University of Antwerp
EMAT | Electron Microscopy for Materials Science

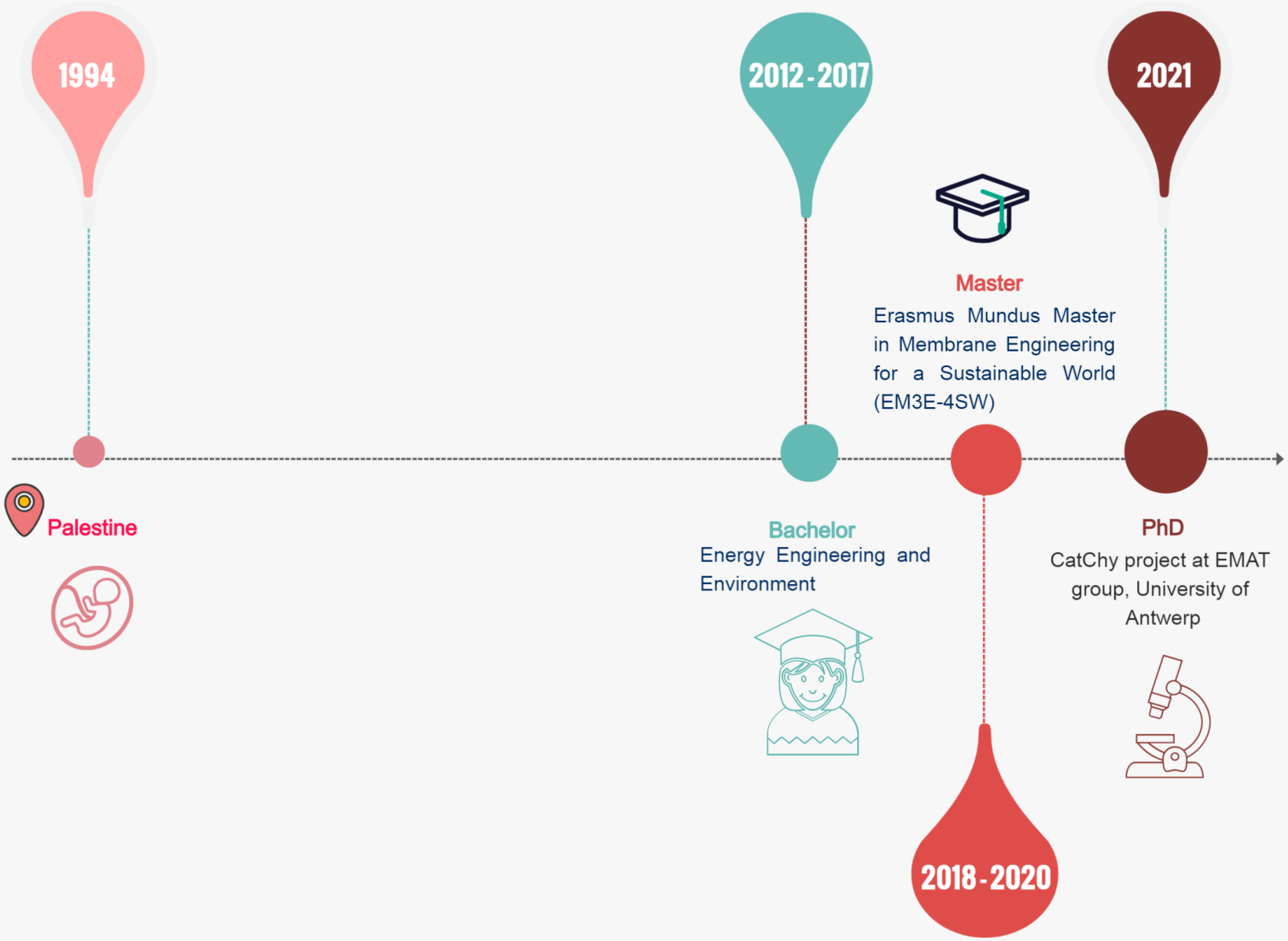
Advanced ex and in situ TEM characterization of cluster electrocatalysts

Mid-term review

ESR10: Deema Balalta

Promoters: Sara Bals and Thomas Altantzis

22 April, 2022



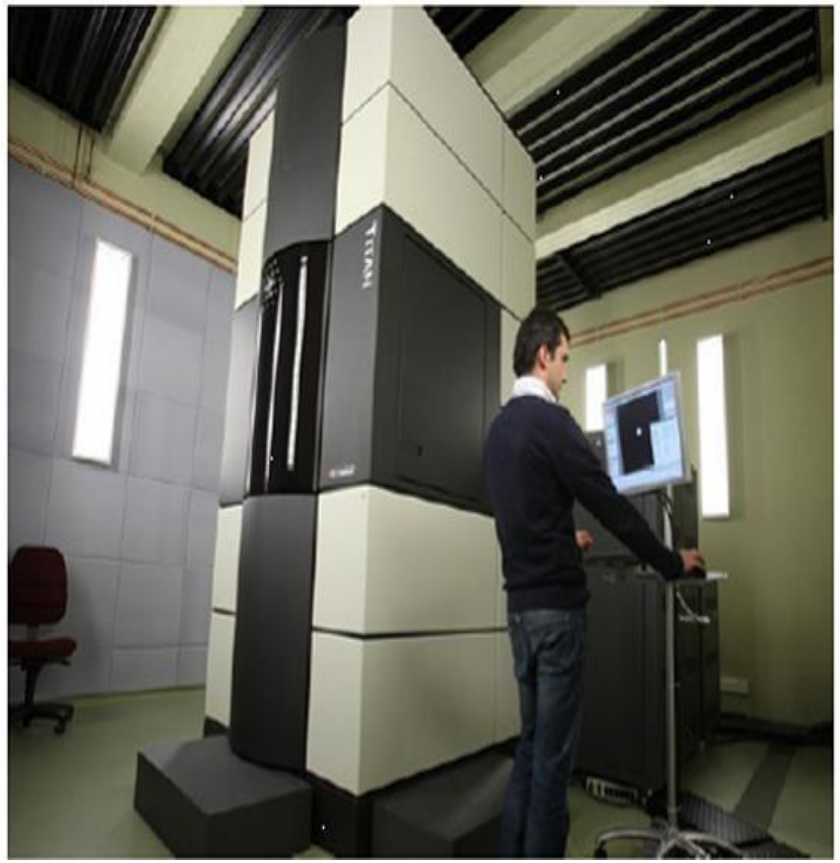
TEM
HRSTEM
EDX mapping
Tomography
StatStem

EMAT at CatCHy

Seeing is Believing

State of the Art Transmission Electron Microscopes:

- TEM + STEM
- Acceleration voltage between 60-300 kV
- Spatial resolution down to: 70 pm in STEM and 50 pm in TEM.
- Highly efficient EDX system (atomic resolution)
- Fast ThermoFisher Ceta camera
- EELS and Direct electron detectors



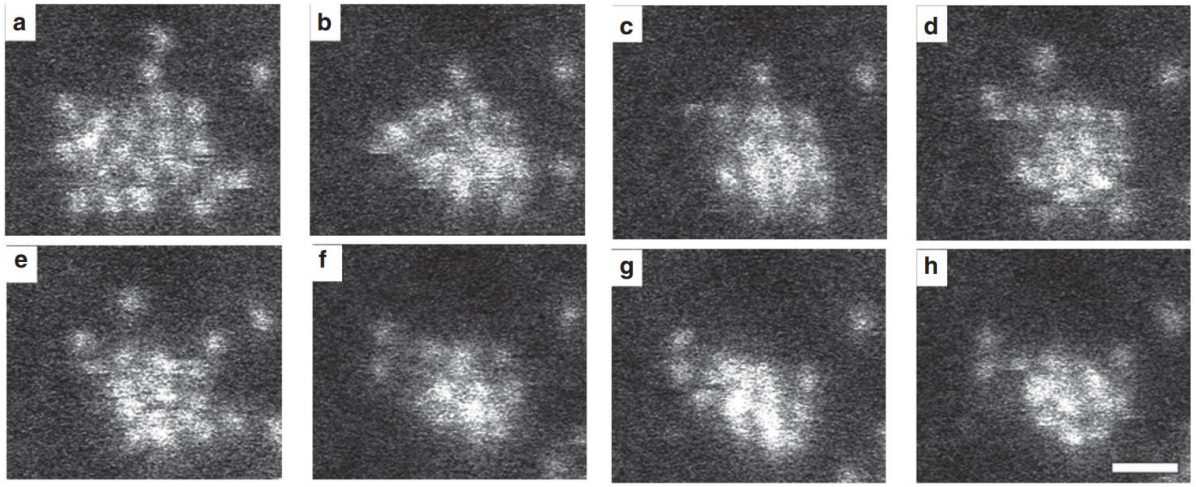
EMAT at CatCHy

Our main contributions to CatCHy:

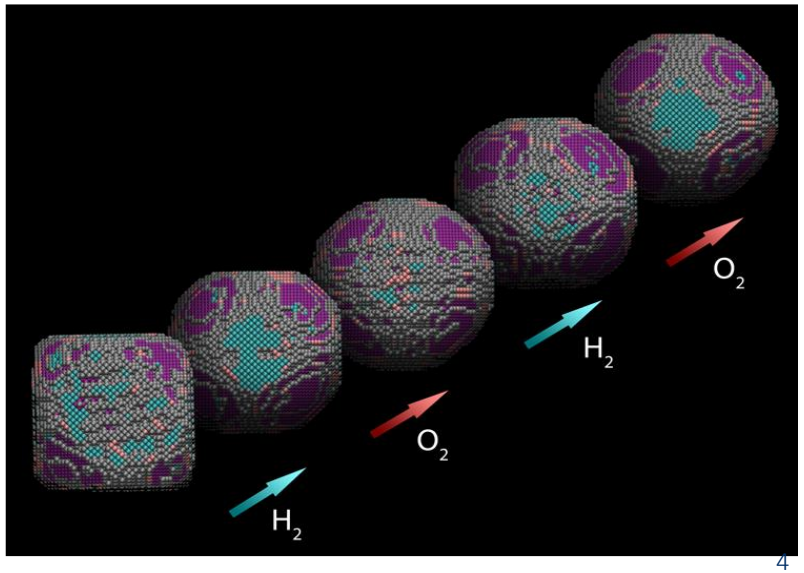
- **Electron tomography** (down to atomic level)
- **TEM for nanomaterials in real conditions**

Prof. Sara Bals

Prof. Thomas Altantzis



S. Bals, S. Van Aert, Nat. Commun., vol. 3, no. ***May 2012***



T. Altantzis, I. Lobato, A. De Backer et al, Nanoletters, ***2019****,* ***19****, 477-481*

Work Packages

- **WP2: Characterization of Deposited Clusters.**

Study the structure, morphology and composition using aberration corrected (S)TEM.
Investigate the deposited clusters under reactive environment with *in situ* TEM

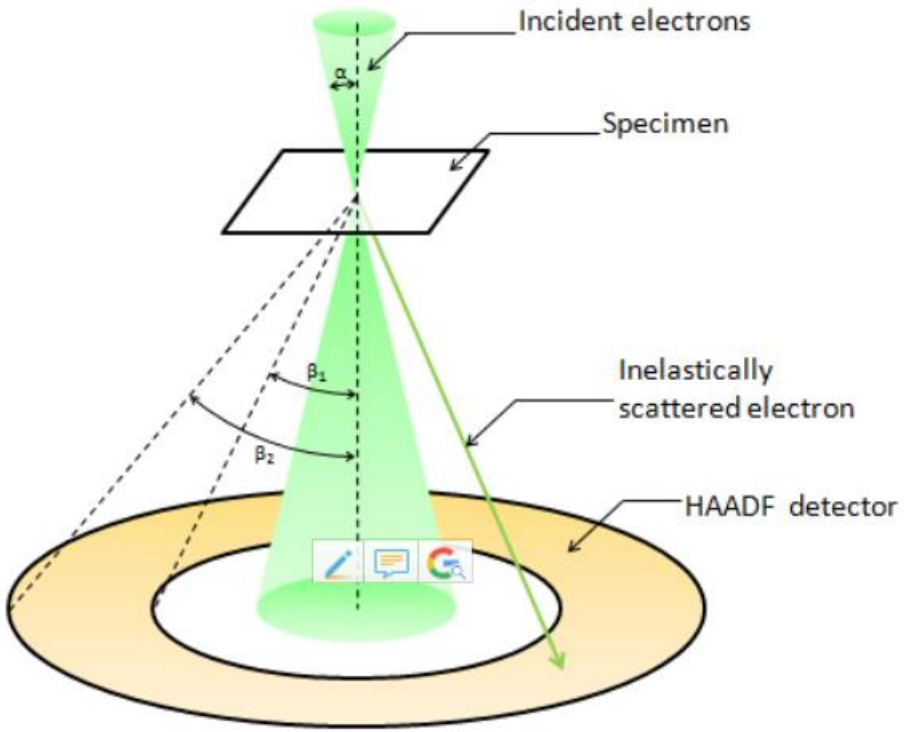
- **WP5: Catalysts Testing** and Prototyping a Model Gas Diffusion Electrode.

