



Fabrication of nanostructured microarrays by combining nanoimprint-assisted microcontact stripping and colloidal lithography techniques

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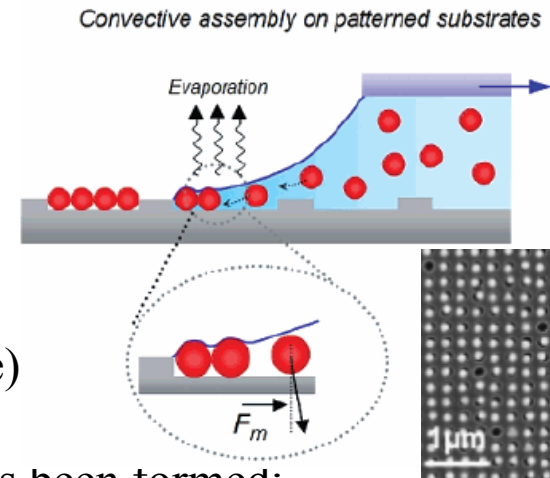
- **Purpose of the work:** fabrication of ordered microstructures of colloidal crystals over large areas

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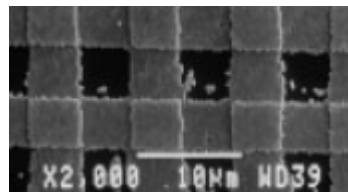
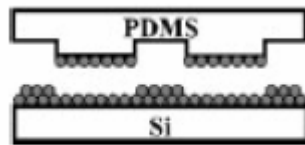
1. Introduction

Bead patterning methods

- Directed self-assembly of nanoparticles →
 - Chemical modification
 - Topographic modification (SAPI, Delamarche)
- Methods for patterning the colloidal film after it has been formed:
 - Soft lithography lift-off processes (PDMS)



* Malaquin et al. *Langmuir*, 200



* Yao et al. *Adv. Mater.*, 2004, 16(1)

Nanoimprint-assisted contact stripping

- Top-down, fine control over the microstructure of the colloidal film
- Control of pressure and temperature during the removal of the nanoparticles
- PMMA stamps are harder than PDMS and less deformable

Applications

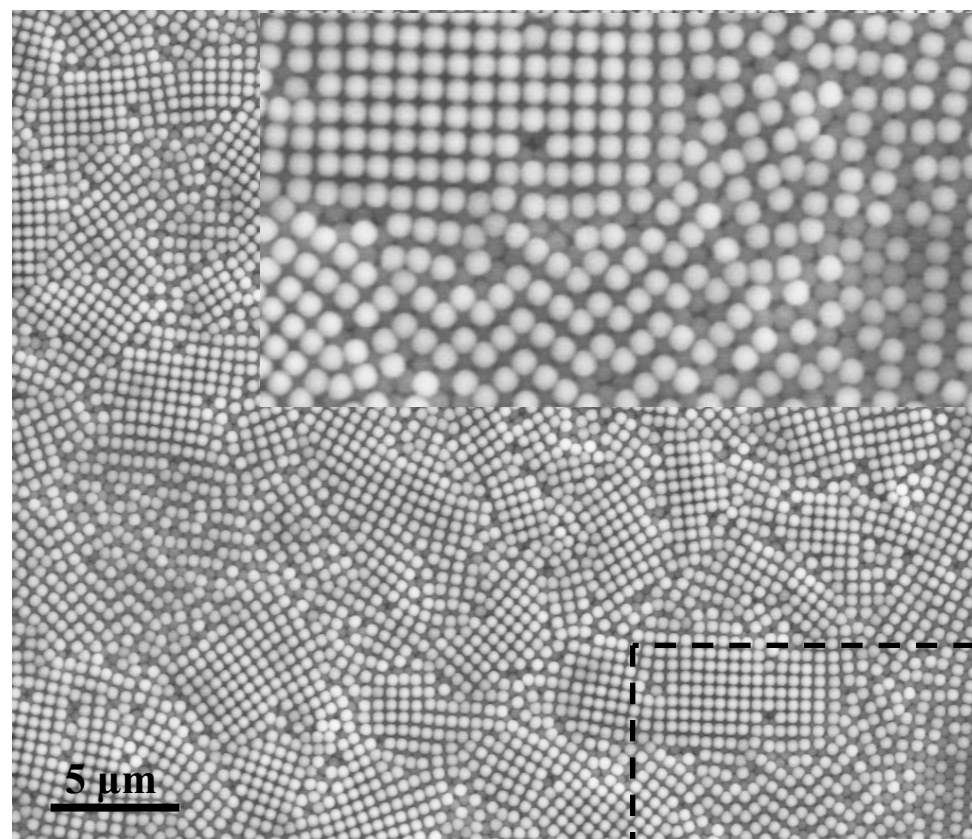
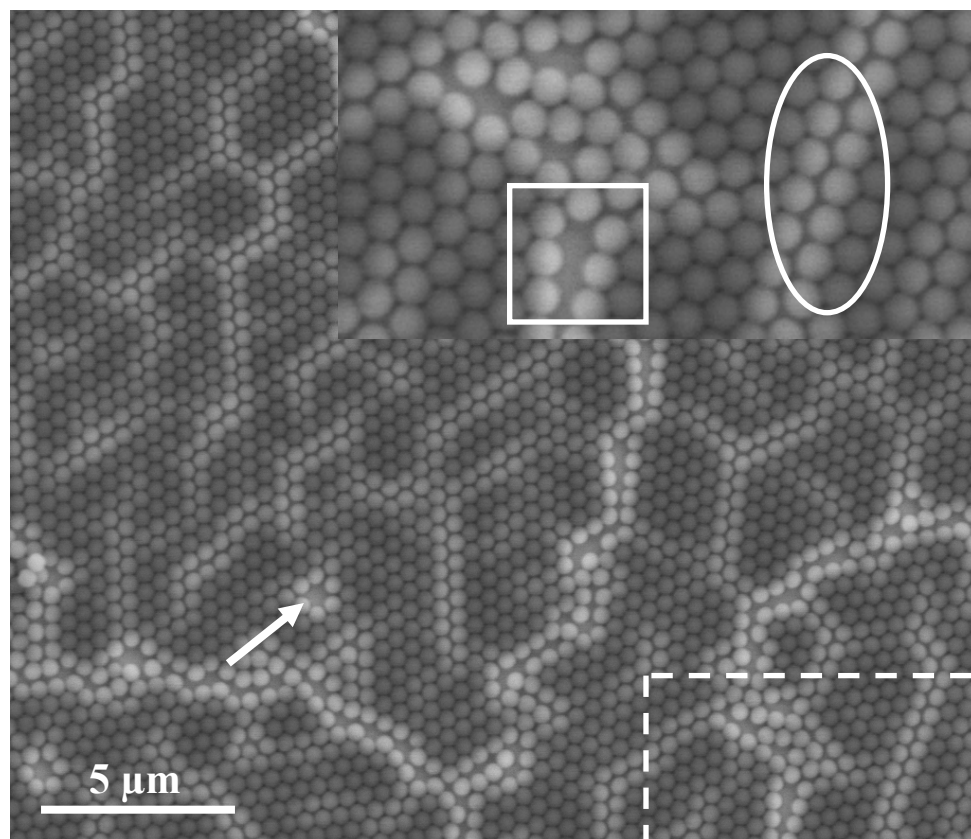
- Cell culture platforms to examine cell-surface interactions
- Sensing platforms for parallel detection



2. Poly(styrene) bead deposition

Spin-coating

PS 500nm \rightarrow Monolayer and bilayer formation



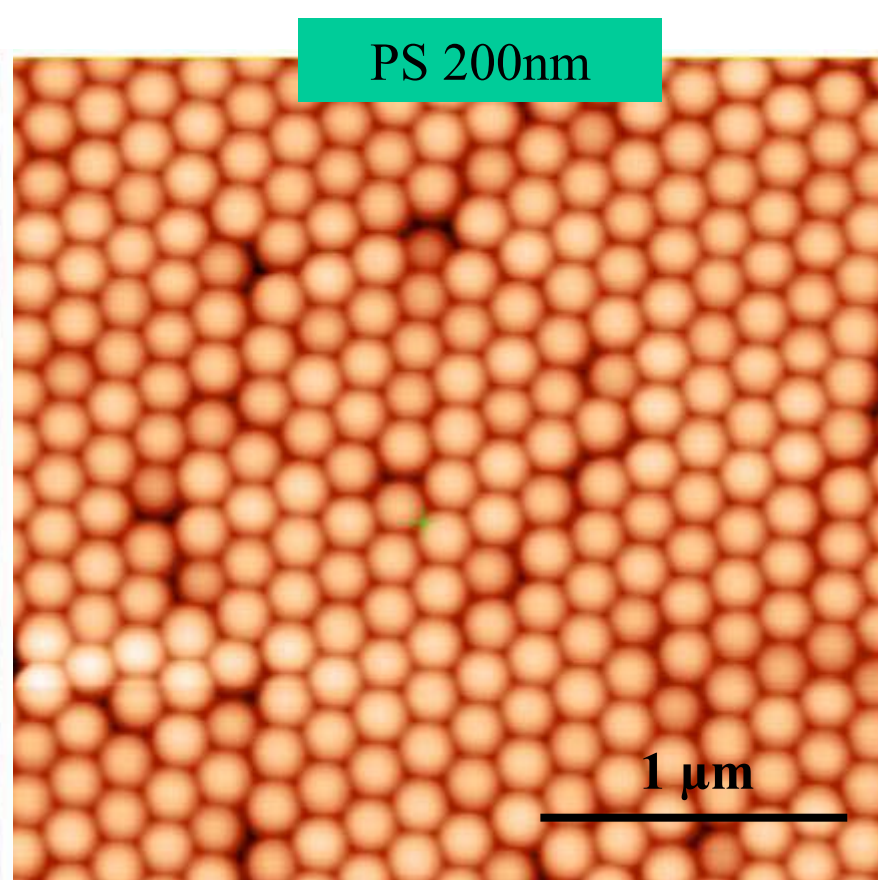
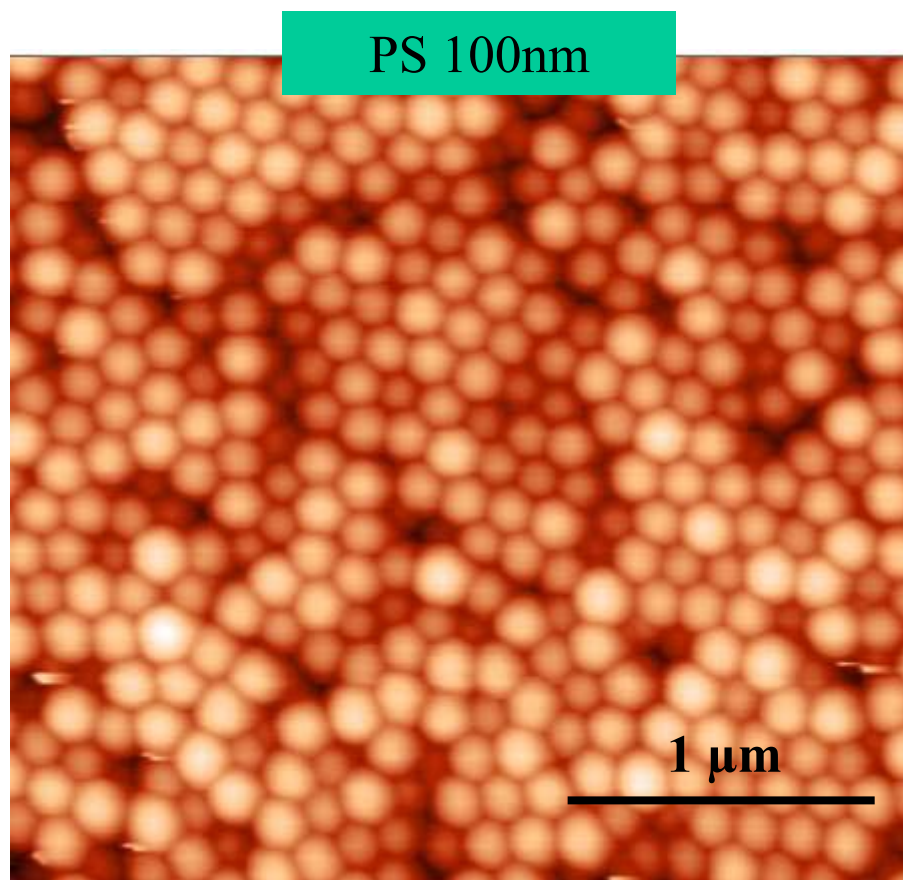


