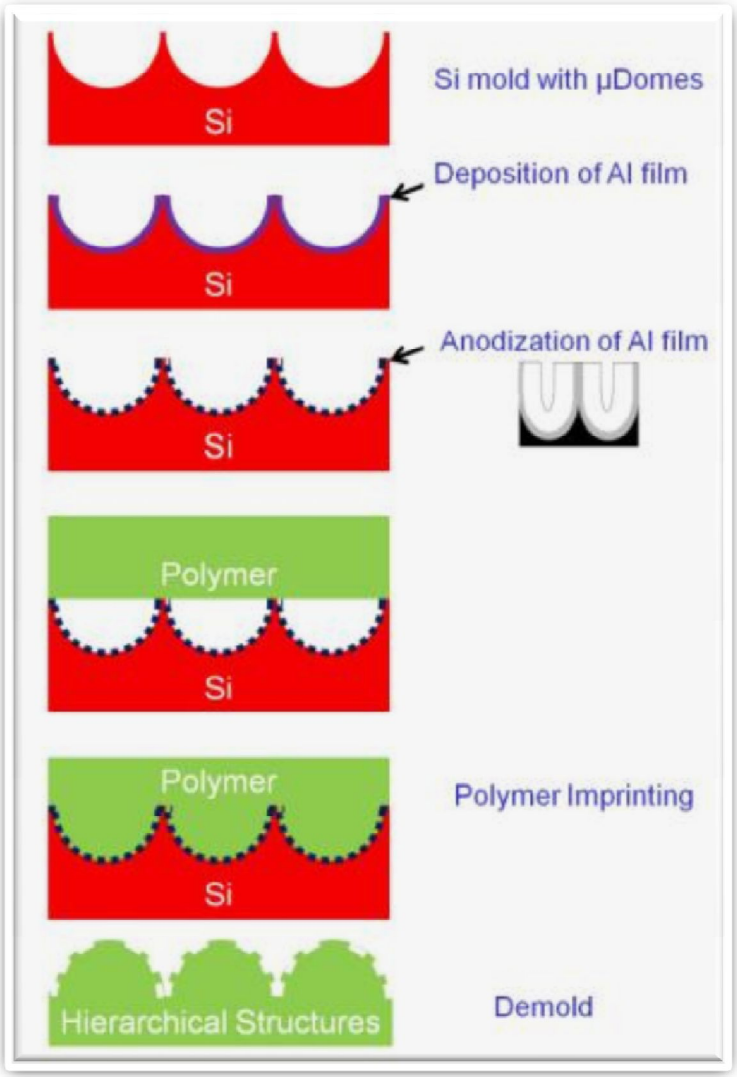
Lotus (Cassie's state)

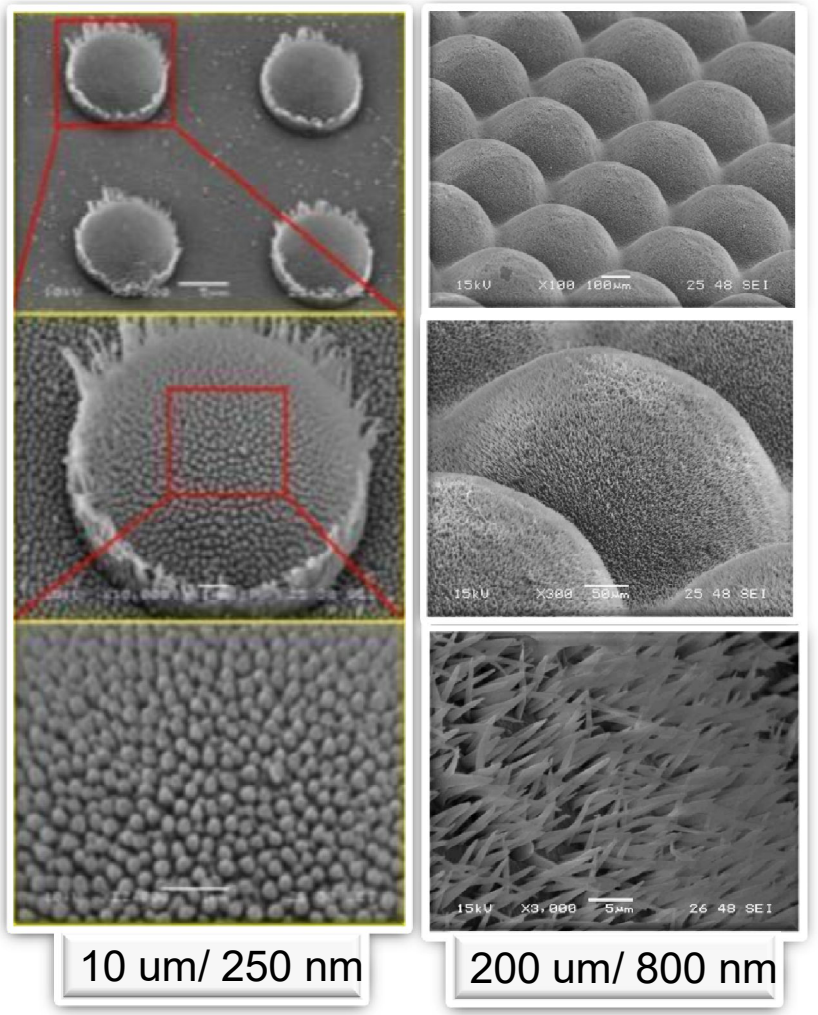
Feng et al. Langmuir 24, 8, 4114-4119

https://en.wikipedia.org/wiki/Ultrahydrophobicity

Lotus-like structure fabrication

Fabrication process steps



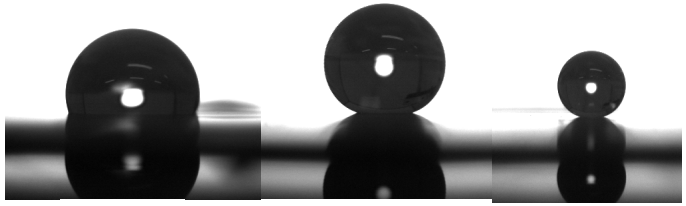


10 um/ 250 nm

200 um/ 800 nm

SHS - Wetting properties

Water Contact Angle

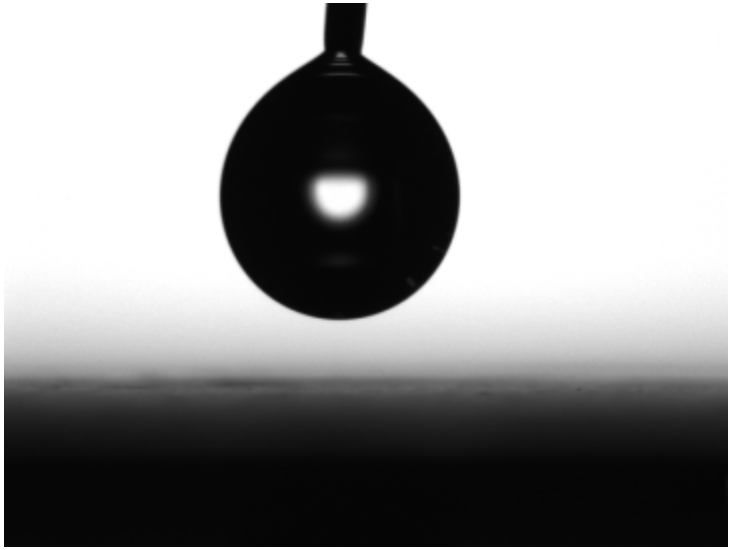


113 º 160 º 163 º

Water contact angle on 10 µm/ 200 nm hierarchy

	Static contact angle(deg)		
Topographies	*Flat*	*Micro*	*Hierarchical*
Pristine (PP)	103 ± 3	-	-
400 µm / 0.8 µm		104 ± 9.1	153 ± 4.6
10 µm /200 nm		113± 2.4	160 ± 2

	Contact angles (deg)		
Topographies	*Static*	*Hysteresis*	*Sliding*
400 µm / 0.8 µm	154 ± 0.5	10 ± 4	8 ± 1.7
10 µm / 200 nm	160 ± 2	9 ± 1	4 ± 0.3



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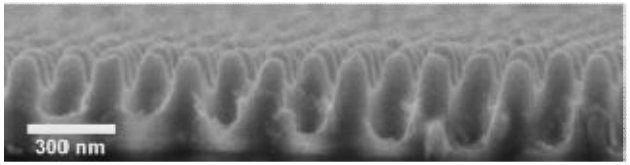
Anti- reflective surfaces

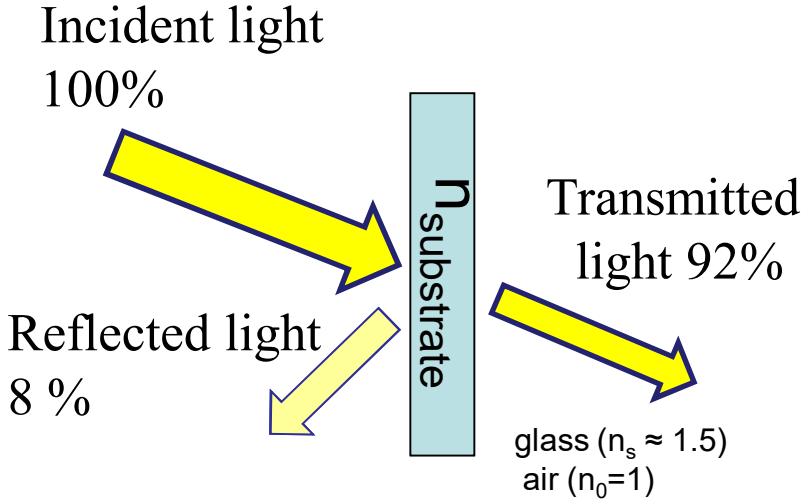
Graded
Refractive Index



Single-imprint Moth-eye Anti-Reflective and Photoinduced Self-cleaning Film with Enhanced Resistance.

Navarro-Baena et al, Nanoscale 2018 . DOI: 10.1039/C8NR02386G

Light Reflection

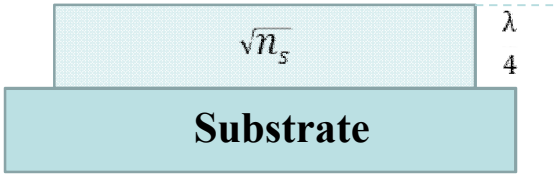


Fresnel's Equation:

$$R = \left[\frac{n_s - n_0}{n_s + n_o}\right]^2$$

Anti-refletion: current solutions available

Single layer



Refractive index for an ideal AR coating:

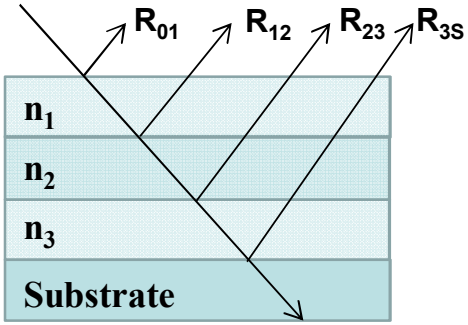
(1) $n_c = (n_a n_s)^{1/2}$
(2) $d = \lambda/4$

Glass ⇨ **n_s=1.2**

MgF_2 (with an index of 1.38)

Few materials and high price!!!

Multiple layer

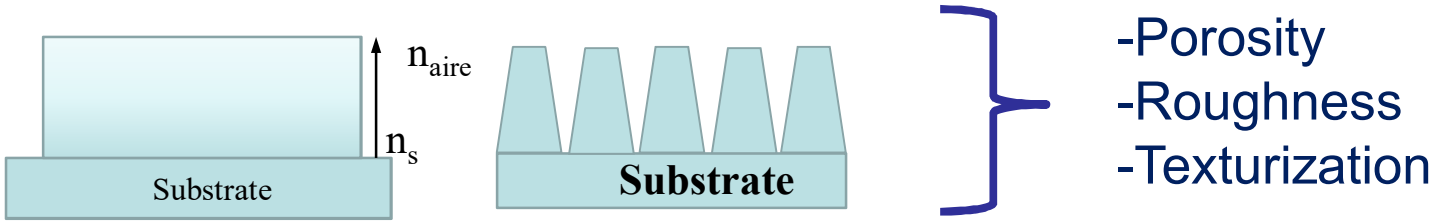


$R_{sum} = R_{01} + R_{12} + R_{23} + R_{3s}$

Expensive approach!!!

