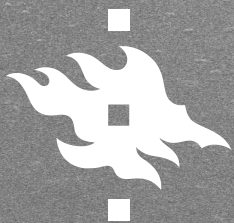
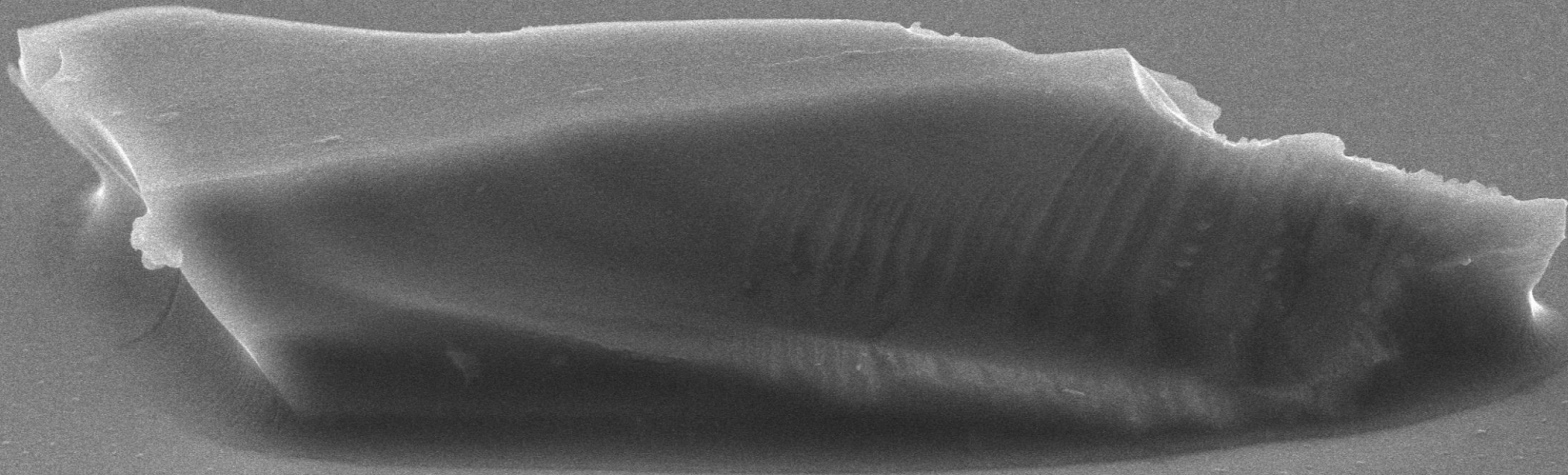


Superconformally selective nanocoatings by capillary condensation



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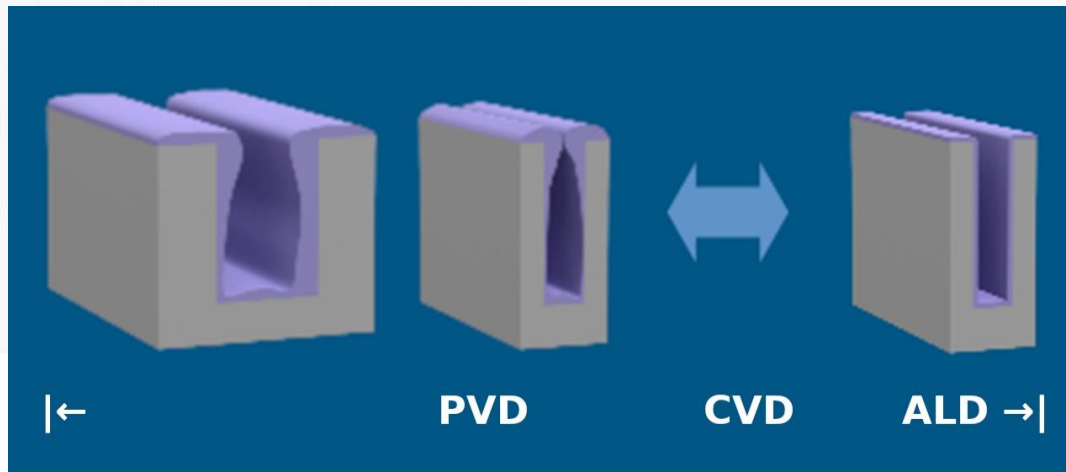
S4800 10.0kV 10.6mm x5.00k SE(M)

10.0um



Introduction: conformality

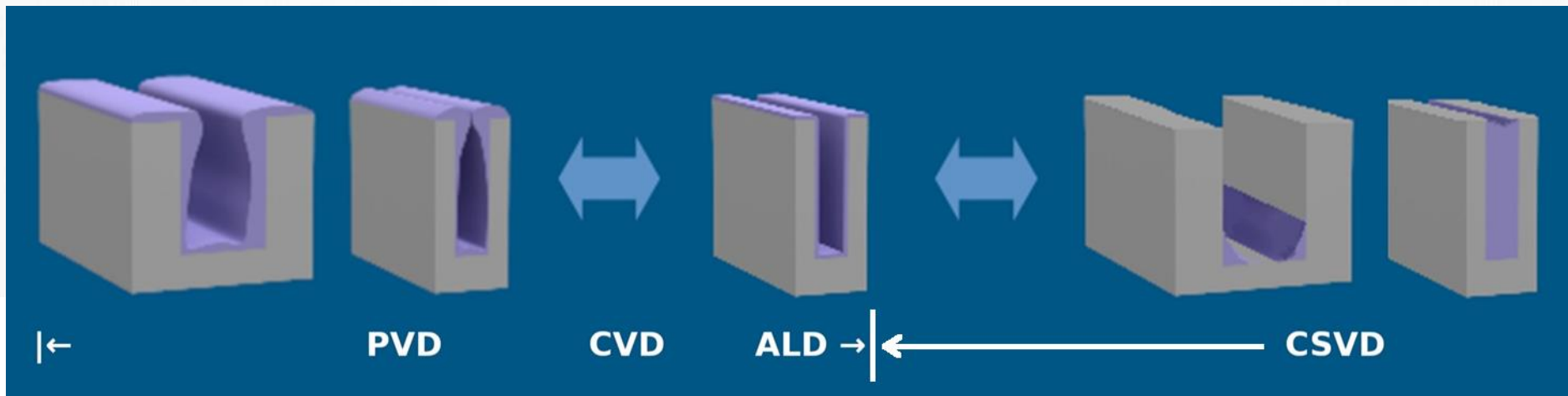
- In vapor deposition, coatings tend to grow thicker on open surfaces than in shadowed areas – internal vs external surfaces





