Istituto Nazionale di Fisica Nucleare

Recent activities in TITAN Lab

Towards autonomous synthesis of VACNTs

Luca Cecchini

PTOLEMY/ANDROMeDa Meeting

September 12°, 2025

“Historical” recap

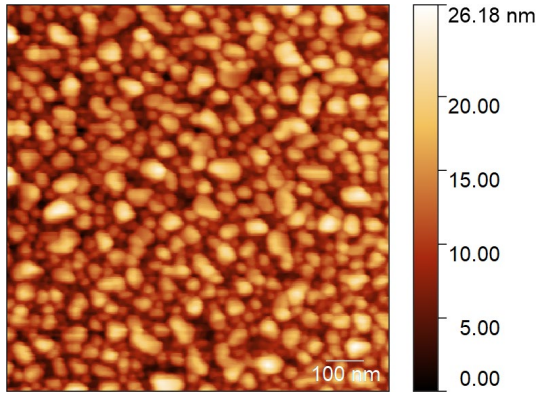
PTOLEMY

TITAN LAB

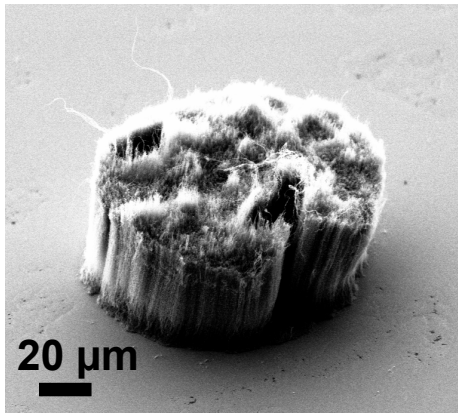
LAboratorio di Spettroscopie Elettroniche e di Correlazione

time

PTOLEMY Italia meeting
17 Febbraio 2025



Internal meeting
12 Settembre 2025



Outline

- Non-lithographic synthesis of VACNTs
- E-beam evaporator
- Iron nanostructuring: dewetting analysis
- TCVD growth: the very first problem
- Substrate cleaning and surface activation
- Increase catalyst reactivity: Plasma dewetting and/or hydrogen flux during growth
- Future activities

Non-lithographic synthesis of VACNTs

0. Substrate selection

Diffusion barrier (SiO_2, Al_2O_3, ...)

Mechanical support (Silicon, ...)

1. Cleaning protocol

2. Catalyst deposition

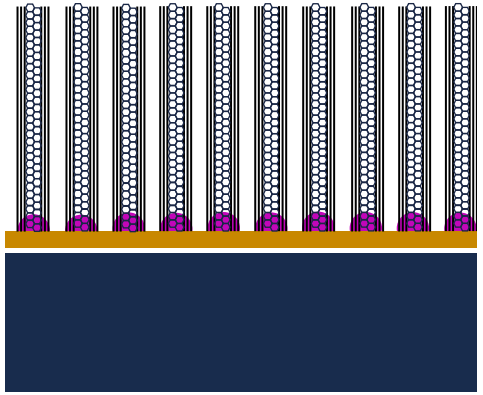
E-beam evaporation (Fe, ...)

3. Dewetting

H_2 reduction

Heat up (720°C, ...)

4. CVD Synthesis (C_2H_2, ...)



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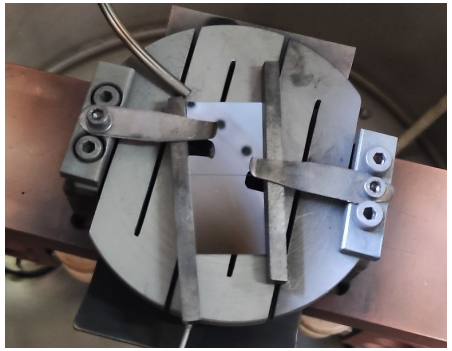
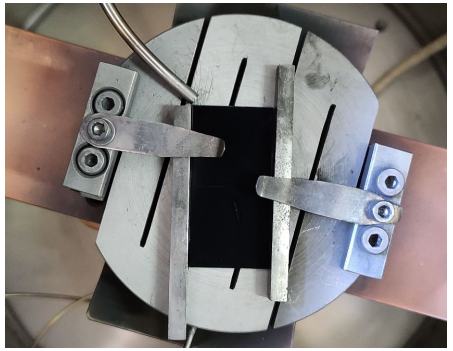
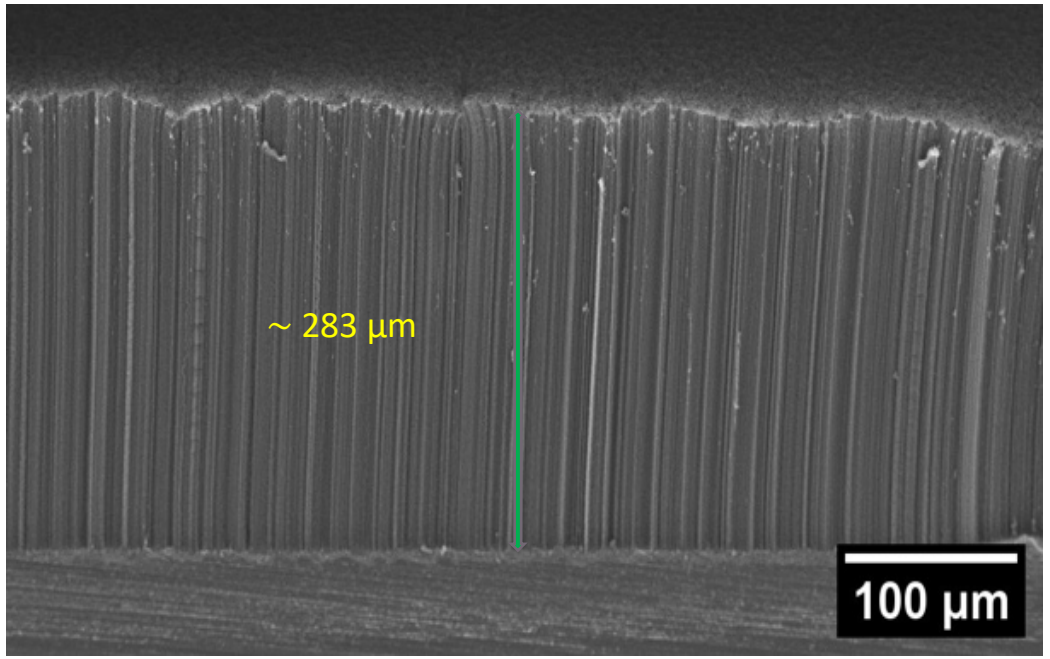
Electron beam evaporator

Fe deposition protocol: PoliFab@PoliMi

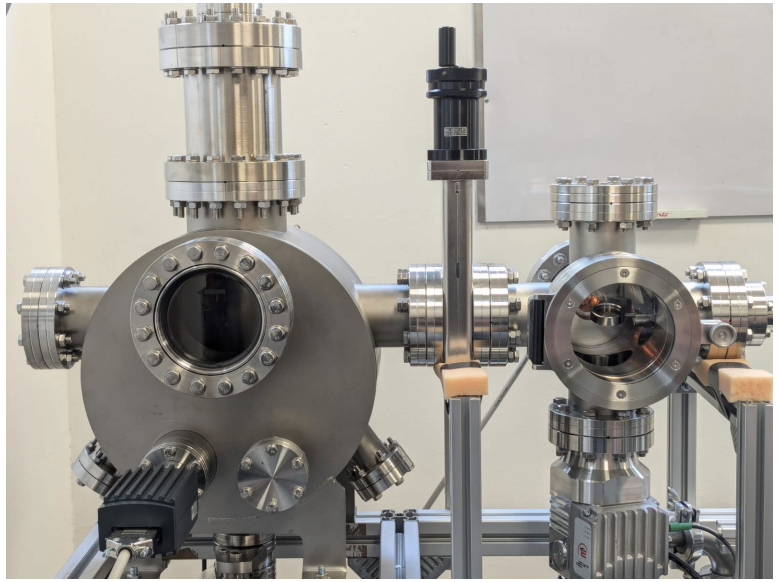
- **Environment:** Cleanroom ISO6
- **Substrate:** Si/SiO2
- **Cleaning:** RCA1
- **Evaporation:** 3nm Fe
- **Transport:** Kitchen vacuum







E-beam evaporator @TitanLab



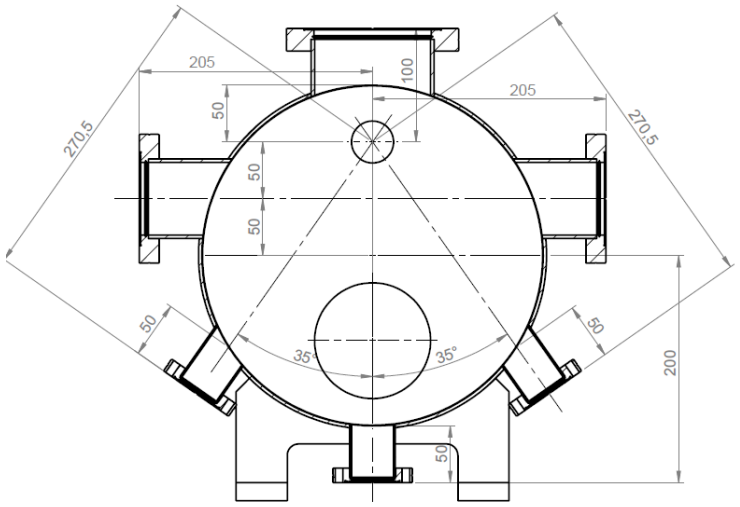
Specifications

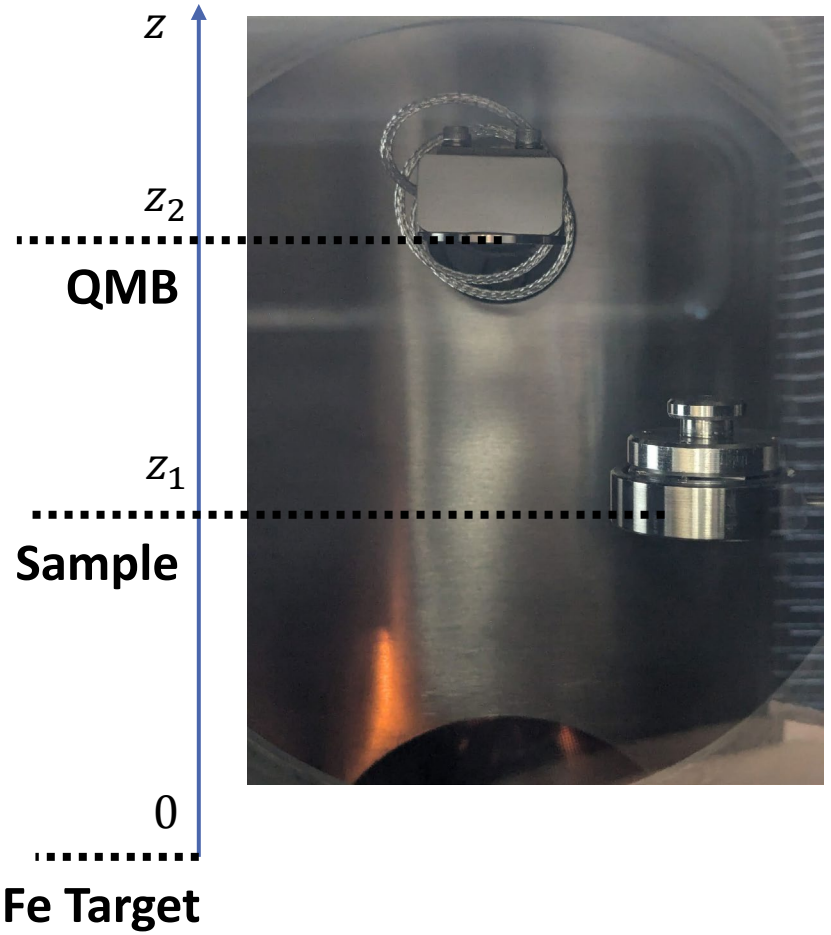
- **Sample dimension** : up to 2×2 cm^2
- **Deposition rate** : Quartz Microbalance
- **Bake-out**: Filament and target 250°C for 3h
  Chamber 110°C for 48h
- **Operation pressure**: 1×10^{-9} mbar
- **Single source**: Fe 99.95%
- **Filament**: Thoriated (1%) tungsten
  Full autonomous technical support
- **Angle aperture**: 6.9°