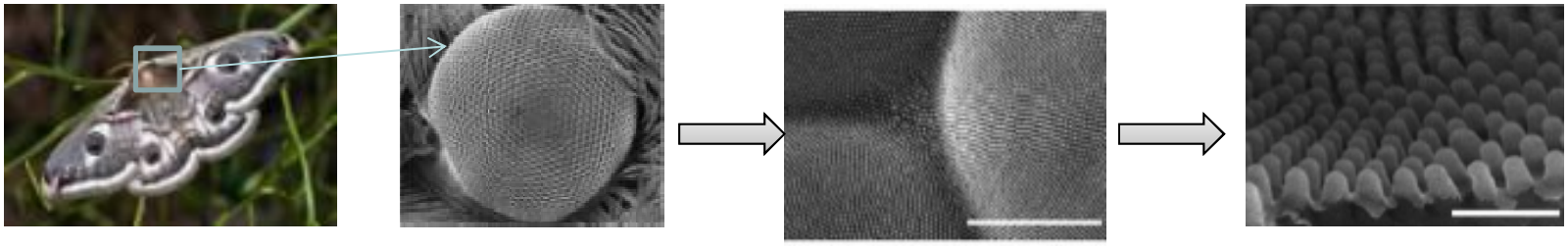
Anti- reflective strategy:

Graded refractive index



-Porosity
-Roughness
-Texturization

Moth´s eye natural antireflective topography – subwavelength nanocone features



Pros of AR textured surfaces

-AR Broad spectral range
-Easy scalable ->R2R
-Cheap

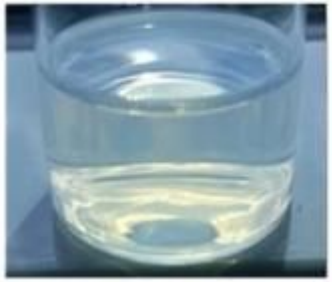
Cons of AR textured surfaces

-Poor mechanical behavior
-Cleaning

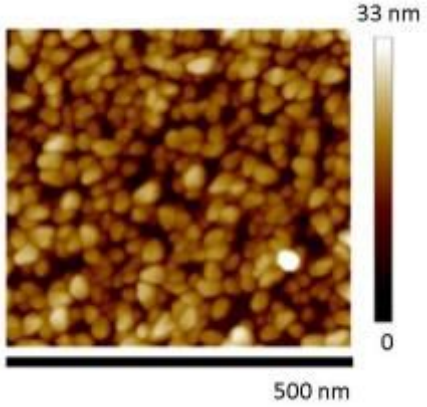
TiO_2 Surface Nanocomposite

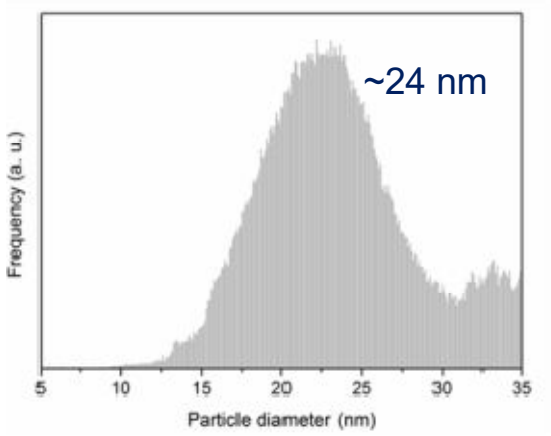
Preparation of polymer nanocomposite

TiO_2 nanoparticles: Hydrothermal synthesis

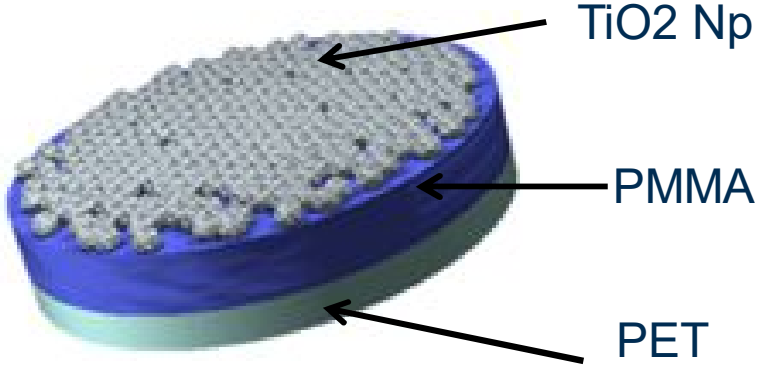


Colloidal suspension

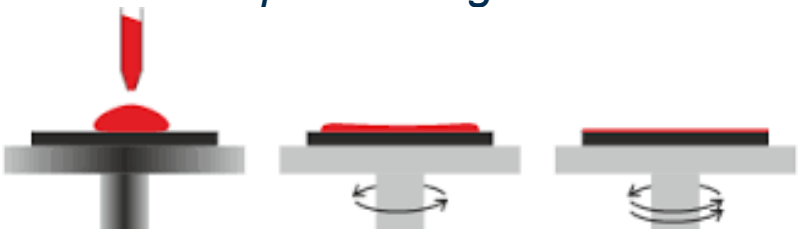




Nanocomposite preparation



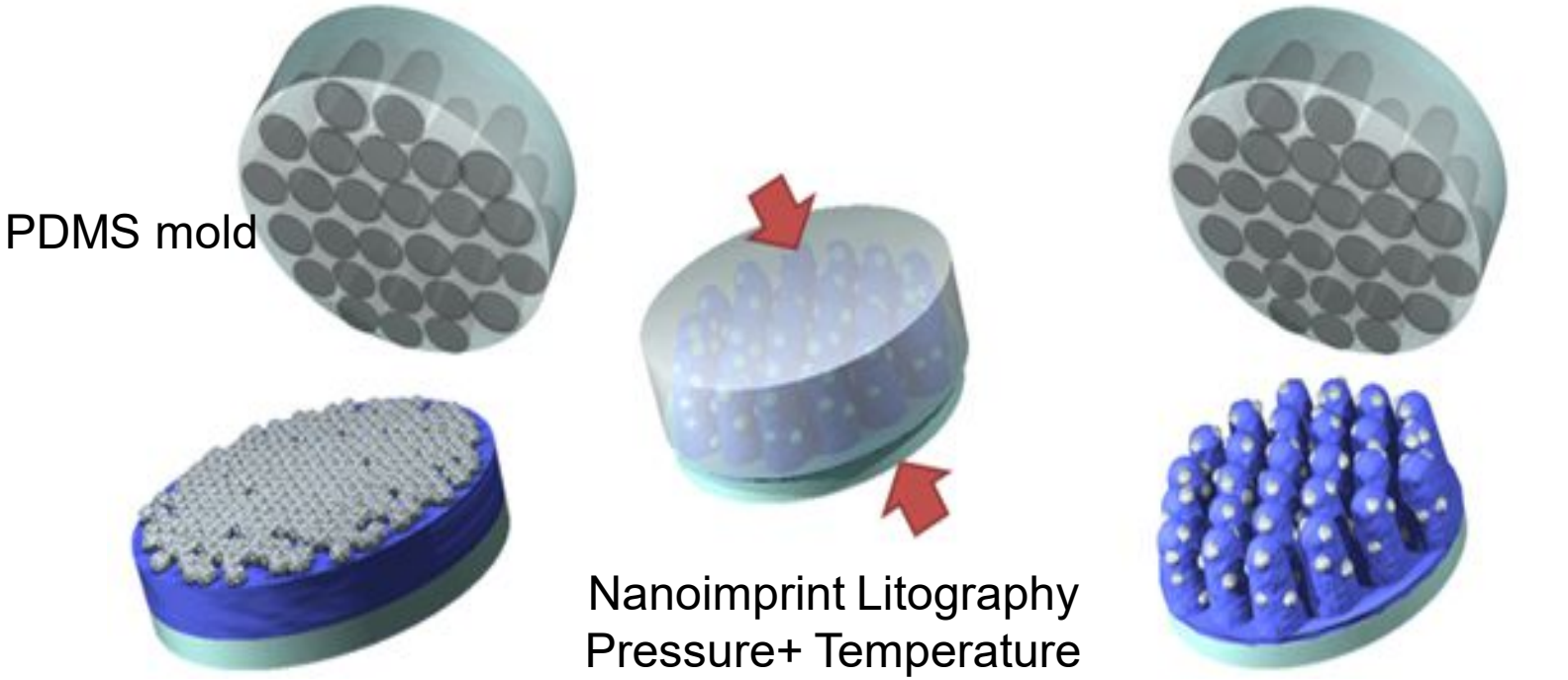
Spin coating



Different ammounts of nanoparticles were deposited

Moth-eye Nanoimprinting

Nanocomposite - Thermal Nanoimprinting



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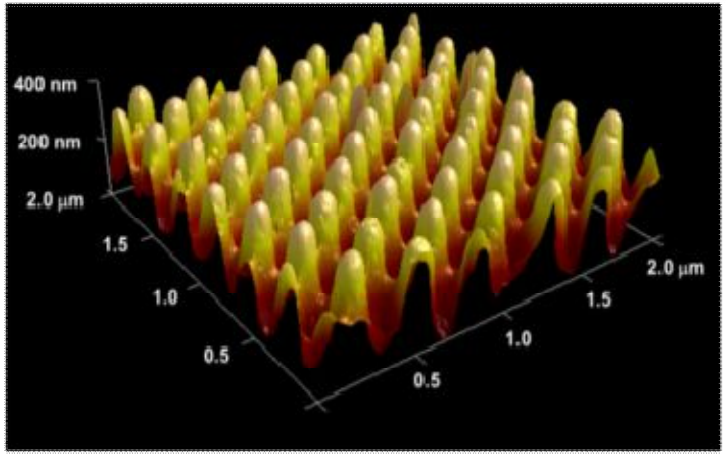
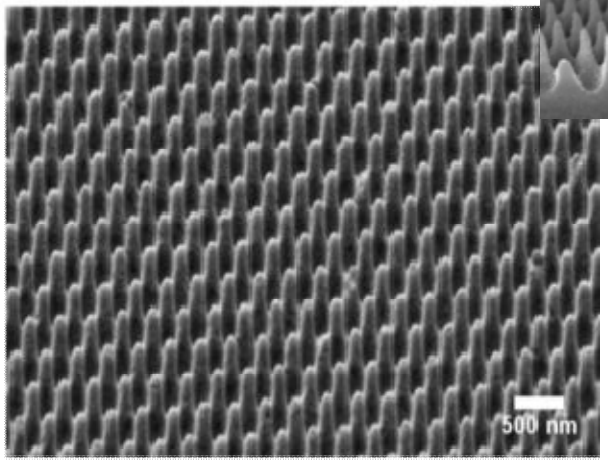
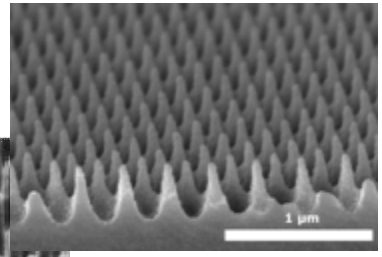
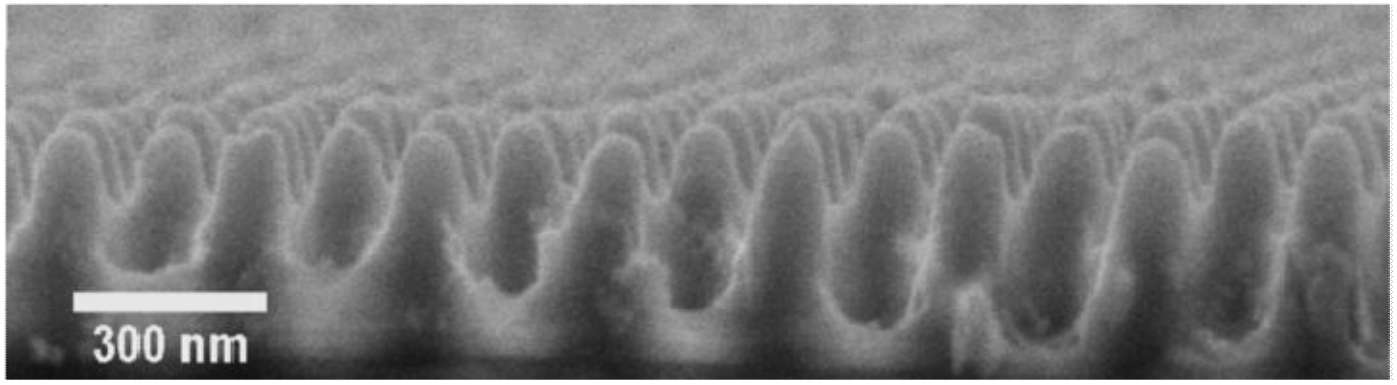
Moth-eye nanostructures