Introduction: conformality

- In vapor deposition, coatings tends to grow thicker on open surfaces than in shadowed areas – internal vs external surfaces
- Extreme selectivity reversion with capillary condensation
 - Cavities stabilize liquid phase. The smaller the cavity, the larger deviation from the saturation pressure is possible without losing the liquid phase
 - Reagent distribution is allowed to settle before fixation
 - Curvature/Capillary Selective Vapor Deposition (CSVD)





Capillary condensation

- Kelvin equation defines the geometrical limit for CC

$$\ln \frac{p}{p_0} = -\frac{2\gamma V_L}{RT r_m}$$

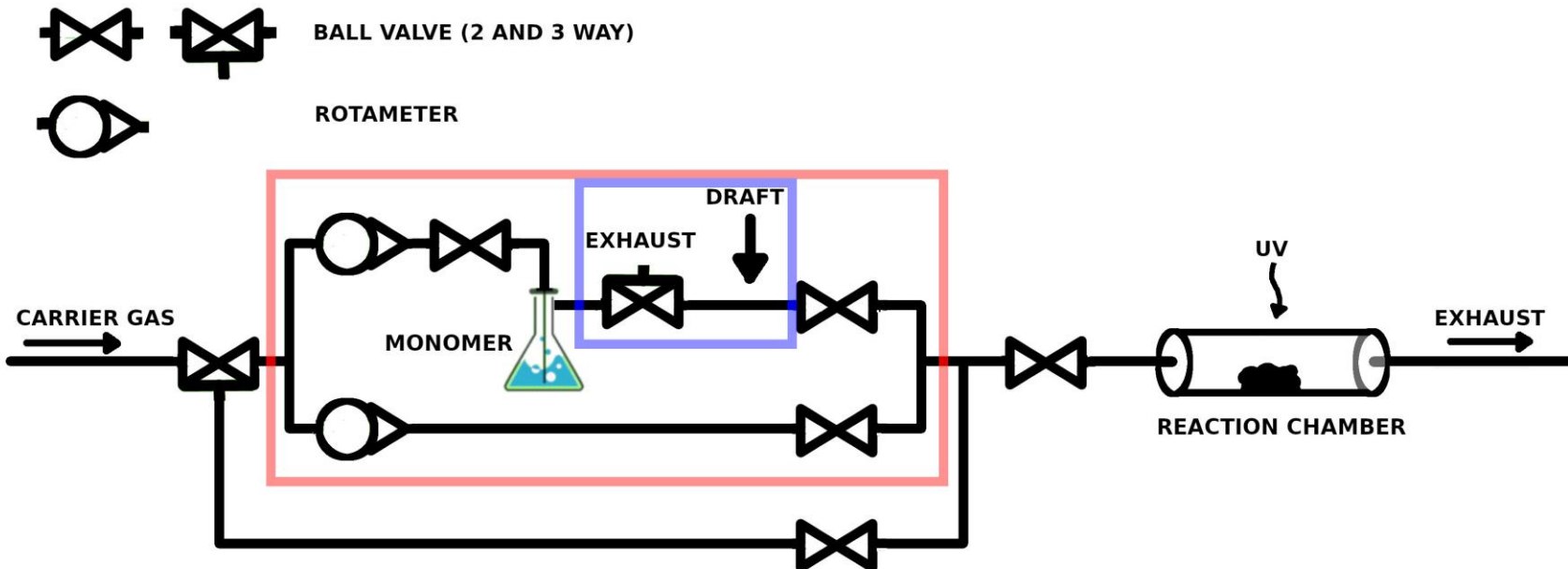
p/p_0 is relative pressure, γ surface tension, V_L molar volume and r_m mean radius of curvature of the liquid-gas interface

- Saturation ratio (SR) = p_m / p_{sat}
 - p_m is the partial pressure of the reagent and p_{sat} its saturation pressure in the given conditions
- Liquid-to-solid reaction is initiated once a gas-liquid equilibrium has been reached



SR control by gas feed mixing

- Carrier gas feed is split in two in a predefined ratio (red rectangle). One branch is saturated with a warm reagent before recombining the branches
 - Process is driven by slight overpressure from the carrier gas inlet
 - Saturation confirmed by condensation near the bubbler
 - (Meth)acrylates and styrene on glass, aluminum oxide and Ni. Initiated by UV (254 nm)

