

nanoscience and nanotechnology: small is different



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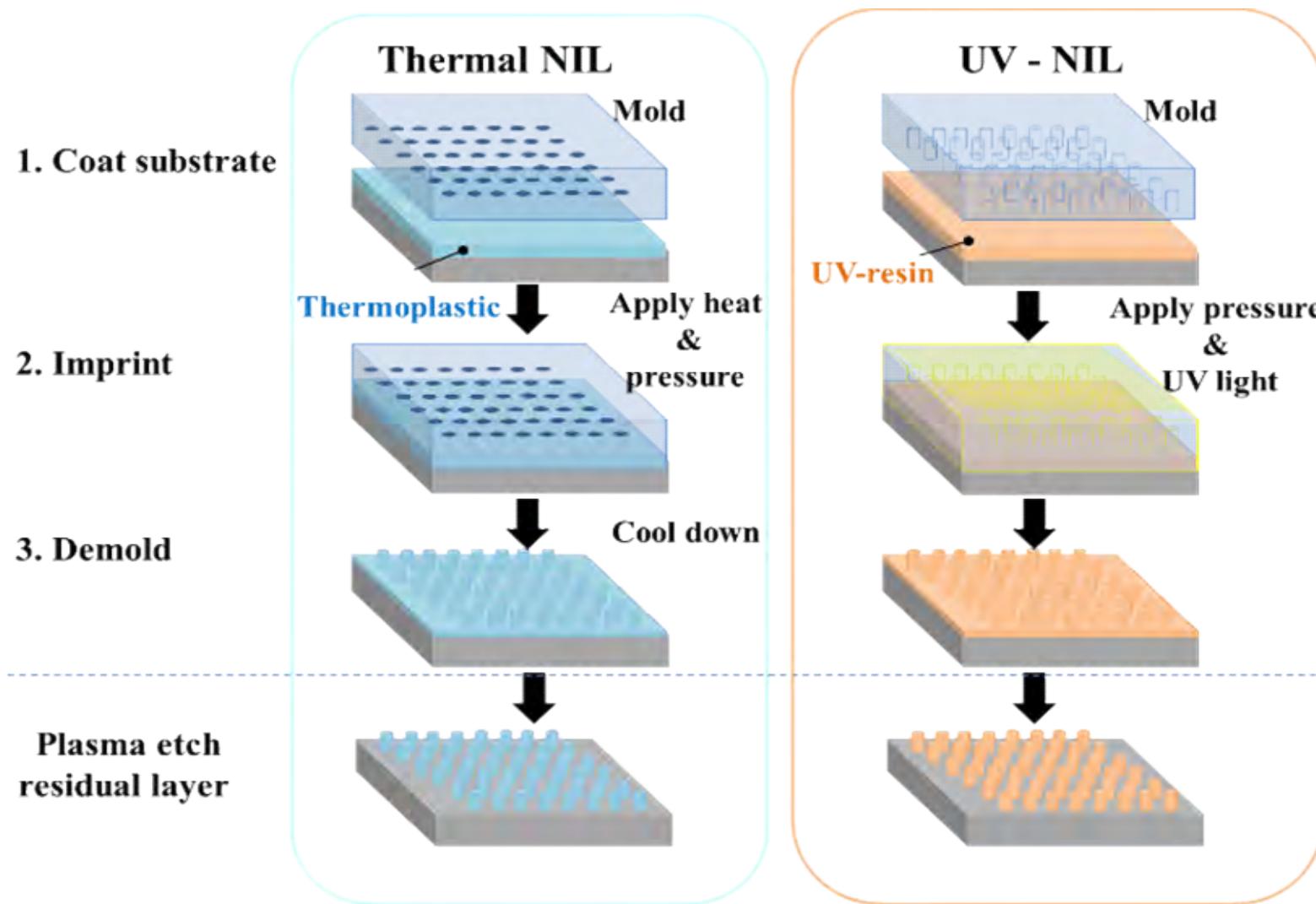
# Nanoimprint lithography and hybrid processes *to produce complex nanostructures*

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# Nano Imprint Lithography - NIL

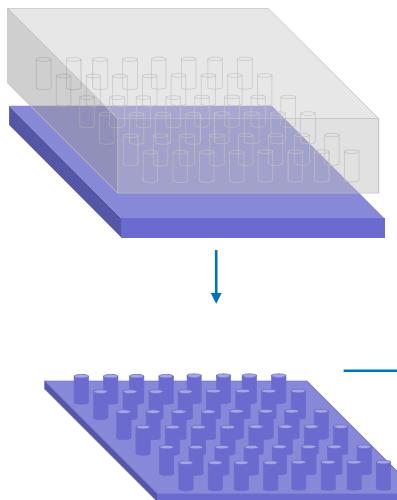
**A replication process :** Pattern transfer by mechanical deformation of a flowing resist material



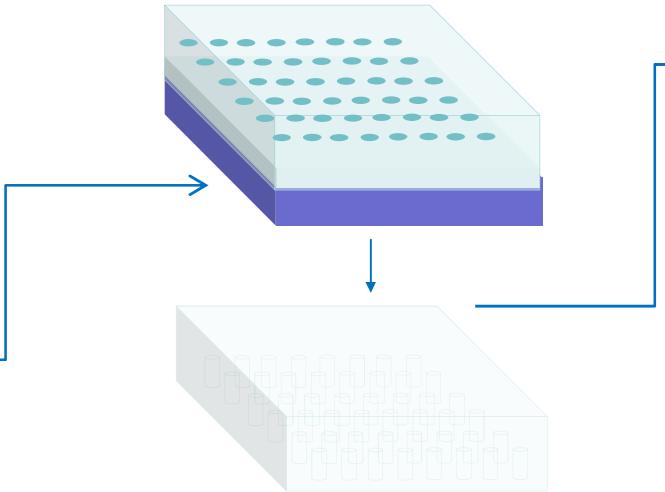
# Soft –NIL

## Thermal-NIL

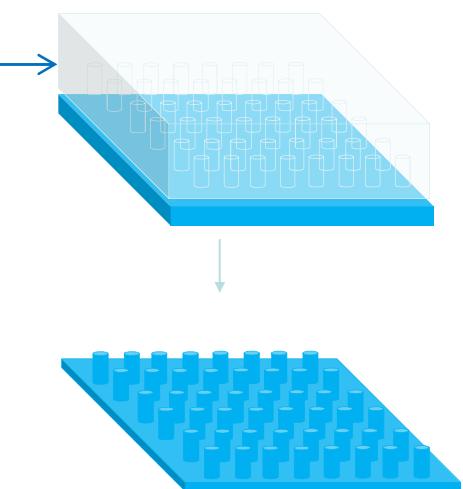
### Hard Mold



## Soft lithography



## Soft NIL



### IPS

Intermediate polymer stamp

### Soft Mold

**PDMS**  
**PFPE**

### Patterned polymer

#### Soft –NIL:

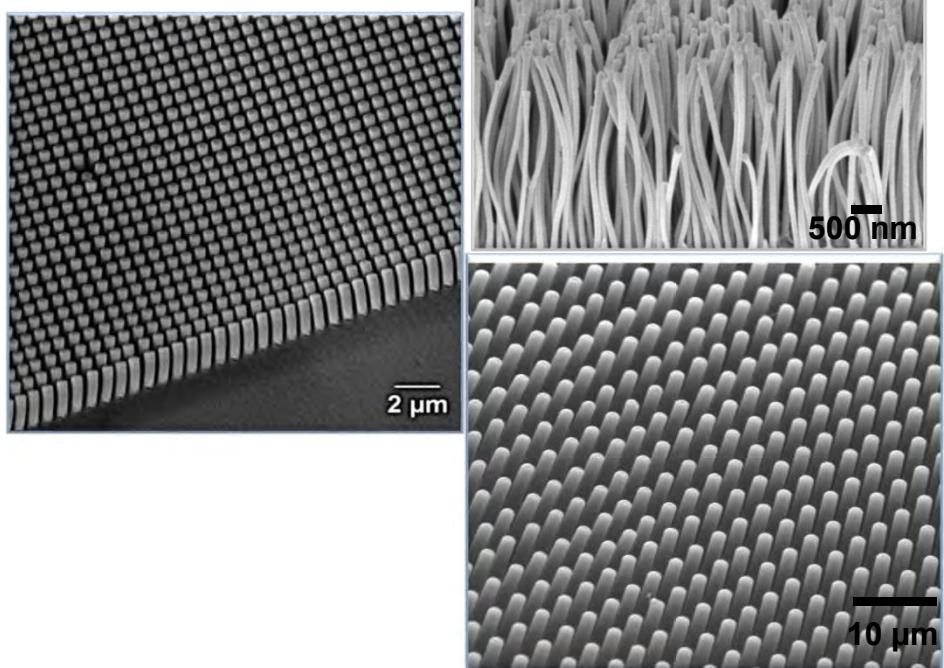
- Sequential action of peeling the mold from substrate
- High gas permeability
- Conformal contact to substrate
- Low surface energy

PDMS: Polydimetilsiloxane

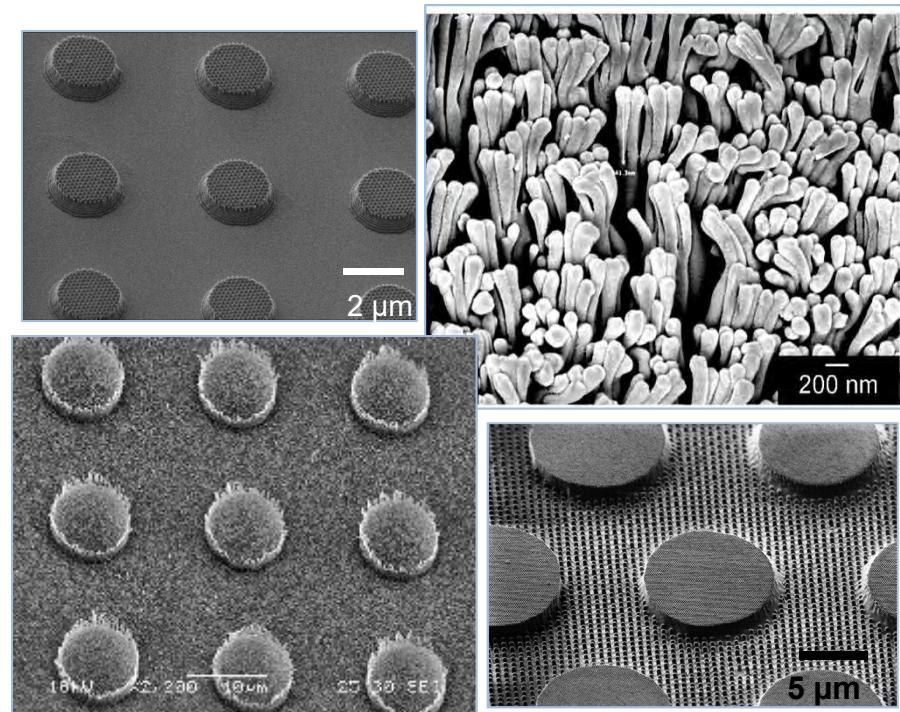
PFPE: Polyurethane based on perfluoropolyether

# Key Technological Expertise

## High Aspect Ratio Topographies



## Complex Hierarchical Topographies

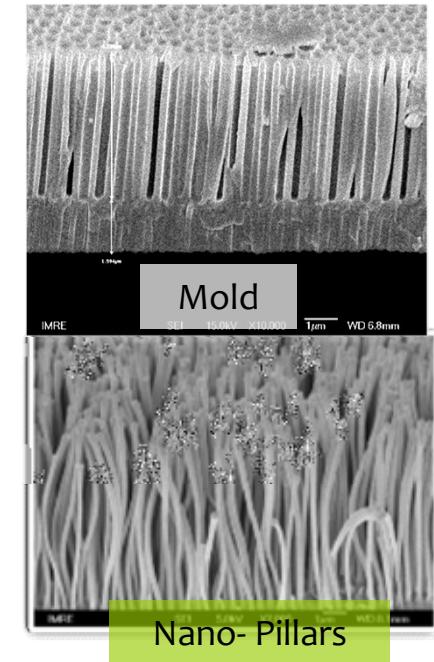
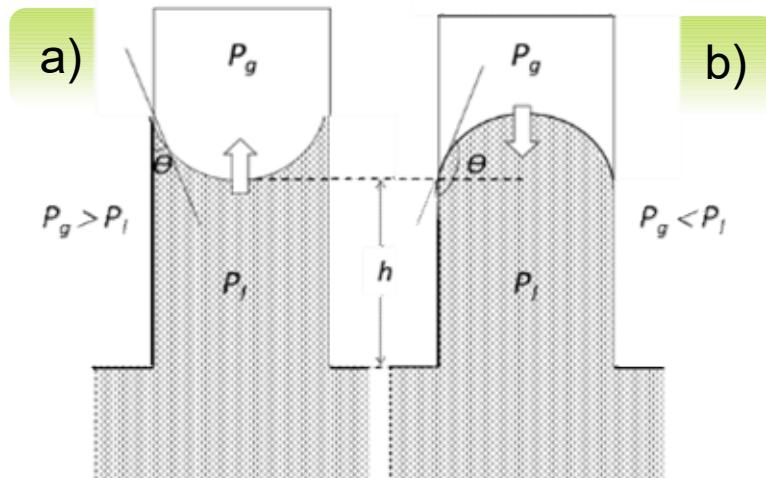


