Advanced Topics in Micro- and Nanomanufacturing

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TU Delft EPFL

Part 4: Single nanoparticle printing

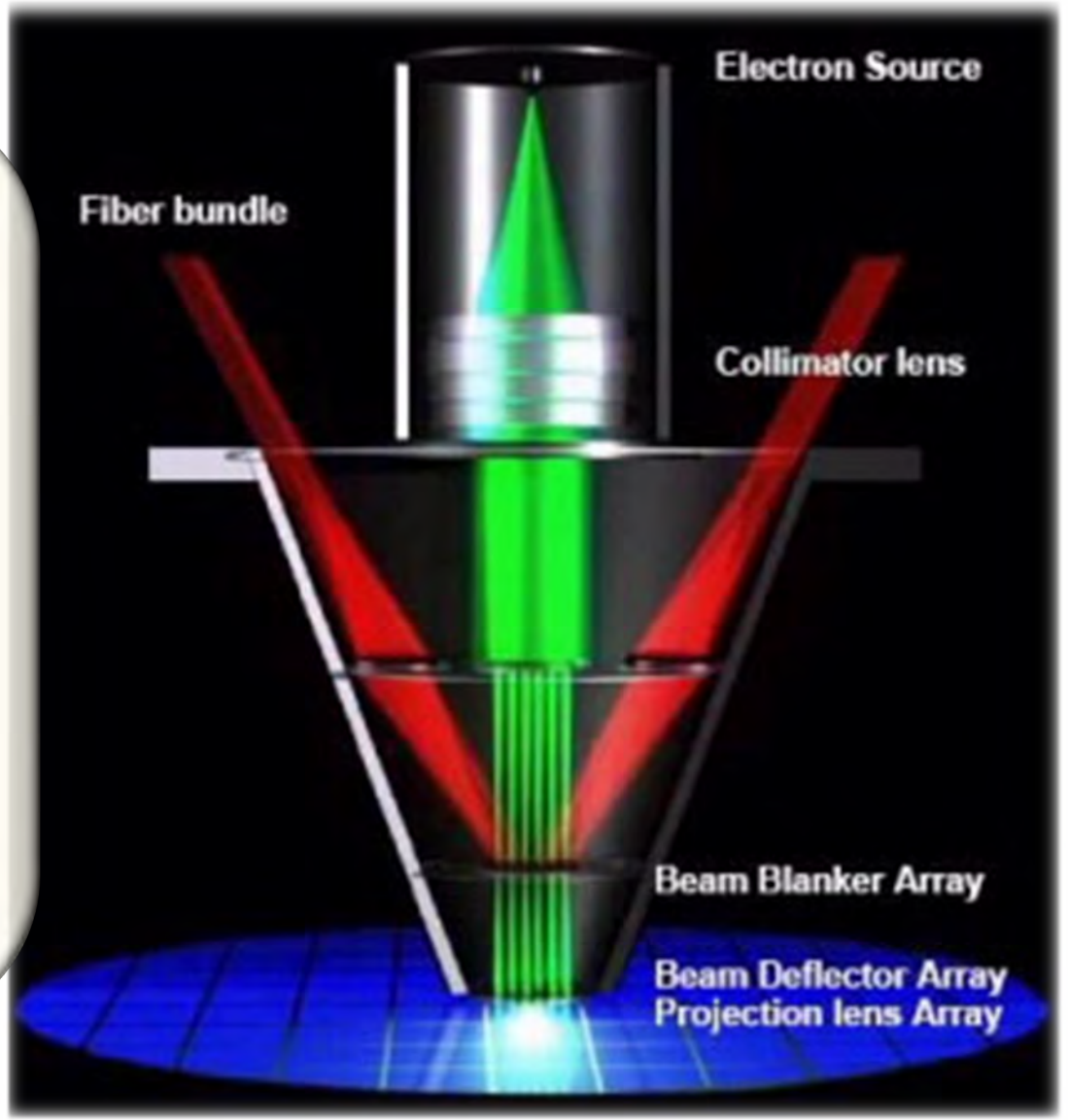
TOP-DOWN MEETS BOTTOM-UP
ELECTRO-TOPOGRAPHICAL TRAPPING
COFFEE RING EFFECT
TOPOGRAPHICALLY-TEMPLATED FLOW COATING
APPLICATION TO MICRO/NANOSYSTEM ASSEMBLY

Beyond top-down micro/nanofabrication

Lithography

- ✓ Ultimate resolution
- ✓ Wafer-level

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



Source: Burn Lin

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

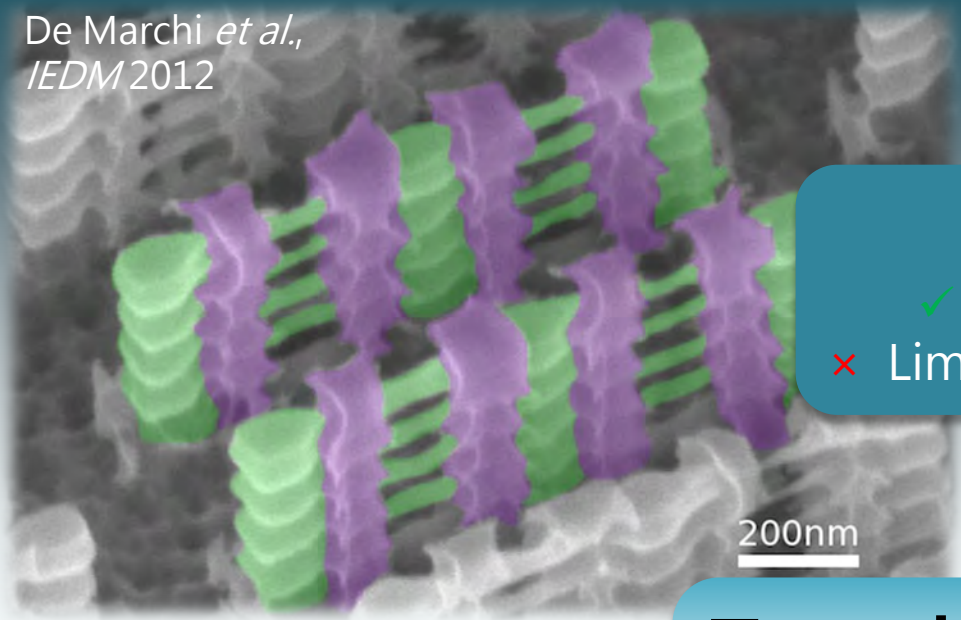
How to build devices out of nanoparticles?

TUDelft EPFL

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

CEES Dekker Lab, TUDelft

De Marchi *et al.*,
IEDM 2012

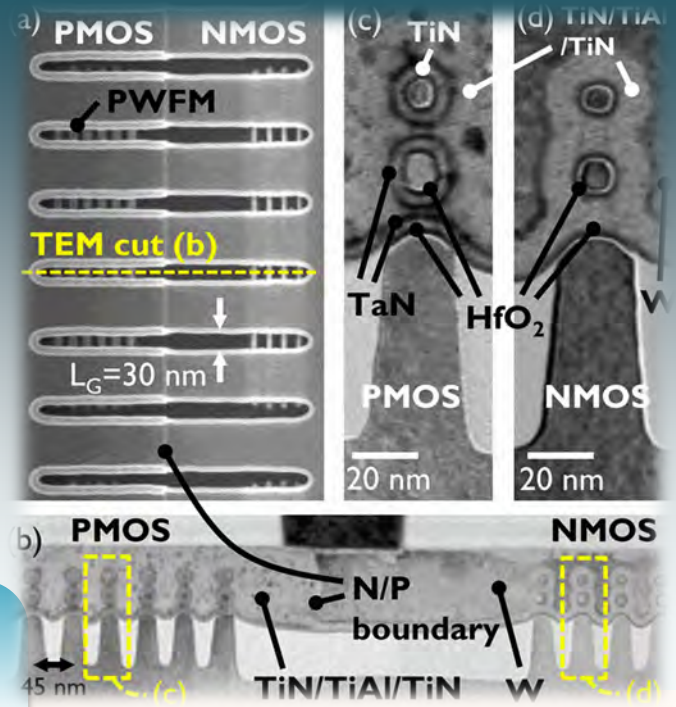


Top-down

✓ Ultimate spatial accuracy

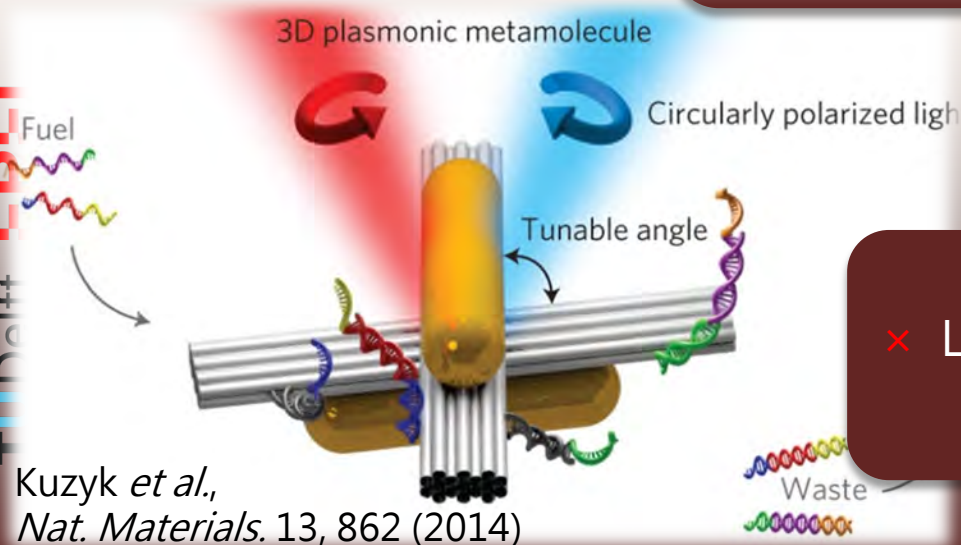
× Limited material choice & quality

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

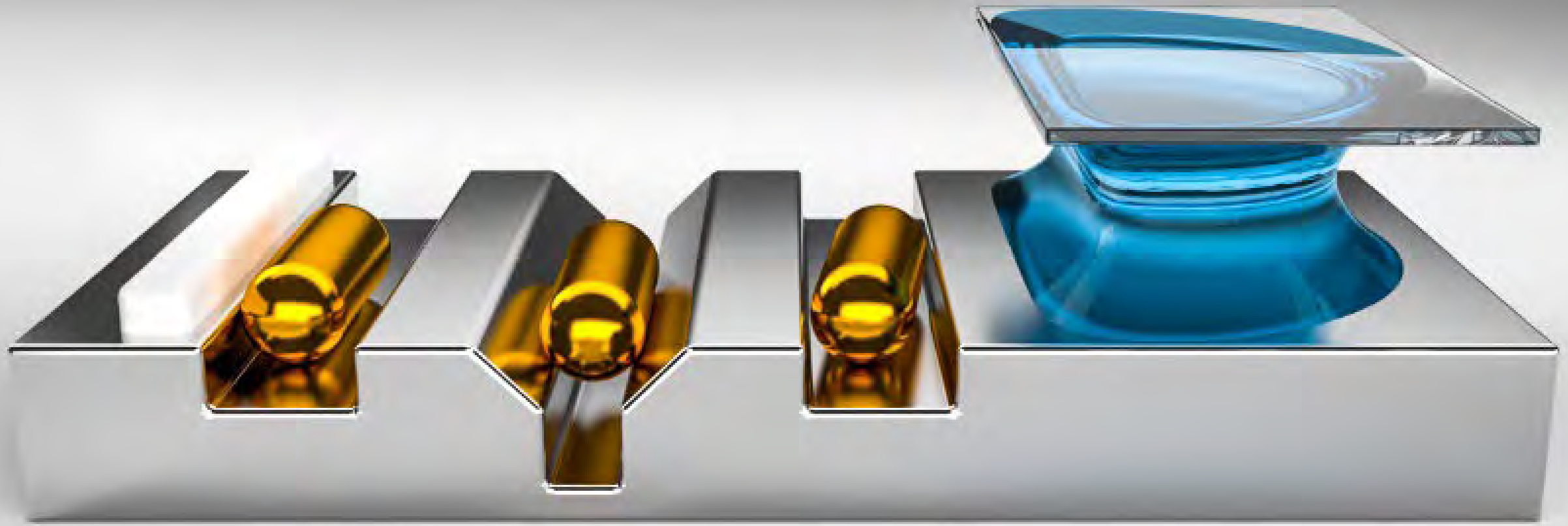
× Limited morphology control

Bottom-up

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

Single nanoparticle printing

Assemby of chemically synthesized NPs
over lithographically patterned substrates



V. Flauraud, M. Mastrangeli, G. Bernasconi, J. Butet, D. Alexander, E. Sharabi, O. Martin, J. Brügger,
Nanoscale Topographical Control of Capillary Assembly of Nanoparticles
Nature Nanotechnology 12, 73-80 (2017)

Eppur si muove: Diffusion

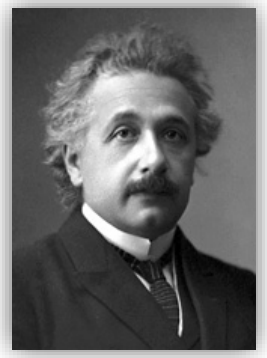
Robert Brown
(1828)

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

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

Pollen grains in water

Jean Perrin
(1908)



Albert Einstein
(1905)

$$J = -D\boldsymbol{\nabla} c \qquad \text{Fick`s 1st law}$$
$$\frac{\partial c}{\partial t} = D\boldsymbol{\nabla}^2 c \qquad \text{Fick`s 2nd law}$$

Paul Langevin
(1908)

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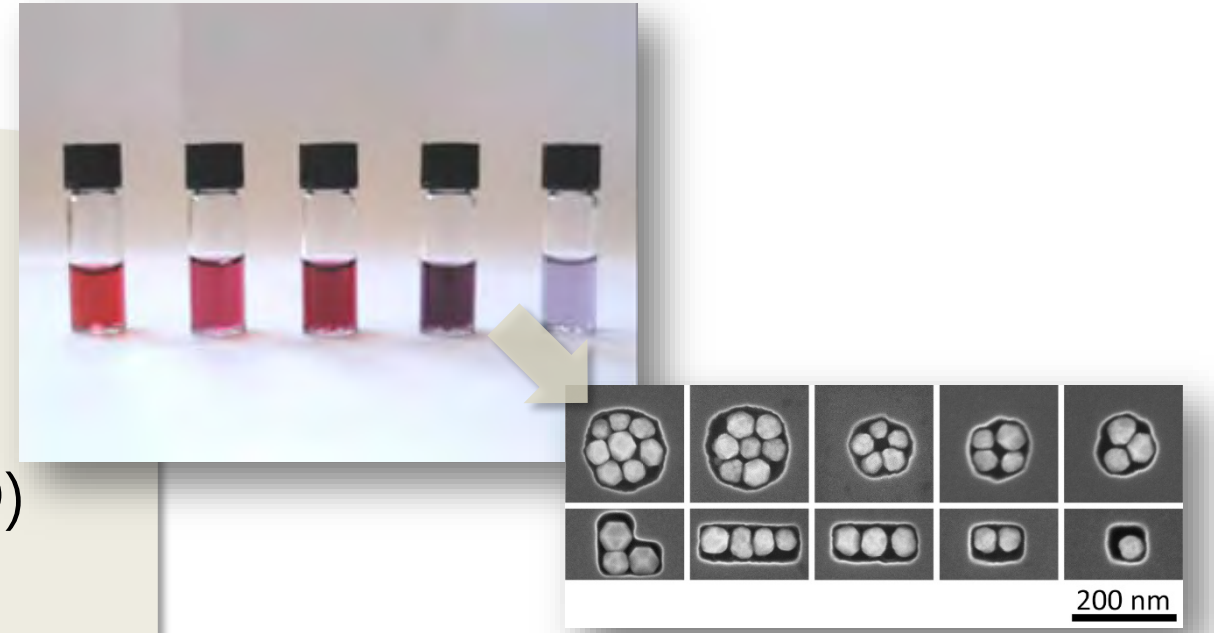
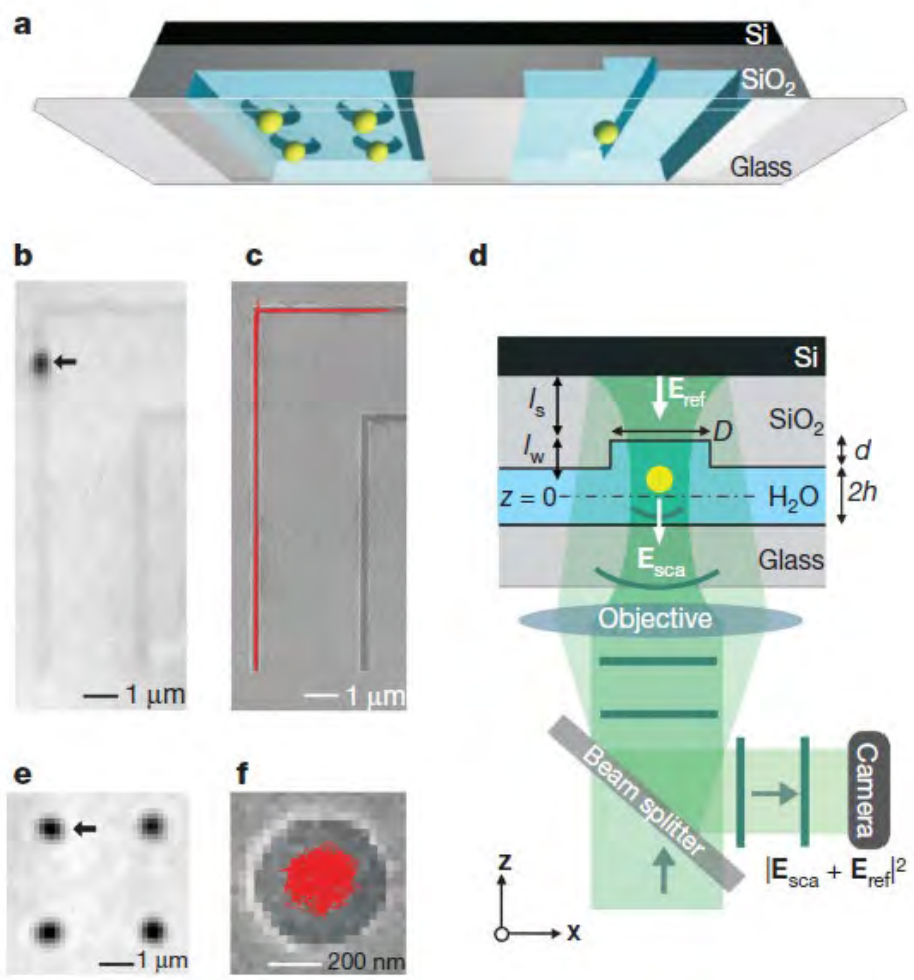
Confinement & templating

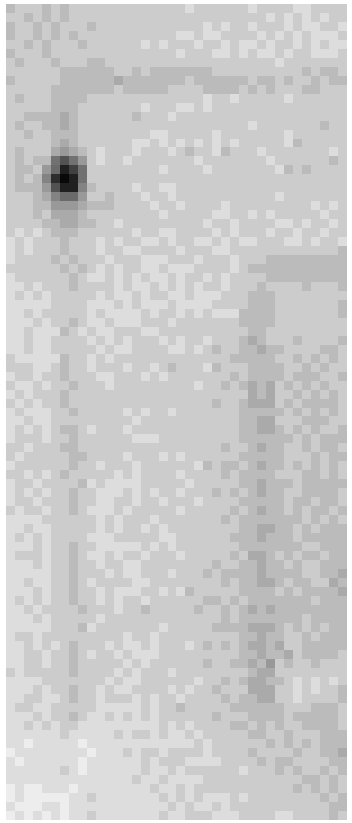
- Dimensionality
  - From suspension… (3D)
    to substrate… (2D)
    to trap… (1D→0D)
- Degrees of freedom
  - From 6 to 0
- Non-interacting particles
  - $\Delta H \approx 0 \rightarrow \Delta G \approx -T\Delta S$

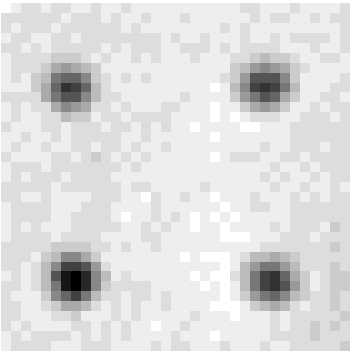


Assembly as **spatial search** problem

Electro-topographical trapping

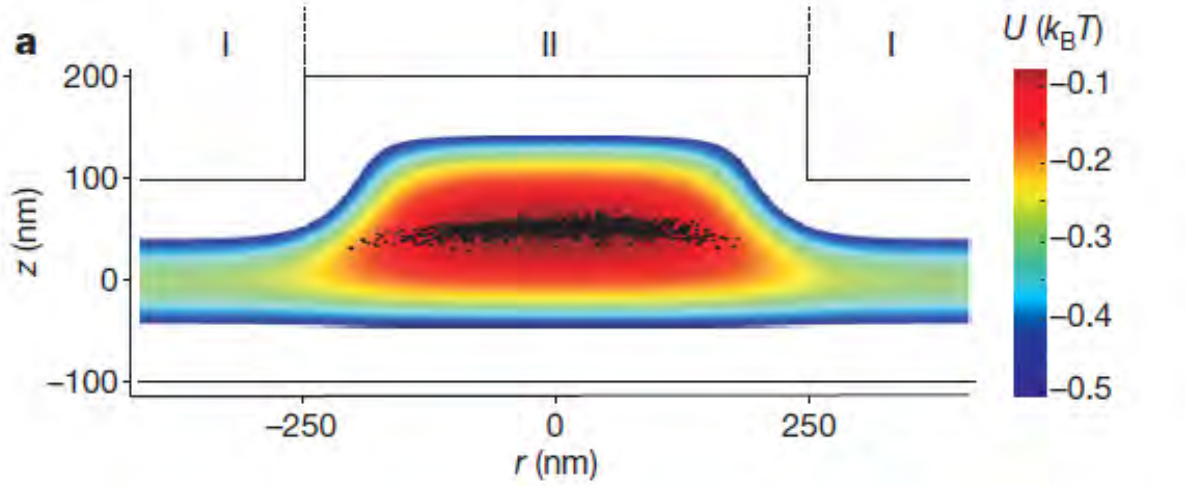


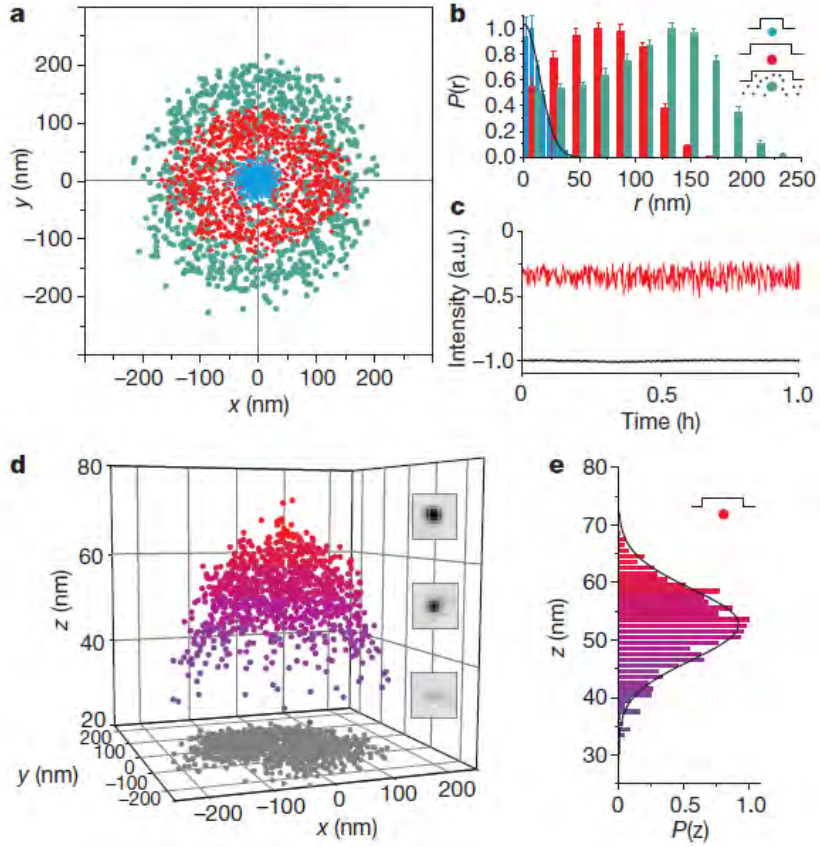




Krishnan *et al.*, *Nature* 467, 692 (2010)

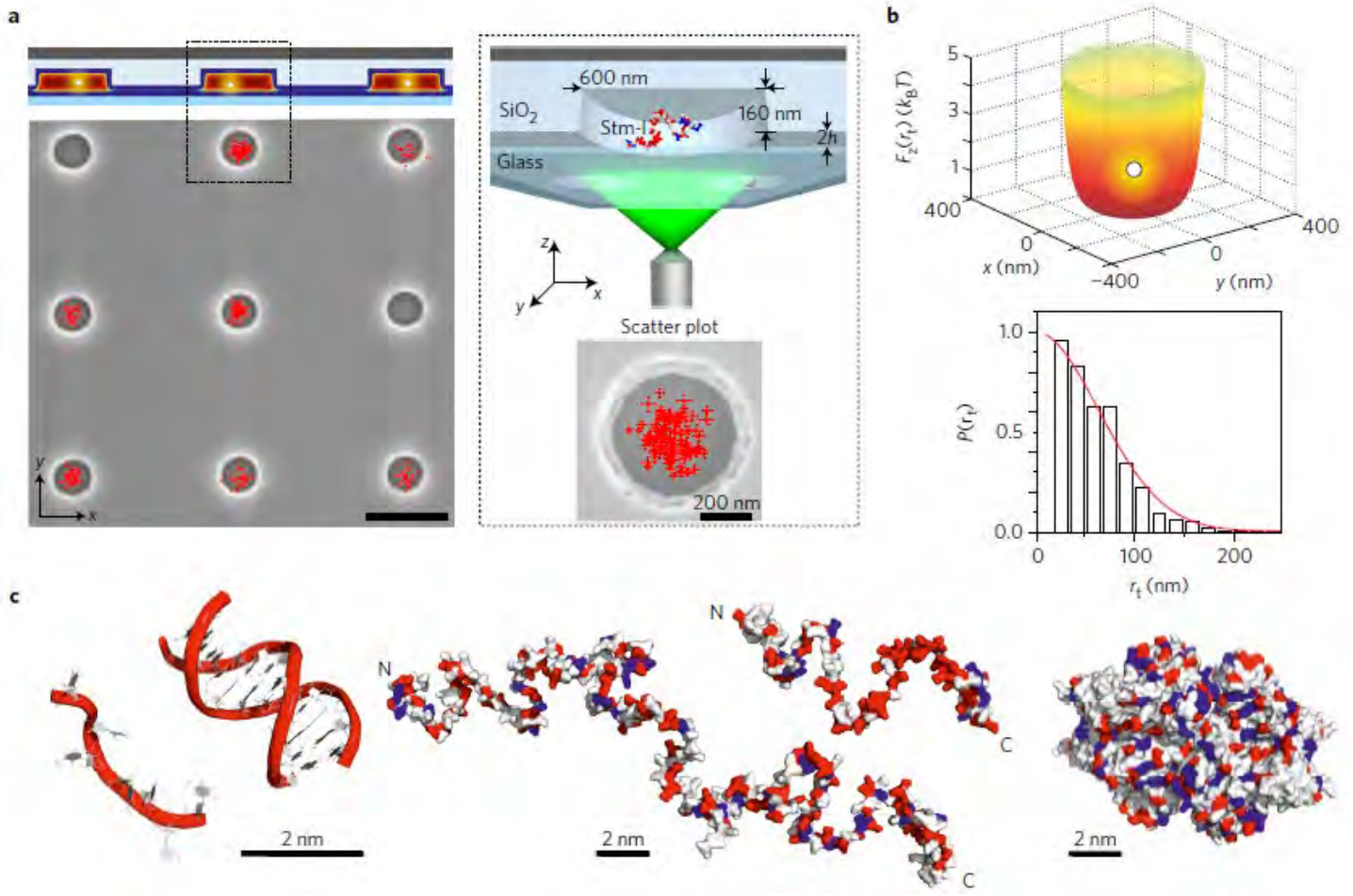
Electro-topographical trapping





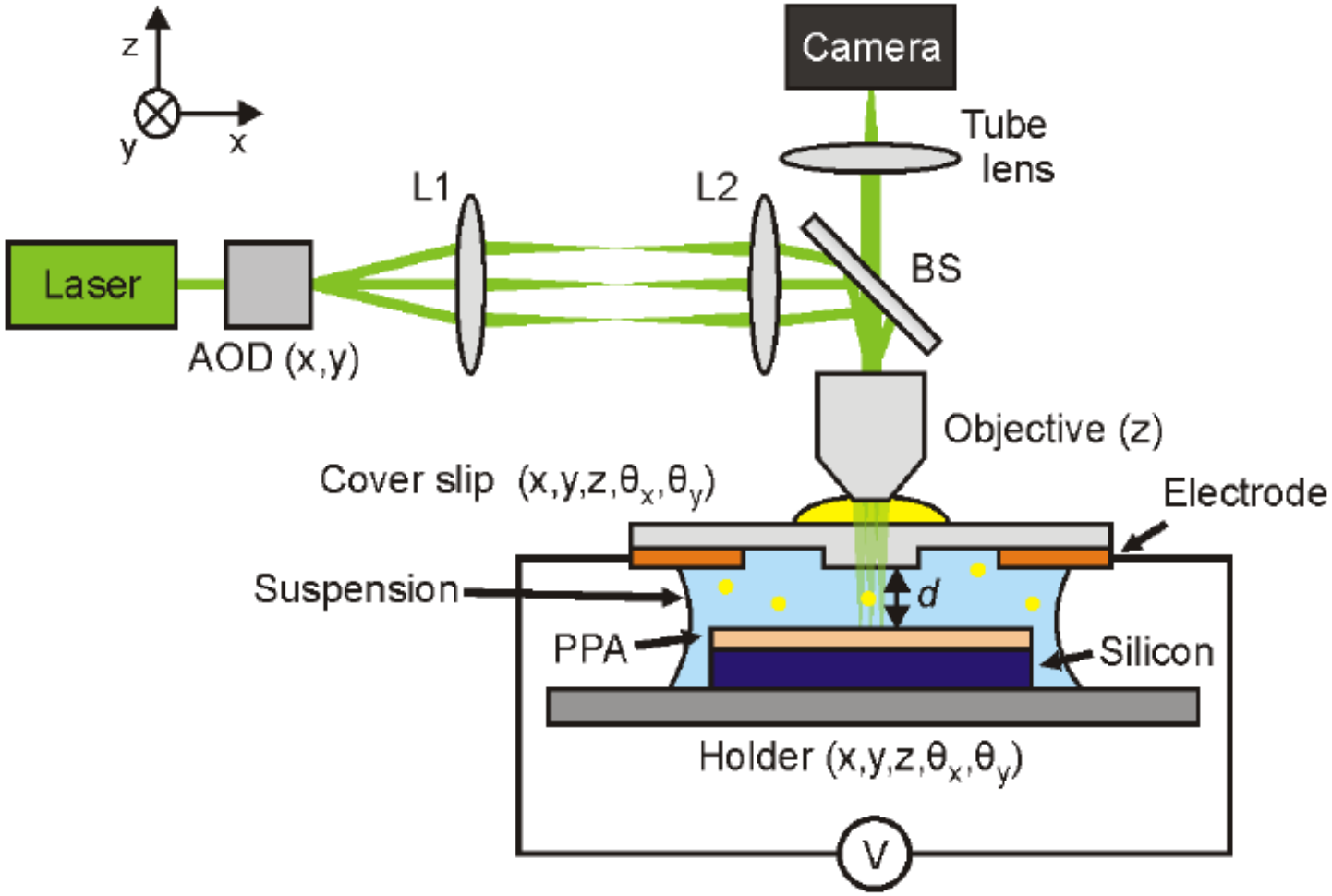
Krishnan *et al.*, *Nature* 467, 692 (2010)

Electro-topographical trapping



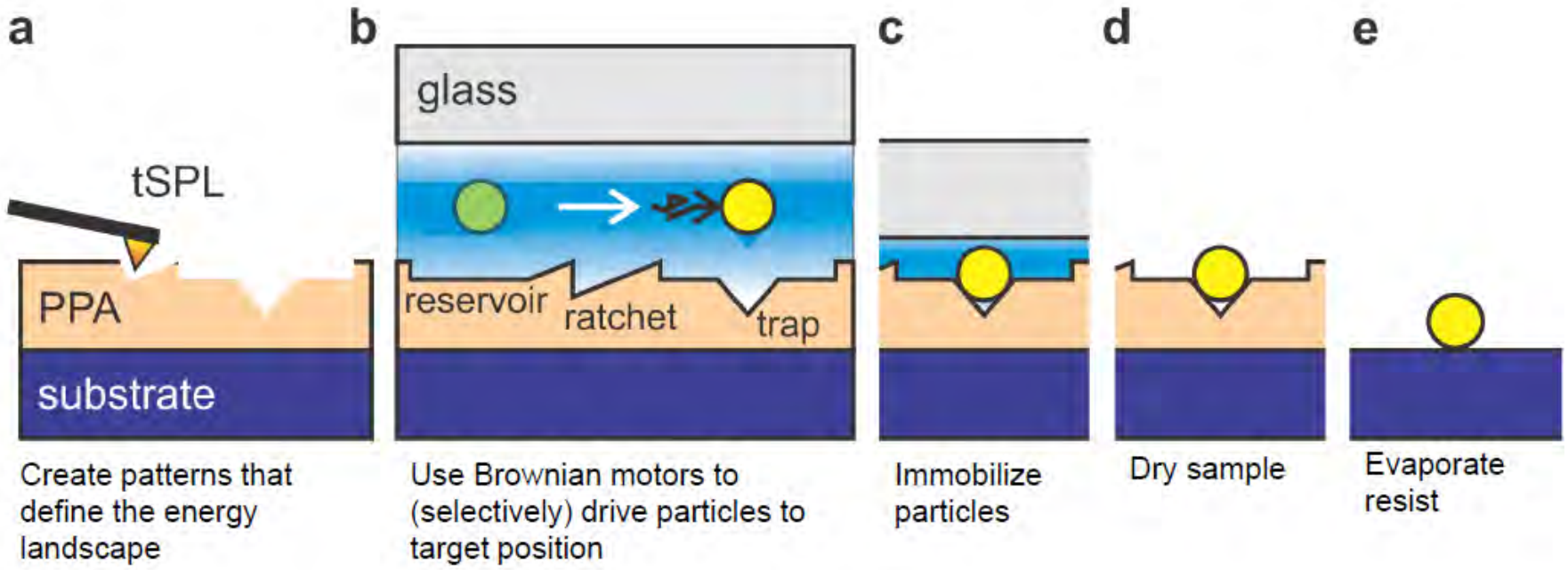
Ruggeri *et al.*, *Nat. Nanotechnol.* 12, 488 (2017)

Rocking Brownian motors



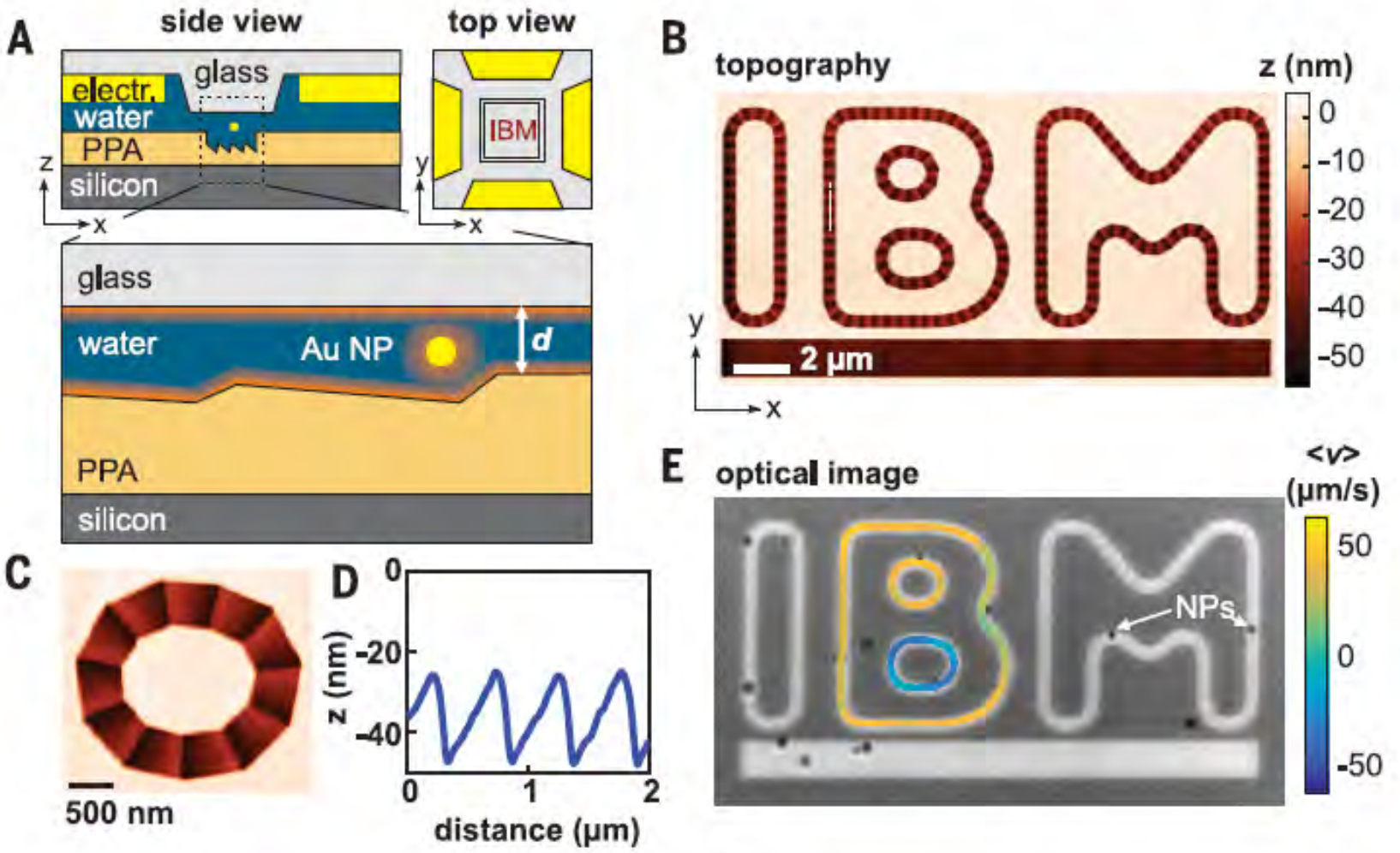
Fringes *et al., J. Appl. Phys.* 2016
Fringes *et al., Bellstein J. Nanotech.* 2018