Morphology: SEM & AFM images

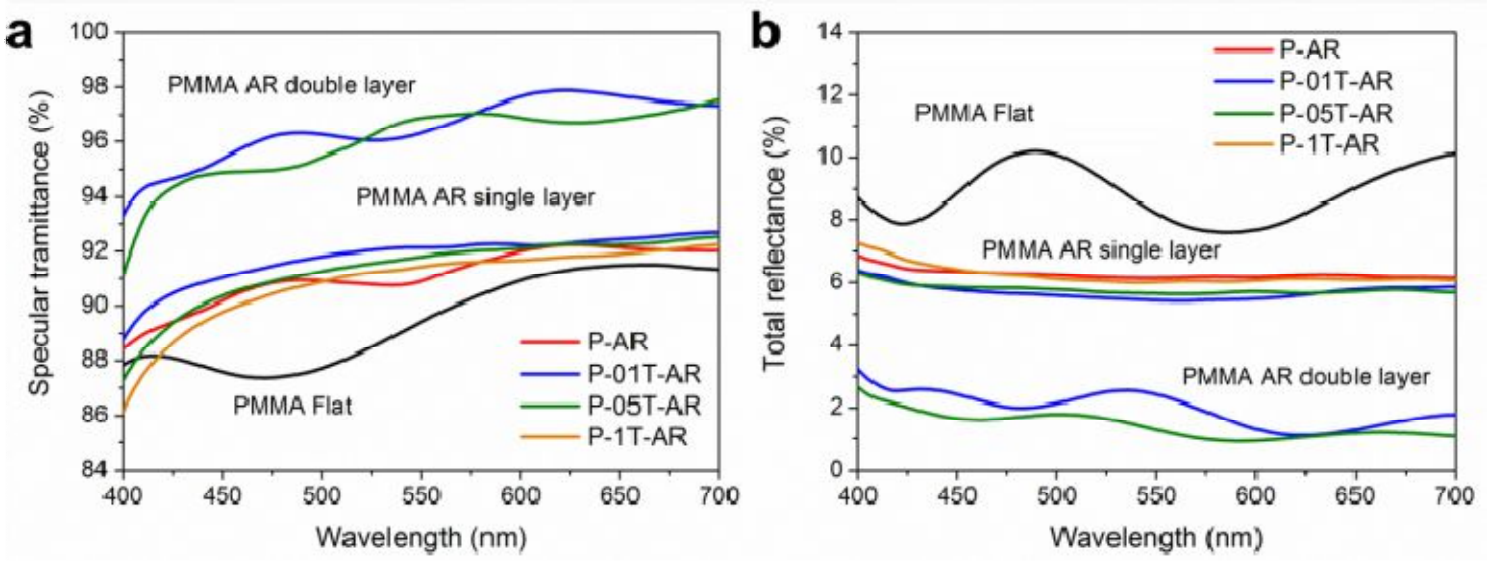








Moth-eye optical characterization

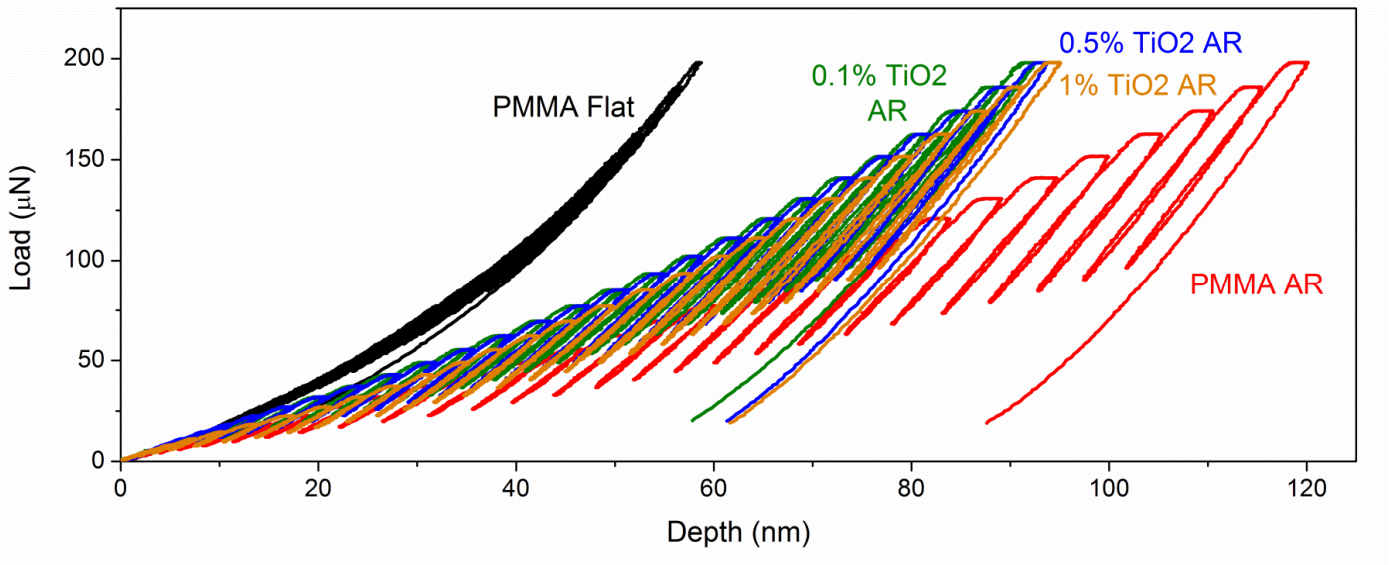


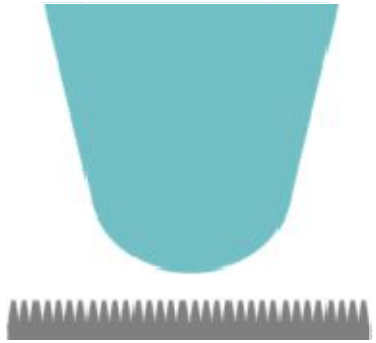
Flat

AR

TiO2 Nps do not impact the optical properties!!!

Mechanical behavior: Nanoindentation

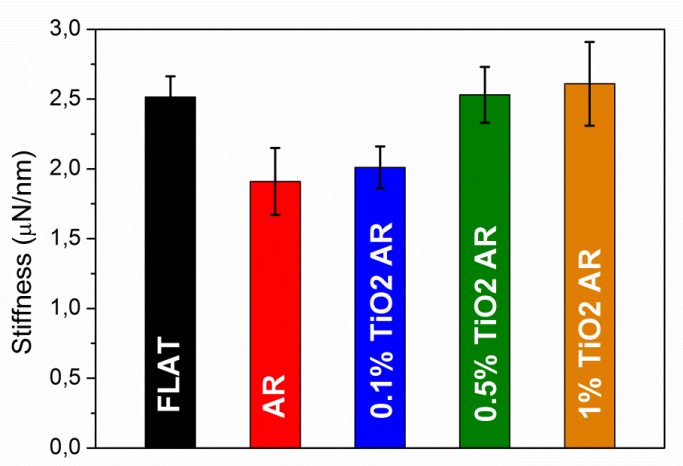


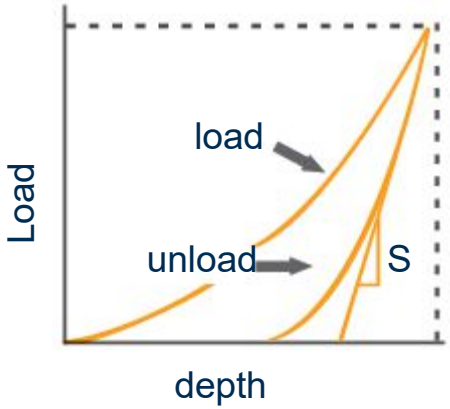


20 load/unload cycles until maximum load of 200 μN

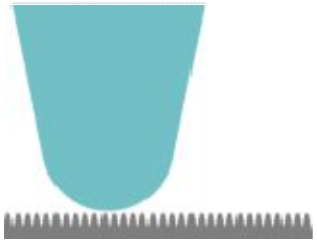
Stiffness

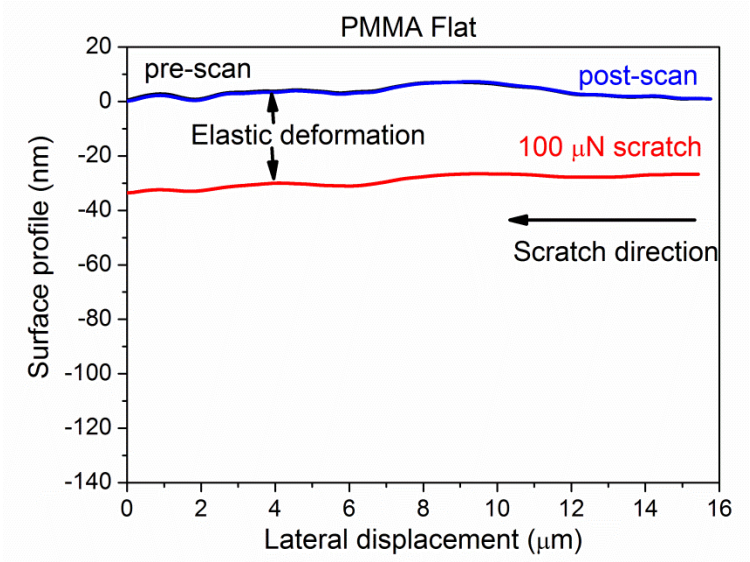
Slope of the curves in the elastic region (maximum of 10 nm)