# High Aspect Ratio NIL

Laplace pressure - Capillary forces



$$\Delta P_c = P_g - P_l = \frac{2 \gamma \cos\theta}{r}$$



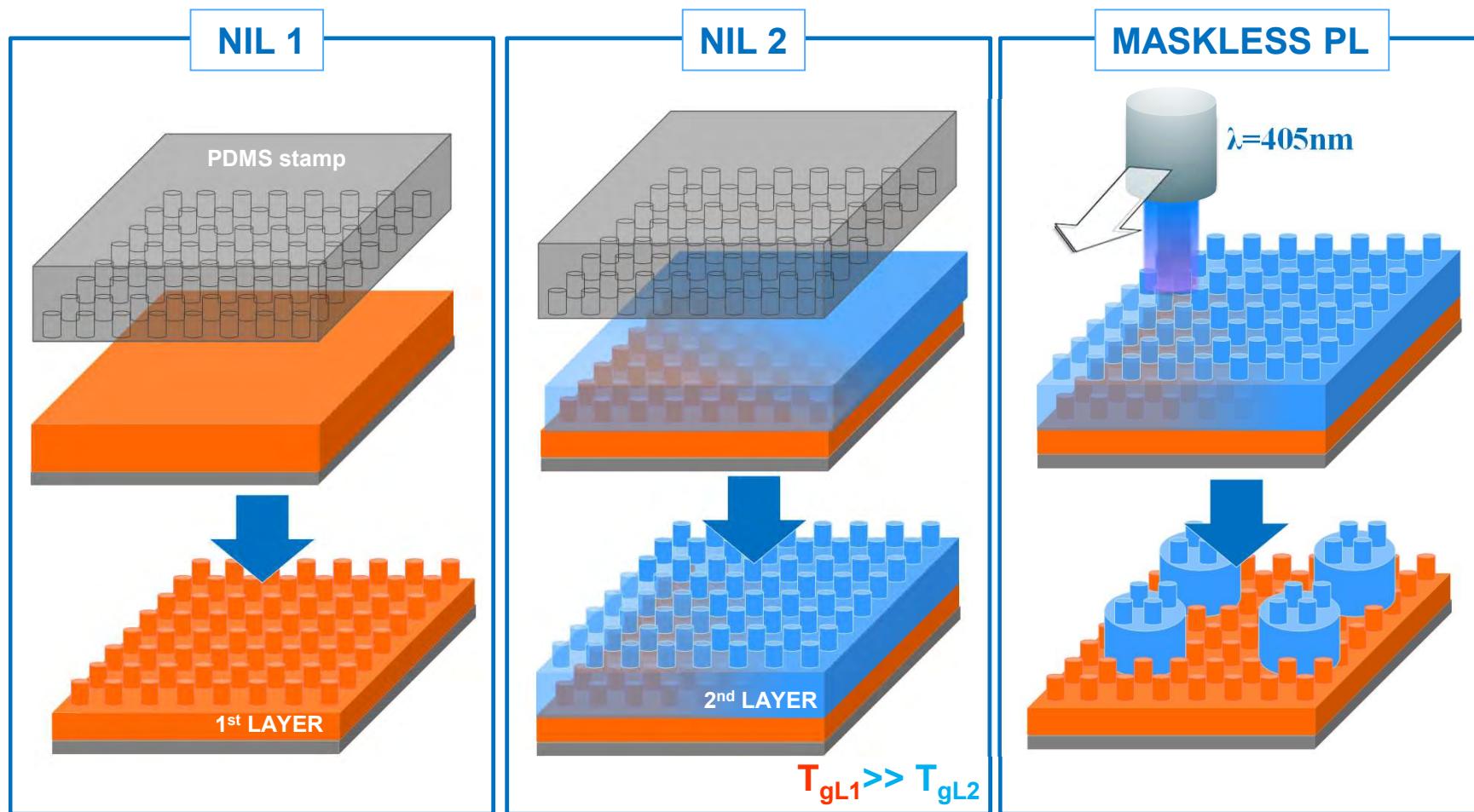
- a) polymer wets the capillary ( $\theta < 90^\circ$ )
- b) polymer does not wet the capillary ( $\theta > 90^\circ$ )

Lucas-Washburn equation:

$$\frac{dh}{dt} = \frac{r \gamma \cos\theta}{4\eta h} \quad t = \frac{2 \eta h^2}{r \gamma \cos\theta}$$

$\gamma_p$  - surface tension of the viscous polymer  
 $\eta$  - the viscosity  
 $\theta$  - the solid-liquid contact angle  
 $r$  - the capillary radius.

# Hybrid fabrication process: NIL + PL

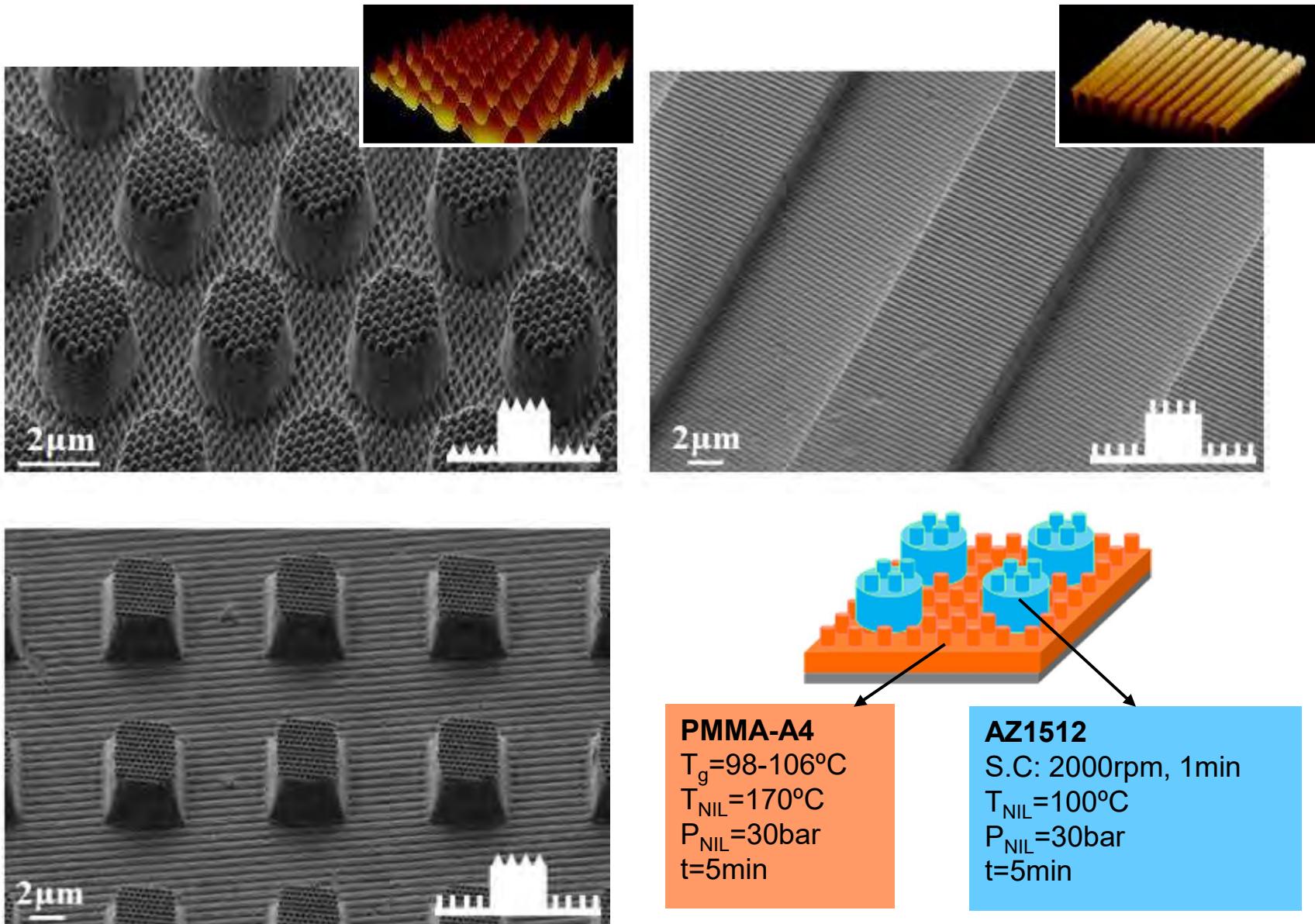


NIL: Nanoimprint Lithography ; PL: Photolithography



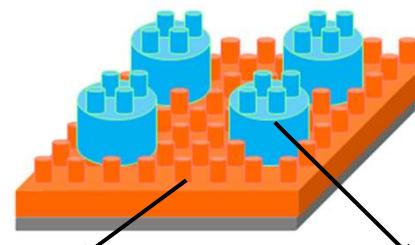
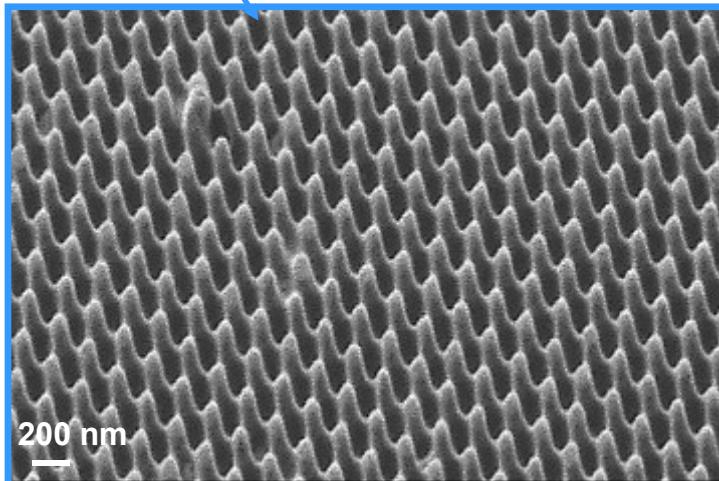
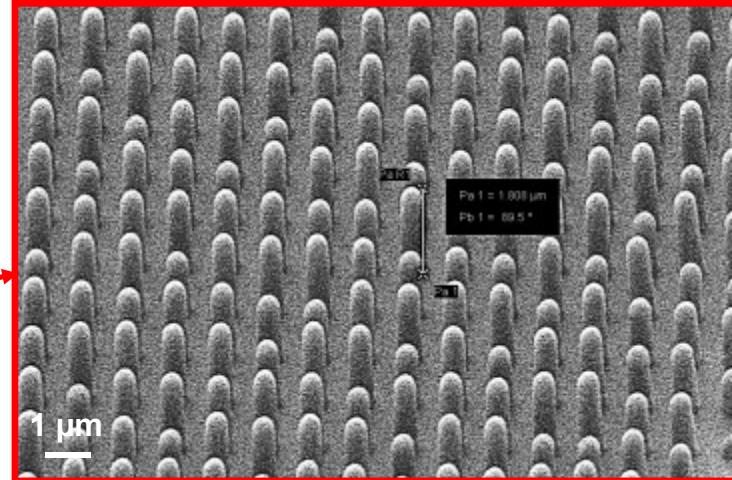
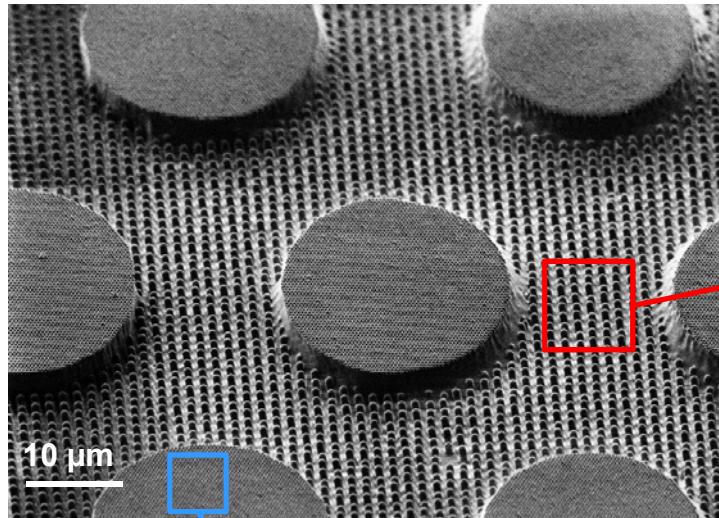
# Micro & Nano Hierarchical Structures

## 1<sup>ST</sup> LAYER: THERMOPLASTIC



# Micro & Nano Hierarchical Structures

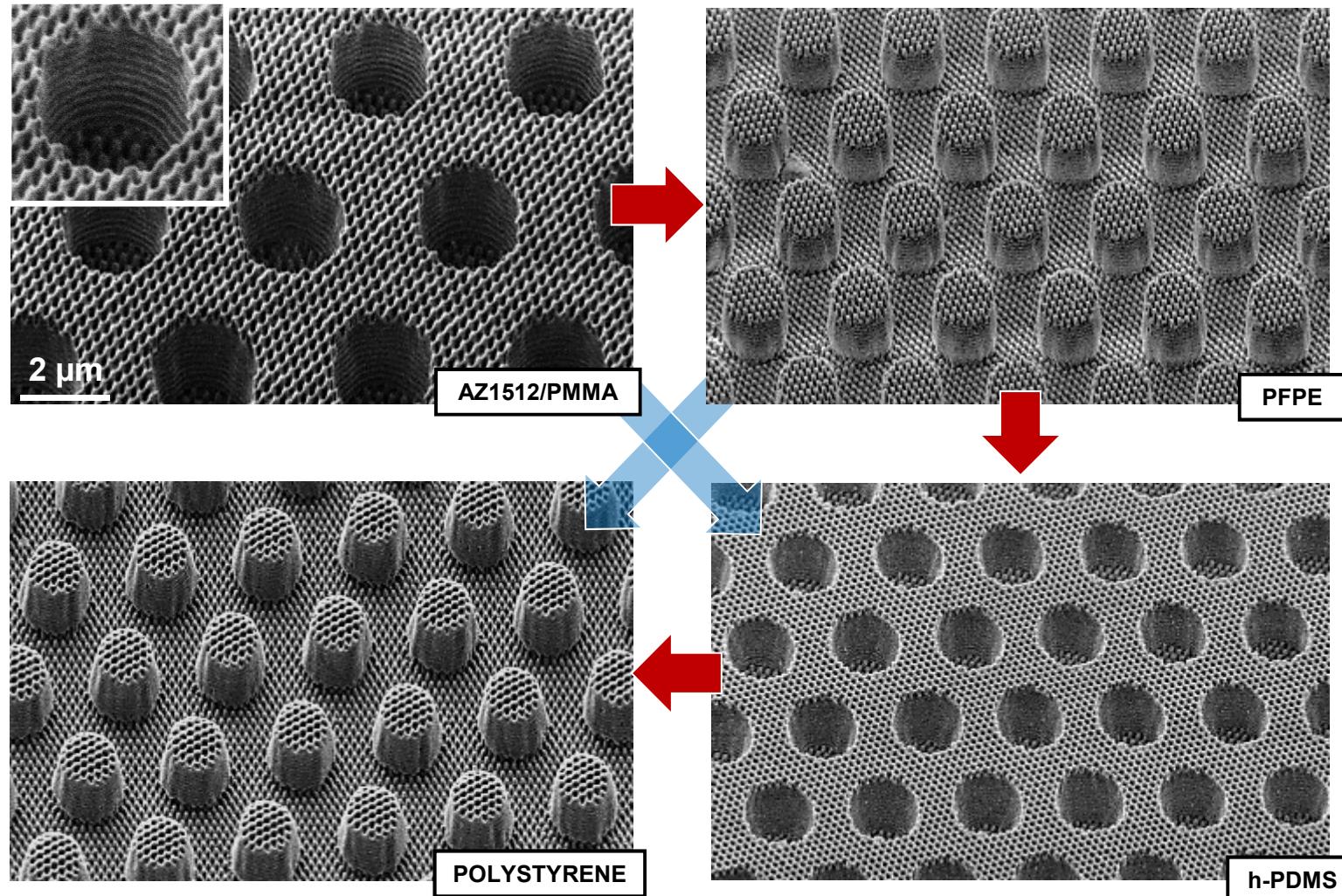
## 1<sup>ST</sup> LAYER: THERMOSET



**EpoTek**  
 $T_{\text{UV-NIL}}=60^\circ\text{C}$   
 $P_{\text{NIL}}=30\text{bar}$   
 $t=5\text{min}$

**AZ1512**  
S.C: 2000rpm, 1min  
 $T_{\text{NIL}}=100^\circ\text{C}$   
 $P_{\text{NIL}}=30\text{bar}$   
 $t=5\text{min}$