Rocking Brownian motors



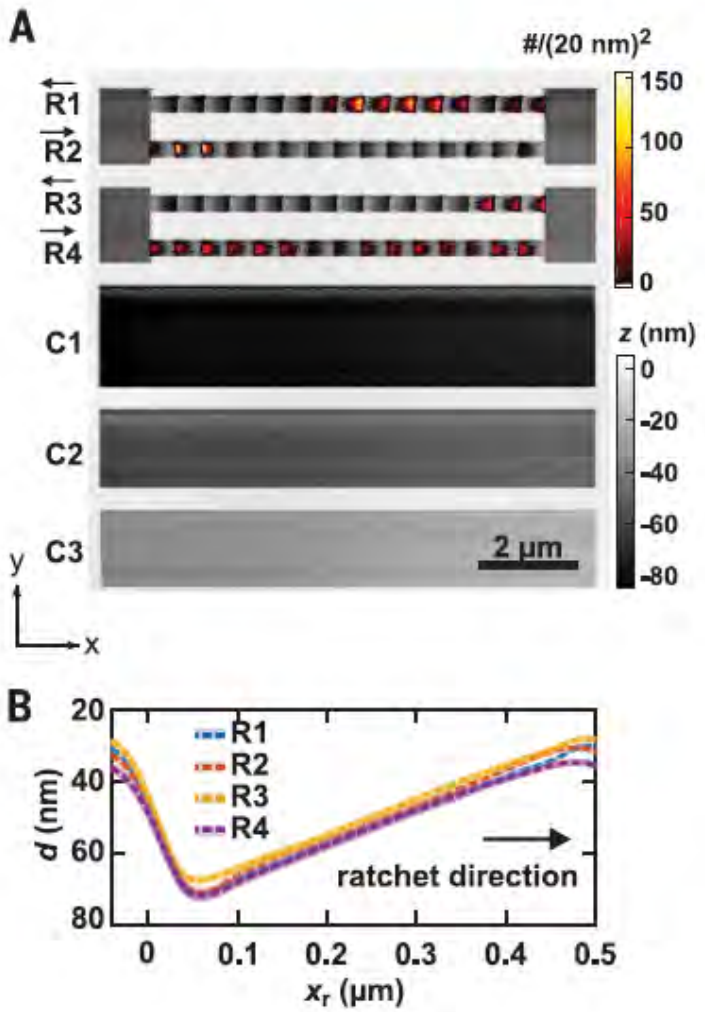
Knoll *et al.*, *TRANSDUCERS 2019*

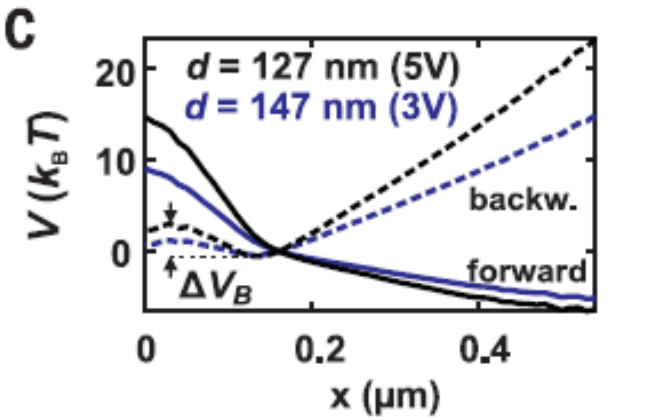
Rocking Brownian motors

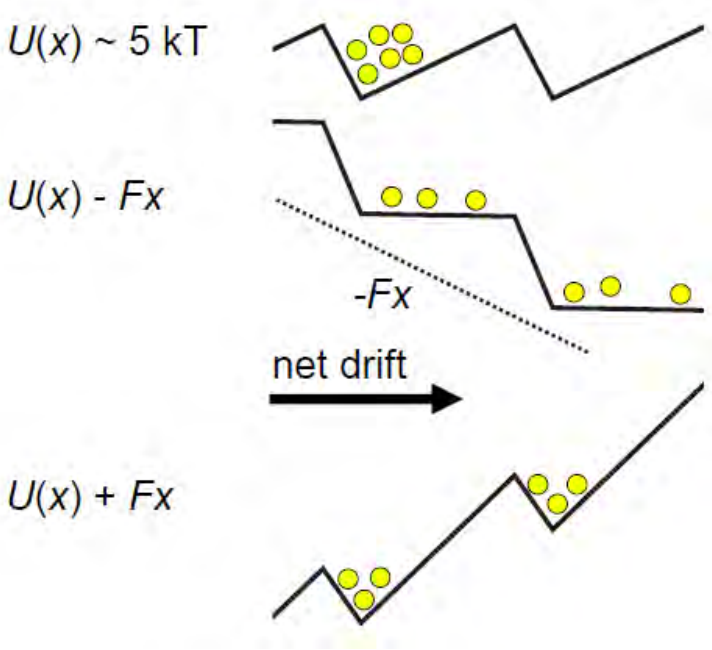


Skaug *et al.*, *Science* 359, 1505 (2018)

Rocking Brownian motors

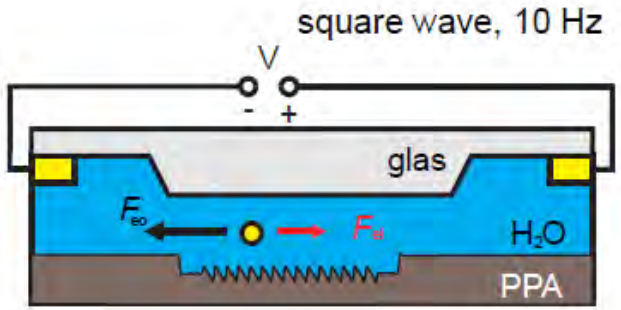


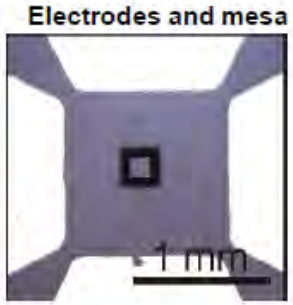


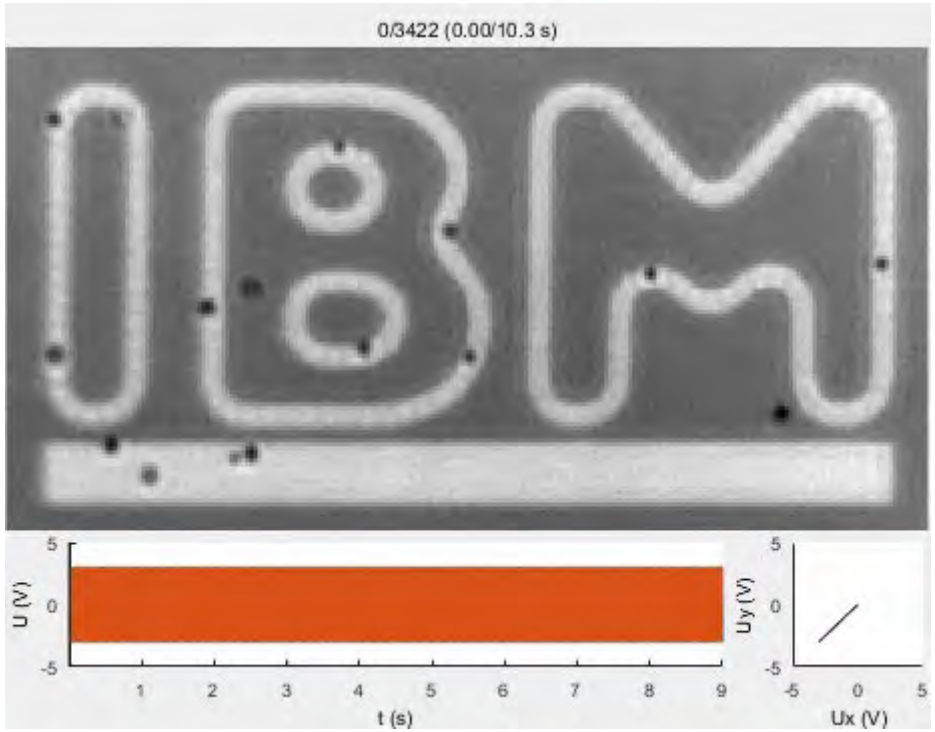


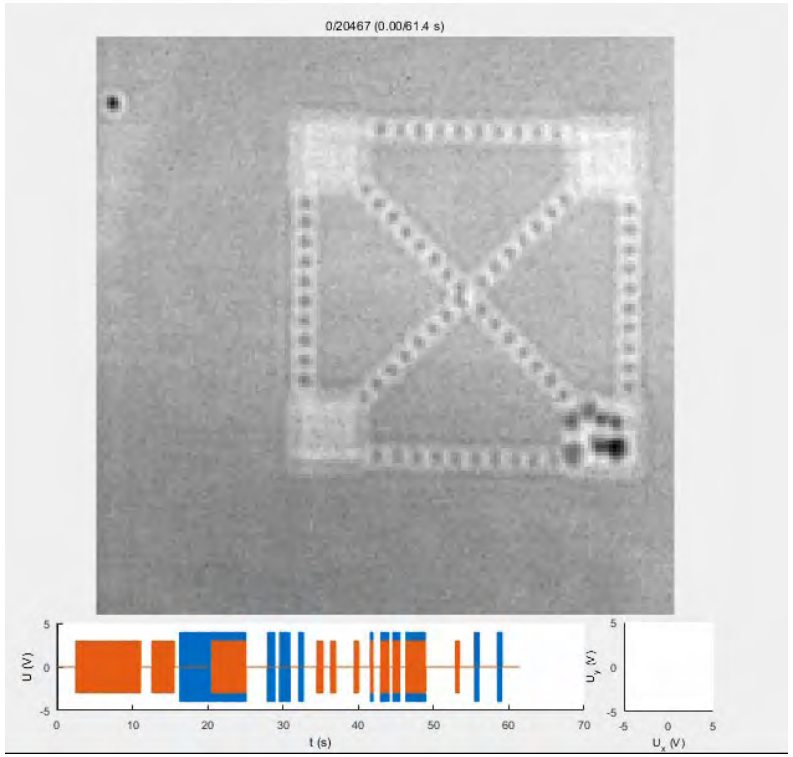
Skaug *et al.*, *Science* 359, 1505 (2018)

Rocking Brownian motors



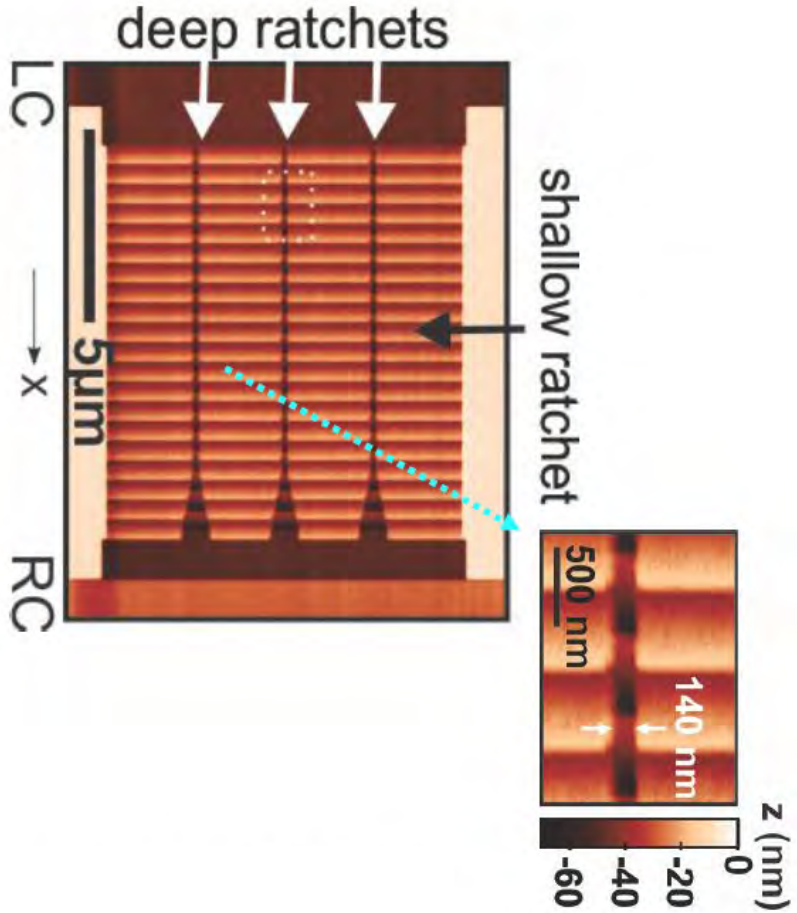


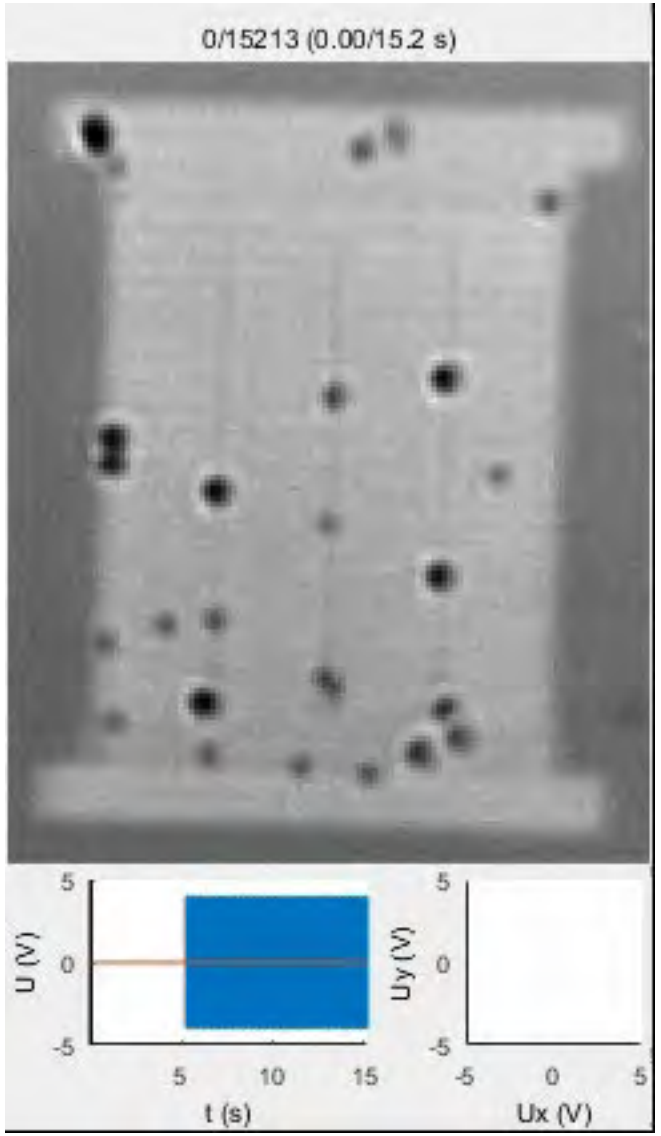




Skaug *et al.*, *Science* 359, 1505 (2018)

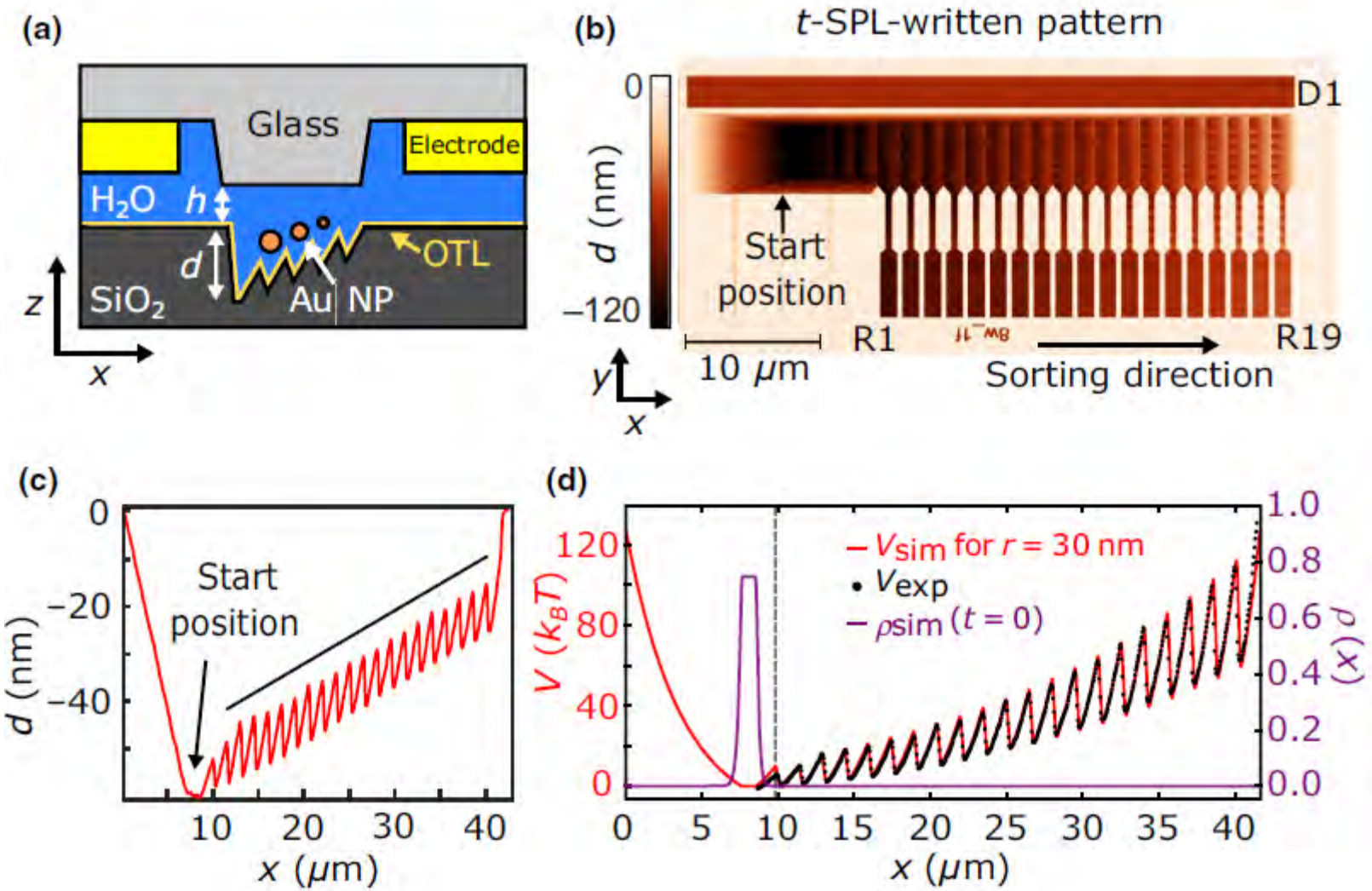
Rocking Brownian motors





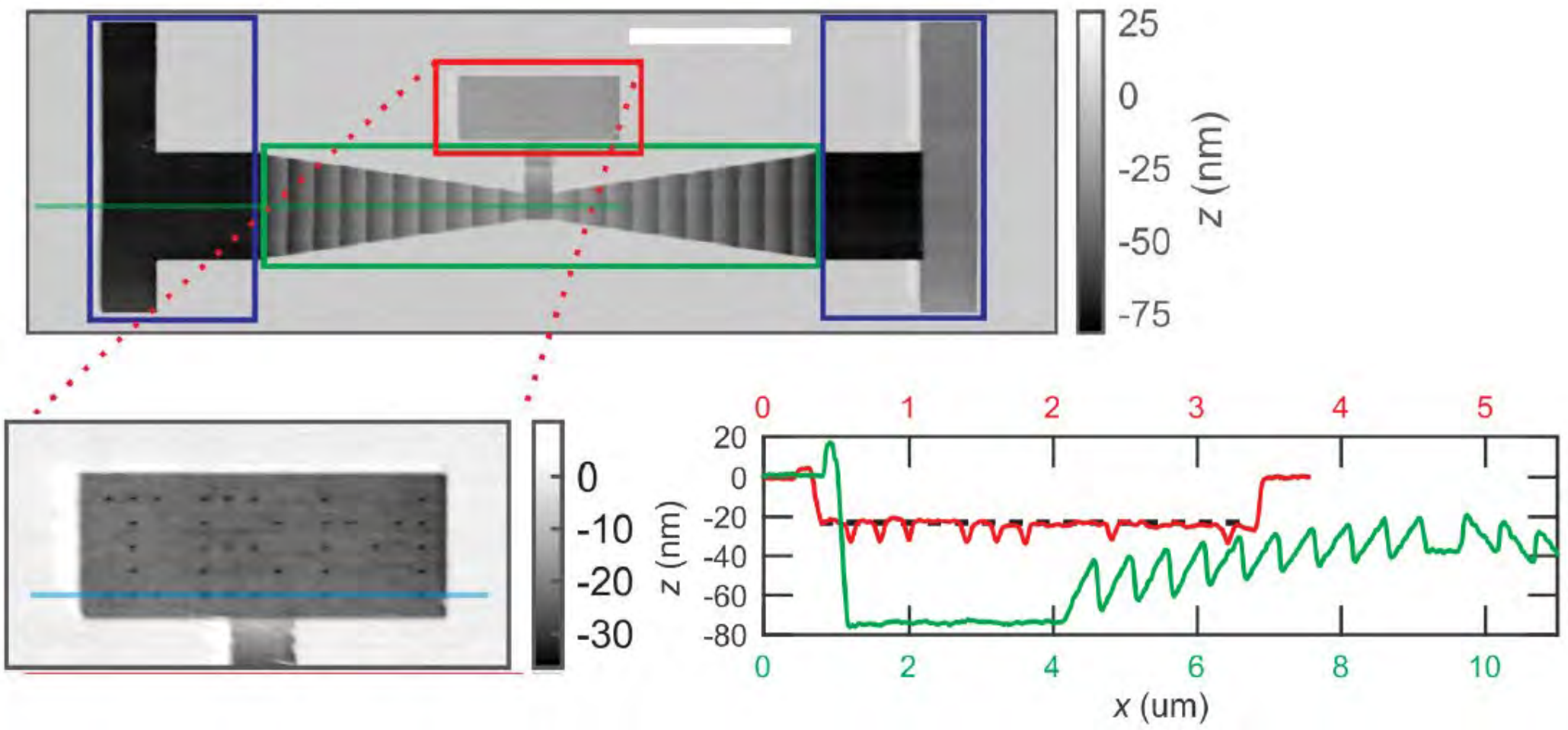
Skaug *et al.*, *Science* 359, 1505 (2018)

Rocking Brownian motors



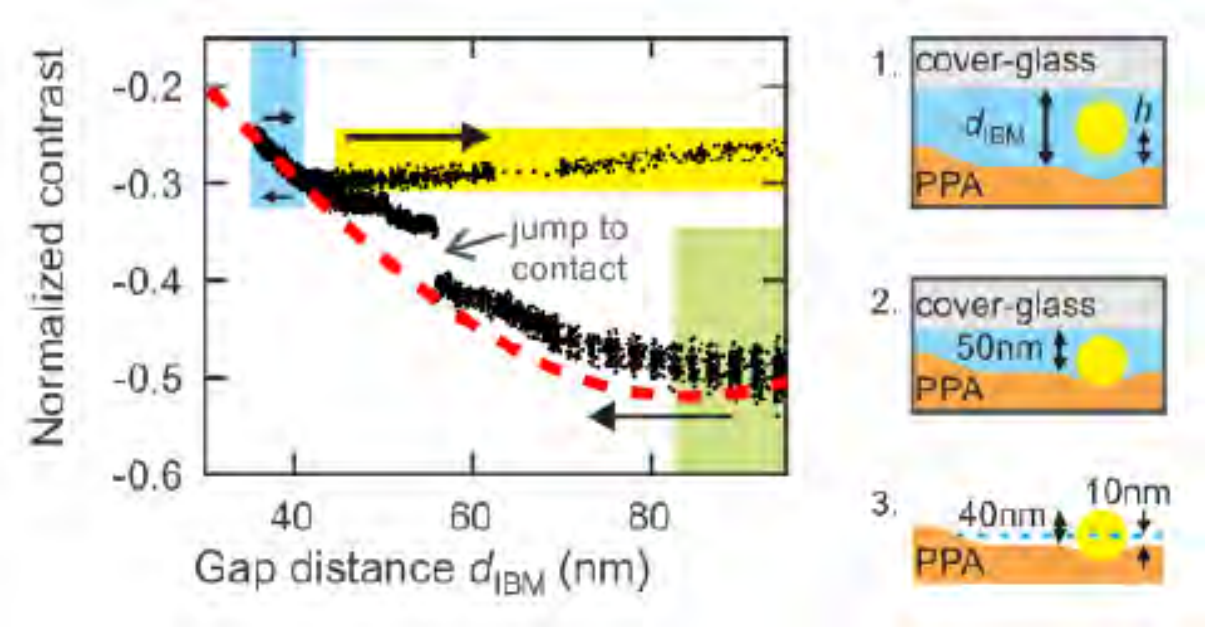
Nicollier *et al.*, *Phys. Rev. Appl.* 15, 034006 (2021)

Rocking Brownian motors



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

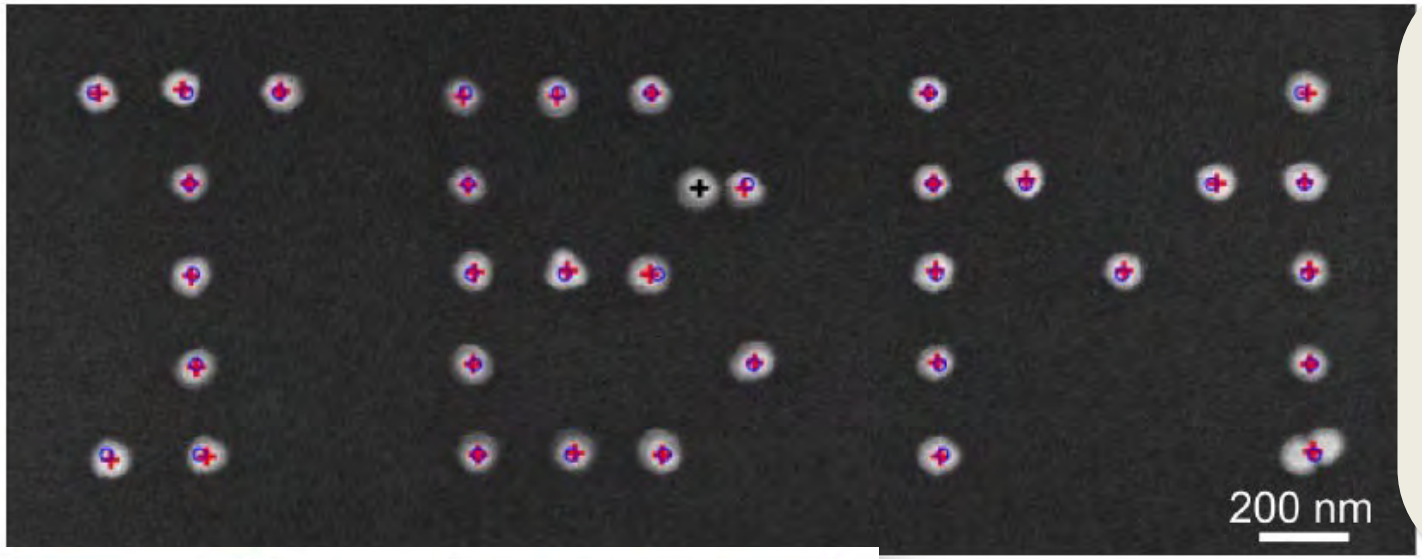
Rocking Brownian motors

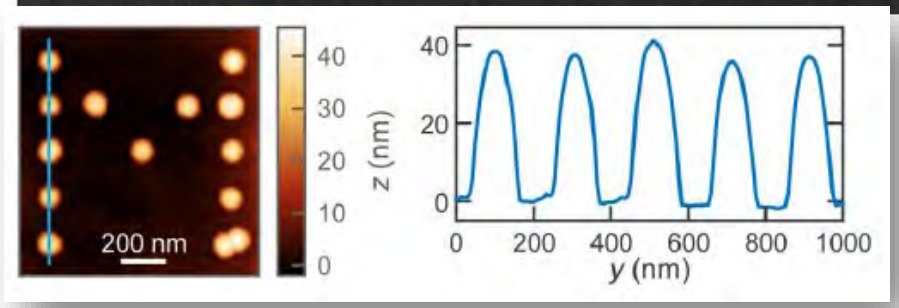


- Deposition pathway
  - First contact with glass (still mobile)
  - Jump into contact with polymer (5 to 9 nm)
  - Elastically compressed system
  - Final particle height: 10 nm above substrate surface

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

Rocking Brownian motors

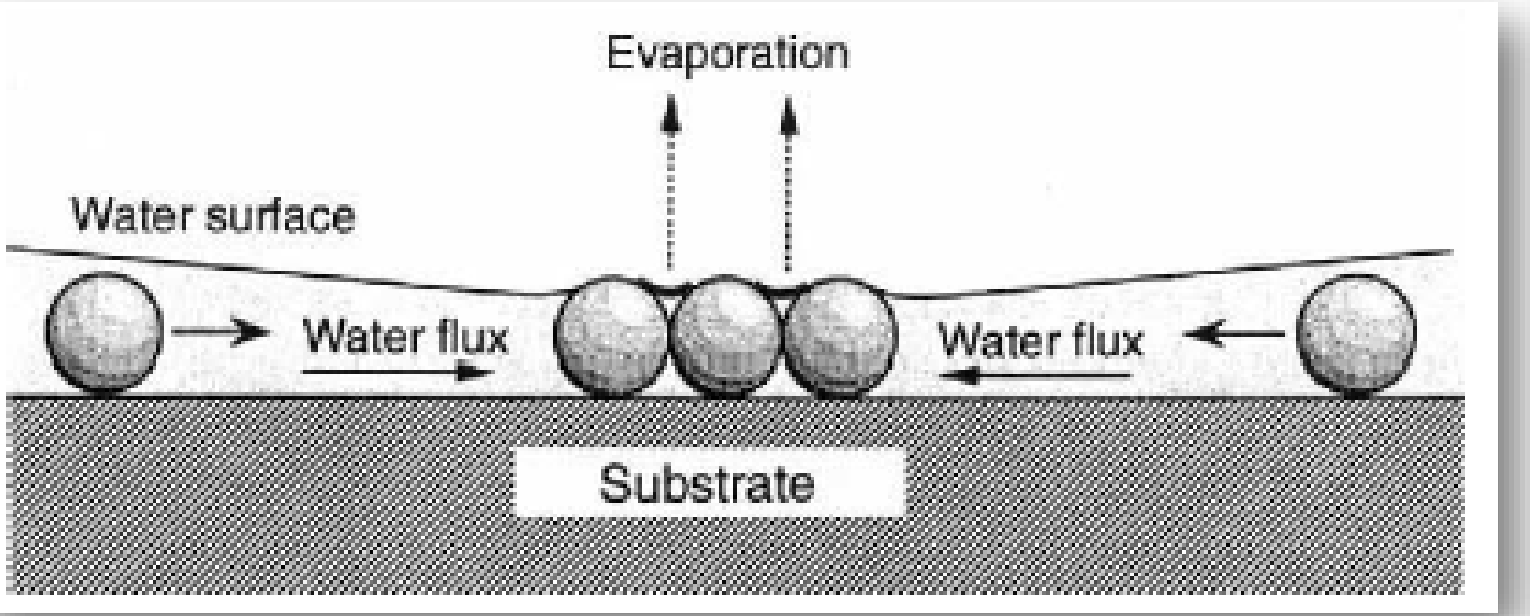




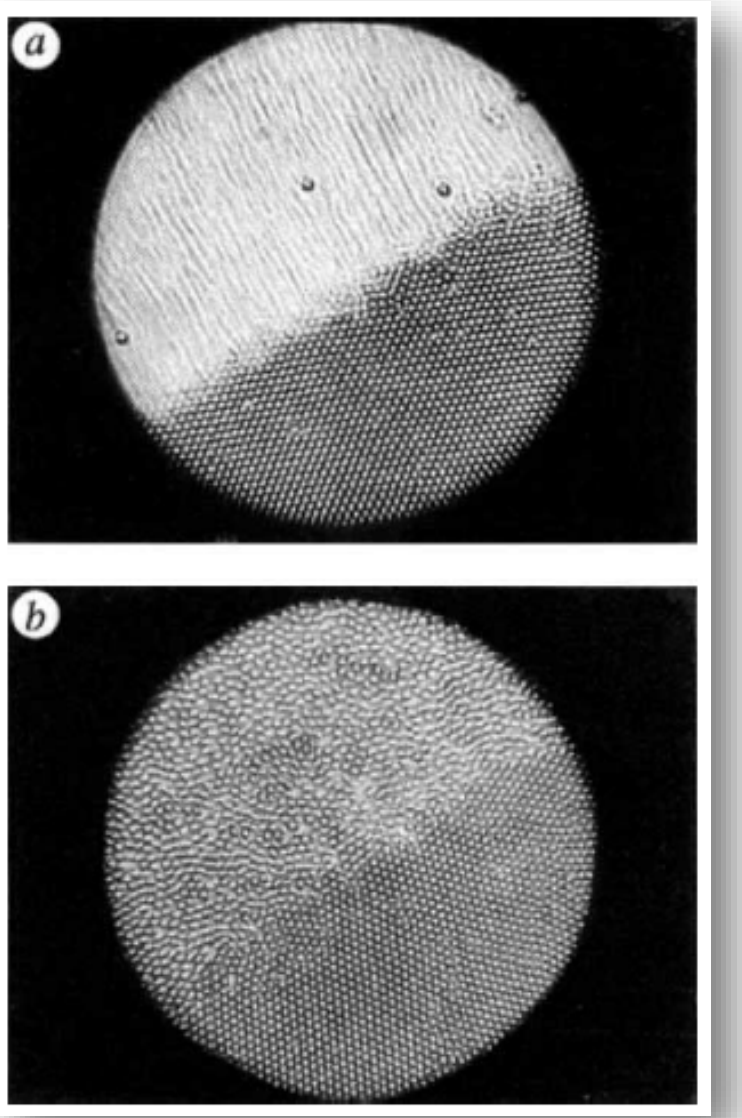
- Error sources
  - Placement
  - Lithography accuracy
  - Particle motion upon resist evaporation
  - SEM distortions (non-linear drift)

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

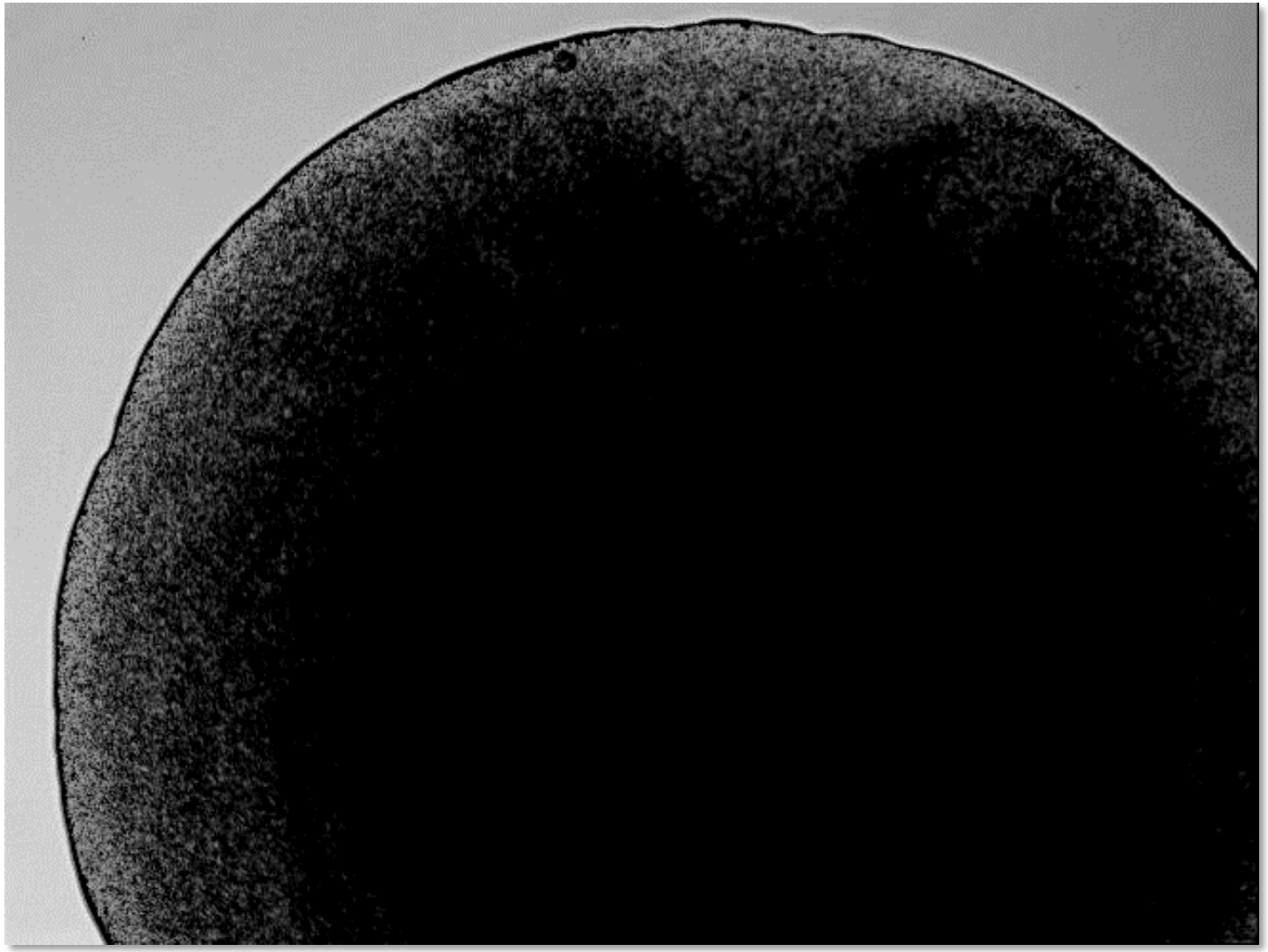
From 3D to 2D: Capillary cristallization



