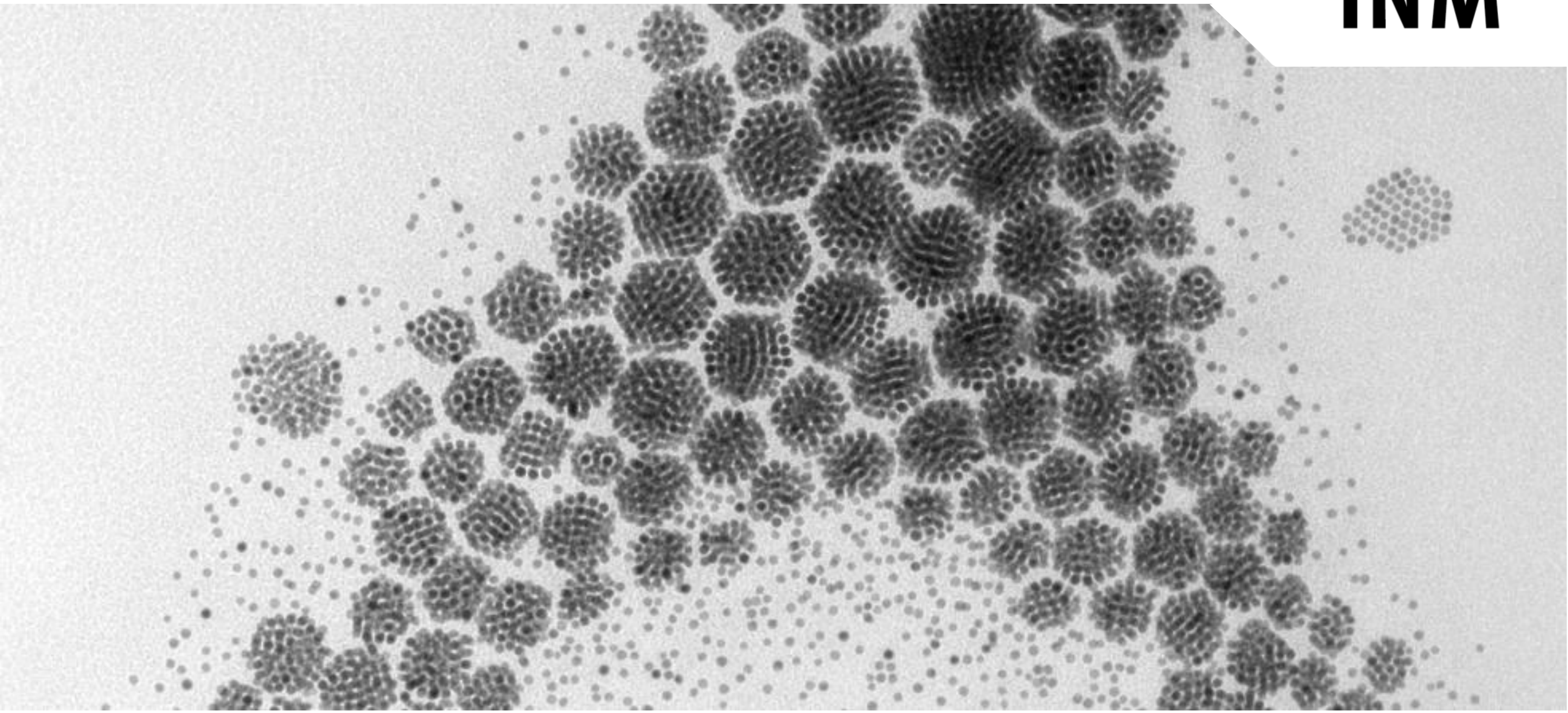
New Ideas. New Materials.

INM



From particle dispersions to rational arrangements

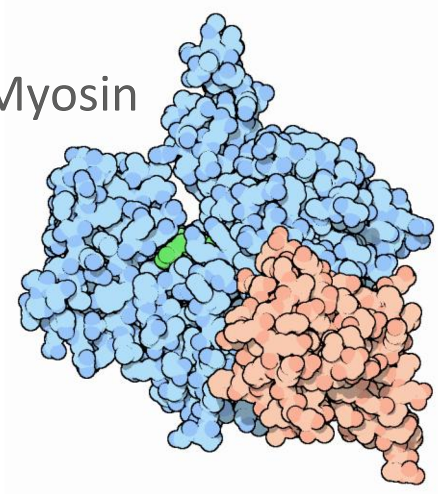
Tobias Kraus, Structure Formation Group, Leibniz-Institute for New Materials

GAFOE 2013, 28 April 2013, Beckman Center, Irvine, USA

Introduction

Structure formation by interacting proteins

Actin + Myosin

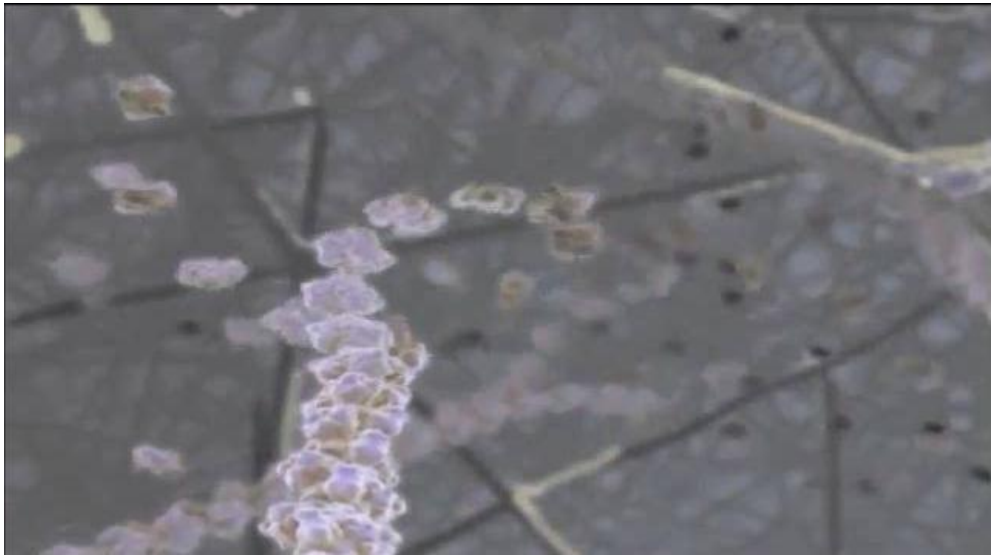


David Goodsell
(RCSB Protein DB)

Proteins

- Typical 10-100 kDa (~10-100 nm)
- Made of C, H, O mostly
- Stable dispersion in water
- Functional combinations: „quaternary structures“

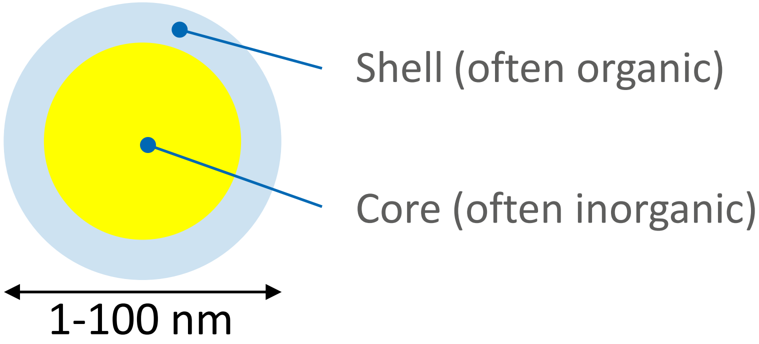
- Specific interactions
- Binding sites
- Precise arrangements



Alain Viel, Robert A. Lue
(Harvard University)

Introduction

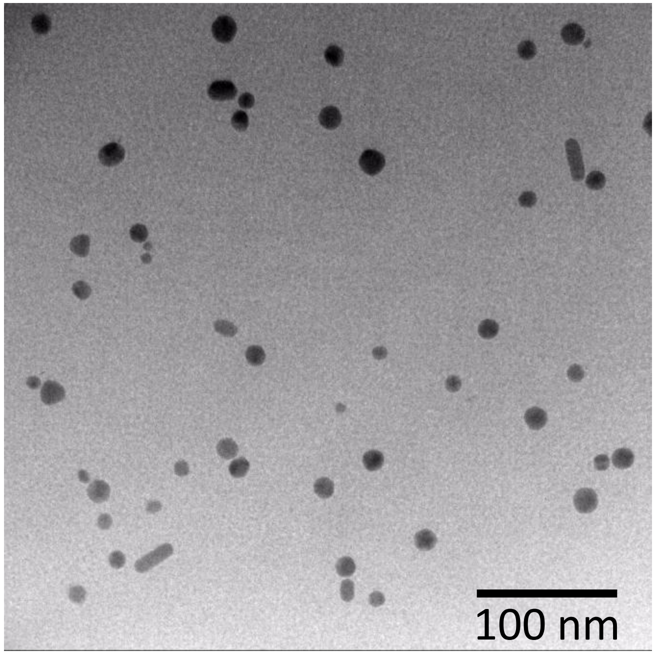
Structure formation by interacting nanoparticles



Nanoparticles

- Typical sizes 1-100 nm
- Made of almost anything you want
- Stable dispersion in solvent
- Functional combinations with polymers: „hybrid materials“

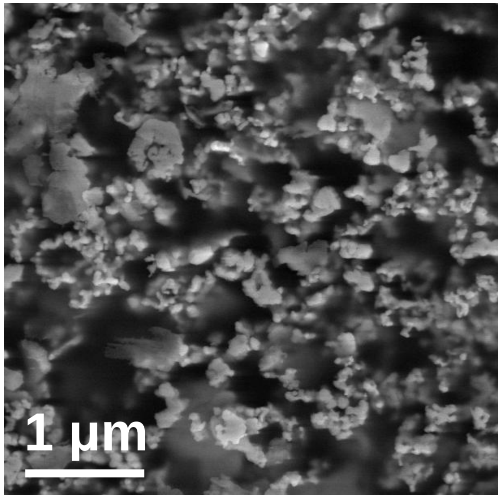
- „Polydispersity“
- Unspecific interactions
- No binding sites
- Random agglomerates



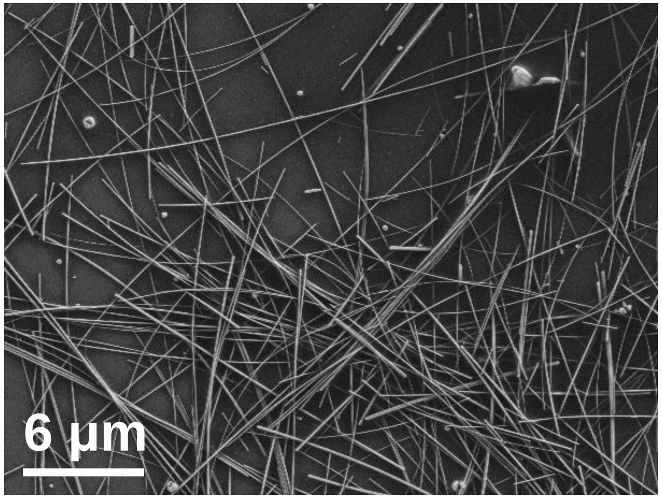
Niels de Jonge and Tobias Kraus, unpublished

Introduction

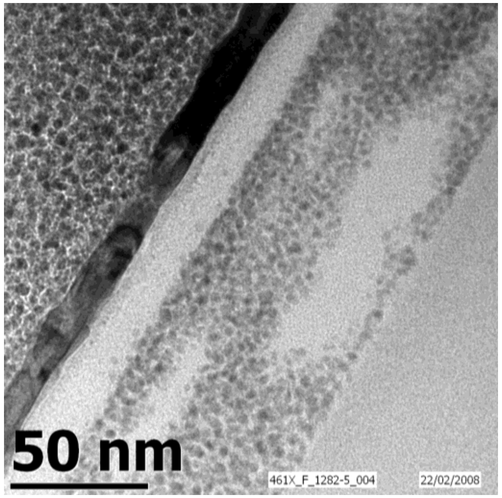
State of the art in particle-based materials



Silver in Epoxy
(Epotek)



Silver nanowires
(INM)