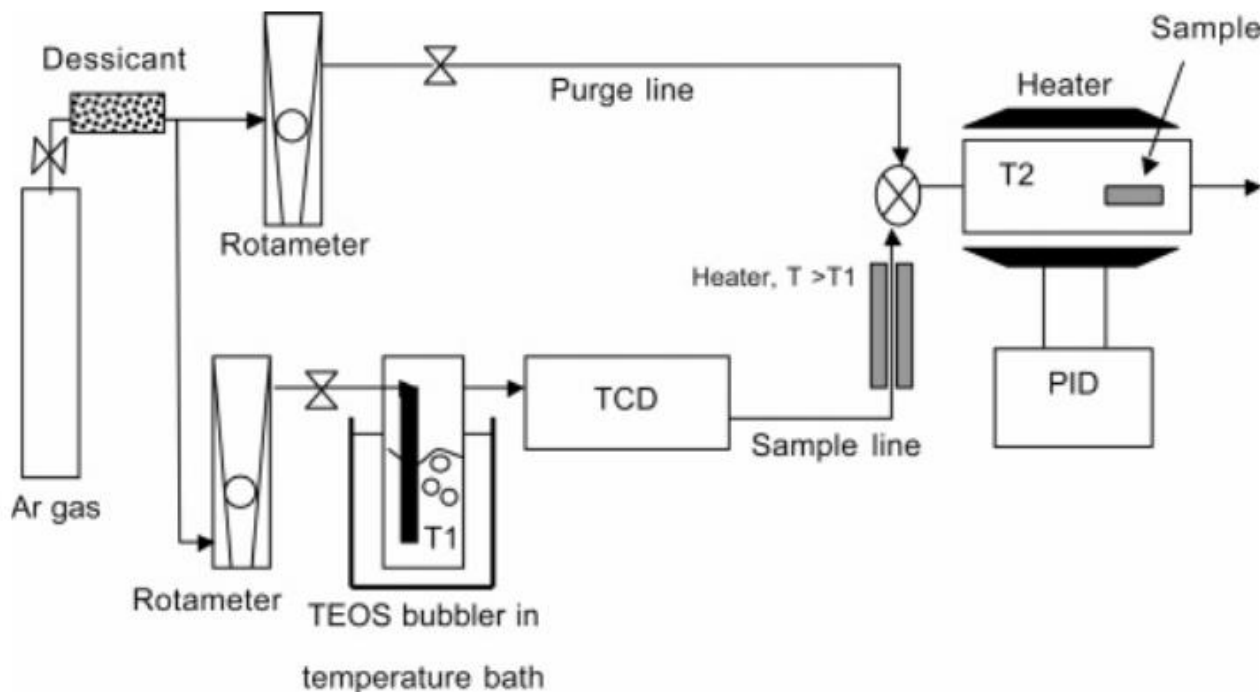


Lovikka et al., Mater. Horiz. 2019, *in press*.
DOI: 10.1039/C8MH01523F



SR control by temperature

- Temperature profile controlled SR
 - Assumed: no reagent saturation. Relatively complex computer-assisted control
 - Silica between titania nanoparticles, initiated by exposure to moisture
 - The reactor line would likely support our approach (previous slide)

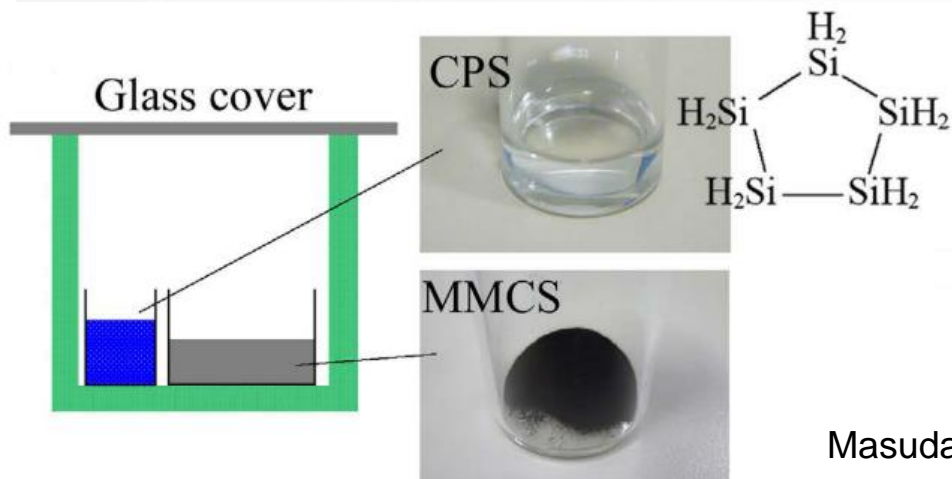


TEOS: Tetraethyl orthosilicate (liquid)
TCD: Thermal Conductive Detector
PID: temperature controller

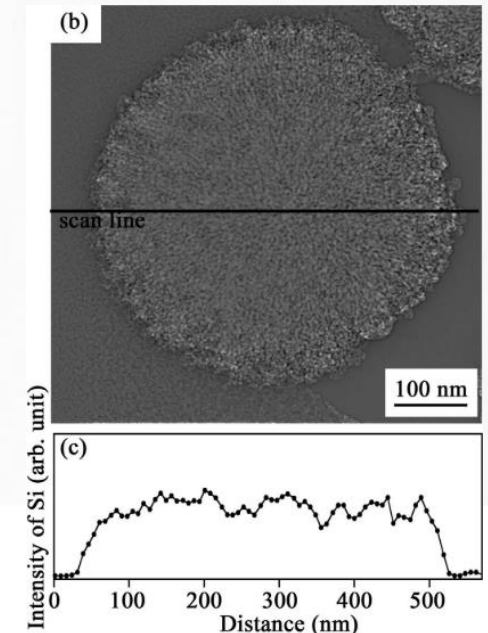


Container with pressure venting

- Simply a container with a pressure release mechanism
 - Liquid reagent added inside in a predefined amount
 - Inefficient SR control: There is reagent loss during pressure release. In addition, some of the reagent will react before evaporation, and thermal initiation may cause evaporation
 - Cyclopentasilane on porous carbon initiated by heating → porous silicon filling