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

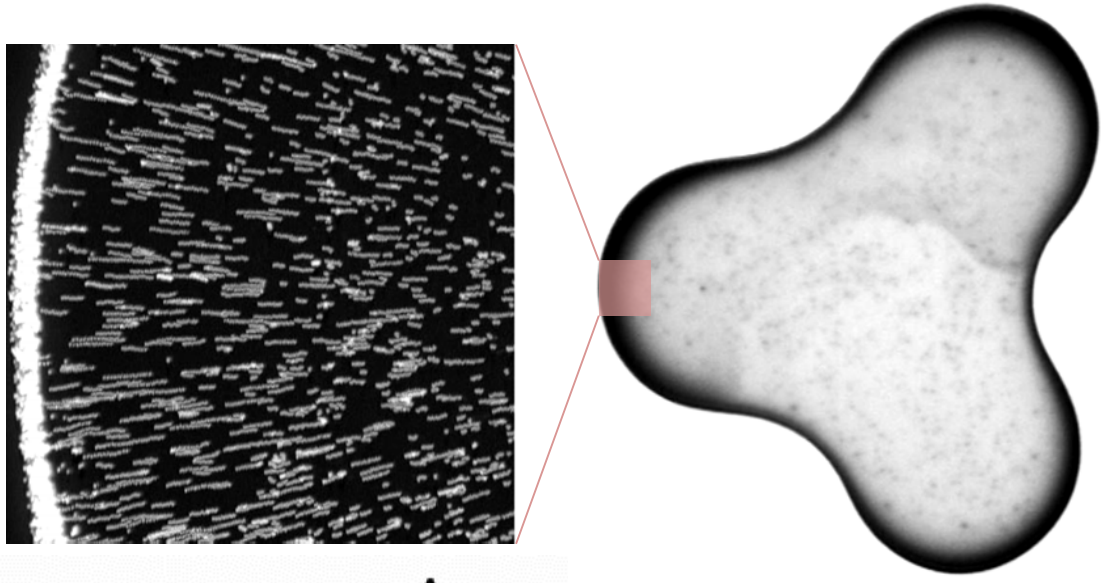


From 3D to 1D: Coffee ring effect



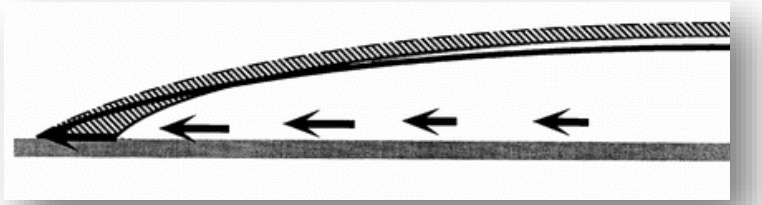
Still *et al.*, *Langmuir* 28, 4984 (2012)

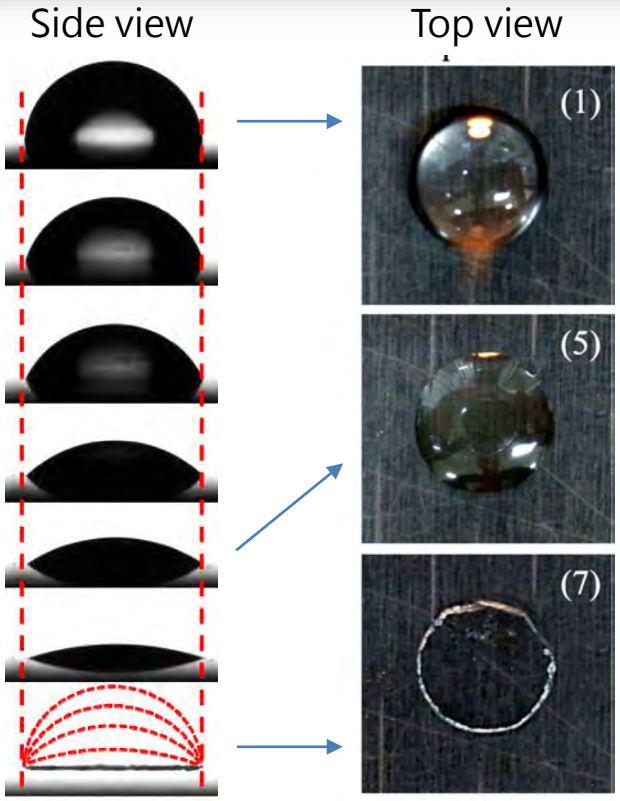
From 3D to 1D: Coffee ring effect

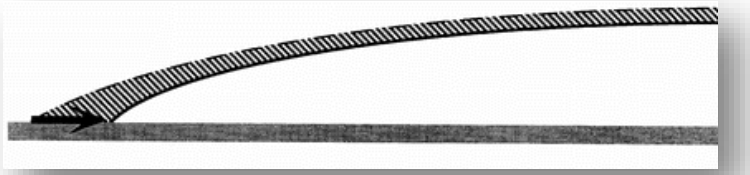


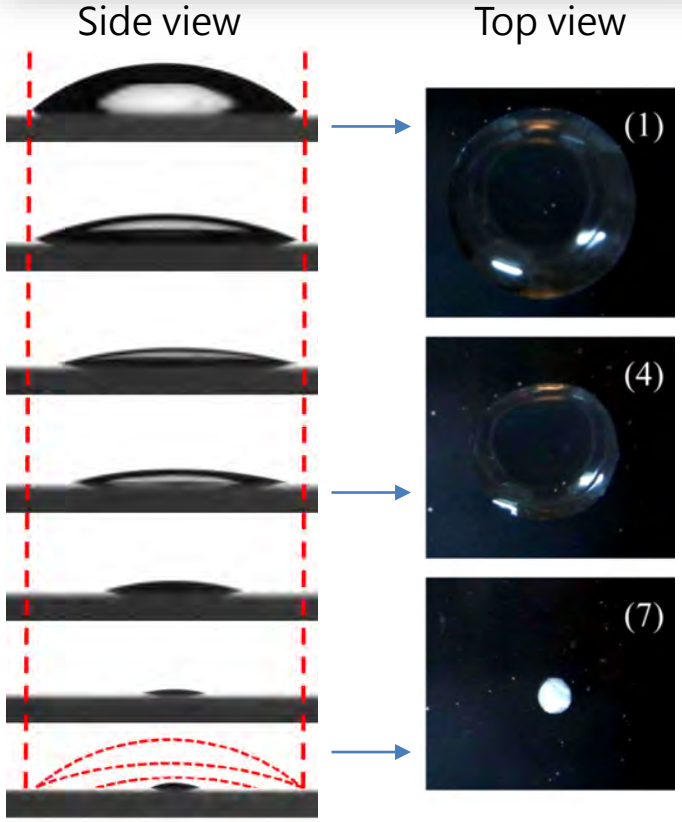
Deegan *et al.*, *Nature* 389, 6653 (1997)

Drop casting



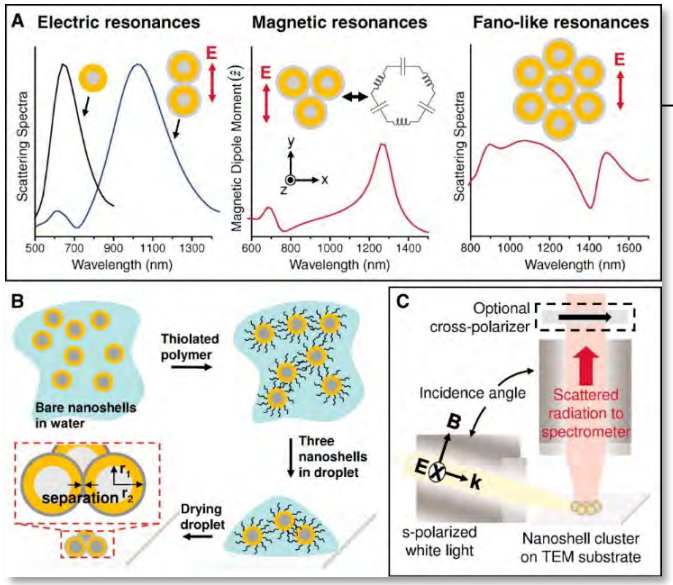




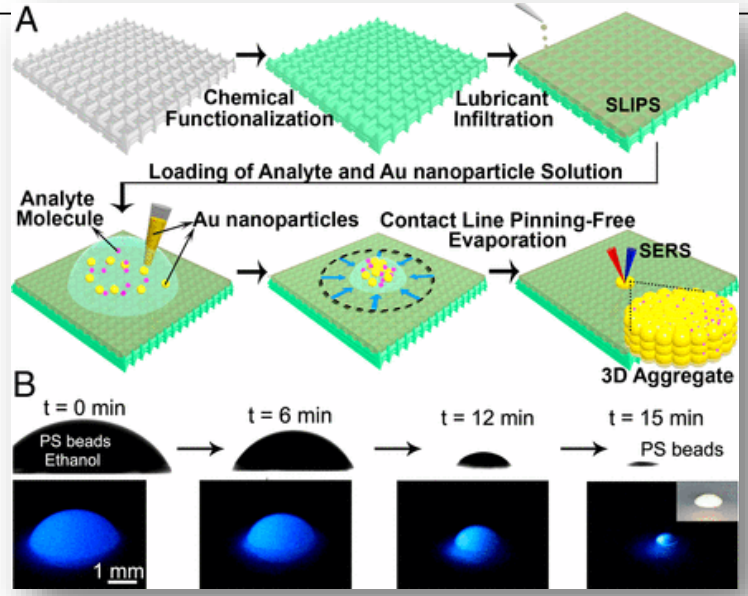


Li *et al.*, *Langmuir* 29, 782 (2013)

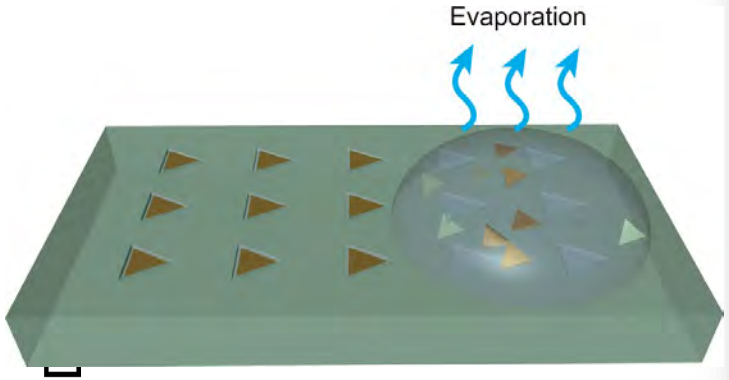
Drop casting



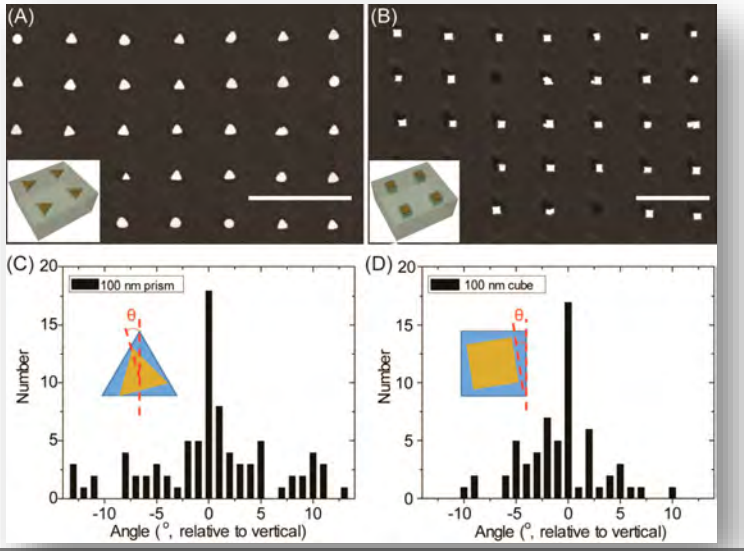
Fan *et al.*, *Science* 328, 1135 (2010)

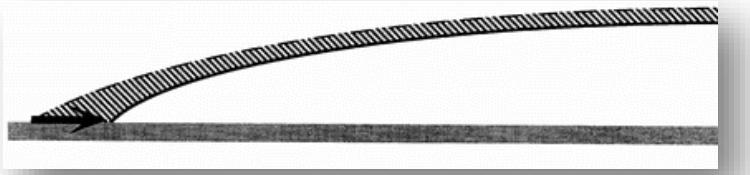


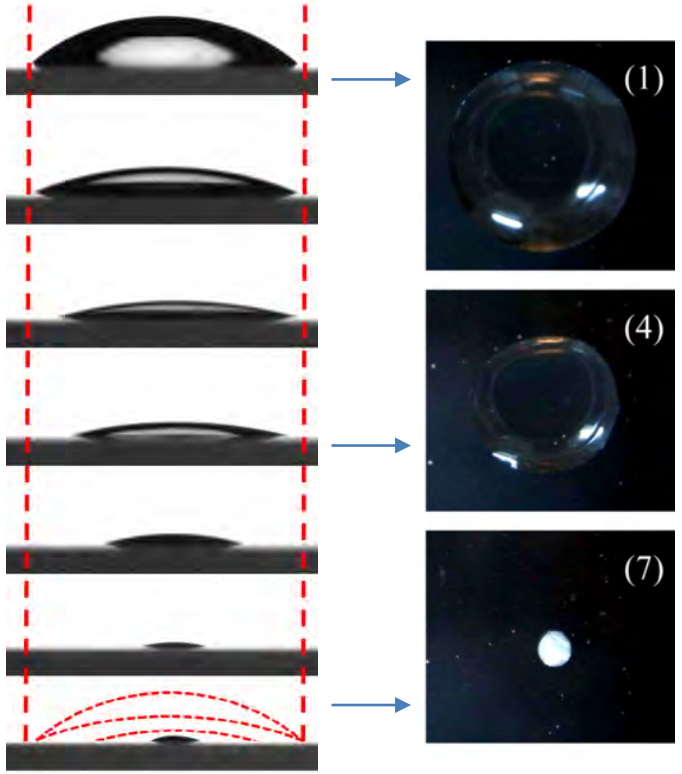
Yang *et al.*, *PNAS* 113, 268 (2016)



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



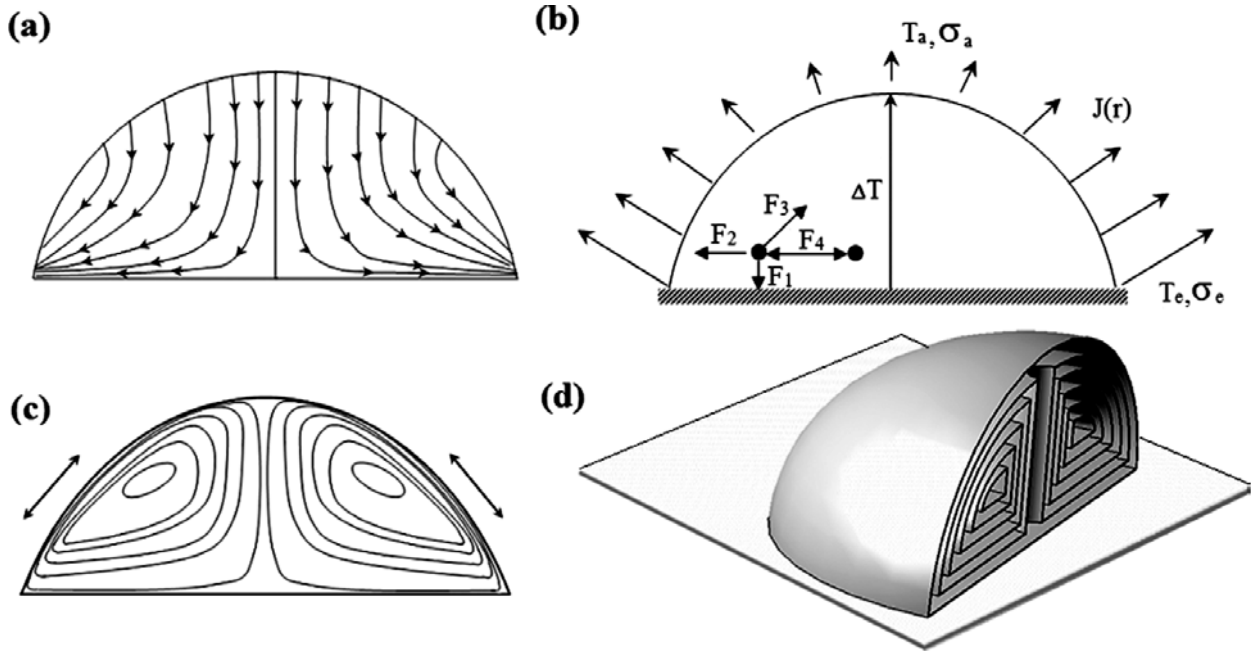




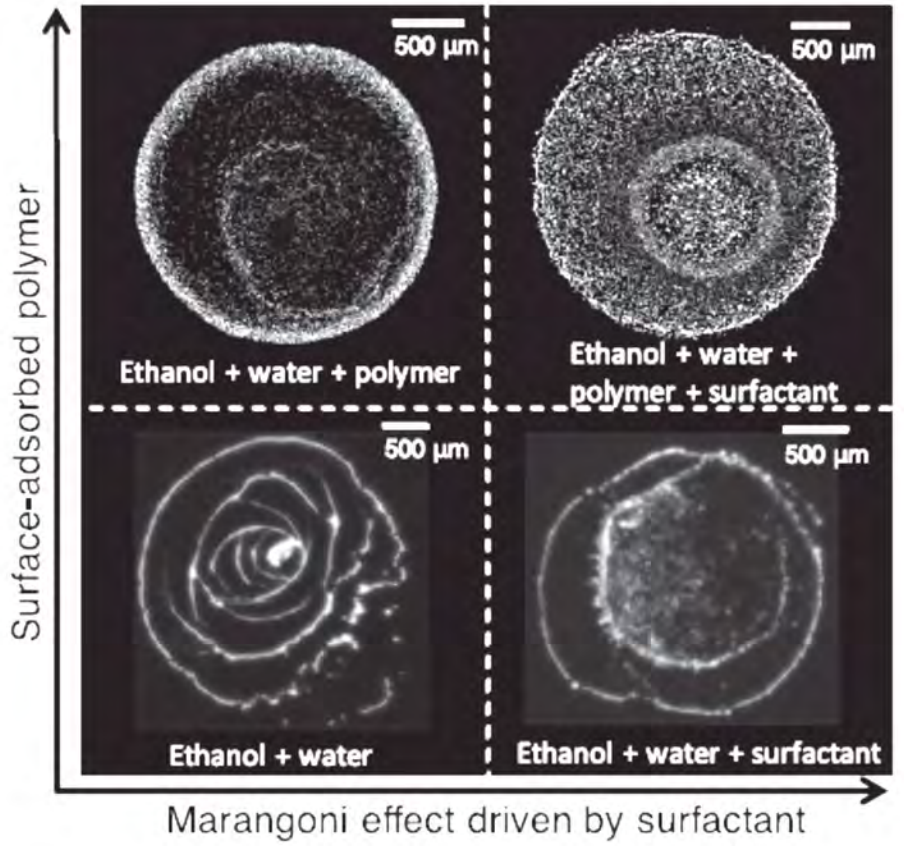
Li *et al.*, *Langmuir* 29, 782 (2013)

From suspension to substrate

Drop casting



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

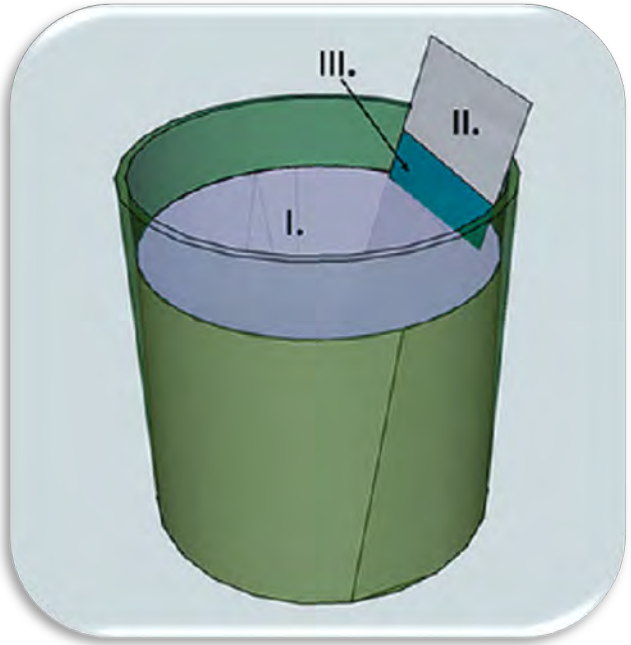


Kim *et al.*, *PRL* 116, 124501 (2016)

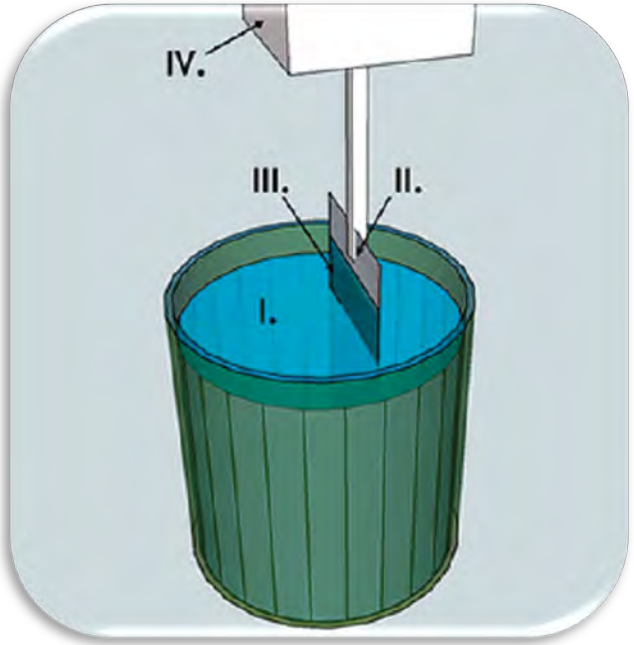
✓ Resource efficient

× Limited control

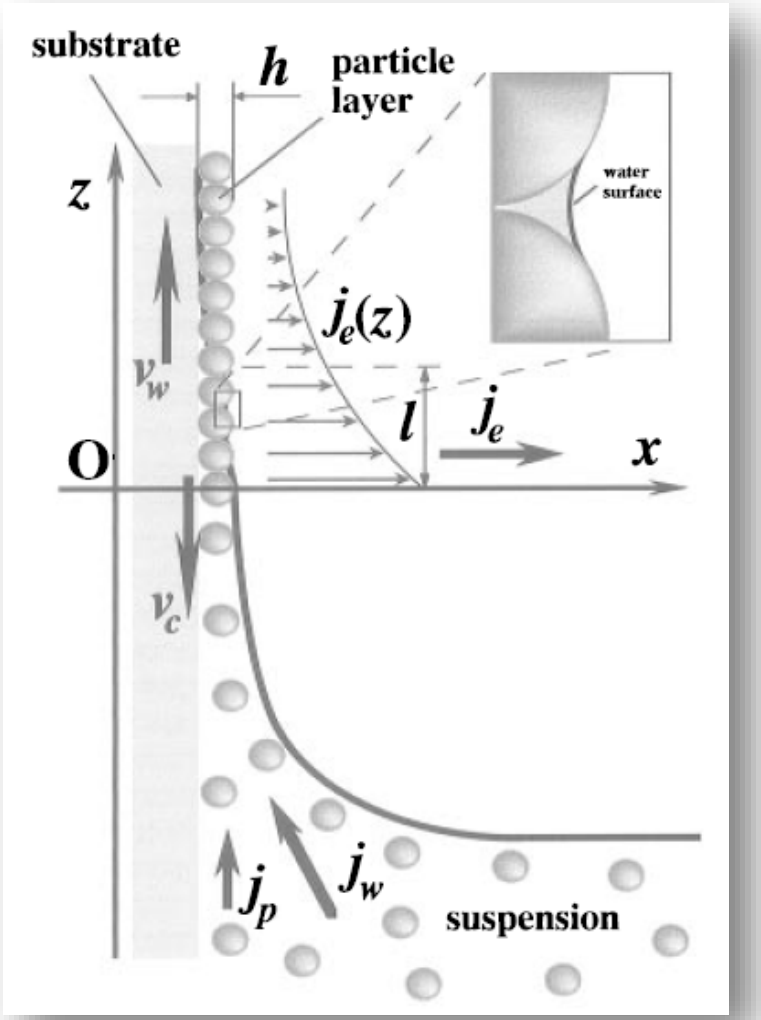
Dip coating



Evaporation-driven



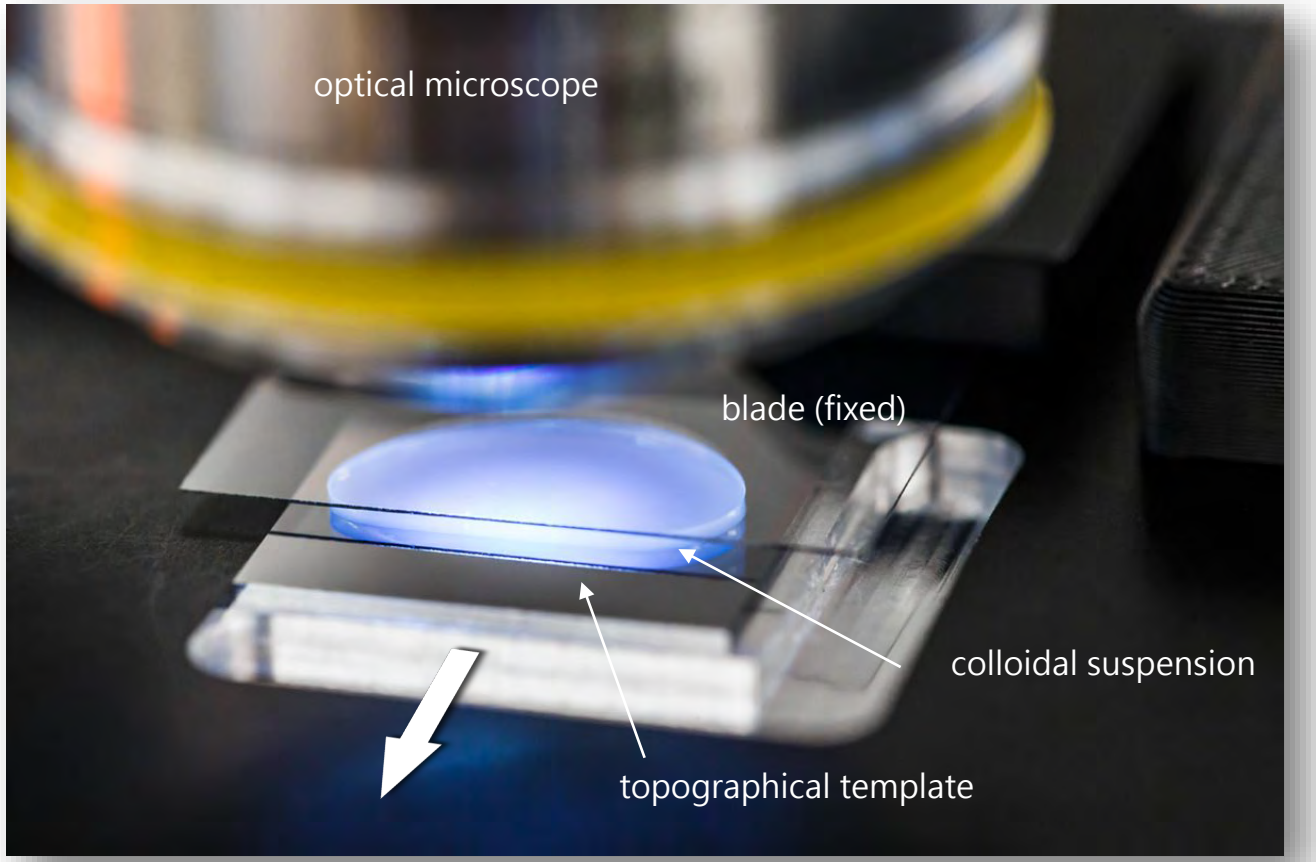
Moving substrate



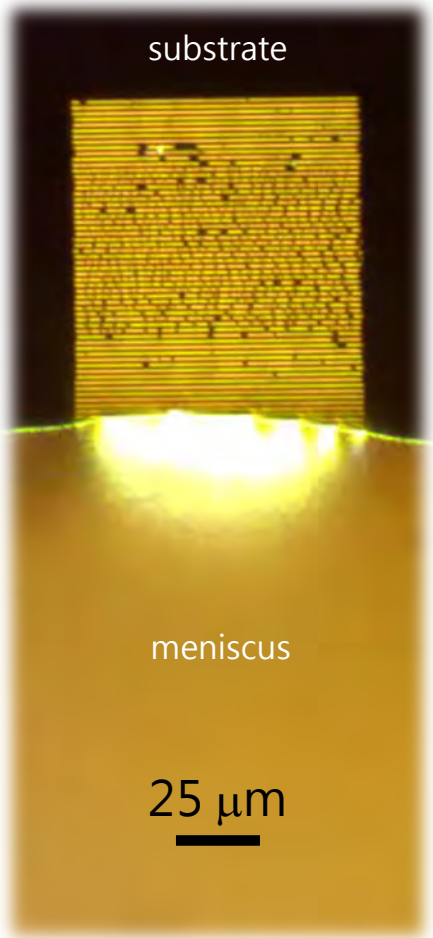
Dimitrov & Nagayama, *Langmuir* 12, 1303 (1996)

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

Blade coating

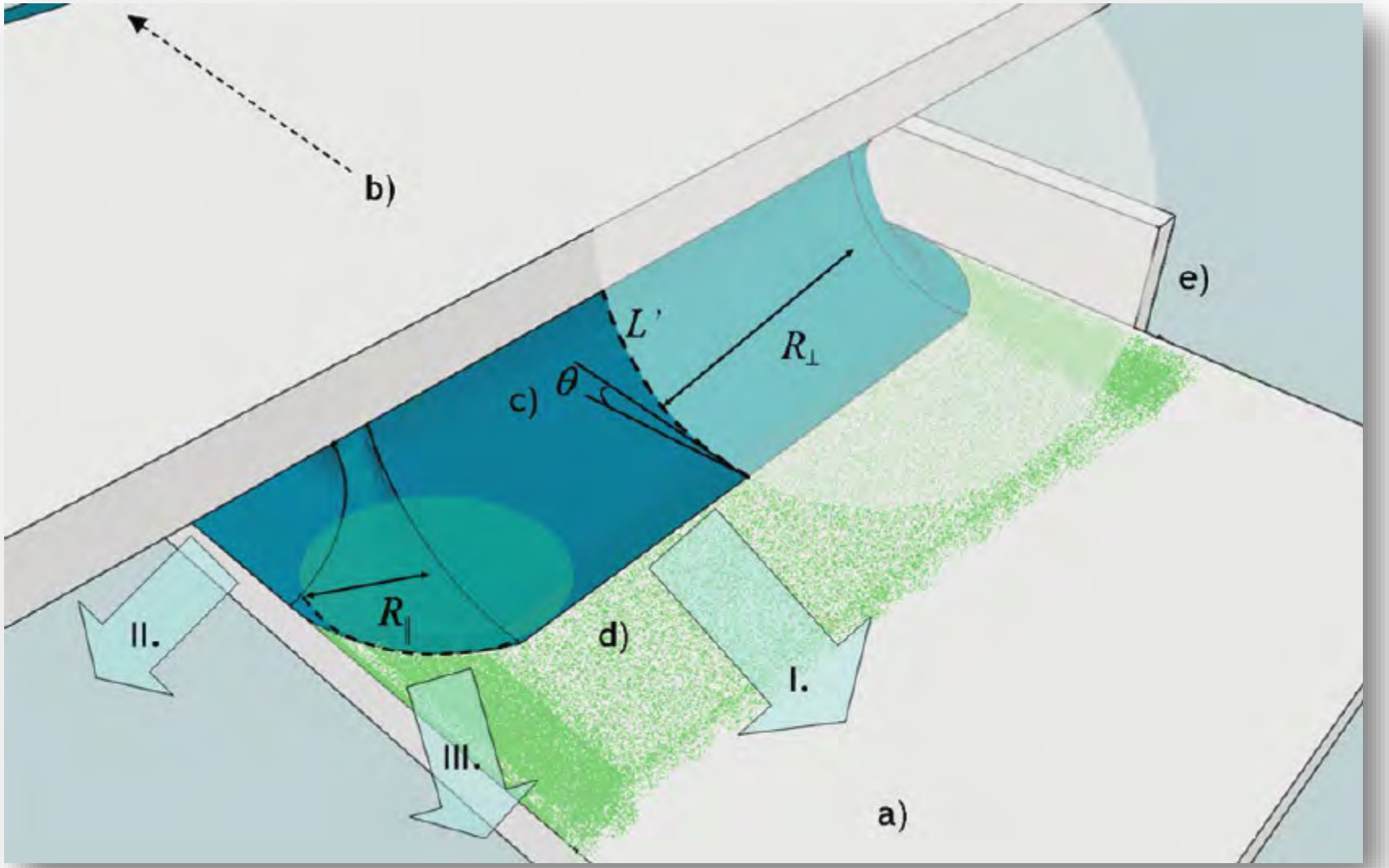


Top view



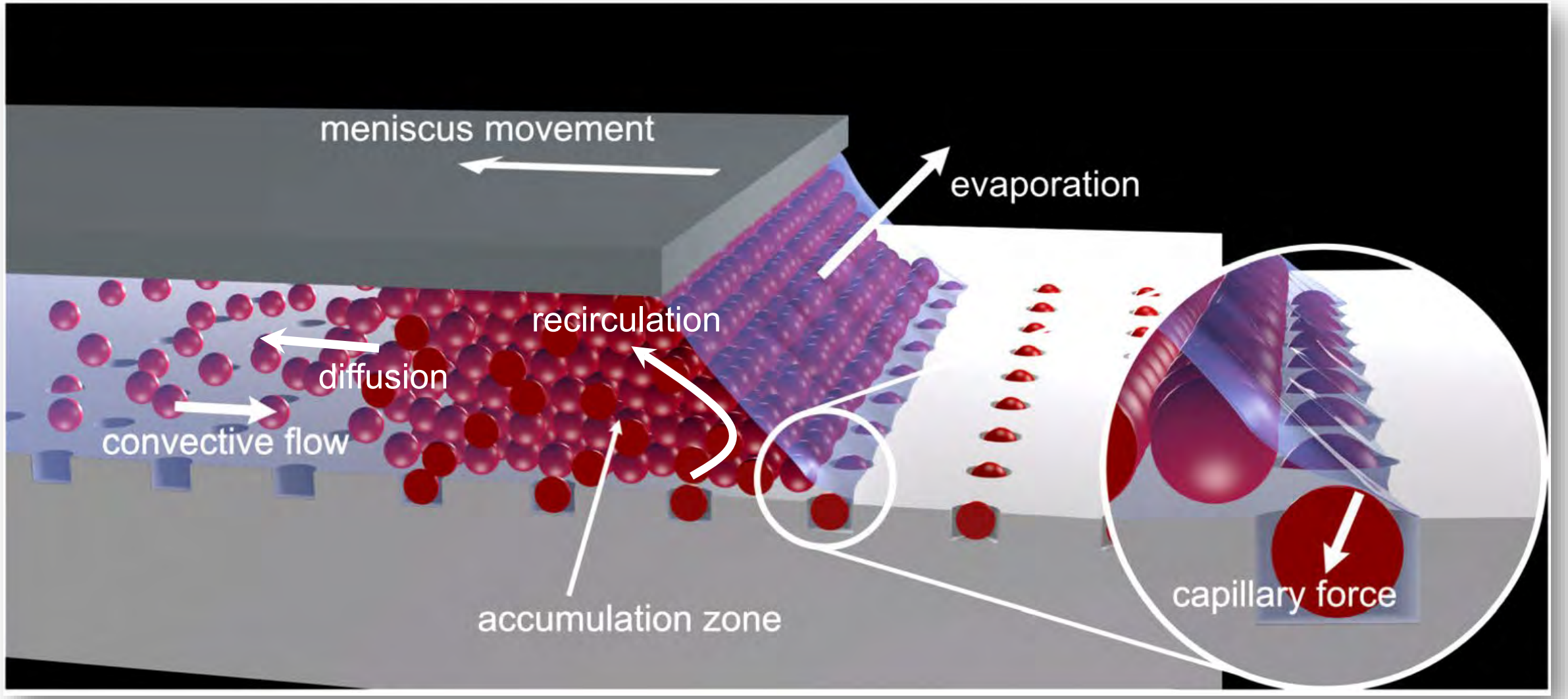
- ✓ Control of meniscus
- ✓ Resource efficient

Blade coating



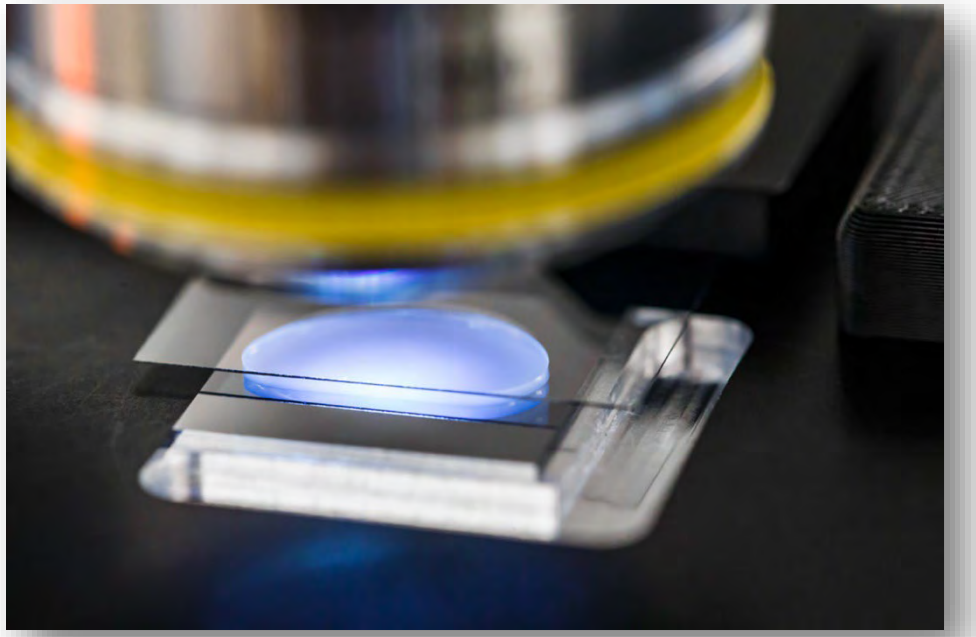
Born *et al.*, *Langmuir* 27, 8621 (2011)