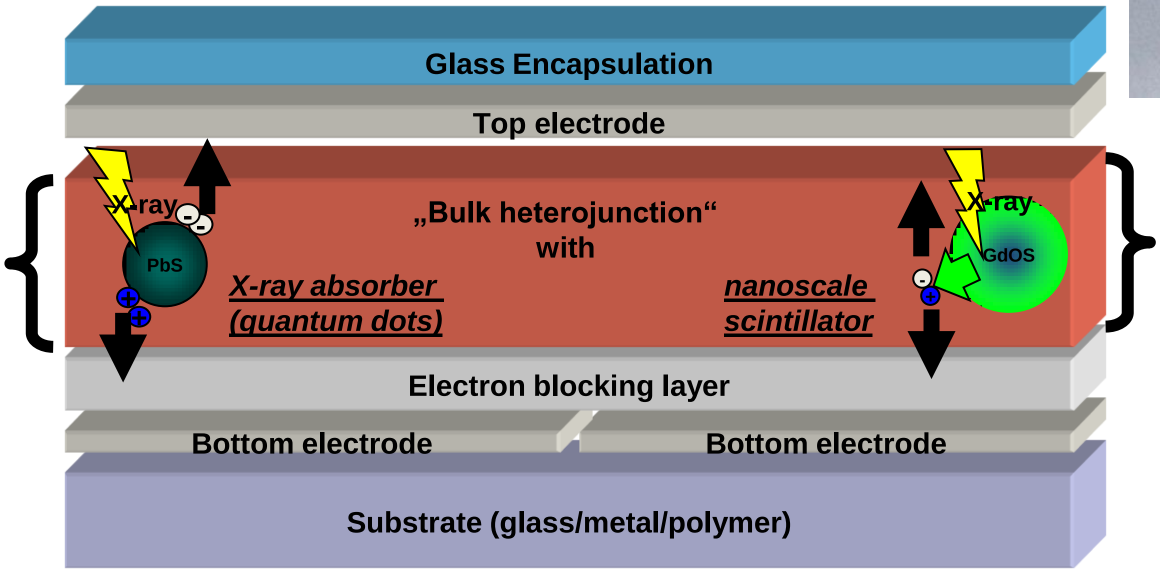


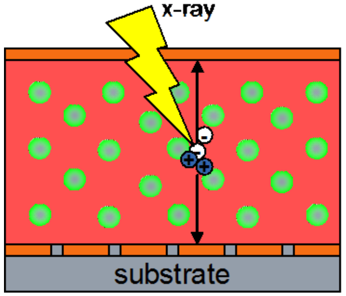
PbS in P3HT:PCBM
(Sandro F. Tedde and Hans Cerva, Siemens AG Corporate Technology)

Introduction

Example: x-ray detector

- Make szintillating nanoparticles (that glow upon x-ray adsorption),
- Embed them in a photovoltaic polymer,
- Create a „soft" photodetector for radiography.



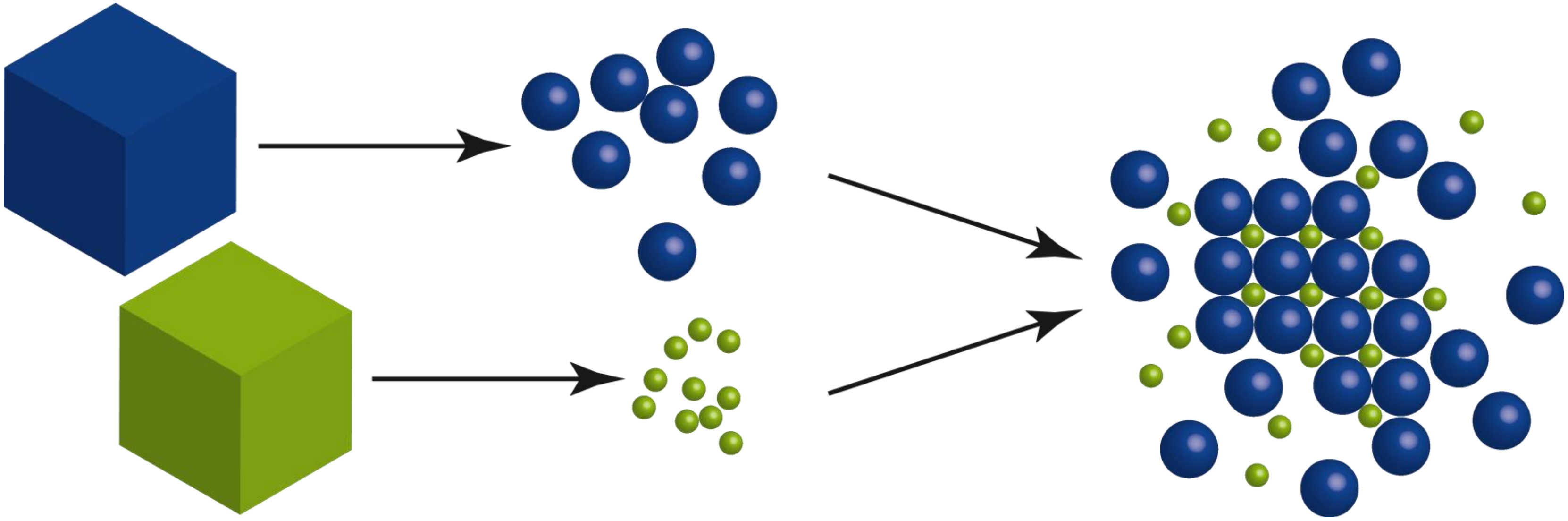


Vision:
Solution-processed photodetector with integrated x-ray absorber

Introduction

Structure formation by interacting nanoparticles

- Assemble nanoparticles with the precision of proteins
- Design the microstructure of particle-based materials



Kraus, *Chemical Monthly* 141 (2010) 1267

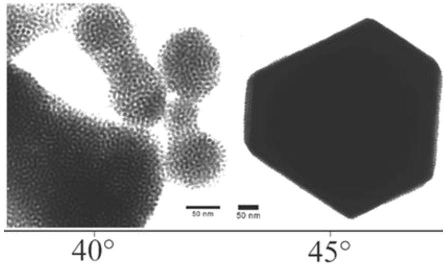
Contents

(Why we think this will work)

Structural control through shells

- Ligands, not core materials, dominate morphology

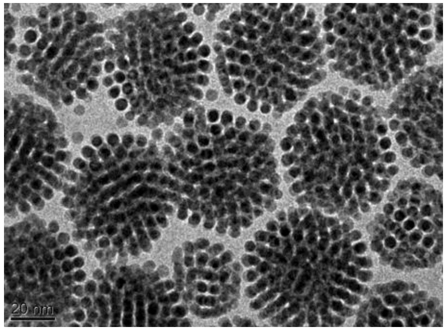
  → Concept independent of core material



Particle clusters in emulsion droplets

- Clusters are known to be free energy minima

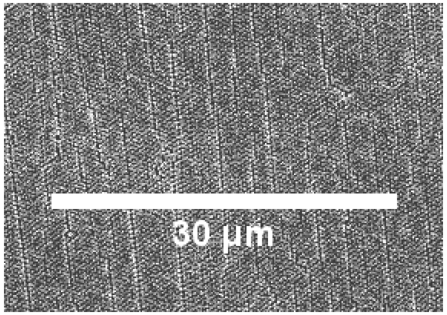
  → Particle can find even complex free energy minima



Wet Coating 2.0

- Regular assemblies in simple coating processes

  → Concept compatible with industry standards



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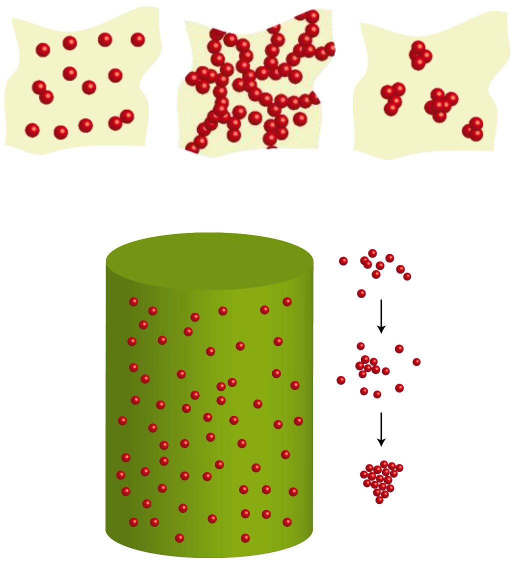

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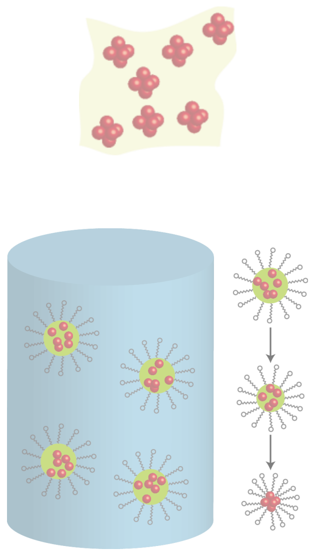

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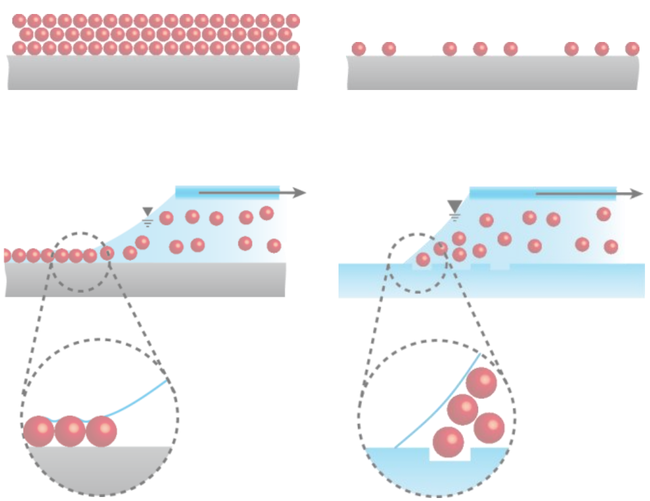
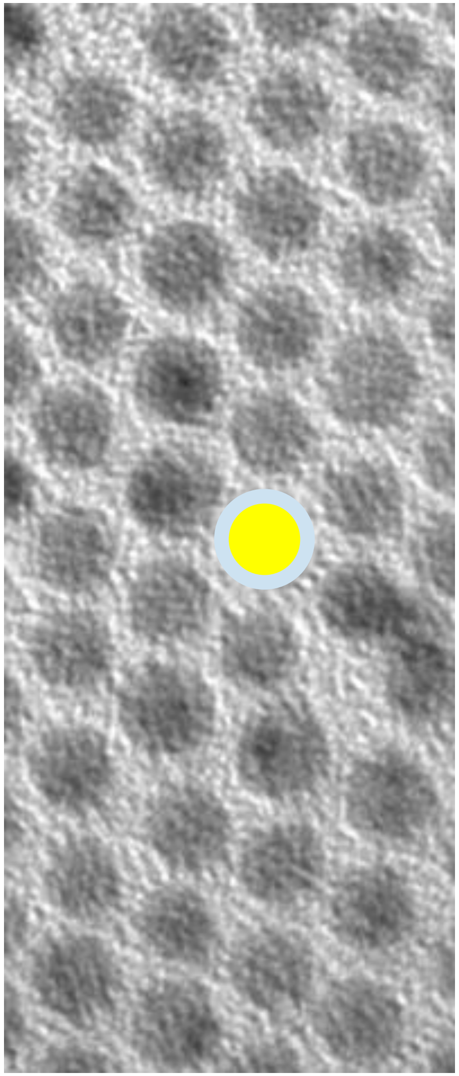


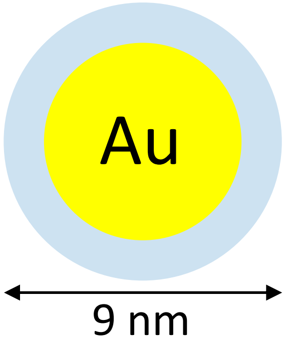
Shell dominates agglomerate structure

Structure of the shell: ligands

Electron microscopy:

