Exploring Big Data for a Deeper Understanding of Electrocatalyst Behavior

- starting…

ElectroCat Laboratory

NATIONAL INSTITUTE OF CHEMISTRY

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Laboratory for ElectroCatalysis

Established in 2020:

Catalyst Synthesis and Characterization

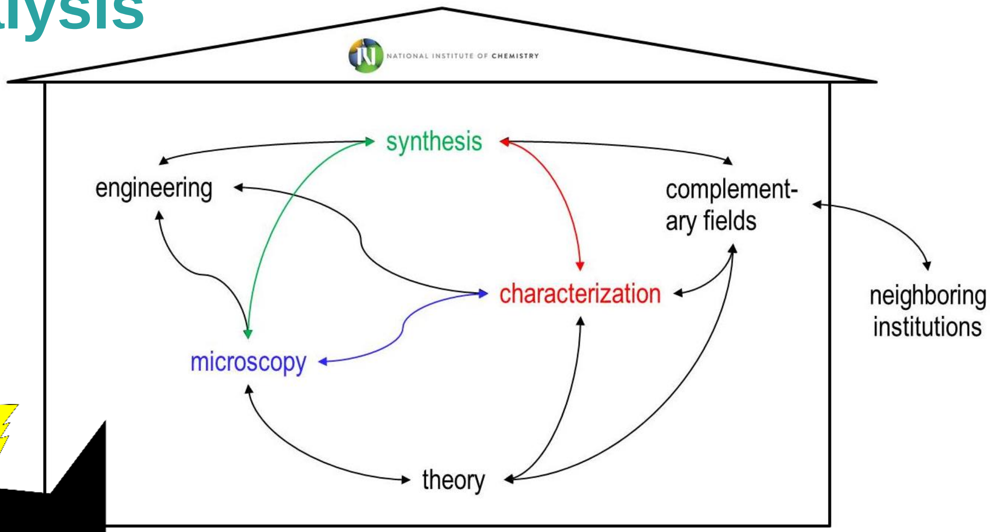
Advanced electrochemical characterization

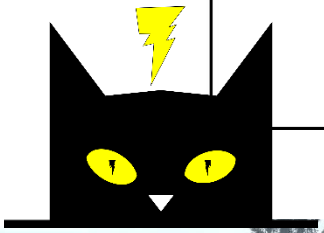
Electron microscopy

Recycling

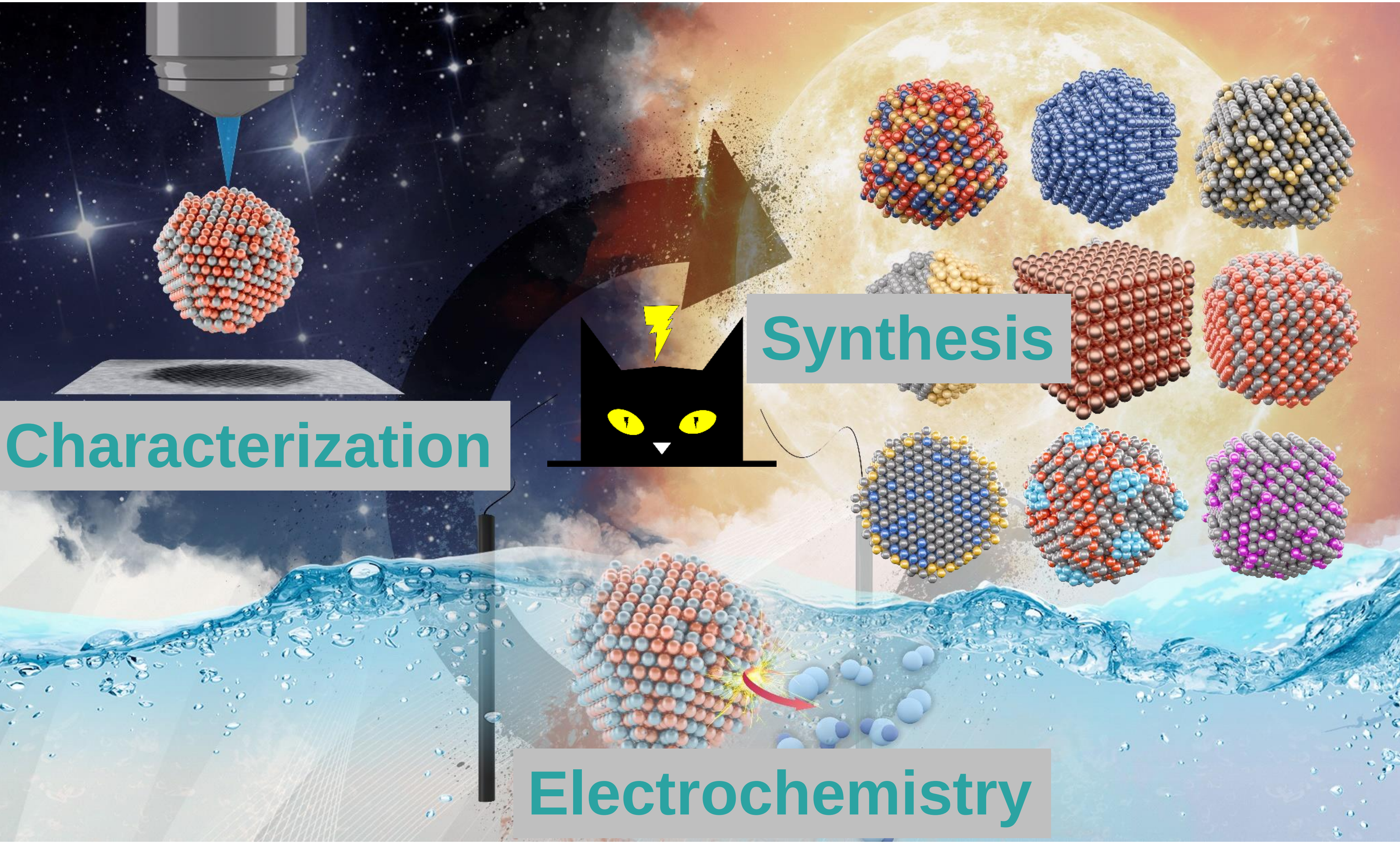
Electrosynthesis

Collaborations…





We support each other to be the best versions of ourselves.


Characterization
Synthesis
Electrochemistry

Electrocatalysis

Very intriguing chemistry that is happening at the metal-electrolyte interface!

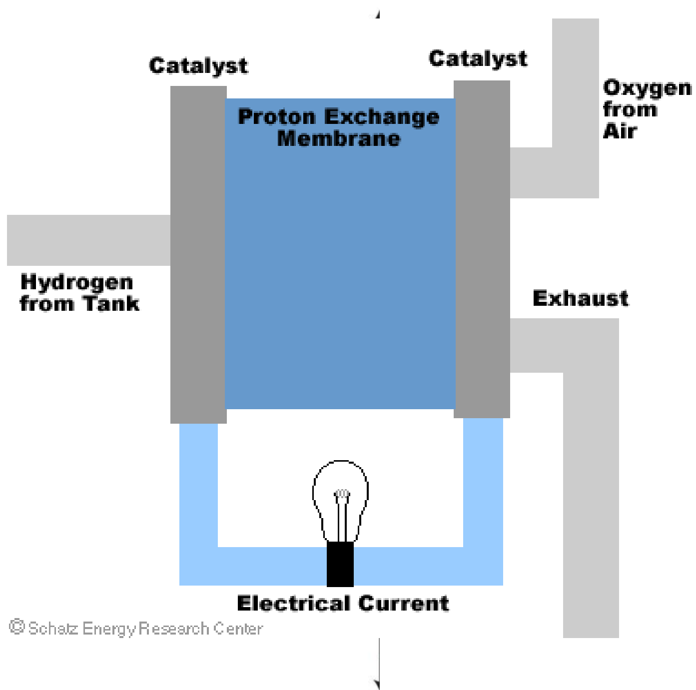
The electrons are decoupled from the reactants by splitting the reaction in two.

Main difference to catalysis is the double layer! *Old field…reinvigorated!*

$2H_2 + O_2 \rightarrow 2H_2O$

$2H_2 \rightarrow 2H^+ + 2e^-$

$CH_3OH + H_2O \rightarrow CO_2 + 6e^- + 6H^+$



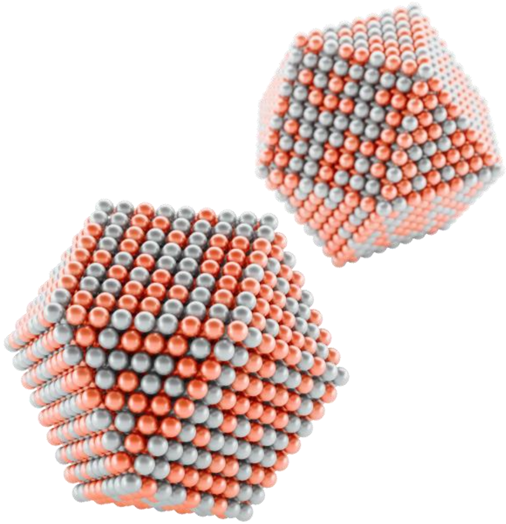
$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

It has relevance to the future possibilities of the energy infrastructure!

N. Markovic, Nature Materials **2013**, 12, 101–102

What are nanoparticles?

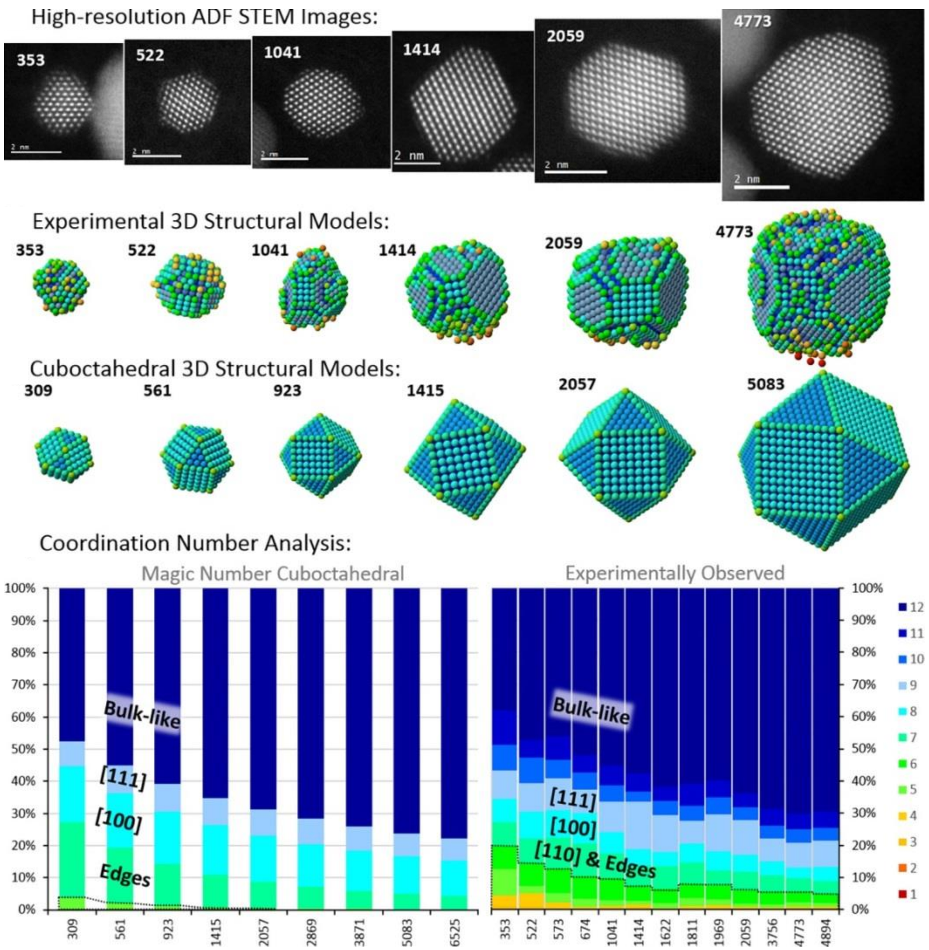
- Nanoparticles are particles ranging in size from 1 to 100 nanometers.
- Hair thickness is approximately one hundred thousand (100 000) nanometers.
- At these sizes, the properties change (large area and more…).
- Nanoparticles are composed of relatively few atoms
  - 2 nm -> 3000 to 5000, 4 nm -> 20000 atoms
  - Nanozymes
  - Electro-Catalysts



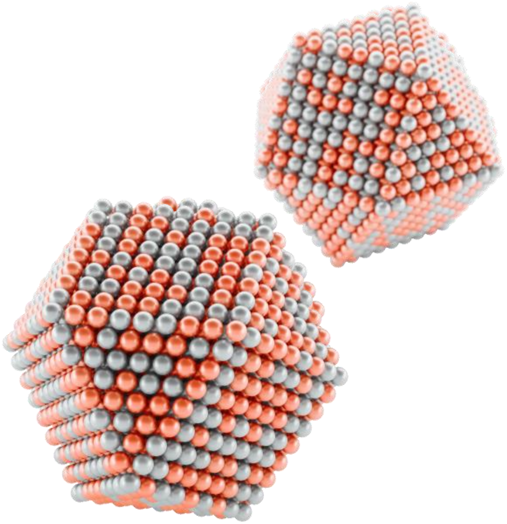
Compared to molecule catalysts (homogeneous) or viruses that have atomically defined structures ours are very complex!

Difference between homo- and heterogeneous-catalysis

No nanoparticle is perfect!



No two particles that we will examine will be alike!



Nanostructured Pt-alloys ORR electrocatalysts

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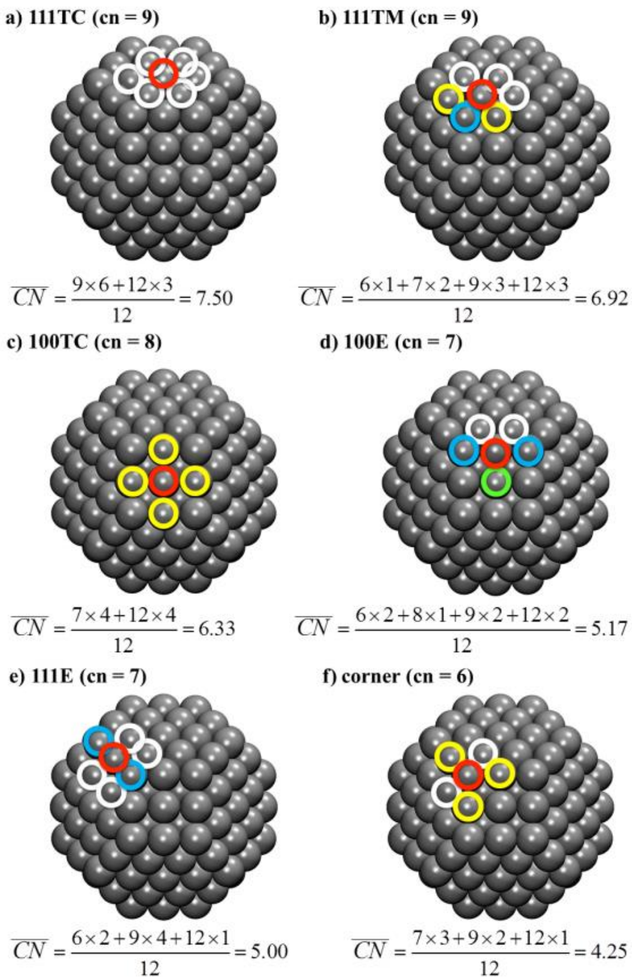

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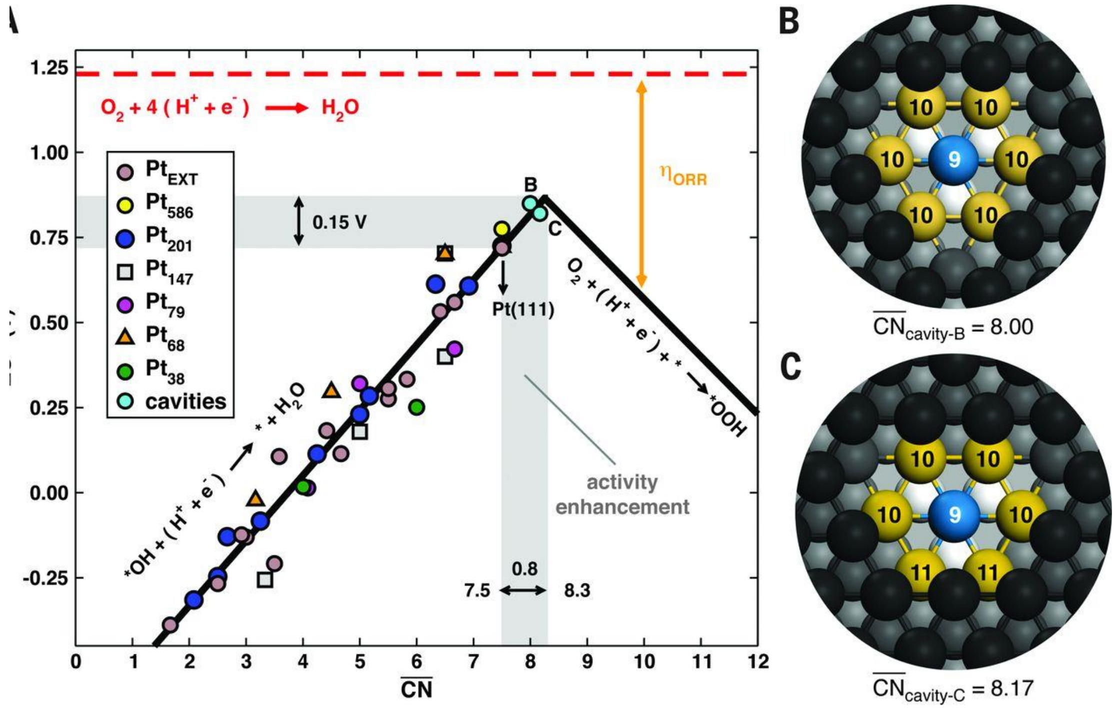
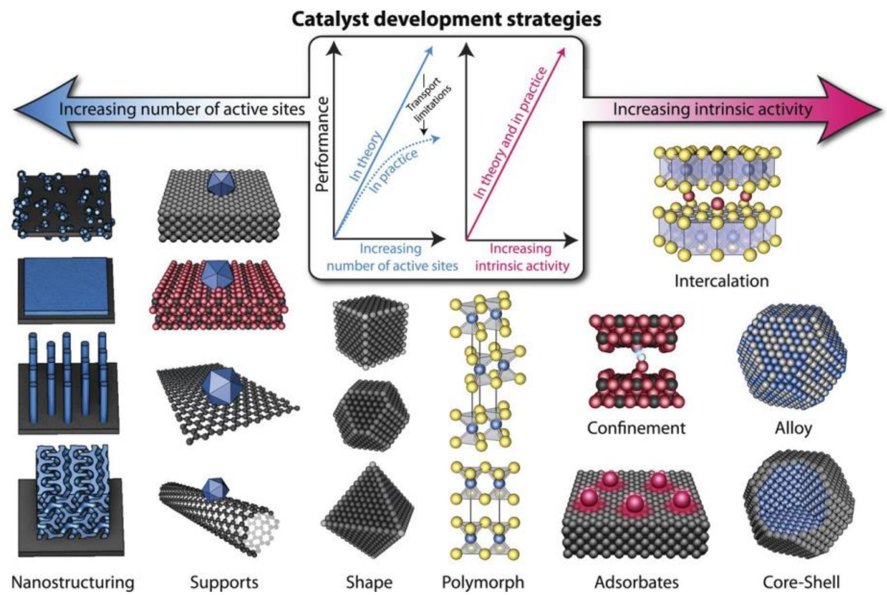


What defines metal electrocatalyst performance?

– double layer structure (what defines that besides the electrolyte…)

-nature of the metal
-size
-morphology (surface facets)
-structure
-composition (presence of second metal)
-presence of defects, steps, kinks, ad-atoms
-alloying ligand and/or strain
-support
-confinement, proximity, ensemble
-surface patterning, nature of electrolyte
-etc.



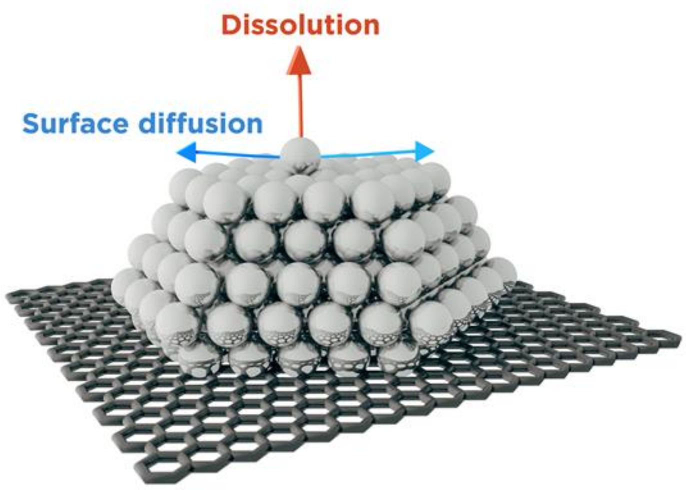
Chorkendorff, Nørskov, Jaramillo*, et al., *Science* **2017**, *355* (6321)

Practically everything we can think of!

Nobel laureate Wolfgang Pauli said, "God made the bulk; surfaces were invented by the devil".

The devil is in the details.