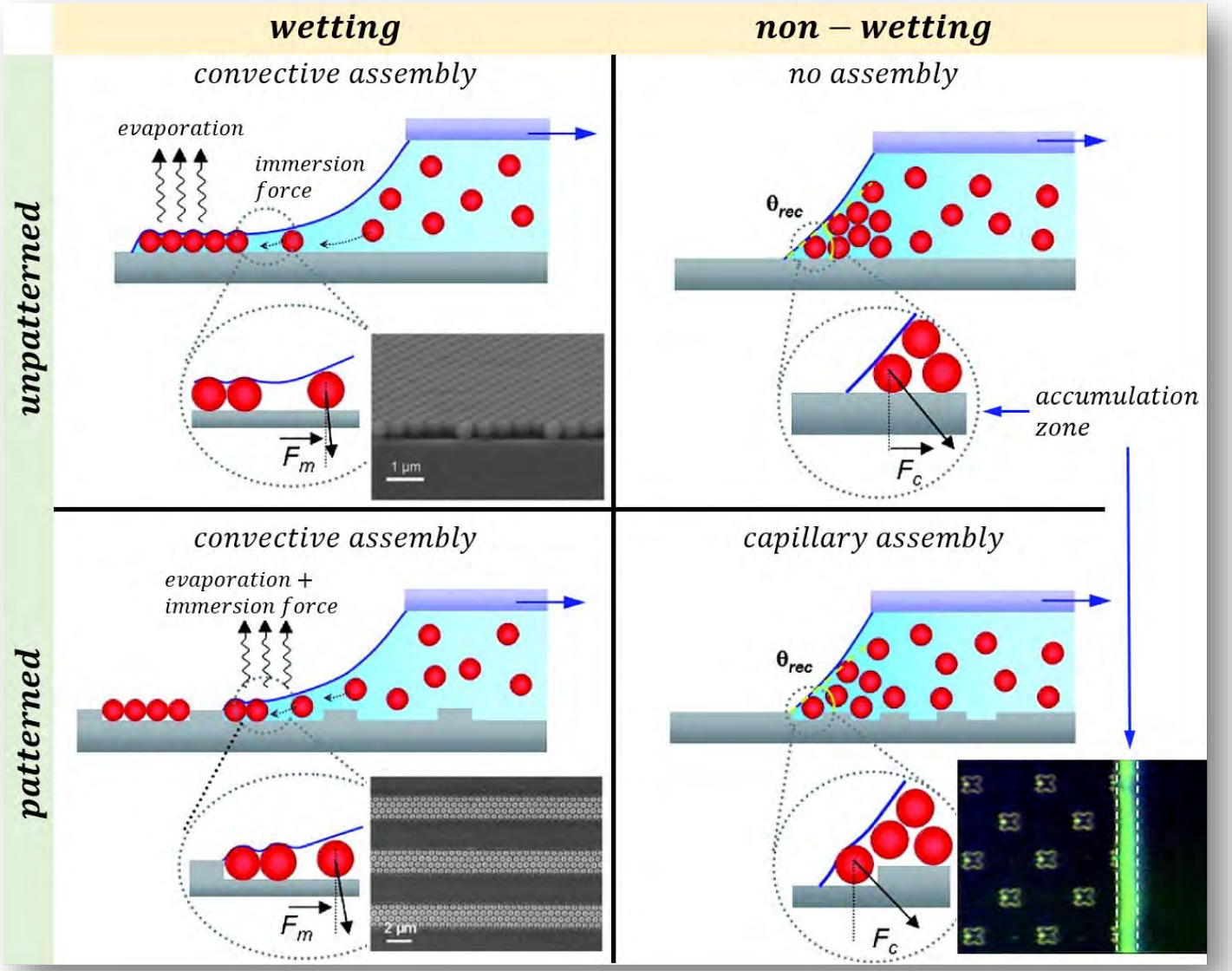
Blade coating



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

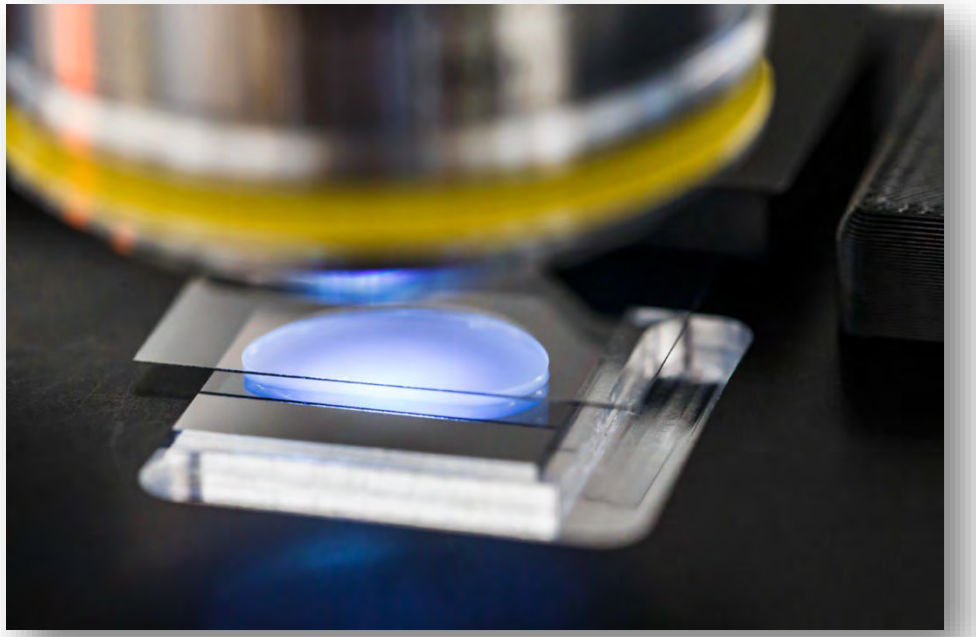
Blade coating





Mastrangeli, *Adv. Mater.* 2015

Top-down meets bottom-up



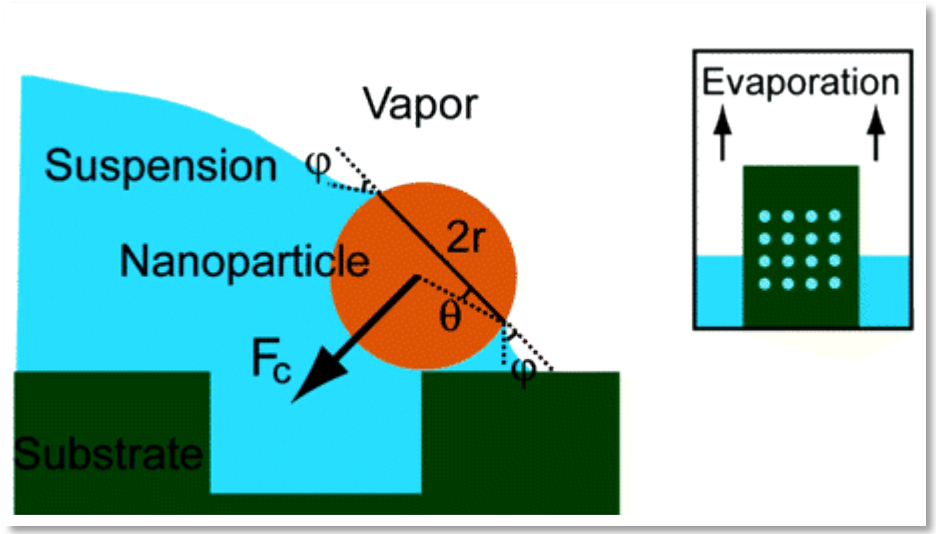
iff

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

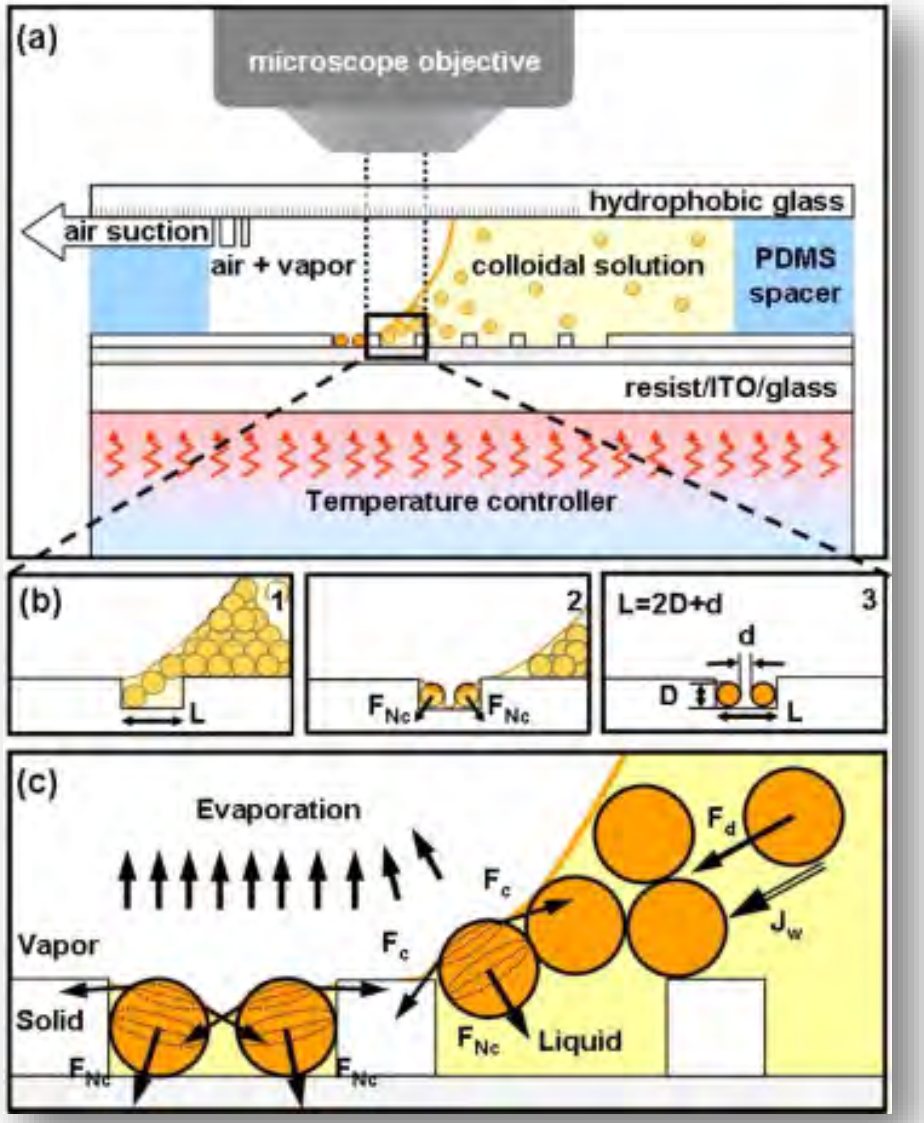
then

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

Capillary push

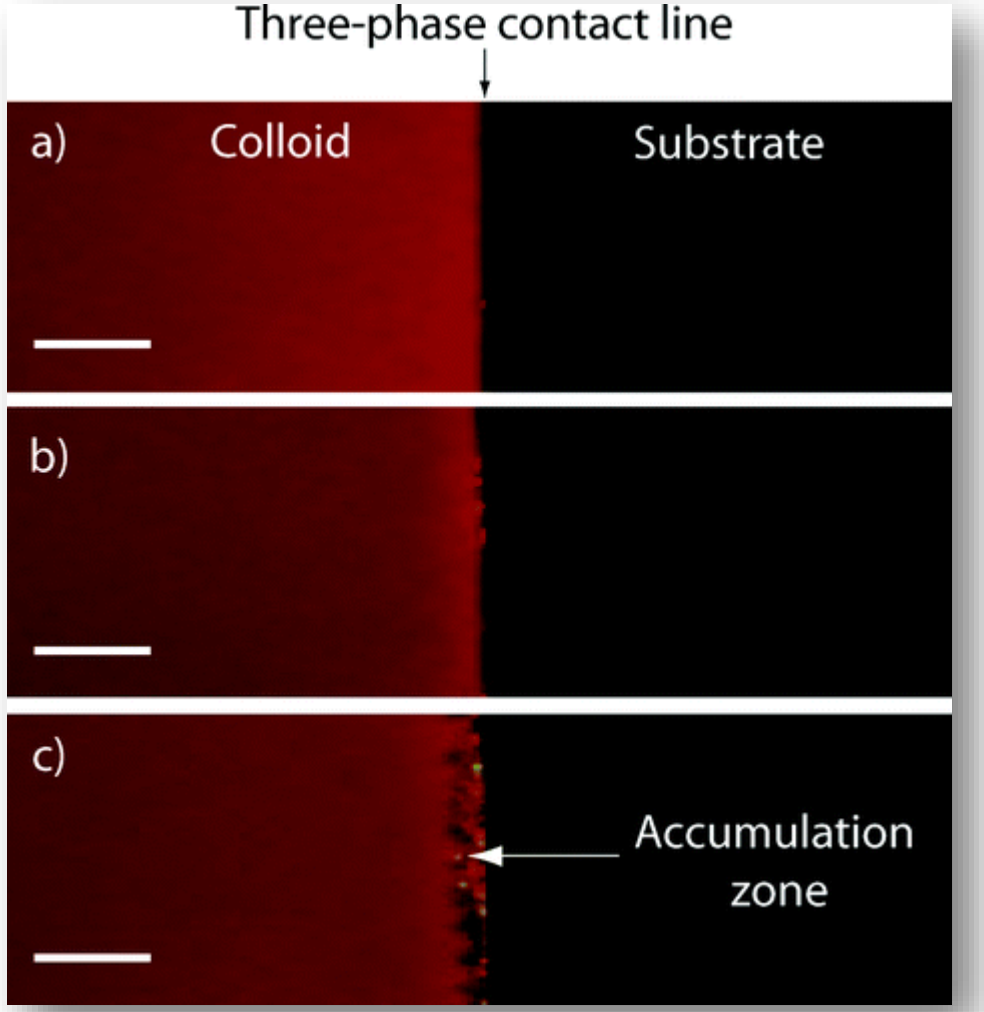


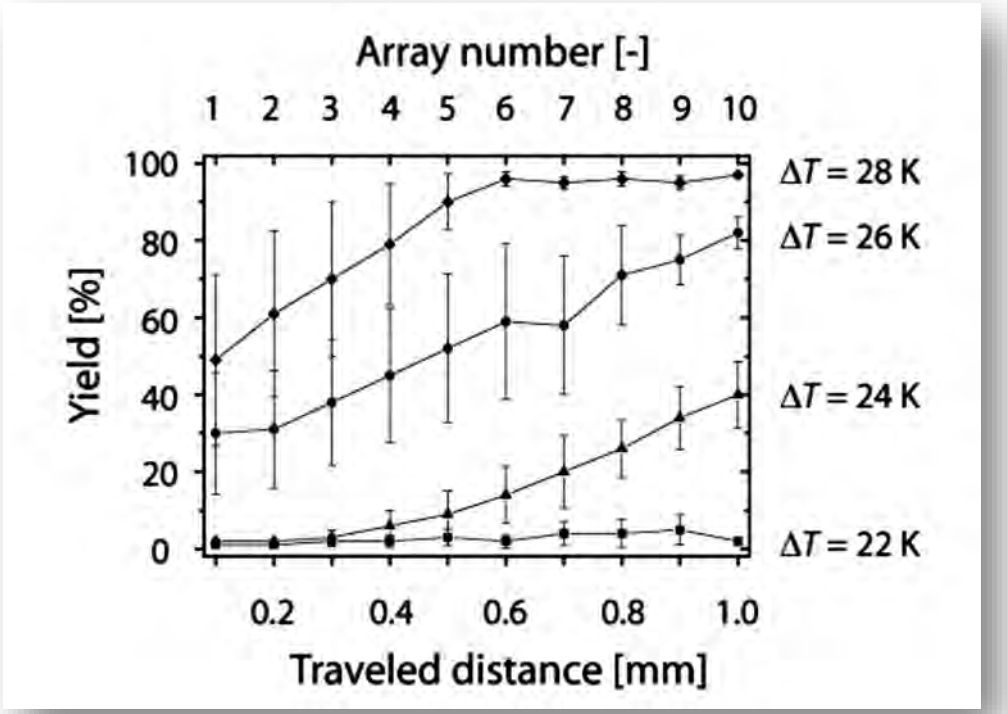
Cui *et al.*, *Nano Lett.* 4, 1093 (2004)



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

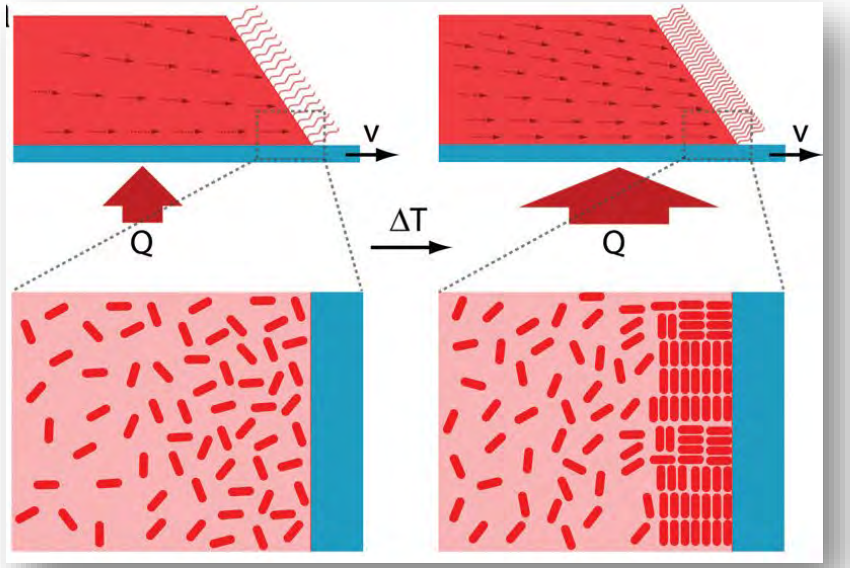
Size of accumulation zone



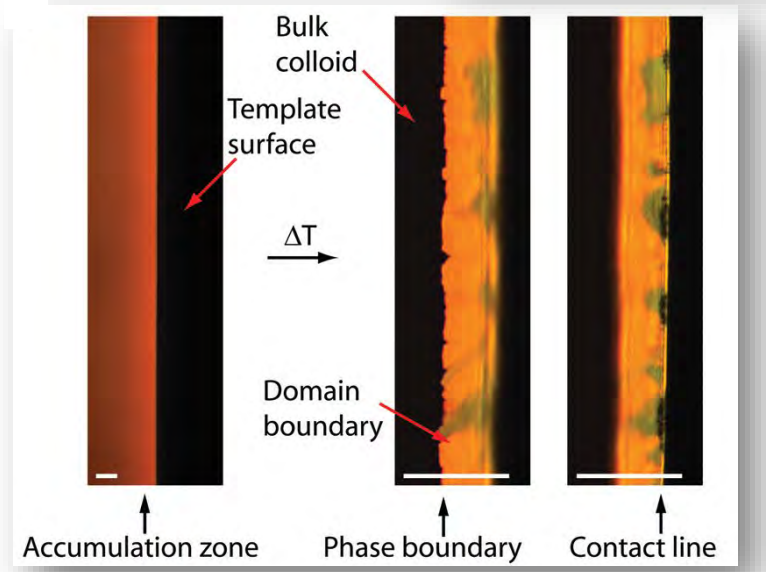


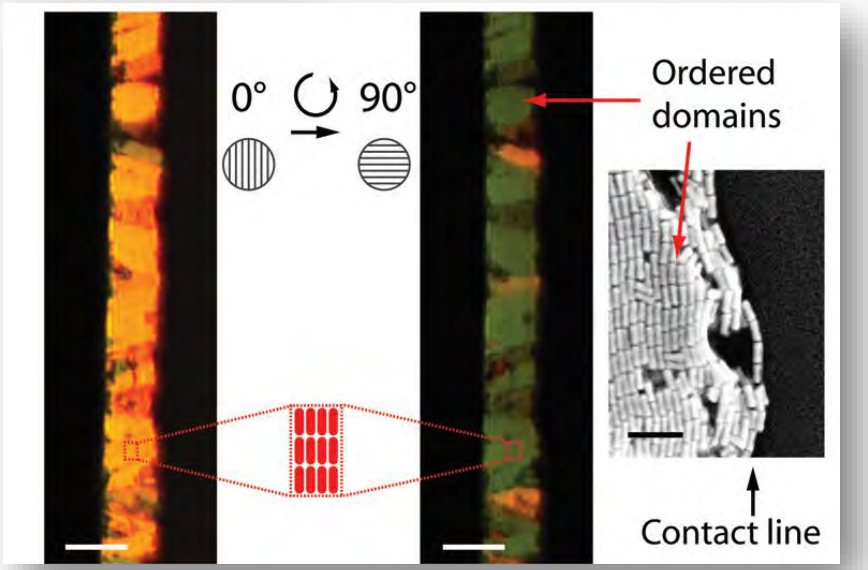
Kuemin *et al.*, *Langmuir* 27, 6305 (2011)

Density-driven phase transition



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

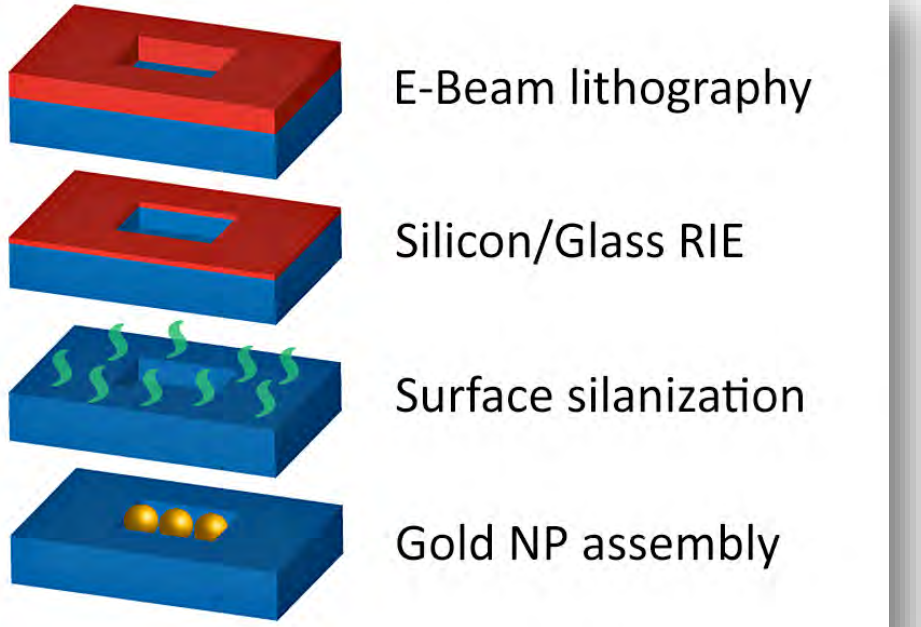


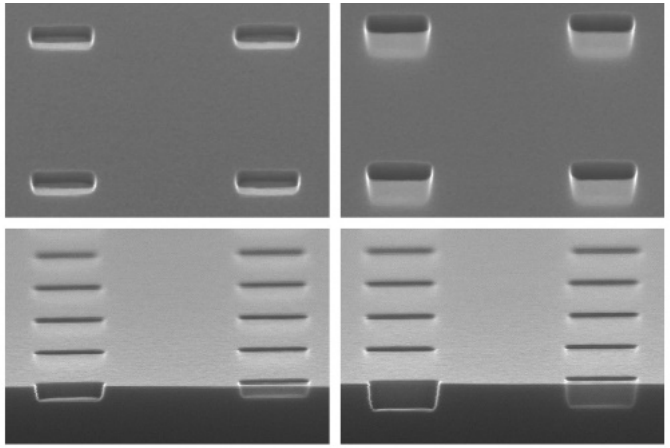


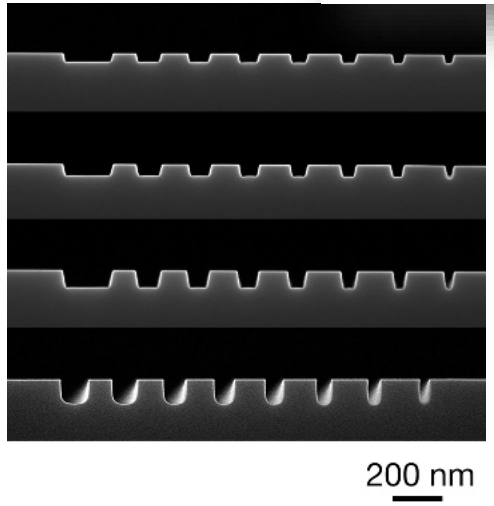
Topographical template fabrication

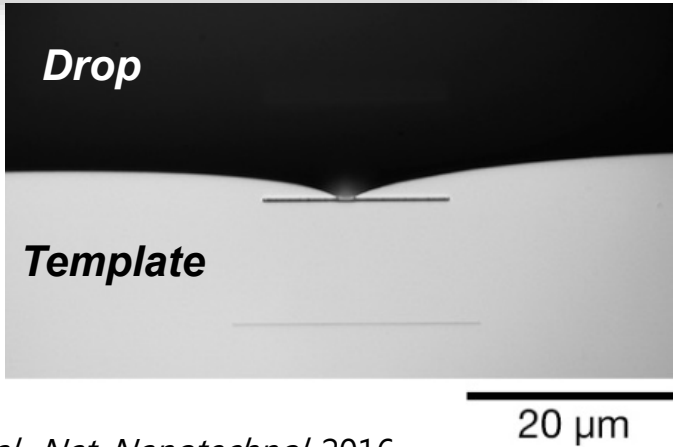
EBL / RIE / Silanisation

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



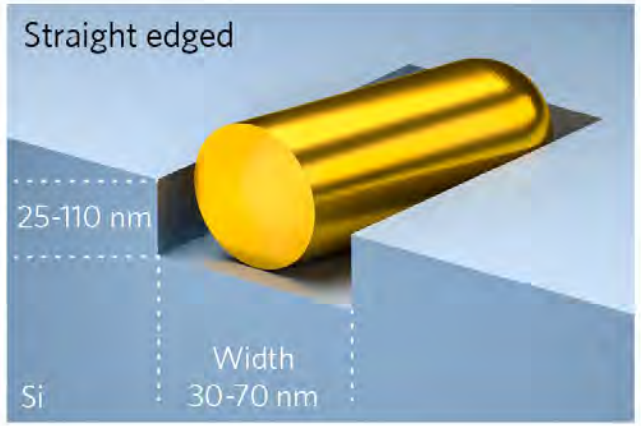


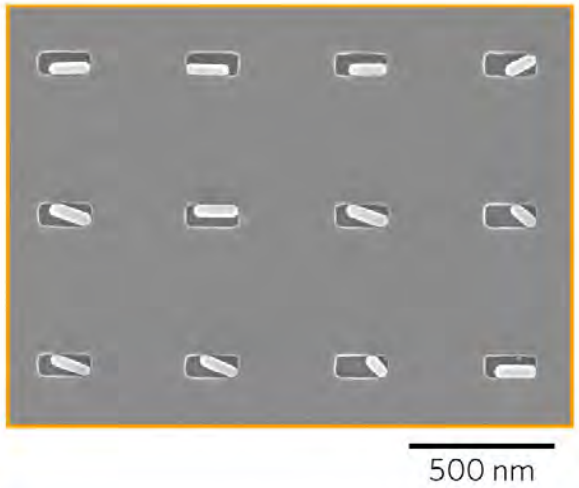


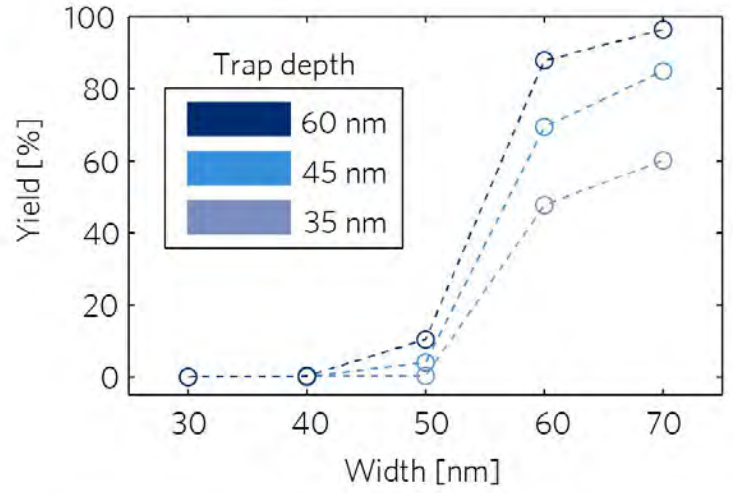


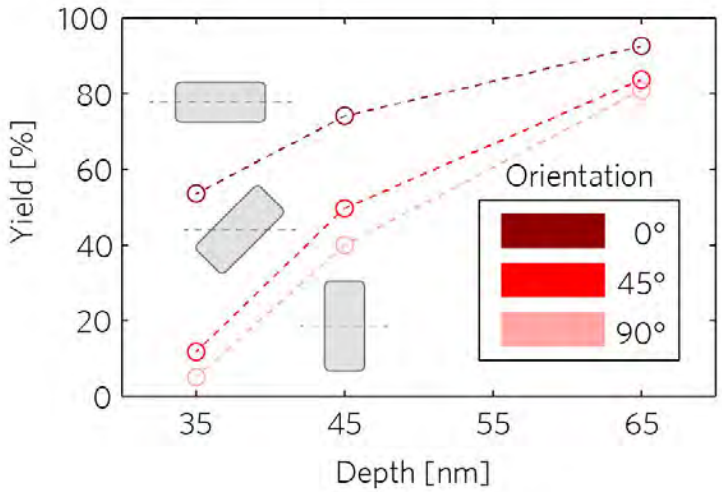
Flauraud *et al., Nat. Nanotechnol.* 2016

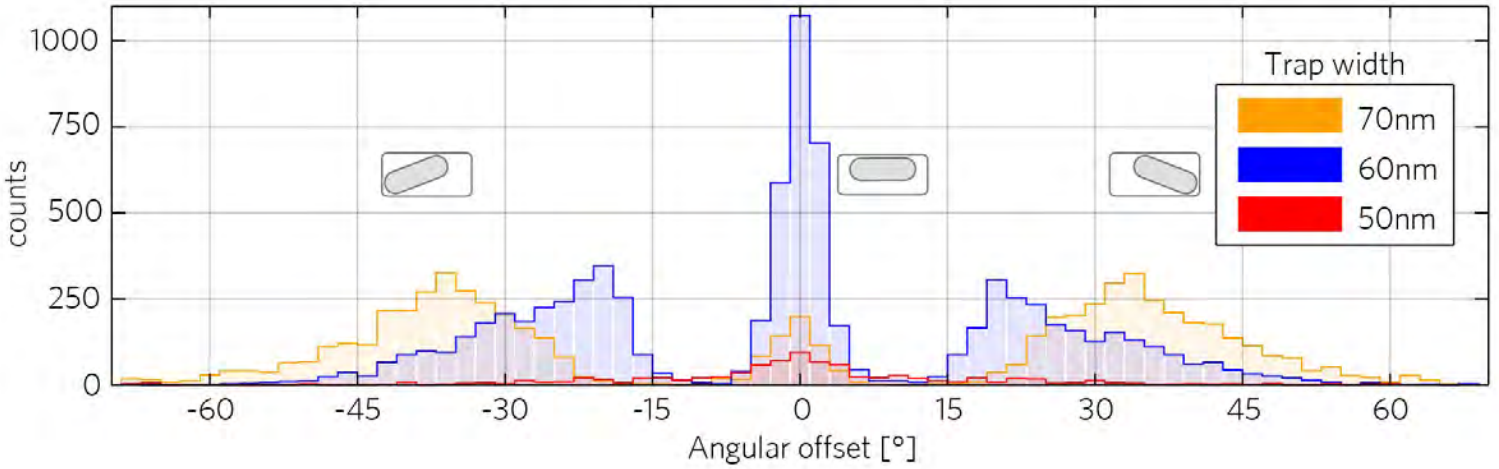
Straight-edged traps





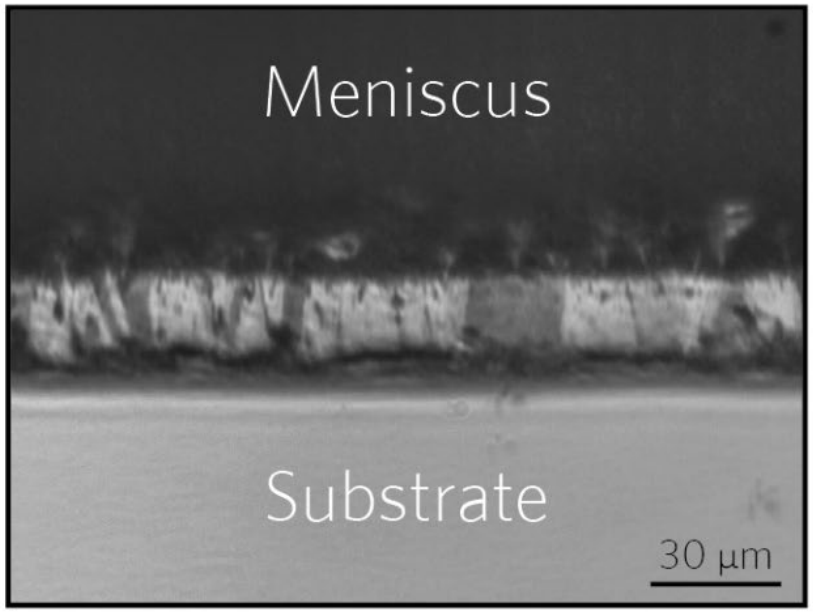


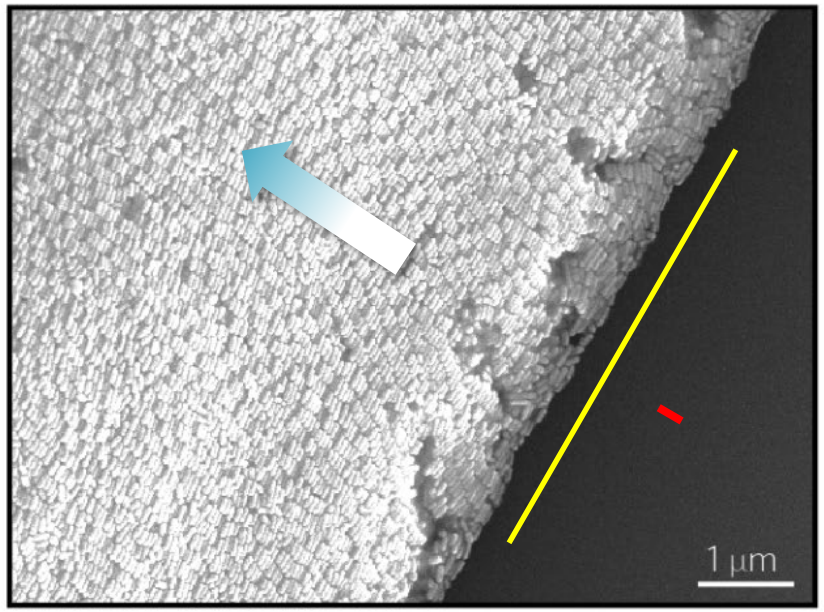




Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Particle accumulation and entropy





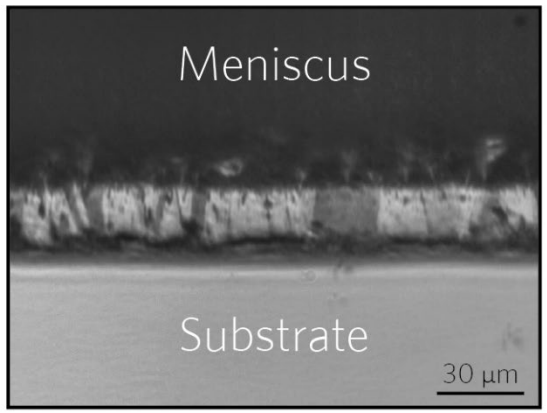
L. Onsager

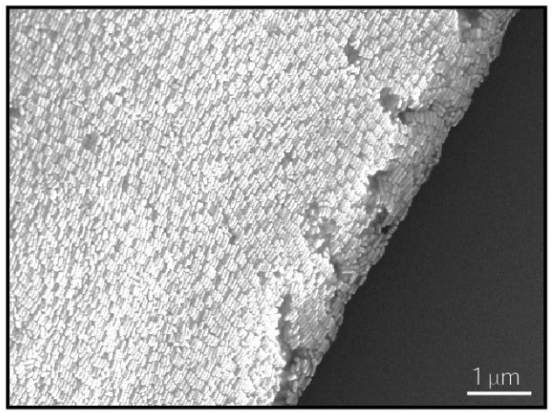
Density-induced phase transition

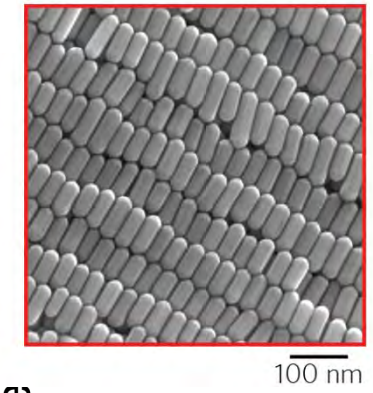
- Rotational entropy traded for translational entropy
- Net entropy gain

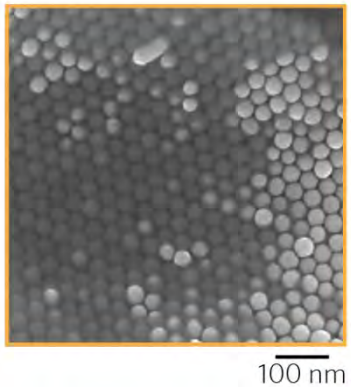
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