# Soft-NIL - Polymer replication

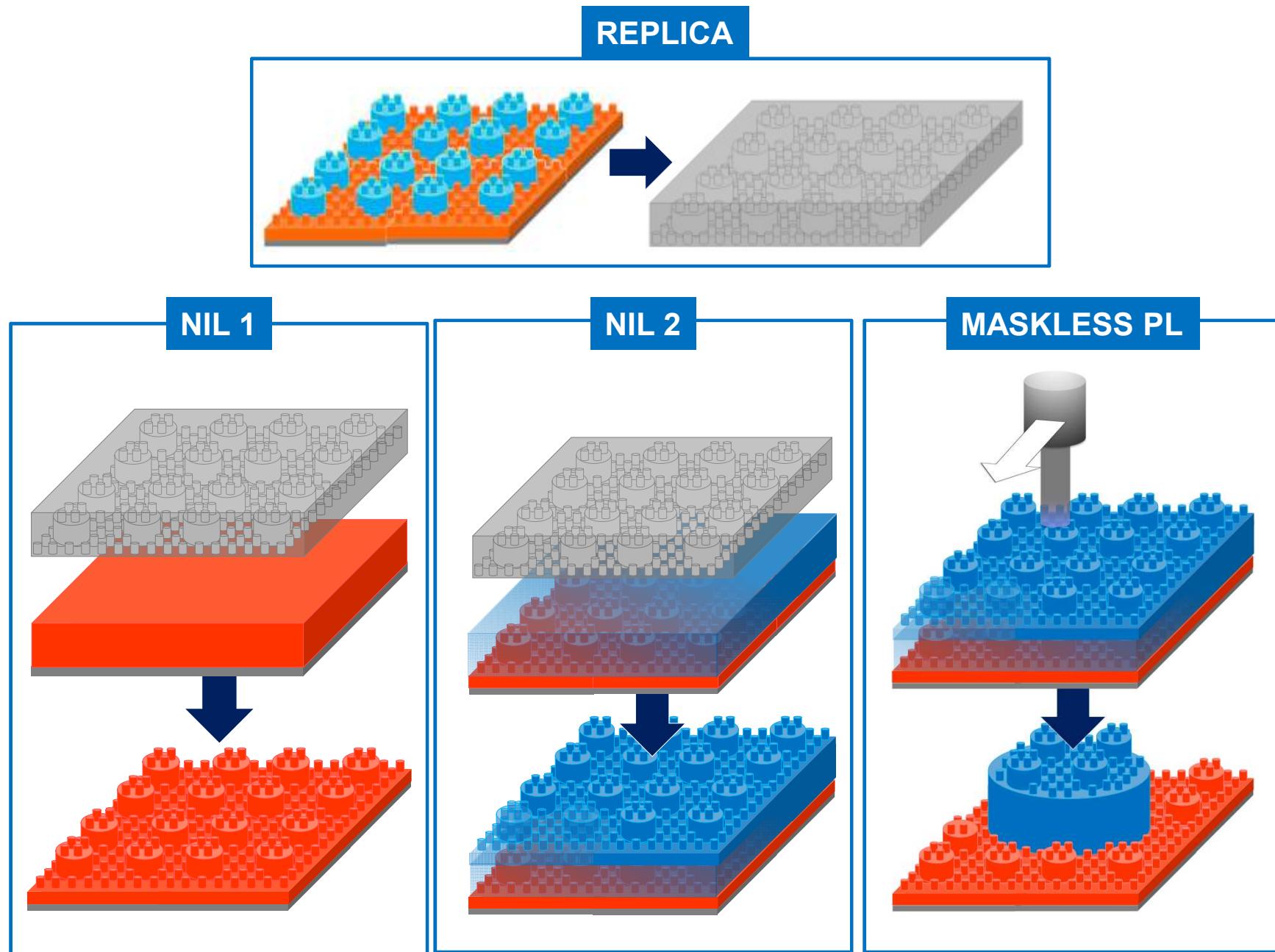


PFPE - Perfluoropolyether

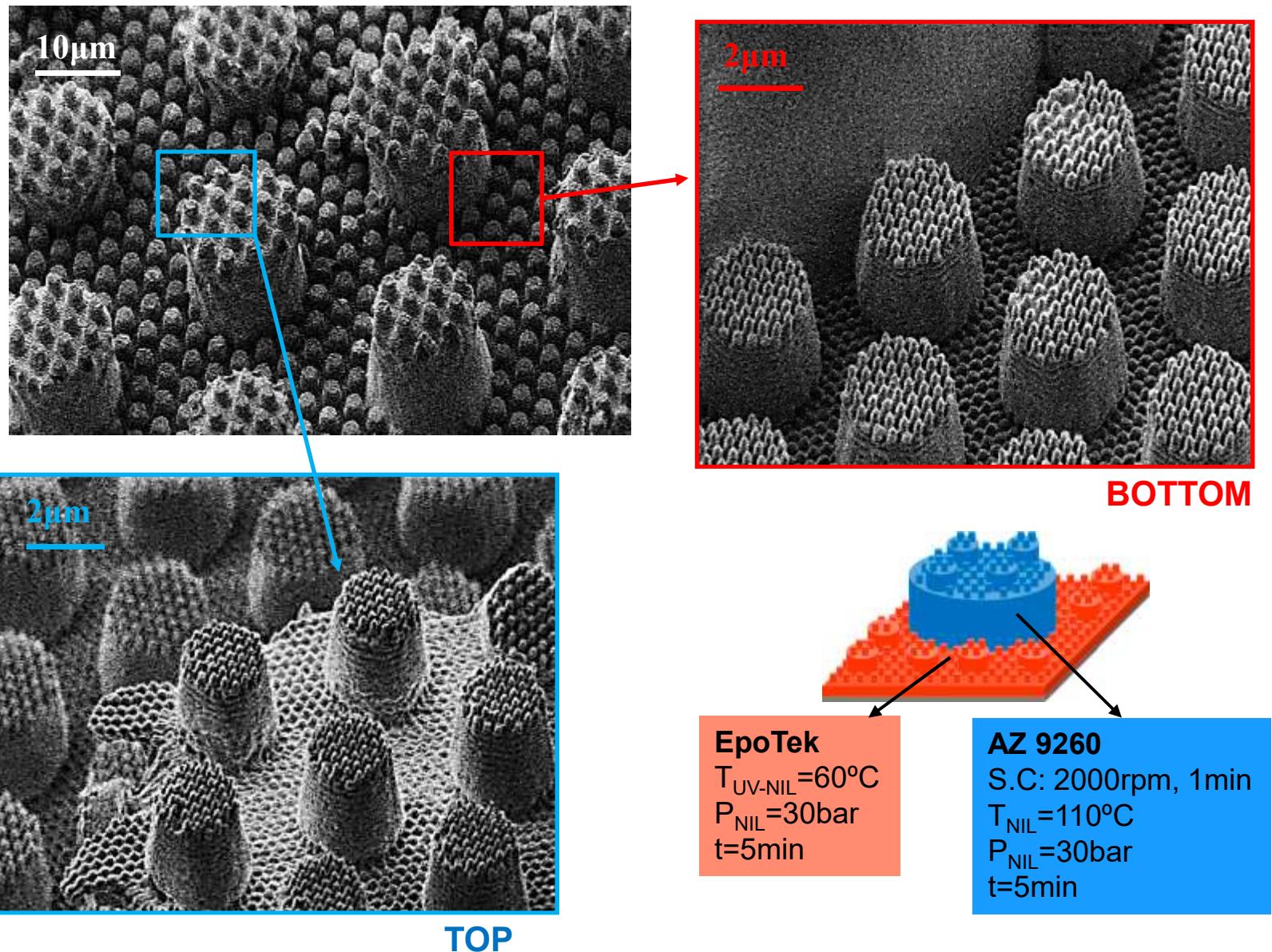
PMMA - Poly(methyl methacrylate)

PDMS - Polydimethylsiloxane

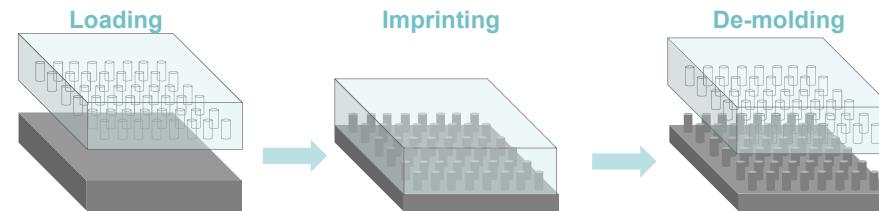
# Multilevel Hierarchical Structures



# Multilevel Hierarchical Structures



# Nanoimprint Lithography (NIL) Tools

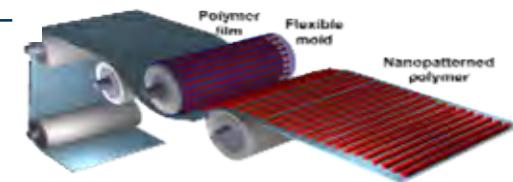


3" wafers - UV & Thermal NIL  
Thermosets & thermoplastic materials

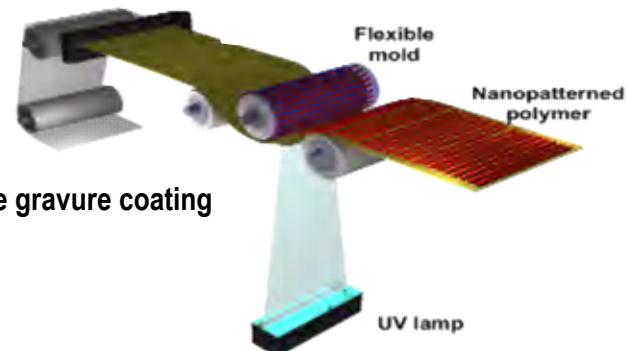
Obducat Eitre® E3



Thermal -NIL



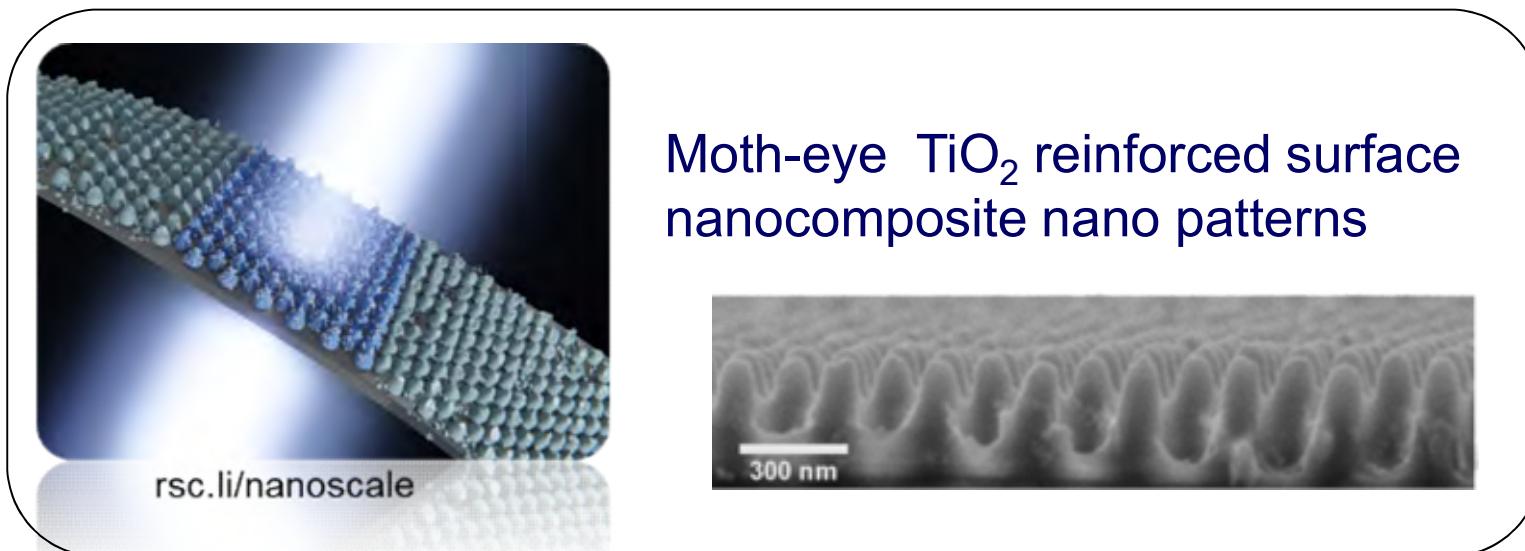
UV-NIL



Reverse gravure coating

Roll to Roll NIL - Pilot facility for scale-up processing (5 m/min)

# Moth-eye biomimetic anti-reflective surfaces



Nanoscale

PAPER

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**Single-imprint moth-eye anti-reflective and self-cleaning film with enhanced resistance†**

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José R. Castro Smirnov,<sup>2</sup> Felipe Viela,<sup>1</sup>\* Miguel A. Monclús,<sup>1</sup>\*  
Manuel R. Osorio,<sup>1</sup>\* Jon M. Molina-Aldareguía,<sup>1</sup>\* and Isabel Rodríguez,<sup>1</sup>\*\*

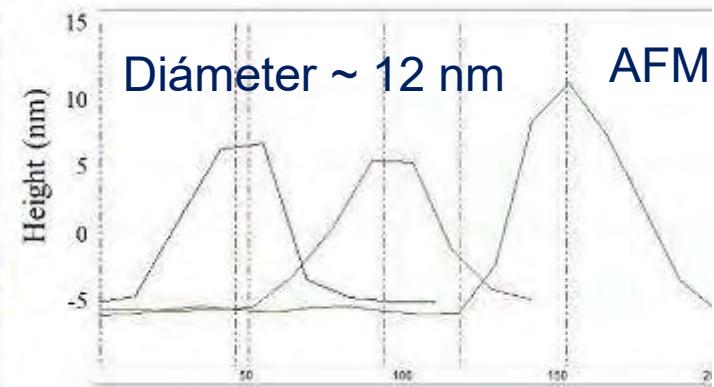
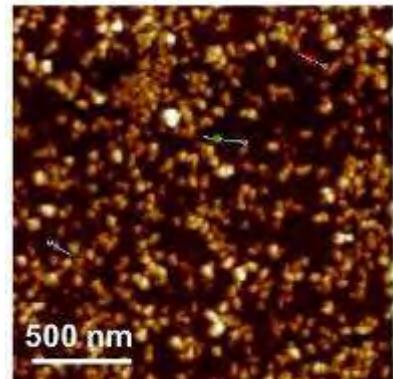
# TiO<sub>2</sub> Surface Nanocomposite