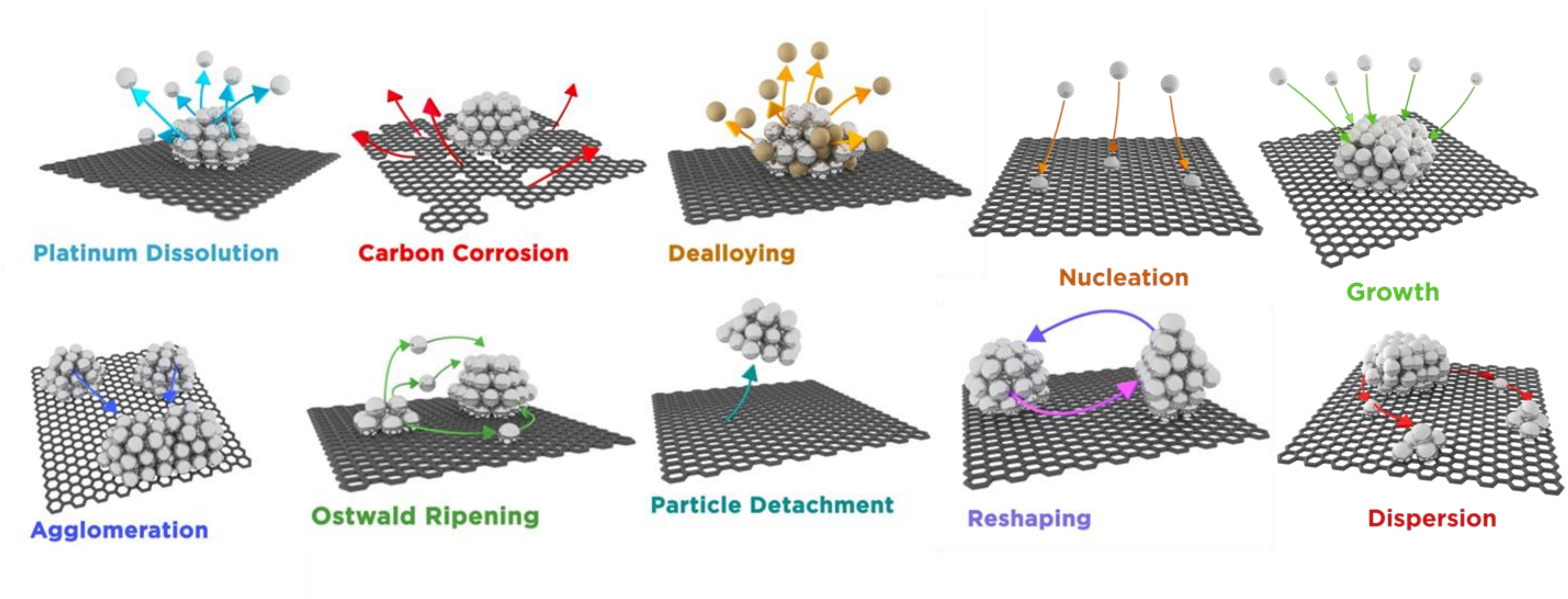
Structure-activity relationship on atomic level is a **state-of-the-art** in electrocatalysis



However we can not synthesize identical (perfect) nanoparticles as a model systems!

Structure-stability relationship at the atomic level is much less explored!
And we have great methods that have (close to) atomic resolution.
It is indeed much harder to measure activity one atom then see how it moves…

Electrochemical degradation mechanisms of nanoparticles

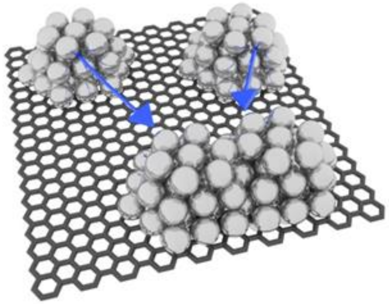


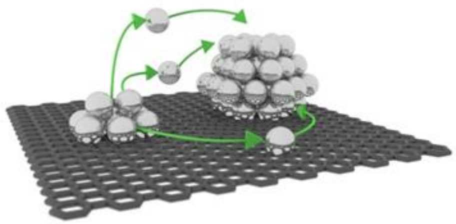
Complex interplay of different mechanisms resulting in the change of active surface area (j_a and ESA)!

Degradation of Pt-based fuel cell catalyst

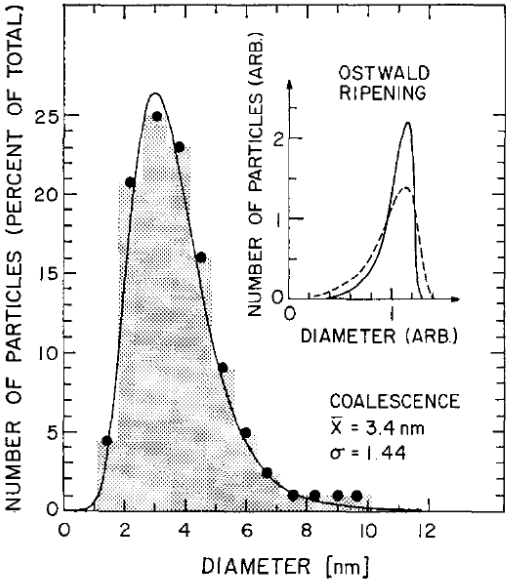
How to distinguish between them?

Postmortem analysis?
No!





Bulk methods like particle size distribution (PSD) obtained by analyzed TEM images and XRD offer only averaged information:
It was shown that PSDs with **tails to larger particle sizes** are associated with particle growth via **migration and coalescence**.
In contrast, a PSD indicative of growth through electrochemical **Ostwald ripening** involves a peak toward large particle sizes with **tailing to smaller sizes**.



Problem: the simple models assume that only one growth mode occurs! – not true!

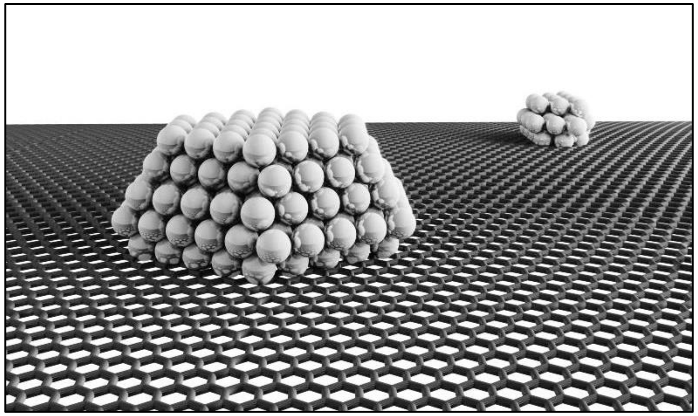
C.G. Granqvist, R.A. Buhrman, Journal of Catalysis , **1976**, 42, 477-479.

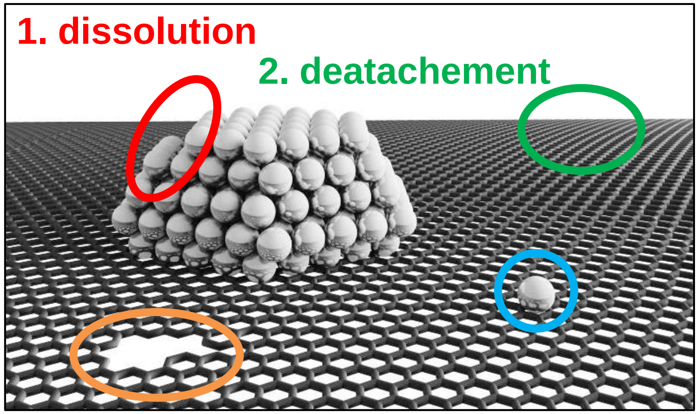
Meier, *ACS Catalysis,* **2012**, 2, 832-843.

Identical Location Electron Microscopy

Spot the difference at the atomic level

Can you spot all 4 differences and mark them?

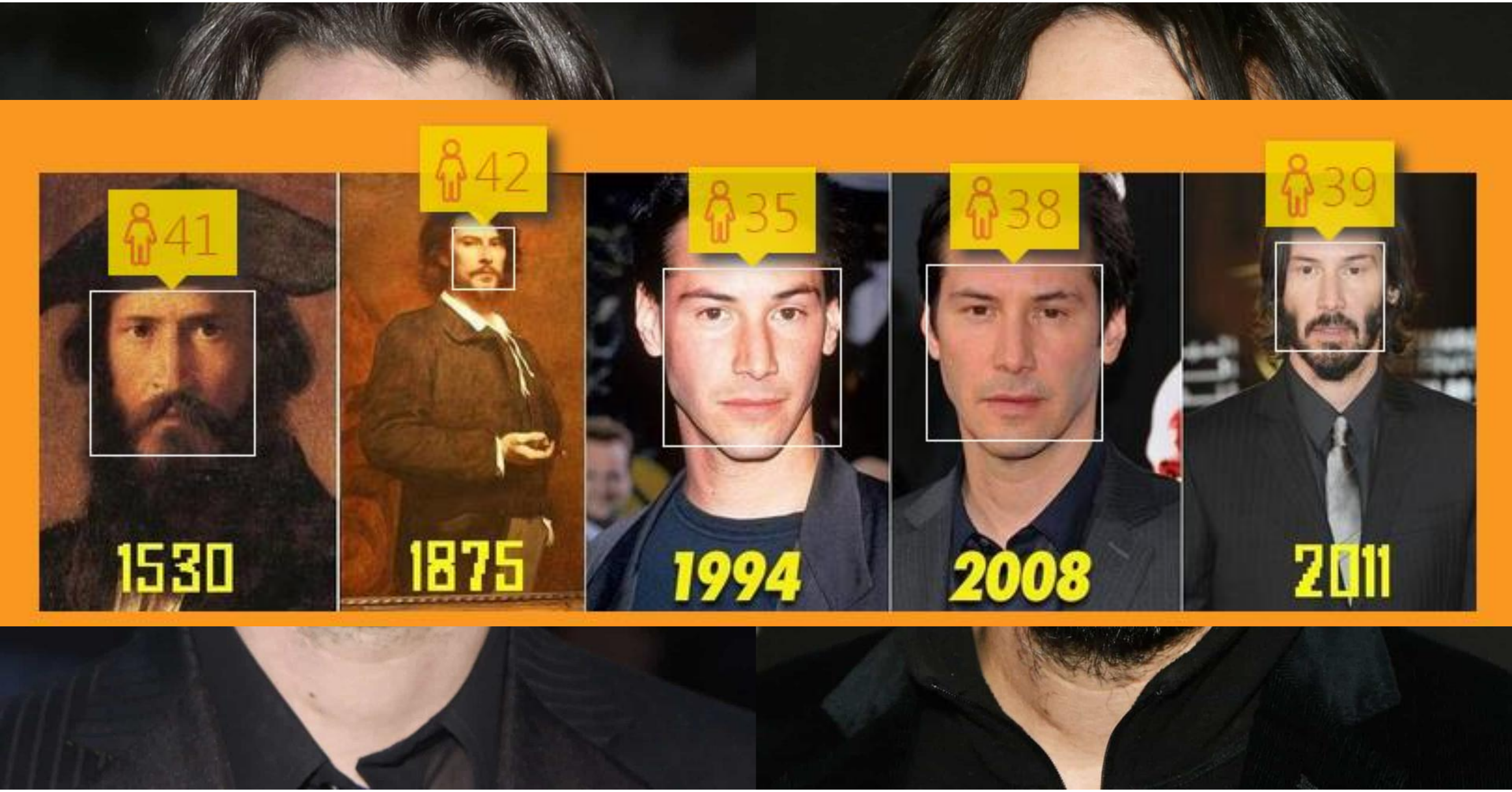




See the two (electrocatalysts) images before and after aging.

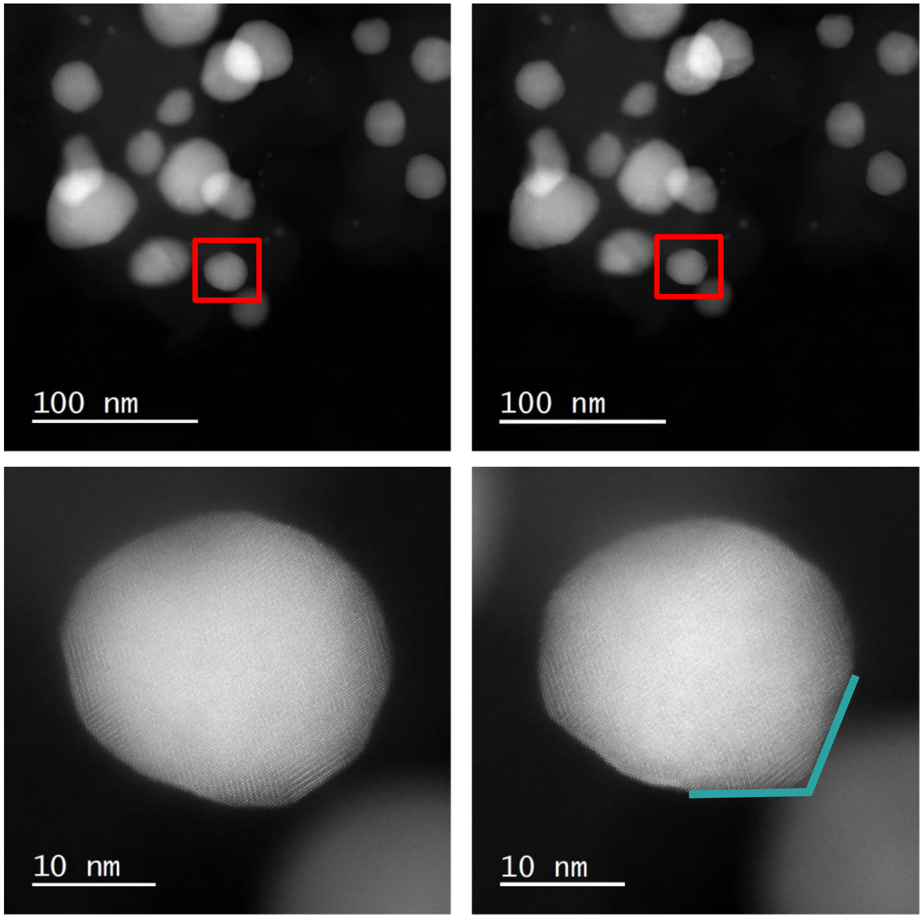
Because the history of the location's physical characteristics is known, reliable conclusions on very complex restructuring events such as degradation mechanisms can be drawn!

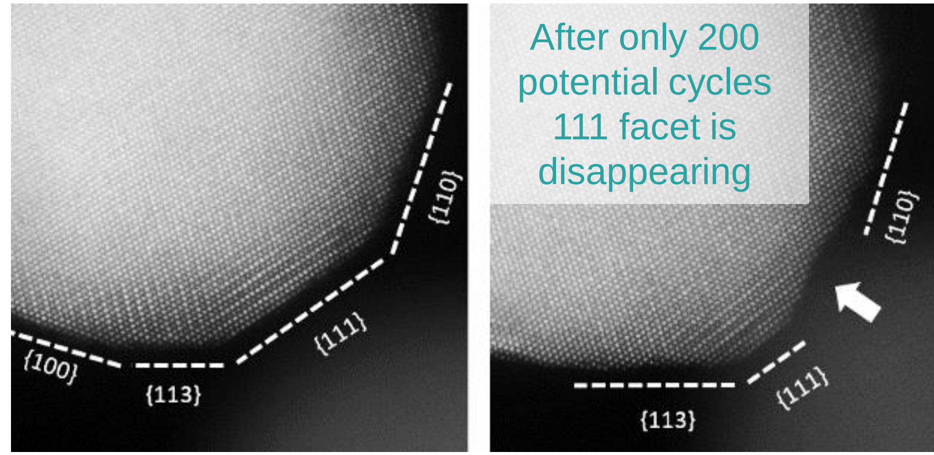
Identical Location …



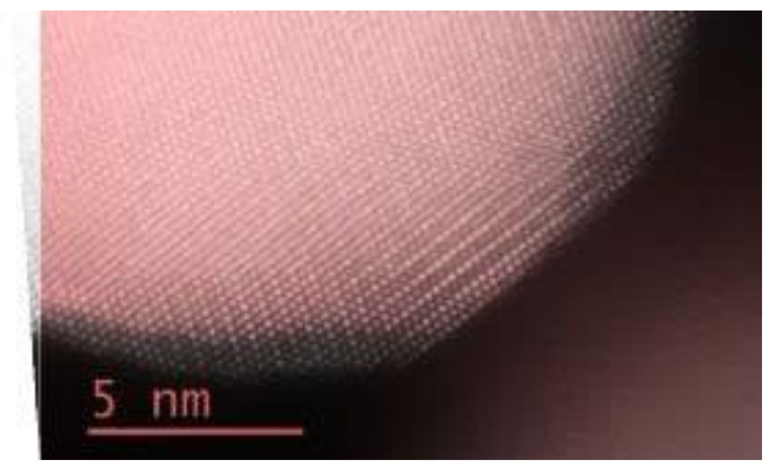
https://www.starsinsider.com/celebrity/392805/the-matrix-of-age-keanu-reeves-is-immortal-and-heres-the-proof
https://www.reddit.com/r/funny/comments/5sqeyu/keanu_doesnt_age_even_the_computer_agrees/

PtM nanoparticles reshaping





Overlay

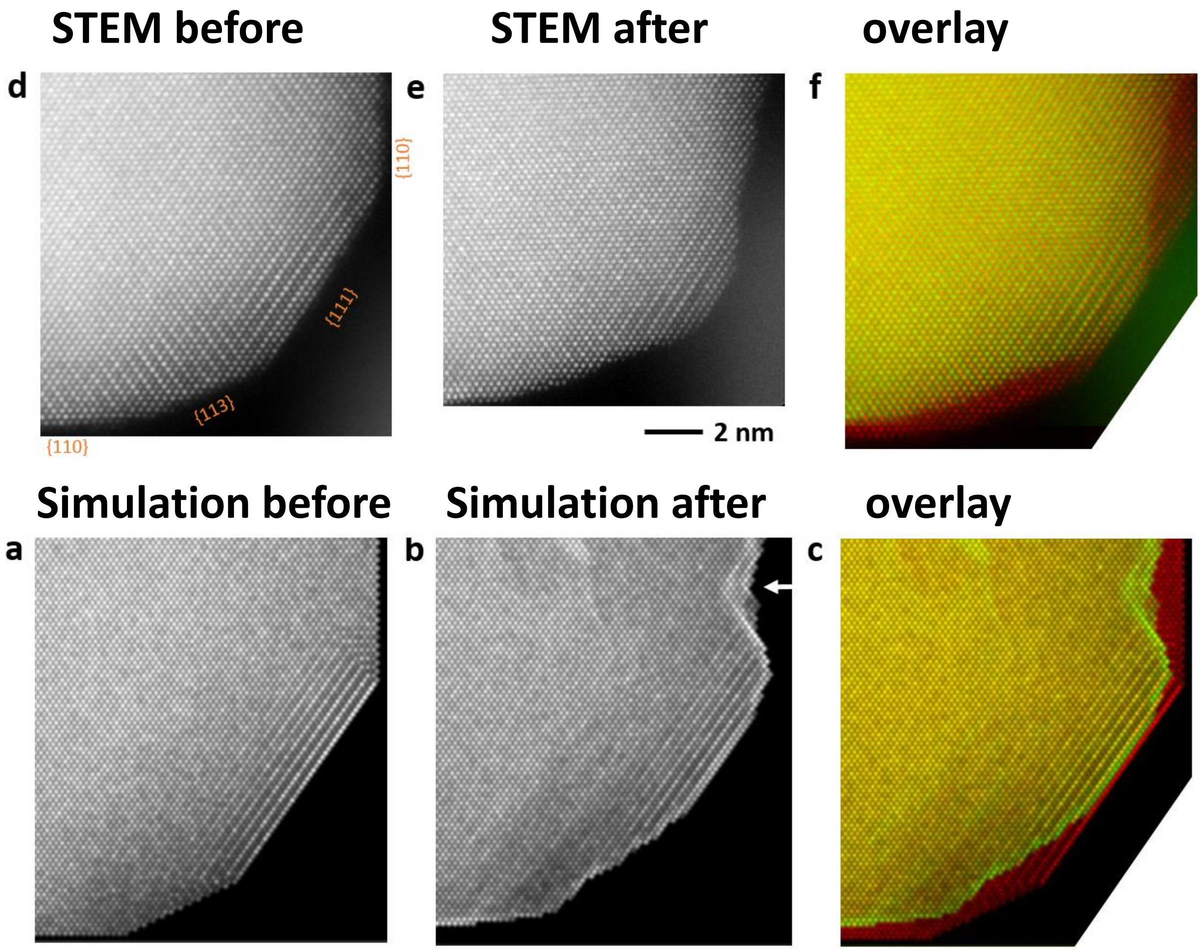


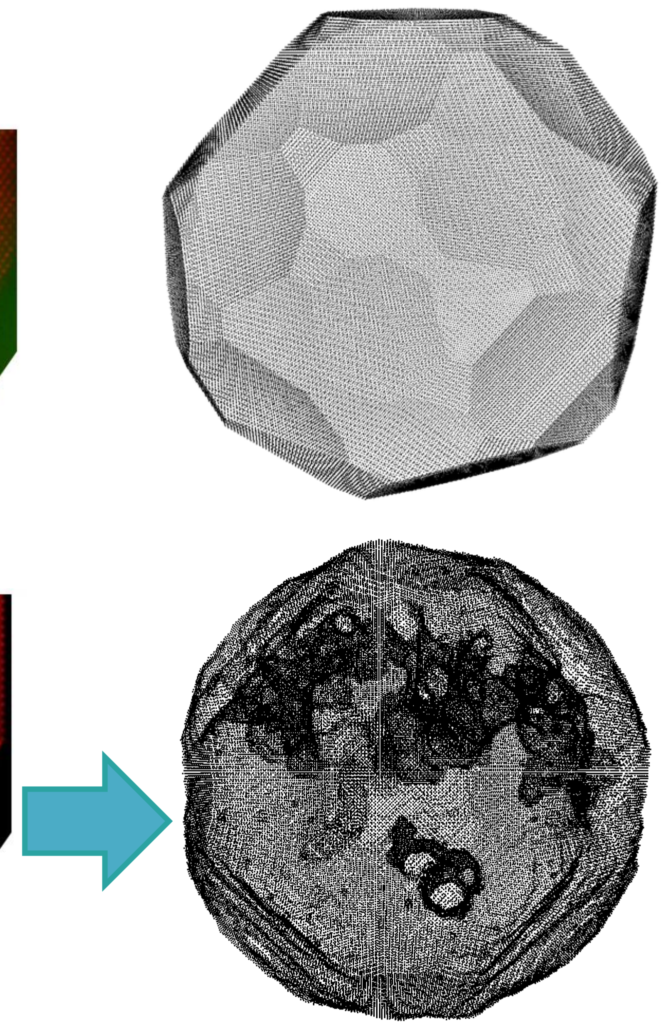
IL-TEM 0,1 M $HClO_4$
200 cyc 0.05 – 1.2 V vs. RHE, 300 mV/s, Ar