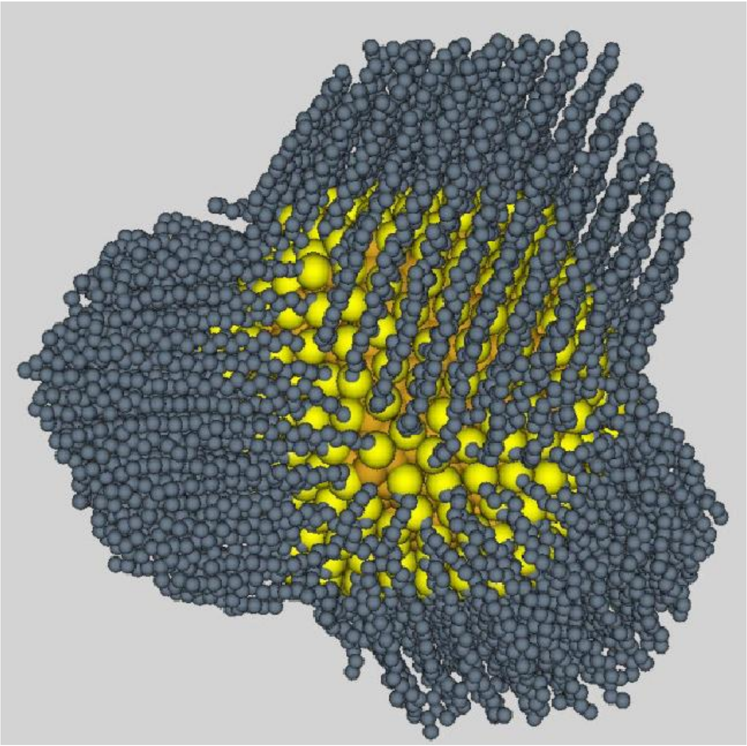


Powerpoint particle:



Dodecanethiol ligand

More realistic (simulation):

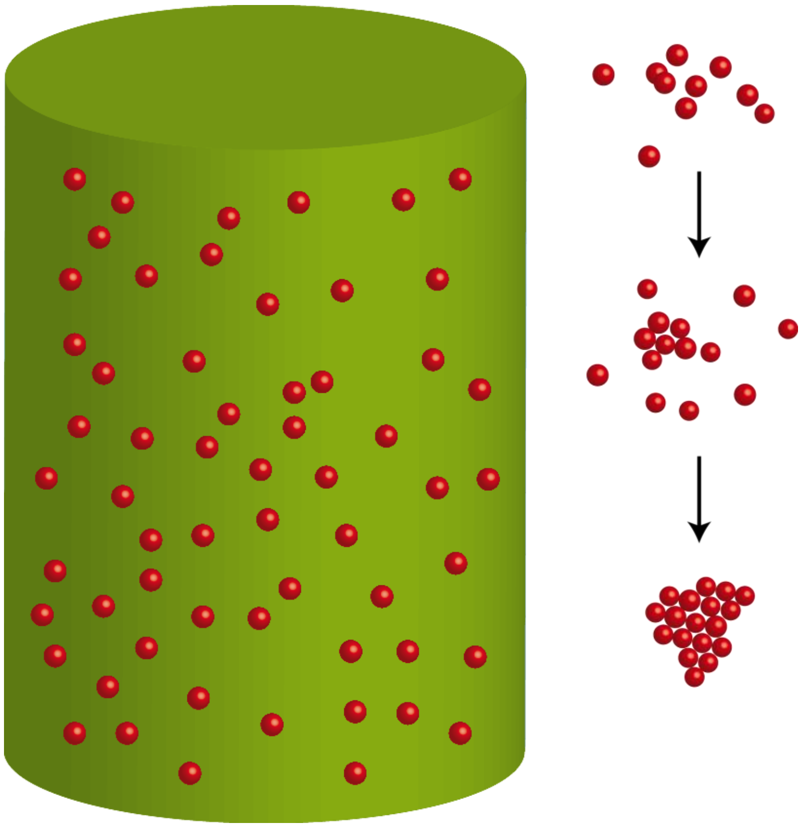


T. Djebaili, J. Richardi, S. Abel and M. Marchi, "Atomistic Simulations of the Surface Coverage of Large Icosahedral Gold Nanocrystals", submitted

Shell dominates agglomerate structure

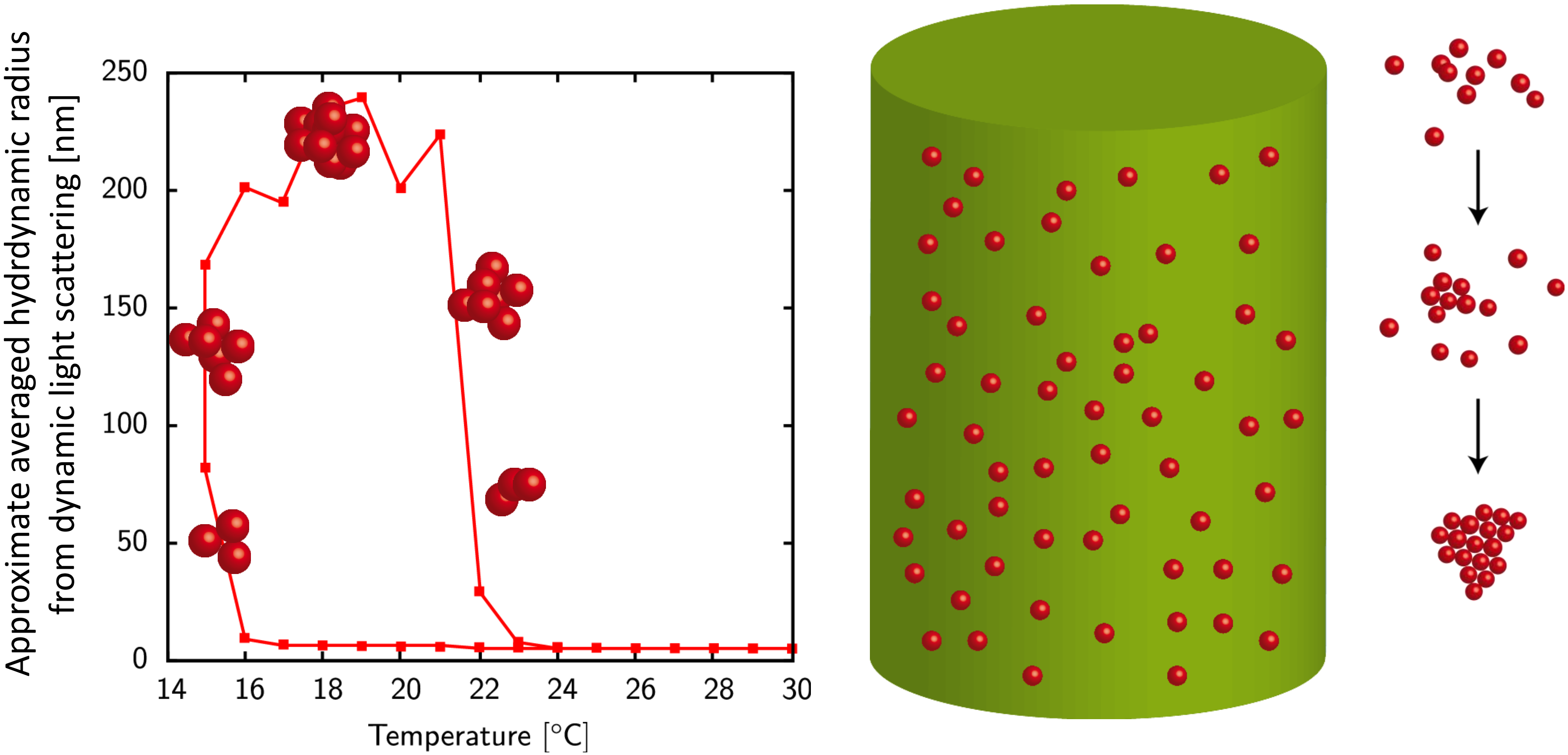
Temperature-induced agglomeration

- Make a stable dispersion of gold particles in heptane.
- Cool it to instability.
- Follow the particles' assembly.
- Look at the morphology of the superstructures.



Shell dominates agglomerate structure

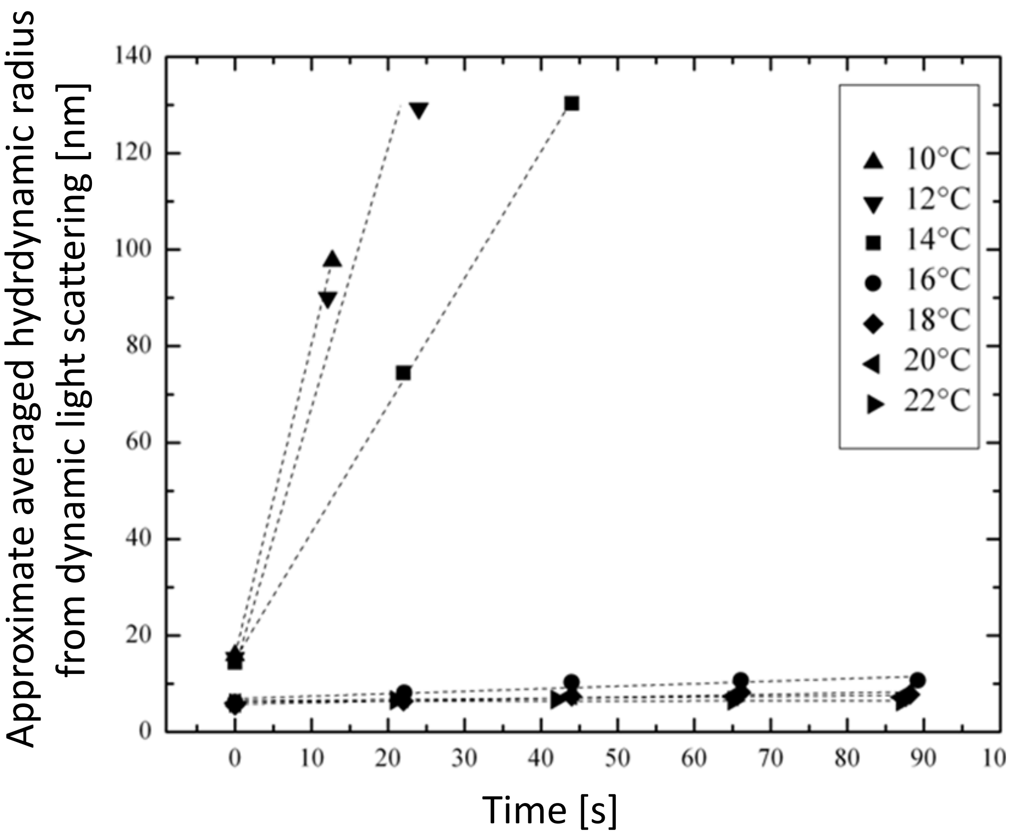
Temperature-induced agglomeration

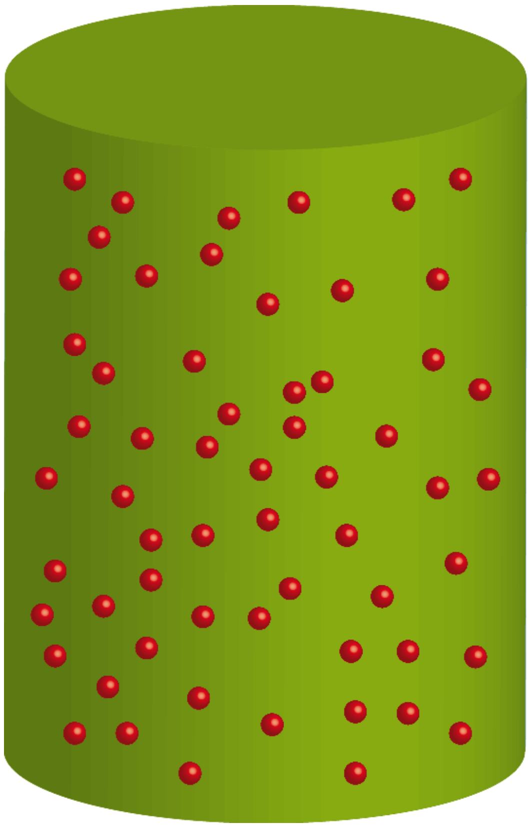


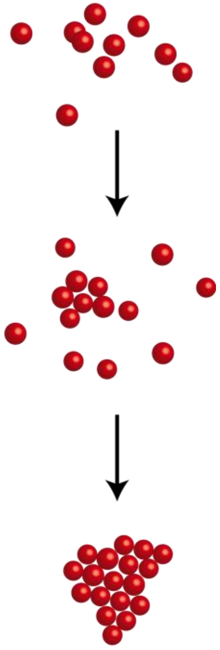
Born and Kraus, *PRE,* manuscript in review