## Preparation of polymer nanocomposite

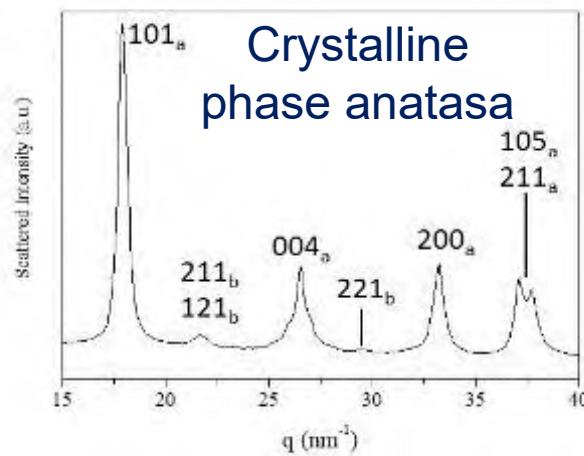
TiO<sub>2</sub> nanoparticles: Hydrothermal synthesis



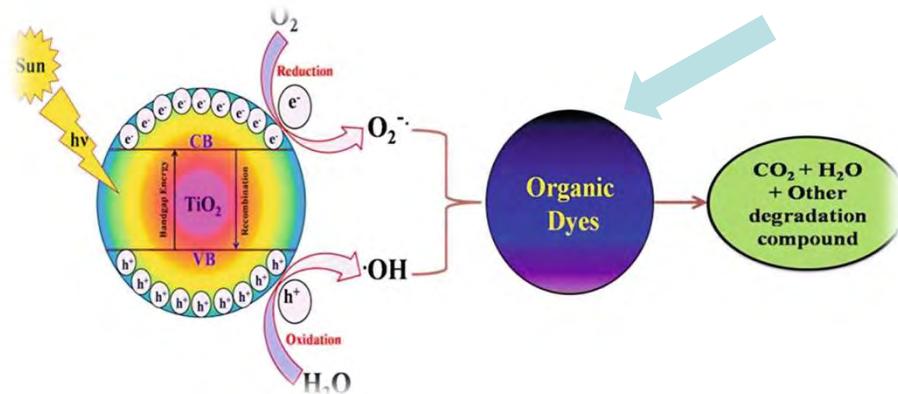
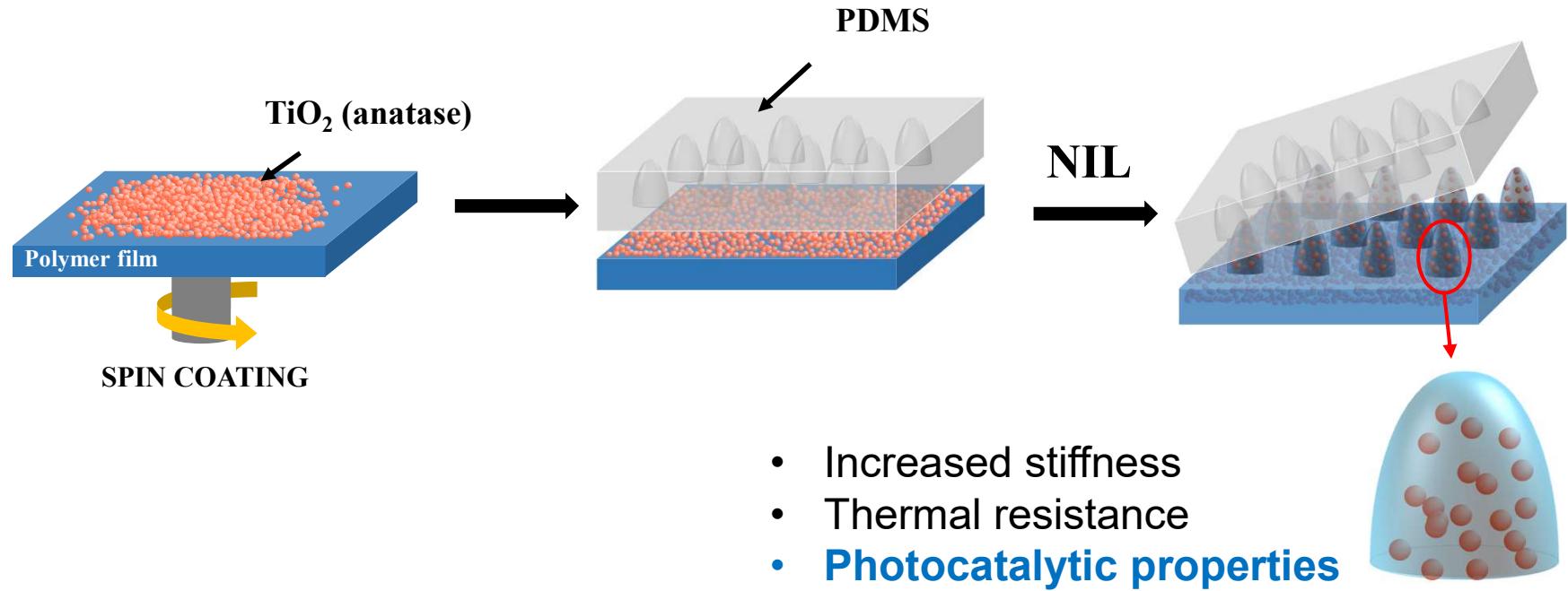
Coloidal suspensión



WAXS

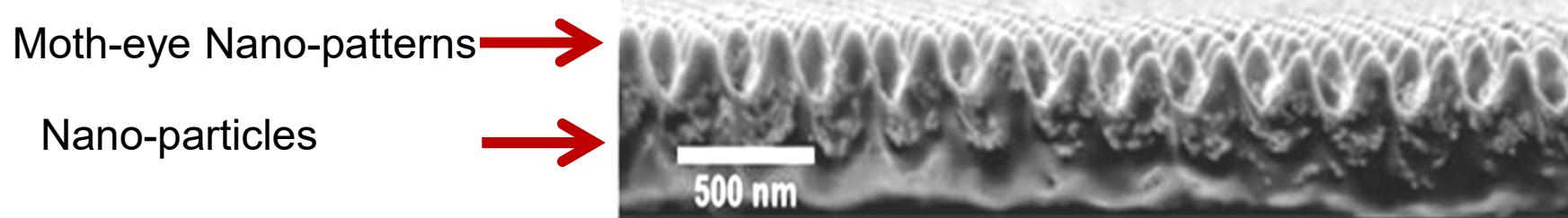
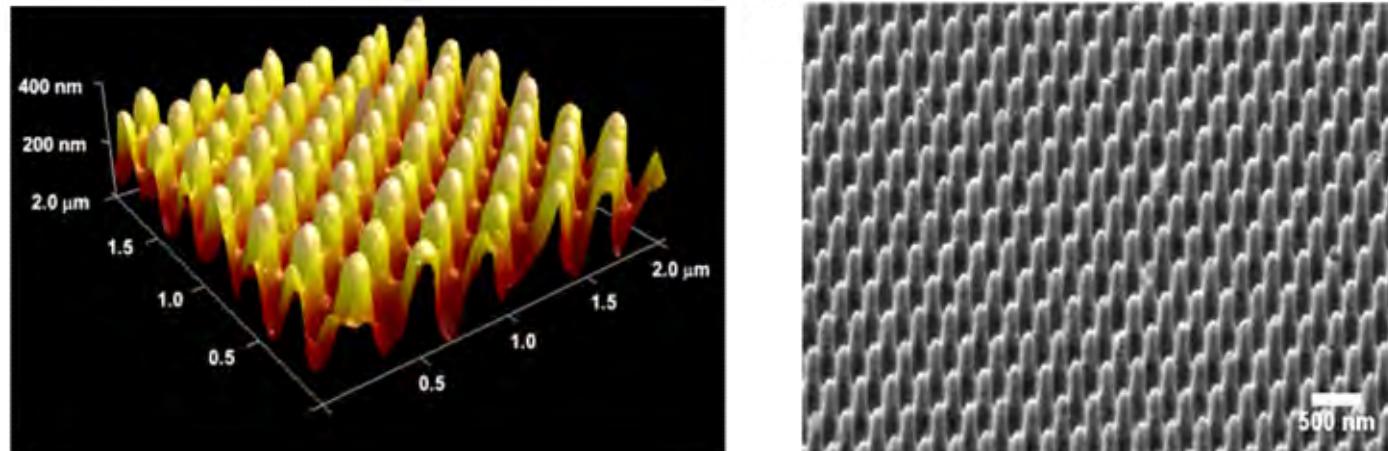


# Anti-reflective surface nanocomposite



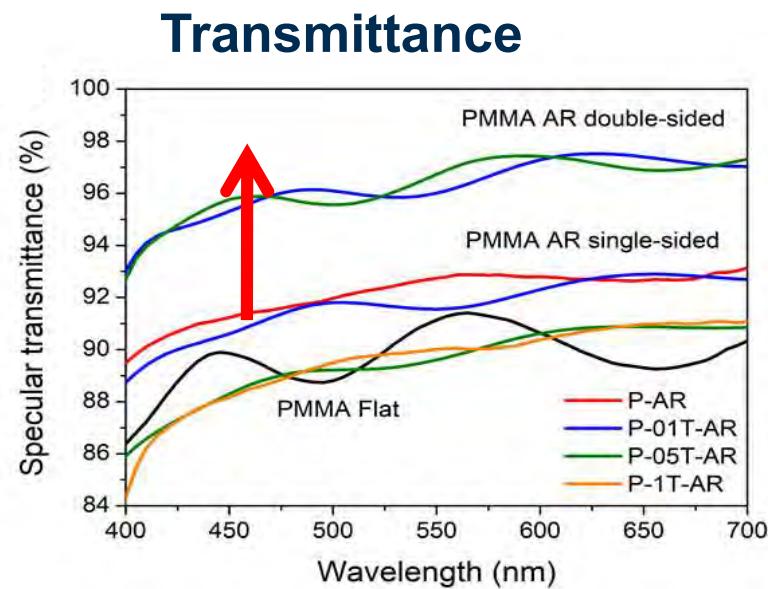
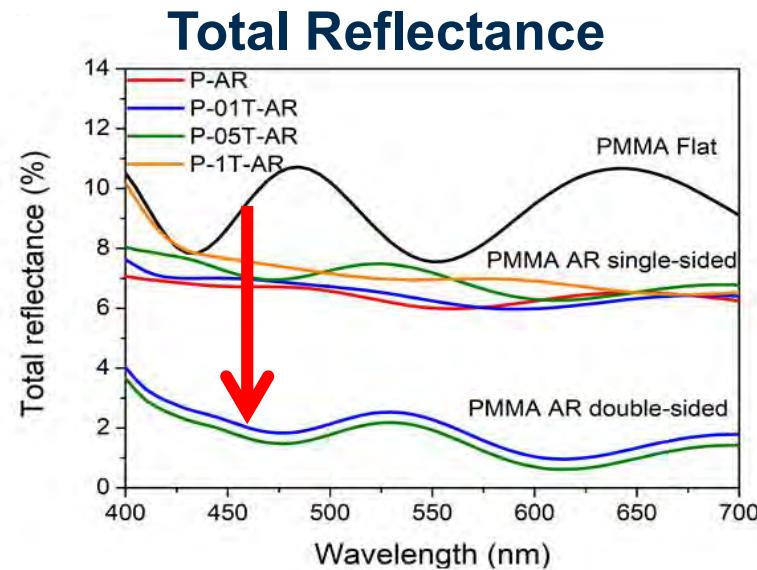
# Moth-eye imprinted topography

Morphology: SEM & AFM images

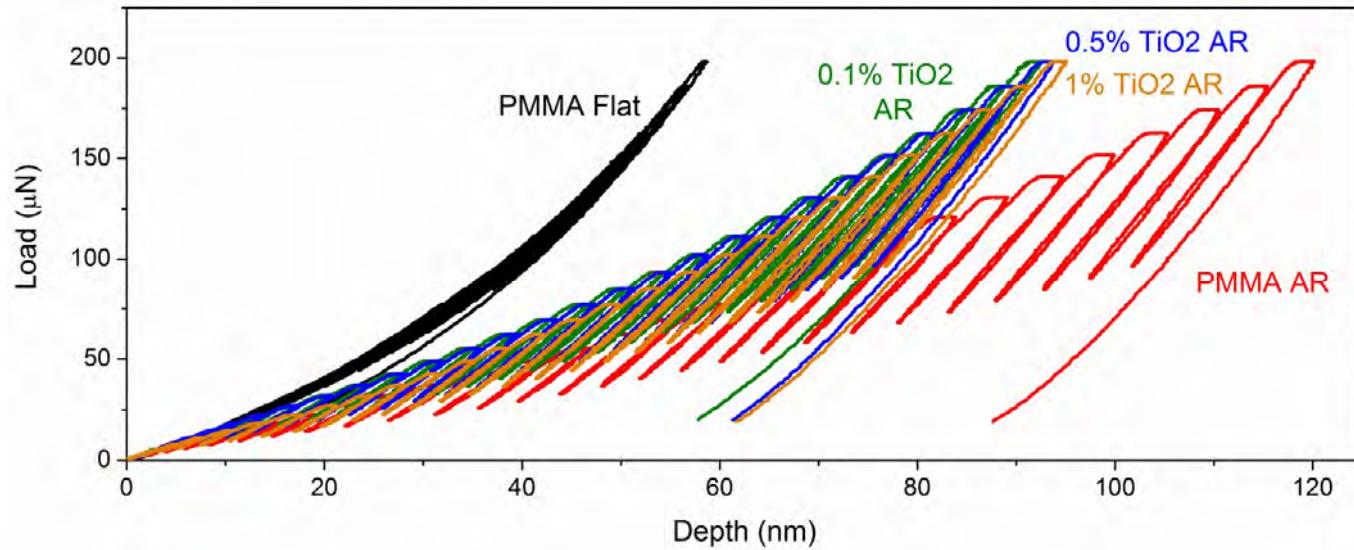


- High fidelity replication of the master mold on PMMA Nanocomposites
- Good nanoparticles dispersion
- Embedded particles within the polymer

# Moth-eye optical characterization



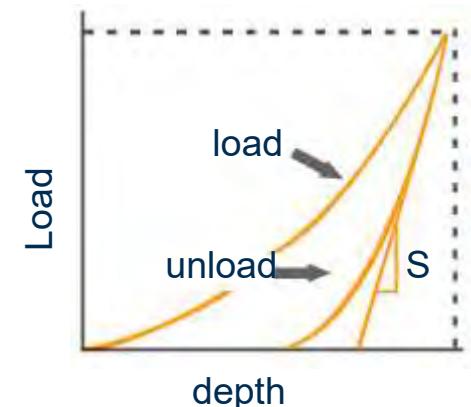
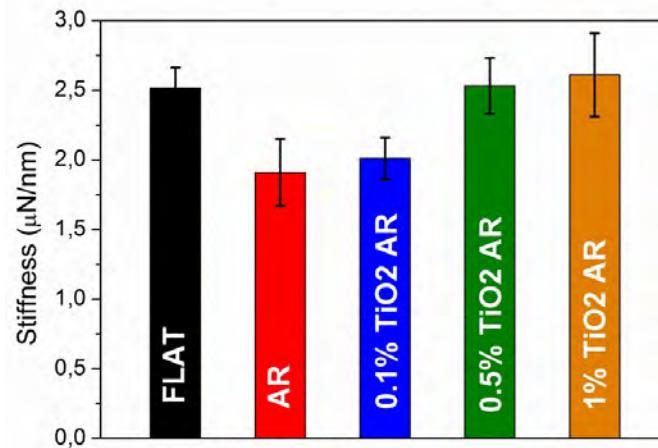
# Mechanical behavior: Nanoindentation