Computer simulation

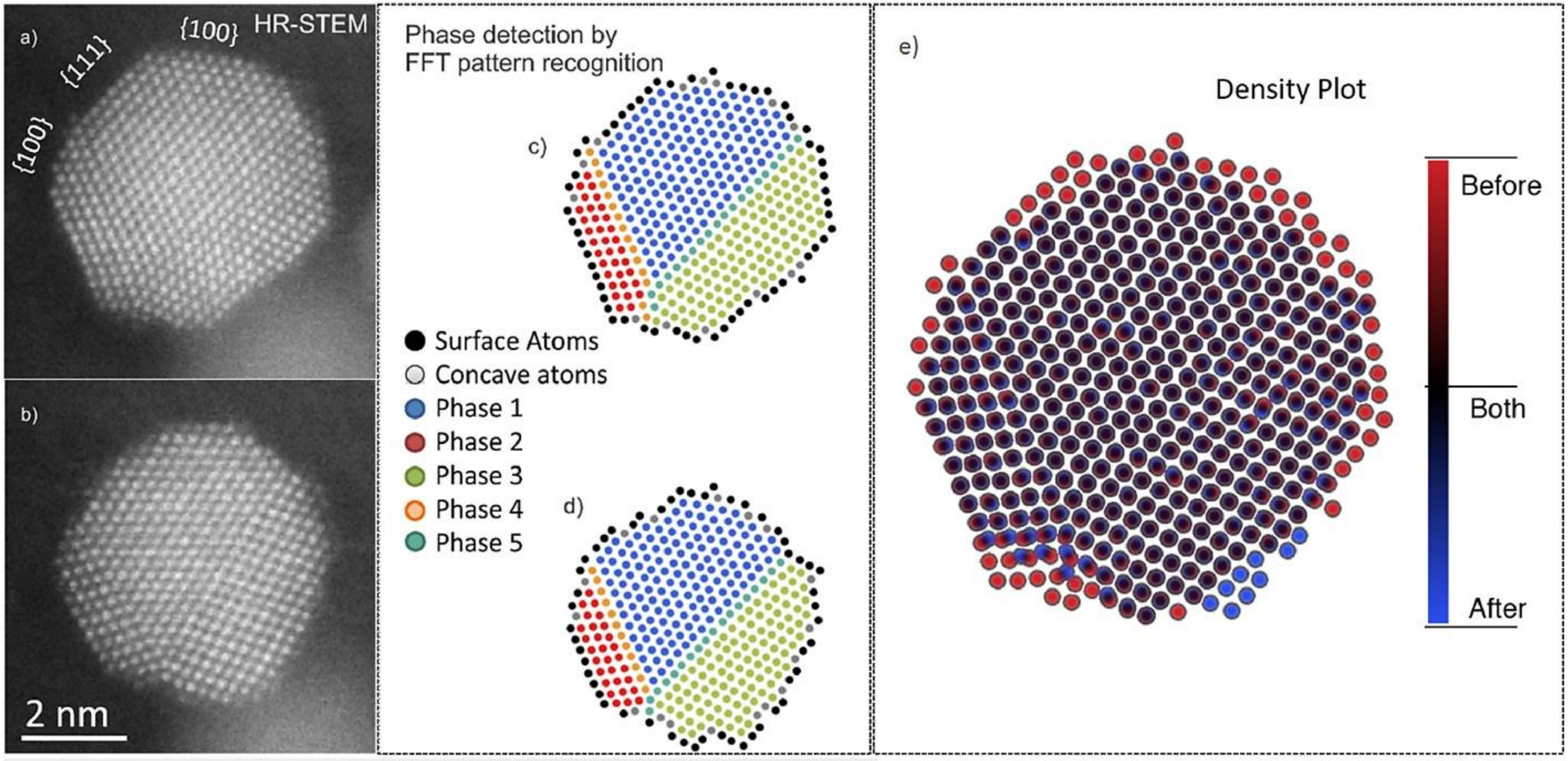
Atomic physical model - KMC!

Pavlisic & **Hodnik** et al. *ACS Catalysis* (2016), 6(8), 5530





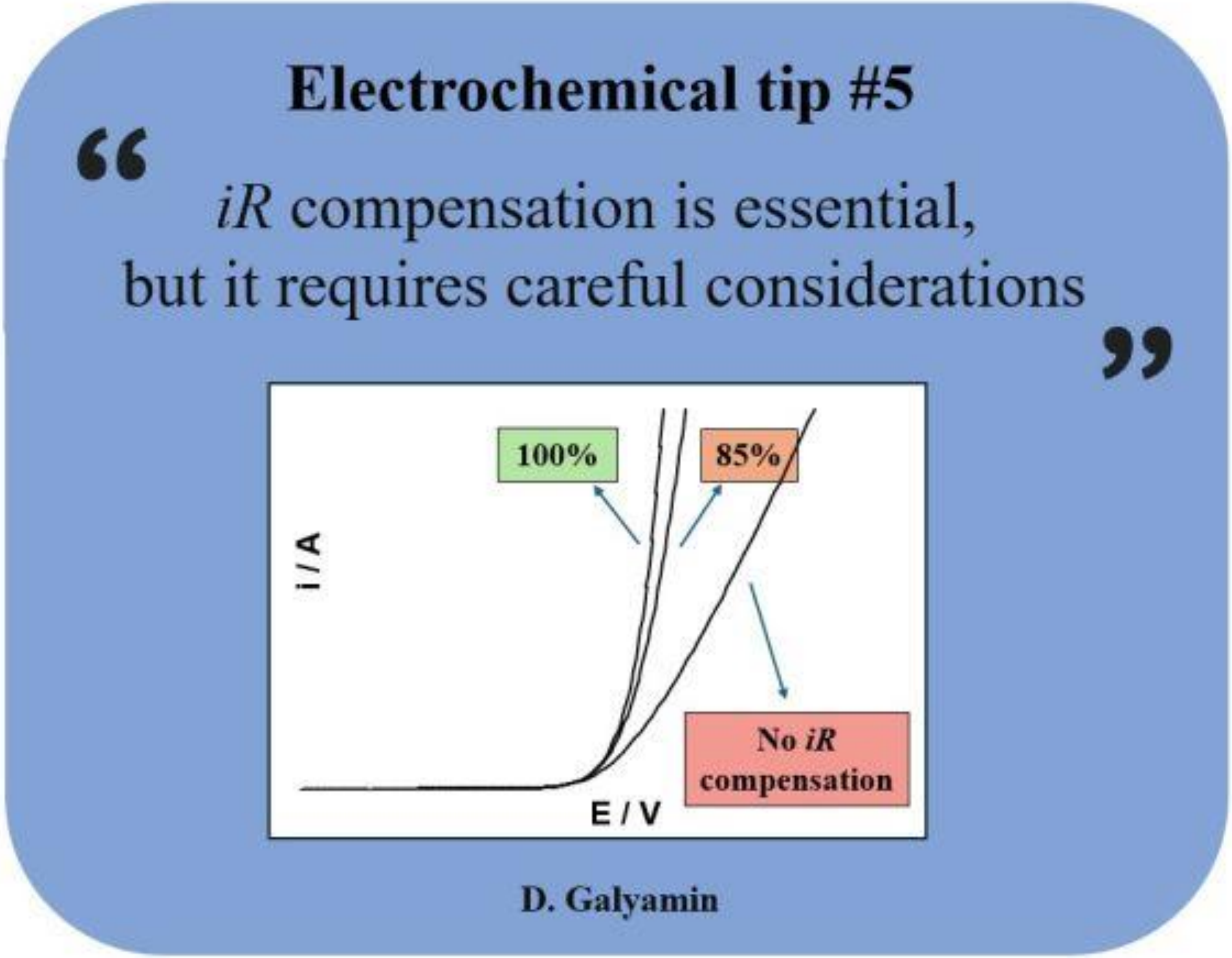
PtM nanoparticles reshaping



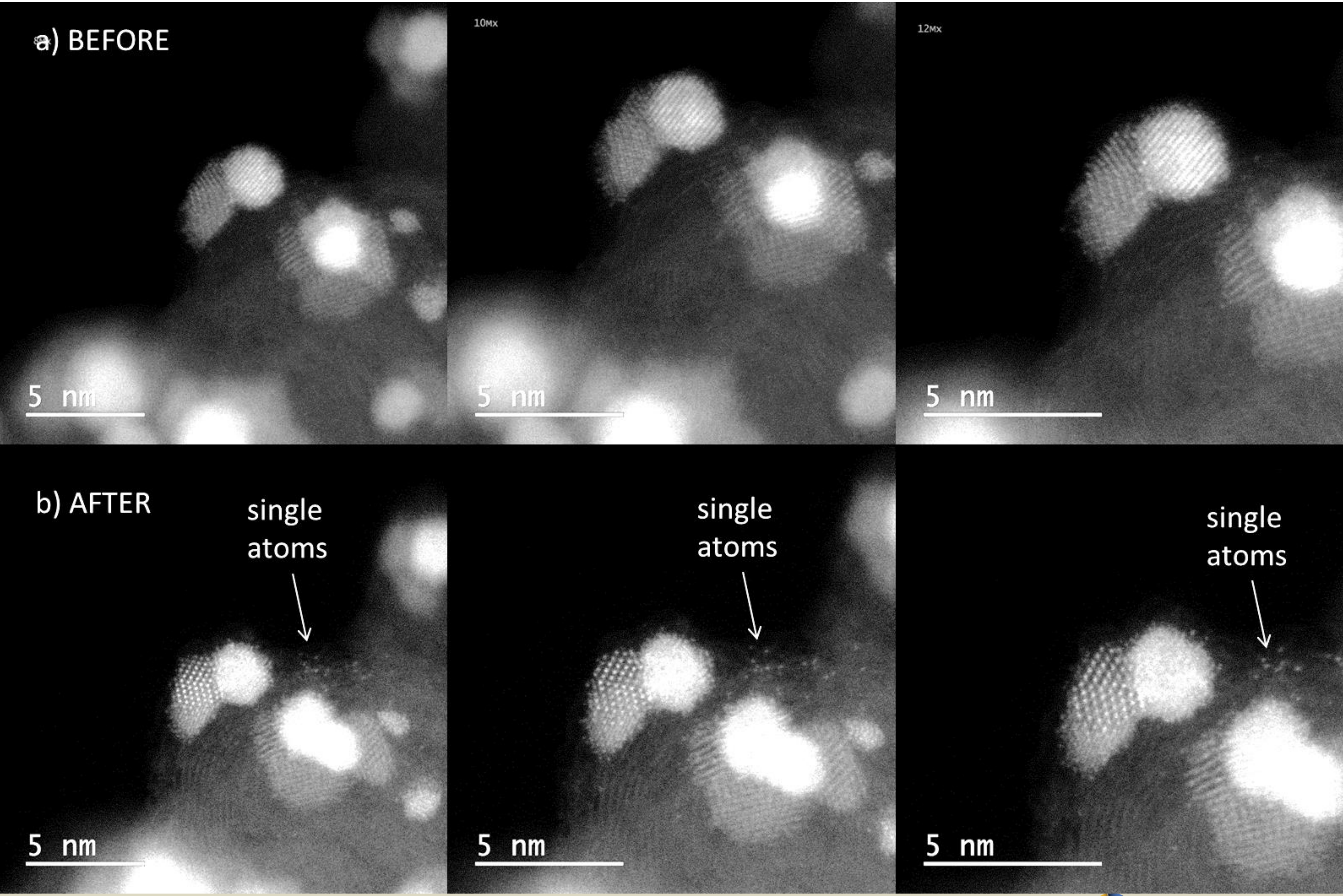
Problems – or my excuses

- How to measure reproducibly?
- How to trust somebody else‘s measurements if we even do not trust ours!
  - iR compensation, catalyst film quality, loading effect, contamination, sample preparation, treatment of data (data massage), use of different potentiostats, reference electrode, …
- Electrochemical signal is an average of signals (bulk)
- Effects od mass transport or local environment like pH
- Impurities (electrochemistry or even some single atom in graphene in TEM)
- Stability issues (electrochemistry or el. beam induced)
- The problem of error and reproducibility (a lot of effects besides just operator; karma or we saw Thursdays and Decembers are the best!)

Problems – electrochemistry



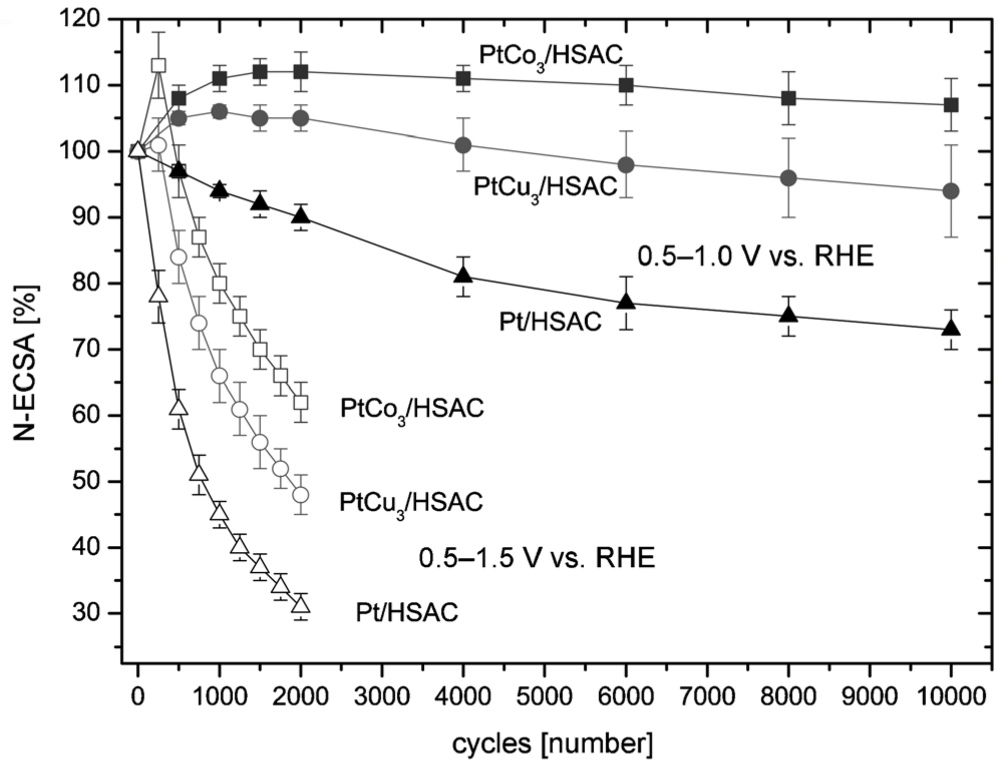
https://www.linkedin.com/posts/mahboobeh-nazarian_why-and-how-much-ir-compensation-should-we-activity-7193188284141871106-zMmL/

