Advanced Topics in Micro- and Nanomanufacturing

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Directed assembly of nanoparticles

TOP-DOWN MEETS BOTTOM-UP
OPTICAL ASSEMBLY
MAGNETIC ASSEMBLY
ELECTRIC ASSEMBLY
CAPILLARY ASSEMBLY

About myself

Massimo Mastrangeli, PhD
Associate professor
TU Delft, the Netherlands

BSc 2003
MSc 2005
Pisa

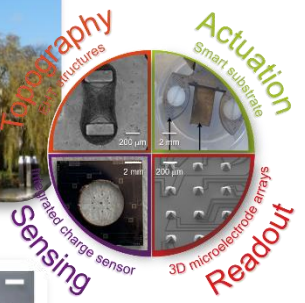
PhD (→`10)
Leuven

Post-Doc (→`13)
Lausanne

Sen. Sci (→`15)
Bruxelles

Res. Ass. (→`17)
Stuttgart

Associate professor
Delft

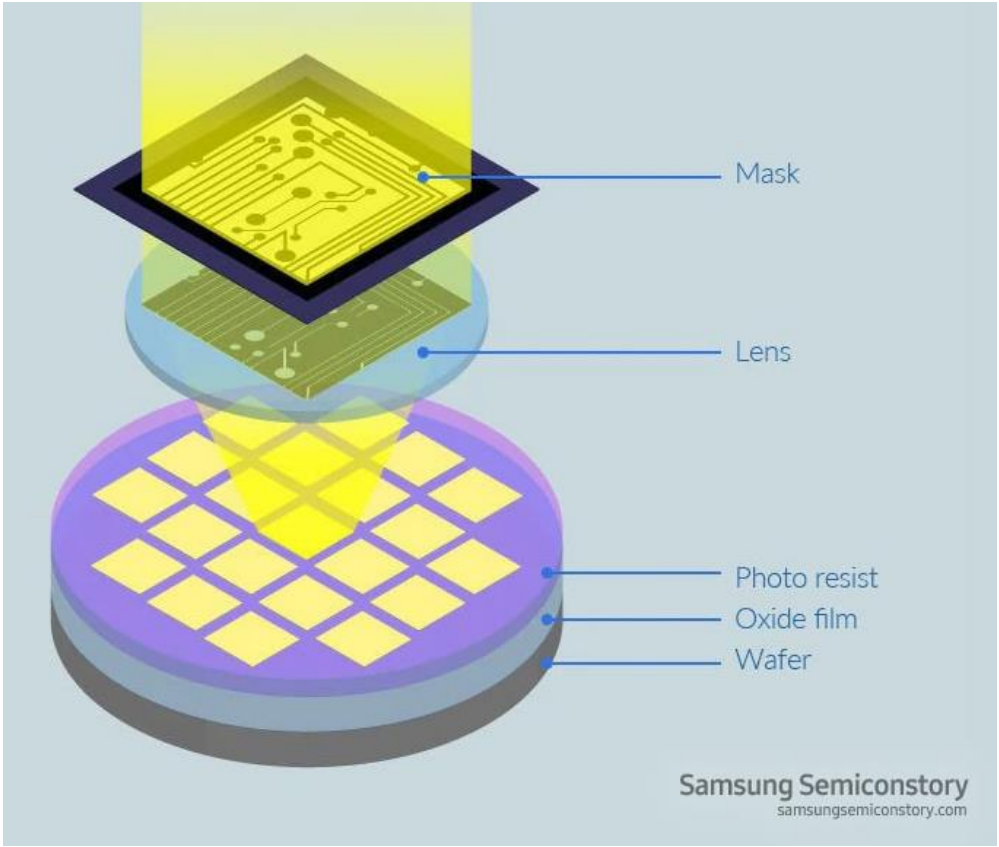


Beyond top-down micro/nanofabrication

Lithography

- ✓ Ultimate resolution
- ✓ Wafer-level

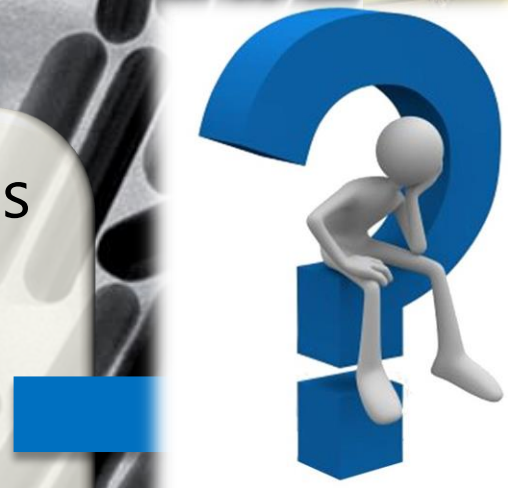
- × Pre-formed layers have low crystalline quality
- × Integration of high-quality materials limited



From nanoparticles to nanodevices

Unique properties of NPs

- Metal, oxide, core/shell
- Carbon-based
  - Graphene
  - Nanotubes
  - Nanodiamonds
- Quantum dots
- Nanowires



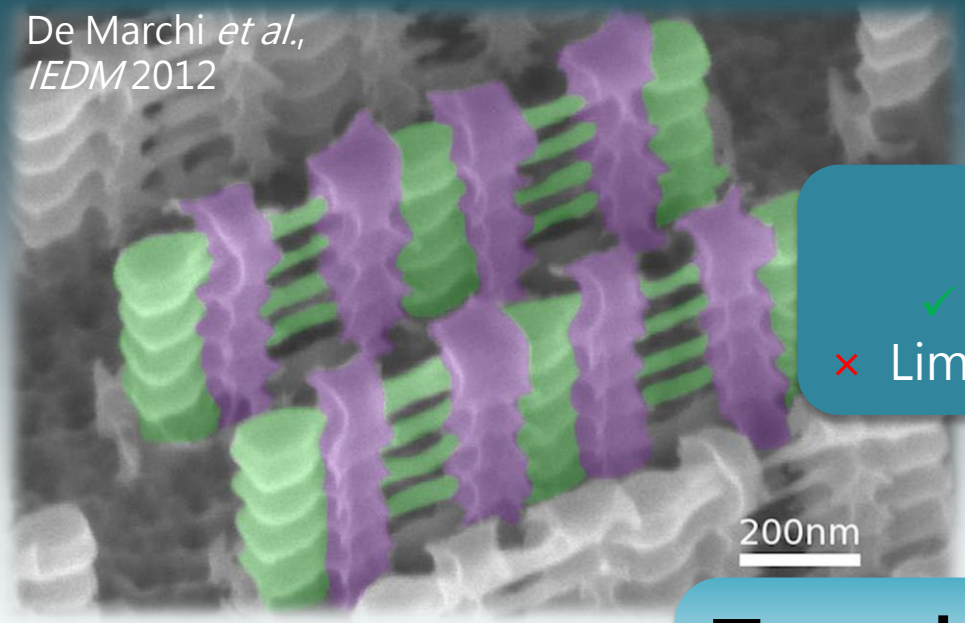
NP-based applications

- Surface-enhanced spectroscopy
- CNT/NW-based FETs
  - Sensor decoration
  - Plasmonic devices
  - Quantum systems
  - Interconnections
  - Metamaterials

How to build devices out of nanoparticles?

Mayer *et al.*, *Farad. Discuss.* 2016

De Marchi *et al.*,
IEDM 2012

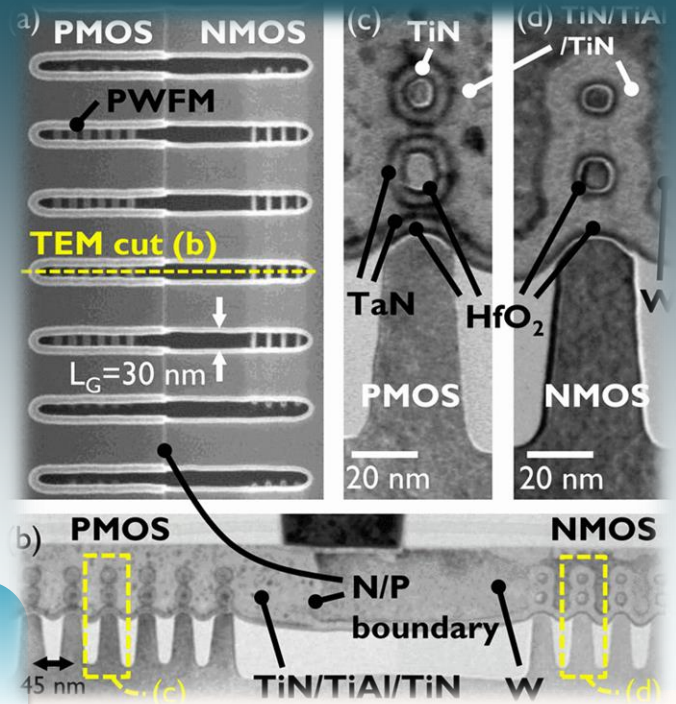


Top-down

✓ Ultimate spatial accuracy

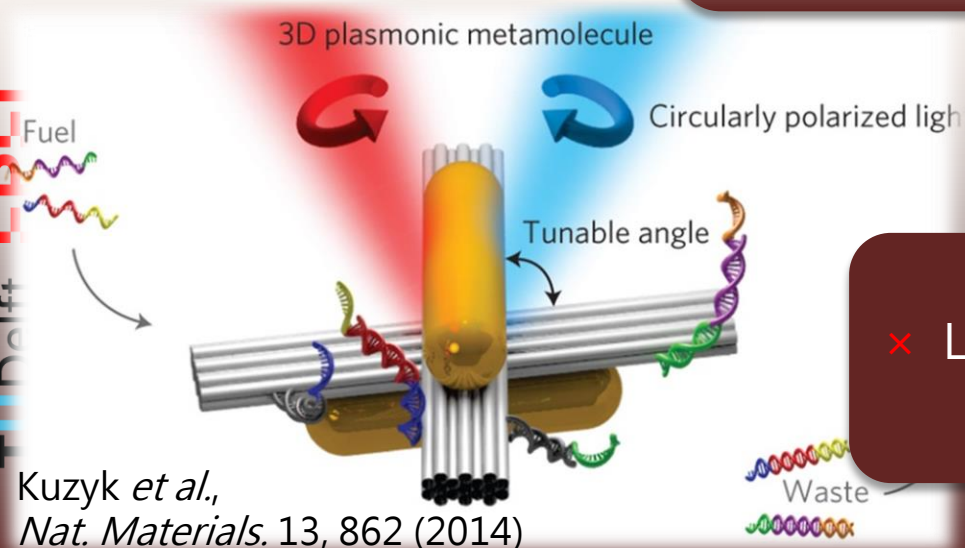
× Limited material choice & quality

H. Mertens *et al.*,
IEDM 2016



Top-down & bottom-up?

Assembly of chemically synthesized NPs over lithographically patterned substrates

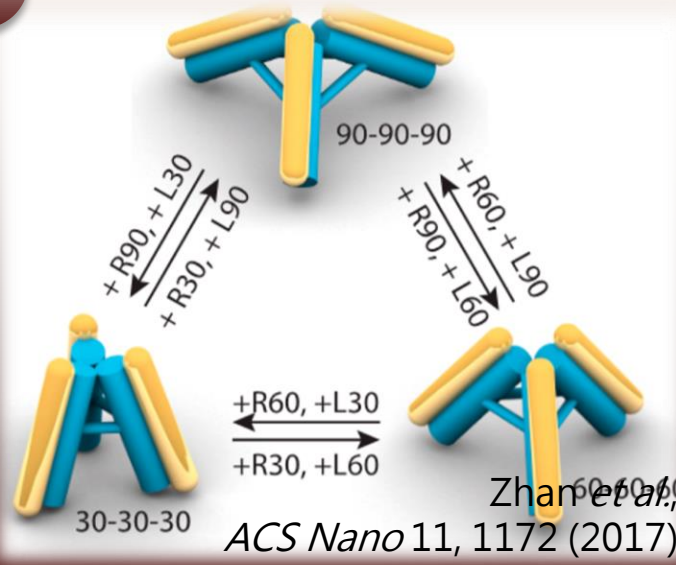


Kuzyk *et al.*,
Nat. Materials. 13, 862 (2014)

✓ Superior NP quality

× Limited morphology control

Bottom-up

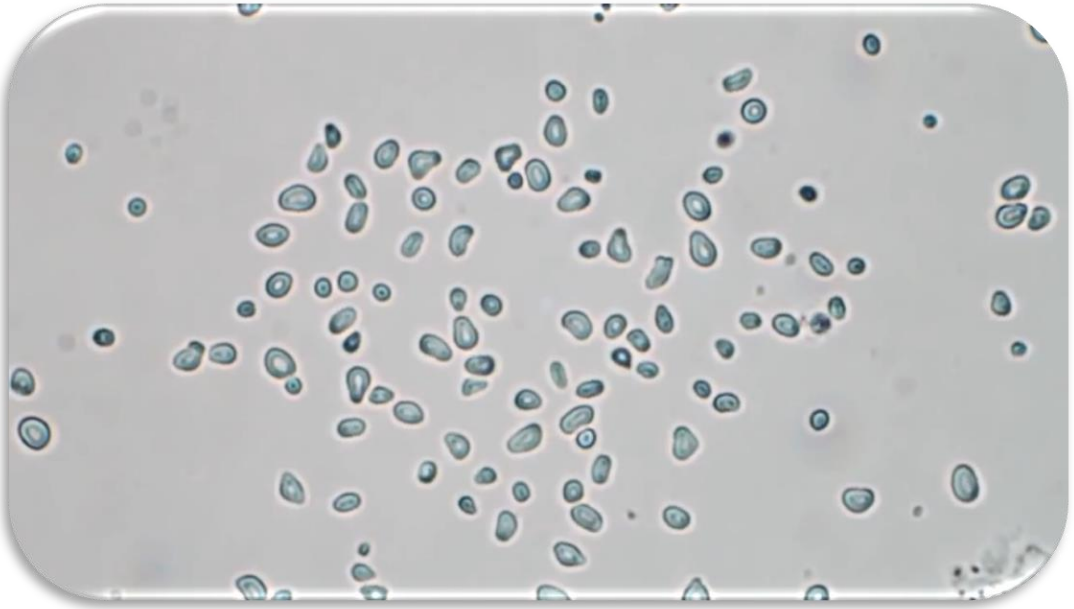


Zhan *et al.*,
ACS Nano 11, 1172 (2017)

Eppur si muove: Diffusion

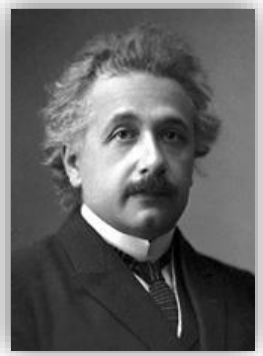
Robert Brown
(1827)

$$\frac{\langle x^2 \rangle}{2t} = \boldsymbol{D} = \mu k_B T = \frac{RT}{6\pi\eta r N_A}$$



[source: Y. Y. Kiat`s YouTube channel]

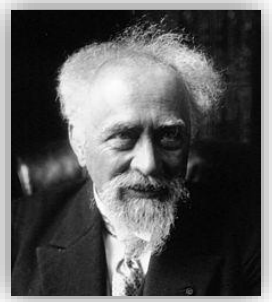
Pollen grains in water



Albert Einstein
(1905)

$$J = -D\boldsymbol{\nabla} c \qquad \text{Fick`s 1st law}$$

$$\frac{\partial c}{\partial t} = D\boldsymbol{\nabla}^2 c \qquad \text{Fick`s 2nd law}$$



Jean Perrin
(1908)

Paul Langevin
(1908)

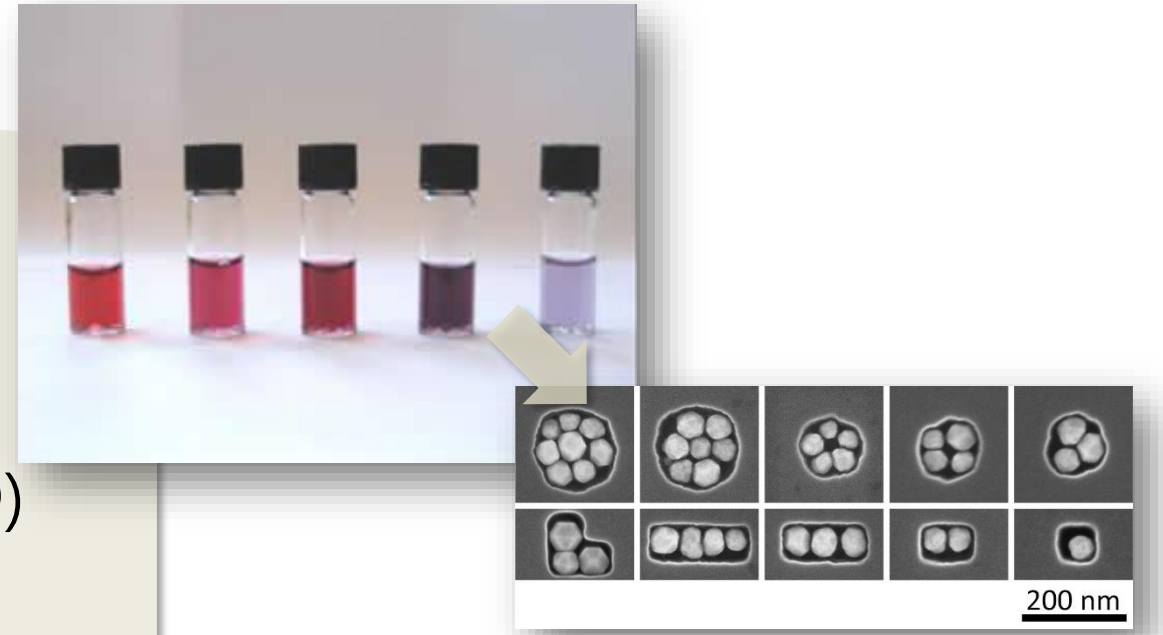
Norbert Wiener
(1923)

Overwriting diffusion: fields & receptors

- **Self-assembly**:
  organizing matter by means of interactions inherent to the components
  - Weak, short-range forces
- **Directed assembly**:
  adding biases (directed motion) and pre-set spatial targets (receptors) to coordinate the (self-)assembly of organized structures
  - Longer-range order

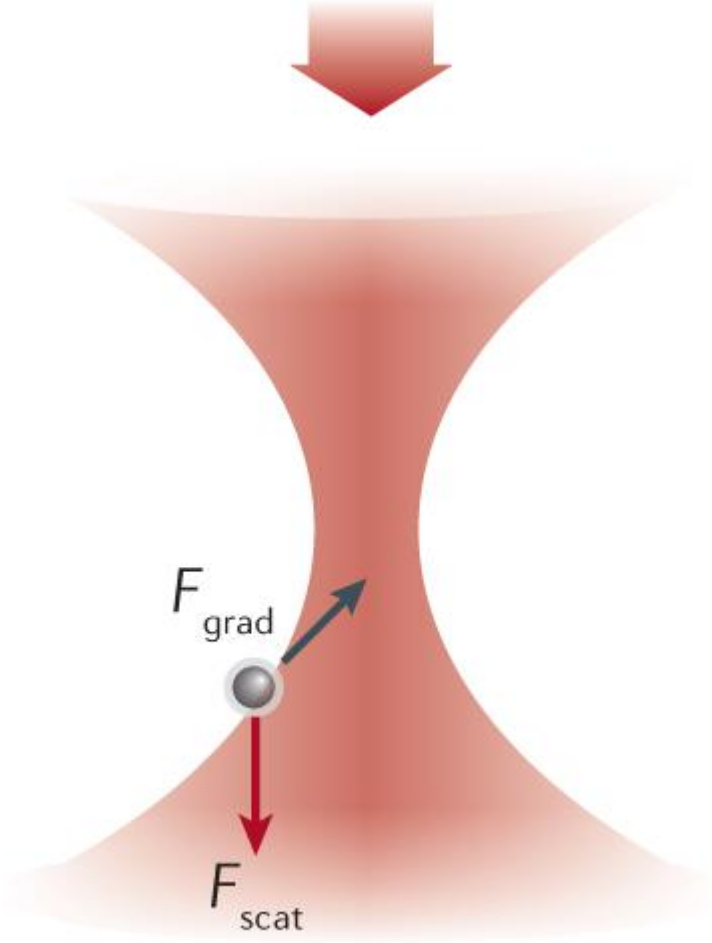
Confinement & templating

- Dimensionality
  - From suspension… (3D)
    to substrate… (2D)
    to trap… (1D→0D)
- Degrees of freedom
  - From 6 to 0
- Non-interacting particles
  - $\Delta H \approx 0 \rightarrow \Delta G \approx -T\Delta S$

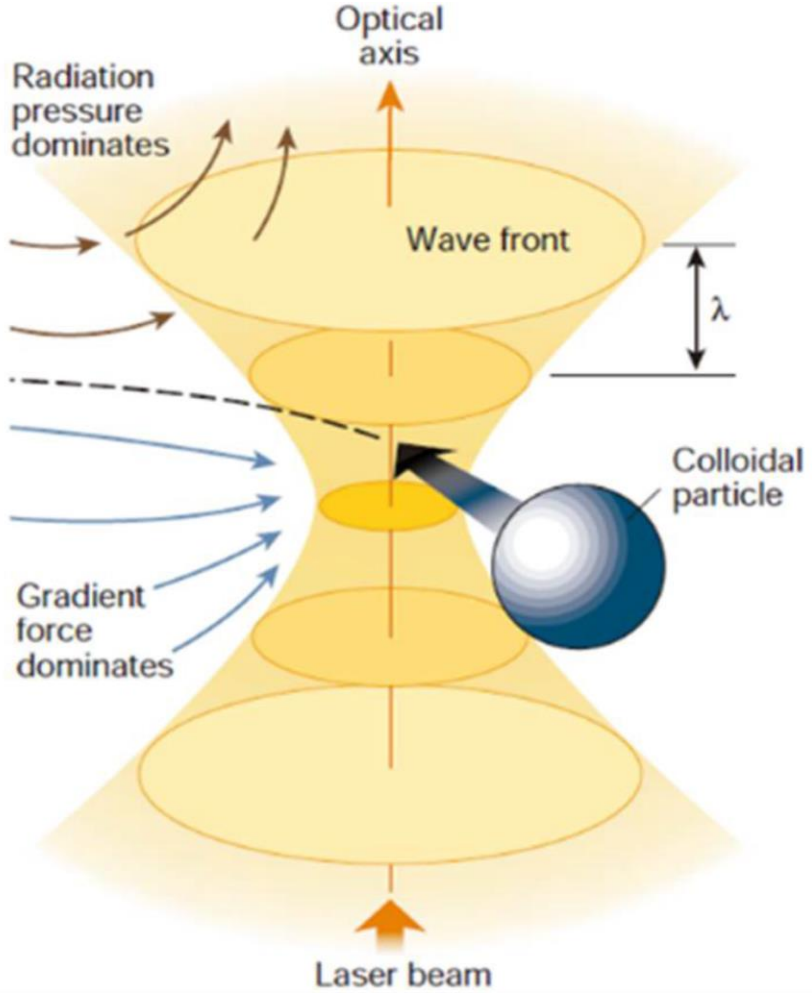


Assembly as **spatial search** problem

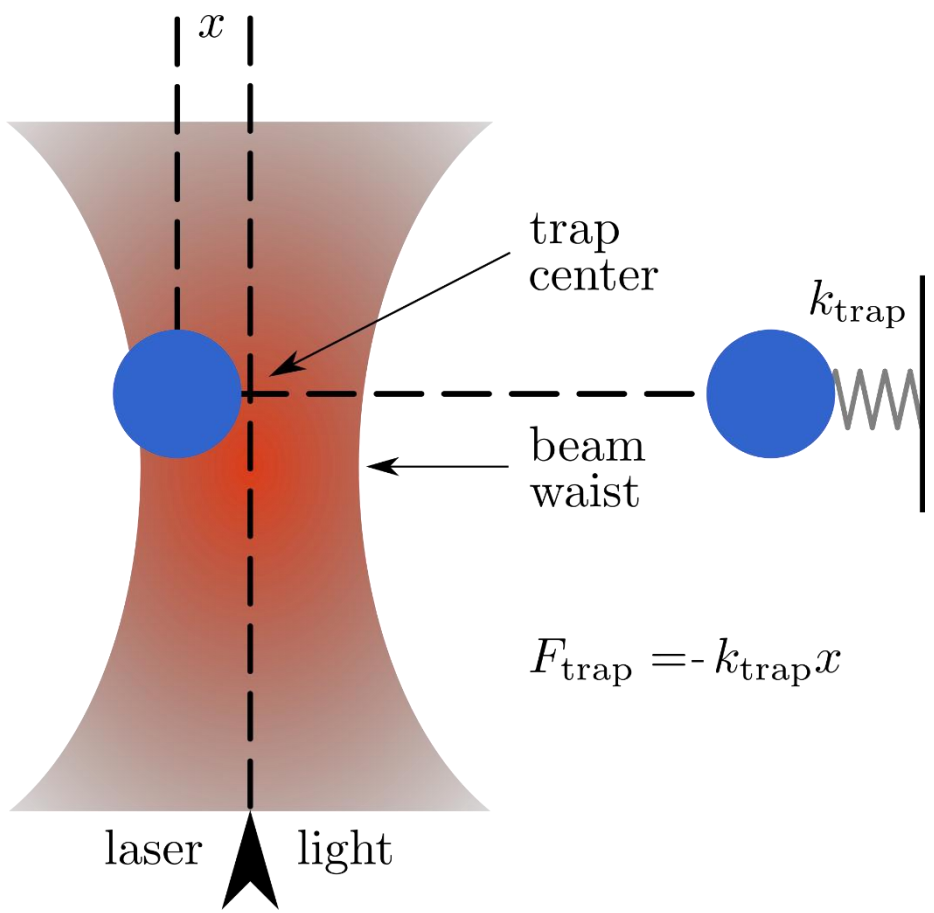
Optical manipulation

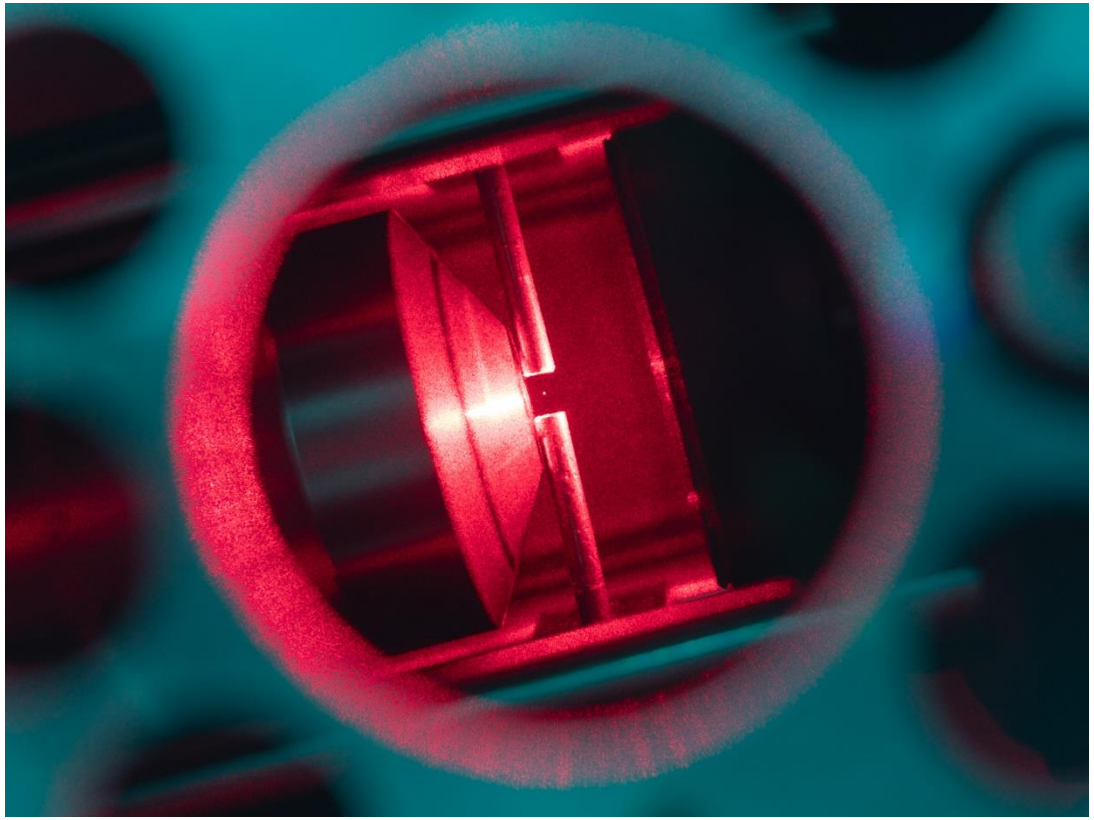


Bustamante *et al.*,
Nat. Rev. Method Primers (2021)

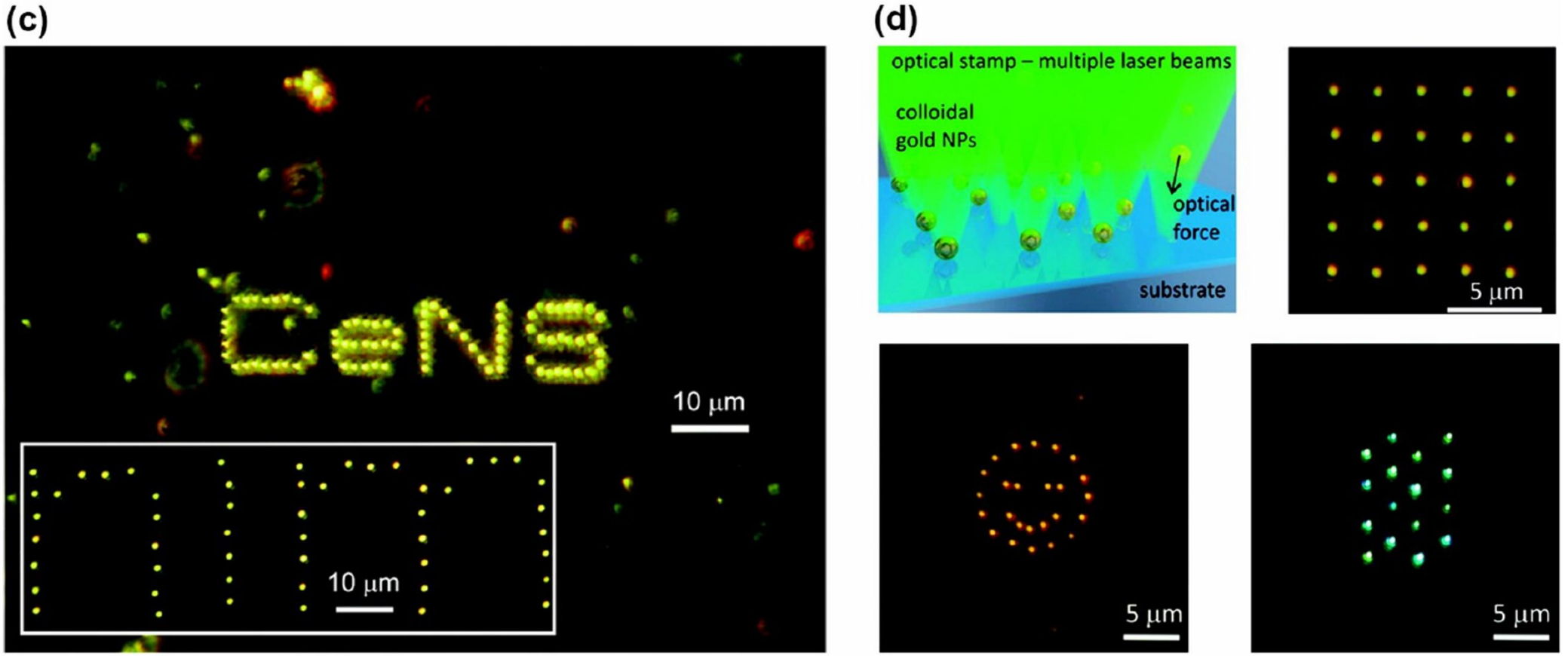


Optical tweezing



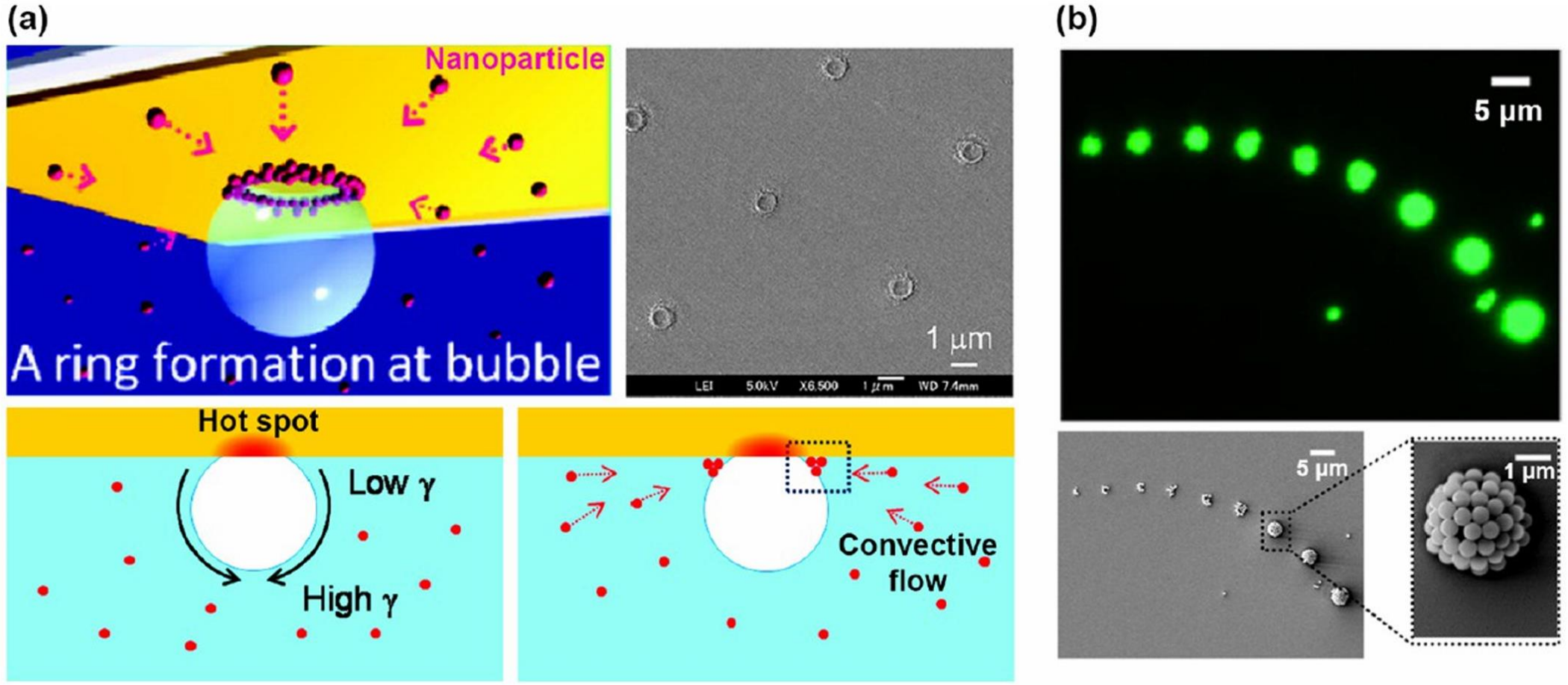


Optical printing



Chai *et al.*, *ACS Nano* 16, 17641-17686 (2022)

Bubble printing



Chai *et al.*, *ACS Nano* 16, 17641-17686 (2022)