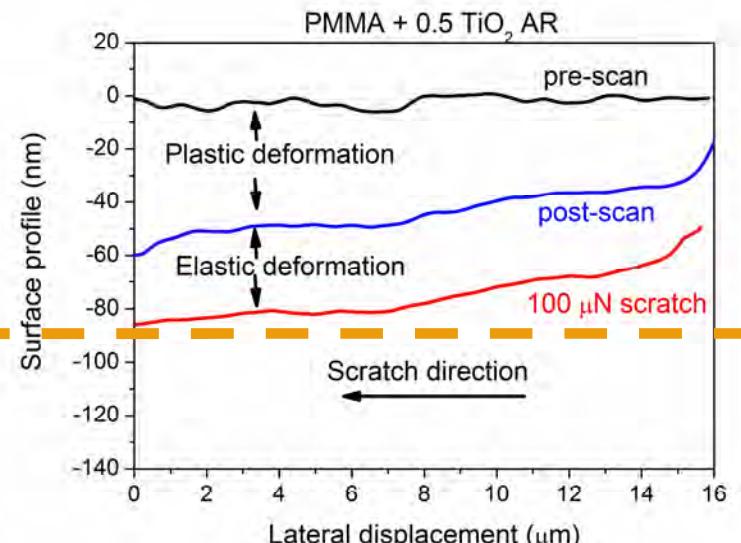
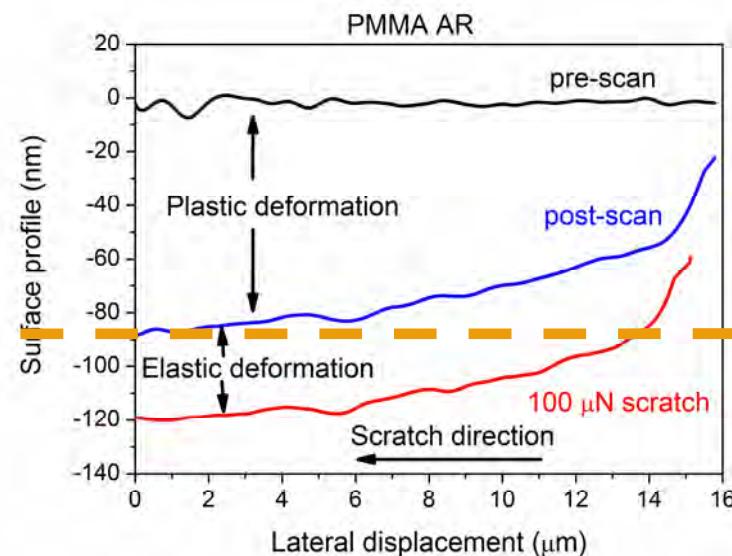
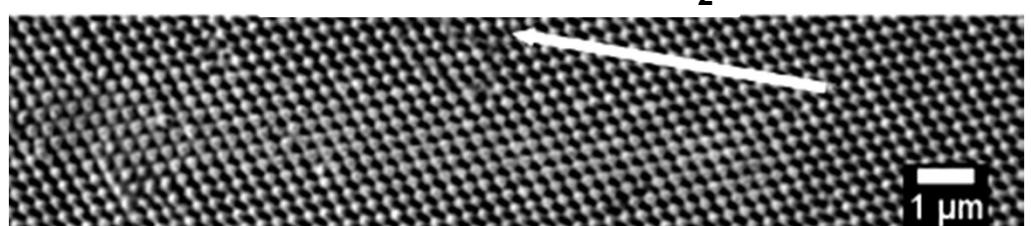
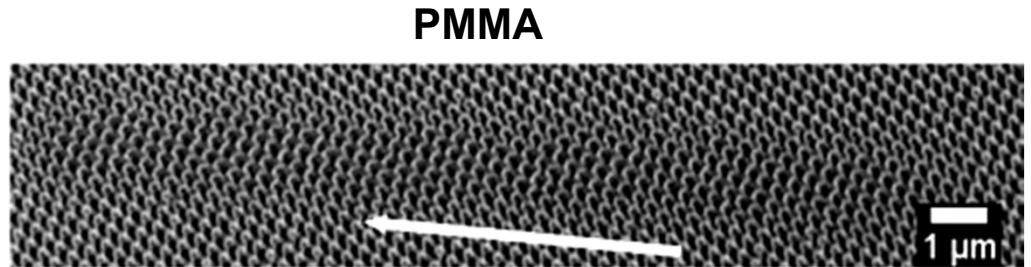
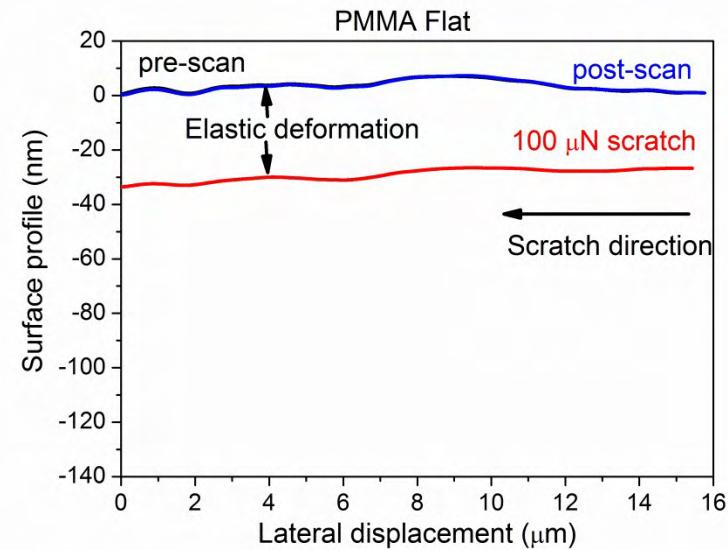
20 load/unload cycles until maximum load of 200  $\mu\text{N}$

## Stiffness

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

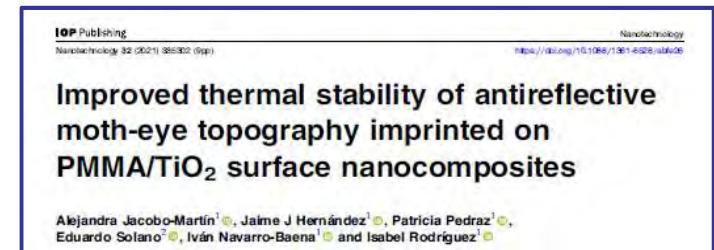
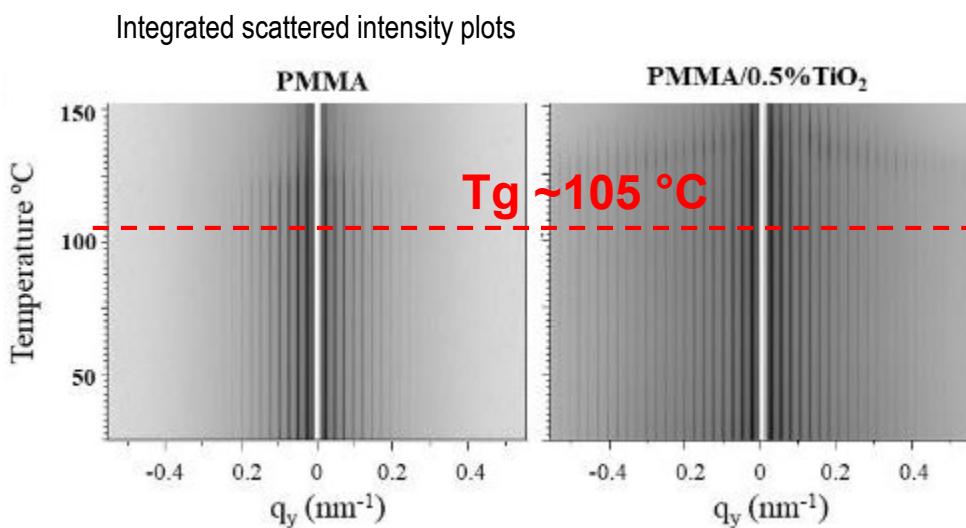
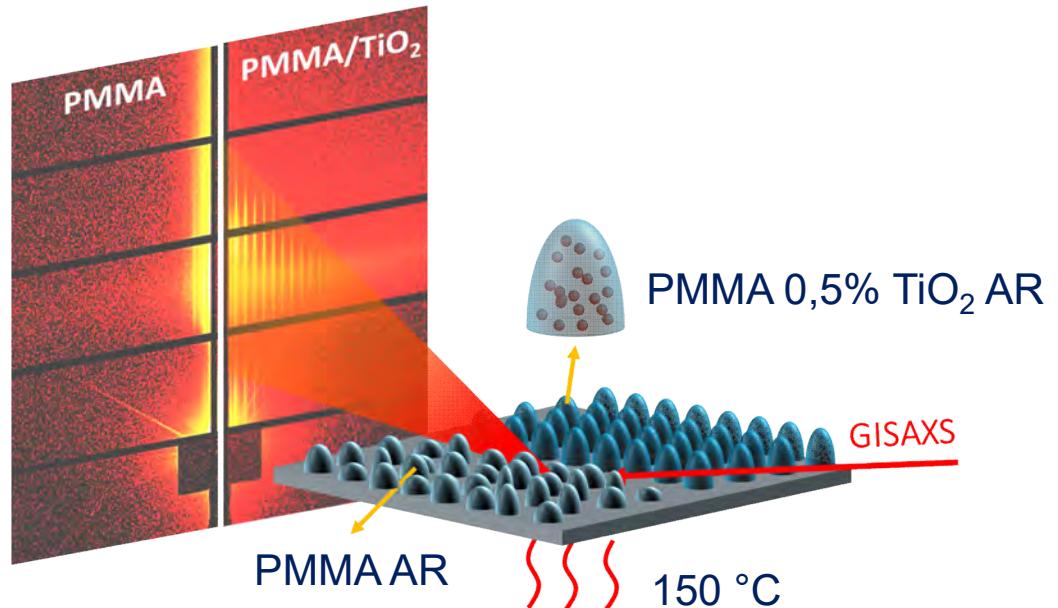