The high performing catalysts from TCs and ECs will be characterized in operando conditions using *in situ* TEM.

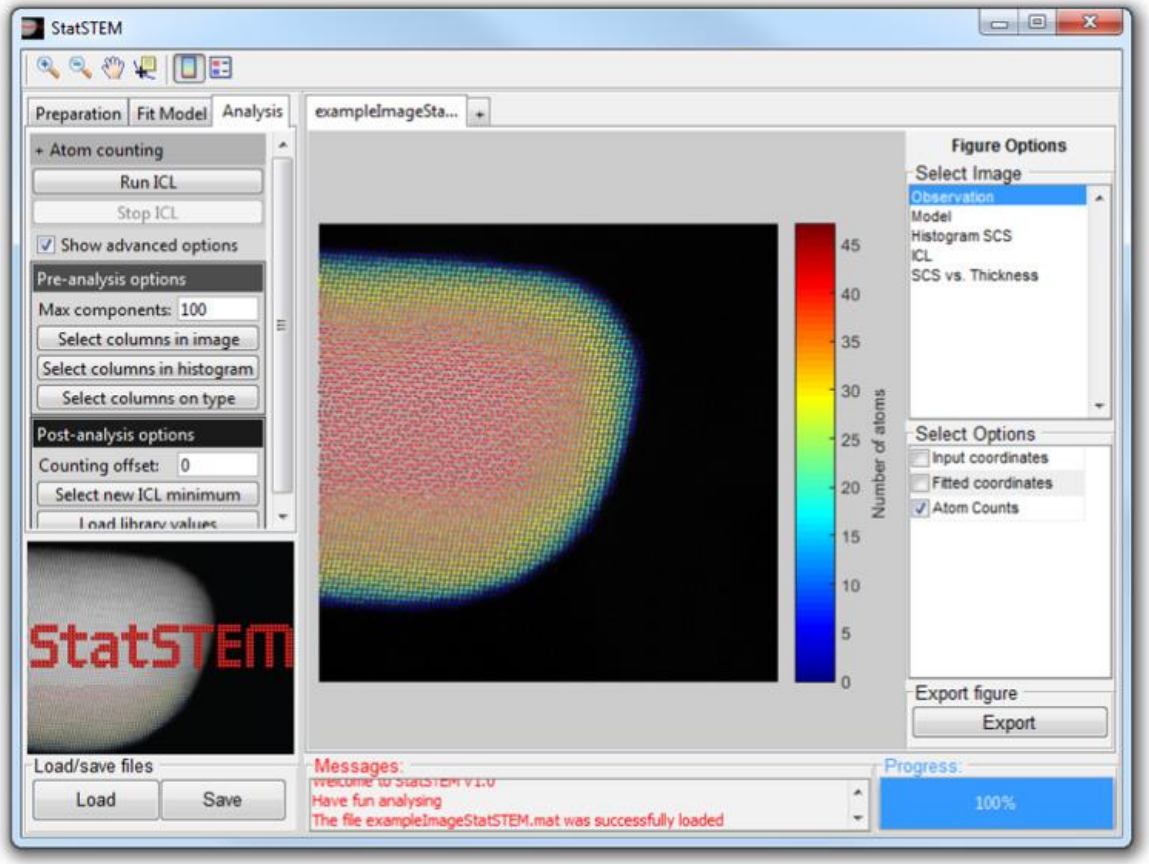
Results obtained

- Structural, morphological and compositional characterization for clusters provided by our partners at TCL and KUL.
- Particle size distribution analysis for the provided clusters.
- Atom Counting.

Data Acquired: HAADF STEM , and Atom counting



HAADF detector

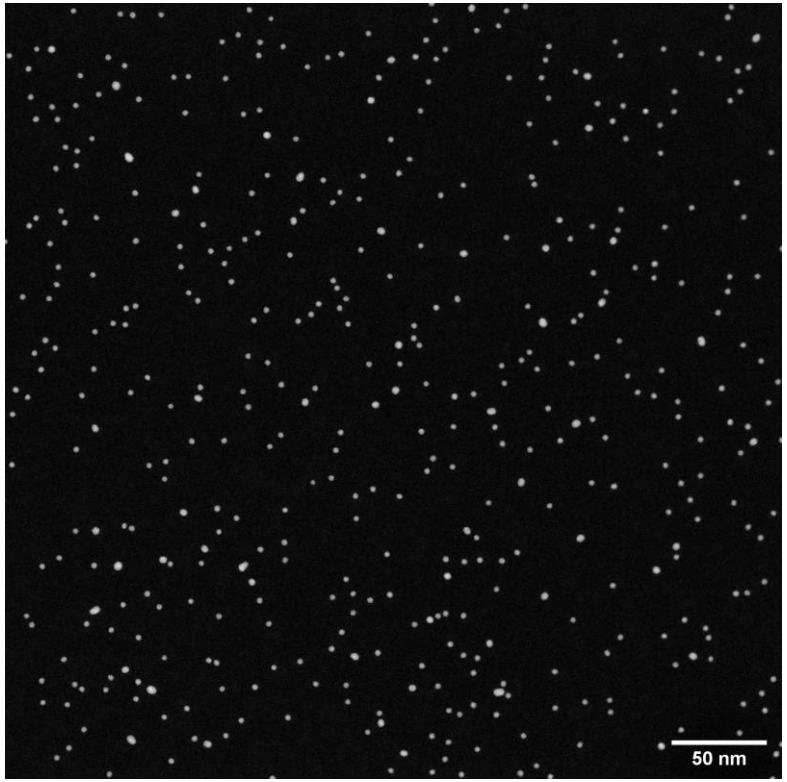


StatSTEM

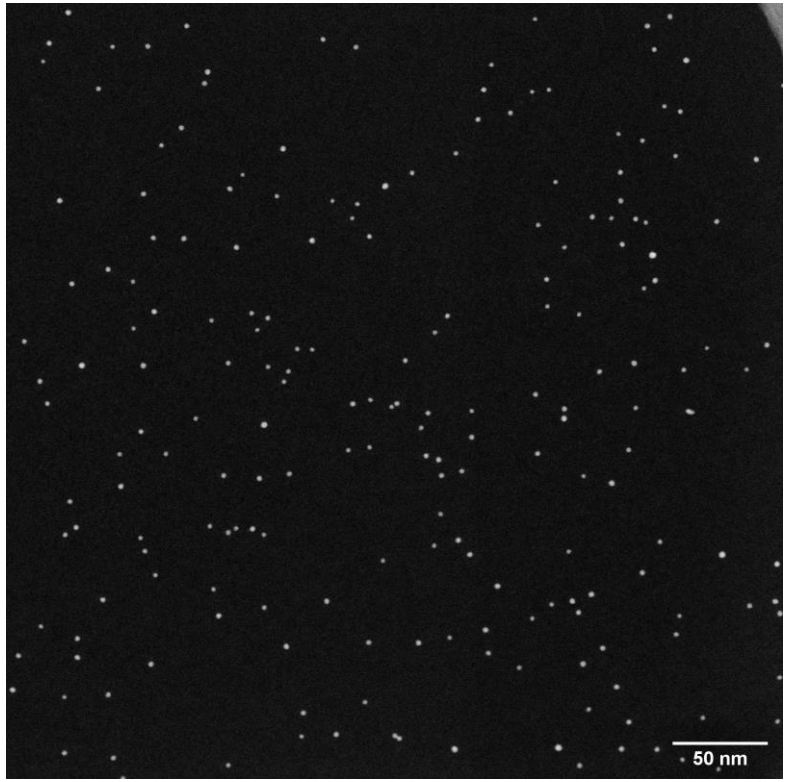
A. De Backer, K.H.W. van den Bos, et. al., Ultramicroscopy 171 (2016), p.104-116

Au clusters from Dimitra Papamichail (ESR 8@KUL)