2. Poly(styrene) bead deposition

Spin-coating

PS 100nm → disordered multilayer

PS 200nm → ordered packing of nanoparticles

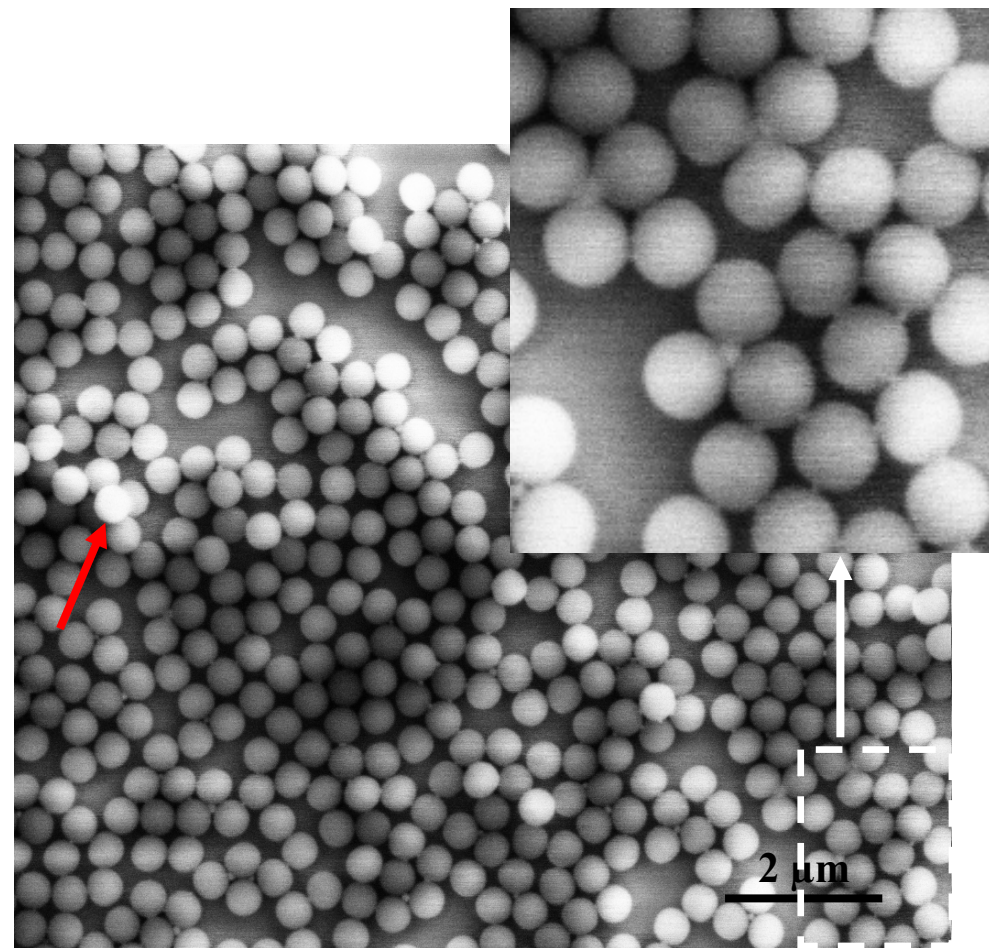
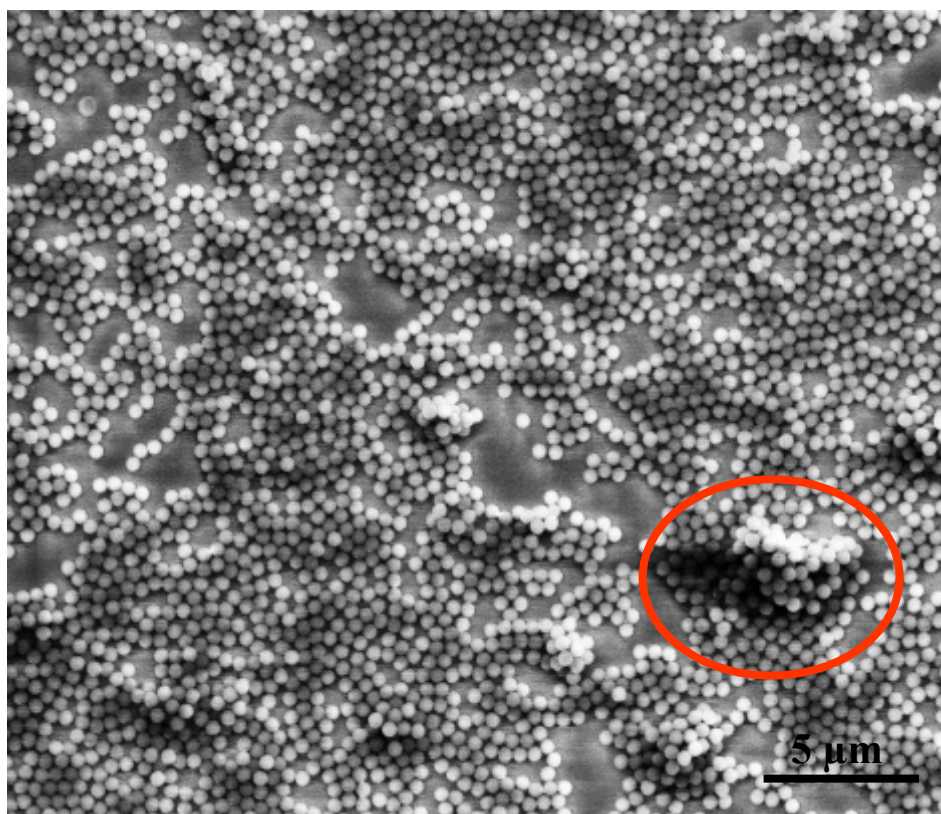




2. Poly(styrene) bead deposition

Langmuir-Blodgett films

Ionic assembly \rightarrow inhomogeneous layers, high adhesion to the substrate





3. Nanoimprint-assisted contact stripping

Nanoimprint Lithography (NIL) – parallel technique

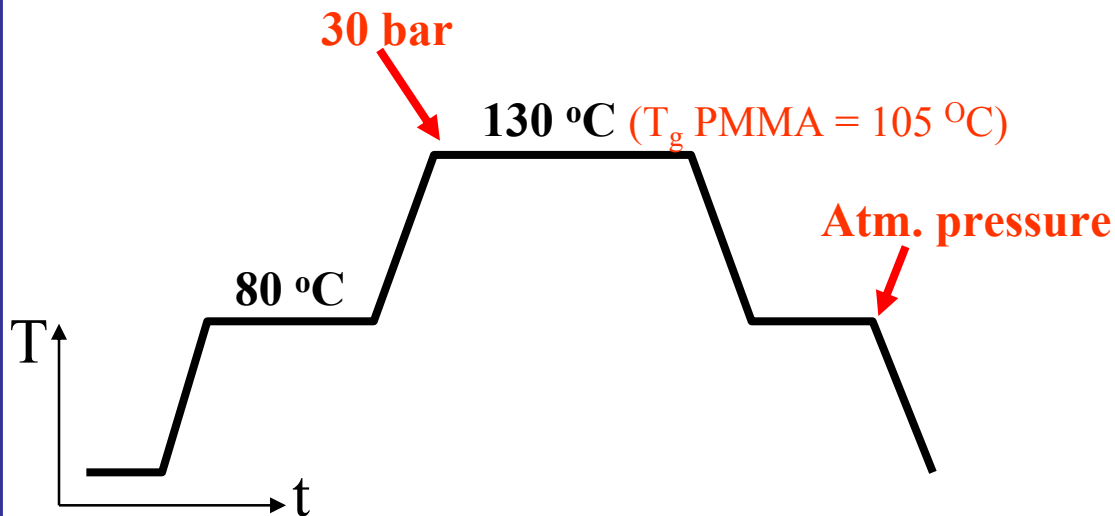
Imprinting: a mould that includes the nanostructures is pressed into a thermoplastic polymer (T, P)

Lateral resolution: 30 nm.