Calibration QMB

Deposition Rate

$$\phi(z_1) = \phi(z_2)\left(\frac{z_2}{z_1}\right)^2$$



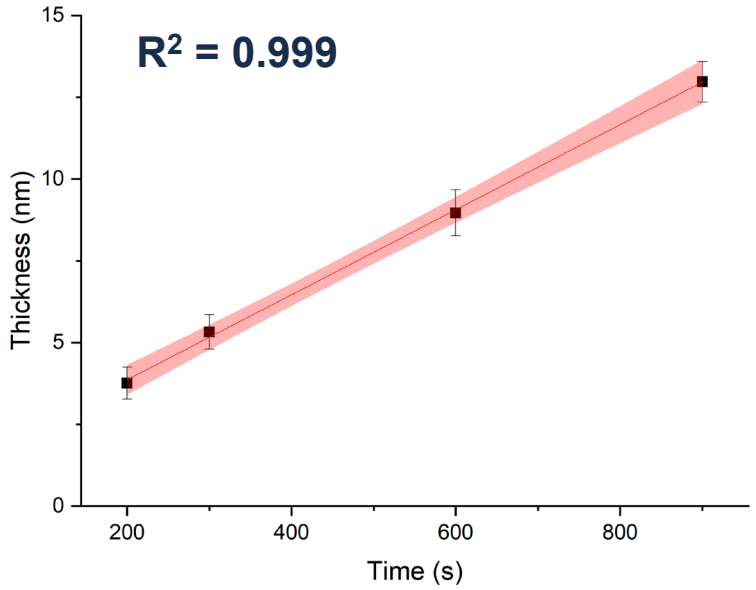


Calibration QMB

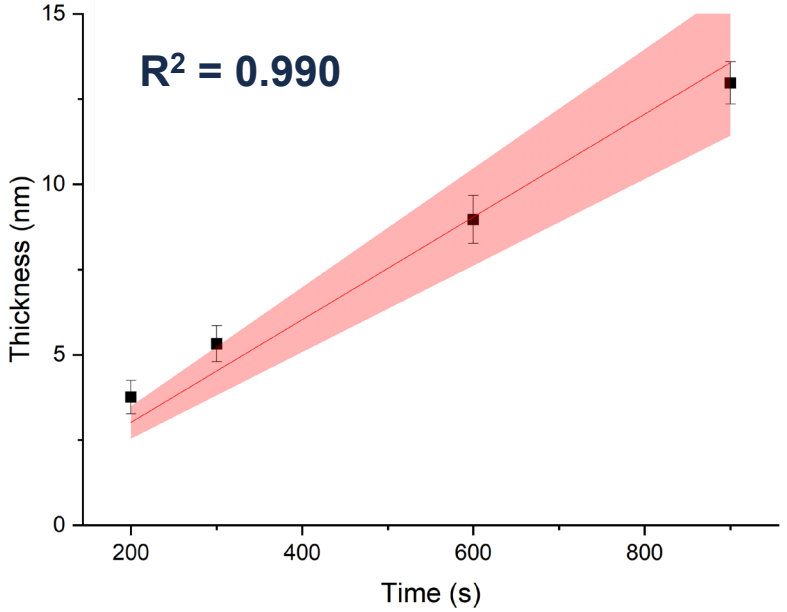
Geometrical estimation

$$\phi(z_1) = \phi(z_2)\left(\frac{z_2}{z_1}\right)^2 = 0.05 \pm 0.01 \frac{\text{Å}}{s}\left(\frac{132}{82}\right)^2 = 0.13 \pm 0.03 \frac{\text{Å}}{s}$$

Linear fit with free intercept $\phi(z_1) = 0.130 \pm 0.002 \ \frac{\text{Å}}{s}$



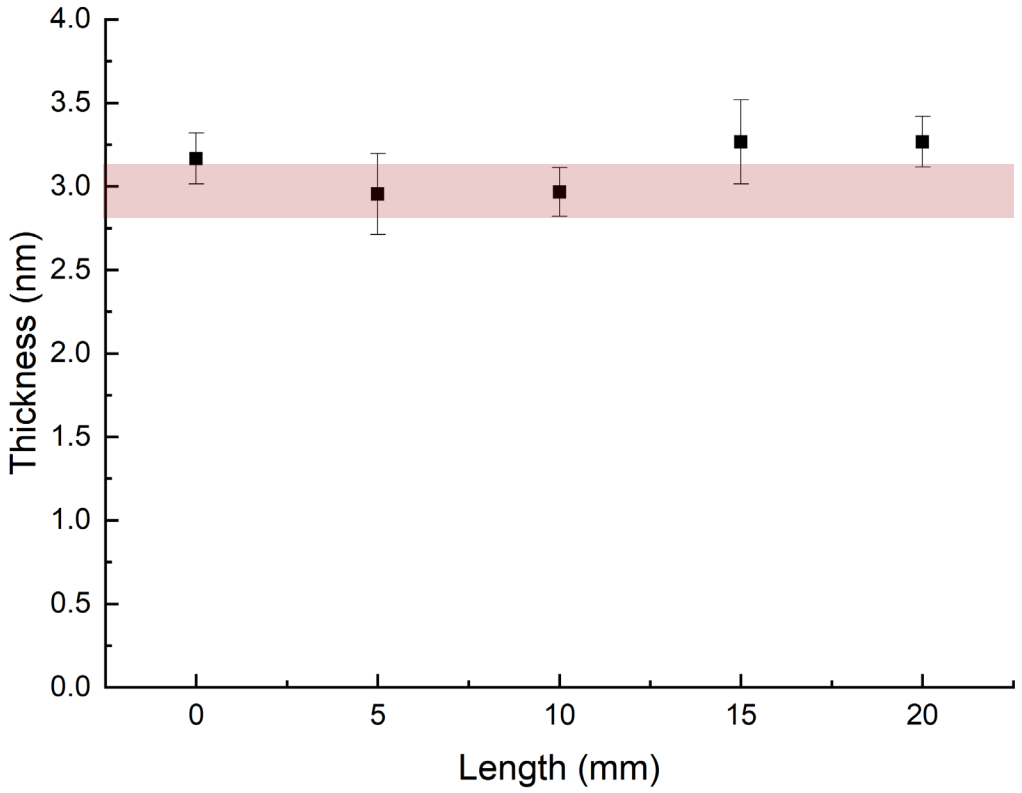
Linear fit with fixed zero intercept $\phi(z_1) = 0.150 \pm 0.007 \ \frac{\text{Å}}{s}$



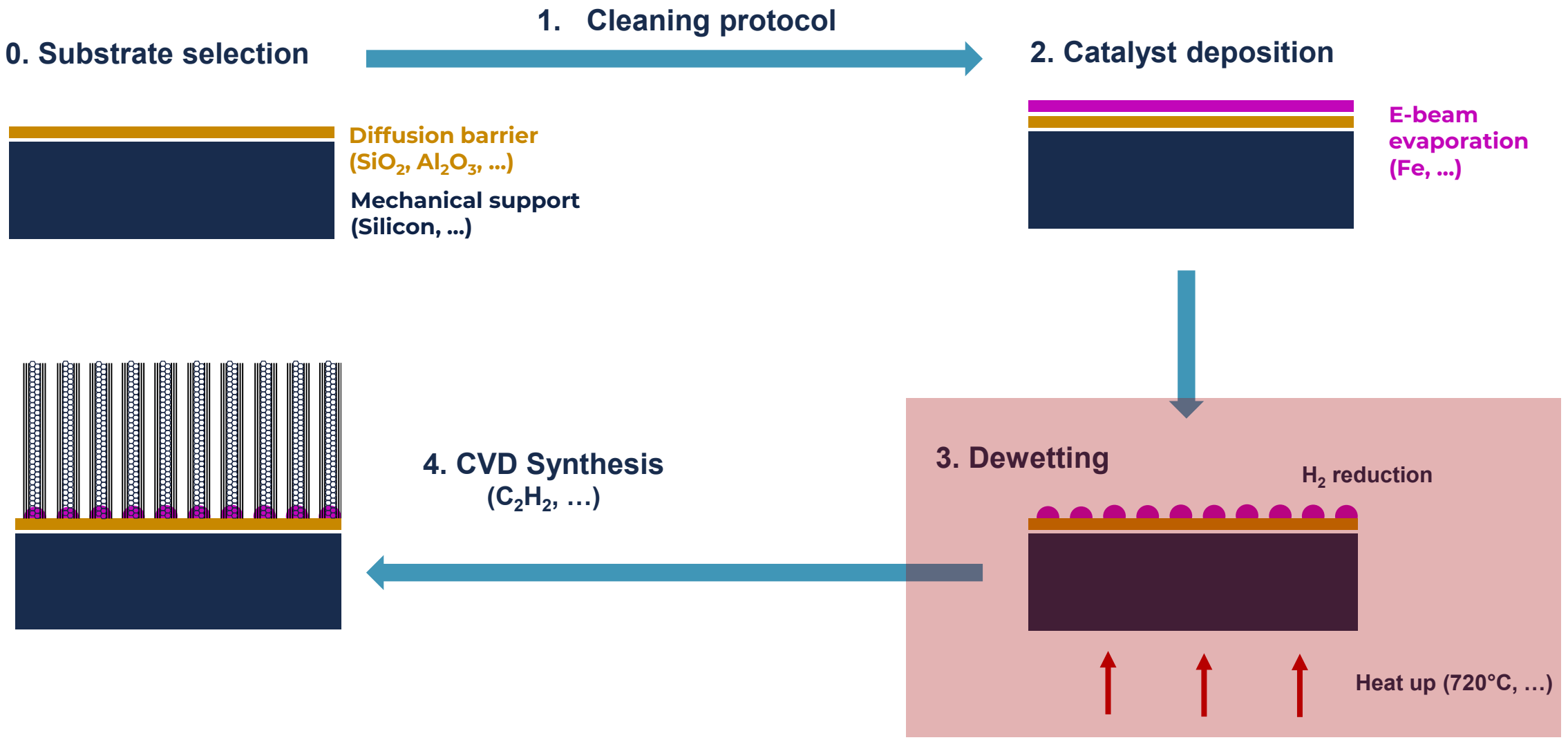
Uniformity Test

There is no statistically significant difference. **Uniform evaporation**.

Increase sensitivity using **ellipsometry**, instead of AFM.