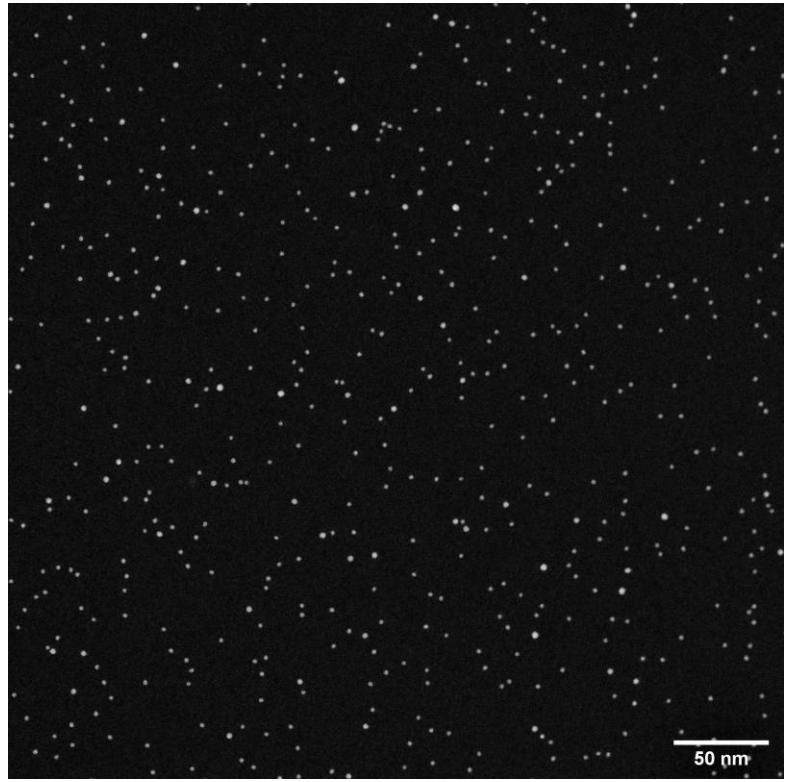
HAADF STEM images



Sample 1: V_{bender} =20 V



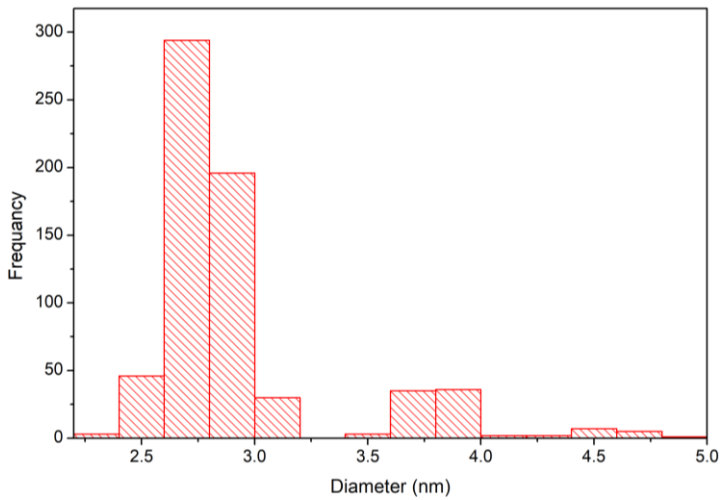
Sample 2: V_{bender} =15 V



Sample 3: V_{bender} =10 V

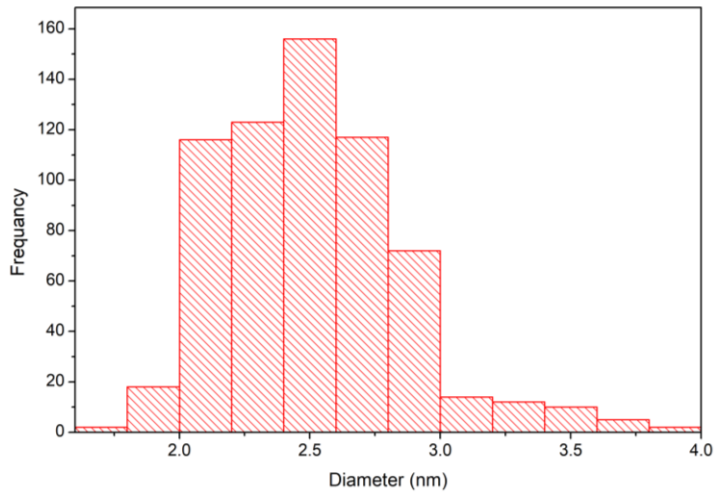
Au clusters from Dimitra Papamichail (ESR 8@KUL)

Particle size distribution



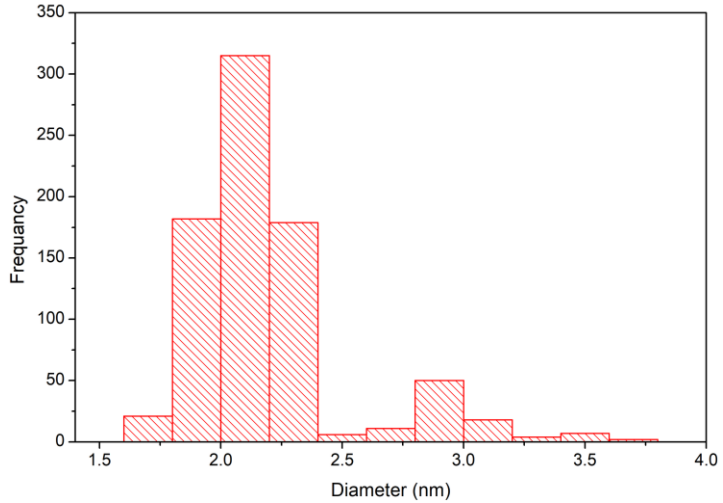
Diameter$_{average}$ = 2.931 ± 0.017 nm
Polydispersity = 14.7 %
Surface coverage$_{2D}$ = 1.811 ± 0.011 %

Sample 1: V_{bender} =20 V



Diameter$_{average}$ = 2.500 ± 0.014 nm
Polydispersity = 13.9 %
Surface coverage$_{2D}$ = 0.547 ± 0.025 %

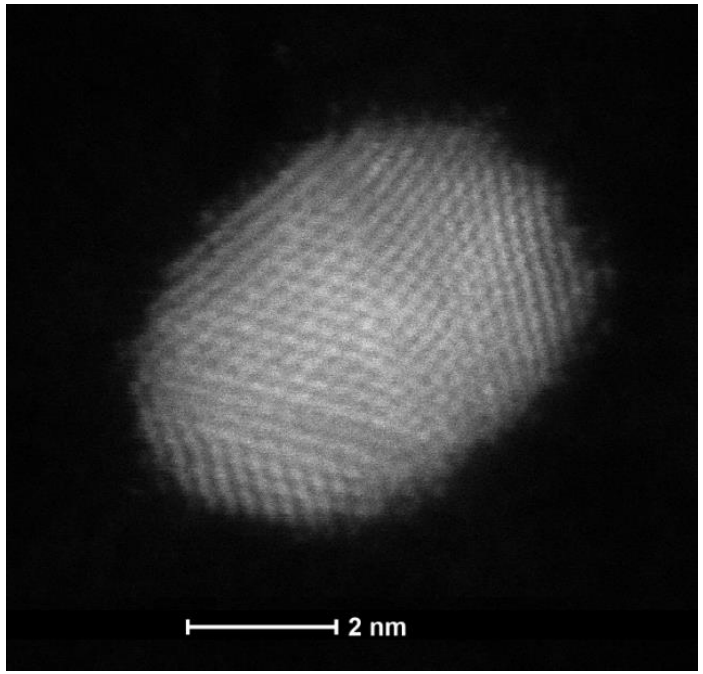
Sample 2: V_{bender} =15 V

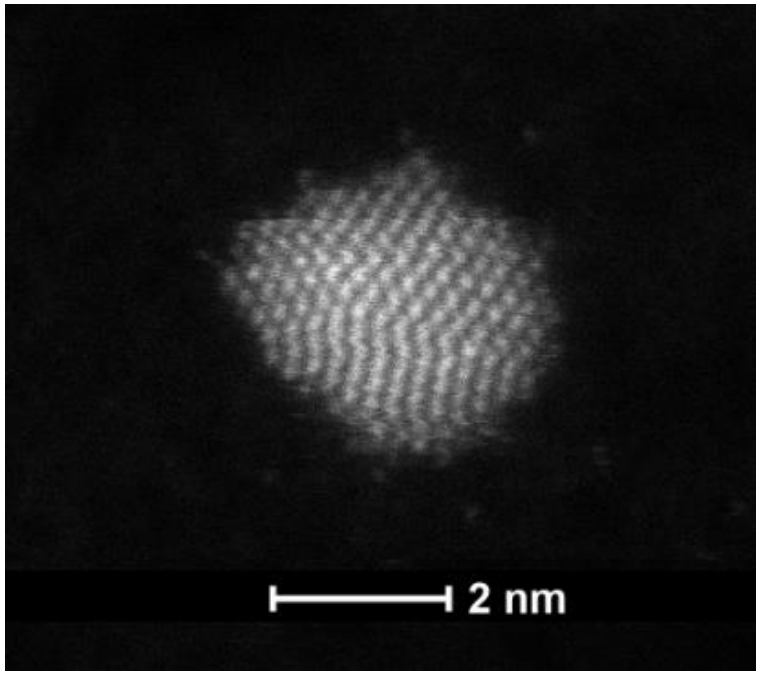


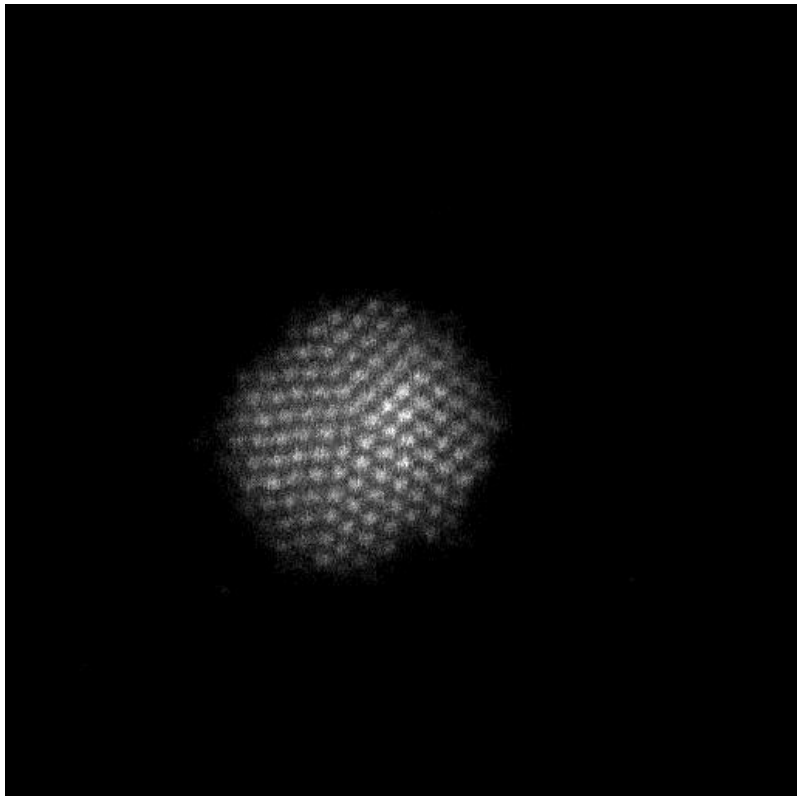
Diameter$_{average}$ = 2.196 ± 0.012 nm
Polydispersity = 15.1 %
Surface coverage$_{2D}$ = 1.205 ± 0.074 %