Working temperature: up to 250°C

Working pressure: from 5 to 70 bar

Typical sequence for imprinting PMMA:



We have used the NIL for nanostructuring polymer surfaces (fabrication of PMMA stamps) and for patterning nanoparticles

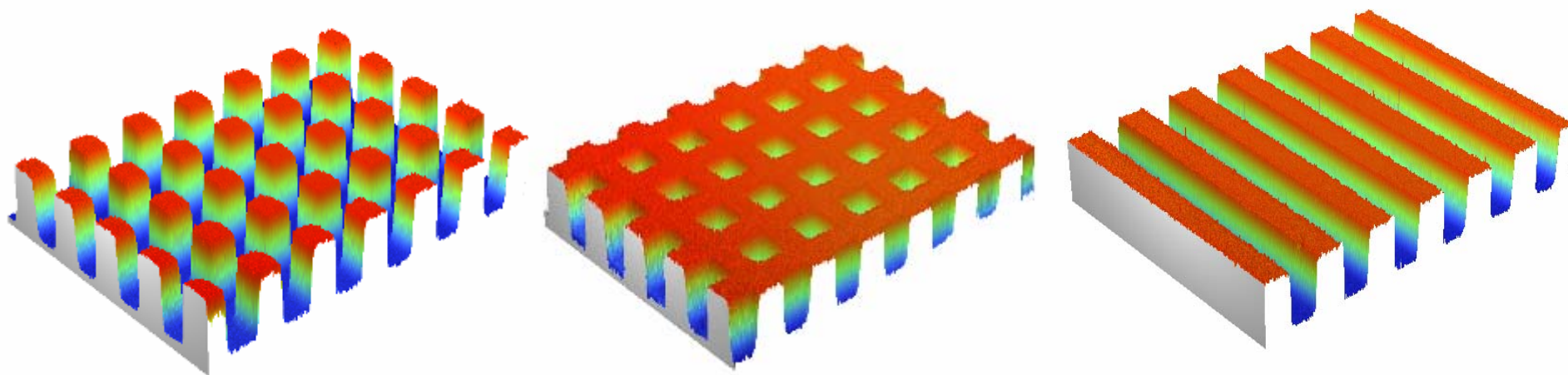


3.1 Stamp production

PMMA moulds by NIL

	$T_{(\text{Imprint})} / \text{K}$	P / Nm^{-2}	t / s	$T_{(\text{Release})} / \text{K}$
PMMA stamp production	403	3×10^6	600	353

Size of structures: 20 μm - 2 μm



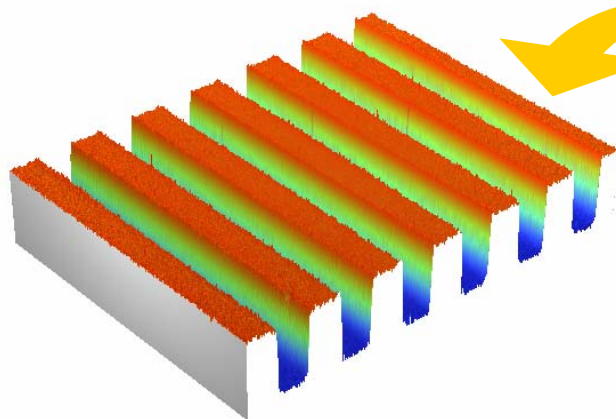
Optical interferometer images of the PMMA replicas



3.2. Patterning of nanoparticles

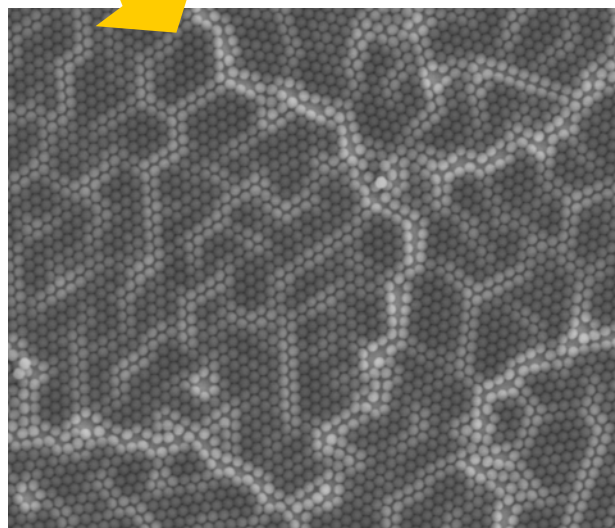
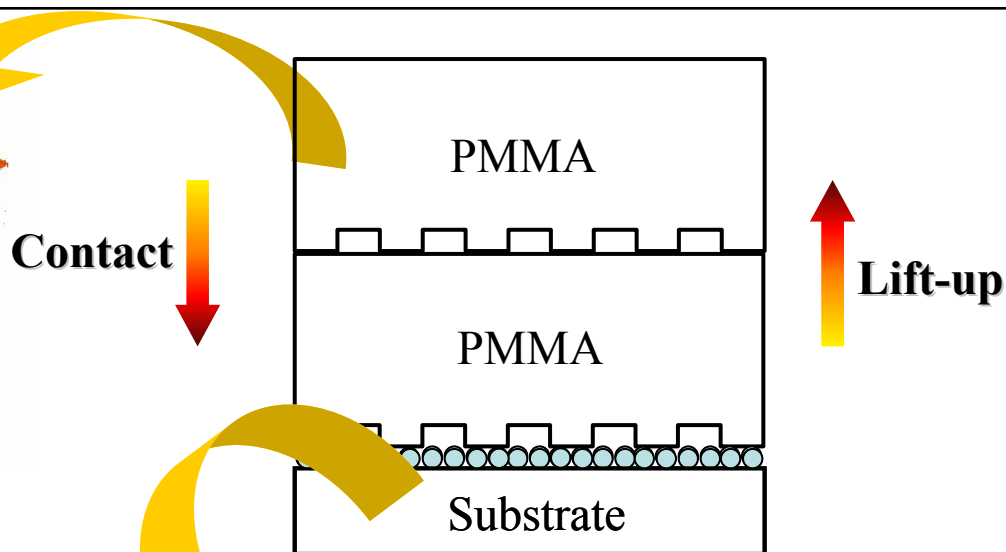
Microcontact Stripping (MCS)

	$T_{(\text{Imprint})} / \text{K}$	P / Nm^{-2}	t / s	$T_{(\text{Release})} / \text{K}$
PS contact stripping	323	5×10^6	200	303



PMMA stamps

Produced by imprinting silicon masters using the nanoimprinter



Substrate with nanoparticles

PS beads 100nm ~ 500nm spin coated on silicon or self-assembled by Langmuir-Blodgett technique



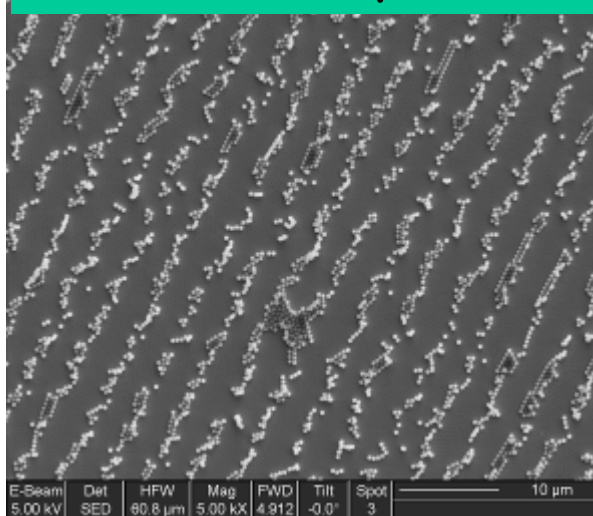
3.2. Patterning of nanoparticles



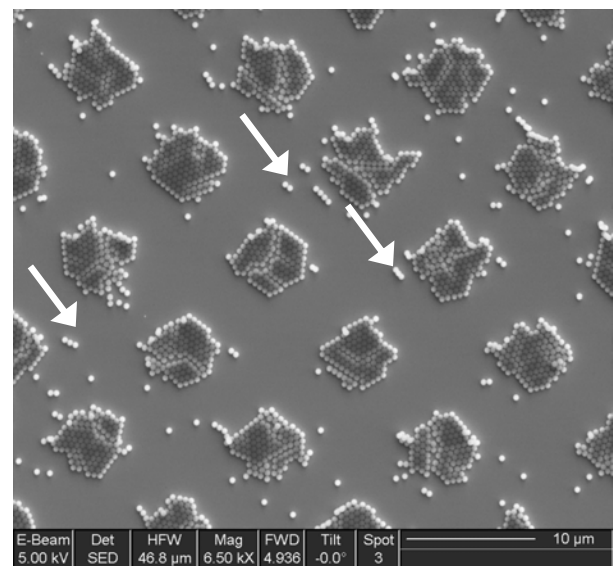
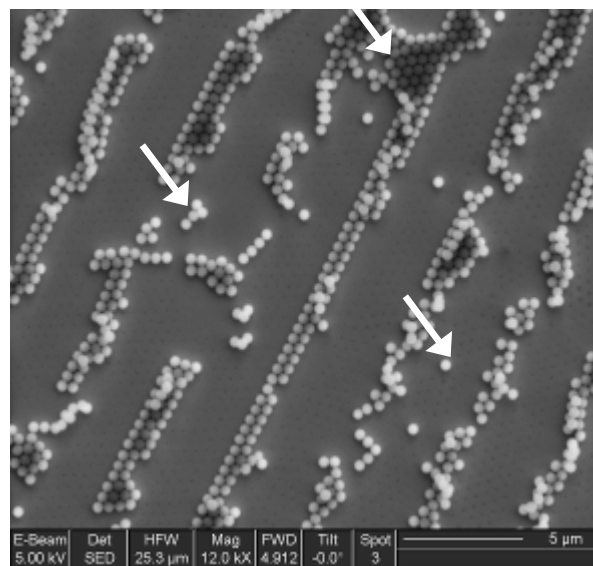
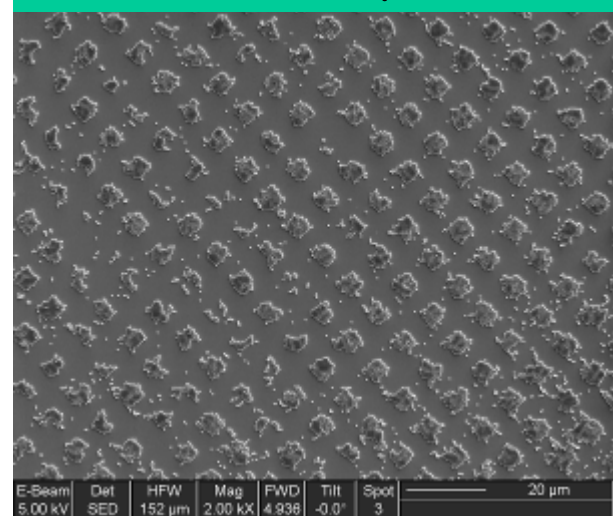
Microcontact Stripping (MCS)