Masuda et al., Sci. Rep. 2016, 37689

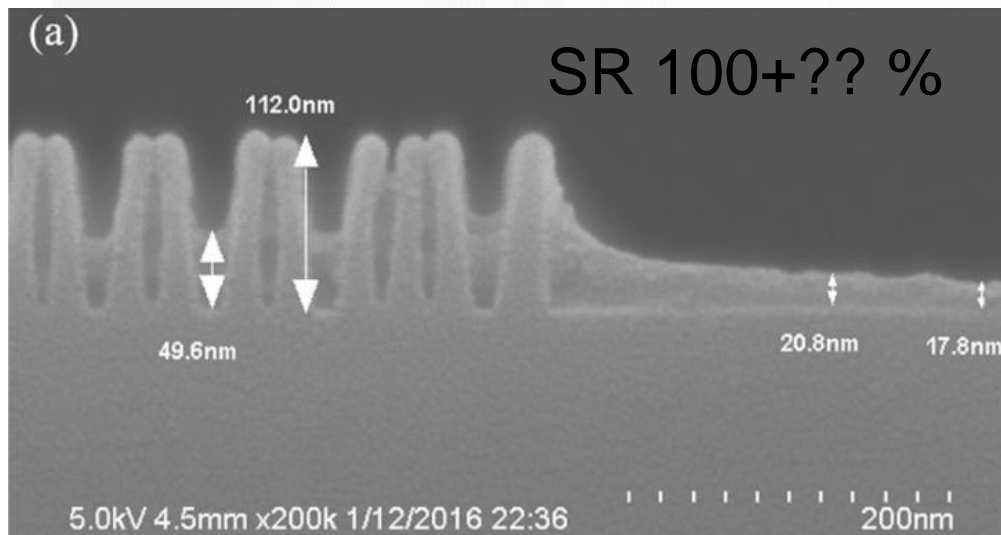




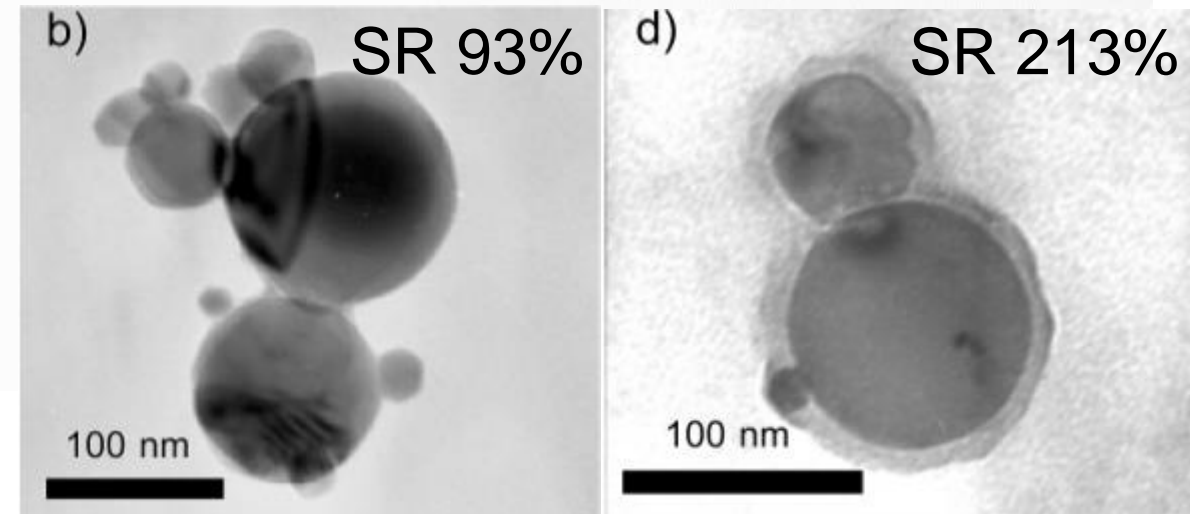
CC with initiated CVD reactor

- Neo-pentyl methacrylate in initiated CVD reactor (vertical flow) with delayed initiation with *t*-butyl peroxide (Ichiki et al. 2017)
 - Non-ideal conditions: supersaturation because of substrate cooling?
 - Compare to Kim&Ehrman (slide 6): controlled temperature differences lead into different SR's and different conformalities
- Many iCVD processes at <100% SR but with simultaneous initiation