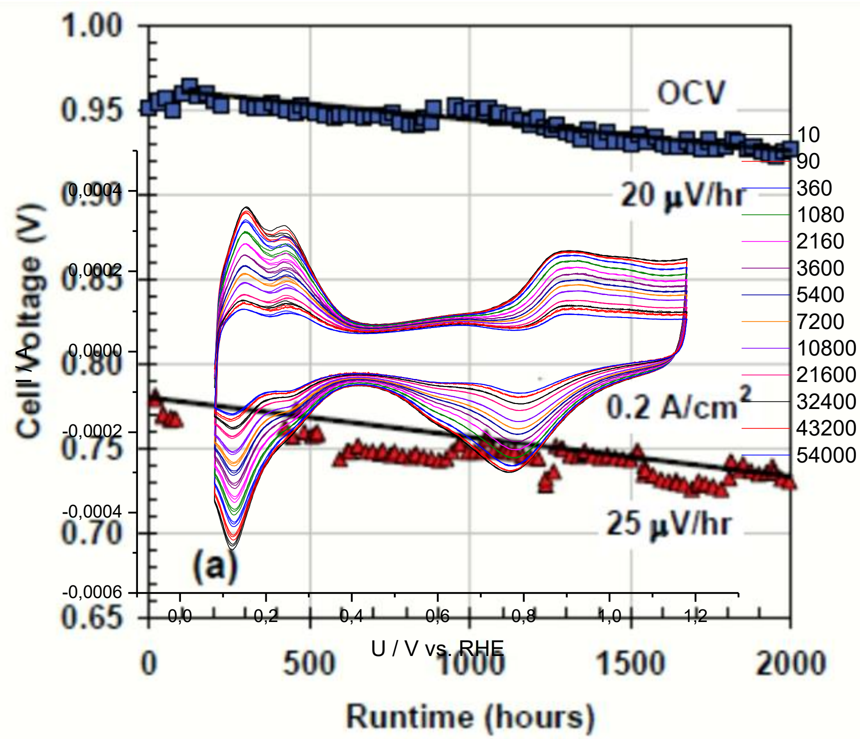


J. Phys. Chem. C 2018, 122, 18, 10050–10058

Proton exchange membrane fuel cell

Device inherently has a averaged behavior

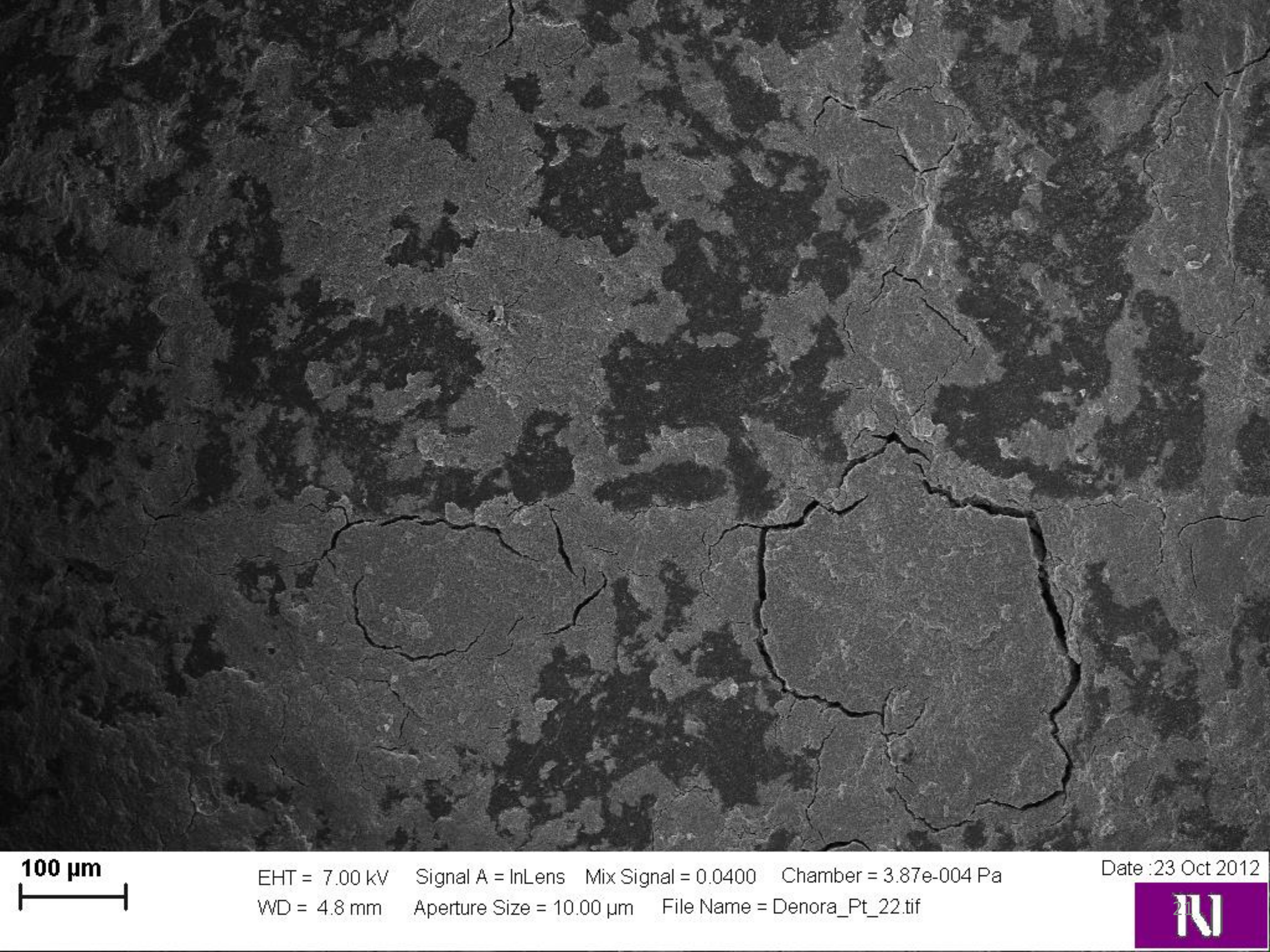




Frédéric Hasché, Activity, *ChemCatChem,* 3, (2011) 1805

Ferreira, *JES,* ***2005***, 152

Is it possible to avoid this – we must truly understand fundamentals first –> ex-situ tests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Aperture Size = 10.00 µm
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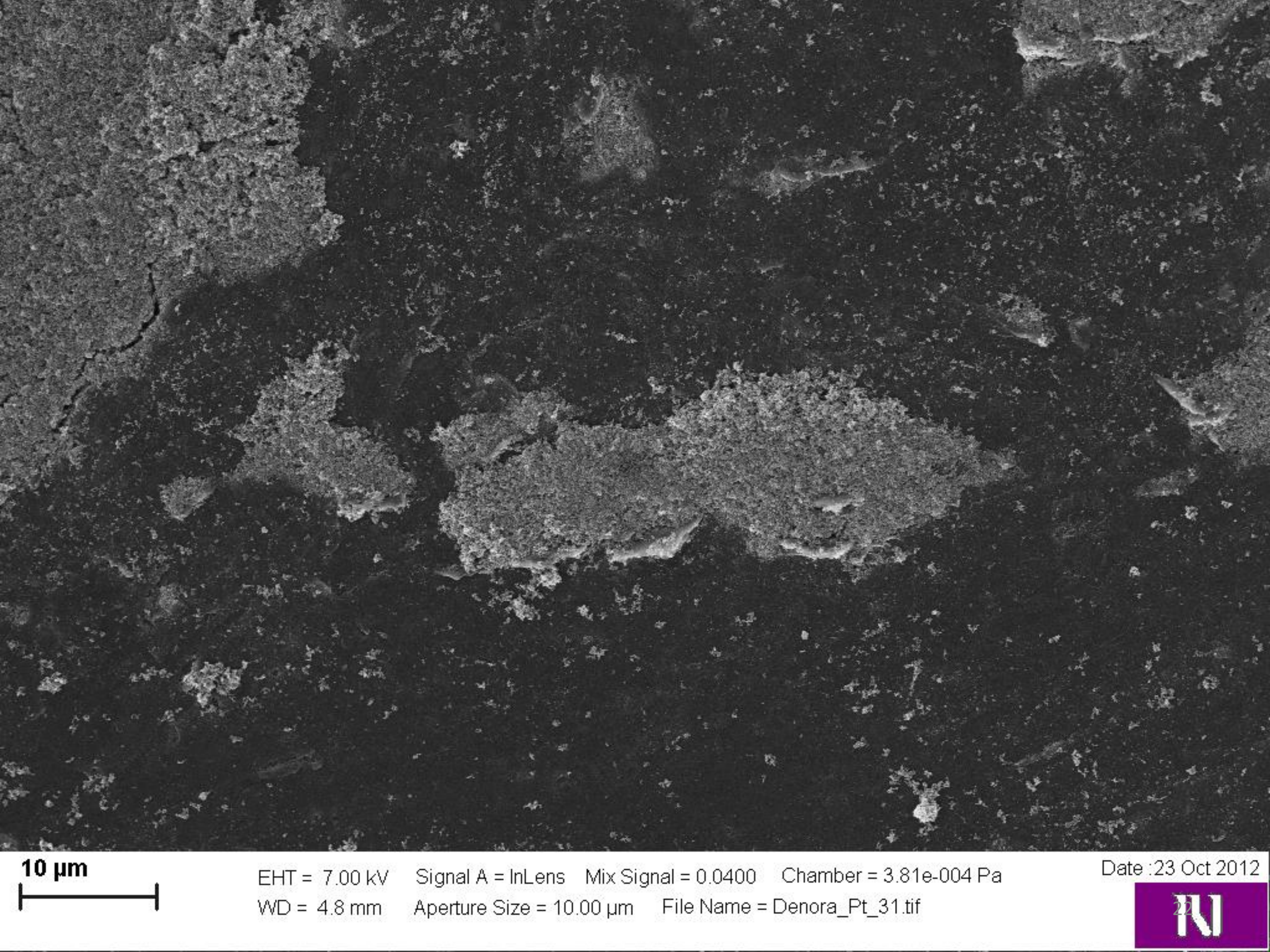
10 µm
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WD = 4.8 mm
Aperture Size = 10.00 µm
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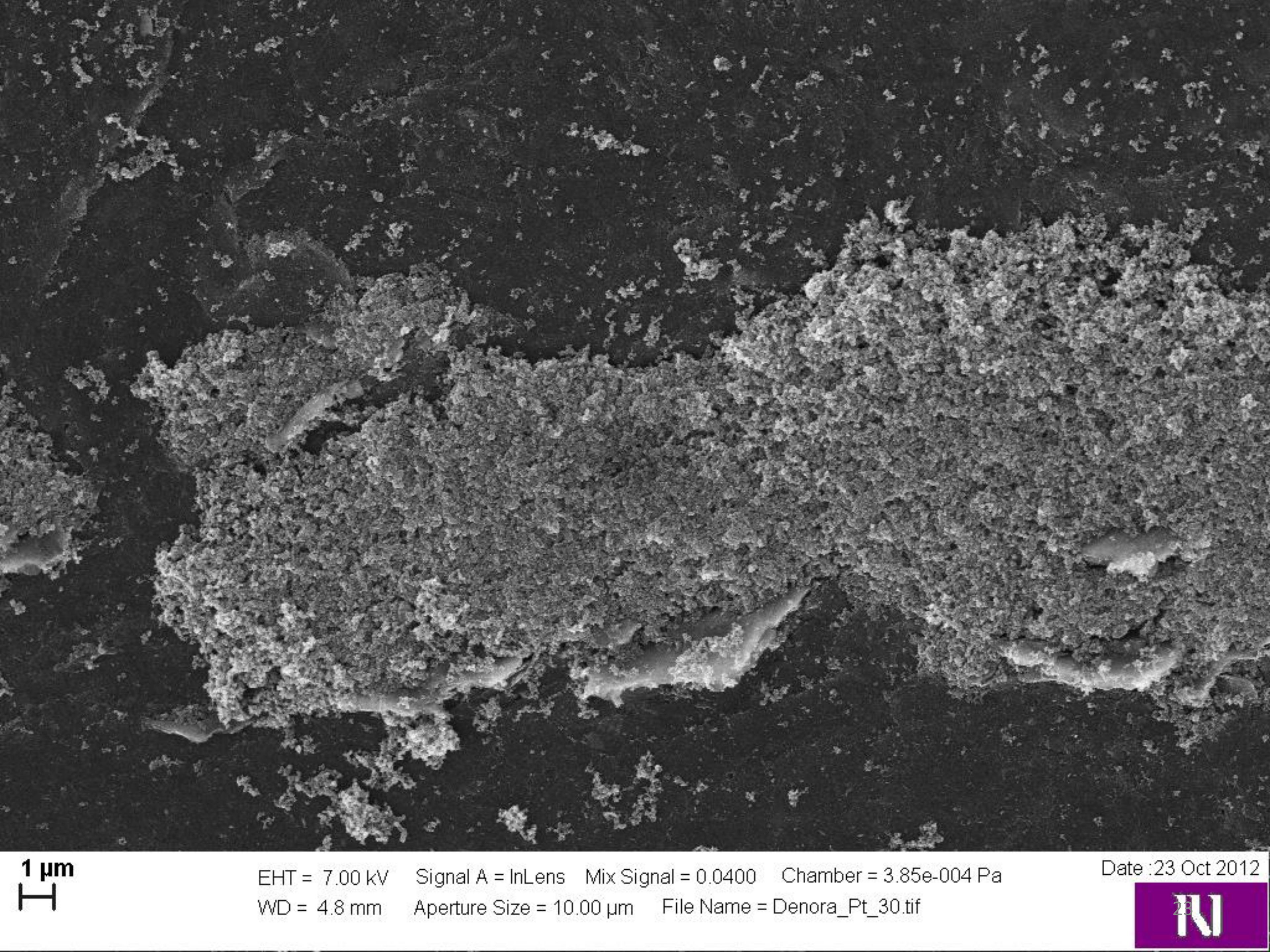
Date :23 Oct 2012