Sample 3: V_{bender} =10 V

HAADF HRSTEM images, crystalline structure

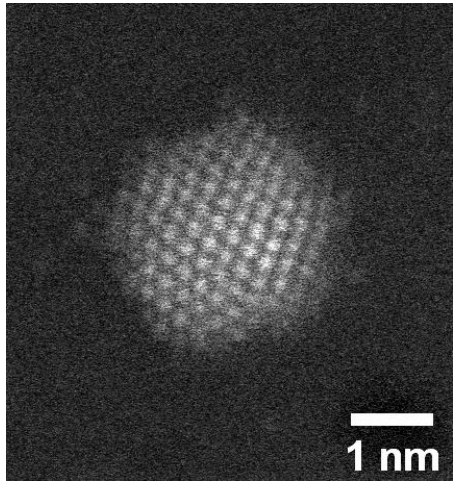


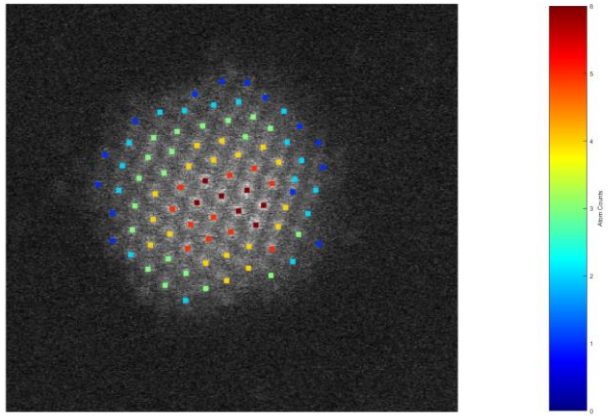




Atom counting

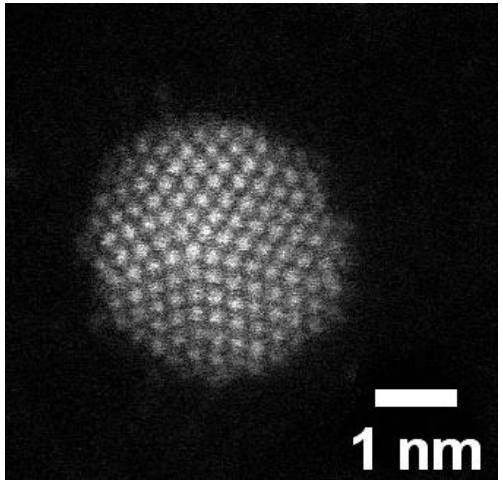
2.5 nm cluster

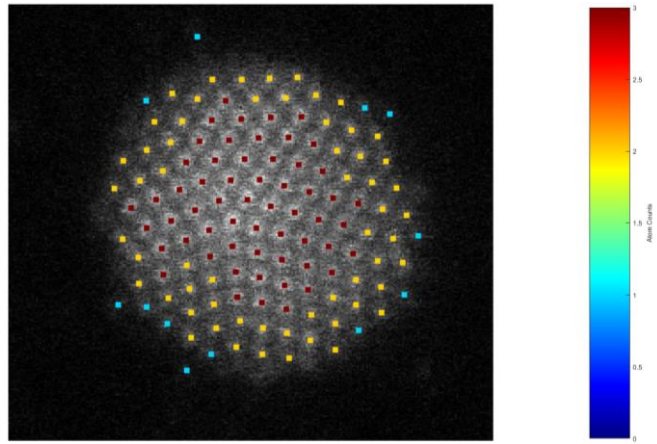




275 atom

3 nm cluster



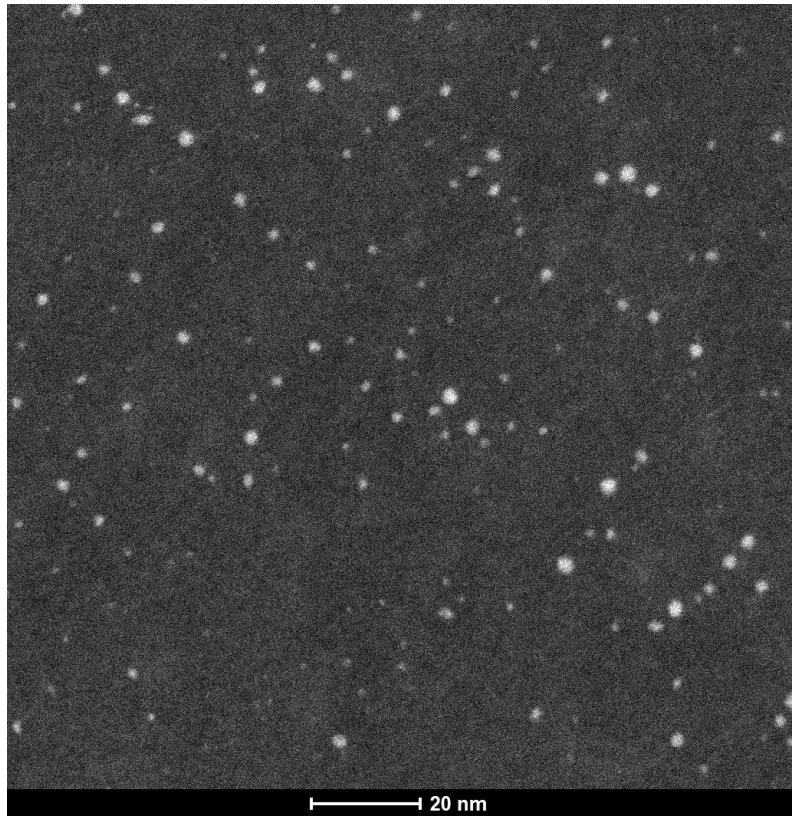


307 atom

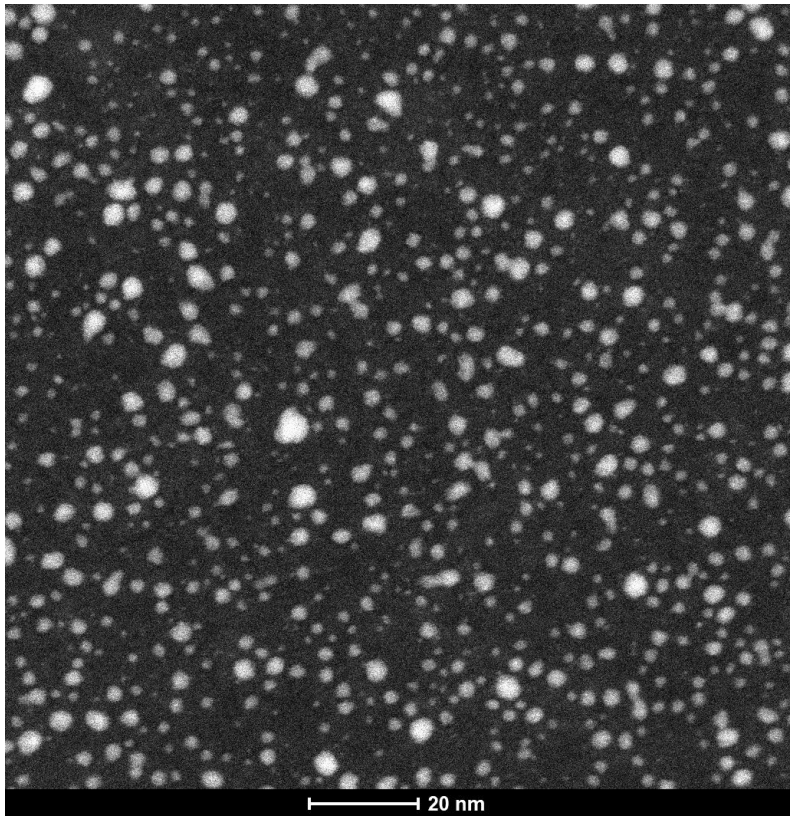
Afterwards…
Relaxed 3D model with Molecular Dynamics Simulations

Pd clusters from João Coroa (ESR 2@TCL)

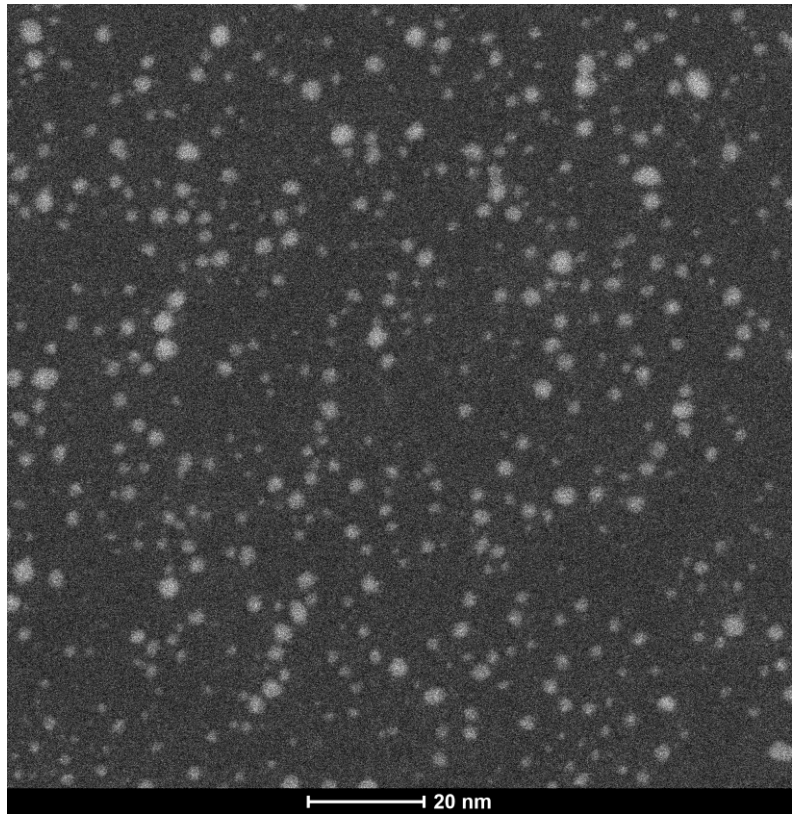
HAADF STEM images



Sample 1: loading= 1.2 µg/cm²



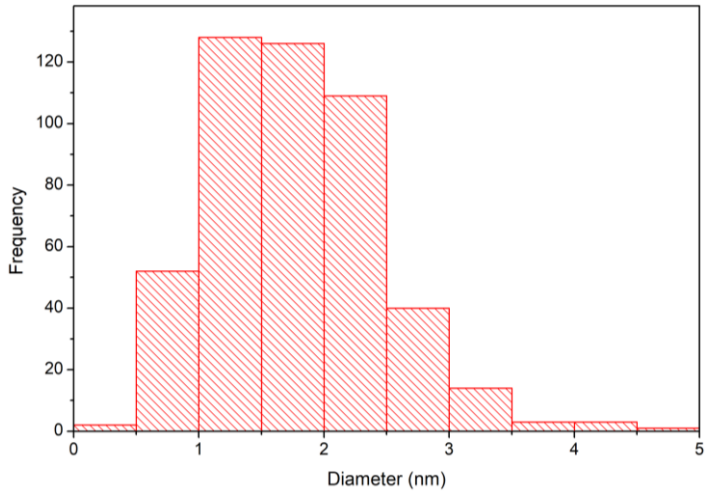
Sample 2: loading= 3.6 µg/cm²



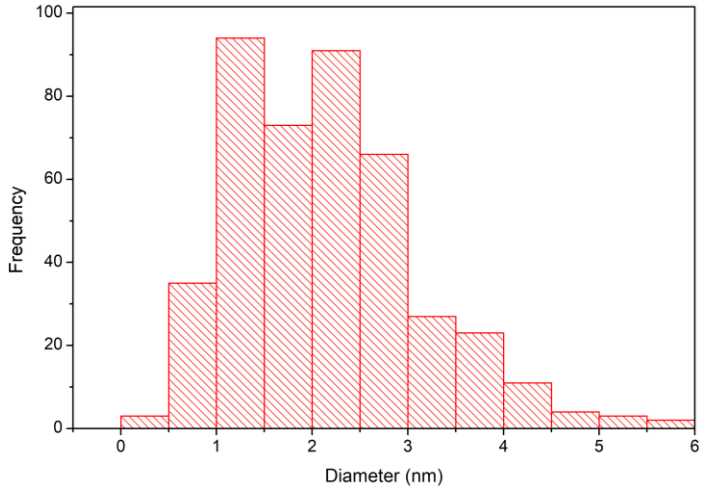
Sample 3: loading= 6 µg/cm²

Pd clusters from João Coroa (ESR 2@TCL)