PDMS stamps

PDMS with 2 μm lines



PDMS with 5 μm holes



Bead “contamination”
between the patterns



3.2. Patterning of nanoparticles



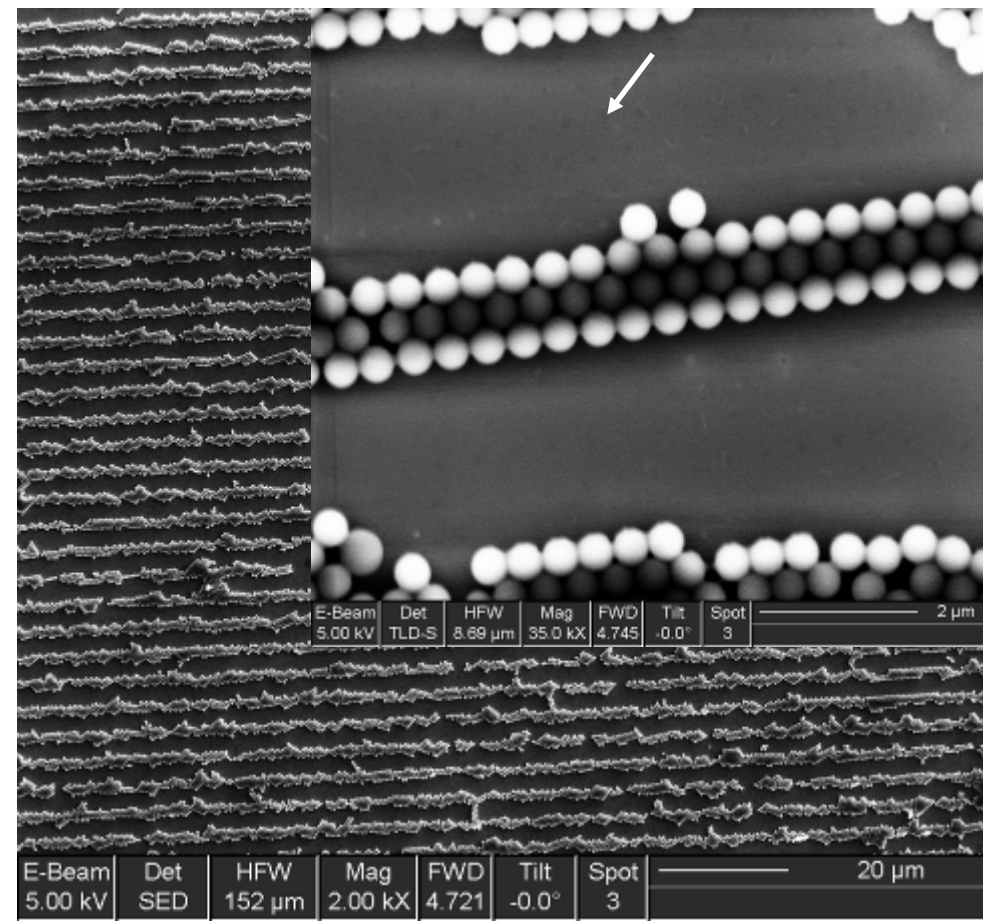
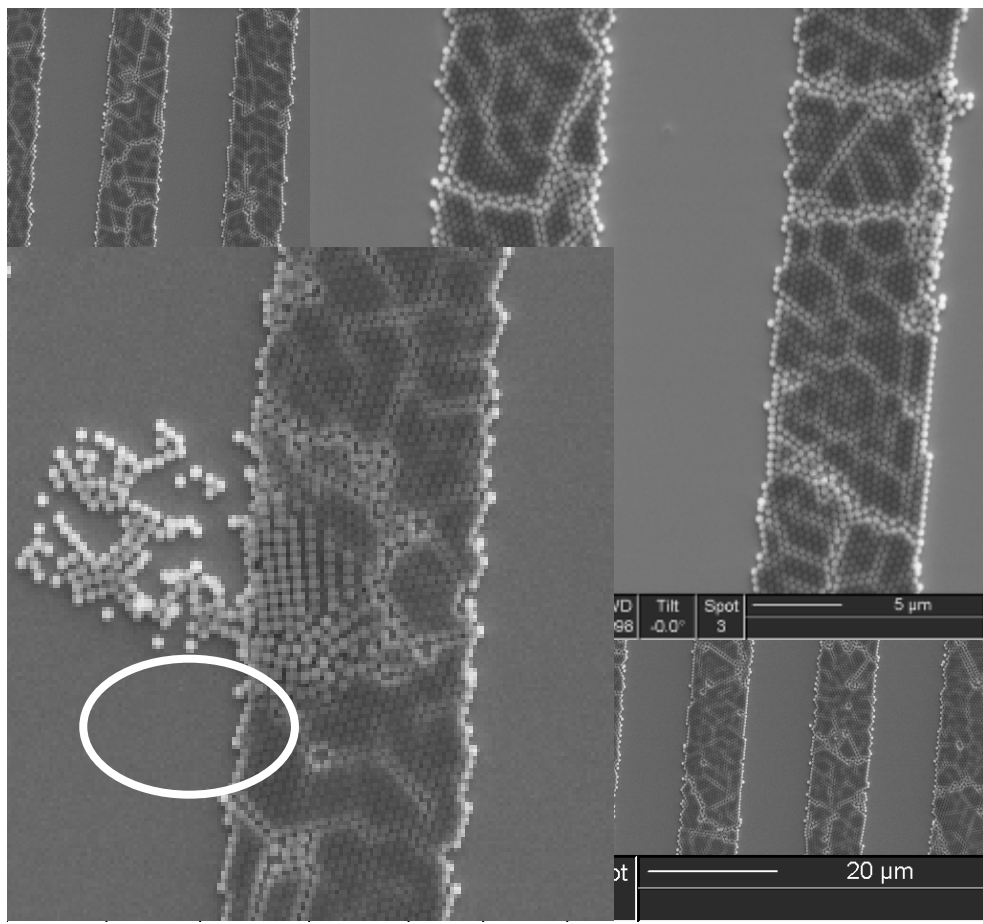
NIL-assisted Microcontact Stripping

PMMA stamps

Stripping routine: 50bar 50 °C

10 μm lines

~2 μm lines



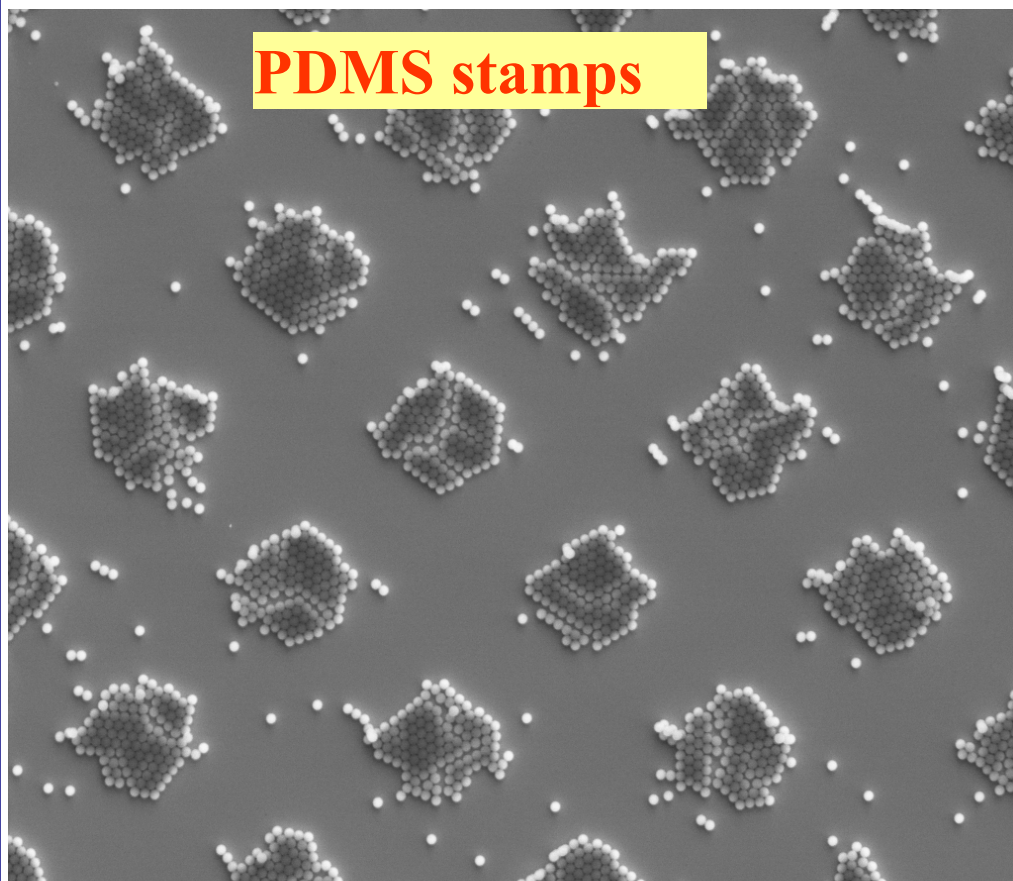
Advantage: larger areas, more homogeneous stripping