Non-lithographic synthesis of VACNTs



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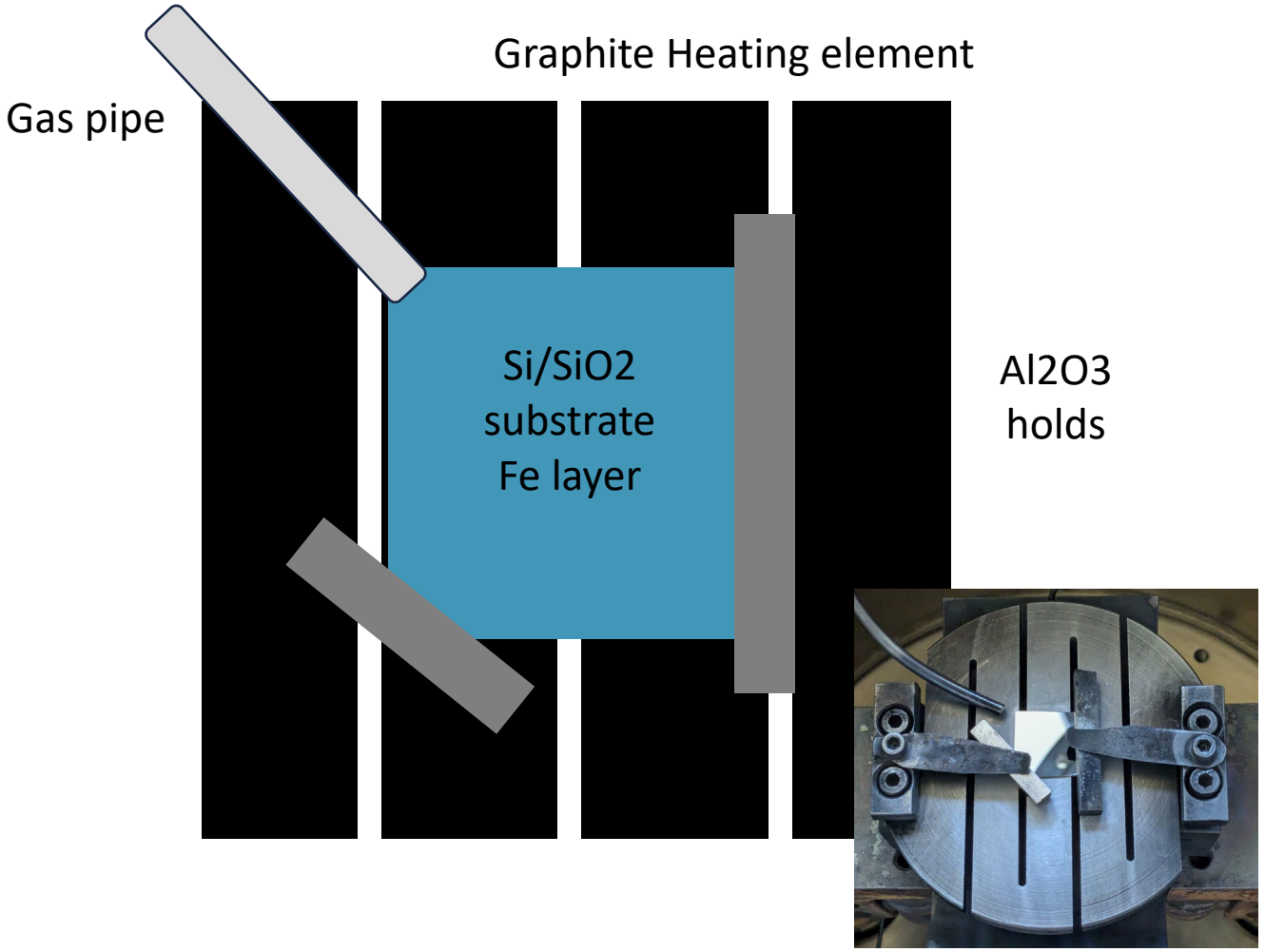
Iron Dewetting

Iron nanostructuring protocol

- Emulate the CleanRoom protocol under chemical hood: RCA1
- Use the standard dewetting protocol:
  720°C for 4mins
  flush H_2 with a linear ramp
  from 10^{-1} mbar to 8×10^{-1} mbar
- Fix sample dimension and holder position to guarantee same temperature gradient.



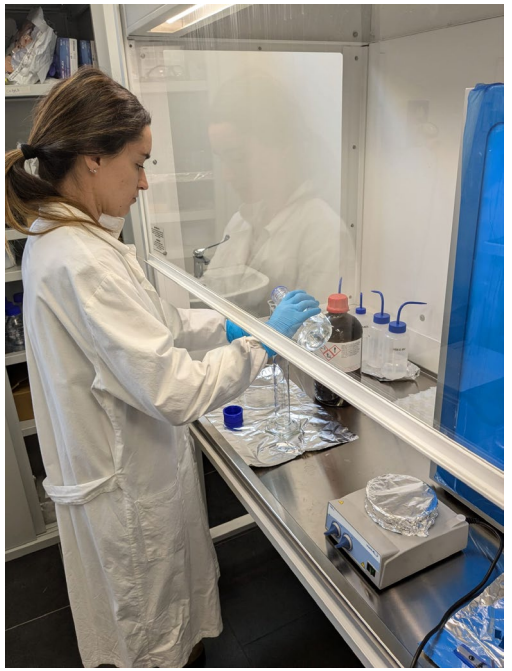
Cleaning protocol: RCA1

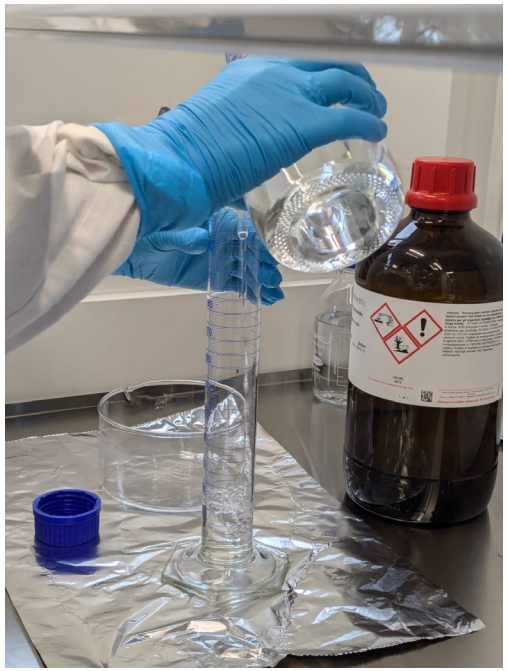
- 150ml DIW
- 30ml Ammonium Hydroxide (30%)

Heat the solution @ 70°C with heating plate (Value 2-3 for 5mins).
Remove the solution from heating plate.

Add:
- 30ml Oxygen Peroxide (28%)

Put the silicon wafer faced-up in the solution for 15mins.
Wash substrate with MilliQ.
Flush with nitrogen.





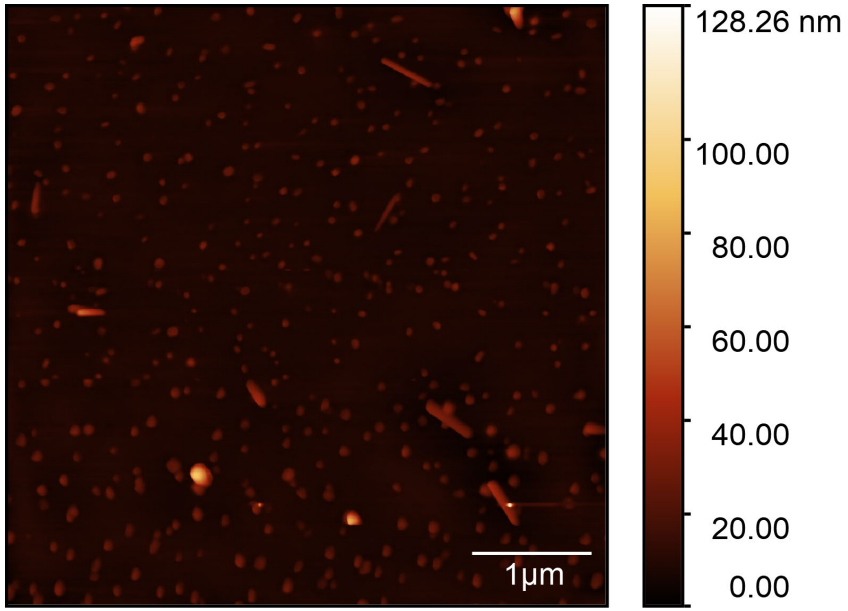
Comparison between cleaning protocols

From thermodynamic point of view, the minimum droplet radius $\boldsymbol{R}_{min}$ is

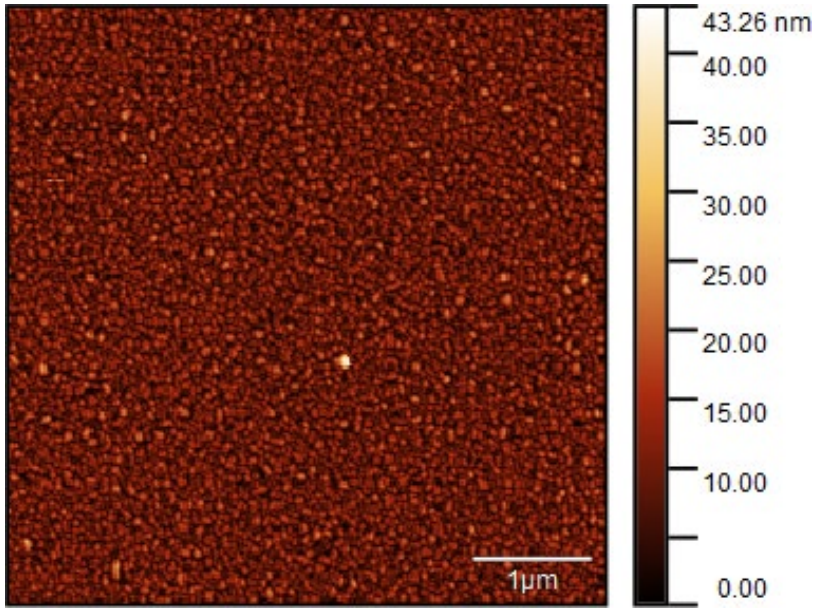
$$R_{min} = \frac{2 V_l}{R \cdot T \cdot \ln(s)} \cdot \sigma_{lv}$$

V_l → molar volume of the droplet
s → degree of supersaturation
σ_{lv} → surface tension at the liquid-vapor interface