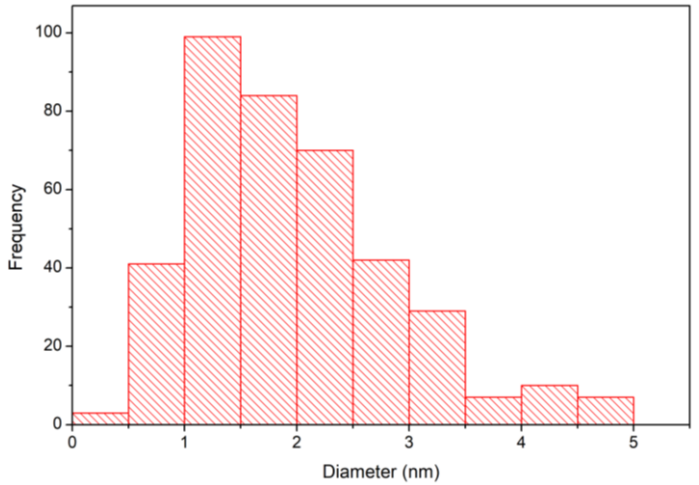
Particle size distribution



Equivalent Diameter$_{average}$ = 1.700 ± 0.0870 nm



Equivalent Diameter$_{average}$ = 1.946 ± 0.0959 nm



Equivalent Diameter$_{average}$ = 1.692 ± 0.0467 nm

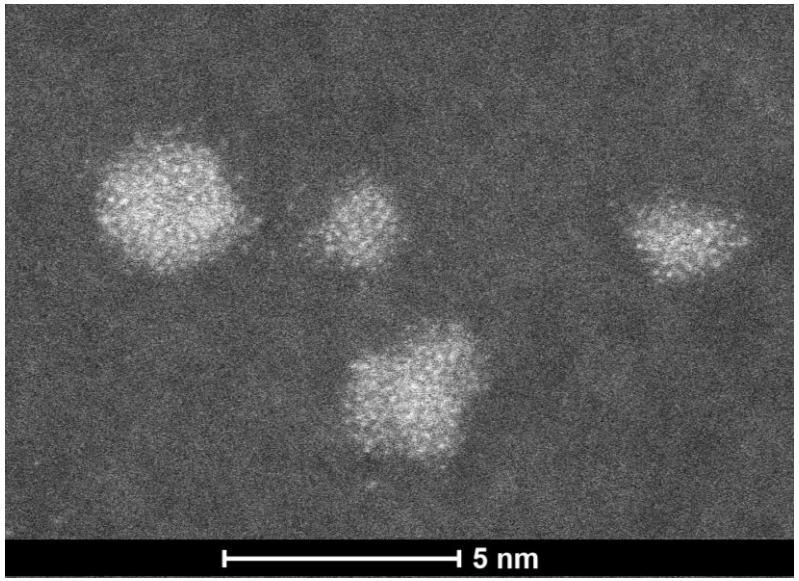
Sample 1: loading= 1.2 µg/cm²

Sample 2: loading= 3.6 µg/cm²

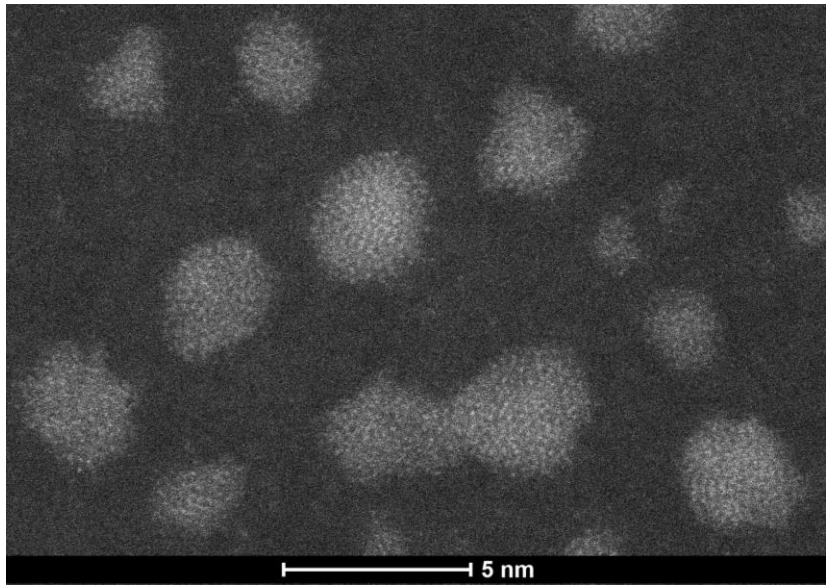
Sample 3: loading= 6 µg/cm²

Pd clusters from João Coroa (ESR 2@TCL)

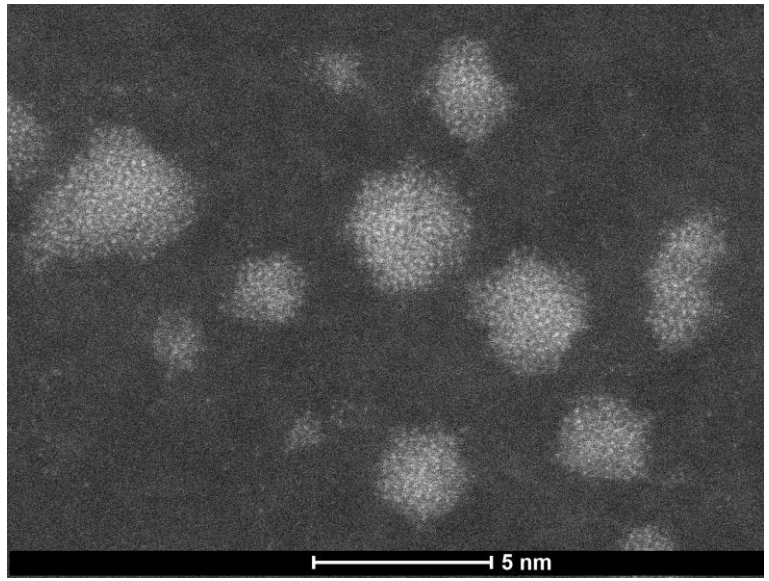
High magnification STEM image, No crystalline structure



Sample 1: loading= 1.2 µg/cm²



Sample 2: loading= 3.6 µg/cm²

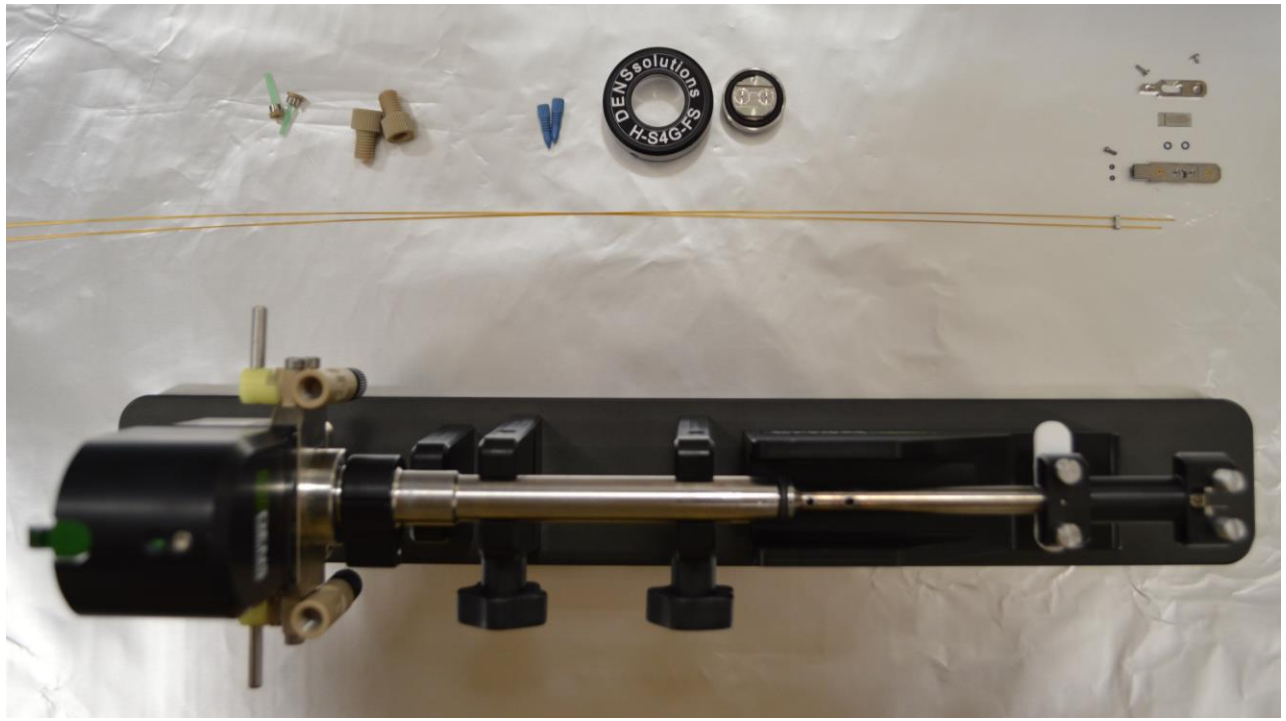


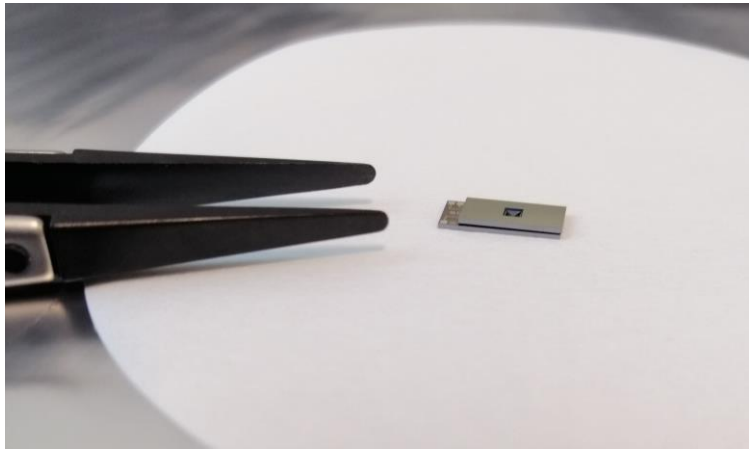
Sample 3: loading= 6 µg/cm²

Advanced in situ TEM studies for electrochemistry applications

EMAT **in-situ** material characterization

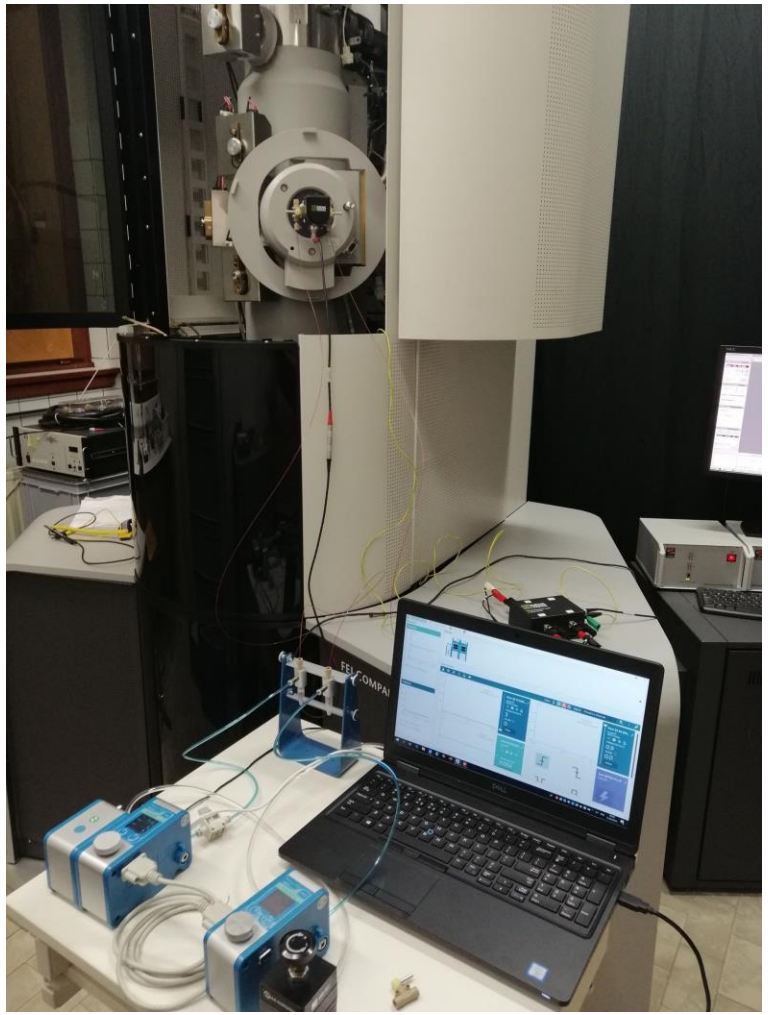
In-situ Stream holder (Liquid-biasing)





Liquid holder tip (Nano reactor)