1 µm
EHT = 7.00 kV
Signal A = InLens
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Date :23 Oct 2012
WD = 4.8 mm
Aperture Size = 10.00 µm
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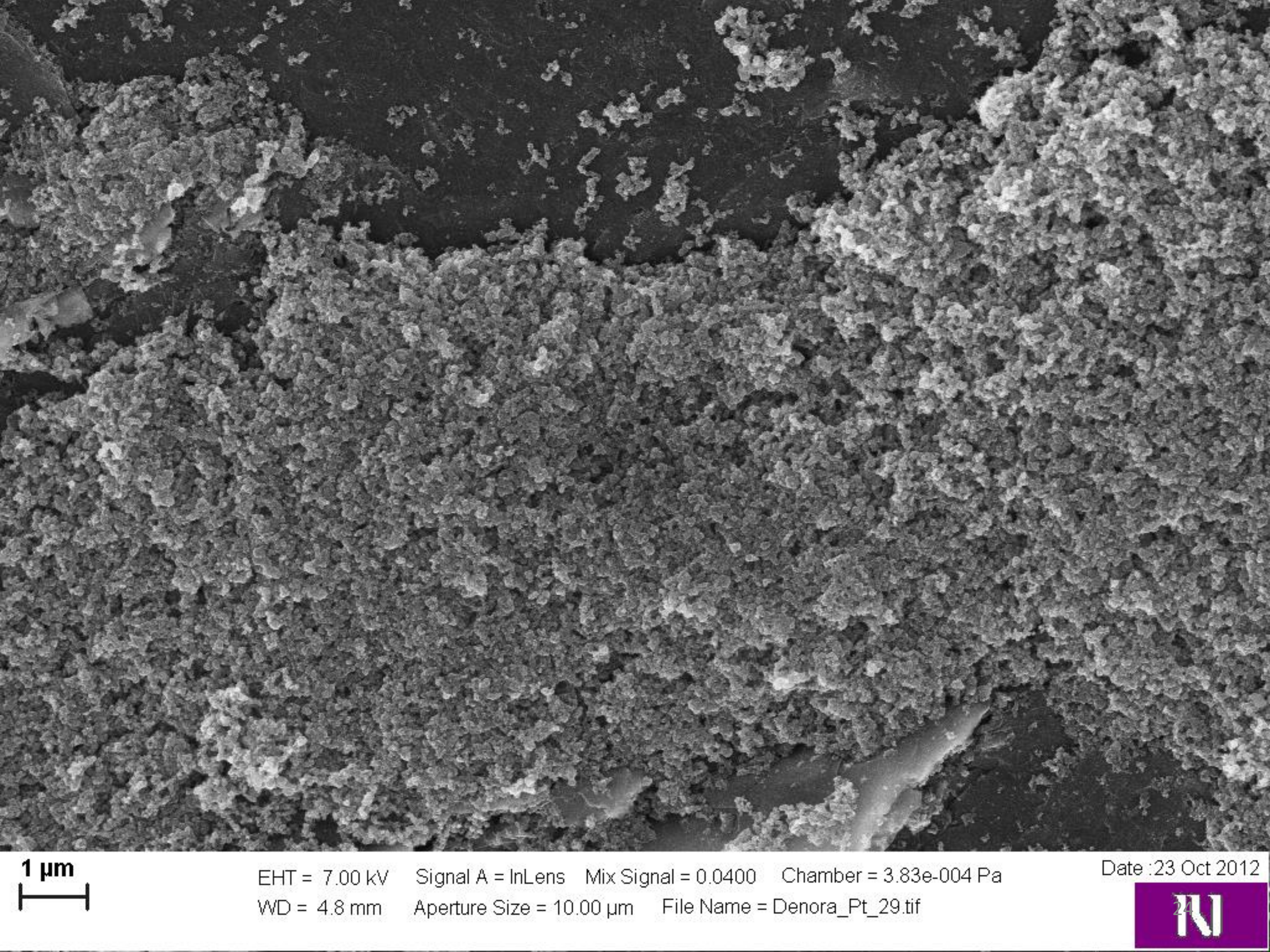
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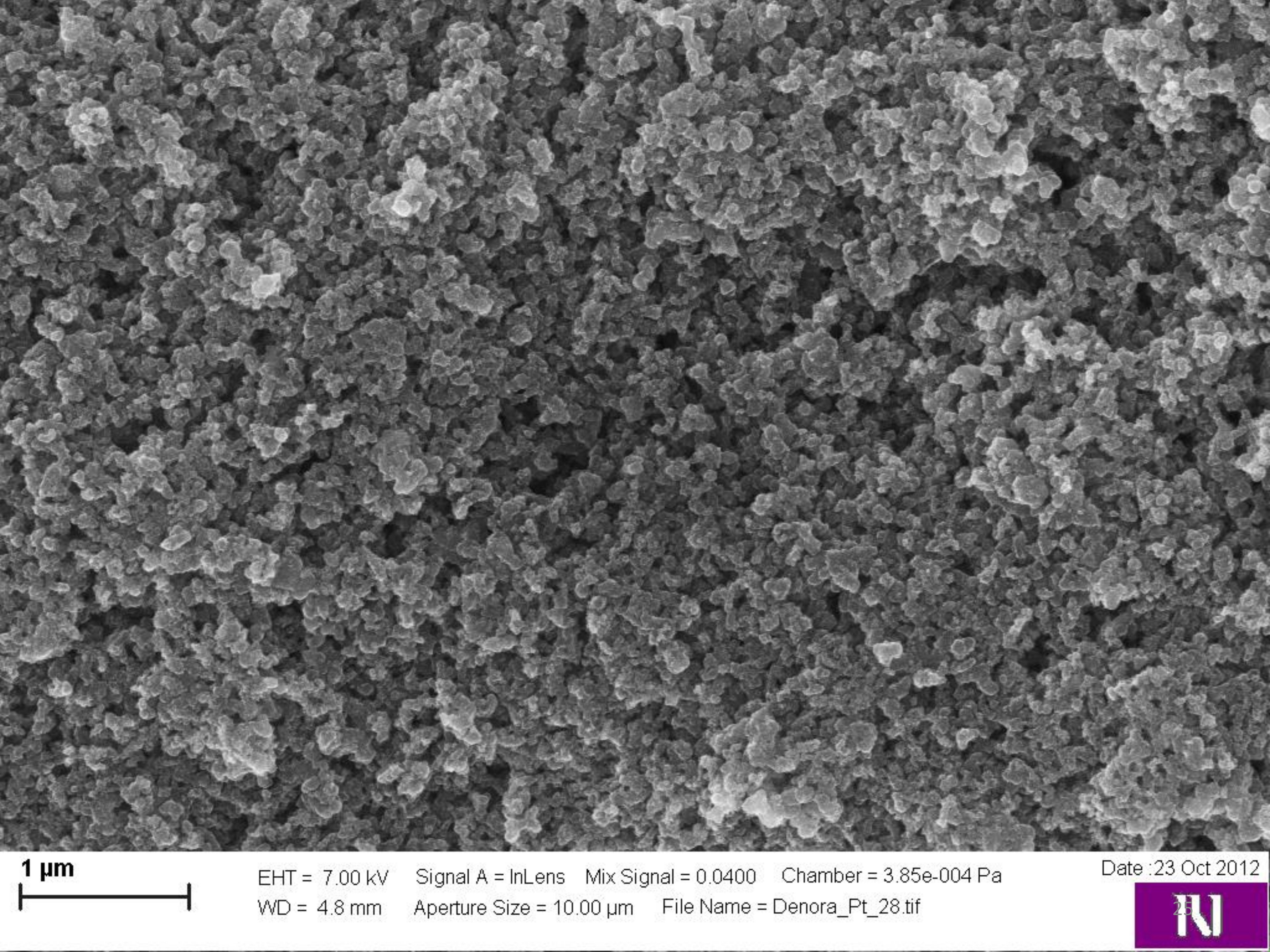
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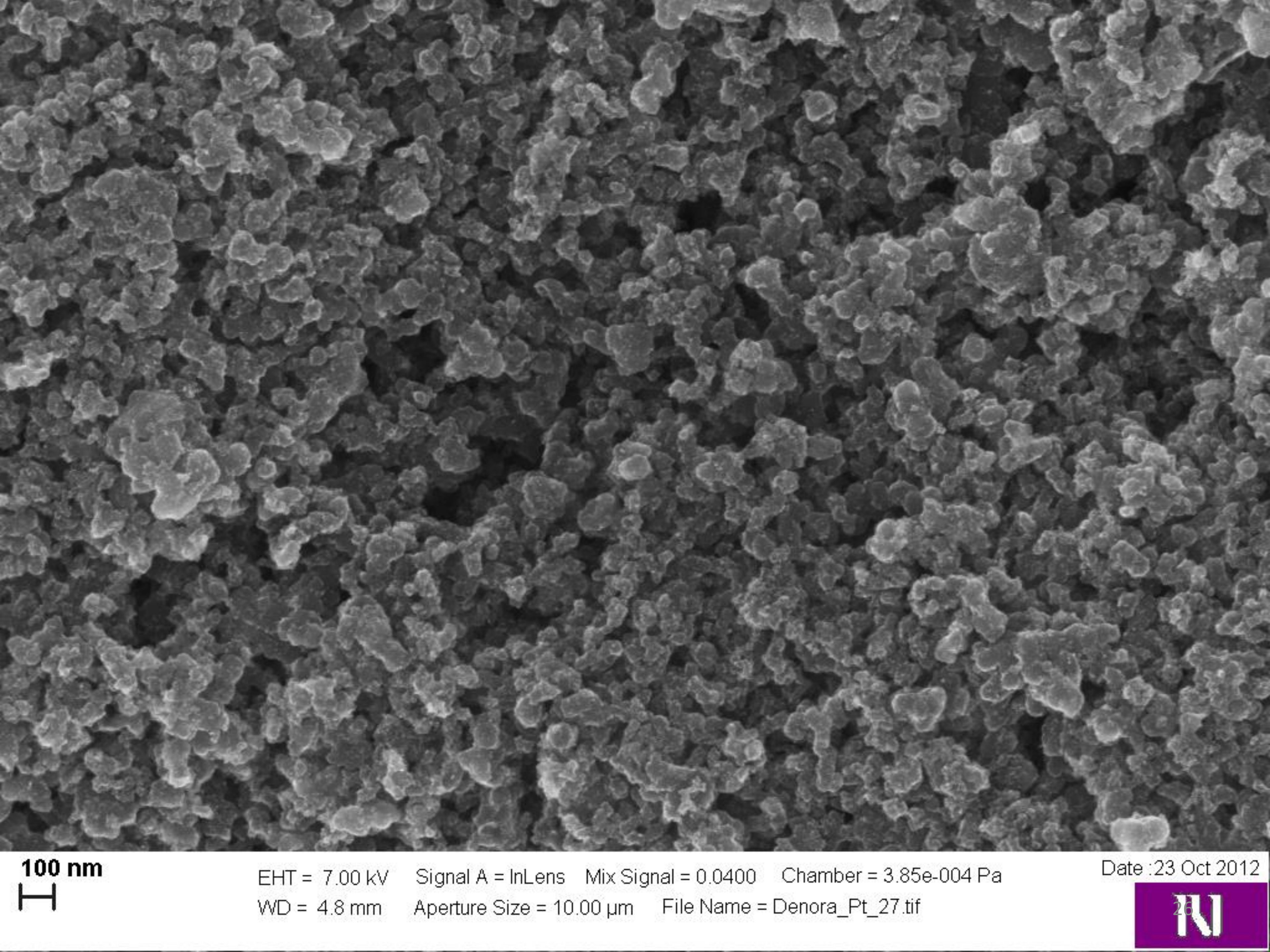
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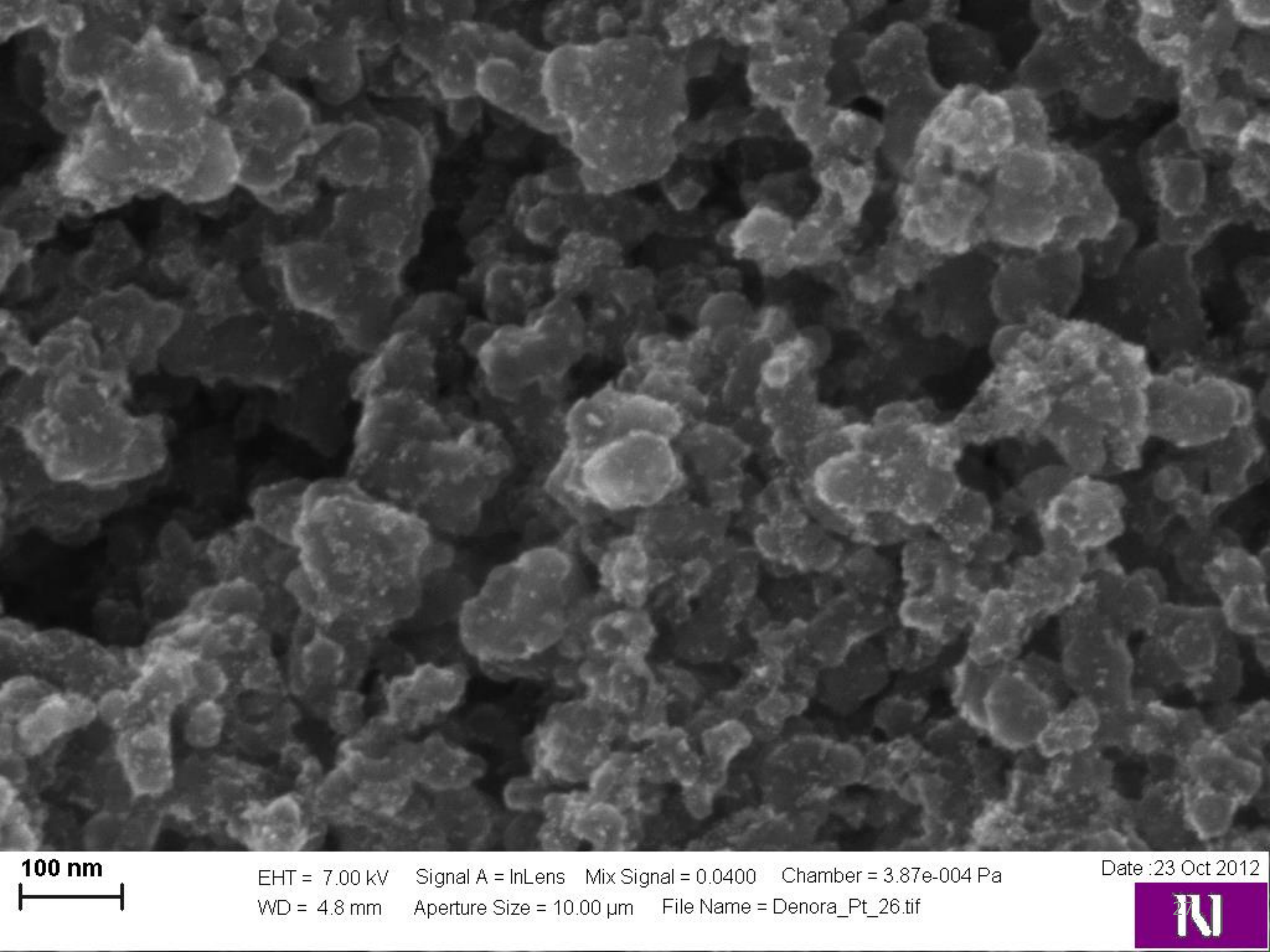
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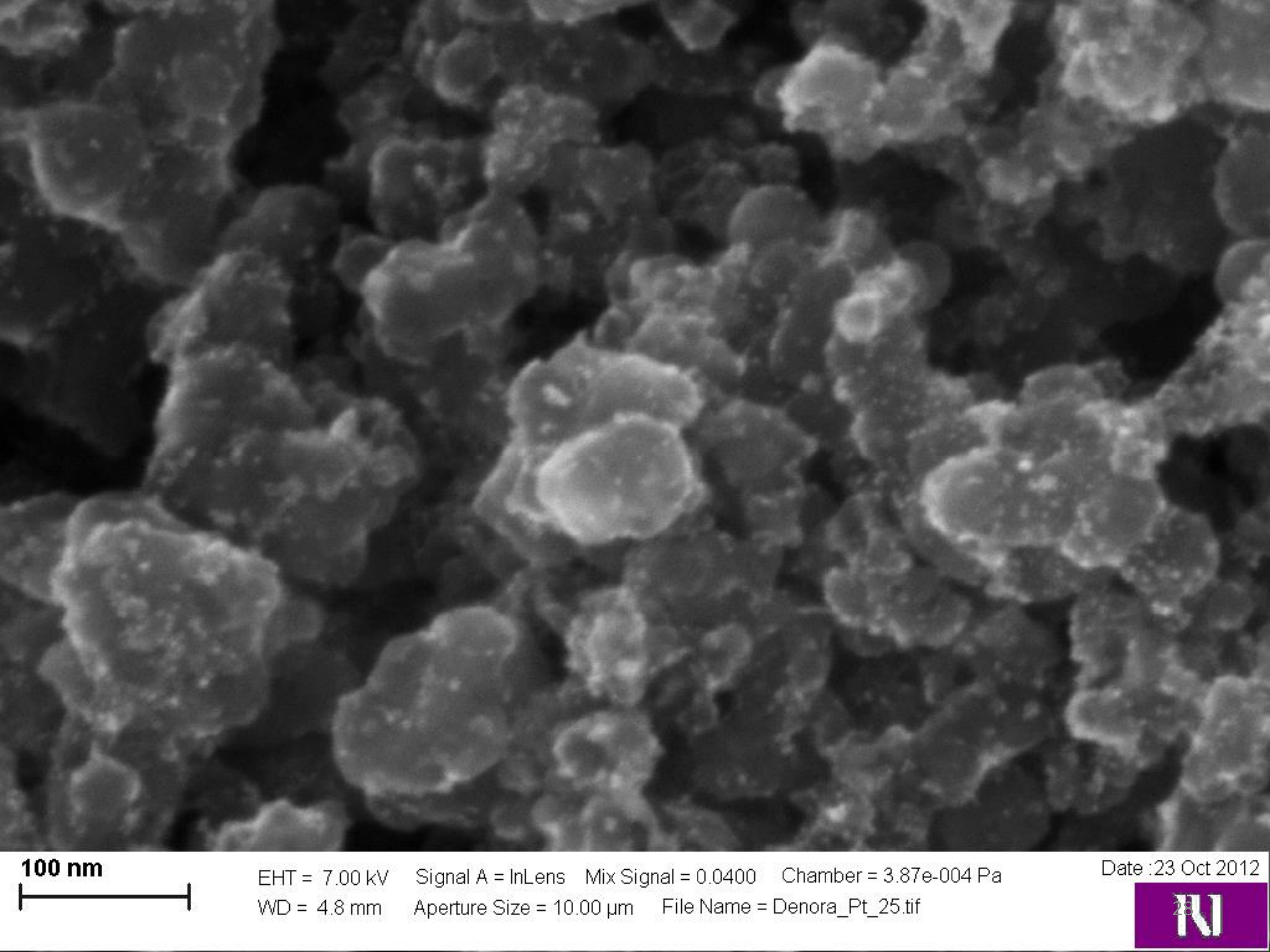
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Aperture Size = 10.00 µm
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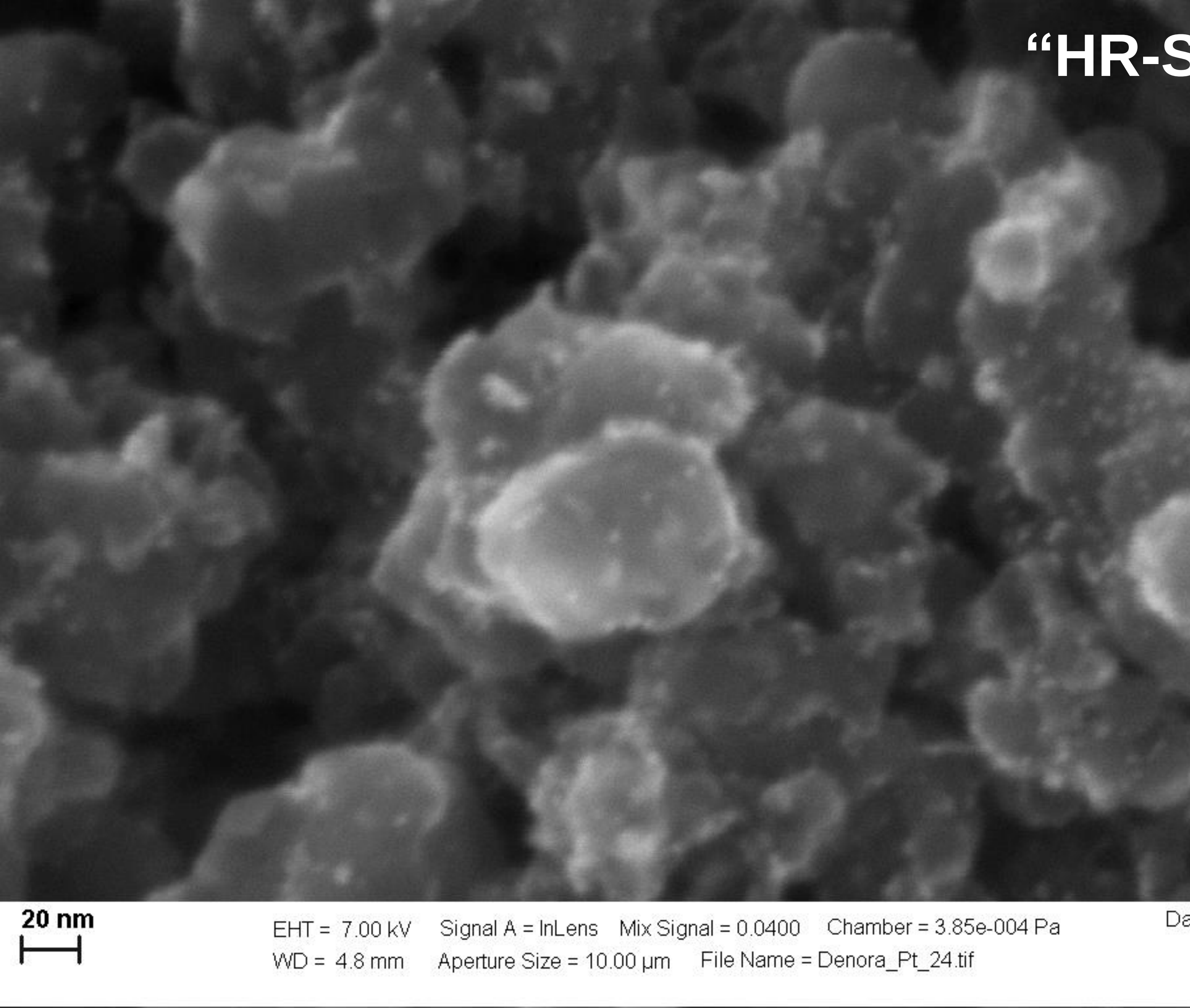
“HR-SEM”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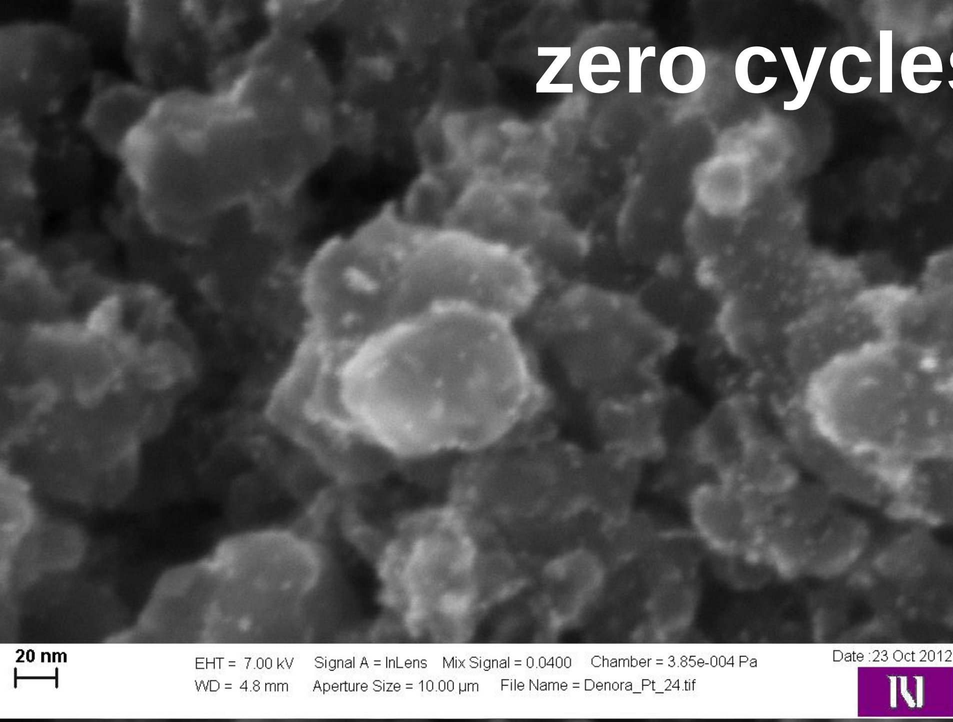
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20 nm
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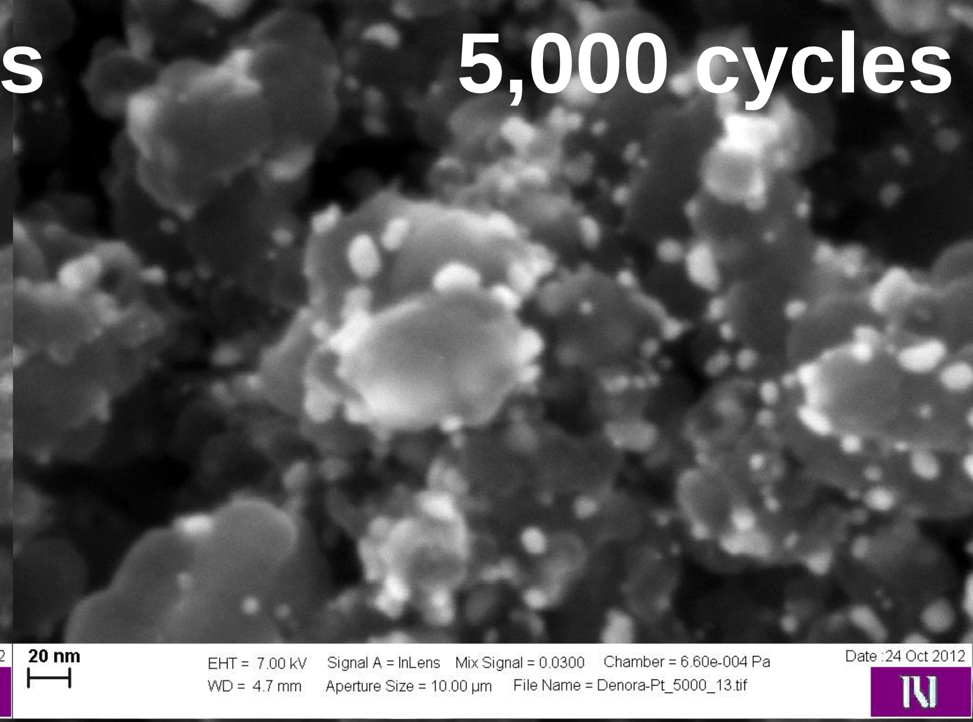
Date :23 Oct 2012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20 nm
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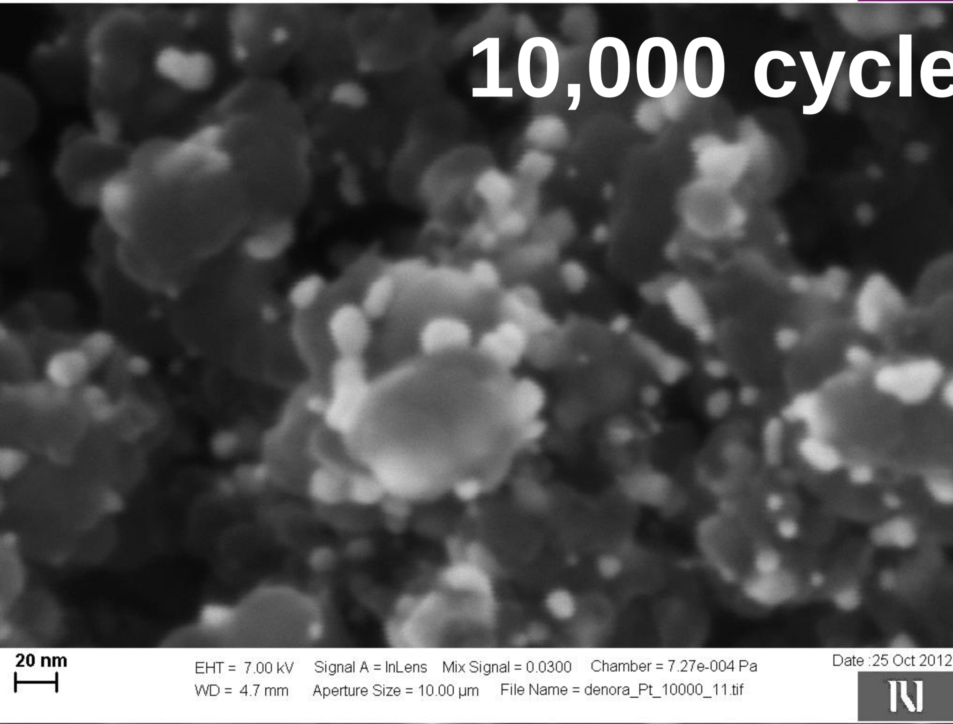
Date :24 Oct 2012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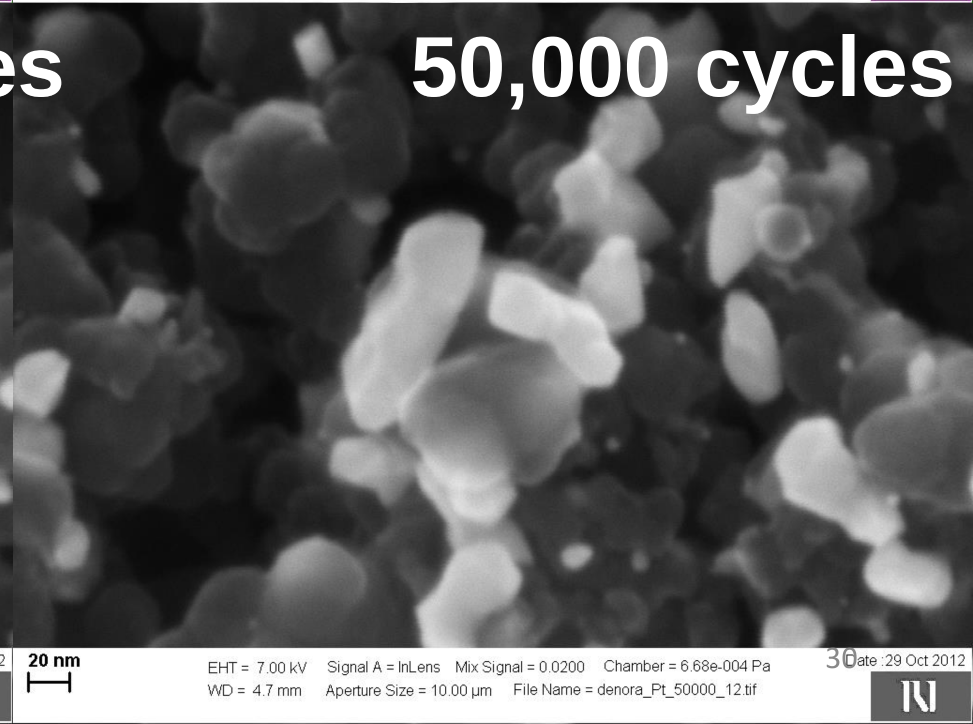
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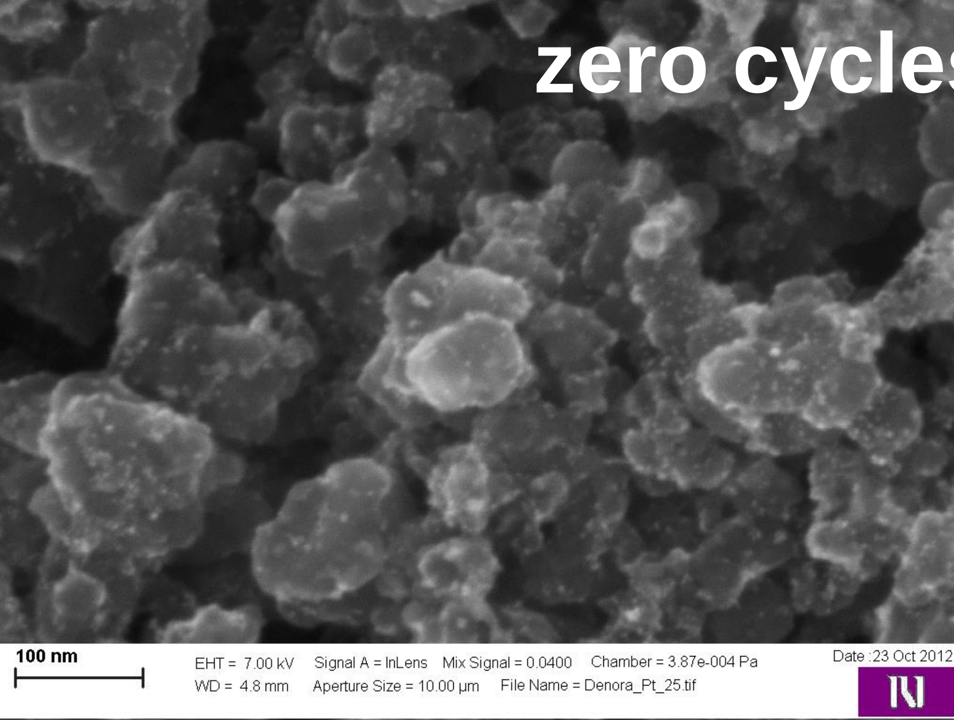