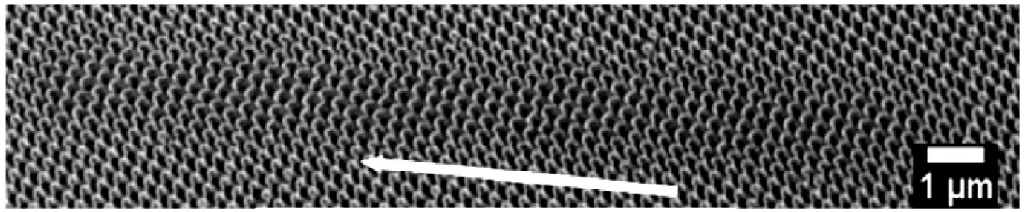


Mechanical behavior: Nanoscratch

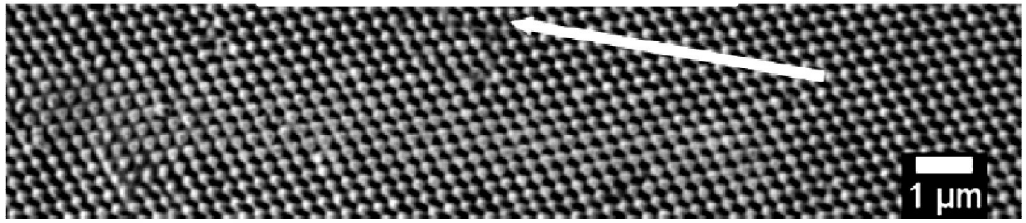


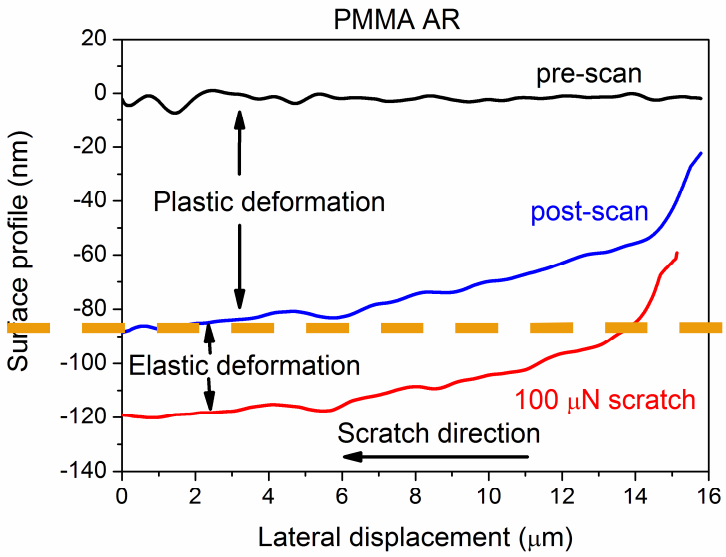


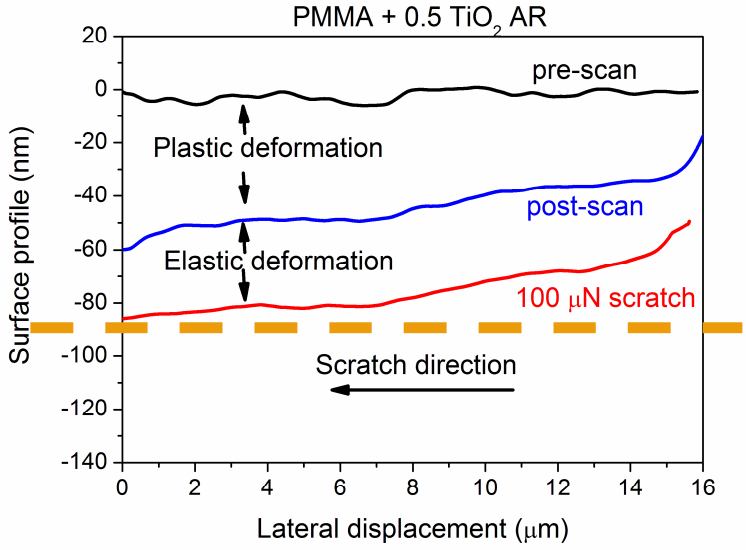
PMMA



PMMA + 0.1 wt% TiO_2

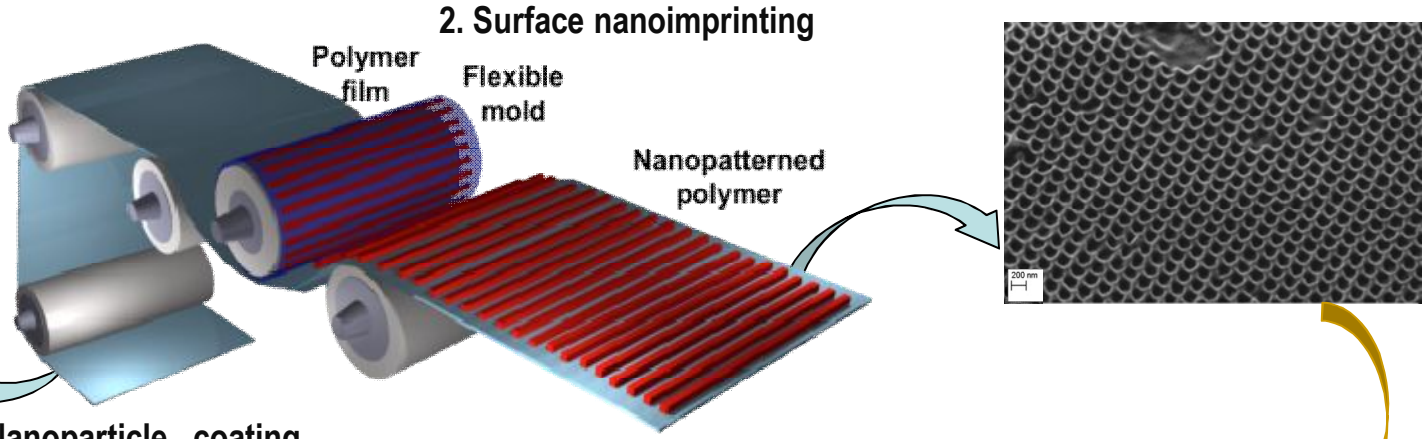


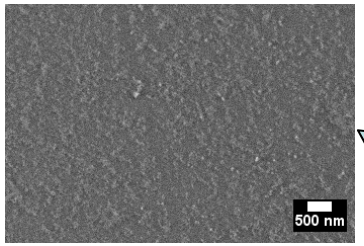




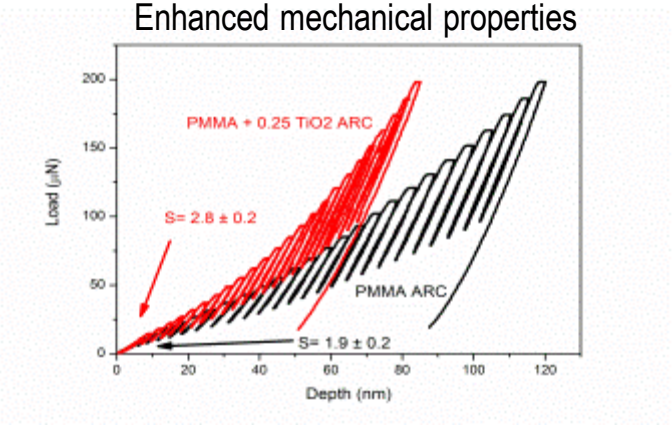
R2R implementation

Continuos proceses

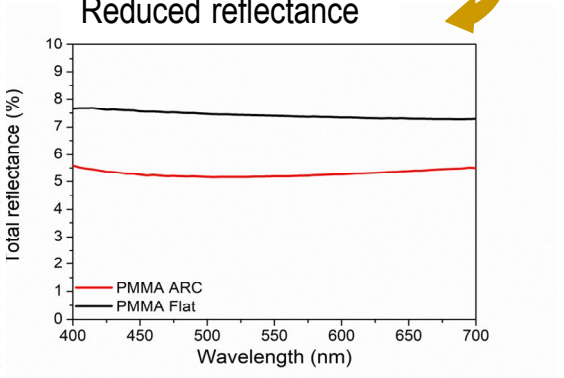




Enhanced mechanical properties



Reduced reflectance



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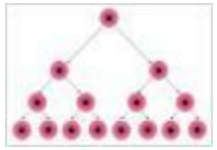
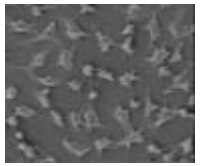
Bio-applications

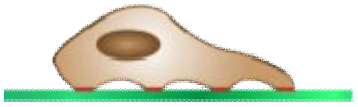
1. Cell Instructive Patterned Topographies