# Mechanical resistance : Nanoscratch

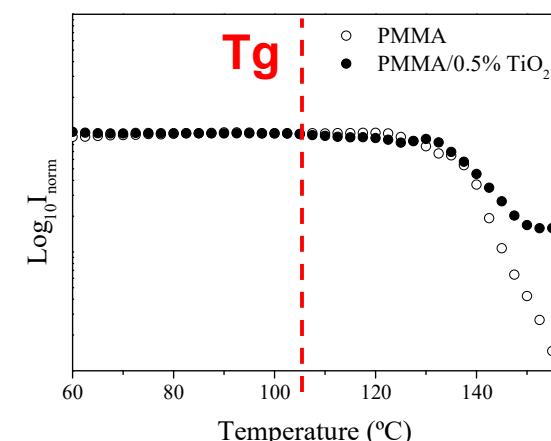


# Thermal stability of AR patterns

## Grazing Incidence Small Angle X-ray Scattering: GISAXS

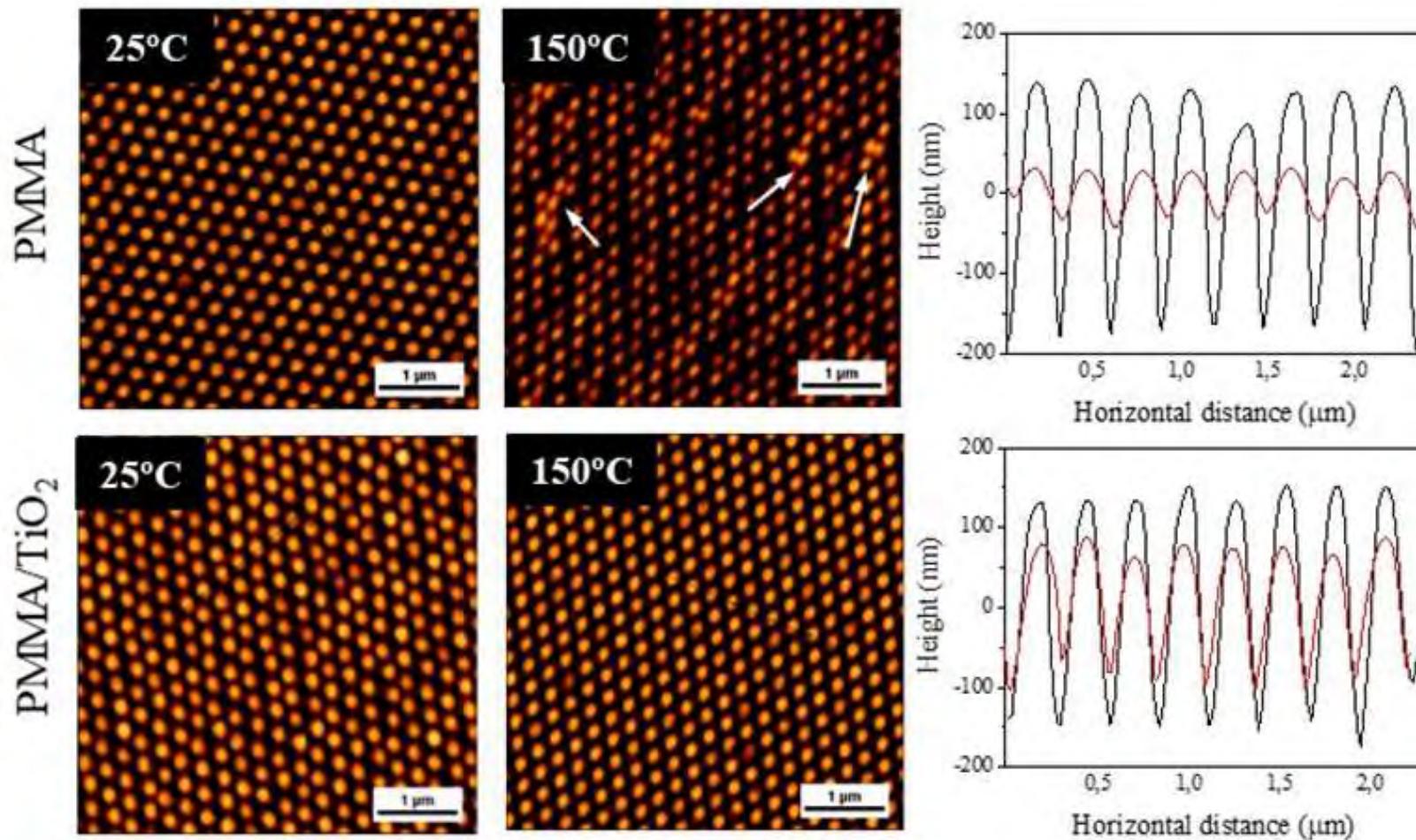


Distortions on the AR pattern  
↓  
Changes on the diffraction pattern



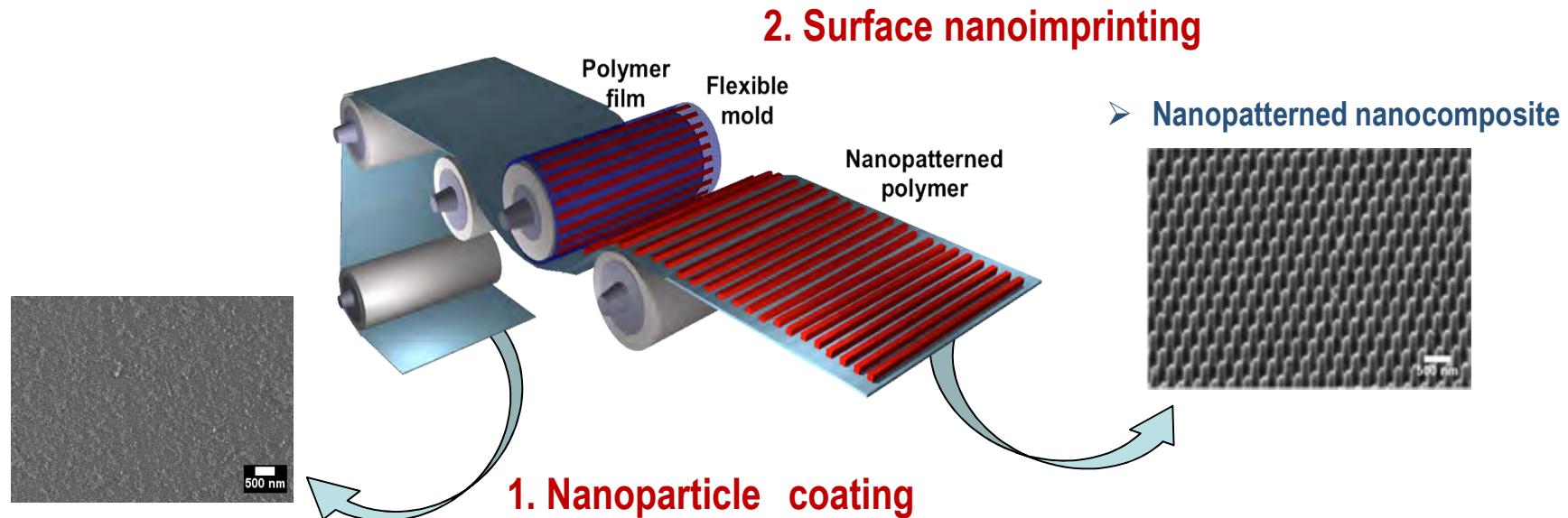
# Improved thermal stability

Moth-eye PMMA/TiO<sub>2</sub> surface nanocomposites

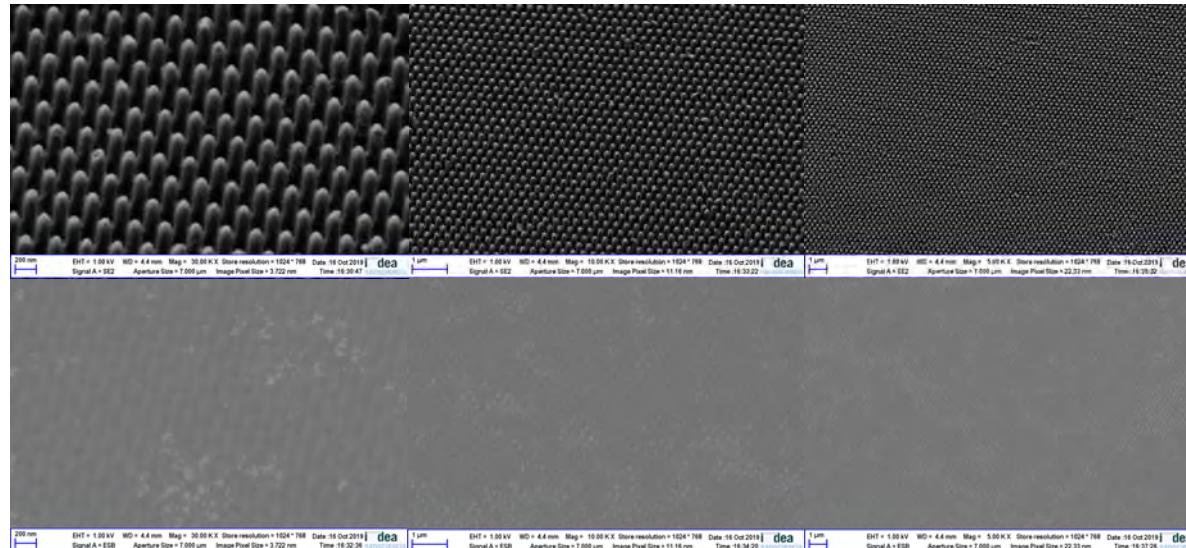


“anchoring effect of the TiO<sub>2</sub> NP to the polymer chain mobility” – pattern stability

# Continuous R2R process

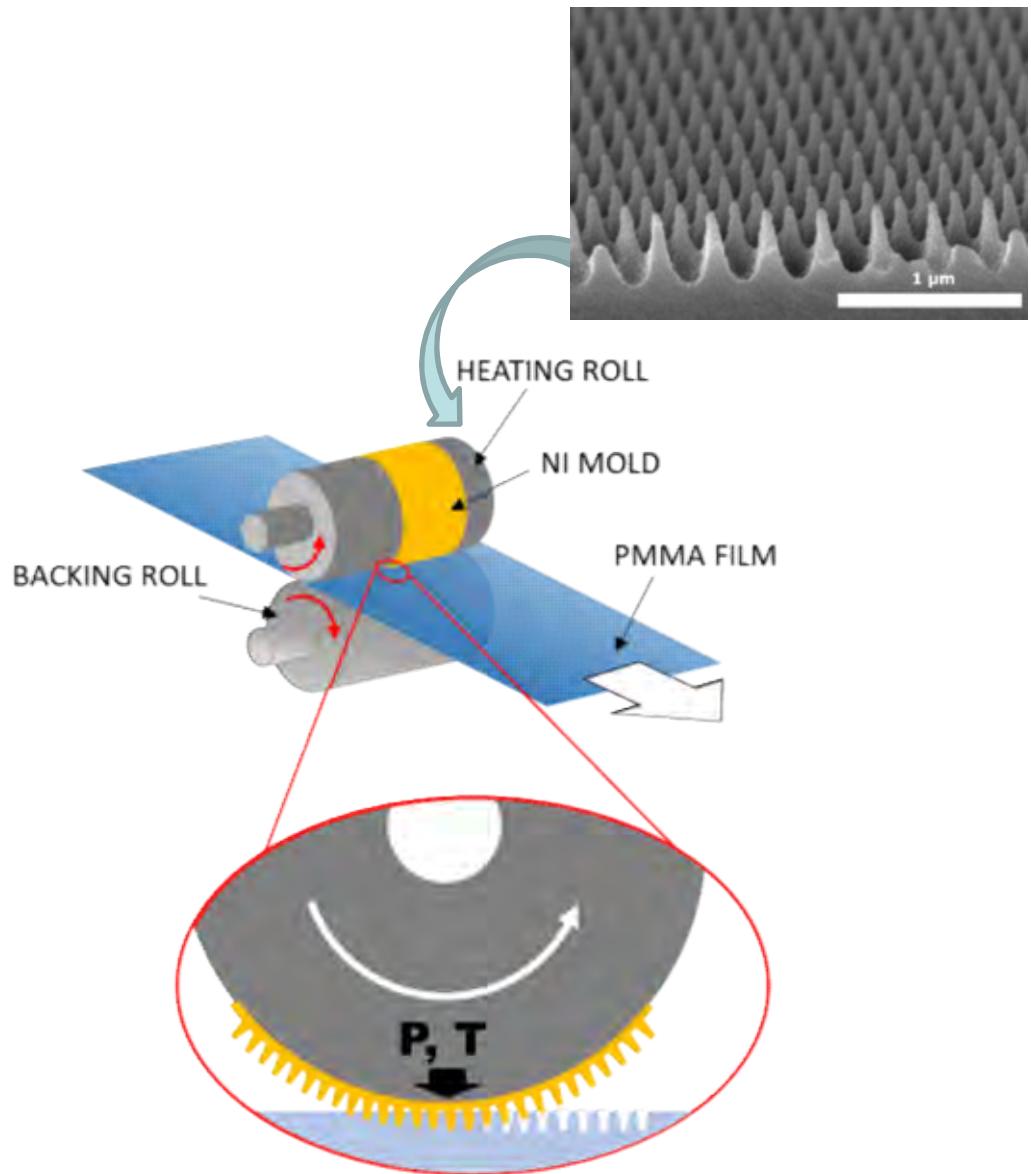
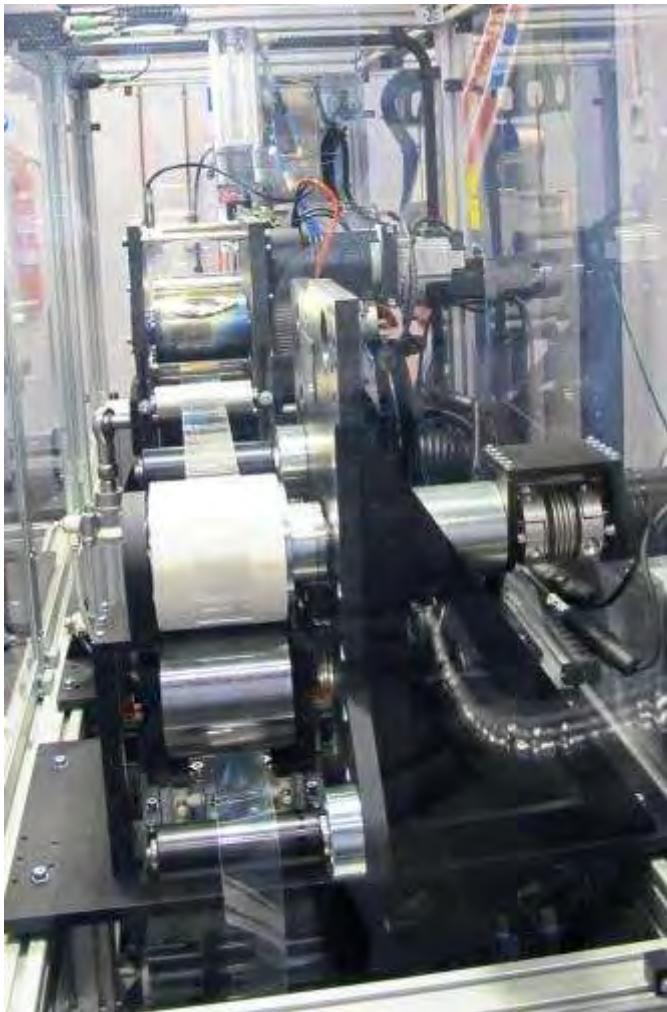


PET + PMMA + 025 % TiO<sub>2</sub> ARC (R2R)



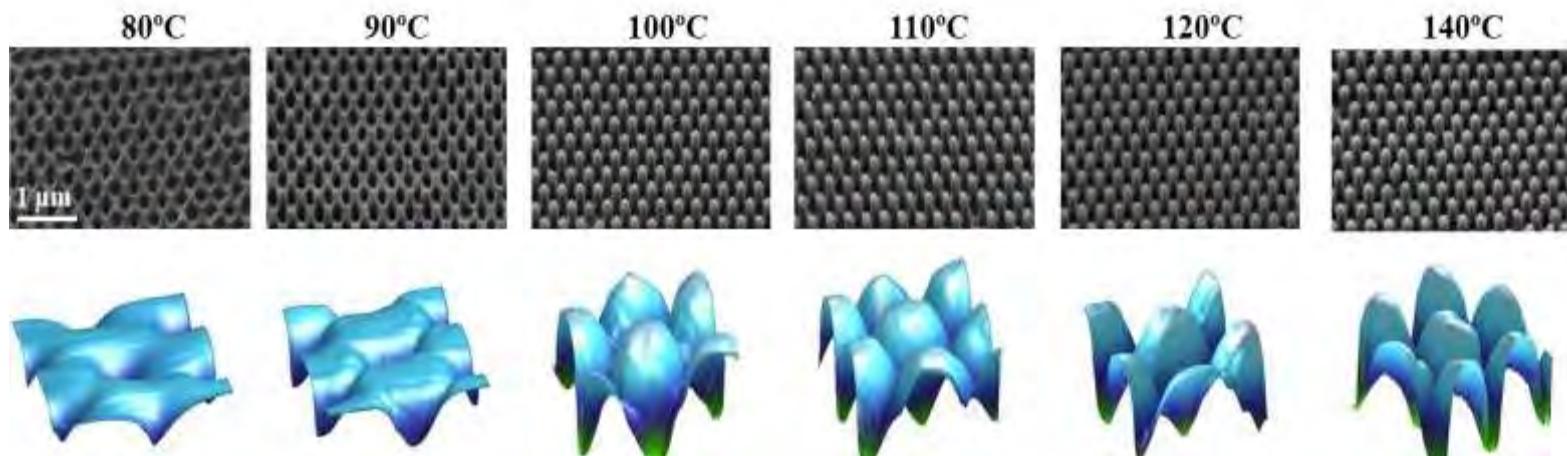
Patent : Polymeric composites with functional surfaces EP3436233B1 0000000