Magnetophoretic assembly

- Magnetic force

$$F_{mag} = \frac{V_p(\chi_p - \chi_m)}{\mu_0}(B \cdot \nabla)\mathrm{B}$$

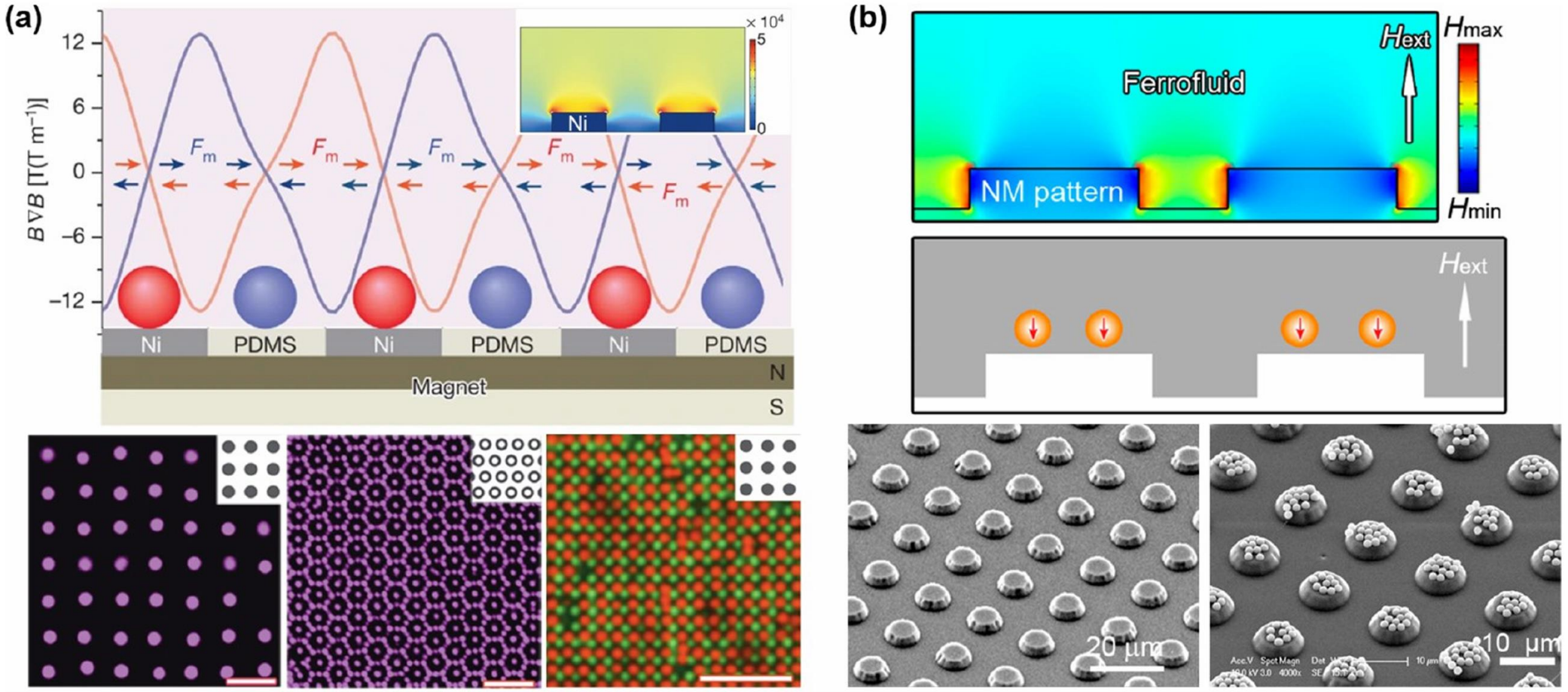
V_p particle volume

μ_0 free space permeability

B magnetic flux density

χ_* susceptibilities

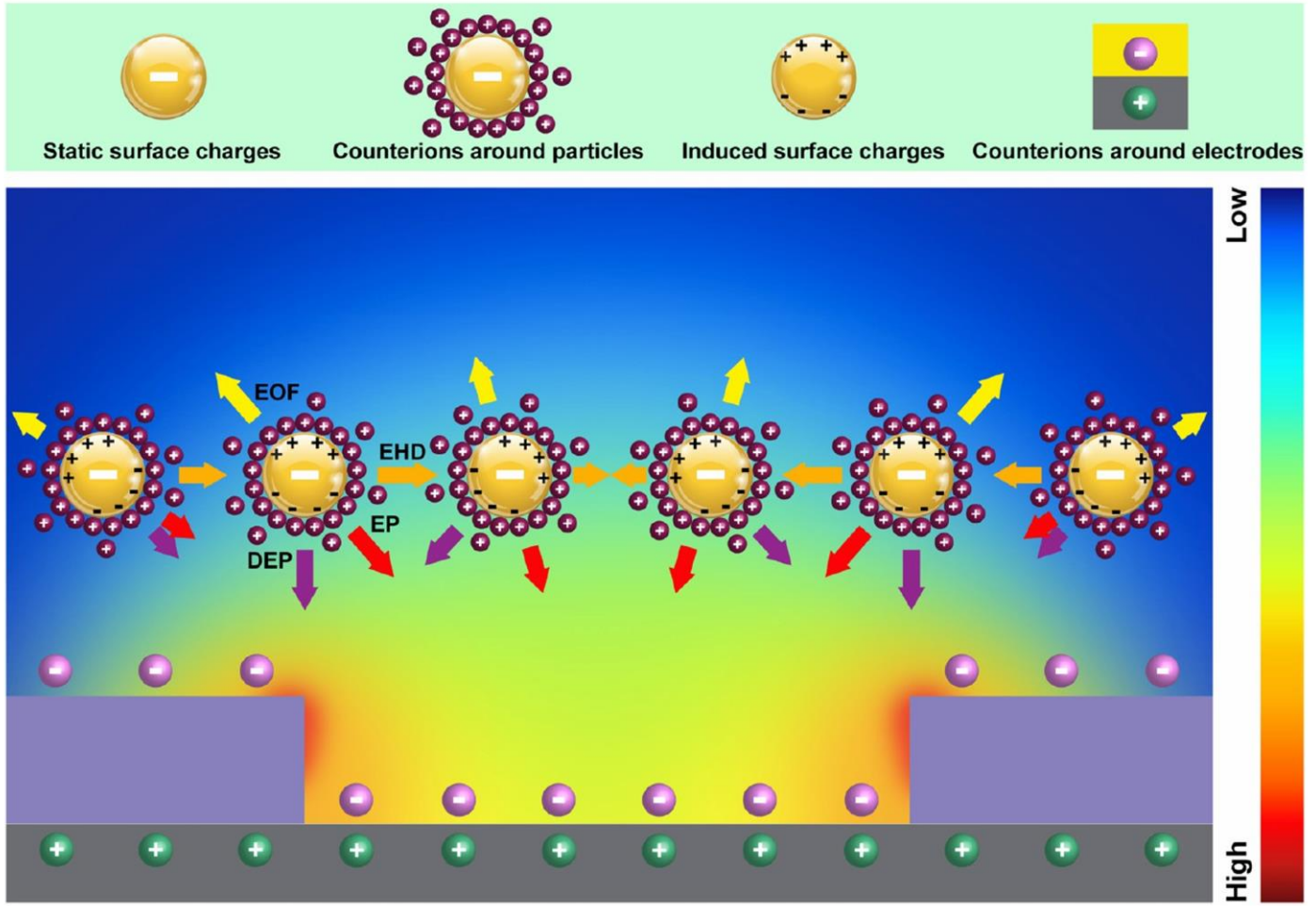
Magnetophoretic assembly



Chai *et al.*, *ACS Nano* 16, 17641-17686 (2022)

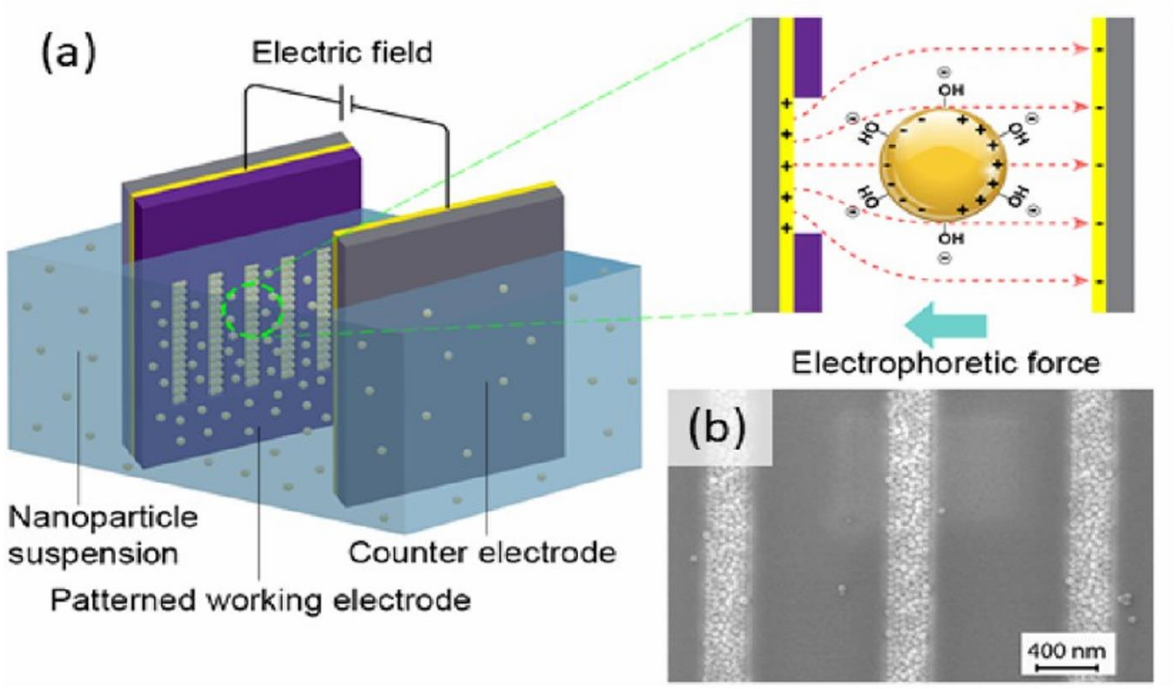
Particles and charges

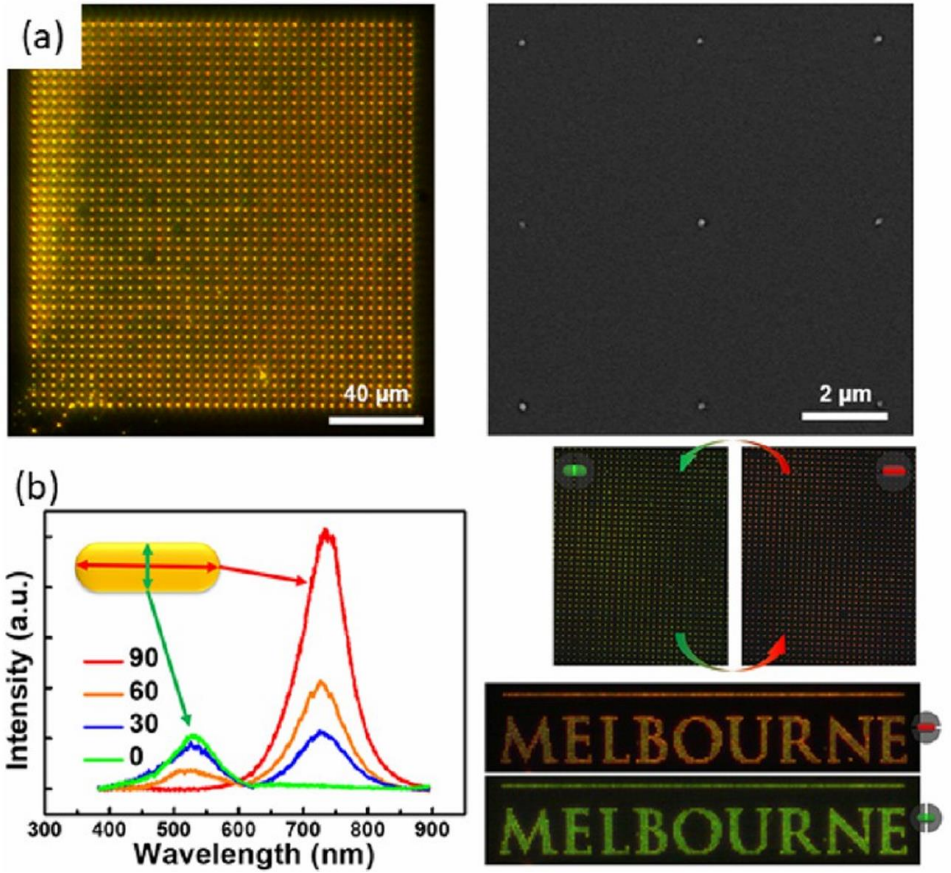
- Electric double layer (EDL)
- Induced charge (polarization)
- DC vs AC
- Fluid drag



Chai *et al.*, *ACS Nano* 16, 17641-17686 (2022)

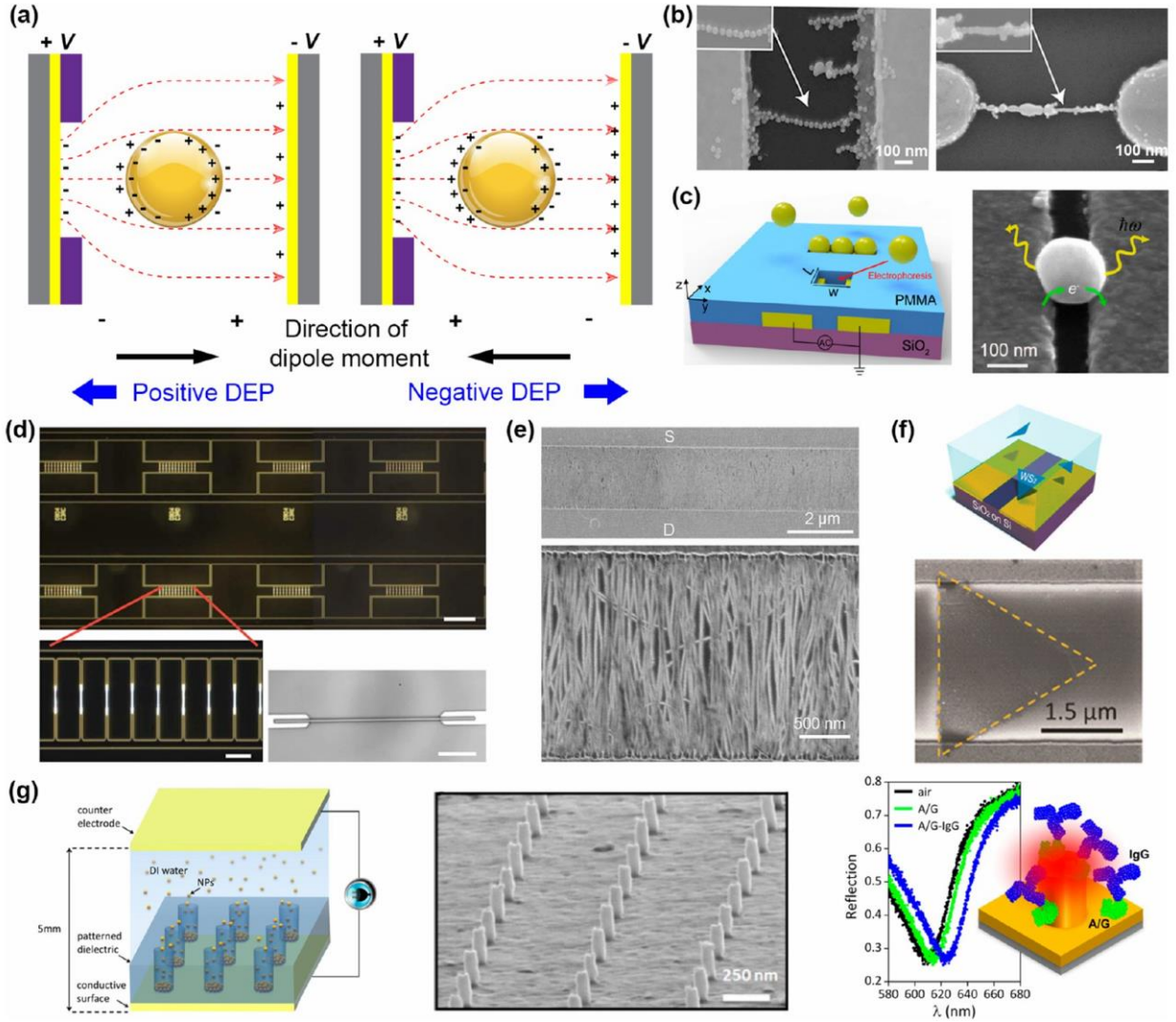
Electrophoretic assembly





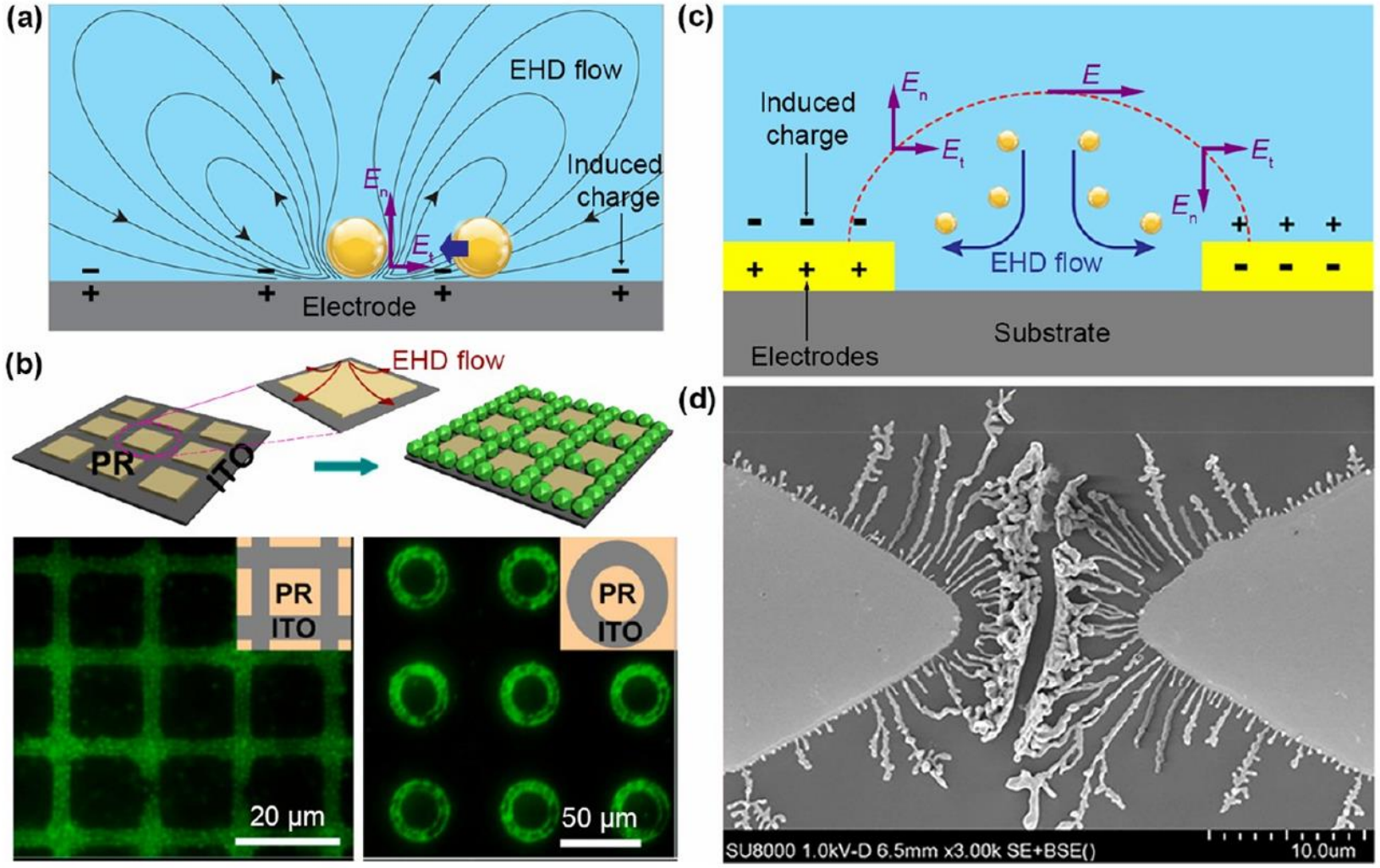
Chai *et al.*, *ACS Nano* 16, 17641-17686 (2022)

Dielectrophoretic assembly



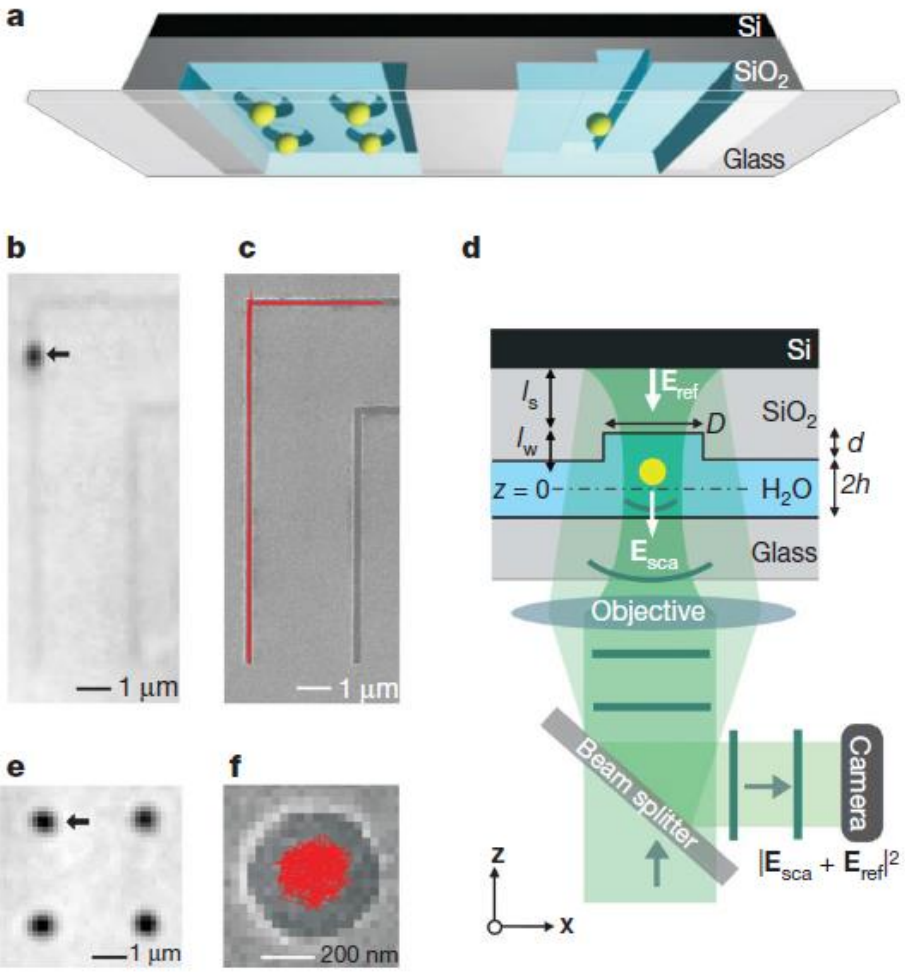
Chai *et al.*, *ACS Nano* 16, 17641-17686 (2022)

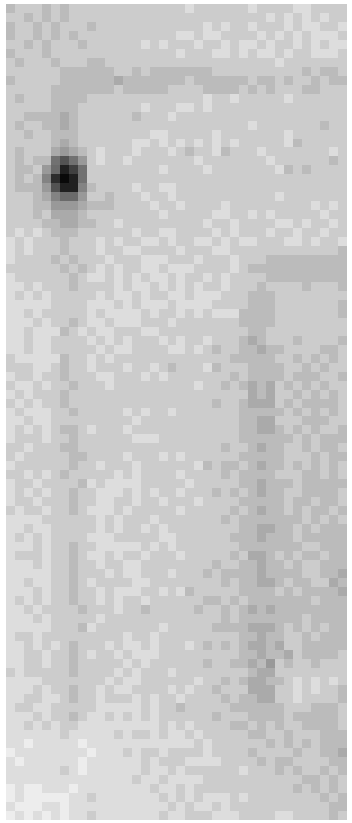
Electrokinetic assembly

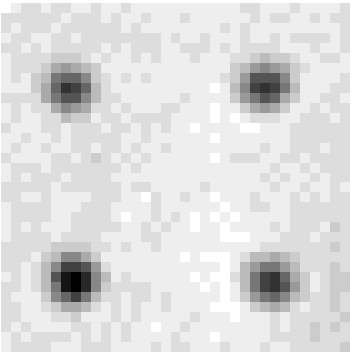


Chai *et al.*, *ACS Nano* 16, 17641-17686 (2022)

Electro-topographical trapping

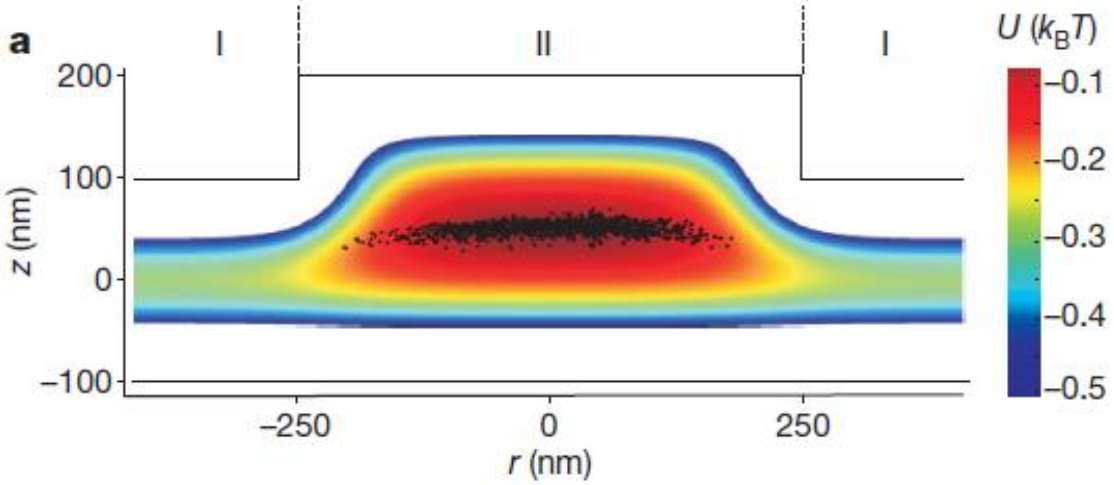


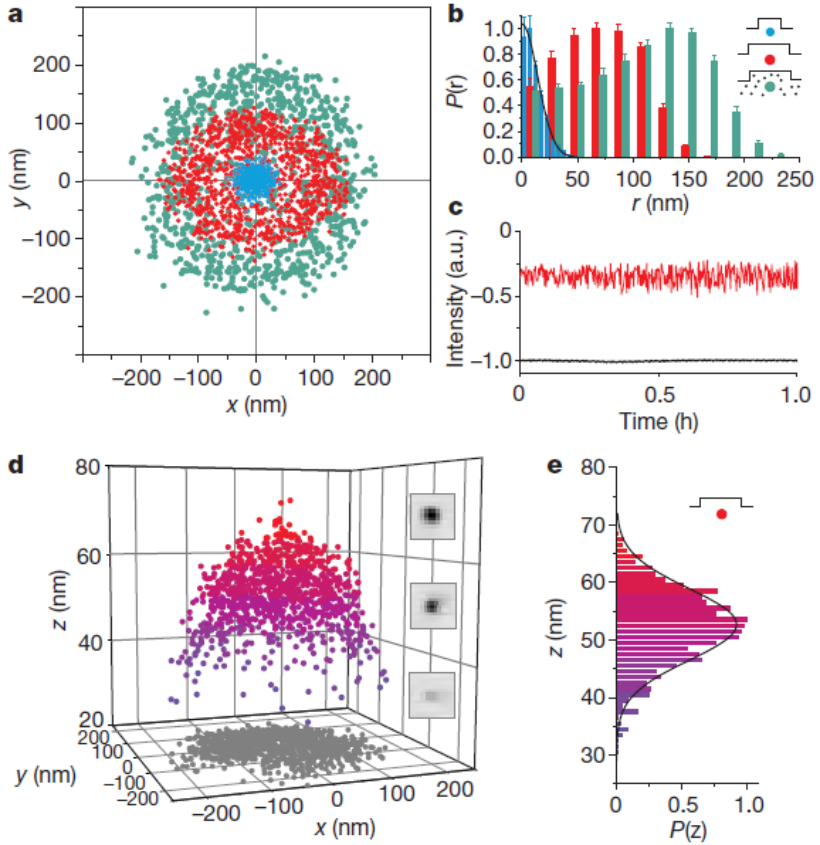




Krishnan *et al.*, *Nature* 467, 692 (2010)

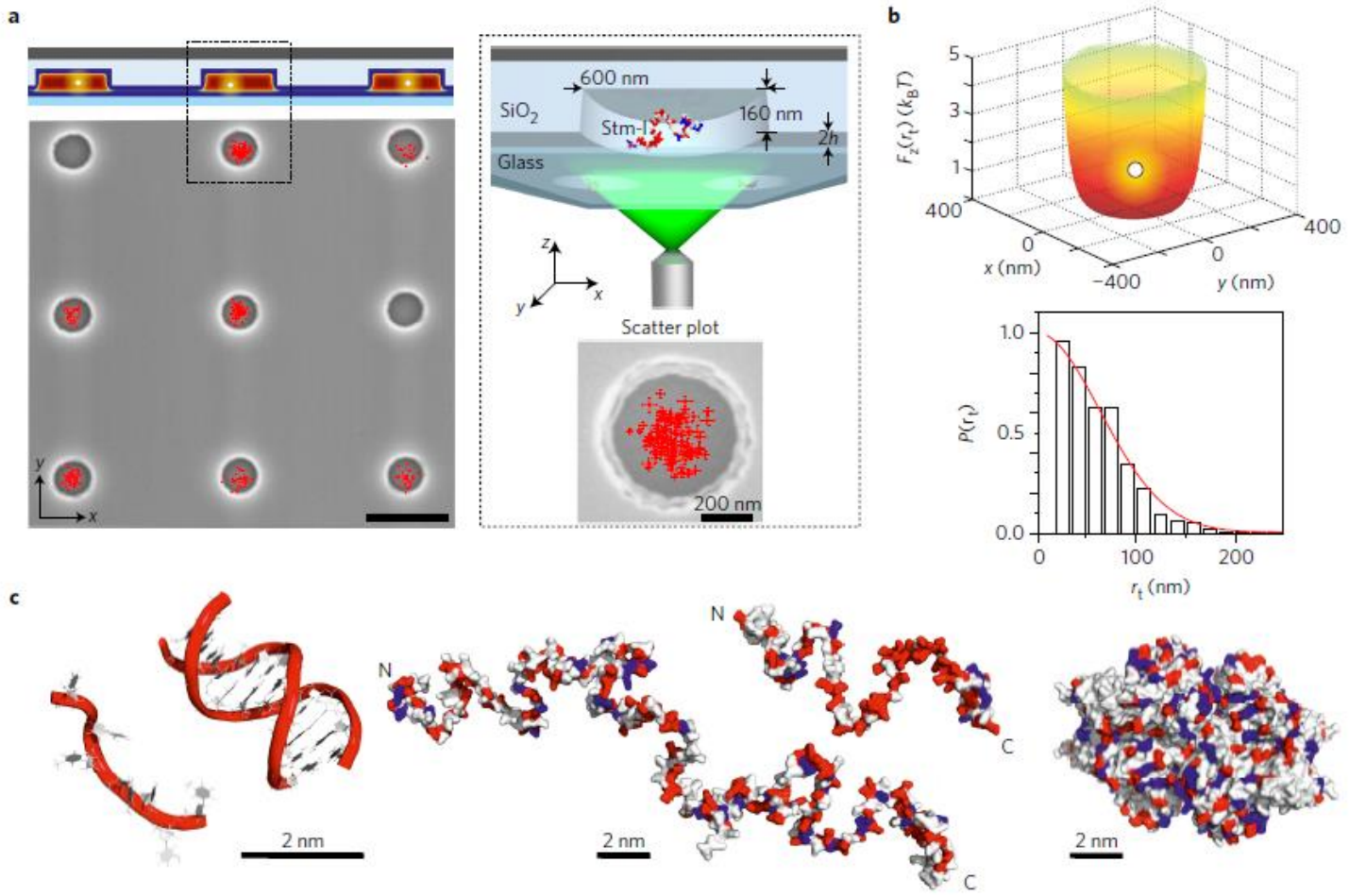
Electro-topographical trapping





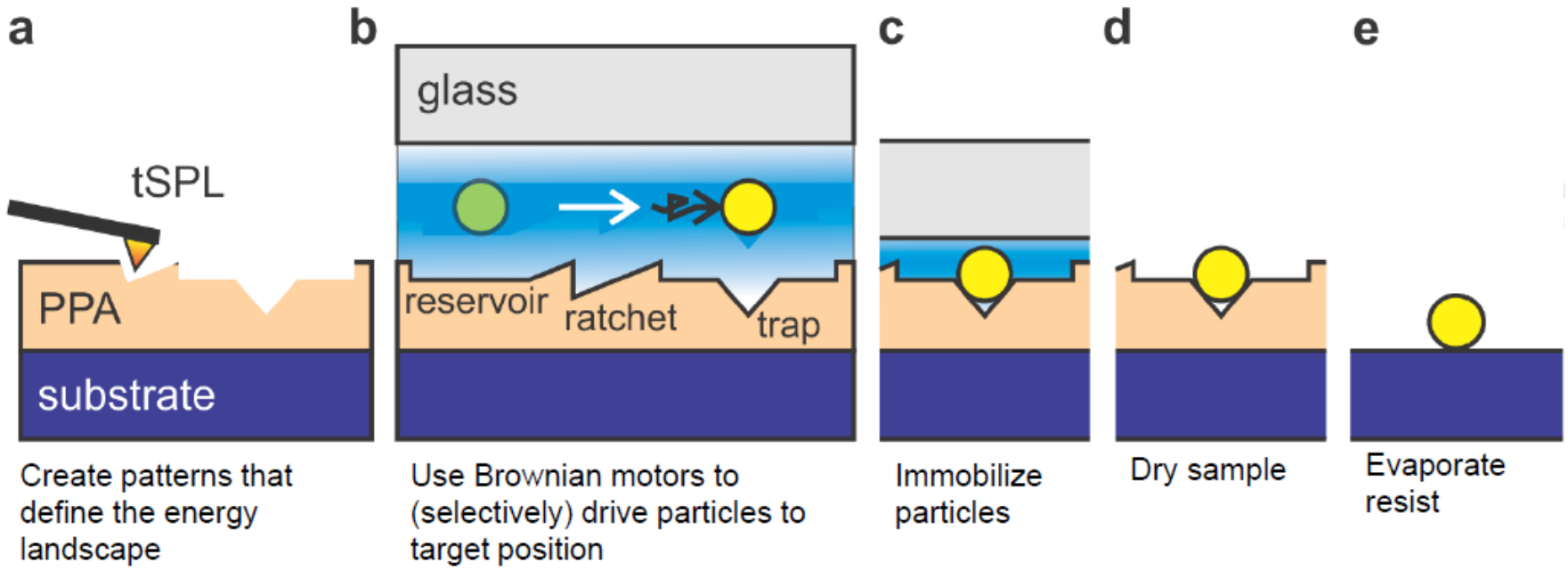
Krishnan *et al.*, *Nature* 467, 692 (2010)

Electro-topographical trapping



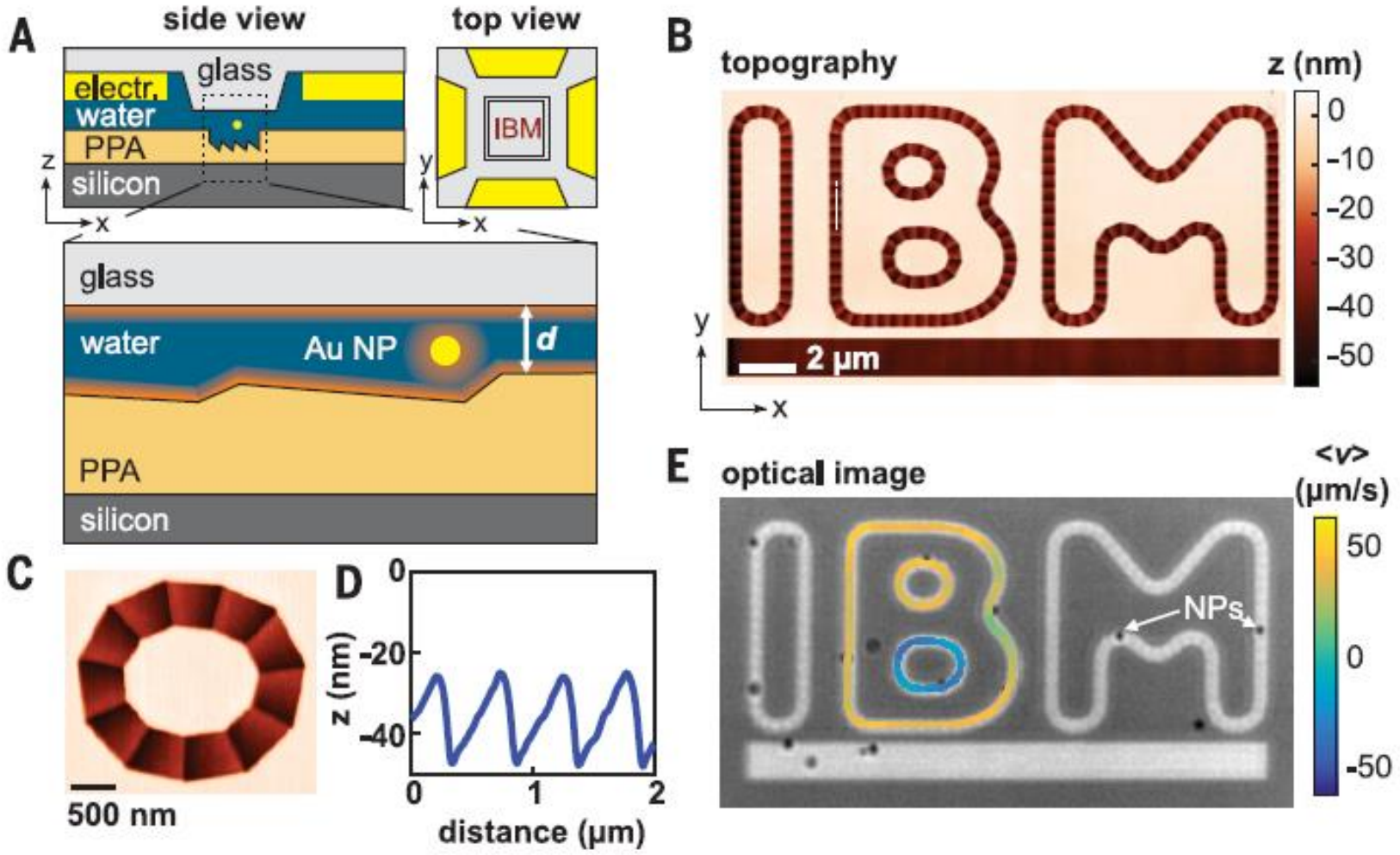
Ruggeri *et al.*, *Nat. Nanotechnol.* 12, 488 (2017)