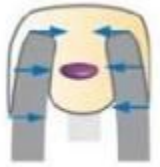
Proliferation



Morphology



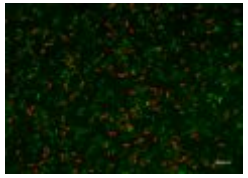
Migration



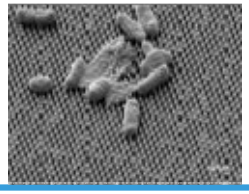
Cell Traction Force

2. Bactericidal Moth Eye Inspired Topography

Fluorescence Microscopy



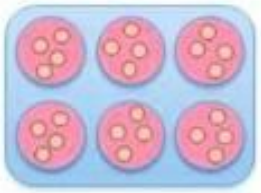
SEM



Cell Instructive Patterned Topographies

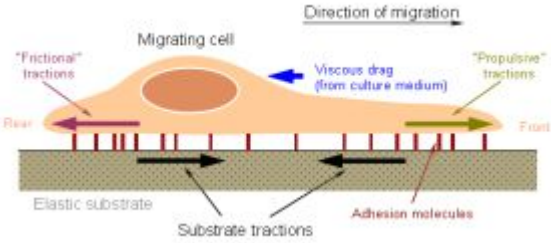
Experimental Setup

Neural Stem Cell suspension

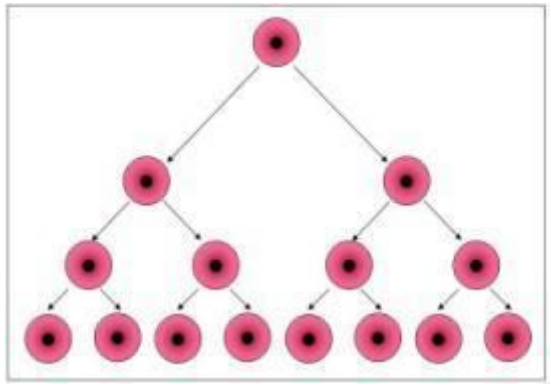


Cell cultured over nano and micropillars surfaces

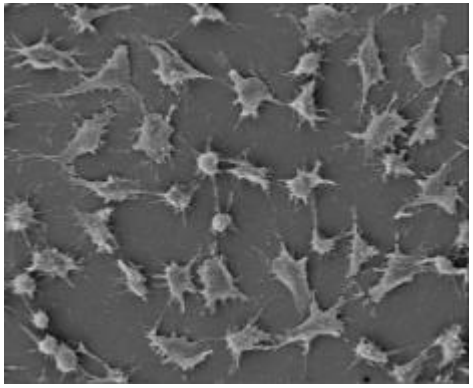
Traction Force



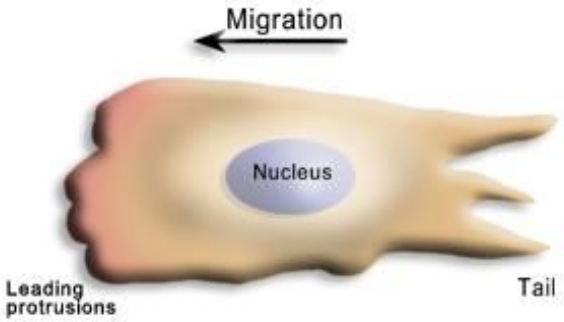
Proliferation



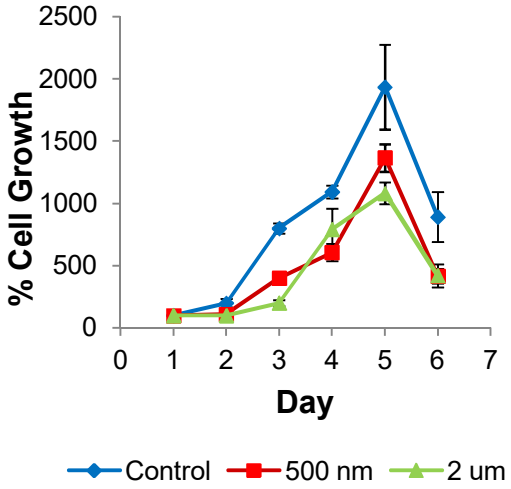
Morphology

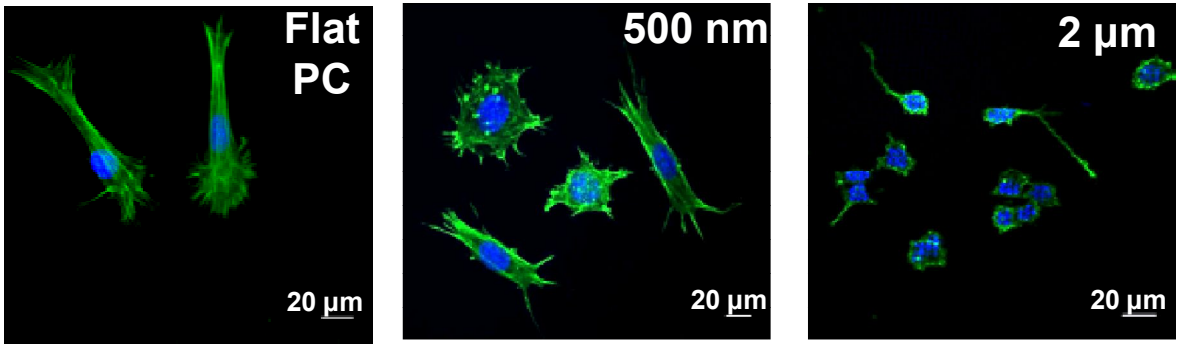


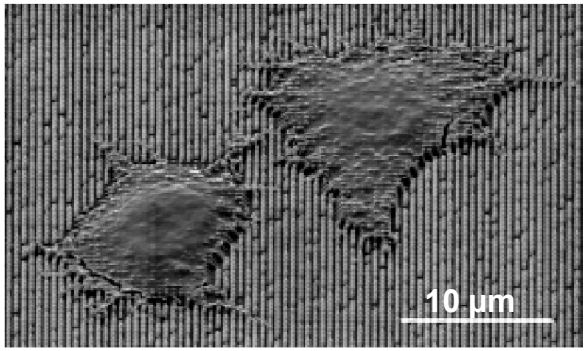
Migration

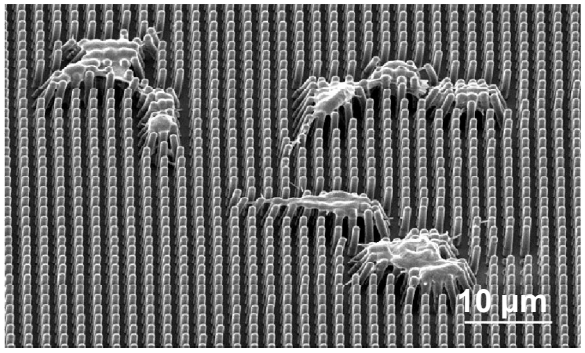


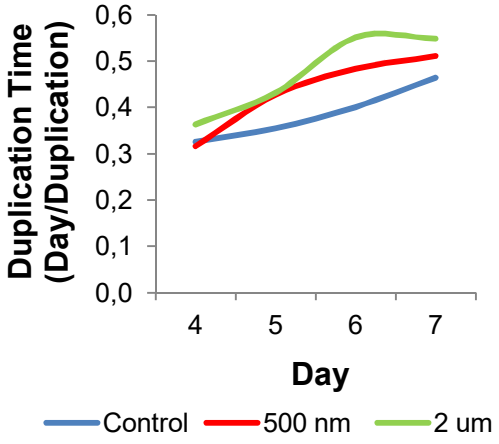
Cell Proliferation & Morphology

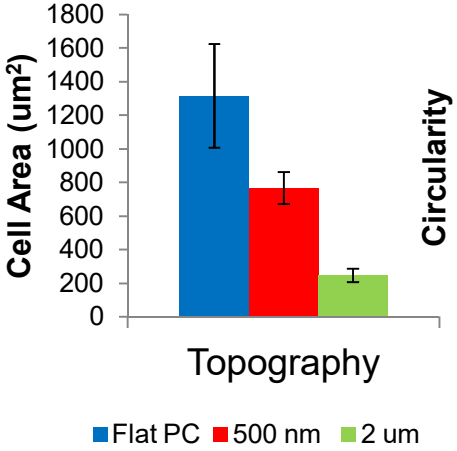


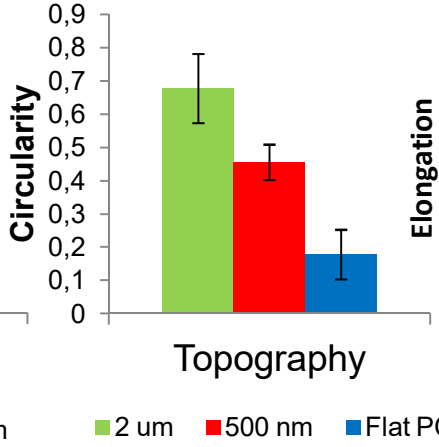


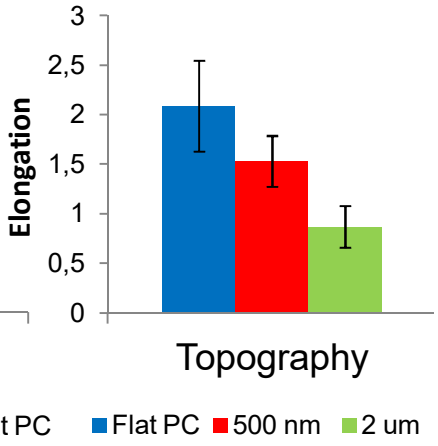






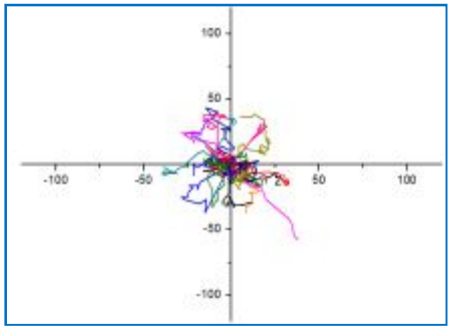


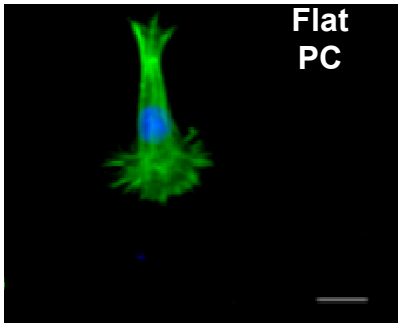


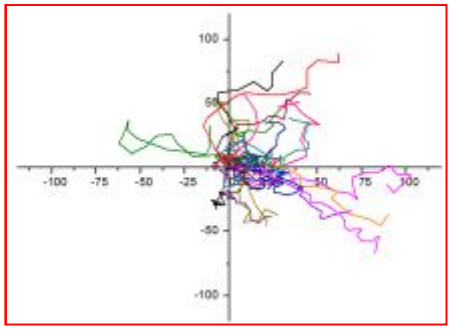


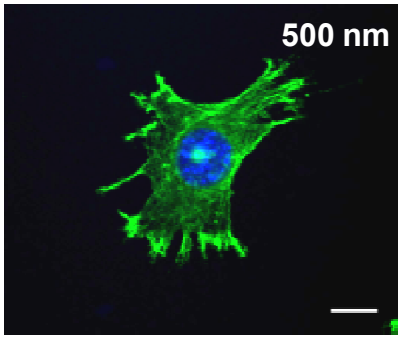
Cell Directional Migration

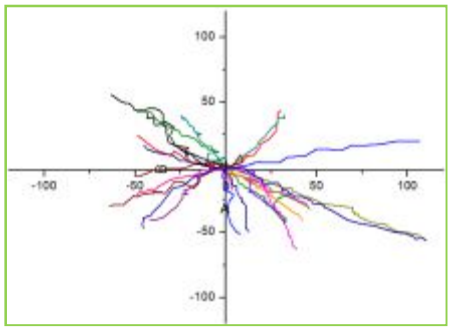
Windrose plots of ell trajectories

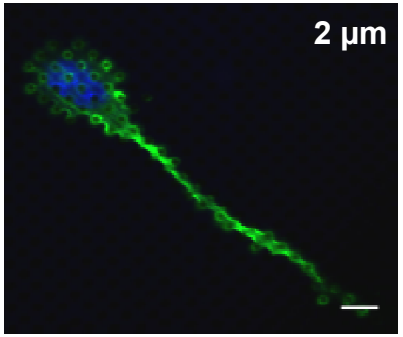


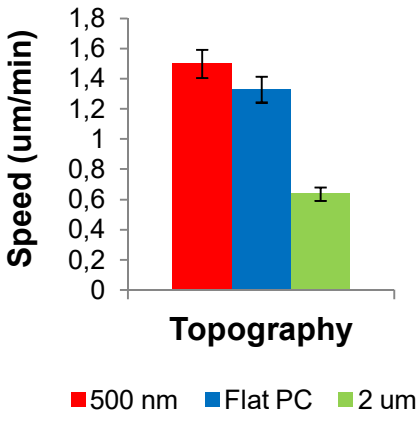


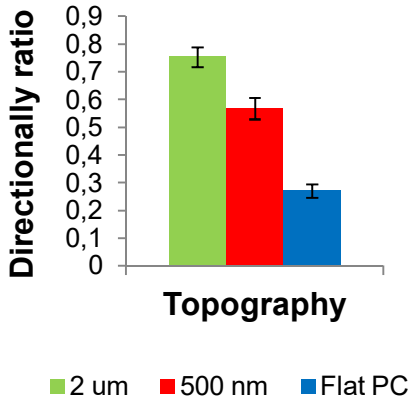


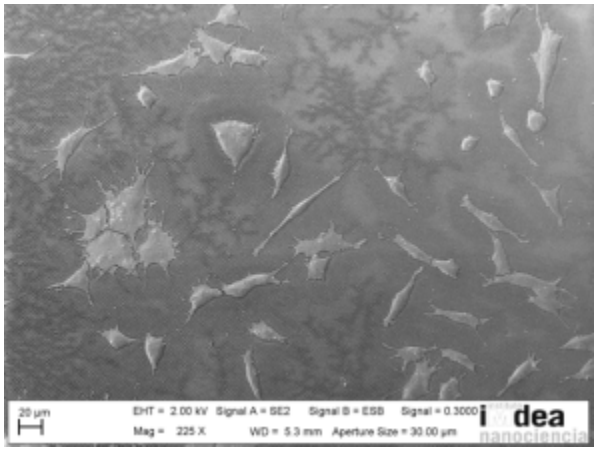




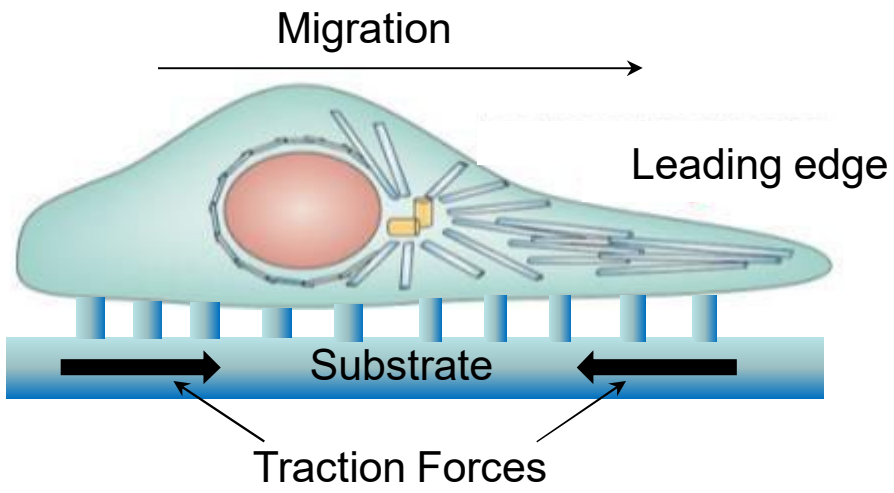








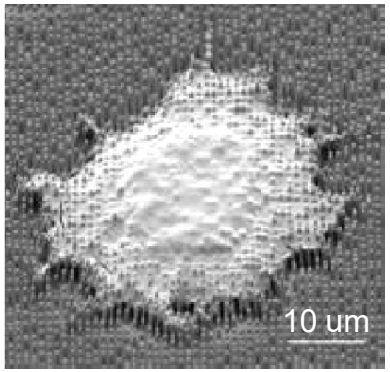
Cell Traction Force



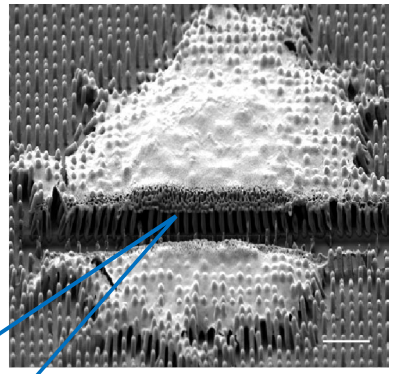
Hooke's Law

$F = k\Delta x$

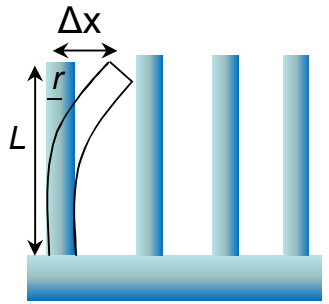
$$k = \frac{3}{4}\pi E \frac{r^4}{l^3}$$