# Thermal R2R imprinting of moth-eye non-reflective films

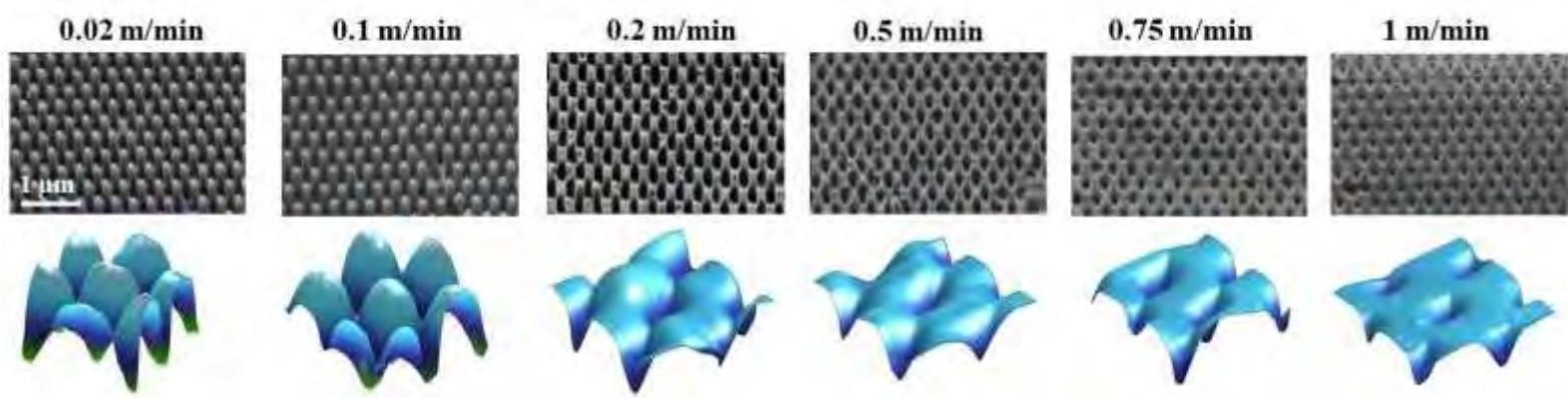


# Thermal R2R imprinting of moth-eye non-reflective films

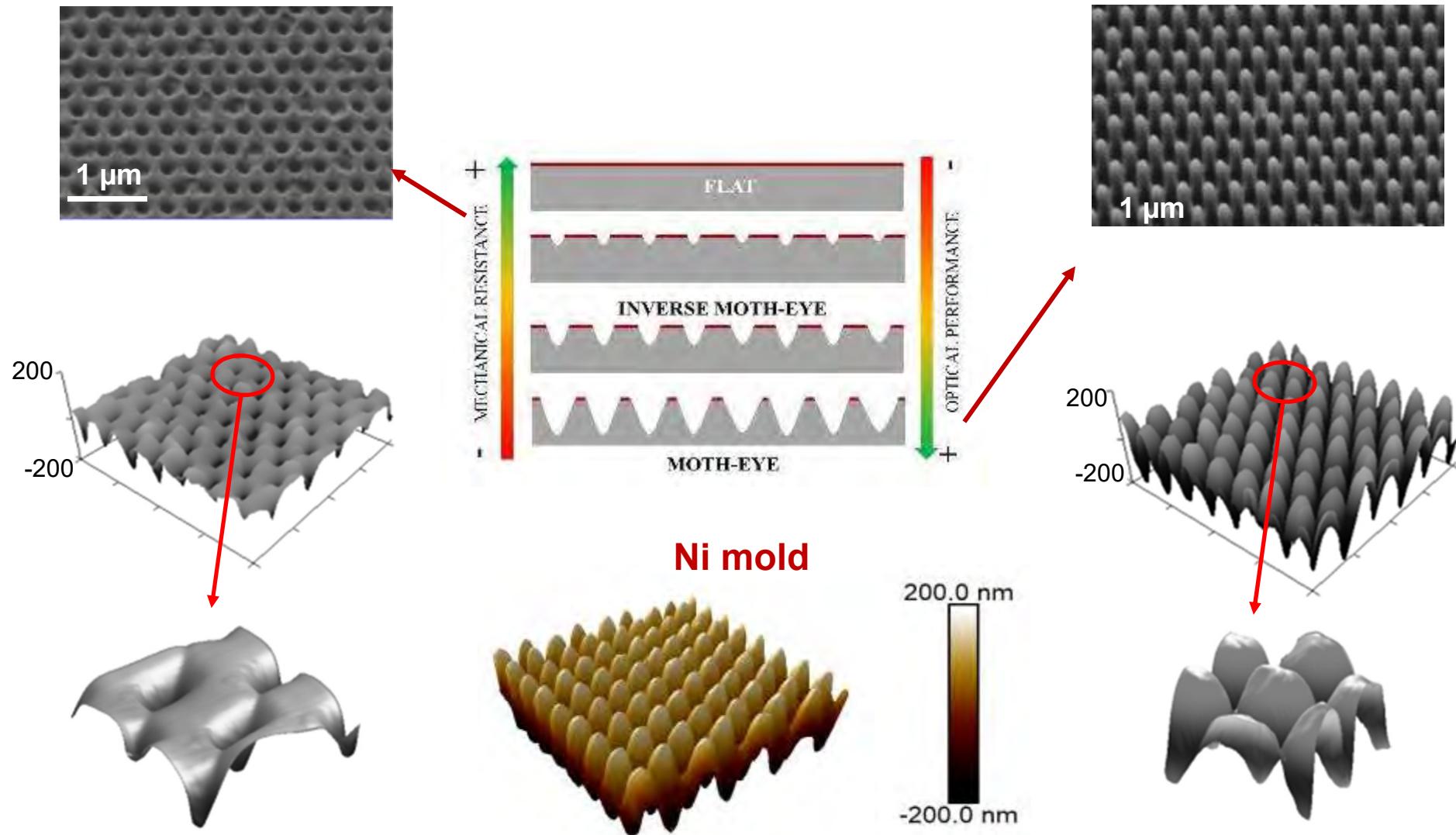
@ Variable temperature



@ Variable speed



# Thermal R2R imprinting of moth-eye non-reflective films

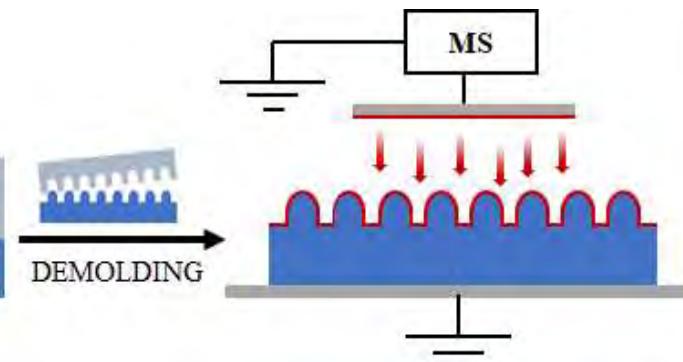


# TiO<sub>2</sub>-PMMA Moth-eye MS coating

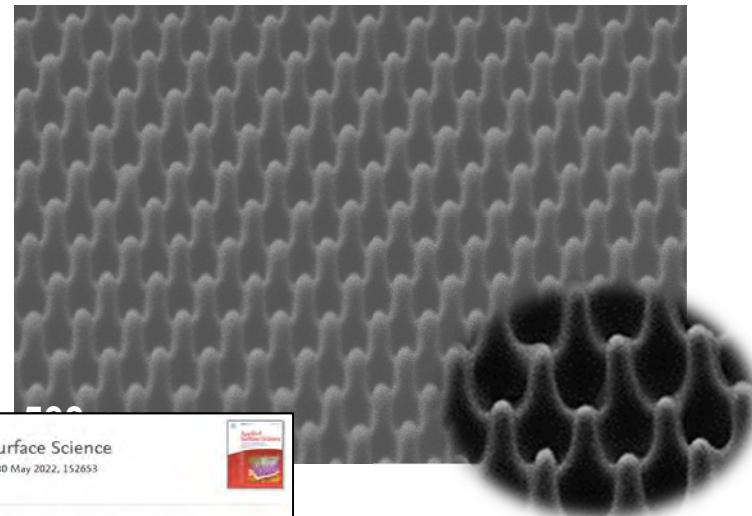
## NANOIMPRINT LITHOGRAPHY



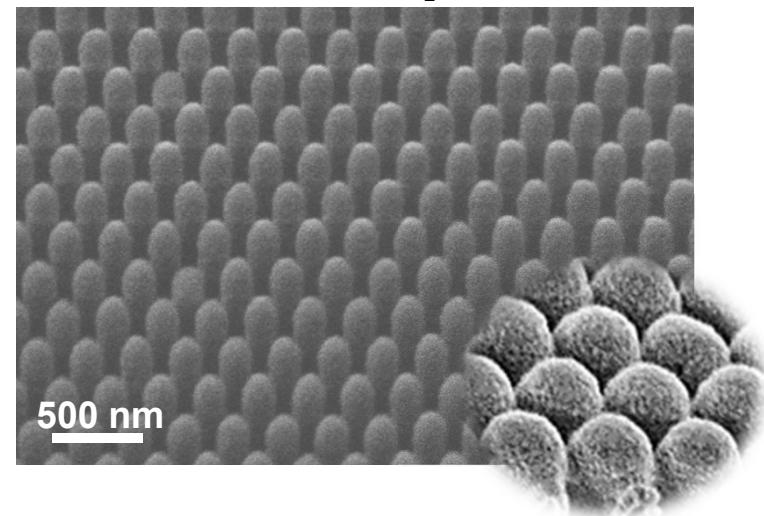
## MAGNETRON SPUTTERING



## PMMA-AR

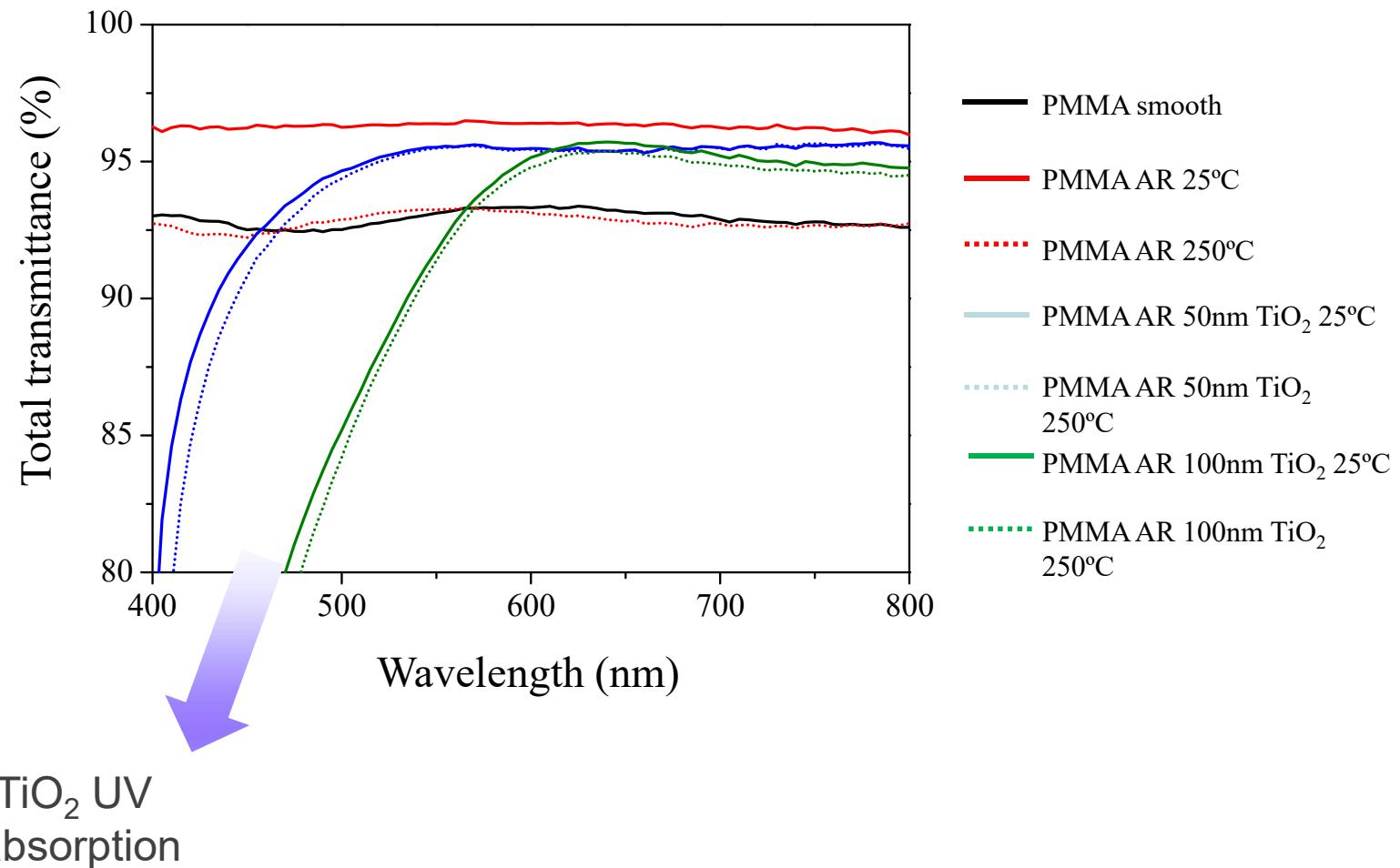


## PMMA-AR-100nm-TiO<sub>2</sub>



Daniel Fernandes  
Tomas Kubart

# Optical transmittance

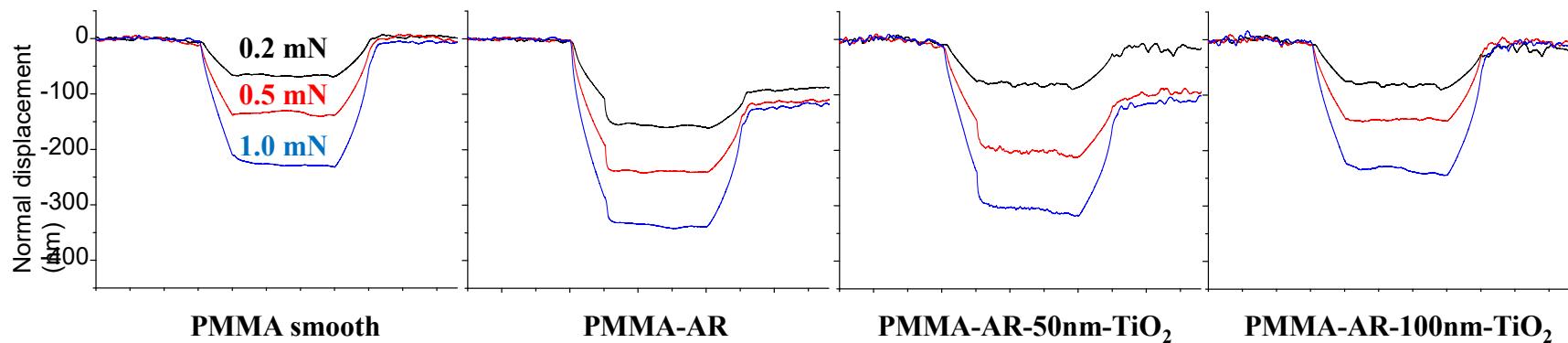
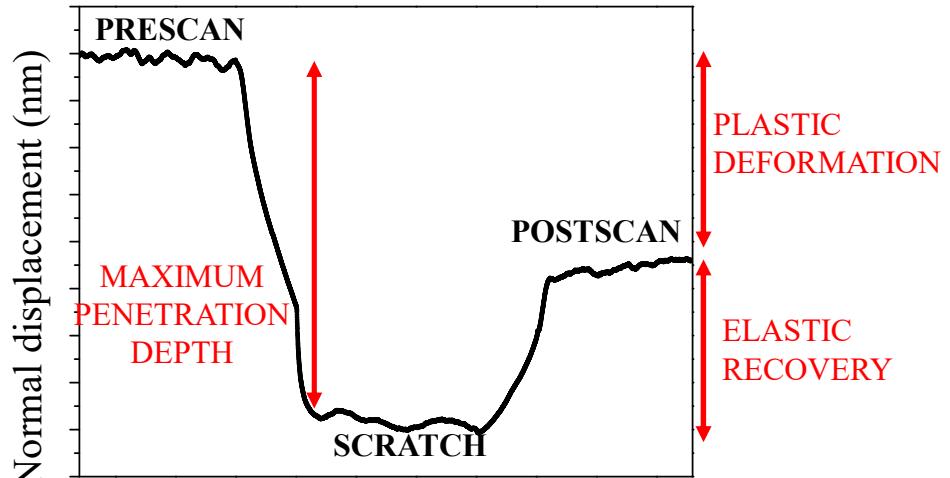
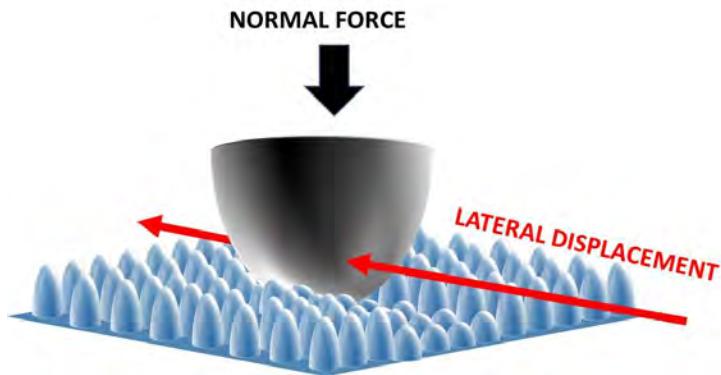