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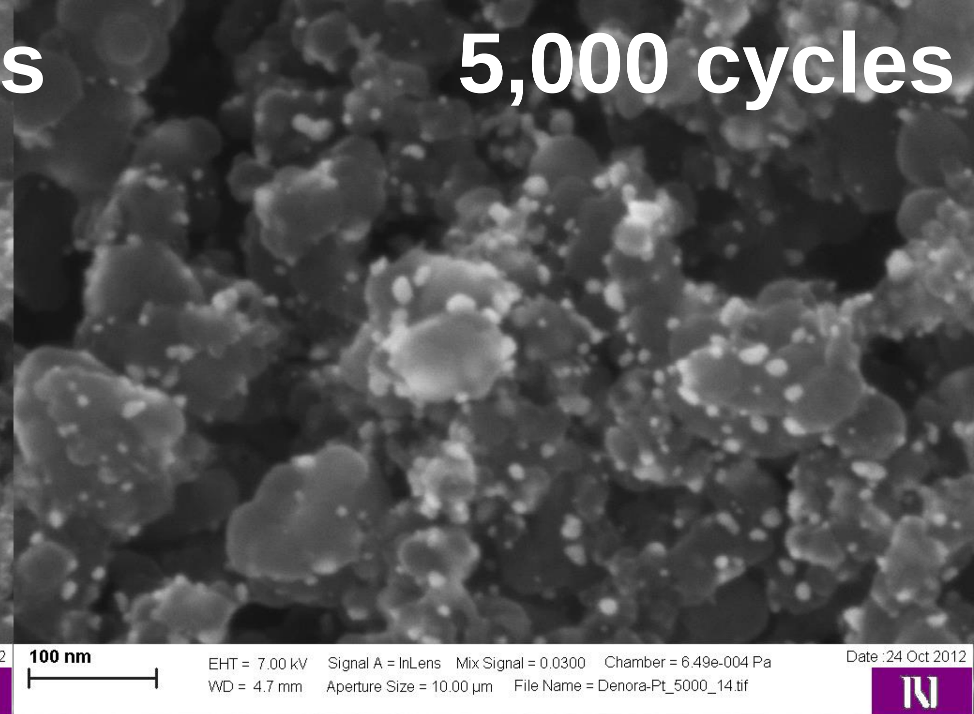
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100 nm
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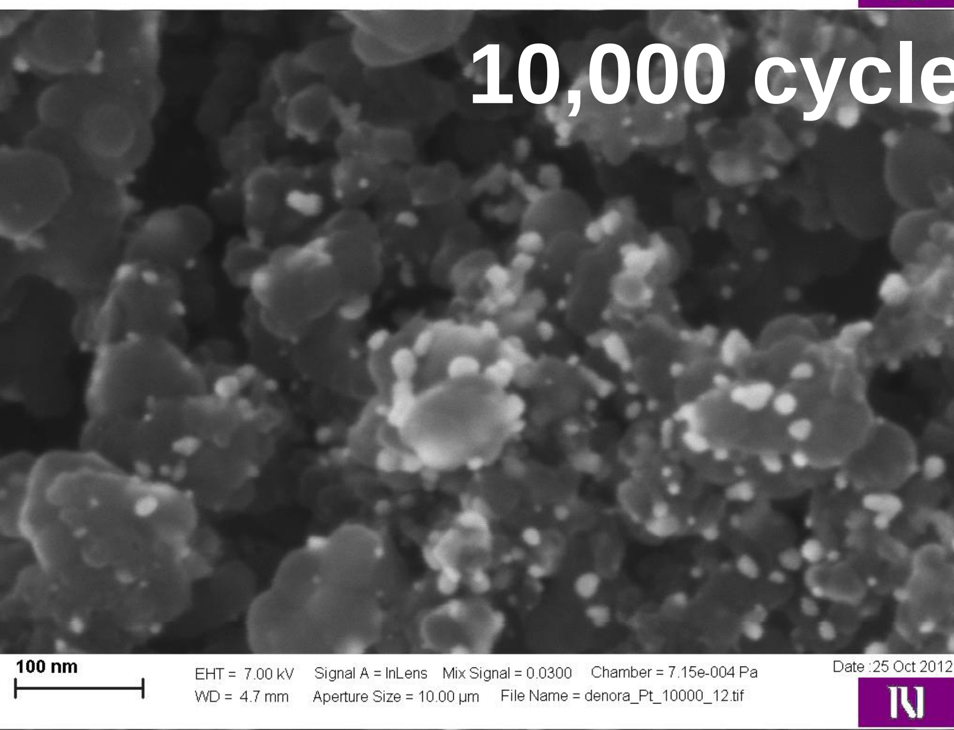
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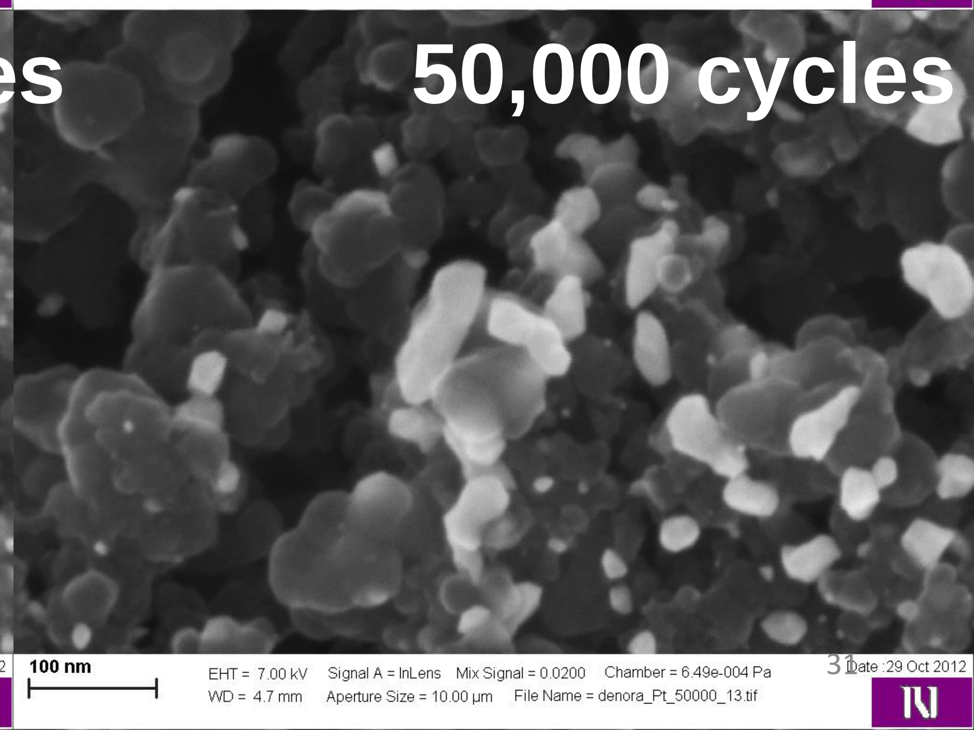
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100 nm
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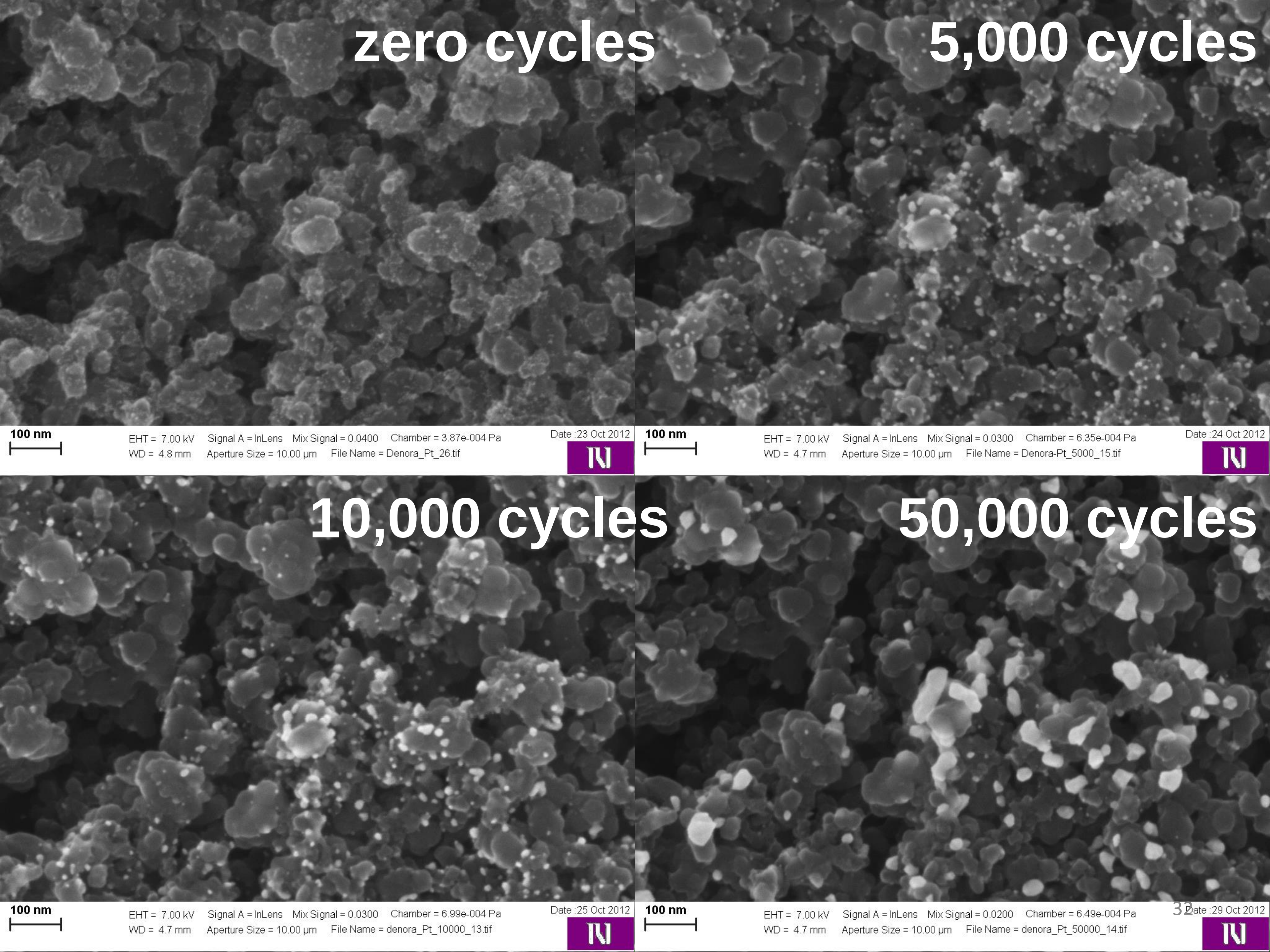
zero cycles
100 nm
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Aperture Size = 10.00 µm
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5,000 cycles
100 nm
EHT = 7.00 kV
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Mix Signal = 0.0300
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Aperture Size = 10.00 µm
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10,000 cycles
100 nm
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Mix Signal = 0.0300
Chamber = 6.99e-004 Pa
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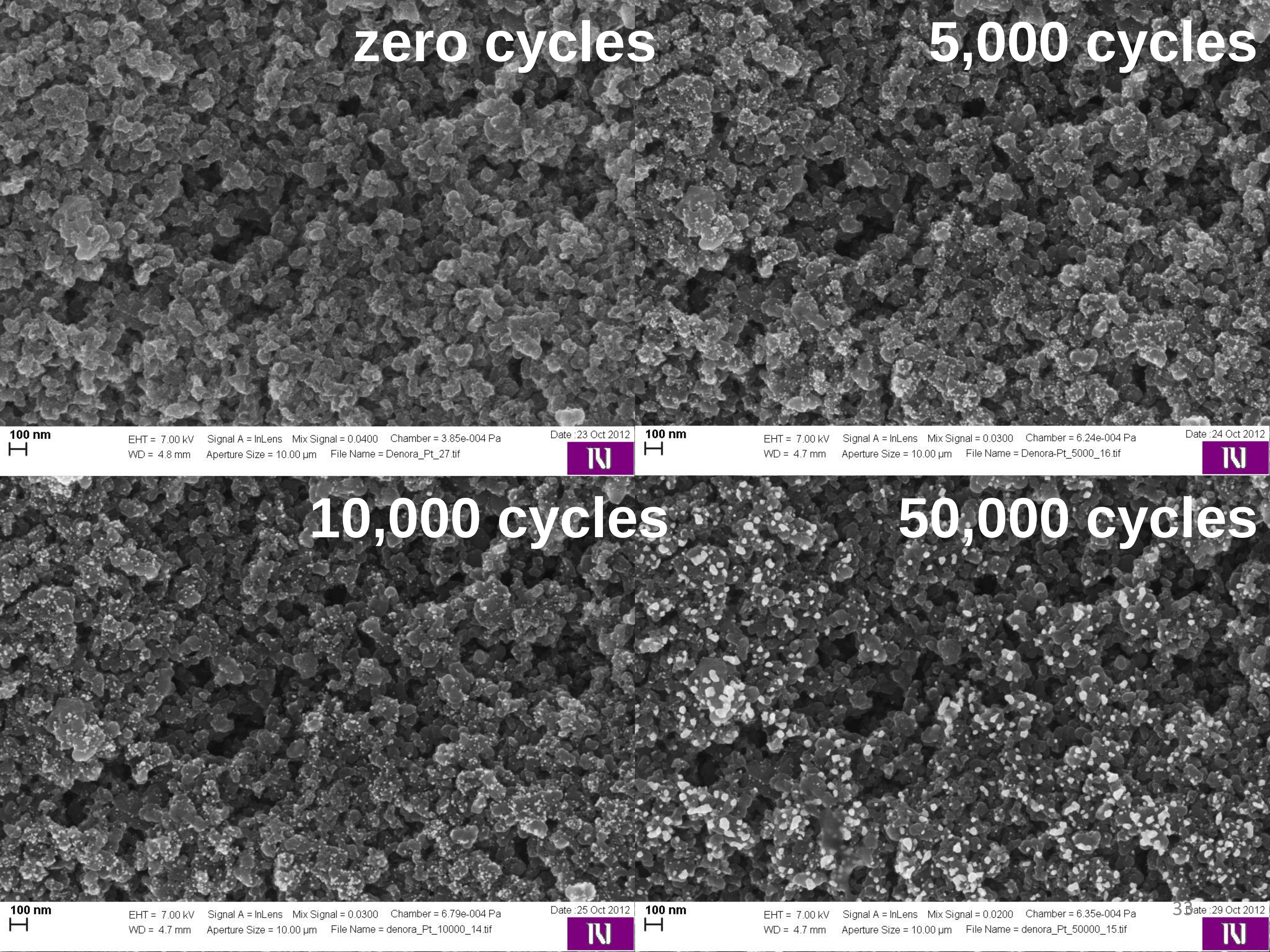
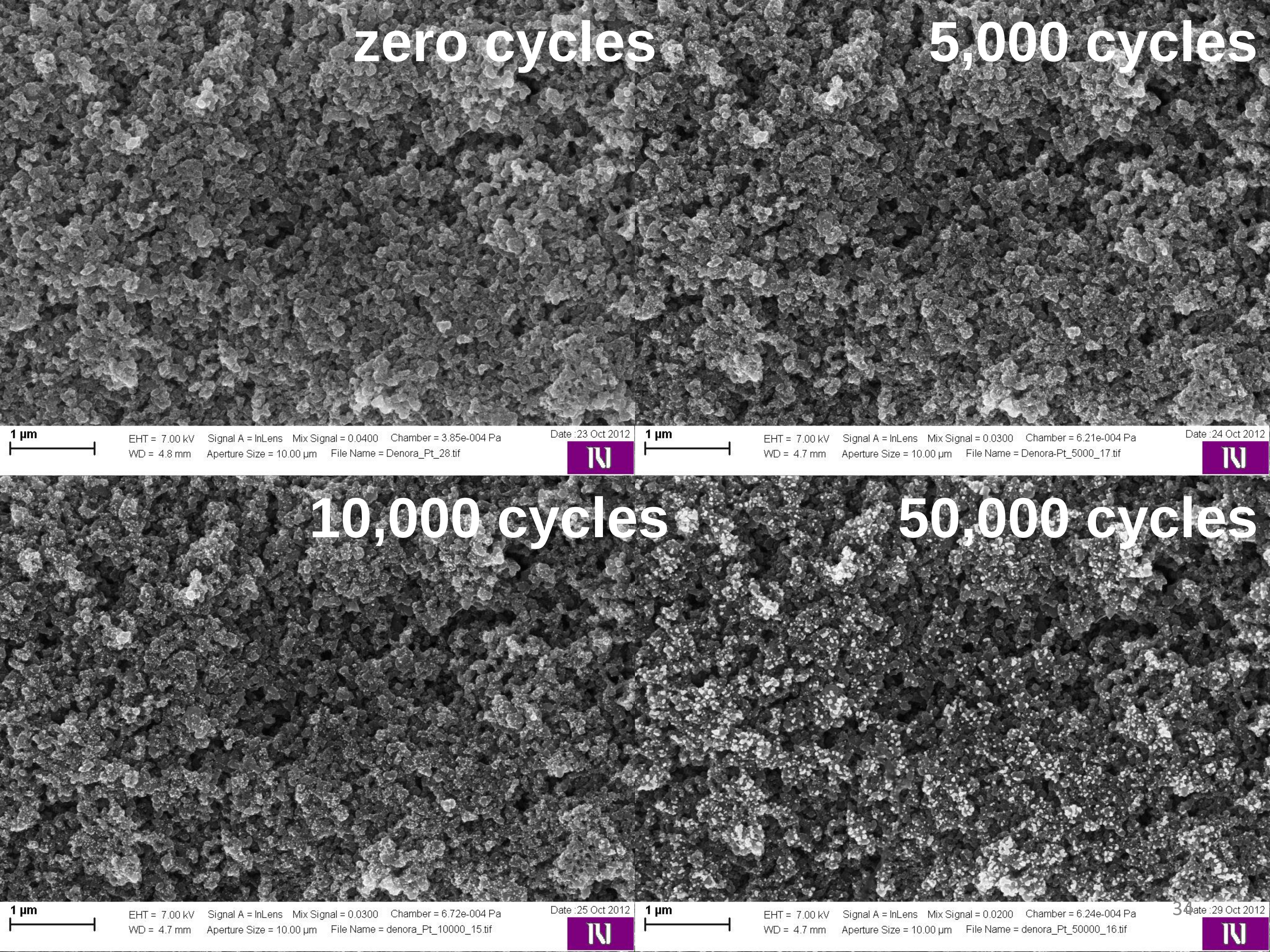
Aperture Size = 10.00 µm
File Name = denora_Pt_10000_13.tif
50,000 cycles
100 nm
EHT = 7.00 kV
Signal A = InLens
Mix Signal = 0.0200
Chamber = 6.49e-004 Pa
Date :29 Oct 2012
WD = 4.7 mm
Aperture Size = 10.00 µm
File Name = denora_Pt_50000_14.tif