Rocking Brownian motors



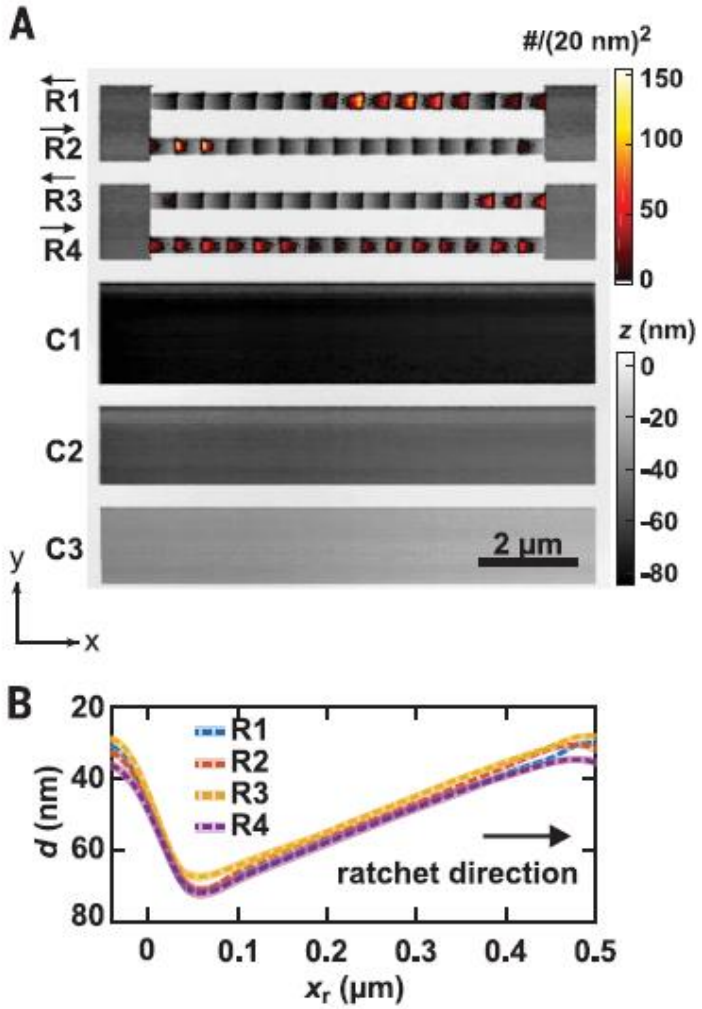
Knoll *et al.*, *TRANSDUCERS 2019*

Rocking Brownian motors

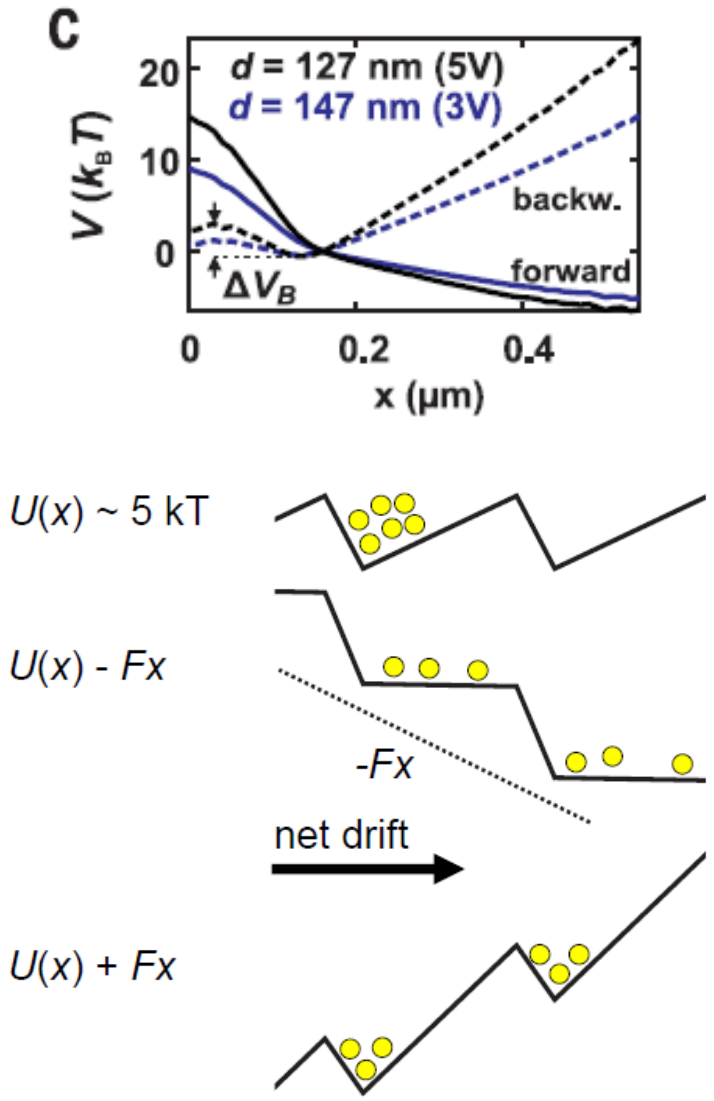


Skaug *et al.*, *Science* 359, 1505 (2018)

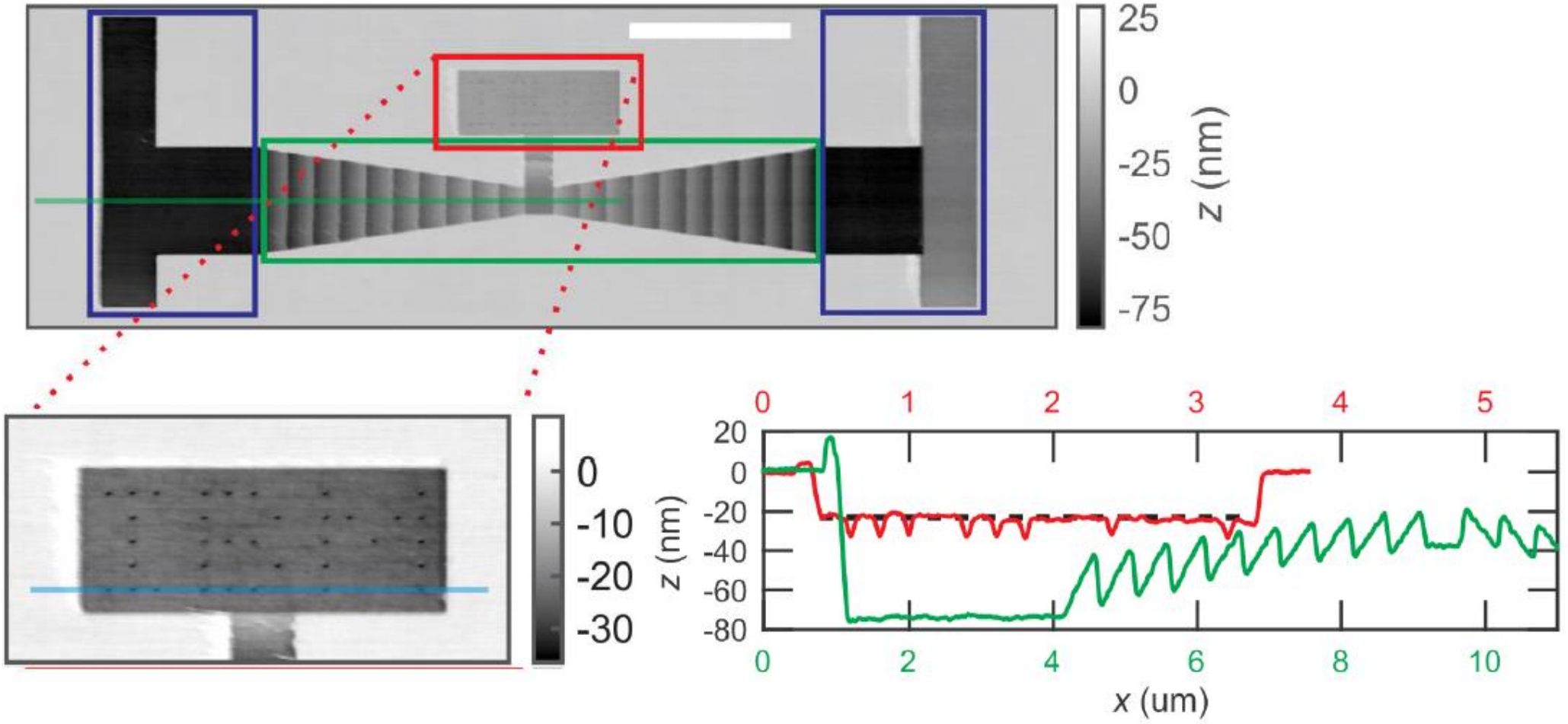
Rocking Brownian motors



Skaug *et al.*, *Science* 359, 1505 (2018)

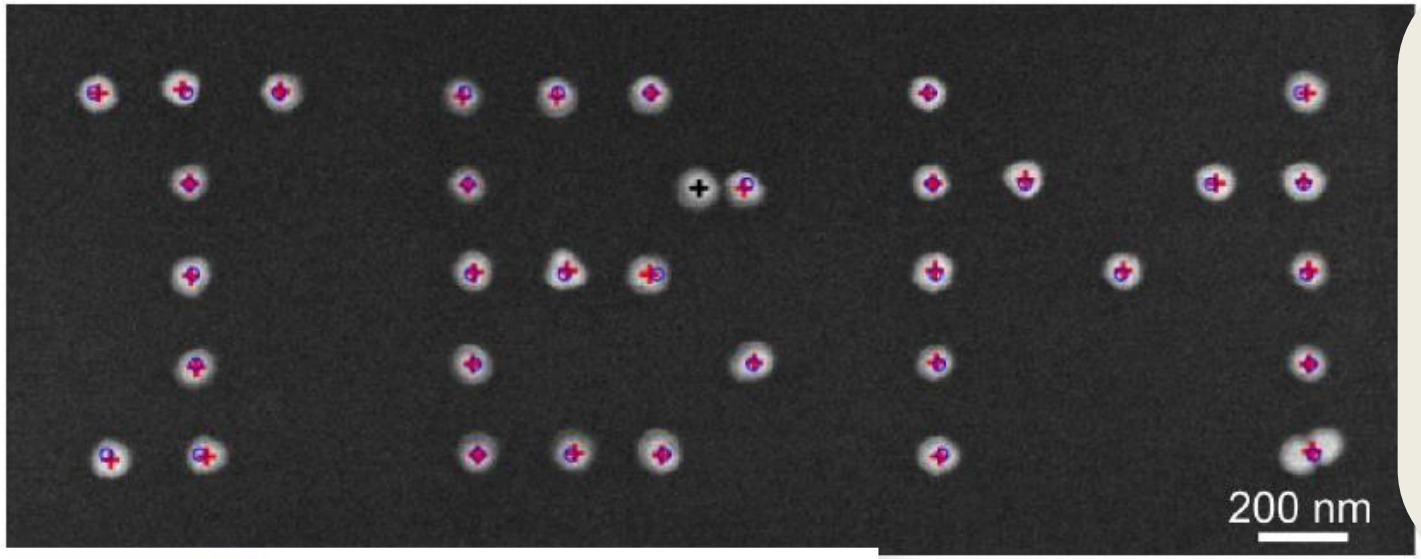


Rocking Brownian motors



Knoll *et al.*, *TRANSDUCERS 2019*
Fringes *et al., Nano Letters* 19, 8855 (2020)

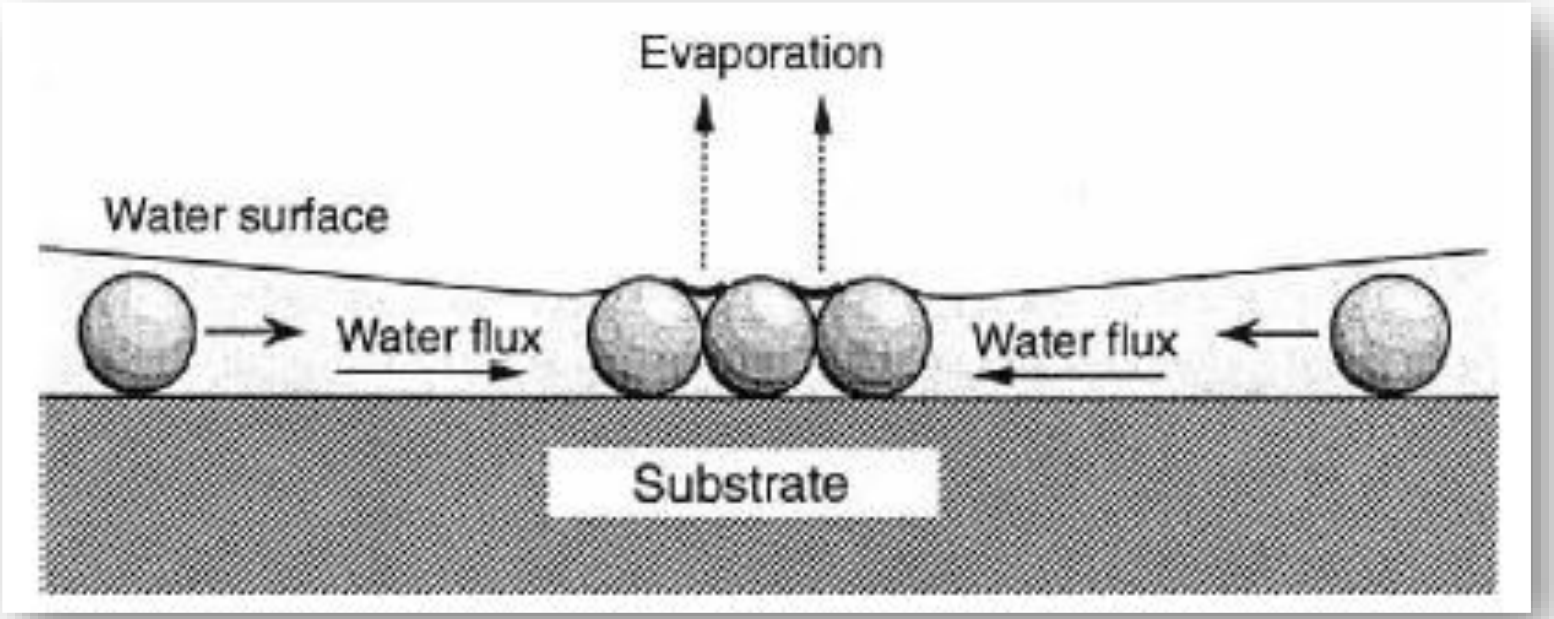
Rocking Brownian motors



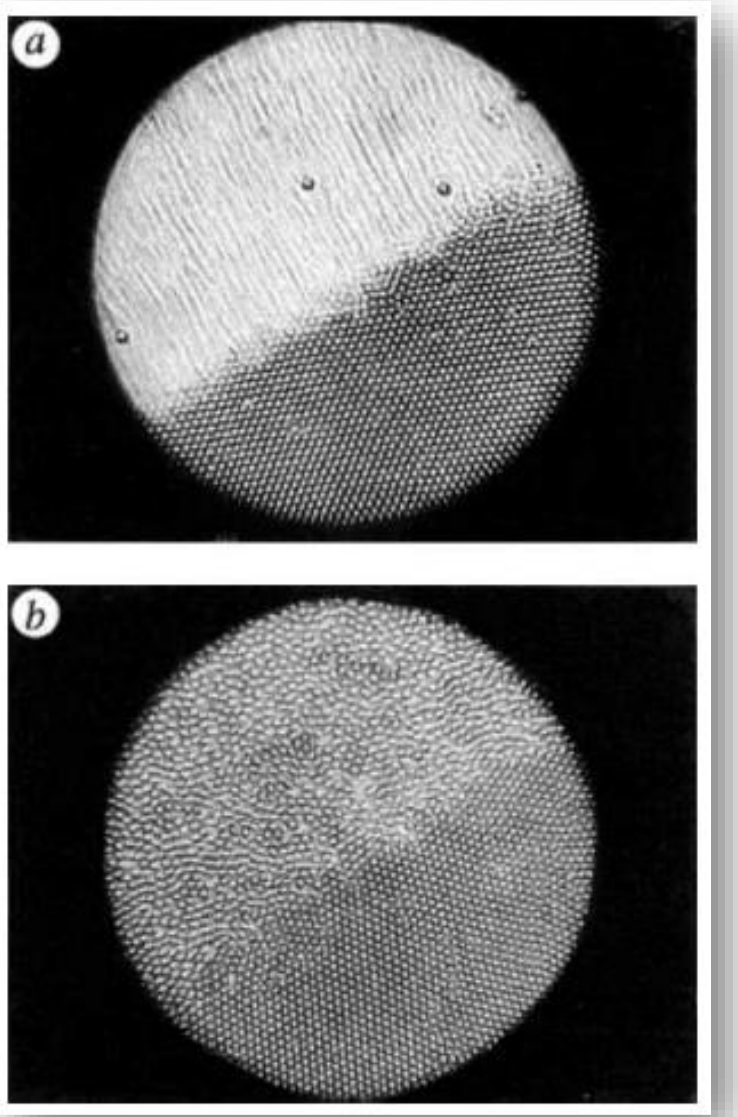
- Error sources
  - Placement
  - Lithography accuracy
  - Particle motion upon resist evaporation
  - SEM distortions (non-linear drift)

Knoll *et al.*, *TRANSDUCERS 2019*
Fringes *et al., Nano Letters* 19, 8855 (2020)

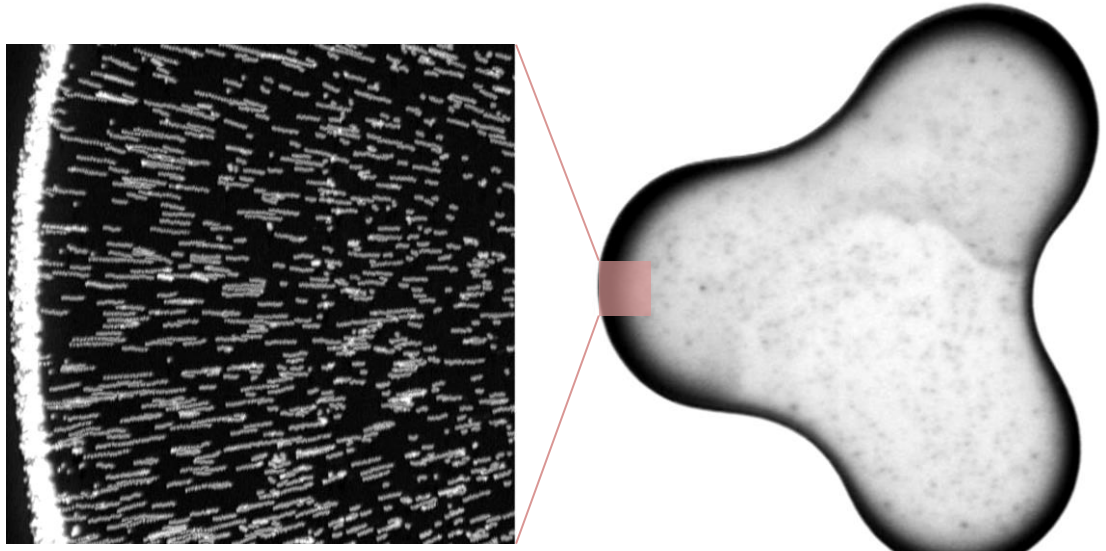
From 3D to 2D: Capillary cristallization

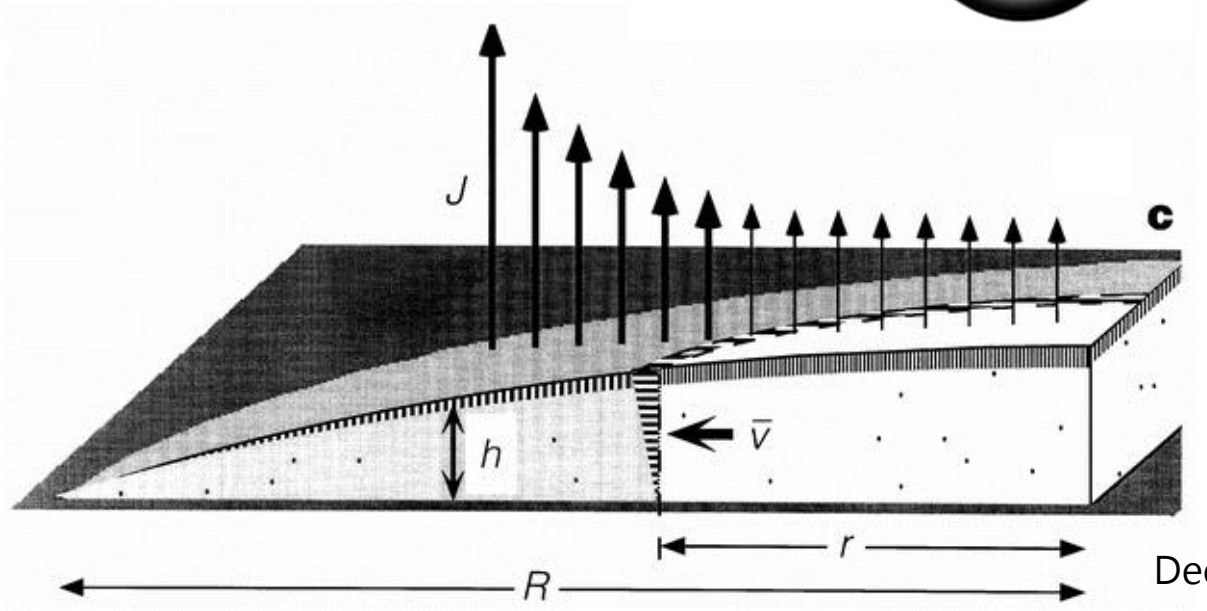


Denkov *et al.*, *Nature* 361, 26 (1993)



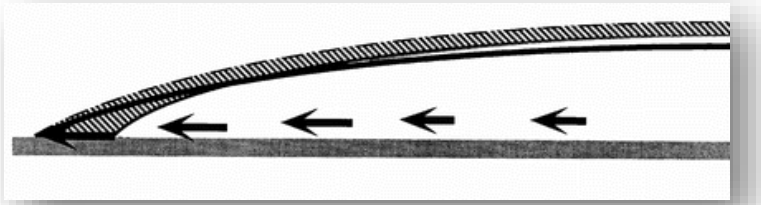
From 3D to 1D: Coffee ring effect

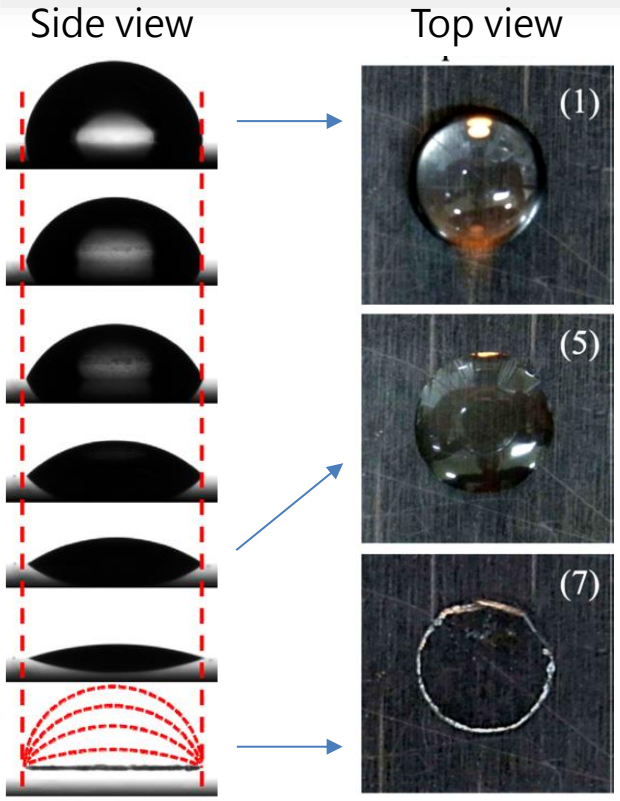


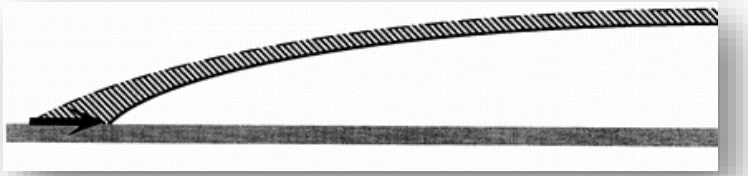


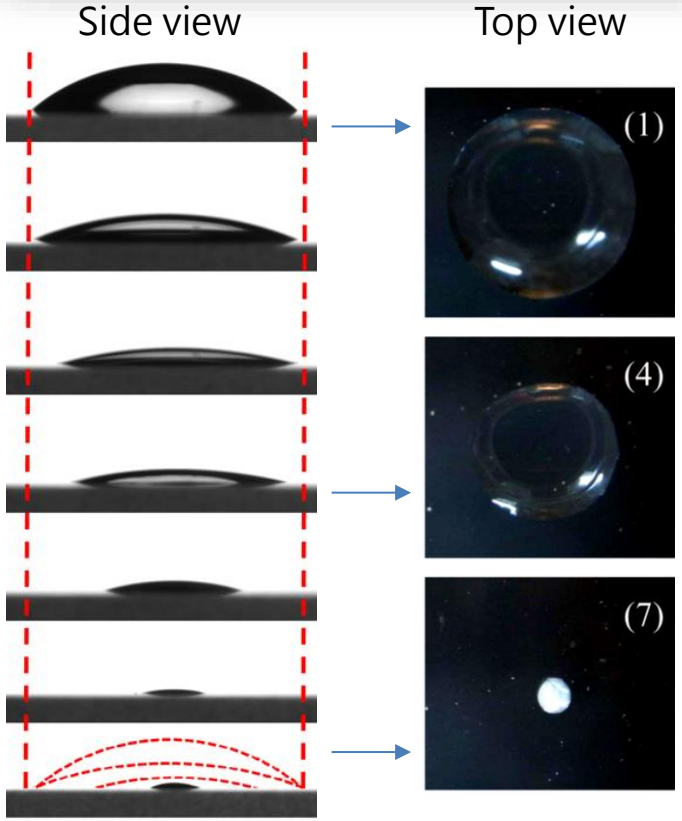
Deegan *et al.*, *Nature* 389, 6653 (1997)

Drop casting



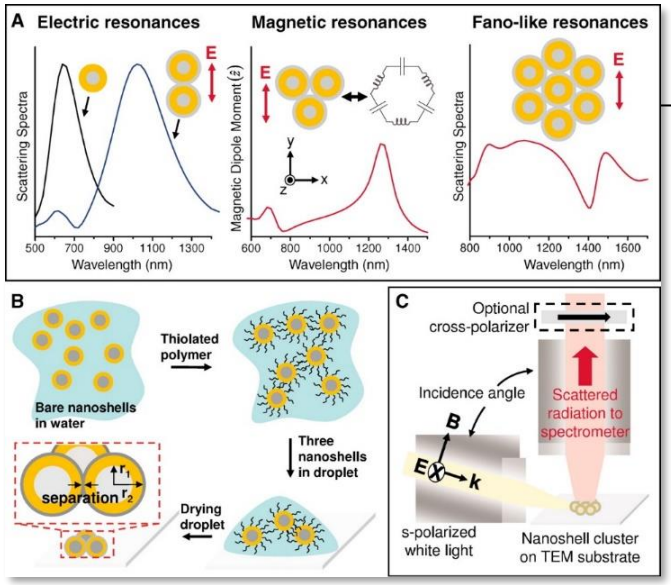




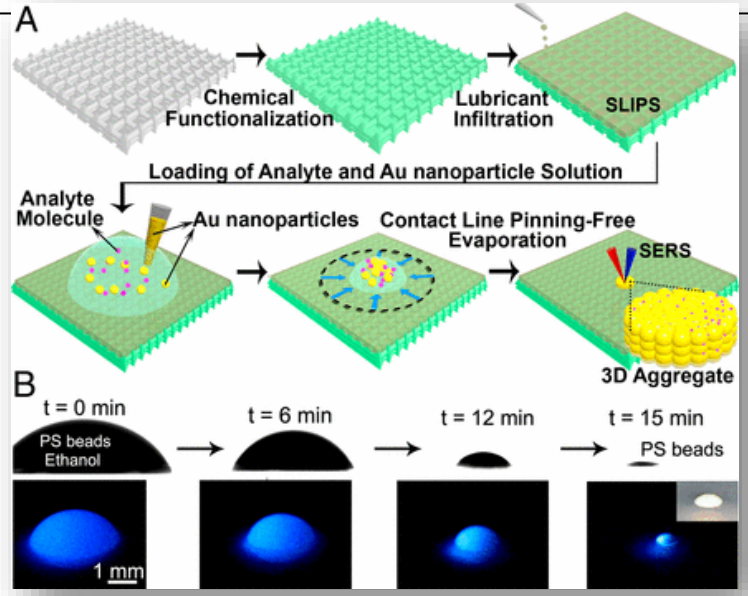


Li *et al.*, *Langmuir* 29, 782 (2013)

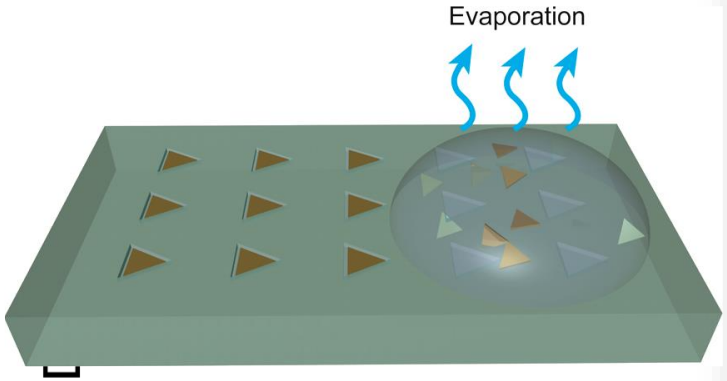
Drop casting



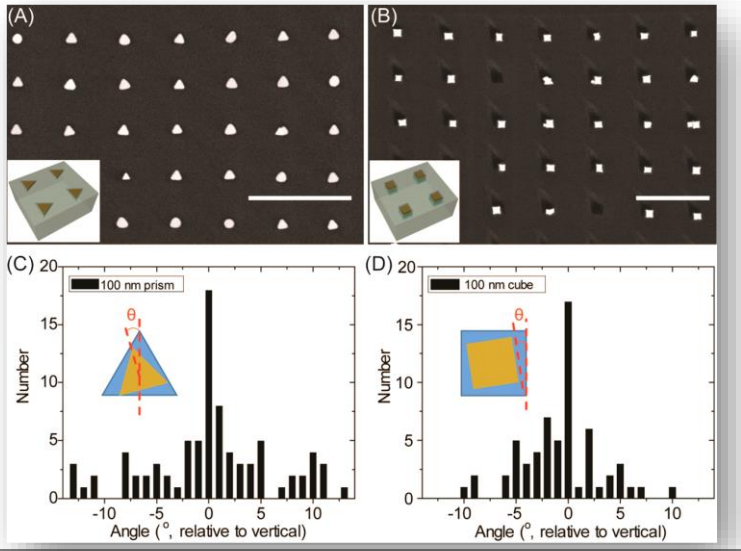
Fan *et al.*, *Science* 328, 1135 (2010)

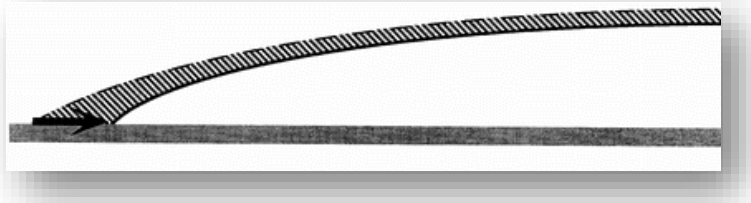


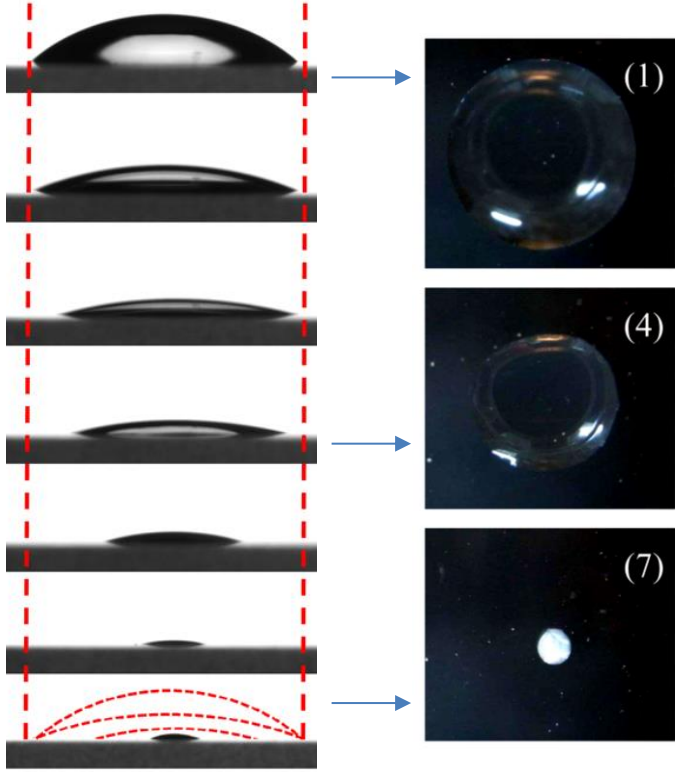
Yang *et al.*, *PNAS* 113, 268 (2016)



Zhou *et al.*,
Nano Lett. 14, 2157 (2014)



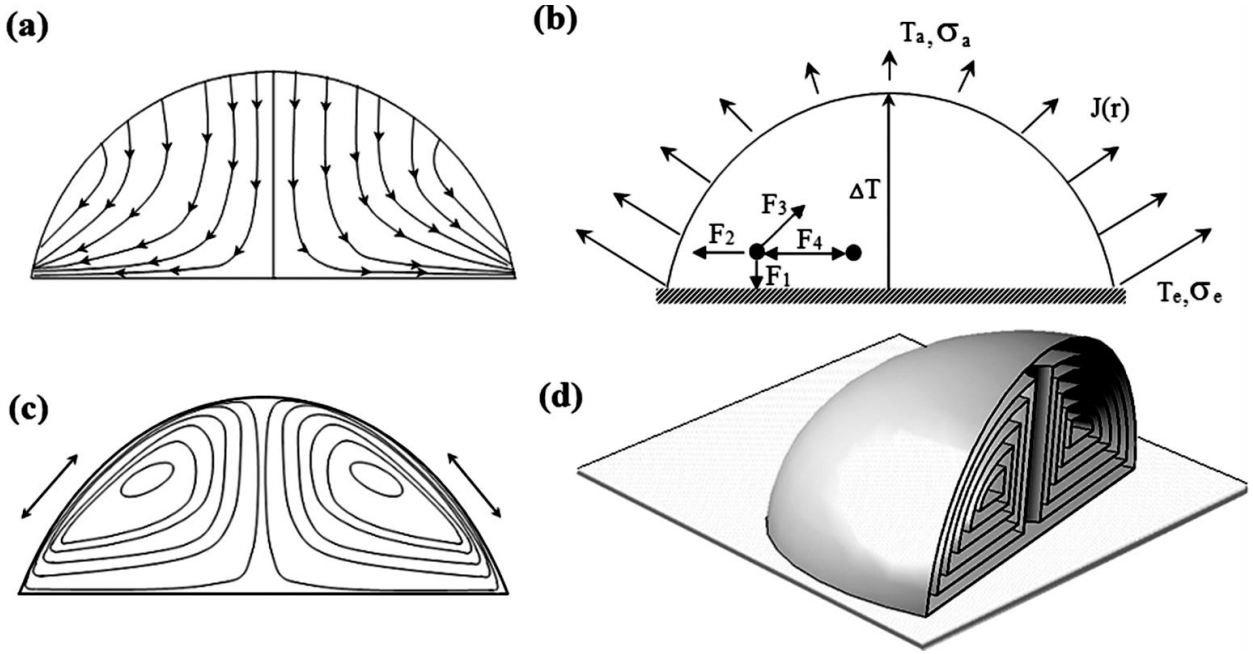




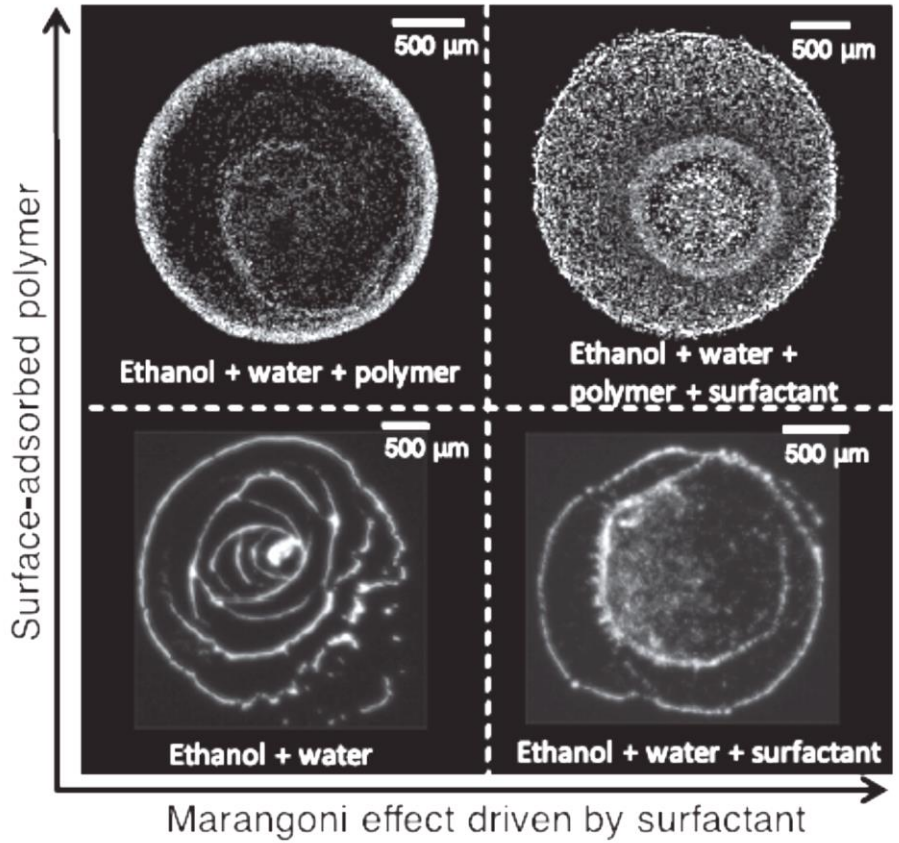
Li *et al.*, *Langmuir* 29, 782 (2013)