ANTIREFLECTIVE FUNCTIONALITY IS PRESERVED AT T>>T<sub>g</sub>

# Mechanical resistance

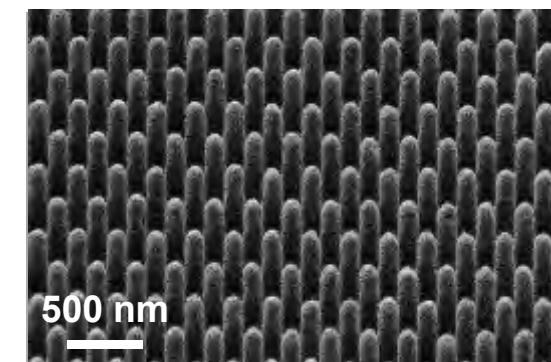
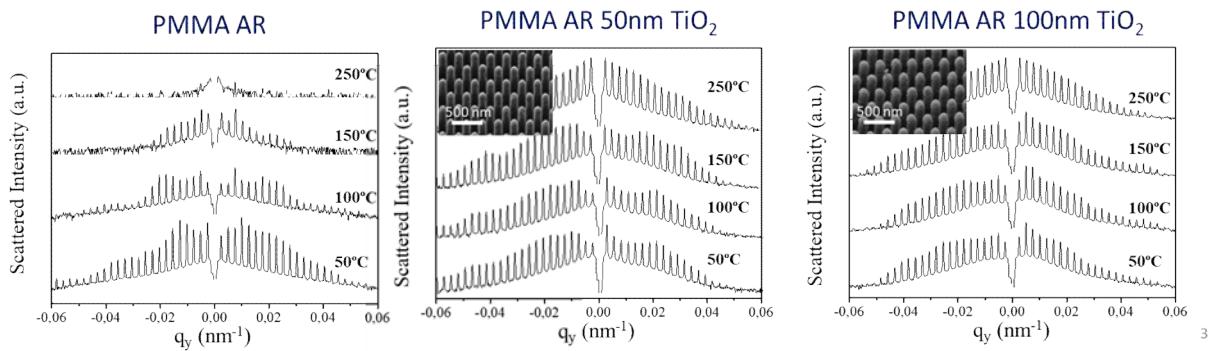
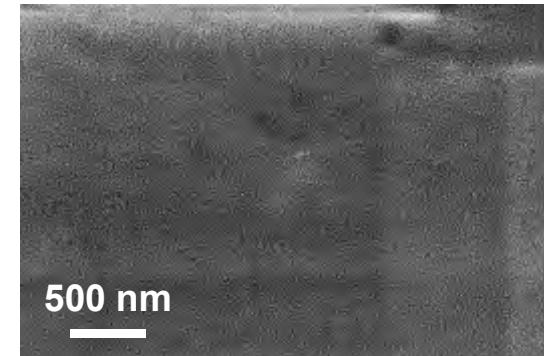
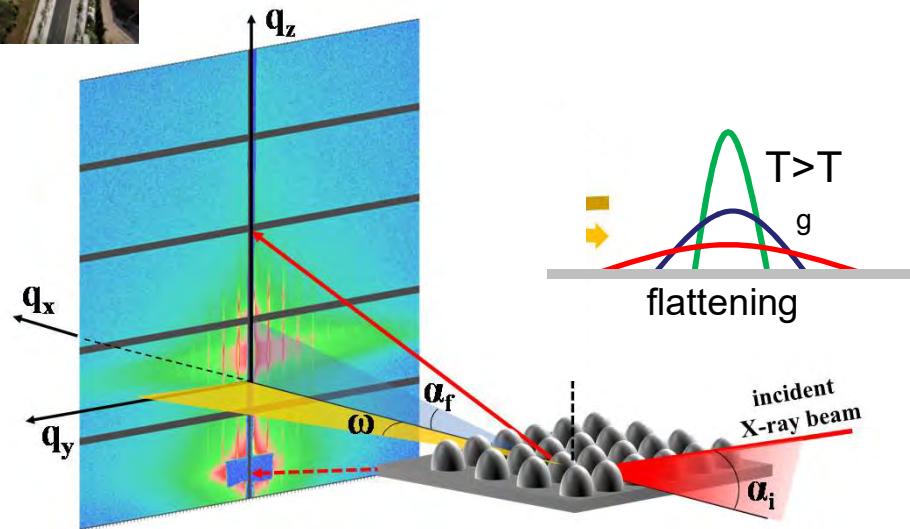
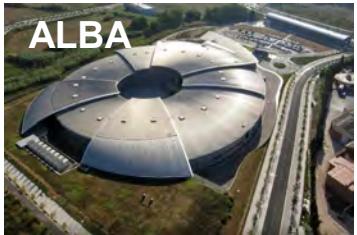
Nanolito 26-27<sup>th</sup> January 2022

## NANOSCRATCH TEST



**TiO<sub>2</sub> ENCAPSULATION IMPROVES SCRATCH RESISTANCE OF AR NANOSTRUCTURES**

# Thermal resistance

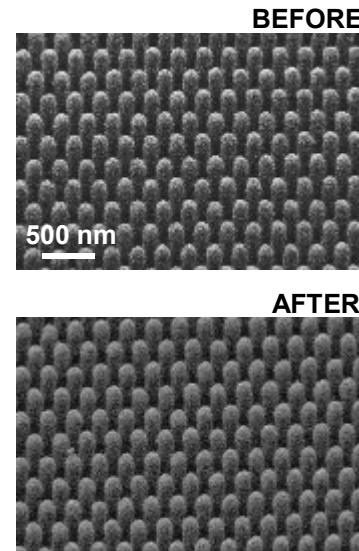


32

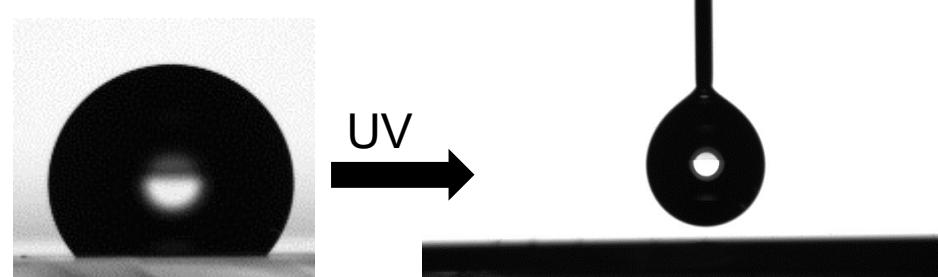
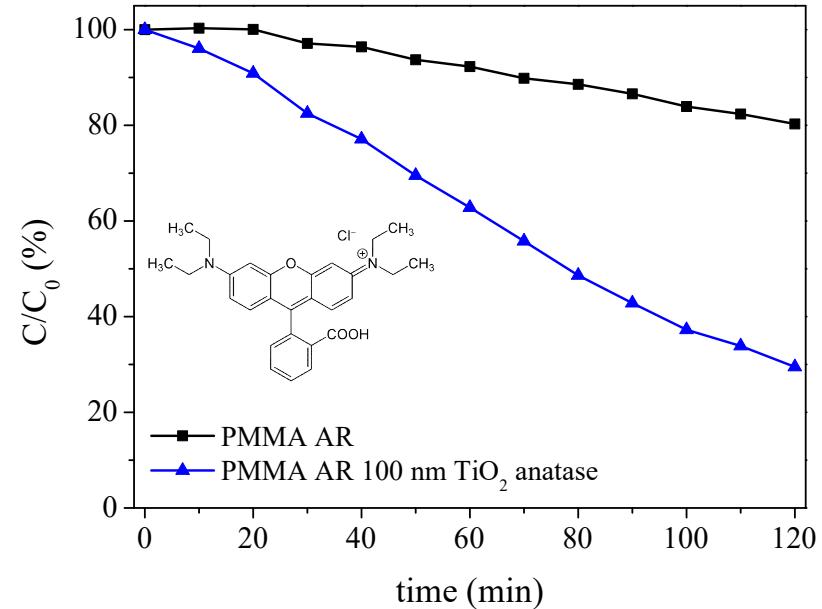
**TiO<sub>2</sub> ENCAPSULATION PREVENTS REFLOW AND DISTORTION EFFECTS up to 250 C**

# Photoinduced self-cleaning

**Amorphous  $\text{TiO}_2 \rightarrow$  anatase**

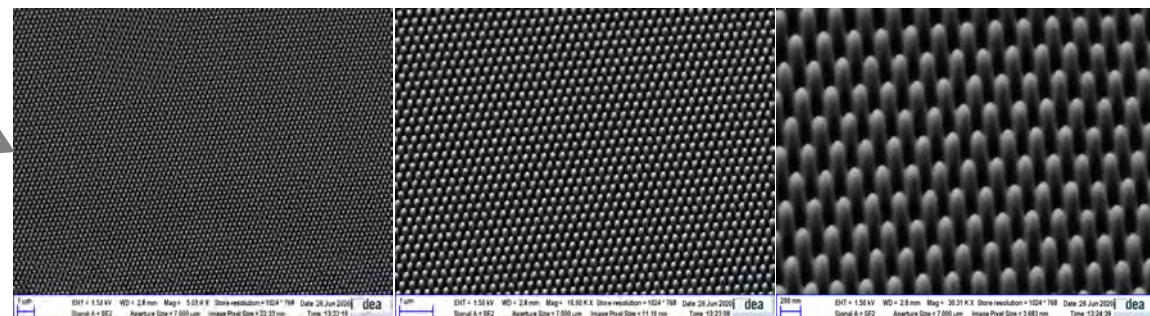
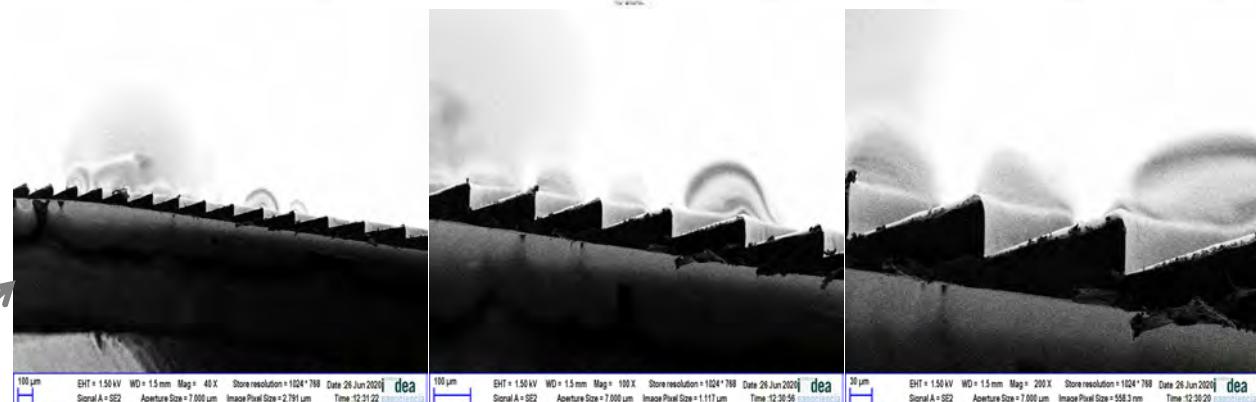
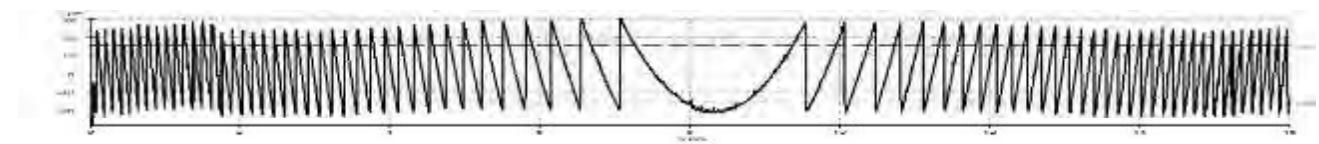
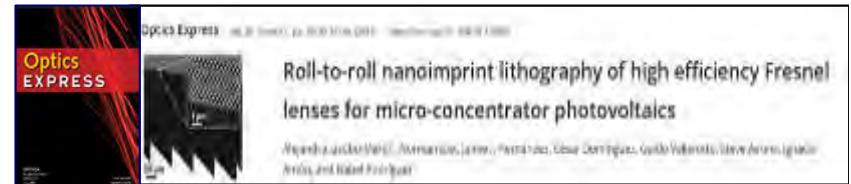
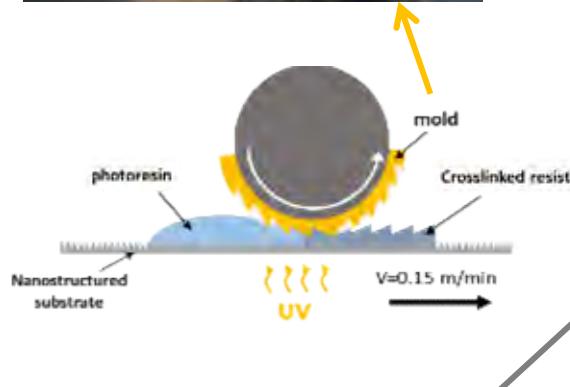


**RhB UV degradation assay**



**POLLUTANT DEGRADATION + SUPERHYDROPHYLICITY = SELF-CLEANING**

# UV R2R NIL Fresnel lens with anti-reflective moth eye



# Acknowledgements

## Group members

Jaime Hernandez  
Alberto Martín Asensio  
Miguel Esteban Lucía  
Sergio Dávila  
Maria Teresa Alameda



Alejandra Jacobo  
Jean Cacheux  
Ivan Navarro Baena



## Collaborators



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UNIVERSITET

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Tomas Kubart



Manuel R Osorio  
Daniel Granados



Miguel Monclús  
Jon Molina



César Domínguez  
Ignacio Antón



Eduardo Solano  
Juan Carlos Martínez

# Thank you for your attention !