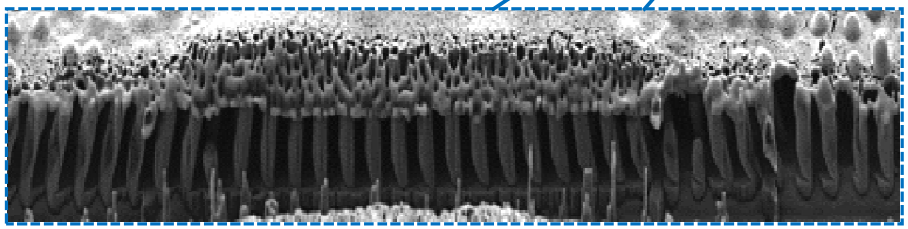


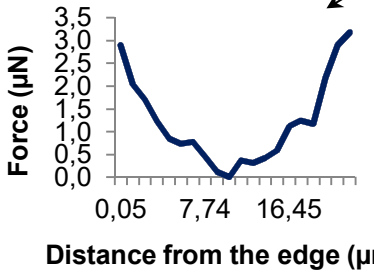
FIB-SEM Visualization

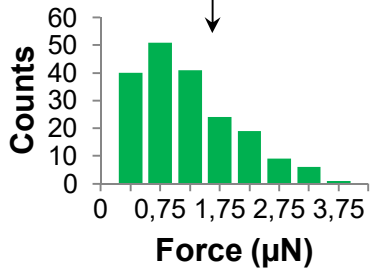


Bending angle measurement



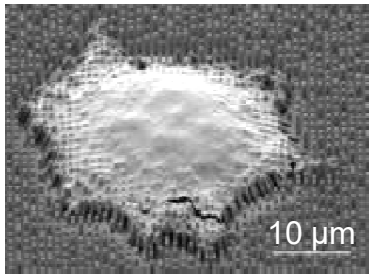




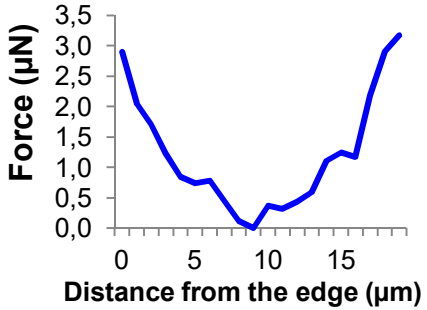


Cell Traction Force

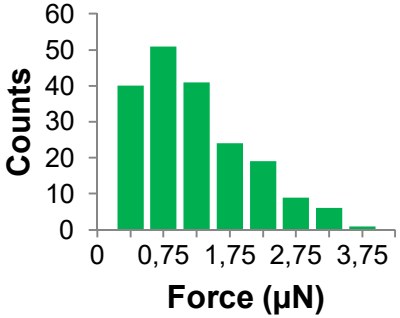
No Migration



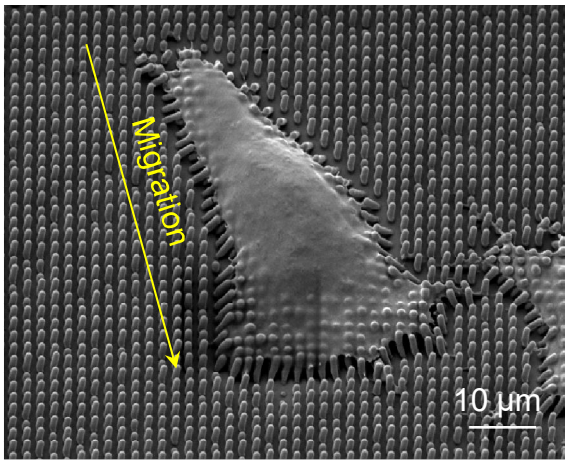
Single cell force profile



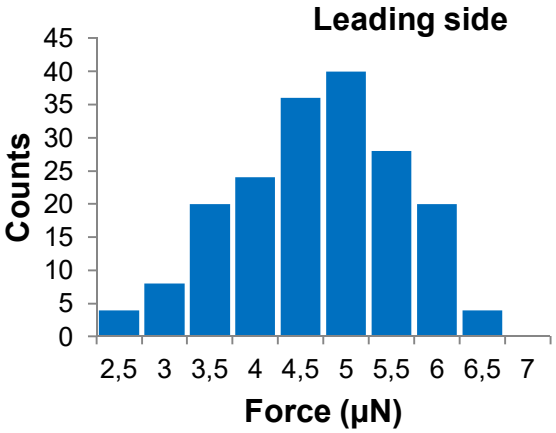
Mean force value



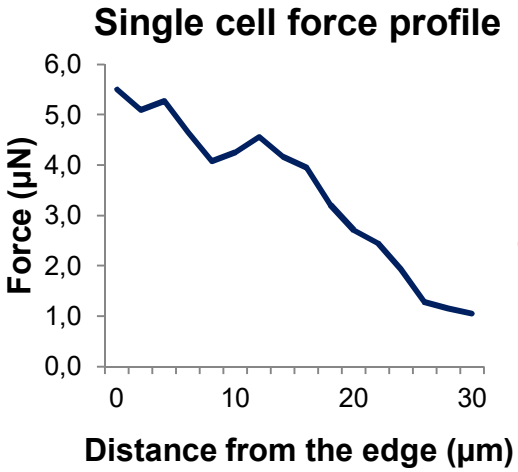
Migration

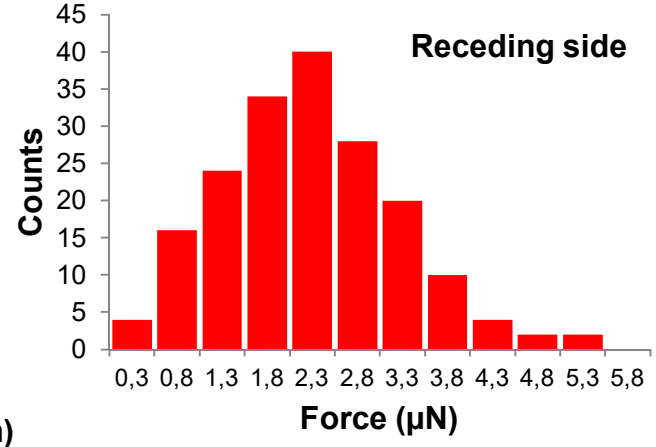


Mean force value



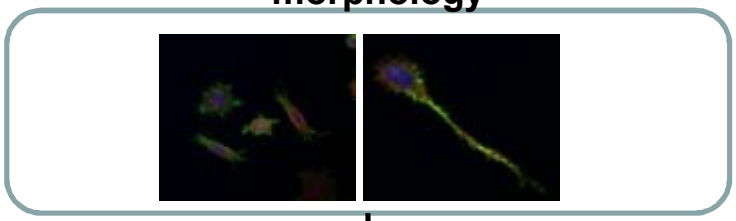
Single cell force profile

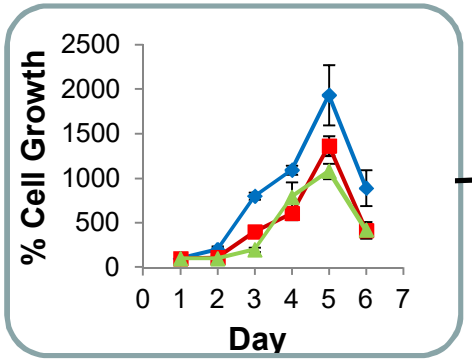




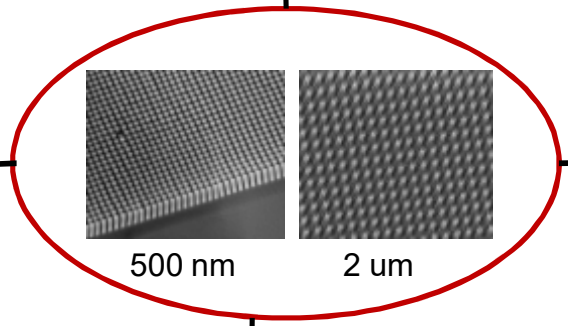
Summary

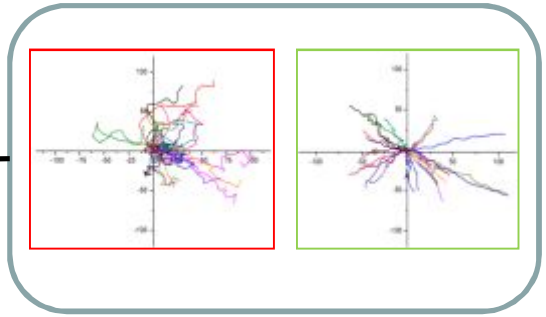
Nano and Microscale determine cell morphology



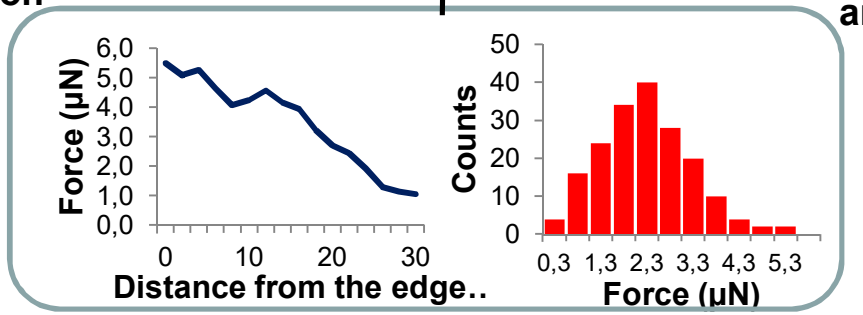


Nano and Microscale reduce cell proliferation





Nanoscale increases mobility
Microscale decreases mobility and induces persistant direction



Microscale increases cell traction forces

Viela, Felipe, et al. "Biomechanical cell regulation by high aspect ratio nanoimprinted pillars." Advanced Functional Materials26.31 (2016): 5599-5609.