Shell dominates agglomerate structure

Temperature-induced agglomeration



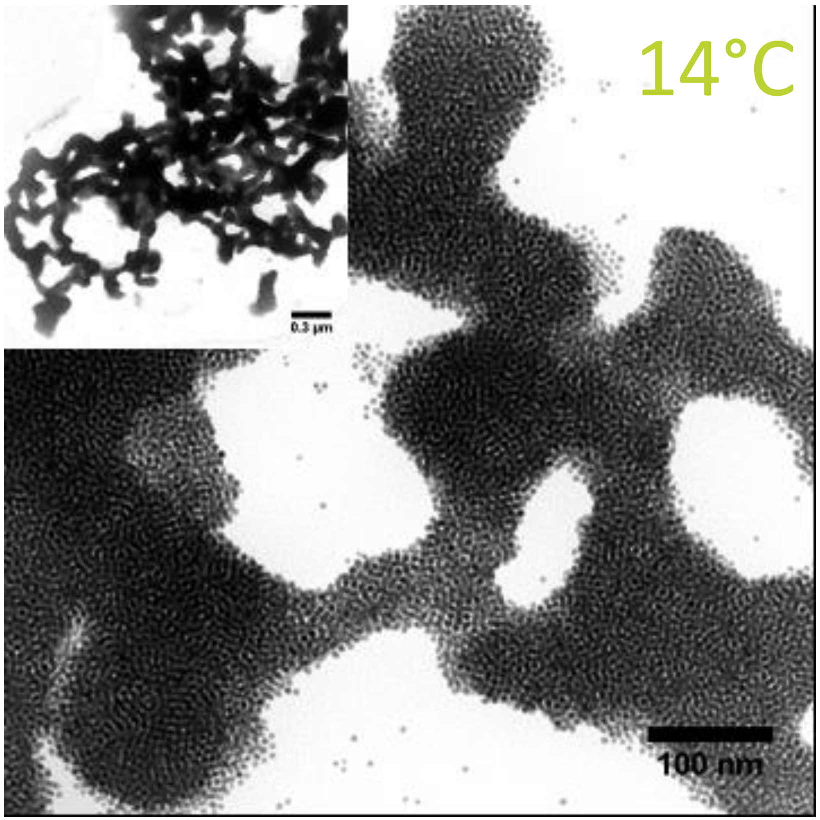


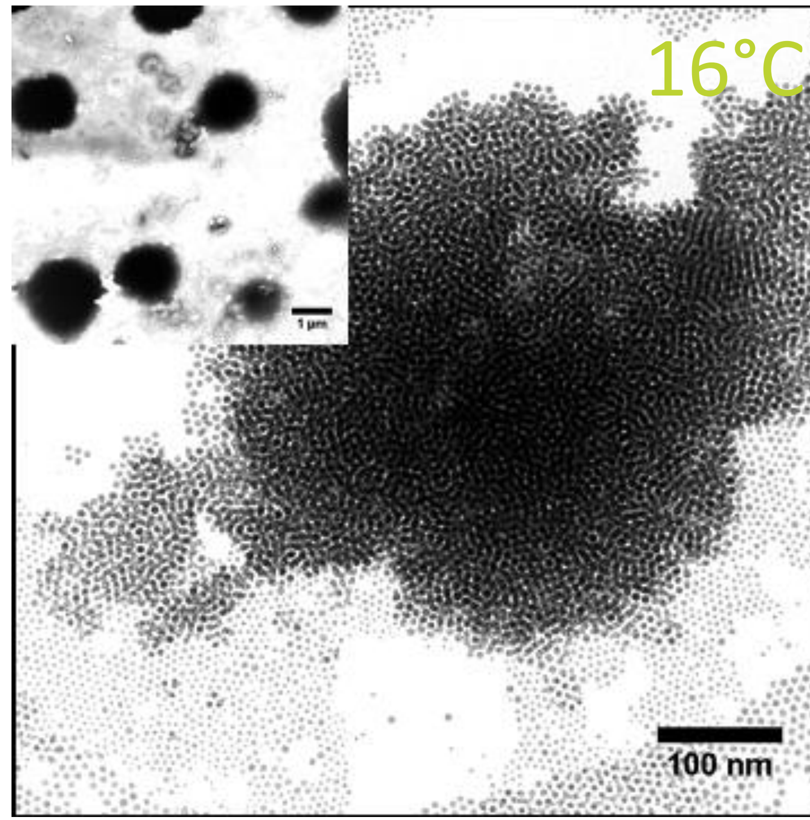


Born and Kraus, *PRE,* manuscript in review

Shell dominates agglomerate structure

Temperature-induced agglomeration



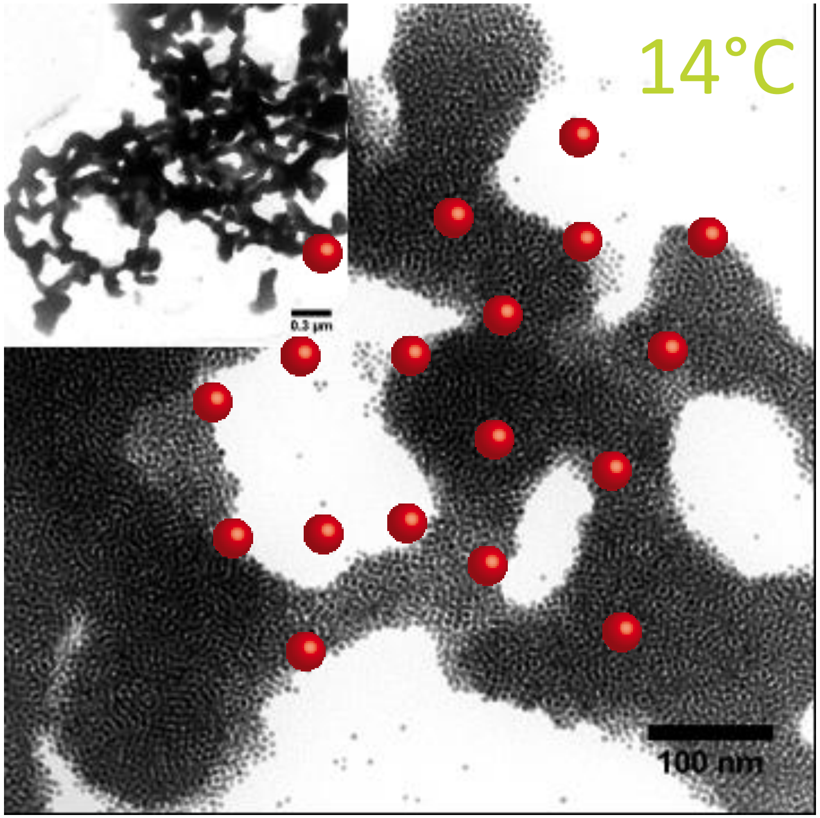


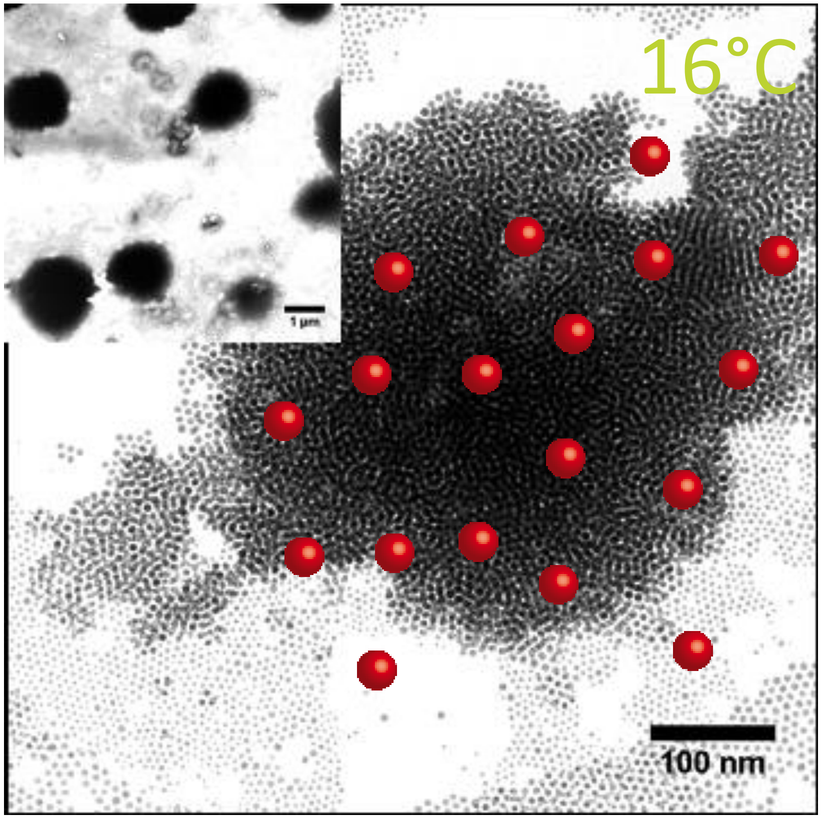
Born and Kraus, *PRE,* manuscript in review

Shell dominates agglomerate structure

Temperature-induced agglomeration

But: no order under any conditions!

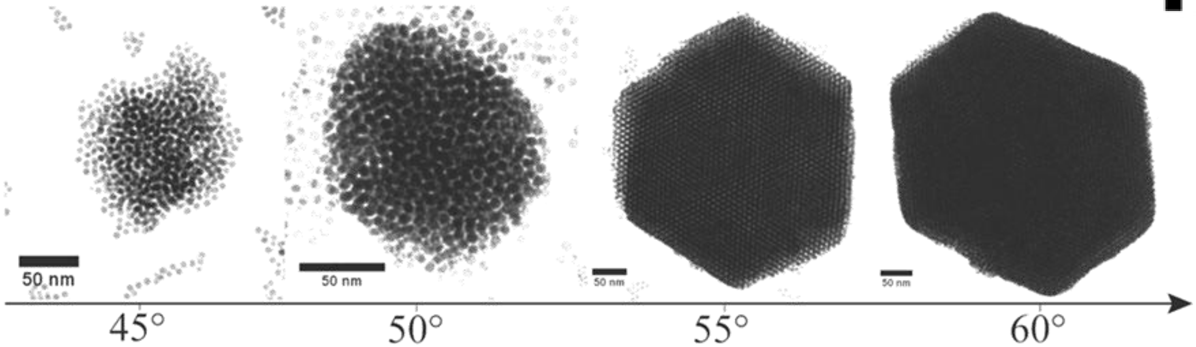




Modify experiment: agglomerate at higher temperatures.