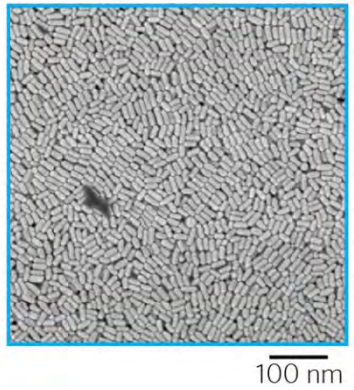
Insight 1: Non-uniform accumulation

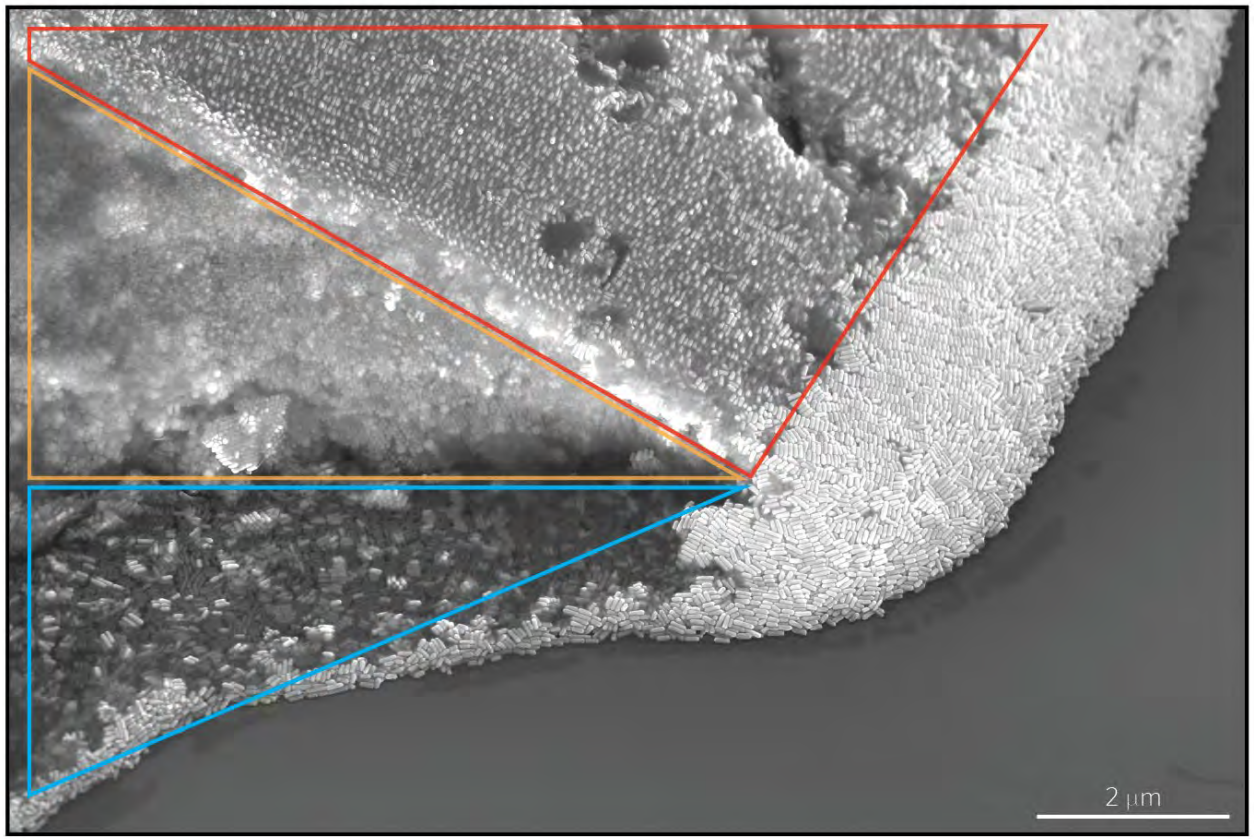






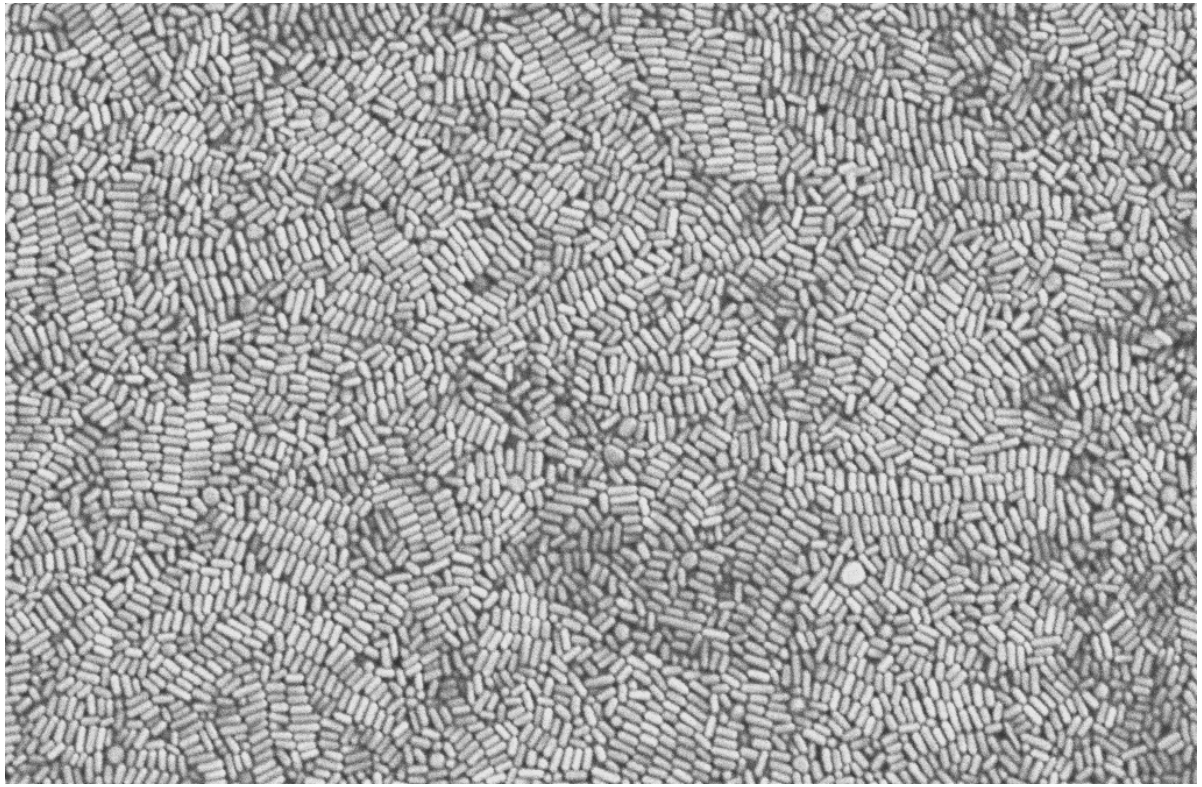


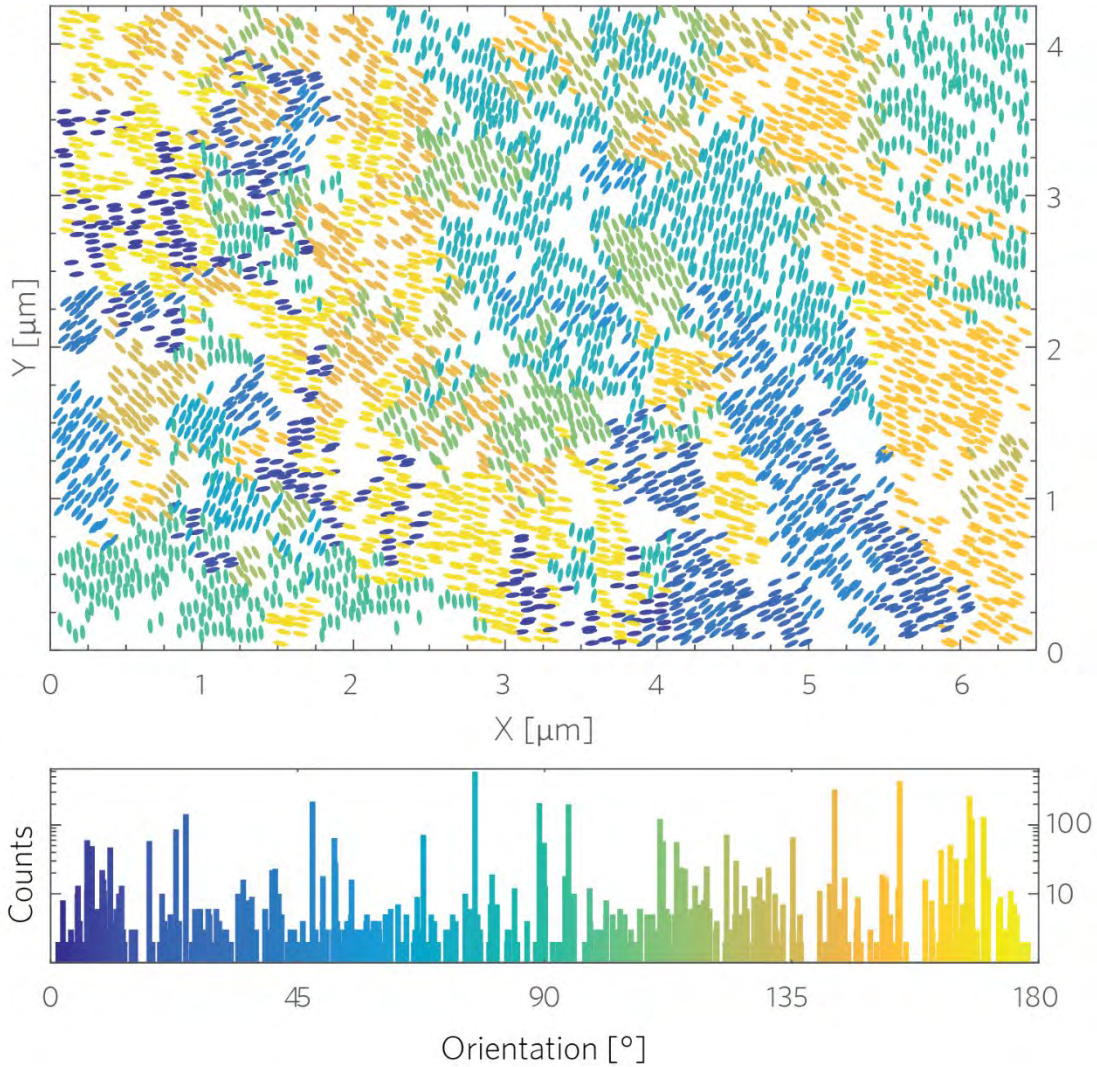




Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

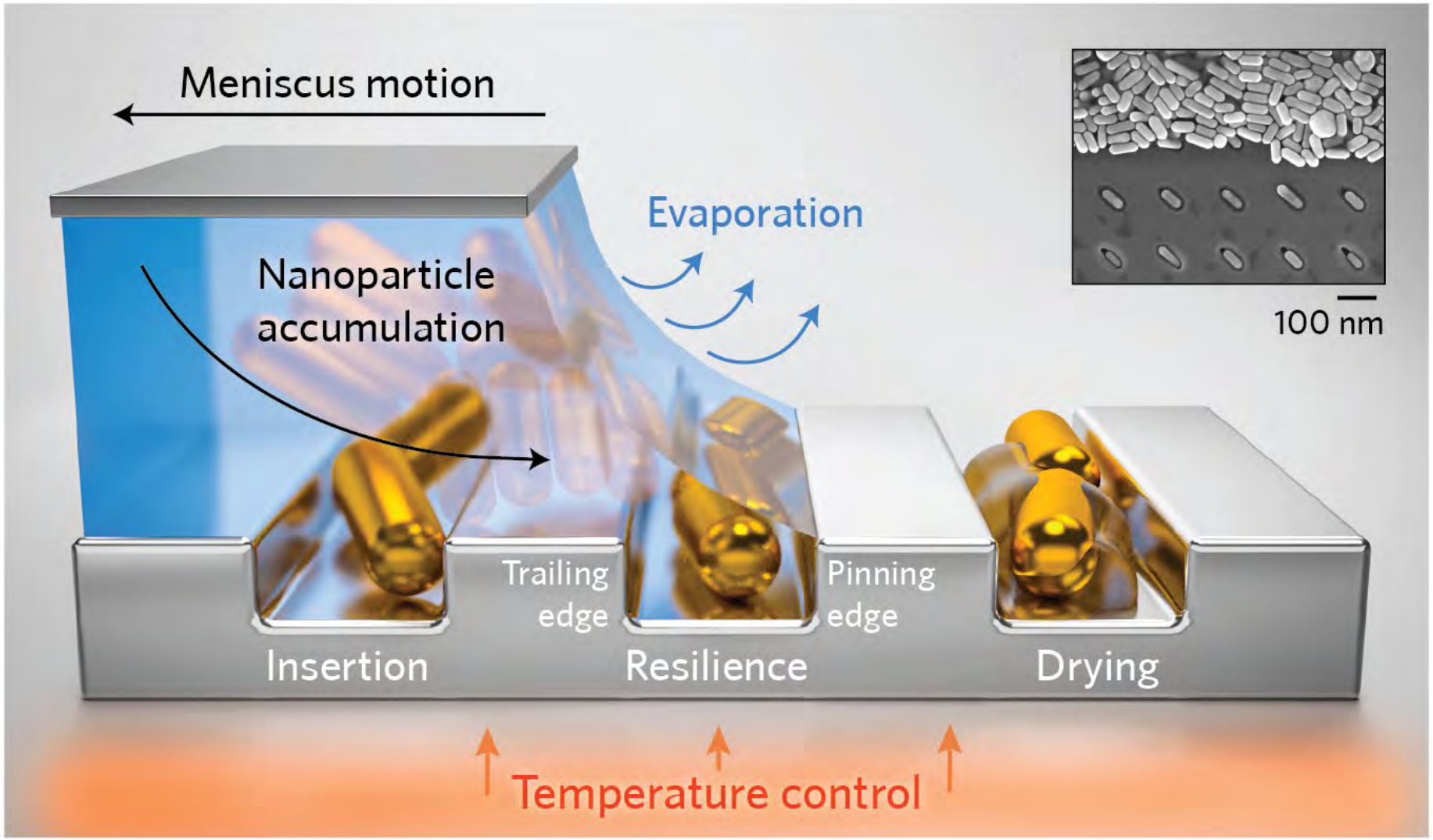
Insight 1: Non-uniform accumulation



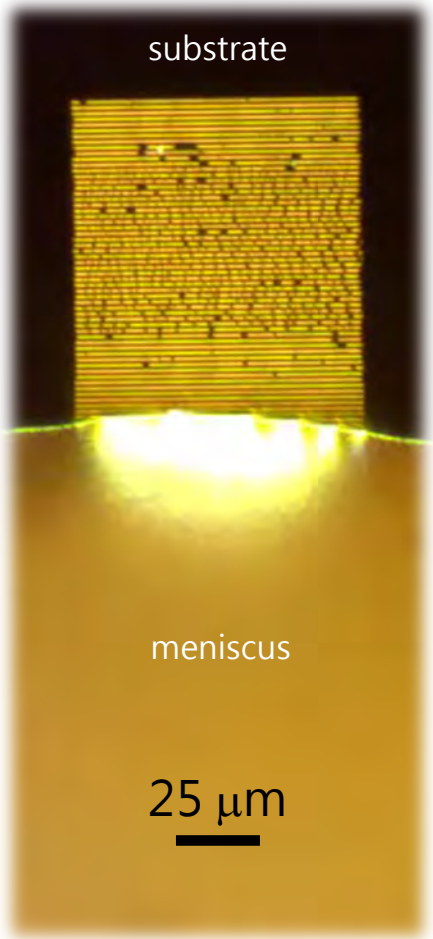


Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

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

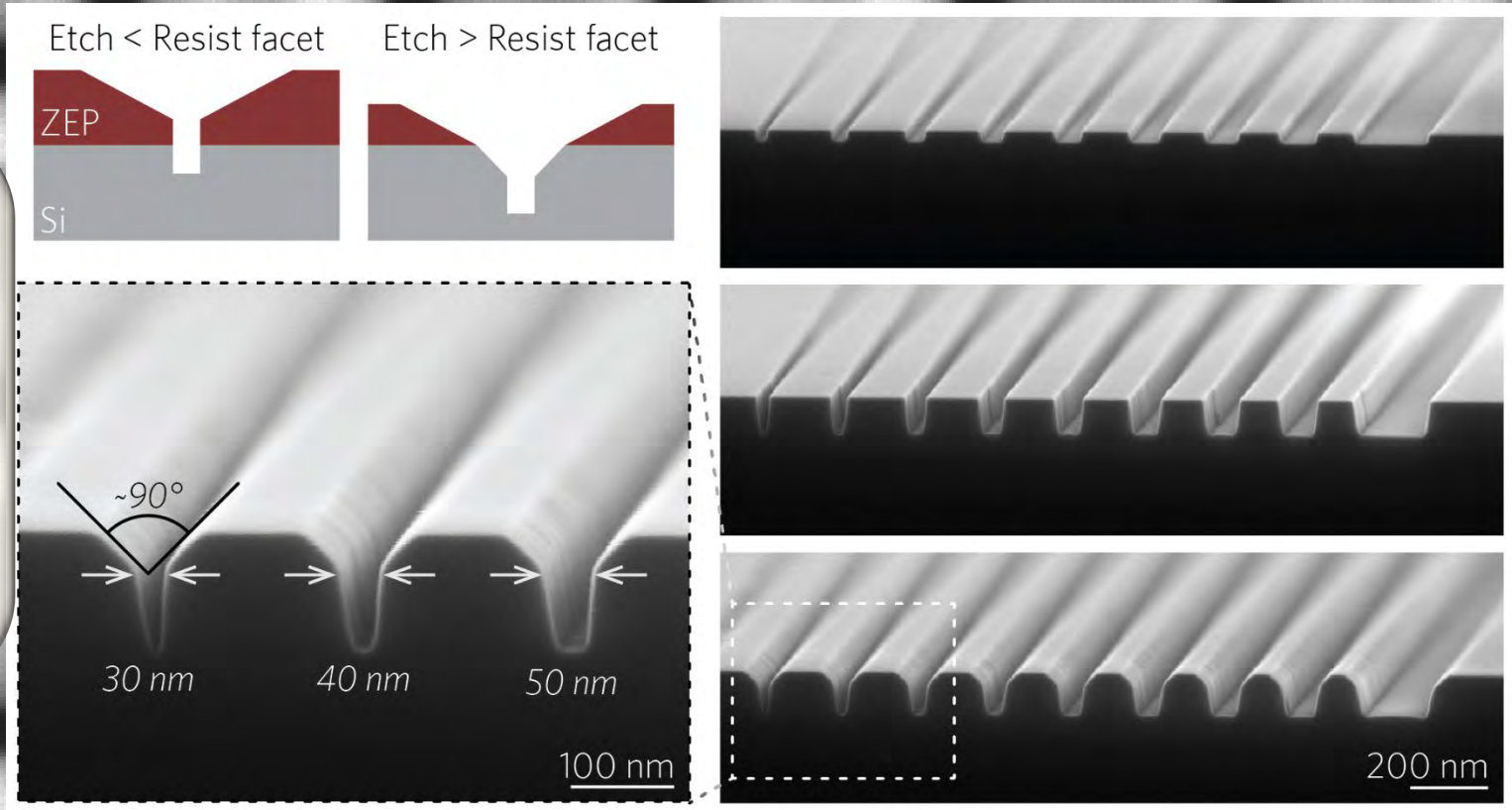
TU Delft EPFL

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

Insight 3: 3D trap geometry

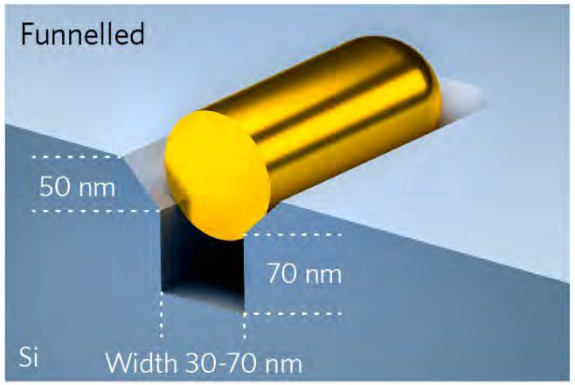
EBL – RIE – Silanisation

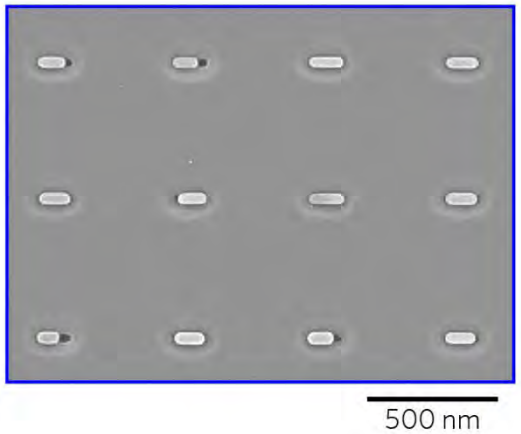
- Cl_2/BCl_3 chemistry
- Progressive resist faceting
- Low roughness transfer to Si
- Compatible with SiO_2 & Si_3N_4

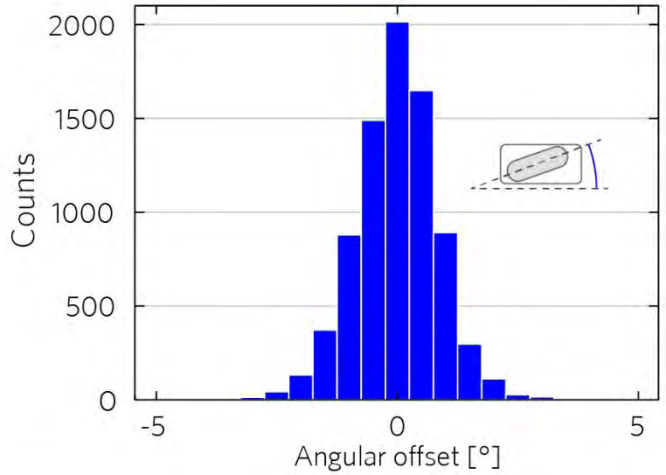


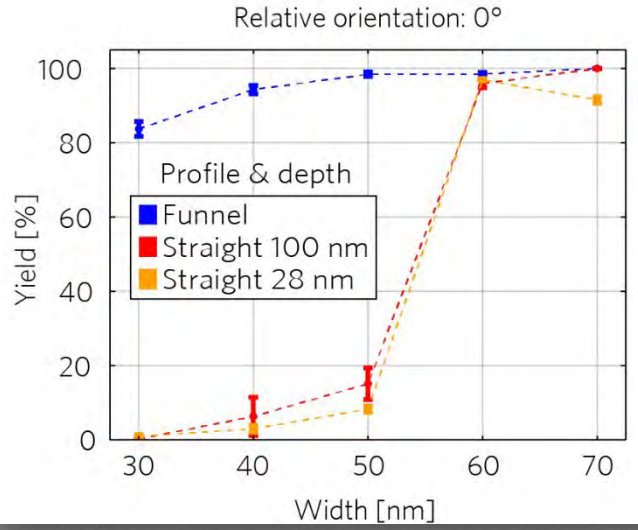
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

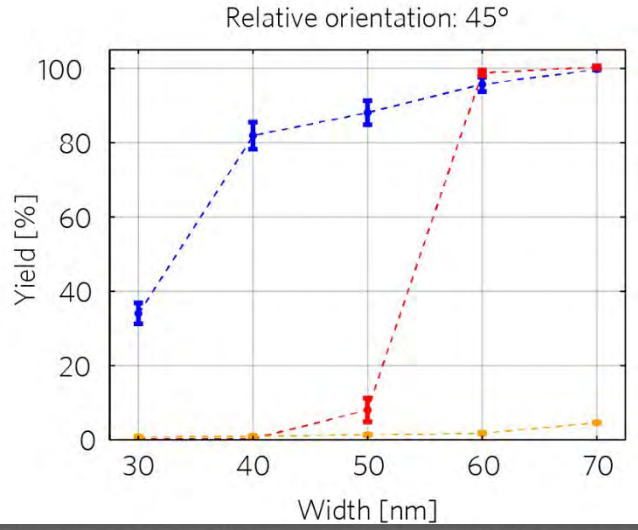
Assembly on funneled traps

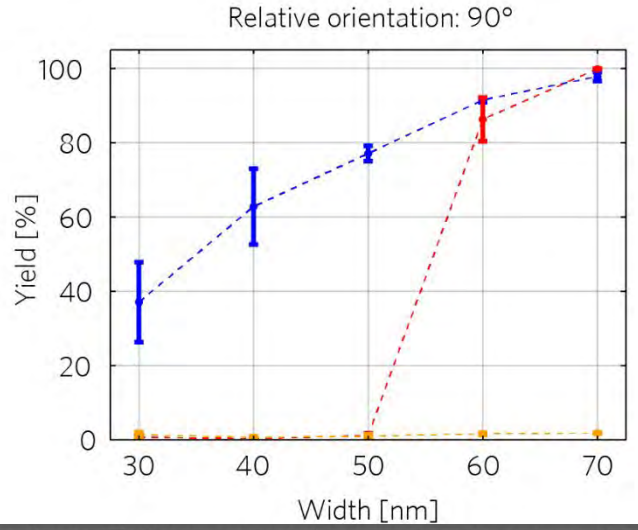












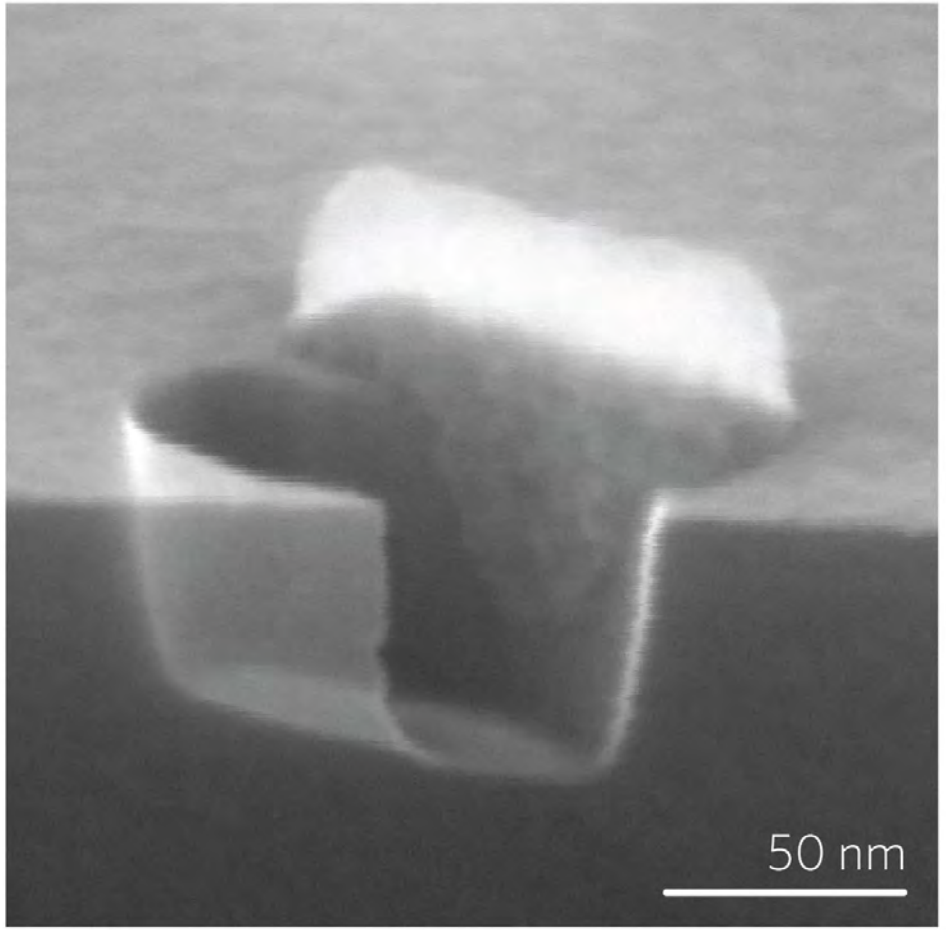
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

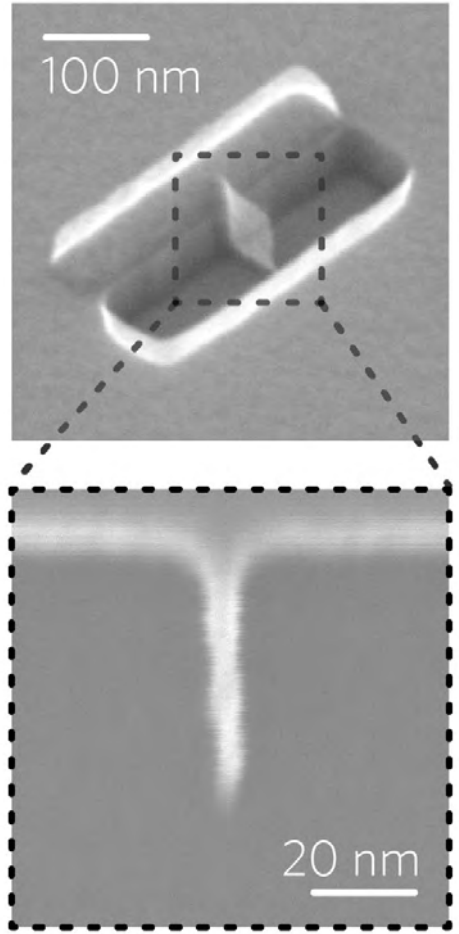
Single auxiliary sidewall

Auxiliary sidewall

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

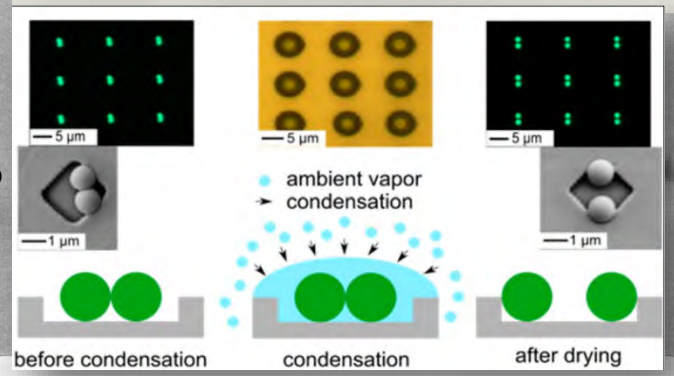
- Counteract NP removal
- Symmetry breaking





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

Straight-edged traps with auxiliary sidewall



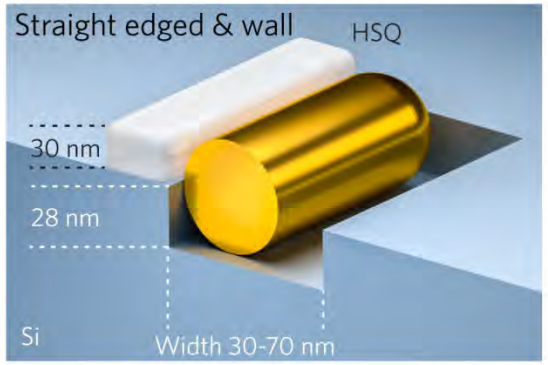
Ni *et al.*, Langmuir 2014

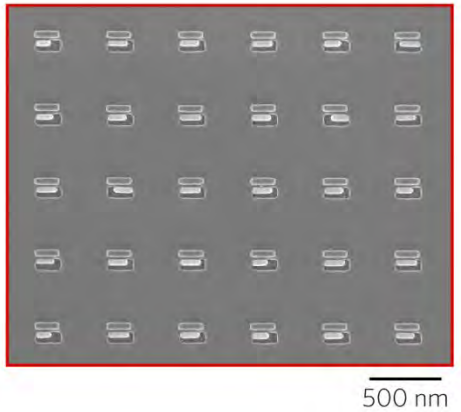
Biased evaporation

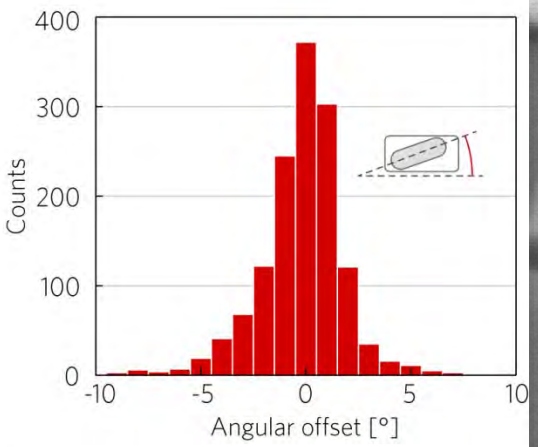
- Deterministic positioning in loose traps