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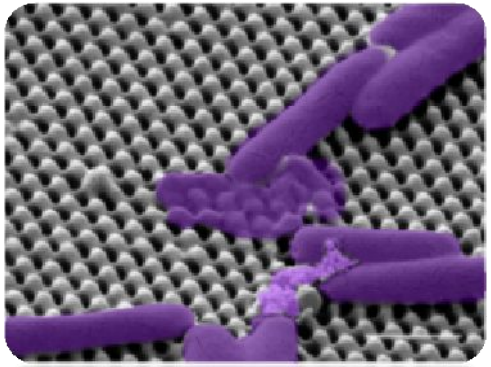
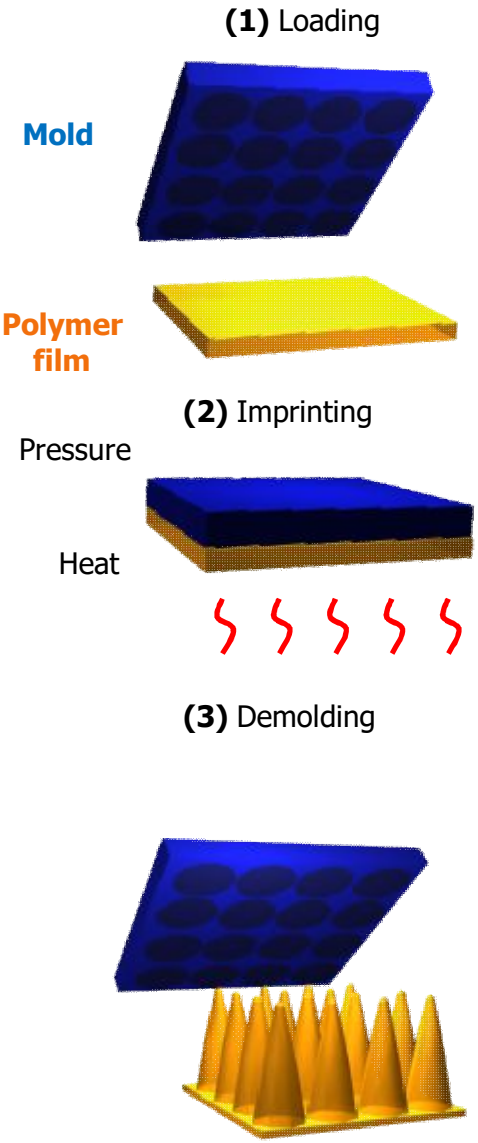
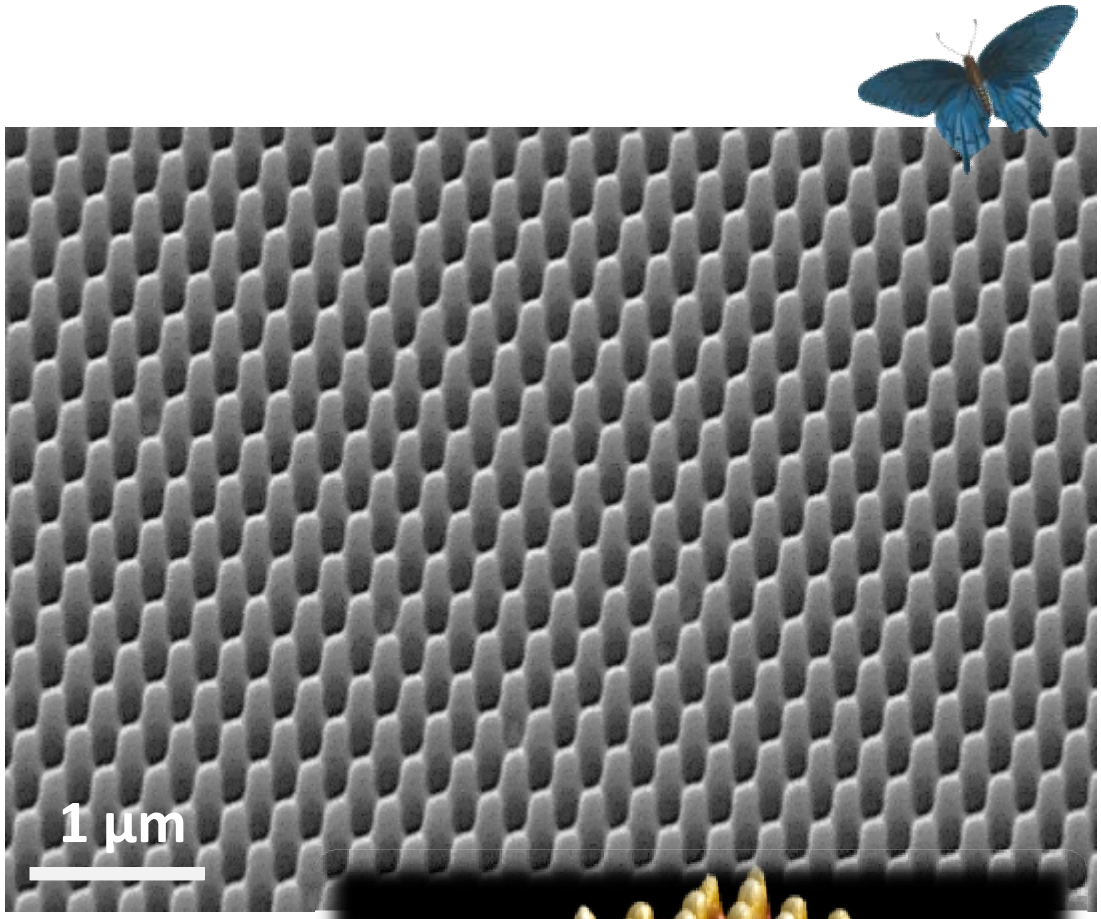
2. Bactericidal Moth Eye Inspired Topography

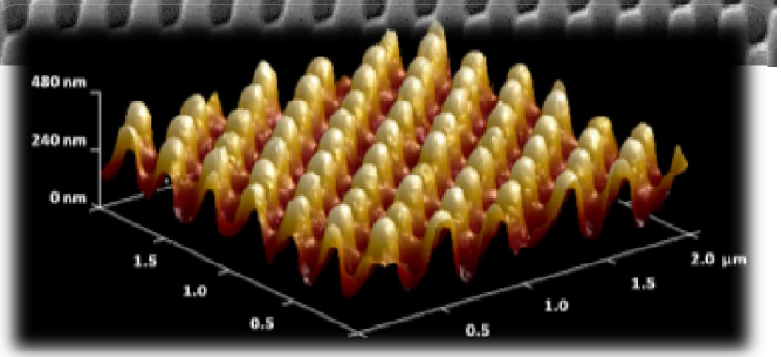


Viela, F, et al. Moth-eye mimetic cytocompatible bactericidal nanotopography: a convergent design. Bioinspiration & Biomimetics, 2018, 13, 026011.

Moth-eye mimetic topography



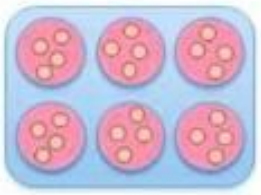




Height: 250 nm
Aspect Ratio: 2.8

EXPERIMENTAL SETUP

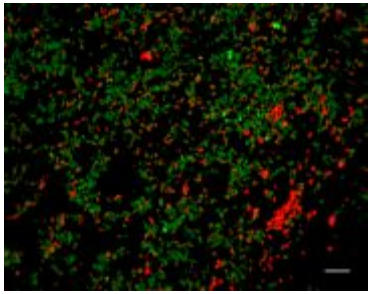
Bacterial/ Cell Supension



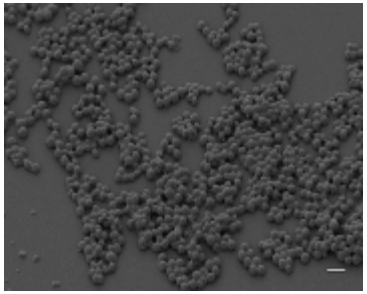
Bacterial/ Cell Culture on moth eye Inspired Topography