Ichiki et al. Thin Solid Films 2017, 23



Kim & Ehrman, Langmuir 2007, 2497

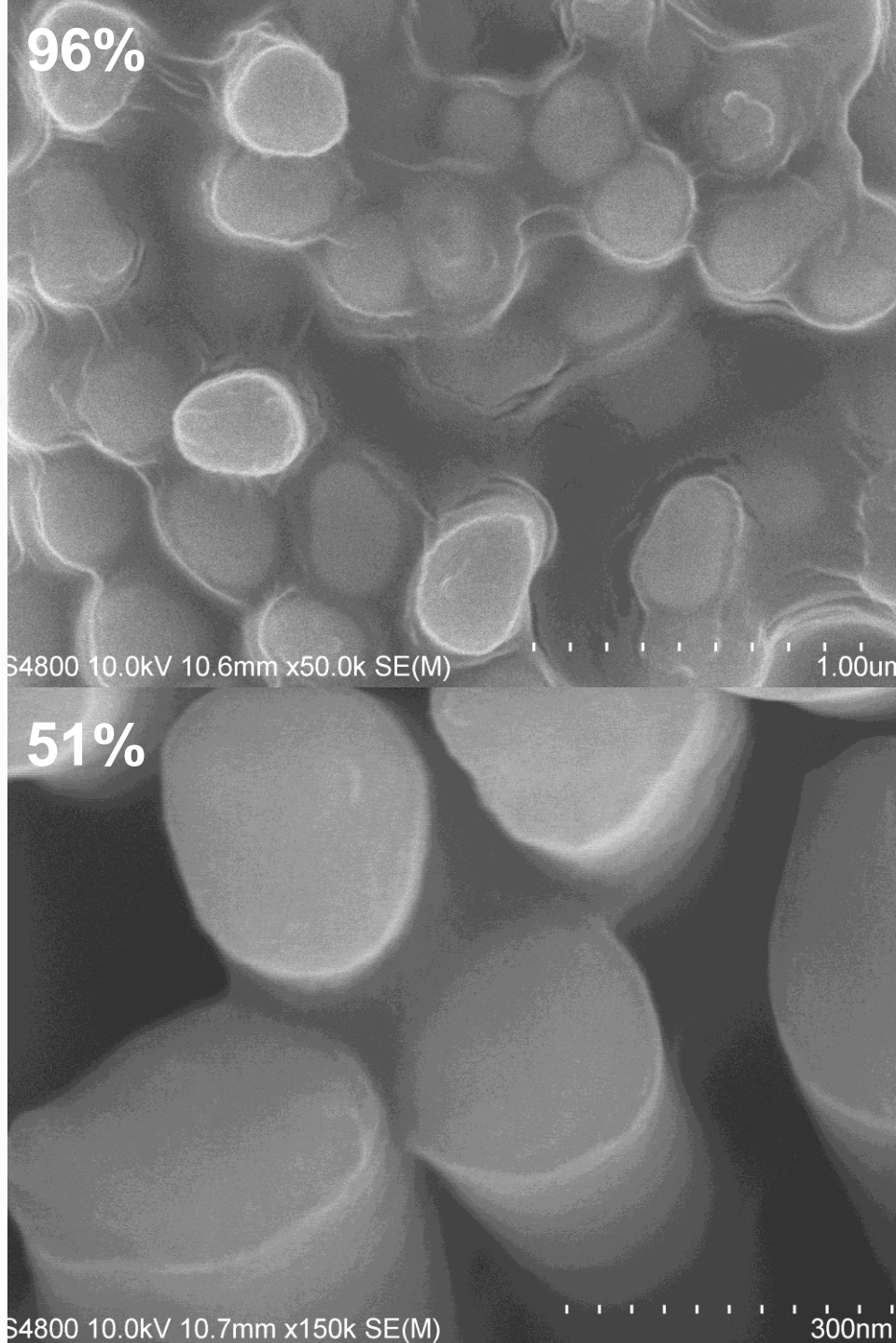
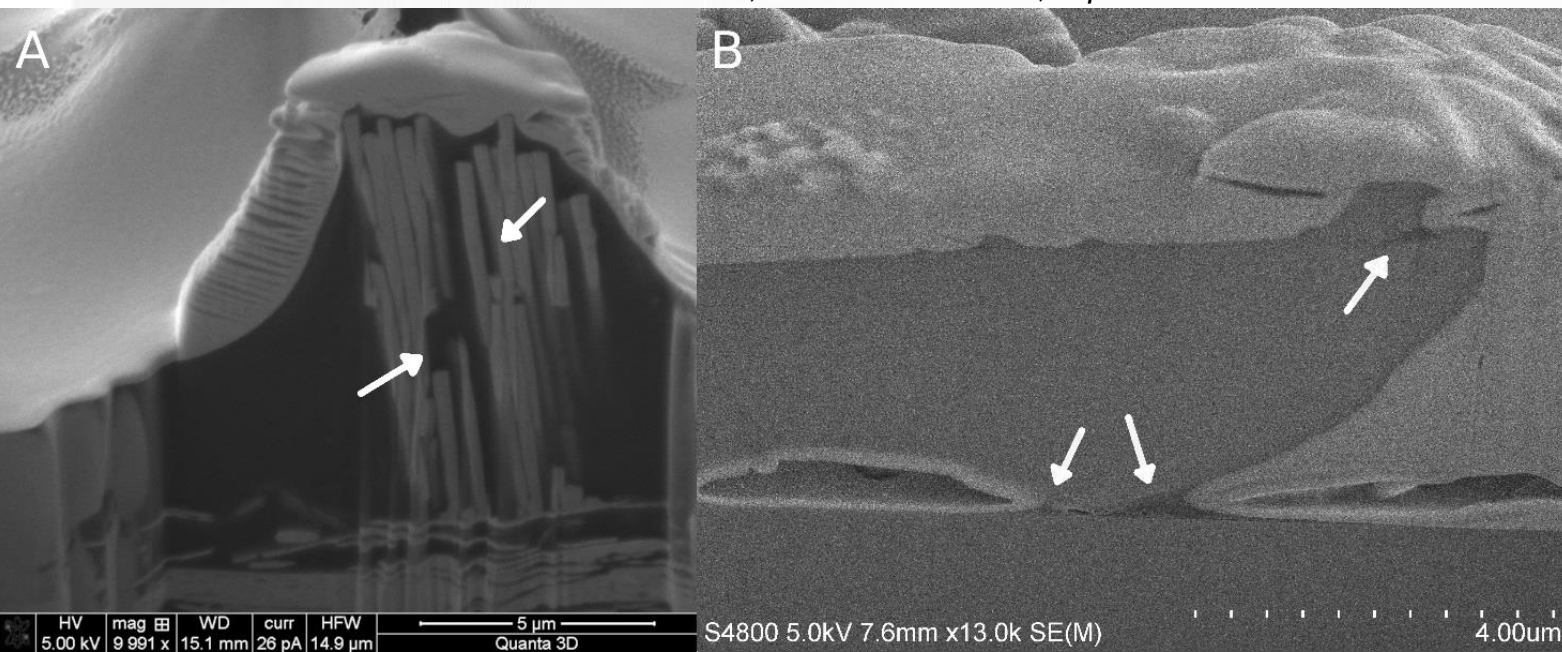




Demo with ethyl acrylate

- Lower SR caused poly(ethyl acrylate) to fill only smaller spaces
- Cross-sectional images show exceptionally good filling between Ni nanopillars (A) and in cavities between glass surfaces (B) (white arrows)