Shell dominates agglomerate structure

Octadecane monolayer

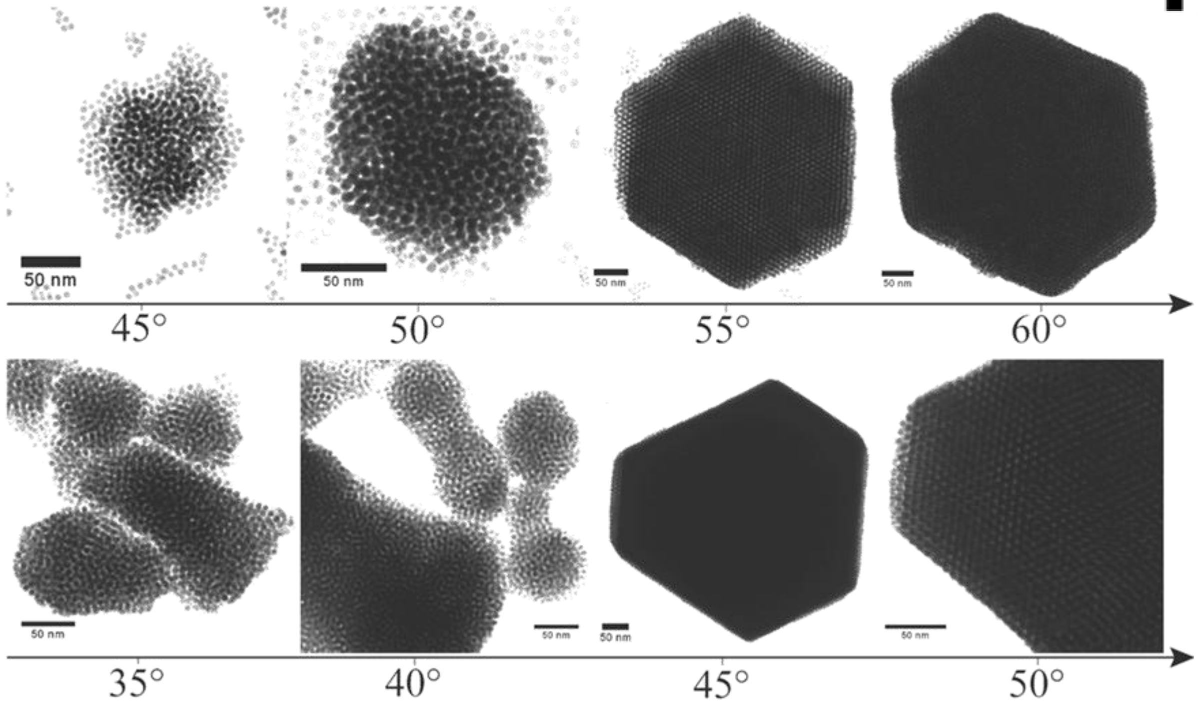


Geyer, Born, Kraus, *Phys. Rev. Lett.* 109 (2012) 128302

Shell dominates agglomerate structure

Octadecane
monolayer

Hexadecane
monolayer



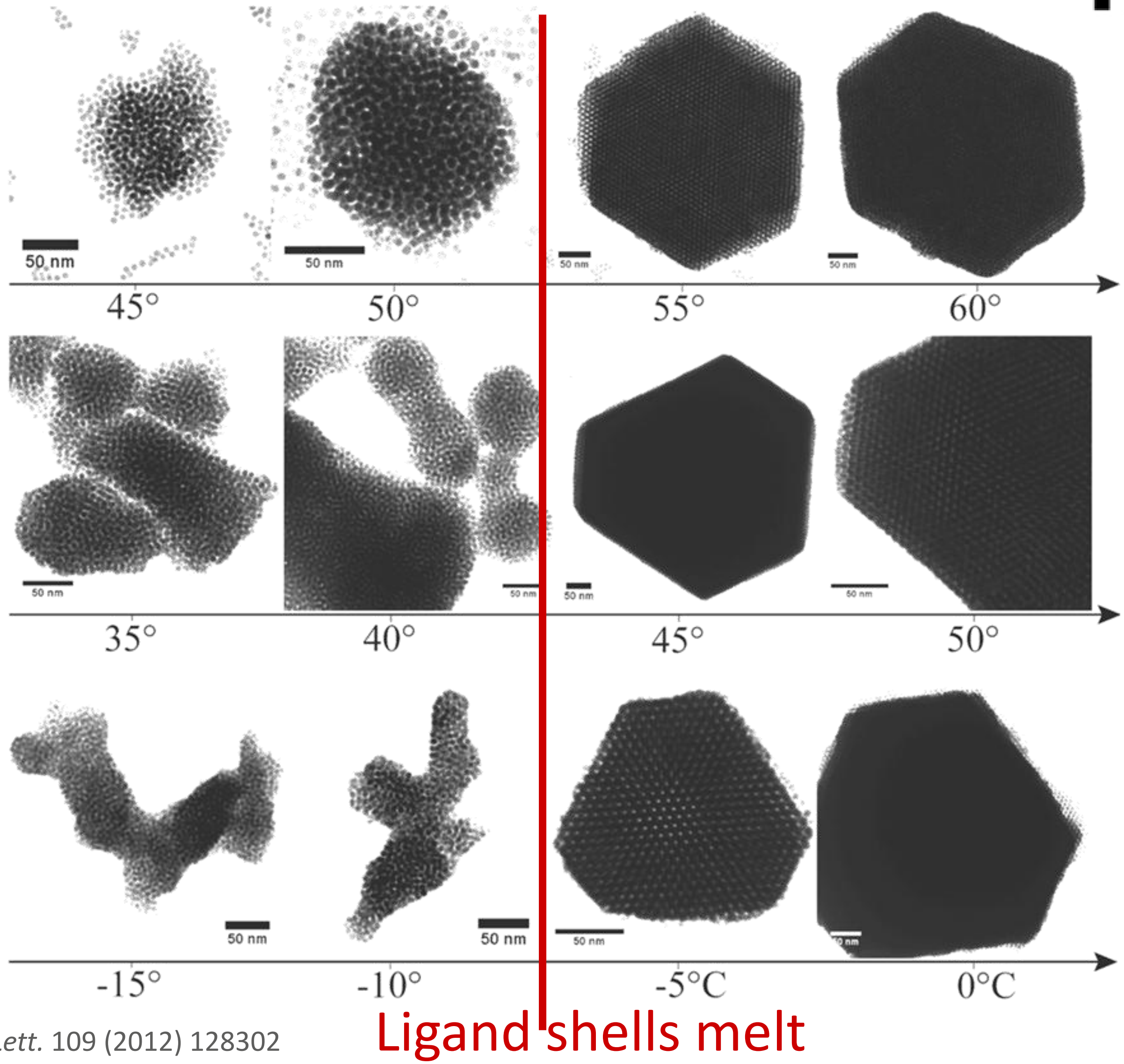
Geyer, Born, Kraus, *Phys. Rev. Lett.* 109 (2012) 128302

Shell dominates agglomerate structure

Octadecane monolayer

Hexadecane monolayer

Dodecane monolayer



Geyer, Born, Kraus, *Phys. Rev. Lett.* 109 (2012) 128302

Shell dominates agglomerate structure
for unpolar nanoparticle dispersions.

Cores interact through van der Waals forces

- Van der Waals is weakly T-dependant

  → Cores do not cause sharp transitions

Ligands interact with solvent

- Particle interactions are dominated by this interaction

  → as in Proteins, solvent-molecule interactions dominate superstructures

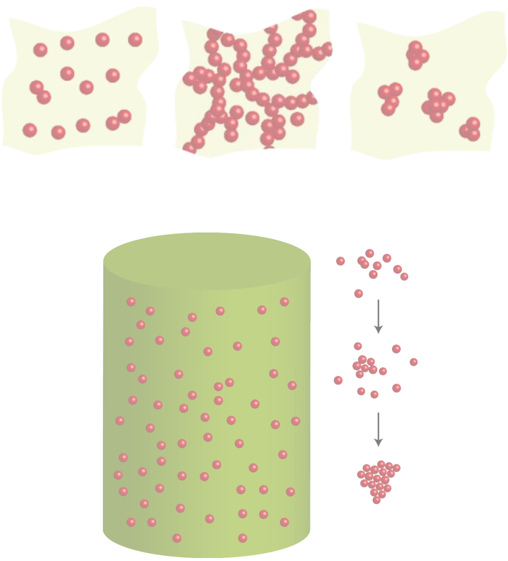
Ligands change conformation with temperature

- Particle packing in agglomerates depends on conformation

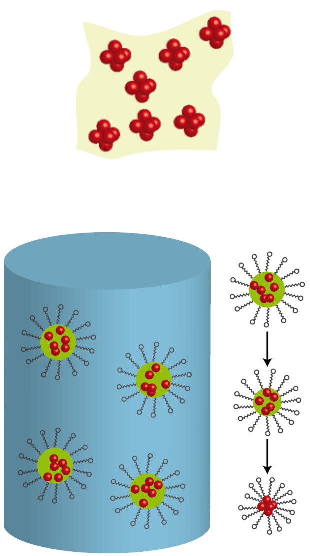
  → as in Proteins, molecular conformation translates into arrangement