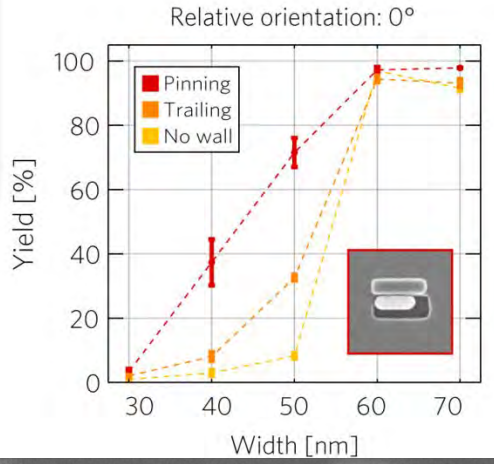
Sidewall position

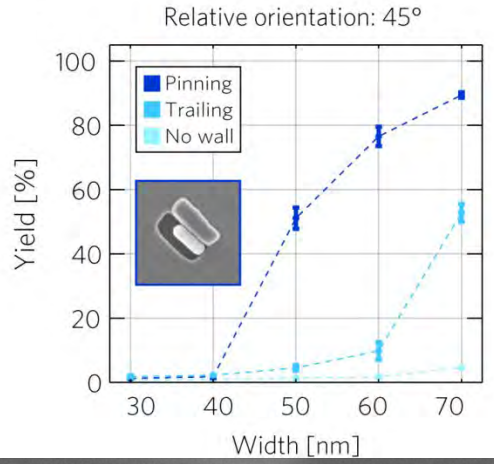
- High yield improvement

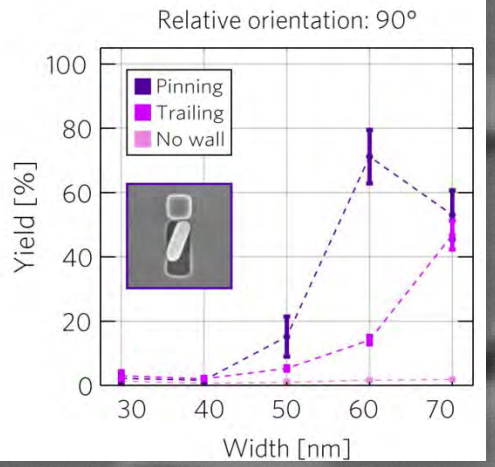










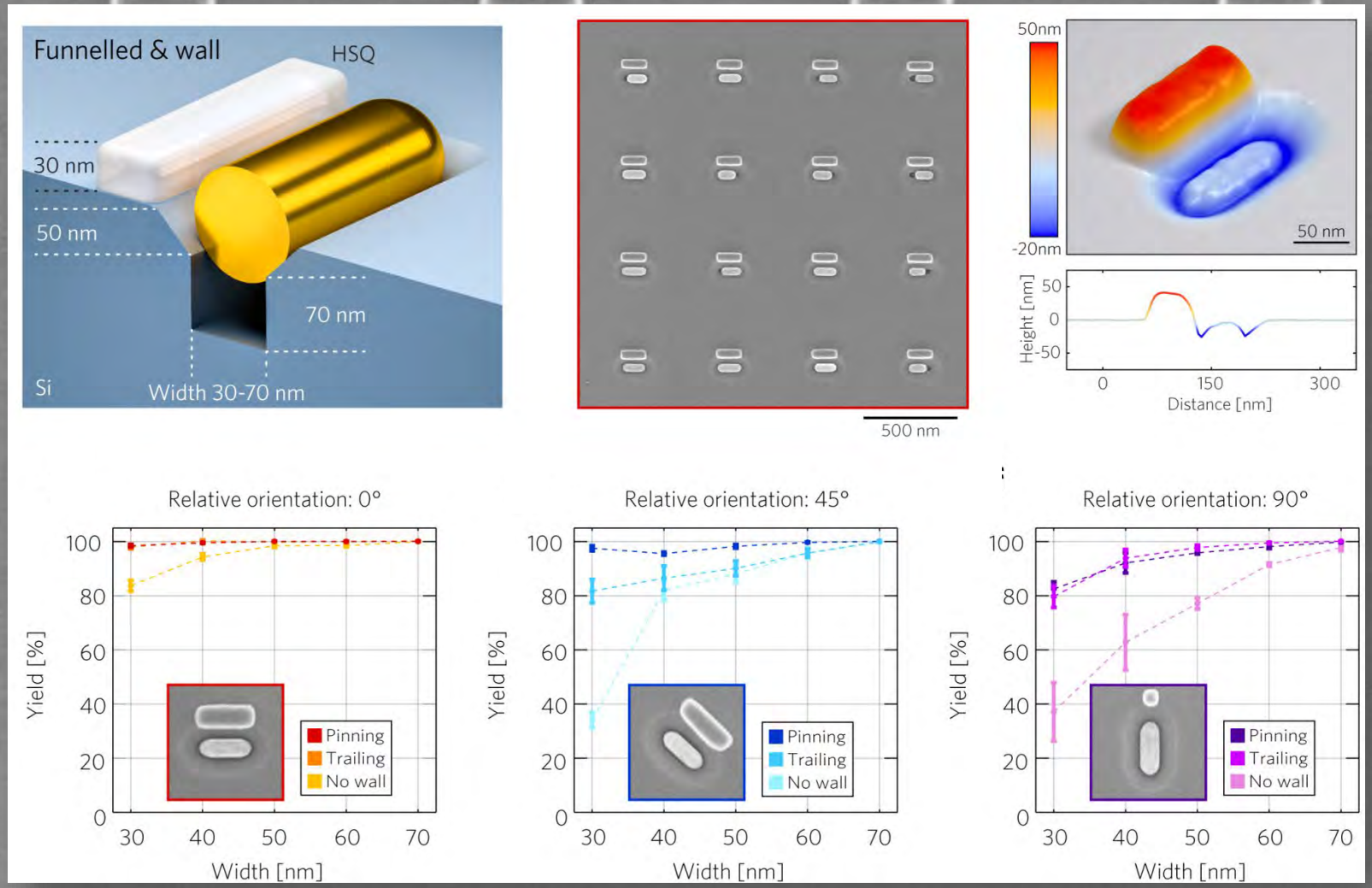


Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

The ideal trap

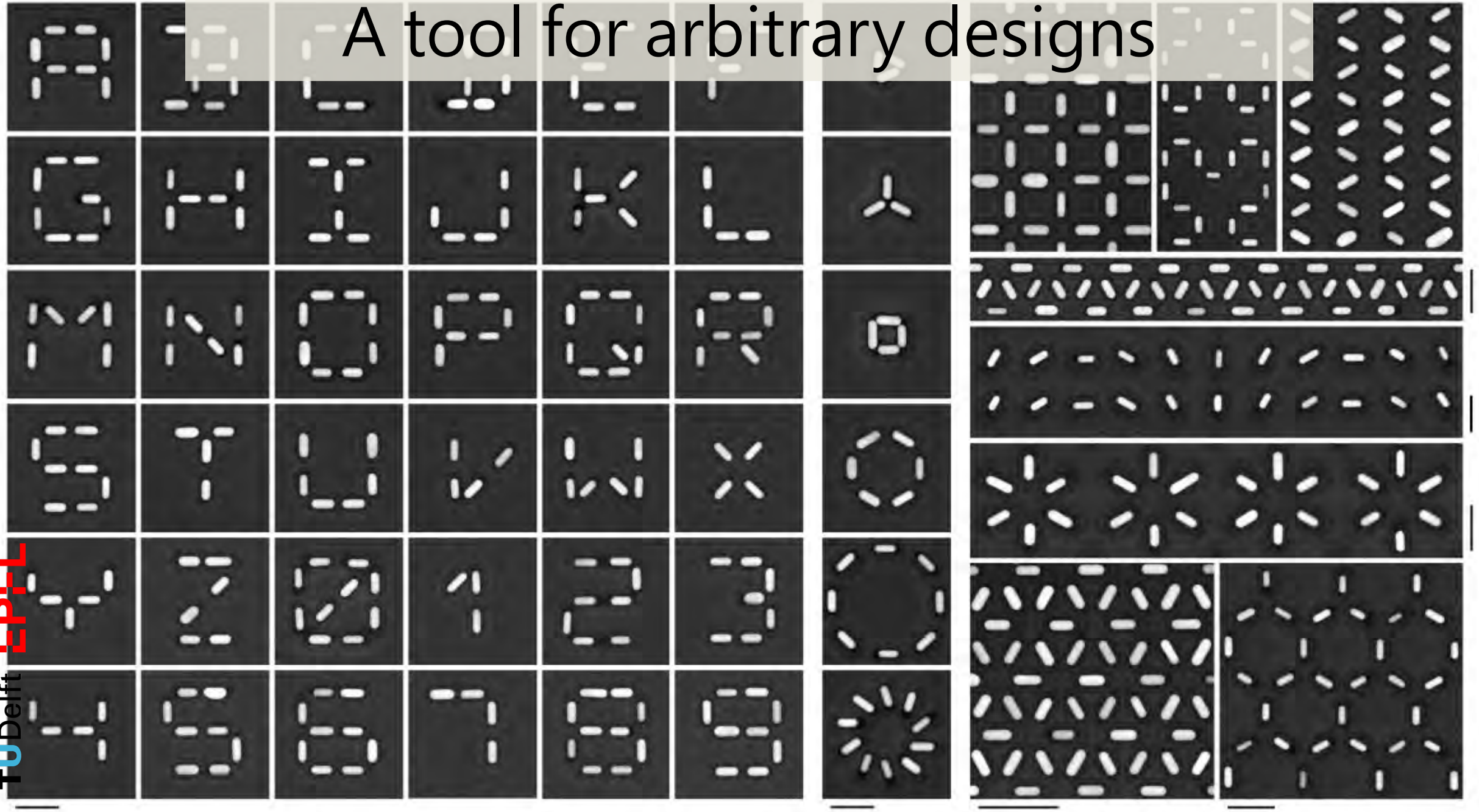
Exploits all three stages of assembly

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



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

A tool for arbitrary designs

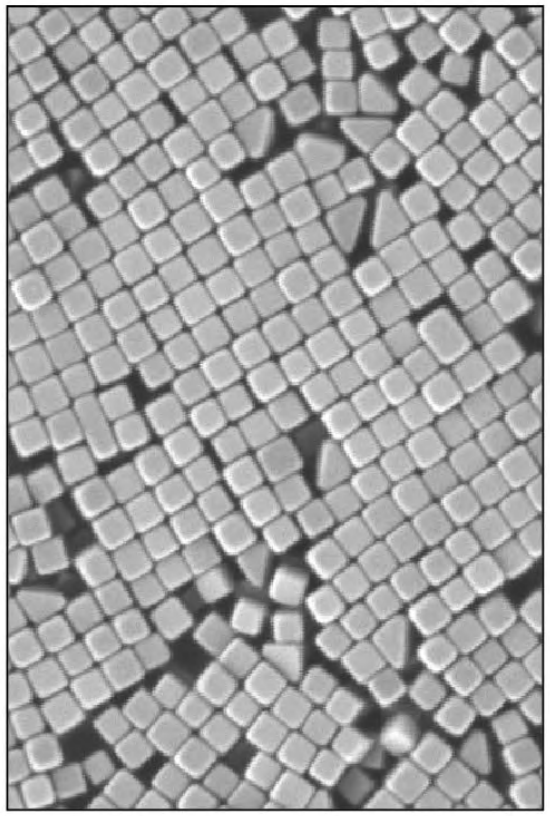


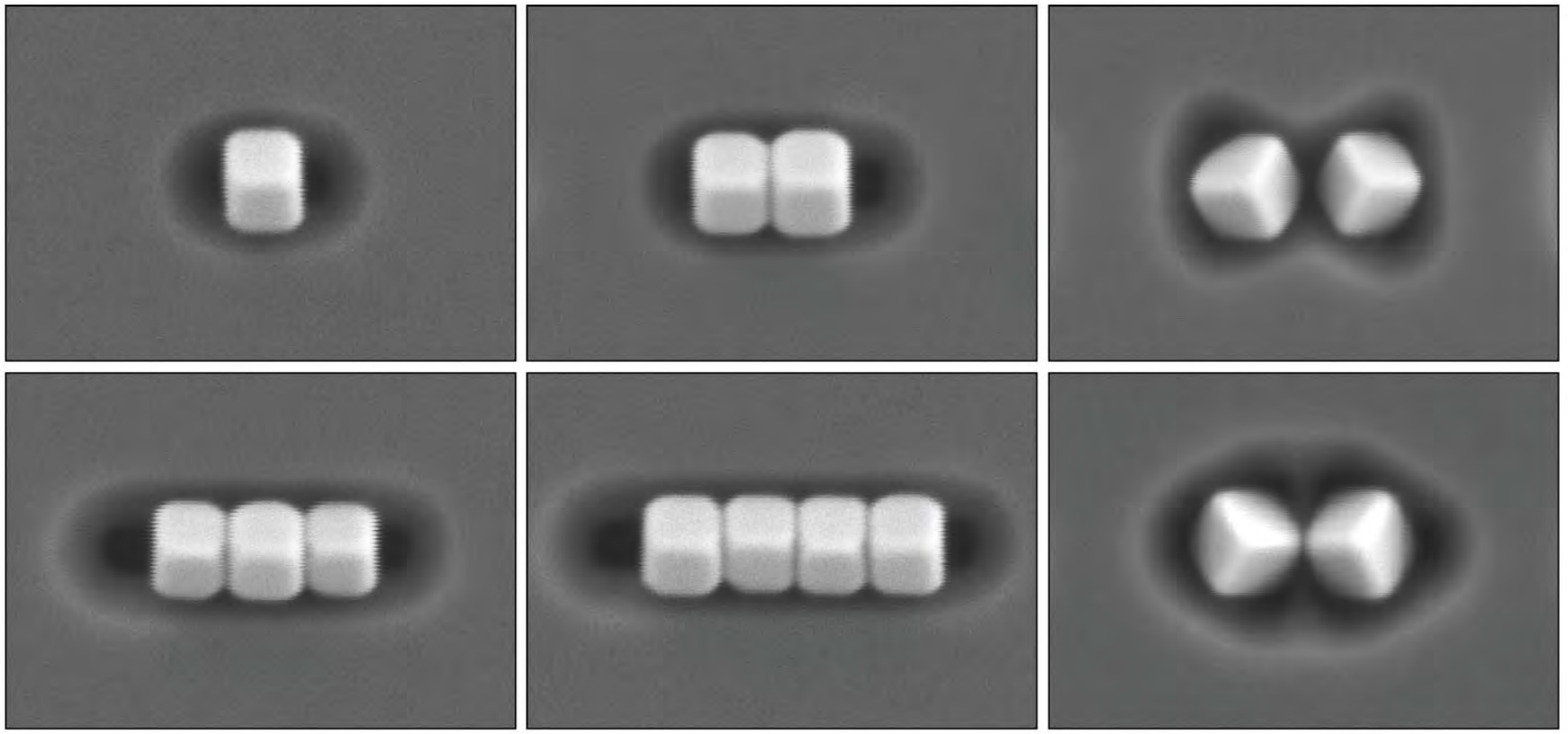
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Scalebars: 250 nm

TU Delft EPFL

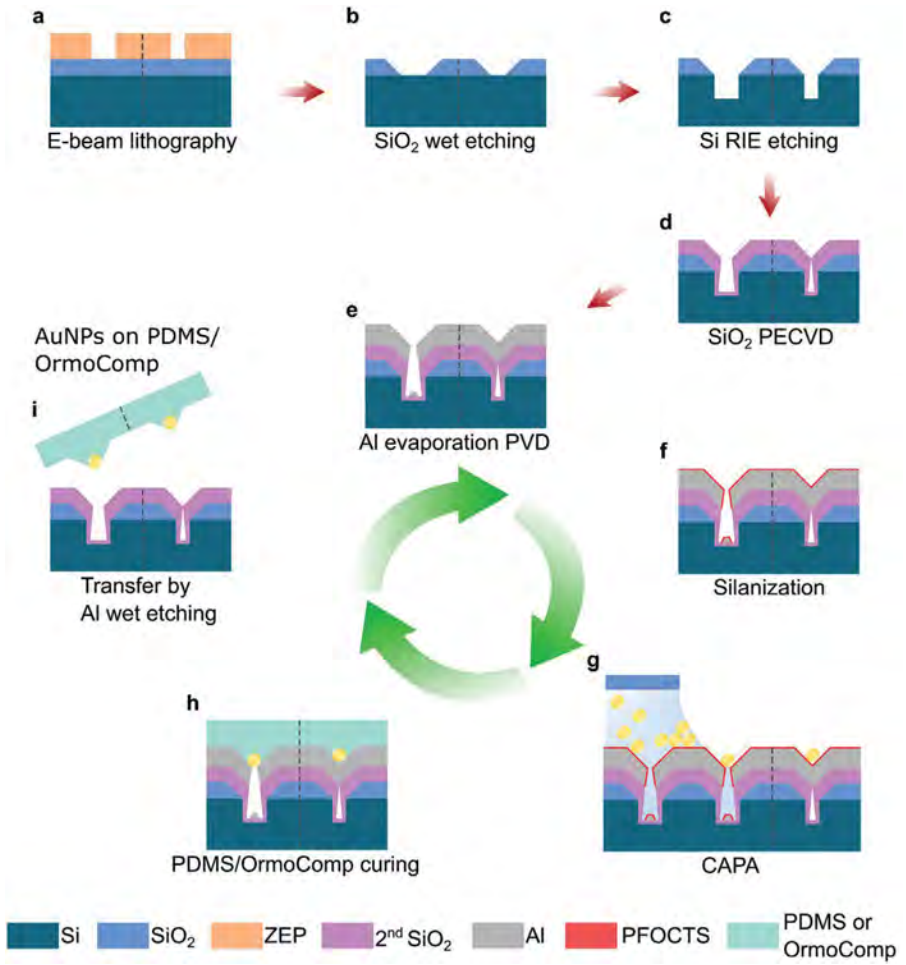
3D orientation of Ag nanocubes

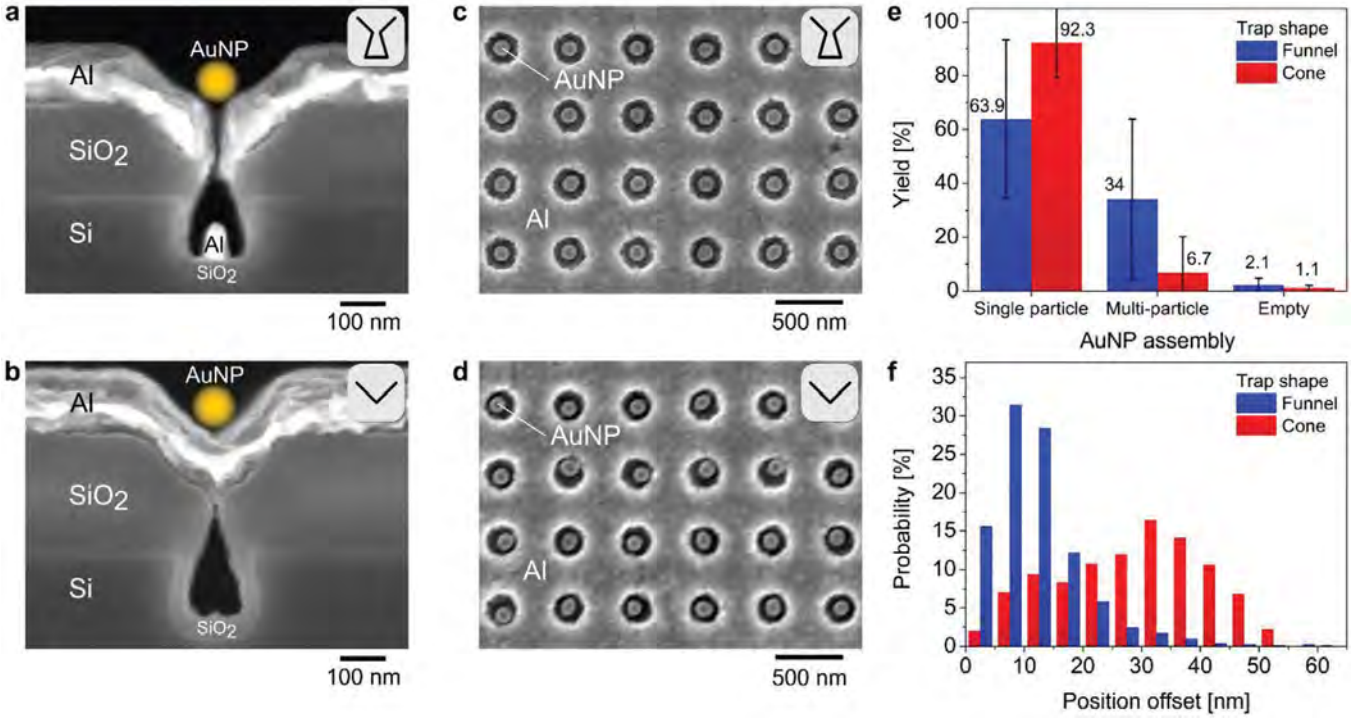




Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Funneled traps in reusable template

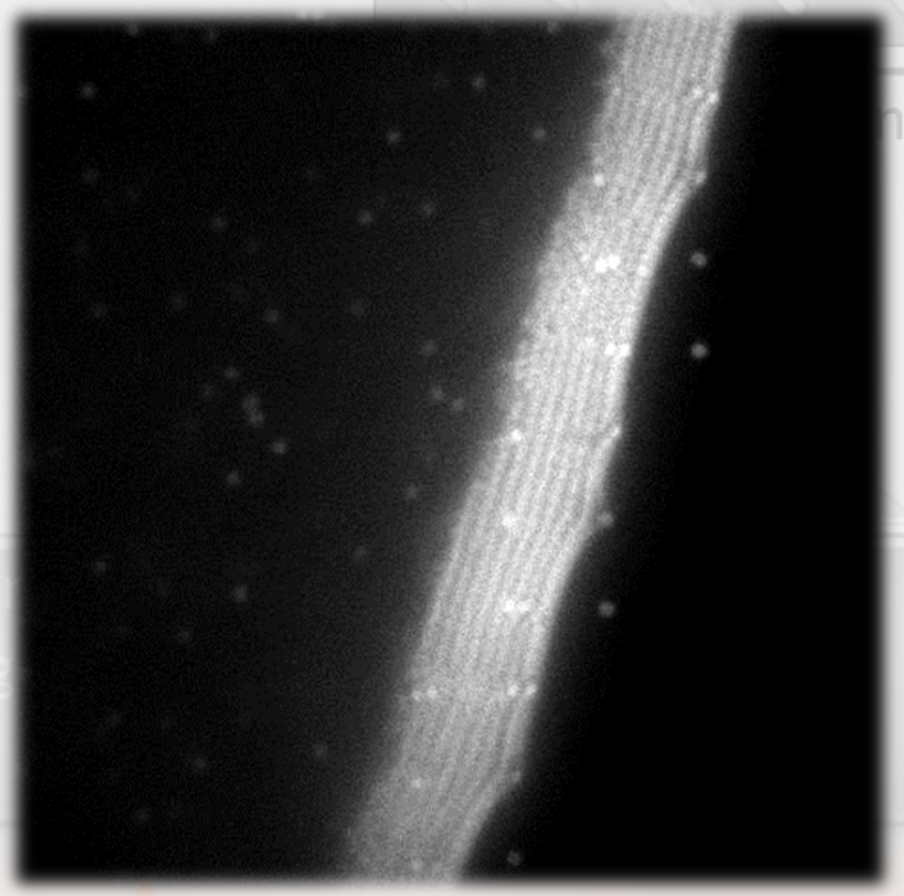




Yu *et al., Part. Part. Syst. Charact.* 39, 2100288 (2022)

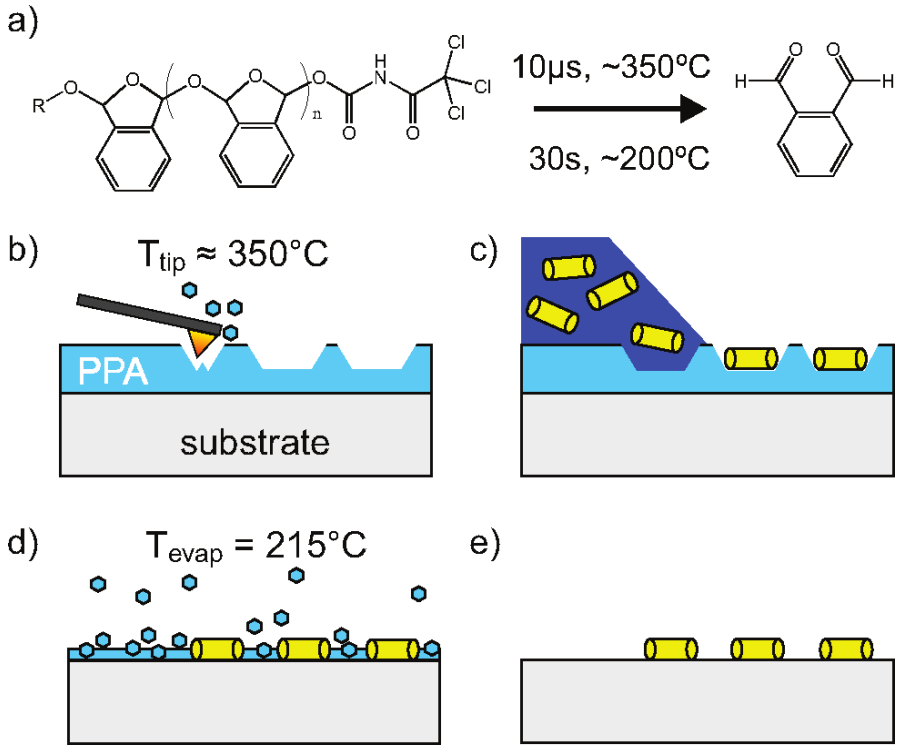
Updated wisdom

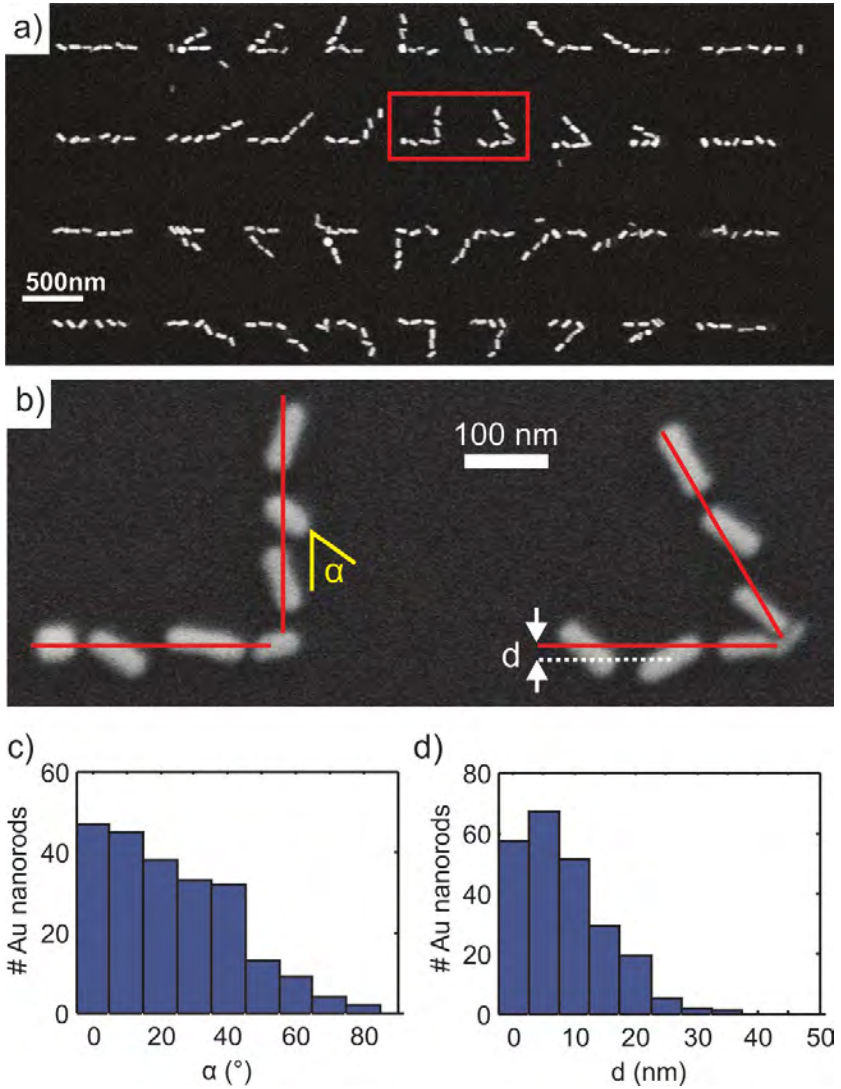
1. Contact line
   - Boundary
   - Drags particles across substrate
   - Last push
2. Accumulation
   - Width facilitates injection
   - Confinement dependent
3. Particle trajectory
   - Advection, immobilization, drag
   - Injection: pressure, entropy
4. Assembly stages
   - All impact assembly yield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



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

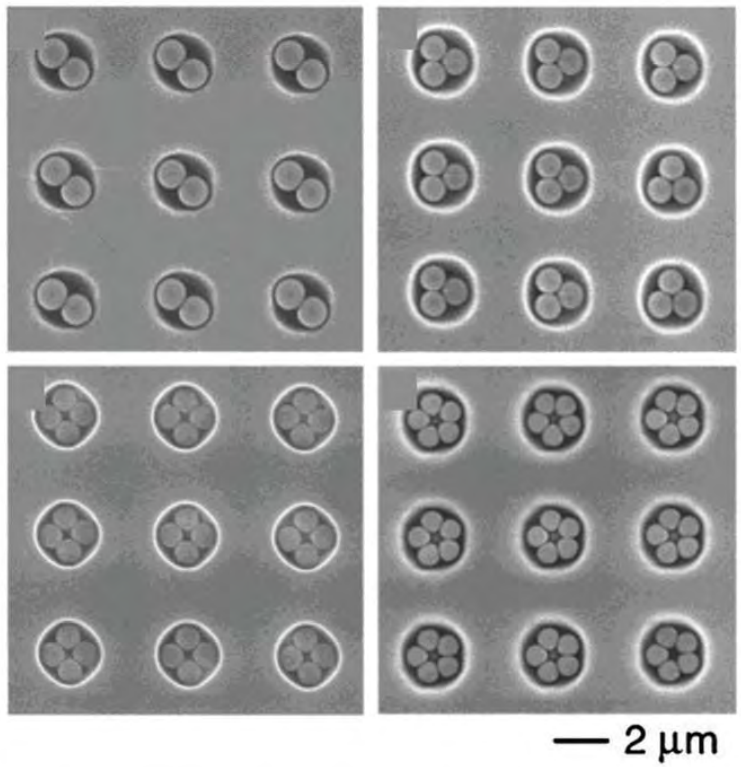
Trap design: t-SPL-based sculpting



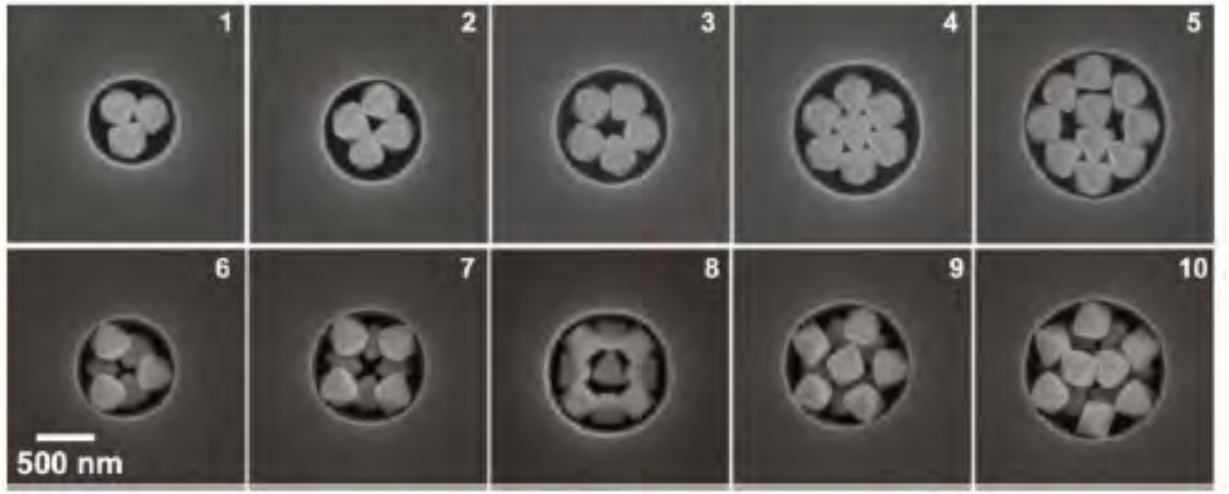


Holzner *et al.*, *Nano Letters* 11, 3957 (2011)

Trap design: Trap-to-particle ratio

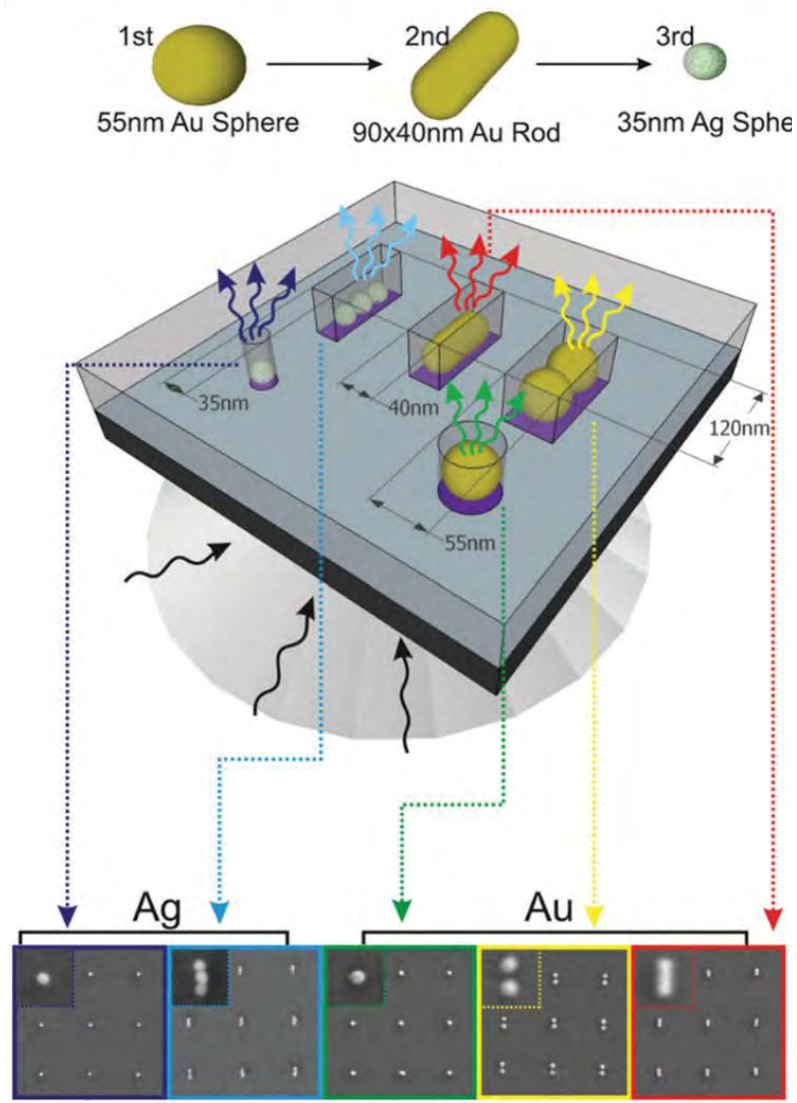


Yin *et al.*, *J. Am. Chem. Soc.* 123, 8718 (2001)

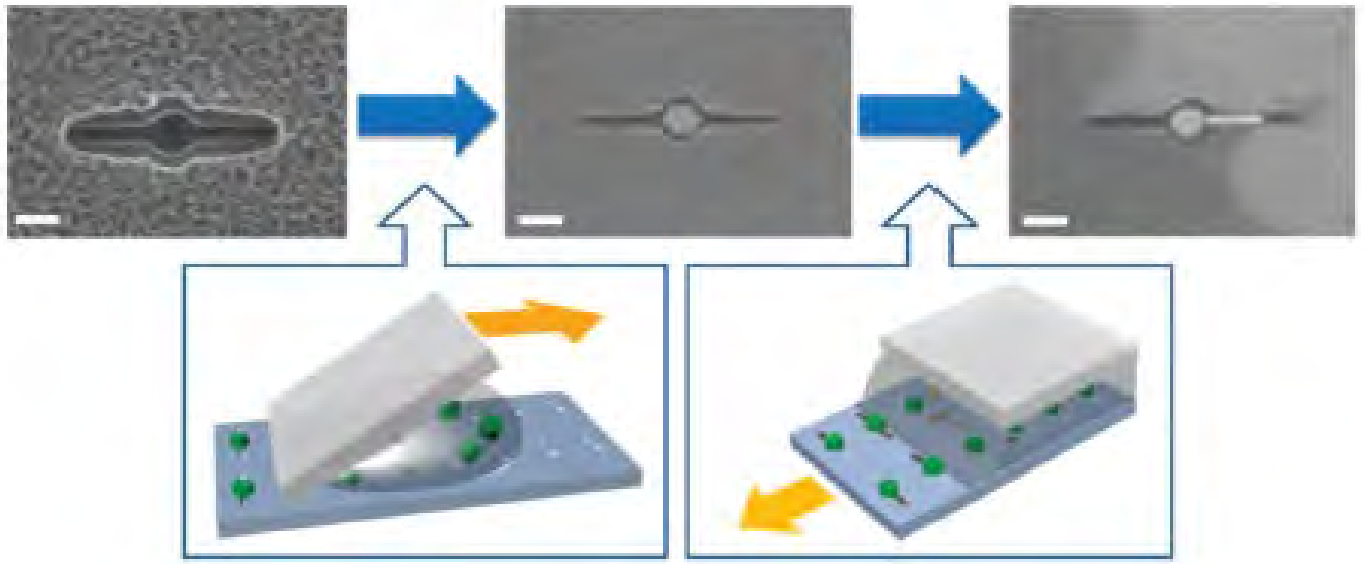


Henzie *et al.*, *Proc. Natl. Acad. Sci* 110, 6640 (2013)

Trap design: Shape matching

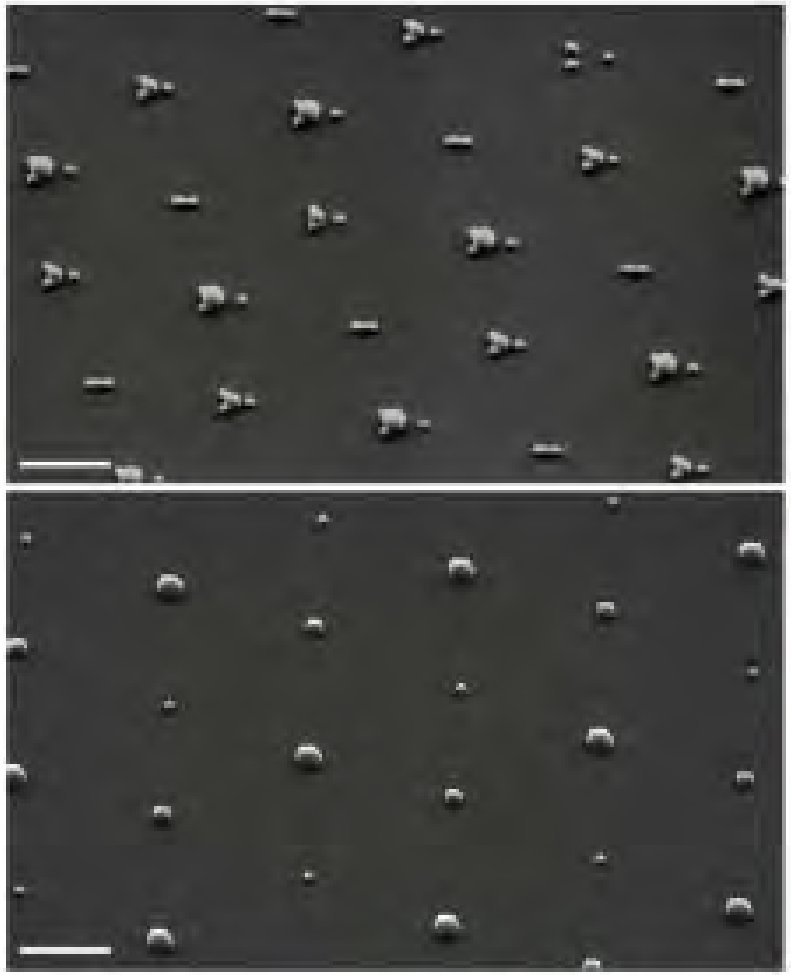


Chen & Reinhard, *Adv. Mater.* 28, 3522 (2016)

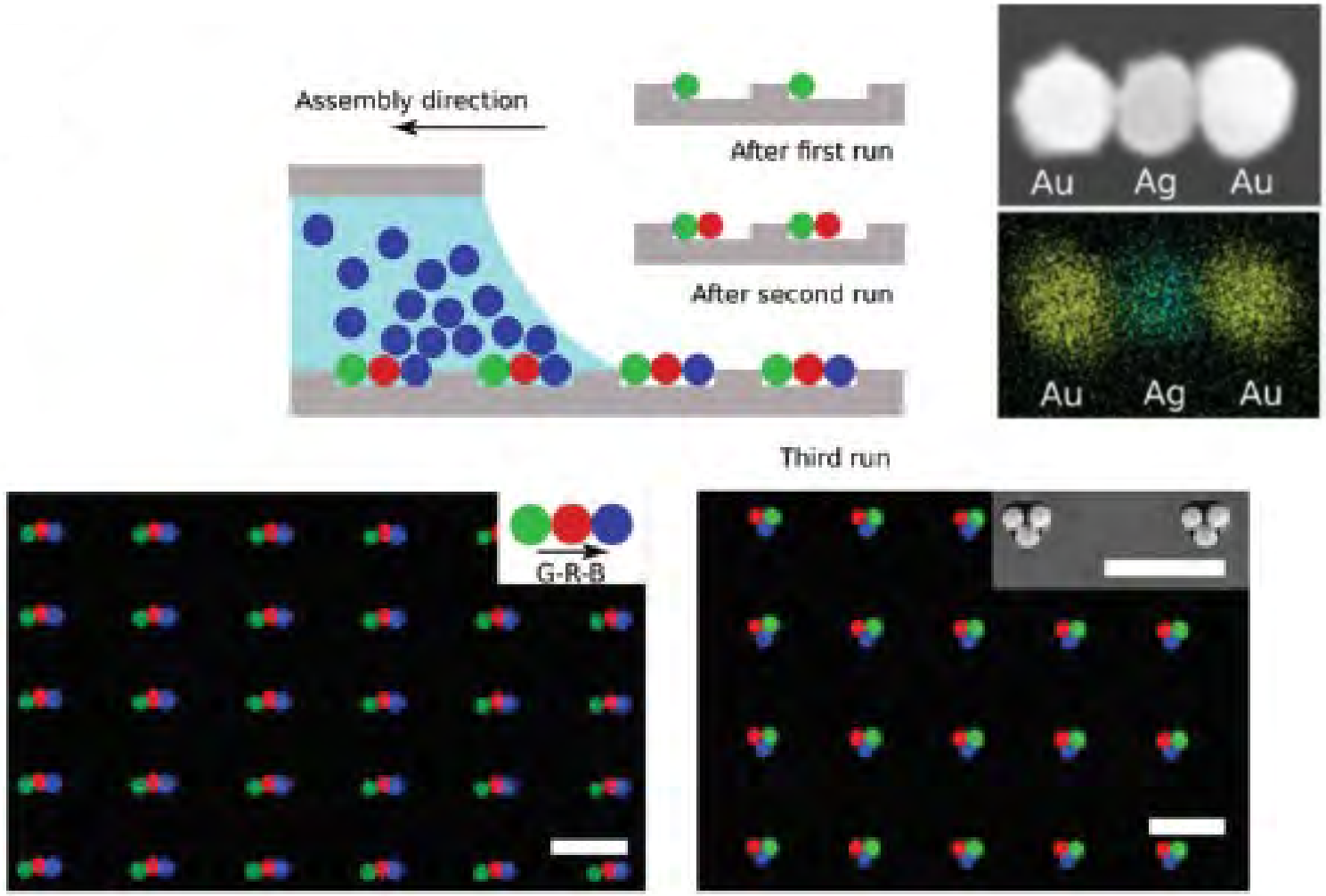


Greybush *et al.*, *ACS Nano* 9, 9482 (2014)

Trap design: Shape matching

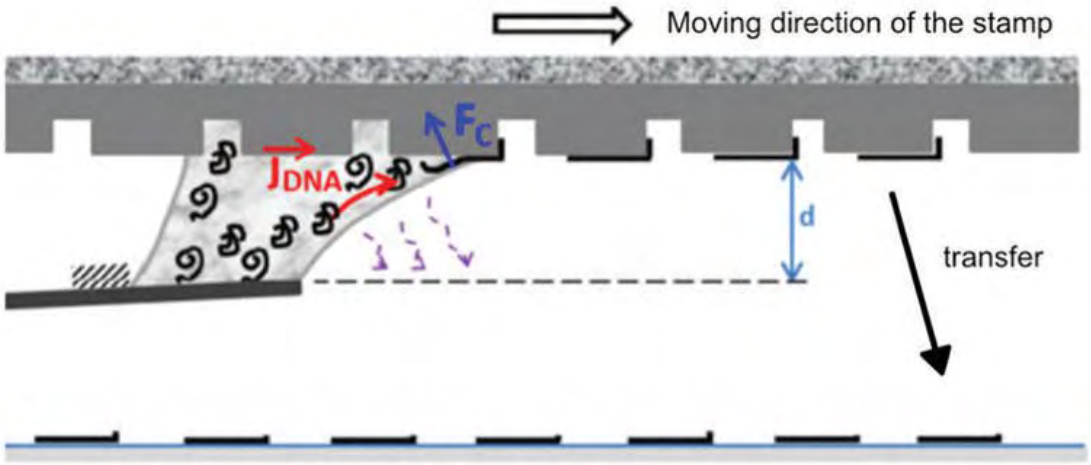


Kuemin *et al., Adv. Mater.* 22, 2804 (2010)