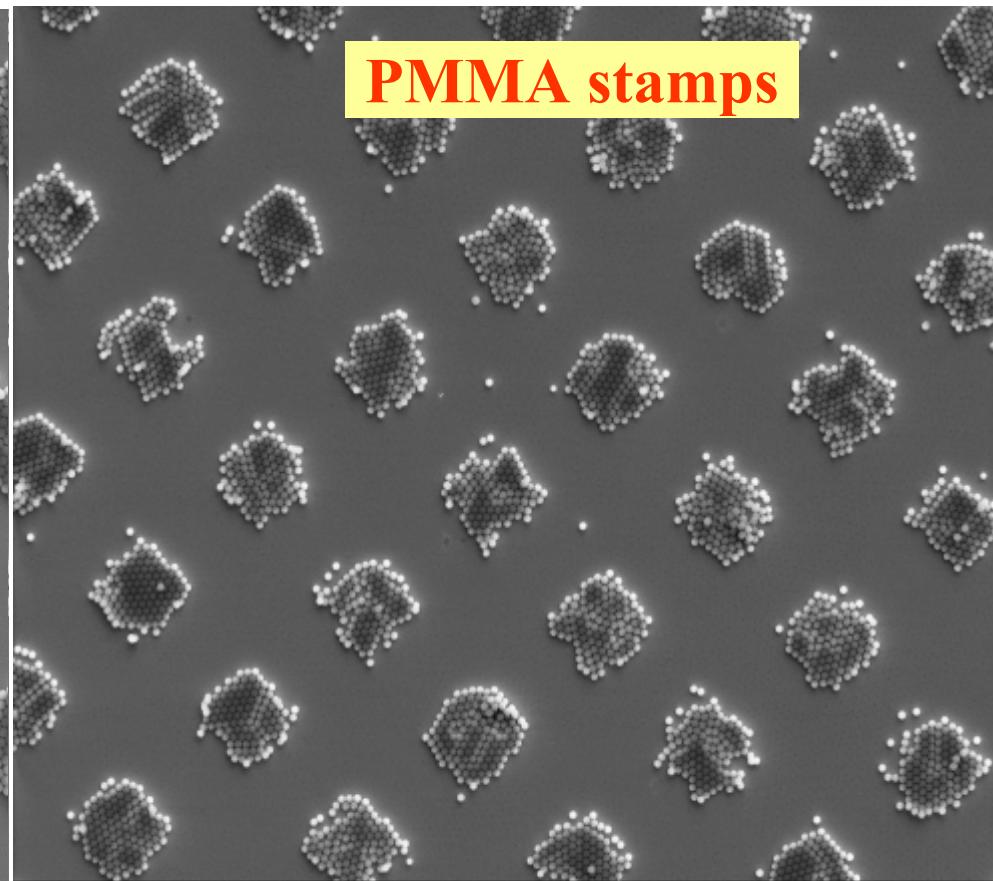
3.2. Patterning of nanoparticles

Conventional PDMS vs NIL-assisted Microcontact Stripping

Stamps with 5 μm holes



PDMS stamps



PMMA stamps

E-Beam	Det	HFW	Mag	FWD	Tilt	Spot	10 μm
5.00 kV	SED	46.8 μm	6.50 kX	4.936	-0.0°	3	

E-Beam	Det	HFW	Mag	FWD	Tilt	Spot	10 μm
5.00 kV	SED	60.8 μm	5.00 kX	5.024	-0.0°	3	



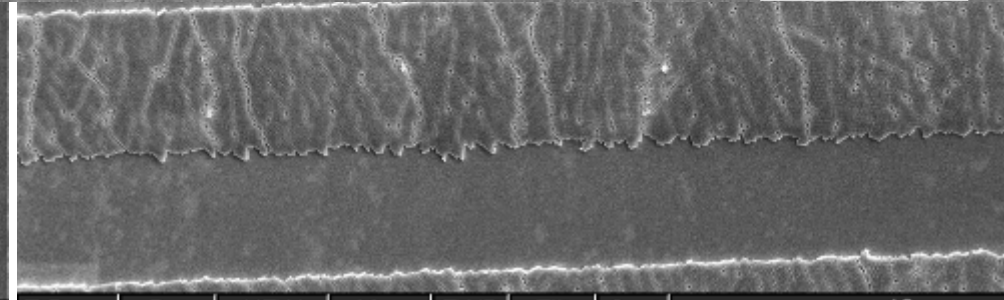
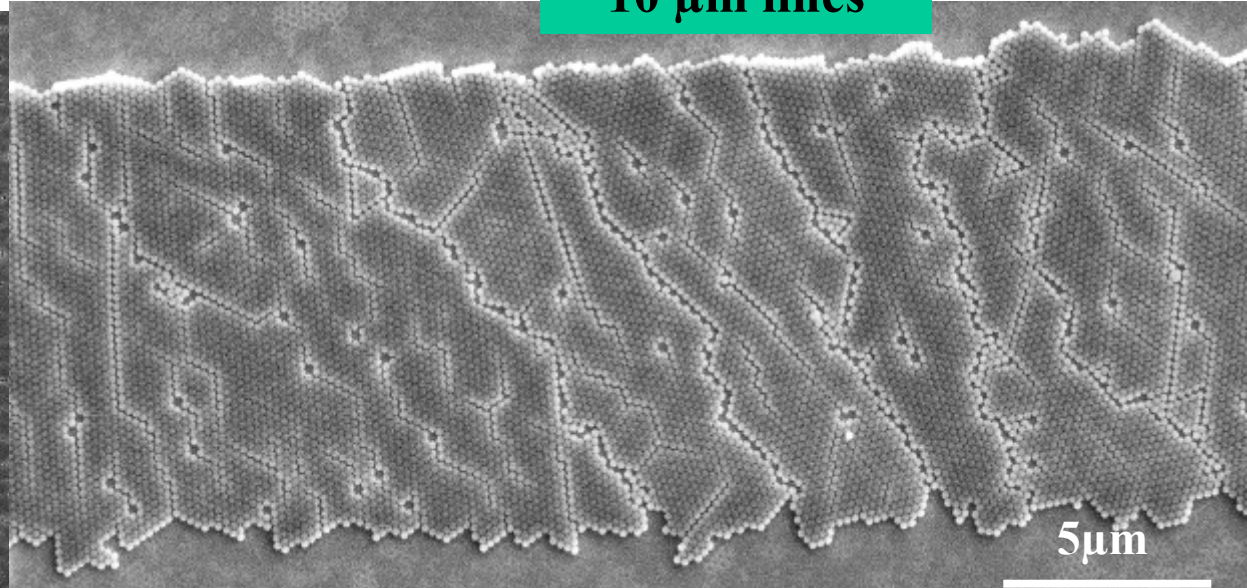
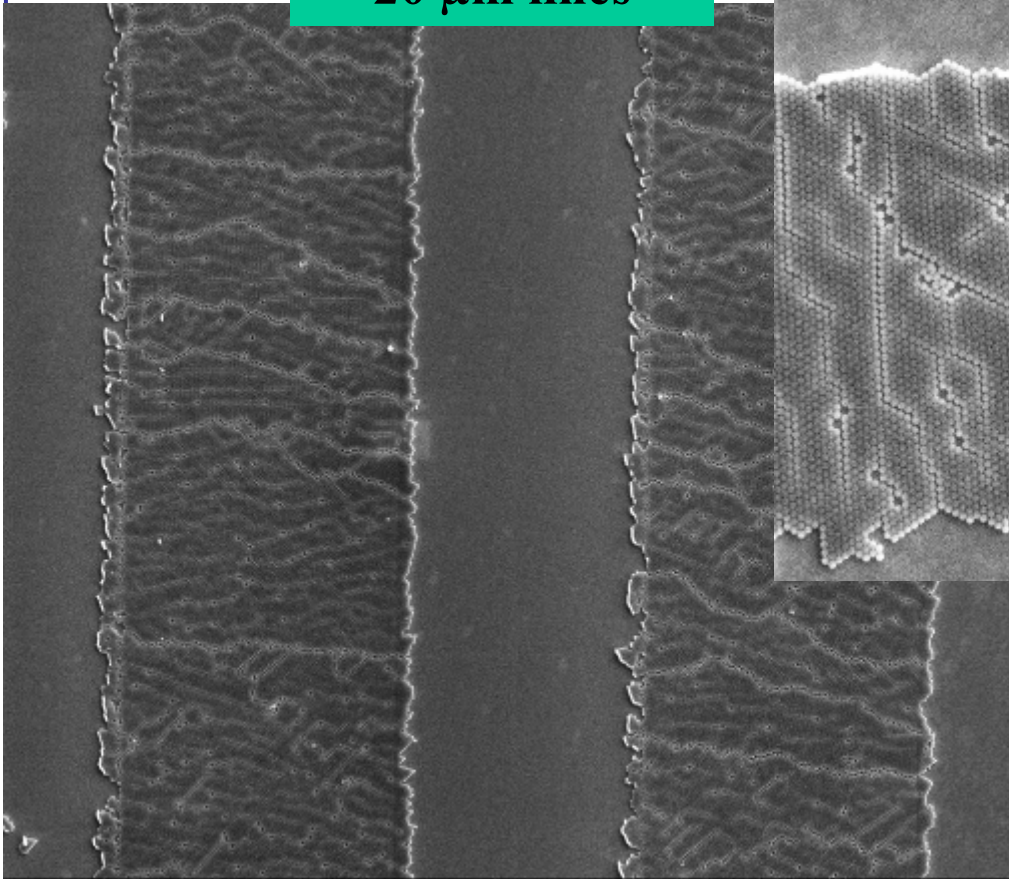
3.2. Patterning of nanoparticles



PMMA stamps – 200nm diameter PS beads

20 μm lines

10 μm lines



E-Beam	Det	HFW	Mag	FWD	Tilt	Spot	10 μm	
5.00 kV	SED	76.0 μm	4.00 kX	5.118	-0.0°	3		

E-Beam	Det	HFW	Mag	FWD	Tilt	Spot	10 μm	
5.00 kV	SED	76.0 μm	4.00 kX	4.986	-0.0°	3		

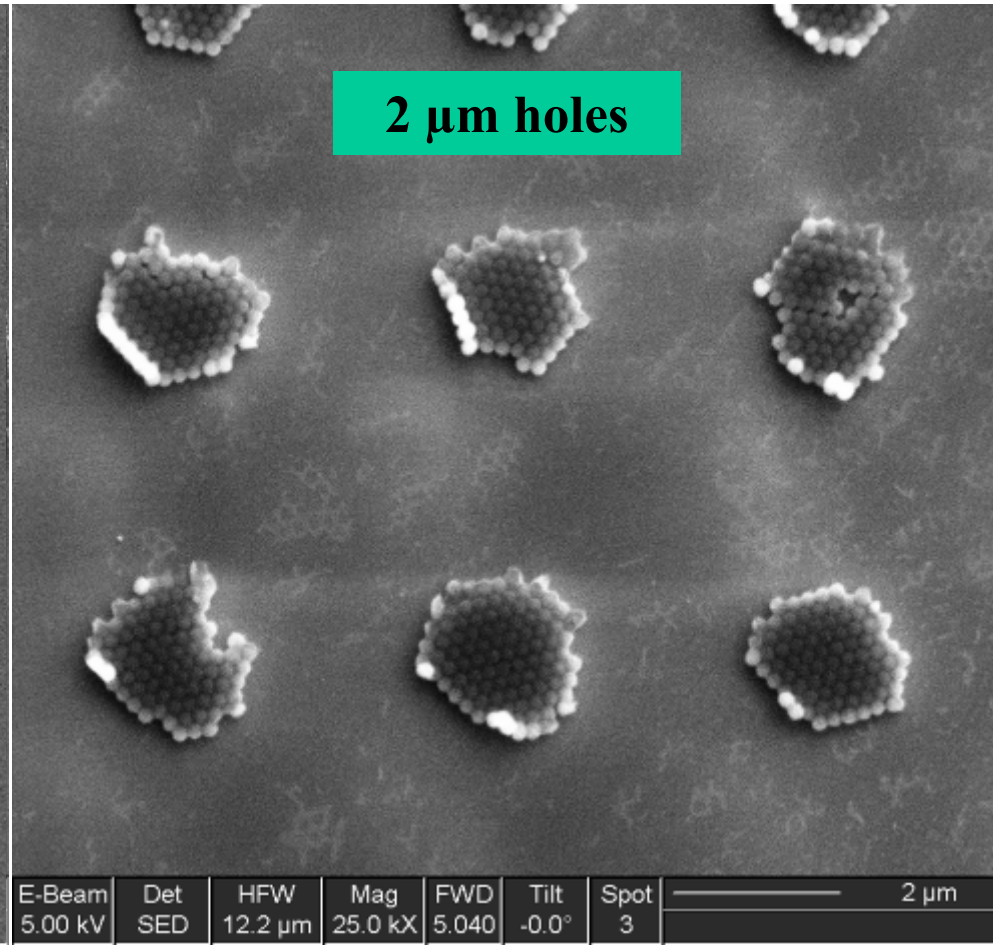
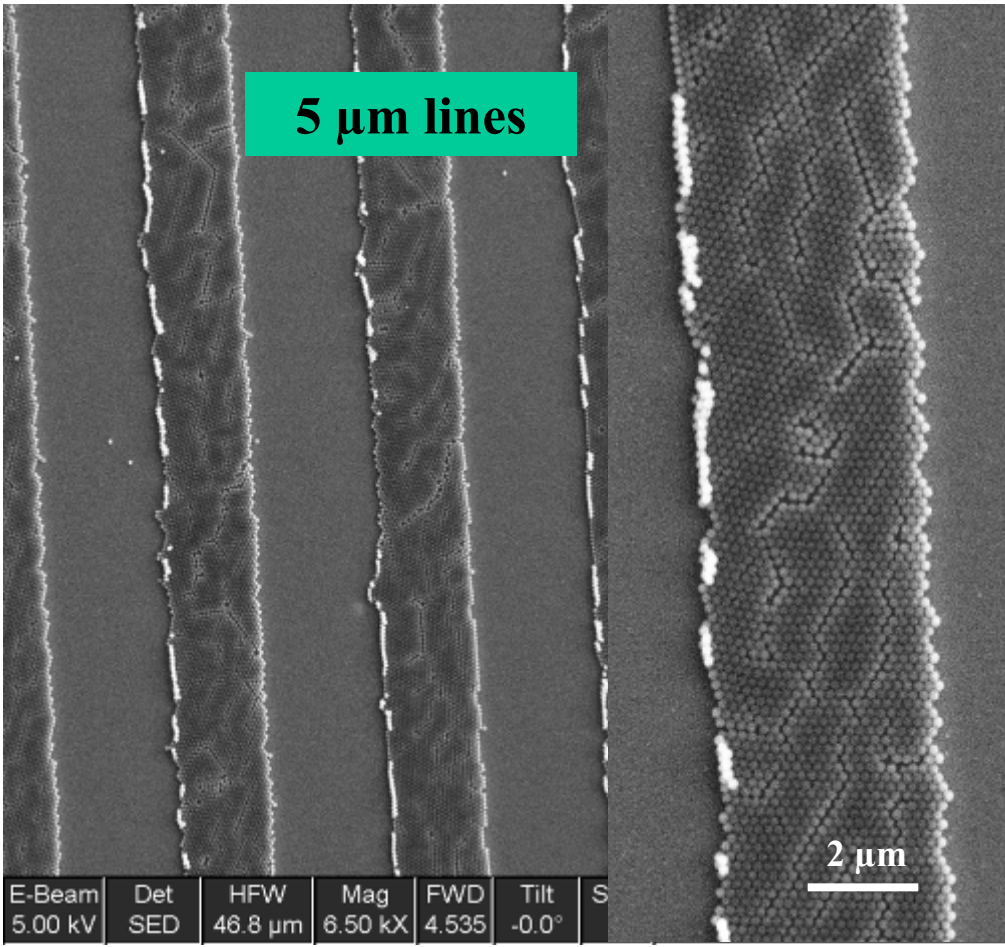