Acetone + IPA + MilliQ

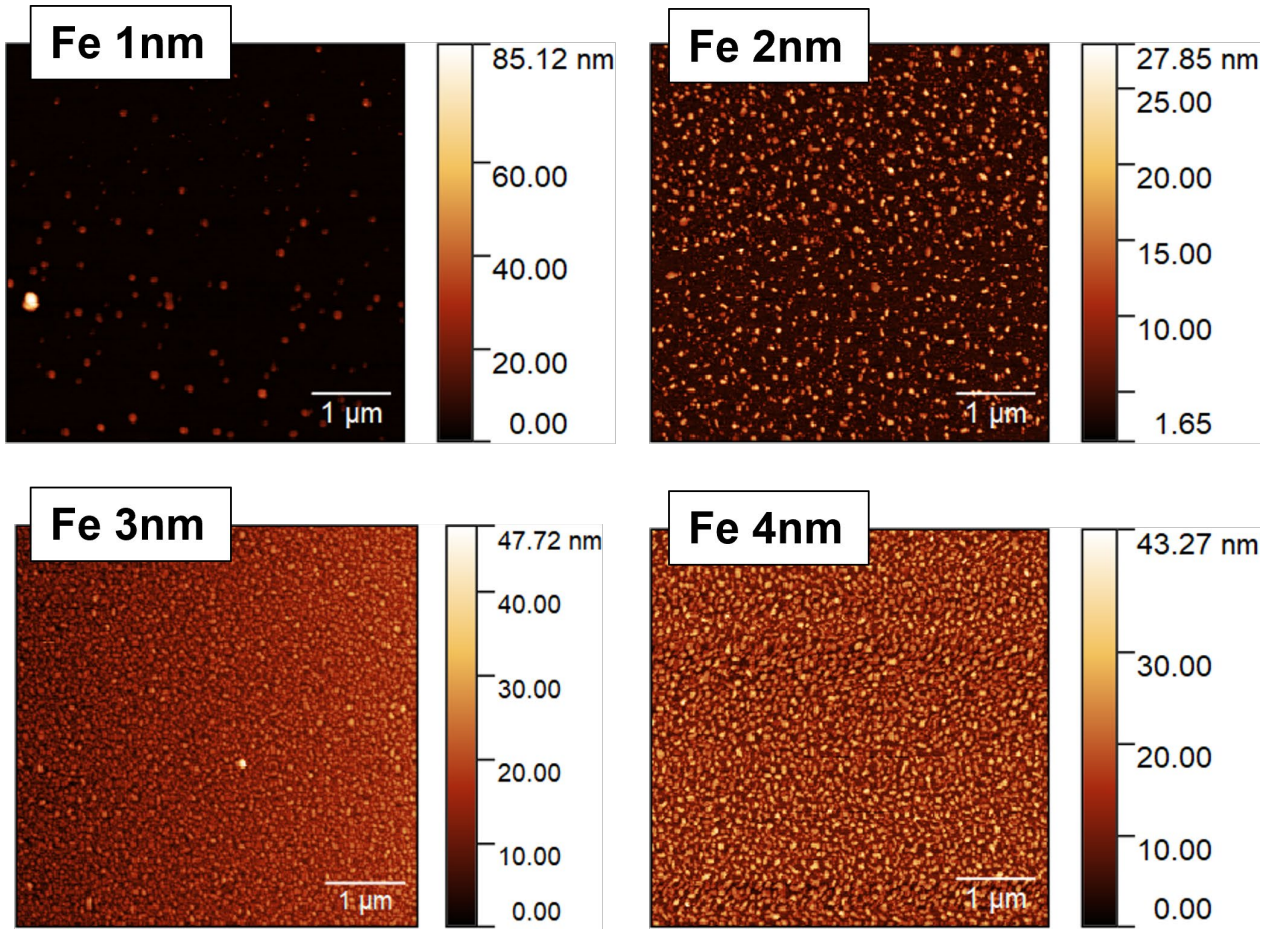


RCA1

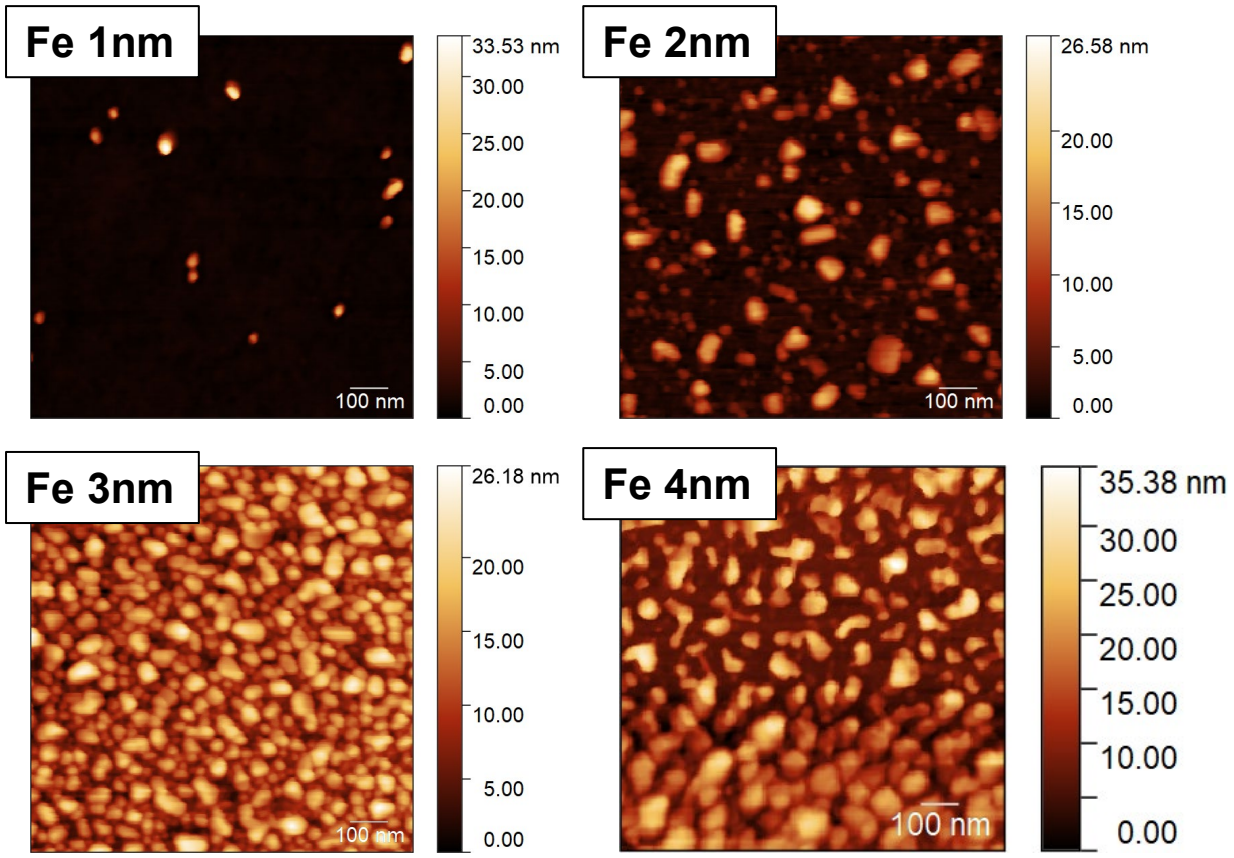


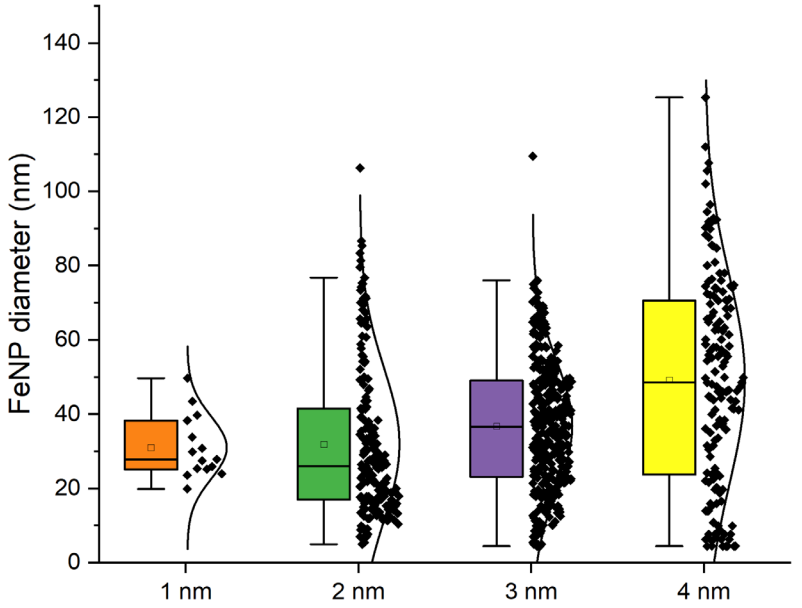
Iron nanostructuring

- AFM characterization in Tapping mode
- Radius tip < 10 nm Si tip (PPP-NCHR)



FeNPs Diameter analysis





Fe Thickness (nm)	$\delta_{FeNP} \times 10^{10}$ cm^{-2}	Surface Coverage
1	0.21	1.2 %
2	1.98	21.9 %
3	3.38	44.1 %
4	1.54	38.7 %

Non-lithographic synthesis of VACNTs

0. Substrate selection

1. Cleaning protocol

2. Catalyst deposition

Diffusion barrier
(SiO_2, Al_2O_3, ...)

Mechanical support
(Silicon, ...)

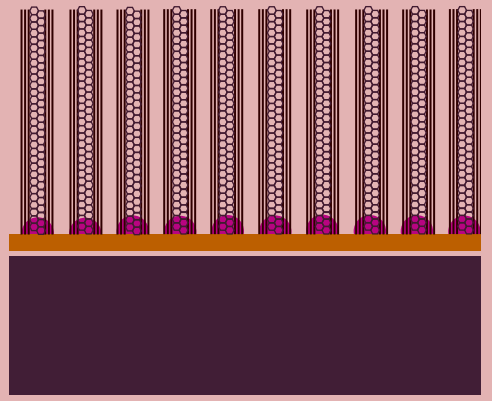
E-beam evaporation
(Fe, ...)

3. Dewetting

H_2 reduction

Heat up (720°C, ...)

4. CVD Synthesis
(C_2H_2, ...)



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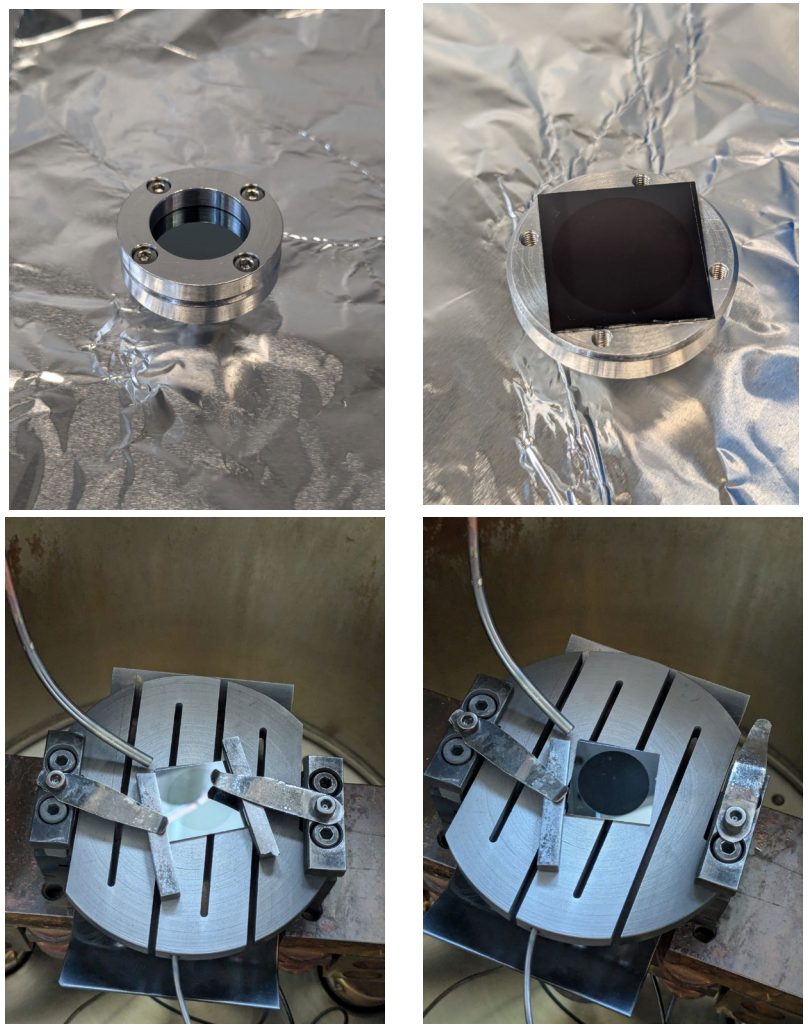
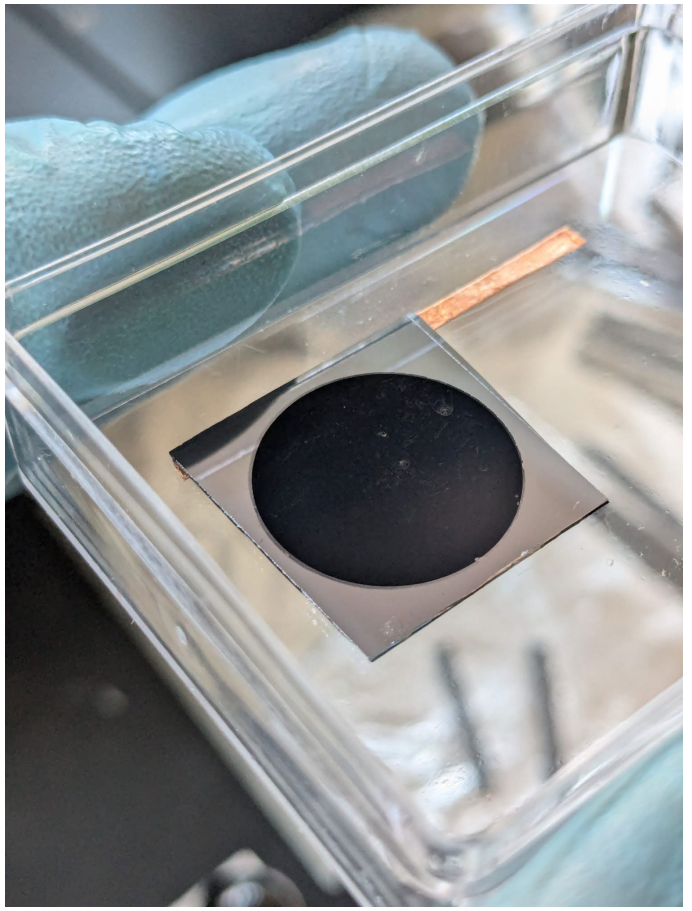
VACNTs synthesis