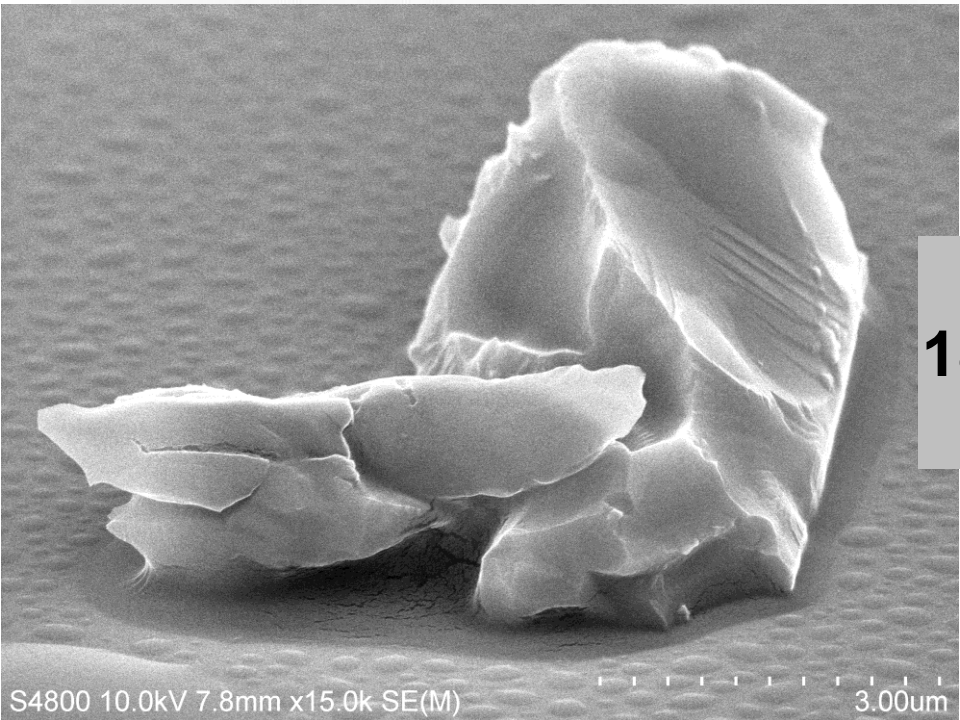
Lovikka et al., Mater. Horiz. 2019, *in press*. DOI: 10.1039/C8MH01523F





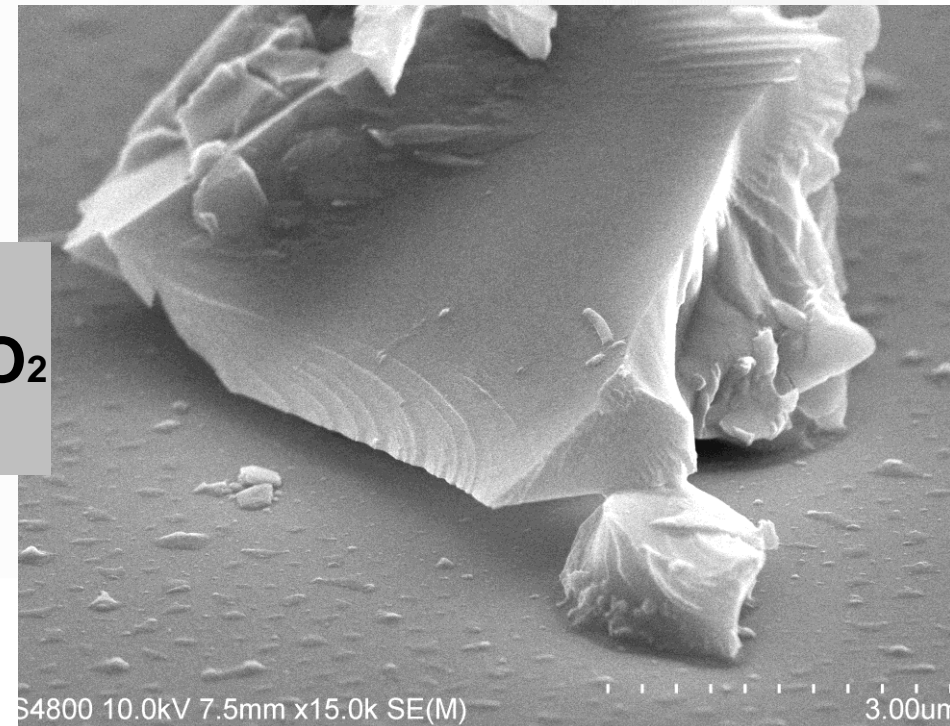
O_2 : inhibitor in gas-liquid interfaces

- Adding oxygen reduced p(EA) growth. As a gas phase additive, it prevents surface growth better than bulk liquid polymerization
 - O_2 /monomer ratio is lower in liquid monomer than at interfaces
 - O_2 favors CSVD growth mode over (p)iCVD one
 - In addition, UV+ozone etching could be happening