From suspension to substrate

Drop casting



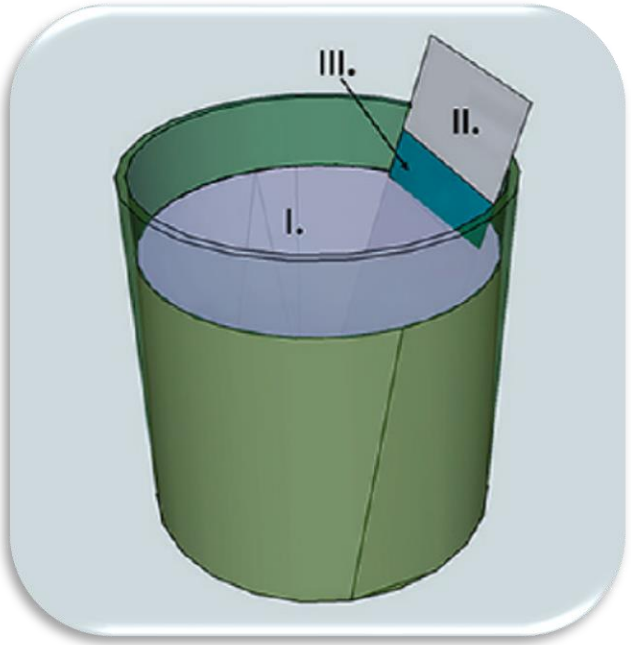
Thokchom *et al.*, *Langmuir* 30, 12144 (2014)



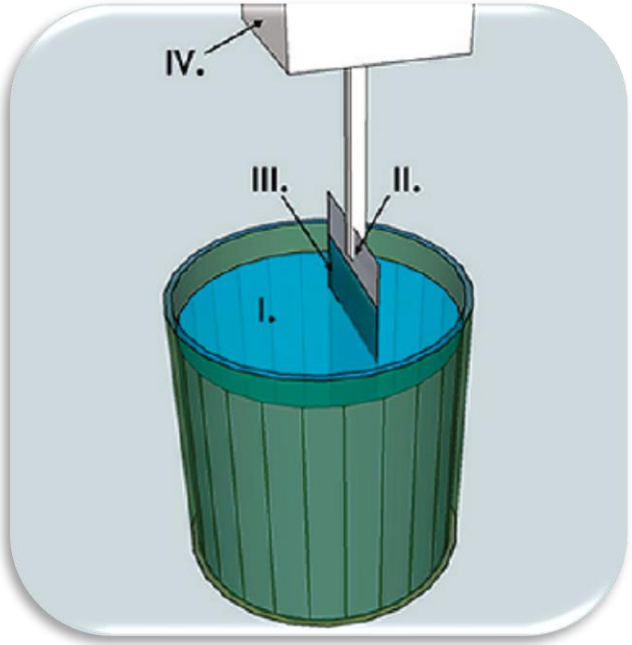
Kim *et al.*, *PRL* 116, 124501 (2016)

- ✓ Resource efficient
- × Limited control

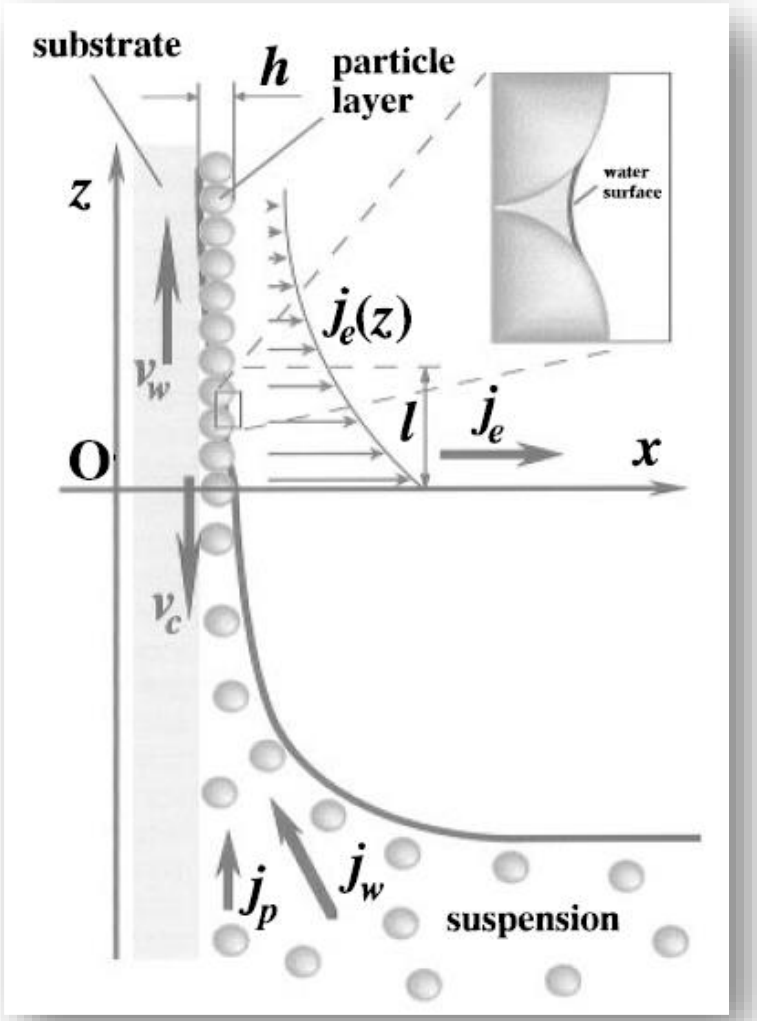
Dip coating



Evaporation-driven



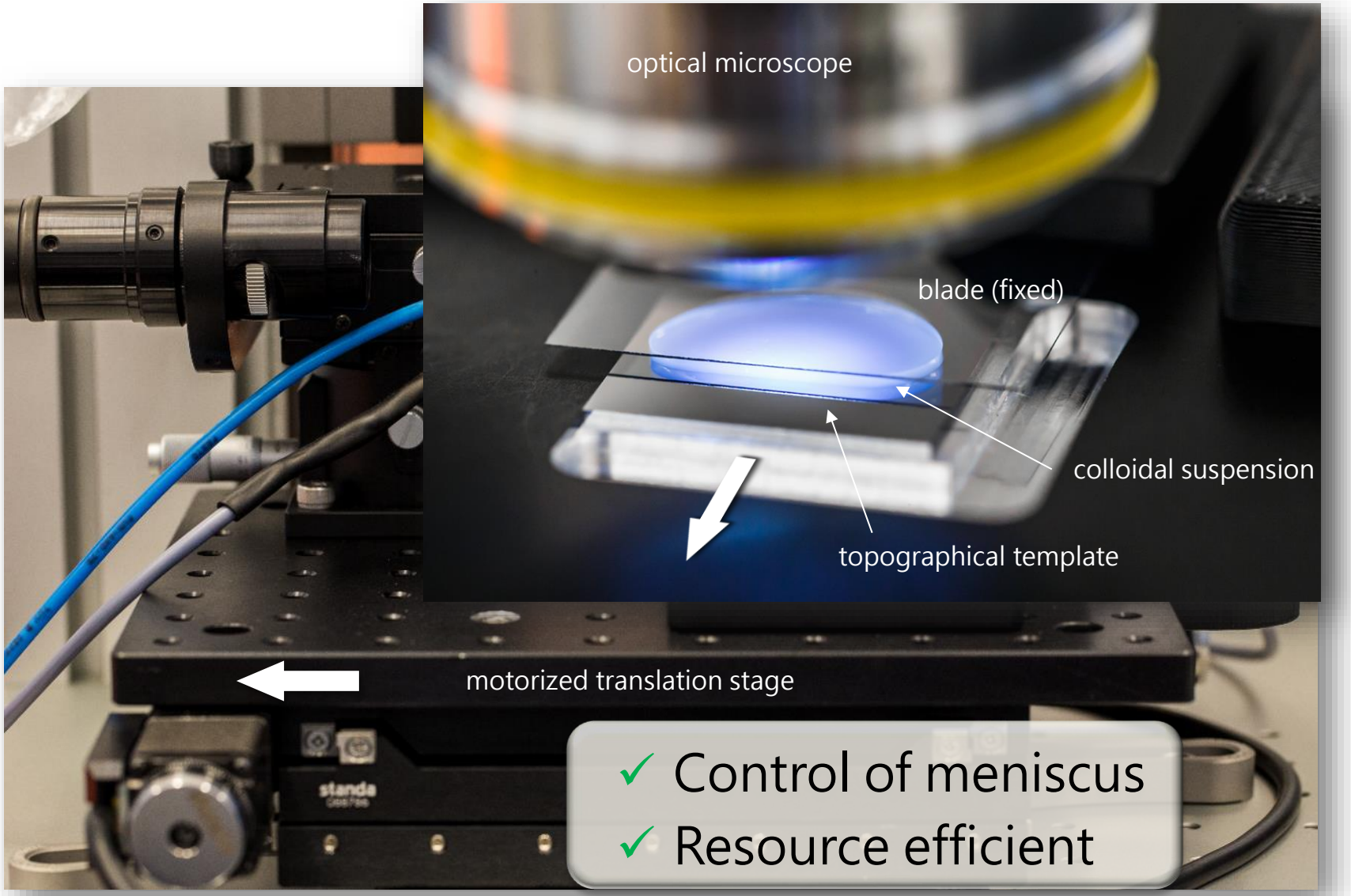
Moving substrate



Dimitrov & Nagayama, *Langmuir* 12, 1303 (1996)

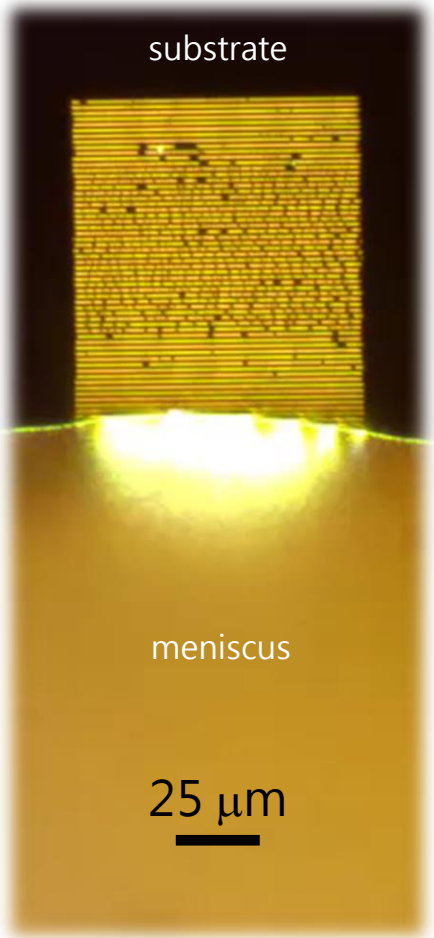
- ✓ Uniform deposition over large areas
- × Limited control on meniscus geometry

Blade coating



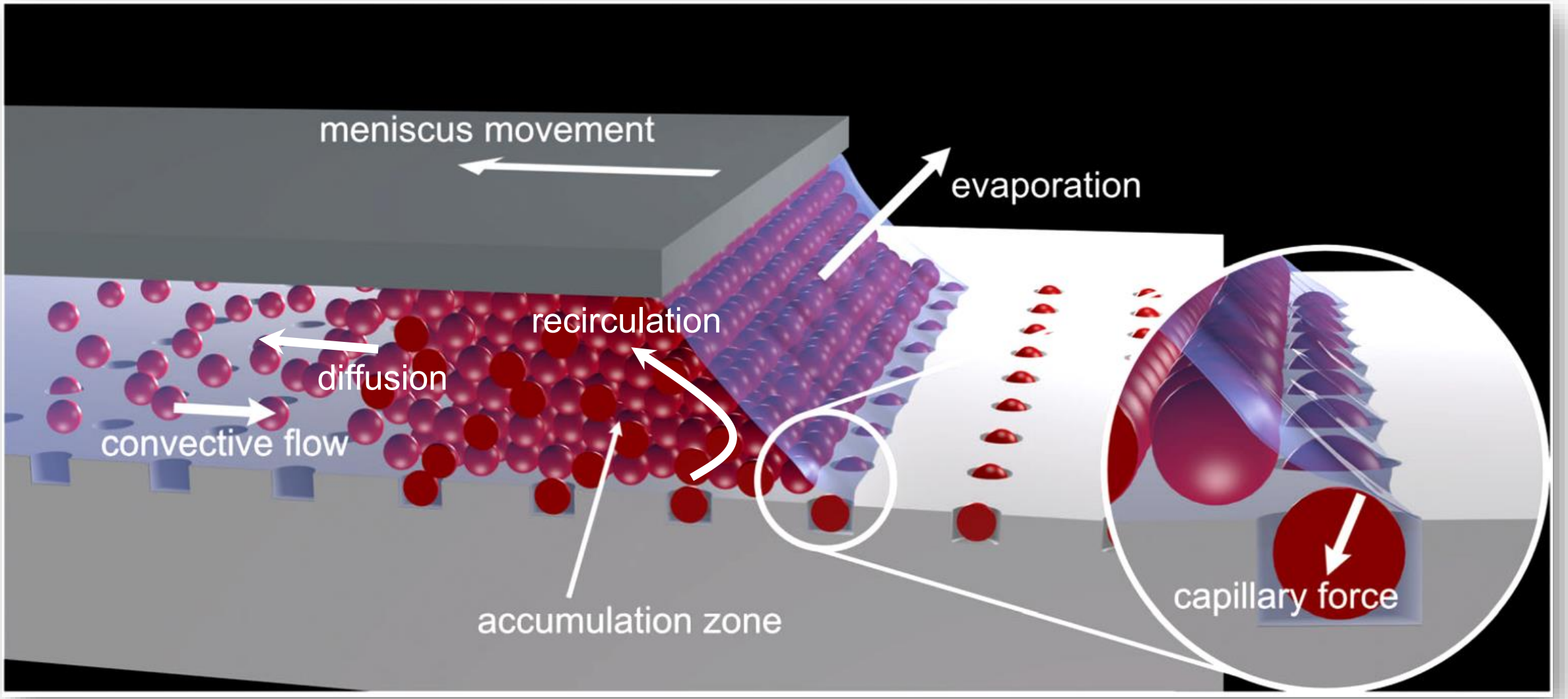
- ✓ Control of meniscus
- ✓ Resource efficient

Top view



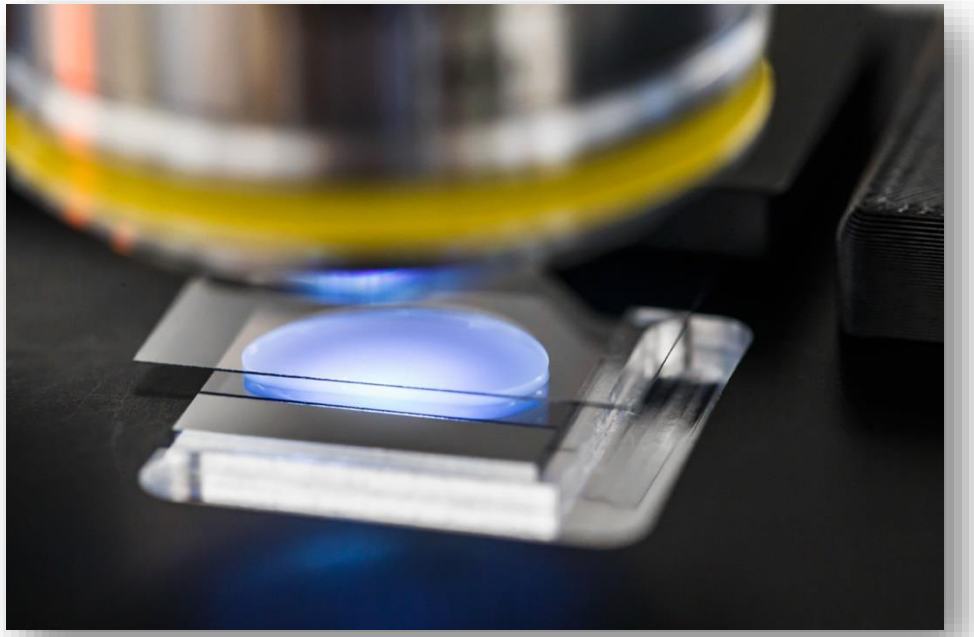
From suspension to substrate

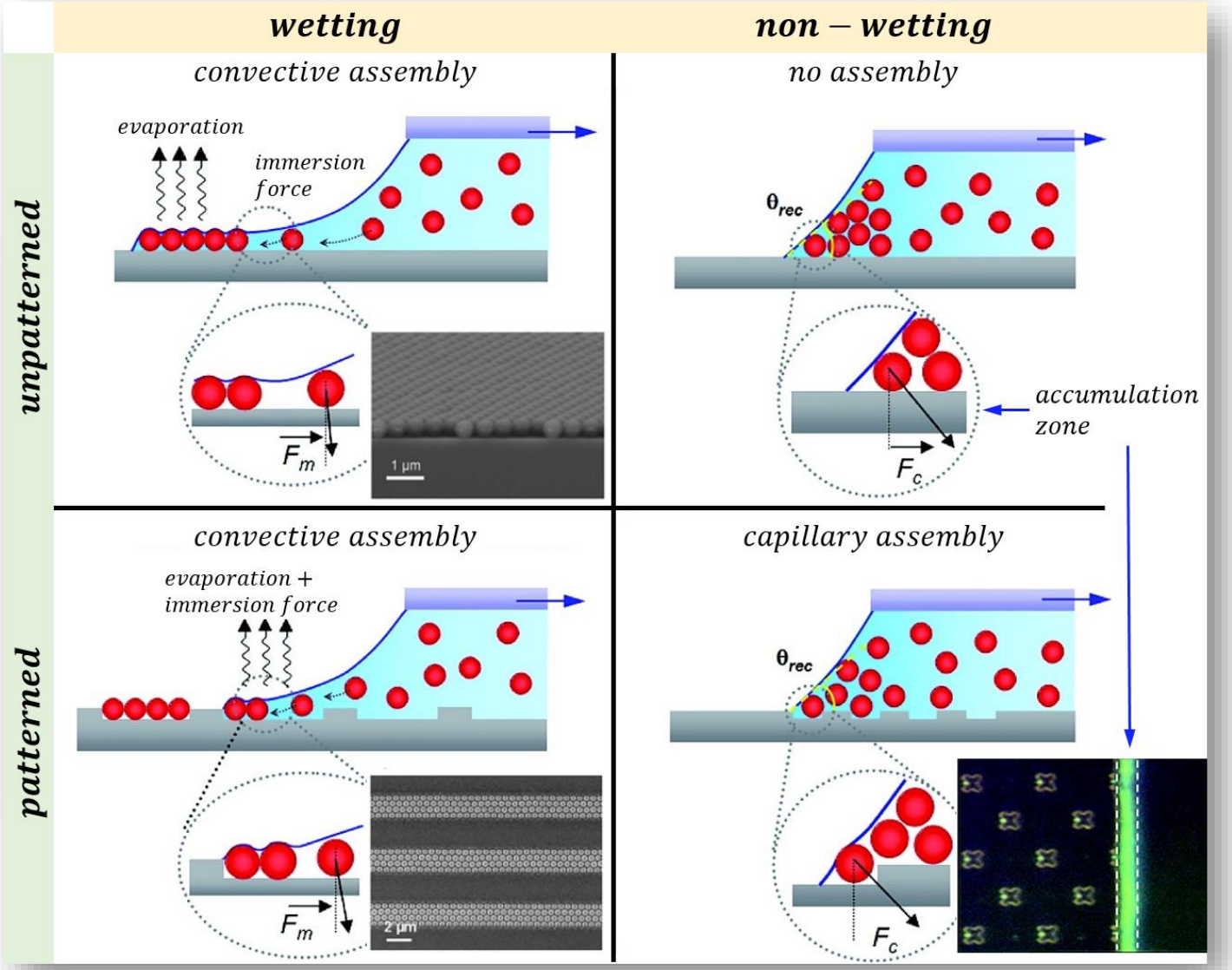
Blade coating



Ni *et al.*, *Soft Matter* 2018

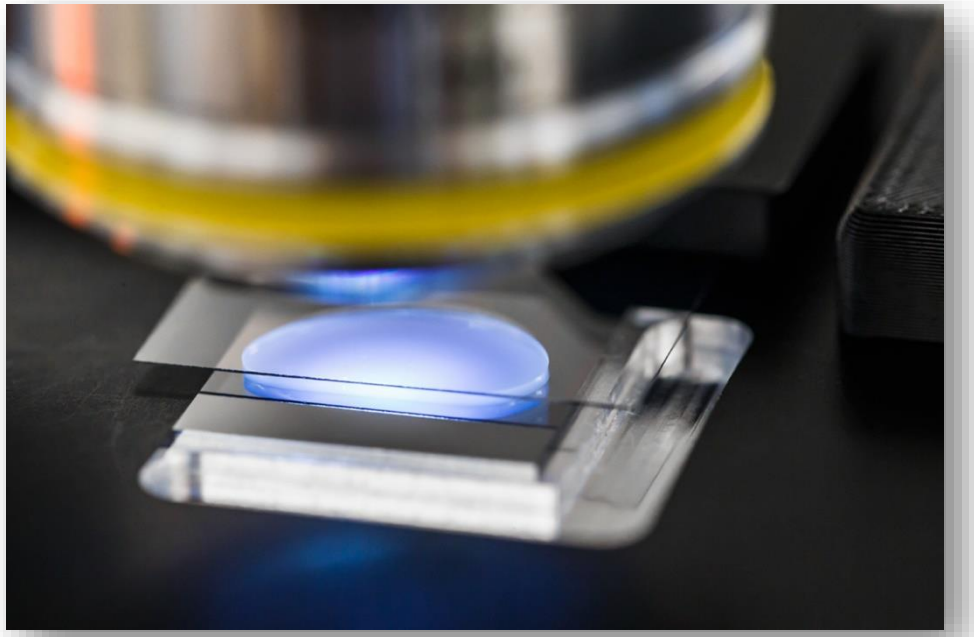
Blade coating





Mastrangeli, *Adv. Mater.* 2015

Top-down meets bottom-up



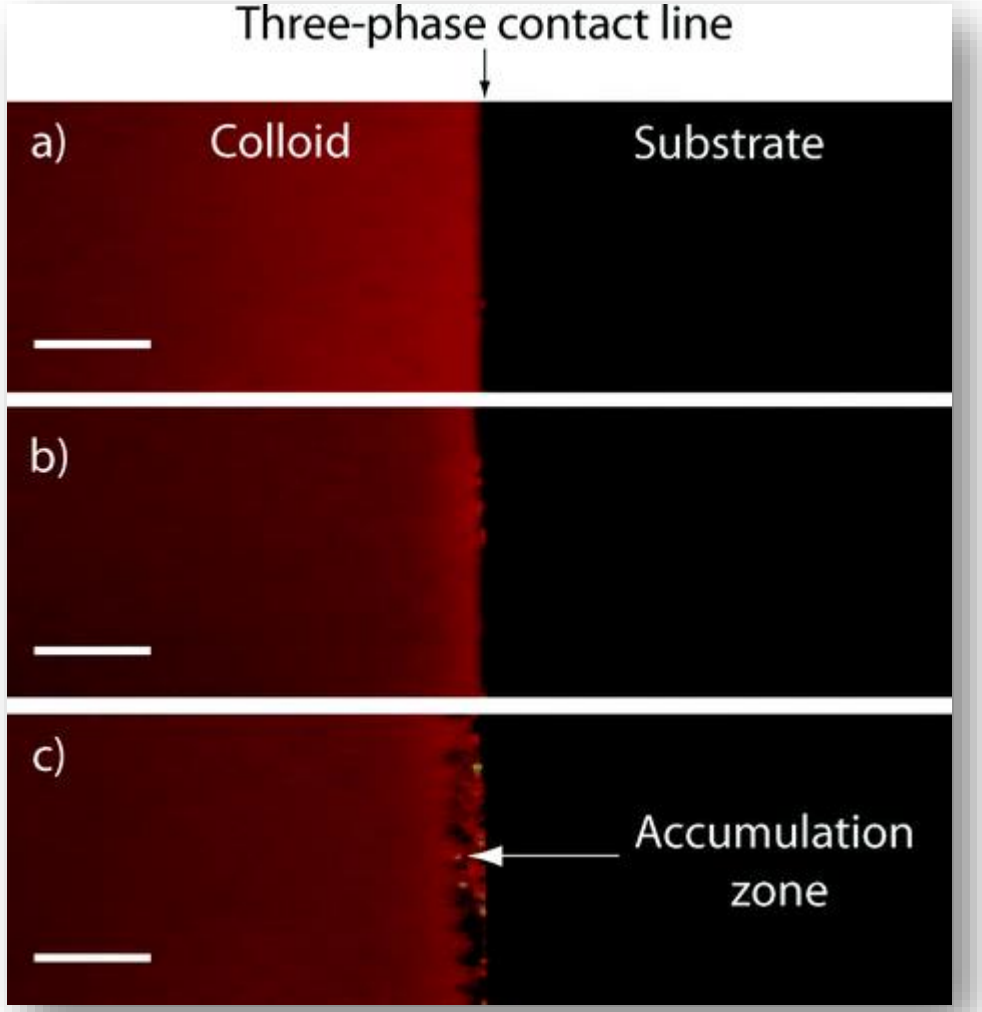
iff

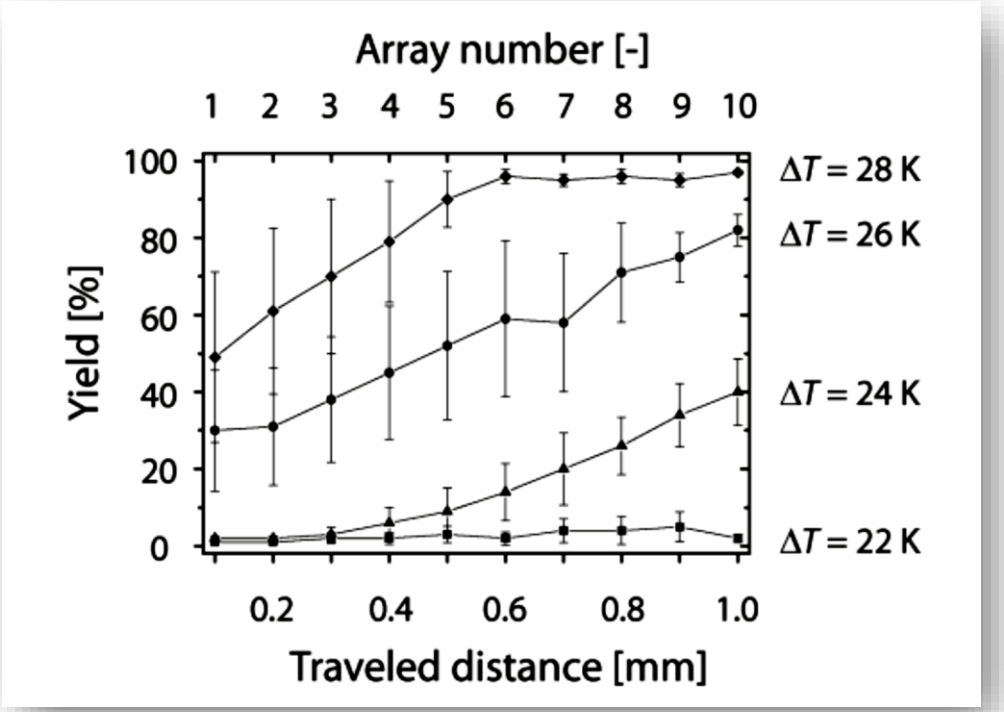
- ✓Stable colloidal suspension
- ✓Control of substrate wetting & patterning

then

Capillary assembly *does not* depend on specificities of particles or substrates

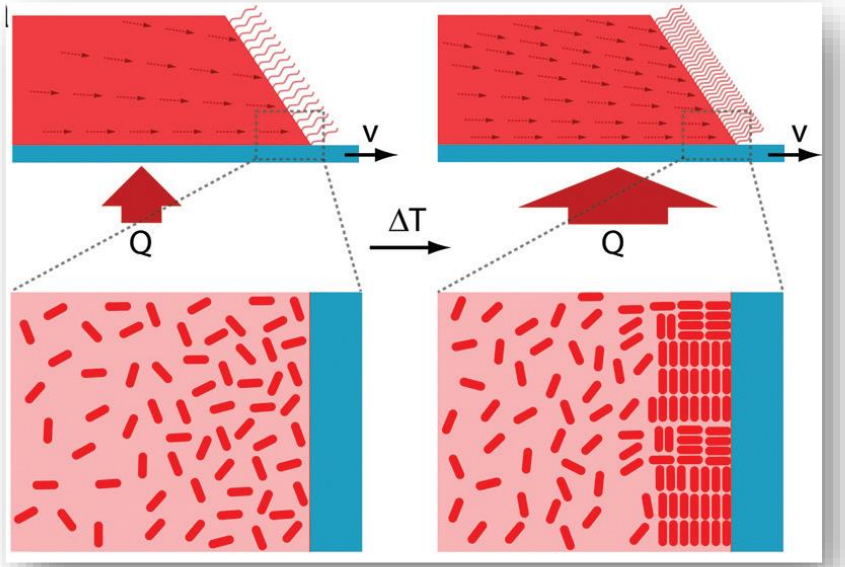
Size of accumulation zone



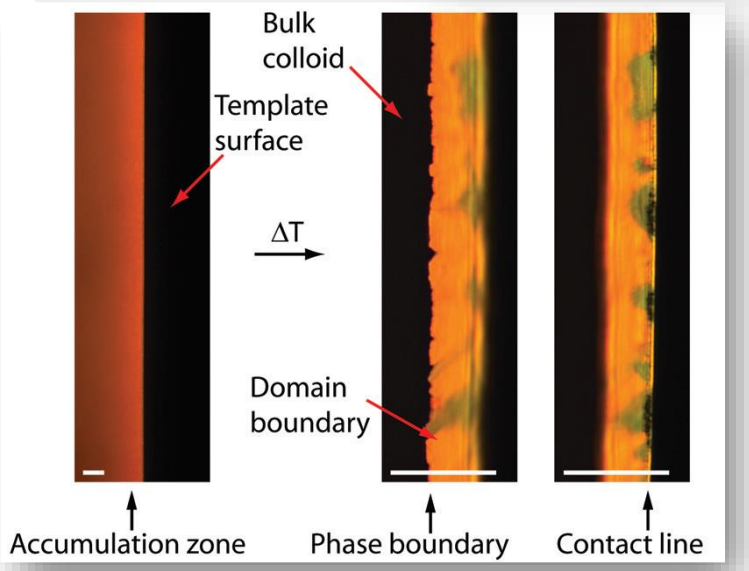


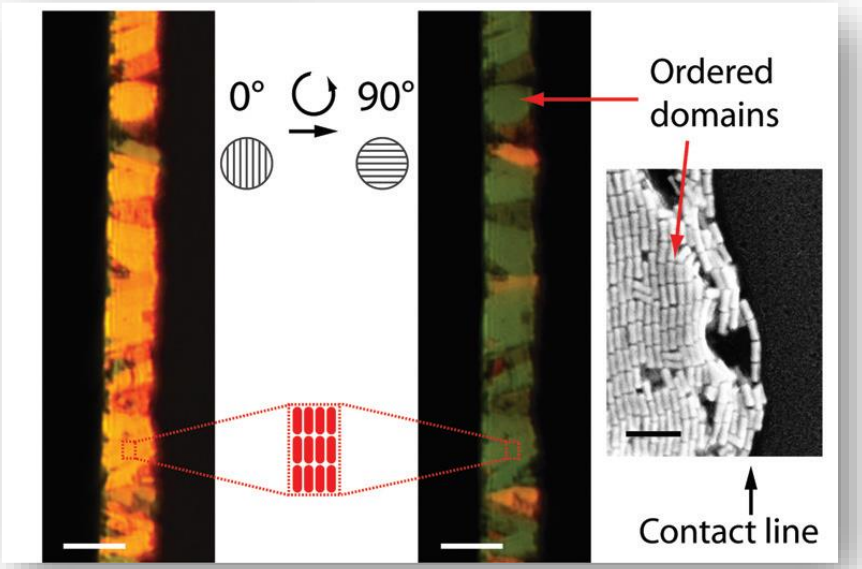
Kuemin *et al.*, *Langmuir* 27, 6305 (2011)

Density-driven phase transition



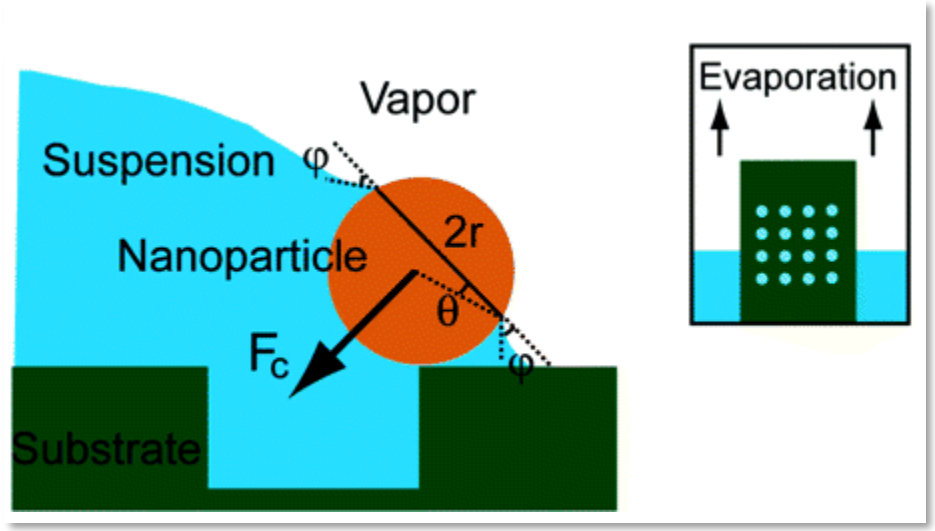
Kuemin *et al.*,
Adv. Funct. Mater. 22, 702 (2012)



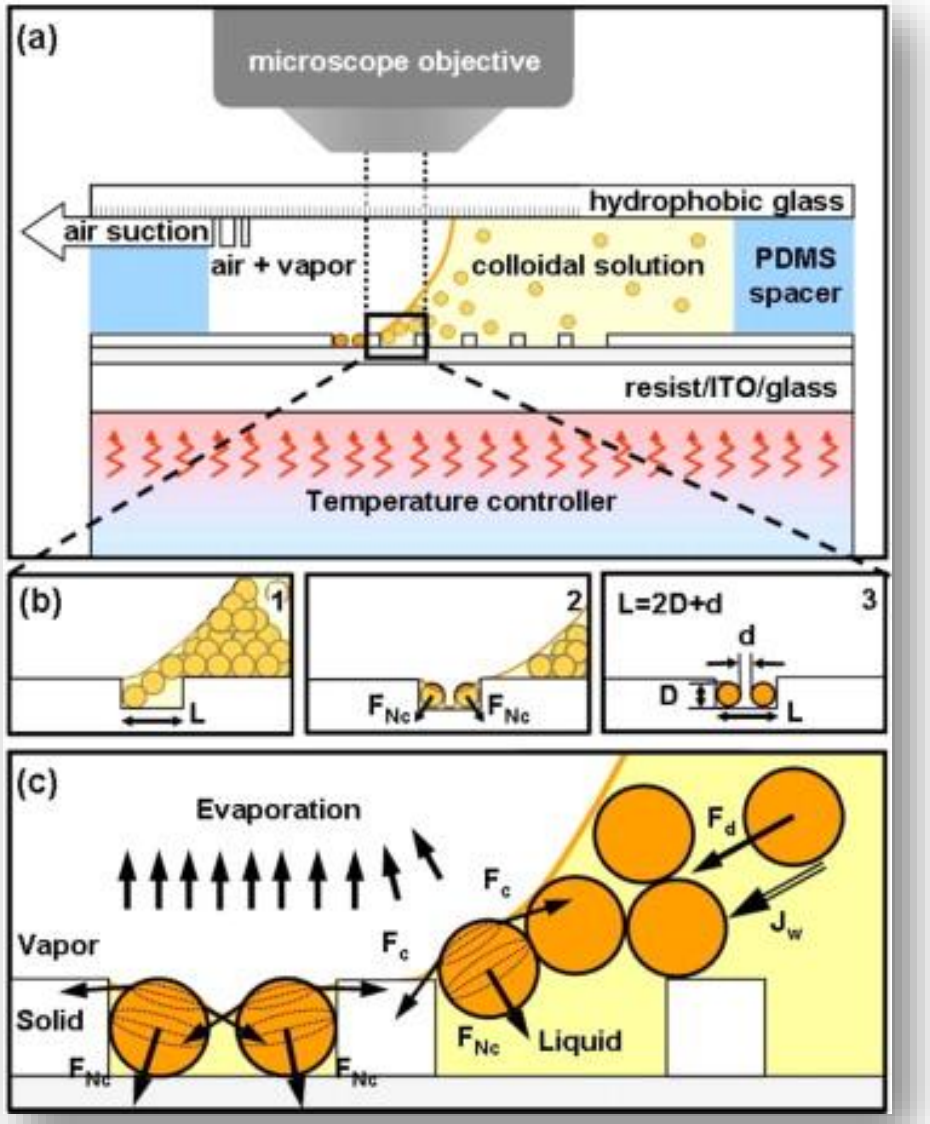


Prior wisdom

Capillary push



Cui *et al.*, *Nano Lett.* 4, 1093 (2004)