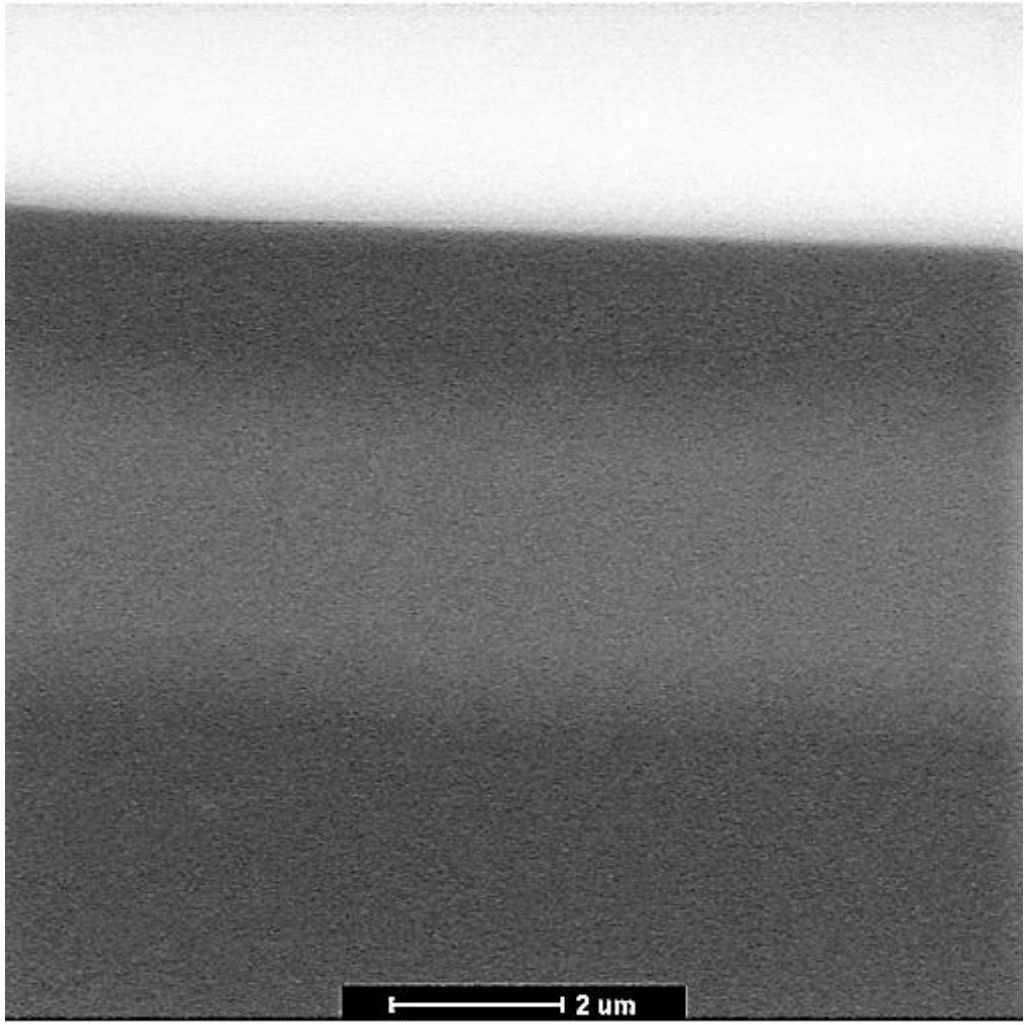
Stream holder

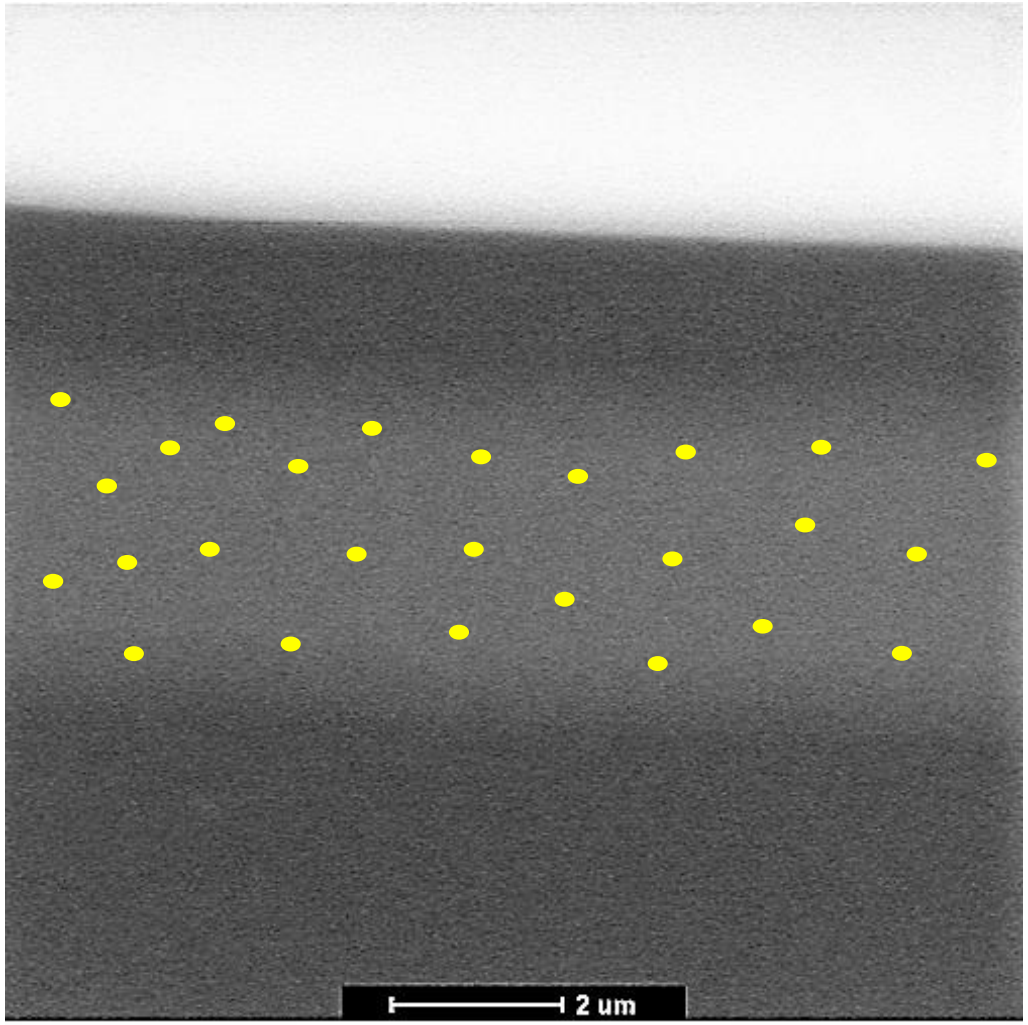


electrical connections

flow system

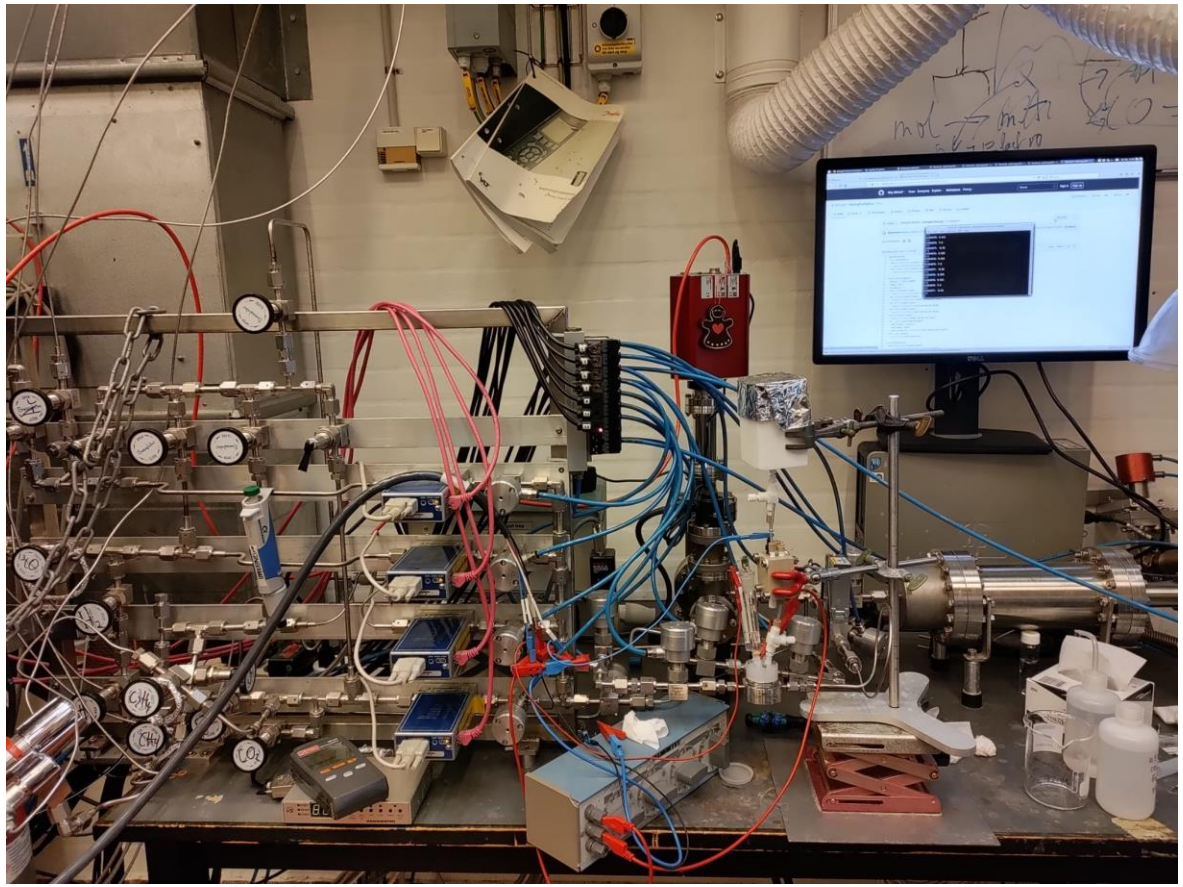
GC electrode inside the Microscope





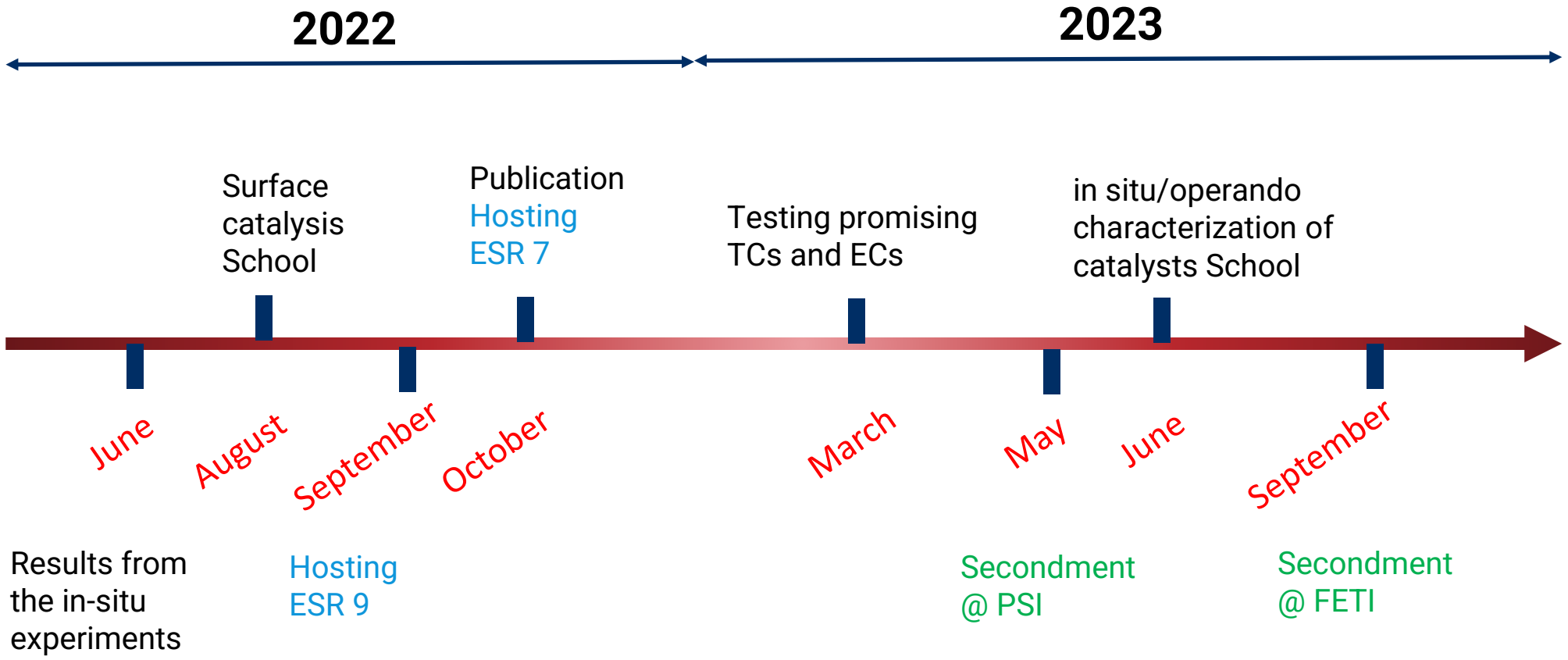
Secondment @DTU

Characterization of clusters with complementary electrochemical characterization techniques