zero cycles
100 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0400 Chamber = 3.85e-004 Pa
WD = 4.8 mm Aperture Size = 10.00 µm File Name = Denora_Pt_27.tif
Date :23 Oct 2012
5,000 cycles
100 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0300 Chamber = 6.24e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = Denora-Pt_5000_16.tif
Date :24 Oct 2012
10,000 cycles
100 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0300 Chamber = 6.79e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_10000_14.tif
Date :25 Oct 2012
50,000 cycles
100 nm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0200 Chamber = 6.35e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_50000_15.tif
Date :29 Oct 2012


zero cycles
1 µm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0400 Chamber = 3.85e-004 Pa
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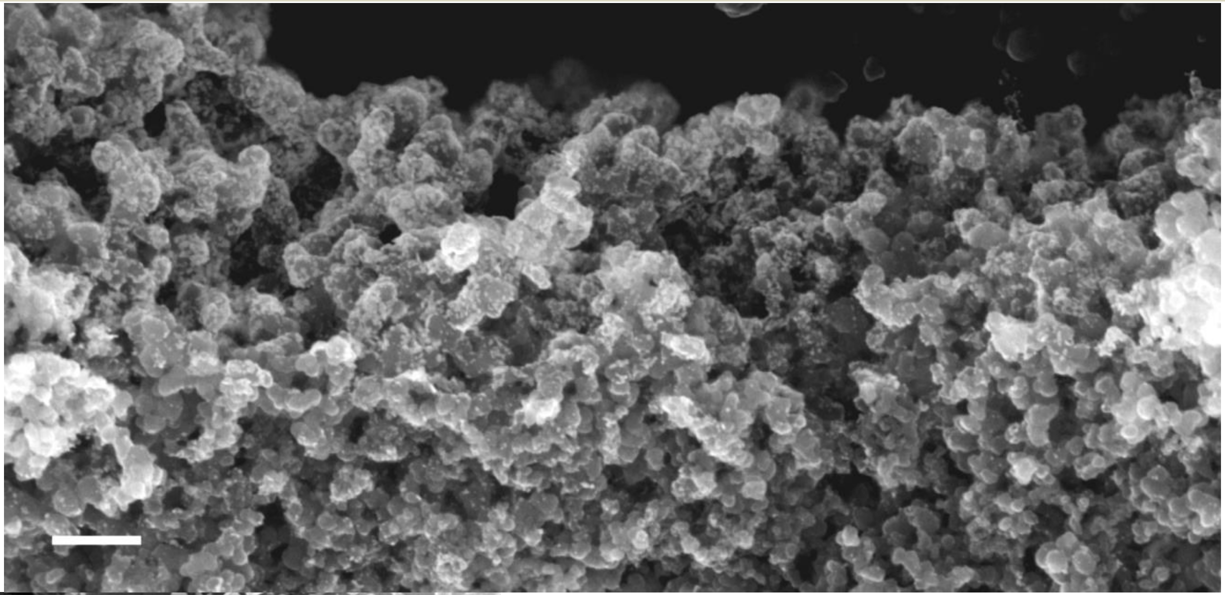
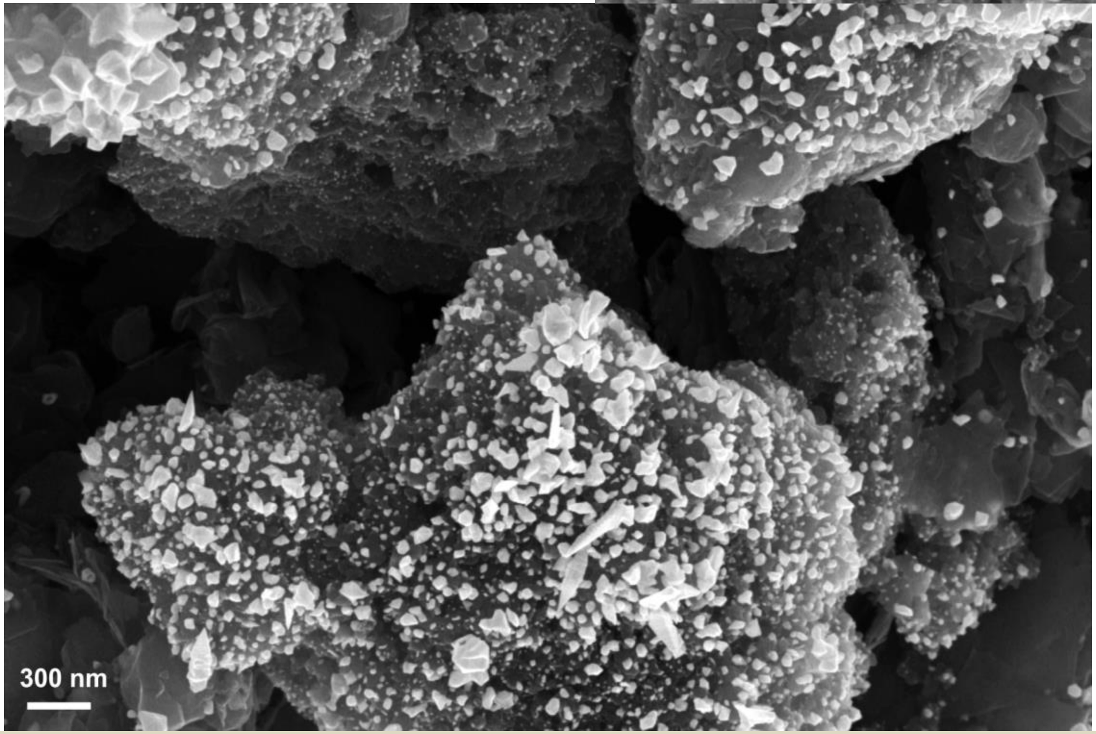
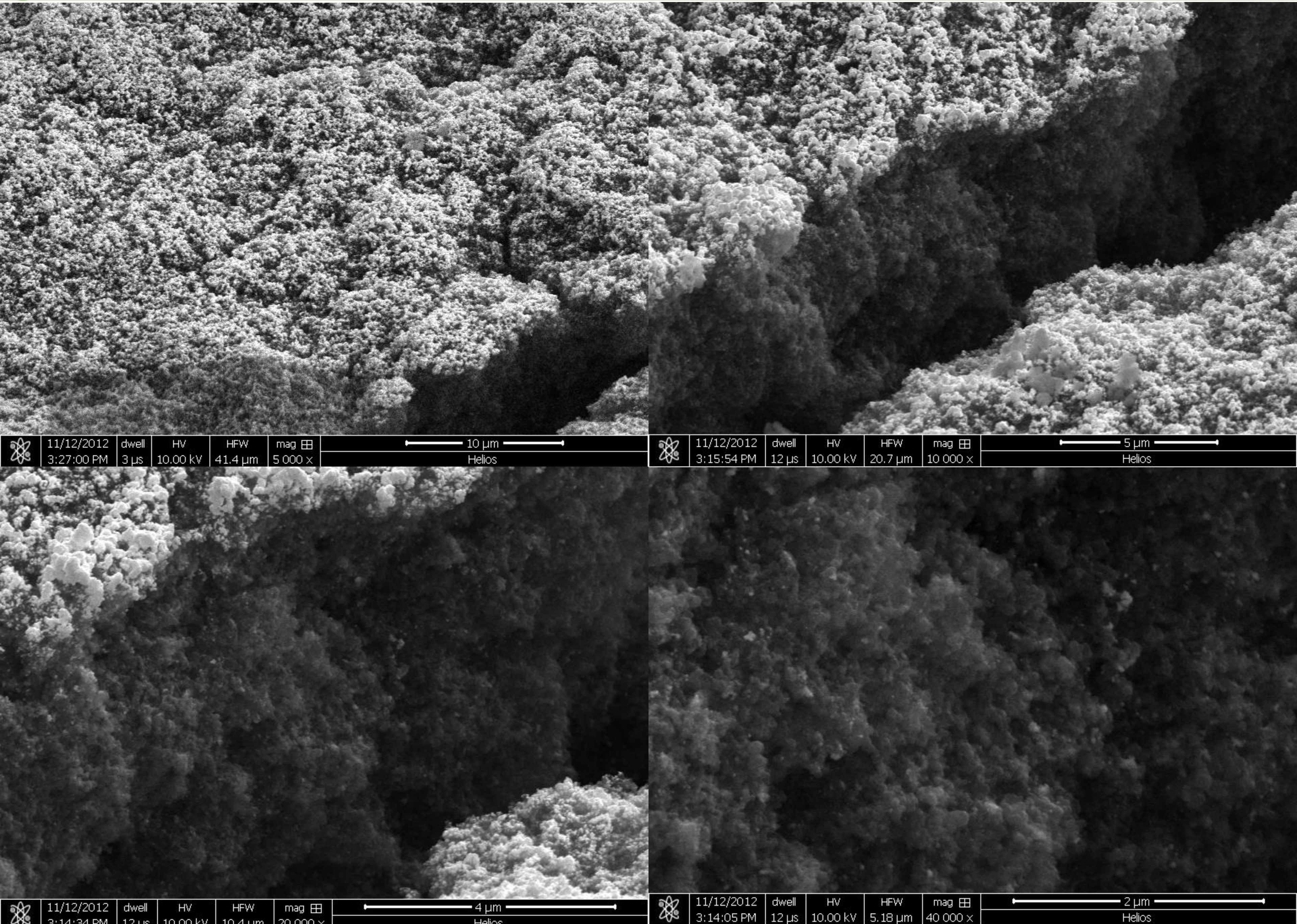
Date :23 Oct 2012
5,000 cycles
1 µm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0300 Chamber = 6.21e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = Denora-Pt_5000_17.tif
Date :24 Oct 2012
10,000 cycles
1 µm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0300 Chamber = 6.72e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_10000_15.tif
Date :25 Oct 2012
50,000 cycles
1 µm
EHT = 7.00 kV Signal A = InLens Mix Signal = 0.0200 Chamber = 6.24e-004 Pa
WD = 4.7 mm Aperture Size = 10.00 µm File Name = denora_Pt_50000_16.tif
Date :29 Oct 2012

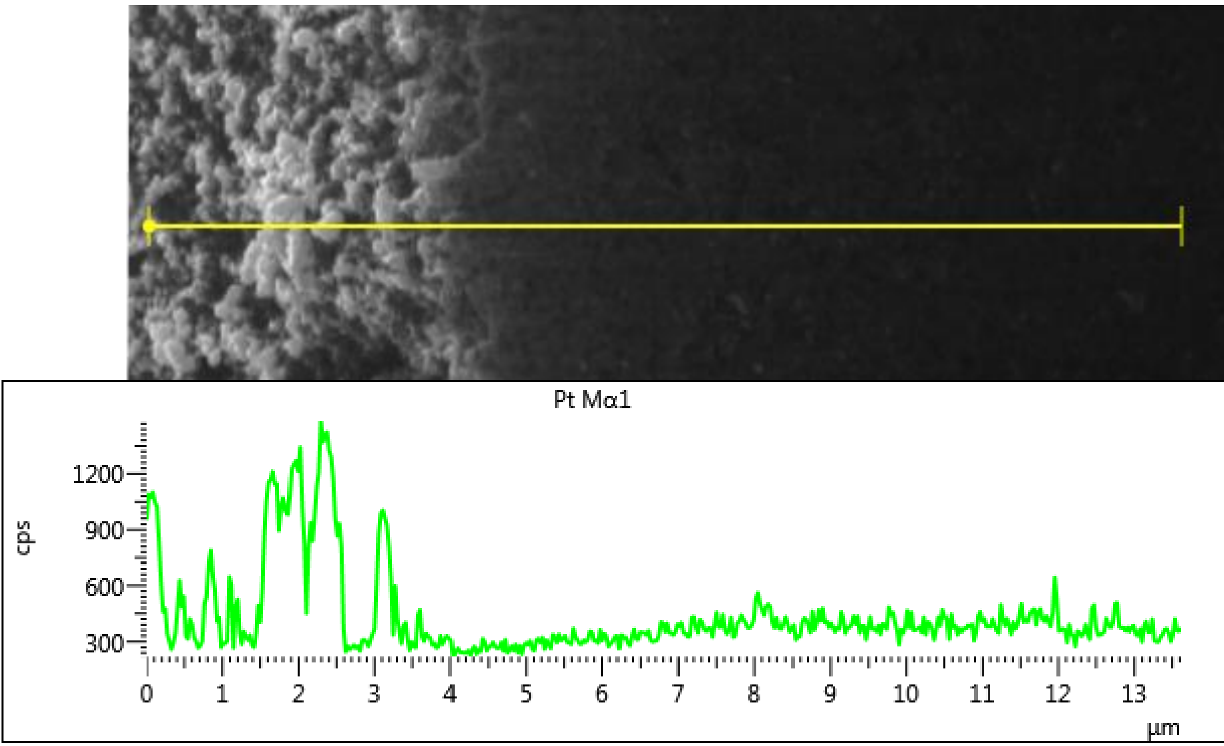


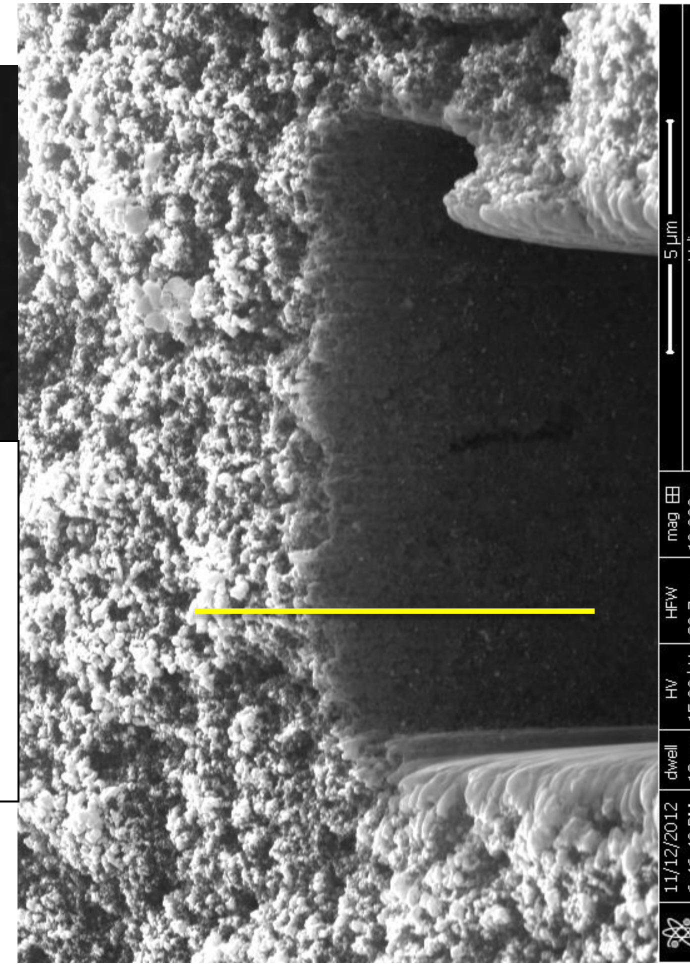

300 nm

Pt/C 50k cyc

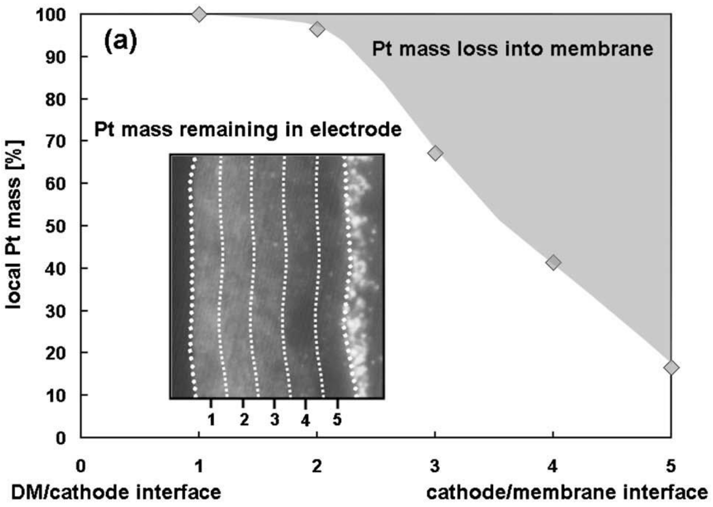

11/12/2012 3:27:00 PM
dwell 3 µs
HV 10.00 kV
HFW 41.4 µm
mag 5 000 x
10 µm
Helios
11/12/2012 3:15:54 PM
dwell 12 µs
HV 10.00 kV
HFW 20.7 µm
mag 10 000 x
5 µm
Helios
11/12/2012 3:14:34 PM
dwell 12 µs
HV 10.00 kV
HFW 10.4 µm
mag 20 000 x
4 µm
Helios
11/12/2012 3:14:05 PM
dwell 12 µs
HV 10.00 kV
HFW 5.18 µm
mag 40 000 x
2 µm
Helios

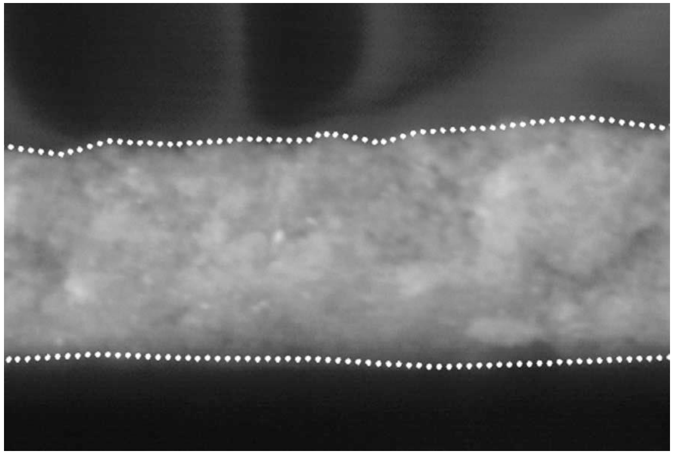
Pt/C 50k cyc

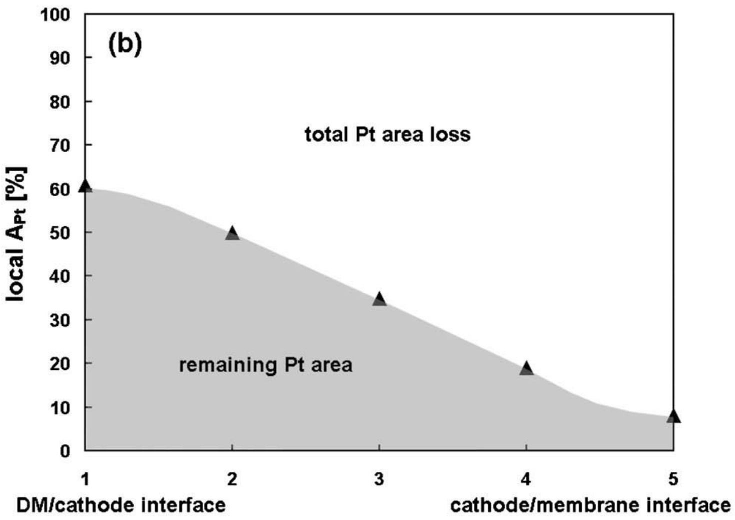

Pt Mα1
cps
1200
900
600
300
0
1
2
3
4
5
6
7
8
9
10
11
12
13
µm

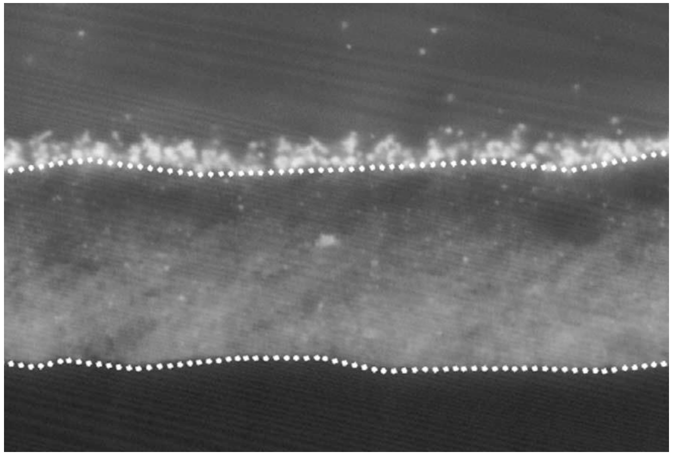

5 µm
Helios
mag ⊞ 10 000 x
HFW 20.7 µm
HV 15.00 kV
dwell 12 µs
11/12/2012 6:46:49 PM

2010_Gasteiger_Shao_Platinum-Alloy Cathode Catalyst Degradation in Proton Exchange Membrane Fuel Cells: Nanometer-Scale Compositional and Morphological Changes









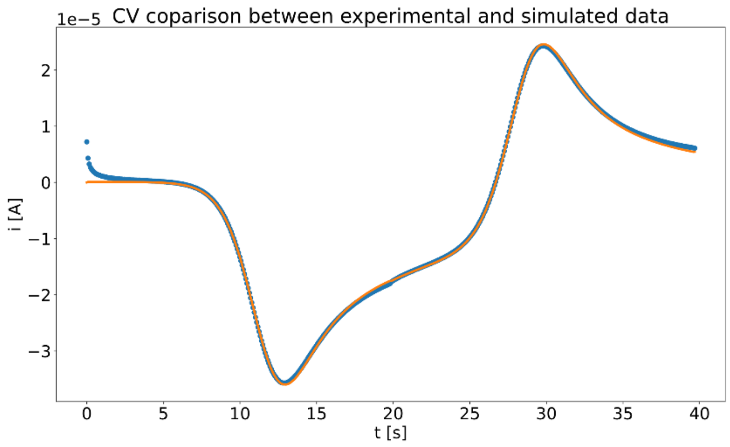
What do we do in the lab on these topics?

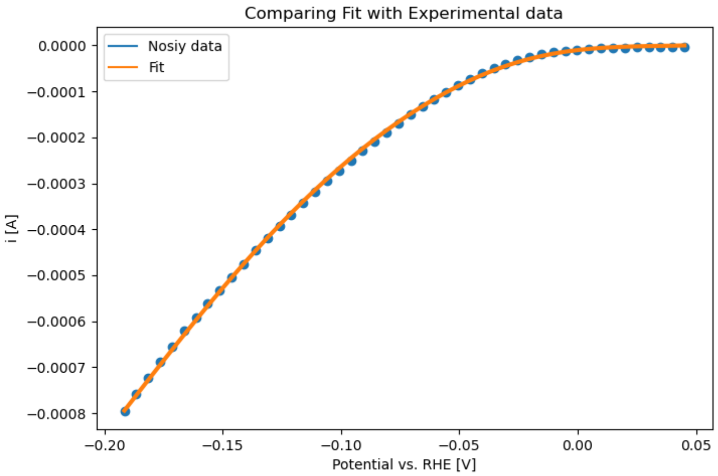
- Computer vision for TEM images
- Pattern recognition for electron diffractions
- Electrochemistry data analysis/simulation
- Automatization of gas diffusion electrode measurement
- Compositionally complex alloys - screening
  - data collection in a readable database; "electronic lab notebook" – Quipnex (our own FAIRmat)

Inferring kinetic parameters from experiments

- Finding optimal parameters:
  - An objective approach to comparing materials
  - Finding and fitting a mechanism onto experimental data using ML approaches

Comparing HER data with simulation

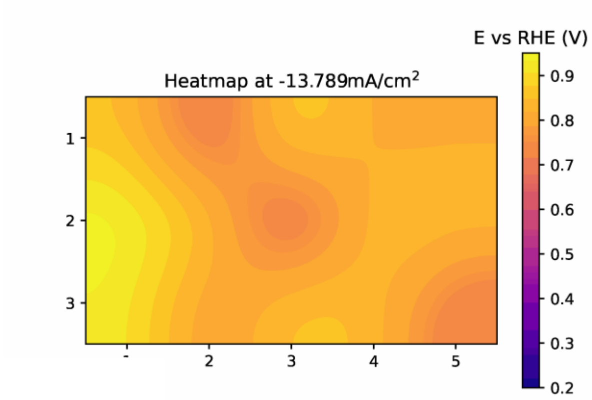


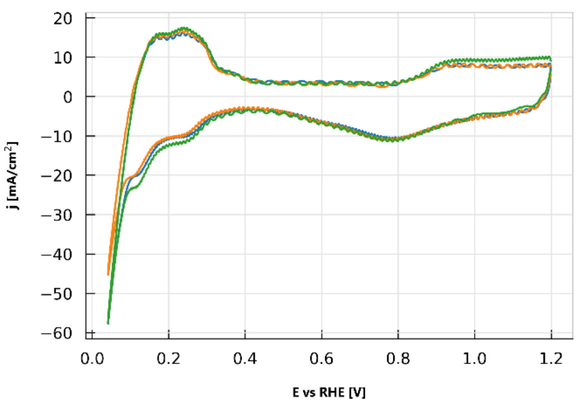


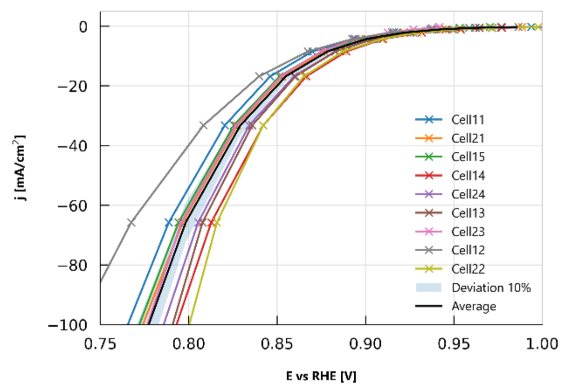
Thanks Ožbej Vodeb!

From Data to Discovery: Designing a Relational Electrocatalyst Database for Machine Learning-Driven Pattern Recognition

- We have begun experimenting with high-throughput measurements – automatization
- To test reproducibility – error bars
- There is a lot of data being generated with the measurements
- It needs to be stored somewhere
- A unified place where data is being gathered (and processed)



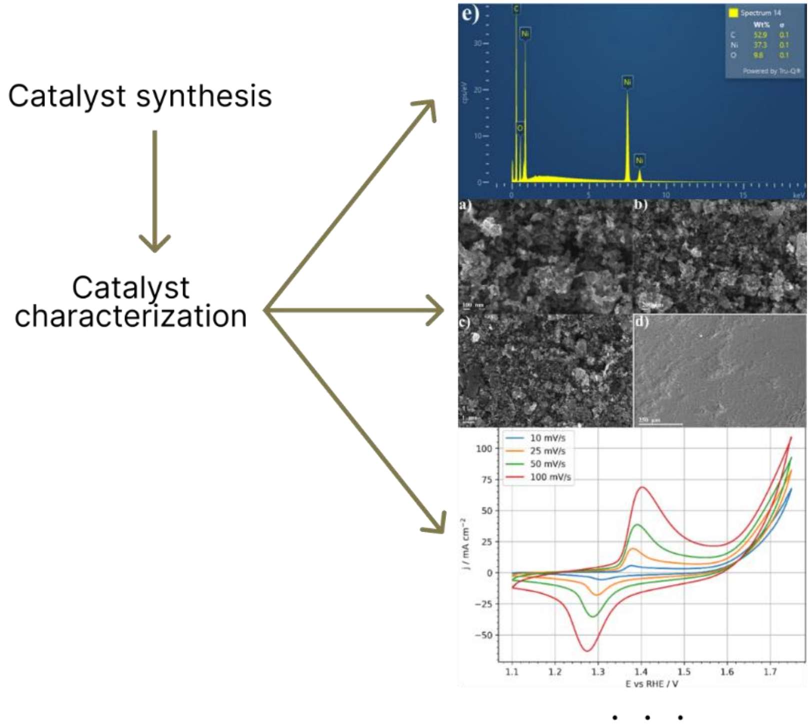




Thanks Aleš Arsel and Miha Hotko!