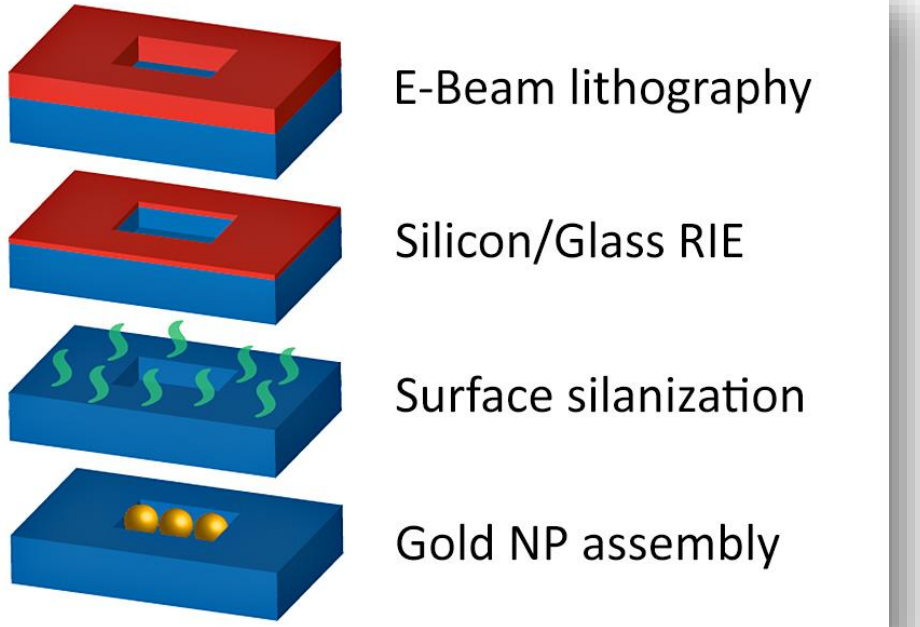


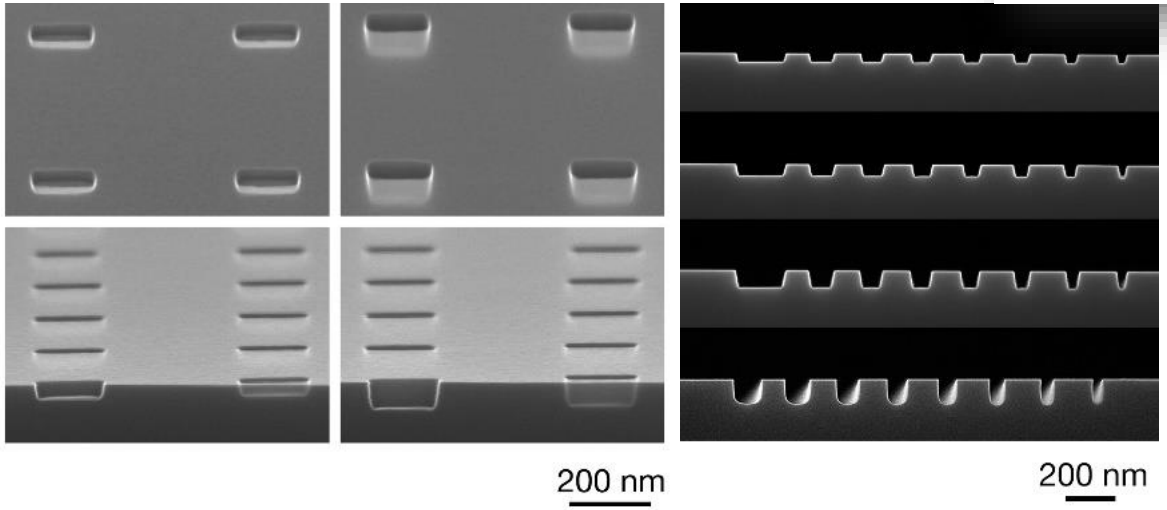
Pinedo Rivera *et al.*, *Microelectron. Eng.* 86, 1089 (2009)

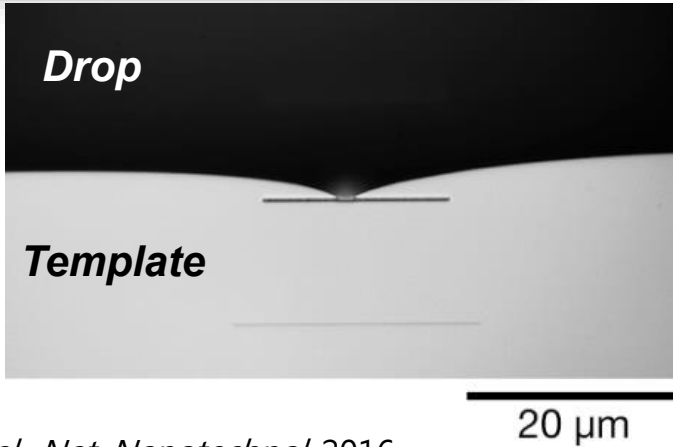
Topographical template fabrication

EBL / RIE / Silanisation

- Features 30nm± 5nm
- Multilayer processes
- Chlorine-based RIE
- water CA: ~110°

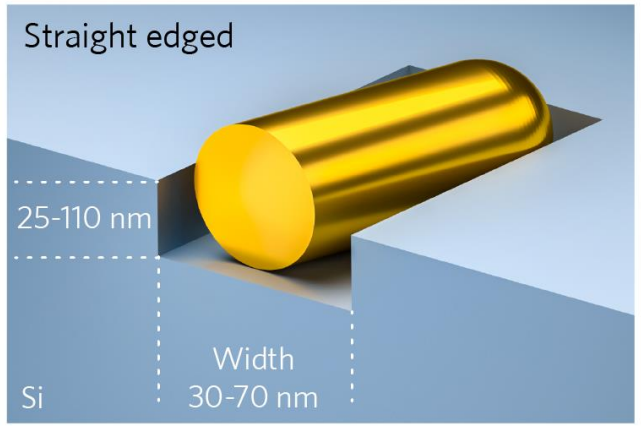


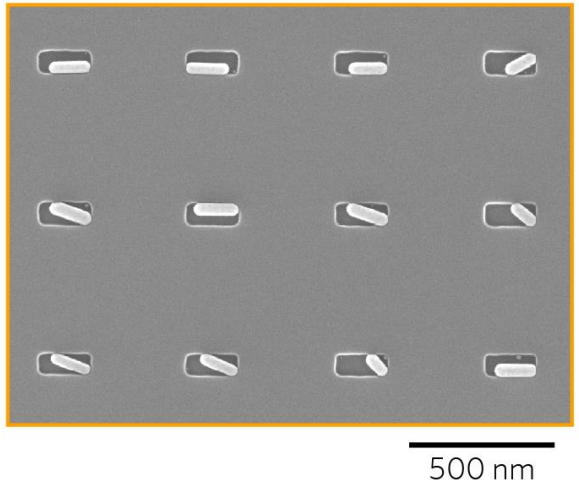


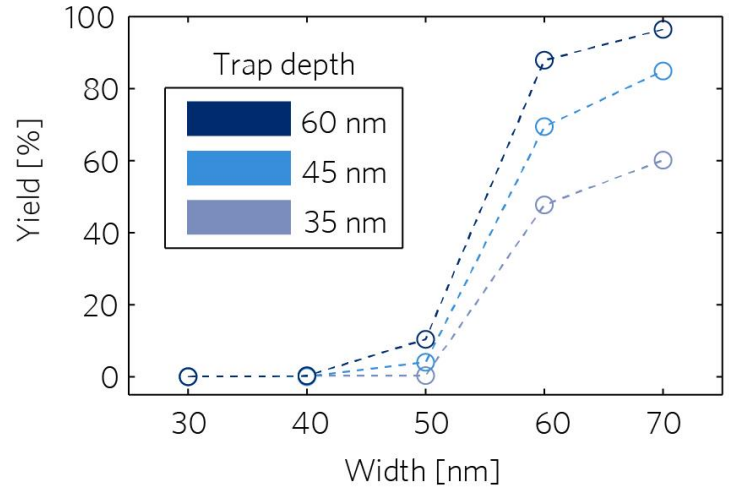


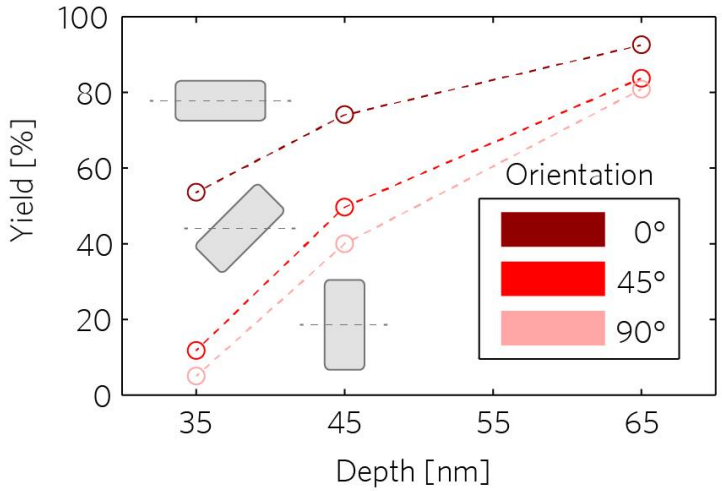
Flauraud *et al., Nat. Nanotechnol.* 2016

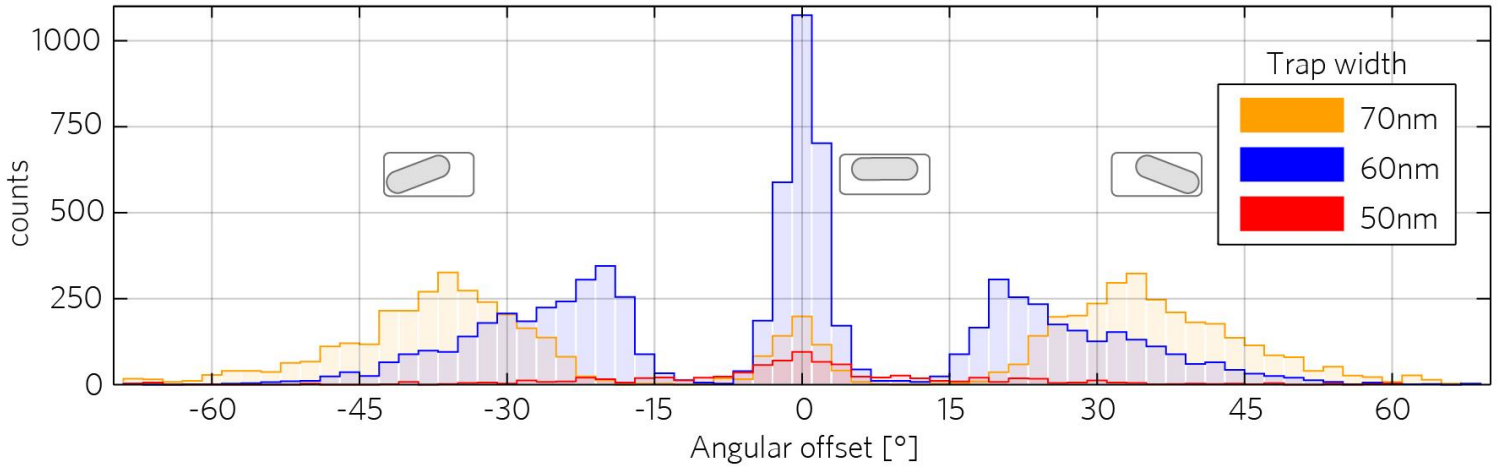
Straight-edged traps





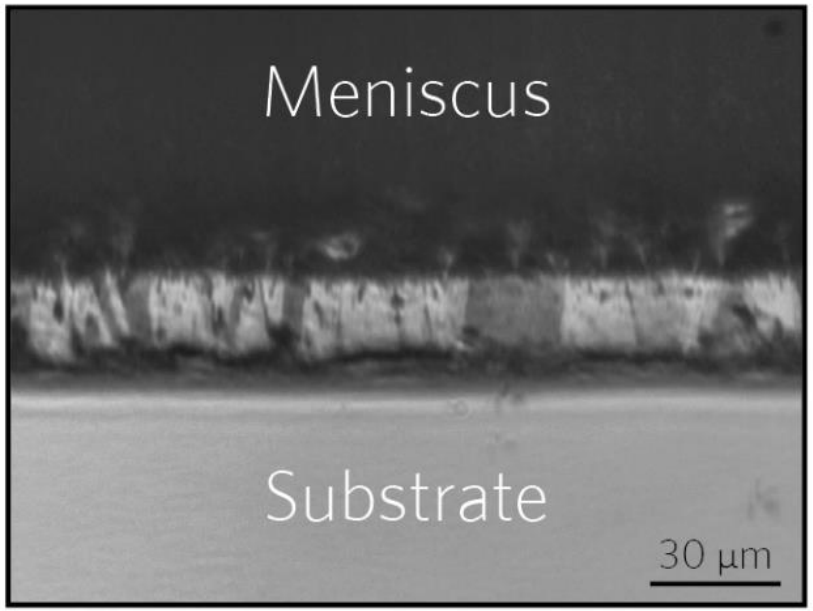


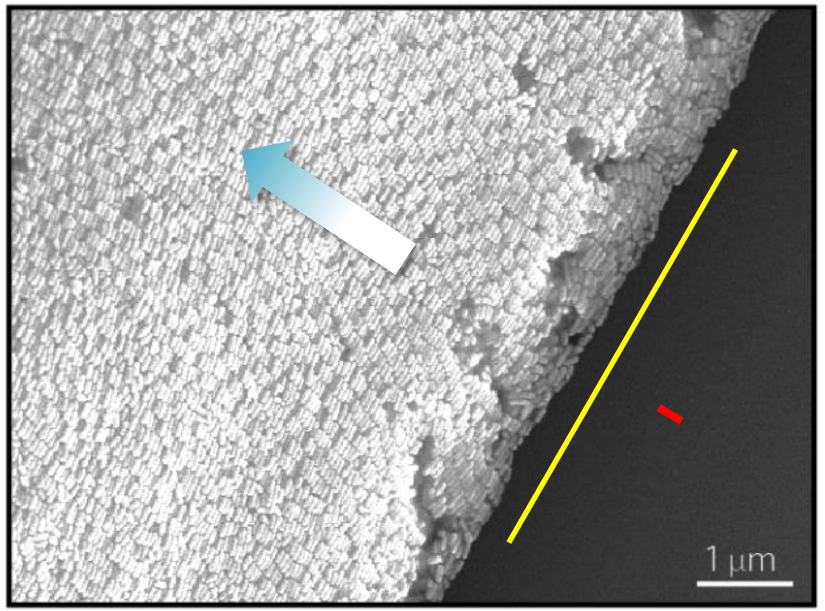


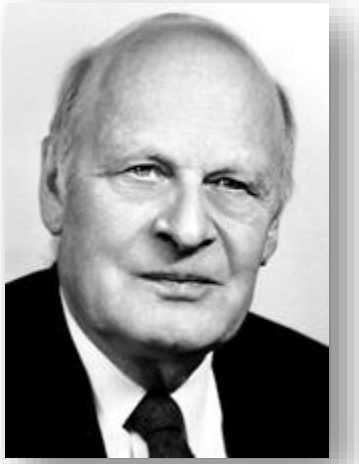


Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Particle accumulation and entropy







L. Onsager

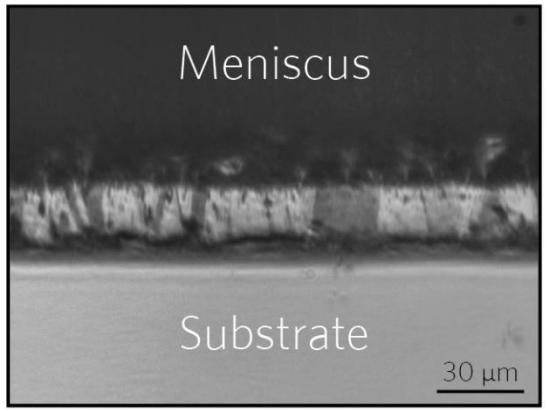
Density-induced phase transition

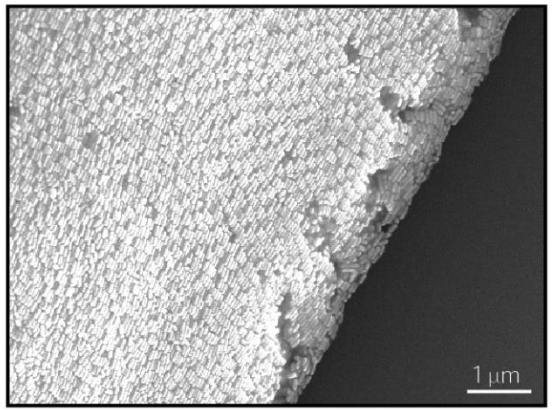
- Rotational entropy traded for translational entropy
- Net entropy gain

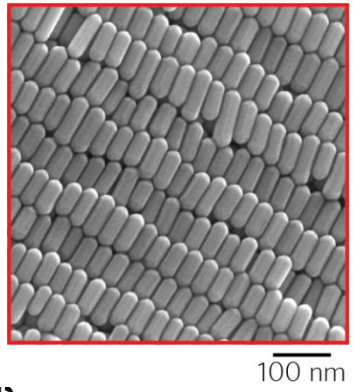
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

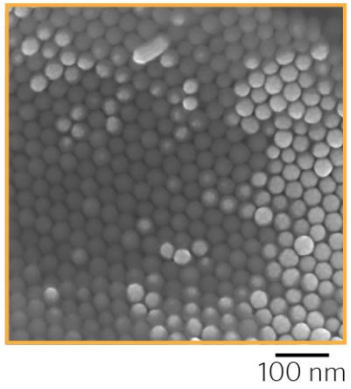
What would Lars think?

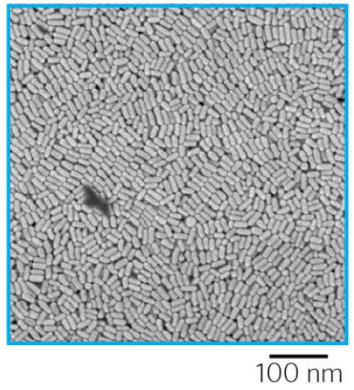
Insight 1: Non-uniform accumulation

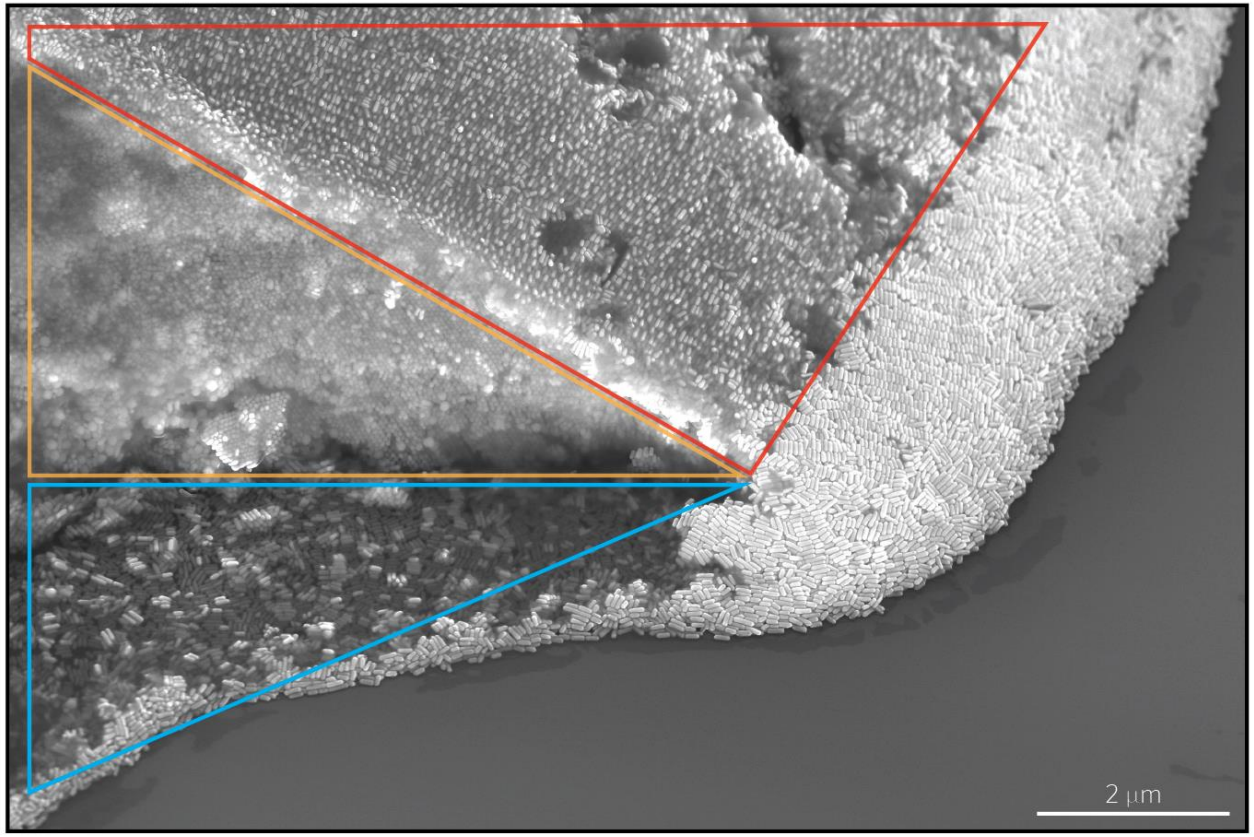






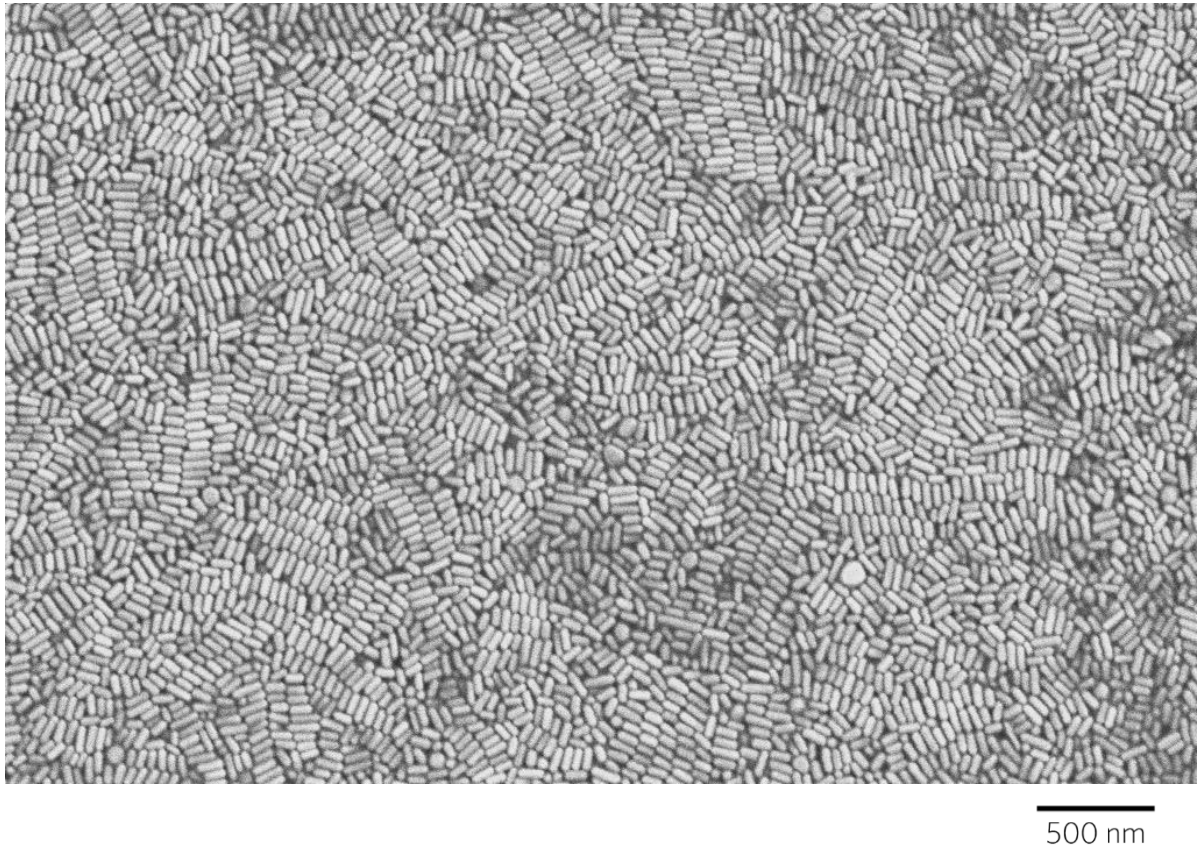


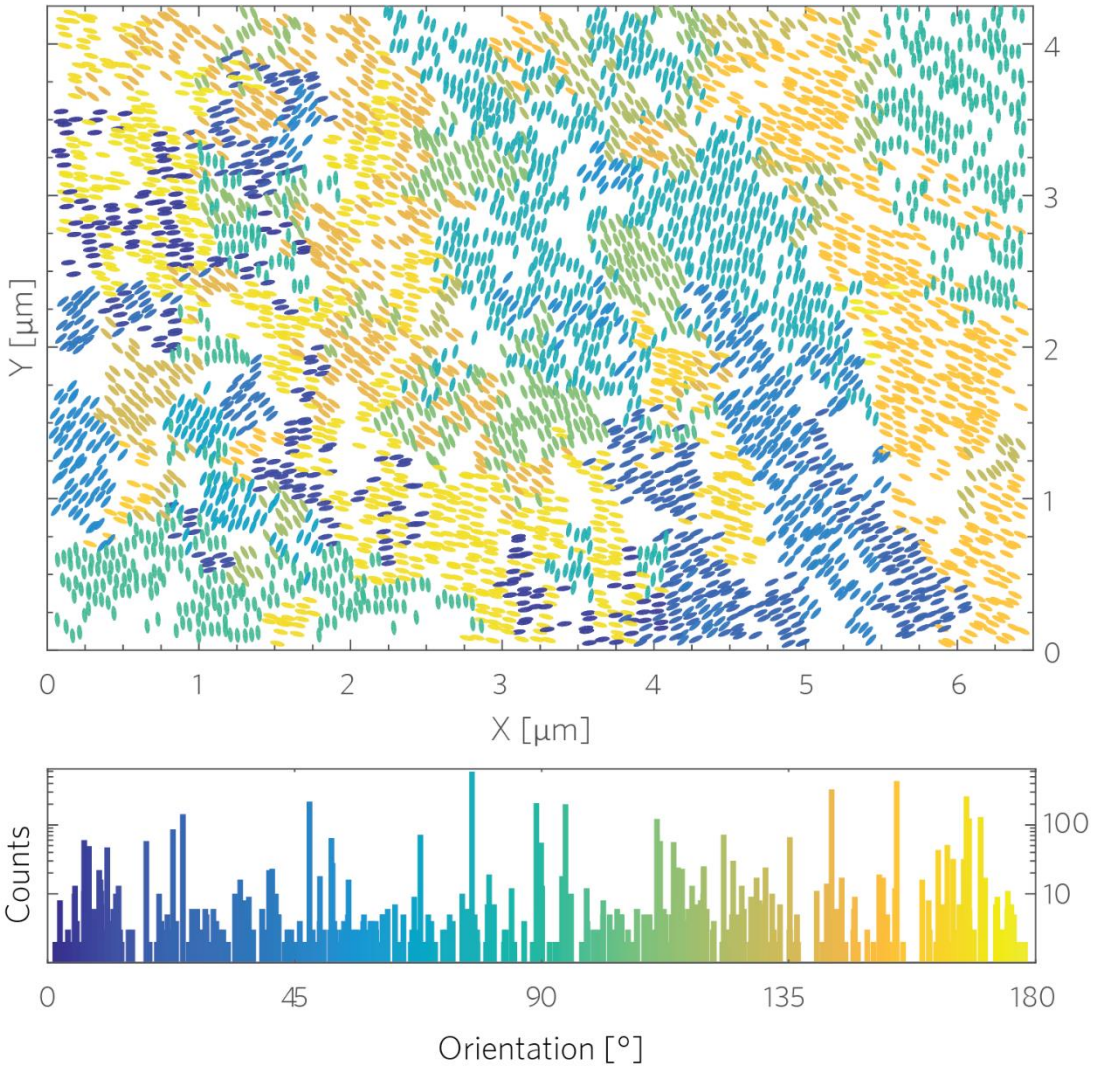




Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

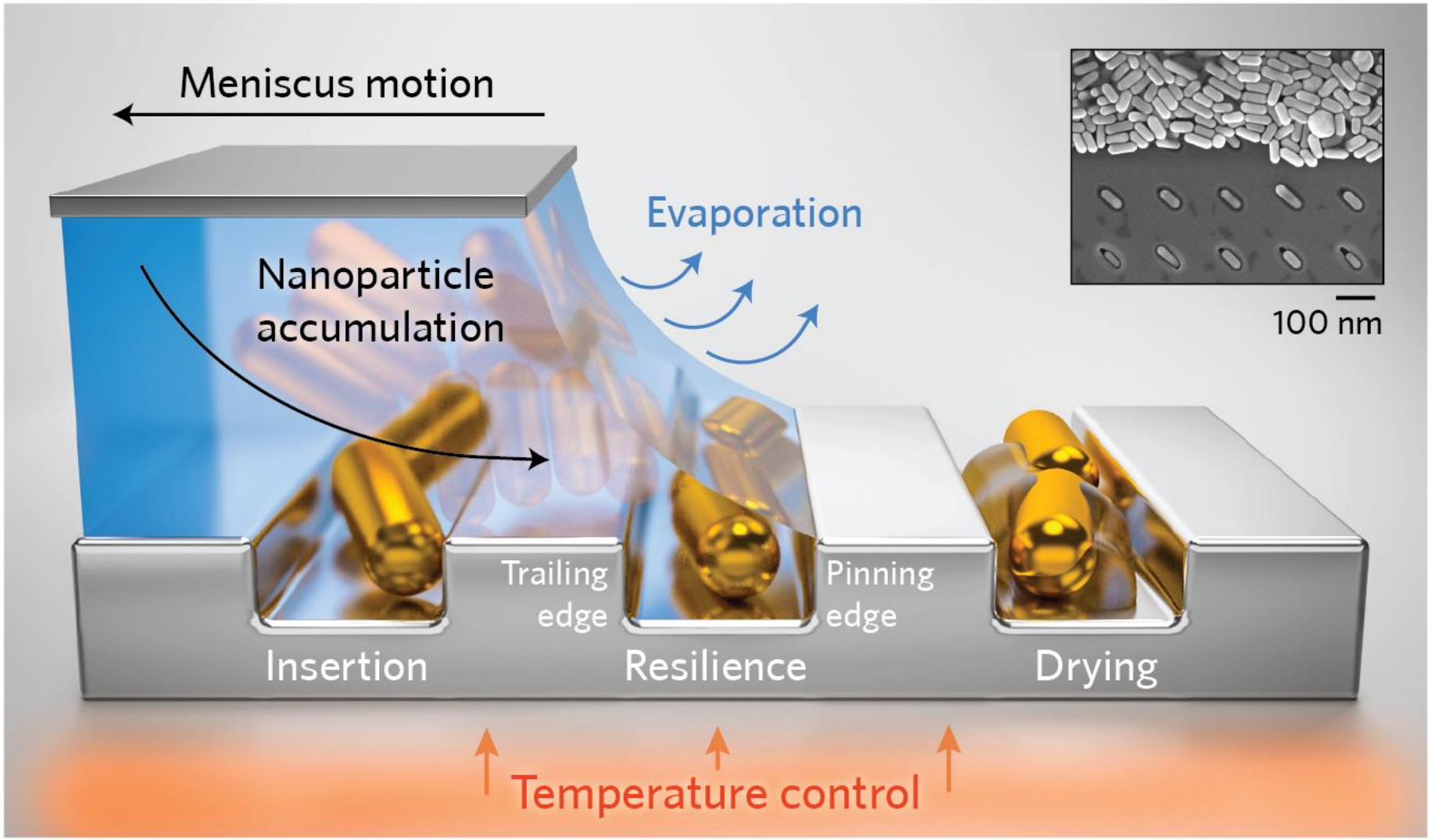
Insight 1: Non-uniform accumulation



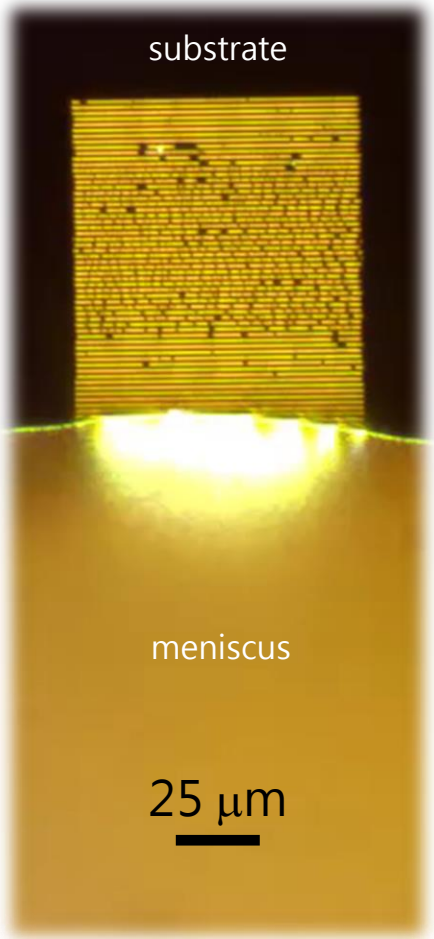


Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Insight 2: Stages of capillary assembly



Top view



Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Limitations of straight-edged traps

- Trap cross-section needs to accommodate effective NPs size…
- …But dry NPs are smaller
- Loose positional control