Bactericidal Effect

Fluorescence Microscopy

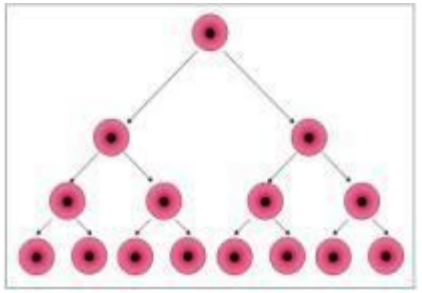


Scaning Electron Microscopy

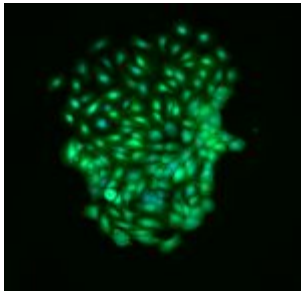


Biocompatibility

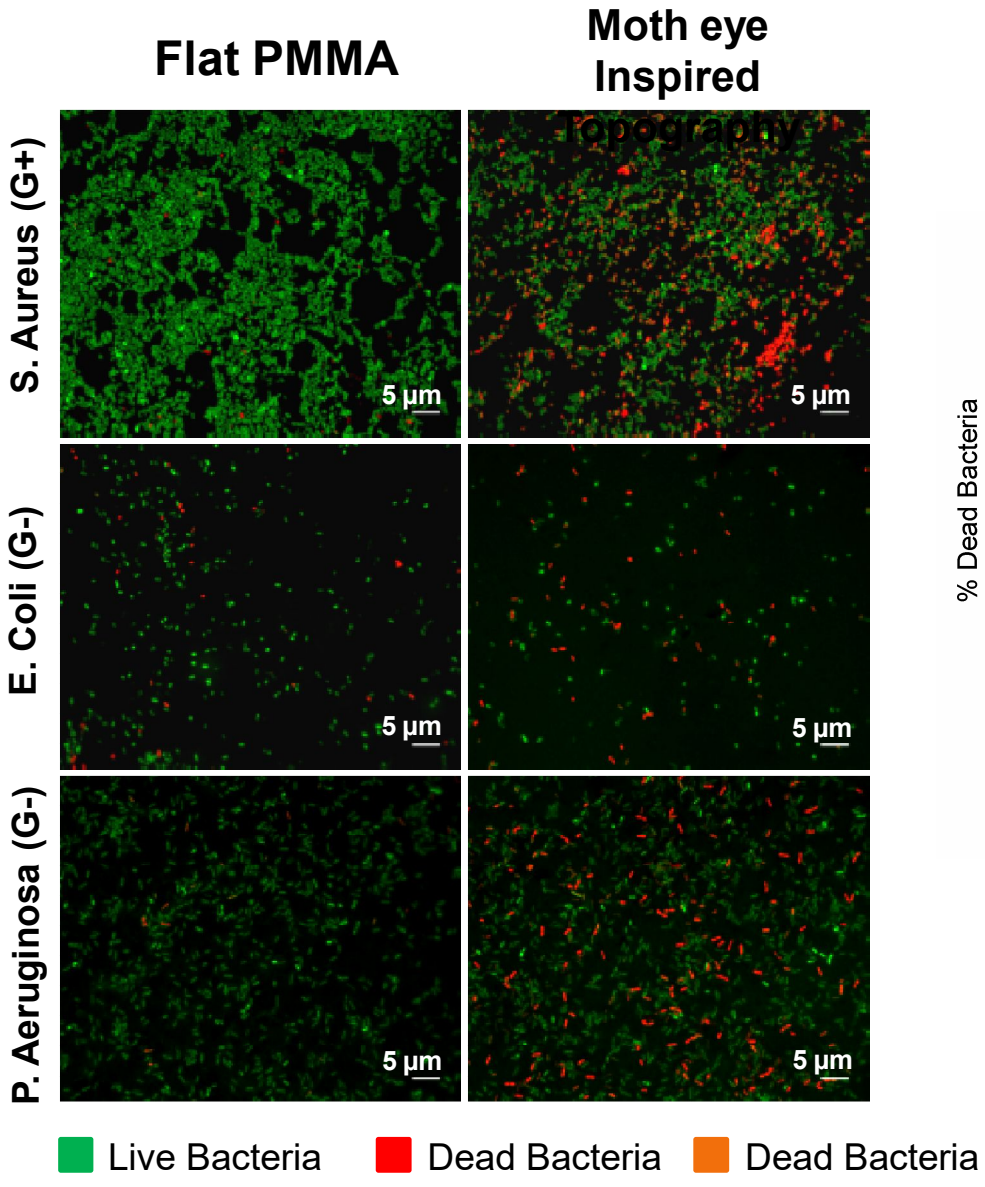
Cell Proliferation

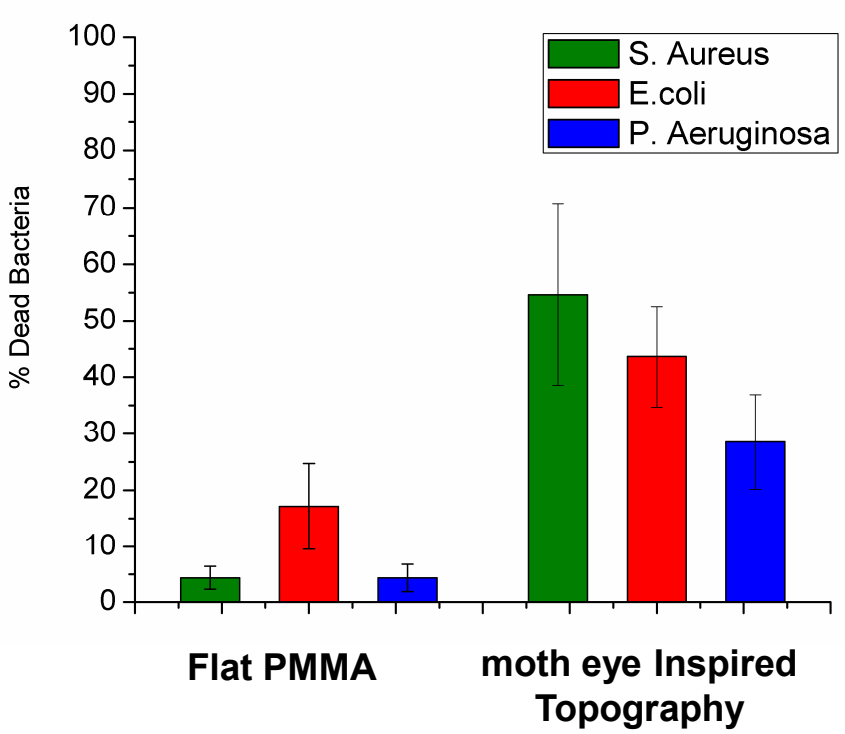


Cell Morphology



Bactericidal Efficacy of Moth Eye Topography





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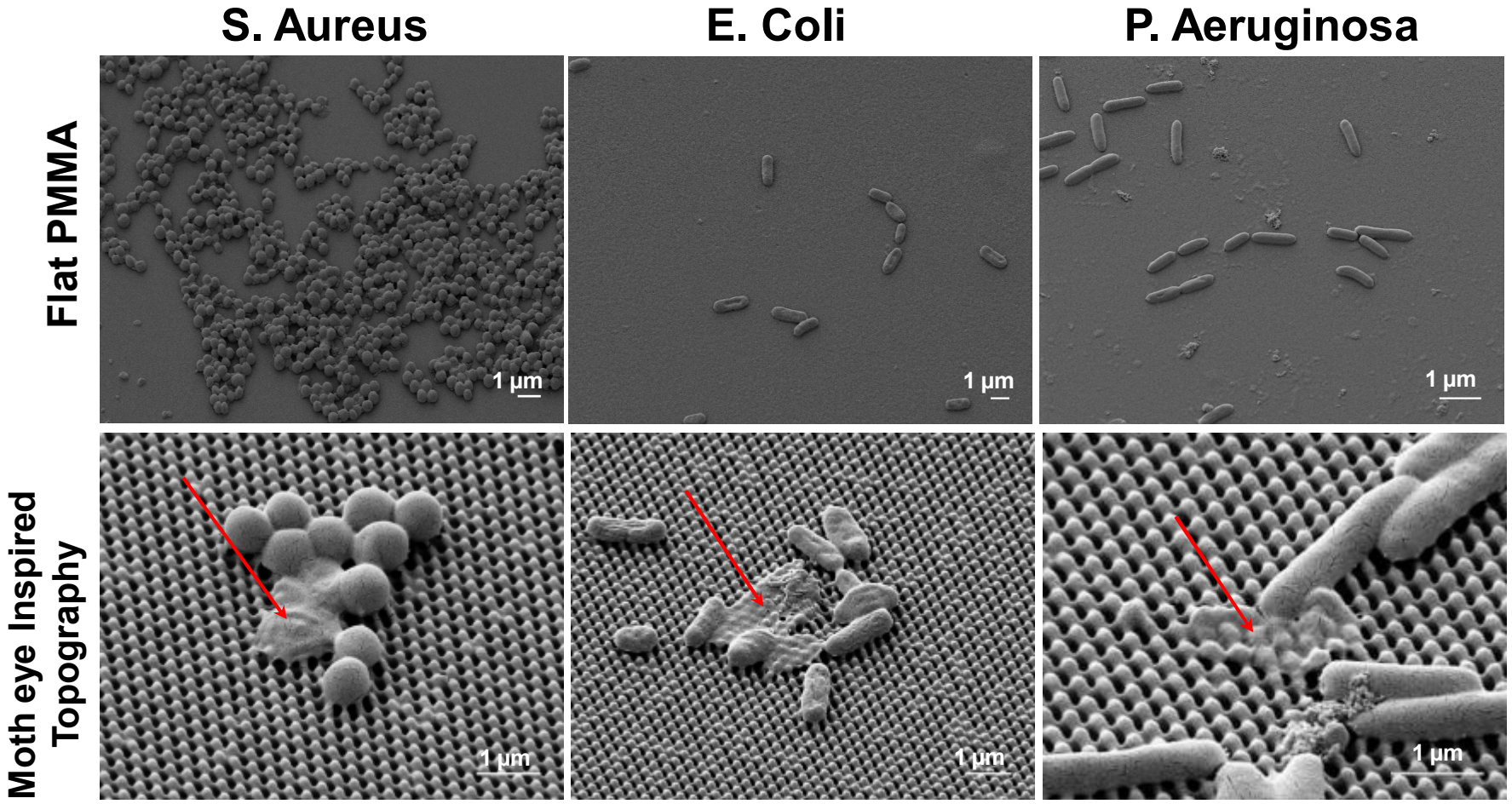
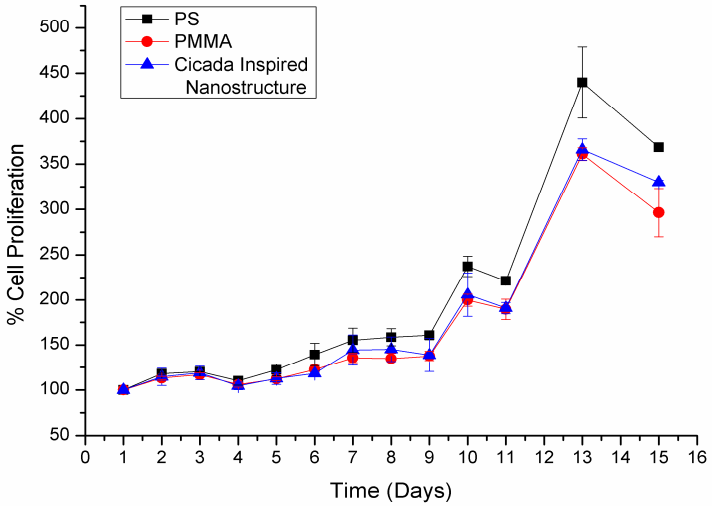
Moth Eye Bactericidal Effect

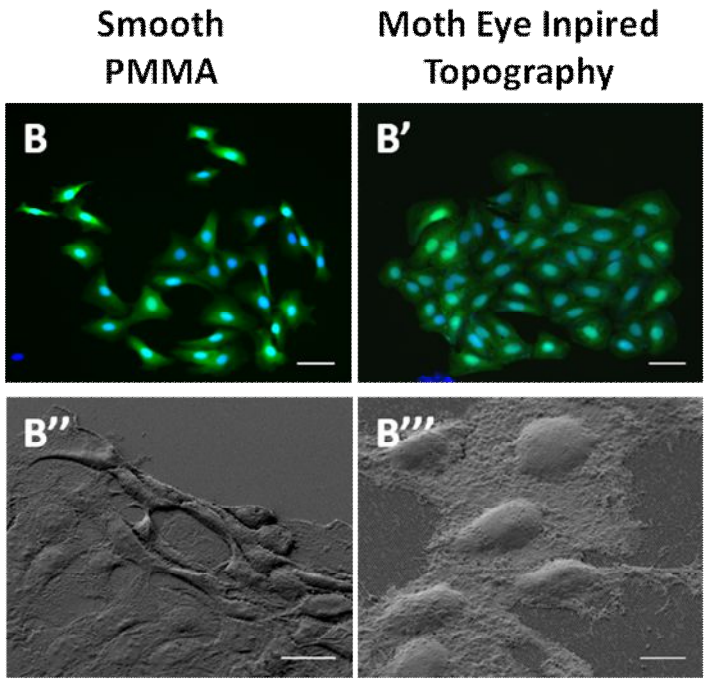


“Mechanical rupture – membrane stretching to optimize adhesion”

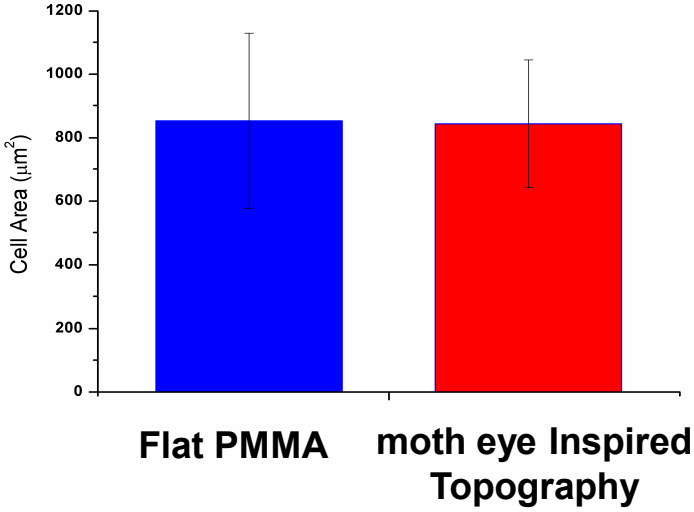
Biocompatibility of Moth Eye Topography

Cell Proliferation- HaCaT cells

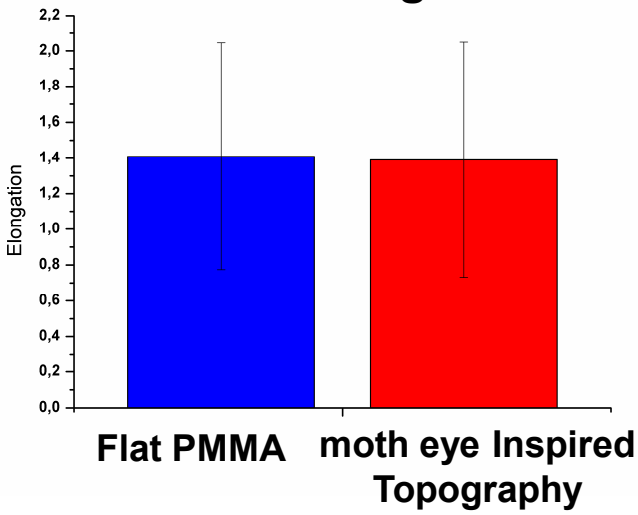




Cell Spreading

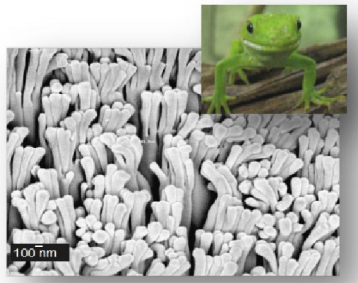


Cell Elongation

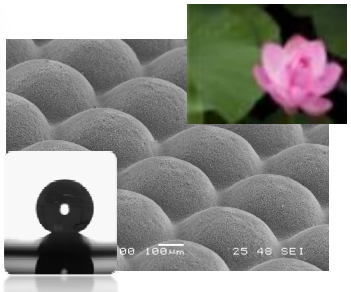


Summary

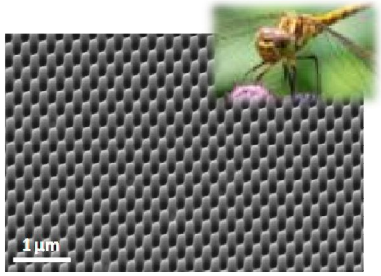
•Polymer micro/nano imprinting



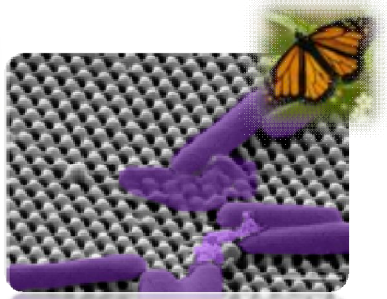
Gecko like dry adhesives



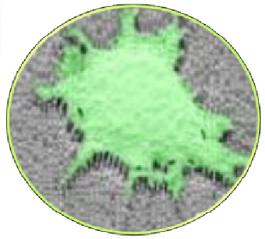
Superhydrophobic,self cleaning



Anti-reflective surfaces



Bactericidal surfaces



Cell substrates

❖Patterning is a valuable tool to exploit the functionality of materials into new applications . Design is key to achieve specific functions.

❖Structuring imparts function by physical means regardless the chemical nature.

❖ Patterning -using replication (NIT) is a suitable methodology for sustainable product development / nanomanufacturing

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