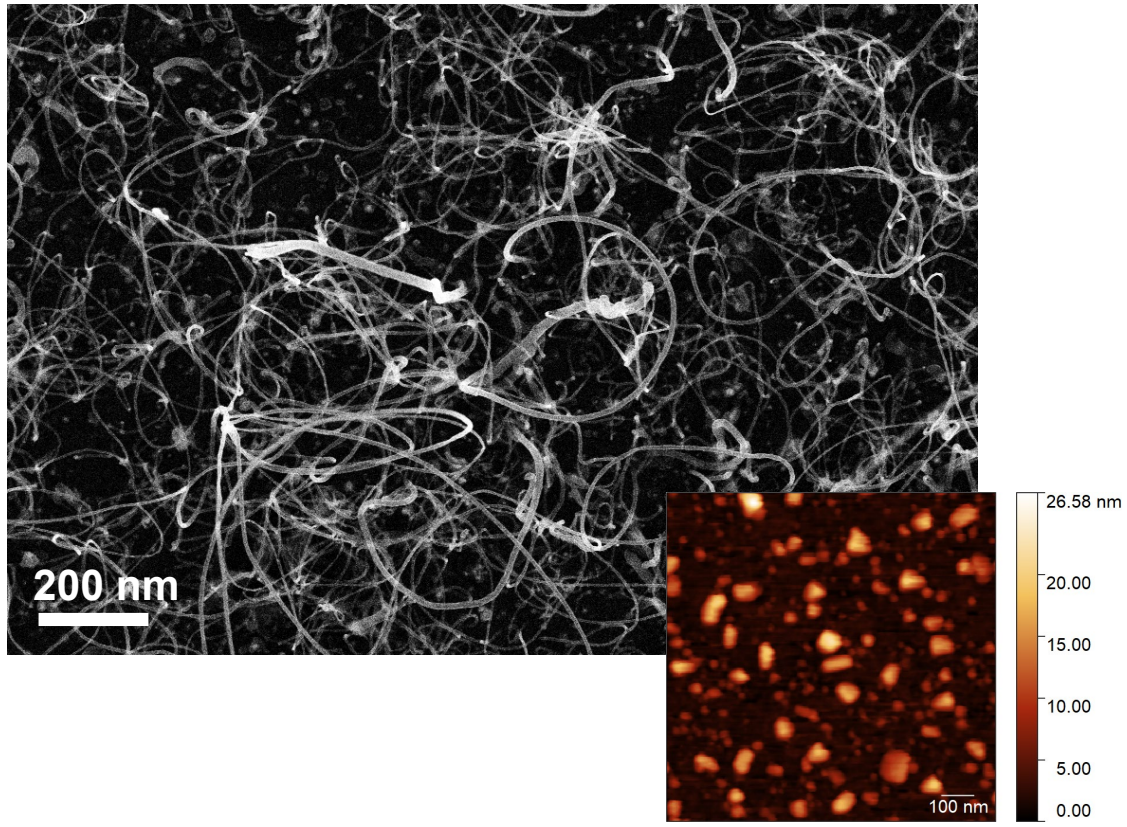
The very first VACNTs growth



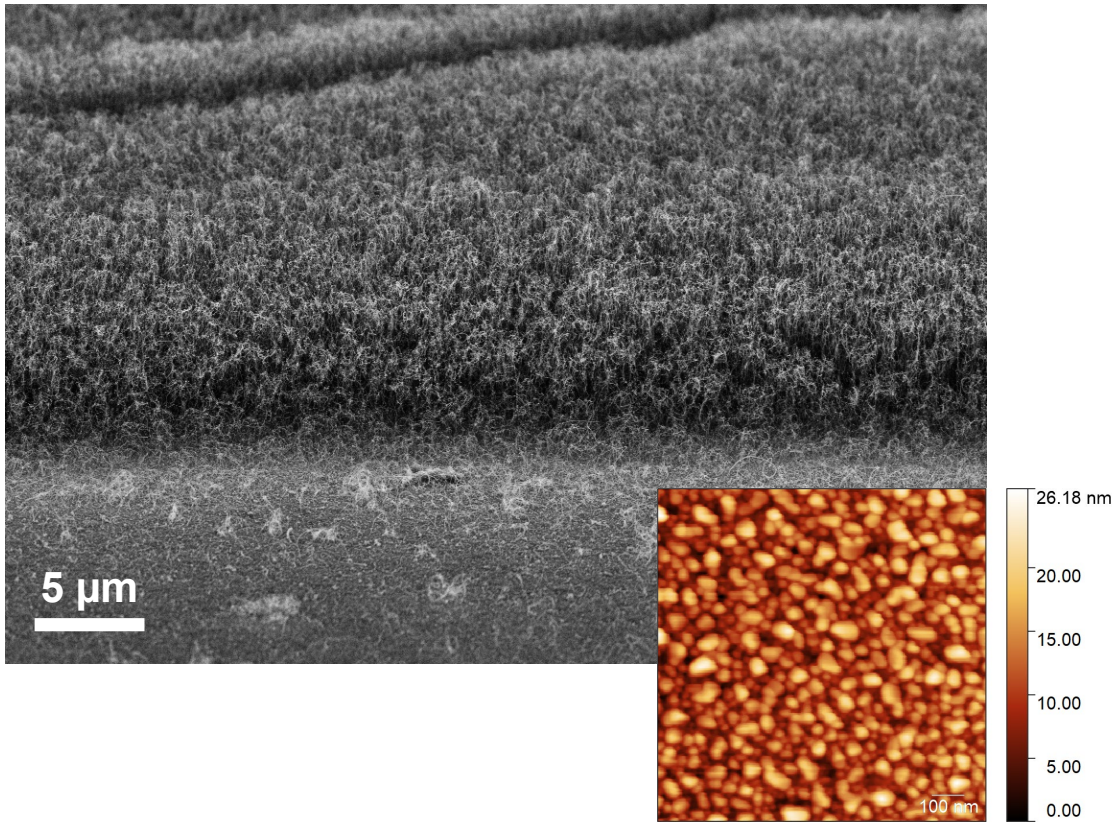


The very first problem

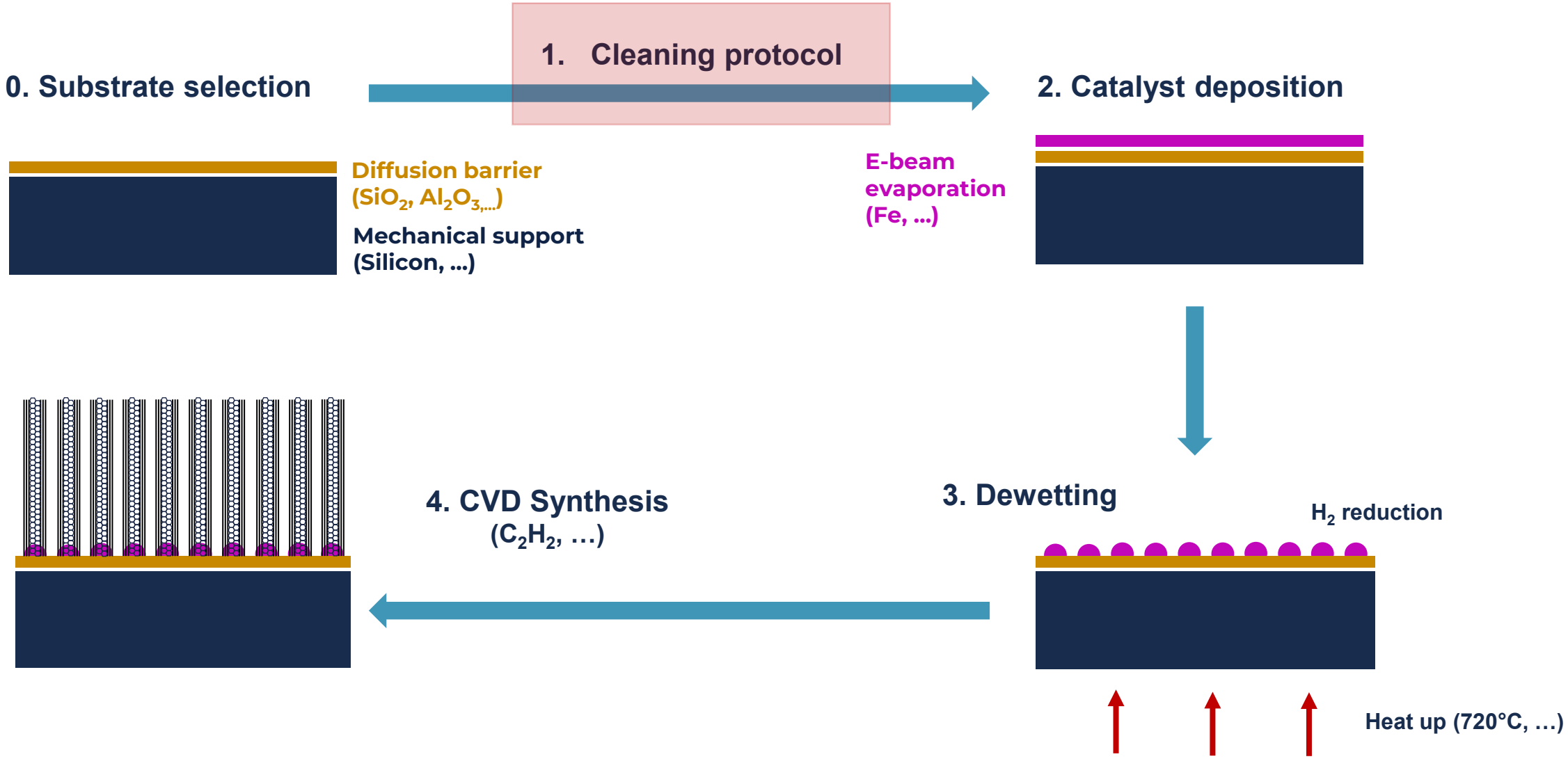
2 nm



3 nm

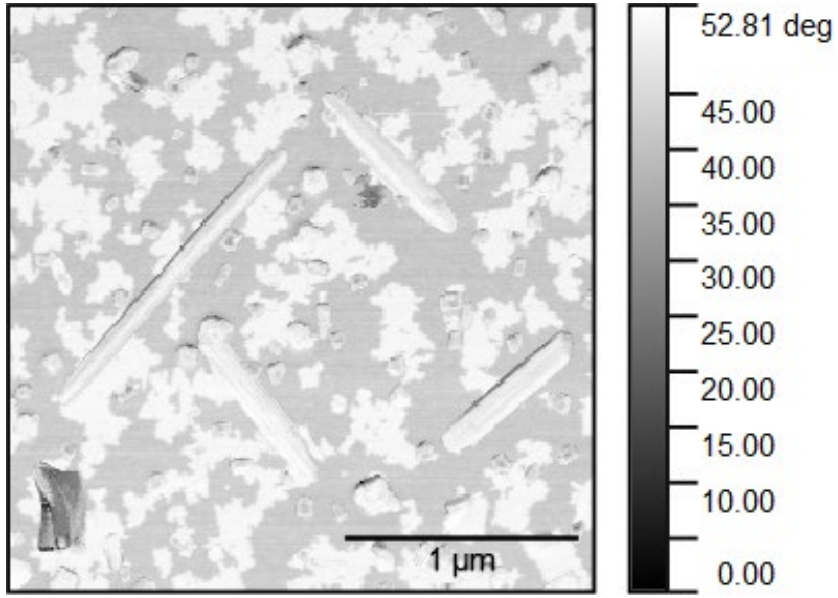


A step back...