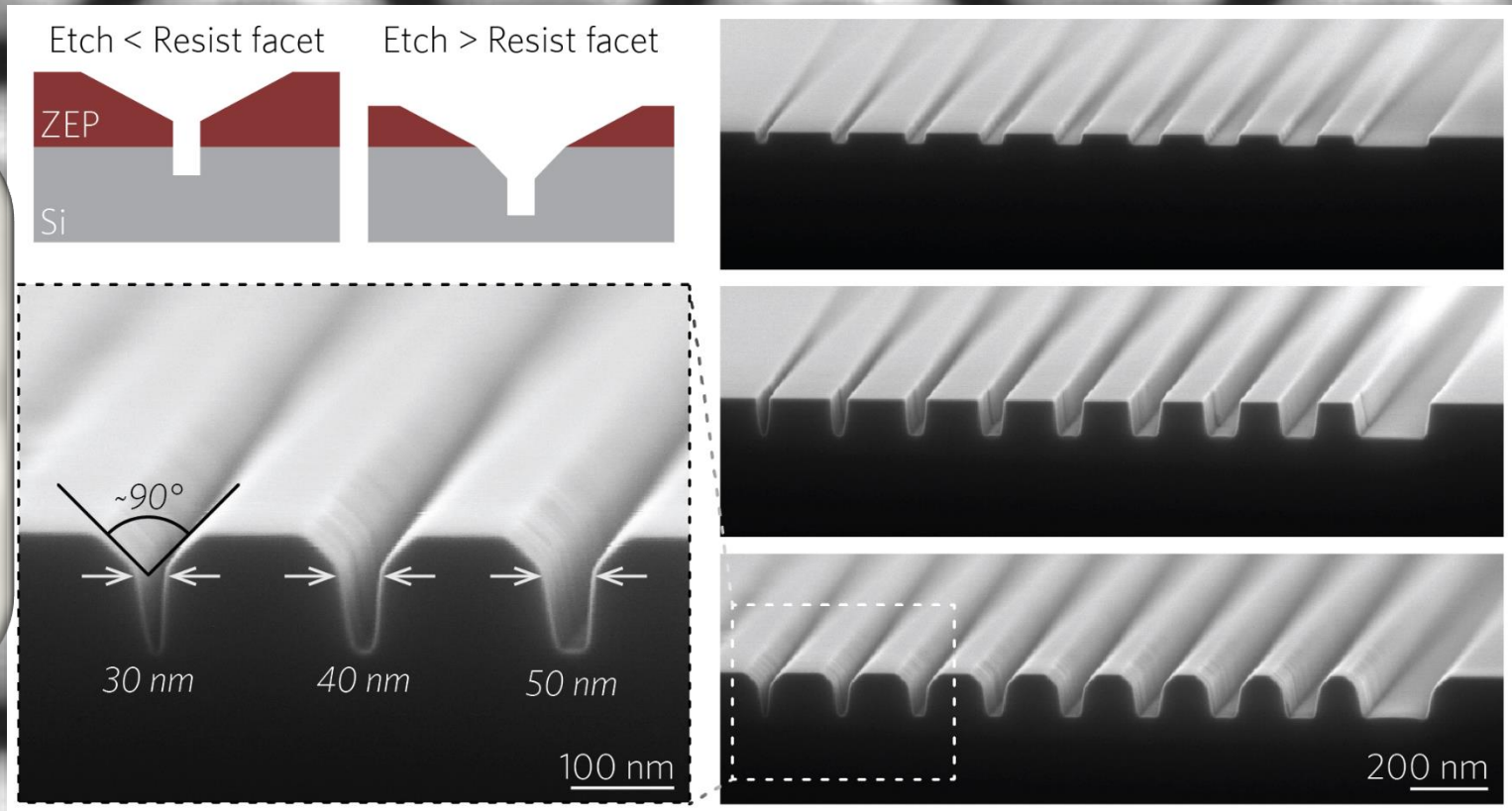
TU Delft EPFL

Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Insight 3: 3D trap geometry

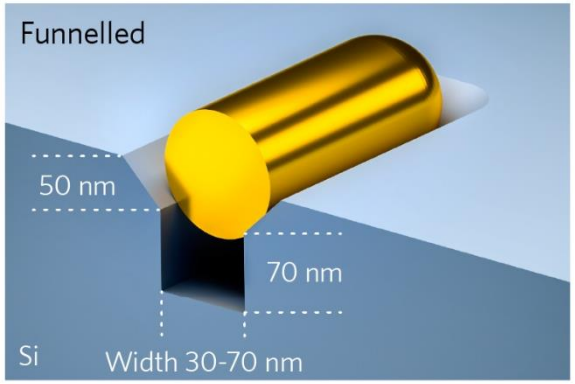
EBL – RIE – Silanisation

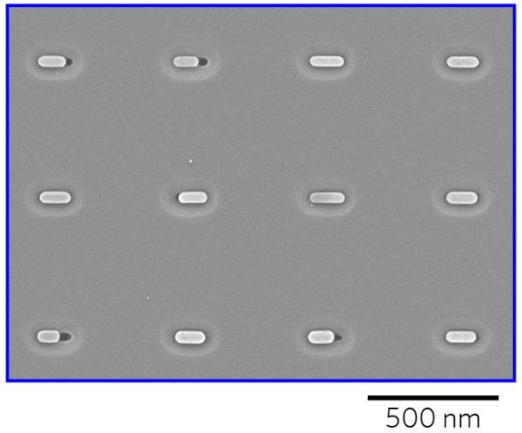
- Cl_2/BCl_3 chemistry
- Progressive resist faceting
- Low roughness transfer to Si
- Compatible with SiO_2 & Si_3N_4

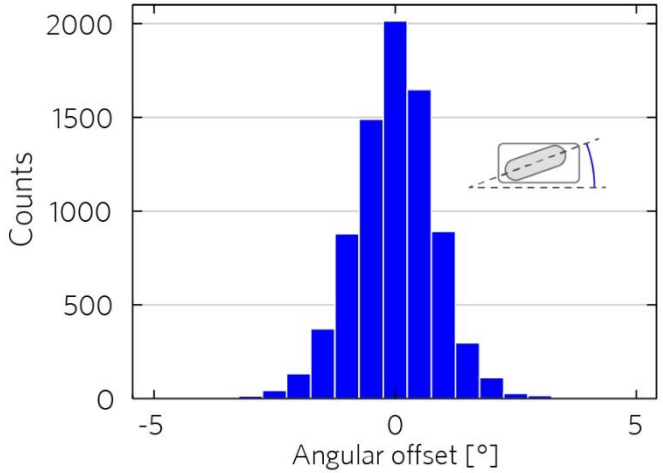


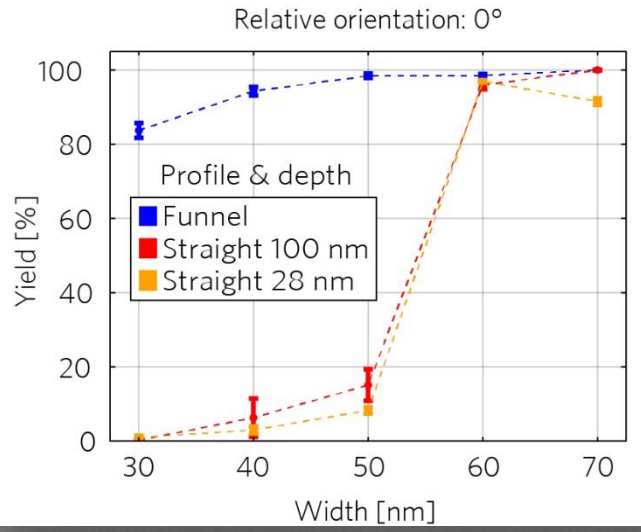
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

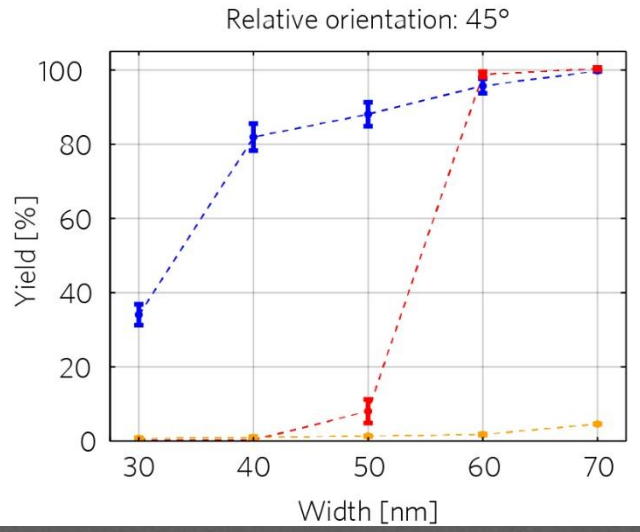
Assembly on funneled traps

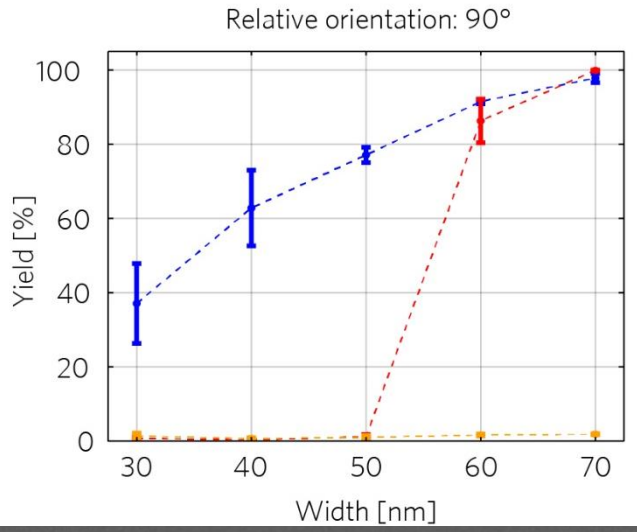












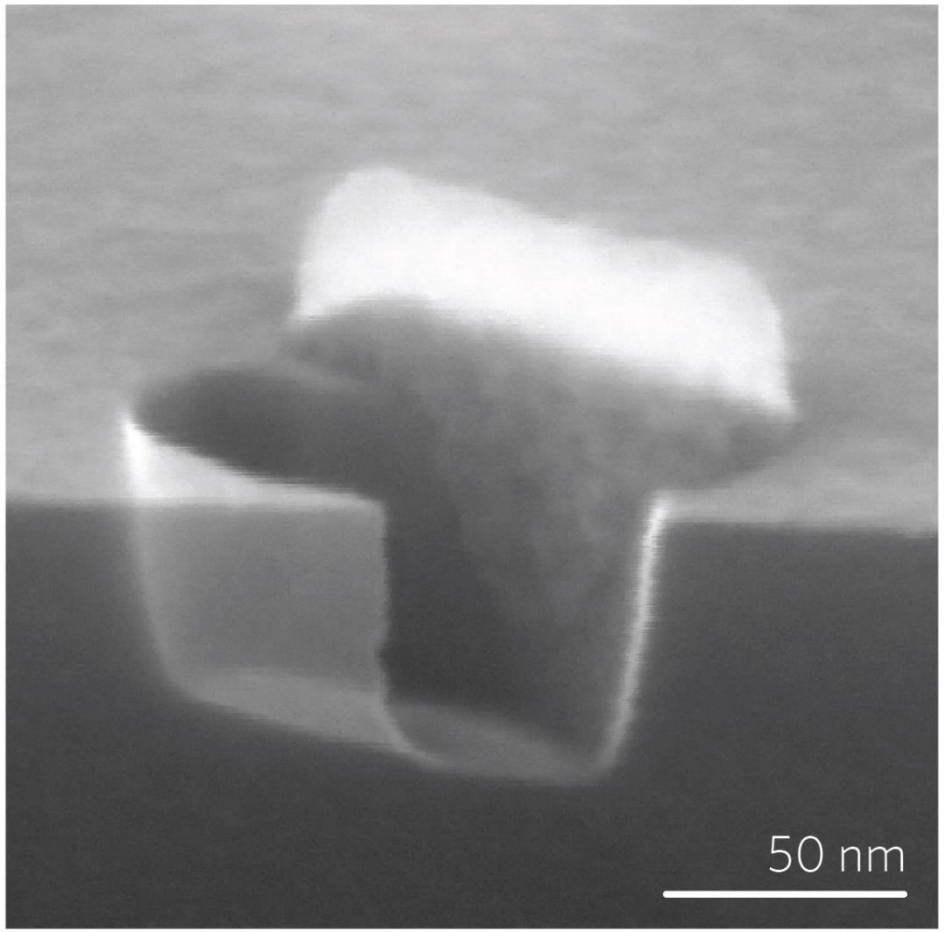
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

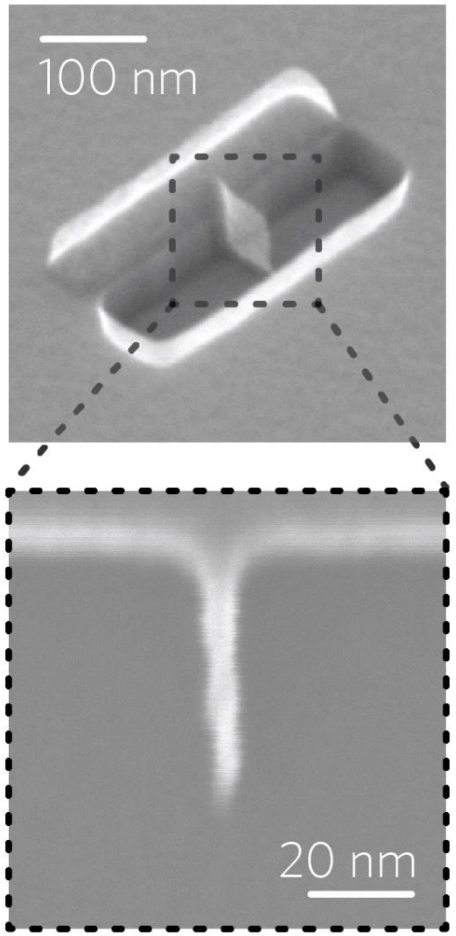
Single auxiliary sidewall

Auxiliary sidewall

- HSQ (SiO_x) EBL resist
- Alignment < 10 nm

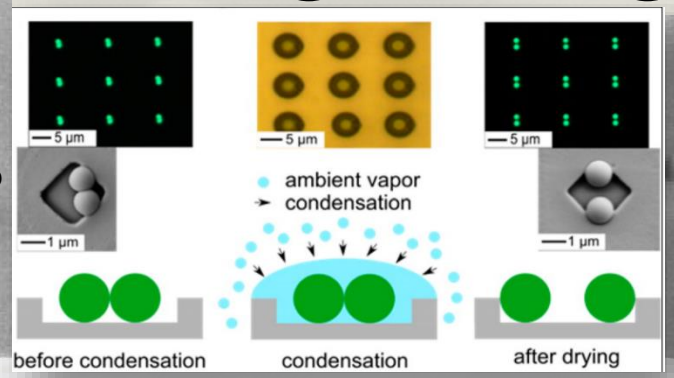
- Counteract NP removal
- Symmetry breaking





Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Straight-edged traps with auxiliary sidewall



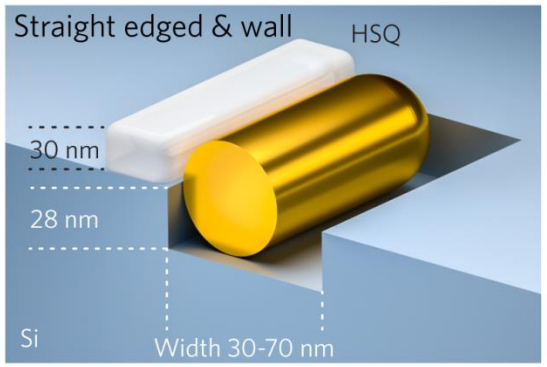
Ni *et al.*, Langmuir 2014

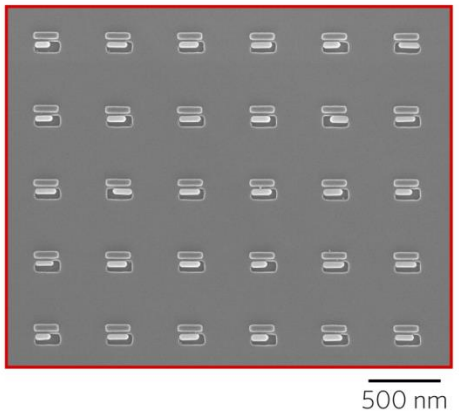
Biased evaporation

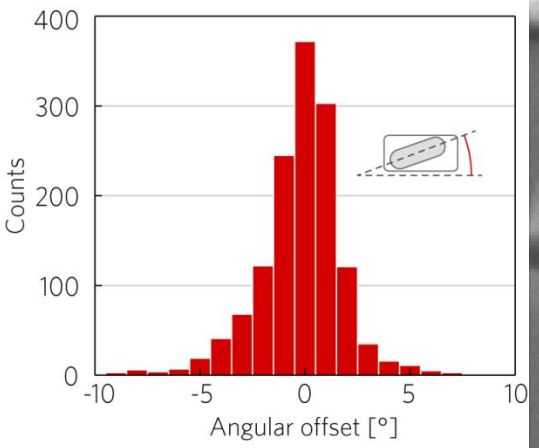
- Deterministic positioning in loose traps

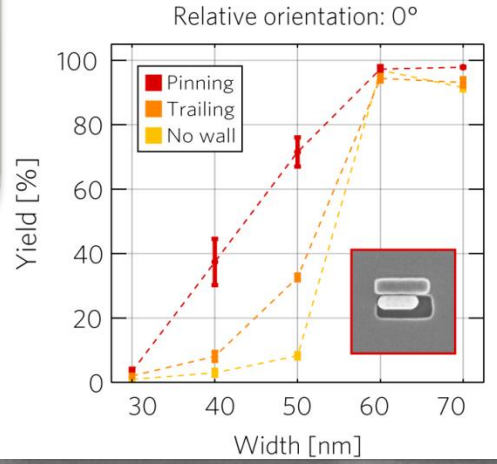
Sidewall position

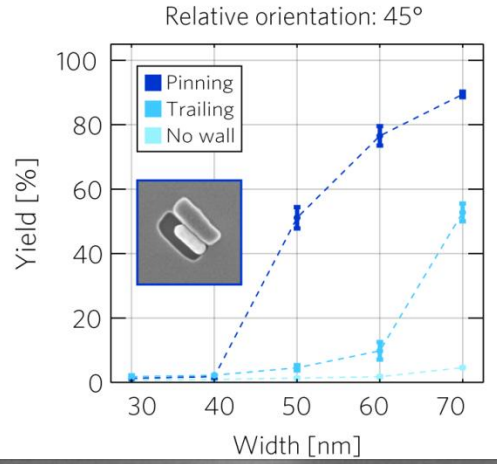
- High yield improvement

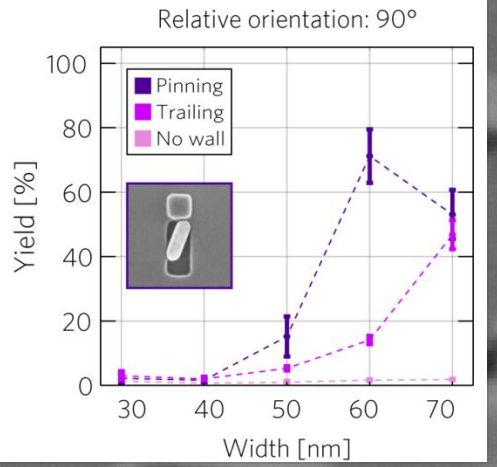












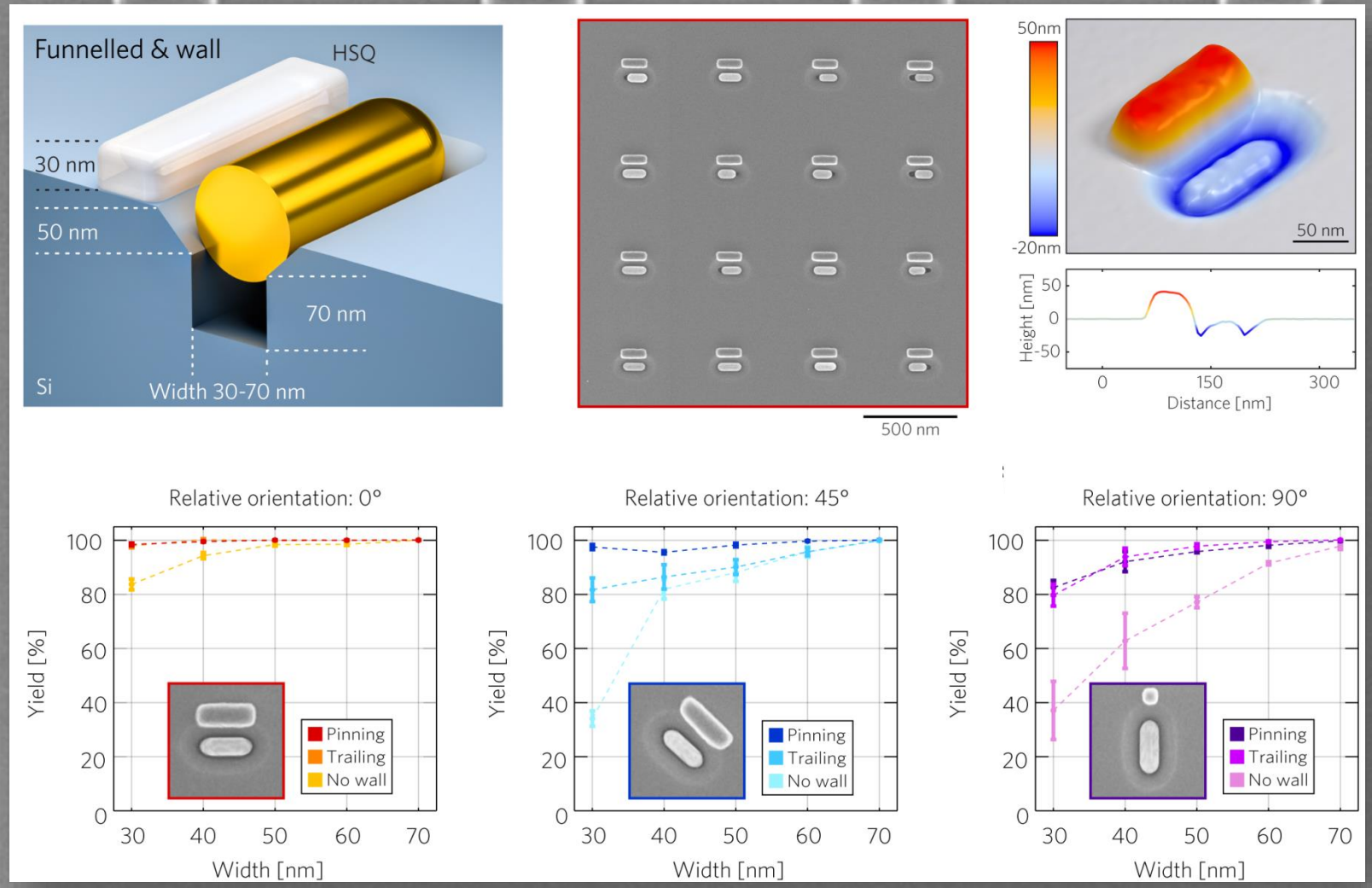
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

TU Delft EPFL

The ideal trap

Exploits all three stages of assembly

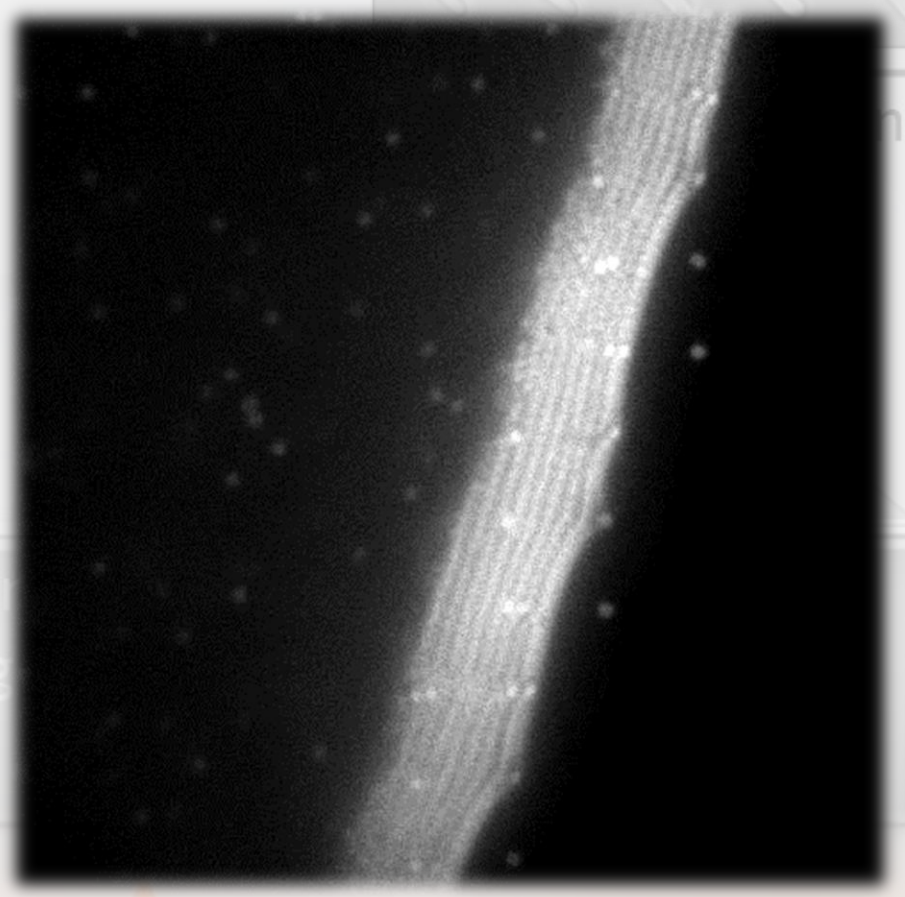
- Up to 100% yield for all orientations
- Absolute positioning control



Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

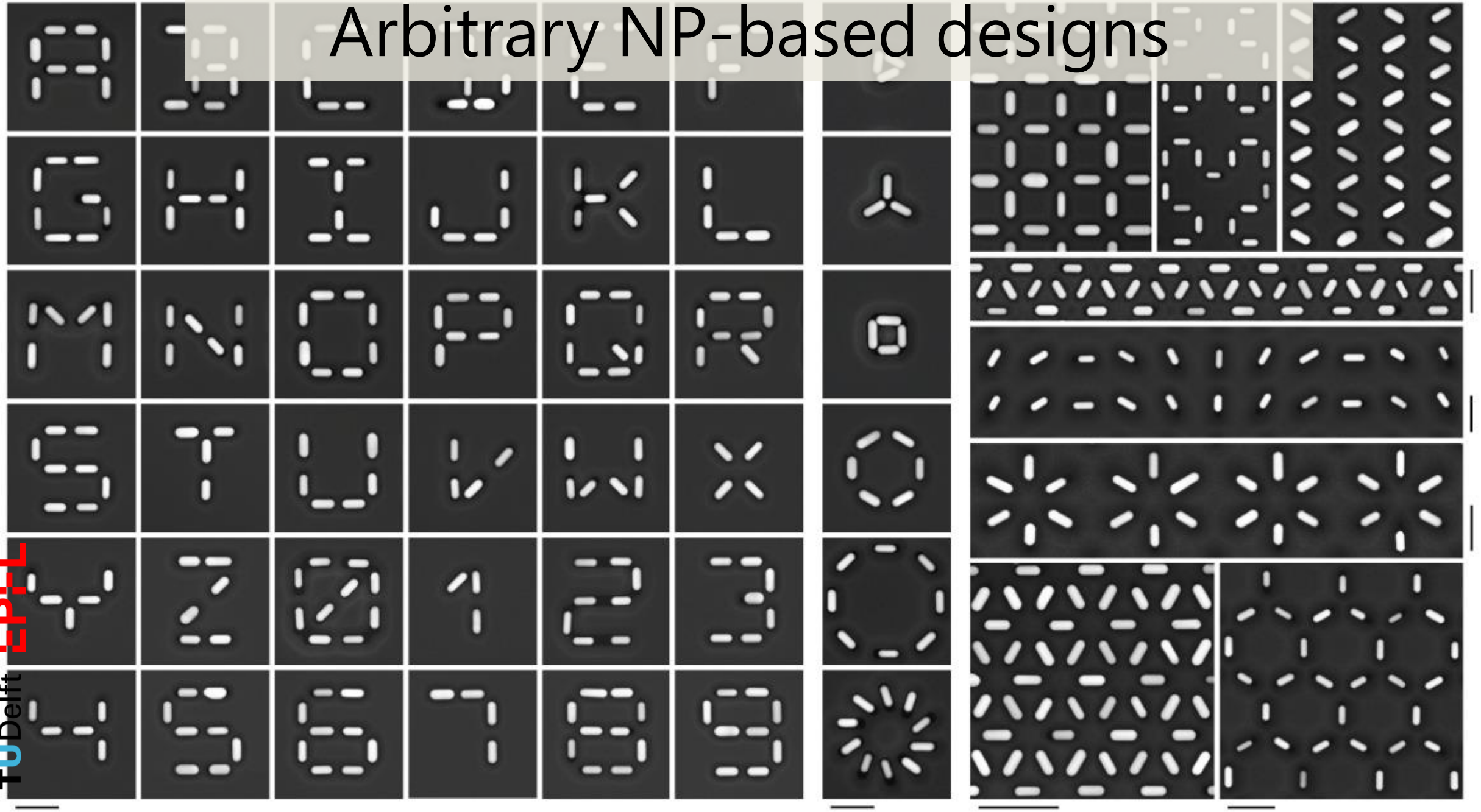
Updated wisdom

1. Contact line
   - Boundary
   - Drags particles across substrate
   - Last push
2. Accumulation
   - Width facilitates injection
   - Confinement dependent
3. Particle trajectory
   - Advection, immobilization, drag
   - Injection: pressure, entropy
4. Assembly stages
   - All impact assembly yield
   - Tailored trap geometry



Ni *et al.*, *Farad. Discuss.* 181, 225 (2015)

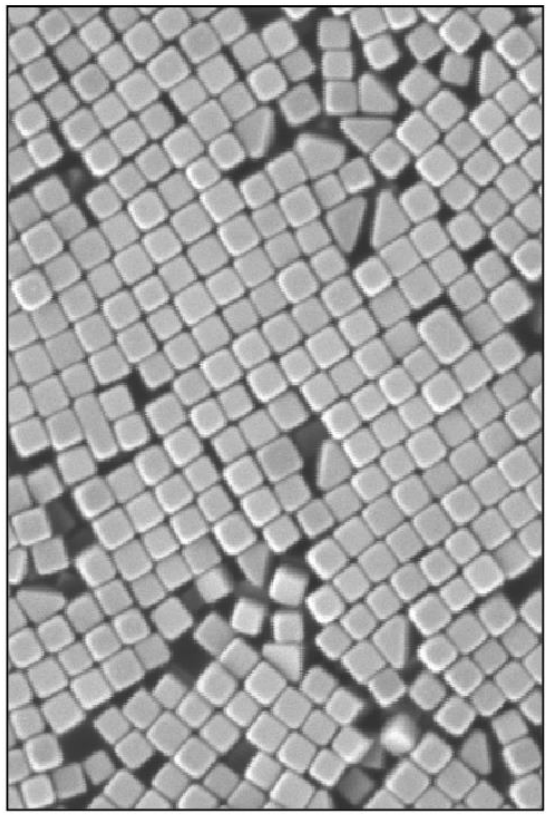
Arbitrary NP-based designs

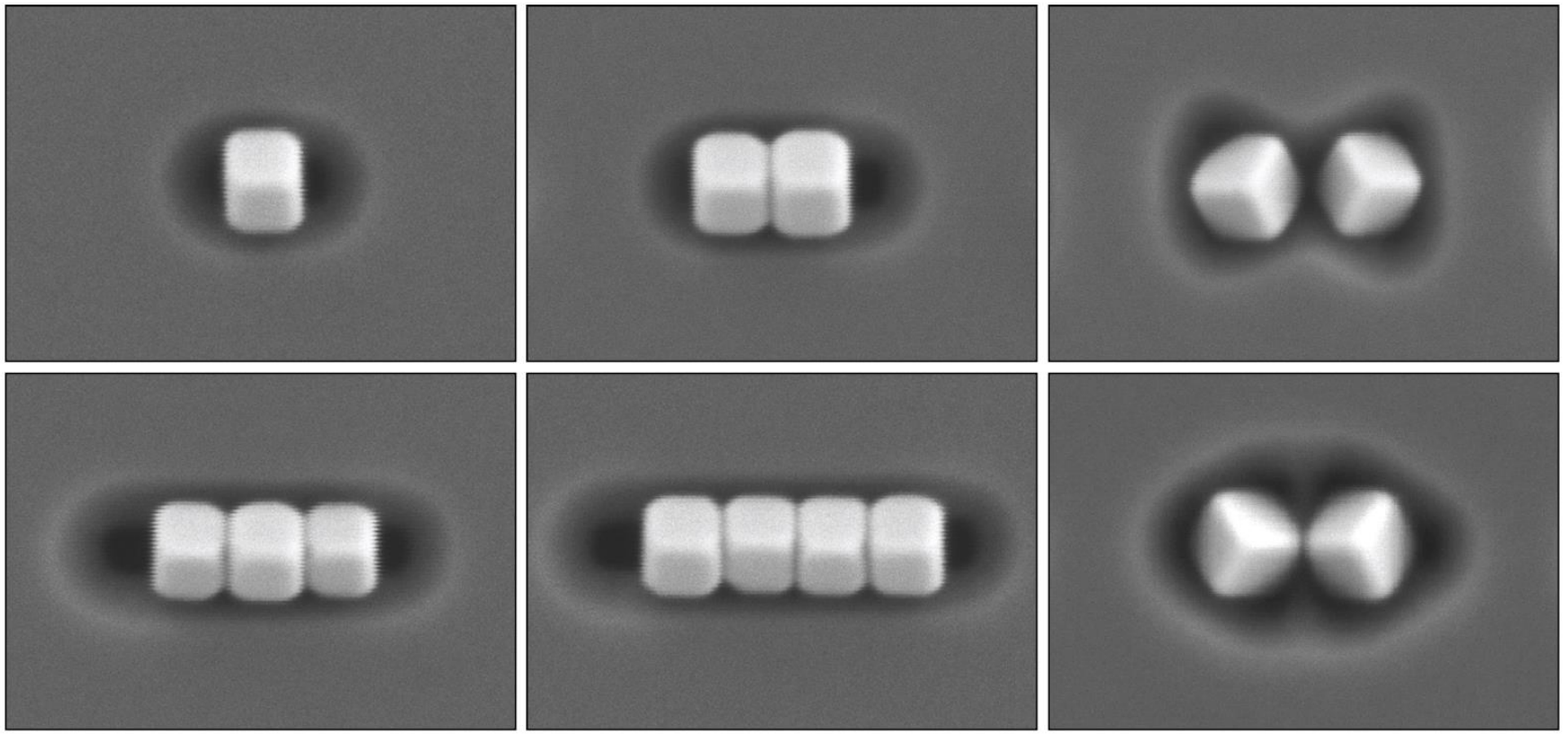


Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Scalebars: 250 nm

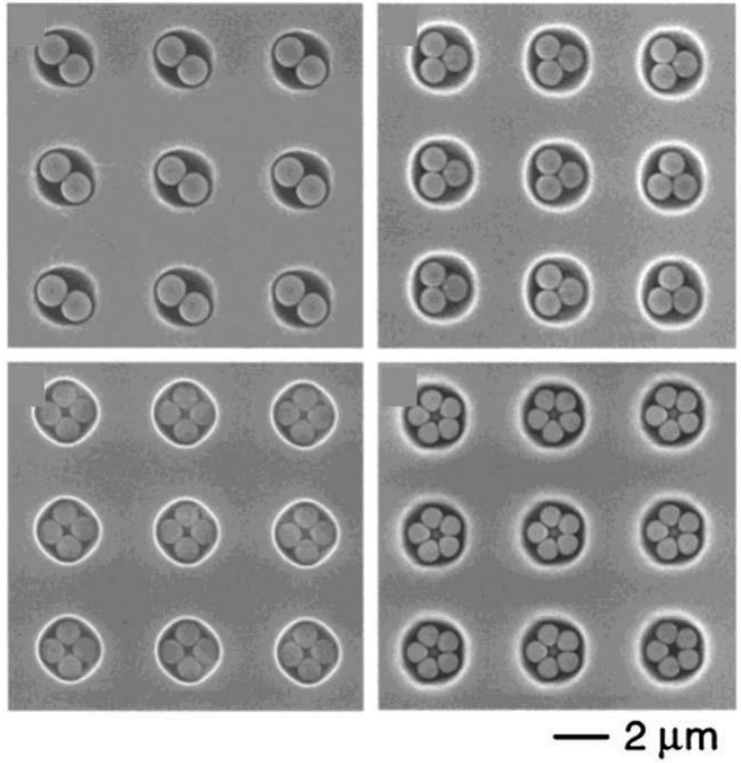
3D orientation of Ag nanocubes



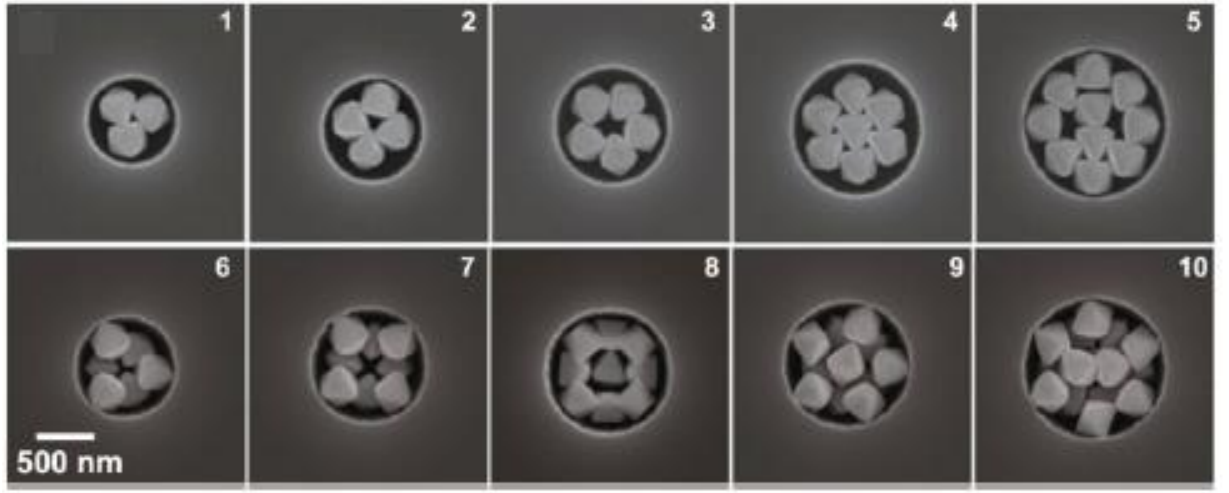


Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Trap design: Trap-to-particle ratio