EC-MS System (the Sniffer)

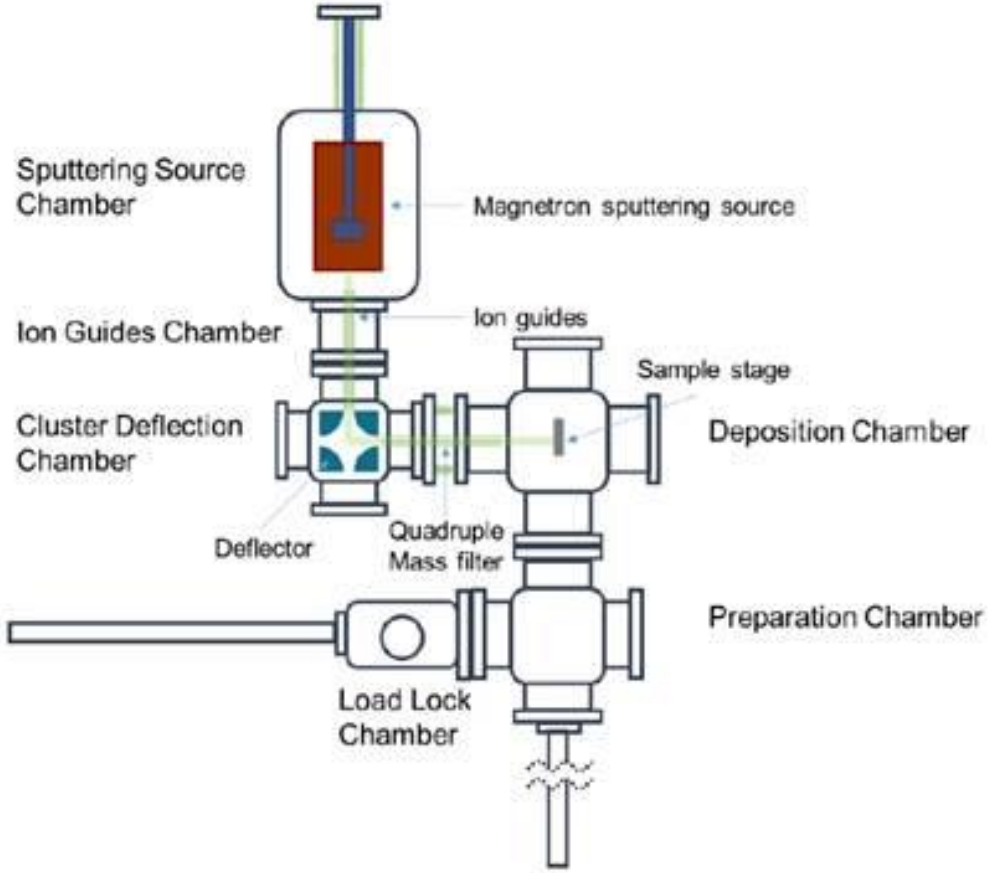
Future Plan


2022
2023
Surface catalysis School
Publication
Hosting ESR 7
Testing promising TCs and ECs
in situ/operando characterization of catalysts School
June
August
September
October
March
May
June
September
Results from the in-situ experiments
Hosting ESR 9
Secondment @ PSI
Secondment @ FETI