pEA on glass
18% (no O_2) \rightarrow 50% + O_2
15 min UV

Lovikka et al., Mater. Horiz. 2019, *in press*
DOI: 10.1039/C8MH01523F

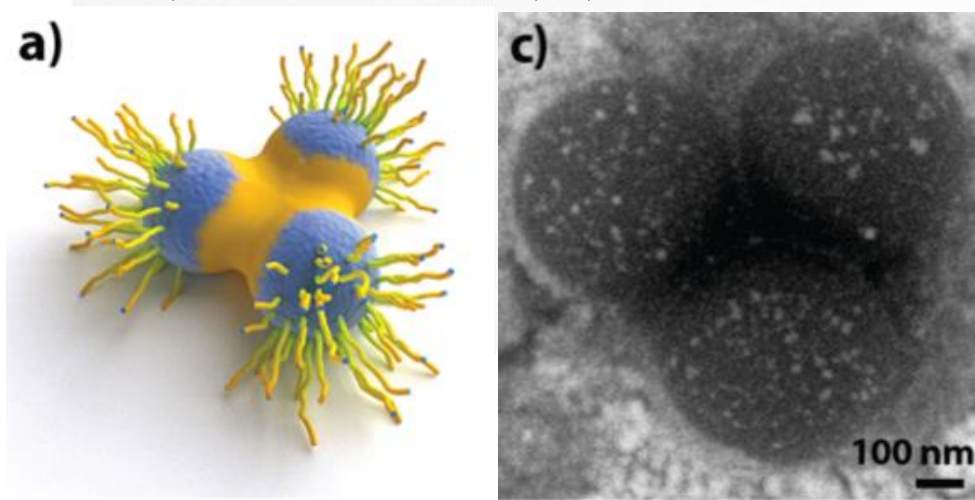




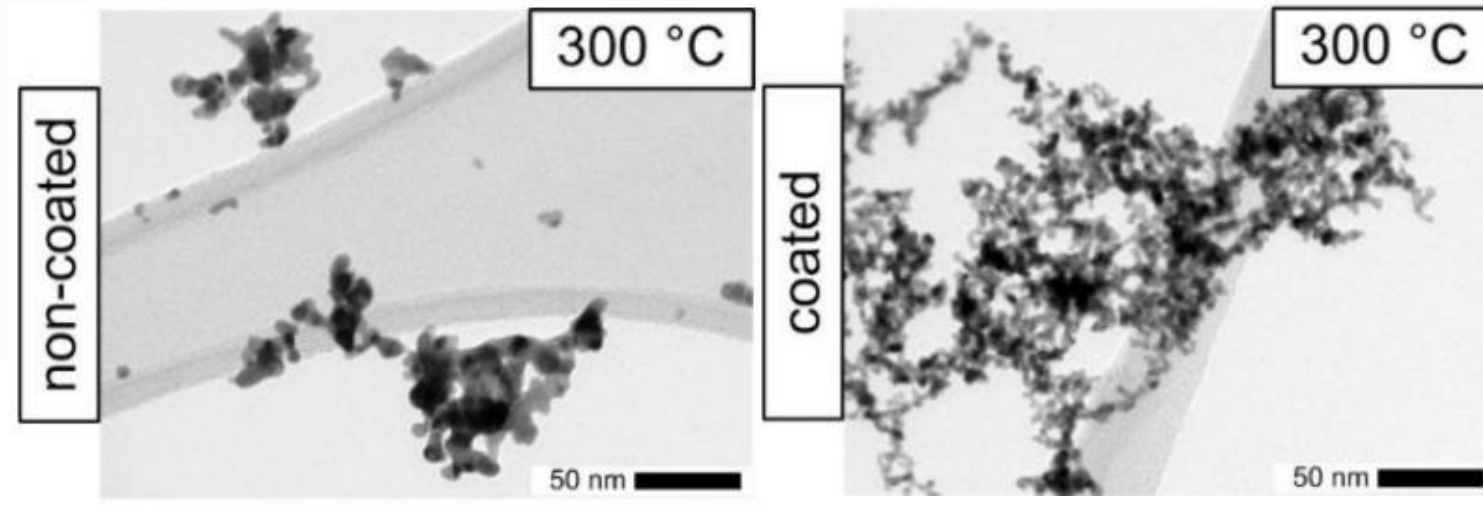
Advantages of CC in aerosol treatment

- Location-selective functionalization
 - a) Schematic of an anisotropically functionalized nanoparticle cluster. c) Au nanoparticles (white spots) attached on non-covered surfaces of amine-functionalized PS particles. (Li&Stein 2019)
- Stabilization with minimized property losses
 - Pt nanoparticles after SiO_x coating. Stability against sintering was increased while surface coverage was minimized -> minimized losses in photocatalytic activity at elevated temperatures. (Post et al. 2016)