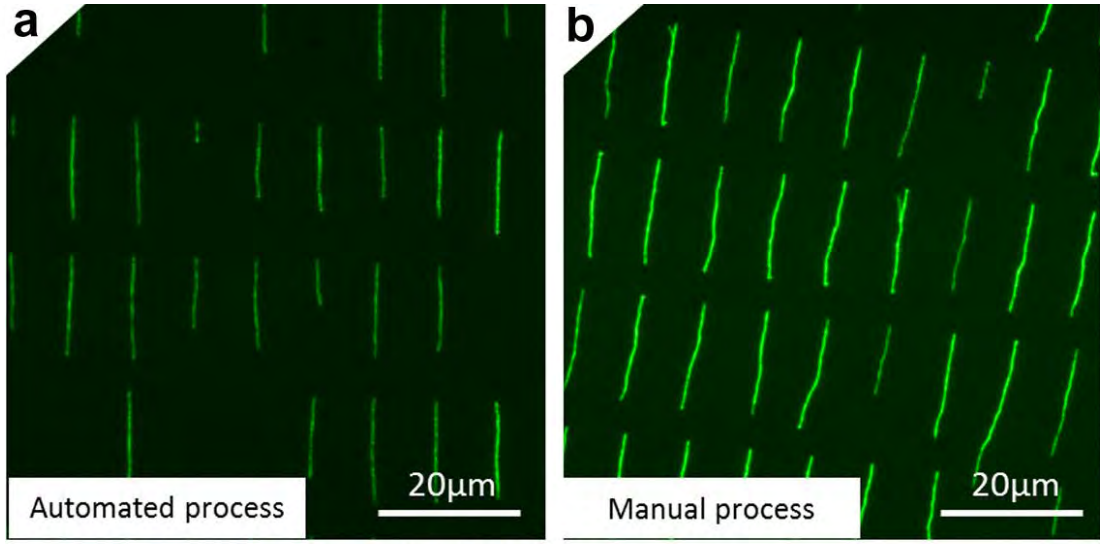


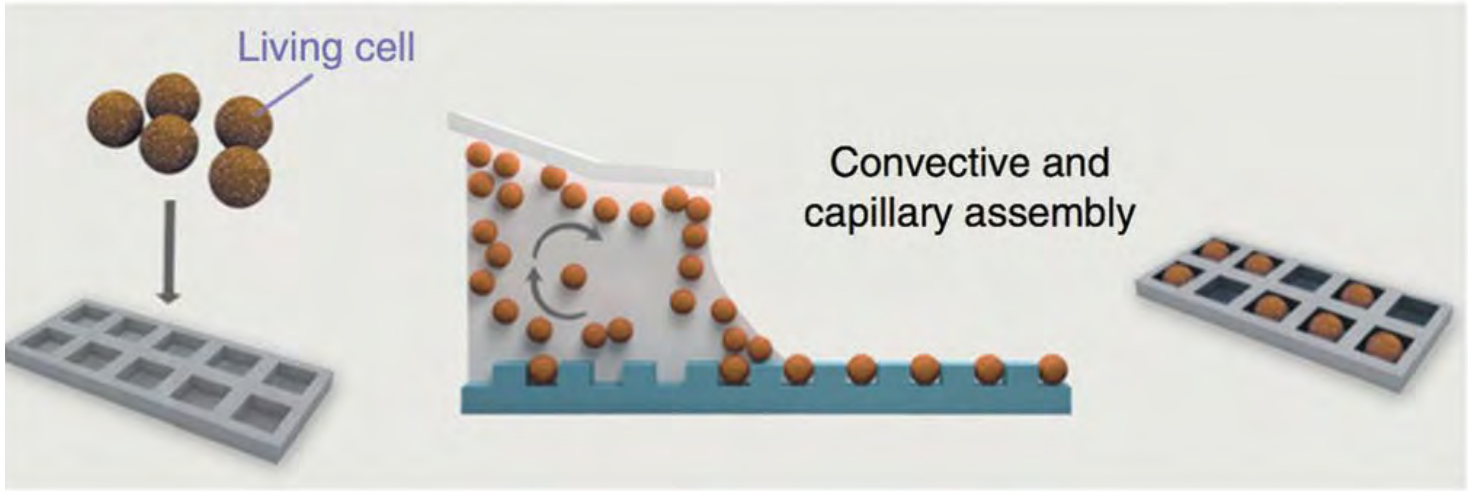
Ni *et al.*, *Soft Matter* 2018

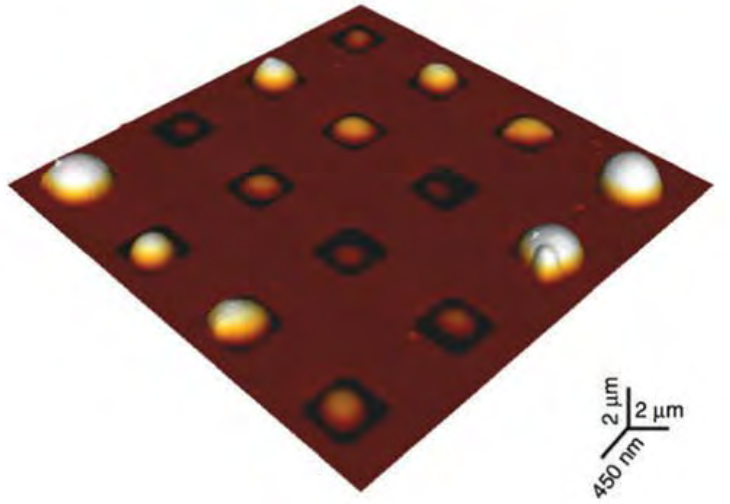
Biomolecules & cells



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

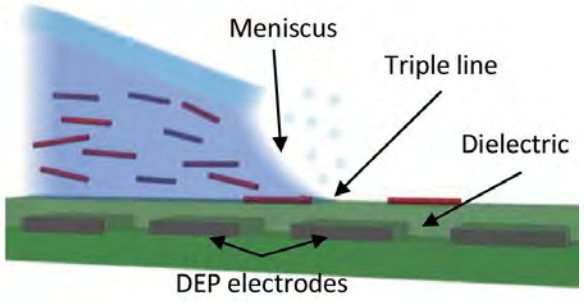


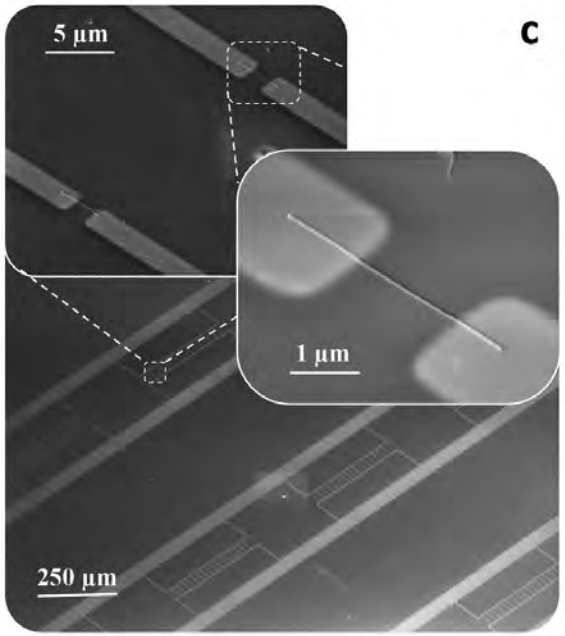


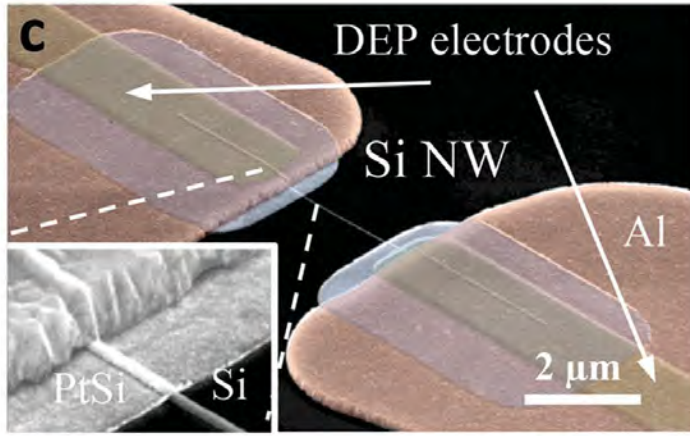


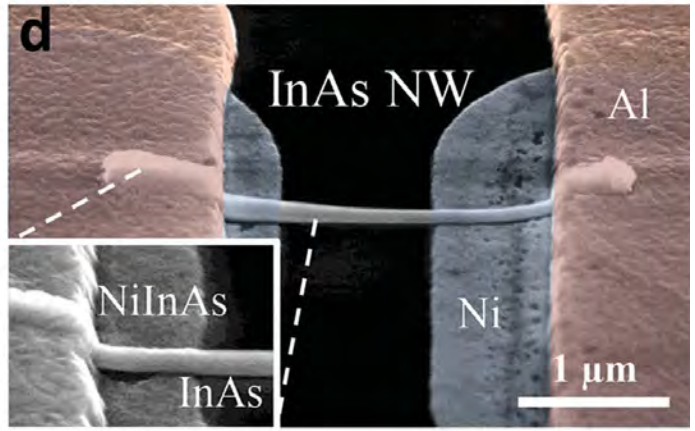
Formosa *et al.*, *Nat. Protoc.* 10, 199 (2015)

Non-topographical traps

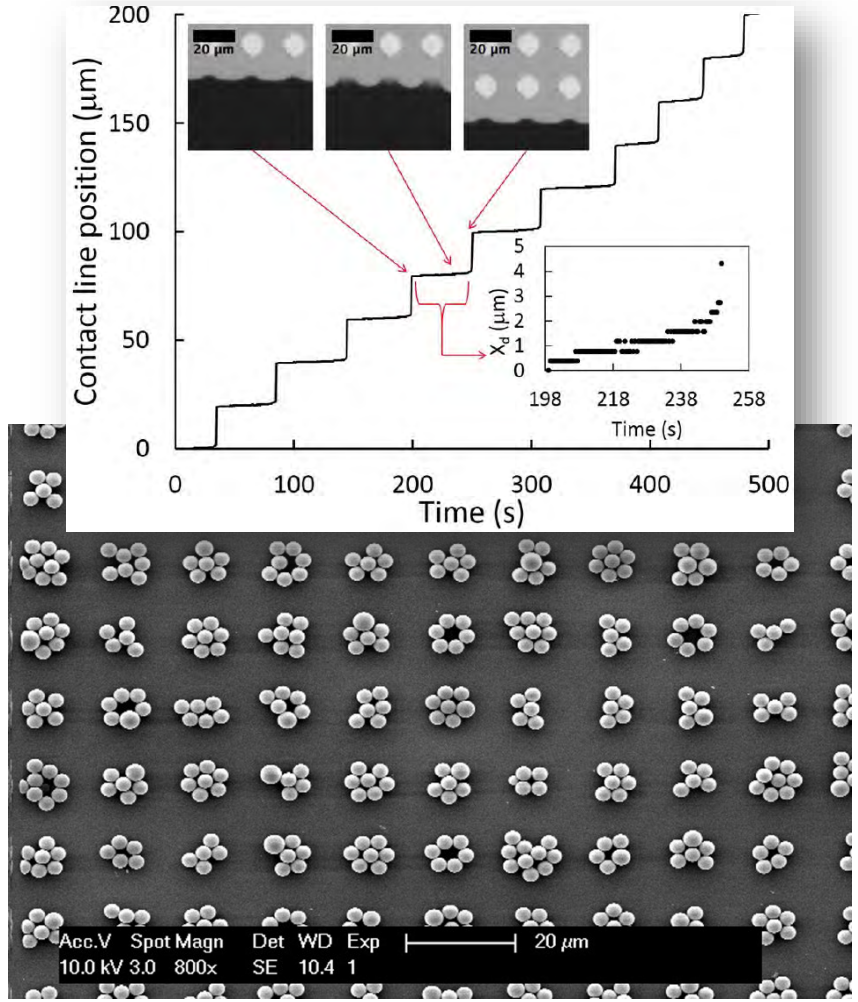






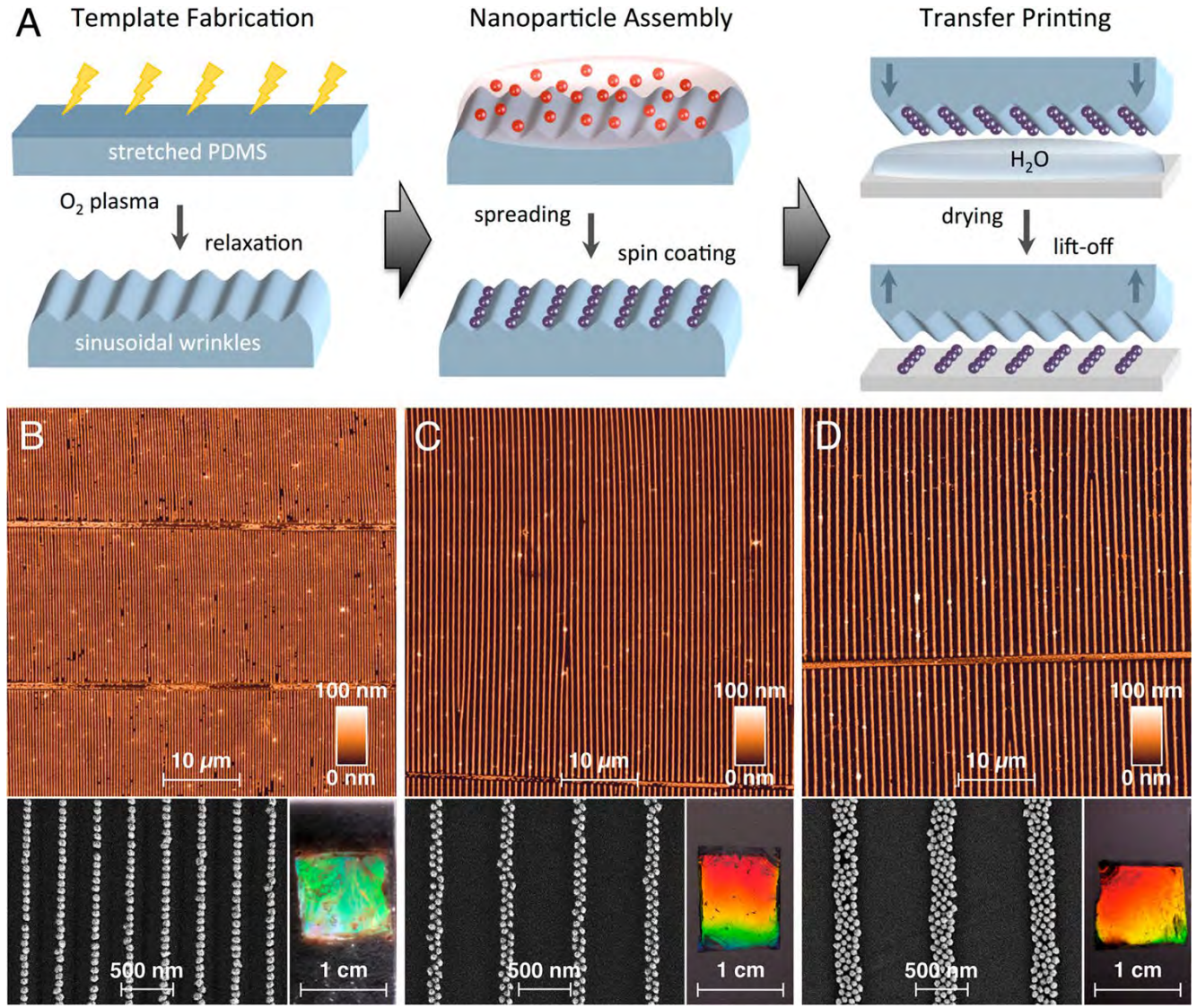


Collet *et al.*, *Adv. Mater.* 27, 1268 (2015)



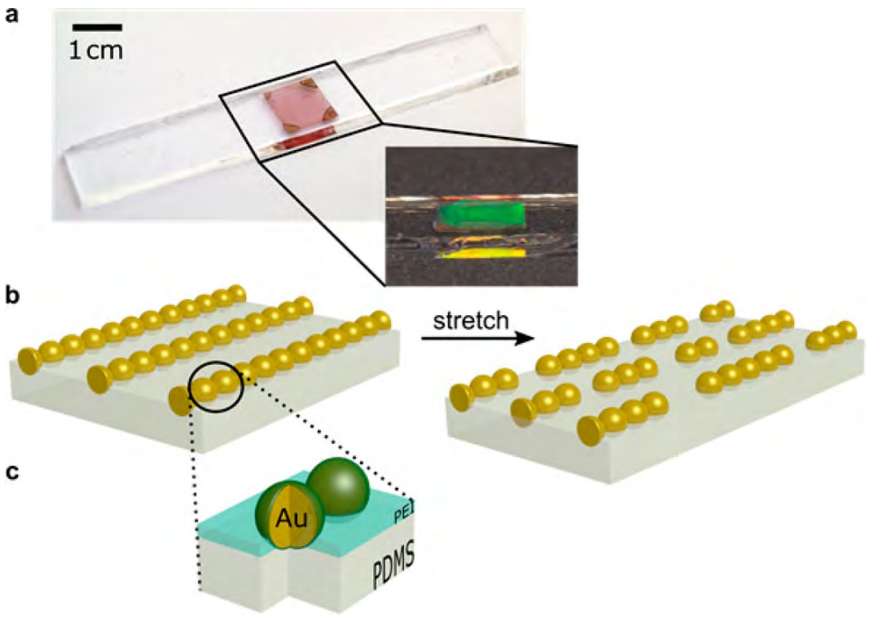
Wirth *et al.*, *Langmuir* 31, 1632 (2015)

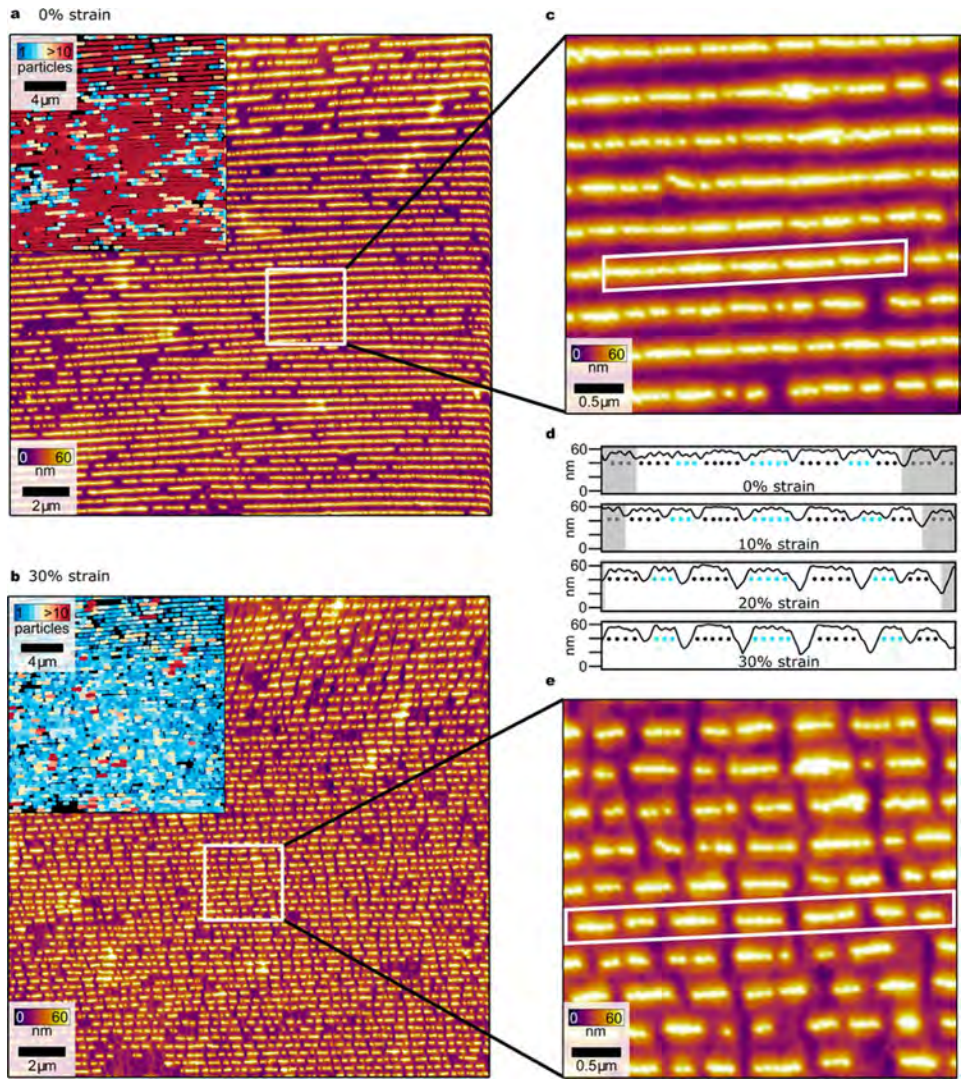
Non-lithographical traps



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

Non-lithographical traps





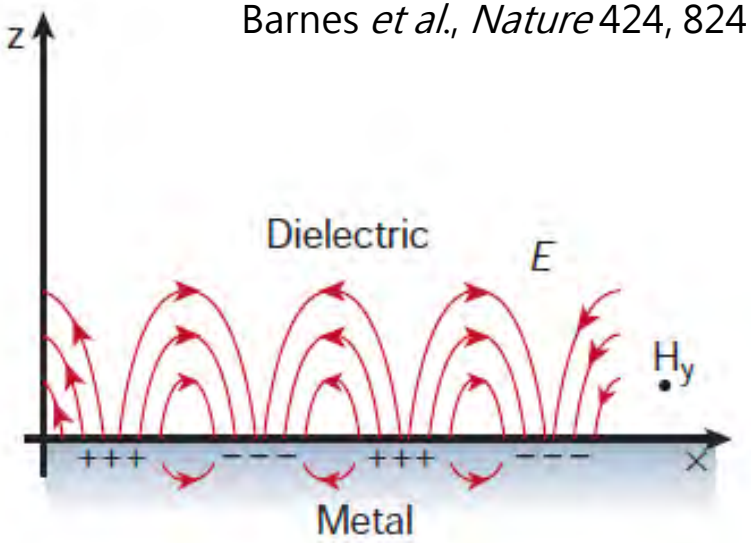
Steiner *et al.*, *ACS Nano* 11, 8871 (2017)

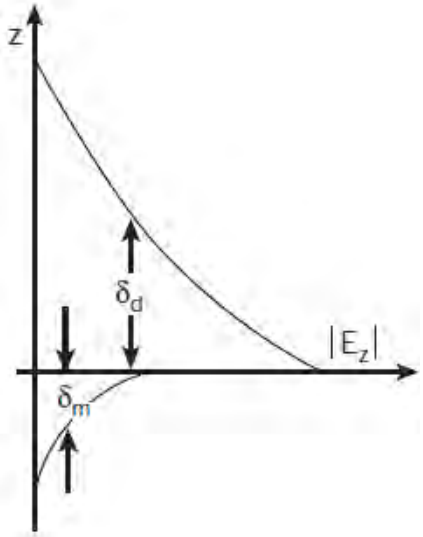
Surface plasmon polaritons

- Combined EM wave & surface charge
- Bound at metal/dielectric interface
- Perpendicular field component
  - enhanced at the surface
  - exponentially decaying

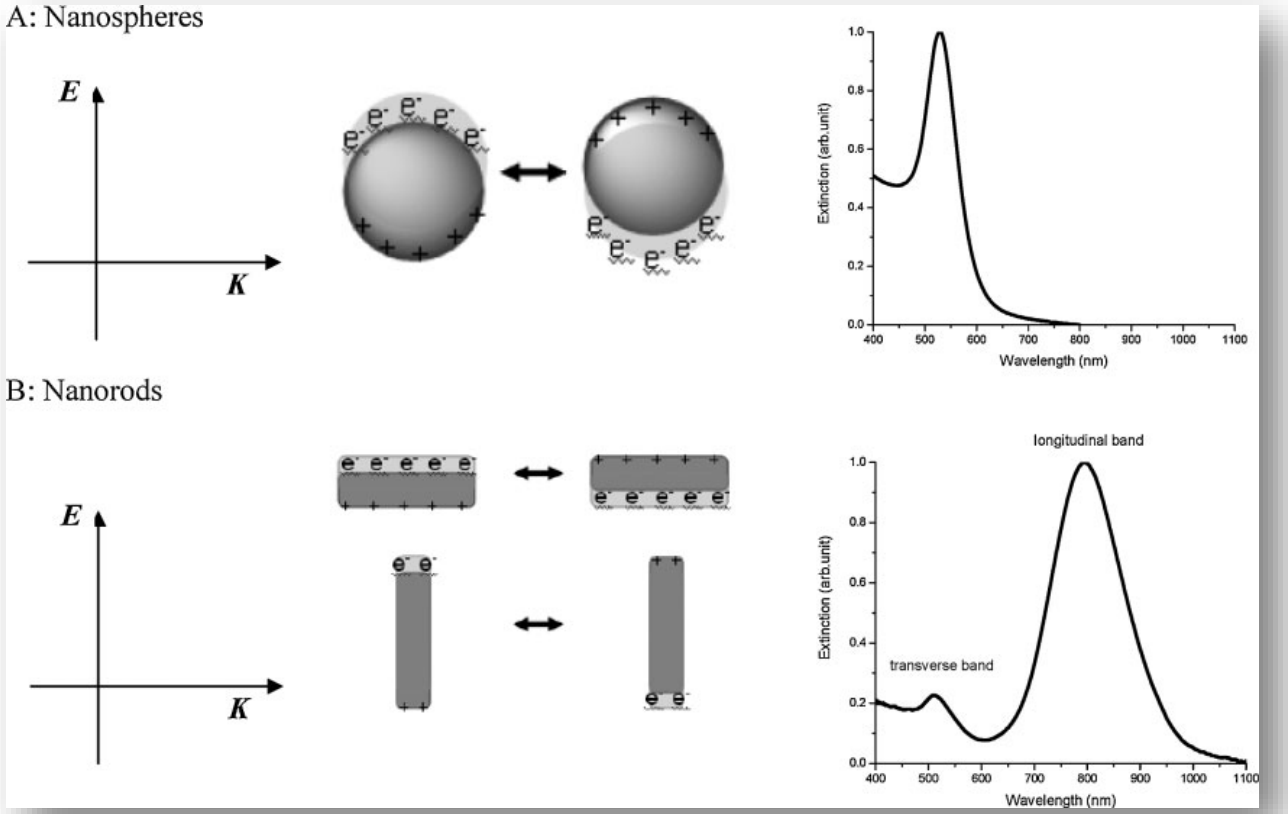
- Confinement of EM energy in sub-wavelength volumes

Barnes *et al.*, *Nature* 424, 824 (2003)

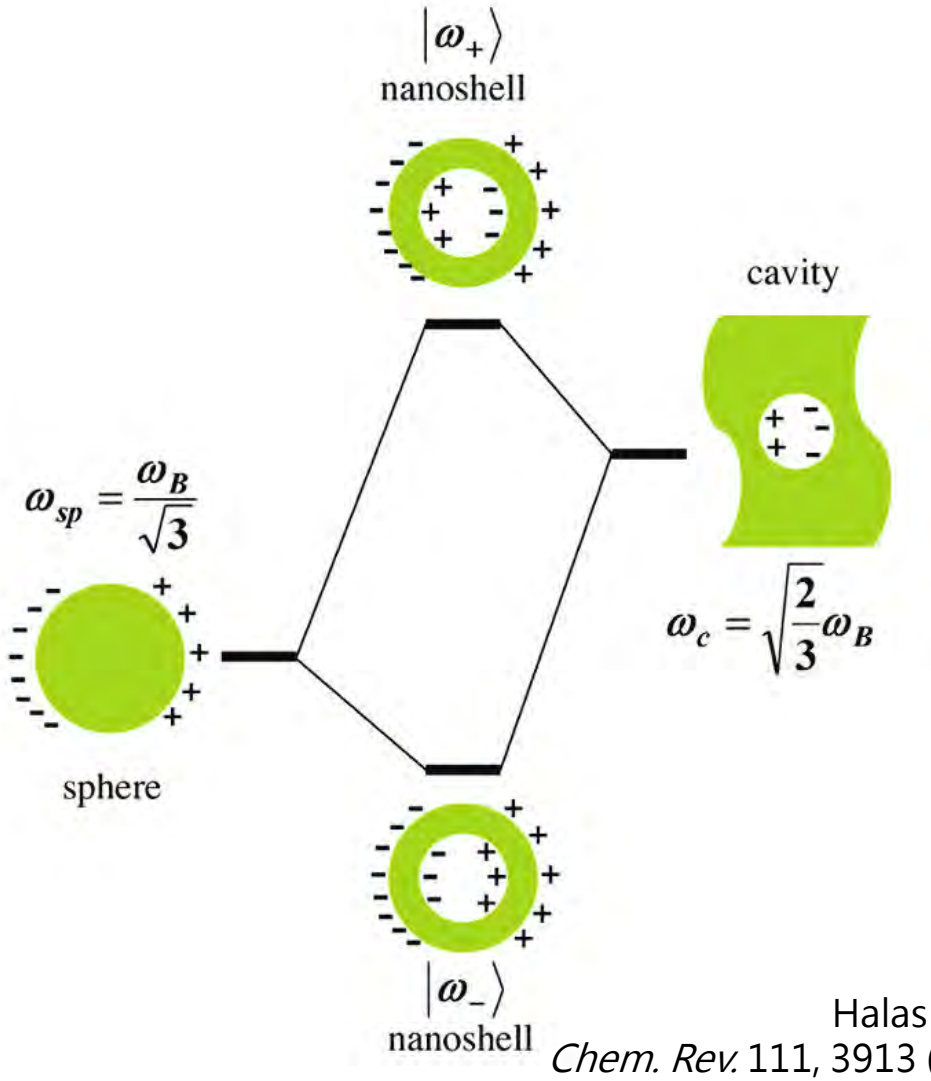




Localized surface plasmon resonances in NPs

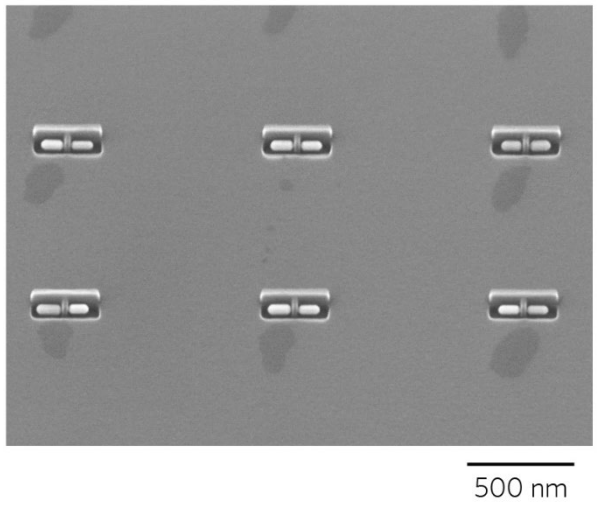


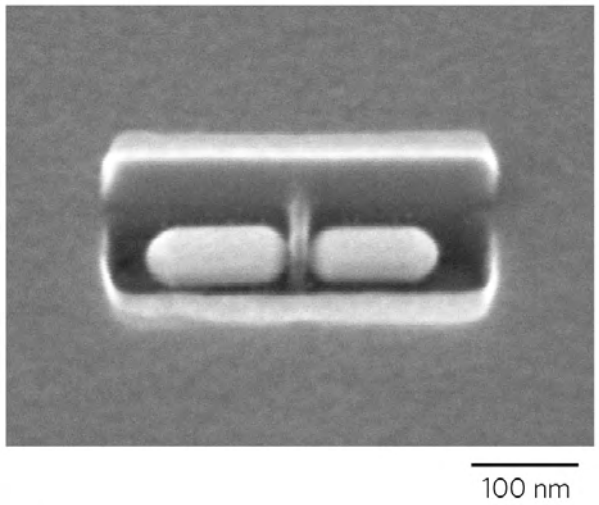
Huang *et al.*, *Adv. Mater.* 21, 4880 (2009)

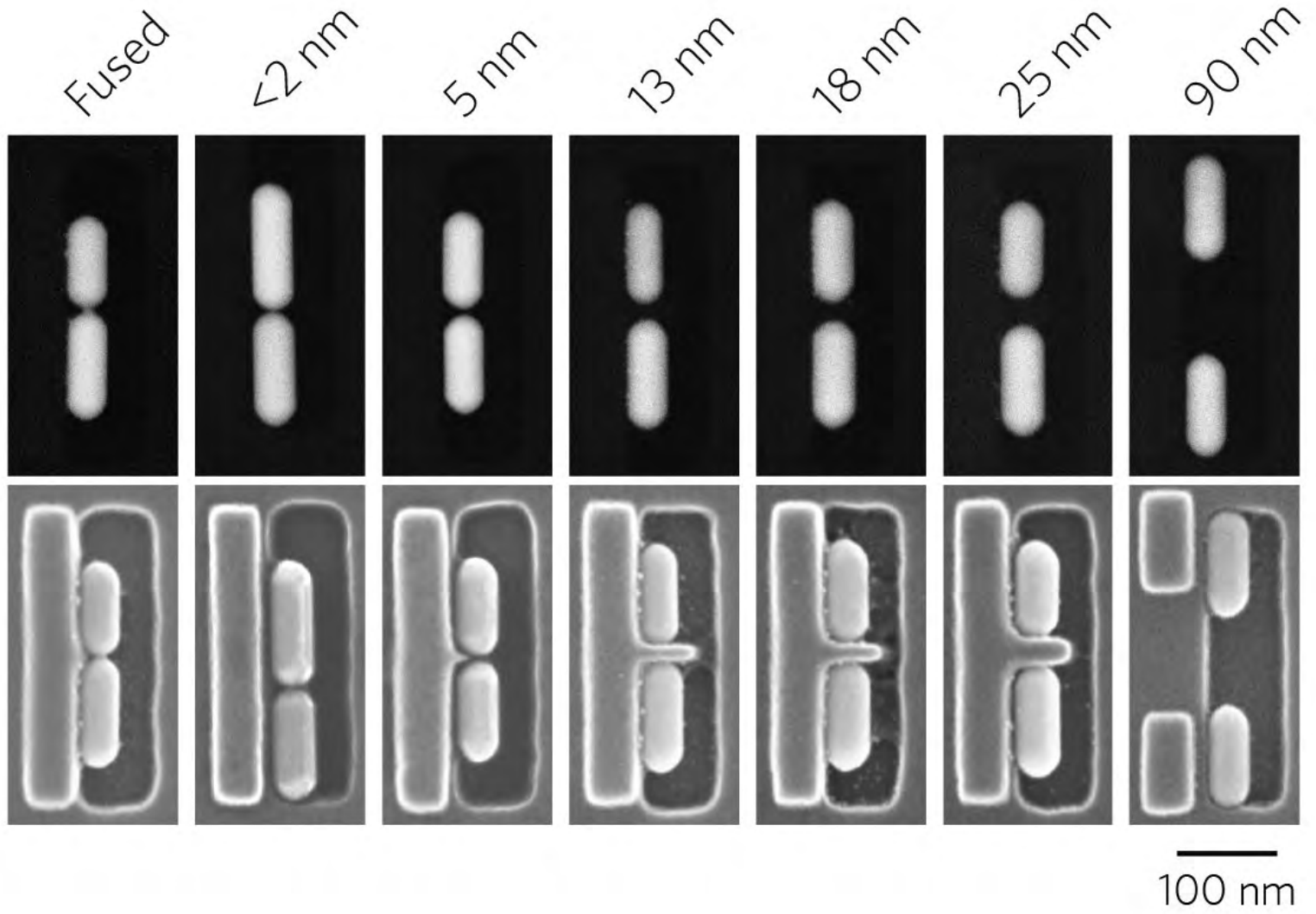


Halas *et al.*, *Chem. Rev.* 111, 3913 (2011)