From Data to Discovery: Designing a Relational Electrocatalyst Database for Machine Learning-Driven Pattern Recognition

- Database tables have key descriptors to store and organize experimental data effectively
  There has to exist a sample table which every other table references
- The interface needs to have an API for the programmatic uploading of data
- Measurements still require a human to determine the reliability of the generated result - **a Trust Factor**
- There needs to be a way to determine why the results aren't trusted
- This data could be used for machine learning once the database has enough information
- Good care has to be taken in designing the database schema.



Thanks Aleš Arsel and Miha Hotko!

Modifications of compositionally complex materials

Various alloys

▼

Electrochemical treatments

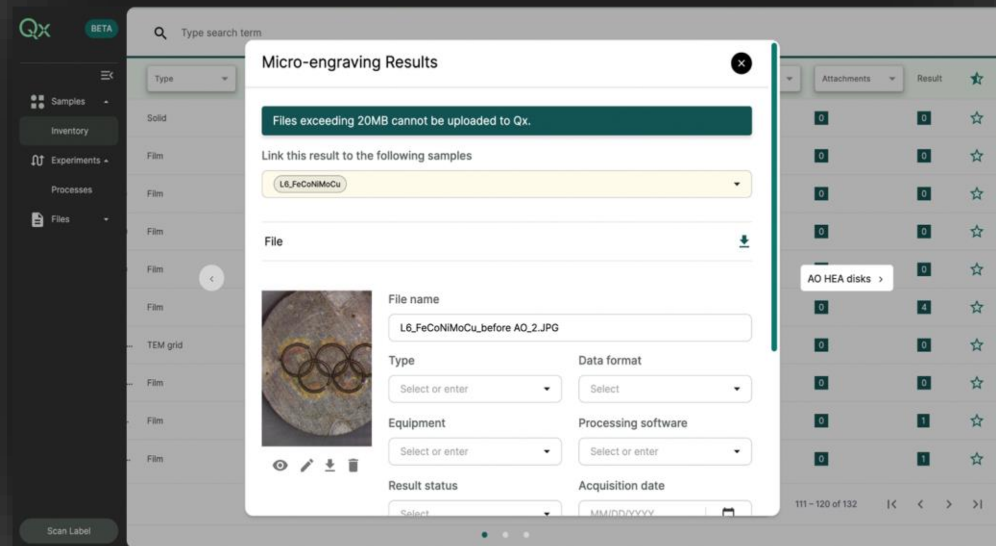
Heat treatments

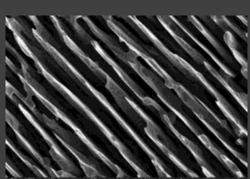
▼

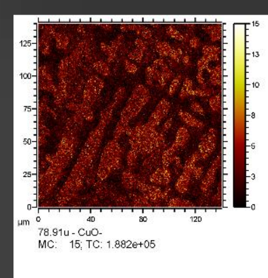
Analyses

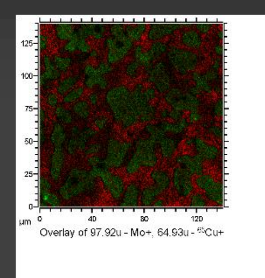
▼

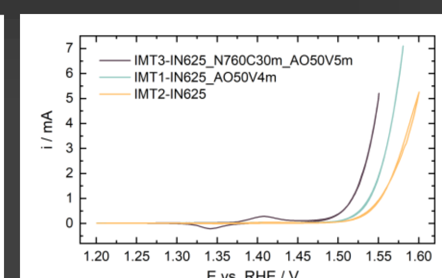
Scale up





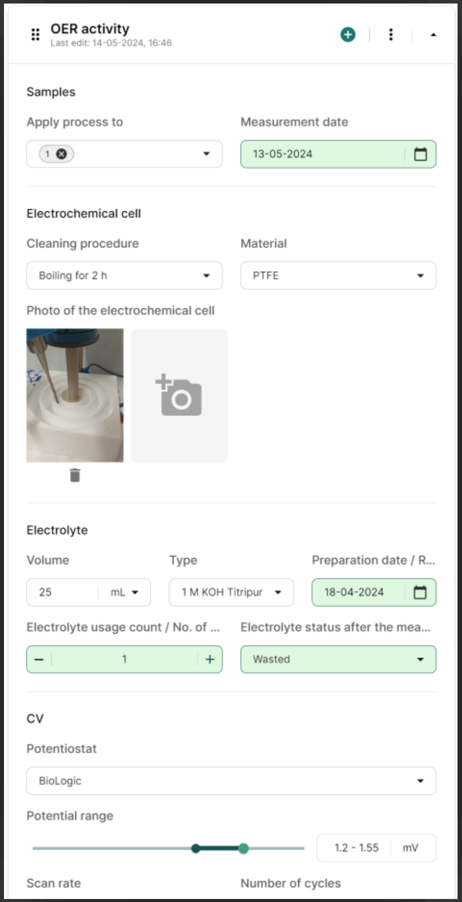






Thanks Luka Suhadolnik!

Data organization – the Qx app



- Hierarchical sample creation and linkage
- Adding of processes, comments, and results
- Creation of process templates with all the important parameters
- Exports for advanced analysis

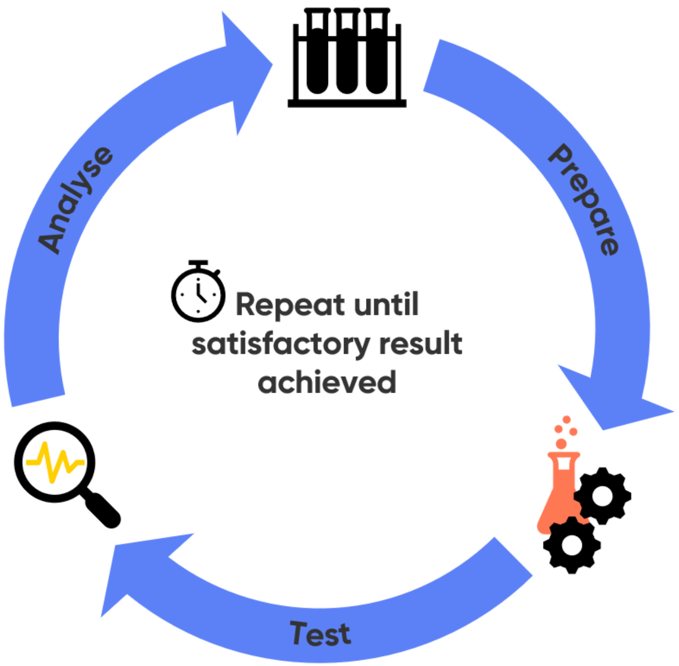
https://www.quipnex.com

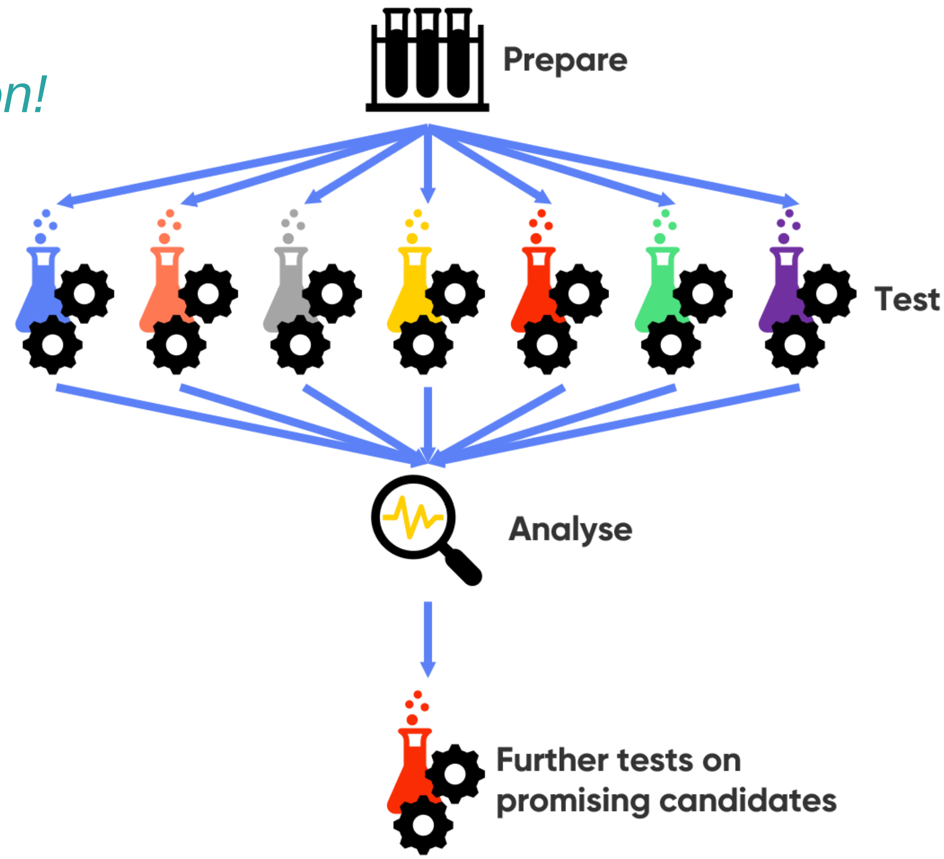
Thanks Luka Suhadolnik!

Our wish! Jubelee for electrocatalysis!

Or, more realistically, just automatization of some of our experiments…

High throughput screening –> solution!





Problems?
Reliable measurements
Reliable data collection
Data processing
Complexity?
Materials discovery?
Black box?
We still try!

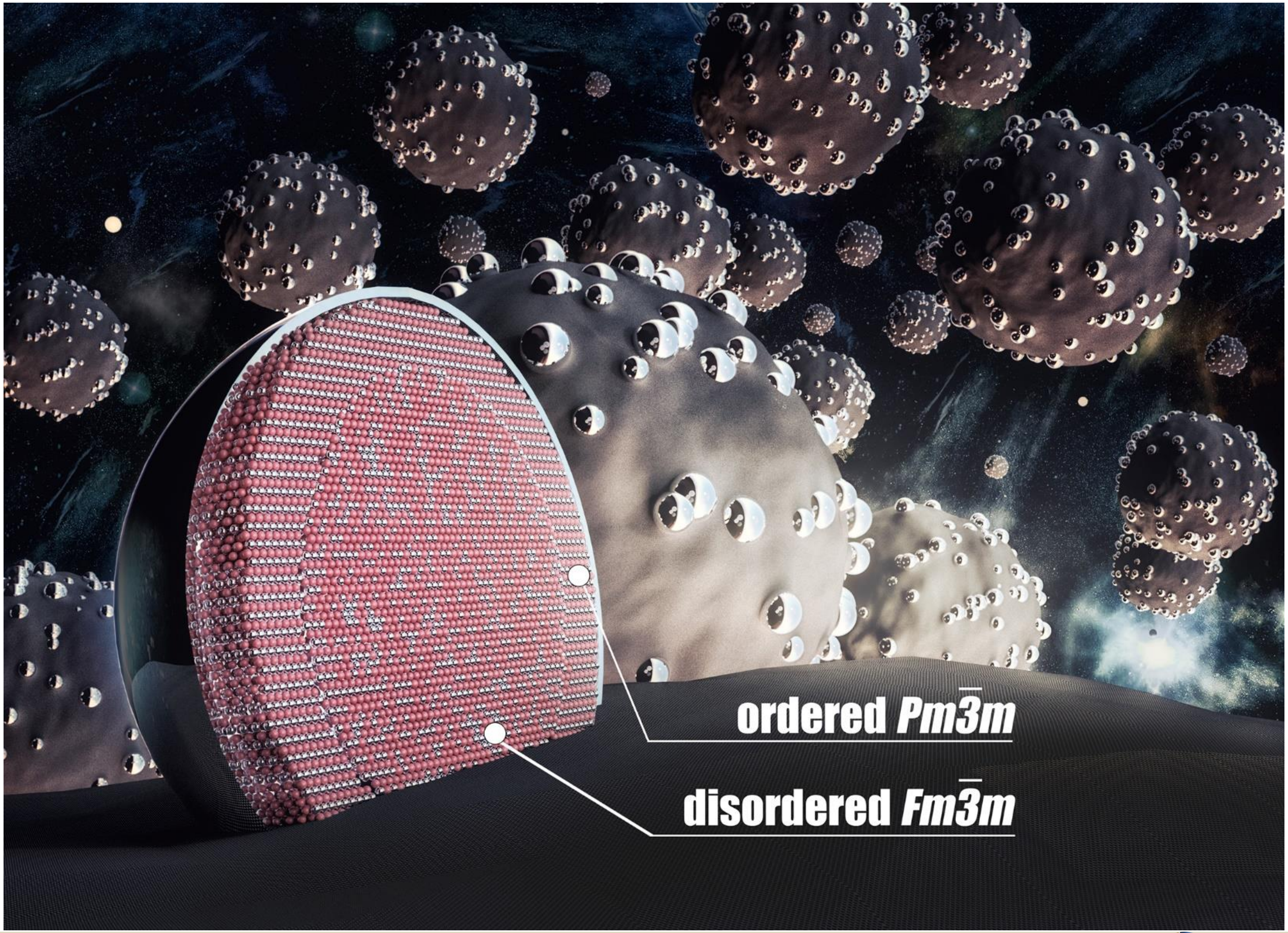
Thank you for your attention!

Slovenian Research and Innovation Agency
European Research Council
Established by the European Commission
This workshop is supported by: The NATO Science for Peace and Security Programme
EKPO FUEL CELL TECHNOLOGIES
ERA-MIN 2 RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY
Johnson Matthey Inspiring science, enhancing life

"Besides improving the technology we should also try to adapt human habits."

The devil is in the details.

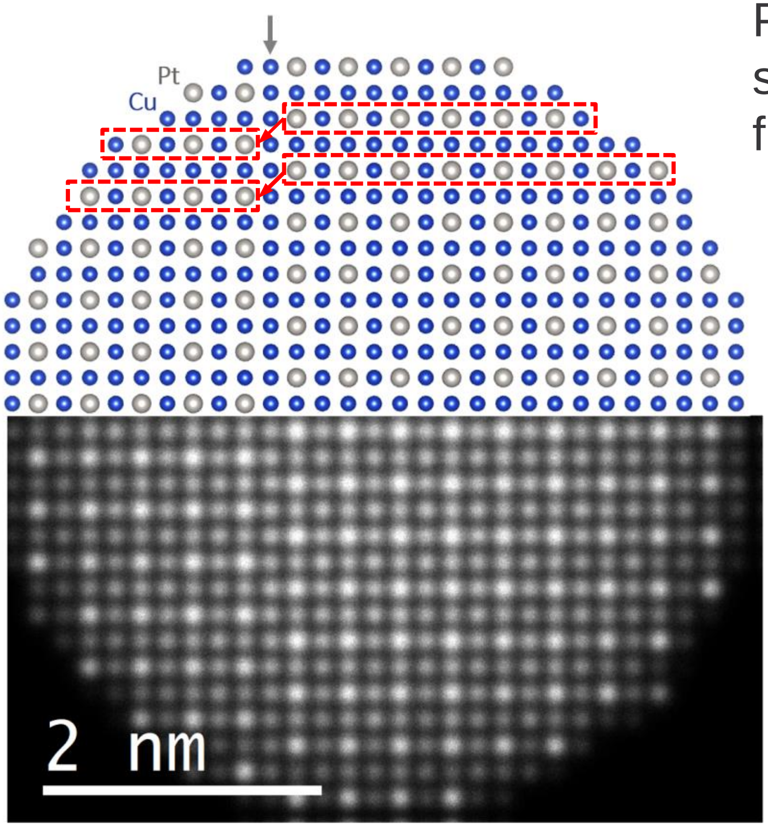
Structurally ordered Pt-alloy nanoparticles (~2010)



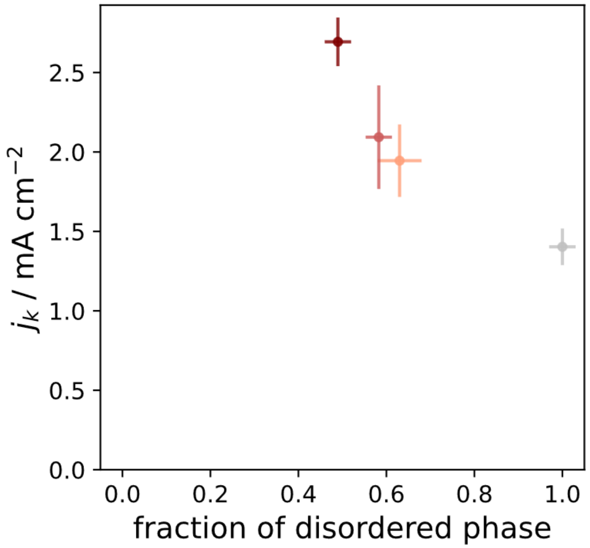
Hodnik et al. Phys. Chem. Chem. Phys., 2014, 16, 13610-13615

The devil is in the details.

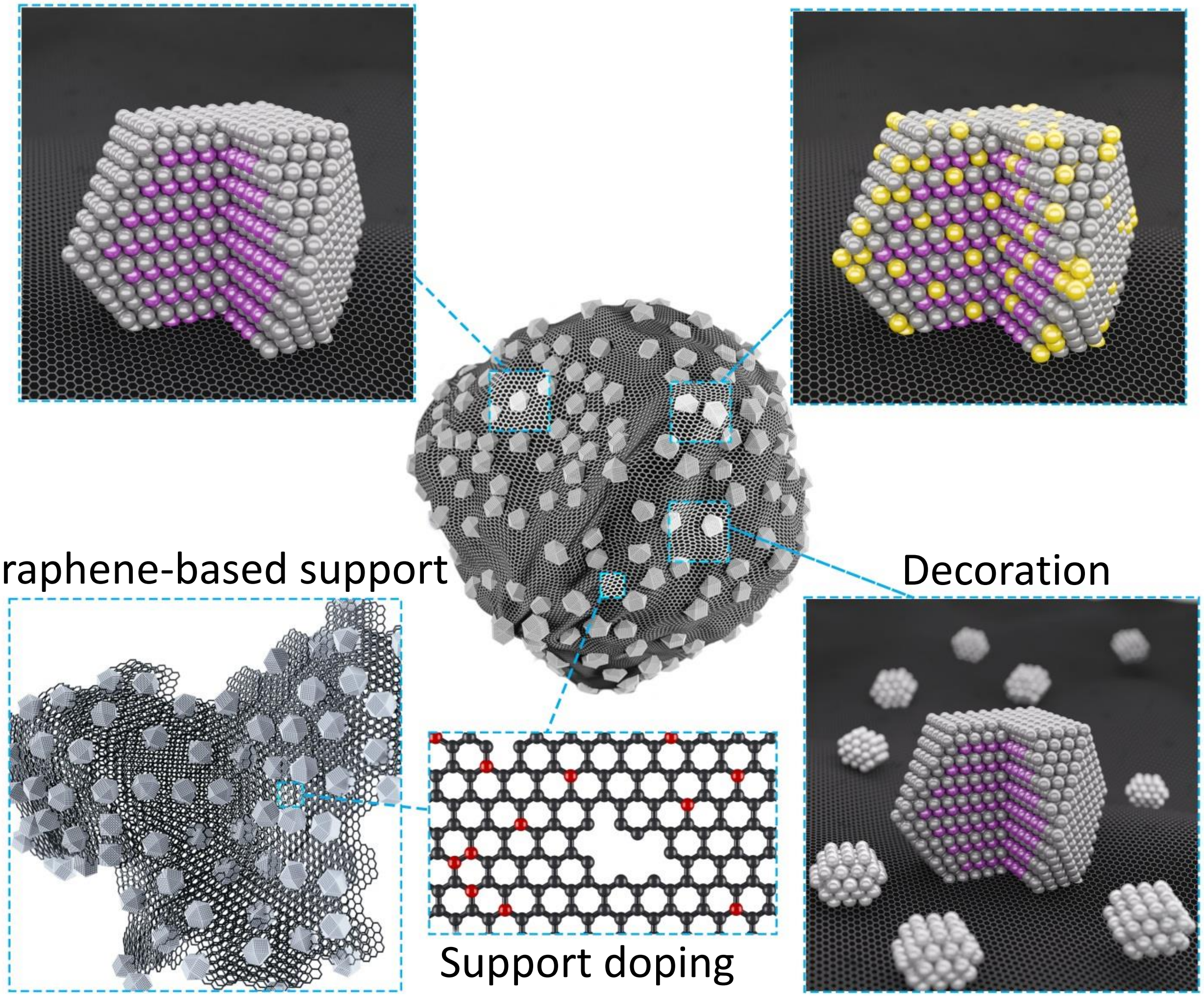
Pt-alloy structure



Periodic anti-phase boundaries and crystal superstructures in $PtCu_3$ nanoparticles as fuel cell catalysts



Short facts of innovative technology



"Unlocking potentials"

KI startups:

MEAs:

mebius

Catalysts:

ReCatalyst

Contact: nejc.hodnik@ki.si