Li & Stein, J. Am. Chem. Soc. 2009, 29, 9920



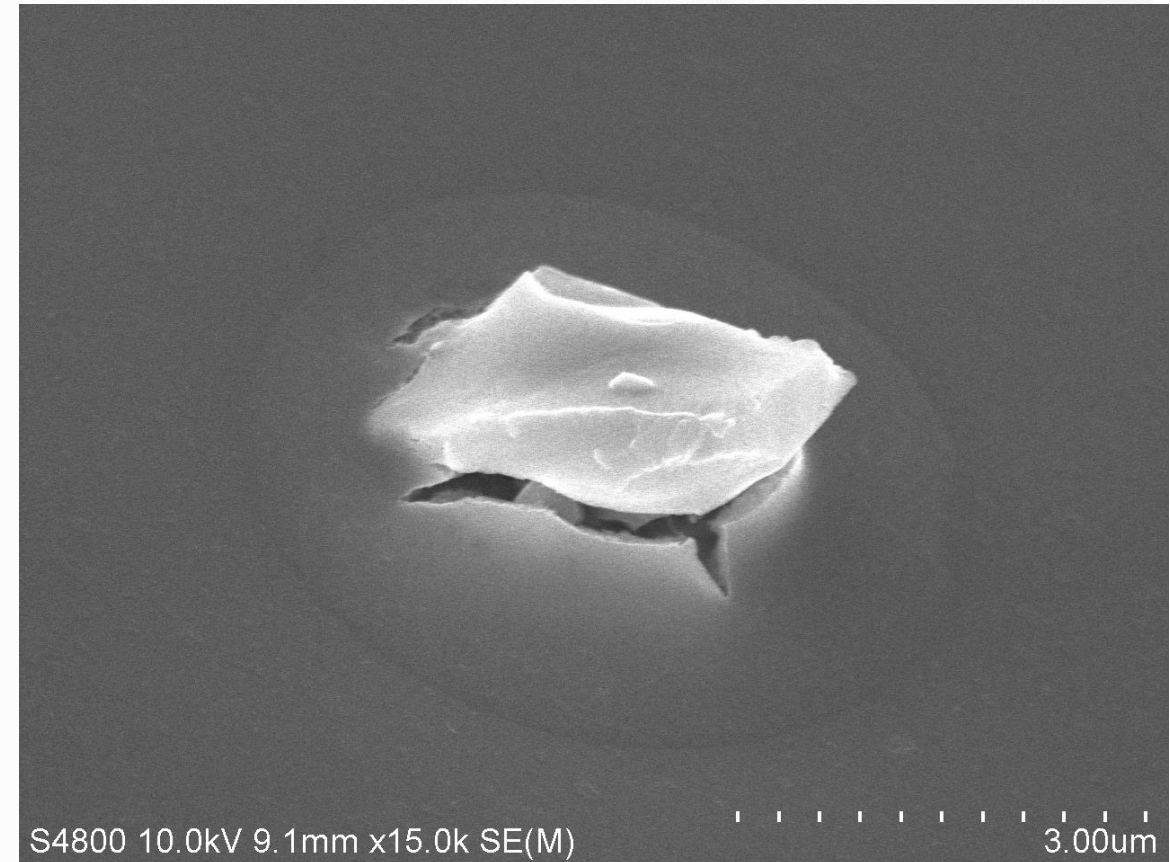
Post et al., Nanomaterials, 2016, 5, 91





Current challenges and future ideas

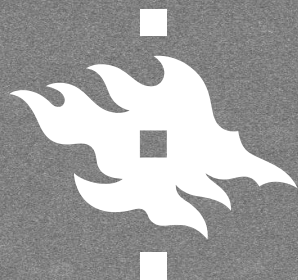
- Polymer as template in vapor phase infiltration (VPI)
 - Optionally subsequent calcination
- Utilizing inherent properties of nanostructures in other ways than CC
 - Plasma. Other ways of electroinitiation?
- CC with immiscible liquids
- Review article being planned
 - The field is new and small but scattered. Only a few citations between groups. Research goes unnoticed
 - If you are about to prepare a manuscript in the field, let me know



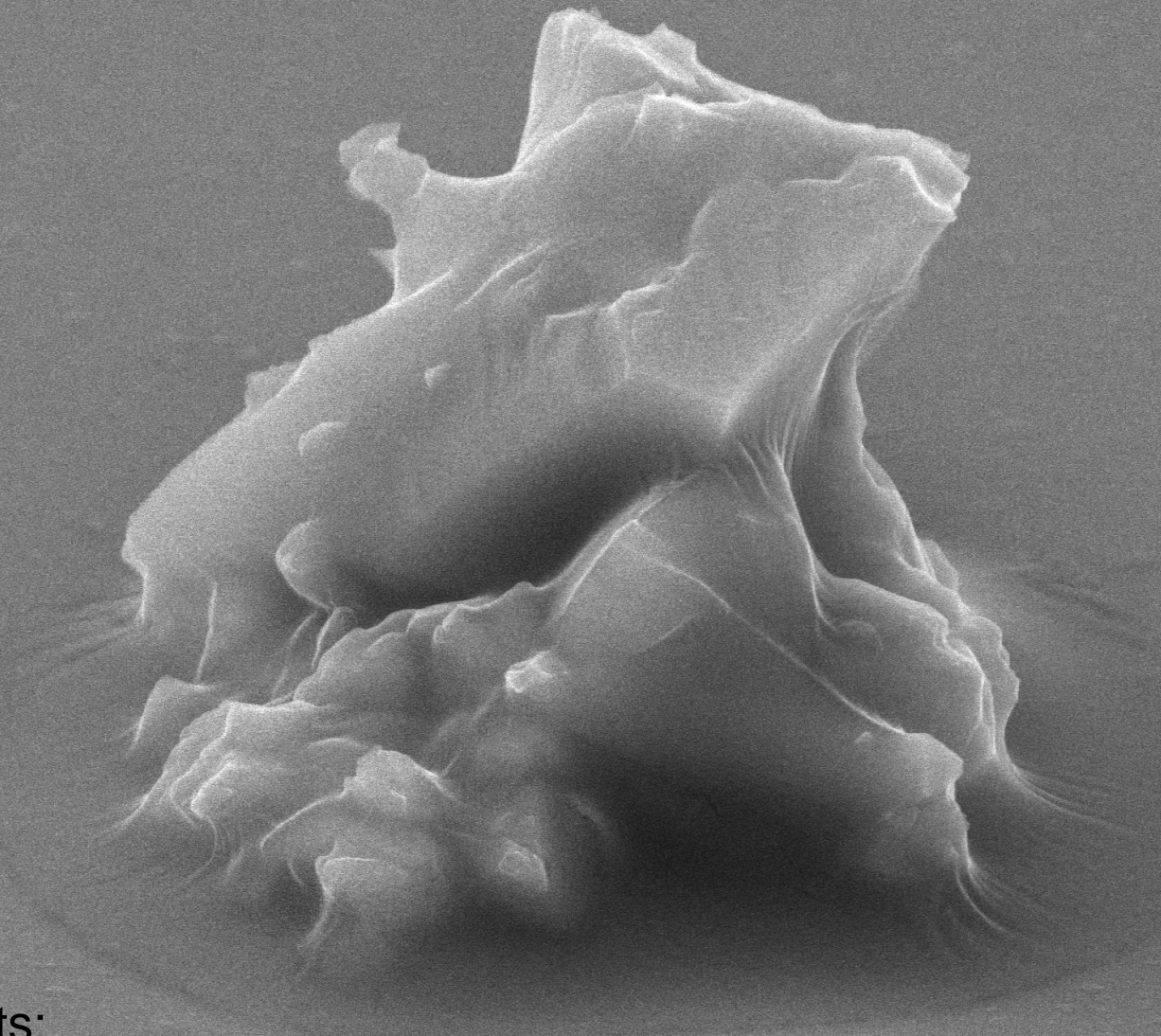


Conclusions

- With CC the surfaces are coated starting from the hardest-to-reach areas
 - Thermodynamic equilibration and surface curvature as a growth limiting factor (cf. ALD)
 - Underresearched field!
- CC can be utilized with a simple reactor setup and relative ease
 - Gives ideas how to utilize current reactors in new ways
 - Gives ideas on more flexible reactor builds and improving old designs?
- Might lay the groundwork for a new complementary paradigm for selective vapor deposition in nano and micron scale
 - Former issues, e.g. O_2 , may instead be advantageous in CSVD
 - Separate optimization for mass transfer and reaction
 - No need for pumping or expensive apparatus
 - Scales controllably down to the nanoscale
 - Etc



¿Q&A?



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3.00um