Contents

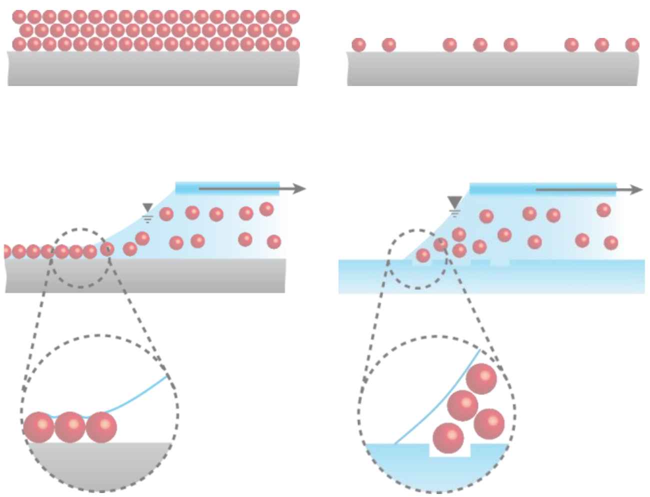
1. Shells



2. Clusters



3. Coating 2.0

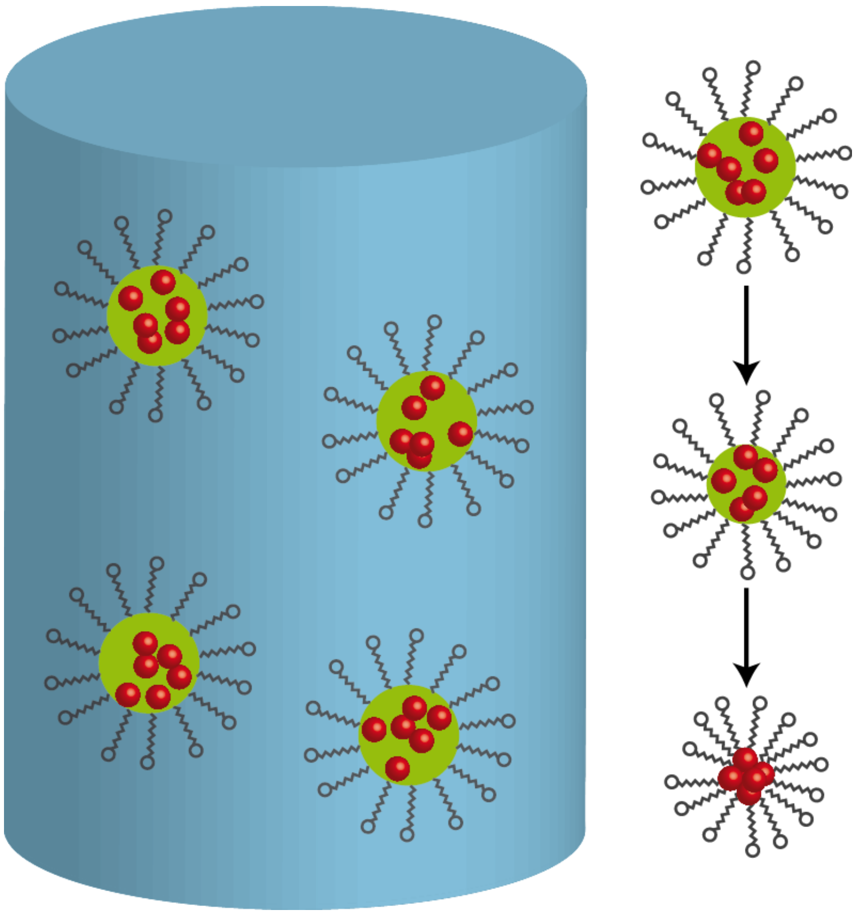


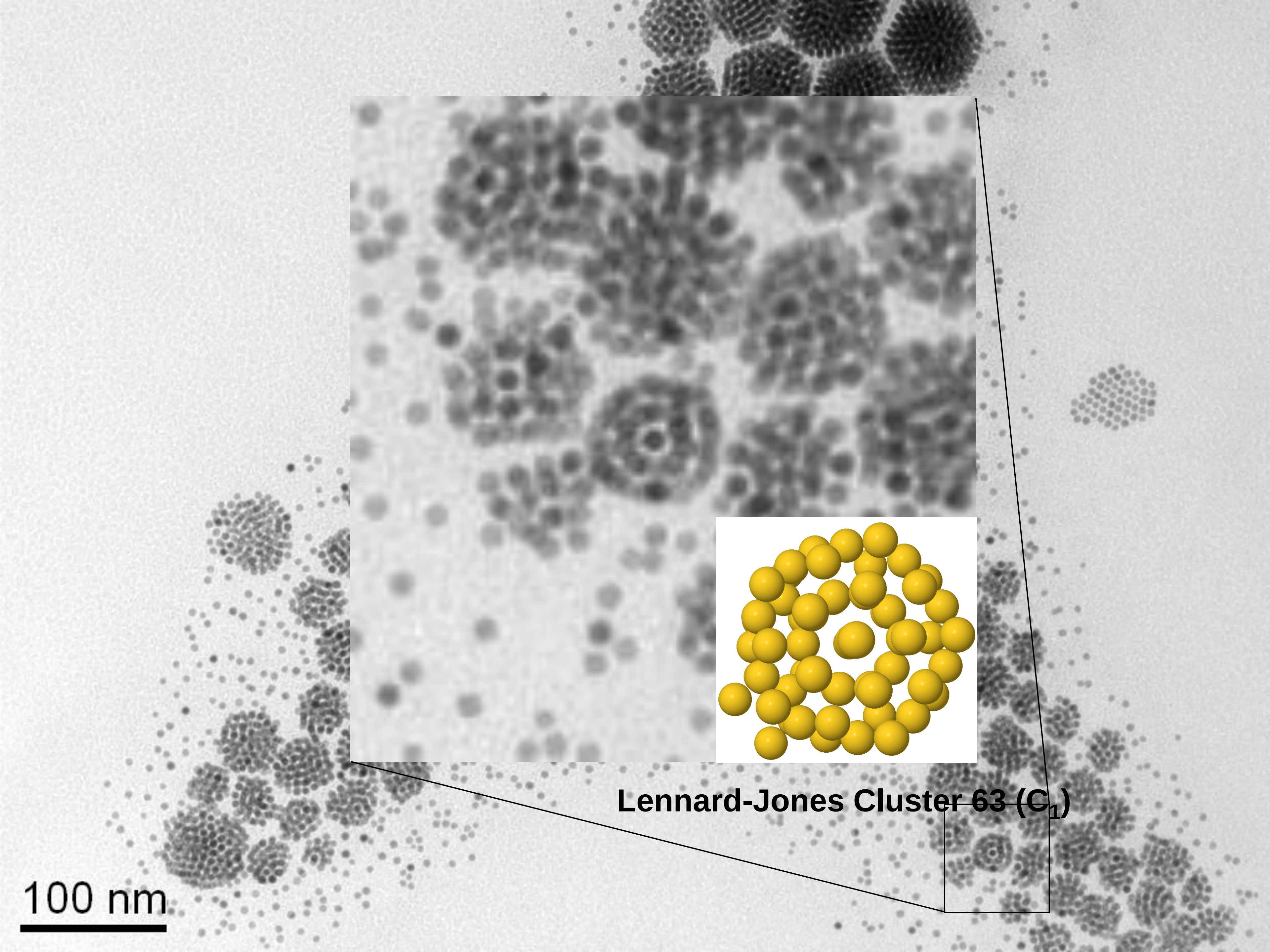
Particle clusters

Emulsion-assisted particle assembly

Prodecure:

- Mix particles in hexane with surfactant and water,
- Emulsify oil phase by shear or ultrasound,
- Gently evaporate hexane,
- Obtain stable dispersion of supraparticles.

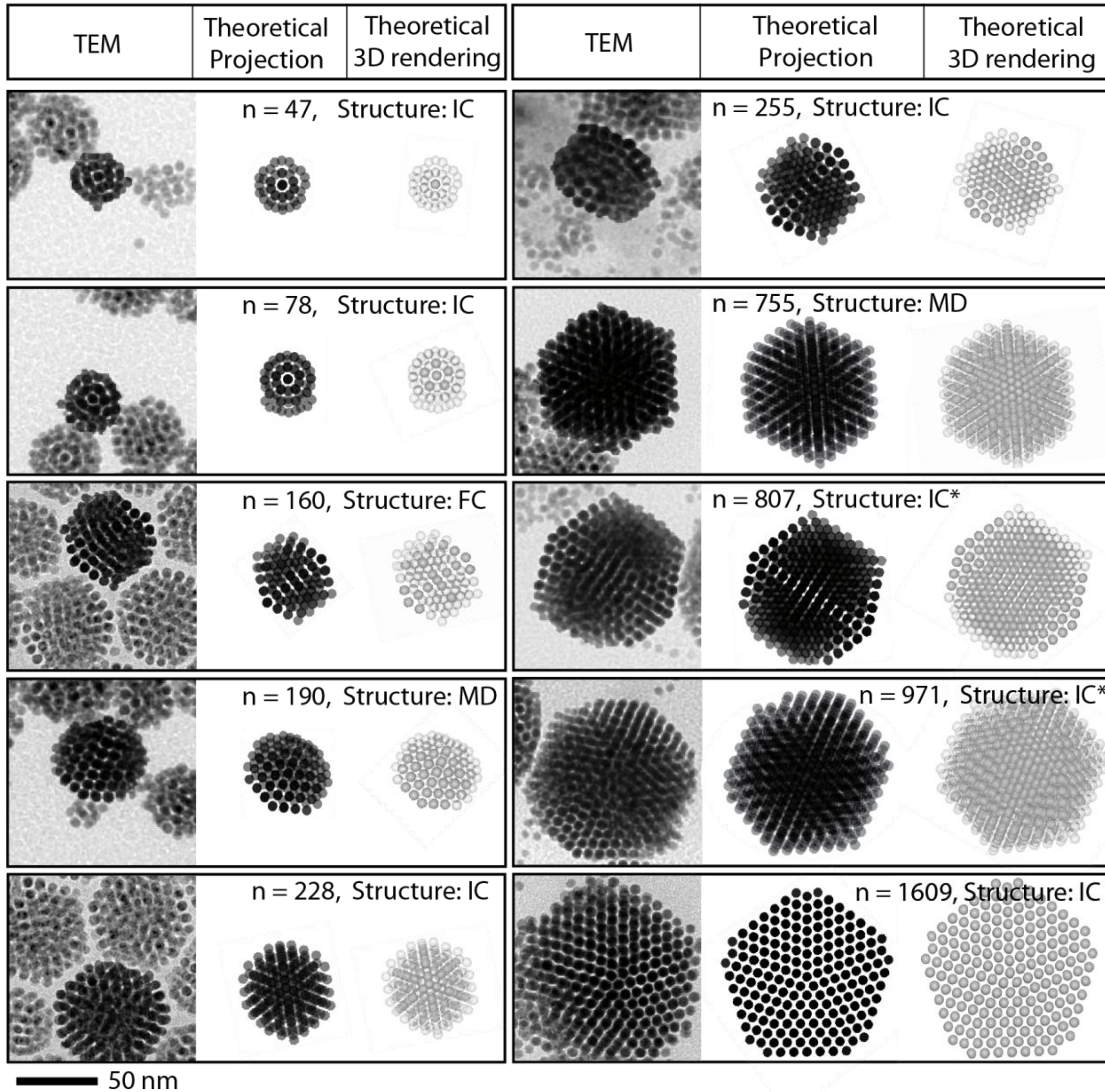




Lennard-Jones Cluster 63 (C_1)
100 nm

Supraparticles

Structures



Lacava, Born, Kraus, *Nano Lett.* 12 (2012) 3279

Supraparticles

are proof that nanoparticles find minima

Particles find a **unique minimum** that is known to be optimal

- Just as proteins, they settle in free energy minima

  → Engineering minima lets you engineer structure

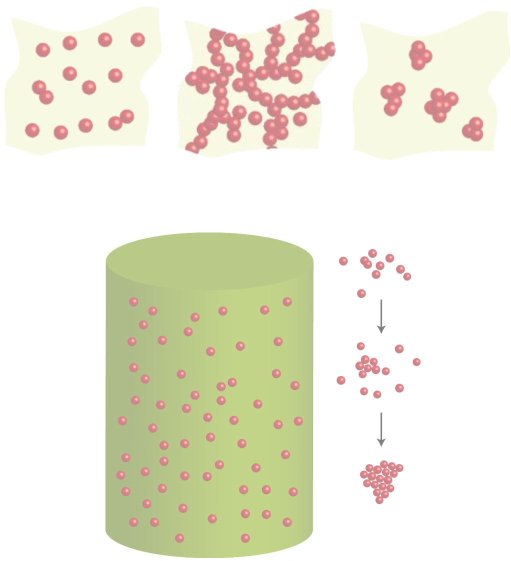
Confinement seems to aid assembly

- Only in confined volume do particles find the minimum

  → as in cells, confinement apparently favours regular assembly

Contents

1. Shells



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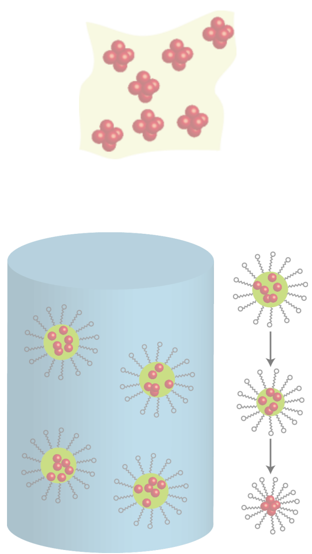

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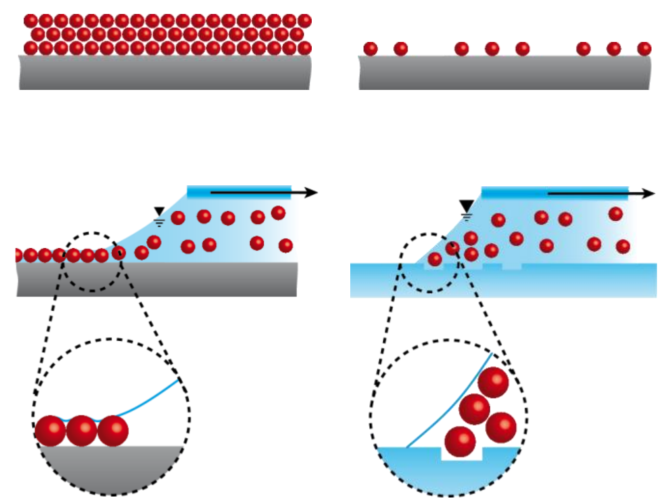
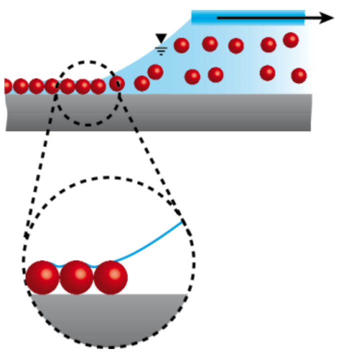
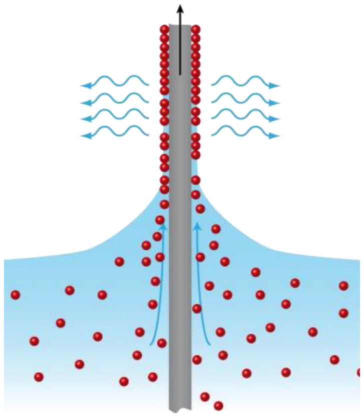


Wet coating 2.0

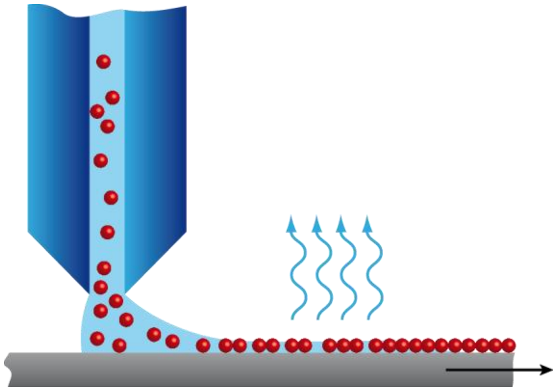
Structural control in standard coating processes:



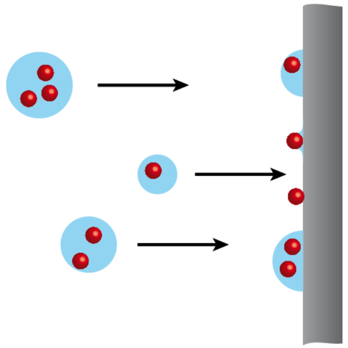
Doctor blading



Dip coating



Slot-die coating



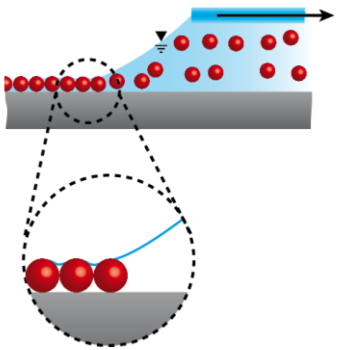
Spray coating

How do we transfer the results ?