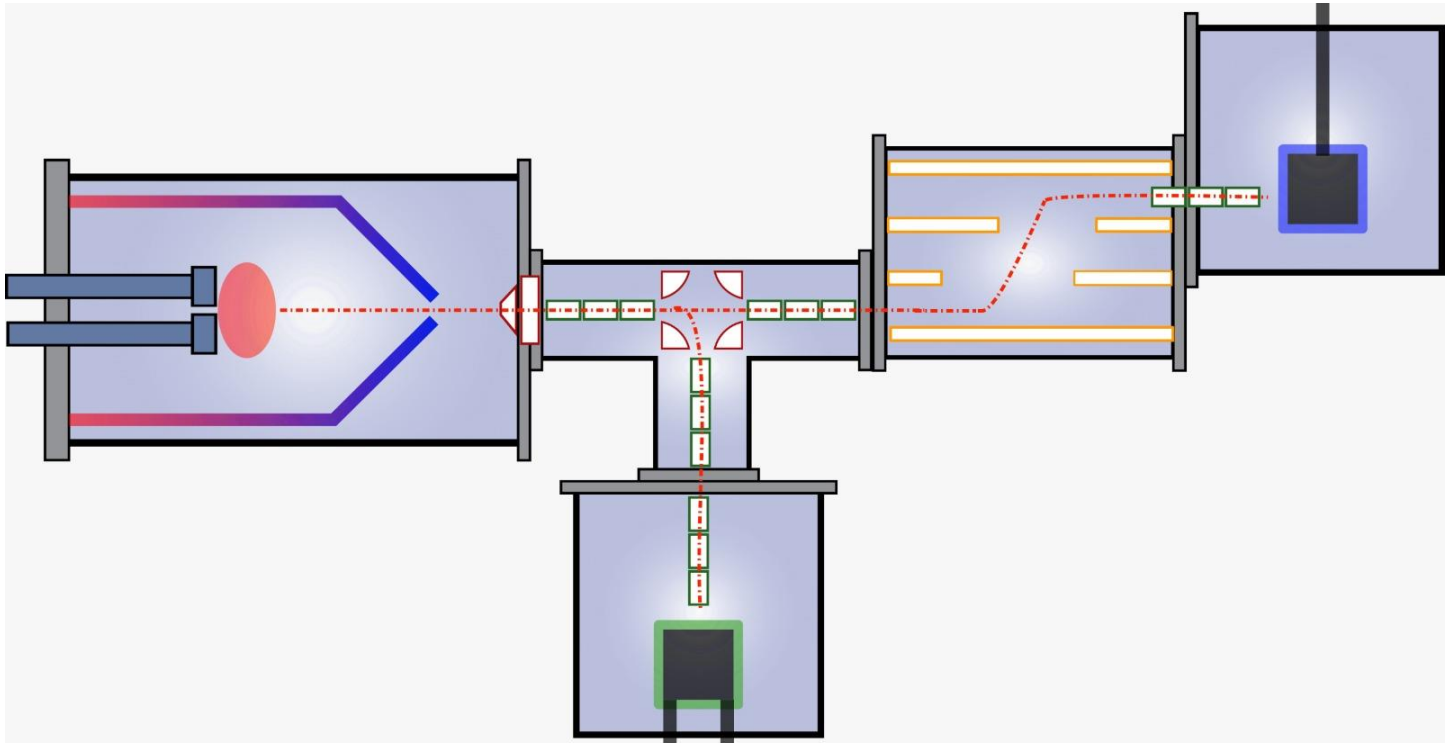
Thank you

Supplementary Slides

Schemes of Magnetron cluster sources at KUL and TCL

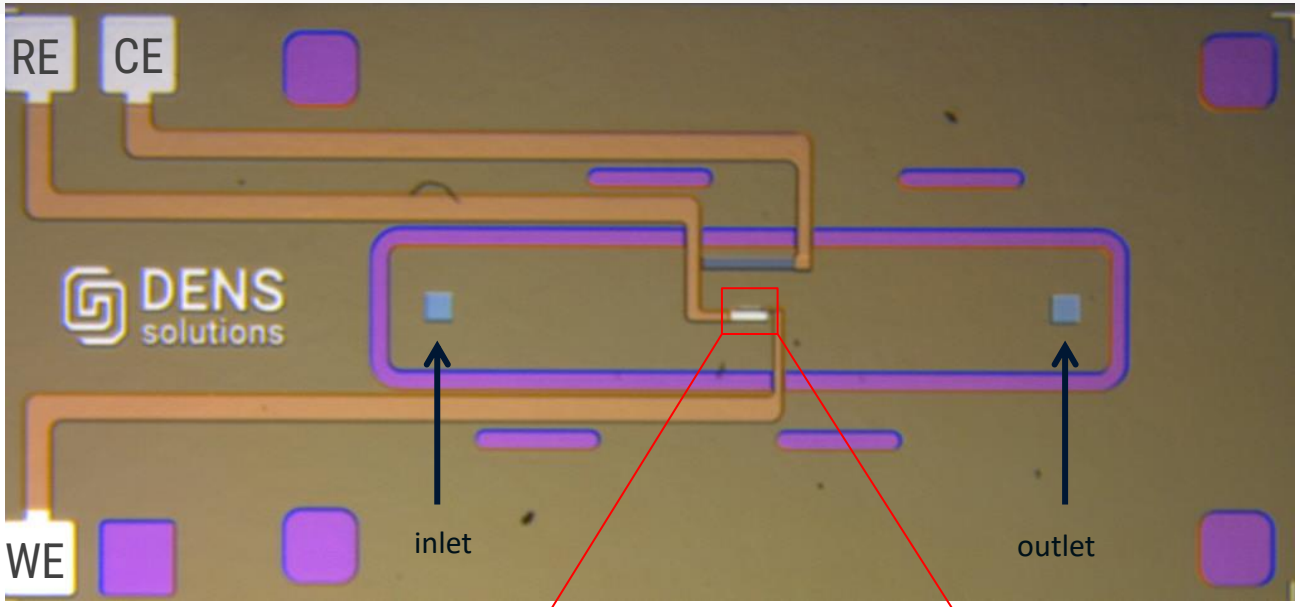


@KUL

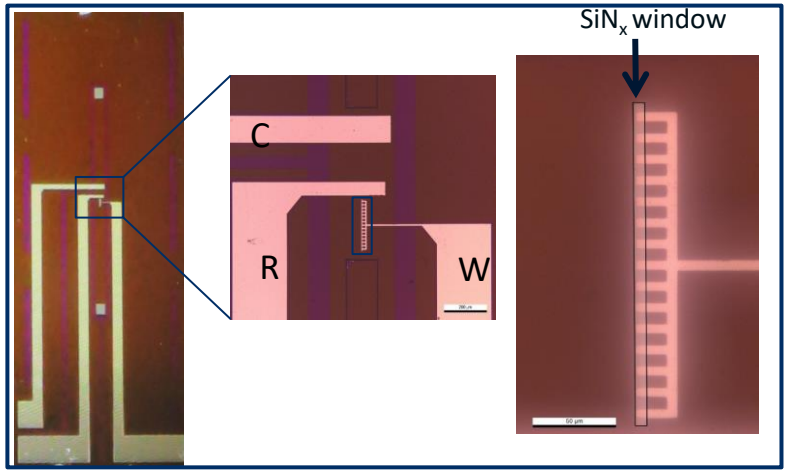


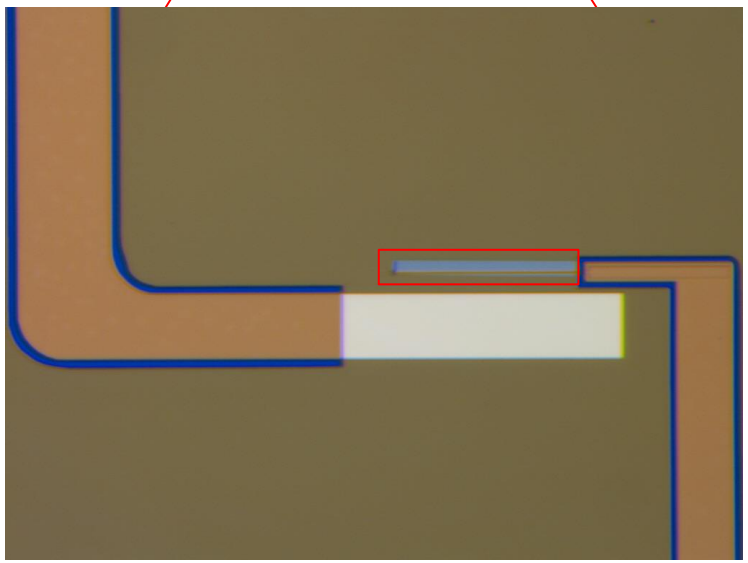
@TCL

Bottom Chip



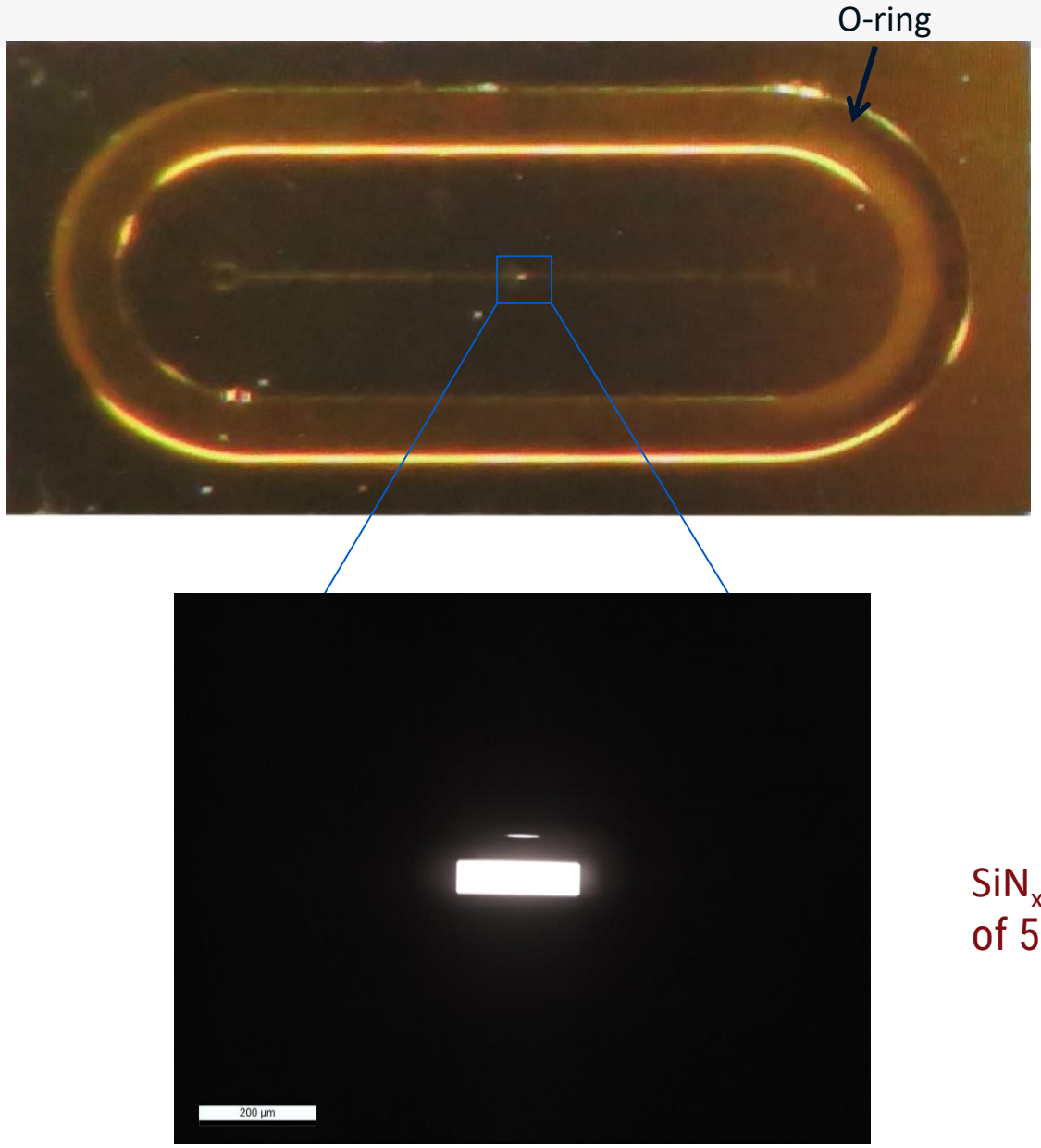
Old Chips





Glassy Carbon electrode
+ SiN_x window

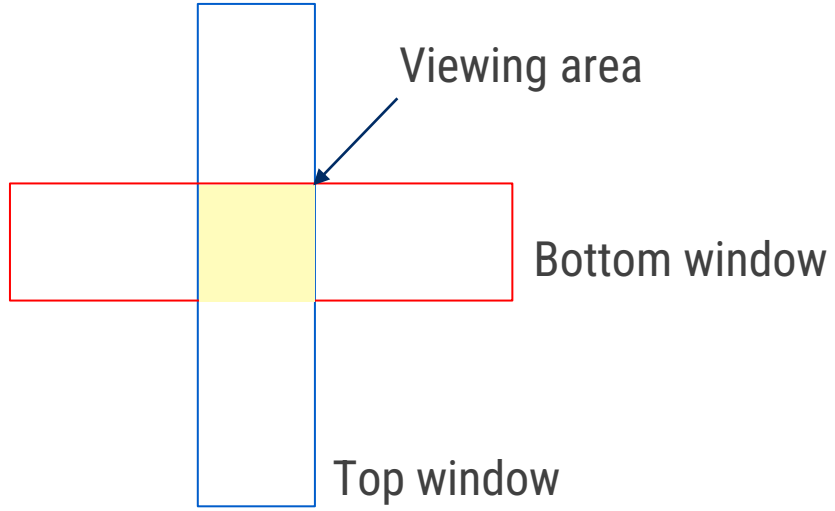
Top Chip



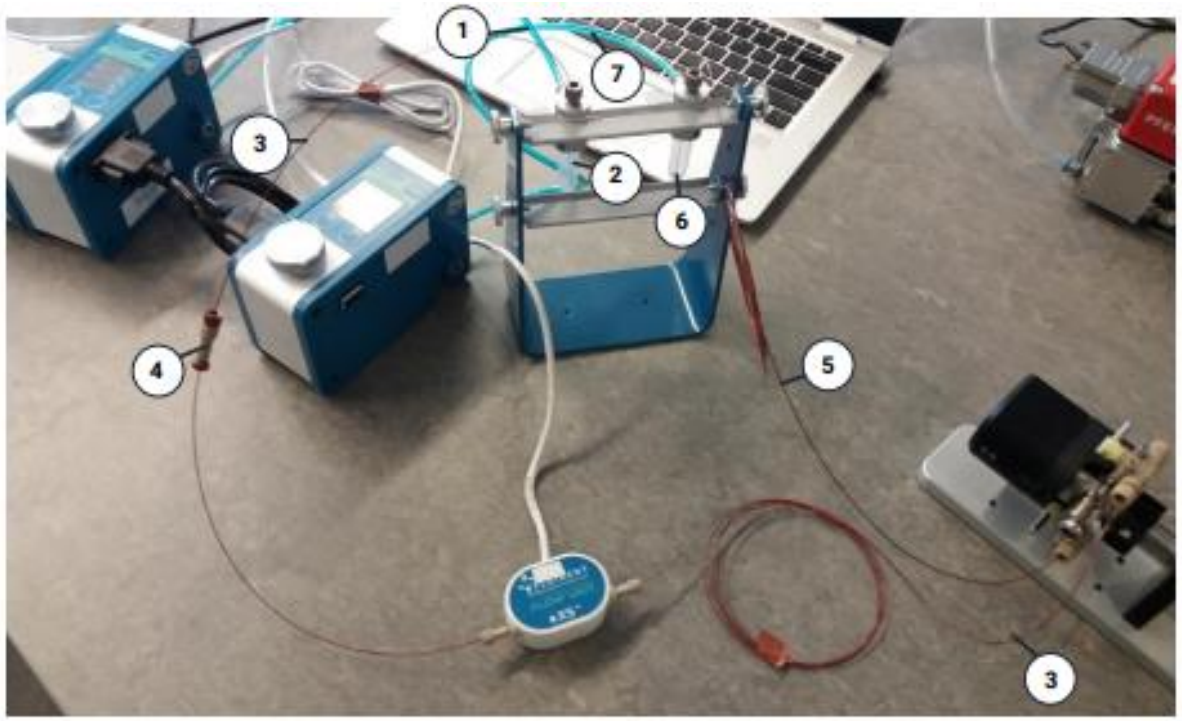
SiN_x window (membrane of 50 nm thickness)

Side view of the assembled tip

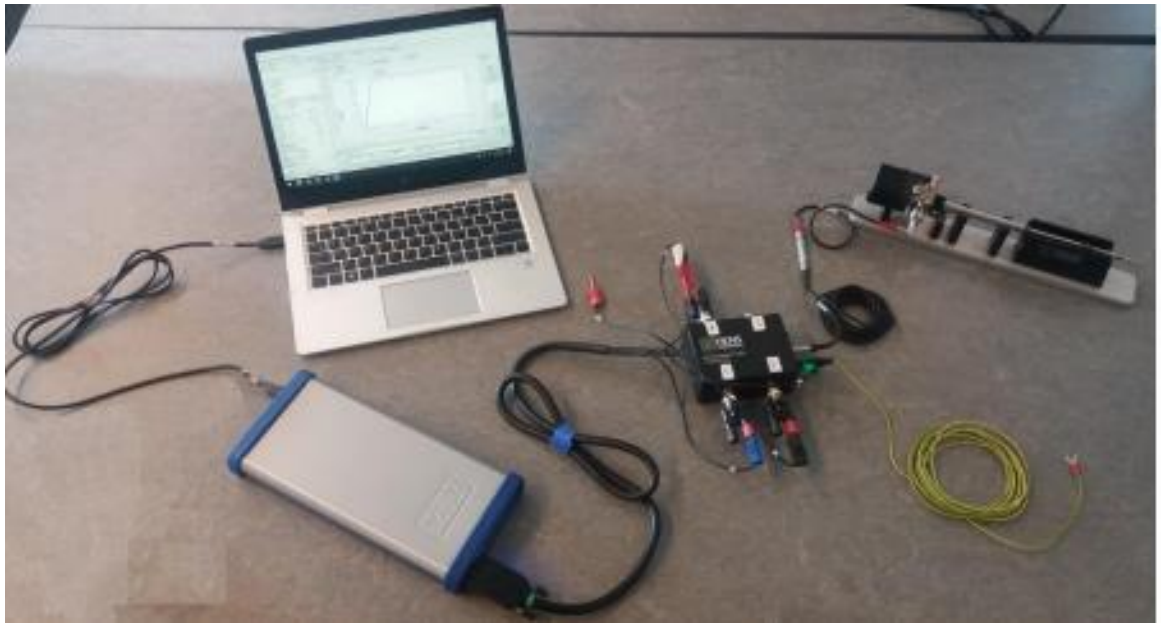
Working volume ~ 80 nL



Top view schematic of the windows



An overview of the flow system



An overview of the electrical connections