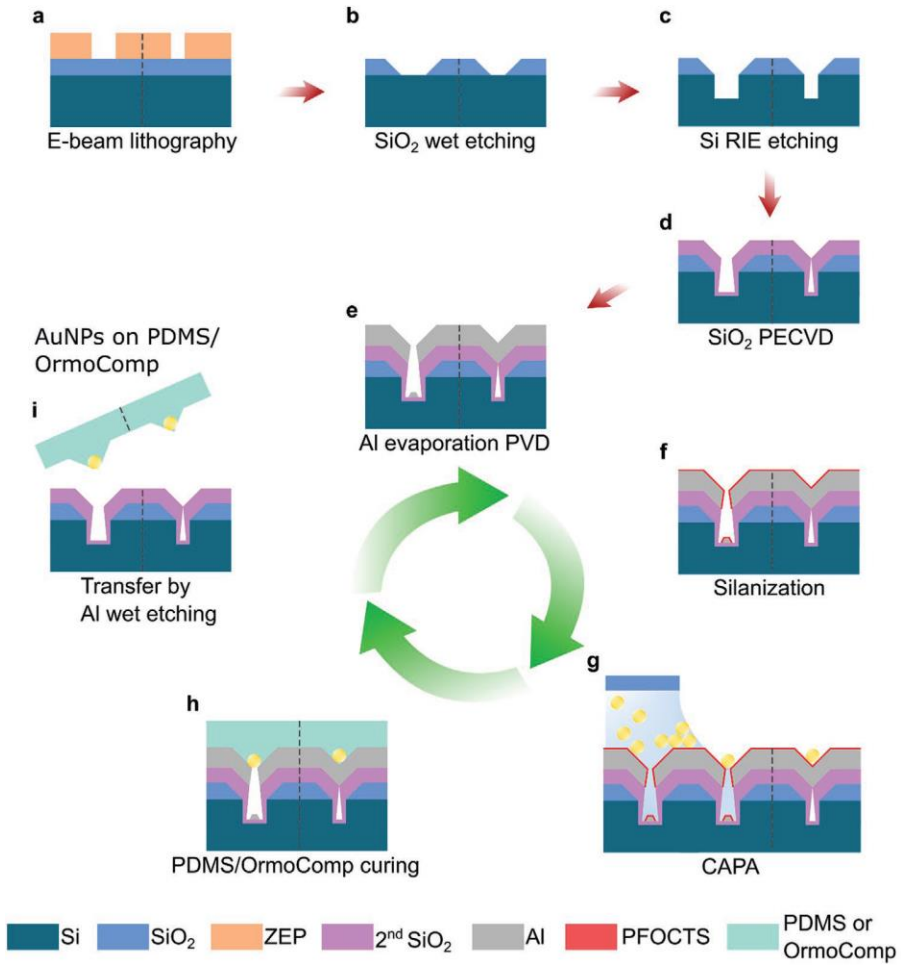


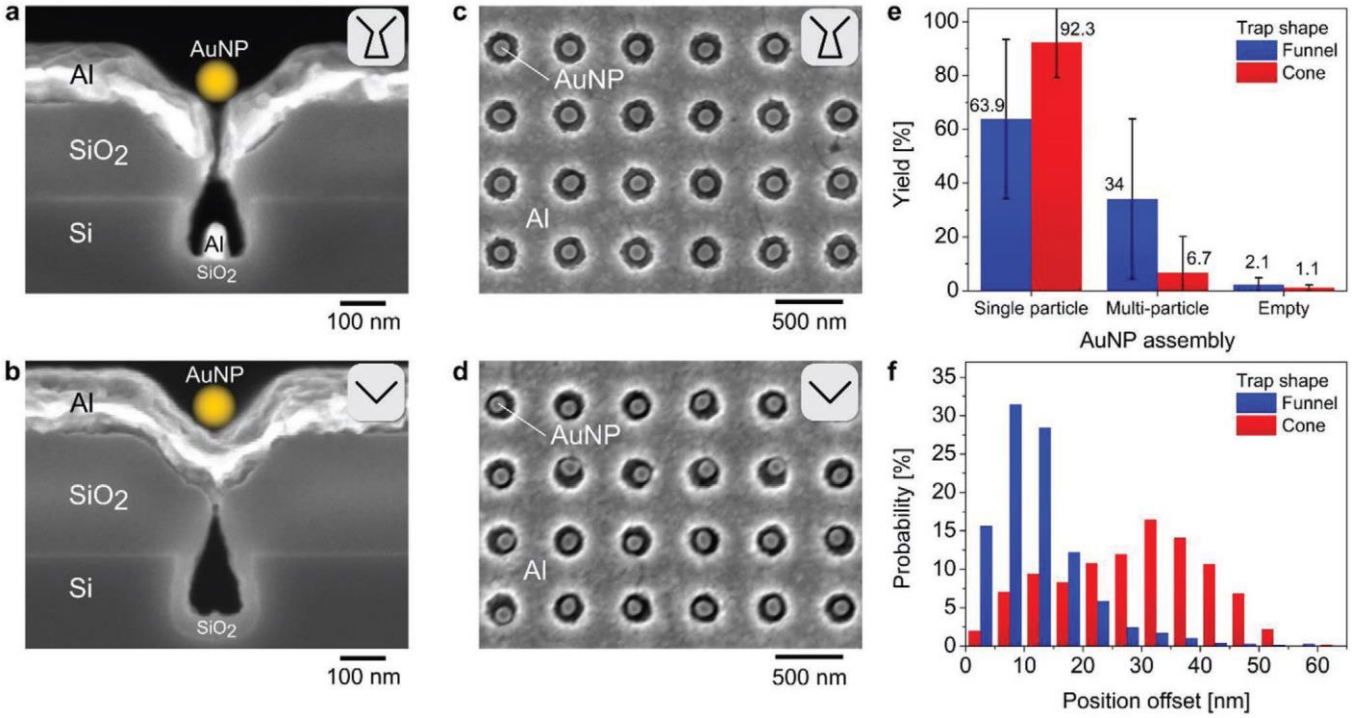
Yin *et al.*, *J. Am. Chem. Soc.* 123, 8718 (2001)



Henzie *et al.*, *Proc. Natl. Acad. Sci* 110, 6640 (2013)

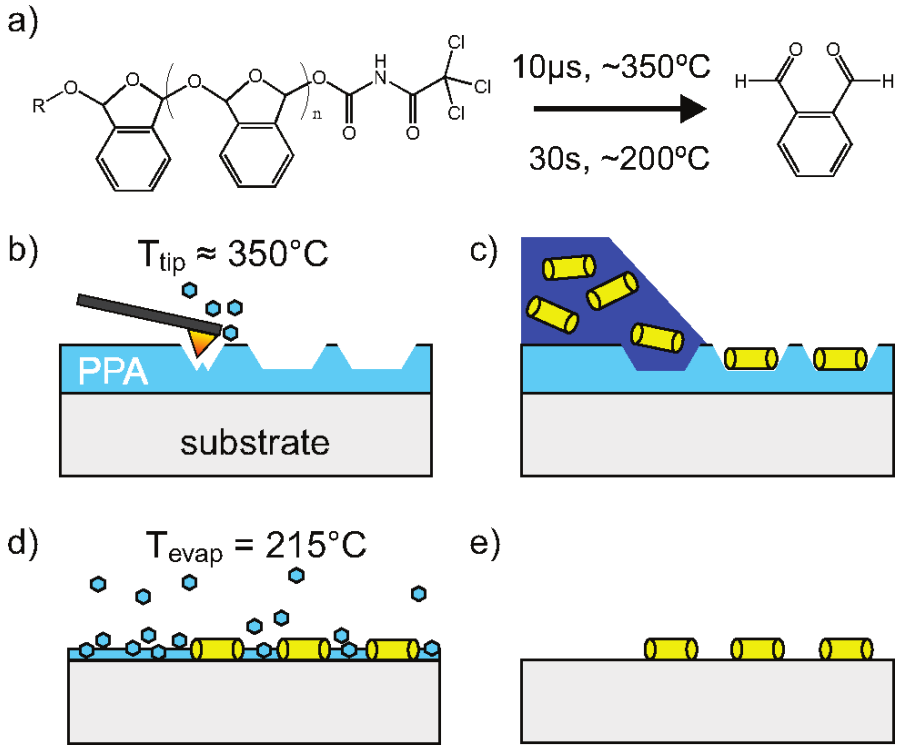
Funneled traps in reusable template

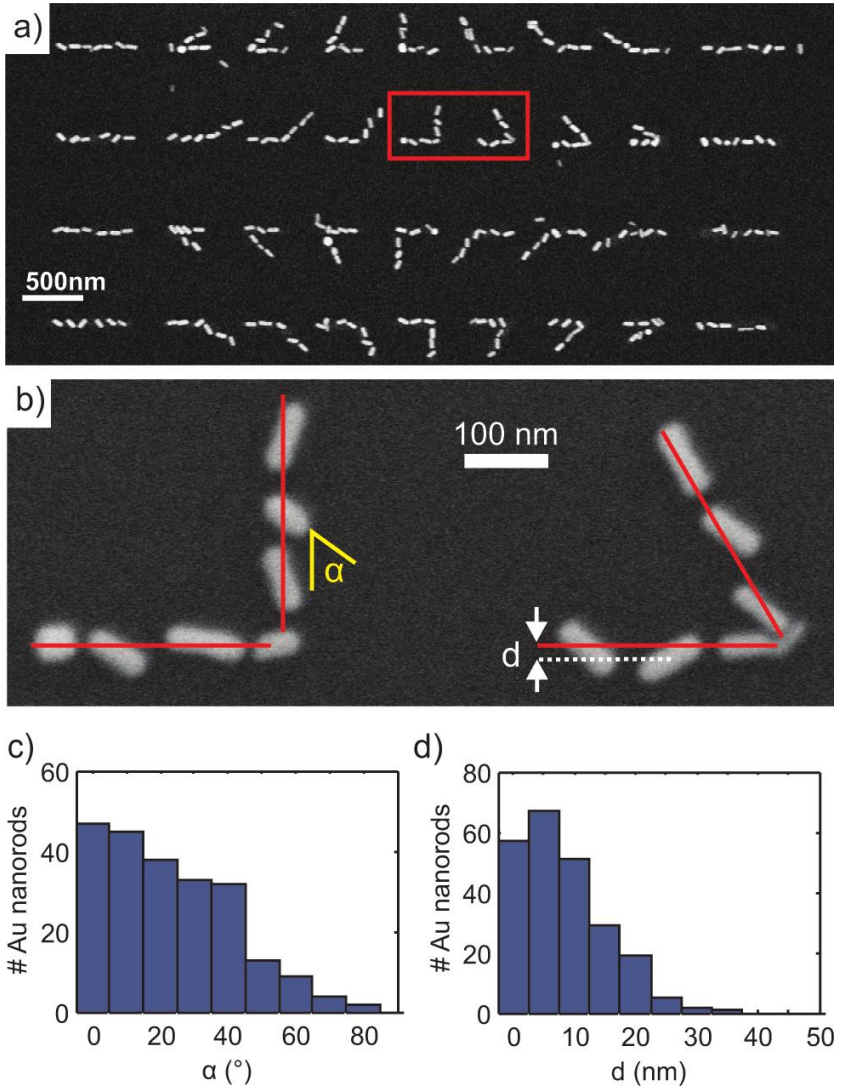




Yu *et al., Part. Part. Syst. Charact.* 39, 2100288 (2022)

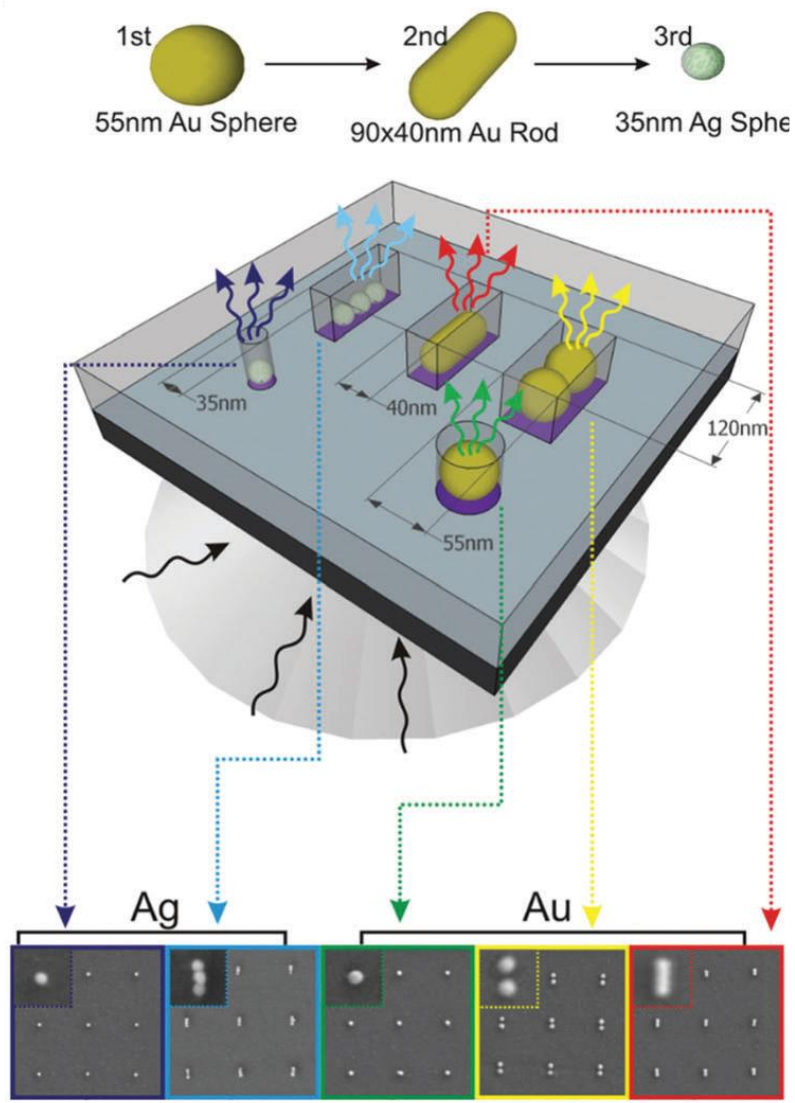
Trap design: t-SPL-based sculpting



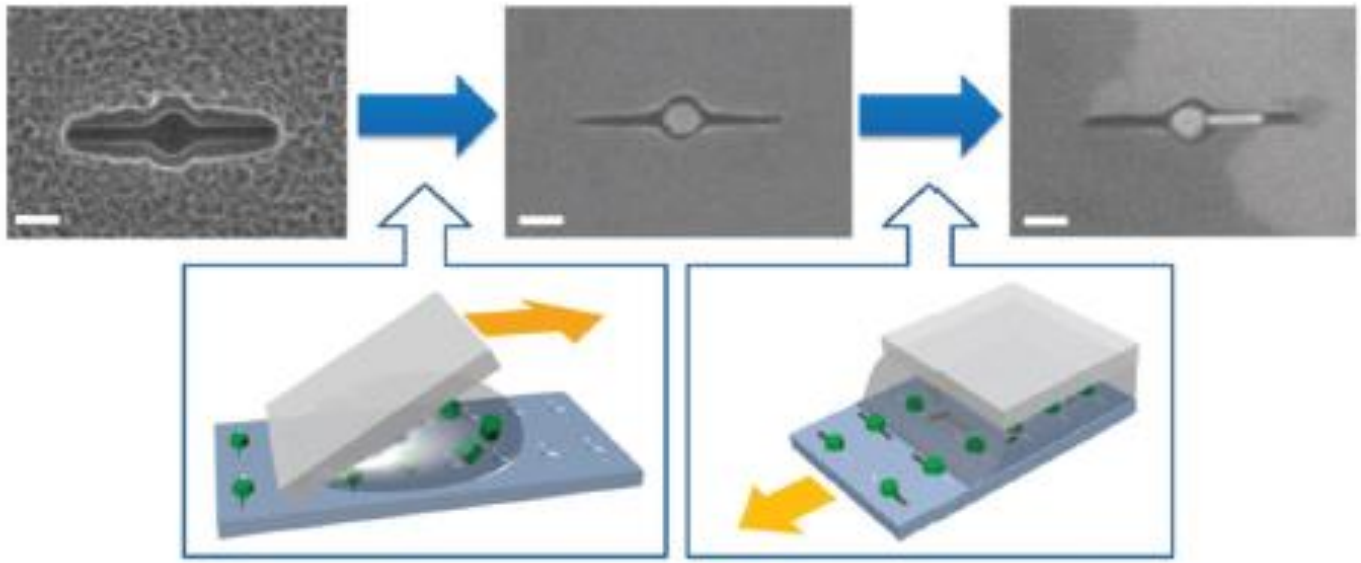


Holzner *et al.*, *Nano Letters* 11, 3957 (2011)

Trap design: Shape matching

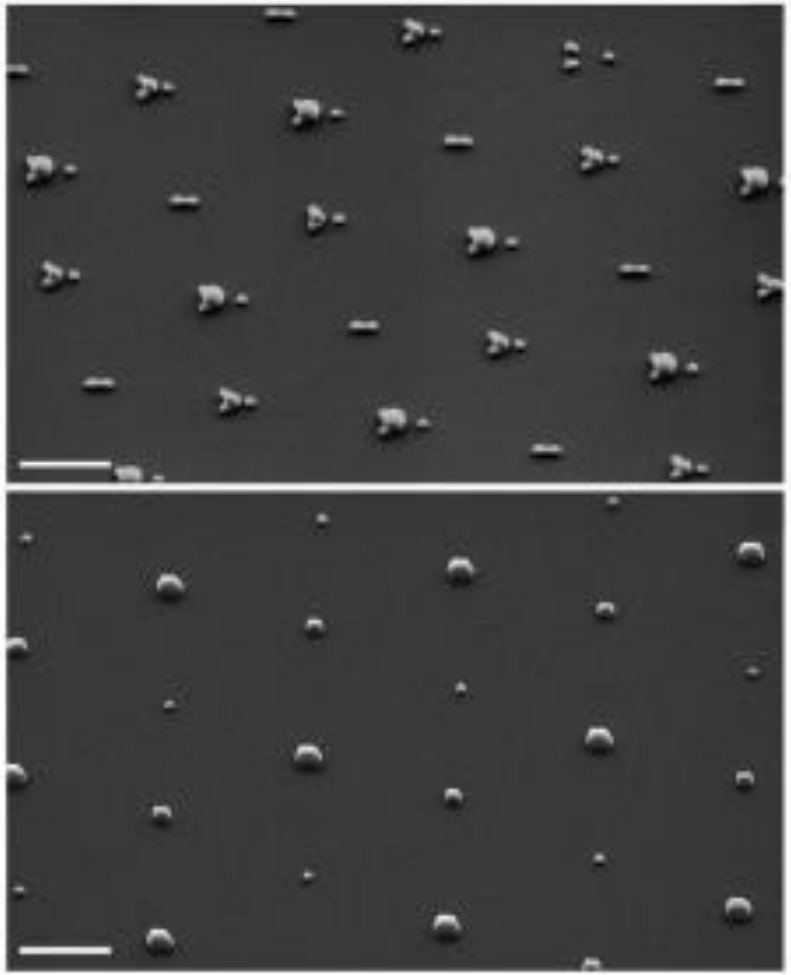


Chen & Reinhard, *Adv. Mater.* 28, 3522 (2016)

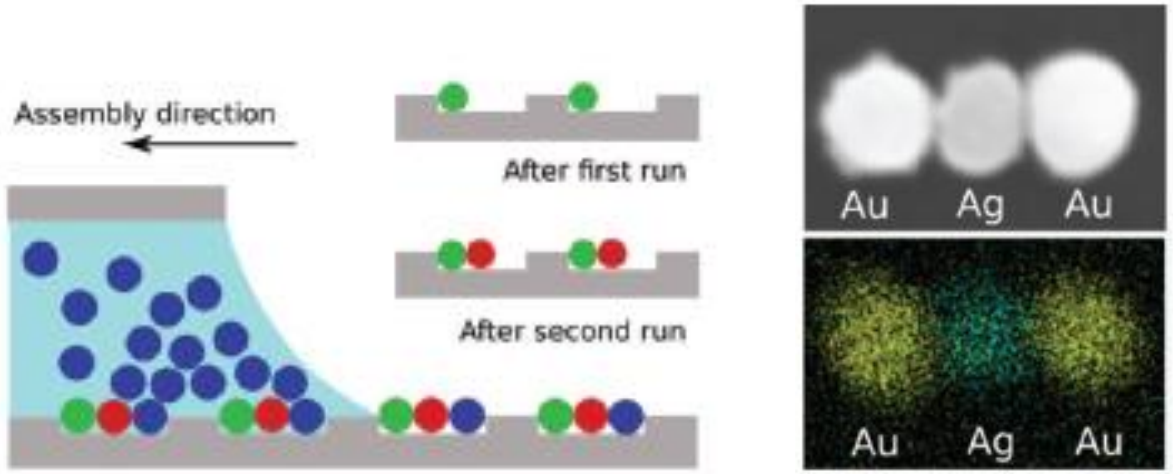


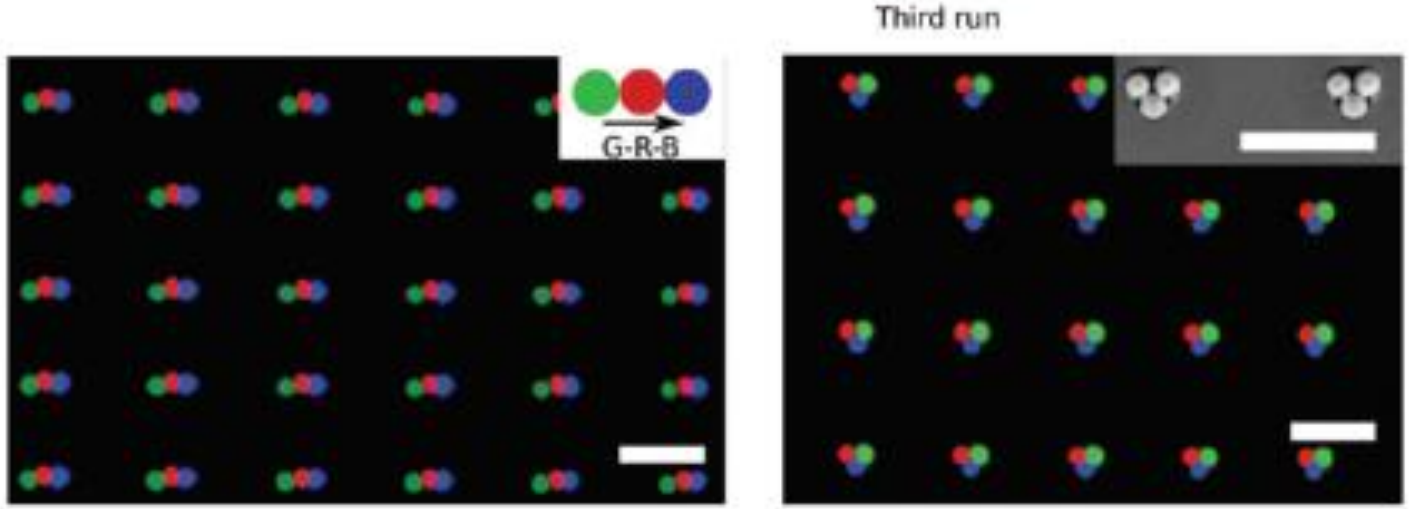
Greybush *et al.*, *ACS Nano* 9, 9482 (2014)

Trap design: Shape matching



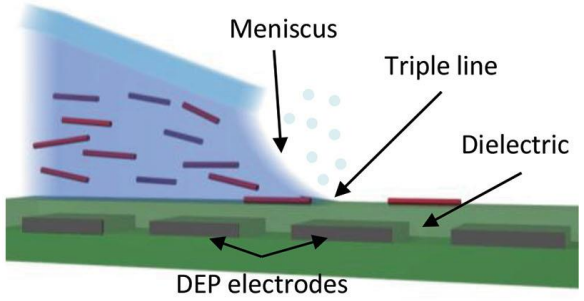
Kuemin *et al., Adv. Mater.* 22, 2804 (2010)

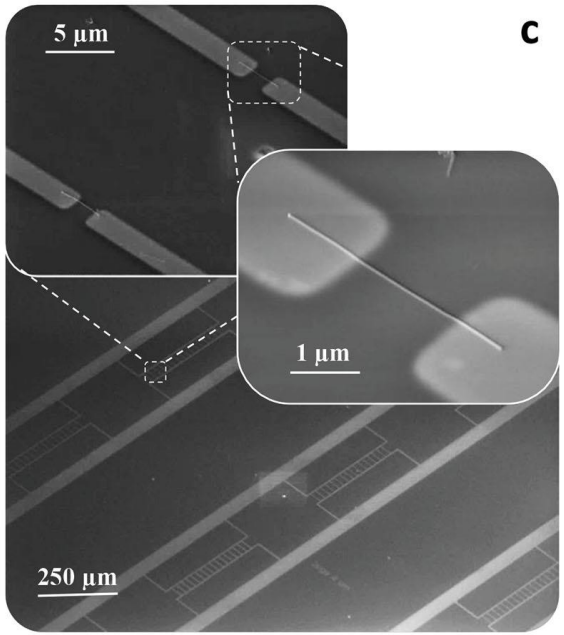


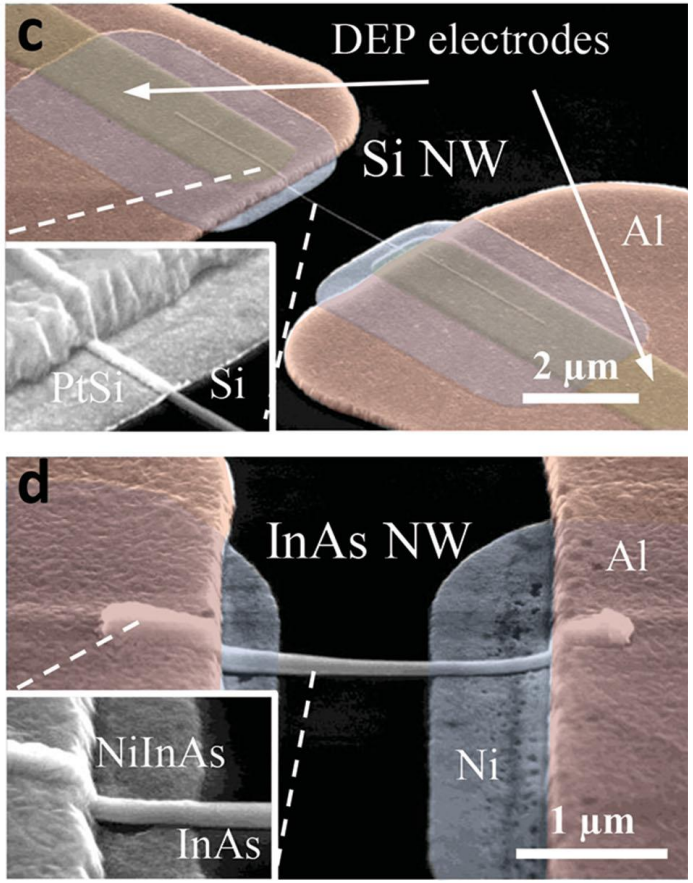


Ni *et al.*, *Soft Matter* 2018

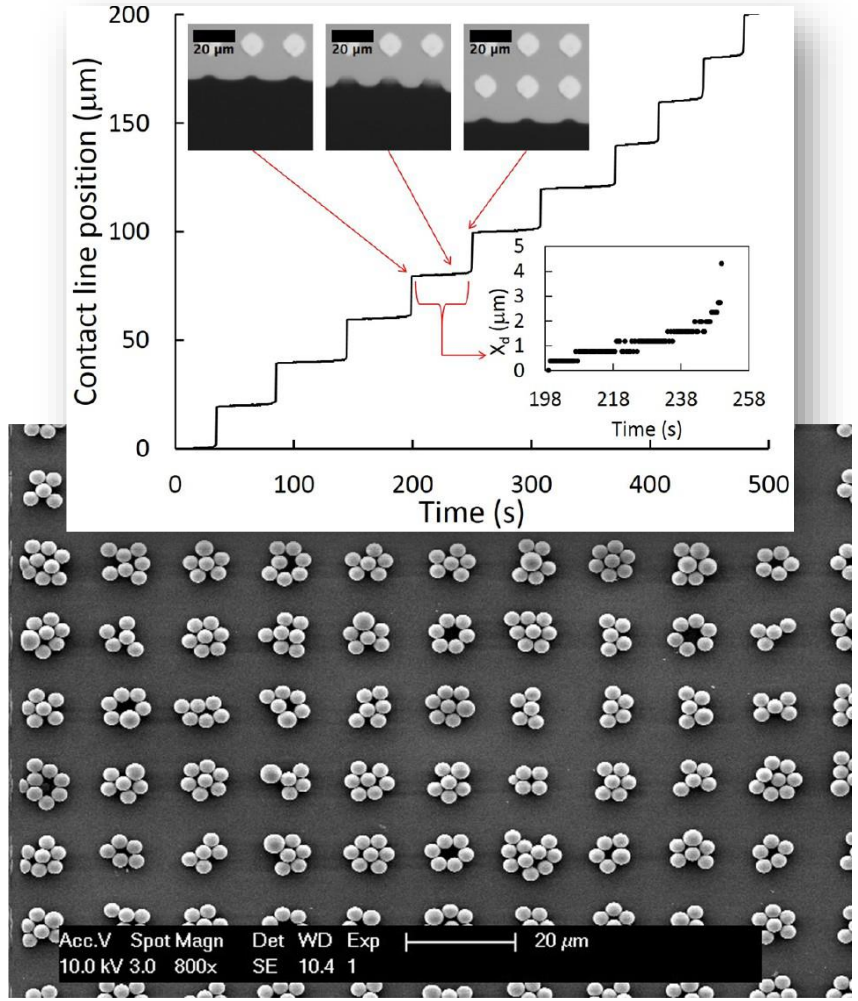
Non-topographical traps





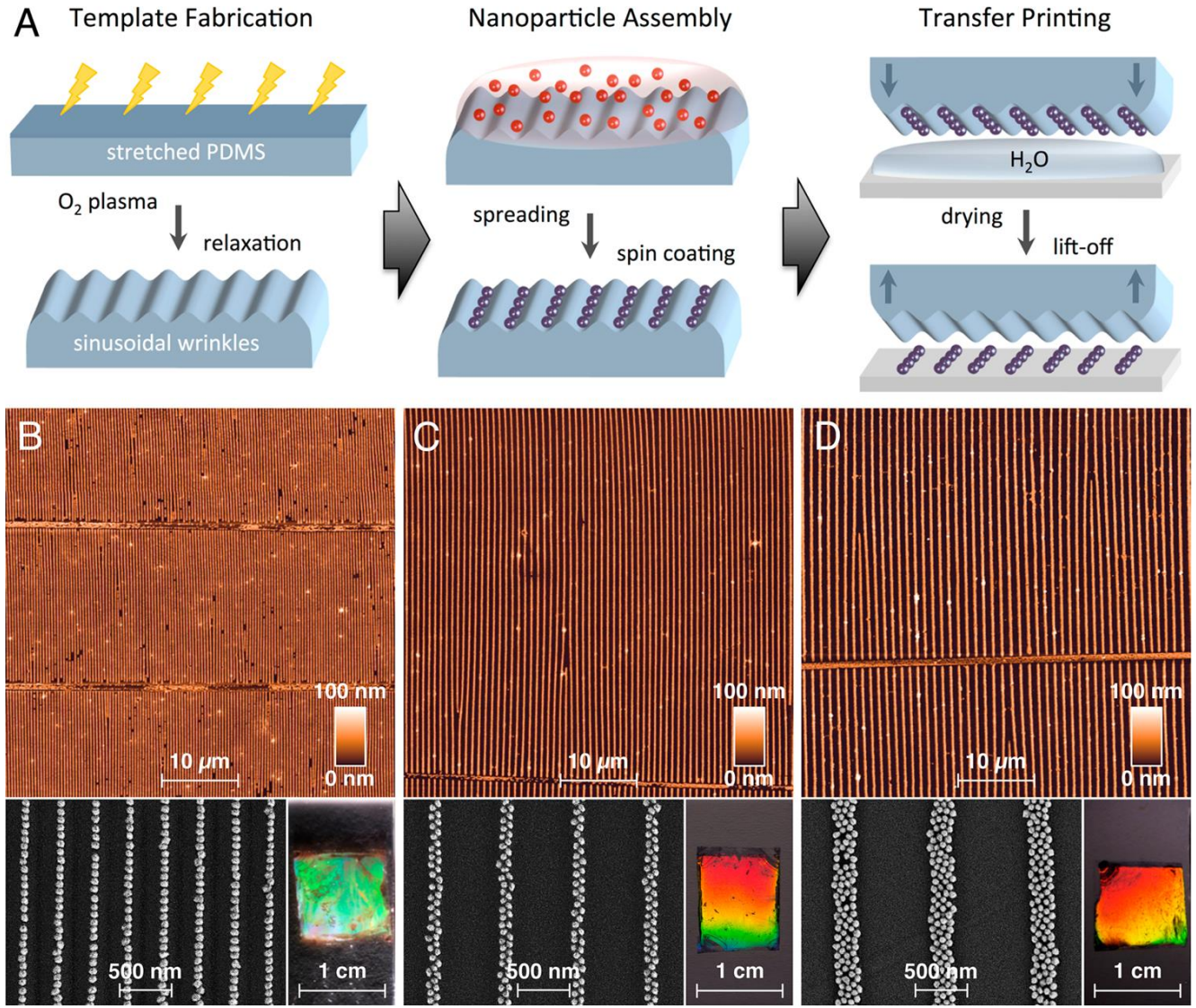


Collet *et al.*, *Adv. Mater.* 27, 1268 (2015)



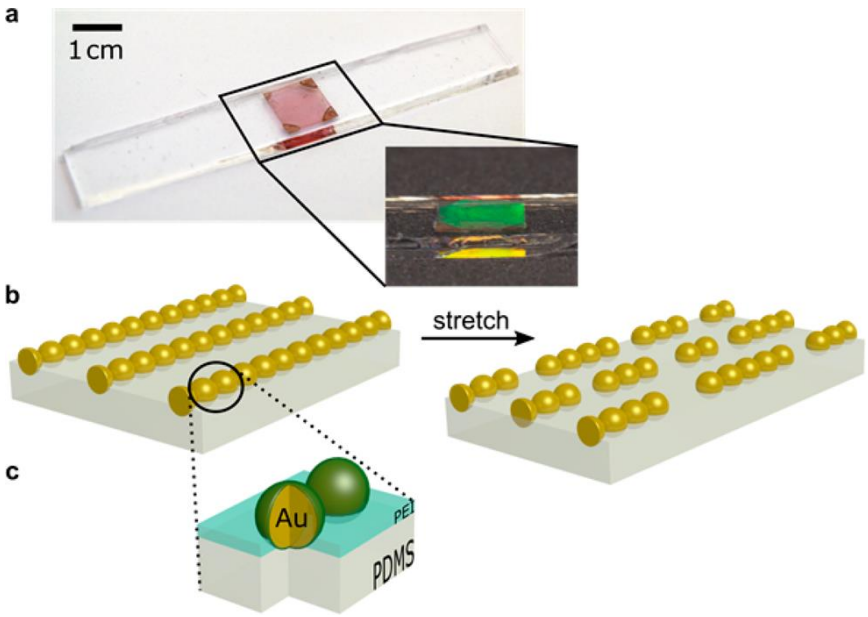
Wirth *et al.*, *Langmuir* 31, 1632 (2015)

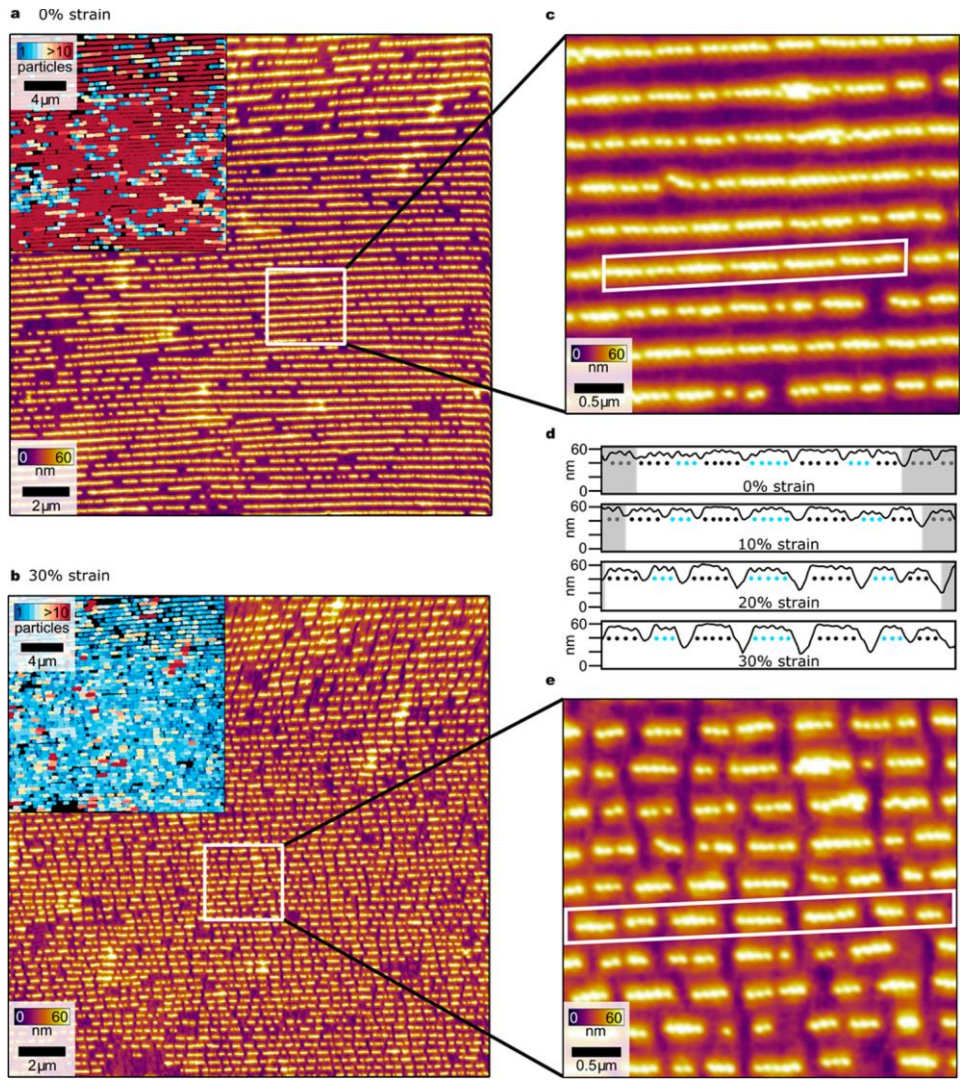
Non-lithographical traps



Hanske *et al.*, *Nano Letters 14*, 6863 (2014)