- Lab-scale coaters with in-situ observation.
- Analysis of particle trajectories and liquid geometry.
- Structural control at realistic speeds.

Wet coating 2.0

Structural control in standard coating processes



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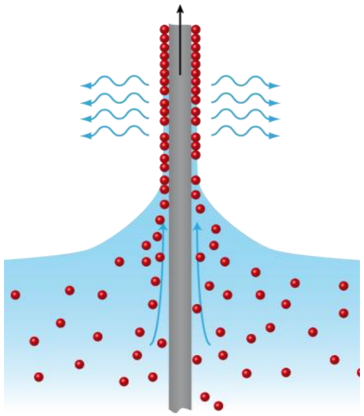

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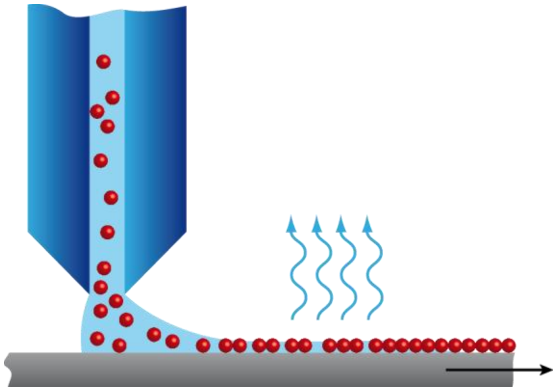

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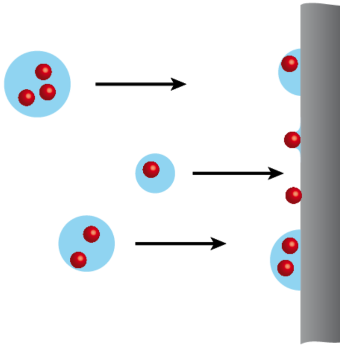

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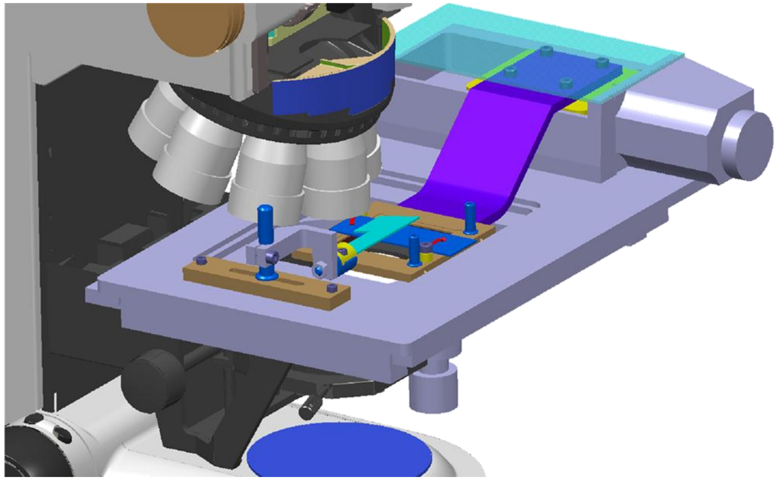
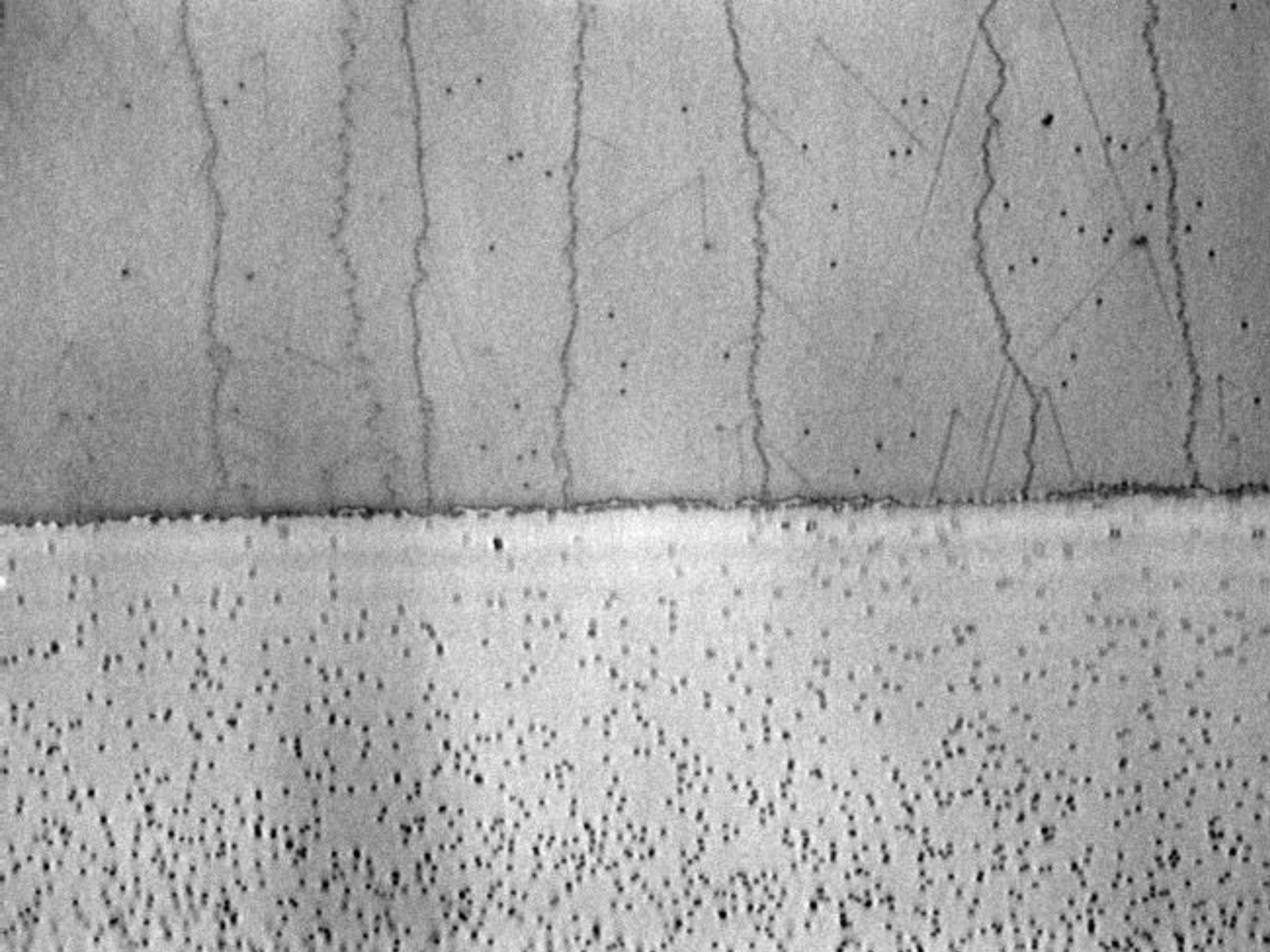
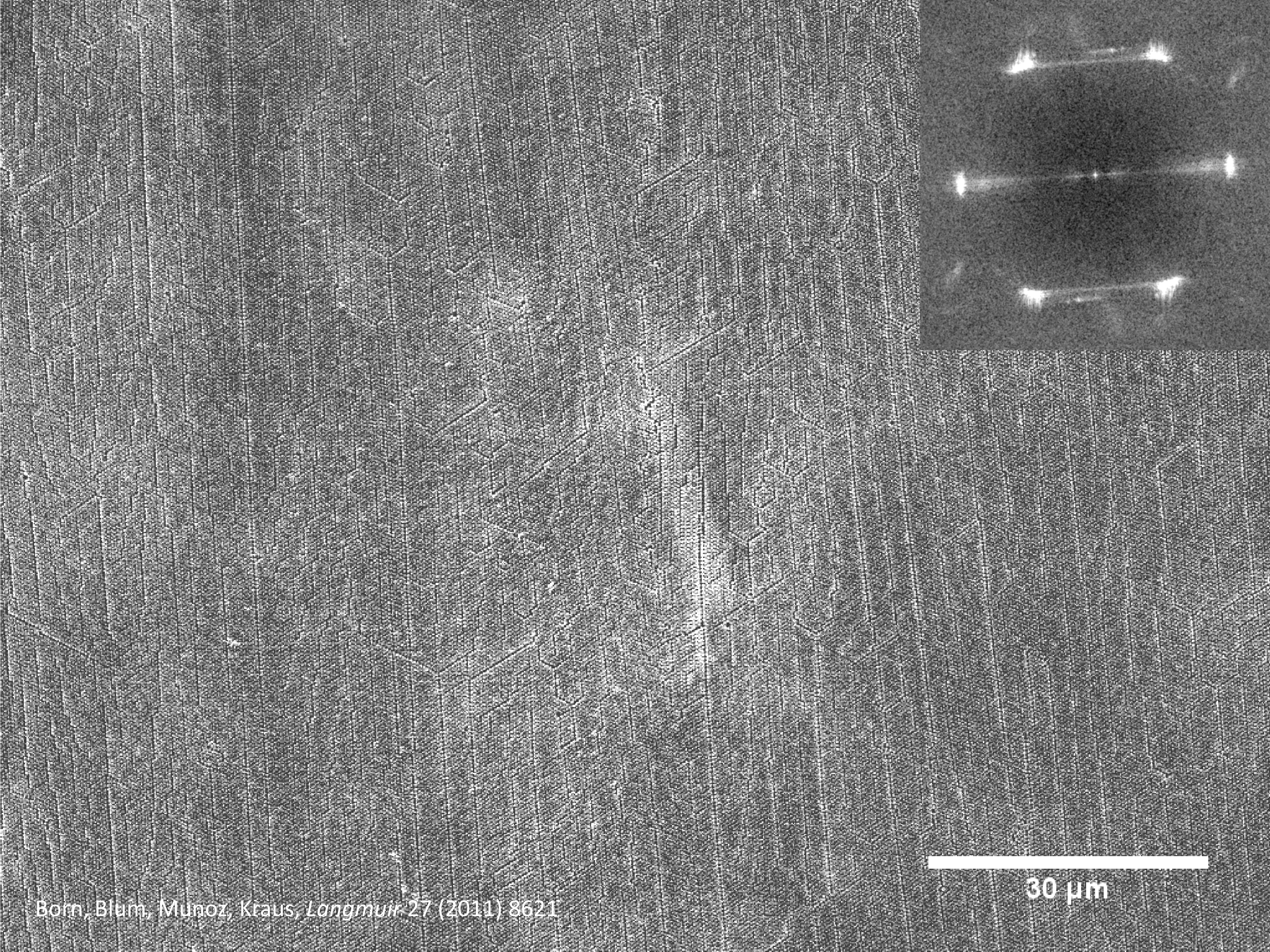
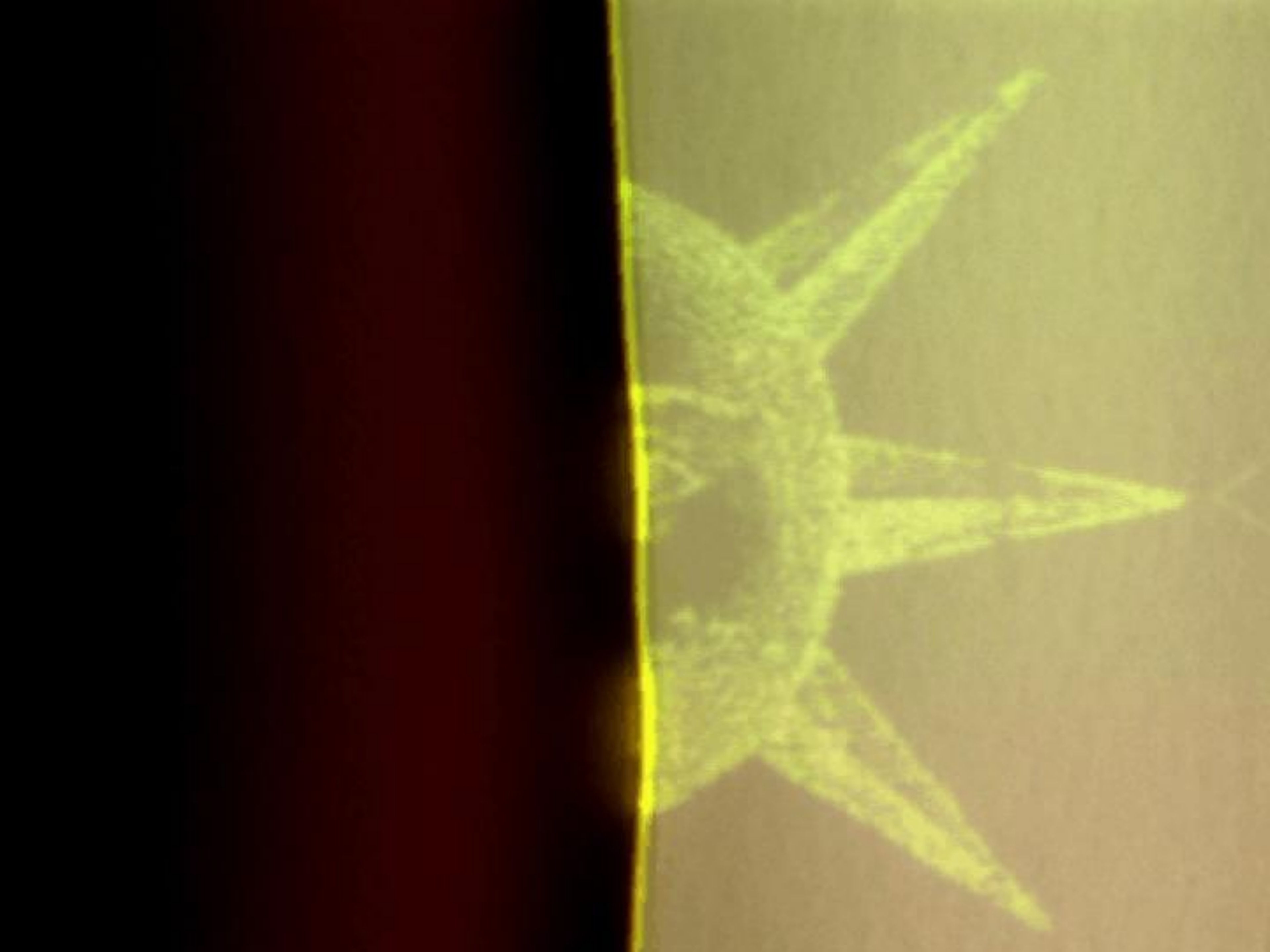
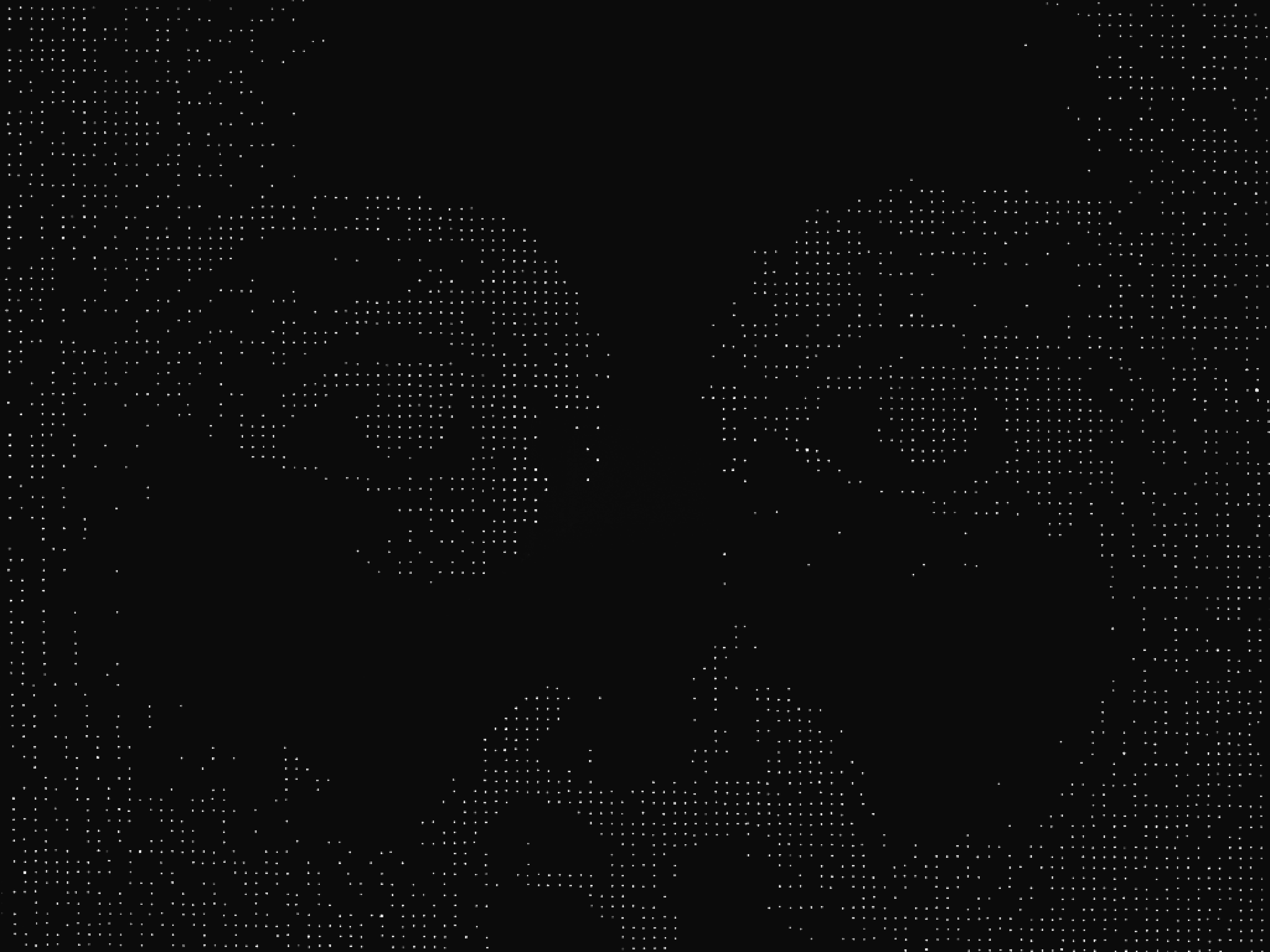