3.2. Patterning of nanoparticles



PMMA stamps – 200nm diameter PS beads

Joint Research Centre

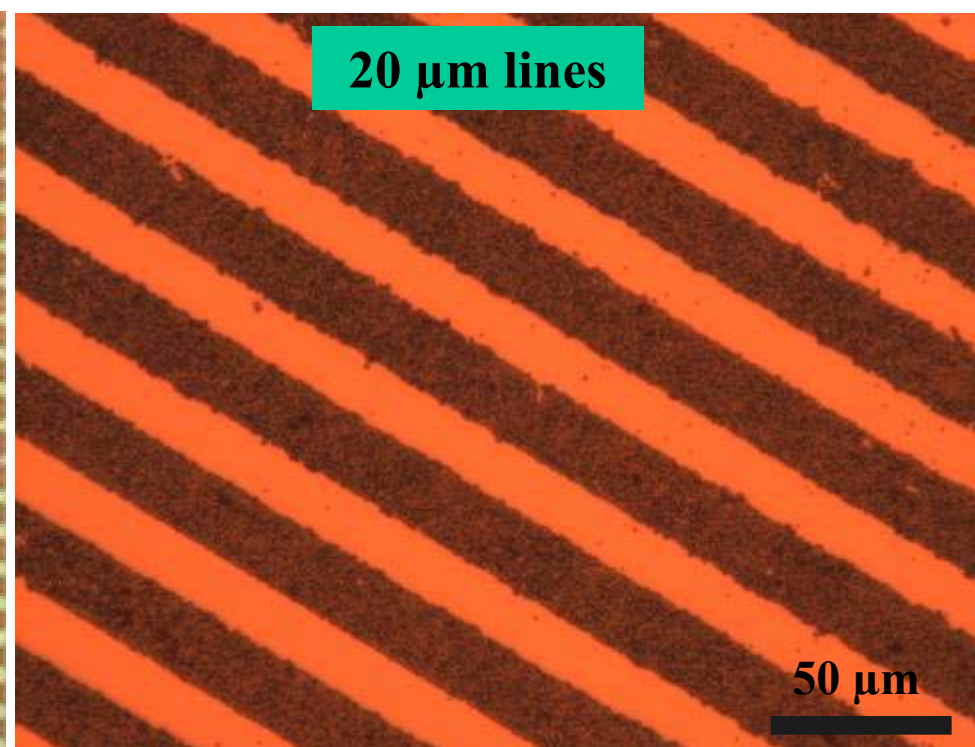
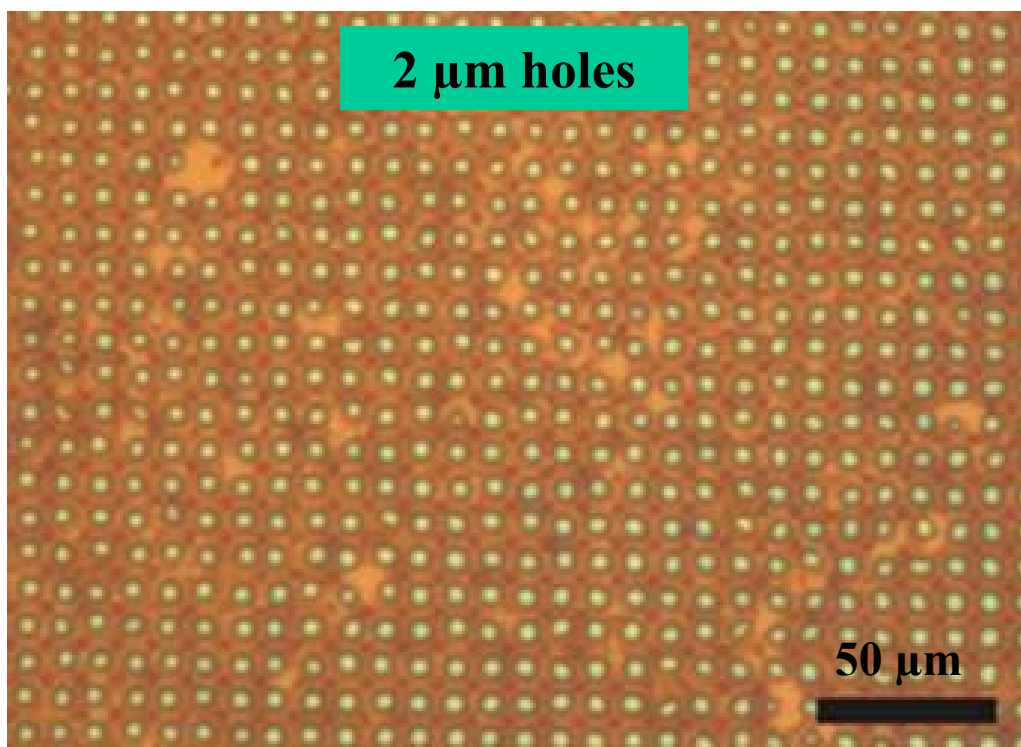




3.2. Patterning of nanoparticles

100nm diameter PS beads
Spin-coated film

500nm diameter PS beads
Langmuir-Blodgett film

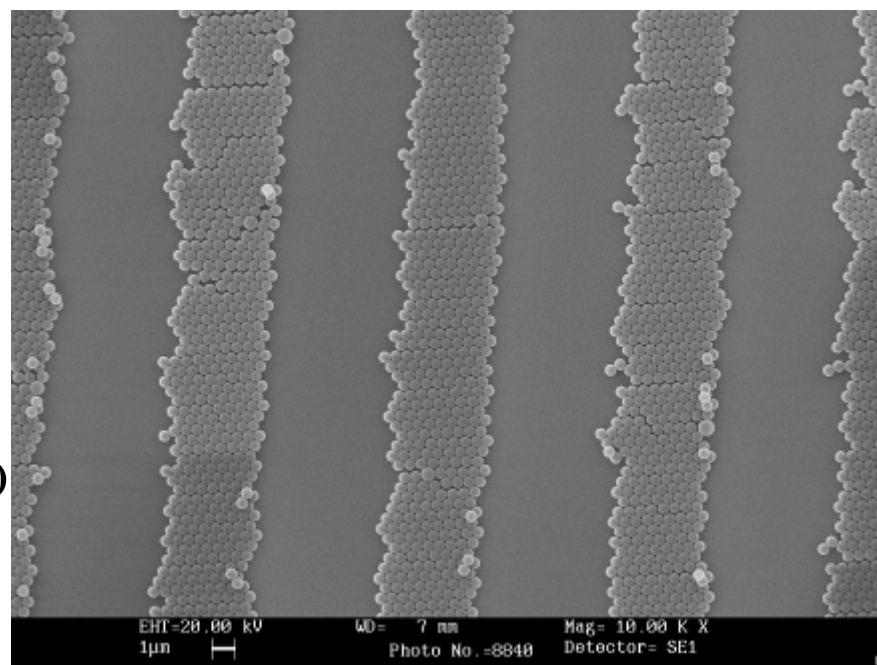
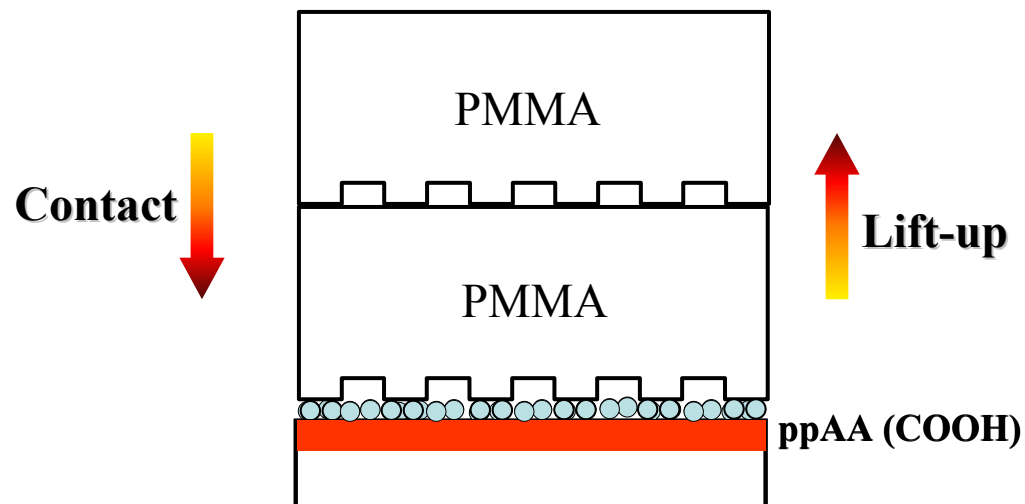