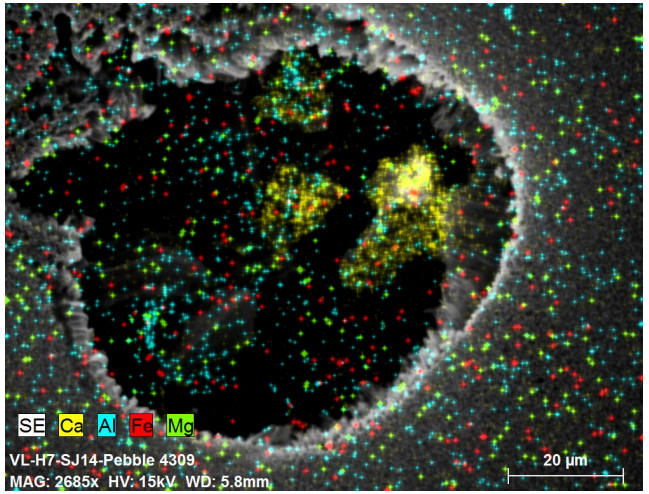

0. Substrate selection
1. Cleaning protocol
2. Catalyst deposition
Diffusion barrier
(SiO_2, $Al_2O_{3,...}$)
Mechanical support
(Silicon, ...)
E-beam
evaporation
(Fe, ...)
3. Dewetting
H_2 reduction
4. CVD Synthesis
(C_2H_2, ...)
Heat up (720°C, ...)

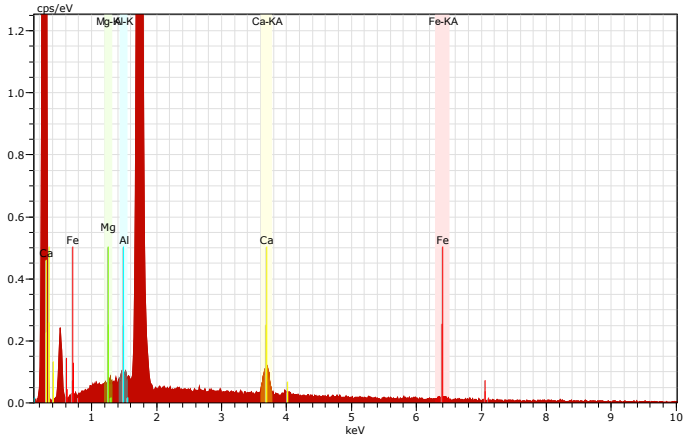
The importance of “fresh” Tipe I water

Phase diagram

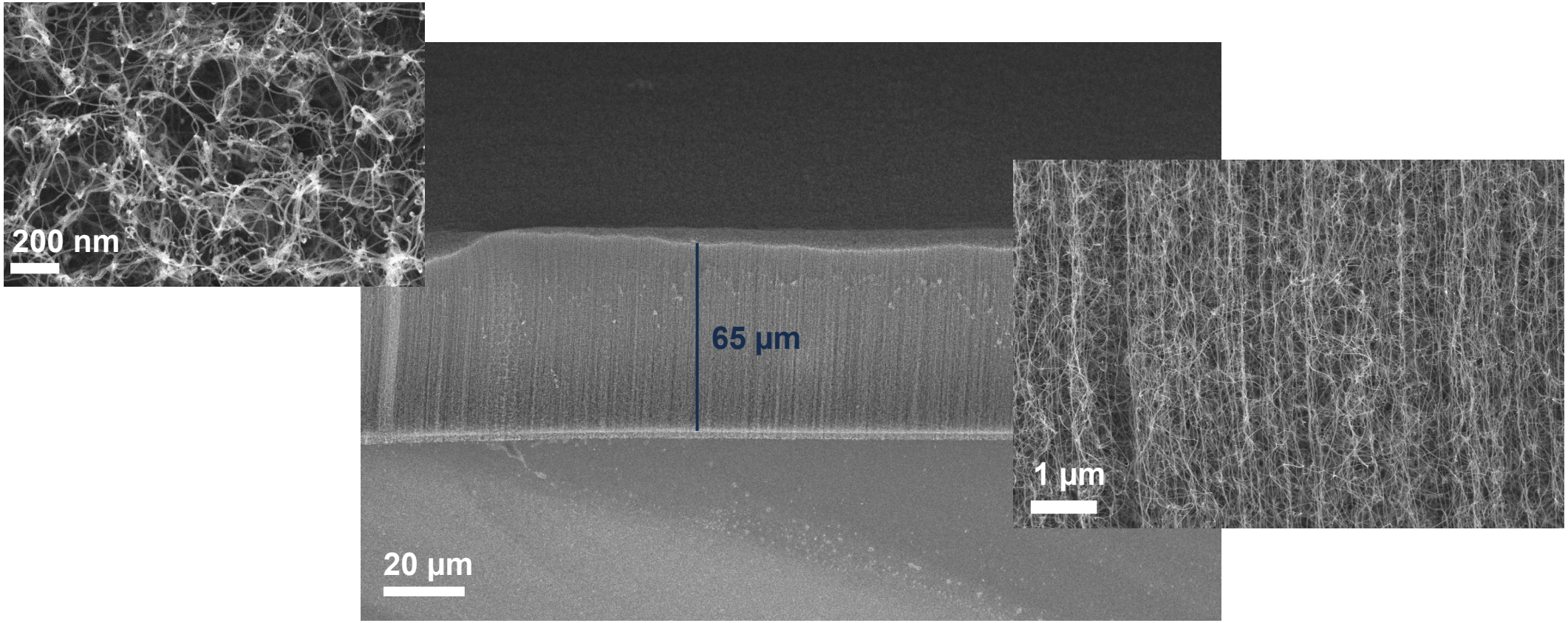


SEM-EDX

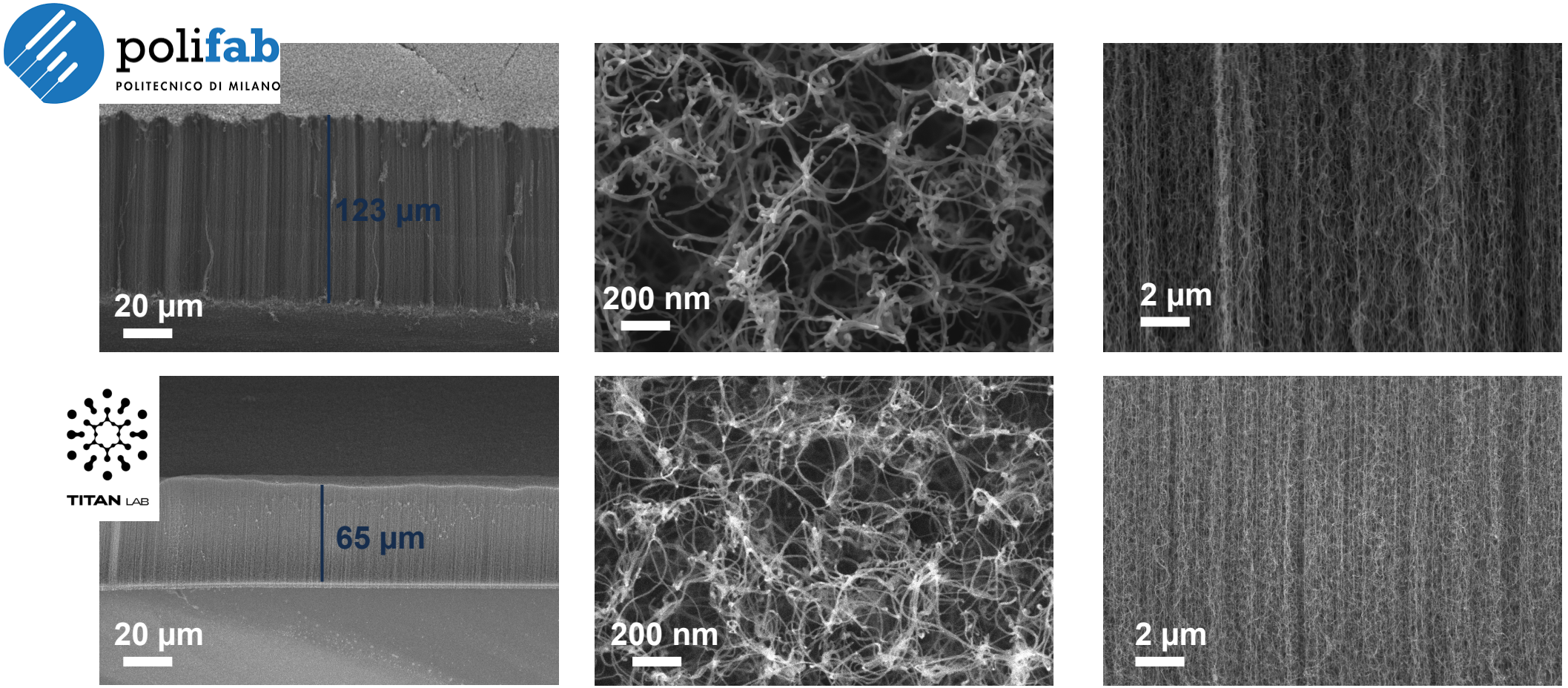




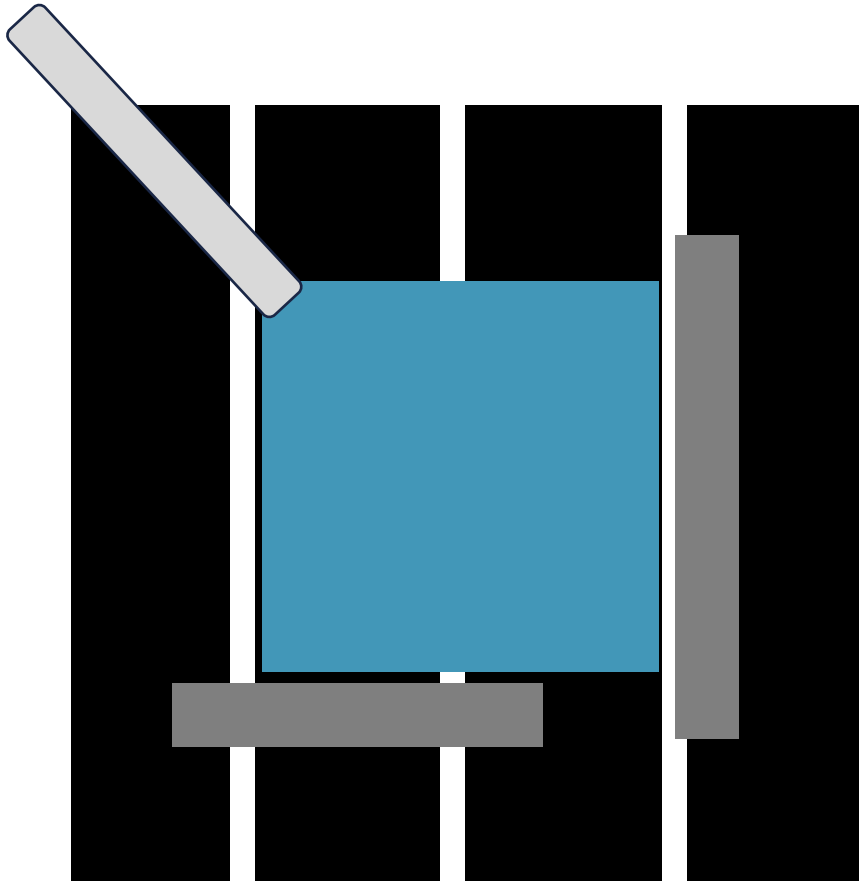
Protocol with “fresh MilliQ”