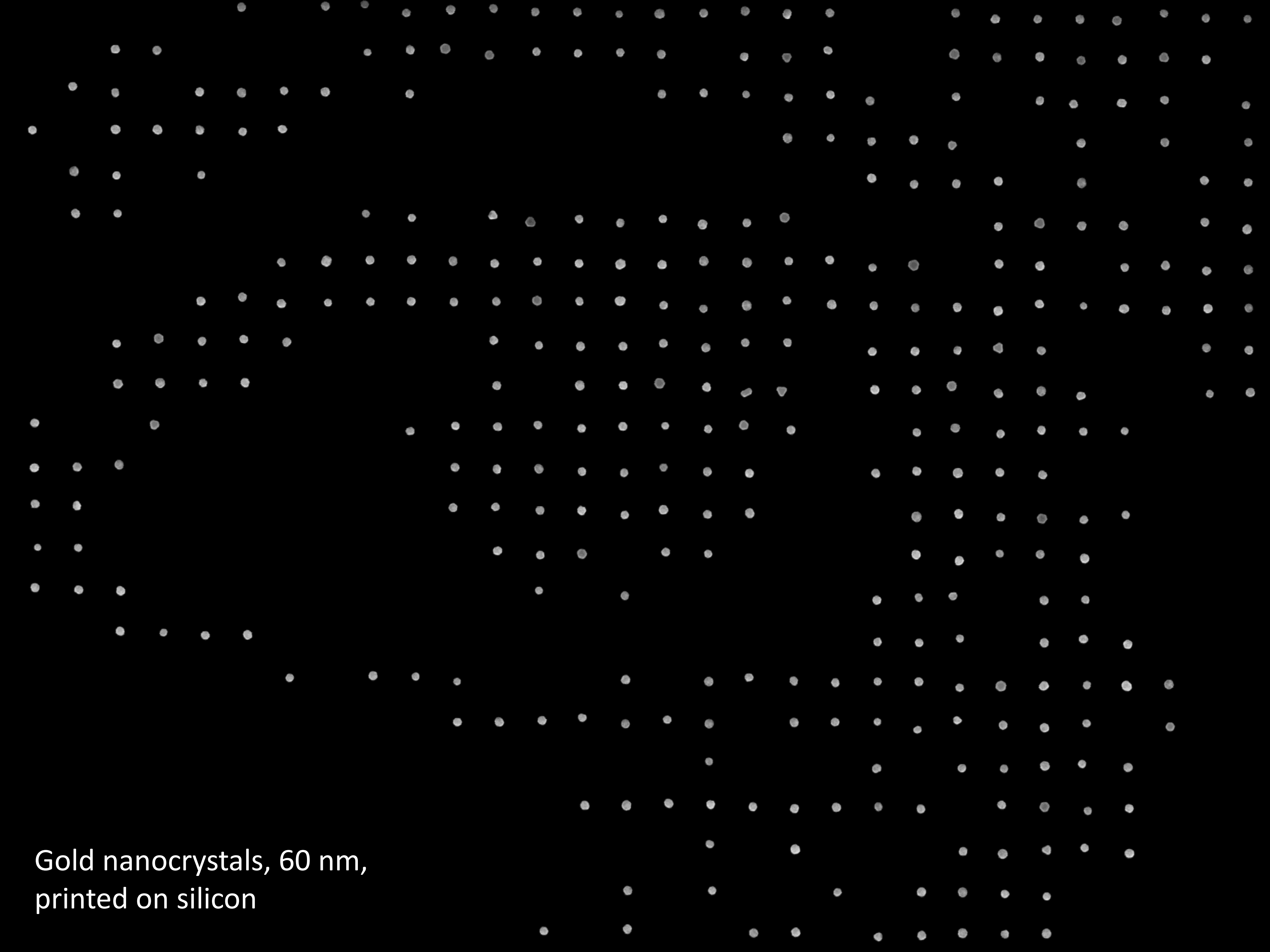



30 µm
Born, Blum, Munoz, Kraus, *Langmuir* 27 (2011) 8621



Kraus, Malaquin, Schmid, Riess,
Spencer, Wolf, *Nature Nanotech.* 2 (2007) 570





Gold nanocrystals, 60 nm,
printed on silicon

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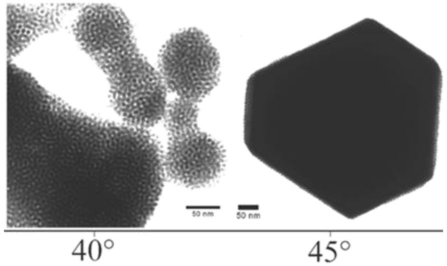

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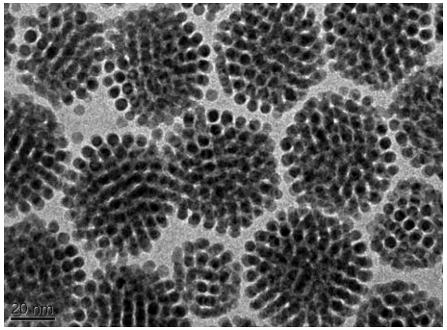

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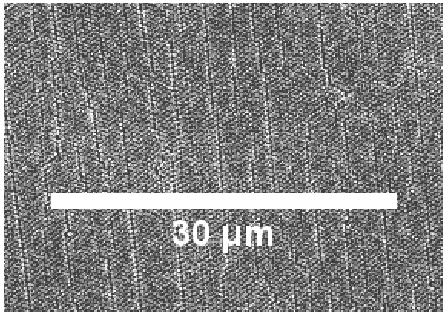

The team:

Philip Born, Christina Bauer, Jonas Becker, Daniel Brodoceanu, Jona Engel, Dominik Gerstner, Johann Lacava, Anika Weber, Anne Wonn

Collaborations: Tihamer Geyer (UdS), Patrick Huber (TUHH), Heiko Wolf (IBM), ...

Funding: DFG, DAAD, BMBF, AiF, INM

New Ideas. New Materials.

INM

Thank you!