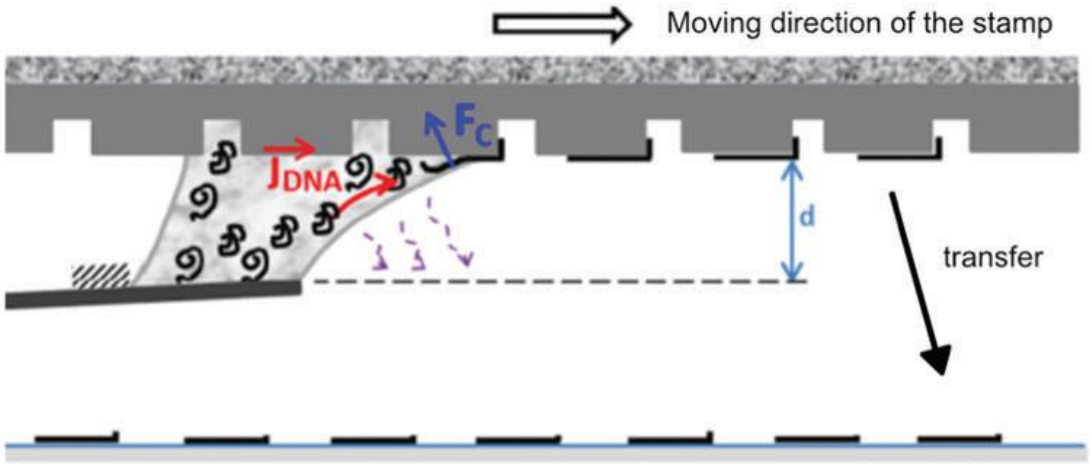
Non-lithographical traps



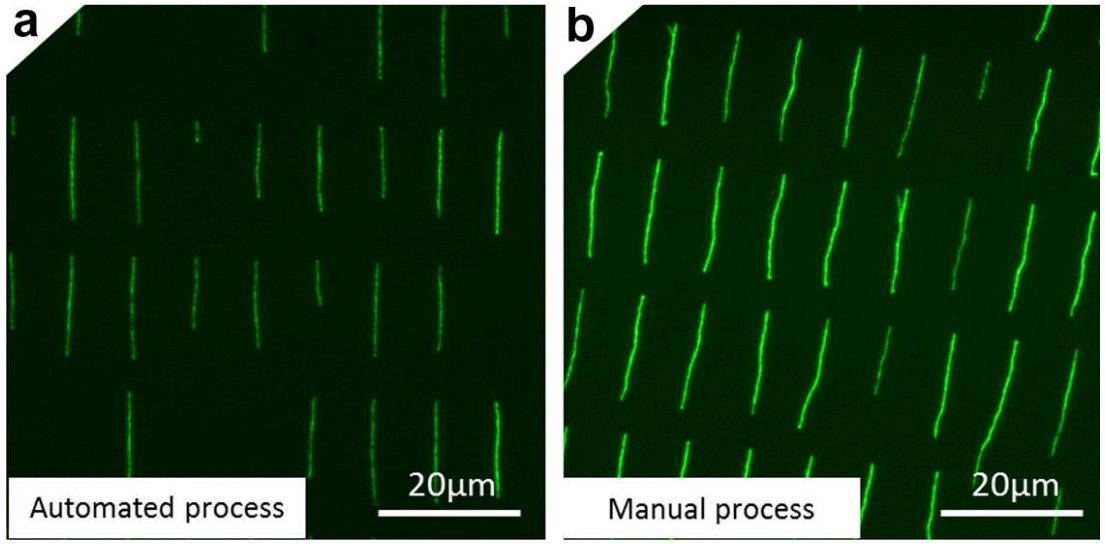


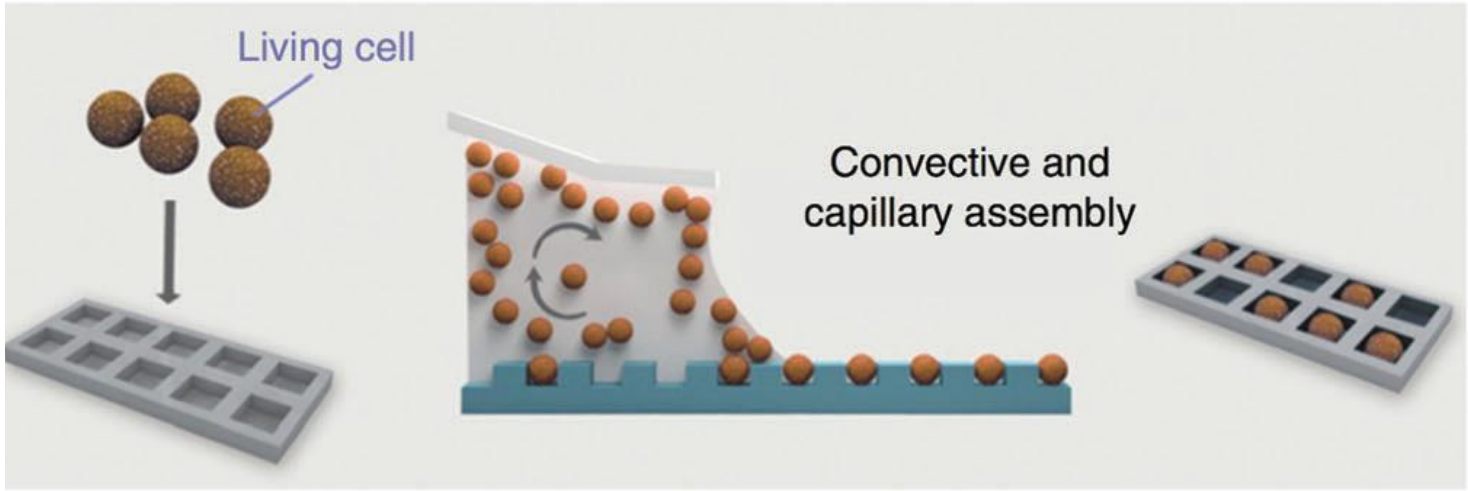
Steiner *et al.*, *ACS Nano* 11, 8871 (2017)

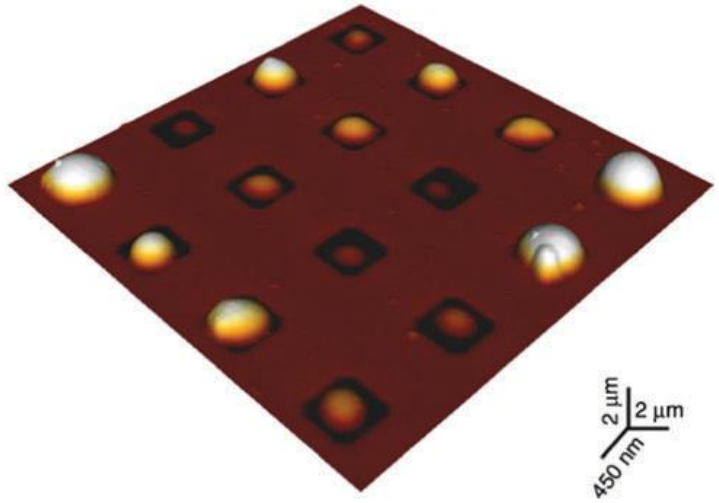
Biomolecules & cells



Cayron *et al.*, *Microelectron. Eng.* 135, 1 (2015)

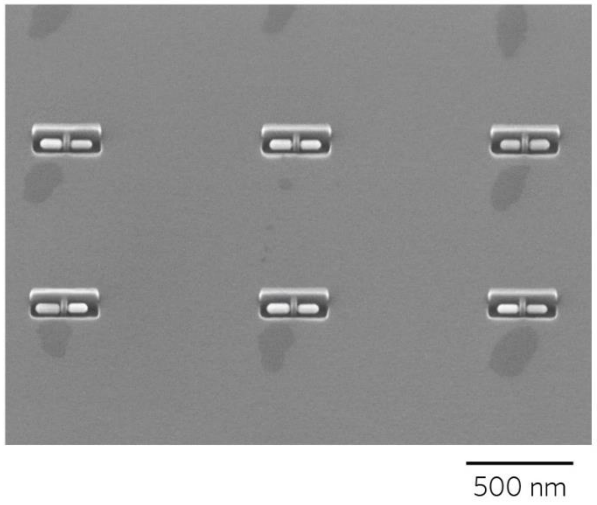


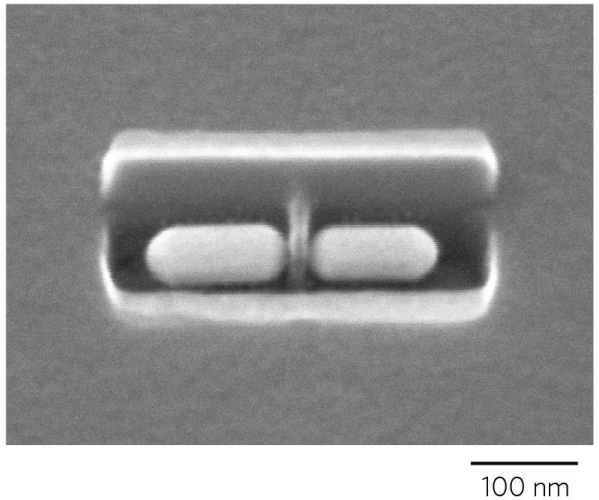


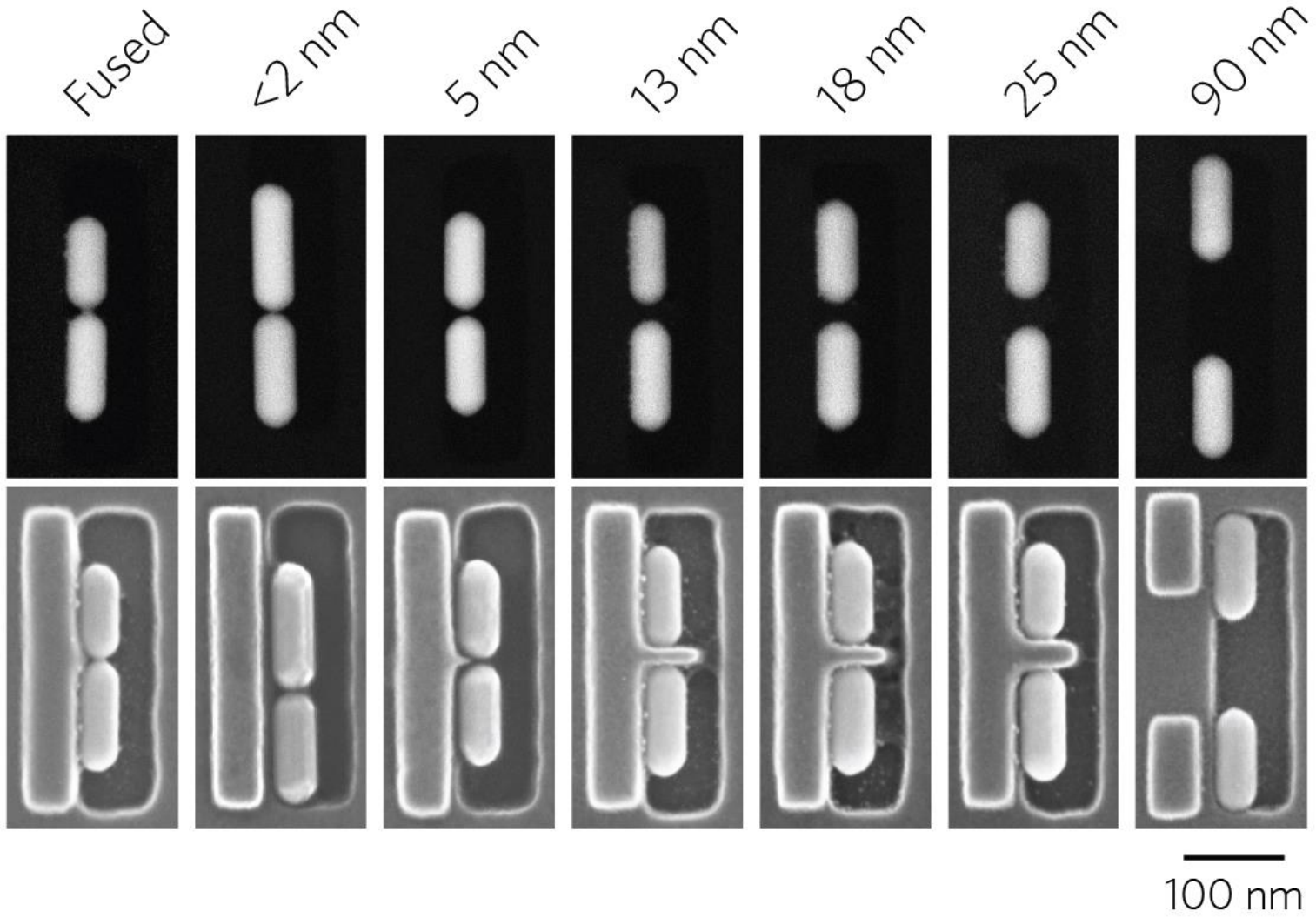


Formosa *et al.*, *Nat. Protoc.* 10, 199 (2015)

Nanogap tuning in nanorod dimers



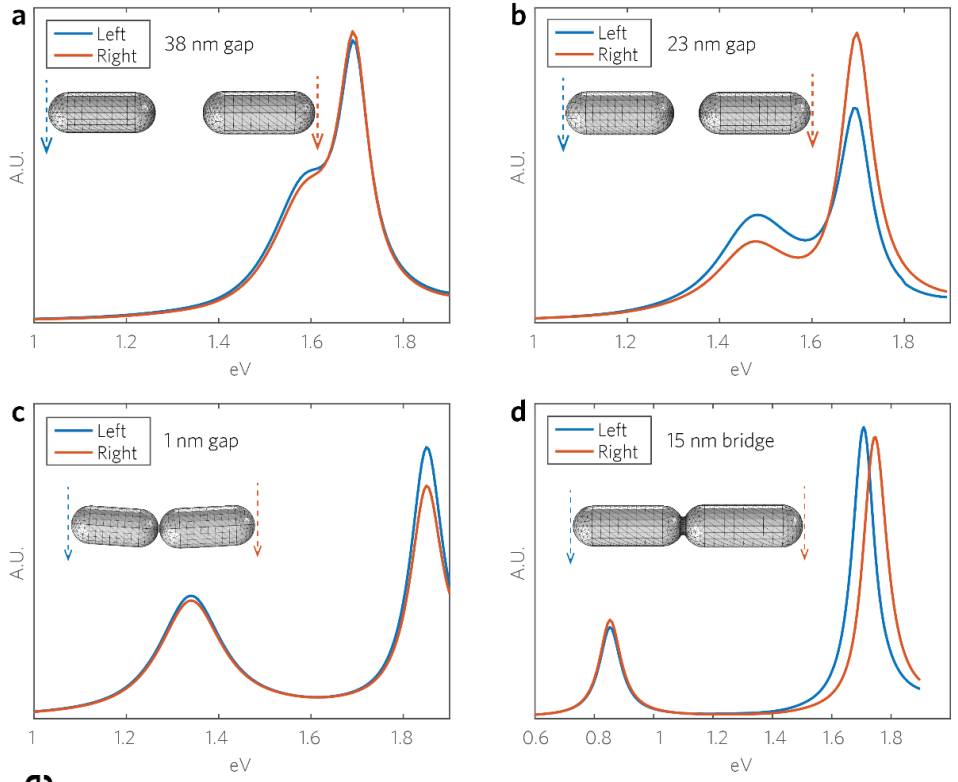


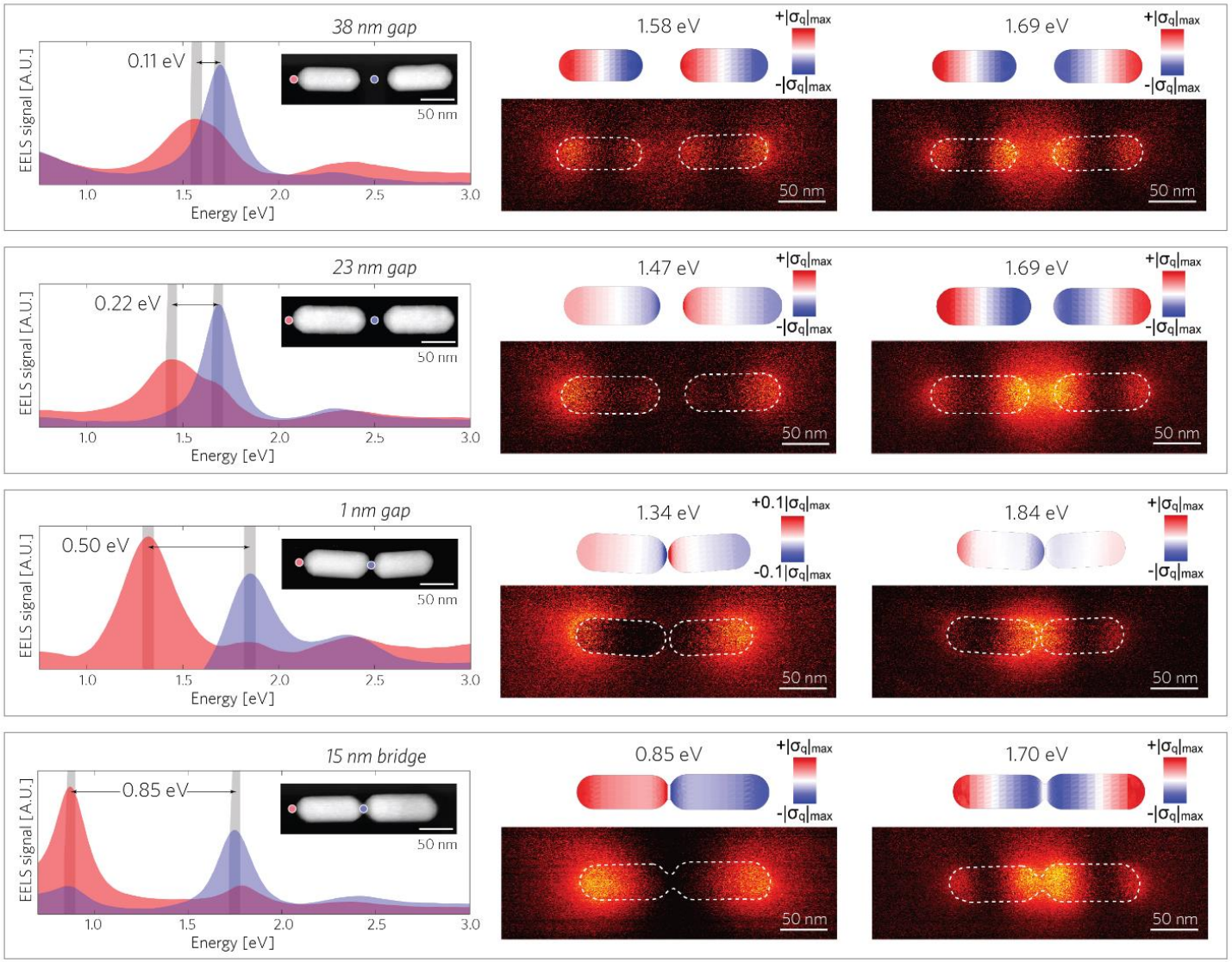


Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

From weak to strong plasmonic coupling

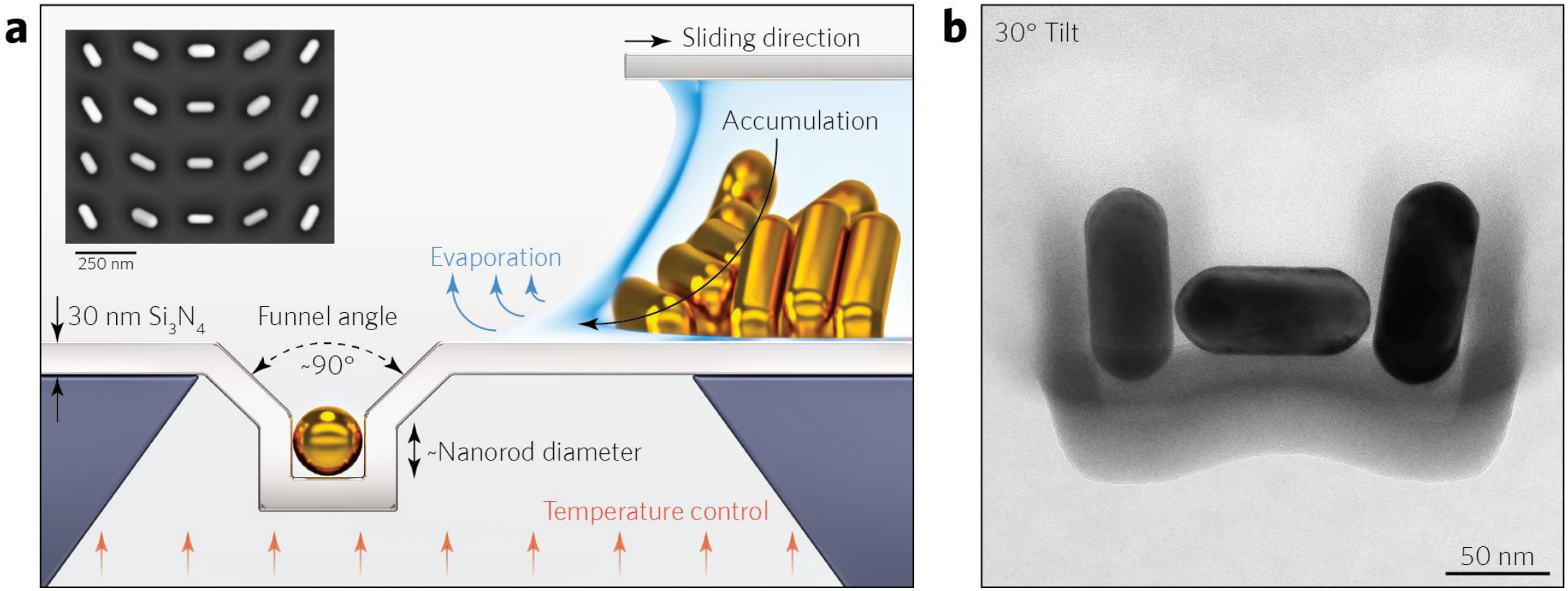
FEM simulations





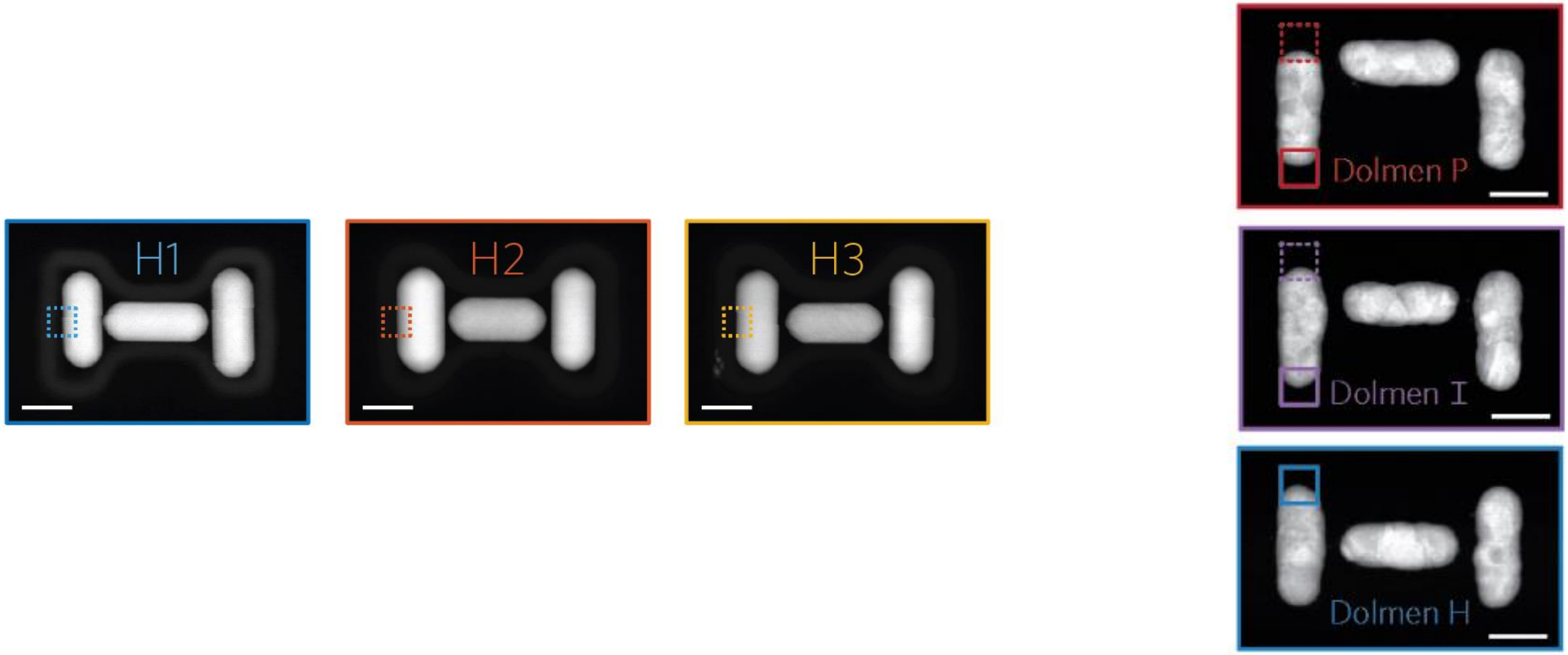
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Plasmonic dolmens



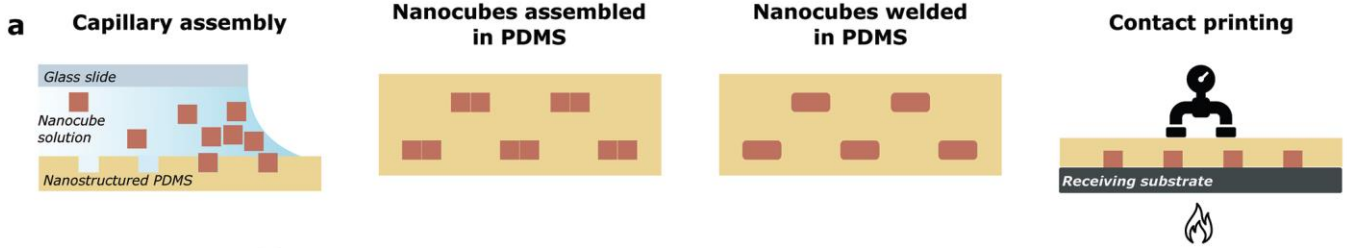
Flauraud *et al.*, *ACS Photon. 4*, 1661 (2017)

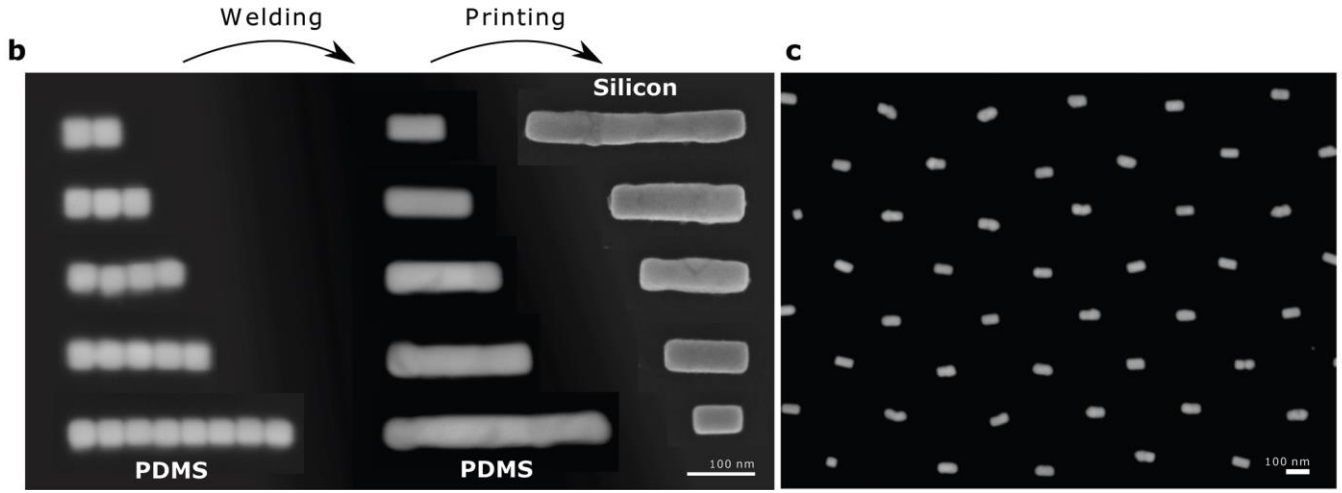
Crystallinity & edge roughness

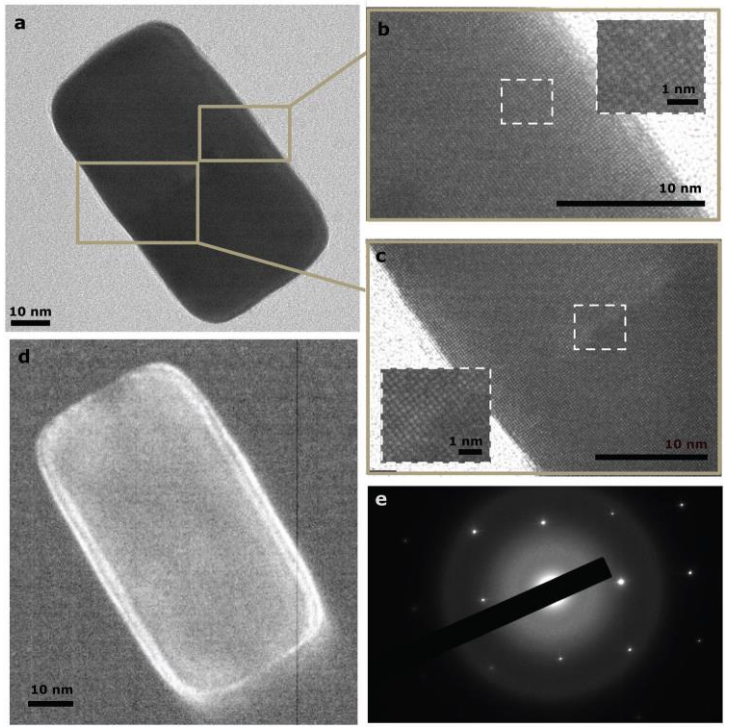


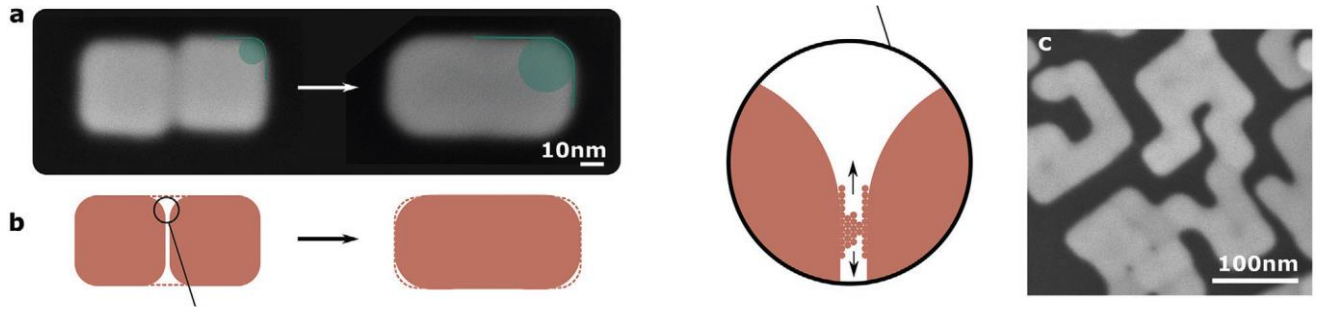
Flauraud *et al.*, *ACS Photon. 4*, 1661 (2017)

Monocrystals from nanocube epitaxy



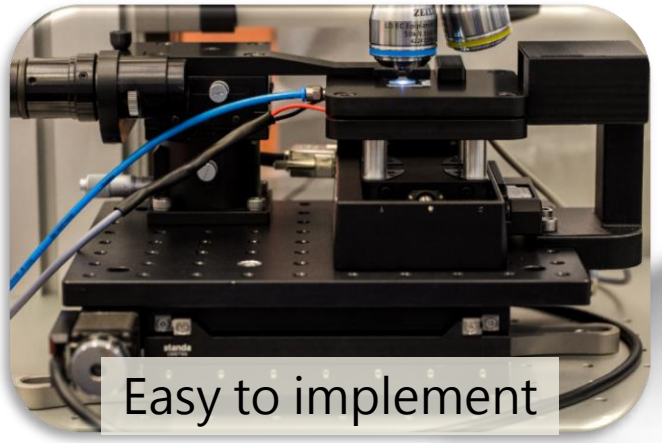






Capitaine & Sciacca, *Adv. Mater.* 34, 2200364 (2022)

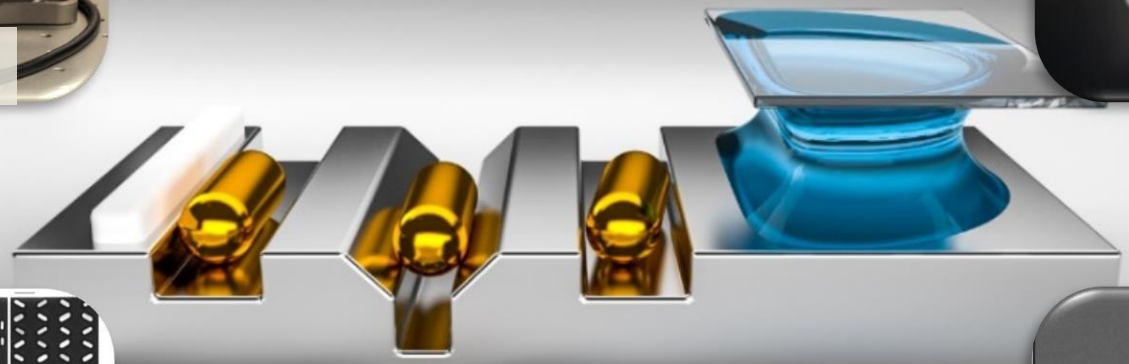
Take home messages

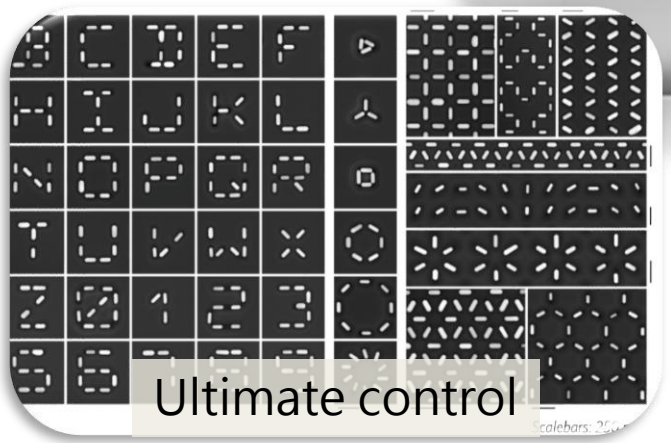


Easy to implement

Top-down patterning

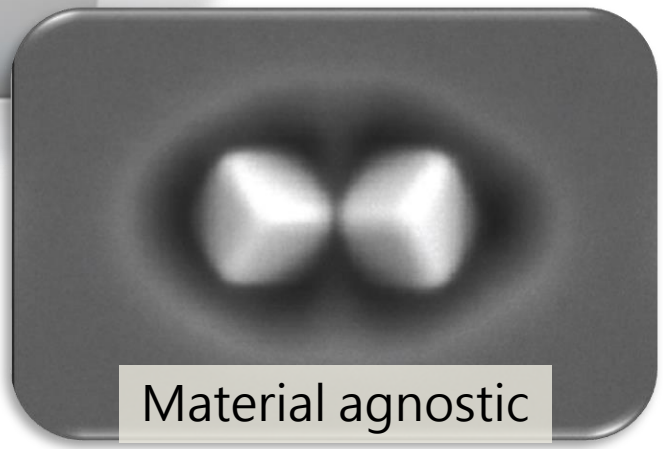
Resource efficient





Ultimate control

Bottom-up assembly



Material agnostic