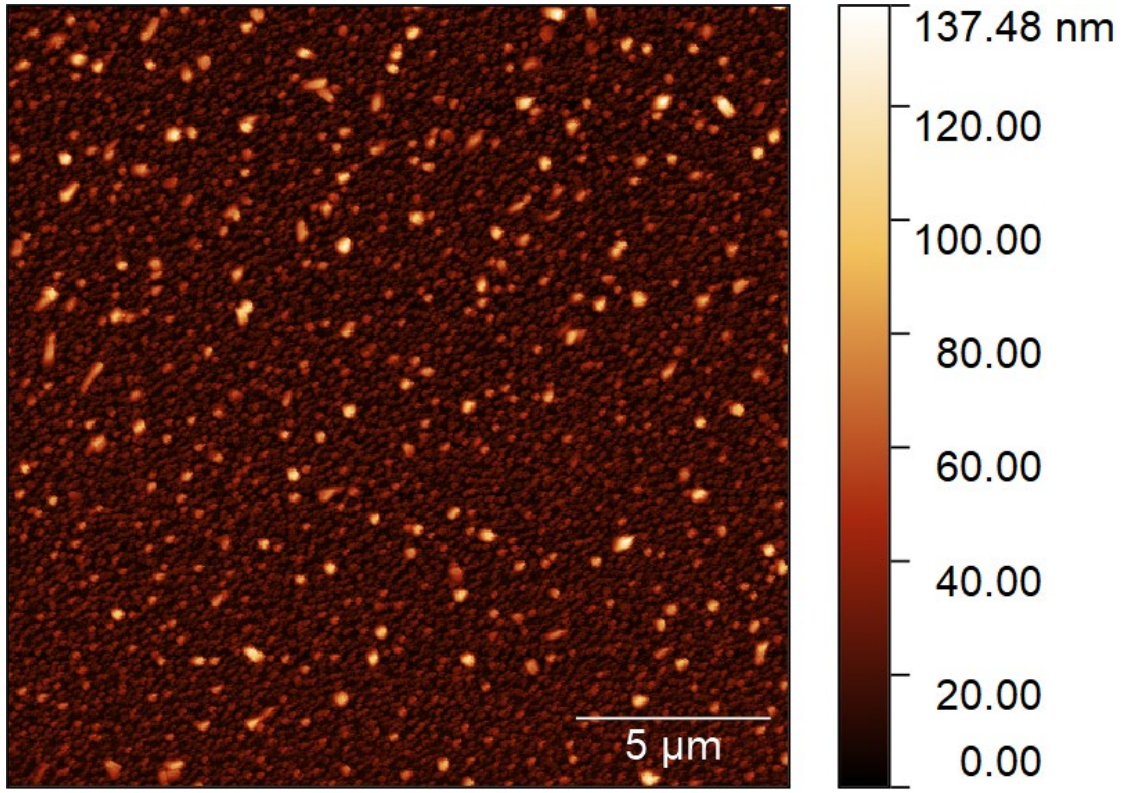


Comparison with Old samples

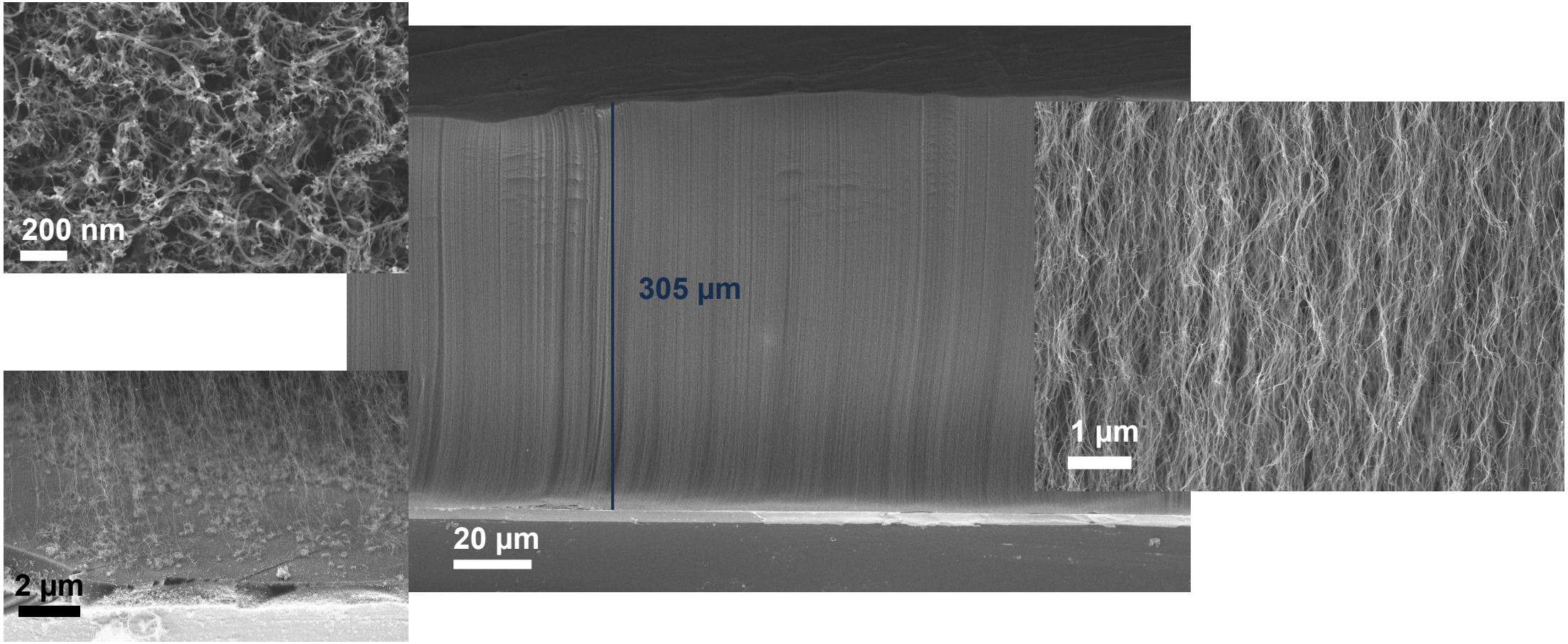


Uniform growth: remove holds



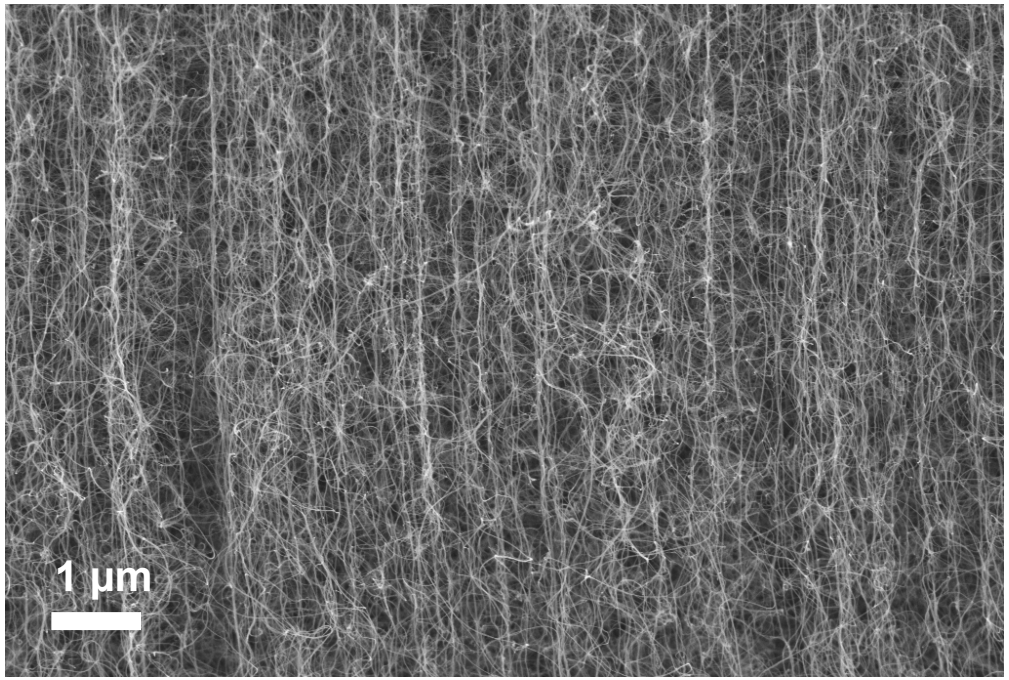


Uniform growth: remove holds

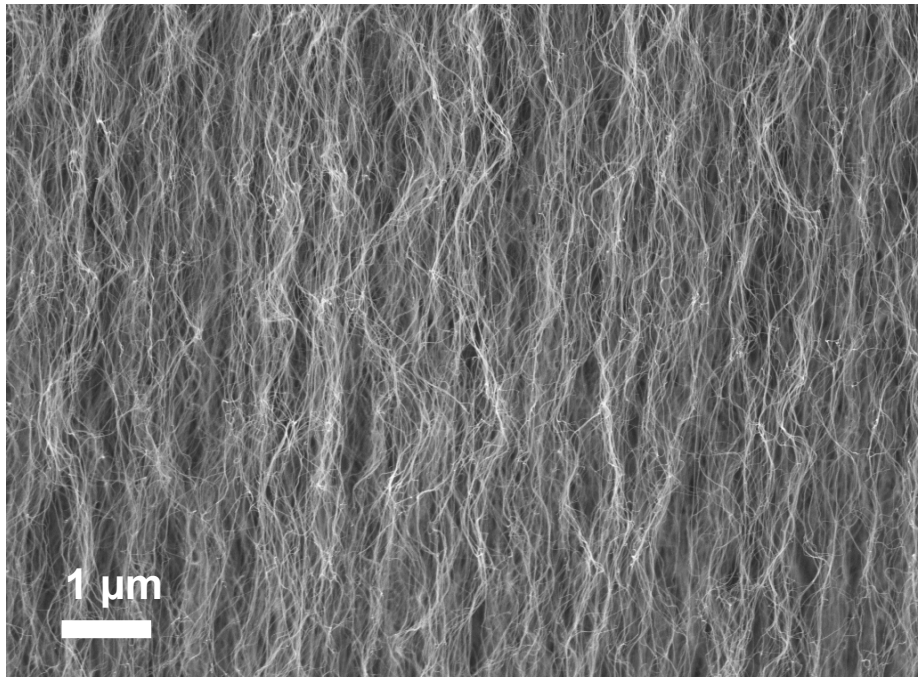


Comparison Fresh MilliQ and NoHolds

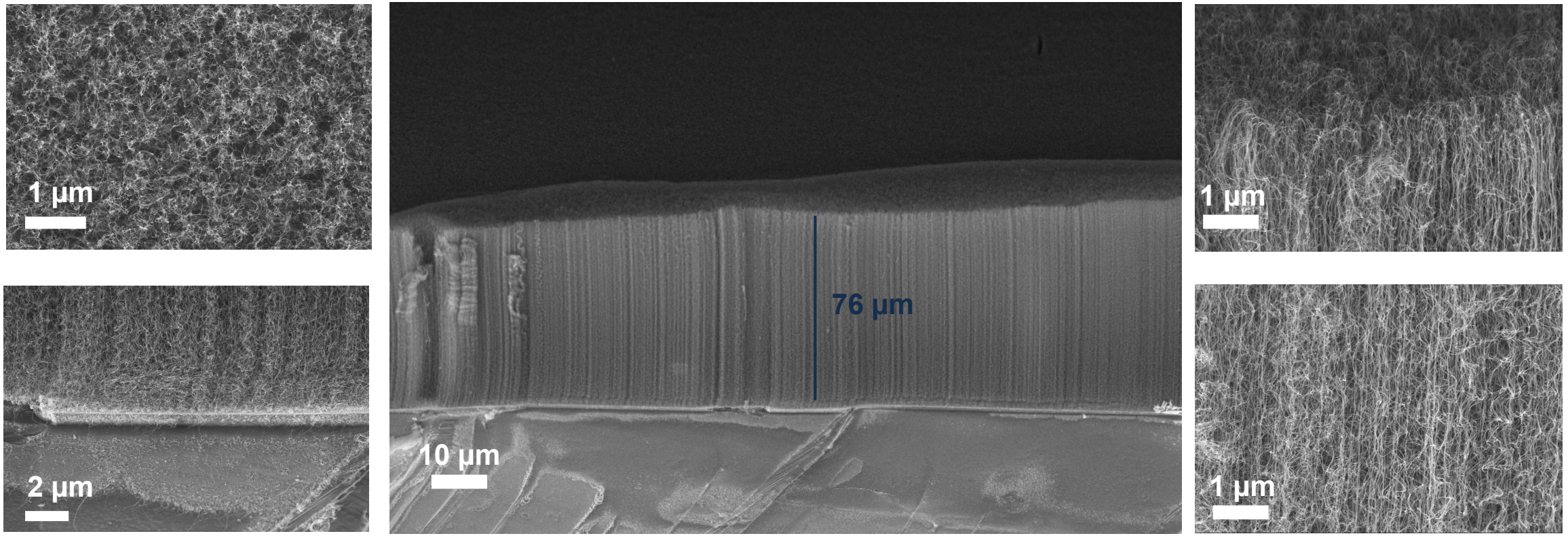
Holds



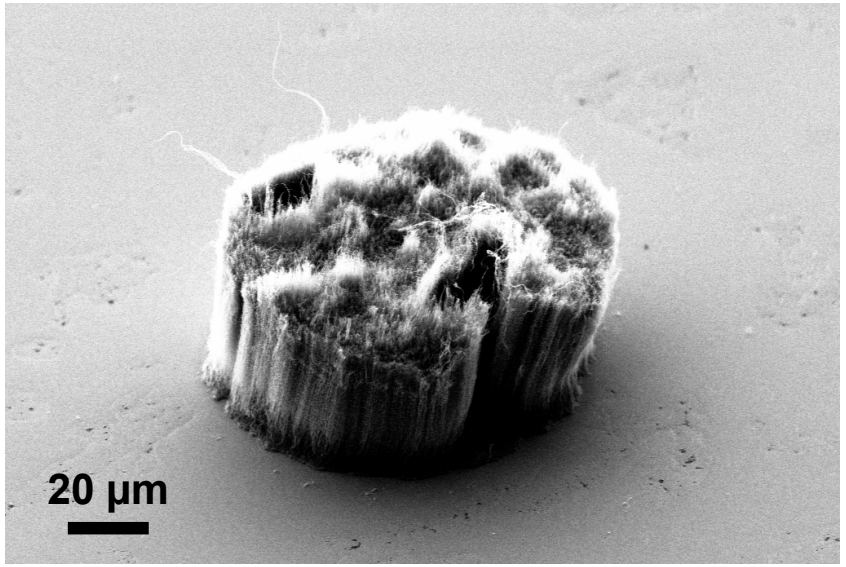
No holds

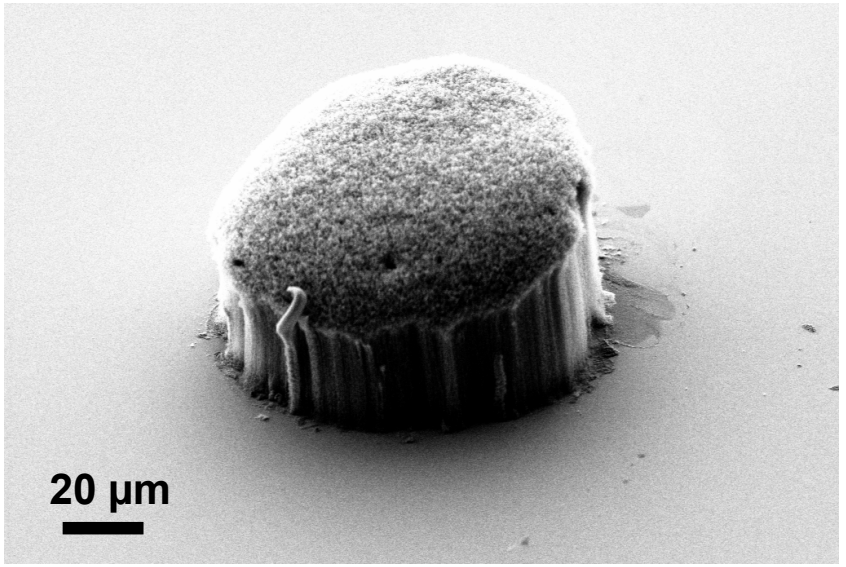


Flux hydrogen during synthesis



Shadow Mask patterning



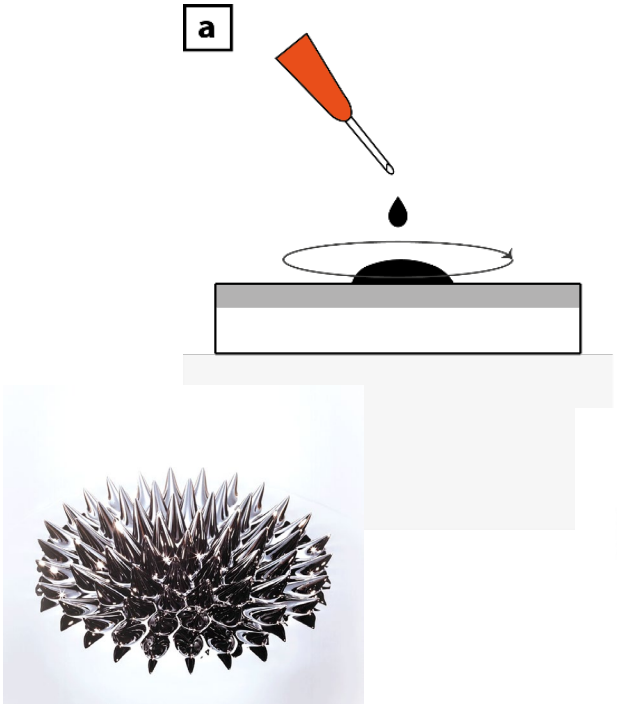


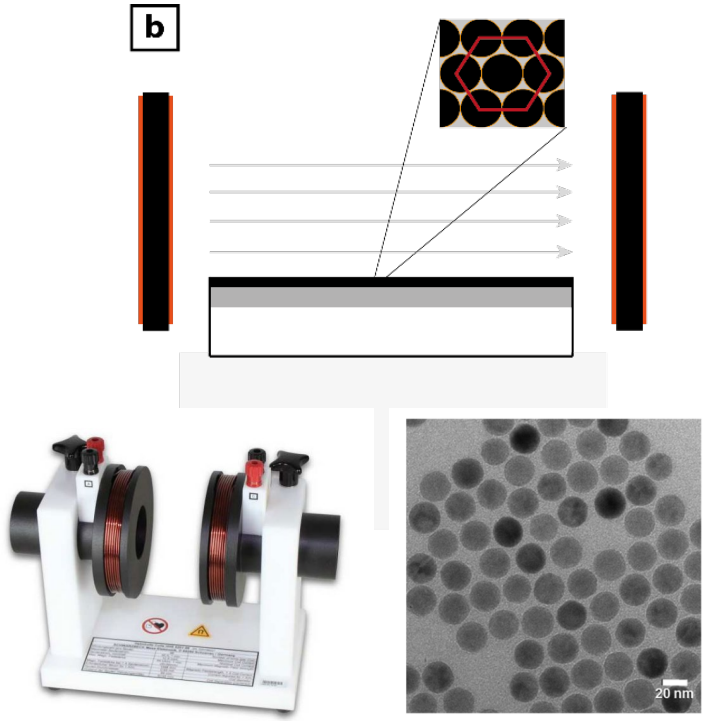
Waiting for new SEM micrographs of EBL patterning (G. Pettinari)

Future activities

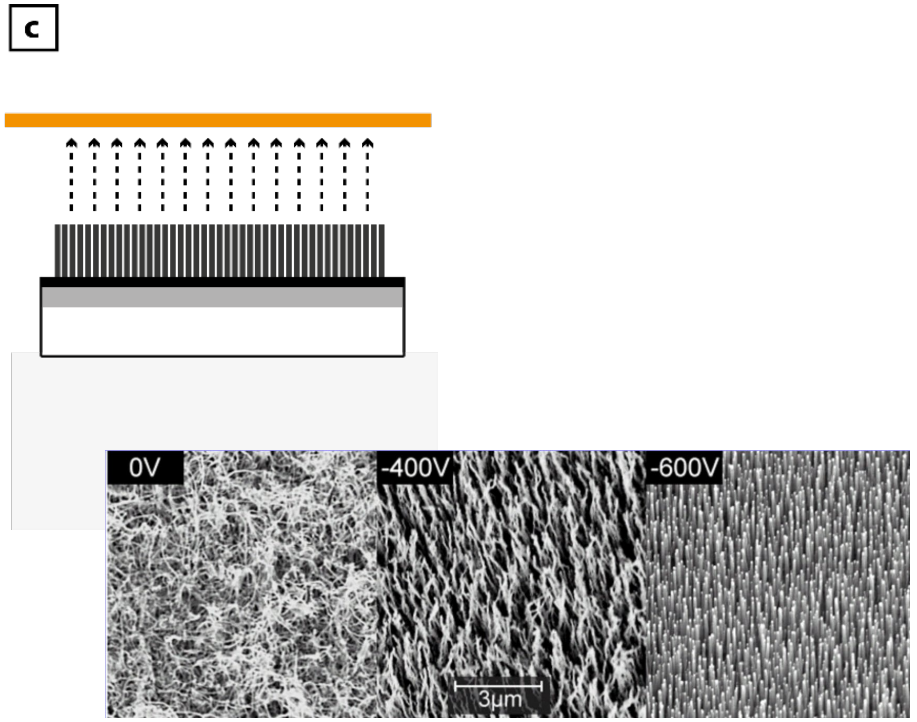
- Define reproducible protocol, **minimizing contamination** during cleaning, iron deposition and synthesis.
- Evaluate feasibility of **micropatterning**.
- Understand the role of **hydrogen plasma during annealing**.
- Evaluate the **crust removal with hydrogen plasma**.
- SEM of **microtome crust** cuts.
- Define a protocol for VACNTs **transfer printing on metal substrates** (copper, aluminium).
- Synthesis with **gas shower** and no more pipeline.

Future activities: Grant proposal





Theis-Bröhl, K. *et al.* Self-Assembled Layering of Magnetic Nanoparticles in a Ferrofluid on Silicon Surfaces. *ACS Appl. Mater. Interfaces* **10**, 5050–5060 (2018).



Chhowalla, M. *et al.* Growth process conditions of vertically aligned carbon nanotubes using plasma enhanced chemical vapor deposition. *Journal of Applied Physics* **90**, 5308–5317 (2001).

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Thank you for the attention.

Any question?

Luca Cecchini

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