Nanogap tuning in nanorod dimers

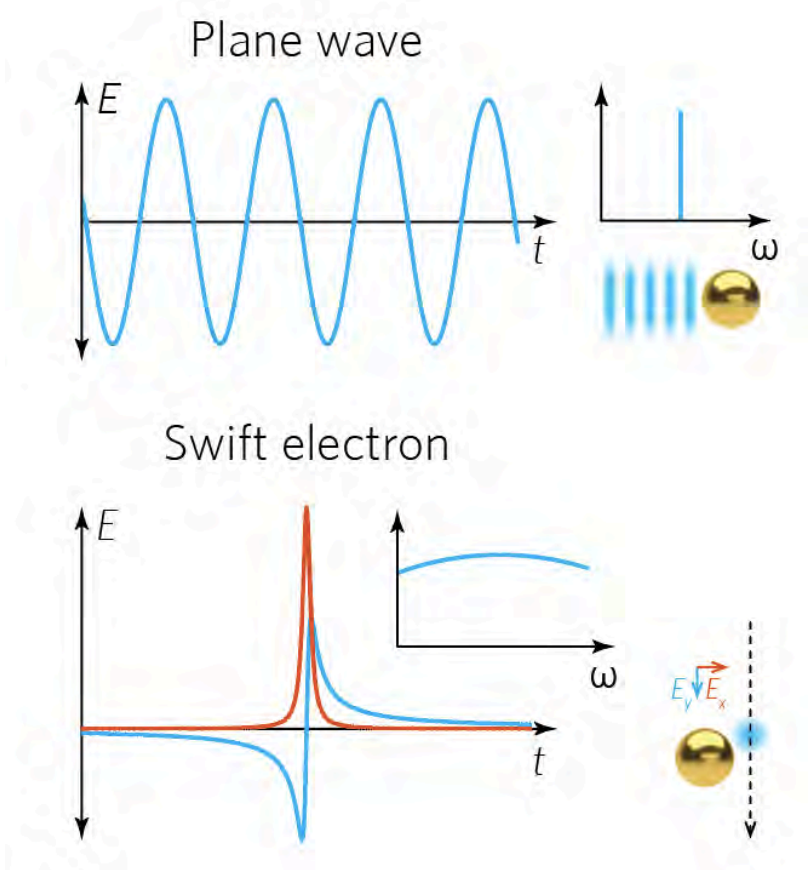


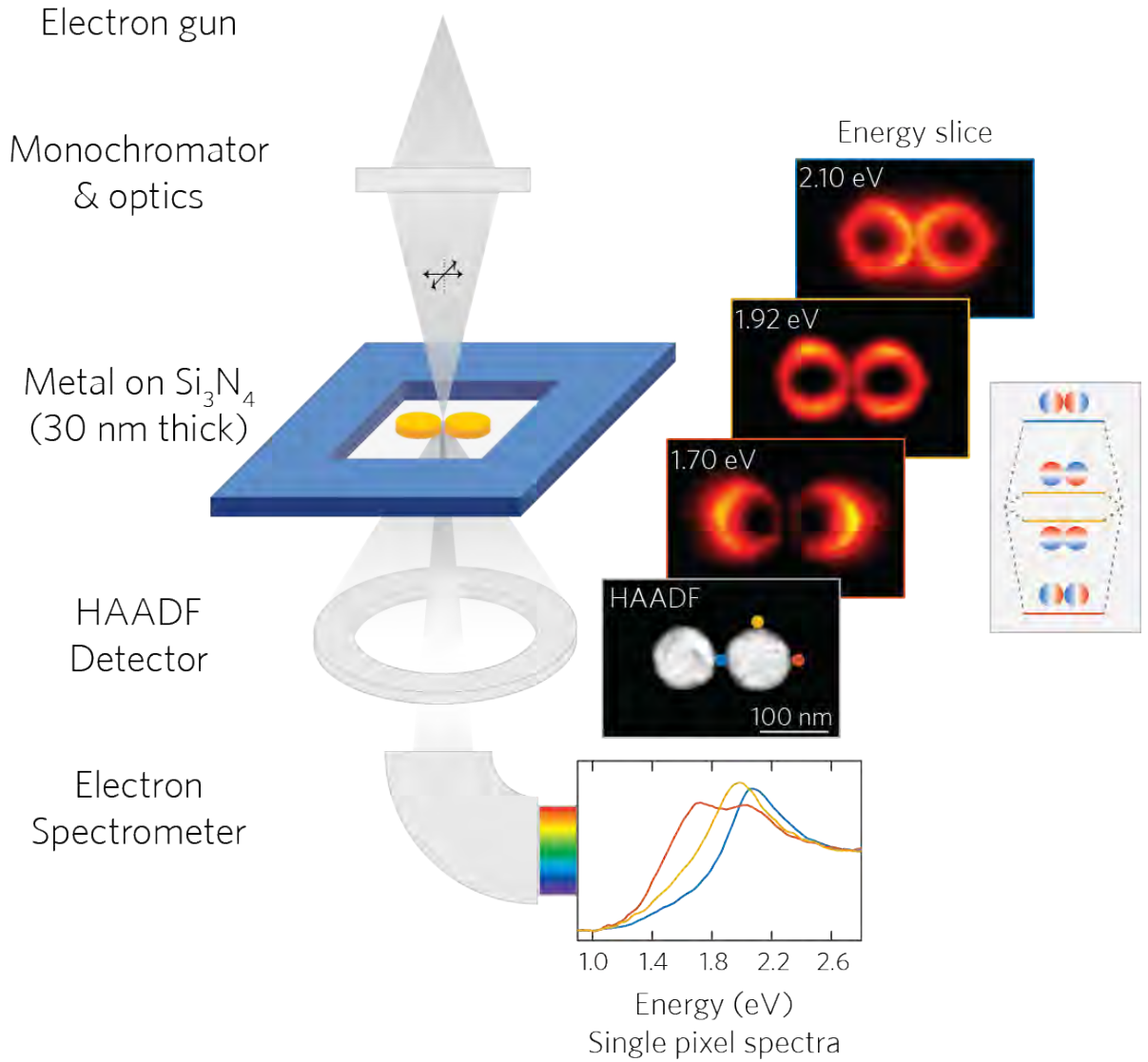




Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

Electron energy-loss spectroscopy: plasmon maps





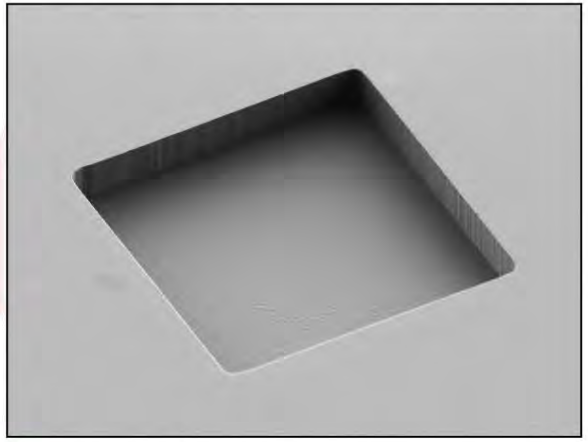
Courtesy of V. Flauraud

Fabrication of TEM compatible substrates

4" wafer: 256 Si_3N_4 TEM samples, 30 nm-thick

Windows: 500x100 µm

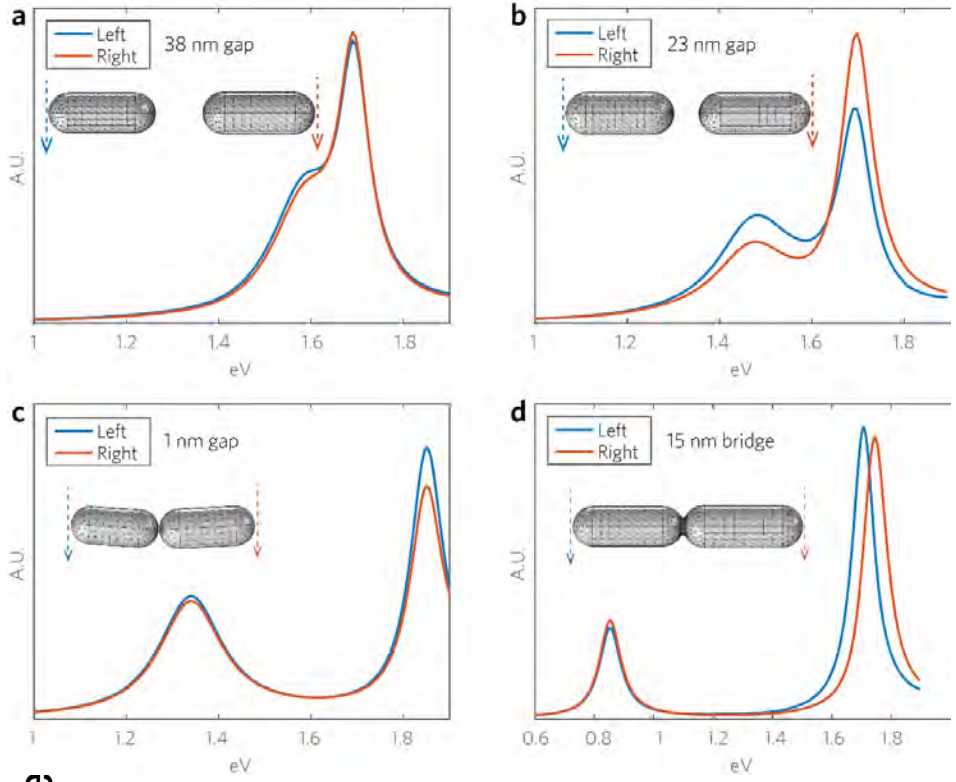
Ebeam alignment markers

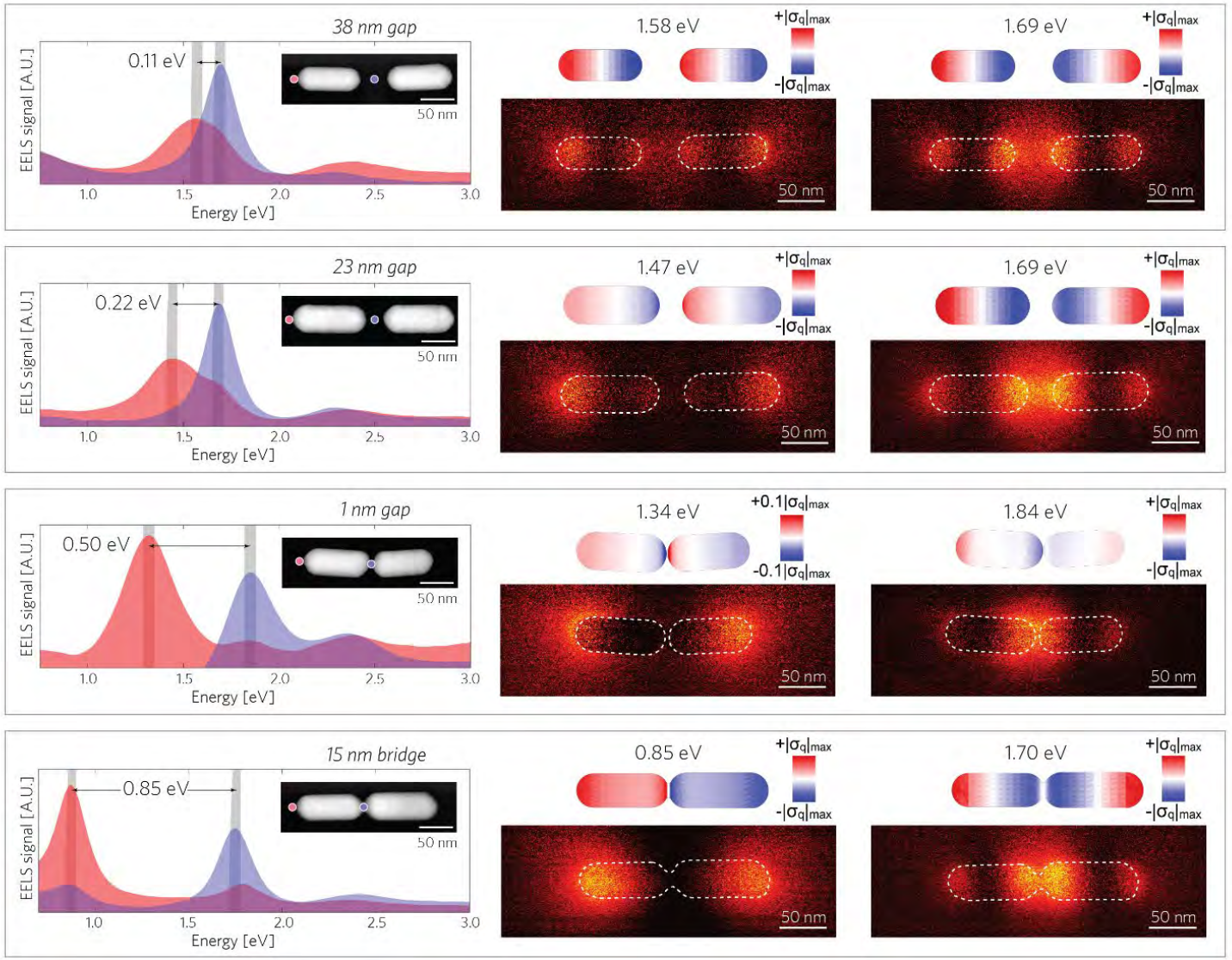


Courtesy of V. Flauraud

From weak to strong plasmonic coupling

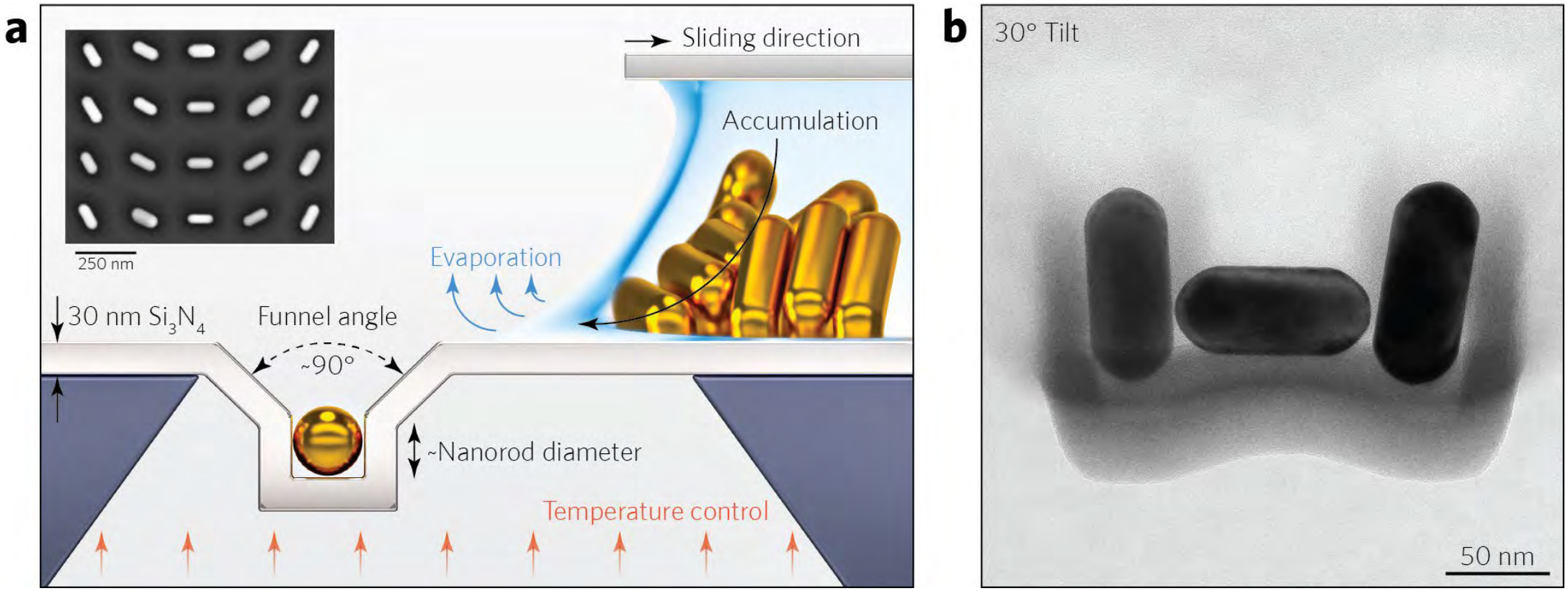
FEM simulations





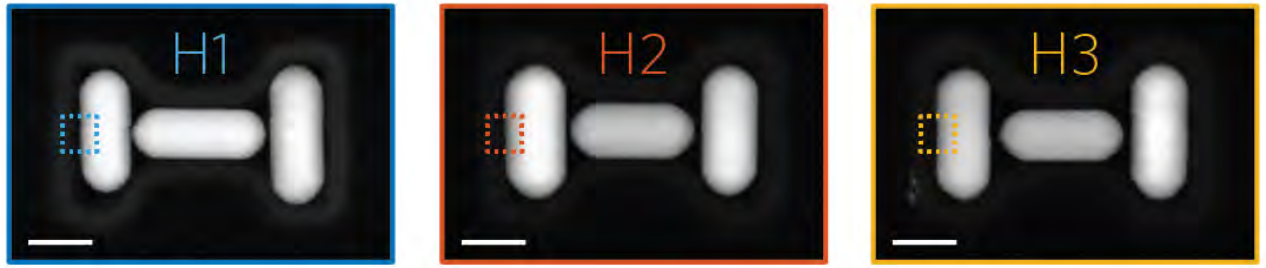
Flauraud *et al., Nat. Nanotechnol.* 12, 73 (2017)

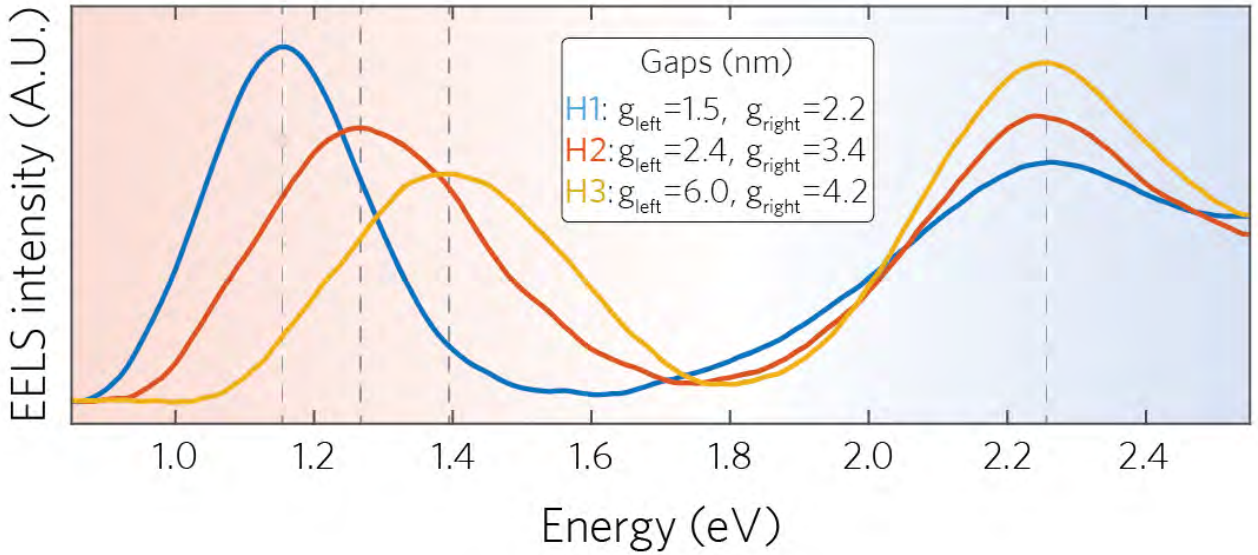
Plasmonic dolmens

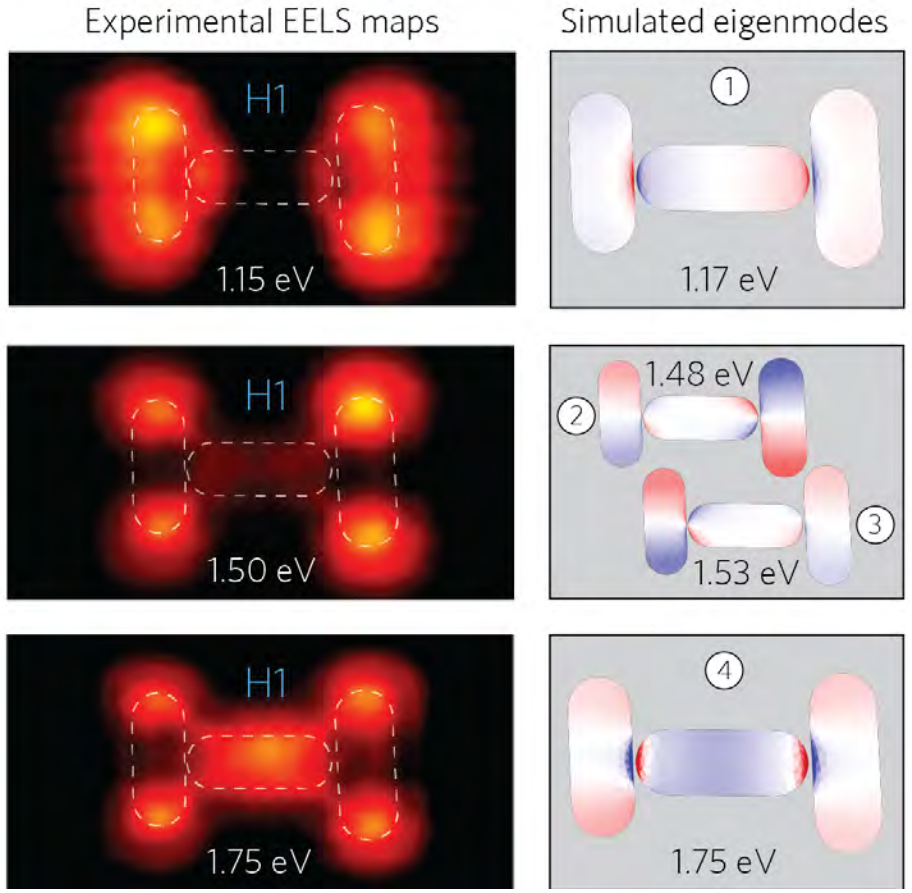


Flauraud *et al.*, *ACS Photon. 4*, 1661 (2017)

Plasmonic dolmens

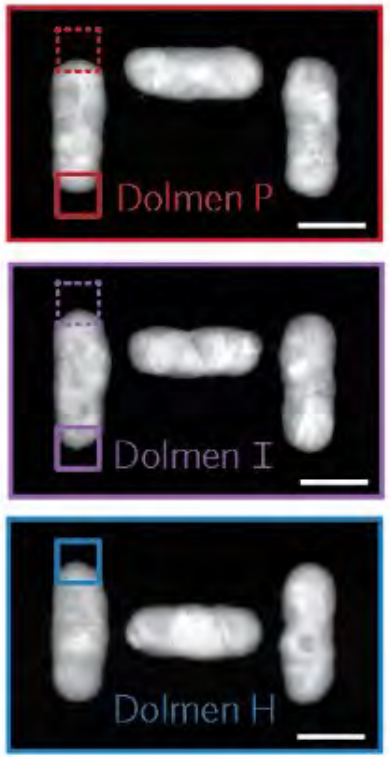


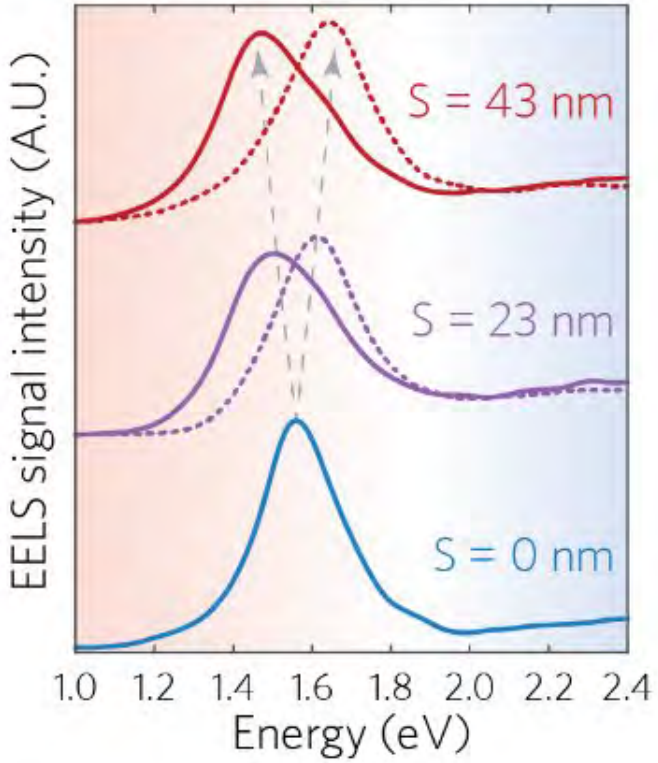


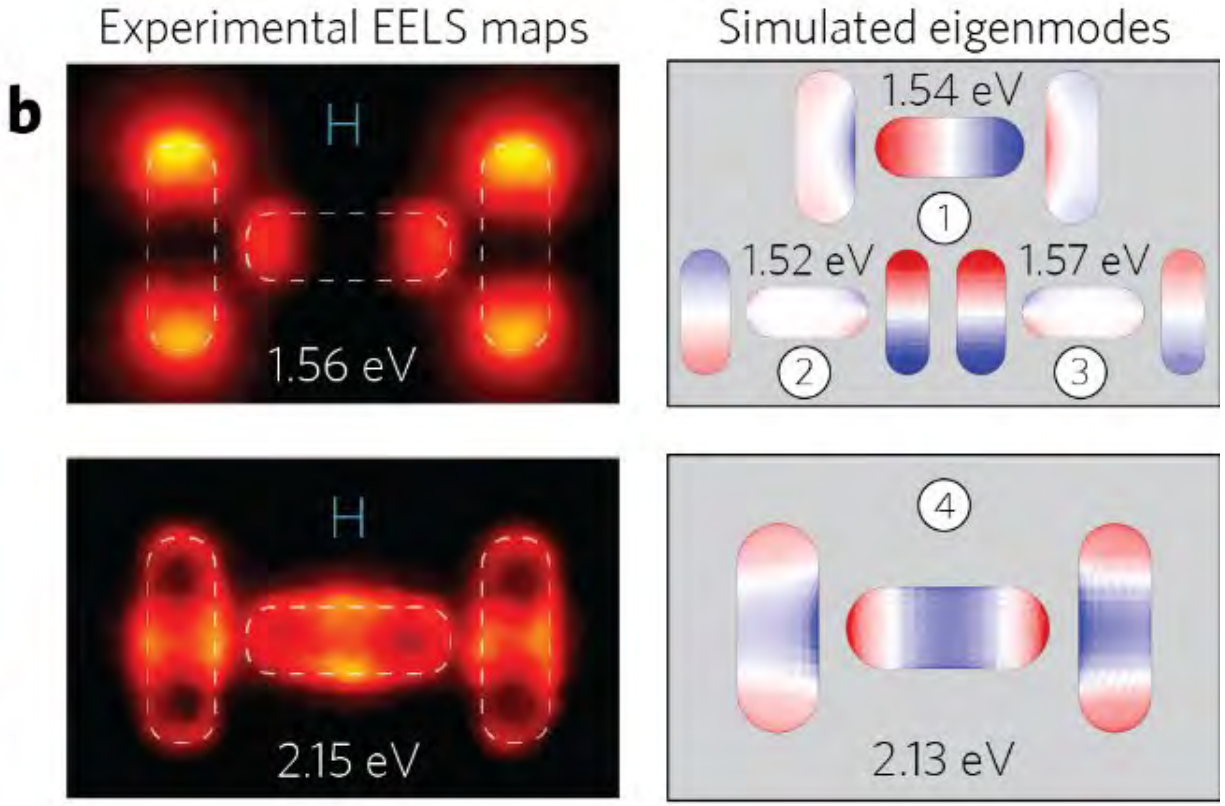


Flauraud *et al.*, *ACS Photon. 4*, 1661 (2017)

Plasmonic dolmens

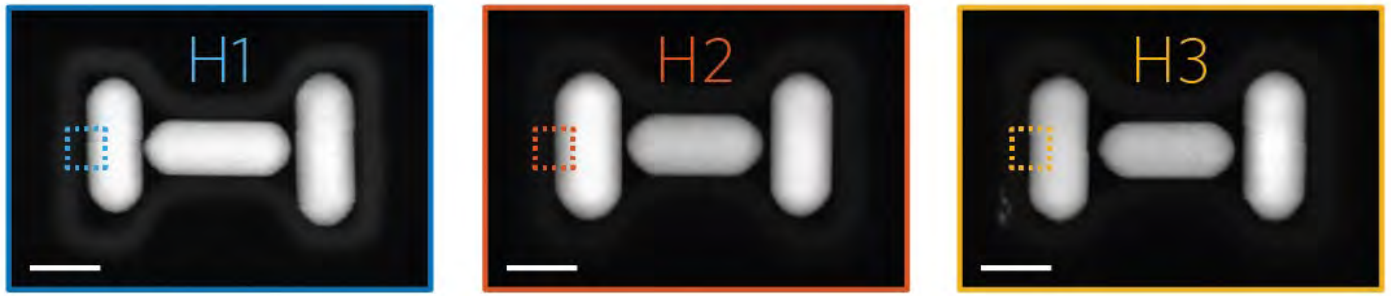


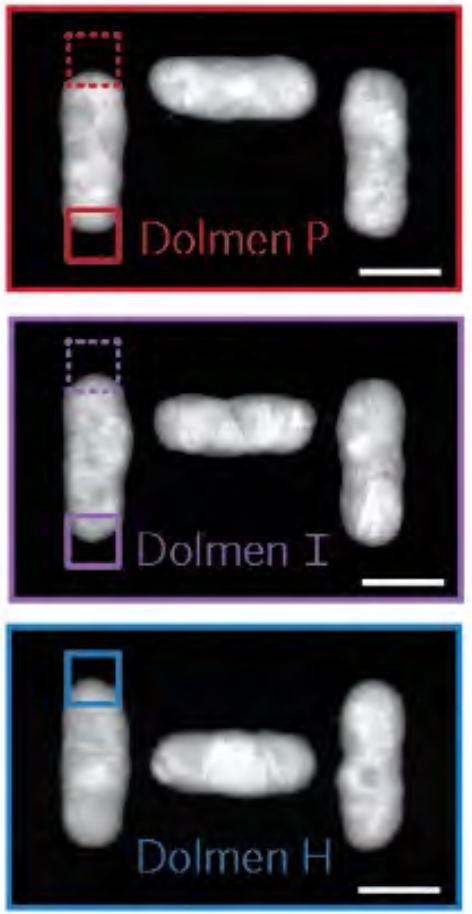




Flauraud *et al.*, *ACS Photon. 4*, 1661 (2017)

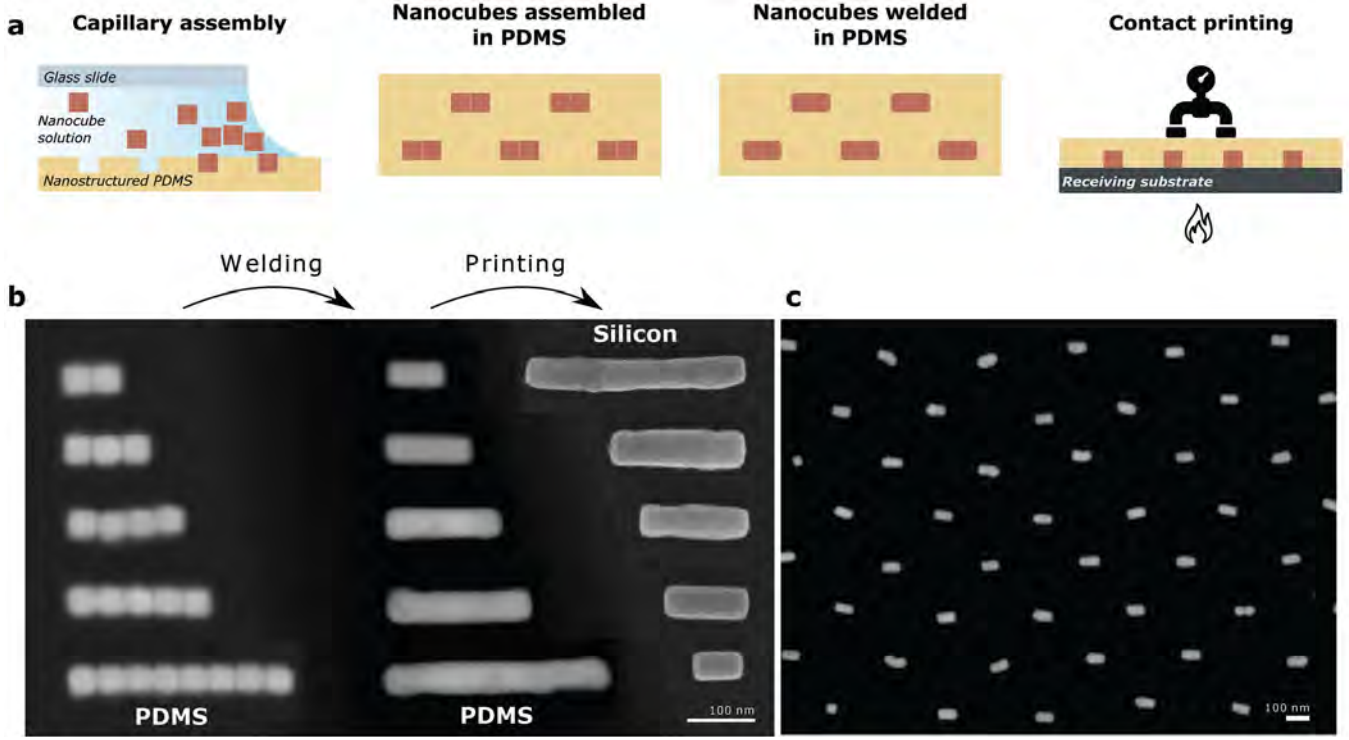
Crystallinity & edge roughness

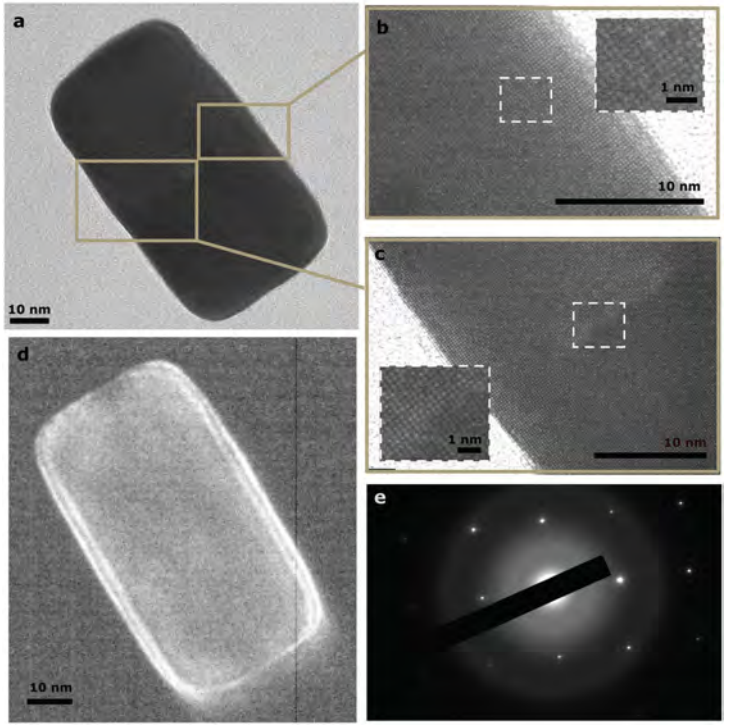


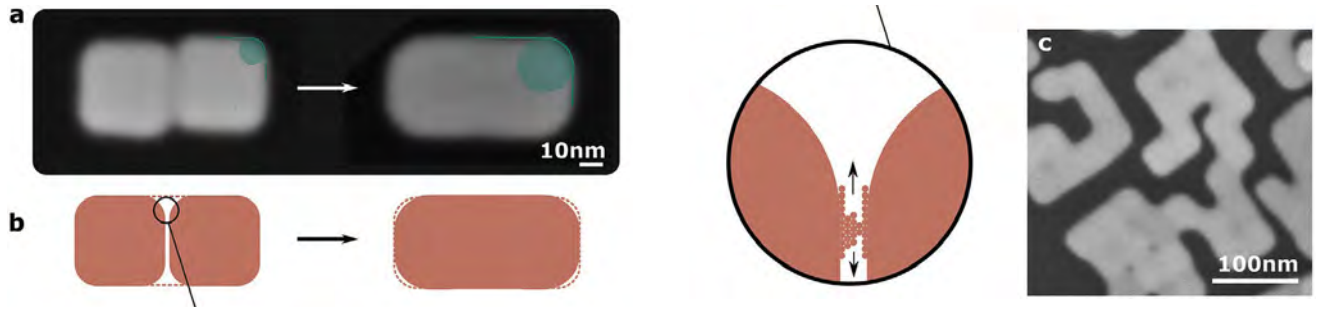


Flauraud *et al.*, *ACS Photon. 4*, 1661 (2017)

Monocrystals from nanocube epitaxy

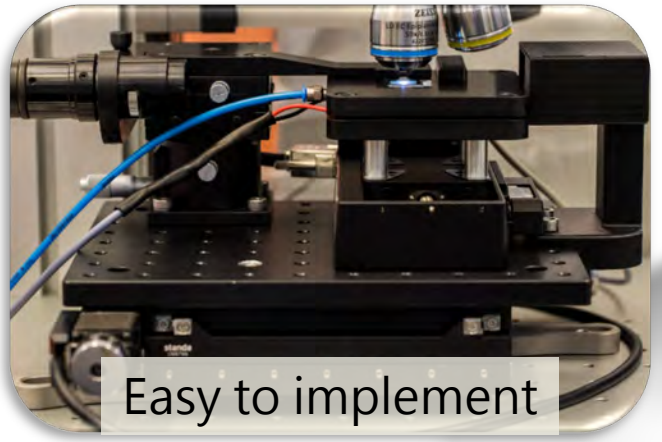






Capitaine & Sciacca, *Adv. Mater.* 34, 2200364 (2022)

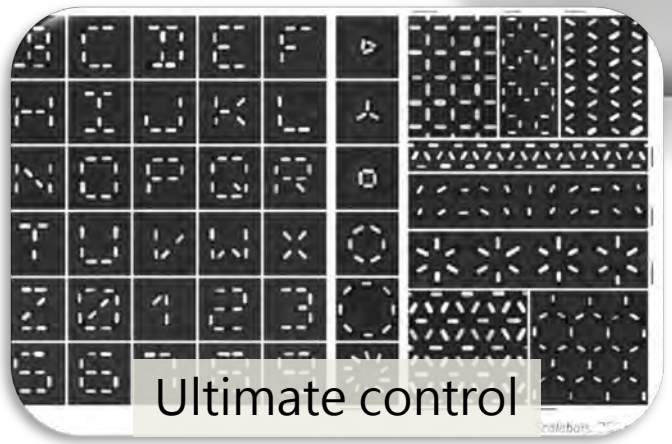
Take home messages



Easy to implement

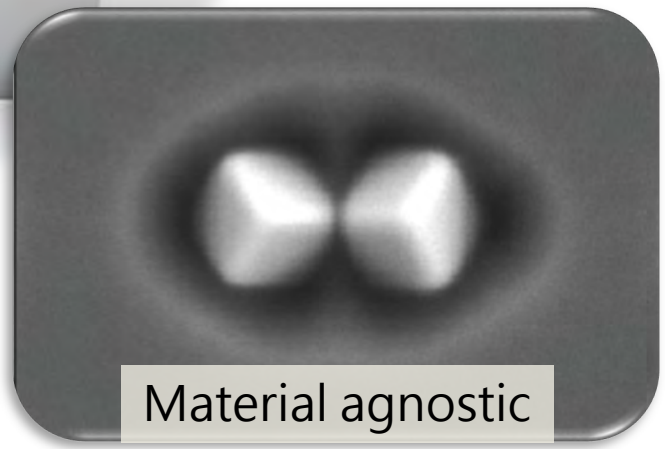
Top-down patterning

Resource efficient



Ultimate control

Bottom-up assembly



Material agnostic

References

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2. L. Malaquin, T. Kraus, H. Schmid, E. Delamarche, H. Wolf, "Controlled particle placement through convective and capillary assembly", *Langmuir* **23** (23), 11513-11521 (2007)
3. T. Kraus, L. Malaquin, H. Schmid, W. Riess, N. D. Spencer, H. Wolf, "Nanoparticle printing with single nanoparticle resolution", *Nat. Nanotechnol.* **2**, 570-576 (2007)
4. M. Mastrangeli, "The fluid joint: The soft spot of micro- and nanosystems", *Adv. Mater.* **27** (29), 5254-4272 (2015)
5. V. Flauraud, M. Mastrangeli, G. D. Bernasconi, J. Butet, D. T. L. Alexander, O. J. F. Martin, J. Brugger, "Nanoscale topographical control of capillary assembly of nanoparticles", *Nat. Nanotechnol.* **12**, 73-80 (2017)
6. V. Flauraud, G. D. Bernasconi, J. Butet, M. Mastrangeli, D. T. L. Alexander, O. J. F. Martin, J. Brugger, "Mode evolution in strongly coupled plasmonic dolmens fabricated by templated assembly", *ACS Photon.* **4** (7), 1661-1668 (2017)
7. S. Ni, L. Isa, H. Wolf, "Capillary assembly as a tool for the heterogeneous integration of micro- and nanoscale objects", *Soft Matter* **14**, 2978 (2018)