4. Microarrays of fouling nanodomains in non-fouling matrix

Fouling Polymer: Poly Acrylicacid (ppAA), COOH functional

Micropatterned nanobeads

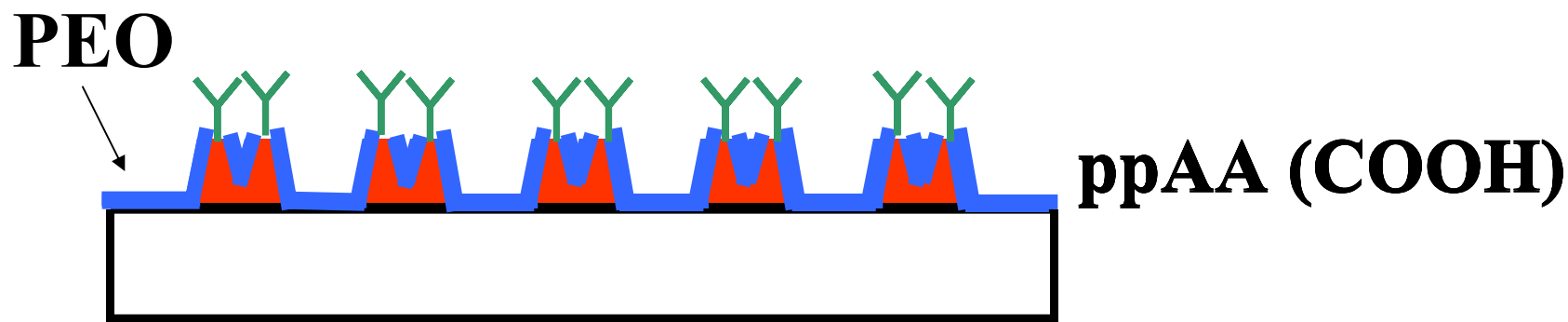




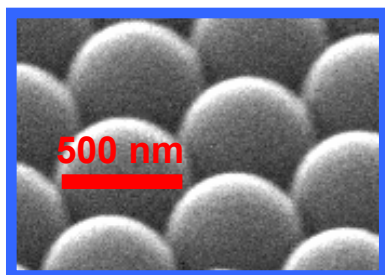
4. Microarrays of fouling nanodots in non-fouling matrix



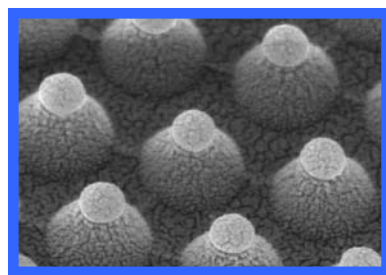
Nanofabrication process



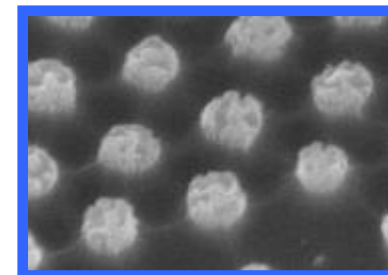
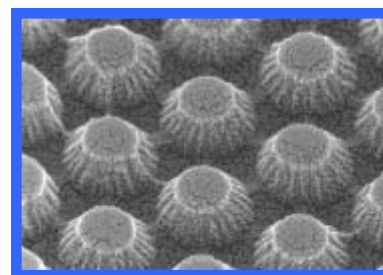
O₂ etching



PEO deposition
+ Lift-off



Protein nanoarray

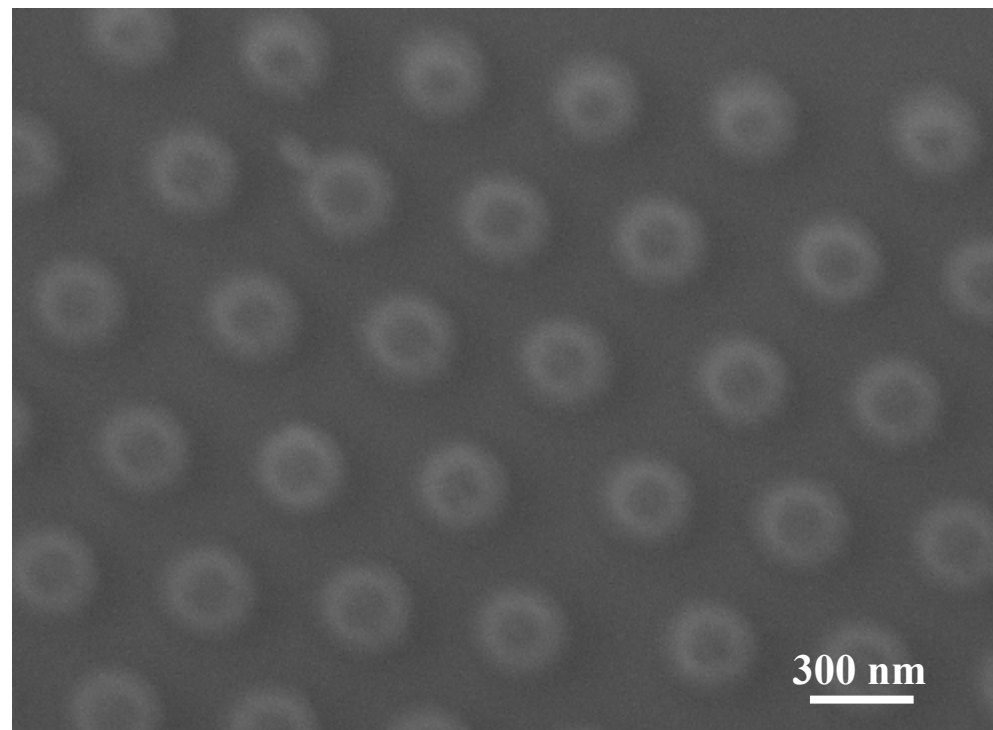
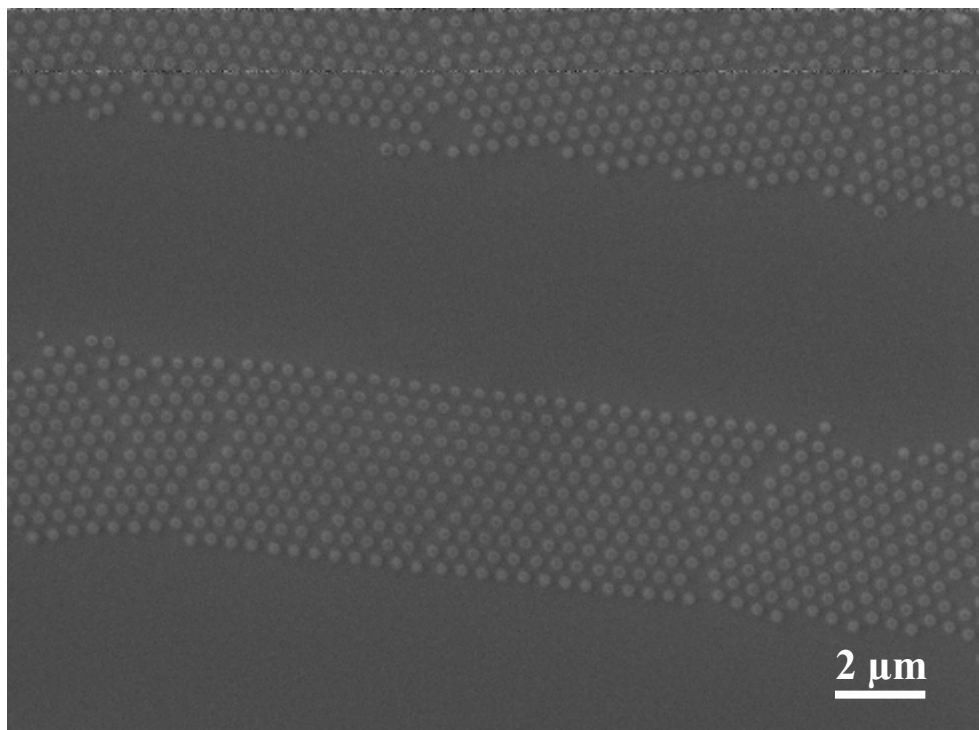


* Valesia et al. *Adv. Func. Mat.*, 2006, 16(9)



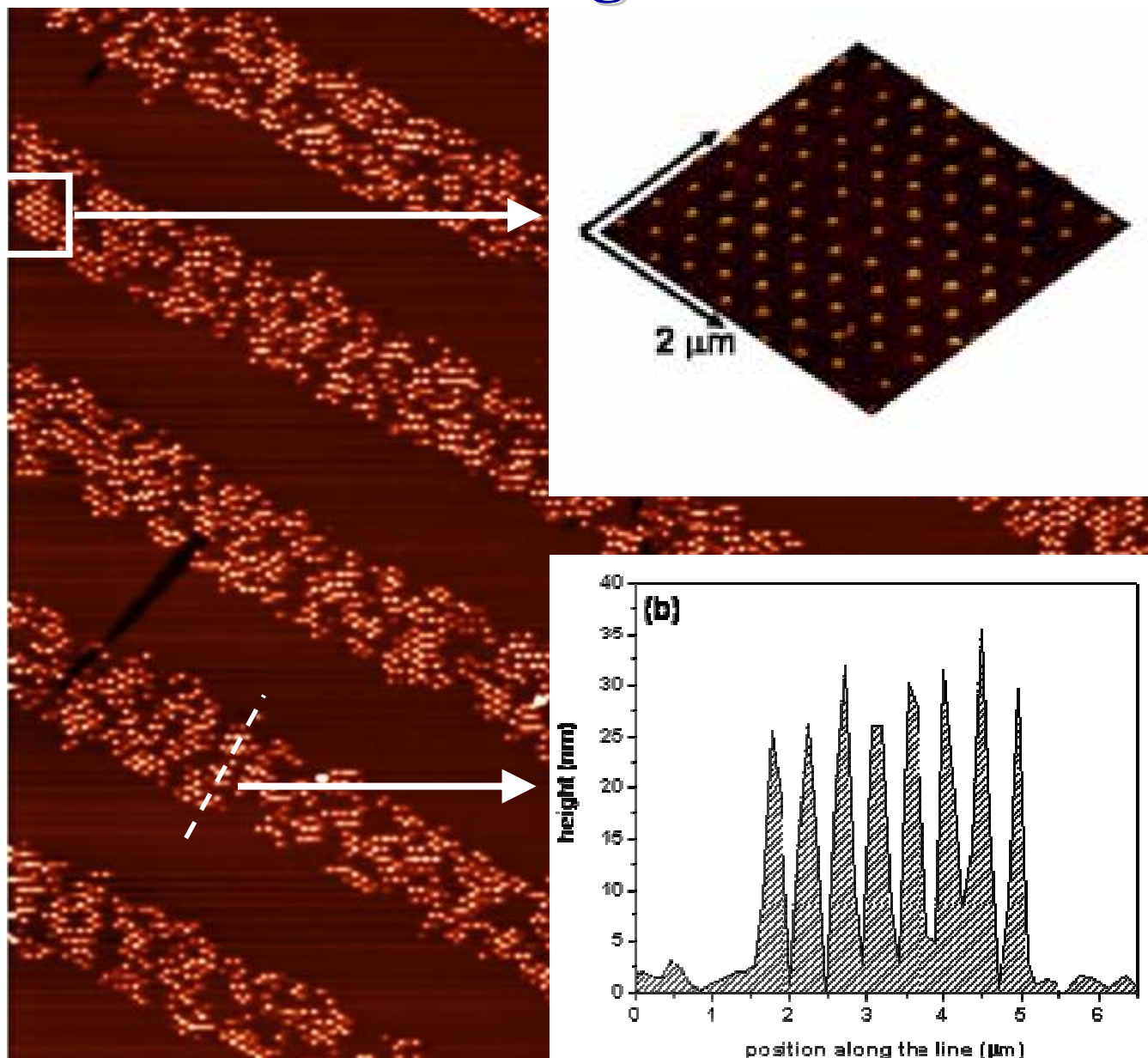
4. Microarrays of fouling nanodots in non-fouling matrix

Nanodomains after etching. 500nm diameter PS beads





4. Microarrays of fouling nanodots in non-fouling matrix





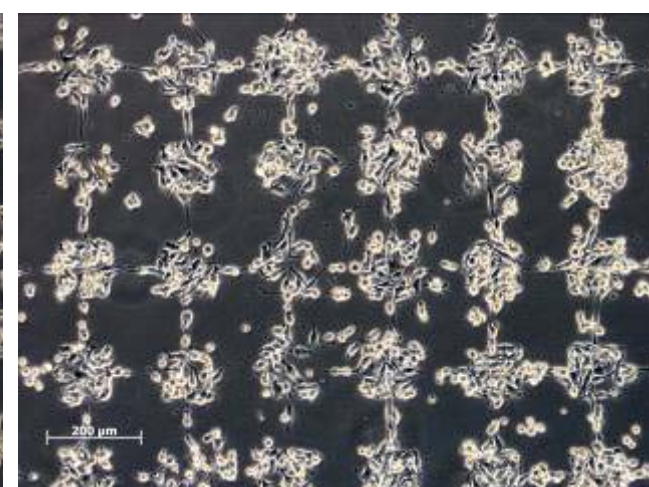
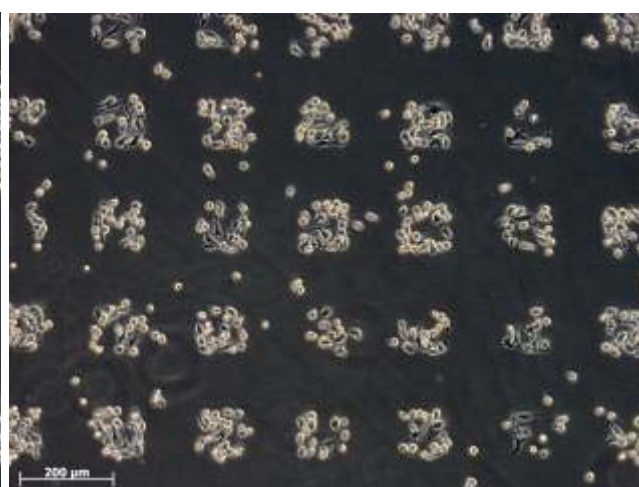
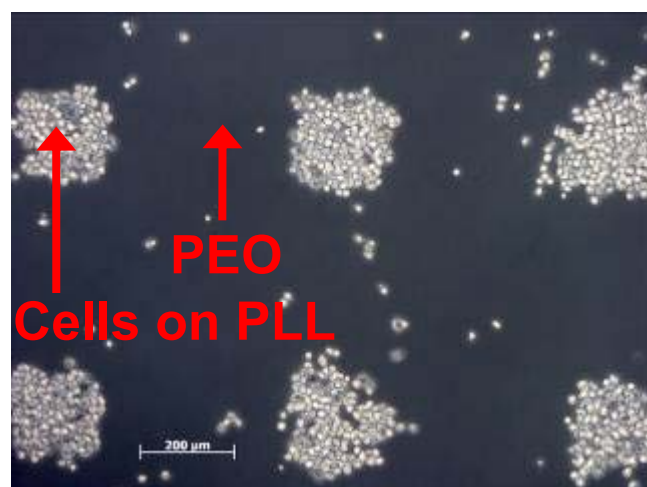
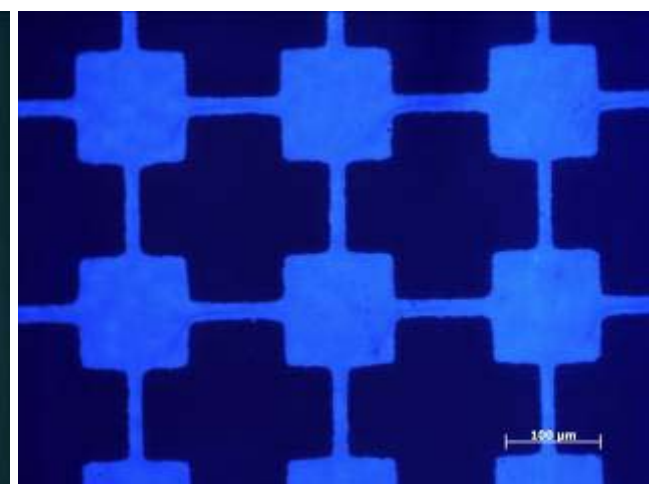
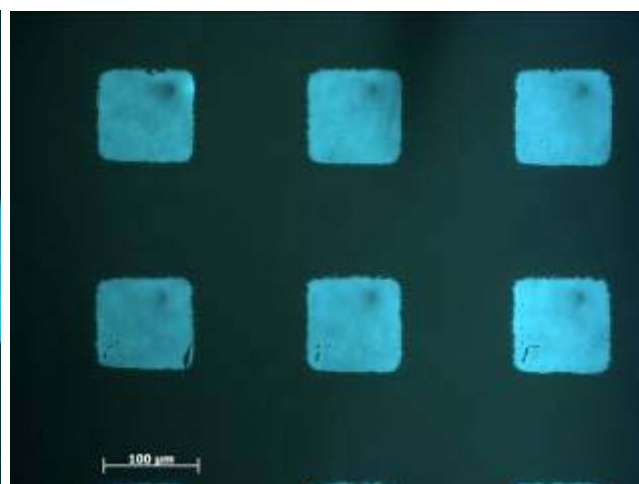
Micro-Patterning by direct printing on antifouling surfaces (MCP)

Designs to study neural stem cell migration and axonal protrusions outgrowth

Migration

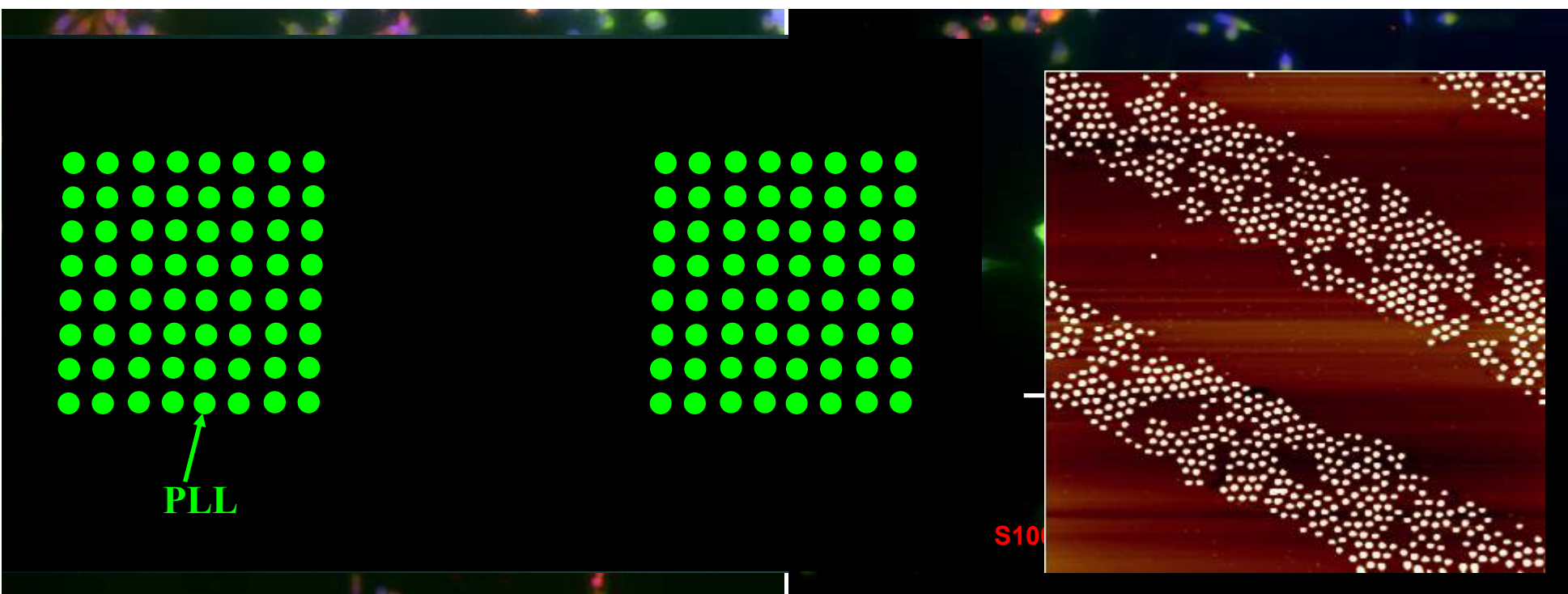


Differentiation





Future applications





5. Conclusions

- **New method for the micro-patterning of nano-beads at large scale**
 - More performant regarding bead-substrate adhesion.
 - High definition of patterned edges
 - Lower bead “contamination” between arrays
 - Highly controllable method possible that can be applied to other non-polymeric particles and substrates

- **Nanoimprint-assisted contact stripping:**
 - Use of homogeneous pressure and temperature to strip nanoparticles using PMMA stamps.
 - Stripping conditions adjustable to the bead-substrate system used.

- **Micro-patterns of PS nano-beads of different diameters and with different level of bead adherence**

- **1st application: Fabrication of surfaces with nanoscale chemical contrast inside the micro-patterns**

- **Other applications:**
 - Study of cell-surface interactions at the nanoscale
 - Fabrication of arrays of photonic crystals



Acknowledgements



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..... **Thank you !**